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Synthesis of Rotationally Restricted and Modular Biphenyl Building Blocks

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A series of modular biphenyl building blocks with stepwise adjusted torsion angles and terminally functionalized with leaving groups have been synthesized. The two phenyl rings of the biphenyl synthon are clamped by alkyl chains of various lengths. The desired building blocks **3** and **4** were obtained by copper-mediated C–C biaryl coupling reactions followed by the construction of interlinking alkyl bridges. The key intermediates **14** and **15** were transformed into the corresponding cycloheptadienones **16** and **17**, which were reduced to the desired propyl-bridged biphenyls **3b** and **3c**. The butyl-bridged derivatives **4b** and **4c** were obtained from **14** and **15** by an allylation reaction followed by ring-closing metathesis (RCM) and hydrogenation. The pentyl chain in precursor **24** was obtained by two aldol C–C bond-forming reactions followed by a sequence of reduction steps. It was subsequently cyclized in an aryl–aryl coupling reaction to the pentyl-bridged biphenyl **26** along with the macrocyclic dimer **25**. The UV absorption spectra of the acetylsulfanyl-functionalized series **1a**–**8a** were recorded and analyzed: A linear correlation between the conjugation band in the UV absorption spectra and the $\cos^2\Phi$ values (Φ is the interplanar torsion angle) is observed.

Introduction

The concept of molecules as minute functional building blocks with atomic precision for electronic applications ranging from single molecules,[1–3] through molecular devices,[4–8] to bulk materials leads to a new perception in organic chemistry. The electronic properties of a functional unit suddenly came to be designed and engineered by synthetic chemists, no longer solely the task of semiconductor engineers. Of particular interest are conjugated π systems as their delocalized electrons are expected to considerably favor electronic transport through their structures. Thus, π-conjugated molecules, either as single-molecule wires[3,9,10] or as polymers,[11–14] have received considerable attention as potential functional subunits or materials in emerging areas, for example, in molecular electronics,[15] photovoltaics,[16,17] or light-emitting systems.[18] A detailed understanding of the structural factors governing electron-transport processes is not only of fundamental interest, but also a crucial requirement for the development of design criteria.

Biphenyls as the smallest structures to comprise two adjacent benzene rings as individual π systems are ideal model compounds to investigate electronic transport properties.[19–21] Particularly appealing features are their rigidity, which results in a well-defined spacing of their terminal units, and their compactness, which provides detectable signals even in poorly conducting conformations. Usually, donor or acceptor subunits are interlinked by biphenyl structures, which allows electron transfer to be studied on a molecular level.[22,23] Thus, the degree of π overlap in the two phenyl rings and the resulting extent of delocalization over both π systems dictates the electronic communication through the synthon, which is expected to vary with the torsion angle Φ between the planes of the two phenyl rings. In other words, a high conducting state is expected for a biphenyl system with both phenyl rings in the same plane, whereas considerably reduced conducting features are expected for systems in which the two rings are perpendicular.[19,24–27]

The ability to modulate or even control the configuration of biphenyl subunits enables the electronic communication along the biphenyl backbone to be regulated. Several examples of biphenyl systems with a partially controlled torsion angle Φ as connector in molecular devices have been reported. McLendon and co-workers used *ortho*-substituted biphenyls with porphyrin termini as model compounds to study the through-bond electron-transfer rate as a function of the torsion angle.[23] By preparing biphenyls with crown ether bridges, Benniston et al. attempted to control the biphenyl conformation by complexation with cations.[28] In a recent study, Venkataraman et al. reported the correlation between calculated molecular conformation and single-molecule conductance of several terminally amine-functionalized biphenyl systems comprising different additional substituents.[29]

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Unfortunately, in all these model compounds the torsion angle between the two phenyl rings was not the only parameter to vary, and thus alterations in physical properties might be the result of several effects. In particular, the electron density in the phenyl rings is affected by different substituents influencing the expected torsion angles. Furthermore, thermal motion leads to variation in the torsion angles of simple biphenyl systems comprising a C–C single bond as the link between the two phenyl rings.

To face these challenges, we would like to present our recent approach to the systematic variation of the torsion angle Φ in biphenyl systems with almost negligible alteration in the electronic properties of the phenyl rings and with considerably reduced thermal variation of the torsion angle. The basic idea was to interlink the two phenyl rings through an additional alkyl chain of various lengths bridging the two *ortho* positions (Figure 1). To achieve a reasonably relaxed conformation of the additional alkyl chain, the inter-ring torsion angle must increase with increasing length of the alkyl chain. All members of the series have an additional alkyl substituent at the *ortho* position and thus a very comparable electronic situation for all the compounds. Finally, as the biphenyl synthon became a subunit of a rather rigid cyclic structure, thermal fluctuations of the torsion angle are considerably reduced compared with the parent biphenyl systems.

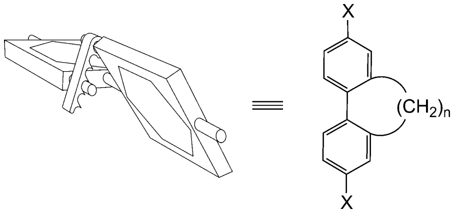
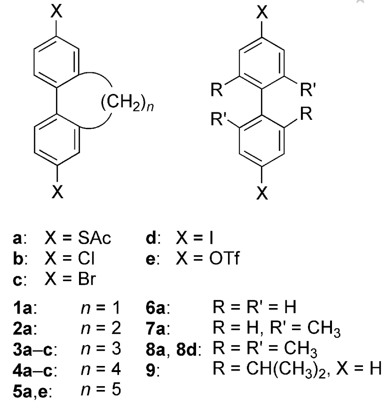
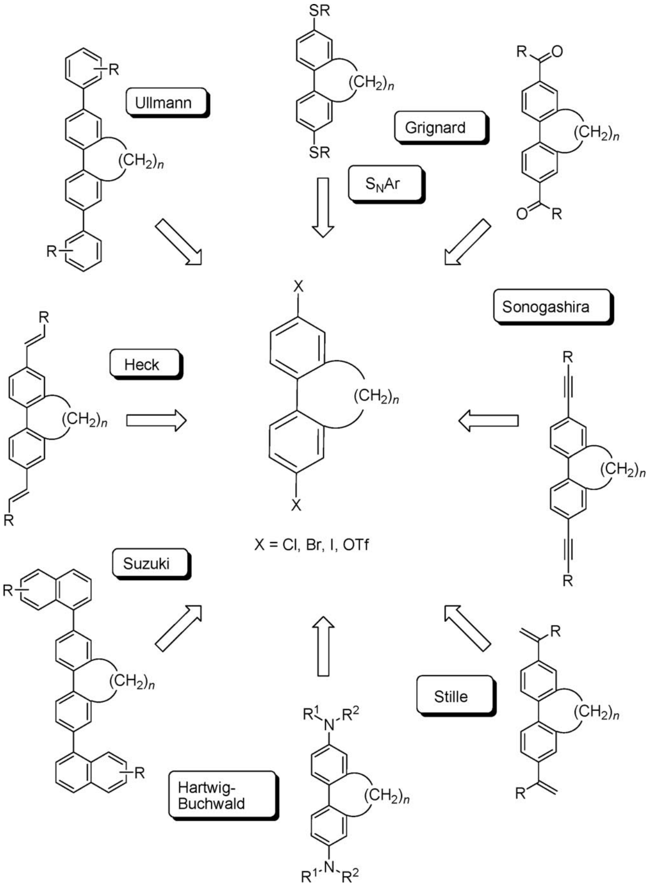


Figure 1. The concept of fixing the torsion angle by a second clamping bridge of defined length is sketched on the left side. On the molecular level, an alkyl chain with n CH$_2$ units interlinks the two phenyl units, adjusting stepwise the interplanar torsion angle. The modular biphenyl building blocks are terminally functionalized with leaving groups X.

Herein we report the synthesis of chemically robust and modular cyclic biphenyl building blocks **3b**,**c**, **4b**,**c**, and **5e** (Scheme 1). Furthermore, *ortho*-alkyl-substituted biphenyl derivatives **6**–**9** were synthesized as additional members of the series. To enable their functionalization and integration into molecular devices[5–8,30,31] and materials,[2,3,32] the biphenyl synthons were further functionalized at the *para* positions by typical leaving groups such as halogen atoms or triflate groups. These bromine-, iodine-, and triflate-functionalized building blocks are suitable candidates for palladium-catalyzed cross-coupling reactions such as the Hartwig–Buchwald,[33–35] Heck,[36,37] Suzuki,[38,39] Stille,[40] or Sonogashira reactions.[41,42] Further, metal-mediated reactions like the Ullmann[43] and Grignard[44] reactions or S$_N$Ar-type reactions can be applied (Scheme 2).



Scheme 1. Biphenyl molecules synthesized in this work. **1a**–**8a** are the bis(acetylsulfanyl) derivatives and **3b**,**c**, **4b**,**c**, **5e**, and **8d** are the terminally chlorine-, bromine-, iodine-, or triflate-functionalized building blocks.



Scheme 2. Possible reactions of the modular building blocks. The various leaving groups provide substrates for Hartwig–Buchwald, Heck, Suzuki, Stille, Sonogashira, Ullmann, Grignard, and S$_N$Ar-type reactions.

As examples, we describe the Pd-catalyzed conversion of the ditriflate **5e** and diiodide **8d** into the *tert*-butylsulfanyl derivatives **28** and **30**, which were subsequently transformed into the acetyl-protected dithiols **5a** and **8a**. Note, the Pd-catalyzed conversion to terminally amine-functionalized building blocks as precursors of model compounds with interesting nonlinear optical properties are described elsewhere.[45] The doubly chlorinated compounds **3b** and **4b** were further functionalized by nucleophilic aromatic substitution reactions to intermediate methylsulfanyl derivatives, which were subsequently transformed into the (acetylsulfanyl)biphenyls **3a** and **4a**. The model compounds were complemented by the *ortho*-substituted alkylbiphenyl derivatives **6**–**9**. The synthesis and characterization of **1a**, **2a**, **6a**, and **7a** and their precursors were reported earlier.[46]

Results and Discussion

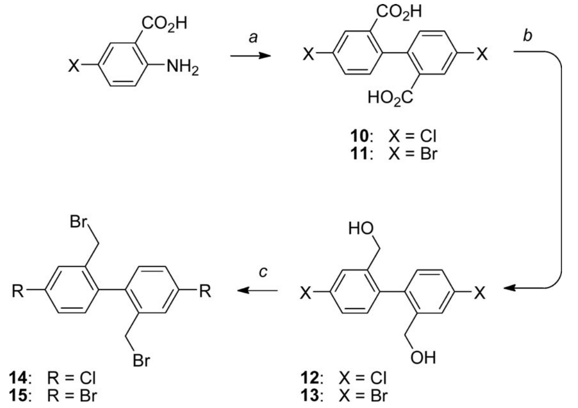
Synthesis

The concept of restricted rotation of biphenyl synthons was inspired by the "Geländer" molecules of Vögtle and co-workers.[47] By clamping the *para*-terphenyl backbone with an additional three atom bridges like thiobis(methylene) or ester-functionalized propyl chains they synthesized *para*-terphenylophanes that display chirality as a result of their screw-type arrangement, which arises from the fixed torsion angles of the biphenyl subunits. However, to keep the electronic features of the substituents as comparable as possible within the series, we avoided heteroatoms in the bridging structure.

Indeed, the synthetic strategy towards the propyl- and butyl-bridged building blocks **3** and **4** starting from benzyl bromides is reminiscent to some extent of the approach of Vögtle and co-workers.[47] The key intermediates **14** and **15** (Scheme 3) were synthesized on a large scale: 4,4′-Dichlorodiphenic acid (**10**) was synthesized from the bulk chemical 5-chloroanthranilic acid according to the procedure of Helms et al.[48] Similarly, we obtained 4,4′-dibromodiphenic acid (**11**) in a good yield (70%). The crude diphenic acids **10** and **11** were reduced to the diols **12** and **13** by using sodium borohydride and $BF_3{\cdot}Et_2O$ as the activating Lewis acid.[49] The crude diol **12** was subsequently transformed into the dibenzyl dibromide by an S_N2 reaction to obtain the key intermediate **14** in a yield of 48% (over two steps).[50] Similarly, we obtained the dibromo homologue **15** in 63% yield. Immediate purification of the crude diols by flash chromatography improved the yields considerably. Interestingly, attempts to repeat an already reported synthesis of **14** based on radical bromination[51] were not successful in our laboratory, and instead of the desired compound a tarry inseparable mixture was obtained.

