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SYNTHESIS OF NOVEL 4,4-DIALKYL- AND 4,4-DIARYLINDENO[1,2-*b*]THIOPHENES AND THEIR 2-BROMO DERIVATIVES*

J. Bucevicius[1], P. Adomenas[2], and S. Tumkevicius[1]**

A series of new 4,4-dialkyl- and 4,4-diaryl-4H-indeno[1,2-b]thiophenes and their 2-bromo derivatives were synthesized and characterized. An economical one-pot method for the preparation of the key starting material 2-(2-thienyl)benzoic acid and improved procedures for the synthesis of indeno[1,2-b]thiophen-4-one and 4,4-dialkyl-4H-indeno[1,2-b]thiophenes have been developed. The described methods were shown to be efficient for the preparation of the title compounds on a multigram scale.

Keywords: indeno[1,2-*b*]thiophenes, sulfur heterocycles, alkylation, bromination, Kumada coupling.

4*H*-Indeno[1,2-*b*]thiophene is an attractive molecule with potentially interesting properties owing to its unique structure highly reminiscent to fluorene. Compounds possessing this heterocyclic moiety were found to display a wide range of functional material properties and are useful for the construction of sensitizers for dye-sensitized solar cells [1, 2], *p*-type organic semiconductors for organic thin film transistors [3-6], chromophores in luminescent materials [7], or as spacers in D-π-A [8] dyes for liquid or solid state solar cells. Continuing our program focused on the search of novel heterocyclic compounds with valuable properties [9-11], we present herein a synthesis of the title compounds and some improved procedures for the preparation of intermediates.

For the construction of 4*H*-indeno[1,2-*b*]thiophene ring system, 2-(2-thienyl)benzoic acid or the corresponding benzoates are the most often used starting materials [3, 12]. These compounds, as well as their precursor, 2-(2-thienyl)benzonitrile, can be obtained by Ullmann coupling [12], palladium-catalyzed desulfinylative [13, 14] or Stille [15, 16] reactions, or using manganese-catalyzed oxidative cross coupling of the corresponding Grignard reagents [17].

Taking into account that manganese-catalyzed reactions require large excess of one of the components and palladium prices are steadily rising, the purpose of the present investigation was to establish a more economical synthesis method, suitable for the preparation of the title compounds on a multigram scale. In this connection, for the synthesis of 2-(2-thienyl)benzoic acid (**4**) we decided to apply the Kumada-type Ni(0)-catalyzed cross-coupling reaction between 2-chlorobenzonitrile (**1**) and 2-thienylmagnesium bromide (**2**) (Scheme 1). Upon optimization of the reaction conditions, it was noticed that the success of the cross-coupling

*Dedicated to Academician G. Duburs on the occasion of his 80th birthday.

**To whom correspondence should be addressed, e-mail: sigitas.tumkevicius@chf.vu.lt.

[1]Vilnius University, 24 Naugarduko St., Vilnius LT-03225, Lithuania.
[2]Fine synthesis Ltd., 201E Kalvarijų St., Vilnius LT-08311, Lithuania; e-mail: p.adomenas@gmail.com.

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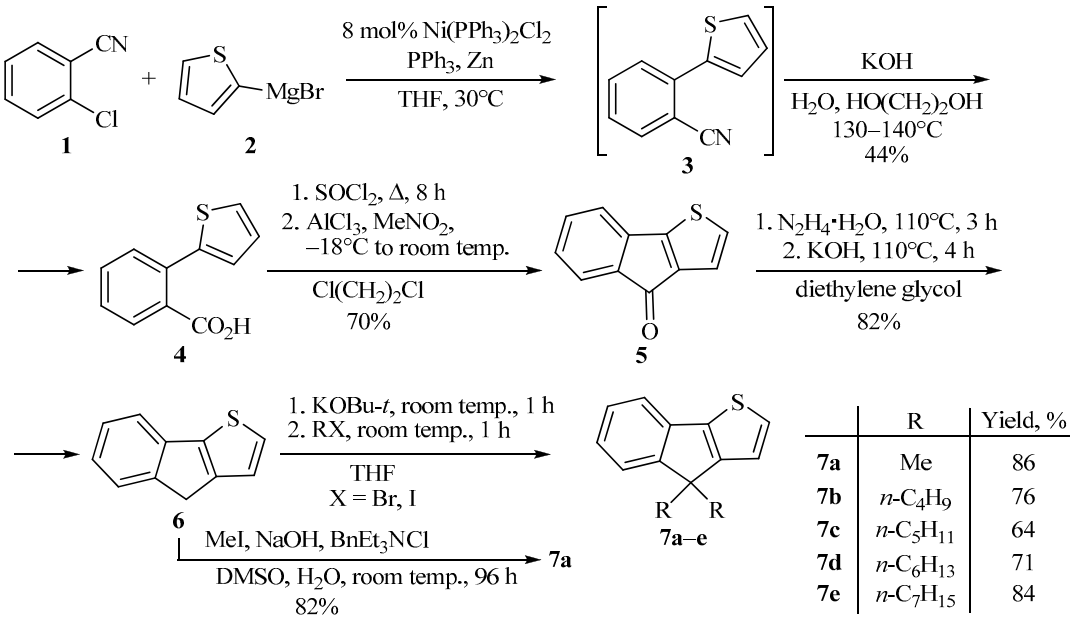
reaction depends on the amount of catalyst. When 2 mol% $NiCl_2(PPh_3)_2$ were used only 10% conversion of nitrile **1** to the desired product **3** was observed. Increase of catalyst loading up to 4 mol% raised the conversion to 30%, and 2-chlorobenzonitrile (**1**) was completely consumed in 8 h when 8 mol% $NiCl_2(PPh_3)_2$ was employed in the reaction. Formation of compound **3** was confirmed, and conversion of the starting material was estimated by GC/MS (*m*/*z* 185.1 $[M]^+$). Distillation of the crude product under reduced pressure gave a mixture consisting of 2-(2-thienyl)-benzonitrile (**3**) and triphenylphosphine. This mixture was used in the next step without any further purification. Hydrolysis of compound **3** with KOH in ethylene glycol furnished 2-(2-thienyl)benzoic acid (**4**) in overall two-step yield 44%.

