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(54) Titre : POLYMERISATION CATIONIQUE D'OLEFINES EN PRESENCE D'EAU AU MOYEN DE CO-AMORCEURS
FLUOROARYLIQUES DINUCLEAIRES
(54) Title: CATIONIC POLYMERIZATION OF OLEFINS IN THE PRESENCE OF WATER USING DINUCLEAR
FLUOROARYL CO-INITIATORS

(57) **Abrégé/Abstract:**

A method is provided for cationically polymerizing olefin monomer by using a novel coinitorator in the presence of water. More specifically, a method is provided for cationically polymerizing olefin monomer by using a novel coinitorator in an aqueous suspension or aqueous emulsion polymerization process.



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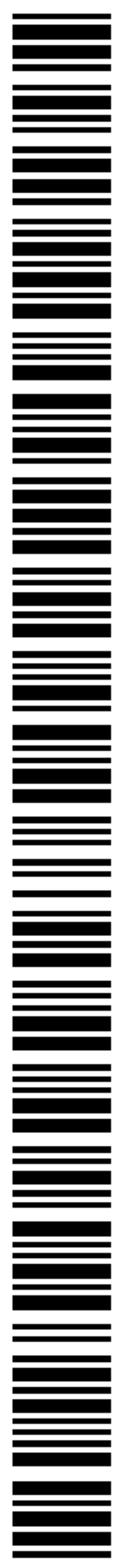
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(54) Title: POLYMERIZATION OF I-BUTENE IN HYDROCARBON MEDIA USING BIS(BORANE) CO-INITIATORS

(57) Abstract: A method is provided for cationically polymerizing olefin monomer by using a novel coinitiator in the presence of water. More specifically, a method is provided for cationically polymerizing olefin monomer by using a novel coinitiator in an aqueous suspension or aqueous emulsion polymerization process.



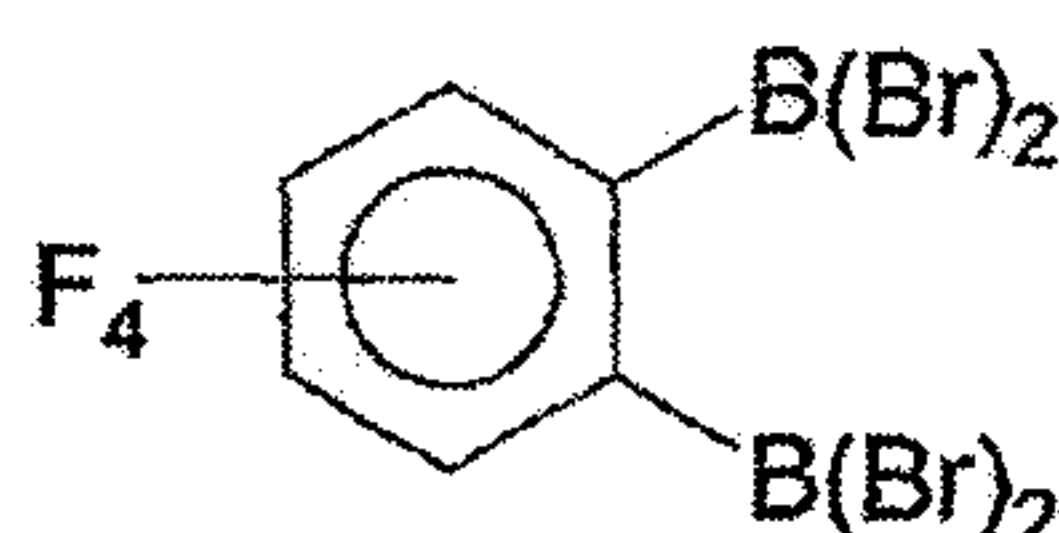
WO 2004/094486 A1

CATIONIC POLYMERIZATION OF OLEFINS IN THE PRESENCE OF WATER USING DINUCLEAR FLUOROARYL CO-INITIATORS

TECHNICAL FIELD

This invention relates to a cationic-polymerization method that uses new coinitiators.

This invention also relates to a method for synthesizing 1,2- $\text{C}_6\text{F}_4[\text{B}(\text{Br})_2]_2$:



BACKGROUND OF THE INVENTION

Poly(isobutene) (PIB) is an important industrial commodity that is prepared by the polymerization of isobutene (IB), a cheap petrochemical obtained by the cracking of higher hydrocarbons. Depending on its molecular weight (MW), PIB is used in hundreds if not thousands of diverse applications, e.g., rubbers, lubricants, adhesives, viscosity control agents, additives. The polymerization of IB is carried out by large companies world-wide, including Exxon-Mobil, BASF, Oronite, BP, Japan Synthetic Rubber, etc.

IB polymerization is effected either in the bulk (BASF) or in the liquid phase by the use of hydrocarbon or chlorinated hydrocarbon diluents at cryogenic temperatures. The typical polymerization initiation systems include strong Lewis acids (BF_3 , AlCl_3 , TiCl_4 , etc); these acids are highly moisture sensitive and rapidly hydrolyze to noxious side products during work-up. Environmental concerns (air, water pollution) present important issues even with state-of-the-art industrial processes.

Cationically polymerized olefins, such as butyl rubber, a co-polymer of i-butene (IB) and isoprene (IP), have long been commercially important synthetic rubbers. For example, about 500 million pounds of butyl rubber (BR) were produced in the United States in 1991. Conventional methods of BR manufacture employ low temperature (as low as -100°C) and the presence of a Lewis acid, such as AlCl_3 , in a chlorinated hydrocarbon solvent. Under these conditions, production of high

MW (> 200,000) BR, occurs at acceptable rates. Chlorinated hydrocarbon solvents are used because they have sufficient polarity to stabilize the transition states, and thus lower the activation energy for ion generation in carbocationic polymerization. The low temperatures are used to slow the termination and chain transfer processes that limit the growth in the molecular weight of the polymer chains. Less polar solvents are generally less effective at stabilizing transition states, and thus fewer carbocations are produced that are active in polymerization. The solvent also needs to act as a fluid heat transfer medium to dissipate the heat of polymerization. The solvent should optimally dissolve the ingredients of the polymerization. Methyl chloride is useful in the synthesis of BR, as it is both a polar solvent (which enhances propagation rates) and a poor solvent for BR so that the process is a suspension polymerization at these low temperatures.

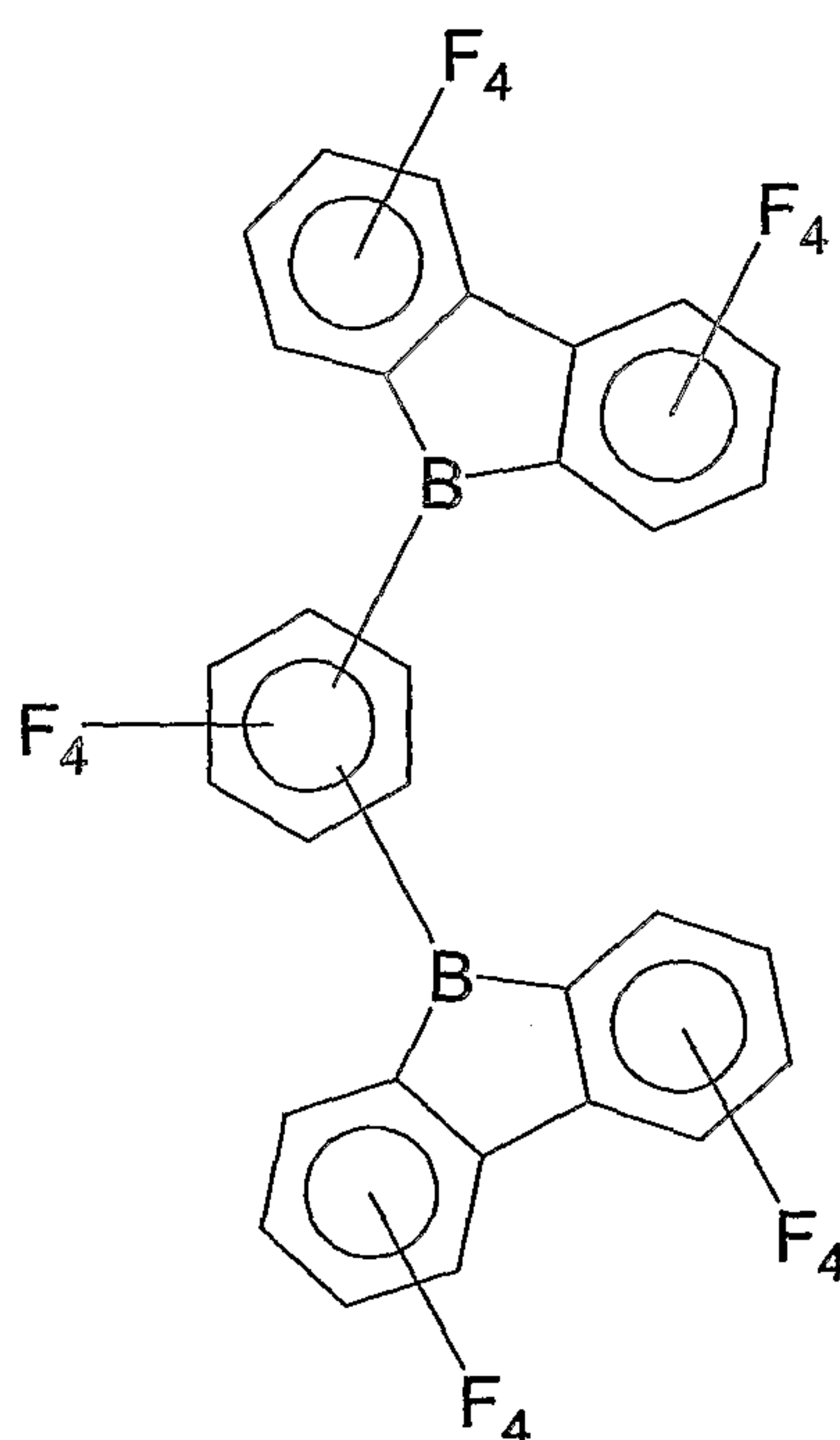
Recent legislation in the United States allows the continued use of methyl chloride in existing facilities, but expanded facilities and/or new plants will be required to use alternative solvents that are not chlorinated. Hence there is a need to develop initiators which will be effective in the absence of a halogenated solvent in producing high MW BR at commercially acceptable rates.

A variety of Lewis acidic, main group and transition metal initiators or co-initiators of i-butene (IB) polymerization have been reported to provide poly(i-butene) (PIB) or co-polymers of IB and IP in the absence of chlorinated solvents or with a minimum amount of chlorinated solvents being present. However, none of these compositions is believed to provide BR of sufficiently high MW at acceptable rates in the absence of chlorinated solvents. Therefore, there is a continuing need to develop alternative initiator compositions.

SUMMARY OF INVENTION

This invention is generally directed to a method for cationically polymerizing olefin monomer comprising the step of using a composition having the chemical structure:

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as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomer comprising the step of using a composition having the chemical structure:



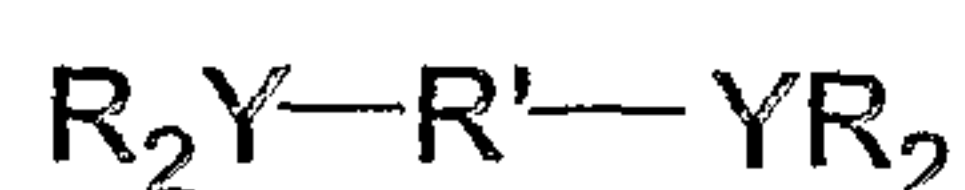
as a coinitiator in the presence of water;

wherein each R is independently selected from the group consisting of a perfluorophenyl; 3,5-bis(trifluoromethyl)phenyl; 1-perfluoronaphthyl; 2-perfluoronaphthyl; 2-perfluorobiphenyl; 3-perfluorobiphenyl; 4-perfluorobiphenyl; and $p-R''_3Si$ -2,3,5,6-tetrafluorophenyl;

wherein R' is 1,2-perfluorophenylene; 1,2-perfluoronaphthalene; 2,3-perfluoronaphthalene; 1,8-perfluoronaphthalene; 1,2-perfluoroanthracene; 2,3-perfluoroanthracene; 1,9-perfluoroanthracene; 1,2-perfluorophenanthrene; 2,3-perfluorophenanthrene; 1,10-perfluorophenanthrene; 9,10-perfluorophenanthrene; 2,2'-perfluorobiphenylene; 2,2'-perfluoro-1,1'-binaphthalene; 3,3'-perfluoro-2,2'-binaphthalene; or 1,1'-ferrocene; and

wherein R'' is a C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, or C₁₀ alkyl.

This invention is generally directed to a method for cationically polymerizing olefin monomer comprising the step of using a composition having the chemical structure:



as a coinitiator in an organic phase or neat monomer reaction phase;

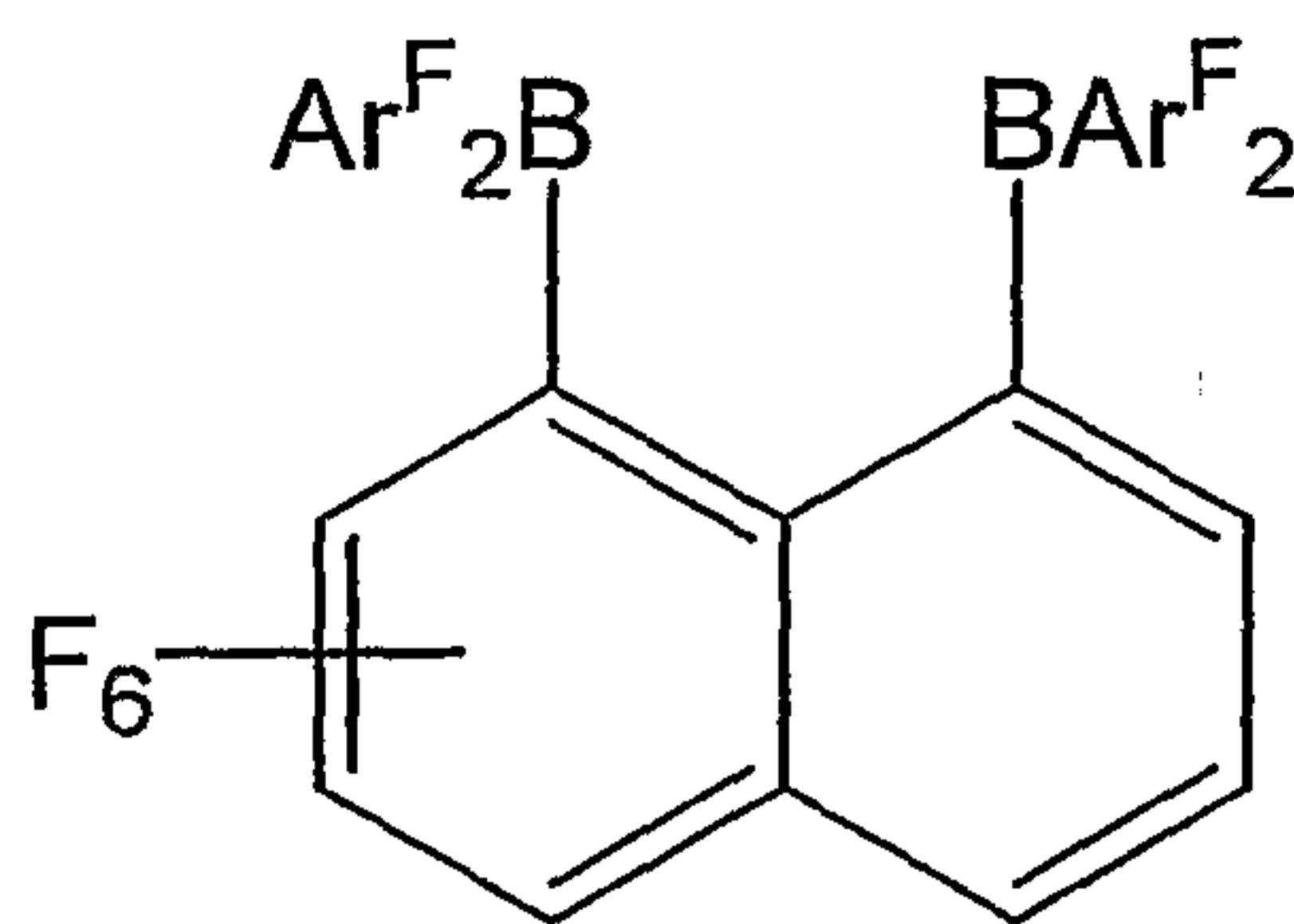
wherein Y is boron or aluminum;

wherein each R is independently selected from the group consisting of a perfluorophenyl; 3,5-bis(trifluoromethyl)phenyl; 1-perfluoronaphthyl; 2-perfluoronaphthyl; 2-perfluorobiphenyl; 3-perfluorobiphenyl; 4-perfluorobiphenyl; and $p-R''_3Si$ -2,3,5,6-tetrafluorophenyl;

wherein R' is 1,2-perfluorophenylene; 1,2-perfluoronaphthalene; 2,3-perfluoronaphthalene; 1,8-perfluoronaphthalene; 1,2-perfluoroanthracene; 2,3-perfluoroanthracene; 1,9-perfluoroanthracene; 1,2-perfluorophenanthrene; 2,3-perfluorophenanthrene; 1,10-perfluorophenanthrene; 9,10-perfluorophenanthrene; 2,2'-perfluorobiphenylene; 2,2'-perfluoro-1,1'-binaphthalene; 3,3'-perfluoro-2,2'-binaphthalene; or 1,1'-ferrocene; and

wherein R'' is a C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, or C₁₀ alkyl.

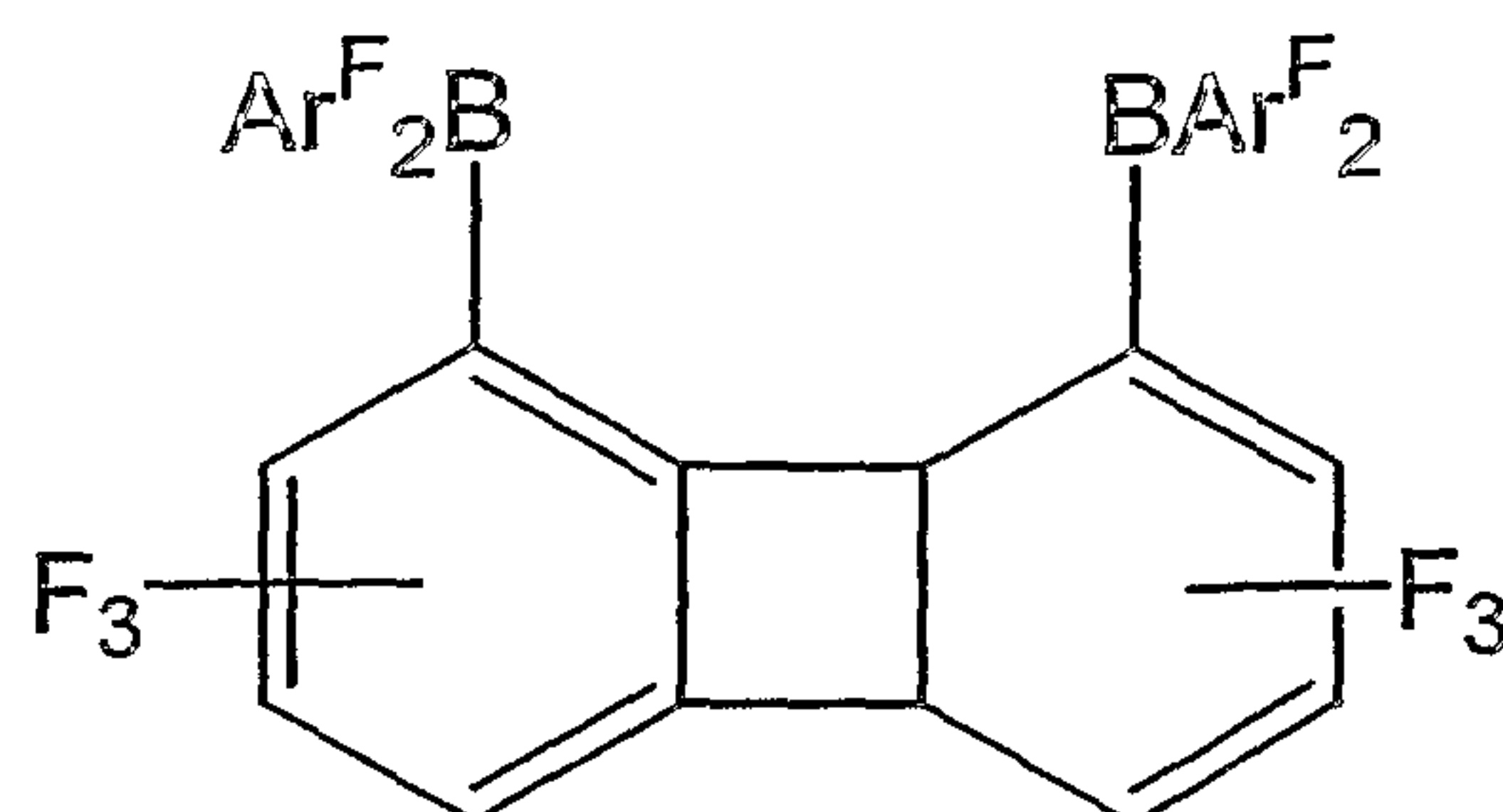
This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:



wherein $Ar^F = C_6F_5$ or $Ar^F_2 = C_{12}F_8$

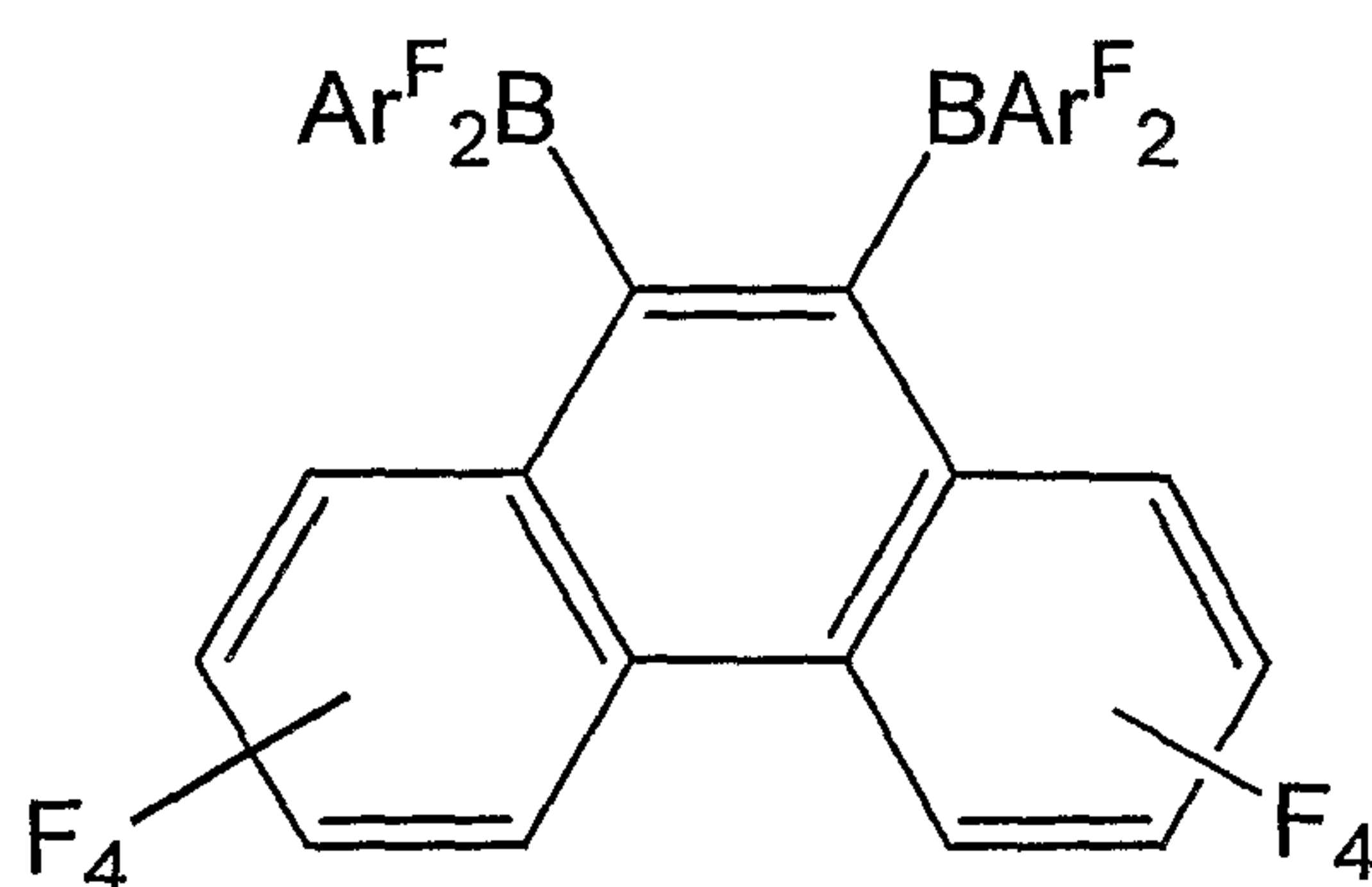
as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:



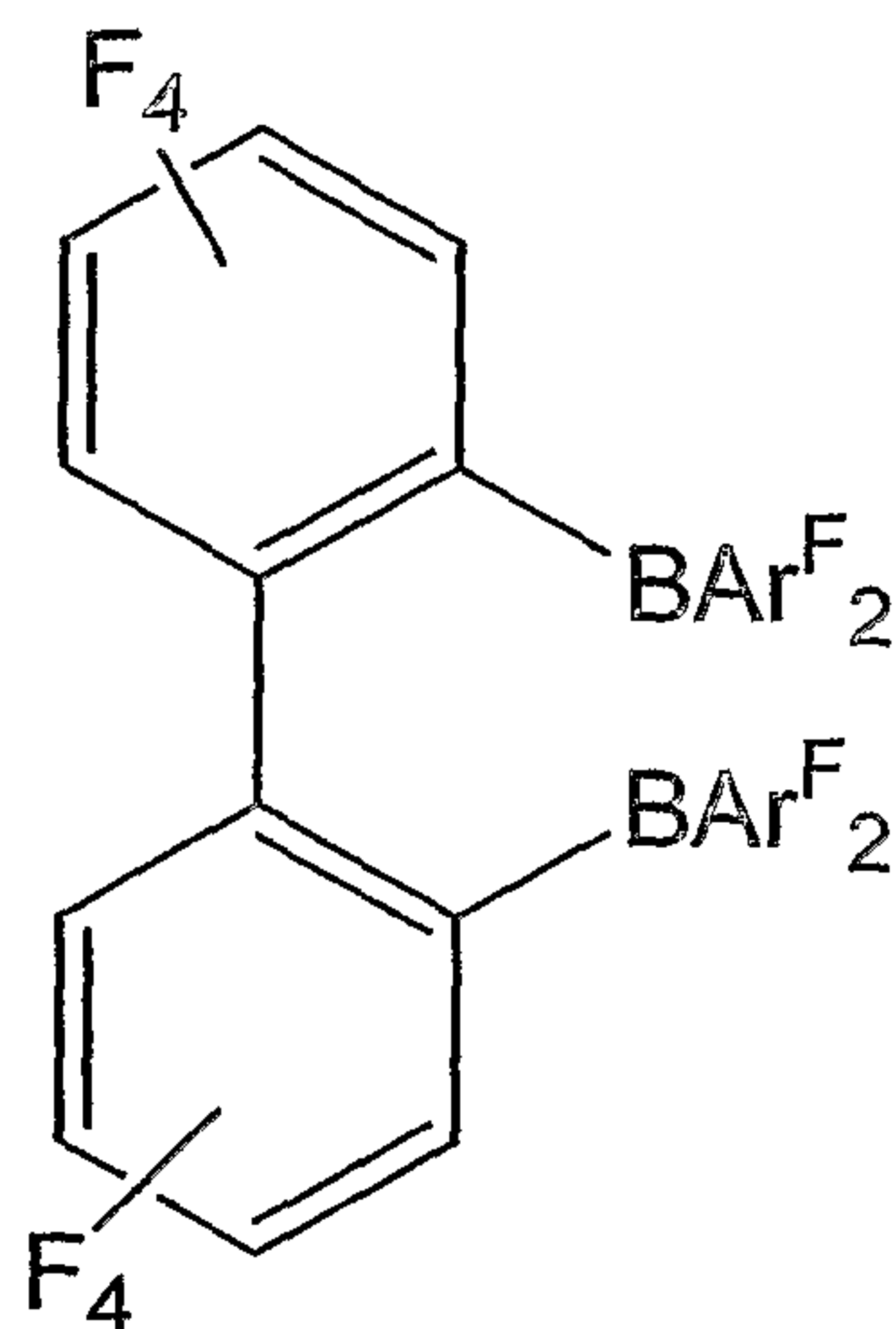
wherein $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$ or $\text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$
as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:



wherein $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$ or $\text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:

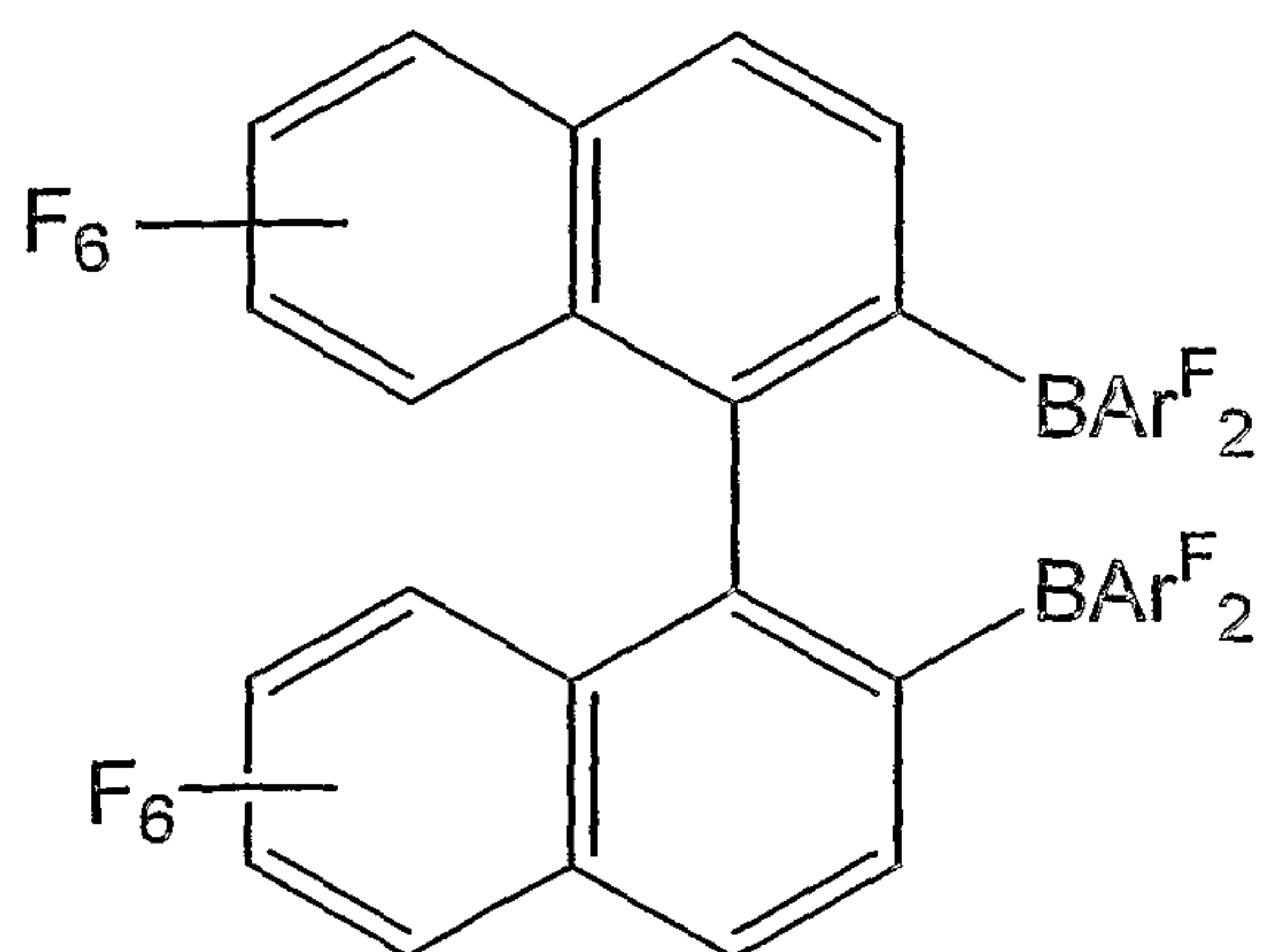


wherein $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$ or $\text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$

as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:

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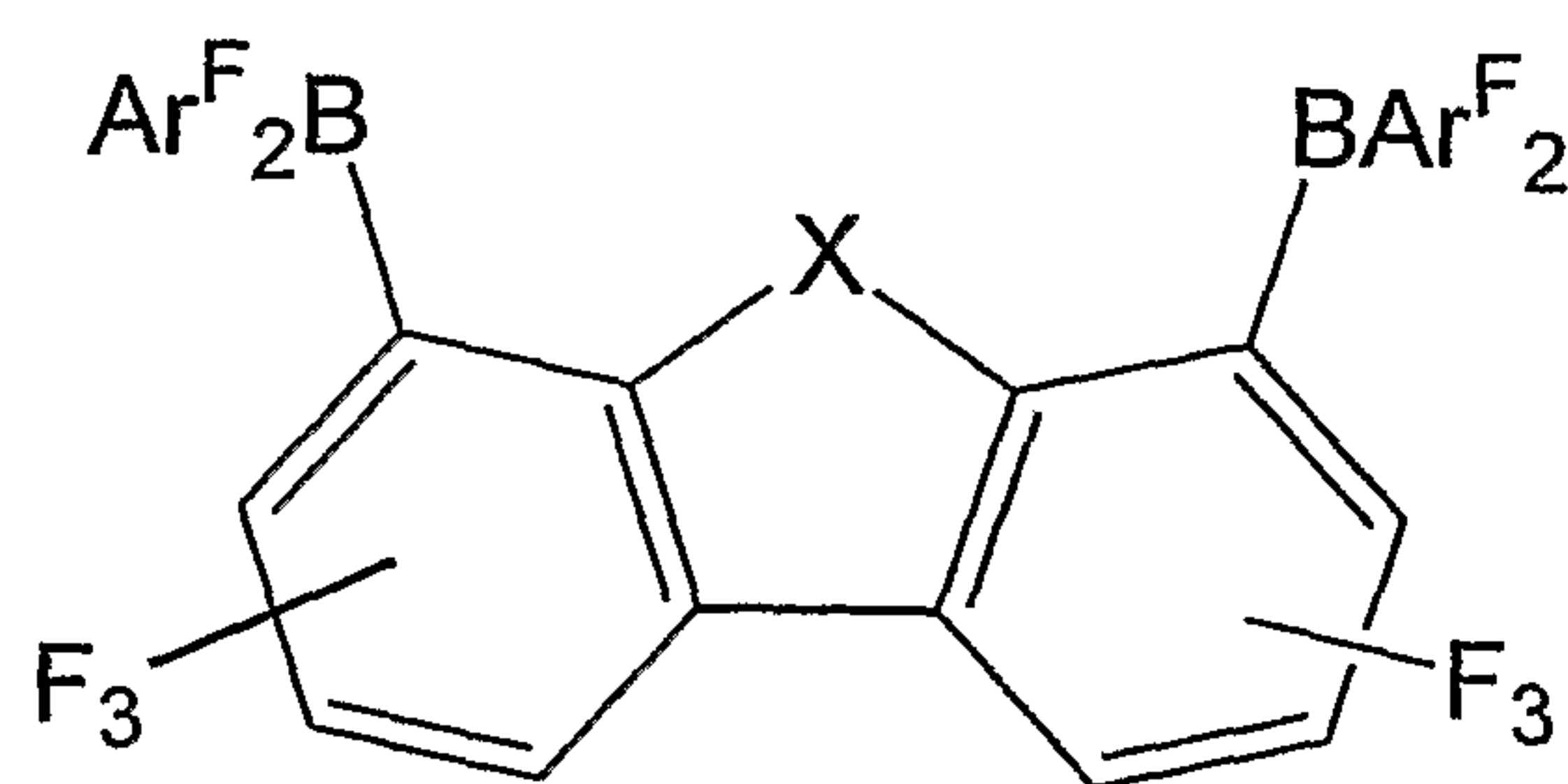


wherein

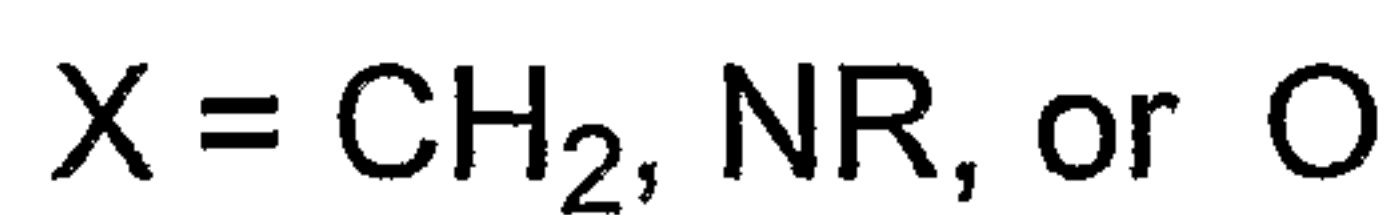


as a coinitiator in the presence of water.

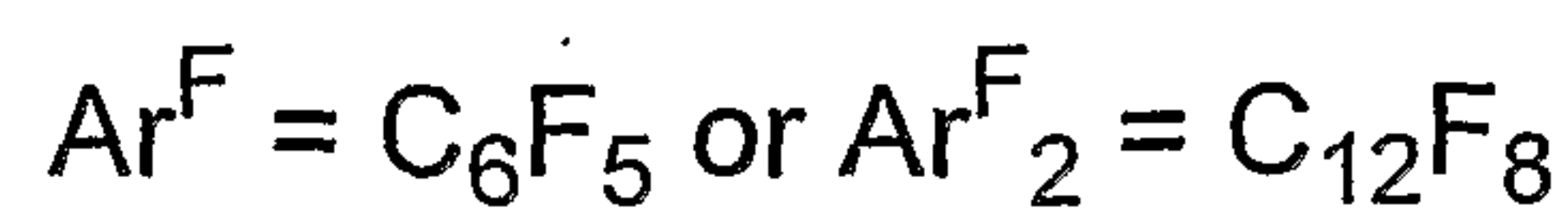
This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:



wherein

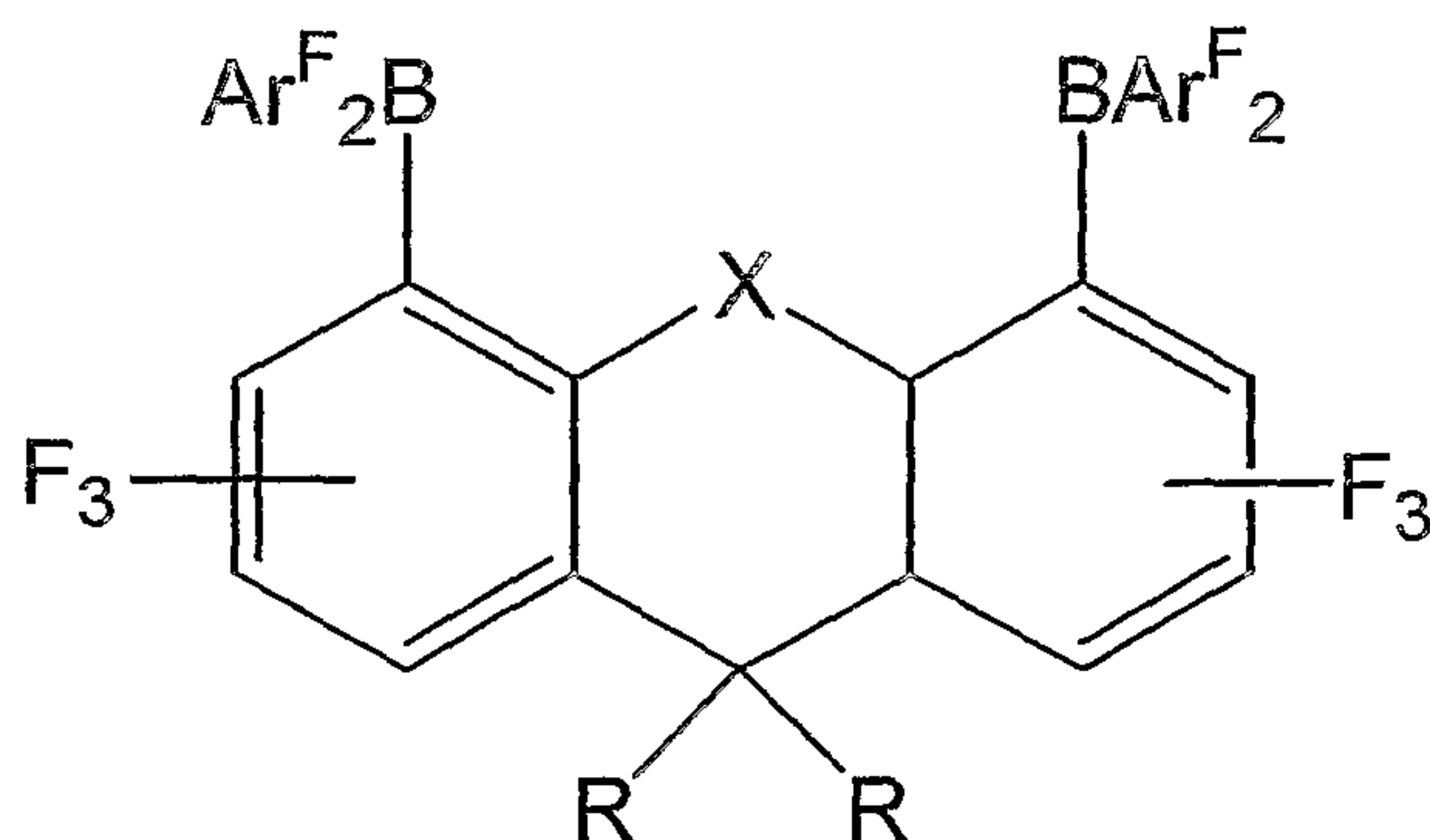


and



as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:

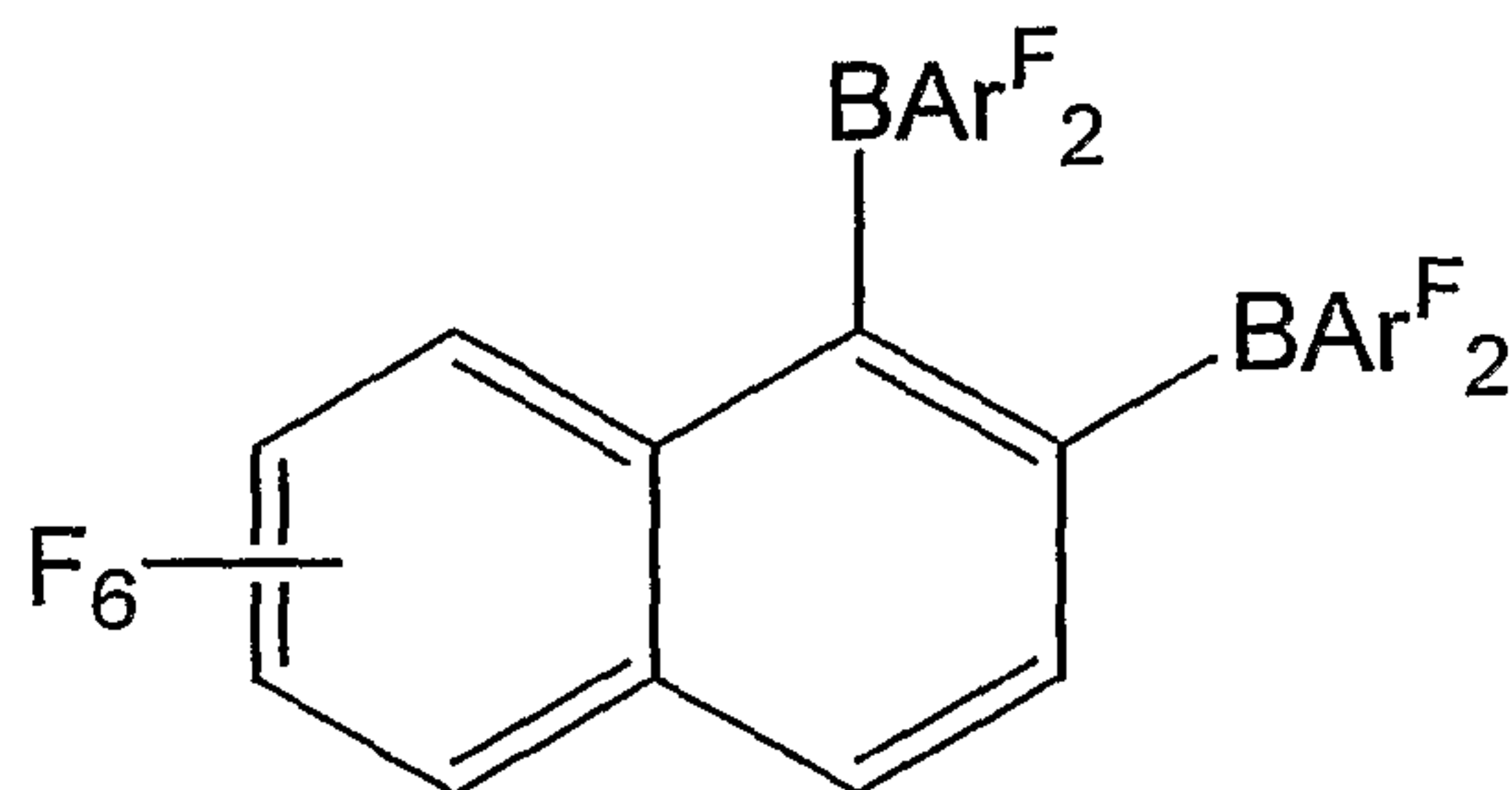


wherein $X = \text{CH}_2, \text{NR}, \text{ or } \text{O}$

and $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5 \text{ or } \text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$

as a coinitiator in the presence of water.

