Synthesis of diimine ligands with cycloalkyl substituents based on 4,6-dibenzofuran- and 4,6-dibenzothiophenedicarboxaldehydes*

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A formic acid-catalyzed reaction of substituted cycloalkylanilines with 4,6-dibenzofuran- and 4,6-dibenzothiophenedicarboxaldehydes in methanol—dichloromethane mixture afforded a number of the corresponding diimines, which can be of interest as components of catalytic systems for polymerization of olefins.

Key words: dibenzofurans, dibenzothiophenes, anilines, imines, aldehydes, ligands.

The synthesis of new postmetallocene catalysts for polymerization of olefins is ensured by a possibility of introduction of various substituents into a ligand and alteration of its framework.[1] A variation of the ligand structure causes a change of electron density and sterical hindrance at an active center of the catalyst and thus affects activity of the catalytic system, which can lead to a change of the mechanism of polymerization.[1,2] The exemplary bis(arylimino)pyridyl complexes of iron chloride and 1,2-bis(arylimino)acenaphthene complexes of nickel bromide demonstrated a possibility to create catalytic systems for polymerization of ethylene, which are active at the temperature higher than 70 °C due to the introduction of cycloalkyl substituents into *ortho*-position of the aryl ring, bearing an imine group.[3]

Earlier,[4] it was shown that the changes of the framework of bis(arylimino)pyridyl complexes of iron and cobalt chlorides affected their catalytic activity in polymerization of olefins. It looks reasonable that the alteration of the framework, bearing arylimino groups, together with the introduction of cycloalkyl substituents into them, may promote creation of new, highly active catalytic systems. When choosing a new framework, a synthetic availability of the corresponding dialdehydes or ketones, as well as a ligating power of the bis(arylimines) obtained, should be taken into account. We chose dibenzofuran and dibenzothiophene frameworks for the synthesis of new ligands, since 4,6-dibenzofuran- and 4,6-dibenzothiophenedicarboxaldehydes can be easily obtained,[5] while their bis(arylimines) are patented as components of catalytic systems for polymerization of olefins.[6]

The reaction of 4,6-dibenzofurandicarboxaldehyde (**1**) or 4,6-dibenzothiophenedicarboxaldehyde (**2**) with anilines leading correspondingly to 4,6-bis(aryliminomethyl)dibenzofuran and 4,6-bis(aryliminomethyl)dibenzothiophene ligands, was implemented on a model reaction of dialdehyde **1** with a number of methyl- and isopropylanilines.[4,6,7] The ligands of dibenzofuran series are obtained by reflux of a mixture of dialdehyde **1** and the corresponding alkylaniline in ethanol or in ethanol—isopropanol mixture in the presence of *p*-toluenesulfonic or acetic acids and molecular sieves.[4,7]

We extended this method to the synthesis of new 4,6-bis(aryliminomethyl)dibenzofurans and -dibenzothiophenes, bearing cycloalkyl substituents, and optimized the reaction conditions (Scheme 1).

2-Cyclopentyl- and 2,6-dicyclopentylanilines **3a—d**, 2-cyclohexyl- and 2,6-dicyclohexylanilines **4a—d**, as well as 2-cyclooctylanilines **5a—c**, upon heating with dialdehydes **1** and **2** in ethanol in the presence of *p*-toluenesulfonic acid or in methanol in the presence of catalytic amounts of formic acid afford the corresponding 4,6-bis(cycloalkylphenyliminomethyl)dibenzofurans and -dibenzothiophenes **6—11**. However, the reaction is not complete even under prolonged heating, and as a result, a mixture of the corresponding mono- and diimines is formed, from which diimines **6—11** can be isolated by column chromatography in only 45—50% yield. When the reaction is carried out in methanol—dichloromethane