Scheme 1

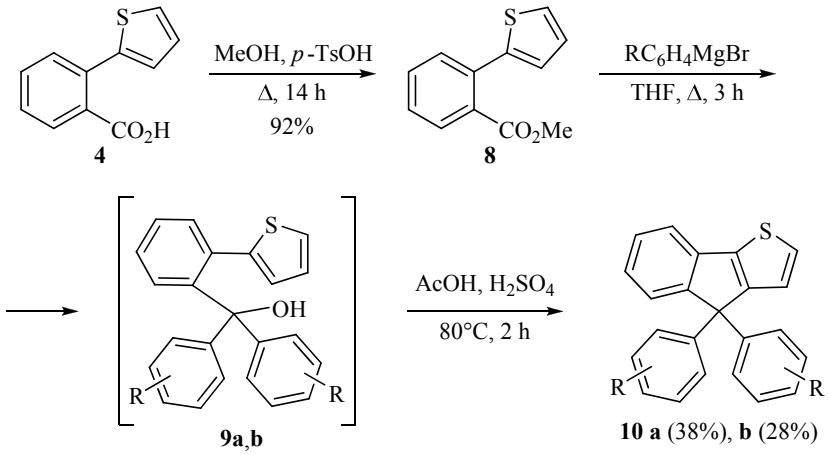


	R	Yield, %
7a	Me	86
7b	*n*-C_4H_9	76
7c	*n*-C_5H_{11}	64
7d	*n*-C_6H_{13}	71
7e	*n*-C_7H_{15}	84

Literature survey revealed that the synthesis of the key intermediate, 4*H*-indeno[1,2-*b*]thiophen-4-one (**5**) is explored insufficiently. To our knowledge, the only method of synthesis of compound **5** from benzoic acid **4** described in the literature includes the synthesis of the corresponding benzoyl chloride and its subsequent cyclization with $SnCl_4$ in dry benzene [3, 12]. Therefore, we decided to investigate other well-known cyclization reactions. First, we tried to apply the direct cyclization reactions using $POCl_3$ or PPA. However, the reaction of compound **4** with $POCl_3$ did not yield even traces of product. Heating compound **4** with PPA at 100°C afforded 4*H*-indeno[1,2-*b*]thiophen-4-one (**5**) in low yield (18%). Further, the corresponding chloro-anhydride was obtained by treating compound **4** with $SOCl_2$. Various Lewis acids were tested in intramolecular Friedel–Crafts acylation reaction. Using $FeCl_3$, $AlCl_3$, and $TiCl_4$ in dichloroethane afforded compound **5** in 36%, 46%, and 52% yields, respectively. The best result was achieved using *in situ* generated $AlCl_3$–$MeNO_2$ complex: indenothiophenone **5** was obtained in 70% yield over two steps (Scheme 1). Wolff–Kishner reduction of compound **5** afforded 4*H*-indeno[1,2-*b*]thiophene (**6**) [12] in 82% yield. Methylation of compound **6** with methyl iodide using phase transfer catalyst benzyltriethylammonium chloride in the two-phase solvent system after 96 h of stirring at room temperature afforded compound **7a** in 82% yield. Alkylation of compound **6** under the same reaction conditions with alkyl halides, which had longer carbon chains, showed even longer reaction times, and 4,4-dialkyl-4*H*-indeno[1,2-*b*]thiophenes **7b-e** could not be separated from the monoalkylated by-products. In order to reduce the reaction time and increase yields of dialkylated compounds **7a-e**, the alkylation reaction using an excess of potassium *tert*-butoxide with alkyl halides was carried out (Scheme 1). This method produced 4,4-dialkyl-4*H*-indeno[1,2-*b*]thiophenes **7a-e** in good yields without any traces of monoalkylated by-products. The total reaction time was 2 h. The method works well with both alkyl bromides and alkyl iodides.

