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(54) **SOLAR CELL DYES FOR COPPER REDOX  
BASED DYE SENSITIZED SOLAR CELLS  
AND COMBINATIONS THEREOF**

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(63) Continuation of application No. 17/003,248, filed on  
Aug. 26, 2020, now Pat. No. 11,286,244, which is a

(57) **ABSTRACT**

The present application discloses compounds and composi-  
tions, useful in the manufacture of dye-sensitized solar cells  
and other similar technology.

**SOLAR CELL DYES FOR COPPER REDOX  
BASED DYE SENSITIZED SOLAR CELLS  
AND COMBINATIONS THEREOF**

**[0001]** The present application is a Continuation of, and claims priority under 35 USC 120 to, U.S. patent application Ser. No. 17/003,248, which was a Continuation of International Application PCT/US2019/040955, filed Jul. 9, 2019, which claimed priority to U.S. Provisional Application 62/696,010, filed Oct. 17, 2018. The contents of these priority applications are incorporated by reference herein in their entirety.

TECHNICAL FIELD

**[0002]** The present invention is in the field of material compositions used to assemble dye sensitized solar cells (DSSC) and other dye sensitized electronic devices such as information storage devices, sensing devices and imaging devices. In particular, it concerns the utility of novel organic chromophores and chromophore combinations as the sensitizing dyes in dye sensitized electronic devices.

BACKGROUND

**[0003]** Sensitization of semiconductor solids such as metal oxides in imaging devices, memories, sensors, and solar cells can serve as an effective means of energy transduction. These devices use metal oxides, such as titanium dioxide that are transparent to light but can be sensitized to the desired spectrum through the use of sensitizing agents that absorb light energy and transduce it into electrical power or an electrical signal. This sensitization occurs through charge injection into the metal oxide from the excited state of the dye sensitizer. Sensitizers such as transition metal complexes, inorganic colloids and organic dye molecules are used.

**[0004]** Prominent among such technologies is the dye-sensitized metal oxide solar cell (DSSC). DSSCs use a dye to absorb light and initiate a rapid electron transfer to a nanostructured oxide such as  $\text{TiO}_2$ . The mesoscopic structure of the  $\text{TiO}_2$  allows building of thick, nanoporous films with active-layer thicknesses of several microns. The dye is then adsorbed on the large surface area of the mesoporous  $\text{TiO}_2$ . Charge balance and transport is achieved by a layer having a REDOX couple, such as iodide/triiodide,  $\text{Co(II)/Co(III)}$  complexes, and  $\text{Cu(I)/Cu(II)}$  complexes.

**[0005]** Dyes based on transition metal complexes are disclosed in Gratzel et al., U.S. Pat. Nos. 4,927,721 and 5,350,644. These dye materials are disposed on mesoporous metal oxides that have a high surface area on which the absorbing, sensitizing layer can be formed. This results in a high absorptivity of light in the cell. Dyes such as  $\text{Ru(II)(2,2'-bipyridyl 4,4' dicarboxylate)}_2 (\text{NCS})_2$  have been found to be efficient sensitizers and can be attached to the metal oxide solid through carboxyl or phosphonate groups on the periphery of the compounds. However, when transition metal ruthenium complexes are used as sensitizers they must be applied to the mesoporous metal oxide layers in a coat as thick as 10 micrometers or thicker in order to absorb enough solar radiation to attain sufficient power conversion efficiencies. Further, the ruthenium complexes are expensive. In addition, such dyes must be applied using volatile organic solvents, co-solvents, and diluents because they are not dispersible in water. Volatile organic compounds (VOCs) are significant pollutants that can affect the environment and

human health. While VOCs are usually not acutely toxic, they may have chronic health and environmental effects. For this reason, governments around the world are seeking to reduce the levels of VOCs.

**[0006]** One type of dye-sensitized solar cell is known as the Gratzel cell. Hamann et al. (2008), "Advancing beyond current generation dye-sensitized solar cells," *Energy Environ. Sci.* 1:66-78 (the disclosure of which is incorporated in its entirety by reference), describes the Gratzel cell. The Gratzel cell includes crystalline titanium dioxide nanoparticles serving as a photoanode in the photovoltaic cell. The titanium dioxide is coated with light sensitive dyes. The titanium dioxide photoanode includes 10-20 nm diameter titanium dioxide particles forming a 12  $\mu\text{m}$  transparent film. The 12  $\mu\text{m}$  titanium dioxide film is made by sintering the 10-20 nm diameter titanium dioxide particles so that they have a high surface area. The titanium dioxide photoanode also includes a 4  $\mu\text{m}$  film of titanium dioxide particles having a diameter of about 400 nm. The coated titanium dioxide films are located between two transparent conducting oxide (TCO) electrodes. Also disposed between the two TCO electrodes is an electrolyte with a redox shuttle.

**[0007]** The Gratzel cell may be made by first constructing a top portion. The top portion may be constructed by depositing fluorine-doped tin dioxide ( $\text{SnO}_2\text{F}$ ) on a transparent plate, which is usually glass. A thin layer of titanium dioxide ( $\text{TiO}_2$ ) is deposited on the transparent plate having a conductive coating. The  $\text{TiO}_2$  coated plate is then dipped into a photosensitized dye such as ruthenium-polypyridine dye in solution. A thin layer of the dye covalently bonds to the surface of the titanium dioxide. A bottom portion of the Gratzel cell is made from a conductive plate coated with platinum metal. The top portion and the bottom portion are then joined and sealed. The electrolyte, such as iodide-triiodide, is then typically inserted between the top and bottom portions of the Gratzel cell.

**[0008]** Typically, thin films for Dye Sensitized Solar Cells (DSSC) are composed of a single metal oxide—usually titanium dioxide, which in addition to nanoparticles, may be utilized in the form of larger 200 to 400 nm scale particles or as dispersed nanoparticles formed in-situ from a titanium alkoxide solution. In one embodiment, the present application discloses the use of multiple morphologies of titanium oxide as well as other metal oxides, which provide a boost in efficiency over the single metal oxide system. The additional metal oxides that may be employed include, but are not limited to, alpha aluminum oxide, gamma aluminum oxide, fumed silica, silica, diatomaceous earth, aluminum titanate, hydroxyapatite, calcium phosphate and iron titanate; and mixtures thereof. These materials may be utilized in conjunction with traditional titanium oxide thin films or with a thin film dye sensitized solar cell system

**[0009]** In operation, the dye absorbs sunlight, which results in the dye molecules becoming excited and transmitting electrons into the titanium dioxide. The titanium dioxide accepts the energized electrons, which travel to a first TCO electrode. Concurrently, the second TCO electrode serves as a counter electrode, which uses a redox couple such as iodide-triiodide ( $\text{I}^-/\text{I}_3^-$ ) to regenerate the dye. If the dye molecule is not reduced back to its original state, the oxidized dye molecule decomposes. As the dye-sensitized solar cell undergoes a large number of the oxidation-reduction cycles in the lifetime of operation, more and more dye

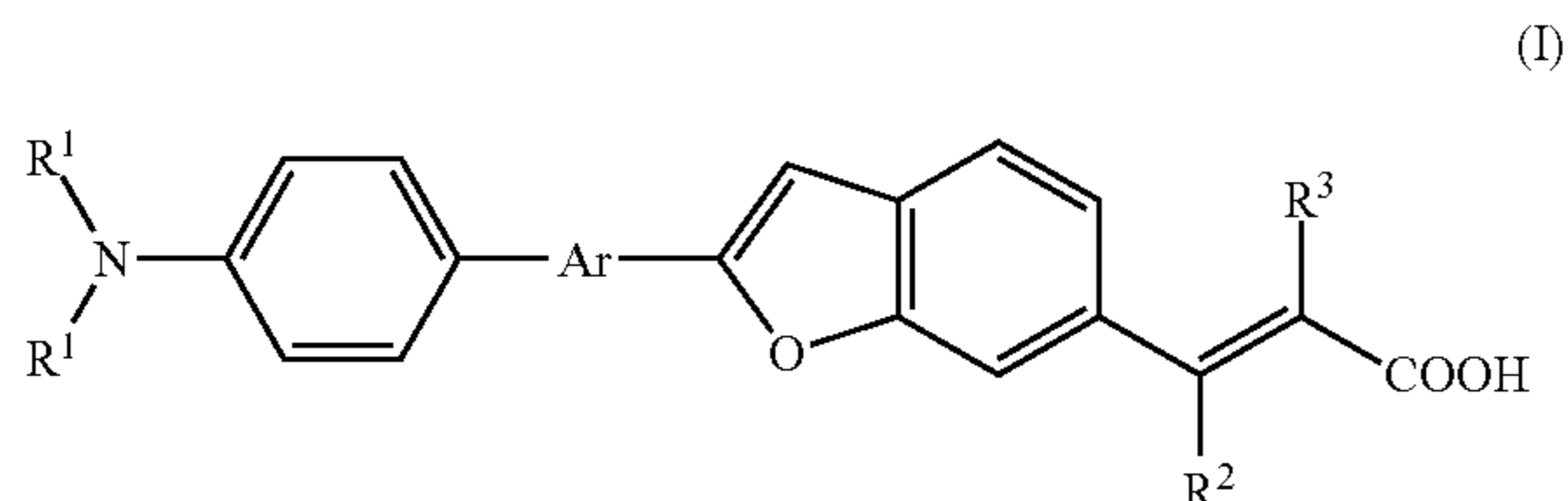
molecules undergo decomposition over time, and the cell energy conversion efficiency decreases.

[0010] Hattori and his coworkers (Hattori, S., et al. (2005) "Blue copper model complexes with distorted tetragonal geometry acting as effective electron-transfer mediators in dye-sensitized solar cells. *J. Am. Chem. Soc.*, 127: 9648-9654) have used copper (I/II) redox couples in DSSCs using ruthenium-based dyes, with very low resulting efficiencies. Peng Wang and his coworkers improved the performance of copper redox-based dye DSSCs using an organic dye (Bai, Y., et al. (2011) *Chem. Commun.*, 47: 4376-4378). The voltage generated from such cells far exceeded voltage generated by any iodide/triiodide based redox couple.

#### SUMMARY OF THE INVENTION

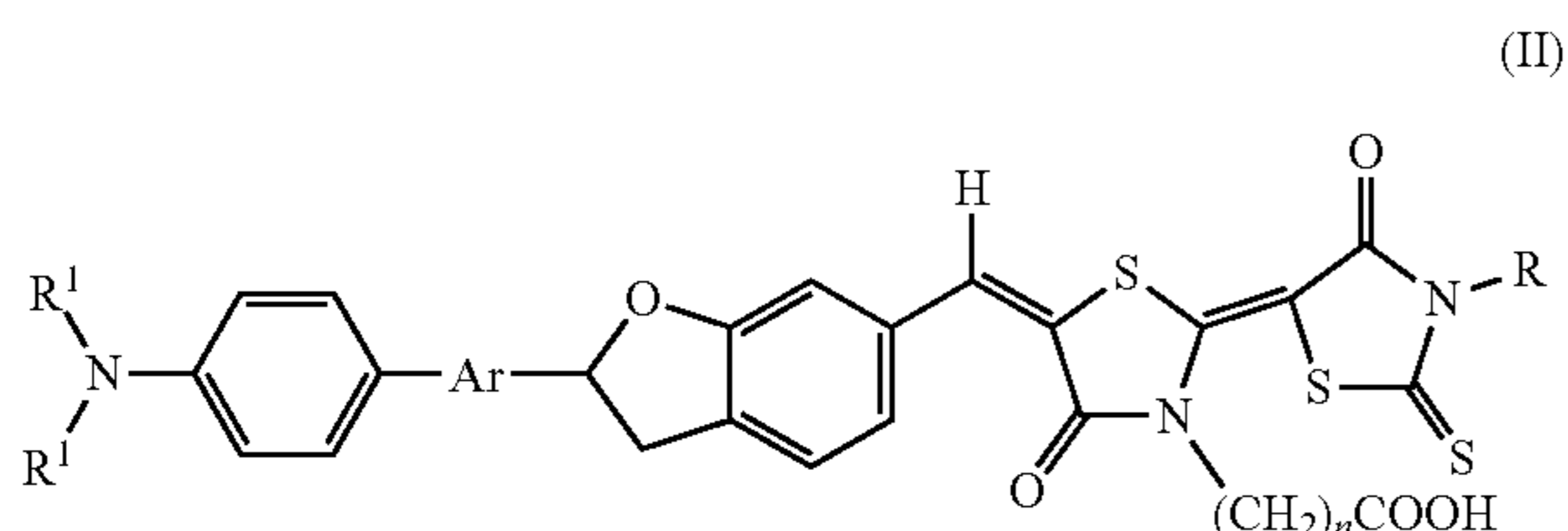
[0011] A dye sensitized solar cell (DSSC) is a low-cost solar cell, often a thin film solar cell. The present application discloses high efficient dye sensitized solar cells, and solar cell dyes for use in such DSSCs. In a particular embodiment, the solar cell is based on a semiconductor that is formed between a photo-sensitized anode and an electrode.

[0012] Described herein is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula I and its structural isomers:



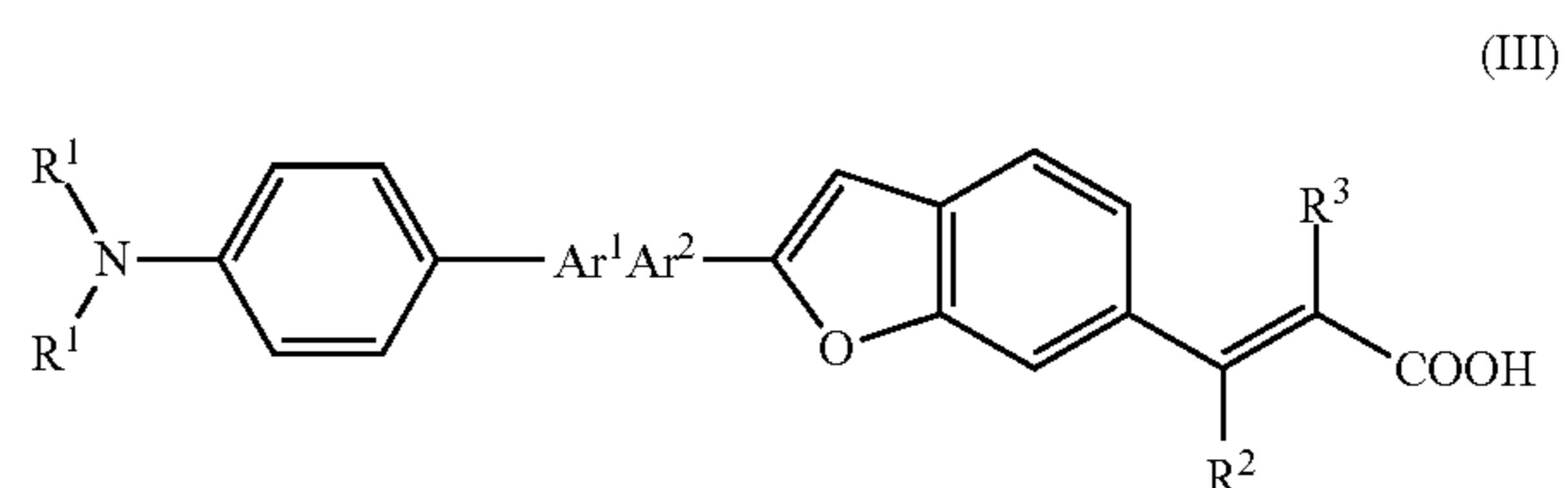
wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar— is a pi-bridge; R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of H, —CN, —COOH, —X, substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, —COOR, —CONHR, —CON(H)OR, —SO<sub>3</sub>R, —SO<sub>2</sub>R—OSO<sub>3</sub>R, —PO<sub>3</sub>HR, and —OPO<sub>3</sub>HR; X is halogen; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

[0013] Also described herein is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula and its structural isomers



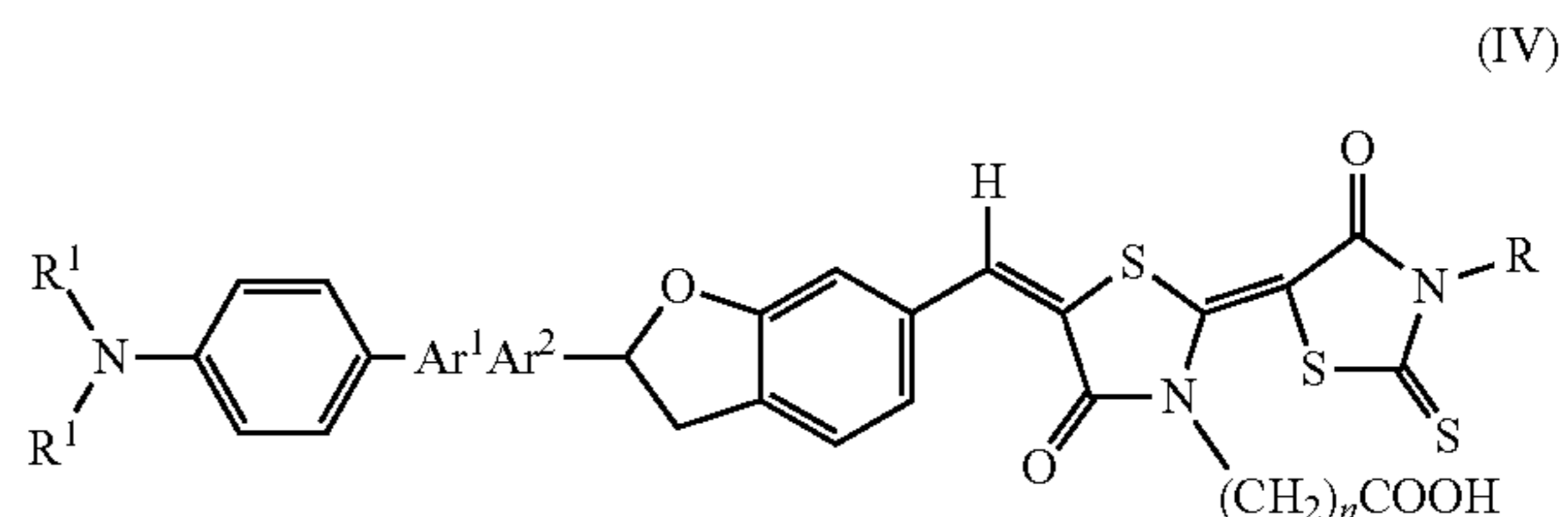
wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar— is a pi-bridge; n is an integer from 1 to 10; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

[0014] Further described herein is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula III and its structural isomers:



wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar<sup>1</sup>— is an electron-withdrawing pi-bridge; —Ar<sup>2</sup>— is an electron-donating pi-bridge; R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of H, —CN, —COOH, —X, substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, —COOR, —CONHR, —CON(H)OR, —SO<sub>3</sub>R, —SO<sub>2</sub>R—OSO<sub>3</sub>R, —PO<sub>3</sub>HR, and —OPO<sub>3</sub>HR; X is halogen; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

[0015] Also described herein is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula IV and its structural isomers:



[0016] wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar<sup>1</sup>— is an electron-withdrawing pi-bridge; —Ar<sup>2</sup>— is an electron-donating pi-bridge; n is an integer from 1 to 10; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

[0017] Further described herein are solar cell dye combinations that exhibit synergistic effect when the combination is used with  $\text{TiO}_2$  in dye sensitized solar cells (DSSCs) in general and copper redox based DSSCs in particular. The voltage generated from the dye combination is higher than that from individual dye-based solar cells; overall current generated is often higher than sum of both dyes using additive effect; and overall power generated is higher than that from individual dye based solar cells. The synergistic effect is seen with both acetonitrile-based volatile electrolytes and sulfolane based stable electrolyte formulations.

[0018] The present inventors have surprisingly discovered unexpected improvements in voltage, current density and overall power density when a benzofuran-containing dye such as WD3 is sensitized with commercial dyes such as XY1b. The generated voltage is higher than that from either WD3 dye-based or XY1b dye-based DSSCs. This synergistic improvement is not seen when two benzofuran containing dyes or two non-benzofuran containing dyes are combined.

[0019] The dye combinations can be used as efficient sensitizers in dye sensitized solar cells. These molecules will also help in using energy mismatched dye molecules (e.g., a blue dye which will not work by itself can be used to harvest light of 600-800 nm wavelength) for making high efficiency solar cells.

[0020] The present application contains the first description of synergistic dye combinations that exhibit performance higher than additive combination of two dyes. Because of this surprising and unexpected synergy, the dye combinations described herein are particularly useful for fabricating high performance solar cells for harvesting sun and indoor light.

[0021] Described herein is a solar cell dye composition comprising a benzofuran-containing dye and a non-benzofuran-containing dye.

[0022] Also described herein are DSSCs incorporating a solar cell dye as described above. Still further described herein are methods of making DSSCs comprising the step of incorporating a solar cell dye as described above.

## DETAILED DESCRIPTION

### Definitions

[0023] Unless specifically noted otherwise herein, the definitions of the terms used are standard definitions used in the art of organic chemistry. Exemplary embodiments, aspects and variations are illustrated in the figures and drawings, and it is intended that the embodiments, aspects and variations, and the figures and drawings disclosed herein are to be considered illustrative and not limiting.

[0024] While particular embodiments are shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example only. Numerous variations, changes, and substitutions will now occur to those skilled in the art. It should be understood that various alternatives to the embodiments described herein may be employed in practicing the methods described herein. It is intended that the appended claims define the scope of the invention and that methods and structures within the scope of these claims and their equivalents be covered thereby.

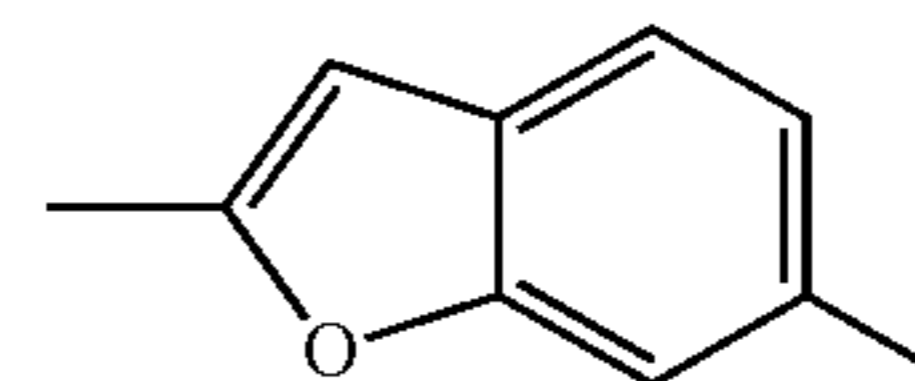
[0025] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is com-

monly understood by one of skill in the art. All patents and publications referred to herein are incorporated by reference.

[0026] As used in the specification and claims, the singular form “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise.

[0027] Unless otherwise stated, structures depicted herein are also meant to include dyes which differ only in the presence of one or more isotopically enriched atoms. For example, dyes as described herein wherein one or more hydrogens are replaced by deuterium or tritium, or the replacement of one or more carbon atoms by the  $^{13}\text{C}$ - or  $^{14}\text{C}$ -enriched carbon isotope. Further, substitution with heavier isotopes, particularly deuterium ( $^2\text{H}$  or D) may afford certain advantages resulting from greater stability, increased half-life, etc. It is understood that deuterium in this context is regarded as a substituent of a dye of the formula (I). The dyes described herein may also contain unnatural proportions of atomic isotopes at one or more of atoms that constitute such dyes. For example, the dyes may be radiolabeled with radioactive isotopes, such as for example tritium ( $^3\text{H}$ ), iodine-125 ( $^{125}\text{I}$ ) or carbon-14 ( $^{14}\text{C}$ ). All isotopic variations of the dyes described herein, whether radioactive or not, are encompassed.

[0028] “Benzofuran-containing” dyes, as used herein, refers to solar cell dyes whose chemical structure comprises a unit having chemical structure



where the open links in this structure indicate where this unit is linked to the rest of the dye structure. One or more of the four ring hydrogens on this unit may be substituted.

[0029] “Non-benzofuran-containing” dyes, as used herein, are solar cell dyes that are not benzofuran-containing dyes.

[0030] “Isomers” are different compounds that have the same molecular formula. “Stereoisomers” are isomers that differ only in the way the atoms are arranged in space. “Enantiomers” are a pair of stereoisomers that are non-superimposable mirror images of each other. A 1:1 mixture of a pair of enantiomers is a “racemic” mixture. The term “(.+-.)” is used to designate a racemic mixture where appropriate. “Diastereoisomers” are stereoisomers that have at least two asymmetric atoms, but which are not mirror-images of each other. The absolute stereochemistry is specified according to the Cahn-Ingold-Prelog R-S system. When a compound is a pure enantiomer the stereochemistry at each chiral carbon can be specified by either R or S. Resolved compounds whose absolute configuration is unknown can be designated (+) or (–) depending on the direction (dextro- or levorotatory) which they rotate plane polarized light at the wavelength of the sodium D line. Certain of the dyes described herein contain one or more asymmetric centers and can thus give rise to enantiomers, diastereomers, and other stereoisomeric forms that can be defined, in terms of absolute stereochemistry, as (R)- or (S)-. The present chemical entities, pharmaceutical compositions and methods are meant to include all such possible isomers, including racemic mixtures, optically pure forms and intermediate mixtures. Optically active (R)- and (S)-isomers can be prepared using chiral synthons or chiral reagents, or resolved using

conventional techniques. The optical activity of a compound can be analyzed via any suitable method, including but not limited to chiral chromatography and polarimetry, and the degree of predominance of one stereoisomer over the other isomer can be determined.

**[0031]** When the dyes described herein contain olefinic double bonds or other centers of geometric asymmetry, and unless specified otherwise, it is intended that the dyes include both E and Z geometric isomers.

**[0032]** A “substituted” or “optionally substituted” group, as used herein, means that a group (such as alkyl, aryl, heterocyclyl, cycloalkyl, heterocyclylalkyl, arylalkyl, heteroaryl, or heteroarylalkyl) unless specifically noted otherwise, may have 1, 2 or 3 —H groups substituted by 1, 2 or 3 substituents selected from halo, trifluoromethyl, trifluoromethoxy, methoxy, —COOH, —CHO, —NH<sub>2</sub>, —NO<sub>2</sub>, —OH, —SH, —SMe, —NHCH<sub>3</sub>, —N(CH<sub>3</sub>)<sub>2</sub>, —CN and the like.

**[0033]** “Tautomers” are structurally distinct isomers that interconvert by tautomerization. “Tautomerization” is a form of isomerization and includes prototropic or proton-shift tautomerization, which is considered a subset of acid-base chemistry. “Prototropic tautomerization” or “proton-

shift tautomerization” involves the migration of a proton accompanied by changes in bond order, often the interchange of a single bond with an adjacent double bond. Where tautomerization is possible (e.g. in solution), a chemical equilibrium of tautomers can be reached. An example of tautomerization is keto-enol tautomerization. A specific example of keto-enol tautomerization is the interconversion of pentane-2,4-dione and 4-hydroxypent-3-en-2-one tautomers. Another example of tautomerization is phenol-keto tautomerization. A specific example of phenol-keto tautomerization is the interconversion of pyridin-4-ol and pyridin-4(1H)-one tautomers.

**[0034]** As used herein, the term “pi-bridge” refers to a chemical moiety, comprising two ends available for covalent linkage (hence “bridge”) and comprising one or more carbon-carbon, heteroatom-carbon, or heteroatom-heteroatom double or triple pi-pi bonds (hence “pi”). The double or triple bonds are conjugated, and one end of a double or triple bond must lie adjacent to each covalent end. Double bonds in each pi-bridge may be part of a linear, cyclic, bicyclic or polycyclic structure.

**[0035]** Pi-bridges contemplated herein include, but are not limited to, those shown in Table 1:

TABLE 1

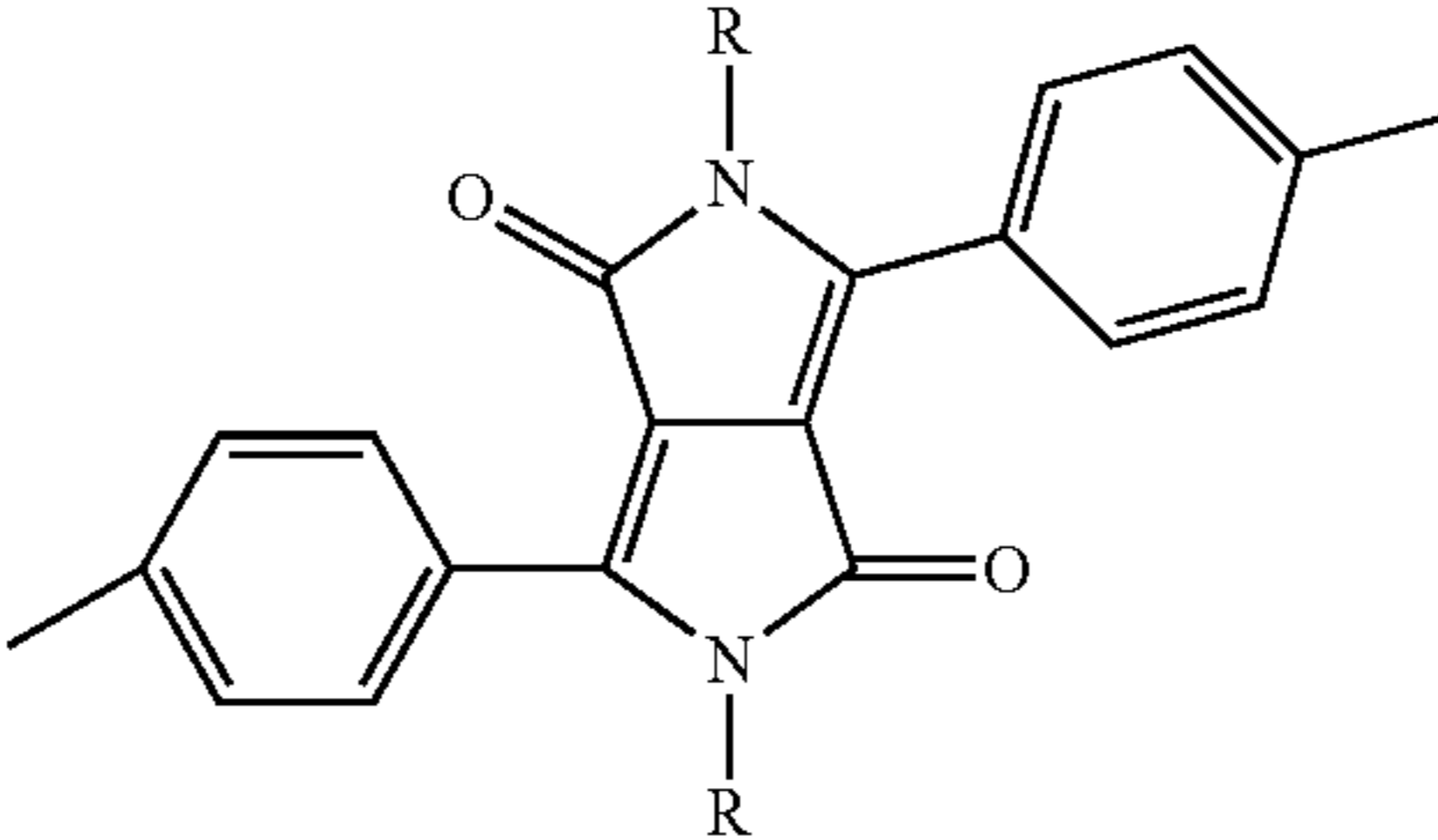
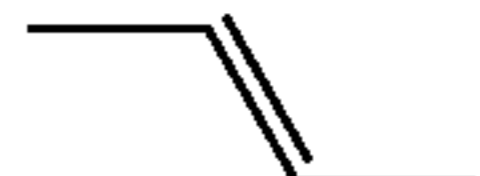
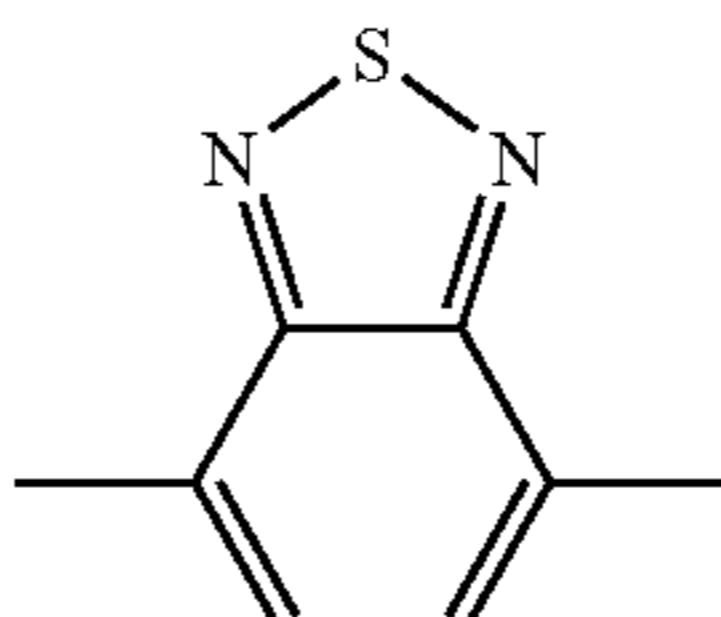
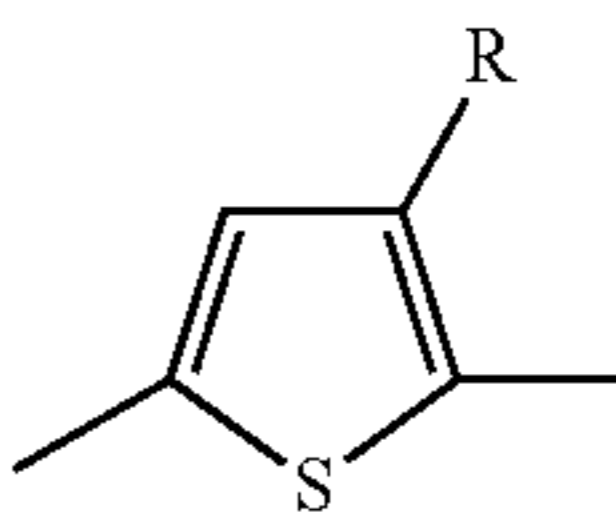
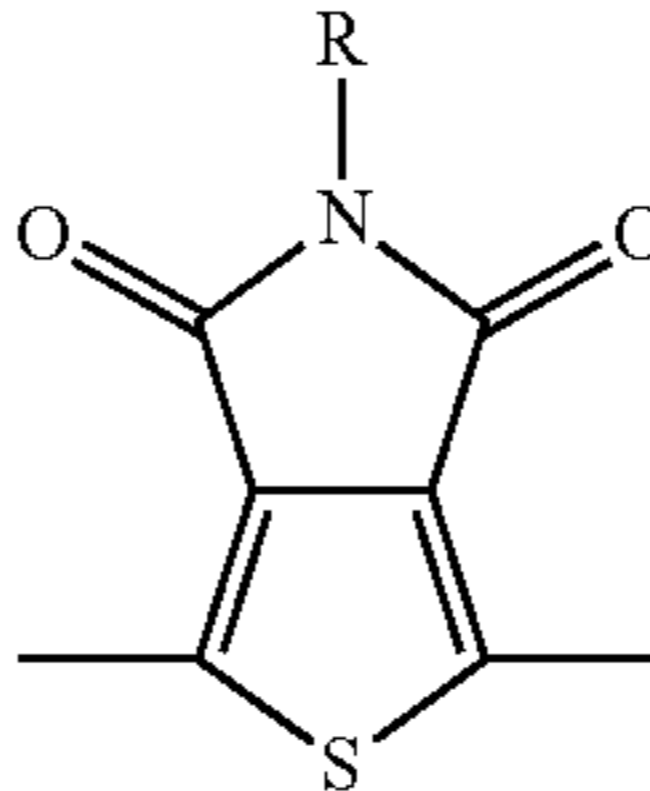
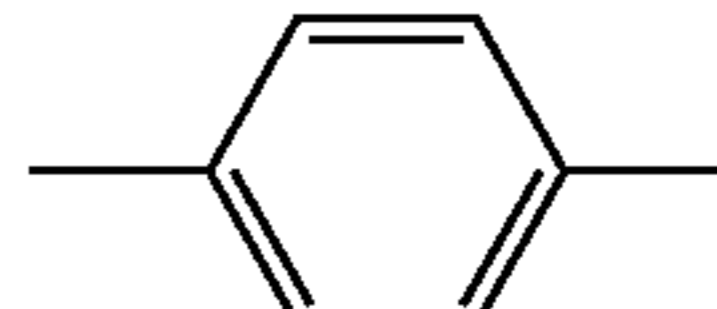
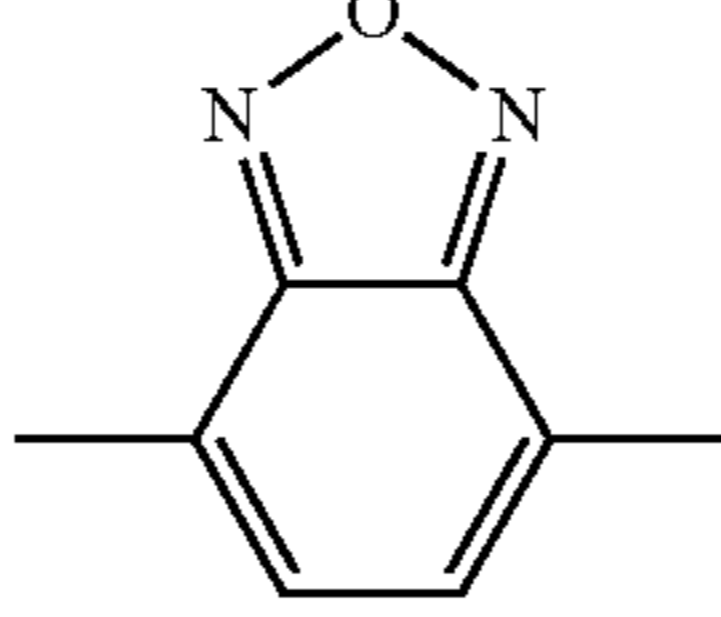
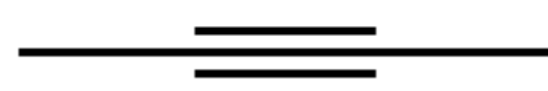
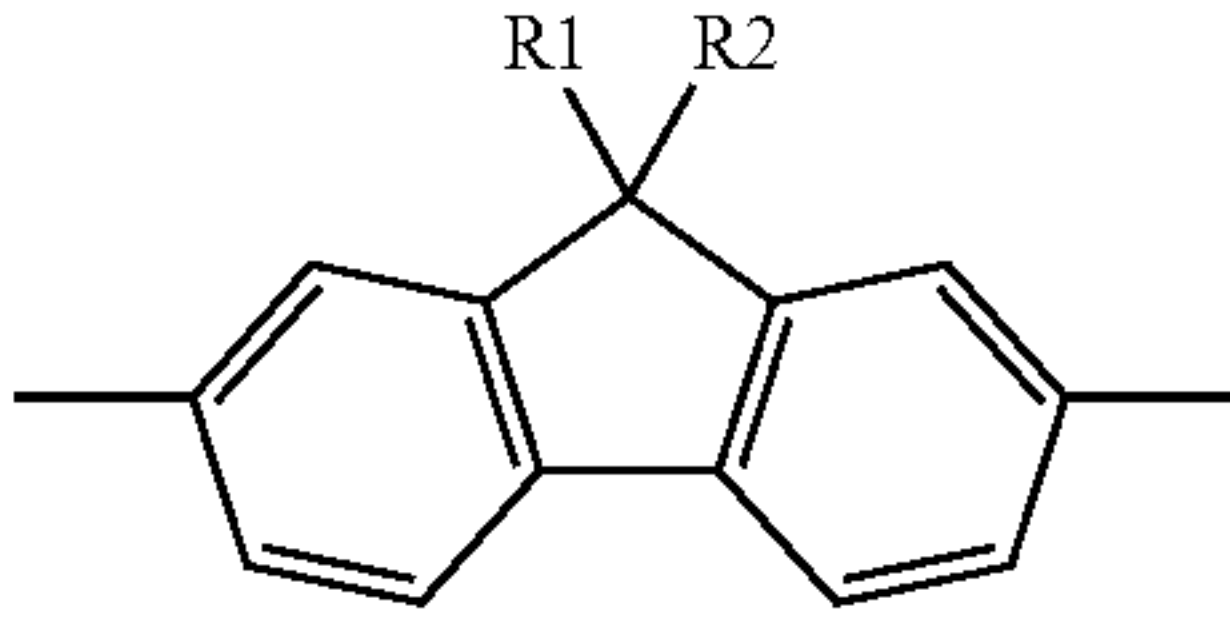
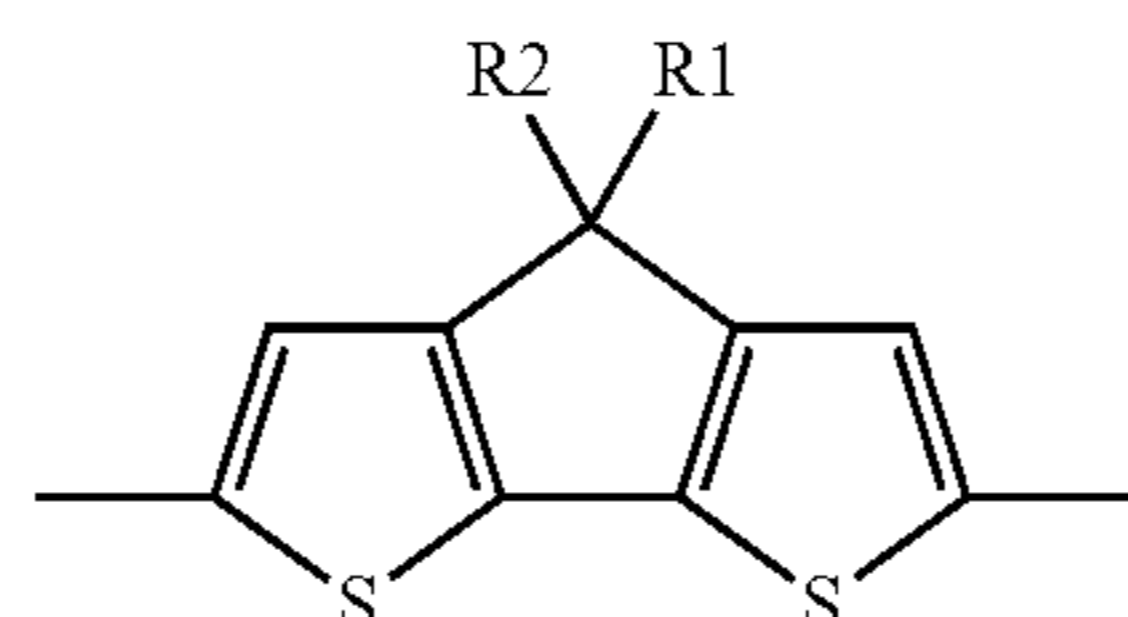
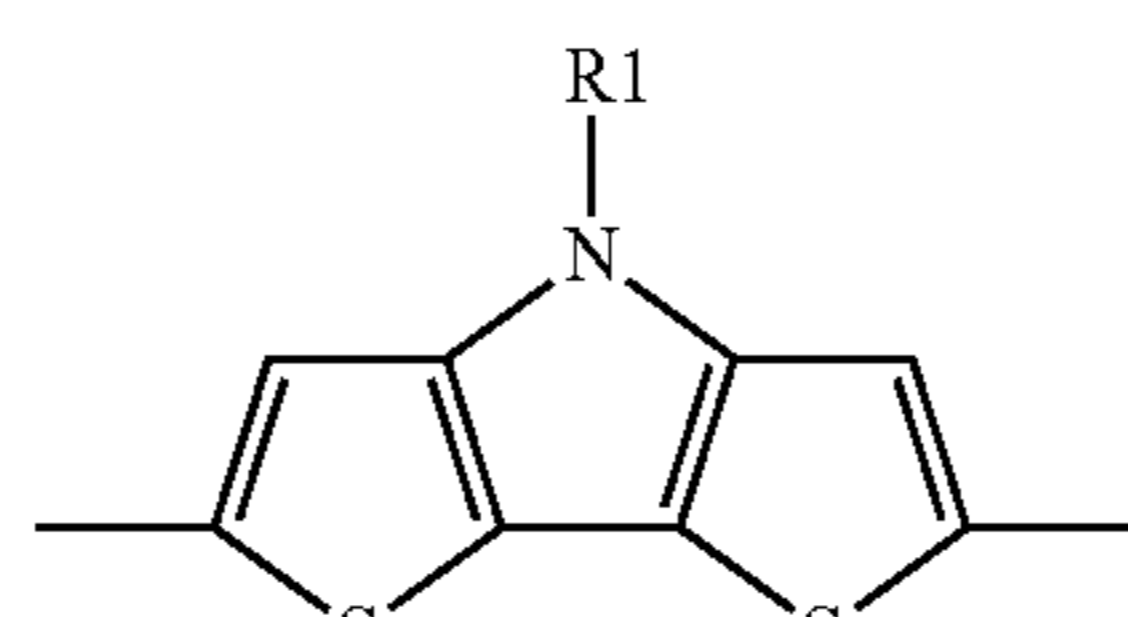
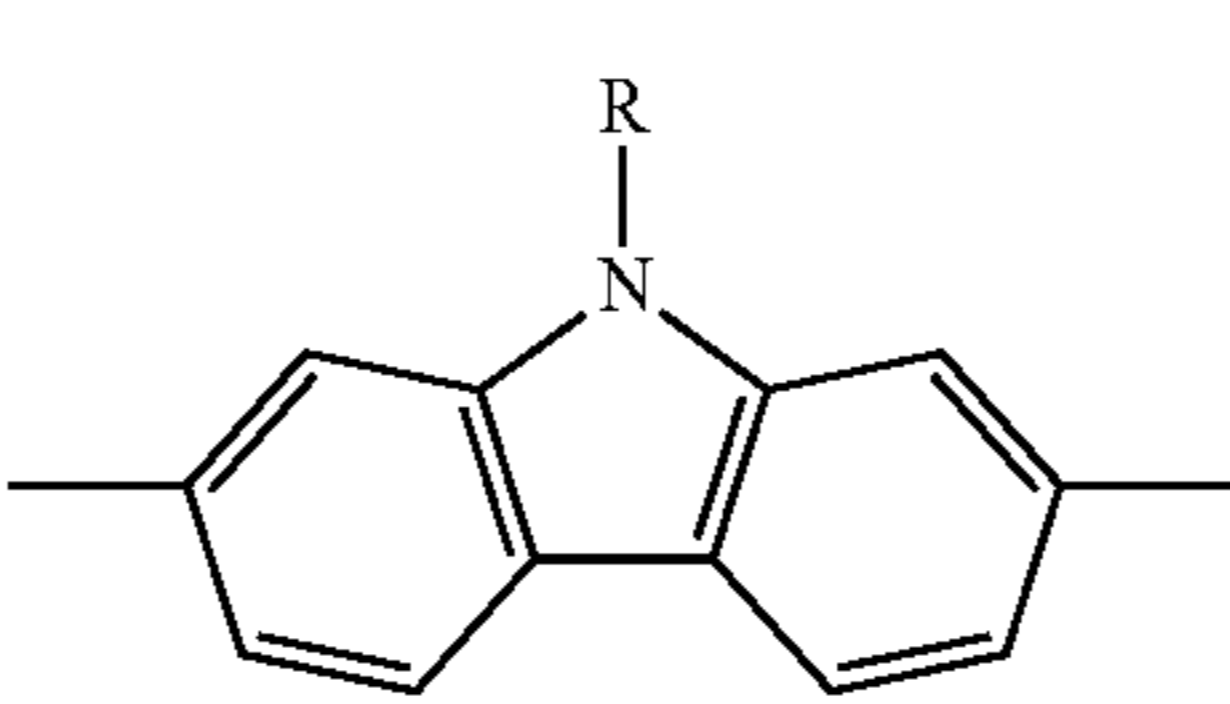
Electron-accepting pi-bridges	Electron-donating pi-bridges
	
	
	
	
	

TABLE 1-continued

Electron-accepting pi-bridges	Electron-donating pi-bridges
	
	
	

In the above Table 1, each R, R<sup>1</sup> and R<sup>2</sup> are independently selected from the group consisting of H, —CN, —COOH, —X, substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, —COOR, CONHR, CON(H)OR, —SO<sub>3</sub>R, —SO<sub>2</sub>R—OSO<sub>3</sub>R, —PO<sub>3</sub>HR, and —OPO<sub>3</sub>HR; X is halogen; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

**[0036]** Dyes described herein also include crystalline and amorphous forms of those dyes, including, for example, polymorphs, pseudopolymorphs, solvates, hydrates, unsolvated polymorphs (including anhydrates), conformational polymorphs, and amorphous forms of the dyes, as well as mixtures thereof. “Crystalline form,” “polymorph,” and “novel form” may be used interchangeably herein, and are meant to include all crystalline and amorphous forms of the dye listed above, as well as mixtures thereof, unless a particular crystalline or amorphous form is referred to.

**[0037]** “Solvent,” “organic solvent,” and “inert solvent” each means a solvent inert under the conditions of the reaction being described in conjunction therewith including, for example, benzene, toluene, acetonitrile, tetrahydrofuran (“THF”), dimethylformamide (“DMF”), chloroform, methylene chloride (or dichloromethane), diethyl ether, methanol, N-methylpyrrolidone (“NMP”), pyridine and the like. Unless specified to the contrary, the solvents used in the reactions described herein are inert organic solvents. Unless specified to the contrary, for each gram of the limiting reagent, one cc (or mL) of solvent constitutes a volume equivalent.

#### Compositions

#### Dye-Sensitized Solar Cells

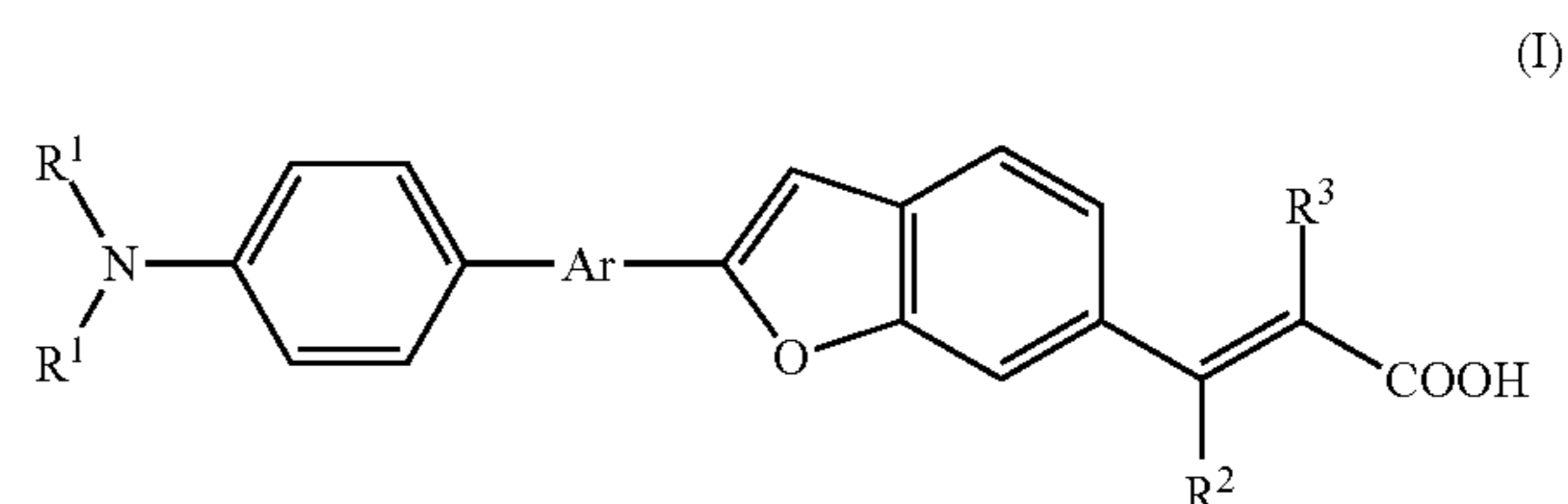
**[0038]** Dye-sensitized solar cells (DSSCs) described herein comprise a photoanode, a photocathode, and a redox electrolyte disposed between the photoanode and the photocathode.

**[0039]** The photoanode comprises a metal oxide such as titanium dioxide. The oxide can be in the form of nanoparticles such as mesoporous titanium oxide nanoparticles. The photoanode is sensitized with a solar cell dye deposited on a flexible metal, a transparent conducting substrate, or a fluorine-doped tin oxide coated glass. The photocathode comprises a catalytic layer comprising one or more thin layers of platinum, polythiophenes including PEDOT, polyanilines, polypyrroles, or carbon (including carbon nanotubes and graphenes). The redox electrolyte is commonly selected from a pair consisting of iodide/triiodide, Co(II)/Co(III) organic ligand complexes, and Cu(I)/Cu(II) organic ligand complexes.

**[0040]** The DSSCs described herein also comprise one or more solar cell dyes as described herein.

#### Benzofuran-Containing Dyes

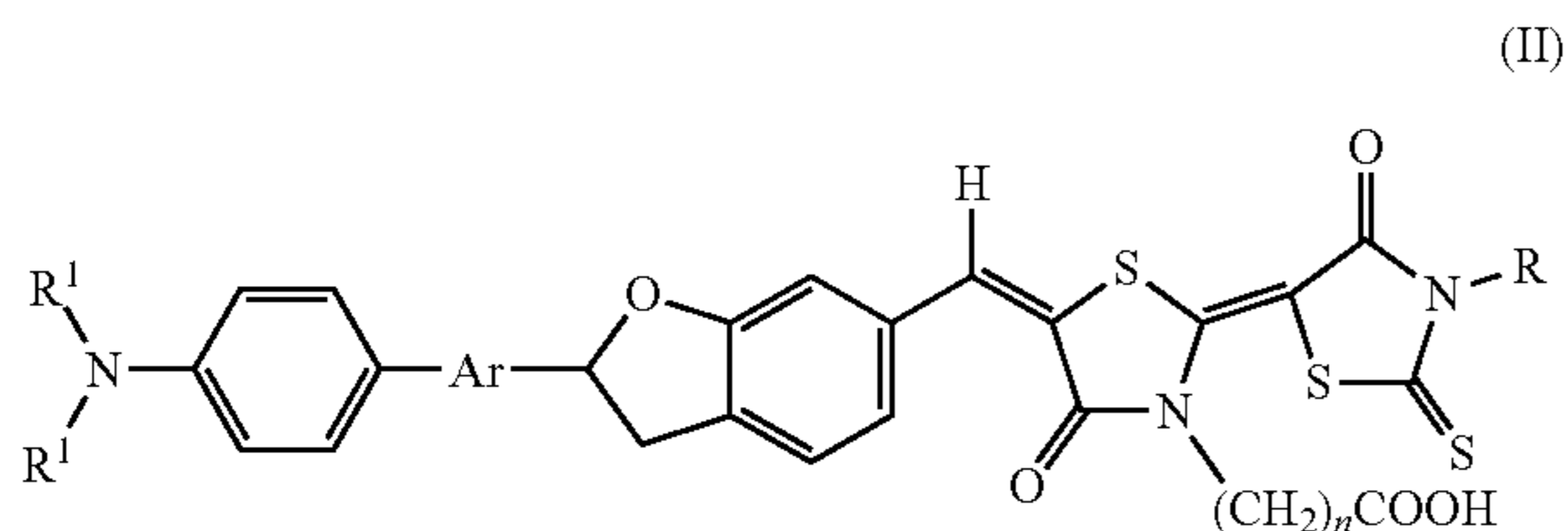
**[0041]** Also described herein are solar cell dyes for use in a DSSC, wherein the dye is a compound of formula I:



wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar— is a pi-bridge; R<sup>2</sup> and R<sup>3</sup> are independently selected from the

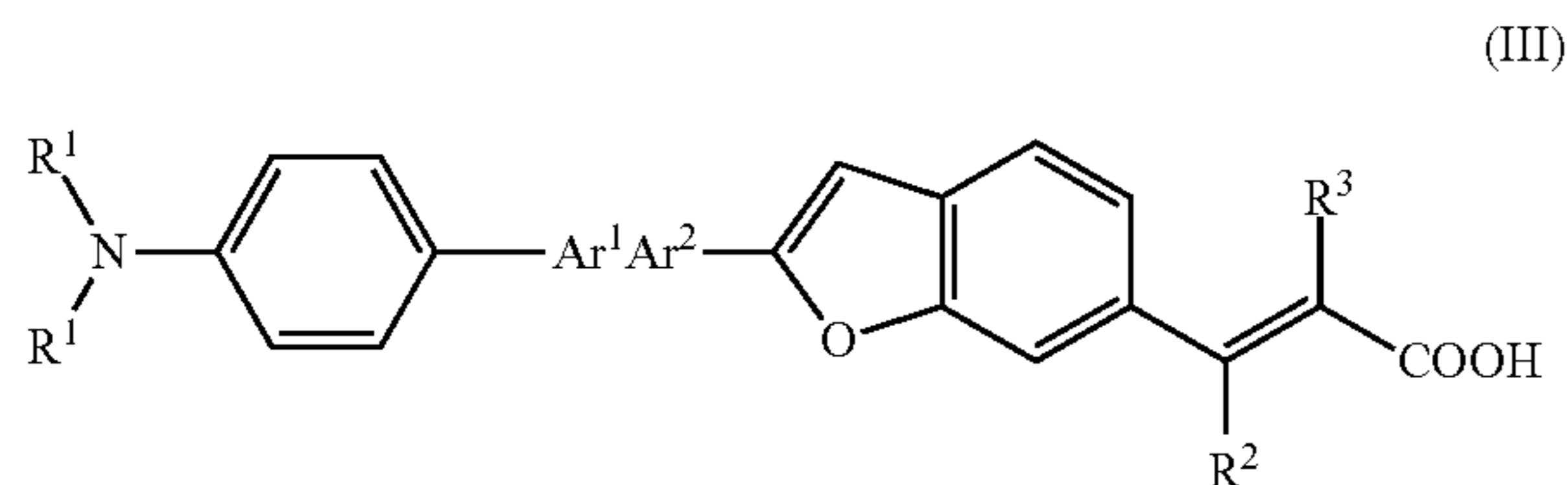
group consisting of H, —CN, —COOH, —X, substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, —COOR, —CONHR, —CON(H)OR, —SO<sub>3</sub>R, —SO<sub>2</sub>R—OSO<sub>3</sub>R, —PO<sub>3</sub>HR, and —OPO<sub>3</sub>HR; X is halogen; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

**[0042]** Also described herein is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula II and its structural isomers:



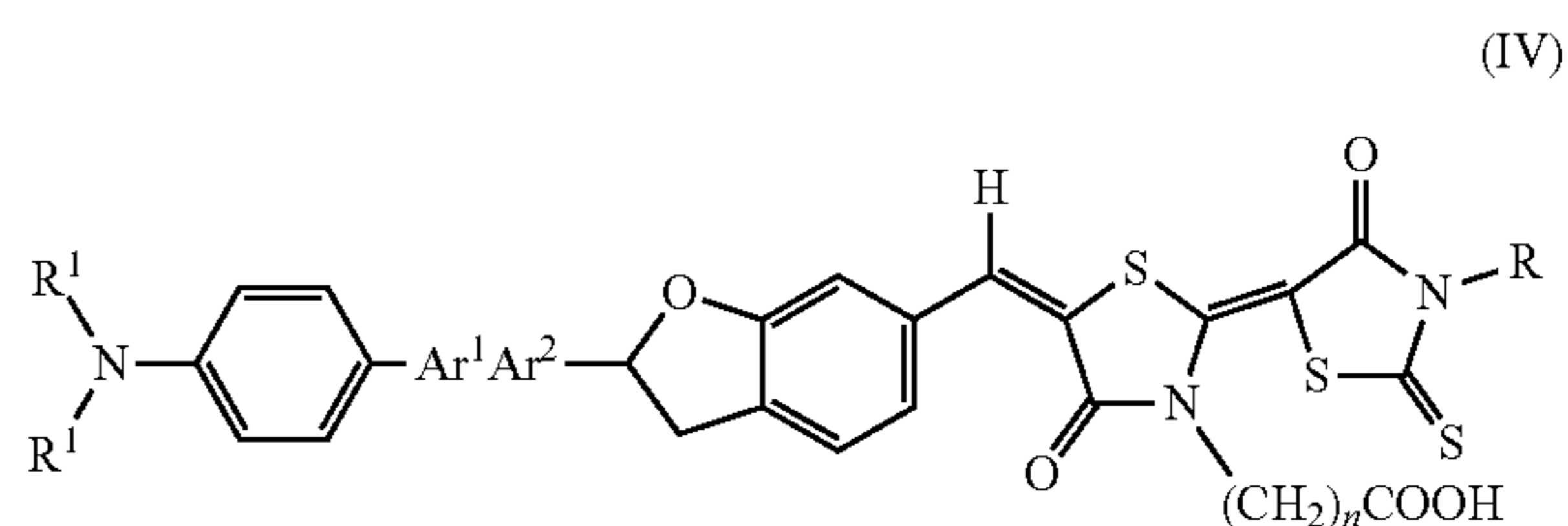
wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar— is a pi-bridge; n is an integer from 1 to 10; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

**[0043]** Further described herein is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula III and its structural isomers:



wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar<sup>1</sup>— is an electron-withdrawing pi-bridge; —Ar<sup>2</sup>— is an electron-donating pi-bridge; R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of H, —CN, —COOH, —X, substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, —COOR, —CONHR, —CON(H)OR, —SO<sub>3</sub>R, —SO<sub>2</sub>R—OSO<sub>3</sub>R, —PO<sub>3</sub>HR, and —OPO<sub>3</sub>HR; X is halogen; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

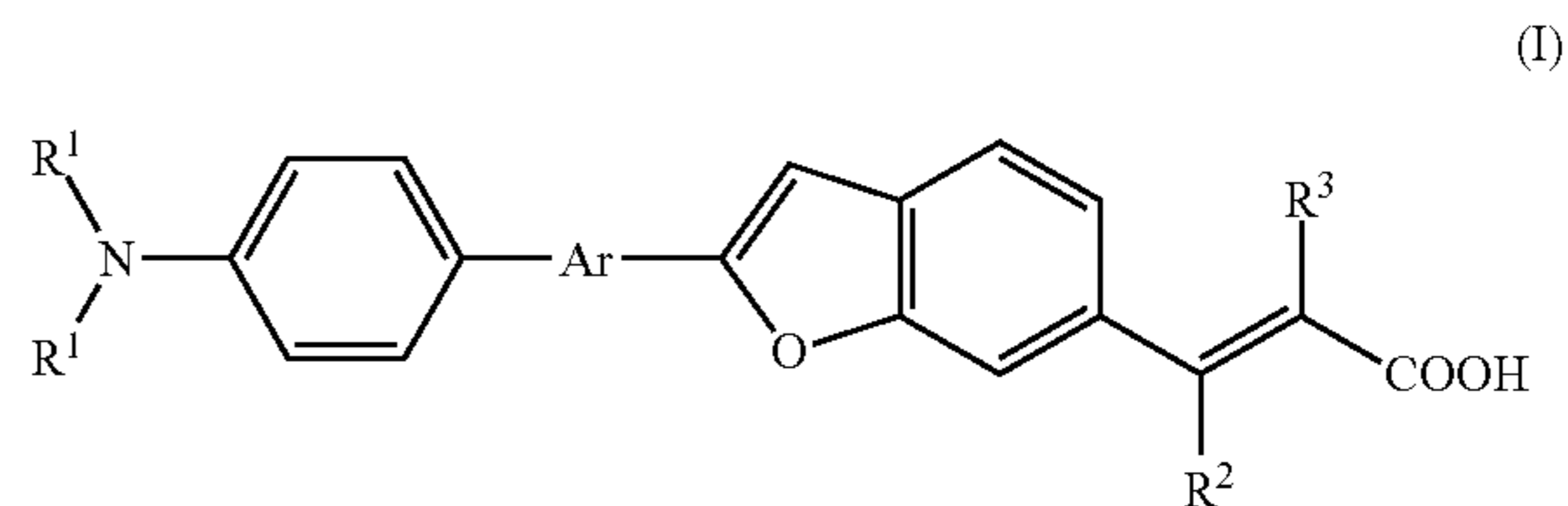
**[0044]** Further described here is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula IV and its structural isomers:



wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar<sup>1</sup>— is an electron-withdrawing pi-bridge; —Ar<sup>2</sup>— is an electron-donating pi-bridge; n is an integer from 1 to 10; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

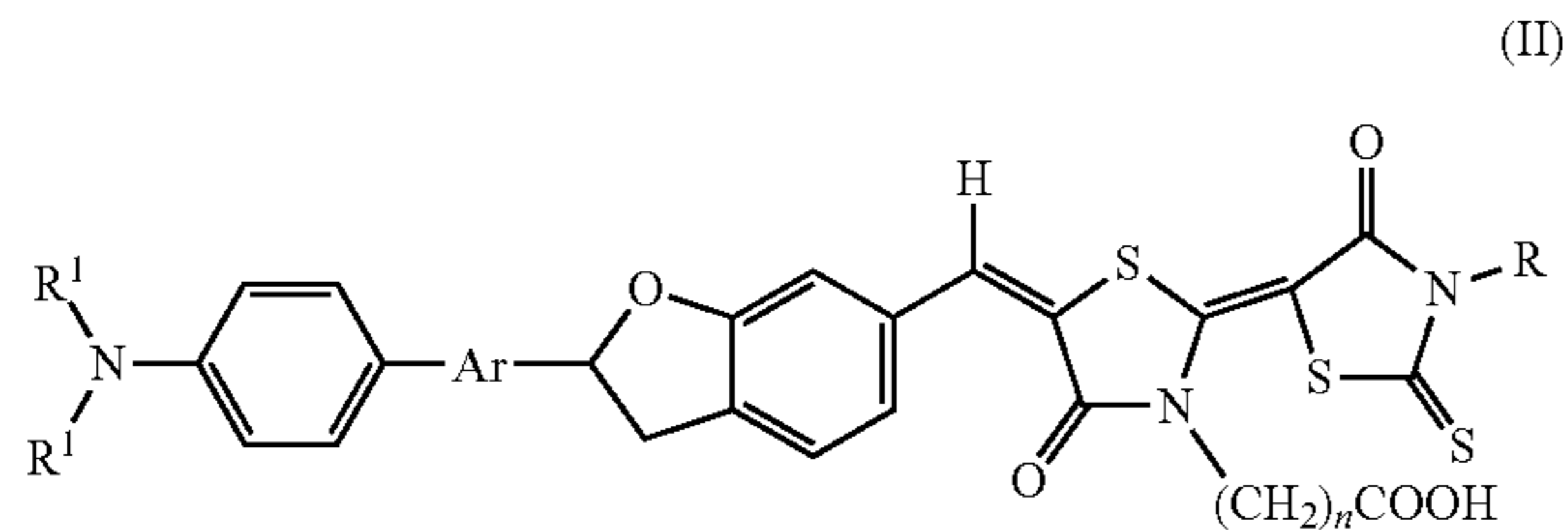
**[0045]** In each of the above formulae (I)-(IV), in some embodiments each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted phenyl, naphthyl, fluorenyl, carbazolyl, biphenyl, thienyl, and pyrrolyl. In other embodiments each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl. In still other embodiments each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl.

**[0046]** The following exemplary solar cell dyes have been synthesized. In each case the molecule identified in the left-hand column (e.g., D0) is represented in three parts, wherein the central portion represents the pi-bridge, with two open covalent bonds. The structure of the entire molecule is visualized by joining the open covalent pi-bridge bonds to the open single bonds from the left and right portions:



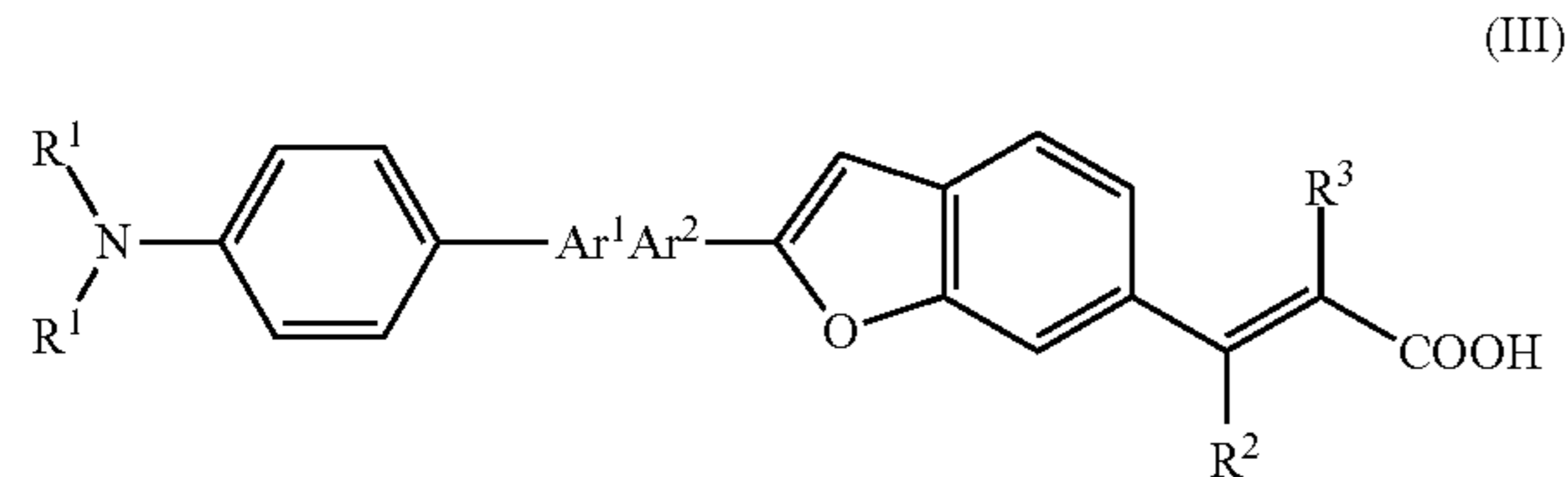
wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl; —Ar— is a pi-bridge; R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of H, —CN, —COOH, —X, substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, —COOR, —CONHR, —CON(H)OR, —SO<sub>3</sub>R, —SO<sub>2</sub>R—OSO<sub>3</sub>R, —PO<sub>3</sub>HR, and —OPO<sub>3</sub>HR; X is halogen; and R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

**[0047]** Also described herein is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula II and its structural isomers:



wherein each  $R^1$  is independently selected from the group consisting of substituted or unsubstituted linear or branched  $C_1$ - $C_{10}$  alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted  $C_6$ - $C_{12}$  aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted  $C_4$ - $C_{12}$  heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted  $C_5$ - $C_{10}$  cycloalkyl, and substituted or unsubstituted  $C_5$ - $C_{10}$  heterocycloalkyl; —Ar— is a pi-bridge; n is an integer from 1 to 10; and R is substituted or unsubstituted linear or branched  $C_1$ - $C_{10}$  alkyl.

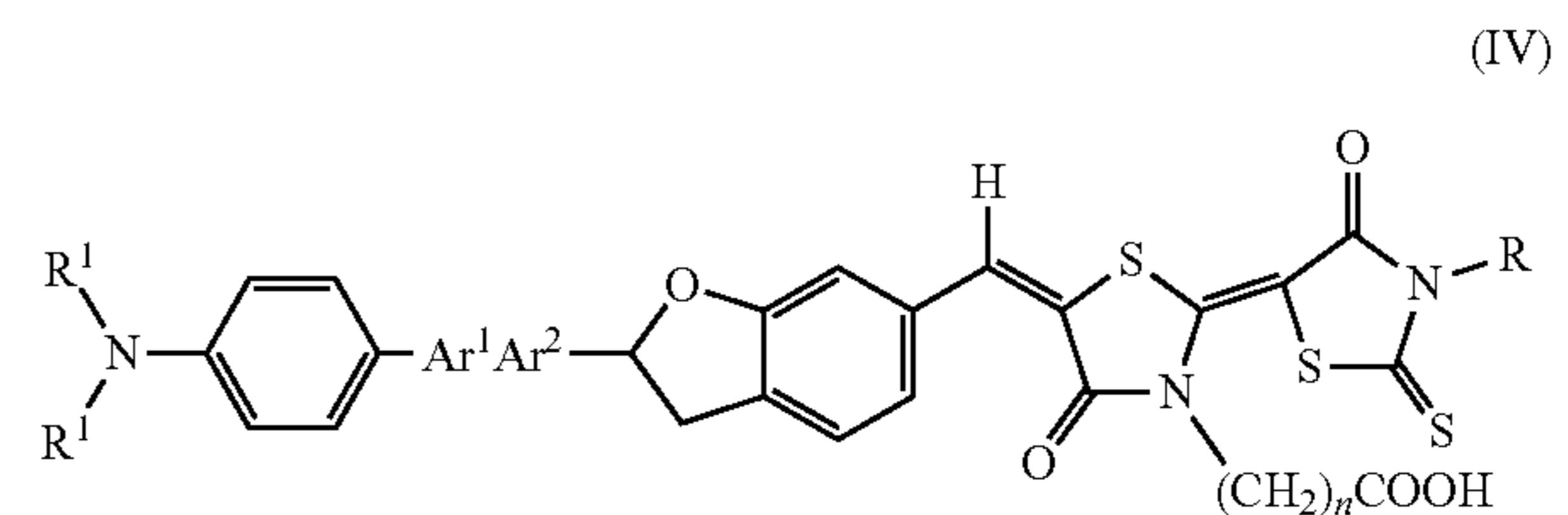
**[0048]** Further described herein is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula III and its structural isomers:



wherein each  $R^1$  is independently selected from the group consisting of substituted or unsubstituted linear or branched  $C_1$ - $C_{10}$  alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted  $C_6$ - $C_{12}$  aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted  $C_4$ - $C_{12}$  heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted  $C_5$ - $C_{10}$  cycloalkyl, and substituted or unsubstituted  $C_5$ - $C_{10}$  heterocycloalkyl; —Ar<sup>1</sup>— is an electron-withdrawing pi-bridge; —Ar<sup>2</sup>— is an electron-donating pi-bridge;  $R^2$  and  $R^3$  are independently selected from the group consisting of H, —CN, —COOH, —X,

substituted or unsubstituted linear or branched  $C_1$ - $C_{10}$  alkyl, —COOR, —CONHR, —CON(H)OR, —SO<sub>3</sub>R, —SO<sub>2</sub>R—, —OSO<sub>3</sub>R, —PO<sub>3</sub>HR, and —OPO<sub>3</sub>HR; X is halogen; and R is substituted or unsubstituted linear or branched  $C_1$ - $C_{10}$  alkyl.

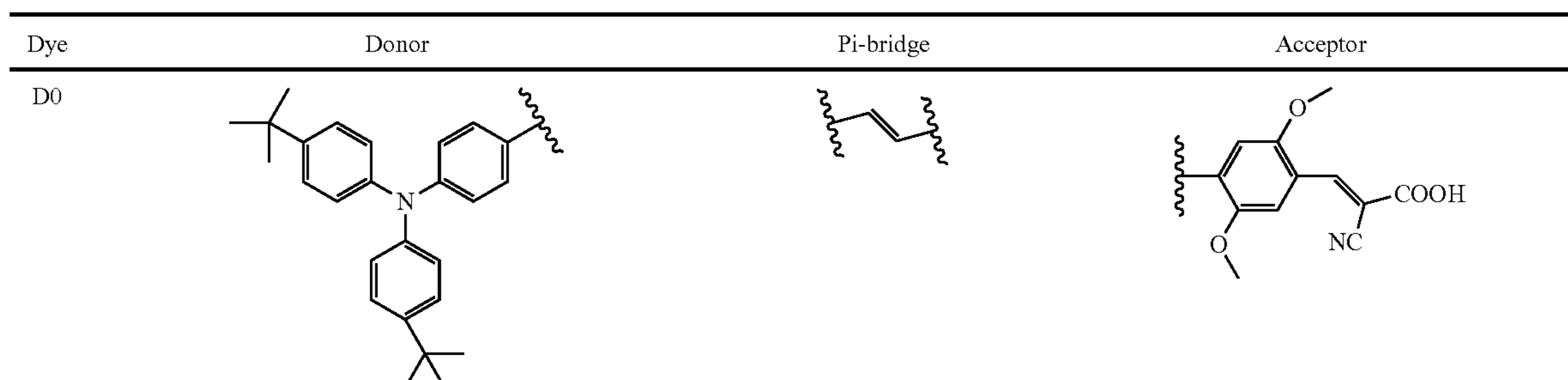
**[0049]** Further described here is a solar cell dye for use in a DSSC, wherein the dye is a compound of formula IV and its structural isomers:



wherein each  $R^1$  is independently selected from the group consisting of substituted or unsubstituted linear or branched  $C_1$ - $C_{10}$  alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted  $C_6$ - $C_{12}$  aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted  $C_4$ - $C_{12}$  heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted  $C_5$ - $C_{10}$  cycloalkyl, and substituted or unsubstituted  $C_5$ - $C_{10}$  heterocycloalkyl; —Ar<sup>1</sup>— is an electron-withdrawing pi-bridge; —Ar<sup>2</sup>— is an electron-donating pi-bridge; n is an integer from 1 to 10; and R is substituted or unsubstituted linear or branched  $C_1$ - $C_{10}$  alkyl.