To achieve the oxo-functionalized propyl bridge in **16**, an additional carbon atom was introduced by an intramolecular cyclization reaction of the dibromide **14** using the masked formaldehyde equivalent (tolylsulfonyl)methyl isocyanide (TosMic)[52] to provide the dichloro ketone **16** in a yield of 77%. In a similar way the dibromo ketone **17** was obtained in 44% yield.

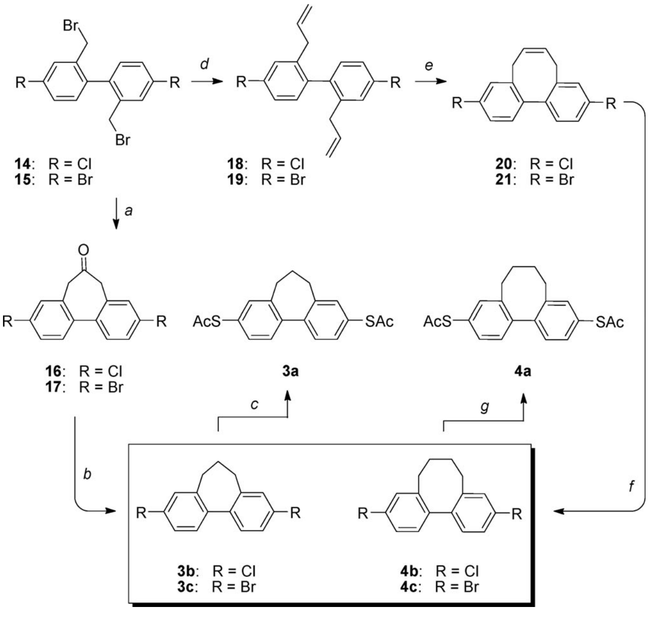
A Lewis acid catalyzed reduction of the oxo group with polymethylhydrosiloxane (PMHS)[53] afforded the doubly chlorinated key building block **3b** in 61% yield. According to the same procedure, **3c** was obtained in 78% yield. These compounds were purified by flash chromatography followed by recrystallization from hexane to remove remaining impurities from the polymeric silane reagent. The aromatic nucleophilic substitution reaction of both chlorine atoms with methylthiolates and in situ transprotection[46,54,55] of the resulting methylsulfanyl functional groups provided the terminally acetylsulfanyl-functionalized and propyl-bridged biphenyl **3a** (49%).



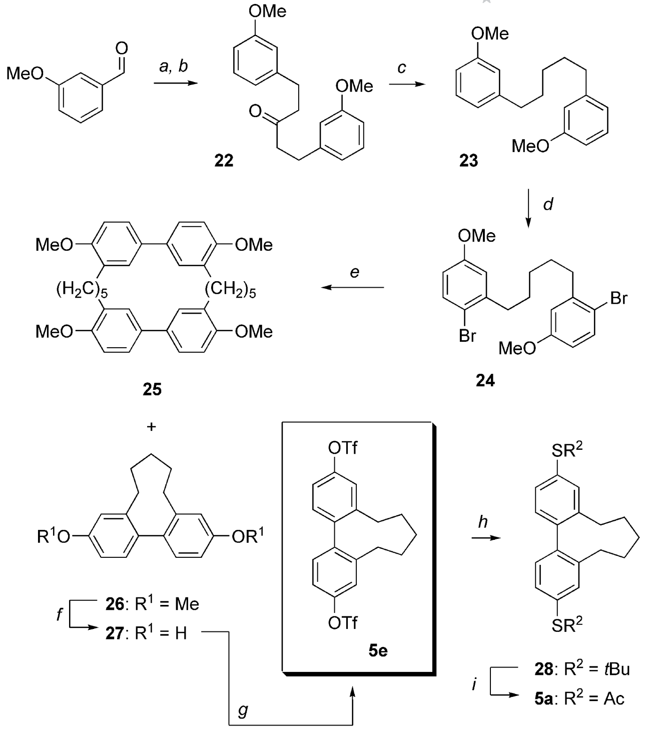
Scheme 3. Reagents and conditions: (a) $NaNO_2$, HCl, 0 °C, then $CuSO_4$, $HONH_2$, NH_4OH, H_2O, 0–70 °C, 69% for **10**, 70% for **11**; (b) $NaBH_4$, $BF_3{\cdot}Et_2O$, THF, 67% for **13**; (c) PBr_3, CH_2Cl_2, 0 °C, 48% for **14** (over two steps), 63% for **15**.

Again, starting from the 4,4′-dihalogenated dibenzyl dibromides **14** and **15**, a copper-mediated Grignard reaction[56] provided the diallylbiphenyls **18** and **19** in 58 and 77% yields, respectively, as odorous oils. In spite of the reported challenges faced during the formation of eight-membered rings[57] by ring-closing metathesis (RCM), the cyclization proceeded smoothly in the case of **18** and **19**, probably due to the conformationally predisposed allyl chains.[58,59] The metathesis reaction, first- and second-generation Grubbs' catalyst were found to be equally effective, afforded **20** and **21** in good yield of 64 and 79%, respectively, as white solids. Subsequent hydrogenation with palladium on charcoal at atmospheric pressure yielded the doubly halogenated key building blocks **4b** and **4c** almost quantitatively. Finally, a similar reaction sequence as described for **3a** resulted in the transformation of the chloro groups into acetylsulfanyl groups to provide the butyl-bridged derivative **4a** in 32% yield (Scheme 4).

An alternative strategy was used to assemble the cyclononane structure in **5e**. As shown in Scheme 5, the interring pentyl chain was established prior to the formation of the biphenyl backbone. The symmetric 1,5-bis(3-methoxyphenyl)pentane (**23**) was synthesized according to a reported procedure.[60–62] Thus, *meta*-anisaldehyde underwent a double aldol condensation with acetone[60,61] followed by a hydrogenation reaction[62] to afford **22** in 46% yield over two steps. The reduction to **23** was achieved by a classic Wolf–Kishner reaction in 72% yield.[62] Subsequent bromination afforded regioselectively the dibromo key intermediate **24** in 42% yield as precursor of the cyclization reaction.[63] Repeated recrystallization turned out to be crucial to remove the regioisomeric side-products formed in this step.



Scheme 4. Reagents and conditions: (a) TosMic, NaOH, TBAB, CH_2Cl_2/H_2O, then HCl, *tert*-butyl methyl ether (*t*BME)/H_2O, 77% for **16**, 44% for **17**; (b) polymethylhydrosiloxane (PMHS), $(C_6F_5)_3B$, CH_2Cl_2, room temp., 61% for **3b**, 78% for **3c**; (c) $NaSCH_3$, 1,3-dimethyl-2-imidazolidinone (DMI), then AcCl, 110 °C, 49%; (d) $CH_2CHMgBr$, CuI, CH_2Cl_2, –40 °C to room temp., 58% for **18**, 79% for **19**; (e) Grubb's catalyst, CH_2Cl_2, reflux, 88% for **20**, 94% for **21**; (f) H_2, 10% Pd/C, room temp., EtOAc, 95% for **4b**, 98% for **4c**; (g) $NaSCH_3$, DMI, then AcCl, 110 °C, 32%.



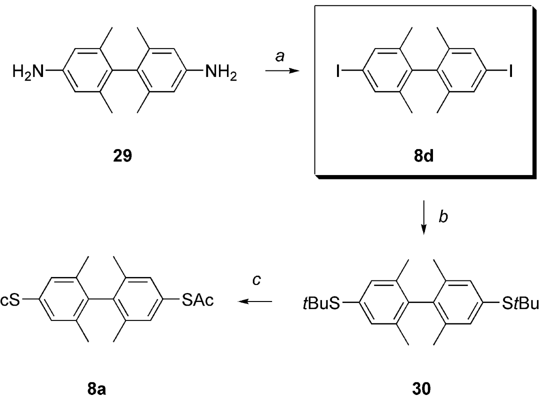
Scheme 5. Reagents and conditions: (a) acetone, NaOH, EtOH;[60,61] (b) 1 atm H_2, 10% Pd/C, EtOAc, 46% (over two steps);[62] (c) hydrazine, 85%, KOH, triethyleneglycol, 190–200 °C, 72%;[62] (d) Br_2, pyridine, –10 °C to room temp., 42% (after recrystallization);[63] (e) *t*BuLi, CuCN, LiBr, MeTHF, –60 °C, then 1,3-dinitrobenzene, 23% for **26**, 27% for **25**; (f) BBr_3, CH_2Cl_2, room temp.; (g) Tf_2O, pyridine, 4 °C to room temp., quant.; (h) *t*BuSNa, $[Pd_2(dba)_3]$, xantphos, *p*-xylene, 140 °C, 62% (over three steps); (i) BBr_3, AcCl, toluene, 61%.

The readily synthesized key substrate **24** underwent a copper-mediated C–C biaryl bond-forming reaction. Whitesides[64] and more recently Lipshutz and co-workers[65–68] applied oxidants to aryl cuprates to form biaryls intermolecularly. By adapting the experimental procedure of Schreiber and co-workers,[69] which allows the synthesis of a series of asymmetric biaryl-containing macrocyclic rings, the cyclononane structure **26** was synthesized successfully. Treatment of the dibromide **24** with *tert*-butyllithium followed by CuCN led to the formation of a cyclic biaryl cuprate as the intermediate. Upon exposure to 1,3-dinitrobenzene as the oxidant, two major products were isolated in about equal amounts after purification by flash chromatography. Intermolecular dimerization of two molecules of **24** gave the undesired dimer **25**, which was formed in a yield of 27%, whereas the intramolecular reaction provided the desired macrocycle **26** in a yield of 23%. Attempts to favor the intramolecular reaction by applying high-dilution conditions did not improve the isolated yield of the monomeric product **26**.

Subsequent functional-group transformations allowed **26** with terminal methoxy groups to be transformed into the key building block **5e** bearing triflate groups. The unfunctionalized pentyl bridge in **26** allowed electrophilic cleavage[70] of the two methyl groups of the biaryl diether with boron tribromide at room temperature. The crude biaryldiol **27** was obtained as a fluffy material that was pure enough to use directly in the next step. Subsequent esterification of the diol **27** with triflic anhydride in pyridine, acting as the base, gave the key building block **5e** as a colorless oil. Slight impurities, probably arising from the reagent, remained after purification by flash chromatography. However, these traces did not interfere with the subsequent reaction steps.