The synthetic route towards 4,4-diarylindeno[1,2-*b*]thiophenes is outlined in Scheme 2. Ester **8**, prepared from acid **4**, reacted with an excess of aryl Grignard reagents to give the corresponding alcohols **9a**,**b** as intermediates. Without further purification, these alcohols were subjected to acid-catalyzed intramolecular annelation to afford 4,4-diaryl-4*H*-indeno[1,2-*b*]thiophenes **10a**,**b** [7].

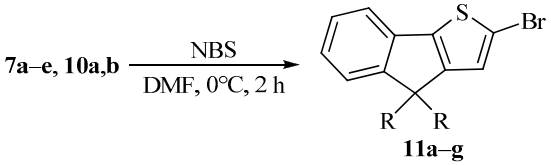
Scheme 2



a R= 4-C_6H_{13}, **b** R = 3-C_6H_{13}

The obtained 4,4-dialkylindeno[1,2-*b*]thiophenes **7a-e** and 4,4-diaryl-4*H*-indeno[1,2-*b*]thiophenes **10a**,**b** were selectively brominated at position 2 by NBS in DMF under exclusion of light to give compounds **11a-g** in high yields (Scheme 3).

Scheme 3



	R	Yield, %
11a	Me	90
11b	*n*-C_4H_9	82
11c	*n*-C_5H_{11}	92
11d	*n*-C_6H_{13}	89
11e	*n*-C_7H_{15}	78
11f	4-(*n*-C_6H_{13})C_6H_4	89
11g	3-(*n*-C_6H_{13})C_6H_4	70

In summary, we have synthesized and characterized a series of new 4,4-dialkyl- and 4,4-diaryl-4*H*-indeno[1,2-*b*]thiophenes and their 2-bromo derivatives. The synthesized compounds can find application as precursors or substrates for the development of novel functional materials with valuable light-emitting and semiconductive properties. Improved procedures for the synthesis of 2-(2-thienyl)benzoic acid and 4,4-dialkyl-4*H*-indeno[1,2-*b*]thiophenes allow the preparation of the title compounds on a multigram scale.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova spectrometer (300 and 75 MHz, respectively) in $CDCl_3$. The NMR chemical shifts were referenced to residual solvent peaks (7.29 and 77.3 ppm for ^{1}H and ^{13}C nuclei, respectively). Mass spectra and conversion of compounds were acquired on an Agilent 5975 GC/MS instrument with EI ionization (70 eV). Elemental analysis was performed on a ThermoFischer Scientific Flash 2000 Elemental Analyzer. Melting points were determined in open capillaries with a digital melting point

ThermoFischer Scientific IA900 series apparatus and are uncorrected. Thin-layer chromatography was performed using TLC-aluminum sheets with silica gel Merck 60 F254. Visualization was accomplished by UV light. Column chromatography was performed using Merck Silica gel 60 (0.040-0.063 mm). All reagents, catalysts, and solvents were purchased from Sigma-Aldrich and were used without further purification.

2-(2-Thienyl)benzoic Acid (4). A mixture of $NiCl_2(PPh_3)_2$ (144.5 g, 0.221 mol), PPh_3 (115.8 g, 0.442 mol), and Zn (14.3 g, 0.221 mol) was stirred at room temperature for 30 min under argon atmosphere till the reaction mixture became dark-red. Then a solution of 2-chlorobenzonitrile (**1**) (379.5 g, 2.760 mol) in THF (1000 ml) was added to the reaction mixture. Thiophene Grignard reagent (**2**), prepared by reacting 2-bromothiophene (500 g, 3.07 mol) with magnesium turnings (76.5 g, 3.15 mol) in THF (1000 ml), was added dropwise to the reaction mixture at such a speed that temperature would not rise above 30°C. The reaction mixture was stirred at room temperature for 2 h and left overnight, then poured into ice water, acidified with concentrated hydrochloric acid to pH 2-4, and extracted with CH_2Cl_2 (2×750 ml). The combined extracts were dried over Na_2SO_4 and filtered. After the removal of the solvent from the filtrate, the obtained viscous dark-brown residue was distilled under vacuum and the fraction with bp 145-155°C/1 mbar was collected to give 300.0 g of 2-(2-thienyl)benzonitrile (**3**) as a viscous yellow oil. The obtained crude 2-(2-thienyl)benzonitrile (**3**) was added to a mixture of ethylene glycol (1200 ml), H_2O (50 ml), and KOH (320 g, 5.7 mol). The reaction mixture was stirred at 130-140°C for 24 h. After cooling to room temperature, the mixture was poured into water, acidified with concentrated HCl to pH 1-2, and extracted with CH_2Cl_2 (3×500 ml). After removal of the solvent, the brown residue was recrystallized from hexane to give 250 g (44%) of compound **4** as a white solid, mp 91-93°C (hexane) (mp 92-94°C (Et_2O) [3]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.08-7.14 (2H, m, H-3,4 thienyl); 7.39 (1H, dd, *J* = 4.8, *J* = 1.5, H-5 thienyl); 7.41-7.54 (2H, m, H-4,5 Ph); 7.57 (1H, dd, *J* = 7.5, *J* = 1.5, H-3 Ph); 7.94 (1H, dd, *J* = 7.5, *J* = 1.5, H-6 Ph); 10,09 (1H, s, COOH). ^{13}C NMR spectrum, δ, ppm: 126.4; 127.1; 127.5; 128.1; 130.5; 130.8; 132.1; 132.2; 135.4; 141.9; 173.9. Found, %: C 64.32; H 3.96. $C_{11}H_8O_2S$. Calculated, %: C 64.69; H 3.95.

