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Polymer-Bound Chiroptical Molecular Switches; Photochemical Modification of the Chirality of Thin Films

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Abstract. Photobistable chiral polymers were obtained by covalent attachment of inherently dissymmetric 2-hydroxy-9-(7'-methyl-1',2',3',4'-tetrahydrophenanthrene-4'-yldiene)-9H-thioxanthene to methacrylate copolymers with appropriate spacers. Upon irradiation at 300 nm the optical activity of thin films of these polymers could be altered.

INTRODUCTION
Photochemical control of structures and functions of organic materials by means of molecular switches has seen rapid progress in recent years.1 A large range of photochromic materials has been developed2 and photo-modulation of conductivity,3 liquid crystalline phases,4,5 gels,6 and helicity of polypeptides,7 as well as photoresponsive host-guest systems,8 are illustrative for the effects that can be controlled. Major advances are furthermore seen in the photoregulation of structure and function of biomaterials.9 The design of optical switches based on bistable organic molecules has particularly been stimulated by the challenge of molecular memory elements. Polymers are excellent supporting materials for practical application of photochromic compounds, as stability and easy processability are notable features. Azobenzenes, fulgides, and spiropyrans, either covalently attached to macromolecules or used as dopant in the polymeric matrix, have been employed to control, for instance, the macroscopic organization in liquid crystalline polymers,10 the helicity of poly(benzyl)-l-glutamate,11 and the permeability of membrane-mimetic systems.12

We have focused on the control of chirality by light13 in bistable photoresponsive materials.

The chiroptical switches developed in our group13-19 consist of chiral overcrowded ethylenes that adopt a helical shape. The photochemically bistable system 1 which is used in the present study is shown in Scheme 1.

Scheme 1. The four different chiral isomers of alkene 1

Compound 1 consists of four stereoisomers which are stable towards racemization (i.e., thermal P-trans UM-trans or M-cis UP-cis interconversions) under ambient conditions. Irradiating with UV light results in the rapid reversible interconversion of the two helical alkene diastereomers, P-trans UM M-cis, with opposite helicity (pseudoenantiomers).14 Irradiation of the switch in n-hexane at 300 nm leads to a cis:trans ratio of 64:36, whereas irradiating at 250 nm or 350 nm results in a...
cis:trans ratio of 68:32. The photostationary states can therefore be modulated by irradiating the chiroptical switch with UV light of different wavelengths. This change in chirality can be monitored by CD spectroscopy.

These materials are particularly interesting for possible use in optical data storage devices and the photomodulation of chiral surfaces and thin films. As a next step towards application we envisioned to incorporate the chiroptical switches into polymer films. This might be achieved by functional polymers in which the switching unit is attached to the polymer backbone through a spacer or by mixing of the switches with polymers. The first method, which is reported here, is particularly attractive as aggregation of the switches is avoided.

Major advantages of the overcrowded alkenes described here are that they can be switched back and forth using UV-Vis light, their photostationary states are stable without thermal isomerization, and nondestructive read-out is possible by chiroptical methods. In azobenzene modified polymers, for instance, thermal instability of the cis form is often encountered. In our current investigation we coupled 2-methoxy-9-(7'-methyl-1',2',3',4'-tetrahydrophenanthrene-4'-ylidene)-9H-thioxanthene (Scheme 1) to a polymer by a spacer. The methoxy group in 1, which is easily converted to a phenol, enables us to attach switching unit 1 to a variety of spacers.

Initially a methacrylate monomer was synthesized with a photoactive chiral unit attached to it via a spacer and subsequently copolymerization of 4 with methyl methacrylate (MMA) using a radical initiator was studied.

Random copolymerization is unlikely to occur this way however and furthermore it was shown that the overcrowded alkenes are not completely inert toward radical conditions of polymerization. The results of this approach, using monomer 4, were not satisfactory. Therefore it was decided to start with a copolymer with reactive side chains and attach the chiroptical switch at a later stage.

RESULTS AND DISCUSSION

Functionalized polymers with different spacers and degrees of loading with photoactive units were prepared according to the route shown in Schemes 3-6.

