Reactivity of 3-halopropynols: X-ray crystallographic analysis of 1,1-dihalocumulenes and 2+2 cycloaddition products

Nurbey Gulia, Bartłomiej Pigulski, and Sławomir Szafert*

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland
Email: slawomir.szafert@chem.uni.wroc.pl

Dedicated to Prof. Oleg A. Rakitin on the occasion of his 65th birthday

Received 04-10-2017  Accepted 06-08-2017  Published on line 07-05-2017

Abstract

Reactions of 3-halopropynols and their butadiyne analogues with BF$_3$·Et$_2$O or HX$_{aq}$ were investigated. Depending on the end group and the reaction conditions, different products were obtained which belonged to two classes: (i) 1,1-dihaloallenes, and (ii) products of 2+2 cycloaddition. The resulting species were identified using single crystal X-ray analysis and NMR spectroscopy.

Keywords: Allenes, 1-haloalkynes, 2+2 cycloaddition, heavy atom effect, $^{13}$C NMR, X-ray crystallography
**Introduction**

During the last few decades enormous progress in the chemistry of allenes has been made and compounds of this type are now being used as versatile synthetic precursors in many organic reactions.\(^1\) Moreover, their extended analogues - cumulenes - are attracting a significant interest in scientific circles as model compounds of the linear, allotropic form of carbon - carbyne.\(^2\) Nevertheless, known 1,1-dihalocumulenes remain rare and only the synthesis and reactivity of tetrafluorobutatriene has been widely explored. The compound was first obtained in 1959 by Martin and Sharkey,\(^3\) but an X-ray solid state structure of this extremely unstable compound was determined in 2002.\(^4\) To date, this perfluorinated butatriene was used as a ligand for organometallic iridium\(^5,6\) and rhodium\(^6\) complexes or as dienophile in Diels-Alder reaction.\(^7\) Perchlorinated,\(^8\) perbrominated\(^9\) and periodinated\(^10\) analogues are known but no reactivity studies were performed. 1,1-Dibromo- or 1,1-diiodo-cumulenes have a significant potential as building blocks for more complex, all-carbon scaffolds and may be obtained from 1-halobutadiynes. In our group, we have been conducting continuous studies on the syntheses and reactivity of 1-haloalkynes and 1-halopolyynes\(^11-16\) and we attempted to use them as precursors of 1,1-dihalocumulenes. On the other hand, (2+2) cycloaddition of allenes has been intensively explored for many years.\(^17,18\) Dimerization proceeds through diradical intermediates affording different isomers of 2-dimethylenecyclobutane derivatives.\(^19\) Their subsequent transformations provide complex molecules with broad carbon core diversification.\(^20-22\) Herein, we report on the preparation and characterization of two 1,1-dihaloallenes and some products of their cycloaddition. Because of the complicated molecular structure of these compounds, we focused on X-ray crystallographic methods for structure determination.

**Results and Discussion**

**Synthesis**

Syntheses of 1-haloalkyne precursors started from commercially available alkynols 1 and 2 as shown in Scheme 1. In the first step, halogenations with the use of \(N\)-bromosuccinimide (NBS) or \(N\)-iodosuccinimide (NIS) were performed to yield 1-haloalkynes 3-5.
Scheme 1. Synthesis of 1-haloalkyne precursors.

Next, 1-bromoalkynes 3 and 5 were used for Cadiot-Chodkiewicz cross-coupling with trimethylsilyl acetylene to give butadiynes 6 and 7. Final 1-halobutadiynes 8 and 9 were obtained using NXS/AgNO₃ halogenations.

