Syntheses of Dithienylcyclopentene Optical Molecular Switches

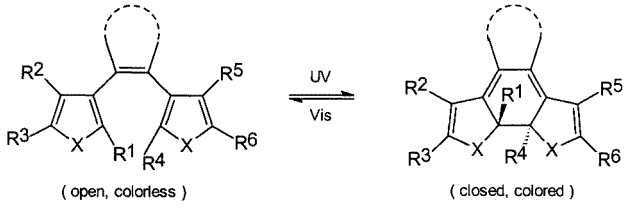
Linda N. Lucas,[a] Jaap J. D. de Jong,[a] Jan H. van Esch,*[a] Richard M. Kellogg,[a,b] and Ben L. Feringa*[a]

Keywords: Photochromism / Electrocyclic reactions / Cross-coupling / Diarylethene

Properly functionalized dithienylethenes show promise for light-induced switching processes. To prevent *cis*/*trans* isomerization from competing with conrotatory 6π-electron ring closure, the ethene segment is usually incorporated in a (perfluorinated) cyclopentene. In the present article syntheses of perhydrocyclopentene **1** and perfluorocyclopentene **2** are described, which are amenable for large-scale conversions. Both compounds have chloro substituents at the 5-position of the thiophene rings to allow further functionalization. The conversion of the chloro substituents of **1** to formyl, carboxylate, boronyl, and hydrogen groups by halogen/lithium exchange at room temperature is described, and examples are given of further elaboration of **1** and **2** by attachment, both in a symmetrical as well as unsymmetrical fashion, of additional functionality by condensation, Friedel–Crafts or Suzuki reactions. The newly prepared thienylperhydrocyclopentene derivatives show reversible photochromism if the substituents at the 5-postions allow for conjugation with the thiophene π-system.

Introduction

Of the many diarylethenes available, dithienylethenes of the sort illustrated in Scheme 1 show particular promise for optical switching processes. As illustrated they undergo reversible ring-closure on irradiation with ultraviolet (UV) or, in some cases, visible light. The closed intermediates are stable to oxidation if R^1 and R^4 are non-hydrogen substituents, methyl groups being an excellent example. In many cases the photochemically induced ring-closure is thermally irreversible and the compounds can show good fatigue resistance.[1] These are promising features for application in optical data storage,[2,3] molecular wires[4,5] and as molecular switches.[6]



Scheme 1. Switching cycle for 3,3′-dithienylethenes

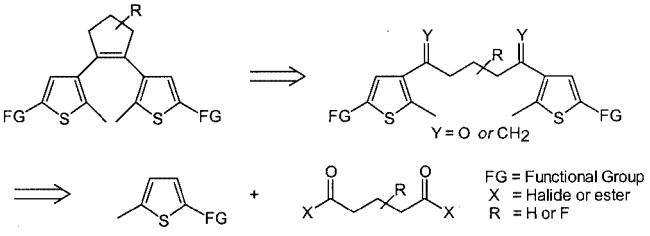
[a] Laboratory of Organic Chemistry, Stratingh Institute, University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands
Fax: (internat.) + 31-50/363-4296
E-mail: esch@chem.rug.nl
[b] Syncom B.V.,
Kadijk 3, 9747 AT Groningen, The Netherlands

The most commonly used diaryl-, and in particular dithienyl-, ethenes are the diarylperfluorocyclopentenes.[7] Diarylmaleic anhydrides[8] and diarylmaleimides are also commonly used.[9] Many functionalized derivatives of these diarylethenes have been synthesized.[6] Although the photochromic properties of these compounds are highly attractive, the synthesis of diarylethenes is not trivial. Diarylperfluorocyclopentenes are prepared by a double substitution reaction on octafluorocyclopentene by a lithiated thiophene derivative. The yields are usually moderate at best, it is not easy to scale up the procedure, and a considerable amount of monosubstituted perfluorocyclopentene product is formed. The major cause of these complications is that octafluorocyclopentene is very volatile (bp. 26−28 °C)[10] and therefore not easy to handle. Only in one case has a very high yield (99%) been reported.[11] Another drawback of this route is that octafluorocyclopentene is very expensive and not regularly available.

Recently we communicated a new and rather easy synthetic procedure wherein perhydro- rather than perfluorocyclopentene derivatives are prepared.[12] The reactions can be performed on a large scale and cheap(er) starting materials can be used. In this paper we present the full details on the synthesis and derivatization of these new dithienylcyclopentenes as well as details of conversions with perfluorocyclopentene derivatives. We also report methods for nonsymmetrical derivatization of these switches, and conclude with preliminary data on the photochromic properties of these compounds.

Results and Discussion

The retrosynthetic approach to functionalized dithienylcyclopentenes is shown in Scheme 2. In this route, the central cyclopentene ring is formed in the last step by a ring closure reaction of a 1,5-diketone by a McMurry reaction.[13,14] Another possibility to form this ring is by a ring-closure metathesis employing a 2,6-diaryl-1,6-heptadiene.[15,16] The latter compound can be obtained from the 1,5-diketone by a Wittig reaction. The generation of substituted cyclopentenes either by a McMurry reaction or a ring-closure metathesis are well established reactions that can be carried out on a multigram scale. The McMurry reaction was preferred, because it is performed in two consecutive steps in a "one-pot" procedure. As an alternative an "instant" method can be used, in which active titanium is prepared in the presence of the substrate.[17]



Scheme 2

The key intermediates in the two synthetic routes shown in Scheme 3 are the 1,5-diaryl-1,5-diketones **4** and **8**. Many procedures for the preparation of aryl ketones are known, the most straightforward of which is a Friedel–Crafts acylation of the corresponding aryl compounds with a 1,5-dicarboxylic dichloride. Alternatively, the addition of a metalated aryl (thienyl) group to a 1,5-dinitrile or 1,5-diester can be employed. The thiophene derivative to be used requires some consideration. The most reactive positions in the thiophene molecule are the 2- and 5-positions, but in the route envisioned in Schemes 2 and 3 the acylation must occur at the 3-position, which is only possible if the 2- and 5-positions are substituted. The functional groups have to be compatible with the reaction conditions and, if nonequivalent, must have the correct directing effects. The Friedel–Crafts reaction is preferred, because it saves one step compared to an addition of a metalated aryl (thienyl) group to a 1,5-dinitrile or 1,5-diester.

First, the synthesis of the simple dithienylcyclopentene **5** was carried out in order to test the viability of the proposed route (Scheme 3). The Friedel–Crafts acylation[18] of **3** with glutaryl dichloride in CS_2 using $AlCl_3$ as a Lewis acid gave a tarry reaction product, from which the desired 1,5-diketone **4** could be isolated by column chromatography in 40% yield. Ring closure of **4** by a McMurry reaction with Mg and $TiCl_3(THF)_3$ in THF at 40 °C[19] gave the desired 1,2-bis(2,5-dimethylthien-3-yl)cyclopentene (**5**) in 58% yield after purification using column chromatography with hexane. Later it was found that unpurified **4** could be subjected to the McMurry ring closure reaction without significant decrease in yield.

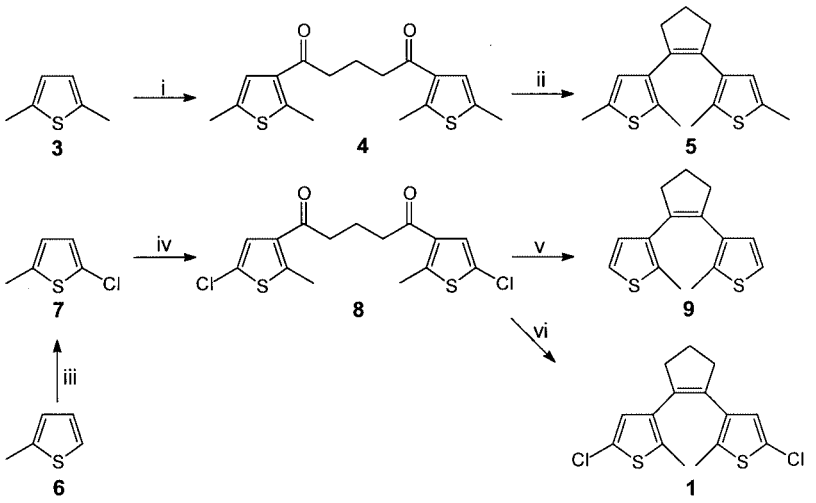
This synthesis can be performed on a large scale and the starting materials are easily accessible, but the drawback of **5** is the lack of functionality for further derivativization. Some attempts were made to brominate the 5-methyl groups of **5** using NBS, but no discrimination could be achieved between the methyl groups. Later it turned out that the photochemical reactions of these simple bis(2,5-dialkylthienyl)cyclopentenes are in fact irreversible, which implies that these compounds are not suitable as photochromic switches.[12]

The second approach shown in Scheme 3 starting from compound **7** offers access to compounds that can be more readily functionalized. Halogens are very versatile functional groups. First 2-bromo-5-methylthiophene was used as a substrate for the Friedel–Crafts acylation. However, this reaction was not successful because it was found that during the Friedel–Crafts acylation the bromo substituent shifted to the 3-position, followed by acylation at the more reactive 2-position. This rearrangement ("halogen dance") has been observed before for bromothiophenes,[20] and iodides are known to behave similarly. However, when 2-chloro-5-methylthiophene[20,21] was subjected to a Friedel–Crafts reaction[18] with $AlCl_3$ and glutaryl dichloride in CS_2 at 0 °C the desired diketone **8** was obtained in 98% yield (Scheme 3). The reasons for this high selectivity and the resulting avoidance of the need for the separation of isomers are not clear.[20]