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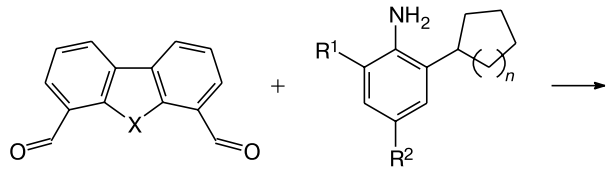
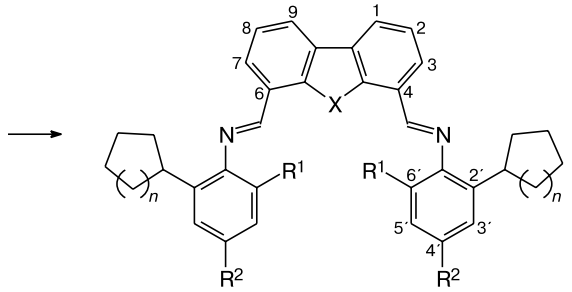
Scheme 1



1, **2** **3a—d**, **4a—d**, **5a—c**



6a—d, **7a—d**, **8a—c**, **9a—d**, **10a—d**, **11a—c**

$R^1 = R^2 = H$ (**a**); R^1 = Me, $R^2 = H$ (**b**); $R^1 = R^2$ = Me (**c**); R^1 = *cyclo*-$(CH_2)_{n+3}CH$, $R^2 = H$ (**d**)
n = 1 (**3**, **6**, **9**), 2 (**4**, **7**, **10**), 4 (**5**, **8**, **11**);
X = O (**1**, **6—8**), S (**2**, **9—11**)

mixture (1 : 1) in the presence of formic acid, dialdehydes **1** and **2** are completely converted to bisimines **6—11** in as high yields as 92—99%.

The structures of obtained 4,6-bis(cycloalkylphenyliminomethyl)dibenzofurans and -dibenzothiophenes **6—11** were established on the basis of analytical and spectral data. In the ^{1}H NMR spectra of diimines **6—8** the H(2) and H(8) protons of the dibenzofuran ring resonate as triplets at δ 7.41—7.51, the H(1) and H(9) protons, as downfield shifted doublets at δ 7.99—8.10, and the H(3) and H(7) protons, as doublets at δ 8.23—8.31. Signals of the H(2), H(8) and H(3), H(7) protons of the dibenzothiophene ring of diimines **9—11** are shifted downfield in comparison with the signals of the dibenzofuran analogs, whereas signals of the H(1) and H(9) protons are shifted upfield. In the ^{1}H NMR spectra of diimines **6—11**, singlets of the N=CH groups are present in region δ 8.53—8.99. Signals of the methylene groups of the cycloalkyl substituents of the Schiff bases **6—11** resonate as multiplets at δ 0.95—2.10, and those of the CH groups, at δ 2.49—3.84. In the spectra of diimines **6b,c—11b,c**, singlets of the Me groups in region δ 2.08—2.63 are present. In the IR spectra of the Schiff bases **6—11**, a strong absorption band is present in region 1623—1640 cm^{-1}, which corresponds to the stretching vibrations of the C=N bond in the imine group.

An intensive peak of the molecular ion is characteristic of the mass spectra of diimines **6—11**.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-200 SY spectrometer with the working frequency of 200 MHz for solutions of compounds in $CDCl_3$. HMDS was used as the internal standard. IR spectra were recorded on a Vector 22 spectrometer for the samples in KBr pellets. The reaction progress and the purity of synthesized compounds were monitored by TLC on Silufol UV-254 plates with chloroform as eluent. Elemental analysis was performed on a Carlo Erba 1106 CHN-analyzer. Molecular formulas of compounds obtained were calculated from the high-resolution mass spectra recorded on a Finnigan MAT 8200 spectrometer. Melting points were determined between glass plates upon heating with the rate of 1 deg min^{-1}.