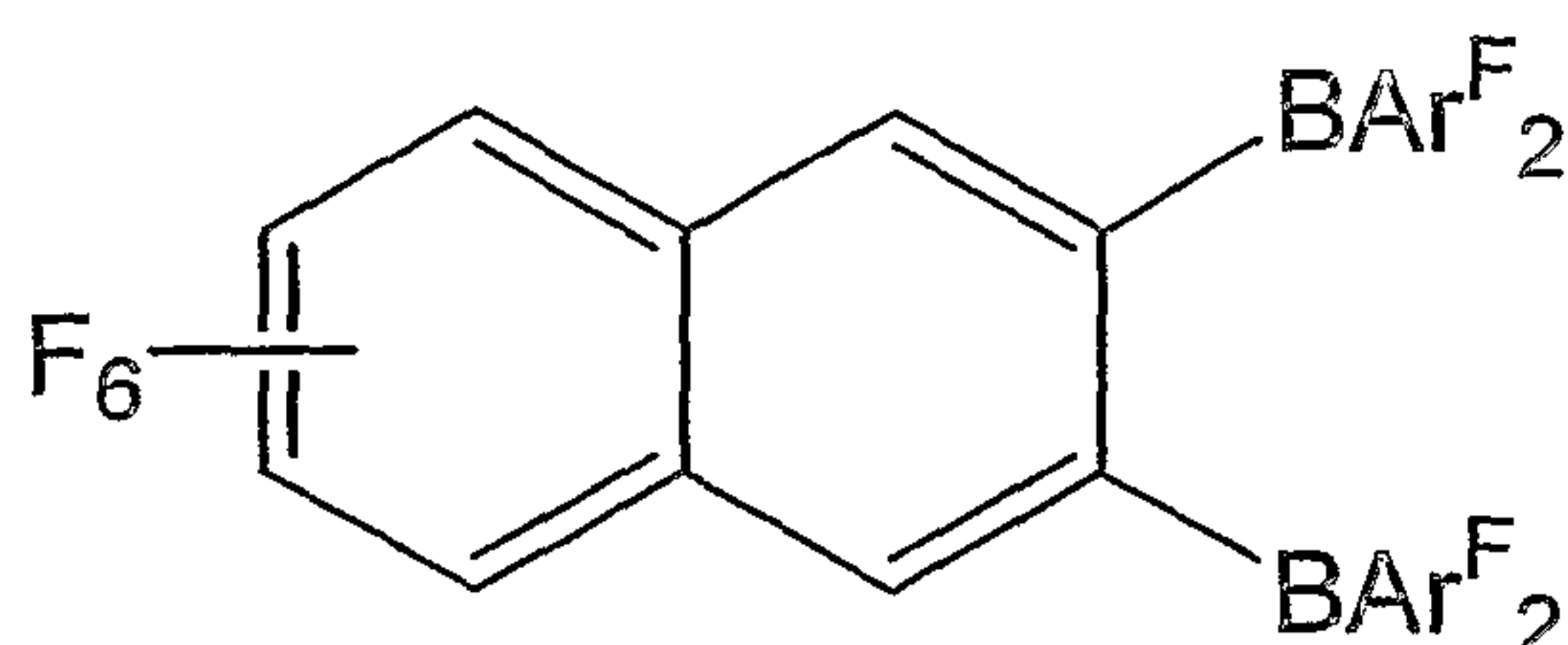
This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:



wherein $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5 \text{ or } \text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$

as a coinitiator in the presence of water.

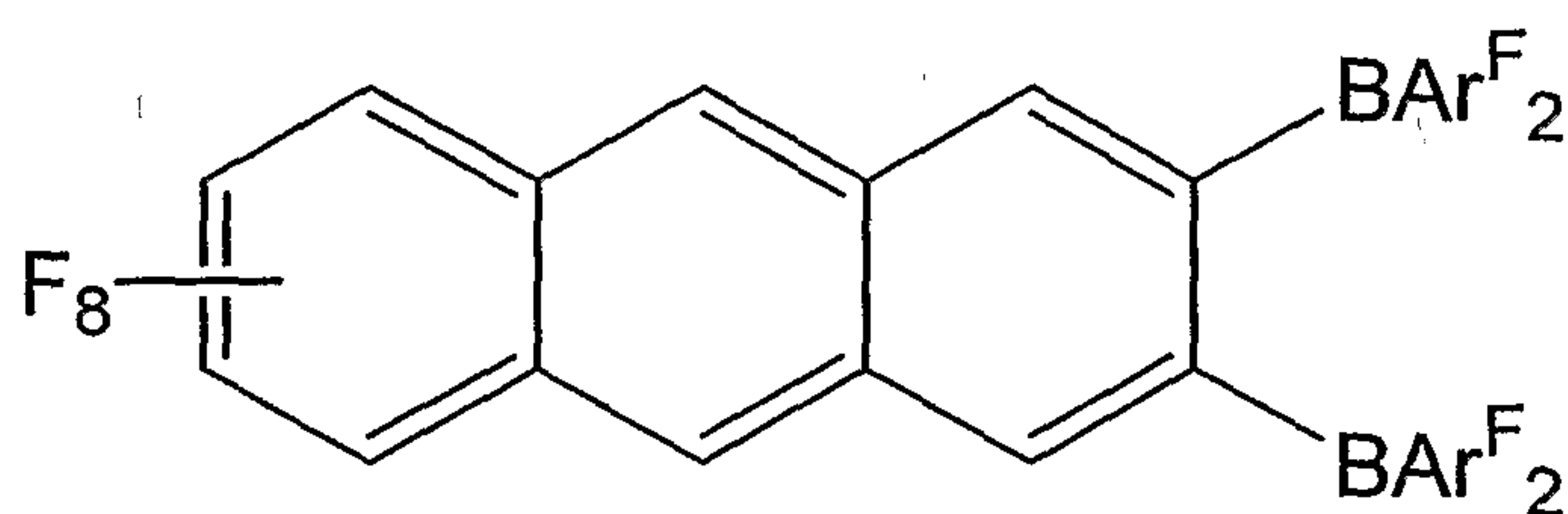
This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:



wherein $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$ or $\text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$

as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:

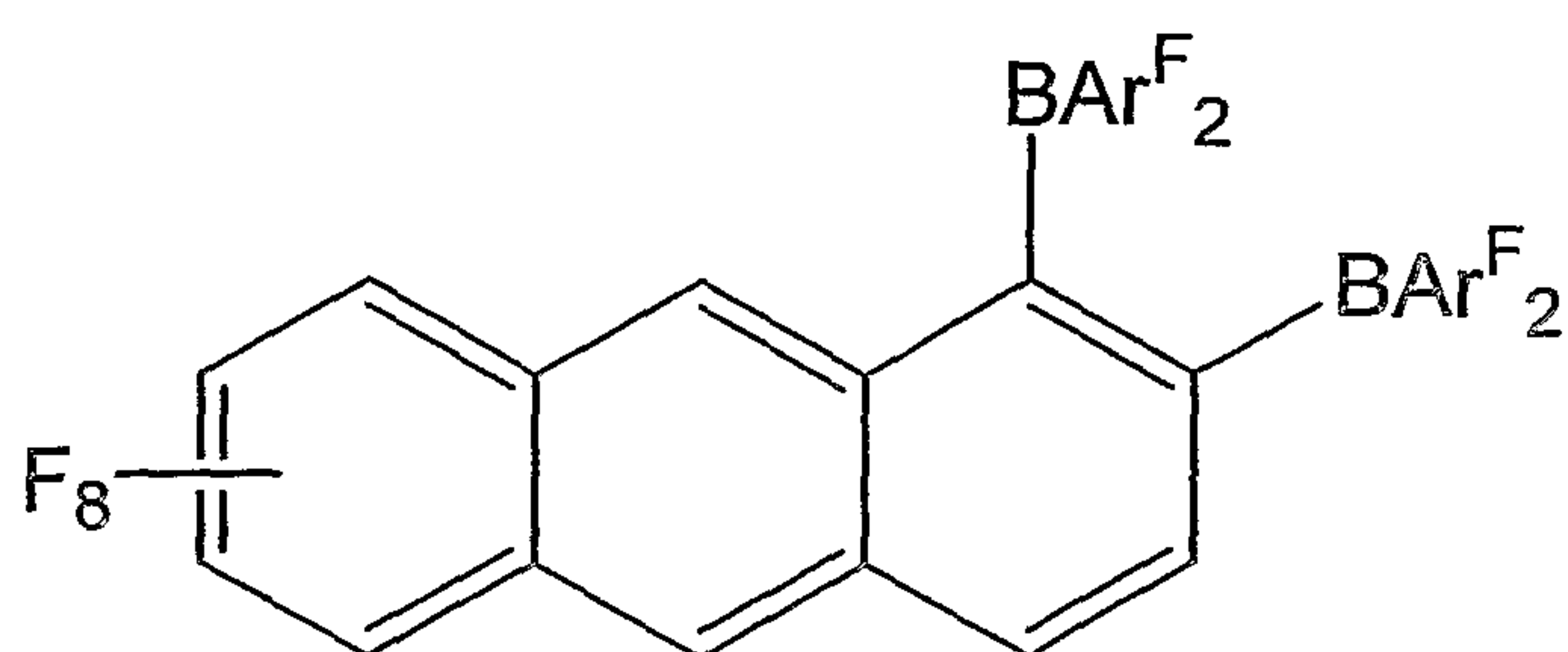


wherein $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$ or $\text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$

as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:

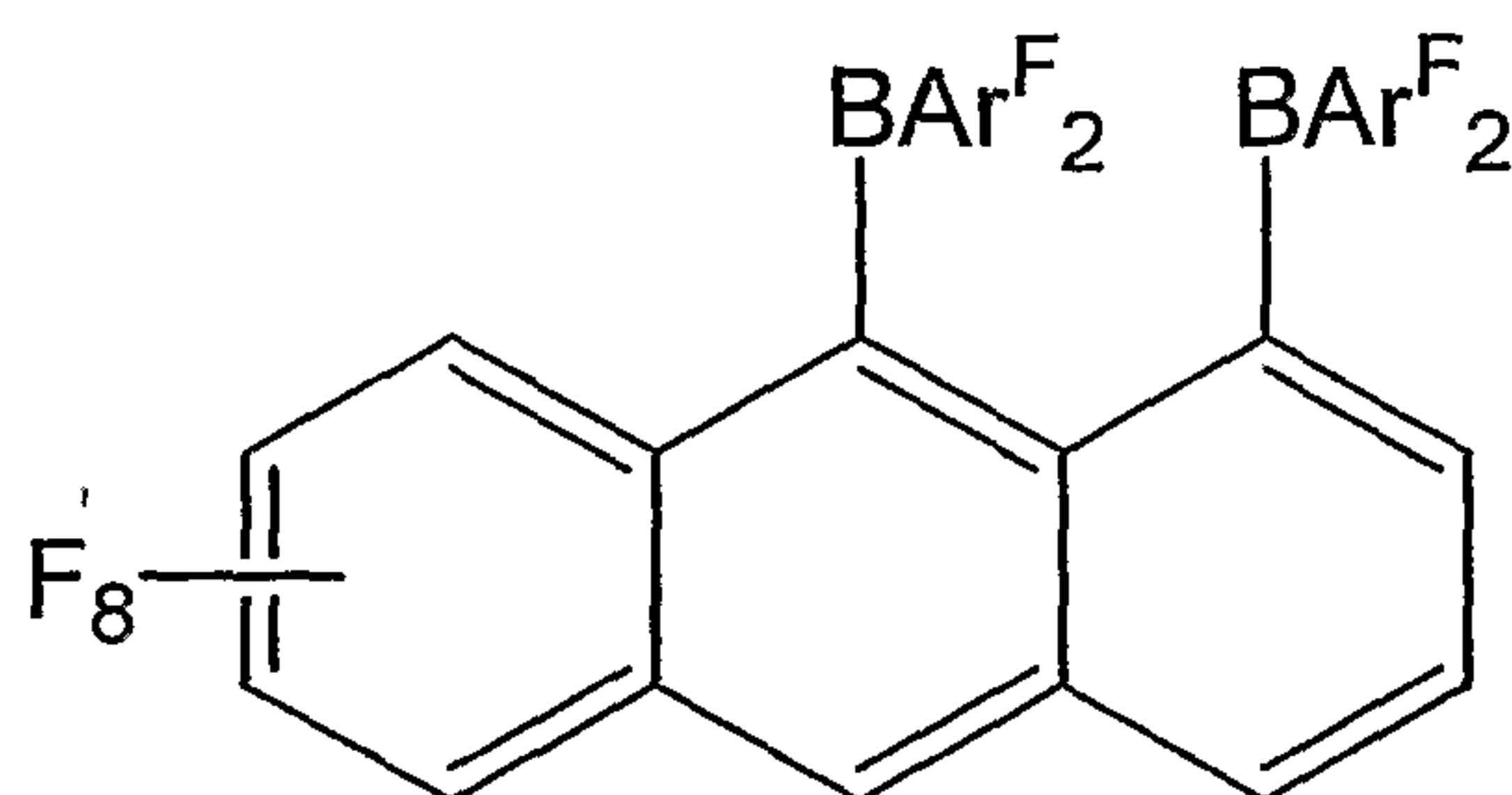
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wherein $Ar^F = C_6F_5$ or $Ar^F_2 = C_{12}F_8$

as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:

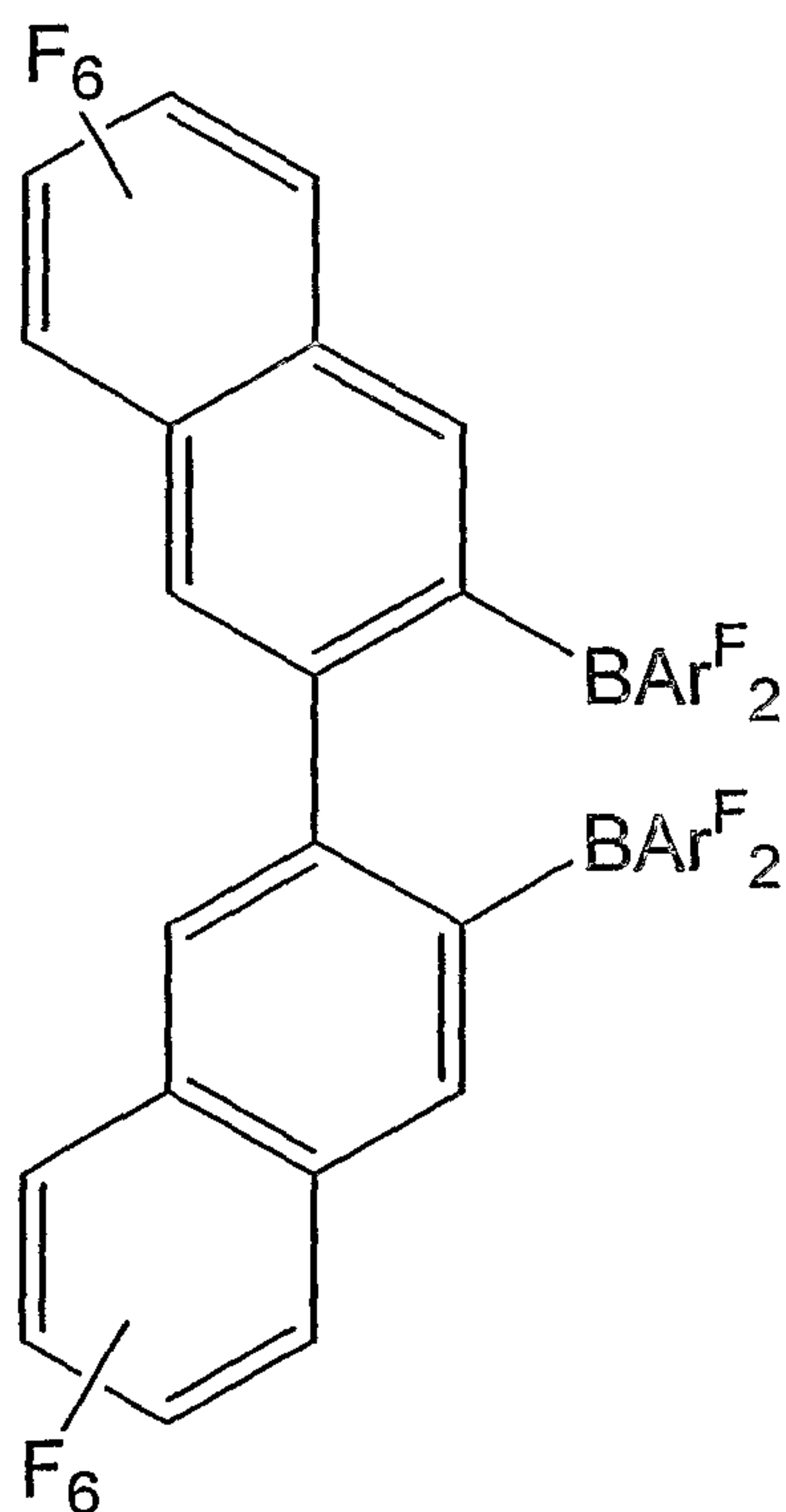


wherein $Ar^F = C_6F_5$ or $Ar^F_2 = C_{12}F_8$

as a coinitiator in the presence of water.

This invention is generally directed to a method for cationically polymerizing olefin monomers comprising the step of using a composition having the chemical structure:

11



wherein



as a coinitiator in the presence of water.

This invention generally provides a cationic-polymerization method that uses new coinitiators. The invention also provides for a cationic-polymerization method that uses new coinitiators in the presence of water. This invention also provides a method for making 1,2- $\text{C}_6\text{F}_4[\text{B}(\text{Br})_2]_2$:

perfluoroanthracenyl; 1,9-perfluoroanthracenyl; 1,2-perfluorophenanthrenyl; 2,3-perfluorophenanthrenyl; 1,10-perfluorophenanthrenyl; 9,10-perfluorophenanthrenyl; 2,2'-perfluorobiphenylenyl; 2,2'-perfluoro-1,1'-binaphthalenyl; 3,3'-perfluoro-2,2'-binaphthalenyl; or 1,1'-ferrocenyl; and

wherein R'' is a C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, or C₁₀ alkyl.