The *tert*-butyl-protected terminal sulfur groups in **28** were obtained from **5e** and NaS*t*Bu by applying palladium-catalyzed cross-coupling conditions. The conversion of the triflates to aryl thioethers is a valuable reaction due to the wide range of phenol derivatives used as pool chemicals. However, only a few examples of this reaction have been described. Zheng[71] (Merck Research Laboratories) and Mispelaere-Canivet and co-workers[72] have shown the cross-coupling of aliphatic and aromatic thiols with aryl triflates mediated by Pd/ligand catalytic systems. However, to the best of our knowledge bis(triflate)-functionalized aromatic systems had never been investigated when we initiated this synthetic investigation. A catalytic amount of $[Pd_2(dba)_3]$ and xantphos as the ligand in *p*-xylene were successfully applied in the cross-coupling reaction of **5e** with NaS*t*Bu to form **28**. However, an elevated reaction temperature of 140 °C turned out to be crucial for the formation of the doubly *tert*-butylated product **28**. A yield of 62% was obtained for this three-step reaction sequence. A final transprotection step of the *tert*-butylsulfanyl groups gave the terminally acetylsulfanyl-functionalized macrocyclic biphenyl **5a**. Thus, **28** was treated with an equimolar amount of boron tribromide to remove the *tert*-butyl groups, whereupon the free thiol groups formed were trapped in situ by acetyl chloride to afford the thioester **5a**.[73,74]

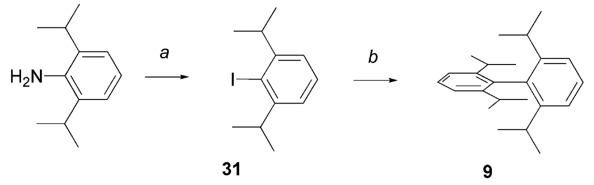
To complement the series of cyclic biphenyls with restricted rotation along the biphenyl axis, we focused on biphenyl systems with sterically demanding substituents at the *ortho* position. An interesting biphenyl building block with an almost perpendicular configuration of the two phenyl rings and thus with poor electronic coupling along its backbone is 4,4′-diiodo-2,2′,6,6′-tetramethylbiphenyl (**8d**; Scheme 6). Starting from the benzidine precursor **29** bearing four methyl groups at the desired position,[75] the amine groups were diazotized with nitrous acid in aqueous media and then treated with an iodide/iodine couple to give the functionalized diiodo building block in a three to four times higher yield than an earlier reported procedure.[76] Interestingly, we were not able to introduce the thioacetate anion by the palladium catalyzed procedure reported by Lai and Backes.[77]



Scheme 6. Reagents and conditions: (a) $NaNO_2$, H_2SO_4, H_2O, KI, I_2, 51%; (b) *t*BuSNa, $[Pd_2(dba)_3]$, xantphos, *p*-xylene, 140 °C, 50%; (c) BBr_3, AcCl, toluene, 84%.

However, the key building block **8d** successfully underwent a palladium-catalyzed coupling reaction by the protocol of Mispelaere-Canivet and co-workers[72] to give the thioether **30** in 50% yield. The acetyl-protected dithiol **8a** was finally achieved in 84% yield by using a standard reprotection procedure as described for the synthesis of compound **5a**. To separate the isomeric impurities emerging from the prior performed benzidine rearrangement (**29**), recrystallization from a mixture of hot hexane and cyclohexane was performed to yield highly pure **8a**.

To obtain a biphenyl structure with a perpendicular conformation, we successfully synthesized the novel sterically demanding synthon 2,2′,6,6′-tetraisopropylbiphenyl (**9**) starting from the commercially available 2,6-diisopropylaniline (Scheme 7). By applying the Sandmeyer reaction, the aryl iodide **31**[78] was obtained in moderate yield, which was subsequently converted into **9** by a copper-mediated aryl–aryl coupling reaction similar to that described before for the preparation of compound **26**. Unfortunately, all attempts to further functionalize the tetraisopropylbiphenyl synthon with leaving groups at the *para* positions failed. Although under mild reaction conditions, for example, bromine in trimethyl phosphate, no conversion of **9** was observed, overbromination was observed in the Lewis acid ($FeCl_3$) catalyzed bromination with bromine in CH_2Cl_2. Further attempts geared towards selective iodination with the hypervalent iodination reagent PIFA [phenyliodine(III) bis(trifluoroacetate)][79] resulted in complex mixtures of mono- and diiodinated derivatives of **9**. Owing to the challenging selective functionalization, **9** was no longer considered as a potential modular biphenyl building block. All synthesized molecules were fully characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis or in a few cases by accurate mass determination.



Scheme 7. Reagents and conditions: (a) $NaNO_2$, *p*TSA, KI, *t*BuOH, H_2O, 40%; (b) *t*BuLi, CuCN, LiBr, MeTHF, –60 °C, then 1,3-dinitrobenzene, 20%.

UV Absorption Spectroscopy

To investigate the correlation between electronic absorption properties and the interplane torsion angle Φ, an entire series of biphenyl derivatives comprising similar terminal groups was required. We focused primarily on the acetylsulfanyl derivatives **1a**–**8a**, which were also considered as suitable model compounds for investigating single-molecule transport properties. The UV absorption spectra of the series **1a**–**8a** were measured in hexane at a concentration of 1.0×10^{-5} M. The absorption spectra obtained are displayed in Figure 2.

The longest-wavelength absorption bands of **1a**[80] and **2a** are at around 312 nm and, in analogy to their terminally unsubstituted counterparts, are assigned to the α-absorption band.[81] Similarly, the broad absorption bands of **1a**–**8a** between 240 and 300 nm can be assigned to the p band of the biphenyl subunit. This p band is also called the conjugation band as its position and intensity is reported to reflect the extent of conjugation in the biphenyl core.[82–84]

Compared with the terminally unfunctionalized biphenyl, we observe for **6a**[24] a bathochromic shift of about 30 nm of the p band, which may be attributed to an enlargement of the π system due to the substitution with lone-pair-containing *S*-acetyl groups.[84]

The onset and λ_{max} values of the p-band absorption of each absorption spectra are listed in Table 1. According to theory, the π–π* transition energy[83,85] and the λ_{max} value of the conjugation band should correlate with the confor-

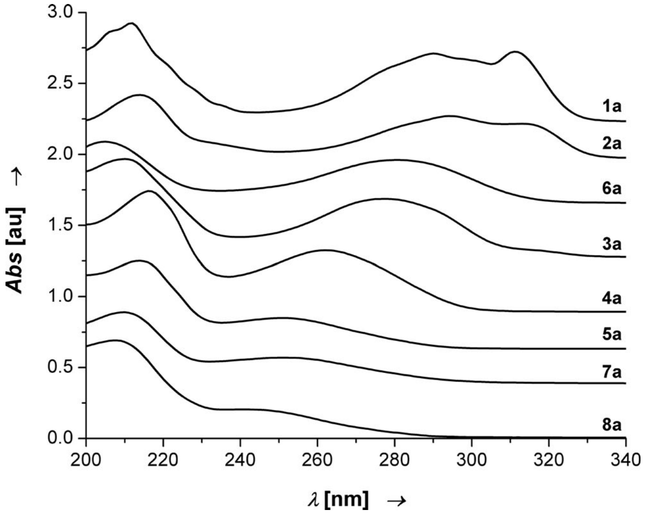


Figure 2. UV adsorption spectra of the bis(acetylsulfanyl)biphenyls in hexane at a concentration of 1×10^{-5} M. The absorption spectra are displayed in a stacked mode.

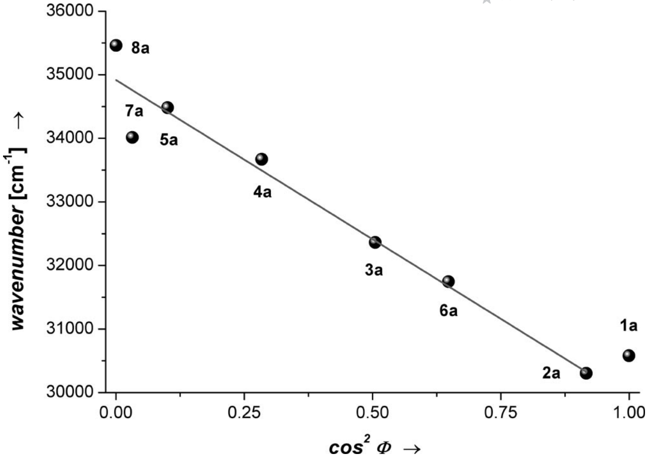


Figure 3. Onset of the UV absorption spectra of the molecules **1a**–**8a** plotted against $\cos^2 \Phi$. Φ is the interplanar torsion angle obtained from the X-ray structures.

mation of the biphenyl core. The orbital overlap of adjacent π systems correlates linearly with the cosine between their planes, and the electron-transfer properties between the two π systems is proportional to $\cos^2$ of their torsion angles.[85–87] Thus, in Figure 3, the longest-wavelength onset of each spectrum, which reflects the HOMO–LUMO band gap of the compound under investigation, is plotted against $\cos^2 \Phi$. The values of the interplane torsion angles Φ were determined by X-ray structural analysis and are reported elsewhere.[27] Within this series of compounds, the expected linear correlation between the HOMO–LUMO band gap and $\cos^2 \Phi$ was observed. The α-absorption band was only observed for fixed biphenyl systems with torsion angles Φ below 45°, that is, **1a**–**3a** (**3a**: shoulder between 310 and 325 nm). Furthermore, a strong increase of this band with decreasing torsion angle was observed in this subseries. Note that the unbridged biphenyl **6a** with Φ = 36.4° also does not exhibit this band.

Table 1. Torsion angles Φ from the solid-state structures[27] and the UV adsorption properties of the series **1a**–**8a**.

	Φ [°][a]	λ_{max} [nm][b]	ε [L mol^{-1} cm^{-1}][c]	λ_{on} [nm][d]
1a	1.1	291	28900	327
2a	16.8	295	30500	330
3a	44.7	278	24000	309
4a	57.8	263	21700	297
5a	71.8	250	17600	290
6a	36.4	281	27000	315
7a	79.7	251	17600	294
8a	89.0	244	18300	282

[a] Φ is the torsion angle between the planes of the phenyl rings. [b] λ_{max} is the wavelength at the maximum of the p band. [c] ε is the extinction coefficient at λ_{max} of the p band. [d] λ_{on} is the absorption onset of the UV spectra.

The plot of the p-band absorption maxima against $\cos^2 \Phi$ is displayed in Figure 4. Again, the expected linear correlation between λ_{max} of the p band and $\cos^2 \Phi$ was observed for the series. The only slightly exceptional behavior was observed for the fluorene derivative **1a**, which displayed a p-band maximum a little below the expected value. Interestingly, a similar trend is also observed in single-molecule transport investigations.[27]

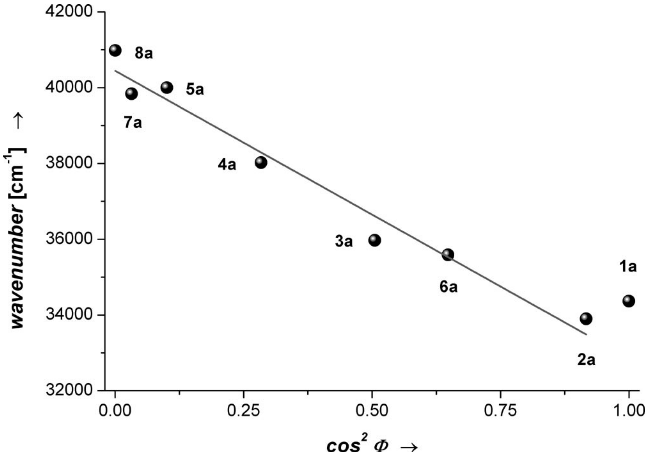


Figure 4. p-Band absorption maxima of the molecules **1a**–**8a** plotted against $\cos^2 \Phi$. Φ is the interplanar torsion angle obtained from the X-ray structures.

X-ray Structure

Single crystals suitable for X-ray analysis were obtained for all acetylsulfanyl-functionalized derivatives **1a**–**8a**, which enabled the determination of their solid-state interplane torsion angles Φ. Although most of these solid-state structures have been reported elsewhere,[27,46] the structures of **8a** and **9** are displayed in Figure 5. Single crystals of **8a** were obtained from a hot hexane/cyclohexane mixture, whereas slow concentration of cold pentane provided single crystals of **9**.

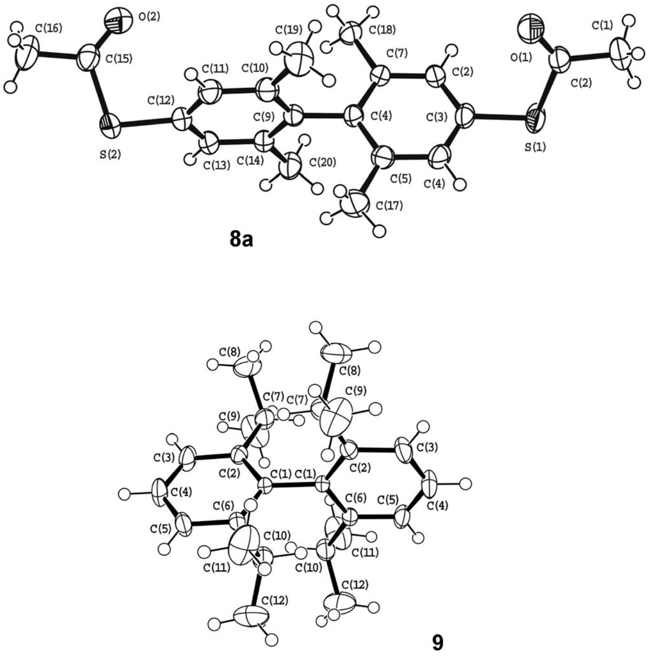


Figure 5. Top: X-ray structure of **8a** with an interplane torsion angle Φ of 89.0°. Bottom: X-ray structure of 2,2′,6,6′-tetraisopropylbiphenyl (**9**) displaying a torsion angle Φ between the two phenyl rings of 86.5°.