6-Bromohexyl methacrylate (BHMA) and 2-bromoethyl methacrylate (BEMA) were prepared from methacryloyl chloride and 6-bromohexanol or 2-bromoethanol in tetrahydrofuran (THF) at 0 °C, using triethylamine as HCl scavenger (Scheme 3). After the reaction, salts were filtered off and the monomer was isolated by distillation. Because of the low stability of the monomer it was immediately used for the polymerization reactions. Copolymerizations were performed in toluene with mixtures (9:1 ratios) of MMA and comonomers BEMA or BHMA using azobisisobutyronitrile (AIBN) as an initiator at 60 °C (Scheme 3). Both polymers 6a and 6b contained around 8% of bromoalkyl side chains, after purification.

The photoactive chiral overcrowded alkene 1 was prepared in a multistep sequence which involved the preparation of the “upper” tetrahydrophenanthrene part and the “lower” thioxanthene part of the molecule, followed by coupling the two halves to form the sterically-demanding double bond. The synthesis of the upper part of 2-methoxy-9-(7’-methyl-1’,2’,3’,4’-tetrahydrophenanthrene-4’-ylidene)-9H-thioxanthene 1 starts with a Friedel-Crafts acylation of 2-methylnaphthalene 7 with succinic anhydride in nitrobenzene at 5 °C, affording acid 8, together with isomeric products due to acylation at other positions in the naphthalene ring. 1H NMR analysis showed that approximately 80% of the product consisted of 8, which was separated from the other isomers via one crystallization from acetic acid according to the procedure of Haworth et al.24 Wolff-Scheme 2. Synthesis of MMA monomer with attached alkene 1

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Scheme 3. Synthesis of 6-bromohexylmethacrylate and 2-bromoethyl methacrylate and copolymerization of MMA with BHMA (n = 6) or BEMA (n = 2)
Kishner reduction of the keto-acid followed by a ring closure in polyphosphoric acid furnished ketone 10 in 30% overall yield. This ketone was easily converted to hydrazone 11 by refluxing with an excess of hydrazine hydrate in ethanol.

The key step, which has been used frequently for the preparation of the basic skeleton of (substituted) 9H-thioxanthene-9-ones, involves a coupling reaction between an aromatic thiol group and an aryl halide (Scheme 5), although several approaches to achieve this transformation can be followed.25

The synthesis of 2-methoxy-9H-thioxanthene-9-one 13 is depicted in Scheme 5 and started from thiosalicylic acid and 4-iodoanisole, and was based on the method described by Vasiliu et al.26 The dipotassium salt of thiosalicylic acid replaced the iodine atom from the 4-iodoanisole in the presence of copper powder in boiling dimethylformamide (DMF) to form an aryl-sulfur bond. The resulting benzoic acid 12 was converted to thioxanthone 14 by stirring in concentrated H2SO4. This was performed at 10 °C in order to suppress sulfonation, which can easily occur due to the presence of the electron-donating methoxy group. Transformation of the ketone into thioketone 1 was accomplished by refluxing with a twofold excess of P2S5 in toluene. The thioketone was isolated as a dark-green solid, which did not show any decomposition even after storage for several months at room temperature.

The strategy used successfully to prepare extremely hindered alkenes is based on the 1,3-dipolar cycloaddition between a diazo compound and a thioketone to form a thiadiazoline, followed by a twofold extrusion reaction as described by Barton27 and Kellogg.28 The hydrazone 11 was oxidized to the unstable dark-red diazo compound 15 with silver(I)oxide in ether at -10°C in the presence of magnesium sulfate as desiccant. After filtration of the salts, the thioxanthone 14 was added to the cold solution of the diazo compound. Evolution of nitrogen was observed until the dark-red color of the solution had faded away. The intermediate thiadiazoline was not detected, indicating rapid decomposition to the more stable episulfide 16 (56%). The episulfides were obtained as cis-trans mixtures and used as such in the next step. Desulfurization of 16 with copper in boiling xylene afforded alkene 1 in 89% yield as a mixture of cis and trans isomers (50:50 ratio).