Our primary synthetic goal was to obtain 1,1-dihaloallenes and 1,1-dihalocumulenes from the 1-haloalkyne precursors 4, 5, 8 and 9. Therefore, their reactions with BF₃·Et₂O (with and without an external source of halogen) and HX(aq) were carried out as shown in Scheme 2. It is known that the reaction of polyynes such as R-(C≡C)n-C(OH)R₂ with BF₃·Et₂O leads to a cationic intermediate. Therefore we hoped that the unstable cationic cumulene can be halogenated by an external source of halogen. Higher cumulenes are highly moisture sensitive and thus we focused on the development of moisture free conditions. In the first thrust, the reaction of 4 with BF₃·Et₂O was performed. As a result we obtained 10 as a main product (19%) but other unknown minor products were also formed. Unfortunately, our attempts to increase the yield of 10 by addition of iodine source (I₂, NaI, NIS, tetrabutylammonium iodide (TBAI)) failed and we decided to switch to ‘wet’ conditions. We used literature procedure and the reaction of 4 with HI(aq) gave 10 in 62% yield. The reaction of 5 with BF₃·Et₂O gave a complex mixture of products. After extensive silica gel chromatography workup we obtained and characterized two major components of this mixture - products of 2+2 cycloaddition 11 and 12. It is noteworthy, that no formation of 13 was observed. The reaction of 5 with HBr(aq) gave expected, pure 13. Unfortunately, the reaction of butadiynes 8 and 9 with BF₃·Et₂O did not occur and only slow decomposition of substrates was observed. The use of HX(aq) caused only much quicker decomposition of substrates.
Scheme 2. Attempts to prepare 1,1-dihaloallenes and 1,1-diahalocumulenes.

We assumed that 11 and 12 might be the result of 2+2 cycloaddition of 5 and 13 formed in situ. Therefore we carried out a reaction of 5 and 13 in pure hexane at 100 °C in a sealed vial as shown in. However, we did not find formation of 11 and/or 12; the main product was the cyclobuta[b]naphthalene 14 in 40% yield. Compound 14 was obtained by dimerization of pure 13 in hexanes solution under the similar condition with only 18%. It is also possible to obtain 14 directly from 5 by Lewis acid mediated dimerization. Therefore, we assume that the precursor of 14 are both compounds that underwent reaction according to the proposed mechanism (Scheme 4).

Scheme 3. The attempted reaction of 13 with 5.
Scheme 4. The proposed mechanism for the formation of 14 from 13 and 5.

We decided to look closer at the $^{13}$C NMR spectra of allenes 10 and 13 (see Figure 1). The chemical shifts of signals of the three allenic carbon atoms of 10 and 13 are given in Table 1. $^{13}$C NMR spectrum of 13 is a standard spectrum of allene with slightly upfield shifted signal of C1 (54.4 ppm). The situation for 10 is different and the carbon signal derived from C1 atom is extremely strongly shifted upfield (-46.4 ppm) which is considerably outside the typical chemical shift range used for $^{13}$C NMR measurements. The examples of 1,1-diiodoallenes are very rare in the literature and the majority of them were obtained in pre-$^{13}$C NMR era. Therefore, it is hard to perform a comparison of the obtained results with the literature data since useful $^{13}$C NMR spectra are available only for perhalobutatrienes. Carbon chemical shifts of allenic part of 10 and 13 are compared in Table 1 with those for butatrienes I$_2$(C=C)$_2$I$_2$ and Br$_2$(C=C)$_2$Br$_2$. The chemical shift of a signal derived from C=Cl$_2$ carbon strongly depends on solvent and in cyclohexanone it is also strongly upfield shifted (-27.5 ppm). The explanation for the very strong shielding may be the heavy atom effect. This phenomenon is observed for instance for an alpha carbon signal in 1-iodoalkynes and also leads to upfield shift of that signal. The strength of that effect intimately depends on Lewis basicity of a solvent. Solvents that are Lewis bases result in less upfield-shifted carbon signal of the C=Cl atom. That may explain the difference between the chemical shift of C=Cl$_2$ atom for 10 (-46.4 ppm in CDCl$_3$) and that for I$_2$C$_4$I$_2$ (-27.5 ppm in cyclohexanone). We suggest that the unusual chemical shift of the signal derived from C1 carbon of 10 is most likely to be due to an extremely strong heavy atom effect.
Figure 1. $^{13}$C NMR spectra of 10 and 13 (CDCl$_3$, 126 MHz, 300 K).

