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Synthesis and Characterization of Nonsymmetric Cyclopentene-Based Dithienylethenes

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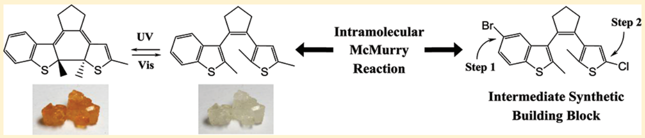
Supporting Information

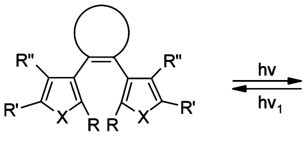


ABSTRACT: Nonsymmetric cyclopentene-based dithienylethenes, containing both thienyl and benzothienyl units, have been synthesized for the first time, employing intramolecular McMurry reaction as a key transformation to target compounds **10** and **16**. Photochromic properties of these compounds were examined in toluene and acetonitrile solutions, PMMA layers, solid films, and crystal phase. To explain an unprecedented single-crystalline photochromism phenomena of **10**, X-ray crystallographic analysis was performed, revealing a significant influence of strong S···S interatomic interactions on the intramolecular distance between two photochemical reaction centers in the molecule. Compound **16** could be further synthetically modified in a step-by-step manner, thus serving as potential key intermediate to various complex bifunctional photochromic molecules.

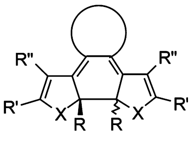
INTRODUCTION

Organic photochromic materials have attracted growing interest due to their employment in construction of various optical devices such as photoswitches,[1] actinometers and dosimeters,[2] and especially in the field of optoelectronics.[3] Recent progress in the laser and information technologies makes photochromic materials promising for use as recording media in devices for recording, storage, and processing of optical information.[3,4] For this purpose, dihetarylethenes of a general formula **1** are most commonly being used, which undergo a reversible interconversion under irradiation from the open **A** form to the cyclic **B** form (Scheme 1).

Scheme 1. Photochromic Interconversion of Dihetarylethenes under Irradiation



1A



1B

Among a variety of photochromes **1**, diarylethenes containing two thiophene-based moieties (dithienylethenes, X = S) are the most promising because of superior thermal stability of their cyclic isomers, high fatigue resistance, rapid response to the effects of radiation, maximum remoteness of absorption bands of open **A** and cyclic **B** forms, sufficient solubility in organic solvents, high reactivity in the solid state, etc.[3,5] Most of the attention in this field has been drawn to dithienylethenes with perfluorocyclopentene bridge, which resulted in numerous syntheses and exploration of physical and chemical properties of these compounds in both solution and solid state.[6] Possibility of a sequential anionic substitution of fluorines in perfluorocyclopentene allows syntheses of either symmetric[7] or nonsymmetric[8] target dithienylethenes. At the same time, dithienylethenes with a cyclopentene bridge are much less studied; however, they also display attractive photochromic properties and could be considered as a promising alternative to dithienylperfluorocyclopentenes. Studies of physical properties of both perfluoro- and perhydrocyclopentene connected dithienylethenes have been performed in a comparative mode in various solutions, showing no major dissemblance in their photochromic behavior.[9] On the other hand, no cyclopentene-based dihetarylethenes are known to date that display photochromic properties in a single-crystalline phase, while among their perfluorocyclopentene-based analogues only a handful reveal this unique ability.[10] This feature is, however, extremely valuable due to thermal stability of the photoinduced form, high fatigue resistance, increased sensitivity, and rapid response of photochromic single crystals of dithienylethenes, extending application of these compounds in switching, optical memory, and display.[5,11]

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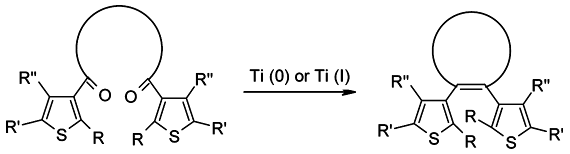
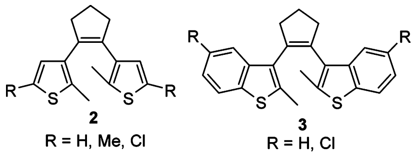
Construction of symmetric dithienylethenes is usually accomplished by intramolecular condensation of the corresponding symmetric 1,5-diketones under McMurry conditions (Scheme 2).[12]

Scheme 2. General Synthesis of Dithienylethenes via McMurry Reaction



Both thienyl **2**[13] and benzothienyl **3**[14,15] (Chart 1) containing photochromes with cyclopentene as a bridge unit have been synthesized by this approach.

Chart 1. Known Symmetric Simple Cyclopentene-Based Dithienylethenes



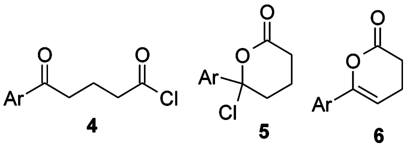
Further transformations of the synthesized molecules were, however, rather limited due to their restrained reactivity. Thus, only formylation[16] and acetylation[17] of benzothiophene fragments of **3** (R = H) were performed with moderate yields, whereas either simultaneous or consecutive lithiation of chlorides in **2** (R = Cl) have been the only means of constructing bigger molecules based on this skeleton, usually via Suzuki coupling.[18] Despite such lack of variety in modification methods, hundreds of new molecules have recently been synthesized from **2** (R = Cl) and studied. This includes a variety of both symmetric[19] and nonsymmetric[20] sophisticated photochromic molecular systems.

The given examples illustrate the growing need in developing other functionalized thienyl-based photochromic scaffolds having a cyclopentene bridge. Ideally, the target structure should be nonsymmetric, with different reactivity of the present functional groups, so it could be easily modified in a step-by-step manner. In this article, we report a novel synthetic approach to nonsymmetric cyclopentene-based photochromes having both thienyl- and benzothienyl- fragments. This approach includes synthesis of nonsymmetric 1,5-diketone followed by intramolecular condensation under McMurry conditions. An unsubstituted representative of this new class of dithienylethenes with a cyclopentene bridge unit displays photochromic properties in a single crystal, which is, to our knowledge, the first example of crystalline photochromism for cyclopentene-connected dihetarylethenes. Another compound having chemically active halogens on both thienyl and benzothienyl moieties can serve as a key intermediate to various complex bifunctional molecules.