4*H*-Indeno[1,2-*b*]thiophen-4-one (5). A mixture of 2-(2-thienyl)benzoic acid (**4**) (150 g, 0.735 mol), $SOCl_2$ (88 g, 0.74 mol), and 1,2-dichloroethane (250 ml) was refluxed for 8 h. Then the reaction mixture was cooled to -18°C, and a solution of $AlCl_3$ (103 g, 0.75 mol) and $MeNO_2$ (122 g, 2 mol) in 1,2-dichloroethane (300 ml) was added dropwise within 1 h. After the addition was complete, the reaction mixture was left to warm to room temperature for 1 h. The mixture was poured into 5 M HCl (500 ml) and stirred for 30 min. The organic layer was separated, washed twice with water, dried over Na_2SO_4, and filtered. After removal of the solvent from the filtrate, the obtained dark-brown residue was distilled under vacuum at 122°C/0.5 mbar and recrystallized from hexane to give 96 g (70%) of compound **5** as orange crystals, mp 101-102°C (hexane) (mp 99-101°C (benzene) [12]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.13-7.22 (4H, m, H-2,3,6,8); 7.35 (1H, td, *J* = 7.5, *J* = 0.9, H-7); 7.46 (1H, dd, *J* = 7.5, *J* = 0.9, H-5). ^{13}C NMR spectrum, δ, ppm: 119.5; 121.7; 123.9; 128.7; 129.3; 134.1; 136.7; 139.0; 142.2; 159.2; 187.5. Found, %: C 70.69; H 3.24. $C_{11}H_6OS$. Calculated, %: C 70.94; H 3.25.

4*H*-Indeno[1,2-*b*]thiophene (6). A mixture of 4*H*-indeno[1,2-*b*]thiophen-4-one (**5**) (40 g, 0.215 mol), hydrazine hydrate (36 g of 50% solution in water, 0.36 mol), and diethylene glycol (150 ml) was heated at 110°C for 3 h, then cooled to 40°C, and KOH (36 g, 0.645 mol) was added. The reaction mixture was heated to 110°C and stirred for 4 h. After cooling to room temperature, the mixture was poured into water (400 ml) and extracted with CH_2Cl_2 (3×150 ml). The organic layer was separated and washed with water until neutral reaction (pH 7). After removal of the solvent, the solid was recrystallized from hexane to give 32 g (82%) of compound **6** as a yellowish solid, mp 68-70°C (hexane) (mp 68-69°C (Et_2O) [12]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.74 (2H, s, CH_2); 7.16 (1H, d, *J* = 4.5, H-3); 7.24-7.34 (2H, m, H-5,8); 7.35 (1H, d, *J* = 4.5, H-2); 7.52-7.55 (2H, m, H-6,7). ^{13}C NMR spectrum, δ, ppm: 34.2; 119.0; 122.9; 125.0; 125.3; 127.1; 127.3; 139.1; 143.4; 146.3; 147.4. Mass spectrum, *m*/*z* (I_{rel}, %): 172 $[M]^+$ (100), 139 (10), 127 (20), 86 (14). Found, %: C 76.46; H 4.63. $C_{11}H_8S$. Calculated, %: C 76.70; H 4.68.

Synthesis of 4,4-Dimethyl-4*H*-indeno[1,2-*b*]thiophene (7a) Under Phase Transfer Catalysis. A mixture of 4*H*-indeno[1,2-*b*]tiophene (**6**) (2.00 g, 11.60 mmol), benzyltriethylammonium chloride (0.18 g,

0.79 mmol), MeI (2.5 ml, 40 mmol), DMSO (20 ml), and 50% aqueous solution of NaOH (20 ml) was stirred at room temperature for at least 96 h. The reaction mixture was quenched with water and extracted with CH_2Cl_2. After removal of the solvent, the product was purified by column chromatography on silica gel (eluent hexane) to give compound **7a**. Yield 1.90 g (82%), white powder, mp 84-85°C (2-PrOH). ^{1}H NMR spectrum: δ, ppm (*J*, Hz): 1.52 (6H, s, $2CH_3$); 7.08 (1H, d, *J* = 5.1, H-3); 7.24-7.32 (2H, m, H-5,8); 7.34 (1H, d, *J* = 5.1, H-2); 7.48-7.50 (2H, m, H-6,7). ^{13}C NMR spectrum, δ, ppm: 26.3; 45.7; 119.1; 120.9; 122.6; 125.4; 127.2; 127.8; 136.8; 140.0; 156.5; 158.6. Found, %: C 77.45; H 6.04. $C_{13}H_{12}S$. Calculated, %: C 77.95; H 6.04.

