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Thermotropic liquid crystals based on ferrocenylbiphenyl and ferrocenylterphenyl

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4′-Ferrocenyl-1,1′-biphenyl-4-yl 4-alkoxybenzoates Fc–$(C_6H_4)_2$–OC(O)–C_6H_4–O–C_nH_{2n+1} (n=8, 10, 12) (**3a**–**c**), representing a new class of ferrocene-containing thermotropic mesogens with nematogenic properties, were prepared. Two approaches were used for the construction of these mesogens: (i) reaction of 4′-ferrocenyl-1,1′-biphenyl-4-ol with 4-alkoxybenzoylchlorides, and (ii) crosscoupling of tris(4-ferrocenylphenyl)boroxine with the corresponding halobenzenes. Crosscoupling was also applied for the synthesis of terphenyl-containing mesogens Fc–$(C_6H_4)_3$–OC(O)–C_6H_4–O–C_nH_{2n+1} (n=10, 12) (**6a,b**) and (RC_5H_4)Fe-[C_5H_4–$(C_6H_4)_3$–OC(O)–C_6H_4–O–$C_{10}H_{21}$] (**11a**, R=Et; **11b**, R=$n-$Bu). The latter compounds also form nematic phases. Mesogens **6a,b** form mesophases with wider temperature ranges than their biphenyl-containing counterparts **3b,c**. The most pronounced mesomorphism was displayed by compounds **11a** and **11b**, which have mesophases in the ranges 141–253°C and 120–238°C, respectively. The purity of compounds was established by ^{1}H NMR spectra and elemental analysis. Mesophases were identified by polarizing optical microscopy and differential scanning calorimetry.

1. Introduction

4,4′-Disubstituted-1,1′-biphenyl is a widely used building block for the construction of calamitic liquid crystals (LCs). Molecules of these LCs have rod-like shapes and contain different groups on opposite ends of a biphenyl system. The nature of these groups exerts a great influence on the properties of mesophases. In particular, the introduction of ferrocene, which is a bulky, easily polarizable moiety, often drastically changes the mesomorphic behavior of LCs.

In previous papers we have demonstrated that the synthesis of 4-derivatives of 4′-ferrocenyl[1,1′]biphenyl and of 4″-ferrocenyl[1″,4′:1′,1]terphenyl, considered by us as prospective precursors of LCs, can be accomplished by two approaches [1, 2].

One of these approaches, outlined in scheme 1, path 1, involves arylation of ferrocene by substituted biphenyldiazonium followed by modification of the *Q* group to introduce a flexible aliphatic chain on the arylferrocene. The second method, shown in scheme 1, path 2, involves crosscoupling of tris(4-ferrocenylphenyl)boroxine with the corresponding halobenzene (scheme 1, iii) or halobiphenyl (scheme 1, iv) derivatives (Suzuki reaction). In the present study, we have applied both of these approaches for the preparation of new LC materials incorporating ferrocenylbiphenyl and ferrocenylterphenyl moieties. The liquid crystalline properties of the ferrocenylbiphenyl and ferrocenylterphenyl derivatives are discussed and compared with the non-ferrocene-containing halobenzene and halophenyl compounds.

2. Synthesis

We used 4′-ferrocenyl-1,1′-biphenyl-4-ol (**2**) as a starting material for the preparation of mesogenic ferrocenylbiphenyl derivatives, which contain a rod-like part that is built up of three phenyl rings. Compound **2** was synthesized in 23% yield by arylation of ferrocene with 4-hydoxyl[1,1′]biphenyldiazonium-4′ tetrafluoroborate (**1**) in acetic acid media (scheme 2). Elongation of the rod-like segment of **2** and introduction of a flexible alkyl chain was accomplished by reaction of the lithium salt of **2** with 4-alkoxybenzoylchlorides. In this way we prepared esters **3a** and **3b**.

Previously, **3** was prepared by crosscoupling of 4-bromophenylferrocene and 4-hydroxyphenylboronic acid (33% yield) in the presence of a large amount of

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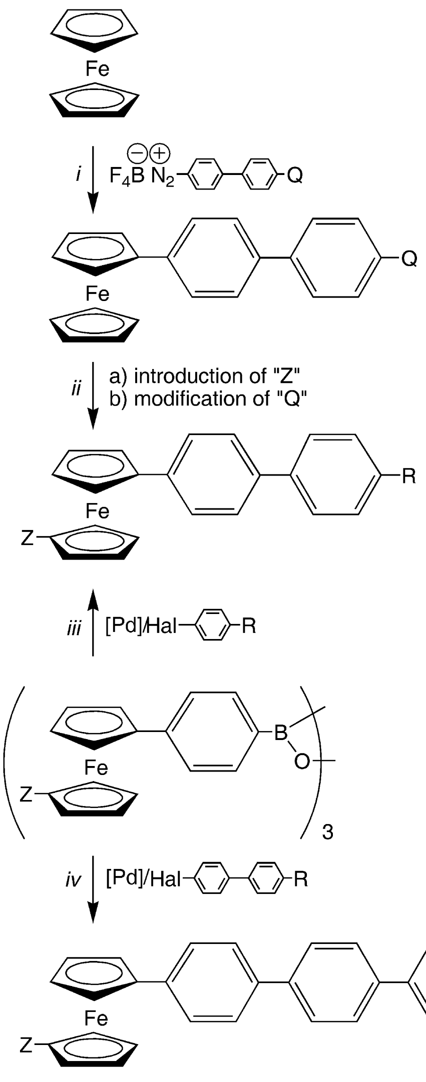


Scheme 1. Two general pathways for synthesis of ferrocenylbiphenyl and ferrocenylterphenyl complexes. Path 1: i + ii; Path 2: iii or iv; Q=OH, Br, CN, NO_2, NH_2; Z=H, acyl, alkyl; R=4-alkoxyphenyl moiety attached via CH=N, C(O)O or C(O)NH groups.