4,6-Dibenzofurandicarboxaldehyde (**1**), 4,6-dibenzothiophenedicarboxaldehyde (**2**), and cycloalkylanilines **3a—d**, **4a—d**, **5a—c** were obtained following the known procedures.[5,8]

4,6-Bis(cycloalkylphenyliminomethyl)dibenzofurans 6—8 and 4,6-bis(cycloalkylphenyliminomethyl)dibenzothiophenes 9—11 (general procedure). A mixture of dialdehyde **1** or **2** (1 mmol), the corresponding cycloalkylaniline **3—5** (2.1 mmol), methanol (10 mL), dichloromethane (10 mL), and anhydrous formic acid (5 mg) was refluxed for 2—6 h up to the full conversion of starting compounds (TLC monitoring). The solvents were evaporated, the residue was triturated with methanol (5 mL), the crystalline precipitate of diimines **6—11** was filtered off and washed with cold methanol (2×3 mL).

4,6-Bis(2-cyclopentylphenyliminomethyl)dibenzofuran (6a). The yield was 97%, m.p. 140—141 °C. HRMS, found: *m/z* 510.2673 $[M]^+$. $C_{36}H_{34}N_2O$. Calculated: M = 510.2671. IR, ν/cm^{-1}: 1626 (N=CH). ^{1}H NMR, δ: 1.50—2.10 (m, 16 H, CH_2); 3.54 (m, 2 H, CH); 6.92—7.22 (m, 8 H, H(3′)—H(6′)); 7.42 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 7.99 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.23 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.99 (s, 2 H, N=CH).

4,6-Bis(6-cyclopentyl-2-methylphenyliminomethyl)dibenzofuran (6b). The yield was 96%, m.p. 145—146 °C. HRMS, found: *m/z* 538.2987 $[M]^+$. $C_{38}H_{38}N_2O$. Calculated: M = 538.2984. IR, ν/cm^{-1}: 1636 (N=CH). ^{1}H NMR, δ: 1.39—2.05 (m, 16 H, CH_2); 2.12 (s, 6 H, Me); 2.98 (m, 2 H, CH); 6.80—7.10 (m, 6 H, H(3′)—H(5′)); 7.48 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.07 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.31 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.82 (s, 2 H, N=CH).

4,6-Bis(6-cyclopentyl-2,4-dimethylphenyliminomethyl)dibenzofuran (6c). The yield was 96%, m.p. 162—163 °C. HRMS, found: *m/z* 566.3293 $[M]^+$. $C_{40}H_{42}N_2O$. Calculated: M = 566.3297. IR, ν/cm^{-1}: 1638 (N=CH). ^{1}H NMR, δ: 1.35—1.98 (m, 16 H, CH_2); 2.08, 2.23 (both s, 6 H each, Me); 2.96 (m, 2 H, CH); 6.77, 6.86 (both s, 2 H each, H(3′), H(5′)); 7.47 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.06 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.29 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.78 (s, 2 H, N=CH).

4,6-Bis(2,6-dicyclopentylphenyliminomethyl)dibenzofuran (6d). The yield was 97%, m.p. 223—224 °C. Found (%): C, 85.60; H, 7.69; N, 4.29. $C_{46}H_{50}N_2O$. Calculated (%): C, 85.45; H, 7.74; N, 4.33. IR, ν/cm^{-1}: 1636 (N=CH). ^{1}H NMR, δ: 1.37—1.97 (m, 32 H, CH_2); 2.96 (m, 4 H, CH); 6.95—7.12 (m, 6 H, H(3′)—H(5′)); 7.51 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.10 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.31 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.77 (s, 2 H, N=CH). MS, *m/z*: 646 $[M]^+$.

4,6-Bis(2-cyclohexylphenyliminomethyl)dibenzofuran (7a). The yield was 96%, m.p. 200—201 °C. HRMS, found: *m/z* 538.2971 $[M]^+$. $C_{38}H_{38}N_2O$. Calculated: M = 538.2984. IR, ν/cm^{-1}: 1627 (N=CH). ^{1}H NMR, δ: 1.10—1.90 (m, 20 H, CH_2); 3.12 (m, 2 H, CH); 6.91—7.22 (m, 8 H, H(3′)—H(6′)); 7.41 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.02 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.23 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.99 (s, 2 H, N=CH).

