



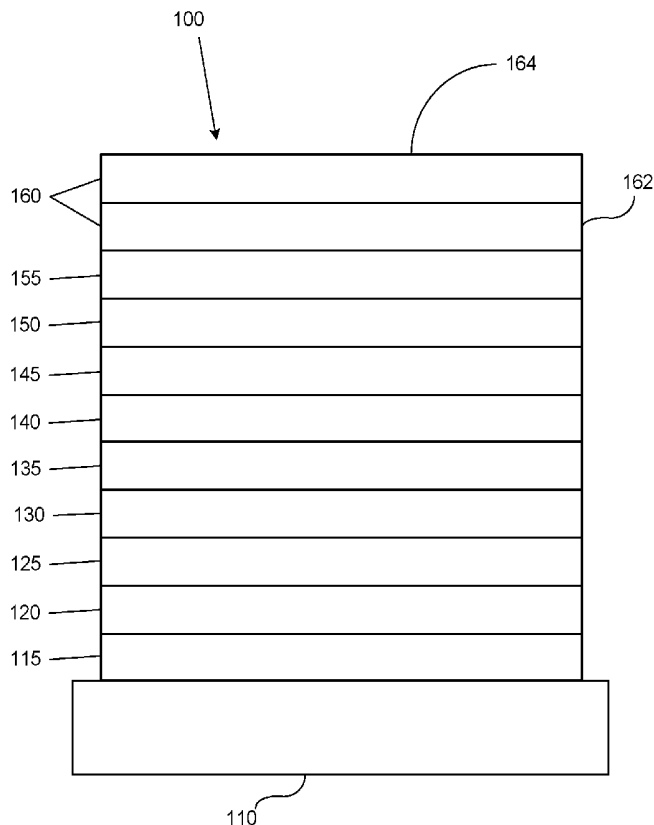
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**LIN et al.**(10) **Pub. No.: US 2017/0077417 A1**(43) **Pub. Date: Mar. 16, 2017**(54) **ORGANIC ELECTROLUMINESCENT  
MATERIALS AND DEVICES****Publication Classification**(71) Applicant: **Universal Display Corporation,**  
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division of application No. 12/647,927, filed on Dec.  
28, 2009, now Pat. No. 9,067,947.(60) Provisional application No. 61/145,370, filed on Jan.  
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(57)

**ABSTRACT**

A new class of compounds containing aza-dibenzothiophene or aza-dibenzofuran are provided. The compounds may be used in organic light emitting devices giving improved stability, improved efficiency, long lifetime and low operational voltage. In particular, the compounds may be used as the host material of an emissive layer having a host and an emissive dopant, or as a material in an enhancement layer.



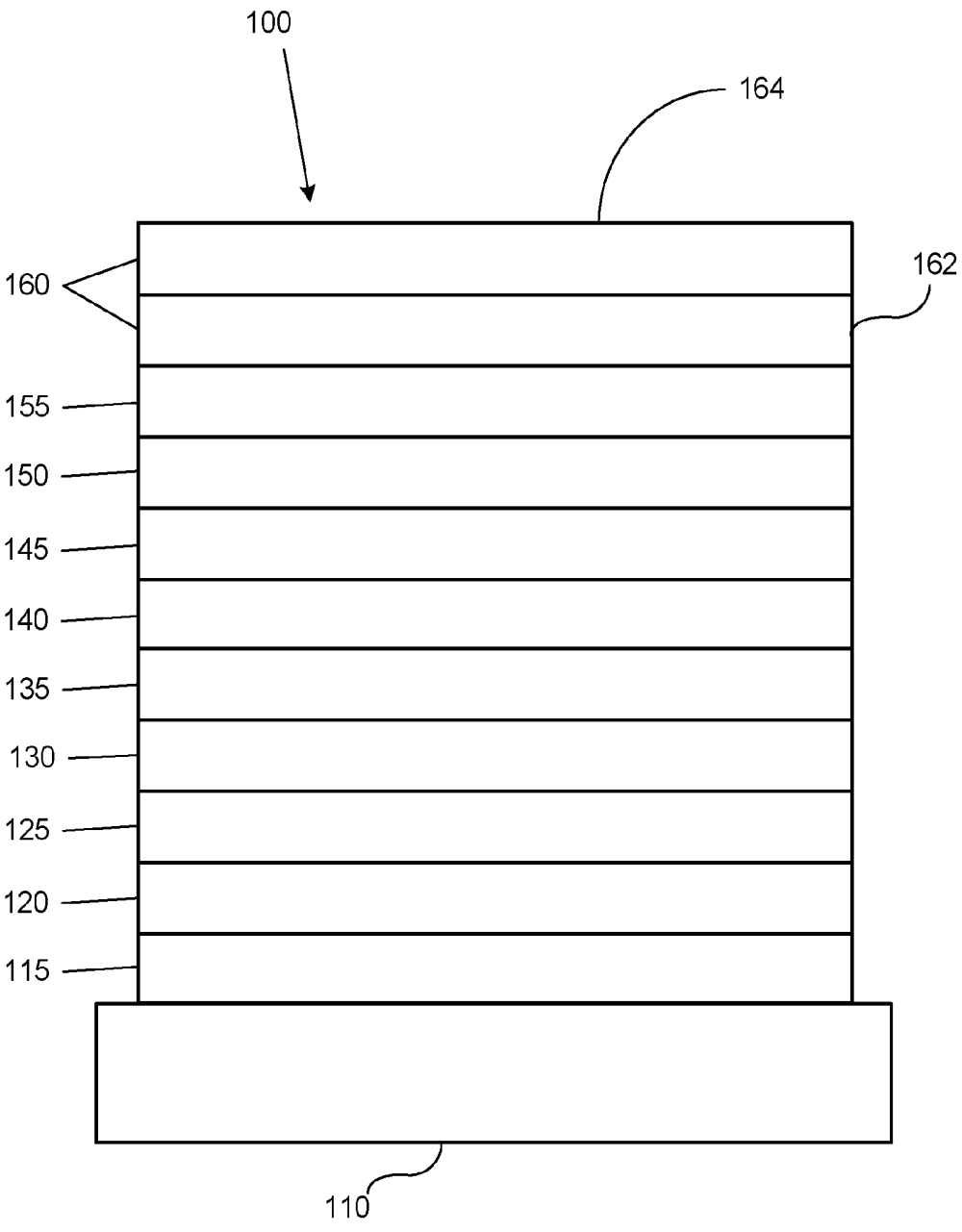


FIGURE 1

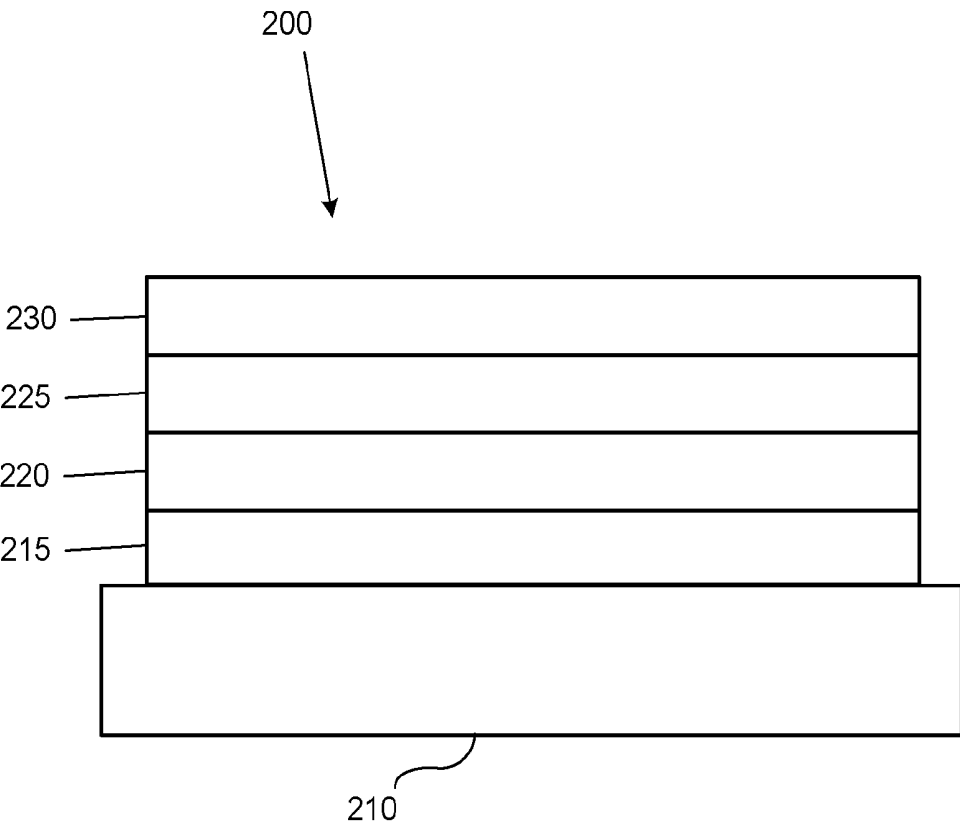


FIGURE 2

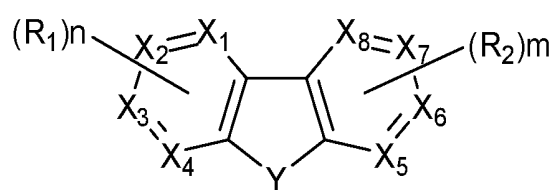


FIGURE 3

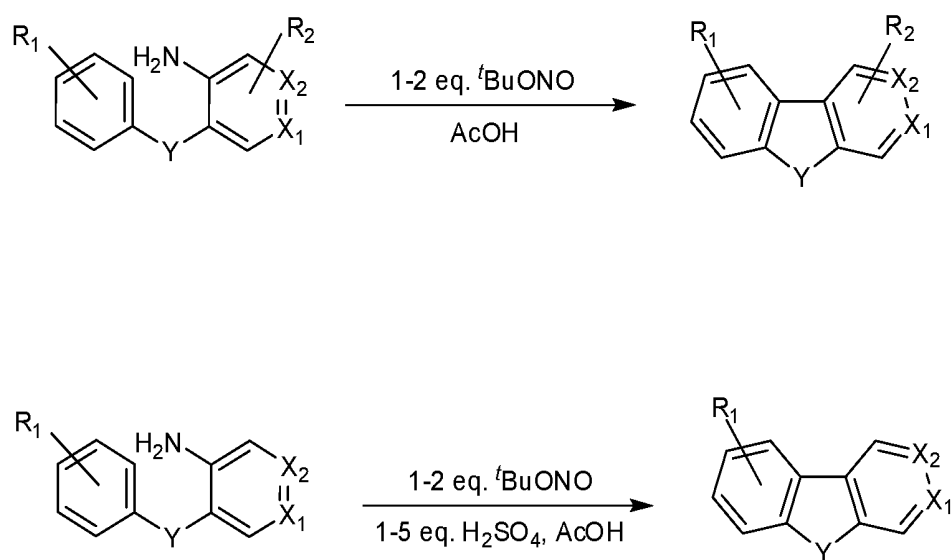


FIGURE 4

## ORGANIC ELECTROLUMINESCENT MATERIALS AND DEVICES

### CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of U.S. patent application Ser. No. 14/735,589, filed on Jun. 10, 2015, which is a divisional application of U.S. patent application Ser. No. 12/647,927, filed Dec. 28, 2009, now patented as U.S. Pat. No. 9,067,947, issued on Jun. 30, 2015, which claims priority to U.S. Provisional Application No. 61/145,370, filed Jan. 16, 2009, the disclosures of which are herein expressly incorporated by reference in their entirety.

[0002] The claimed invention was made by, on behalf of, and/or in connection with one or more of the following parties to a joint university corporation research agreement: Regents of the University of Michigan, Princeton University, The University of Southern California, and the Universal Display Corporation. The agreement was in effect on and before the date the claimed invention was made, and the claimed invention was made as a result of activities undertaken within the scope of the agreement.

### FIELD OF THE INVENTION

[0003] The present invention relates to novel organic complexes containing aza-dibenzothiophene or aza-dibenzofuran. The materials may be useful in organic light emitting devices (OLEDs),

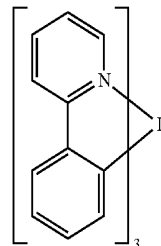
### BACKGROUND

[0004] Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

[0005] OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and configurations are described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, which are incorporated herein by reference in their entirety.

[0006] One application for phosphorescent emissive molecules is a full color display. Industry standards for such a display call for pixels adapted to emit particular colors, referred to as “saturated” colors. In particular, these standards call for saturated red, green, and blue pixels. Color may be measured using CIE coordinates, which are well known to the art.

[0007] One example of a green emissive molecule is tris(2-phenylpyridine) iridium, denoted Ir(ppy)<sub>3</sub>, which has the structure:



[0008] In this, and later figures herein, we depict the dative bond from nitrogen to metal (here, Ir) as a straight line,

[0009] As used herein, the term “organic” includes polymeric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. “Small molecule” refers to any organic material that is not a polymer, and “small molecules” may actually be quite large. Small molecules may include repeat units in some circumstances. For example, using a long chain alkyl group as a substituent does not remove a molecule from the “small molecule” class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as apart of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core moiety of a dendrimer may be a fluorescent or phosphorescent small molecule emitter. A dendrimer may be a “small molecule,” and it is believed that all dendrimers currently used in the field of OLEDs are small molecules.

[0010] As used herein, “top” means furthest away from the substrate, while “bottom” means closest to the substrate. Where a first layer is described as “disposed over” a second layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is “in contact with” the second layer. For example, a cathode may be described as “disposed over” an anode, even though there are various organic layers in between.

[0011] As used herein, “solution processible” means capable of being dissolved, dispersed, or transported in and/or deposited from a liquid medium, either in solution or suspension form.

[0012] A ligand may be referred to as “photoactive” when it is believed that the ligand directly contributes to the photoactive properties of an emissive material. A ligand may be referred to as “ancillary” when it is believed that the ligand does not contribute to the photoactive properties of an emissive material, although an ancillary ligand may alter the properties of a photoactive ligand.

[0013] As used herein, and as would be generally understood by one skilled in the art, a first “Highest Occupied Molecular Orbital” (HOMO) or “Lowest Unoccupied Molecular Orbital” (LUMO) energy level is “greater than” or “higher than” a second HOMO or LUMO energy level if the first energy level is closer to the vacuum energy level. Since ionization potentials (IP) are measured as a negative energy relative to a vacuum level, a higher HOMO energy level corresponds to an IP having a smaller absolute value (an IP that is less negative). Similarly, a higher LUMO energy level corresponds to an electron affinity (EA) having

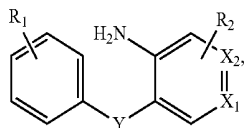
a smaller absolute value (an EA that is less negative). On a conventional energy level diagram, with the vacuum level at the top, the LUMO energy level of a material is higher than the HOMO energy level of the same material. A “higher” HOMO or LUMO energy level appears closer to the top of such a diagram than a “lower” HOMO or LUMO energy level.

**[0014]** As used herein, and as would be generally understood by one skilled in the art, a first work function is “greater than” or “higher than” a second work function if the first work function has a higher absolute value. Because work functions are generally measured as negative numbers relative to vacuum level, this means that a “higher” work function is more negative. On a conventional energy level diagram, with the vacuum level at the top, a “higher” work function is illustrated as further away from the vacuum level in the downward direction. Thus, the definitions of HOMO and LUMO energy levels follow a different convention than work functions.

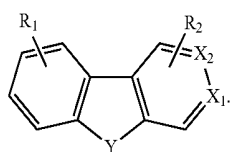
**[0015]** More details on OLEDs, and the definitions described above, can be found in U.S. Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

#### SUMMARY OF THE INVENTION

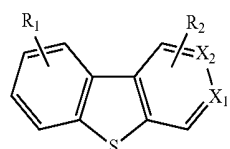
**[0016]** A process is provided for making aza-dibenzothiophene compounds or aza-dibenzofuran compounds. The process, comprising treating an acetic acid solution of an amino-arylthio pyridine intermediate having the formula



wherein one of  $X_1$  and  $X_2$  is nitrogen and the other of  $X_1$  and  $X_2$  is carbon and wherein  $Y$  is S or O, with  $^t\text{BuONO}$  to produce an aza complex having the formula

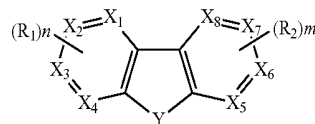


$R_1$  and  $R_2$  may represent mono, di, tri or tetra substitutions.  $R_1$  is selected from the group consisting of hydrogen, alkyl, aryl, heteroaryl and halide. Preferably,  $R_1$  is halide.  $R_2$  is selected from the group consisting of hydrogen, alkyl, aryl and halide. Preferably, one of  $X_1$  and  $X_2$  may be carbon and the other may be nitrogen. More preferably,  $X_1$  is nitrogen and  $X_2$  is carbon or  $X_1$  is carbon and  $X_2$  is nitrogen. Preferably,  $Y$  is S. Alternatively,  $Y$  may preferably be O.  $R_2$  may include at least one halide, and  $R_2$  may include only halide substituents. The process may be used to make compounds where  $R_2$  is not halide and the amino-arylthio pyridine intermediate is treated with  $\text{H}_2\text{SO}_4$  prior to treatment with  $^t\text{BuONO}$ . The yield of

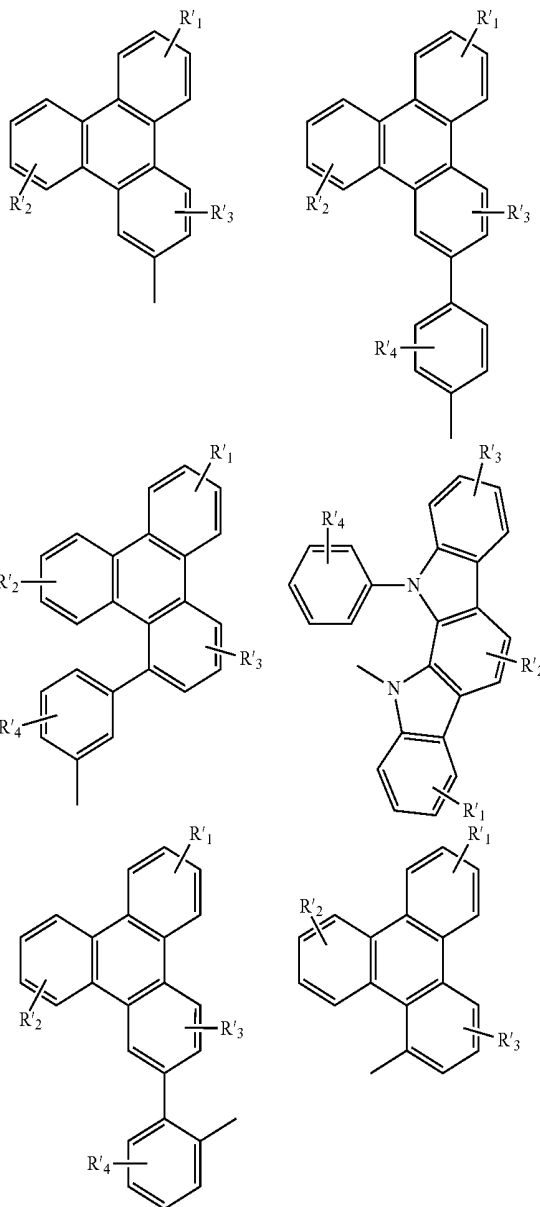


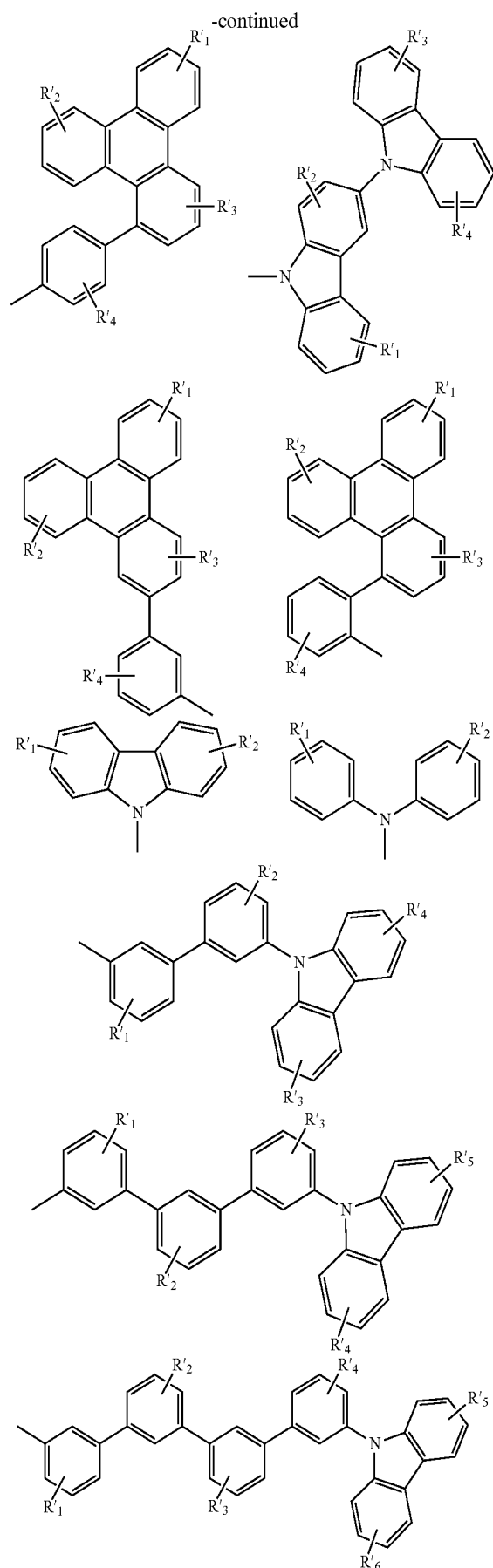
may be greater than 50%.

**[0017]** A novel class of aza-dibenzothiophene and aza-dibenzofuran compounds are provided. The compounds have the formula:



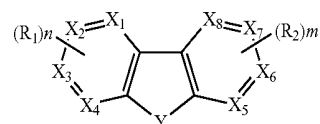
FORMULA I.  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$  are independently selected from the group consisting of a carbon atom and a nitrogen atom, and at least one of  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$  is a nitrogen atom.  $Y$  is S or O.  $R_1$  and  $R_2$  may represent mono, di, tri, or tetra substitutions.  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen, alkyl, aryl and halide, and at least one of  $R_1$  and  $R_2$  is selected from the group consisting of:



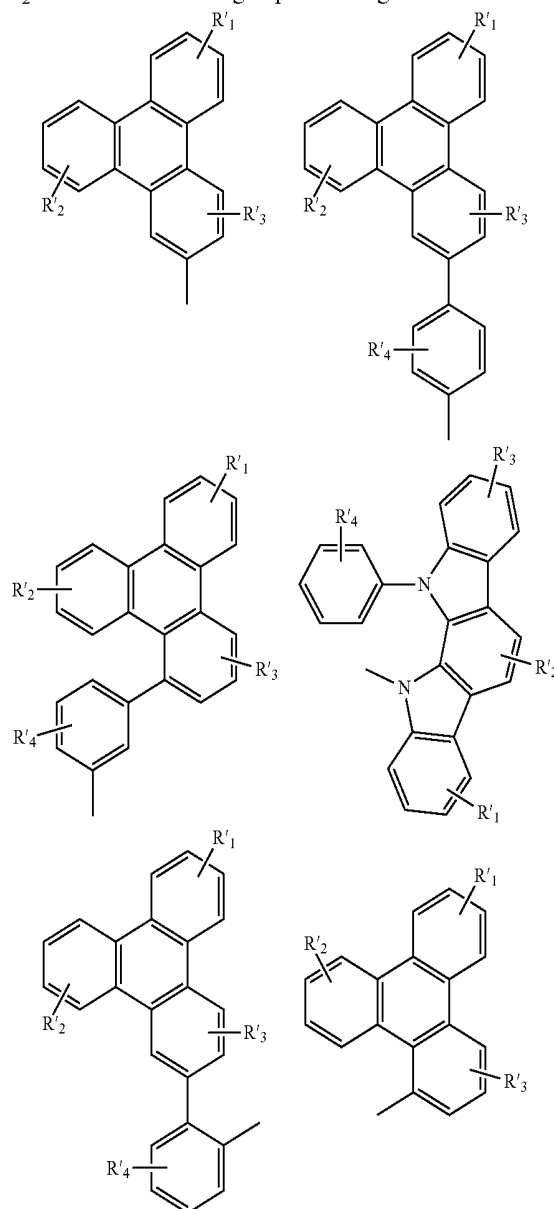


$R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  may represent mono, di, tri, tetra or penta substitutions, and  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably,  $m$  and  $n$  are 0, 1, 2, 3, or 4; and wherein  $m+n$  is equal to or greater than 2 and  $m+n$  is equal to or less than 6. Preferably,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are each independently hydrogen or methyl.

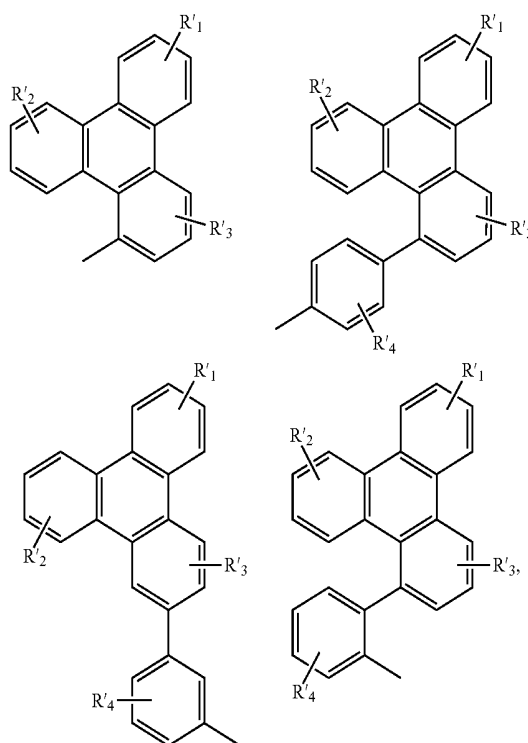
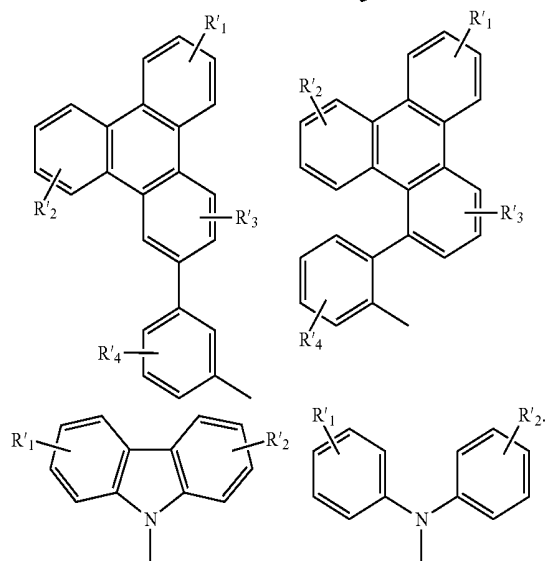
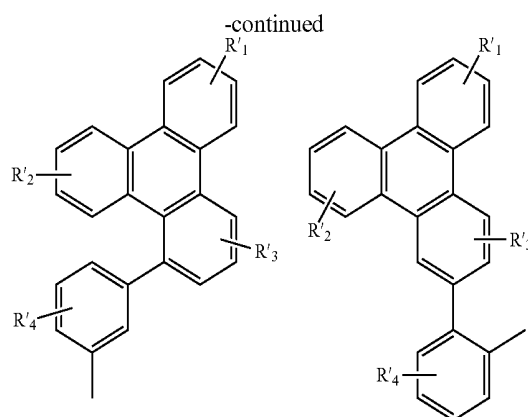
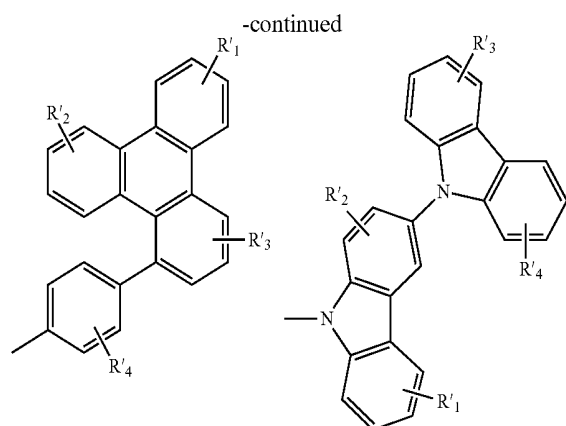
[0018] Additionally, a novel class of aza-dibenzothio-  
phene and aza-dibenzofuran compounds are provided. The  
compounds have the formula:



FORMULA I.  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$  are independently selected from the group consisting of a carbon atom and a nitrogen atom, and at least one of  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$  is a nitrogen atom.  $Y$  is S or O.  $R_1$  and  $R_2$  may represent mono, di, tri, or tetra substitutions.  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen, alkyl, aryl and halide, and at least one of  $R_1$  and  $R_2$  is selected from the group consisting of:

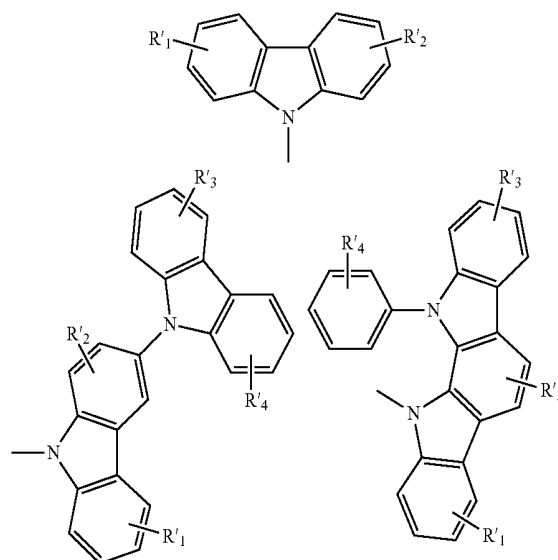
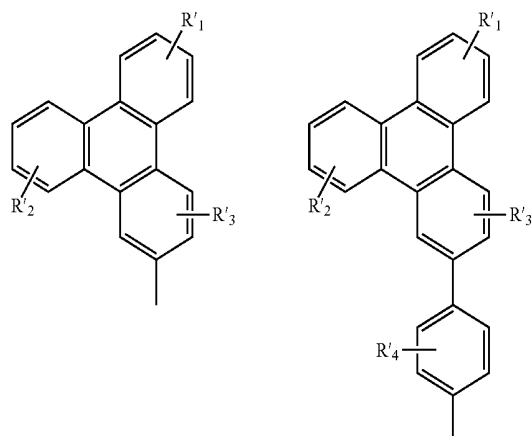


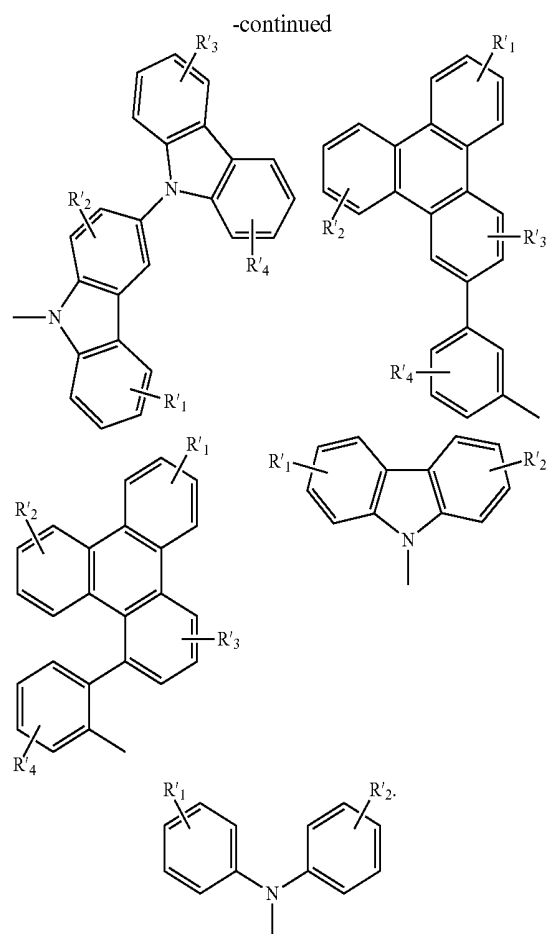
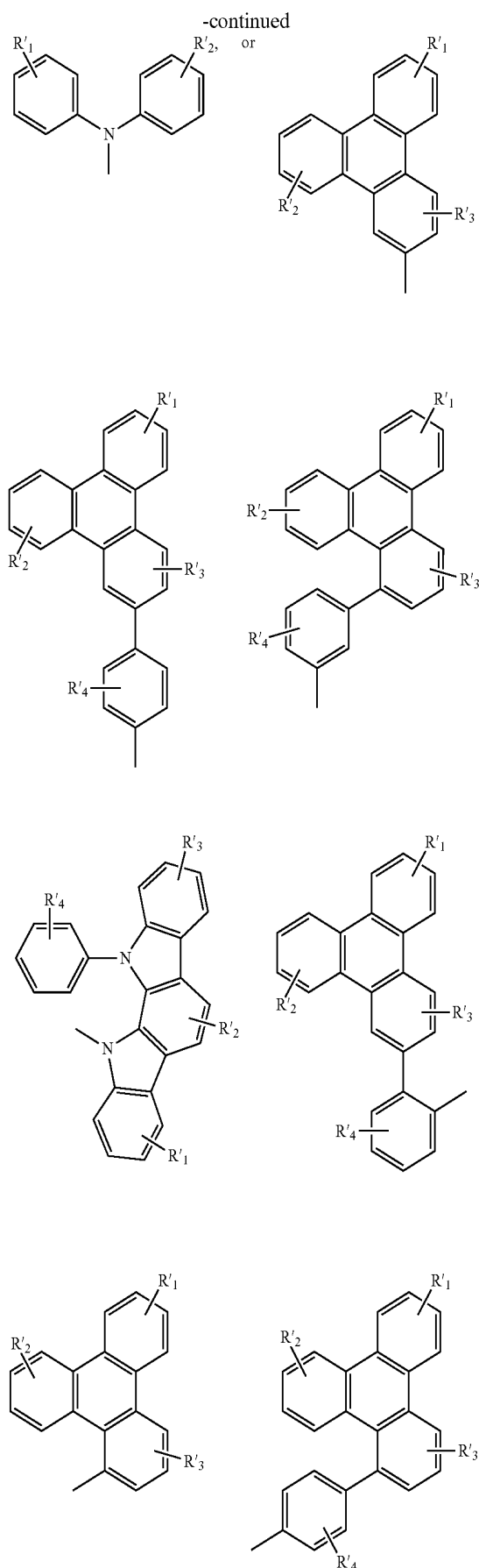




R'<sub>1</sub>, R'<sub>2</sub>, R'<sub>3</sub>, and R'<sub>4</sub> may represent mono, di, tri, tetra or penta substitutions, and R'<sub>1</sub>, R'<sub>2</sub>, R'<sub>3</sub>, and R'<sub>4</sub> are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably, m and n are 0, 1, 2, 3, or 4; and wherein m+n is equal to or greater than 2 and m+n is equal to or less than 6. Preferably, R'<sub>1</sub>, R'<sub>2</sub>, R'<sub>3</sub>, and R'<sub>4</sub> are each independently hydrogen or methyl.

**[0019]** Compounds are also provided where one of R<sub>1</sub> and R<sub>2</sub> is hydrogen and the other of R<sub>1</sub> and R<sub>2</sub> is selected from the groups consisting of





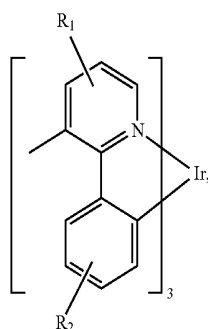
**[0020]** Specific examples of the aza-dibenzothiophene compounds and aza-dibenzofuran compounds are provided including Compounds 1-93.

**[0021]** Specific examples of the aza-dibenzothiophene compounds and aza-dibenzofuran compounds are provided including Compounds 1-79.

**[0022]** A first device comprising an organic light emitting device is provided. The device further comprises an anode, a cathode, and an organic layer disposed between the anode and the cathode. The organic layer comprises a compound having FORMULA I. In particular, the organic layer of the device may comprise a compound selected from Compounds 1-93.

[0023] In one aspect, the first device is a consumer product.

**[0024]** An organic light emitting device is also provided. The device comprises an anode, a cathode, and an organic layer disposed between the anode and the cathode. The organic layer comprises a compound having FORMULA I. In particular, the organic layer of the device may comprise a compound selected from Compound 1-79. Preferably, the organic layer is an emissive layer and the compound having FORMULA I is a host. The emissive layer may further comprise an emissive dopant. Preferably, the emissive dopant has the formula



where  $R_1$  and  $R_2$  are each independently selected from the group consisting of hydrogen, alkyl, and aryl.

[0025] Additionally, a consumer product is also provided. The product contains a device that has an anode, a cathode, and an organic layer disposed between the anode and the cathode, where the organic layer comprises a compound having FORMULA I.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0026] FIG. 1 shows an organic light emitting device.

[0027] FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

[0028] FIG. 3 shows aza-dibenzothiophene compounds and aza-dibenzofuran compounds.

[0029] FIG. 4 shows reactions in synthetic pathways.

#### DETAILED DESCRIPTION

[0030] Generally, an OLED comprises at least one organic layer disposed between and electrically connected to an anode and a cathode. When a current is applied, the anode injects holes and the cathode injects electrons into the organic layer(s). The injected holes and electrons each migrate toward the oppositely charged electrode. When an electron and hole localize on the same molecule, an “exciton,” which is a localized electron-hole pair having an excited energy state, is formed. Light is emitted when the exciton relaxes via a photoemissive mechanism. In some cases, the exciton may be localized on an excimer or an exciplex. Non-radiative mechanisms, such as thermal relaxation, may also occur, but are generally considered undesirable.

[0031] The initial OLEDs used emissive molecules that emitted light from their singlet states (“fluorescence”) as disclosed, for example, in U.S. Pat. No. 4,769,292, which is incorporated by reference in its entirety. Fluorescent emission generally occurs in a time frame of less than 10 nanoseconds.

[0032] More recently, OLEDs having emissive materials that emit light from triplet states (“phosphorescence”) have been demonstrated. Baldo et al., “Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices,” *Nature*, vol. 395, 151-154, 1998; (“Baldo-I”) and Baldo et al., “Very high-efficiency green organic light-emitting devices based on electrophosphorescence,” *Appl. Phys. Lett.*, vol. 75, No. 3, 4-6 (1999) (“Baldo-III”), which are incorporated by reference in their entireties. Phosphorescence is described in more detail in U.S. Pat. No. 7,279,704 at cols. 5-6, which are incorporated by reference.

[0033] FIG. 1 shows an organic light emitting device 100. The figures are not necessarily drawn to scale. Device 100 may include a substrate 110, an anode 115, a hole injection layer 120, a hole transport layer 125, an electron blocking layer 130, an emissive layer 135, a hole blocking layer 140, an electron transport layer 145, an electron injection layer 150, a protective layer 155, and a cathode 160. Cathode 160 is a compound cathode having a first conductive layer 162 and a second conductive layer 164. Device 100 may be fabricated by depositing the layers described, in order. The properties and functions of these various layers, as well as example materials, are described in more detail in U.S. Pat. No. 7,279,704 at cols. 6-10, which are incorporated by reference.

[0034] More examples for each of these layers are available. For example, a flexible and transparent substrate-anode combination is disclosed in U.S. Pat. No. 5,844,363, which is incorporated by reference in its entirety. An example of a p-doped hole transport layer is m-MTDATA doped with F.sub.4-TCNQ at a molar ratio of 50:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. Examples of emissive and host materials are disclosed in U.S. Pat. No. 6,303,238 to Thompson et al., which is incorporated by reference in its entirety. An example of an n-doped electron transport layer is BPhen doped with Li at a molar ratio of 1:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated by reference in their entireties, disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electrically-conductive, sputter-deposited ITO layer. The theory and use of blocking layers is described in more detail in U.S. Pat. No. 6,097,147 and U.S. Patent Application Publication No. 2003/0230980, which are incorporated by reference in their entireties. Examples of injection layers are provided in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety.

[0035] FIG. 2 shows an inverted OLED 200. The device includes a substrate 210, a cathode 215, an emissive layer 220, a hole transport layer 225, and an anode 230. Device 200 may be fabricated by depositing the layers described, in order. Because the most common OLED configuration has a cathode disposed over the anode, and device 200 has cathode 215 disposed under anode 230, device 200 may be referred to as an “inverted” OLED. Materials similar to those described with respect to device 100 may be used in the corresponding layers of device 200. FIG. 2 provides one example of how some layers may be omitted from the structure of device 100.

[0036] The simple layered structure illustrated in FIGS. 1 and 2 is provided by way of non-limiting example, and it is understood that embodiments of the invention may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost

factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as a mixture of host and dopant, or more generally a mixture, may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device **200**, hole transport layer **225** transports holes and injects holes into emissive layer **220**, and may be described as a hole transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an "organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to FIGS. **1** and **2**.

**[0037]** Structures and materials not specifically described may also be used, such as LEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190 to Friend et al., which is incorporated by reference in its entirety. By way of further example, OLEDs having a single organic layer may be used. OLEDs may be stacked, for example as described in U.S. Pat. No. 5,707,745 to Forrest et al, which is incorporated by reference in its entirety. The OLED structure may deviate from the simple layered structure illustrated in FIGS. **1** and **2**. For example, the substrate may include an angled reflective surface to improve out-coupling, such as a mesa structure as described in U.S. Pat. No. 6,091,195 to Forrest et al., mod/or a pit structure as described in U.S. Pat. No. 5,834,893 to Bulovic et al., which are incorporated by reference in their entireties.

**[0038]** Unless otherwise specified, any of the layers of the various embodiments may be deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. patent application Ser. No. 10/233,470, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink-jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution processibility than those having symmetric structures, because asymmetric materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

**[0039]** Devices fabricated in accordance with embodiments of the invention may be incorporated into a wide variety of consumer products, including flat panel displays, computer monitors, televisions, billboards, lights for interior or exterior illumination and/or signaling, heads up displays, fully transparent displays, flexible displays, laser printers, telephones, cell phones, personal digital assistants (PDAs), laptop computers, digital cameras, camcorders, viewfinders, micro-displays, vehicles, a large area wall, theater or stadium screen, or a sign. Various control mechanisms may be used to control devices fabricated in accordance with the present invention, including passive matrix and active matrix. Many of the devices are intended for use in a temperature range comfortable to humans, such as 18 degrees C. to 30 degrees C., and more preferably at room temperature (20-25 degrees C.).

**[0040]** The materials and structures described herein may have applications in devices other than OLEDs. For example, other optoelectronic devices such as organic solar cells and organic photodetectors may employ the materials and structures. More generally, organic devices, such as organic transistors, may employ the materials and structures.

**[0041]** The terms halo, halogen, alkyl, cycloalkyl, alkenyl, alkynyl, arylkyl, heterocyclic group, aryl, aromatic group, and heteroaryl are known to the art, and are defined in U.S. Pat. No. 7,279,704 at cols. 31-32, which are incorporated herein by reference.

**[0042]** A new class of compounds containing an aza-dibenzothiophene or aza-dibenzofuran core are provided (illustrated in FIG. **3**). In particular, aza-dibenzothiophene compounds or aza-dibenzofuran compounds further substituted with triphenylene and/or nitrogen-containing substituents are provided. These compounds may be advantageously used in phosphorescent organic light emitting devices. Preferably, these compounds may be used as a host material in an emissive layer or as a material in an enhancement layer.

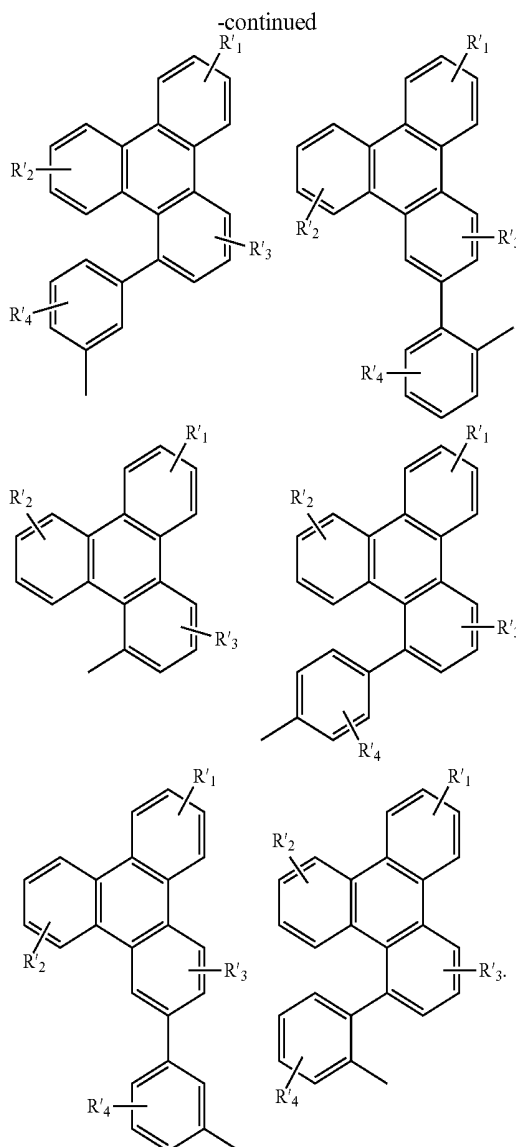
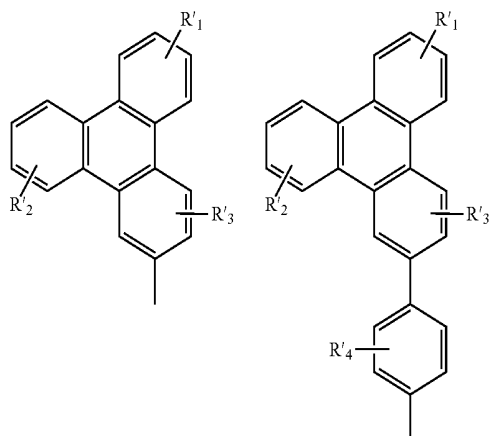
**[0043]** While there are existing syntheses for aza-dibenzothiophene compounds and aza-dibenzofuran compounds, these synthetic routes may have limited practicality. For example, substrates of aza-dibenzothiophene and aza-dibenzofuran were first synthesized by the well-known Pschorr Cyclization method which involves the formation of diazonium salt followed by cyclization in an aqueous medium with or without catalysts, such as Cu, CuCl. However, the general yield of the Pschorr Cyclization method is not consistent and can be less than 10%. Therefore, it is desirable to provide a process for making aza-dibenzothiophene compounds and aza-dibenzofuran compounds in improved yields. A new process for making aza-dibenzothiophene compounds is provided herein (illustrated in FIG. **4**). The processes described in this invention differ from the existing synthesis at least by using acetic acid, not aqueous medium, and do not employ any metal catalyst. Preferably, the acetic acid is pure(or glacial) acetic acid. The process provided herein may provide yields higher than 50% or yields higher than 70%.

**[0044]** Dibenzothiophene-containing and dibenzofuran-containing materials are typically hole transporting materials that have a relatively high triplet energy. Given the beneficial properties of dibenzothiophene and dibenzofuran, these compounds have been used in the OLED area and some of these compounds have achieved good device performance. See Lin et al., *Dibenzothiophene-containing Materials in Phosphorescent Light Emitting Diodes*, 2008, U.S. application Ser. No. 12/208,907 and Ma et al., *Benzo-fused Thiophene/Triphenylene Hybrid Materials*, 2008, PCT/US2008/072499. Without being bound by theory, it is

thought that anion injection and anion stability may play an important role in device stability. In order to have high anion stability and a lower energy barrier for anion injection to the emissive layer, compounds with a lower LUMO level are desired. In particular, dibenzothiophene and dibenzofuran containing compounds having a lower LUMO value (i.e., compounds that are more easily reduced) may be beneficial.

**[0045]** The compounds provided herein contain an aza-dibenzothiophene or aza-dibenzofuran core further substituted with particular chemical groups having desirable properties. Specifically, these aza-type compounds are substituted with triphenylene groups and/or nitrogen-containing groups (e.g., carbazole) to maintain high triplet energy and provide improved charge transport properties. Therefore, these substituted aza-dibenzothiophene compounds and aza-dibenzofuran compounds may provide devices having improved stability, improved efficiency, and a longer lifetime. In addition, these aza-type compounds have been demonstrated to be more easily reduced than their dibenzothiophene or dibenzofuran counterparts, and thus may provide devices having low operating voltage.

**[0046]** Triphenylene is a polyaromatic hydrocarbon with high triplet energy, yet high  $\pi$ -conjugation and a relatively small energy difference between the first singlet and first triplet levels. This would indicate that triphenylene has relatively easily accessible HOMO and LUMO levels compared to other aromatic compounds with similar triplet energy (e.g., biphenyl). These characteristics of triphenylene make it a good molecular building block in OLED hosts to stabilize charges (hole or electron). One advantage of using triphenylene and its derivatives as hosts is that it can accommodate red, green and even blue phosphorescent dopants to give high efficiency without energy quenching. Triphenylene hosts may be used to provide high efficiency and stability PHOLEDs. See Kwong and Alleyne, *Triphenylene Hosts in Phosphorescent Light Emitting Diodes*, 2006, 60 pp, U.S. 2006/0280965 A1. A compound containing an aza-dibenzothiophene or aza-dibenzofuran core and a triphenylene moiety may be beneficial as a host in PHOLEDs. More specifically, the triplet energy of both portions of the compound are relatively high thereby maintaining an overall high triplet energy. In addition, the combination of these two groups in one compound may also offer improved charge balance thus improving device efficiency and lifetime. Non-limiting examples triphenylene groups that may be the triphenylene moiety of such compounds may include



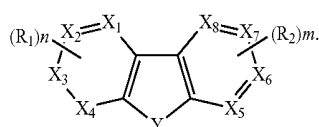
**[0047]** Nitrogen containing groups may also be used as substituents of the aza-dibenzothiophene compounds and aza-dibenzofuran compounds. Such nitrogen containing groups may include carbazole, oligocarbazole, indolocarbazole, and diphenylamine. Carbazole is a nitrogen containing heteroaromatic, having high triplet energy, and has hole transporting and electron transporting properties. One advantage to using carbazole-containing compounds (i.e., carbazole, oligocarbazole and indolocarbazole) as host materials is that they simultaneously possess sufficiently large triplet energies and carrier transport properties. For example, the indolocarbazole and 3-(9-carbazolyl)carbazole have a relatively low electrochemical oxidation potential. As such, these compounds are easier to oxidize and to reverse the oxidation, which improves overall host stability. Another advantage is that these carbazole building blocks can serve as donors, while coupling with aza-dibenzothiophenes or aza-dibenzofurans which are acceptors here, to form a donor-acceptor type molecule. It is believed that these molecules having a donor-acceptor molecular arrangement contribute, at least in part, to the low voltage character in the device.

**[0048]** The compounds provided herein may be used as host materials in blue, green and red PHOLEDs. In particu-

lar, aza-dibenzothiophene or aza-dibenzofuran compounds substituted with triphenylene may be used in blue, green and red devices as these compounds can accommodate blue, green and red emissive dopants. Preferably, these compounds may be used in blue devices. The aza-type compounds provided herein may also be substituted with both triphenylene and nitrogen-containing substituents. These compounds substituted with both triphenylene and nitrogen-containing groups may be used in green and red devices as these compounds can accommodate green and red emissive dopants. Preferably, these compounds may be used in green devices.

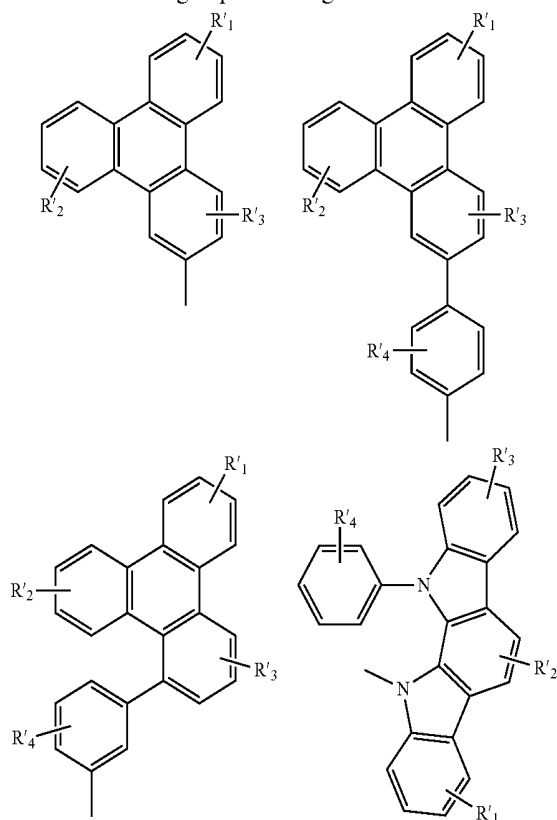
**[0049]** The heteroaromatic compounds (i.e., aza-dibenzothiophene and aza-dibenzofuran) described herein may be more easily reduced than their dibenzothiophene or dibenzofuran counterparts, in particular by 0.2 V to 0.5 V. As a result, these aza-type compounds may provide devices having low operational voltage and long lifetimes. Without being bound by theory, it is thought that the more easily reduced compounds may provide better anion stability and easier anion injection from the electron transport layer (ETL) to the emissive layer (EML) in the device.

[0050] The compounds described herein have the formula:

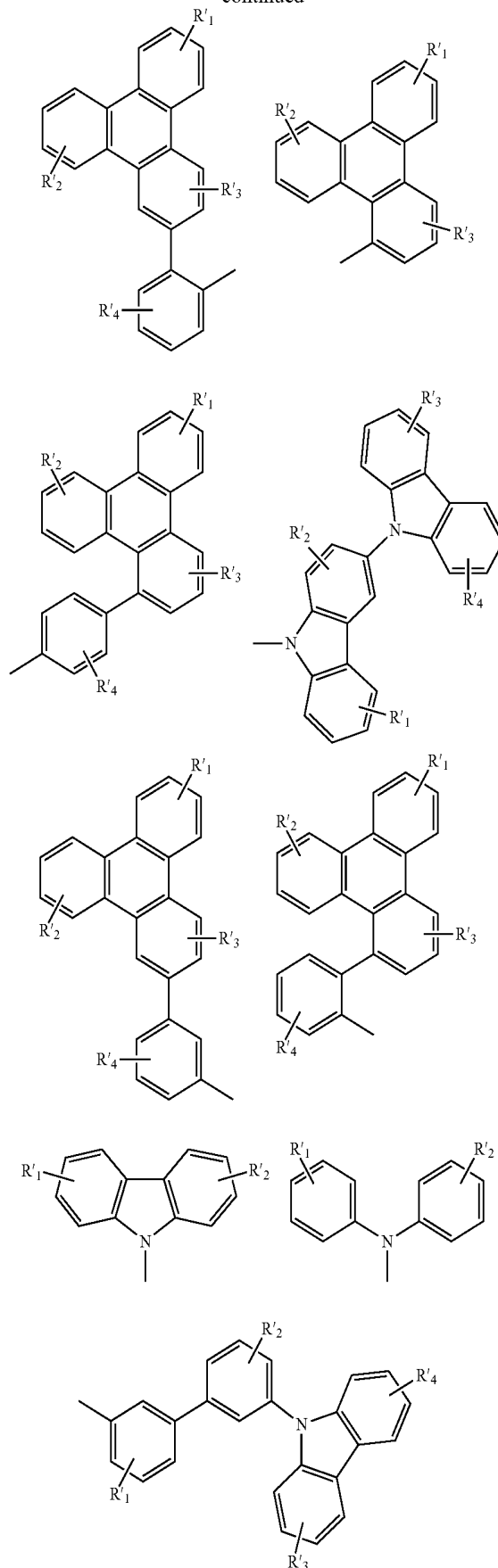


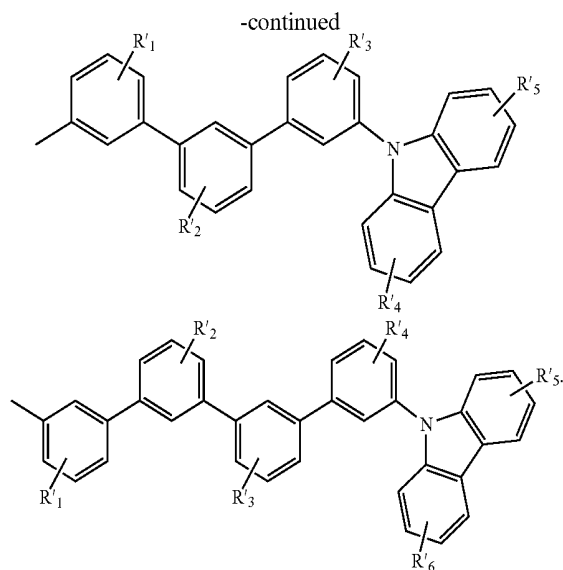
FORMULA I

**[0051]**  $X_1, X_2, X_3, X_4, X_5, X_6, X_7$ , and  $X_8$  are independently selected from the group consisting of a carbon atom and a nitrogen atom, and at least one of  $X_1, X_2, X_3, X_4, X_5, X_6, X_7$ , and  $X_8$  is a nitrogen atom. Y is S or O.  $R_1$  and  $R_2$  may represent mono, di, tri, or tetra substitutions.  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen, alkyl, aryl and halide. At least one of  $R_1$  and  $R_2$  is selected from the group consisting of:



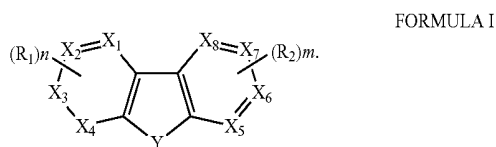
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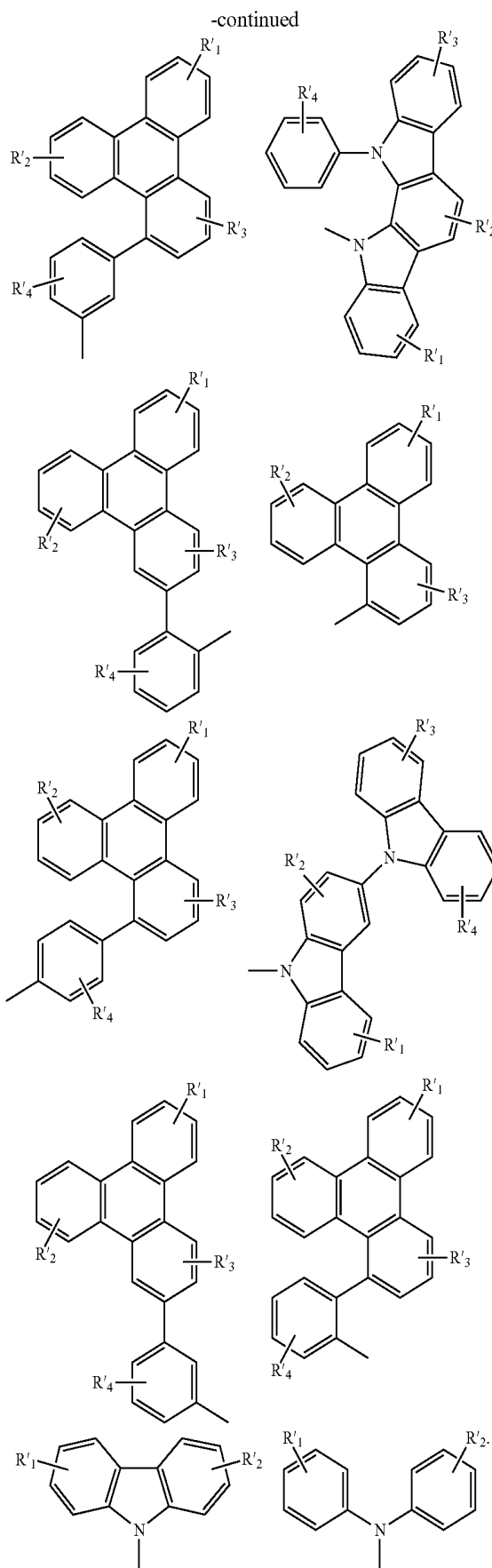
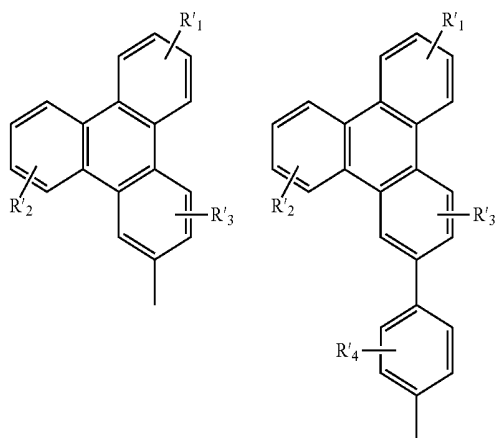


$R'_1$ ,  $R'_2$ ,  $R'_3$  and  $R'_4$  may represent mono, di, tri, or tetra or penta substitutions; and  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are each independently hydrogen or methyl.