The cis and trans isomers of methoxy-substituted chiral alkene 1 are readily distinguished by their 1H-NMR spectra. The methoxy singlet found in trans-1 at 3.89 ppm, the normal position for this group, is shifted to 2.97 ppm in cis-1 due to shielding by the upper naphthalene moiety. The mixture of alkenes cis-1 and trans-1 was separated into the four stereoisomers M-cis-1, P-cis-1, M-trans-1, and P-trans-1 by HPLC using a (+)-poly(triphenylmethylmethacrylate) column with hexane/isopropanol 9:1 as eluent. The thermal racemization barrier for cis-1 was determined by polarimetry. Upon heating of enantiomerically pure M-cis-1 in p-xylene, racemization into P-cis-1 was observed with ΔG° = 26.4 kcal mol⁻¹ without the occurrence of thermal racemization.
cis-trans isomerization (e.g., M-cis Ü P-trans). To avoid any racemization in the final steps towards functionalized polymers 17a-d, mild conditions had to be employed both in the deprotection step and the attachment to the copolymers 6a and 6b (Scheme 7). Following a number of procedures for cleaving the arene moiety—ether it was found that treatment of 1 with BBr3 in dichloromethane at 0 °C met this requirement to afford 2 in 93% yield. Coupling of both racemic and enantiomerically pure 2 to the functionalized PMMA copolymers was achieved using Cs2CO3 in DMF at 40 °C, followed by extensive purification to remove any uncoupled 2. Initially these coupling reactions were performed at 40 °C. Repeated washing and reprecipitation of the polymers did not result in removal of the switching unit, and 1H NMR spectra showed absorptions at 3.1 and 4.0 ppm originating from the methylene groups of the aryl-alkyl ether moiety (cis-trans), indicating that the switches are covalently bound. The functionalized polymers prepared via this route are given in Table 1. The amount of chiroptical switch per polymer was determined by 1H NMR comparing the integrations of the aryl-CH$_2$ absorptions at 2.35 ppm and the methoxy group of methylmethacrylate units at 3.60 ppm. The degree of functionalization in the copolymers could independently be determined by UV-Vis spectroscopy, using the known extinction coefficients of the switching unit at 309 and 332 nm. Infrared spectroscopy also clearly indicated the presence of arene units in the polymers. The new functionalized copolymers, bearing 1.5-4.7% chiroptical switches attached via two- and six-carbon spacers, showed excellent film-forming properties. High quality transparent films were obtained by solution casting from a 5% solution in chloroform or toluene of the polymer on quartz slides. As expected, none of the polymers coupled to a mixture of the four isomers of the switching units showed any CD signal. The CD spectrum of the uncoupled switching unit (P-trans) in dioxane, compared well to that of P-trans-1 in hexane, whereas the CD spectrum of the polymer-bound switch in dioxane (polymer 17d) still shows the typical absorption for P-trans in solution, but it shows a cutoff below 260 nm due to absorptions of the polymer backbone. Mixing polymers 6a and 6b with free M-trans isomer 1 resulted in the inverse CD-spectrum compared to the CD-spectrum of polymer 17d with covalently bound P-trans-1, as expected. The intensity of the CD spectrum of the freshly prepared film of polymer 17d was lower (approximately 10%) than estimated using the known amount of polymer and degree of functionalization.

This is probably due to the fact that some thermal racemization during the coupling of the switching unit to the polymer cannot be completely avoided. It is known that the used switches racemize rather fast at elevated temperatures, especially in solution.

Irradiation of P-trans-1 with UV light at 300 nm results in a photostationary state composed of 64% M-cis-1 and 36% P-trans-1 in hexane, whereas irradiation with 350 nm light results in a photostationary state composed of 68% M-cis-1 and 32% P-trans-1. Irradiation of thin films of polymer 17d with covalently bound P-trans-1 leads to a distinct change of CD signal. A typical example is seen in Fig. 1. The irradiation times needed to reach the photostationary states are, however, much longer for polymer films (90 min) than for solutions (30-60 s)$^{14}$ of the same chiroptical switch. It should be noted that the films remain optically active after irradiation; the decrease in CD absorptions is a result of formation of a photostationary state between M and P helices (approximately 65:35 ratio on the basis of the measured CD effect). The irradiation times may be shortened by switching above the glass transition temperature (Tg), while the photostationary states can be stabilized below Tg, but more stable switches are required to achieve this improvement. Subsequent switching by alternatively irradiating with 350 nm and 300 nm did not result in significant changes in the CD spectra. Due to the low loading in the chiral polymer 17d and the

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Table 1. Polymer chiroptical switches

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Basic polymer</th>
<th>Chiroptical switch</th>
<th>Coupling T (°C)</th>
<th>Functionalization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17a</td>
<td>6b</td>
<td>mixture of isomers</td>
<td>60</td>
<td>1.5</td>
</tr>
<tr>
<td>17b</td>
<td>6a</td>
<td>mixture of isomers</td>
<td>40</td>
<td>4.0</td>
</tr>
<tr>
<td>17c</td>
<td>6b</td>
<td>mixture of isomers</td>
<td>40</td>
<td>4.3</td>
</tr>
<tr>
<td>17d</td>
<td>6b</td>
<td>P-trans</td>
<td>40</td>
<td>4.7</td>
</tr>
</tbody>
</table>

$^a$Number of switches relative to the number of monomeric units, as determined by UV and 1H NMR spectroscopy.

