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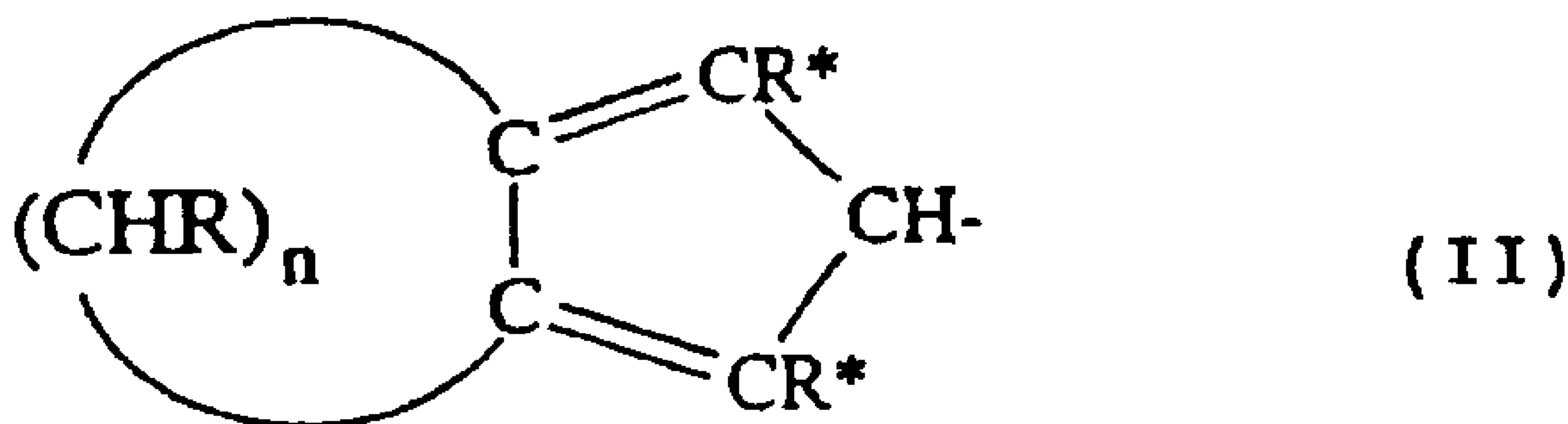
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(54) Title: BRIDGED CYCLOPENTADIENYL DERIVATIVES AND PROCESS FOR THEIR PREPARATION



(57) **Abrégé/Abstract:**

Bridged cyclopentadienyl derivatives having general formula (I) A-X-B (I) wherein: 1) A is a monofunctional hydrocarbyl radical having general formula (II) (see formula II) 2) -X- is the bridge between A and B and consists of a bifunctional radical selected from an alkylene group, a silanylene group, an alkyl substituted silaalkylene group, a siloxasilanylene group; 3) B is a monofunctional hydrocarbyl radical selected from: e) any of the A radicals defined above, f) a cyclopentadienyl radical, the bridged cyclopentadienyl derivatives being used as soluble catalysts for the homo- and co-polymerization of α -olefins.

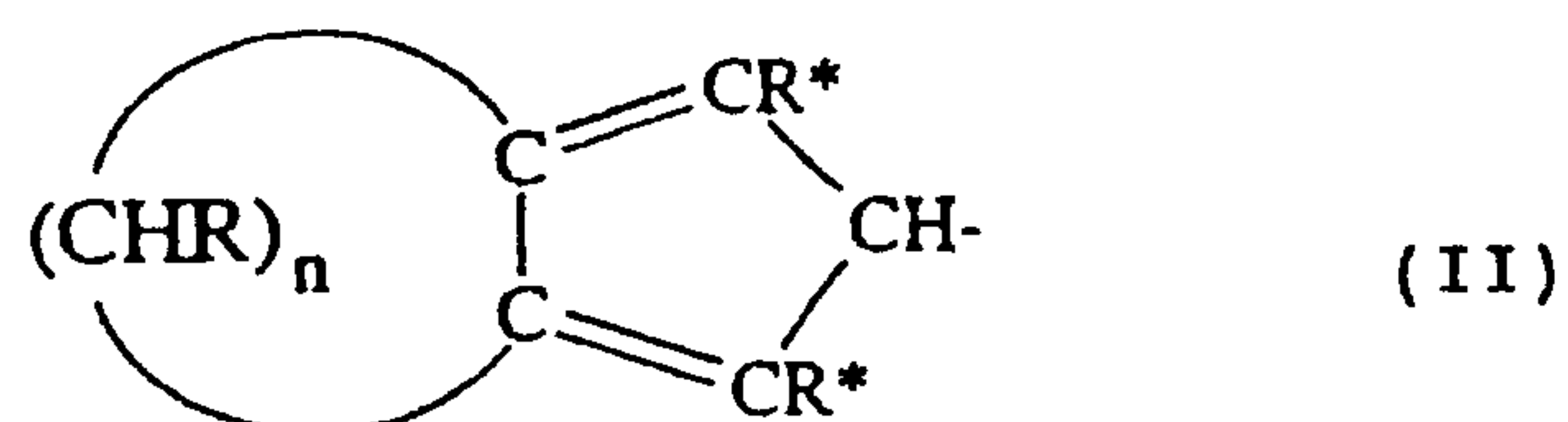
ABSTRACT

Bridged cyclopentadienyl derivatives having general formula (I)



wherein:

- 1) A is a monofunctional hydrocarbyl radical having general formula (II)



- 2) -X- is the bridge between A and B and consists of a bifunctional radical selected from an alkylene group, a silanylene group, an alkyl substituted silaalkylene group, a siloxasilanylene group;
- 3) B is a monofunctional hydrocarbyl radical selected from:
- e) any of the A radicals defined above,
 - f) a cyclopentadienyl radical,

the bridged cyclopentadienyl derivatives being used as soluble catalysts for the homo- and co-polymerization of α -olefins.

BRIDGED CYCLOPENTADIENYL DERIVATIVES AND PROCESS
FOR THEIR PREPARATION

The present invention relates to new bridged compounds of the cyclopentadienyl type and the process for their preparation.

It is known that the most useful soluble catalysts for the homo- and copolymerization of alpha-olefins consist of complexes of zirconium or titanium having ligands of the bis-indenyl, bis-fluorenyl type, or mixed, such as fluorenyl cyclopentadienyl ligands (P.C. Mohring, N.J. Coville, J. Organomet. Chem. 479, 1, 1994).

The ligands can be bridged or non-bridged. The best results, particularly in terms of high molecular weights, are obtained with bridged ligands (see J.C.W. Chien and D. He, Journal of Polymer Science, Part A: Polymer Chemistry, Vol. 29 (1991), page 1585).

Tetrahydroindenyl derivatives are more efficient than the corresponding unsaturated derivatives, particularly in the incorporation of co- and ter-monomers, and are therefore at present

among the most widely selected catalysts.

There is the problem, however, that whereas ligands of the indenyl and fluorenyl type are easily available, the corresponding 5 tetrahydroindenyl derivatives are obtained by the direct hydrogenation of the zirconium complex as it is difficult to chemoselectively hydrogenate the starting ligands.

The hydrogenation process of the complex with 10 zirconium has various disadvantages. In fact, as indicated by several experts (see E. Samuel, Bull. Soc. Chim. Fr, 3548, 1966 and S. Collins et al. in J. Organometallic Chem., 342, 21, 1988) there are difficulties in carrying out this hydrogenation due 15 to low yields and/or drastic conditions. In addition, the hydrogenation process of indenyl complexes of zirconium produces two identical ligands of the tetrahydroindenyl type; in fact it is not possible to obtain with this method 20 asymmetrical complexes having one tetrahydroindenyl and one indenyl ligand.

New bridged cyclopentadienyl derivatives have now been found which overcome the disadvantages mentioned above owing to the fact that, as a result 25 of their structure, they do not necessitate the

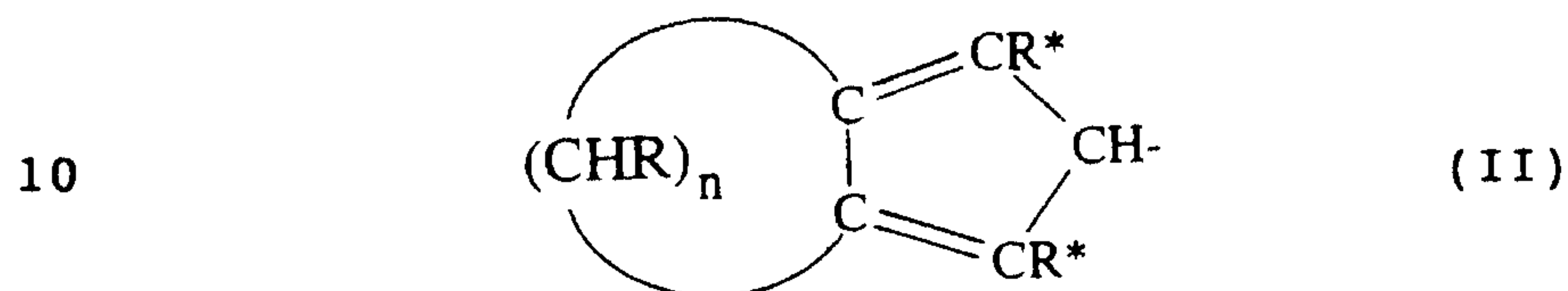
above hydrogenation step.

In accordance with this, the present invention relates to bridged derivatives of cyclopentadienyl having general formula (I)



wherein

1) A is a monofunctional hydrocarbyl radical having general formula (II)



wherein R and R' are selected from:

-- H,

-- monofunctional alkyl radicals having from 1 to 3

15 carbon atoms,

-- monofunctional alkylaryl or aryl radicals, with

the proviso that:

-- the number of R different from H is not more than 2;

20 -- at least one R' is H;

preferably all the R = H and R' is selected from H and CH₃;

2) n is an integer from 2 to 20, and is preferably selected from 3, 4, 5, 6, 10;

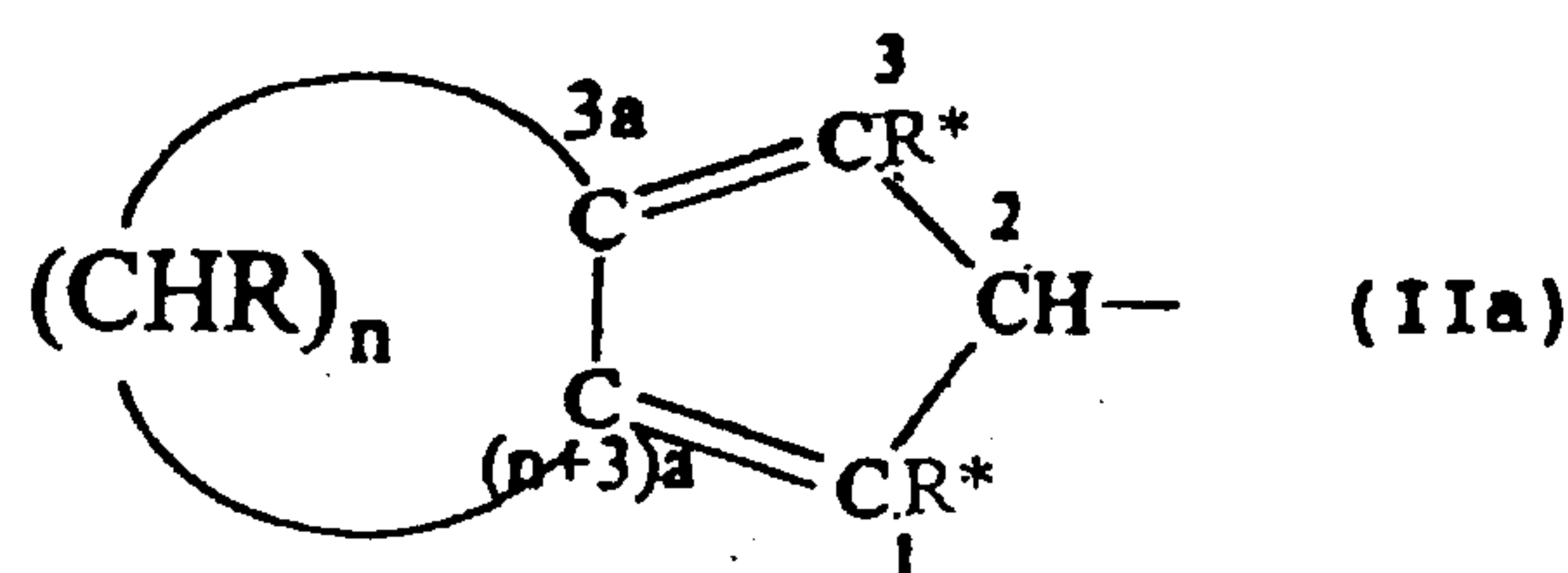
25 3) -X- is the bridge between A and B and consists

of a bifunctional radical selected from:

- a) a linear, branched or cyclic C₂-C₂₀ alkylene group;
 - b) an alkyl or aryl substituted silanylene group having from 1 to 2 silicon atoms;
 - c) an alkyl substituted silalkylene group;
 - d) a siloxasilanylene group or -Si(R₁)₂-O-Si(R₂)₂- tetraalkyl or tetraaryl substituted;
- 4) B is a monofunctional hydrocarbyl radical selected from:
- e) any of the A radicals defined above;
 - 10 f) a cyclopentadienyl radical.

The groups A are monofunctional cyclopentadienyl radicals whose corresponding hydrocarbons, in short hereinafter called AH, are described in copending European patent application EP-A-0 760 355.

Typical examples of the hydrocarbons AH, having both R* = H, are indicated in Table 1. The names of the above hydrocarbons were obtained using the Autonom program of the Beilstein Institute - Beilstein Information System and the number of carbon atoms is the same as in formula (IIa):



In an embodiment, the hydrocarbons AH, and therefore the corresponding monofunctional hydrocarbyl radicals A, are selected from:

- 2,4,5,6,7,8-hexahydroazulene ($R'=R=H$ and $n=5$),
- 5 - 4,5,6,7,8,9-hexahydro-2H-cyclopentacyclooctene ($R'=R=H$ and $n=6$),
- 4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene ($R'=R=H$ and $n=10$),
- 1-methyl-4,5,6,7,8,9,10,11,12,13-decahydro-2H-
10 cyclopentacyclododecene ($R'=CH_3$, $R=H$, $n=10$).

In one embodiment, -X- is a linear, branched or cyclic alkylene radical, having from 2 to 20 carbon atoms. Typical examples of linear -X- are ethylene, propylene, butylene, pentylene, hexylene.
15 Typical examples of branched -X- are isopropylidene (CH_3-C-CH_3), isobutylidene ($CH_3-C-C_2H_5$), 3-pentylene ($C_2H_5-C-C_2H_5$), diphenylmethylen ($C_6H_5-C-C_6H_5$). Typical examples of cyclic alkylene -X- radical are cyclobutylene, cyclopentylene, cyclohexylene.

20 In another embodiment -X- is an alkyl or aryl substituted silanylene group having from 1 to 2 silicon atoms, for example dimethylsilanylene, or -Si(CH₃)₂-, diethyl silanylene, tetramethyl disilylanylene, or -Si(CH₃)₂-Si(CH₃)₂-, dimethyl
25 diethyl disilanylene, preferably

dimethylsilanylene.

In another form of embodiment, the -X- group consists of Silicon-Carbon sequences, i.e. an alkyl substituted silaalkylene group, for example,

5 -Si(R')₂-C(R'')₂-, wherein R' is a low alkyl and R'' is hydrogen or a low alkyl. Typical examples of silaalkylene groups are:

-- 1-sila-1,1-dimethylethylene,

-- 2-sila-2,2-dimethylpropylene,

10 -- 1,3-disila-1,1,3,3-tetramethylpropylene.

In another embodiment the X group is a tetraalkyl or tetraaryl substituted

siloxasilanylene, i.e. -Si(R₁)₂-O-Si(R₂)₂,

wherein R₁ and R₂, the same or different, can be

15 alkyl or aryl radicals.

In the preferred embodiment -X- is selected from linear or branched alkylene derivatives and dialkylsilanylenes, even more preferably it is selected from ethylene, isopropylidene and
20 dimethylsilanylene.

As far as B is concerned, this is a monofunctional hydrocarbyl radical selected from:

(e) any of the A radicals defined above,

(f) a cyclopentadienyl radical.

25 When B is equal to any of the A derivatives

defined above, the product having general formula (I) will consist of two cyclopentadienyl A derivatives, the same or different, joined to each other in position 2 from the bridge -X-.

5 We will call these structures A-X-A', wherein A and A', the same or different, both have general formula (II), with the specification that, in the bridged product A-X-A', the double bonds of the cyclopentadienyl ring can be situated in positions
10 3,3a- and 1,(n+3)a- or in positions 1,2- and 3a,(n+3)a-, where n has the meaning defined above and the numbering of the positions, represented in general formula (IIa) is obtained from the Autonom program mentioned above.

15 Typical examples of A-X-A' structures, wherein A' is the same or different from A, are indicated in tables 2a, 2b, 2c, 2d.

When B does not belong to the hydrocarbyl radicals having general formula (II), B is a
20 monofunctional cyclopentadienyl radical (f) selected from cyclopentadienyl, indenyl, fluorenyl and the relative alkyl, aryl, trialkylsilyl substituted derivatives; (f) is preferably selected from cyclopentadienyl, indenyl and fluorenyl. For
25 the sake of simplicity we shall call these

compounds A-X-C.

It should be noted that, as specified above for the A-X-A' products, in the bridged product A-X-C, the double bonds of the cyclopentadienyl 5 ring of the hydrocarbyl radical A can be situated in positions 3,3a- and 1,(n+3)a- or 1,2- and 3a,(n+3)a- where n has the meaning defined above and the numbering of the positions, represented in general formula IIa, is obtained from the Autonom 10 program mentioned above. We shall call the hydrocarbons corresponding to the monofunctional cyclopentadienyl radicals (f) FH.

The joining point to the bridge -X- of the above cyclopentadienyl derivatives (f) is that 15 which is usually obtained in the known art. For example, indene will be linked to the bridge -X- in position 1 and fluorene in the only non-condensed position of the 5-term cycle.

Tables 3a-3d provide examples of structures of 20 the type A-X-C, wherein C is any of the monofunctional cyclopentadienyl radicals (f).

A further object of the present invention relates to a process for the preparation of the compounds having general formula (I) wherein -X- is 25 selected from branched or cyclic alkylene

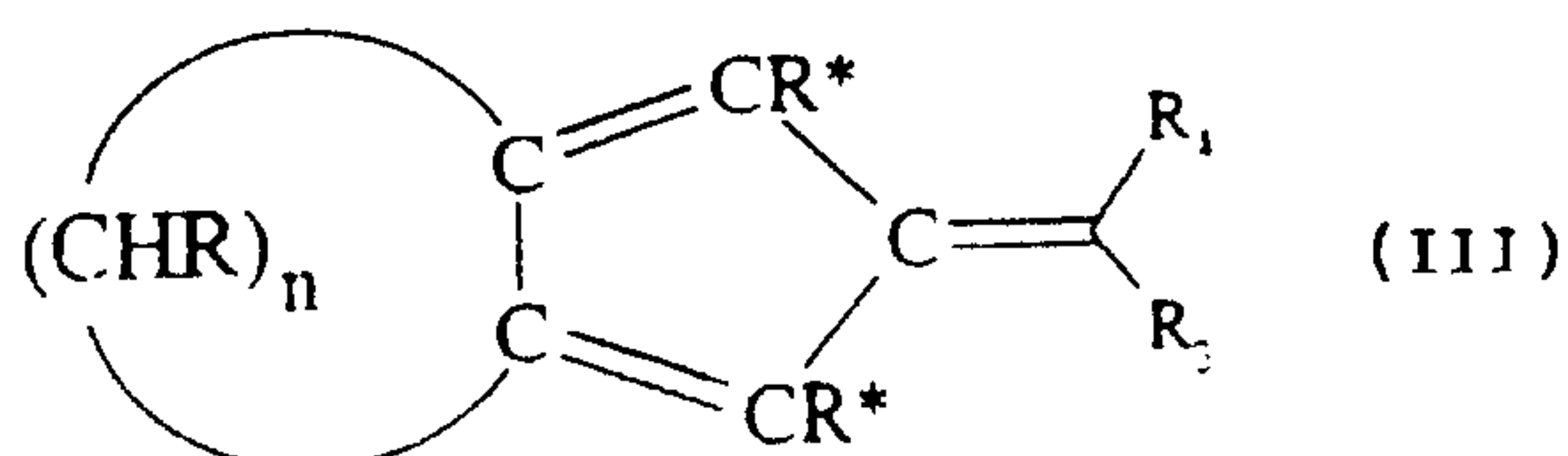
derivatives and from dialkyl substituted silanylenes.

The above compounds are prepared starting from the hydrocarbons A-H as defined above (i.e. from 5 hydrocarbons corresponding to the radicals A having general formula IIa) and with a process which varies according to the structure of -X-.

When -X- is a difunctional derivative of the type R_3-C-R_4 , wherein R_3 and R_4 are selected from 10 monofunctional C_1-C_5 alkyl radicals, phenyl, or R_3 and R_4 jointly form a C_4-C_5 alkylene radical, the reaction takes place in two steps.

In accordance with this the present invention relates to a process for the preparation of the 15 compounds having general formula A-X-B, wherein A and B have the meaning defined above and -X- is a radical of the type R_3-C-R_4 , wherein R_3 and R_4 have the above meaning, which involves the following steps:

20 i) Condensation between the compound having the general formula A-H defined above and a ketone having the general formula R_3-CO-R_4 to give the fulvene compound having general formula (III):



ii) Addition to the fulvene compound obtained in step (i) of the hydrocarbon BH, the above hydrocarbon BH being selected from any of the hydrocarbons AH and FH defined above.

5 Step (i) of the above reaction takes place in a basic environment, preferably with an alcoholate of a tertiary alcohol, even more preferably with potassium *tert*-butylate.

Step (ii) of the above process is preferably
10 carried out by preparing the anion of the hydrocarbon BH and subsequently interacting the above anion with the product (III) obtained in step (i).

It should be noted that the process described
15 above enables the preparation of compounds in which -X- forms a bridge between the radical A always in position 2 and the cyclopentadienyl radical B in the position specified by the known art.

A further object of the present invention
20 relates to intermediates, of the fulvene type, having general formula (III), wherein n , R , R' , R_3 and R_4 have the meaning defined above; preferably $R=H$, R' is selected from H and CH_3 , $R_3=R_4=CH_3$ or C_6H_5 , n is selected from 3,4,5,6,10.

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Another object of the present invention relates to a process for obtaining the compounds having general formula $Al-X-Al$ wherein X is a dialkylsilanylene and the Al radicals, the same as each other, are selected from the A radicals defined above, which comprises the reaction of the hydrocarbon AlH with a dialkyl dihalogen silane, preferably a dialkyl dichlorosilane, in a molar ratio AlH /dialkyl dihalogen silane of about 2/1.

10 In a preferred embodiment, the process is carried out by preparing the anion of the hydrocarbon AlH , preferably with an alkyl lithium, and interacting the anion thus prepared with the dihalogen silane.

15 A further object of the present invention relates to a process for obtaining the compounds having general formula $Al-X-B$ wherein:

-X- is a dialkylsilanylene;

Al is a monofunctional hydrocarbyl radical
20 selected from the A radicals defined above;

B is selected from:

-- A_2 , where A_2 is any of the A radicals defined above provided it is different from Al ,

-- a cyclopentadienyl radical (f),

25 the above process being carried out in two steps,

the first of which (step a) comprising the reaction of the compound AlH with a dialkyl dihalogen silane, preferably a dialkyl dichlorosilane, in a molar ratio AlH/dialkyl dihalogen silane of about 5 1/1; the second step comprising the reaction of the compound obtained in step (a) with a hydrocarbon BH in an essentially equimolar ratio with respect to the product obtained in step (a).

In the preferred embodiment, the process is 10 carried out by preparing the anion of the hydrocarbon AlH, preferably with alkyllithium, and subsequently reacting, in the first step, the above anion with the dihalogen silane, in a molar ratio essentially consisting of 1/1. In the second step 15 the anion of the hydrocarbon BH is prepared, preferably with an alkyllithium, and the above anion is reacted with the compound obtained in the first step, in a molar ratio of about 1/1.

The following examples provide a better 20 illustration of the present invention.

EXAMPLE 1 - Synthesis of bis(2,4,5,6,7,8-hexahydroazulen-2-yl)dimethylsilane

12 ml of a solution of n-butyllithium 2.5 M in hexane are added, at room temperature, to a 25 solution in 100 ml of THF containing 4.1 grams

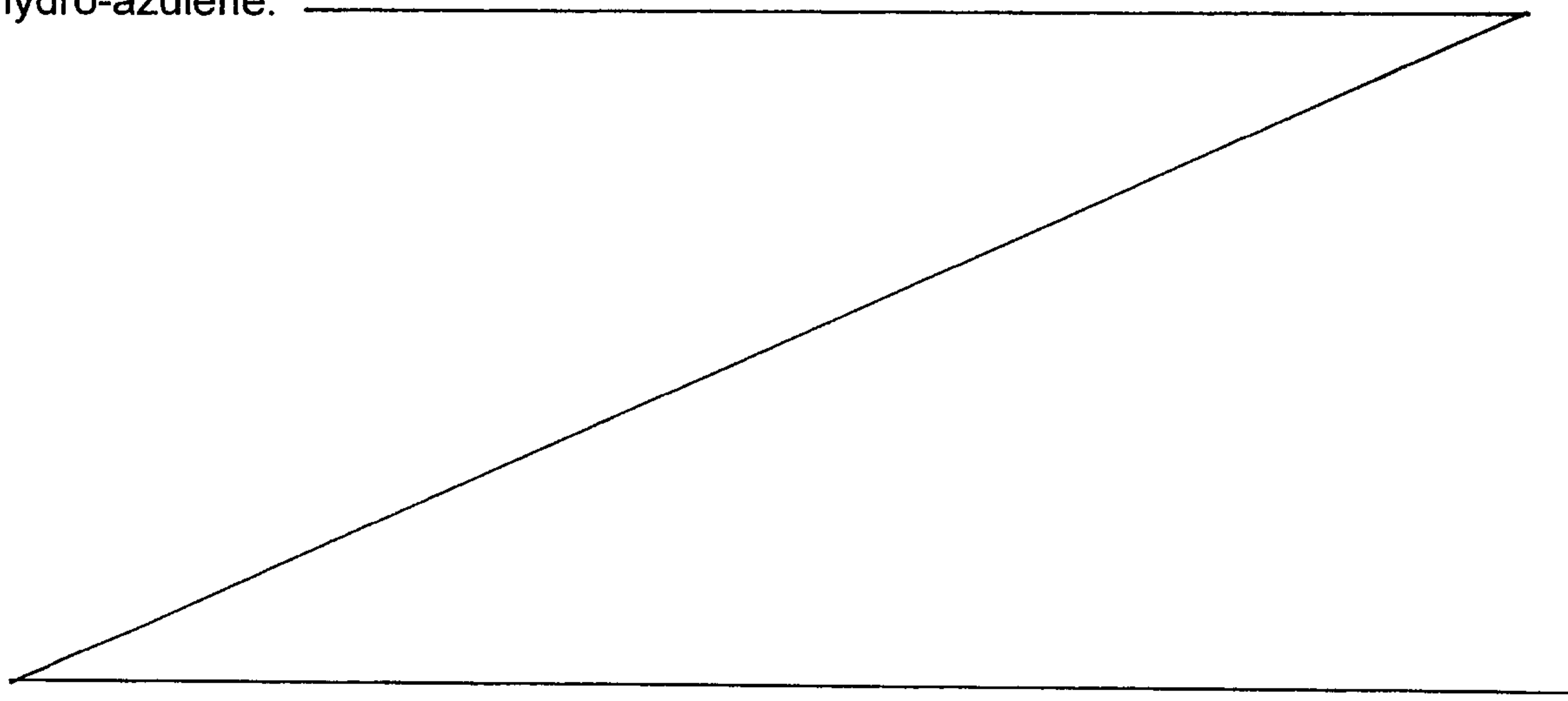
(0.03 moles) of 2,4,5,6,7,8-hexahydroazulene (prepared as described in the copending European patent application of the same applicant EP-A-0 760 355). There is an exothermic reaction with the formation of a white solid. The mixture is left under stirring for 2 hours and is then cooled to -70°C and 1.93 grams (0.015 moles) of dimethyldichlorosilane are added, over a period of about 20 minutes. The temperature is left to rise overnight and a yellow solution is finally obtained.

10 After evaporation of the solvent, the product is purified on a silica gel column eluting with petroleum ether.

The product obtained is polluted with the starting diene which is removed maintaining the fraction under mechanical vacuum for 24 hours.

2.2 grams of product are obtained (45% yield), which is pure upon NMR and GC analysis.

20 The ^1H -NMR spectrum (CDCl_3 , ppm rel. to TMS) is the following: 6.03 (bs, 4H), 3.07 (bs, 2H), 2.50 (m, 8H), 1.90-1.50 (bs, 12H), -0.2 (s, 6H).
EXAMPLE 2 - Synthesis of 2-[1H-Inden-1-yl]-1-methyl-ethyl]-1,4,5,6,7,8-hexahydro-azulene.



A solution is prepared in 10 ml of MeOH and 10 ml of acetone, of 4.5 grams (0.033 moles) of 2,4,5,6,7,8 hexahydroazulene and 0.3 grams of Potassium terbutylate. The above solution is left 5 at reflux temperature for 20 hours, at the end of which a further 2.7 grams of Potassium terbutylate are added. The mixture is maintained at reflux temperature for a further 25 hours, at the end of which the mixture is poured into water and is 10 extracted with ethyl ether.

After neutralisation and anhydrification, the ether extract is evaporated and the residue is purified by elution on a silica gel column with petroleum ether.

15 3.8 grams of fulvene derivative
2-isopropylidene-2,4,5,6,7,8-hexahydro-azulene are obtained as a yellow solid (66% yield). The ¹H-NMR spectrum of this compound (CDCl₃, ppm rel. TMS) is the following: 6.13 (s, 2H), 2.47 (m, 4H), 2.09 (s, 20 6H), 1.64 (m, 6H).

An ether solution (100 ml) of Indene (4.0 grams, 0.034 moles) is prepared. 12 ml of a 2.5 M solution in hexane of Butyllithium are added and the mixture is left under stirring for 3 hours.

25 The fulvene derivative is then added to the

above solution, cooled to about -70°C . The temperature is left to rise and the mixture is left under stirring for 48 hours.