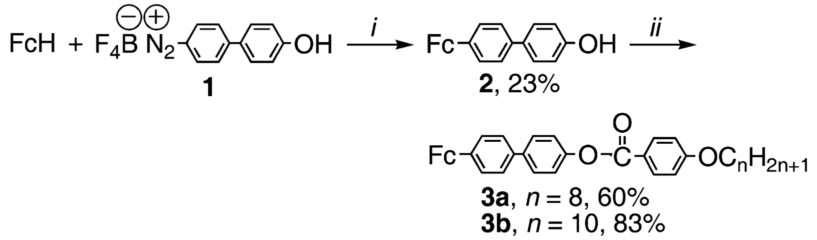
palladium catalyst (17 mol%) [3]. While arylation of ferrocene with the diazonium salt **1** is a reasonable alternative to crosscoupling, the low yield of the desired phenol motivated us to try an alternative method of preparation. Thus we carried out crosscoupling reactions of tris(4-ferrocenylphenyl)boroxine (**4**) and halobenzene derivatives, **5a–c**, possessing elongated rod-like shapes, favourable for the display of mesomorphism. Scheme 3 illustrates the conditions and yields of products in these crosscoupling reactions.

Crosscoupling of **4** with iodide **5a** proceeded successfully and gave the target compound in good yield, while reactions with the bromo derivatives **5b,c** were accompanied by the formation of side products in significant amounts (according to TLC data). This result agrees with the fact that iodobenzenes are more reactive in crosscoupling reactions than the corresponding bromides.

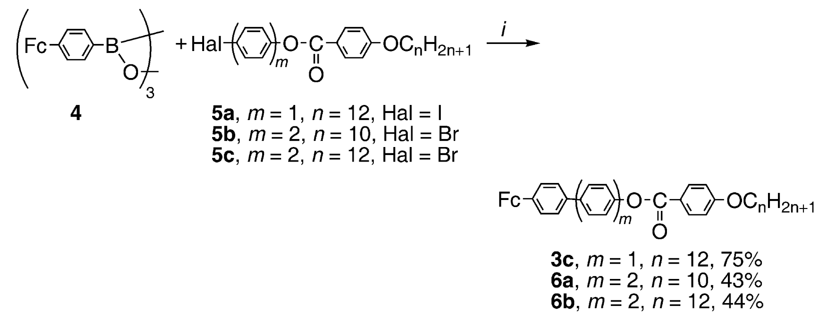
Crosscoupling of boron-containing reagents of type **4** with halobiphenyls is the best strategy for the synthesis of ferrocenylmesogens that contain a terphenyl moiety bound directly to ferrocenyl. It should be noted that crosscoupling reactions have been used for the preparation of ferrocenylbiphenyls but not mesogens [4]. This strategy is especially convenient for the preparation of many new compounds as prospective LC materials because boroxine **4** can be coupled with many different haloarenes.

We also made use of crosscoupling reactions for the preparation of 1,1′-disubstituted ferrocenes containing terphenyl groups. Ethyl and butyl groups were introduced on the second cyclopentadienyl ring in order to reduce the temperature of the transition between the crystalline phase and mesophase. Mesogenic ferrocene derivatives of this type are uncommon. In fact, only one representative of this structural type (related to 1′-alkylferrocenecarboxylic acid esters) was previously reported [5].

We prepared compounds **11a** and **11b** according to the synthetic route presented in scheme 4. The first step in the reaction sequence is acylation of bromide **7** with



Scheme 2. Synthesis of **3a,b**. i, (a) glacial acetic acid, (b) ascorbic acid/H_2O, Et_2O; ii, (a) n-BuLi, hexane, 0°C, (b) $ClC(O)C_6H_4O(CH_2)_nH_{2n+1}$, Et_2O, 20°C.

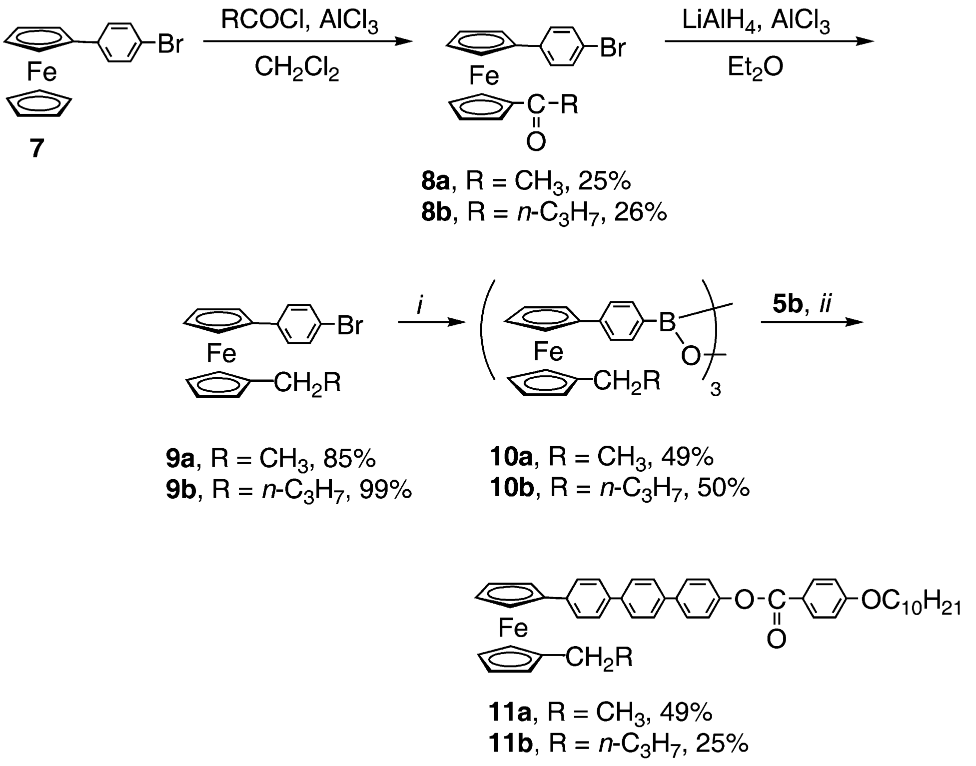


Scheme 3. Synthesis of **3c, 6a,b**. i, DMF, H_2O, K_2CO_3, 3.3–4.2% $Pd(PPh_3)_2Cl_2$, 65°C.