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Fig. 1. CD spectra of a film of polymer 17d before (A) and after (B) irradiation with 300 nm.
small changes in diastereomeric excess upon irradiation at different wavelengths with this particular helical alkene, accurate detection of the photomodulation of the film was not feasible. Furthermore, slight racemization of the switching unit due to the long periods that the film is exposed to the UV light can not be excluded at present.

By employing these new photoactive chiral polymers we have demonstrated that the chirality of the polymeric film can be modified by irradiation. Despite the shortcomings, such as long irradiation times, these materials have potential for optical data storage.

**EXPERIMENTAL SECTION**

**Methods**

All reactions and purifications were performed under a nitrogen or argon atmosphere unless otherwise stated. Toluene and tetrahydrofuran (THF) were distilled from sodium. Dimethylformamide (DMF) and dichloromethane were purified by a distillation from P2O5. Azobis-isobutyronitrile (AIBN) was recrystallized from ethanol and kept under a nitrogen atmosphere at -5 °C. Methyl methacrylate was purified by distillation from CaH2 under a reduced nitrogen atmosphere. Irradiation experiments at 350 and 300 nm were performed using low-pressure 28 × 1-cm 8 W mercury lamps. 1H NMR spectra were recorded on a Nicolet NT-200 or a sphere. Irradiation experiments at 350 and 300 nm were performed using a low-pressure 28 × 1-cm 8 W mercury lamps. 1H NMR spectra were recorded on a Nicolet NT-200 or a Varian VXR300 spectrometer, UV spectra were recorded on a Philips PUL8700 single-beam spectrophotometer, differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC-7, circular dichroism (CD) spectra were recorded on a Jobin Yvon autodichrograph mark V, IR spectra were recorded on a Perkin Elmer 841 spectrophotometer. Solution of the alkenes was achieved with HPLC using a water-cooled 4.6 × 250 mm (or 20 × 250 mm) (+)-poly(triphenylmethyl methacrylate) column (Daicel OT”) with hexane/isopropanol (9/1) as an eluent.

2-Bromoethyl Methacrylate (BEMA) (5a), 6-Bromohexyl Methacrylate (BHMA) (5b)

5a and 5b were prepared from methacryloyl chloride and 2-bromoethanol or 6-bromohexanol in THF at 0 °C, using triethylamine as a HCl scavenger.29 After the reaction, salts were removed by filtration and the monomers were isolated by distillation. The reaction was characterized by 1H NMR spectroscopy (CDCl3: δ(CH2-Br) 3.4 ppm). Because of the low stability of the monomer it was immediately used for the polymerization reactions.

**Copolymers 6a and 6b**

The copolymers were prepared in toluene using AIBN as an initiator at 60 °C. MMA was mixed with the comonomer BEMA (5a) or BHMA (5b) in a 9:1 ratio.30 The products were isolated by precipitation in pet-ether 40-60 and purified by recrystallization from dichloromethane in pet-ether 40-60. The polymers were dried under vacuum at 40 °C for two days. P(MMA-co-BEMA) (polymer 6a): 1H NMR: -COO-CH2-: 4.3 ppm, -CH2-Br: 3.5 ppm. Anal. Calcd (from monomer feed): C, 55.9; H, 7.4; Br, 7.3. Found: C, 56.7; H, 7.5; Br, 6.0. DSC: Ts: 103 °C, GPC: Mw = 60000; Mn = 160000. P(MMA-co-BHMA) (polymer 6b): 1H NMR; -COO-CH2-: 3.9 ppm, -CH2-Br: 3.4 ppm. Anal. Calcd (from monomer feed): C, 57.4; H, 7.7; Br, 6.9. Found: C, 57.9; H, 7.8; Br, 5.8. DSC: Ts: 85 °C; GPC: Mw = 20000, Mn = 65000.

