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A Rational Approach to Tetra-Functional Photo-Switches

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α,ω-Bis(1,8-dichloroanthracen-10-yl)alkanes with (CH$_2$)$_n$-linker units (n = 1–4) were synthesized starting from 1,8-dichloroanthracen-10(9H)-one. This was transformed into anthracenes with allyl, bromomethyl and propargyl substituents in position 10; these were converted in various C—C-bond formation reactions (plus hydrogenation), leading to two anthracene units flexibly linked by α,ω-alkandiyl groups. 1,2-Ethandiyl- and 1,3-propandiyl-linked derivatives were functionalized with ethynyl groups in positions 1, 8, 1' and 8', and these terminally functionalized by Me$_3$Sn groups using Me$_2$NSnMe$_3$. All linked bisanthracenes were subjected to UV light induced cyclomerization and a series of 9,10:9',10'-photo-cyclomers were obtained. Their thermal cycloreversion and (repeated) switchability was demonstrated. 1,3-Bis{1,8-bis[(trimethylstannyl)ethynyl]anthracen-10-yl}propane served as model compound for photoswitchable acceptor molecules and its open and closed forms were characterized by NMR and DOSY experiments.

Introduction

Functionalized anthracenes provide well-defined distances and orientations of the substituents. Thus, they are frequently used for organic and organometallic applications where defined geometries of several functions are needed.[1,2] Photo-dimerization of these rigid frameworks doubles the number of directed functions. In most cases, irradiation with UV light induces a [4π+4π] cycloaddition reaction and 9,10:9',10'-photo-dimers are formed, but usually more than one photo-isomer is obtained.[3] In the case of 1,8-substituted anthracenes the formation of two isomers [*head-to-head*- (**A**) and *head-to-tail*-photo-dimer (**B**)] is observed (Scheme 1). Due to steric repulsion and symmetry considerations in electronic effects, the *head-to-tail*-isomer is generally favored and formed in excess.[2e,4]

Different approaches are known to control this regioselectivity, for instance by dimerization of anthracene derivatives in the ordered solid state[5] or in preorganized supramolecular assemblies, e.g. inside cyclodextrins[6] or within nanoflasks.[7] Furthermore, a common strategy to avoid *head-to-tail*-photo-dimerization is to introduce a short linker unit between two anthracene subunits, usually in positions 9/9'. As shown in Scheme 1, compounds **C**–**E** are interesting examples for these bichromphoric systems.[8–10]
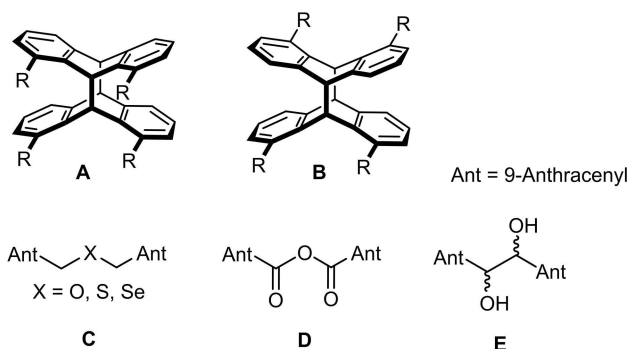
Scheme 1. The photo-dimers **A** (*head-to-head*) and **B** (*head-to-tail*) are obtained upon UV irradiation of 1,8-substituted anthracenes. Compounds **C**–**E** are examples for bichromophoric anthracenes connected by flexible linker units.[8–10]

Our present search for new selectively complexing poly-Lewis acids makes it necessary to decorate rigid and donor-free frameworks with Lewis acid functions. In this context, systems based on flexibly bridged bisanthracenes could be of special interest for the reversible complexation of guest molecules by switching from open to closed isomers. The synthesis of the required organic frameworks is the main element of this contribution. Recently, we synthesized a series of 1,8-dichlorinated anthracene derivatives, with two such units flexibly bridged with —Me$_2$Si—(CH$_2$)$_n$—SiMe$_2$— linkers. For these systems we found the bulky dimethylsilyl groups to inhibit any cyclomerizing.[11] In contrast, bisanthracenyl compounds with short α,ω-alkandiyl chains are known to be well-suited for 9,10:9',10'-photo-cyclomerization,[3,8] at least for the unsubstituted derivatives. For our purpose, the use of substituted analogues could be a suitable access to photo-switchable poly-Lewis acids.

Herein, we report the syntheses of molecules with two 1,8-substituted anthracene units, connected by methylene, 1,2-ethandiyl, 1,3-propandiyl and 1,4-butandiyl chains in positions 10/10'. For comparison bisanthracenes with even longer linker

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units were synthesized. All of these compounds were tested for UV-induced [4π+4π] cycloaddition and the resulting photo-cyclomers for thermal cycloreversion. Moreover, fourfold (trimethylstannyl)ethynyl-functionalized bisanthracenes were synthesized as model compounds for photo-switchable acceptor molecules.

Results and Discussion

There are several literature protocols for the synthesis of α,ω-bis(anthracen-9-yl)alkanes, usually starting from anthrone, anthraldehyde or dihydroanthracene.[12] An efficient synthesis was recently reported by Klaper and Linker. They converted anthracene in a Birch reduction, followed by alkylation with α,ω-dibromoalkanes.[13] Since we are interested in chloro-substituted anthracenes, which can be further modified with rigid alkynyl-spacers in Kumada cross-coupling reactions, completely new strategies for the synthesis of α,ω-bis(1,8-dichloro-anthracen-10-yl)alkanes had to be developed in this work.

Initially, 1,8-dichloroanthracenes bearing different functional groups in position 10 were required. They were subsequently subjected to C—C-bond formation reactions, in order to interconnect two anthracene building blocks. As shown in Scheme 2, the methyl-, vinyl- and allyl-substituted derivatives **2**, **3** and **4** were synthesized by reacting the corresponding Grignard reagent with 1,8-dichloroanthracen-10(9H)-one (**1**). The latter is easily available by reduction of 1,8-dichloroanthraquinone with sodium dithionite in DMF.[14] After aqueous workup, rearomatisation and purification by column
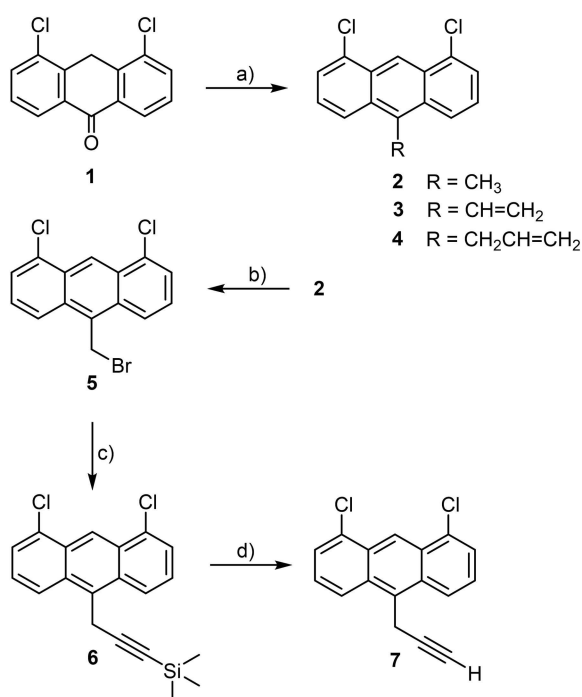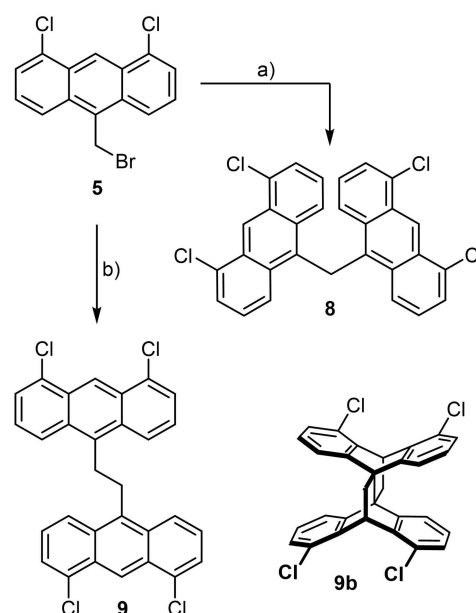
chromatography, the substituted anthracenes were obtained as bright yellow crystals.

Bromination of **2** in benzylic position with N-bromosuccinimide (NBS) gave 10-(bromomethyl)-1,8-dichloro-anthracene (**5**) in a very good yield of 95%. **5** was further converted with (trimethylsilyl)-ethinylmagnesium bromide in the presence of copper(I) iodide, forming the propargyl-substituted anthracene derivative **6**. Cleavage of the trimethylsilyl protecting groups had to be carried out under mild conditions using silver nitrate and water in acetone. The use of potassium carbonate in methanol did not afford the desired propargyl-substituted anthracene **7**, but quantitatively 1,8-dichloro-10-(prop-1-yn-1-yl)-anthracene (**7b**) (Scheme S2, SI). All new compounds were characterized by multinuclear NMR spectroscopy and high resolution mass spectrometry. In case of vinylanthracene **3**, bromomethylanthracene **5** and propargylanthracene **7** the molecular structures in the crystalline state were determined by X-ray diffraction (Figures S32–S34, SI).

The methylene- and ethylene-linked dichloroanthracenes **8** and **9** were synthesized each in one step from bromomethylanthracene **5** (Scheme 3). Therefore, compound **5** was lithiated with n-butyllithium at −78°C. For the preparation of compound **8** the lithiated species was used for a nucleophilic addition reaction with anthrone **1**. The elimination of water and the subsequent aromatization was achieved by addition of phosphorus pentoxide and keeping the mixture at 80°C for three hours. In order to form the ethylene linked bisanthracene **9**, the lithiated species was converted in a salt elimination reaction with a second equivalent of **5** (Scheme 3). Due to very low solubility, bis-(anthracen-10-yl)ethane **9** was solely charac-

Scheme 2. Syntheses of the 1,8-10-substituted anthracenes **2**–**7**. Reagents and conditions: a) RMgBr, THF, r.t., 16 h, 71% (**2**), 33% (**3**), 85% (**4**); b) NBS, AIBN, benzene, reflux, 2 h, 95%; c) Me₃Si–C≡C–MgBr, CuI, THF, 0°C to r.t., 16 h, 91%; d) AgNO₃, H₂O, acetone, 4 d, 85%.
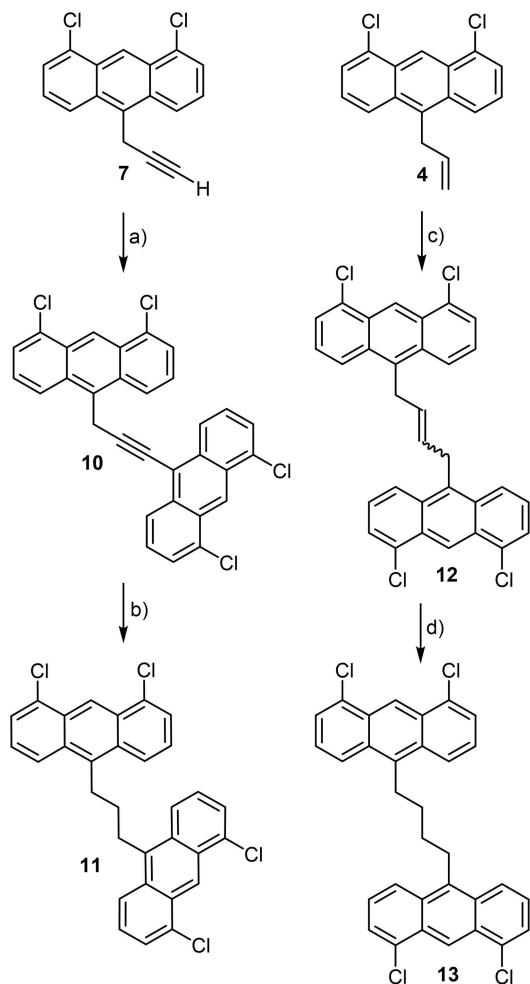
Scheme 3. Syntheses of the bisanthracenylalkanes **8** and **9**. Reagents and conditions: a) n-butyllithium (1 eq), THF, −78°C, 0.5 h, 1,8-dichloroanthracen-10(9H)-one (**1**), −78°C to r.t., 16 h, 25%; b) n-butyllithium (0.5 eq), THF, −78°C to r.t., 16 h, 84%. Tetrachlorolepidopterene **9b** is observed as a by-product of bisanthracenylethane **9**.

terized by ^{1}H NMR spectroscopy and high resolution mass spectrometry.