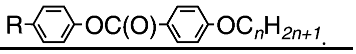
acyl chloride. This reaction gives the target ketones **8a** and **8b** in low yields. Nevertheless, such yields are good for this reaction because acylation of substituted ferrocenes usually proceeds with poor selectivity [6]. Transformation of **8a**,**b** into compounds **9** was accomplished by the use of $LiAlH_4$ in the presence of $AlCl_3$. This reductive system is especially good for conversion of bromine-containing ferrocenyl ketones into the corresponding alkylferrocenes because it does not cause reductive debromination [7]. Boroxines **10a** and **10b** were prepared in the same manner that we previously applied for the synthesis of boroxine **4** [2]. Finally, the crosscouplings of compounds **10** were carried out analogously to the preparation of terphenyl derivatives **6a**,**b**.

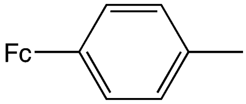
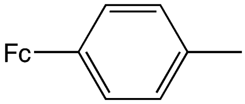
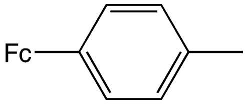
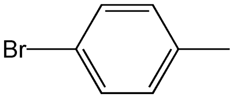
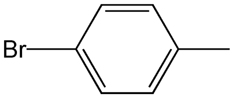
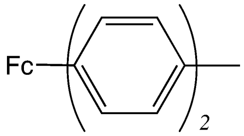
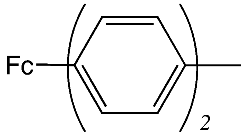
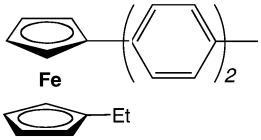
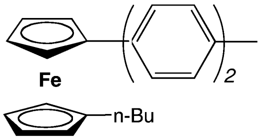
3. Liquid crystalline properties

Investigations of the thermal behaviour of compounds **3a–c, 5a–c** and **6a,b** by polarizing optical microscopy (POM) revealed that they all form mesophases. Temperatures of the phase transitions and types of mesophases are presented in table 1. Representative structures of molecules from each series are shown in figure 1. The transition temperatures for the ferrocene-mesogens **3a, 3c, 6a, 6b** and **11a**, determined by POM,



Scheme 4. Synthesis of **11a,b**. i, (a) *n*-BuLi, THF/Et_2O, −50°C, (b) $B(OBu)_3$, (c) HCl/H_2O; ii, DMF, H_2O, K_2CO_3, 3.3 % $Pd(PPh_3)_2Cl_2$, 65°C.

Table 1. Thermal properties of compounds **3a–c, 5a–c, 6a,b** and **11 a,b** with general formula: 

			POM phase transition temperatures/°C		DSC phase transition temperatures/°C	
Compound	*R*	*n*	cooling from isotropic melts[a]	mesophase range, ΔT	heating (ΔH/kJ mol^{-1})	cooling (ΔH/kJ mol^{-1})
3a		8	Cr 154 N N 161 I	7	K 156 N (46.7) N 163 I (2.1)	—
3b		10	Cr 148 N N 155 I	7	—	—
3c		12	K 133 N N 148 I	15	K 135 N (66) N 149 I (2.4)	K 123 N (25.6) N 149 I (2.5)
5a[b]	I	12	K 85 I I (84 SmA)[c] Cr	−1	—	—
5b		10	S_A 205 I	[d]	—	—
5c		12	S_x 201 I	[d]	K 104 S_x (45.9) S_x 204 I (7.3)	K 65 S_x (20.2) S_x 96 S_{xc} (1.9) S_x 199 I (7.0)
6a		10	K 204 N N 270 I	66	K 209 N (38.5) decomposes >250	—
6b		12	K 202 N N 262 I	60	Cr 117 Cr_2 (20.5) K_2 175 K_3 (5.2) K_3 210 N (26.9) decomposes >250	K 172 K_2 (2.6) K_2 191 K_3 (3.0) K_3 197 N (8.3)
11a		10	K 141 LC LC 253 I	112	K 136 K_2 (13.1) K_2 145 S_x (28.7) S_x 159 N (1.0) decomposes >250	K 117 S_x (19.2) S_x 154 N (0.8)
11b		10	K 120 Sx Sx 161 N N 238 I	41(smectic) 77(nematic)	—	—

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[a] Scan rate, 10° min^{-1} except **3a** which was 2° min^{-1}. [b] This compound was prepared previously [8]. [c] Monotropic transition. [d] Mesophase exists to room temperature.

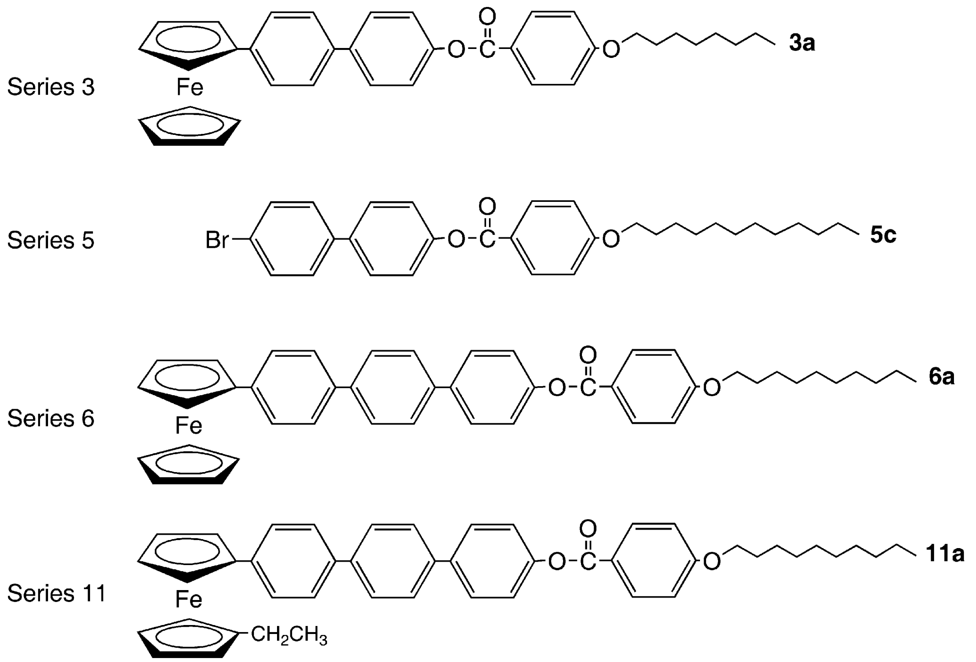

Figure 1. Representative structures of molecules from series **3**, **5**, **6** and **11**.

were confirmed by differential scanning calorimetry (DSC); the corresponding transition enthalpies are included in table 1. Haloarenes **5a–c** form smectic phases. In the case of the iodo-derivative **5a** this was established by observing a fan texture that is characteristic for smectics.