4,4-Dialkyl-4*H*-indeno[1,2-*b*]thiophenes 7a-e (General Method). Potassium *tert*-butoxide (3.9 g, 34.8 mmol) was added to a solution of 4*H*-indeno[1,2-*b*]-thiophene (**6**) (2.0 g, 11.6 mmol) in THF (30 ml). The reaction mixture was stirred at room temperature for 1 h. Then the corresponding alkyl iodide (for compounds **7a**,**b**,**e**) or bromide (for compounds **7c**,**d**) (34.8 mmol) was added, and the reaction mixture was stirred for an additional hour. The reaction was quenched with water and extracted with CH_2Cl_2 (3×50 ml); the organic layer was separated and washed with water until neutral reaction (pH 7). After evaporation of the solvent, the product was recrystallized from 2-PrOH (compound **7a**) or purified by column chromatography (eluent hexane) (compounds **7b-e**).

4,4-Dimethyl-4*H*-indeno[1,2-*b*]thiophene (7a). Yield 2.0 g (86%).

4,4-Dibutyl-4*H*-indeno[1,2-*b*]thiophene (7b). Yield 2.5 g (76%), yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.69-0.85 (4H, m, $2CH_2C\underline{H}_2CH_2CH_3$); 0.75-0.87 (6H, t, *J* = 7.5, $2CH_3$); 1.13-1.21 (4H, m, $2CH_2CH_2C\underline{H}_2CH_3$); 1.89-1.99 (4H, m, $2C\underline{H}_2CH_2CH_2CH_3$); 7.20 (1H, d, *J* = 4.8, H-3); 7.31-7.33 (3H, m, H-5,6,7); 7.38 (1H, d, *J* = 4.8, H-2); 7.45 (1H, d, *J* = 7.5, H-8). ^{13}C NMR spectrum, δ, ppm: 14.1; 23.3; 26.6; 39.0; 54.0; 118.8; 121.8; 122.8; 125.2; 126.9; 127.3; 138.5; 141.4; 154.1; 155.6. Found, %: C 80.22; H 9.03. $C_{19}H_{24}S$. Calculated, %: C 80.22; H 8.59.

4,4-Dipentyl-4*H*-indeno[1,2-*b*]thiophene (7c). Yield 2.3 g (64%), yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.71-0.89 (4H, m, $2CH_2C\underline{H}_2(CH_2)_2CH_3$); 0.83 (6H, t, *J* = 7.2, $2CH_3$); 1.14-1.23 (8H, m, $2(CH_2)_2(C\underline{H}_2)_2CH_3$); 1.97-2.07 (4H, m, $2C\underline{H}_2(CH_2)_3CH_3$); 7.04 (1H, d, *J* = 4.8, H-3); 7.30-7.36 (3H, m, H-5,6,7); 7.39 (1H, d, *J* = 4.8, H-2); 7.51 (1H, d, *J* = 7.2, H-8). ^{13}C NMR spectrum, δ, ppm: 14.3; 22.6; 24.1; 32.6; 39.3; 54.1; 118.9; 121.8; 122.8; 125.3; 127.0; 127.4; 138.6; 141.5; 154.2; 155.6. Mass spectrum, *m*/*z* (I_{rel}, %): 312 $[M]^+$ (70), 241 (90), 185 (100), 171 (35), 152 (14). Found, %: C 80.7; H 9.03. $C_{21}H_{28}S$. Calculated, %: C 80.71; H 9.03.

4,4-Dihexyl-4*H*-indeno[1,2-*b*]thiophene (7d). Yield 2.8 g (71%), yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.72-0.89 (4H, m, $2CH_2C\underline{H}_2(CH_2)_3CH_3$); 0.88 (6H, t, *J* = 7.5, $2CH_3$); 1.12-1.21 (12H, m, $2(CH_2)_2(C\underline{H}_2)_3CH_3$); 1.96-2.06 (4H, m, $2C\underline{H}_2(CH_2)_4CH_3$); 7.07 (1H, d, *J* = 4.8, H-3); 7.27-7.38 (3H, m, H-5,6,7); 7.38 (1H, d, *J* = 4.8, H-2); 7.51 (1H, d, 7.2, H-8). ^{13}C NMR spectrum, δ, ppm: 14.3; 22.9; 24.4; 30.0; 31.9; 39.3; 54.1; 118.9; 121.8; 122.8; 125.2; 127.0; 127.4; 138.6; 141.5; 154.1; 155.6. Mass spectrum, *m*/*z* (I_{rel}, %): 340 $[M]^+$ (63), 255 (85), 185 (100), 171 (32), 152 (12). Found, %: C 80.92; H 9.44. $C_{23}H_{32}S$. Calculated, %: C 81.11; H 9.47.