A byproduct, generally observed in the preparation of bis-(anthracen-10-yl)ethanes, is the corresponding tetrabenzotetra-cyclotetradecatetraene, also referred to as lepidopterene.[15] In our case, this species is the peritetrachlorolepidopterene **9b**, first reported by Becker and co-workers.[16] Actually, we found the formation of compounds **9** and **9b** in competition to each other. However, we were able to avoid the formation of **9b** by heating the reactive solution to room temperature immediately after adding *n*-butyllithium and thus obtaining the precipitated product **9** in 84% yield. Stirring the mixture at −78 °C for several hours instead, lepidopterene **9b** was found to be the main product. However, in larger scales, the formation of **9b** cannot be avoided. Its solid state structure was determined in X-ray diffraction experiments (Figure S35, SI).

1,3-Propandiyl- and 1,4-butandiyl-linked anthracenes **11** and **13** were both obtained in two-step syntheses (Scheme 4). The three-membered spacer was introduced by a Sonogashira-Hagihara cross-coupling reaction of the propargyl-substituted anthracene **7** with 10-bromo-1,8-dichloroanthracene,[17] yielding

compound **10**. The 1,4-but-2-endiyl-linked bisanthracene **12** was obtained in nearly quantitative yield by subjecting the allyl-functionalized anthracene **4** to olefin metathesis using Grubbs I catalyst. Note, that no reaction was observed when 1,8-dichloro-10-vinylanthracene (**3**) was treated under the same conditions. The unsaturated linker units of compounds **10** and **12** were reduced by use of hydrogen at room temperature in the presence of palladium/carbon, yielding the desired compounds **11** and **13**.

Compounds **11**–**13** were characterized by X-ray diffraction. The molecular structures of **11** and **13** in the crystalline state are shown in Figure 1 for comparison (see Figure S34, SI for solid state structure of **12**). All structural parameters of **11** and **13** are in good agreement with the values of the non-chlorinated derivatives, crystallized by Arslan and co-workers.[18,19] Compared to each other, no differences within experimental error can be observed for the anthracene skeletons, solely for the C(10)–CH₂–CH₂ bond angle [115.2(2)°

Scheme 4. Syntheses of the bisanthracenylalkanes **11** and **13**. Reagents and conditions: a) 10-bromo-1,8-dichloroanthracene, PdCl₂(PPh₃)₂, CuI, diisopropylamine, reflux, 3d, 33%; b) H₂, Pd/C, CH₂Cl₂, 2d, 87%; c) Grubbs' I cat. (5 mol%), CH₂Cl₂, 40 °C, 16 h, 95%; d) H₂, Pd/C, CH₂Cl₂, 1d, 63%.
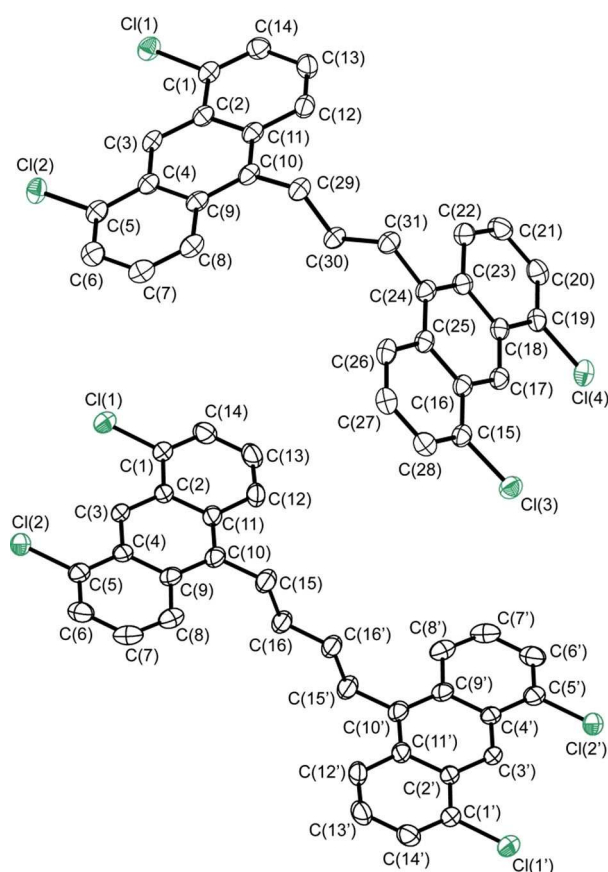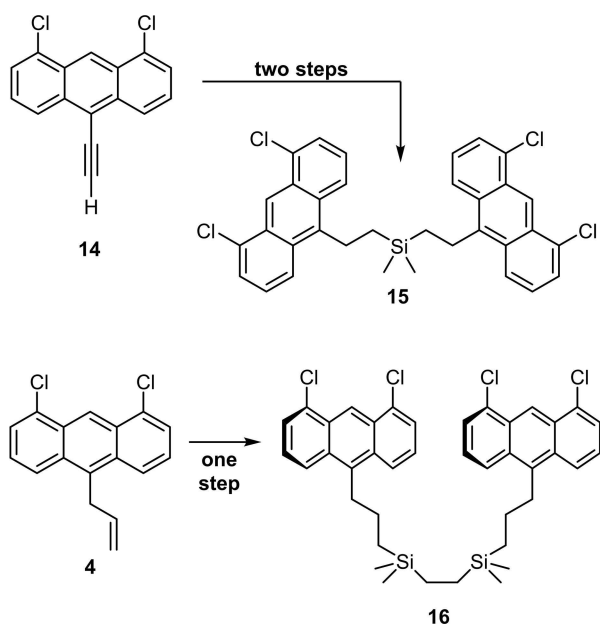
Figure 1. Molecular structures of 1,3-bis(1,8-dichloranthracen-10-yl)propane (**11**, above) and 1,4-bis(1,8-dichloroanthracen-10-yl)butane (**13**, below) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **11/13**: C(1)–C(2) 1.433(4)/1.424(2), C(1)–C(14) 1.353(4)/1.354(2), C(1)–Cl(1) 1.750(3)/1.743(2), C(2)–C(3) 1.394(4)/1.387(2), C(2)–C(11) 1.440(4)/1.438(2), C(10)–C(11) 1.413(4)/1.405(2), C(10)–C(29/15) 1.514(4)/1.513(2), C(15)–C(16)–/1.524(2), C(16)–C(16')–/1.516(3), C(29)–C(30) 1.537(4)/–; C(1)–C(2)–C(3) 122.6(3)/122.8(2), C(1)–C(2)–C(11) 117.6(3)/117.6(1), C(2)–C(1)–Cl(1) 118.4(2)/118.8(1), C(2)–C(3)–C(4) 120.9(3)/121.5(2), C(2)–C(11)–C(10) 119.6(3)/119.7(2), C(10)–CH₂–CH₂ 115.2(2)/113.9(1), C(11)–C(10)–CH₂ 120.3(3)/120.1(2), C(15)–C(16)–C(16')–/113.1(2), C(29)–C(30)–C(31) 110.3(2)/–.

for **11** and 113.9(1)° for **13**]. In general, the bond angles of the carbon atoms in the linker units show higher diversity for propane **11** [110.3(2)–115.2(2)], than for butane **13** [113.1(2)–113.9(1)].

In order to investigate the influence of the chain length in terms of the ability to form photo-cyclomers, polymethylene-linked bisanthracenes with more than four members would be interesting. However, the formation of such compounds might require more sophisticated synthetic strategies. Assuming that dimethylsilyl groups within the bridging moiety should not significantly affect the photochemistry of the corresponding bisanthracenes, we synthesized derivatives **15** and **16**; they are linked by five and ten-membered chains containing one and two dimethylsilyl groups, respectively. As shown in Scheme 5, 10-allyl-1,8-dichloroanthracene (**4**) and 1,8-dichloro-10-ethynylanthracene (**14**) were used as starting materials and converted in one or two steps (for experimental details and solid state structures, see SI).

Photo-Cyclomerizing Reactions

The UV/VIS-absorption spectra of compunds **8**, **9**, **11** and **13** (see Figures S27 and S28, SI) are highly consistent with characteristic p absorption bands located at 320–420 nm, as it is observed for 1,8-dichloroanthracene.[20] These four bisanthracenes were investigated in UV light induced photo-cyclomerization experiments (Scheme 6). Therefore, small amounts of the yellow solids were dissolved or suspended in degassed deuterated chloroform in an NMR tube and the mixtures were irradiated with UV light (365 nm) for a certain period of time. The conversion was indicated by a rapid change of the sample's colour from yellow to colorless. ¹H NMR spectroscopic experi-
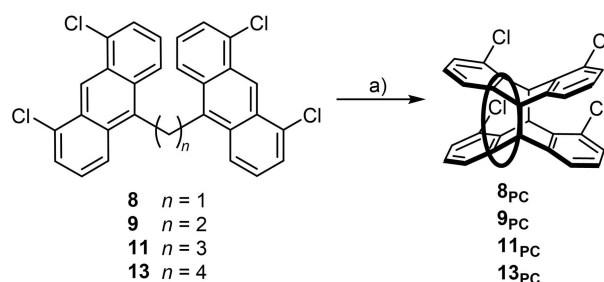
Scheme 6. UV light irradiation of compounds **8**, **9**, **11** and **13** and formation of the corresponding [4π + 4π] photo-cyclomers; a) CDCl₃, UV light (365 nm), 1–3 h. The photo-cyclomers **8**$_{PC}$, **9**$_{PC}$ and **11**$_{PC}$ are formed quantitatively. In addition to cyclomer **13**$_{PC}$, photo-oligomers were formed by intermolecular cycloaddition.

ments demonstrated the quantitative formation of the photo-cyclomers **8**$_{PC}$, **9**$_{PC}$ and **11**$_{PC}$. Compounds **8**$_{PC}$ and **9**$_{PC}$ were found to be much better soluble than their non-irradiated precursors **8** and **9**. However, the NMR signals of compound **8**$_{PC}$ rapidly disappeared after a few minutes and a colorless solid precipitated, which could not be dissolved in any common organic solvent. Irradiating butane **13**, a mixture of different species was obtained. Besides cyclomer **13**$_{PC}$, which could be explicitly identified, a colorless precipitate is obtained. We suppose that hardly soluble photo-dimers and oligomers were formed due to intermolecular cycloaddition, indicated by additional characteristic resonances in the ¹H NMR spectrum. Evidence to this assumption was further provided by the entire recovery of **13**, if the sample is heated to 220 °C for 1 h.

The cyclomers **8**$_{PC}$, **9**$_{PC}$, **11**$_{PC}$ and **13**$_{PC}$ were further characterized by ¹³C NMR spectroscopy and by (high) resolution mass spectrometry. Their molecular structures in the crystalline state were determined by X-ray diffraction studies and are depicted in Figure 2 (for details see SI). To the best of our knowledge, these structures are the first known examples for substituted 9,10:9′,10′-photo-cyclomers with four functional groups, pointing in the same direction. The structural parameters of all four compounds are well comparable to each other, except for the corresponding linker units.