■ RESULTS AND DISCUSSION

Synthesis. 1,5-Dicarbonyl compounds are indispensable intermediates in synthesis of cyclopentene-based photochromes via the McMurry reaction. To date there are only a few examples in the literature of acylations of thiophenes under Friedel−Crafts conditions with glutaric anhydride,[21] although analogous aryl-substituted 5-ketoacids are well documented.[22] The latter could be transformed to 5-ketoacid chlorides; however, depending on structural characteristics or employed reagents normal **4** and pseudo **5** forms have been reported for this reaction.[23,24] Pseudo acid chlorides easily give substituted corresponding enol lactones **6** that appear to be major side-reaction products (Chart 2).

Chart 2. Reported Products of Substituted 5-Ketoacid to Acid Chloride Conversion

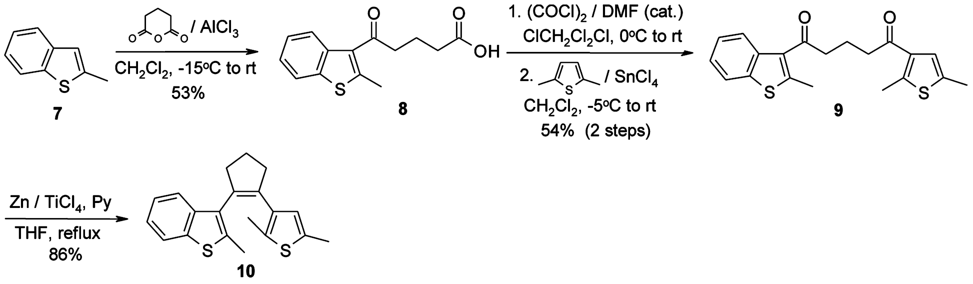


We decided to test this approach on a simple object, such as 2-methylbenzothiophene **7** (Scheme 3). The obtained 5-ketoacid **8** was converted to acid chloride under mild conditions followed by $SnCl_4$-promoted acylation of 2,5-dimethylthiophene. The McMurry cyclization of nonsymmetric diketone **9** proceeded smoothly to give dithienylethene **10** in excellent yield.

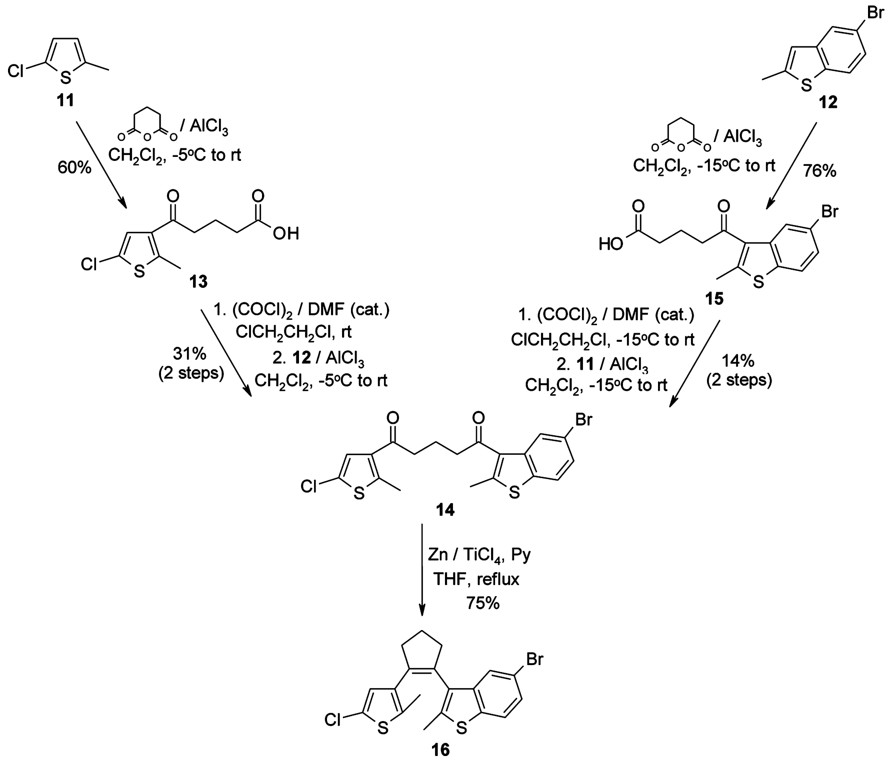
Encouraged by these results, we initiated research for a bifunctional nonsymmetric photochrome. 2-Chloro-5-methylthiophene **11** and 5-bromo-2-methylbenzothiophene **12** appeared to be most practical starting material for this purpose (Scheme 4). Thus, acylation of **11** with glutaric anhydride gave acid **13** in good yield. Unfortunately, the conversion of **13** to the acid chloride followed by the second Friedel−Crafts reaction turned out to be rather difficult. Both small scale loads and further upscaling of the target diketone furnished only moderate yields for the two-step procedure. An attempt of approaching **14** starting from **12** was also accomplished. 5-Ketoacid **15** was obtained in high yield; however, the following two-step transformation gave a moderate yield as well. It is known that pseudo form of acid chloride **5** dominates when the substituent has an electron-withdrawing nature,[23] which apparently turned out to be an issue in our case. Thus, the presence of either a chlorine in the thiophene ring or a bromine in the benzothiophene fragment significantly affected the fraction of linear 5-ketoacid chloride. It was found that mild reagents and conditions should be applied for the acid chloride conversion step, such as oxalyl dichloride in dichloroethane, while upon using $SOCl_2$ only traces of the desired product were detected. $AlCl_3$ was necessary to be used in the Fridel−Crafts acylation step, since $SnCl_4$ was not potent enough for less active **11** and **12**, as compared to 2,5-dimethylthiophene, giving no desired product. Yet, the McMurry cyclization of diketone **14** proceeded efficiently, giving the target photochrome in high yield.[25]