**[0052]** The compounds described herein have the formula:



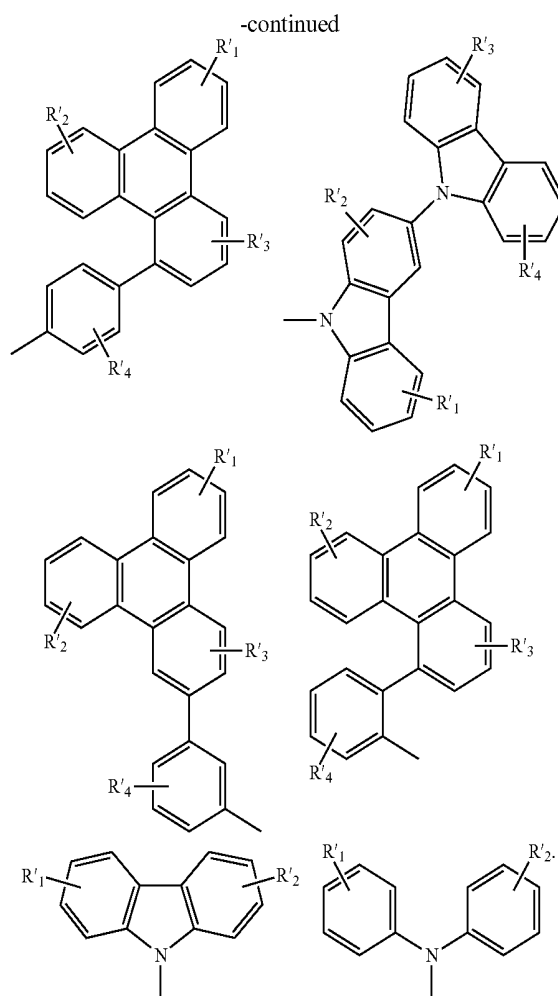
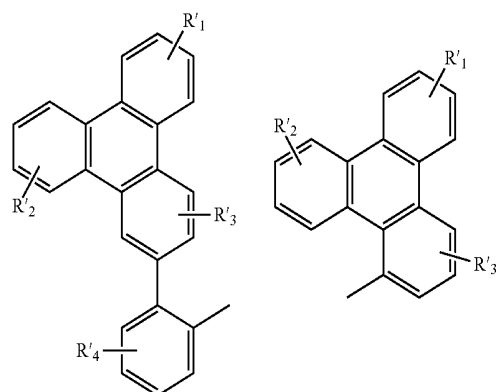
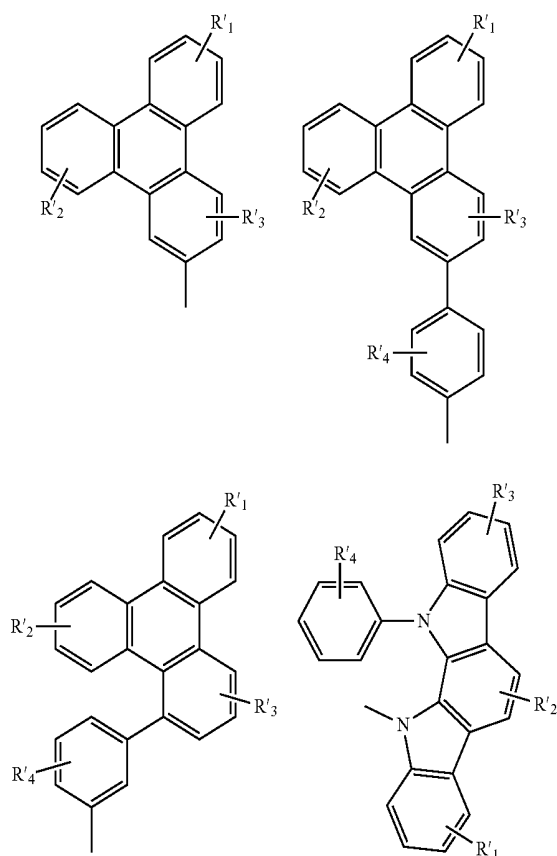
**[0053]** Where  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$  are independently selected from the group consisting of a carbon atom and a nitrogen atom, and at least one of  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$  is a nitrogen atom.  $Y$  is S or O, wherein  $R_1$  and  $R_2$  represent mono, di, tri, or tetra substitutions.  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen, alkyl, aryl and halide and at least one of  $R_1$  and  $R_2$  is selected from the group consisting of:



$R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  may represent mono, di, tri, or tetra or penta substitutions; and  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are each independently hydrogen or methyl.

**[0054]** Preferably,  $m$  and  $n$  are 0, 1, 2, 3, or 4, and  $m+n$  is equal to or greater than 2 and  $m+n$  is equal to or less than 6. Without being bound by theory, it is thought that at least 2 provides better electron transport properties by providing a preferred amount of electron transport moieties. Moreover, it is thought that greater than 6 may result in an increase in sublimation temperature so that the manufacturing of devices with such compounds is not as practical.

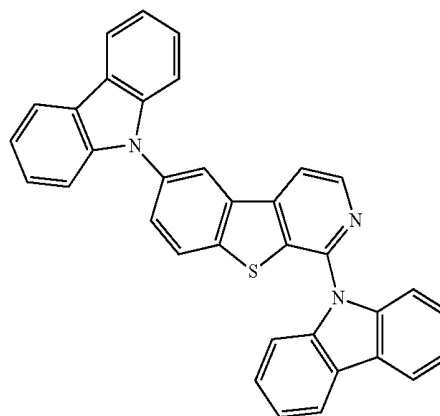
**[0055]** In one aspect, at least one of  $R_1$  and  $R_2$  is selected from the group consisting



$R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are each independently hydrogen or methyl.

**[0056]** Specific examples of the compounds are provided, and include compounds selected from the group consisting of:

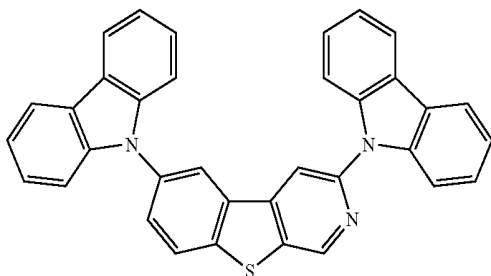
Compound 1



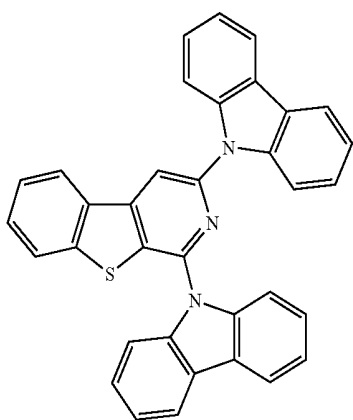


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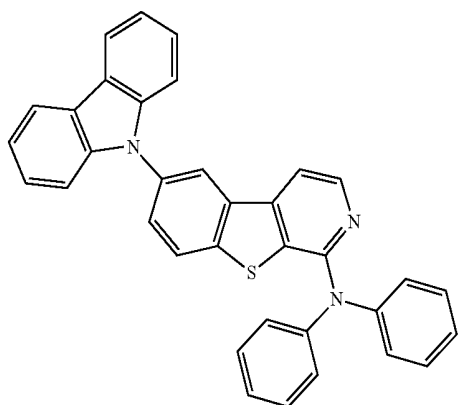
Compound 2



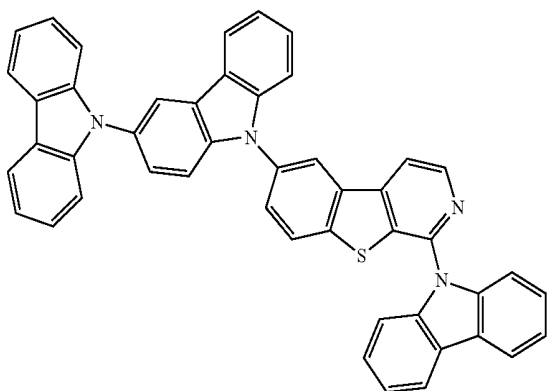
Compound 3



Compound 4

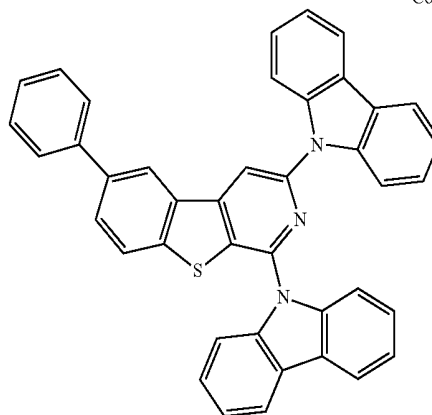


Compound 5

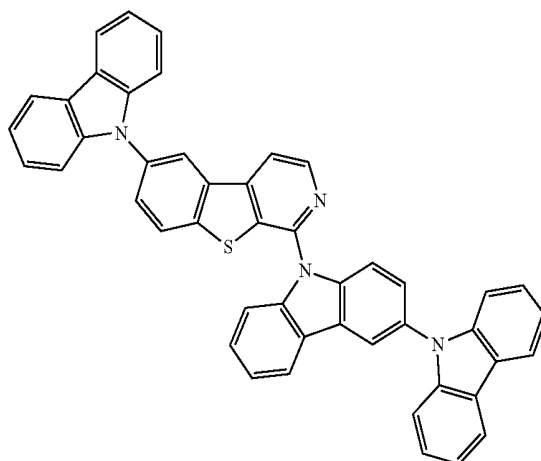


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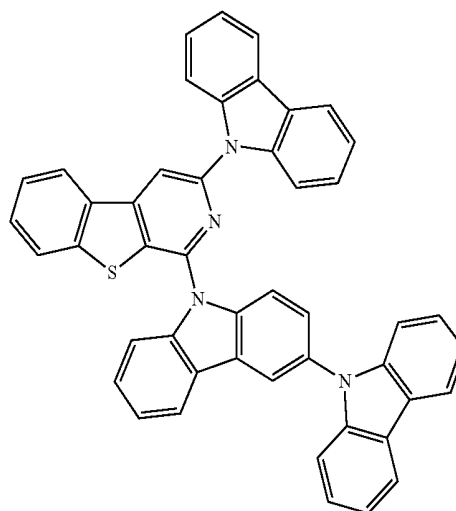
Compound 6



Compound 7

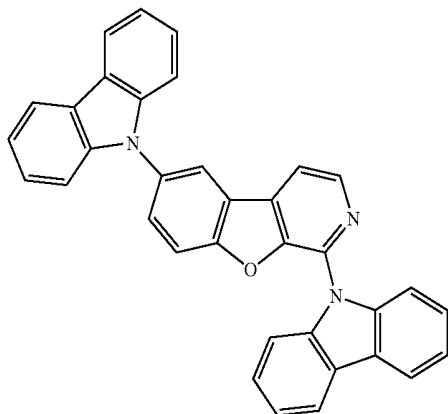


Compound 8



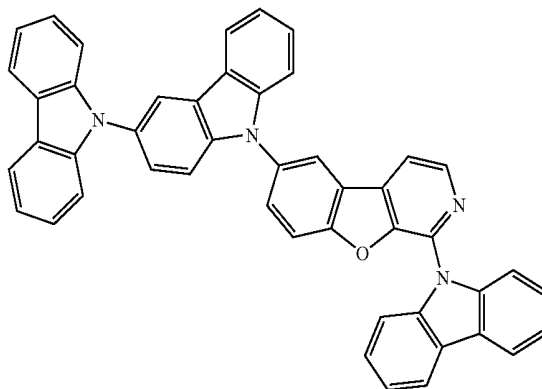
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Compound 9

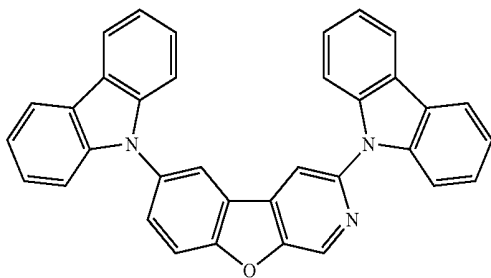


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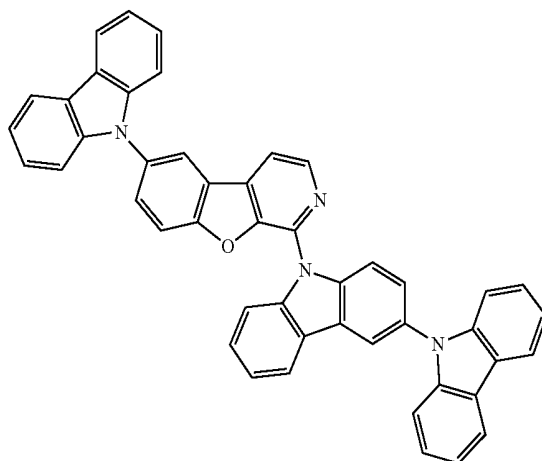
Compound 13



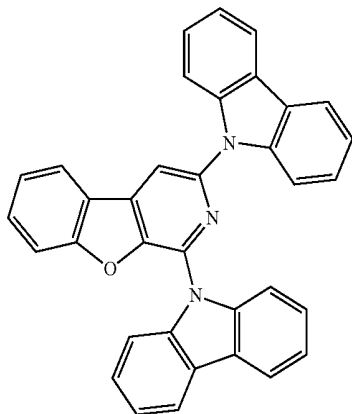
Compound 10



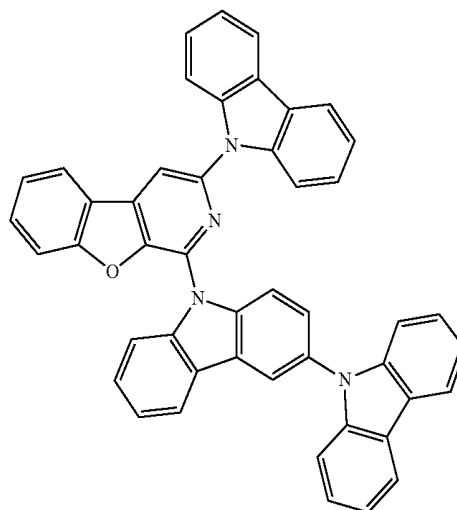
Compound 14



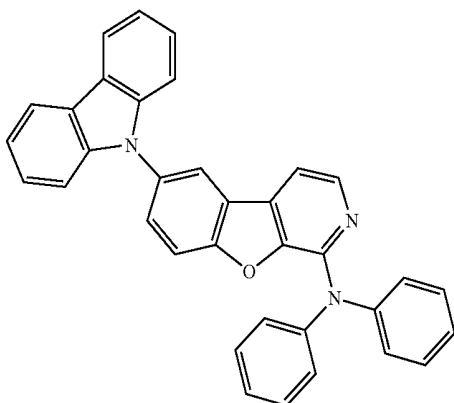
Compound 11



Compound 15

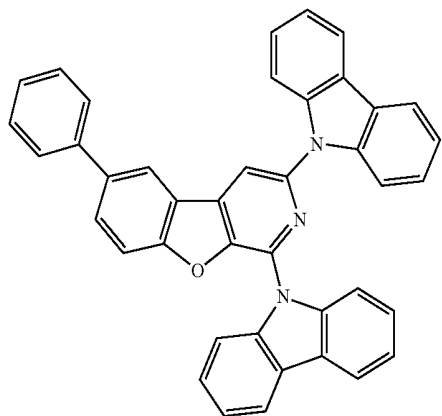


Compound 12



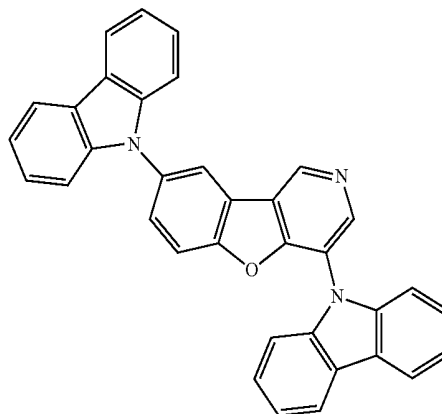
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Compound 16

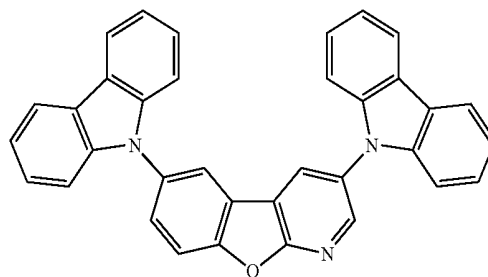


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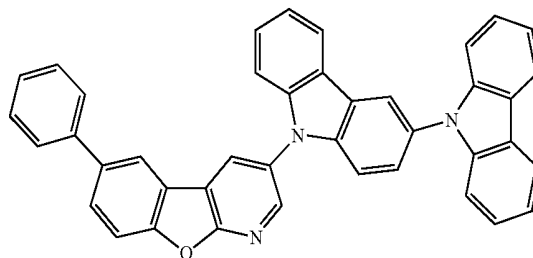
Compound 20



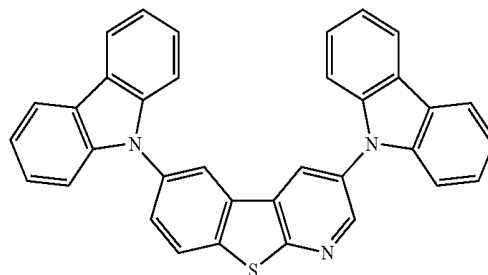
Compound 21



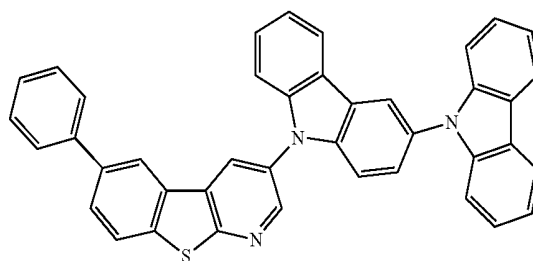
Compound 22



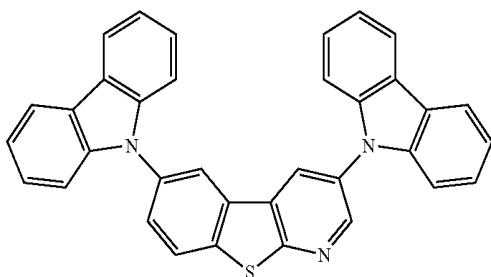
Compound 23



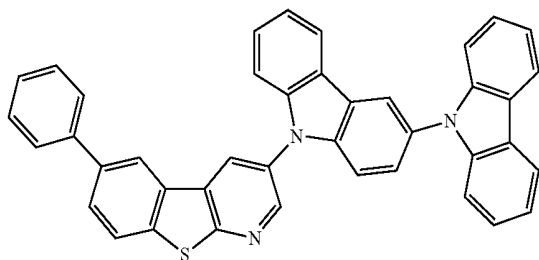
Compound 24



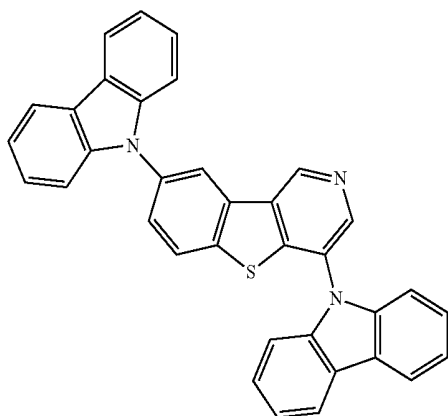
Compound 17



Compound 18

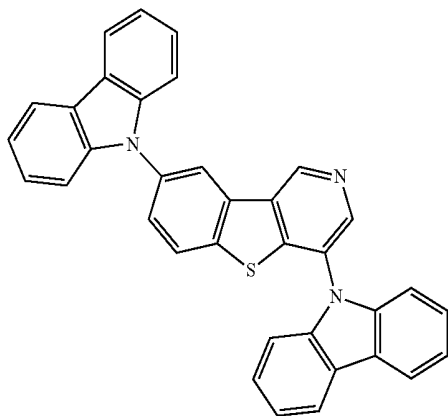


Compound 19



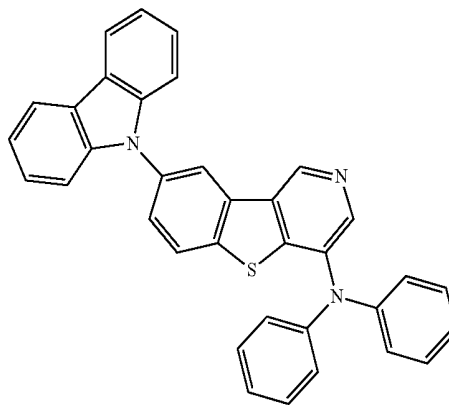
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Compound 25

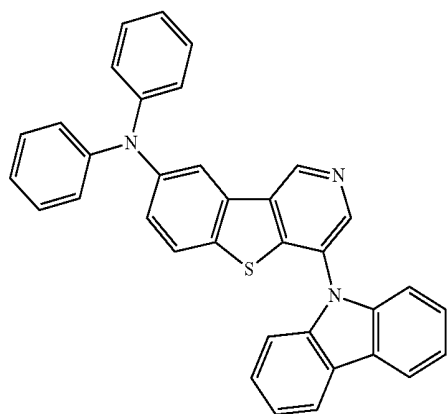


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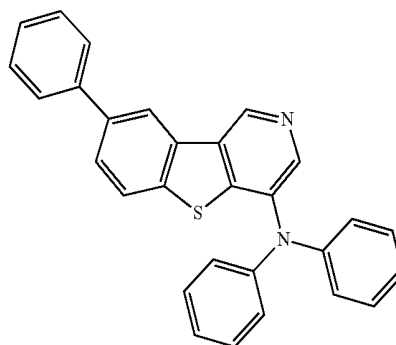
Compound 29



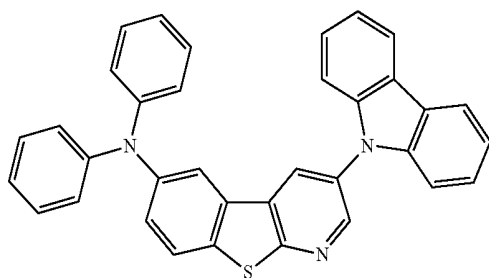
Compound 26



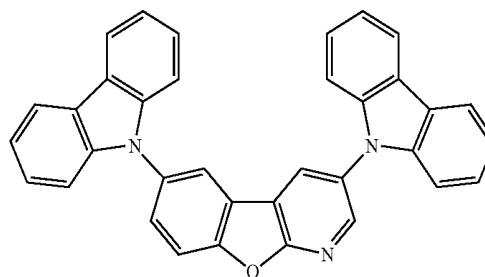
Compound 30



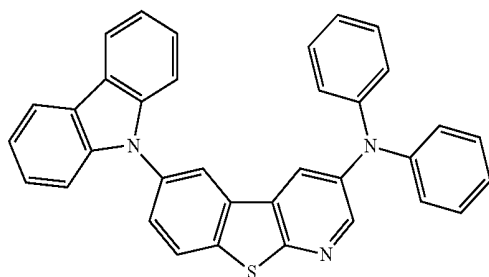
Compound 27



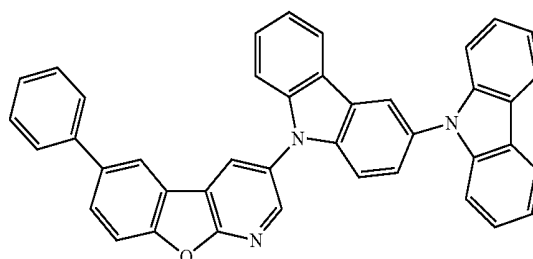
Compound 31



Compound 28

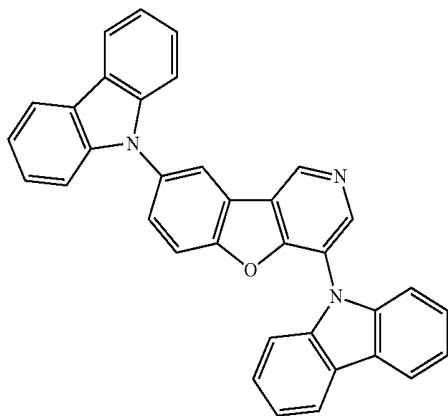


Compound 32



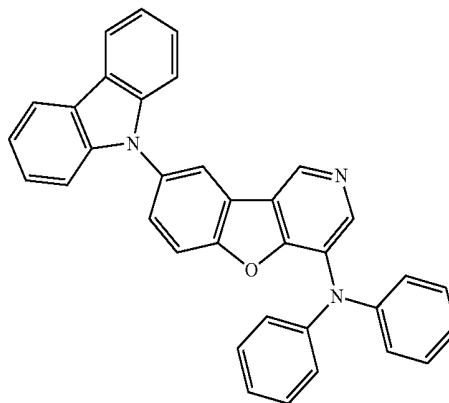
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Compound 33



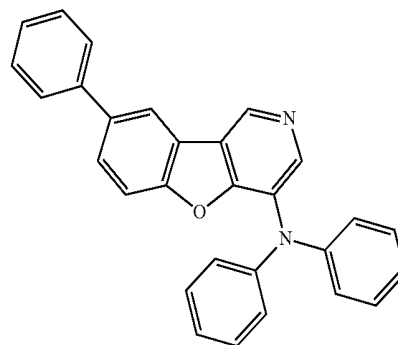
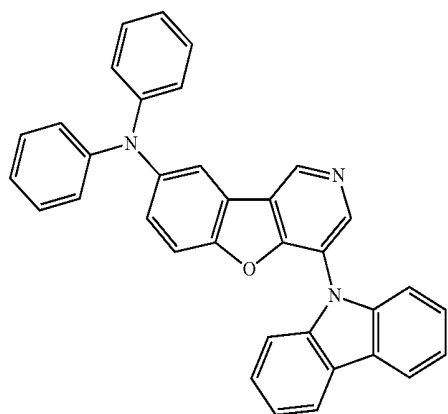
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Compound 37



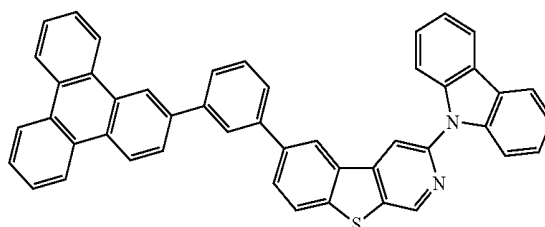
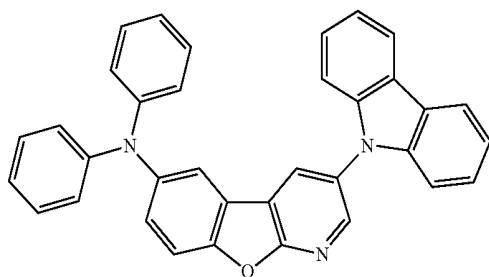
Compound 38

Compound 34



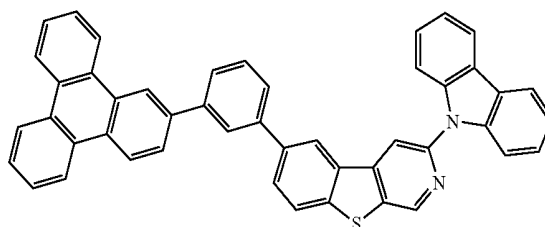
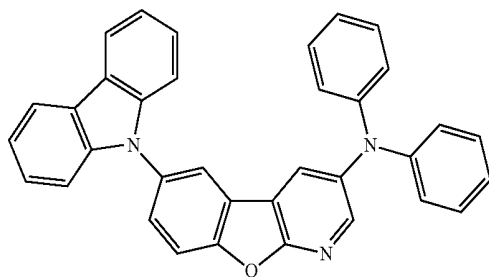
Compound 39

Compound 35

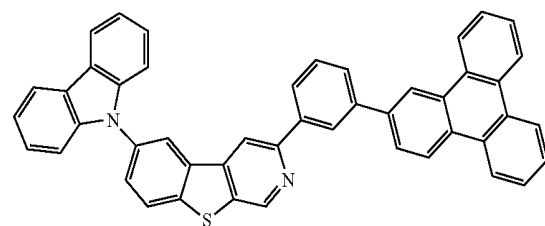


Compound 40

Compound 36

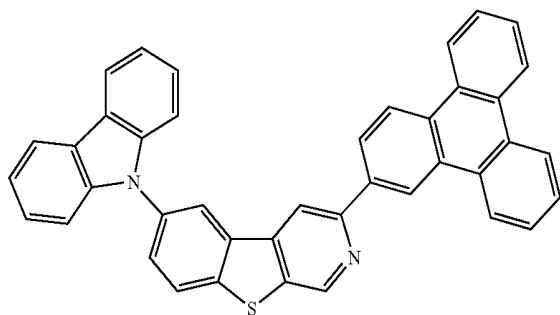


Compound 41



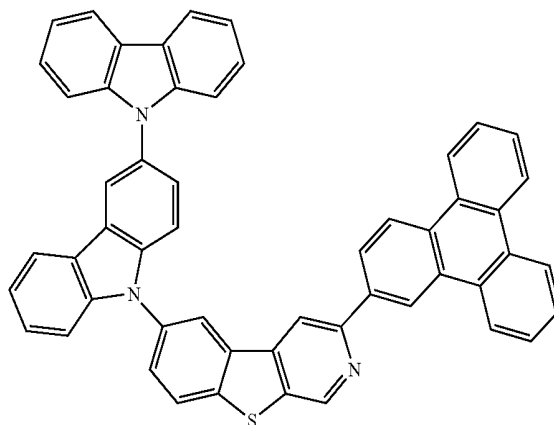
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Compound 42

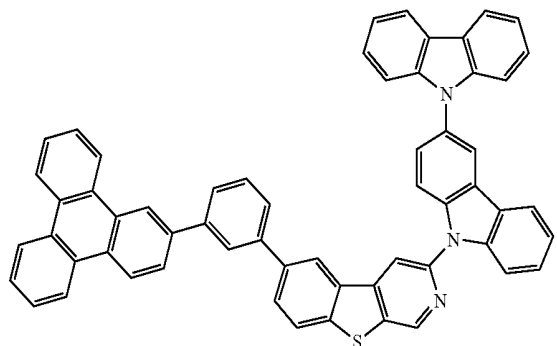


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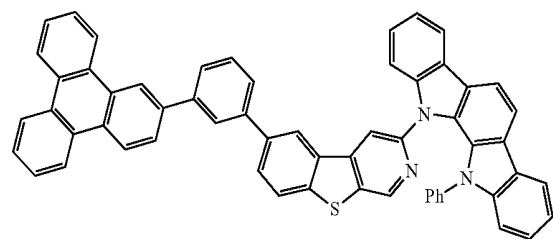
Compound 46



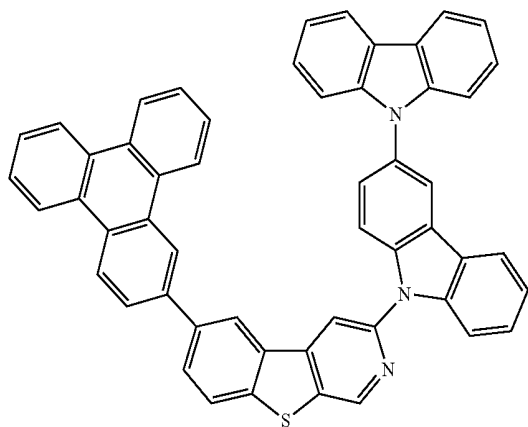
Compound 43



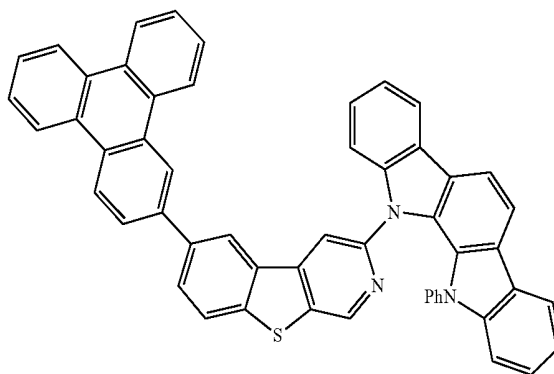
Compound 47



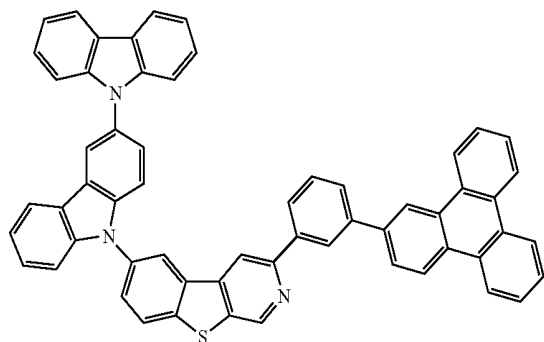
Compound 44



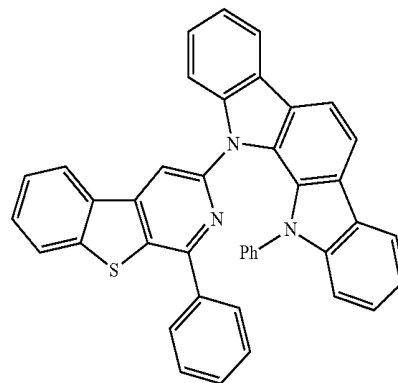
Compound 48



Compound 45

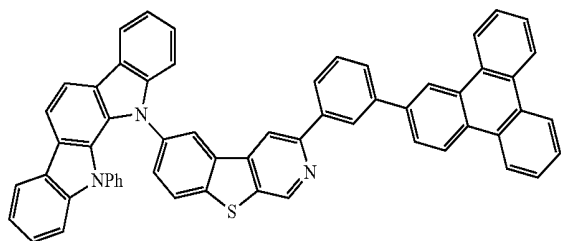


Compound 49



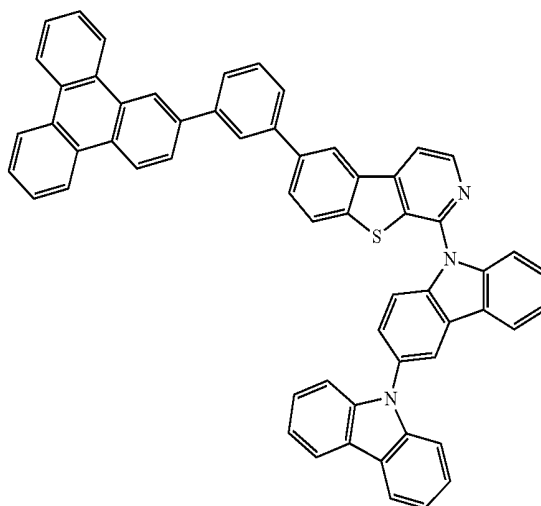
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Compound 50

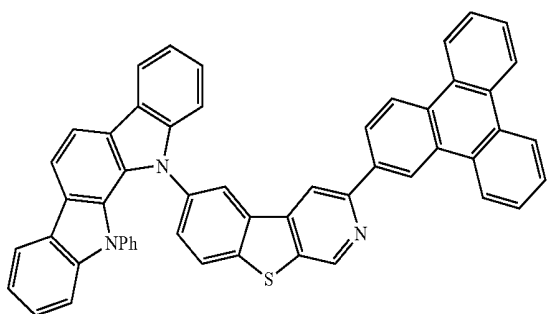


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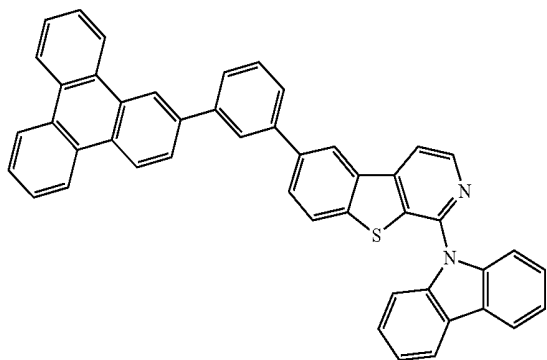
Compound 54



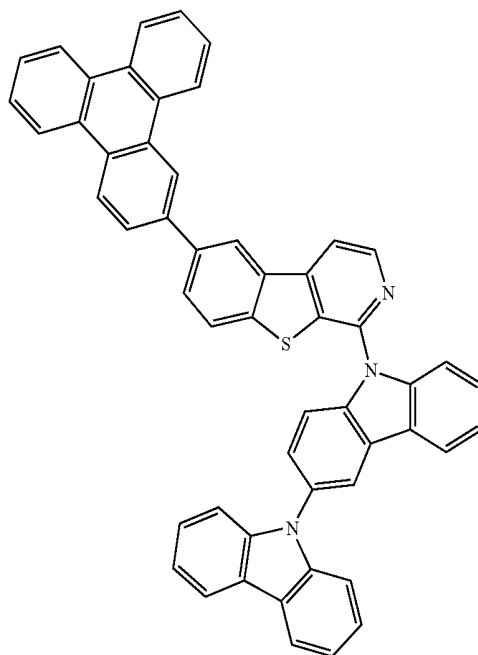
Compound 51



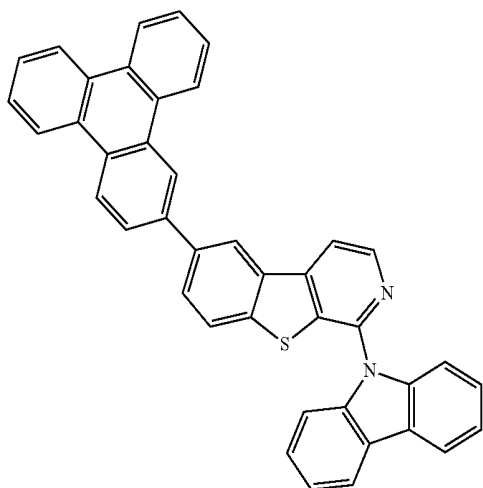
Compound 52



Compound 55

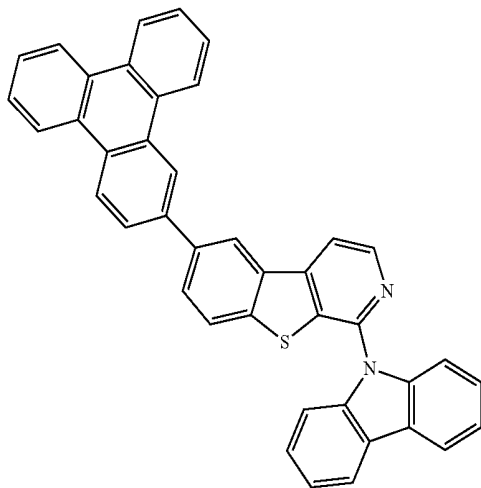


Compound 53



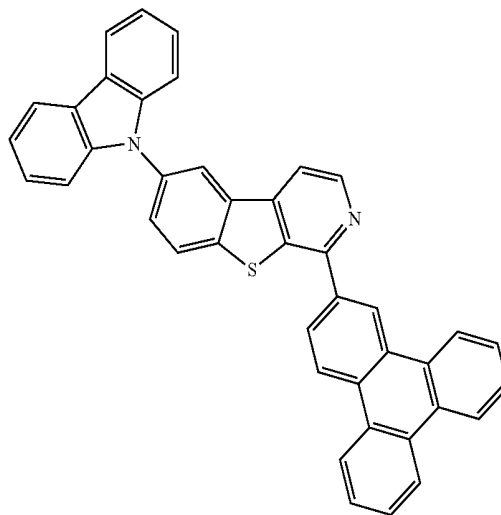
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Compound 56

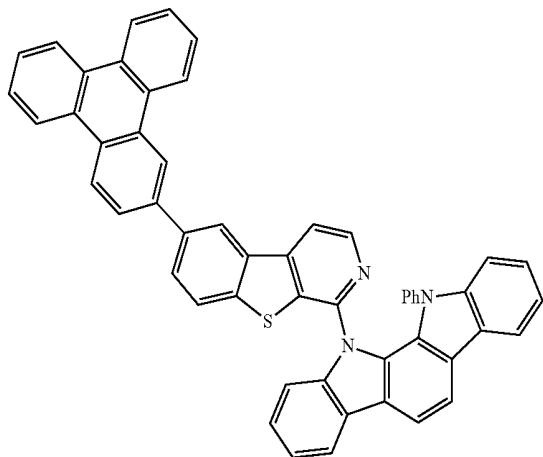


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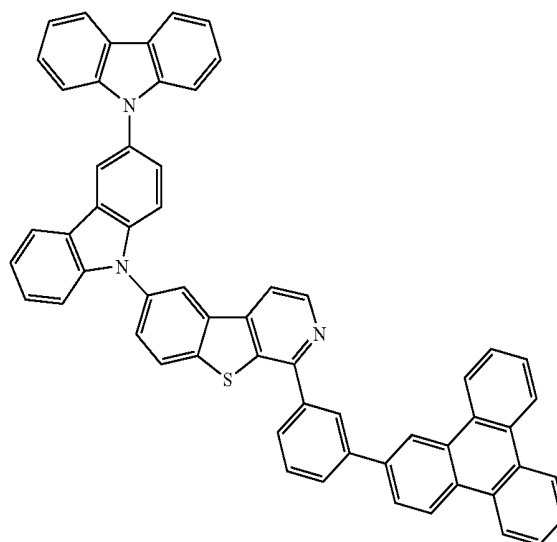
Compound 59



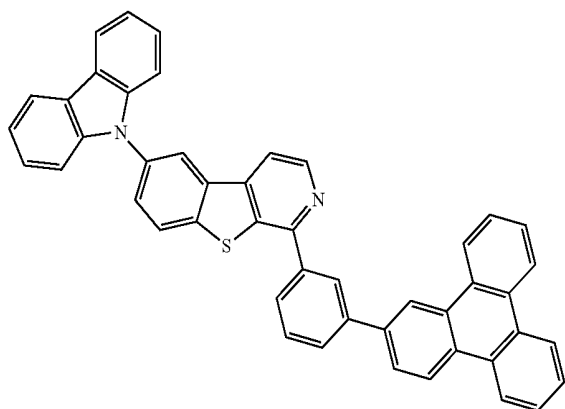
Compound 57



Compound 60



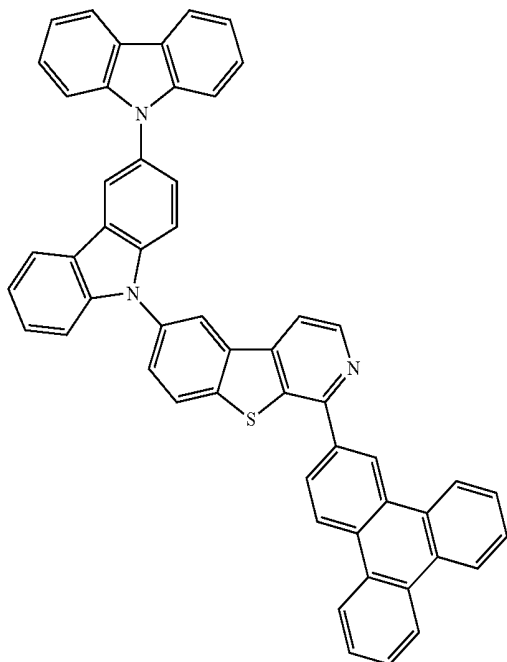
Compound 58



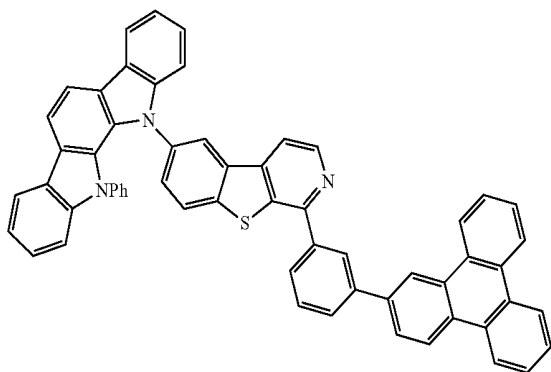


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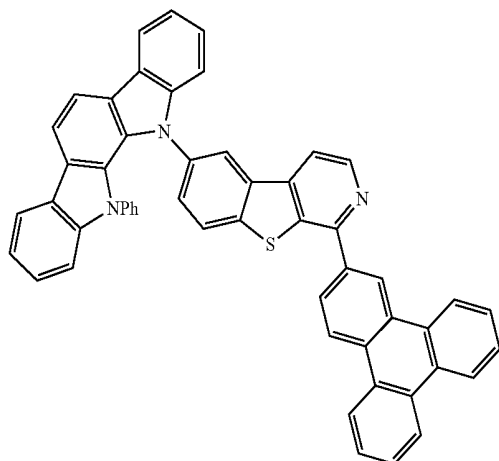
Compound 61



Compound 62

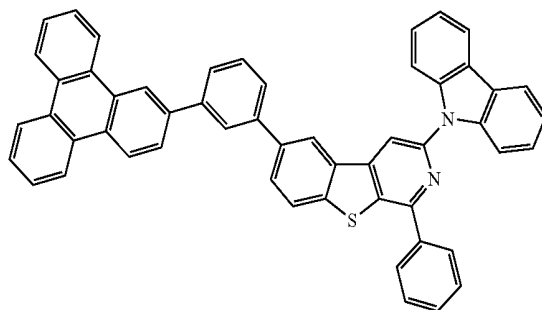


Compound 63

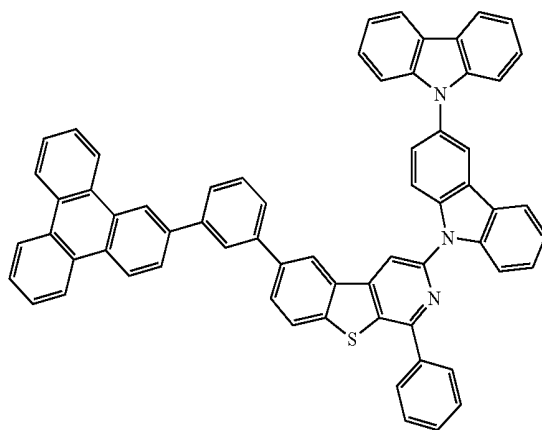


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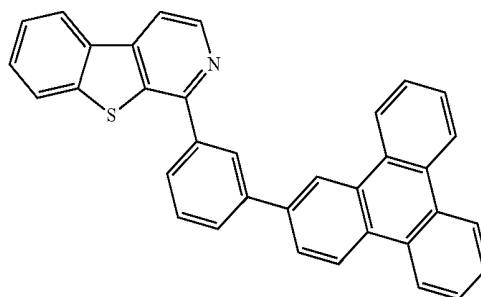
Compound 64



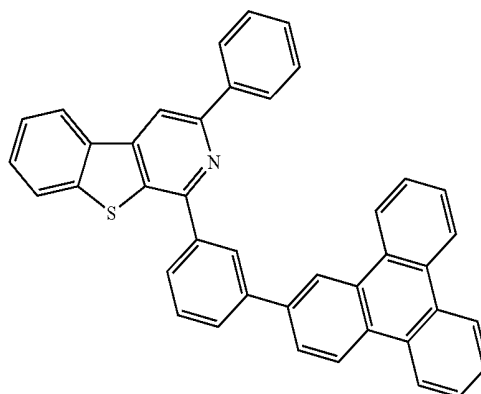
Compound 65



Compound 66

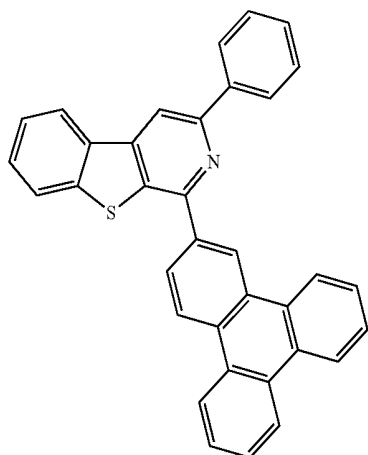


Compound 67



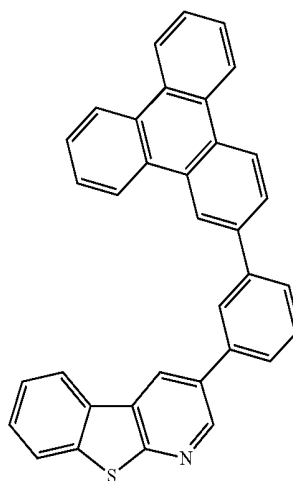
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Compound 68

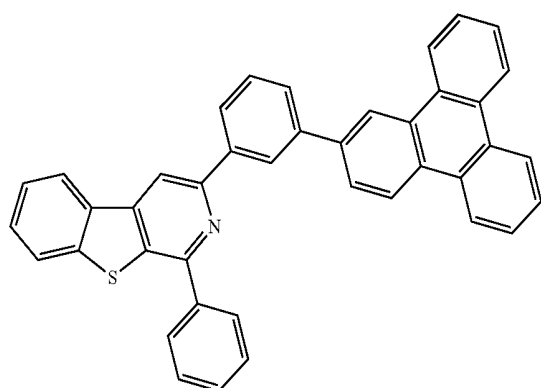


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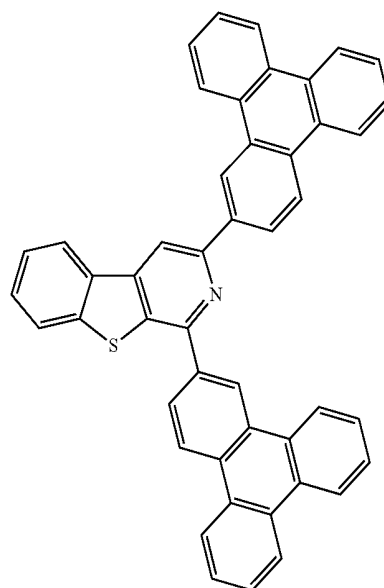
Compound 71



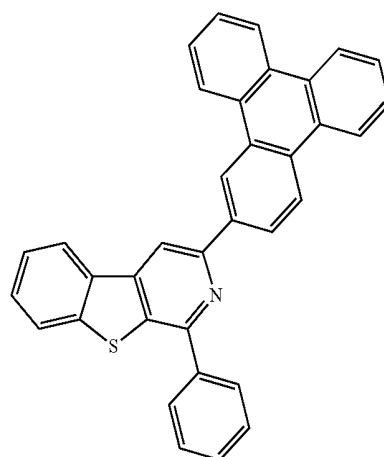
Compound 69



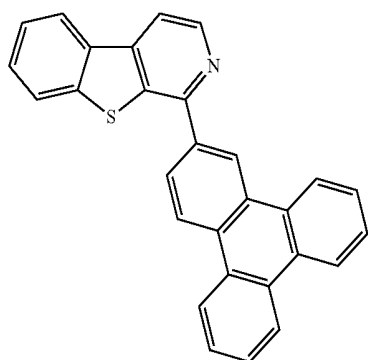
Compound 72



Compound 73

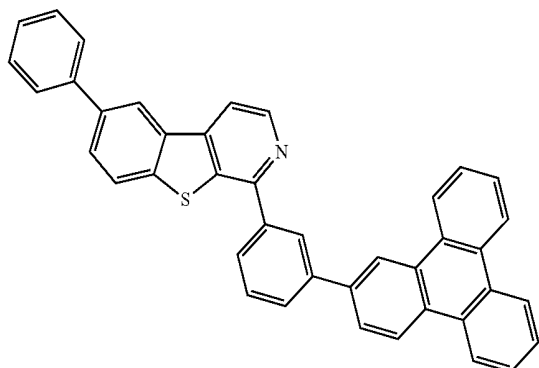


Compound 70



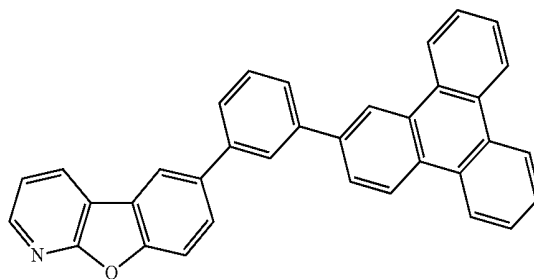
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Compound 74

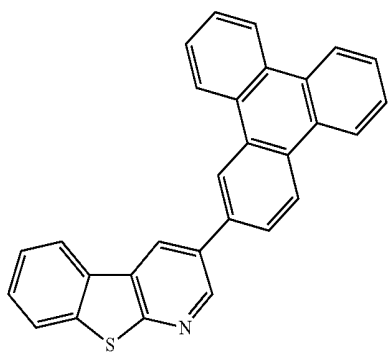


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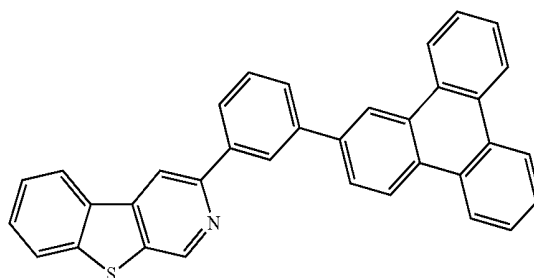
Compound 78



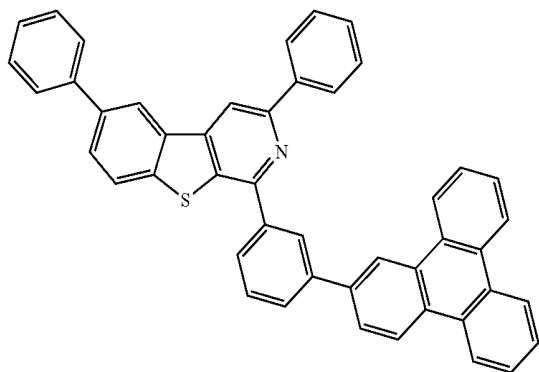
Compound 75



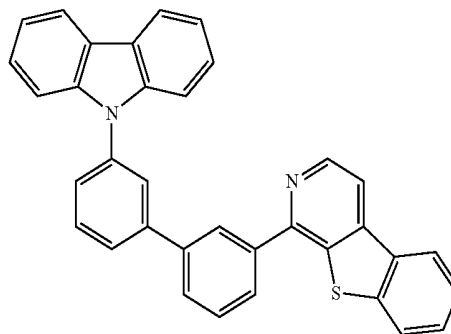
Compound 79



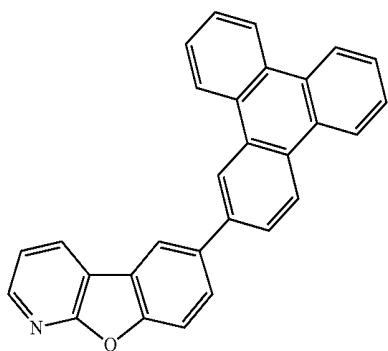
Compound 76



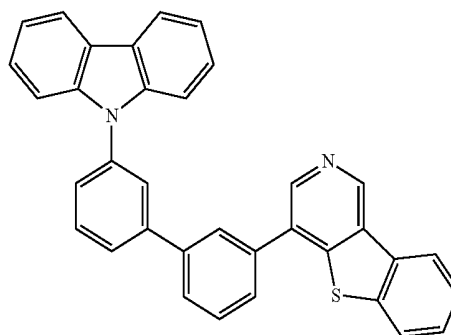
Compound 80



Compound 77

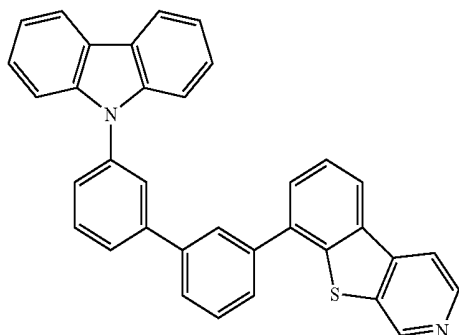


Compound 81



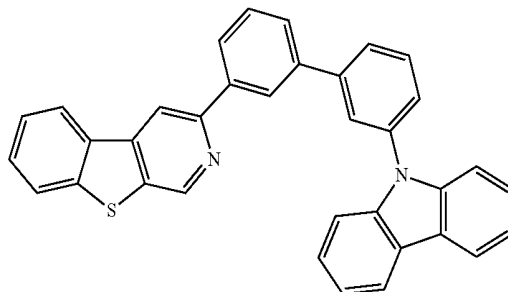
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Compound 82

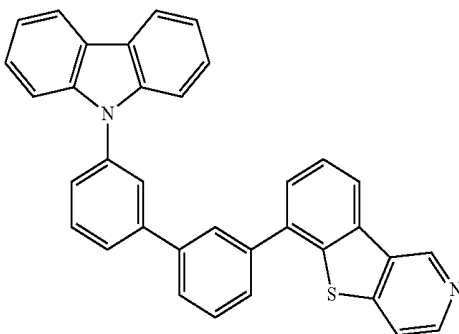


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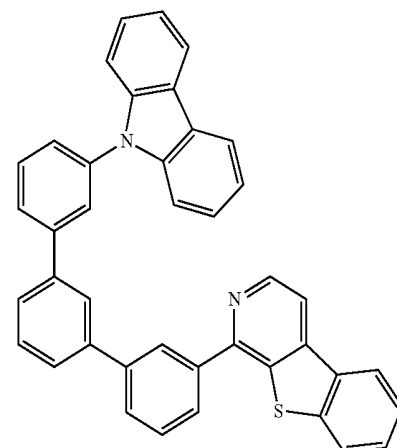
Compound 86



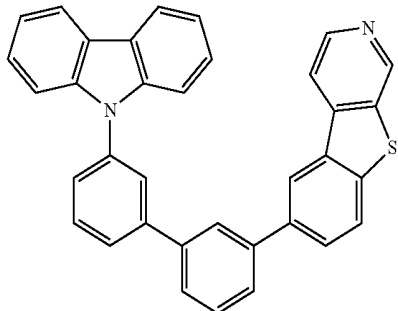
Compound 83



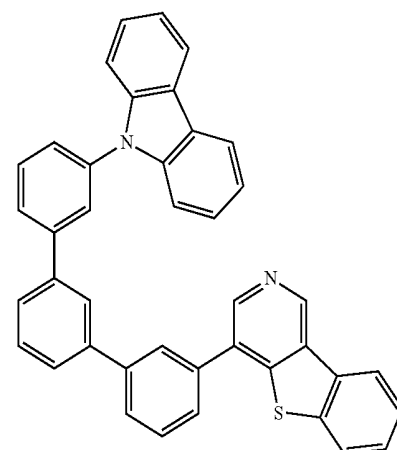
Compound 87



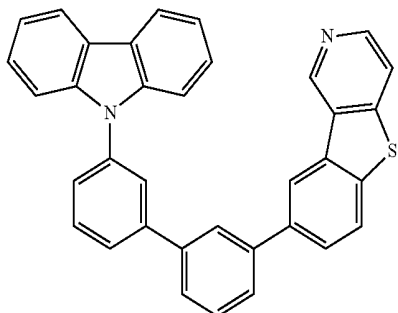
Compound 84



Compound 88

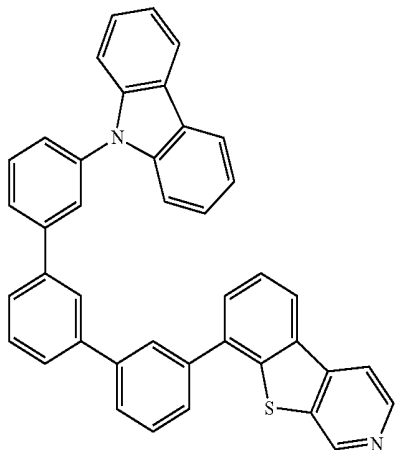


Compound 85



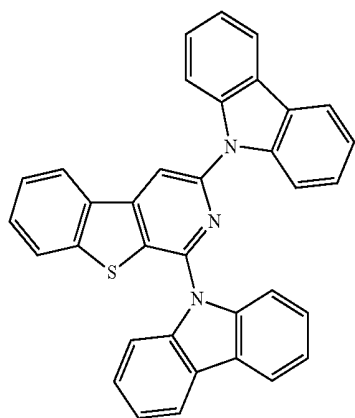
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Compound 89

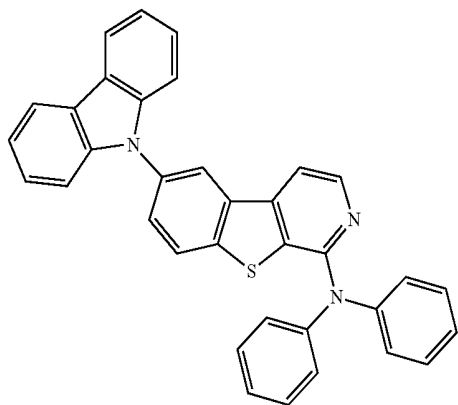


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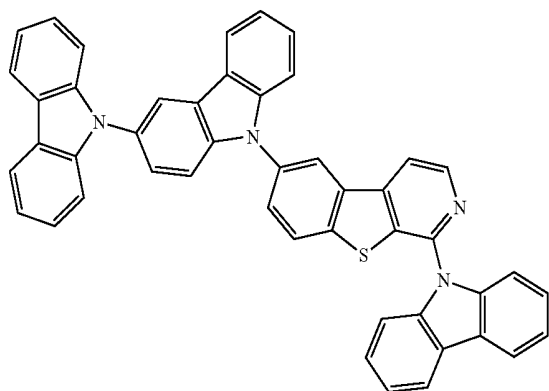
Compound 3



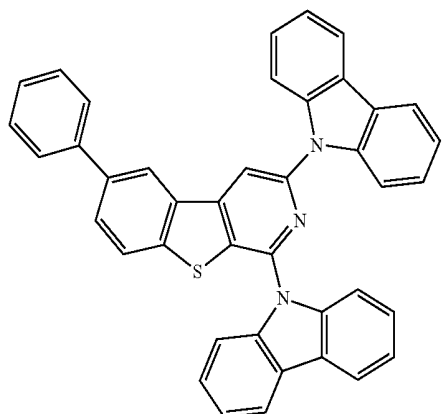
Compound 4



Compound 5

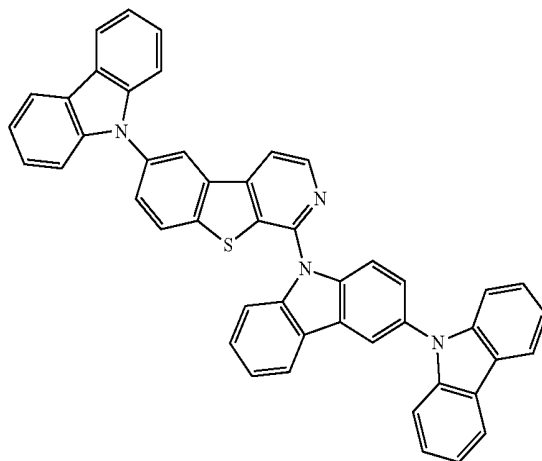


Compound 6

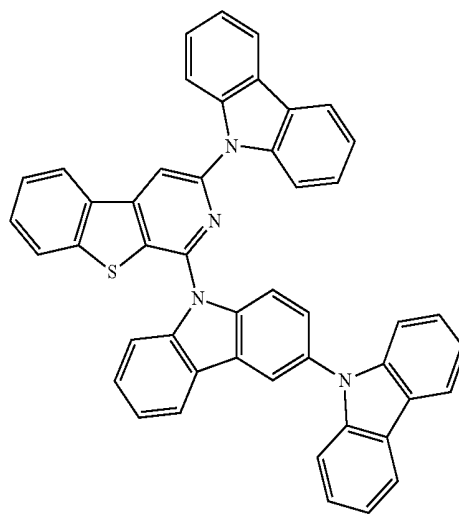


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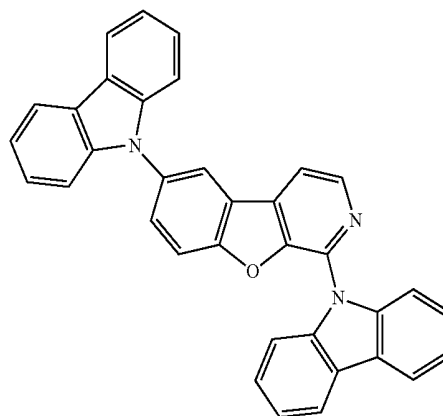
Compound 7



Compound 8

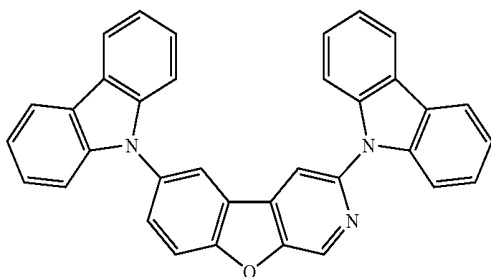


Compound 9

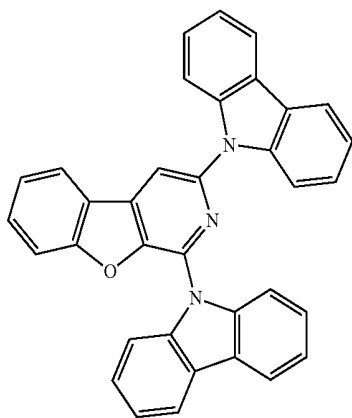


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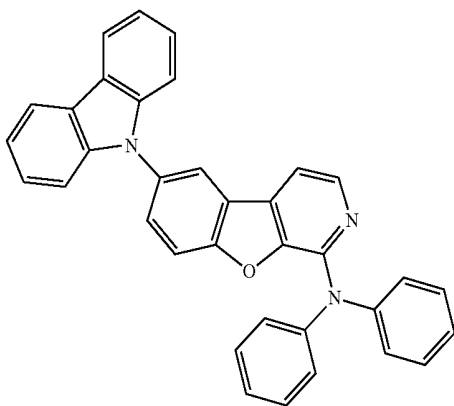
Compound 10