Cooling of isotropic melts of bromobiphenyls **5b,c** from 205 and 201°C, respectively, leads to enantiotropic LC phases with oily streak textures and homeotropic domains that are typical for smectic mesophases. Cooling of the mesophases to room temperature (about 25°C) did not lead to crystallization of samples **5b** and **5c**, so the Cr→Sm transition temperatures were not determined by POM. The significant difference in thermal properties between **5a** and **5b,c** is probably caused by the different lengths of the rod-like segments in these compounds. The longer biphenyl segment in **5b** and **5c** causes higher clearing temperatures and more pronounced mesomorphism for **5b** and **5c**. A similar situation is observed for ferrocene-containing derivatives of biphenyl, **3a–c**, compared with the corresponding terphenyl derivatives, **6a**,**b** (see table 1).

All ferrocenylmesogens investigated give enantiotropic nematic phases with schlieren or marble textures. For biphenyl derivatives **3a–c**, as the length of the alkyl chain increases there is a monotonic decrease in the phase transition temperatures and an increase in the mesophase temperature range. This phenomenon is quite common for a homological series of ferrocene-containing LC compounds [9].

Compounds **3b,c** and **5b,c** contain the same rod-like fragment and differ from each other only in the terminal substituent (ferrocenyl moiety or bromine atom) but their thermal behaviours are quite different. Ferrocene-containing LCs **3b,c** exhibit different types of mesophases, drastically reduced mesophase temperature ranges and lower phase transition temperatures. The influence of the ferrocene moiety is probably a consequence of its great volume [4, 10]. Smectic layers of molecules **5b,c** are formed due to intermolecular π–π interactions between the phenyl rings and weaker van der Waals interactions between the alkyl chains. The bulky ferrocenyl group hinders formation of these layers, and derivatives **3b,c** give only nematic phases.

Terphenyl derivatives **6a,b** contain an extra phenyl ring compared with analogues **3b,c**, i.e. **6a,b** have longer rod-like portions and consequently their mesophases have wider temperature ranges and the phase transition temperatures also rise significantly. Thus, the presence of three phenyl rings in the organic core of ferrocenylmesogens is favourable for stabilizing the nematic phase, which is in agreement with results published previously [4, 10]. Another important property of compounds **6a,b** is their high thermal stability. This is also in agreement with previously reported mesogens based on monosubstituted ferrocenes containing the same number of phenyl rings, which decompose at temperatures above 250°C [4].

The data in table 1 demonstrate that an increase of the alkyl chain length, when going from compound **6a** to homologue **6b**, causes only a small decrease in the melting and clearing temperatures. As far as mesogenic properties are concerned, it is very important to achieve a decrease of the Cr→N transition temperature. Accordingly, we modified molecule **6a** by introducing flexible ethyl and butyl groups in the unsubstituted Cp ring of this structure to obtain compounds **11a** and **11b**. These compounds give nematic mesophases, which were identified by characteristic marble and schlieren textures. Furthermore, modification of the second Cp ring as mentioned above, gives rise to smectogenic mesomorphism for **11a** and **11b**.

We hypothesized that compounds **11a** and **11b** would undergo phase transitions at lower temperatures in comparison with compound **6a** that has no ethyl or butyl group. As expected, the first liquid crystalline phase transition for **11a** takes place at 141°C and for **11b** at 120°C, compared with 204°C for **6a**. This large decrease of the Cr→LC transition temperature leads to a wider mesophase temperature range for **11a** and **11b** than for **6a** in spite of the relatively small change in the clearing temperature.

The results reveal that ferrocene derivatives containing a terphenyl moiety show more remarkable mesogenic properties than do their counterparts that contain biphenyl cores. It should be noted that the presence of the ferrocene moiety in mesogens plays an important role in their thermal behaviour. This moiety promotes formation of the nematic phase. In addition, the presence of ferrocene provides new opportunities for effective regulation of the phase transition temperatures and the width of the mesophase temperature range by modification of the unsubstituted Cp ring.

4. Experimental

4-Decyloxy- and 4-dodecyloxy-benzoylchlorides [11], 4′-amino-1,1′-biphenyl-4-ol [12] and tris(4-ferrocenylphenyl)boroxine (**4**) [2] were prepared according to published procedures. 4′-Bromo-1,1′-biphenyl-4-ol was purchased from Aldrich. Aluminum chloride was sublimed avoiding moisture. All solvents were purified by standard methods: ether and THF, by use of sodium ketyl; hexane and petroleum ether, by distillation over sodium; and methylene chloride and chloroform were successively washed with sulphuric acid and water, dried over $MgSO_4$ and distilled over phosphorus pentoxide.

Crosscoupling reactions, synthesis of 4′-ferrocenyl-1,1′-biphenyl-4-ol (**2**), and experiments using *n*-butyllithium were performed with an Ar purge. When necessary, compounds were purified by column chromatography on Al_2O_3 (activity II by Brockmann). Monitoring of the reactions was performed by TLC on 'Silufol' sheets. Phase transition temperatures of the mesogenic compounds are presented in table 1.

^1H NMR spectra were obtained on a Varian VXR-400 spectrometer (400 MHz). Chloroform-d was used as a solvent. POM data were obtained by using a Polam P-211 microscope (LOMO, Russia) supplied with a Mettler FP 80 hotstage. Samples were heated quickly into the isotropic phase. The isotropic sample was then cooled at a rate of approximately $10°C\,min^{-1}$. Formation of liquid crystalline phases followed by transformation into the crystal phase were observed. DSC data were recorded by a Mettler DSC 20 instrument. The heating and cooling rate for the DSC experiments was $10°C\,min^{-1}$. Elemental analyses were performed in the Organic Microanalysis Laboratory of MSU (Chem. Dept.).