The reaction mixture is then hydrolysed in water and is extracted with ethyl ether which, after evaporation, gives a solid which is purified on a silica gel column using petroleum ether as eluant.

4.5 grams of product are obtained (74% yield).

10 Its ^1H -NMR spectrum (CDCl_3 , ppm rel. TMS) is the following: 7.4-7.0 (m, 4H), 6.8 (dd, 1H), 6.45 (dd, 1H), 5.95 (s, 1H), 3.60 (bs, 1H), 3.10 (bs, 2H), 2.40 (m, 6H), 1.23 (s, 3H), 0.94 (s, 3H).

EXAMPLE 3 - Synthesis of bis (decahydrocyclopentacyclododecen-2-yl) dimethyl silanes.

20 22 ml of BuLi 2.5 M in hexane are added to a solution of 11 grams of 4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene, prepared as described in the copending European patent application of the same applicant EP-A-0 760 355 in 100 ml of pentane. The mixture is kept under stirring for a night, the solid obtained is filtered and is dried obtaining 9.0 grams of the corresponding Lithium salt.

A solution is prepared in THF (100 ml) of 3.4 grams (0.16 moles) of the above Lithium salt.

1.0 grams (0.008 moles) of dimethyldichlorosilane are added, at -70C in about 5 20 minutes, to this solution in THF. The temperature is then left to rise during a night, obtaining at the end a yellow solution.

After evaporation of the solvent, ethyl ether is added and the mixture is hydrolyzed with dilute 10 hydrochloric acid. The ether extract is washed to neutrality, dried and evaporated. The residue (3.7 grams) is purified on a silica gel column eluting with petroleum ether.

2.2 grams (62% yield) of product are obtained 15 which upon NMR analysis proves to be a mixture of bis(4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecen-2-yl)dimethyl silane. ¹H-NMR (CDCl₃, pm rel. TMS): 6.62 (s), 6.39 (bs), 6.21 (bs), 6.12 (bs), 3.23 (m), 2.91 (s), 2.35 (m), 1.88-0.84 (m), 20 0.08 (bs), -0.21 (bs).

¹³C-NMR (CDCl₃, ppm rel. TMS): 153.35, 146.07, 146.02, 141.49, 141.04, 138.44, 132.29, 132.01, 127.09, 125.09, 124.89, 121.46, 61.37, 46.25, 39.49, 32.30, 30.96, 30.76, 28.94, 28.90, 24.30.

25 Example 4 - Synthesis of

1,2-bis-(1-methyl-4,5,6,7,8,9,10,11,12,13-decahydro-2-H-cyclopentacyclopentacyclododecen-2-yl)-dimethyl silane.

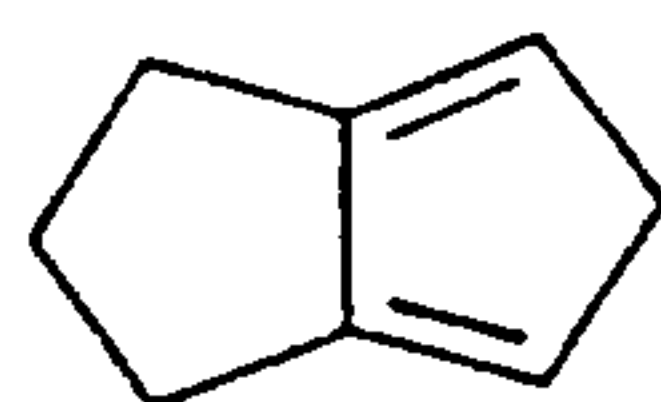
28 ml ($70 \cdot 10^{-3}$ moles) of BuLi in hexane are added to 15.1 g. ($69.2 \cdot 10^{-3}$ moles) of 1-methyl-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene, prepared according to example 4 of EP-A-0 760 355, diluted with 100 ml of pentane. The mixture is stirred for a night and then filtered. The solid is recovered and dried: 12 g. of the corresponding Lithium salt are obtained.

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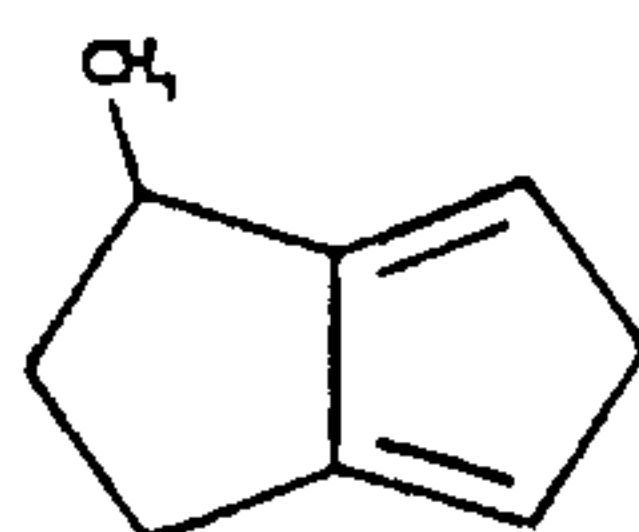
To 5.6 g. ($25.7 \cdot 10^{-3}$ moles) of the above Lithium salt, dissolved in 100 ml of anhydrous THF and cooled to -70°C , are added 1.7 g. ($13.2 \cdot 10^{-3}$ moles) of dichlorosilane; the temperature is then left to rise to 20°C during a night. After evaporation of the solvent, diethyl ether is added and the reaction mixture is hydrolysed with diluted HCl. The organic phase is washed to neutrality, dried and evaporated. The residue is purified on a silica gel column eluting with petroleum ether.

3.5 g. (55% yield of 1,2-bis-(1-methyl-4,5,6,7,8,9,10,11,12,13-decahydro-2-H-cyclopentacyclododecen-2-yl)-dimethyl silane are obtained.

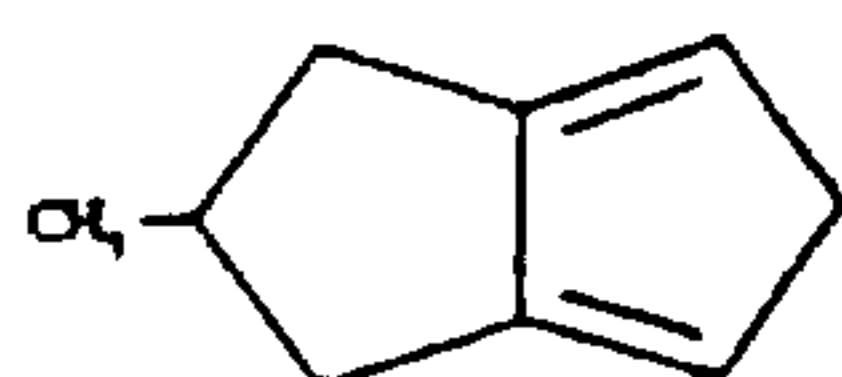
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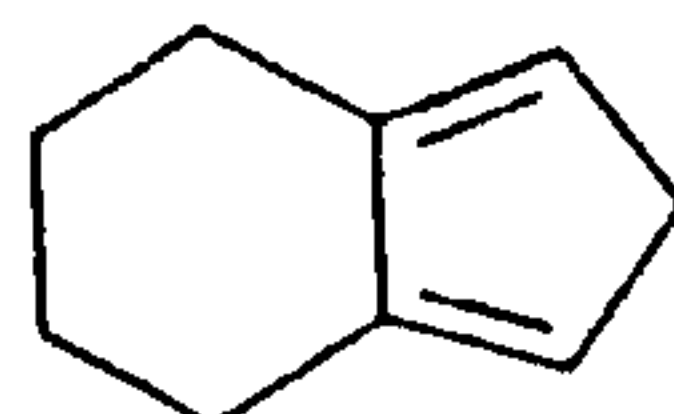
1,2,3,5-tetrahydro-pentalene



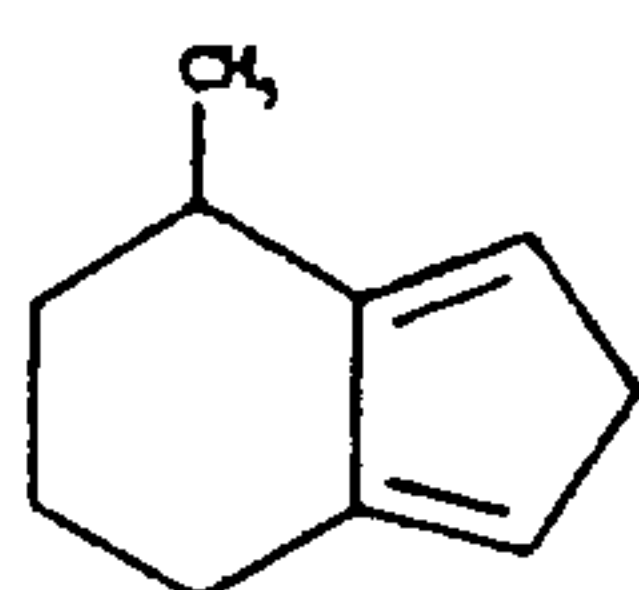
1-methyl-1,2,3,5-tetrahydro-pentalene



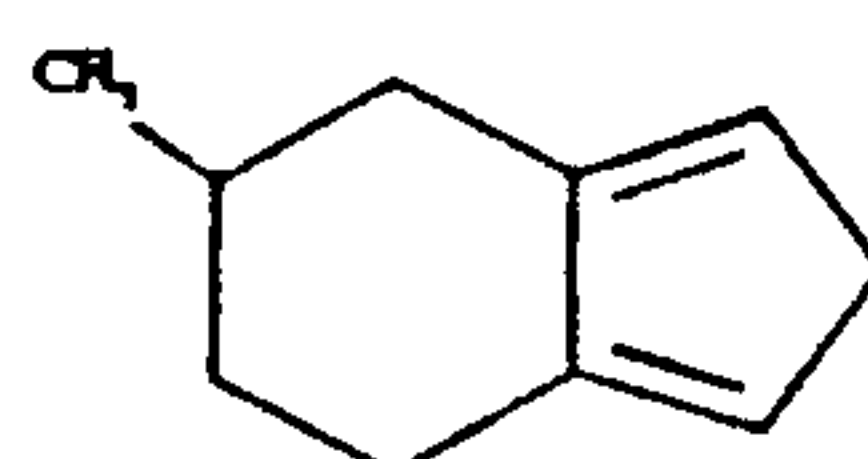
2-methyl-1,2,3,5-tetrahydro-pentalene



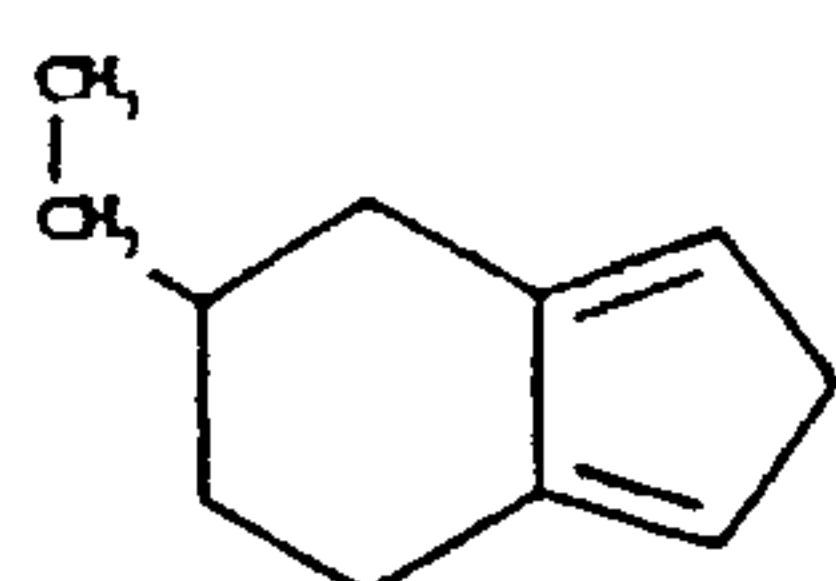
4,5,6,7-tetrahydro-2H-indene



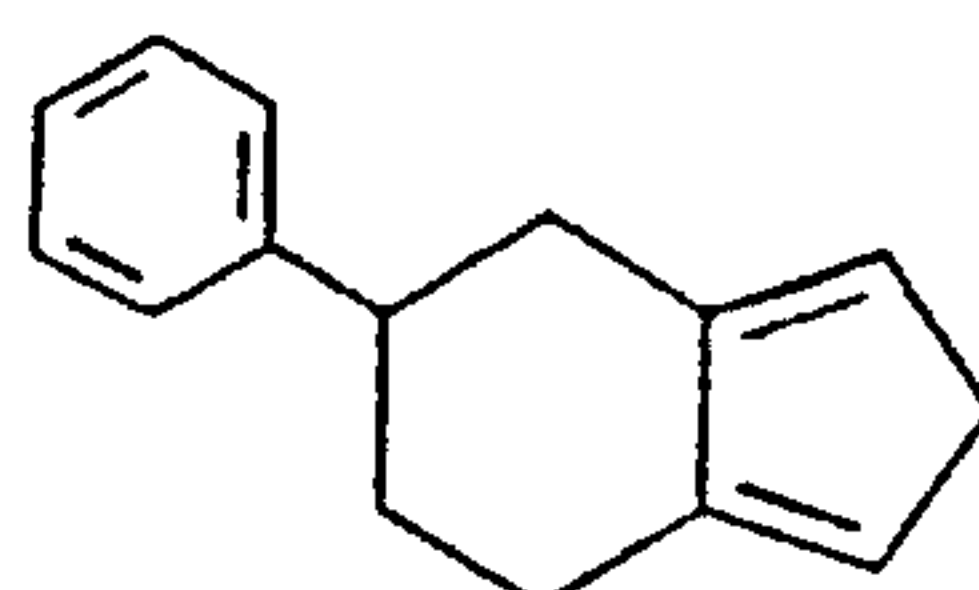
7-methyl-4,5,6,7-tetrahydro-2H-indene



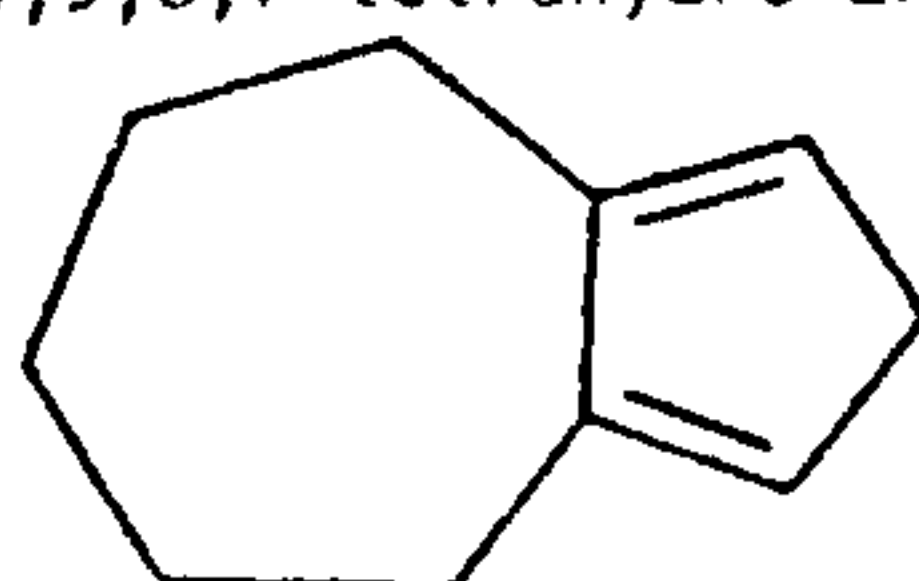
6-methyl-4,5,6,7-tetrahydro-2H-indene



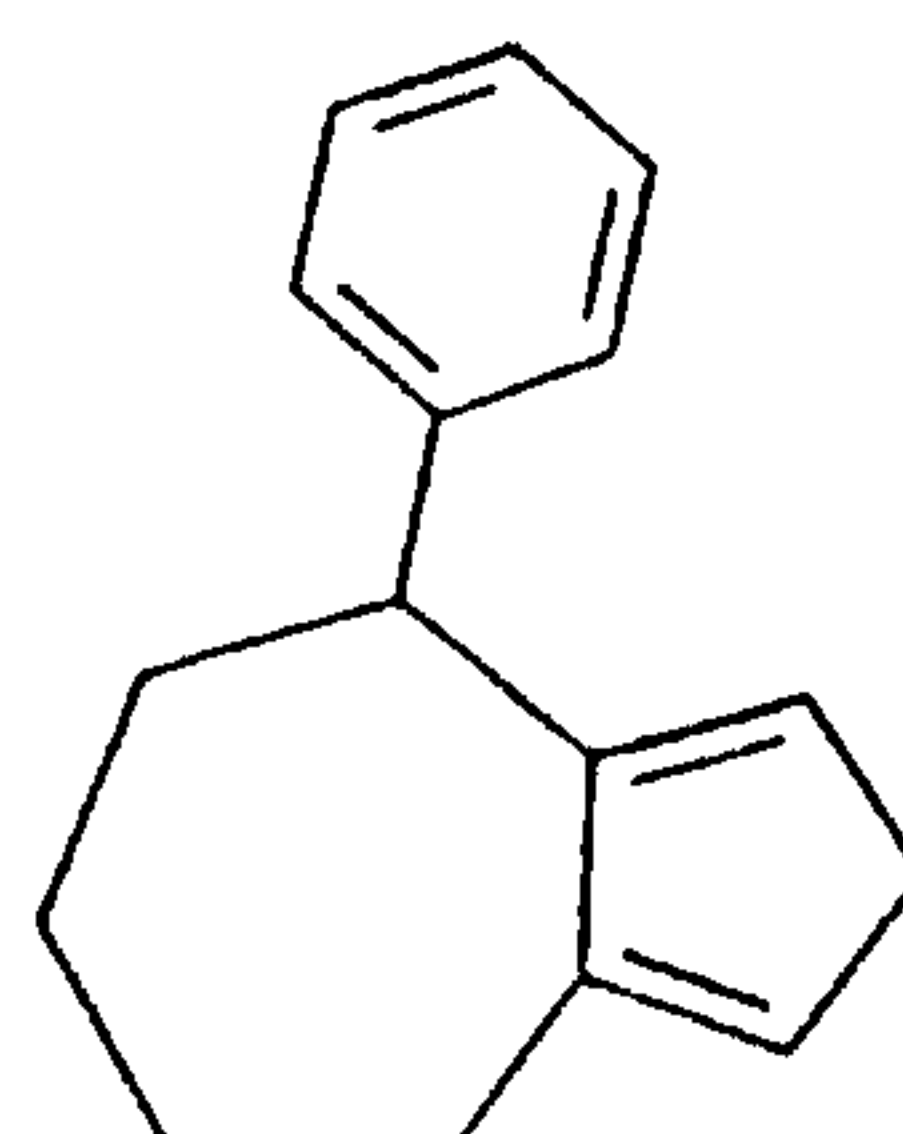
6-ethyl-4,5,6,7-tetrahydro-2H-indene



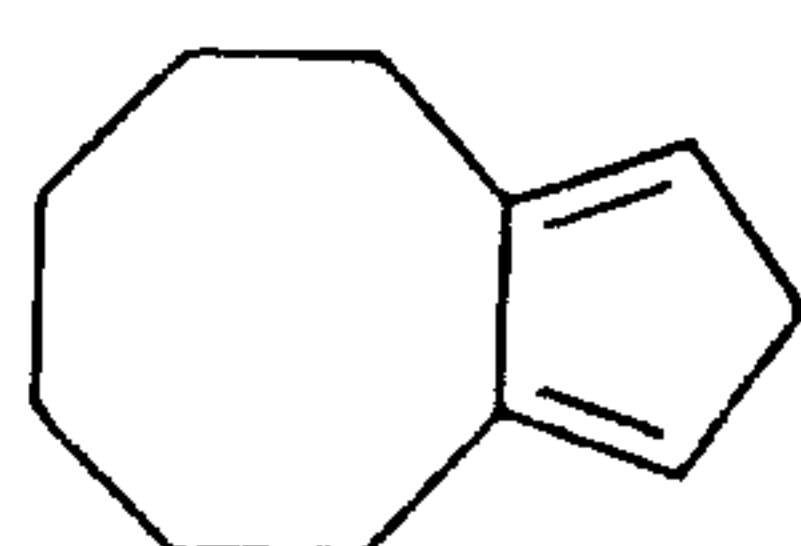
6-phenyl-4,5,6,7-tetrahydro-2H-indene



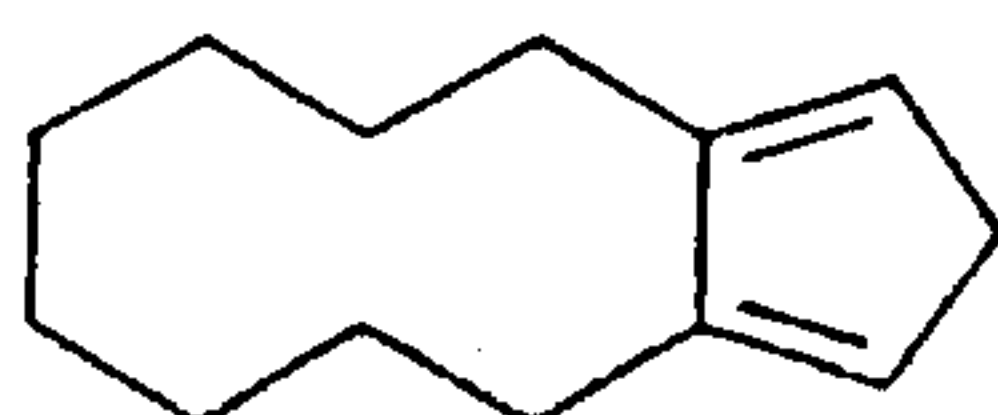
2,4,5,6,7,8-hexahydroazulene



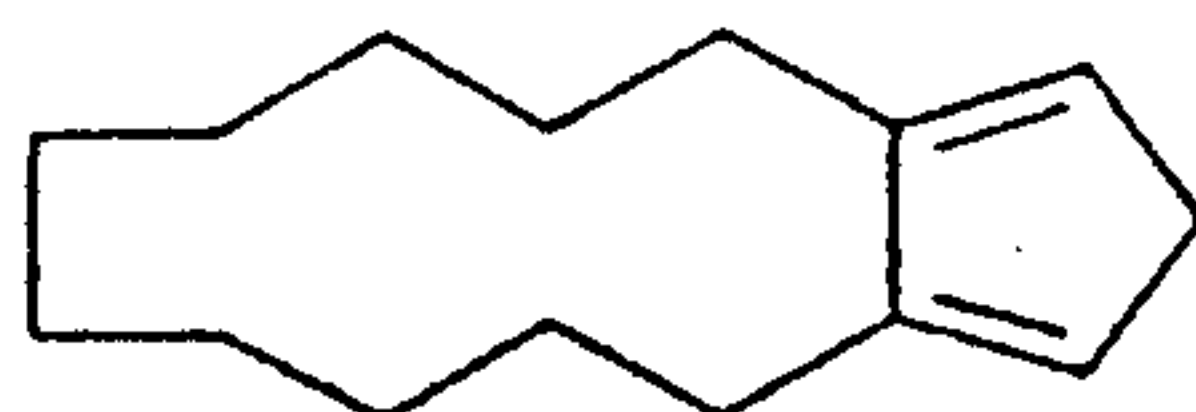
8-phenyl-2,4,5,6,7,8-hexahydro-azulene



4,5,6,7,8,9-hexahydro-2H-cyclopentacyclooctene

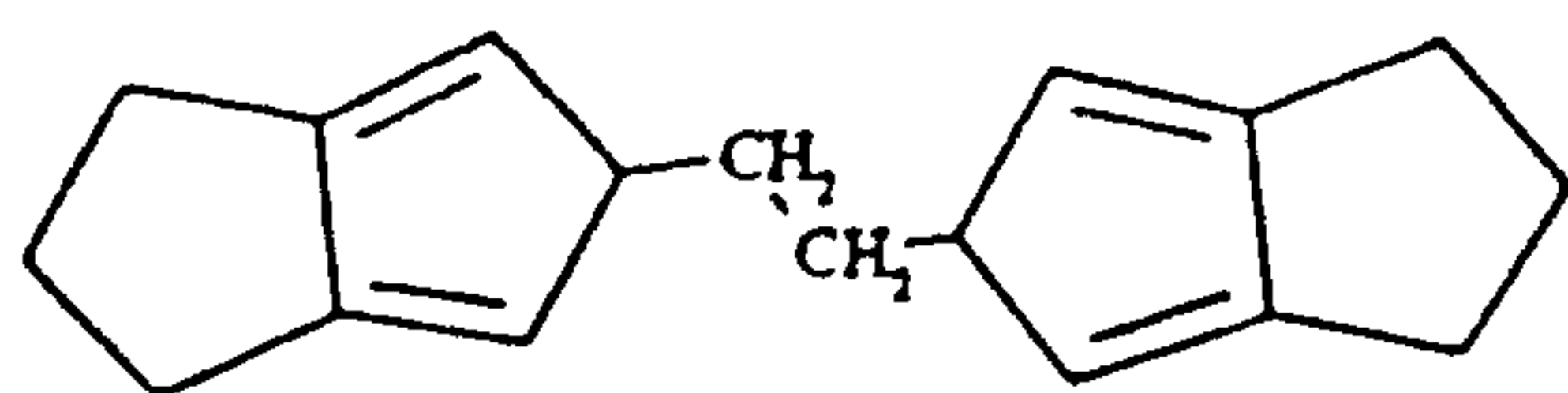


4,5,6,7,8,9,10,11-octahydro-2H-cyclopentacyclodecene

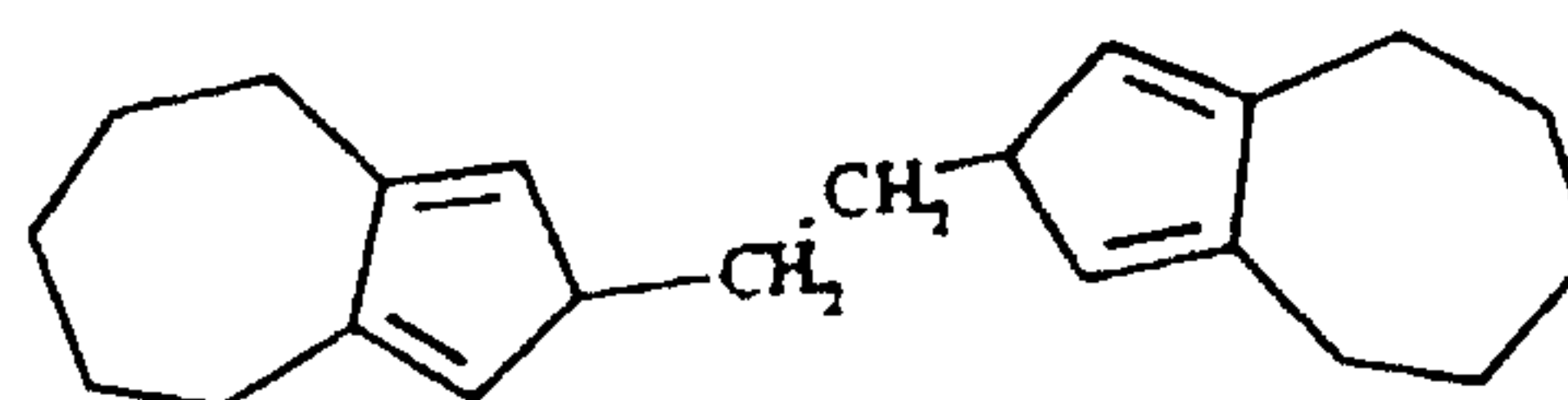


4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene

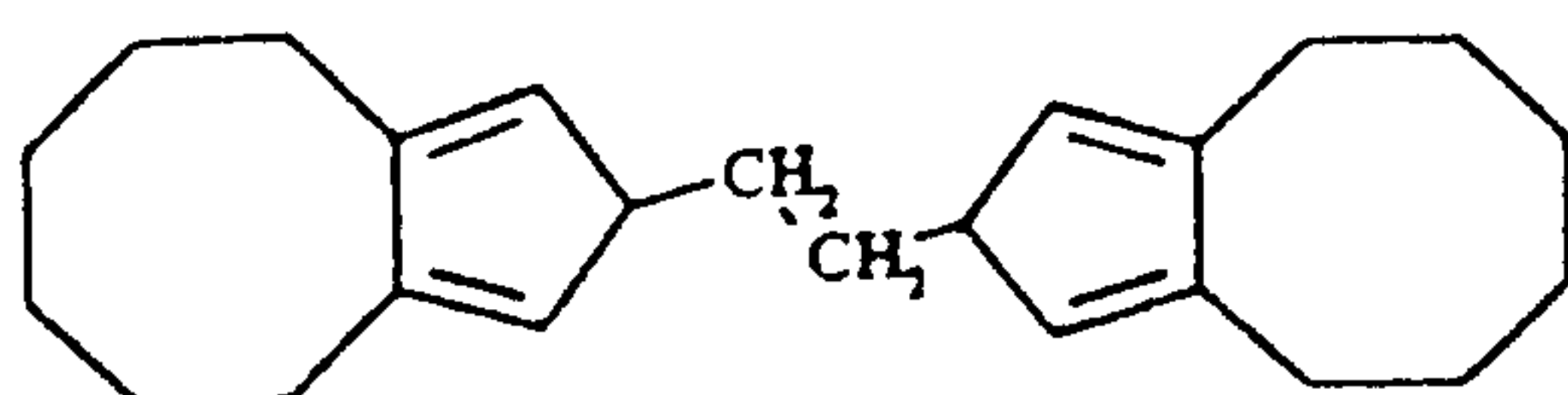
Table 1.