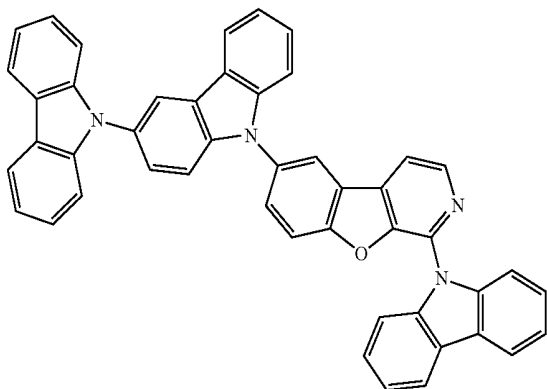
Compound 11



Compound 12

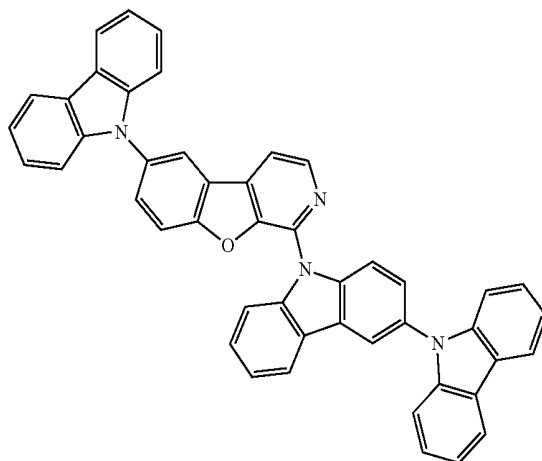


Compound 13

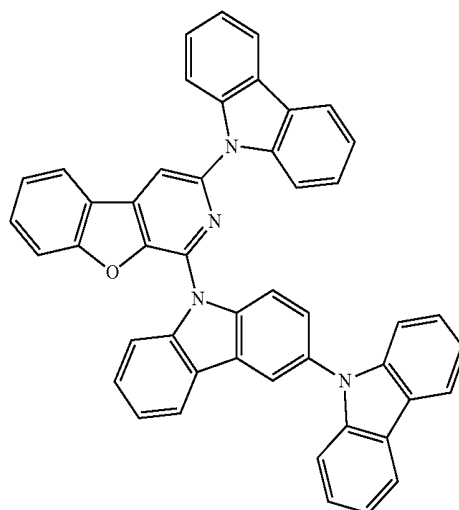


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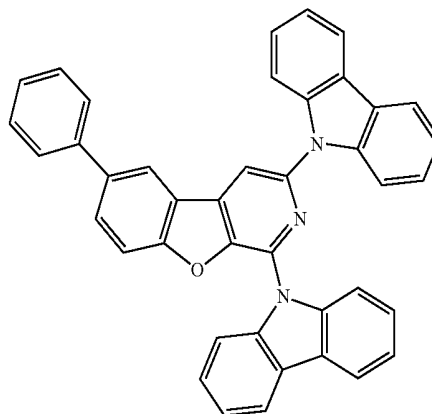
Compound 14



Compound 15

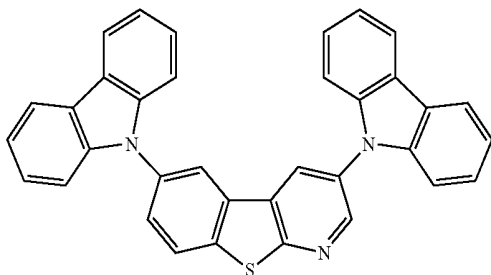


Compound 16



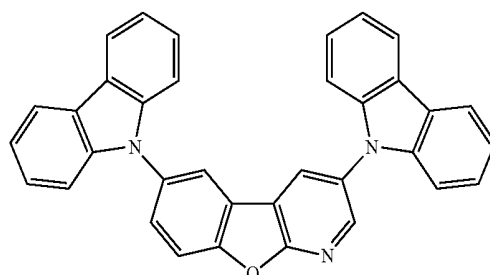
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Compound 17

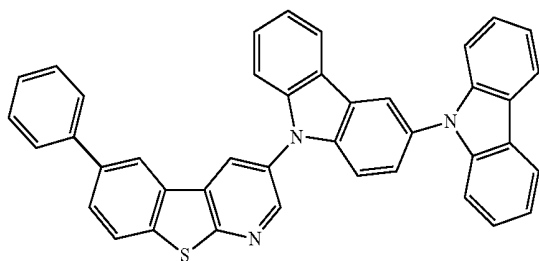


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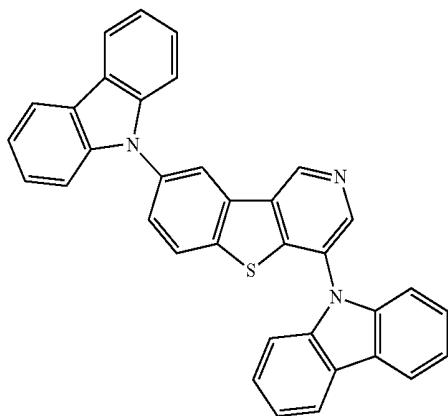
Compound 21



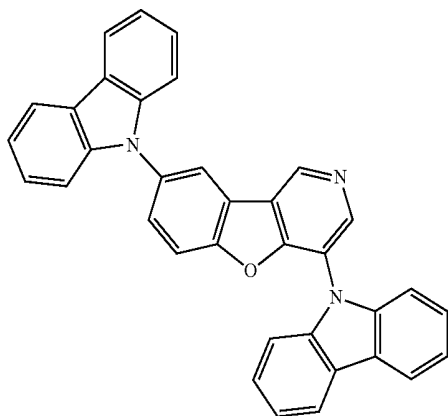
Compound 18



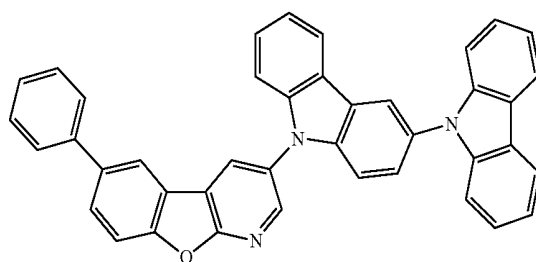
Compound 19



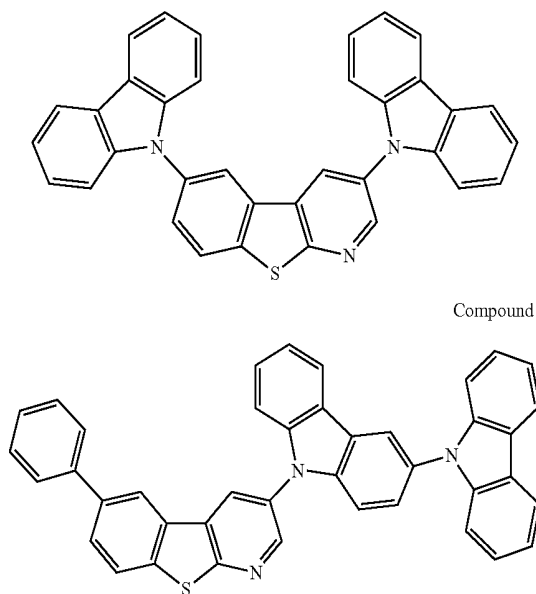
Compound 20



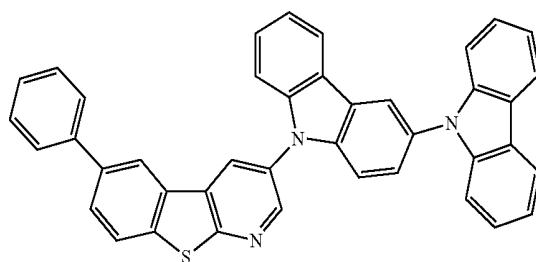
Compound 22



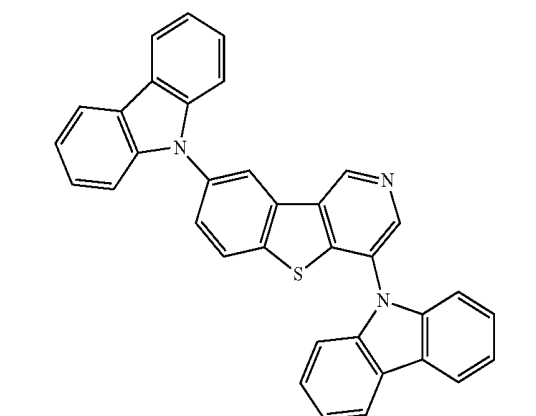
Compound 23



Compound 24



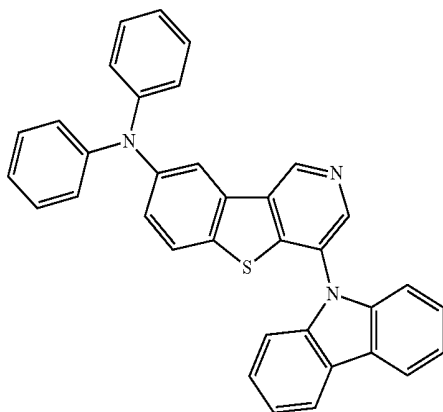
Compound 25





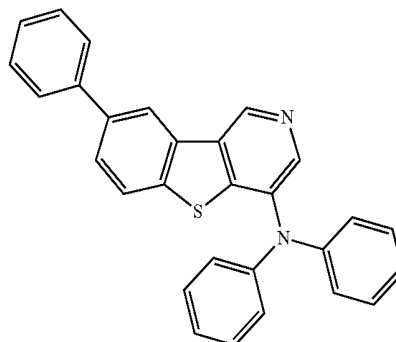
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Compound 26

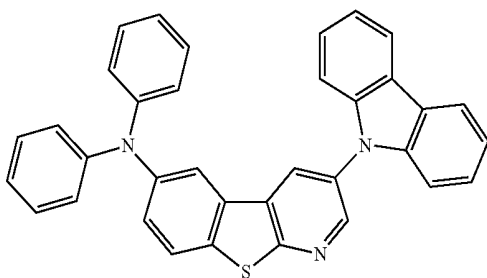


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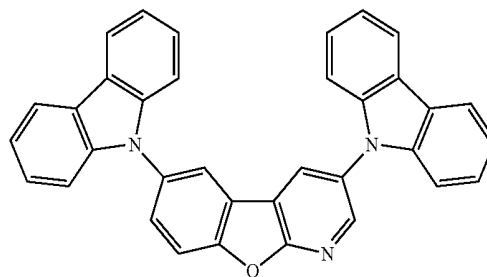
Compound 30



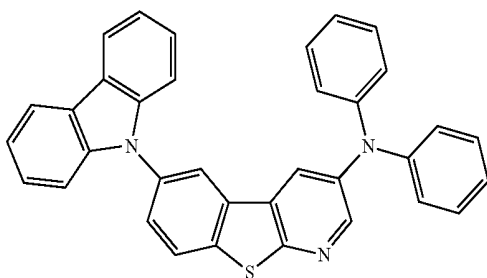
Compound 27



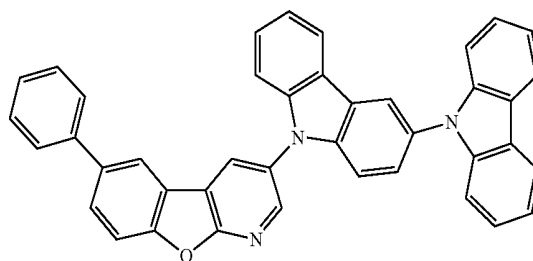
Compound 31



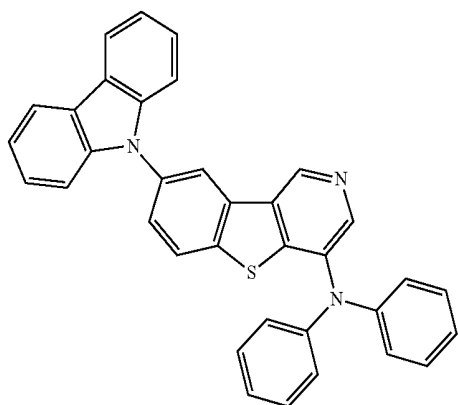
Compound 28



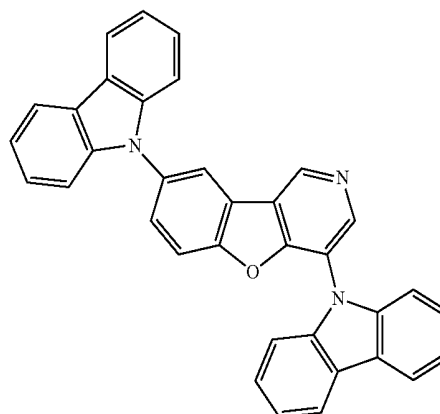
Compound 32



Compound 29

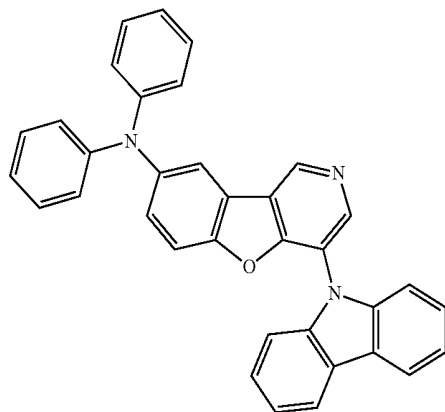


Compound 33



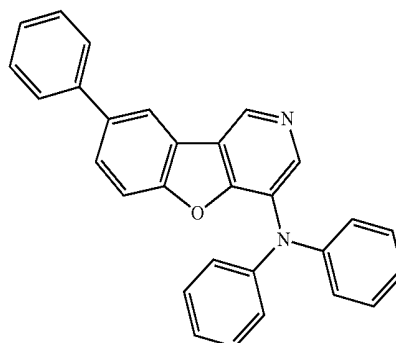
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Compound 34

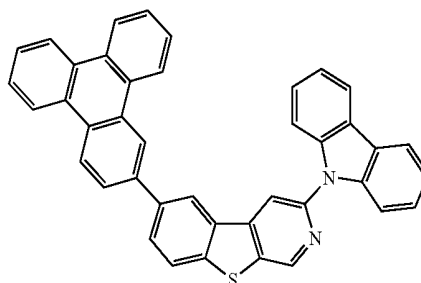


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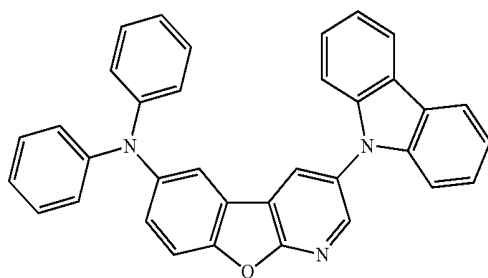
Compound 38



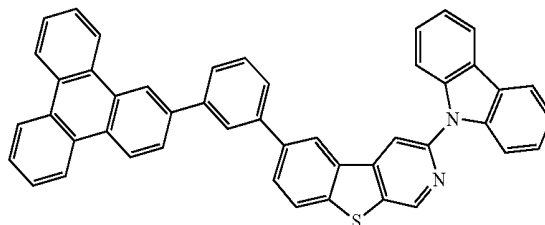
Compound 39



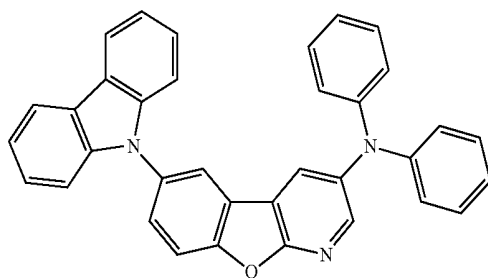
Compound 35



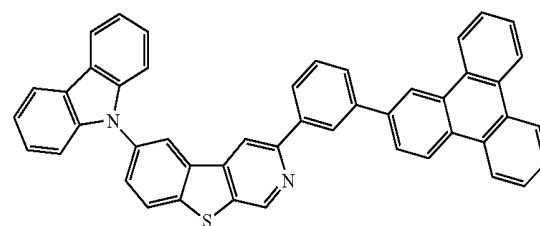
Compound 40



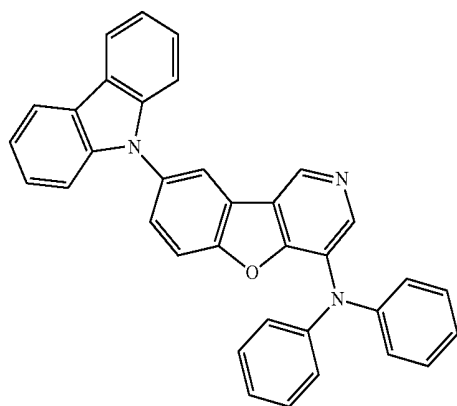
Compound 36



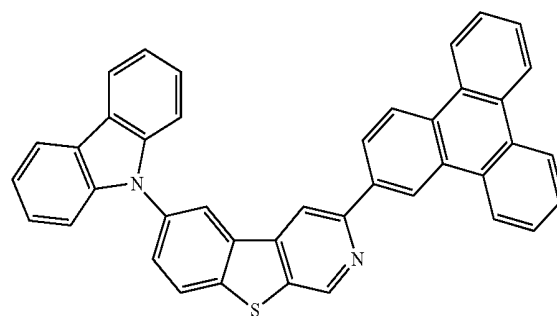
Compound 41



Compound 37

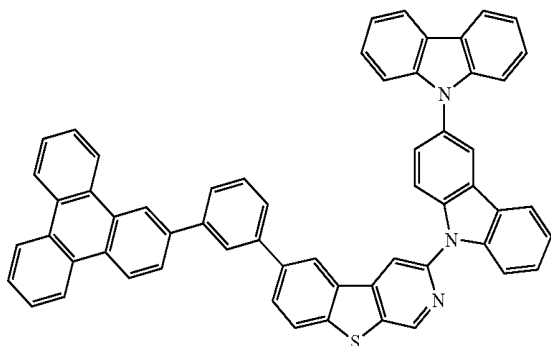


Compound 42

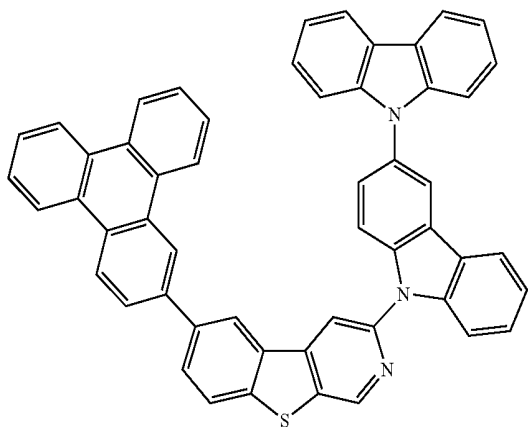


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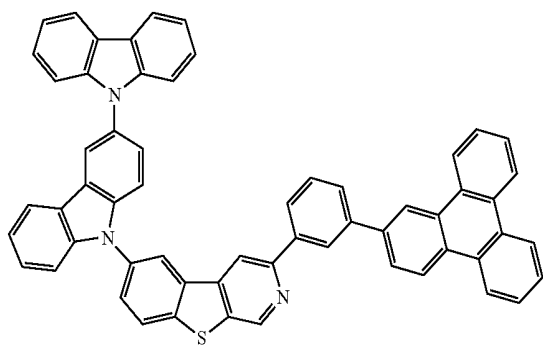
Compound 43



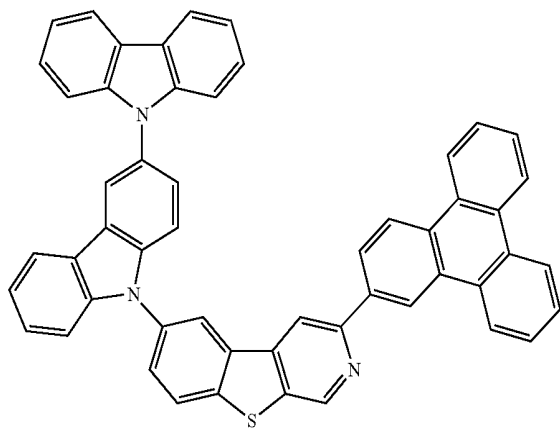
Compound 44



Compound 45

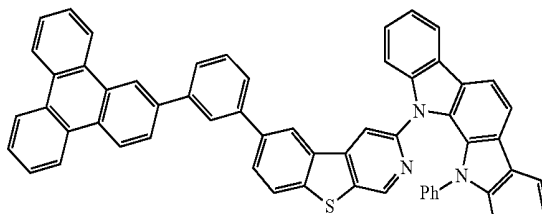


Compound 46

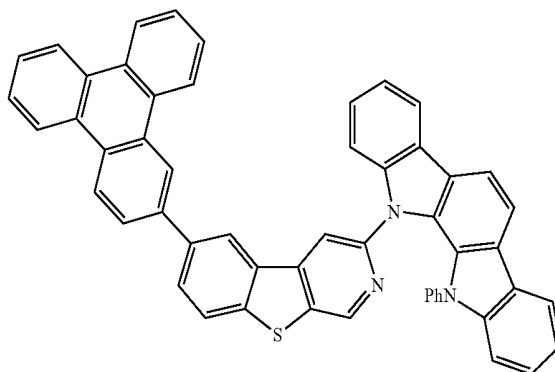


-continued

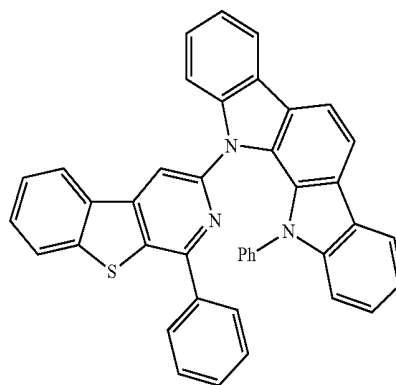
Compound 47



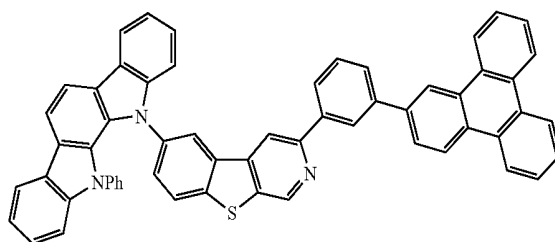
Compound 48



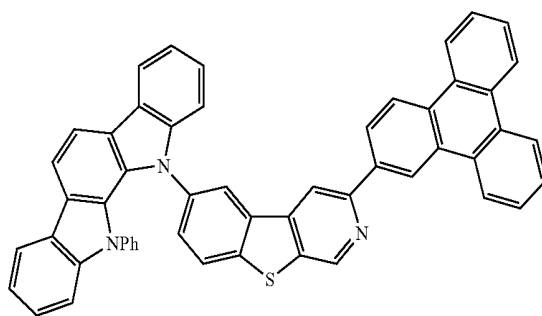
Compound 49



Compound 50

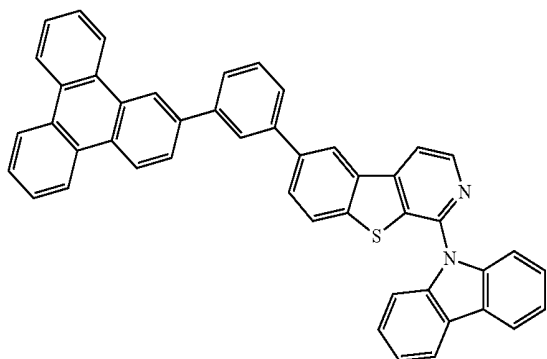


Compound 51



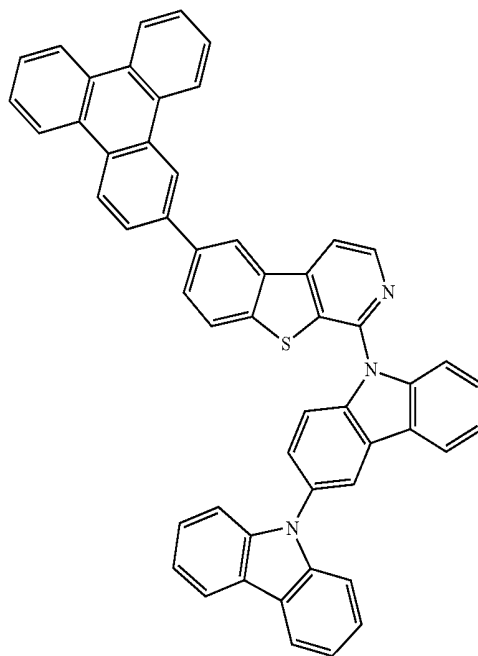
-continued

Compound 52

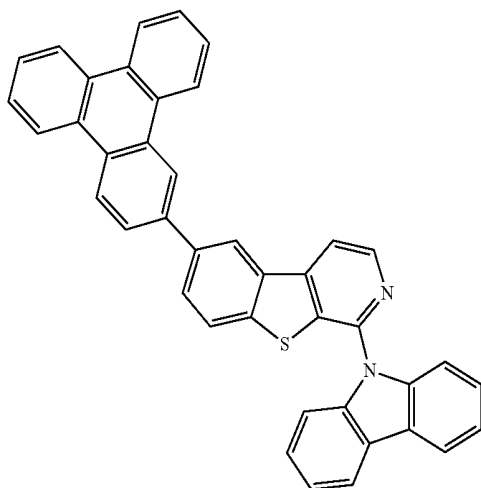


-continued

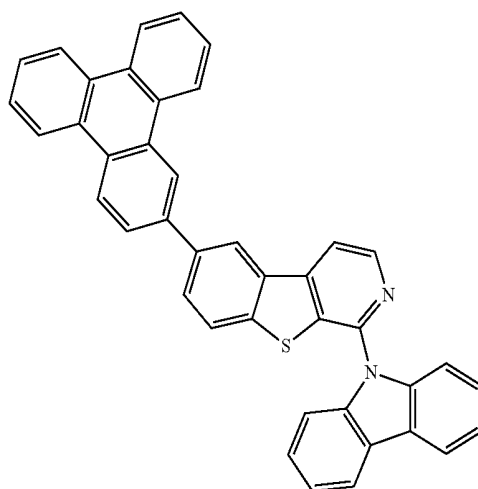
Compound 55



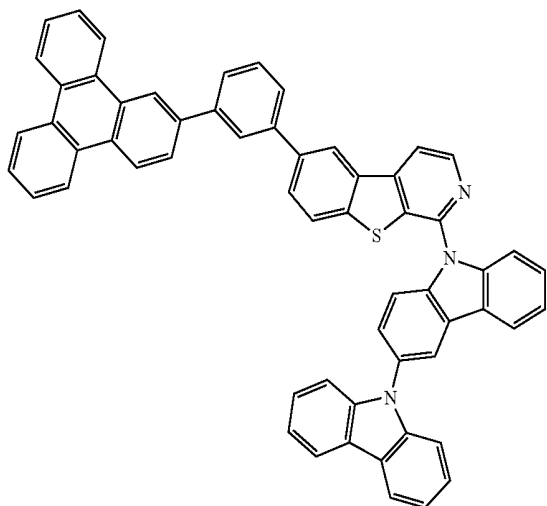
Compound 53



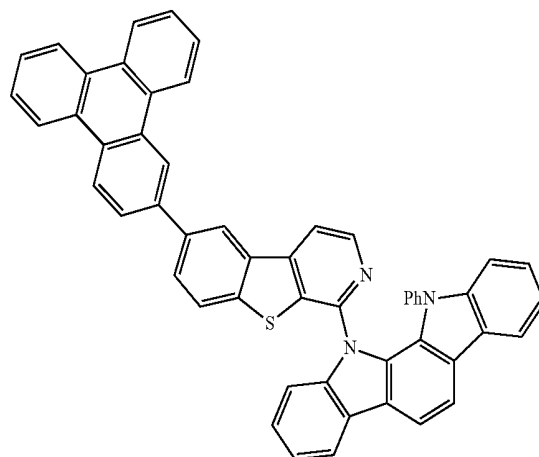
Compound 56



Compound 54

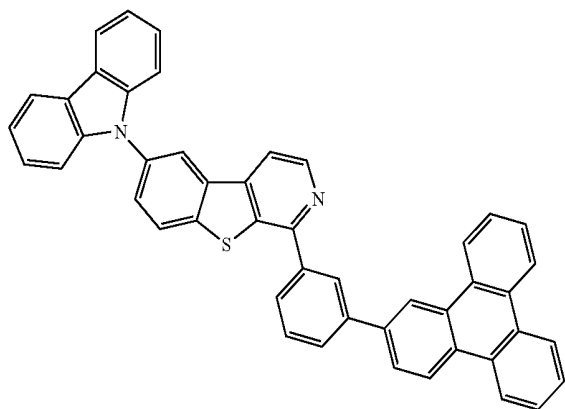


Compound 57

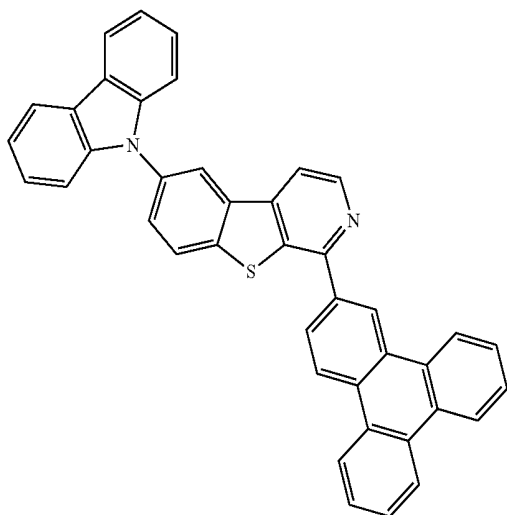


-continued

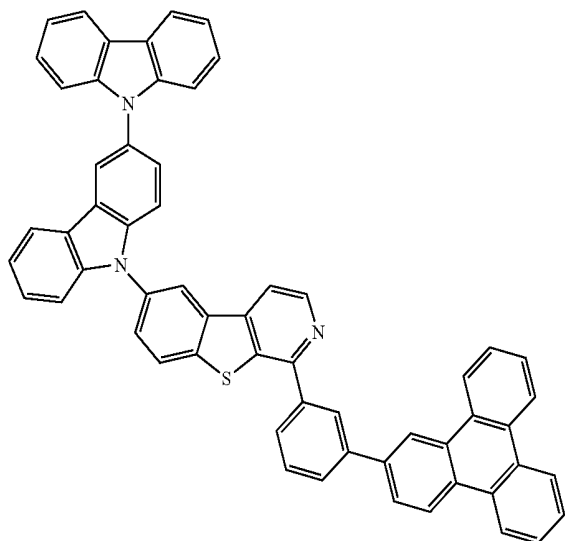
Compound 58



Compound 59

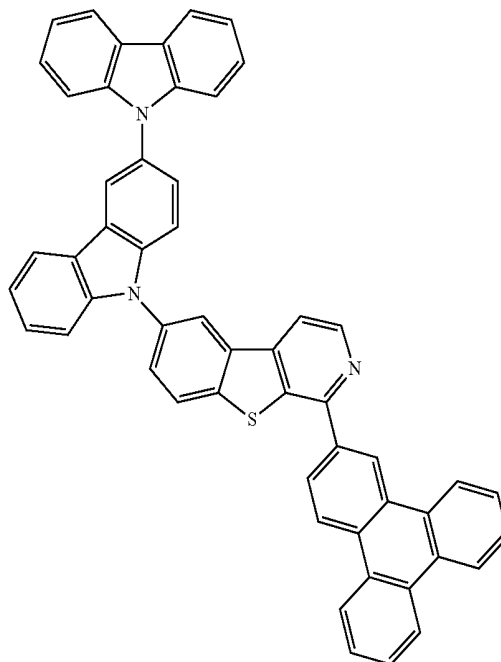


Compound 60

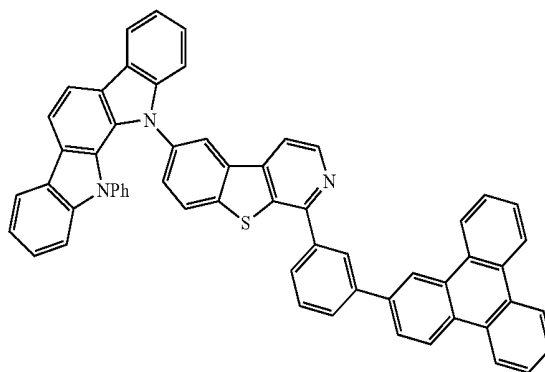


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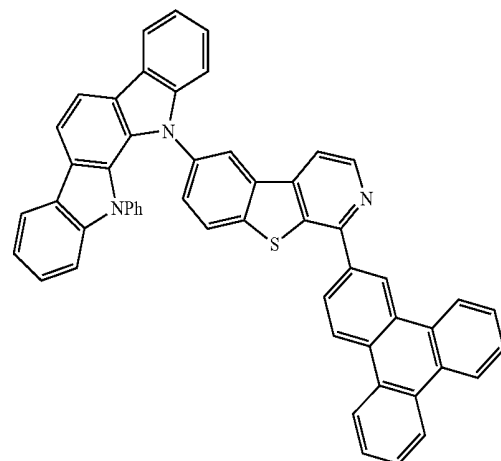
Compound 61



Compound 62

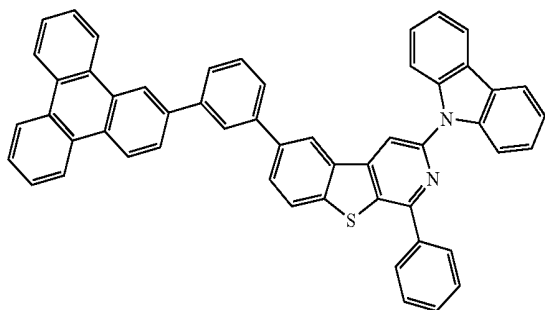


Compound 63



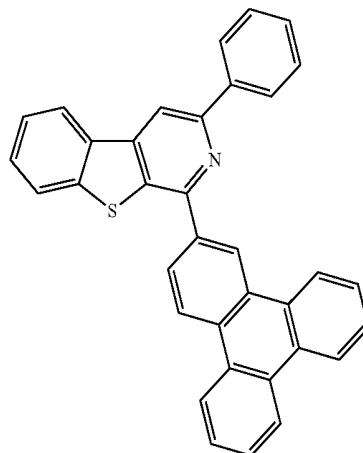
-continued

Compound 64

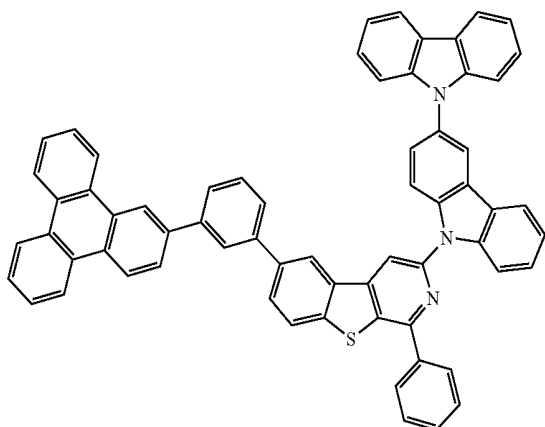


-continued

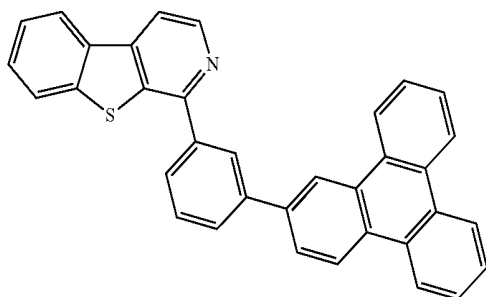
Compound 68



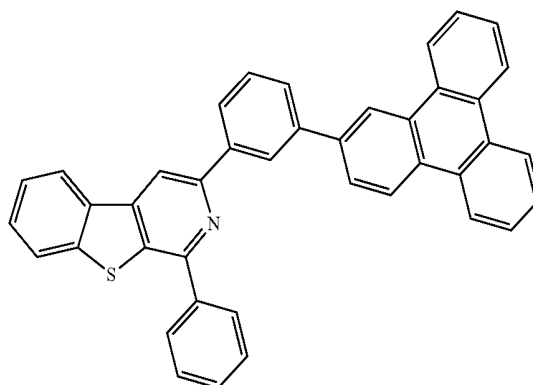
Compound 65



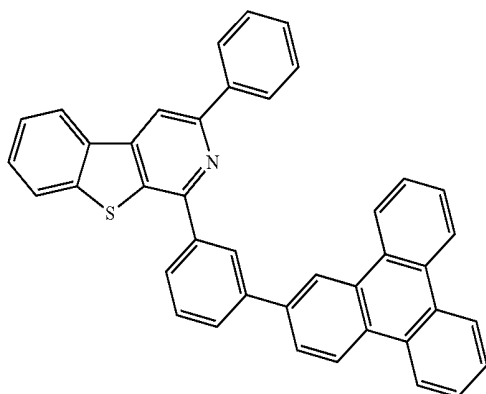
Compound 66



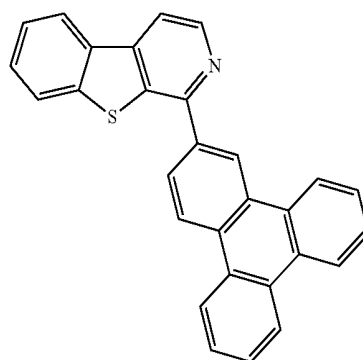
Compound 69



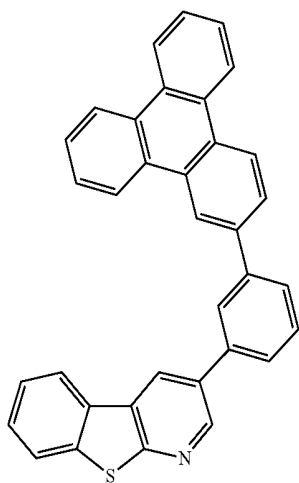
Compound 67



Compound 70

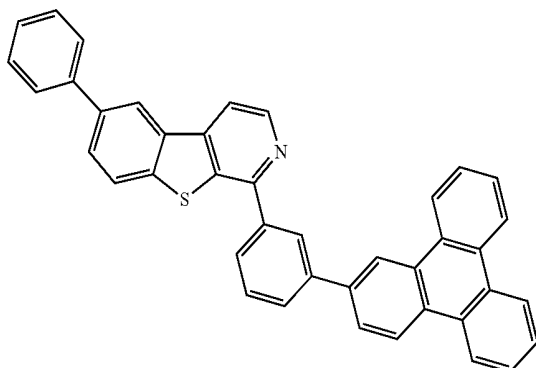


-continued



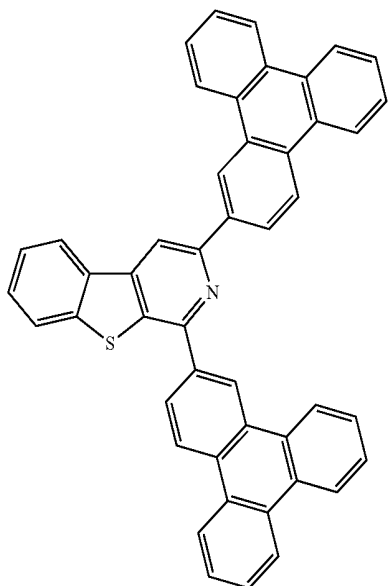
Compound 71

-continued

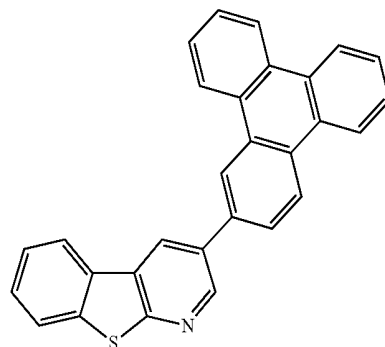


Compound 74

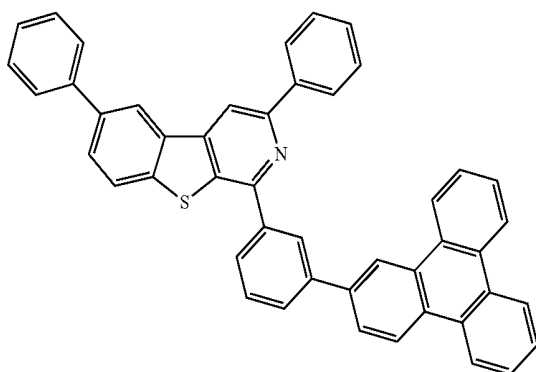
Compound 72



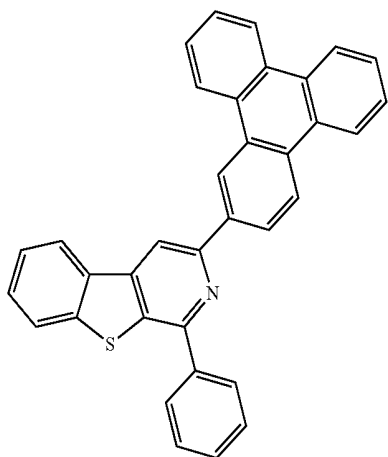
Compound 75



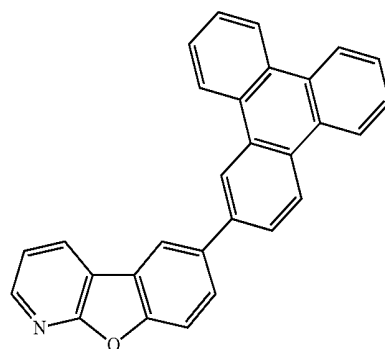
Compound 76



Compound 73

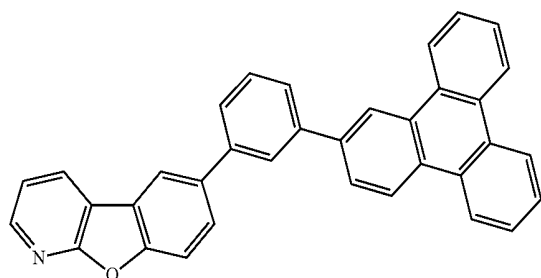


Compound 77

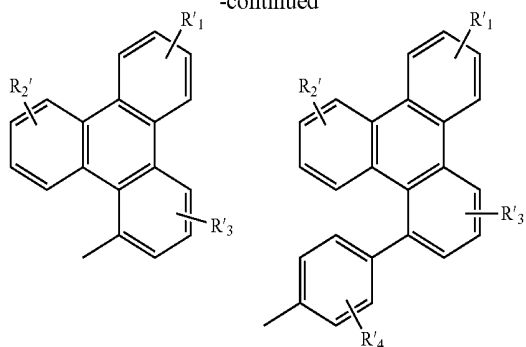


-continued

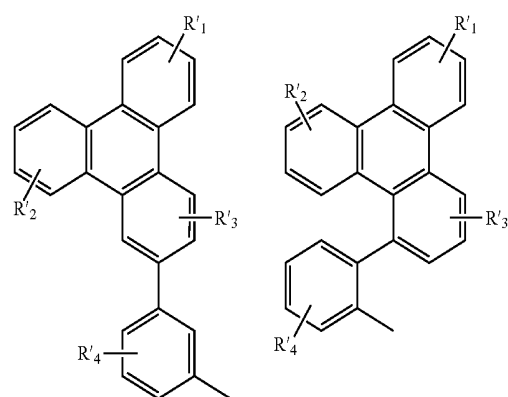
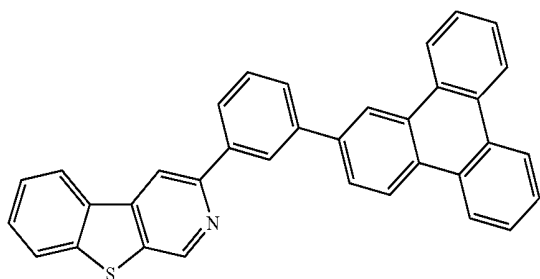
Compound 78



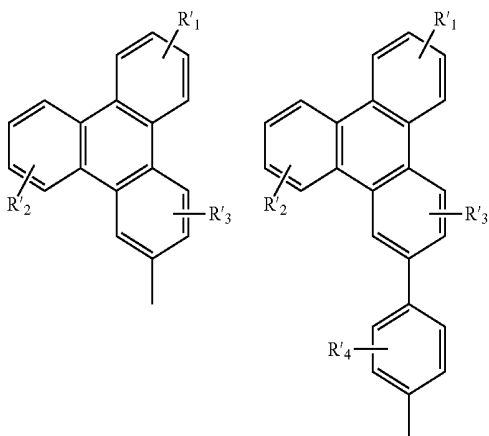
-continued



Compound 79



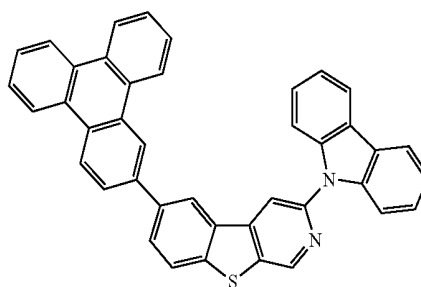
[0058] In another aspect, at least one of  $R_1$  and  $R_2$  is selected from the group consisting of:



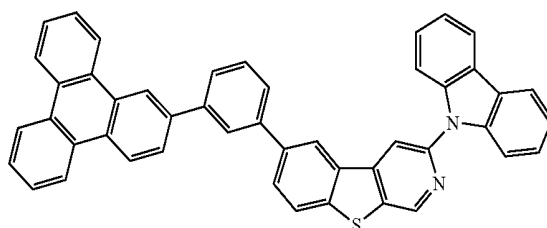
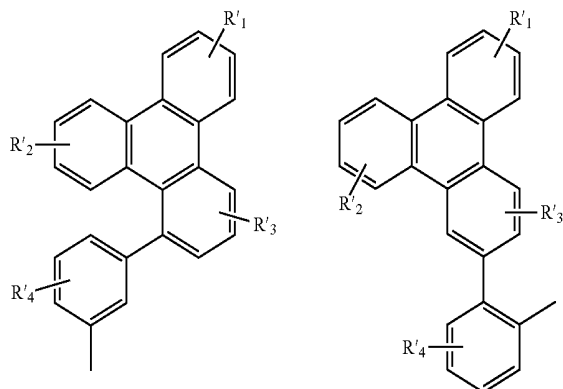
$R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are each independently hydrogen or methyl.

[0059] Specific examples of such compounds include compounds selected from the group consisting of:

Compound 39



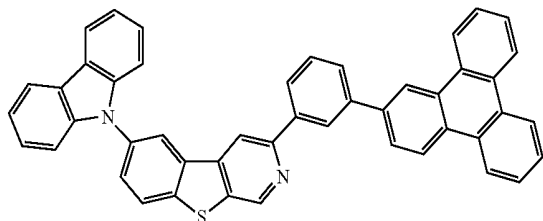
Compound 40





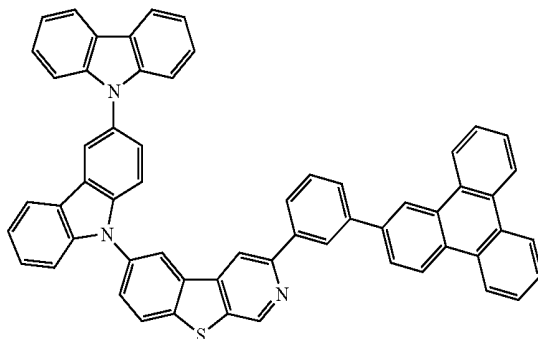
-continued

Compound 41

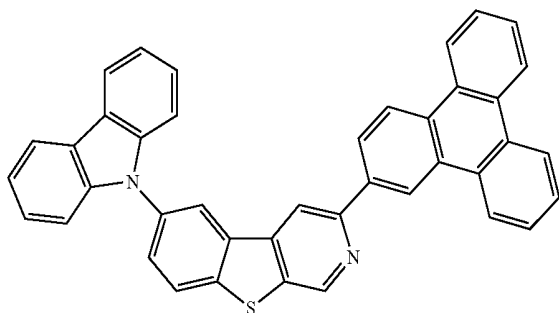


-continued

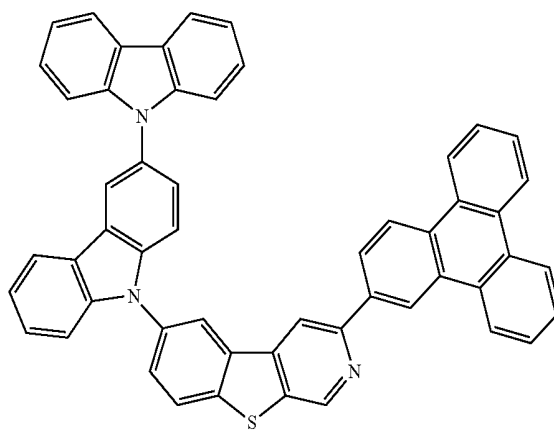
Compound 45



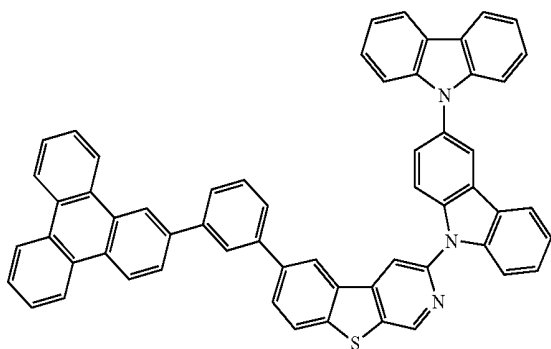
Compound 42



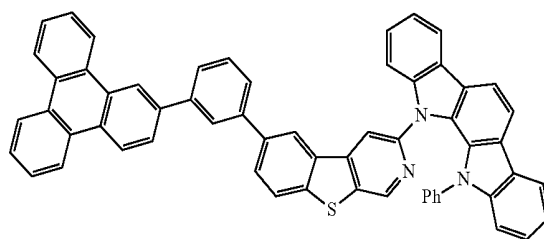
Compound 46



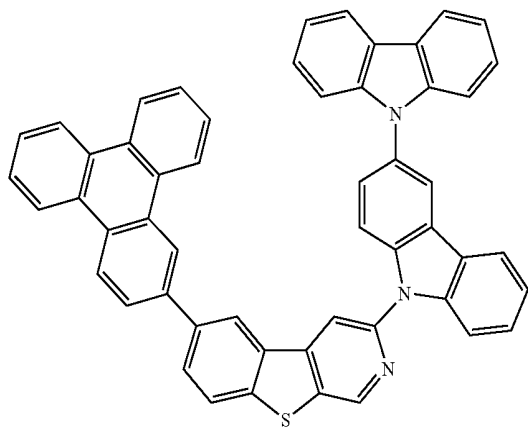
Compound 43



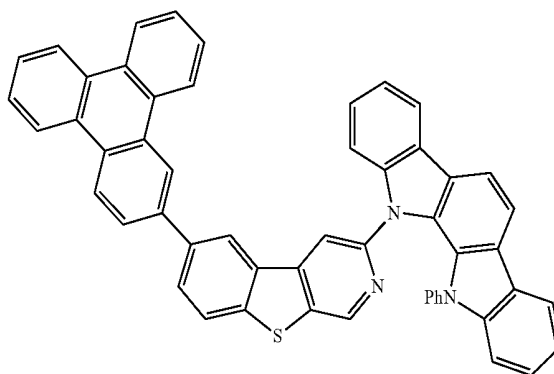
Compound 47



Compound 44

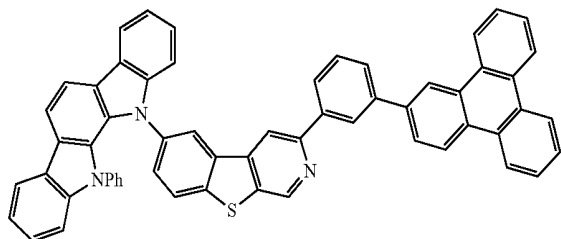


Compound 48



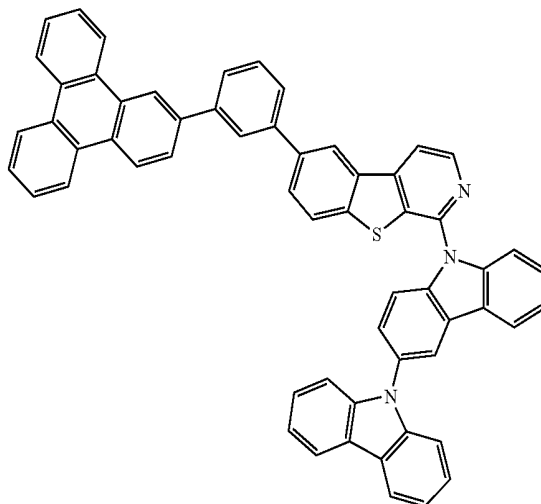
-continued

Compound 50

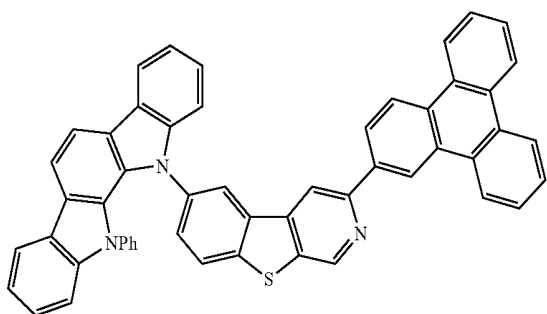


-continued

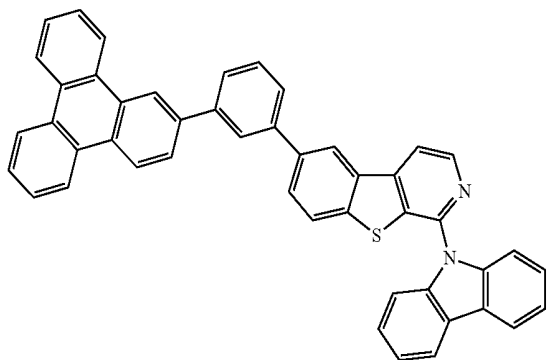
Compound 54



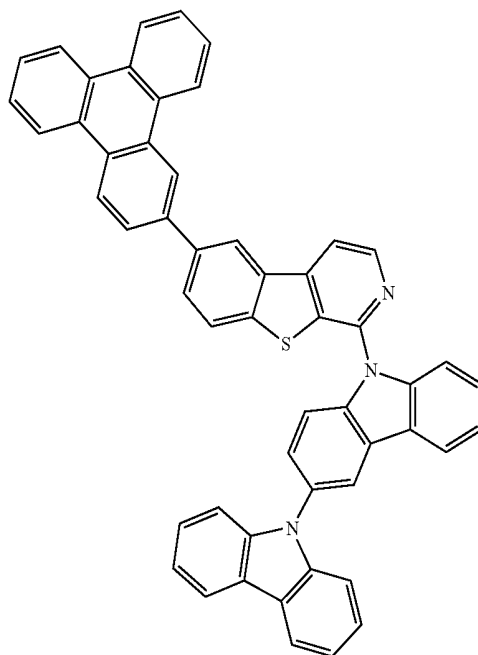
Compound 51



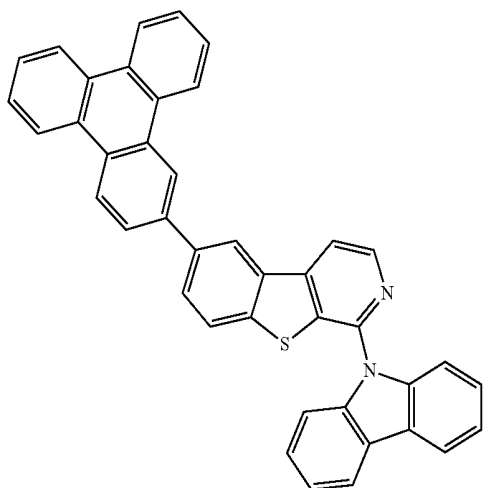
Compound 52



Compound 55

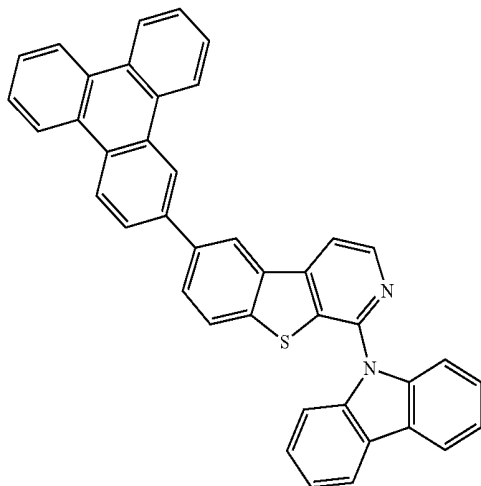


Compound 53



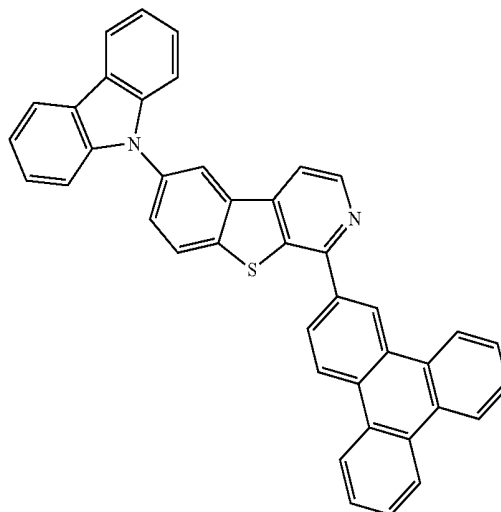
-continued

Compound 56

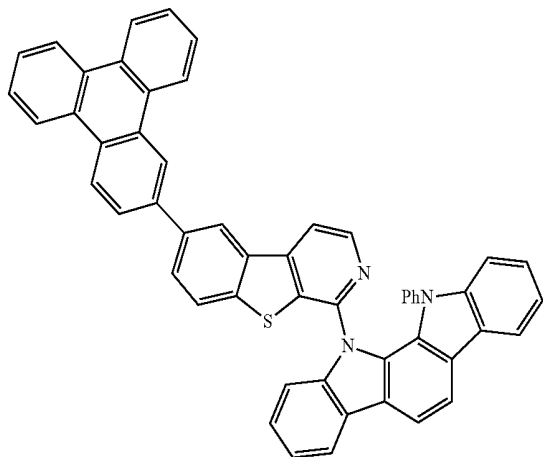


-continued

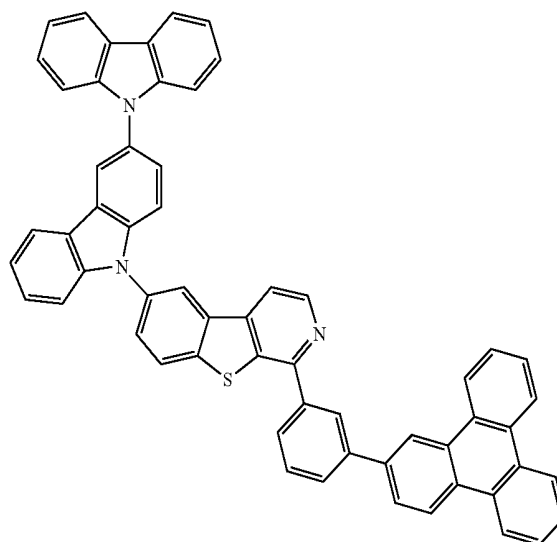
Compound 59



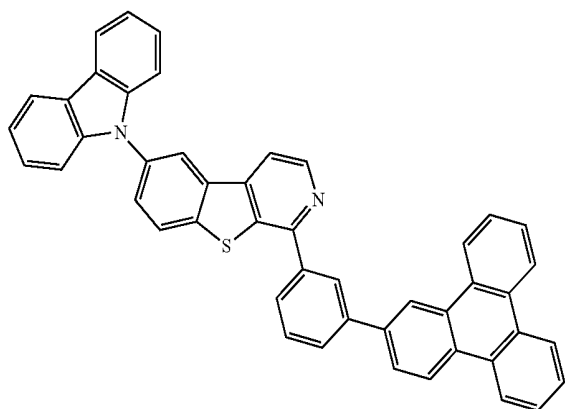
Compound 57



Compound 60

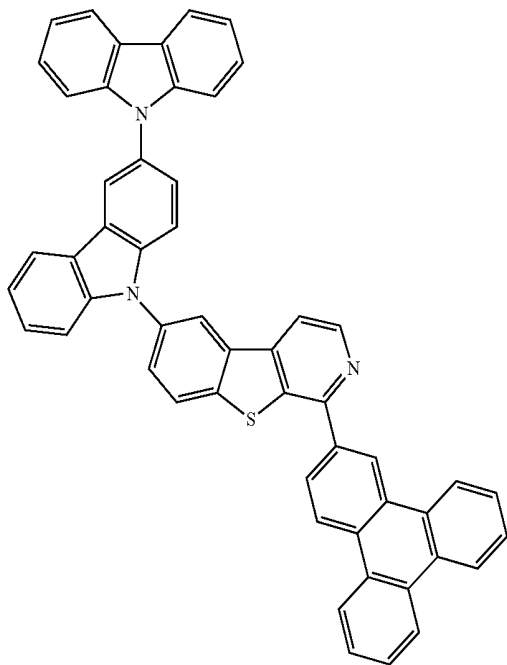


Compound 58

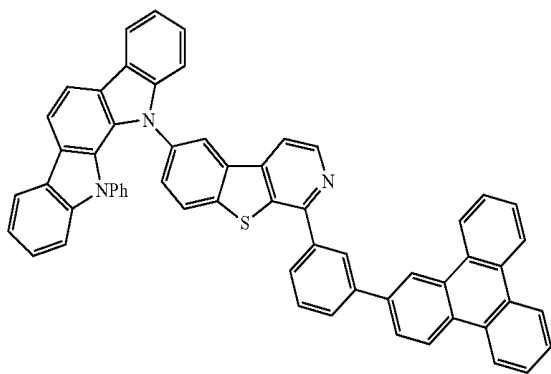


-continued

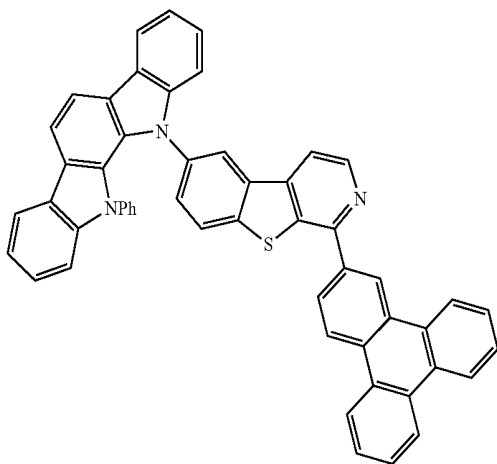
Compound 61



Compound 62

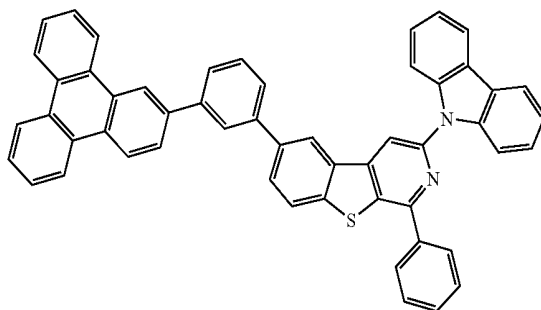


Compound 63

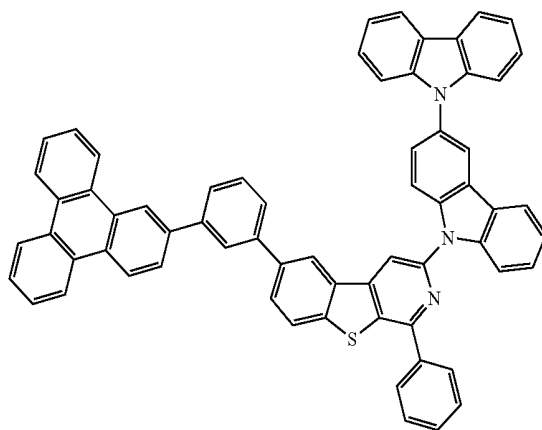


-continued

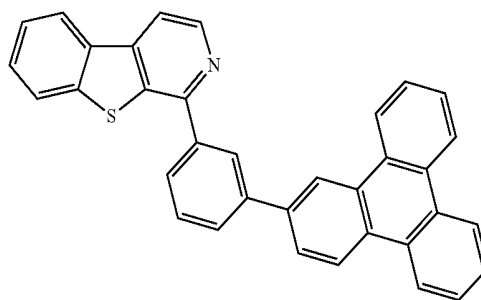
Compound 64



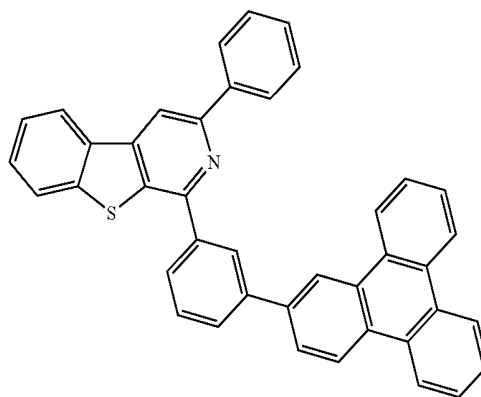
Compound 65



Compound 66

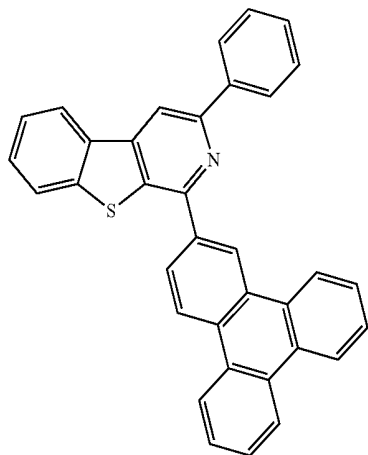


Compound 67



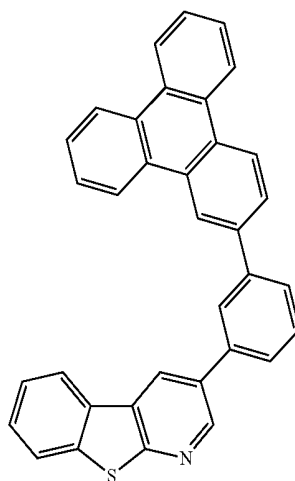
-continued

Compound 68

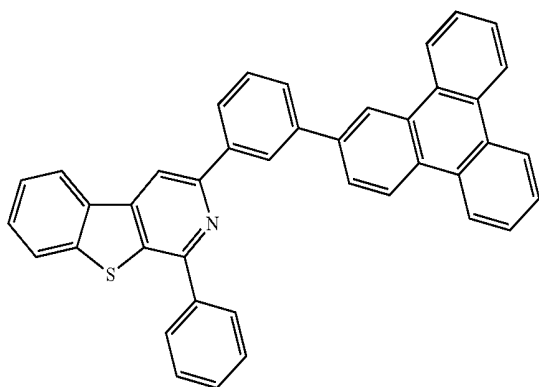


-continued

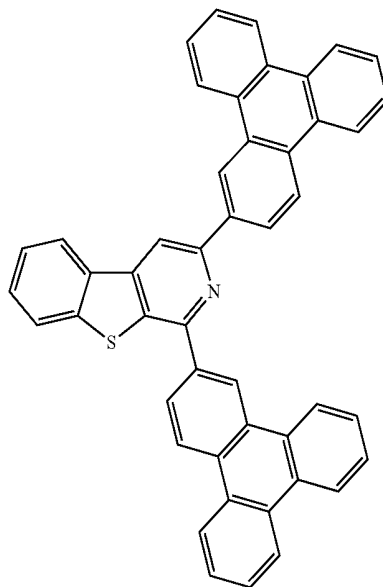
Compound 71



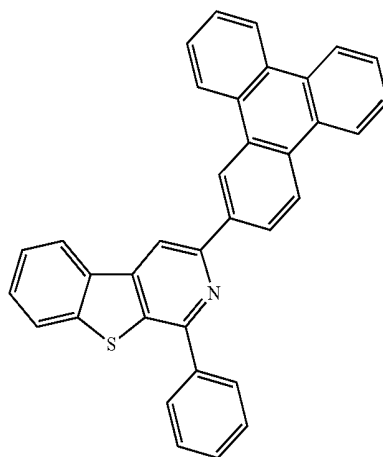
Compound 69



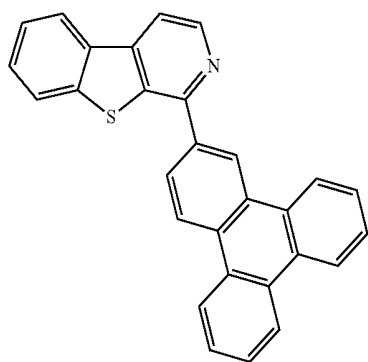
Compound 72



Compound 73

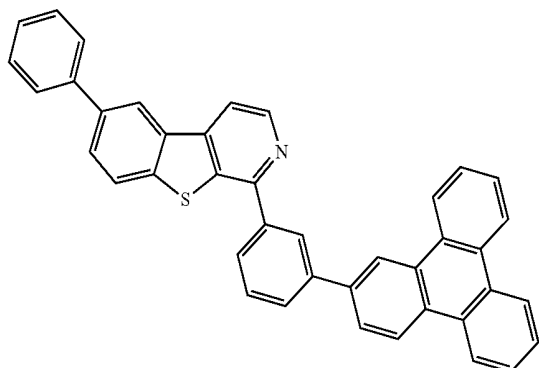


Compound 70



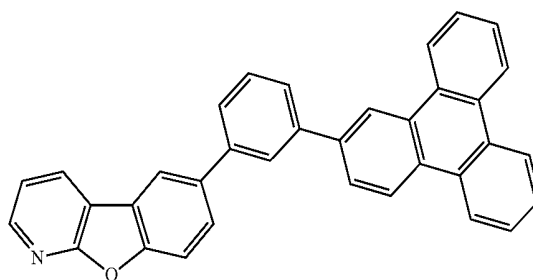
-continued

Compound 74

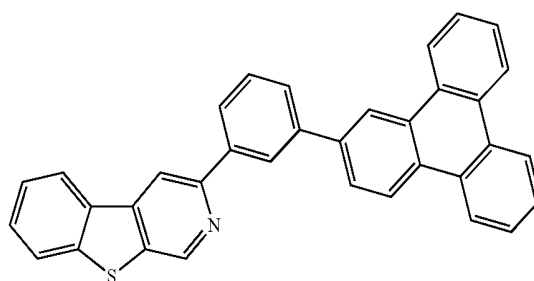


-continued

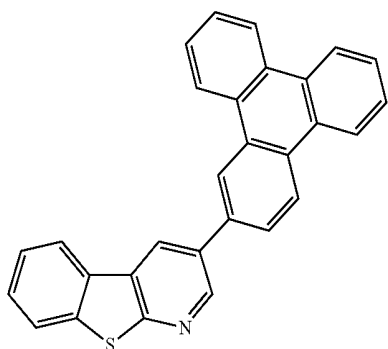
Compound 78



Compound 79

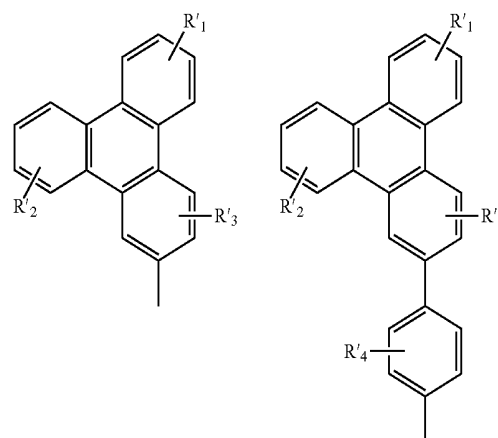
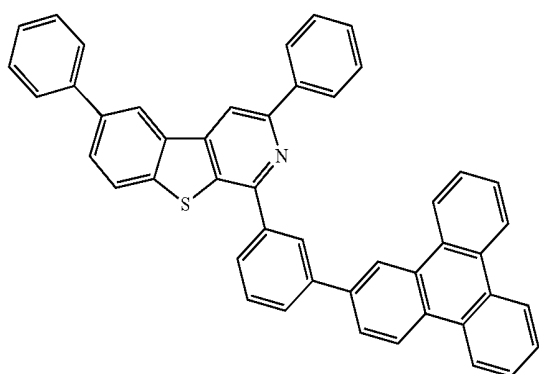


Compound 75

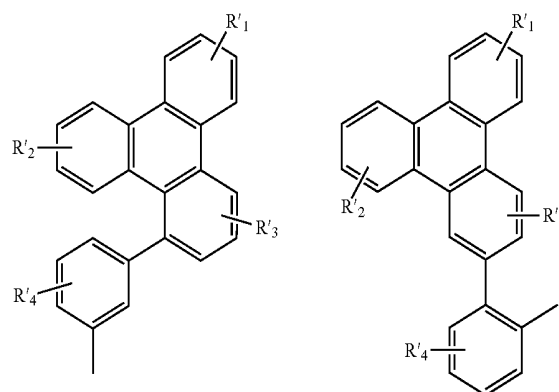
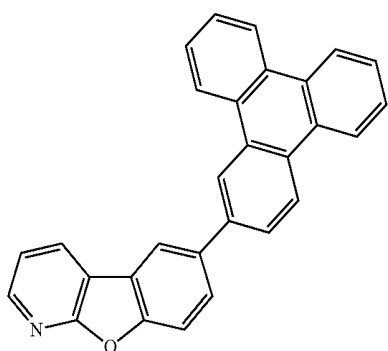


[0060] In another aspect,  $R_1$  and  $R_2$  are each independently selected from the group consisting of hydrogen and

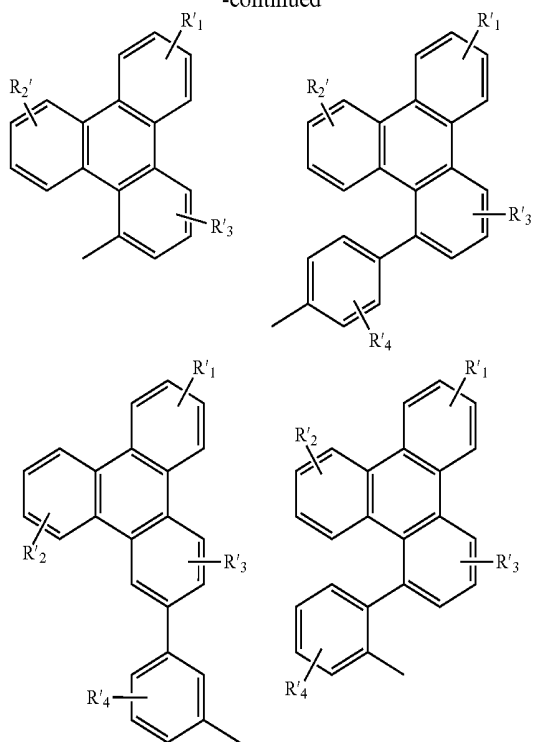
Compound 76



Compound 77



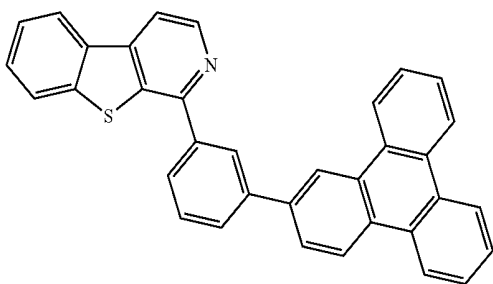
-continued



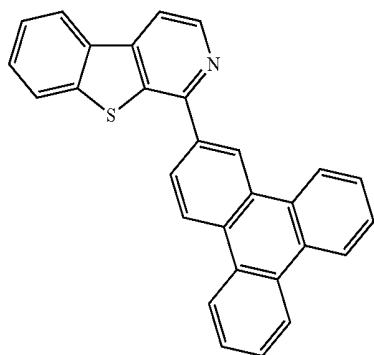
$R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably,  $R'_1$ ,  $R'_2$  and  $R'_4$  are each independently hydrogen or methyl.

**[0061]** Specific examples of such compounds include compounds selected from the group consisting of:

Compound 66

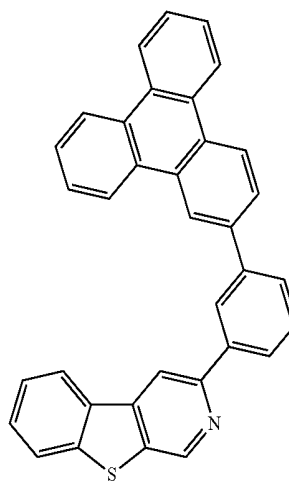


Compound 70

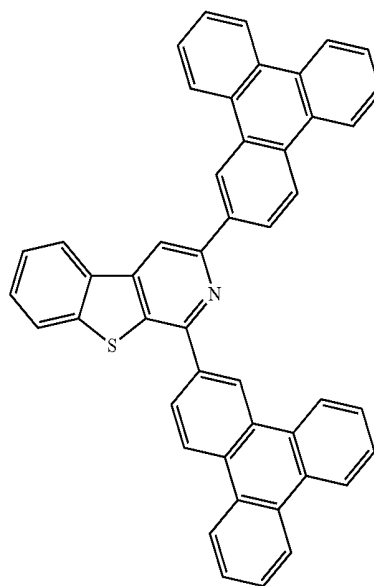


-continued

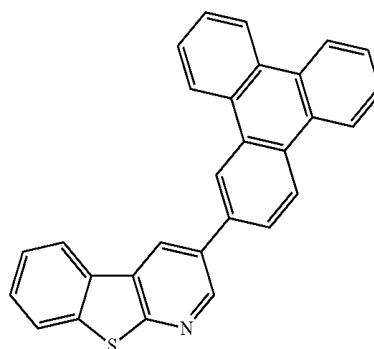
Compound 71



Compound 72

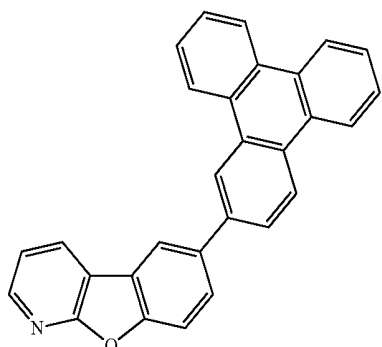


Compound 75

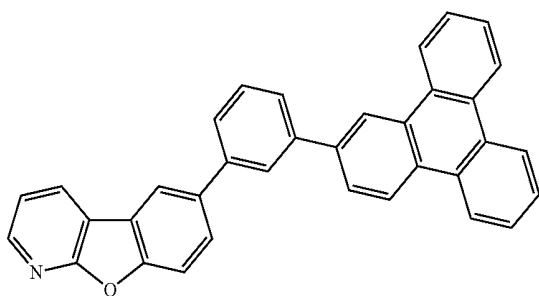


-continued

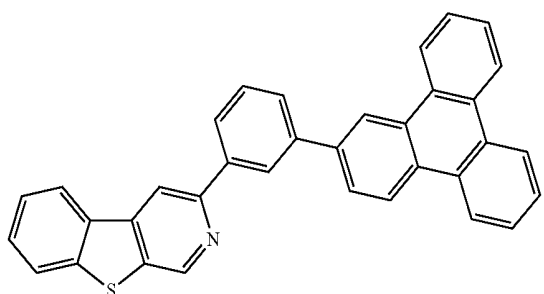
Compound 77



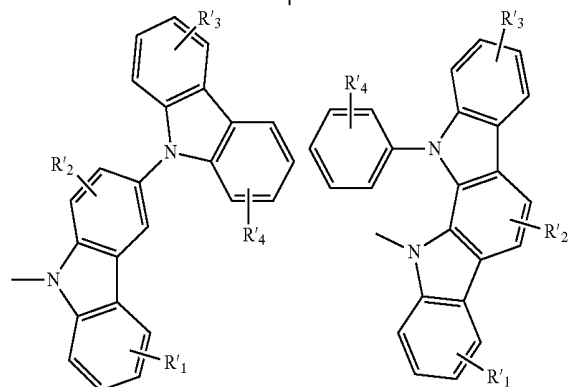
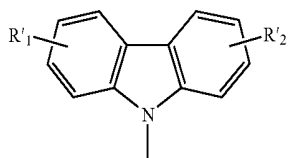
Compound 78



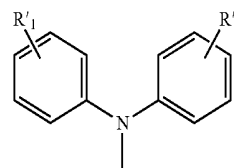
Compound 79



[0062] In one aspect, at least one of  $R_1$  and  $R_2$  is selected from the group consisting



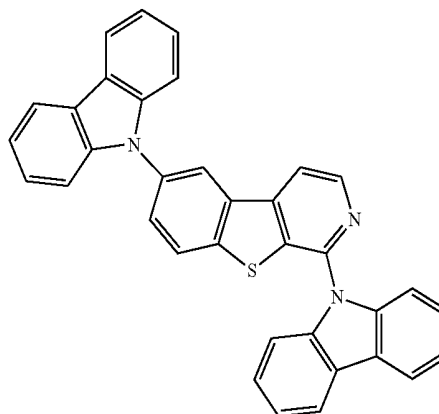
-continued



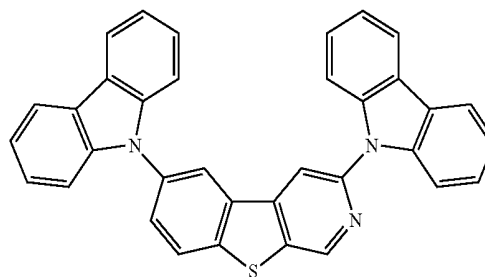
$R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably,  $R'_1$ ,  $R'_2$  and  $R'_4$  are each independently hydrogen or methyl.

[0063] Specific examples of such compounds include compounds selected from the group consisting of:

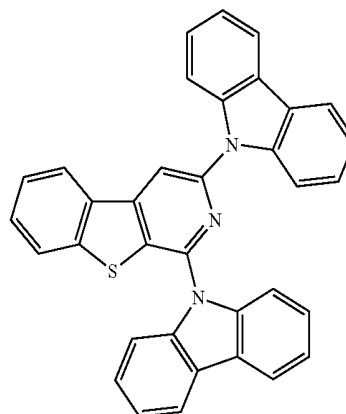
Compound 1



Compound 2



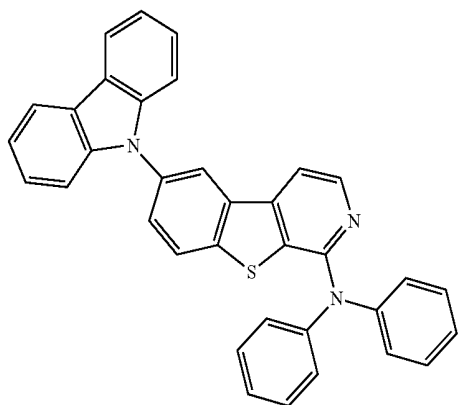
Compound 3





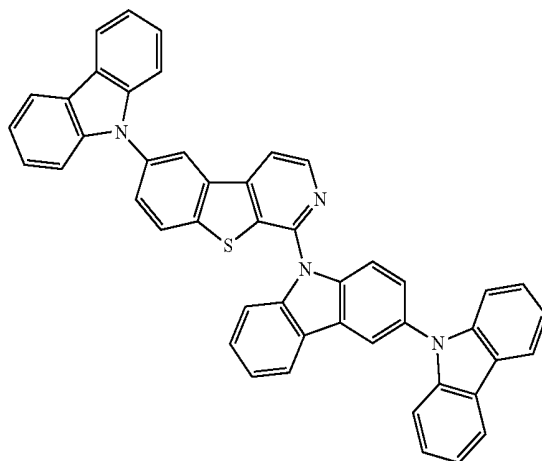
-continued

Compound 4

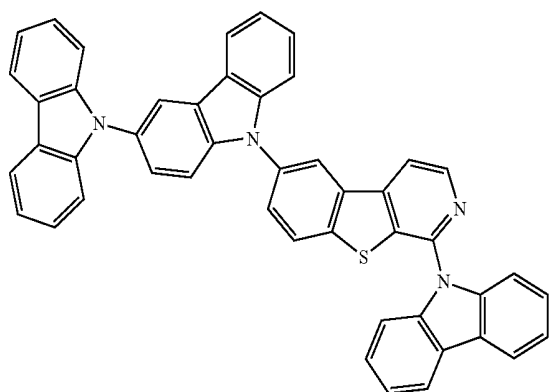


-continued

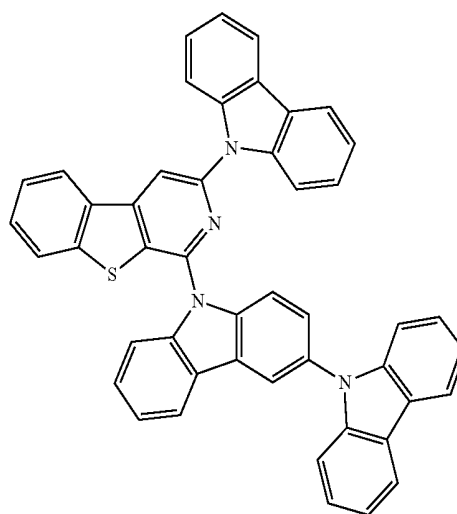
Compound 7



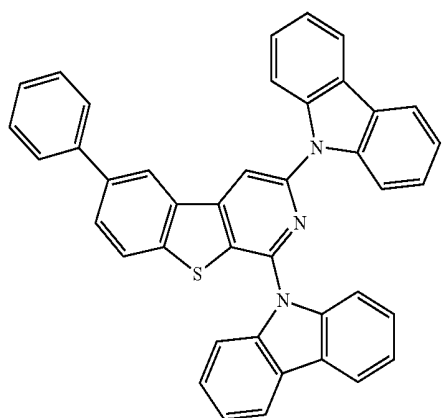
Compound 5



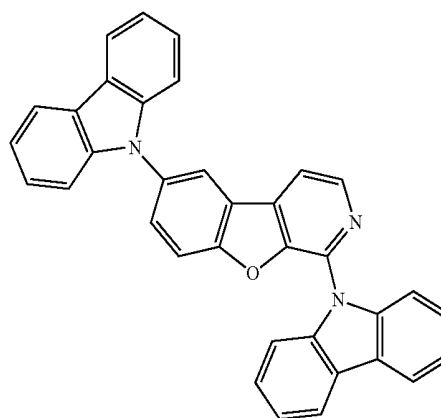
Compound 8



Compound 6

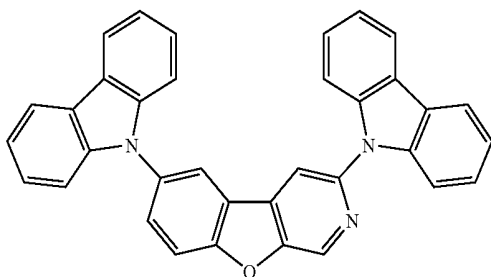


Compound 9

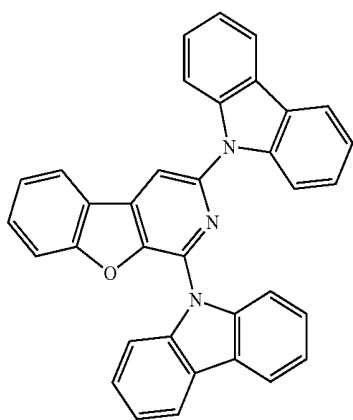


-continued

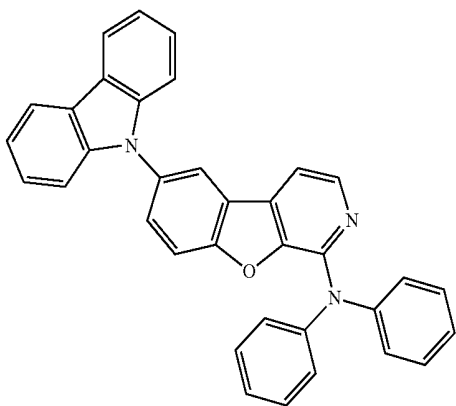
Compound 10



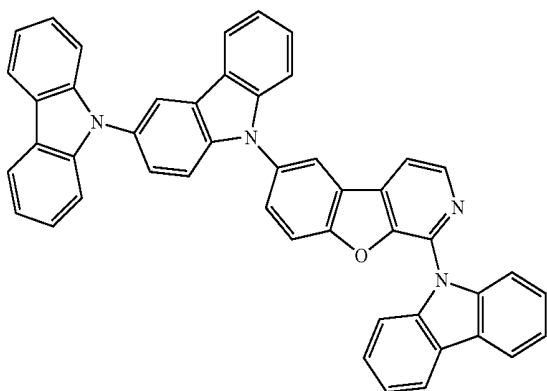
Compound 11



Compound 12

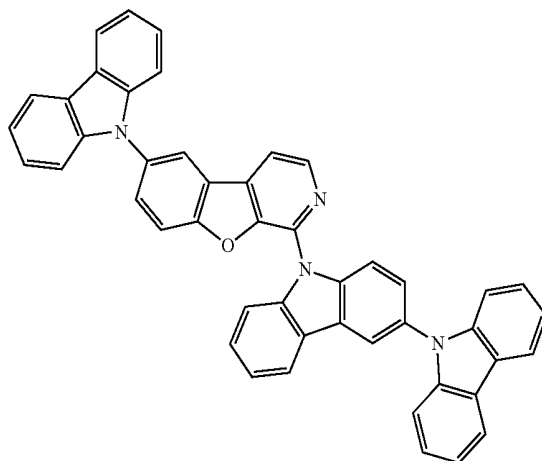


Compound 13

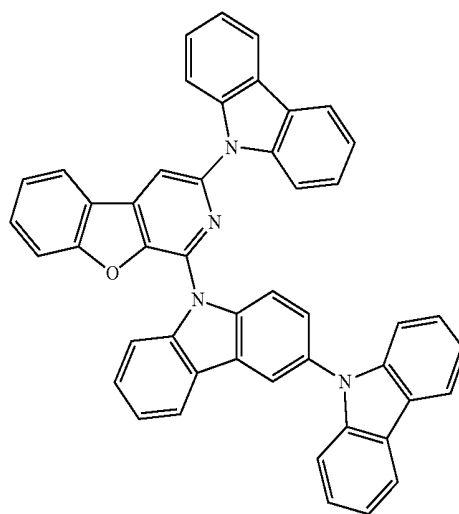


-continued

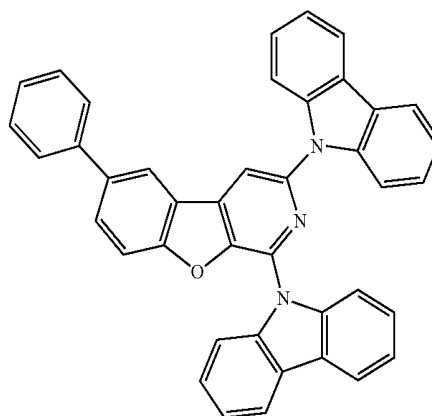
Compound 14



Compound 15

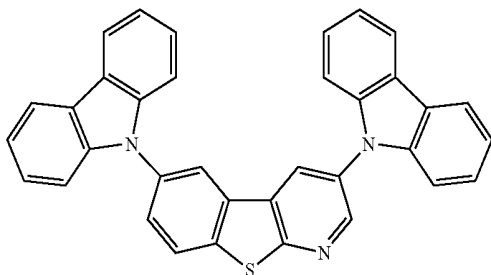


Compound 16



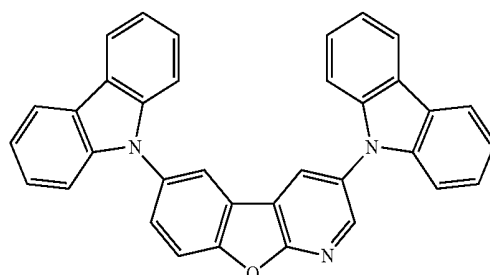
-continued

Compound 17

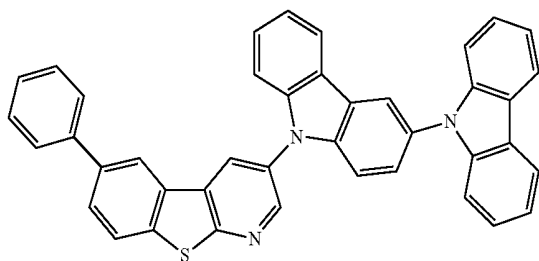


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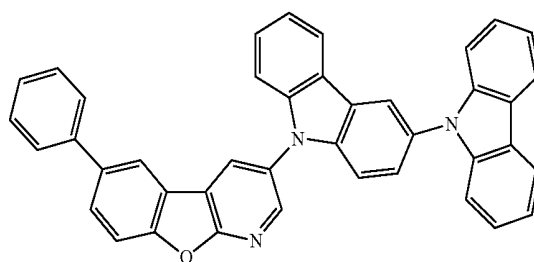
Compound 21



Compound 18

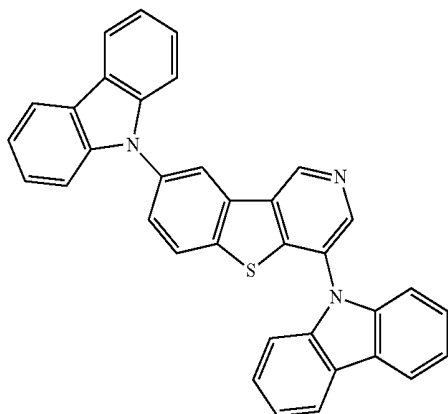


Compound 22

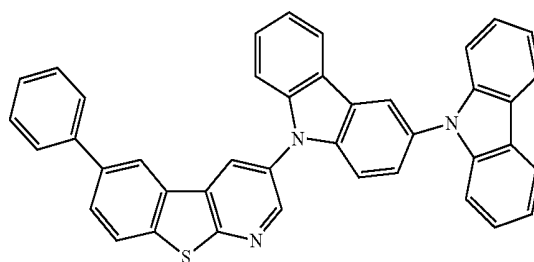


Compound 23

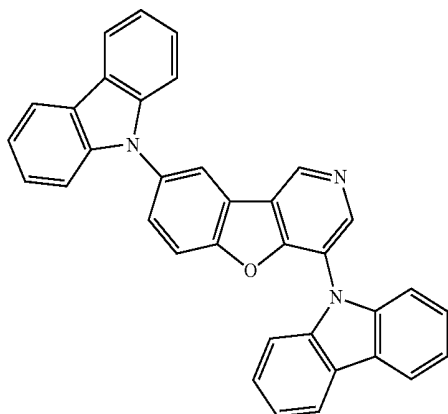
Compound 19



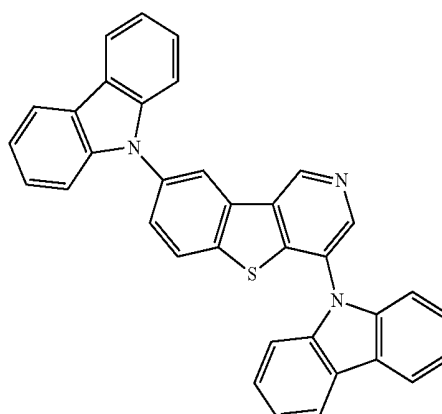
Compound 24



Compound 20

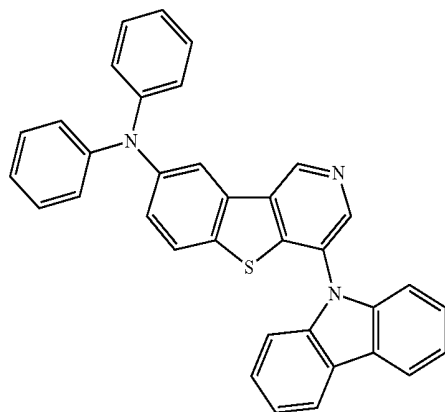


Compound 25



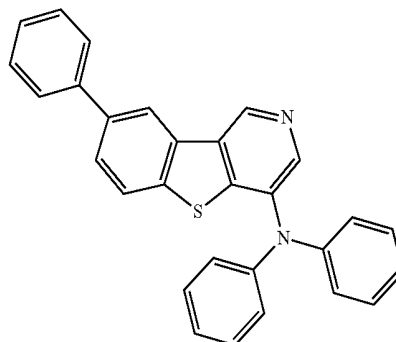
-continued

Compound 26

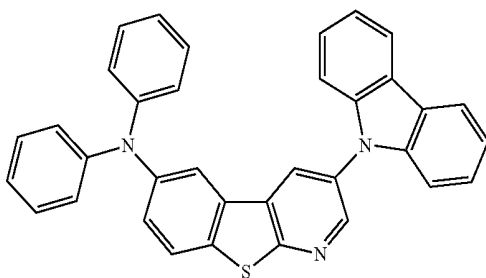


-continued

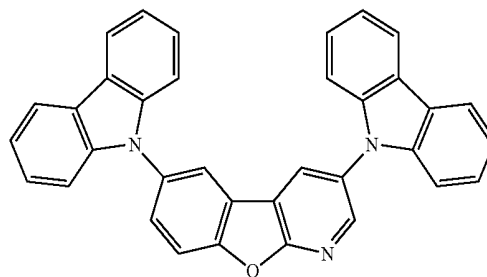
Compound 30



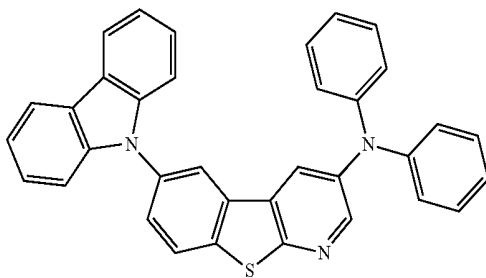
Compound 27



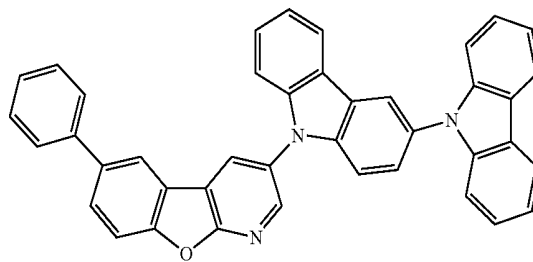
Compound 31



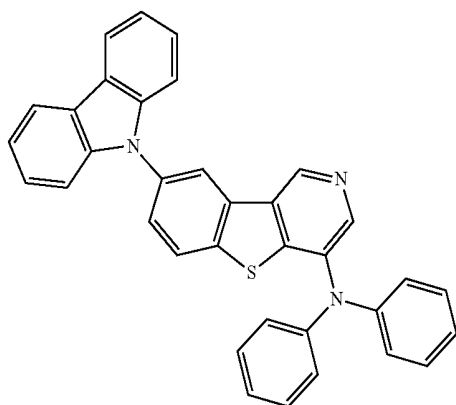
Compound 28



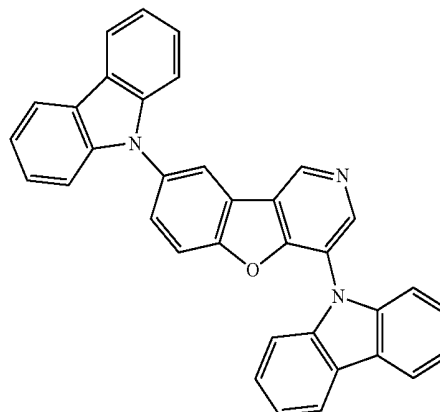
Compound 32



Compound 29

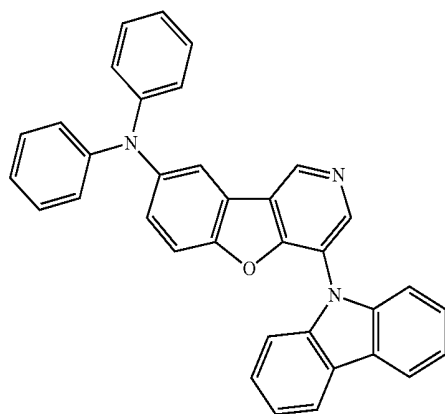


Compound 33



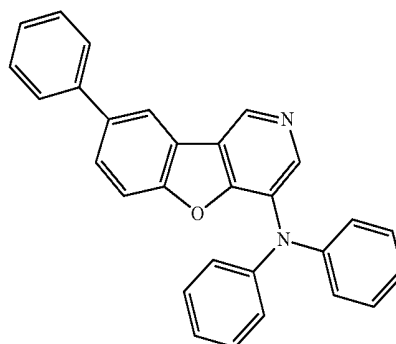
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Compound 34

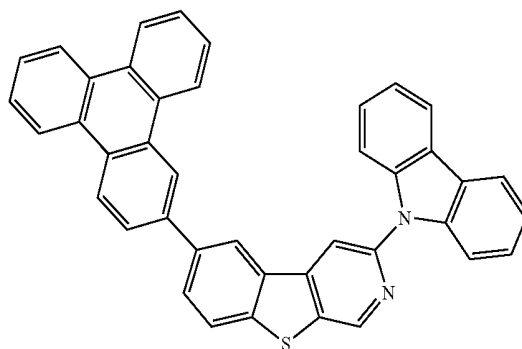


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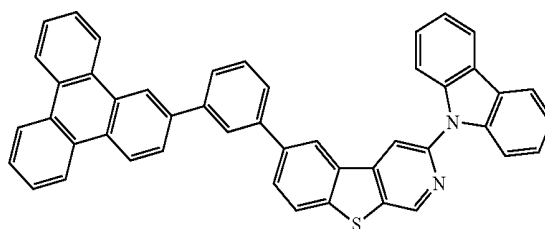
Compound 38



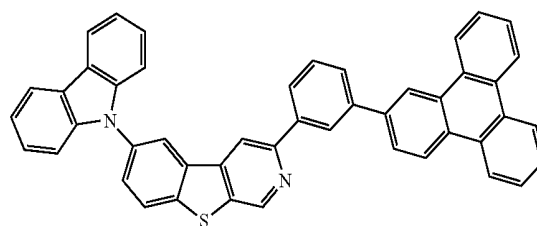
Compound 39



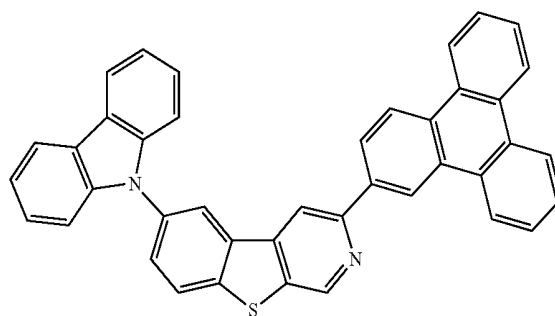
Compound 40



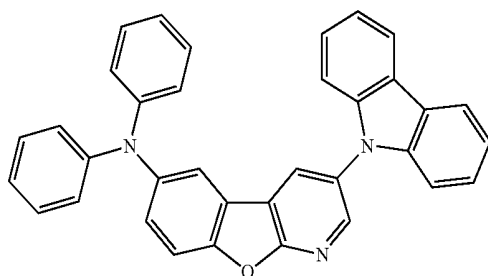
Compound 41



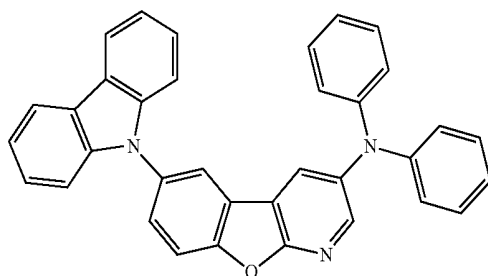
Compound 42



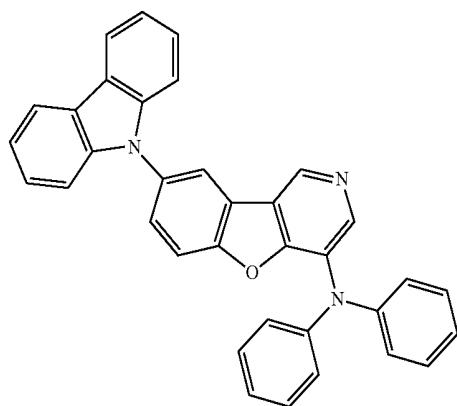
Compound 35



Compound 36

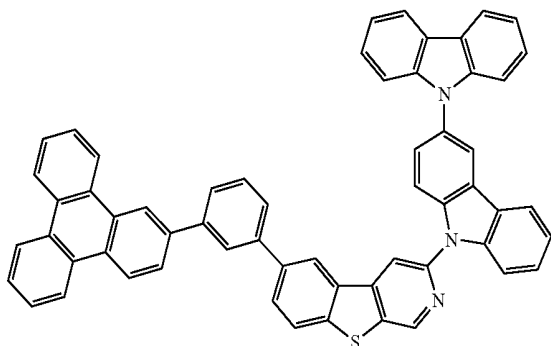


Compound 37

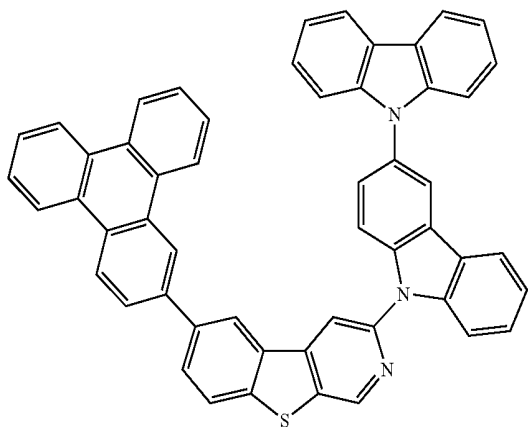


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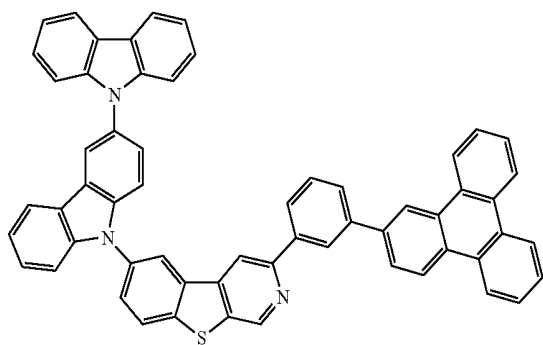
Compound 43



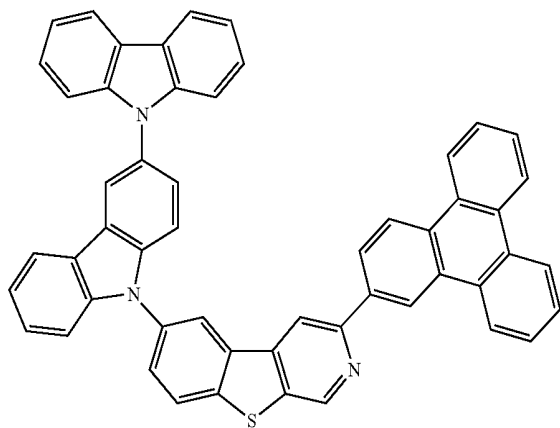
Compound 44



Compound 45

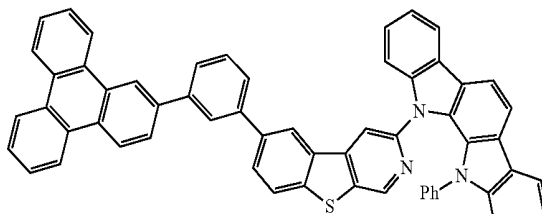


Compound 46

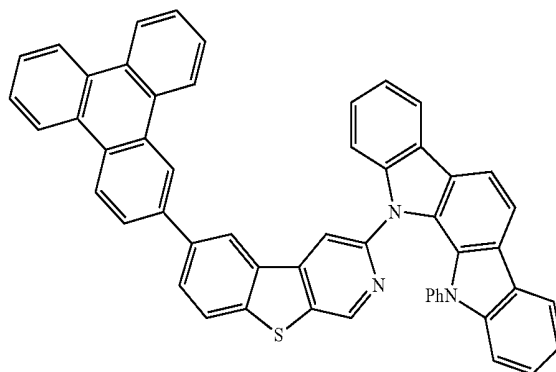


-continued

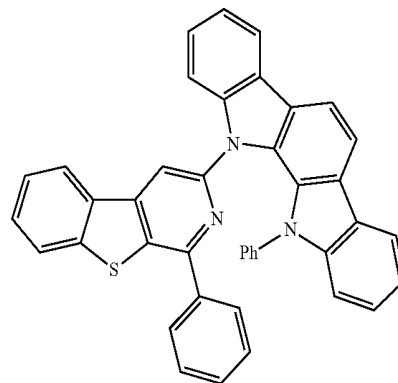
Compound 47



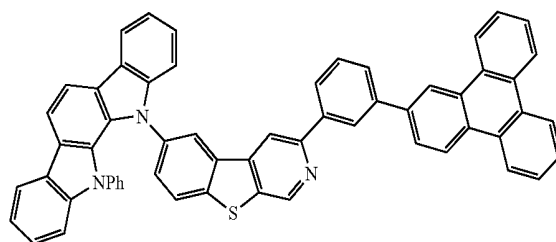
Compound 48



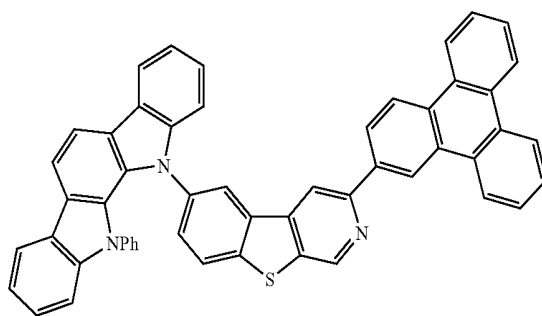
Compound 49



Compound 50

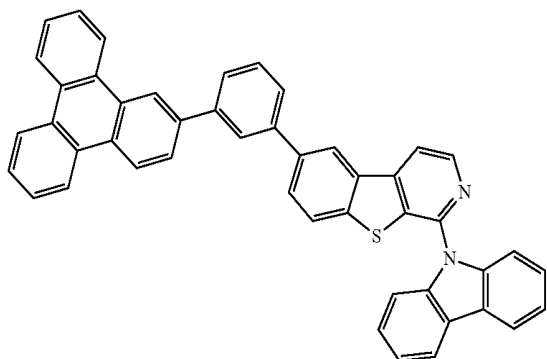


Compound 51



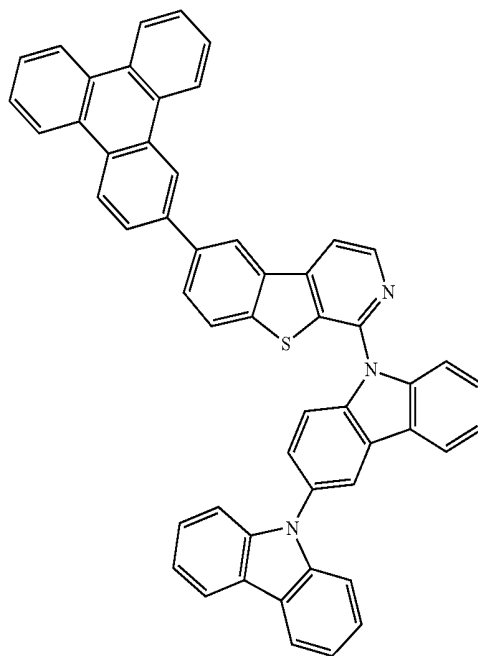
-continued

Compound 52

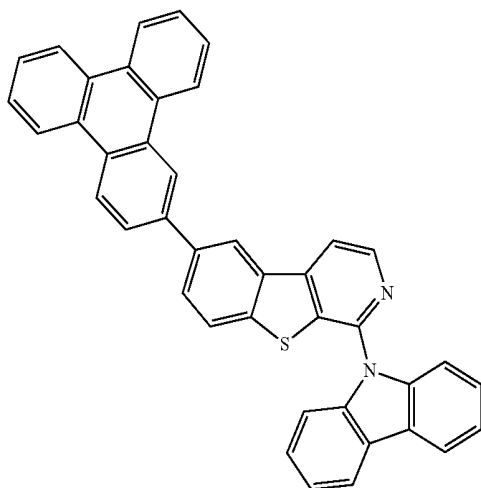


-continued

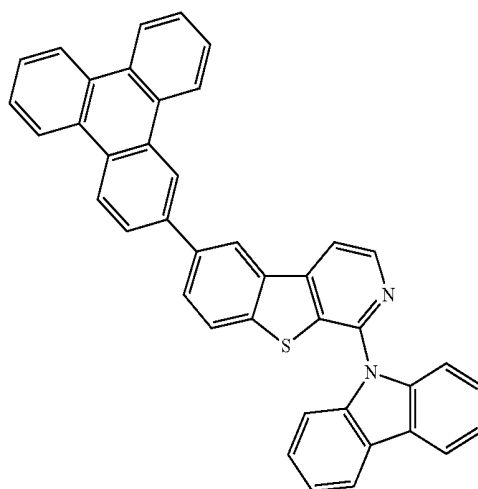
Compound 55



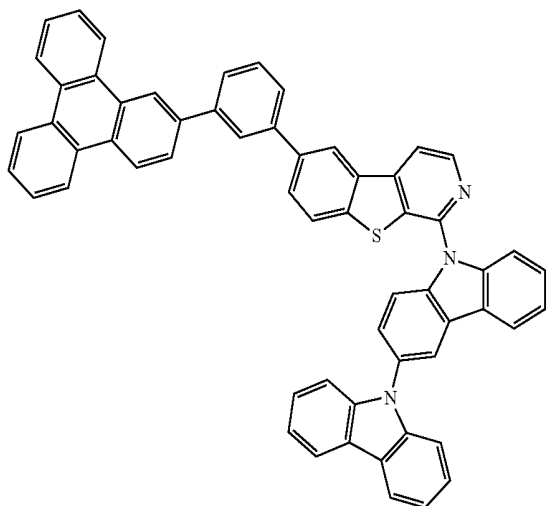
Compound 53



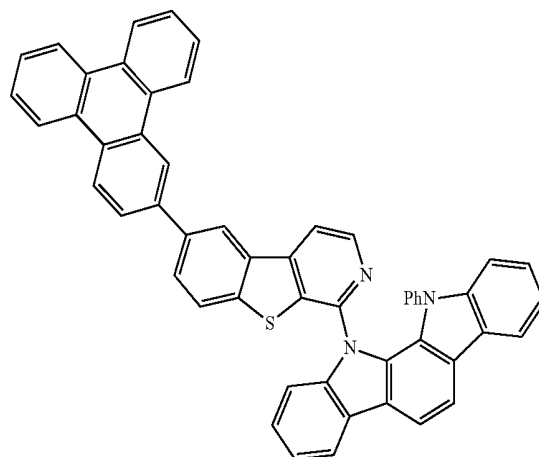
Compound 56



Compound 54

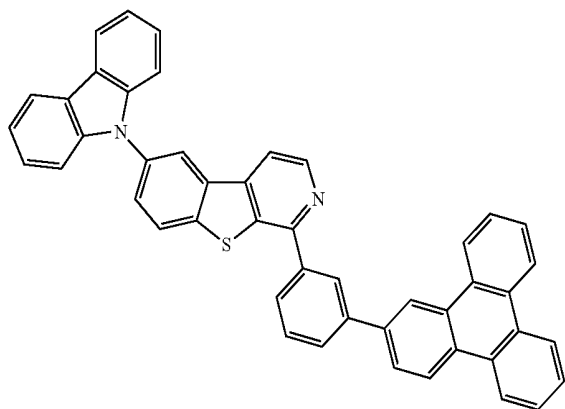


Compound 57



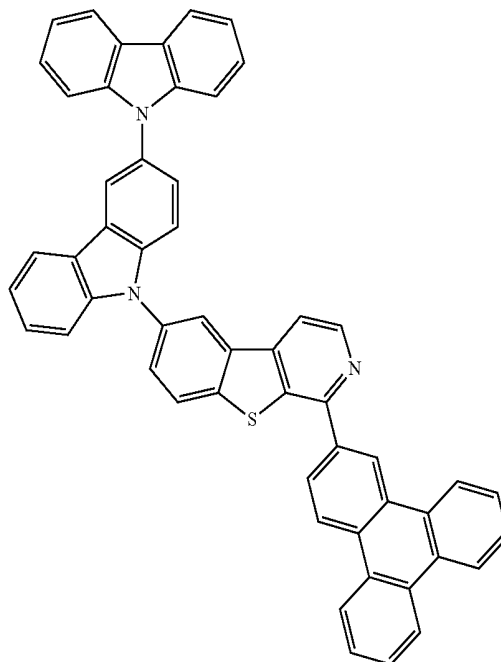
-continued

Compound 58

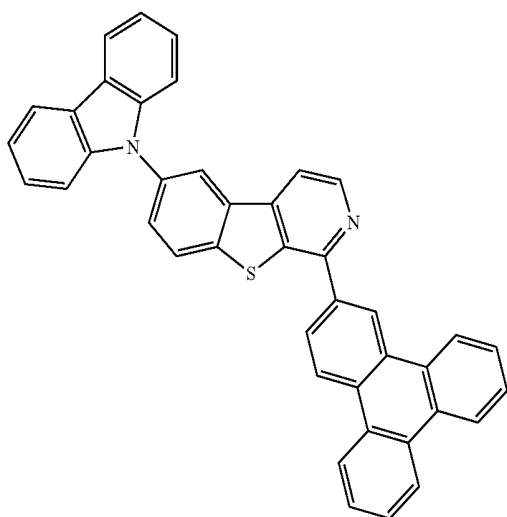


-continued

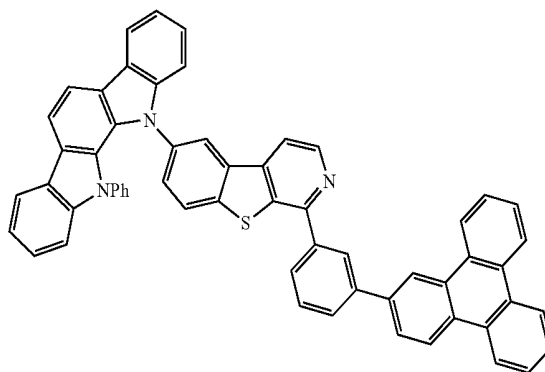
Compound 61



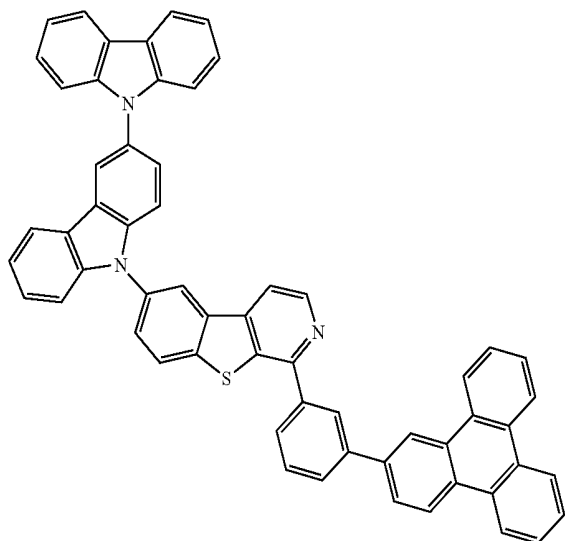
Compound 59



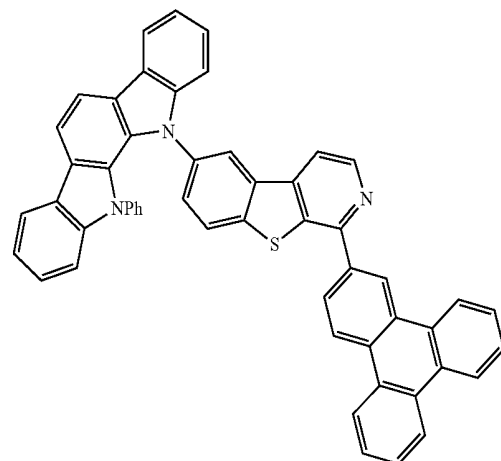
Compound 62



Compound 60



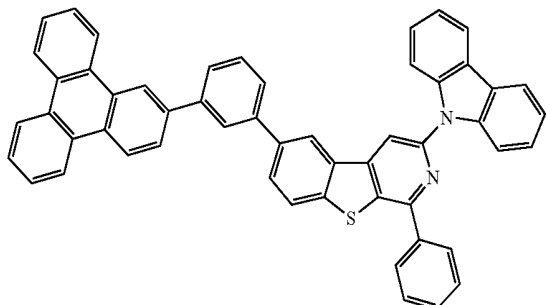
Compound 63



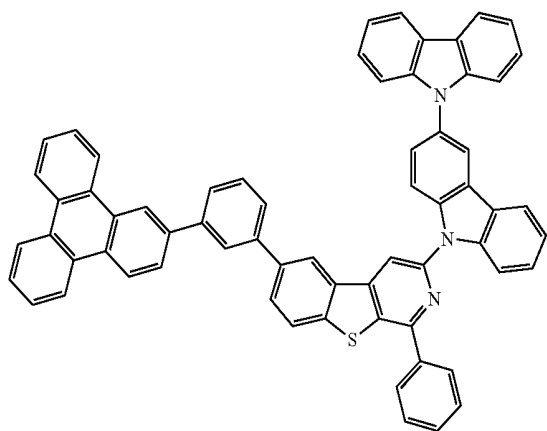


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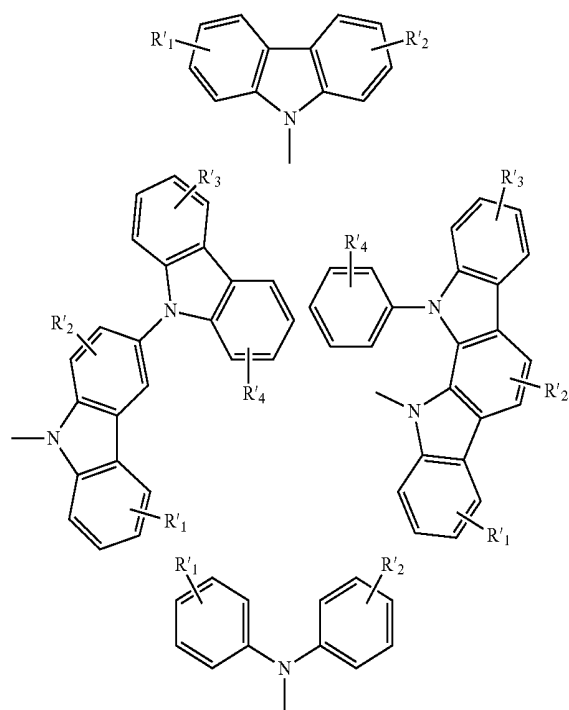
Compound 64



Compound 65



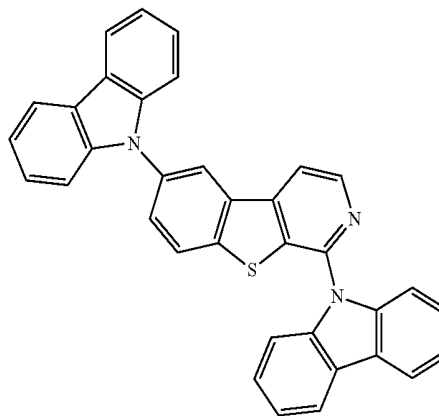
[0064] In another aspect,  $R_1$  and  $R_2$  are each independently selected from the group consisting of hydrogen and



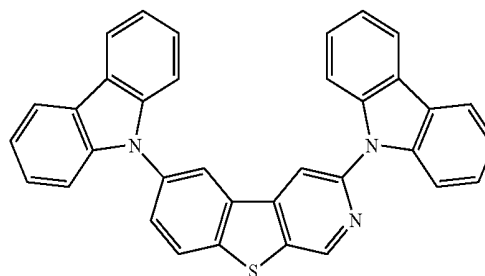
$R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are each independently hydrogen or methyl.