Table 1. Chemical shifts of selected $^{13}$C NMR signals for 10, 13, I$_2$C$_4$I$_2$ and Br$_2$C$_4$Br$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>C1 [ppm]</th>
<th>C2 [ppm]</th>
<th>C3 [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>CDCl$_3$</td>
<td>-46.4</td>
<td>204.3</td>
<td>105.7</td>
</tr>
<tr>
<td>13</td>
<td>CDCl$_3$</td>
<td>54.4</td>
<td>203.7</td>
<td>118.8</td>
</tr>
<tr>
<td>I$_2$C$_4$I$_2$</td>
<td>DMSO-$d_6$</td>
<td>37.7</td>
<td>121.2</td>
<td>-</td>
</tr>
<tr>
<td>I$_2$C$_4$I$_2$</td>
<td>pyridine-$d_5$</td>
<td>-14.9</td>
<td>163.5</td>
<td>-</td>
</tr>
<tr>
<td>I$_2$C$_4$I$_2$</td>
<td>cyclohexanone with cyclohexane-$d_{12}$</td>
<td>-27.5</td>
<td>162.9</td>
<td>-</td>
</tr>
<tr>
<td>Br$_2$C$_4$Br$_2$</td>
<td>DMSO-$d_6$</td>
<td>65.4</td>
<td>153.5</td>
<td>-</td>
</tr>
</tbody>
</table>

X-ray single crystal diffraction

Monocrystals of allenes 10 and 13 were obtained by slow evaporation of their hexane solutions. Compound 10 crystallizes in $P1$ space group, triclinic system with $Z = 4$, whereas 13 crystallizes in $P2_1/n$ space group, monoclinic system with $Z = 8$ (see the Table S1 in the Supplementary Material). In both crystal structures there are two molecules in the asymmetric unit. Molecular structures are shown in Figures 2 and 3.
Figure 2. The molecular structure of 10. Two molecules in the asymmetric unit.

Figure 3. The molecular structure of 13. Two molecules in the asymmetric unit.

Selected bond lengths and angles for 10 and 13 are given in the supplementary material Table S2. Single diffraction X-ray structures of 1,1-dibromo and 1,1-diiodoallenes are rare in the literature and only the structures of tetrabromo and tetraiodobutatrienes are known.\textsuperscript{9-10} For both 10 and 13 C1-C2 double bond (1.276-1.295 Å) are shorter than C2-C3 double bond (1.306-1.339 Å). Analogous bond lengths for tetraiodobutatriene are C1-C2 = 1.316 Å and C2-C3 = 1.225 Å, whereas for tetrabromobutatriene they are C1-C2 = 1.296 and C2-C3 = 1.285 Å. The angles between the plane containing C1, X1 and X2 atoms and the plane containing C3 atom and carbon atoms directly connected with it are nearly 90° and the exact values are 86.4° and 87.9° for 10 and 89.6° and 85.8° for 13. Those values are typical for allenes.

Monocrystals of 11, 12 and 14 were obtained under identical conditions i.e. by slow evaporation of DCM from DCM/hexane solutions (1/1). All three compounds crystallize in monoclinic system in \textit{P}2\textsubscript{1}/\textit{n} (11, 14) and \textit{Cc} (12) space groups (see the Table S1 in the Supplementary Material). The molecular structures of 11, 12 and 14 are shown in Figures 7-9. The interatomic distances and angles within carbon four-membered rings were...
analyzed. In all three structures this part of the molecules is almost ideally planar, however, the distances and angles between carbon atoms in these fragments contain substantial distortions from the ideal four-membered ring. In each structure, the smallest bond angle “lies” at the carbon with the biggest substituent. In 14 (molecule 14B) it is 82.3(2)° for angle C2B-C1B-C4B. Structures 11 and 12 contain similar angle distortion at corresponding atoms (see the Table S3 in the Supplementary Material). The bond length in four-membered rings of 11 and 12 are within the normal range for the corresponding bond types. However, in 14 we observed unusually long C(sp³)-C(sp³) bonds in both molecules (two molecules in the asymmetric unit) which are 1.644(5) and 1.662(5) Å for C2A-C1A and C2B-C1B. Such extremely long C(sp³)-C(sp³) covalent bond may occur in some other cyclobutanaphthalene derivatives.²²,₃¹