4.1. *4-Hydroxy[1,1′]biphenyldiazonium-4′ tetrafluoroborate, 1*

A mixture of 4′-amino-1,1′-biphenyl-4-ol (1.36 g, 7.3 mmol), hydrochloric acid (36%, 10 ml) and water (35 ml) was heated under reflux for 5 min. An additional amount of water (55 ml) was added and the mixture was cooled to 3°C. Then a solution of sodium nitrite (0.69 g, 10 mmol) in water (5 ml) was added dropwise to the stirred reaction mixture at 3°C. Stirring was continued for 30 min at 3°C followed by addition of an aqueous solution of ammonium tetrafluoroborate (1.05 g, 10 mmol). After 30 min of stirring, the diazonium salt was filtered off, dried in air and dissolved in acetone (50 ml). The acetone solution was filtered, and pure diazonium salt precipitated by addition of ether. Compound **1** (1.16 g, 55%) was obtained as a yellow–brown crystalline powder (decomp. >118°C). Calculated for $C_{12}H_9BF_4N_2O$., C 50.75, H 3.19, N 9.86; found, C 50.46, H 3.11, N 9.99%.

4.2. *4′-Ferrocenyl[1,1′]biphenyl-4-ol, 2*

Diazonium salt **1** (0.60 g, 2.1 mmol) was added to a stirred solution of ferrocene (0.59 g, 3.2 mmol) in glacial acetic acid (40 ml). The reaction mixture was stirred for 3 h at room temperature and left for 12 h without stirring. Then an aqueous solution of ascorbic acid (1.2 g) and ether (100 ml) were added to the mixture. The organic layer was separated, washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo*. The residue was subjected to chromatography on Al_2O_3 (column: *l* 15 cm, *d* 2.5 cm). Ferrocene was eluted with petroleum ether; crude **2** was eluted with a 3/2 petroleum ether/Et_2O mixture. After crystallization from aqueous ethanol (12 ml of EtOH and 4 ml of water) **2** was obtained (0.17 g, 23%), m.p. 173–175°C (cf.

m.p. 172–174°C [13]). ^{1}H NMR, δ: 4.05 (s, 5 H, C_5H_5); 4.31 (m, 2 H); 4.65 (m, 2 H); 4.90 (s, 1 H, OH); 6.89 (m, 2 H); 7.46–7.51 (m, 6 H).

4.3. *4′-Ferrocenyl[1,1′]biphenyl-4-yl 4-decyloxybenzoate, 3b*

2.5 N *n*-Butyllithium (0.23 ml, 0.6 mmol) in hexane was added to an ice-cold solution of **2** (0.16 g, 0.45 mmol) in Et_2O (28 ml). The resulting suspension of the lithium salt was stirred for 20 min, then a solution of 4-decyloxybenzoyl chloride (0.19 g, 0.64 mmol) in Et_2O (5 ml) was added. The cooling bath was removed and the reaction mixture stirred for 3 h at 20°C, then left for 12 h without stirring. The resulting mixture was poured into water, and benzene was added. The organic layer was separated, washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue recrystallized from $CHCl_3$/petroleum ether (at –3°C). Compound **3b** (0.23 g, 83%) was obtained as a light yellow, fine crystalline powder. Calculated for $C_{39}H_{42}FeO_3$, C 76.22, H, 6.89, Fe, 9.09; found, C 76.38, H 6.72, Fe 9.24%. ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3), 1.29 (m, 12 H, $(CH_2)_6$), 1.47 (m, 2 H), 1.81 (m, 2 H), 4.04 (t, 2 H, OCH_2), 4.06 (s, 5 H, C_5H_5), 4.32 (m, 2 H), 4.66 (m, 2 H), 6.97 (m, 2 H), 7.26 (m, 2 H), 7.52 (m, 4 H), 7.64 (m, 2 H), 8.15 (m, 2 H).

4.4. *4′-Ferrocenyl[1,1′]biphenyl-4-yl 4-octyloxybenzoate, 3a*

This compound was prepared in 60% yield by the synthetic procedure used for the preparation of **3b**. Calculated for $C_{37}H_{38}FeO_3$, C 75.77, H 6.53; found, C 75.50, H 6.38%. ^{1}H NMR, δ: 0.87 (t, 3 H, CH_3), 1.29 (m, 8 H, $(CH_2)_4$), 1.47 (m, 2 H), 1.81 (m, 2 H), 4.04 (t, 2 H OCH_2), 4.06 (s, 5 H, C_5H_5), 4.33 (m, 2 H), 4.67 (m, 2 H), 6.97 (m, 2 H), 7.26 (m, 2 H), 7.52 (m, 4 H), 7.64 (m, 2 H), 8.15 (m, 2 H).

4.5. *4-Iodophenyl 4-dodecyloxybenzoate, 5a*

4-Iodophenol (0.66 g, 3 mmol), 4-dodecyloxybenzoyl chloride (1.95 g, 6 mmol) and pyridine (1.5 ml,18 mmol) were dissolved in methylene chloride (20 ml). This solution was heated under reflux for 11 h, and then water and CH_2Cl_2 were added. The organic layer was separated, washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo*. The residue was subjected to chromatography on Al_2O_3 (column: *l* 15 cm, *d* 2.5 cm); a mixture of benzene and petroleum ether (1/1) was used as eluant. The solvent was removed *in vacuo*, and crystallization of the residue from petroleum ether (b.p. 70–100°C, 30 ml) gave 1.19 g (78%) of compound **5a** as colourless needles. ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3), 1.26 (m, 16 H, $(CH_2)_8$), 1.46 (m, 2 H), 1.81 (m, 2 H), 4.03 (t, 2 H. OCH_2), 6.94–6.99 (m, 4 H), 7.69–7.73 (m, 2 H), 8.08–8.12 (m, 2 H).

4.6. *4′-Bromo[1,1′]biphenyl-4-yl 4-dodecyloxybenzoate, 5c*

4′-Bromo-1,1′-biphenyl-4-ol (0.40 g, 1.6 mmol), 4-dodecyloxybenzoyl chloride (1.04 g, 3.2 mmol) and pyridine (0.77 ml, 9.6 mmol) were dissolved in methylene chloride (15 ml). This solution was heated under reflux for 9 h, and then water and CH_2Cl_2 (90 ml) were added. The organic layer was separated, washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the residue recrystallized from petroleum ether, b.p. 70–100°C (55 ml). Compound **5c** (0.71 g, 82%) was obtained as a white powder. Calculated for $C_{31}H_{37}BrO_3$, C 69.27, H 6.94; found, C 69.14, H 6.91%. ^{1}H NMR, δ: 0.87 (t, 3 H, CH_3), 1.26 (m, 16 H, $(CH_2)_8$), 1.46 (m, 2 H), 1.81 (m, 2 H), 4.03 (t, 2 H, OCH_2), 6.96 (m, 2 H), 7.26 (m, 2 H), 7.43 (m, 2 H), 7.54–7.58 (m, 4 H), 8.14 (m, 2 H).