[0065] Specific examples of such compounds include compounds selected from the group consisting of:

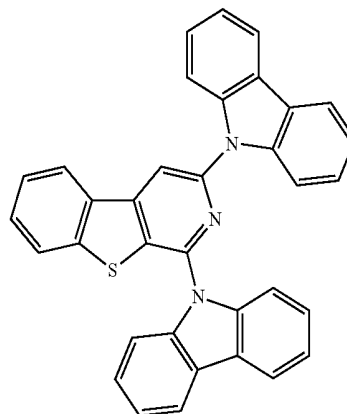
Compound 1



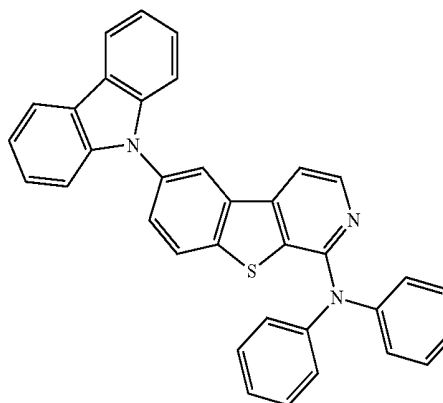
Compound 2



Compound 3

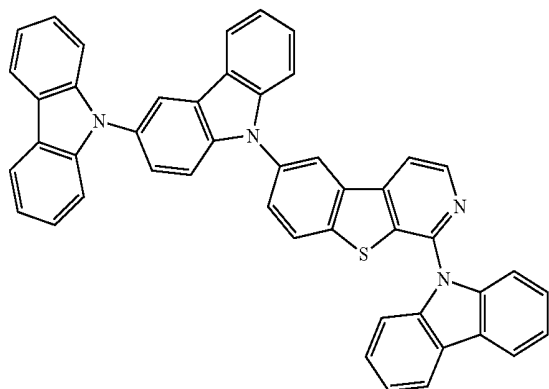


Compound 4



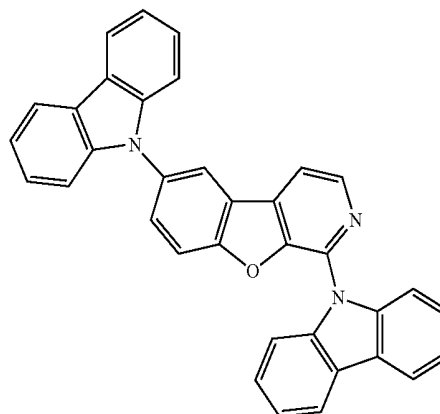
-continued

Compound 5

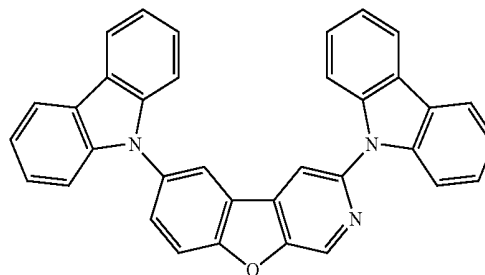


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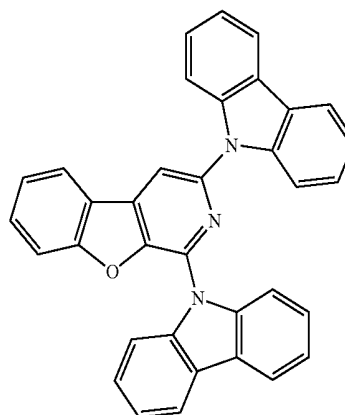
Compound 9



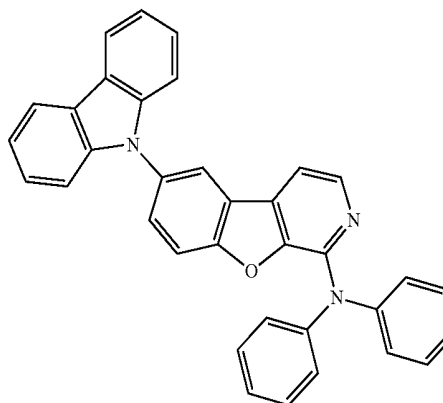
Compound 10



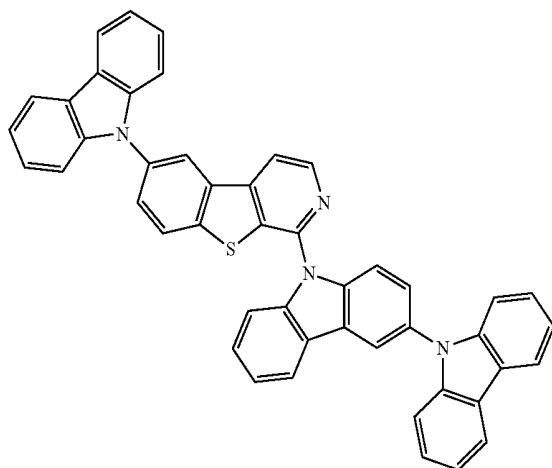
Compound 11



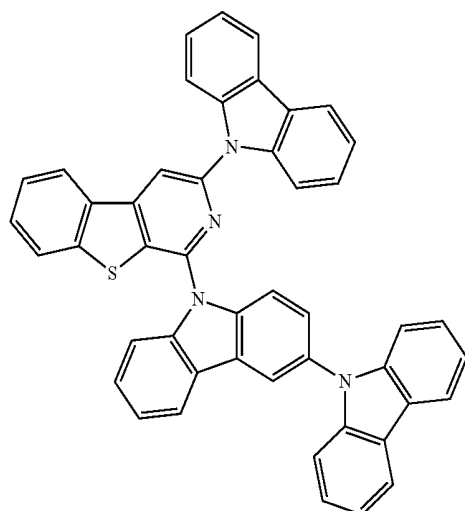
Compound 12



Compound 7

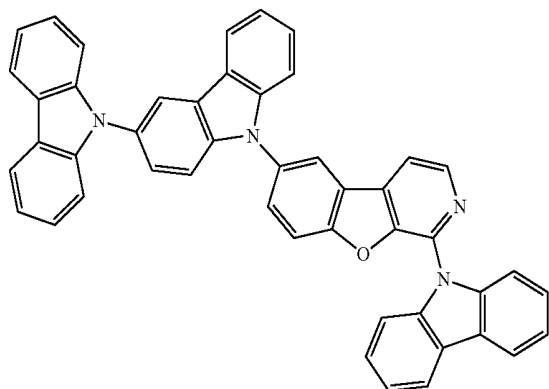


Compound 8



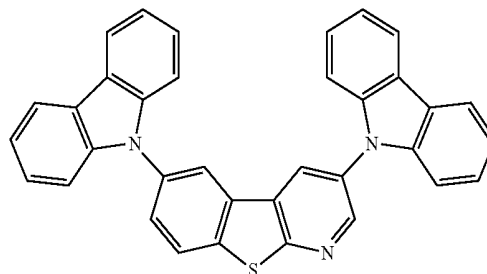
-continued

Compound 13

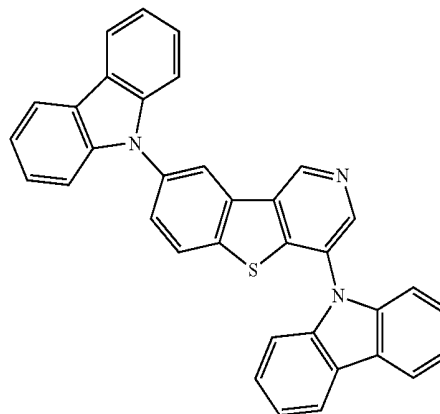


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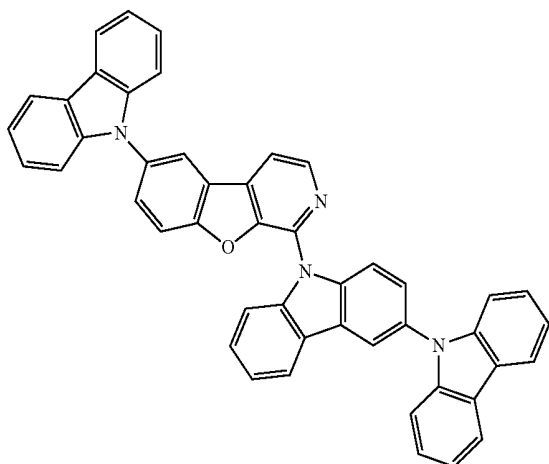
Compound 17



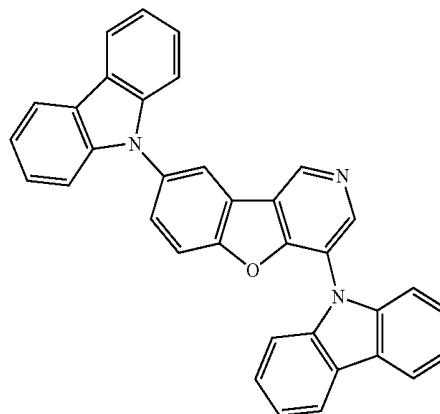
Compound 19



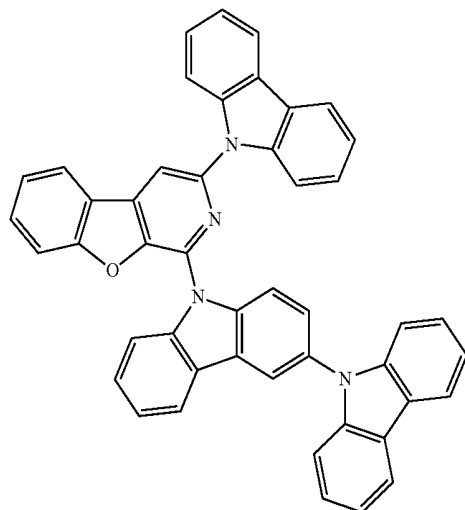
Compound 14



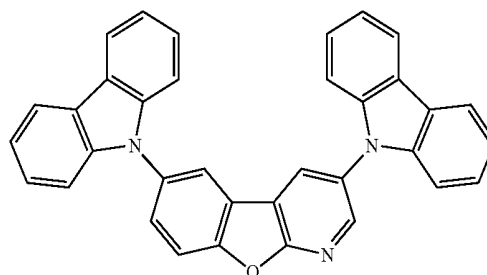
Compound 20



Compound 15

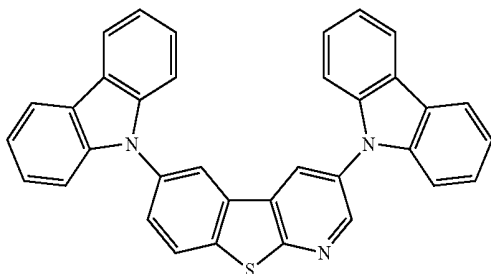


Compound 21



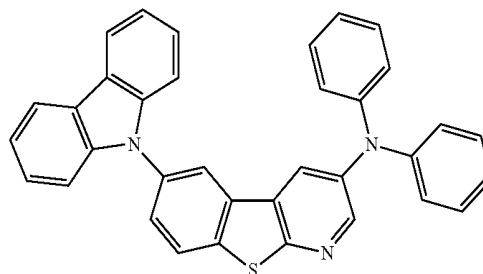
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Compound 23

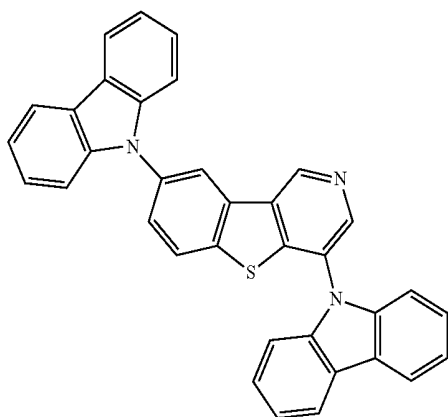


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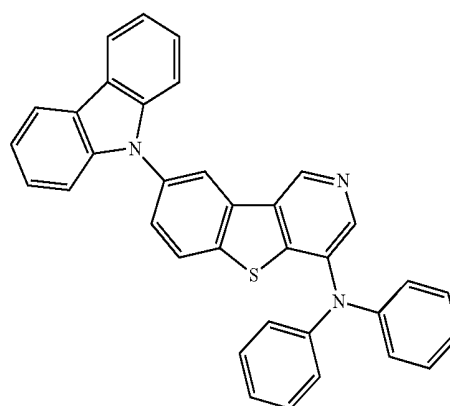
Compound 28



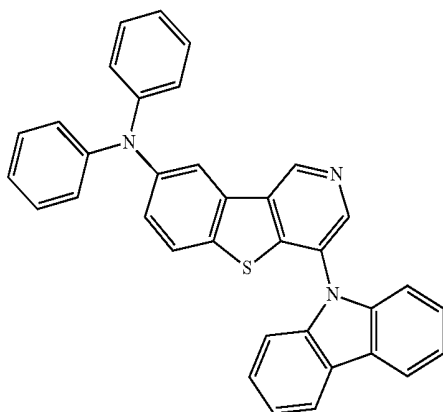
Compound 25



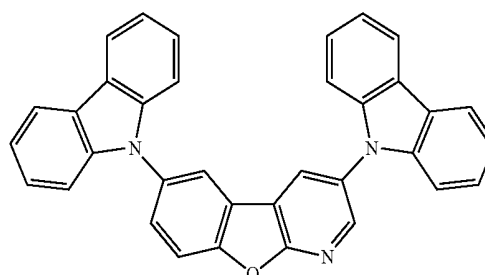
Compound 29



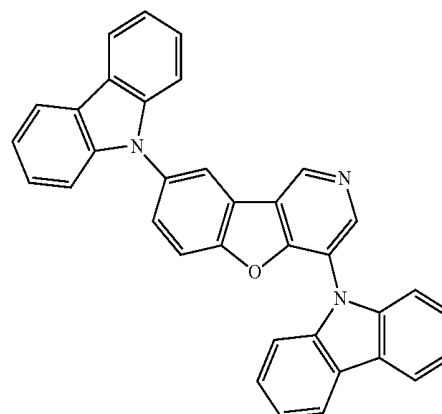
Compound 26



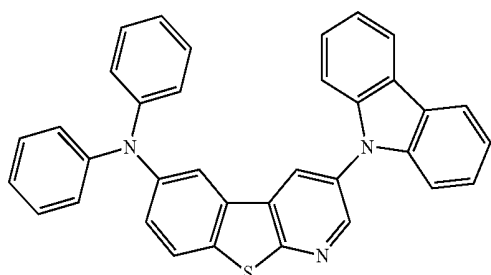
Compound 31



Compound 33

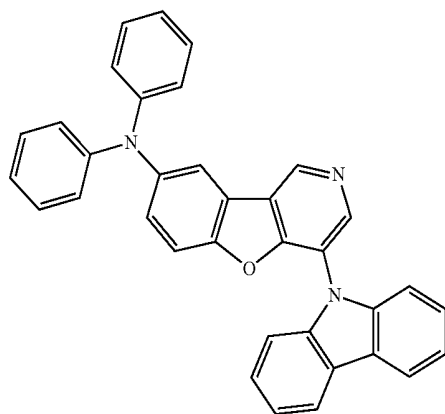


Compound 27

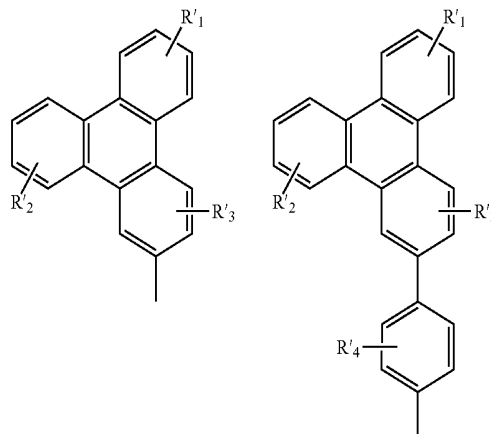


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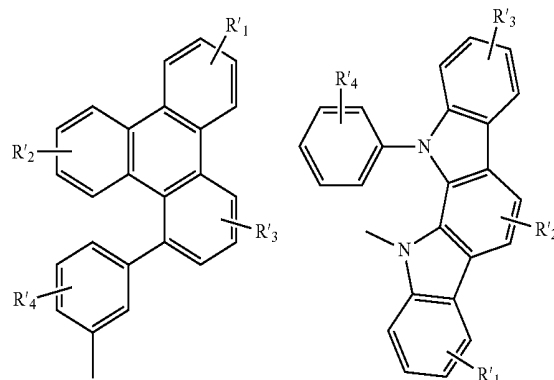
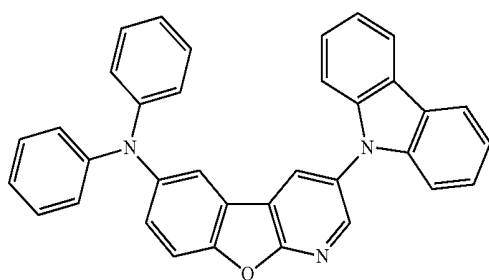
Compound 34



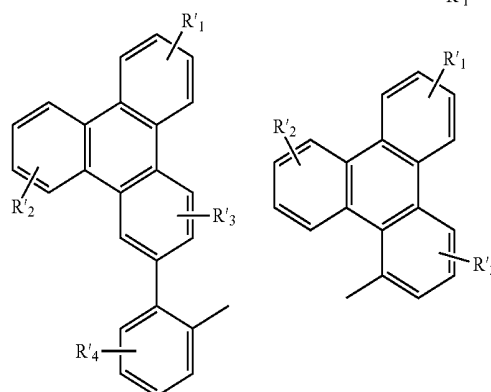
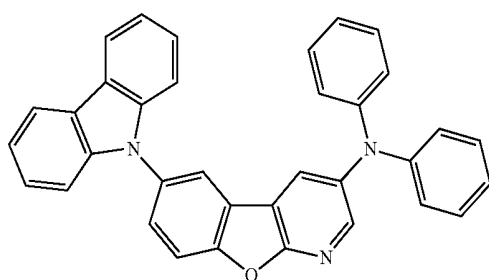
[0066] In one aspect,  $R_1$  and  $R_2$  are each independently selected from the group consisting of hydrogen and



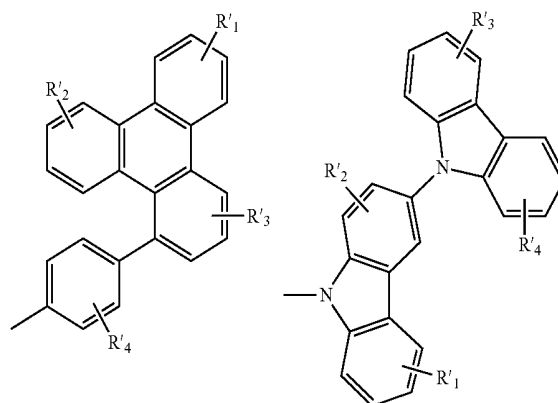
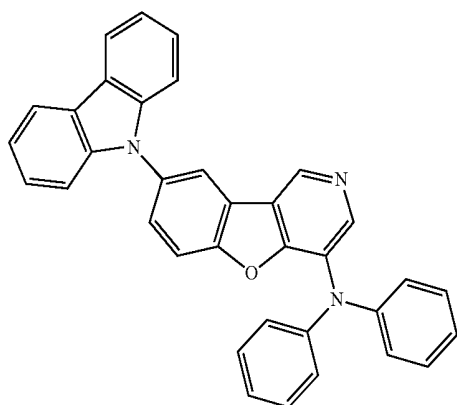
Compound 35

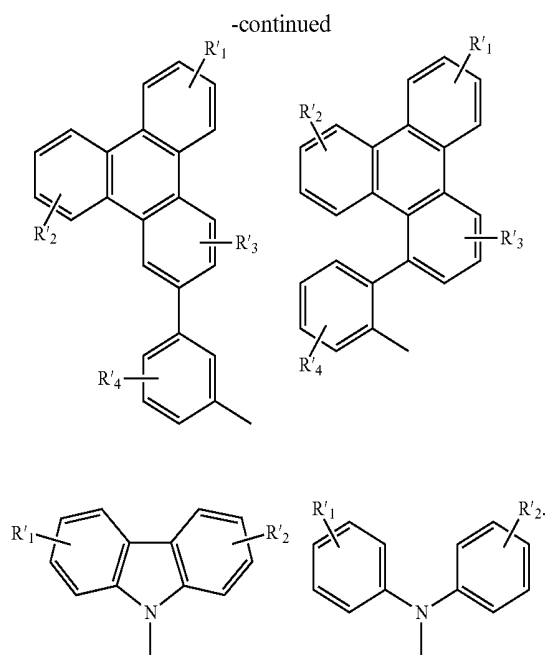


Compound 36



Compound 37

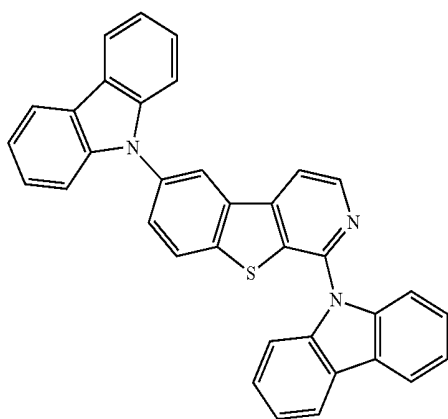




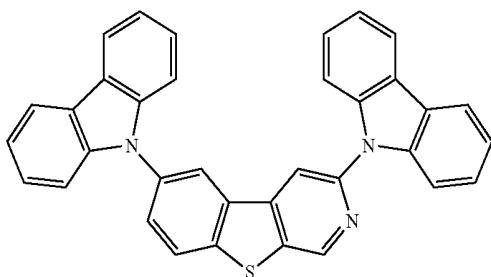
R'<sub>1</sub>, R'<sub>2</sub>, R'<sub>3</sub>, and R'<sub>4</sub> are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl. Preferably, R'<sub>1</sub>, R'<sub>2</sub>, R'<sub>3</sub>, and R'<sub>4</sub> are each independently hydrogen or methyl.

[0067] Specific examples of such compounds include compounds selected from the group consisting of:

Compound 1

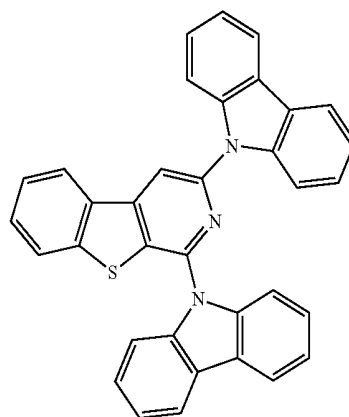


Compound 2

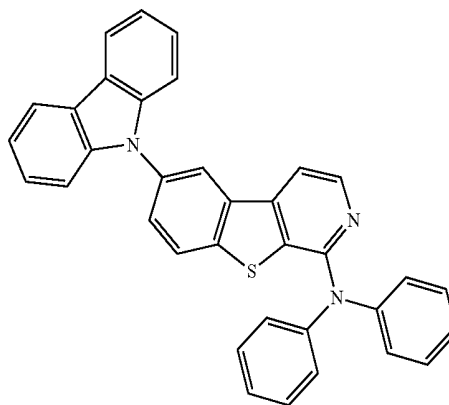


-continued

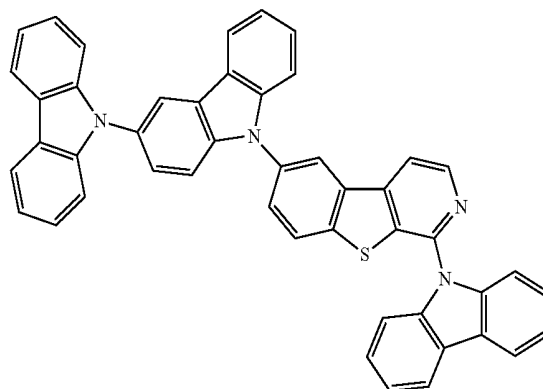
Compound 3



Compound 4

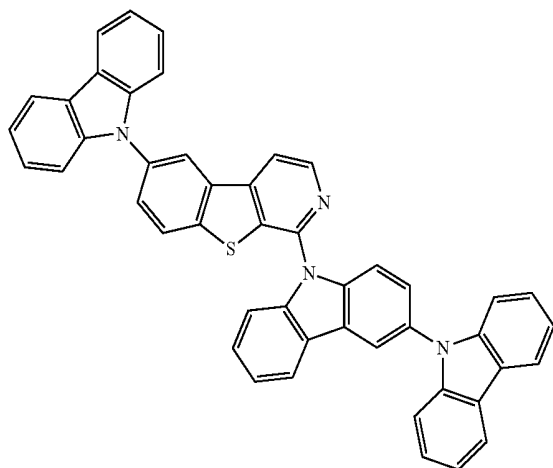


Compound 5

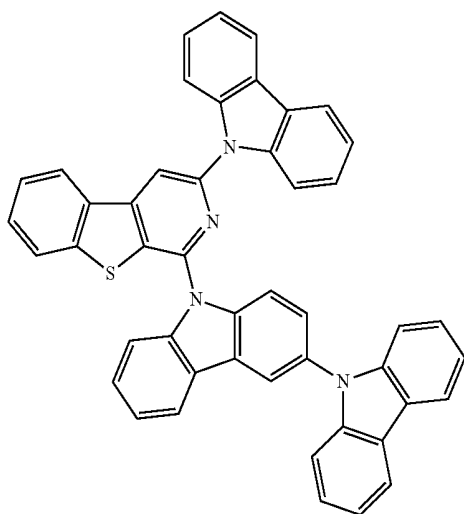


-continued

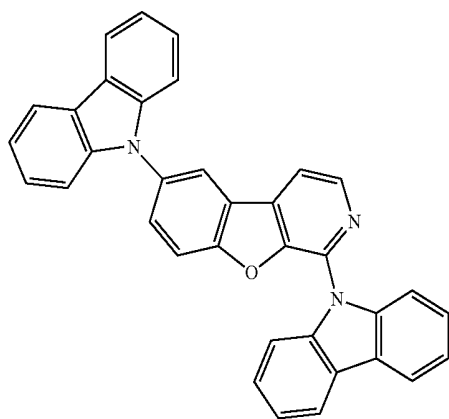
Compound 7



Compound 8

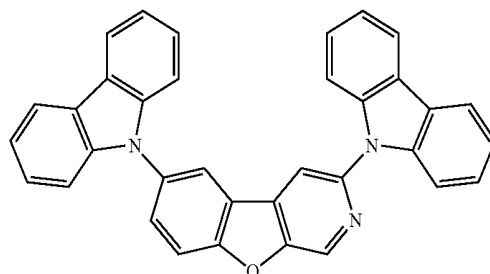


Compound 9

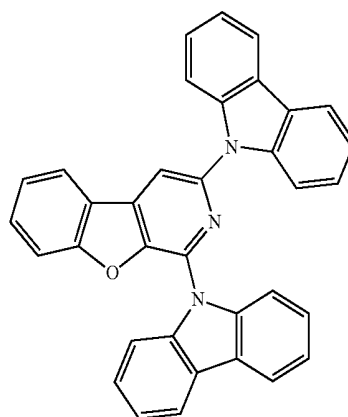


-continued

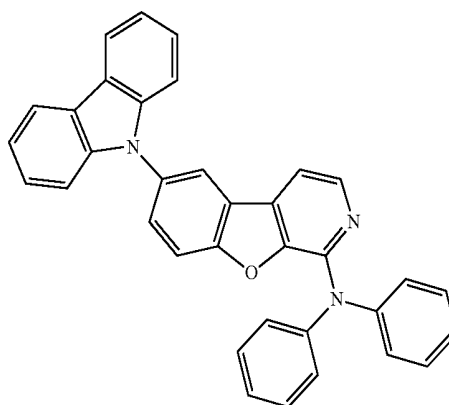
Compound 10



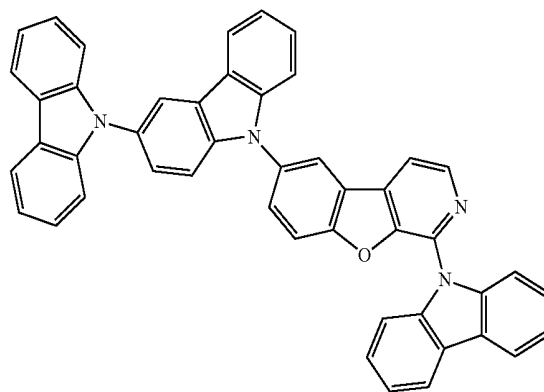
Compound 11



Compound 12

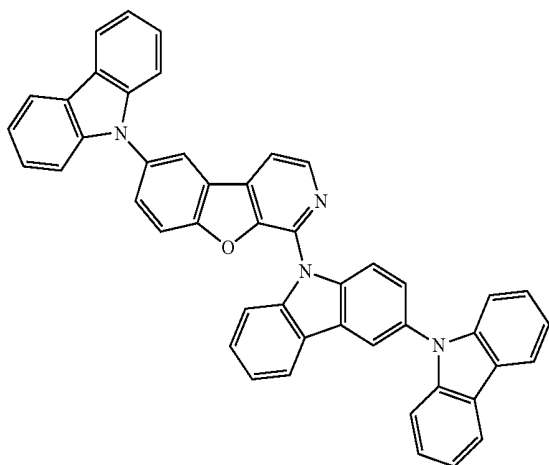


Compound 13



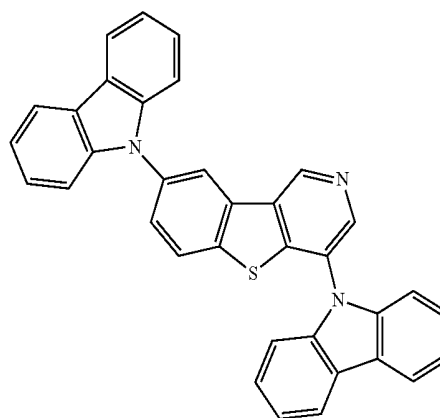
-continued

Compound 14

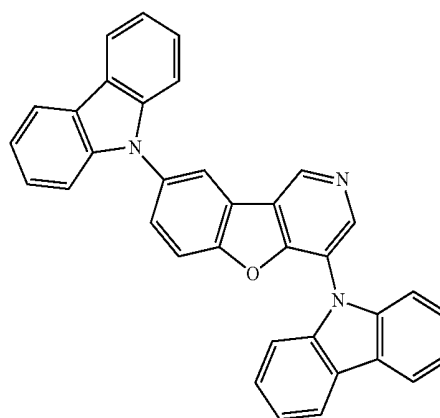


-continued

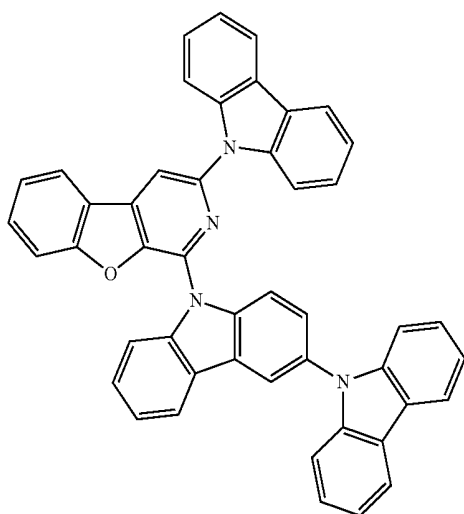
Compound 19



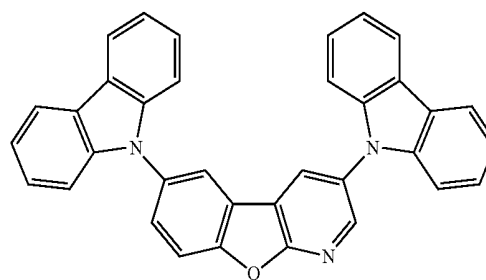
Compound 20



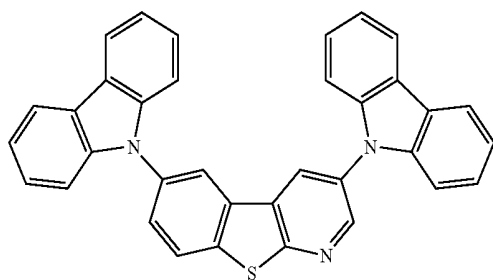
Compound 15



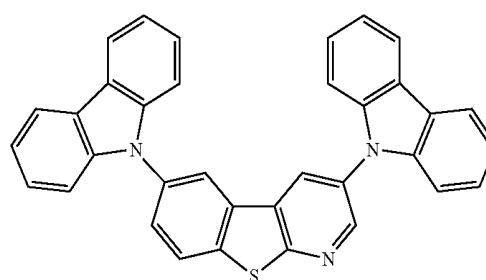
Compound 21



Compound 17



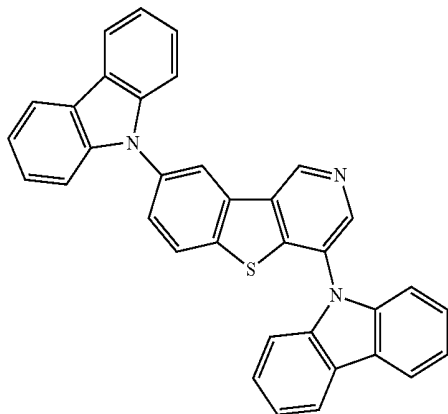
Compound 23





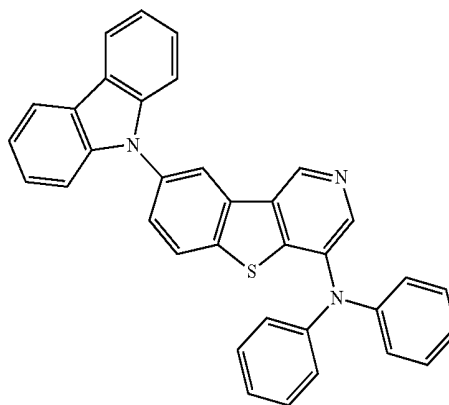
-continued

Compound 25

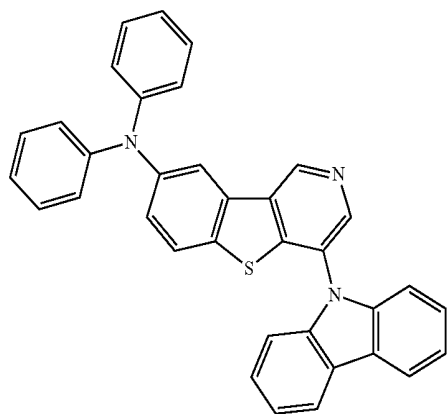


-continued

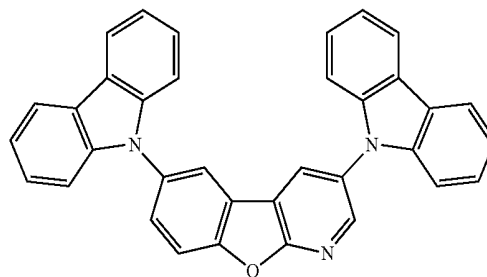
Compound 29



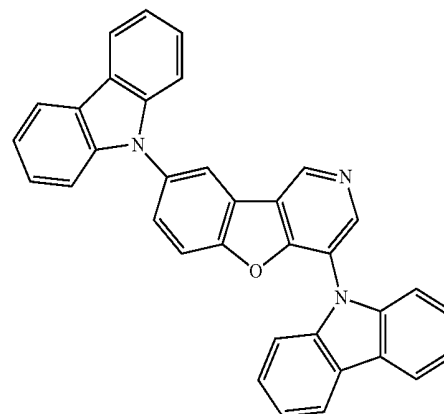
Compound 26



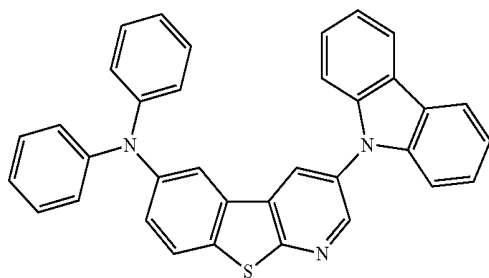
Compound 31



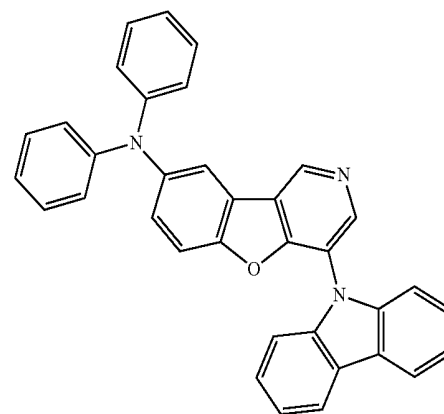
Compound 33



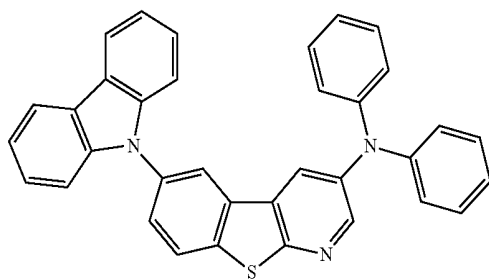
Compound 27



Compound 34

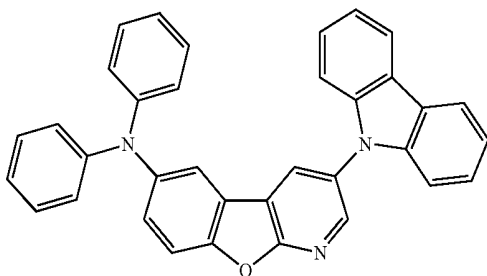


Compound 28

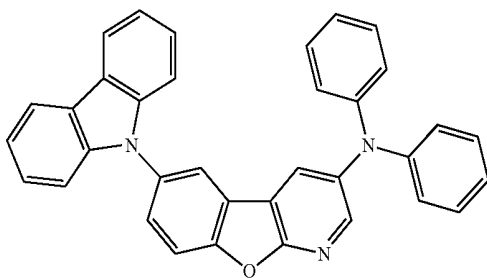


-continued

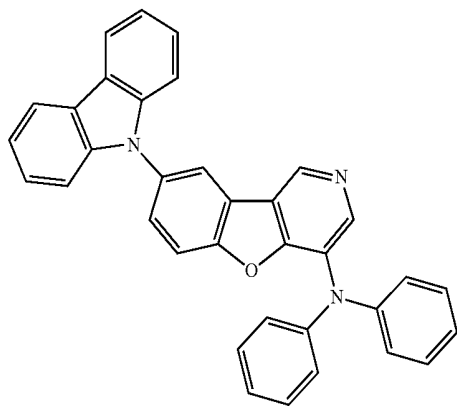
Compound 35



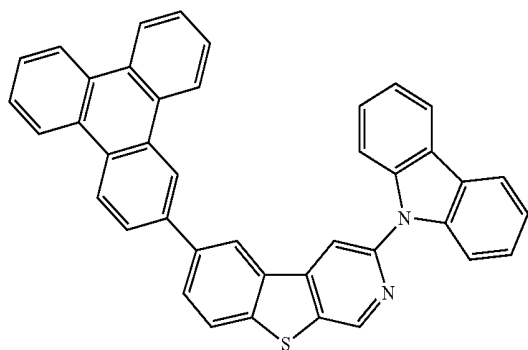
Compound 36



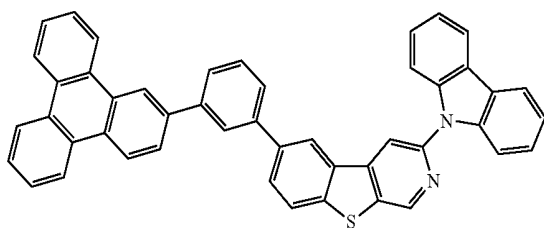
Compound 37



Compound 39

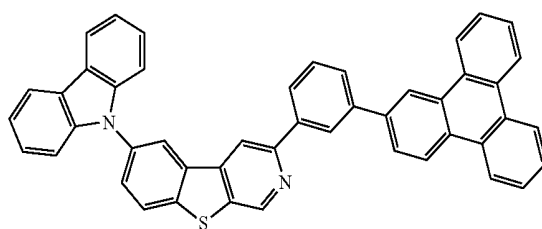


Compound 40

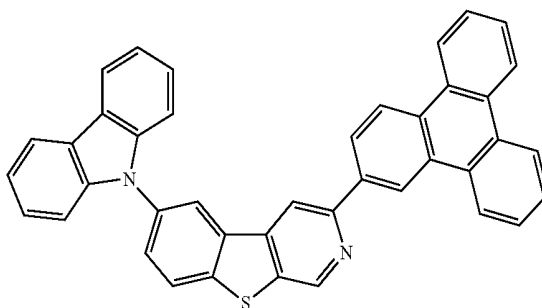


-continued

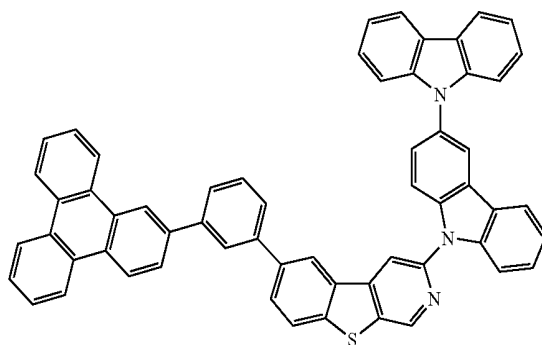
Compound 41



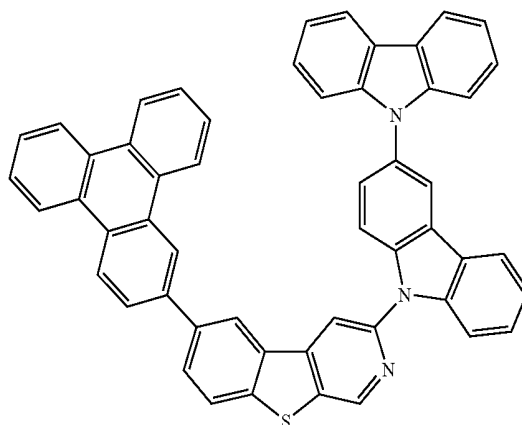
Compound 42



Compound 43

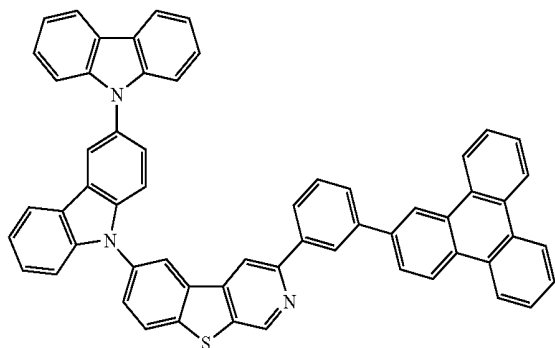


Compound 44



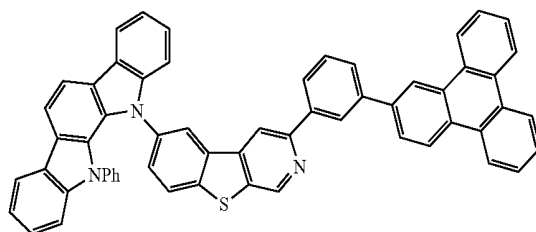
-continued

Compound 45

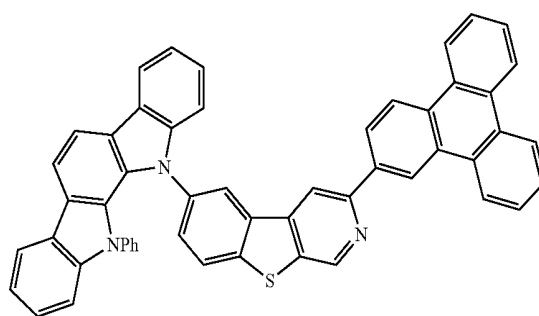


-continued

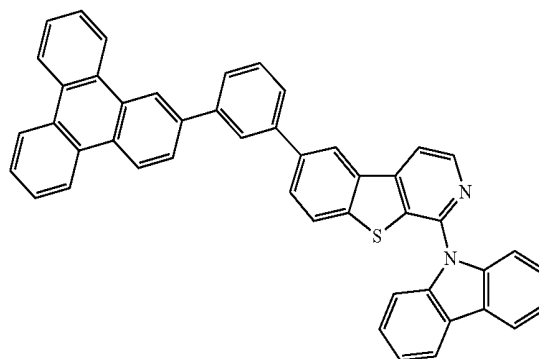
Compound 50



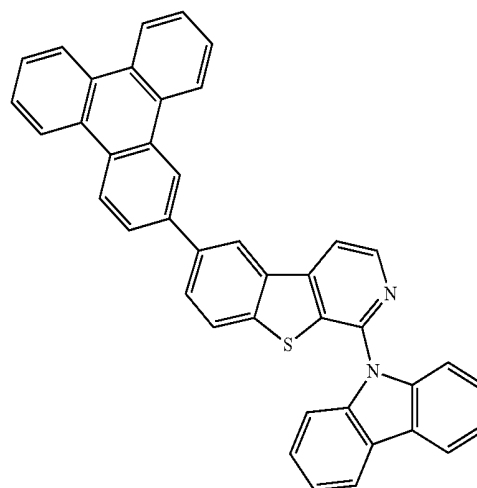
Compound 51



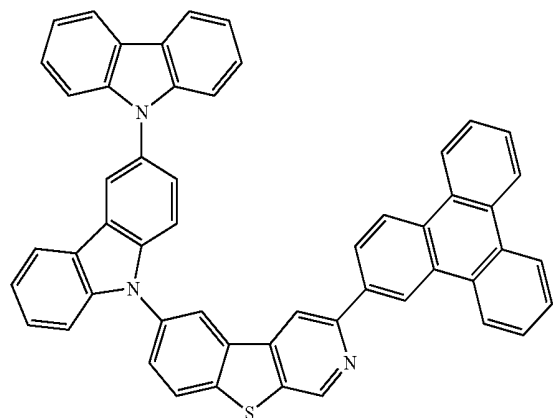
Compound 52



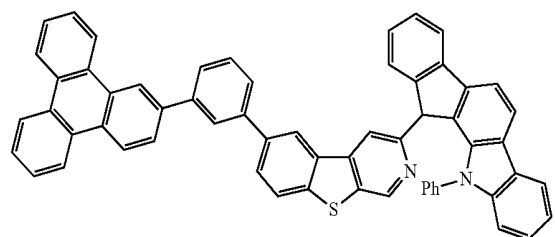
Compound 53



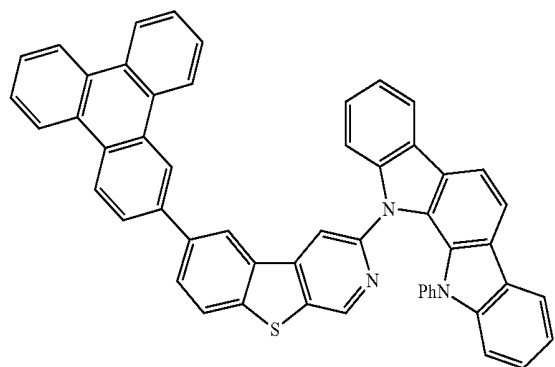
Compound 46



Compound 47

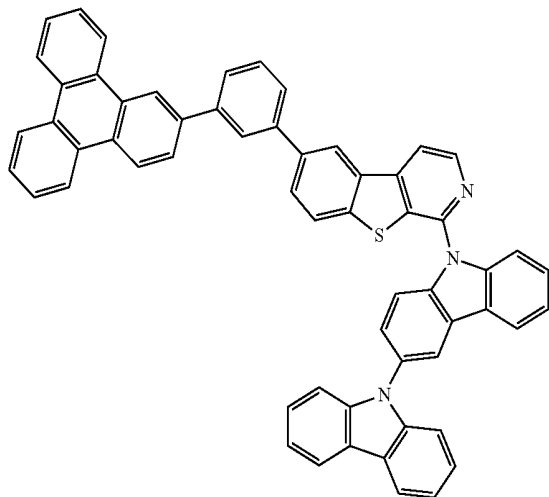


Compound 48



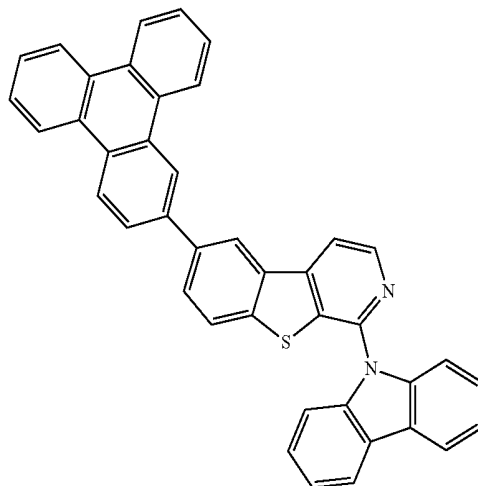
-continued

Compound 54

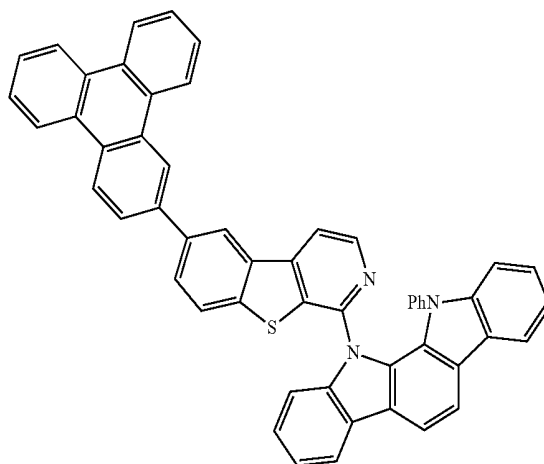


-continued

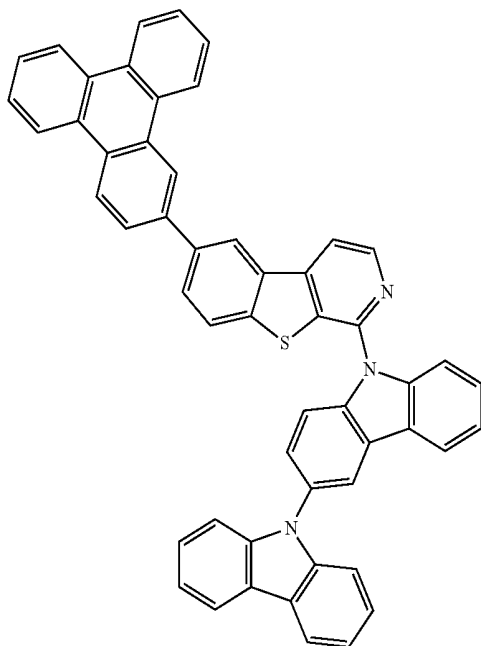
Compound 56



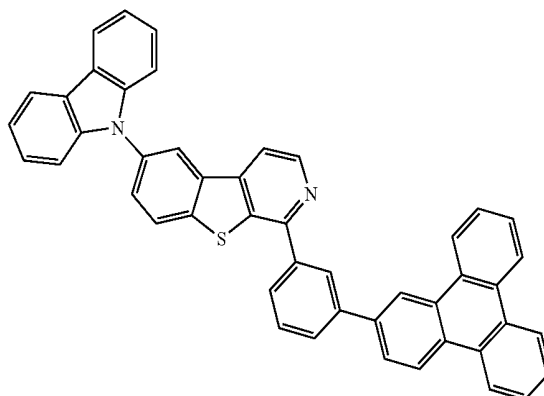
Compound 57



Compound 55

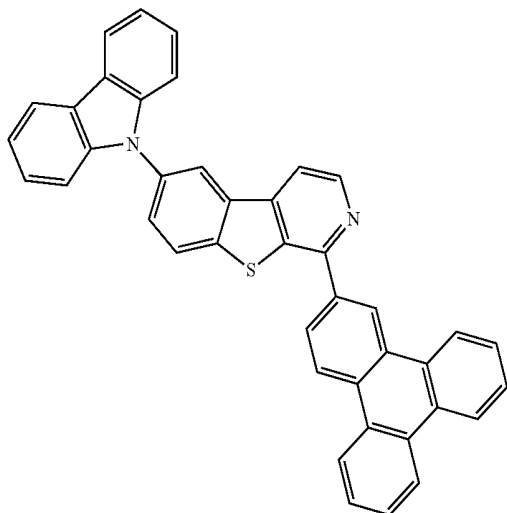


Compound 58



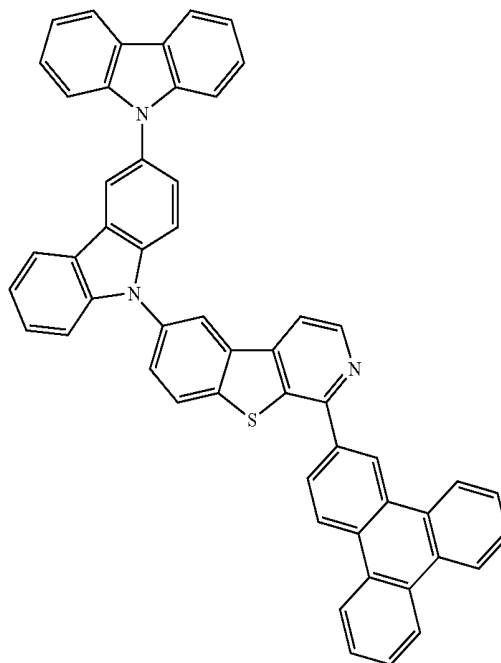
-continued

Compound 59



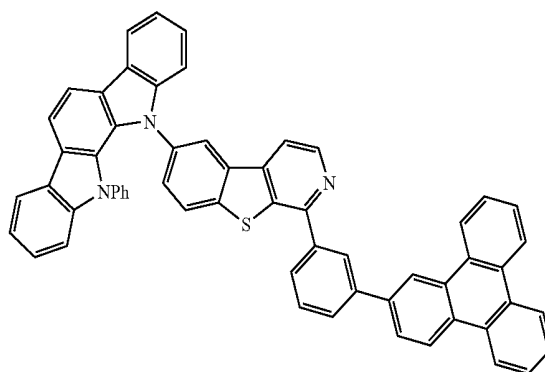
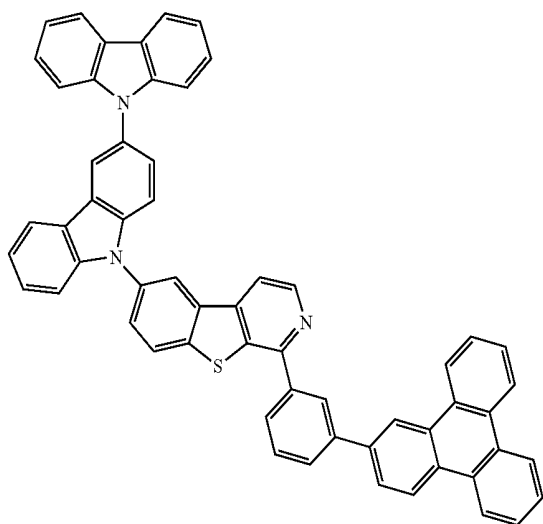
-continued

Compound 61

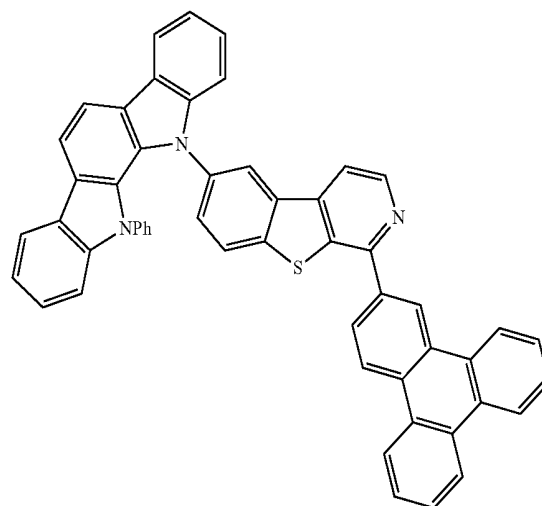


Compound 62

Compound 60

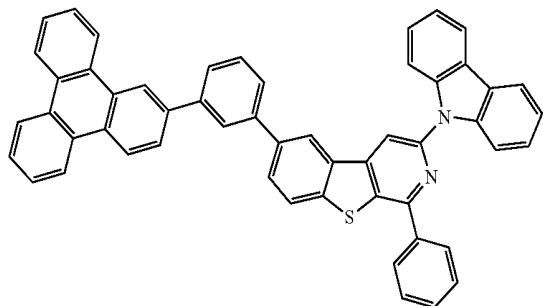


Compound 63

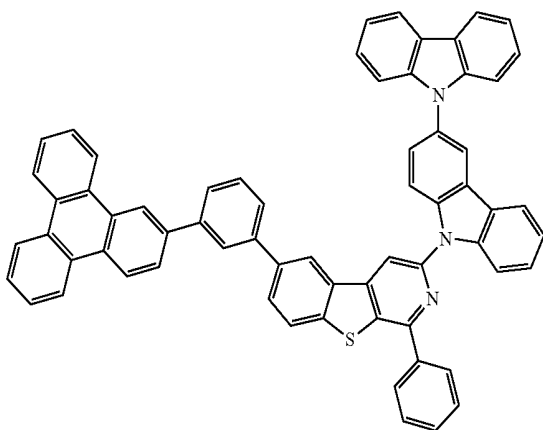


-continued

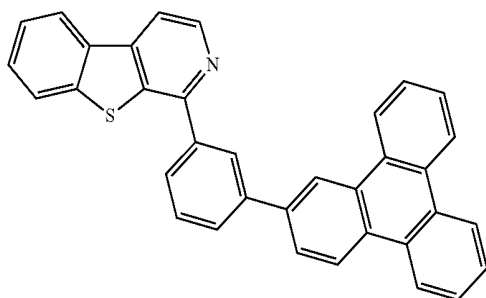
Compound 64



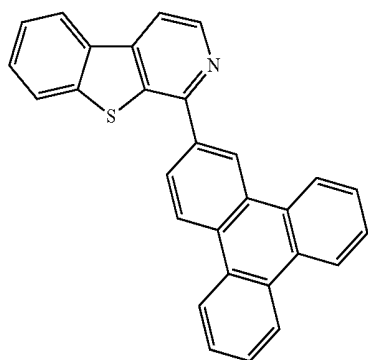
Compound 65



Compound 66

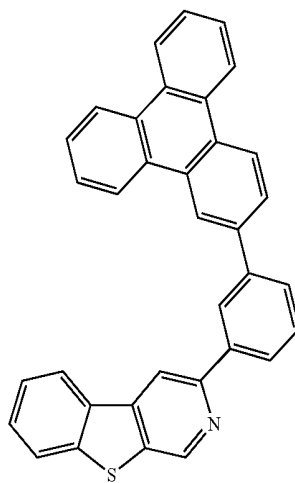


Compound 70

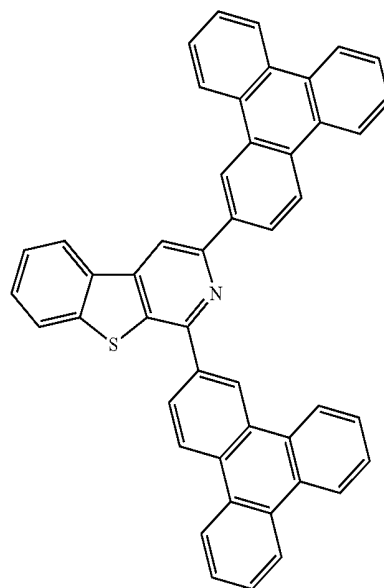


-continued

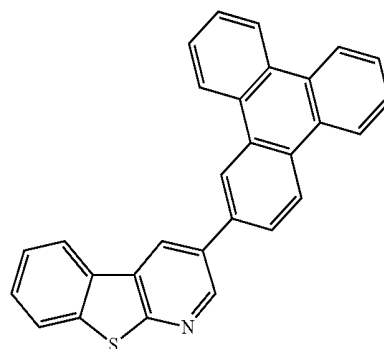
Compound 71



Compound 72

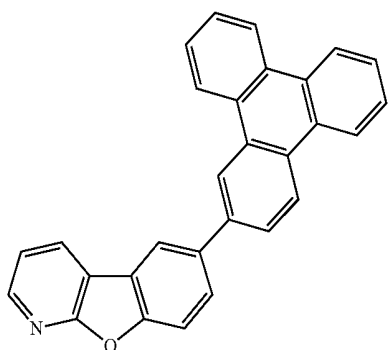


Compound 75

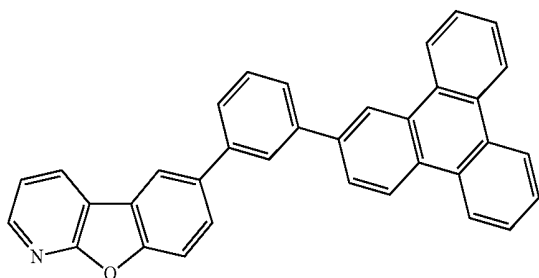


-continued

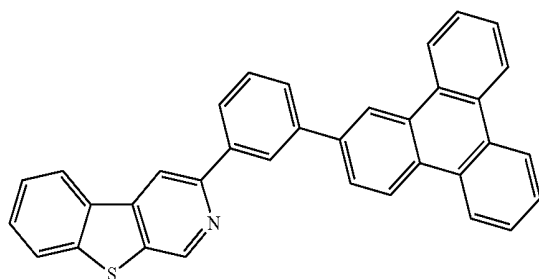
Compound 77



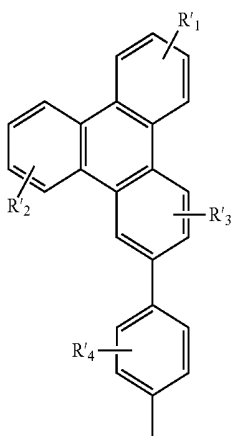
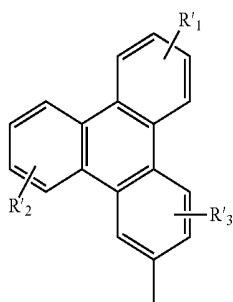
Compound 78



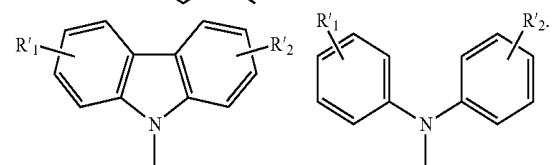
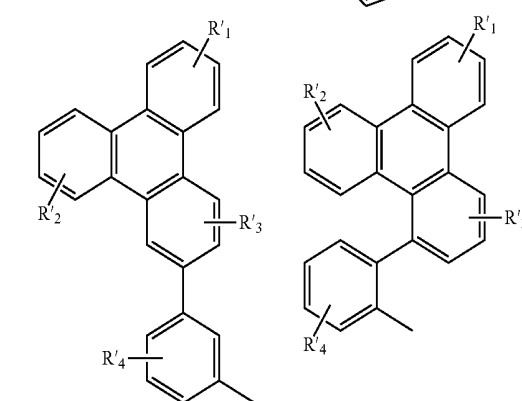
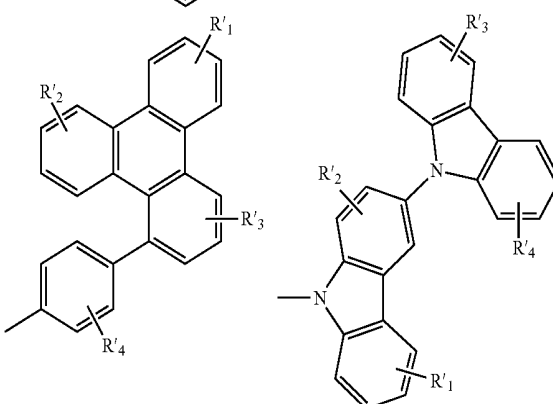
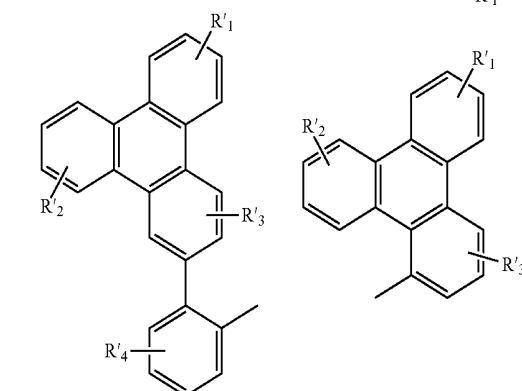
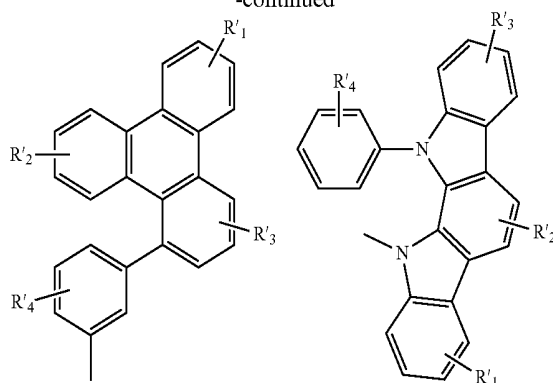
Compound 79



[0068] In another aspect,  $R_1$  is selected from the group consisting of:



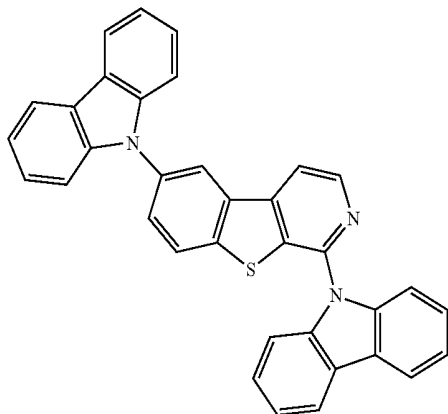
-continued



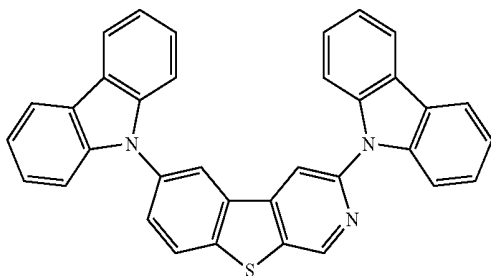
$R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl.  $R_2$  is hydrogen. Preferably,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are each independently hydrogen or methyl.