4,6-Bis(6-cyclohexyl-2-methylphenyliminomethyl)dibenzofuran (7b). The yield was 95%, m.p. 186—187 °C. HRMS, found: *m/z* 566.3304 $[M]^+$. $C_{40}H_{42}N_2O$. Calculated: M = 566.3297. IR, ν/cm^{-1}: 1638 (N=CH). ^{1}H NMR, δ: 1.12—1.85 (m, 20 H, CH_2); 2.15 (s, 6 H, Me); 2.57 (m, 2 H, CH); 6.82—7.17 (m, 6 H, H(3′)—H(5′)); 7.49 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.08 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.31 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.81 (s, 2 H, N=CH).

4,6-Bis(6-cyclohexyl-2,4-dimethylphenyliminomethyl)dibenzofuran (7c). The yield was 94%, m.p. 219—220 °C. HRMS, found: *m/z* 566.3293 $[M]^+$. $C_{42}H_{46}N_2O$. Calculated: M = 566.3297. IR, ν/cm^{-1}: 1641 (N=CH). ^{1}H NMR, δ: 1.05—1.80 (m, 20 H, CH_2); 2.09, 2.26 (both s, 6 H each, Me); 2.57 (m, 2 H, CH); 6.77, 6.82 (both s, 2 H each, H(3′), H(5′)); 7.47 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.06 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.29 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.78 (s, 2 H, N=CH).

4,6-Bis(2,6-dicyclohexylphenyliminomethyl)dibenzofuran (7d). The yield was 95%, m.p. 253—254 °C. Found (%): C, 85.56; H, 8.20; N, 4.03. $C_{50}H_{58}N_2O$. Calculated (%): C, 85.47; H, 8.26; N, 3.99. IR, ν/cm^{-1}: 1637 (N=CH). ^{1}H NMR, δ: 0.95—1.85 (m, 40 H, CH_2); 2.49 (m, 4 H, CH); 6.92—7.30 (m, 6 H, H(3′)—H(5′)); 7.51 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.11 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.30 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.74 (s, 2 H, N=CH). MS, *m/z*: 702 $[M]^+$.

4,6-Bis(2-cyclooctylphenyliminomethyl)dibenzofuran (8a). The yield was 99%, m.p. 63—64 °C. HRMS, found: *m/z* 594.3617 $[M]^+$. $C_{42}H_{46}N_2O$. Calculated: M = 594.3610. IR, ν/cm^{-1}: 1625 (N=CH). ^{1}H NMR, δ: 1.38—1.88 (m, 28 H, CH_2); 3.47 (m, 2 H, CH); 6.85—7.23 (m, 8 H, H(3′)—H(6′)); 7.47 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.04 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.29 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.99 (s, 2 H, N=CH).

4,6-Bis(6-cyclooctyl-2-methylphenyliminomethyl)dibenzofuran (8b). The yield was 99%, m.p. 131—132 °C. HRMS, found: *m/z* 622.3923 $[M]^+$. $C_{44}H_{50}N_2O$. Calculated: M = 622.3926. IR, ν/cm^{-1}: 1638 (N=CH). ^{1}H NMR, δ: 1.30—1.85 (m, 28 H, CH_2); 2.11 (s, 6 H, Me); 2.93 (m, 2 H, CH); 6.82—7.05 (m, 6 H, H(3′)—H(5′)); 7.49 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.08 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.33 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.83 (s, 2 H, N=CH).

4,6-Bis(6-cyclooctyl-2,4-dimethylphenyliminomethyl)dibenzofuran (8c). The yield was 99%, m.p. 172—173 °C. Found (%): C, 84.76; H, 8.20; N, 4.23. $C_{46}H_{54}N_2O$. Calculated (%): C, 84.92; H, 8.31; N, 4.31. IR, ν/cm^{-1}: 1640 (N=CH). ^{1}H NMR, δ: 1.25—1.80 (m, 28 H, CH_2); 2.18, 2.25 (both s, 6 H each, Me); 2.90 (m, 2 H, CH); 6.76, 6.80 (both s, 2 H each, H(3′), H(5′)); 7.48 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 8.07 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.31 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.80 (s, 2 H, N=CH). MS, *m/z*: 650 $[M]^+$.