The steric repulsion caused by the four methyl groups at the *ortho* positions of the biphenyl derivative **8a** resulted in an almost perpendicular arrangement of the planes of the two phenyl rings with a torsion angle Φ of 89.0°. Interestingly, at first glance the sterically even more demanding four isopropyl groups at the *ortho* positions of **9** caused a slightly reduced interplane torsion angle Φ of only 86.5°. Currently, the origin of this unexpected difference remains unclear. As attempts to synthesize the acetylsulfanyl-functionalized derivative **9a** have failed, the optical analysis of a dissolved species to enable a comparison with **1a**–**8a** is unavailable. Thus, this difference in Φ might either be a general trend for such *ortho*-alkyl-functionalized biphenyl compounds or a simple packing effect in the solid-state structures.

Conclusions

A series of modular biphenyl building blocks bridged with alkyl chains of various lengths and functionalized at the *para* positions have been synthesized. The ring-interlinking alkyl bridges, which affect the torsion angle Φ, keeps the electronic structure of the biphenyl subunit within the series as uniform as possible. The π–π coupling of the biphenyl synthon is thus dominated by the interplane torsion angle Φ. Further, the synthesis was optimized to obtain the building blocks **3b**–**8d** easily on a gram-scale.

The medium-sized ring structures were constructed in the case of the seven-membered ring by carbon insertion with the formaldehyde equivalent TosMic and in the case of the eight-membered ring by ring-closing metathesis as the key steps. The nine-membered ring was obtained by first constructing a pentyl chain by two aldol C–C bond-forming reactions and a subsequent oxidative aryl–aryl coupling reaction. The *para* functionalization of the modular building blocks with chlorine, bromine, iodine, or triflate as leaving groups enables their integration into molecular devices and materials by a wide range of chemical coupling reactions. Terminal acetylsulfanyl derivatives were obtained for all members of the series. The chlorine-functionalized building blocks **3b** and **4b** were converted into **3a** and **4a** by an S_NAr reaction. Compounds **5a** and **8a** were obtained by palladium-catalyzed cross-coupling reactions of **5e** and **8d**.

The UV absorption spectra of the acetylsulfanyl derivatives **1a**–**8a** as model compounds were recorded. A linear correlation between the conjugation band of the UV absorption and the $\cos^2$ of the torsion angle Φ was observed.

These terminally thiol-functionalized biphenyl synthons have already been integrated on a single-molecule level into a scanning tunneling microscope (STM) junction.[27] Furthermore, a series of NLO model compounds based on torsionally restricted biphenyls is currently under investigation.[45] In addition, these rigid rod-type structures are currently being functionalized with different anchor groups.

Experimental Section

General: All chemicals were directly used in the syntheses without purification unless otherwise indicated. All reactions were performed under argon with oven-dried glassware. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX-400 or -250 spectrometer. ^1H NMR chemical shifts are internally referenced to the residual solvent proton resonance ($CDCl_3$: δ = 7.26 ppm; [D_6]DMSO: δ = 2.49 ppm). ^{13}C NMR chemical shifts are internally referenced to the deuteriated solvent signal ($CDCl_3$: δ = 77.16 ppm; [D_6]DMSO: δ = 39.7 ppm). Mass spectra were recorded with an Esquire 3000 plus (Bruker) for electron spray ionization (ESI) MS or with a Finnigan MAT 95Q spectrometer for electron impact (EI) MS. Elemental analyses were carried out with a Perkin–Elmer Analysator 240. For TLC analysis, silica gel 60 F254 glass plates with a thickness of 0.25 mm from Merck were used. Flash chromatography was performed on silica gel 60 (40–63 µm) from Merck.

4,4′-Dichlorobiphenyl-2,2′-dicarboxylic Acid (10): 2-Amino-5-chlorobenzoic acid (23.90 g, 0.14 mmol) was suspended in HCl (49.6 mL, 0.600 mol, 37%) and water (110 mL). At 0 °C the amine was diazotized by adding slowly a solution of $NaNO_2$ (11.50 g, 0.169 mol, 1.2 equiv.) in water (40 mL). After stirring at 0 °C for 1 h, the solution was carefully introduced through a cannula into a freshly prepared solution of $CuSO_4{\cdot}5H_2O$ (69.30 g, 0.278 mol, 2.0 equiv.), NH_4OH (148 mL, 0.96 mmol, 6.9 equiv., 25%), water (250 mL), and hydroxylamine·HCl (20.70 g, 0.30 mmol, 2.1 equiv.) dissolved in a NaOH solution (49.5 mL, 0.300 mol, 2.1 equiv.). Then stirring was continued at 25 °C, and the reaction mixture was heated up to 70 °C over 1 h. The mixture was cooled. The mixture was cooled to room temperature and acidified with HCl (37%). After filtering, washing with water, and drying in an oven (70 °C), 4,4′-dichlorobiphenyl-2,2′-dicarboxylic acid (**10**) was obtained as a beige powder (15.10 g, 48.53 mmol, 69%). M.p. 246–250 °C. TLC: R_f = 0.06 (ethyl acetate). ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 7.18 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H), 7.59 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H), 7.85 (s, 2 H), 13.0 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 130.0, 131.4, 132.0, 133.2, 141.7, 167.4 ppm. MS (EI): *m/z* (%) = 310.0 (30) [M]$^+$, 292.0 (21) [M – H_2O]$^+$, 292.0 (21), 265.0 (100) [M – CO_2]$^+$, 248 (68), 186.0 (42), 150.1 (31).

4,4′-Dibromobiphenyl-2,2′-dicarboxylic Acid (11): By applying the same conditions as described above for the synthesis of **10**, target compound **11** was obtained from 2-amino-5-bromobenzoic acid as a deep-red powder (70%). M.p. 246–250 °C. TLC: R_f = 0.06 (ethyl acetate). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 7.05–7.20 (m, 2 H), 7.67–7.50 (m, 2 H), 7.94 (br. s, 2 H), 13.1 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 121.4, 133.5, 134.7 ppm. MS (EI): *m/z* (%) = 397.9, 399.9, 401.9 [M]$^+$.

4,4′-Dichlorobiphenyl-2,2′-dimethanol (12): Under an inert gas, 4,4′-dichlorobiphenyl-2,2′-dicarboxylic acid (**10**; 17.10 g, 54.96 mmol) was dissolved in dry THF (200 mL). $NaBH_4$ (6.24 g, 0.165 mol, 3.0 equiv.) was added in portions keeping the temperature below 30 °C. After stirring at room temperature for 1 h, $BF_3{\cdot}Et_2O$ (31.1 mL, 0.253 mol, 4.6 equiv.) was added dropwise to the reaction mixture keeping the temperature between 10 and 25 °C. The mixture was stirred overnight and quenched with HCl (5%), diluted with ethyl acetate (450 mL), and filtered through a Celite pad. The brown solution was washed with satd. Na_2CO_3 and then brine and dried with $MgSO_4$. After evaporation of the solvents, 4,4′-dichlorobiphenyl-2,2′-dimethanol (**12**) was obtained as a brown oily solid (16.40 g), which was used without further purification in the next step. For analytical purposes a sample was purified by flash chromatography (silica gel; hexane/ethyl acetate, 7:3). M.p. 121 °C. TLC: R_f = 0.15 (hexane/ethyl acetate, 7:3). ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): δ = 4.08 (dd, $^2J_{\mathrm{H,H}}$ = 14.1, $^3J_{\mathrm{H,H}}$ = 5.4 Hz, 2 H), 4.19 (dd, $^2J_{\mathrm{H,H}}$ = 14.1, $^3J_{\mathrm{H,H}}$ = 5.4 Hz, 2 H), 5.26 (dd, $^3J_{\mathrm{H,H1}}$ = 5.4, $^3J_{\mathrm{H,H2}}$ = 5.4 Hz, 2 H), 7.11 (d, $^3J_{\mathrm{H,H1}}$ = 8.1 Hz, 2 H), 7.36 (dd, $^3J_{\mathrm{H,H}}$ = 8.1, $^4J_{\mathrm{H,H}}$ = 2.3 Hz, 2 H), 7.58 (d, $^4J_{\mathrm{H,H}}$ = 2.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 61.0, 127.2, 127.5, 131.7, 133.4, 136.4, 143.3 ppm. No accurate MS was obtained. $C_{14}H_{12}Cl_2O_2$ (283.15): C 59.39, H 4.27; found C 59.40, H 4.23.

4,4′-Dibromobiphenyl-2,2′-dimethanol (13): Target compound **13** was synthesized by applying the same conditions as used for synthesis of the dichloro compound **12** (67%). M.p. 133–134 °C. TLC: R_f = 0.40 (hexane/ethyl acetate, 1:1). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 4.05 (dd, $^2J_{\mathrm{H,H}}$ = 14.1, $^3J_{\mathrm{H,H}}$ = 5.5 Hz, 4 H), 4.15 (dd, $^2J_{\mathrm{H,H}}$ = 14.1, $^3J_{\mathrm{H,H}}$ = 5.4 Hz, 2 H), 5.23 (dd, $^3J_{\mathrm{H,H1}}$ = 5.5, $^3J_{\mathrm{H,H2}}$ = 5.5 Hz, 2 H), 7.01 (d, $^3J_{\mathrm{H,H1}}$ = 8.1 Hz, 2 H), 7.47 (dd, $^3J_{\mathrm{H,H}}$ = 8.0, $^4J_{\mathrm{H,H}}$ = 1.9 Hz, 2 H), 7.69 (d, $^4J_{\mathrm{H,H}}$ = 1.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 61.0, 122.0, 130.1, 130.4, 131.9, 136.8, 143.4 ppm. MS (FAB): *m/z* (%) = 372.9 [M + H]$^+$. $C_{14}H_{12}Br_2O_2$ (372.05): calcd. C 45.20, H 3.25; found C 44.63, H 3.43.

2,2′-Bis(bromomethyl)-4,4′-dichlorobiphenyl (14): 4,4′-Dichlorobiphenyl-2,2′-dimethanol (**12**; 16.40 g, assuming 54.96 mmol) was dissolved in dry CH_2Cl_2 (100 mL). The brown solution was cooled to 5 °C, and PBr_3 (12.9 mL, 0.136 mol, 2.5 equiv.) was slowly added dropwise to the reaction mixture. After stirring at 0–25 °C (30 h), water (40 mL) was carefully added to quench the reaction. The aqueous phase was separated and extracted with CH_2Cl_2 (40 mL), and the combined organic phases were filtered through a silica pad. After evaporation of the solvents and purification by flash chromatography (silica; CH_2Cl_2 in hexane, 10–80%), 2,2′-bis(bromomethyl)-4,4′-dichlorobiphenyl (**14**) was obtained as yellow crystals (10.70 g, 26.17 mmol, 48% over two steps). M.p. 120–121 °C. TLC: R_f = 0.44 (hexane/CH_2Cl_2, 95:5). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.10 (d, $^2J_{\mathrm{H,H}}$ = 10.3 Hz, 2 H), 4.25 (d, $^2J_{\mathrm{H,H}}$ = 10.3 Hz, 2 H), 7.19 (d, $^3J_{\mathrm{H,H}}$ = 8.2 Hz, 2 H), 7.36 (dd, $^3J_{\mathrm{H,H}}$ = 8.2, $^4J_{\mathrm{H,H}}$ = 2.2 Hz, 2 H), 7.54 (d, $^4J_{\mathrm{H,H}}$ = 2.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 30.6, 128.8, 130.8, 131.5, 134.7, 136.6, 137.9 ppm. MS (EI): *m/z* (%) = 405.9, 407.9, 409.9, 411.9 [M]$^+$. $C_{14}H_{10}Br_2Cl_2$ (408.94): calcd. C 41.12, H 2.46; found C 40.98, H 2.48.