In contrast to the α,ω-alkandiyl-based bisanthracenes, the irradiation of the SiMe₂-containing bisanthracenes **15** and **16** did not lead to intramolecular photo-cyclomers. ¹H NOESY NMR experiments indicate the formation of intermolecular photo-oligomers by revealing the proximity of the linker protons to those in position 9 of the anthracene dimer units (Figures S22–S25, SI). These results are consistent with previous observations that typically no photo-cyclomers are obtained for bisanthracenes bearing more than four-membered (polymethylene) linker units.[3]

Since compounds **9** and **11** were found to be most suitable for photo-cyclomerization, only these two bisanthracenes were used for further modifications. In order to expand the aromatic systems with rigid alkynyl substituents, **9** and **11** were functionalized in quadruple Kumada cross-coupling reactions with (trimethylsilyl)ethynyl-substituents (Scheme 7). A subsequent cleavage of the trimethylsilyl protecting groups using
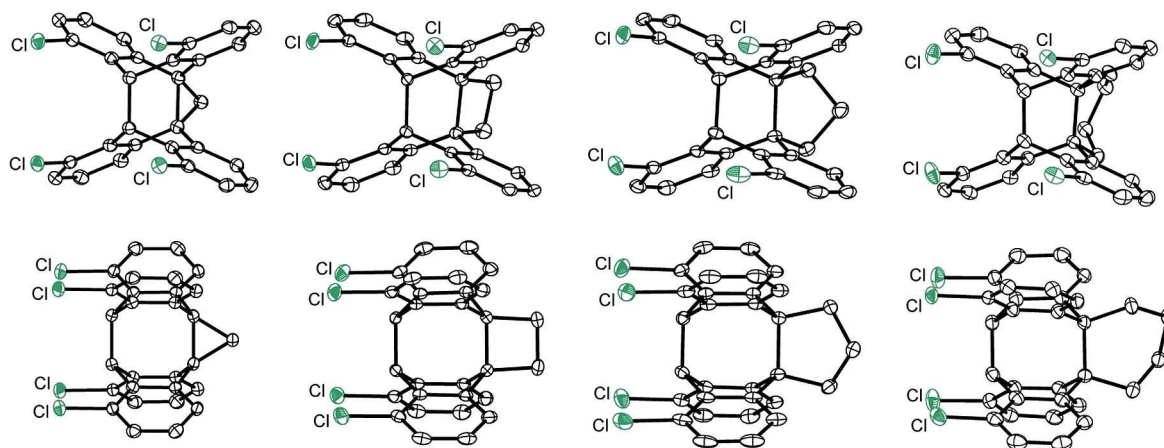

Scheme 5. Syntheses of bis[(1,8-dichloroanthracene-10-yl)ethyl]dimethylsilane (**15**) and 1,2-bis{[3-(1,8-dichloroanthracen-10-yl)propyl]dimethylsilyl}ethane (**16**). For experimental details see SI.

Figure 2. Angled views (above) and side views (below) of the molecular structures of photo-cyclomers 8_{PC}, 9_{PC}, 11_{PC} and 13_{PC} (from left to right) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. The intramolecular distances between the chlorine substituents are found to be 4.6–4.8 Å (shown horizontally) and 3.7–3.9 Å (shown vertically). Selected bond lengths and angles are listed in Table S1 (SI).

potassium carbonate in methanol afforded the ethynyl-substituted derivatives **19** and **20**.

According to a literature protocol by Wrackmeyer et al.[21] the terminal alkynes **19** and **20** were reacted with (dimethylamino)trimethylstannane in amine elimination reactions, to afford the tetrastannanes **21** and **22**, respectively, in quantitative yield. They were characterized by multinuclear NMR spectroscopy, elemental analysis and X-ray diffraction experiments. Their molecular structures are depicted in Figure 3. Both compounds crystallize in stretched configurations. The intramolecular distances between Sn(1) and Sn(2) as well as Sn(3) and Sn(4) range from 5.4 to 6.0 Å. The coordination sphere of the tin atoms is distorted from local threefold symmetry, most significantly demonstrated for compound **22** by the bond angles C(16)—Sn(1)—C(17) [101.6(1)°] and C(17)—Sn(1)—C(19) [117.0(1)°]. Repulsive interactions between the bulky Me₃Sn-groups are indicated by the torsion angles Sn(1)—C(1)—C(5)—Sn

(2) and Sn(3)—C(25)—C(29)—Sn(4) ranging from ±11° to 13° and by a considerable bending of the alkynyl-groups.

Combining the attributes of flexibly linked anthracene backbones and fourfold directed metal-containing substituents, tetrastannanes **21** and **22** were tested as model compounds for photo-switchable acceptor molecules.

Initially, appropriate investigations were carried out for the unsubstituted tetraalkynes **19** and **20** according to the previously described experiments. Due to the more extended π-systems, the UV/VIS-absorption spectra of **19** and **20** (see Figure S30, SI) show bathochromic shifts of about 20 nm for the p absorption bands (340–440 nm), compared to the analogous chloro-substituted derivatives **9** and **11**. The maxima are located at 423 nm for **19** and 420 nm for **20**, which is considerably red-shifted compared to simple 1,8-diethynylanthracene at 405 nm.[20] As for the tetrachlorides **9** and **11**, the products of intramolecular 9,10:9',10'-cycloaddition 19_{PC} and 20_{PC} were obtained upon UV-light induced photo-cyclomerization (Scheme 8). In the case of propane **20**, traces of an unknown
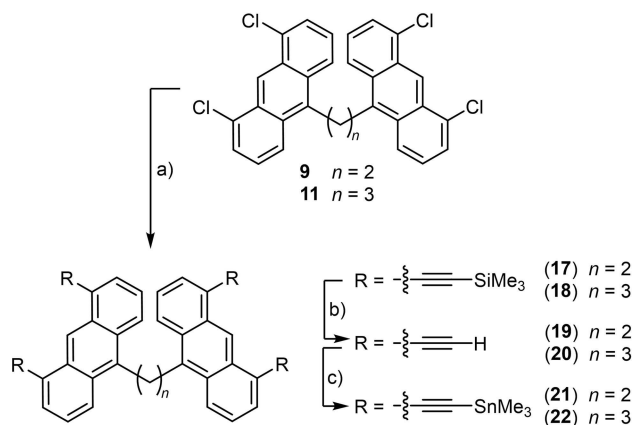
Scheme 7. Syntheses of the bisanthracenylalkanes **17**–**22**. Reagents and conditions: a) Me₃Si–C≡C–MgBr, Ni(acac)₂, PPh₃, THF, reflux, 67% (**17**), 49% (**18**); b) K₂CO₃, MeOH, 16 h, quant. (**19/20**); c) Me₃Sn–NMe₂, THF, 60°C, 2–4 h, quant. (**21/22**).

$n = 2$	$n = 3$	R	$n = 2$	$n = 3$
9	**11**	$-\xi-Cl$	9_{PC}	11_{PC}
19	**20**	$-\xi-{\equiv}-H$	19_{PC}	20_{PC}
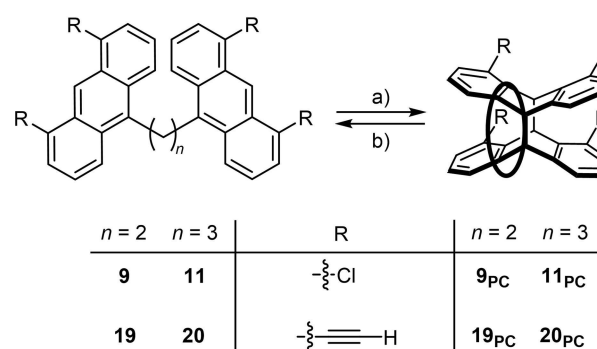
Scheme 8. UV light induced photo-cyclomerization of the bisanthracenylalkanes **9**, **11**, **19** and **20** and thermal cycloreversion: a) CDCl₃, UV light (365 nm); b) 1,2-dichlorobenzene-d₄, 160–220°C.
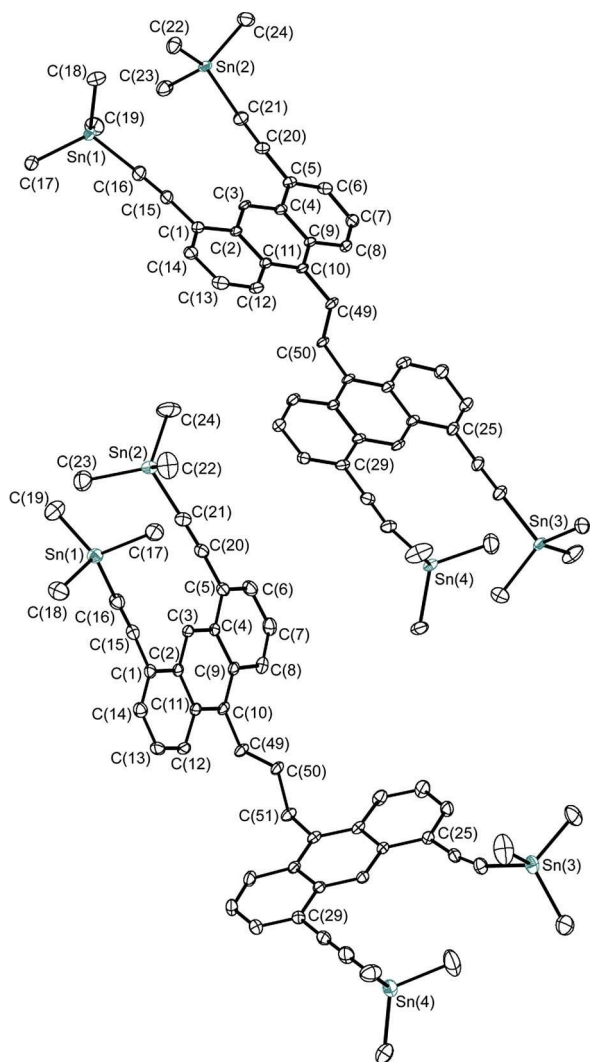
Figure 3. Molecular structures of 1,2-bis{1,8-bis[(trimethylstannyl)ethynyl]anthracen-10-yl}ethane (**21**, above) and 1,3-bis{1,8-bis[(trimethylstannyl)ethynyl]anthracen-10-yl}propane (**22**, below) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **21/22**: C(1)–C(2) 1.447(3)/1.443(3), C(1)–C(15) 1.443(4)/1.439(3), C(2)–C(3) 1.388(3)/1.392(2), C(2)–C(11) 1.442(3)/1.432(2), C(10)–C(11) 1.413(3)/1.415(3), C(10)–C(49) 1.514(3)/1.511(2), C(15)–C(16) 1.205(4)/1.207(3), C(16)–Sn(1) 2.108(3)/2.118(2), C(17)–Sn(1) 2.131(3)/2.136(2), C(49)–C(50) 1.545(3)/1.534(2), C(50)–C(51)–/1.537(3); C(1)–C(2)–C(3) 121.5(2)/120.8(2), C(1)–C(2)–C(11) 118.9(2)/119.5(2), C(1)–C(15)–C(16) 177.0(3)/174.6(2), C(2)–C(3)–C(4) 121.5(2)/121.2(2), C(2)–C(11)–C(10) 119.6(2)/120.0(2), C(10)–C(49)–C(50) 111.7(2)/112.9(2), C(11)–C(10)–C(49) 120.4(2)/118.4(2), C(15)–C(16)–Sn(1) 177.0(3)/165.1(2), C(16)–Sn(1)–C(17) 110.0(1)/101.6(1), C(17)–Sn(1)–C(19) 109.0(1)/117.0(1), C(49)–C(50)–C(51)–/111.3(2).

photo-product (probably an intermolecular formed photo-dimer) were observed in its ^{1}H NMR spectrum.