4,6-Bis(2-cyclopentylphenyliminomethyl)dibenzothiophene (9a). The yield was 96%, m.p. 211—212 °C. HRMS, found: *m/z* 526.2410 $[M]^+$. $C_{36}H_{34}N_2S$. Calculated: M = 526.2443. IR, ν/cm^{-1}: 1626 (N=CH). ^{1}H NMR, δ: 1.20—1.92 (m, 16 H, CH_2); 3.84 (m, 2 H, CH); 6.92—7.30 (m, 8 H, H(3′)—H(6′)); 7.59 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 7.81 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.35 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.54 (s, 2 H, N=CH).

4,6-Bis(6-cyclopentyl-2-methylphenyliminomethyl)dibenzothiophene (9b). The yield was 93%, m.p. 74—75 °C. HRMS, found: *m/z* 554.2790 $[M]^+$. $C_{38}H_{38}N_2S$. Calculated: M = 554.2776. IR, ν/cm^{-1}: 1635 (N=CH). ^{1}H NMR, δ: 1.15—1.95 (m, 16 H, CH_2); 2.17 (s, 6 H, Me); 3.12 (m, 2 H, CH); 6.90—7.19 (m, 6 H, H(3′)—H(5′)); 7.60 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 7.76 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.35 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.54 (s, 2 H, N=CH).

4,6-Bis(6-cyclopentyl-2,4-dimethylphenyliminomethyl)dibenzothiophene (9c). The yield was 95%, m.p. 86—87 °C. HRMS, found: *m/z* 582.3069 $[M]^+$. $C_{40}H_{42}N_2S$. Calculated: M = 582.3068. IR, ν/cm^{-1}: 1638 (N=CH). ^{1}H NMR, δ: 1.35—1.90 (m, 16 H, CH_2); 2.13, 2.27 (both s, 6 H each, Me); 3.13 (m, 2 H, CH); 6.80, 6.88 (both s, 2 H each, H(3′), H(5′)); 7.58 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 7.74 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.33 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.54 (s, 2 H, N=CH).

4,6-Bis(2,6-dicyclopentylphenyliminomethyl)dibenzothiophene (9d). The yield was 97%, m.p. 223—224 °C. Found (%): C, 83.50; H, 7.61; N, 4.79. $C_{46}H_{50}N_2S$. Calculated (%): C, 83.38; H, 7.55; N, 4.83. IR, ν/cm^{-1}: 1633 (N=CH). ^{1}H NMR, δ: 1.25—2.00 (m, 32 H, CH_2); 3.06 (m, 4 H, CH); 6.91—7.15 (m, 6 H, H(3′)—H(5′)); 7.60 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 7.76 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.37 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.51 (s, 2 H, N=CH). MS, *m/z*: 662 $[M]^+$.

4,6-Bis(2-cyclohexylphenyliminomethyl)dibenzothiophene (10a). The yield was 95%, m.p. 272—273 °C. HRMS, found: *m/z* 554.2752 $[M]^+$. $C_{38}H_{38}N_2S$. Calculated: M = 554.2756. IR, ν/cm^{-1}: 1624 (N=CH). ^{1}H NMR, δ: 1.05—1.95 (m, 20 H, CH_2); 3.24 (m, 2 H, CH); 6.93—7.20 (m, 8 H, H(3′)—H(6′)); 7.59 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 7.75 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.35 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.82 (s, 2 H, N=CH).