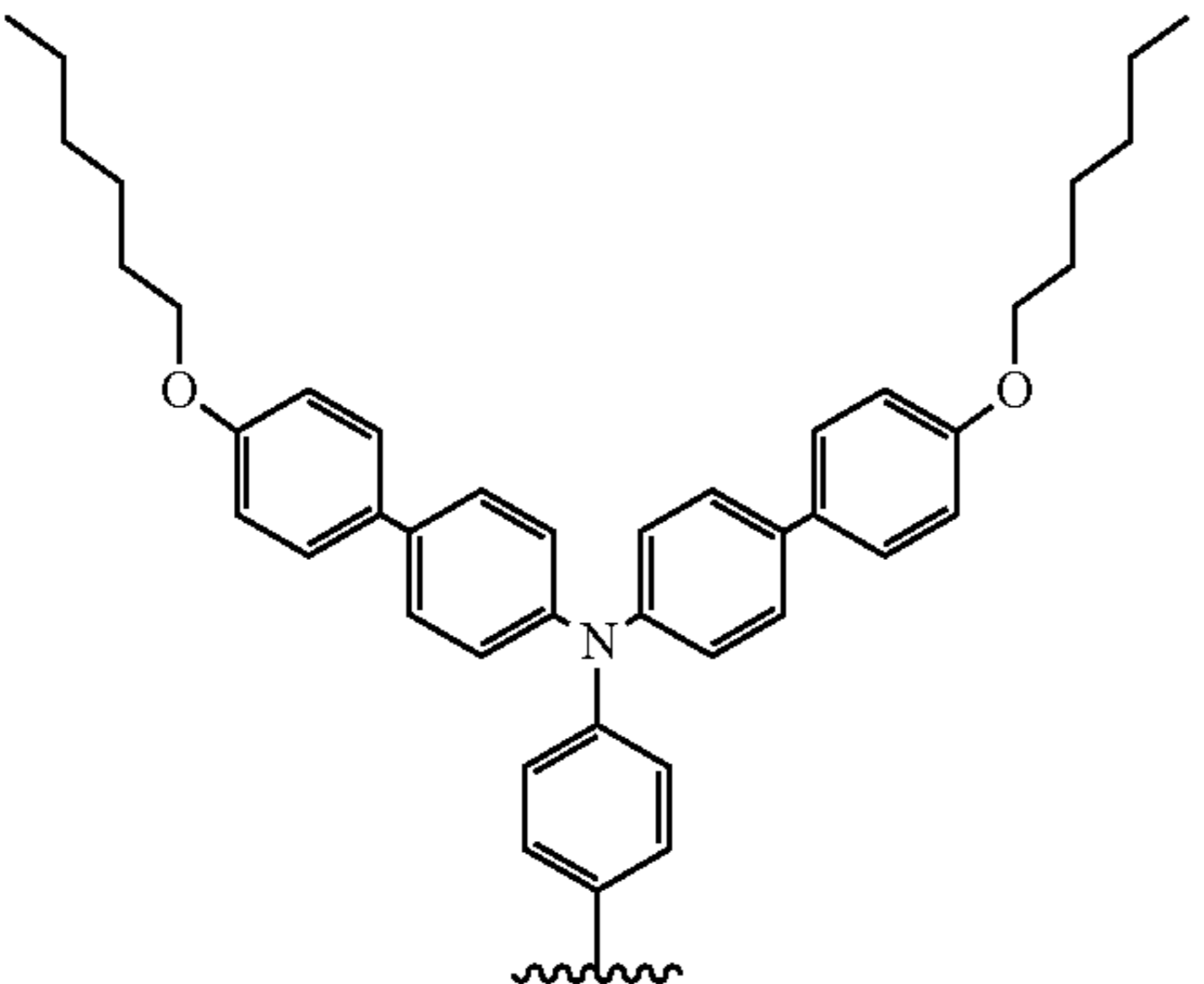
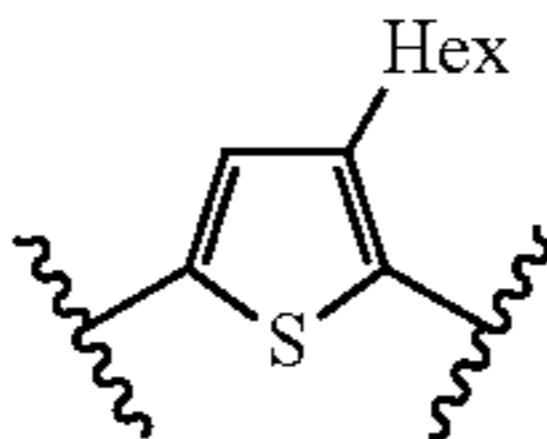
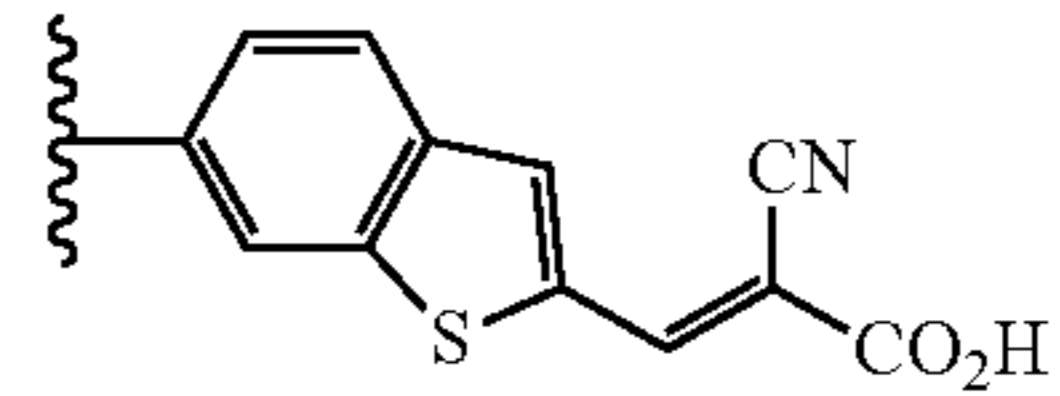
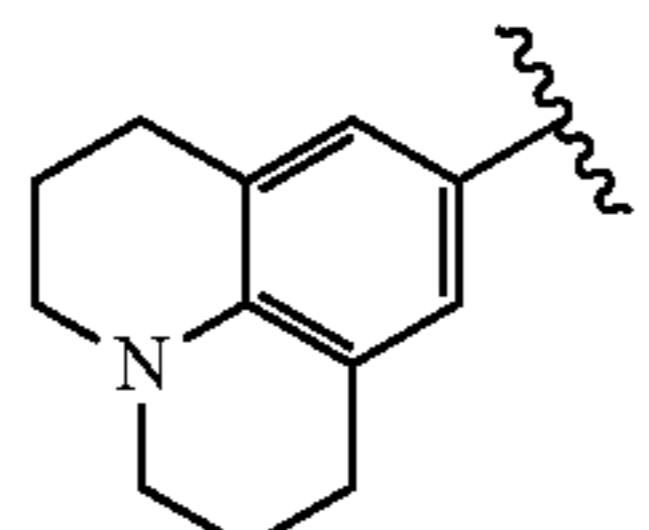
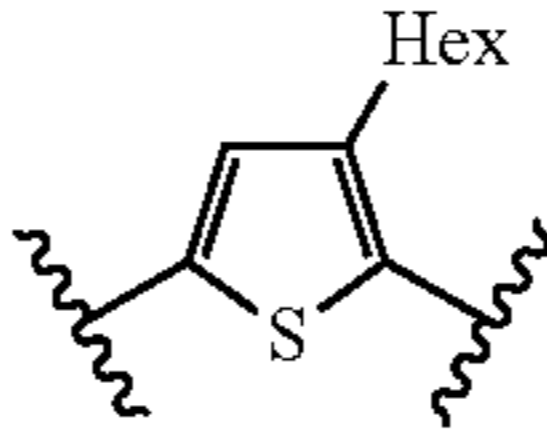
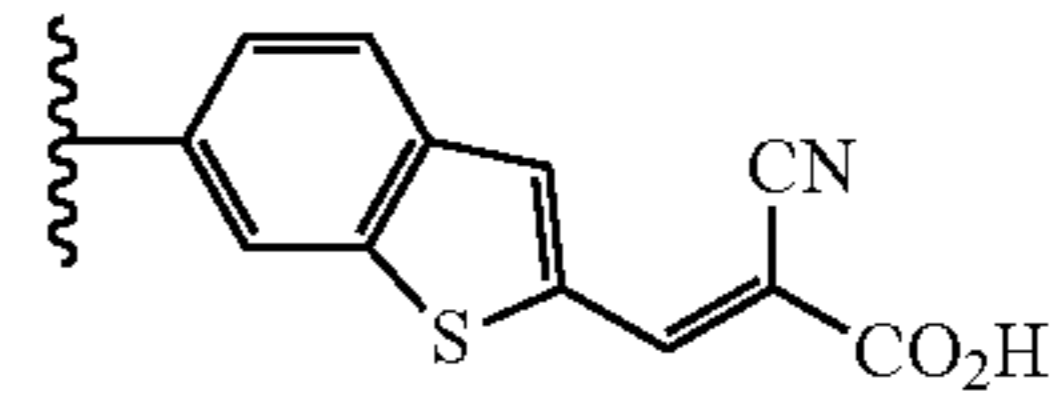
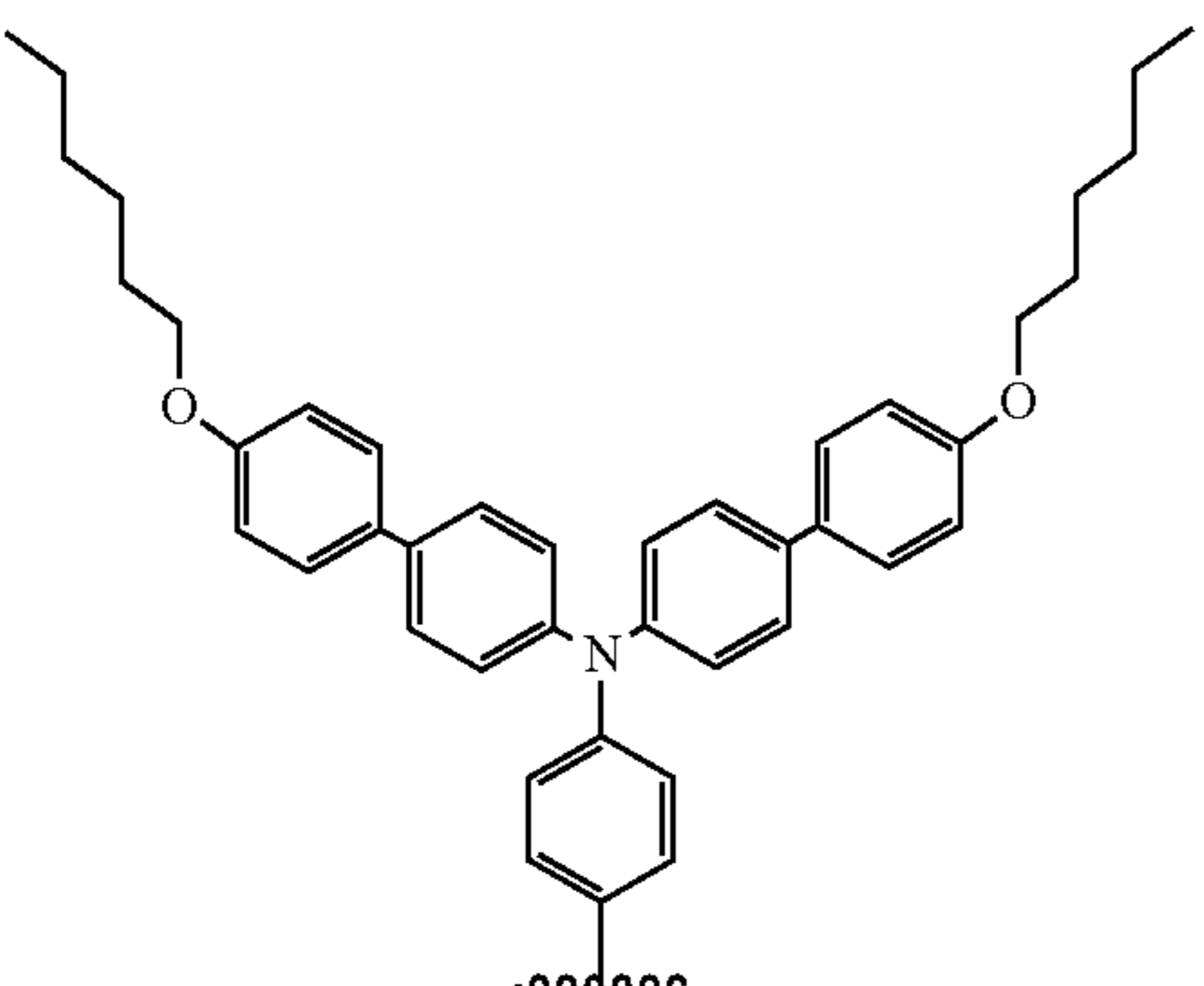
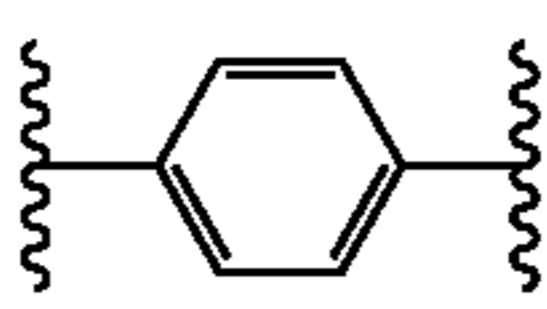
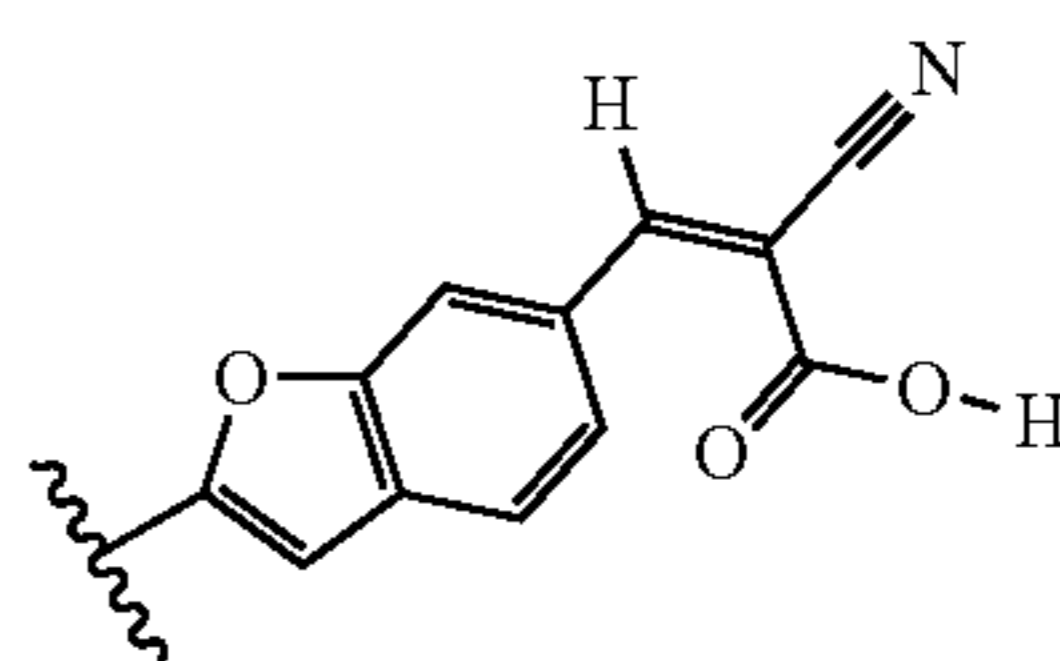
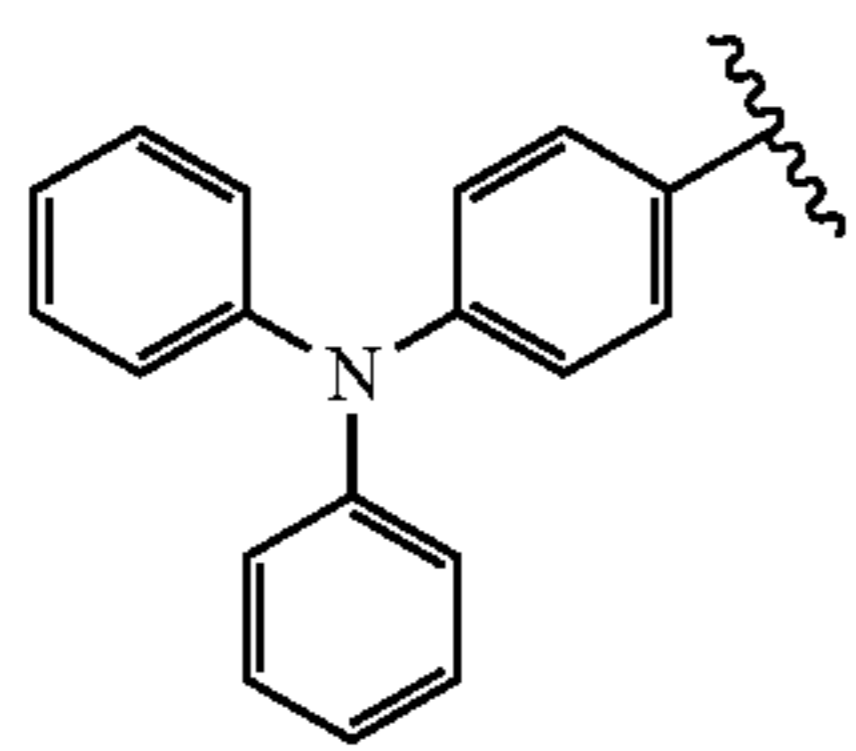
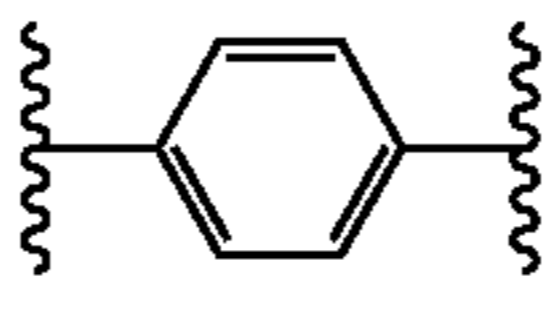
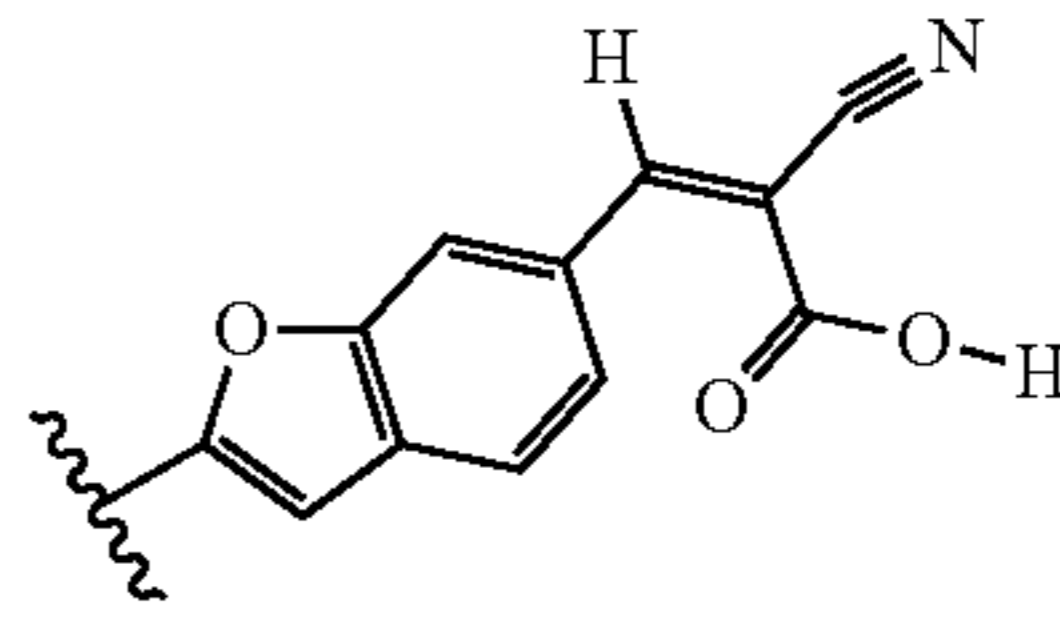
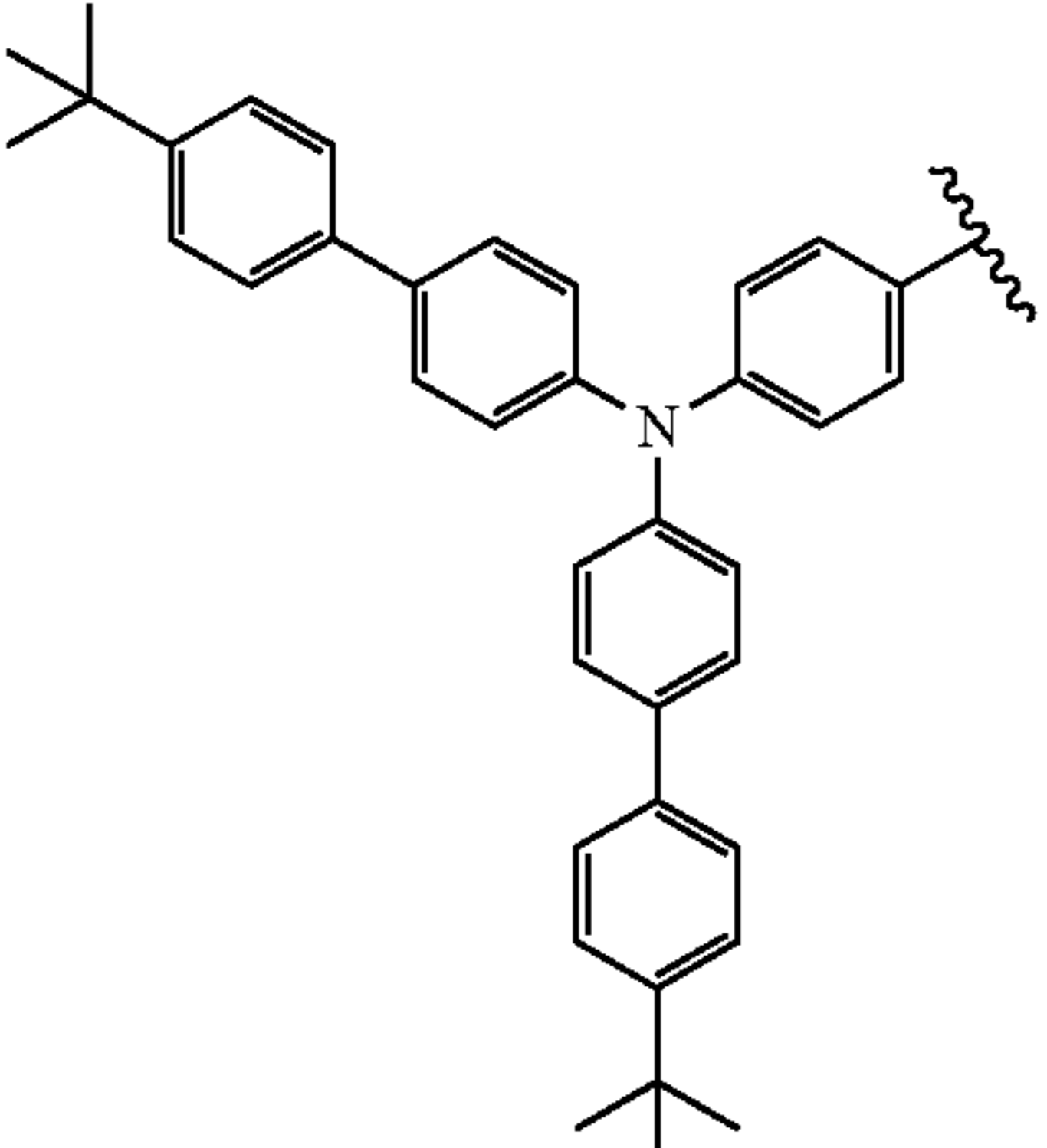
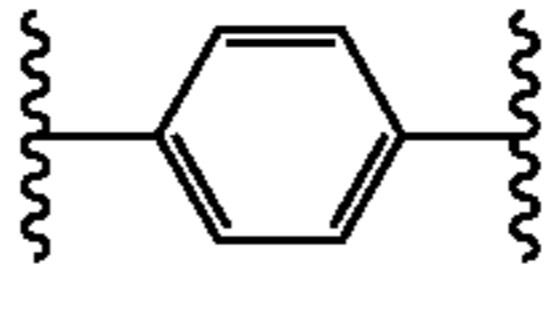
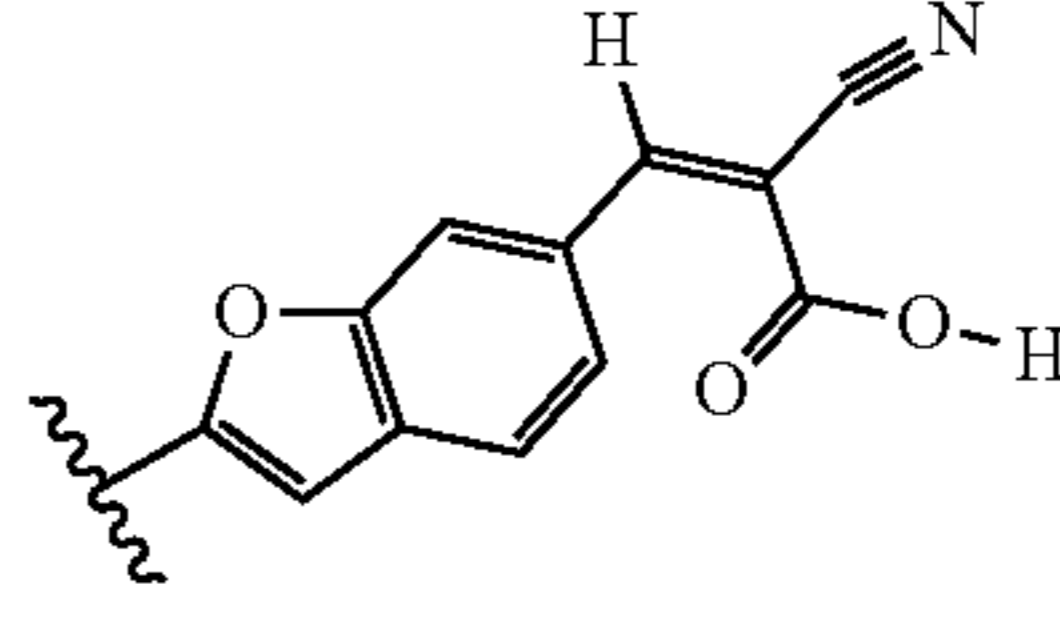
**[0050]** In each of the above formulae (I)-(IV), in some embodiments each  $R^1$  is independently selected from the group consisting of substituted or unsubstituted phenyl, naphthyl, fluorenyl, carbazolyl, biphenyl, thienyl, and pyrrolyl. In other embodiments each  $R^1$  is independently selected from the group consisting of substituted or unsubstituted linear or branched  $C_1$ - $C_{10}$  alkyl. In still other embodiments each  $R^1$  is independently selected from the group consisting of substituted or unsubstituted  $C_5$ - $C_{10}$  cycloalkyl.

**[0051]** The following exemplary solar cell dyes have been synthesized. In each case the molecule identified in the left-hand column (e.g., D0) is represented in three parts, wherein the central portion represents the pi-bridge, with two open covalent bonds. The structure of the entire molecule is visualized by joining the open covalent pi-bridge bonds to the open single bonds from the left and right portions:

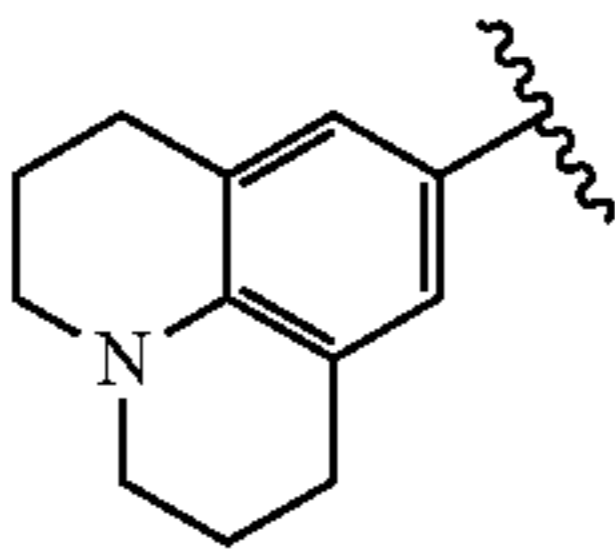
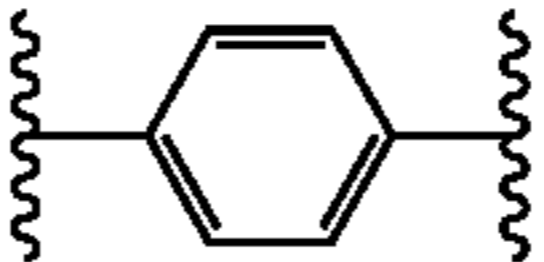
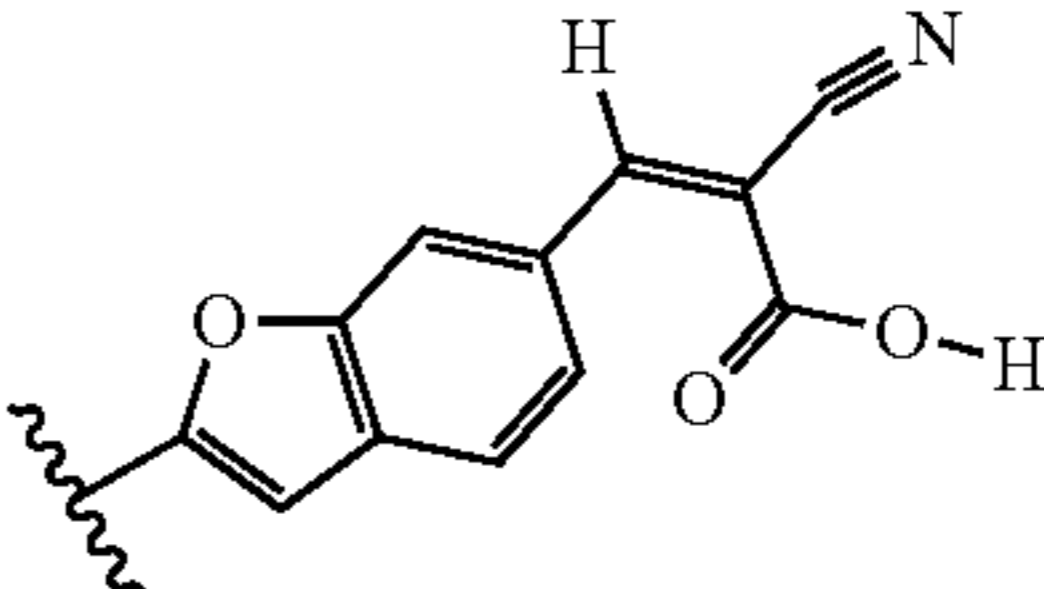
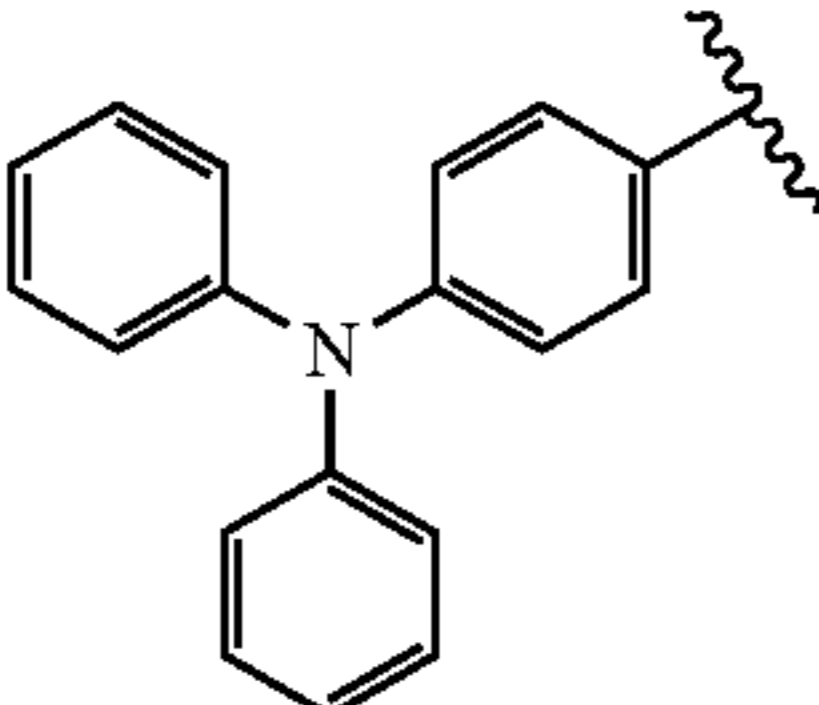
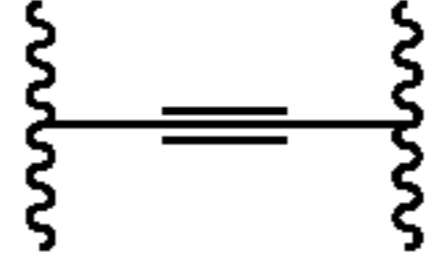
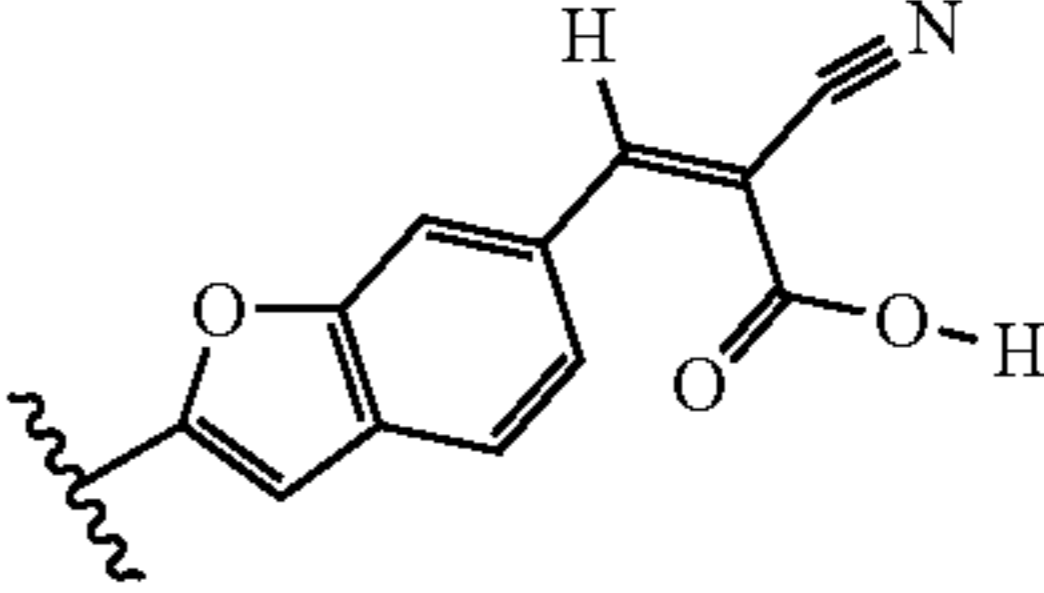
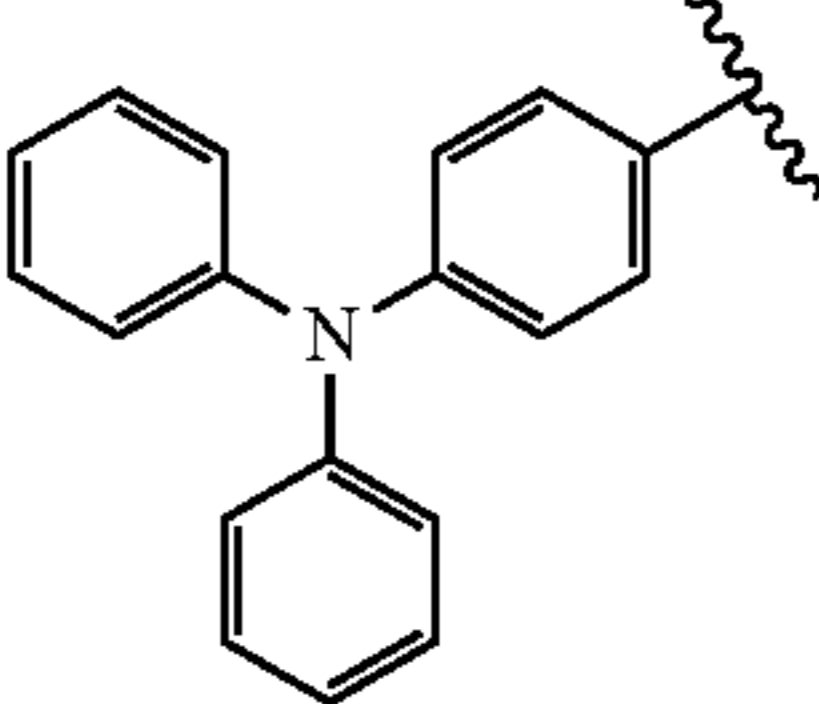
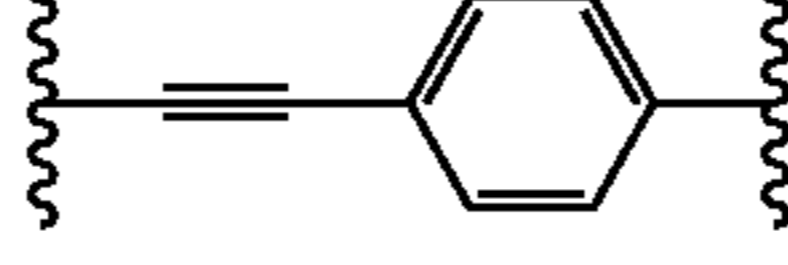
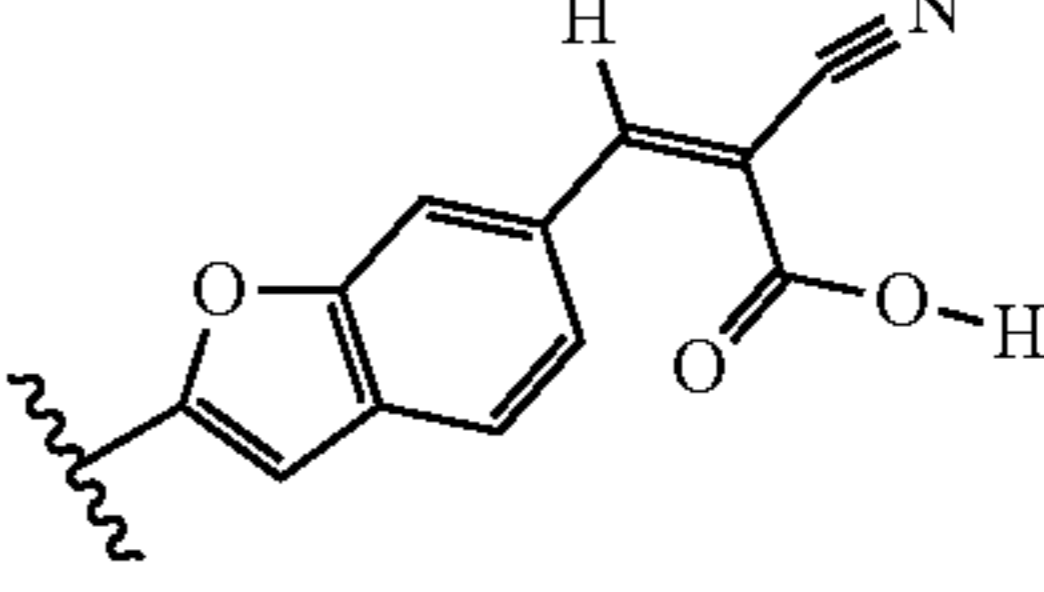
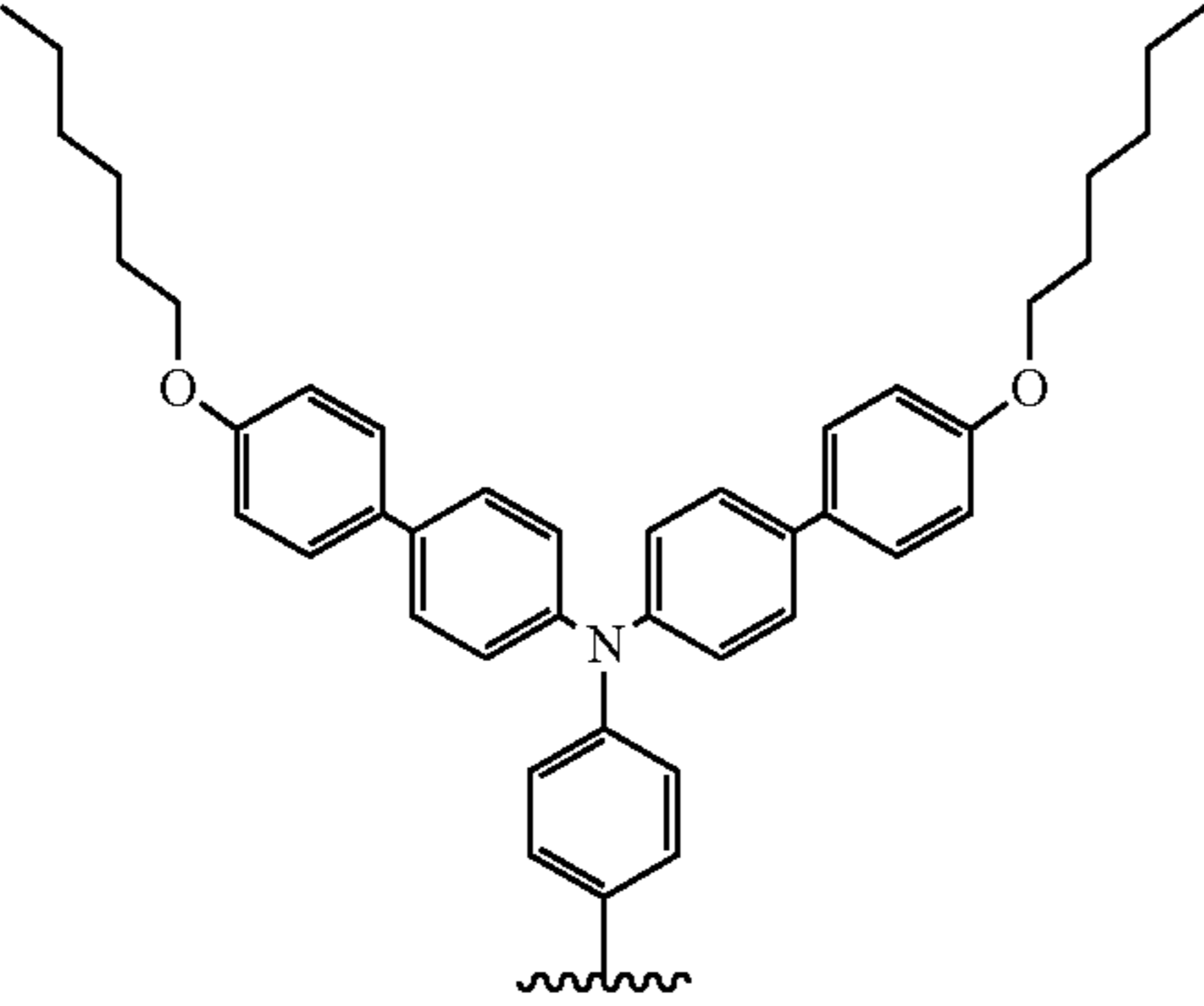
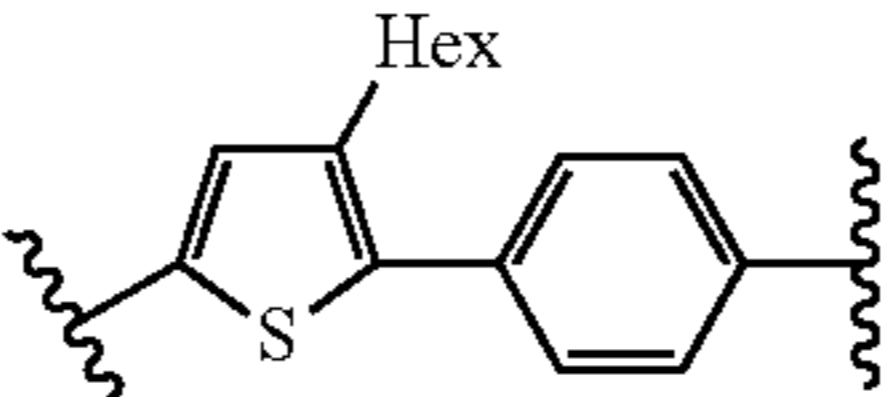
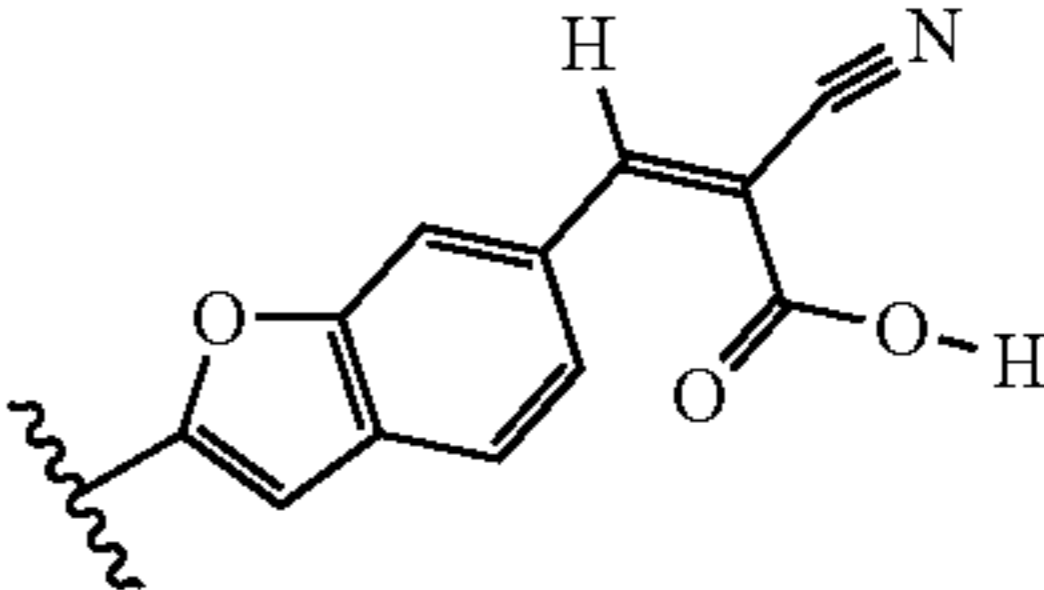
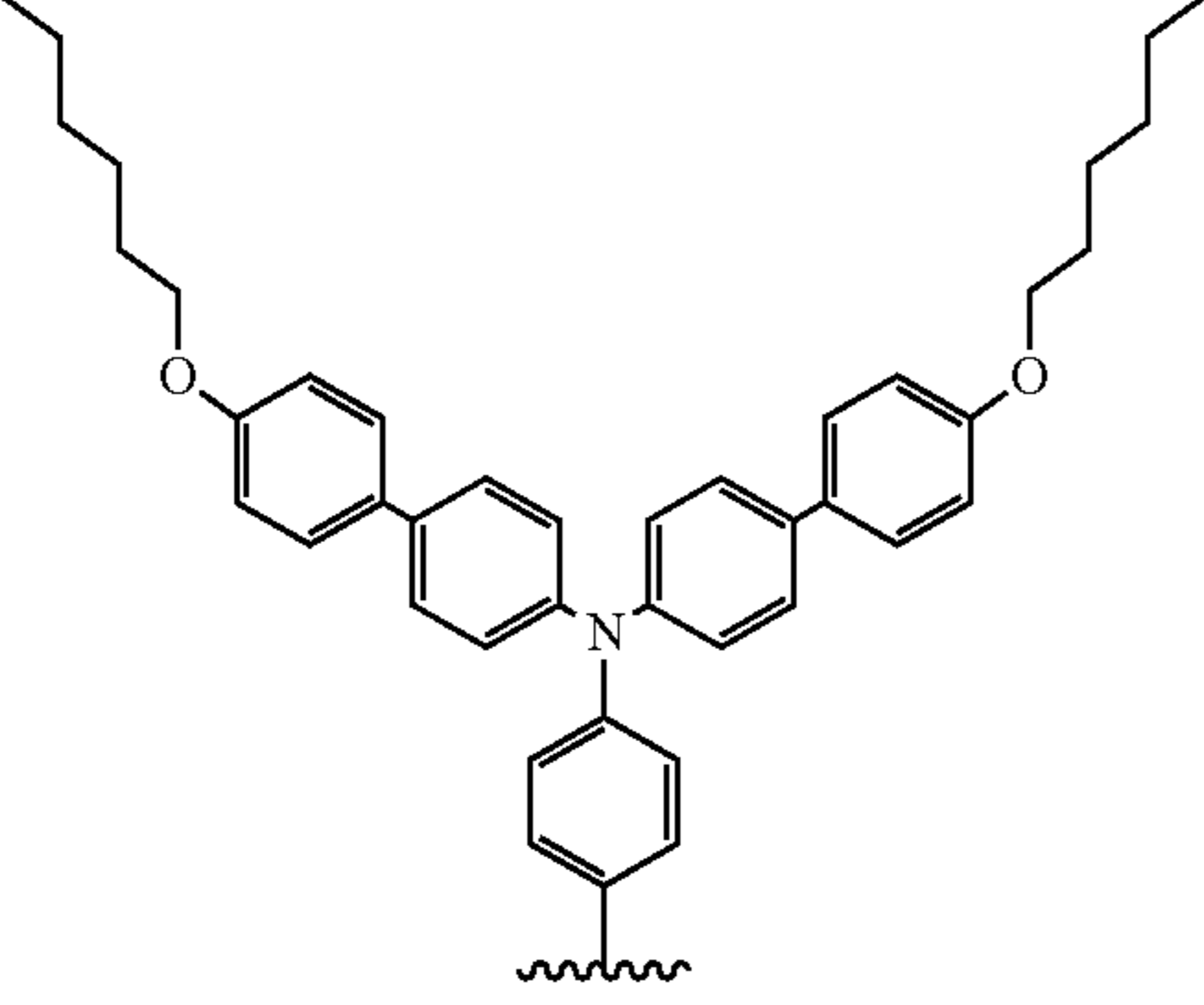
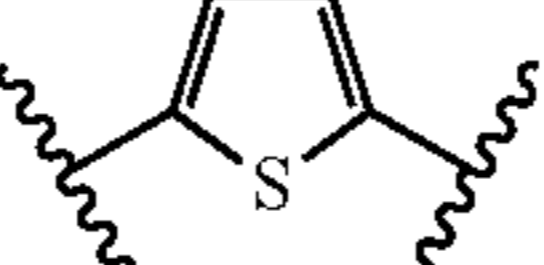
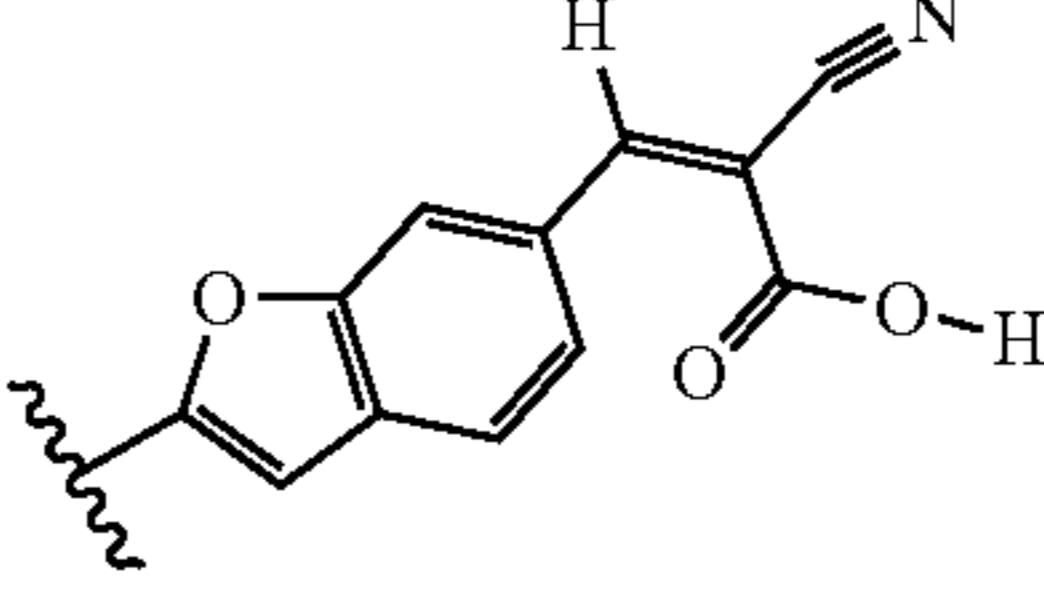
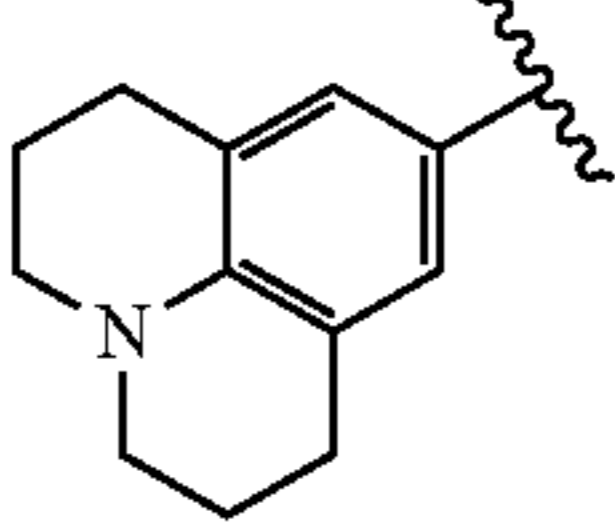
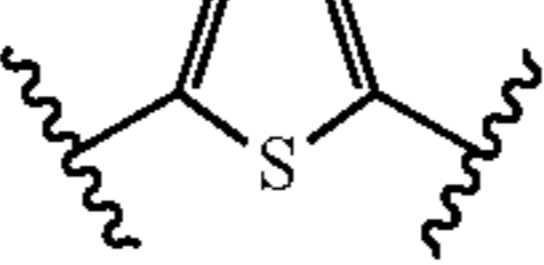
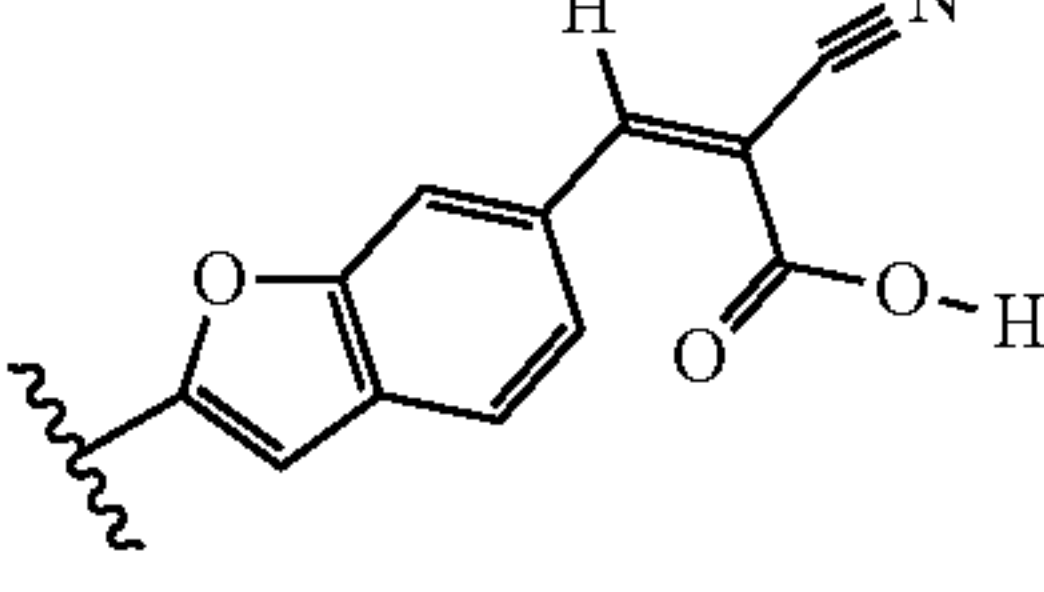




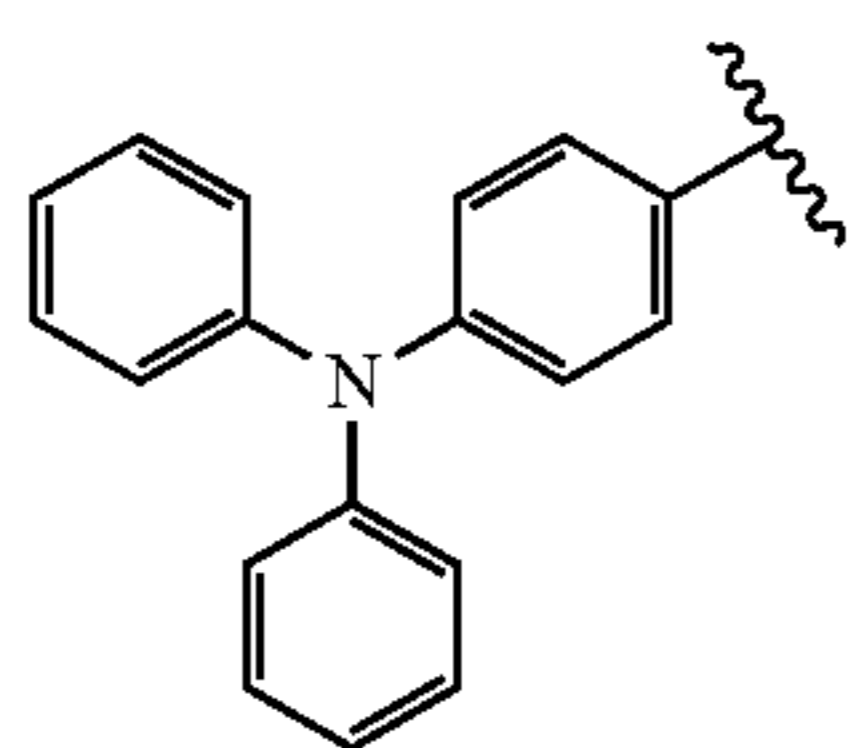
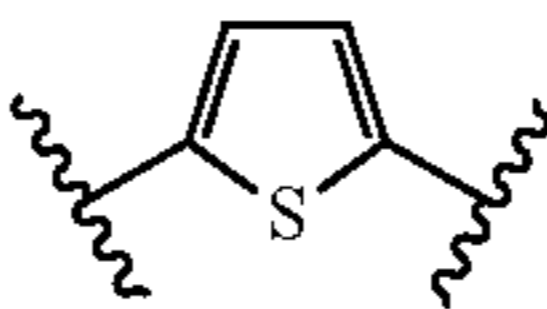
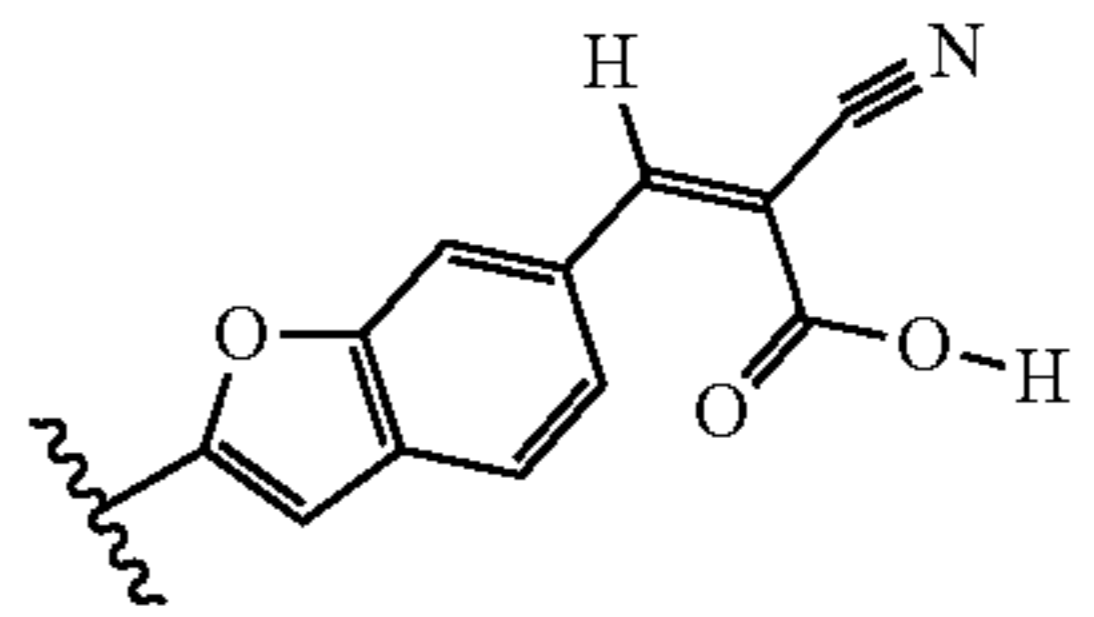
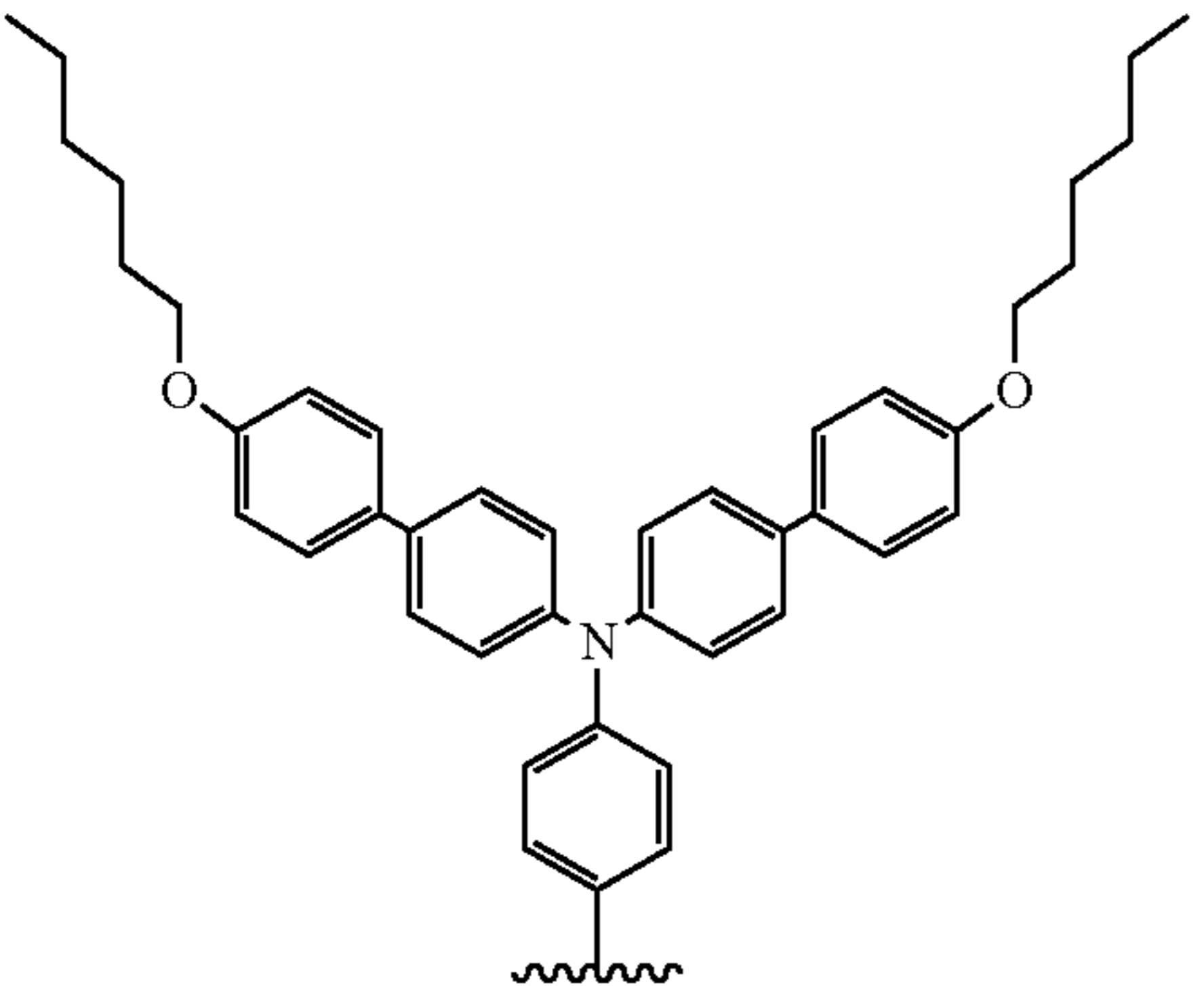
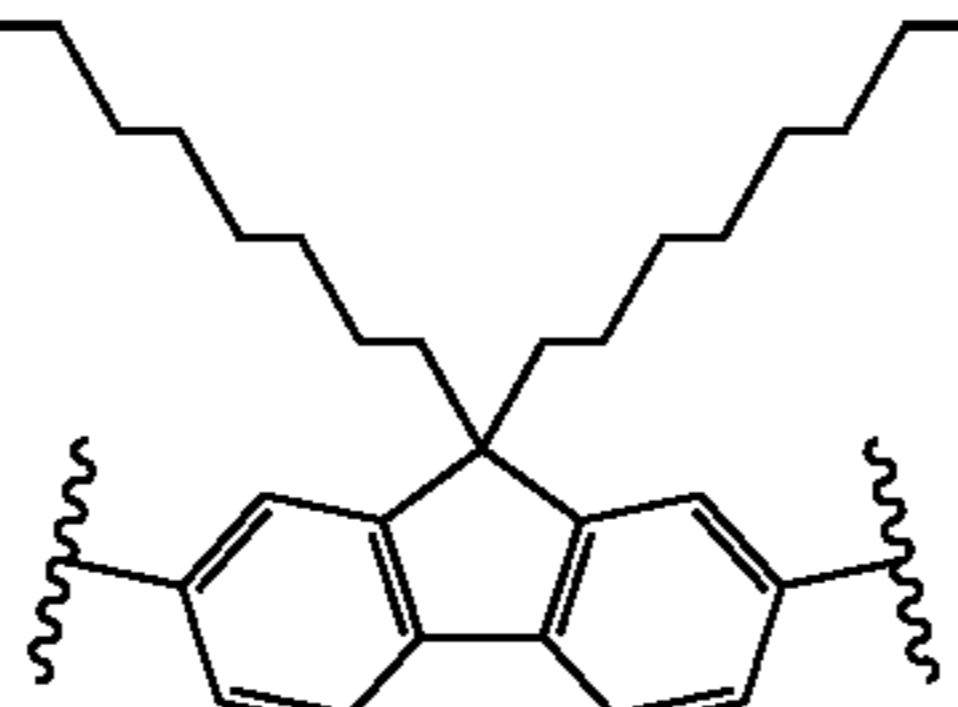
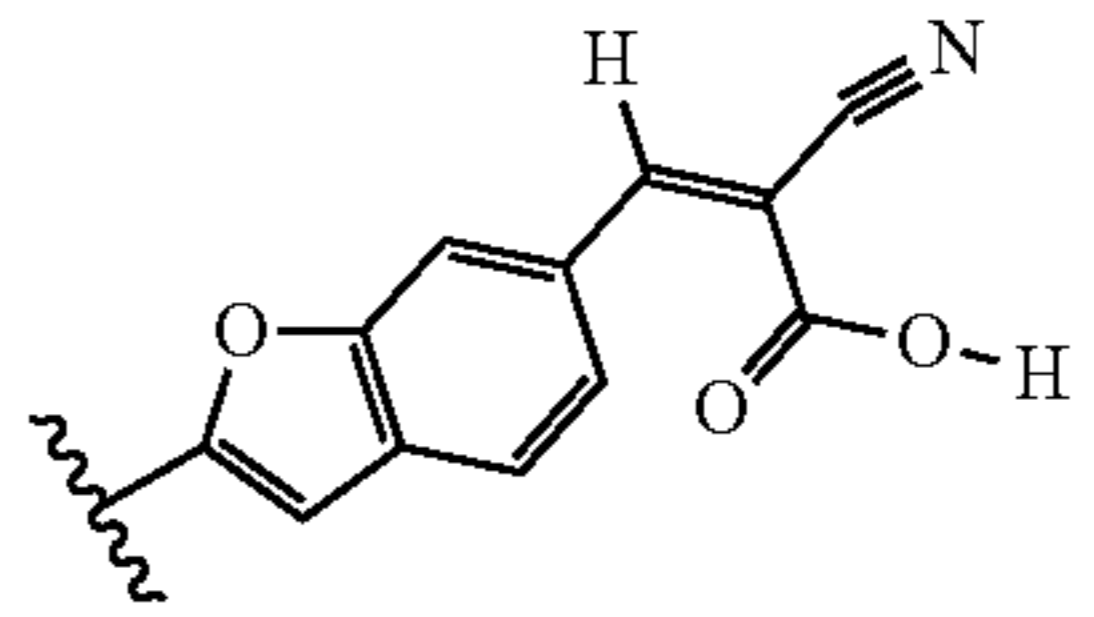
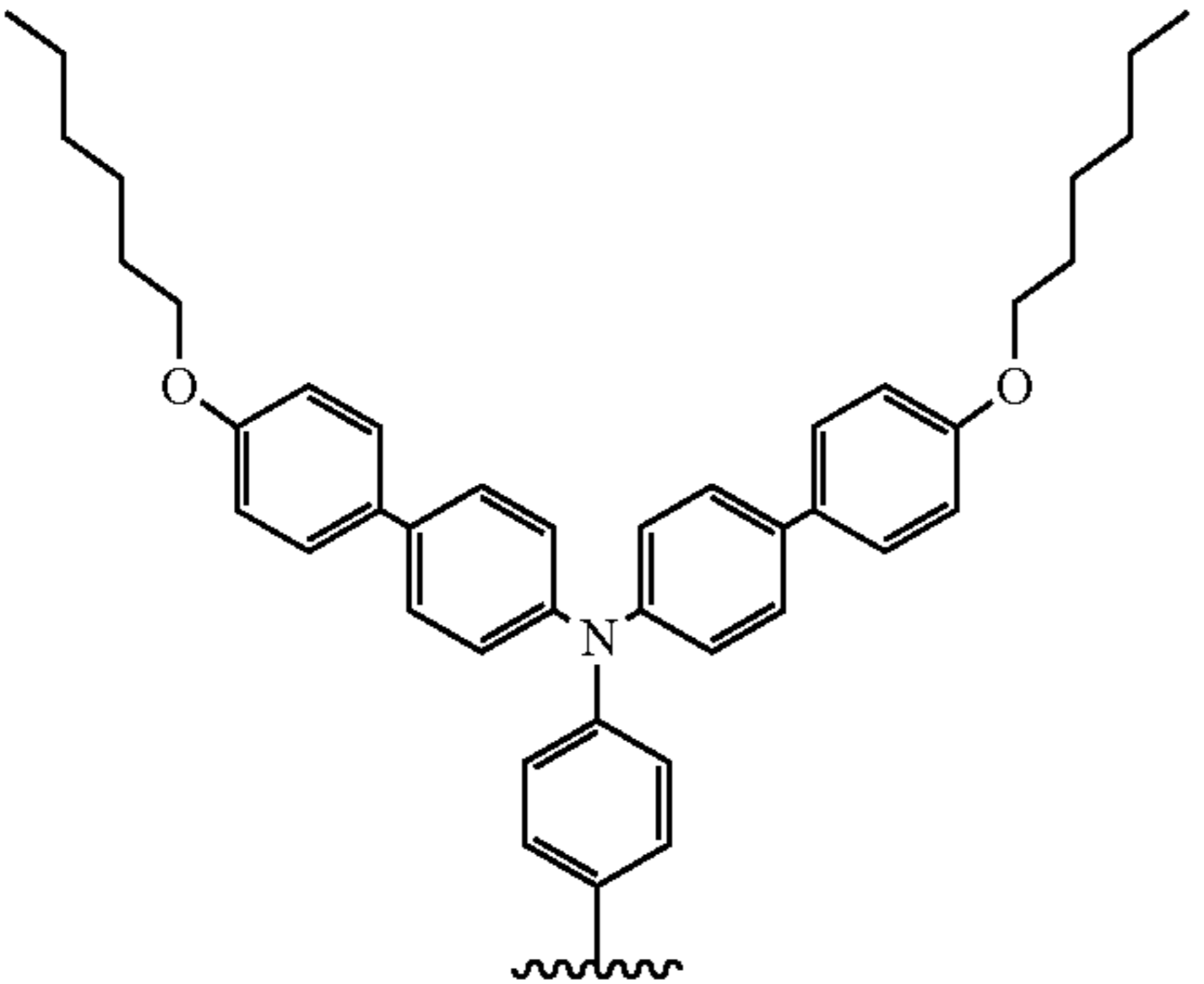
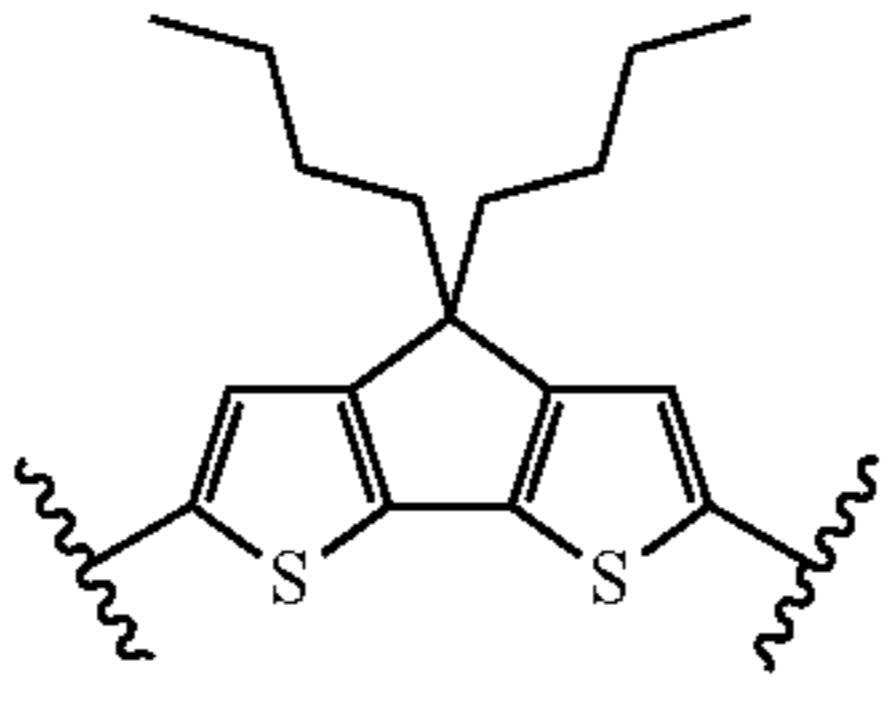
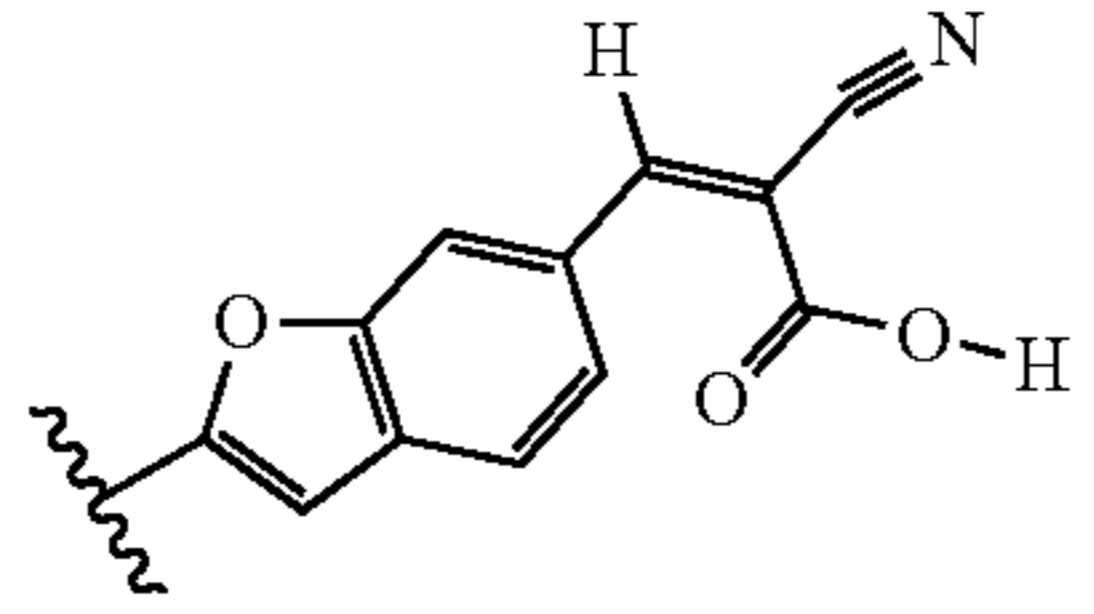
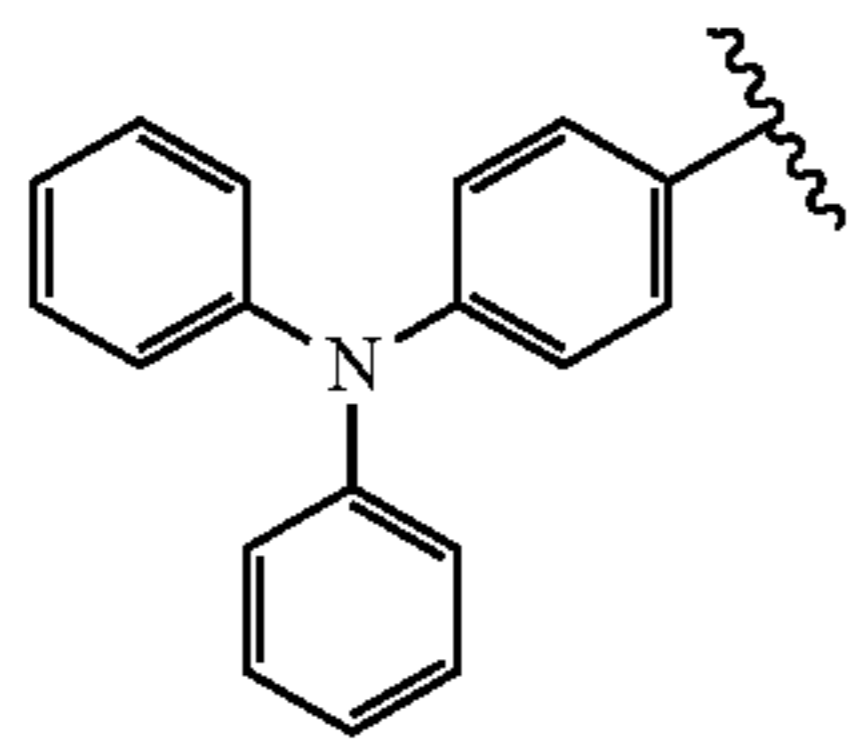
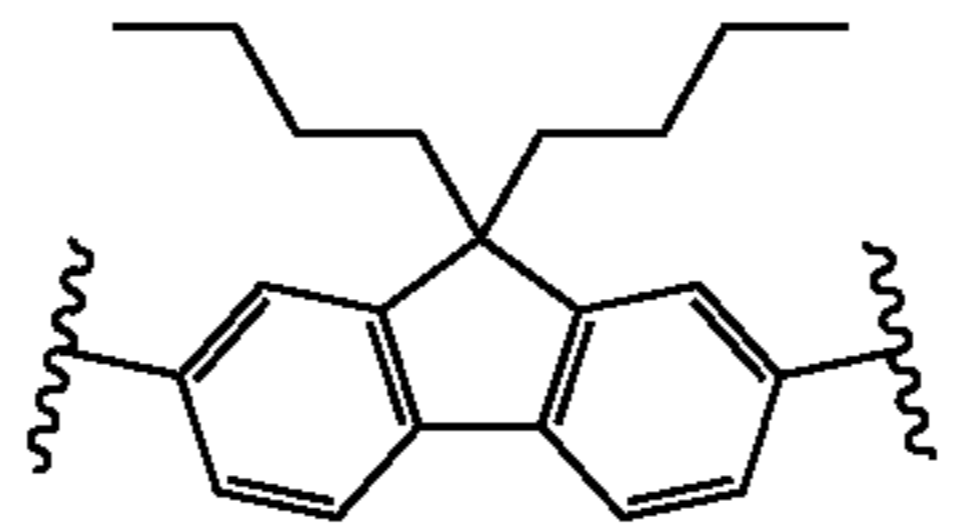
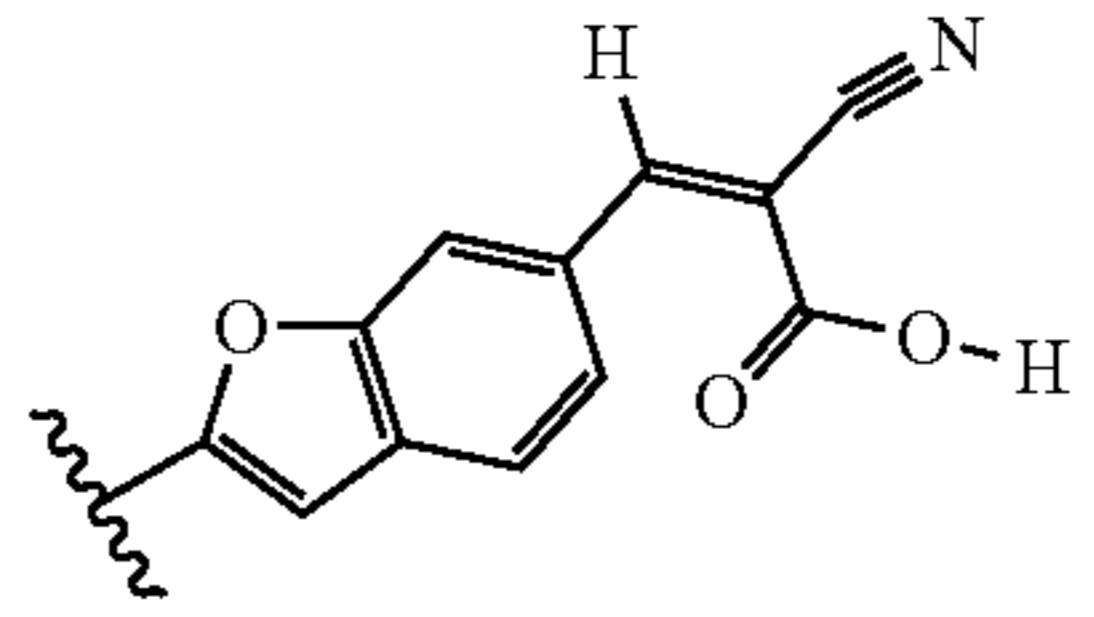
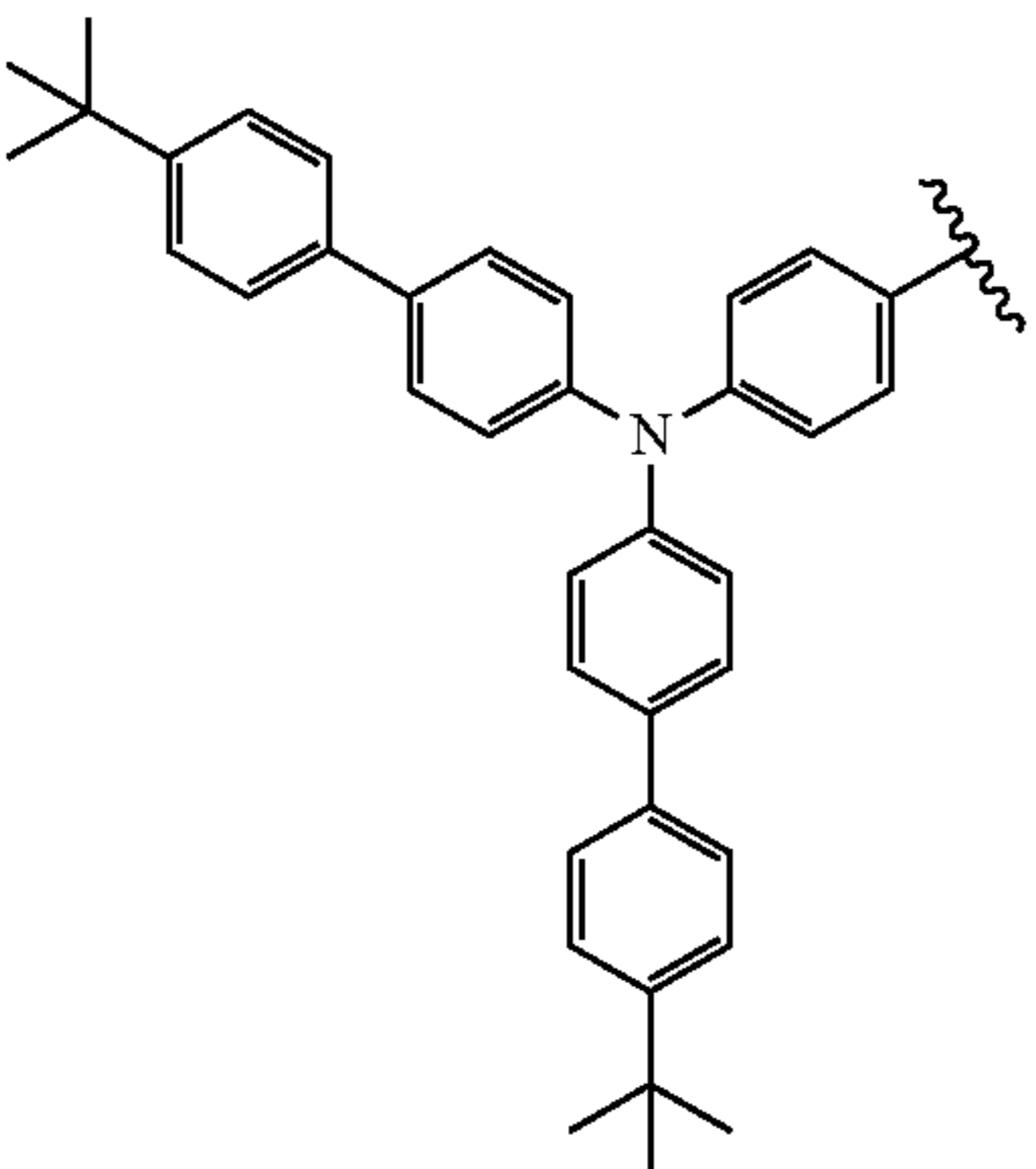
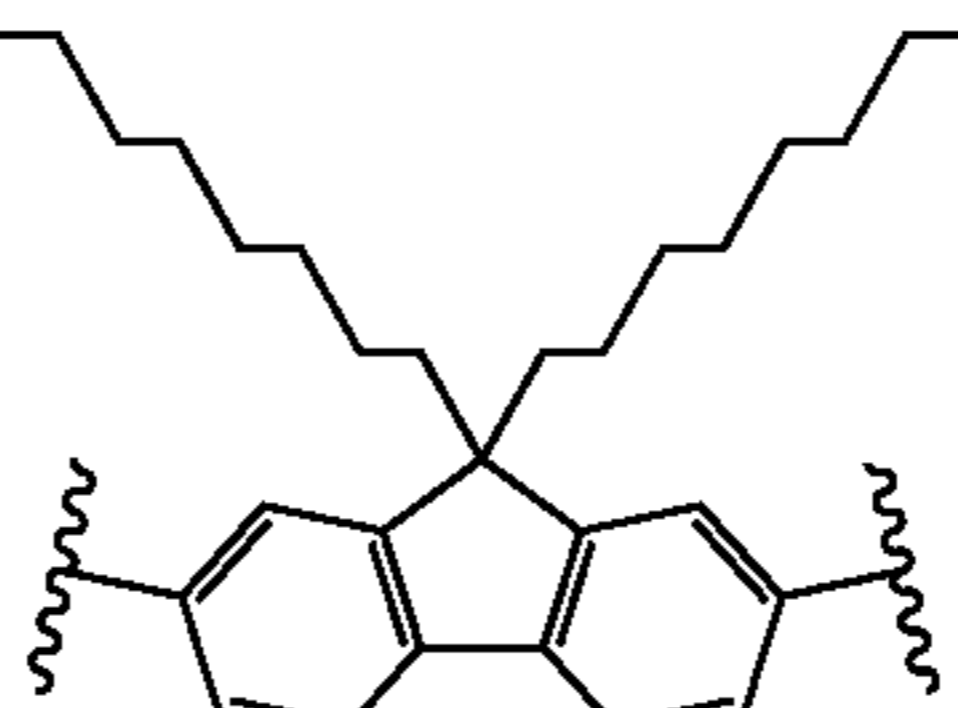
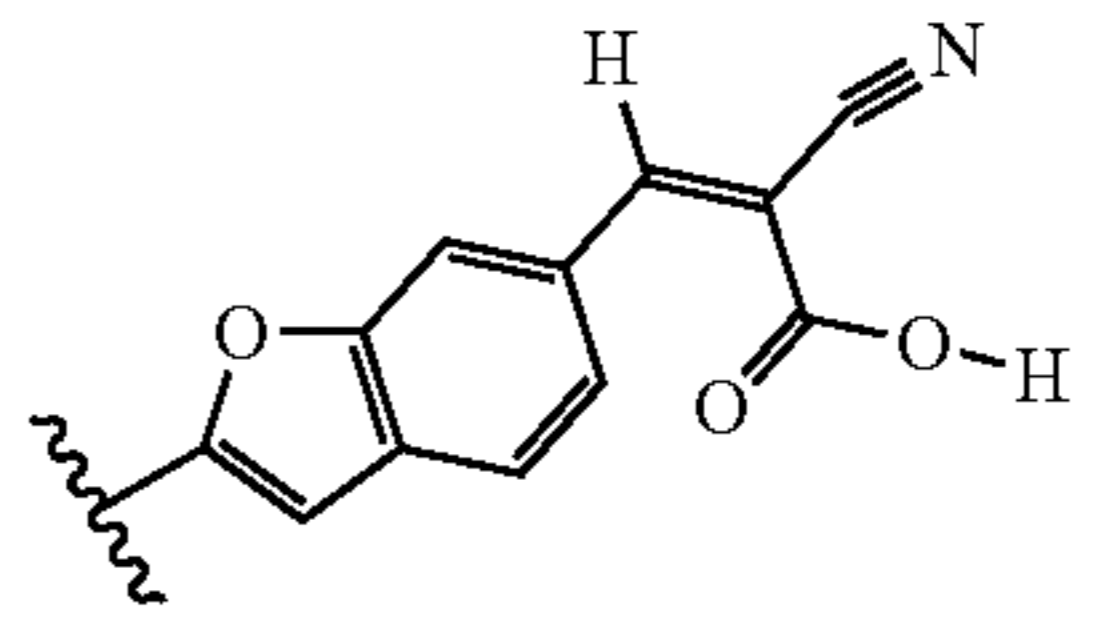
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Dye	Donor	Pi-bridge	Acceptor
D1			
D2			
D3			
D4			
D5			