cis- and trans-2-Hydroxy-9-(7'-methyl-1',2',3',4'-tetrahydro-phenanthrene-4'-yliden)-9H-thioxanthene (2)

To a magnetically stirred solution of alkene 1 (400 mg, 0.97 mmol) in CH2Cl2 cooled at 0 °C was added Br2 (10 mL, 10 mmol, 1.0 M Br2 in CH2Cl2, 10 equiv), whereupon the color of the reaction mixture immediately turned red. After 30 min the temperature of the mixture was allowed to rise slowly. The conversion to 2 was complete in 2.5 h (TLC, SiO2, CH2Cl2/hexane, 1/1, Rf 1 = 0.45, Rf 2 = 0.12). The dark brown mixture was poured into 100 mL of a well stirred mixture of H2O and CH2Cl2, 1:1. The organic layer immediately turned purple; it was separated and the water layer was extracted with CH2Cl2 (100 mL). The combined organic layers were washed with water and dried over Na2SO4. The solvent was removed under reduced pressure and 2 was obtained as a foam (357 mg, 91.9 mmol, 93%). 1H NMR (200 MHz) δ: 1.86-2.27 (m, 2H), 2.34 (s, 3H), 2.94-3.17 (m, 2H), 3.28-3.43 (m, 1H), 5.90 (d, 1H), 6.29 (d, 1H), 6.37-6.51 (m, 1H), 6.66 (dd, 1H), 6.74-6.98 (m, 3H), 7.17-7.68 (m, 7H).

**Polymers 17a-d**

40 mg of alkene 2 was dissolved in DMF (10 mL) and the solution was heated to 40 °C. Then slowly 90 mg of Cs2CO3 was added, upon which the color of the solution turned from purple to brown. 0.11 g of the functionalized PMMA in 10 mL DMF was added and the mixture was allowed to react for 16 h. The reaction mixture was precipitated in water, resulting in a pink solid. The solid was reprecipitated from CH2Cl2 in pet-ether 40-60 and dried in vacuo. Yield: 50%; Anal. Calcd for P(MMA-BHMA) (assuming all alkyl bromide groups have reacted): C, 66.5; H, 7.5; Br, 6.9. Found: C, 66.8; H, 7.3; Br, 6.9. DSC; Tg: 103 °C, GPC; Mn = 60000; Mw = 160000. P(MMA-co-BHMA) (polymer 6b): 1H NMR; -COO-CH2-: 3.9 ppm, -CH2-Br: 3.4 ppm. Anal. Calcd (from monomer feed): C, 55.9; H, 7.4; Br, 7.3. Found: C, 56.7; H, 7.5; Br, 6.0. DSC: Ts: 103 °C, GPC; Mw = 60000; Mn = 160000. P(MMA-co-BHMA) (polymer 6b): 1H NMR; -COO-CH2-: 3.9 ppm, -CH2-Br: 3.4 ppm. Anal. Calcd (from monomer feed): C, 57.4; H, 7.7; Br, 6.9. Found: C, 57.9; H, 7.8; Br, 5.8. DSC: Ts: 85 °C; GPC: Mw = 20000, Mn = 65000.

**Preparation of the Thin Films**

Polymer films were prepared by solution casting of a 5%
solution of the polymer in toluene on a quartz slide. The film of the polymer coupled to an optically-pure switch (polymer 17d) was cast in the dark to avoid premature switching. The CD spectrum of the freshly prepared film was compared to that of polymer 17d in solution (dioxane). The sample was irradiated with UV light (300 nm) and the CD spectrum was monitored as a function of irradiation time. After 90 min the CD spectrum did not change any more, indicating that a photostationary state had been reached. As a control, irradiations of solutions of 1 were performed (see also ref 14).

4-Oxo-4-[2-(6-methylphenyl)]butanoic acid (8)

This compound was prepared according to the method described by Haworth et al.22 Starting from succinic anhydride (73.1 g, 0.73 mol) and 2-methylphenylthene (7, 102.3 g, 0.72 mol), crystallization from acetic acid (700 mL) afforded pure 8 as a slightly brown solid (70.3 g, 0.29 mol, 40.3%): mp 158.3-161.0 °C (lit:24 mp 162-163 °C); 1H NMR (300 MHz) δ 0.89 (t, J = 7.0 Hz, 2H), 2.26-2.40 (m, 2H), 2.40 (s, 3H), 2.75 (t, J = 7.0 Hz, 2H), 7.17 (m, 5H), 8.40 (s, 1H); the acidic proton was not observed due to the presence of small amounts of acetic acid.