**Figure 4.** The molecular structure of 11; the intermolecular halogen bond.

In structures of 11, 12 and 14, van der Waals forces are the predominant intermolecular interactions. Nevertheless, in the structure of 11 halogen bond Br-O of 3.115(2) Å (the sum of vdW radii of Br and O is 3.37 Å, Figure 7) occurs. Additionally, the OH group of 11 remains disengaged in the hydrogen bond. To confirm that we used infrared spectroscopy. The IR spectrum showed the stretching frequency and signal shapes (sharp peak at 3592 cm⁻¹) supporting non-hydrogen-bonded OH groups. The relative position of two molecules of 11 enables the hydrogen O-H···Br bonding after rotation around O1-C18 bond (Figure 7). However, halogen bond better stabilizes the structure in this particular example.

**Figure 5.** The molecular structure of 12.

**Figure 6.** The molecular structure of 14 (two molecules in the asymmetric unit).
Conclusions

Two 1-haloalkynes and two 1-halobutadiynes were investigated as precursors of 1,1-dihaloallenes and 1,1-dihalocumulenes. All new compounds were fully characterized by spectroscopic methods. For 1,1-diodoallene an extremely strong heavy atom effect on the $^{13}$C NMR spectrum was observed. Five products presented in this work were characterized by X-ray crystallography. They belong to two classes: 1,1-dihaloallenes and products of 2+2 cycloaddition of allenes that contain a carbon four-membered ring in their structure.

Experimental Section

General. All reactions were conducted under N$_2$ by using standard Schlenk techniques unless stated otherwise. Glassware was pre-dried at 120 °C. Solvents were treated as follows: THF was distilled from Na/benzophenone, CH$_2$Cl$_2$ and CH$_3$CN were distilled from P$_2$O$_5$, Et$_2$O, AcOH and hexane (pure for analysis) were used as received. AgNO$_3$ (puriss p.a., POCH), AgF (98%, Alfa Aesar), KF (puriss p.a., POCH), NaI (puriss p.a., POCH), I$_2$ (puriss p.a., POCH), NIS (97% Alfa Aesar), NBS (99%, Aldrich), TBAI (98%, Aldrich), HI$_{aq}$ (57%, Fluka), HBr$_{aq}$ (48%, Lancaster), BF$_3$·Et$_2$O (Aldrich), Pd(PPh$_3$)$_2$Cl$_2$ (99.5% Aldrich), CuI (99.999%, Aldrich), trimethylsilylacetylene (98%, Aldrich), NH$_2$Pr$_2$ (99.5%, Aldrich) ethynyltrimethylsilane (98%, Fluorochem) were used as received. Silica gel (0.063-0.200) were used for column chromatography. Syntheses were started from commercially available 1 and 2 and compounds 3, 6, and 7 are known.

$^1$H and $^{13}$C NMR spectra were recorded using a 500 MHz Bruker Avance spectrometer with an inverse broadband probe. For all the $^1$H NMR spectra, the chemical shifts are given in ppm relative to the solvent residual peaks (CDCl$_3$, $^1$H: 7.26 ppm, $^{13}$C: 77.16 ppm). Coupling constants are given in Hz. $^{13}$C NMR spectra were measured with proton decoupling. HRMS spectra were recorded using Bruker MicOTOF-Q spectrometers with ESI ion source and time-of-flight mass analyzer. IR spectra were recorded using a Bruker 66/s FTIR spectrometer. Microanalyses were conducted with an Elementar CHNS Vario EL III analyzer.

X-ray diffraction. X-ray diffraction data were collected with a KUMA KM4 CCD or an Agilent Sapphire diffractometer (ω scan technique). The space groups were determined from systematic absences and Lorentz and polarization corrections were applied. Absorption correction was applied with the use of CrysAlisPro software. The structures were solved by direct methods and refined by full-matrix, least-squares on $F^2$ by use of the SHELXTL Package. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations but were not refined. The position of H-O (11) was found in electron density map then hydrogen was placed and refined (AFIX 147).