4,4′-Dibromo-2,2′-bis(bromomethyl)biphenyl (15): By applying the same procedure as used for the synthesis of the dichloro compound **14** described above, 4,4′-dibromobiphenyl-2,2′-dimethanol (**13**) was converted into 4,4′-dibromo-2,2′-bis(bromomethyl)biphenyl (**15**; 63%). M.p. 147 °C. TLC: R_f = 0.27 (hexane/*t*-BME, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.09 (d, $^2J_{\mathrm{H,H}}$ = 10.3 Hz, 2 H), 4.26 (d, $^2J_{\mathrm{H,H}}$ = 10.3 Hz, 2 H), 7.12 (d, $^3J_{\mathrm{H,H}}$ = 8.2 Hz, 2 H), 7.50 (dd, $^3J_{\mathrm{H,H}}$ = 8.2, $^4J_{\mathrm{H,H}}$ = 2.0 Hz, 2 H), 7.69 ($^4J_{\mathrm{H,H}}$ = 2.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 30.7, 123.1, 131.98, 132.00, 134.0, 137.5, 138.4 ppm. MS (EI): *m/z* (%) = 493.7, 495.7, 497.7, 499.7 [M]$^+$. $C_{14}H_{10}Br_4$ (497.85): calcd. C 33.78, H 2.02; found C 33.67, H 2.01.

2,2′-Diallyl-4,4′-dichlorobiphenyl (18): Under argon 2,2′-bis(bromomethyl)-4,4′-dichlorobiphenyl (**14**) (673 mg, 1.65 mmol) was dissolved in CH_2Cl_2 (15 mL). CuI (313 mg, 1.64 mmol, 1.0 equiv.) was added at once, and the reaction mixture was cooled to –70 °C. In the absence of light, vinylmagnesium bromide (9.4 mL, 6.58 mmol, 4.0 equiv., 0.7 M) in dry THF was slowly added dropwise to the reaction mixture, and stirring was continued at –70 °C for 1 h. After stirring overnight (0–25 °C), the reaction was quenched with satd. NH_4Cl (50 mL) and brine (50 mL). The mixture was extracted with *t*-BME (3 × 50 mL), separated, and the combined organic phases were dried with $MgSO_4$. The crude product was purified by flash chromatography to afford 2,2′-diallyl-4,4′-dichlorobiphenyl (**18**) as a smelly and colorless oil (290 mg, 0.96 mmol, 58%). TLC: R_f = 0.76 (hexane/CH_2Cl_2, 95:5). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.02 (dddd, $^2J_{\mathrm{H,H}}$ = 15.5, $^3J_{\mathrm{H,H}}$ = 6.6, $^4J_{\mathrm{H,H1}}$ = 1.5, $^4J_{\mathrm{H,H2}}$ = 1.5 Hz, 2 H), 3.08 (dddd, $^2J_{\mathrm{H,H}}$ = 15.5, $^3J_{\mathrm{H,H}}$ = 6.7, $^4J_{\mathrm{H,H1}}$ = 1.5, $^4J_{\mathrm{H,H2}}$ = 1.5 Hz, 2 H), 4.87 (dddd, $^2J_{\mathrm{H,H1}}$ = 1.7, $^3J_{\mathrm{H,H}Z}$ = 17.0, $^4J_{\mathrm{H,H1}}$ = 1.5, $^4J_{\mathrm{H,H2}}$ = 1.5 Hz, 2 H), 5.00 (dddd, $^2J_{\mathrm{H,H}}$ = 1.7, $^3J_{\mathrm{H,H}E}$ = 10.0, $^4J_{\mathrm{H,H1}}$ = 1.5, $^4J_{\mathrm{H,H2}}$ = 1.5 Hz, 2 H), 5.74 (dddd, $^3J_{\mathrm{H,H1}}$ = 17.0, $^3J_{\mathrm{H,H2}}$ = 10.0, $^3J_{\mathrm{H,H3}}$ = 6.7, $^3J_{\mathrm{H,H3}}$ = 6.6 Hz, 2 H), 7.01 (d, $^3J_{\mathrm{H,H}}$ = 8.0 Hz, 2 H), 7.19 (dd, $^3J_{\mathrm{H,H}}$ = 7.8, $^4J_{\mathrm{H,H}}$ = 2.2 Hz, 2 H), 7.36 (d, $^4J_{\mathrm{H,H}}$ = 2.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 37.9, 117.2, 126.6, 129.7, 131.6, 134.0, 136.4, 138.4, 140.3 ppm. MS (EI): *m/z* (%) = 302.1 (35) [M]$^+$, 267.1 (98) [M – Cl]$^+$, 238.0 (62), 226.1 (100) [M – Cl – C_3H_5 (allyl)]$^+$, 203.1 (66), 191.1 (61), 101.0 (20). $C_{18}H_{16}Cl_2$ (303.23): calcd. C 71.30, H 5.32; found C 71.07, H 5.30.

2,2′-Diallyl-4,4′-dibromobiphenyl (19): According to the procedure used for the synthesis of **18** target compound **19** (79%) was obtained as a colorless oil. TLC: R_f = 0.46 (hexane/CH_2Cl_2, 95:5). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.13–2.97 (m, 4 H), 4.87 (dd, $^2J_{\mathrm{H,H}}$ = 1.6, $^3J_{\mathrm{H,H}}$ = 17.0 Hz, 2 H), 5.01 (dd, $^2J_{\mathrm{H,H}}$ = 1.6, $^3J_{\mathrm{H,H}}$ = 10.1 Hz, 2 H), 5.80–5.67 (m, 2 H), 6.95 (d, $^3J_{\mathrm{H,H}}$ = 8.1 Hz, 2 H), 7.37 (dd, $^3J_{\mathrm{H,H}}$ = 8.4, $^4J_{\mathrm{H,H}}$ = 2.1 Hz, 2 H), 7.43 (d, $^4J_{\mathrm{H,H}}$ = 2.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 37.3, 116.8, 121.8, 129.1, 131.3, 132.2, 135.9, 138.4, 140.1 ppm. MS (EI): *m/z* (%) = 390.0, 392.0, 394.0 [M]$^+$. $C_{18}H_{16}Br_2$ (392.13): calcd. C 55.13, H 4.11; found C 55.24, H 4.19.

3,10-Dichloro-5,8-dihydrodibenzo[*a*,*c*]cyclooctene (20): 2,2′-Diallyl-4,4′-dichlorobiphenyl (**18**; 121 mg, 0.40 mmol) and Grubbs' catalyst (2nd generation, 20.4 mg, 24 µmol, 6.0 mol-%) was heated at reflux in CH_2Cl_2 (30 mL). After 3 h, the solvent was evaporated, and the crude product was purified by flash chromatography (silica gel; 0–5% CH_2Cl_2 in hexane) to yield 3,10-dichloro-5,8-dihydrodibenzo[*a*,*c*]cyclooctene (**20**) as an off-white solid (97 mg, 0.35 mmol, 88%). M.p. 129–130 °C. TLC: R_f = 0.51 (hexane/CH_2Cl_2, 98:2). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.82–3.13 (m, 4 H), 5.81–5.85 (m, 2 H), 7.14–7.21 (m, 4 H), 7.23–7.27 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 33.4, 126.8, 129.1, 129.3, 129.4, 129.6, 134.5, 139.0, 139.7 ppm. MS (EI): *m*/*z* (%) = 274.0 (80) $[M]^+$, 239.1 (82) $[M - Cl]^+$, 204.1 (100) $[M - 2\ Cl]^+$, 176.1 (21), 101.0 (33). $C_{16}H_{12}Cl_2$ (275.17): calcd. C 69.84, H 4.40; found C 69.35, H 4.50.

3,10-Dibromo-5,8-dihydrodibenzo[*a*,*c*]cyclooctene (21): According to the protocol described above target compound **21** was obtained as a white solid (94%). M.p. 147 °C. TLC: R_f = 0.61 (hexane/CH_2Cl_2, 95:5). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.91 (d, $^2J_{H,H}$ = 14.7 Hz, 2 H), 3.02–3.13 (m, 2 H), 5.79–5.87 (m, 2 H), 7.11 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.37 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H), 7.42 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 2.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 32.9, 122.3, 128.7, 129.2, 129.3, 132.1, 138.8, 139.7 ppm. MS (EI): *m*/*z* (%) = 361.9, 363.9, 365.9 $[M]^+$. $C_{16}H_{12}Br_2$ (364.07): calcd. C 52.78, H 3.32; found C 52.66, H 3.35.

3,10-Dichloro-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (4b): 3,10-Dichloro-5,8-dihydrodibenzo[*a*,*c*]cyclooctene (**20**; 102 mg, 0.37 mmol) was dissolved in ethyl acetate (6 mL), and Pd/C (10% Pd, 10.0 mg, 2.5 mol-%) was added. The mixture war stirred under hydrogen (1 atm) for 3 h and then filtered through a silica pad, washed with ethyl acetate, and the solvent was evaporated. 3,10-Dichloro-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (**4b**) was collected as a white solid (98 mg, 0.36 mmol, 95%). M.p. 163–164 °C. TLC: R_f = 0.51 (hexane/CH_2Cl_2, 98:2). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.42–1.56 (m, 2 H), 2.04–2.14 (m, 4 H), 2.63–2.76 (m, 2 H), 7.12–7.17 (m, 2 H), 7.19–7.31 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 29.6, 32.9, 126.3, 129.7, 129.9, 130.6, 134.1, 138.3, 144.9 ppm. MS (EI): *m*/*z* (%) = 276.0 (100) $[M]^+$, 241 (24) $[M - Cl]^+$, 212.0 (32), 178.1 (35), 88.0 (13). $C_{16}H_{14}Cl_2$ (277.19): calcd. C 69.33, H 5.09; found C 69.88, H 5.40.

3,10-Dibromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (4c): By applying the same reaction conditions as used for the conversion of the dichloro compound **20** to **4b**, the dibromo compound **4c** was obtained from **21** as a white solid (98%). M.p. 168–170 °C. TLC: R_f = 0.75 (hexane/CH_2Cl_2, 95:5). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.45–1.53 (m, 2 H), 2.03–2.14 (m, 4 H), 2.69 (dd, $^2J_{H,H}$ = 13.4, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.07 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.37 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 2.0 Hz, 2 H), 7.43 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 29.3, 32.6, 122.1, 129.0, 130.6, 132.4, 138.5, 144.9 ppm. MS (EI): *m*/*z* (%) = 363.9, 365.9, 367.9 $[M]^+$. $C_{16}H_{14}Br_2$ (366.09): calcd. C 52.49, H 3.85; found C 52.45, H 3.81.

3,10-Bis(acetylsulfanyl)-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (4a): Under an inert gas, 3,10-dichloro-5,6,7,8-tetrahydrodibenzo-[*a*,*c*]cyclooctene (**4b**; 175 mg, 0.63 mmol) was dissolved in dry and degassed DMI (10 mL), and sodium methanethiolate (620 mg, 8.85 mmol, 14.0 equiv.) was added. The reaction mixture was kept at 110 °C overnight. AcCl (7.0 mL) was carefully added to the cooled reaction mixture, and the milky mixture was stirred at room temperature overnight. The reaction was then quenched with ice and the mixture extracted with toluene (3 × 20 mL). The organic phase was washed with brine/water (1:1, 3 × 15 mL) and brine (1 × 20 mL), filtered through wool, and the solvent was evaporated. The crude product was separated by flash column chromatography (silica gel; 10–20% *t*-BME in hexane). 3,10-Bis(acetylsulfanyl)-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (**4a**) was obtained (72.0 mg, 0.20 mmol, 32%). Recrystallization from cyclohexane yielded single crystals suitable for X-ray analysis. M.p. 144 °C. TLC: R_f = 0.23 (hexane/*t*-BME, 8:2). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.51–1.59 (m, 2 H), 2.07–2.19 (m, 4 H), 2.48 (s, 6 H), 2.74–2.78 (m, 2 H), 7.29–7.36 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 29.6, 31.0, 33.2, 128.1, 130.5, 132.3, 135.9, 141.6, 144.4, 194.9 ppm. UV/Vis: λ_{max} (ε) = 217 (40200), 263 (21700 $M^{-1}cm^{-1}$) nm. MS (EI): *m*/*z* (%) = 356.2 (26) $[M]^+$, 314.1 (31) $[M - CH_3CO]^+$, 272.1 (100) $[M - 2\ CH_3CO]$. $C_{20}H_{20}O_2S_2$ (356.50): calcd. C 67.38, H 5.65; found C 67.39, H 5.91.