Aside from NMR spectroscopic investigations, absorption spectroscopy is a well suited tool to monitor the photo-reactions. This was exemplarily performed for bisanthracenylethane **19** (Figure 4). In case of a low concentrated solution (2.5×10^{-5} mol L^{-1}), upon UV irradiation the absorption bands of **19** rapidly decrease. After only four minutes, the maxima at 261 nm (β band) and 423 nm (p band) disappeared
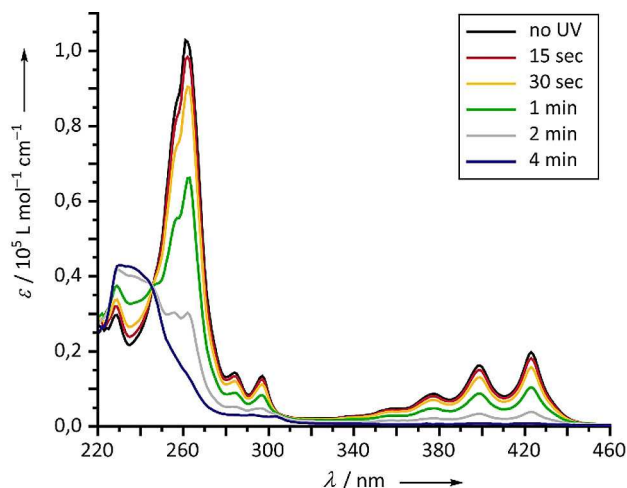

Figure 4. UV/VIS spectrum of bisanthracene **19** (2.5×10^{-5} mol L^{-1}) and the formed photo-cyclomer **19$_{PC}$** as a function of UV irradiation duration.

and a new hypsochromically shifted band arises at about 230–250 nm. These observations result from the loss of the larger anthracene π-system in favor of multiple non-conjugated benzene rings of the cyclomer.

Bergmark and Jones reported the cycloreversion of photo-cyclomers by thermal dissociation.[22] In case of bisanthracenyl-alkanes they used the high boiling 1,2-dichlorobenzene as solvent, since temperatures far above 100 °C are required. In order to reobtain the bisanthracenylethanes and -propanes, analogous experiments concerning the thermal dissociation were performed for cyclomers **9$_{PC}$**, **11$_{PC}$**, **19$_{PC}$** and **20$_{PC}$**, respectively (Scheme 8). An entire reversibility of the cyclomerization, monitored by ^{1}H NMR spectroscopy, could be demonstrated for **9$_{PC}$**, **11$_{PC}$** and **19$_{PC}$** by heating 1,2-dichloro-benzene-d$_4$ solutions up to 160–200 °C (for details see Experimental Section). Compound **20$_{PC}$** could be partially dissociated as well at 220 °C, however, the corresponding isomer **20** was not completely reobtained, even after heating for several days. Instead, the loss in intensity of the signals indicates slow decomposition. In general, lower temperatures (160–180 °C) and faster reaction times are required for the cycloreversion of the ethylene-linked compounds, compared to the analogous propanes (200–220 °C). This might be due to the higher ring strain, caused by the cyclobutane unit. By alternating irradiating and heating the NMR samples of **9/9$_{PC}$**, **11/11$_{PC}$** and **19/19$_{PC}$** under the above mentioned conditions photo-cylomerization and cycloreversion could be repeated several times for these compounds (four cycles could be carried out effortlessly), proving their ability to be used as photo-switches. However, the high temperatures required for ring opening could be a disadvantage for later applications.

The solid state structures of **19** and **20** and their corresponding photo-cyclomers **19$_{PC}$** and **20$_{PC}$** were determined by X-ray diffraction experiments. Exemplarily, those of **20** and **20$_{PC}$** are depicted in Figure 5. Expectedly, the bond angles C(2)–C(3)–C(4) [121.2(2) for **20** and 107.4(1) for **20$_{PC}$**] as well as C(9)–C(10)–C(11) [119.6(2) for **20** and 106.3(1) for **20$_{PC}$**] indicate
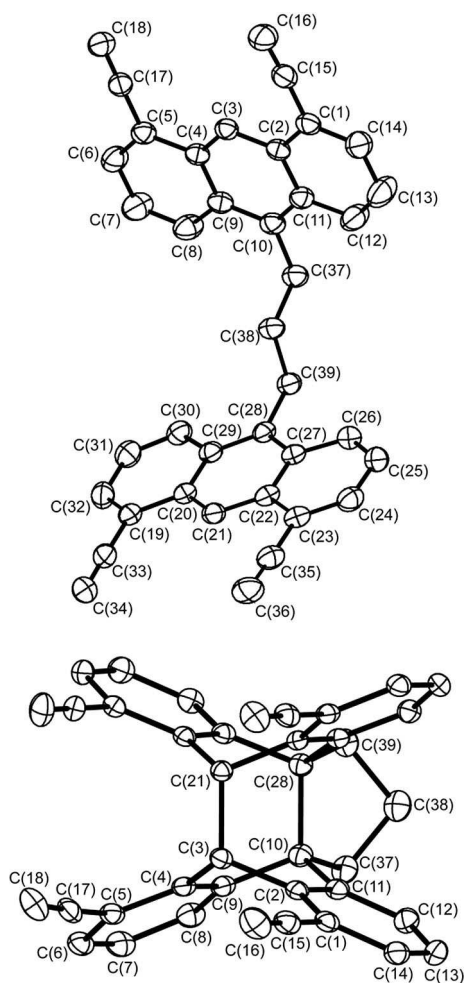
Figure 5. Molecular structures of 1,3-bis(1,8-diethynylanthracen-10-yl) propane (**20**, above) and its 9,10:9',10'-photo-cyclomer **20**$_{PC}$ (below) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms and a half disordered benzene solvent molecule in **20** are omitted for clarity. Selected bond lengths [Å] and angles [°] for **20/20**$_{PC}$: C (1)—C(2) 1.441(3)/1.405(2), C(1)—C(15) 1.436(3)/1.436(2), C(2)—C(3) 1.395(3)/ 1.511(1), C(2)—C(11) 1.438(3)/1.400(2), C(3)—C(21) —/1.606(1), C(10)—C(11) 1.407(3)/1.536(2), C(10)—C(28) —/1.662(2), C(10)—C(37) 1.514(3)/1.545(2), C (15)—C(16) 1.181(3)/1.193(2), C(37)—C(38) 1.536(3)/1.521(2); C(1)—C(2)—C(3) 121.1(2)/122.0(1), C(1)—C(15)—C(16) 177.8(2)/178.7.(1), C(2)—C(3)—C(4) 121.2(2)/107.4(1), C(2)—C(3)—C(21) —/112.8(1), C(2)—C(11)—C(10) 120.0(2)/ 117.4(1), C(9)—C(10)—C(11) 119.6(2)/106.3(1), C(10)—C(37)—C(38) 110.6(2)/ 105.5(1), C(11)—C(10)—C(28) —/110.0(1), C(37)—C(38)—C(39) 114.4(2)/100.1(1).

the change from trigonal planar to tetrahedral geometry at the bridgehead atoms. Furthermore, the bonds C(2)—C(3), C(3)—C(4), C(9)—C(10) and C(10)—C(11) are increased from about 1.4 Å to approximately 1.5 Å. No or only slight differences are found for the outer benzene rings and the ethynyl-functions. As a characteristic for photo-dimers and photo-cyclomers, the new bonds formed by cycloaddition, C(3)—C(21) [1.606(1) Å] and C (10)—C(28) [1.662(2)], are very long compared to the standard C—C single bond with 1.52 Å.[23] They are in the range of very long C—C bonds like those in diamantoid dimers and longer than the central bond in diamantyl-diamantane [solid state, XRD: 1.647(4), gas-phase, GED: 1.630(5) Å].[24]

No cyclomerization reaction takes place in case of the tin-functionalized ethylene derivate **21**. After several hours of UV irradiation, slow decomposition can be observed in the ¹H NMR spectrum. In contrast, the propylene-linked bisanthracene **22** is converted completely into its 9,10:9',10'-photo-cyclomer **22**$_{PC}$ (Scheme 9) under these conditions at very low concentrations.
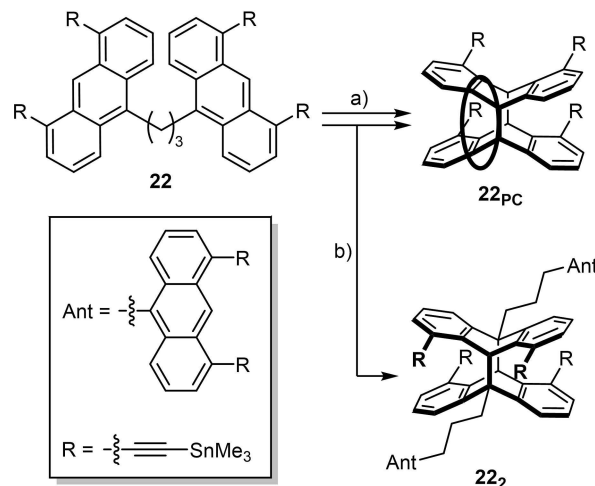
Scheme 9. UV light induced photo-reactions of the bisanthracenylpropane **22**, forming the intramolecular photo-cyclomer **22**$_{PC}$ and the intermolecular photo-dimer **22**$_2$, respectively: a) CDCl₃, UV light (365 nm), high dilution; b) CDCl₃, UV light (365 nm), low dilution.

The *head-to-tail* photo-dimer **22**$_2$ is obtained beside **22**$_{PC}$ if more concentrated solutions of **22** are irradiated. The ratio of both photo-products, depending on the concentration of **22** in different (NMR-)solvents is given in Table 1.

Table 1. Ratio between photo-cyclomer **22**$_{PC}$ and photo-dimer **22**$_2$, formed upon UV irradiation (365 nm) depending on the concentration of the reactant **22** in different solvents.

solvent	[**22**]/10^{-4} mol L⁻¹	**22**$_{PC}$ [%]	**22**$_2$ [%]
CDCl₃	9.7	100	0
o-Cl₂C₆D₄	26.2	100	0
C₆D₆	61.2	73	27
CDCl₃	157.1	63	37
CDCl₃	201.6	53	47

Both compounds can be easily differentiated by means of multinuclear and two-dimensional NMR spectroscopy. Diffusion ordered NMR experiments (DOSY) were performed to determine the diffusion coefficient *D* of the reaction products. *D* correlates inversely to the molecular size.[25–27] The diffusion coefficient of the non-reacted bisanthracene **22** has also been determined and was used as reference (Table 2). The results clearly demonstrate the significantly different molecular sizes of **22**$_{PC}$ and **22**$_2$. While the diffusion coefficients of **22** and of **22**$_{PC}$ indicate similar molecular sizes the diffusion coefficient of **22**$_2$ was found to be considerably smaller as it is expected for a bulkier molecule [see Figure S26 (SI) for a DOSY plot of **22**$_{PC}$ and

Table 2. Diffusion coefficients D [10^{-10} m^{2}s^{-1}] of compounds **22**, **22$_{PC}$** and **22$_2$** in CDCl$_3$ solution, determined by means of DOSY NMR measurements.

	22	22$_{PC}$	22$_2$
D	6.03	6.62	4.42

22$_2$]. The assembly of a photo-polymer, containing more than two monomeric units can be excluded. Thus, the results from ordinary NMR spectroscopy and DOSY NMR studies are in good agreement.

As for the previous bisanthracenes, the thermal dissociation of compound **22$_{PC}$** was attempted. However, no indications for a successful cycloreversion were obtained under the tested conditions. At temperatures higher than 80 °C, **22$_{PC}$** is starting to decompose. Notwithstanding, **22** is rebuild from a mixture of **22$_{PC}$** and **22$_2$** at 160 °C, illustrating that photo-dimer **22$_2$** can be dissociated without any difficulties.

Conclusions

First steps on the way to photo-switchable poly-Lewis acids have been made. In this context, different "anthracene mono-mers", bearing functional groups at the central ring were used to synthesize α,ω-bis(1,8-dichloroanthracen-10-yl)alkanes and some derivatives. UV irradiation experiments were performed for these bisanthracenes, obtaining their corresponding 9,10:9′,10′-photo-cyclomers or intermolecular photo-oligomers, respectively. The ethylene- and propylene-linked derivatives were found to be optimal for photo-cylomerization and thus the modification by replacing the chloro-substituents with rigid ethynyl-groups was performed. The capability as reversible photo-switches was proven by multiple cycles of photo-cylomerization and thermal retro-Diels-Alder cycloreversion. The terminal alkynes were functionalized with trimethylstannyl groups, obtaining quadruply metalated bis-anthracenes. DOSY NMR experiments were used to differentiate between intra-molecular cylomers and intermolecular dimers, proving the shape of the formed photo-products. All in all, the presented results are an important step on the way to generate systems that are capable of reversible guest complexation by photo-switchable poly-Lewis acids.