4,6-Bis(6-cyclohexyl-2-methylphenyliminomethyl)dibenzothiophene (10b). The yield was 96%, m.p. 196—197 °C. HRMS, found: *m/z* 582.3074 $[M]^+$. $C_{40}H_{42}N_2S$. Calculated: M = 582.3069. IR, ν/cm^{-1}: 1636 (N=CH). ^{1}H NMR, δ: 0.98—1.85 (m, 20 H, CH_2); 2.17 (s, 6 H, Me); 2.85 (m, 2 H, CH); 6.85—7.11 (m, 6 H, H(3′)—H(5′)); 7.60 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 7.74 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.35 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.55 (s, 2 H, N=CH).

4,6-Bis(6-cyclohexyl-2,4-dimethylphenyliminomethyl)dibenzothiophene (10c). The yield was 95%, m.p. 213—214 °C. HRMS, found: *m/z* 610.3387 $[M]^+$. $C_{42}H_{46}N_2S$. Calculated: M = 610.3382. IR, ν/cm^{-1}: 1634 (N=CH). ^{1}H NMR, δ: 1.01—1.83 (m, 20 H, CH_2); 2.14, 2.27 (both s, 6 H each, Me); 2.89 (m, 2 H, CH); 6.82, 6.86 (both s, 2 H each, H(3′), H(5′)); 7.60 (t, 2 H, H(2), H(8), *J* = 7.8 Hz); 7.76 (d, 2 H, H(1), H(9), *J* = 7.8 Hz); 8.37 (d, 2 H, H(3), H(7), *J* = 7.8 Hz); 8.53 (s, 2 H, N=CH).

4,6-Bis(2,6-dicyclohexylphenyliminomethyl)dibenzothiophene (10d). The yield was 95%, m.p. 278—279 °C. Found (%): C, 85.56; H, 8.20; N, 4.03. $C_{50}H_{58}N_2O$. Calculated (%): C, 85.47; H, 8.26; N, 3.99. IR, ν/cm^{-1}: 1632 (N=CH). ^{1}H NMR, δ: 0.95—1.85 (m, 40 H, CH_2); 2.73 (m, 4 H, CH); 6.92—7.30 (m, 6 H, H(3′)—H(5′)); 7.51 (t, 2 H, H(2), H(8), *J* = 7.8 Hz);

8.11 (d, 2 H, H(1), H(9), J = 7.8 Hz); 8.30 (d, 2 H, H(3), H(7), J = 7.8 Hz); 8.74 (s, 2 H, N=CH). MS, m/z: 702 $[M]^+$.

4,6-Bis(2-cyclooctylphenyliminomethyl)dibenzothiophene (11a). The yield was 93%, m.p. 229—230 °C. HRMS, found: m/z 610.3281 $[M]^+$. $C_{42}H_{46}N_2S$. Calculated: M = 610.3381. IR, ν/cm^{-1}: 1625 (N=CH). ^{1}H NMR, δ: 0.96—1.95 (m, 28 H, CH_2); 3.66 (m, 2 H, CH); 6.82—7.20 (m, 8 H, H(3′)—H(6′)); 7.60 (t, 2 H, H(2), H(8), J = 7.8 Hz); 7.82 (d, 2 H, H(1), H(9), J = 7.8 Hz); 8.35 (d, 2 H, H(3), H(7), J = 7.8 Hz); 8.68 (s, 2 H, N=CH).

4,6-Bis(6-cyclooctyl-2-methylphenyliminomethyl)dibenzothiophene (11b). The yield was 97%, m.p. 213—214 °C. HRMS, found: m/z 638.3686 $[M]^+$. $C_{44}H_{50}N_2S$. Calculated: M = 638.3694. IR, ν/cm^{-1}: 1637 (N=CH). ^{1}H NMR, δ: 1.10—1.85 (m, 28 H, CH_2); 2.14 (s, 6 H, Me); 3.14 (m, 2 H, CH); 6.89—7.12 (m, 6 H, H(3′)—H(5′)); 7.61 (t, 2 H, H(2), H(8), J = 7.8 Hz); 7.77 (d, 2 H, H(1), H(9), J = 7.8 Hz); 8.39 (d, 2 H, H(3), H(7), J = 7.8 Hz); 8.55 (s, 2 H, N=CH).