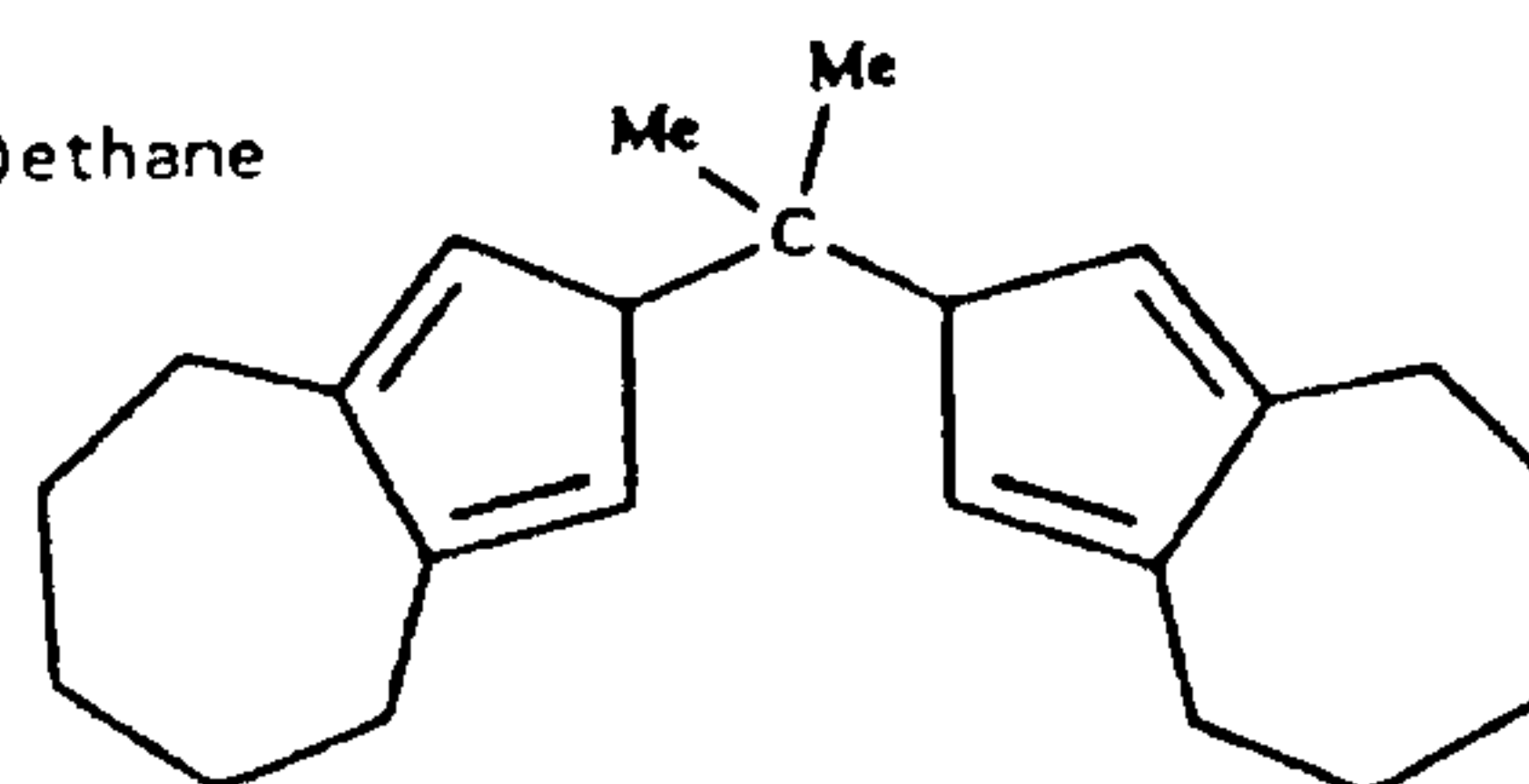
1,2-bis-(2,4,5,6-tetrahydropentalen-2-yl)ethane



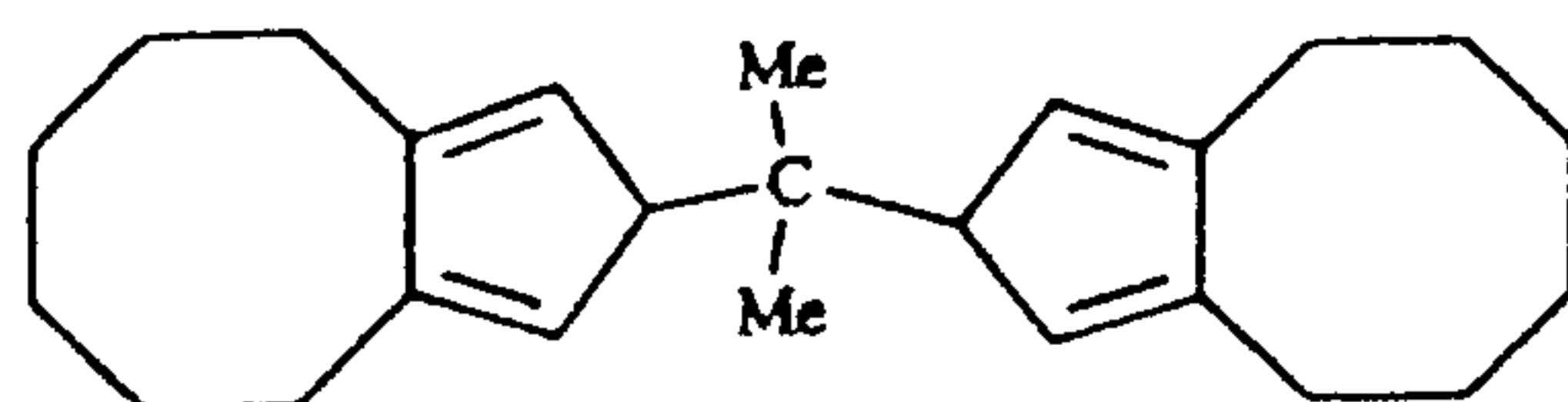
1,2-bis-(2,4,5,6,7,8-hexahydroazulen-2-yl)ethane



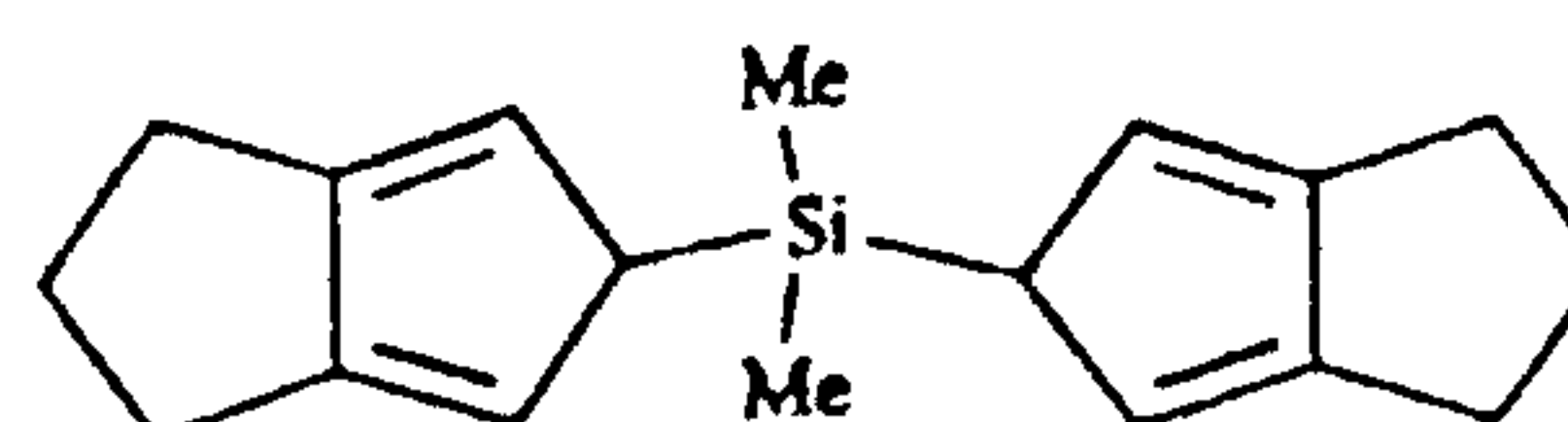
1,2-bis-(4,5,6,7,8,9-hexahydro-2H-cyclopentacycloocten-2-yl)ethane



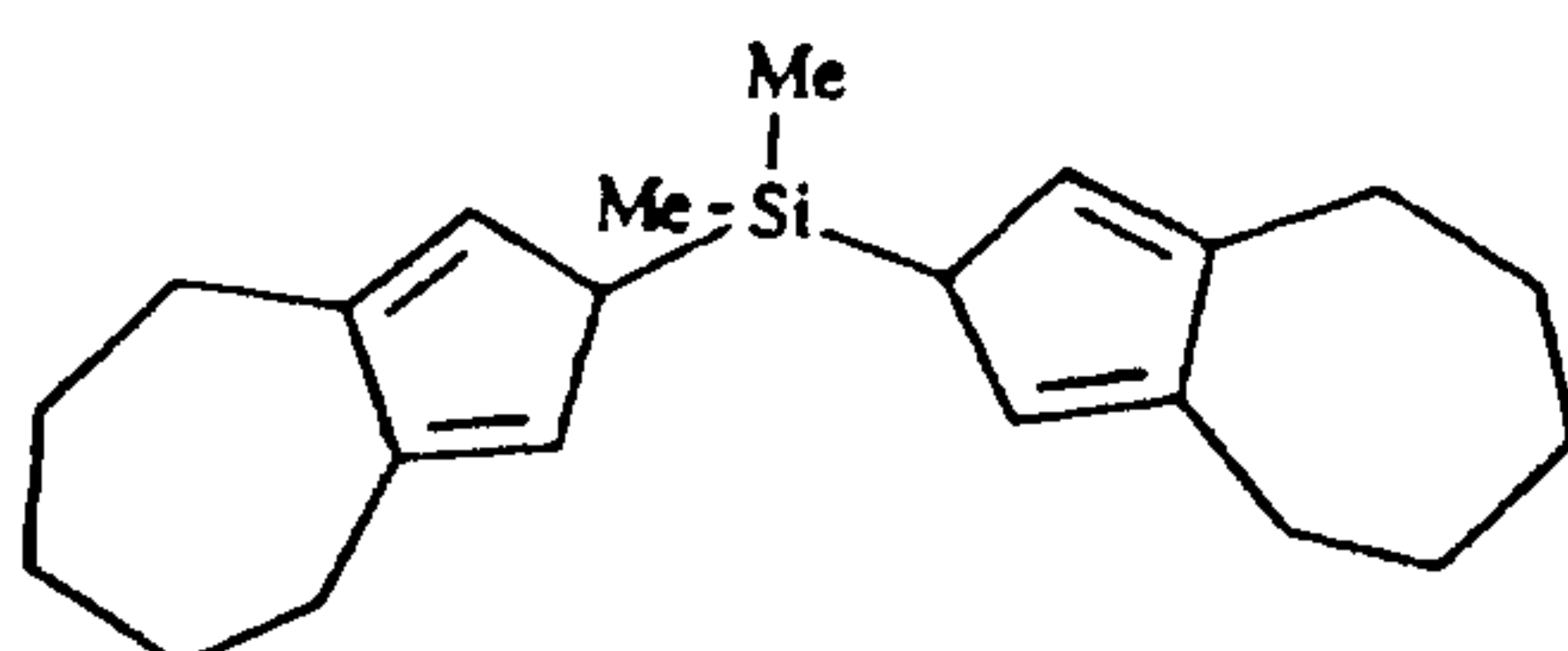
1,1-bis-(2,4,5,6,7,8-hexahydroazulen-2-yl)-1-methyl-ethane



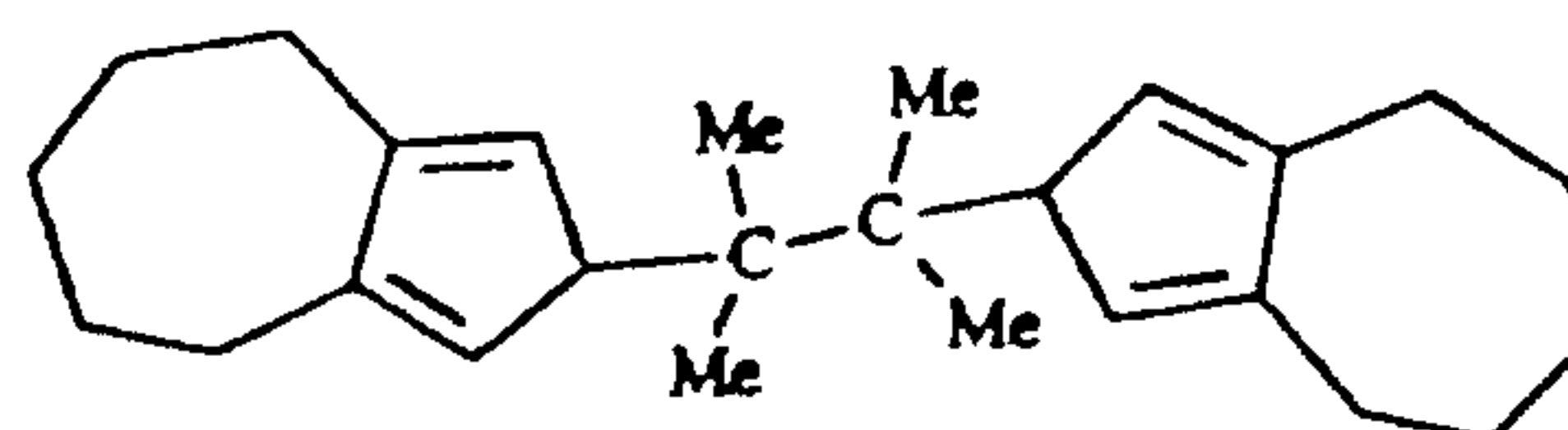
1,1-bis-(4,5,6,7,8,9-hexahydro-2H-cyclopentacycloocten-2-yl)-1-methyl-ethane



bis-(2,4,5,6-tetrahydropentalen-2-yl)dimethylsilane

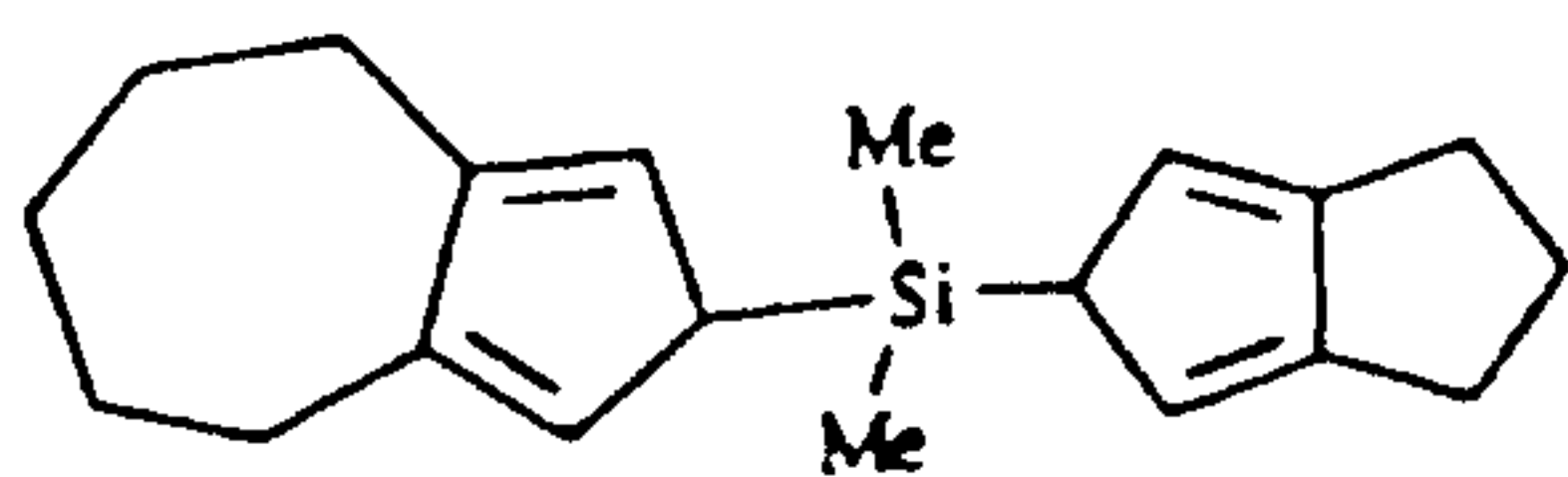


bis-(2,4,5,6,7,8-hexahydroazulen-2-yl)dimethylsilane

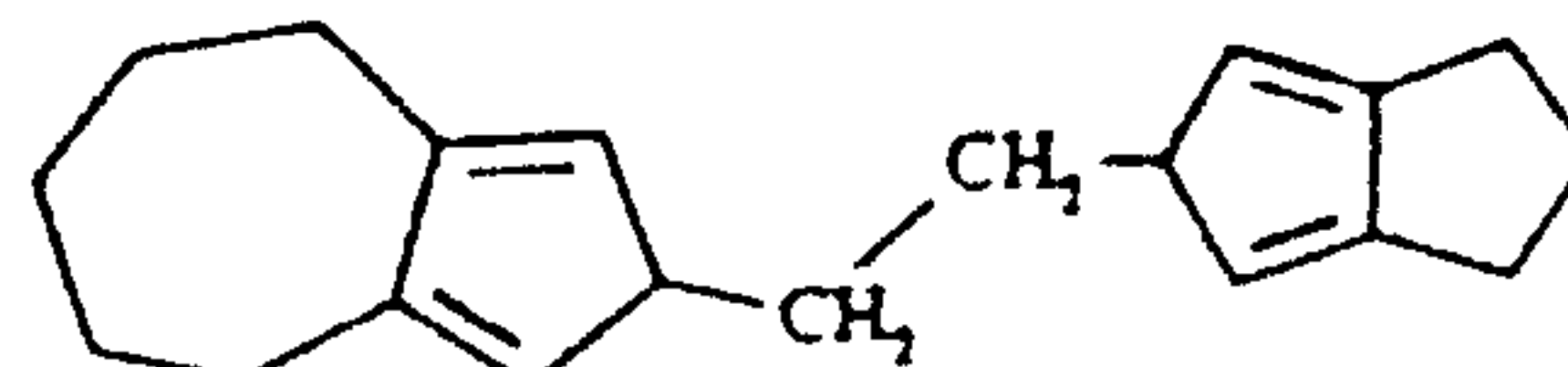


1,2-bis-(1,1,2-trimethyl-(2,4,5,6,7,8-hexahydroazulen-2-yl))propane

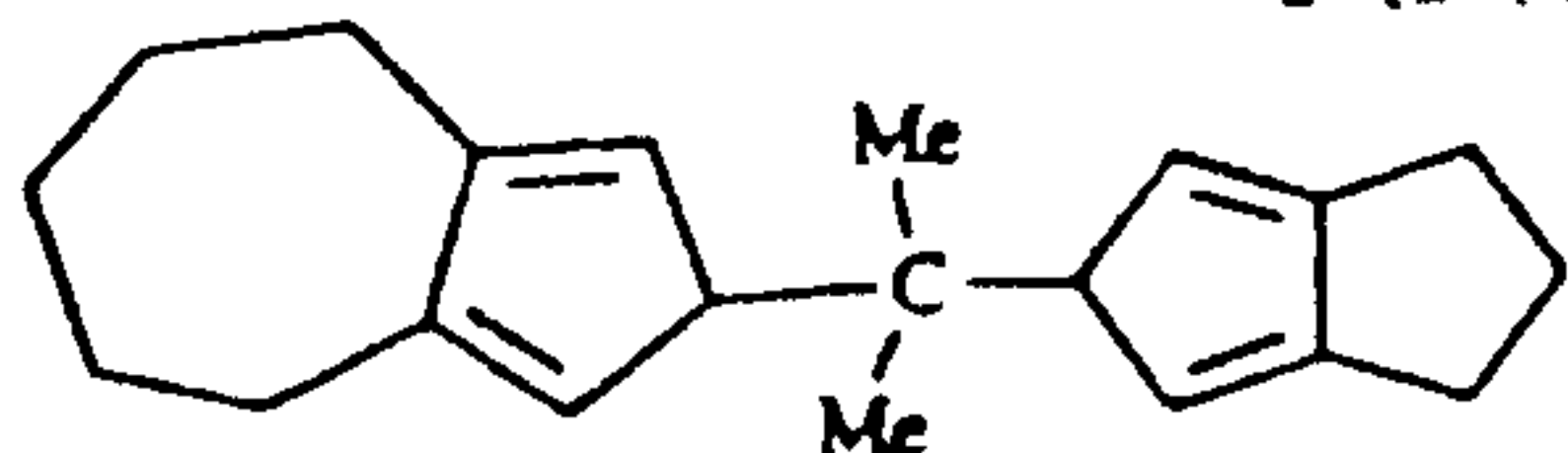
Table 2a



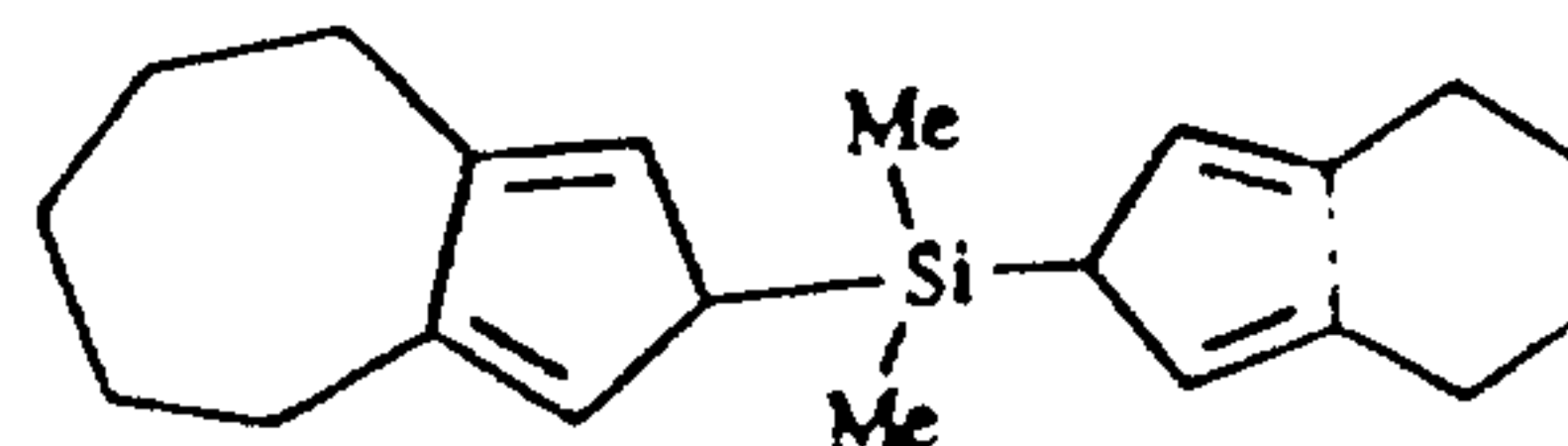
2-(Dimethyl-(2,4,5,6-tetrahydro-pentalen-2-yl)-silanyl)-2,4,5,6,7,8-hexahydro-azulene



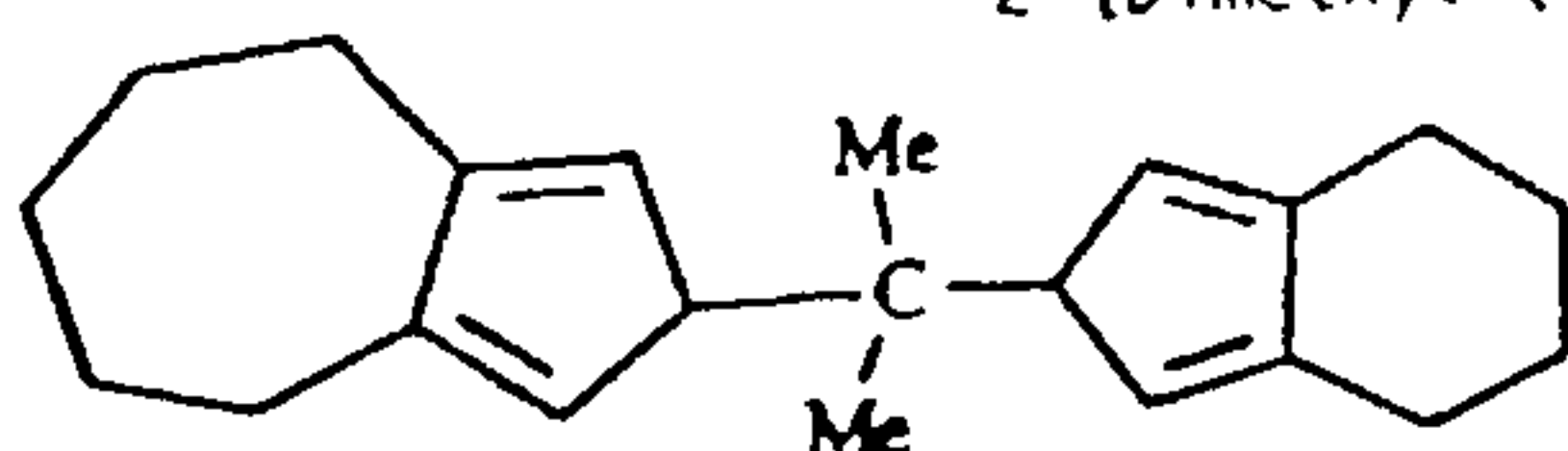
2-(2-(2,4,5,6-Tetrahydro-pentalen-2-yl)-ethyl)-2,4,5,6,7,8-hexahydro-azulene



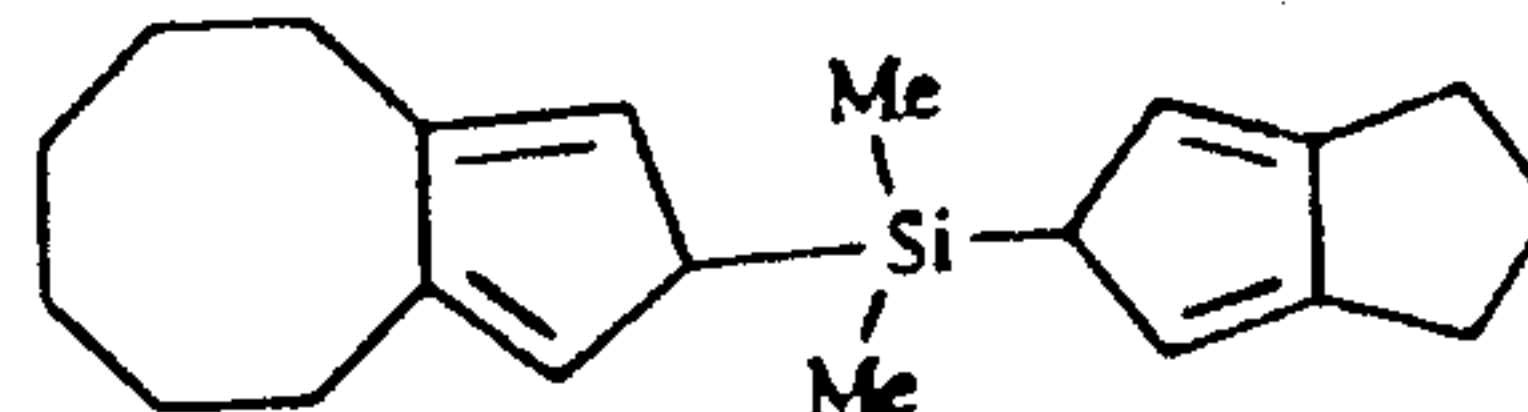
2-[1-Methyl-1-(2,4,5,6-tetrahydro-pentalen-2-yl)-ethyl]-2,4,5,6,7,8-hexahydro-azulene



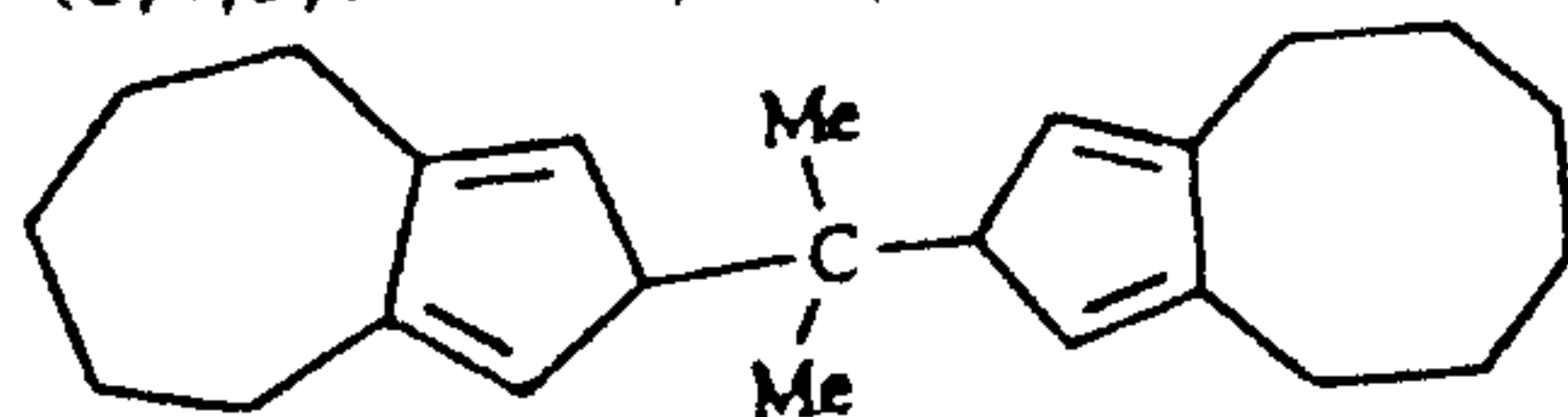
2-(Dimethyl-(4,5,6,7-tetrahydro-2H-inden-2-yl)-silanyl)-2,4,5,6,7,8-hexahydro-azulene



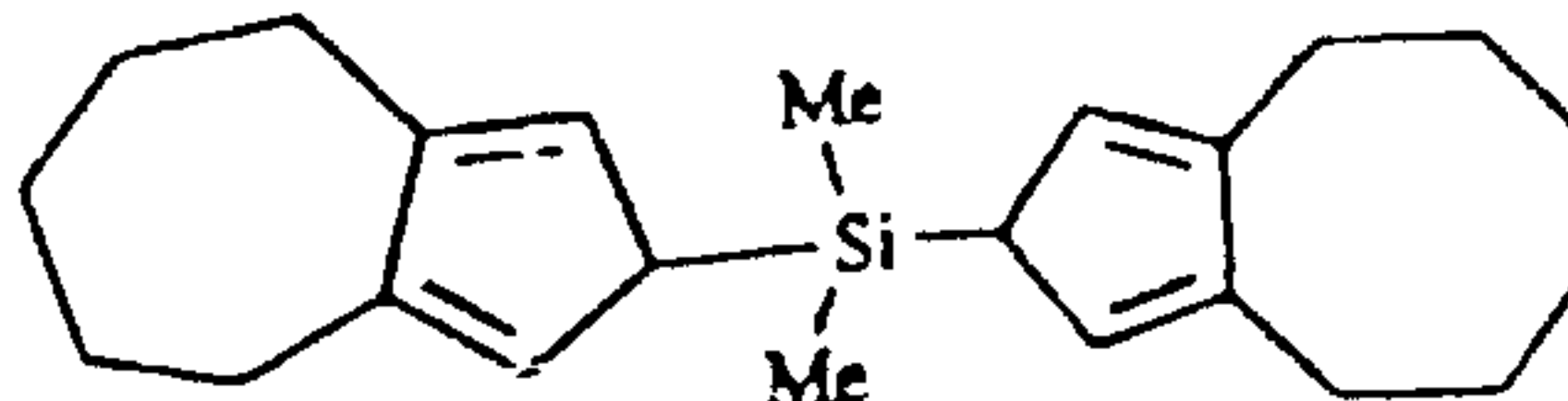
2-[1-Methyl-1-(4,5,6,7-tetrahydro-2H-inden-2-yl)-ethyl]-2,4,5,6,7,8-hexahydro-azulene