[0069] Specific examples of such compounds include compounds selected from the group consisting of:

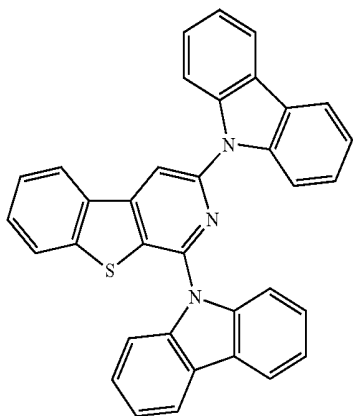
Compound 1



Compound 2

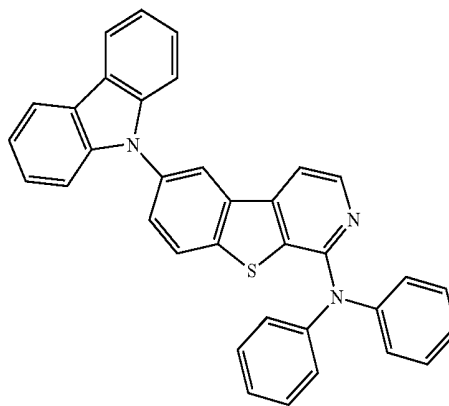


Compound 3

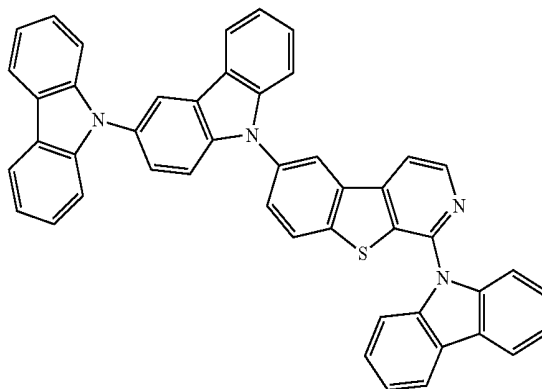


-continued

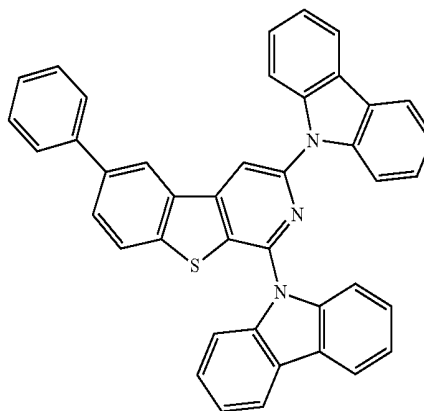
Compound 4



Compound 5



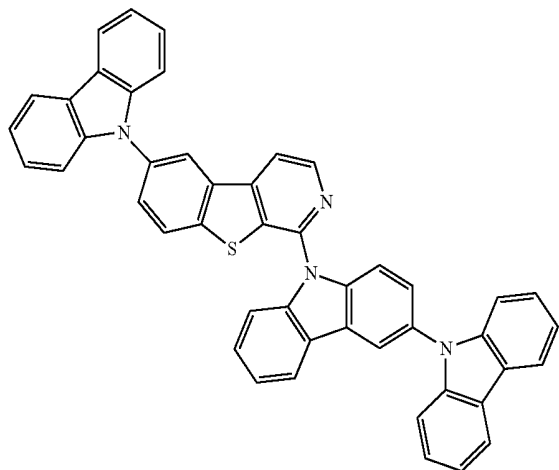
Compound 6



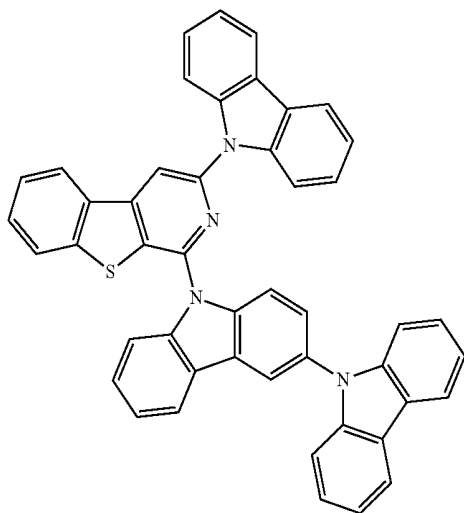


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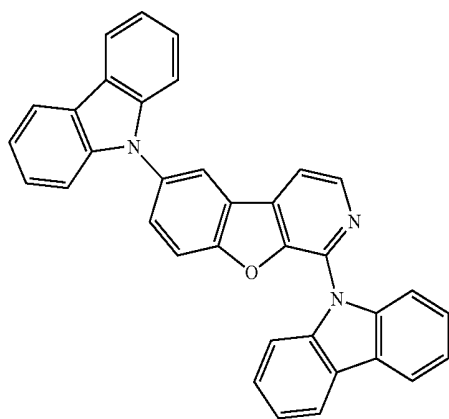
Compound 7



Compound 8

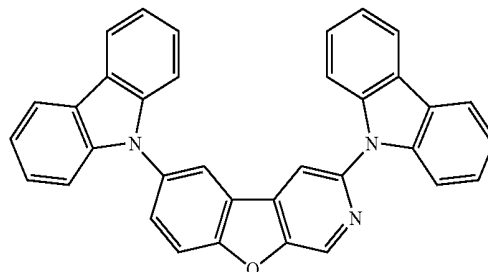


Compound 9

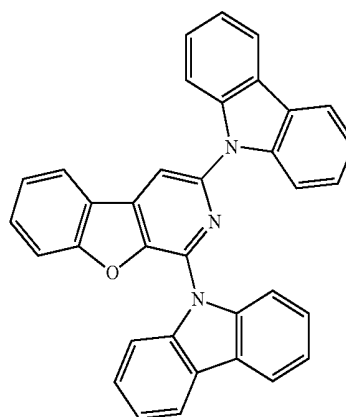


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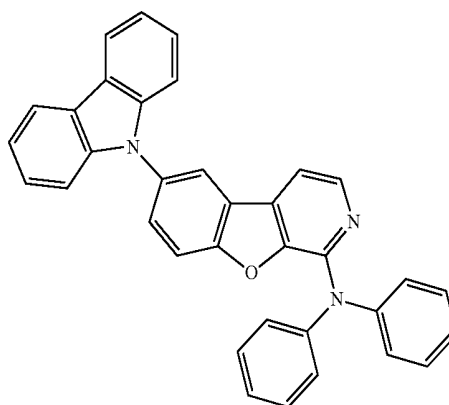
Compound 10



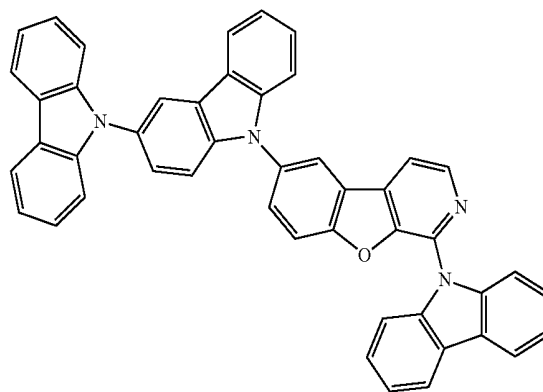
Compound 11



Compound 12

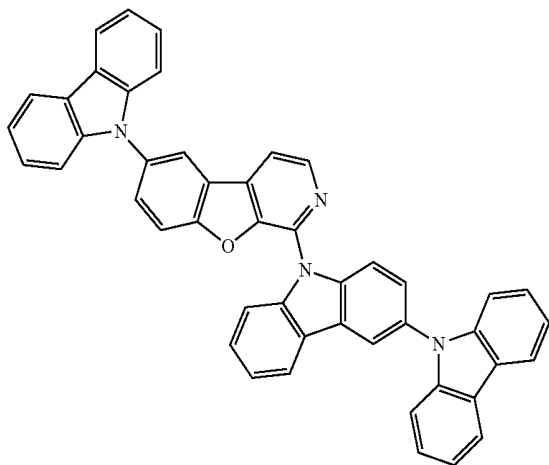


Compound 13



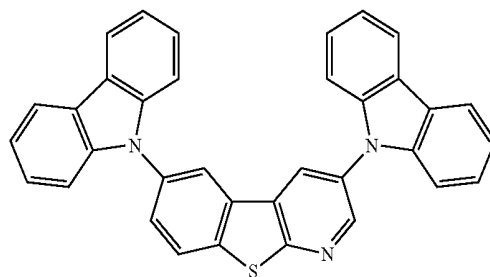
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Compound 14

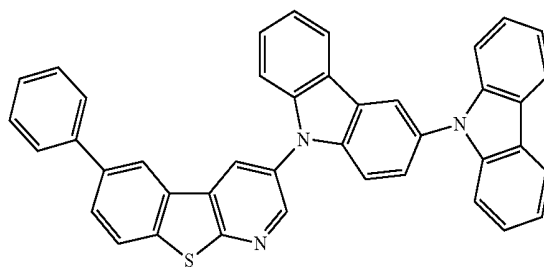


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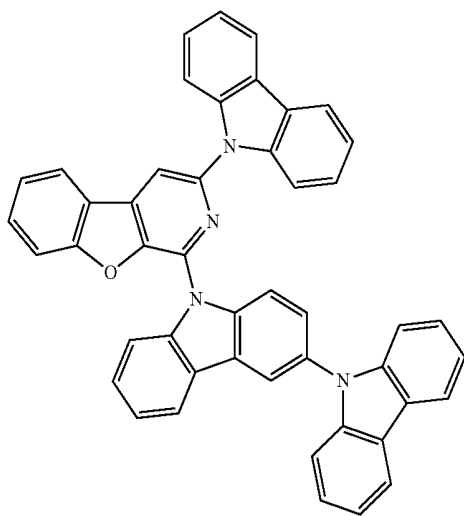
Compound 17



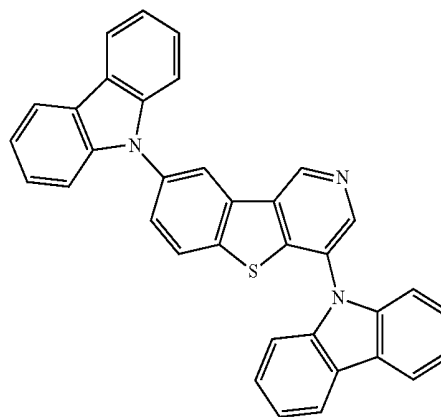
Compound 18



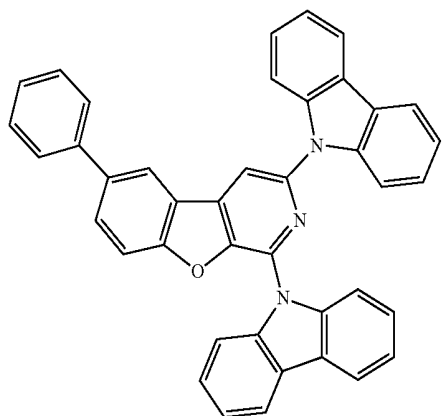
Compound 15



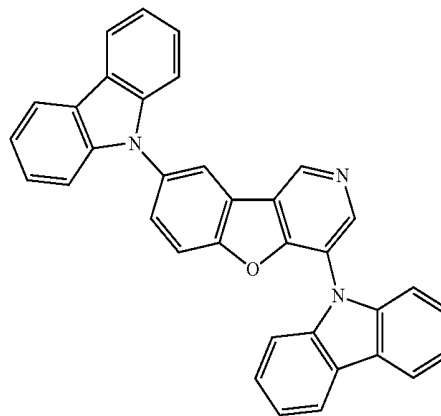
Compound 19



Compound 16

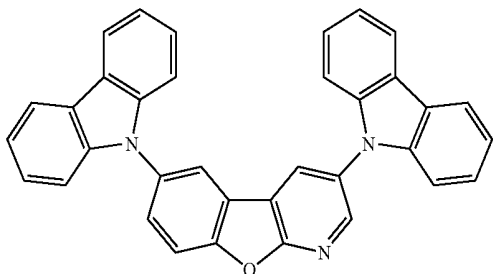


Compound 20

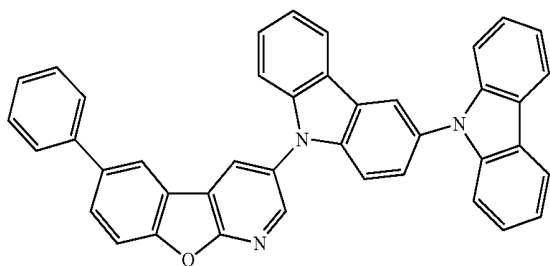


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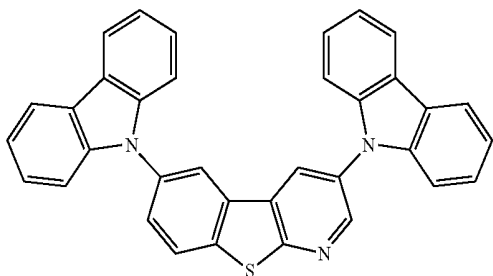
Compound 21



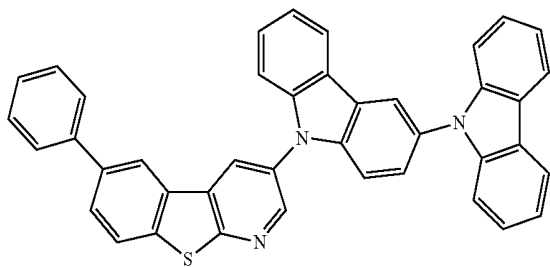
Compound 22



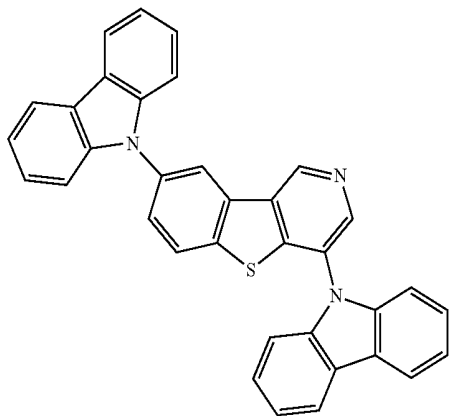
Compound 23



Compound 24

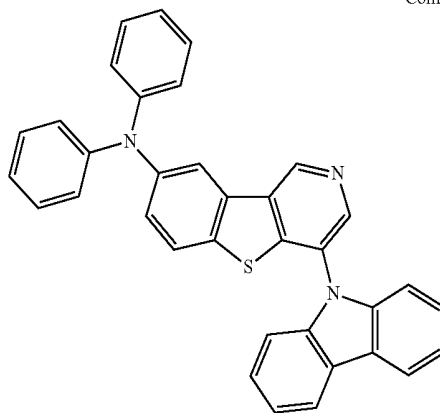


Compound 25

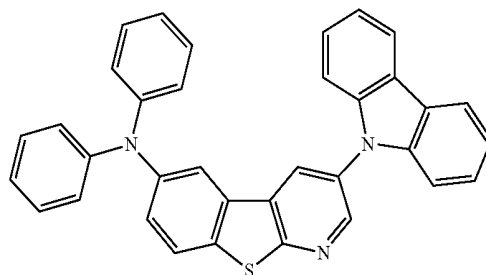


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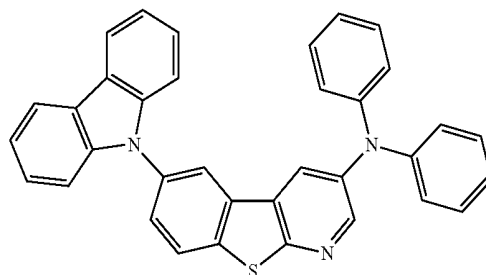
Compound 26



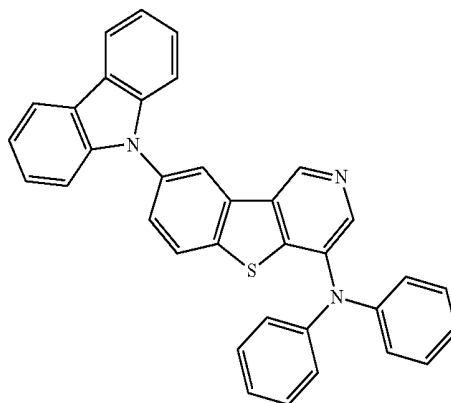
Compound 27



Compound 28

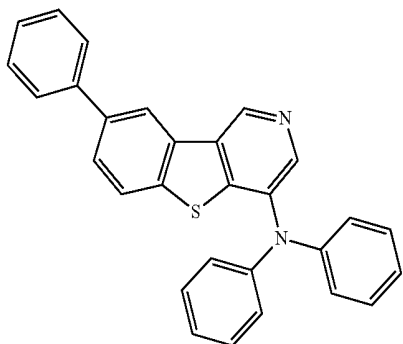


Compound 29



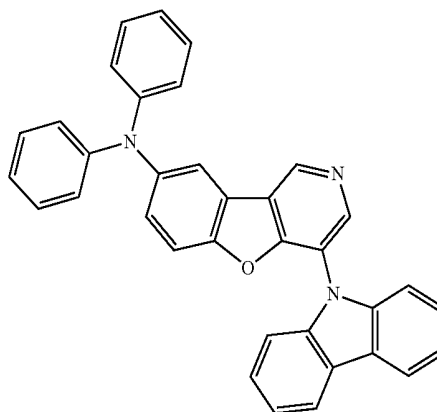
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Compound 30

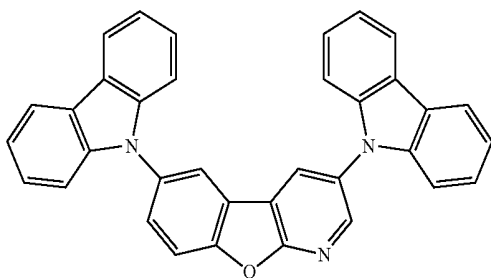


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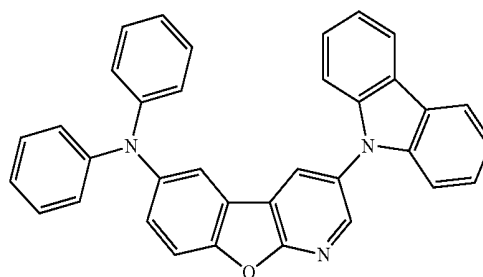
Compound 34



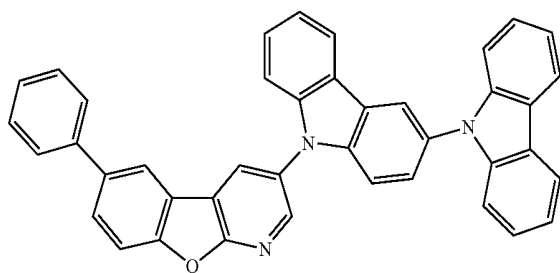
Compound 31



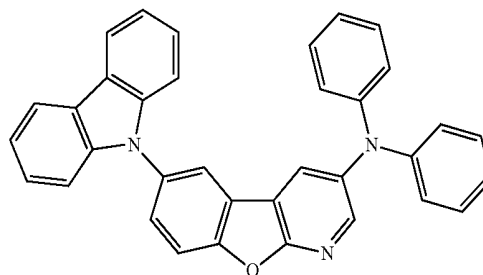
Compound 35



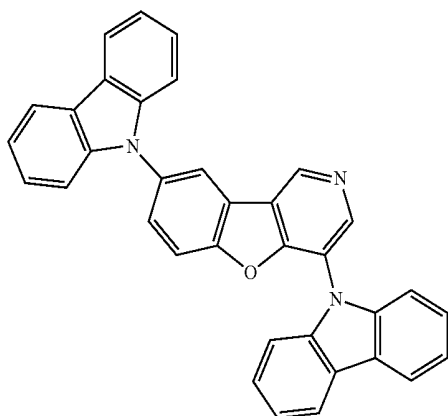
Compound 32



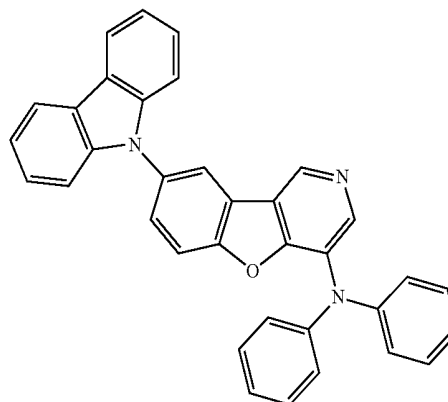
Compound 36



Compound 33

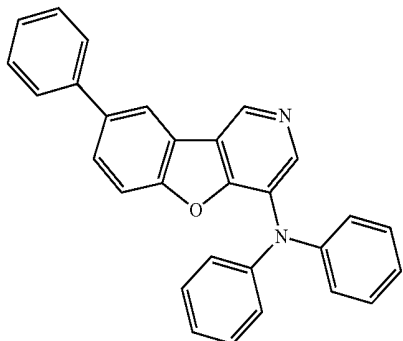


Compound 37



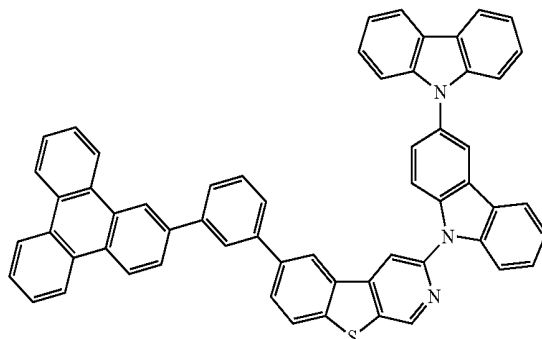
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Compound 38

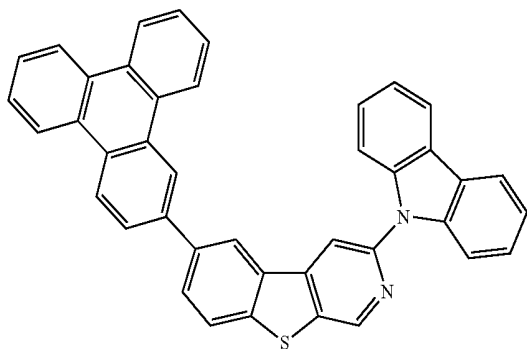


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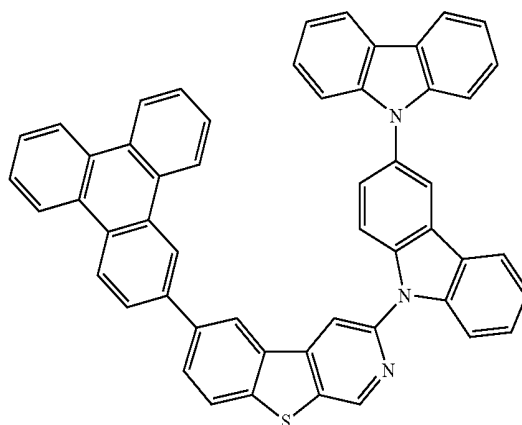
Compound 43



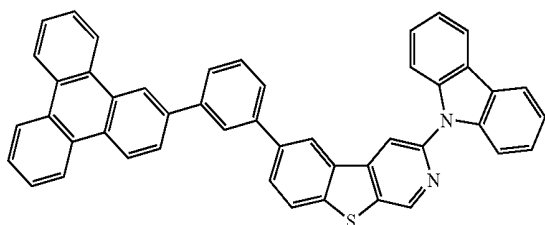
Compound 39



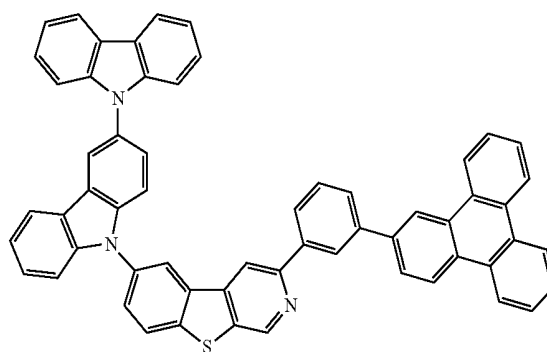
Compound 44



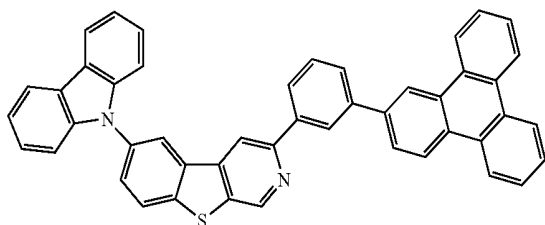
Compound 40



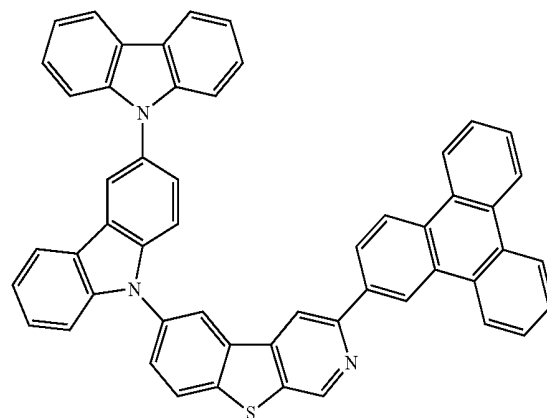
Compound 45



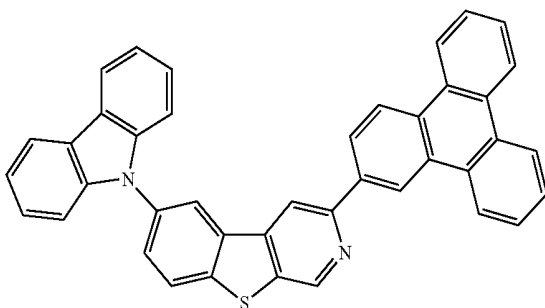
Compound 41



Compound 46

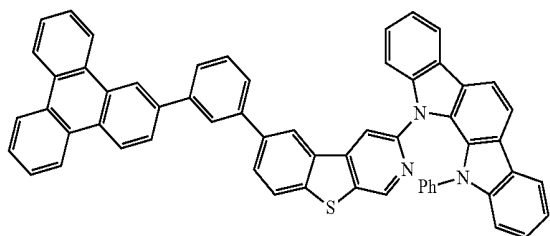


Compound 42

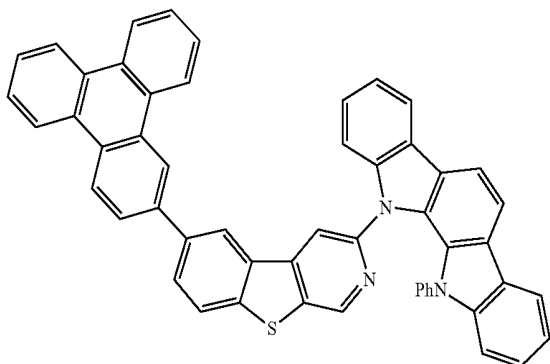


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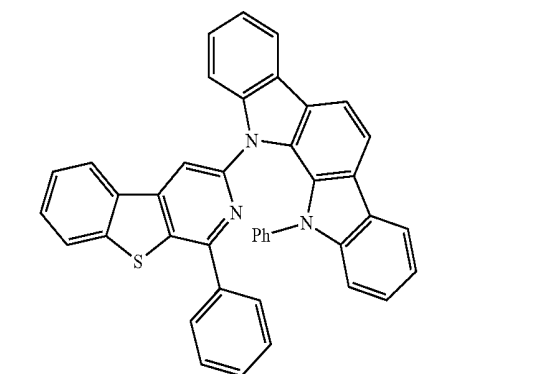
Compound 47



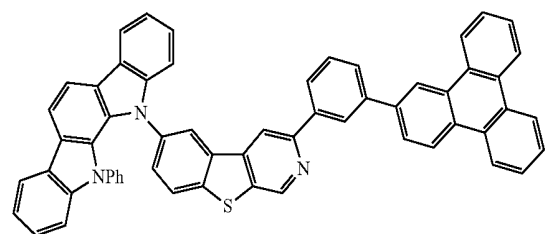
Compound 48



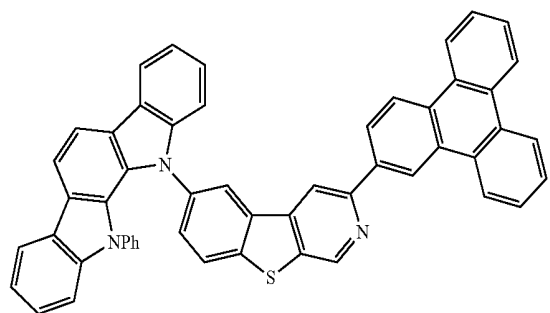
Compound 49



Compound 50

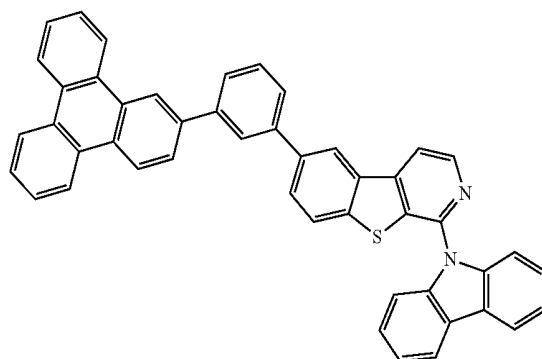


Compound 51

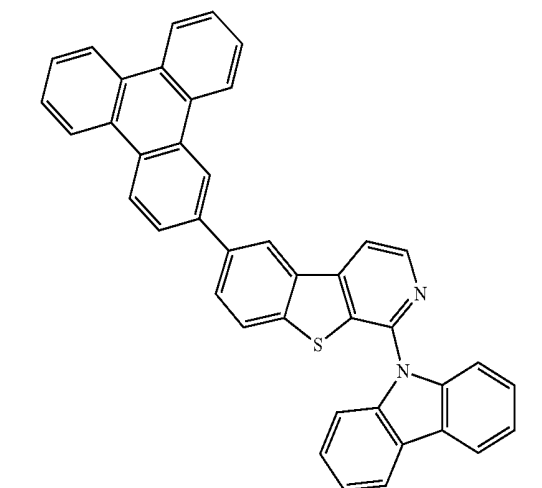


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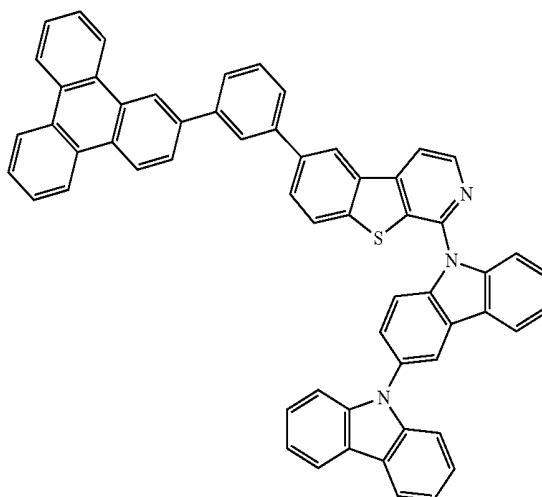
Compound 52



Compound 53

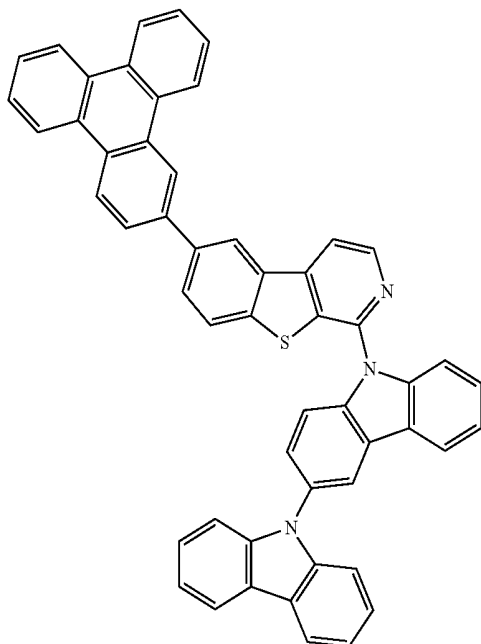


Compound 54

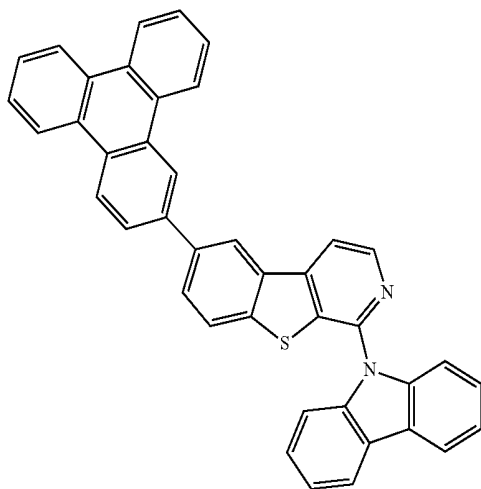


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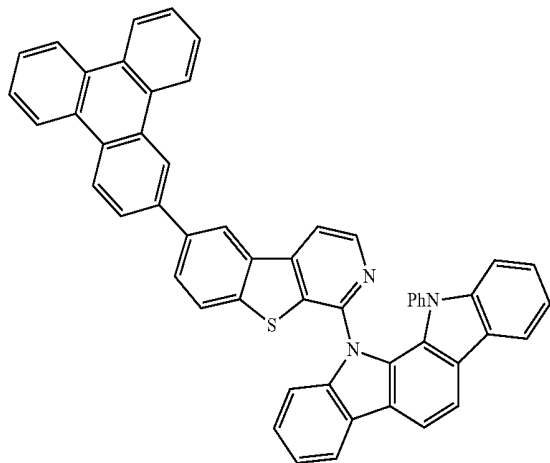
Compound 55



Compound 56

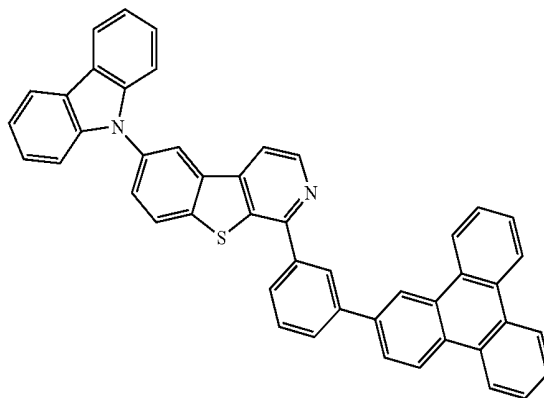


Compound 57

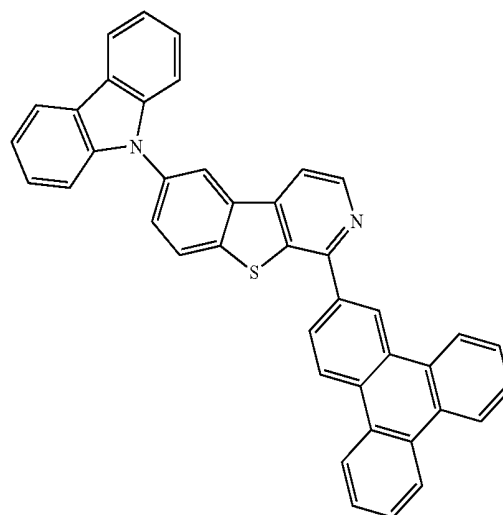


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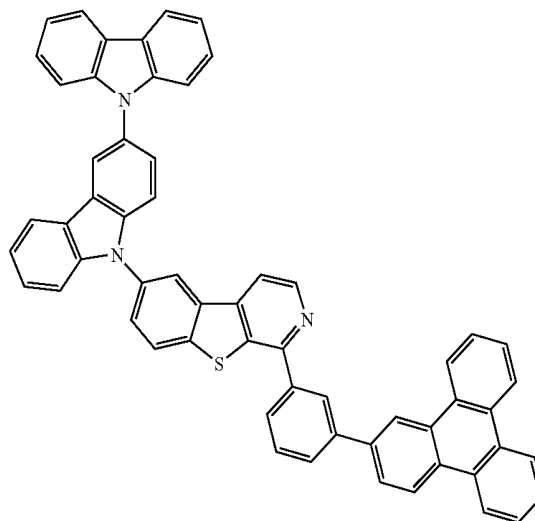
Compound 58



Compound 59

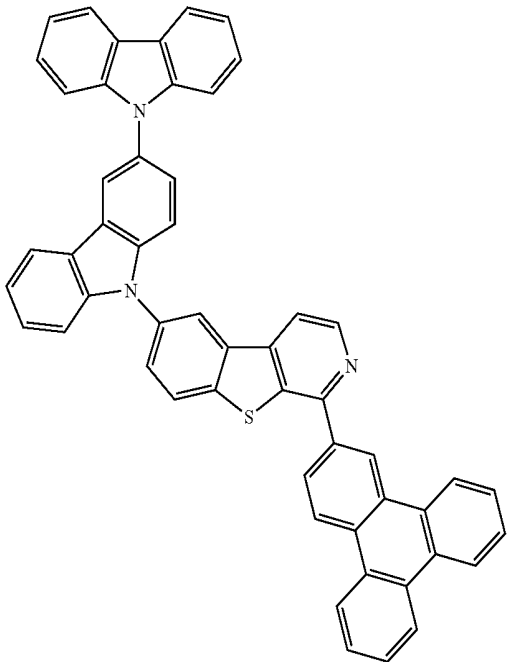


Compound 60

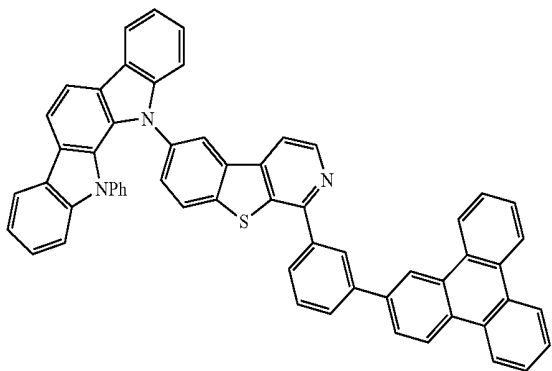


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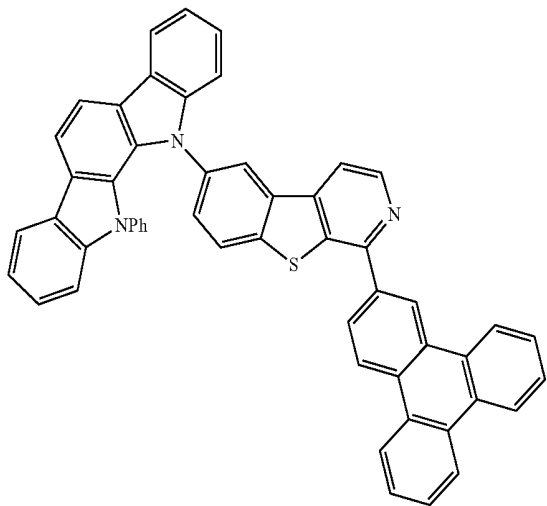
Compound 61



Compound 62

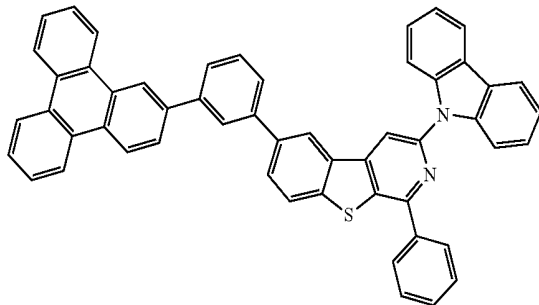


Compound 63

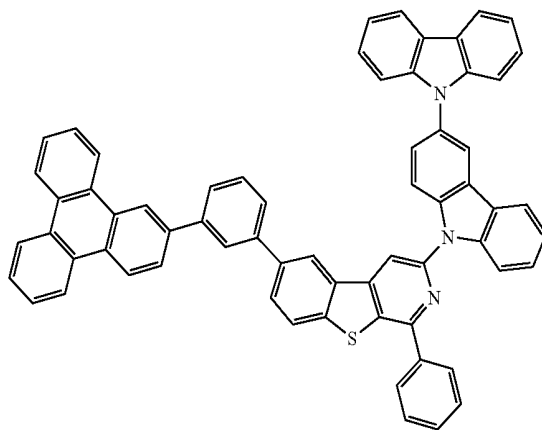


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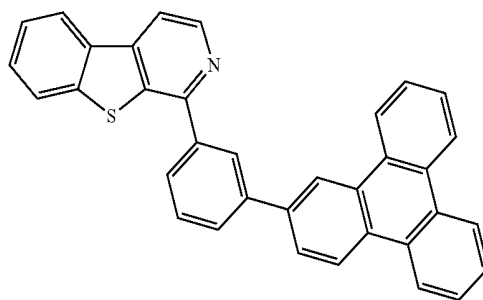
Compound 64



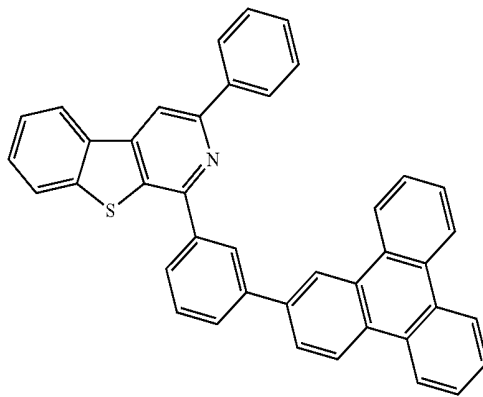
Compound 65



Compound 66



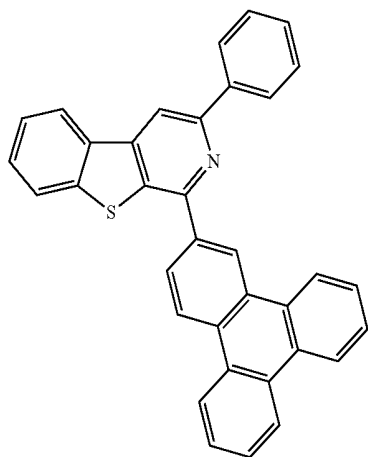
Compound 67





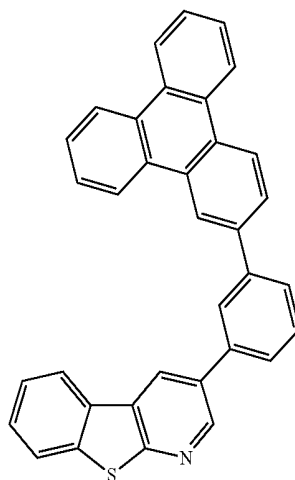
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Compound 68

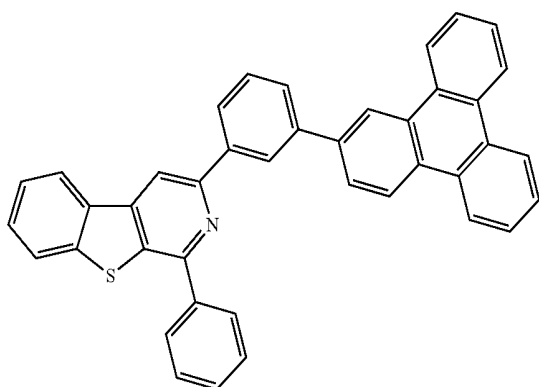


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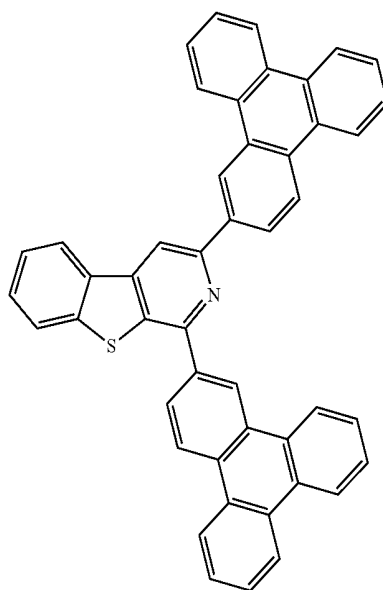
Compound 71



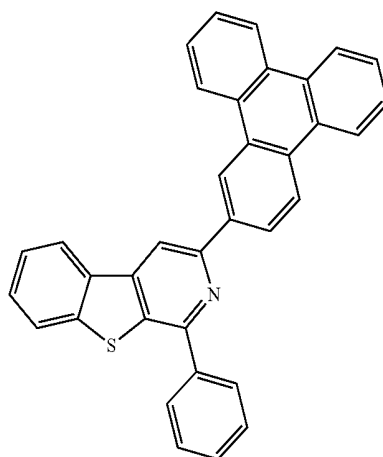
Compound 69



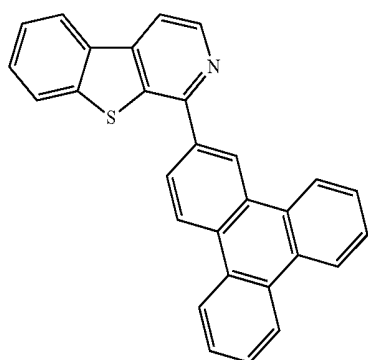
Compound 72



Compound 73

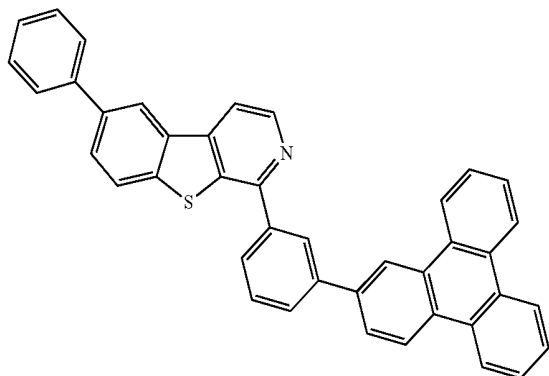


Compound 70

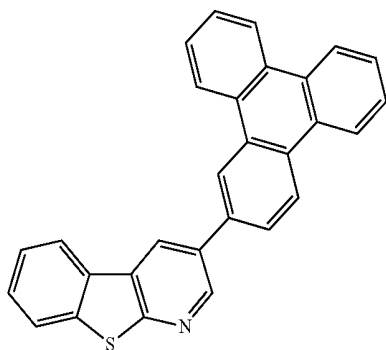


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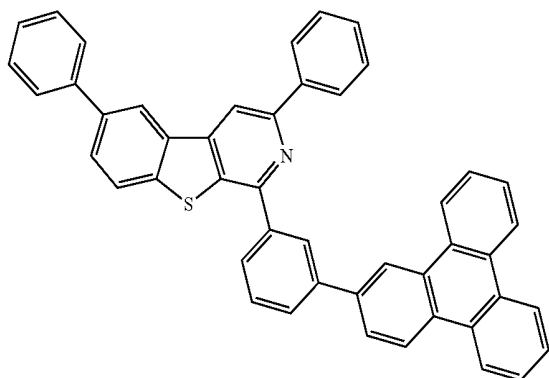
Compound 74



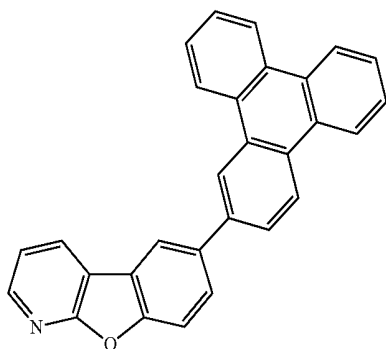
Compound 75



Compound 76

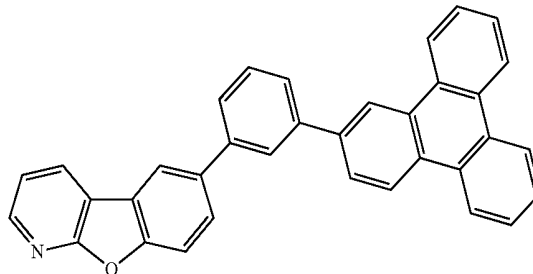


Compound 77

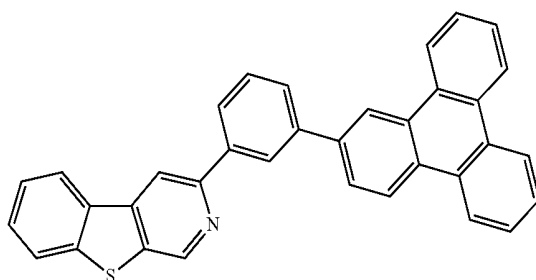


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Compound 78

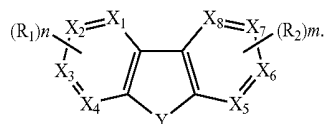


Compound 79

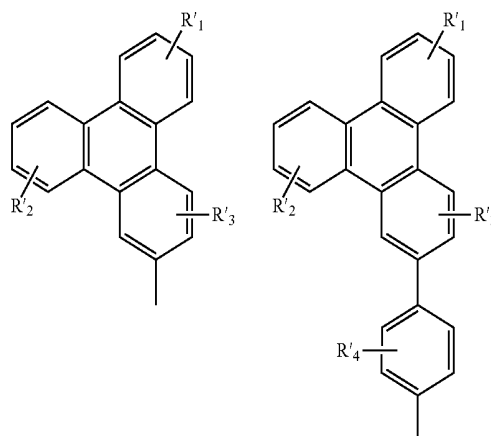


**[0070]** A first device comprising an organic light emitting device is also provided. The device further comprises an anode, a cathode, and an organic layer disposed between the anode and the cathode. The organic layer further comprising a compound having the formula:

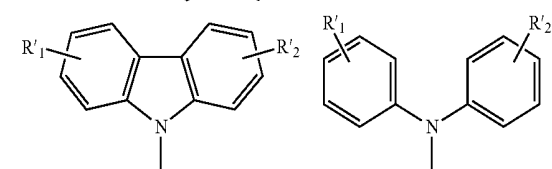
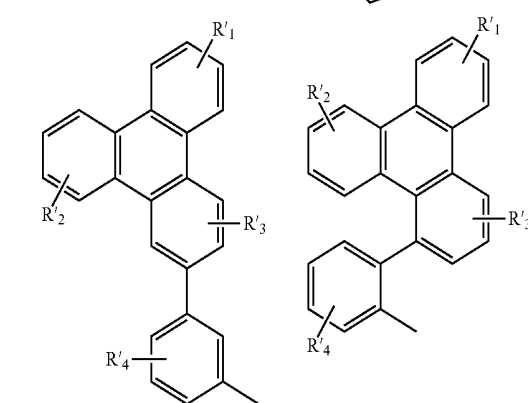
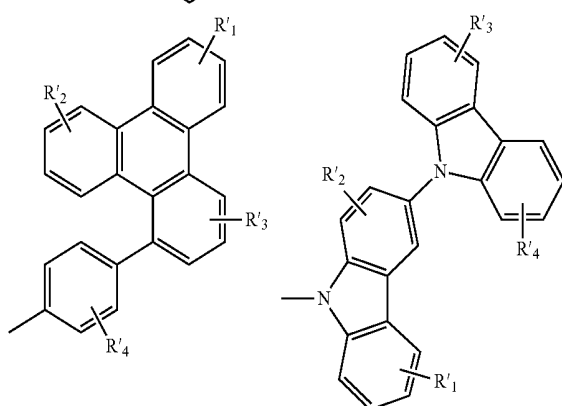
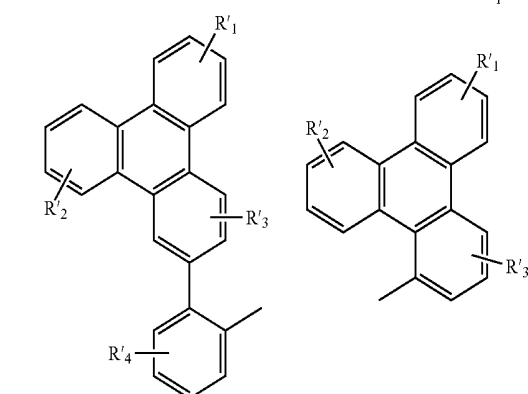
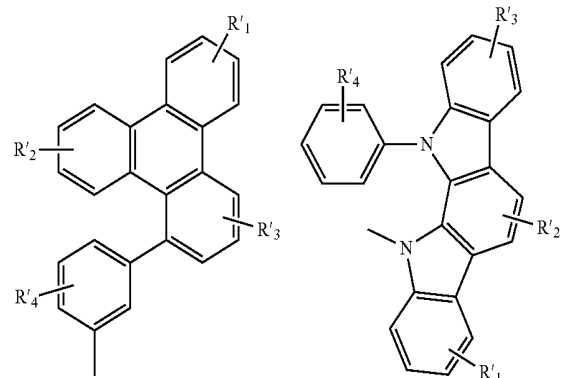
FORMULA I



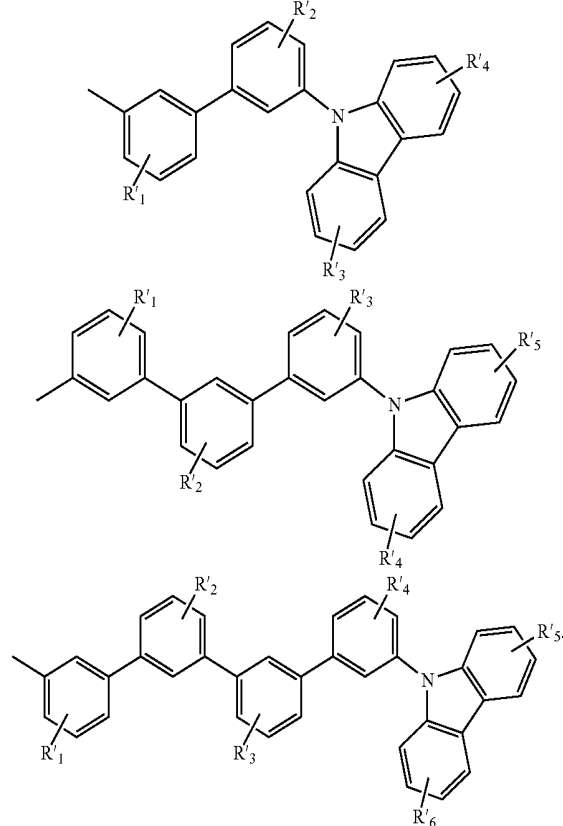
$X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$  are independently selected from the group consisting of a carbon atom and a nitrogen atom. At least one of  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$ ,  $X_5$ ,  $X_6$ ,  $X_7$ , and  $X_8$  is a nitrogen atom, Y is S or O. R1 and R2 may represent mono, di, tri, or tetra substitutions. R1 and R2 are independently selected from the group consisting of hydrogen, alkyl, aryl and halide. At least one of R1 and R2 is selected from the group consisting of:



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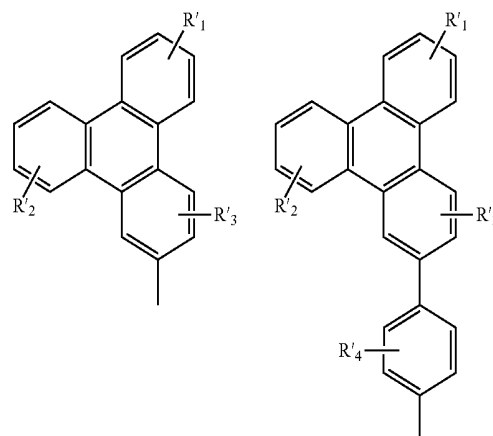


R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> may represent mono, di, tri, tetra or penta substitutions. R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl.

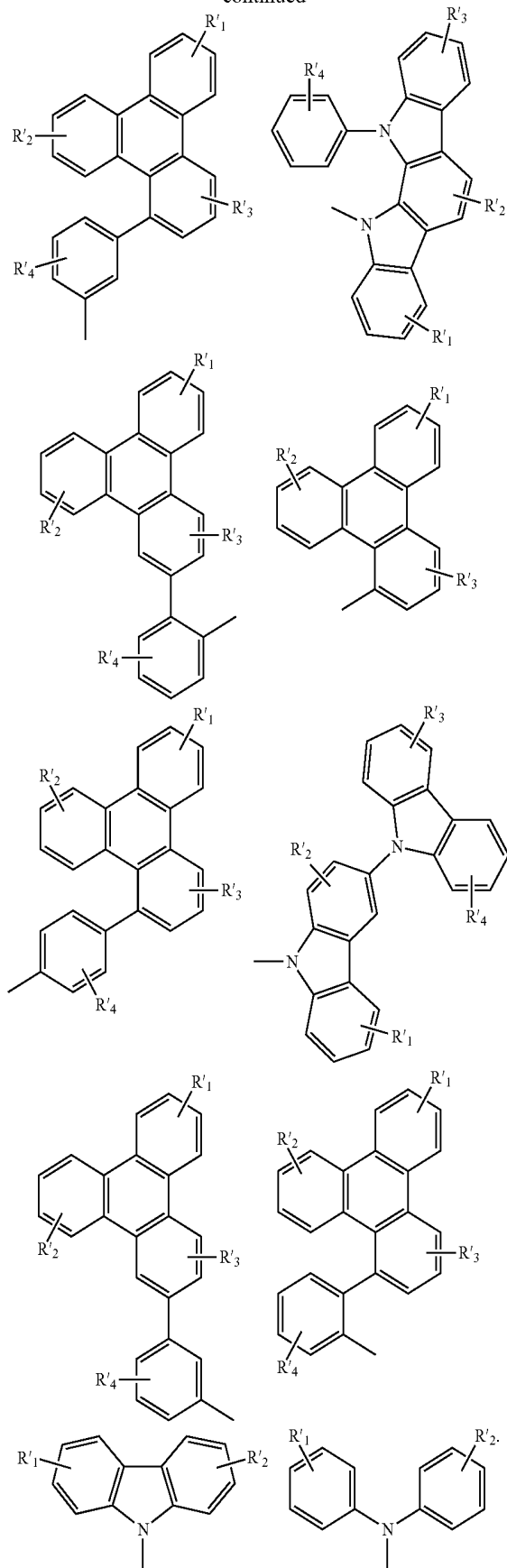
[0071] In one aspect, the first device is a consumer product.

[0072] Additionally, an organic light emitting device is also provided. The device comprises an anode, a cathode, and an organic emissive layer disposed between the anode and the cathode, wherein the organic layer further comprises a compound having FORMULA I. Preferably, m and n are 0, 1, 2, 3, or 4; and m+n is equal to or greater than 2 and m+n is equal to or less than 6.

[0073] In one aspect, at least one of R<sub>1</sub> and R<sub>2</sub> is selected from the group consisting of:

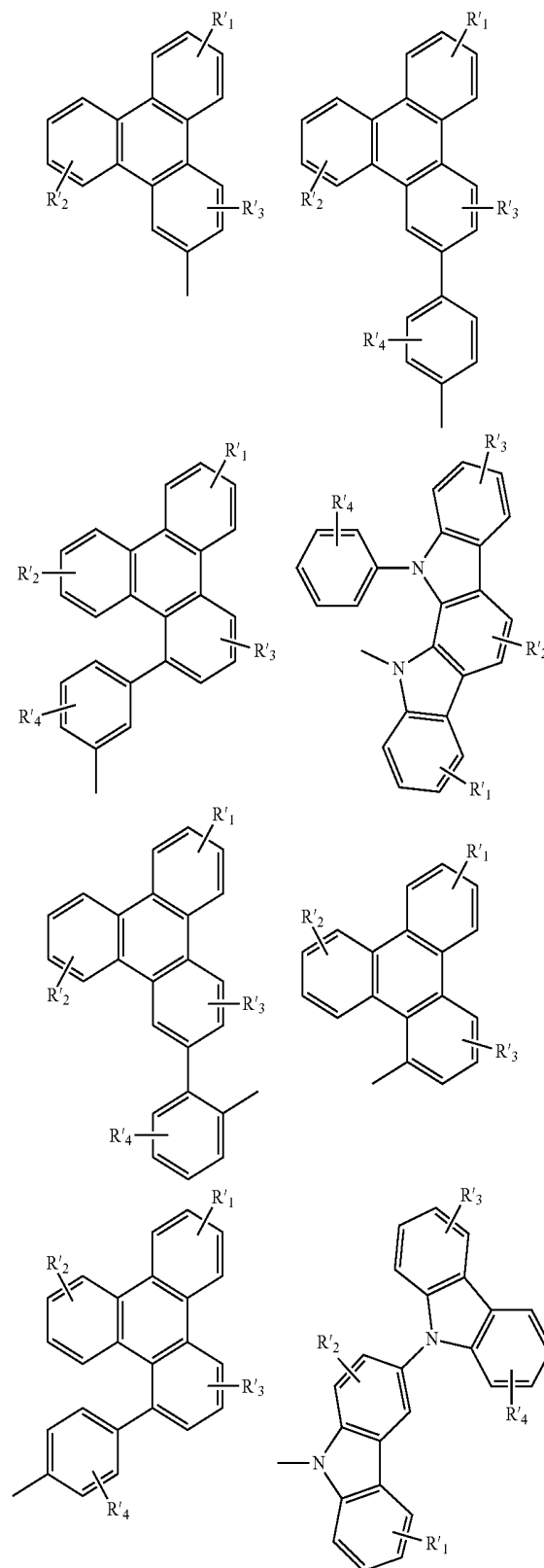


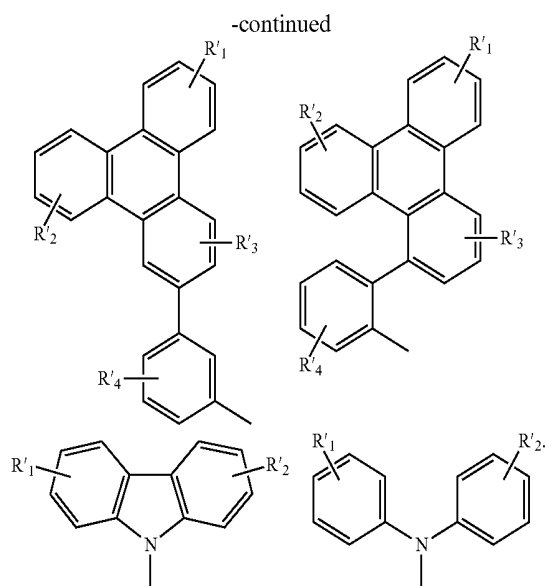
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R'<sub>1</sub>, R'<sub>2</sub>, R'<sub>3</sub>, and R'<sub>4</sub> are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl.