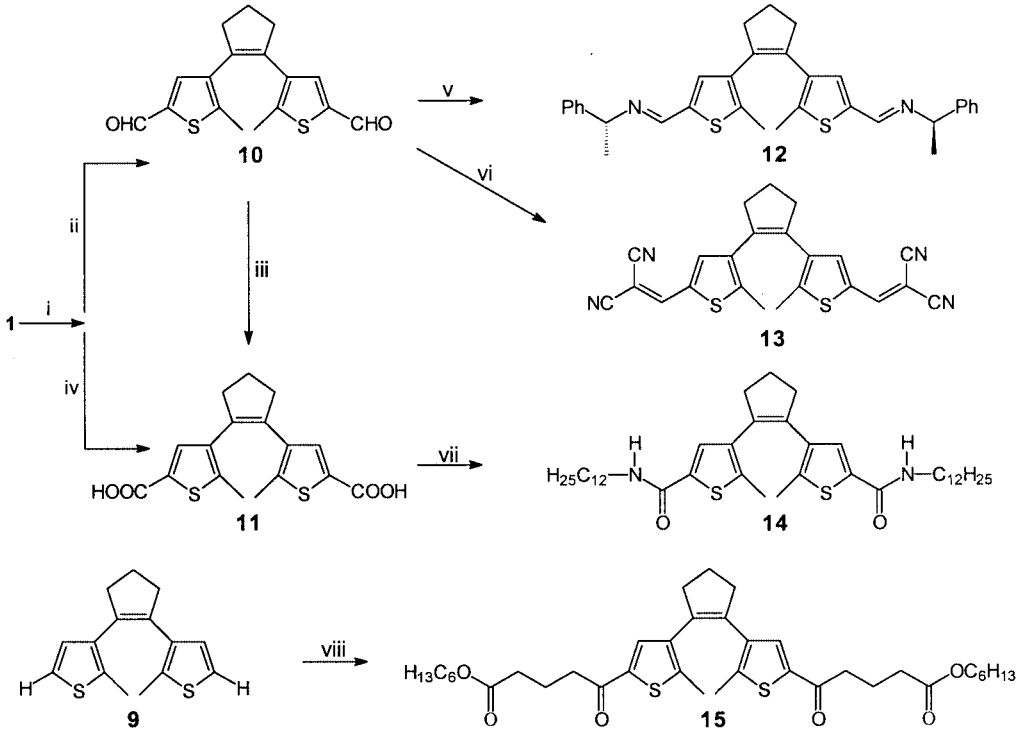
Diketone **8** was then used in a McMurry reaction[19] with $TiCl_3(THF)_3$ and Mg in THF at 40 °C.[13] NMR analysis revealed that instead of the expected product **1**, the dechlorinated ring-closed product **9** had been formed. Catalytic dechlorination of aromatic chlorides using Grignard reagents in the presence of $(C_2H_5)_2TiCl_2$ has also been reported by Takahashi et al.[22] They observed that the use of THF as a solvent dramatically improves the reactivity in this dehalogenation reaction. Compound **9** is not very stable, and deteriorates even at 4 °C within a week. McMurry reactions can also be carried out with milder reducing agents like zinc to prepare the Ti^0 species in situ.[17] When the reaction was carried out with $TiCl_3(THF)_3$ and Zn in THF at 40 °C, the desired diarylethene **1** could be obtained. Later it was found that instead of $TiCl_3$, which was suddenly removed from the commercial market, easier to handle $TiCl_4$ also could be used. The synthesis of compound **1** can be performed on a large scale (largest scale used to date was 1 mol) and requires only cheap starting materials.

The photochromic switch **1** can easily be functionalized in many different ways. Compound **1** can readily undergo a chlorine/lithium exchange at *ambient temperature* (Scheme 4) thus providing a versatile handle for the introduction of functionality.

Quenching of the doubly lithiated **1** with, for instance, DMF gave the dialdehyde **10** in 52% yield (Scheme 4). The diacid **11** (Scheme 4) can be obtained by oxidation of **10**,[23] or directly by adding CO_2(s) to a solution of lithiated **1**.[24]



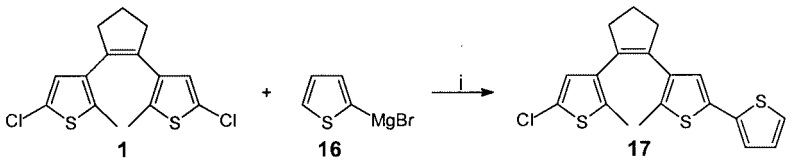
Scheme 3. Reagents: (i) glutaryl dichloride, $AlCl_3$, CS_2, 40%; (ii) Mg, $TiCl_3(THF)_3$, THF, 55%; (iii) NCS, HOAc, C_6H_6, 82%; (iv) glutaryl dichloride, $AlCl_3$, CS_2, 98%; (v) Mg, $TiCl_3(THF)_3$, THF, 55%; (vi) Zn, $TiCl_3(THF)_3$, THF, 50%



Scheme 4. Reagents: (i) *n*BuLi, room temperature., THF; (ii) DMF, THF, 52%; (iii) $AgNO_3$, NaOH, H_2O; (iv) CO_2(s), THF, 81%; (v) (*R*)-(+)-1-phenylethylamine, MeOH, 26%; (vi) malonitrile, piperidine, reflux, EtOH, 72%; (vii) *N*-methylmorpholine, 2-chloro-4,6-dimethoxytriazine, dodecylamine, CH_2Cl_2, 53%; (viii) hexyl 5-chloro-5-oxovalerate, $AlCl_3$, CS_2, 54%

This compound can for instance be used to synthesize amides **14**,[25] or alkyl esters. The dialdehyde **10** is a precursor for the bis[(phenylethyl)imino] derivative **12**.[26] Furthermore a condensation reaction with malonitrile has been carried out to yield **13**.[27] Lithiated **1** can also be quenched with a Brønsted acid to give **9**. Although this compound is not very stable, it can be used to synthesize compound **15** under standard Friedel−Crafts conditions using hexyl 5-chloro-5-oxovalerate.[28] Substitution occurs exclusively at the most reactive 5-position.

Photochromic switches with an extended aromatic system are currently the focus of much attention. It would be useful if an approach to diarylcyclopentene-based switches were available, in which an aromatic moiety could readily be coupled with a dithienylcyclopentene building block. The bis(chlorothienyl)cyclopentene switch **1** is in principle such



Scheme 5. Reagents: (i) Ni(dppp)Cl_2, reflux, EtO_2, 40%

a building block. The most straightforward method to extend the aromatic system of **1** is by a cross coupling reaction using organometallic reagents with organic halides and related electrophiles. Cross coupling methods[29] available for synthesis of biaryls are the Kumada coupling, the Suzuki coupling, the Stille coupling, or aryl C−C bond formation reactions mediated by organozinc reagents and aryl halides. In order to attach an aryl group to **1** it can be allowed to react with an organometallic reagent or the corresponding boronic acid derivative. Alternatively, **1** can be transformed into the organometallic compound or a boronic acid. Because many arylboronic acids and organometallic compounds are commercially available, it is easier to use **1** as the aryl halide.

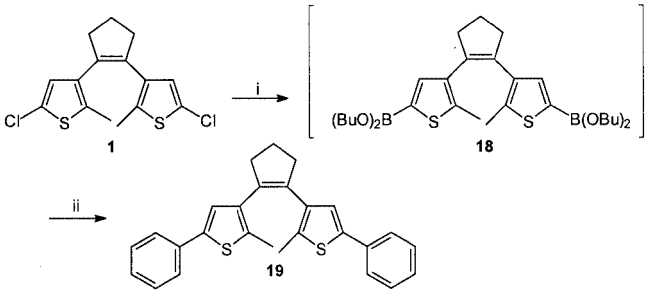
The first approach to synthesize the oligoaryl switch was by the Kumada[30] cross coupling reaction, because of the good experience in our group with this reaction for the synthesis of oligothiophene derivatives.[31] First a coupling between **1** and **16** in diethyl ether with Ni(dppp)Cl_2 as catalyst was performed,[32] but unfortunately only a single cross coupling took place to give **17** in 40% yield together with a small amount of starting material (Scheme 5).

Increasing the amount of catalyst to even stoichiometric quantities did not improve this result and only the monoadduct could be obtained. Compound **17** is, of course, interesting for the synthesis of nonsymmetric switches.

Another (phosphane)Ni complex often used in the Kumada cross coupling is [Ni(PPh_3)$_2Cl_2$]. On use of 1 equiv. of this catalyst under the same conditions as described above (Scheme 5), the starting material, the mono- and the bis(adduct) were recovered from the reaction mixture in a 1:1:4 ratio. Reduction of the amount of catalyst resulted in a lower yield of the bis(adduct), and at 10 mol % of catalyst or less no bis(adduct) was formed at all. This route clearly is not suitable. Most likely, the decreased reactivity of the chloride compared to bromides or iodides is the main problem in this Kumada cross coupling reaction.[33]