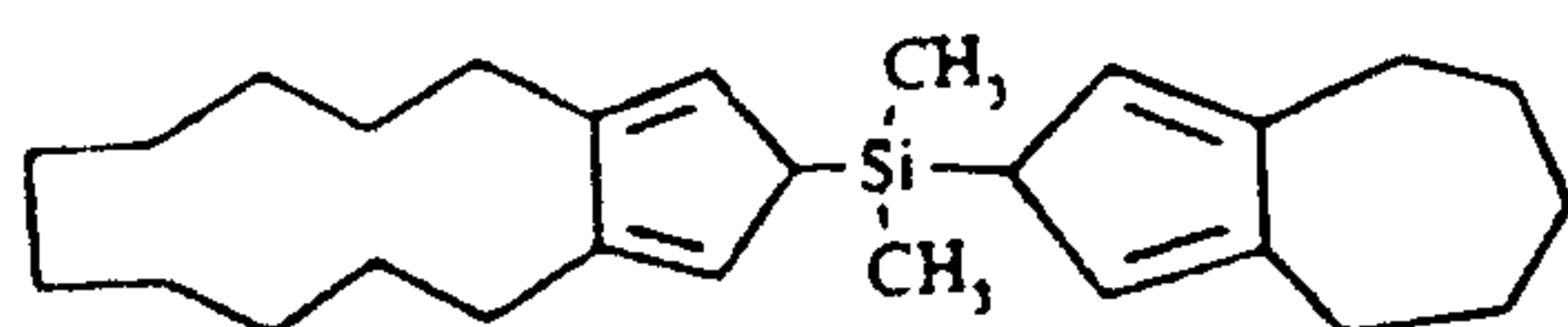
2-(Dimethyl-(2,4,5,6-tetrahydro-pentalen-2-yl)silanyl)-4,5,6,7,8,9-hexahydro-2H-cyclopentacyclooctene



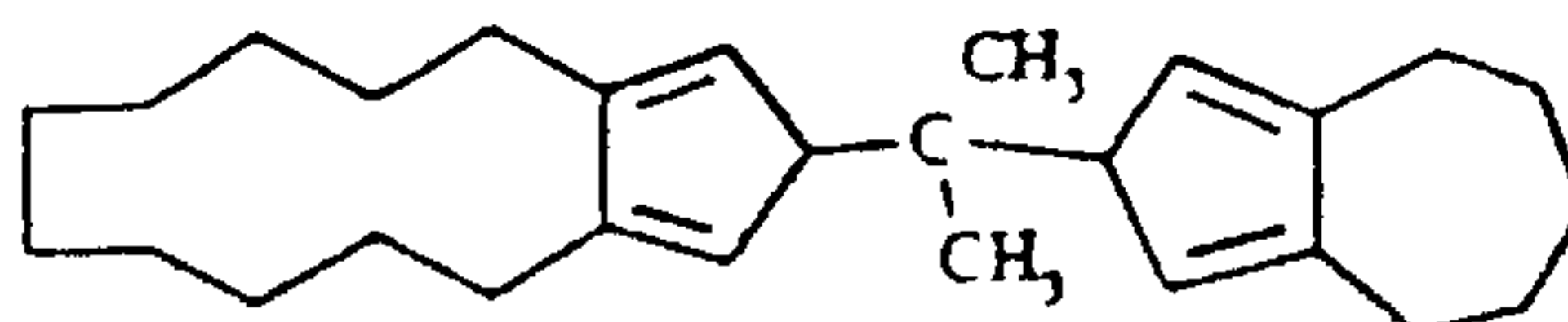
2-[1-(2,4,5,6,7,8-Hexahydro-azulen-2-yl)-1-methyl-ethyl]-4,5,6,7,8,9-hexahydro-2H-cyclopentacyclooctene



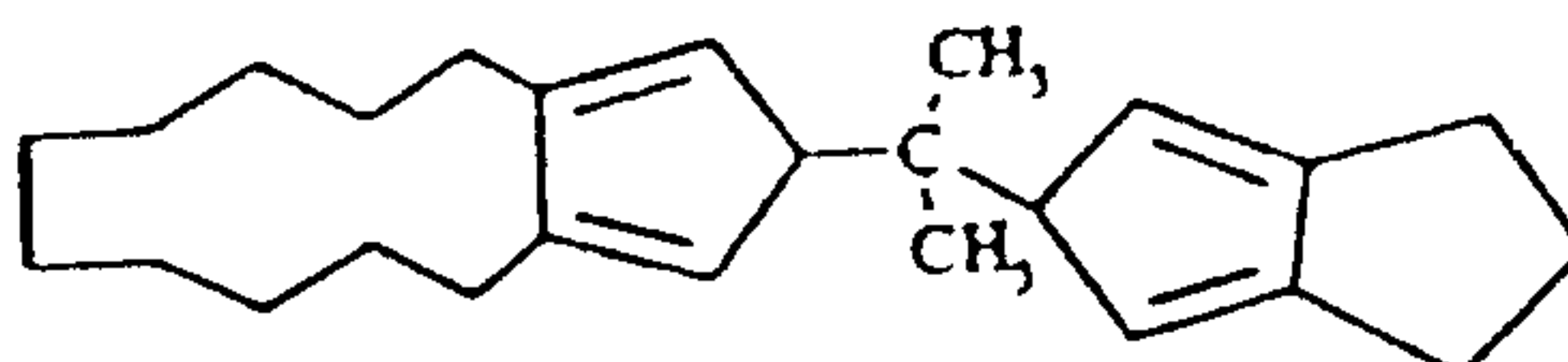
2-[(2,4,5,6,7,8-Hexahydro-azulen-2-yl)-dimethyl-silanyl]-4,5,6,7,8,9-hexahydro-2H-cyclopentacyclooctene



2-[(2,4,5,6,7,8-Hexahydro-azulen-2-yl)-dimethyl-silanyl]-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene

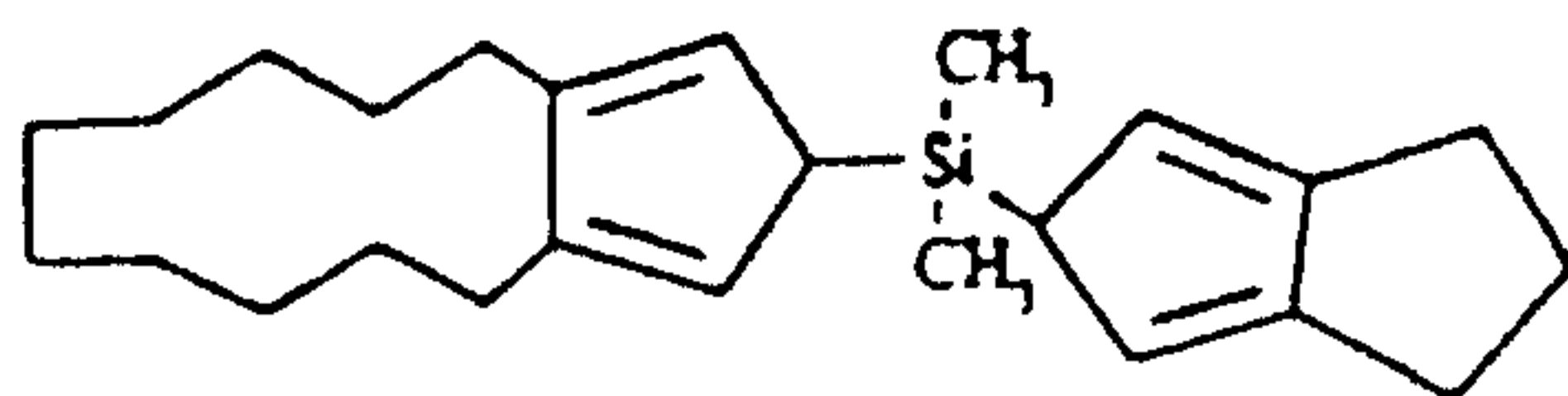


2-[1-(2,4,5,6,7,8-Hexahydro-azulen-2-yl)-1-methyl-ethyl]-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene

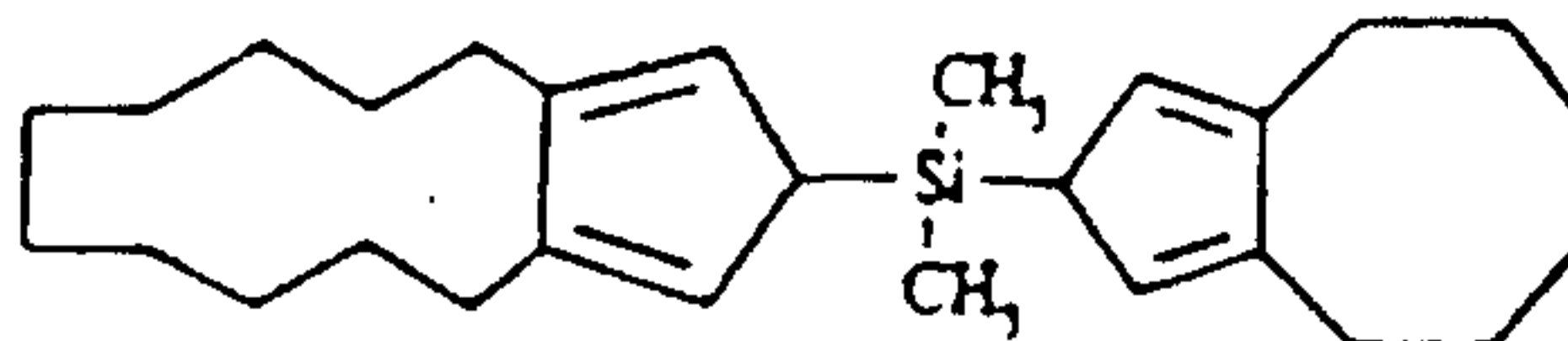


2-[1-Methyl-1-(2,4,5,6-tetrahydro-pentalen-2-yl)-ethyl]-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene

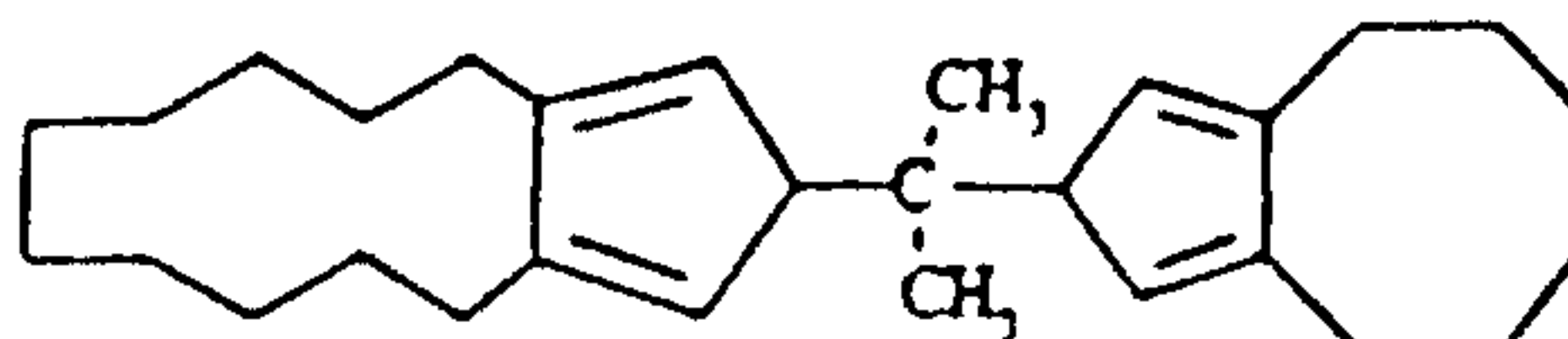
Table 2b



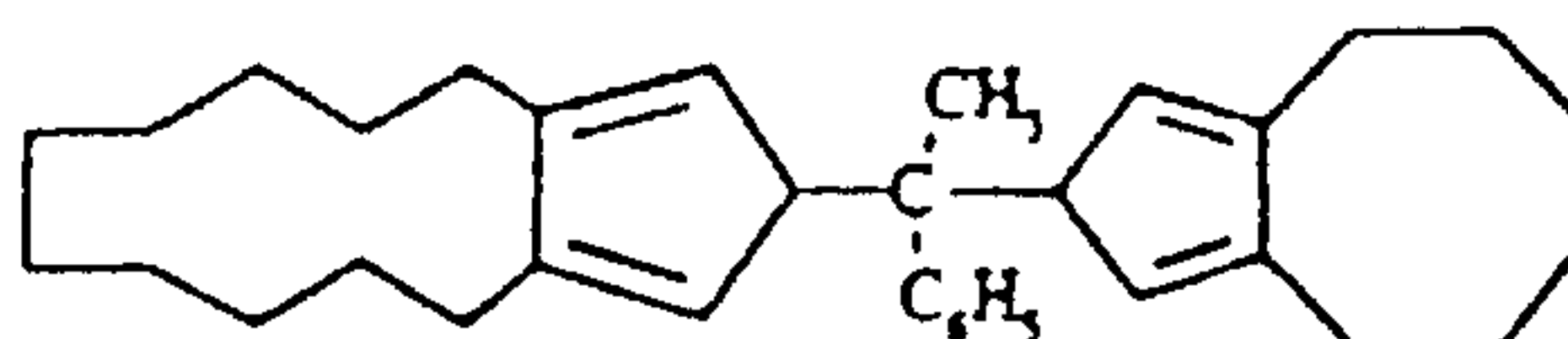
2-[(Dimethyl-(2,4,5,6-tetrahydro-pentalen-2-yl)-silyl)-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene



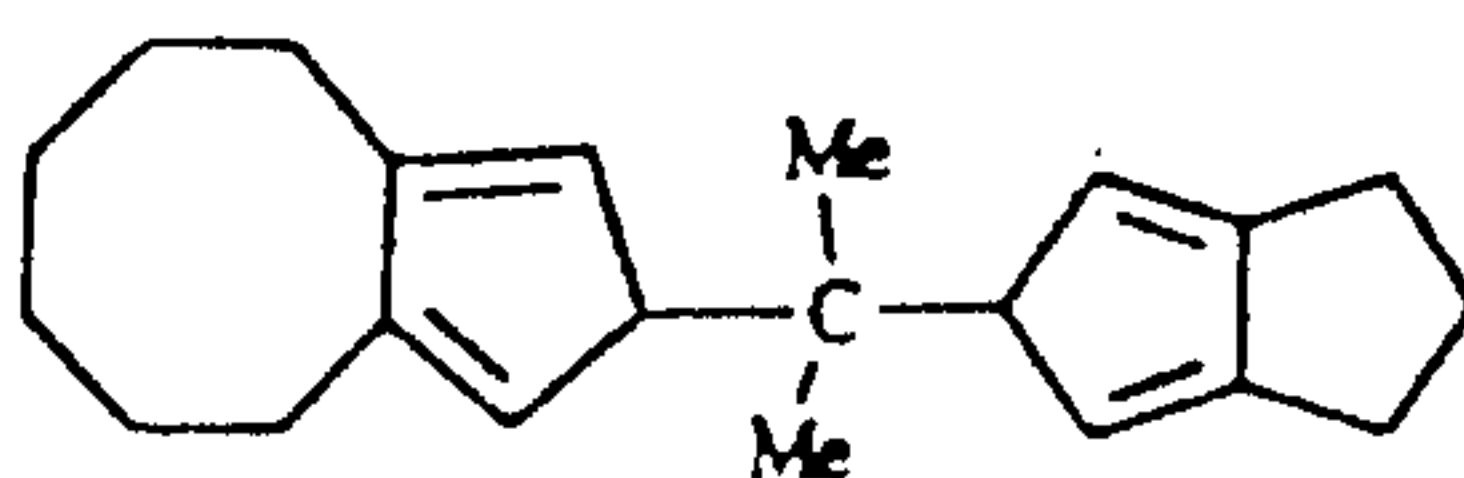
2-[(4,5,6,7,8-hexahydro-2H-cyclopentacycloocten-2-yl)-dimethyl-silyl]-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene



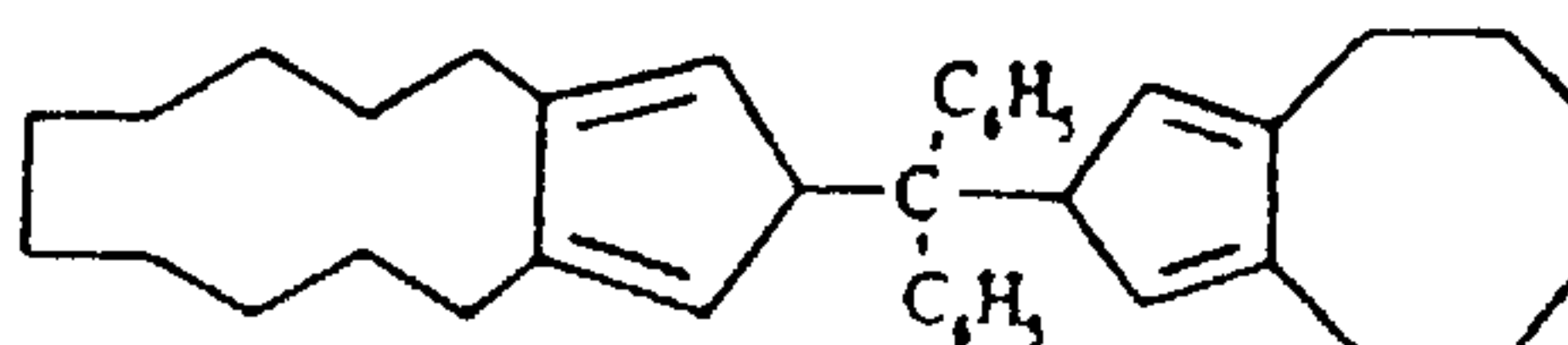
2-[1-(4,5,6,7,8,9-hexahydro-2H-cyclopentacycloocten-2-yl)-1-methyl-ethyl]-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene



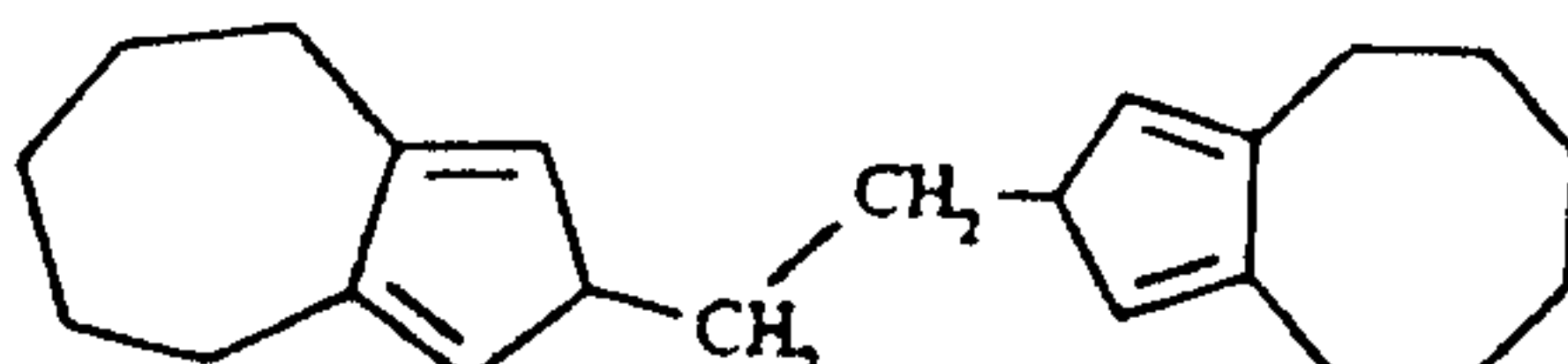
2-[1-(4,5,6,7,8,9-hexahydro-2H-cyclopentacycloocten-2-yl)-1-phenyl-ethyl]-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene



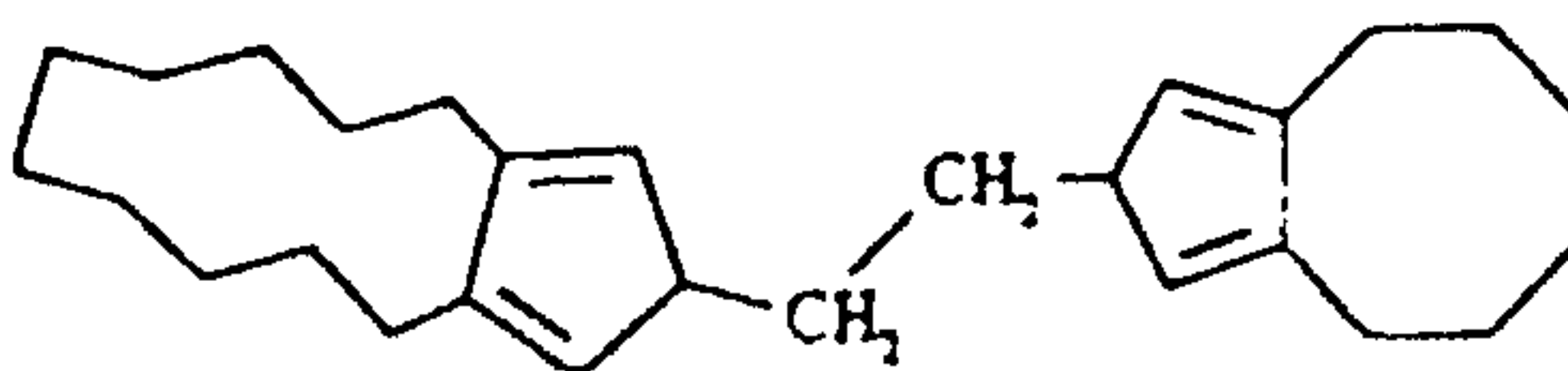
2-[1-Methyl-1-(2,4,5,6-tetrahydro-pentalen-2-yl)-ethyl]-4,5,6,7,8,9-hexahydro-2H-cyclopentacyclooctene



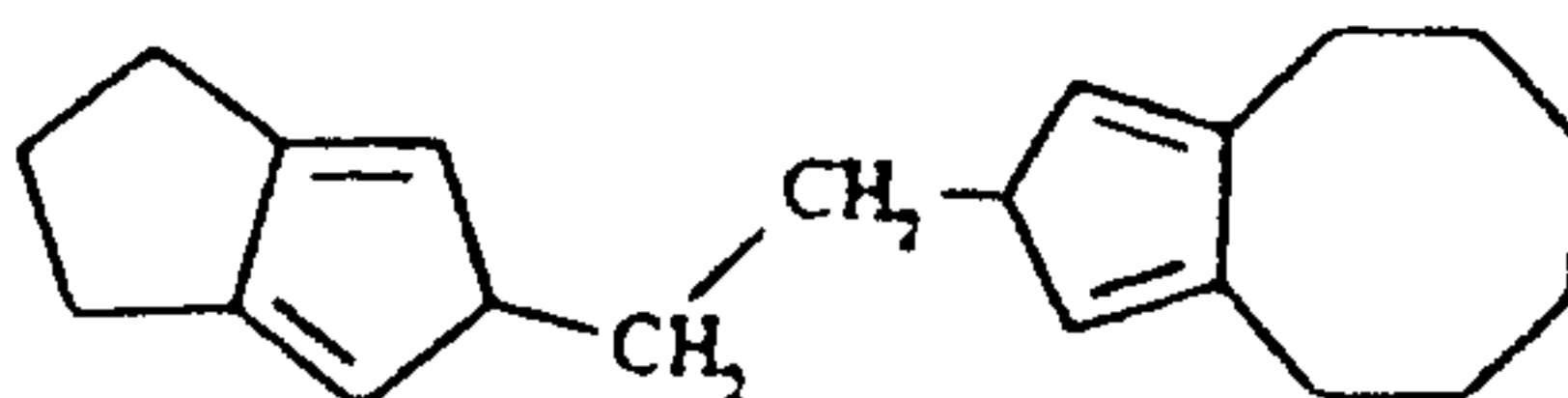
2-[(4,5,6,7,8,9-hexahydro-2H-cyclopentacycloocten-2-yl)-diphenyl-methyl]-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene



2-[2-(2,4,5,6,7,8-hexahydro-azulen-2-yl)-ethyl]-4,5,6,7,8,9-hexahydro-2H-cyclopentacyclooctene

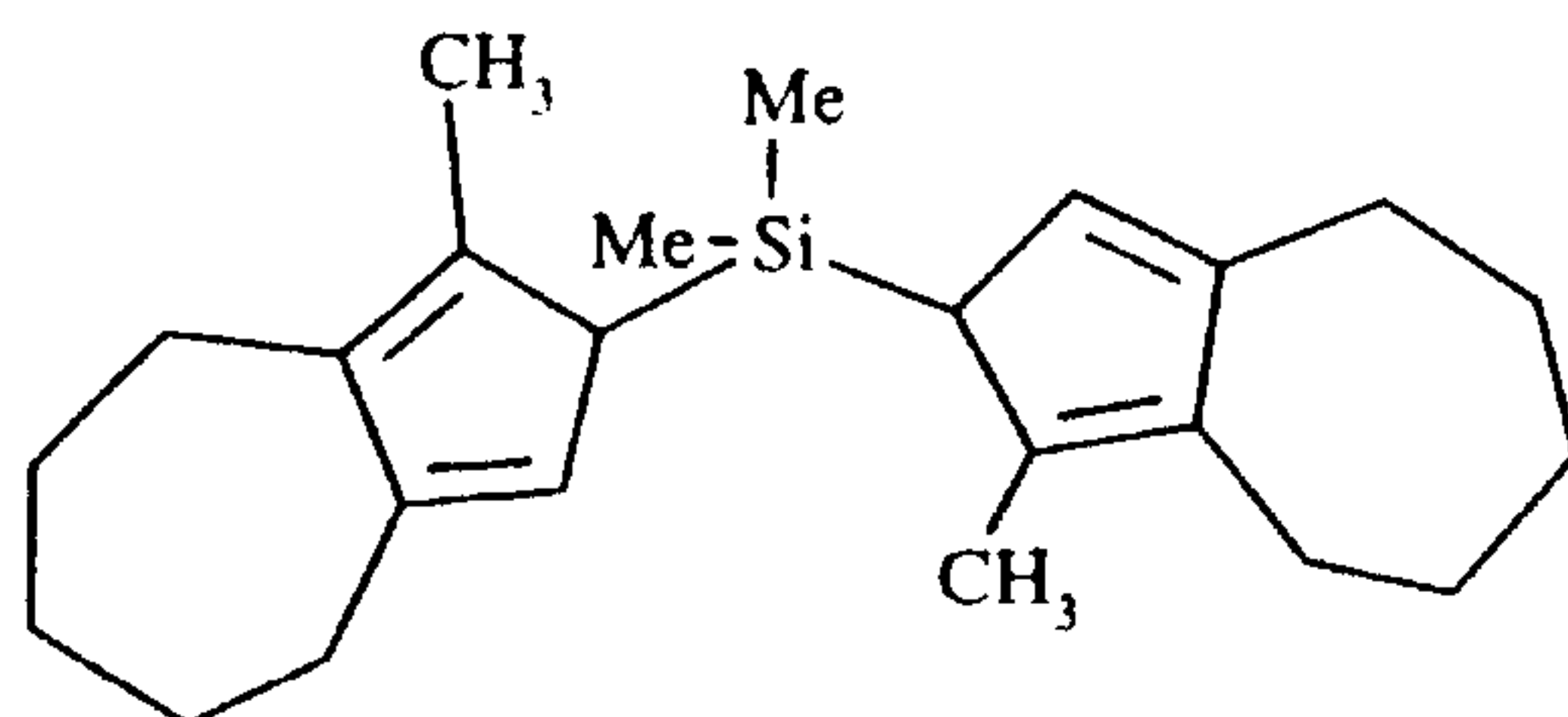


2-[2-(4,5,6,7,8,9-hexahydro-2H-cyclopentacycloocten-2-yl)-ethyl]-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecene

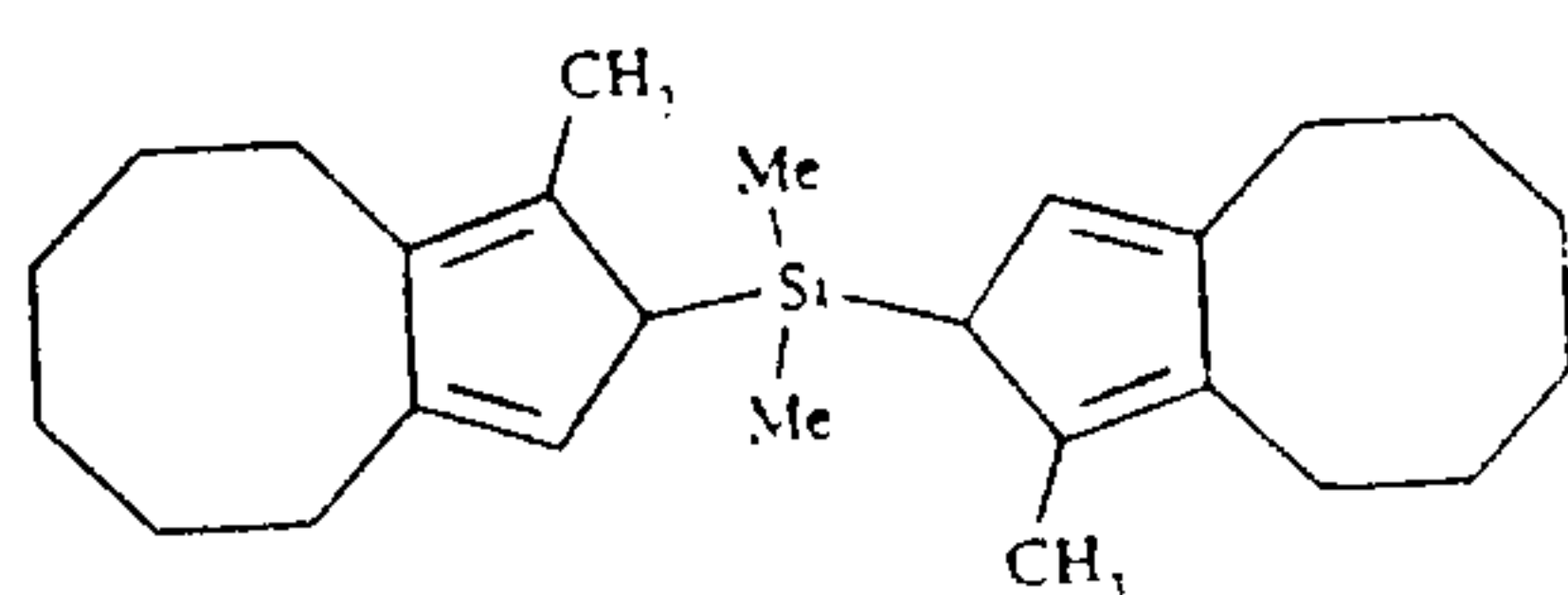


2-[2-(2,4,5,6-tetrahydro-pentalen-2-yl)-ethyl]-4,5,6,7,8,9-hexahydro-2H-cyclopentacyclooctene