[0074] In another aspect, R<sub>1</sub> and R<sub>2</sub>, are each independently selected from the group consisting of hydrogen and

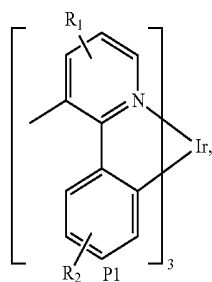




**[0075]** In one aspect, devices are provided that contain a compound selected from the group consisting of Compounds 1-93.

**[0076]** In particular, devices are provided wherein the compound is selected from the group consisting of Compounds 1-79.

**[0077]** In one aspect, the organic layer is an emissive layer and the aza-dibenzothiophene and aza-dibenzofuran having FORMULA I is a host in the organic layer. The organic layer may further comprise an emissive dopant. Preferably, the emissive dopant has the formula



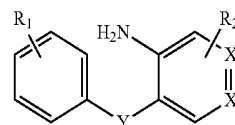
where  $R_1$  and  $R_2$  are each independently selected from the group consisting of hydrogen, alkyl, and aryl.

**[0078]** As discussed above, the aza-dibenzothiophene and aza-dibenzofuran compounds having FORMULA I may be advantageously used as a host material in an emissive layer. However, these compounds may also be used as materials in an enhancement layer. In particular, the compounds described herein may be used the material in a blocking layer.

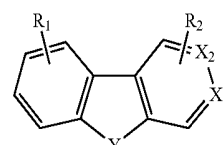
**[0079]** A consumer device is also provided, wherein the device further comprises an anode, a cathode and an organic layer. The organic layer further comprises an aza-dibenzothiophene or aza-dibenzofuran compound having FORMULA I.

**[0080]** Additionally, a process for making an aza-dibenzothiophene compound or an aza-dibenzofuran compound is provided (illustrated in FIG. 4, top). The process comprises

treating an acetic acid solution of an amino-arylthio pyridine intermediate having the formula:

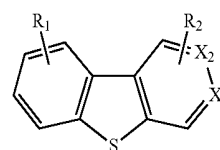


with  $t\text{BuONO}$  to produce an aza complex having the formula



$Y$  is S or O.  $X_1$  or  $X_2$  is nitrogen.  $R_1$  and  $R_2$  may be a mono, di, tri, or tetra substitution.  $R_1$  is selected from the group consisting of hydrogen, alkyl, aryl and heteroaryl; and  $R_2$  is selected from the group consisting of hydrogen, alkyl, aryl and halide. For example, an acetic acid solution of the intermediate 3-amino-4-arylthio pyridine with halide substituents on the pyridine ring or an acetic acid solution of the intermediate 3-arylthio-4-amino pyridine with halide substituents on the pyridine ring may be treated with 1-2 eq. of  $t\text{BuONO}$  at room temperature until no gas evolved, usually around 1-3 hours.

**[0081]** Particular examples of the process include intermediates and aza-complexes where  $Y$  is S (i.e., dibenzothiophene intermediates and aza-dibenzothiophene complexes). Alternatively, the process may preferably include intermediates and aza-complexes where  $Y$  is O (i.e., dibenzofuran intermediates and aza-dibenzofuran complexes). The process provided herein may yield greater than 50% or greater than 70% of the aza-complexes. In particular, the yield of



may be greater than 50%.

**[0082]** Examples of the process to make aza-dibenzothiophene or aza-dibenzofuran compounds include intermediates where one of  $X_1$  and  $X_2$  is carbon and the other is nitrogen. In a particular example of the process,  $X_1$  is nitrogen and  $X_2$  is carbon. In another particular example,  $X_1$  is carbon and  $X_2$  is nitrogen.

**[0083]** Examples of the process to make aza-dibenzothiophene or aza-dibenzofuran compounds include compounds where  $R_2$  includes at least one halide. In a particular example of the process,  $R_2$  includes only halide substituents. Moreover,  $R_1$  is preferably halide. Halide substituents may include, but are not limited to, bromide, chloride, fluoride, and iodide.

**[0084]** The process may also be used to make aza-dibenzothiophene or aza-dibenzofuran compounds where  $R_2$ , is

not a halide (i.e. there are no further substituents on the pyridine ring). For these aza-compounds lacking a halide substituent on the pyridine ring, the amino-arylthio pyridine intermediate is treated with  $\text{H}_2\text{SO}_4$  prior to treatment with  $\text{tBuONO}$  (illustrated in FIG. 4, bottom). For example, an acetic acid solution of the intermediate 3-amino-4-arylthio pyridine or an acetic acid solution of the intermediate 3-arylthio-4-amino pyridine may be treated with 1-5 eq. of  $\text{H}_2\text{SO}_4$ , followed by 1-2 eq. of  $\text{tBuONO}$  until no gas evolved, usually around 1-5 hours.

**[0085]** The materials described herein as useful for a particular layer in an organic light emitting device may be used in combination with a wide variety of other materials present in the device. For example, emissive dopants disclosed herein may be used in conjunction with a wide variety of hosts, transport layers, blocking layers, injection layers,

electrodes and other layers that may be present. The materials described or referred to below are non-limiting examples of materials that may be useful in combination with the compounds disclosed herein, and one of skill in the art can readily consult the literature to identify other materials that may be useful in combination.

**[0086]** In addition to and/or in combination with the materials disclosed herein, many hole injection materials, hole transporting materials, host materials, dopant materials, exciton/hole blocking layer materials, electron transporting and electron injecting materials may be used in an OLED. Non-limiting examples of the materials that may be used in an OLED in combination with materials disclosed herein are listed in Table 1 below. Table 1 lists non-limiting classes of materials, non-limiting examples of compounds for each class, and references that disclose the materials.

TABLE 1

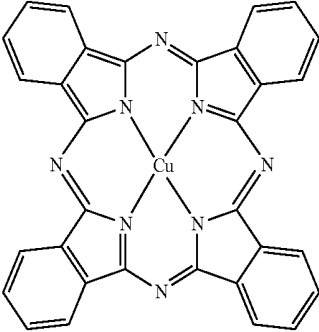
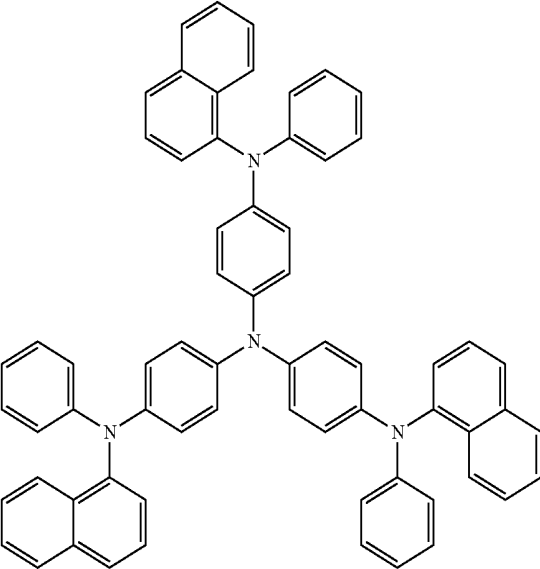
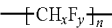
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Hole injection materials		
Phthalocyanine and porphyrin compounds		Appl. Phys. Lett. 69, 2160 (1996)
Starburst triarylamines		J. Lumin. 72-74, 985 (1997)
$\text{CF}_x$ Fluorohydrocarbon polymer		Appl. Phys. Lett. 78, 673 (2001)

TABLE 1-continued

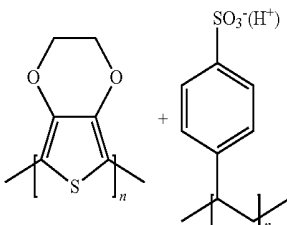
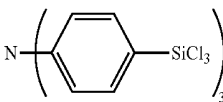
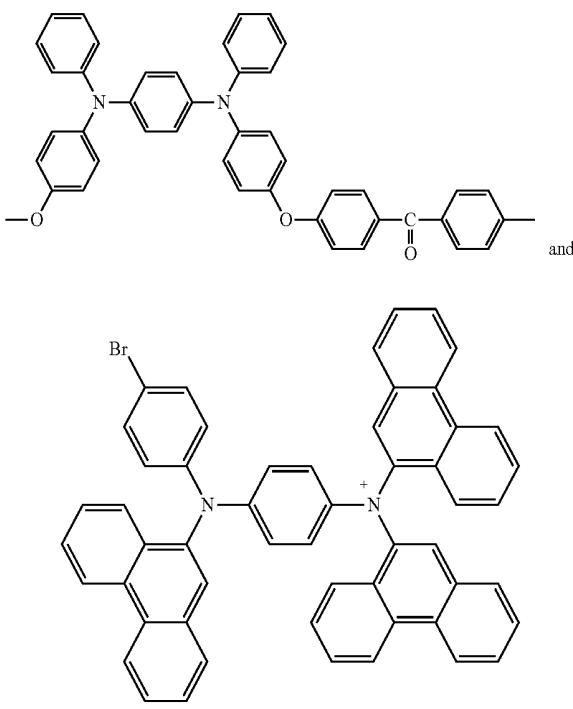
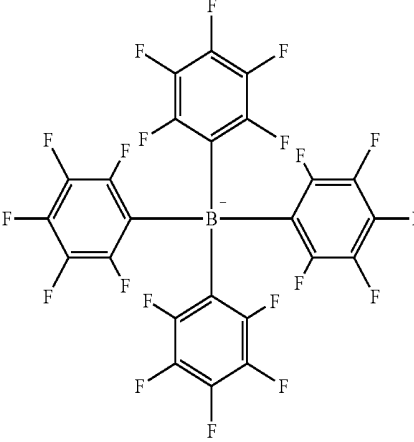
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Conducting polymers (e.g., PEDOT: PSS, polyaniline, polythiophene)		Synth. Met. 87, 171 (1997) WO2007002683
Phosphonic acid and silane SAMs		US20030162053
Triarylamine or polythiophene polymers with conductivity dopants		EA01725079A1
		

TABLE 1-continued

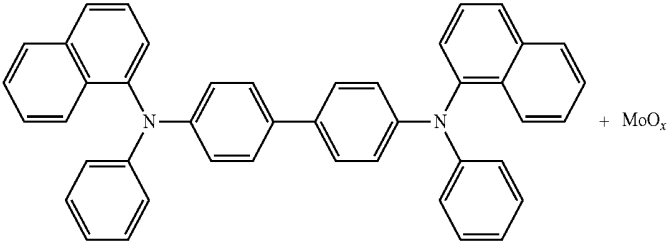
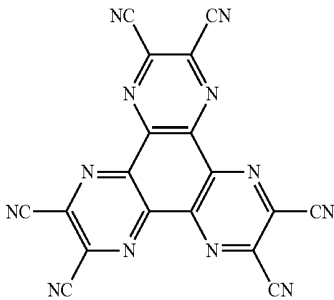
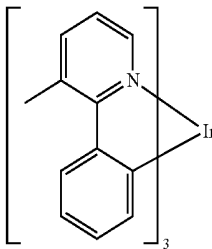
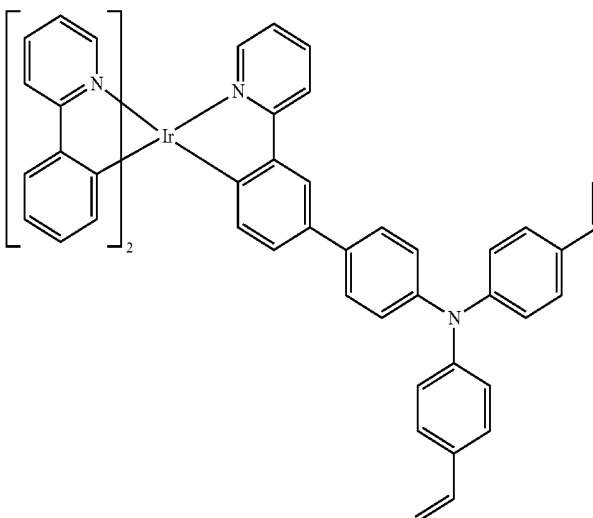
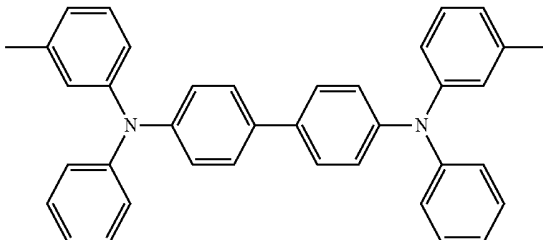
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Arylamines complexed with metal oxides such as molybdenum and tungsten oxides	 $+ \text{MoO}_x$	SID Symposium Digest, 37, 923 (2006) WO2009018009
p-type semiconducting organic complexes		US20020158242
Metal organometallic complexes		US20060240279
Cross-linkable compounds		US20080220265
Hole transporting materials		
Triarylamines (e.g., TPD, $\alpha$ -NPD)		Appl. Phys. Lett. 511, 913 (1987)



TABLE 1-continued

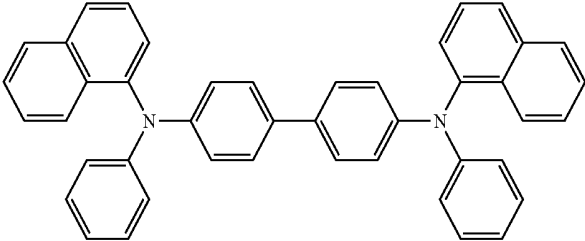
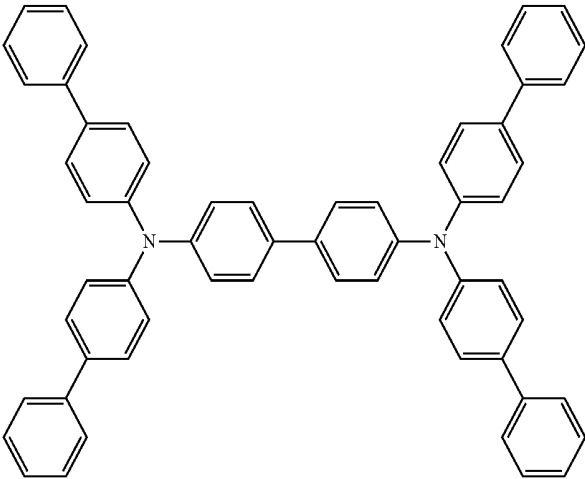
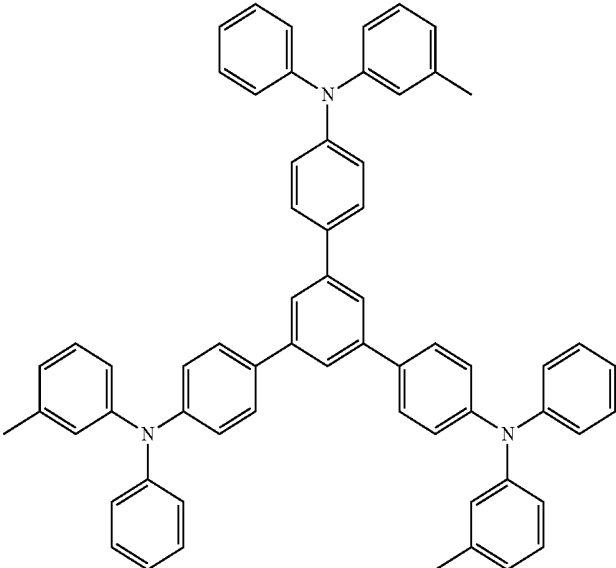
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. Pat. No. 5,061,569
		EP650955
		J. Mater. Chem. 3, 319 (1993)

TABLE 1-continued

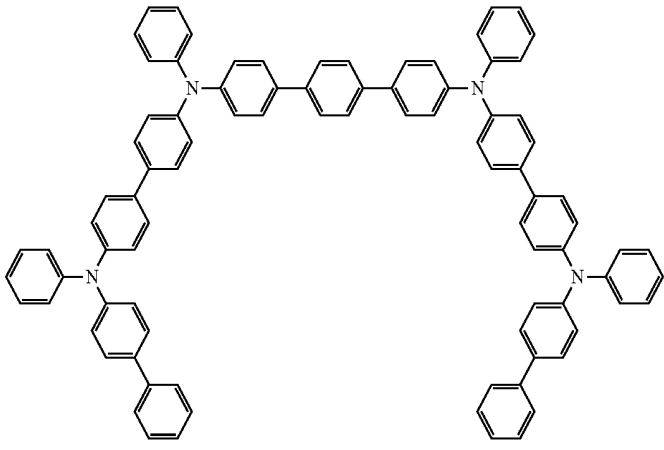
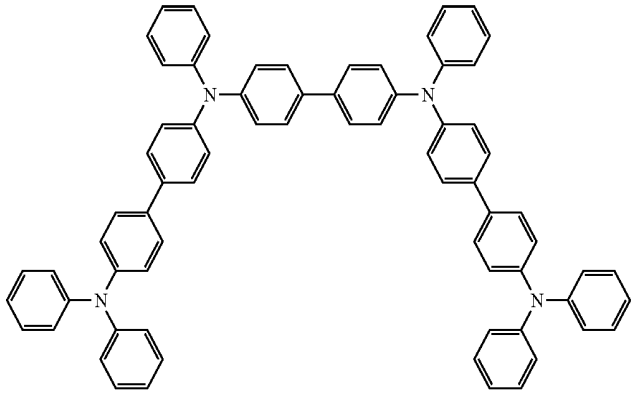
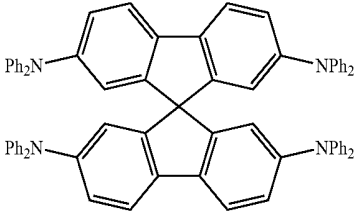
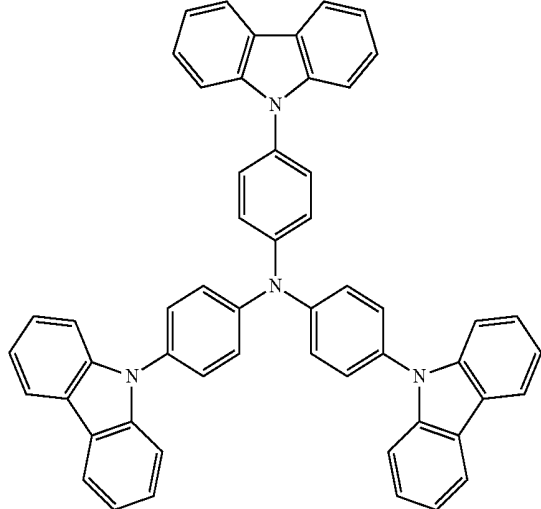
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Appl. Phys. Lett. 90, 183503 (2007)
		Appl. Phys. Lett. 90, 183503 (2007)
Triarylamine on spirofluorene core		Synth. Met. 91, 209 (1997)
Arylamine carbazole compounds		Adv. Mater. 6, 677 (1994), US20080124572

TABLE 1-continued

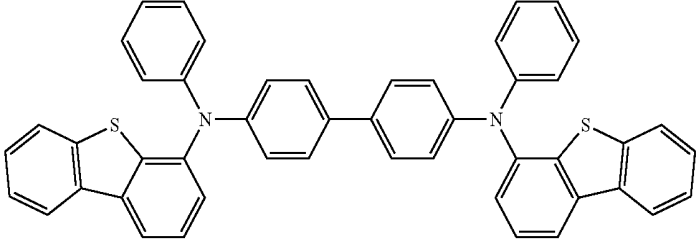
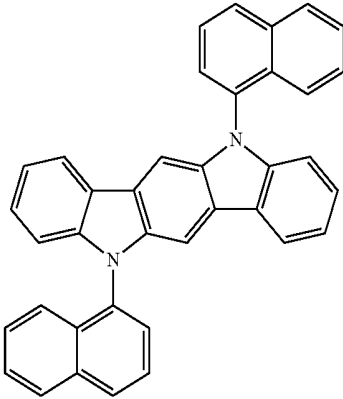
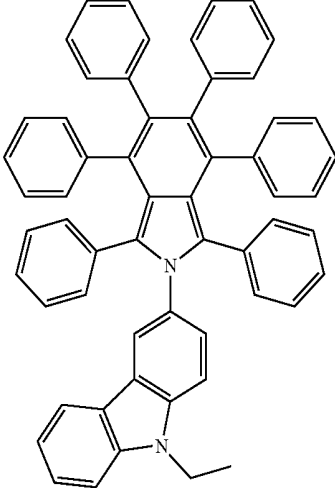
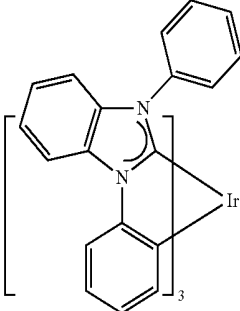
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triarylamine with (di)benzothiophene/(di) benzofuran		US20070278938, US20080106190
Indolocarbazoles		Synth. Met. 111, 421 (2000)
Isoindole compounds		Chem. Mater. 15, 3148 (2003)
Metal carbene complexes		US20080018221

TABLE 1-continued

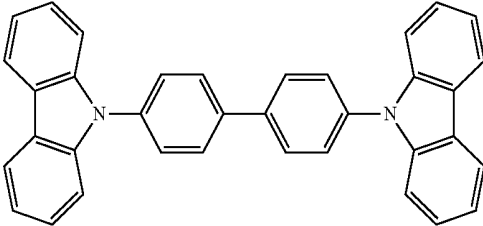
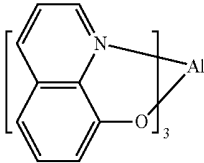
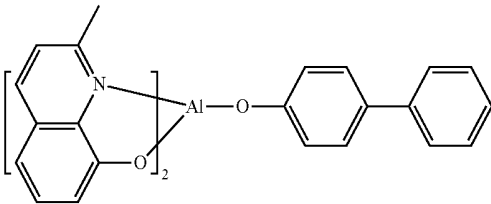
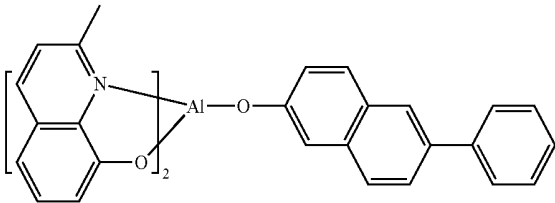
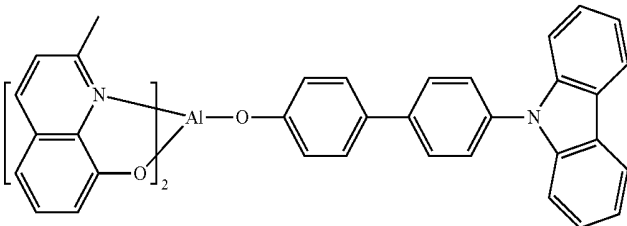
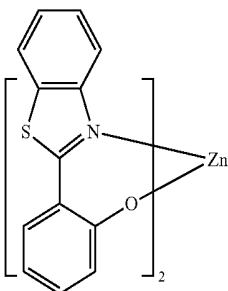
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Phosphorescent OLED host materials		
Red hosts		
Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
Metal 8-hydroxyquinolates (e.g., Alq <sub>3</sub> , BAlq)		Nature 395, 151 (1998)
		US20060202194
		WO2005014551
		WO2006072002
Metal phenoxybenzothiazole compounds		Appl. Phys. Lett. 90, 123509 (2007)

TABLE 1-continued

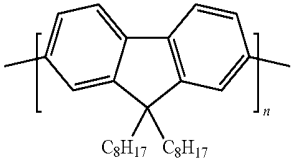
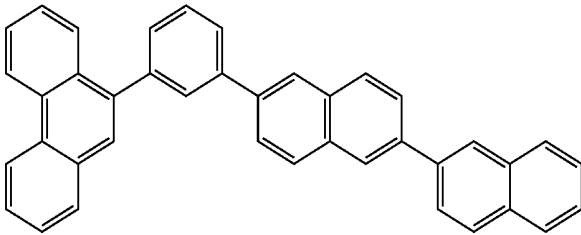
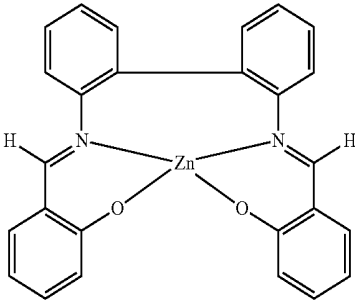
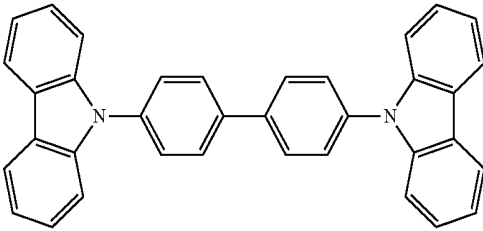
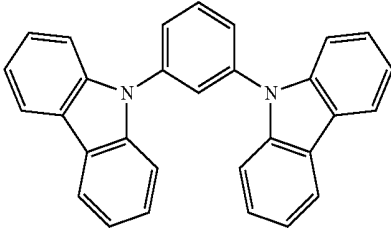
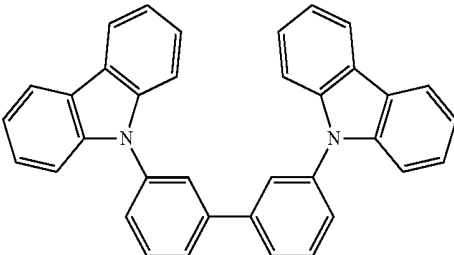
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Conjugated oligomers and polymers (e.g., polyfluorene)		Org. Electron. 1, 15 (2000)
Aromatic fused rings		WO2009066779, WO2009066778, WO2009063833, US20090045731, US20090045730, WO2009008311, US20090008605, US20090009065
Zinc complexes		WO2009062578
Green hosts		
Arylcarbazoles	  	Appl. Phys. Lett. 78, 1622 (2001)  US20030175553  WO2001039234

TABLE 1-continued

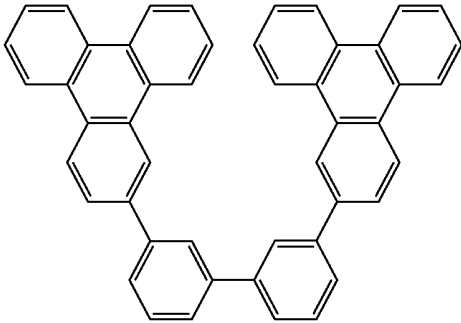
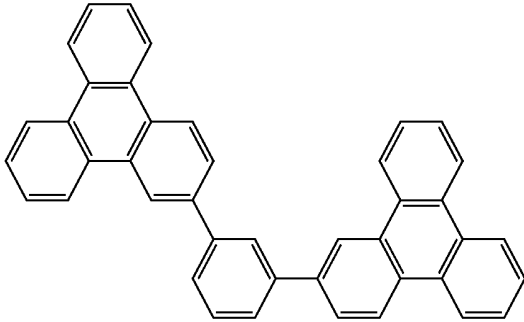
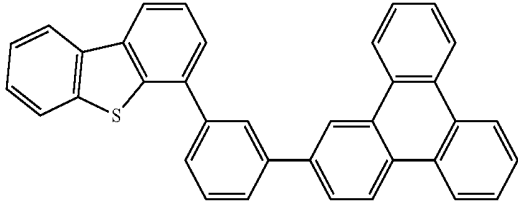
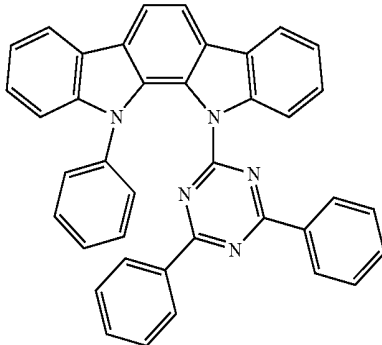
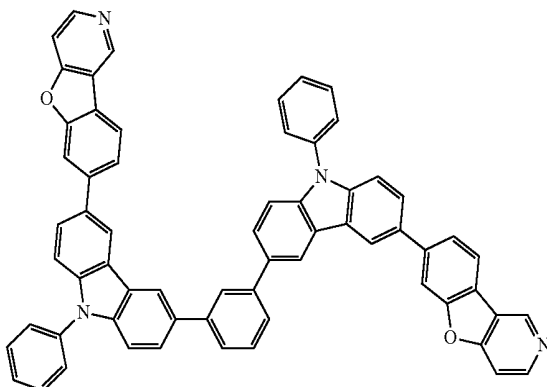
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Aryltriphenylene compounds		US20060280965
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		WO2009021126
Donor acceptor type molecules		WO2008056746
Aza-carbazole/DBT/DBF		JP2008074939

TABLE 1-continued

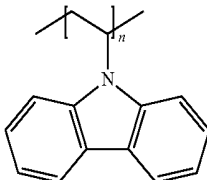
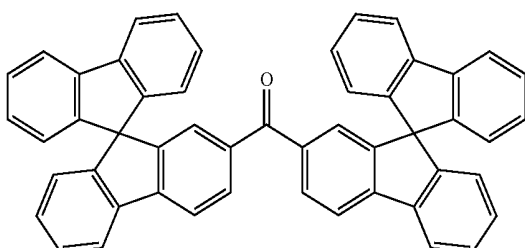
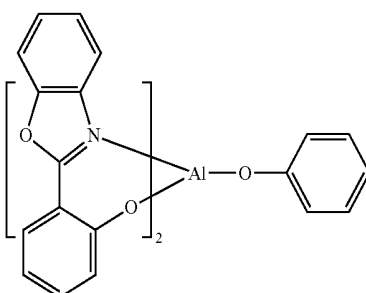
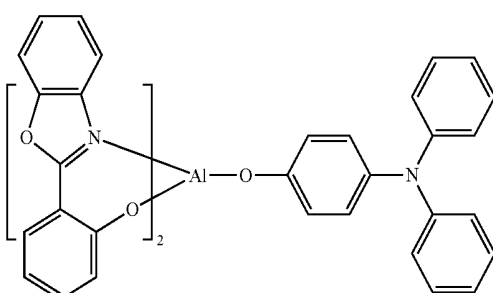
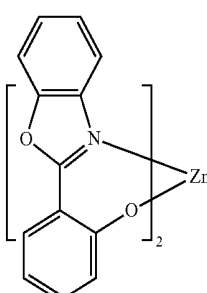
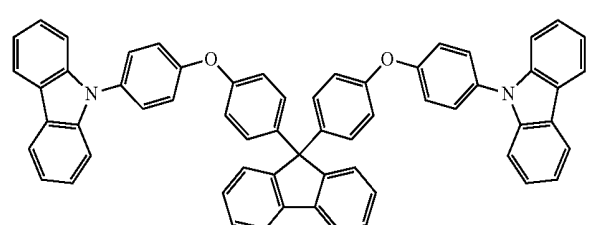
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Polymers (e.g., PVK)		Appl. Phys. Lett. 77, 2280 (2000)
Spirofluorene compounds		WO2004093207
Metal phenoxybenzoxazole compounds		WO2005089025
		WO2006132173
		JP200511610
Spirofluorene-carbazole compounds		JP2007254297

TABLE 1-continued

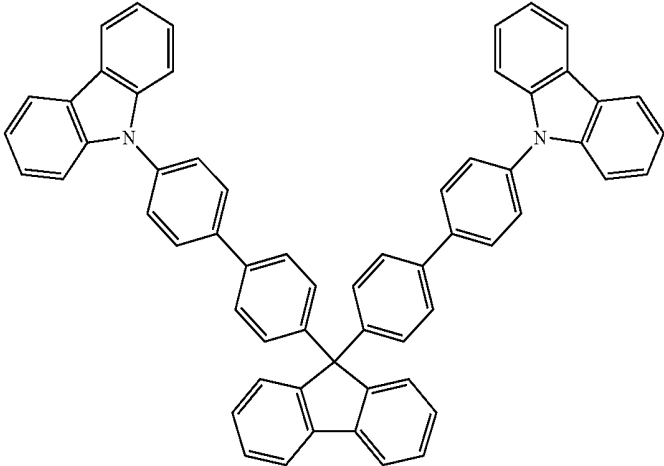
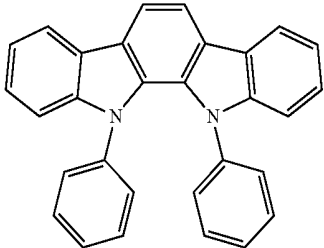
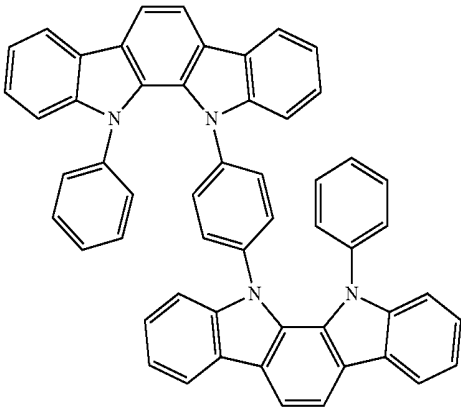
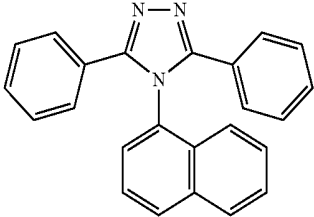
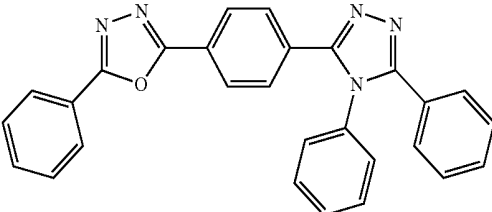
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		JP2007254297
Indolocabazoles		WO2007063796
		WO2007063754
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole)		J. Appl. Phys. 90, 5048 (2001)
		WO2004107822



TABLE 1-continued

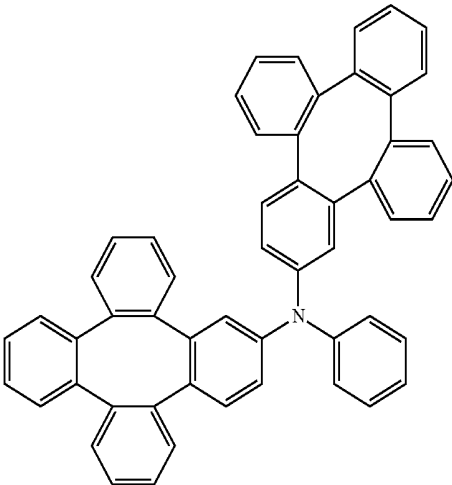
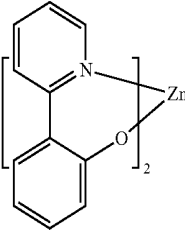
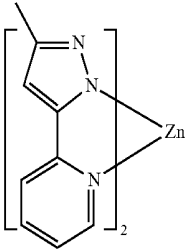
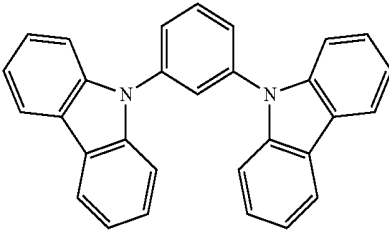
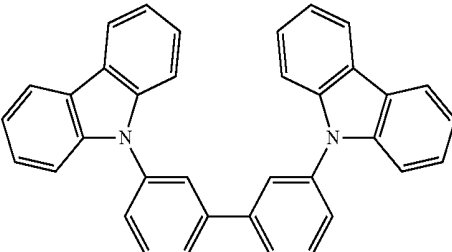
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Tetraphenylene complexes		US20050112407
Metal phenoxypyridine compounds		WO2005030900
Metal coordination complexes (e.g., Zn, Al with N-N ligands)		US20040137268, US20040137267
Blue hosts		Appl. Phys. Lett, 82, 2422 (2003)
Arylcarbazoles		US20070190359

TABLE 1-continued

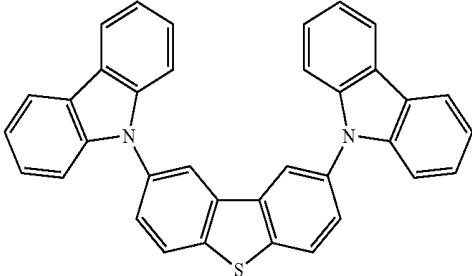
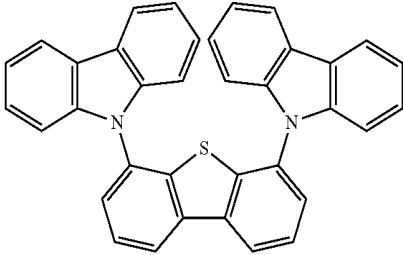
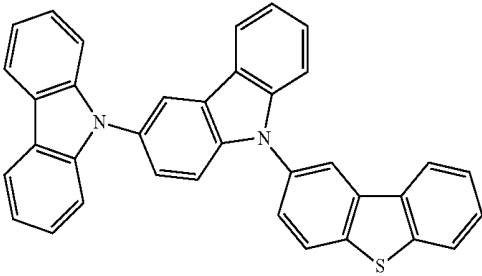
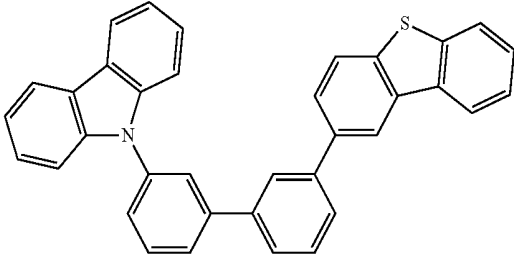
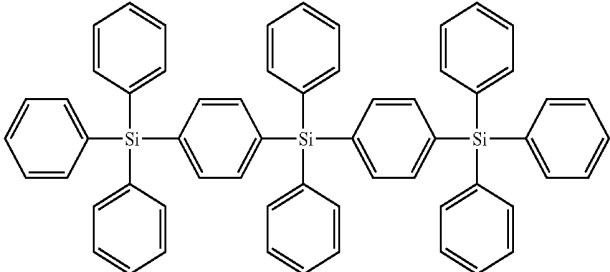
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Dibenzothiophene/ Dibenzofuran-carbazole compounds		WO2006114966, US20090167162
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		WO2009086028
		US20090030202, US20090017330
Silicon aryl compounds		US20050238919

TABLE 1-continued

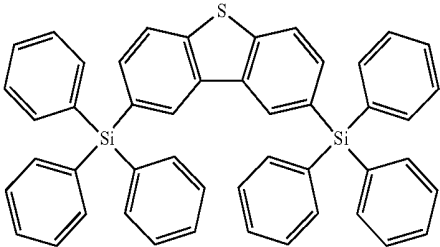
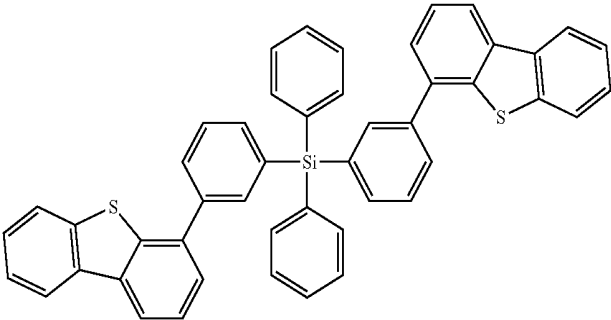
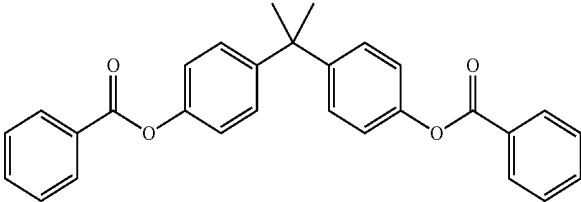
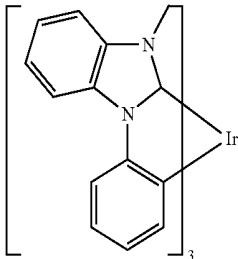
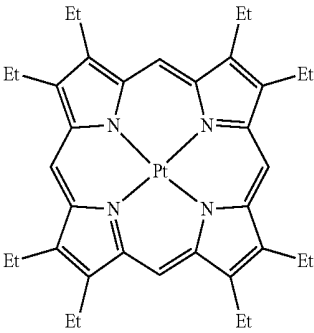
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO2009003898
Silicon/Germanium aryl compounds		EP2034538A
Aryl benzoyl ester		WO2006100298
High triplet metal organometallic complex		U.S. Pat. No. 7,154,114
	Phosphorescent dopants	
Red dopants		
Heavy metal porphyrins (e.g., PtOEP)		Nature 395, 151 (1998)

TABLE 1-continued

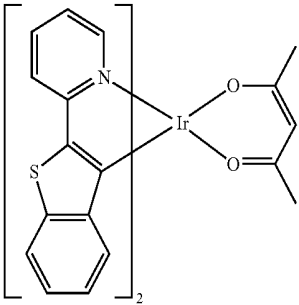
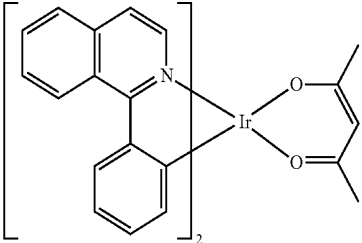
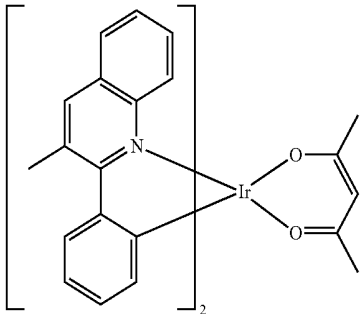
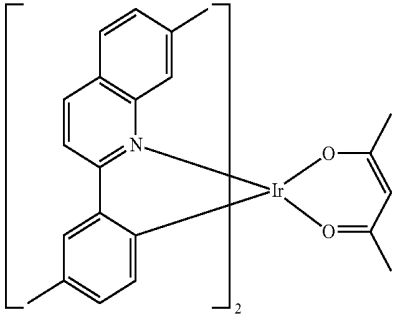
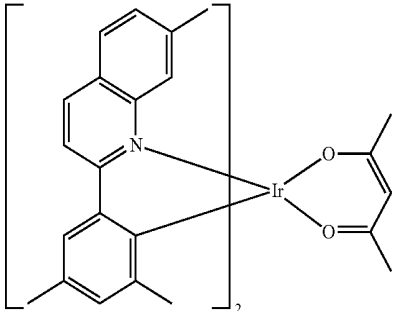
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Iridium (III) organometallic complexes		Appl. Phys. Lett. 78, 1622 (2001)
		US2006835469
		US2006835469
		US20060202194
		US20060202194

TABLE 1-continued

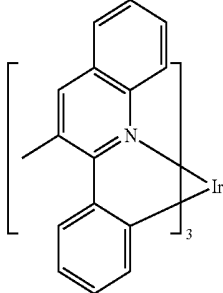
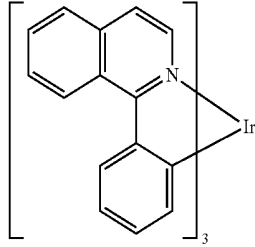
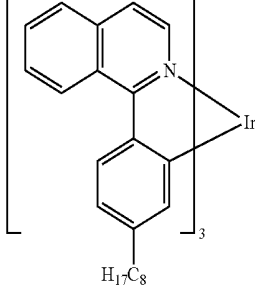
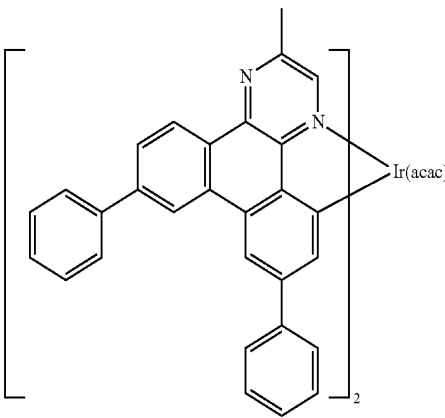
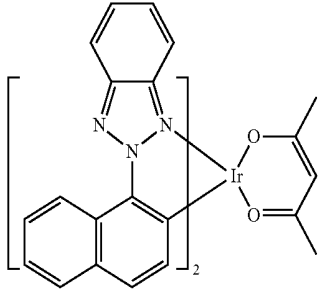
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		Adv. Mater. 19, 739 (2007)
		WO2009100991
		WO2008101842

TABLE 1-continued

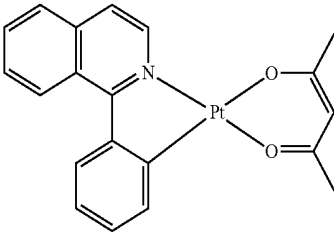
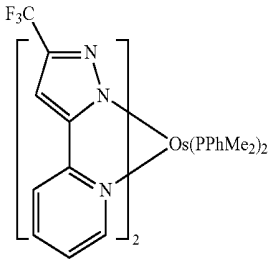
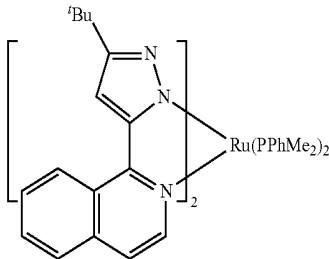
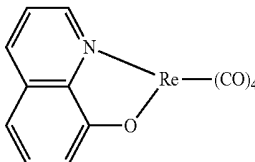
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Platinum (II) organometallic complexes		WO2003040257
Osmium (III) complexes		Chem. Mater. 17, 3532 (2005)
Ruthenium (II) complexes		Adv. Mater. 17, 1059 (2005)
Rhenium (I), (II), and (III) complexes		US20050244673

TABLE 1-continued

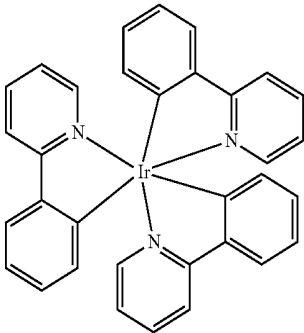
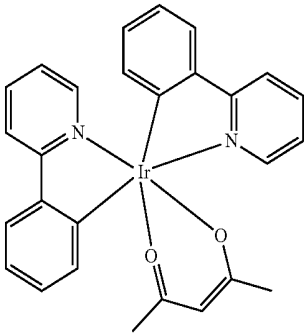
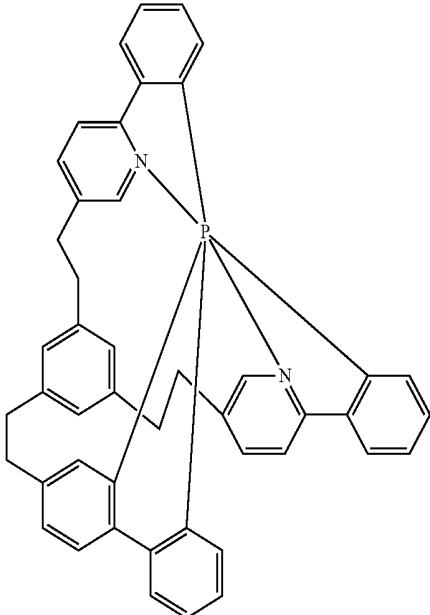
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Green dopants		
Iridium (III) organometallic complexes	<div data-bbox="639 533 943 864"></div> <p data-bbox="724 875 858 898">and its derivatives</p>	Inorg. Chem. 40, 1704 (2001)
	<div data-bbox="639 1005 943 1337"></div>	US20020034656
	<div data-bbox="576 1442 1007 2054"></div>	U.S. Pat. No. 7,332,232

TABLE 1-continued

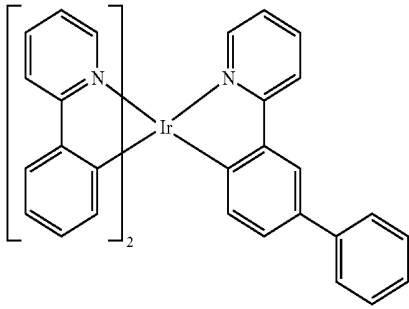
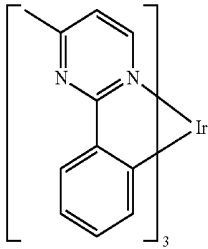
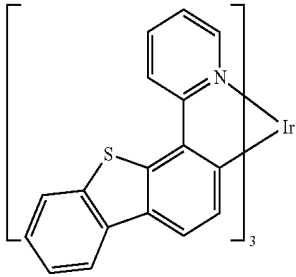
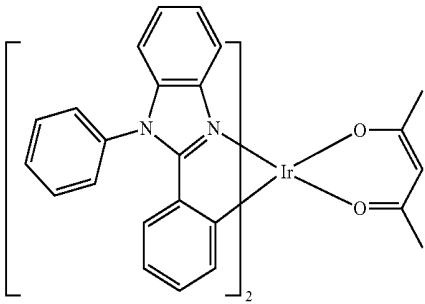
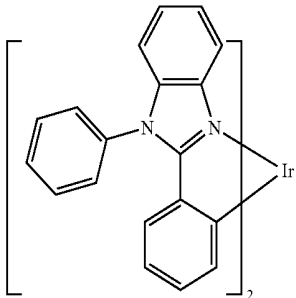
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20090108737
		US20090039776
		U.S. Pat. No. 6,921,915
		U.S. Pat. No. 6,687,266
		Chem. Mater. 16, 2480 (2004)



TABLE 1-continued

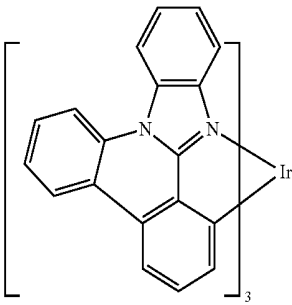
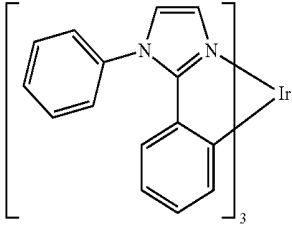
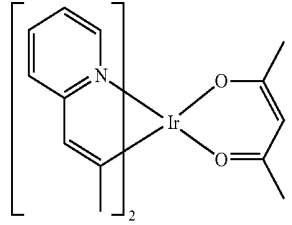
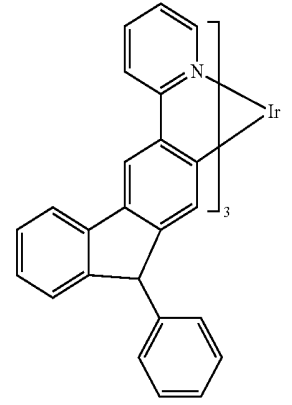
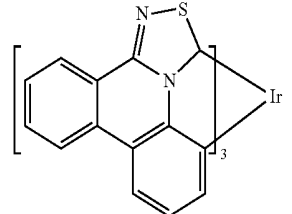
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20070190359
		US 20060008670 JP2007123392
		Adv. Mater. 16, 2003 (2004)
		Angew. Chem. Int. Ed. 2006, 45, 7800
		WO2009050290

TABLE 1-continued

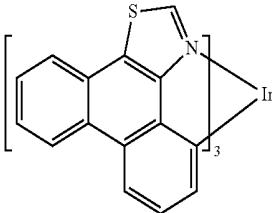
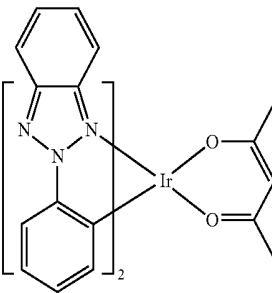
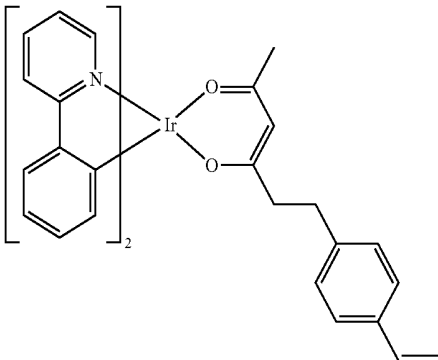
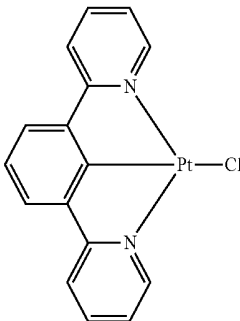
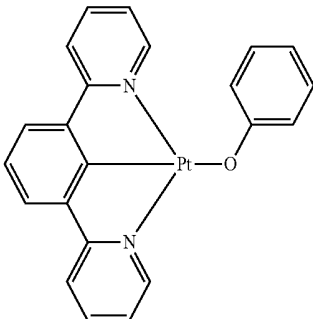
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20090165846
		US20080015355
Monomer for polymeric metal organometallic compounds		U.S. Pat. No. 7,250,226, U.S. Pat. No. 7,396,598
Pt (II) organometallic complexes, including polydentate ligands		Appl. Phys. Lett. 86, 153505 (2005)
		Appl. Phys. Lett. 86, 153505 (2005)

TABLE 1-continued

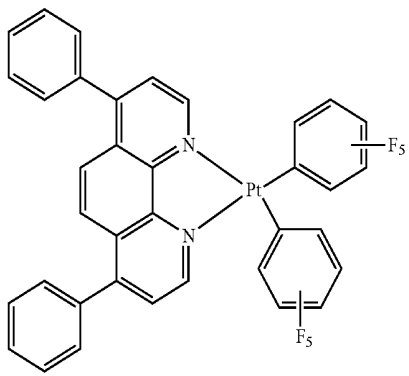
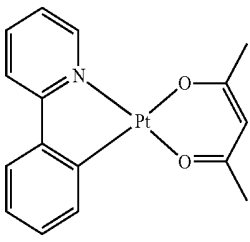
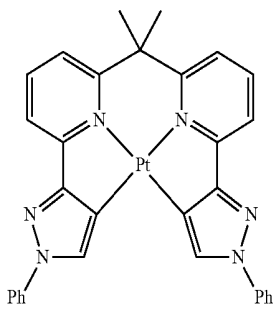
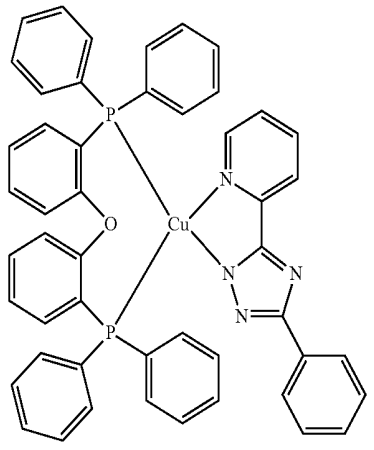
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
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		WO2002015645
		US20060263635
Cu complexes		WO2009000673

TABLE 1-continued

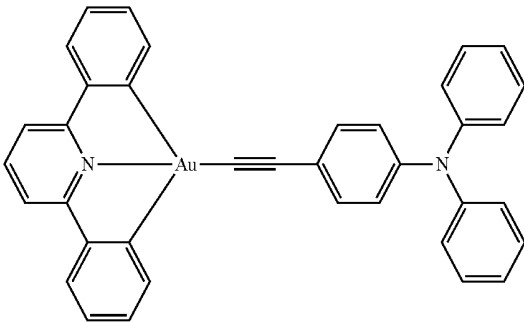
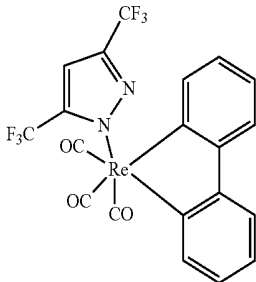
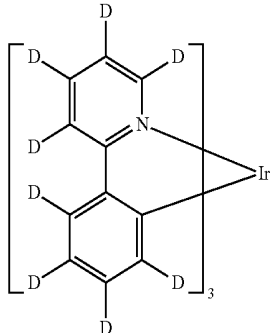
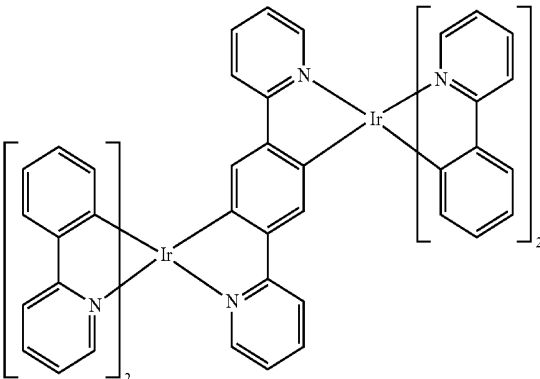
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Gold complexes		Chem. Commun. 2906 (2005)
Rhenium (III) complexes		Inorg. Chem. 42, 1248 (2003)
Deuterated organometallic complexes		US20030138657
Organometallic complexes with two or more metal centers		US20030152802

TABLE 1-continued

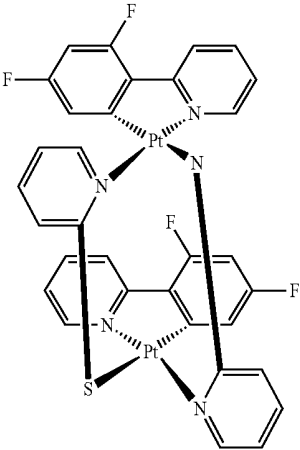
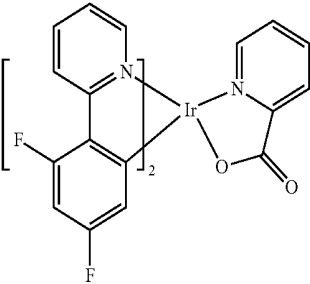
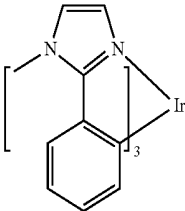
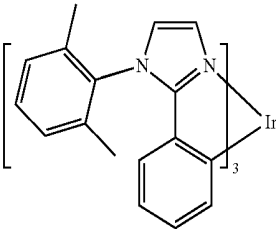
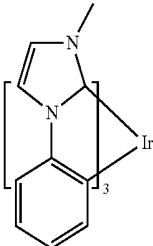
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. Pat. No. 7,090,928
Blue dopants		
Iridium (III) organometallic complexes		WO2002002714
		WO2006009024
		US2006021923
		U.S. Pat. No. 7,393,599, WO2006056418, US20050260441, WO2005019373

TABLE 1-continued

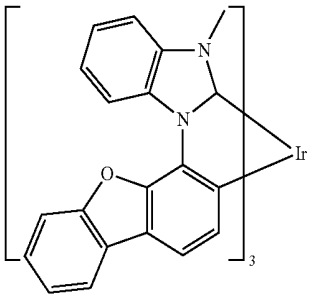
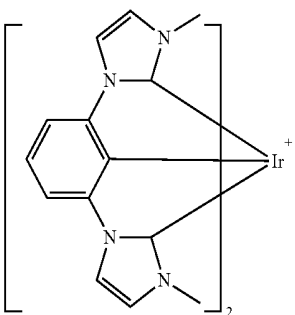
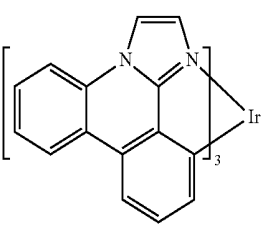
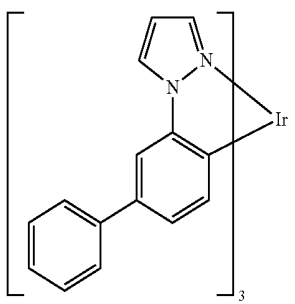
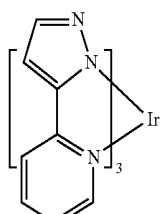
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		U.S. Pat. No. 7,445,855
		US20070190359, US20080297033
		U.S. Pat. No. 7,338,722
		US20020134984

TABLE 1-continued

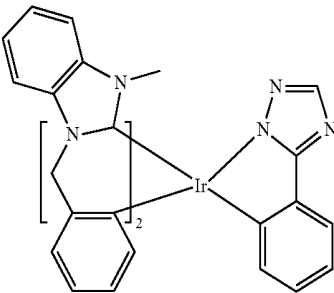
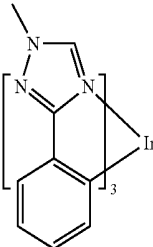
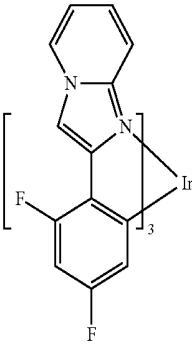
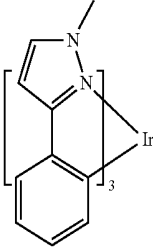
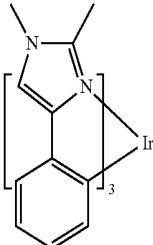
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		Inorg. Chem. 46, 4308 (2007)
		WO2005123873
		WO2005123873

TABLE 1-continued

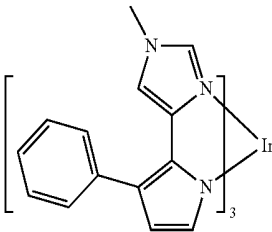
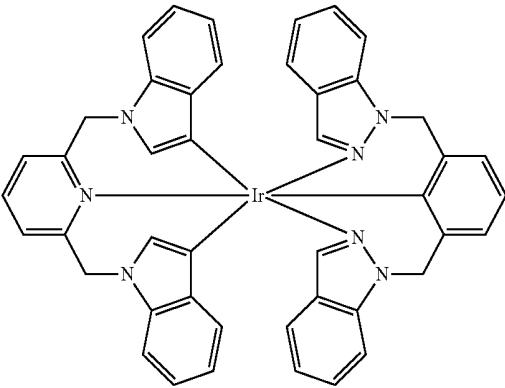
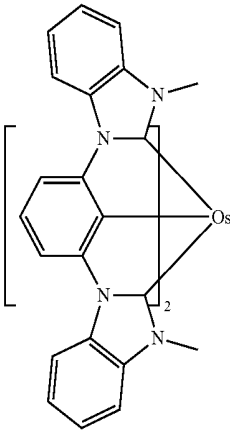
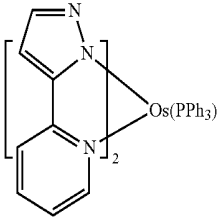
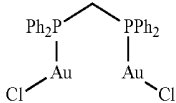
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO2007004380
		WO2006082742
Osmium (II) complexes		U.S. Pat. No. 7,279,704
		Organometallics 23, 3745 (2004)
Gold complexes		Appl. Phys. Lett. 74, 1361 (1999)