Experimental Section

General: 1,8-Dichloroanthracene-10-(9*H*)-one (**1**),[14] 1,8-bis[(trime-thylsilyl)ethynyl]-10-methylanthracene (**2b**),[28] bis[(1,8-dichloroan-thracene-10-yl)ethynyl]dimethylsilane (**14b**)[29] and 10-bromo-1,8-dichloroanthracene[17] were synthesized according to literature protocols. For the syntheses of compounds **2**–**7**, **10**, **12**, **15**, **16**, 1,8-bis[(trimethylsilyl)ethynyl]-10-(bromomethyl)anthracene (**2c**), 1,8-di-chloro-10-(prop-1-yn-1-yl)anthracene (**7b**), 10,10′-(prop-1-ene-1,3-diyl)bis(1,8-dichloroanthracene) (**11b**), its photo-cyclomer **11b$_{PC}$** and lepidopterene **17b** see Supporting Information. Methylmagne-sium bromide (3.0 M in Et$_2$O), vinylmagnesium bromide (1.0 M in THF), allylmagnesium bromide (1.0 M in Et$_2$O), ethylmagnesium bromide (3.0 M in Et$_2$O), n-butyllithium (1.6 M in n-hexane; all

purchased from Sigma Aldrich), *N*-bromosuccinimide, copper(I) iodide, nickel(II) acetylacetonate (from Acros Organics), dichloro-dimethylsilane (from Alfa Aesar), phosphorus pentoxide, palla-dium/charcoal activated (10% Pd, oxidic form), AIBN, diisopropyl-amine (from Merck), Karstedt catalyst (2% Pt in xylol, from abcr), bis(triphenylphosphine)-palladium(II)dichloride, 1,2-bis(dimethylsil-yl)ethane, trimethylsilylacetylene, (from Fluorochem) and PPh$_3$ (from Fluka) were used without further purification. First gener-ation Grubbs I catalyst was purchased from Strem Chemicals and hydrogen from Linde. (Dimethylamino)trimethylstannane (from abcr) was used after condensation. All reactions using metal organic reagents, as well as Kumada cross-coupling reactions were carried out under an anhydrous, inert atmosphere of nitrogen using standard Schlenk techniques in dry solvents (THF dried over potassium, Et$_2$O dried over LiAlH$_4$, both freshly distilled before use). All photo-cyclomerization reactions were performed using a UVGL-25 Compact UV Lamp (365 nm, 4 W, 230 V, 0.16 A). The distance between UV lamp and NMR tube/flask was about 1 cm. Column chromatography was performed on silica gel 60 (0.04–0.063 mm). NMR spectra were recorded on a Bruker *Avance III 300*, a Bruker *DRX 500*, a Bruker *Avance III 500*, a Bruker *Avance III 500 HD* and a Bruker *Avance 600* at ambient temperature (298 K). The chemical shifts (δ) were measured in ppm with respect to the solvent [CDCl$_3$: ^{1}H NMR $\delta = 7.26$ ppm, ^{13}C NMR $\delta = 77.16$ ppm; C$_6$D$_6$: ^{1}H NMR $\delta = 7.16$ ppm, ^{13}C NMR $\delta = 128.06$ ppm; o-Cl$_2$C$_6$D$_4$ (from deutero): ^{1}H NMR $\delta = 6.93$ and 7.19 ppm] or referenced externally (^{29}Si: SiMe$_4$, ^{119}Sn: SnMe$_4$). EI mass spectra were recorded using an *Autospec X* magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. MALDI experiments were performed using a Q-IMS-TOF mass spectrometer *Synapt G2Si* (Waters, Manchester, UK) in resolution mode, inter-faced to a MALDI ion source or with an *Ultraflex* MALDI-TOF/TOF mass spectrometer (Bruker Daltonik, Bremen, Germany) operated in reflectron mode (Thermo Scientific TSQ 7000, ThermoFinnigen). No HRMS could be measured for a few compounds e.g. non-isolated photo-cyclomers, or if the intensity of the signal was too low due to fragmentation or H/D exchange of the acid ethynyl protons during the UV irradiation. Elemental analyses were performed with CHNS elemental analyzer HEKAtech EURO EA or by Mikroanalytisches Labor Kolbe (Oberhausen). UV/VIS spectra were recorded on a Thermo Evolution 300 UV-Visible spectro-photometer using Hellma Analytics QX absorption cells with PTFE stopper (10.00 mm, 200–3500 nm). The numbering scheme for NMR assignments of the anthracenes (Scheme 10) is based on IUPAC guidelines.
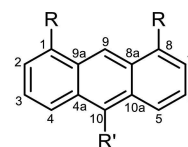
Scheme 10. Numbering scheme for NMR spectroscopic assignments.

Bis(1,8-dichloroanthracen-10-yl)methane (8): A solution of *n*-bu-tyllithium (1.6 M in *n*-hexane, 0.62 mL, 0.99 mmol) was added dropwise to a solution of 10-(bromomethyl)-1,8-dichloroanthracene (**5**, 326 mg, 1.00 mmol) in THF (14 mL) at −78 °C. After stirring for 0.5 hours, a solution of 1,8-dichloroanthracen-10(9*H*)-one (**1**, 315 mg, 1.20 mmol) in THF (24 mL) was added at −78 °C and the mixture was allowed to warm to ambient temperature. After stirring for 16 h and hydrolyzing with an aqueous saturated solution of NH$_4$Cl (30 mL), the aqueous layer was extracted with dichloro-methane (4×20 mL) and the combined organic phases were dried

over MgSO$_4$. The solvent was evaporated and the residue was dissolved in dry toluene (40 mL). P$_2$O$_5$ (two tips of a spatula) was added and the mixture was heated to 80 °C for 3 h. The hot mixture was filtered and the solid was washed with toluene (30 mL). After removing the solvent, the residue was washed with chloroform (3× 10 mL). Air-drying afforded **8** as a yellow solid. Yield: 126 mg (25 %). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 9.40$, (s, 2H, *H9*), 8.14 (d, $^3J_{H,H} = 9.1$ Hz, 4H, *H4/H5*), 7.57 (d, $^3J_{H,H} = 7.2$ Hz, 4H, *H2/H7*), 7.20 (dd, $^3J_{H,H} = 9.1$, 7.2 Hz, 4H, *H3/H6*), 5.97 (s, 2H, Ar*CH$_2$*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): $\delta = 133.8$, 131.6, 129.6, 126.4 (*C3/C6*), 125.9 (*C2/C7*), 123.6 (*C4/C5*), 121.5 (*C9*), 30.2 [solely observable by HMQC (Ar*CH$_2$*)] ppm. One signal missing due to low solubility. MS (MALDI-TOF, positive ions, DCTB): *m/z* [assignment] = 504.0 [M]$^+$, 469.0 [M−Cl]$^+$. HRMS (MALDI-TOF): calculated for C$_{29}$H$_{16}$Cl$_4^+$: 504.00006; measured: 503.9995, dev. [ppm]: 1.11, dev. [mmu]: 0.56.

1,2-Bis(1,8-dichloroanthracen-10-yl)ethane (9): A solution of *n*-butyllithium (1.6 M in *n*-hexane, 0.20 mL, 0.32 mmol) was added dropwise to a solution of 10-(bromomethyl)-1,8-dichloroanthracene (**5**, 224 mg, 0.66 mmol) in THF (18 mL) at −78 °C. After stirring for ten minutes the mixture was allowed to warm to ambient temperature, whereat a yellow solid precipitated. After stirring for 16 h and hydrolyzing with water (5 mL), the suspension was filtered and the residue washed with *n*-pentane and dichloromethane (5 mL each). Air-drying afforded **9** as a yellow solid. Yield: 142 mg (84 %). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 9.29$, (s, 2H, *H9*), 8.00 (d, $^3J_{H,H} = 8.9$ Hz, 4H, *H4/H5*), 7.60 (d, $^3J_{H,H} = 7.1$ Hz, 4H, *H2/H7*), 7.32 (dd, $^3J_{H,H} = 8.9$, 7.1 Hz, 4H, *H3/H6*), 4.07 (s, 4H, *CH$_2$*) ppm. ^{1}H NMR (500 MHz, *o*-Cl$_2$C$_6$D$_4$): $\delta = 9.28$, (s, 2H, *H9*), 8.11 (d, $^3J_{H,H} = 9.0$ Hz, 4H, *H4/H5*), 7.46 (d, $^3J_{H,H} = 7.1$ Hz, 4H, *H2/H7*), 7.28 (dd, $^3J_{H,H} = 8.9$, 7.2 Hz, 4H, *H3/H6*), 3.94 (s, 4H, *CH$_2$*) ppm. Due to the extreme low solubility of the compound, a ^{13}C{^{1}H} NMR spectrum could not be recorded. MS (EI, 70 eV): *m/z* [assignment] = 518.3 [M]$^+$, 259.0 [C$_{15}$H$_9$Cl$_2$]$^+$, 225.0 [C$_{15}$H$_9$Cl]$^+$, 189.0 [C$_{15}$H$_9$]$^+$. HRMS (EI): calculated for C$_{30}$H$_{18}$Cl$_4^+$: 518.01571; measured: 518.01459; dev. [ppm]: 2.16, dev. [mmu]: 1.12.

When the mixture was stirred for several hours at −78 °C before warming to ambient temperature, peritetrachlorolepidopterene **9 b** was formed as the main product. Analytical data of **9 b**: ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.10$, (dd, $^3J_{H,H} = 8.0$ Hz, 4H, *H2/H7*), 6.80 (t, $^3J_{H,H} = 7.9$ Hz, 4H, *H3/H6*), 6.69 (d, $^3J_{H,H} = 7.8$ Hz, 4H, *H4/H5*), 5.82 (t, $^3J_{H,H} = 2.9$ Hz, 2H, *H9*), 2.86 (d, $^3J_{H,H} = 2.9$ Hz, 4H, *CH$_2$*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): $\delta = 145.2$, 139.5, 129.8, 126.6 (*C3/C6*), 126.6 (*C2/C7*), 121.6 (*C4/C5*), 54.5 (*C10*), 37.3 (*C9*), 27.7 (*CH$_2$*) ppm. MS (EI, 70 eV): *m/z* [assignment] = 517.9 [M]$^+$, 258.9 [C$_{15}$H$_9$Cl$_2$]$^+$, 189.0 [C$_{15}$H$_9$]$^+$. Elemental analysis calcd (%) for C$_{30}$H$_{18}$Cl$_4$: C 69.26, H 3.49; found: C 68.84, H 3.67.