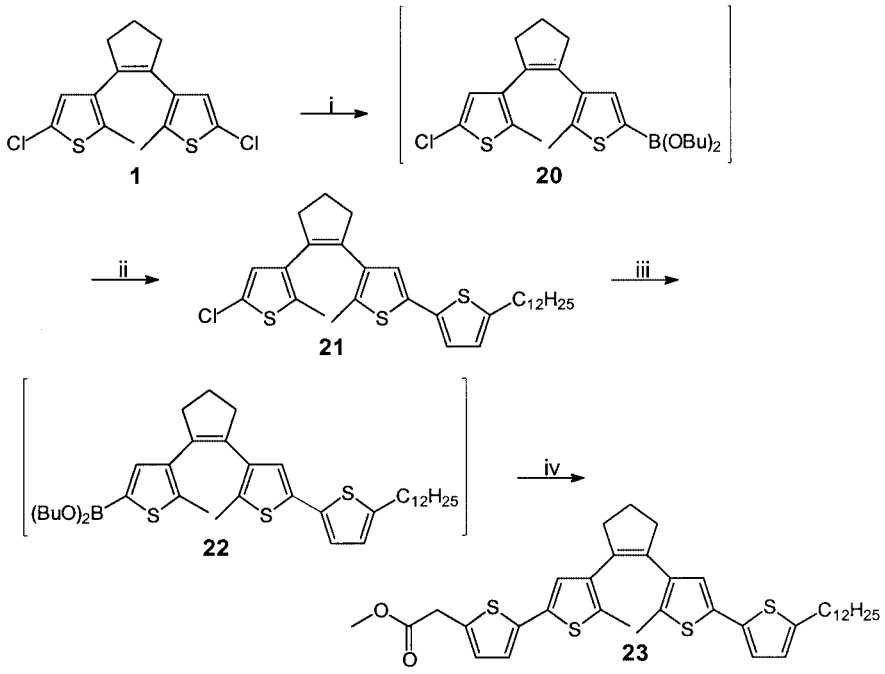
As an alternative to the Kumada cross coupling the two aryl fragments might be coupled using a Suzuki reaction.[29] These cross coupling reactions often proceed under mild conditions, provided the organoboron compound is activated with a suitable base. Because of their higher reactivity chiefly aryl bromides, iodides, and triflates have been used as starting materials for Suzuki reactions. There is currently a great deal of interest in the coupling of aryl chlorides with arylboronic acids.[34] Although nickel catalysts are useful for this reaction as has been demonstrated by Indolese[35] and Saito et al.,[36] most studies have focussed on palladium catalysts. Recently significant breakthroughs in this area have been made by Fu,[37] Buchwald,[38] Nolan,[39] Beller[40] and Trudell.[41] Suzuki coupling of chlorothiophene derivatives has not been reported yet, but the recently developed systems looked promising for our purpose. A series of reactions were carried out under the various conditions as reported.[37−41] Unfortunately none of these attempts led to a cross-coupled product, and starting compound **1** was recovered in all cases. Apparently, also in the Suzuki reaction the low reactivity of the chloro−thienyl bond prevents the coupling reaction from taking place. The most obvious solution to this problem is to convert the chloride switch **1** into the more reactive bromide derivative or to the boronic ester derivative. This latter approach has been applied before in the synthesis of diarylperfluorocyclopentene derivatives by Lehn et al.[5] It was found that **1** could also be converted into a boronic acid by means of an organolithium reagent followed by reaction with a borate, which was then allowed to react with an aryl halide in a Suzuki cross coupling reaction.

First, **1** was lithiated with *n*BuLi in THF at room temperature, and then treated with $B(OBu)_3$ to provide the bis(boronic ester) **18** (Scheme 6). The unpurified material was used directly in the Suzuki reaction without any workup because it was found that it easily hydrolyses to the dehalogenated switch **9** during isolation. A similar observation was made by Lehn et al.[5]



Scheme 6. Reagents: (i) *n*BuLi, room temperature, $B(OBu)_3$, THF; (ii) C_6H_5Br, Pd(PPh_3)$_4$, Na_2CO_3, ethylene glycol, H_2O, THF, 70%

For the Suzuki cross coupling reaction, Pd(PPh_3)$_4$ was used as palladium source, Na_2CO_3 as base, THF as solvent and several drops of ethylene glycol were added as cosolvent. In this particular case phenyl bromide was used as aryl halide source (Scheme 6). This procedure worked well, and after column chromatography, isolated yields of up to 70% were reached. The method described above for the Suzuki reaction to provide symmetrical **19** could also be used to



Scheme 7. Reagents: (i) *n*BuLi, room temperature, $B(OBu)_3$; (ii) 2-bromo-5-dodecylthiophene, $Pd(PPh_3)_4$, Na_2CO_3, ethylene glycol, reflux, H_2O, THF, 37%; (iii) *t*BuLi, room temperature, $B(OBu)_3$; (iv) methyl 2-(5-bromo-2-thienyl)acetic acid, $Pd(PPh_3)_4$, Na_2CO_3, ethylene glycol, reflux, H_2O, THF, 32%

synthesize nonsymmetrical switches after a slight modification. In this way compound **21** (Scheme 7) was synthesized.

Using 1 equiv. of *n*BuLi and subsequent reaction with $B(OBu)_3$ provided the monoboronic ester **20**. This product was allowed to react in the Suzuki reaction with 2-bromo-5-dodecylthiophene[42] to provide **21**. The amount of the disubstituted or unsubstituted compound was less than 5%. Compound **21** was subjected to a second Suzuki reaction. In this case *t*BuLi was used in order to promote lithiation because neither *n*BuLi nor *s*BuLi were effective. The same reaction sequence was repeated, this time with methyl 2-(5-bromo-2-thienyl)acetic acid[43] as aryl halide source to provide **23** in 12% overall yield starting from switch **1** (Scheme 7). All the dithienylcyclopentenes described in this article synthesized starting form compound **1** show photochromic behavior similar to that of known diarylethenes.[44]

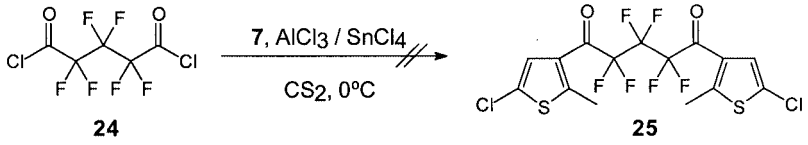
We investigated whether dithienylperfluorocyclopentene switches could also be synthesized according to the route developed for **1**. A Friedel−Crafts acylation of thiophene **7** with hexafluoroglutaryl dichloride (**24**),[45] $AlCl_3$ and benzene or toluene has been described in the literature.[46,47]

Unfortunately this reaction did not work for the combination of 2-chloro-5-methyl-thiophene (**7**) and hexafluoroglutaryl dichloride (**24**), and only an undefined black tar was obtained (Scheme 8). The use of $SnCl_4$ as Lewis acid did not lead to any improvement. Most likely, the acylation does not occur because the acylium intermediate is so difficult to obtain owing to the strongly electron-withdrawing fluorine atoms.

The diethyl ester of hexafluoroglutaric acid (**27**) has been used in a reaction with phenyllithium to obtain the corresponding diketone.[48] That same approach was used here. Diethyl hexafluoroglutarate (**27**) was synthesized[49] in quantitative yield by a standard acid-catalysed esterification of hexafluoroglutaric acid.

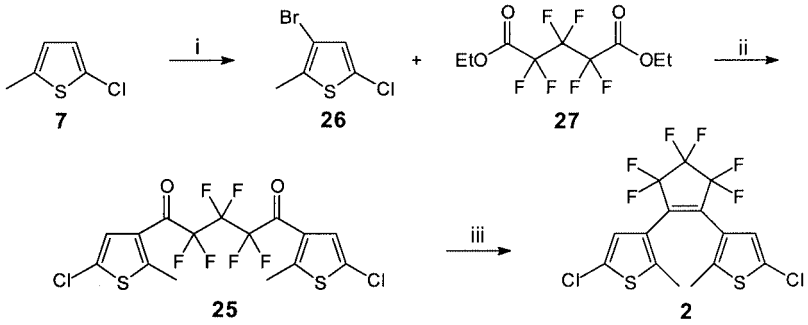
In this alternative approach[50] 2-chloro-5-methylthiophene (**7**) was used as the starting material (Scheme 9). Treatment of this compound with a lithiating reagent would result in lithium/halogen exchange of the chlorine atom at the 2-position instead of deprotonation at the 4-position. Therefore this compound was first brominated at the 4-position using Br_2 in chloroform to give 3-bromo-5-chloro-2-methylthiophene (**26**). Compound **26** was then lithiated at −78 °C in anhydrous diethyl ether using *n*BuLi. Under these conditions exclusive lithium/halogen exchange occurs with the bromine atom at the 3-position, and the chlorine substituent is not affected. Lithiated **26** was then treated with a solution of **27** in diethyl ether at the same temperature. After acidic workup, the 1,5-diketone **25** was obtained in good yield, and other regioisomers were not formed.

Ring closure was achieved by the McMurry coupling with $TiCl_3(THF)_3$ and Zn in THF at 40 °C to provide **2**, which was purified by column chromatography. It is, of course, in principle possible to use thiophene derivatives other than **26** in this route, provided that they can be lithiated exclusively at the 3-position. However, it was found that 3-bromo-5-chloro-2-methylthiophene is an extremely versatile intermediate for the introduction of functional groups at a later stage at the 5,5′-positions of the diarylperfluorocyclopentenes. Compound **2** can also easily be derivatized as described for compound **1**. Also in the case of **2**



24 25

Scheme 8. Attempted Friedel–Crafts acylation



7 26 27 25 2

Scheme 9. Reagents: (i) Br_2, $CHCl_3$, 93%; (ii) *n*BuLi, −78 °C, Et_2O, 70%; (iii) Zn, $TiCl_3(THF)_3$, THF, 55%

the compound can readily undergo a chlorine/lithium exchange at ambient temperature (Scheme 4) thus providing a versatile handle to introduce functionality. In this way the diformyl compound could be obtained as described before by Lehn.[27] Also the Suzuki reaction could be performed in the way described before for **1**, but **2** gave much lower yields than **1** in the Suzuki reaction with phenyl bromide, even when Lehn's conditions[5] were applied.

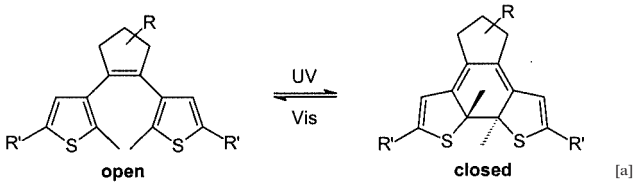
The photochromic behaviour of **1** and **2** and derivatives thereof was studied by irradiation with a high-pressure mercury lamp at selected wavelengths, and monitored by UV/Vis spectroscopy. Table 1 shows the absorption maxima for the open and closed forms of a number of the synthesized derivatives described in this article and their corresponding extinction coefficients. The absorption maxima of the open forms of **1**, **5** and **9** all appear at wavelengths < 240 nm, but extension of the switches with functional groups which can participate in conjugation with the thienyl groups, like with compounds **10**–**19** of Table 1, results in a bathochromic shift of the absorption maxima to wavelengths between 250 and 340 nm. Upon irradiation at wavelengths near their absorption maxima, the solutions of compounds **10**–**19** turn red to purple and two new absorption maxima appear in the visible region at 340–450 nm and 520–732 nm, respectively (Table 1 and Figure 1). The appearance of these bands is characteristic for the formation of the closed form.[1] It should be noted that in all cases a photostationary state (PSS) is obtained, and the extinction coefficients reported in Table 1 are those of the PSS. Due to nonzero absorption of the closed form in the UV spectral region, both ring closure and ring opening take place after photoexcitation, leading to an equilibrium situation (PSS) determined by the quantum yields of ring closing and ring opening. However, quantum yields obtained for diarylethenes showed that the cyclization is more efficient than the ring opening,[1] and therefore it can be assumed that the PSS represents the closed form of the switch.