Synthetic procedures

9-{Bromoethyl(1)-9H-fluoren-9-ol}$_3$ (3). 9-Ethynyl-9H-fluoren-9-ol (1, 1.083 g, 5.25 mmol) and NBS (1.133 g, 6.30 mmol) were dissolved in 25 mL of acetonitrile. Next, KF (0.305 g, 5.25 mmol) and AgNO$_3$ (0.892 g, 5.25 mmol) were added. The mixture was stirred for 2 h and after this time solvent was removed under reduced pressure. Crude product was purified by elution through short silica gel plug (hexane/Et$_2$O; v/v; 1/1) yielding 1.362 g of yellow solid (4.78 mmol, 75%). IR (cm$^{-1}$, nujol mull) 2211 (C=C), 3524 (OH). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.71 – 7.68 (m, 2H), 7.63 – 7.60 (m, 2H), 7.41 (td, $J$ 7.5, 1.2 Hz, 2H), 7.36 (td, $J$ 7.4, 1.2 Hz, 2H), 2.65 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 146.4, 139.1, 130.0, 128.7, 124.4, 120.4, 80.0, 75.6, 44.4. Elemental analysis: calcd for C$_{15}$H$_9$BrO (285.14): C 63.18, H 3.18. Found: C, 62.97; H, 3.01 %.

9-{Iodoethyl(1)-9H-fluoren-9-ol} (4)
According to the procedure for 3, 9-ethynyl-9H-fluoren-9-ol (1, 0.986 g of, 4.78 mmol), AgNO₃ (0.812 g, 4.78 mmol),KF (0.278 g, 4.78 mmol), NIS (1.330 g, 5.73 mmol), H₂O (172 μl), and acetonitrile (40 mL) were used. Time: 24 h, purification: silica gel plug (hexane/DCM; v/v; 1/2), yield: 0.953 g (2.87 mmol, 60%), yellow solid. 

¹H NMR (500 MHz, CDCl₃) δ 7.70 (ddd, J 7.4, 1.1, 0.7 Hz, 2H), 7.62 (ddd, J 7.5, 1.1, 0.7 Hz, 2H), 7.41 (td, J 7.5, 1.2 Hz, 2H), 7.36 (td, J 7.4, 1.2 Hz, 2H), 2.54 (bs, 1H). 

³C NMR (126 MHz, CDCl₃) δ 146.6, 139.3, 130.0, 128.8, 124.5, 120.4, 94.0, 76.3, 1.5. HRMS(ESI): m/z calcd for C₁₉H₂₀O₄Na: 354.9590 [M+Na]⁺; found: 354.9564.

3-Bromo-1,1-diphenylprop-2-yn-1-ol³⁵ (5). 1,1-Diphenylprop-2-yn-1-ol (2, 1.00 g, 4.80 mmol) was dissolved in acetonitrile (30 mL) with an addition of water (0.220 mL, 12.2 mmol). The flask was wrapped with aluminum foil and NBS (1.04 g, 5.84 mmol), AgNO₃ (0.245 g, 1.44 mmol), and KF (0.167 g, 2.87 mmol) were added. The mixture was stirred for 20 h. After this time solvent was removed on rotary evaporator. Mixture of DCM/hexane (v/v; 1/1) was poured onto greasy residual and this mixture was passed through a short (10 cm) silica gel plug. 5 (1.203 g, 4.19 mmol, yield 87%) was obtained as beige solid. 

¹H NMR (500 MHz, CDCl₃) δ 7.60 – 7.56 (m, 4H), 7.37 – 7.32 (m, 4H), 7.31 – 7.27 (m, 2H), 2.80 (s, 1H). 

³C NMR (126 MHz, CDCl₃) δ 144.5, 128.5, 128.1, 126.2, 82.8, 75.6, 48.4.