4,4-Diheptyl-4*H*-indeno[1,2-*b*]thiophene (7e). Yield 3.6 g (84%), yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.75-0.91 (4H, m, $2CH_2C\underline{H}_2(CH_2)_4CH_3$); 0.91 (6H, t, *J* = 7.2, $2CH_3$); 1.17-1.29 (16H, m, $2(CH_2)_2(C\underline{H}_2)_4CH_3$); 1.91-2.07 (4H, m, $2C\underline{H}_2(CH_2)_5CH_3$); 7.03 (1H, d, *J* = 5.1, H-3); 7.24-7.36 (3H, m, H-5,6,7); 7.36 (1H, d, *J* = 5.1, H-2); 7.47 (1H, d, *J* = 7.2, H-8). ^{13}C NMR spectrum, δ, ppm: 14.3; 22.8; 24.4; 29.3; 30.3; 32.1; 39.3; 54.1; 118.9; 121.8; 122.8; 125.3; 127.0; 127.3; 138.5; 141.4; 154.1; 155.6. Found, %: C 80.96; H 9.87. $C_{25}H_{36}S$. Calculated, %: C 81.46; H 9.84.

Methyl 2-(2-Thienyl)benzoate (8). A mixture of 2-(2-thienyl)benzoic acid (**4**) (30 g, 0.147 mol), *p*-TsOH (5 g, 0.022 mol), and MeOH (100 ml) was refluxed for 14 h. Then the reaction mixture was cooled and poured into ice water (300 ml) and extracted with CH_2Cl_2 (2×100 ml). Removal of the solvent gave 29 g (91%) of yellowish oil (slightly-yellow oil [3]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.77 (3H, s, $COOCH_3$); 7.06-7.10 (2H, m, H-3,4 thienyl); 7.37 (1H, dd, *J* = 5.0, *J* = 1.5, H-2 thienyl); 7.43-7.52 (3H, m, H-4,5,6 Ph); 7.75 (1H, td, *J* = 7.6, *J* = 1.5, H-3 Ph). ^{13}C NMR spectrum, δ, ppm: 52.2; 125.9; 126.3; 127.2; 127.7; 129.4; 131.0; 131.1; 131.7; 134.1; 142.0; 169.1.

4,4-Diaryl-4*H*-indeno[1,2-*b*]thiophenes 10a,b (General Method). Grignard reagent prepared from 1-bromo-4-hexylbenzene or 1-bromo-3-hexylbenzene (13.3 g, 0.055 mol) and magnesium turnings (1.45 g, 0.06 mol) in THF (25 ml) was added to a stirred solution of methyl 2-(2-thienyl)benzoate (**8**) (5 g, 0.023 mol) in THF (50 ml). After the addition was complete, the reaction mixture was refluxed for 3 h, then cooled to room temperature and poured into 1 M NH_4Cl solution (200 ml), extracted with CH_2Cl_2, and washed with water twice. After removal of the solvent, the obtained yellow oil was dissolved in acetic acid (40 ml) and heated to 80°C. When the required temperature was reached, 2 drops of concentrated H_2SO_4 was added, and stirring at 80°C was continued for 2 h. The reaction mixture was poured to ice water, extracted with CH_2Cl_2, and washed with water 3 times. Removal of the solvent gave the crude product, which was recrystallized from 2-PrOH.

4,4-Bis(4-hexylphenyl)-4*H*-indeno[1,2-*b*]thiophene (10a). Yield 4.3 g (38%), white solid, mp 61-63°C (2-PrOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.94 (6H, t, *J* = 6.0, $2CH_3$); 1.35-1.63 (16H, m, $2CH_2(C\underline{H}_2)_4CH_3$); 2.59 (4H, t, *J* = 7.5, $2C\underline{H}_2(CH_2)_4CH_3$); 7.08-7.24 (10H, m, H-2,3, H-2,3,5,6 2Ar); 7.31-7.35 (2H, m, H-6,7); 7.43 (1H, d, *J* = 7.5, H-5); 7.51 (1H, d, *J* = 7.5, H-8). ^{13}C NMR spectrum, δ, ppm: 14.3; 22.8; 29.3; 31.6; 31.9; 35.8; 63.1; 119.5; 123.4; 125.8; 126.6; 127.5; 128.0; 128.1; 128.5; 137.5; 141.2; 141.5; 142.2; 154.0; 156.2. Mass spectrum, *m*/*z* (I_{rel}, %): 492 $[M]^+$ (100), 459 (9), 407 (18), 331 (16), 260 (14). Found, %: C 85.02; H 7.89. $C_{35}H_{40}S$. Calculated, %: C 85.31; H 8.18.