The structure of the closed form was confirmed by ^{1}H NMR spectroscopy. The ^{13}C and ^{1}H NMR spectra of the open form of **1**–**19** showed clearly that these compounds have C_2 symmetry. Upon irradiation of solutions of the open form of **10**, **12**, **13** and **19**, a second set of peaks appeared which are slightly shifted with respect to those of the open form indicating that a photochemical reaction has occurred, but splitting or doubling of the peaks was not observed, which is in agreement with the C_2 symmetry of the closed form. The differences in chemical shift between the open and closed form are most pronounced for the thiophene proton and methyl group, and are summarized in Table 2.

Irradiation of solutions of **10**–**19** in the PSS with visible light ($\lambda > 450$ nm) causes the absorption bands in the visible region to disappear and the absorption band in the UV between 250 and 340 nm was restored. Apparently, photochemical switching between the ring-open and ring-closed form of **10**–**19** is reversible. Especially the photochromic switching of compounds **12**–**19** is excellent, and at least 5 photochemical switching cycles between the open and closed form can be performed without any sign of degradation. The dialdehyde switch **10** is photochemically less stable as became clear from the ± 8% decrease in intensity of the band at 280 nm of the open form after one cycle, which is similar to the photochemical stability of the perfluorinated dialdehyde as reported by Lehn et al.[27]

The photochemical behavior of compounds **1**, **5** and **9** is different. The open form of **1** showed a distinct absorption in the UV region after irradiation, and a clear absorption appeared in the visible region ($\lambda_{max} = 444$ nm). After longer irradiation times ($t > 10$ min), the absorption bands started to decrease indicating that **1** is degrading, probably

Table 1. UV/Vis spectroscopic data of the open and closed (PSS) form of several compounds



[a]

Compound	R/R′	λ_{max} open (ε)	λ_{max} PSS (ε)
1	H/Cl	240 (19.0)	276, 444 (1.2)
2	F/Cl	242 (24.9), 300 (4.8)	334 (19.3), 331 (5.71), 501 (3.9)
5	H/Me	233 (24.0), 275[b] (8.1)	201 (12.8)
9	H/H	229 (21.0), 270[b] (9.2)	231[b] (10.0)
10[c]	H/CHO	280 (41.0), 318 (14.9)	383 (16.6), 379 (15.8), 580 (14.7)
11[d]	H/COOH	252 (29.7), 290[b] (9.9)	253 (15.0), 347 (8.7), 531 (6.8)
12	H/CH=NCH(Me)Ph	271 (54.0), 308[b] (23.6)	366 (12.7), 555 (12.4)
13[c]	H/CH=C(CN)$_2$	334 (27.4), 392 (30.3)	358 (18.3), 448 (17.9), 732 (21.8)
14[d]	H/CONHC$_{12}$H$_{25}$	264 (28.7), 298[b] (9.9)	269 (12.9), 347 (8.0), 522 (8.9)
19	H/Ph	277 (33.3), 303[b] (23.1)	269 (24.8), 287 (21.2), 354 (11.1), 364 (12.0) 529 (14.6)

[a] UV/Vis spectroscopic data are obtained for *n*-hexane solutions at 25 °C, unless noted otherwise, and reported in nm (λ_{max}) and 10^3 cm^{-1} M^{-1} (ε). The PSS were obtained by irradiation of solutions of the open form with a 150-W mercury lamp with a 313-nm band pass filter (compounds **2**, **10**, **11**, **12**, **14**, **19**), a 405-nm band pass filter (compound **13**), or without filter (**1**, **5**, **9**). [b] Shoulder. [c] Benzene as solvent. [d] Methanol as solvent.

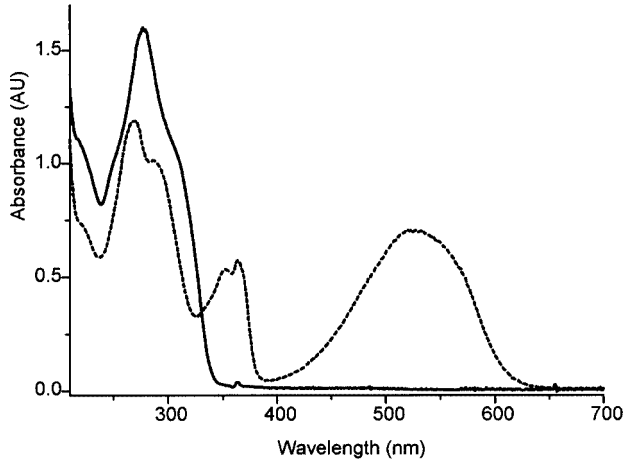


Figure 1. (a) UV/Vis spectra of **19** (4.8×10^{-5} M in *n*-hexane) in the open form (−) and the closed form (PSS, ---)

Table 2. ^{1}H NMR chemical shift data before and after irradiation

Compound[a]	δCH$_3$ open	δCH$_3$ closed	δCH open	δCH closed
10[b]	2.04	2.17	7.42	6.72
12[b]	1.97	1.94	6.95	7.37
13[b]	2.14	2.05	7.40	6.56
19[c]	1.98	2.25	7.04	6.27

[a] ^{1}H NMR spectra were obtained for 1 mM solutions of the compounds before and after irradiation at 25 °C (δ in ppm), using lamp and filters as described in Table 1. [b] $CDCl_3$ as solvent. [c] [D$_8$]Toluene as solvent.

to the compound proposed by Branda et al.[51] Apparently the photochemical switching of **1** can take place, but the process is not fully reversible due to degradation processes, which makes **1** unsuitable as a photochromic switch. Compounds **5** and **9** do not show maxima in the visible region after irradiation with UV light, and prolonged irradiation also leads to degradation of the compounds. Here the perfluoro compound **2** behaves more favorable. Irradiation of switch **2** showed a distinct absorption in the visible region (λ_{max} = 501 nm) due to formation of the closed form, and irradiation of the closed form with visible light ($\lambda >$ 460 nm) caused a complete conversion into the open form. Apparently, for the perfluoro switch **2** it is possible to switch selectively between the open and the closed form.

A very important property of the dithienylcyclopentene switches is the thermal irreversibility of the photochemical cyclization, and especially the closed form of the perfluorocyclopentene switches are stable up to temperatures well above 100 °C.[1] The thermal stability of the closed forms (PSS) of **13** and **19** were tested, because the thermal stability of their perfluoro derivatives were known from literature.[52,27] For compound **19** it was found that the closed form shows excellent thermal stability up to 80 °C for prolonged periods (> 14 h), although at 100 °C slowly reverts to the open form. The ring-closed form of switch **13** appeared to be less stable at elevated temperatures, and reverts to the ring-open form with a half-life time of 4.27 min at 60 °C in benzene, which is in fact slower then the perfluorocyclopentene analogues compound ($t_{1/2}$ = 3.3 min).[27] ^{1}H NMR spectroscopy revealed the closed form only reverts to the open form, as there is no sign of any decomposition products in the spectra.

In summary, a facile synthetic route to diarylethenes **1** and **2** has been described. The reactions can be performed on a large scale and cheap starting materials can be used compared to the commonly employed syntheses. The dithienylcyclopentene **1** is a highly versatile starting material for

a variety of dithienylcyclopentene-based compounds that can be used as molecular switches, and both symmetrical and nonsymmetrical derivatives are readily accessible. It appears that if the conjugation of switch **1** is increased, the dithienylcyclopentenes shows excellent switching behavior and little fatigue. It is foreseen that these favorable properties together with the facile synthetic procedures reported here will strongly stimulate the application of dithienylcyclopentene-based photochromic switches in advanced systems like switchable molecular wires and antenna systems, molecular electronics, and smart materials.

Experimental Section

General Procedures: Melting points were determined with a Büchi melting point apparatus or a Mettler FP1 melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 200 MHz, 300 MHz or 500 MHz, ^{13}C NMR spectra were recorded at 50.3 MHz, 75.4 MHz or 125.7 MHz, and ^{19}F NMR spectra were recorded at 188.2 MHz or 470.3 MHz. All spectra were taken at ambient temperature, with the residual protons from the solvent as an internal reference and the chemical shifts are reported relative to TMS. Mass spectrometry was performed using CI^+, DEI or EI^+ ionization procedures. The dithienylethenes are sometimes hard to sublime and only by means of DEI (desorption electron ionization) it is possible in these cases to obtain the mass spectrum. Derivatives synthesized starting from compound **1** are light-sensitive and were therefore exclusively handled in the dark using brown glassware, and column chromatography was performed in yellow light.

Materials: Reagents and starting materials were used as supplied. The solvents were distilled and dried before use, if necessary, using standard methods. Aldrich silica gel grade 9385 (230−400 mesh) was used for column chromatography. Hexyl 5-chloro-5-oxovalerate,[28] 2-bromo-5-dodecylthiophene,[42] methyl 2-(5-bromo-2-thienyl)acetic acid[43] and diethyl hexafluoroglutarate (**27**)[48] were synthesized according to literature procedures. The petroleum ether used had a boiling range of 40−60 °C.