4.7. *4′-Bromo[1,1′]biphenyl-4-yl 4-decyloxybenzoate, 5b*

The synthesis of this substance was carried out as described for compound **5c**. After two crystallizations from petroleum ether, the yield of **5b** was 65%. Calculated for $C_{29}H_{33}BrO_3$, C 68.37, H 6.53; found, C 68.33, H 6.37%. ^{1}H NMR, δ: 0.87 (t, 3 H, CH_3), 1.27 (m, 12 H, $(CH_2)_6$), 1.46 (m, 2 H), 1.81 (m, 2 H), 4.03 (t, 2 H, OCH_2), 6.96 (m, 2 H), 7.26 (m, 2 H), 7.43 (m, 2 H), 7.54–7.58 (m, 4 H), 8.14 (m, 2 H).

4.8. *4″-Ferrocenyl[1″,4′:1′,1]terphenyl-4-yl 4-decyloxybenzoate, 6a*

In a Schlenk flask $Pd(PPh_3)_2Cl_2$ (0.0173 g, 0.025 mmol), **4** (0.17 g, 0.2 mmol), **5b** (0.31 g, 0.6 mmol), potassium carbonate (0.22 g), water (1.5 ml) and DMF (7 ml) were placed in succession. This mixture was stirred at 60–70°C (water bath) for 2 h. The reaction mixture gradually turned yellow–brown and palladium black formed. After the appearance of palladium black, the mixture was stirred for another 1.5 h, and was then cooled to room temperature and poured into water. The precipitate (the product of the crosscoupling reaction) was extracted with methylene chloride (50 ml). The organic layer was separated, washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo*. The residue was purified by chromatography on Al_2O_3 (column: *l* 15 cm, *d* 2.5 cm). A petroleum ether/benzene (3/1) mixture was used as eluant. In the process of chromatography three yellow bands were formed. After the first band was eluted and discarded, the elution was continued with a 1/1 mixture of petroleum ether/benzene. The second fraction was also discarded. The main and third fraction was eluted with benzene. From this latter fraction, 0.21 g of substance was isolated. Recrystallization from a mixture of CH_2Cl_2 and MeOH at −3°C gave 0.18 g (43%) of compound **6a**. Calculated for $C_{45}H_{46}FeO_3$, C 78.25, H 6.71; found, C 78.15, H 7.00%. ^{1}H NMR, δ: 0.87 (t, 3 H, CH_3), 1.28 (m, 12 H, $(CH_2)_6$), 1.49 (m, 2 H), 1.81 (m, 2 H), 4.04 (t, 2 H, OCH_2), 4.25 (s, 5 H, C_5H_5), 4.57 (m, 2 H), 4.93 (m, 2 H), 6.97 (m, 2 H), 7.30 (m, 2 H), 7.38 (m, 2 H), 7.52 (m, 2 H), 7.66 (m, 6 H), 8.15 (m, 2 H).

4.9. *4″-Ferrocenyl[1″,4′:1′,1]terphenyl-4-yl 4-dodecyloxybenzoate, 6b*

In a Schlenk flask $Pd(PPh_3)_2Cl_2$ (0.020 g, 0.028 mmol), **4** (0.18 g, 0.2 mmol), **5c** (0.36 g, 0.7 mmol), potassium carbonate (0.22 g), water (1.5 ml) and DMF (9.5 ml) were placed in succession. The crosscoupling reaction and isolation of the product were carried out according to the procedure described for the synthesis of **6a**. After recrystallization from a mixture of CH_2Cl_2 and EtOH at –3°C, compound **6b** (0.20 g, 44%) was obtained. Calculated for $C_{47}H_{50}FeO_3$, C 78.54, H 7.01; found, C 78.69, H 6.96%. ^{1}H NMR, δ: 0.87 (t, 3 H, CH_3), 1.26 (m, 16 H, $(CH_2)_8$), 1.47 (m, 2 H), 1.81 (m, 2 H), 4.04 (t, 2 H, OCH_2), 4.14 (s, 5 H, C_5H_5), 4.42 (m, 2 H), 4.77 (m, 2 H), 6.97 (m, 2 H), 7.28 (m, 2 H), 7.49 (m, 2 H), 7.54 (m, 2 H), 7.66 (m, 6 H), 8.15 (m, 2 H).

4.10. *4′-Ferrocenyl-1,1′-biphenyl-4-yl 4-dodecyloxybenzoate, 3c*

In a Schlenk flask $Pd(PPh_3)_2Cl_2$ (0.0143 g, 0.02 mmol), **4** (0.173 g, 0.2 mmol), **5a** (0.305 g, 0.6 mmol), potassium carbonate (0.22 g), water (1.5 ml) and DMF (8.5 ml) were placed in succession. The reaction was carried out according to the procedure described for compound **6a**. The product was extracted from the reaction mixture with CH_2Cl_2. The extract was washed with water, and evaporation of the methylene chloride afforded 0.38 g of a yellow powder. TLC of the powder showed that only one compound was present, so the product was purified by a single crystallization from a mixture of CH_2Cl_2 and petroleum ether at −3°C. The yield of compound **3c** was 0.29 g (75%). Calculated for $C_{41}H_{46}FeO_3$, C 76.63, H 7.21; found, C 76.73, H 7.32%. ^{1}H NMR, δ: 0.87 (t, 3 H, CH_3), 1.26 (m, 16 H, $(CH_2)_8$), 1.47 (m, 2 H), 1.81 (m, 2 H), 4.04 (t, 2 H, OCH_2), 4.08 (s, 5 H, C_5H_5), 4.35 (m, 2 H), 4.70 (m, 2 H), 6.97 (m, 2 H), 7.26 (m, 2 H), 7.50 (m, 4 H), 7.63 (m, 2 H), 8.15 (m, 2 H).