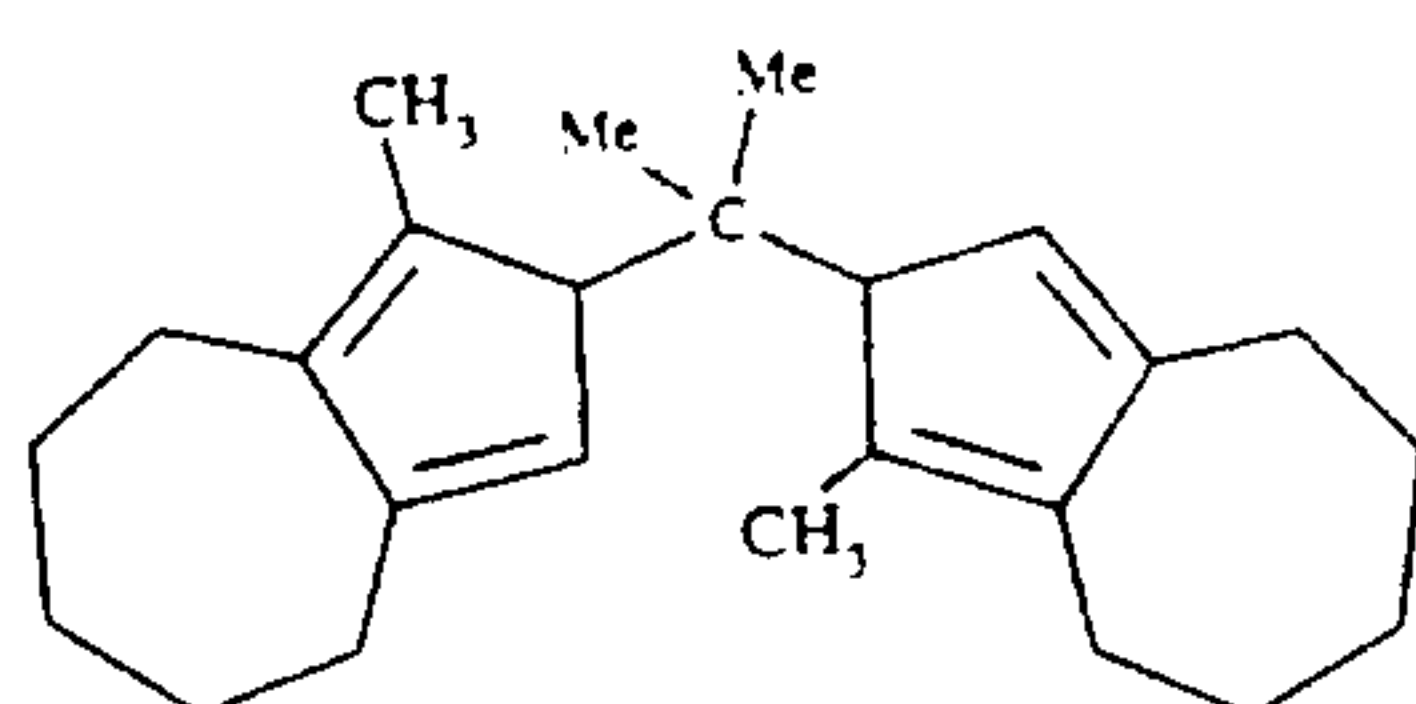
Table 2c



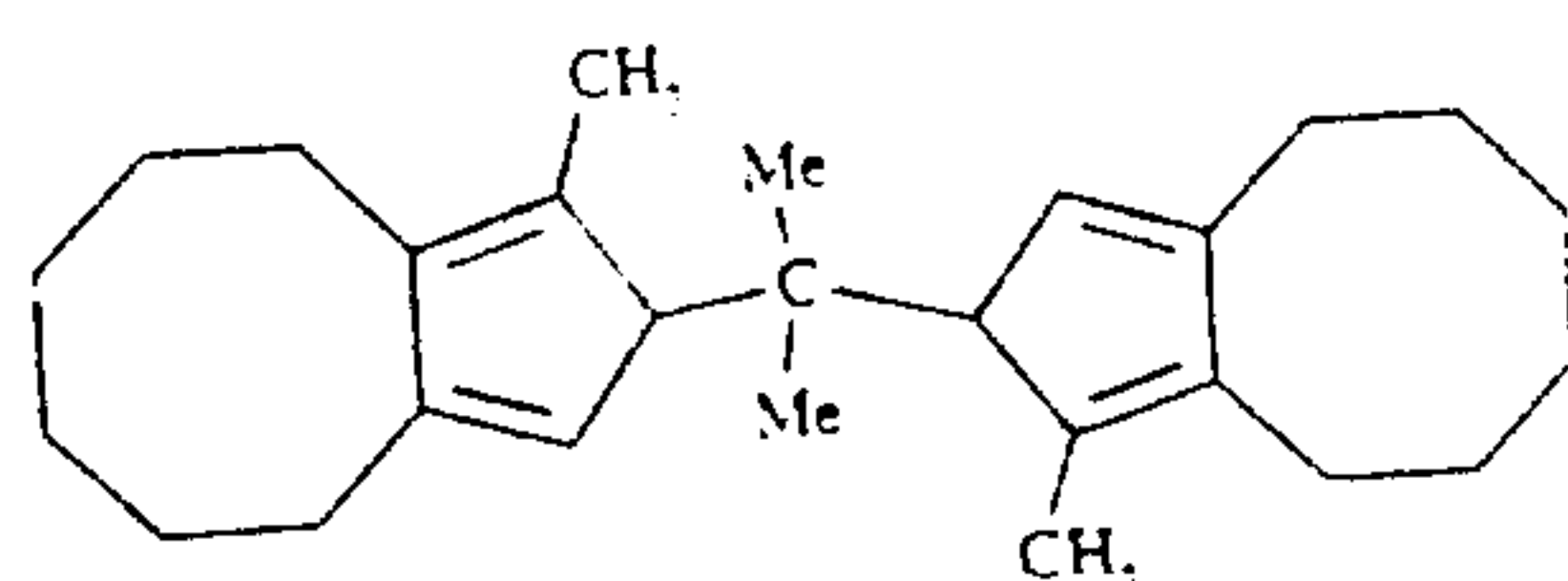
bis-(1-methyl-2,4,5,6,7,8-exahydroazulen-2-yl)dimethylsilane



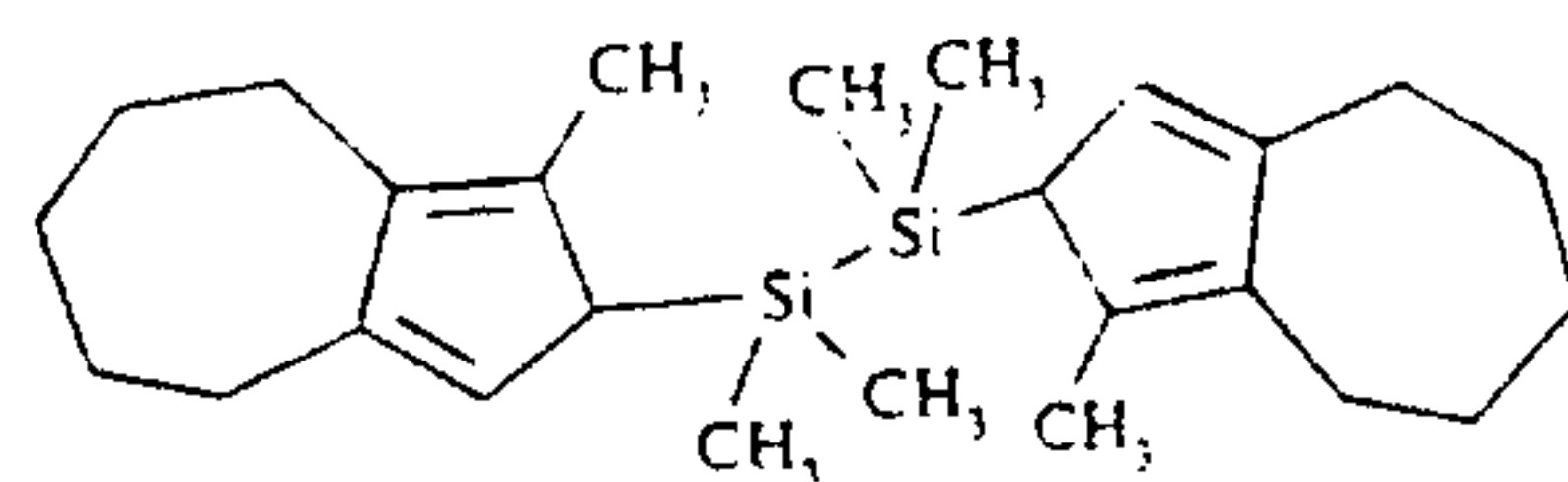
bis-(1-methyl-4,5,6,7,8,9-exahydro-2H-cyclopentacycloocten-2-yl)dimethylsilane



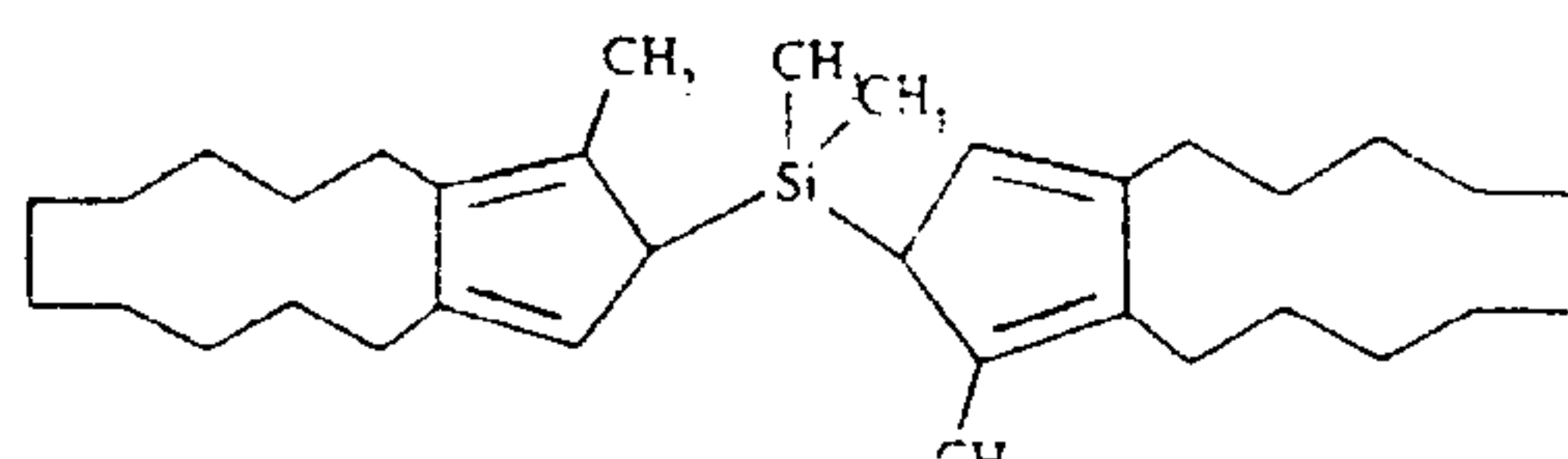
1,1-bis-(1-methyl-2,4,5,6,7,8-exahydroazulen-2-yl)-1-methyl-ethane



1,1-bis-(1-methyl-4,5,6,7,8,9-hexahydro-2H-cyclopentacycloocten-2-yl)-1-methyl-ethane

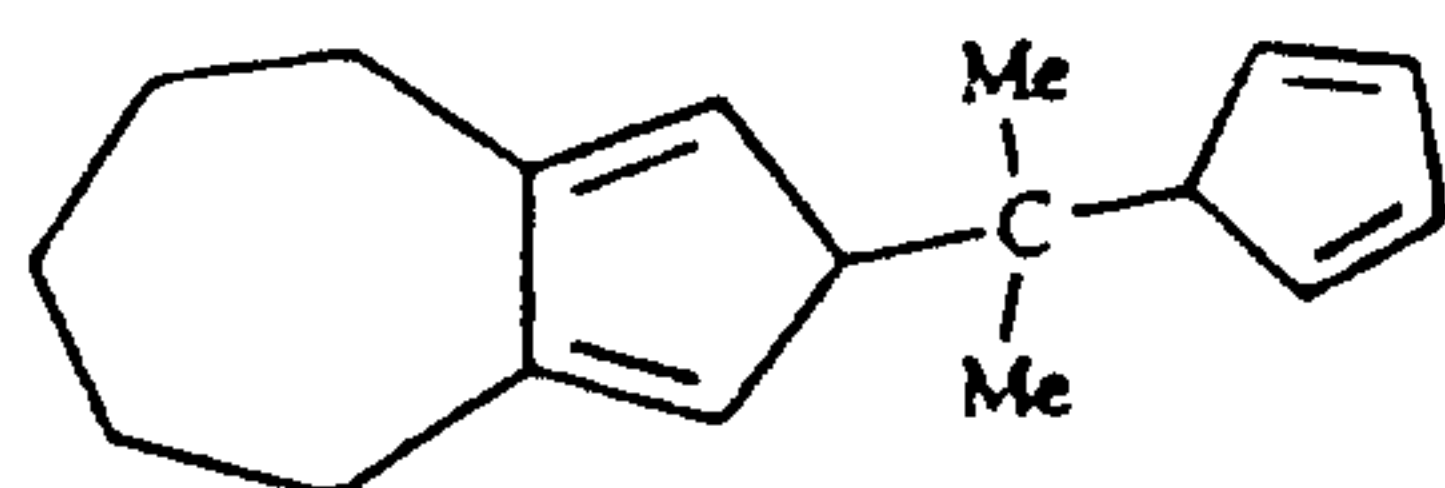


1,2-bis-(1-methyl-2,4,5,6,7,8-exahydroazulen-2-yl)tetramethyldisilane

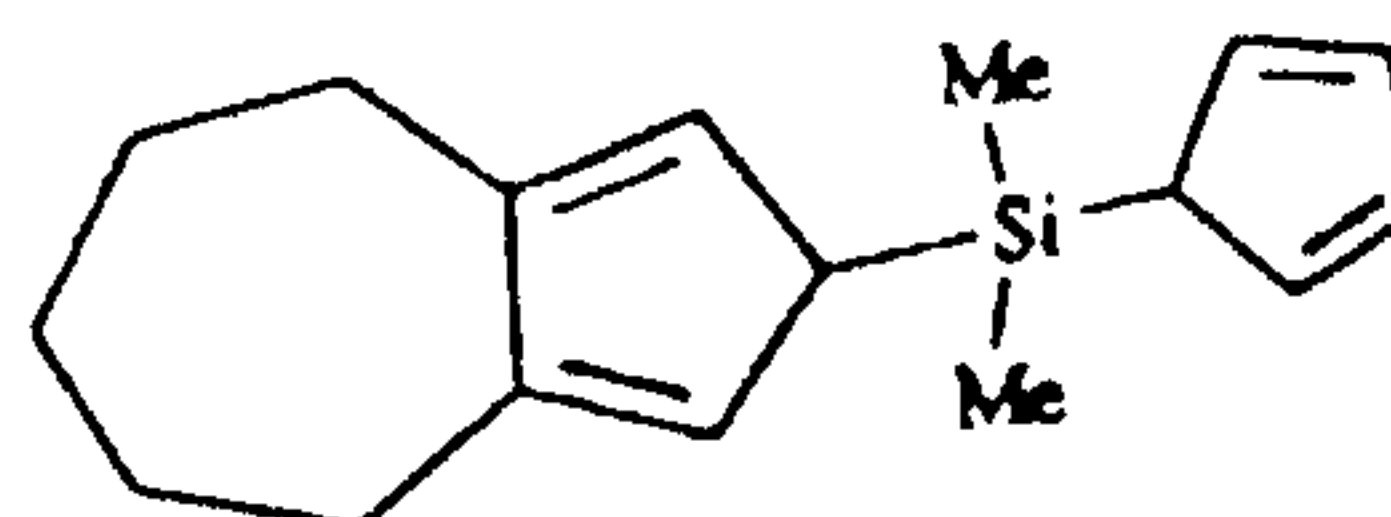


bis-(1-methyl-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclopentacyclododecen-2-yl)-dimethylsilane

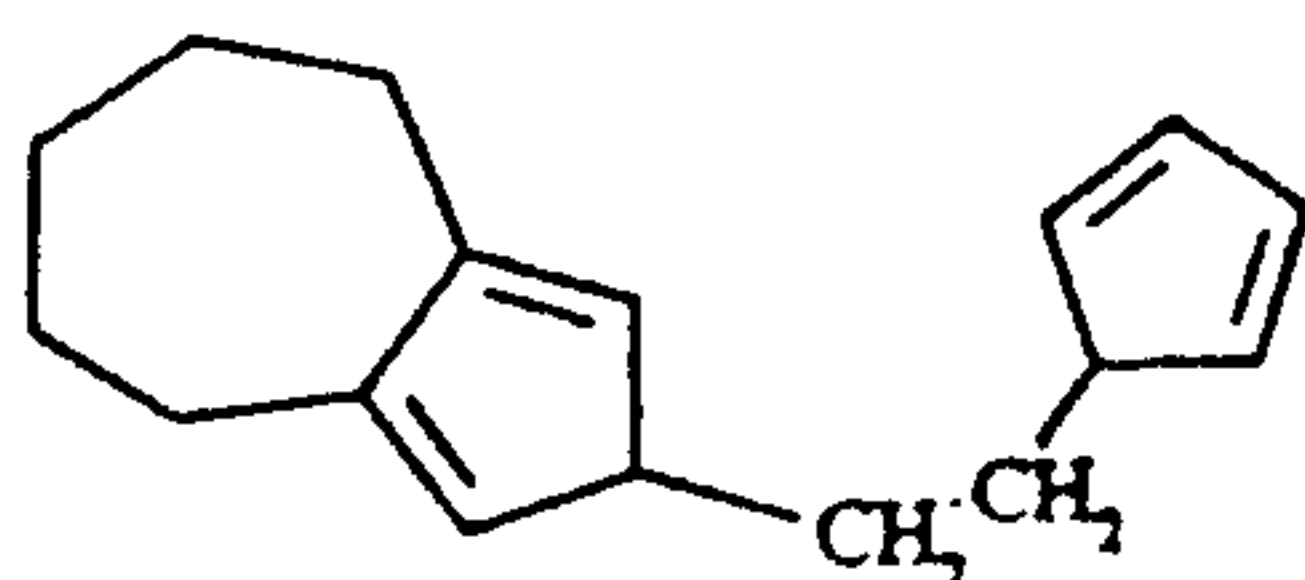
Table 2d



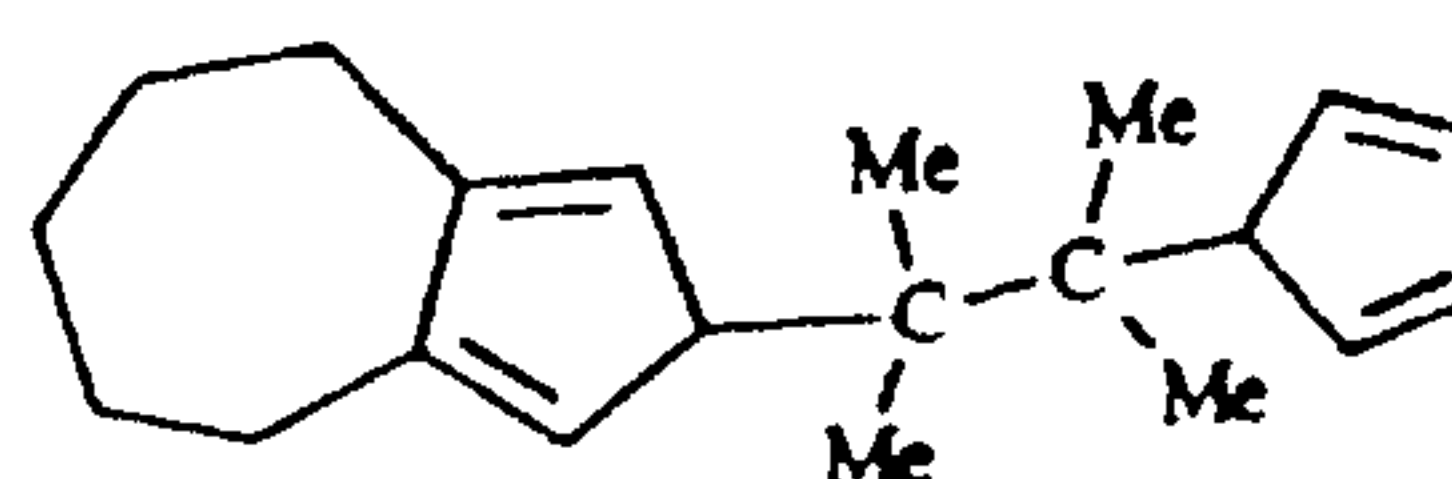
2-(1-Cyclopenta-2,4-dienyl-1-methyl-ethyl)-2,4,5,6,7,8-hexahydro-azulene



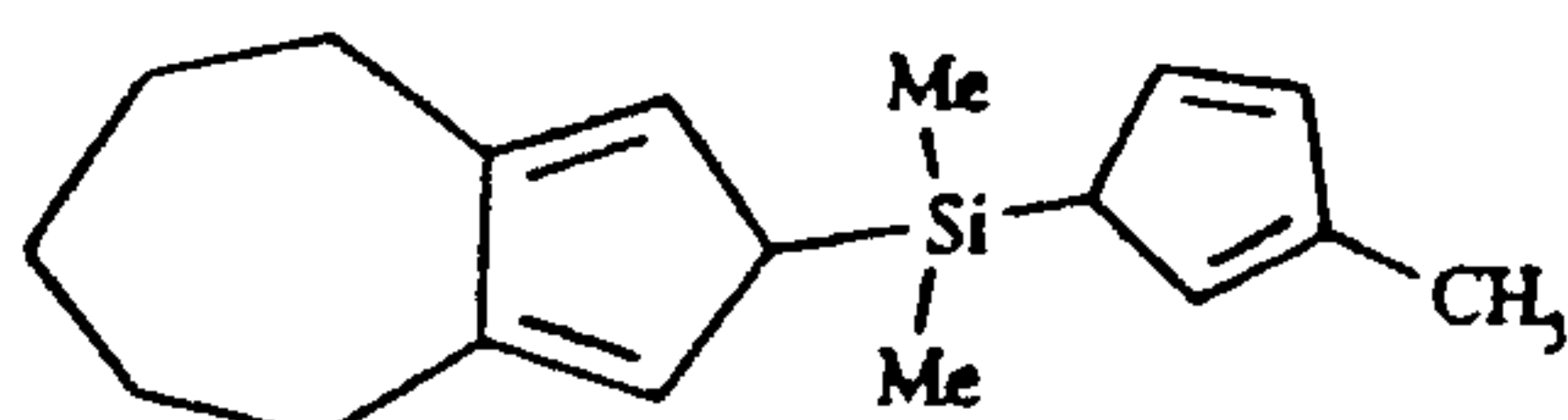
2-(Cyclopenta-2,4-dienyl-dimethyl-silanyl)-2,4,5,6,7,8-hexahydro-azulene



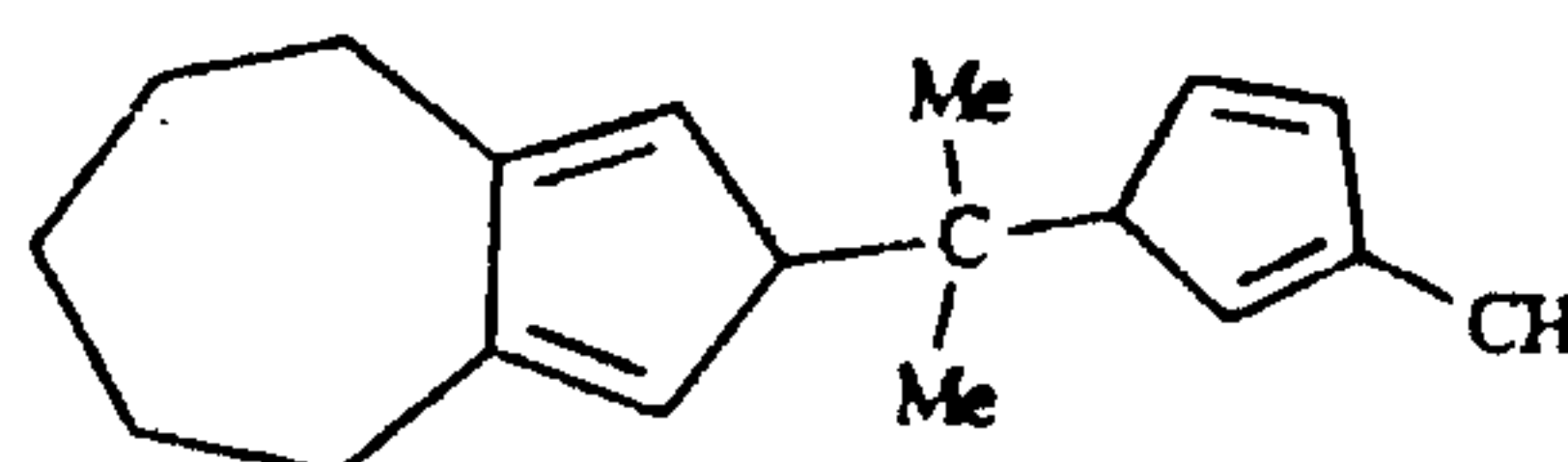
2-(2-Cyclopenta-2,4-dienyl-ethyl)-2,4,5,6,7,8-hexahydro-azulene



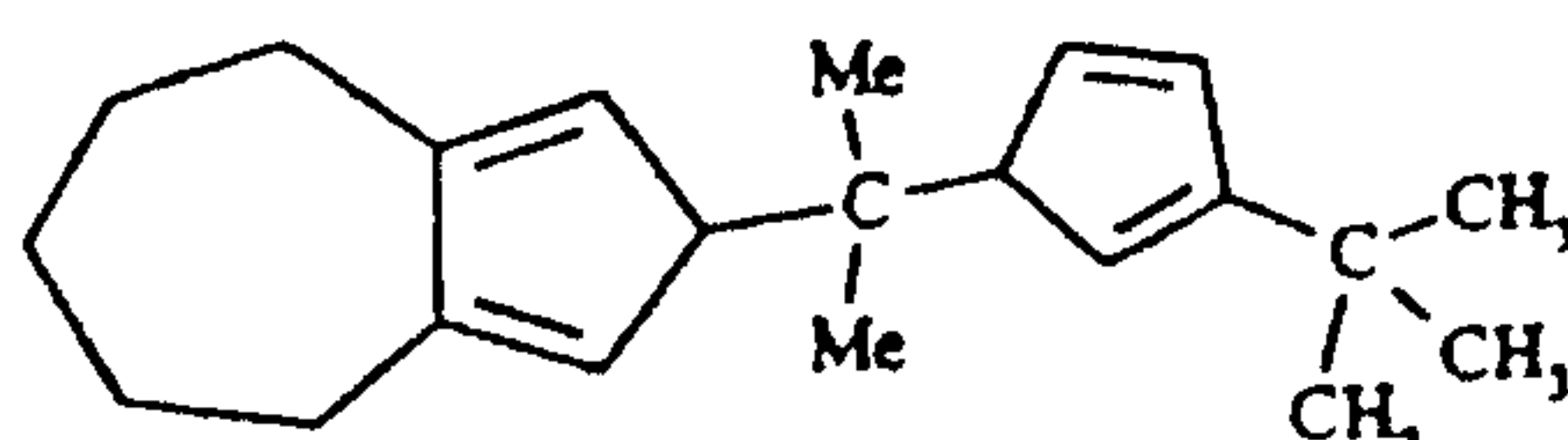
2-(2-Cyclopenta-2,4-dienyl-1,1,2-trimethyl-propyl)-2,4,5,6,7,8-hexahydro-azulene