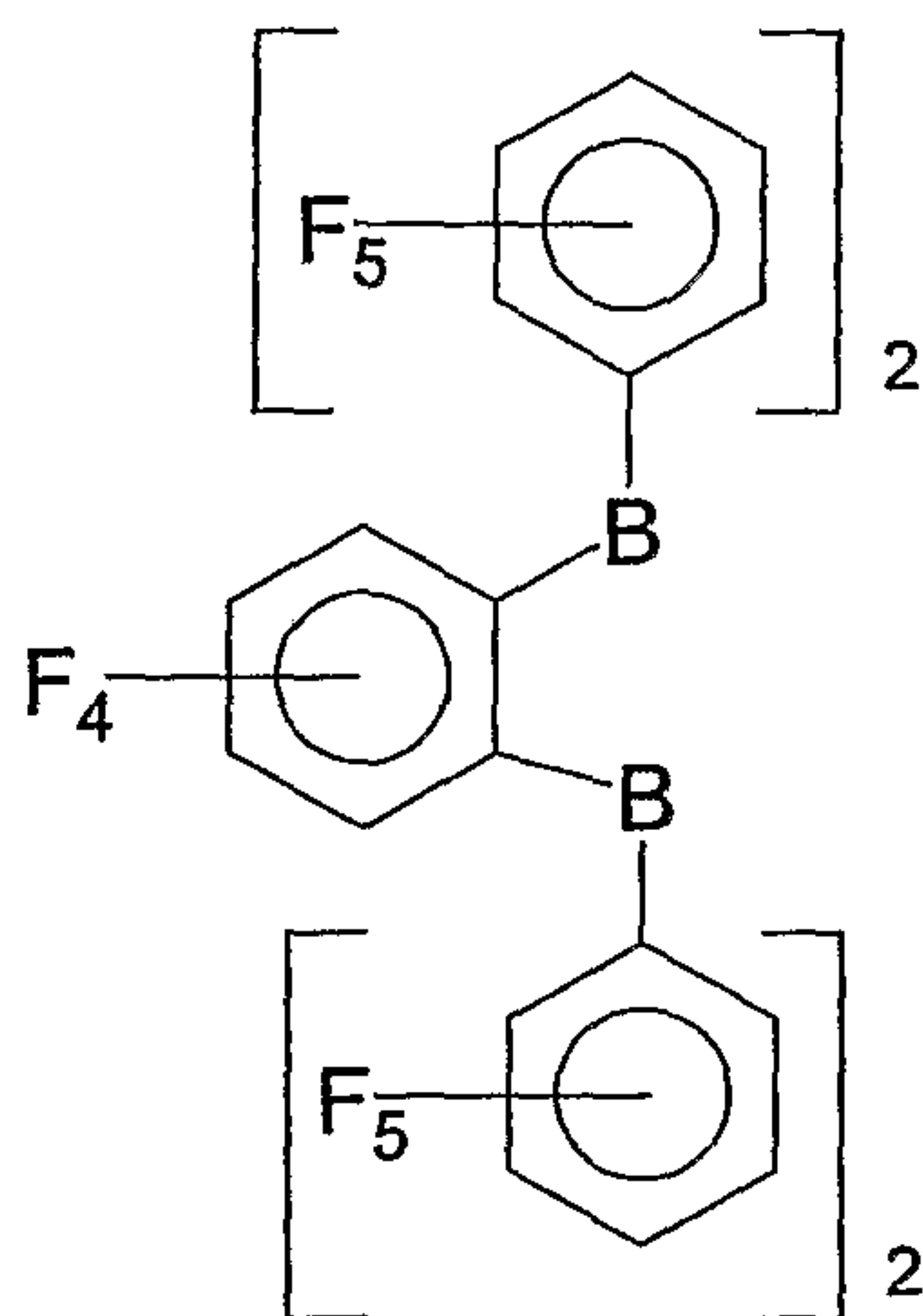
2)



wherein Y is boron or aluminum;

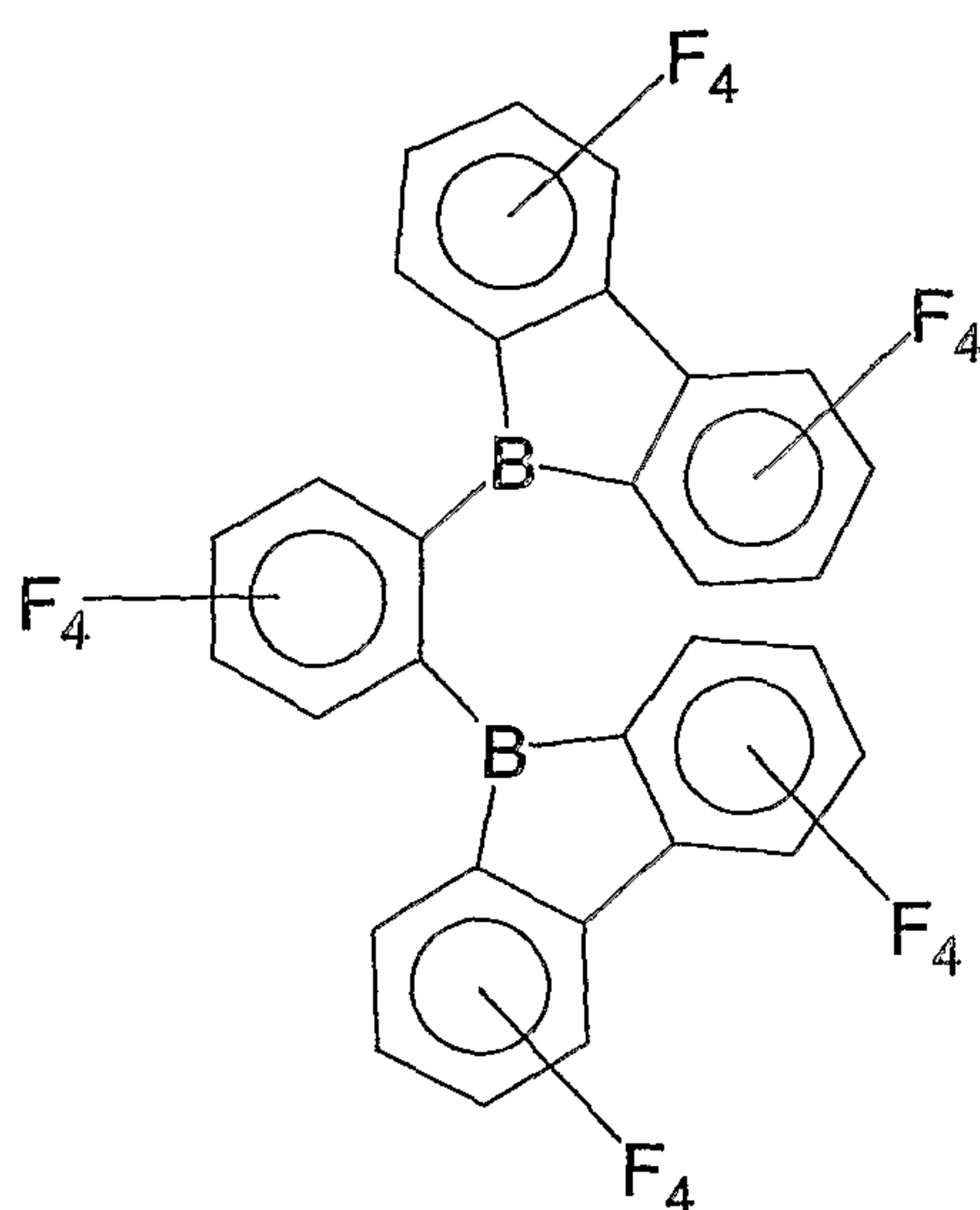
wherein R, R', and R'' is as described above.

3)

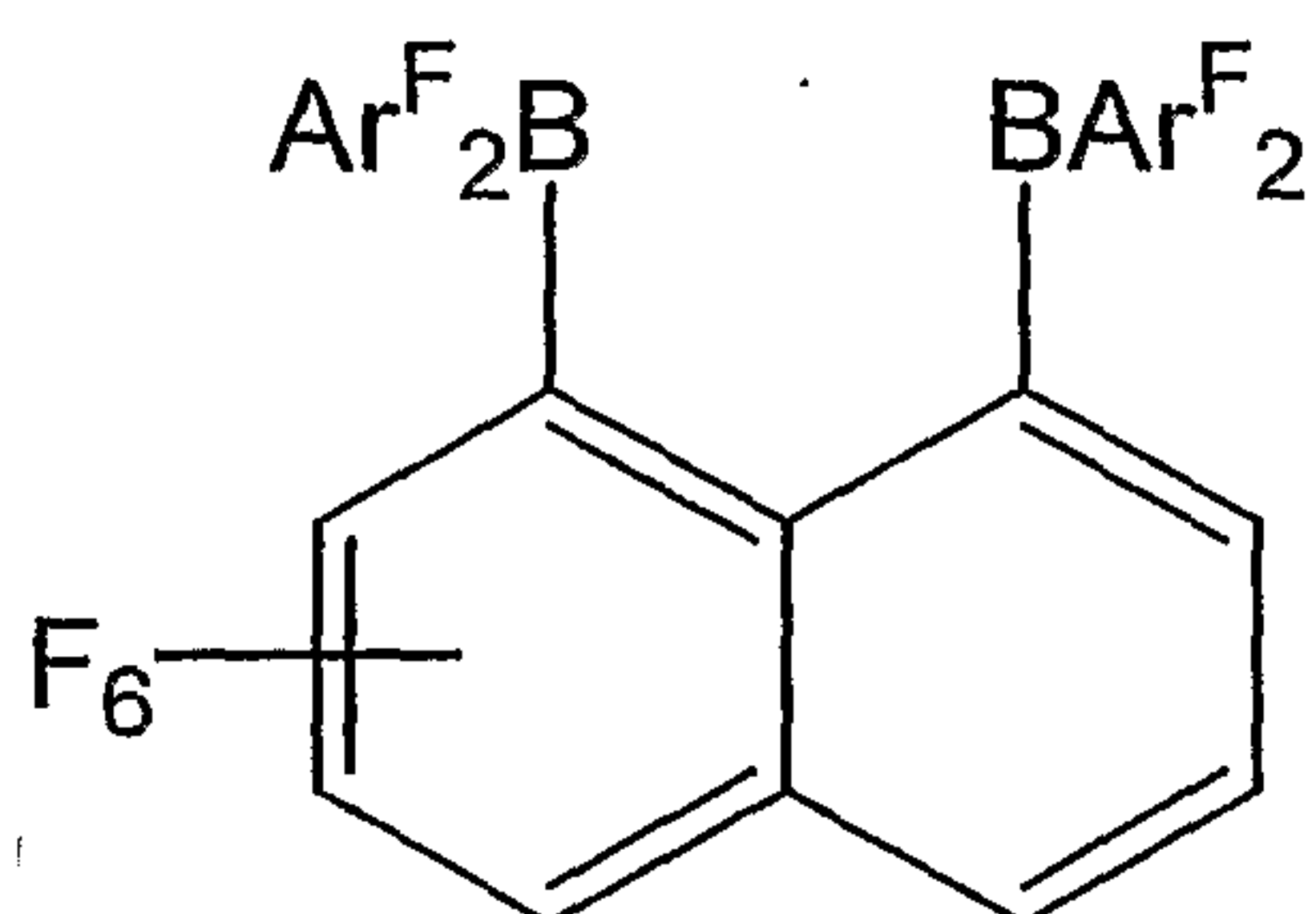


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4)



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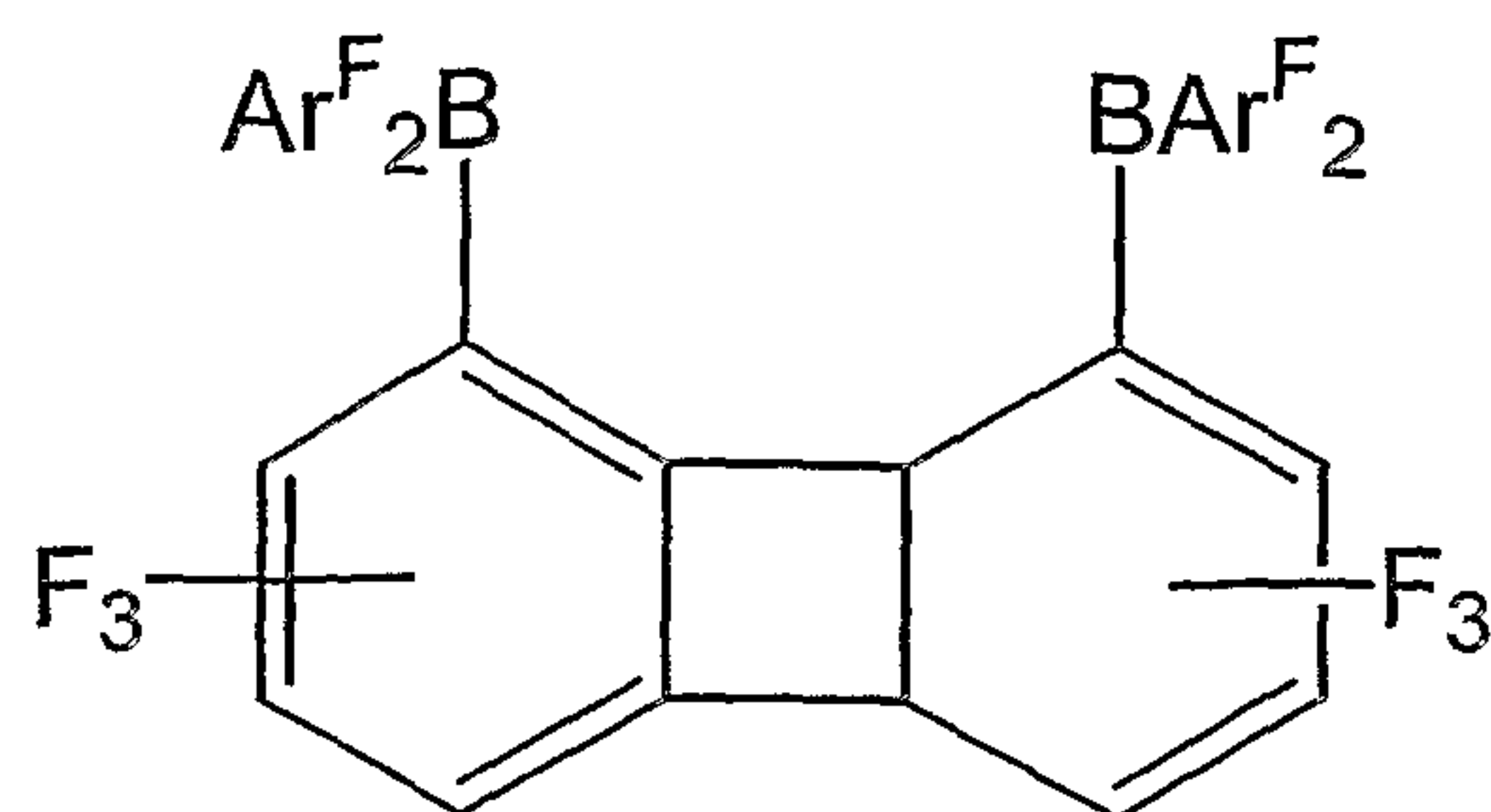


wherein

$$\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5 \text{ or } \text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$$

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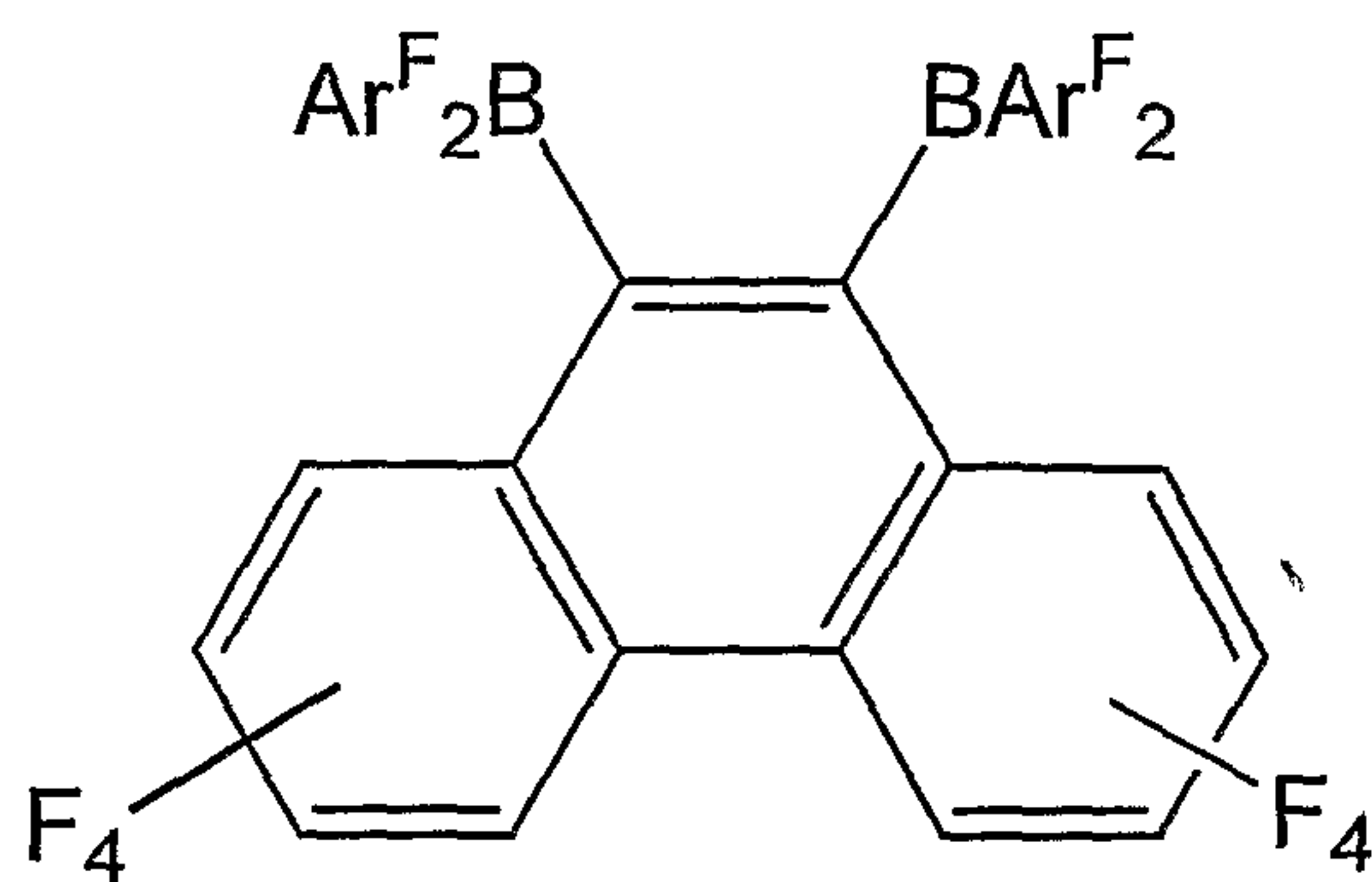
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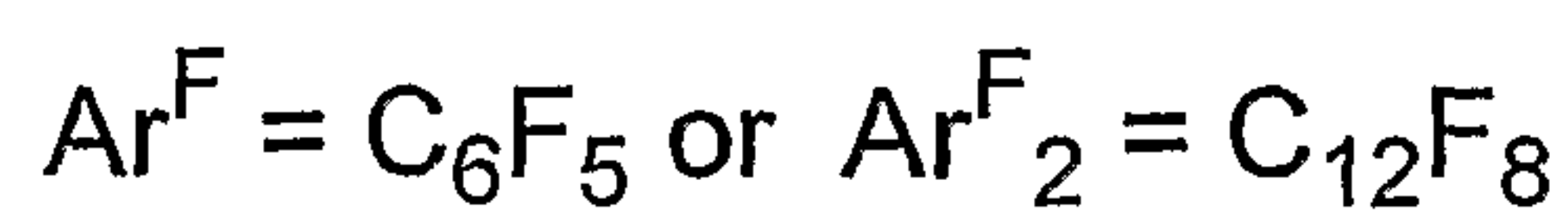
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7)