To confirm the desired possibility of consequent substitution of halogen atoms in **16**, we chose palladium/BINAP-catalyzed amination under Buchwald conditions.[26] First, chemical transformation under such mild conditions should not have affected the chlorine substituent in the thiophene ring; second, a variety of amines could be used in this reaction yielding photochromes of various structures, especially those having two different functionalities. For this purpose, we chose two heterocyclic amines bearing another functional group, 1-

Scheme 3. Synthetic Route to Photochrome 10

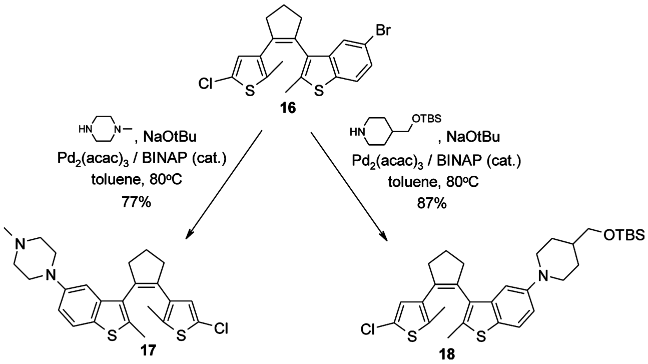


Scheme 4. Synthetic Routes to Photochrome 16



methylpiperazine and hydroxyl-protected 4-piperidinemethanol (Scheme 5).

Scheme 5. Catalytic Amination of 16



The desired products were obtained with excellent yields under these conditions. Further lithiation of 2-chlorothienyl unit with *t*-BuLi is a trivial procedure that has numerous examples in the literature.[13,27] Thus, the reported here dithienylethene **16** could be successively functionalized at both ends of the molecule, thus serving as an intermediate building block in construction of complicated photochromic molecules.

Spectral and Kinetic Characteristics. Spectral and kinetic studies of synthesized compounds **10** and **16** were performed in solutions (toluene, acetonitrile, $C = 2 \times 10^{-4}$ M), poly(methyl methacrylate) (PMMA) layers, and solid films obtained by slow evaporation of the corresponding toluene solutions.

Typical photoinduced spectral changes of photochromes **10** and **16** in acetonitrile solution are presented in Figure 1. As can be seen, for both compounds absorption spectra of the initial open form (curves 1) and photoinduced closed form (curves 2) are very alike, showing no critical dependence between the spectral properties and structural substituents.

Analogously, photocyclization under UV irradiation in the toluene solution for both photochromes **10** and **16** resulted in appearance of an absorption band located in the short wavelength visible spectral region. In this solvent, introduction of mediocre electron acceptors such as chlorine and bromine into thienyl and benzothienyl fragments, respectively, led to a

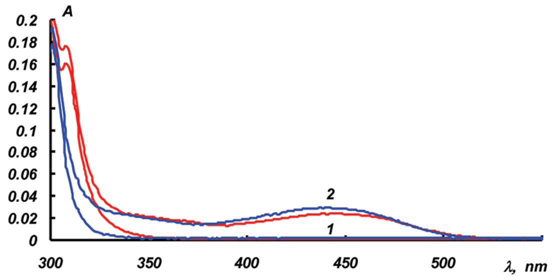


Figure 1. Absorption spectra of dithienylethenes **10** (blue) and **16** (red) in acetonitrile before (1) and after (2) UV irradiation.

slight bathochromic spectral shift (5 nm) of absorption bands for both open and closed forms for compound **16**, as compared to **10** (Table 1).

Table 1. Spectral and Kinetic Characteristics for Dithienylethenes 10 and 16[a]

compound	system	λ_A, nm	D_A	λ_B, nm	ΔD_B^{phot}
10	solution in toluene	300 sh	0.3	445	0.05
	solution in acetonitrile	300 sh	0.2	440	0.03
	solid film	300 sh	0.3	450	0.04
	PMMA film	300 sh	0.7	450	0.12
16	solution in toluene	305 sh	0.2	450	0.04
	solution in acetonitrile	305 sh	0.2	440	0.02
	solid film	305 sh	0.9	455	0.08
	PMMA film	305 sh	0.6	450	0.13

[a] λ_A and λ_B are wavelengths of absorption band maxima for open and cyclic forms, respectively; D_A is a value of optical density at the absorption maximum of the open form; ΔD_B^{phot} is a value of the photoinduced optical density at the absorption maximum of the cyclic form in the photoequilibrium state; sh stands for absorption shoulder.

Very similar absorption spectra for open and cyclic forms for these compounds were also obtained by UV irradiation of acetonitrile solutions, PMMA, and solid films.

In all cases, the absorption band of the open form for **16** was shifted to the long wavelength spectral region as compared to **10**. At the same time, replacement of toluene by polar acetonitrile resulted in small hypsochromic spectral shifts. The opposite displacement induced by molecular packing was observed for these compounds in polymer and solid films.

Both compounds are characterized by comparable sensitivity to UV irradiation in solution (Table 1). In either toluene or acetonitrile the values of photoinduced optical density (ΔD_B^{phot}) are analogous for **10** and **16**, while the values of optical density for the open form (D_A) for these two compounds remain identical. On the other hand, with the D_A growth, and as a result with an increase of absorbed activating UW irradiation, as it happens in PMMA films containing either compound or in the solid film of **16**, a consequent increase in the ΔD_B^{phot} value was observed accordingly.

Reversible photoinduced transformations of photochromes **10** and **16** between open and cyclic forms (Scheme 1) is demonstrated by kinetic curves for photocoloration under UV irradiation followed by photobleaching under visible light (Figure 2) with all measurements being carried out at the maximum of the absorption band of the cyclic form. As could be seen, structural differences between these compounds had a very little effect on the photobleaching process.