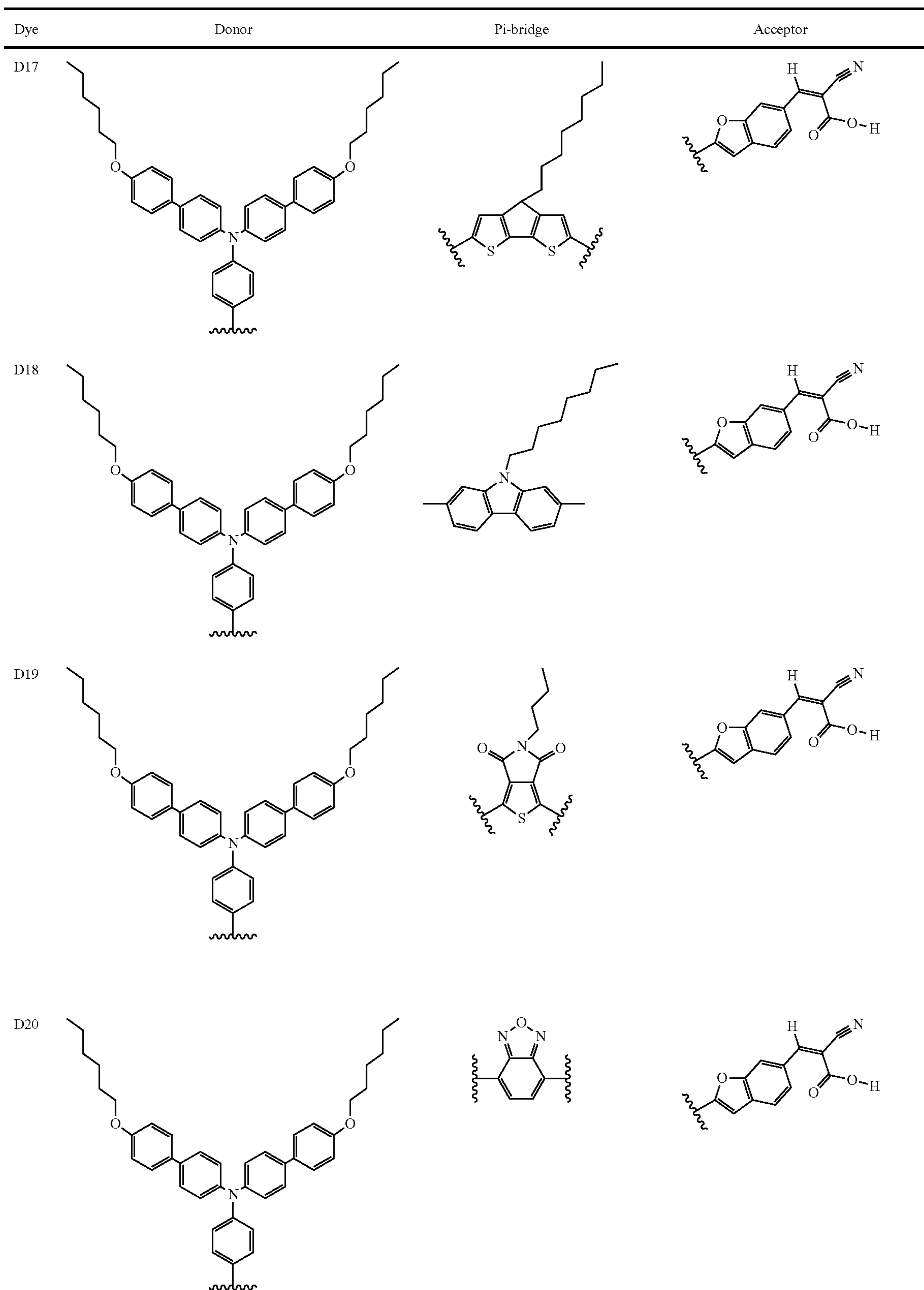
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Dye	Donor	Pi-bridge	Acceptor
D6			
D7			
D8			
D9			
D10			
D11			

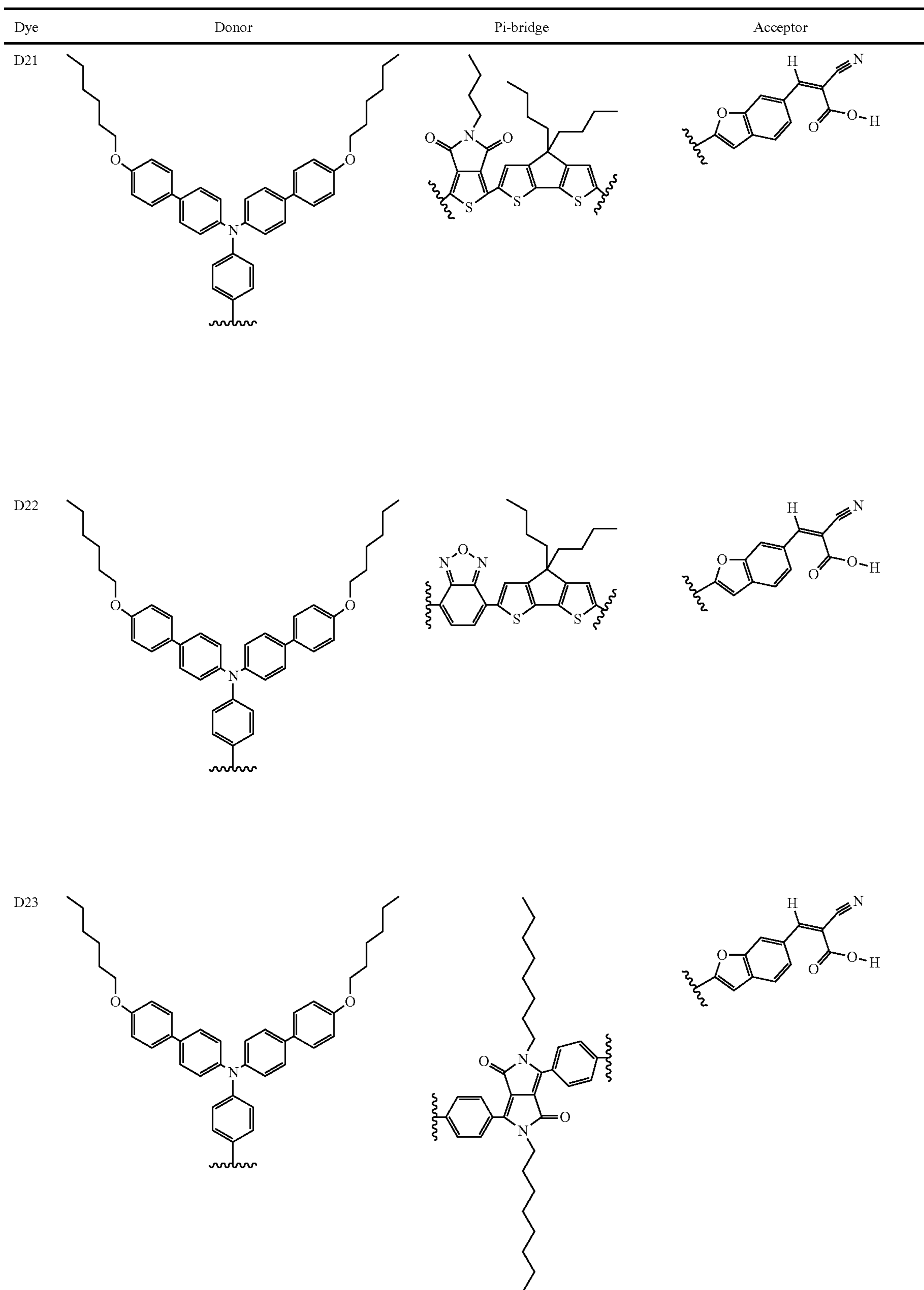
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Dye	Donor	Pi-bridge	Acceptor
D12			
D13			
D14			
D15			
D16			

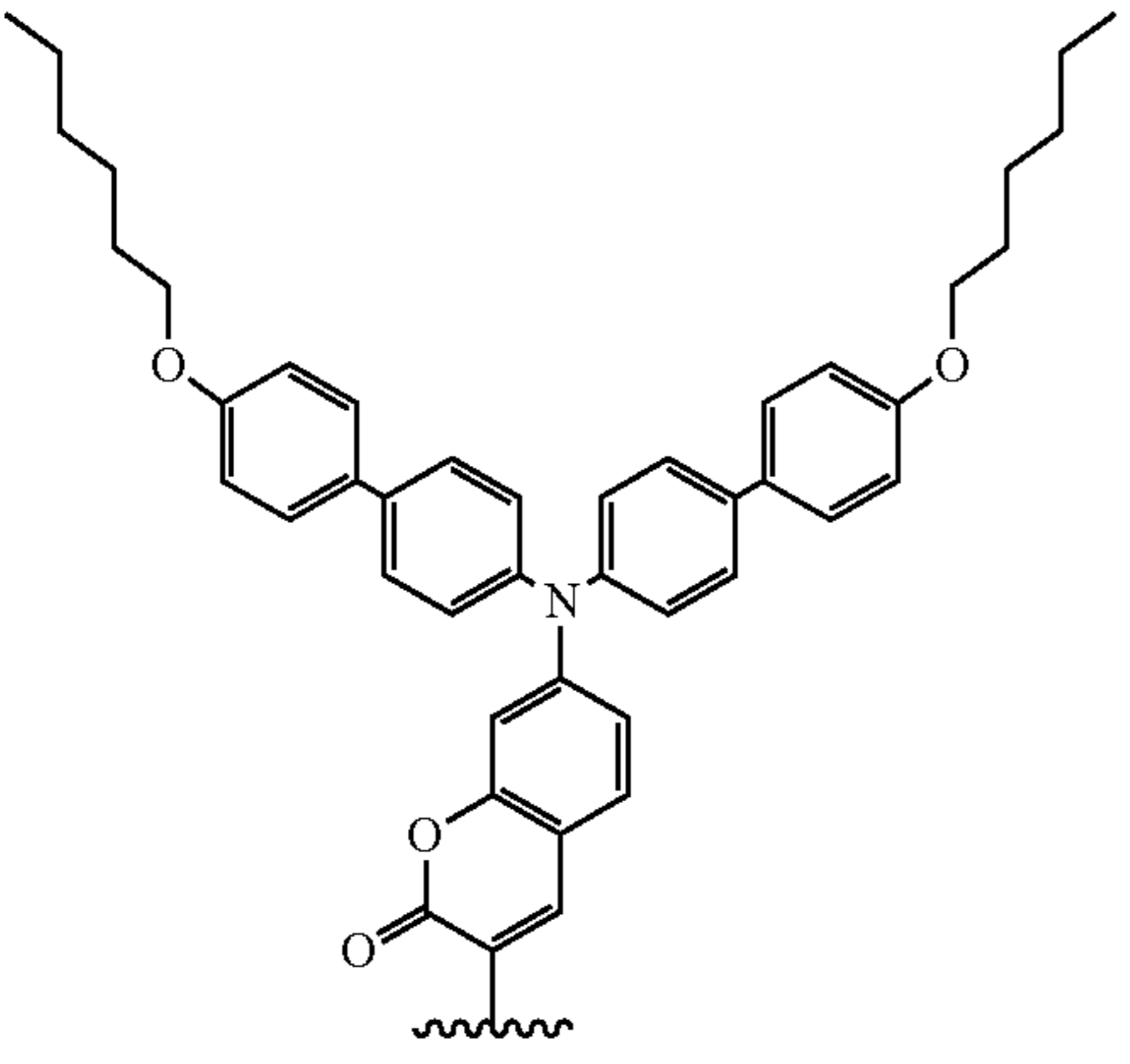
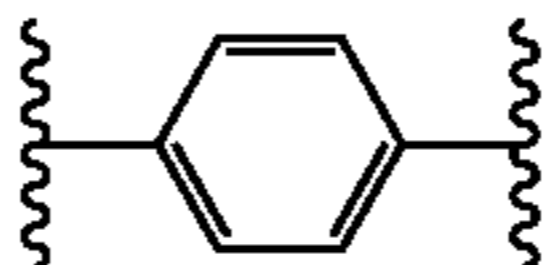
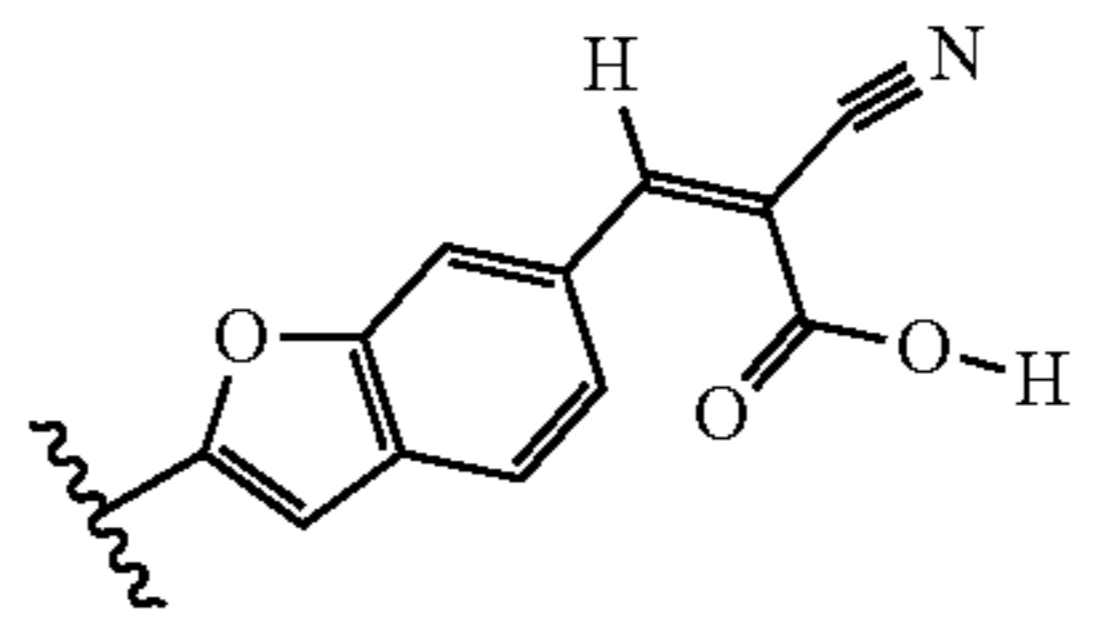
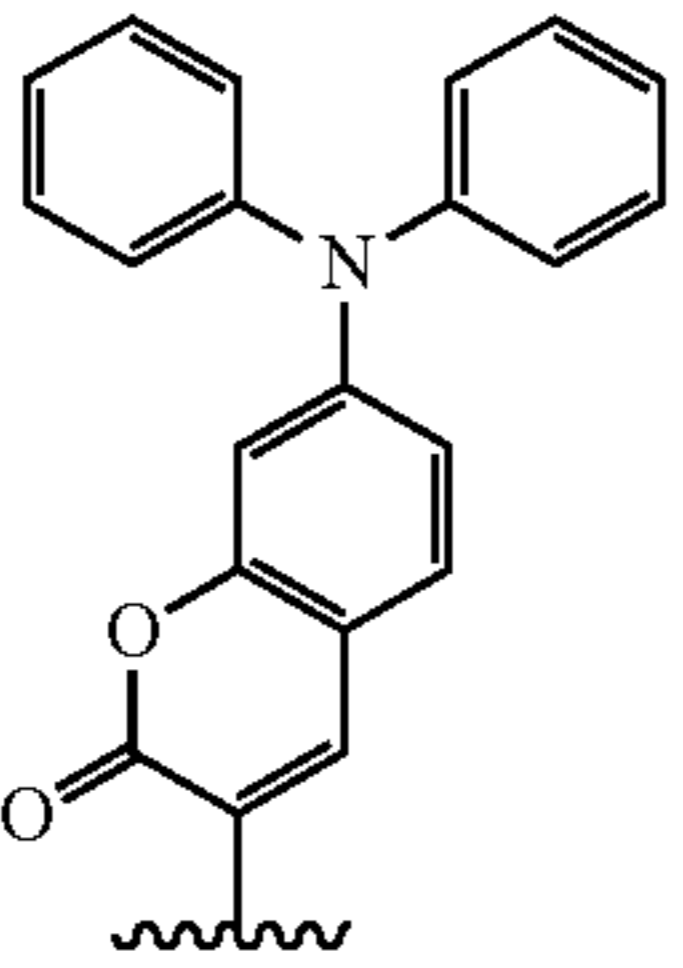
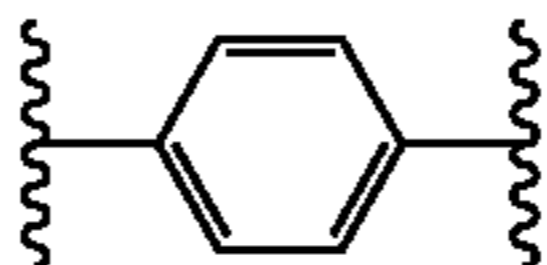
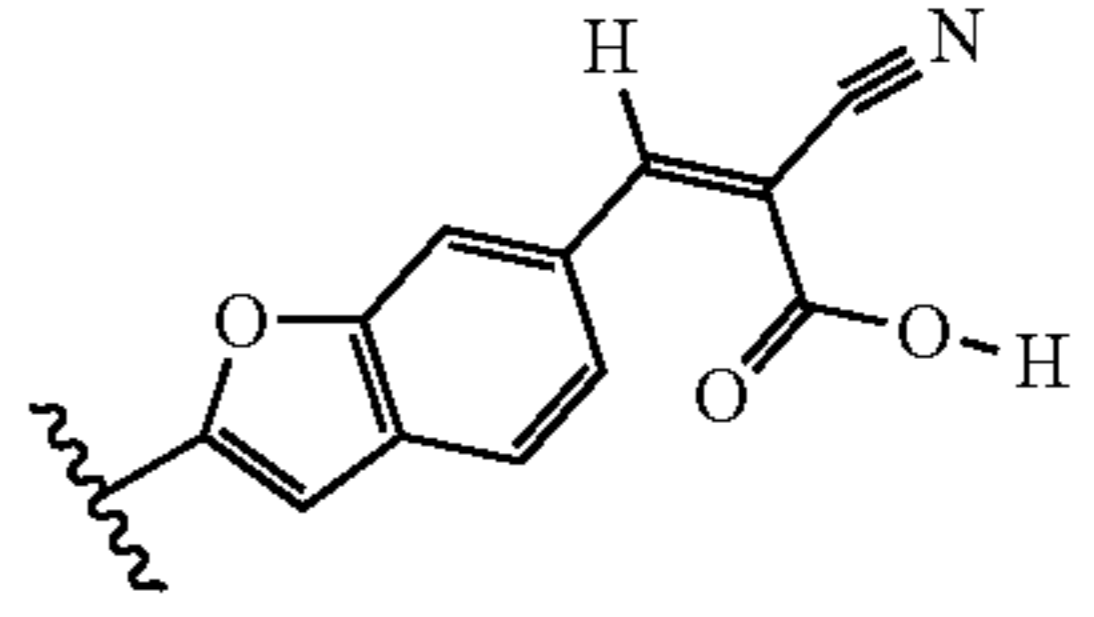
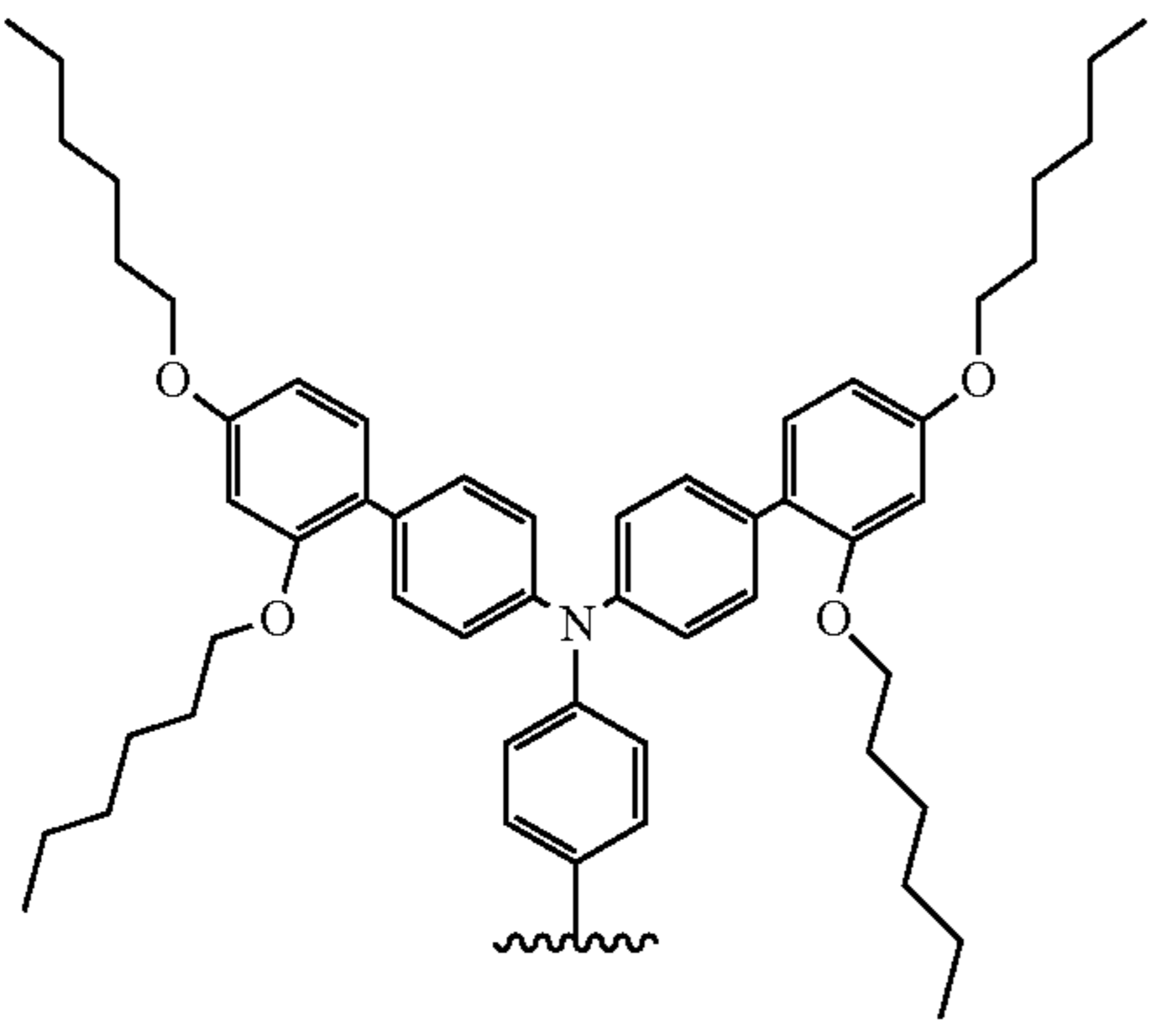
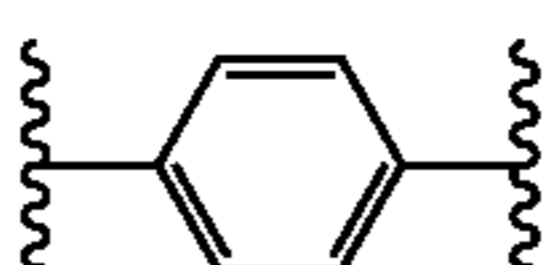
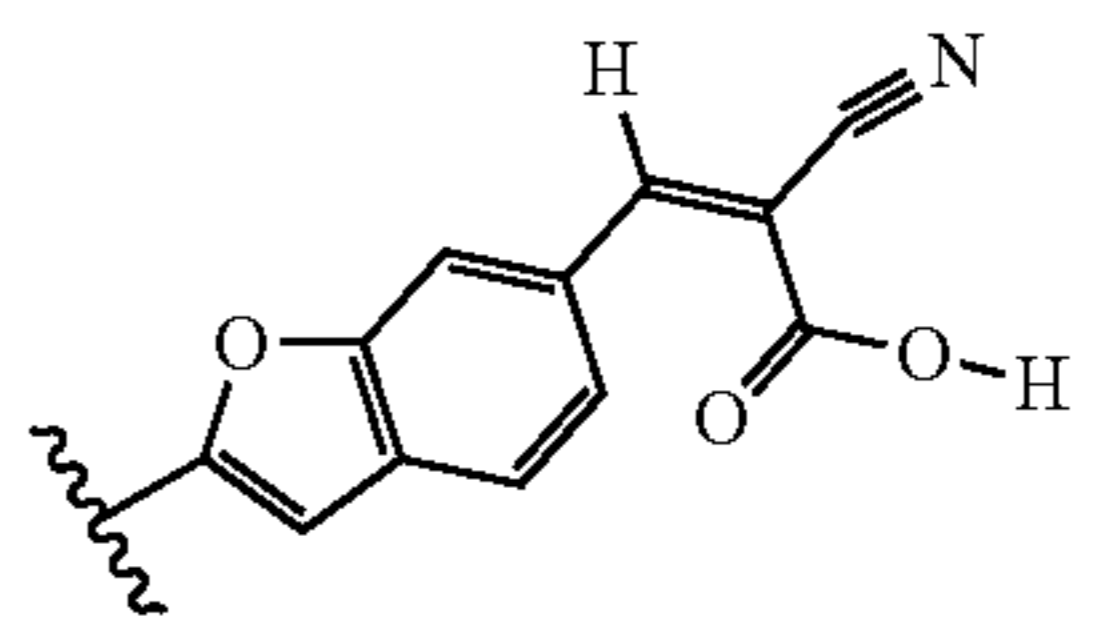
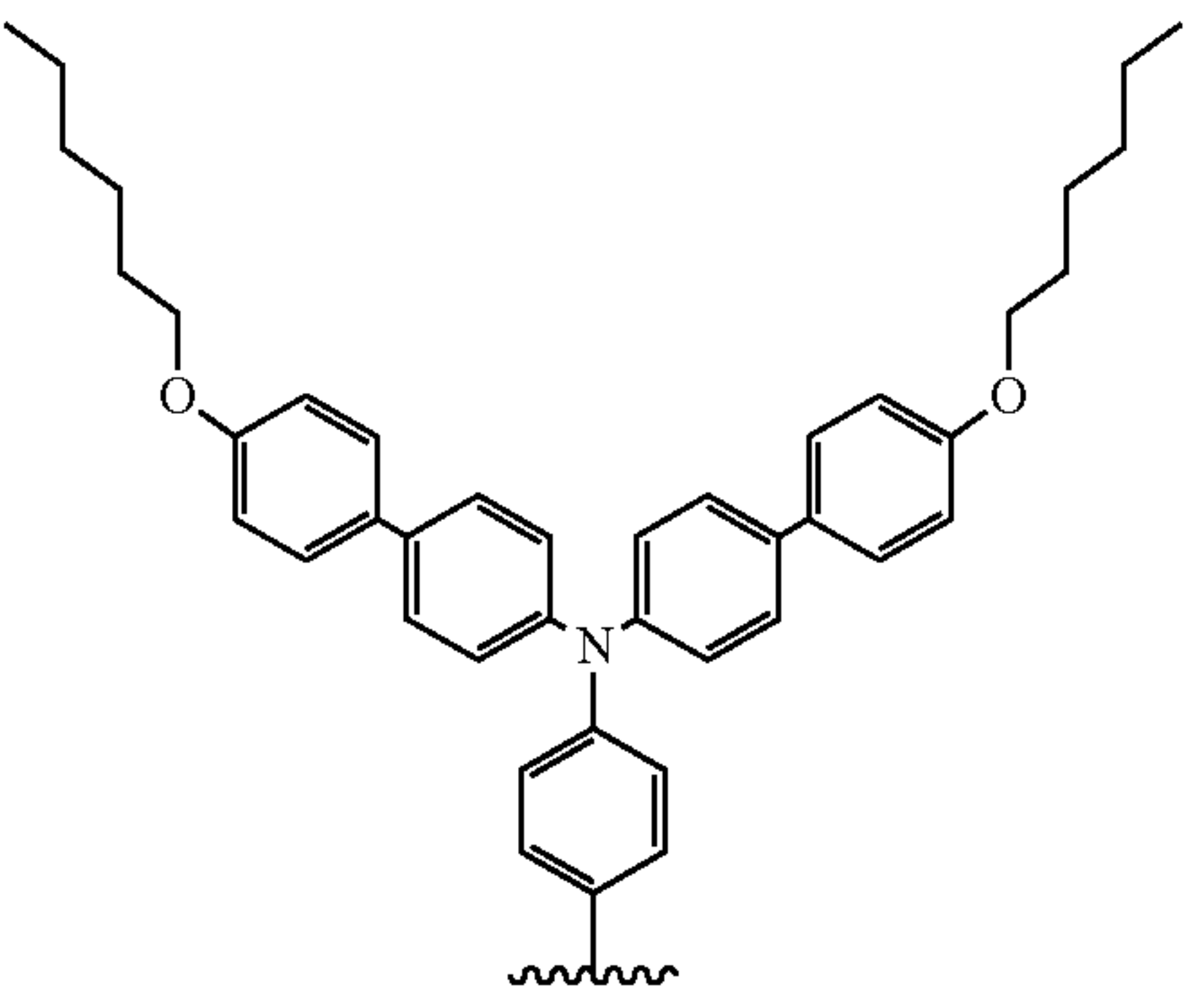
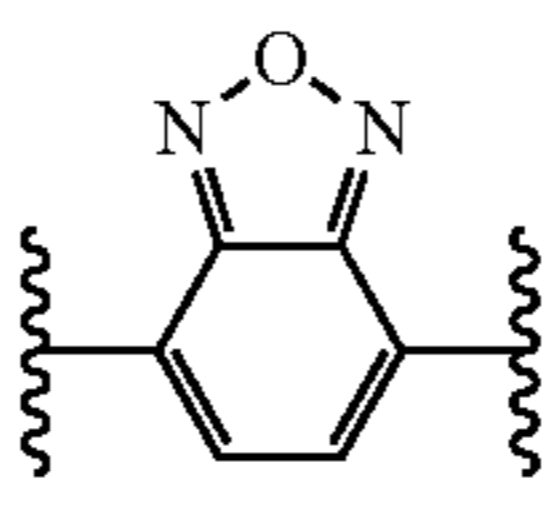
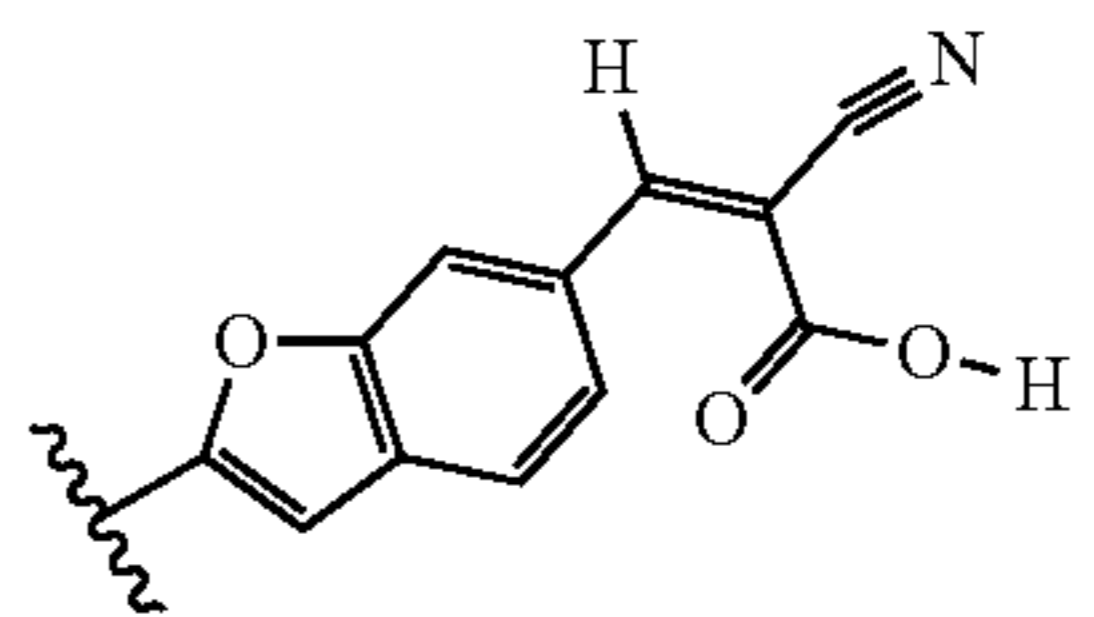
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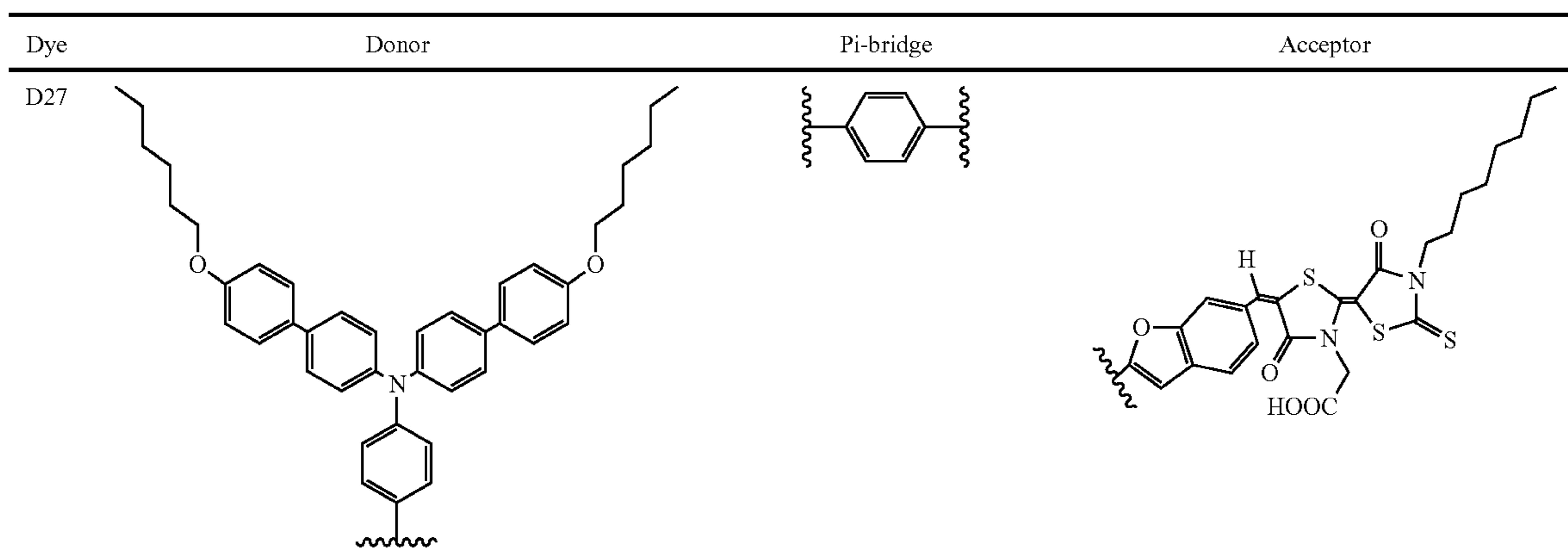
-continued



-continued

Dye	Donor	Pi-bridge	Acceptor
D24			
D25G			
D25H			
D26			

-continued



**[0052]** Isolation and purification of the chemical entities and intermediates described herein can be effected, if desired, by any suitable separation or purification procedure such as, for example, filtration, extraction, crystallization, column chromatography, thin-layer chromatography or thick-layer chromatography, or a combination of these procedures. Specific illustrations of suitable separation and isolation procedures can be had by reference to the examples herein. However, other equivalent separation or isolation procedures can also be used.

**[0053]** When desired, the (R)- and (S)-isomers of the solar cell dyes described herein, if present, may be resolved by methods known to those skilled in the art, for example by formation of diastereomeric salts or complexes which may be separated, for example, by crystallization; via formation of diastereomeric derivatives which may be separated, for example, by crystallization, gas-liquid or liquid chromatography; selective reaction of one enantiomer with an enantiomer-specific reagent, for example enzymatic oxidation or reduction, followed by separation of the modified and unmodified enantiomers; or gas-liquid or liquid chromatography in a chiral environment, for example on a chiral support, such as silica with a bound chiral ligand or in the presence of a chiral solvent. Alternatively, a specific enantiomer may be synthesized by asymmetric synthesis using optically active reagents, substrates, catalysts or solvents, or by converting one enantiomer to the other by asymmetric transformation.

**[0054]** The solar cell dyes described herein can be optionally contacted with an acceptable acid to form the corresponding acid addition salts. Acceptable forms of the solar cell dyes recited herein include salts, chelates, non-covalent complexes or derivatives, precursors, and mixtures thereof. In certain embodiments, the dyes described herein are in the form of salts. In addition, if the dye described herein is

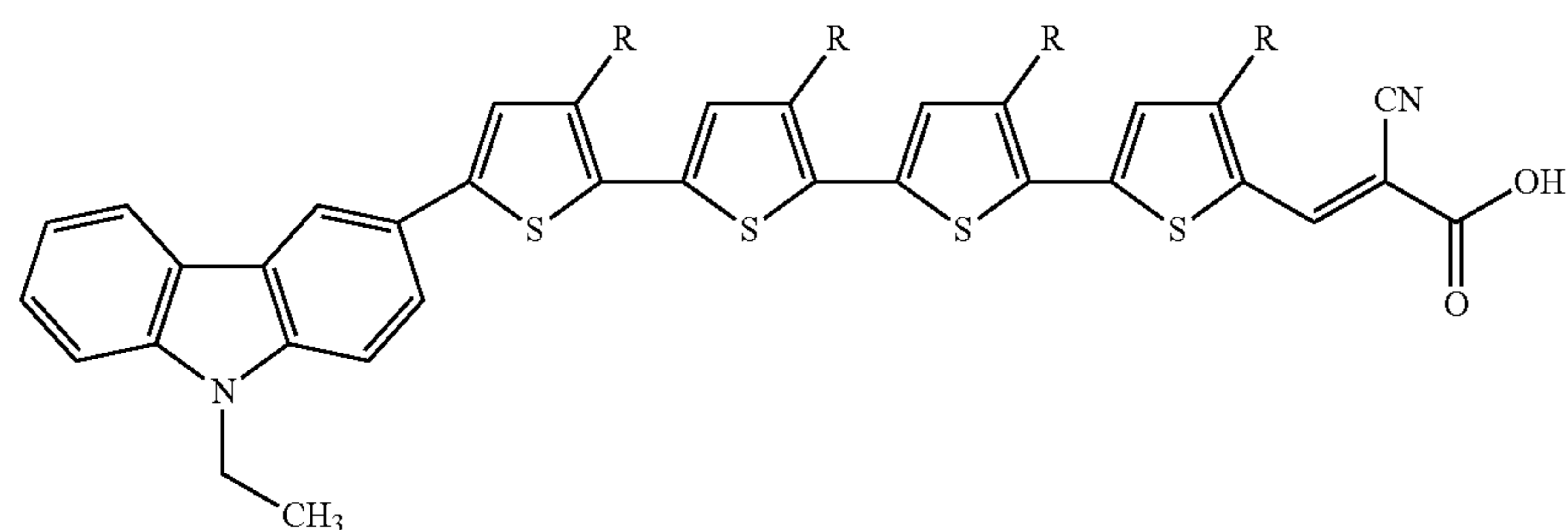
obtained as an acid addition salt, the free base can be obtained by basifying a solution of the acid salt. Conversely, if the product is a free base, an addition salt may be produced by dissolving the free base in a suitable organic solvent and treating the solution with an acid, in accordance with conventional procedures for preparing acid addition salts from base compounds. Those skilled in the art will recognize various synthetic methodologies that may be used to prepare non-toxic addition salts.

**[0055]** When ranges are used herein for physical properties, such as molecular weight, or chemical properties, such as chemical formulae, all combinations and subcombinations of ranges and specific embodiments therein are intended to be included. The term “about” when referring to a number or a numerical range means that the number or numerical range referred to is an approximation within experimental variability (or within statistical experimental error), and thus the number or numerical range may vary from, for example, between 1% and 15% of the stated number or numerical range. The term “comprising” (and related terms such as “comprise” or “comprises” or “having” or “including”) include those embodiments, for example, an embodiment of any composition of matter, composition, method, or process, or the like, that “consist of” or “consist essentially of” the described features.

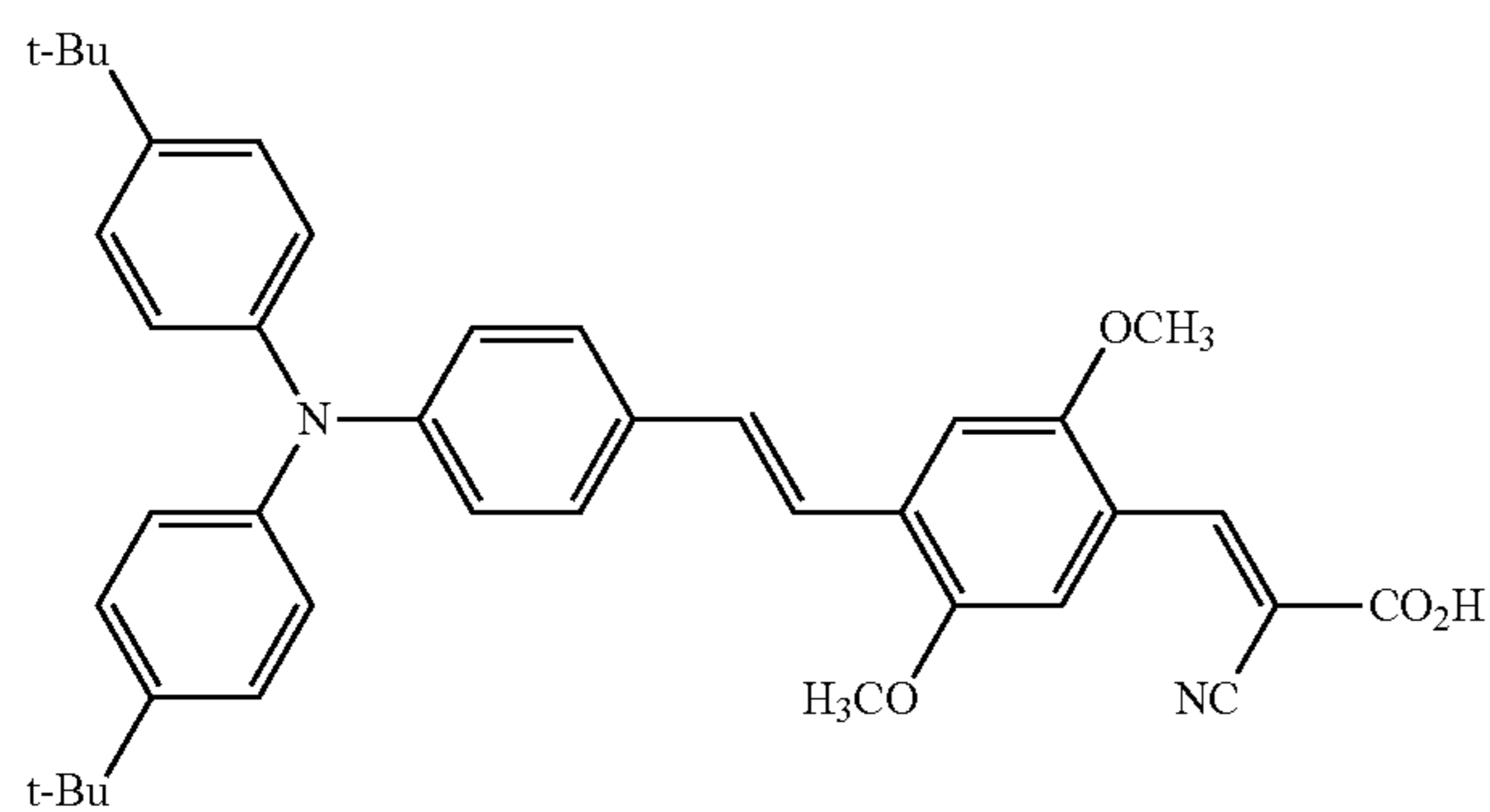
#### Non-Benzofuran-Containing Dyes

**[0056]** Non-benzofuran-containing dyes as described herein are any dyes that (a) are useful in DSSCs and (b) do not contain a benzofuran ring in their structure. There are currently many commercially available non-benzofuran containing dyes.

**[0057]** In some embodiments, the non-benzofuran containing dye is selected from the group consisting of MK2, BOD4, XY1b, WE10 and WE11. The first three of these dyes are commercially available and have the following structures:

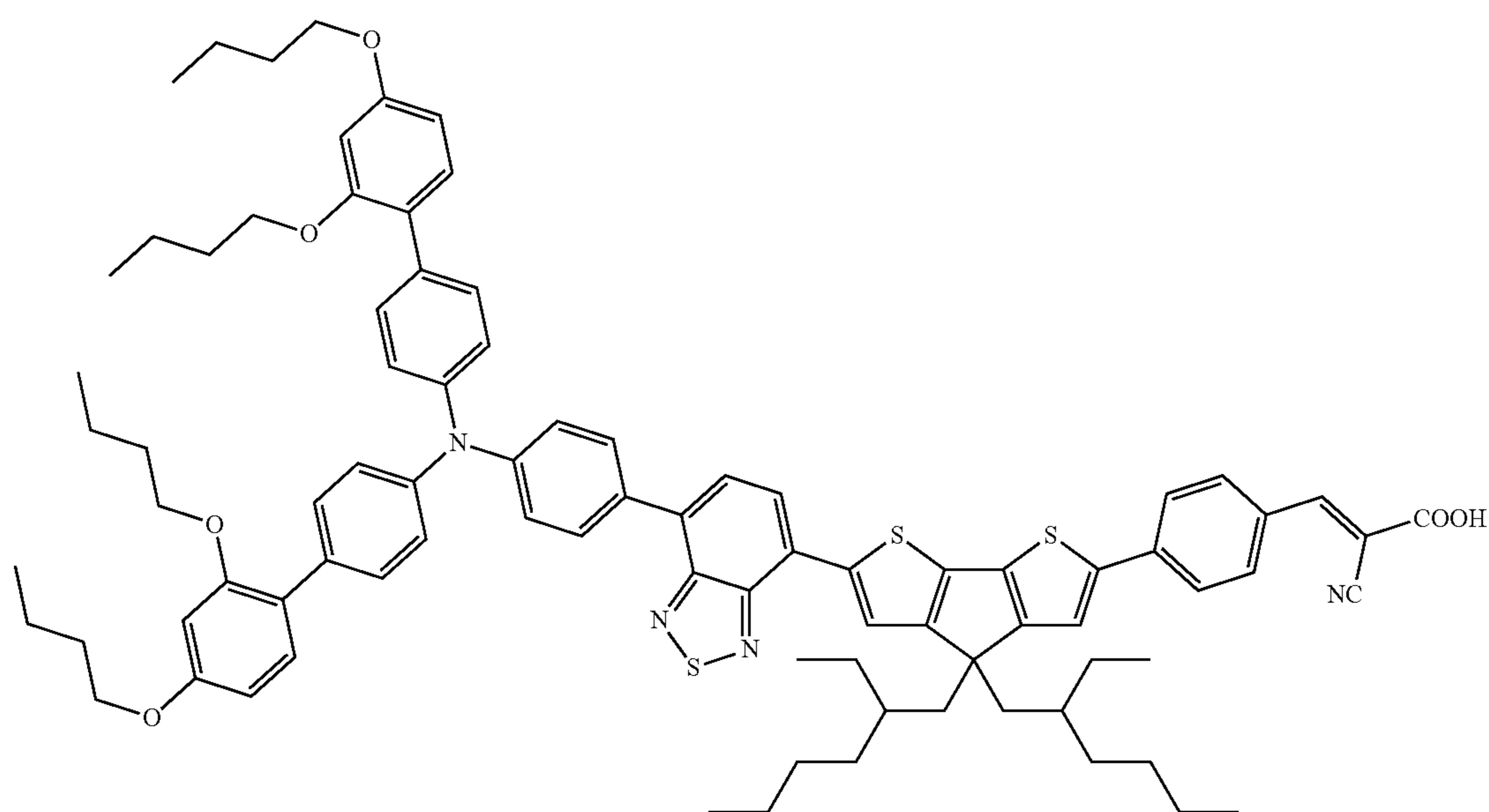


MK2 dye  
 R  $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$



BOD4 dye

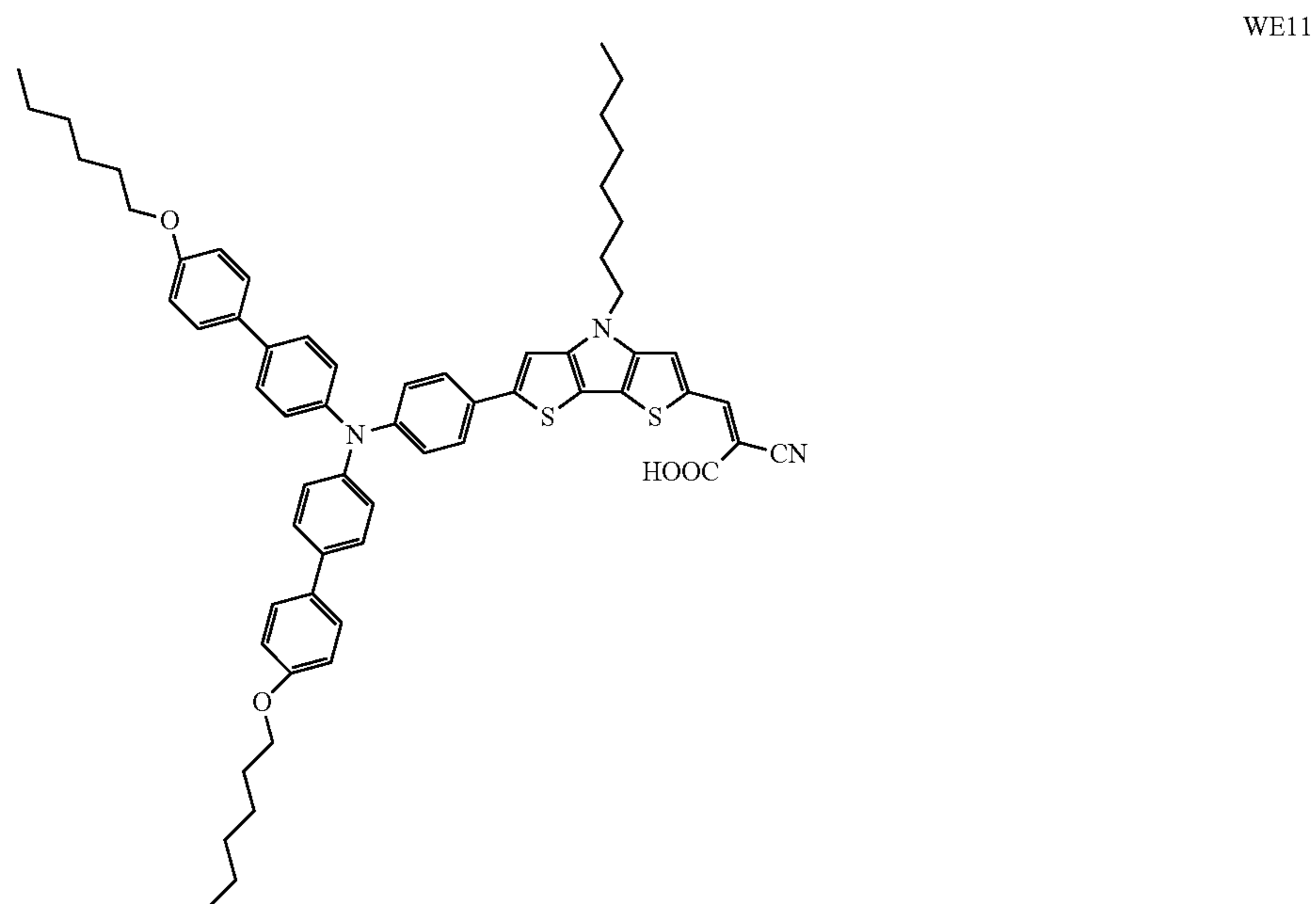
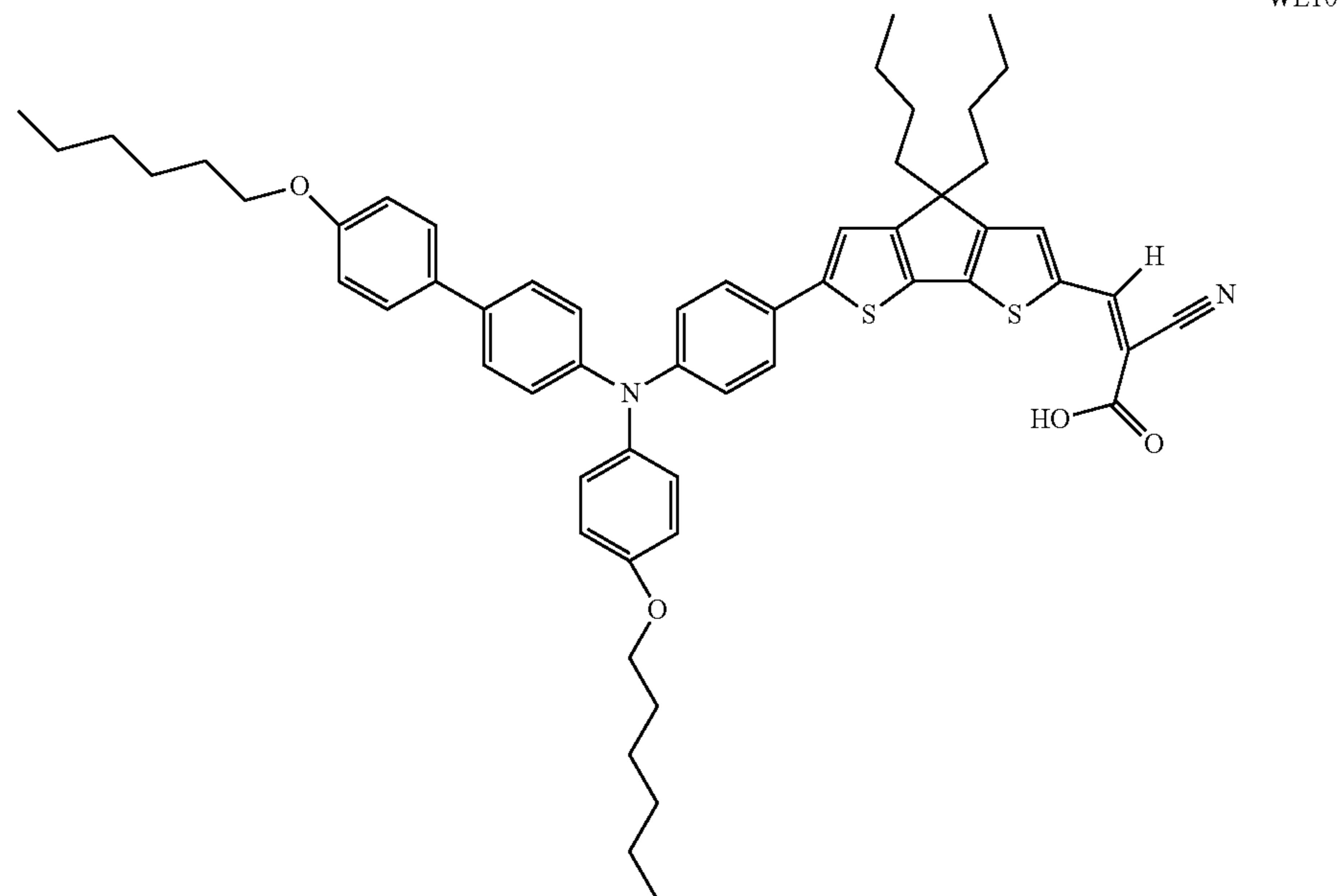
XY1b



Ⓢ indicates text missing or illegible when filed



[0058] The latter two dyes have the following structures:



#### Combinations of Solar Cell Dyes

[0059] Solar cell dye combinations described herein comprise a benzofuran-containing dye and a non-benzofuran-containing dye. In some embodiments, the benzofuran-containing dye is a compound having the structure shown in formulae I, II, III or IV as shown herein. In some embodiments, the non-benzofuran-containing dye is MK2, BOD4, XY1b, WE10 or WE11.

#### EXPERIMENTAL

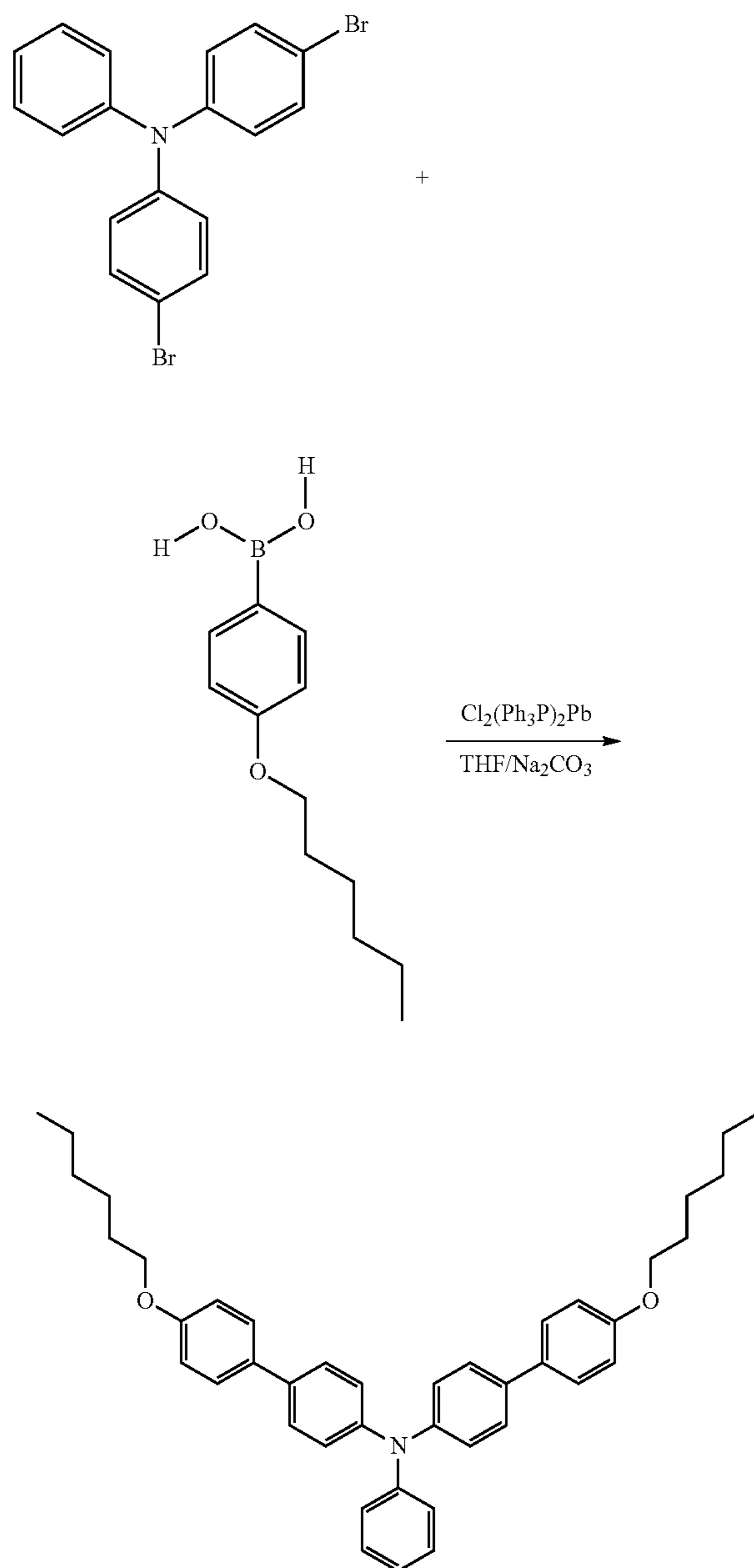
[0060] All reagents were purchased from commercial suppliers and used as supplied unless stated otherwise. Reactions were carried out in air unless stated otherwise. 400 MHz  $^1\text{H}$  NMR spectra were obtained on a JEOL AS 400 spectrometer. Low-resolution mass spectra (LRMS) were obtained on a JEOL JMS-T100LC DART/AccuTOF mass spectrometer. Measurement of reversal of protein aggregation may be carried out using such assays as Bis-ANS Fluorescence as described in, for example, W. T. Chen et al. (2011), *J. Biol. Chem.*, 286 (11): 9646.

## Synthesis of Solar Cell Dyes

Example 1. Synthesis of (Z)-2-cyano-3-[6-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-hexyl-2-thienyl]benzothiophen-2-yl]prop-2-enoic Acid (D1)

A. 4,4'-Bis(4-n-hexyloxyphenyl)triphenylamine

[0061]

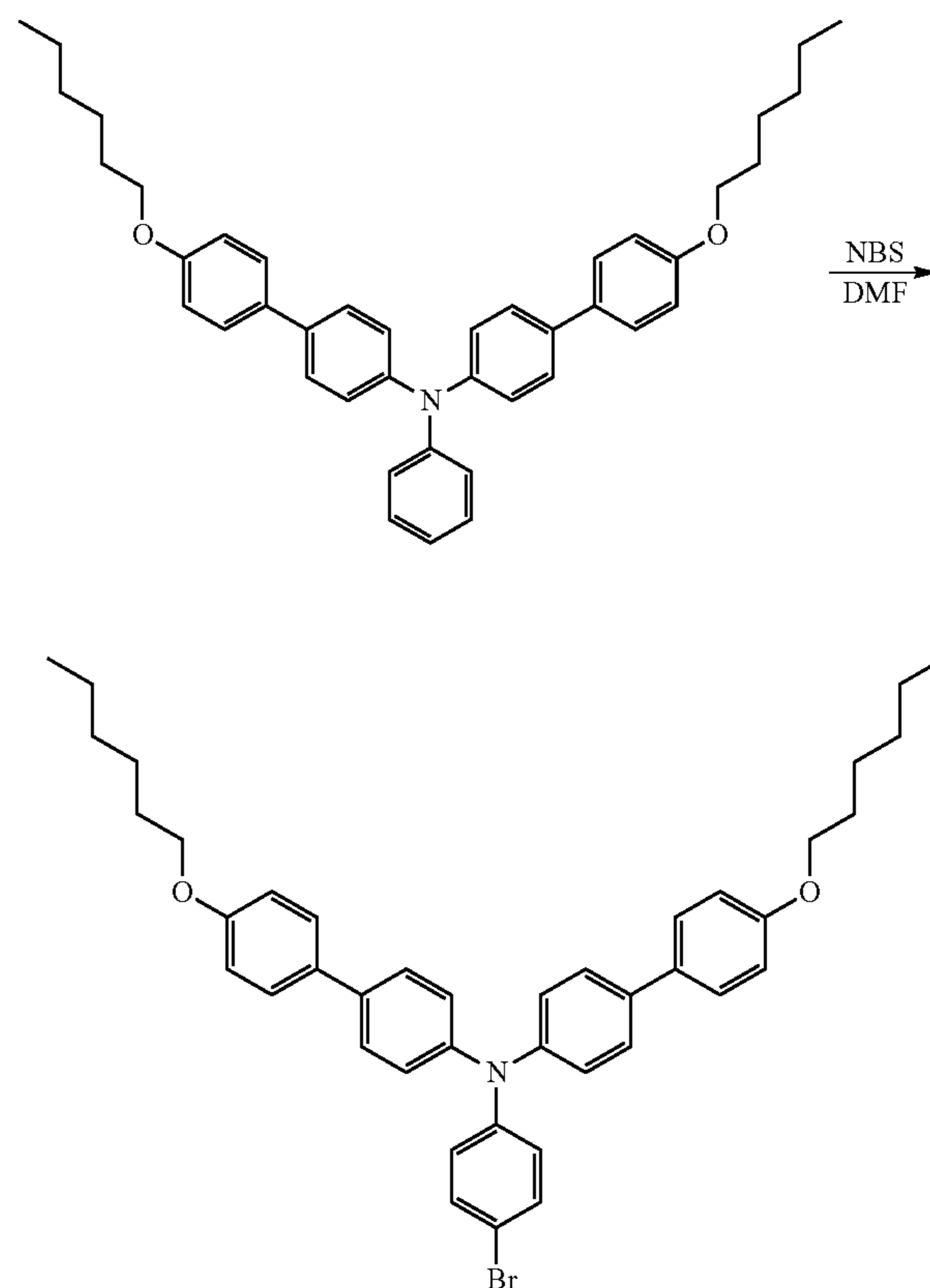


[0062] In a round bottom flask, 6.0 g (14.9 mmol) dibromo-triphenylamine, 8.9 g (38.2 mmol) 4-n-hexyloxybenzeneboronic acid and 0.2 g (0.25 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 50 mL THF and 30 mL 10%  $\text{Na}_2\text{CO}_3$ . The batch was held

at reflux for 24 h and HPLC showed complete reaction. Mixture was poured into a beaker with 300 mL water and the product was filtered off, washed with water, and dried. Crude product was dissolved in methylene chloride then passed through a plug of silica gel and washed through with dichloromethane. The solvent was removed and replaced with acetonitrile. The resulting solid was filtered off, washed with acetonitrile and dried, yielding 8 g tan solid (90% yield). UV/Vis max 325 nm, LCMS  $m/z=598.4$ .

B. N-(4-bromophenyl)-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]aniline

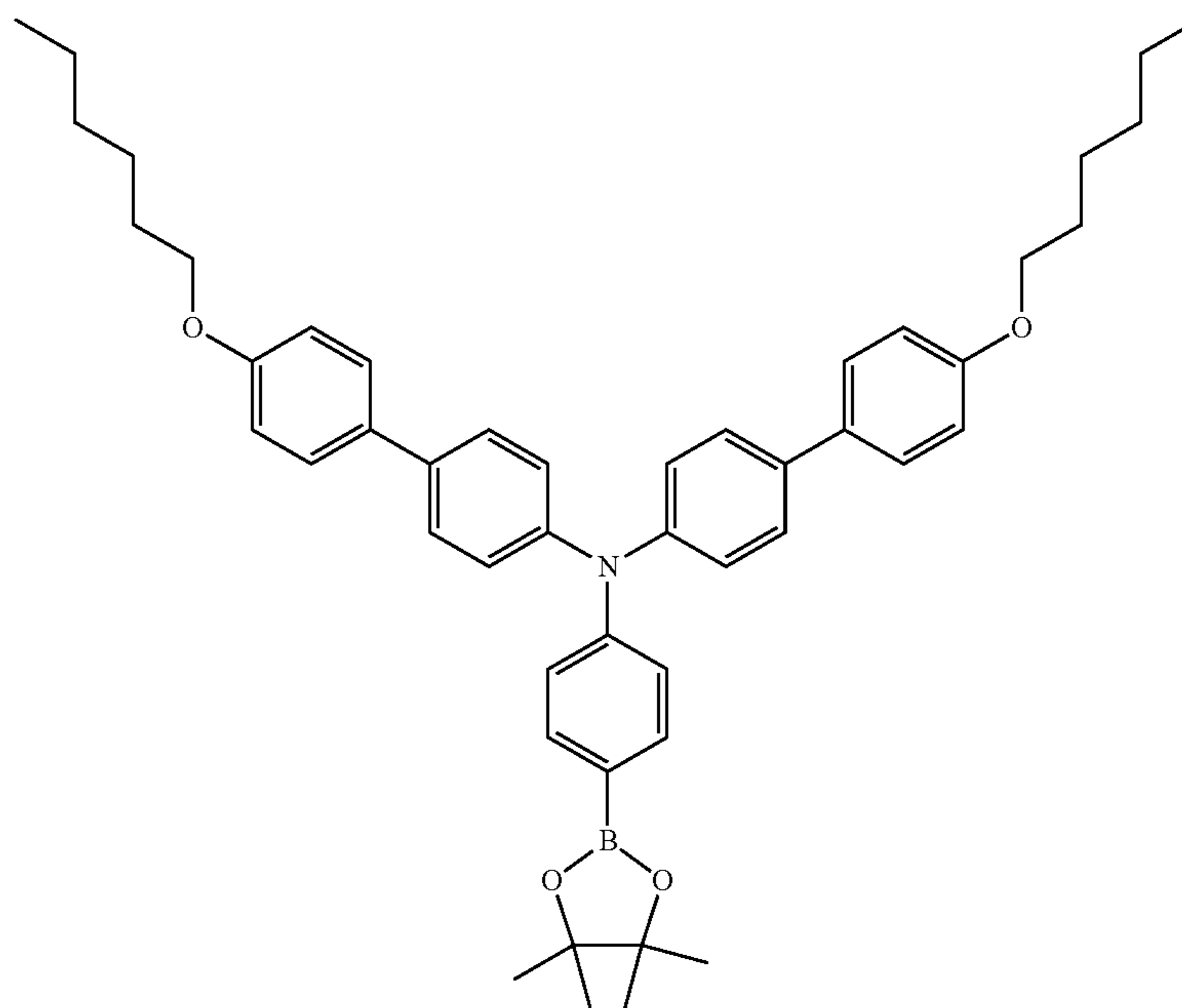
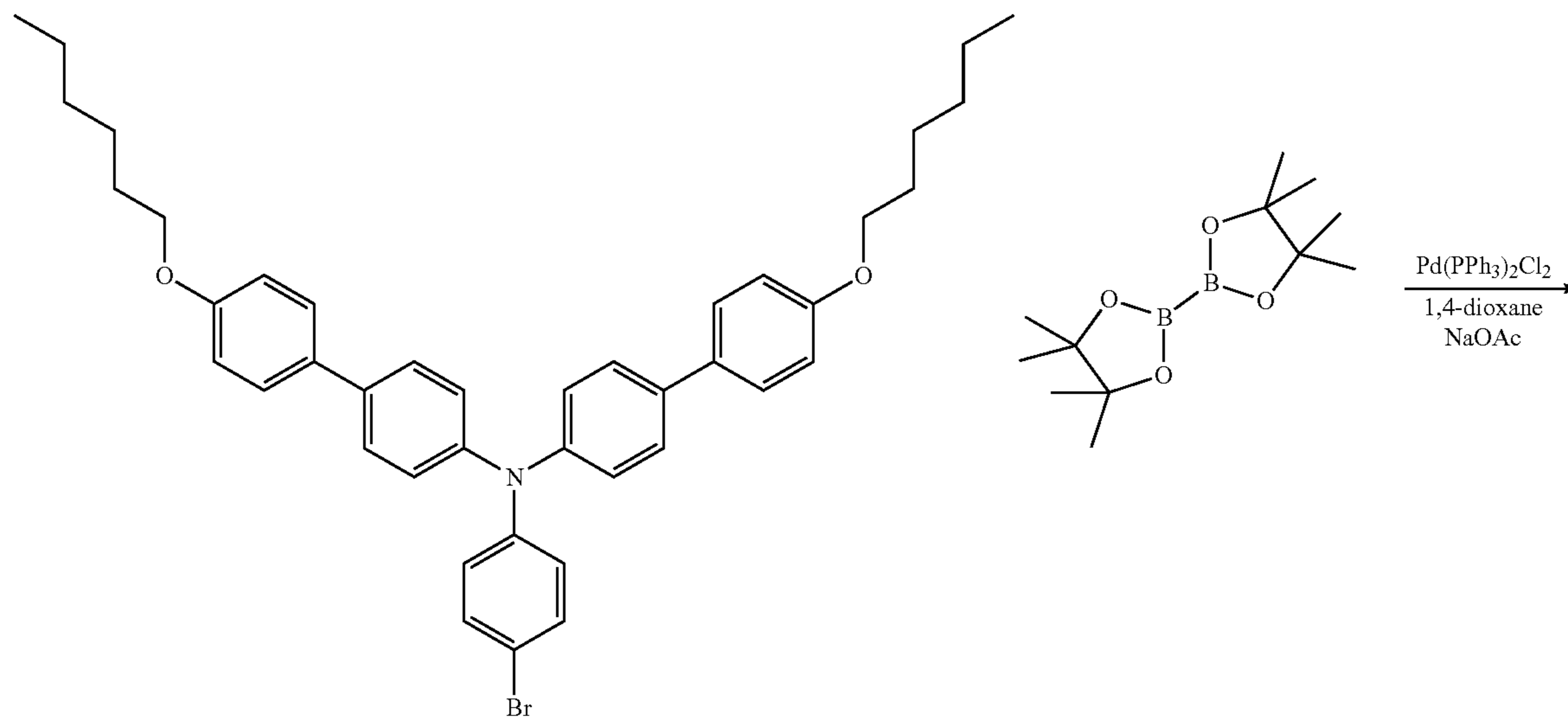
[0063]



[0064] In a round bottom flask, 4.25 g (7.1 mmol) 4,4'-Bis(4-n-hexyloxyphenyl)triphenylamine and 1.5 g (8.4 mmol) N-bromosuccinimide was combined in 45 mL DMF at 25° C. for 2 h. Mixture was poured into a beaker with 300 mL water and the product was extracted into dichloromethane. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , evaporated to dryness and the residue was crystallized from ethanol, yielding 3.55 g white solid (5.25 mmol, 73.9% yield). UV/Vis max 330 nm, LCMS  $m/z=678.2$ .

C. N,N-bis[4-(4-hexoxyphenyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline

[0065]

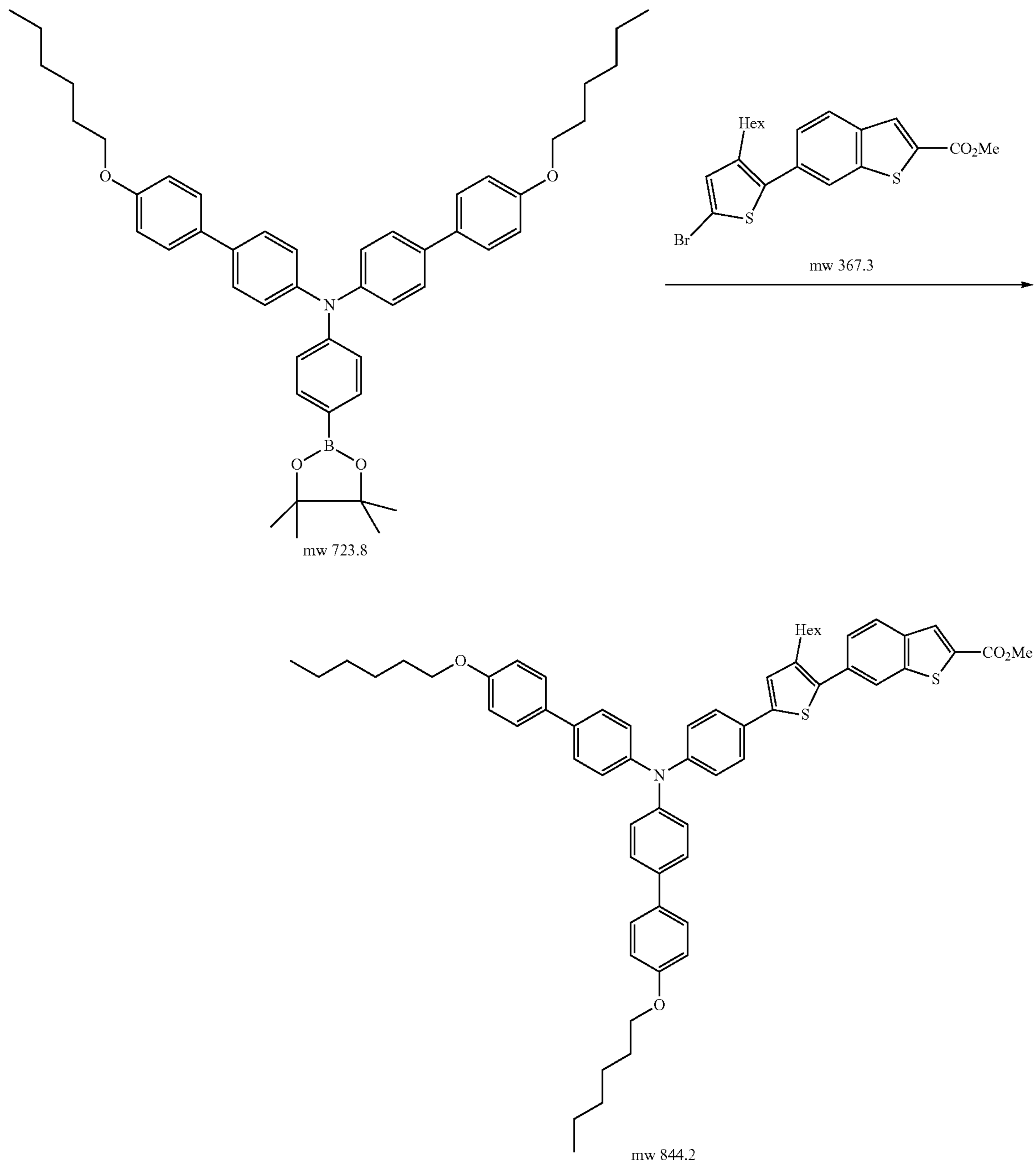


[0066] In a round bottom flask, 7.7 g (11.38 mmol) N-(4-bromophenyl)-4-(4-hexoxyphenyl)-N'-[4-(4-hexoxyphenyl)phenyl]aniline, 3.6 g (17.07 mmol) bis(pinacolato)diborane and 4 g KOAc was combined in 80 mL 1,4-dioxane. 0.3 g (0.4 mmol) dichloro 1,1'-bis(diphenylphosphino)ferrocene palladium(II) was added and the batch was held at reflux for 2 h. Reaction completed. Batch was cooled to rt then poured

into 400 mL of water. Solid was filtered off, washed with water and dried. Solid was dissolved in methylene chloride and passed through a silica gel plug and washed through with methylene chloride to remove original material. Solvent was displaced with ethyl acetate causing the product to crystallize, yielding 5.46 g white solid (7.54 mmol, 66% yield). UV/Vis max 335 nm, LCMS  $m/z=724.4$

D. Methyl 6-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-methyl-2-thienyl]benzothiophene-2-carboxylate

[0067]

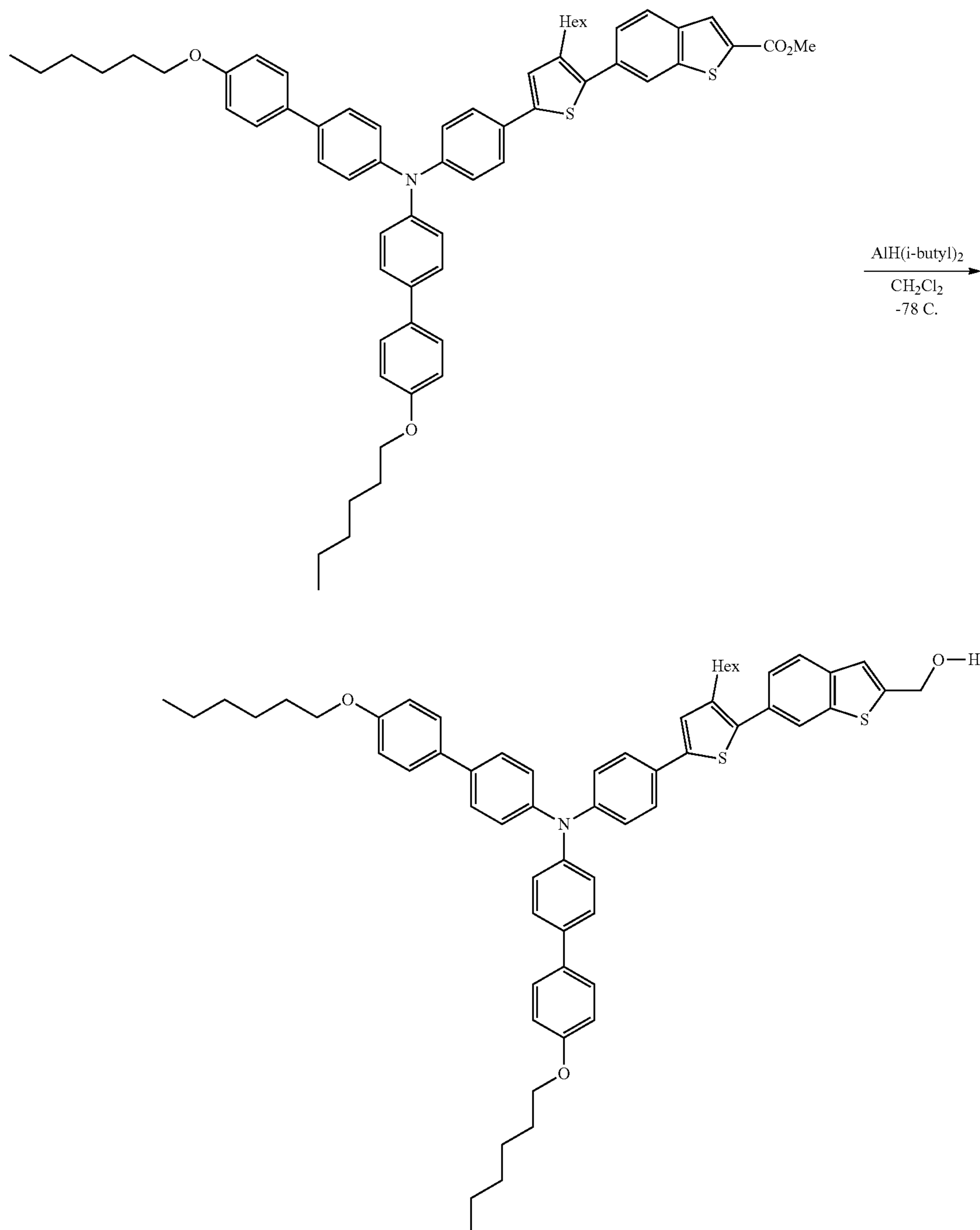


[0068] In a round bottom flask, 1 g (1.38 mmol) N,N-bis[4-(4-hexoxyphenyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 0.56 g (1.5 mmol) methyl 6-(5-bromo-3-methyl-2-thienyl)benzothiophene-2-carboxylate was combined in 20 mL THF and 3 mL 10% Na<sub>2</sub>CO<sub>3</sub> (0.44 g dry, 4.2 mmol). 0.1 g (0.13 mmol) dichloro-bis(diphe-

nylphosphino) ferrocene palladium (II) was added and the batch was refluxed for 2 h. HPLC (C18, 10% up to 80% THF/water) indicated complete reaction. Batch was poured into 100 mL water and product was extracted into dichloromethane. Product was purified using chromatography (EtOAc/Hexane) yielding 250 mg yellow solid (21% yield).

E. [6-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-methyl-2-thienyl]benzothiophen-2-yl]methanol

[0069]

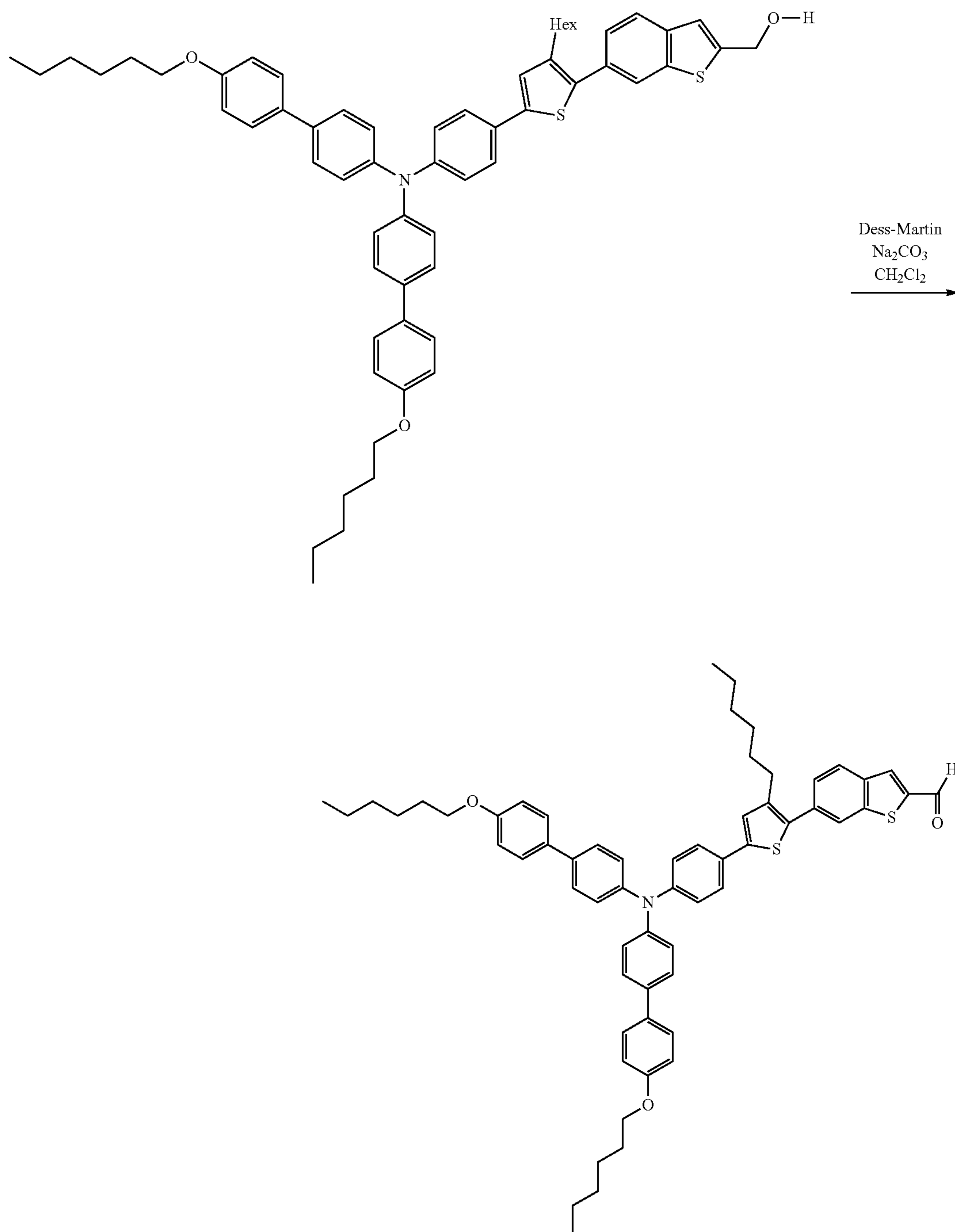


[0070] In a round bottom flask, 0.3 g (0.31 mmol) methyl 6-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-3-methyl-2-thienyl]benzothiophene-2-carboxylate in 10 mL methylene chloride was cooled to ~-78 C. 0.35 mL (0.35 mmol) DIBAL (1M in hexane) was added dropwise. After 3 h, reaction stalled at ~60% completion. 0.2

mL additional DIBAL was added. Reaction was completed in ~15 min. 5 mL ethyl acetate was slowly added, along with 200 mg of water. Batch was allowed to warm to rt overnight. Product was purified on silica gel (hexane/methylene chloride) yielding 0.257 g (0.28 mmol, 90% yield).