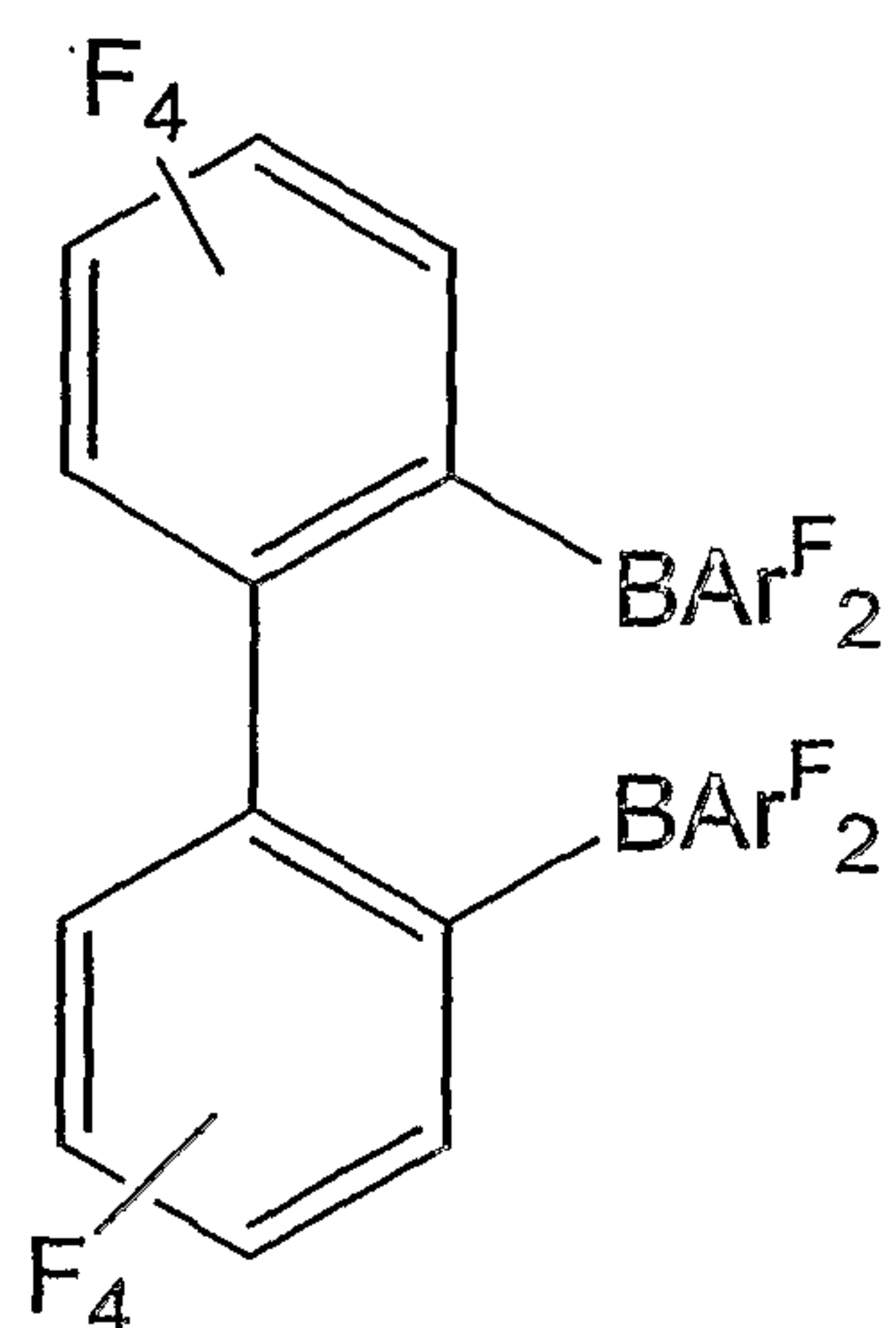


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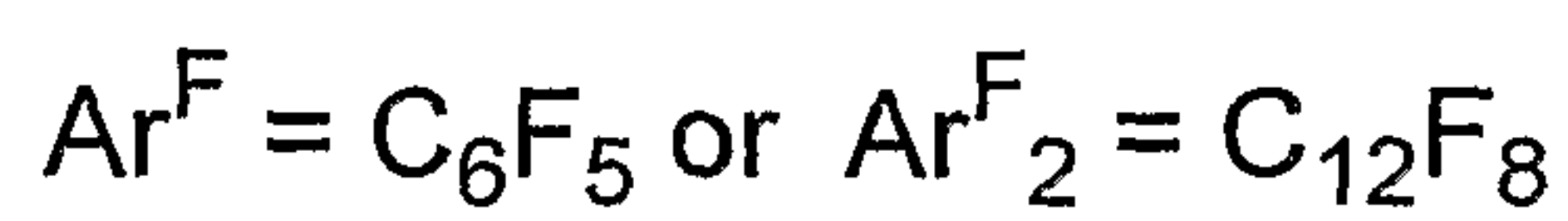


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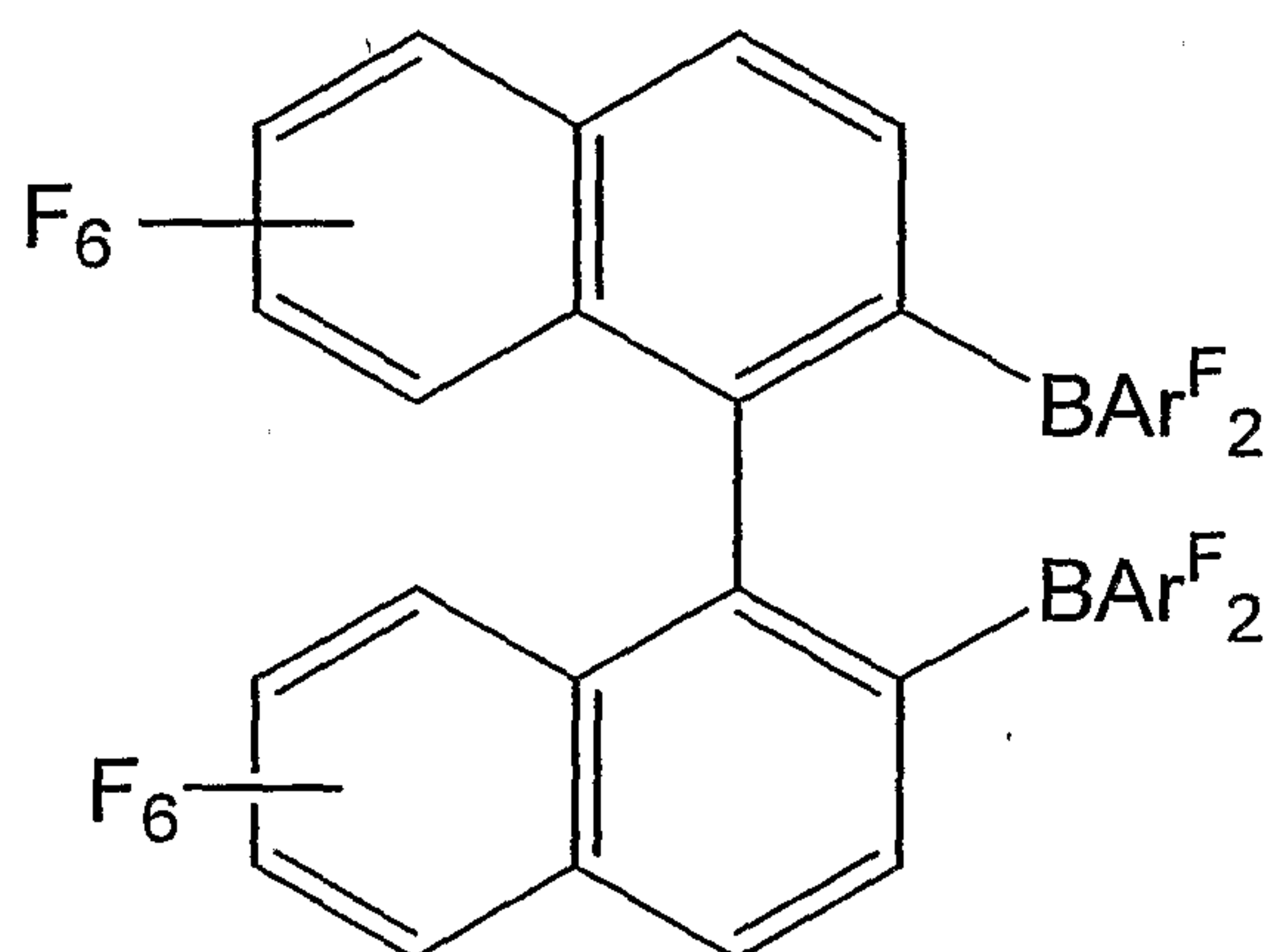
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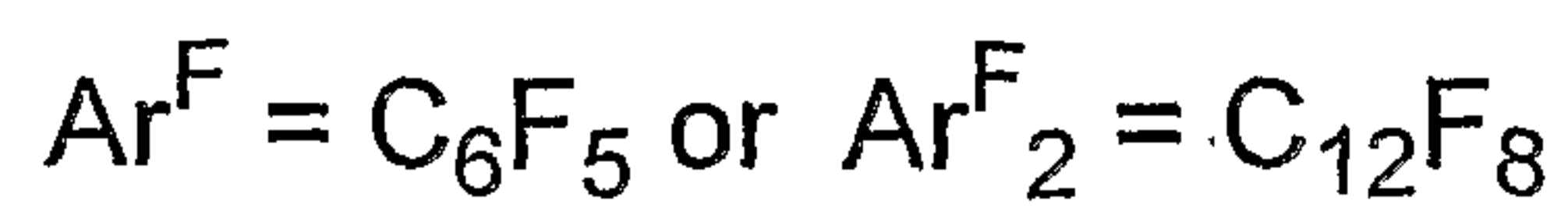
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9)

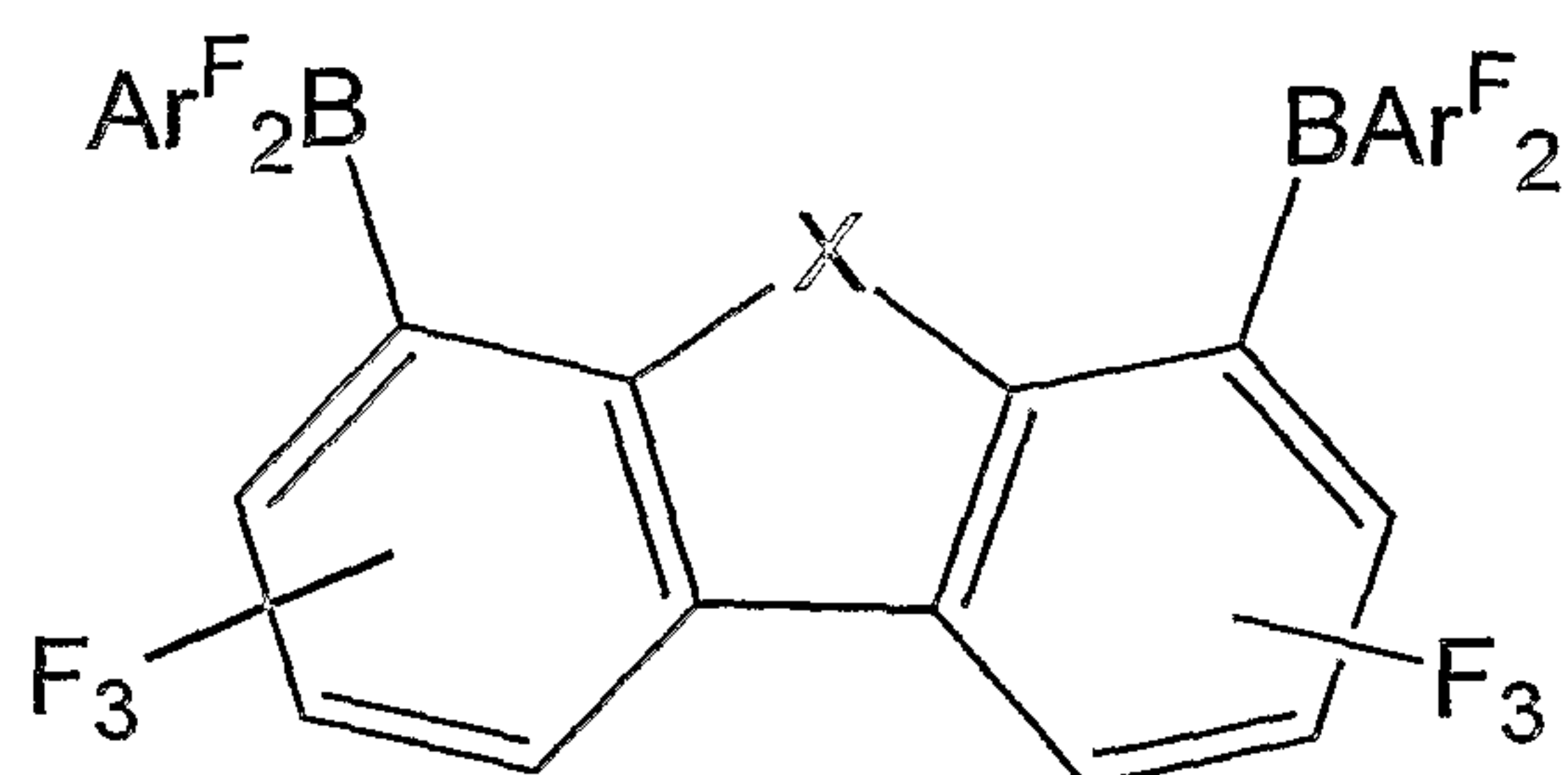


wherein



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10)



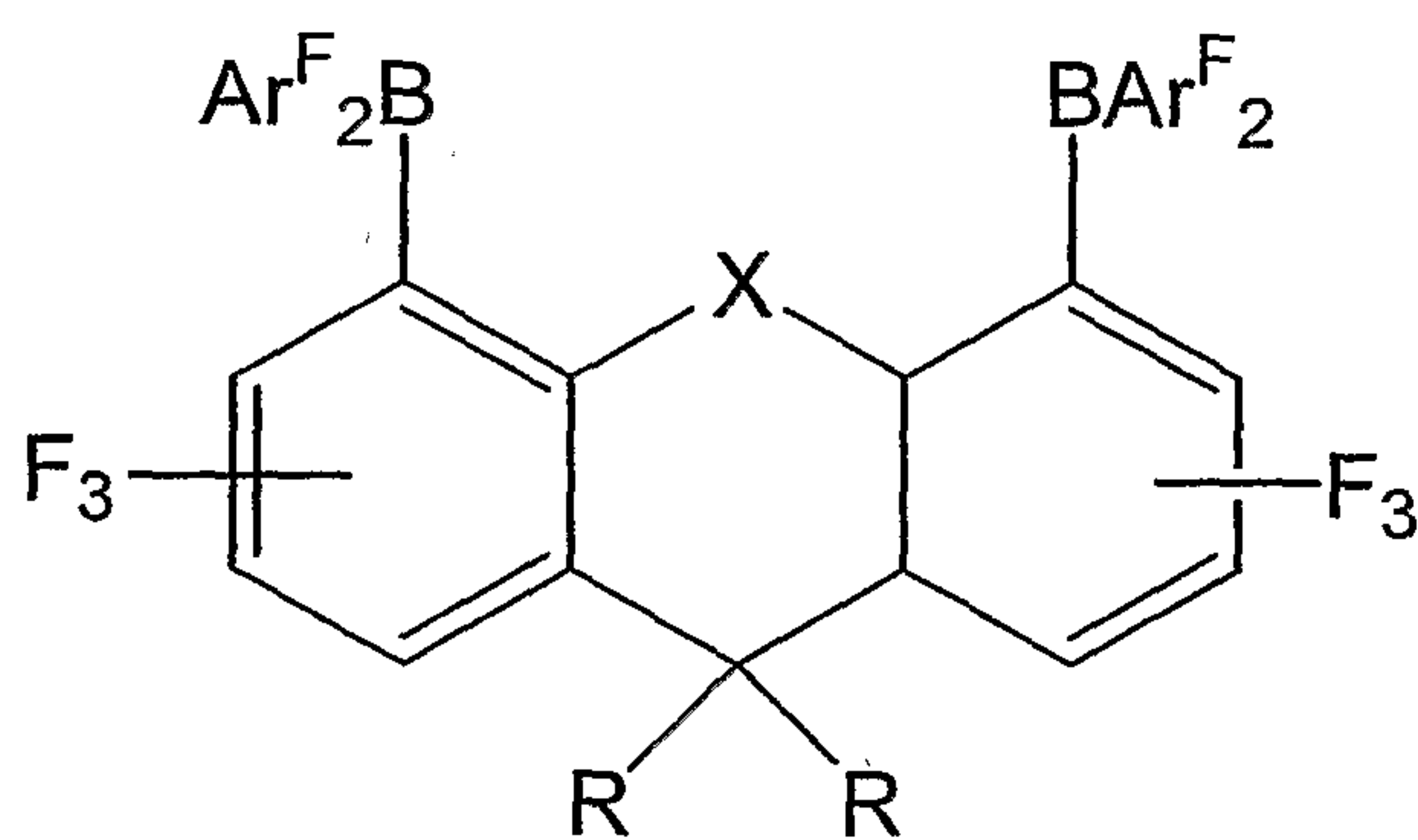
wherein

 $X = \text{CH}_2, \text{NR}, \text{ or } \text{O}$

and

 $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5 \text{ or } \text{Ar}^{\text{F}_2} = \text{C}_{12}\text{F}_8$

11)



wherein

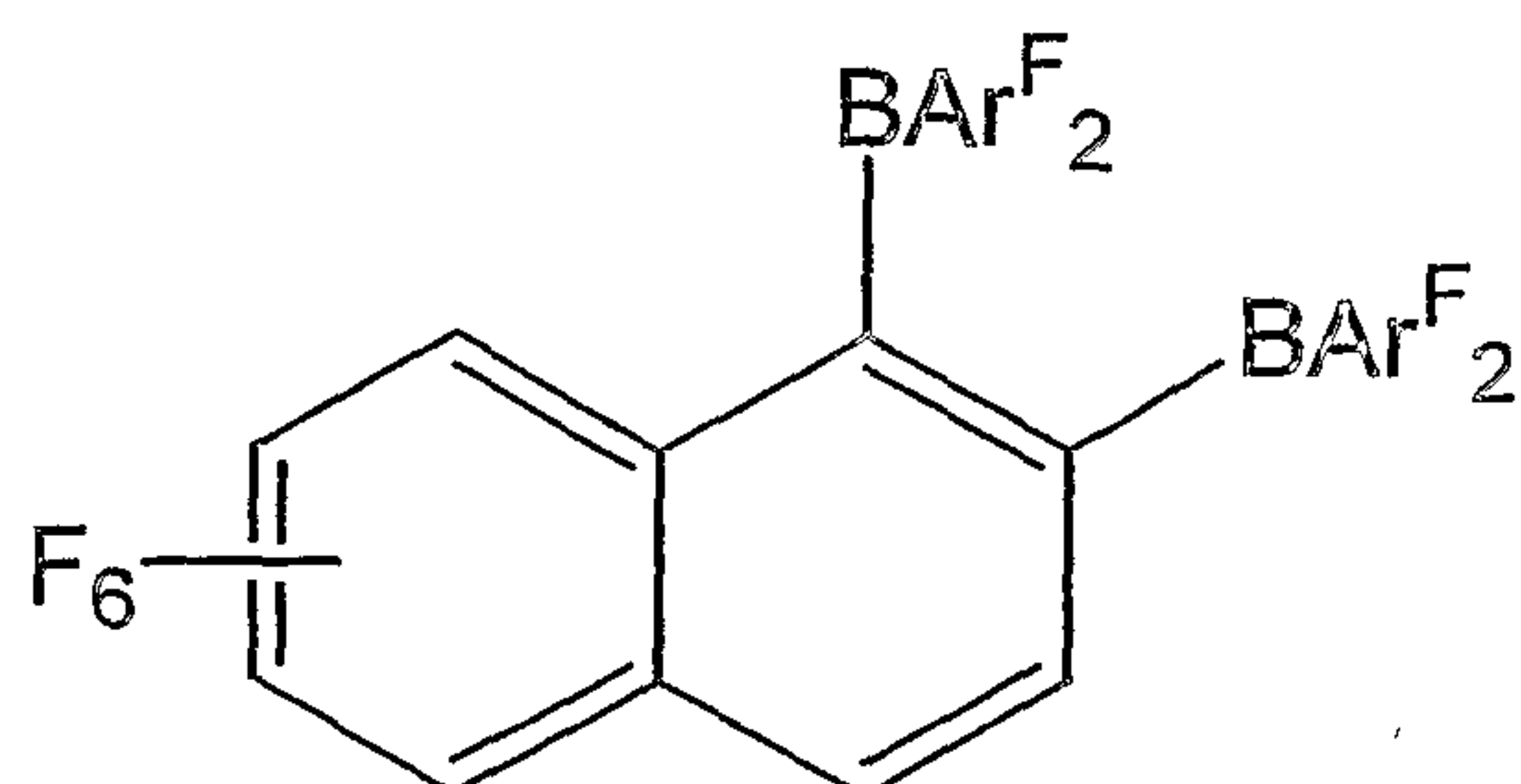
 $X = \text{CH}_2, \text{NR}, \text{ or } \text{O}$

and

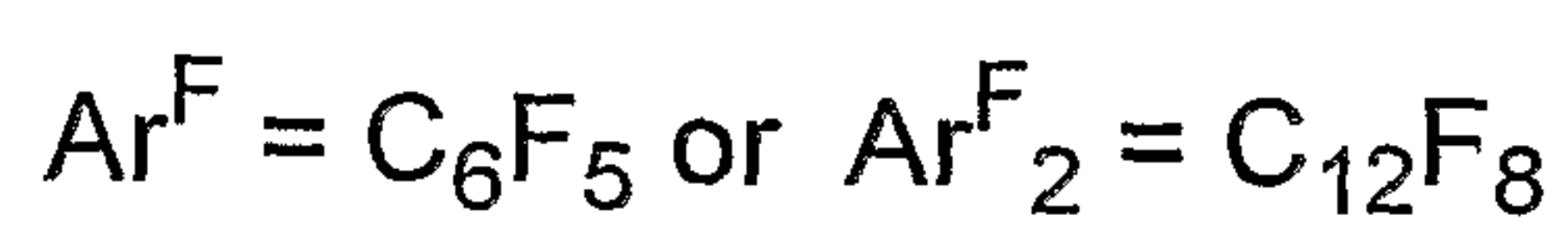
 $\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5 \text{ or } \text{Ar}^{\text{F}_2} = \text{C}_{12}\text{F}_8$