4.11. *4-Bromophenylferrocene, 7*

A mixture of 4-bromoaniline (5.0 g, 0.029 mol), water (40 ml) and conc. H_2SO_4 (8 ml) was heated to boiling. The resulting solution of the anilinium salt was cooled to 4°C and then a solution of sodium nitrite (2.4 g, 0.035 mol) in water (10 ml) was added dropwise. The solution of diazonium salt was filtered and urea (0.4 g) added to the filtrate. This filtrate was added during 30 min to a stirred, cold (+5°C) solution of ferrocene (5.4 g, 0.029 mol) in a mixture of glacial acetic acid (120 ml) and 1,2-dichloroethane (30 ml) containing AcONa•3H_2O (2.5 g). Stirring was continued at 20°C for an additional 1.5 h and the reaction mixture was left at 20°C overnight, then poured into 300 ml of water. Chloroform (40 ml) was added, the organic layer was separated and the water layer extracted with chloroform (4 × 30 ml). The combined organic layers were dried over $MgSO_4$ and filtered; the filtrate was evaporated *in vacuo*. The oily residue was subjected to steam distillation, which removed an excess of ferrocene and volatile organic admixtures. The non-volatile residue was dried in air and crude **7** was extracted from the residue with petroleum ether (6 × 50 ml). After removal of the solvent *in vacuo*, the remaining **7** was purified by column chromatography on Al_2O_3 (column: *l* 18 cm, *d* 2.5 cm; petroleum ether eluant). The eluate was evaporated to dryness *in vacuo* and the residue was recrystallized from methanol (about 120 ml). Compound **7** was obtained (2.3 g, 23%) as orange crystals, m.p. 122–124°C (m.p.121–123°C [14]). ^{1}H NMR, δ: ppm): 4.03 (s., 5H), 4.32 (m., 2H), 4.60 (m., 2H), 7.33 (m., 2H), 7.39 (m., 2H).

4.12. *1-Acetyl-1′-(4-bromophenyl)ferrocene, 8a*

Aluminum chloride (0.80 g, 6 mmol) was added to a solution of acetyl chloride (0.26 ml, 0.28 g, 3.6 mmol) in CH_2Cl_2 (10 ml). This mixture was stirred for 20 min, and then a solution of **7** (1.02 g, 3 mmol) in CH_2Cl_2 (25 ml) was added. The reaction mixture was stirred for 6 h and left for 12 h without stirring; it was then poured onto ice. Methylene chloride and hydrochloric acid were then added, and the organic layer was separated, washed with water and dried over $MgSO_4$. The organic solution was evaporated *in vacuo* to dryness, and the residue subjected to chromatography on Al_2O_3 (column: *l* 15.5 cm, *d* 2.5 cm). Unreacted starting material **7** (0.046 g, 4.5% of the initial amount) was eluted with petroleum ether. The crude compound **8a** was eluted with a mixture of petroleum ether and benzene (1/1). Recrystallization of the oily product (0.41 g) from petroleum ether, b.p. 70–100°C (25 ml) gave pure **8a** (0.29 g, 25%) as fine needles, m.p. 99–101°C (cf. 97–98°C [6]). Calc. for $C_{18}H_{15}BrFeO$, C 56.44, H

3.95; found, C 56.79, H 3.89%. ^{1}H NMR, δ: 2.14 (s, 3 H, CH_3), 4.35 (m, 4 H), 4.61 (m,4 H), 7.27–7.30 (m, 2 H), 7.42–7.44 (m, 2 H).

4.13. *1-Butanoyl-1′-(4-bromophenyl)ferrocene, 8b*

This compound was prepared analogously to compound **8a**. From **7** (3.41 g, 0.01 mol), butanoyl chloride (1.28 g, 0.012 mol) and aluminum chloride (2.66 g, 0.02 mol) in CH_2Cl_2 (30 ml), **8b** (1.06 g, 26%) was obtained as red–orange brilliant plates, m.p. 97–99°C (from methanol/water 5/1). Calculated for $C_{20}H_{19}BrFeO$, C 58.43, H 4.66; found, C 58.40, H 4.25. ^{1}H NMR, δ (ppm, *J*/Hz): 0.93 (t, 3 H, CH_3, ^3J=8), 1.60 (m, 2H, CH_3CH_2), 2.41 (t, 2H, ^3J=6, $CH_3CH_2CH_2$), 4.33–4.35 (m, 4 H), 4.61–4.62 (m, 4 H), 7.27–7,29 (m, 2 H), 7.41–7.43 (m, 2 H).

4.14. *1-(4-Bromopheny)-1′-ethylferrocene, 9a*

Aluminum chloride (0.16 g, 0.0012 mol) was added to a suspension of $LiAlH_4$ (assay 85%, 0.07 g, 0.0015 mol) in diethyl ether (10 ml). This mixture was stirred for 10 min, and then a solution of **8a** (0.44 g, 0.0011 mol) in ether (35 ml) was added dropwise to the stirred mixture during 10 min. After addition was complete, the reaction mixture was stirred with reflux for 40 min. Water was added, and the organic layer was separated, washed with water and dried over Na_2CO_3. The organic solution was filtered and evaporated *in vacuo* to dryness to give 0.36 g (85%) of **9a** as an orange oil, which gradually transformed to a crystalline mass. Calc. for $C_{18}H_{17}BrFe$, C 58.58, H 4.64; found, C 58.46, H 4.56%. ^{1}H NMR, δ: 1.06 (t, 3 H, CH_3, ^3J=6 Hz), 2.16 (quartet, 2 H, CH_2, ^3J=8 Hz), 3.92 (m, 4 H), 4.29 (m, 2 H), 4.55 (m, 2 H), 7.29–7.31 (m, 2 H), 7.37–7.39 (m, 2 H).

4.15. *1-(4-Bromopheny)-1′-butylferrocene, 9b*

This compound was prepared analogously to compound **9a**. From **8b** (1.11 g, 0.0027 mol), $LiAlH_4$ (assay 85%, 0.15 g, 0.0034 mol), aluminum chloride (0.36 g, 0.0027 mol) and ether (10 ml), **9b** (1.06 g, 99%) was obtained as an orange oil which gradually crystallized. Calc. for $C_{20}H_{21}BrFe$, C 60.49, H 5.33; found, C 60.48, H 5.22%. ^{1}H NMR, δ (ppm, *J*/Hz): 0.86 (t, 3 H, CH_3, ^3J=8), 1.25 (m, 2 H, $CpCH_2CH_2CH_2$), 1.36 (m, 2H, $CpCH_2CH_2$), 2.10 (t, 2H, $CpCH_2$, ^3J=6), 3.90–3.92 (m, 4 H), 4.27 (m, 2 H), 4.54 (m, 2 H), 7.29–7.31 (m, 2 H), 7.37–7.39 (m, 2 H).