3,9-Dichloro-5,7-dihydro-6*H*-dibenzo[*a*,*c*]cyclohepten-6-one (16): NaOH (430 mg, 10.80 mmol, 5.1 equiv.) was dissolved in H_2O (5 mL) and added to a solution of 2,2′-bis(bromomethyl)-4,4′-dichlorobiphenyl (**14**; 866 mg, 2.12 mmol), (tolylsulfonyl)methyl isocyanide (TosMic; 462 mg, 2.37 mmol, 1.1 equiv.), and tetrabutylammonium bromide (161 mg, 0.50 mmol, 24.0 mol-%) in CH_2Cl_2 (20 mL) at 0 °C. The two-phase mixture was stirred vigorously at room temperature overnight. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (6 mL). *t*-BME (15 mL) and HCl (6 mL, 37%) were added to the organic mixture, which was then stirred vigorously for 3 h. The phases were separated, and the organic layer was washed with water (5 mL) and satd. $NaHCO_3$ (8 mL), dried with Na_2SO_4, and the solvent evaporated. The crude product was purified by flash chromatography (silica gel; 20–80% CH_2Cl_2 in hexane) to afford 3,9-dichloro-5,7-dihydro-6*H*-dibenzo[*a*,*c*]cyclohepten-6-one (**16**) as a white solid (454 mg, 1.64 mmol, 77%). M.p. 223–224 °C. R_f = 0.24 (hexane/CH_2Cl_2, 6:4). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.53 (d, $^2J_{H,H}$ = 13.0 Hz, 2 H), 3.56 (d, $^2J_{H,H}$ = 13.0 Hz, 2 H), 7.27–7.30 (m, 2 H), 7.38–7.43 (m, 2 H), 7.44–7.49 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 49.2, 128.4, 129.8, 130.9, 134.6, 134.8, 137.1, 208.5 ppm. MS (EI): *m*/*z* (%) = 276.0 (89) $[M]^+$, 248.0 (33) $[M - CO]^+$, 213.1 (84) $[M - CO - Cl]^+$, 178.1 (100) $[M - CO - 2\ Cl]^+$, 151.1 (9), 106.0 (18), 88.0 (36). $C_{15}H_{10}Cl_2O$ (277.15): calcd. C 65.01, H 3.64; found C 64.71, H 3.74.

3,9-Dibromo-5,7-dihydro-6*H*-dibenzo[*a*,*c*]cyclohepten-6-one (17): According to the procedure used for the synthesis of **16**, target compound **17** was isolated as a white solid (44%). M.p. 242–244 °C. TLC: R_f = 0.13 (hexane/CH_2Cl_2, 1:1). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.48 (d, $^2J_{H,H}$ = 14.0 Hz, 2 H), 3.54 (d, $^2J_{H,H}$ = 14.0 Hz, 2 H), 7.38–7.43 (m, 4 H), 7.54–7.58 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 49.1, 122.8, 131.0, 131.4, 132.8, 135.0, 137.6, 208.5 ppm. MS (EI): *m*/*z* (%) = 363.9, 365.9, 367.9 $[M]^+$. $C_{15}H_{10}Br_2O$ (366.05): calcd. C 49.22, H 2.75; found C 49.21, H 2.70.

3,9-Dichloro-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (3b): Tris-(pentafluorophenyl)borane (55.0 mg, 0.11 mmol, 2.0 mol-%) was added to a solution of 3,9-dichloro-5,7-dihydro-6*H*-dibenzo[*a*,*c*]-cyclohepten-6-one (**16**; 1.44 g, 5.20 mmol) in CH_2Cl_2 (40 mL). While maintaining the reaction temperature at room temperature, polymethylhydrosiloxane (PMHS; 6.0 mL) was slowly added. After 20 min, another portion of catalyst (80.0 mg, 0.16 mmol, 3.0 mol-%) was added (foaming!). After TLC showed full conversion of the starting material, the solvent was evaporated. The resulting gel was extracted with hexane (4 × 80 mL) and filtered through a silica pad. The concentrated extract was recrystallized from MeOH/H_2O (15 mL and 0.3 mL) to obtain 3,9-dichloro-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (**3b**) as long white needles (835 mg, 3.17 mmol, 61%). M.p. 87–88 °C. TLC: R_f = 0.74 (hexane/CH_2Cl_2, 6:4). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.21 (m, 2 H), 2.49 (m, 4 H), 7.24–7.37 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 31.6, 33.3, 127.2, 129.0, 129.8, 133.7, 138.8, 141.6 ppm. MS (EI): *m*/*z* (%) = 262.0 (100) $[M]^+$, 227.1 (25) $[M - Cl]^+$, 212.1 (32), 192.1 (58) $[M - 2\ Cl]^+$, 176.1 (11), 94.5 (16). $C_{15}H_{12}Cl_2$ (263.16): calcd. C 68.46, H 4.60; found C 68.39, H 4.67.

3,9-Dibromo-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (3c): Tris(pentafluorophenyl)borane (18.2 mg, 35.5 µmol, 5.3 mol-%) was added to a solution of 3,9-dibromo-5,7-dihydrodibenzo[*a*,*c*]cyclohepten-6-one (**17**; 260 mg, 0.71 mmol) in CH_2Cl_2 (13 mL). While maintaining the temperature at 25 °C, polymethylhydrosiloxane (0.85 mL) was slowly added. After 5 min the solvent was evaporated. The resulting gel was extracted with hexane (7 × 30 mL). The combined organic layers were concentrated in vacuo and purified by column chromatography (silica, hexane/CH_2Cl_2, 6:4). The oil obtained was then recrystallized from methanol/water (100:1) to afford 3,9-dibromo-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (**3c**; 195 mg, 4.60 mmol, 78%) as a colorless powder. M.p. 114–115 °C. TLC: R_f = 0.61 (silica, hexane/CH_2Cl_2, 6:4). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.14–2.47 (m, 2 H), 2.43–2.47 (m, 4 H), 7.19 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.39 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H), 7.46 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 2.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 31.0, 32.9, 121.5, 129.6, 129.7, 131.4, 138.9, 141.5 ppm. HRMS (ESI): calcd. for $C_{15}H_{13}Br_2$ $[M + H]^+$ 350.9383; found 350.9385.

3,9-Bis(acetylsulfanyl)-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (3a): Under an inert gas, 3,9-dichloro-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (**3b**; 383 mg, 1.46 mmol) was dissolved in dry and degassed DMI. Sodium methanethiolate (2.00 g, 28.53 mmol, 19.5 equiv.) was added at once, and the reaction mixture was stirred at 110 °C overnight. After cooling to room temperature, AcCl (9 mL) was carefully added, and stirring was continued at room temperature overnight. The reaction mixture was poured onto ice, and the phases were separated and extracted with toluene (4 × 40 mL). The organic phase was washed with brine/water (1:1, 4 × 10 mL) and brine (1 × 10 mL), filtered through wool, and the solvent was evaporated. The crude product was separated by flash column chromatography (silica gel; hexane/*t*-BME, 8:2) to afford pure 3,9-bis(acetylsulfanyl)-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (**3a**; 242 mg, 0.71 mmol, 49%). Crystallization by using cyclohexane yielded single crystals suitable for X-ray analysis. M.p. 134 °C. TLC: R_f = 0.27 (hexane/*t*-BME, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.20 (m, 2 H), 2.45 (s, 6 H), 2.50 (m, 4 H), 7.29–7.31 (m, 2 H), 7.38–7.44 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 30.7, 31.6, 33.5, 127.5, 129.6, 133.1, 134.7, 141.0, 141.8, 194.7 ppm. UV/Vis: λ_{max} (ε) = 211 (36200), 278 (24000), 317 (2600) nm. MS (EI): *m*/*z* (%) = 342.0 (28) $[M]^+$, 300.0 (26) $[M - CH_3CO]^+$, 258.0 (100) $[M - 2\,CH_3CO]^+$, 192.1 (10), 165.1 (7). $C_{19}H_{18}O_2S_2$ (342.48): calcd. C 66.63, H 5.30; found C 66.32, H 5.32.

1,5-Bis(3-methoxyphenyl)-1,4-pentadien-3-one: A solution of *m*-anisaldehyde (20.0 g, 0.147 mol, 2.0 equiv.) and acetone (5.4 mL, 0.073 mol, 1.0 equiv.) in EtOH (30 mL) was added dropwise to a solution of NaOH (15.0 g, 0.375 mol, 5.1 equiv.) in EtOH (125 mL) and water (125 mL) while maintaining the reaction temperature at 20 °C with a water bath. After stirring the mixture at room temperature for 2 h, CH_2Cl_2 (100 mL) was added, and the phases were separated. The organic layer was washed with brine/water (80 mL, 1:1) and dried with $MgSO_4$. After evaporation of the solvent, a yellow viscous oil (22.5 g) was obtained, which was used without further purification in the next step. For analytical purposes a sample was recrystallized from EtOH/water. M.p. 109 °C. TLC: R_f = 0.55 (hexane/ethyl acetate, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.85 (s, 6 H), 6.93–6.98 (m, 2 H), 7.06 (d, $^3J_{H,H}$ = 15.9 Hz, 2 H), 7.12–7.14 (m, 2 H), 7.19–7.23 (m, 2 H), 7.33 (m, 2 H), 7.70 (m, $^3J_{H,H}$ = 15.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 55.8, 113.7, 116.8, 121.1, 126.1, 130.4, 136.6, 143.6, 160.4, 189.3 ppm. MS (EI): *m*/*z* (%) = 294.1 (100) $[M]^+$, 263.1 (32) $[M - CH_3O]^+$, 161.1 (23), 121.1 (23). $C_{19}H_{18}O_3$ (294.34): calcd. C 77.53, H 6.16; found C 77.39, H 6.27.

1,5-Bis(3-methoxyphenyl)-3-pentanone (22): The crude 1,5-bis(3-methoxyphenyl)-1,4-pentadien-3-one (assuming 73.45 mmol) was dissolved in ethyl acetate (200 mL) and Pd/C (0.50 g, 10% Pd) was added under an inert gas. The suspension was saturated with hydrogen gas and then vigorously stirred until the required volume of hydrogen (3.3 L, 147 mmol, 2.0 equiv.) was consumed. The suspension was degassed and filtered through a short silica pad. After evaporation of the solvent, flash chromatography (silica gel; 30–60% ethyl acetate in hexane) was performed to obtain 1,5-bis(3-methoxyphenyl)-3-pentanone (**22**; 10.10 g, 33.85 mmol, 46% over two steps) as an oil. TLC: R_f = 0.43 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.71 (t, $^3J_{H,H}$ = 8.0 Hz, 4 H), 2.85 (t, $^3J_{H,H}$ = 8.0 Hz, 4 H), 3.79 (s, 6 H), 6.73 (m, 6 H), 7.16–7.22 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 30.2, 44.8, 55.6, 111.8, 114.5, 121.1, 129.9, 143.1, 160.1, 209.4 ppm. MS (EI): *m*/*z* (%) = 298.2 (34) $[M]^+$, 163.1 (22), 135.1 (100), 121.1 (40), 91.1 (14). $C_{19}H_{22}O_3$ (298.38): calcd. C 76.48, H 7.43; found C 75.55, H 7.43.