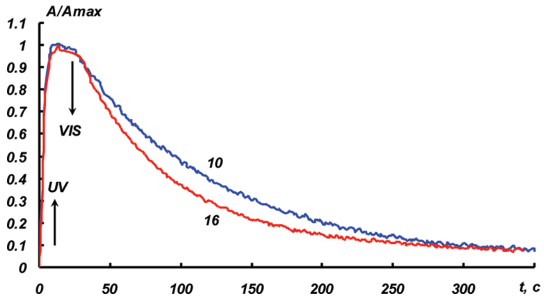


Figure 2. Kinetic curves for **10** (blue) and **16** (red) in acetonitrile for processes of photocoloration under UV irradiation (I = 12 mW/cm^2) and photobleaching under visible light (I = 190 mW/cm^2).

It is worth mentioning that dithienylethenes **10** and **16** displayed thermal irreversibility in either solution, polymer, or solid film. The value of its photoinduced optical density in the photoequilibrium state remained unchanged within 24 h in the dark at room temperature.

Thus, compounds **10** and **16** display standard photochromic properties in both solution and solid state typical for this class of dithienylethenes. Introduction of halogens into thiophene and benzothiophene rings does not significantly influence their spectral or kinetic behavior.

Solid State Properties. Finding a photochromic compound that would display photochromism in a crystalline phase was never a trivial task. Not only must two substituents at the reaction centers in the photochromic molecule acquire antiparallel conformation in the crystal for such photocyclizations to proceed, but also the distance between these centers should be shorter than an allowed limit of ~4.2 Å calculated by Irie.[28] Despite the fact that quite a few perfluorocyclopentene-based photochromes displaying single-crystalline photochromism are known, there are no examples in the literature to date of cyclopentene-based dihetarylethenes that possess such properties in a crystal state. Our earlier attempts to obtain crystals of **3** (R = Cl) displaying photocromic activity under UV irradiation were also fruitless.[15]

Crystallization of **10** from hexane furnished colorless transparent crystals of different size. To our content, these crystals quickly acquired deep orange color under UV irradiation, decolorizing within a minute under a visible light exposure (Figure 3). Multiple repetitions of this procedure influenced neither the intensity of orange color nor the swiftness of decolorization. At the same time, UV-irradiated crystals of **10** could be stored at room temperature in a dark place for months without any noticeable loss of color. These experiments suggested high fatigue resistance of **10** and high thermal stability of the closed form **10B** in the single-crystalline state.

Figure 3. Photographs of crystal of **10** before and after photoirradiation with UV light.

In order to understand the nature of packing of molecules of **10** in a crystal lattice, X-ray analysis was performed. High quality single crystals were grown from hexane by slow evaporation.

The X-ray diffraction (XRD) analysis showed that molecular geometry of **10** has been significantly affected by crystal packing effects. Initially, we attempted to obtain the diffraction data at 100 K, but at this temperature and up to 150 K all single crystals had cracking upon mounting on the goniometric head. At 150 K, however, we managed to X-ray a crystal of **10** and found that this compound had crystallized in space group $P2_1/c$ with two independent molecules **A** and **B** in a unit cell. Despite an apparent pseudosymmetry, which caused the doubling of the crystallographic axis *a*, two independent molecules displayed some significant differences in molecular geometry;[29] the latter is crucial for the photocyclization process. Although the bond lengths distribution and even the conformation (dihedral angles between the central ring and the heterocycles) for molecules **A** and **B** were almost identical, the difference in the intramolecular distances between the reactive centers C(2′) and C(2″) in **A** and **B** (3.839(2) and 3.699(2) Å, respectively) attained 0.140(2) Å. As could be seen, both values are smaller than the mentioned above limit of ~4.2 Å, while antiparrallel conformation of C(2′)−C(8′) and C(2″)−C(8″) bonds was observed for both **A** and **B** molecules in the crystal (Figure 4).

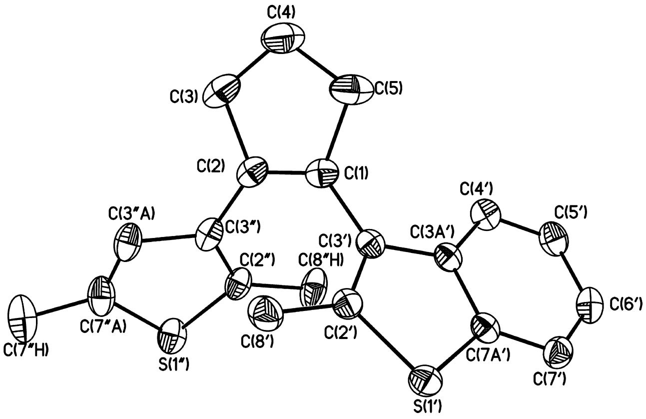


Figure 4. General view of one of the independent molecules at 150 K with representation of atoms via thermal ellipsoids (p = 50%). Hydrogen atoms are omitted for clarity.

Two different C(2′)···C(2″) distances for molecules **A** and **B**, mentioned above, are likely to be governed by crystal packing effects, especially by shortened intermolecular contact S(1″)···S(2″) (3.643(1) Å), responsible for assembling molecules **A** into chains. The analogous interaction between molecules **B** is much weaker (S···S = 3.808(2) Å). At the same time, in both cases these S···S contacts are characterized by the pronounced directionality with the S(1′)···S(1″)−C(7″A) angle being close to 160° and thus attributing to the n(S)−σ*(C−S) charge transfer.[30] As a consequence of the above differences in the molecular geometry and intermolecular interactions, the crystal of **10** at 153 K is formed by alternating layers (parallel to the crystallographic plane *bc*) that contain either **A** or **B** molecules (Figure 5).

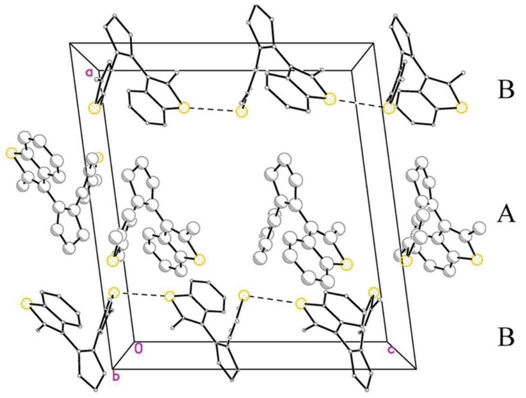


Figure 5. Fragment of the crystal packing of **10** at 150 K. Carbon atoms of the independent molecule **A** are shown by larger balls.