1,3-Bis(1,8-dichloroanthracen-10-yl)propane (11): A suspension of 10,10′-(prop-1-yne-1,3-diyl)bis(1,8-dichloroanthracene) (**10**, 250 mg, 0.47 mmol) and Pd/C (50 mg, 10 % Pd, oxidic form) in dichloromethane (50 mL) was stirred under hydrogen atmosphere (starting at $p = 1.6$ bar) at ambient temperature. After each day the pressure was increased by 0.3 bar until 2.2 bar and finally stirred for further 4 h. The mixture was filtered, the residue washed with dichloromethane (5 mL) and the filtrate evaporated. Washing the residue with *n*-pentane (10 mL) afforded **11** as a yellow solid. Yield: 218 mg (87 %). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 9.28$, (s, 2H, *H9*), 8.02 (d, $^3J_{H,H} = 8.9$ Hz, 4H, *H4/H5*), 7.61 (d, $^3J_{H,H} = 7.2$ Hz, 4H, *H2/H7*), 7.35 (dd, $^3J_{H,H} = 8.9$, 7.2 Hz, 4H, *H3/H6*), 3.77 (t, $^3J_{H,H} = 7.9$ Hz, 4H, Ar*CH$_2$*), 2.34 (p, $^3J_{H,H} = 7.9$ Hz, 2H, Ar*CH$_2$CH$_2$*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): $\delta = 135.9$ (*C10*), 133.6, 130.9, 129.4, 125.9 (*C3/C6*), 125.8 (*C2/C7*), 123.5 (*C4/C5*), 120.4 (*C9*), 32.7 (Ar*CH$_2$CH$_2$*), 28.4 (Ar*CH$_2$*) ppm. ^{1}H NMR (500 MHz, *o*-Cl$_2$C$_6$D$_4$): $\delta = 9.25$, (s, 2H, *H9*), 7.99 (d, $^3J_{H,H} = 9.0$ Hz, 4H, *H4/H5*), 7.45 (d, $^3J_{H,H} = 7.1$ Hz, 4H, *H2/H7*), 7.21 (dd, $^3J_{H,H} = 8.9$, 7.3 Hz, 4H, *H3/H6*), 3.69 (t, $^3J_{H,H} = 8.0$ Hz, 4H, Ar*CH$_2$*), 2.21 (p, $^3J_{H,H} = 7.9$ Hz, 2H, Ar*CH$_2$CH$_2$*) ppm. MS (MALDI-TOF, positive ions, DCTB): *m/z*

[assignment] = 532.0 [M]$^+$. HRMS (MALDI-TOF): calculated for C$_{31}$H$_{12}$Cl$_4^+$: 532.03136; measured: 532.0327, dev. [ppm]: 2.52, dev. [mmu]: 1.34. Elemental analysis calcd (%) for C$_{31}$H$_{20}$Cl$_4$: C 69.69, H 3.77; found: C 70.37, H 3.98.

1,4-Bis(1,8-dichloroanthracen-10-yl)butane (13): A suspension of 1,4-Bis(1,8-dichloroanthracene-10-yl)but-2-ene (**12**; 209 mg, 0.38 mmol) and Pd/C (12 mg, 10 % Pd, oxidic form) in dichloromethane (40 mL) was stirred under hydrogen atmosphere ($p = 5.0$ bar) at ambient temperature for one day. After removing the solvent, the residue was treated with boiling toluene (25 mL) and the mixture was filtered. The solid was washed with small amounts of toluene. Cooling the solution to ambient temperature afforded **13** as yellow crystals. Yield: 133 mg (63 %). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 9.28$ (s, 1H, *H9*), 8.16 (d, $^3J_{H,H} = 8.9$ Hz, *H4/H5*), 7.64 (d, $^3J_{H,H} = 7.1$ Hz, *H2/H7*), 7.43 (dd, $^3J_{H,H} = 8.9$, 7.1 Hz, *H3/H6*), 3.65–3.71 (m, 4H, Ar*CH$_2$*), 2.04–2.10 (m, 4H, Ar*CH$_2$CH$_2$*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): $\delta = 136.4$ (*C10*), 133.6, 130.8, 129.5, 125.8 (*C2/C3/C6/C7*), 123.7 (*C4/C5*), 120.3 (*C9*), 31.9 (Ar*CH$_2$CH$_2$*), 28.7 (Ar*CH$_2$*) ppm. ^{1}H NMR (500 MHz, *o*-Cl$_2$C$_6$D$_4$): $\delta = 9.22$ (s, 1H, *H9*), 8.09 (d, $^3J_{H,H} = 8.9$ Hz, *H4/H5*), 7.47 (d, $^3J_{H,H} = 7.0$ Hz, *H2/H7*), 7.20–7.29 (m, *H3/H6*), 3.51–3.64 (m, 4H, Ar*CH$_2$*), 1.98–2.10 (m, 4H, Ar*CH$_2$CH$_2$*) ppm. MS (EI, 70 eV): *m/z* [assignment] = 546.0 [M]$^+$, 259.0 [C$_{15}$H$_9$Cl$_2$]$^+$. HRMS (EI): calculated for C$_{32}$H$_{22}$Cl$_4^+$: 546.04701; measured: 546.04455; dev. [ppm]: 4.51, dev. [mmu]: 2.46. Elemental analysis calcd (%) for C$_{32}$H$_{22}$Cl$_4$: C 70.10, H 4.04; found: C 68.74, H 4.37.

General procedure for Kumada cross-coupling reactions: [(Trimethylsilyl)ethynyl]magnesium bromide was obtained by adding trimethylsilylacetylene to a solution of ethylmagnesium bromide in THF at 0 °C. The mixture was stirred at room temperature for 16 h and gas evolution was observed. The freshly prepared [(trimethylsilyl)ethynyl]magnesium bromide (1 M in THF, ca. 12 eq.) was added to a solution of the bis(1,8-dichloroanthracen-10-yl)alkane, Ni(acac)$_2$ and PPh$_3$ in THF at room temperature. The color of the solution changed from yellow to dark red and the mixture was heated to reflux for several days. After hydrolyzing with a saturated aqueous solution of NH$_4$Cl, the aqueous layer was extracted with dichloromethane for several times. The combined organic phases were dried over MgSO$_4$. The solvent was evaporated and the crude yellow brownish solid was purified by either washing with dichloromethane or column chromatography on silica gel.

1,2-Bis{1,8-bis[(trimethylsilyl)ethynyl]anthracen-10-yl}ethane (17): Synthesis according to the general procedure for Kumada cross-coupling reactions using 1,2-bis(1,8-dichloroanthracen-10-yl)ethane (**9**, 205 mg, 0.39 mmol), PPh$_3$ and Ni(acac)$_2$ (one spatula tip of each compound), reflux for 6 d. Washing the crude product with *n*-pentane/dichloromethane (2:1, 20 mL) and dichloromethane (5 mL) afforded **17** as bright yellow solid. Yield: 201 mg (67 %). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 9.35$, (s, 2H, *H9*), 8.18 (d, $^3J_{H,H} = 9.1$ Hz, 4H, *H4/H5*), 7.77 (d, $^3J_{H,H} = 6.7$ Hz, 4H, *H2/H7*), 7.38 (dd, $^3J_{H,H} = 8.5$, 7.1 Hz, 4H, *H3/H6*), 4.03 (s, 4H, *CH$_2$*), 0.39 (s, 36H, *CH$_3$*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): $\delta = 135.2$ (*C10*), 132.2 (*C2/C7*), 131.2, 129.8, 125.3 (*C4/C5*), 125.2 (*C3/C6*), 123.7 (*C9*), 122.4, 104.0 (C≡CSi), 100.2 (C≡CSi), 29.6 (*CH$_2$*), 0.6 (*CH$_3$*) ppm. Due to the extreme low solubility of the compound, a ^{29}Si{^{1}H} NMR spectrum could not be recorded. MS (MALDI-TOF, positive ions, ABS): *m/z* [assignment] = 766.3 [M]$^+$, 383.2 [C$_{25}$H$_{27}$Si$_2$]$^+$. HRMS (MALDI-TOF): calculated for C$_{50}$H$_{54}$Si$_4^+$: 766.3303; measured: 766.3314, dev. [ppm]: 1.49, dev. [mmu]: 1.14. Elemental analysis calcd (%) for C$_{50}$H$_{54}$Si$_4$: C 78.27, H 7.09; found: C 77.89, H 7.25.

1,3-Bis{1,8-bis[(trimethylsilyl)ethynyl]anthracen-10-yl}propane (18): Synthesis according to the general procedure for Kumada cross-coupling reactions using 1,3-bis(1,8-dichloroanthracen-10-yl)propane (**11**; 218 mg, 0.41 mmol), PPh$_3$ and Ni(acac)$_2$ (one spatula tip of each compound), reflux for 3 d. Column chromatography

[Ø = 3 cm, *l* = 9 cm, eluent: *n*-pentane/dichloromethane (8:1)] afforded **18** as bright yellow solid. R_f = 0.1 [*n*-pentane/dichloromethane (8:1)]. Yield: 154 mg (49%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.33, (s, 2H, *H9*), 8.08 (d, $^3J_{H,H}$ = 8.9 Hz, 4H, *H4/H5*), 7.76 (d, $^3J_{H,H}$ = 6.9 Hz, 4H, *H2/H7*), 7.36 (dd, $^3J_{H,H}$ = 8.9, 6.9 Hz, 4H, *H3/H6*), 3.73 (t, $^3J_{H,H}$ = 7.8 Hz, 4H, ArCH$_2$), 2.31 (p, $^3J_{H,H}$ = 7.8 Hz, 2H, ArCH$_2$CH$_2$), 0.38 (s, 36H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 135.5 (*C10*), 132.2 (*C2/C7*), 131.2, 129.5, 125.4 (*C4/C5*), 125.2 (*C3/C6*), 123.3 (*C9*), 122.3, 104.0 (C≡CSi), 100.1 (C≡CSi), 32.8 (ArCH$_2$CH$_2$), 28.0 (ArCH$_2$), 0.6 (CH$_3$) ppm. ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$): δ = −17.5 ppm. MS (MALDI-TOF, positive ions, DCTB): *m/z* [assignment] = 780.3 [M]$^+$. HRMS (MALDI-TOF): calculated for C$_{51}$H$_{56}$Si$_4^+$: 780.34536; measured: 780.3468, dev. [ppm]: 1.85, dev. [mmu]: 1.44.

1,2-Bis(1,8-diethynylanthracen-10-yl)ethane (19): A suspension of 1,2-bis{1,8-bis[(trimethylsilyl)ethynyl]anthracen-10-yl}ethane (**17**, 171 mg, 0.22 mmol) and K$_2$CO$_3$ (300 mg, 2.17 mmol) in methanol (120 mml) was heated to reflux for 1d. After cooling to ambient temperature, the suspension was filtered. Washing the crude product with methanol (10 mL) and water (10 mL) afforded **19** as yellow solid. Yield: 107 mg (quantitative). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.48, (s, 2H, *H9*), 8.15 (d, $^3J_{H,H}$ = 8.9 Hz, 4H, *H4/H5*), 7.76 (d, $^3J_{H,H}$ = 6.7 Hz, 4H, *H2/H7*), 7.38 (dd, $^3J_{H,H}$ = 8.7, 7.1 Hz, 4H, *H3/H6*), 4.06 (s, 4H, CH$_2$), 3.26 (s, 4H, C≡CH) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 133.1 (*C10*), 131.6, 131.3 (*C2/C7*), 129.8, 125.4 (*C4/C5*), 125.2 (*C3/C6*), 123.5 (*C9*), 121.4, 82.9 (C≡CH), 82.0 (C≡CH), 29.4 (ArCH$_2$) ppm. ^{1}H NMR (500 MHz, *o*-Cl$_2$C$_6$D$_4$): δ = 9.59, (s, 2H, *H9*), 8.23 (d, $^3J_{H,H}$ = 8.9 Hz, 4H, *H4/H5*), 7.68 (d, $^3J_{H,H}$ = 6.8 Hz, 4H, *H2/H7*), 7.34 (dd, $^3J_{H,H}$ = 8.9, 7.0 Hz, 4H, *H3/H6*), 3.95 (s, 4H, CH$_2$), 3.64 (s, 4H, C≡CH) ppm. MS (MALDI-TOF, positive ions, DCTB): *m/z* [assignment] = 478.3 [M]$^+$. HRMS (MALDI-TOF): calculated for C$_{38}$H$_{22}^+$: 478.17160; measured: 478.1715, dev. [ppm]: 0.21, dev. [mmu]: 0.10. Elemental analysis calcd (%) for C$_{38}$H$_{22}$: C 95.37, H 4.63; found: C 89.67, H 4.59. Too low carbon values are known for hydrocarbons with terminal alkynes.