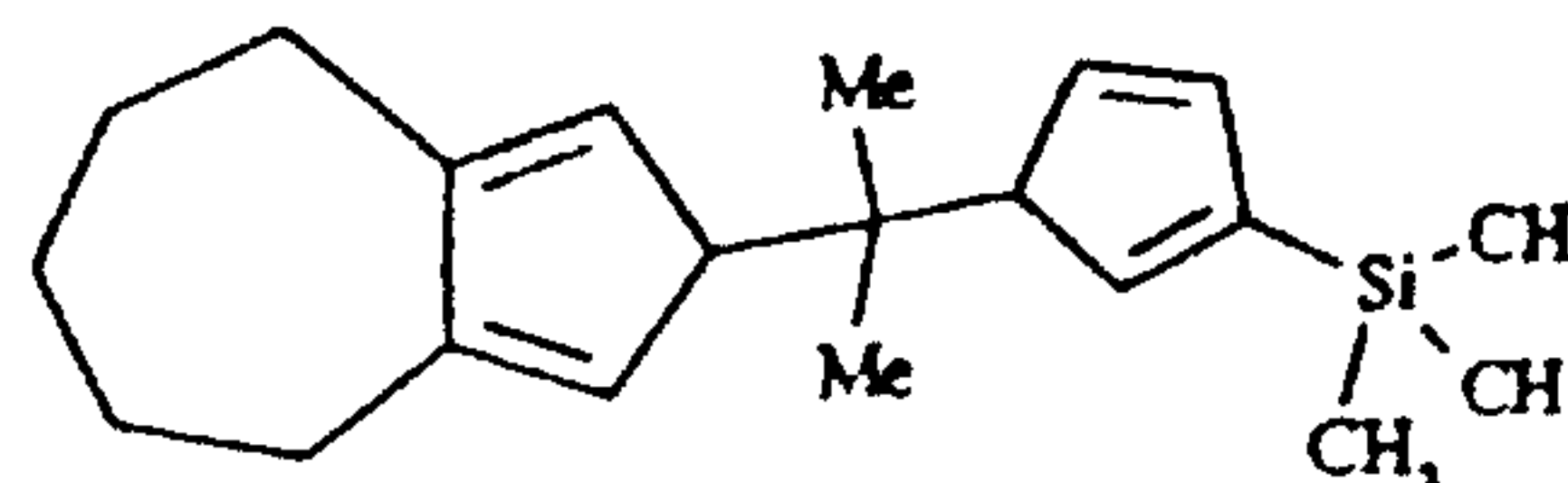
2-[Dimethyl-(3-methyl-cyclopenta-2,4-dienyl)-silanyl]-2,4,5,6,7,8-hexahydro-azulene



2-[1-Methyl-1-(3-methyl-cyclopenta-2,4-dienyl)-ethyl]-2,4,5,6,7,8-hexahydro-azulene

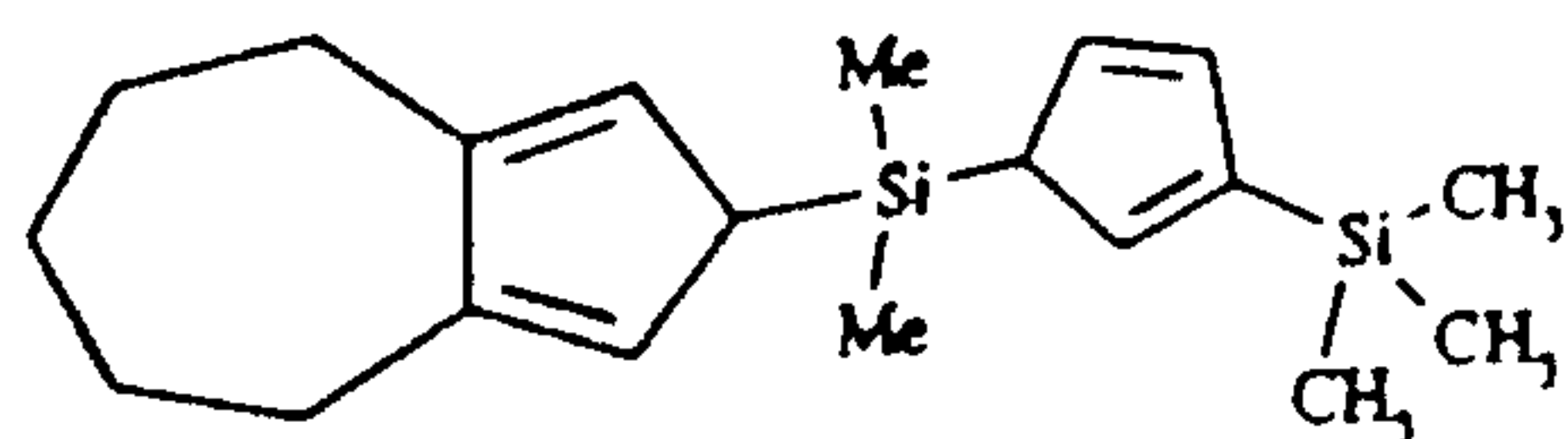


2-[1-(3-ter-Butyl-cyclopenta-2,4-dienyl)-1-methyl-ethyl]-2,4,5,6,7,8-hexahydro-azulene

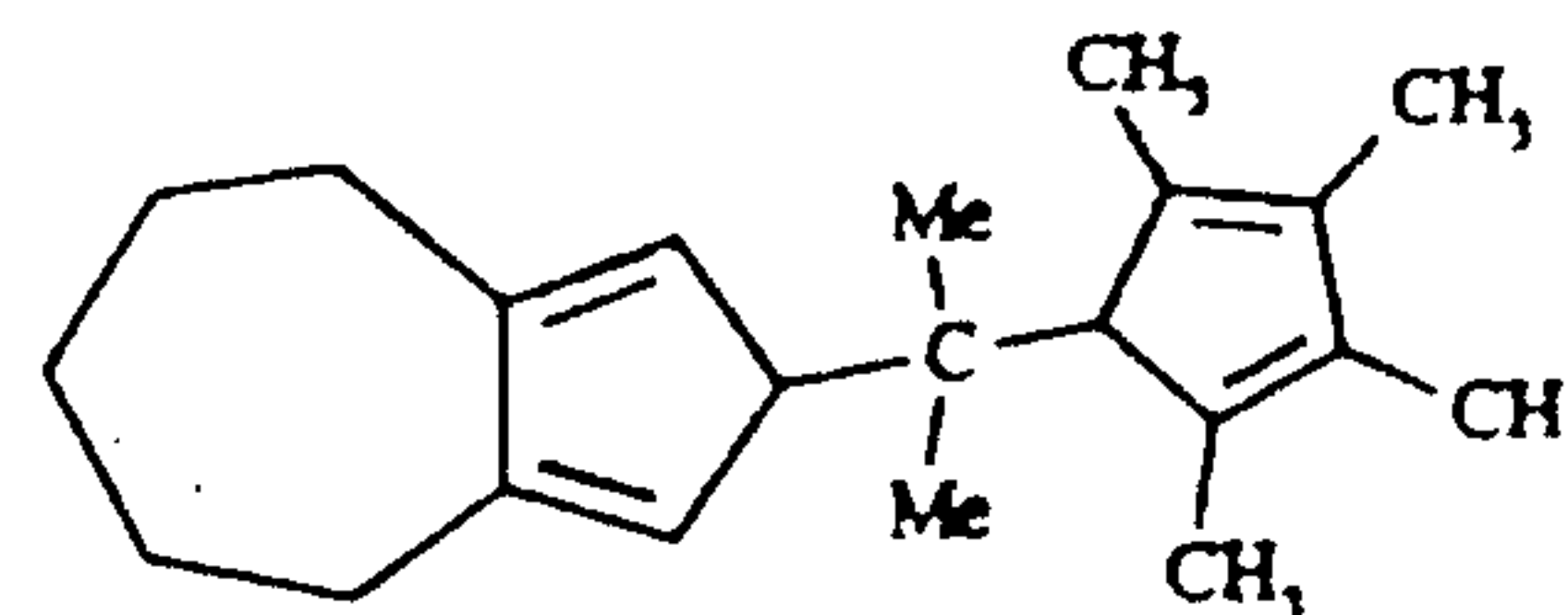


2-[1-(1-Methyl-1-(3-trimethylsilyl-cyclopenta-2,4-dienyl)-ethyl)-2,4,5,6,7,8-hexahydro-azulene

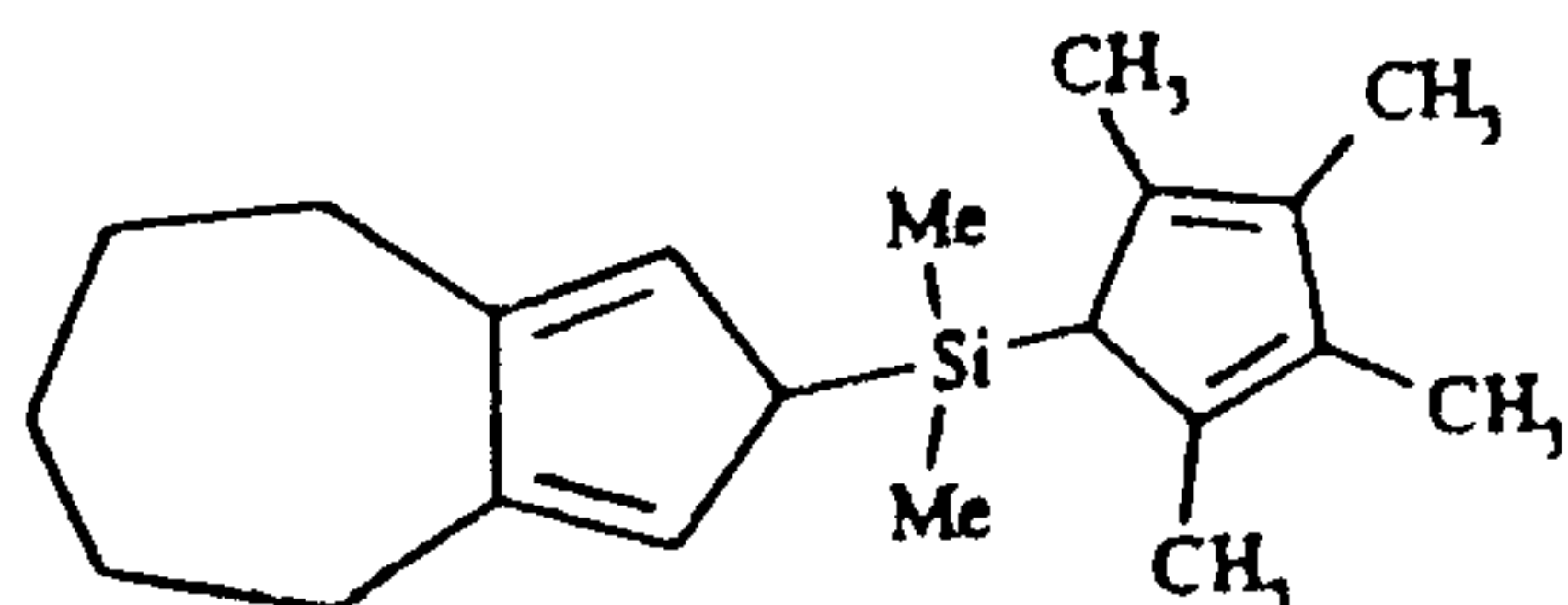
Table 3a



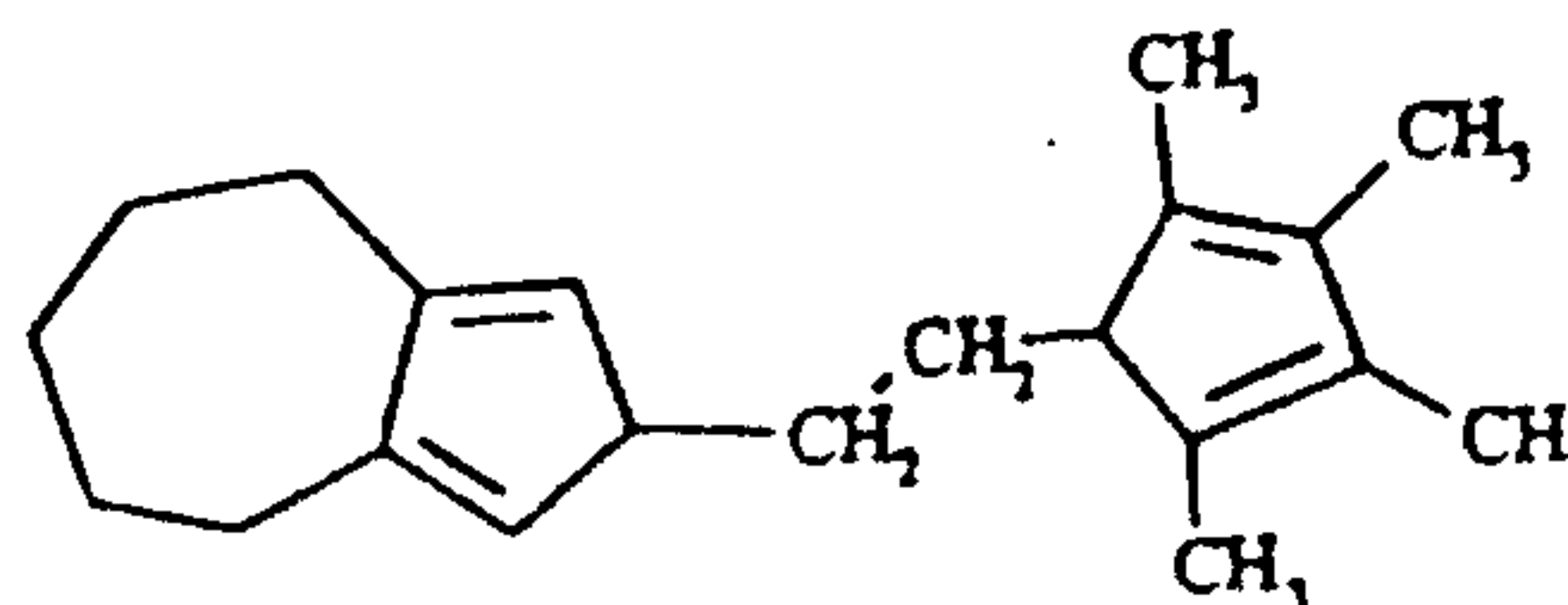
2-[dimethyl-(3-trimethylsilyl-cyclopenta-2,4-dienyl)-silyl]-2,4,5,6,7,8-hexahydro-azulene



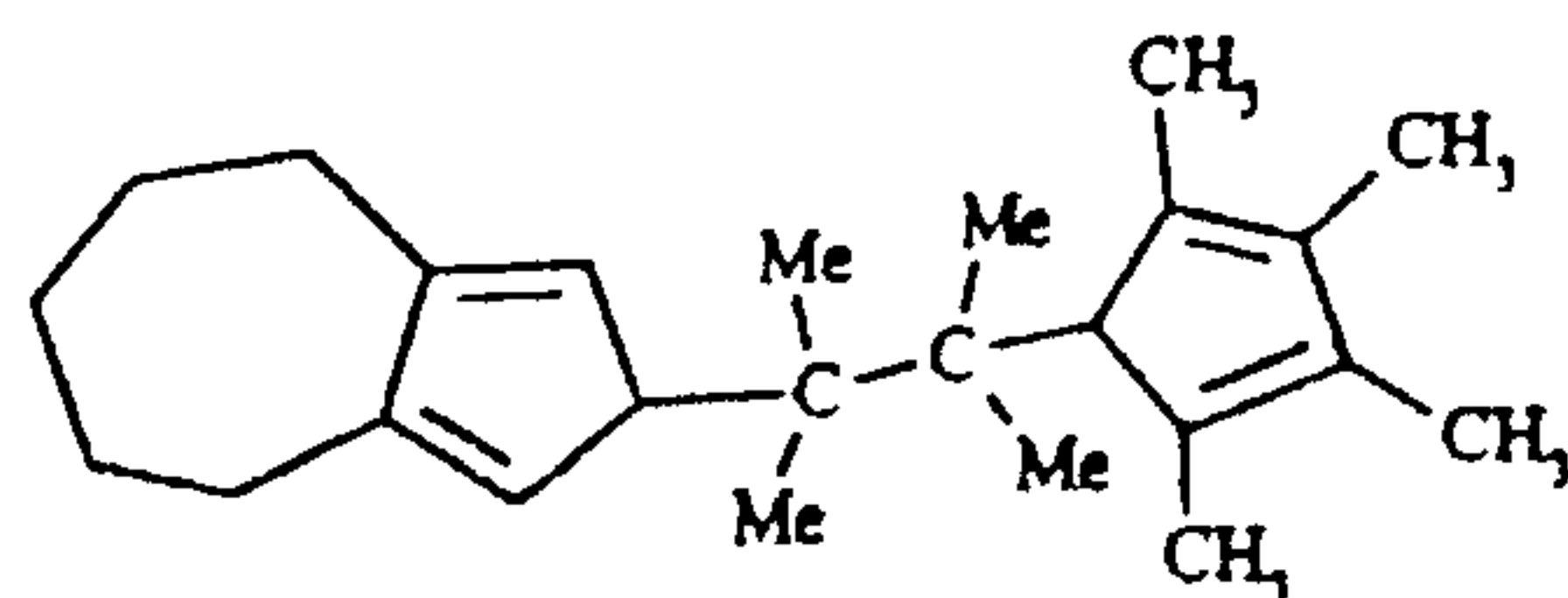
2-[1-methyl-1-(2,3,4,5-tetramethyl-cyclopenta-2,4-dienyl)-ethyl]-2,4,5,6,7,8-hexahydro-azulene



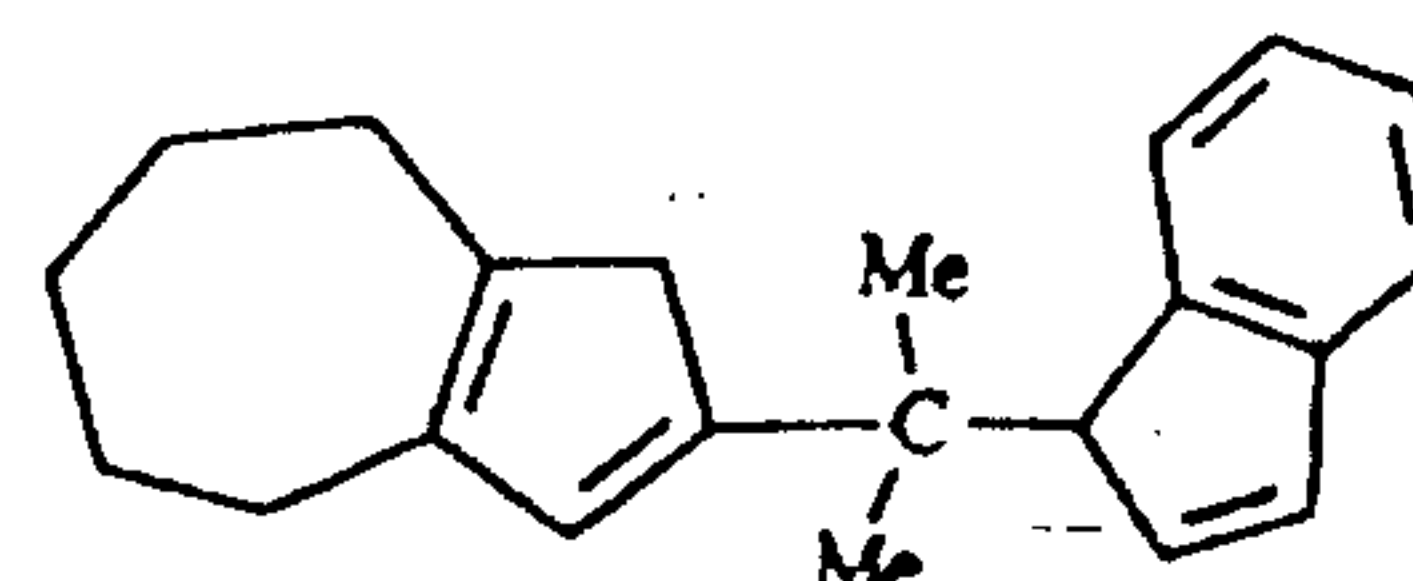
2-[Dimethyl-(2,3,4,5-tetramethyl-cyclopenta-2,4-dienyl)-silyl]-2,4,5,6,7,8-hexahydro-azulene



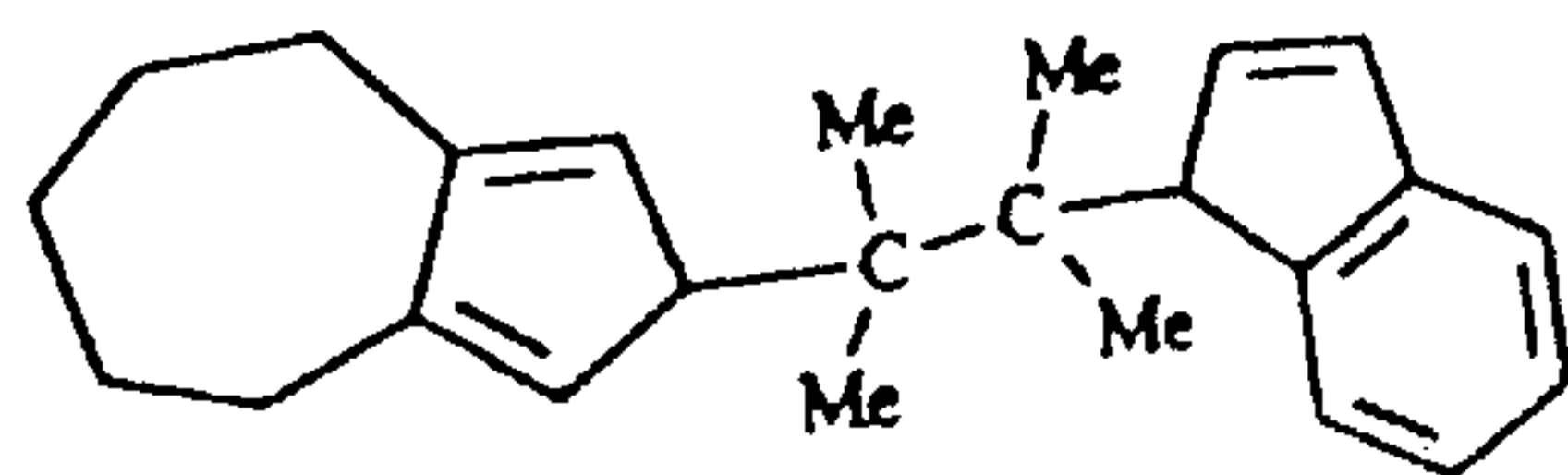
2-[2-(2,3,4,5-Tetramethyl-cyclopenta-2,4-dienyl)-ethyl]-2,4,5,6,7,8-hexahydro-azulene



2-[1,1,2-Trimethyl-2-(2,3,4,5-Tetramethyl-cyclopenta-2,4-dienyl)-propyl]-2,4,5,6,7,8-hexahydro-azulene

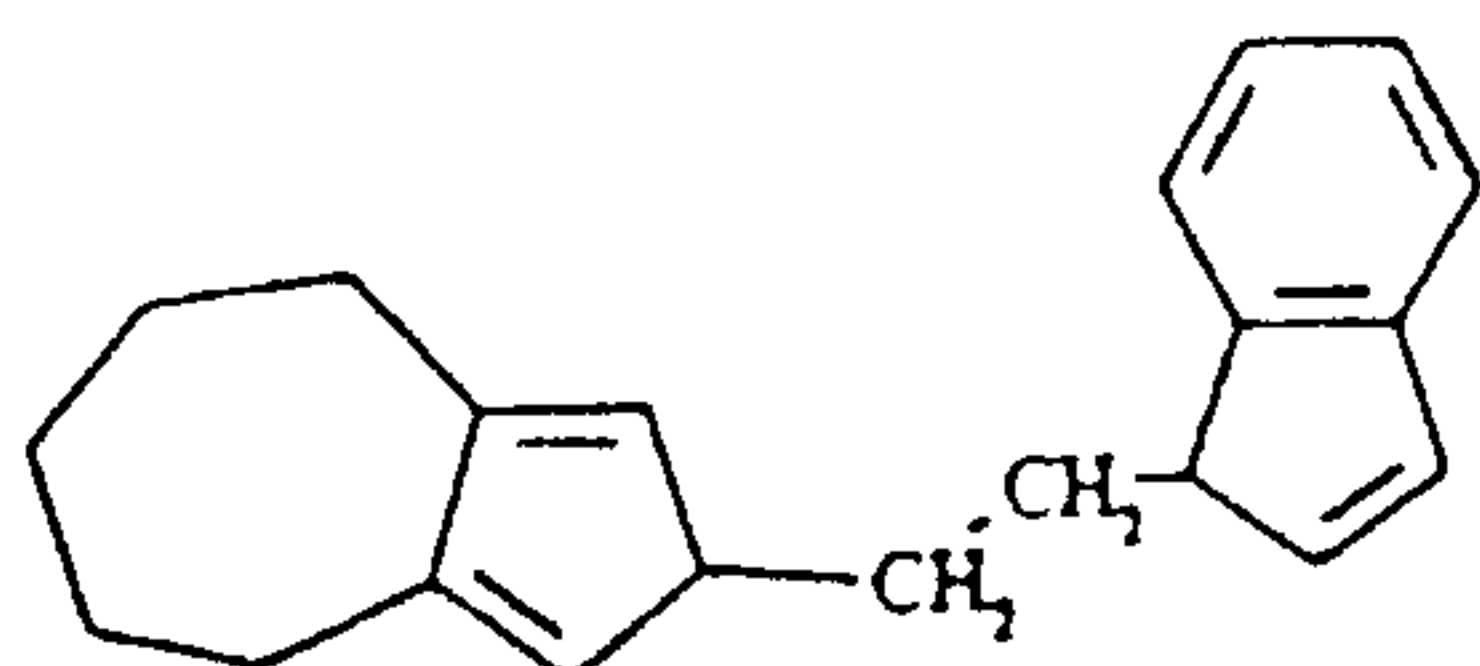


2-[1-(1H-Inden-1-yl)-1-methyl-ethyl]-1,4,5,6,7,8-hexahydro-azulene

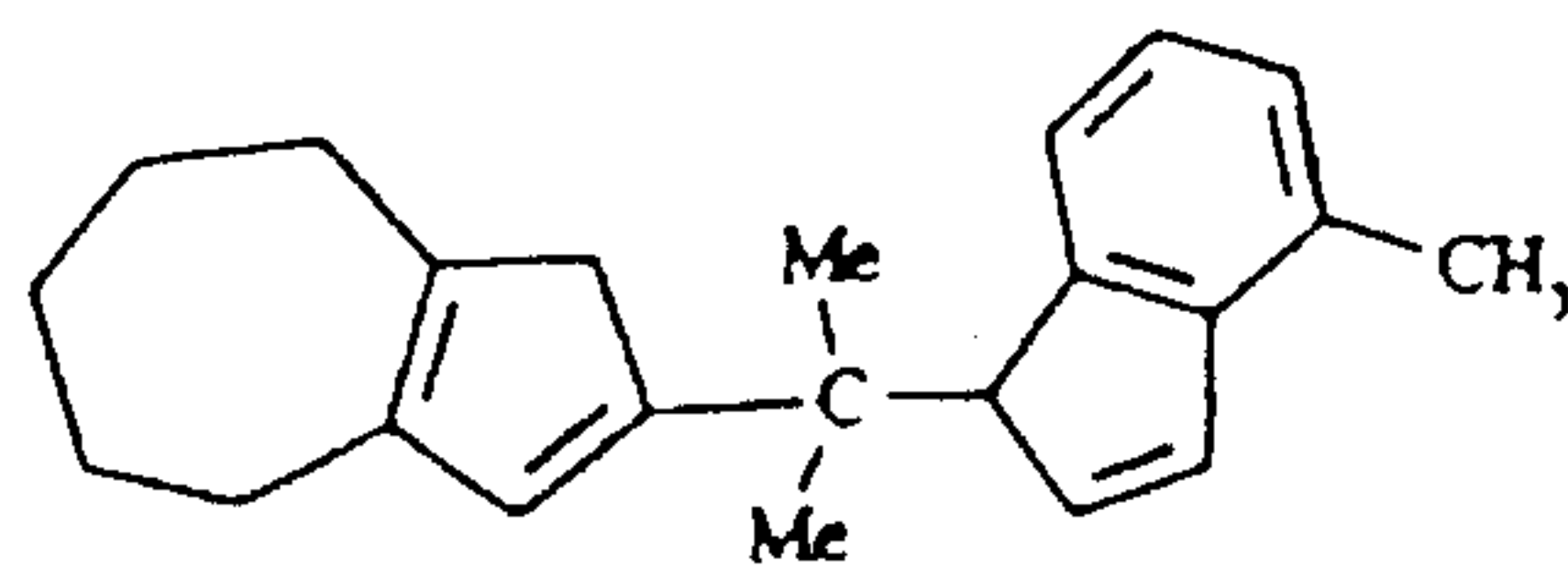


2-[2-(1H-Inden-1-yl)-1,1,2-trimethyl-propyl]-2,4,5,6,7,8-hexahydro-azulene

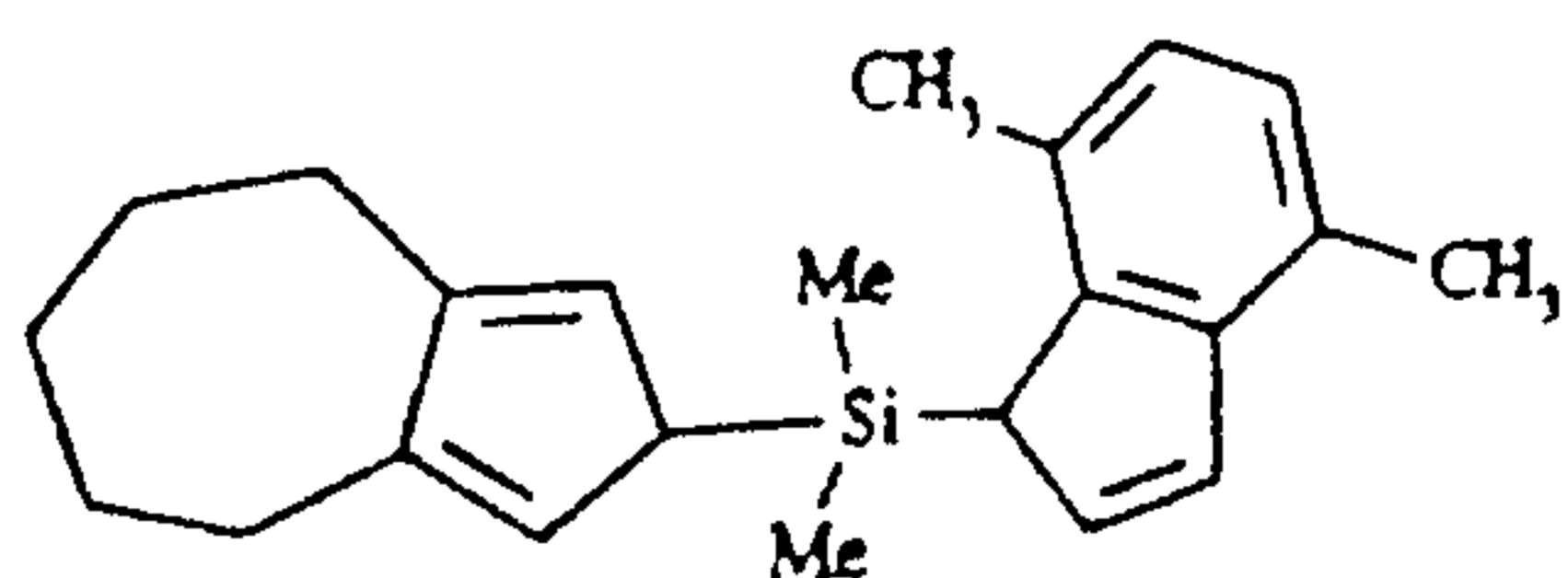
Table 3b



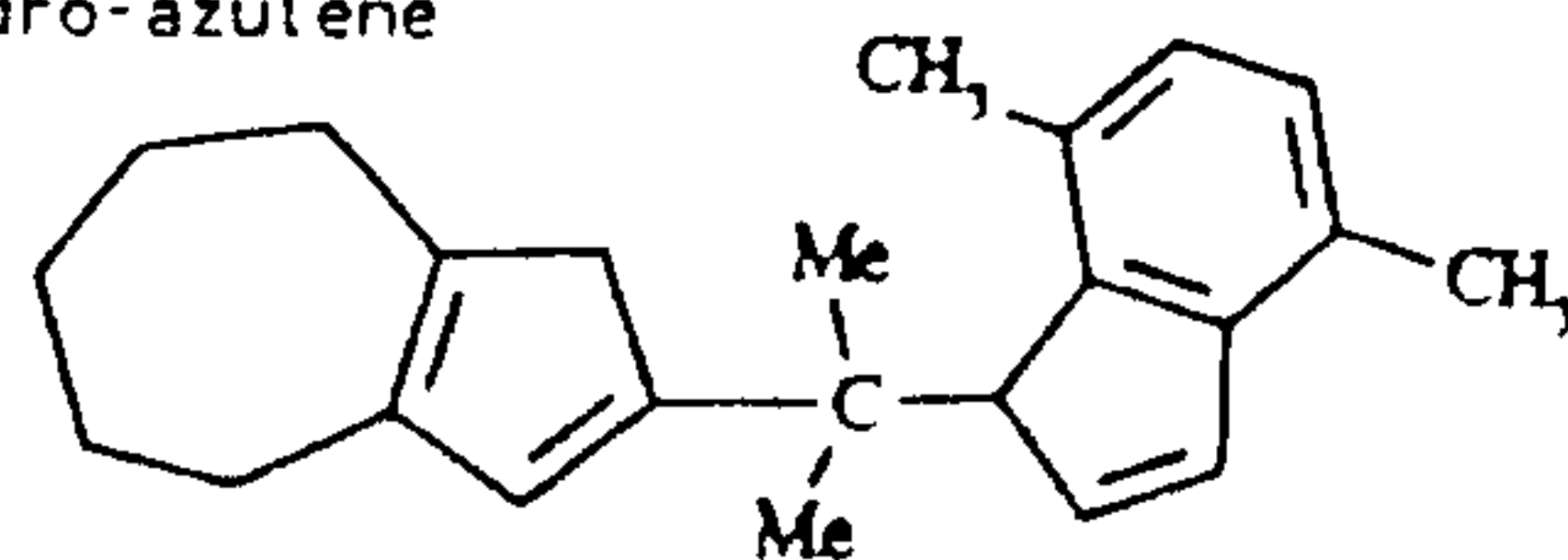
2-[2-(1H-inden-1-yl)-ethyl]-2,4,5,6,7,8-hexahydro-azulene