9-[(Trimethylsilyl)buta-1,3-diyne-1-yl]-9H-fluoren-9-ol (6). 9-(Bromoethyl)-9H-fluoren-9-ol (3, 0.721 g, 2.53 mmol), Pd(PPh₃)₂Cl₂ (0.036 g, 0.511 mmol), Cul (0.019 g, 0.10 mmol), ethynyltrimethylsilane (0.43 mL, 3.0 mmol) were dissolved in 20 mL of THF. Next NH₄Pr₂ (0.89 mL, 6.3 mmol) was added and the mixture was stirred for 2 h. After this time solvent was removed under reduced pressure and product was purified by silica gel chromatography (hexane/Et₂O; v/v; 1/1) yielding 6 (0.545 g, 1.80 mmol, 71%) as yellow oil. IR (cm⁻¹, nujol mull) 2104 (C≡C), 2222 (C≡C). 

¹H NMR (500 MHz, CDCl₃) δ 7.70 – 7.67 (m, 2H), 7.63 – 7.60 (m, 2H), 7.41 (td, J 7.5, 1.2 Hz, 2H), 7.35 (td, J 7.5, 1.2 Hz, 2H), 2.52 (bs, 1H, OH), 0.16 (s, 9H). 

³C NMR (126 MHz, CDCl₃) δ 146.2, 139.3, 130.1, 128.8, 124.5, 120.5, 88.1, 87.5, 77.5, 75.2, 68.1, -0.4.

1,1-Diphenyl-5-(trimethylsilyl)penta-2,4-diyne-1-ol³⁶ (7). To the solution of 3-bromo-1,1-diphenylprop-2-yn-1-ol (5, 0.627 g, 2.18 mmol) in THF (15 mL) ethynyltrimethylsilane (0.453 mL, 3.27 mmol), Cul (0.021 g, 0.11 mmol), and Pd(PPh₃)₂Cl₂ (0.077 g, 0.11 mmol) were added. Next, NH₄Pr₂ (0.770 mL, 5.49 mmol) was added dropwise and the mixture was stirred for 2 h. Next, the solvent was removed under reduced pressure and the residue was purified by silica gel flash-chromatography (DCM/hexane, 1/1). 7 (0.423 g, 1.39 mmol, 64%) was obtained as beige solid. 

¹H NMR (500 MHz, CDCl₃) δ 7.59 – 7.52 (m, 4H), 7.37 – 7.31 (m, 4H), 7.31 – 7.26 (m, 2H), 2.77 (s, 1H), 0.21 (m, 9H). 

³C NMR (126 MHz, CDCl₃) δ 144.1, 128.6, 128.2, 126.2, 89.5, 87.3, 79.4, 75.1, 72.4, -0.3.

9-(Iodobuta-1,3-diyne-1-yl)-9H-fluoren-9-ol (8). According to the procedure for 3, 9-[(trimethylsilyl)buto-1,3-diyne-1-yl]-9H-fluoren-9-ol (6, 0.210 g, 0.695 mmol), AgF (0.091 g, 0.69 mmol), NIS (0.194 g, 0.836 mmol), H₂O (25 μL, 1.4 mmol), and acetonitrile (20 mL) were used. Time: 16 h, purification: silica gel plug (hexane/Et₂O, 1:1, v/v), yield: 0.236 g (0.663 mmol, 95%), white solid. IR (cm⁻¹, nujol mull) 2221 (C≡C). 

¹H NMR (500 MHz, CDCl₃) δ 7.69 – 7.66 (m, 2H), 7.62 (dd, J 7.3, 0.9 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.35 (td, J 7.5, 1.1 Hz, 2H), 2.51 (s, 1H). 

³C NMR (126 MHz, CDCl₃) δ 146.1, 139.3, 130.2, 128.8, 124.5, 120.5, 78.1, 74.9, 74.7, 68.7, 0.7. HRMS(ESI): m/z calcd for C₁₉H₁₉O₂: 378.9590 [M+Na]⁺; found: 378.9552.

5-Bromo-1,1-diphenylpenta-2,4-diyne-1-ol (9). According to the procedure for 3, 1,1-diphenyl-5-(trimethylsilyl)penta-2,4-diyne-1-ol (7, 0.152 g, 0.500 mmol), AgNO₃ (0.026 g, 0.15 mmol), KF (0.029 g, 0.50 mmol), NBS (0.107 g, 0.601 mmol), H₂O (23 μL, 1.3 mmol), and acetonitrile (10 mL) were used. Time: 20 h, purification: silica gel (hexane/DCM, 1:1, v/v), yield: 0.114 g (0.366 mmol, 73%), beige viscous oil. IR (cm⁻¹, KBr) 3411 (O-H, broad), 2234 (C≡C), 2138 (C≡C), 1490, 1450, 697. 