F. 6-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-hexyl-2-thienyl]benzothiophene-2-carbaldehyde

[0071]

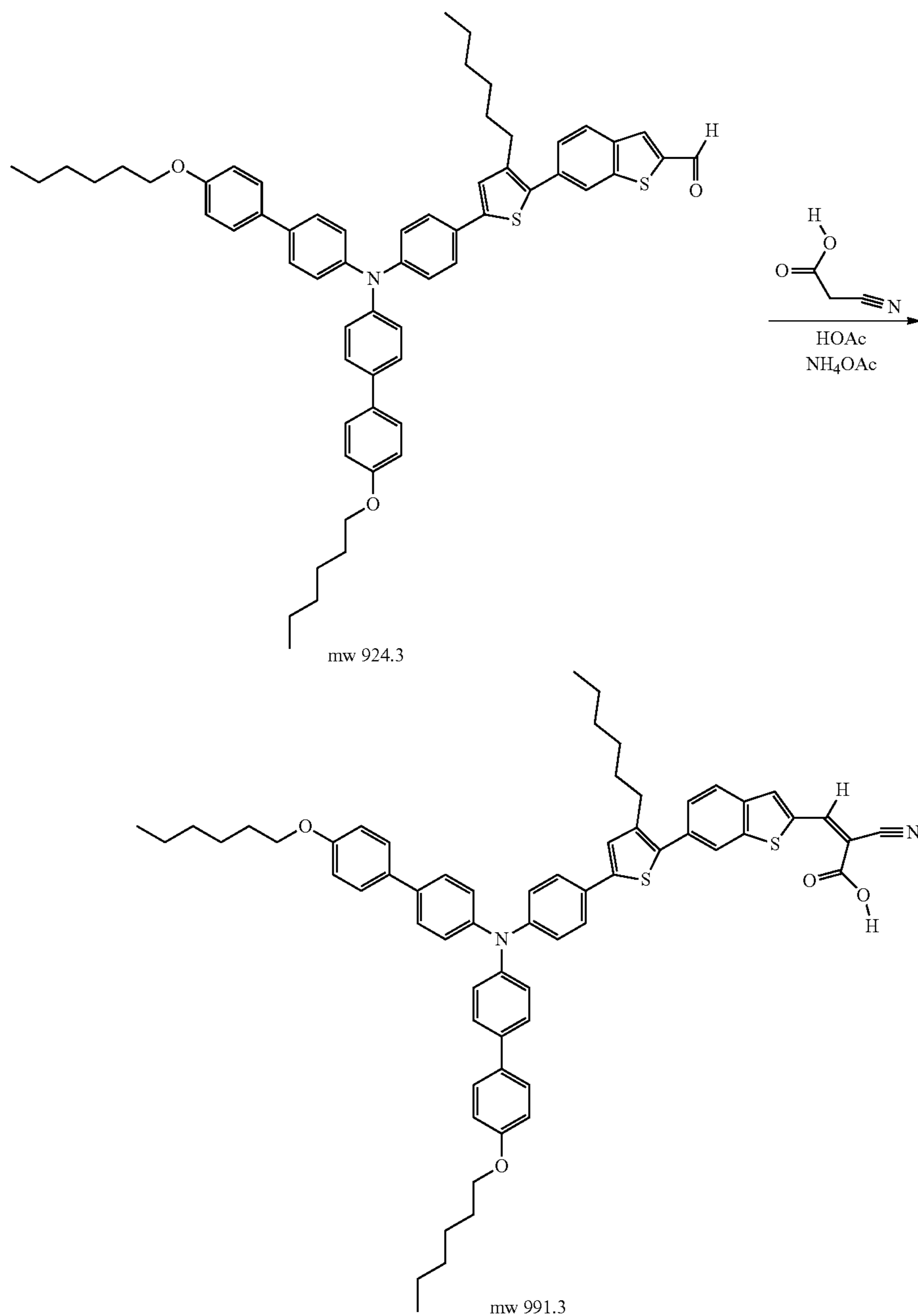


[0072] In a round bottom flask, 0.257 g (0.28 mmol) [6-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-methyl-2-thienyl]methanol was dissolved in 10 mL methylene chloride. 0.3 g (2.8 mmol) Na<sub>2</sub>CO<sub>3</sub> and 0.14 g (0.33 mmol) Dess-Martin

reagent was added. HPLC showed ~60% conversion to a new material. An additional 0.1 g was added, causing the reaction to go to completion. Product was purified on silica gel (hexane/methylene chloride), yielding 0.257 g (0.28 mmol, 100% yield).

G. (Z)-2-cyano-3-[6-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-hexyl-2-thienyl]benzothiophen-2-yl]prop-2-enoic Acid (D1)

[0073]



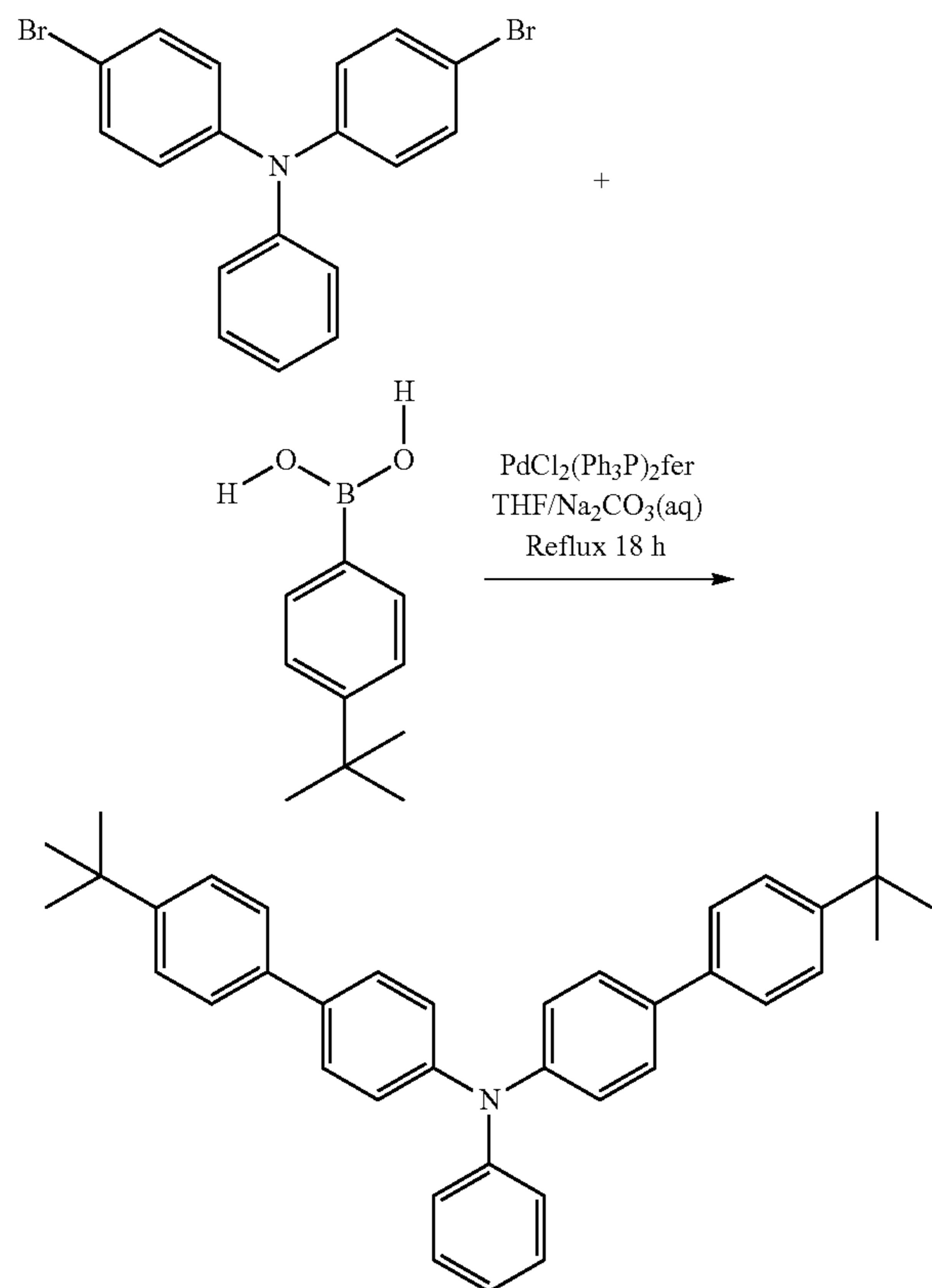
[0074] In a round bottom flask, 0.242 g (0.26 mmol) 6-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-3-hexyl-2-thienyl]benzothiophene-2-carbaldehyde, 0.067 g (0.79 mmol) cyanoacetic acid and 0.13 g (1.68 mmol) ammonium acetate was combined in 10 mL HOAc at reflux for 8 h. HPLC indicated complete reaction. Product was oiled out upon cooling. HOAc layer was removed and the product (still in rb-flask) was vacuum

dried to remove residual HOAc. Crude product was dissolved in ~6 mL methylene chloride and passed through a plug of silica gel and eluted with ~50 mL methylene chloride (product remains on the plug). The product was washed off the silica using 30% MeOH in CH<sub>2</sub>Cl<sub>2</sub>. Solvent was stripped off and product was vacuum dried yielding 0.142 g (55% yield).

Example 2. Synthesis of (Z)-3-[2-[4-[4-[4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)-phenyl]anilino]phenyl]phenyl]benzofuran-6-yl]-2-cyano-prop-2-enoic Acid (D5)

A. 4,4'-Bis(4-t-butylphenyl)triphenylamine

[0075]

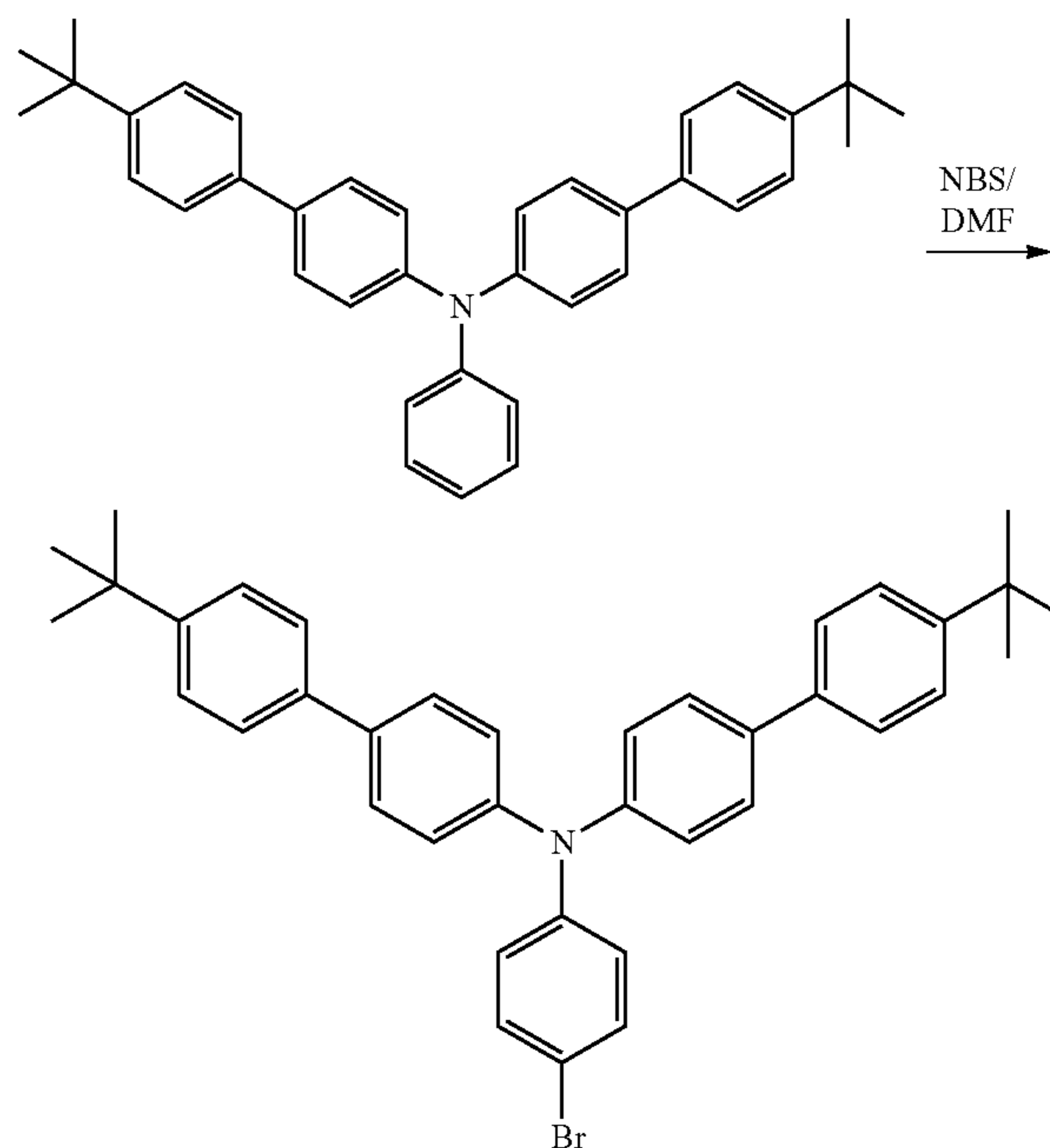


[0076] In a round bottom flask, 5.25 g (13 mmol) 4,4'-Dibromotriphenylamine, 5.8 g (32.5 mmol) 4-t-butylphenylboronic acid, 0.2 g (0.26 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 80 mL THF and 20 mL 10%  $\text{Na}_2\text{CO}_3$ . Batch was held at reflux for 18 h (LC showed complete reaction). Reaction mixture

was poured into 300 mL water and extracted product into methylene chloride. The organic layer was dried, then passed through a bed of silica gel. The solvent was stripped off and replaced with methanol resulting in a white solid (5.4 g, 81% yield).

B. N-(4-bromophenyl)-4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)-phenyl]aniline

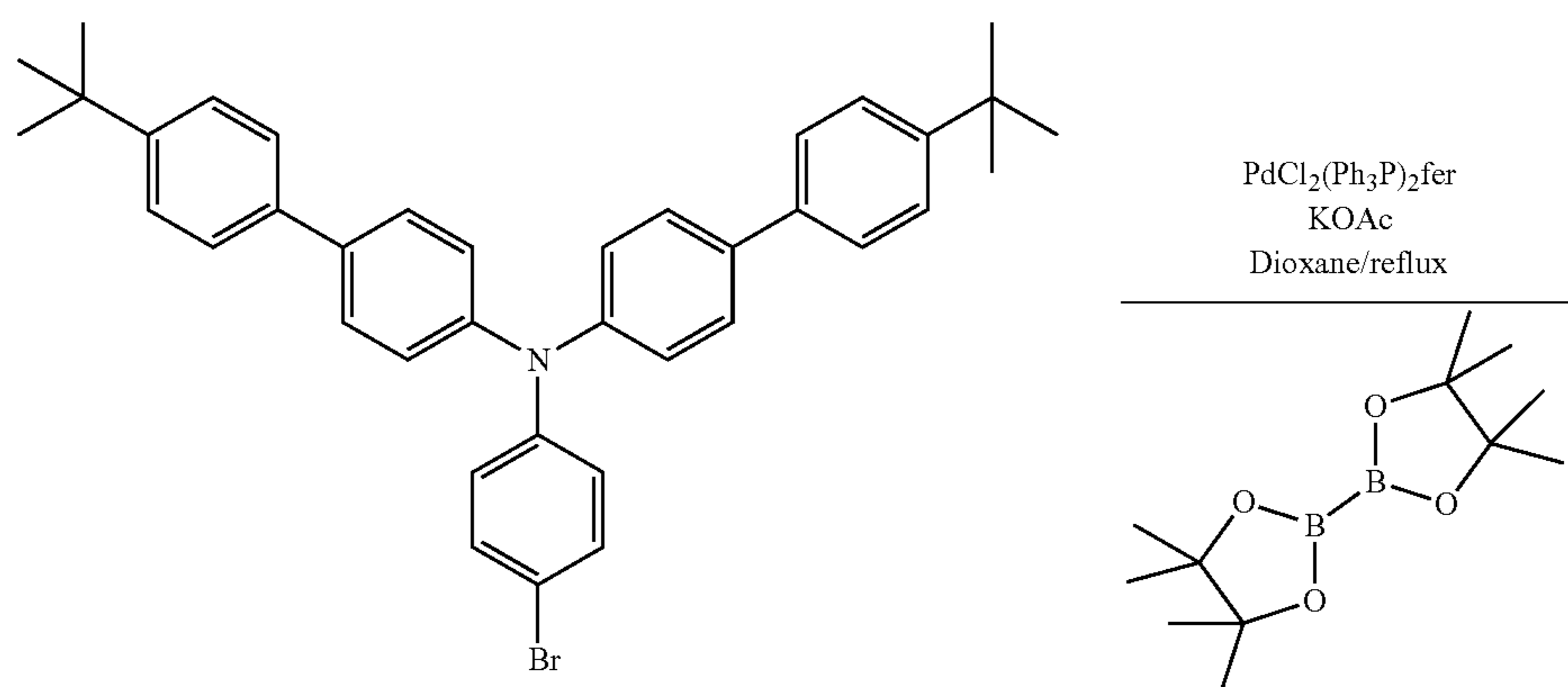
[0077]



[0078] In a round bottom flask, 5.4 g (10.6 mmol) 4,4'-Bis(4-t-butylphenyl)triphenylamine in 50 mL DMF at 5° C. was added. 2.27 g (12.7 mmol) NBS was added in 3 portions, resulting in a green solution. Batch was held at rt for 1 h (complete by LC) then precipitated into 300 mL water. Solid was filtered off slowly, washed with water, and dried, yielding 5.7 g white solid (9.7 mmol, 92% yield). UV/Vis max 330 nm, LCMS  $m/z=590.2$

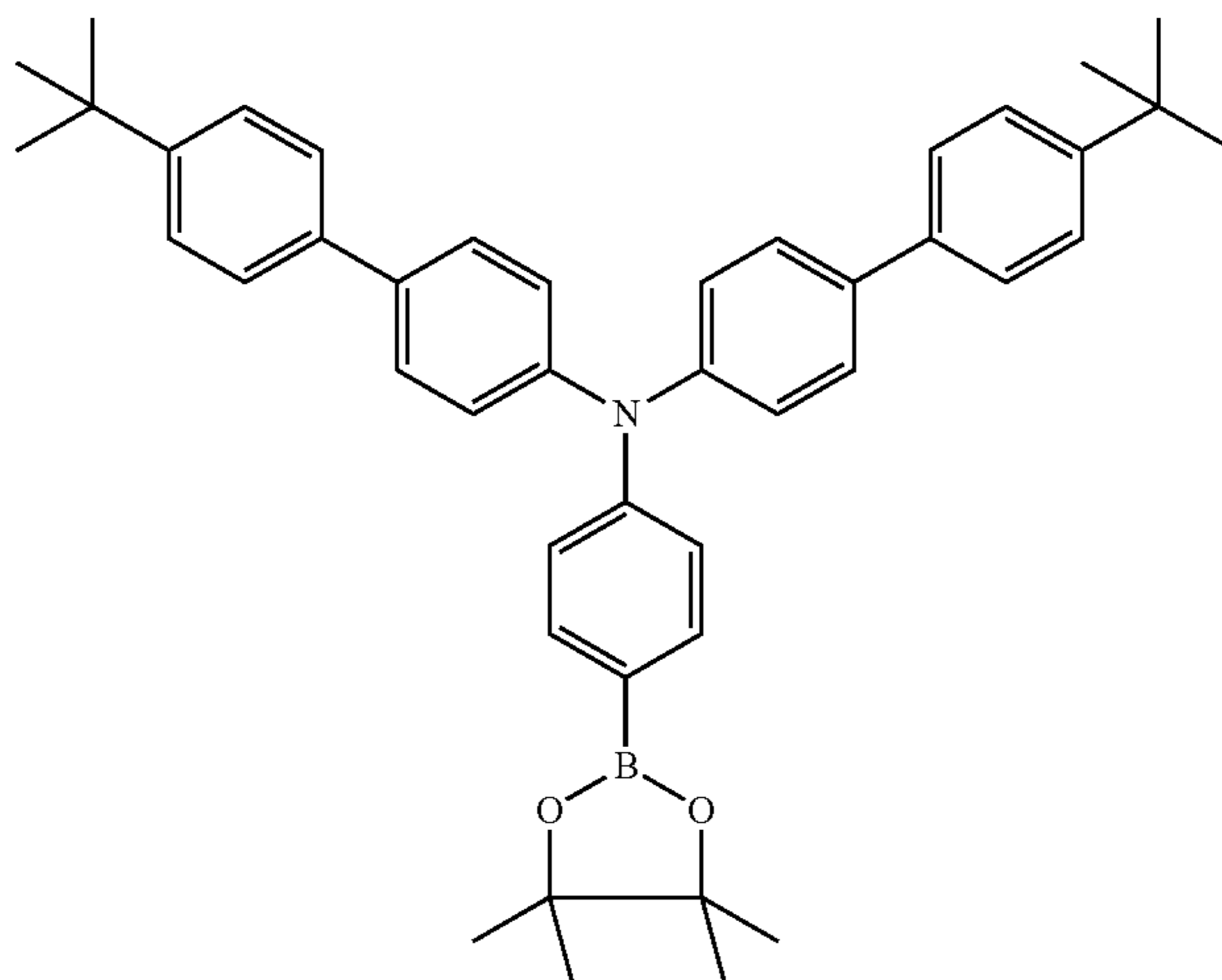
C. N,N-bis[4-(4-tert-butylphenyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline

[0079]





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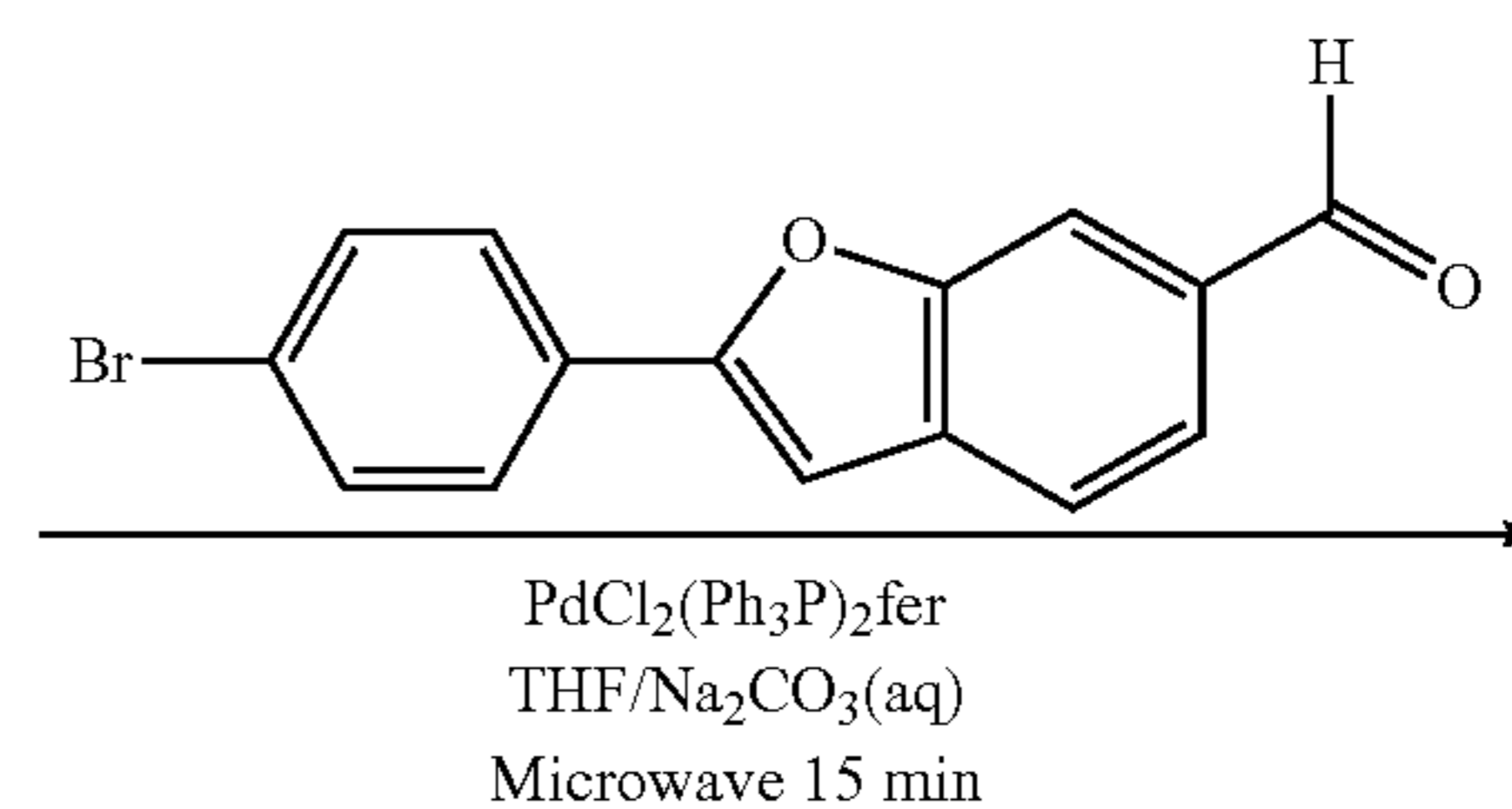
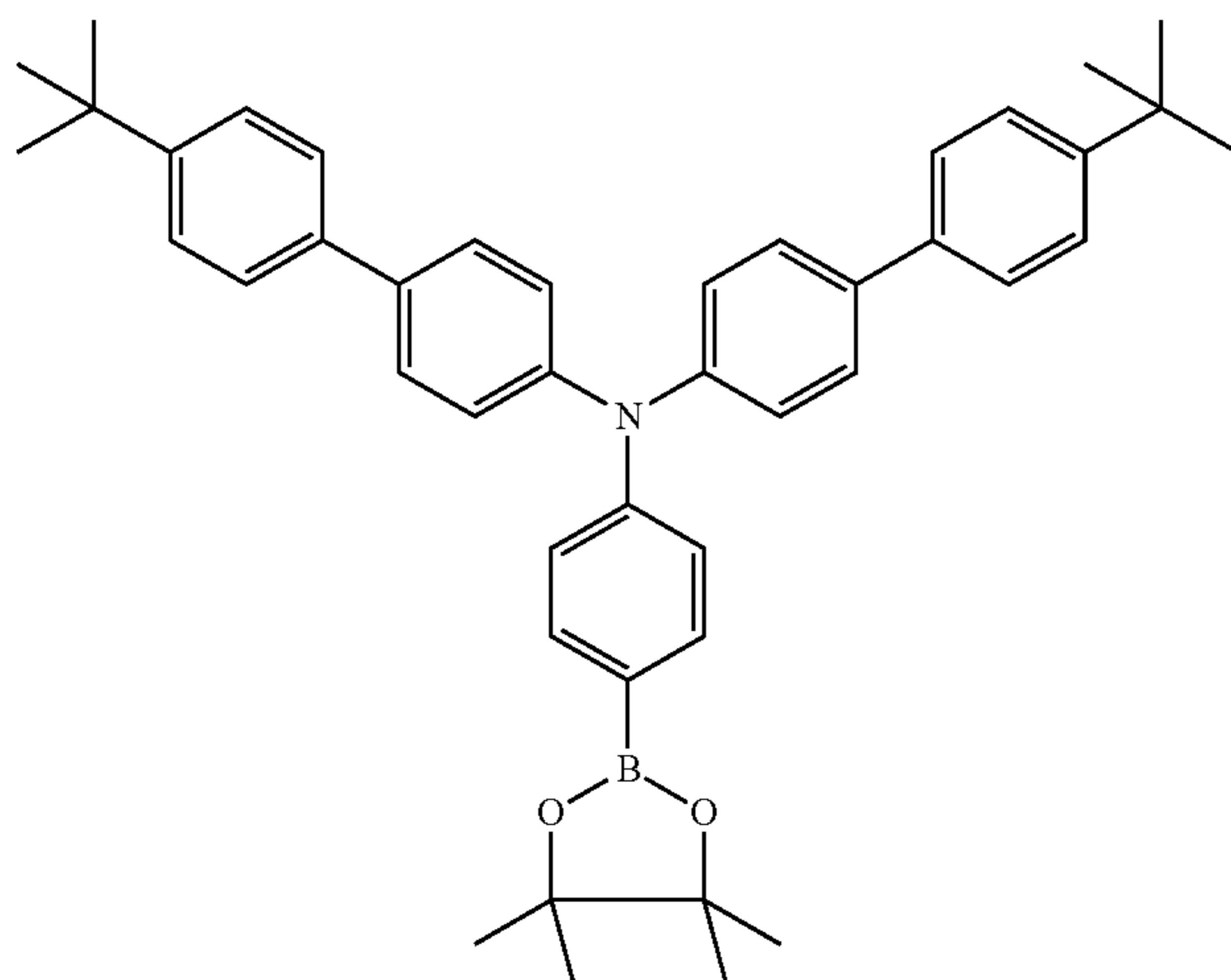


[0080] In a round bottom flask, 3 g (5.1 mmol) N-(4-bromophenyl)-4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]aniline, 0.2 g (0.26 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II), 1.5 g (5.5 mmol) bis(pinacolato)diborane and 1.6 g KOAc was combined in 30 mL 1,4-dioxane. Batch was held at reflux for 2 h. HPLC indicated a complete reaction. Batch was cooled to rt then poured into 200 mL water. Solid was filtered off, washed with water, then washed with acetonitrile and vacuum dried at 60° C. (3.5 g). Solid dissolved in methylene chloride and

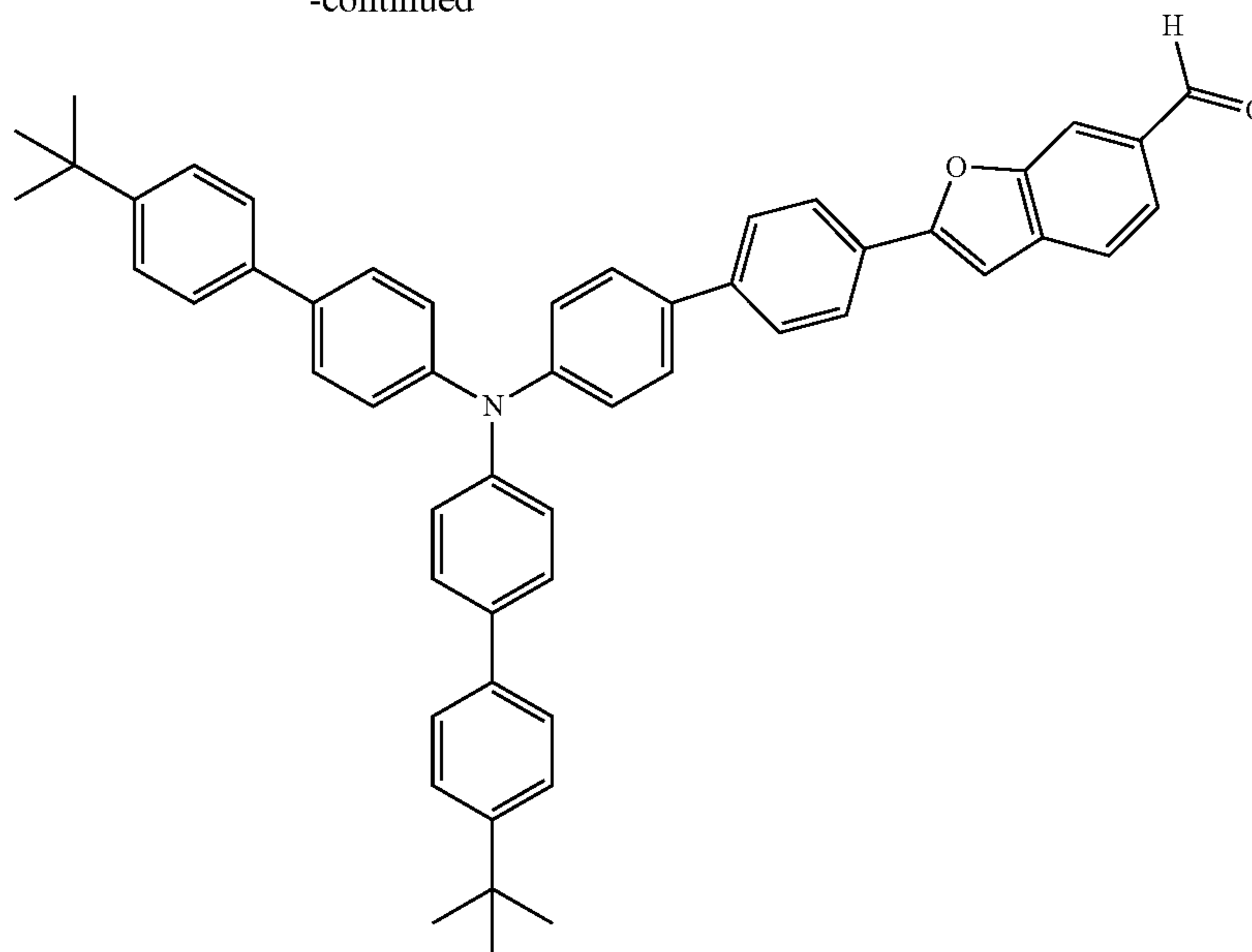
passed through a silica gel plug and washed through with methylene chloride to remove origin material. Solvent stripped off and replaced with ethanol. Solid filtered off and washed with ethanol yielding 2.3 g (3.6 mmol, 71% yield). UV/Vis max 335 nm, LCMS m/z=636.4.

D. 2-[4-[4-[4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)-phenyl]anilino]phenyl]phenyl]benzofuran-6-carbaldehyde

[0081]



-continued

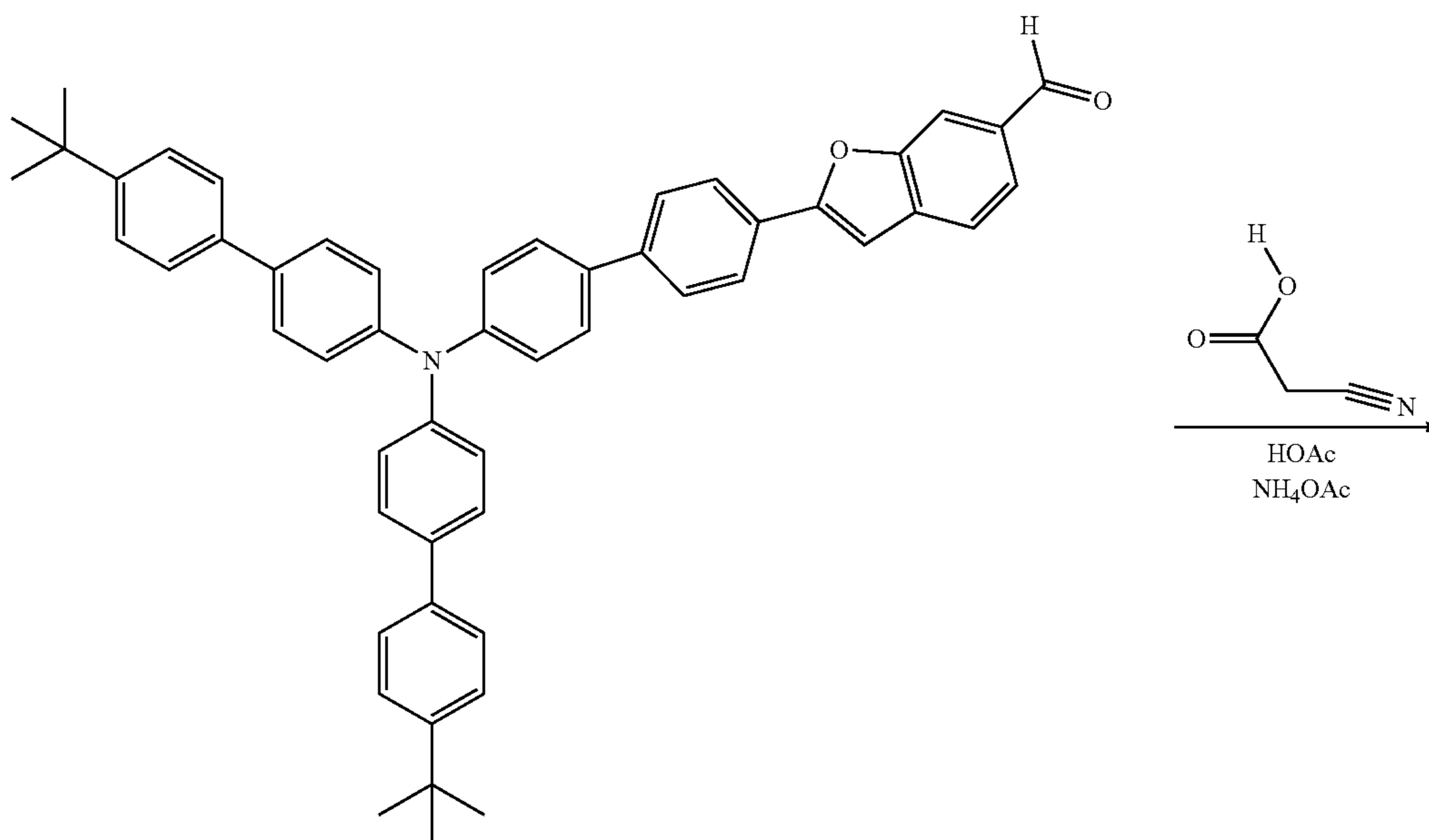


[0082] In a round bottom flask, 634 mg (1.0 mmol) N,N-bis[4-(4-tert-butylphenyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 320 mg (1.06 mmol) 2-(4-bromophenyl)benzofuran-6-carbaldehyde and 60 mg (0.08 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 8 mL THF and 3 mL 10% Na<sub>2</sub>CO<sub>3</sub>. Batch was microwaved at 100° C. for 15 min. Batch was poured into 100 mL water and product was extracted into methylene chloride. The organic layer was

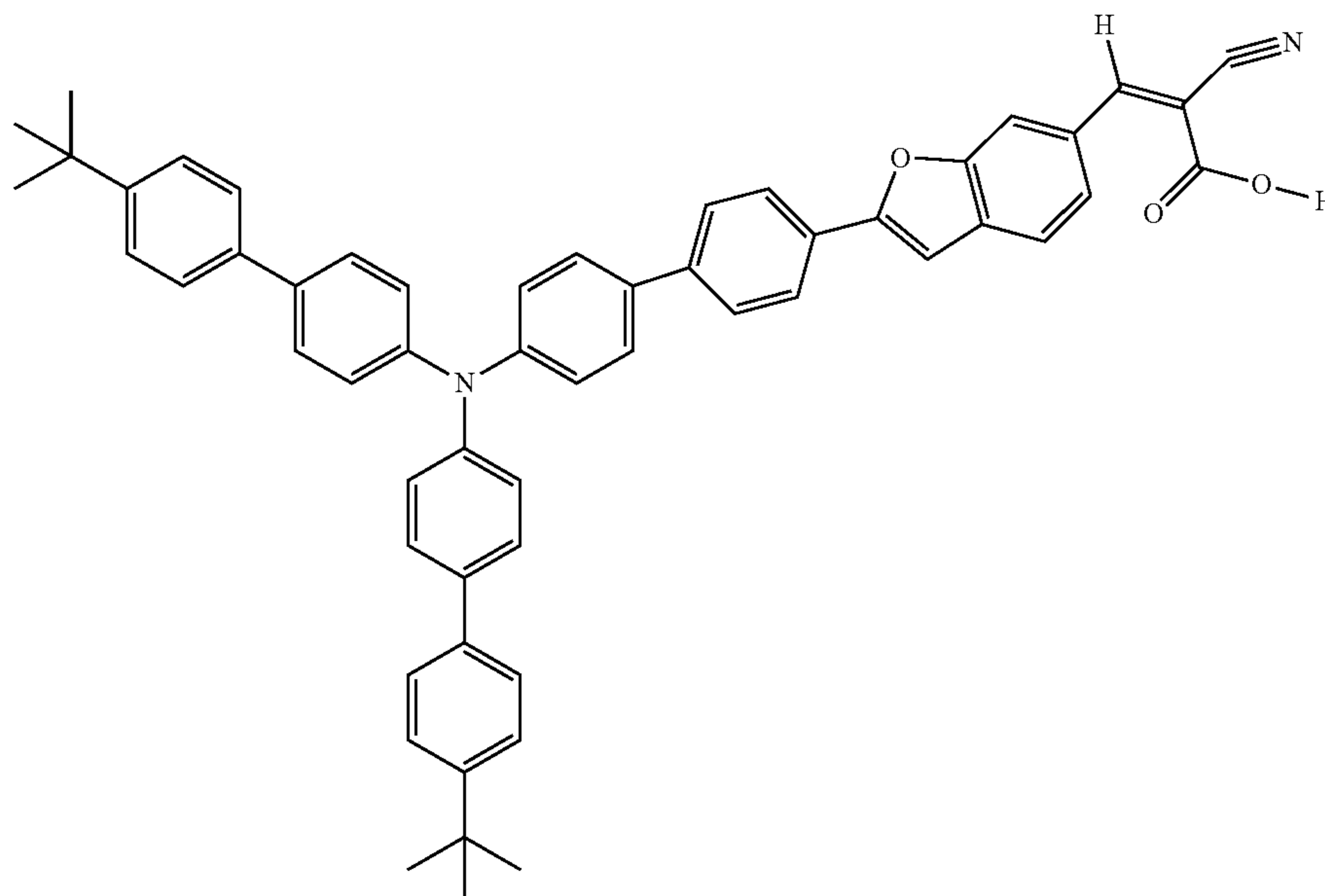
dried, then passed through a silica gel plug. Product was washed through with methylene chloride. Solvent was stripped off and product crystallized from ethanol. 338 mg (0.46 mmol, 46% yield). UV/Vis max 340 nm & 390 nm, LCMS m/z=730.4.

E. (Z)-3-[2-[4-[4-[4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)-phenyl]anilino]phenyl]phenyl]benzofuran-6-yl]-2-cyano-prop-2-enoic Acid

[0083]



-continued

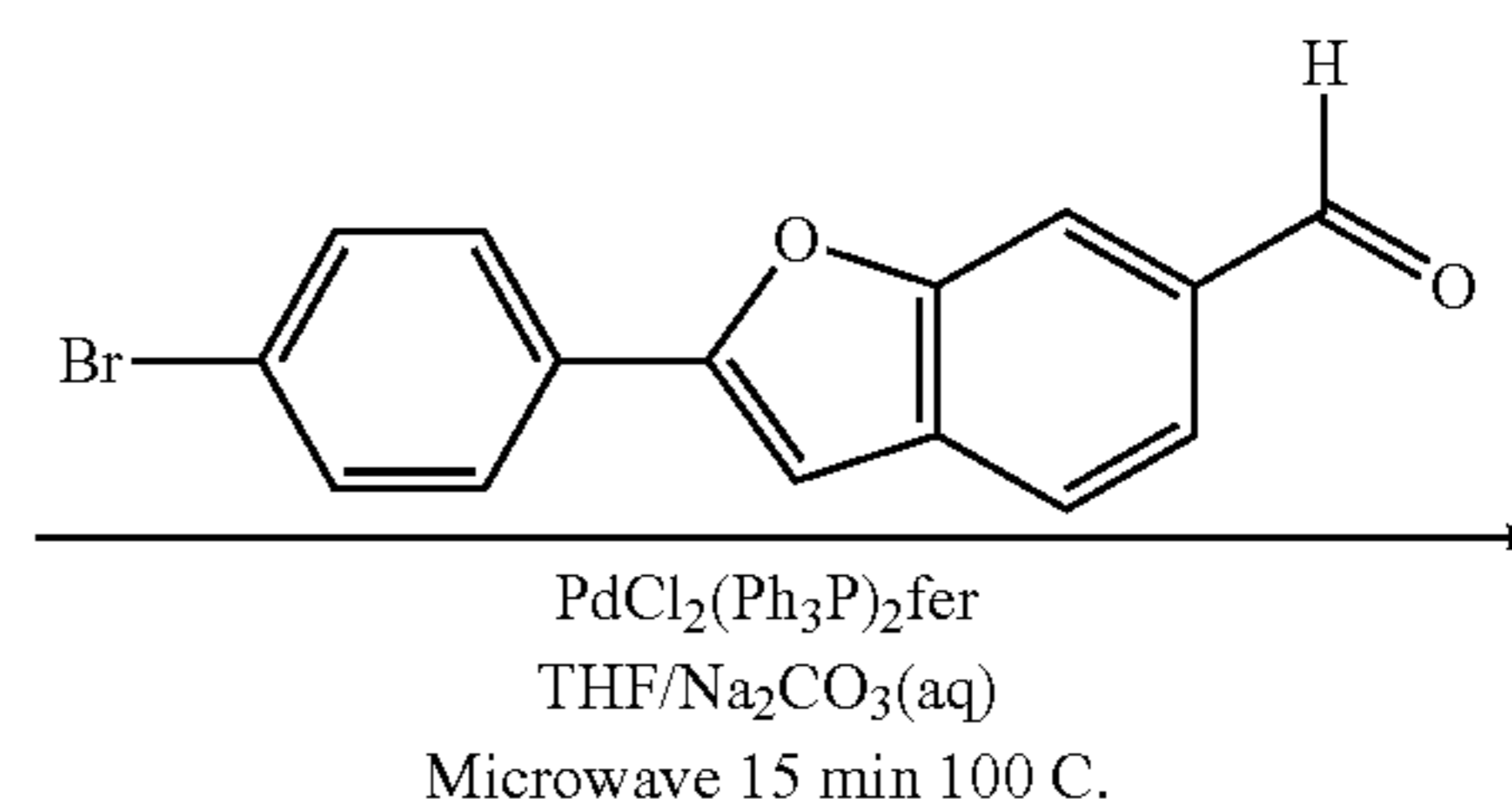
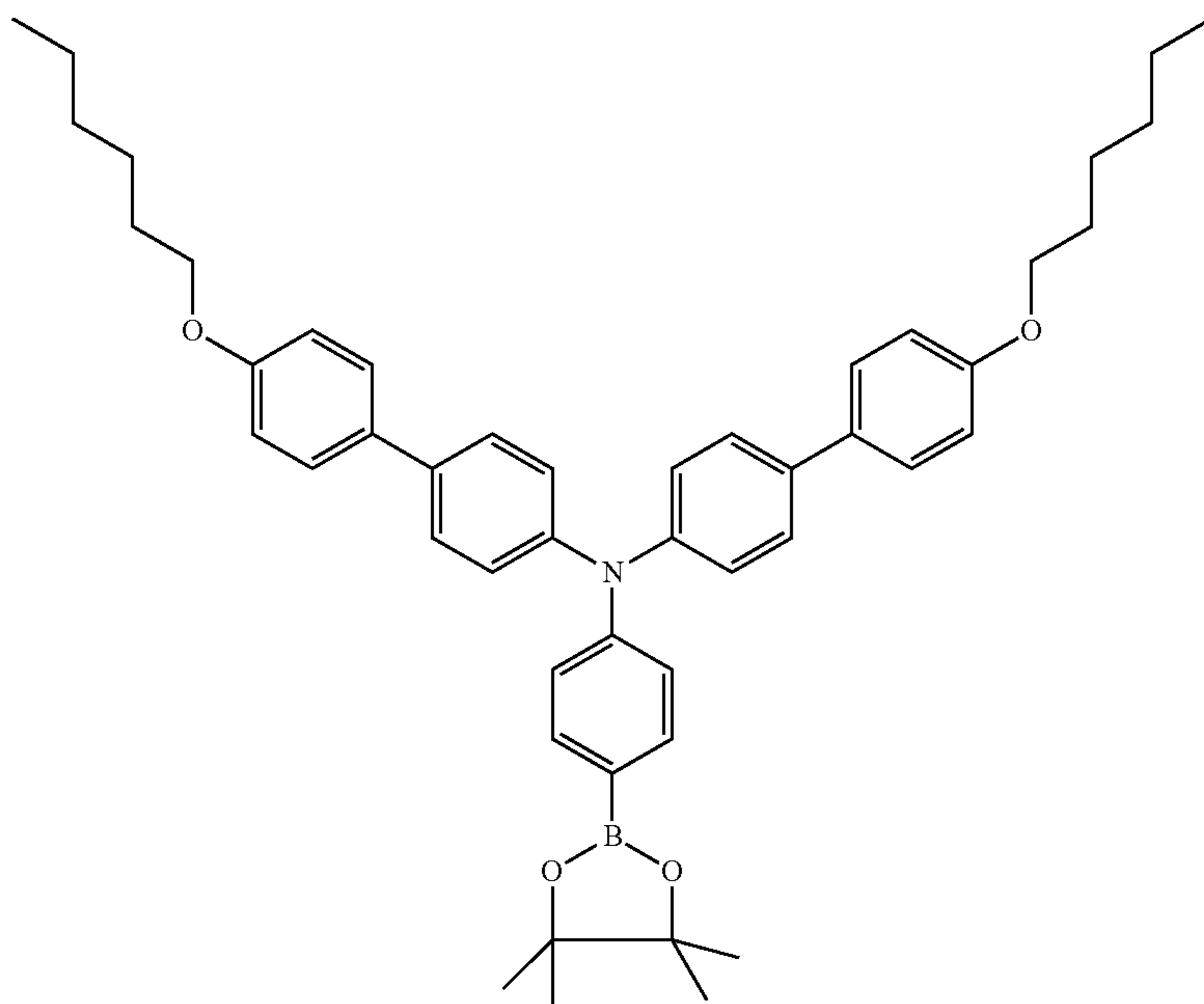


**[0084]** In a round bottom flask, 330 mg (0.45 mmol) 2-[4-[4-[4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]anilino]phenyl]phenyl]benzofuran-6-carbaldehyde, 200 mg (1.85 mmol) cyanoacetic acid and 450 mg (3.6 mmol) ammonium acetate was combined in 12 mL acetic acid and held at reflux for 3 h. Batch was cooled and combined with 50 mL water. Product was filtered off and washed with water (3x5 mL) yielding 300 mg orange solid (83% yield, 92 Area % @ 350 nm, 3% unreacted aldehyde and 5% unknown). UV/Vis max 340 nm & 420 nm, LCMS  $m/z=797.2$ .

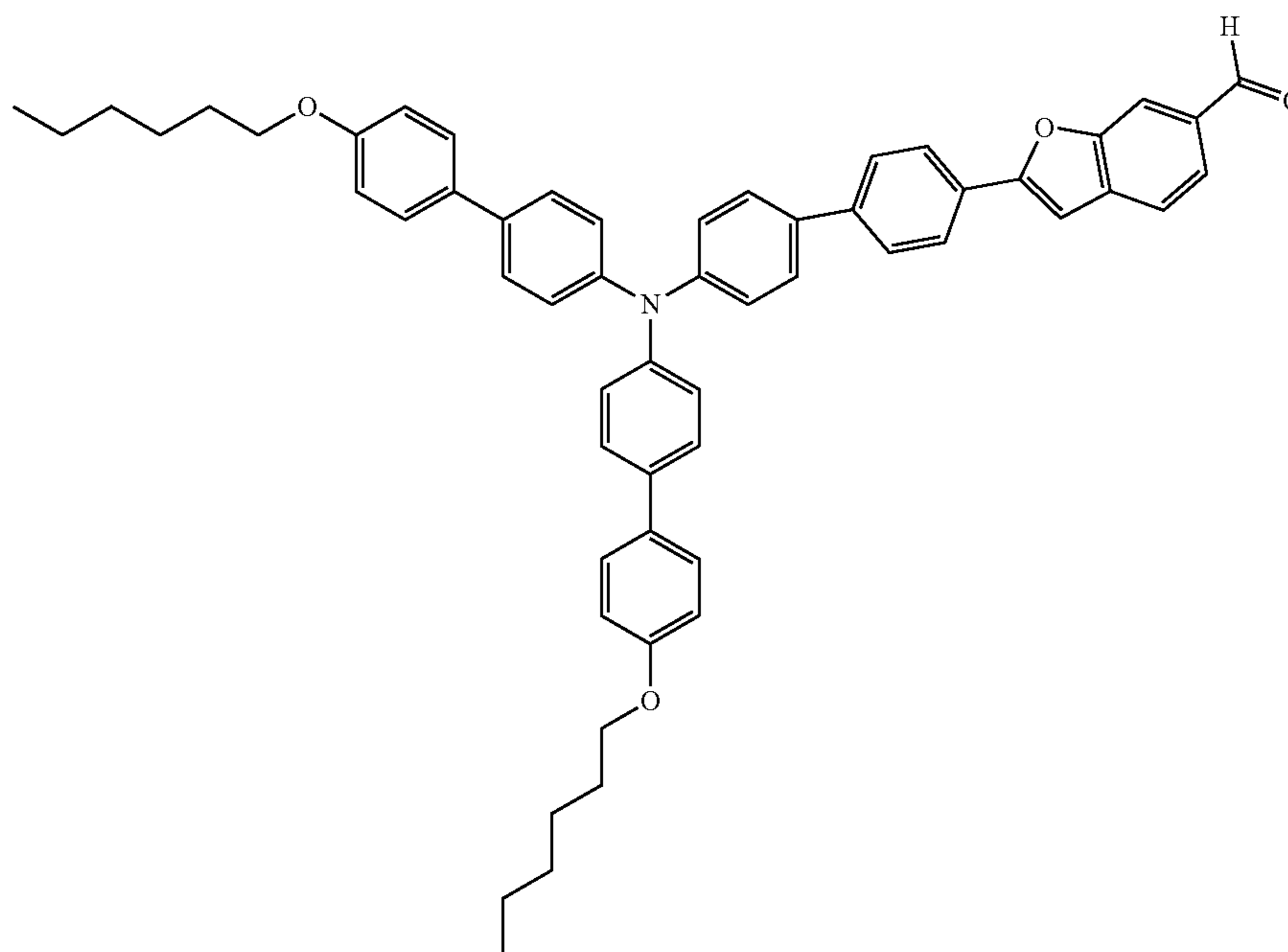
Example 3. Synthesis of (Z)-2-cyano-3-[2-[4-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]phenyl]benzofuran-6-yl]prop-2-enoic Acid (D3)

A. 2-[4-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]phenyl]benzofuran-6-carbaldehyde

**[0085]**



-continued

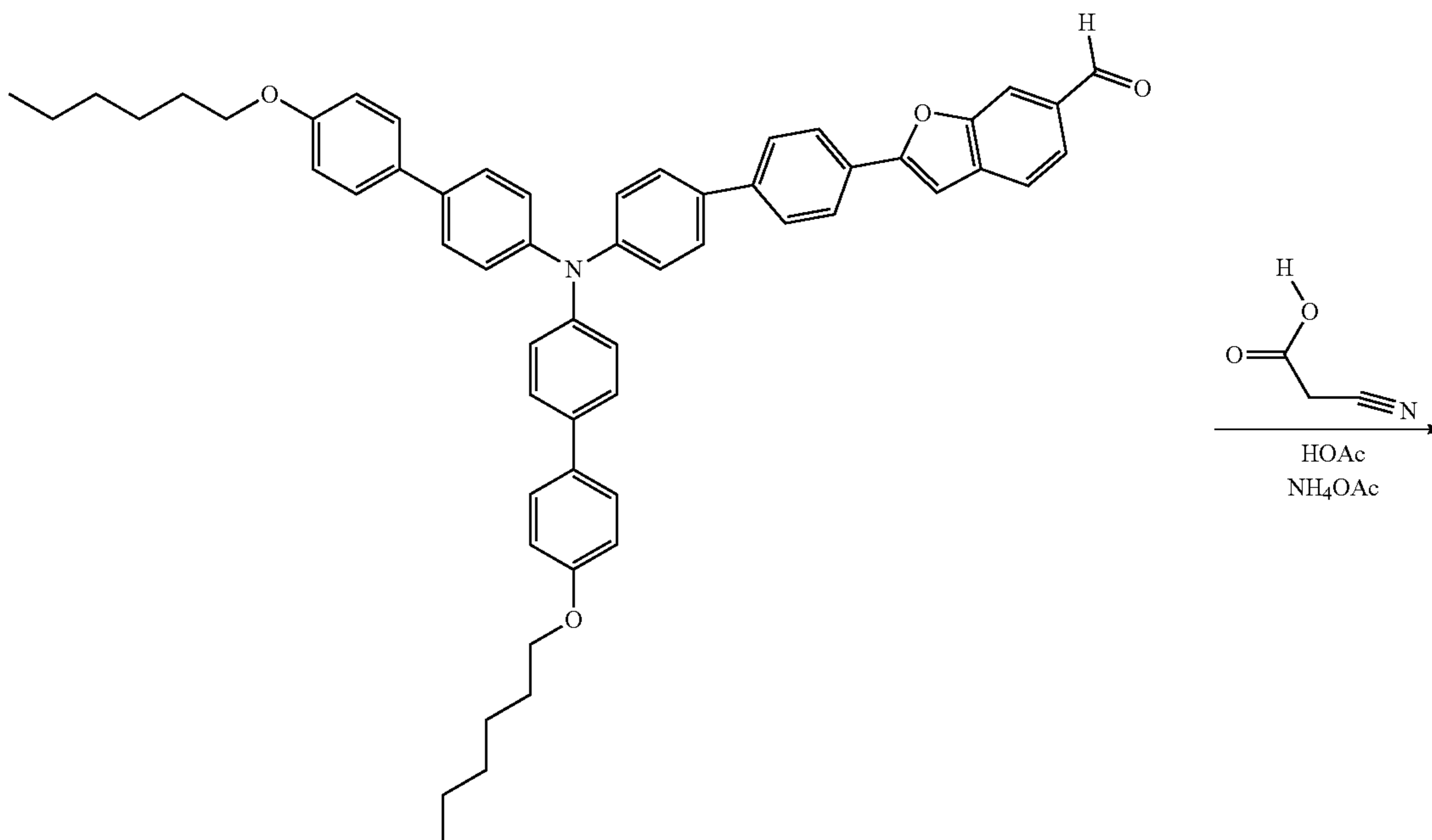


**[0086]** In a round bottom flask, 900 mg (1.24 mmol) N,N-bis[4-(4-hexoxyphenyl)phenyl]-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)aniline (see Example 1.C), 411 mg (1.38 mmol) 2-(4-bromophenyl)benzofuran-6-carbaldehyde, 100 mg dichloro 1,1'-bis(diphenylphosphino)-ferrocene palladium(II) was combined in 12 mL THF and 3 mL 10% Na<sub>2</sub>CO<sub>3</sub>. Batch was microwaved at 100° C. for 20 min. Mixture was poured into water and product extracted into methylene chloride. Product was purified on silica gel

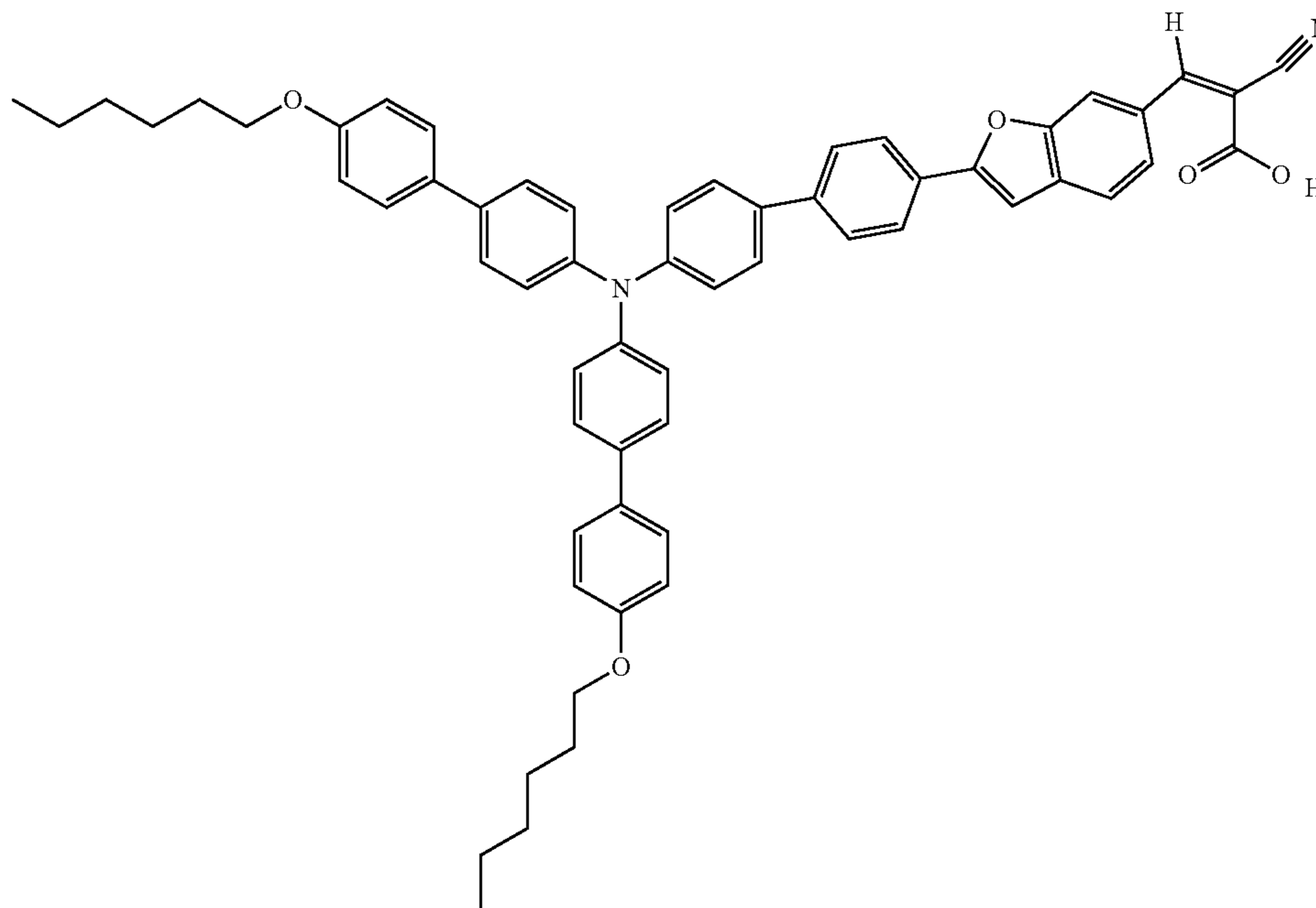
(hexane/methylene chloride 0% to 70%), yielding 468 mg (0.572 mmol, 46% yield). LCMS m/z=818.4.

B. (Z)-2-cyano-3-[2-[4-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]phenyl]benzofuran-6-yl]prop-2-enoic Acid

**[0087]**



-continued

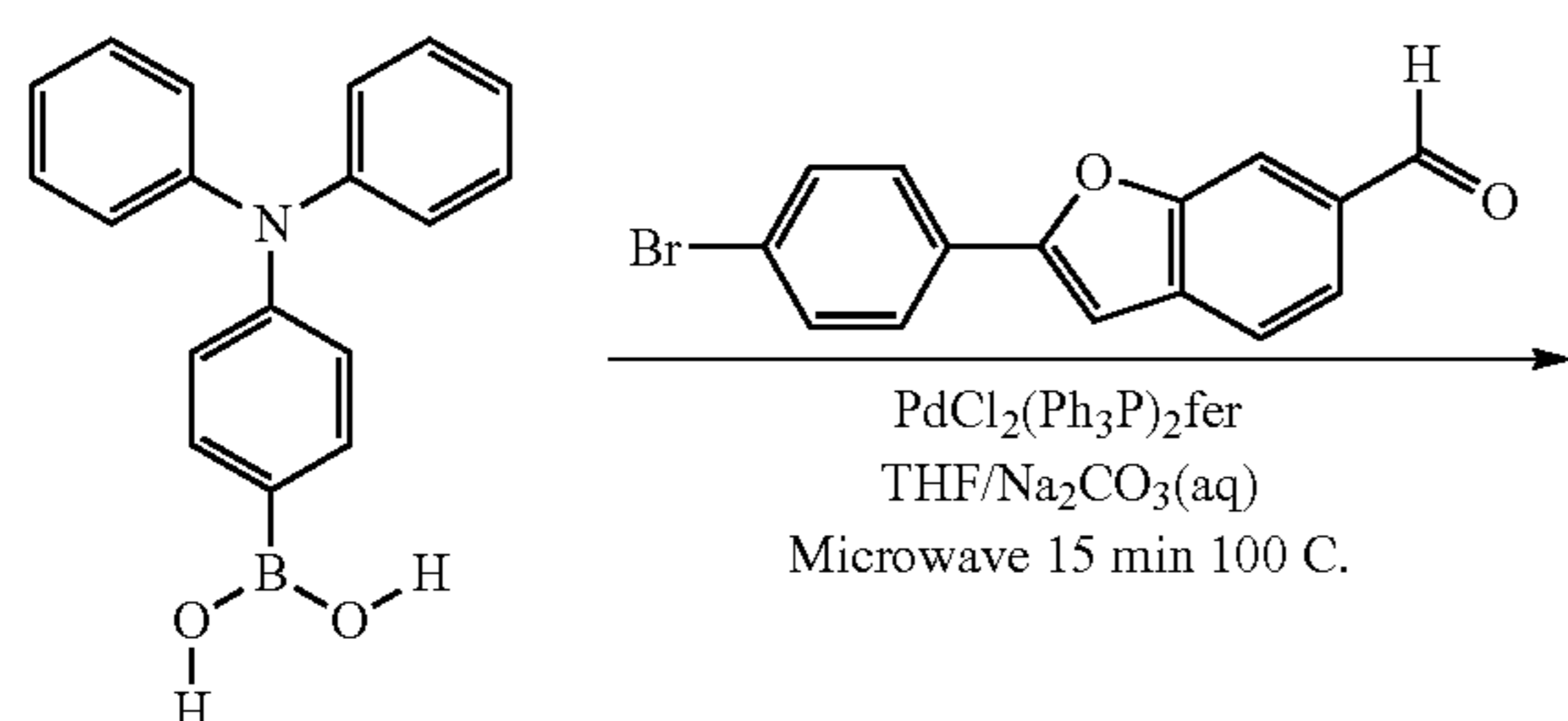


**[0088]** In a round bottom flask, 460 mg (0.56 mmol) 2-[4-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]phenyl]benzofuran-6-carbaldehyde, 239 mg (2.8 mmol) cyanoacetic acid and 433 mg ammonium acetate (5.6 mmol) was combined in 12 mL acetic acid and held at reflux for 3 h. Batch was cooled and the product was filtered off, washed with 1 mL HOAc, then washed with water (3x5 mL) and dried, yielding 495 mg orange solid (100% yield). UV/Vis max 340 nm & 420 nm, LCMS  $m/z=885.8$ .

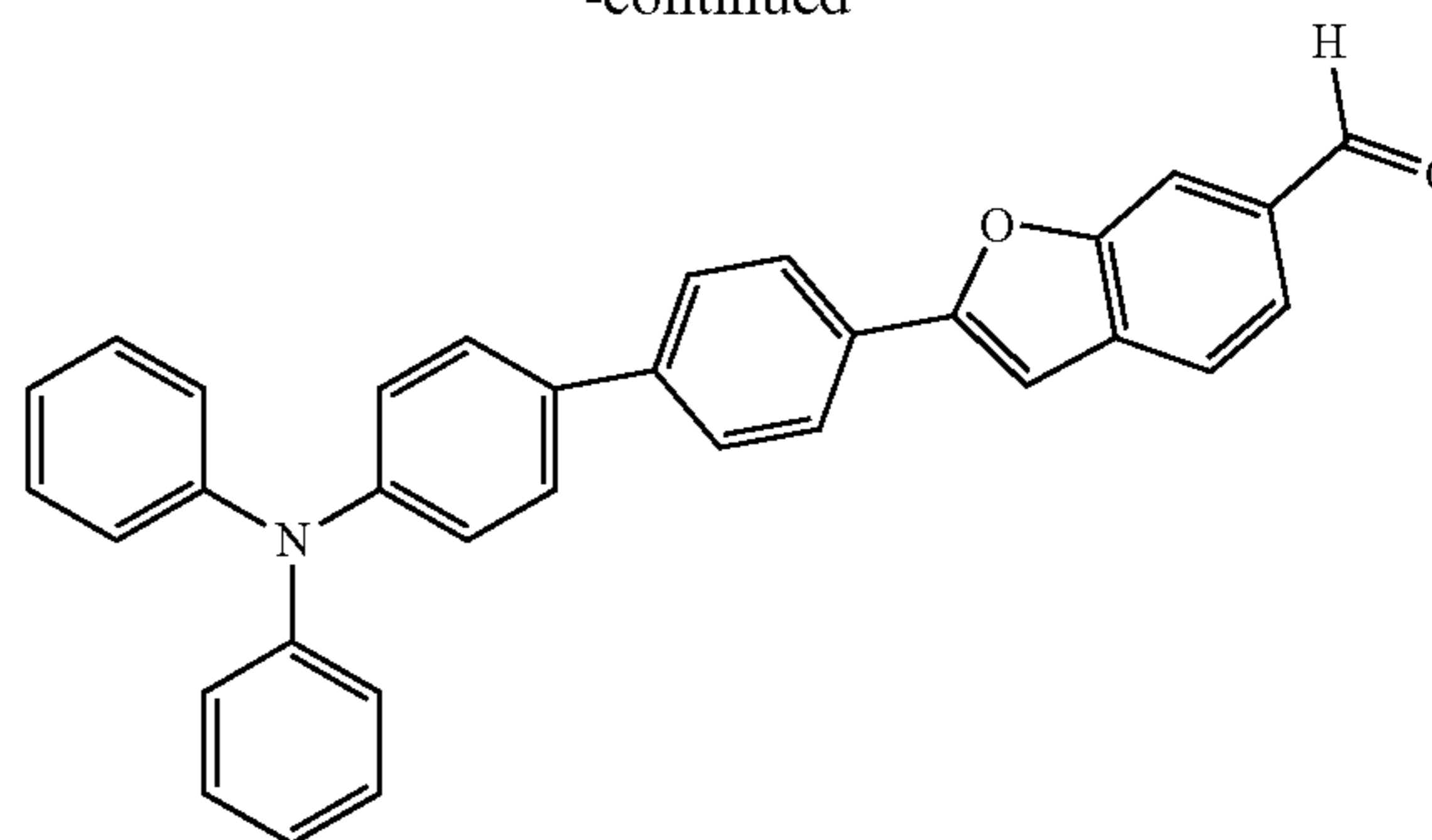
Example 4. Synthesis of (Z)-2-cyano-3-[2-[4-[4-(N-phenylanilino)phenyl]phenyl]benzofuran-6-yl]prop-2-enoic Acid (D4)

A. 2-[4-[4-(N-phenylanilino)phenyl]phenyl]benzofuran-6-carbaldehyde

**[0089]**

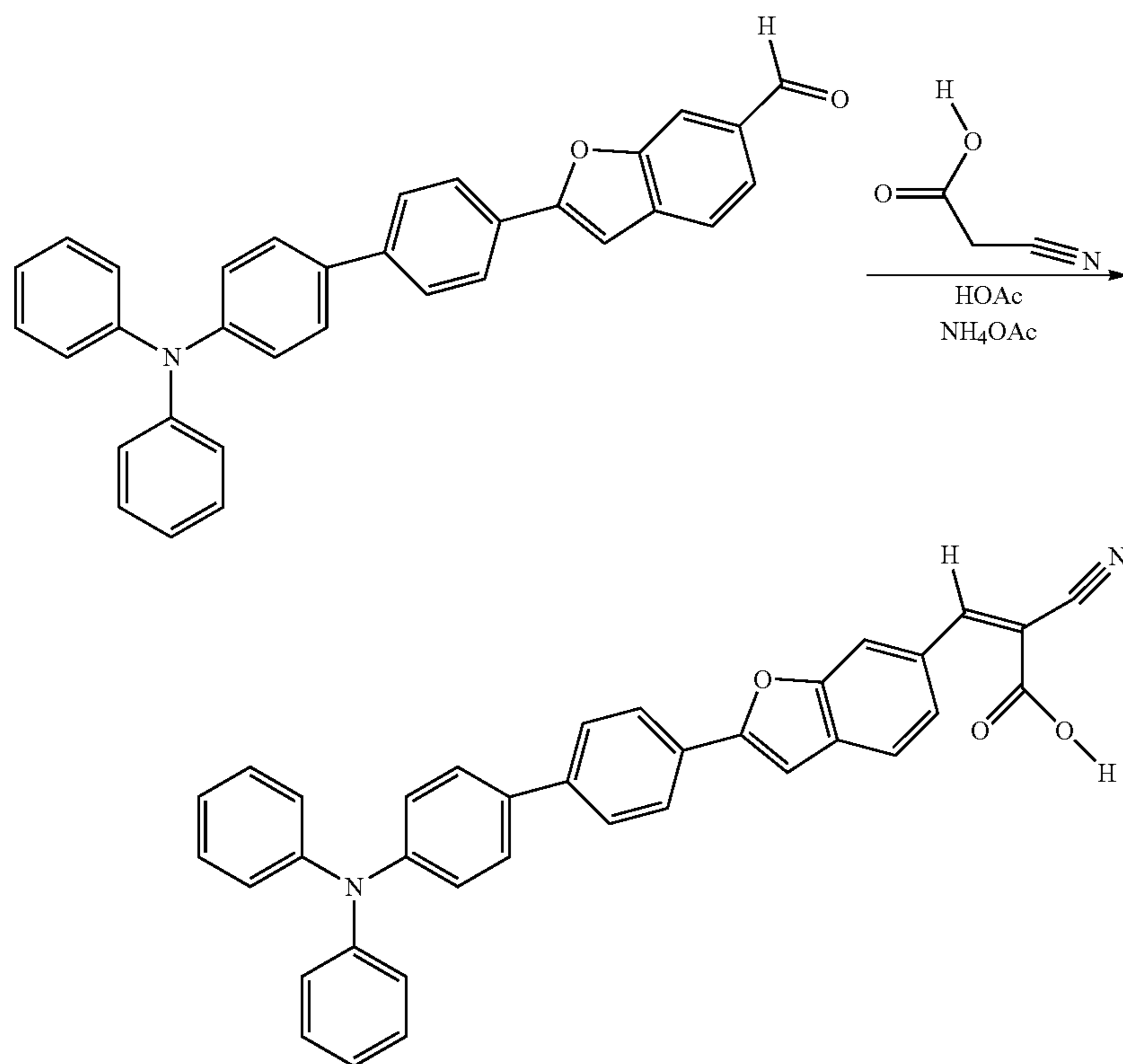


-continued



**[0090]** In a round bottom flask, 0.125 g (0.43 mmol) 4-triphenylamine boronic acid, 0.135 g (0.45 mmol) 2-(4-bromophenyl)benzofuran-6-carbaldehyde, and 0.2 g (0.26 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 4 mL THF and 1.5 mL 10%  $\text{Na}_2\text{CO}_3$ . Batch was microwaved at 100° C. for 15 min. Product was purified on silica gel (hexane/ $\text{CH}_2\text{Cl}_2$ ). Three fractions were collected. 1 (77 mg), 2 (50 mg) and 3 (26 mg). Fraction 1 was 100 area %, Fractions 2 & 3 were approximately 95 area %. UV/Vis max 380 nm, LCMS  $m/z=466.2$ .

B. (Z)-2-cyano-3-[2-[4-[4-(N-phenylanilino)phenyl]phenyl]benzofuran-6-yl]prop-2-enoic Acid  
[0091]

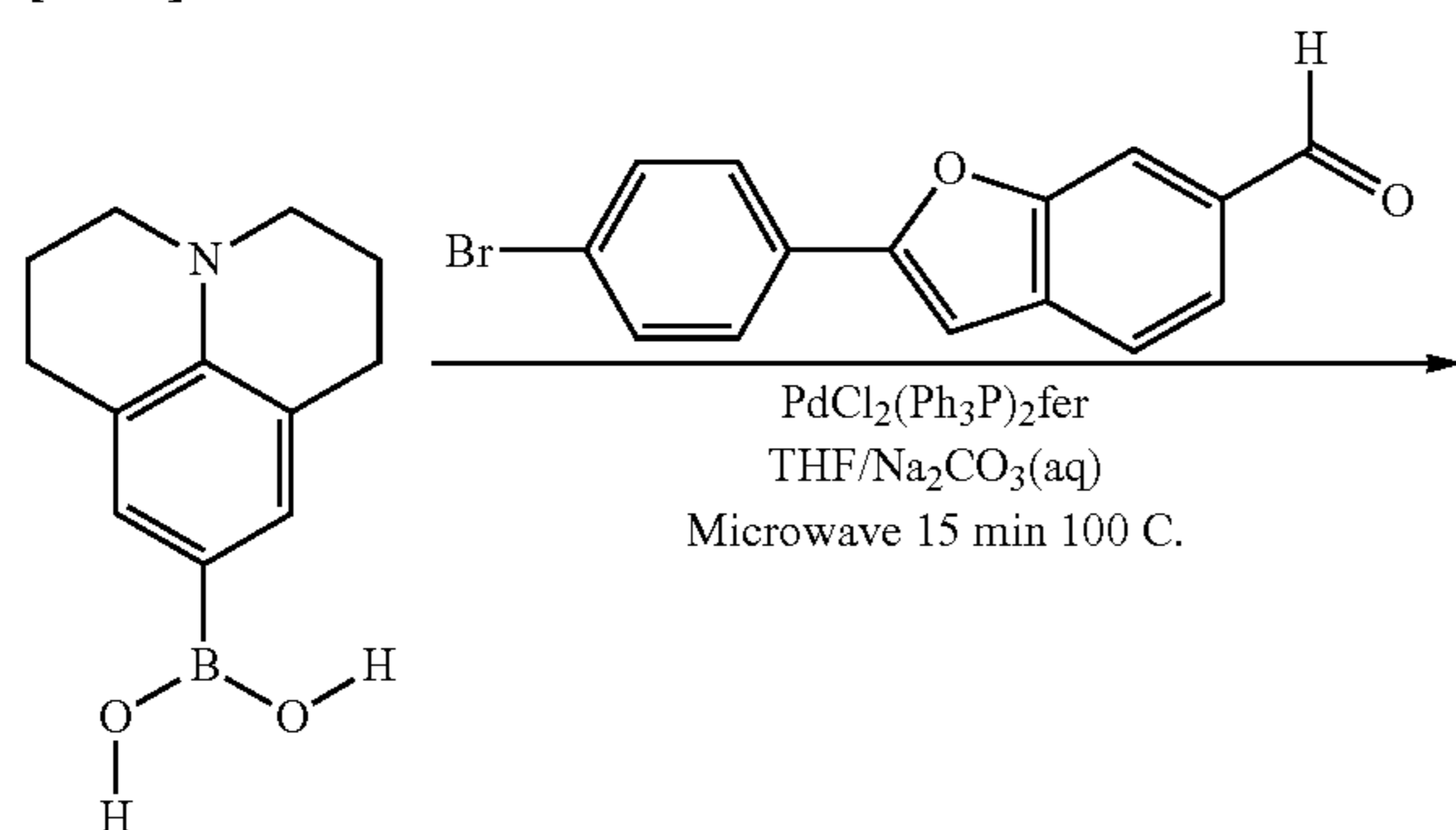


[0092] In a round bottom flask, 77 mg (0.163 mmol) 2-[4-[4-(N-phenylanilino)phenyl]phenyl]benzofuran-6-carbaldehyde, 54 mg (0.6 mmol) cyanoacetic acid, and 130 mg ammonium acetate was combined in 5 mL acetic acid and refluxed for 4 h. LCMS showed complete conversion to desired product. Product was filtered off, washed with water and dried yielding 85 mg (0.159 mmol, 97% yield). UV/Vis max 415 nm, LCMS  $m/z=533.2$ .