All of these differences between the independent molecules **A** and **B** persist only up to 173 K. Starting from this temperature and up to room temperature, the number of independent molecules in the unit cell decrease to one (Z' = 1) with crystallographic axis *a* becoming two times smaller. The main geometric parameters of **10** at 173 K are similar to those measured at 150 K, but the C(2′)···C(2″) separation is equal to 3.776(2) Å while the interatomic distance for the above S···S contact is 3.709(2) Å. In other words, the stronger the intermolecular S···S binding is, the longer is the distance between the reactive centers in a molecule of **10**.

Hence, we can conclude that in the temperature range 150−293 K the molecular arrangement in a crystal and thus the intramolecular separation between the two reactive centers govern the photocyclization reaction in solid. Moreover, the significant variation of the C(2′)···C(2″) distance as a consequence of the intermolecular S···S interaction clearly indicates the flexibility of **10**, which could further contribute to the photocyclization in the solid state.

Conclusion. A new synthetic approach to nonsymmetric cyclopentene-based photochromes has been designed and accomplished. Compounds **10** and **16** containing both thienyl and benzothienyl units have been synthesized as representatives of this new class of dithienylethenes. Their syntheses included formation of a corresponding nonsymmetric 1,5-diketone, which underwent intramolecular McMurry condensation. It was shown that compound **16** could be consequently transformed into different bifunctional photochromic objects by step-by-step substitution of halogens. In the first step bromide in the benzothiophene ring was substituted by different amines having other functional groups in the molecule via catalytic amination, followed by lithiation of chloride in the thiophene ring. Spectral and kinetic studies of synthesized compounds were performed in toluene and acetonitrile solutions, PMMA layers, and solid films and showed standard photochromic properties typical for dithienylethenes. Absorption spectra and kinetic curves recorded for **10** and **16** showed almost no structural influence on photochromic properties for these compounds. At the same time, compound **10** displayed photochromism in a single-crystalline phase, which is the first example of this phenomenon to date for cyclopentene-based dihetarylethenes. X-ray analysis of **10** discovered the close relation between the intermolecular S···S interactions and the intramolecular distance between two reaction centers.

■ EXPERIMENTAL SECTION

General. All reactions were carried out under argon atmosphere. Solvents were dried by the usual methods and then distilled prior to use. NMR spectra were obtained at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR with chemical shift values in the spectra being

Table 2. Crystal Data and Structure Refinement Parameters for **10** at 150 and 173 K

temperature	150 K	173 K
empirical formula	$C_{20}H_{20}S_2$	
formula weight	324.48	
crystal color, habit	colorless, prism	
crystal system	monoclinic	
space group	$P2_1/c$	
Z (Z')	8(2)	4(1)
a, Å	16.6382(16)	8.3268(8)
b, Å	13.2364(14)	13.2672(11)
c, Å	15.3904(16)	15.4463(13)
β, deg	97.490(2)	97.4242(17)
V, Å^3	3360.5(6)	1692.1(3)
d_{calc} (g cm^{-1})	1.283	1.274
linear absorption, μ (cm^{-1})	3.11	3.09
F(000)	1376	688
$2\theta_{max}$, deg	58	58
reflections measured	19368	13205
independent reflections (R_{int})	8908 (0.0522)	4476 (0.0200)
observed reflections [$I > 2\sigma(I)$]	6507	3669
parameters	403	202
final $R(F_{hkl})$: R_1	0.0448	0.0407
wR_2	0.1283	0.1254
GOF	0.993	0.941
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.424/−0.361	0.356/−0.279

referenced to the solvent. Elemental analyses were carried out with a Perkin−Elmer CHN analyzer (2400 series II). High resolution mass spectra (HR MS) were measured on the Bruker micrOTOF II instrument using electrospray ionization (ESI).[31] The measurements were done in a positive ion mode (interface capillary voltage −4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. Spectral and kinetic studies were conducted with Cary 50 bio (Varian) spectrophotometer using a quartz cell with a path length of 0.2 cm. Concentration of the photochromic compounds in solution was 2×10^{-4} M. Toluene and acetonitrile from Aldrich were used as solvents. Polymer solid films were prepared by casting the corresponding chloroform solution (1 mL) of poly(methyl methacrylate) (PMMA) (100 mg) and dithienylethene (0.5 mg) into an open poly(ethylene terephthalate) (PET) box followed by evaporation in the dark. Solid films were obtained by evaporation of the corresponding toluene solutions ($C = 10^{-3}$ M) from a quartz plate. The slightly opaque film obtained from **10** was unevenly surfaced due to its polycrystalline origin. Compound **16** formed a smooth amorphous transparent film that retained its transparency throughout the measurements.

5-(2-Methylbenzo[*b*]thiophen-3-yl)-5-oxopentanoic Acid (8). To a solution of 2-methylbenzo[*b*]thiophene (4.2 g, 28.4 mmol) and glutaric anhydride (3.9 g, 34.1 mmol) in dry dichloromethane (40 mL) at −15 °C was added aluminum(III) chloride (9.4 g, 70.9 mmol) in portions within 1 h under argon atmosphere. The formed suspension was stirred at −5 to 0 °C for 2 h and then at rt for 5 h. The reaction mixture was quenched with ice, and the aqueous layer was additionally extracted with chloroform (4 × 30 mL). The combined organic extract was dried with anhydrous sodium sulfate. After evaporation of the solvent the residue was crystallized from dichloromethane/hexanes to give 2.1 g of gray powder. Filtrate was evaporated, and the residue was subjected to silica gel flash column chromatography (ethyl acetate/hexanes) to give additionally 1.8 g of **8**. Combination of two portions provided 3.9 g (53%) of gray solid: mp 108−110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (tt, 2H, J = 7.1, 7.1 Hz), 2.52 (t, 2H, J = 7.1 Hz), 2.77 (s, 3H), 3.04 (t, 2H, J = 7.1 Hz), 7.30−7.43 (m, 2H), 7.73 (d, 1H, J = 7.8 Hz), 8.10 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.8, 19.0, 33.0, 42.3, 121.6, 123.4, 124.3, 125.1, 132.6, 137.2, 138.1, 148.2, 179.5, 197.9. Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38; S, 12.22. Found: C, 64.09; H, 5.38; S, 12.25.