¹H NMR (500 MHz, CDCl₃) δ 7.57 – 7.53 (m, 4H), 7.37 – 7.32 (m, 4H), 7.31 – 7.27 (m, 2H), 2.77 (s, 1H). 

³C NMR (126 MHz, CDCl₃) δ 144.0, 128.6, 128.3, 126.2,
75.0, 72.4, 64.9, 43.7 (1C is missing). HRMS(ESI): m/z calcd for C_{12}H_{11}BrONa: 332.9885 [M+Na]^+; found: 332.9886.

9-(2,2-Diiodovinylidene)-9H-fluorene (10)

Procedure A: 9-(iodoethenyl)-9H-fluoren-9-ol (4, 0.475 g, 1.43 mmol) was dissolved in 25 mL of THF and the solution was cooled to 0 °C. BF3·Et2O (0.21 mL, 1.70 mmol) was added and the mixture was stirred for 1 h. After this time solvent was removed under reduced pressure and product was purified by elution through short silica gel plug (hexane) yielding 0.120 g (0.271 mmol, 19%) of white solid.

Procedure B: 9-(iodoethenyl)-9H-fluoren-9-ol (4, 0.232 g, 0.699 mmol) was dissolved in 10 mL of AcOH and cooled down to 0 °C. Next HI(aq) (0.74 mL, 57%) in 2 mL of H2O was added dropwise. The mixture was stirred for 2 h at room temperature and the product precipitated as yellow solid. Crude product was filtered off and 48% recovery was obtained as yellow solid. IR (cm⁻¹, KBr) 1927, 1442, 770, 730, 691, 574.

[2-Bromo-3-(dibromomethylene)-4,4-diphenylcyclobut-1-en-1-yl]diphenylmethanol (11) and 2-(Dibromo-methylene)-4-(diphenylmethyleny)-3,3-diphenylcyclobutan-1-one (12). 3-Bromo-1,1-diphenylprop-2-yn-1-ol (5, 0.330 g, 1.15 mmol) was dissolved in dry hexane (10 mL) and BF3·Et2O (0.170 mL, 1.38 mmol) was added in one portion. After 24 h at room temperature hexane was evaporated under reduce pressure and the residue was separated using column chromatography (silica gel, hexane/DCM 50→100%).

(11) (0.033 g, 0.052 mmol, yield 9%) was obtained as yellow solid. Rf = 0.50 (silicagel, hexane/DCM 50%). IR (cm⁻¹, KBr) 3592 (O: 556.9933 [M+H]^+; found: 556.9932.

(12) (0.007 g, 0.013 mmol, yield 2%) was obtained as yellow solid. Rf = 0.36 (silicagel, hexane/DCM 50%). IR (cm⁻¹, KBr) 1725, 1568, 1095, 755, 700, 556. ¹H NMR (500 MHz, CDCl3) δ 7.44 – 7.22 (m, 15H), 7.16 (t, J 7.8 Hz, 1H), 6.97 (t, J 7.8 Hz, 2H), 6.65 (d, J 7.8 Hz, 2H). ¹³C NMR (126 MHz, CDCl3) δ 183.5, 155.6, 150.7, 149.9, 140.4, 138.6, 137.9, 130.0, 129.6, 129.1, 128.5, 128.2, 128.1, 127.9, 127.3, 126.5, 94.6, 67.3. HRMS(ESI): m/z calcd for C_{30}H_{21}BrONa: 658.9014 [M+Na]^+; found: 658.9046.