Example 5. Synthesis of (Z)-3-[2-[4-(1-azatricyclo[7.3.1.0<sup>5,13</sup>]trideca-5(13),6,8-trien-7-yl)phenyl]benzofuran-6-yl]-2-cyano-prop-2-enoic Acid (D6)

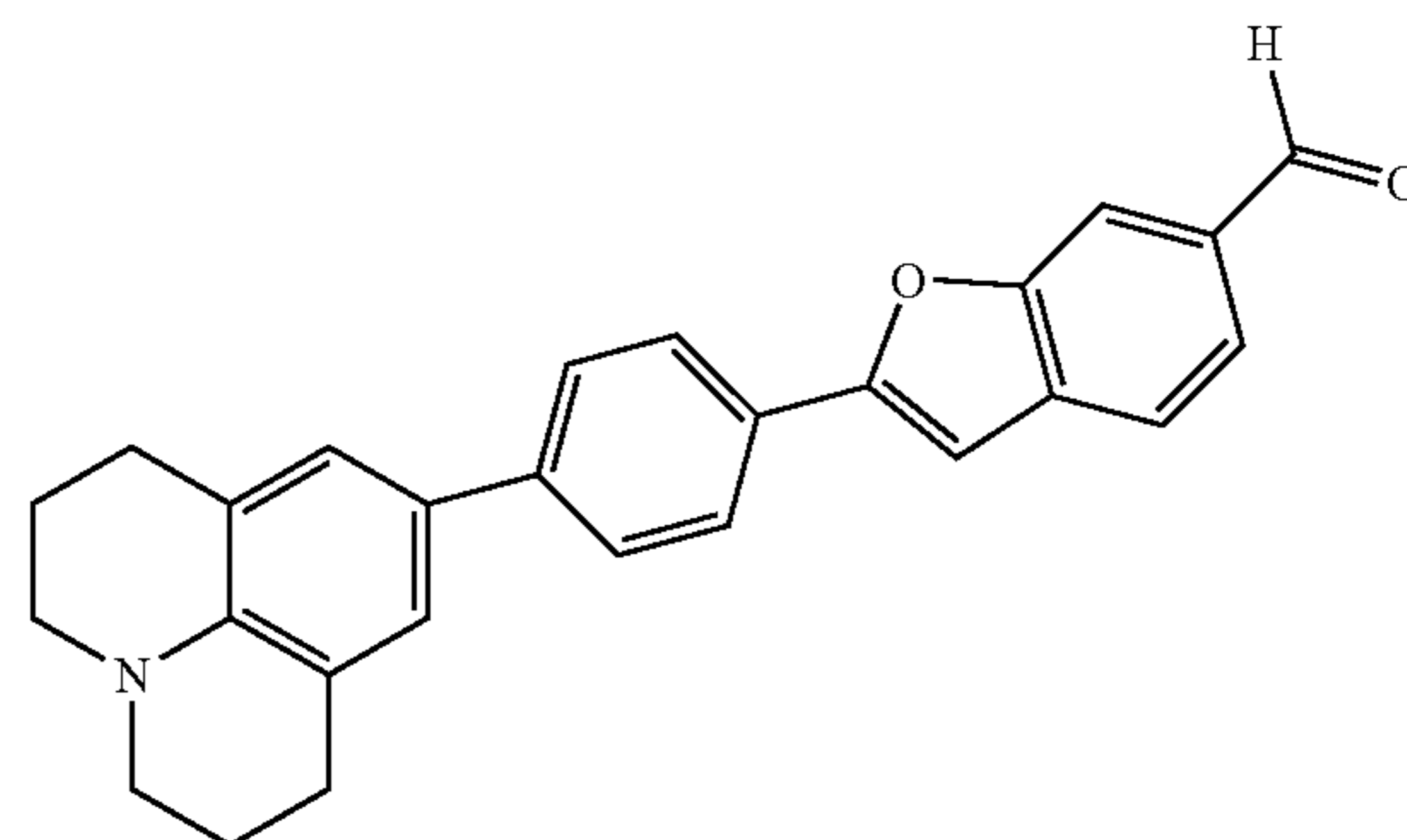
A. 2-[4-(1-azatricyclo[7.3.1.0<sup>5,13</sup>]trideca-5,7,9(13)-trien-7-yl)phenyl]benzofuran-6-carbaldehyde

[0093]



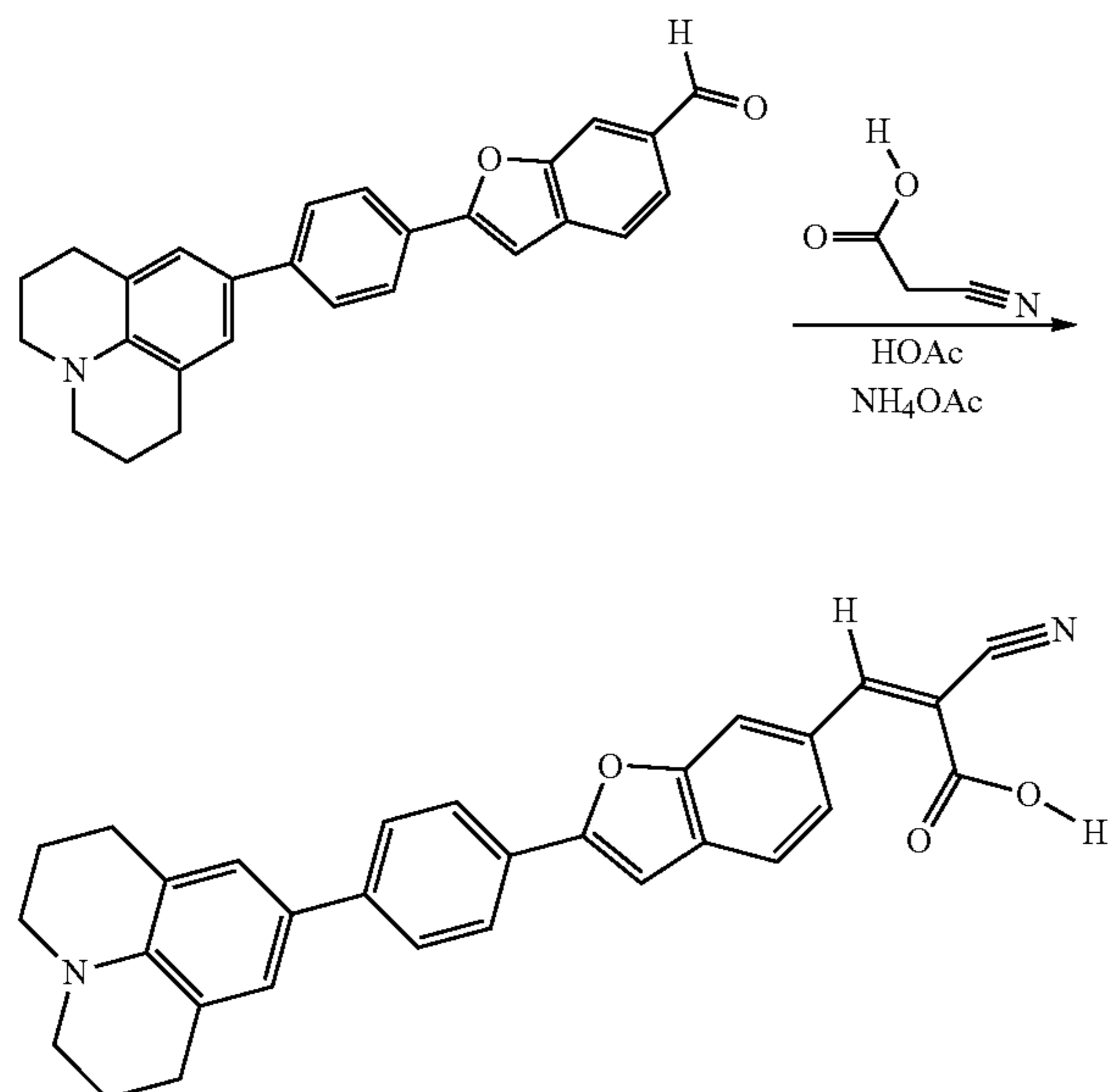
[0094] In a round bottom flask, 0.217 g (1 mmol) julolidine boronic acid, 0.33 g (1.1 mmol) 2-(4-bromophenyl)benzofuran-6-carbaldehyde and 30 mg (0.04 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 4 mL THF and 1.5 mL 10%  $\text{Na}_2\text{CO}_3$ . Batch was microwaved at 100° C. for 15 min, then purified on silica gel ( $\text{CH}_2\text{Cl}_2$ /hexane), yielding 124 mg (31% yield). UV/Vis max 400 nm, LCMS  $m/z=394.0$ .

-continued



B. (Z)-3-[2-[4-(1-azatricyclo[7.3.1.0<sup>5,13</sup>]trideca-5(13),6,8-trien-7-yl)phenyl]benzofuran-6-yl]-2-cyano-prop-2-enoic Acid

[0095]

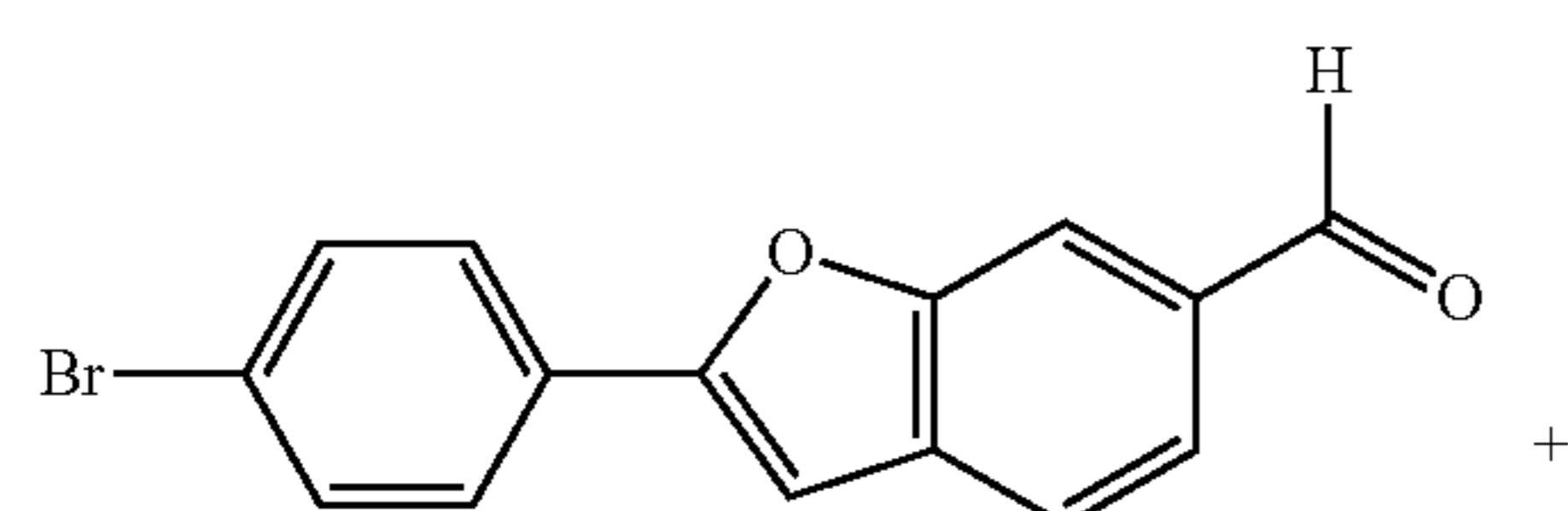


[0096] In a round bottom flask, 124 mg (0.315 mmol) 2-[4-(1-azatricyclo[7.3.1.0<sup>5,13</sup>]trideca-5,7,9(13)-trien-7-yl)phenyl]benzofuran-6-carbaldehyde, 133 mg (1.57 mmol) cyanoacetic acid and 243 mg (3.15 mmol) ammonium acetate was combined in 6 mL acetic acid and held at reflux for 3 h. Batch was cooled and combined with 20 mL water. Product was extracted into methylene chloride (3x2 mL) then the organic layer was washed with water (1x5 mL). Product was purified on silica gel, resulting in significant loss of product. Only 15 mg was obtained. UV/Vis max 435 nm, LCMS  $m/z=461.2$ .

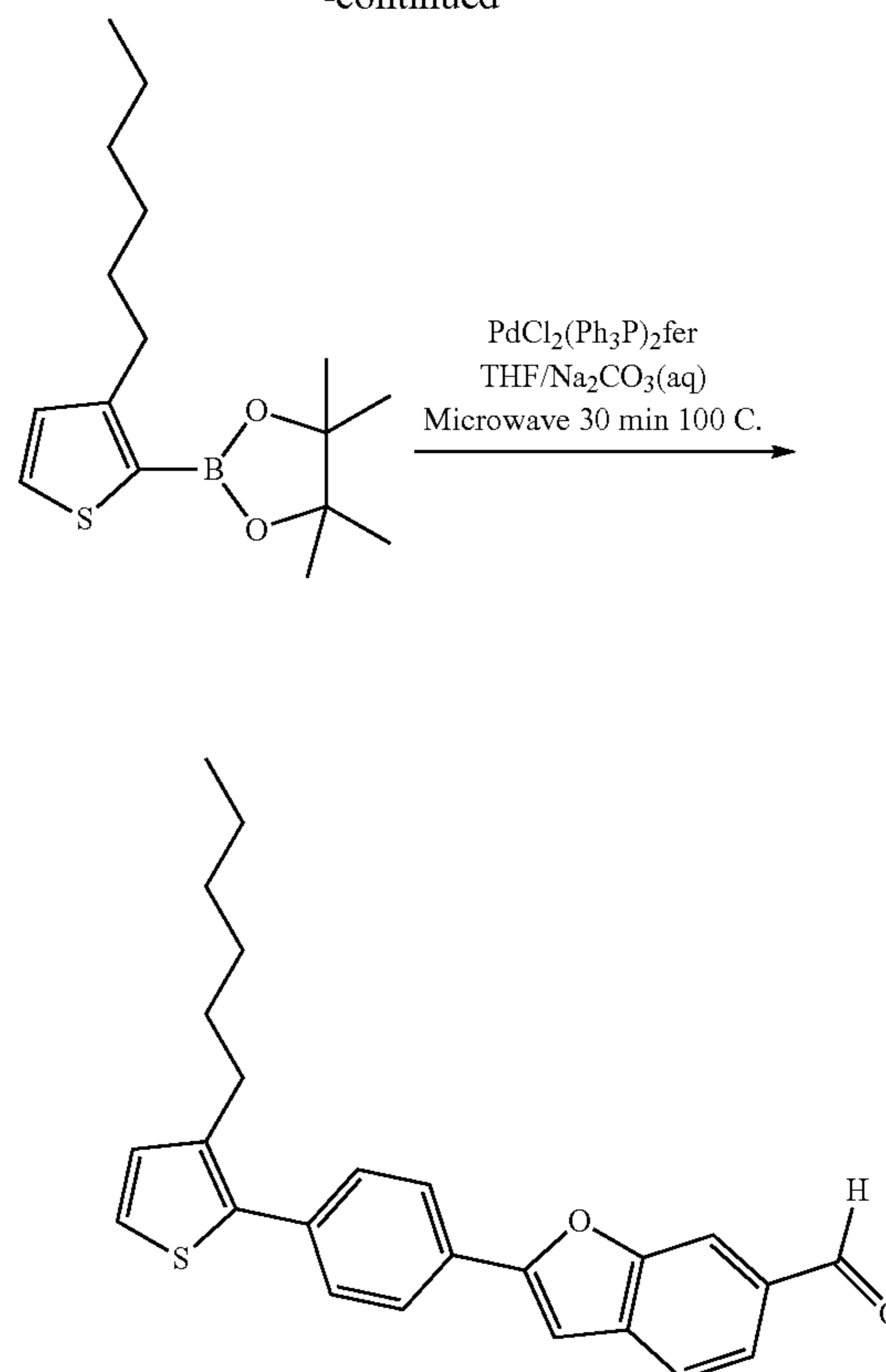
Example 6. Synthesis of (Z)-2-cyano-3-[2-[4-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-hexyl-2-thienyl]phenyl]benzofuran-6-yl]prop-2-enoic Acid (D9)

A. 2-[4-(3-hexyl-2-thienyl)phenyl]benzofuran-6-carbaldehyde

[0097]



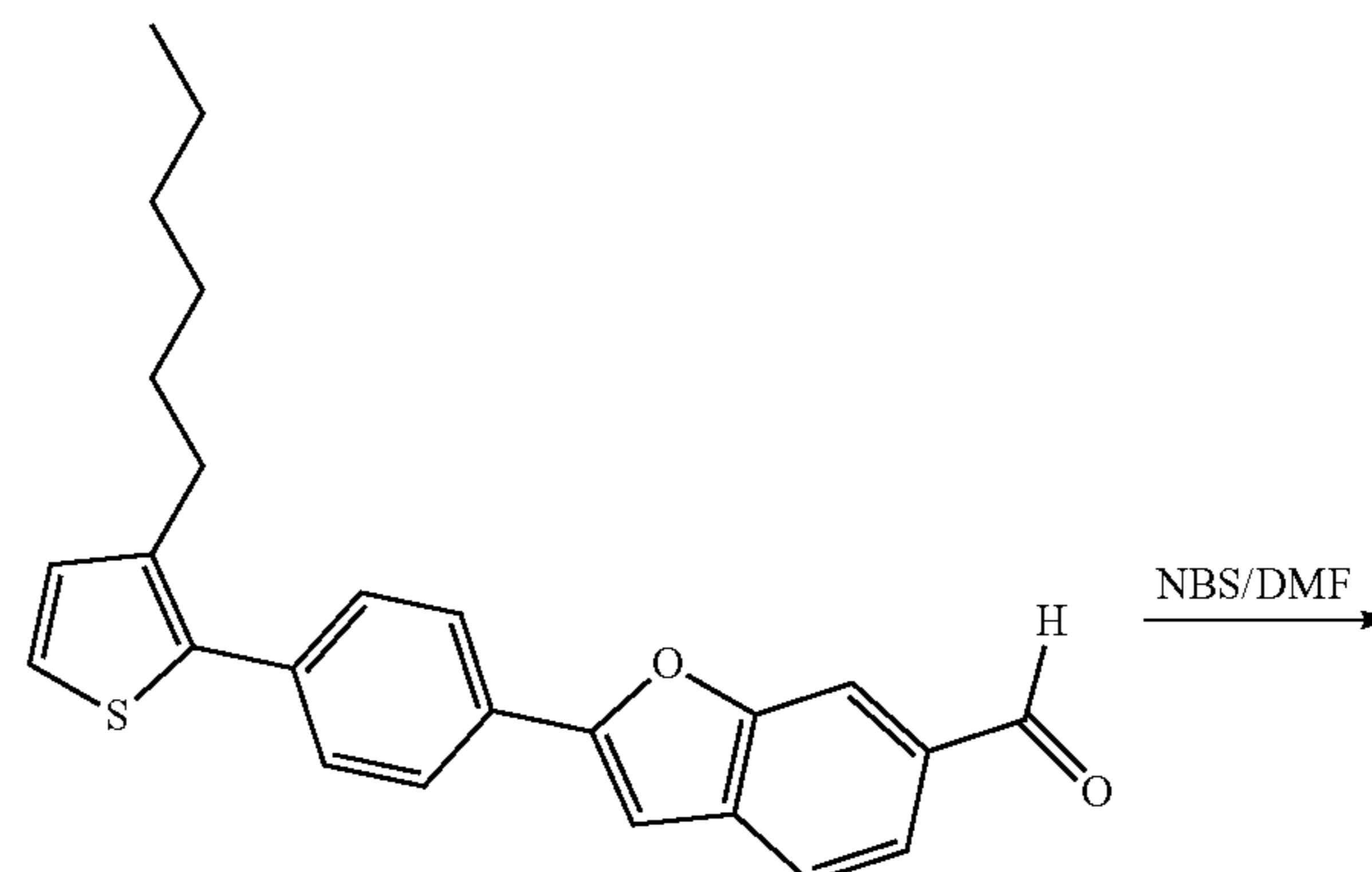
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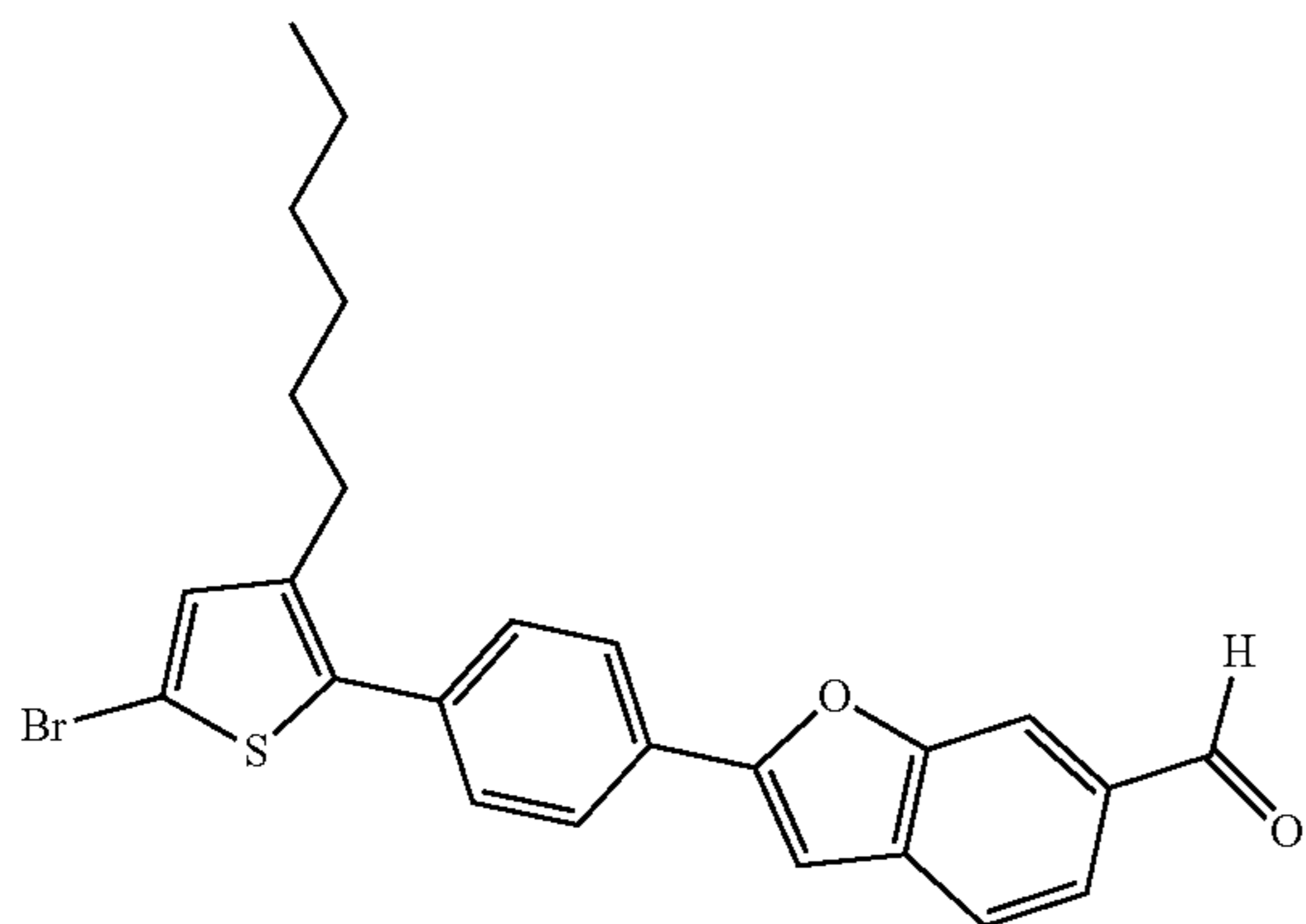
[0098] In a round bottom flask, 225 mg (0.75 mmol) 2-(4-bromophenyl)benzofuran-6-carbaldehyde, 242 mg (0.82 mmol), 3-hexylthiophene-2-boronic acid pinacol ester and 30 mg (0.04 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 4 mL THF and 1.5 mL 10%  $\text{Na}_2\text{CO}_3$ . Batch was microwaved at 100° C. for 30 min and purified on silica gel ( $\text{CH}_2\text{Cl}_2$ /hexane), yielding 205 mg (0.527 mmol, 70% yield). UV/Vis max 350 nm, LCMS  $m/z=389.1$ .

B. 2-[4-(5-bromo-3-hexyl-2-thienyl)phenyl]benzofuran-6-carbaldehyde

[0099]

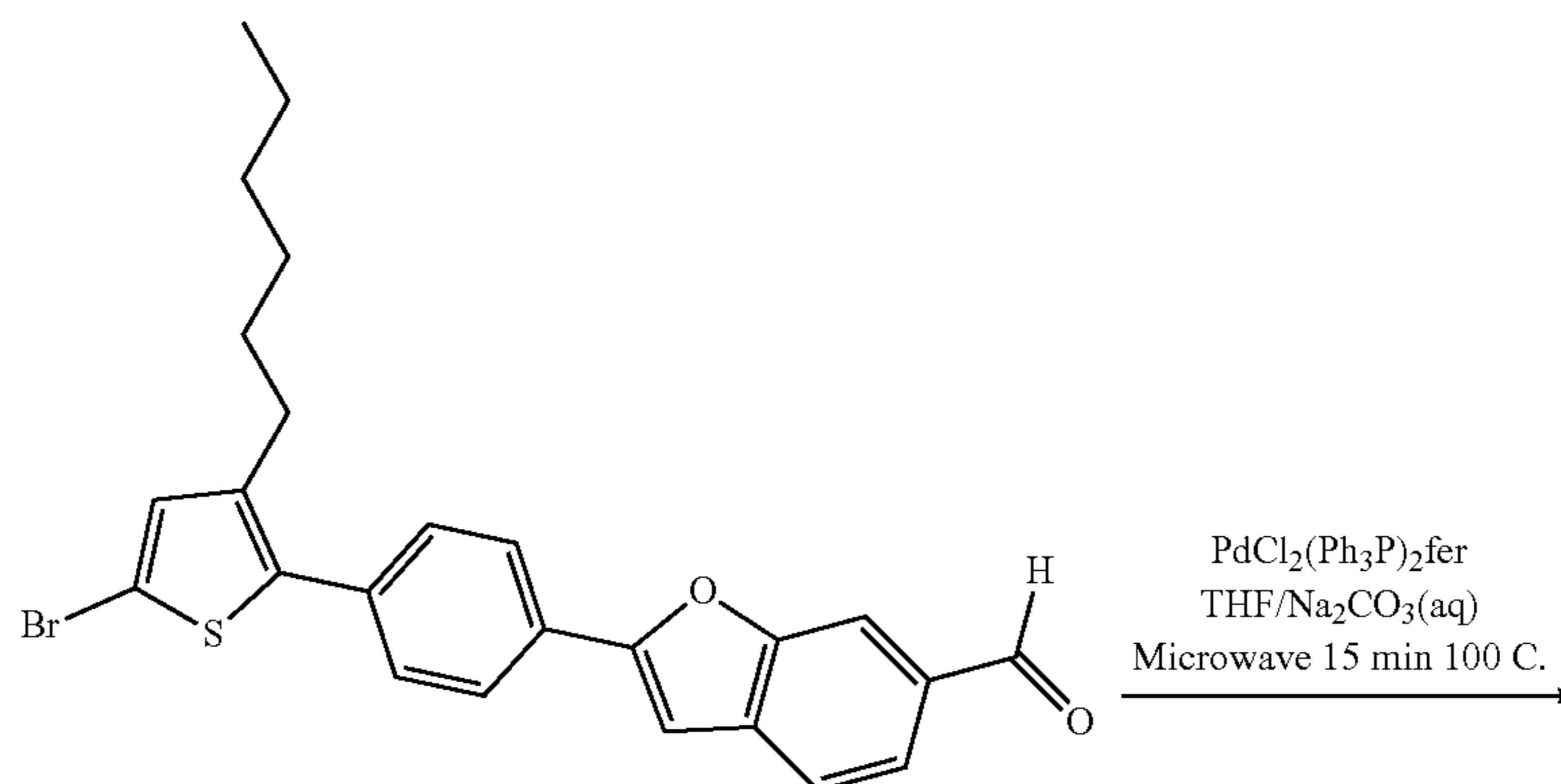
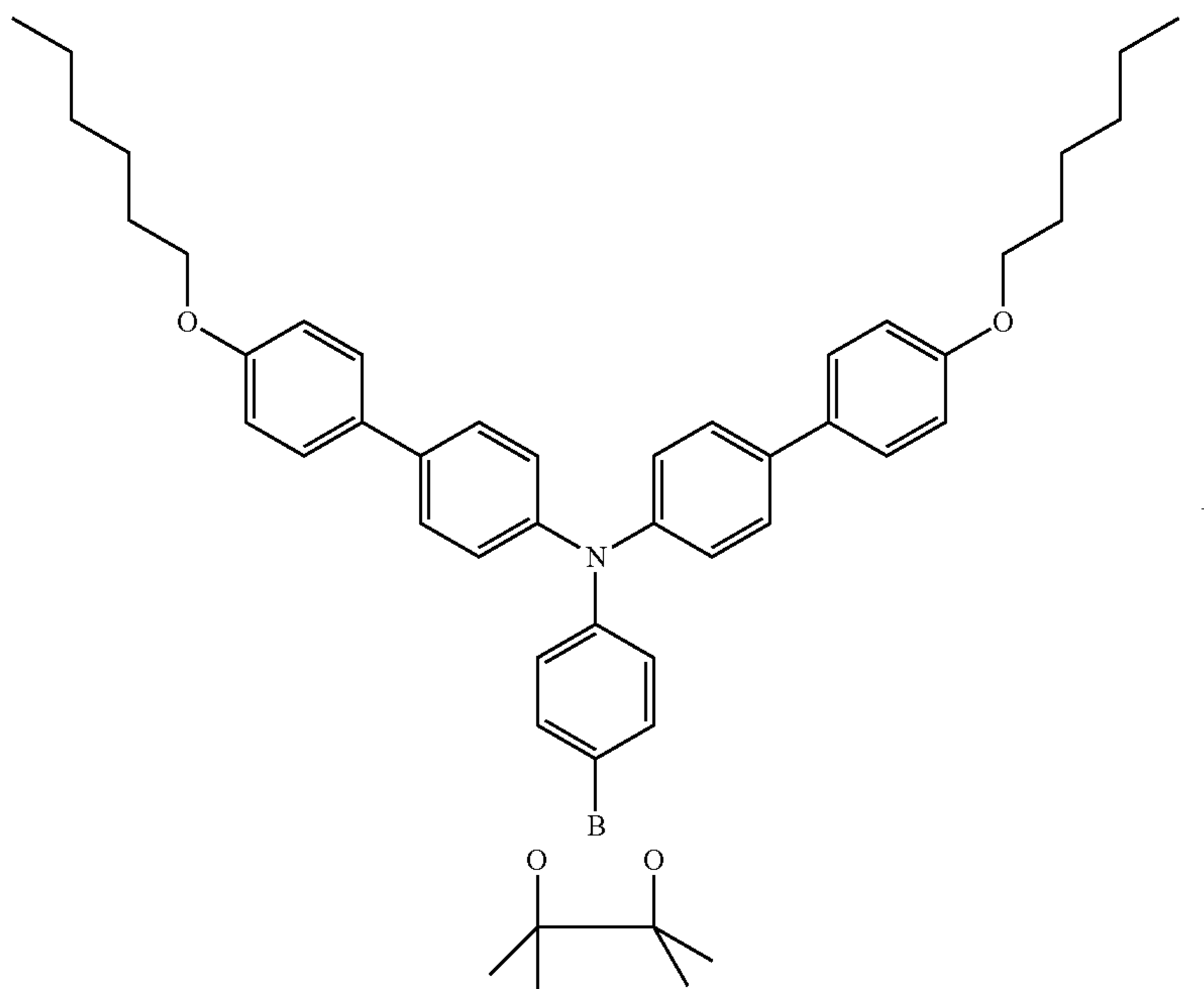


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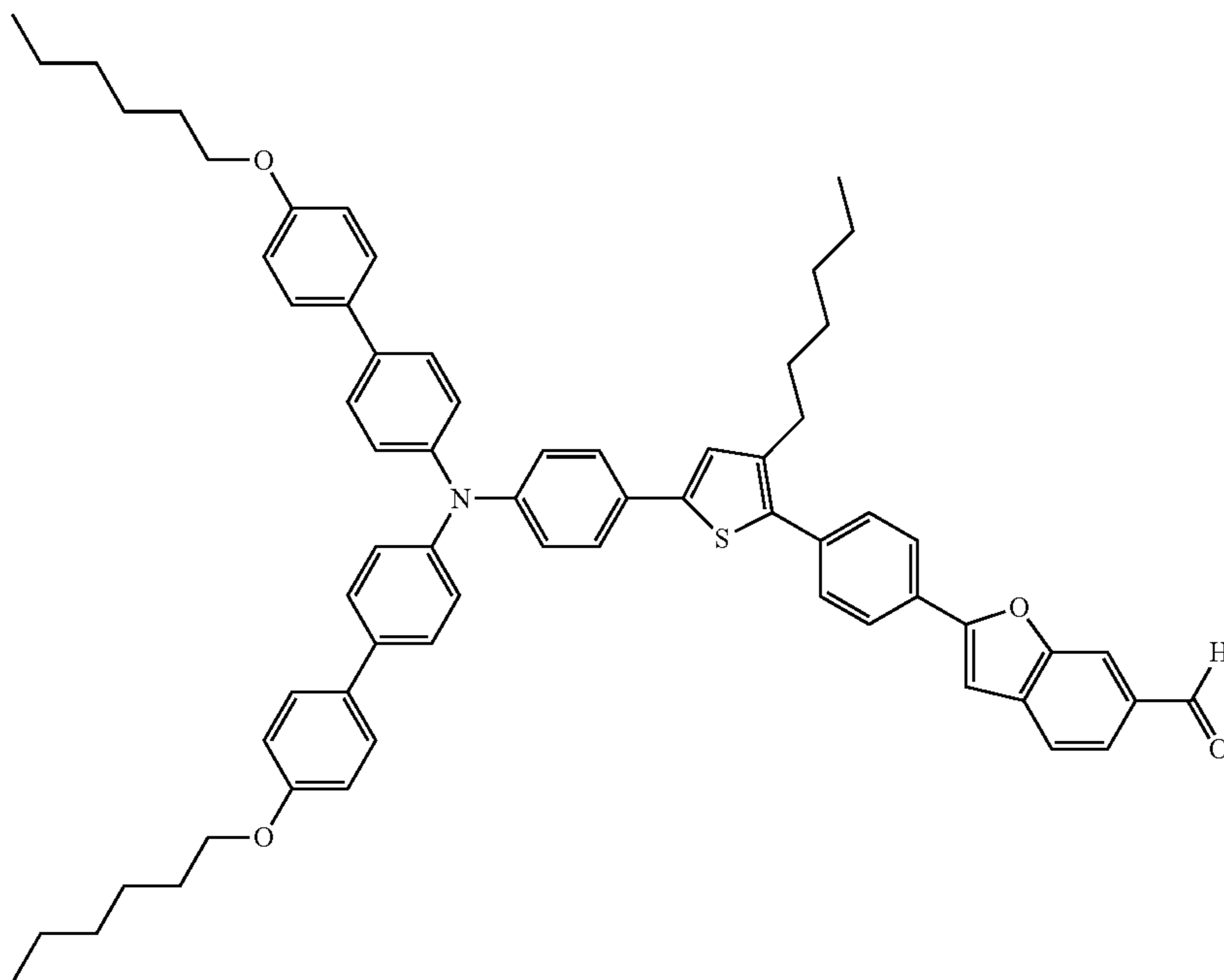
**[0100]** In a round bottom flask, 205 mg (0.53 mmol) 2-[4-(3-hexyl-2-thienyl)phenyl]benzofuran-6-carbaldehyde in 5 mL DMF was cooled to 5° C. A solution of 93 mg NBS (0.53 mmol) in 3 mL DMF was added dropwise and the batch was allowed to warm to rt. Batch was poured into 20 mL water and the product was extracted into methylene chloride and purified on silica gel, yielding 60 mg (0.13 mmol, 24% yield). UV/Vis max 350 nm, LCMS m/z=467.0, 469.0.

C. 2-[4-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-hexyl-2-thienyl]phenyl]benzofuran-6-carbaldehyde

**[0101]**



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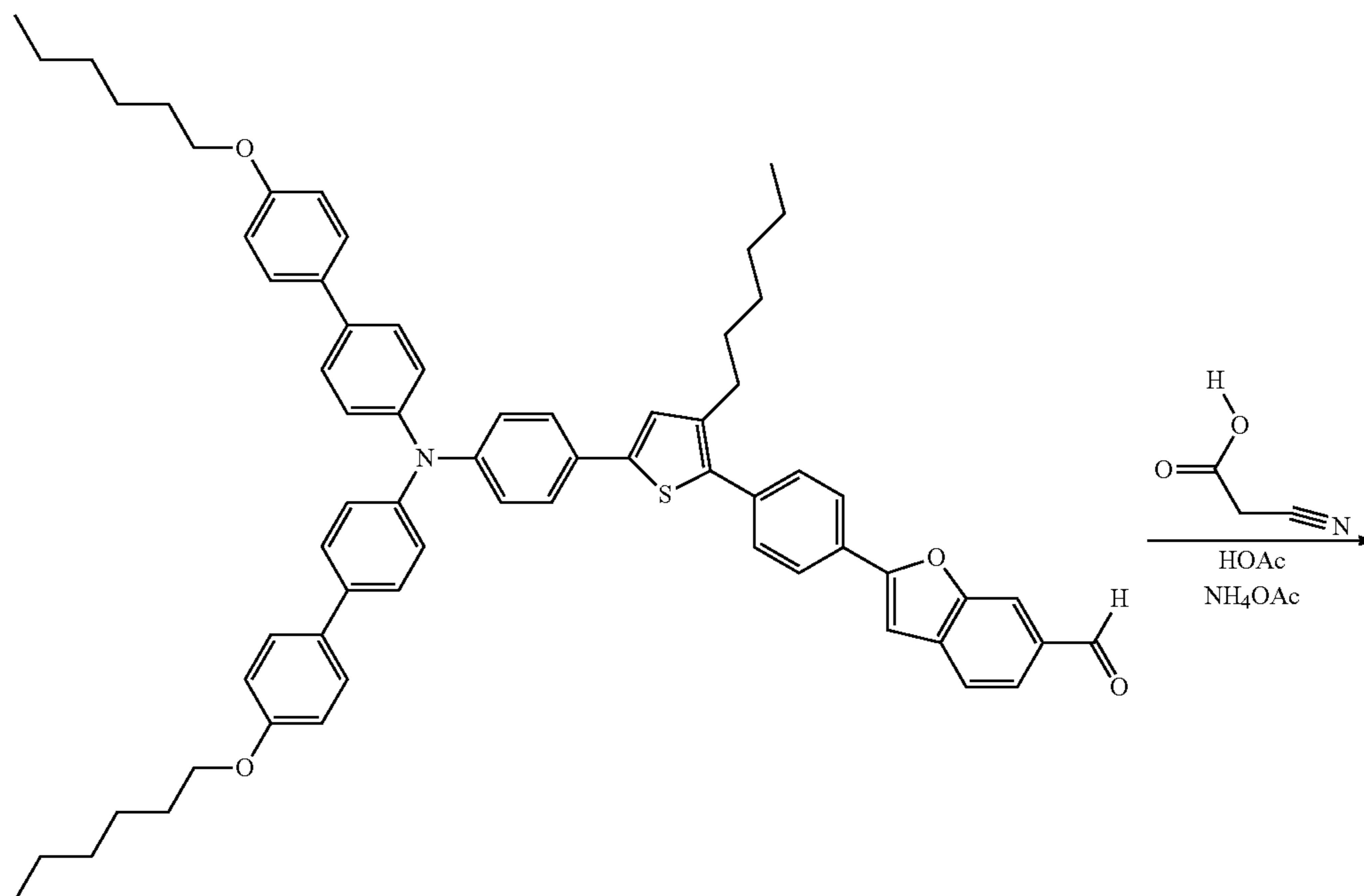


[0102] In a round bottom flask, 92 mg (0.13 mmol) N,N-bis[4-(4-hexoxyphenyl)phenyl]-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)aniline (see Example 1.C), 60 mg (0.13 mmol) aldehyde intermediate (Lot DJ1374), and 20 mg (0.026 mmol) dichloro-bis(diphenylphosphino)ferrocene palladium (II) was combined in 4 mL THF and 1.5 mL 10% Na<sub>2</sub>CO<sub>3</sub>. Batch was microwaved at 100° C. for 15 min. Product was purified on silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub>), yielding

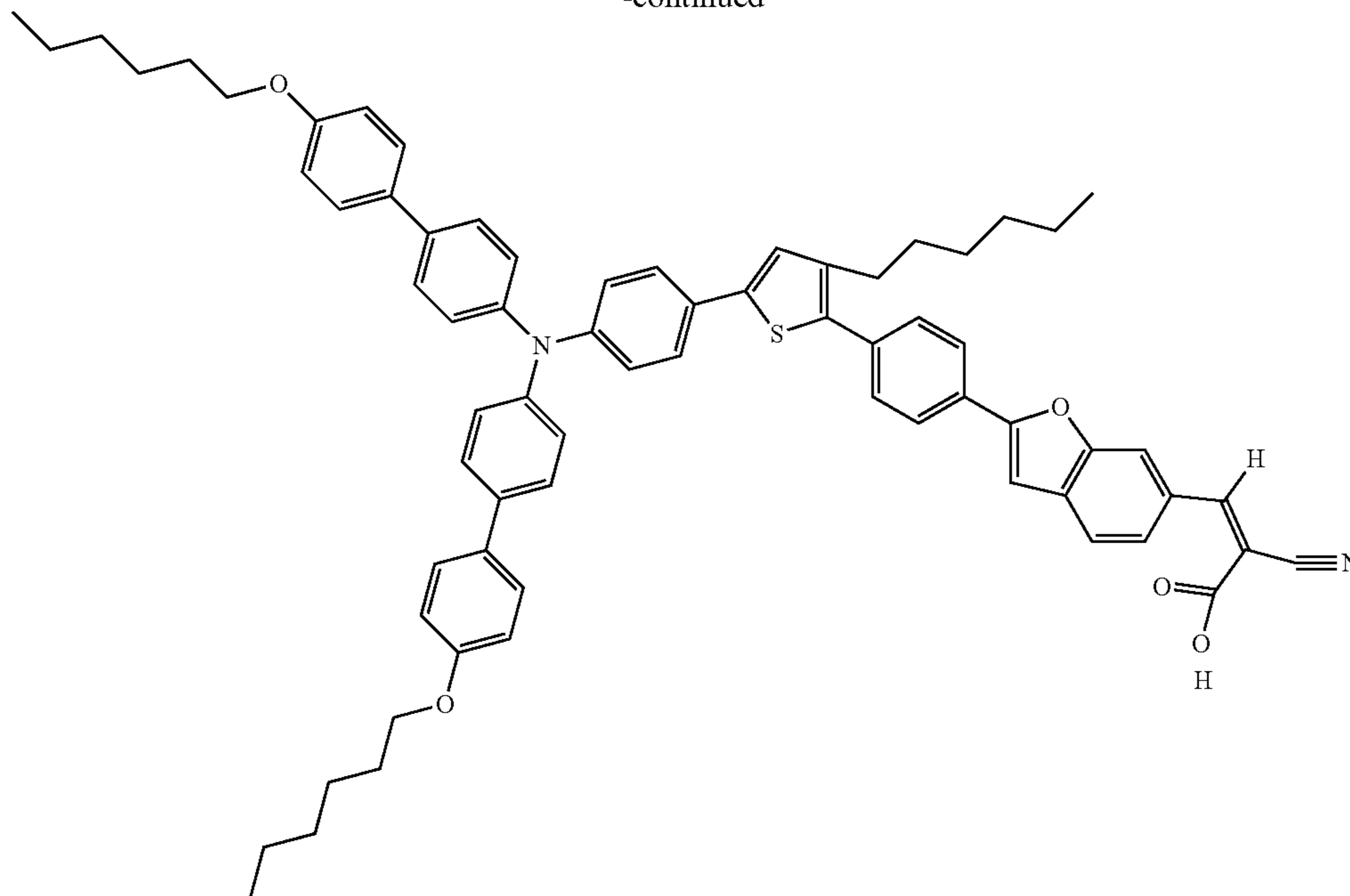
52 mg (0.052 mmol, 40% yield). UV/Vis max 345 nm & 495 nm, LCMS m/z=984.6.

D. (Z)-2-cyano-3-[2-[4-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-3-hexyl-2-thienyl]phenyl]benzofuran-6-yl]prop-2-enoic Acid

[0103]



-continued

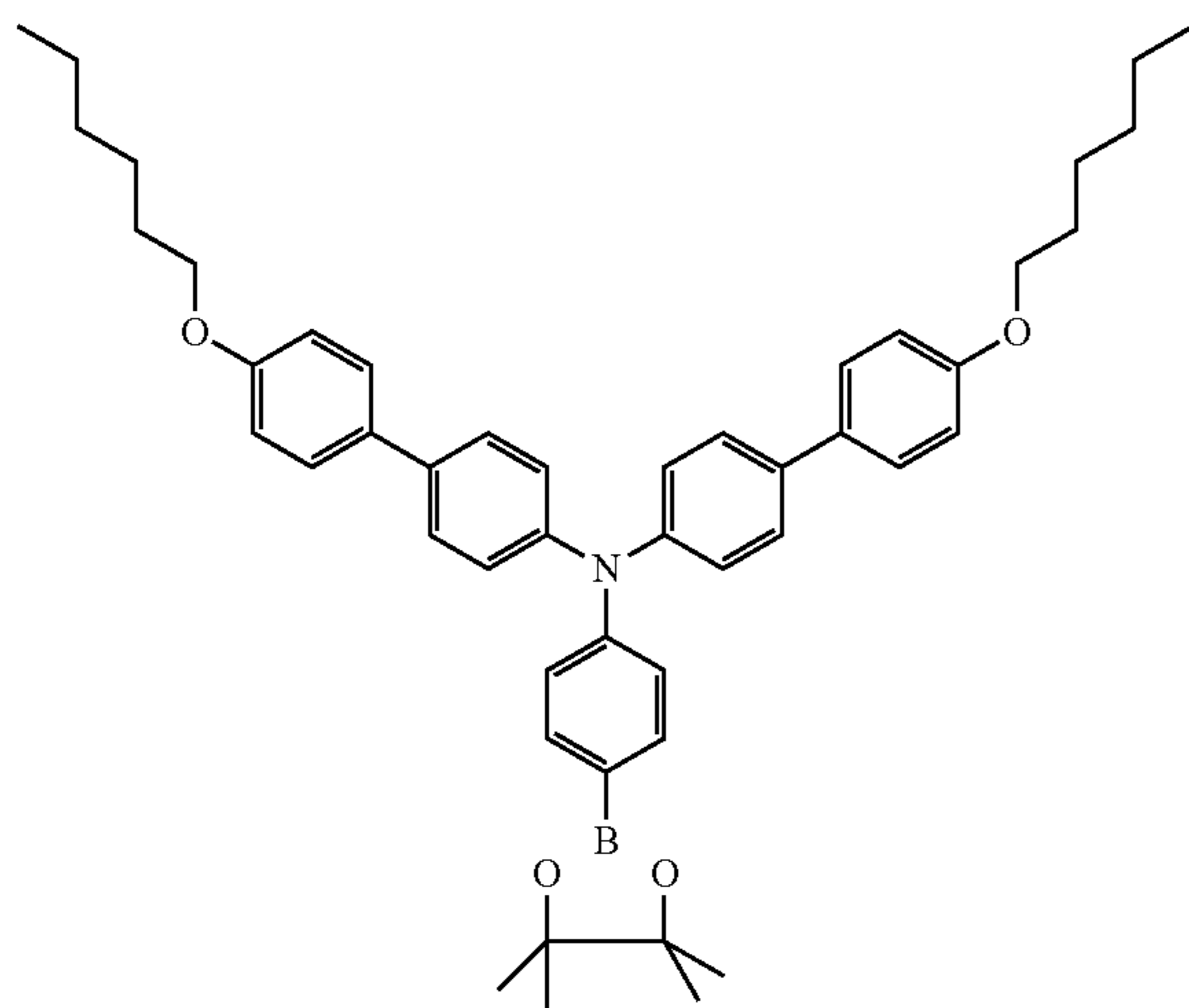


**[0104]** In a round bottom flask, 52 mg (0.052 mmoles) 2-[4-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-3-hexyl-2-thienyl]phenyl]benzofuran-6-carbaldehyde, 21 mg (0.25 mmol) cyanoacetic acid and 38 mg (0.5 mmol) ammonium acetate was combined in 6 mL HOAc and refluxed for 2 h. Batch was cooled and combined with 20 mL water. Product was filtered off, washed with water and dried, yielding 58 mg (0.05 mmol, 100% yield). UV/Vis max 350 nm & 410 nm, LCMS  $m/z=1051.4$ .

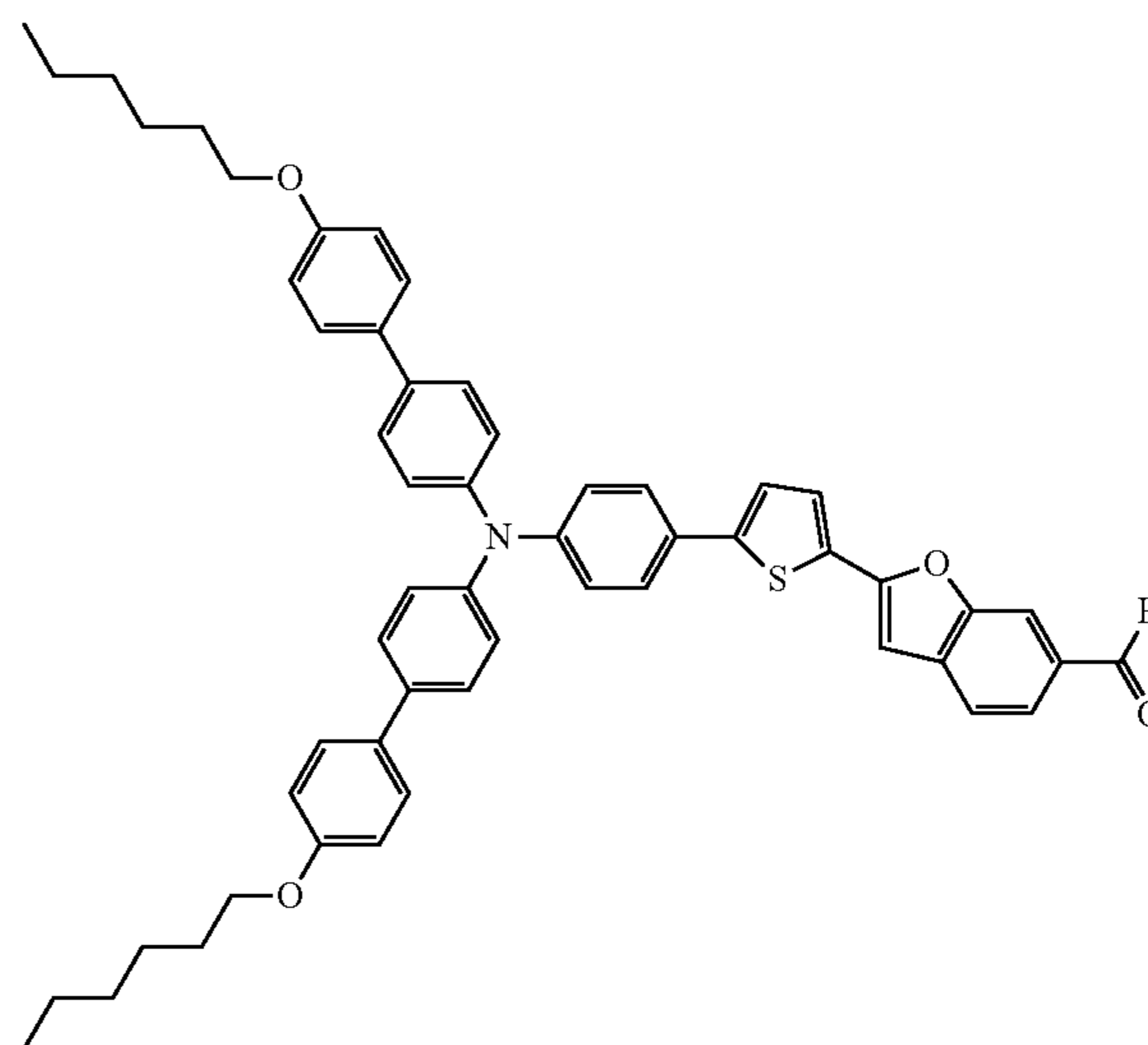
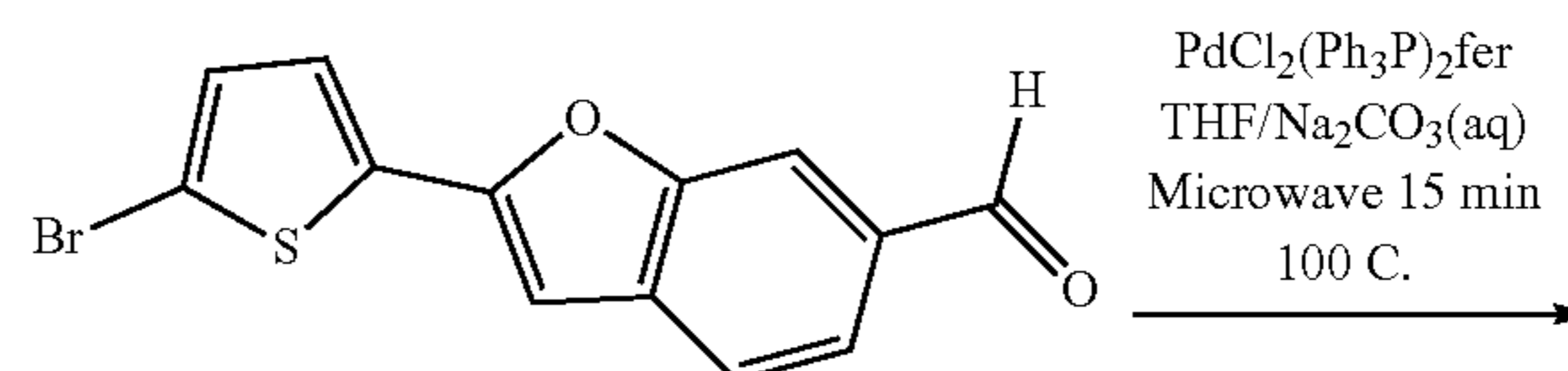
Example 7. Synthesis of (Z)-2-cyano-3-[2-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-2-thienyl]benzofuran-6-yl]prop-2-enoic Acid (D10)

A. 2-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-2-thienyl]benzofuran-6-carbaldehyde

**[0105]**



-continued



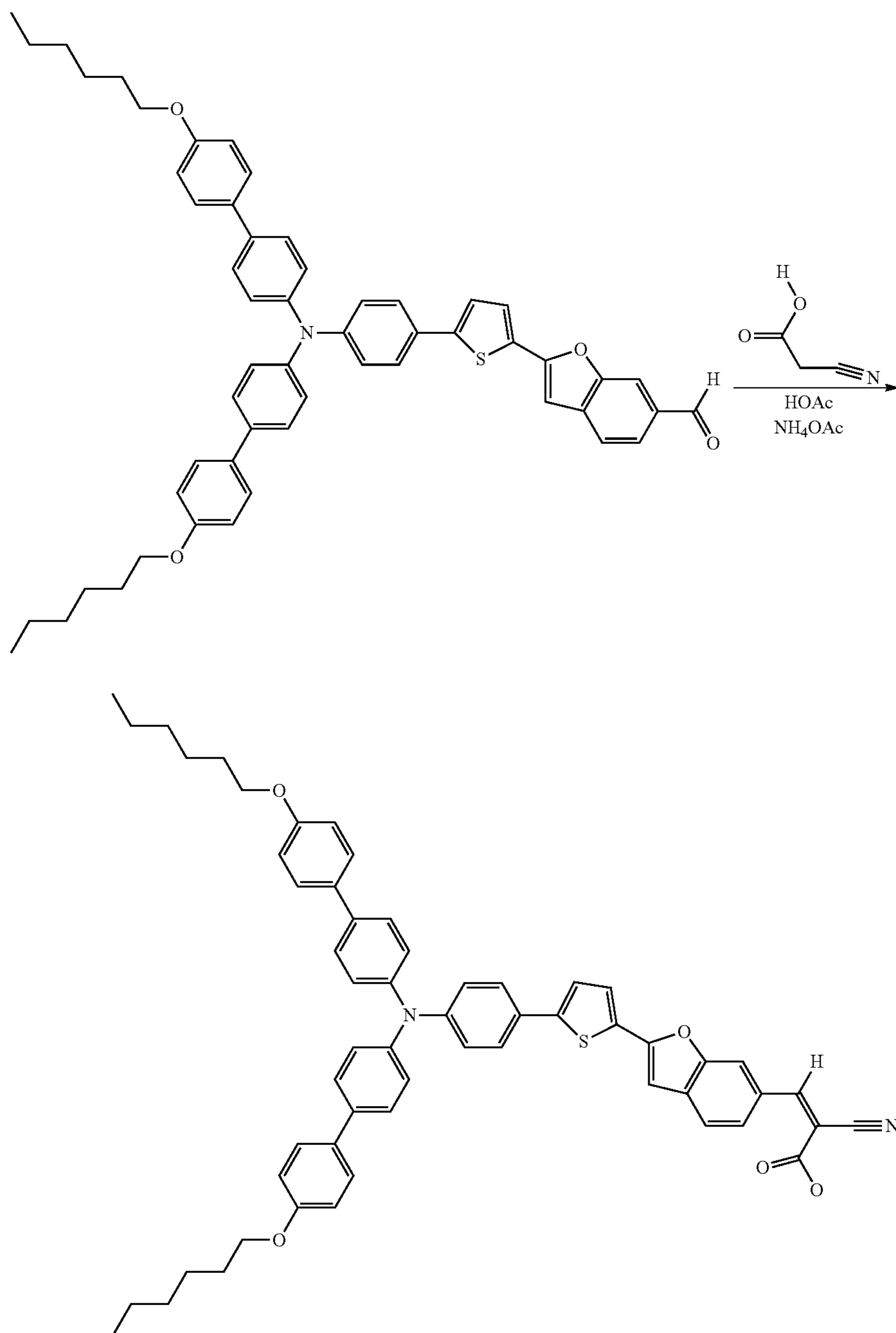
**[0106]** In a round bottom flask, 276 mg (0.38 mmol) N,N-bis[4-(4-hexoxyphenyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (see Example 1.C), 130 mg (0.42 mmol) 2-(5-bromo-2-thienyl)benzofuran-6-carbaldehyde, and 50 mg (0.06 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 4

mL THF and 1.5 mL 10% Na<sub>2</sub>CO<sub>3</sub>. Batch was microwaved at 100° C. for 15 min. Product was purified on silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub>) yielding 160 mg (0.19 mmol, 50% yield).

[0107] UV/Vis max 340 nm & 425 nm, LCMS m/z=824.4

B. (Z)-2-cyano-3-[2-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-2-thienyl]benzofuran-6-yl]prop-2-enoic Acid

[0108]

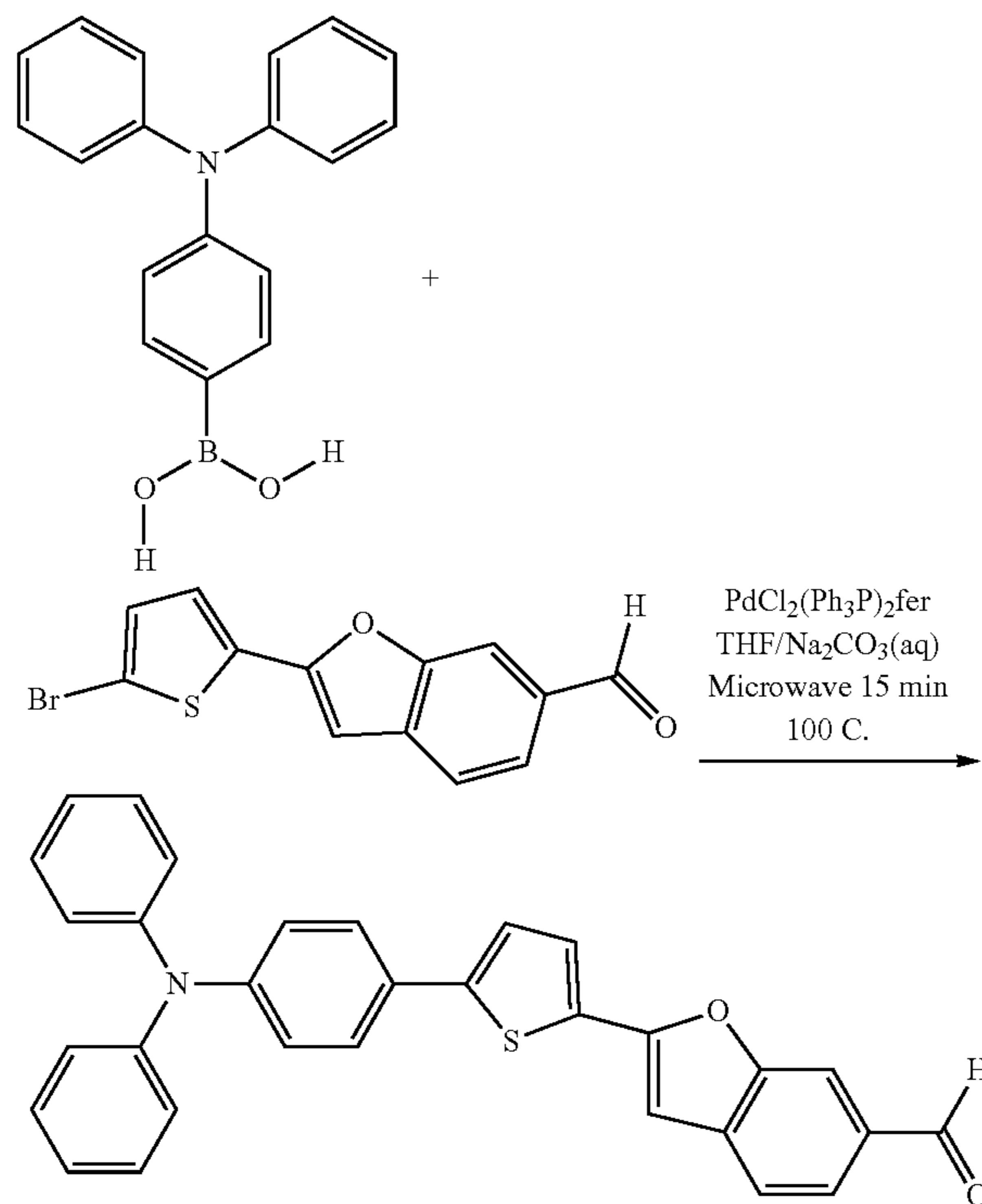


[0109] In a round bottom flask, 250 mg (0.3 mmoles) 2-[5-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-2-thienyl]benzofuran-6-carbaldehyde, 129 mg (1.5 mmol) cyanoacetic acid and 231 mg (3 mmol) ammonium acetate was combined in 6 mL HOAc and refluxed for 2 h. Batch was cooled. Product was filtered off, washed with 2 mL acetic acid then water and dried, yielding 247 mg (0.28 mmol, 93% yield). UV/Vis max 345 nm & 455 nm, LCMS m/z=891.6.

Example 8. Synthesis of (Z)-2-cyano-3-[2-[5-[4-(N-phenylanilino)phenyl]-2-thienyl]benzofuran-6-yl]prop-2-enoic Acid (D12)

A. 2-[5-[4-(N-phenylanilino)phenyl]-2-thienyl]benzofuran-6-carbaldehyde

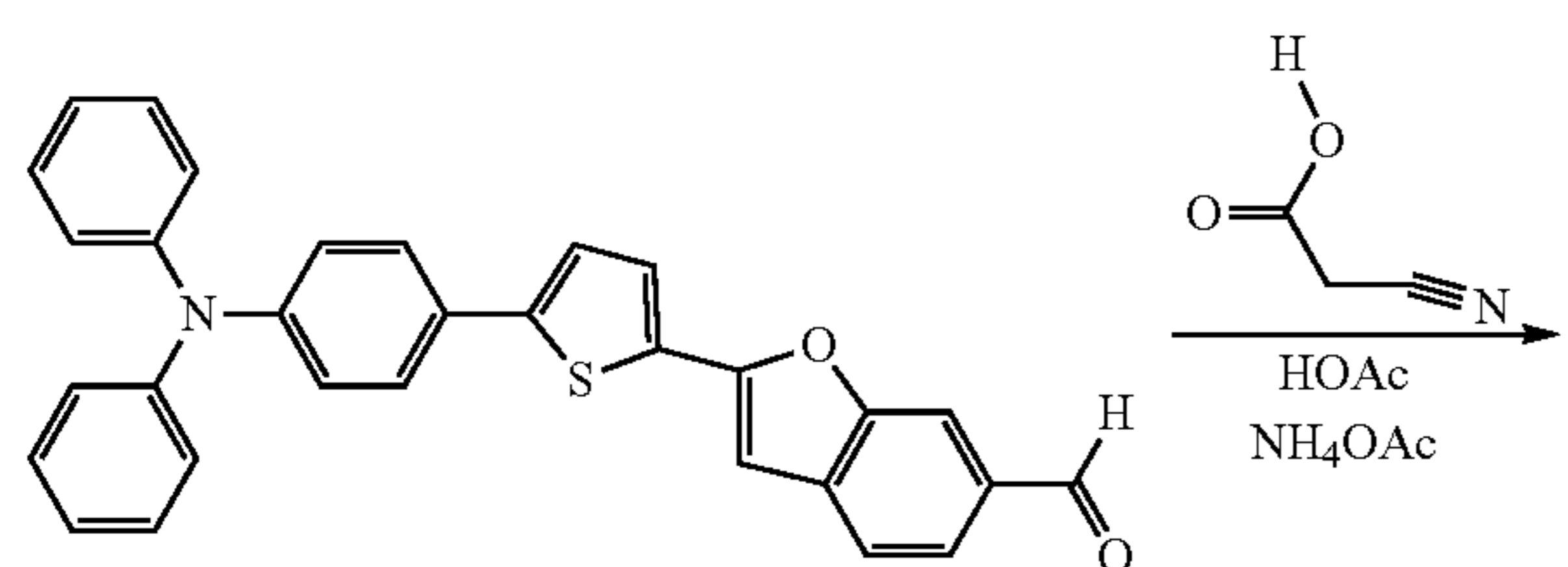
[0110]



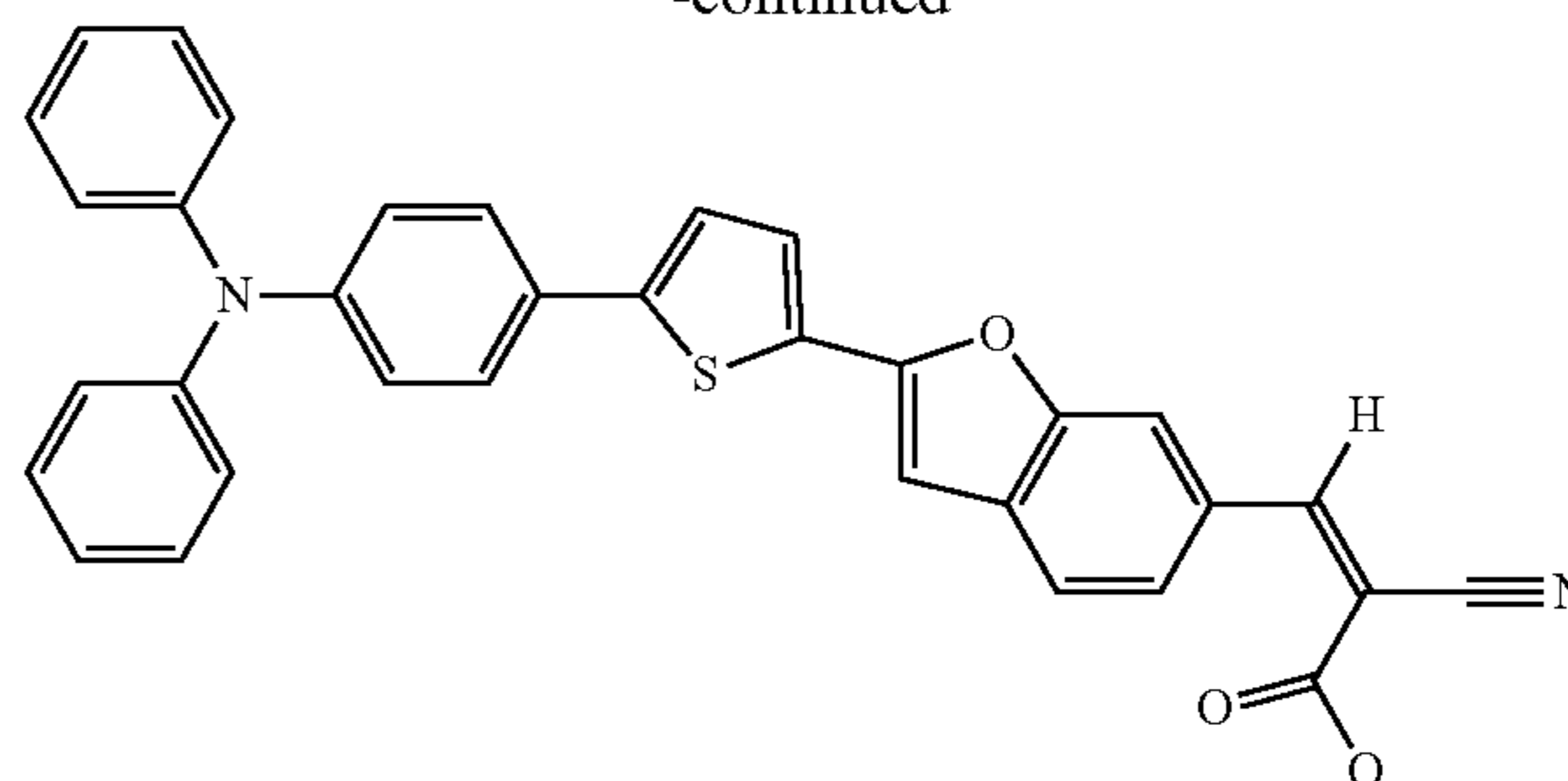
[0111] In a round bottom flask, 144 mg (0.5 mmol) 4-diphenylamino phenylboronic acid, 168 mg (~0.5 mmol assuming ~90% pure) 2-(5-bromo-2-thienyl)benzofuran-6-carbaldehyde, and 20 mg (0.026 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 4 mL THF and 1.5 mL 10% Na<sub>2</sub>CO<sub>3</sub>. Batch was microwaved at 100° C. for 15 min. Product was purified on silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub>) yielding 80 mg (0.17 mmol, 34% yield). UV/Vis max 415 nm, LCMS m/z=472.2.

B. (Z)-2-cyano-3-[2-[5-[4-(N-phenylanilino)phenyl]-2-thienyl]benzofuran-6-yl]prop-2-enoic Acid

[0112]



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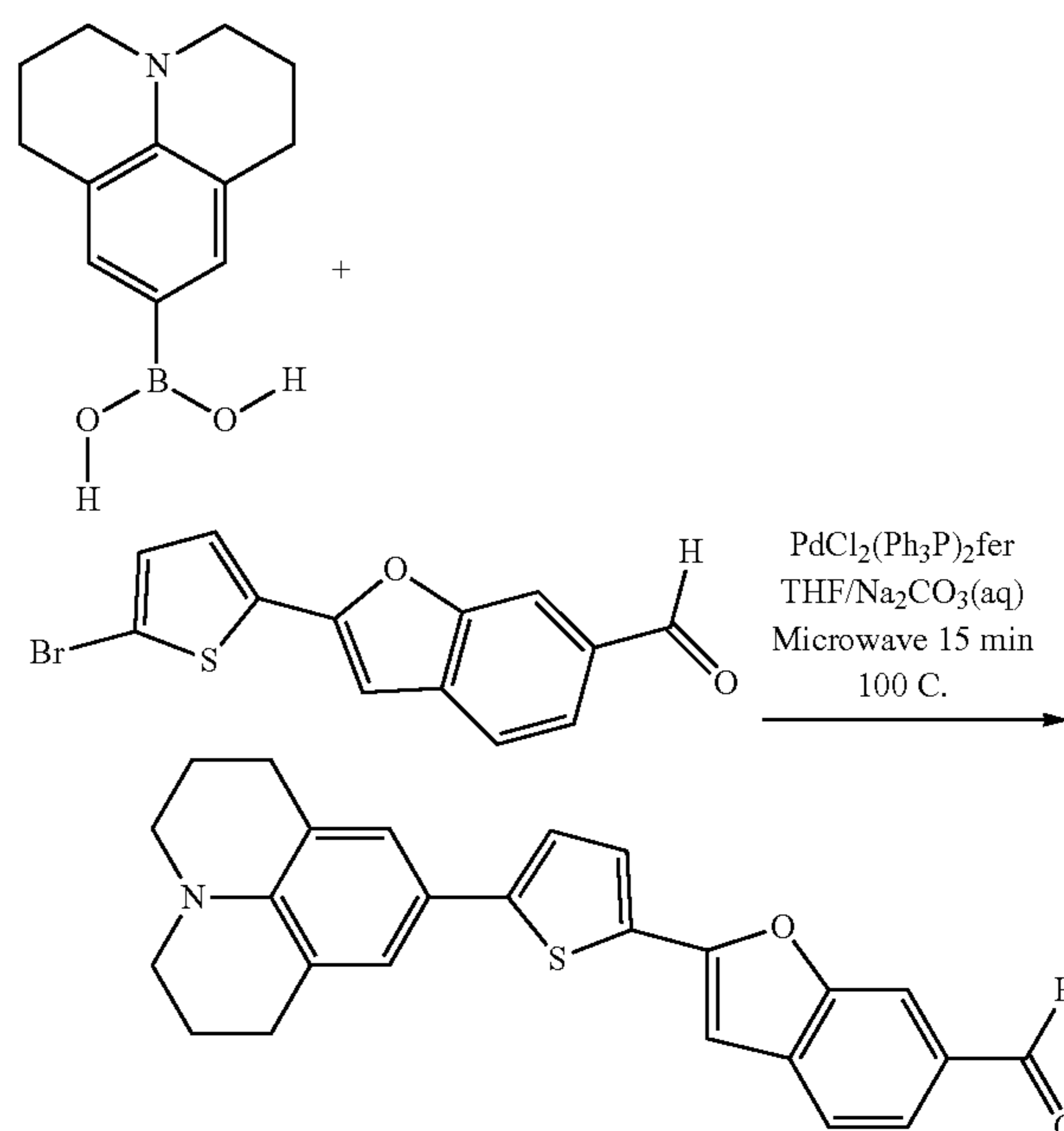


[0113] In a round bottom flask, 80 mg (0.17 mmoles) 2-[5-[4-(N-phenylanilino)phenyl]-2-thienyl]benzofuran-6-carbaldehyde, 72 mg (0.85 mmol) cyanoacetic acid and 130 mg (1.7 mmol) ammonium acetate was combined in 6 mL HOAc and refluxed for 2 h. Batch was cooled and combined with 20 mL water. Product was filtered off, washed with water and dried yielding 90 mg (0.16 mmol, 94% yield). UV/Vis max 445 nm, LCMS m/z=539.2.

Example 9. Synthesis of (Z)-3-[2-[5-(1-azatricyclo[7.3.1.05,13]trideca-5(13),6,8-trien-7-yl)-2-thienyl]benzofuran-6-yl]-2-cyano-prop-2-enoic Acid (D11)

A. 2-[5-(1-azatricyclo[7.3.1.05,13]trideca-5,7,9(13)-trien-7-yl)-2-thienyl]benzofuran-6-carbaldehyde

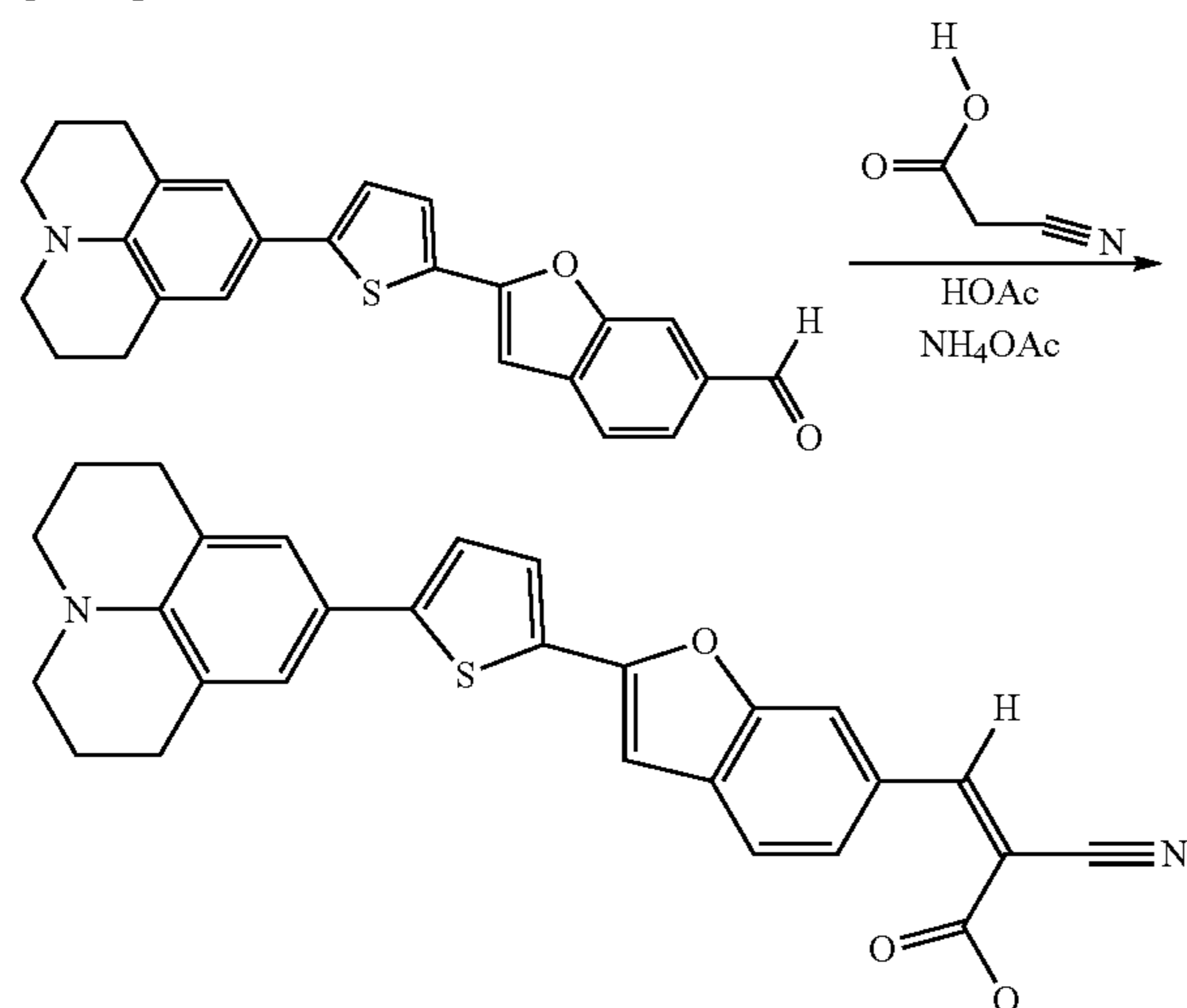
[0114]



[0115] In a round bottom flask, 141 mg (0.65 mmol) julolidine boronic acid, 200 mg (~0.65 mmol) 2-(5-bromo-2-thienyl)benzofuran-6-carbaldehyde, and 20 mg (0.026 mmol) dichloro-bis(diphenylphosphino) ferrocene palladium (II) was combined in 4 mL THF and 1.5 mL 10% Na<sub>2</sub>CO<sub>3</sub>. Batch was microwaved at 100° C. for 15 min. Product was purified on silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub>), yielding 50 mg (0.125 mmol, 19% yield). UV/Vis max 420 nm, LCMS m/z=400.2.

B. (Z)-3-[2-[5-(1-azatricyclo[7.3.1.0<sup>5,13</sup>]trideca-5(13),6,8-trien-7-yl)-2-thienyl]benzofuran-6-yl]-2-cyano-prop-2-enoic Acid

[0116]

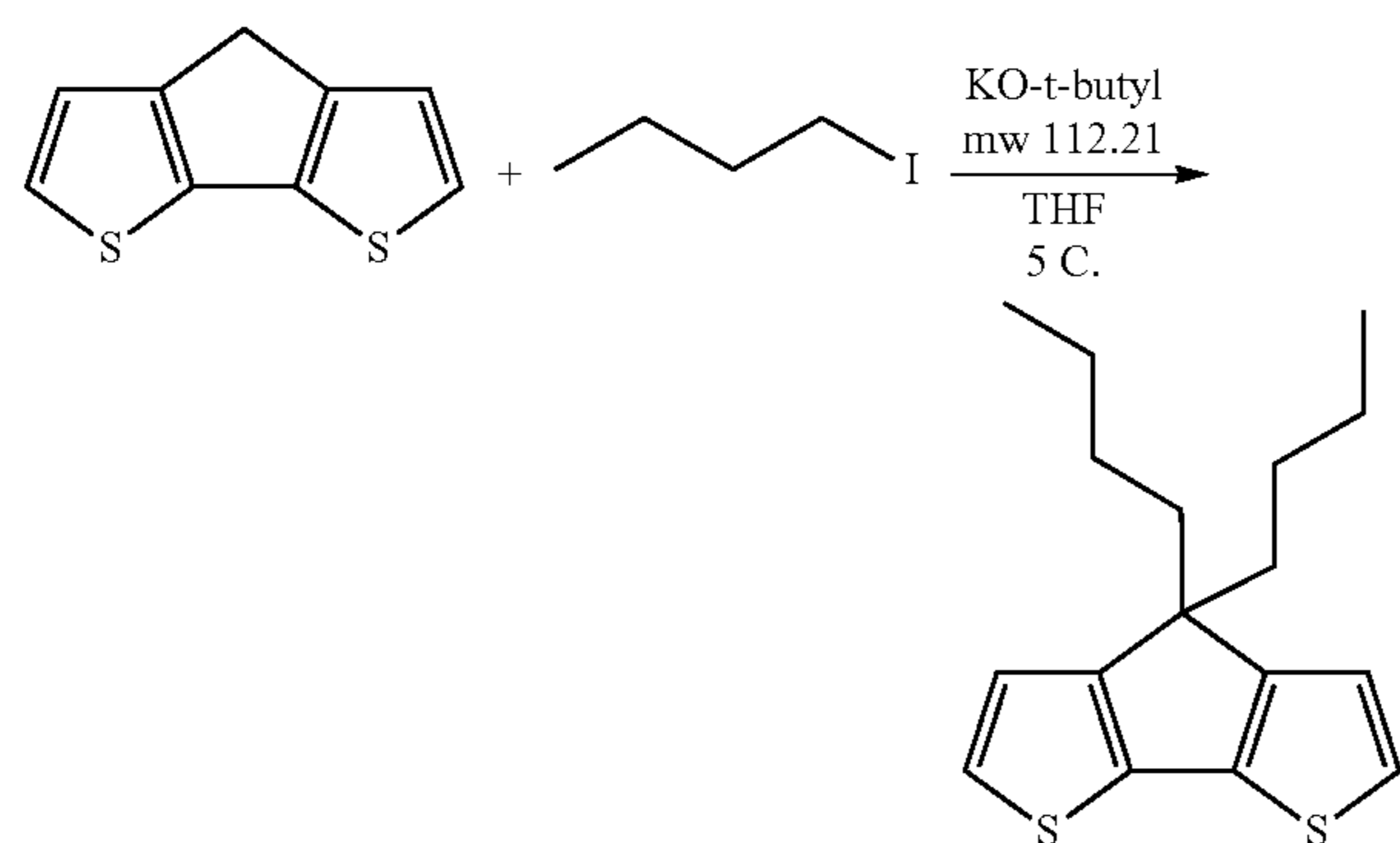


[0117] In a round bottom flask, 50 mg (0.12 mmoles) 2-[5-(1-azatricyclo[7.3.1.0<sup>5,13</sup>]trideca-5,7,9(13)-trien-7-yl)-2-thienyl]benzofuran-6-carbaldehyde, 53 mg (0.63 mmol) cyanoacetic acid and 96 mg (1.2 mmol) ammonium acetate was combined in 6 mL HOAc at 90° C. for 6 h. Reaction was stopped at 90% completion. Batch was cooled and product filtered off, washed with water and dried, yielding 50 mg (0.11 mmol, 85% yield). UV/Vis max 475 nm, LCMS m/z=467.2.

Example 10. Synthesis of (Z)-2-cyano-3-[2-[7,7-dibutyl-10-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-3,11-dithiatricyclo[6.3.0.0<sup>2,6</sup>]undeca-1(8),2(6),4,9-tetraen-4-yl]benzofuran-6-yl]prop-2-enoic Acid (D14)

A. 7,7-dibutyl-3,11-dithiatricyclo[6.3.0.0<sup>2,6</sup>]undeca-1(8),2(6),4,9-tetraene

[0118]

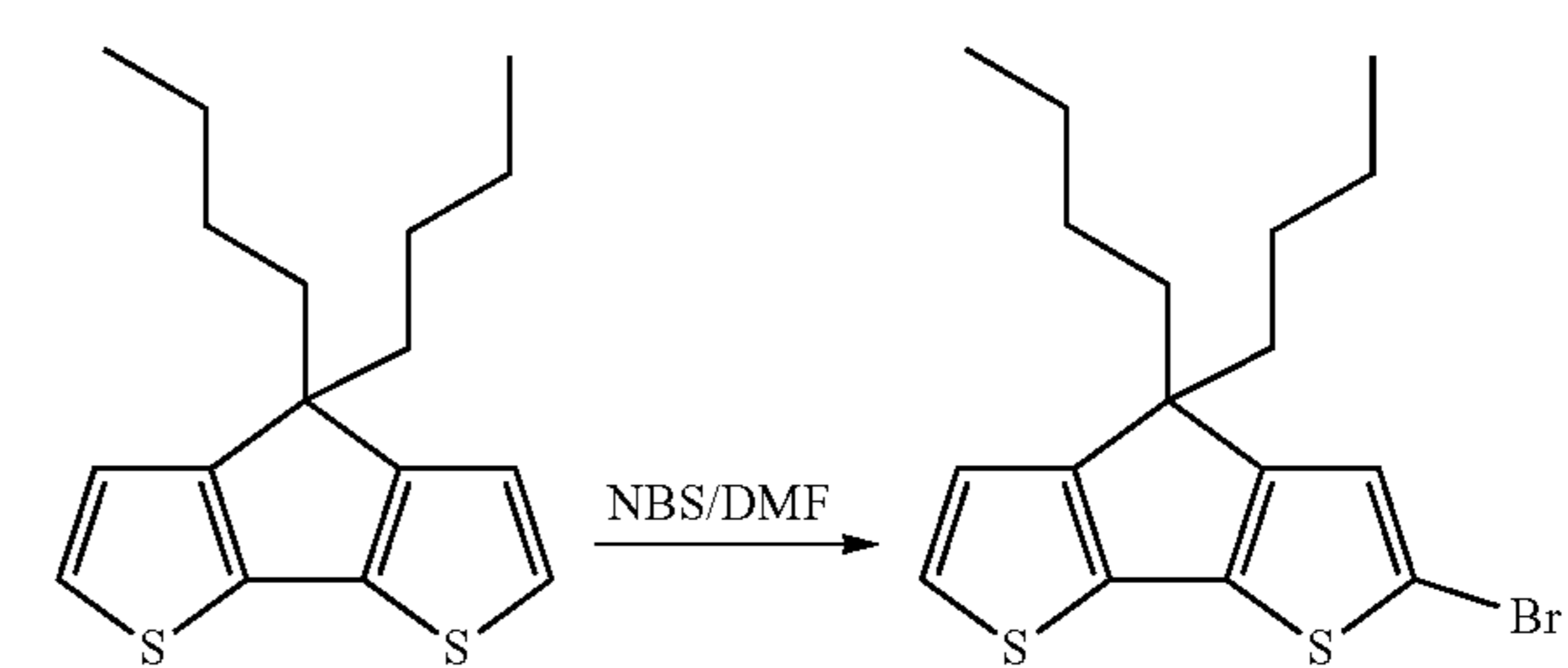


[0119] In a round bottom flask, 2.3 g (12.9 mmol) 4H-Cyclopenta[1,2-b:5,4-b']dithiophene in 25 mL THF at 5° C. was treated with 4.15 g (37 mmol) potassium t-butoxide followed by the addition of 4.76 g (25.9 mmol) 1-iodobutane. Batch was poured into water and extracted into methylene chloride. The organic layer was concentrated and passed thru a silica gel column (80 g), eluted with hexane

and concentrated, yielding 3.1 g light yellow solid (oily crystals). 97 A % by HPLC (85% yield). UV/Vis max 315 nm, LCMS m/z=291.1.