1,5-Bis(2,5-dimethylthien-3-yl)pentane-1,5-dione (4): $AlCl_3$ (7.02 g, 52.7 mmol) and 2,5-dimethylthiophene (5.0 mL, 44 mmol) were added to CS_2 (100 mL). The mixture was heated to reflux and glutaryl dichloride (3.71 g, 22.0 mmol) in CS_2 (25 mL) was added dropwise. After the addition of glutaryl dichloride, the reaction mixture was refluxed for 2 h. After cooling to room temperature, cold H_2O (50 mL) was carefully added to the reaction mixture and the water layer was extracted with diethyl ether (3 × 75 mL). The combined organic phases were washed with a saturated $NaHCO_3$ solution (1 × 50 mL) and water (1 × 50 mL), dried (Na_2SO_4), filtered and the solvent was evaporated in vacuo to yield a yellow solid (3.78 g, 54%), m.p. 57.0−58.2, which was used in subsequent reactions without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.85 (s, 6 H), 1.95−2.09 (m, 2 H), 2.34 (s, 6 H), 2.73 (t, J = 7.2, 9.6 Hz, 4 H), 6.41 (s, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.9 (q), 16.0 (q), 18.5 (t), 40.6 (t), 126.0 (d), 134.9 (s), 135.3 (s), 147.1 (s), 195.9 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1669 cm^{-1} (C=O). MS (EI): m/z = 320 [M^+]. $C_{17}H_{20}O_2S_2$: calcd. C 63.72, H 6.29; found C 64.14, H 6.33.

1,2-Bis(2,5-dimethylthien-3-yl)cyclopentene (5): $TiCl_3(THF)_3$ (0.42 g, 1.1 mmol) and Mg (69 mg, 2.8 mmol) were stirred under nitrogen in dry THF (30 mL) at 40 °C until the blue colour of $TiCl_3(THF)_3$ had disappeared and then **4** (0.36 g, 1.1 mmol) was added to the black solution. After stirring for 2 h at 40 °C, the mixture was poured into aqueous hydrochloric acid (6 N, 50 mL). After extraction with diethyl ether (2 × 50 mL), the combined diethyl ether layers were washed with a saturated sodium bicarbonate solution (2 × 25 mL) and H_2O (1 × 25 mL), dried (Na_2SO_4), filtered and the solvent was evaporated in vacuo to yield a brown oil (0.28 g, 86%). Chromatography on silica gel (hexane/ethyl acetate, 9:1) afforded the product as a white solid (0.19 g, 58%), m.p. 89.0−90.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (s, 6 H), 1.95−2.09 (m, 2 H), 2.34 (s, 6 H), 2.73 (t, J = 7.4 Hz, 4 H), 6.41 (s, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.8 (q), 14.9 (q), 22.7 (t), 38.2 (t), 125.9 (d), 131.9 (s), 134.0 (s), 134.8 (s), 135.3 (s) ppm. MS (EI): m/z = 288 [M^+]. $C_{17}H_{20}S_2$: calcd. C 70.78, H 6.99; found C 70.13, H 6.92.

2-Chloro-5-methylthiophene (7): 2-Methylthiophene (100 mL, 1.03 mol) and *N*-chlorosuccinimide (152 g, 1.13 mol) were added to a stirred solution of benzene (400 mL) and acetic acid (400 mL). The suspension was stirred for 30 min at room temperature, then, after 1 h of heating at reflux, the cooled mixture was poured into a 3 M aq. NaOH solution (300 mL). The organic phase was washed with a 3 M aq. NaOH solution (3 × 300 mL), dried (Na_2SO_4), filtered and the solvent evaporated in vacuo to yield a slightly yellow liquid. Purification of the product by vacuum distillation (19 Torr, 55 °C) afforded a colourless liquid (111 g, 84%), b.p. 55 °C (19 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 6.40−6.42 (m, 1 H), 6.58 (d, J = 2.2 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.2 (q), 124.3 (s), 125.7 (s), 126.4 (s), 138.4 (s) ppm. MS (EI): m/z = 131 [M^+]. C_5H_5ClS: calcd. C 45.29, H 3.80; found C 45.76, H 3.77.

1,5-Bis(5-chloro-2-methylthien-3-yl)pentane-1,5-dione (8): Under vigorous stirring $AlCl_3$ (48 g, 0.36 mol) was added in portions to an ice-cooled solution of **7** (32.3 mL, 0.298 mol) and glutaryl dichloride (25 g, 0.15 mmol) in CS_2 (300 mL). After addition of $AlCl_3$, the reaction mixture was stirred for 2 h at room temperature. Then ice-cold water (100 mL) was carefully added to the reaction mixture and the water layer was extracted with diethyl ether (3 × 150 mL). The combined organic phases were washed with water (1 × 100 mL), dried (Na_2SO_4), filtered and the solvent was evaporated in vacuo to yield a brown tar (53 g, 98%). This tar can be purified by flash chromatography (hexane/ethyl acetate, 9:1) to provide a white solid (25.9 g, 48%), m.p. 82.0−85.0. For further reactions it is, however, not necessary to purify this tar. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.98−2.12 (m, 2 H), 2.66 (s, 6 H), 2.86 (t, J = 6.8 Hz, 2 H), 7.19 (s, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 16.0 (q), 18.1 (t), 40.4 (t), 125.2 (d), 126.7 (s), 134.7 (s), 147.6 (s), 194.7 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 1675 cm^{-1} (C=O). MS (EI): m/z = 360 [M^+]. $C_{15}H_{14}Cl_2O_2S_2$: calcd. C 49.87, H 3.91; found C 49.46, H 3.94.

1,2-Bis(2-methylthien-3-yl)cyclopentene (9): $TiCl_3(THF)_3$ (1.57 g, 4.23 mmol) and Mg (0.26 g, 11 mmol) were stirred under nitrogen in dry THF (30 mL) at 40 °C until the blue colour of $TiCl_3(THF)_3$ had disappeared, whereupon **8** (1.53 g, 4.23 mmol) was added to the black solution. After stirring for 30 min at 40 °C, the mixture was cooled to room temperature and poured into aqueous hydrochloric acid (6 N, 50 mL). The resulting mixture was extracted with diethyl ether (2 × 50 mL). The combined organic layers were washed with a saturated $NaHCO_3$ solution (2 × 25 mL) and H_2O (1 × 25 mL), dried (Na_2SO_4), filtered and the solvent was evaporated in vacuo to yield a brown oil (0.79 g, 72%). Chromatography of the oil on silica gel (petroleum ether) afforded the compound as a yellow oil (0.22 g, 20%). Due to its instability further purification

was not successful. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.92 (s, 6 H), 1.97−2.14 (m, 2 H), 2.79 (t, *J* = 7.5 Hz, 4 H), 6.74 (d, *J* = 5.0 Hz, 2 H), 6.95 (d, *J* = 5.0 Hz, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.9 (q), 22.9 (t), 38.3 (t), 121.0 (d), 128.0 (s), 134.3 (d), 136.5 (s), 143.2 (s) ppm. MS (EI): *m*/*z* = 260 [M^+].

1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene (1): "Instant method": A mixture of **8** (1.13 g, 3.13 mmol), $TiCl_3(THF)_3$ (2.32 g, 6.26 mmol), Zn dust (0.82 g, 7.8 mmol) and THF (30 mL) was stirred under nitrogen at 40 °C for 1 h. The mixture was cooled to room temperature and poured through a glass filter containing silica gel that was pretreated with petroleum ether. The silica was rinsed with petroleum ether. After evaporation of the solvent, a yellow solid (0.97 g, 94%) remained. Pure **1** was obtained as a white solid (0.45 g, 44%) after purification by chromatography on silica gel (petroleum ether), m.p. 75.6−78.0. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.98 (s, 6 H),1.94−2.09 (m, 2 H), 2.71 (t, *J* = 7.5 Hz, 4 H), 6.58 (s, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.9 (q), 23.6 (t), 39.1 (t), 125.9 (d), 127.4 (s), 134.0 (s), 135.1 (s), 135.5 (s) ppm. MS (EI): *m*/*z* = 328 [M^+]. $C_{15}H_{14}Cl_2S_2$: calcd. C 54.71, H 4.29; found C 54.54, H 4.24.

1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene (1): Due to lack of $TiCl_3$ the reaction was later on carried out with $TiCl_4$. THF (50 mL) and Zn dust (2.5 g) were placed in a three-necked flask under nitrogen. $TiCl_4$ (6.2 mL, 29 mmol) was added very cautiously using a glass syringe. The solution turned yellow and was refluxed for 45 min. Next it was cooled in an ice bath and **8** (6.90 g, 19.2 mmol) was added in portions. This mixture was refluxed for 2 h, subsequently quenched with 10% aq. K_2CO_3 (50 mL) and extracted with diethyl ether (4 × 20 mL). The combined organic layers were washed with H_2O (1 × 25 mL), dried (Na_2SO_4) and the solvent was removed in vacuo. The compound was purified by column chromatography in the same way as described before in this case to yield (3.16 g, 50%) of a white solid. The properties of **1** synthesized by this route are identical to those described for **1** prepared with $TiCl_3(THF)_3$.

1,2-Bis(5-formyl-2-methylthien-3-yl)cyclopentene (10): *n*BuLi (7.85 mL of a 1.6 M solution in hexane, 12.6 mmol) was added to a stirred solution of **1** (1.97 g, 5.98 mmol) in anhydrous THF (20 mL) under nitrogen at room temperature. 1 h after the addition, the reaction mixture was quenched with anhydrous dimethylformamide (0.97 mL, 12 mmol). The mixture was stirred then for an additional hour at room temperature, before it was poured into aqueous HCl (2 N, 50 mL). The mixture was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with a saturated $NaHCO_3$ solution (2 × 25 mL) and H_2O (1 × 25 mL), and dried (Na_2SO_4), filtered and the solvents evaporated in vacuo to yield a brown solid (1.89 g, 90%). Chromatography on silica gel (hexane/ethyl acetate, 9:1) afforded the product as a brown/orange solid (0.98 g, 52%), m.p. 116.1−117.9 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.04 (s, 6 H), 2.07−2.17 (m, 2 H), 2.83 (t, *J* = 7.5 Hz, 4 H), 7.42 (s, 2 H), 9.74 (s, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.3 (q), 22.8 (t), 38.3 (t), 134.9 (d), 136.9 (s), 137.3 (s), 140.1 (s), 146.3 (s), 182.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 1662 cm^{-1} (C=O). MS (EI): *m*/*z* = 316 [M^+]. HRMS: calcd. for $C_{17}H_{16}O_2S_2$ 316.059, found 316.061.