1-(2,5-Dimethylthiophen-3-yl)-5-(2-methylbenzo[*b*]thiophen-3-yl)pentane-1,5-dione (9). Carboxylic acid **8** (630 mg, 2.4 mmol) was added in portions to a stirred solution of oxalyl chloride (2.4 g, 18.9 mmol) and catalytical amount of dimethylformamide in dry 1,2-dichloroethane (10 mL) at 0 °C under argon atmosphere. The formed solution was stirred at rt for 12 h. Solvents were evaporated, and the residue was dried in vacuo to give 670 mg of dark solid. It was dissolved in dry dichloromethane (10 mL), and 2,5-dimethylthiophene (540 mg, 4.8 mmol) was added. Tin(IV) chloride (1.9 g, 7.3 mmol) was then added in a dropwise manner within 30 min to the formed solution at −5 °C under argon atmosphere. The suspension was stirred at rt for 16 h, quenched with ice, and filtered, and the aqueous layer was additionally extracted with chloroform (3 × 10 mL). The combined organic extract was washed with aqueous sodium carbonate and brine and then dried with anhydrous sodium sulfate. After evaporation of the solvent the residue was subjected to silica gel flash column chromatography (dichloromethane). Fractions containing **9** were combined and evaporated. Crystallization of the residue from ether/hexanes provided 460 mg (54%) of beige solid: mp 95−98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (tt, 2H, J = 7.0, 7.0 Hz), 2.39 (s, 3H), 2.66 (s, 3H), 2.77 (s, 3H), 2.92 (t, 2H, J = 7.0 Hz), 3.05 (t, 2H, J = 7.0 Hz), 6.99 (s, 1H), 7.29−7.42 (m, 2H), 7.73 (d, 1H, J = 8.0 Hz), 8.11 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 15.9, 16.8, 18.8, 40.5, 42.7, 121.6, 123.5, 124.2, 125.0, 125.9, 132.9, 135.0, 135.3, 137.3, 138.2, 147.2, 147.8, 195.7, 198.6; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{20}O_2S_2$, 357.0977; found 357.0974.

3-(2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-enyl)-2-methylbenzo[*b*]thiophene (10). Titanium(IV) chloride (490 mg, 2.6 mmol) was added in a dropwise manner to a well-stirred suspension of zinc dust (510 mg, 7.8 mmol) in dry tetrahydrofuran (15 mL) at −10 °C under argon atmosphere. The suspension was stirred at rt for 1 h, then dry pyridine (200 mg, 2.6 mmol) was added followed by addition of **9** (460 mg, 1.3 mmol) in one portion. The suspension was refluxed for 9 h, and after this time TLC analysis showed no starting material left in the reaction mixture. Several drops of water were added with stirring, and the suspension was filtered through a silica plug. After evaporation of the filtrate the residue was subjected to silica gel flash column chromatography (hexanes) to give 360 mg (86%) of white powder. Colorless crystals of **10** could be obtained by crystallization from hexane, and high quality single crystals suitable for X-ray diffraction were grown from hexane by slow evaporation: mp 97−98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89 (s, 3H), 2.20 (s, 3H), 2.21 (m, 2H), 2.37 (s, 3H), 2.67−2.91 (broad m, 2H), 2.99−3.15 (m, 2H), 6.45 (s, 1H), 7.28−7.39 (m, 2H), 7.63 (d, 1H, J = 7.5 Hz), 7.78 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.5, 15.0, 23.6, 37.8, 38.0, 121.8, 122.3, 123.2, 123.7, 125.7, 130.9, 132.3, 132.9, 134.7, 134.8, 135.5, 137.8, 138.3, 139.7. Anal. Calcd for $C_{20}H_{20}S_2$: C, 74.03; H, 6.21; S, 19.76. Found: C, 74.16; H, 6.21; S, 19.49.

5-(5-Chloro-2-methylthiophen-3-yl)-5-oxopentanoic Acid (13). To a solution of 2-chloro-5-methylthiophene[27] (15.3 g, 115 mmol) and glutaric anhydride (15.7 g, 138 mmol) in dry dichloromethane (200 mL) at −5 °C was added aluminum(III) chloride (38.2 g, 287 mmol) in portions within 1.5 h under argon atmosphere. The reaction mixture was stirred at 0 °C for 2 h and then at rt for 12 h. Ice was added, and the aqueous layer was additionally extracted with chloroform (3 × 100 mL). The combined organic layer was washed with brine, dried with anhydrous sodium sulfate, and evaporated. The crude product was purified with silica gel flash column chromatography (ethyl acetate/hexanes) to give 17 g (60%) of beige solid: mp 79−80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (tt, 2H, J = 7.1, 7.1 Hz), 2.48 (t, 2H, J = 7.1 Hz), 2.65 (s, 3H), 2.87 (t, 2H, J = 7.1 Hz), 7.18 (s, 1H), 11.12 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.9, 18.7, 32.9, 40.2, 125.3, 126.6, 134.7, 147.8, 179.4, 194.4. Anal. Calcd for $C_{10}H_{11}ClO_3S$: C, 48.68; H, 4.49; Cl, 14.37; S, 13.00. Found: C, 48.61; H, 4.53; Cl, 14.29; S, 12.92.