19

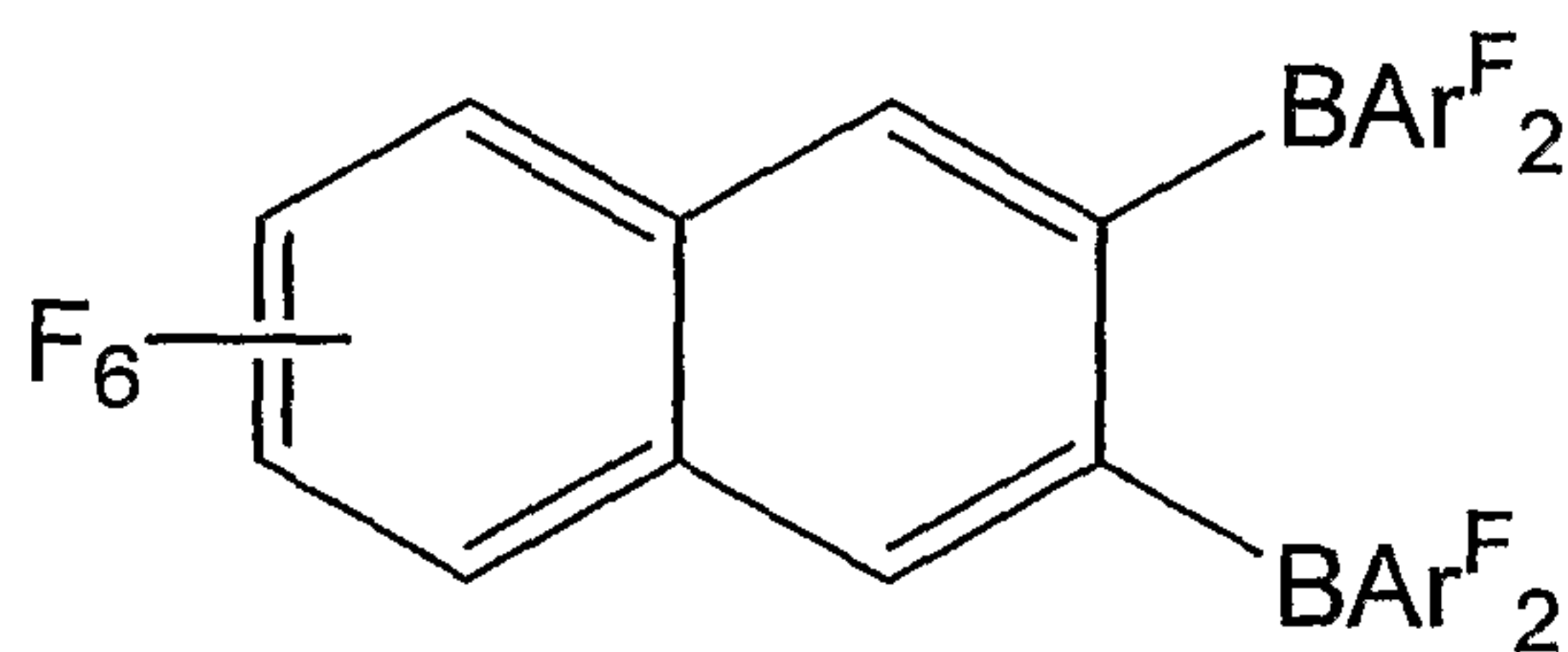
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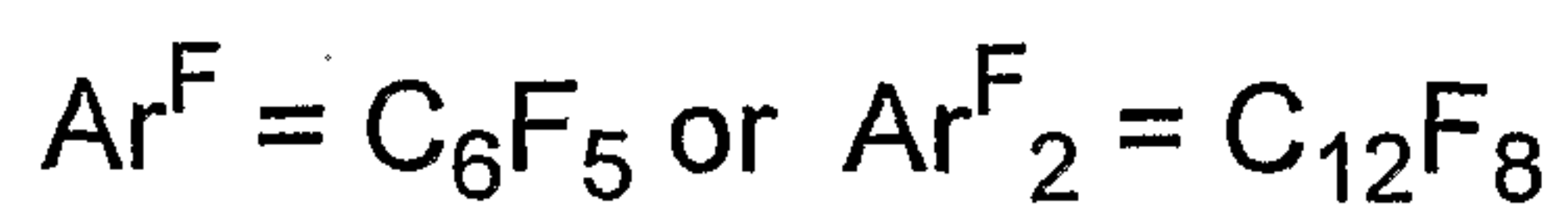
wherein



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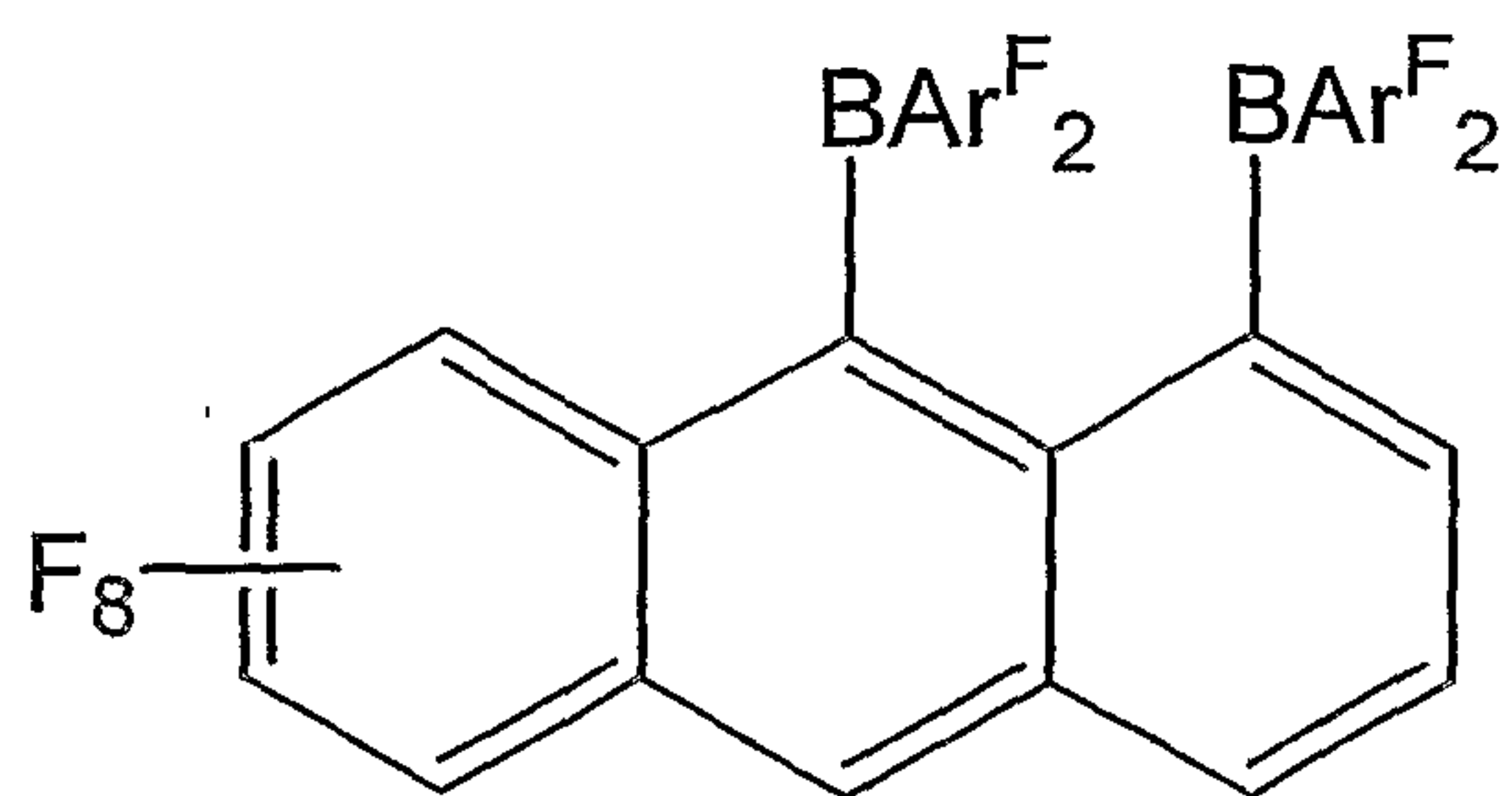


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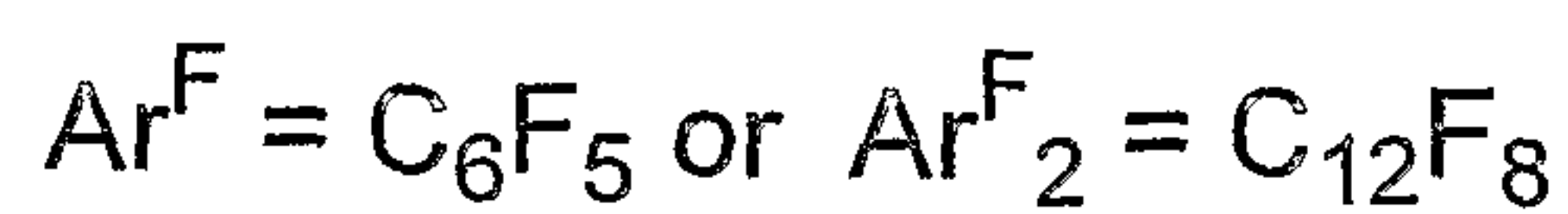


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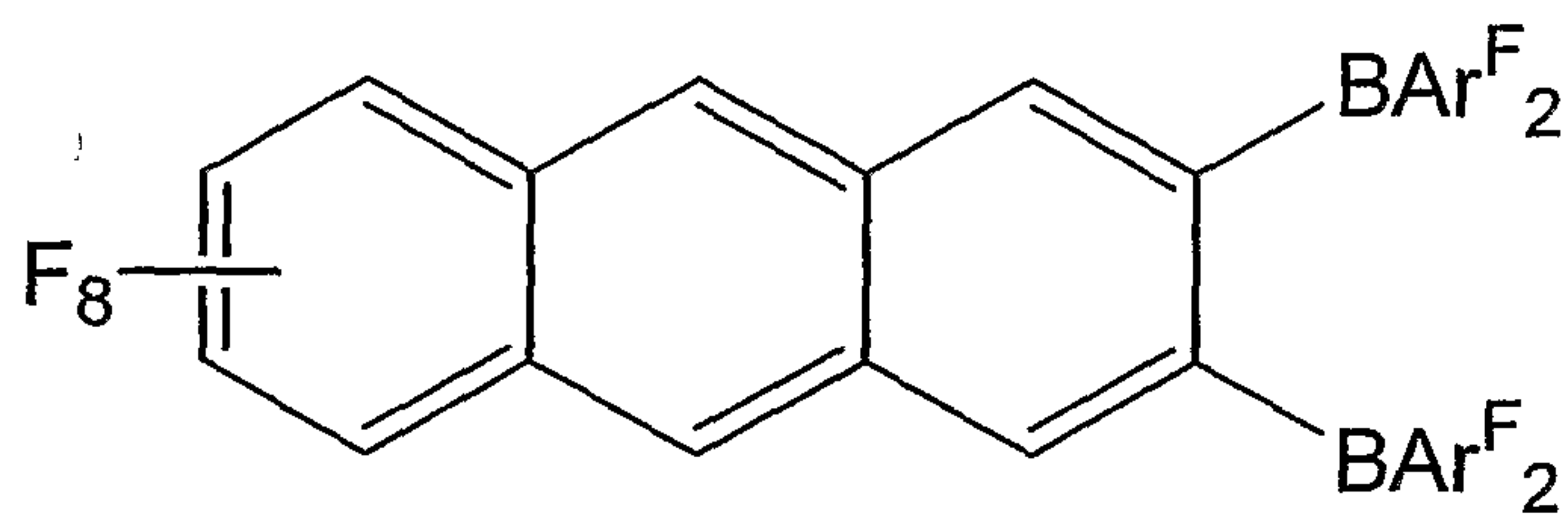
14)



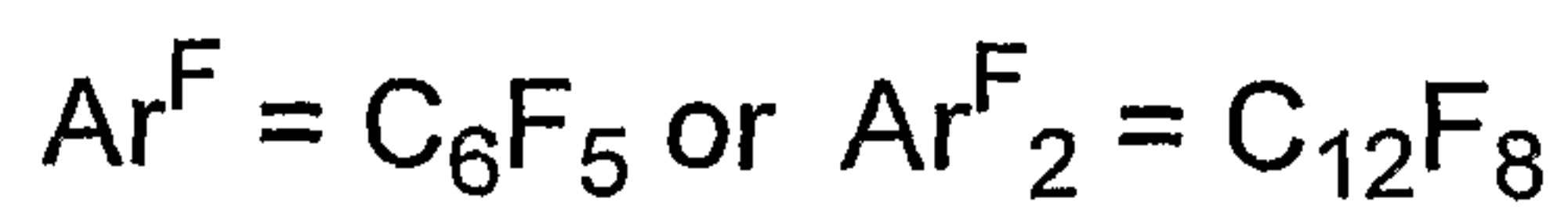
wherein



15)

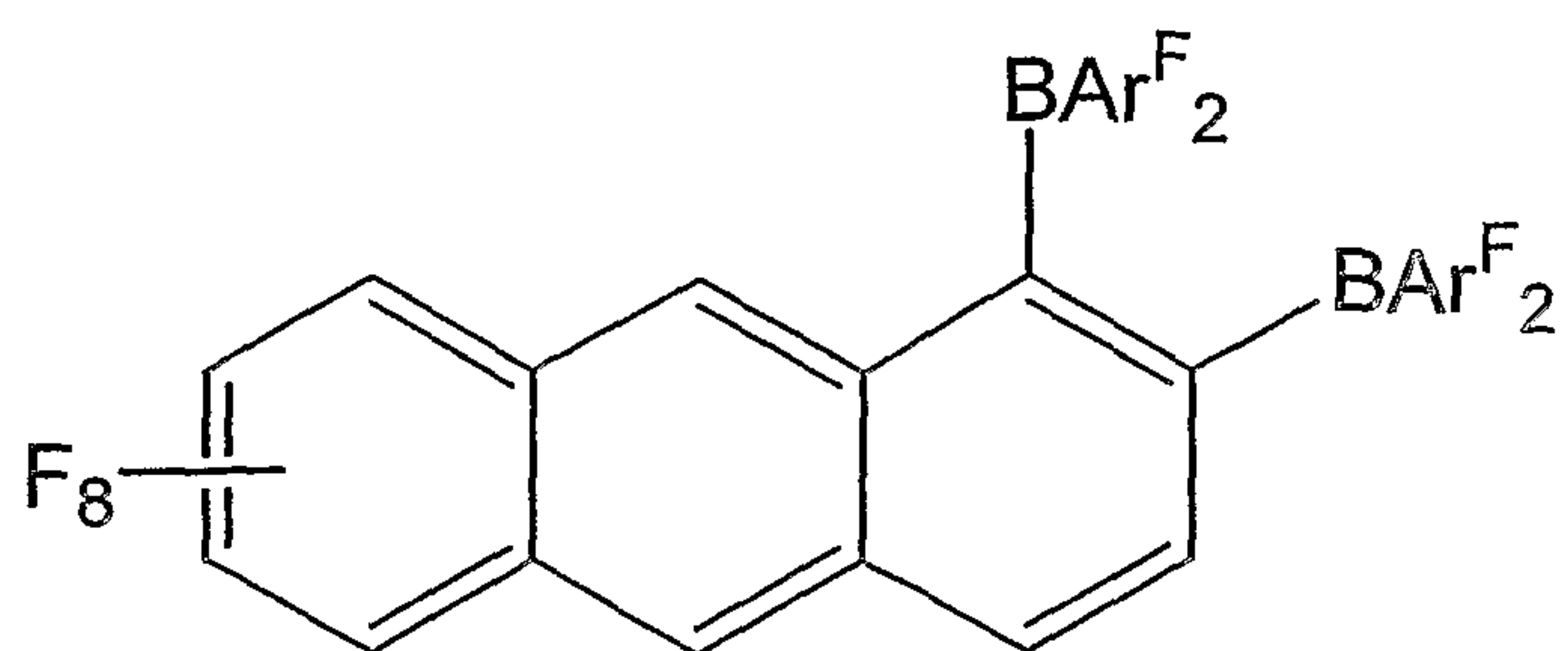


wherein

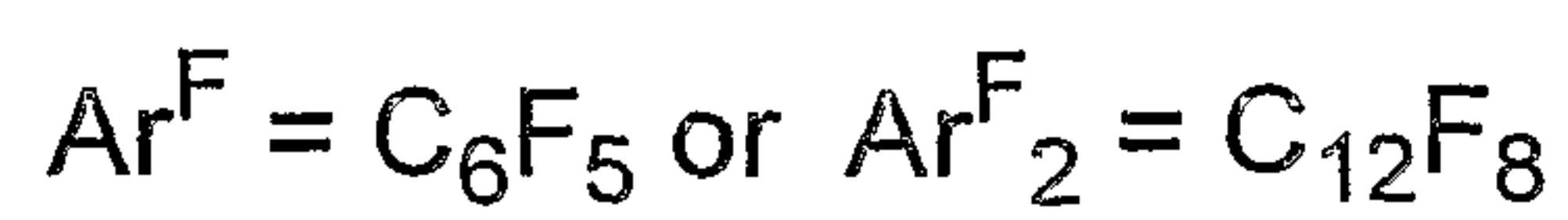


21

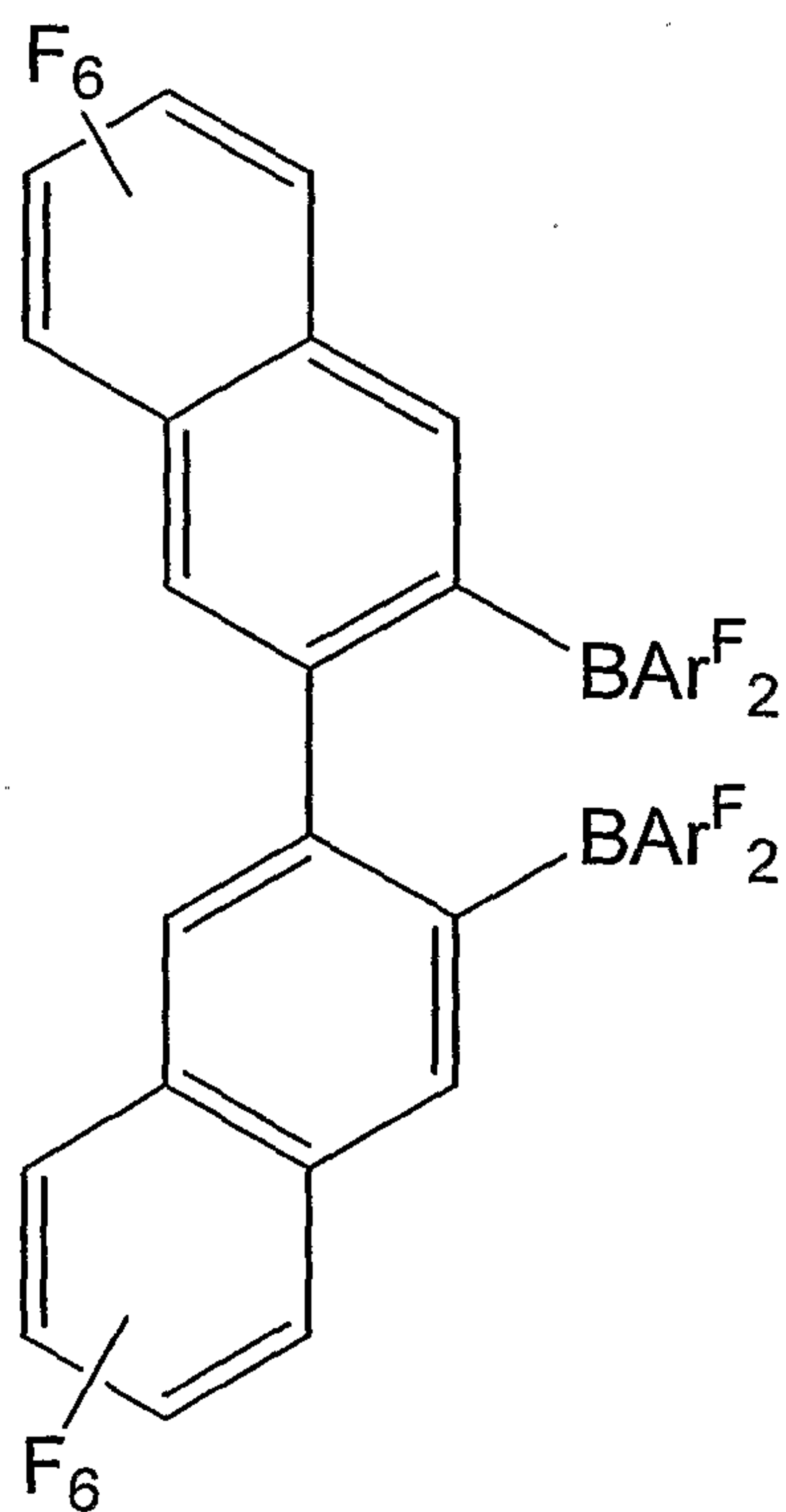
16)