B. 4-bromo-7,7-dibutyl-3,11-dithiatricyclo[6.3.0.0<sup>2,6</sup>]undeca-1(8),2(6),4,9-tetraene

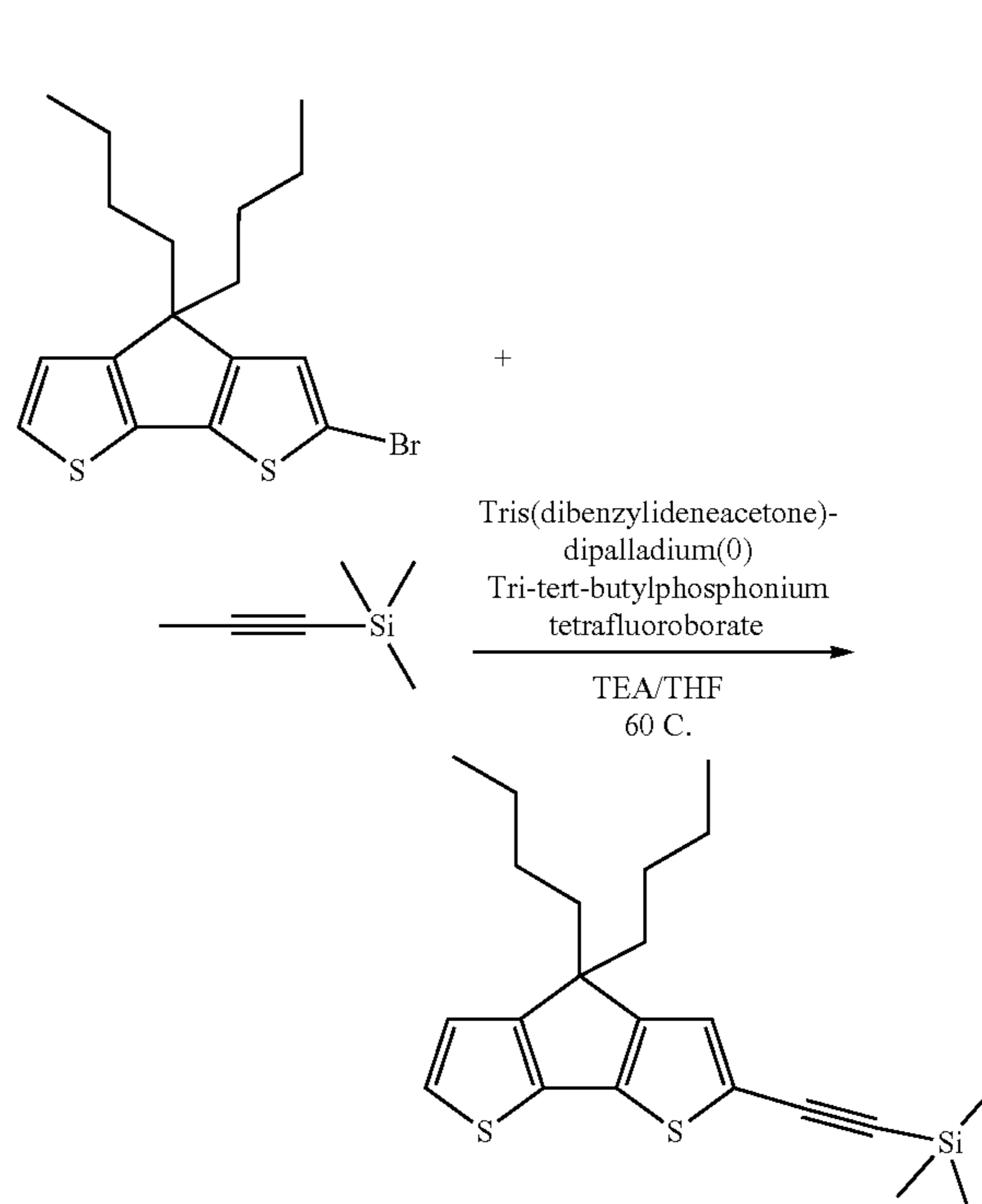
[0120]



[0121] In a round bottom flask, 1.6 g (5.5 mmol) 7,7-dibutyl-3,11-dithiatricyclo[6.3.0.0<sup>2,6</sup>]undeca-1(8),2(6),4,9-tetraene was dissolved in 15 mL DMF was cooled to 5° C. A solution 0.95 g (5.3 mmol) N-bromosuccinamide in 5 mL DMF was added dropwise over 30 min. The mixture was poured into 100 mL water and extracted with methylene chloride. The organic layer was separated, concentrated and passed through a silica gel column (hexane) yielding 0.91 g (2.46 mmol, 45% yield) yellow oil. UV/Vis max 325 nm, LCMS m/z=368.9, 370.9.

C. 2-(7,7-dibutyl-3,11-dithiatricyclo[6.3.0.0<sup>2,6</sup>]undeca-1(8),2(6),4,9-tetraen-4-yl)ethynyl-trimethylsilane

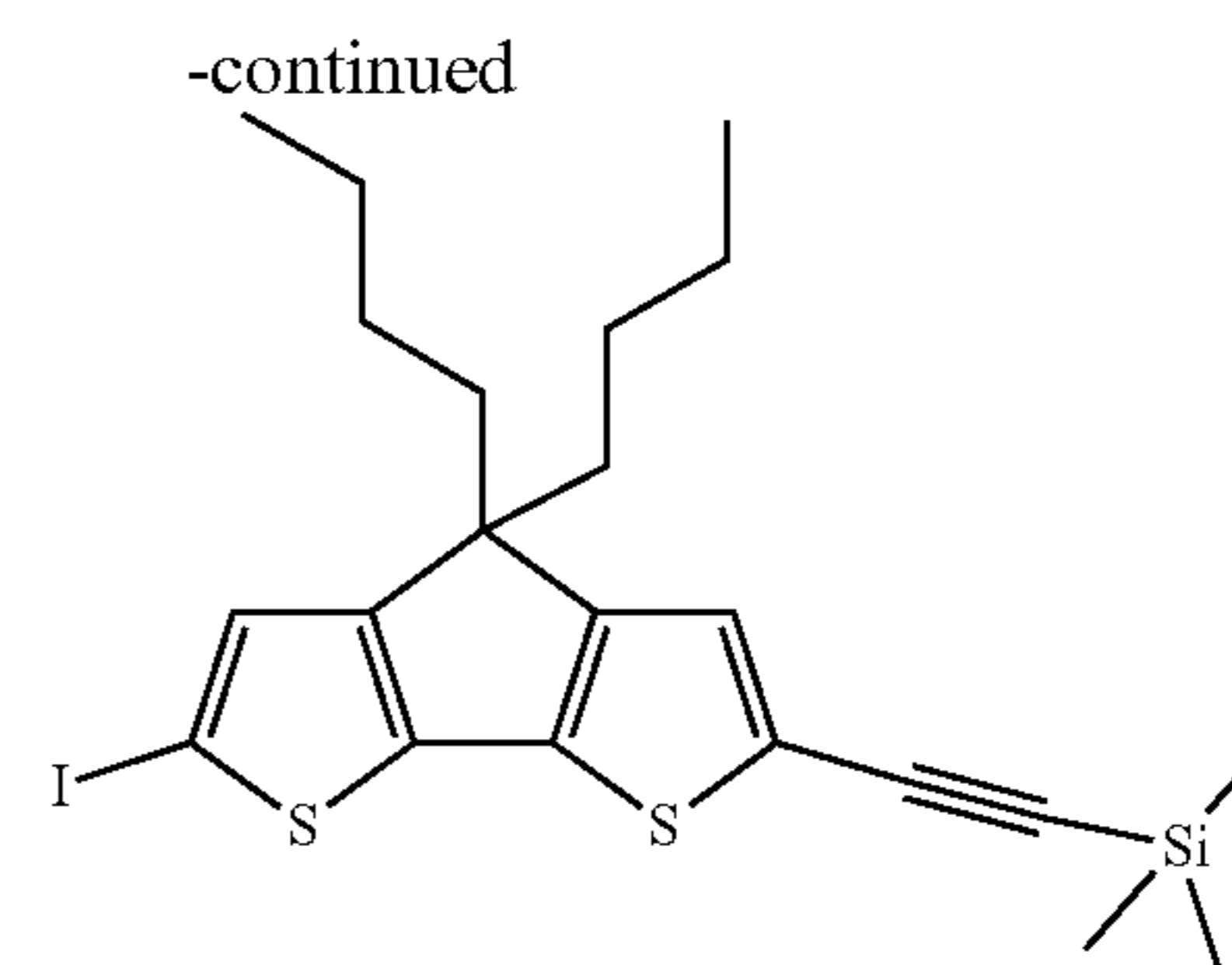
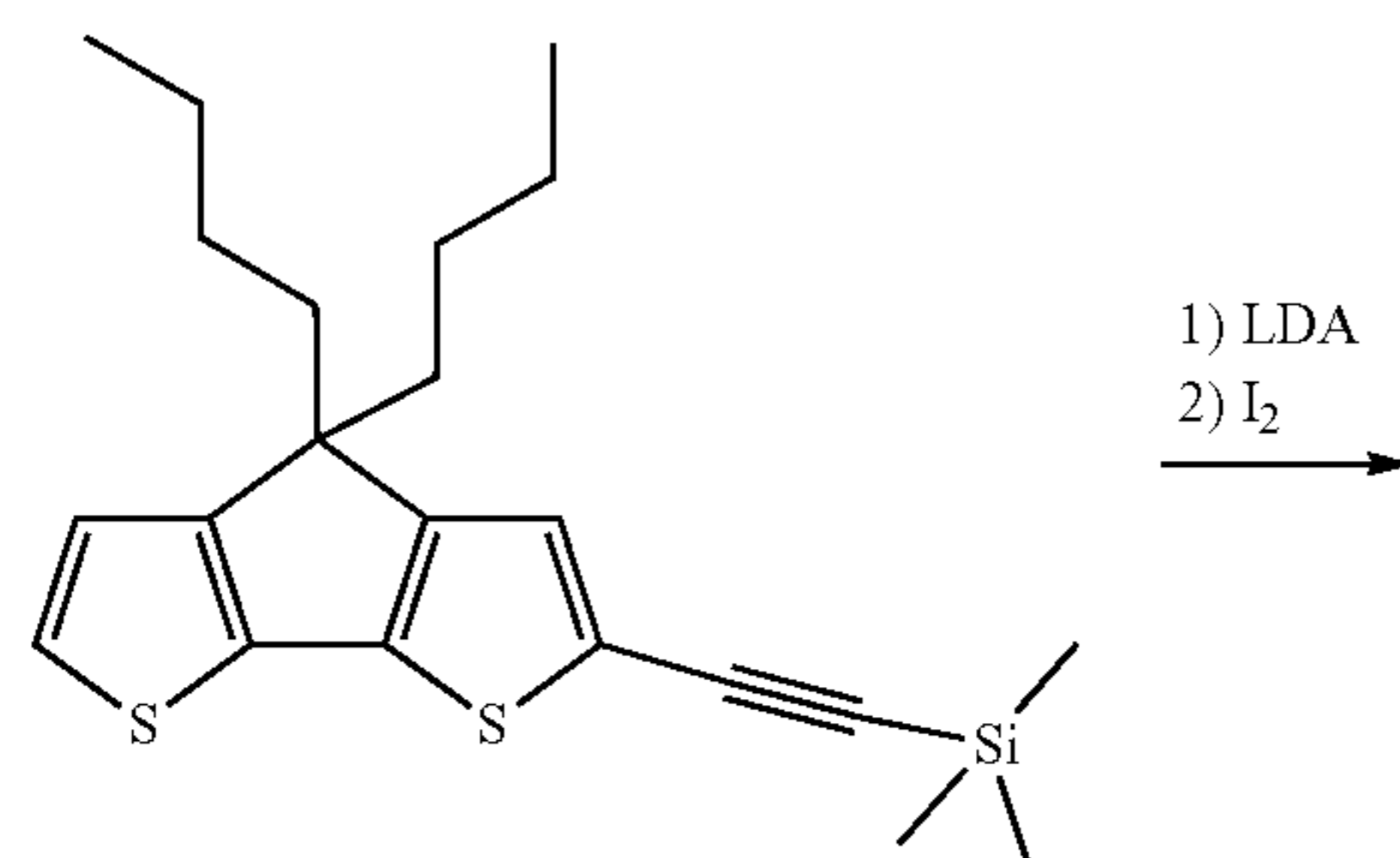
[0122]



**[0123]** In a round bottom flask, 0.91 g (2.46 mmol) 4-bromo-7,7-dibutyl-3,11-dithiatricyclo[6.3.0.0<sup>2,6</sup>]undeca-1(8),2(6),4,9-tetraene, 100 mg tri-tert-butylphosphonium tetrafluoroborate, 110 mg tris(dibenzylideneacetone) dipalladium(0) and 0.725 g (7.4 mmol) TMS-acetylene was combined in 6 mL TEA in a sealed pressure tube. Mixture was held at 60° C. for 18 h then poured into 25 mL water containing 5 mL of acetic acid (pH 6-7). The product was extracted into methylene chloride, concentrated and purified on silica gel (hexane) yielding 640 mg dark oil, (67% yield). UV/Vis max 360 nm, LCMS m/z=387.2.

D. 2-(7,7-dibutyl-10-iodo-3,11-dithiatricyclo[6.3.0.0<sup>2,6</sup>]undeca-1(8),2(6),4,9-tetraen-4-yl)ethynyl-trimethyl-silane

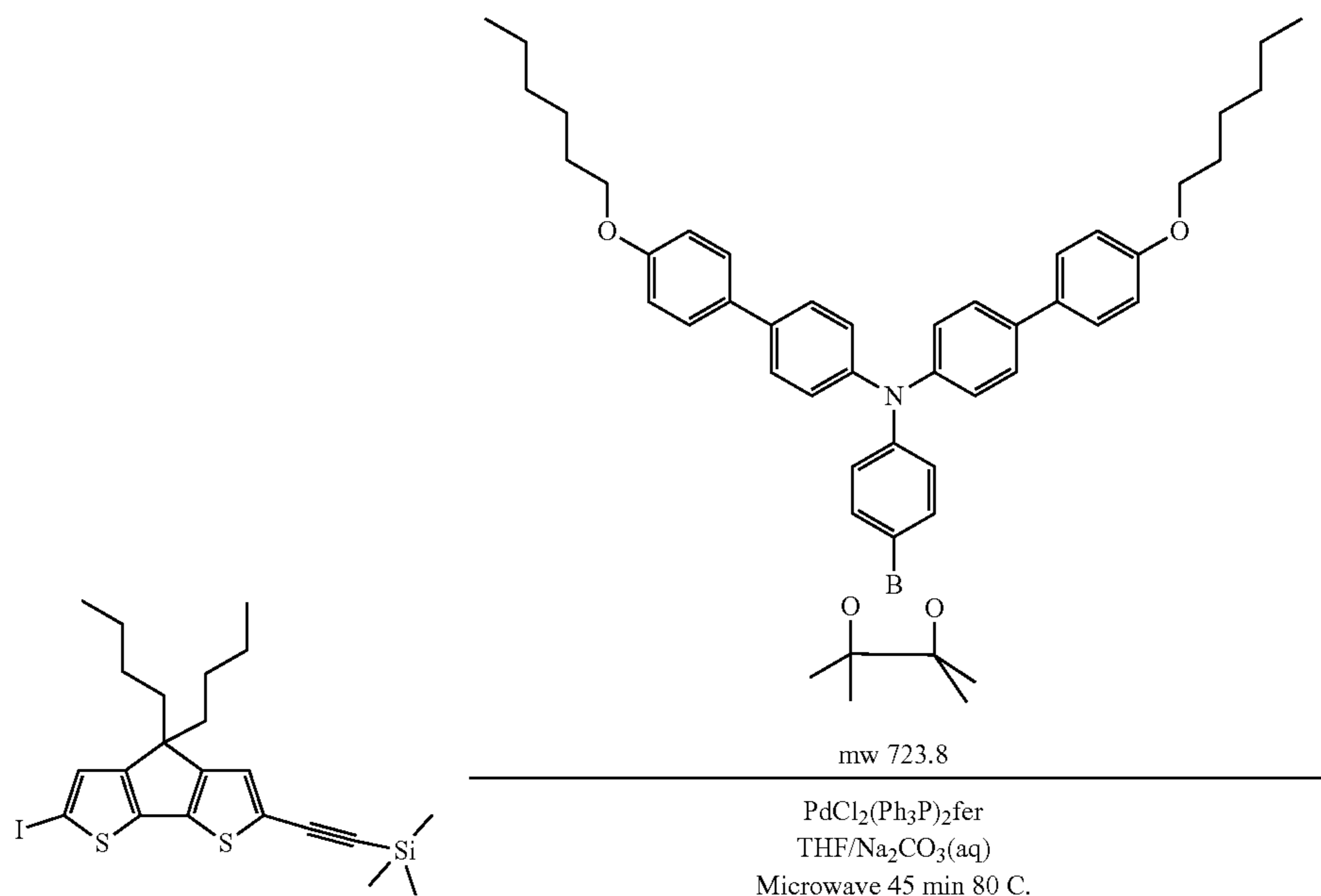
**[0124]**



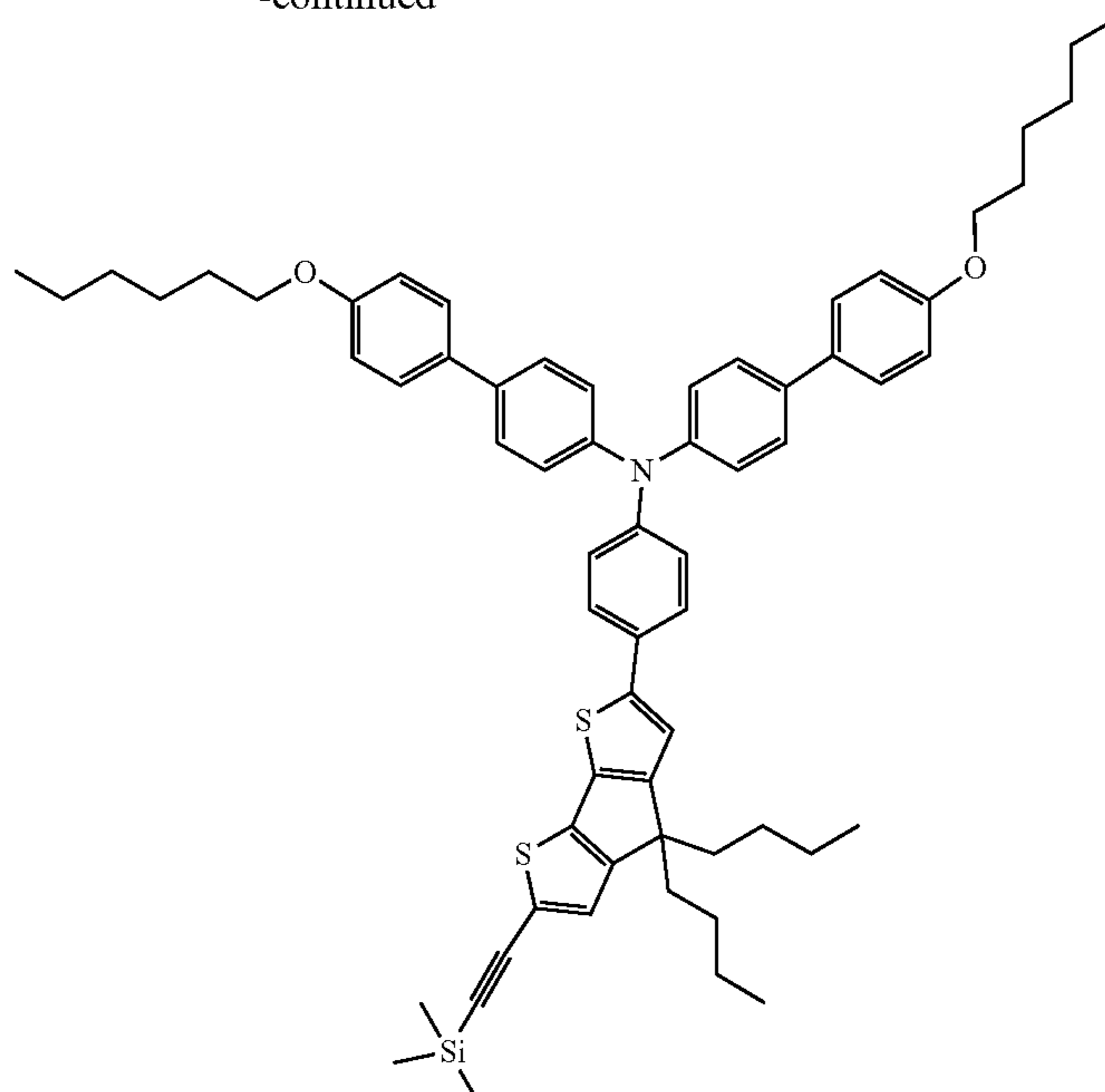
**[0125]** In a round bottom flask, 300 mg (0.775 mmol) 4,4-dibutyl-2-TMS-acetylene-cyclopentadithiophene was added to 4 mL diethyl ether at -78° C. 1.5 mL LDA (1 M solution, 1.5 mmol) was added, then batch was warmed to 0° C. for 15 min. Batch was cooled back to -78° C. and 381 mg (1.5 mmol) iodine in 4 mL ether added. Batch was warmed to rt. HPLC showed complete reaction. Purification on silica gel (hexane) yielded 300 mg yellow oil (75% yield). UV/Vis max 370 nm, LCMS m/z=512.9.

E. N-[4-[7,7-dibutyl-10-(2-trimethylsilylethynyl)-3,11-dithiatricyclo[6.3.0.0<sup>2,6</sup>]undeca-1(8),2(6),4,9-tetraen-4-yl]phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline

**[0126]**



-continued

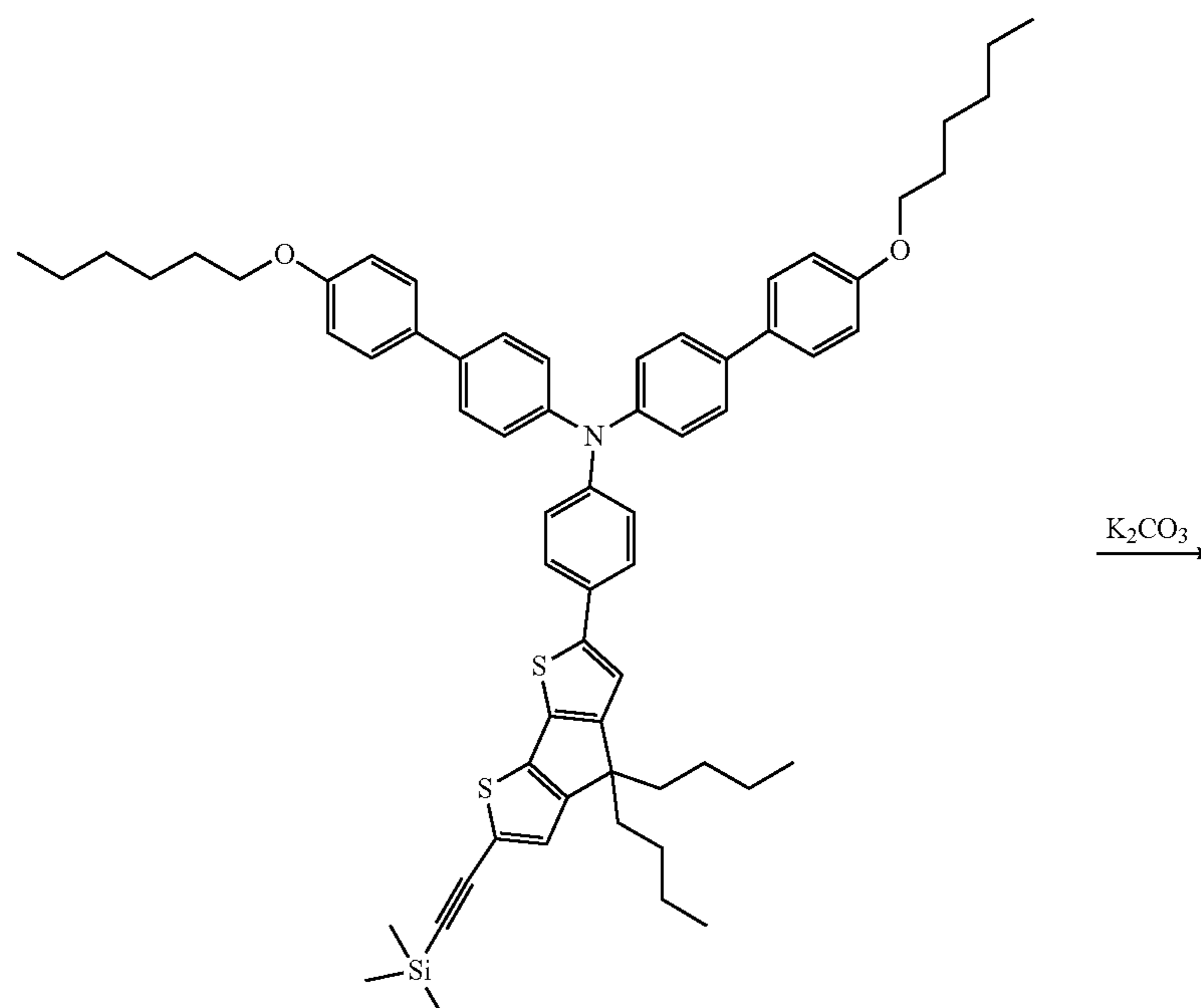


**[0127]** In a round bottom flask, 100 mg (0.195 mmol) 2-(7,7-dibutyl-10-iodo-3,11-dithiatricyclo[6.3.0.0.2,6]undeca-1(8),2(6),4,9-tetraen-4-yl)ethynyl-trimethyl-silane, 141 mg (0.195 mmol) N,N-bis[4-(4-hexoxyphenyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline and 30 mg (0.04 mmol) dichloro 1,1'-bis(diphenylphosphino)ferrocene palladium(II) was combined in 3 mL THF and 2 mL 10% Na<sub>2</sub>CO<sub>3</sub>. Mixture was microwaved at 80° C. for 45 min then poured into 20 mL water. The product was

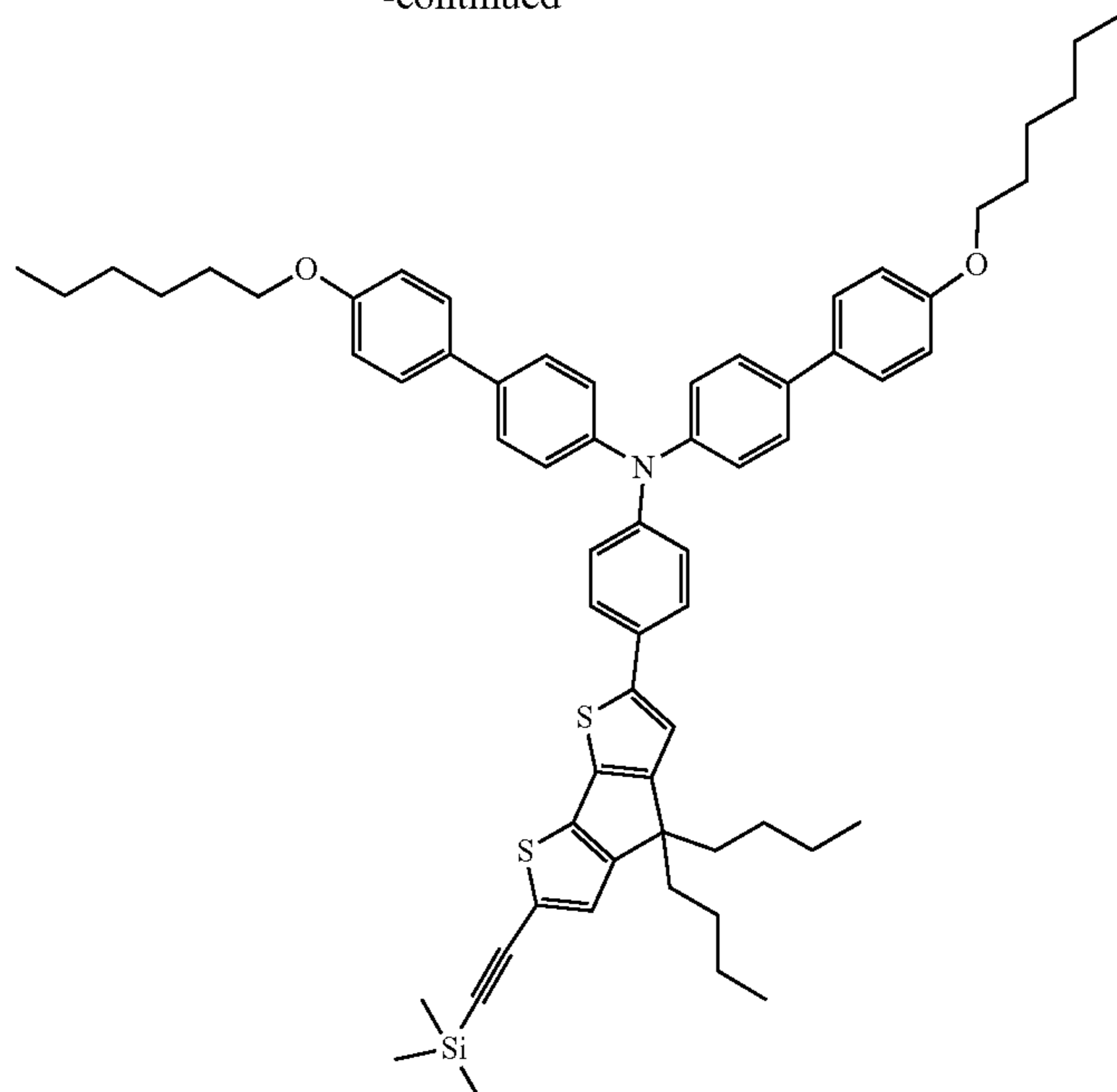
extracted into methylene chloride and purified on silica gel (hexane/methylene chloride) yielding 86 mg (0.087 mmol, 44.6% yield). UV/Vis max 420 nm, LCMS m/z=982.4.

F. N-[4-(7,7-dibutyl-10-ethynyl-3,11-dithiatricyclo[6.3.0.0.2,6]undeca-1(8),2(6),4,9-tetraen-4-yl)phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline

**[0128]**



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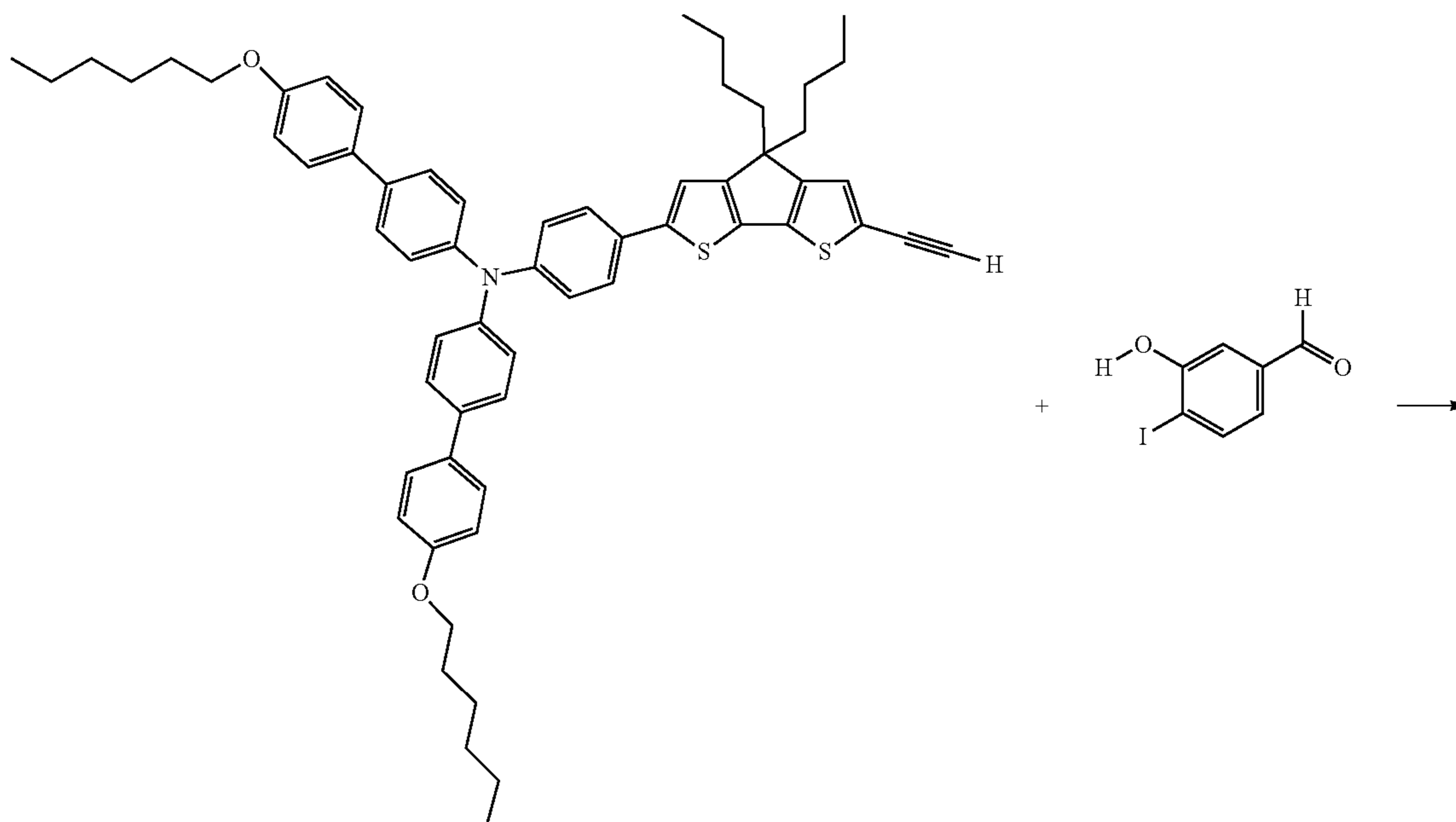


**[0129]** In a round bottom flask, 86 mg (0.087 mmol) N-[4-[7,7-dibutyl-10-(2-trimethylsilylethynyl)-3,11-dithiatricyclo[6.3.0.02,6]undeca-1(8),2(6),4,9-tetraen-4-yl]phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline and 200 mg  $K_2CO_3$  was combined in 3 mL  $CH_2Cl_2$  and 3 mL methanol stirred at rt for 1 h. 10 mL water was added, organic layer separated, dried and concentrated, yielding 69 mg (87% yield).

UV/Vis max 420 nm, LCMS  $m/z=910.6$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.44-7.51 (m, 10H; CH<sub>arom</sub>), 7.09-7.18 (m, 8H; CH<sub>arom</sub>), 6.93-6.96 (m, 4H; CH<sub>arom</sub>), 3.98 (t, 4H;

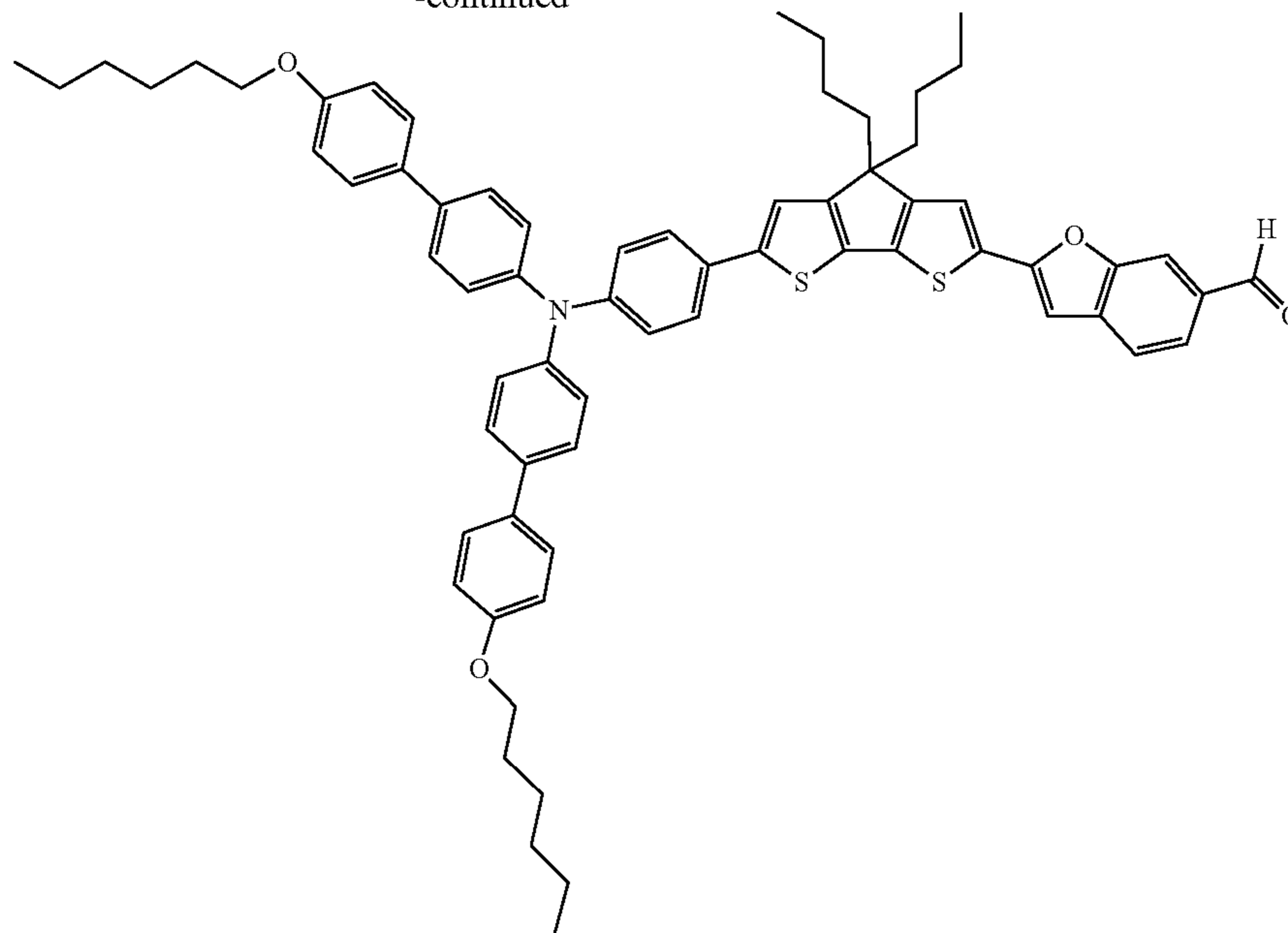
—OCH<sub>2</sub>-), 3.45 (s, 1H; acetylene-H), 1.75-1.84 (m, 8H; —CH<sub>2</sub>-arom, —CH<sub>2</sub>-), 1.43-1.48 (m, 4H; —CH<sub>2</sub>-), 1.33-1.36 (m, 8H; —CH<sub>2</sub>-), 1.13-1.18 (m, 4H; —CH<sub>2</sub>-), 0.88-0.92 (m, 10H; —CH<sub>2</sub>-, —CH<sub>3</sub>), 0.76 (t, 6H; —CH<sub>3</sub>).

G. 2-[7,7-dibutyl-10-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-3,11-dithiatricyclo[6.3.0.02,6]undeca-1(8),2(6),4,9-tetraen-4-yl]benzofuran-6-carbaldehyde

**[0130]**



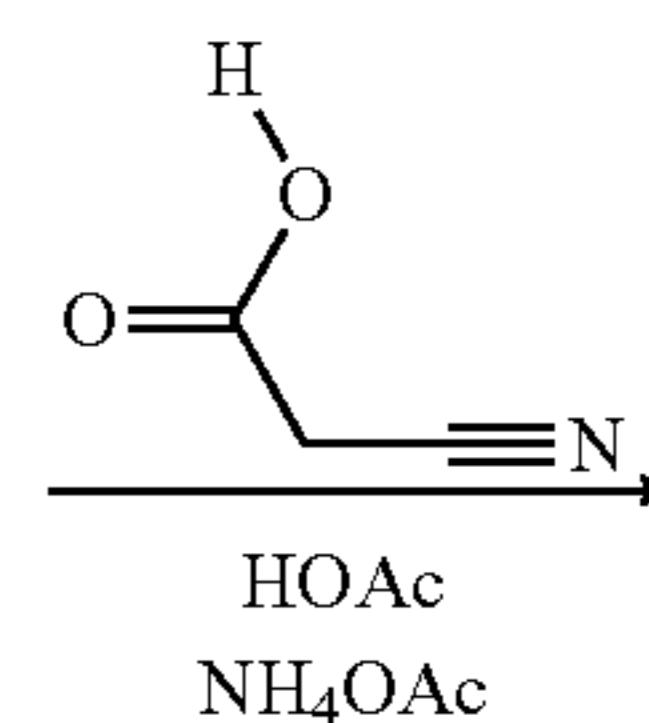
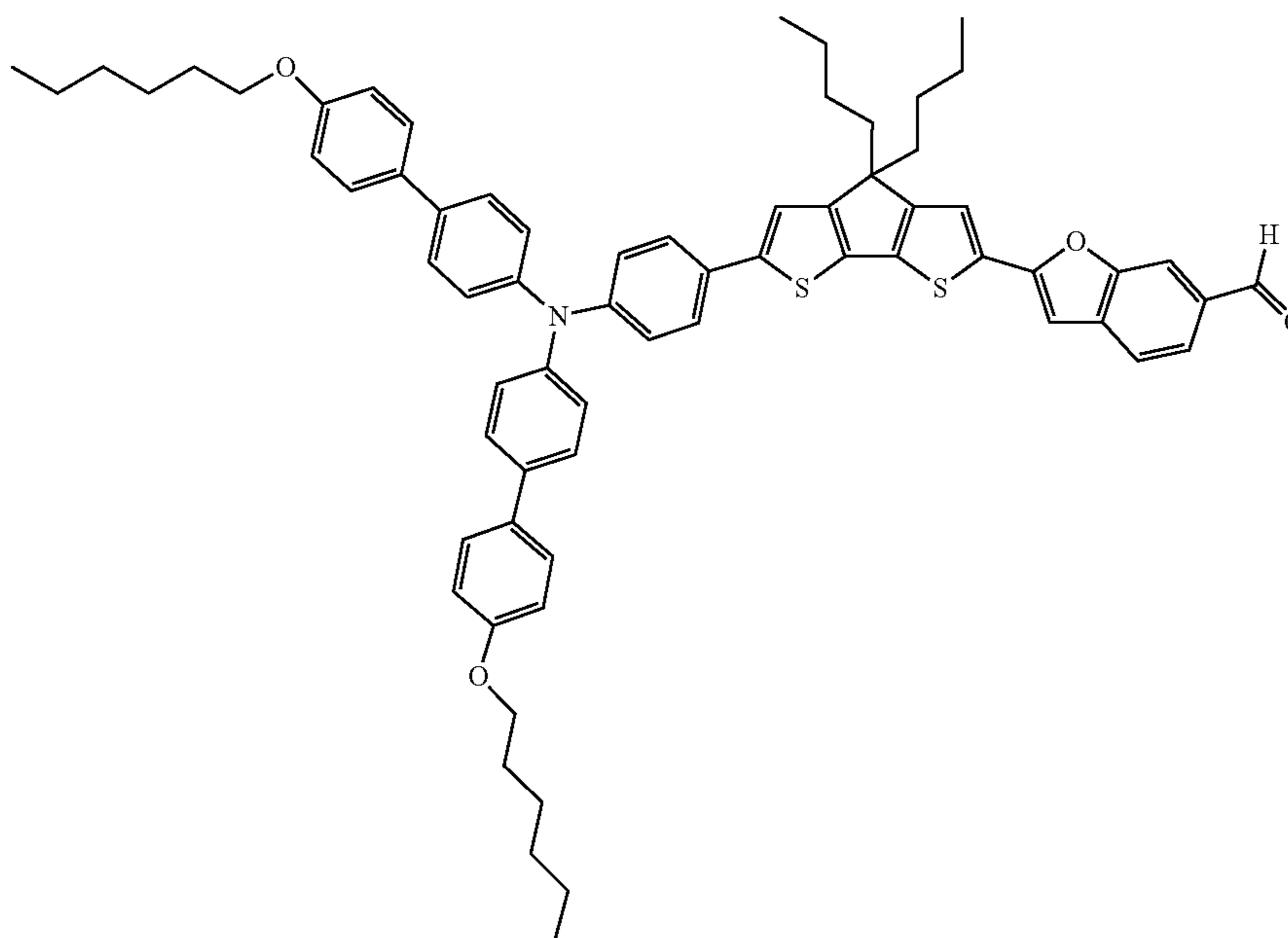
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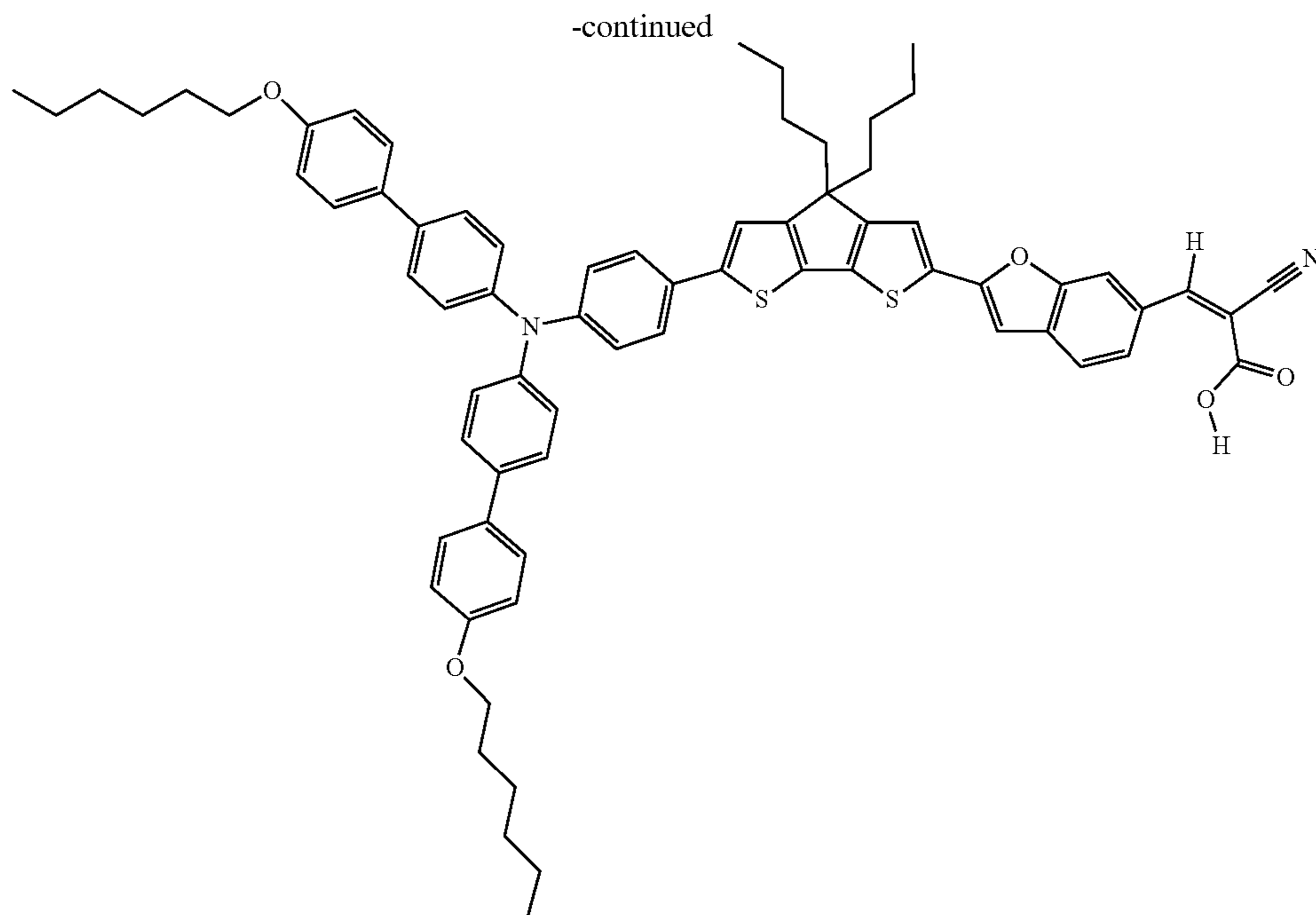


**[0131]** In a round bottom flask, 69 mg (0.0757 mmol) N-[4-(7,7-dibutyl-10-ethynyl-3,11-dithiatricyclo[6.3.0.0.2,6]undeca-1(8),2(6),4,9-tetraen-4-yl)phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline, 18 mg (0.072 mmol) 3-hydroxy-4-iodobenzaldehyde, 10 mg bis (triphenylphosphine)palladium dichloride and 10 mg CuI was combined in 4 mL tiethylamine. Batch was held at 40° C. for 3 h. Reaction mixture was poured into 20 mL water and the mixture n was adjusted to pH 6-7 using acetic acid. Product was extracted into methylene chloride. Organic layer was concentrated and product was purified on silica gel (hex/CH<sub>2</sub>Cl<sub>2</sub>), yielding 9 mg (0.0087 mmol, 12% yield) orange solid. UV/Vis max 470 nm, LCMS m/z=1031.6. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 9.97 (s, 1H; —CHO), 7.89 (s, 1H; CHarom), 7.68-7.70 (m, 1H; CHarom), 7.53, 7.55 (d, 1H;

CHarom), 7.36-7.47 (m, 10H; CHarom), 7.07-7.14 (m, 8H; CHarom), 6.88-6.91 (m, 4H; CHarom), 6.795, 6.798 (d, 1H; CHarom), 3.92 (t, 4H; —OCH<sub>2</sub>-), 1.83-1.87 (m, 4H; —CH<sub>2</sub>-), 1.70-1.78 (m, 4H; —CH<sub>2</sub>-arom), 1.37-1.45 (m, 4H; —CH<sub>2</sub>-), 1.26-1.31 (m, 8H; —CH<sub>2</sub>-), 1.10-1.18 (m, 8H; —CH<sub>2</sub>-), 0.88-0.94 (m, 4H; —CH<sub>2</sub>-), 0.82-0.86 (m, 6H; —CH<sub>3</sub>), 0.72 (t, 6H; —CH<sub>3</sub>).

H. (Z)-2-cyano-3-[2-[7,7-dibutyl-10-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-3,11-dithiatricyclo[6.3.0.0.2,6]undeca-1(8),2(6),4,9-tetraen-4-yl]benzofuran-6-yl]prop-2-enoic Acid

**[0132]**

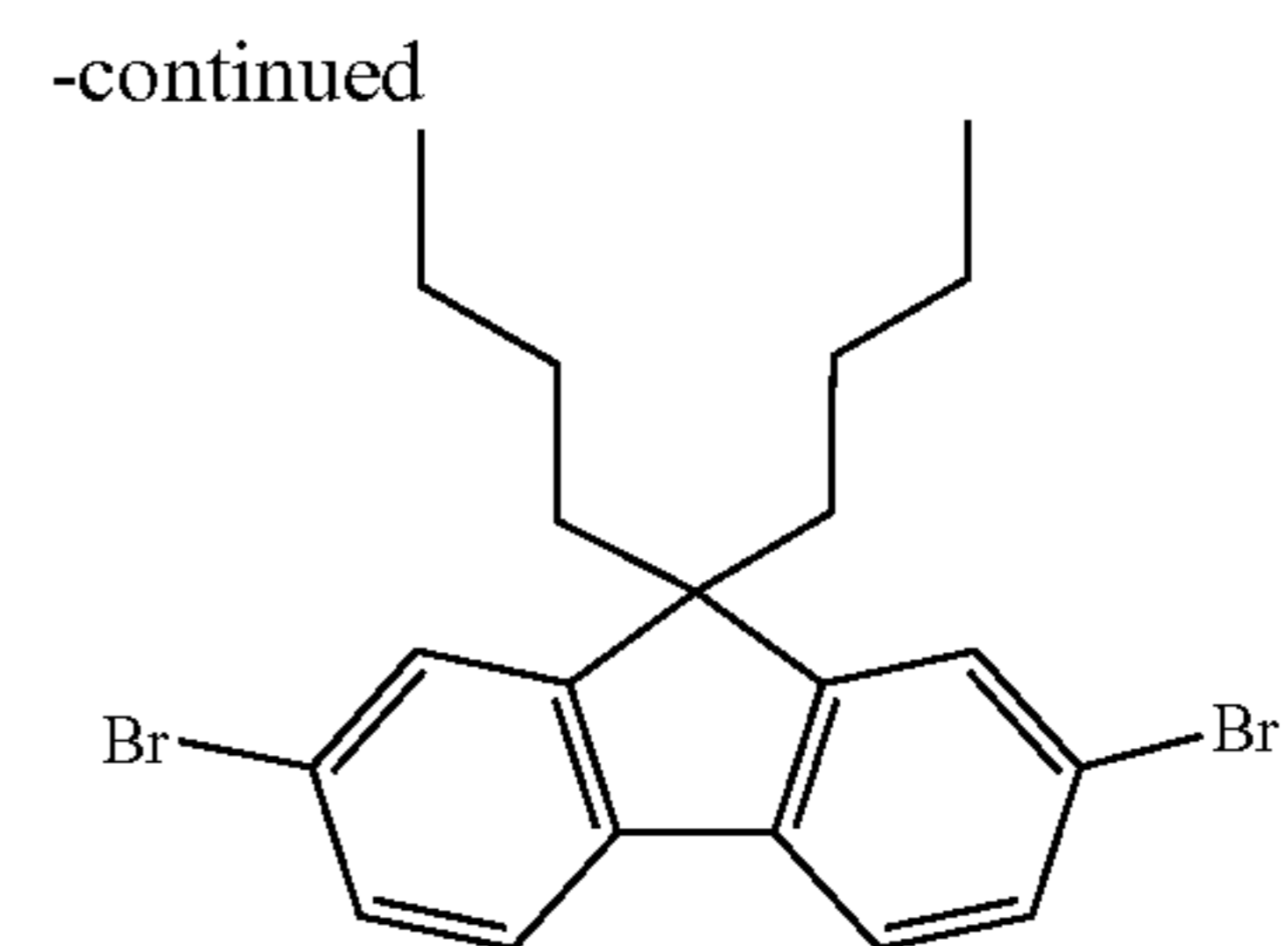
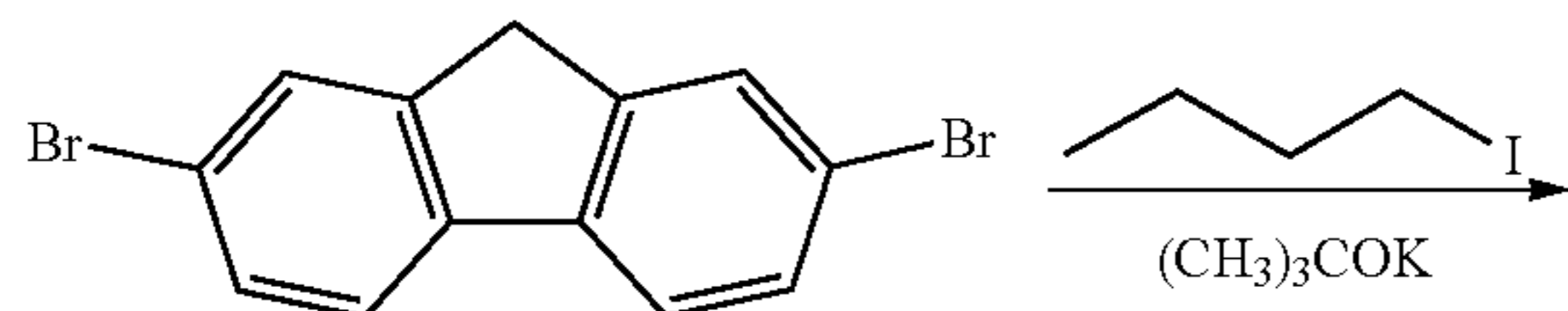


**[0133]** In a round bottom flask, 9 mg (0.0087 mmol) 2-[7,7-dibutyl-10-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-3,11-dithiatricyclo[6.3.0.0.2,6]undeca-1(8),2(6),4,9-tetraen-4-yl]benzofuran-6-carbaldehyde, 5 mg (0.06 mmol) cyanoacetic acid and 15 mg (0.19 mmol) ammonium acetate was combined in 5 mL acetic acid. Batch was held at reflux for 8 h. 20 mL of water was added and product was extracted into methylene chloride, yielding 10.3 mg red solid. UV/Vis max 500 nm, LCMS  $m/z=1098.4$ .

Example 11. Synthesis of (Z)-2-cyano-3-[2-[9,9-dibutyl-7-[4-(N-phenylanilino)phenyl]fluoren-2-yl]benzofuran-6-yl]prop-2-enoic Acid (D15)

A. 2,7-dibromo-9,9-dibutyl-fluorene

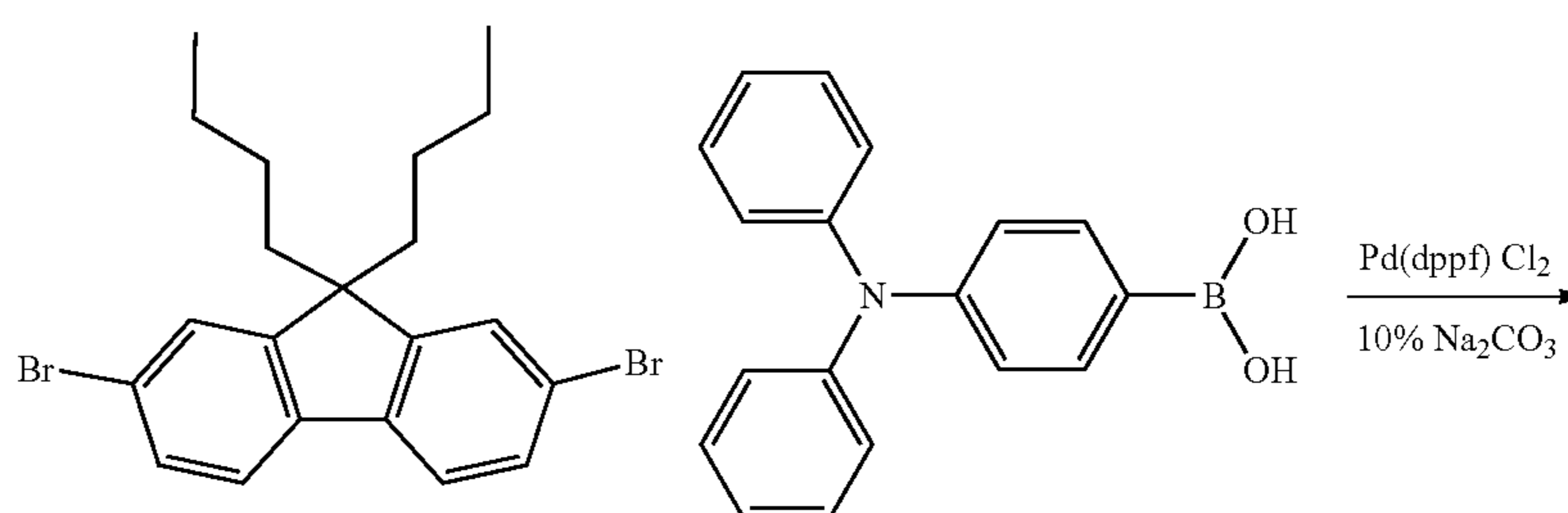
**[0134]**



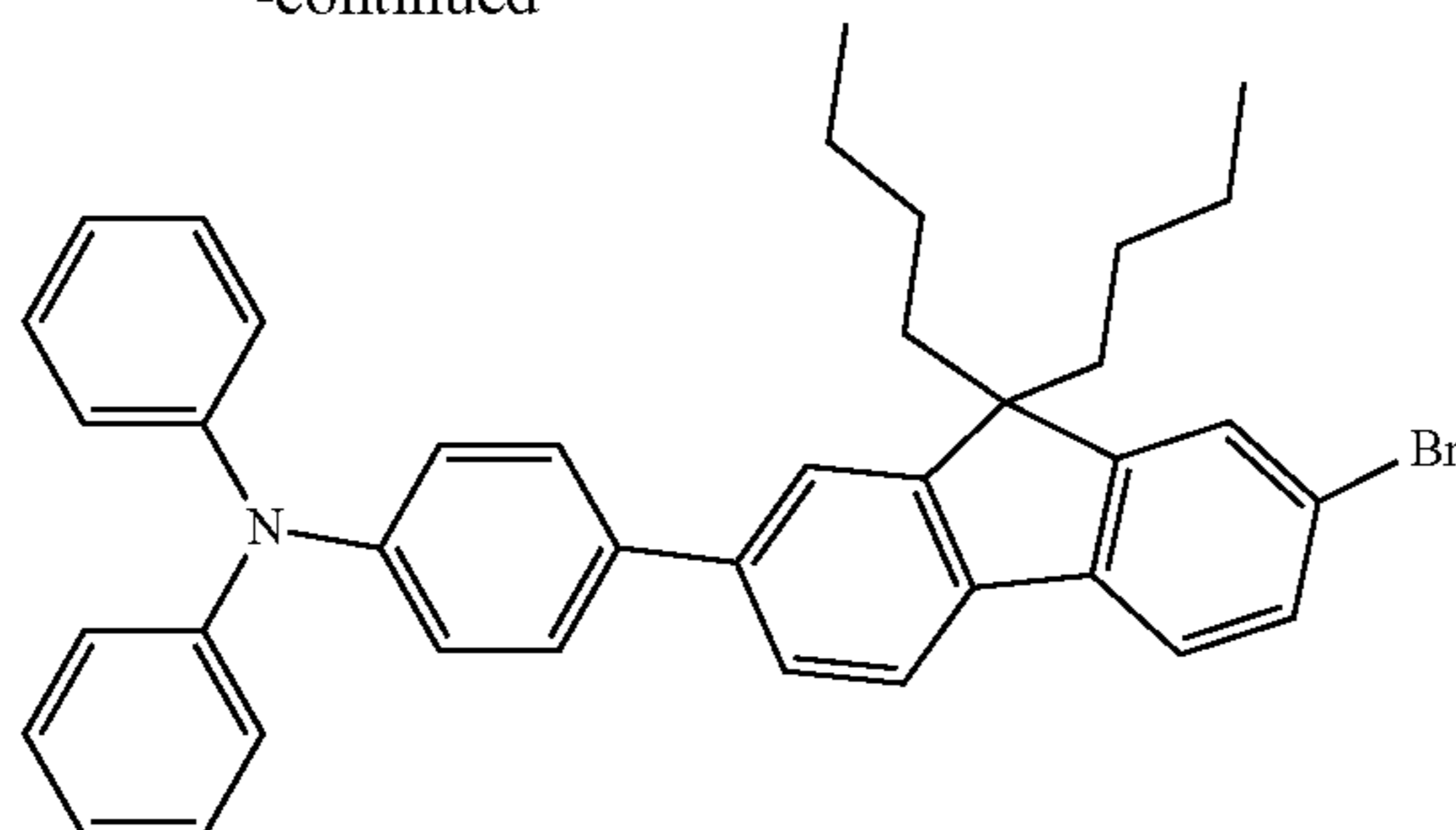
**[0135]** To a 50 mL flask, 2,7-dibromofluorene (2.50 g, 7.76 mmol) and anhydrous tetrahydrofuran (30 mL) were added and cooled to 0° C. To this reaction mixture sodium tert-butoxide (1.86 g, 19.41 mmol) was added and stirred for 30 min at 0° C., then n-iodobutane (3.21 g, 17.47 mmol) was added slowly to it. The reaction temperature was brought to room temperature and mixture was stirred overnight. To terminate the reaction, cold water (20 mL) was added and then extracted with ethylacetate. Organic layer was dried over anhydrous sodium sulfate and concentrated. The residue was purified by chromatography on silica gel (hexane is the elutant) to afford 2,7-dibromo-9,9-dibutyl-fluorene (2.5 g). UV/Vis max 280 nm.

B. 4-(7-bromo-9,9-dibutyl-fluoren-2-yl)-N,N-diphenyl-aniline

**[0136]**

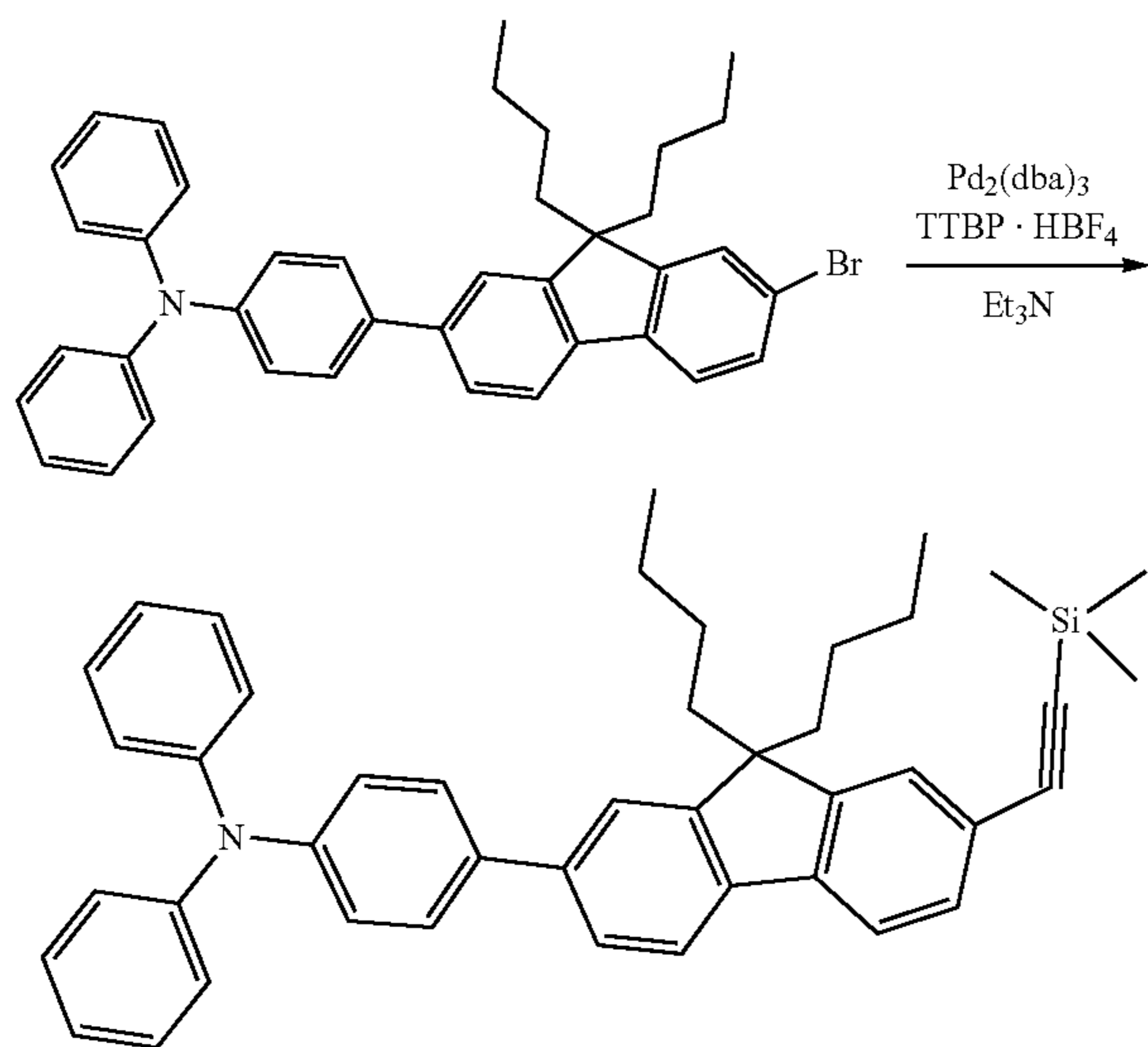


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**[0137]** 2,7-dibromo-9,9-dibutyl-fluorene (0.36 g, 0.83 mmol), [4-(N-phenylanilino)phenyl]boronic acid (0.08 g, 0.27 mmol), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.04 g, 0.05 mmol), 10% aqueous sodium carbonate solution (6 mL), and tetrahydrofuran (15 mL) were added into a 20 mL microwave vial and reacted for 15 min at 100° C. by microwave. The reaction mixture was extracted with ethylacetate (15 mL) and organic layer was washed with water (10 mL) and brine solution (10 mL), respectively. Organic layer was dried over anhydrous sodium sulfate and concentrated. This crude was purified using column chromatography on silica gel (0 to 10% ethyl acetate in hexanes) to obtain 4-(7-bromo-9,9-dibutyl-fluoren-2-yl)-N,N-diphenyl-aniline (0.08 g). UV/Vis max 350 nm, LCMS  $m/z=600$ .

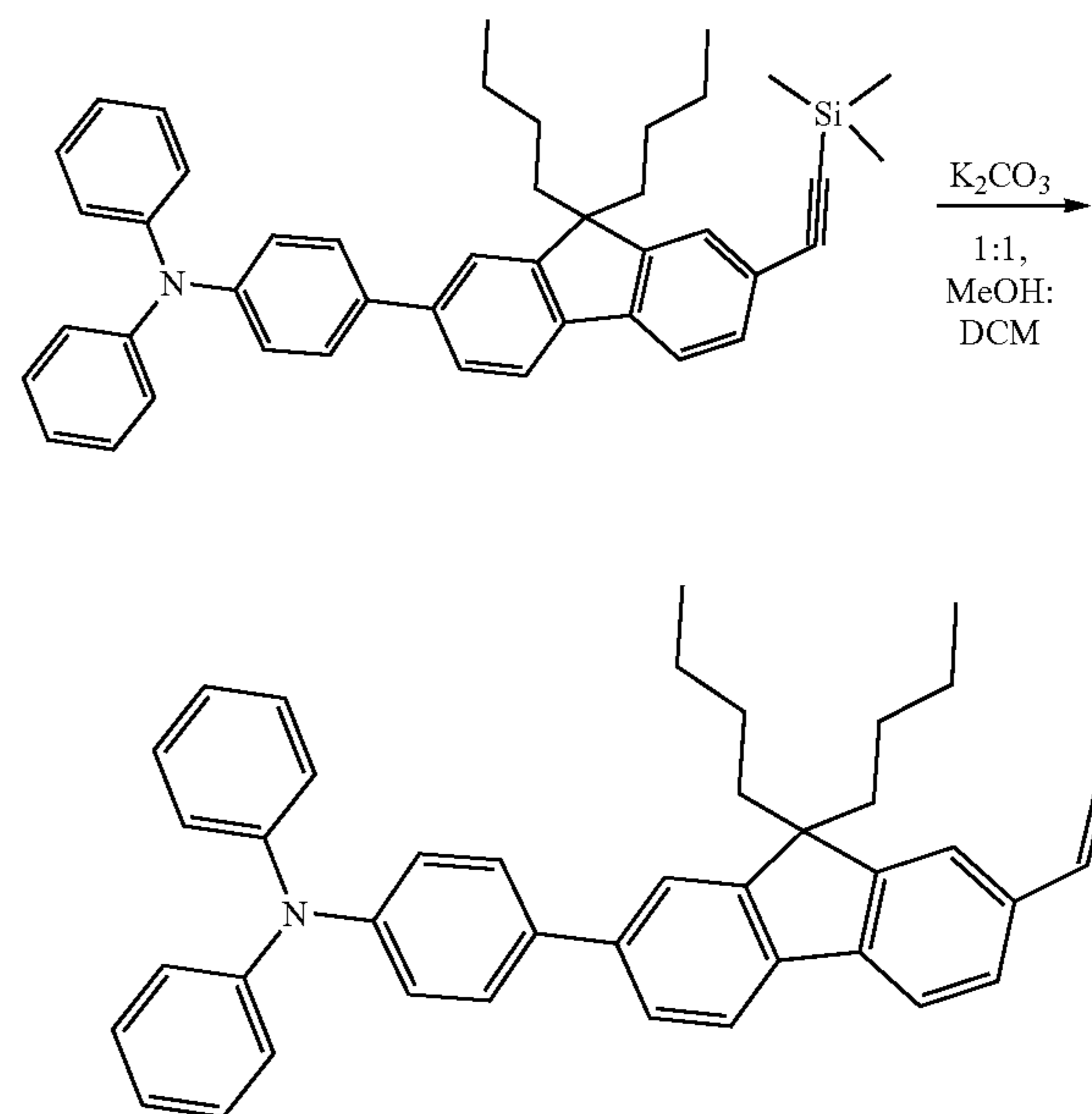
C. 4-[9,9-dibutyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]-N,N-diphenyl-aniline

**[0138]**

**[0139]** To a 50 mL flask Tris(dibenzylideneacetone)dipalladium(0) (0.28 g, 0.30 mmol), Tri-tert-butylphosphonium tetrafluoroborate (0.087 g, 0.30 mmol), 4-(7-bromo-9,9-dibutyl-fluoren-2-yl)-N,N-diphenyl-aniline (0.9 g, 1.50 mmol), trimethylsilylacetylene (0.44 g, 4.50 mmol) and triethylamine (0. G, mmol) were added under nitrogen. The reaction mixture was stirred for 20 h at 45° C. The reaction

mixture was extracted with ethylacetate (30 mL) and washed with water (10 mL) and brine solution (10 mL). Organic layer was dried over anhydrous sodium sulfate and concentrated. The crude product was purified using column chromatography on silica gel (0 to 10% ethylacetate in hexanes) to obtain 4-[9,9-dibutyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]-N,N-diphenyl-aniline (0.72 g). UV/Vis max 350 nm, LCMS  $m/z=618$ .

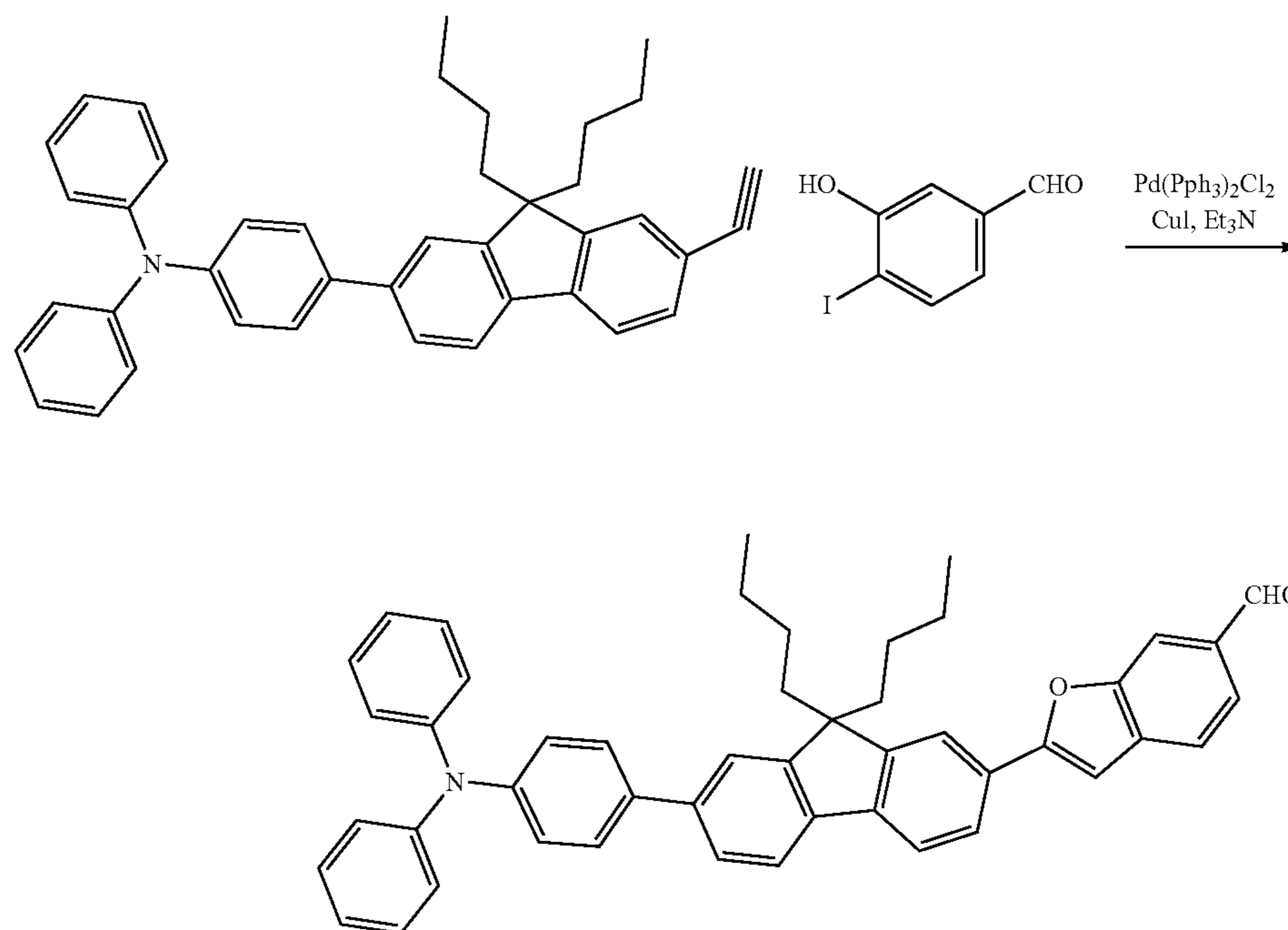
D. 4-(9,9-dibutyl-7-ethynyl-fluoren-2-yl)-N,N-diphenyl-aniline

**[0140]**

**[0141]** 4-[9,9-dibutyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]-N,N-diphenyl-aniline (0.72 g, 1.17 mmol) was added to a 50 mL flask, then dichloromethane (10 mL) and methanol (10 mL) were added under nitrogen. To this reaction mixture, anhydrous  $K_2CO_3$  (0.64 g, 4.66 mmol) was added and stirred for 3 h. The reaction mixture evaporated and the resulting crude product was dissolved in dichloromethane (30 mL) and filtered through the filtering funnel and mother liquor concentrated to obtain 4-(9,9-dibutyl-7-ethynyl-fluoren-2-yl)-N,N-diphenyl-aniline (0.62 g). UV/Vis max 350 nm, LCMS  $m/z=546$ .

## E. 2-[9,9-dibutyl-7-[4-(N-phenylanilino)phenyl]fluoren-2-yl]benzofuran-6-carbaldehyde

[0142]

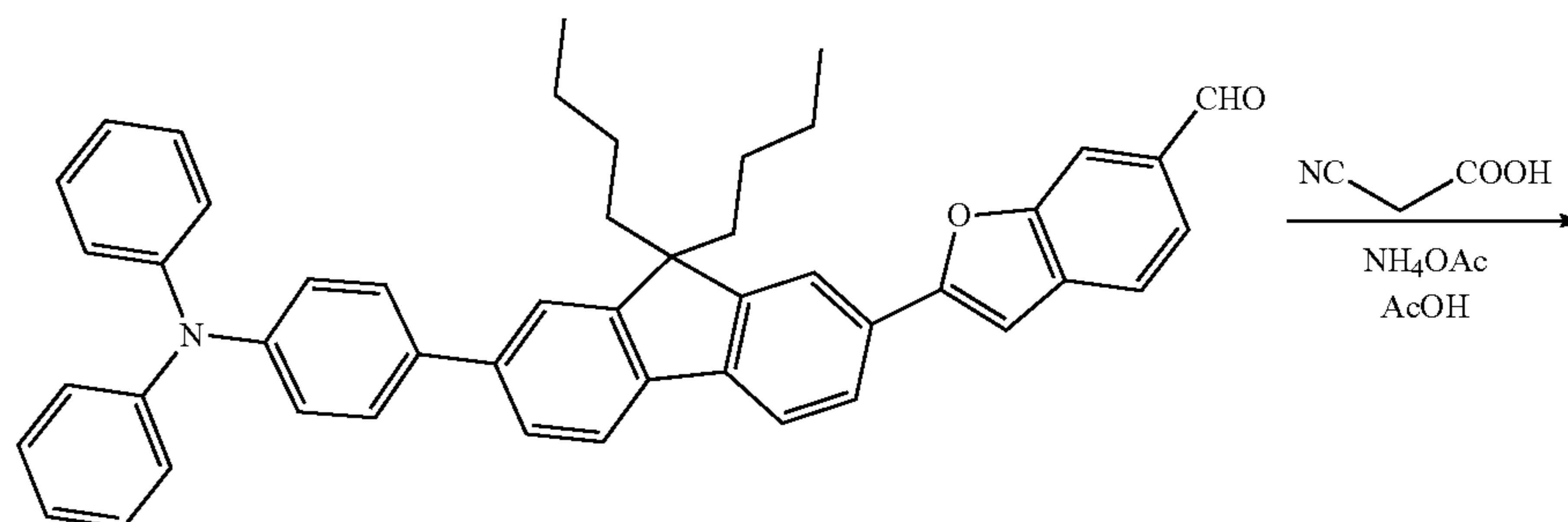


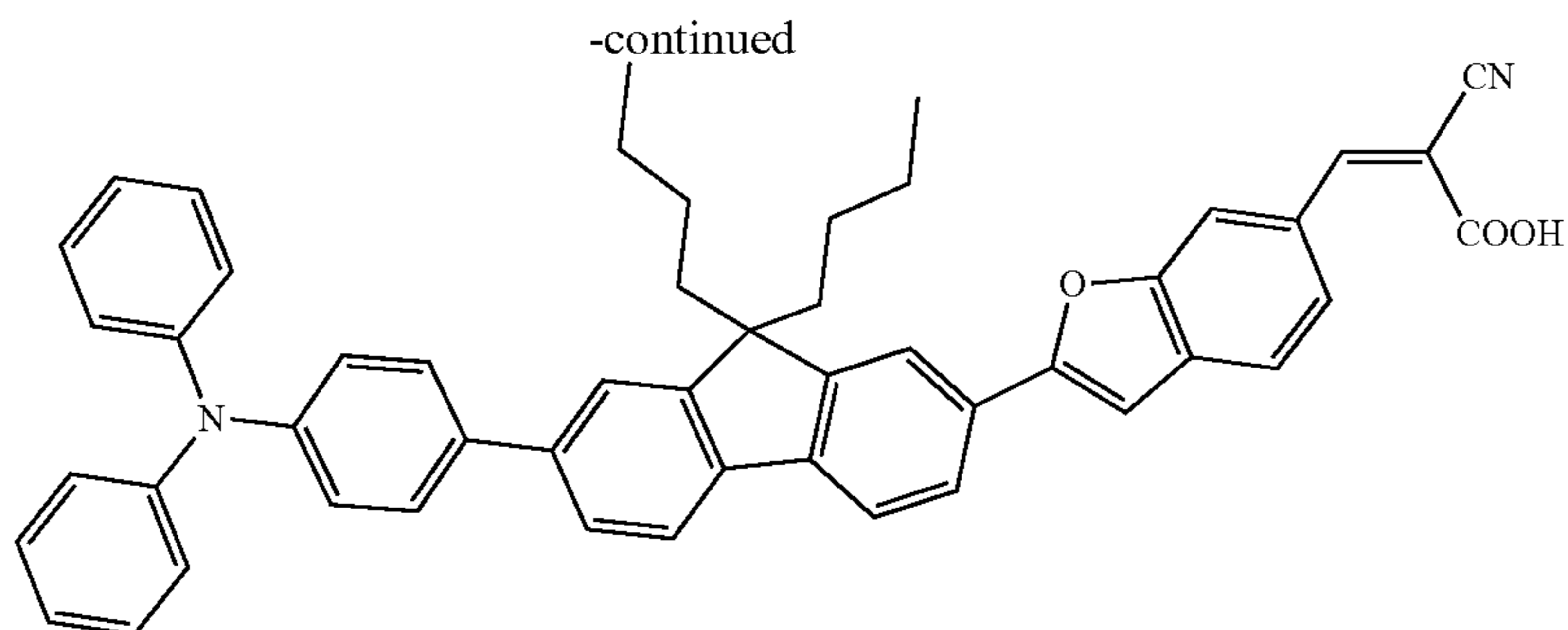
[0143] To a 50 mL flask 3-hydroxy-4-iodobenzaldehyde (0.27 g, 1.10 mmol), bis(triphenylphosphine)palladium dichloride (0.015 g, 0.22 mmol), and copper(I) iodide (0.0042 g, 0.22 mmol) were added under nitrogen. The flask was purged with nitrogen for 20 min, then a solution of 4-(9,9-dibutyl-7-ethynylfluoren-2-yl)-N,N-diphenylaniline (0.60 g, 1.10 mmol) in triethylamine (15 mL) degassed with nitrogen was added. The reaction was heated at 50° C. for 3 h, then cooled down to room temperature and quenched with water (25 mL). The reaction mixture was extracted with ethyl acetate (30 mL) and the organic layer washed with

brine solution and dried over sodium sulfate. The organic layer was filtered and concentrated. Crude product was purified using chromatography on silica gel (0 to 13% ethyl acetate in hexanes) to afford 2-[9,9-dibutyl-7-[4-(N-phenylanilino)phenyl]fluoren-2-yl]benzofuran-6-carbaldehyde (0.2 g). UV/Vis max 395 nm, LCMS m/z=666.