1,2-Bis(5-carboxy-2-methylthien-3-yl)cyclopentene (11): *n*BuLi (2.4 mL of a 1.6 M solution in hexane, 3.8 mmol) was added to a stirred solution of **1** (0.50 g, 1.5 mmol) in anhydrous THF (15 mL) under nitrogen at room temperature. After 1 h, solid CO_2 (excess) was added. After 30 min, water (15 mL) was added. The water layer was washed with diethyl ether and then acidified with 30% HCl until pH = 1 was reached. The precipitated product was filtered with care and washed with 1 M HCl. The residual water was azeotropically removed with toluene to yield an off-white solid (0.43 g, 1.2 mmol, 81%). ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 1.91 (s, 6 H, CH_3), 1.95−2.05 (m, 2 H), 2.77 (t, *J* = 7.8 Hz, 4 H), 7.40 (s, 2 H,) ppm. ^{13}C NMR (75.4 MHz, [D_6]DMSO): δ = 14.3 (q), 22.3 (t), 37.9 (t), 130.4 (s), 133.8 (d), 134.3 (s), 136.4 (s), 141.7 (s), 162.6 (s) ppm. IR: $\tilde{\nu}$ = 1550, 1663, 2578, 2841, 2953 cm^{-1}, MS (EI): *m*/*z* = 348 [M^+]. $C_{17}H_{16}O_4S_2$: calcd. C 58.60, H 4.63; found C 58.77, H 4.73.

1,2-Bis(2-methyl-5-{[(1-phenylethyl)imino]methyl}thien-3-yl)cyclopentene (12): 10 (40.3 mg, 0.130 mmol) was dissolved in (+)-(1*R*)-1-phenylethylamine (3.4 mL of a stock solution of 1 mL of amine in 99 mL of methanol). After 18 h of stirring at room temperature, the solvent was removed in vacuo. The mixture was diluted with dichloromethane and dried (Na_2SO_4), filtered and the solvents were evaporated in vacuo to yield a brown oil. Chromatography on Al_2O_3 (hexane/ethyl acetate/Et_3N, 2:1:0.02) afforded a purple oil (17.6 mg, 26%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.55 (d, *J* = 6.6 Hz, 6 H), 1.97 (s, 6 H), 1.94−2.10 (m, 2 H), 2.76 (t, *J* = 7.7 Hz, 4 H), 4.45 (q, *J* = 6.8, *J* = 6.4 Hz, 2 H), 6.95 (s, 2 H), 7.24−7.36 (m, 10 H), 8.25(s, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.9 (q), 22.9 (t), 24.8 (q), 38.3 (t), 69.1 (d), 126.6 (d), 126.73 (d), 128.4(d), 131.6 (s), 134.4 (s), 135.9 (s), 138.5 (s), 139.0 (s), 145.1 (s), 152.7 (d) ppm. IR: $\tilde{\nu}$ = 1631 cm^{-1}. HRMS: calcd. for $C_{33}H_{34}N_2S_2$ 522.216, found 522.216.

1,2-Bis[5-(2,2-dicyanoethenyl)-2-methylthien-3-yl]cyclopentene (13): A mixture of malonitrile (15 mg, 0.23 mmol), **10** (35.0 mg, 0.111 mmol) and a catalytic amount of piperidine (1 drop of a stock solution of 1 drop of amine in 2 mL of absolute ethanol) in absolute ethanol (1.5 mL) was heated to reflux. After 17 h, the solution was cooled to room temperature and the solvent was removed in vacuo. Trituration of the crude product in methanol resulted in the formation of a brown/orange solid, which was isolated by filtration in the dark and dried in vacuo (33 mg, 72%), m.p. 154−156 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.14 (s, 6 H), 2.05−2.20 (m, 2 H), 2.82 (t, *J* = 7.2 Hz, 4 H), 7.40 (s, 2 H), 7.63 (s, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.4 (q), 22.8 (t), 38.3 (t), 113.1 (s), 113.9 (s), 132.1 (d), 135.2 (s), 137.7 (s), 139.0 (s), 148.8 (s), 150.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2343 cm^{-1}, 2223 cm^{-1} (C≡N), 1574 cm^{-1} (C=C−CN)$_2$. MS (EI): *m*/*z* = 412 [M^+]. HRMS: calcd. for $C_{23}H_{16}N_4S_2$ 412.0816, found 412.0822.

1,2-Bis{5-[(dodecylamino)carbonyl]-2-methylthien-3-yl}cyclopentene (14): 11 (0.20 g, 0.60 mmol) was suspended in CH_2Cl_2 (5 mL) and placed in an ice bath. Subsequently *N*-methylmorpholine (0.13 mL, 1.2 mmol) was added and the solid material dissolved. Then 2-chloro-4,6-dimethoxytriazine (0.20 g, 1.2 mmol) was added, and a white precipitate was formed immediately after this addition. The reaction mixture was stirred for 2 h at 0 °C, and then another 2 equiv. of *N*-methylmorpholine (0.13 mL, 1.2 mmol) were added followed by dodecylamine (0.26 mL, 1.2 mmol). Stirring was continued for 1 h at 0 °C, and subsequently overnight at room temperature. CH_2Cl_2 (50 mL) was added and the solution was washed with 1 M HCl (2 × 20 mL), brine (1 × 20 mL), a saturated aq. bicarbonate solution (1 × 20 mL) and H_2O (1 × 20 mL). The organic phase was dried (Na_2SO_4) and evaporation of the solvent gave a solid product. After purification by column chromatography (CH_2Cl_2/MeOH, 40:1) an off-white solid was obtained (0.22 g, 53%), m.p. 102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.24 (m,18 H), 1.56 (m, 4 H), 1.92 (s, 6 H), 1.97−2.07 (m, 2 H), 2.77 (t, *J* = 7.5 Hz, 4 H), 3.35 (m, 4 H), 5.77 (t, 2 H, NH), 7.17 (s, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$):

δ = 14.1 (q), 14.6 (q), 22.7 (t), 22.8 (t), 26.8 (t), 26.9 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t, 2×), 31.9 (t), 38.4 (t), 40.0 (t), 129.3 (d), 134.4 (s), 134.7 (s), 136.2 (s), 139.5 (s), 161.8 (s) ppm. IR (neat): $\tilde{\nu}$ = 1535, 1561, 1618, 2852, 2922, 3298 cm^{-1}. MS (DEI): 682 [M^+]. HRMS: calcd. for $C_{41}H_{66}N_2O_2S_2$ 682.457, found 682.455.

1,2-Bis[5-(5-hexyloxy-1,5-dioxopentyl)-2-methylthien-3-yl]cyclopentene (15): $AlCl_3$ (3.50 g, 26.2 mmol) was added in three portions to a solution of **9** (3.10 g, 11.9 mmol) and hexyl 5-chloro-5-oxovalerate (5.60 g, 23.8 mmol) in CS_2 (90 mL) at 0 °C. After addition, the ice bath was removed and the mixture was stirred at room temperature for 2 h. The mixture was then cautiously quenched with ice-cold water and the water layer was extracted with diethyl ether (2 × 75 mL). The combined organic layers were washed with a saturated aq. bicarbonate solution (2 × 50 mL) and brine (1 × 50 mL). The organic layer was dried with Na_2SO_4 and the solvent evaporated to leave a dark oil. This oil was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH, 40:1) to afford a pure product as colorless oil (4.01 g, 54%), ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.87 (t, *J* = 6.6 Hz, 3 H), 1.29 (s, 6 H), 1.5−1.64 (m, 2 H), 1.94−2.05 (m, 2 H), 1.96 (s, 6 H), 2.0−2.13 (m, 2 H), 2.38 (t, *J* = 7.2 Hz, 2 H), 2.80 (t, *J* = 7.8 Hz, 4 H), 2.84 (t, *J* = 7.2 Hz, 2 H), 4.05 (t, *J* = 6.8 Hz, 4 H), 7.38 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.9 (q), 15.0 (q), 19.7 (t), 22.5 (t), 22.8 (t), 25.5 (t), 28.5 (t), 31.4 (t), 33.3 (t), 37.7 (t), 38.4 (t), 64.5 (t), 132.8 (s), 134.8 (d), 136.8 (s), 139.87 (s), 144.3 (s), 173.1 (s), 191.8 (s) ppm. HRMS: calcd. for $C_{37}H_{52}O_6S_2$ 656.321, found 656.319.

2-Thienylmagnesium Bromide (16): A solution of 2-bromothiophene (1.00 mL, 10.3 mmol) in anhydrous diethyl ether (8 mL) was added dropwise to magnesium turnings (0.30 g, 12 mmol) in diethyl ether (2 mL). The mixture spontaneously started to reflux, became turbid and the amount of magnesium diminished in time. After 1 h of reflux, the Grignard reagent was ready for use in the Kumada coupling.