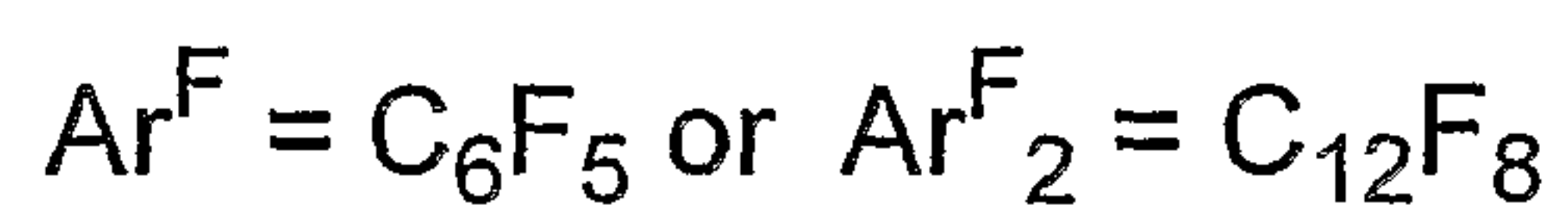
wherein



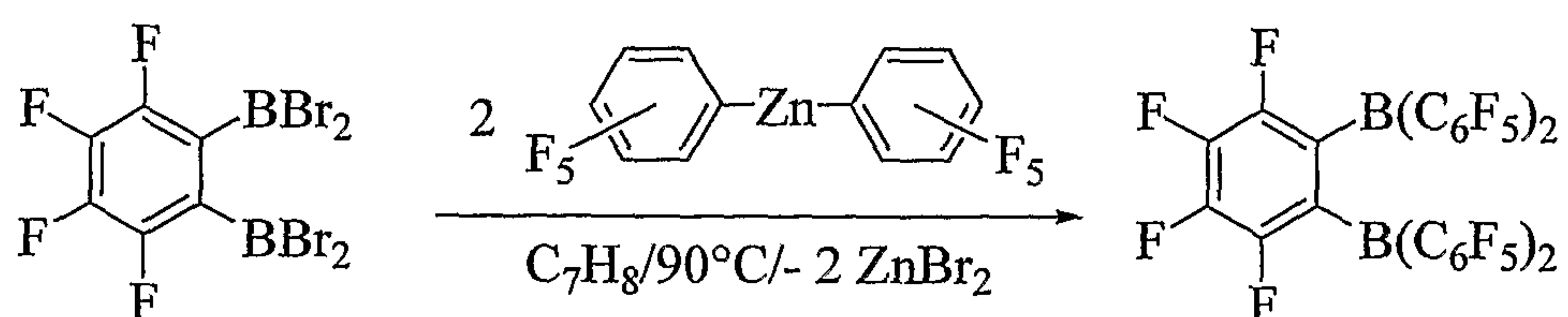
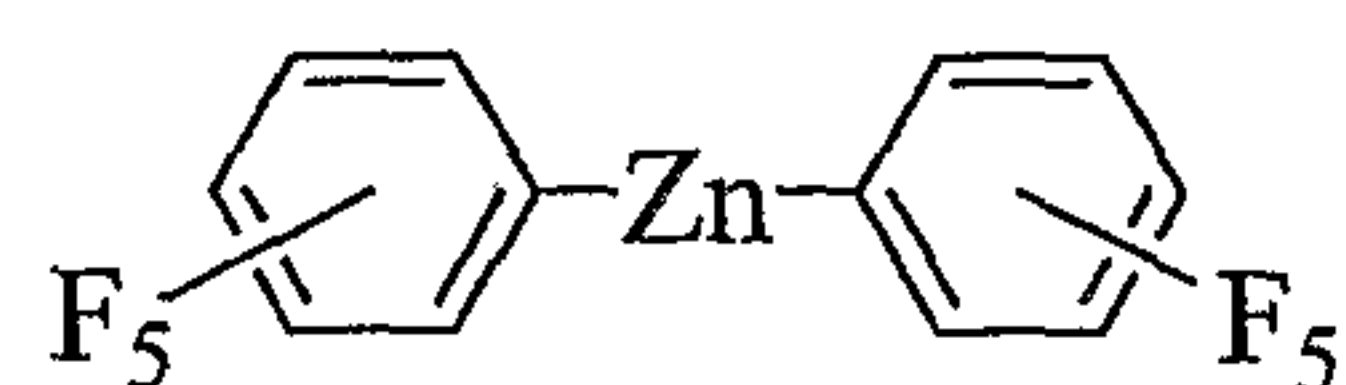
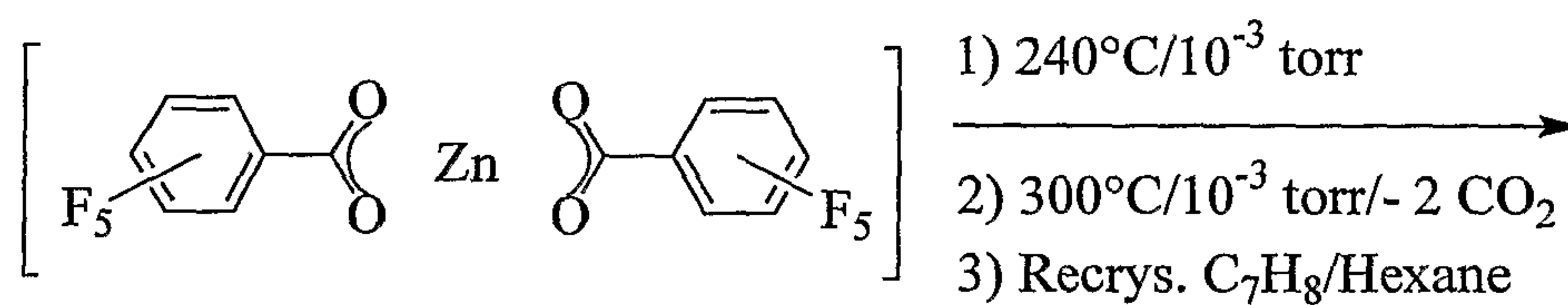
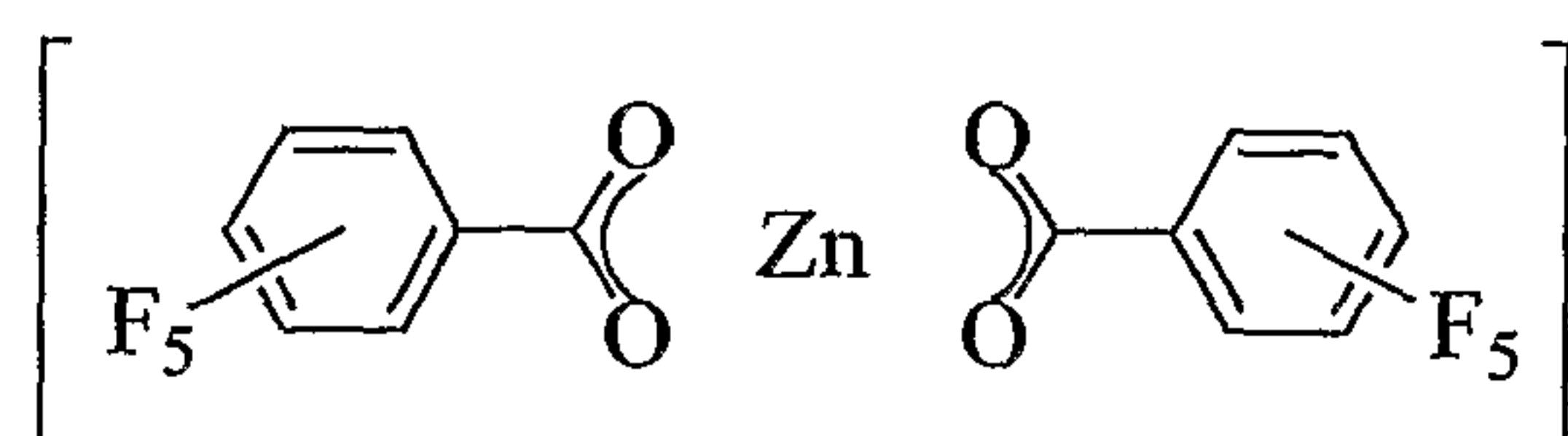
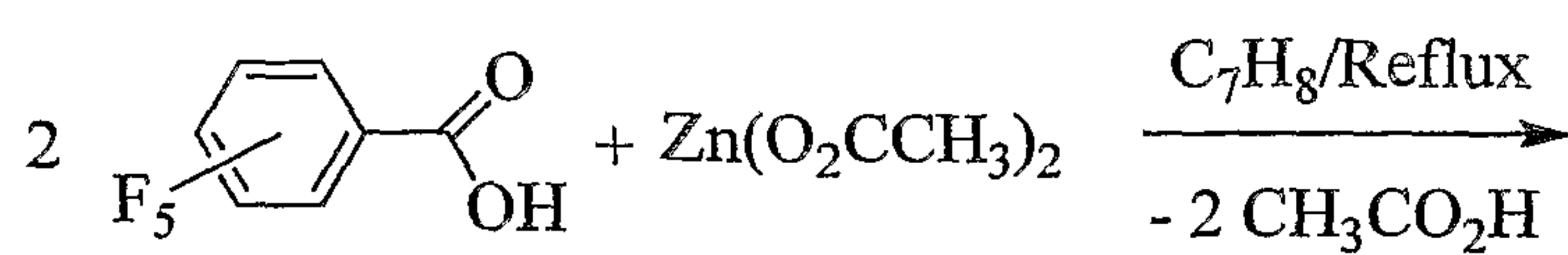
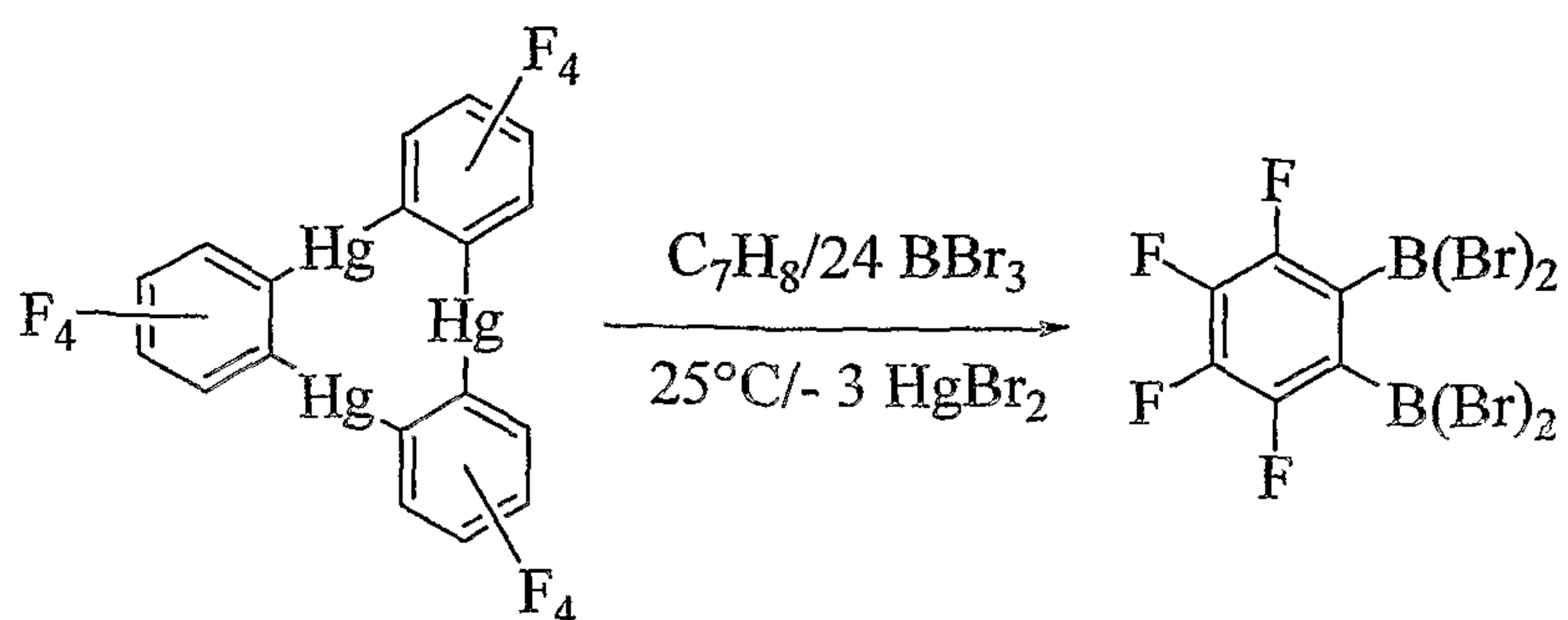
17)

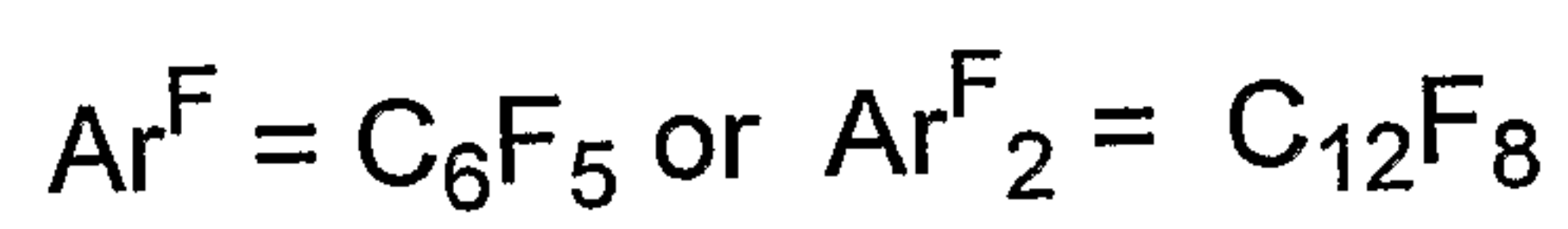
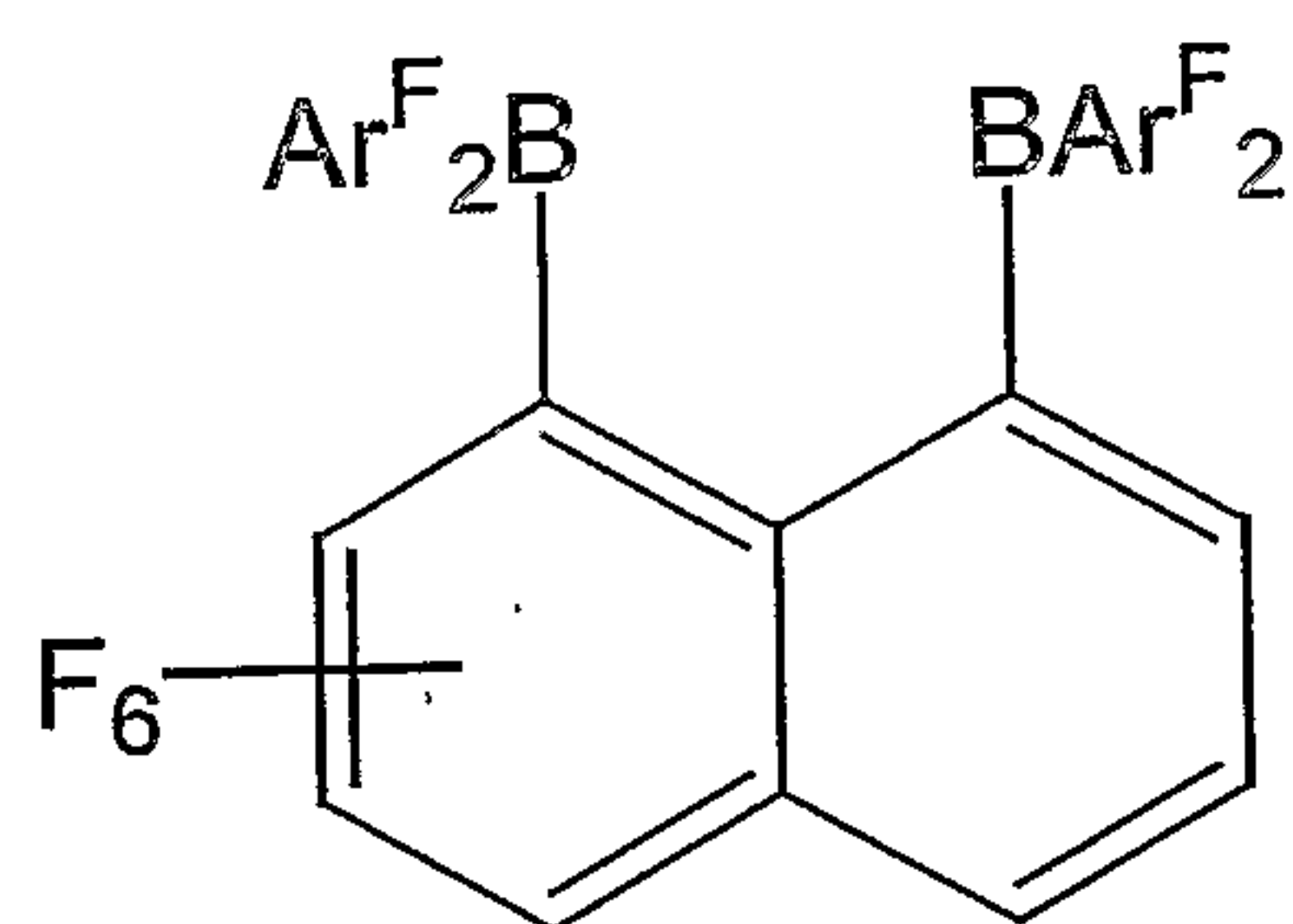


wherein



23



3/15**FIG. 3.**

4/15

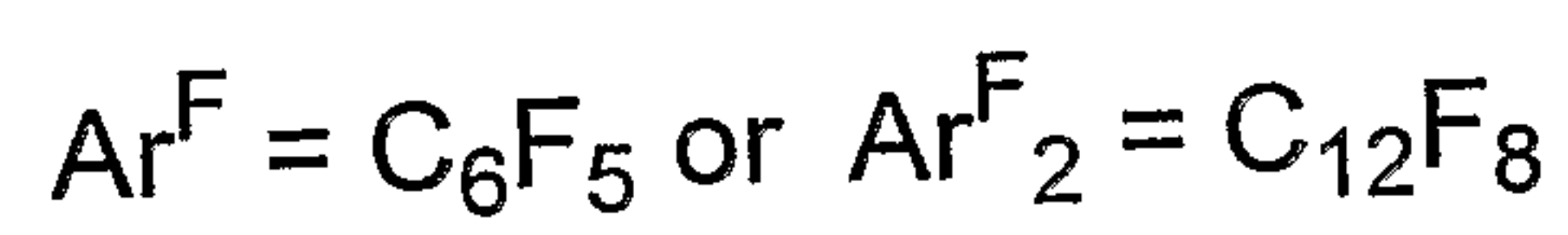
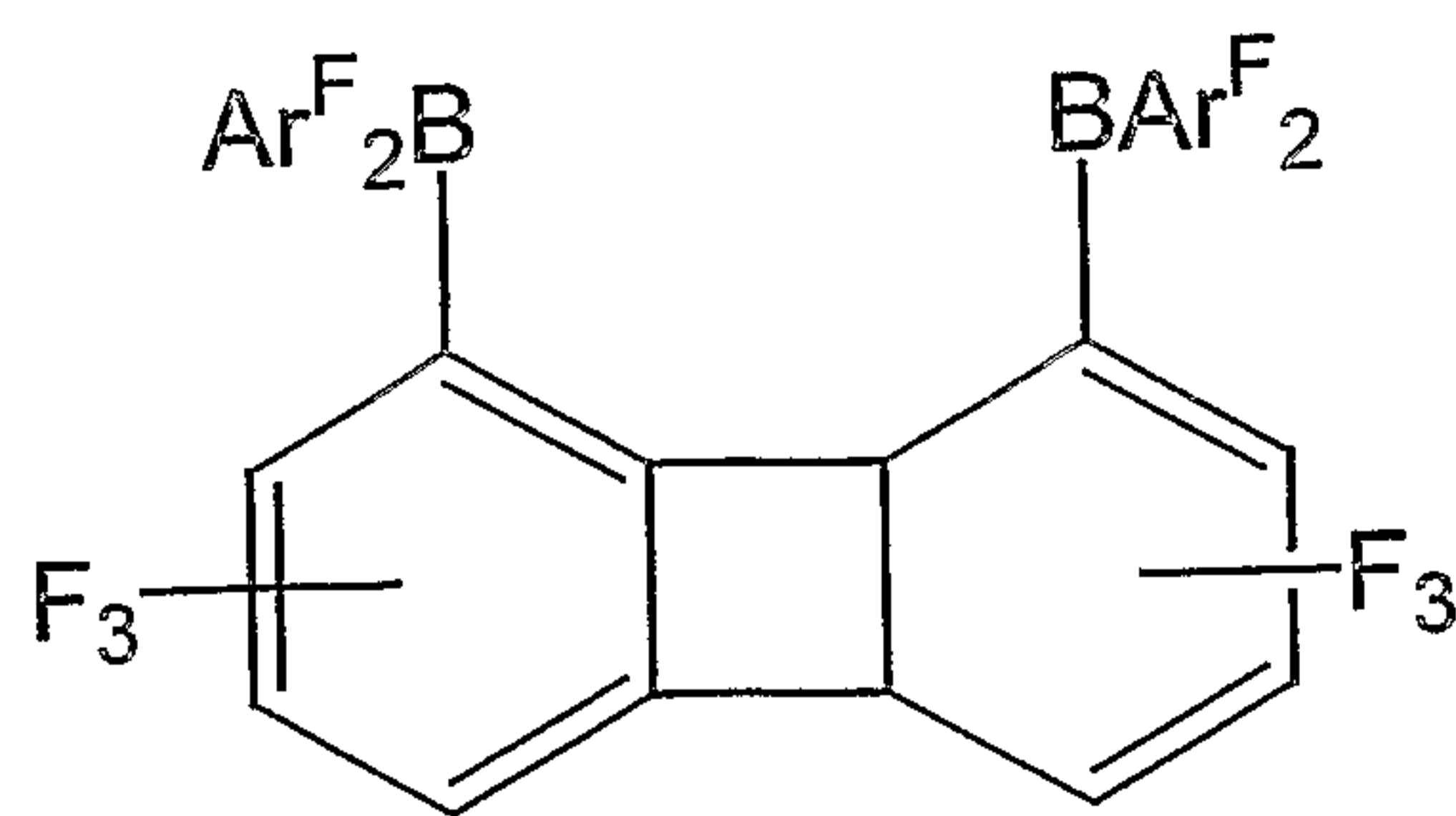
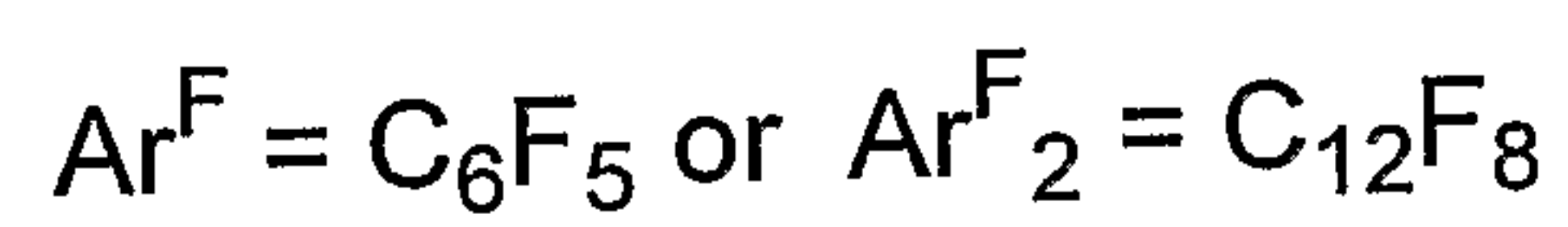
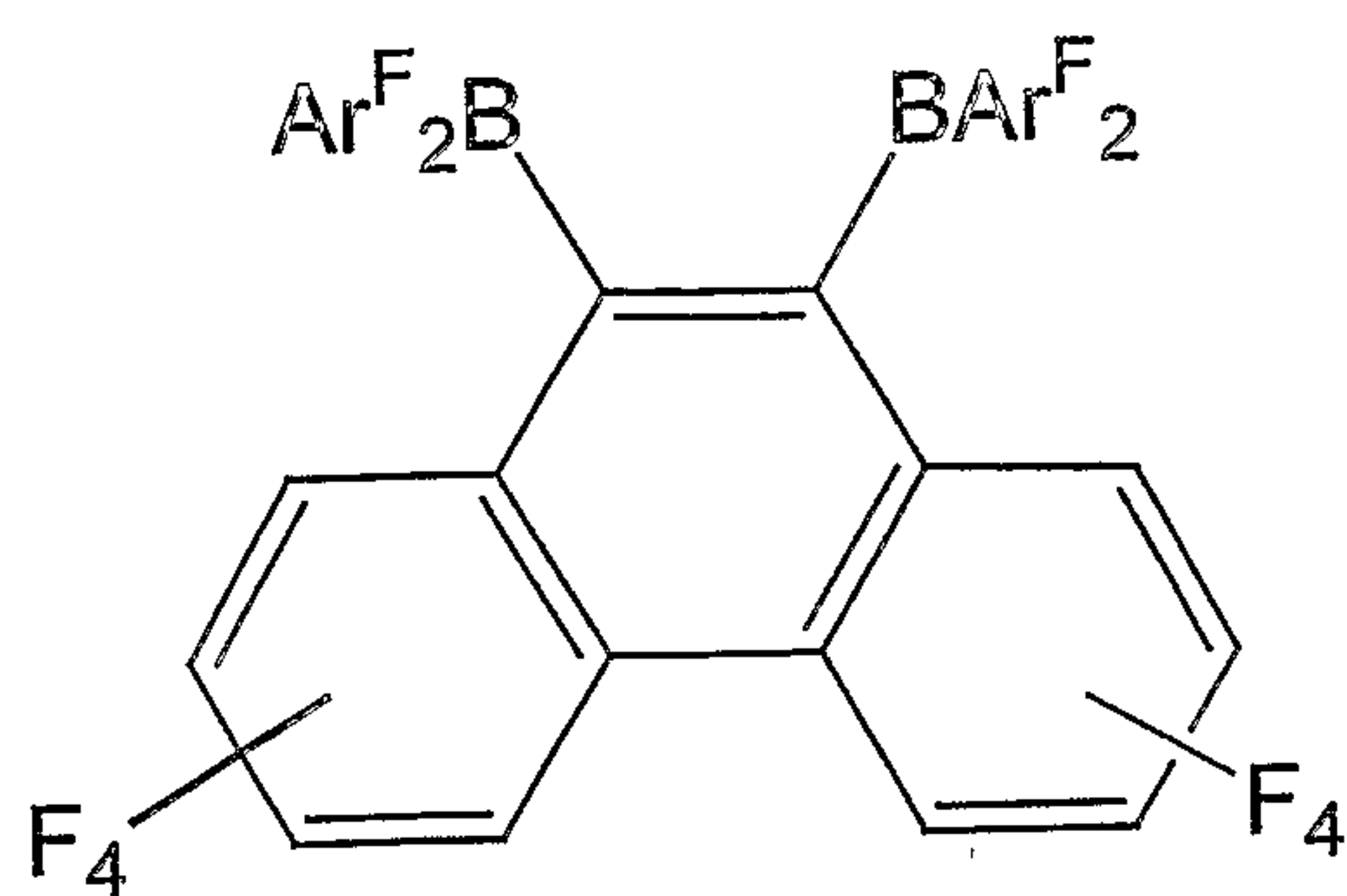