Synthesis of 1-(5-Bromo-2-methylbenzo[*b*]thiophen-3-yl)-5-(5-chloro-2-methylthiophen-3-yl)pentane-1,5-dione (14) from 13. Carboxylic acid **13** (570 mg, 2.3 mmol) was added in portions to a stirred solution of oxalyl chloride (2.9 g, 22.8 mmol) and a catalytical amount of dimethylformamide in dry 1,2-dichloroethane (10 mL) at −5 °C under argon atmosphere. The formed solution was stirred at rt for 4 h. Solvents were evaporated, and the residue was dried in vacuo to give 605 mg of dark oily solid. It was dissolved in dry dichloromethane (10 mL), and 5-bromo-2-methylbenzo[*b*]thiophene[32] (570 mg, 2.5 mmol) was added. Aluminum(III) chloride (670 mg, 5 mmol) was then added in portions to the formed solution at −5 °C under argon atmosphere. The suspension was stirred at rt for 16 h, quenched with ice, and filtered, and the aqueous layer was additionally extracted with chloroform (3 × 10 mL). The combined organic extract was washed with aqueous sodium carbonate and brine and then dried with anhydrous sodium sulfate. After evaporation of the solvent the residue was subjected to silica gel flash column chromatography (dichloromethane). Fractions containing **14** were combined and evaporated to give 330 mg (31%) of brown solid: mp 142−145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (tt, 2H, J = 6.9, 6.9 Hz), 2.67 (s, 3H), 2.79 (s, 3H), 2.91 (t, 2H, J = 6.9 Hz), 3.02 (t, 2H, J = 6.9 Hz), 7.19 (s, 1H), 7.42 (dd, 1H, J = 8.5, 1.9 Hz), 7.58 (d, 1H, J = 8.5 Hz), 8.37 (d, 1H, J = 1.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.9, 17.2, 18.5, 40.5, 42.5, 119.6, 122.6, 125.3, 126.6, 126.7, 127.5, 132.1, 134.8, 135.7, 140.0, 147.6, 149.7, 194.7, 197.5; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{16}BrClO_2S_2$, 454.9536; found 454.9527.

5-(5-Bromo-2-methylbenzo[*b*]thiophen-3-yl)-5-oxopentanoic Acid (15). To a solution of 5-bromo-2-methylbenzo[*b*]thiophene[32] (4 g, 17.6 mmol) and glutaric anhydride (2.4 g, 21.1 mmol) in dry dichloromethane (35 mL) at −15 °C was added aluminum(III) chloride (6.3 g, 47.5 mmol) in portions within 1 h under argon atmosphere. The reaction mixture was stirred at −5 to 0 °C for 2 h and then at rt for 5 h. The solvent was evaporated, and the solid was washed on filter with excess of water. After drying beige solid was extracted with hot ethyl acetate (50 mL) and hot chloroform (3 × 40 mL). After evaporation of solvents from the combined filtrate the residue was refluxed in ether and filtered to give 4.6 g (76%) of beige powder after drying. Analytically pure sample could be obtained by crystallization from ethyl acetate as white crystals: mp 170−173 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.89 (tt, 2H, J = 7.2, 7.1 Hz), 2.32 (t, 2H, J = 7.2 Hz), 2.80 (s, 3H), 3.02 (t, 2H, J = 7.1 Hz), 7.51 (dd, 1H, J = 8.5, 1.5 Hz), 7.92 (d, 1H, J = 8.5 Hz); 8.36 (d, 1H, J = 1.5 Hz); 12.07 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 16.9, 19.2, 32.8, 42.1, 118.8, 123.7, 126.0, 127.1, 131.3, 135.5, 139.9, 150.6, 174.3, 197.4. Anal. Calcd for $C_{14}H_{13}BrO_3S$: C, 49.28; H, 3.84; Br, 23.42; S, 9.40. Found: C, 49.27; H, 3.96; Br, 23.29; S, 9.34.

Synthesis of 1-(5-Bromo-2-methylbenzo[*b*]thiophen-3-yl)-5-(5-chloro-2-methylthiophen-3-yl)pentane-1,5-dione (14) from 15. Carboxylic acid **15** (2 g, 5.9 mmol) was added in portions to a stirred solution of oxalyl chloride (6.4 g, 50 mmol) and a catalytical amount of dimethylformamide in dry 1,2-dichloroethane (25 mL) at −15 °C under argon atmosphere. The formed suspension was slowly warmed and stirred at rt for 5 h. Solvents were evaporated, and the residue was dried in vacuo to give 2.1 g of brown solid. It was dissolved in dry dichloromethane (30 mL), and 2-chloro-5-methylthiophene[27] (1 g, 7.5 mmol) was added. Aluminum(III) chloride (2.3 g, 17.4 mmol) was then added in portions to the formed solution at −15 °C under argon atmosphere. The suspension was stirred at rt for 16 h, quenched with ice, and filtered, and the aqueous layer was additionally extracted with chloroform (3 × 20 mL). The combined organic extract was washed with aqueous sodium carbonate and brine and then dried with anhydrous sodium sulfate. After evaporation of the solvent the residue was subjected to silica gel flash column chromatography (dichloromethane) to give 370 mg (14%) of light-brown solid with analytical data identical to that of the earlier obtained sample (from **13**).

5-Bromo-3-(2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-enyl)-2-methylbenzo[*b*]thiophene (16). Titanium(IV) chloride (3.7 g, 19.5 mmol) was added in a dropwise manner to a well-stirred suspension of zinc dust (4.8 g, 73.8 mmol) in dry tetrahydrofuran (50 mL) at −10 °C under argon atmosphere. The suspension was refluxed for 1 h and then cooled to rt, and dry pyridine (1.5 g, 19 mmol) was added followed by addition of **14** (2.3 g, 5 mmol) in one portion. The suspension was refluxed for 8 h, and after this time TLC analysis showed no starting material left in the reaction mixture. Water (1.3 g, 72.2 mmol) was added with stirring; the precipitate was filtered and washed with hot ethyl acetate/hexanes 1/1 solution (3 × 35 mL). After evaporation of the combined filtrate the residue was subjected to silica gel flash column chromatography (hexanes) to give 1.6 g (75%) of colorless gum: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80 (s, 3H), 2.14 (s, 3H), 2.15 (m, 2H), 2.61−2.90 (broad m, 2H), 2.85−3.02 (m, 2H), 6.51 (s, 1H), 7.33 (dd, 1H, J = 8.4, 1.8 Hz), 7.57 (d, 1H, J = 8.4 Hz), 7.60 (d, 1H, J = 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.7, 23.4, 37.7, 37.9, 118.0, 123.2, 124.8, 125.0, 126.3, 126.4, 129.9, 133.4, 133.7, 134.4, 136.7, 137.3, 137.8, 140.9; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{16}BrClS_2$, 424.9617; found 424.9624.