1-(5-Chloro-2-methylthien-3-yl)-2-[2-methyl-5-(thien-2-yl)thien-3-yl]cyclopentene (17): A Grignard reagent was prepared of 2-bromothiophene (0.57 mL, 4.8 mmol), Mg (0.12 g, 5.1 mmol) and diethyl ether (5 mL) according to the procedure described for **16**. At the same time **1** (0.40 g, 1.2 mmol) was added to a suspension of Ni(dppp)Cl_2 (21 mg, 0.04 mmol) in anhydrous diethyl ether (10 mL). The thienylmagnesium bromide solution was added dropwise at 0 °C. The mixture turned black immediately. After addition, the mixture was refluxed for 20 h. Subsequently the reaction mixture was quenched with 2 N HCl at 0 °C, extracted with diethyl ether (3 × 50 mL) and dried (Na_2SO_4). After column chromatography (petroleum ether), **17** was obtained as a red oil (0.18 g, 40%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.90 (s, 3 H), 1.95 (s, 3 H), 2.00−2.09 (m, 2 H), 2.72−2.82 (m, 4 H), 6.62 (s, 1 H), 6.86 (s, 1 H), 6.99 (d, *J* = 4.2 Hz, 1 H), 7.05 (d, *J* = 3.6 Hz, 1 H), 7.15 (d, *J* = 5.1 Hz, 1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.2 (q), 14.2 (q), 22.9 (t), 38.3 (t), 38.4 (t), 122.9 (d), 123.7 (d), 124.3 (d), 126.7 (d), 127.6 (d), 133.1 (s), 133.22 (s), 133.9 (s), 135.0 (s), 135.0 (s), 136.0 (s), 137.6 (s) ppm. MS (EI): 377 [M^+]. HRMS: calcd. for $C_{19}H_{17}ClS_3$ 376.017, found 376.018.

1,2-Bis[5-(dibutoxyboryl)-2-methylthien-3-yl]cyclopentene (18): **1** (1.75 g, 5.30 mmol) was dissolved in anhydrous THF (12 mL) and *n*BuLi (4.5 mL of 2.5 M solution in hexane, 11.2 mmol) was added under nitrogen at room temperature in 5 portions using a syringe. This solution was stirred for 30 min at room temperature, then $B(OBu)_3$ (4.3 mL, 16 mmol) was added in one portion. This reddish solution was stirred for 1 h at room temperature and was then used in the Suzuki cross coupling reaction without any workup because the product is deboronized during isolation.

1,2-Bis(2-methyl-5-phenylthien-3-yl)cyclopentene (19): Bromobenzene (1.12 mL, 9.29 mmol) was dissolved in THF (12 mL), $Pd(PPh_3)_4$ (0.37 g, 0.30 mmol) was added, and the resulting solution was stirred for 15 min at room temperature. Then aqueous Na_2CO_3 (23 mL, 2 M) and 6 drops of ethylene glycol were added. This two-phase system was heated in an oil bath just below reflux at a temperature of 60 °C and the solution of **18** was added dropwise via a syringe in a short time period of approximately 5 min. Subsequently the mixture was refluxed for 2 h and cooled to room temperature, after which diethyl ether (50 mL) and H_2O (50 mL) were added. The organic layer was separated and dried (Na_2SO_4). After concentration, the compound was purified by column chromatography on silica (hexane) to yield a brown/yellowish solid (1.80 g, 70%), m.p. 85 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.98 (s, 6 H), 2.03−2.13 (m, 2 H), 2.84 (t, *J* = 7.5 Hz, 4 H), 7.03 (s, 2 H), 7.19−7.25 (m, 2 H), 7.32 (dd, *J* = 6.9, *J* = 7.5 Hz, 4 H), 7.49 (d, *J* = 7.2 Hz, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.4 (q), 23.0 (t), 38.5 (t), 123.9 (s), 125.2 (d), 126.8 (d), 128.7 (d), 134.4 (s), 134.5 (s), 136.6 (s), 139.5 (s) ppm. $C_{27}H_{24}S_2$ (412.6): calcd. C 78.60, H 5.86; found C 78.65, H 5.90.

1-(5-Chloro-2-methylthien-3-yl)-2-[5-(dibutoxyboryl)-2-methylthien-3-yl]cyclopentene (20): **1** (0.47 g, 1.4 mmol) was dissolved in anhydrous THF (10 mL) and *n*BuLi (0.89 mL of 1.6 M solution in hexane, 1.4 mmol) was added dropwise under nitrogen using a syringe. The mixture was stirred for 30 min at room temperature and $B(OBu)_3$ (0.58 mL, 2.1 mmol) was added in one portion. This solution was stirred for 1 h at room temperature and was used in the nonsymmetrical Suzuki cross coupling reaction without further workup.

1-(5-Chloro-2-methylthien-3-yl)-2-[5-(5-dodecylthien-2-yl)-2-methylthien-3-yl]cyclopentene (21): 2-Bromo-5-dodecylthiophene (0.49 g, 1.4 mmol) was dissolved in THF (12 mL), $Pd(PPh_3)_4$ (53 mg, 3 mol %) was added, and this solution was stirred for 15 min at room temperature. Then aq. Na_2CO_3 (6 mL, 2 M) and 8 drops of ethylene glycol were added. This two-phase system was heated in an oil bath just below reflux (60 °C) and the solution of **20** (1.4 mmol) in THF (8 mL) was added dropwise via a syringe over a short time. After that, the mixture was heated at reflux for 2 h. After cooling, diethyl ether (100 mL) and H_2O (50 mL) were added. The organic layer was washed with H_2O (1 × 50 mL), 2 M HCl (2 × 50 mL), brine (2 × 50 mL) and dried (Na_2SO_4). After evaporation of the solvent, the product was purified by column chromatography (petroleum ether) on silica to yield a pink oil (0.28 g, 37%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.87 (t, *J* = 6.3, *J* = 6.9, 3 H), 1.20−1.34 (m, 20 H), 1.58−1.71 (m, 2 H), 1.87 (s, 3 H), 1.91 (s, 3 H), 1.97- 2.08 (m, 2 H), 2.68−2.81 (m, 4 H), 6.59 (s, 1 H), 6.62 (d, *J* = 3.6 Hz, 1 H), 6.76 (s, 1 H), 6.84 (d, *J* = 3.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 14.1 (q), 14.2 (q), 22.7 (t), 22.9 (t), 29.1 (t), 29.3 (t), 29.5 (t), 29.6 (t), 30.1 (t), 31.6 (t), 31.9 (t), 38.4 (t), 38.5 (t), 122.6 (d), 123.5 (d), 123.9 (s), 124.6 (d), 125.0 (s), 126.8 (d), 133.2 (s), 133.3 (s), 133.7 (s), 133.7 (s), 135.0 (s), 135.1 (s), 135.9 (s), 144.8 (s) ppm. HRMS: calcd. for $C_{31}H_{41}S_3Cl$ 554.206, found 554.205.

1-[5-(Dibutoxyboryl)-2-methylthien-3-yl]-2-[5-(5-dodecylthien-2-yl)-2-methylthien-3-yl]cyclopentene (22): **21** (0.30 g, 0.55 mmol) was dissolved in anhydrous THF (5 mL) and *t*BuLi (0.35 mL of 1.7 M solution in pentane, 0.61 mmol) was added dropwise under nitrogen at 0 °C using a syringe. The mixture was stirred for 45 min at room temperature and $B(OBu)_3$ (0.22 mL, 0.83 mmol) was added in one portion. This solution was stirred for 1 h at room temperature and was used in the nonsymmetrical Suzuki cross coupling

reaction without further workup because the product is hydrolyzed during isolation.

1-[5-(5-Dodecylthien-2-yl)-2-methylthien-3-yl]-2-[(5-{5-[(methoxycarbonyl)methyl]thien-2-yl})-2-methylthien-3-yl]cyclopentene (23): Methyl 2-(5-bromothien-2-yl)acetic acid (0.13 g, 0.55 mmol) was dissolved in THF (12 mL) and $Pd(PPh_3)_4$ (53 mg, 3 mol %) was added, this solution was stirred for 15 min at room temperature. Then aq. Na_2CO_3 (6 mL, 2 M) and 6 drops of ethylene glycol were added. This two-phase system was heated in an oil bath just below reflux (60 °C) and the solution of **22** (0.55 mmol) in THF (5 mL) was added dropwise via a syringe over a short time, followed by reflux of the mixture for 4 h. After cooling, diethyl ether (100 mL) and H_2O (50 mL) were added. The organic layer was washed with H_2O (1 × 20 mL), saturated aq. NH_4Cl (1 × 25 mL), a saturated aq. bicarbonate solution (1 × 25 mL), brine (2 × 25 mL) and dried (Na_2SO_4). After concentration, the compound was purified by column chromatography (hexane/ethyl acetate, 9:1) on silica to yield an oil (0.12 g, 32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.3, *J* = 6.9, 3 H), 1.20−1.34 (m, 20 H), 1.58−1.71 (m, 2 H), 1.90 (s, 3 H), 1.91 (s, 3 H), 1.98- 2.09 (m, 2 H), 2.71−2.81 (m, 4 H), 3.73 (s, 3 H), 3.78 (s, 2 H), 6.62 (d, *J* = 3.6 Hz, 1 H), 6.78 (d, *J* = 3.9 Hz, 1 H), 6.80 (s, 1 H), 6.83 (d, *J* = 3.3 Hz, 1 H), 6.84 (s, 1 H), 6.87 (d, *J* = 3.3 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 14.1 (q), 14.3 (q), 22.7 (t), 22.9 (t), 29.1 (t), 29.3 (t), 29.5 (t), 29.6 (t), 30.1 (t), 31.6 (t), 31.9 (t), 35.4 (t), 38.5 (t), 52.3 (q), 122.5 (d), 123.63 (d), 124.3 (d), 124.5 (d), 127.5 (d), 132.9 (s), 133.3 (s), 133.6 (s), 133.9 (s), 134.3 (s), 134.6 (s), 135.1 (s), 136.1 (s), 136.3 (s), 137.6 (s), 144.4 (s), 144.7 (s), 170.7 (s) ppm. HRMS: calcd. for $C_{38}H_{48}O_2S_4$ 664.254, found 664.252.