1,5-Bis(3-methoxyphenyl)pentane (23): Hydrazine hydrate (2.3 mL, 39.00 mmol, 3.0 equiv., 85%) was added to a suspension of 1,5-bis(3-methoxyphenyl)-3-pentanone (**22**; 3.83 g, 12.84 mmol) and powdered KOH (2.88 g, 51.33 mmol, 4.0 equiv.) in triethyleneglycol (13 mL) under cooling. The mixture was heated at reflux for 2 h. The water and excess hydrazine were distilled off at an oil bath temperature of 190 °C. After 4 h at this reaction temperature, the reaction was stopped. Water was added to the cooled reaction mixture, and the mixture was extracted with hexane/ethyl acetate (4:1; 3 × 60 mL). The combined organic layers were washed with water (3 × 15 mL) and brine (50 mL), and dried with $MgSO_4$. After evaporation of the solvent and purification by flash chromatography (silica gel; hexane/ethyl acetate, 6:1) 1,5-bis(3-methoxyphenyl)pentane (**23**; 2.64 g, 9.30 mmol, 72%) was obtained as a colorless oil. TLC: R_f = 0.53 (hexane/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.41 (m, 2 H), 1.65 (m, 4 H), 2.59 (t, $^3J_{H,H}$ = 8.0 Hz, 4 H), 3.82 (s, 6 H), 6.72–6.78 (m, 6 H), 7.18–7.22 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 29.4, 31.7, 36.4, 55.5, 111.3, 114.6, 121.3, 129.6, 144.9, 159.9 ppm. MS (EI): *m*/*z* (%) = 284.2 (54) $[M]^+$, 163.1 (8), 135.1(23), 122.1 (100), 91.1 (15). $C_{19}H_{24}O_2$ (284.39): calcd. C 80.24, H 8.51; found C 80.36, H 8.62.

1,5-Bis(2-bromo-5-methoxyphenyl)pentane (24): A solution of bromine (5.30 g, 33.16 mmol, 2.3 equiv.) in CH_2Cl_2 (20 mL) was added dropwise to a solution of 1,5-bis(3-methoxyphenyl)pentane (**23**; 4.10 g, 14.42 mmol) and dry pyridine (4.0 mL, 49.65 mmol, 3.5 equiv.) in CH_2Cl_2 (40 mL) at –10 °C over 30 min. After stirring at room temperature for another 2 h, the reaction mixture was washed with satd. $NaHCO_3$ and dried with $MgSO_4$. After evaporation of the solvent, short-column flash chromatography (silica gel; CH_2Cl_2/hexane, 1:1) was performed to obtain 6.3 g of the crude product. The chromatographically inseparable impurities were removed by recrystallization from pentane (60 mL) at 4 °C. The pure 1,5-bis(2-bromo-5-methoxyphenyl)pentane (**24**; 2.65 g, 5.99 mmol, 42%) was collected as fine white crystals. M.p. 44–45 °C. TLC: R_f = 0.53 (hexane/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.43–1.51 (m, 2 H), 1.62–1.72 (m, 4 H), 2.70 (t, $^3J_{H,H}$ = 8.0 Hz, 4 H), 3.78 (s, 6 H), 6.62 (dd, $^4J_{H,H}$ = 3.0, $^3J_{H,H}$ = 8.7 Hz, 2 H), 6.78 (d, $^4J_{H,H}$ = 3.0 Hz, 2 H), 7.41 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 29.5, 30.1, 36.7, 55.8, 113.4, 115.3, 116.4, 133.6, 143.4, 159.3 ppm. MS (EI): *m*/*z* (%) = 440.0, 442.0, 444.0 $[M]^+$. $C_{19}H_{22}Br_2O_2$ (442.18): calcd. C 51.61, H 5.01; found C 51.63, H 5.03.

3,11-Dimethoxy-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (26): Under an inert gas, 1,5-bis(2-bromo-5-methoxyphenyl)pentane (**24**; 2.00 g, 4.50 mmol) was dissolved in dry MeTHF (170 mL). The solution was cooled to –60 °C in a dry ice/acetone bath, and *t*BuLi (11.1 mL, 18.0 mmol, 4.0 equiv.) was added dropwise. After the addition was completed, the yellow solution was stirred at this temperature for another 15 min. A fresh solution of anhydrous LiBr (825 mg, 9.50 mmol, 2.1 equiv.) and CuCN (425 mg, 4.75 mmol, 1.1 equiv.) in MeTHF (10 mL) was prepared. This almost clear green copper solution was transferred to the reaction mixture over 10 min while keeping the reaction temperature below –50 °C. The cloudy reaction mixture was then stirred at –20 °C for another 1 h and then cooled again to –40 °C. 1,3-Dinitrobenzene (3.00 g, 18.0 mmol, 4.0 equiv.) was added at once, and the cooling reservoir was removed. After stirring at room temperature overnight, the black reaction mixture was quenched with a mixture of NH_4Cl (40 mL, 10%) and NH_4OH (40 mL, 25%). The layers were separated, and the aqueous phase was extracted with *t*-BME (2 × 80 mL). The combined organic layers were washed with brine and dried with $MgSO_4$. After evaporation of the solvent, flash chromatography (silica; *t*-BME in hexane, 0–20%) was performed to obtain the monomer fraction **26** (568 mg) and a fraction containing the dimer **25** according to the MS analysis (343 mg, 0.61 mmol, 27%). Recrystallization of the monomer fraction from hexane (10 mL) afforded the pure monomer **26** (292 mg, 1.03 mmol, 23%) as colorless crystals. **26:** M.p. 112–113 °C. TLC: R_f = 0.53 (hexane/*t*-BME, 5:1). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.37–1.43 (m, 2 H), 1.48–1.56 (m, 2 H), 1.71–1.77 (m, 2 H), 2.06–2.13 (m, 2 H), 2.57–2.64 (m, 2 H), 3.80 (s, 6 H), 6.76–6.78 (m, 4 H), 7.03–7.06 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 28.6, 29.5, 33.9, 55.6, 111.2, 114.5, 130.5, 134.7, 144.1, 159.3 ppm. MS (EI): *m*/*z* (%) = 282.2 (100) $[M]^+$, 267.2 (6) $[M - CH_3]^+$, 239.1 (10), 225.1 (9), 211.1 (7), 165.1 (6), 122.1 (6). $C_{19}H_{22}O_2$ (282.38): calcd. C 80.82, H 7.85; found C 80.47, H 7.93. **25:** Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.00–1.13 (m, 4 H), 1.30–1.52 (m, 8 H), 2.33 (t, $^3J_{H,H}$ = 7.3 Hz, 8 H), 3.84 (s, 12 H), 6.70 (dd, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 2.6 Hz, 4 H), 6.80 (d, $^4J_{H,H}$ = 2.6 Hz, 4 H), 6.92 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 29.3, 29.6, 33.6, 55.5, 110.7, 113.7, 131.7, 133.5, 141.9, 158.9 ppm. MS (EI): *m*/*z* (%) = 564.3 (100) $[M]^+$, 282.2 (8), 239.1 (10), 121.1 (11).

3,11-Dihydroxy-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (27): A solution of BBr_3 (4.1 mL, 4.10 mmol, 4.0 equiv., 1.0 M) in CH_2Cl_2 was slowly added dropwise to a solution of 3,11-dimethoxy-6,7,8,9-tetrahydro-5*H*-dibenzo-[*a*,*c*]cyclononene (**26**; 288 mg, 1.02 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C. Then stirring was continued at room temperature until TLC showed full conversion of the starting material (1.5 h). The reaction was quenched with MeOH under ice-cooling. The reaction mixture was then washed with water (10 mL), dried with $MgSO_4$, and the solvents were evaporated. The crude 3,11-dihydroxy-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (**27**) was obtained as a white powder, which was pure enough to use in the next step. TLC: R_f = 0.40 (hexane/*t*-BME, 1:2). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.31–1.37 (m, 2 H), 1.41–1.52 (m, 2 H), 1.65–1.76 (m, 2 H), 2.00–2.09 (m, 2 H), 2.47–2.56 (m, 2 H), 6.64–6.70 (m, 4 H), 6.93 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 28.1, 29.0, 33.2, 112.4, 115.3, 130.1, 133.8, 143.7, 155.4 ppm. MS (EI): *m*/*z* (%) = 254.1 (100) $[M]^+$, 211.1 (25), 198.1 (15), 108.1 (16).

3,11-Bis(trifluoromethylsulfonyloxy)-6,7,8,9-tetrahydro-5*H*-dibenzo-[*a*,*c*]cyclononene (5e): The crude 3,11-dihydroxy-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (**27**; assuming 1.02 mmol) from the previous step was dissolved in dry pyridine (8 mL). Then triflic anhydride (677 µL, 4.02 mmol, 4.0 equiv.) was slowly added dropwise to the solution. Stirring was continued at room temp. (30 min), and the beige solution was quenched with a cold $NaHCO_3$ solution. The product was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic phases were dried with $MgSO_4$. After evaporation of the solvent, flash chromatography (silica; hexane/CH_2Cl_2, 7:3) was performed to afford 3,11-bis(trifluoromethylsulfonyloxy)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (**5e**; 620 mg) as a colorless oil that contained some inseparable material that did not affect the next step. Upon standing at room temperature, a sample of the triflate solidified after a few weeks. TLC: R_f = 0.73 (hexane/*t*-BME, 1:2). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.34–1.39 (m, 2 H), 1.47–1.56 (m, 2 H), 1.76–1.87 (m, 2 H), 1.99–2.06 (m, 2 H), 2.67–2.73 (m, 2 H), 7.15–7.22 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 28.3, 29.1, 33.7, 119.1, 119.2 (q, $J_{C,F}$ = 321 Hz), 122.1, 130.9, 140.8, 145.2, 149.7 ppm. MS (EI): *m*/*z* (%) = 518.0 $[M]^+$, 385.1 (17) $[M - SOCF_3]^+$, 252.1 (34) $[M - 2\ SOCF_3]^+$, 235.1 (44), 107 (23). $C_{19}H_{16}F_6O_6S_2$ (518.45): calcd. C 44.02, H 3.11; found C 44.15, H 3.04.

3,11-Bis(*tert*-butylsulfanyl)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (28): Under an inert gas, 3,11-bis(trifluoromethylsulfonyloxy)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (**5e**; 336 mg, assuming 0.55 mmol) was dissolved in degassed *p*-xylene (10 mL). Then $[Pd_2(dba)_3 \cdot CHCl_3]$ (78.0 mg, 75.4 µmol, 11.6 mol-%), xantphos (52.0 mg, 89.9 µmol, 13.8 mol-%), and sodium *tert*-butanethiolate (290 mg, 2.58 mmol, 4.0 equiv.) were added. The reaction mixture was stirred at 140 °C for 6 h. Then toluene (20 mL) was added, and the mixture was washed with brine (2 mL). The aqueous phase was extracted with toluene (2 × 20 mL), and the combined organic phases were dried with $MgSO_4$. After evaporation of the solvent, flash chromatography (silica; *t*-BME in hexane, 1–5%) was performed to afford 3,11-bis(*tert*-butylsulfanyl)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (**28**; 134 mg, 0.34 mmol, 62% over three steps) as a bright-yellow solid. M.p. 108–110 °C. TLC: R_f = 0.58 (hexane/*t*-BME, 97:3). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.31–1.41 (m, 20 H), 1.48–1.56 (m, 2 H), 1.72–1.83 (m, 2 H), 1.99–2.06 (m, 2 H), 2.62–2.68 (m, 2 H), 7.09 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.37–7.43 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 28.5, 29.5, 31.4, 33.5, 46.2, 129.1, 132.0, 134.9, 138.4, 142.3, 142.4 ppm. MS (EI): *m*/*z* (%) = 398.2 (24) $[M]^+$, 342.1 (7) $[M - C_4H_8]^+$, 286.1 (100) $[M - 2\ C_4H_8]^+$. HRMS (ESI): calcd. for $C_{25}H_{35}S_2$ $[M + H]^+$ 399.2180; found 399.2185.