## F. (Z)-2-cyano-3-[2-[9,9-dibutyl-7-[4-(N-phenylanilino)phenyl]fluoren-2-yl]benzofuran-6-yl]prop-2-enoic Acid

[0144]



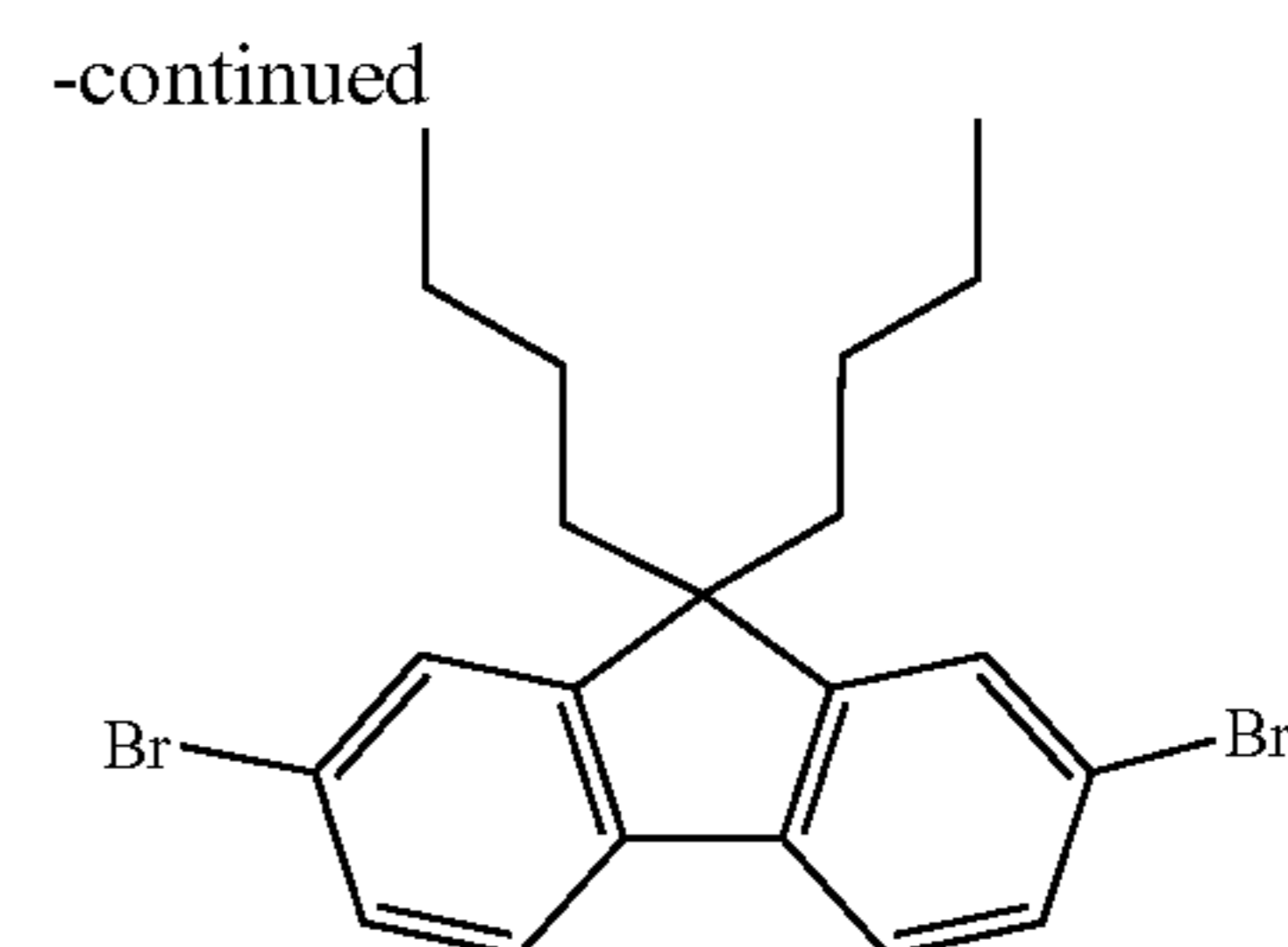
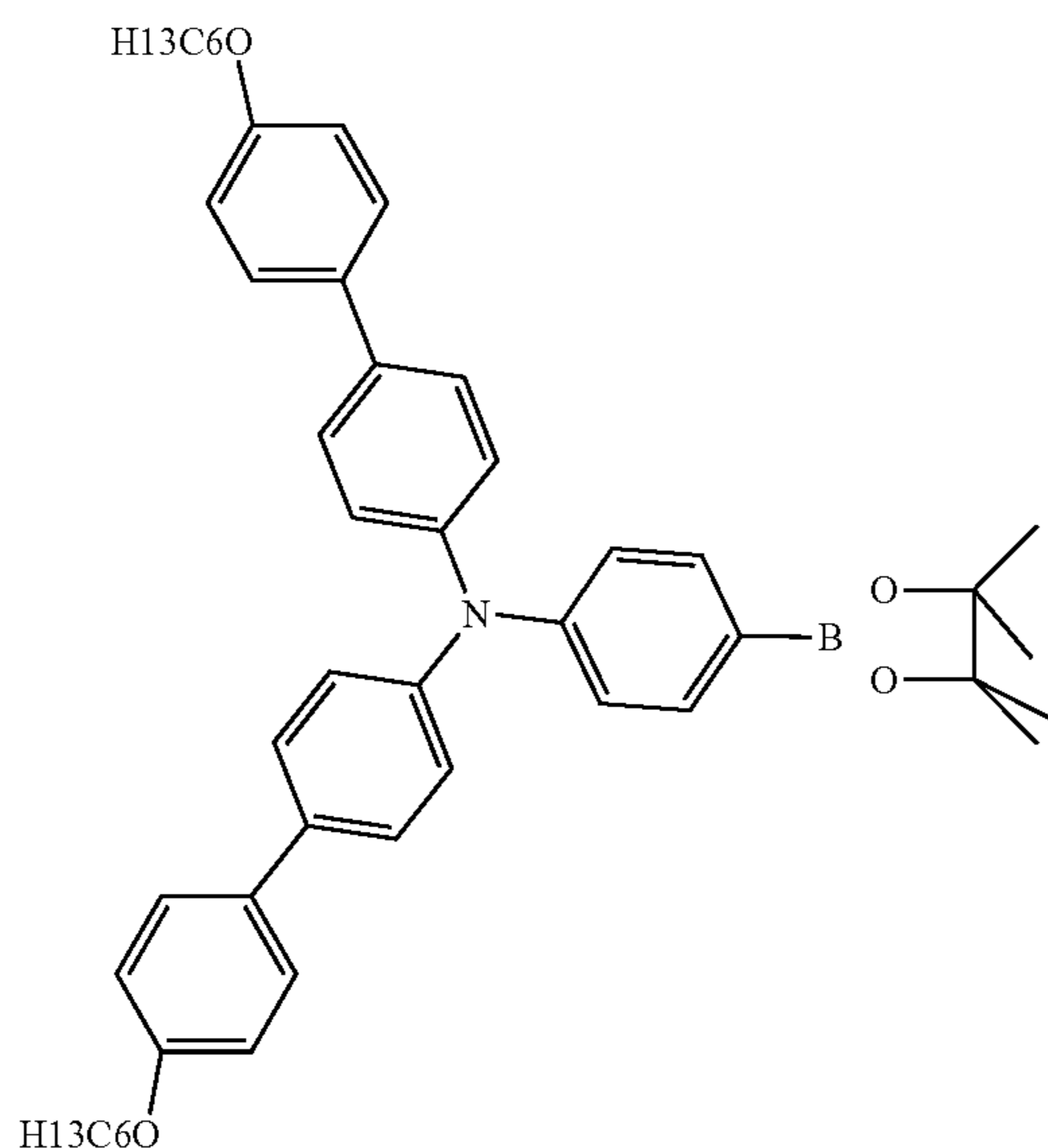
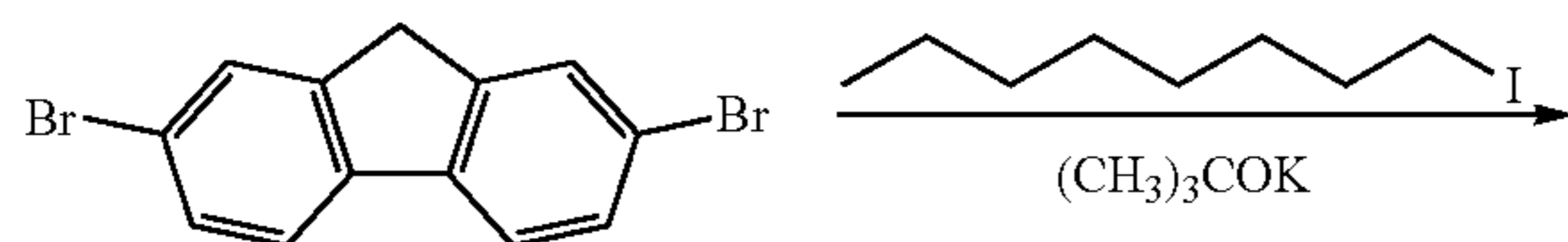


**[0145]** Acetic acid (5.0 mL) was added to 2-[9,9-dibutyl-7-[4-(N-phenylanilino)phenyl]fluoren-2-yl]benzofuran-6-carbaldehyde (0.2 g, 0.30 mmol), cyanoacetic acid (0.127 g, 1.50 mmol), and ammonium acetate (0.23 g, 3.0 mmol) and the reaction was heated to reflux for 1.5 h. The reaction was cooled to room temperature and diluted with dichloromethane (35 mL). The dichloromethane (35 mL) was washed with water (2×10 mL) and brine solution (10 mL). The organic layer dried over anhydrous sodium sulfate and concentrated to afford (Z)-2-cyano-3-[2-[9,9-dibutyl-7-[4-(N-phenylanilino)-phenyl]fluoren-2-yl]benzofuran-6-yl]prop-2-enoic acid (0.17 g), unidentified olefin isomer. UV/Vis max 425 nm, LCMS m/z=733.

Example 12. Synthesis of (E)-2-cyano-3-[2-[7-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-yl]prop-2-enoic Acid (D13)

A. 2,7-dibromo-9,9-dioctyl-fluorene

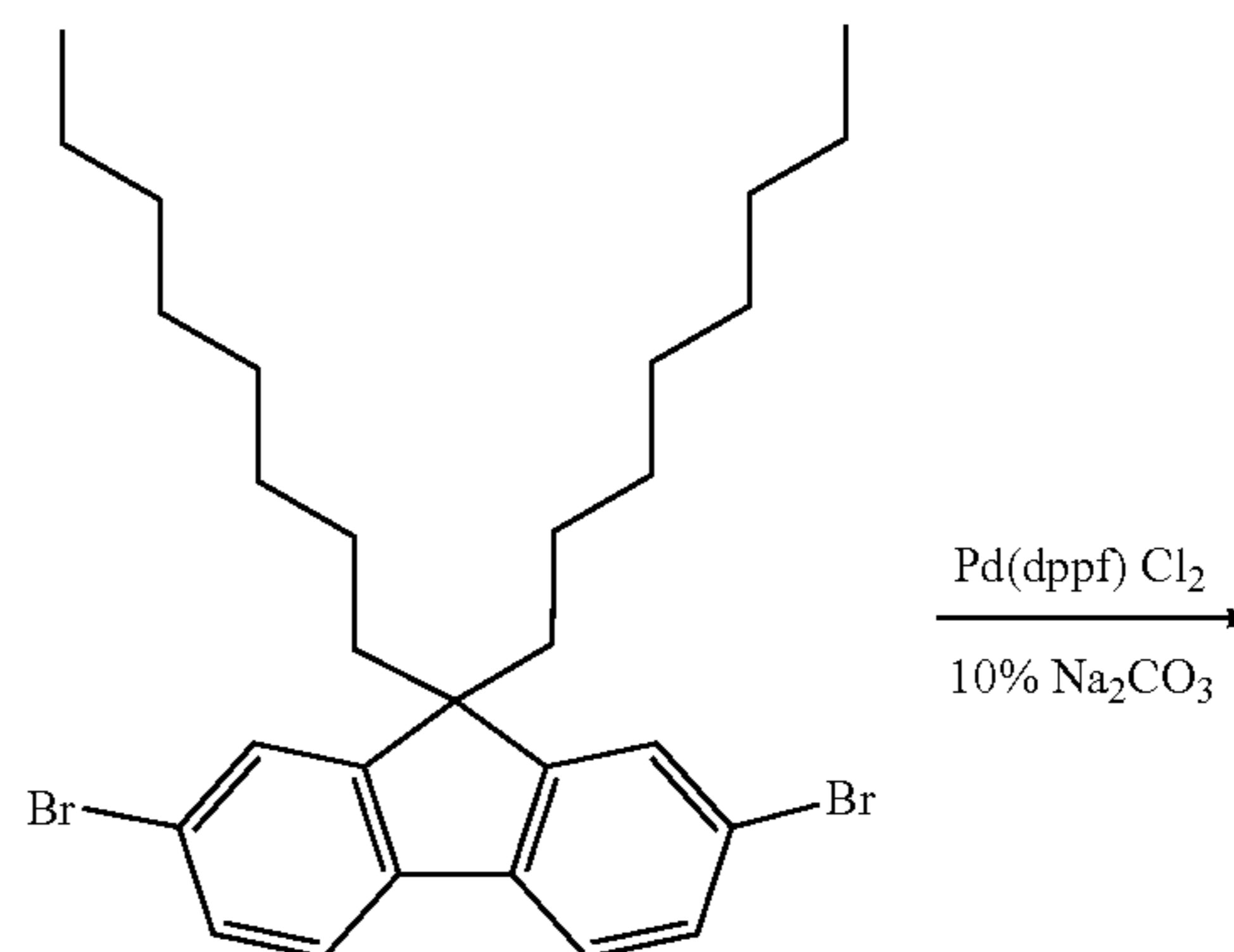
**[0146]**

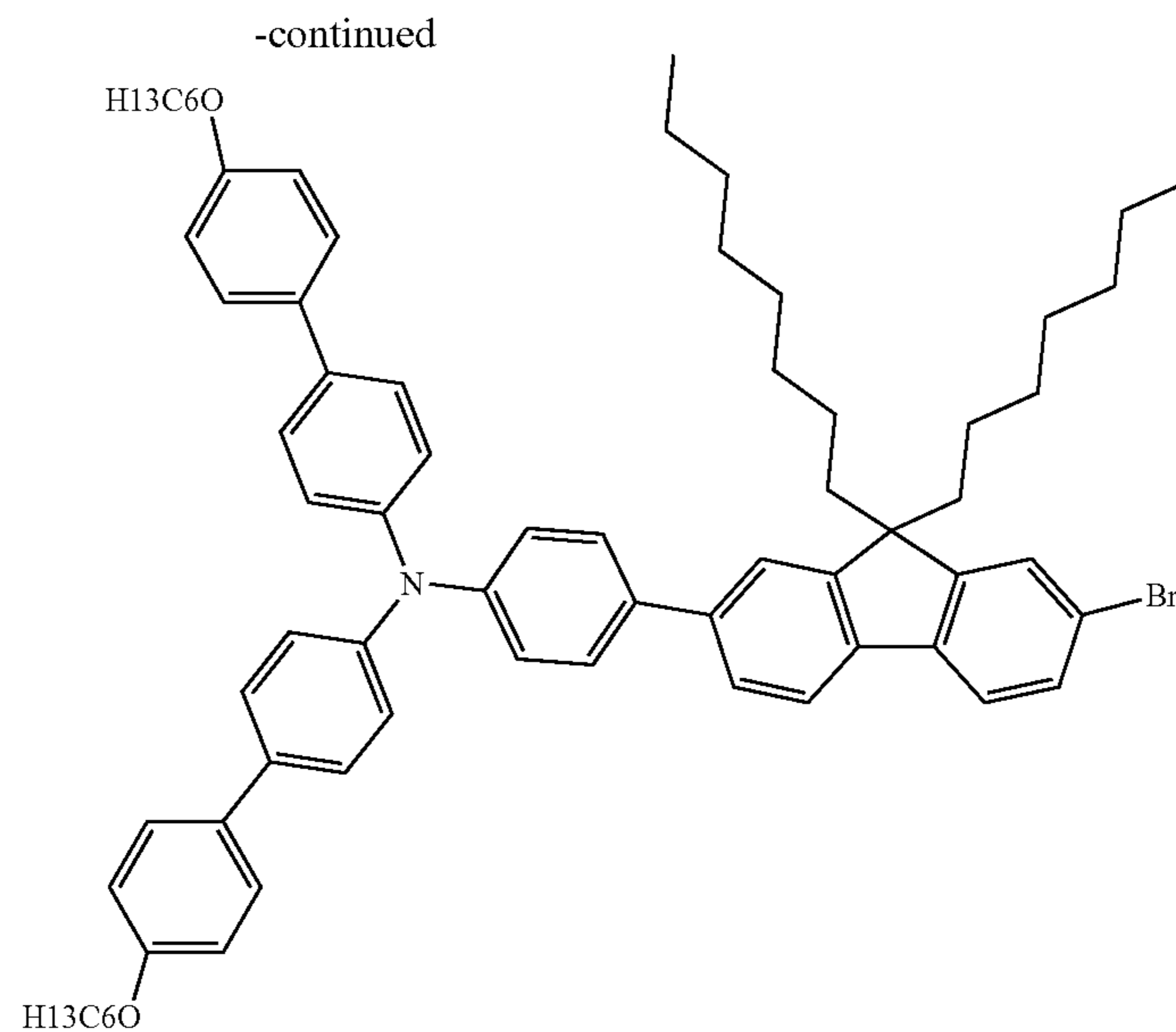


**[0147]** To a 50 mL flask, 2,7-dibromofluorene (4.0 g, 12.4 mmol) and anhydrous tetrahydrofuran (60 mL) were added and cooled to 0° C. To this reaction mixture, potassium tert-butoxide (3.48 g, 31.06 mmol) was added and stirred for 30 min at 0° C. and then n-iodooctane (6.56 g, 27.34 mmol) was added slowly. The reaction temperature was brought to room temperature stirred overnight. To terminate the reaction, cold water (20 mL) was added and then extracted with ethylacetate. Organic layer was dried over anhydrous sodium sulfate and concentrated. The residue was purified by chromatography on silica gel (hexane is the elutant) to afford 2,7-dibromo-9,9-dioctyl-fluorene (6.0 g). UV/Vis max 280 nm.

B. N-[4-(7-bromo-9,9-dioctyl-fluoren-2-yl)phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline

**[0148]**



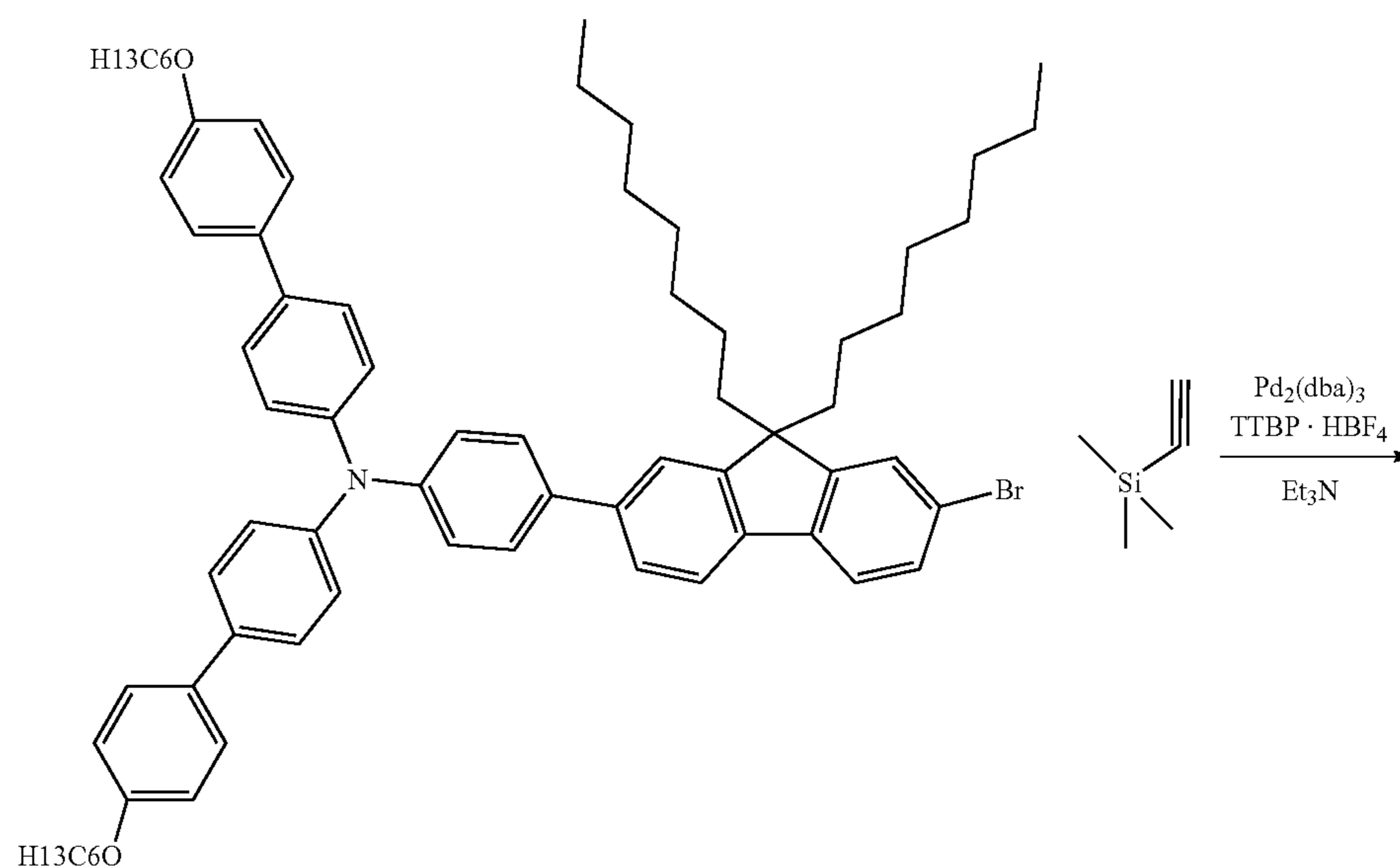


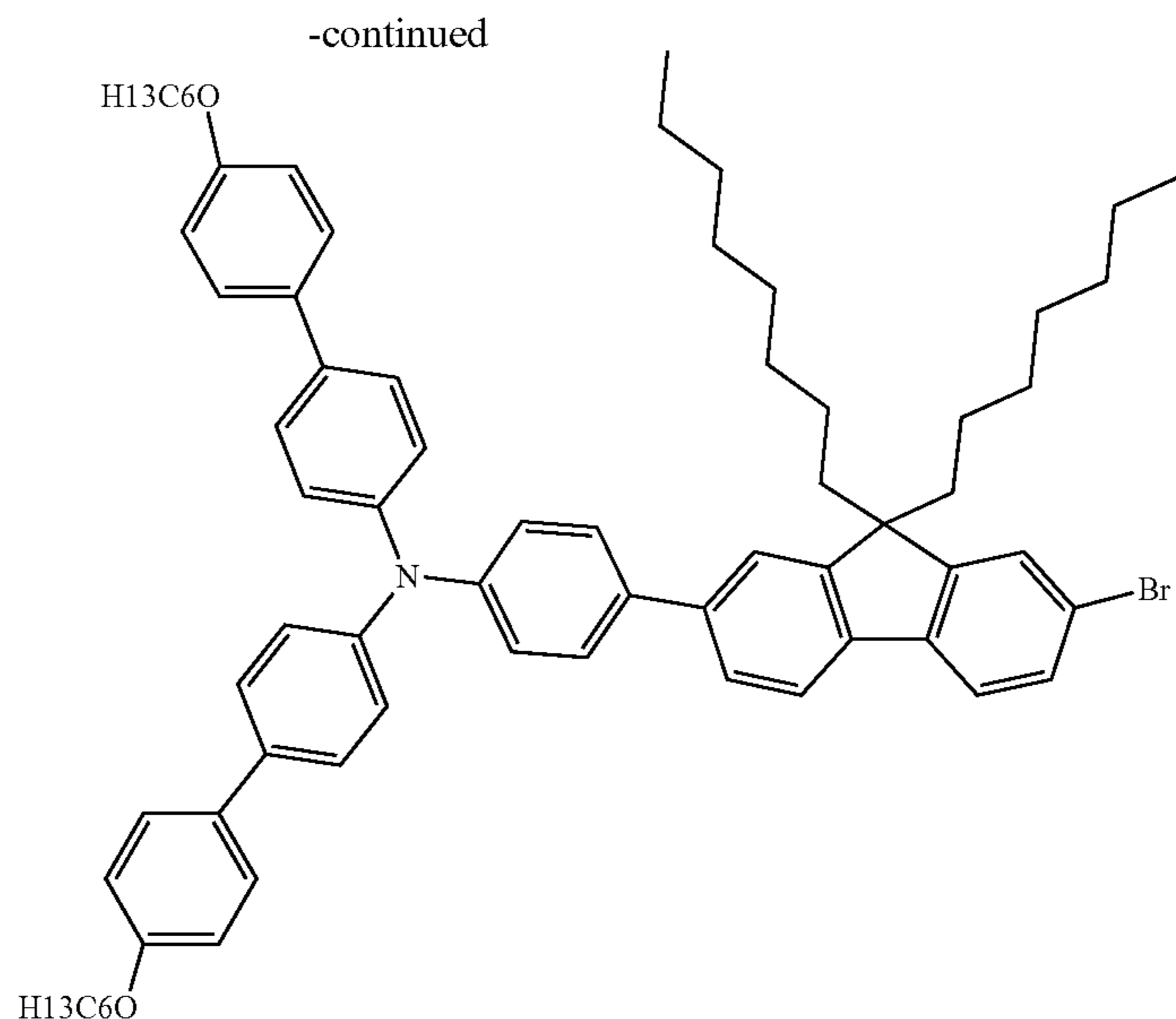
**[0149]** 2,7-dibromo-9,9-dioctyl-fluorene (0.34 g, 0.62 mmol), N,N-bis[4-(4-hexoxyphenyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (0.15 g, 0.20 mmol), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.03 g, 0.04 mmol), 10% aqueous sodium carbonate solution (6 mL), and tetrahydrofuran (15 mL) were added to a 20 mL microwave vial and reacted for 15 min at 100° C. by microwave. The reaction mixture was extracted with ethylacetate (15 mL) and organic layer washed with water (10 mL) and brine solution (10 mL), respectively.

Organic layer was dried over anhydrous sodium sulfate and concentrated. The crude product was purified using column chromatography on silica gel (0 to 10% ethyl acetate in hexanes) to obtain N-[4-(7-bromo-9,9-dioctyl-fluoren-2-yl)phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline (0.07 g). UV/Vis max 350 nm, LCMS m/z=1064.

C. N-[4-[9,9-dioctyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline

**[0150]**



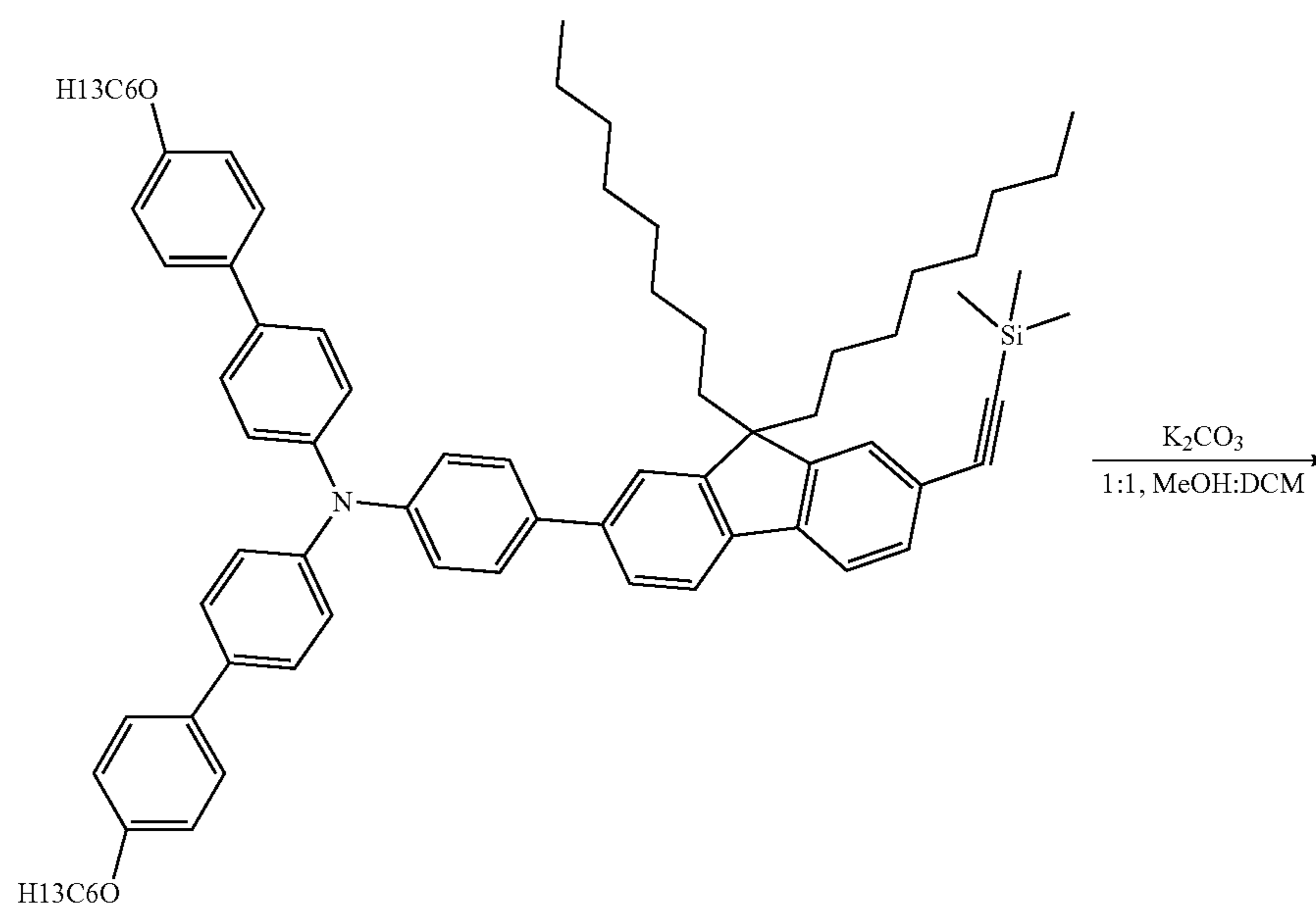


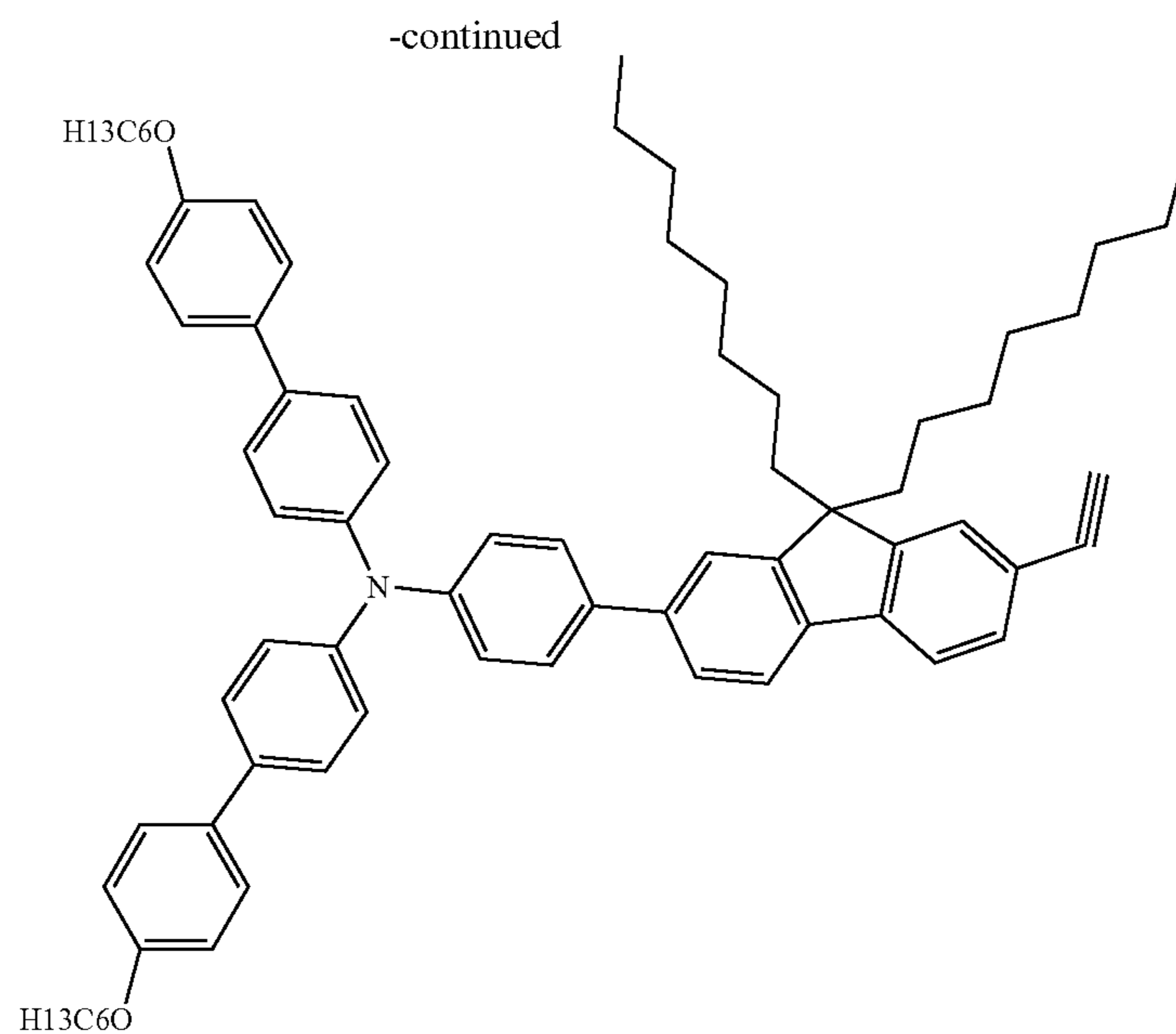
**[0151]** To a 50 mL flask Tris(dibenzylideneacetone)dipalladium(0) (0.09 g, 0.10 mmol), Tri-tert-butylphosphonium tetrafluoroborate ((0.03 g, 0.10 mmol), N-[4-(7-bromo-9,9-dioctyl-fluoren-2-yl)phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline (0.55 g, mmol), trimethylsilylacetylene (0.15 g, 1.55 mmol) and triethylamine (15 mL) were added under nitrogen. The reaction mixture was stirred for 20 h at 45° C. The reaction mixture was extracted with ethylacetate (30 mL) and washed with water (10 mL) and brine solution (10 mL). Organic layer was dried over anhy-

drous sodium sulfate and concentrated. The crude product was purified using column chromatography on silica gel (0 to 10% ethylacetate in hexanes) to obtain N-[4-[9,9-dioctyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline (0.37 g). UV/Vis max 350 nm, LCMS m/z=1082.

D. N-[4-(7-ethynyl-9,9-dioctyl-fluoren-2-yl)phenyl]-  
4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]  
aniline

**[0152]**



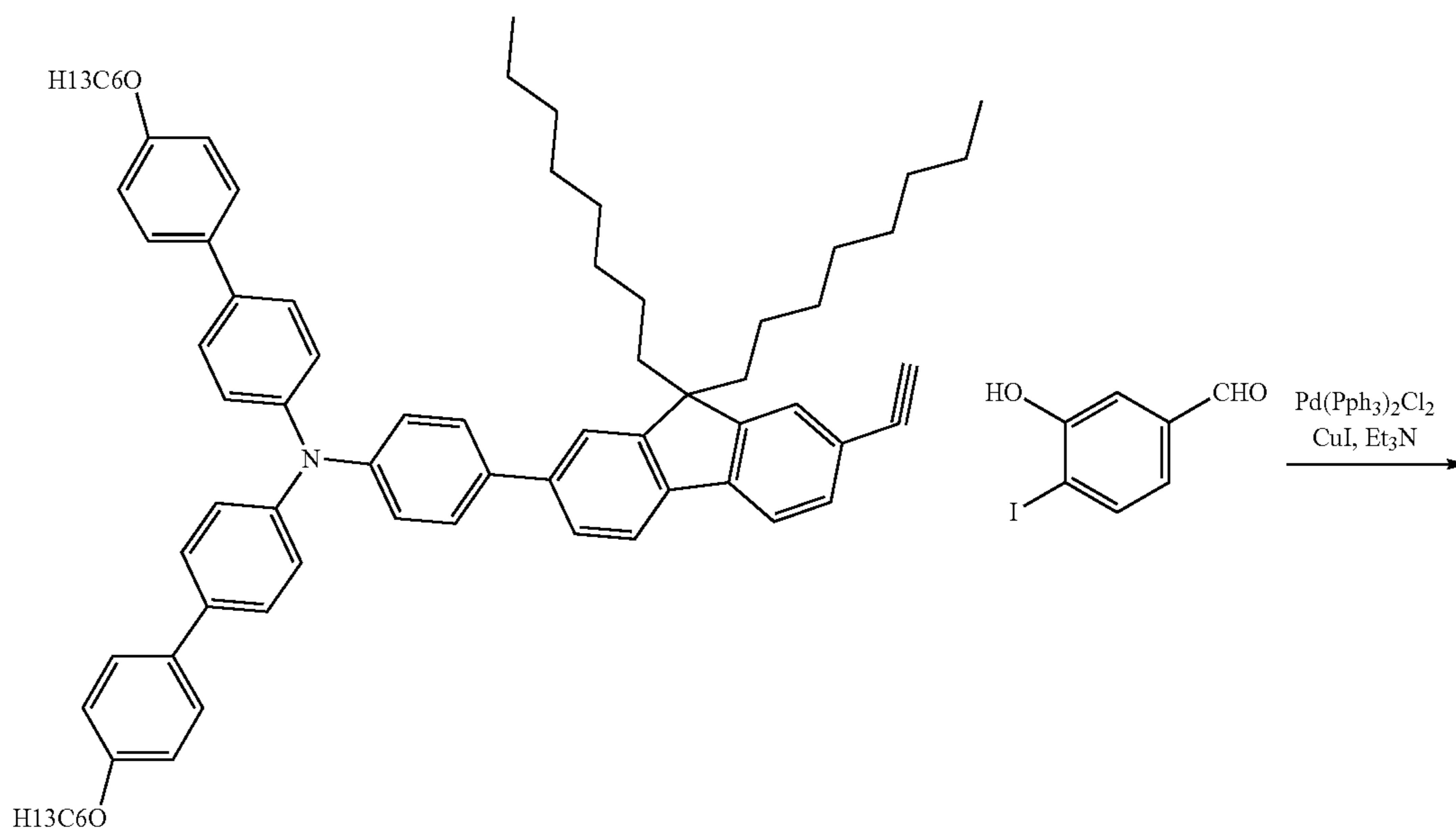


**[0153]** N-[4-[9,9-dioctyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline (0.37 g, 0.34 mmol) was added to a 50 mL flask and then dichloromethane (10 mL) and methanol (10 mL) were added under nitrogen. To this reaction mixture, anhydrous  $K_2CO_3$  (0.19 g, 1.30 mmol) was added and stirred for 3 h. The reaction mixture evaporated and the resulting crude product was dissolved in dichloromethane (30 mL) and filtered through filtering funnel and mother

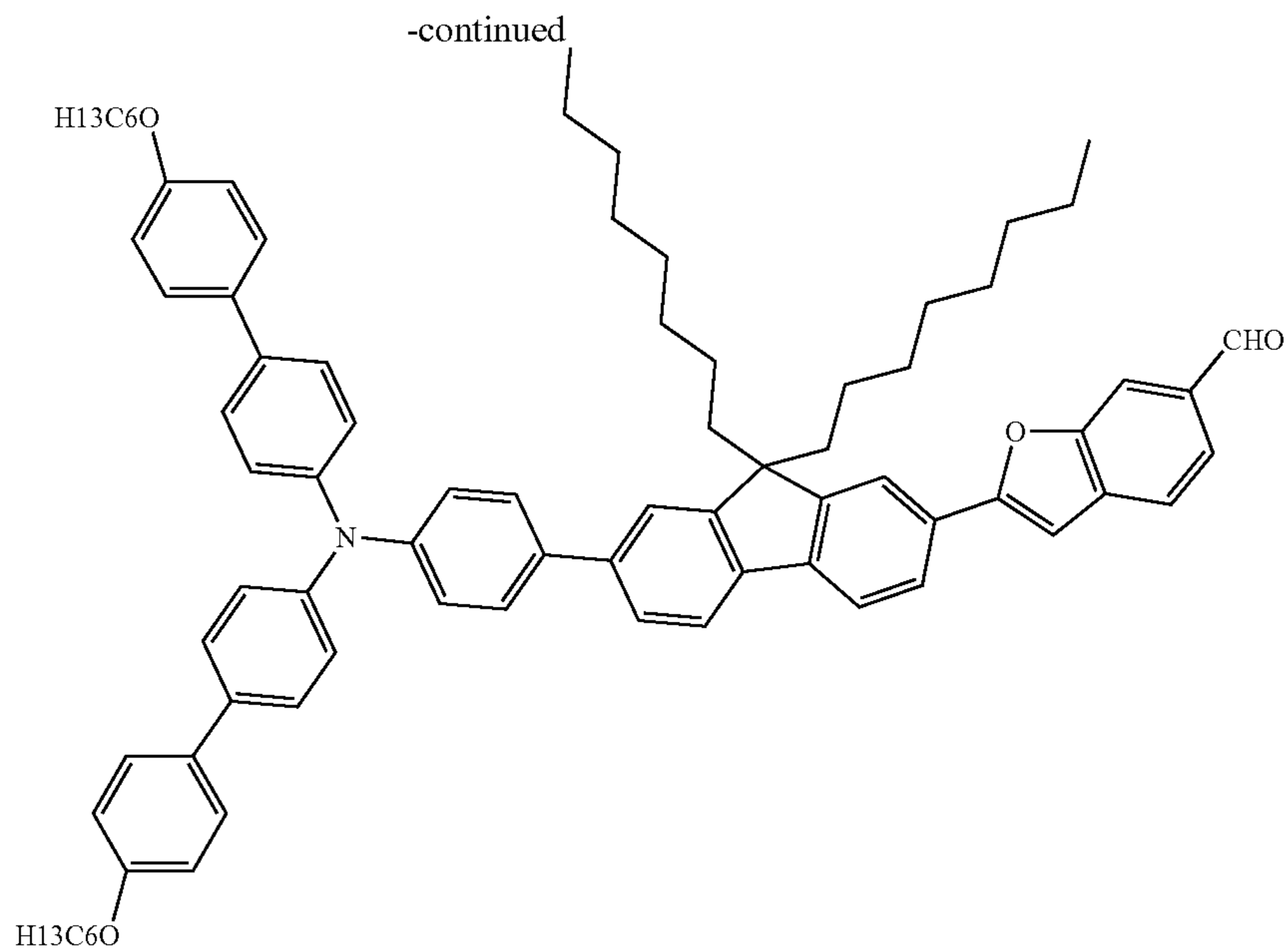
liquor concentrated to obtain N-[4-(7-ethynyl-9,9-dioctylfluoren-2-yl)phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline (0.32 g). UV/Vis max 350 nm, LCMS  $m/z=1010$ .

E. 2-[7-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-9,9-dioctylfluoren-2-yl]benzofuran-6-carbaldehyde

**[0154]**





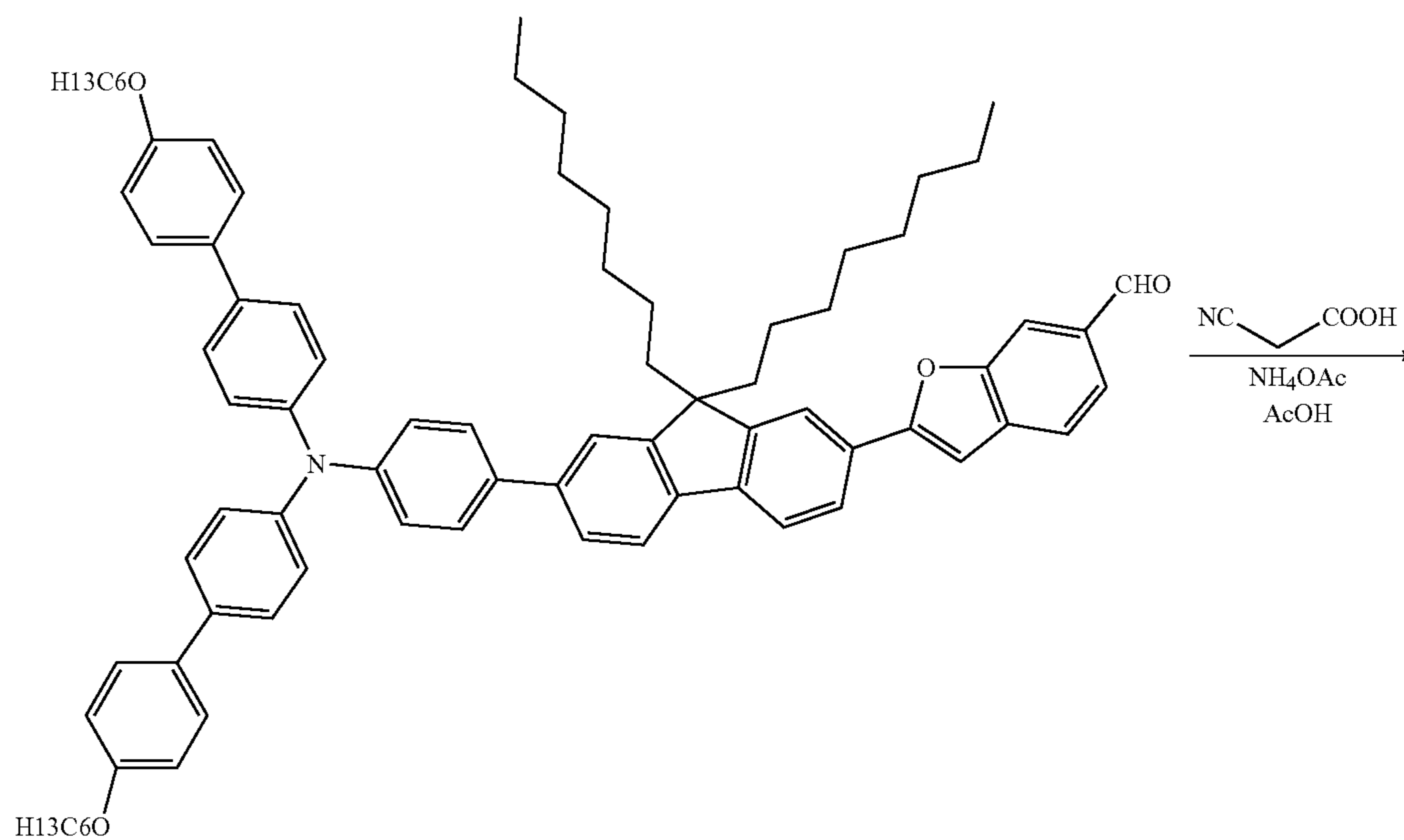


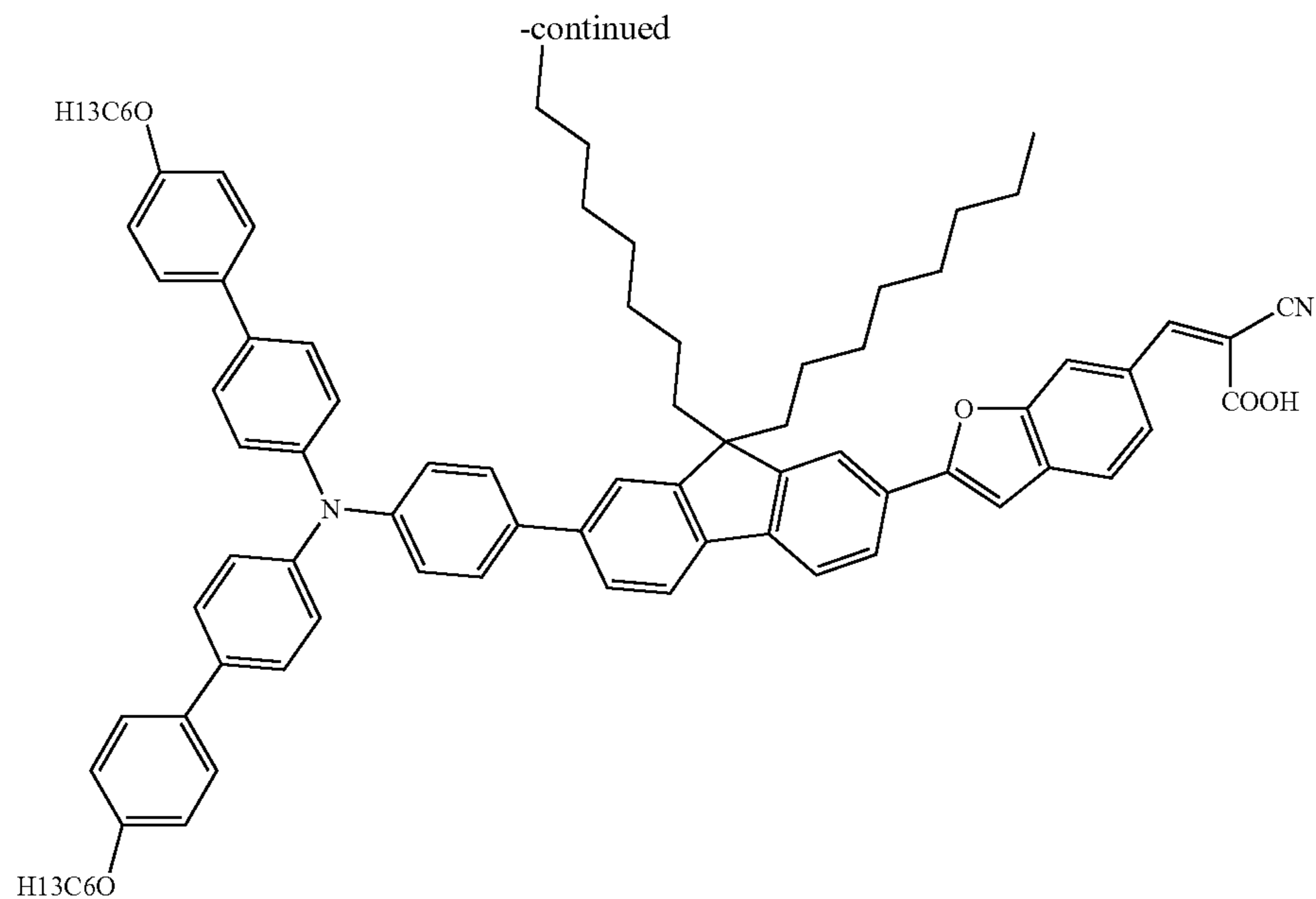
**[0155]** To a 50 mL flask 3-hydroxy-4-iodobenzaldehyde (0.073 g, 0.30 mmol), bis(triphenylphosphine)palladium dichloride (0.043 g, 0.06 mmol), and copper(I) iodide (0.02 g, 0.06 mmol) were added under nitrogen. The flask was purged with nitrogen for 20 min, then a solution of N-[4-(7-ethynyl-9,9-dioctyl-fluoren-2-yl)phenyl]-4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]aniline (0.6 g) in triethylamine (2.18 mL) degassed with nitrogen was added. The reaction was heated at 50° C. for 3 h, cooled down to room temperature, then quenched with water (25 mL). The reaction mixture was extracted with ethyl acetate (30 mL) and organic layer washed with brine solution and dried over

sodium sulfate. The organic was filtered and concentrated. Crude product was purified using chromatography on silica gel (0 to 13% ethyl acetate in hexanes) to afford 2-[7-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-carbaldehyde (0.09 g). UV/Vis max 395 nm, LCMS m/z=1130.

F. (E)-2-cyano-3-[2-[7-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-yl]prop-2-enoic Acid

**[0156]**





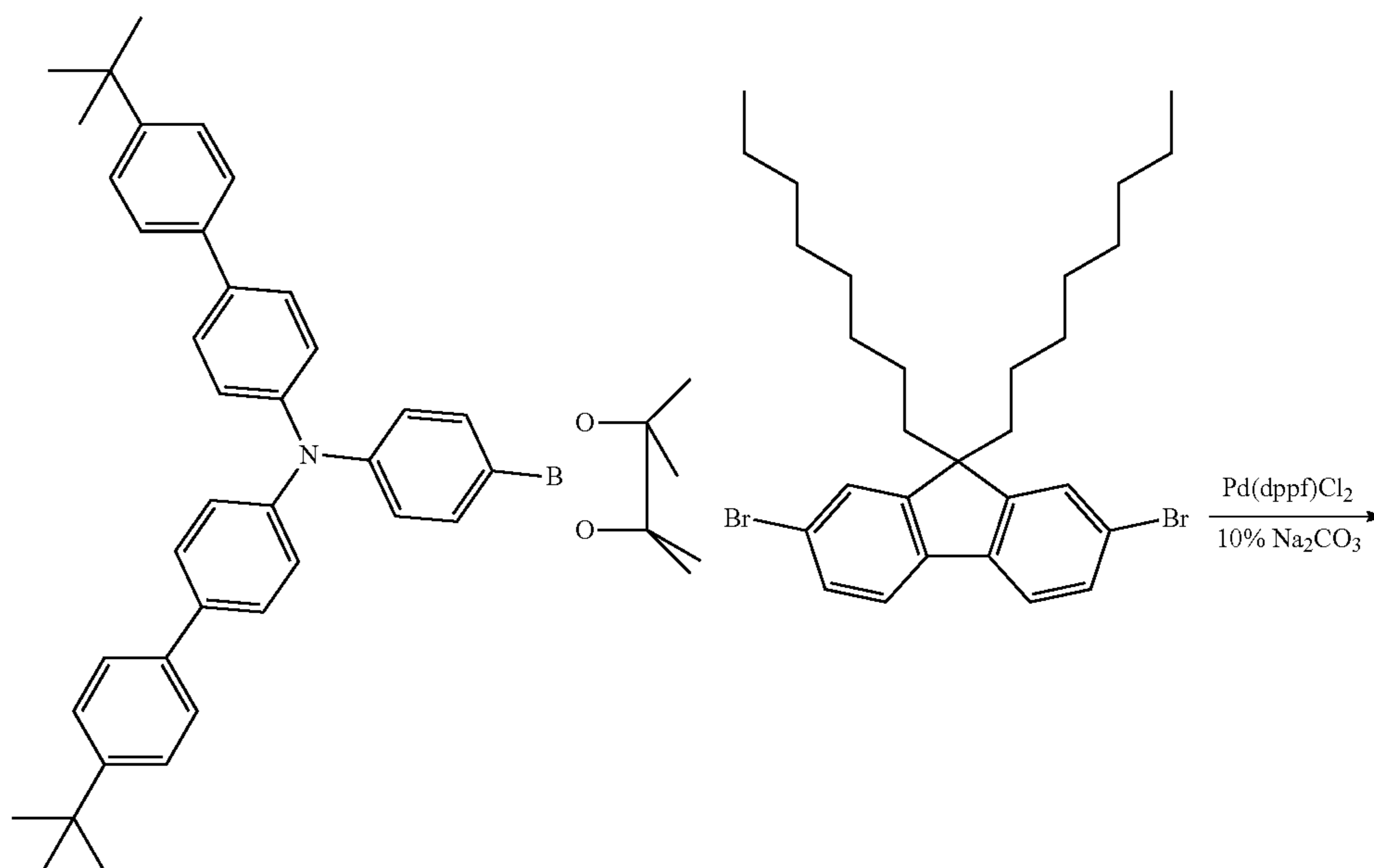
**[0157]** Acetic acid (1.70 mL) was added to 2-[7-[4-[4-(4-hexoxyphenyl)-N-[4-(4-hexoxyphenyl)phenyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-carbaldehyde (0.2 g), cyanoacetic acid (0.07 g, 0.9 mmol), and ammonium acetate (0.14 g, 1.80 mmol) in a round bottom flask, and the reaction was heated to reflux for 1.5 h. The reaction was cooled to room temperature and diluted with dichloromethane (35 mL). The dichloromethane (35 mL) was washed with water (2×10 mL) and brine solution (10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated to afford (E)-2-cyano-3-[2-[7-[4-[4-(4-hexoxy-

phenyl)-N-[4-(4-hexoxyphenyl)-phenyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-yl]prop-2-enoic acid, unidentified olefin isomer. UV/Vis max 425 nm, LCMS  $m/z=1197$ .

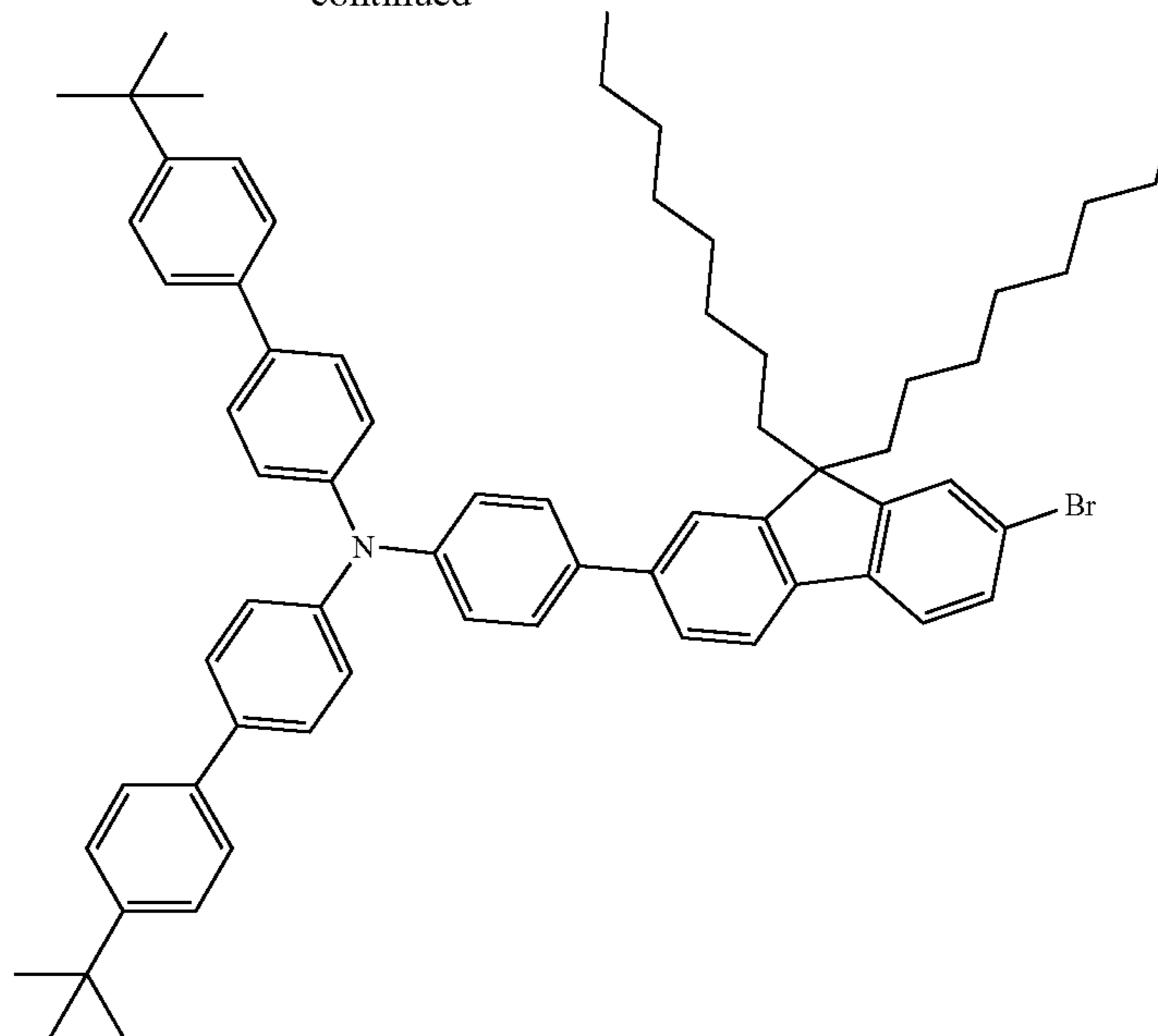
### Example 13. Synthesis of D16

A. N-[4-(7-bromo-9,9-dioctyl-fluoren-2-yl)phenyl]-4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]aniline

**[0158]**



-continued

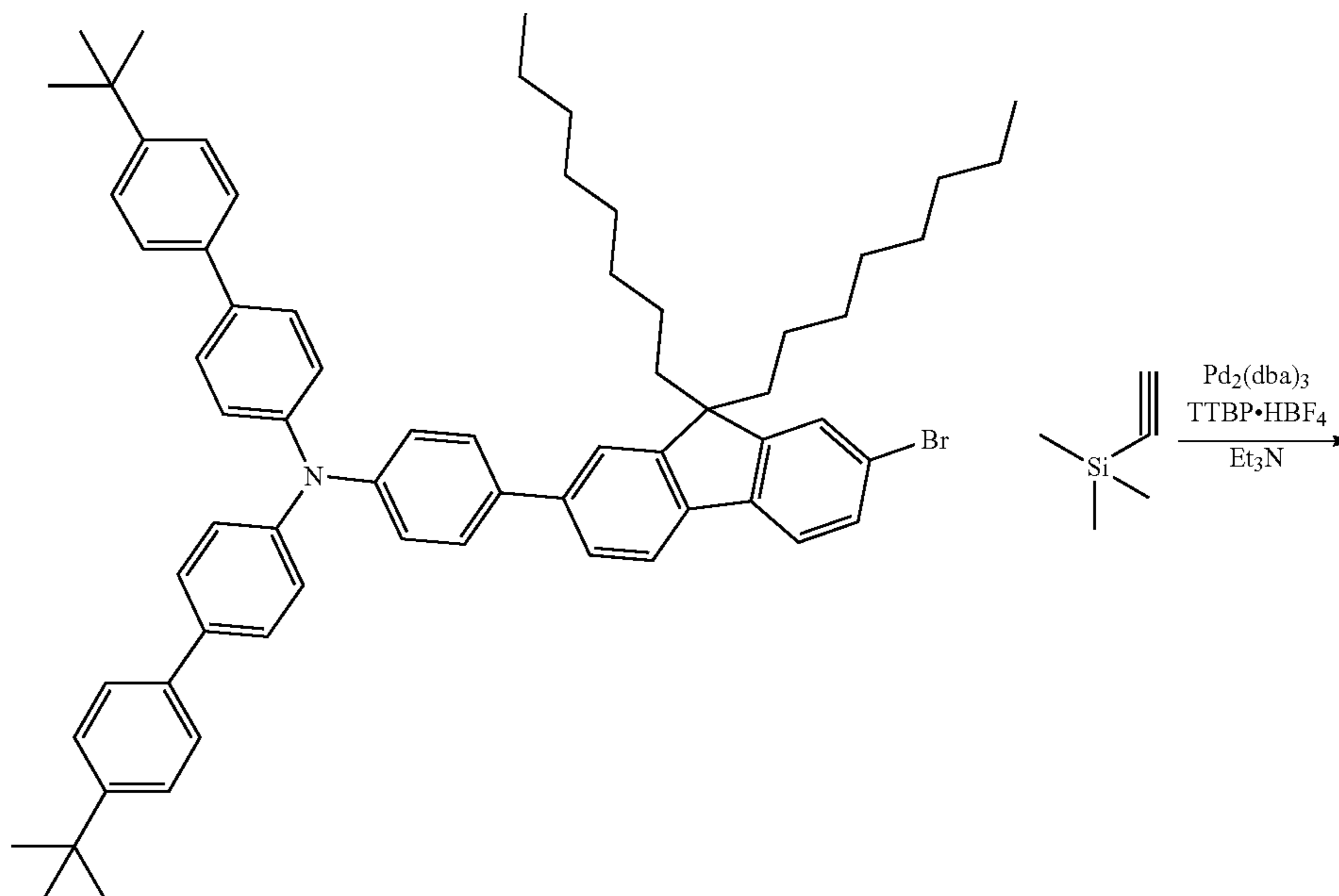


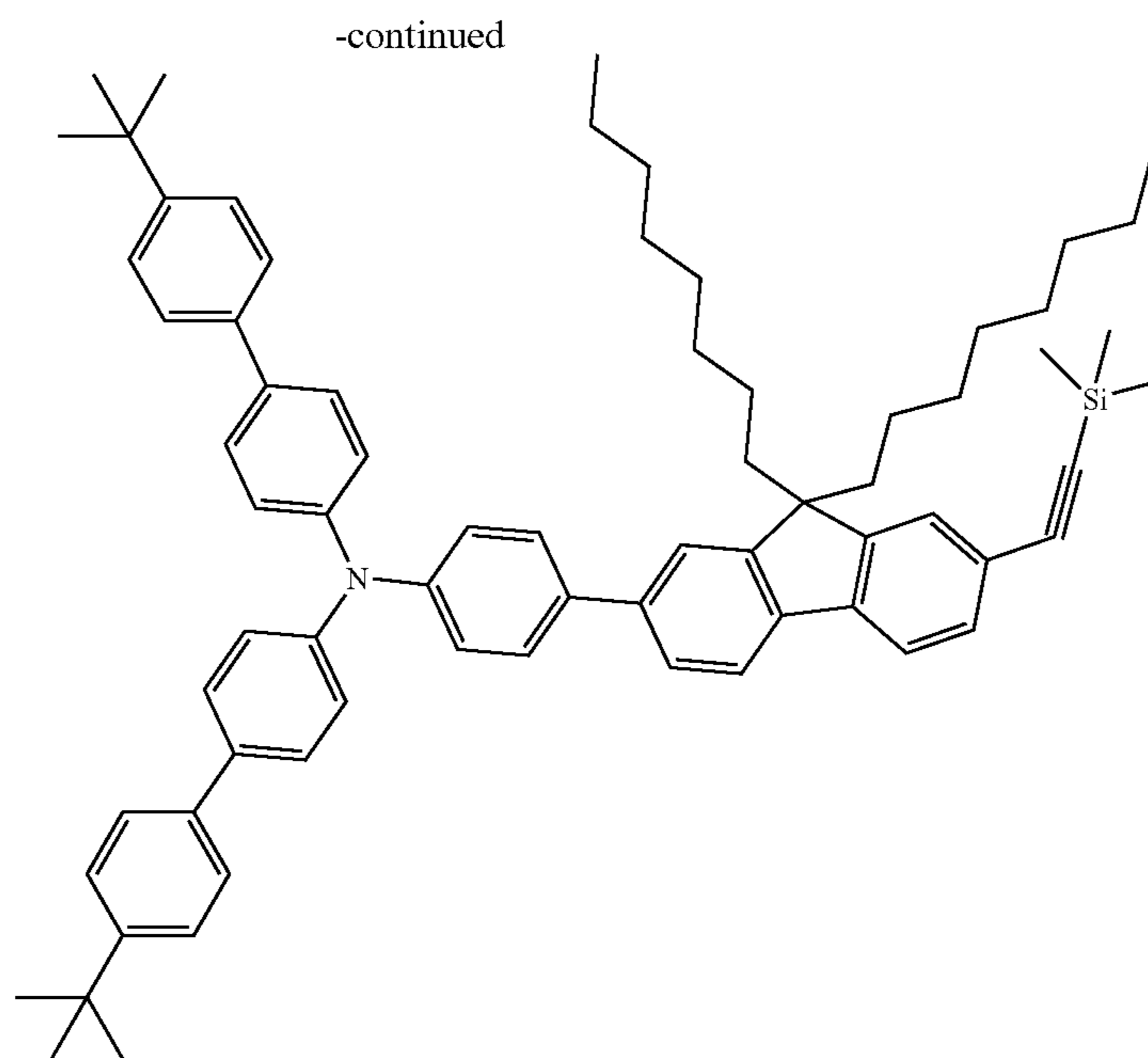
**[0159]** 2,7-dibromo-9,9-dioctyl-fluorene (0.75 g, 1.34 mmol) (see Example 12.A), N,N-bis[4-(4-tert-butylphenyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (0.25 g, 0.40 mmol) (see Example 2.C), [1,1'-bis(diphenylphosphino)ferrocene]dichloro-palladium(II) (0.08 g, 0.57 mmol), 10% aqueous sodium carbonate solution (5 mL), and tetrahydrofuran (15 mL) were added in a 20 mL microwave vial and reacted for 15 min at 100° C. by microwave. The reaction mixture was extracted with ethylacetate (15 mL) and organic layer washed with water (10 mL) and brine solution (10 mL), respectively. Organic layer

was dried over anhydrous sodium sulfate and concentrated. The crude product was purified using column chromatography on silica gel (0 to 10% ethyl acetate in hexanes) to obtain N-[4-(7-bromo-9,9-dioctyl-fluoren-2-yl)phenyl]-4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]aniline (0.2 g). UV/Vis max 350 nm, LCMS m/z=976.

B. 4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]-N-[4-[9,9-dioctyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]phenyl]aniline

**[0160]**



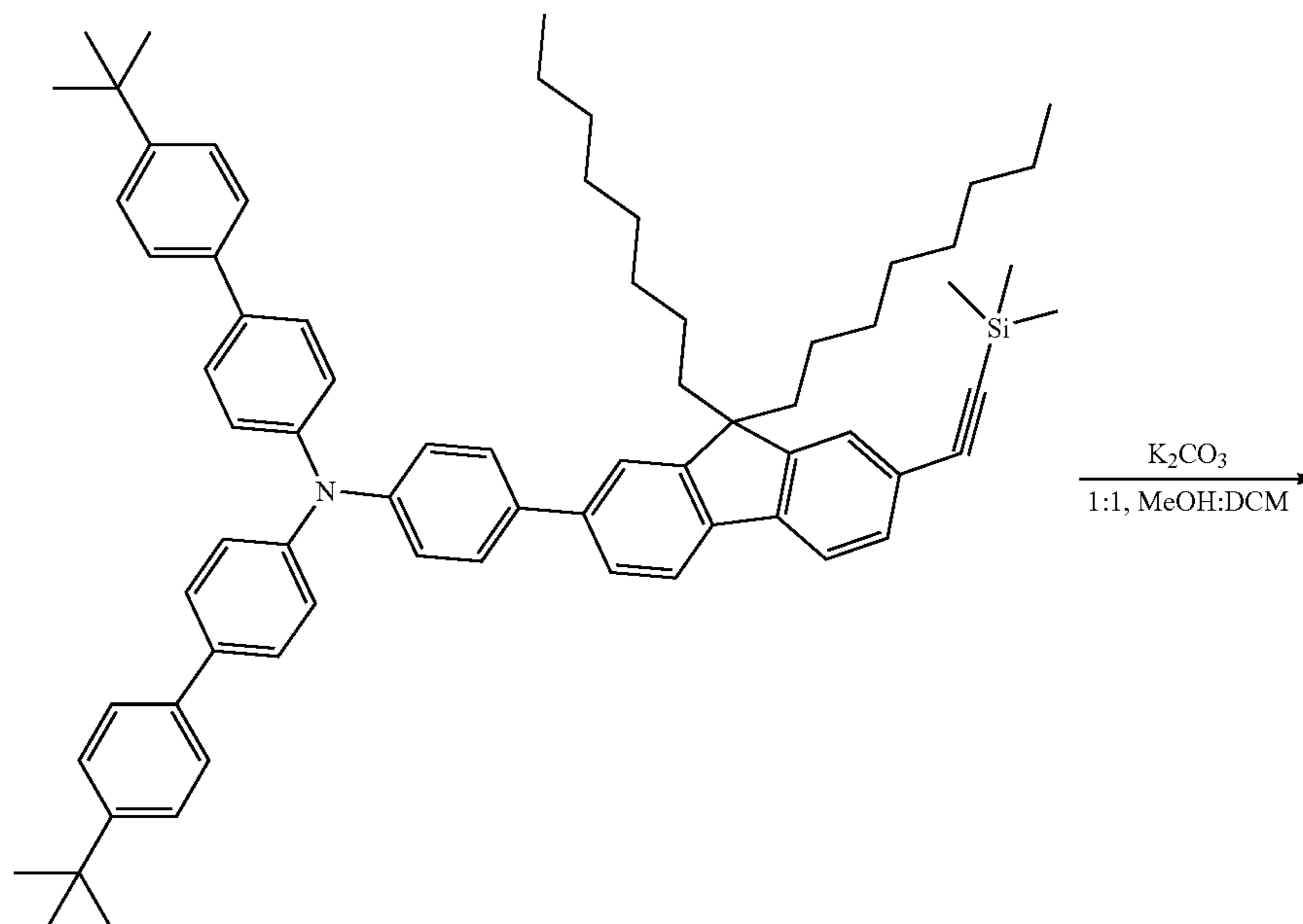


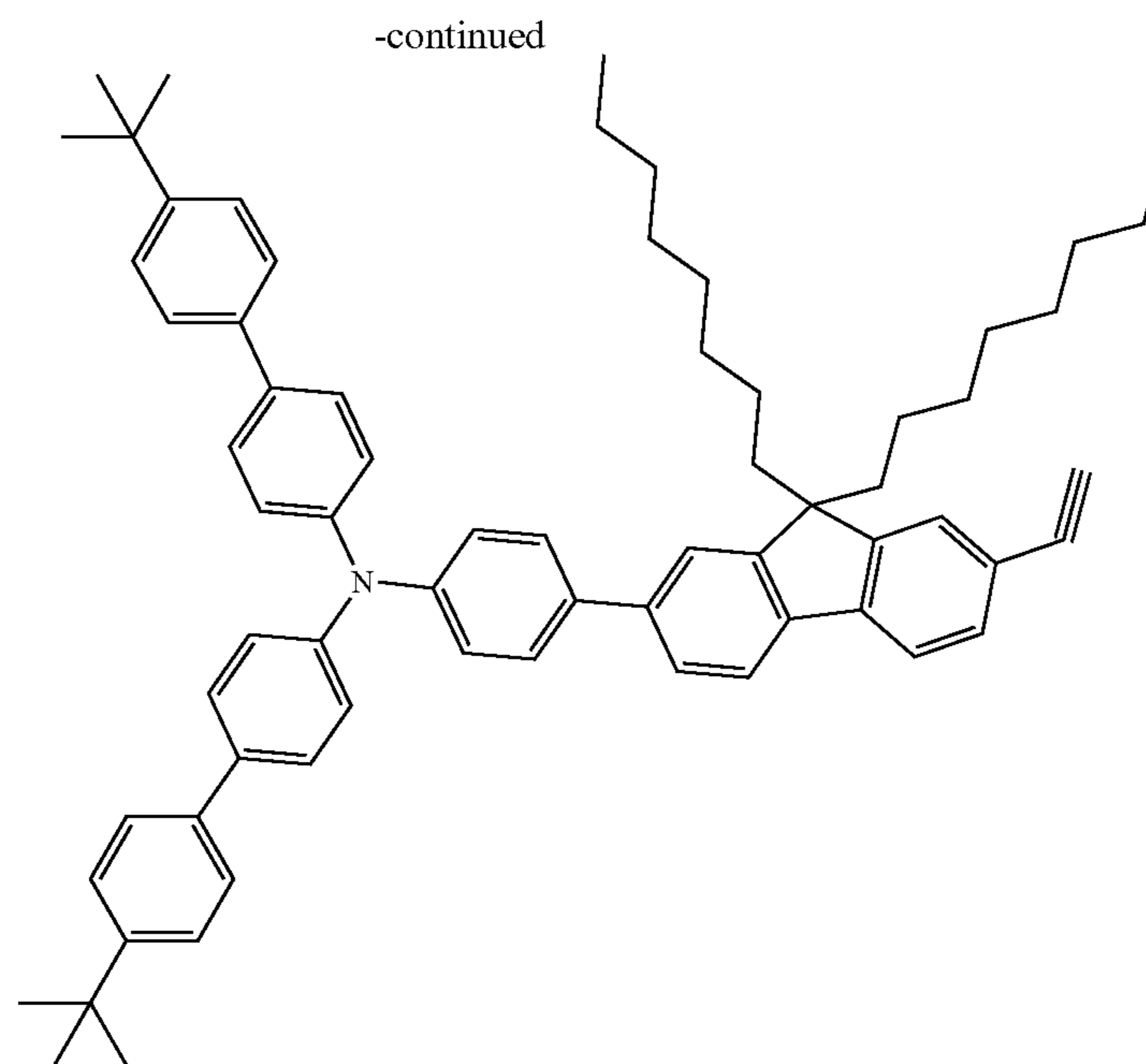
**[0161]** To a 50 mL flask Tris(dibenzylideneacetone)dipalladium(0) (0.09 g, 0.10 mmol), Tri-tert-butylphosphonium tetrafluoroborate (0.03 g, 0.10 mmol), N-[4-(7-bromo-9,9-dioctyl-fluoren-2-yl)phenyl]-4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]aniline (0.50 g, 0.51 mmol), trimethylsilylacetylene (0.15 g, 1.50 mmol) and triethylamine (15 mL) were added under nitrogen. The reaction mixture was stirred for 20 h at 45° C. The reaction mixture extracted with ethylacetate (30 mL) and washed with water (10 mL) and brine solution (10 mL). Organic layer was dried over anhydrous sodium sulfate and concentrated. The crude

product was purified using column chromatography on silica gel (0 to 10% ethylacetate in hexanes) to obtain 4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]-N-[4-[9,9-dioctyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]phenyl]aniline (0.34 g). UV/Vis max 350 nm, LCMS m/z=994.

C. 4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]-N-[4-(7-ethynyl-9,9-dioctyl-fluoren-2-yl)phenyl]aniline

**[0162]**



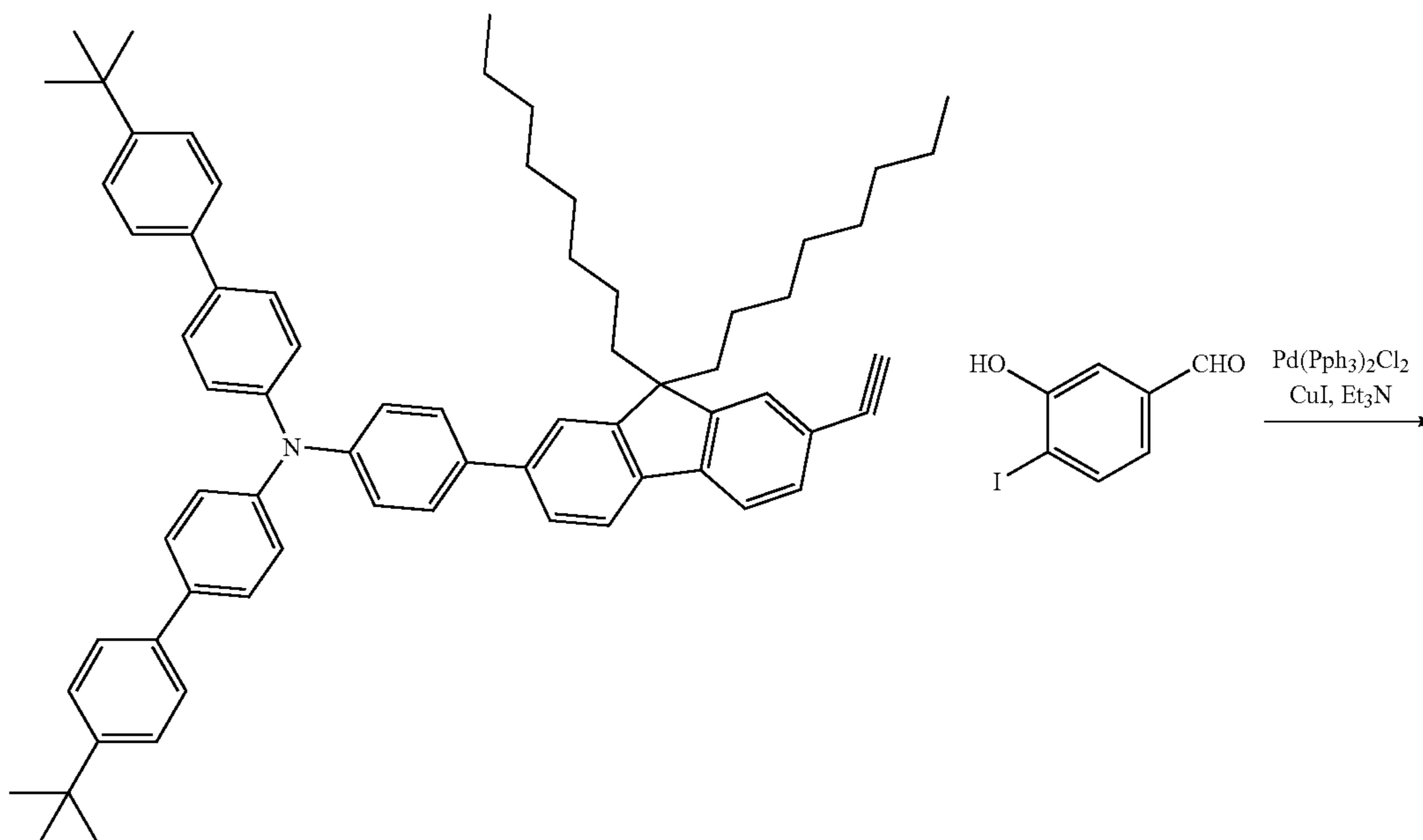


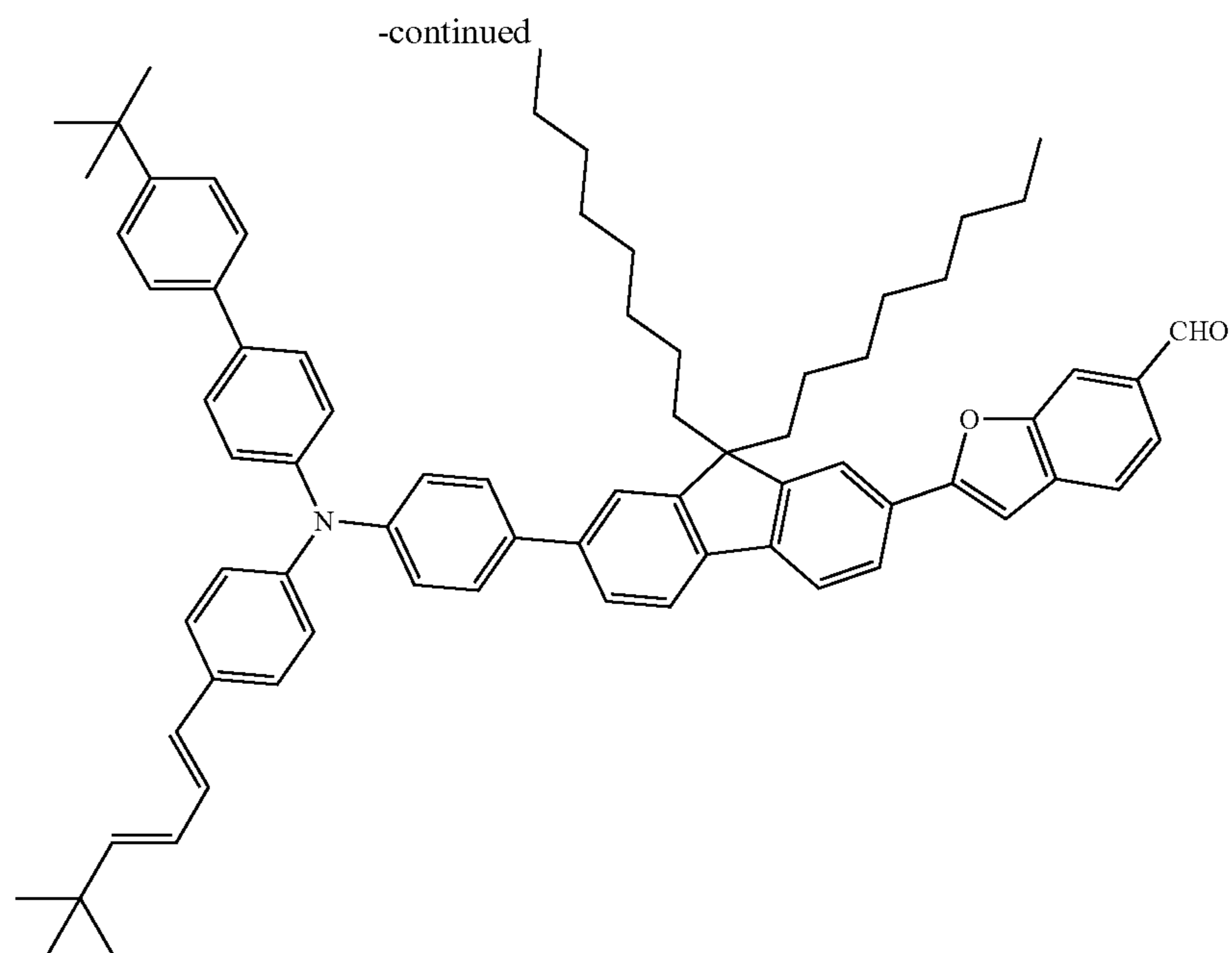
**[0163]** 4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]-N-[4-[9,9-dioctyl-7-(2-trimethylsilylethynyl)fluoren-2-yl]phenyl]aniline (0.30 g, 0.32 mmol) was added to a 50 mL flask and then dichloromethane (10 mL) and methanol (10 mL) were added under nitrogen. To this reaction mixture anhydrous  $K_2CO_3$  (0.17 g, 1.20 mmol) was added and stirred for 3 h. The reaction mixture evaporated and the resulting crude product was dissolved in dichloromethane (30 mL) and filtered through filtering funnel and mother

liquor concentrated to obtain 4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]-N-[4-(7-ethynyl-9,9-dioctylfluoren-2-yl)phenyl]aniline (0.27 g). UV/Vis max 350 nm, LCMS  $m/z=922$ .