3-Bromo-5-chloro-2-methylthiophene (26): A solution of bromine (3.78 mL, 73.3 mmol) in $CHCl_3$ (20 mL) was added slowly to an ice-cooled solution of **7** (9.72 g, 73.3 mmol) in $CHCl_3$ (75 mL). After addition of the bromine, the reaction mixture was stirred for 2 h at room temperature, and subsequently poured into H_2O (150 mL). The water layer was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4), filtered and the solvent was evaporated in vacuo to yield a yellow/brown oil (14.4 g, 93%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.32 (s, 6 H), 6.73 (s,1 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.5 (q), 107.4 (s), 126.7 (d), 128.3 (s), 133.0 (s) ppm. MS (EI): 211 [M^+]. C_5H_4BrClS: calcd. C 28.39, H 1.91; found C 28.74, H 1.97.

1,5-Bis(5-chloro-2-methylthien-3-yl)hexafluoropentane-1,5-dione (25): *n*BuLi (1.6 M in hexane, 5.4 mL, 8.6 mmol) was added to a stirred solution of **26** (1.75 g, 8.29 mmol) in anhydrous diethyl ether (25 mL) under nitrogen at −78 °C. After 15 min of stirring at that temperature, **27** (0.91 mL, 4.2 mmol) in anhydrous diethyl ether (2 mL) was added slowly to the mixture in about 30 min. The reaction mixture was quenched with hydrochloric acid (2 N, 10 mL) and extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with a saturated aq. sodium bicarbonate solution (1 × 25 mL) and H_2O (1 × 25 mL), dried (Na_2SO_4), filtered and the solvent was evaporated in vacuo to yield a brown/reddish oil, which was used in the next step without further purification (1.36 g, 70%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.70 (s, 6 H), 7.31 (s, 2 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 17.1 (q), 110.4 (t), 111.1 (t), 125.8 (d), 126.2 (s), 128.9 (s), 155.4 (s), 177.9 (s) ppm. ^{19}F NMR (470.3 MHz, $CDCl_3$): δ = −116.18 (dd, 4 F), −122.73 (dd, 2 F) ppm. IR (Nujol): $\tilde{\nu}$ = 1696 cm^{-1} (C=O). MS (EI): 467[M^+]. HRMS: calcd. for $C_{15}H_8Cl_2F_6O_2S_2$ 467.925, found 467.925.

1,2-Bis(5-chloro-2-methylthien-3-yl)hexafluorocyclopentene (2): "Instant method": A mixture of **25** (0.96 g, 2.1 mmol), $TiCl_3(THF)_3$ (1.50 g, 4.12 mmol), Zn dust (0.53 g, 8.2 mmol) and THF (25 mL) were stirred under nitrogen at 40 °C for 1 h. The mixture was cooled and poured through a glass filter containing silica gel that was pretreated with petroleum ether. The silica was rinsed with petroleum ether. A white solid (0.49 g, 55%) was obtained after purification by chromatography on silica gel (petroleum ether), m.p. 132 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.88 (s, 6 H), 6.88 (s, 2 H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 14.3 (q), 110.7 (t), 117.7 (t), 123.9 (d), 125.4 (s), 127.9 (s), 135.8 (s), 140.4 (s) ppm. ^{19}F NMR (470.3 MHz, $CDCl_3$): δ = −114.78 (dd, *J* = 5.5, 5.0 Hz, 4 F), −136.37 (dd, *J* = 6.2, 5.0 Hz, 2 F) ppm. $C_{15}H_8Cl_2F_6S_2$ (437.3): calcd. C 41.20, H 1.84; found C 41.25, H 1.87.

Acknowledgments

The Royal Netherlands Academy of Sciences is gratefully acknowledged for a fellowship for J. v. E. The authors thank Patrick van Rijn for his contribution to the synthetic work.

[1] M. Irie, *Chem. Rev.* **2000**, *100*, 1685.
[2] P. Ball, L. Garwin, *Nature* **1992**, *355*, 761.
[3] D. M. Eigler, C. P. Lutz, W. E. Rudge, *Nature* **1991**, *352*, 600.
[4] G. M. Tsivgoulis, J.-M. Lehn, *Adv. Mater.* **1997**, *9*, 39.
[5] G. M. Tsivgoulis, J.-M. Lehn, *Chem. Eur. J.* **1996**, *2*, 1399.
[6] B. L. Feringa (Ed.), *Molecular Switches*, Wiley-VCH, Weinheim, **2001**.
[7] M. Hanazawa, R. Sumiya, Y. Horikawa, M. Irie, *J. Chem. Soc., Chem. Commun.* **1992**, 206.
[8] M. Irie, M. Mohri, *J. Org. Chem.* **1988**, *53*, 803.
[9] T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **1997**, *119*, 6066.
[10] R. D. Chambers, R. Edwards, *J. Chem. Soc., Perkin Trans. 1* **1997**, *24*, 3623.
[11] Y. Yokoyama, N. Hosoda, Y. T. Osano, C. Sasaki, *Chem. Lett.* **1998**, 1093.
[12] L. N. Lucas, J. van Esch, R. M. Kellogg, B. L. Feringa, *Chem. Commun.* **1998**, 2313.
[13] J. E. McMurry, *J. Am. Chem. Soc.* **1974**, *96*, 1708.
[14] J. E. McMurry, *Chem. Rev.* **1989**, *89*, 1513.
[15] M. T. Crimmins, B. W. King, *J. Org. Chem.* **1996**, *61*, 4192.
[16] For a recent review see: A. Fürstner, *Angew. Chem. Int. Ed.* **2000**, *39*, 3013.
[17] A. Fürstner, A. Hupperts, A. Ptock, E. Janssen, *J. Org. Chem.* **1994**, *59*, 5215.
[18] G. M. Badger, H. J. Rodda, W. H. F. Sasse, *J. Chem. Soc.* **1954**, 4162.
[19] S. Tyrlik, I. Wolochowicz, *Bull. Soc. Chim. Fr.* **1973**, 2147.
[20] D. R. Arnold, C. P. Hadjiantoniou, *Can. J. Chem.* **1978**, *56*, 1970.
[21] E. Campaigne, W. M. LeSuer, *J. Am. Chem. Soc.* **1948**, *70*, 415.
[22] R. Hara, K. Sato, W.-H. Sun, T. Takahashi, *Chem. Commun.* **1999**, 845.
[23] S. Gronowitz, K. Stenhamar, L. Svensson, *Heterocycles* **1981**, *15*, 947.
[24] T. B. Norsten, N. R. Branda, *J. Am. Chem. Soc.* **2001**, *123*, 1784.
[25] L. N. Lucas, J. van Esch, R. M. Kellogg, B. L. Feringa, *Chem. Commun.* **2001**, 759.
[26] C. Denekamp, B. L. Feringa, *Adv. Mater.* **1998**, *10*, 1080.
[27] S. L. Gilat, S. H. Kawai, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 275.
[28] S. Lartillot, C. Baron, *Bull. Soc. Chim. Fr.* **1964**, 783.
[29] F. Diederich, P. J. Stang (Eds.), *Metal-catalyzed Cross coupling Reactions*, Wiley-VCH, Weinheim, **1998**.
[30] K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374.
[31] F. S. Schoonbeek, J. H. van Esch, B. Wegewijs, D. B. A Rep,

M. P. de Haas, T. M. Klapwijk, R. M. Kellogg, B. L. Feringa, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1393.
[32] K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S.-I. Kodama, I. Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.
[33] Usually aryl bromides or iodides are used in the Kumada cross coupling because of their higher reactivity, although recent studies showed that also chlorobenzene derivatives can be successfully coupled with Grignard reagents by means of $Pd_2(dba)_3$ with N-heterocyclic carbenes as ligands rather than phosphanes. See: [33a] H. Juang, S. P. Nolan, *J. Am. Chem. Soc.* **1999**, *121*, 9889. [33b] V. P. W. Böhm, T. Weskamp, C. W. K. Gstöttmayr, W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 1602.
[34] R. Stürmer, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 3307.
[35] A. F. Indolese, *Tetrahedron Lett.* **1997**, *38*, 3513.
[36] S. Saito, S. Oh-tani, N. Miyaura, *J. Org. Chem.* **1997**, *62*, 8024.
[37] A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 3387.
[38] J. P. Wolfe, S. L. Buchwald, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 2413.
[39] C. Zhang, J. Huang, M. L. Trudell, S. P. Nolan, *J. Org. Chem.* **1999**, *64*, 3804.
[40] A. Zapf, M. Beller, *Chem. Eur. J.* **2000**, *6*, 1830.
[41] C. Zhang, M. L. Trudell, *Tetrahedon Lett.* **2000**, *41*, 595.
[42] P. Bäuerle, F. Würthner, G. Götz, F. Effenberger, *Synthesis* **1993**, 1099.
[43] S. Gronowitz, S. Liljefors, *Chem. Scr.* **1979**, *13*, 39.
[44] L. N. Lucas, *Dithienyl Optical Switches, Towards Photoresponsive Supramolecular Materials*, PhD Thesis, Groningen, **2001**.
[45] G. G. Rozantsev, G. I. Braz, A. Y. Yakubovich, *Zh. Obshch. Khim.* **1964**, *34*, 2974.
[46] C. Tamborski, *J. Fluorine Chem.* **1979**, *14*, 243.
[47] B. F. Malichenko, Z. S. Prikhod'ko, *Zh. Org. Khim.* **1969**, *5*, 2192.
[48] L. S. Chen, C. Tamborski, *J. Fluorine Chem.* **1982**, *19*, 43.
[49] E. T. McBee, A. W. Park, G. B. Bachman, *Ind. Eng. Chem.* **1947**, *39*, 415.
[50] L. N. Lucas, J. van Esch, R. M. Kellogg, B. L. Feringa, *Tetrahedron Lett.* **1999**, *40*, 1775.
[51] A. Peters, N. R. Branda, *Adv. Mater. Opt. Electron.* **2000**, *10*, 245.
[52] M. Irie, T. Lifka, K. Uchida, S. Kobatake, N. Kato, *J. Am. Chem. Soc.* **2000**, *122*, 4871.

Received July 16, 2002
[O02392]