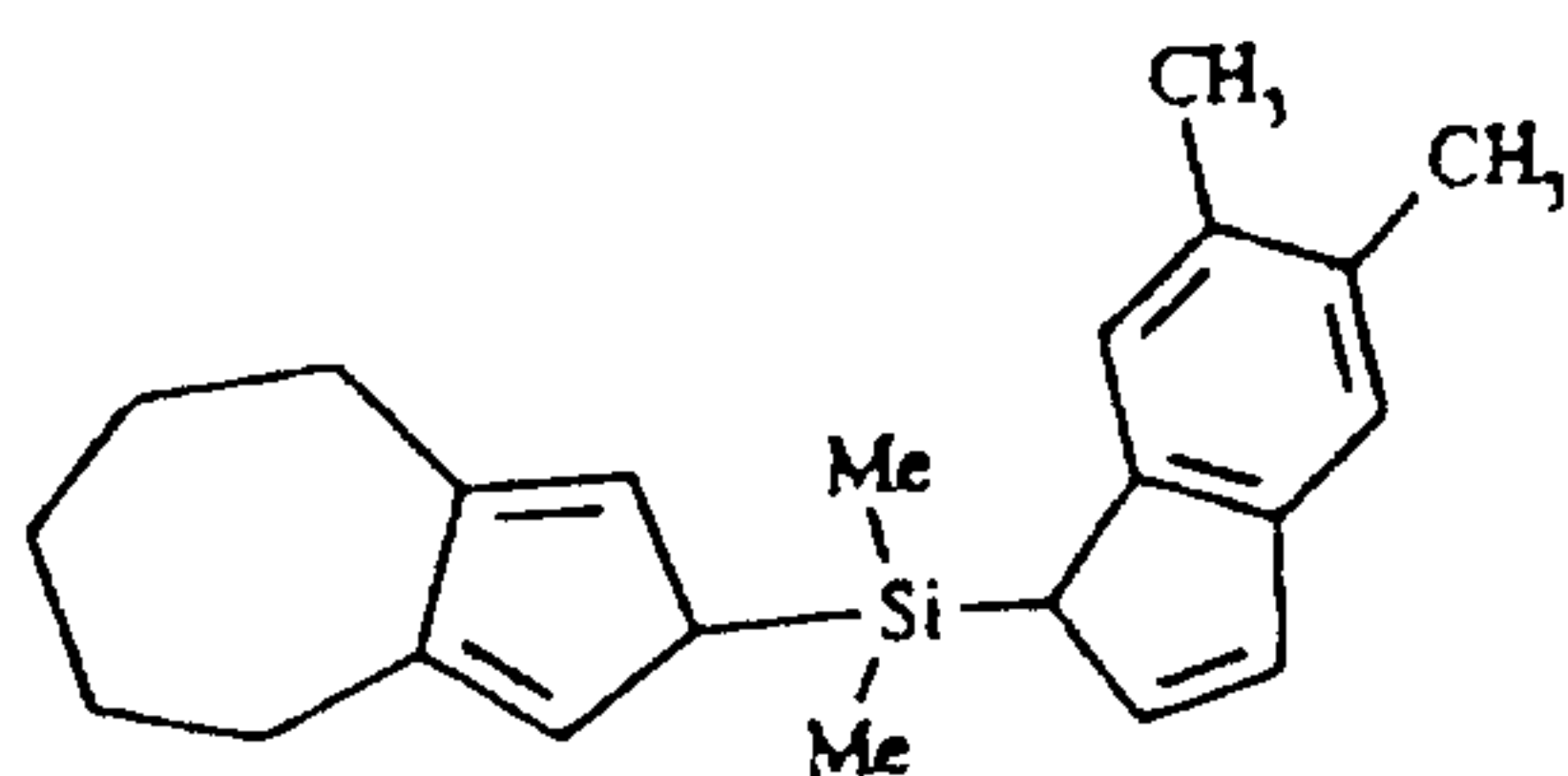
2-[1-methyl-1-(4-methyl-1H-inden-1-yl)-ethyl]-1,4,5,6,7,8-hexahydro-azulene



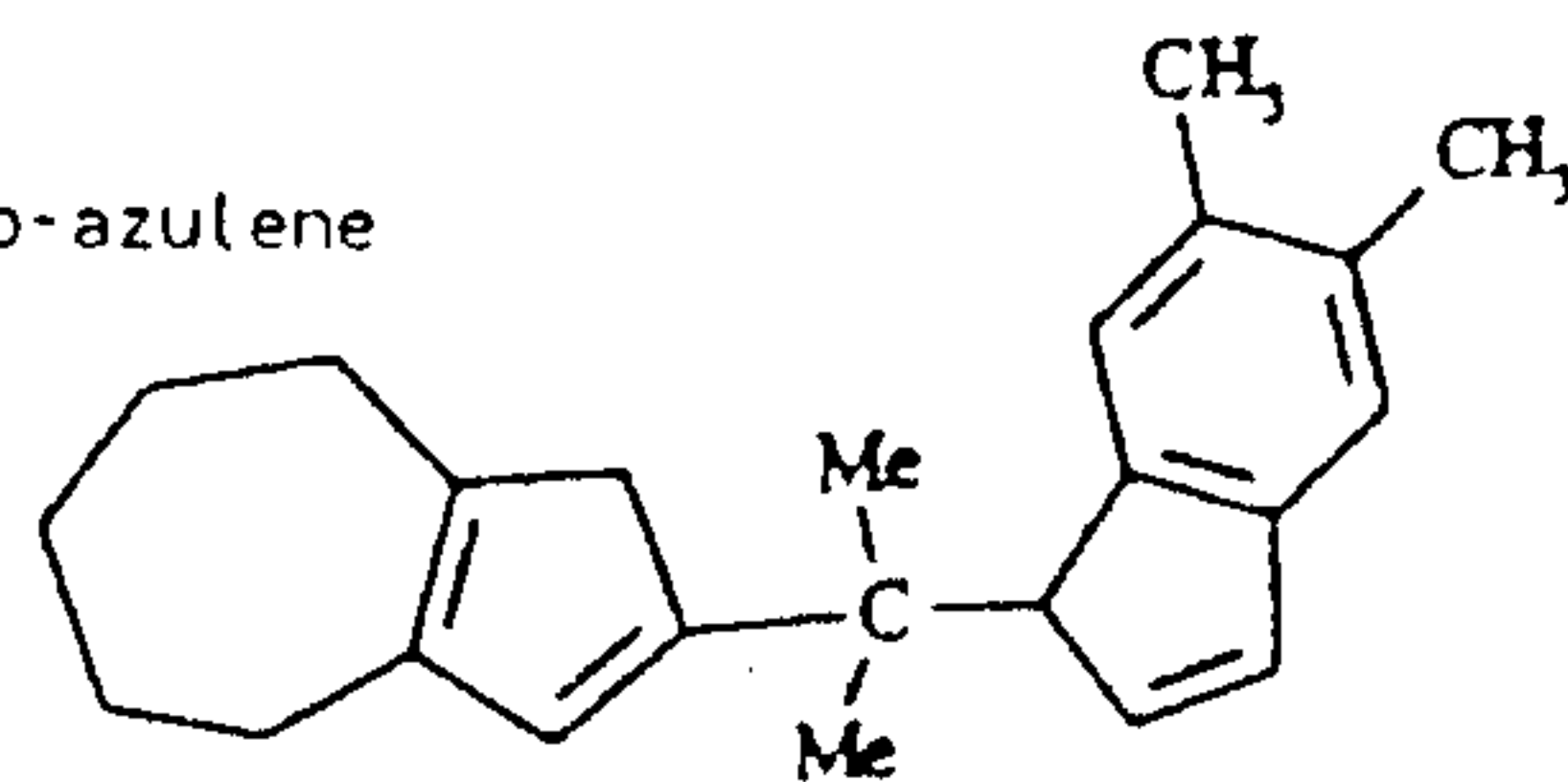
2-[(4,7-dimethyl-1H-inden-1-yl)-dimethyl-silanyl]-2,4,5,6,7,8-hexahydro-azulene



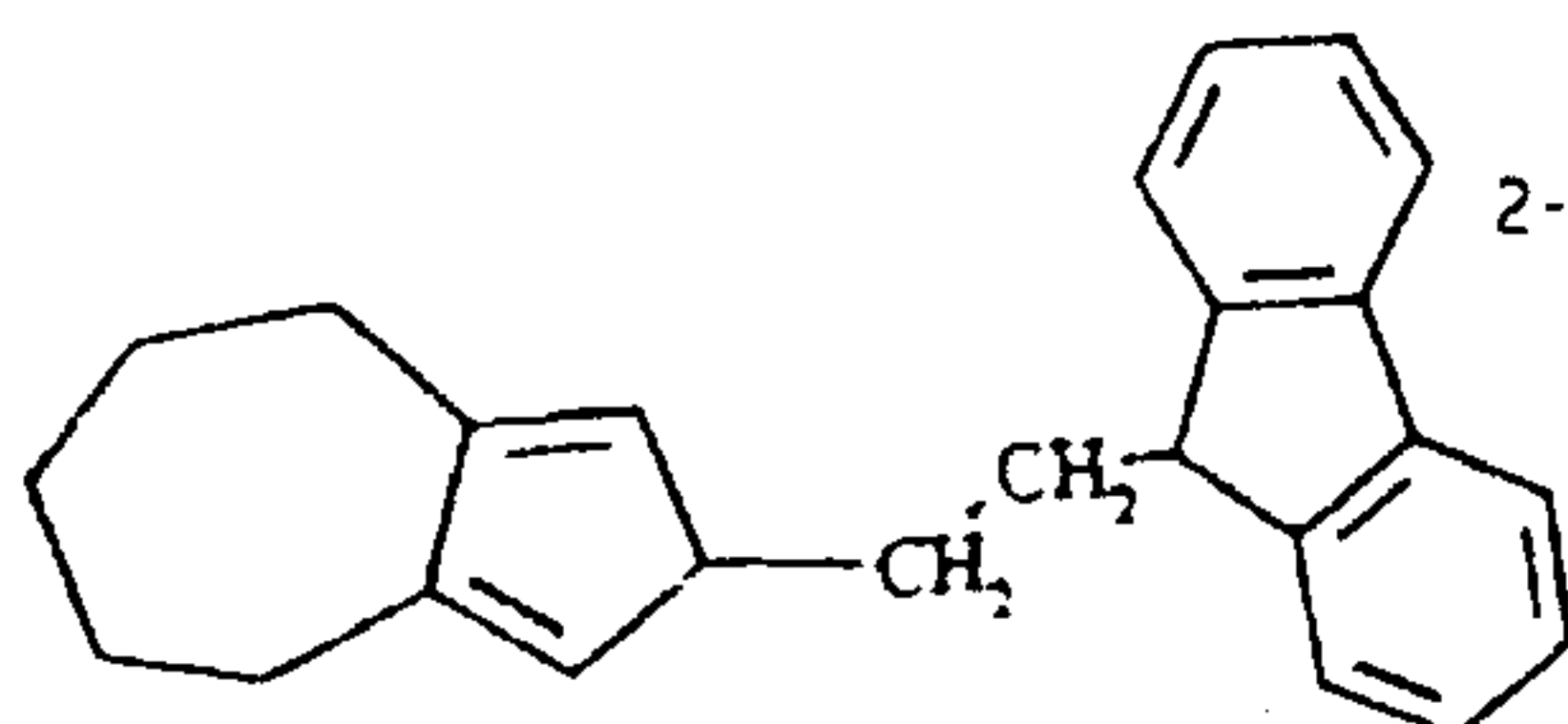
2-[1-(4,7-dimethyl-1H-inden-1-yl)-1-methyl-ethyl]-1,4,5,6,7,8-hexahydro-azulene



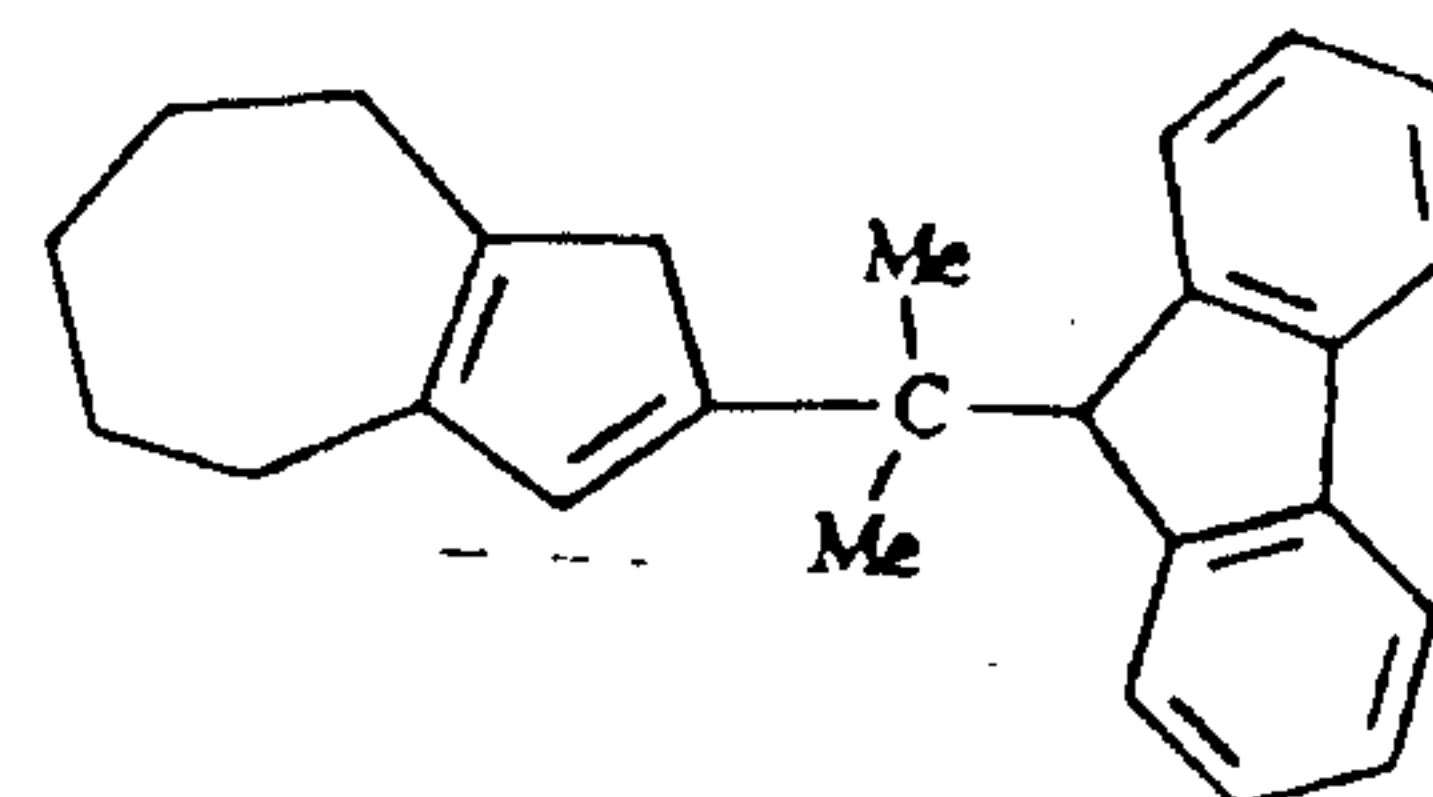
2-[(5,6-dimethyl-1H-inden-1-yl)-dimethyl-silanyl]-2,4,5,6,7,8-hexahydro-azulene



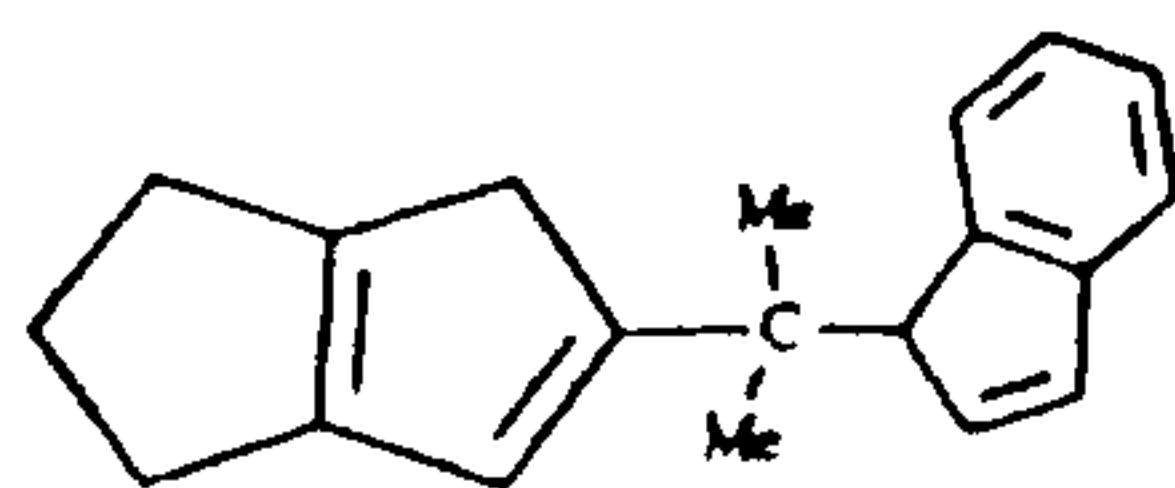
2-[1-(5,6-dimethyl-1H-inden-1-yl)-1-methyl-ethyl]-1,4,5,6,7,8-hexahydro-azulene



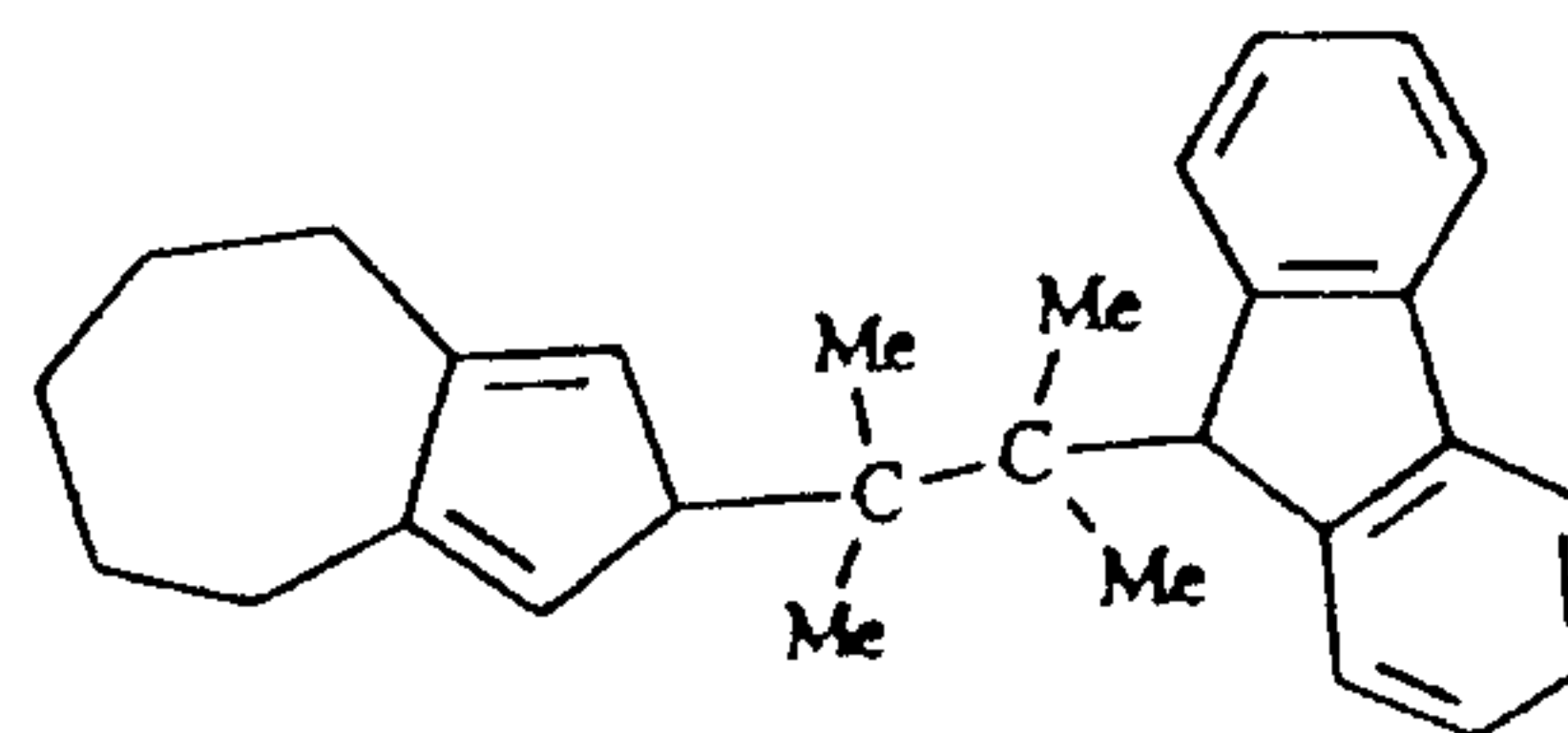
9-[2-(2,4,5,6,7,8-hexahydro-azulen-2-yl)-ethyl]-9H-fluorene