4.16. *Tris[4-(1′-ethylferrocenyl)phenyl]boroxine, 10a*

A 2.6N solution of *n*-butyllithium (0.9 ml, 2.3 mmol) in hexane was added to a stirred solution of **9a** (0.72 g, 2 mmol) in a mixture of THF (15 ml) and Et_2O (10 ml) at −55°C. The reaction mixture was stirred at this temperature for 40 min, then tributylborate (0.6 ml, 0.51 g, 2.2 mmol) was added. The solution was allowed to warm gradually to 20°C, and mixed with water and a solution of conc. hydrochloric acid (3 ml) in water (30 ml). The organic layer was separated, diluted with benzene (20 ml), and washed with water to remove excess acid. The organic solution was dried over Na_2SO_4 and filtered. The solvent was removed *in vacuo*, and the residue treated with petroleum ether (15 ml). A coloured solution was discarded, and the solid residue was treated three times with petroleum ether (10 ml). The resulting powder was recrystallized from a mixture of CH_2Cl_2 and hexane to give 0.30 g (49%) of **10a** as orange–red needles. Calc. for $C_{54}H_{51}B_3Fe_3O_3$, C 68.42, H 5.42; found, C 68.59, H 5.02%. ^{1}H NMR, δ (ppm, *J*/Hz): 1.07 (t, 3 H, CH_3, ^3J=8), 2.18 (quartet, 2 H, CH_2, ^3J=8), 3.95 (m, 4 H), 4.35 (m, 2 H), 4.70 (m, 2 H), 7.59–7.61 (m, 2 H), 8.16–8.18 (m, 2 H).

4.17. *Tris[4-(1′-butylferrocenyl)phenyl]boroxine, 10b*

This compound was prepared analogously to compound **10a**. From **9b** (0.99 g; 0.0025 mol), **10b** (0.43 g; 50%) was obtained as an orange powder. Calculated for $C_{60}H_{63}B_3Fe_3O_3$ (%): C, 69.82; H, 6.15. Found (%): C, 69.87; H, 6.35. ^{1}H NMR, δ (ppm, *J*/Hz): 0.87 (t, 3 H, CH_3, ^3J=6), 1.27 (m, 2H, CH_3CH_2), 1.39 (m, 2H, $CH_3CH_2CH_2$), 2.14 (t, 2 H, Cp-CH_2, ^3J=6), 3.93–3.96 (m, 4 H), 4.35 (m, 2 H), 4.70 (m, 2 H), 7.59–7.61 (m, 2 H), 8.16–8.18 (m, 2 H).

4.18. *4″-(1′-Ethylferrocenyl) [1″,4′:1′,1]terphenyl-4-yl 4-decyloxybenzoate, 11a*

In a Schlenk flask, $Pd(PPh_3)_2Cl_2$ (0.020 g, 0.029 mmol), **10a** (0.19 g, 0.2 mmol), **5b** (0.31 g, 0.6 mmol), potassium carbonate (0.23 g), water (1.5 ml) and DMF (8.5 ml) were placed in succession. The crosscoupling reaction and isolation of the product were performed according to the procedure described for the synthesis of **6a**. Water was added to the reaction mixture and the crosscoupling product was extracted with CH_2Cl_2. After evaporation of the solvent *in vacuo* a yellow powder was obtained. This substance was subjected to chromatography on SiO_2 (column: *l* 5 cm, *d* 2 cm). A mixture of petroleum ether and benzene (1/1) was used for the elution of the first yellow fraction that was discarded. Elution of a second orange fraction was carried out with a mixture of petroleum ether and 1,2-dichloroethane (1/1). The substance isolated from the last fraction was dissolved in hot 1,2-dichloroethane (10 ml). Ethanol (60 ml) was added to the solution in dichloroethane causing precipitation of compound **11a** (0.21 g, 49%). Calc. for $C_{47}H_{50}FeO_3$, C 78.54, H, 7.01; found, C 78.83, H 6.79%. ^1H NMR, δ (ppm, J/Hz): 0.89 (t, 3 H, CH_3, $^3J=8$), 1.08 (t, 3 H, Cp–CH_2–CH_3, $^3J=8$), 1.28 (m, 12 H, $(CH_2)_6$), 1.48 (m, 2 H), 1.83 (quintet, 2 H, $^3J=8$), 2.20 (quartet, 2 H, Cp–CH_2–CH_3, $^3J=8$), 3.96–3.97 (m, 4 H), 4.05 (t, 2 H, OCH_2, $^3J=8$), 4.31 (m, 2 H), 4.64 (m, 2 H), 6.97–6.99 (m, 2 H), 7.29–7.31 (m, 2 H), 7.52–7.59 (m, 4 H), 7.66–7.72 (m, 6 H), 8.15–8.17 (m, 2 H).

4.19. *4′-(1′-Butylferrocenyl) [1″,4′:1′,1]terphenyl-4-yl 4-decyloxybenzoate, 11b*

This compound was prepared analogously to compound **11a**. From **10b** (0.26 g, 0.00025 mol), **5b** (0.38 g, 0.00075 mol), $Pd(PPh_3)_2Cl_2$ (0.0202 g, 0.00029 mol), potassium carbonate (0.25 g), water (2 ml) and DMF (12 ml), compound **11b** (0.14 g, 25%) was obtained. Calc. for $C_{49}H_{54}FeO_3$, C 78.81, H 7.29; found, C 78.79, H 7.14%. ^1H NMR δ (ppm, J/Hz): 0.83–0.90 (2 t, 3H each, 2 CH_3), 1.22–1.40 (m, 16H), 1.48 (m, 2H), 1.83 (quintet, 2H, $^3J=7$), 2.10 (t, 2H, Cp–CH_2–CH_2, $^3J=8$), 4.02–4.07 (m, 6H), 4.37 (m, 2H), 4.70 (m, 2H), 6.97–6.99 (m, 2H), 7.29–7.31 (m, 2H), 7.47–7.49 (m, 2H), 7.55–7.57 (m, 2H), 7.67–7.70 (m, 6H), 8.15–8.17 (m, 2H).

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