4,4-Bis(3-hexylphenyl)-4*H*-indeno[1,2-*b*]thiophene (10b). Yield 3.2 g (28%), white solid, mp 45-46°C (2-PrOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.91 (6H, t, *J* = 6.0, $2CH_3$); 1.25-1.57 (16H, m, $2CH_2(C\underline{H}_2)_4CH_3$); 2.53 (4H, t, *J* = 7.8, $C\underline{H}_2(CH_2)_4CH_3$); 6.96-7.08 (7H, m, H-2, H-2,4,6 2Ar); 7.16 (2H, t, *J* = 7.5, H-5 2Ar); 7.22 (1H, d, *J* = 7.5, H-5); 7.30-7.41 (3H, m, H-3,6,7); 7.51 (1H, d, *J* = 7.5, H-8). ^{13}C NMR spectrum, δ, ppm: 14.3; 22.8; 29.1; 31.7; 31.9; 36.2; 63.6; 119.5; 123.3; 125.2; 125.8; 126.5; 127.0; 127.6; 128.1; 128.2; 128.5; 137.5; 141.3; 143.1; 144.9; 153.8; 156.0. Mass spectrum, *m*/*z* (I_{rel}, %): 492 $[M]^+$ (100), 459 (10), 407 (20), 331 (16), 260 (14). Found, %: C 84.96; H 8.11. $C_{35}H_{40}S$. Calculated, %: C 85.31; H 8.18.

2-Bromo-4,4-dialkyl- and 4,4-Diaryl-4*H*-indeno[1,2-*b*]thiophenes 11a-g (General Method). NBS (1.47 g, 8.25 mmol) was added in portions to a solution of the corresponding 4,4-dialkyl- or 4,4-diaryl-4*H*-indeno[1,2-*b*]thiophene **7a-e**, **10a**,**b** (7.5 mmol) in DMF (25 ml), cooled to 0°C, and protected from the daylight. The reaction mixture was stirred at 0°C for 2 h and then allowed to reach room temperature. The reaction was quenched with water (100 ml) and extracted with CH_2Cl_2. After removal of the solvent, the products were purified by column chromatography on silica gel (eluent hexane).

2-Bromo-4,4-dimethyl-4*H*-indeno[1,2-*b*]thiophene (11a). Yield 1.9 g (90%), white solid, mp 54-55°C (hexane). ^{1}H NMR spectrum, δ, ppm: 1.48 (6H, s, $2CH_3$); 7.08 (1H, s, H-3); 7.25-7.33 (2H, m, H-5,6); 7.38-7.40 (2H, m, H-7,8). ^{13}C NMR spectrum, δ, ppm: 26.1; 46.7; 113.7; 119.0; 122.0; 124.2; 125.7; 127.3; 136.4; 140.2; 155.1; 157.4. Found, %: C 56.23; H, 3.98. $C_{13}H_{11}BrS$. Calculated, %: C 55.92; H 3.97.

2-Bromo-4,4-dibutyl-4*H*-indeno[1,2-*b*]thiophene (11b). Yield 2.2 g (82%), white solid, mp 61-63°C (hexane). ^{1}H NMR spectrum, δ (*J*, Hz): 0.73-0.84 (4H, m, $2CH_2C\underline{H}_2CH_2CH_3$); 0.77 (6H, t, *J* = 7.2, $2CH_3$); 1.12-1.17 (4H, m, $2CH_2CH_2C\underline{H}_2CH_3$); 1.81-1.92 (4H, m, $2C\underline{H}_2CH_2CH_2CH_3$); 7.02 (1H, s, H-3); 7.20-7.29 (2H, m, H-5,6); 7.31-7.39 (2H, m, H-7,8). ^{13}C NMR spectrum, δ, ppm: 14.1; 23.2; 26.5; 38.9; 55.0; 113.3; 118.8; 122.8; 124.8; 125.5; 127.1; 138.1; 141.7; 152.7; 154.4. Mass spectrum, *m*/*z* (I_{rel}, %): 364 $[M]^+$ (60), 307 (50), 251 (20), 226 (100), 198 (46), 184 (75), 139 (24). Found, %: C 63.13; H 6.55. $C_{19}H_{23}BrS$. Calculated, %: C 62.80; H 6.38.

2-Bromo-4,4-dipentyl-4*H*-indeno[1,2-*b*]thiophene (11c). Yield 2.7 g (92%), yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.77-0.82 (4H, m, $2CH_2C\underline{H}_2(CH_2)_2CH_3$); 0.81 (6H, t, *J* = 6.9, $2CH_3$); 1.11-1.16 (8H, m, $2(CH_2)_2(C\underline{H}_2)_2CH_3$); 1.72-1.98 (4H, m, $2C\underline{H}_2(CH_2)_3CH_3$); 7.01 (1H, s, H-3); 7.20-7.30 (2H, m, H-5,6); 7.31-7.41 (2H, m, H-7,8). ^{13}C NMR spectrum, δ, ppm: 14.2; 22.6; 24.0; 32.4; 39.1; 55.1; 113.3; 118.8; 122.8; 124.8; 125.5; 127.1; 138.1; 141.7; 152.7; 154.7. Found, %: C 64.92; H 7.06. $C_{21}H_{27}BrS$. Calculated, %: C 64.44; H 6.95.