9-[1-(3,4,5,6,7,8-hexahydro-azulen-2-yl)-1-methyl-ethyl]-9H-fluorene

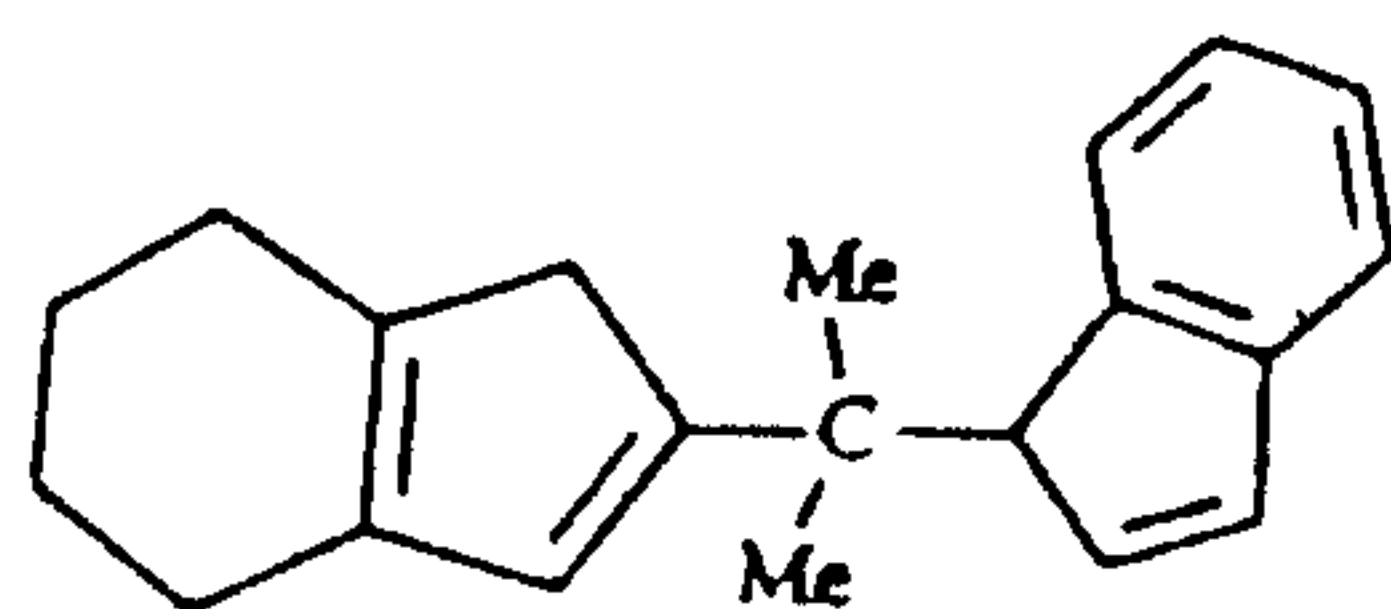


1-[1-methyl-1-(3,4,5,6-tetrahydro-pentalen-2-yl)-ethyl]-1H-indene

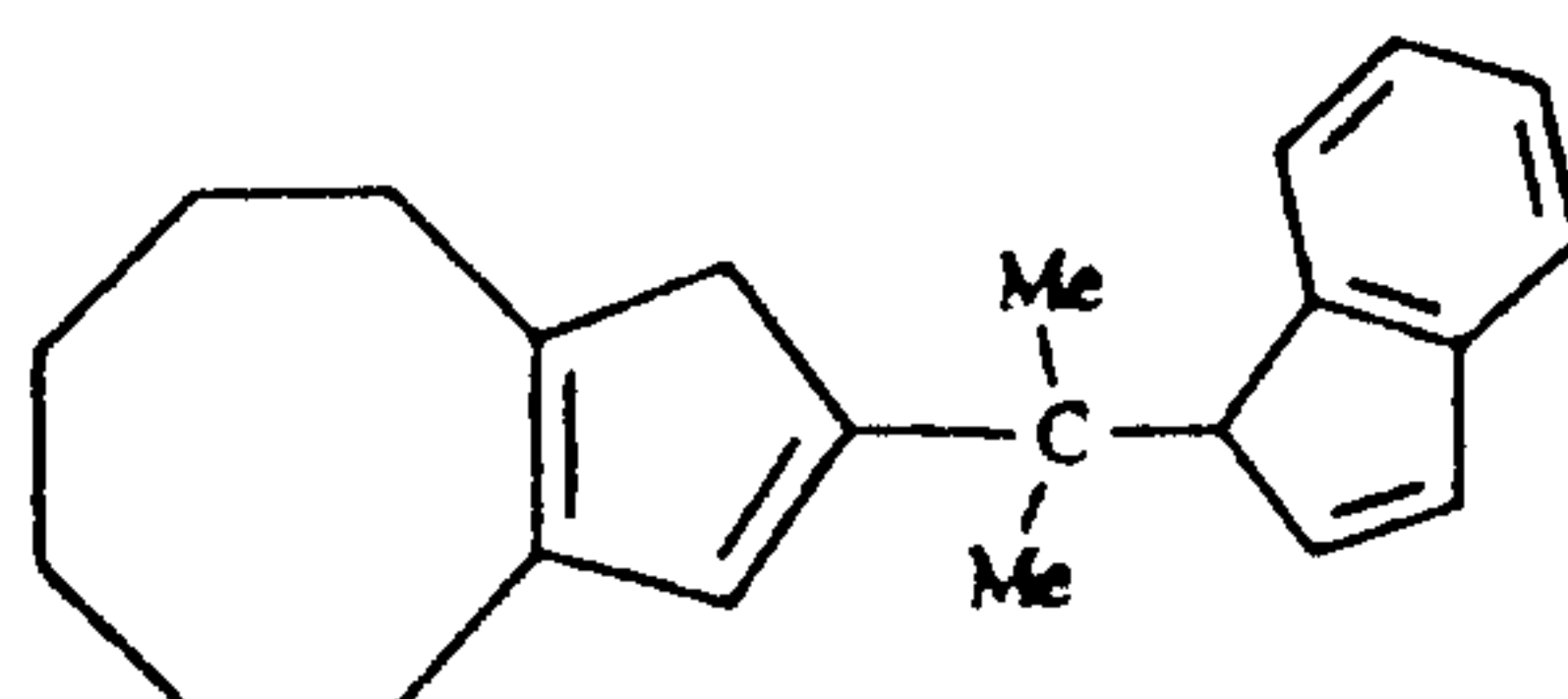


9-[2-(2,4,5,6,7,8-hexahydro-azulen-2-yl)-1,1,2-trimethyl-propyl]-9H-fluorene

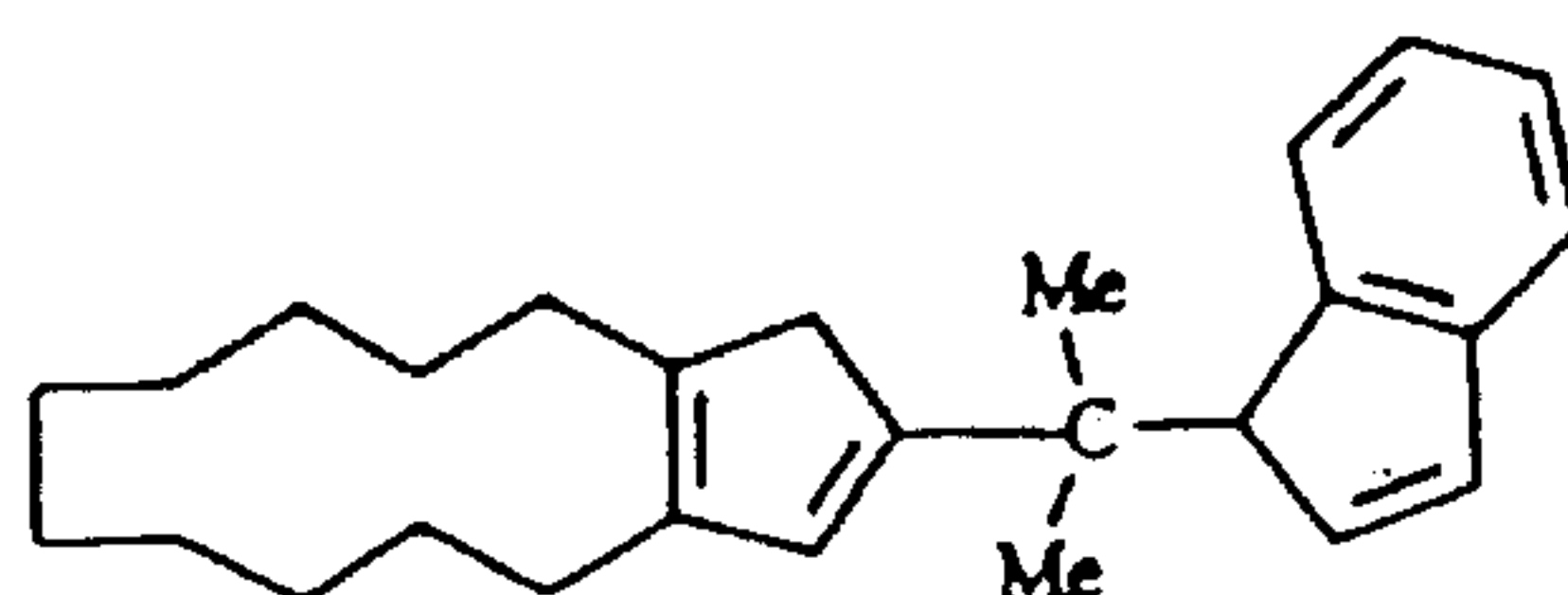
Table 3c



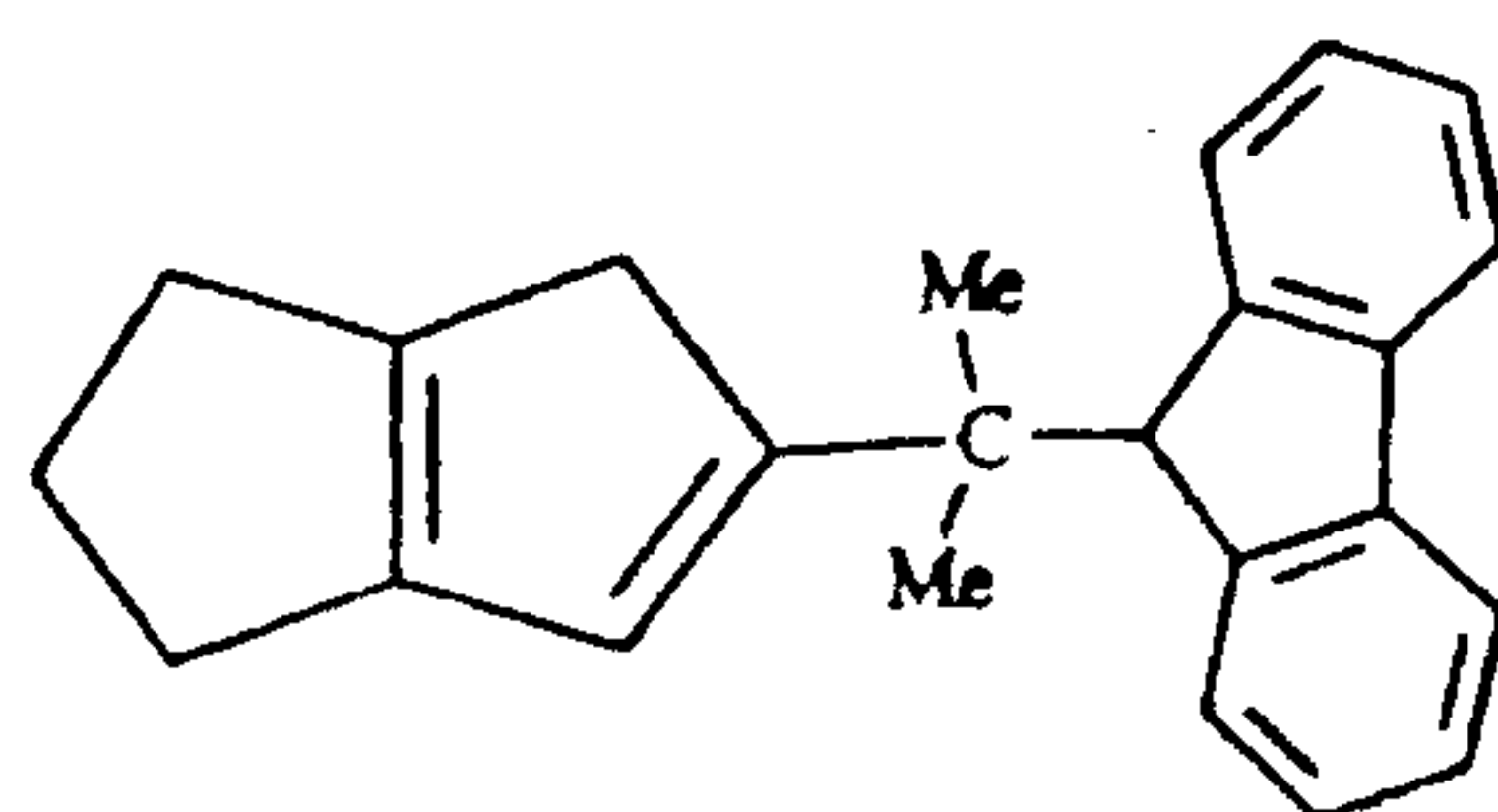
1-[1-Methyl-1-(4,5,6,7-tetrahydro-3H-inden-2-yl)-ethyl]-1H-indene



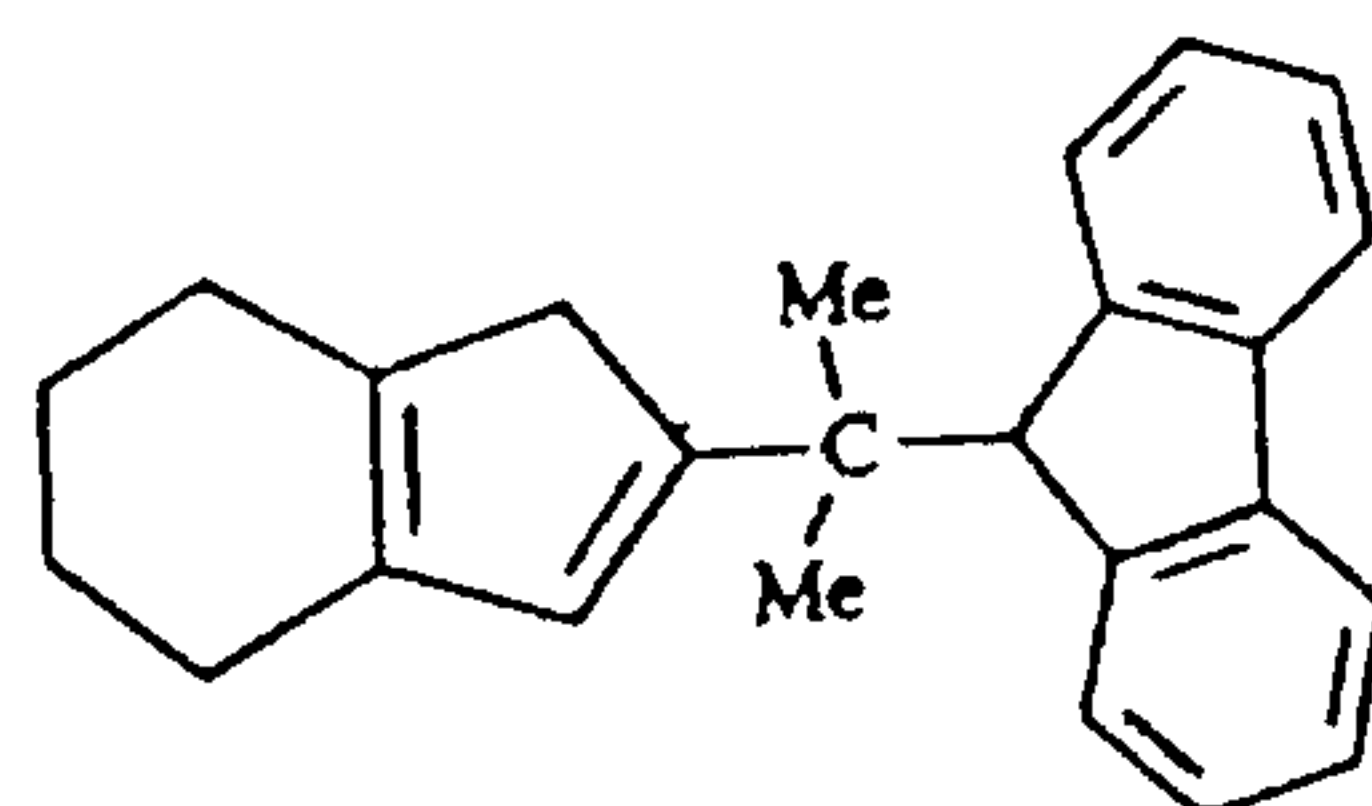
2-[1-(1H-Inden-1-yl)-1-methyl-ethyl]-4,5,6,7,8,9-hexahydro-1H-cyclopentacyclooctene



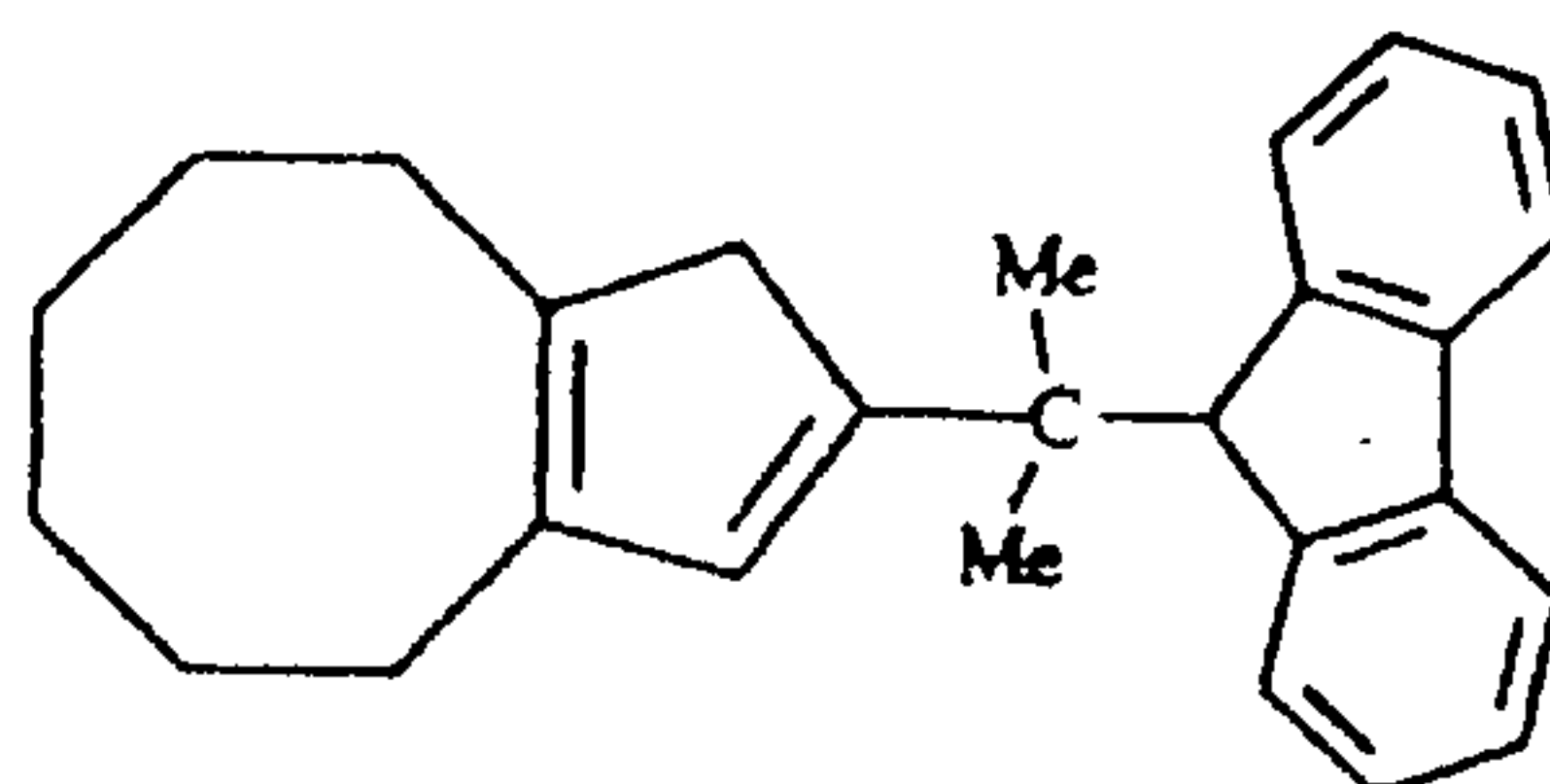
2-[1-(1H-Inden-1-yl)-1-methyl-ethyl]-4,5,6,7,8,9,10,11,12,13-decahydro-1H-cyclopentacyclododecene



9-[1-Methyl-1-(3,4,5,6-tetrahydro-pentalen-2-yl)-ethyl]-9H-fluorene



9-[1-Methyl-1-(4,5,6,7-tetrahydro-3H-inden-2-yl)-ethyl]-9H-fluorene

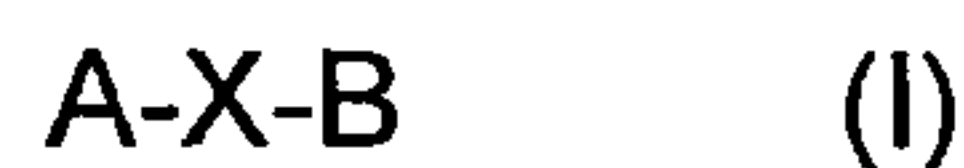


9-[1-(4,5,6,7,8,9-hexahydro-3H-cyclopentacycloocten-2-yl)-1-methyl-ethyl]-9H-fluorene

Table 3d

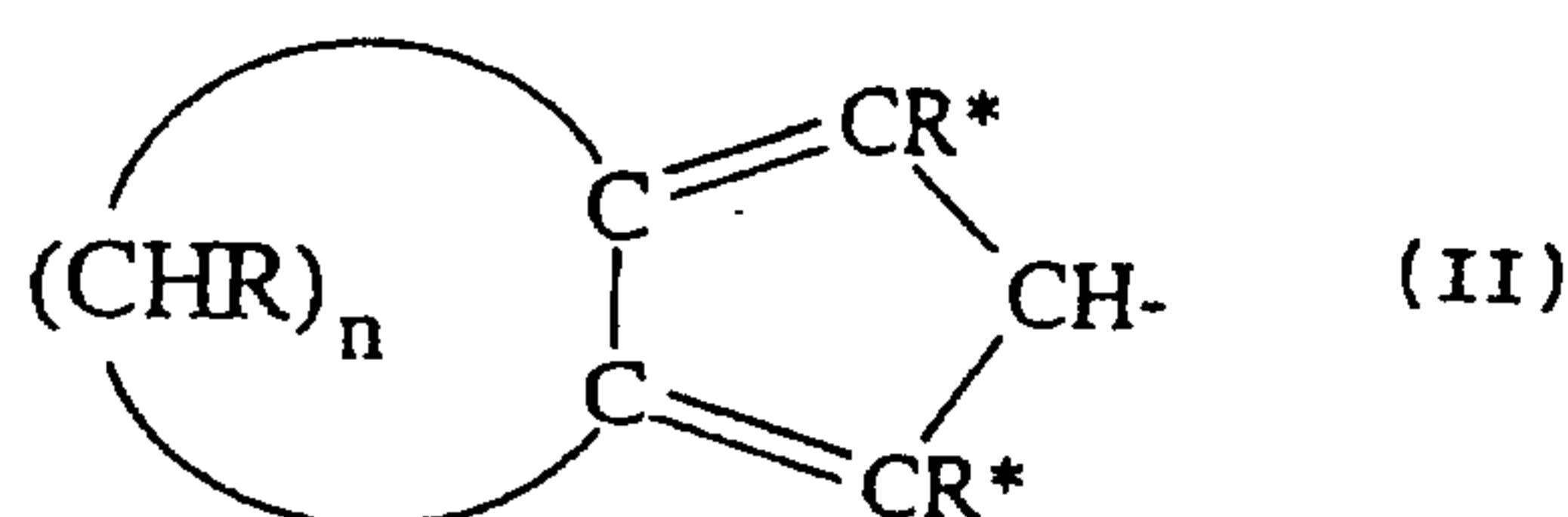
WHAT IS CLAIMED IS:

1. Bridged cyclopentadienyl derivatives having general formula (I)



wherein

- 1) A is a monofunctional hydrocarbyl radical having general formula (II):



wherein R and R* are selected from:

- H,
- monofunctional alkyl radicals having from 1 to 3 carbon atoms, and
- monofunctional alkylaryl or aryl radicals, with the proviso that the number of R different from H is not more than 2 and that at least one R* is H;

- 2) n is an integer from 2 to 20;

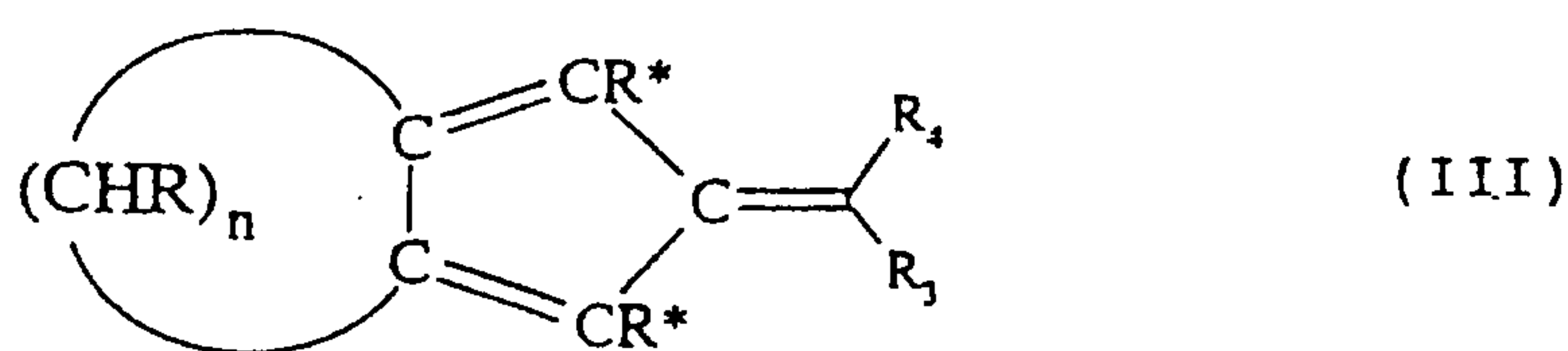
- 3) -X- is the bridge between A and B and consists of a bifunctional radical selected from:

- a) a linear, branched or cyclic C₂-C₂₀ alkylene group;
- b) an alkyl or aryl substituted silanylene group having from 1 to 2 silicon atoms;
- c) an alkyl substituted silaalkylene group; and
- d) a siloxasilanylene group or -Si(R₁)₂-O-Si(R₂)₂- tetraalkyl or tetraaryl substituted;

- 4) B is a monofunctional hydrocarbyl radical selected from:
 - e) any of the A radicals defined above; and
 - f) a cyclopentadienyl radical.
2. The cyclopentadienyl derivatives according to claim 1, wherein all the $R=H$, R^* is selected from H and CH_3 .
3. The cyclopentadienyl derivatives according to claim 1, wherein n is selected from 3,4,5,6 and 10.
4. The cyclopentadienyl derivatives according to claim 1, wherein $R=R^*=H$ and n is selected from 5, 6 and 10.
- 10 5. The cyclopentadienyl derivatives according to claim 1, wherein -X- is selected from linear or branched alkylene derivatives and dialkylsilanylenes.
6. The cyclopentadienyl derivatives according to claim 5, wherein -X- is selected from ethylene, isopropylidene and dimethylsilanylene.
7. The cyclopentadienyl derivatives according to claim 1, wherein B is a monofunctional cyclopentadienyl radical (f) selected from cyclopentadienyl, indenyl, fluorenyl and the corresponding alkyl, aryl and trialkylsilyl substituted derivatives.
- 20 8. The cyclopentadienyl derivatives according to claim 7, wherein B is a monofunctional cyclopentadienyl radical (f) selected from cyclopentadienyl, indenyl and fluorenyl.
9. A process for the preparation of a compound having the general formula A-X-B, wherein A and B have the meaning as defined in claim 1 and -X- is a radical of the type $-C(R_3R_4)-$, wherein R_3 and R_4 are selected from

monofunctional C₁-C₅ alkyl radicals and phenyl, or R₃ and R₄ jointly form a C₄-C₅ alkylene radical, which involves the following steps:

- i) condensation between a hydrocarbon having the general formula A-H defined in claim 1 and a ketone having the general formula: R₃-CO-R₄ to give a fulvene compound having general formula (III)



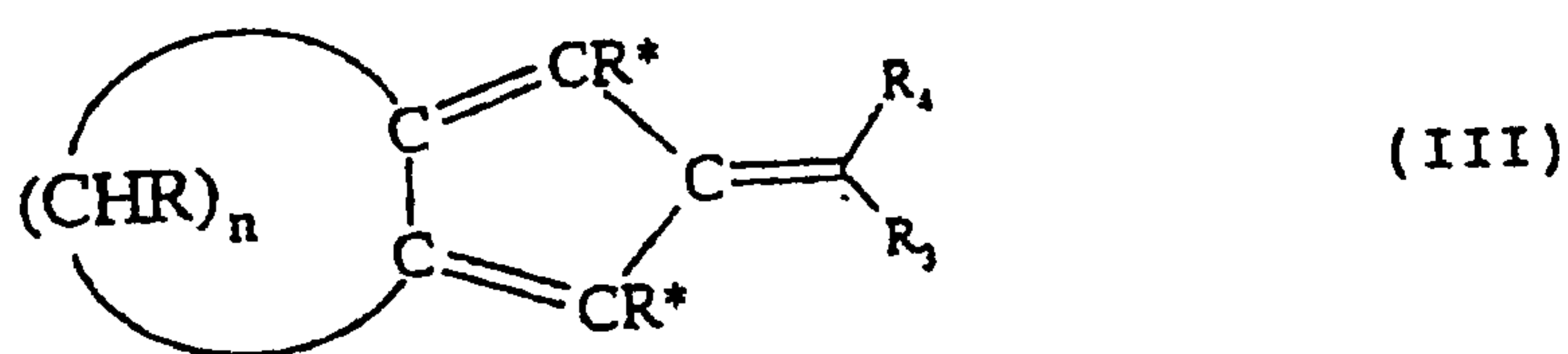
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- ii) a addition to the fulvene compound having general formula (III) obtained in step (i), of a hydrocarbon BH, the above hydrocarbon BH being selected from the group of hydrocarbons corresponding to the monofunctional hydrocarbyl radicals (e) and (f) defined in claim 1.

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10. The process according to claim 9, characterized in that:
 step (i) takes place in a basic environment,
 step (ii) is carried out by preparing an anion of the hydrocarbon BH and subsequently interacting the above anion with the fulvene compound (III) obtained in step (i).
11. The process according to claim 10, characterized in that step (i) takes place with an alcoholate of a tertiary alcohol.
12. The process according to claim 10, characterized in that step (i) takes place with potassium tert-butyrate.

13. The process according to claim 9, wherein R^* is selected from H and CH_3 , $R=H$, $R_3=R_4=CH_3$ or C_6H_5 , and n is selected from 3,4,5,6 and 10.
14. The process according to claim 13, wherein the ketone having the general formula R_3-CO-R_4 is acetone and n is selected from 5,6 and 10.
15. Fulvene derivatives having general formula (III)



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wherein n , R^* , R , R_3 and R_4 have the meaning as defined in claim 1.

16. Fulvene derivatives according to claim 15, wherein $R=H$, R^* is selected from H and CH_3 , $R_3=R_4=CH_3$, and n is selected from 3,4,5,6 and 10.
17. A process for obtaining a compound having general formula $A1-X-A1$ wherein $-X-$ is a dialkylsilanylene and the $A1$ radicals, the same as each other, are selected from the group of A radicals defined in claim 1, which comprises the reaction of an $A1H$ hydrocarbon with a dialkyl dihalogen silane, in a molar ratio $A1H$ /dialkyl dihalogen silane of about 2/1.
- 20 18. The process according to claim 17, wherein the dialkyldihalogen silane is dialkyldichlorosilane.
19. A process for obtaining a compound having the general formula $A1-X-B$ wherein:
 $-X-$ is a dialkylsilanylene;
 $A1$ is a monofunctional hydrocarbyl radical selected from the A radicals defined in claim 1;

B is selected from:

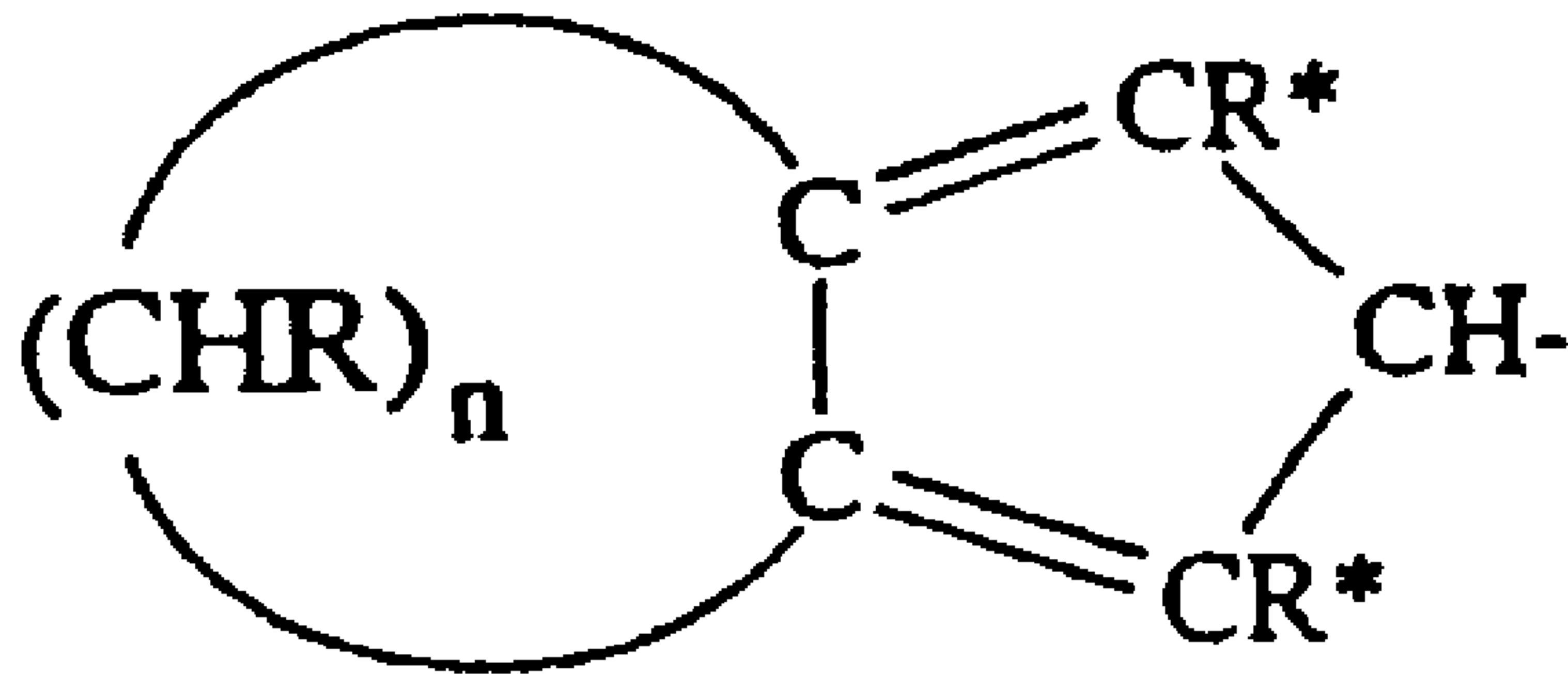
-- A2, where A2 is any of the A radicals defined in claim 1 provided it is different from A1, and

-- a cyclopentadienyl radical (f),

the above process being carried out in two steps, the first of which (step a) comprising the reaction of the compound A1H with a dialkyl dihalogen silane, in a molar ratio A1H/dialkyl dihalogen silane of about 1/1; the second step comprising the reaction of the compound obtained in step (a) with a hydrocarbon BH in an essentially equimolar ratio with respect to the product obtained in step (a).

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20. Process according to claim 19, characterized in that the dialkyl dihalogen is a dialkyl dichlorosilane.



(II)