(3,3-Dibromoprop-1,2-diene-1,1-diyldibenze (13). 3-Bromo-1,1-diphenylprop-2-yn-1-ol (5, 0.574 g, 2.00 mmol) was dissolved in diethyl ether (5 mL) and a mixture of HBr(aq) (48%, 5 mL) and water (5 mL) was added in one portion. Two phase clear solution was mixed vigorously over 2h. Product was extracted with diethyl ether and passed through 10 cm of silica gel with hexane to yield 0.189 g (26%) of white crystalline solid. IR (cm⁻¹, KBr) 1927, 1442, 770, 730, 691, 574. ¹H NMR (500 MHz, CDCl3) δ 7.46 – 7.36 (m, 10H). ¹³C NMR (126 MHz, CDCl3) δ 203.7, 133.7, 129.8, 129.5, 128.9, 118.8, 54.4.

1,1,3-Tribromo-2,2,8-triphenyl-1,2-dihydrocyclobuta[b]naphthalene (14). (3,3-Dibromoprop-1,2-diene-1,1-diyldibenze (13, 0.020 g, 0.057 mmol), 3-bromo-1,1-diphenylprop-2-yn-1-ol (5, 0.016 g, 0.056 mmol) and dry hexane (2 mL) were sealed in a screw cap vial and stirred at 100 °C for 24 h. 14 was isolated by chromatography (silica gel, hexane/DCM 5→30%), Rf = 0.30 (silicagel, hexane/DCM 20%). Yield 0.014 g (40%). ¹H NMR (500 MHz, CDCl3) δ 8.42 (d, J 8.5 Hz, 1H), 7.82 (d, J 8.5 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.59 – 7.51 (m, 4H), 7.50 – 7.44 (m, 4H), 7.41 – 7.34 (m, 6H). ¹³C NMR (126 MHz, CDCl3) δ 144.0, 140.6, 139.0, 135.7, 135.1, 135.0, 133.7, 130.7, 130.5, 128.6, 128.4, 128.1, 128.1, 127.7 (2C), 127.3, 127.1, 116.2, 67.1, 29.9.
Acknowledgements

The authors thank the National Science Centre Poland (Grants UMO-2015/19/B/ST5/02917) and Foundation for Polish Science (START scholarship) for support of this research.

Supplementary Material

For full details, including copies of $^1$H, $^{13}$C and NMR spectra and X-ray crystallography details, see the Supporting Information. CCDC 1540598(10), 1540596(11), 1540595(12), 1540599(13) and 1540597 (14) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

References

   [https://doi.org/10.1002/chem.201502737](https://doi.org/10.1002/chem.201502737)

   [https://doi.org/10.1021/acs.joc.6b02685](https://doi.org/10.1021/acs.joc.6b02685)

   [https://doi.org/10.1039/B913749A](https://doi.org/10.1039/B913749A)

   [https://doi.org/10.1002/chem.201002366](https://doi.org/10.1002/chem.201002366)

   [https://doi.org/10.1021/jo302176k](https://doi.org/10.1021/jo302176k)

   [https://doi.org/10.1021/ol049967o](https://doi.org/10.1021/ol049967o)

   [https://doi.org/10.1002/ejoc.200600905](https://doi.org/10.1002/ejoc.200600905)

   [https://doi.org/10.1021/ja981927q](https://doi.org/10.1021/ja981927q)

   [https://doi.org/10.1016/S0022-328X(00)00201-1](https://doi.org/10.1016/S0022-328X(00)00201-1)

   [https://doi.org/10.1002/anie.201309355](https://doi.org/10.1002/anie.201309355)

   [https://doi.org/10.1016/S0040-4020(68)80131-9](https://doi.org/10.1016/S0040-4020(68)80131-9)

   [https://doi.org/10.1021/ja102848z](https://doi.org/10.1021/ja102848z)

   [https://doi.org/10.1021/jo015882e](https://doi.org/10.1021/jo015882e)

   [https://doi.org/10.1016/0040-4020(68)80131-9](https://doi.org/10.1016/0040-4020(68)80131-9)

   [https://doi.org/10.1021/ja016290g](https://doi.org/10.1021/ja016290g)

   [https://doi.org/10.1002/anie.199700481](https://doi.org/10.1002/anie.199700481)


   [https://doi.org/10.1107/S0108767307043930](https://doi.org/10.1107/S0108767307043930)


   https://doi.org/10.1039/c39790000840