2-Bromo-4,4-dihexyl-4*H*-indeno[1,2-*b*]thiophene (11d). Yield 2.8 g (89%), yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.79-0.85 (4H, m, $2CH_2C\underline{H}_2(CH_2)_3CH_3$); 0.82 (6H, t, *J* = 6.9, $2CH_3$); 1.15-1.22 (12H,

m, $2(CH_2)_2(C\underline{H}_2)_3CH_3$); 1.81-198 (4H, m, $2C\underline{H}_2(CH_2)_4CH_3$); 7.03 (1H, s, H-3); 7.21-7.32 (2H, m, H-5,6); 7.37-7.44 (2H, m, H-7,8). ^{13}C NMR spectrum, δ, ppm: 14.2; 22.8; 24.3; 29.8; 31.8; 39.0; 55.1; 113.3; 118.8; 122.8; 124.9; 125.5; 127.1; 138.1; 141.7; 152.7; 154.6. Found, %: C 65.69; H 7.43. $C_{23}H_{31}BrS$. Calculated, %: C 65.86; H 7.45.

2-Bromo-4,4-diheptyl-4*H*-indeno[1,2-*b*]thiophene (11e). Yield 2.61 g (78%), yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.78-0.84 (4H, m, $2CH_2C\underline{H}_2(CH_2)_4CH_3$); 0.86 (6H, t, *J* = 7.0, $2CH_3$); 1.12-126 (16H, m, $2(CH_2)_2(C\underline{H}_2)_4CH_3$); 1.78-1.95 (4H, m, $2C\underline{H}_2(CH_2)_5CH_3$); 7.01 (1H, s, H-3); 7.20-7.30 (2H, m, H-5,6); 7.32-7.39 (2H, m, H-7,8). ^{13}C NMR spectrum, δ, ppm: 14.3; 22.8; 24.3; 29.2; 30.2; 32.0; 39.1; 55.1; 113.3; 118.8; 122.8; 124.9; 125.5; 127.1; 138.1; 141.7; 152.7; 154.5. Found, %: C 66.93; H 7.92. $C_{25}H_{35}BrS$. Calculated, %: C 67.10; H 7.88.

2-Bromo-4,4-bis(4-hexylphenyl)-4*H*-indeno[1,2-*b*]thiophene (11f). Yield 3.8 g (89%), white powder, mp 93-95°C (hexane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.94 (6H, t, *J* = 6.6, $2CH_3$); 1.36-1.63 (16H, m, $2CH_2(C\underline{H}_2)_4CH_3$); 2.61 (4H, t, *J* = 7.8, $2C\underline{H}_2(CH_2)_4CH_3$); 7.08-7.19 (8H, m, H-2,3,5,6 2Ar); 7.14 (1H, s, H-3); 7.23-7.45 (4H, m, H-5,6,7,8). ^{13}C NMR spectrum, δ, ppm: 14.3; 22.8; 29.4; 31.6; 32.0; 35.8; 63.9; 114.2; 119.5; 120.6; 126.1; 126.5; 127.8; 127.9; 128.6; 137.1; 141.5; 141.6; 141.8; 152.8; 155.0. Found, %: C 73.52; H 6.96. $C_{35}H_{39}BrS$. Calculated, %: C 73.54; H 6.88.

2-Bromo-4,4-bis(3-hexylphenyl)-4*H*-indeno[1,2-*b*]thiophene (11g). Yield 3.0 g (70%), yellow viscous oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.92 (6H, t, *J* = 6.9, $2CH_3$); 1.29-1.61 (16H, m, $2CH_2(C\underline{H}_2)_4CH_3$); 2.56 (4H, t, *J* = 7.8, $2C\underline{H}_2(CH_2)_4CH_3$); 6.97 (2H, dt, *J* = 7,5, *J* = 1.5, H-6 2Ar); 7.05 (2H, s, H-2 2Ar); 7.07-7.14 (3H, m, H-3, H-4 2Ar); 7.17 (2H, t, *J* = 7.5, H-5 2Ar); 7.23 (1H, dd, *J* = 7.5, *J* = 0.9, H-5); 7.33 (1H, td, *J* = 7.5, *J* = 0.9, H-6); 7.37-7.45 (2H, m, H-7,8). ^{13}C NMR spectrum, δ, ppm: 14.3; 22.9; 29.1; 31.6; 31.9; 36.2; 64.5; 114.2; 119.5; 125.1; 126.1; 126.3; 126.5; 127.2; 127.7; 128.4; 128.4; 137.1; 141.5; 143.2; 144.3; 152.6; 154.8. Found: C 73.54; H 6.91. $C_{35}H_{39}BrS$. Calculated, %: C 73.54; H 6.88.

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