3,11-Bis(acetylsulfanyl)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (5a): BBr_3 (0.93 mL, 0.93 mmol, 3.0 equiv., 1.0 M in CH_2Cl_2) was slowly added dropwise to a solution of 3,11-bis(*tert*-butylsulfanyl)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (**28**; 124 mg, 0.31 mmol) in AcCl (13 mL) and dry toluene (30 mL) at 0 °C. Then stirring was continued at room temperature. After TLC showed full conversion (1 h) of the starting material, the reaction mixture was quenched with ice, and the organic phase was separated. The aqueous phase was extracted with toluene (2 × 30 mL). The combined organic layers were dried with $MgSO_4$ and the solvents evaporated in vacuo. The crude product was purified by flash chromatography (silica; *t*-BME/hexane, 1:1) followed by recrystallization from pentane (4 °C) to afford 3,11-bis(acetylsulfanyl)-6,7,8,9-tetrahydro-5*H*-dibenzo[*a*,*c*]cyclononene (**5a**; 70.0 mg, 0.19 mmol, 61%) as colorless crystals. M.p. 151 °C. TLC: R_f = 0.53 (hexane/*t*-BME, 5:1). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.38–1.42 (m, 2 H), 1.44–1.55 (m, 2 H), 1.63–1.82 (m, 2 H), 2.04–2.11 (m, 2 H), 2.45 (s, 6 H), 2.63–2.70 (m, 2 H), 7.18–7.20 (m, 2 H), 7.28–7.30 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 28.5, 29.3, 30.7, 33.5, 127.5, 129.9, 132.0, 135.3, 142.7, 143.3, 194.7 ppm. UV/Vis: λ_{max} (ε) = 214 (48200), 250 (17600 $M^{-1}cm^{-1}$) nm. MS (EI): *m*/*z* (%) = 370.1 (28) $[M]^+$, 328.1

(39) [M – CH_3CO]$^+$, 286.1(100) [M – 2 CH_3CO]. $C_{21}H_{22}O_2S_2$ (370.53): calcd. C 68.07, H 5.98; found C 68.03, H 6.04.

1,2-Bis(3,5-dimethylphenyl)hydrazine: A suspension of 3,5-dimethylnitrobenzene (10.00 g, 66.20 mmol) and zinc powder (25.0 g, 0.382 mol, 5.8 equiv.) in EtOH (40 mL) was heated at reflux under an inert gas. Then the heating source was removed, and a solution of NaOH (15.0 g, 0.375 mol, 5.7 equiv.) in water (50 mL) was added dropwise to the reaction mixture at such a rate that the solution boiled vigorously. After addition of about a third of the base, heating was needed to maintain a steady reflux. After all of the base had been added, heating was continued at reflux for 4 h, and more zinc powder (10.0 g, 0.153 mol, 2.3 equiv.) was added in portions over this period of time. The hot suspension was filtered through Celite and washed with hot EtOH (60 mL) into a mixture of AcOH (150 mL, 30%) and sodium bisulfite (1.0 g, 9.6 mmol, 0.15 equiv.). The slurry was cooled to 10 °C, and the solid was filtered off. Recrystallization from hot heptane (80 mL) afforded 1,2-bis(3,5-dimethylphenyl)hydrazine (3.96 g, 16.48 mmol, 50%) as long white needles. M.p. 119–123 °C. TLC: R_f = 0.77 (ethyl acetate/hexane, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.24 (s, 12 H), 5.46 (s, 2 H), 6.52 (s, 6 H) ppm.

2,2′,6,6′-Tetramethylbenzidine (29): Diluted HCl (175 mL, 10%) was degassed with nitrogen for 30 min. Then 1,2-bis(3,5-dimethylphenyl)hydrazine (3.70 g, 15.4 mmol) was added, and the reaction mixture was heated at reflux. After 2 h, TLC showed full conversion of the starting material. The solution was cooled to room temperature, and NaOH was added until pH = 10. The product was extracted with *t*-BME (3 × 60 mL), and the combined organic phases were washed with brine and dried with $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from benzene/hexane to obtain 2,2′,6,6′-tetramethylbenzidine (**29**; 2.87 g, 11.90 mmol, 77%) as a pink powder. For further purification, the free base was recrystallized several times from EtOH/water; however, traces of isomeric impurities remained in the sample. M.p. 163–165 °C. TLC: R_f = 0.47 (ethyl acetate/hexane, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.82 (s, 12 H), 3.52 (br. s, 4 H), 6.48 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 20.4, 114.7, 131.1, 137.7, 145.0 ppm. MS (EI): *m*/*z* (%) = 240.2 (100) [M]$^+$, 225.1 (14) [M – CH_3]$^+$, 210.1 (30) [M – 2 CH_3]$^+$, 105.1 (11).

4,4′-Diiodo-2,2′,6,6′-tetramethylbiphenyl (8d): A solution of $NaNO_2$ (600 mg, 8.70 mmol, 2.2 equiv.) in water (2.0 mL) was added to a suspension of 2,2′,6,6′-tetramethylbenzidine (**29**; 0.93 g, 3.87 mmol) in water (15 mL) and H_2SO_4 (8 mL, 0.142 mol, 36.4 equiv., 95%) at 4 °C. After stirring at this temperature for another 30 min, all the starting materials had dissolved, and the reaction mixture was transferred to a cold solution of I_2 (2.70 g, 10.64 mmol, 2.8 equiv.) and NaI (2.70 g, 18.00 mmol, 4.7 equiv.) in water (5 mL). After 20 min, more water (20 mL) and CH_2Cl_2 (50 mL) were added to dissolve the reaction components again. After stirring at room temperature overnight, sodium thiosulfate (2.00 g, 12.7 mmol, 3.3 equiv.) was added, and the reaction mixture was stirred for 10 min. The black precipitate was filtered off and the phases separated. The aqueous phase was extracted with $CHCl_3$ (2 × 30 mL), and the combined organic layers were washed again with a thiosulfate solution (25 mL, 10%) and brine. After drying with $MgSO_4$ and evaporation of the solvent, flash chromatography was performed to obtain 4,4′-diiodo-2,2′,6,6′-tetramethylbiphenyl (**8d**; 908 mg, 1.97 mmol, 51%) as bright-yellow crystals. M.p. 196 °C. TLC: R_f = 0.52 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.83 (s, 12 H), 7.48 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 19.8, 93.3, 136.9, 138.2, 138.9 ppm. MS (EI): *m*/*z* (%) = 461.9 (20) [M]$^+$, 336.0 (100) [M – iodine]$^+$, 209.1 (13) [M – 2 iodine]$^+$, 194.1 (76), 179.1 (36). $C_{16}H_{16}I_2$ (462.11): calcd. C 41.59, H 3.49; found C 42.53, H 3.52.

4,4′-Bis(*tert*-butylsulfanyl)-2,2′,6,6′-tetramethylbiphenyl (30): Under an inert gas, 4,4′-diiodo-2,2′,6,6′-tetramethylbiphenyl (**8d**; 690 mg, 1.49 mmol) was dissolved in degassed *p*-xylene (15 mL). Then [$Pd_2(dba)_3 \cdot CHCl_3$] (155 mg, 150 µmol, 10.0 mol-%), xantphos (104 mg, 180 µmol, 12.1 mol-%), and sodium *tert*-butanethiolate (503 mg, 4.48 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 140 °C for 16 h. Then toluene (20 mL) and brine (20 mL) were added, and the phases were separated. The aqueous phase was extracted with *t*-BME (2 × 30 mL), and the combined organic phases were dried with $MgSO_4$. After evaporation of the solvent, flash chromatography (silica; Et_2O in hexane, 3%) was performed to afford 4,4′-bis(*tert*-butylsulfanyl)-2,2′,6,6′-tetramethylbiphenyl (**30**; 289 mg, 0.75 mmol, 50%) as a yellow oil. TLC: R_f = 0.52 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.32 (s, 18 H), 1.88 (s, 12 H), 7.30 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 20.0, 31.5, 46.0, 131.2, 136.0, 136.8, 140.5 ppm. MS (EI): *m*/*z* (%) = 386 (33) [M]$^+$, 330 (7) [M – C_4H_8]$^+$, 274 (100) [M – 2 C_4H_8]$^+$.

4,4′-Bis(acetylsulfanyl)-2,2′,6,6′-tetramethylbiphenyl (8a): BBr_3 (1.0 mL, 1.00 mmol, 2.9 equiv., 1.0 M in CH_2Cl_2) was slowly added dropwise to a solution of 4,4′-bis(*tert*-butylsulfanyl)-2,2′,6,6′-tetramethylbiphenyl (**30**; 130 mg, 0.34 mmol) in AcCl (13 mL) and dry toluene (35 mL) at 0 °C. Then stirring was continued at room temperature. After TLC showed full conversion (45 min) of the starting material, the reaction mixture was quenched with ice, and the organic phase was separated. The aqueous phase was extracted with toluene (2 × 30 mL). The combined organic layers were dried with $MgSO_4$ and the solvents evaporated in vacuo. The crude product was purified by flash chromatography (silica; *t*-BME/hexane, 1:1) followed by recrystallization from a mixture of hexane (2 mL) and cyclohexane (4 mL) to afford 4,4′-bis(acetylsulfanyl)-2,2′,6,6′-tetramethylbiphenyl (**8a**; 101 mg, 0.28 mmol, 84%) as colorless crystals. M.p. 141 °C. TLC: R_f = 0.52 (hexane/*t*-BME, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.91 (s, 12 H), 2.43 (s, 6 H), 7.20 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 20.2, 30.6, 126.7, 133.8, 137.0, 140.9, 193.8 ppm. UV/Vis: λ_{max} (ε) = 209 (57500), 244 (18300 $M^{-1}cm^{-1}$) nm. MS (EI): *m*/*z* (%) = 358.1 (20) [M]$^+$, 316.1 (27) [M – CH_3CO]$^+$, 274.1 (100) [M – 2 CH_3CO]$^+$. $C_{20}H_{22}O_2S_2$ (358.52): calcd. C 67.00, H 6.10; found C 67.10, H 6.16.

X-ray Crystallographic Study: X-ray analyses were performed on single crystals with a Nonius–KappaCCD diffractometer at 173 K by using graphite-monochromated Mo-K_α-radiation (λ = 0.71073 Å). CCDC-746122 (**8a**) and -746123 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. **8a:** $C_{20}H_{22}O_2S_2$, M_r = 358.53, *F*(000) = 760, colorless block crystals, 0.07 × 0.11 × 0.19 mm, monoclinic, space group $P2_1/c$, *Z* = 4, *a* = 12.1700(3), *b* = 10.9870(2), *c* = 15.5093(4) Å, β = 111.3660(10)°, *V* = 1931.25(8) Å^3, $D_{calcd.}$ = 1.233 Mg m^{-3}, θ_{max} = 32.923°. Min/max transmission 0.97/0.98, μ = 0.284 mm^{-1}. From a total of 40834 reflections, 7002 were independent (merging *r* = 0.030). Of these, 4062 were considered as observed [$I > 3.0\sigma(I)$] and were used to refine 217 parameters. *R* = 0.0428 (observed data), *wR* = 0.0680 (all data), GOF = 1.0536. Min/max residual electron density = –0.49/0.57 e Å^{-3}. **9:** $C_{24}H_{34}$, M_r = 322.53, *F*(000) = 712, colorless plate crystals, 0.04 × 0.11 × 0.33 mm, orthorhombic, space group *Aba*2, *Z* = 4, *a* = 13.7511(4), *b* = 14.9038(4), *c* = 9.8716(3) Å, *V* = 2023.12(10) Å^3, $D_{calcd.}$ = 1.059 Mg m^{-3}, θ_{max} = 33.835°. Min/max transmission 0.99/1.00, $\mu = 0.059\ \mathrm{mm}^{-1}$. Of a total of 7763 reflections, 2125 were independent (merging $r = 0.028$). Of these, 1535 were considered as observed [$I > 3.0\sigma(I)$] and were used to refine 109 parameters. $R = 0.0447$ (observed data), $wR = 0.0489$ (all data), GOF = 1.1954. Min/max residual electron density = –0.15/0.27 $e\text{Å}^{-3}$.

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