4,6-Bis(6-cyclooctyl-2,4-dimethylphenyliminomethyl)dibenzothiophene (11c). The yield was 98%, m.p. 170—171 °C. Found (%): C, 82.76; H, 8.18; N, 4.31. $C_{46}H_{54}N_2S$. Calculated (%): C, 82.88; H, 8.11; N, 4.20. IR, ν/cm^{-1}: 1634 (N=CH). ^{1}H NMR, δ: 1.15—1.82 (m, 28 H, CH_2); 2.11, 2.26 (both s, 6 H each, Me); 3.10 (m, 2 H, CH); 6.81, 6.83 (both s, 2 H each, H(3′), H(5′)); 7.60 (t, 2 H, H(2), H(8), J = 7.8 Hz); 7.76 (d, 2 H, H(1), H(9), J = 7.8 Hz); 8.37 (d, 2 H, H(3), H(7), J = 7.8 Hz); 8.53 (s, 2 H, N=CH). MS, m/z: 666 $[M]^+$.

References

1. H. Makio, N. Kashiwa, and T. Fujita, *Adv. Synth. Catal.*, 2002, 344; M. Mitani, J. Saito, S. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J. Mohri, R. Furuyama, H. Terao, H. Bando, H. Tanaka, and T. Fujita, *Chem. Rec.*, 2004, **4**, 137.
2. S. Matsui, M. Mitani, J. Saito, N. Matsukawa, H. Tanaka, T. Nakano, and T. Fujita, *Chem. Lett.*, 2000, **29**, 1263; J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojoh, N. Kashiwa, and T. Fujita, *Angew. Chem., Int. Ed.*, 2001, **40**, 2918; S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847; M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327.
3. N. I. Ivancheva, V. K. Badaev, I. I. Oleynik, S. S. Ivanchev, and G. A. Tolstikov, *Dokl. Akad. Nauk*, 2000, **374**, 648 [*Dokl. Chem.*, 2000 (Engl. Transl.)]; S. S. Ivanchev, G. A. Tolstikov, V. K. Badaev, N. I. Ivancheva, I. I. Oleynik, M. I. Serushkin, and I. V. Oleynik, *Vysokomolekulyar. Soedineniya, Ser. A*, 2001, **43**, 2053 [*Polym. Sci., Ser. A*, 2001, **43** (Engl. Transl.)]; Pat. RF 2194056; *Byul. Izobret.*, 2002, 34; S. S. Ivanchev, G. A. Tolstikov, V. K. Badaev, N. I. Ivancheva, I. I. Oleynik, S. Ya. Khaykin, and I. V. Oleynik, *Vysokomolekulyar. Soedineniya, Ser. A*, 2002, **44**, 1478 [*Polym. Sci., Ser. A*, 2002, **44** (Engl. Transl.)]; Pat. RF 2202559; *Byul. Izobret.*, 2003, 11.
4. G. J. P. Britovsek, V. C. Gibson, O. D. Hoarau, S. K. Spitzmesser, A. J. P. White, and D. J. Williams, *Inorg. Chem.*, 2003, **42**, 3454.
5. Y. Deng, C. J. Chang, and D. G. Nocera, *J. Am. Chem. Soc.*, 2000, **122**, 410; C. Kuehm-Caubère, S. Adach-Becker, Y. Fort, and P. Caubère, *Tetrahedron*, 1996, **52**, 9087.
6. Jpn Pat. 2001172273; *Chem. Abstrs*, 2001, **135**, 61746.
7. W. Zhang, L. Su, W.-H. Sun, and X. Jin, *J. Chem. Res. S*, 2003, 734.
8. I. I. Oleynik, I. V. Oleynik, I. B. Abdrakhmanov, S. S. Ivanchev, and G. A. Tolstikov, *Zh. Obshch. Khim*, 2004, **74**, 1534 [*Russ. J. Gen. Chem.*, 2004, **74** (Engl. Transl.)].

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