1,3-Bis(1,8-diethynylanthracen-10-yl)propane (20): A suspension of 1,3-bis{1,8-bis[(trimethylsilyl)ethynyl]anthracen-10-yl}propane (**18**, 140 mg, 0.18 mmol) in methanol (100 mL) was temporarily heated to reflux and then cooled to ambient temperature. After addition of K$_2$CO$_3$ (150 mg, 1.09 mmol), the mixture was stirred for 16 h. Evaporation of the solvent and filtration of the crude product over silica gel with dichloromethane afforded **20** as yellow solid. Yield: 88 mg (quantitative). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.46, (s, 2H, *H9*), 8.10 (d, $^3J_{H,H}$ = 9.0 Hz, 4H, *H4/H5*), 7.75 (d, $^3J_{H,H}$ = 6.8 Hz, 4H, *H2/H7*), 7.37 (dd, $^3J_{H,H}$ = 9.0, 6.8 Hz, 4H, *H3/H6*), 3.75 (t, $^3J_{H,H}$ = 7.9 Hz, 4H, ArCH$_2$), 3.61 (s 4H, C≡CH), 2.32 (p, $^3J_{H,H}$ = 7.9 Hz, 2H, ArCH$_2$CH$_2$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 135.6 (*C10*), 131.6, 131.3 (*C2/C7*), 129.5, 125.6 (*C4/C5*), 125.3 (*C3/C6*), 123.2 (*C9*), 121.4, 82.9 (C≡CH), 82.0 (C≡CH), 32.9 (ArCH$_2$CH$_2$), 27.9 (ArCH$_2$) ppm. ^{1}H NMR (500 MHz, *o*-Cl$_2$C$_6$D$_4$): δ = 9.57, (s, 2H, *H9*), 8.07 (d, $^3J_{H,H}$ = 9.0 Hz, 4H, *H4/H5*), 7.67 (d, $^3J_{H,H}$ = 6.7 Hz, 4H, *H2/H7*), 7.26 (dd, $^3J_{H,H}$ = 8.9, 6.9 Hz, 4H, *H3/H6*), 3.69 (t, $^3J_{H,H}$ = 7.9 Hz, 4H, ArCH$_2$), 3.60 (s 4H, C≡CH), 2.19 (p, $^3J_{H,H}$ = 7.9 Hz, 2H, ArCH$_2$CH$_2$) ppm. MS (EI, 70 eV): *m/z* [assignment] = 492.3 [M]$^+$. Elemental analysis calcd (%) for C$_{39}$H$_{24}$: C 95.09, H 4.70; found: C 87.91, H 4.70. Too low carbon values are known for hydrocarbons with terminal alkynes.

General procedure for the syntheses of the trimethylstannyl-substituted compounds 21 and 22: The gas elimination reactions were carried out analogous to a procedure described by Wrackmeyer and co-workers.[20] For that purpose, (dimethylamino)trimethylstannane (ca. 6 eq) was added to a solution of the corresponding tetraalkyne in dry THF. The mixture was heated to 60 °C for 2–4 h. After removing all volatile compounds in *vacuo*, the fourfold (trimethylstannyl)ethynyl-functionalized bisanthracenes were quantitatively obtained as yellow solids.

1,2-Bis{1,8-bis[(trimethylstannyl)ethynyl]anthracen-10-yl}ethane (21): Synthesis according to the general procedure using 1,2-bis(1,8-diethynylanthracen-10-yl)ethane (**19**, 50 mg, 0.10 mmol), (dimethylamino)trimethylstannane (0.1 mL, 0.6 mmol) and THF (5 mL). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.47, (s, 2H, *H9*), 8.18 (d, $^3J_{H,H}$ = 8.9 Hz, 4H, *H4/H5*), 7.75 (d, $^3J_{H,H}$ = 6.8 Hz, 4H, *H2/H7*), 7.38 (dd, $^3J_{H,H}$ = 8.9, 6.8 Hz, 4H, *H3/H6*), 4.02 (s, 4H, CH$_2$), 0.47 (s, 36H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 135.1 (*C10*), 131.7 (*C2/C7*), 131.4, 129.8, 125.3 (*C3/C6*), 124.8 (*C4/C5*), 124.0 (*C9*), 122.9, 107.8 (C≡CSn), 99.5 (C≡CSn), 29.6 (CH$_2$), −6.9 (CH$_3$) ppm. ^{119}Sn{^{1}H} NMR (186 MHz, CDCl$_3$): δ = −63.9 ppm. Elemental analysis calcd (%) for C$_{50}$H$_{54}$Sn$_4$N$_4$: C 53.15, H 4.82; found: C 53.22, H 4.96.

1,3-Bis{1,8-bis[(trimethylstannyl)ethynyl]anthracen-10-yl}propane (22): Synthesis according to the general procedure using 1,3-bis(1,8-diethynylanthracen-10-yl)propane (**20**, 36 mg, 0.07 mmol), (dimethylamino)trimethylstannane (0.07 mL, 0.4 mmol) and THF (5 mL). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.44, (s, 2H, *H9*), 8.06 (d, $^3J_{H,H}$ = 9.0 Hz, 4H, *H4/H5*), 7.73 (d, $^3J_{H,H}$ = 6.8 Hz, 4H, *H2/H7*), 7.34 (dd, $^3J_{H,H}$ = 8.7, 7.2 Hz, 4H, *H3/H6*), 3.73 (t, $^3J_{H,H}$ = 7.8 Hz, 4H, ArCH$_2$), 2.32 (p, $^3J_{H,H}$ = 8.1 Hz, 2H, ArCH$_2$CH$_2$), 0.45 (s, 36H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 135.3 (*C10*), 131.7 (*C2/C7*), 131.3, 129.6, 125.2 (*C3/C6*), 124.9 (*C4/C5*), 123.7 (*C9*), 122.8, 107.8 (C≡CSn), 99.4 (C≡CSn), 32.8 (ArCH$_2$CH$_2$), 28.1 (ArCH$_2$), −7.0 (CH$_3$) ppm. ^{119}Sn{^{1}H} NMR (186 MHz, CDCl$_3$): δ = −64.1 ppm. Elemental analysis calcd (%) for C$_{51}$H$_{56}$Sn$_4$N$_4$: C 53.55, H 4.93; found: C 53.87, H 4.84.

General procedure for photo-cyclomerization reactions: In an NMR tube small amounts (3–5 mg) of the particular bisanthracene were dissolved or suspended in dry and degassed CDCl$_3$ (0.5 mL). The mixtures were irradiated with UV light (365 nm) until no more signals of the reactant could be observed in the ^{1}H NMR spectrum (1–3 h), respectively.

Photo-cyclomer of bis(1,8-dichloroanthracen-10-yl)methane (8$_{PC}$): Synthesis according to the general procedure for photo-cyclomerization reactions. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 6.95, (dd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 4H, *H2/H7*), 6.80 (t, $^3J_{H,H}$ = 7.5 Hz, 4H, *H3/H6*), 6.77 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.5 Hz, 4H, *H4/H5*), 5.98 (s, 2H, *H9*), 2.75 (s, 2H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 133.1, 127.3 (*C3/C6*), 127.0 (*C2/C7*), 122.4 (*C4/C5*), 44.2 (*C9*), 14.3 [solely observable by HMQC, (CH$_2$)] ppm. Three signals missing due to low solubility. MS (MALDI-TOF, positive ions, DCTB): *m/z* [assignment] = 504.0 [M]$^+$. HRMS (MALDI-TOF): calculated for C$_{29}$H$_{16}$Cl$_4^+$: 504.00006; measured: 504.0006, dev. [ppm]: 1.07, dev. [mmu]: 0.54.

Photo-cyclomer of 1,2-bis(1,8-dichloroanthracen-10-yl)ethane (9$_{PC}$): Synthesis according to the general procedure for photo-cyclomerization reactions. For the synthesis of **9$_{PC}$** on a preparative scale see the following protocol: A suspension of 1,2-bis(1,8-dichloroanthracen-10yl)ethane (**9**, 83 mg, 0.16 mmol) in oxygen-free dichloromethane (20 mL) was irradiated with UV light (365 nm) for one day. Removing the solvent afforded **9$_{PC}$** as a colourless solid. Yield: Quantitative. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.03, (d, $^3J_{H,H}$ = 7.7 Hz, 4H, *H4/H5*), 7.00 (d, $^3J_{H,H}$ = 7.7 Hz, 4H, *H2/H7*), 6.88 (t, $^3J_{H,H}$ = 7.7 Hz, 4H, *H3/H6*), 5.99 (s, 2H, *H9*), 3.00 (s, 4H, CH$_2$CH$_2$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ = 145.3, 139.4, 133.5, 127.1 (*C2/C3/C6/C7*), 121.8 (*C4/C5*), 62.6 (*C10*), 44.2 (*C9*), 17.0 (CH$_2$CH$_2$) ppm. ^{1}H NMR (500 MHz, *o*-Cl$_2$C$_6$D$_4$): δ = 6.87, (d, $^3J_{H,H}$ = 7.6 Hz, 4H, *H4/H5*), 6.83 (d, $^3J_{H,H}$ = 7.9 Hz, 4H, *H2/H7*), 6.73 (t, $^3J_{H,H}$ = 7.8 Hz, 4H, *H3/H6*), 6.03 (s, 2H, *H9*), 2.80 (s, 4H, CH$_2$CH$_2$) ppm. MS (EI, 70 eV): *m/z* [assignment] = 518.3 [M]$^+$, 259.2 [C$_{15}$H$_9$Cl$_2$]$^+$. Elemental analysis calcd (%) for C$_{30}$H$_{18}$Cl$_4$: C 69.26, H 3.49; found: C 68.00, H 3.53.

Photo-cyclomer of 1,3-bis(1,8-dichloroanthracen-10-yl)propane (11$_{PC}$): Synthesis according to the general procedure for photo-cyclomerization reactions. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.07 (d, $^3J_{H,H}$ = 7.9 Hz, 4H, *H4/H5*), 7.00 (d, $^3J_{H,H}$ = 7.9 Hz, 4H, *H2/H7*), 6.82 (t,

$^3J_{H,H}=7.9$ Hz, 4H, $H3/H6$), 6.09 (s, 2H, $H9$), 2.70 (t, $^3J_{H,H}=6.1$ Hz, 4H, $CH_2CH_2CH_2$), 2.42 (p, $^3J_{H,H}=6.1$ Hz, 2H, $CH_2CH_2CH_2$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=147.0$, 140.3, 133.2, 127.1 ($C2/C7$), 126.8 ($C3/C6$), 122.6 ($C4/C5$), 64.3 ($C10$), 44.1 ($C9$), 35.3 ($CH_2CH_2CH_2$), 26.9 ($CH_2CH_2CH_2$) ppm. ^1H NMR (500 MHz, $o\text{-}Cl_2C_6D_4$): $\delta=6.90$ (d, $^3J_{H,H}=$ 7.9 Hz, 4H, $H4/H5$), 6.83 (d, $^3J_{H,H}=7.9$ Hz, 4H, $H2/H7$), 6.68 (t, $^3J_{H,H}=$ 7.9 Hz, 4H, $H3/H6$), 6.12 (s, 2H, $H9$), 2.48 (t, $^3J_{H,H}=5.9$ Hz, 4H, $CH_2CH_2CH_2$), 2.23 (p, $^3J_{H,H}=5.9$ Hz, 2H, $CH_2CH_2CH_2$) ppm. MS (MALDI-TOF, positive ions, DCTB): m/z [assignment] = 532.0 [M]$^+$. HRMS (MALDI-TOF): calculated for $C_{31}H_{20}Cl_4^+$: 532.03136; measured: 532.0322, dev. [ppm]: 1.58, dev. [mmu]: 0.84.