D. 2-[7-[4-[N-[4-(4-tert-butylphenyl)phenyl]-4-[(1E,3E)-5,5-dimethylhexa-1,3-dienyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-carbaldehyde

**[0164]**



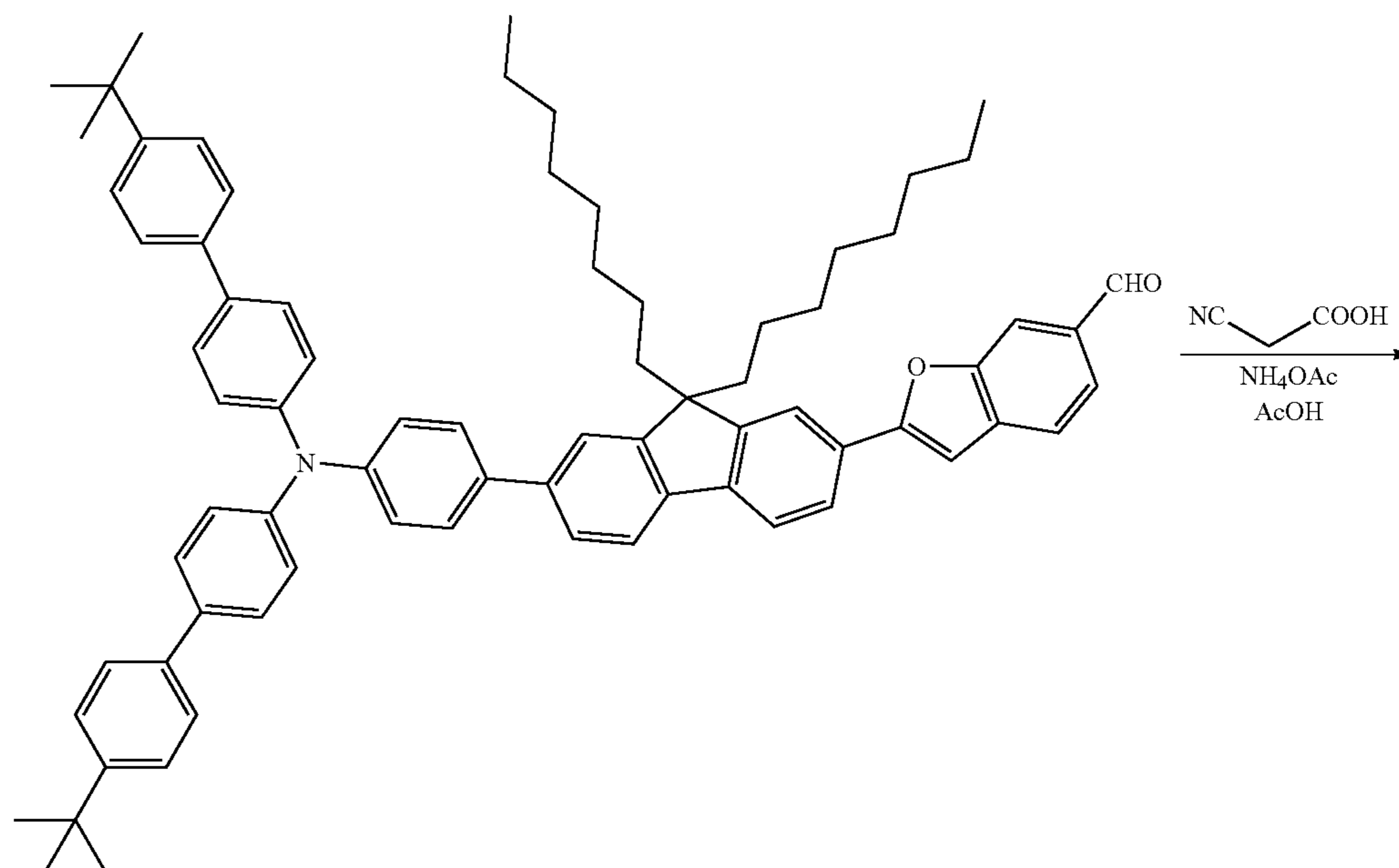


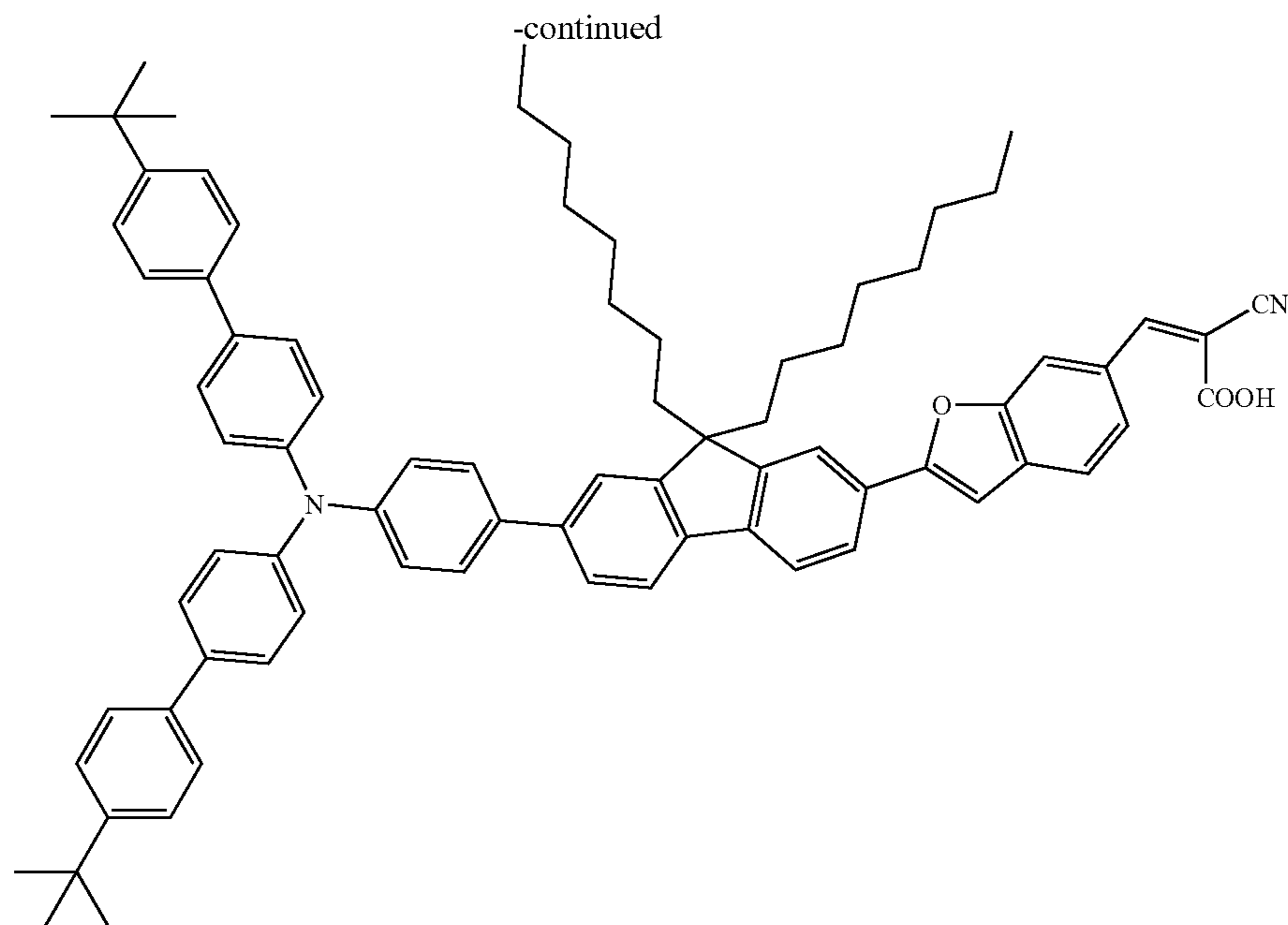
**[0165]** To a 50 mL flask, 3-hydroxy-4-iodobenzaldehyde (0.07 g, 0.08 mmol), bis(triphenylphosphine)palladium dichloride (0.04 g, 0.06 mmol), and copper(I) iodide (0.01 g, 0.06 mmol) were added under nitrogen. The flask was purged with nitrogen for 20 min and then added a solution of 4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]-N-[4-(7-ethynyl-9,9-dioctyl-fluoren-2-yl)phenyl]aniline (0.27 g, 0.30 mmol) in triethylamine (10 mL) which was degassed by bubbling nitrogen through for 20 min. The reaction was heated at 50° C. for 3 h. The reaction was cooled down to room temperature and then reaction quenched with water (25 mL). The reaction mixture extracted with ethyl acetate (30 mL) and organic layer washed with brine solution and dried over sodium sulfate.

The organic was filtered and concentrated. Crude product was purified using chromatography on silica gel (0 to 13% ethyl acetate in hexanes) to afford 2-[7-[4-[N-[4-(4-tert-butylphenyl)phenyl]-4-[(1E,3E)-5,5-dimethylhexa-1,3-dienyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-carbaldehyde (0.045 g). UV/Vis max 395 nm, LCMS  $m/z=1042$ .

(Z)-3-[2-[7-[4-[4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-yl]-2-cyano-prop-2-enoic Acid

**[0166]**



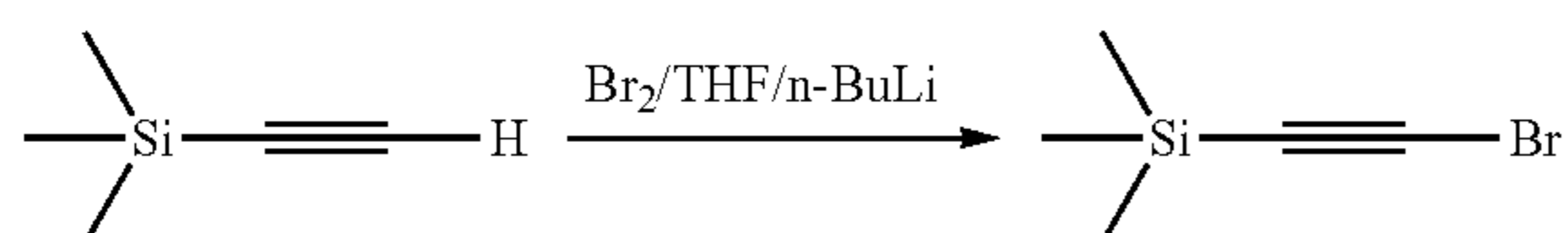


**[0167]** Acetic acid (4 mL) was added to 2-[7-[4-[N-[4-(4-tert-butylphenyl)phenyl]-4-[(1E,3E)-5,5-dimethylhexa-1,3-dienyl]anilino]phenyl]-9,9-dioctyl-fluoren-2-yl]benzofuran-6-carbaldehyde (0.045 g, 0.043 mmol), cyanoacetic acid (0.02 g, 0.2 mmol), and ammonium acetate (0.03 g, 0.43 mmol) and the reaction was heated to reflux for 1.5 h. The reaction was cooled to room temperature and diluted with dichloromethane (25 mL). The dichloromethane layer was washed with water (2×10 mL) and brine solution (10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated to afford 4-(4-tert-butylphenyl)-N-[4-(4-tert-butylphenyl)phenyl]-N-[4-[9,9-dioctyl-7-(6-vinylbenzofuran-2-yl)fluoren-2-yl]phenyl]aniline (0.03 g), unidentified olefin isomer. UV/Vis max 425 nm, LCMS  $m/z=1109$ .

Example 14. Synthesis of (Z)-2-cyano-3-[2-[2-[4-(N-phenylanilino)phenyl]-ethynyl]benzofuran-6-yl]prop-2-enoic Acid (D7)

A. 2-bromoethynyl(trimethyl)silane

**[0168]**

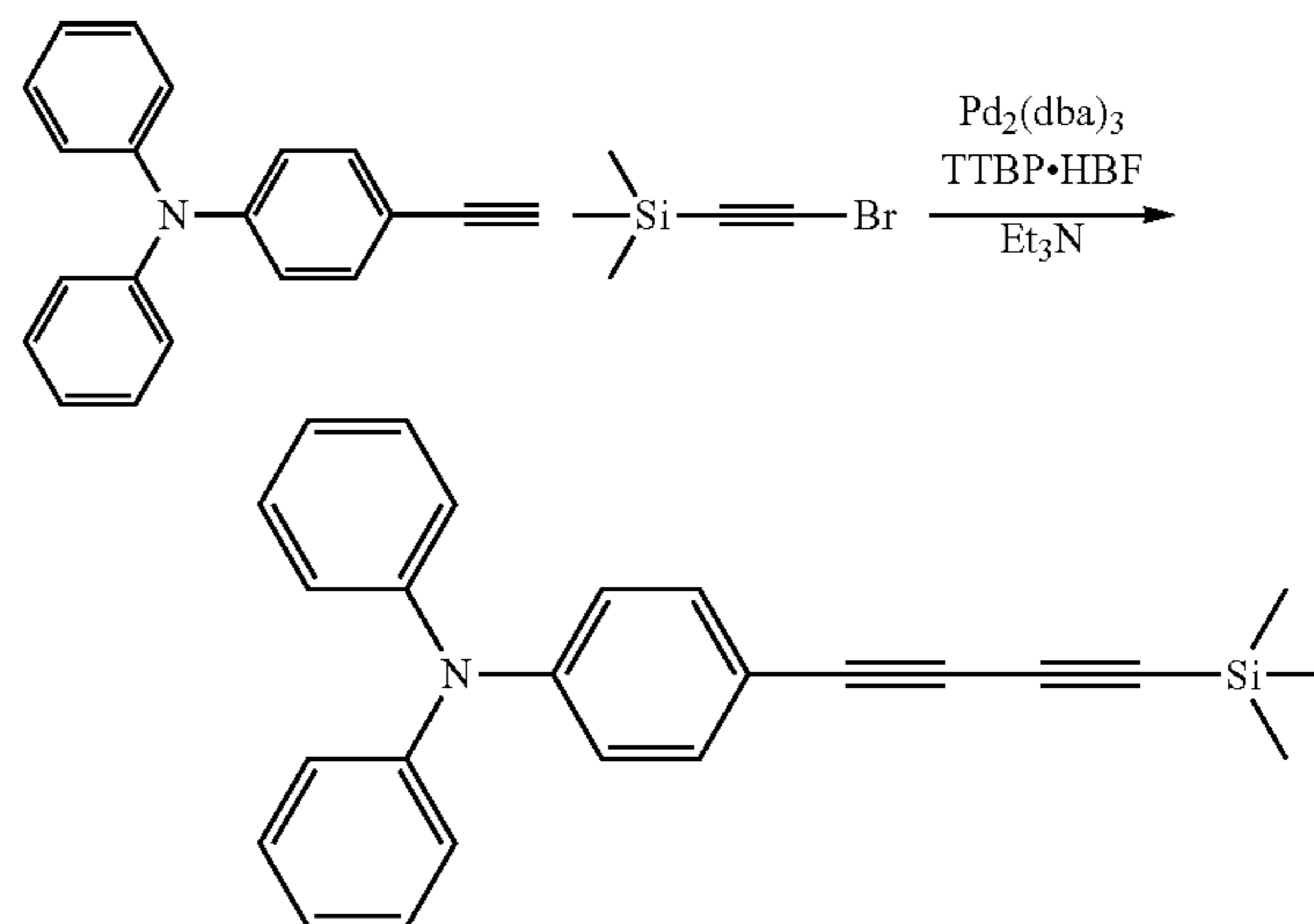


**[0169]** n-BuLi was added dropwise to a stirred solution of ethynyl(trimethyl)silane (2.0 g, 20.40 mmol) in THF (25 mL) at  $-78^{\circ}\text{C}$ ., then stirred further for 30 min at  $-78^{\circ}\text{C}$ . To this reaction mixture, bromine (3.26 g, 20.40 mmol) was added dropwise at  $-78^{\circ}\text{C}$ . and stirring was continued 30 more min. Reaction was quenched with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  (5 mL) and then warmed to room temperature. Reaction mixture was extracted with diethyl ether (30 mL), then the

organic layers were combined and concentrated to obtain 2-bromoethynyl(trimethyl)silane (3.5 g). LCMS  $m/z=175$ .

B. N,N-diphenyl-4-(4-trimethylsilylbuta-1,3-diyne)aniline

**[0170]**

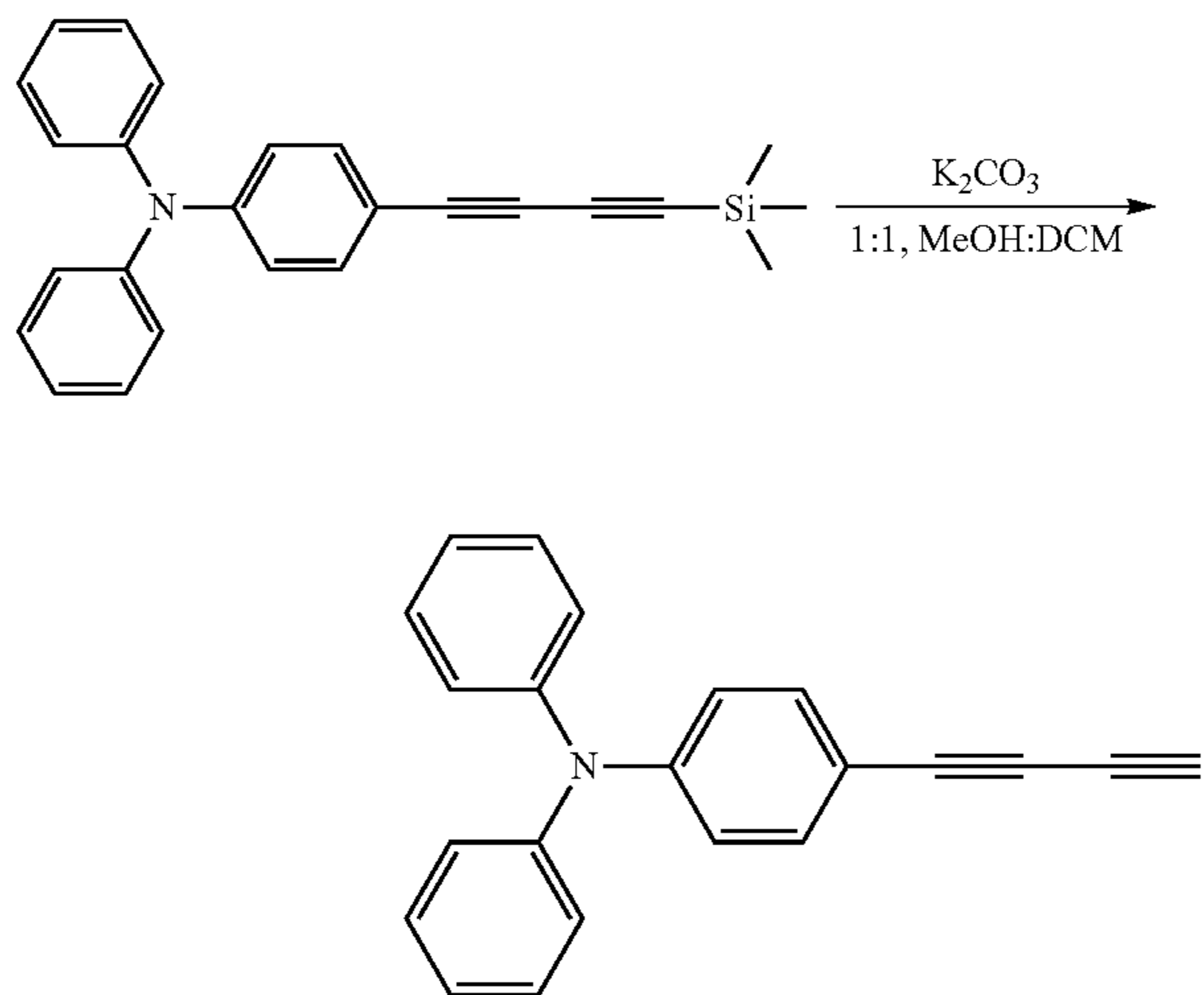


**[0171]** To a 50 mL flask Tris(dibenzylideneacetone)dipalladium(0) (1.02 g, 1.11 mmol), Tri-tert-butylphosphonium tetrafluoroborate (0.32 g, 1.11 mmol) 4-ethynyl-N,N-diphenyl-aniline (1.50 g, 5.57 mmol), 2-bromoethynyl(trimethyl)silane (0.98 g, 5.57 mmol), triethylamine (15 mL), and anhydrous tetrahydrofuran (15 mL) were added under nitrogen. The reaction mixture was stirred for 20 h at room temperature. The reaction mixture extracted with ethylacetate (30 mL) and washed with water (10 mL) and brine solution (10 mL). Organic layer was dried over anhydrous sodium sulfate and concentrated. The crude product was purified using column chromatography on silica gel (0 to 5%

ethylacetate in hexanes) to obtain N,N-diphenyl-4-(4-trimethylsilylbuta-1,3-diyne)aniline (1.60 g). LCMS  $m/z=366$ .

C. 4-buta-1,3-diyne-N,N-diphenyl-aniline

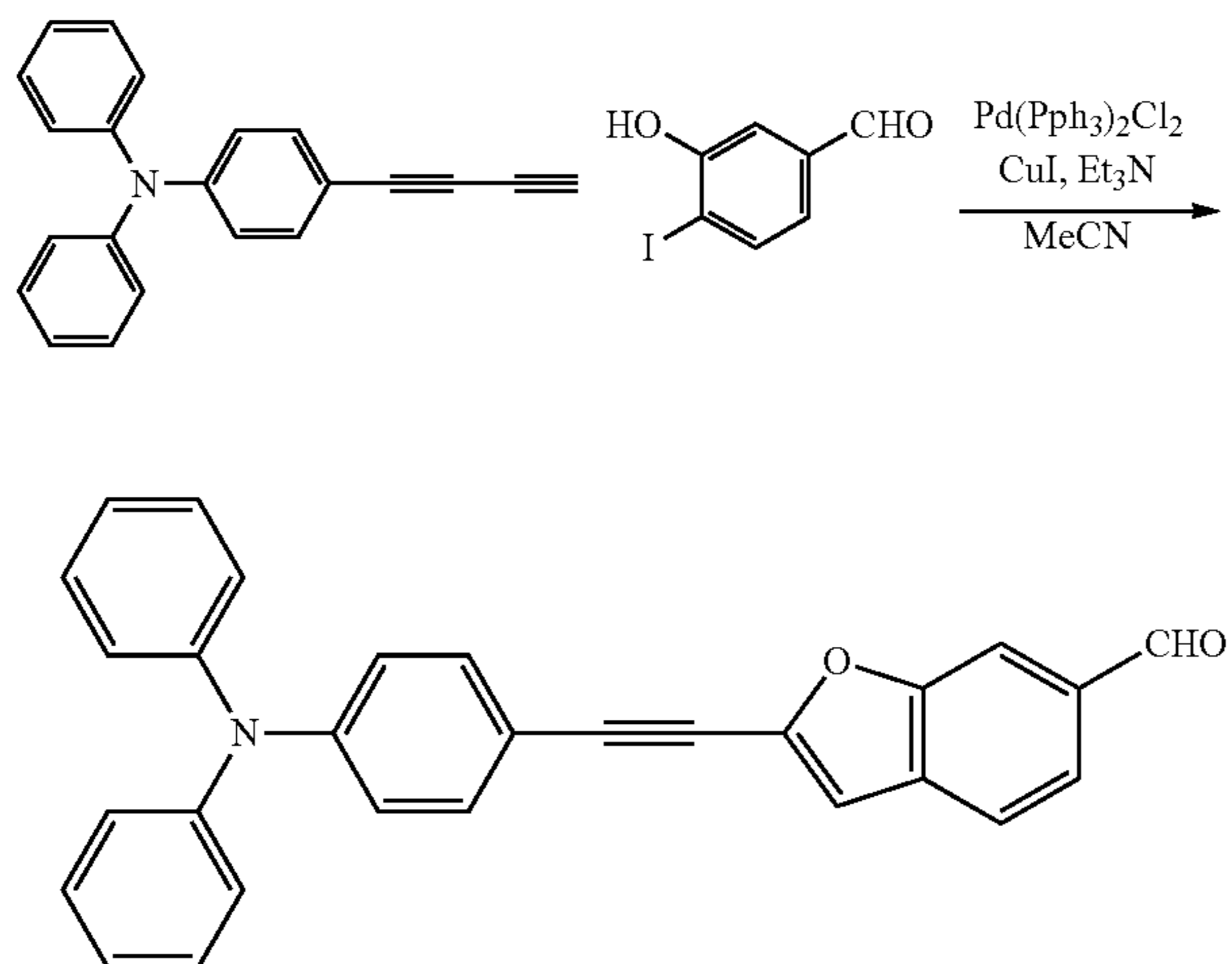
[0172]



[0173] N,N-diphenyl-4-(4-trimethylsilylbuta-1,3-diyne)aniline (0.8 g, 2.20 mmol) was added to a 50 mL flask and then DCM (10 mL) and methanol (10 mL) were added under nitrogen. To this reaction mixture anhydrous  $K_2CO_3$  (1.21 g, 8.76 mmol) was added and stirred for 3 h. The reaction mixture evaporated and then resulted crude product was dissolved in dichloromethane (30 mL) and filtered through filtering funnel and mother liquor concentrated to obtain 4-buta-1,3-diyne-N,N-diphenyl-aniline (0.6 g). LCMS  $m/z=294$ .

D. 2-[2-[4-(N-phenylanilino)phenyl]ethynyl]benzofuran-6-carbaldehyde

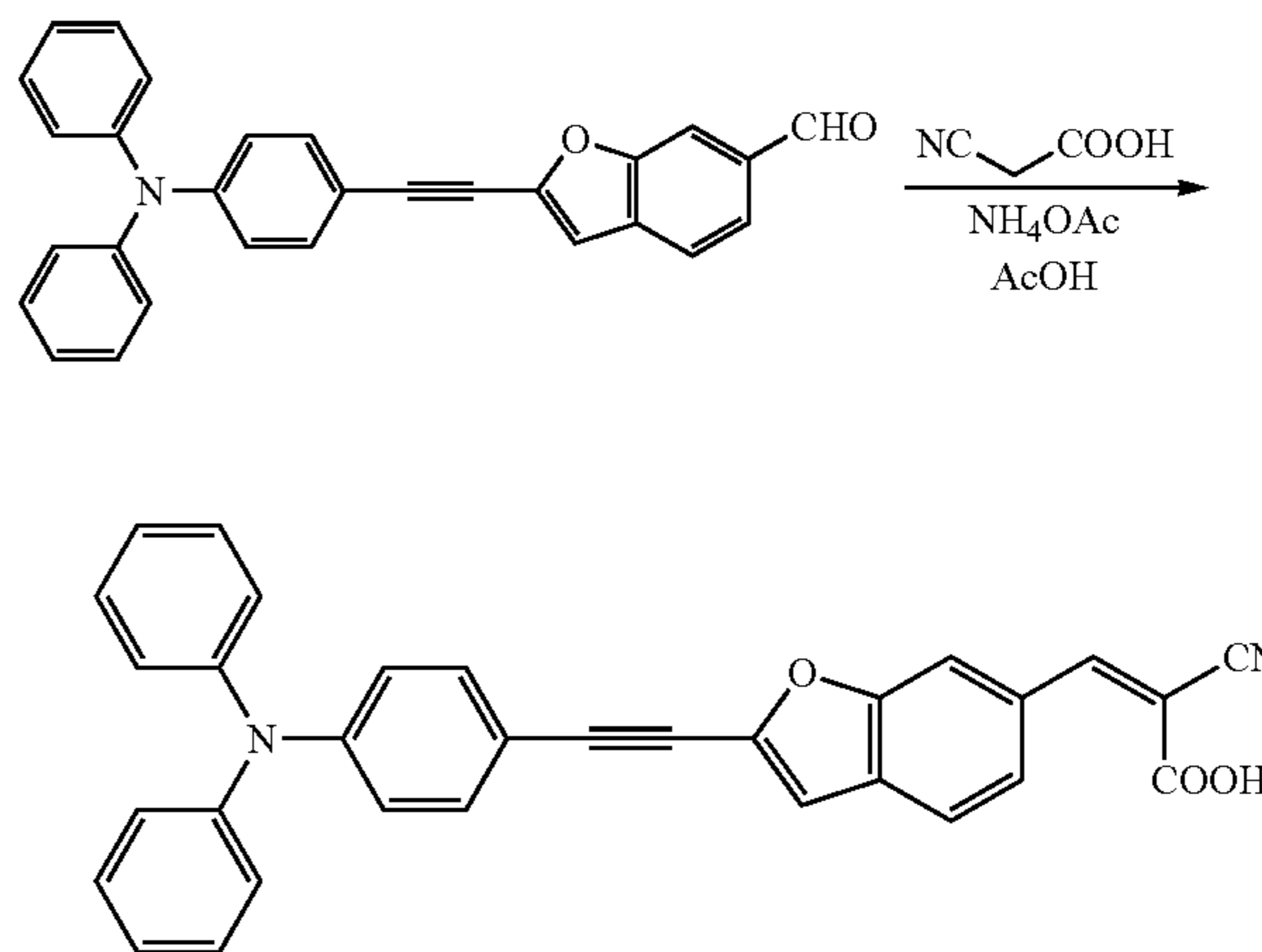
[0174]



[0175] To a 50 mL flask, 3-hydroxy-4-iodobenzaldehyde (0.25 g, 1.02 mmol), 4-buta-1,3-diyne-N,N-diphenyl-aniline (0.30 g, 1.02 mmol), bis(triphenylphosphine)palladium dichloride (0.15 g, 0.20 mmol), and copper(I) iodide (0.04 g, 0.20 mmol) were added under nitrogen. The flask was purged with nitrogen for 20 min, then degassed triethylamine (2 mL) and acetonitrile (20 mL) were added. The reaction was heated at 50° C. for 3 h. The reaction was cooled down to room temperature, then quenched with water (20 mL). The reaction mixture was extracted with ethyl acetate (25 mL) and the organic layer was washed with brine solution and dried over sodium sulfate. The organic was filtered and concentrated. Crude product was purified using chromatography on silica gel (0 to 10% ethyl acetate in hexanes) to afford 2-[2-[4-(N-phenylanilino)phenyl]ethynyl]benzofuran-6-carbaldehyde (0.15 g). UV/Vis max 390 nm, LCMS  $m/z=414$ .

E. (Z)-2-cyano-3-[2-[2-[4-(N-phenylanilino)phenyl]ethynyl]benzofuran-6-yl]prop-2-enoic Acid

[0176]



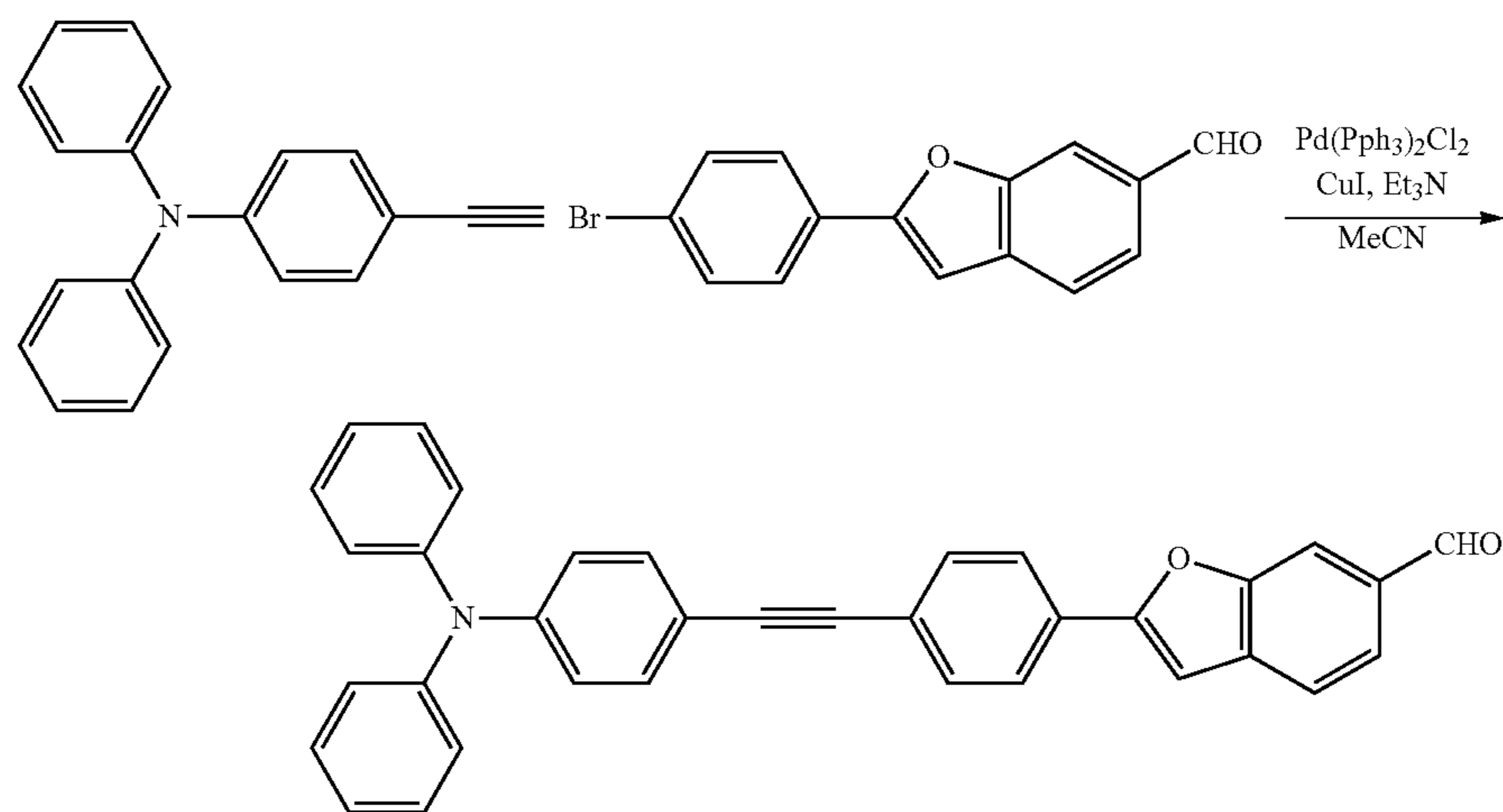
[0177] Acetic acid (8 mL) was added to 2-[2-[4-(N-phenylanilino)phenyl]ethynyl]benzofuran-6-carbaldehyde (0.075 g, 0.02 mmol), cyanoacetic acid (0.05 g, 0.05 mmol), and ammonium acetate (0.04 g, 0.05 mmol) in a round bottom flask, and the reaction was heated to reflux overnight. The reaction was cooled down to room temperature, water (10 mL) was added, then stirred for 1 h. Resulting precipitate was filtered, washed with water (2x20 mL), and dried using vacuum oven at 50° C. for 6 h to afford (Z)-2-cyano-3-[2-[2-[4-(N-phenylanilino)phenyl]ethynyl]benzofuran-6-yl]prop-2-enoic acid (0.07 g), unidentified olefin isomer. UV/Vis max 365 nm.



Example 15. Synthesis of (Z)-2-cyano-3-[2-[4-[2-[4-(N-phenylanilino)-phenyl]ethynyl]phenyl]benzofuran-6-yl]prop-2-enoic Acid

A. 2-[4-[2-[4-(N-phenylanilino)phenyl]ethynyl]phenyl]benzofuran-6-carbaldehyde

[0178]

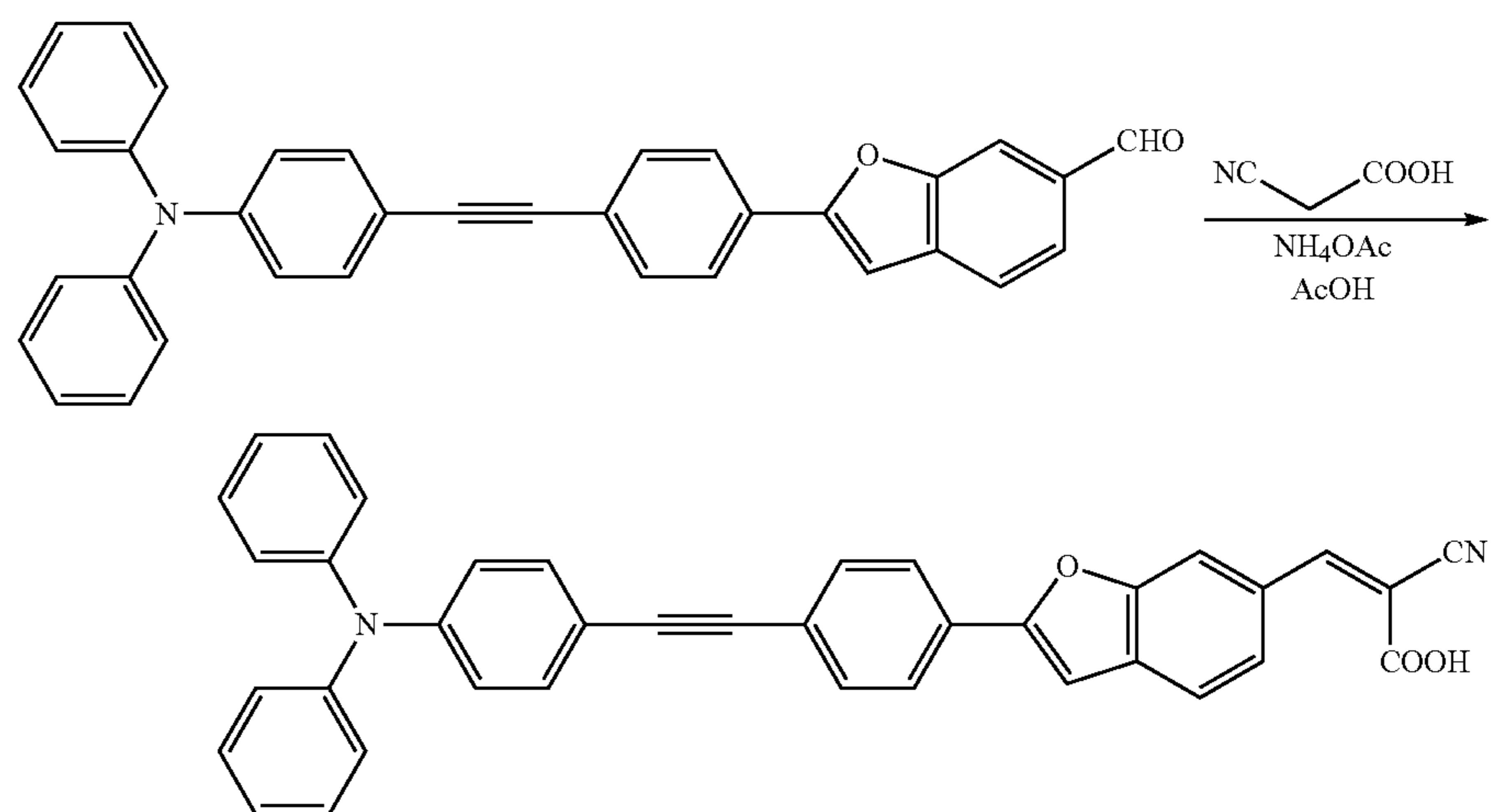


[0179] To a 50 mL flask, 2-(4-bromophenyl)benzofuran-6-carbaldehyde (0.28 g, 0.94 mmol), 4-ethynyl-N,N-diphenyl-aniline (0.25 g, 0.93 mmol), bis(triphenylphosphine) palladium dichloride (0.13 g, 0.20 mmol), and copper(I) iodide (0.04 g, 0.20 mmol) were added under nitrogen. The flask was purged with nitrogen for 20 min, then degassed triethylamine (3 mL) and acetonitrile (20 mL) were added. The reaction was heated at 50° C. for 3 h, then cooled down to room temperature and quenched with water (20 mL). The reaction mixture was extracted with ethyl acetate (25 mL).

The organic layer was washed with brine solution, dried over sodium sulfate, then filtered and concentrated. Crude product was purified using chromatography on silica gel (0 to 10% ethyl acetate in hexanes) to afford 2-[4-[2-[4-(N-phenylanilino)phenyl]ethynyl]phenyl]benzofuran-6-carbaldehyde (0.05 g). UV/Vis max 350 nm, LCMS m/z 490.

B. (Z)-2-cyano-3-[2-[4-[2-[4-(N-phenylanilino)-phenyl]ethynyl]phenyl]benzofuran-6-yl]prop-2-enoic Acid

[0180]



**[0181]** 2-[4-[2-[4-(N-phenylanilino)phenyl]ethynyl]phenyl]benzofuran-6-carbaldehyde (0.05 g, 0.1 mmol), cyanoacetic acid (0.03 g, 0.3 mmol), and ammonium acetate (0.02 g, 0.42 mmol) were added to 4 mL acetic acid and the reaction was heated to reflux overnight. The reaction was cooled down to room temperature. Water (10 mL) was added, then stirred for 1 h. Resulted precipitate was filtered, washed with water (2×20 mL), and dried using vacuum oven at 50° C. for 6 h to afford (Z)-2-cyano-3-[2-[4-[2-[4-(N-phenylanilino)phenyl]ethynyl]phenyl]benzofuran-6-yl]prop-2-enoic acid (0.04 g), unidentified olefin isomer. UV/Vis max 370 nm.

### Example 16

#### Solar Cell Fabrication and Photovoltaic Characterization

**[0182]** FTO (fluorine-doped tin oxide)-coated glass slides were cut into 2 cm×2 cm squares and washed successively with 1% aqueous Triton X-100 solution, DI-water, and iso-propanol. After drying at room temperature, the cleaned slides were treated with corona discharge (~13000V) for approximately 20 s on the conductive side. A 20% aqueous P25 dispersion was blade coated (8 microns thick) on the FTO side. The coated area was trimmed to 1.0 cm<sup>2</sup>. The TiO<sub>2</sub> coated anode was sintered at 450° C. for 30 min, cooled to about 80° C. and dropped into a solution containing 0.3 mM dye and 0.3 mM chenodeoxycholic acid in 1:1 acetonitrile/t-butanol. The anodes were kept in dye solution overnight, rinsed with acetonitrile and air dried in the dark. The dye sensitized anode was sandwiched with electrochemically deposited catalyst (PEDOT or platinum) on an FTO-coated glass slide using Surlyn (Meltonix 1170-60PF from Solaronix, Switzerland) window by hot pressing at 125° C. for 45 s. A copper redox electrolyte solution (A or B as defined below) was injected between anode and cathode using a pinhole on the cathode. The pinhole was sealed using a surlyn/glass cover by a heat sealing process. A conductive silver paint was applied on the contact areas of the anode and cathode and dried to form an electrical contact. The photovoltaic performance of the fabricated cell was measured under AM 1.5 conditions (1.5 atm) at a light intensity of 97 mW/cm<sup>2</sup>. The results of this experiment using various dyes, electrolytes and catalysts are shown in Table 2 below.

**[0183]** Electrolyte Solution A: 200 mM bis(6,6'-dimethyl-2,2'-bipyridine) copper (I) bis(trifluorosulfon)imide, 50 mM bis(6,6'-dimethyl-2,2'-bipyridine) copper (II) bis(trifluorosulfon)imide, 100 mM of Lithium bis(trifluorosulfon)imide and 0.5 M 4-(tertiarybutyl)pyridine in acetonitrile

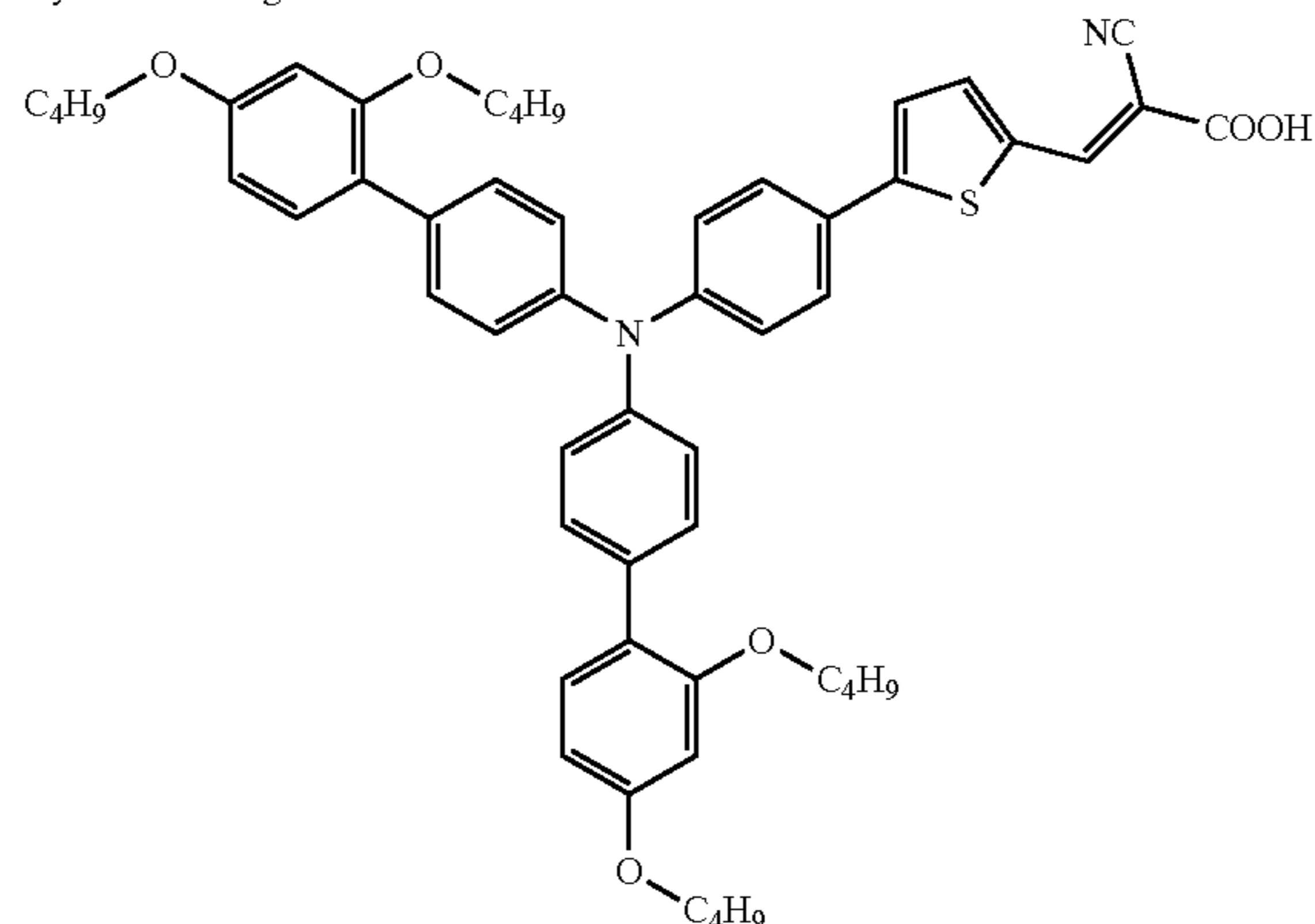
**[0184]** Electrolyte Solution B: 200 mM bis(2,9-dimethyl-1,10-phenanthroline) copper (I) bis(trifluorosulfon)imide, 50 mM bis(2,9-dimethyl-1,10-phenanthroline) copper (II) bis(trifluorosulfon)imide, 100 mM of Lithium bis(trifluorosulfon)imide and 0.5 M 4-(tertiarybutyl)pyridine in acetonitrile

TABLE 2

Experimental conditions and measurements.						
Dye	Catalyst	Electrolyte Solution	Open Circuit Voltage (mV)	Short Circuit Current Density (mA/cm <sup>2</sup> )	Fill Factor	Solar Conversion Efficiency (%)
D1	PEDOT	A	982	6.53	0.507	3.27
D2	PEDOT	A	778	1.25	0.643	0.63
D3	PEDOT	A	1123	8.21	0.493	4.64
D3	PEDOT	B	1198	6.75	0.519	4.14
D5	PEDOT	A	1129	6.99	0.510	4.11
D6	PEDOT	A	789	1.97	0.672	1.06
D7	PEDOT	A	854	2.87	0.636	1.60
D9	PEDOT	A	1130	6.7	0.454	3.59
D9	PEDOT	B	1160	5.06	0.545	3.24
D10	PEDOT	A	1110	7.06	0.462	3.67
D10	PEDOT	B	1129	7.41	0.516	4.37
D11	PEDOT	A	688	0.927	0.48	0.31
D12	PEDOT	A	987	6.09	0.528	3.21
D13	Pt	A	1100	5.5	0.528	3.26
D15	Pt	A	978	4.85	0.6	2.90
D16	Pt	A	1181	5.27	0.492	3.16
D16	PEDOT	A	1197	6.12	0.551	4.16
D35	PEDOT	B	1116	8.2	0.472	4.37

(Dyename, Sweden)

Dyename Orange D35



#### Solar Cell Dye Combinations

### Example 17

**[0185]** Fluorine-doped tin oxide (FTO) coated glasses were cut into 2 cm×2 cm size and cleaned by washing with successive 1% aqueous Triton X-100 solution, deionized (D1) water, and isopropanol. After drying at room temperature, the cleaned FTO glasses were treated with Corona discharge (~13000V) for approximately 20 seconds on the conducting side. An aqueous dispersion containing 20% by weight of TiO<sub>2</sub> (Degussa P25 with a particle size of 21+5 nm) and 5% by weight of poly(4-vinyl pyridine) was prepared and blade coated (6-8 microns thick) on the FTO coated side of the glass. The coating area was trimmed to 1.0 cm<sup>2</sup>. The TiO<sub>2</sub> coated anode was sintered at 450° C. for 30 minutes, cooled to about 80° C. and dropped into a dye solution containing 0.3 mM overall concentration of mix dye with various dye molar ratios (shown in Table 3) and 0.3 mM chenodeoxycholic acid in 1:1 acetonitrile/t-butanol. The anodes were kept in dye solution for overnight, rinsed

with acetonitrile and air dried in the dark. The dye sensitized anode was sandwiched with either electrochemically deposited PEDOT catalyst or pyrolytic platinum catalyst on a FTO coated glass slide using surlyn (Meltonix 1170-60PF from Solaronix, Switzerland) window by hot pressing at 125° C. for 45 seconds. A copper redox electrolyte solution consisting of 200 mM bis(6,6'-dimethyl-2,2'-bipyridine) copper (I) bis(trifluorosulfon)imide, 50 mM bis(6,6'-dimethyl-2,2'-bipyridine) copper (II) bis(trifluorosulfon)imide, 100 mM of Lithium bis(trifluorosulfon)imide and 0.5 M 4-(t-butyl)pyridine in a select solvent was injected between anode and cathode using pinhole on the cathode. The pinhole was sealed using surlyn/glass cover using heat sealing process. A conductive silver paint was applied on the contact areas of anode and cathode and dried to form electrical contact. The photovoltaic performance of the fabricated cells was measured under indoor light exposure conditions at 740 lux and is shown in Table 3.

TABLE 3

Photovoltaic characteristics of solar cells made with various co-sensitizer combinations at 740 lux indoor light exposure with volatile and stable electrolytes						
Dye composition in the sensitizer solution	Catalyst on the cathode	Electrolyte Solvent	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	ff	Power density (uW/cm <sup>2</sup> )
WD3	PEDOT	Acetonitrile	791.02	0.024	0.75	14.18
WD10	PEDOT	Acetonitrile	822.76	0.045	0.67	24.92
WD14	PEDOT	Acetonitrile	699.23	0.043	0.62	18.58
WE11	PEDOT	Acetonitrile	630.67	0.019	0.45	5.44
80/20	PEDOT	Acetonitrile	712.40	0.028	0.70	13.86
WD3/WD14						
80/20	PEDOT	Acetonitrile	878.77	0.067	0.71	41.86
WD3/WE11						
80/20	PEDOT	Acetonitrile	762.28	0.047	0.61	21.96
WD10/WD14						
80/20	PEDOT	Acetonitrile	772.79	0.062	0.63	30.09
WD10/WE11						
WD3	PEDOT	sulfolane	944.86	0.022	0.72	15.01
WD10	PEDOT	sulfolane	957.11	0.05	0.66	34.11
WD14	PEDOT	sulfolane	700.39	0.04	0.70	18.63
WE11	PEDOT	sulfolane	666.21	0.02	0.68	9.89
80/20	PEDOT	sulfolane	885.38	0.06	0.66	33.69
WD3/WD14						
80/20	PEDOT	sulfolane	947.80	0.07	0.66	45.11
WD3/WE11						
80/20	PEDOT	sulfolane	856.48	0.06	0.68	33.63
WD10/WD14						
80/20	PEDOT	sulfolane	921.00	0.07	0.64	40.14
WD10/WE11						
WD3	Pt	sulfolane	926.88	0.03	0.69	16.08
WD10	Pt	sulfolane	936.50	0.05	0.63	28.18
WD14	Pt	sulfolane	698.18	0.04	0.67	16.35
WE11	Pt	sulfolane	668.97	0.03	0.64	11.60
80/20	Pt	sulfolane	844.56	0.05	0.64	25.25
WD3/WD14						
80/20	Pt	sulfolane	937.78	0.07	0.62	41.35
WD3/WE11						
80/20	Pt	sulfolane	880.45	0.06	0.61	32.82
WD10/WD14						
80/20	Pt	sulfolane	902.22	0.07	0.61	37.12
WD10/WE11						

## Example 18

[0186] Fluorine-doped tin oxide (FTO) coated glasses were cut into 2 cm×2 cm size and cleaned by washing with successive 1% aqueous Triton X-100 solution, deionized (DI) water, and isopropanol. After drying at room tempera-

ture, the cleaned FTO glasses were treated with Corona discharge (~13000V) for approximately 20 seconds on the conducting side. An aqueous dispersion containing 20% by weight of TiO<sub>2</sub> (Degussa P25 with a particle size of 21+5 nm) and 5% by weight of poly(4-vinyl pyridine) was prepared and blade coated (6-8 microns thick) on the FTO coated side of the glass. The coating area was trimmed to 1.0 cm<sup>2</sup>. The TiO<sub>2</sub> coated anode was sintered at 450° C. for 30 minutes, cooled to about 80° C. and dropped into a dye solution containing 0.3 mM overall concentration of mix dye with various dye molar ratios (shown in Tables 4-6) and 0.3 mM chenodeoxycholic acid in 1:1 acetonitrile/t-butanol. The anodes were kept in dye solution for overnight, rinsed with acetonitrile and air dried in the dark. The dye sensitized anode was sandwiched pyrolytic platinum catalyst on a FTO coated glass slide using surlyn (Meltonix 1170-60PF from Solaronix, Switzerland) window by hot pressing at 125° C. for 45 seconds. A copper redox electrolyte solution consisting of 250 mM bis(6,6'-dimethyl-2,2'-bipyridine) copper (I) bis(trifluorosulfon)imide, 50 mM bis(6,6'-dimethyl-2,2'-bipyridine) copper (II) bis(trifluorosulfon)imide, 100 mM of Lithium bis(trifluorosulfon)-imide and 0.5 M 4-(t-butyl)pyridine in sulfolane was injected between anode and cathode using pinhole on the cathode. The pinhole was sealed using surlyn/glass cover using heat sealing process. A conductive silver paint was applied on the contact areas of anode and cathode and dried to form electrical contact. The photovoltaic performance of the fabricated cells was measured under indoor light exposure conditions and are shown in Tables 4-6.

TABLE 4

Photovoltaic characteristics of solar cells made with various co-sensitizer combinations at 360 lux indoor light exposure							
Dye combination	Dye 1	Dye 2	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	fill factor	Power density (uW/cm <sup>2</sup> )	
WD3	100% WD3	—	931.15	0.012	0.78	8.73	
cosensitized with XY1b dye	90% WD3	10% XY1b	940.64	0.043	0.60	24.15	
	85% WD3	15% XY1b	942.41	0.047	0.62	27.46	
	85% WD3	100% XY1b	874.82	0.038	0.54	17.98	
WD3	100% WD3	—	931.15	0.012	0.78	8.73	
cosensitized with WD14 dye	90% WD3	10% WD14	895.03	0.026	0.59	13.75	
	80% WD3	20% WD14	879.61	0.032	0.56	15.79	
	70% WD3	30% WD14	867.11	0.036	0.50	15.55	
	50% WD3	50% WD14	807.31	0.033	0.53	14.04	
	—	100% WD14	697.94	0.024	0.65	10.95	
WD3	100% WD3	—	931.15	0.012	0.78	8.73	
cosensitized with WE11 dye	90% WD3	10% WE11	937.44	0.029	0.61	16.53	
	80% WD3	20% WE11	944.03	0.036	0.58	19.58	
	70% WD3	30% WE11	901.71	0.037	0.60	20.02	
	50% WD3	50% WE11	907.38	0.04	0.55	20.00	
	—	100% WE11	795.75	0.035	0.54	15.10	
WD3	100% WD3	—	931.15	0.012	0.78	8.73	
cosensitized with WE10 dye	90% WD3	10% WE10	944.07	0.031	0.65	18.99	
	80% WD3	20% WE10	948.54	0.037	0.58	20.50	
	70% WD3	30% WE10	950.37	0.038	0.59	21.16	
	50% WD3	50% WE10	917.23	0.043	0.56	22.21	
	—	100% WE10	840.97	0.04	0.61	20.35	

TABLE 5

Photovoltaic characteristics of solar cells made with various co-sensitizer combinations at 740 lux indoor light exposure						
Dye combination	Dye 1	Dye 2	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	fill factor	Power density (uW/cm <sup>2</sup> )
WD3	100% WD3	—	952.78	0.022	0.68	14.34
cosensitized with XY1b dye	90% WD3 85% WD3	10% XY1b 15% XY1b	966.94 962.39	0.084 0.090	0.51 0.51	41.75 44.09
WD3	100% WD3	—	952.78	0.022	0.68	14.34
cosensitized with WD14 dye	90% WD3 80% WD3 70% WD3 50% WD3	10% WD14 20% WD14 30% WD14 50% WD14	922.74 908.49 894.52 851.37	0.050 0.061 0.064 0.058	0.50 0.48 0.40 0.40	23.25 26.38 23.07 19.85
—	—	100% WD14	725.40	0.046	0.58	19.29
WD3	100% WD3	—	952.78	0.022	0.68	14.34
cosensitized with WE11 dye	90% WD3 80% WD3 70% WD3 50% WD3	10% WE11 20% WE11 30% WE11 50% WE11	959.96 961.54 934.88 947.10	0.056 0.067 0.071 0.076	0.55 0.51 0.53 0.48	29.62 32.92 34.98 34.77
—	—	100% WE11	865.69	0.070	0.44	26.91
WD3	100% WD3	—	952.78	0.022	0.68	14.34
cosensitized with WE10 dye	90% WD3 80% WD3 70% WD3 50% WD3	10% WE10 20% WE10 30% WE10 50% WE10	957.94 964.11 964.86 943.71	0.060 0.075 0.075 0.088	0.57 0.46 0.51 0.49	32.93 33.48 36.62 41.02
—	—	100% WE10	876.21	0.081	0.52	36.62

TABLE 6

Photovoltaic characteristics of solar cells made with various co-sensitizer combinations at 1100 lux indoor light exposure						
Dye combination	Dye 1	Dye 2	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	fill factor	Power density (uW/cm <sup>2</sup> )
WD3	100% WD3	—	968.70	0.035	0.66	22.41
cosensitized with XY1b dye	90% WD3 85% WD3	10% XY1b 15% XY1b	979.55 970.71	0.123 0.131	0.48 0.48	57.23 60.53
—	—	100% XY1b	920.96	0.108	0.43	42.47
WD3	100% WD3	—	968.70	0.035	0.66	22.41
cosensitized with WD14 dye	90% WD3 80% WD3 70% WD3 50% WD3	10% WD14 20% WD14 30% WD14 50% WD14	945.32 930.14 917.26 874.46	0.078 0.092 0.098 0.089	0.47 0.44 0.39 0.39	34.88 37.99 34.88 30.04
—	—	100% WD14	757.38	0.070	0.52	27.41
WD3	100% WD3	—	968.70	0.035	0.66	22.41
cosensitized with WE11 dye	90% WD3 80% WD3 70% WD3 50% WD3	10% WE11 20% WE11 30% WE11 50% WE11	983.97 975.89 951.06 964.80	0.083 0.097 0.106 0.112	0.51 0.46 0.49 0.43	41.57 43.64 49.30 46.79
—	—	100% WE11	890.68	0.102	0.42	38.43
WD3	100% WD3	—	968.70	0.035	0.66	22.41
cosensitized with WE10 dye	90% WD3 80% WD3 70% WD3 50% WD3	10% WE10 20% WE10 30% WE10 50% WE10	983.61 983.98 982.44 963.36	0.092 0.111 0.111 0.129	0.54 0.44 0.44 0.44	48.96 47.62 48.42 54.80
—	—	100% WE10	905.80	0.117	0.46	49.07

## Example 19

[0187] Fluorine-doped tin oxide (FTO) coated glasses were cut into 2 cm×2 cm size and cleaned by washing with successive 1% aqueous Triton X-100 solution, deionized (DI) water, and isopropanol. After drying at room temperature, the cleaned FTO glasses were treated with Corona discharge (~13000V) for approximately 20 seconds on the

conducting side. An aqueous dispersion containing 20% by weight of TiO<sub>2</sub> (Degussa P25 with a particle size of 21+5 nm) and 5% by weight of poly(4-vinyl pyridine) was prepared and blade coated (6-8 microns thick) on the FTO coated side of the glass. The coating area was trimmed to 1.0 cm<sup>2</sup>. The TiO<sub>2</sub> coated anode was sintered at 450° C. for 30 minutes, cooled to about 80° C. and dropped into a dye solution containing 0.3 mM overall concentration of mix dye with various dye molar ratios (shown in Table 7) and 0.3 mM chenodeoxycholic acid in 1:1 acetonitrile/t-butanol. The anodes were kept in dye solution for overnight, rinsed with acetonitrile and air dried in the dark. The dye sensitized anode was sandwiched pyrolytic platinum catalyst on a FTO coated glass slide using surlyn (Meltonix 1170-60PF from Solaronix, Switzerland) window by hot pressing at 125° C. for 45 seconds. A copper redox electrolyte solution consisting of 250 mM bis(6,6'-dimethyl-2,2'-bipyridine) copper (I) bis(trifluorosulfon)imide, 50 mM bis(6,6'-dimethyl-2,2'-bipyridine) copper (II) bis(trifluorosulfon)imide, 100 mM of Lithium bis(trifluorosulfon)imide and 0.5 M 4-(t-butyl)pyridine in sulfolane was injected between anode and cathode using pinhole on the cathode. The pinhole was sealed using surlyn/glass cover using heat sealing process. A conductive silver paint was applied on the contact areas of anode and cathode and dried to form electrical contact. The photovoltaic performance of the fabricated cells was measured under indoor light exposure conditions and is shown in Table 7.

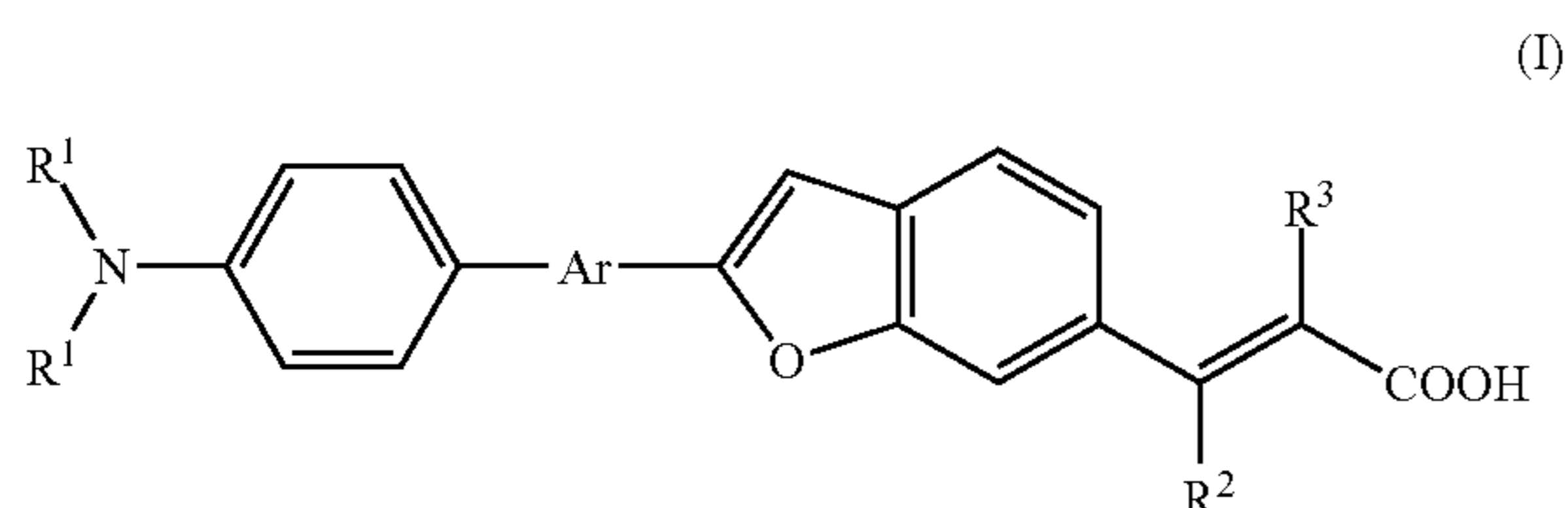
TABLE 7

Photovoltaic characteristics of solar cells made with various co-sensitizer combinations at 740 lux indoor light exposure						
Dye 1	Dye 2	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	Fill factor	Power density (uW/cm <sup>2</sup> )	Synergism
100% WD3	—	931.15	0.012	0.78	8.73	N/A
100% MK2	—	686.35	0.029	0.676	13.46	N/A
100% XY1b	—	861.47	0.06	0.584	30.19	N/A
100% WE11	—	851.71	0.067	0.605	34.52	N/A
100% D35	—	919.85	0.057	0.69	36.18	N/A
100% WD13	—	878.54	0.016	0.717	10.08	N/A
90% WD3	10% MK2	967.33	0.042	0.735	29.86	Yes
90% WD3	10% WD14	923.66	0.049	0.646	29.24	No
90% WD3	10% WE11	974.22	0.054	0.694	36.51	Yes
80% WD3	20% WE11	978.23	0.064	0.635	39.76	Yes
90% WD3	10% WE11	979.94	0.054	0.66	34.93	Yes
80% WD3	20% WE11	975.99	0.07	0.674	46.05	Yes
50% WD3	50% WE11	957.48	0.038	0.69	25.11	No
80% WD3	20% WD9	958.47	0.039	0.71	26.54	Yes
90% WD3	10% BOD4	882.30	0.056	0.659	32.56	No
80% D35	20% WD14	823.37	0.039	0.657	21.10	No
50% D35	50% WD14	753.87	0.037	0.657	18.33	No
D35	WD14					

TABLE 7-continued

Photovoltaic characteristics of solar cells made with various co-sensitizer combinations at 740 lux indoor light exposure						
Dye 1	Dye 2	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	Fill factor	Power density (uW/cm <sup>2</sup> )	Synergism
90% D35	10% WE11	918.34	0.065	0.64	38.20	No
90% WD13	10% WE11	964.95	0.061	0.664	39.08	Yes
90% WD13	10% MK2	933.35	0.041	0.693	26.52	Yes
90% WD13	10% XY1b	980.91	0.083	0.661	53.82	Yes

1. A compound of formula I:



wherein

each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, substituted or unsubstituted phenyl, substituted or unsubstituted C<sub>6</sub>-C<sub>12</sub> aryl (including fused, bicyclic and tricyclic aryl), substituted or unsubstituted C<sub>4</sub>-C<sub>12</sub> heteroaryl (including fused, bicyclic and tricyclic heteroaryl), substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, and substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> heterocycloalkyl;

—Ar— is a pi-bridge;

R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of H, —CN, —COOH, —X, substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl, —COOR, CONHR, CON(H)OR, —SO<sub>3</sub>R, —SO<sub>2</sub>R—OSO<sub>3</sub>R, —PO<sub>3</sub>HR, and —OPO<sub>3</sub>HR;

X is halogen; and

R is substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

2. (canceled)

3. (canceled)

4. (canceled)

5. The compound of claim 1 wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted phenyl, naphthyl, fluorenyl, carbazolyl, biphenyl, thienyl, and pyrrolyl.

6. The compound of claim 1 wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl.

7. The compound of claim 1 wherein each R<sup>1</sup> is independently selected from the group consisting of substituted or unsubstituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl.

8. A dye sensitized solar cell comprising a solar cell dye, wherein the solar cell dye is the compound of claim 1.

9. A method of making a DSSC comprising the step of incorporating the solar cell dye of claim 1 into the DSSC.

10. (canceled)

11. (canceled)

12. (canceled)

13. (canceled)

14. (canceled)

15. (canceled)

16. (canceled)

17. (canceled)

18. (canceled)

19. (canceled)

20. (canceled)

21. (canceled)

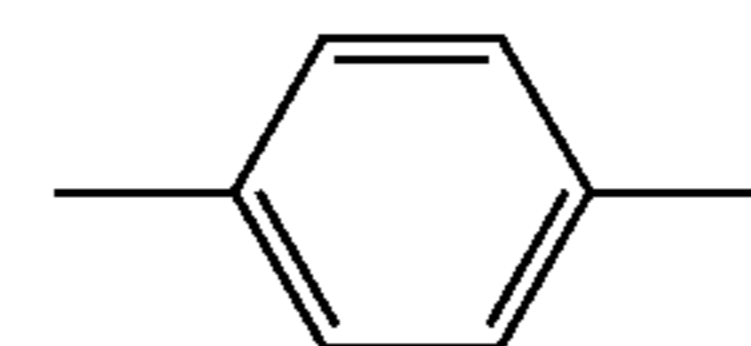
22. (canceled)

23. (canceled)

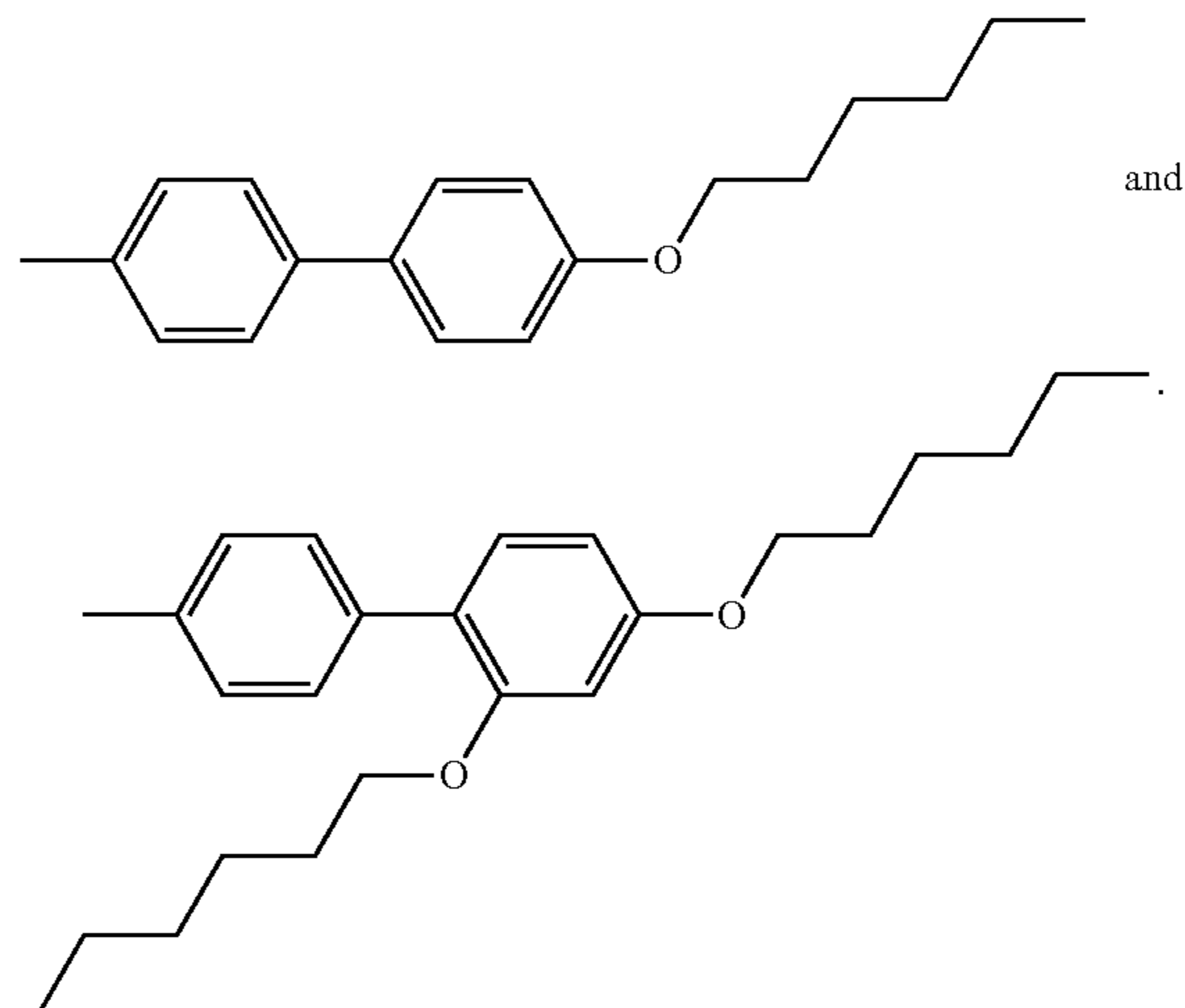
24. (canceled)

25. The compound of claim 1, wherein R<sup>2</sup> is H and R<sup>3</sup> is CN.

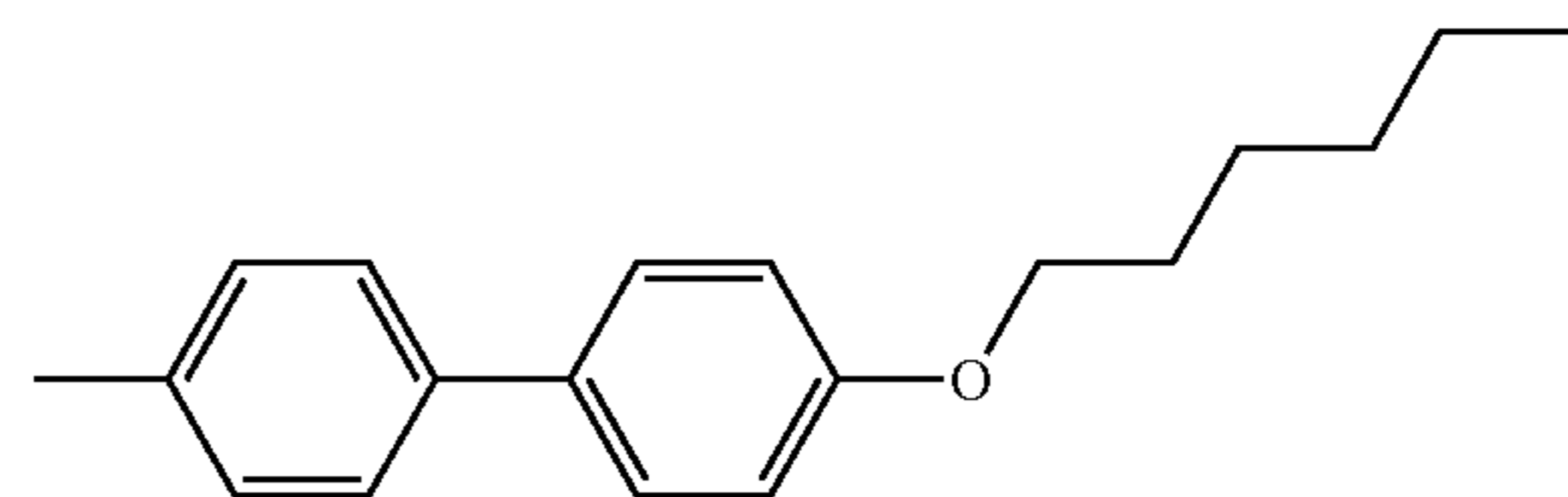
26. The compound of claim 1, wherein the Pi-bridge is



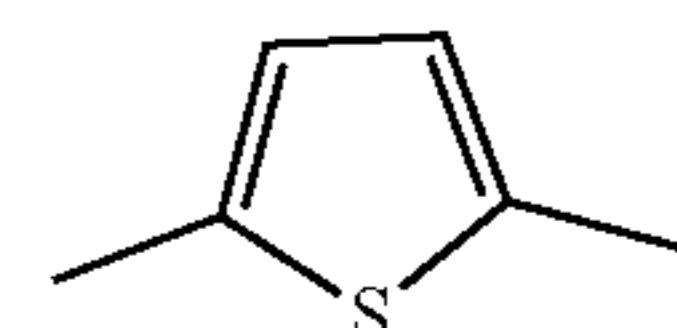
27. The compound of claim 1, wherein R<sup>1</sup> is selected from



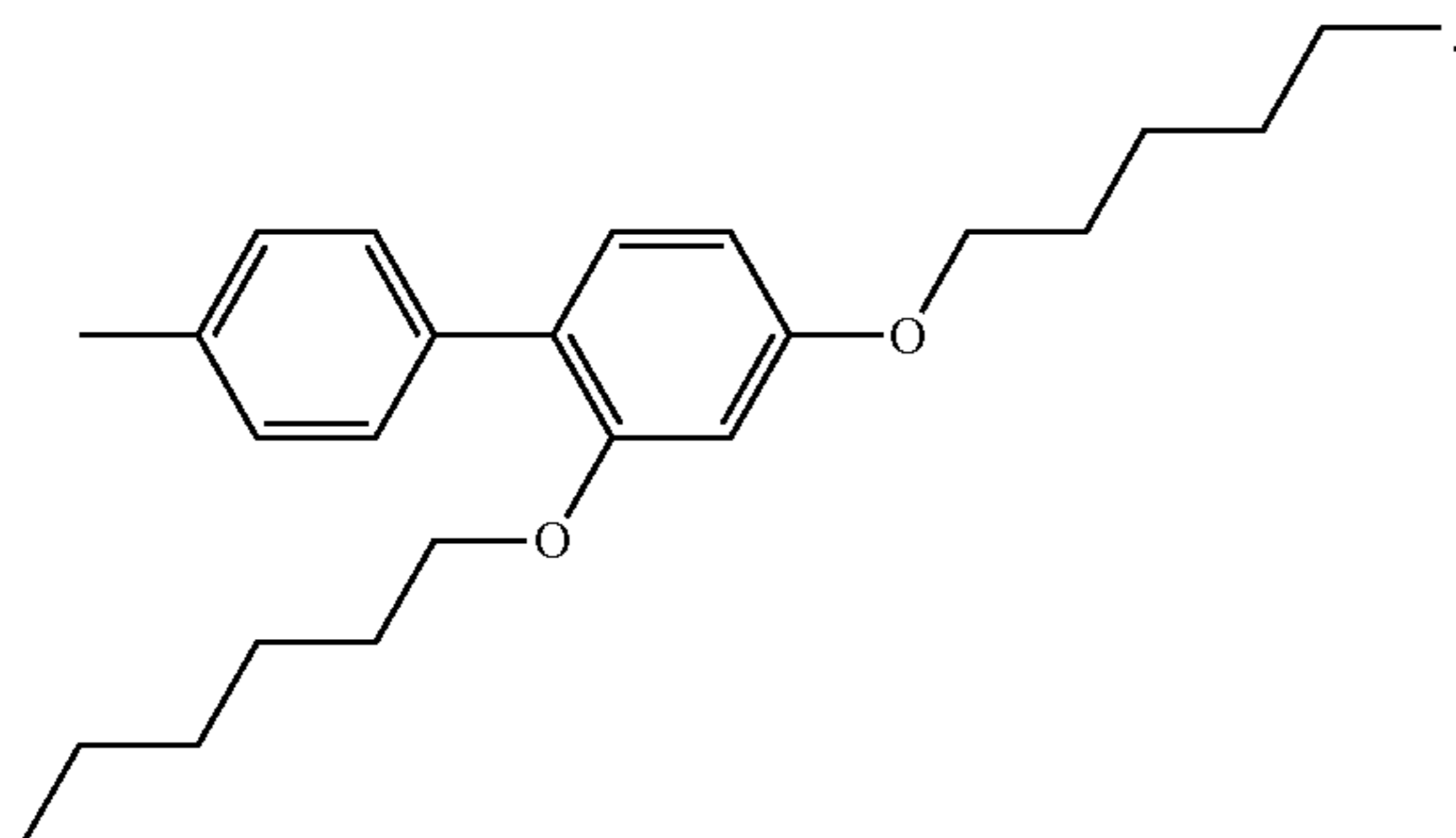
28. The compound of claim 25, wherein R<sup>1</sup> is



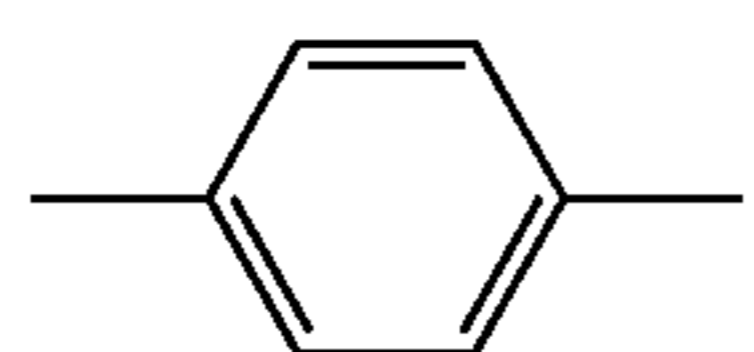
29. The compound of claim 28, wherein the Pi-bridge is



30. The compound of claim 25, wherein R<sup>1</sup> is



31. The compound of claim 30, wherein the Pi-bridge is



\* \* \* \* \*