1-(3-(2-(5-Chloro-2-methylthiophen-3-yl)cyclopent-1-enyl)-2-methylbenzo[*b*]thiophen-5-yl)-4-methylpiperazine (17). Dithienylethene **16** (460 mg, 1.1 mmol), tris(dibenzyledeneacetone)-dipalladium (0) (20 mg, 2 mol %), BINAP (41 mg, 6 mol %), sodium *tert*-butoxide (220 mg, 2.3 mmol), and 1-methylpiperazine (160 mg, 1.6 mmol) were sequentially placed into a Schott tube under argon atmosphere. Toluene (5 mL) was then added, washing all the solids from the walls of the tube. The reaction mixture was stirred at 80 °C for 20 h, and after this time TLC analysis showed no starting material left in the reaction mixture. Ethyl acetate (5 mL) was added, and the formed suspension was filtered. After evaporation of the filtrate the residue was subjected to silica gel flash column chromatography (hexanes/ethyl acetate) to give 368 mg (77%) of brown gum: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (s, 3H), 2.16 (m, 2H), 2.20 (s, 3H), 2.39 (s, 3H), 2.62 (m, 4H), 2.68−2.98 (m, 4H), 3.19 (m, 4H), 6.61 (s, 1H), 6.92 (d, 1H, J = 2.3 Hz), 6.97 (dd, 1H, J = 8.7, 2.3 Hz), 7.57 (d, 1H, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 14.8, 23.4, 37.8, 37.9, 46.1, 50.3, 55.2, 109.4, 115.2, 122.0, 124.7, 126.4, 130.3, 130.4, 133.4, 134.5, 134.6, 136.1, 136.5, 140.0, 148.8; HRMS (m/z) $[M + H]^+$ calcd for $C_{24}H_{27}ClN_2S_2$, 443.1377; found 443.1369.

4-(*tert*-Butyldimethylsilanyloxymethyl)piperidine. 4-Piperidinemethanol (500 mg, 4.4 mmol), *tert*-butylchlorodimethylsilane (660 mg, 4.4 mmol), and imidazole (590 mg, 8.7 mmol) were dissolved in dimethylformamide (2.5 mL), and the solution was kept at rt for 16 h. After dilution with water the mixture was extracted with *tert*-butyl methyl ether (3 × 10 mL). To the well-stirred combined organic extract was added water followed by acetic acid (1.3 g, 22 mmol). Aqueous layer was separated, neutralized with sodium bicarbonate, and then extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic extract was dried with anhydrous sodium sulfate and evaporated. Bulb-to-bulb distillation of the residue provided 520 mg (52%) of light yellow liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.90 (s, 9H), 1.05−1.18 (m, 2H), 2.59 (m, 1H), 2.70 (m, 2H), 2.81 (s, 1H), 2.60 (m, 2H), 3.09 (m, 2H), 3.42 (d, 2H, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.5, 18.3, 25.8, 30.0, 39.0, 46.3, 68.3; HRMS (m/z) $[M + H]^+$ calcd for $C_{12}H_{27}NOSi$, 230.1935; found 230.1930.

4-(*tert*-Butyldimethylsilanyloxymethyl)-1-(3-(2-(5-chloro-2-methylthiophen-3-yl)-cyclopent-1-enyl)-2-methylbenzo[*b*]thiophen-5-yl)piperidine (18). Dithienylethene **16** (424 mg, 1 mmol), tris(dibenzyledeneacetone)dipalladium (0) (15 mg, 1.6 mol %), BINAP (20 mg, 3.2 mol %), sodium *tert*-butoxide (300 mg, 3 mmol), and 4-(*tert*-butyldimethylsilanyloxymethyl)piperidine (458 mg, 2 mmol) were sequentially placed into a Schott tube under argon atmosphere. Toluene (5 mL) was then added, washing all the solids from the walls of the tube. The reaction mixture was stirred at 80 °C for 20 h, and after this time TLC analysis showed no starting material left in the reaction mixture. Ethyl acetate (5 mL) was added, and the formed suspension was filtered. After evaporation of the filtrate the residue was subjected to silica gel flash column chromatography (hexanes/ethyl acetate) to give 495 mg (87%) of yellow gum: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 6H), 0.93 (s, 9H), 1.43 (m, 2H), 1.63 (m, 1H), 1.76 (s, 3H), 1.89 (m, 2H), 2.15 (m, 2H), 2.22 (s, 3H), 2.68 (m, 2H), 2.70−2.99 (m, 4H), 3.52 (d, 2H, J = 6.4 Hz), 3.59 (m, 2H), 6.61 (s, 1H), 6.91 (d, 1H, J = 2.2 Hz), 6.99 (dd, 1H, J = 8.7, 2.2 Hz), 7.55 (d, 1H, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.4, 14.3, 14.9, 18.3, 23.4, 25.9, 29.1, 37.8, 38.0, 38.5, 51.0, 51.4, 68.0, 109.9, 116.2, 121.9, 124.8, 126.5, 130.1, 130.5, 133.5, 134.6, 134.7, 136.0, 136.3, 139.9, 149.7; HRMS (m/z) $[M + H]^+$ calcd for $C_{31}H_{42}ClNOS_2Si$, 572.2238; found 572.2239.

X-ray Crystallography. High quality single crystals of **10** were grown by slow evaporation from hexane. All diffraction data were collected on a Bruker SMART APEX II CCD diffractometer [λ(Mo Kα) = 0.71072 Å, ω-scans] for the same single crystal at 150 and 173 K. The substantial redundancy in data allows empirical absorption correction to be performed with SADABS, using multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The positions of hydrogen atoms were calculated from geometrical point of view and refined within the riding model. All calculations were performed with the SHELXTL software package.[33] Crystal data and structure refinement parameters are listed in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary no. CCDC-827043 (at 150 K) and CCDC-827044 (at 173 K).

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for compounds **8−10** and **13−18** and crystallographic data in CIF format for **10** at 150 and 173 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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