Photo-cyclomer of 1,4-bis(1,8-dichloroanthracen-10-yl)butane (13$_{PC}$): Synthesis according to the general procedure for photo-cyclomerization reactions. ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.22$ (d, $^3J_{H,H}=7.9$ Hz, 4H, $H4/H5$), 7.01 (d, $^3J_{H,H}=7.9$ Hz, 4H, $H2/H7$), 6.82 (t, $^3J_{H,H}=7.9$ Hz, 4H, $H3/H6$), 6.13 (s, 2H, $H9$), 2.54–2.60 (m, 4H, ArCH_2), 2.33–2.38 (m, 4H, ArCH$_2CH_2$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=149.0$, 140.8, 133.0, 127.1 ($C2/C7$), 126.7 ($C3/C6$), 123.3 ($C4/C5$) 57.3 ($C10$), 44.5 ($C9$), 29.5 (ArCH_2), 20.8 (ArCH$_2CH_2$) ppm. ^1H NMR (500 MHz, $o\text{-}Cl_2C_6D_4$): $\delta=7.07$ (d, $^3J_{H,H}=8.0$ Hz, 4H, $H4/H5$), 6.84 (d, $^3J_{H,H}=7.7$ Hz, 4H, $H2/H7$), 6.69 (t, $^3J_{H,H}=7.8$ Hz, 4H, $H3/H6$), 6.18 (s, 2H, $H9$), 2.33–2.39 (m, 4H, ArCH_2), 2.16–2.22 (m, 4H, ArCH$_2CH_2$) ppm. MS (EI, 70 eV): m/z [assignment] = 546.0 [M]$^+$, 259.0 [$C_{15}H_9Cl_2$]$^+$.

Photo-cyclomer of 1,2-bis(1,8-diethynylanthracen-10-yl)ethane (19$_{PC}$): Synthesis according to the general procedure for photo-cyclomerization reactions. ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.08$–7.12 (m, 8H, $H2/H4/H5/H7$), 6.89 (t, $^3J_{H,H}=7.7$ Hz, 4H, $H3/H6$), 6.15 (s, 2H, $H9$), 3.31 (s, 4H, C≡CH), 2.99 (s, 4H, CH_2CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=145.1$, 143.7, 130.1 ($C2/C7$), 125.6 ($C3/C6$), 123.7 ($C4/C5$), 121.1, 82.0 (C≡CH), 81.5 (C≡CH), 61.6 ($C10$), 47.1 ($C9$), 16.4 (CH_2CH_2) ppm. ^1H NMR (500 MHz, $o\text{-}Cl_2C_6D_4$): $\delta=6.94$–7.01 (m, 8H, $H2/H4/H5/H7$), 6.77 (t, $^3J_{H,H}=7.7$ Hz, 4H, $H3/H6$), 6.33 (s, 2H, $H9$), 3.40 (s, 4H, C≡CH), 2.83 (s, 4H, CH_2CH_2) ppm. MS (MALDI-TOF, positive ions, DCTB): m/z [assignment] = 478.2 [M]$^+$. HRMS (MALDI-TOF): calculated for $C_{38}H_{22}^+$: 478.1716; measured: 478.1707, dev. [ppm]: 1.88, dev. [mmu]: 0.90.

Monitoring the photo-cyclomerization of **19** to **19$_{PC}$** by UV/VIS spectroscopy was performed by irradiating a solution of **19** in dichloromethane (2.5×10^{-5} mol L^{-1}) in an absorption cell with PTFE stopper (10.00 mm, 200–3500 nm) and recording absorption spectra in defined time intervals (0, 0.25, 0.5, 1, 2 and 4 minutes).

Photo-cyclomer of 1,3-bis(1,8-diethynylanthracen-10-yl)propane (20$_{PC}$): Synthesis according to the general procedure for photo-cyclomerization reactions. ^1H NMR (500 MHz, $CDCl_3$): $\delta=7.13$ (dd, $^3J_{H,H}=7.9$ Hz, $^4J_{H,H}=0.9$ Hz, 4H, $H4/H5$), 7.10 (dd, $^3J_{H,H}=7.7$ Hz, $^4J_{H,H}=$ 0.9 Hz, 4H, $H2/H7$), 6.83 (t, $^3J_{H,H}=7.8$ Hz, 4H, $H3/H6$), 6.27 (s, 2H, $H9$), 3.30 (s, 4H, C≡CH), 2.69 (t, $^3J_{H,H}=6.1$ Hz, 4H, $CH_2CH_2CH_2$), 2.41 (p, $^3J_{H,H}=6.1$ Hz, 2H, $CH_2CH_2CH_2$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=146.0$, 145.4, 130.2 ($C2/C7$), 125.4 ($C3/C6$), 124.5 ($C4/C5$), 120.8, 82.2 (C≡CH), 81.4 (C≡CH), 63.4 ($C10$), 47.2 ($C9$), 34.8 ($CH_2CH_2CH_2$), 26.9 ($CH_2CH_2CH_2$) ppm. ^1H NMR (500 MHz, $o\text{-}Cl_2C_6D_4$): $\delta=6.98$–7.01 (m, 8H, $H2/H4/H5/H7$), 6.72 (t, $^3J_{H,H}=7.8$ Hz, 4H, $H3/H6$), 6.43 (s, 2H, $H9$), 3.41 (s, 4H, C≡CH), 2.49 (t, $^3J_{H,H}=6.0$ Hz, 4H, $CH_2CH_2CH_2$), 2.25 (p, $^3J_{H,H}=6.0$ Hz, 2H, $CH_2CH_2CH_2$) ppm. MS (EI, 70 eV): m/z [assignment] = 492.3 [M]$^+$.

Photo-cyclomer 22$_{PC}$ and Photo-dimer 22$_2$ of 1,3-bis{1,8-bis[(trimethylstannyl)ethynyl]anthracen-10yl}propane: Differently concentrated solutions of 1,3-bis{1,8-bis[(trimethylstannyl)ethynyl]anthracen-10yl}propane (**22**) in dry and degassed $CDCl_3$, benzene-d_6 or 1,2-dichlorobenzene-d_4 were irradiated with UV light (365 nm) until no more signals of the reactant could be observed in the ^1H NMR spectrum, respectively. Depending on the concentration, the

photo-cyclomer **22$_{PC}$** was formed exclusively or in a mixture with the photo-dimer **22$_2$** (see Table 1, main text).

NMR data for photo-cyclomer **22$_{PC}$**: ^1H NMR (500 MHz, $CDCl_3$): $\delta=$ 7.03–7.09, (m, 8H, $H2/H4/H5/H7$), 6.76 (t, $^3J_{H,H}=7.7$ Hz, 4H, $H3/H6$), 6.01 (s, 2H, $H9$), 2.65 (t, $^3J_{H,H}=6.1$ Hz, 4H, $CH_2CH_2CH_2$), 2.39 (p, $^3J_{H,H}=$ 6.1 Hz, 2H, $CH_2CH_2CH_2$), 0.39 (s, 36H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=145.5$, 145.4, 131.8 ($C2/C7$), 124.9 ($C3/C6$), 123.5 ($C4/C5$), 122.6, 109.1 (C≡CSn), 97.3 (C≡CSn), 63.0 ($C10$), 48.2 ($C9$), 35.1 ($CH_2CH_2CH_2$), 27.0 ($CH_2CH_2CH_2$), −6.5 (CH_3) ppm. $^{119}Sn\{^1H\}$ NMR (186 MHz, $CDCl_3$): $\delta=-63.7$ ppm.

NMR data for photo-dimer **22$_2$**: ^1H NMR (500 MHz, $CDCl_3$): $\delta=9.33$ (s, 2H, $H9_a$), 8.21 (d, $^3J_{H,H}=9.0$ Hz, 4H, $H4_a/H5_a$), 7.69 (d, $^3J_{H,H}=6.8$ Hz, 4H, $H2_a/H7_a$), 7.34–7.39 (m, 8H, $H3_a/H6_a/H4_b/H5_b$), 7.02 (d, $^3J_{H,H}=$ 7.7 Hz, 4H, $H2_b/H7_b$), 6.86 (t, $^3J_{H,H}=7.8$ Hz, 4H, $H3_b/H6_b$), 5.43 (s, 2H, $H9_b$), 3.72–3.79 (m, 4H, Ar$_a$CH_2), 3.55–3.62 (m, 4H, Ar$_b$CH_2), 1.65–1.74 (m, 4H, CH_2—CH_2—CH_2), 0.55 (s, 32H, CH_3), 0.42 (s, 32H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta=144.8$, 143.3, 135.5, 131.5 ($C2_a/C7_a$), 131.2, 130.9 ($C2_b/C7_b$), 129.2, 125.1 ($C3_a/C6_a/C4_a/C5_b$), 125.0 ($C3_b/C6_b$), 124.8 ($C4_a/C5_a$), 123.5($C9_a$), 122.8, 122.4, 109.7 (C≡CSn), 107.8 (C≡CSn), 99.2 (C≡CSn), 97.1 (C≡CSn), 58.8 ($C10$), 57.2 ($C9$), 37.5 (Ar$_b$CH_2), 30.2 (Ar$_a$CH_2), 28.1 ($CH_2CH_2CH_2$), −6.8 (CH_3), −7.0 (CH_3) ppm. $^{119}Sn\{^1H\}$ NMR (186 MHz, $CDCl_3$): $\delta=-64.2$, −66.4 ppm.

General procedure for thermal cyclo-reversion reactions: In a Young-NMR tube small amounts (3–5 mg) of the particular photo-cyclomer were dissolved in degassed 1,2-dichlorobenzene-d_4 (0.5 mL). The solutions were heated in a sand bath to different temperatures until the cycloreversion, monitored by ^1H NMR spectroscopy, was completed (**9$_{PC}$**, **11$_{PC}$** and **19$_{PC}$**) or no more progress in the reaction was observed (**20$_{PC}$**). Reaction conditions for **9$_{PC}$**: 1 h at 180 °C or 1 d at 170 °C; **11$_{PC}$**: 3 d at 200 °C; **19$_{PC}$**: 0.5 h at 180 °C or 2 h at 160 °C; **20$_{PC}$**: 1 d at 220 °C (no complete conversion).

In the special case of compound **13$_{PC}$**, the entire cyclo-reversion of this intramolecular species and the additionally obtained intermolecular photoproducts was performed by heating the mixture to 220 °C for 1 h.

Reversibility of the photo-switches: Switching (at least four times) between the open bisanthracenes (**9**, **11**, and **19**) and their closed photo-cyclomers (**9$_{PC}$**, **11$_{PC}$** and **19$_{PC}$**) could be performed by treating NMR samples of these compounds (in 1,2-dichlorobenzene-d_4 0.5 mL) in accordance to the general protocols for photo-cyclomerization and thermal cyclo-reversion reactions, alternately.

Crystal Structure Determination: Suitable crystals of the compounds **2 c**, **3**, **5**, **7**, **9 b**, **11**, **11 b**, **12**, **13**, **15**, **16**, **17**, **17 b**, **19**, **20**, **21**, **22**, **8$_{PC}$**, **9$_{PC}$**, **11$_{PC}$**, **11b$_{PC}$**, **13$_{PC}$**, **19$_{PC}$** and **20$_{PC}$** were obtained by slow evaporation of saturated solutions of chloroform (**2 c**, **5**, **11 b**, **21**, **22**, **9$_{PC}$**, **20$_{PC}$**), n-pentane (**3**, **11b$_{PC}$**), dichloromethane (**7**, **15**), n-pentane/dichloromethane (4:1) mixture (**9 b**), benzene (**11**, **12**, **16**, **17**, **20**, **11$_{PC}$**, **13$_{PC}$**, **19$_{PC}$**), p-xylene (**13**), toluene (**17 b**, **8$_{PC}$**) and 1,2-dichlorobenzene (**19**). They were selected, coated with paratone-N oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a Rigaku SuperNova diffractometer, a SuperNova, Dual, Cu at zero, Atlas diffractometer, a SuperNova, Single Source at Offset, Eos diffractometer, a Nonius KappaCCD diffractometer and a Bruker AXS X8 Prospector Ultra with APEX II diffractometer. Using Olex2[30] the structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX).[31] Crystal and refinement details, as well as CCDC numbers are provided in Tables S2–S4 (SI). CCDC 1872908 (**2**), 1003191 (**3**), 1872909–1872914 (**5**, **7**, **9 b**, **11**, **11 b**, **12**), 1003193 (**13**), 1872915–1872922 (**15**, **16**, **17**, **17 b**, **19**, **20**, **21**, **22**) and 1872923–1872929 (**8$_{PC}$**, **9$_{PC}$**, **11$_{PC}$**, **11b$_{PC}$**, **13$_{PC}$**, **19$_{PC}$**, **20$_{PC}$**) 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.ac.uk/data_request/cif.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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