4-[2-(6-Methylphenyl)]butanoic acid (9)

Keto-acid 8 (60.0 g, 0.25 mol), KOH (42.0 g, 0.75 mol) and NH2NH2.H2O (33.0 g, 32 mL, 0.63 mol) were successively added to magnetically stirred diethylene glycol (300 mL). This mixture changed to blue, and after stirring for 45 min the now green-brown solution was poured onto ice (≈ 3 kg). The dark green residue obtained after refluxing ketone 10 (20.0 g, 95.2 mmol) and 2-methylnaphthalene (73.1 g, 0.73 mol) and 2-Methoxy-9H-thioxanthene-9-thione (14) To a stirred solution of 13 (15.0 g, 62.0 mmol) in dry toluene (200 mL) was added P2S5 (27.5 g, 124.0 mmol). After 1 h TLC analysis (SiO2, hexane/Et2O 85:15, starting material Rf = 0.25, product Rf = 0.42) indicated the total conversion of 13 to thikoketone 14. The dark green residue obtained after evaporation of the solvents was dissolved in CH2Cl2 (200 mL) and filtered. Hexane (200 mL) was added, whereupon the thikoketone began to separate from the solution. Upon cooling at -18 °C, 14 was obtained as dark green small needles in a
cis- and trans-Dispiro[7-methyl-1,2,3,4-tetrahydrophenanthrene-4, 2'-thiirane-3', 9''-(2''-methyl)9''H-thioxanthene] (16)

A stirred solution of hydrazone 11 (672 mg, 3.00 mmol) in dry ether was cooled to -10°C, whereupon MgSO₄ (approximately 1500 mg), AgNO₃ (1.04 g, 4.50 mmol, 1.5 equiv) and a saturated solution of KOH in ethanol (1 mL) were successively added. The red solution of diazo compound 15 was filtered into another ice-cooled solution. To this cooled solution 2-methoxy-9H-thioxanthene-9-thione (14, 490 mg, 1.90 mmol) was added. Evolution of nitrogen was observed and the red color disappeared. The mixture of episulfides cis-16 and trans-16 precipitated from the Et₂O solution as a slightly yellow solid (ratio cis:trans, 50:50). Crystallization from ethanol yielded episulfides cis-16 and trans-16 (481 mg, 1.06 mmol, 55.8%, based on the amount of added thiokeitone), as a cis and trans mixture (ratio cis:trans, 17:83). No further attempts were made to separate these compounds. Only the NMR data of trans-16 were fully resolved and are given: H NMR (300 MHz) δ 1.25-1.50 (m, 2H), 1.90-1.95 (m, 1H), 2.30-2.38 (m, 1H), 2.35 (s, 3H), 2.41-2.57 (m, 1H), 3.47-3.58 (m, 1H), 3.77 (s, 3H, trans-OCH₃), the cis-OCH₃ was found at 2.98 ppm), 3.81 (dd, J = 8.1, 7.3, 1.5 Hz, 1H), 3.69 (dd, J = 8.8, 7.3 Hz, 1H, 1.5 Hz, 1H), 6.77 (dd, J = 8.1, 2.9 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H, 1H, 6.88 (d, J = 8.1 Hz, 1H, 1H, 7.14-7.53 (m, 6H), 9.31 (d, J = 8.8 Hz, 1H). 13C NMR δ 20.94 (t), 21.11 (q), 29.76 (t), 34.99 (t), 55.44 (q), 59.93 (s, C-S), 61.48 (s, C-S), 124.64 (d), 125.30 (d), 126.21 (d), 126.26 (d), 126.63 (d), 126.82 (d), 126.87 (d), 127.16 (d), 127.57 (d), 128.99 (d), 129.20 (d), 129.39 (d), 130.33 (d), 131.07 (s), 132.50 (s), 132.58 (s), 133.02 (s), 133.92 (s), 134.42 (s), 135.06 (s), 140.01 (s), 158.20 (s); HRMS Calcd for C₃₉H₂₄O₃: 452.127, found 452.126.

cis- and trans-2-Methoxy-9-(7''-methyl-1',2',3',4'-tetrahydroph

REFERENCES AND NOTES


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(22) See, for instance, ref 20c.
(23) Hattijema, H.J.; Feringa, B.L., unpublished results.