FIG. 4.

5/15**FIG. 5**

6/15

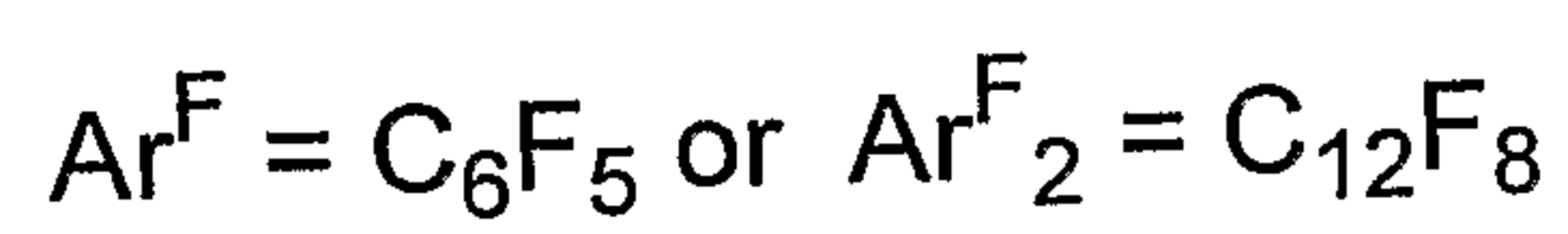
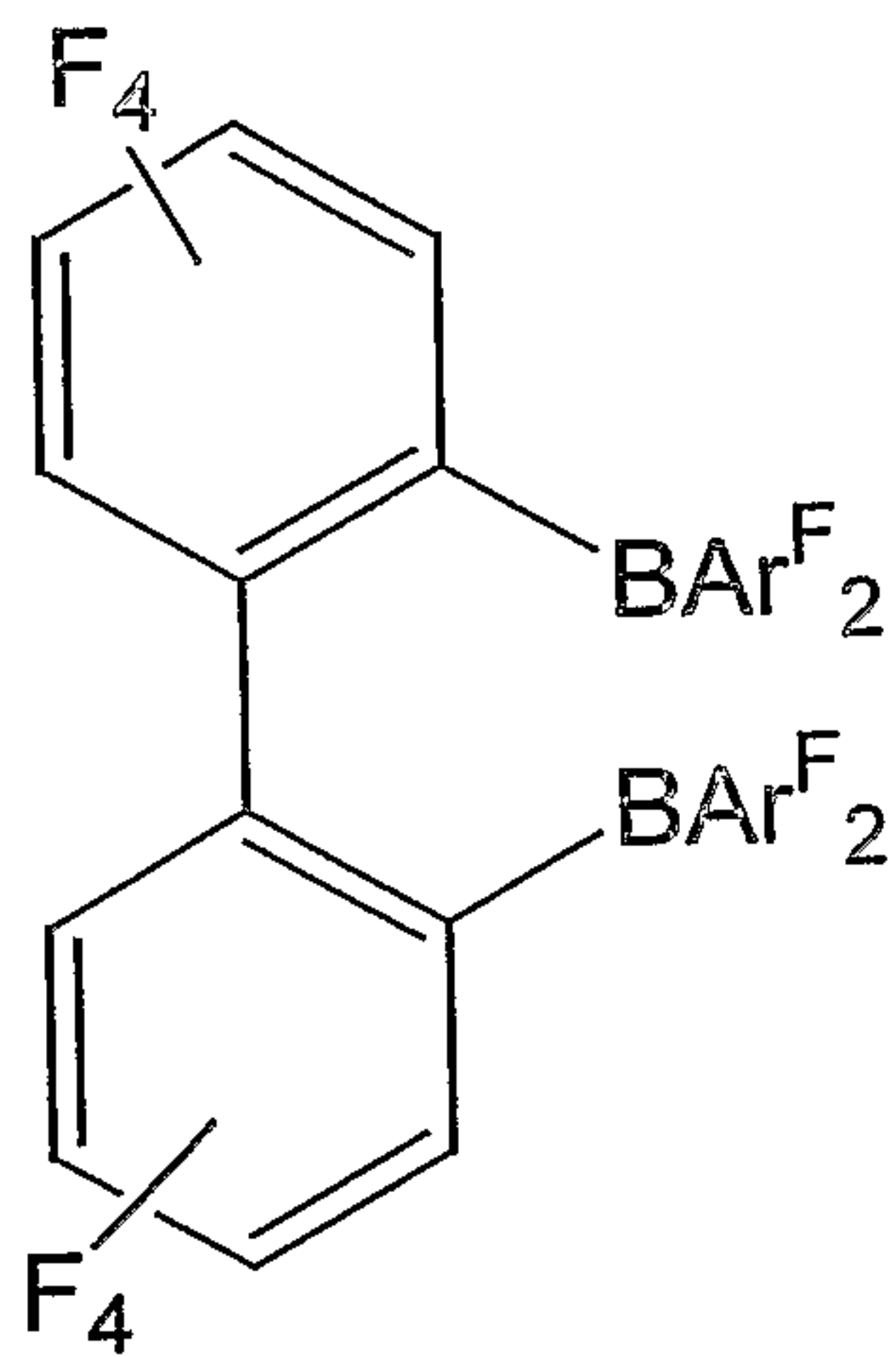


FIG. 6

7/15

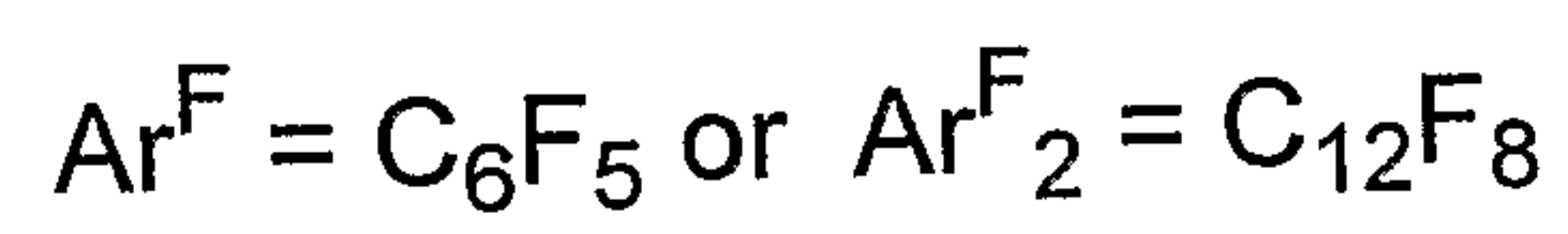
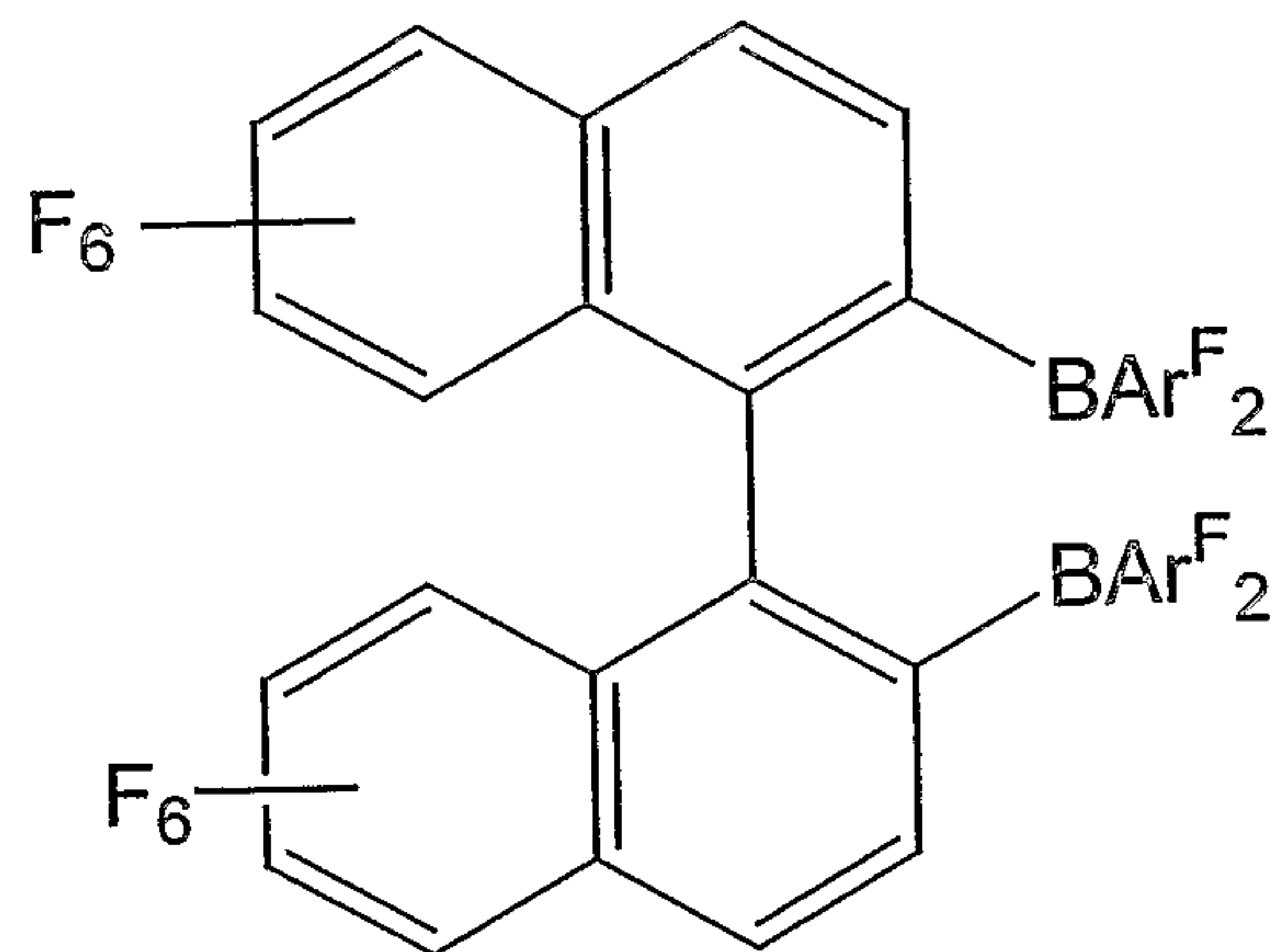
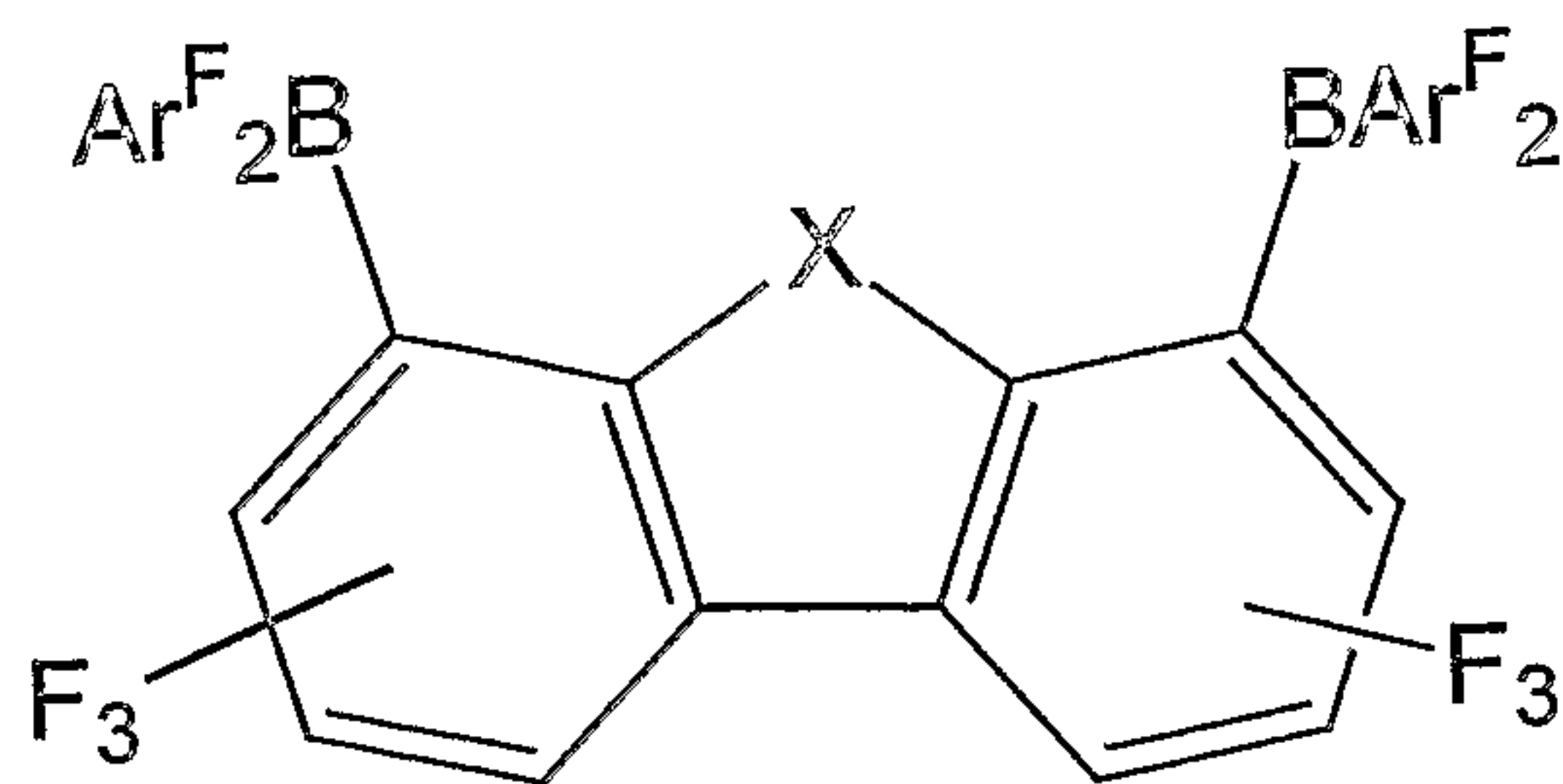


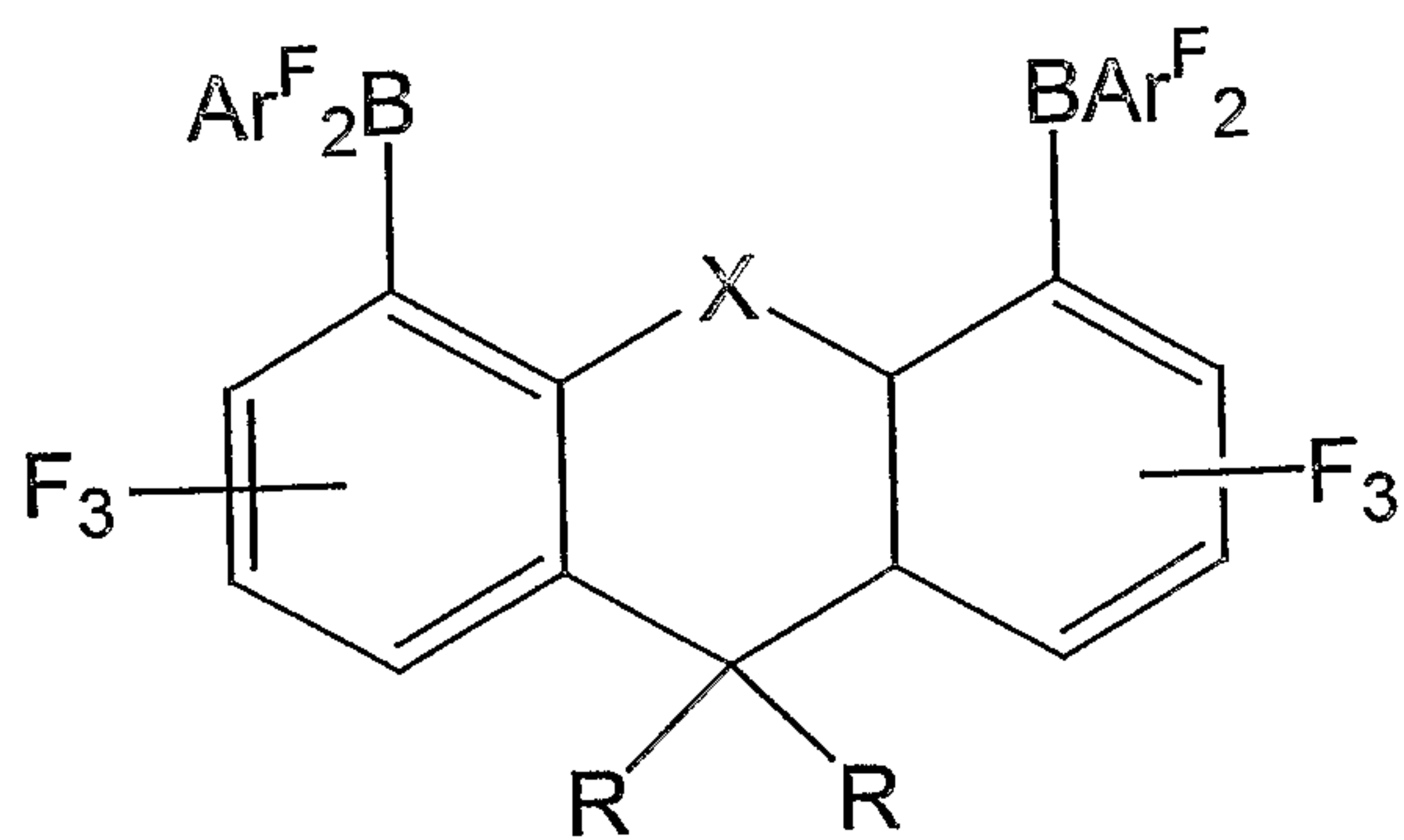
FIG. 7.

8/15

$X = \text{CH}_2, \text{NR}, \text{ or } \text{O}$

$\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5 \text{ or } \text{Ar}^{\text{F}}_2 = \text{C}_{12}\text{F}_8$

FIG. 8.

9/15

X = CH₂, NR, or O

Ar^F = C₆F₅ or Ar^F₂ = C₁₂F₈

FIG. 9.