TABLE 1-continued

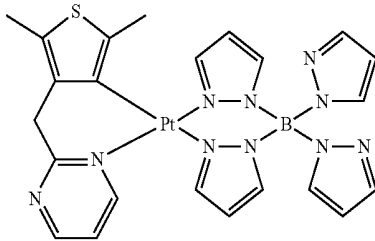
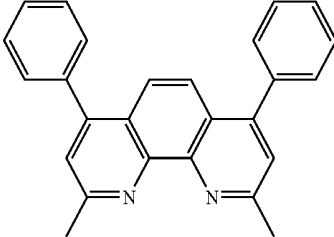
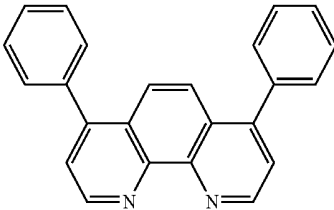
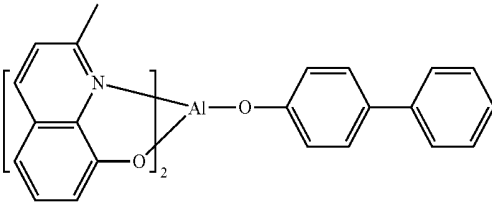
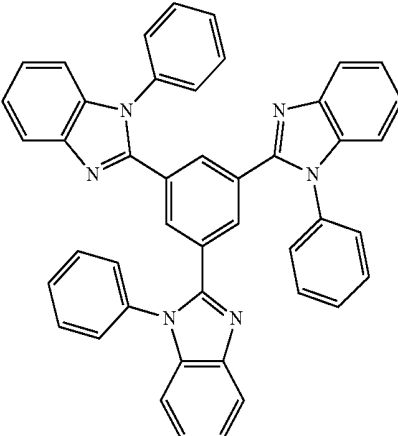
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Platinum (II) complexes		WO2006098120, WO2006103874
Exciton/hole blocking layer materials		
Bathocuprine compounds (e.g., BCP, BPhen)		Appl. Phys. Lett. 75, 4 (1999)
		Appl. Phys. Lett. 49, 449 (2001)
Metal 8-hydroxyquinolates (e.g., BALq)		Appl. Phys. Lett. 81, 162 (2002)
5-member ring electron deficient heterocycles such as triazole, oxadiazole, imidazole, benzoimidazole		Appl. Phys. Lett. 81, 162 (2002)

TABLE 1-continued

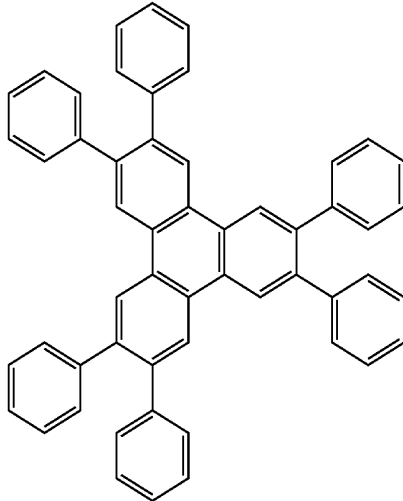
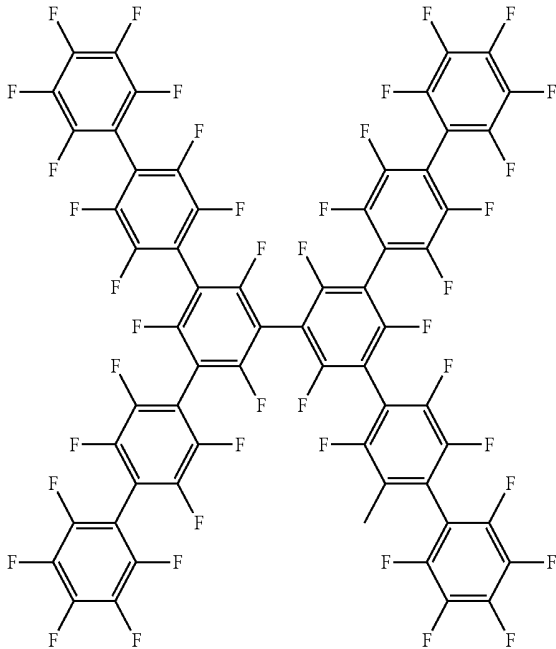
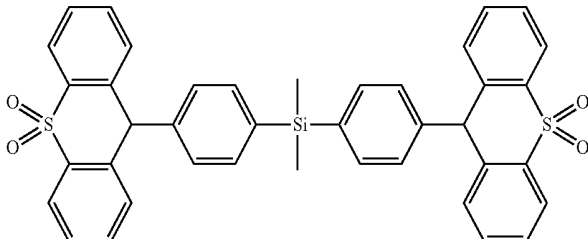
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triphenylene compounds		US20050025993
Fluorinated aromatic compounds		Appl. Phys. Lett. 79, 156 (2001)
Phenothiazine-S-oxide		WO2008132085

TABLE 1-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Electron transporting materials		
Anthracene-benzimidazole compounds		WO2003060956
		US20090179554
Aza triphenylene derivatives		US20090115316
		Appl. Phys. Lett. 89, 063504 (2006)
Metal 8-hydroxyquinolates (e.g., Alq <sub>3</sub> , Zrqq <sub>4</sub> )		Appl. Phys. Lett. 51, 913 (1987) U.S. Pat. No. 7,230,107

TABLE 1-continued

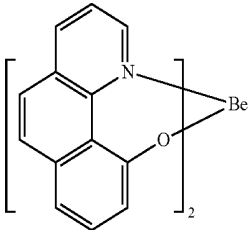
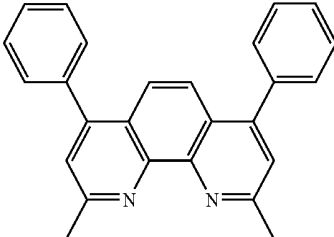
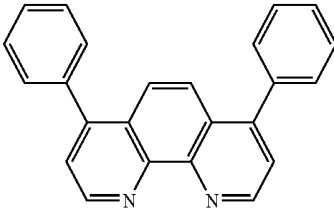
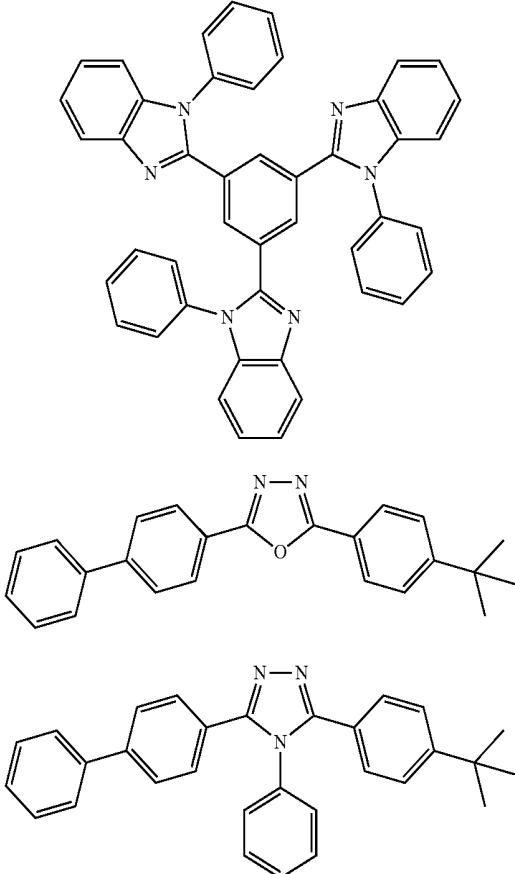
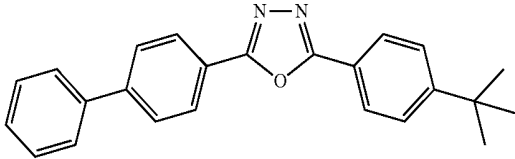
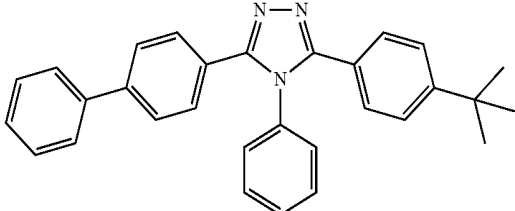
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Metal hydroxybenzoquinolates		Chem. Lett. 5, 905 (1993)
Bathocuprine compounds such as BCP, BPhen, etc		Appl. Phys. Lett. 91, 263503 (2007)
Bathocuprine compounds such as BCP, BPhen, etc		Appl. Phys. Lett. 79, 449 (2001)
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole, imidazole, benzimidazole)		Appl. Phys. Lett. 74, 865 (1999)
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole, imidazole, benzimidazole)		Appl. Phys. Lett. 55, 1489 (1989)
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole, imidazole, benzimidazole)		Jpn. J. Apply. Phys. 32, L917 (1993)

TABLE 1-continued

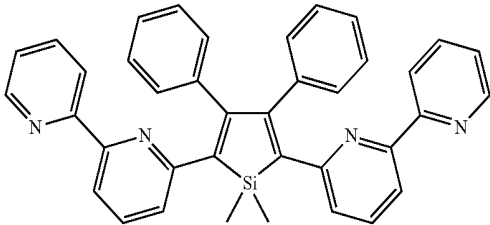
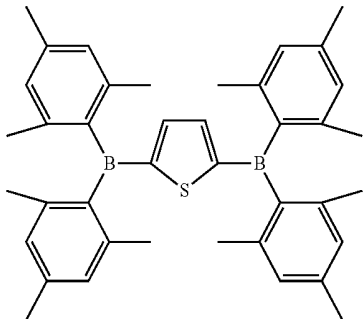
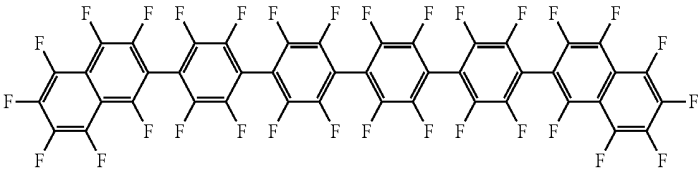
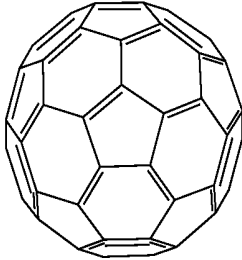
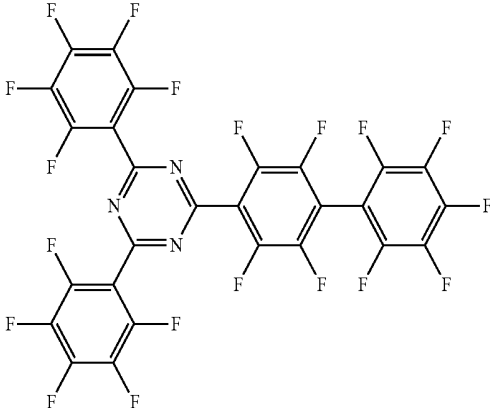
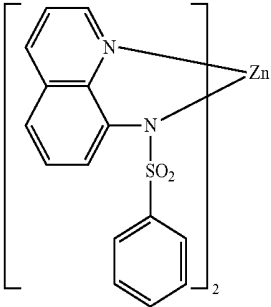
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Silole compounds		Org. Electron. 4, 113 (2003)
Arylborane compounds		J. Am. Chem. Soc. 120, 9714 (1998)
Fluorinated aromatic compounds		J. Am. Chem. Soc. 122, 1832 (2000)
Fullerene (e.g., C60)		US20090101870
Triazine complexes		US20040036077

TABLE 1-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Zn (N,N) complexes		U.S. Pat. No. 6,528,187

## EXPERIMENTAL

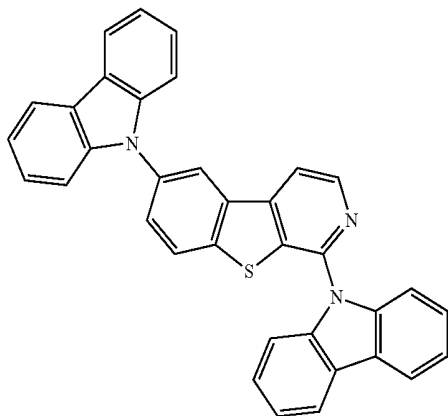
## COMPOUND EXAMPLES

## Example 1

## Synthesis of Compound 1

[0087]

Compound 1



[0088] Step 1. To a 500 mL round flask was added 2-chloro-3-iodo-4-aminopyridine (10 g, 39 mmol), 4-bromothiophenol (7.0 g, 34 mmol), CuI (0.4 g, 2.0 mmol), ethylene glycol (4.9 g, 78 mmol), potassium carbonate (10.8 g, 74 mmol), and 200 mL of isopropanol. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield of 2-chloro-3-(4-bromophenylthio)-4-aminopyridine was 7.4 g.

[0089] Step 2. To a 500 mL round flask was added 2-chloro-3-(4-bromophenylthio)-4-aminopyridine (7.0 g, 22 mmol), and 400 mL of AcOH. To this clear solution, Bu'ONO (2.3 g, 22 mmol) was added drop by drop. After stirring at room temperature for 1 h, another 10 mmol of Bu'ONO was added. The mixture was continued to stir for another 2 h. The reaction was quenched by water, and the product was purified by a silica gel column. Yield of 1-chloro-6-bromo-[1]MBenzothieno[2,3-c]pyridine was 6.5 g.

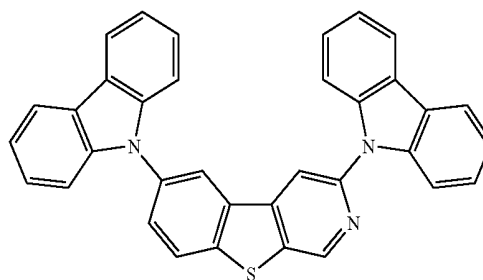
[0090] Step 3. To a 500 mL round flask was added 1-chloro-6-bromo-[1]MBenzothieno[2,3-c]pyridine (3.6 g, 12 mmol), carbazole (6.0 g, 36 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (1.1 g, 1.2 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 2.0 g, 4.8 mmol), sodium t-butoxide (6.9 g, 72 mmol), and 250 mL of xylene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield was 4.0 g. The product was further purified by vacuum sublimation. <sup>1</sup>H NMR results confirmed the desired compound.

## Example 2

## Synthesis of Compound 2

[0091]

Compound 2



[0092] Step 1. To a 500 mL round flask was added 2-chloro-4-amino-5-iodopyridine (11.5 g, 45 mmol), 4-bromothiophenol (8.1 g, 42.8 mmol), CuI (0.4 g, 2.3 mmol), ethylene glycol (5.6 g, 90.4 mmol), potassium carbonate (12.4 g, 90.4 mmol), and 200 mL of isopropanol. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield of 2-chloro-5-(4-bromophenylthio)-4-aminopyridine was 9.2 g.

[0093] Step 2. To a 500 mL round flask was added 2-chloro-5-(4-bromophenylthio)-4-aminopyridine (11 g, 35 mmol), and 600 mL of AcOH. To this clear solution, Bu'ONO (3.6 g, 35 mmol) was added drop by drop. After stirring at room temperature for 1 hr, another 15 mmol of Bu'ONO was added. The mixture was continued to stir for another 2 h. The reaction was quenched by water, and the

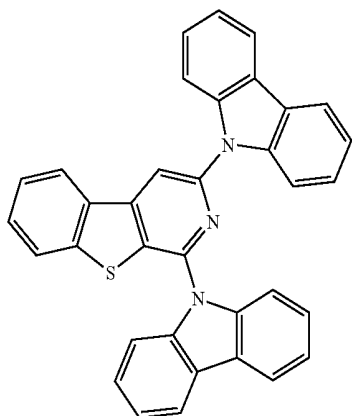
product was purified by a silica gel column. Yield of 3-chloro-6-bromo-[1]Benzothieno[2,3-c]pyridine was 10 g. **[0094]** Step 3. To a 500 mL round flask was added 3-chloro-6-bromo-[1]Benzothieno[2,3-c]pyridine (3.0 g, 10 mmol), carbazole (4.2 g, 25 mmol), Pd(OAc)<sub>2</sub> (0.1 g, 0.5 mmol), P(Bu<sup>t</sup>)<sub>3</sub> (1M in toluene, 1.5 mL, 1.5 mmol), sodium t-butoxide (6.3 g, 66 mmol), and 250 mL of xylene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield was 4.2 g. The product was further purified by vacuum sublimation. <sup>1</sup>H NMR results confirmed the desired compound.

## Example 3

## Synthesis of Compound 3

**[0095]**

Compound 3



**[0096]** Step 1. To a 500 mL round flask was added 2,6-dichloro-3-iodo-4-aminopyridine (7.0 g, 28.8 mmol), thiophenol (3.2 g, 34.8 mmol), CuI (0.2 g, 1.2 mmol), ethylene glycol (3.0 g, 57.6 mmol), potassium carbonate (6.6 g, 57.6 mmol), and 200 mL of isopropanol. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield of 2,6-dichloro-3-phenylthio-4-aminopyridine was 4.0 g.

**[0097]** Step 2. To a 500 mL round flask was added 2,6-dichloro-3-phenylthio-4-aminopyridine (4.0 g, 14.7 mmol), and 200 mL of AcOH. To this clear solution, Bu<sup>t</sup>ONO (1.5 g, 15 mmol) was added drop by drop. After stirring at room temperature for 1 h, another 8 mmol of Bu<sup>t</sup>ONO was added. The mixture was continued to stir for another 2 h. The reaction was quenched by water, and the product was purified by a silica gel column. Yield of 1,3-dichloro-[1]Benzothieno[2,3-c]pyridine was 3.2 g.

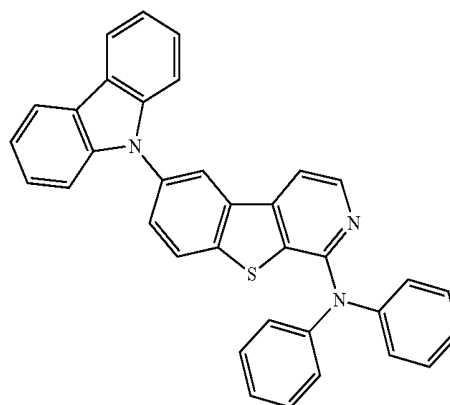
**[0098]** Step 3. To a 500 mL round flask was added 1,3-dichloro-[1]Benzothieno[2,3-c]pyridine (2.5 g, 10 mmol), carbazole (4.2 g, 25 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.9 g, 1.0 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 1.6 g, 4.0 mmol), sodium t-butoxide (4.8 g, 50 mmol), and 200 mL of xylene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield was 4.2 g. The product was further purified by vacuum sublimation. <sup>1</sup>H NMR results confirmed the desired compound.

## Example 4

## Synthesis of Compound 4

**[0099]**

Compound 4



**[0100]** Step 1. To a 500 mL round flask was added 1-chloro-6-bromo-[1]Benzothieno[2,3-c]pyridine (5.0 g, 16.7 mmol), carbazole (2.8 g, 16.7 mmol), Pd(OAc)<sub>2</sub> (0.1 g, 0.4 mmol), P(Bu<sup>t</sup>)<sub>3</sub> (1.0 M solution in toluene, 1.2 mL, 1.2 mmol), sodium t-butoxide (4.8 g, 50.1 mmol), and 400 mL of xylene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield of 1-chloro-6-(9-carbazole)-[1]Benzothieno[2,3-c]pyridine was 1.9 g.

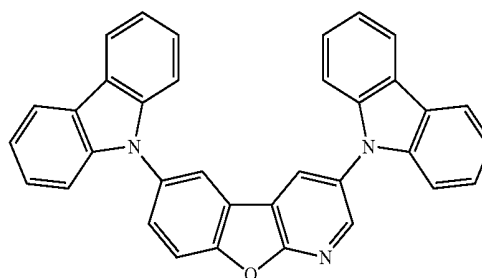
**[0101]** Step 2. To a 500 mL round flask was added 1-chloro-6-(9-carbazole)-[1]Benzothieno[2,3-c]pyridine (1.3 g, 3.4 mmol), diphenylamine (0.7 g, 4.0 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.09 g, 0.1 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.2 g, 0.4 mmol), sodium t-butoxide (0.8 g, 8.0 mmol), and 100 mL of toluene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield of compound 4 was 1.1 g.

## Example 5

## Synthesis of Compound 21

**[0102]**

Compound 21



**[0103]** Step 1. The solution of 2-amino-5-chloropyridine (10.0 g, 77.8 mmol) potassium acetate (7.63 g, 77.8 mmol) in 100 mL of acetic acid was heated to 85° C. and CLI (12.6 g, 77.8 mmol) in 50 mL of acetic acid was added dropwise.

Reaction mixture was kept 2 h at this temperature, diluted with 1 L of water, neutralized with NaOH 1N solution to pH 7 and extracted with ethyl acetate (4×75 mL). Organic fraction were combined, washed with NaHCO<sub>3</sub>, filtered through celite and evaporated. The residue was subjected to column chromatography on silica (eluent—hexane/ethyl acetate 1/1) providing 5-chloro-3-iodopyridin-2-amine as yellow solid (11.9 g, 60%).

**[0104]** Step 2. Mixture of 5-chloro-2-methoxyphenylboronic acid (5.0 g, 26.8 mmol), 5-chloro-3-iodopyridin-2-amine (6.83 g, 26.8 mmol), sodium carbonate (8.53 g, 80.5 mmol in 50 mL of water), Pd(PPh<sub>3</sub>)<sub>4</sub> (621 mg, 2. mol.%) and 100 mL of toluene was refluxed overnight under N<sub>2</sub>. reaction mixture was cooled down to room temperature, organic layer was separated and concentrated in vacuum. The residue was subjected to column chromatography on silica gel with hexane/ethyl acetate gradient mixture as eluent, providing 3.3 g (46% yield) of 5-chloro-3-(5-chloro-2-methoxyphenyl)pyridin-2-amine.

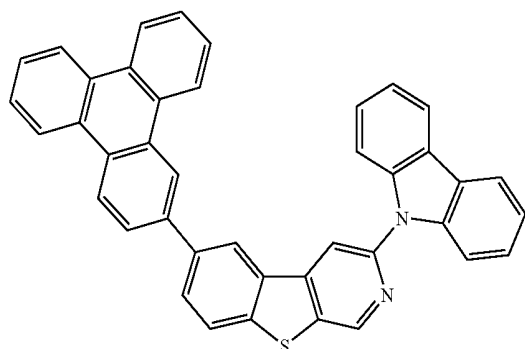
**[0105]** Step 3. Solution of 5-chloro-3-(5-chloro-2-methoxyphenyl)pyridin-2-amine (5.2 g, 19.3 mmol) in 50 mL of glacial acetic acid and 20 mL of THF was cooled down to -10° C. and tert-butyl nitrite (4.6 mL) was added dropwise. The reaction mixture was stirred overnight at 0° C., warmed to room temperature, diluted with 100 mL of water. Solid material was filtered and dried, providing 2.9 g of pure 3,6-dichlorobenzofuro[2,3-b]pyridine.

**[0106]** Step 4. The mixture of 3,6-dichlorobenzofuro[2,3-b]pyridine (2.86 g, 12.01 mmol), carbazole (5.02 g, 30.003 mmol), sodium tert-butoxide (4.62 g, 48.05 mmol), 2-dicyclohexyl-phosphino-2',6'-dimethoxybiphenyl (S-Phos, 430 mg), Pd<sub>2</sub>(dba)<sub>3</sub> (910 mg) in 150 mL of dry xylenes was refluxed under N<sub>2</sub> for 48 h. Then reaction mixture was cooled down to room temperature, diluted with 100 mL H<sub>2</sub>O and extracted with ethyl acetate (4×50 mL). Organic fractions were combined, dried over Na<sub>2</sub>SO<sub>4</sub> anhydr., filtered and evaporated. The residual material was purified by column chromatography on silica gel (eluent—gradient mixture hexane-dichloromethane), then crystallized from hexane/dichloromethane mixture, providing target material as white tiny needles. Additional purification by sublimation (288° C. at 10<sup>-5</sup> mm Hg) resulted 1.86 g of pure target compound.

#### Example 6

##### Synthesis of Compound 39

**[0107]**



Compound 39

**[0108]** Step 1. The mixture of 3-chloro-6-bromo-[1]benzothieno[2,3-c]pyridine (1.7 g, 5.8 mmol), triphenylboronic acid (1.6 g, 5.8 mmol), potassium phosphate tribasic (3.7 g, 17 mmol), 200 mL toluene and 10 mL water was prepared and bubbled with nitrogen for twenty minutes. Then the tris(dibenzylideneacetone)dipalladium (53 mg, 0.060 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (96 mg, 0.23 mmol) were added. The mixture was bubbled with nitrogen for another twenty minutes. After refluxed overnight under nitrogen, then reaction mixture was cooled to room temperature and filtered through a silica plug and washed with dichloromethane. The first several portions were discarded since they only contained impurities. The combined filtrate was concentrated to give crude product, which was recrystallized from hot dichloromethane and hexanes to give 1.8 g 3-chloro-6-(2-triphenylenyl)-[1]Benzothieno[2,3-c]pyridine as yellow solid (4.0 mmol, 70% yield).

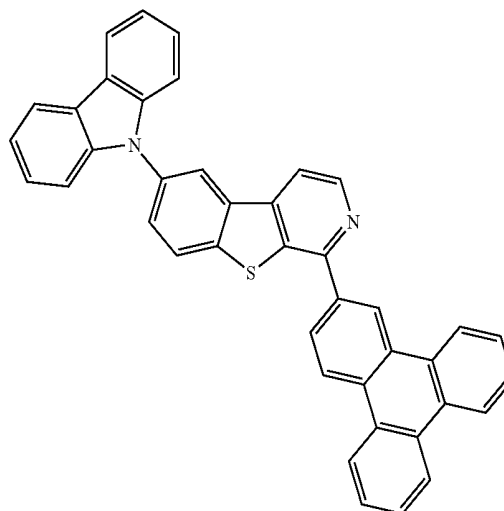
**[0109]** Step 2. The mixture of 3-chloro-6-(2-triphenylenyl)-[1]Benzothieno[2,3-c]pyridine (1.6 g, 3.6 mmol), carbazole (0.72 g, 4.3 mmol), Pd(OAc)<sub>2</sub> (20 mg, 0.090 mmol), sodium t-butoxide (1.0 g, 11 mmol), and 300 mL of xylene was prepared and bubbled with nitrogen for 15 minutes. Then PBu<sub>3</sub> (1.0 M solution in toluene, 0.27 mL, 0.27 mmol) was added and the mixture was bubbled with nitrogen for another 15 minutes. After refluxed overnight, the reaction mixture was cooled to room temperature and filtered through a silica gel plug, which was then washed with dichloromethane. The xylene portion was discarded. The combined dichloromethane filtrate was concentrated and the crude product was stirred in 100 mL mixture of 20% dichloromethane in hexanes overnight. The residue was collected by filtration to give 1.7 g light yellow solid (2.9 mmol, 80% yield).

#### Example 7

##### Synthesis of Compound 59

**[0110]**

Compound 59



**[0111]** Step 1. The mixture of 1-chloro-6-(9-carbazole)-[1]benzothieno[2,3-c]pyridine (1.0 g, 1.6 mmol), triph-



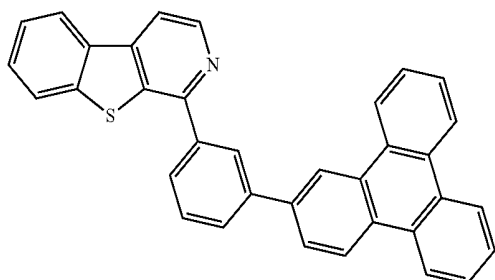
enylen-2-ylboronic acid (0.85 g, 3.1 mmol), potassium phosphate tribasic (1.7 g, 7.8 mmol), 100 mL toluene and 5 mL water was prepared and bubbled with nitrogen for twenty minutes. Then the tris(dibenzylideneacetone)dipalladium (24 mg, 0.030 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (43 mg, 0.10 mmol) were added. The mixture was bubbled with nitrogen for another twenty minutes. After refluxed overnight under nitrogen, the reaction was cooled to room temperature and concentrated. The obtained solid was redissolved in 800 mL refluxing toluene and filtered through a thin celite plug. The collected filtrate was concentrated to about 100 mL and then refluxed under nitrogen for one hour. After slowly cooled to room temperature, the precipitation was collected by filtration. The residue was stirred in 100 mL hot mixture of 20% dichloromethane in methanol and stirred overnight after it cooled to room temperature. The residue was collected by filtration and dried under vacuum to provide 1.2 g white solid (2.1 mmol, 81% yield).

#### Example 8

##### Synthesis of Compound 66

[0112]

Compound 66



[0113] Step 1. To a 250 mL round flask was added 2-chloro-3-iodo-4-aminopyridine (5.0 g, 19.6 mmol), thiophenol (2.16 g, 19.6 mmol), CuI (0.187 g, 0.98 mmol), ethylene glycol (2.5 g, 39 mmol), potassium carbonate (5.4 g, 39 mmol), and 150 mL of isopropanol. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield (91%) of 2-chloro-3-phenylthio-4-aminopyridine was 4.2 g.

[0114] Step 2. To a 250 mL round flask was added 2-chloro-3-phenylthio-4-aminopyridine (2.7 g, 11.4 mmol), and 60 mL of glacial AcOH. To this clear solution, Bu'ONO (1.36 g, 11.45 mmol) was added drop by drop. After stirring at room temperature for 1 h, another (1.36 g 11.45) mmol of Bu'ONO was added. The mixture was continued to stir at room temperature for 18 h. The reaction was quenched by water, and the product was purified by a silica gel column. Yield (88%) of 1-chloro-benzothieno[2,3-c]pyridine was 2.2 g.

[0115] Step 3. The mixture of 1-chloro-benzothieno[2,3-c]pyridine (1.5 g, 6.8 mmol), 3-(triphenyl-2-yl)phenylboronic acid (2.5 g, 7.2 mmol), synthesized according to U.S. Provisional Application Ser. No. 60/963,944, potassium phosphate tribasic (4.4 g, 20.4 mmol), 100 mL toluene and 10 mL water was prepared and bubbled with nitrogen for

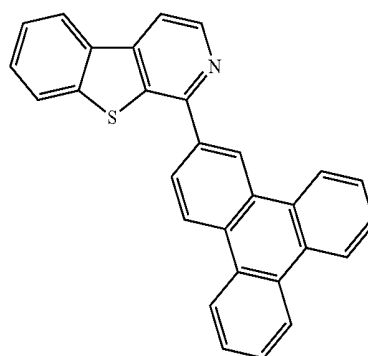
fifteen minutes. Then the tris(dibenzylideneacetone)dipalladium (63 mg, 0.068 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (116 mg, 0.28 mmol) were added. The mixture was bubbled with nitrogen for another twenty minutes. After refluxed overnight under nitrogen, the reaction mixture was cooled to room temperature. The product was purified by silica gel chromatography column. ~2.7 g (81%) Compound 66 was obtained.

#### Example 9

##### Synthesis of Compound 70

[0116]

Compound 70



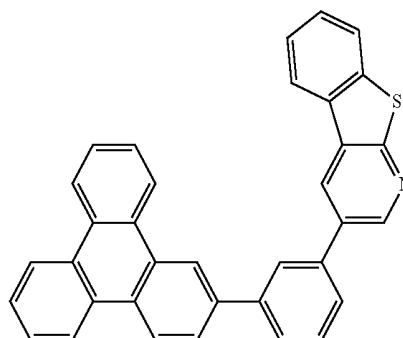
[0117] Step 1. The mixture of 1-chloro-benzothieno[2,3-c]pyridine (1.0 g, 4.5 mmol), 2-triphenyleneboronic acid (1.25 g, 4.5 mmol), synthesized according to U.S. Provisional Application Ser. No. 60/963,944, potassium phosphate tribasic (3.0 g, 18.0 mmol), 100 mL toluene and 10 mL water was prepared and bubbled with nitrogen for fifteen minutes. Then the tris(dibenzylideneacetone)dipalladium (42 mg, 0.045 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (77 mg, 0.18 mmol) were added. The mixture was bubbled with nitrogen for another twenty minutes. After refluxed overnight under nitrogen, the reaction mixture was cooled to room temperature. The product was purified by silica gel chromatography column. ~1.5 g (84%) Compound 70 was obtained.

#### Example 10

##### Synthesis of Compound 71

[0118]

Compound 71



**[0119]** Step 1. The solution of 2-amino-5-chloropyridine (10.0 g, 77.8 mmol) potassium acetate (7.63 g, 77.8 mmol) in 100 mL of acetic acid was heated to 85° C. and ClI (12.6 g, 77.8 mmol) in 50 mL of acetic acid was added dropwise. Reaction mixture was kept 2 h at this temperature, diluted with 1 L of water, neutralized with NaOH 1N solution to pH 7 and extracted with ethyl acetate (4×75 mL). Organic fraction were combined, washed with NaHCO<sub>3</sub>, filtered through celite and evaporated. The residue was subjected to column chromatography on silica (eluent—hexane/ethyl acetate 1/1) providing 5-chloro-3-iodopyridin-2-amine as yellow solid (11.9 g, 60%).

**[0120]** Step 2. Mixture of 2-(methylthio)phenylboronic acid (5.0 g, 29.8 mmol), 5-chloro-3-iodopyridin-2-amine (7.56 g, 29.8 mmol), sodium carbonate (9.0 g, in 50 mL of water), Pd(PPh<sub>3</sub>)<sub>4</sub> (621 mg) and 100 mL of toluene was refluxed overnight under N<sub>2</sub>. reaction mixture was cooled down to room temperature, organic layer was separated and concentrated in vacuum. The residue was subjected to column chromatography on silica gel with hexane/ethyl acetate gradient mixture as eluent, providing 3.5 g of 5-chloro-3-(2-(methylthio)phenyl)pyridin-2-amine.

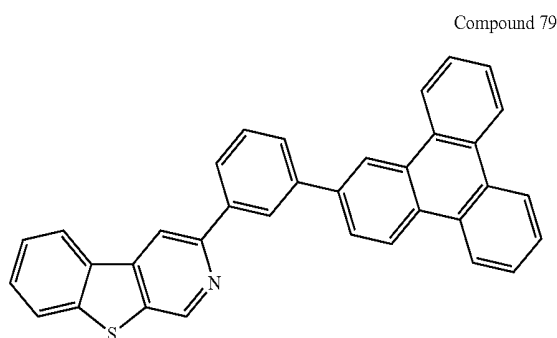
**[0121]** Step 3. Solution of 5-chloro-3-(2-(methylthio)phenyl)pyridin-2-amine (5.2 g, 19.3 mmol) in 50 mL of glacial acetic acid and 20 mL of THF was cooled down to -10° C. and tert-butyl nitrite (4.6 mL) was added dropwise. The reaction mixture was stirred overnight at 0° C., warmed to room temperature, diluted with 100 mL of water. Solid material was filtered and dried, providing 2.5 g of pure 3-chlorobenzothieno[2,3-b]pyridine.

**[0122]** Step 4. The mixture of 3-chloro-[1]Benzothieno[2,3-b]pyridine (1.3 g, 5.9 mmol), 4,4,5,5-tetramethyl-2-(3-(triphenyl-2-yl)phenyl)-1,3,2-dioxaborolane (3.1 g, 7.1 mmol), potassium phosphate tribasic (3.8 g, 18 mmol), 100 mL toluene and 10 mL water was prepared and bubbled with nitrogen for fifteen minutes. Then the tris(dibenzylideneacetone)dipalladium (54 mg, 0.060 mmol) and 2-di cyclohexylphosphino-2',6'-dimethoxybiphenyl (97 mg, 0.24 mmol) were added. The mixture was bubbled with nitrogen for another twenty minutes. After refluxed overnight under nitrogen, the reaction mixture was cooled to room temperature and filtered to collect the precipitation. The residue was washed by methanol and then redissolved in hot toluene. The solution was filtered through a magnesium sulfate plug, which was washed with dichloromethane. The combined filtrate was concentrated to provide 700 mg white solid (1.4 mmol, 24% yield).

#### Example 11

##### Synthesis of Compound 79

**[0123]**



**[0124]** Step 1. To a 250 mL round flask was added 2-chloro-5-iodo-4-aminopyridine (5.0 g, 19.6 mmol), thio-phenol (2.16 g, 19.6 mmol), Cul (0.187 g, 0.98 mmol), ethylene glycol (2.5 g, 39 mmol), potassium carbonate (5.4 g, 39 mmol), and 150 mL of isopropanol. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield (97%) of 2-chloro-3-phenylthio-4-aminopyridine was 4.5 g.

**[0125]** Step 2. To a 250 mL round flask was added 2-chloro-3-phenylthio-4-aminopyridine (3.7 g, 16.8 mmol), and 60 mL of glacial AcOH. To this clear solution, Bu'ONO (1.8 g, 16.8 mmol) was added drop by drop. After stirring at room temperature for 1 h, another (1.8 g 16.8) mmol of Bu'ONO was added. The mixture was continued to stir at room temperature for 18 h. The reaction was quenched by water, and the product was purified by a silica gel column. Yield (33%) of 3-chloro-benzothieno[2,3-c]pyridine was 1.2 g.

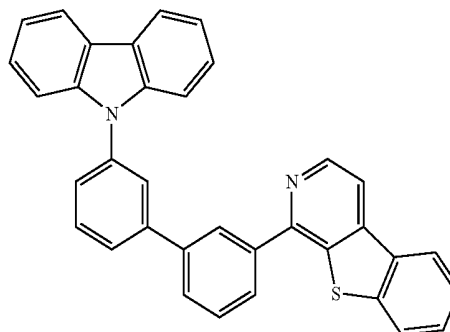
**[0126]** Step 3. The mixture of 3-chloro-benzothieno[2,3-c]pyridine (1.0 g, 4.5 mmol), 3-(triphenyl-2-yl)phenylboronic acid (2.1 g, 4.8 mmol), synthesized according to U.S. Provisional Application Ser. No. 60/963,944, potassium phosphate tribasic (2.9 g, 13.5 mmol), 100 mL toluene and 10 mL water was prepared and bubbled with nitrogen for fifteen minutes. Then the tris(dibenzylideneacetone)dipalladium (63 mg, 0.068 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (116 mg, 0.28 mmol) were added. The mixture was bubbled with nitrogen for another twenty minutes. After refluxed overnight under nitrogen, the reaction mixture was cooled to room temperature. The product was purified by silica gel chromatography column. ~1.2 g (55%) Compound 79 was obtained.

#### Example 12

##### Synthesis of Compound 80

**[0127]**

Compound 80



**[0128]** Step 1. Carbazole (7.3 g, 43.7 mmol), 3-bromiodobenzene (25 g, 87.3 mmol) and sodium t-butoxide (8.4 g, 87.3 mmol) is suspended in 150 mL of dry xylene under nitrogen atmosphere. Tris(dibenzylideneacetone)dipalladium (200 mg) and 1,1'-bis(diphenylphosphino) ferrocene (400 mg) are added as one portion and the reaction is heated to reflux and stirred under nitrogen atmosphere for 24 h. After cooling the xylene is evaporated and the residue is

subjected to column chromatography on silica gel, providing 3-bromophenyl carbazole (9.5 g, yellow solidified oil).

**[0129]** Step 2. 3-Bromophenyl carbazole (9.5 g, 29.5 mmol), bis(pinacolato)diboron (11.2 g, 44.2 mmol), potassium acetate (8.7 g), tris(dibenzylideneacetone)dipalladium (200 mg) and 1,1'-bis(diphenylphosphino)ferrocene (400 mg) are suspended in 200 mL of dioxane and heated to reflux under nitrogen atmosphere overnight. After cooling down and evaporation the residue is subjected to column chromatography on silica gel, providing 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole b(6.0 g, colorless crystals).

**[0130]** Step3. 1,3-Dibromobenzene (16 g, 64.9 mmol), 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole b(6.0 g, 11.6 mmol), potassium acetate (saturated solution of 6.6 g in water) and tetrakis(triphenylphosphine)palladium (0) (380 mg) are heated to reflux in 150 mL of toluene overnight under nitrogen atmosphere. After cooling down, evaporation and column chromatography 9-(3'-bromo-[1,1'-biphenyl]-3-yl)-9H-carbazole (5.8 g) is obtained.

**[0131]** Step 4. Reaction of bis(pinacolato)diboron and 9-(3'-bromo-[1,1'-biphenyl]3-yl)-9H-carbazole in dioxane, catalyzed with tris(dibenzylideneacetone)dipalladium and 1,1'-bis(diphenylphosphino)ferrocene with potassium acetate as base in the same conditions as Step 2 provides 9-(3'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)1,1'-biphenyl]-3-yl)-9H-carbazole which is purified by column chromatography on silica gel.

**[0132]** Step 5. 1-Chlorobenzo[4,5]thieno[2,3-c]pyridine (described as Compound 66, Step 2) and 9-(3'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-3-yl)-9H-carbazole are dissolved in toluene (150 mL). Catalyst tris(dibenzylideneacetone)dipalladium, 400 mg and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl, 200 mg and base (potassium phosphate tribasic) are added as one portion and reaction is heated to reflux under nitrogen atmosphere overnight. The product is purified by silica gel column, providing Compound 80.

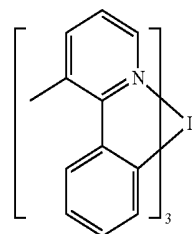
#### Device Examples

**[0133]** All example devices were fabricated by high vacuum ( $<10^{-31}$  Torr) thermal evaporation. The anode electrode is 800 Å of indium tin oxide (ITO). The cathode consisted of 10 Å of LiF followed by 1000 Å of Al. All devices are encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glove box ( $<1$  ppm of  $H_2O$  and  $O_2$ ) immediately after fabrication, and a moisture getter was incorporated inside the package.

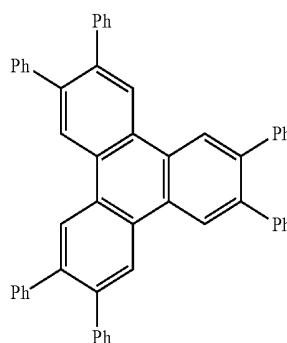
**[0134]** Particular devices are provided wherein P1 is the emissive dopant and an invention compound, Compound 1, Compound 2 or Compound 3, is the host. The organic stack of Device Examples 1-3 consisted of, sequentially from the ITO surface, 100 Å of P1 as the hole injecting layer (HIL), 300 Å of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl ( $\alpha$ -NPD) as the hole transport layer (HTL), 300 Å of the invention compound doped with 15% of P1, an Ir phosphorescent compound, as the emissive layer (EML), 100 Å of invention compound as ETL2 and 400 Å of  $Alq_3$  (tris-8-hydroxyquinoline aluminum) as the ETL1.

**[0135]** Comparative Example 1 was fabricated similarly to the Device Examples, except that the EML comprised CBP as the host doped with 10% of P1, and P2 was used as the blocking layer material.

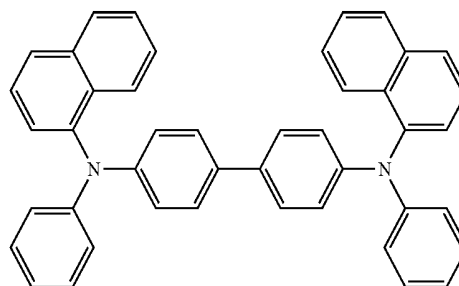
**[0136]** As used herein, the following compounds have the following structures:



P1



P2



NPD

**[0137]** Particular materials for use in an OLED are provided which may lead to devices having particularly good properties. The materials may be used as the host of an emissive layer or as a material in an enhancement layer. The emissive layer materials and blocking layer materials of Device Examples 1-3 are shown in Table 2. The devices were tested and the results measured are provided in Table 3. Cmpd is an abbreviation for Compound. Devices having an emissive layer and a blocking layer using Compounds 1-3 show high device efficiency, long lifetime, and reduced operating voltage.

TABLE 2

Device example	Cmpd	Dopant %	BL
1	1	P1 15%	1
2	2	P1 15%	2
3	3	P1 15%	3
Comparative 1	CBP	P1 10%	P2

TABLE 3

Device example	CIE		$\lambda$ max (nm)	FWHM (nm)	V (V)	At L = 1000 cd/m <sup>2</sup>				At RT 40 mA/cm <sup>2</sup>		
	X	Y				LE (cd/A)	EQE (%)	PE lm/W	LE per EQE	Lo (cd/m <sup>2</sup> )	LT <sub>80%</sub> (hr)	Gnits <sup>2</sup> (hr)
1	0.366	0.602	530	79	5	60.9	16.9	38.4	3.6	17,697	113	35.37
2	0.362	0.605	530	76	5.2	64.3	17.6	38.7	3.7	18,976	85	30.61
3	0.359	0.604	528	76	6	47.6	13.1	24.9	3.6	15582	106	25.81
Comparative 1	0.345	0.615	524	75	5.8	61	16.7	33	3.7	16148	83	21.64

[0138] From Device Examples 1-3, it can be seen that the invention Compounds as hosts in green phosphorescent OLEDs give high device efficiency (i.e., LE >60 cd/A at 1000 cd/m<sup>2</sup>), indicating aza-dibenzothiophene as a chromophore has triplet energy high enough for efficient green electrophosphorescence. Also notable is the high stability of the device incorporating Compounds 1 and 2 as the host. The lifetime, T<sub>80%</sub> (defined as the time required for the initial luminance, L<sub>0</sub>, to decay to 80% of its value, at a constant current density of 40 mA/cm<sup>2</sup> at room temperature) are 113 hrs and 85 hrs for Compounds 1 and 2, respectively, with higher L<sub>0</sub> than the comparative example 1. This translates to a 1.5 fold improvement in the device stability. Thus, the invention compounds may function well as the enhancement layer.

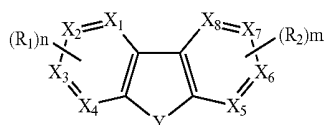
[0139] Another notable feature is that Compounds 1 and 2 both gave lower device voltage, 5 V at 1000 cd/m<sup>2</sup> and 5.2 V at 1000 cd/m<sup>2</sup>, respectively, compared to CBP which has 5.8 V at 1000 cd/m<sup>2</sup>.

[0140] The data suggests that aza-dibenzothiophenes can be excellent hosts and enhancement layer materials for phosphorescent OLEDs, providing higher efficiency, lower voltage and an improvement in device stability multiple times better than the commonly used host, CBP.

[0141] It is understood that the various embodiments described herein are by way of example only, and are not intended to limit the scope of the invention. For example, many of the materials and structures described herein may be substituted with other materials and structures without deviating from the spirit of the invention. The present invention as claimed may therefore includes variations from the particular examples and preferred embodiments described herein, as will be apparent to one of skill in the art. It is understood that various theories as to why the invention works are not intended to be limiting.

We claim:

1. A compound having the formula:



wherein m and n are 0, 1, 2, 3, or 4;

wherein X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, X<sub>5</sub>, X<sub>6</sub>, X<sub>7</sub>, and X<sub>8</sub> are independently selected from the group consisting of a carbon atom and a nitrogen atom;

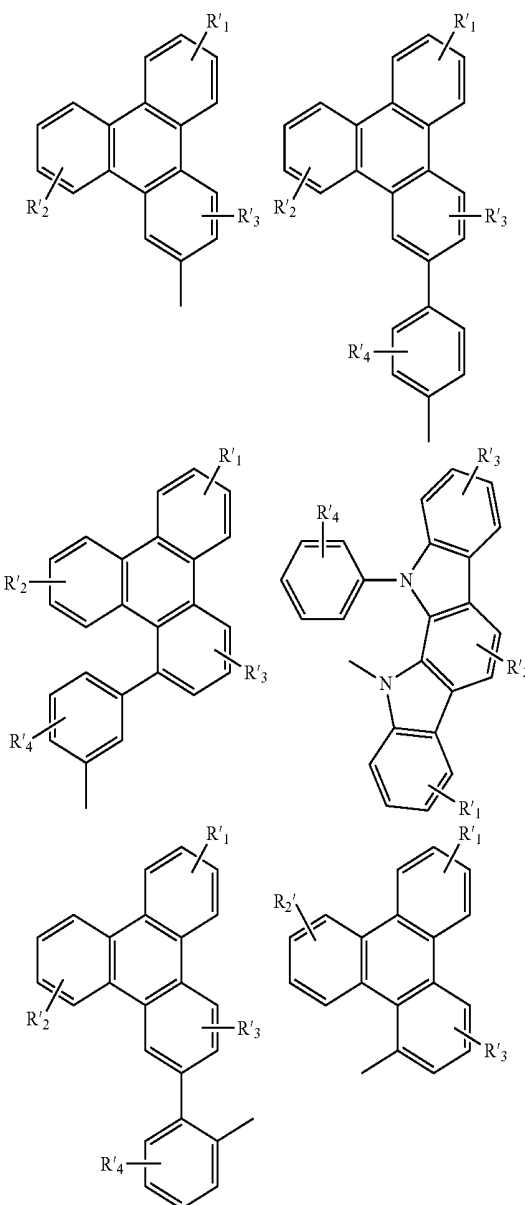
wherein at least one of X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, X<sub>5</sub>, X<sub>6</sub>, X<sub>7</sub>, and X<sub>8</sub> is a nitrogen atom;

wherein Y is S or O;

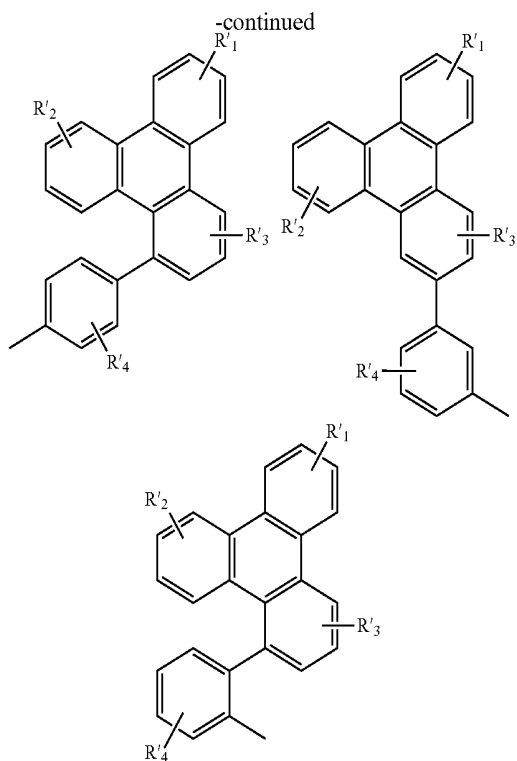
wherein R<sub>1</sub> and R<sub>2</sub> may represent mono, di, tri, or tetra substitutions;

wherein R<sub>1</sub> and R<sub>2</sub> are independently selected from the group consisting of hydrogen, alkyl, aryl and halide; and

wherein at least one of R<sub>1</sub> and R<sub>2</sub> is selected from the group consisting of:

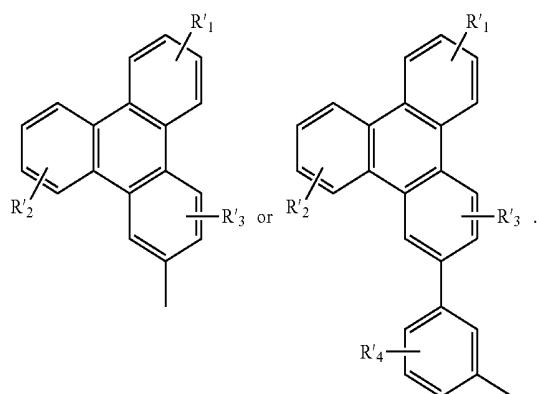


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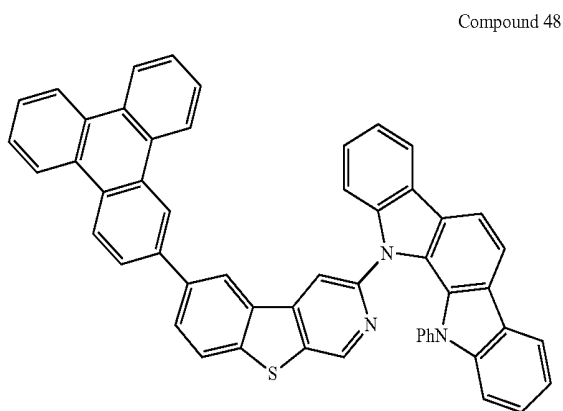
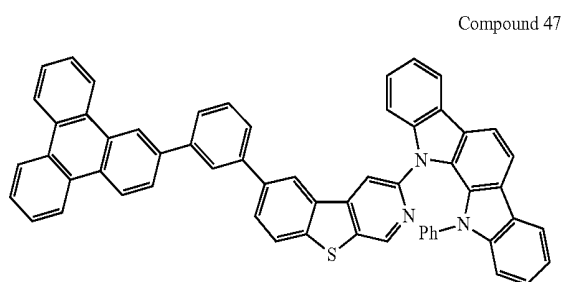
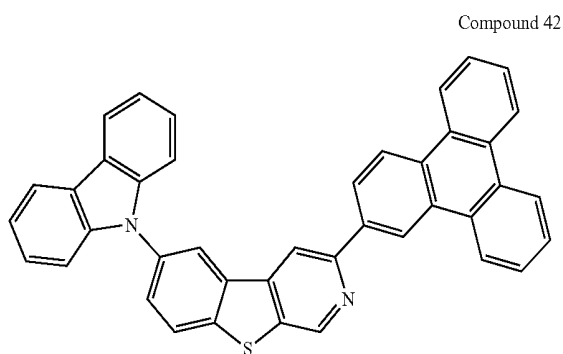
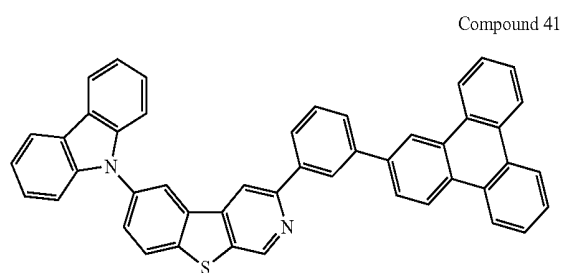
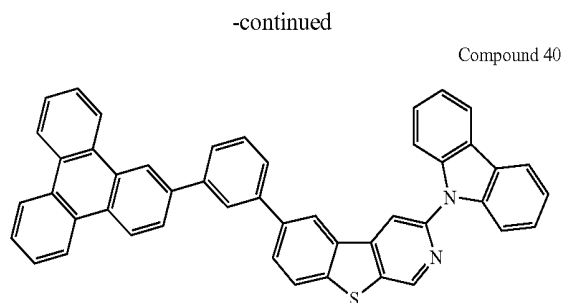
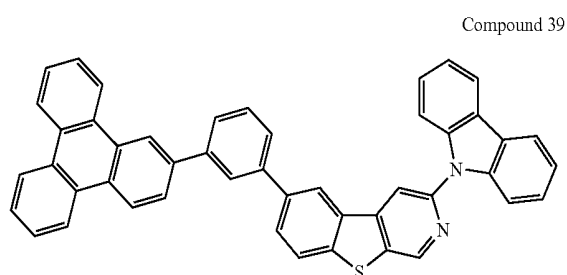
wherein  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  may represent mono, di, tri, tetra or penta substitutions; and wherein  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl.

2. The compound of claim 1, wherein at least one of  $R_1$  and  $R_2$  is



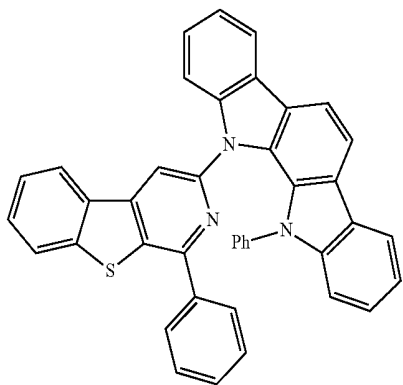
3. The compound of claim 2, wherein  $m+n$  is equal to or greater than 2 and  $m+n$  is equal to or less than 6.

4. The compound of claim 1, wherein the compound is selected from the group consisting of:



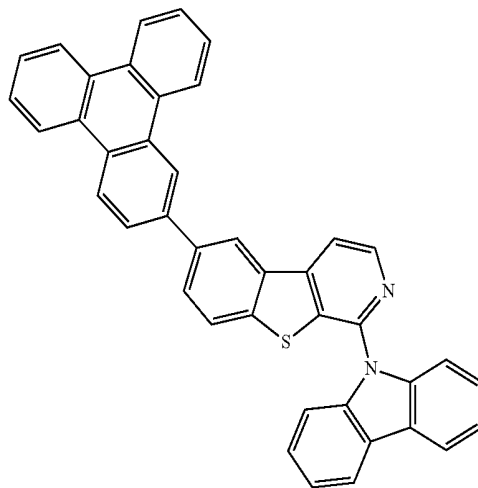
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Compound 49

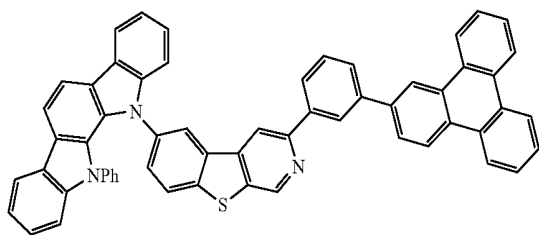


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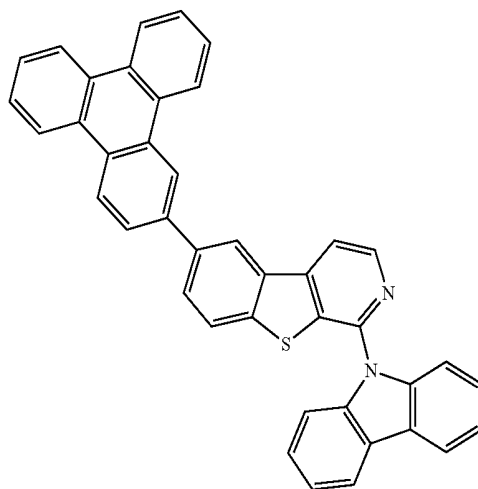
Compound 53



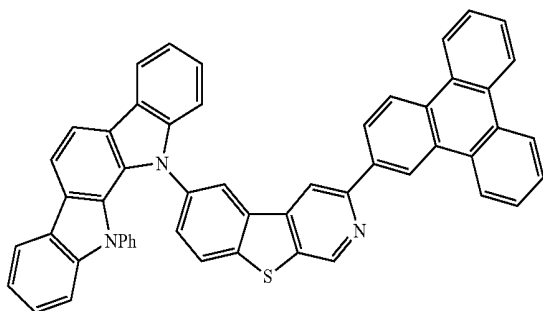
Compound 50



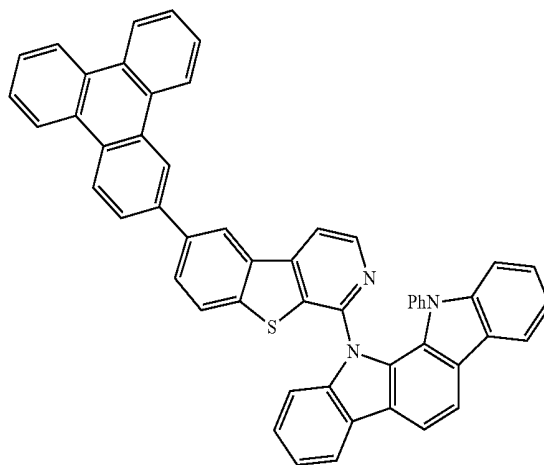
Compound 56



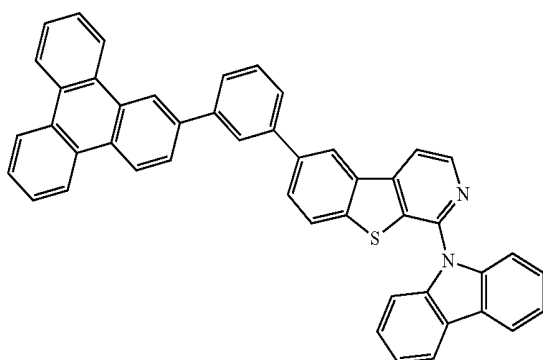
Compound 51



Compound 57

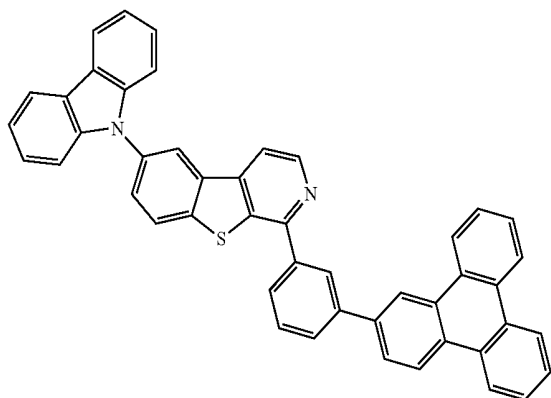


Compound 52



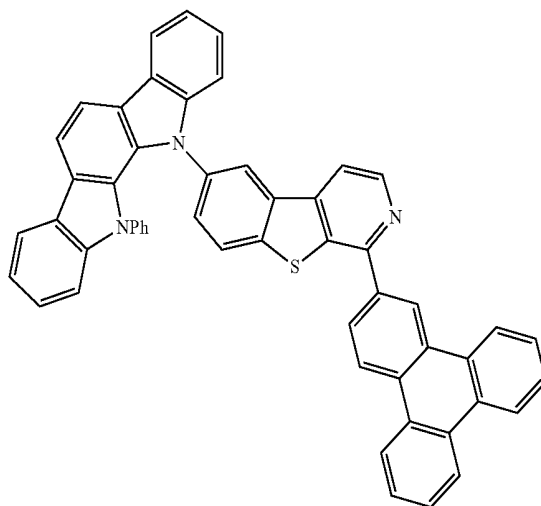
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Compound 58

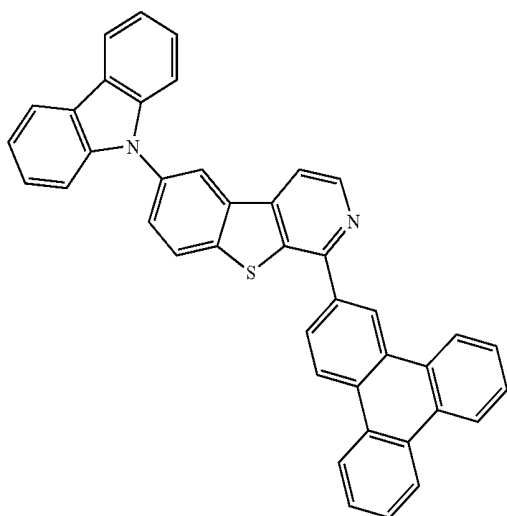


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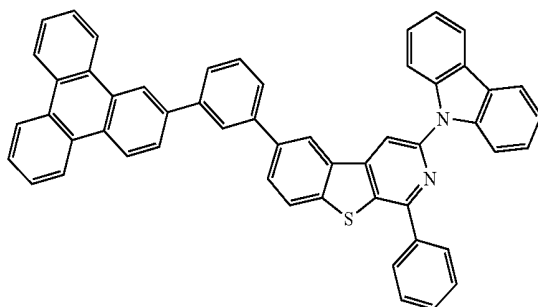
Compound 63



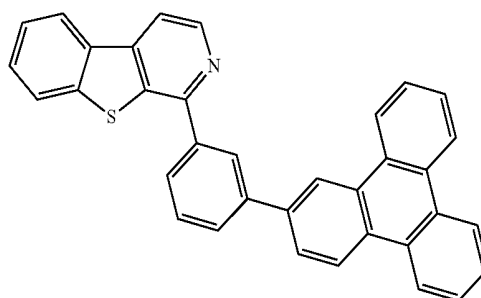
Compound 59



Compound 64

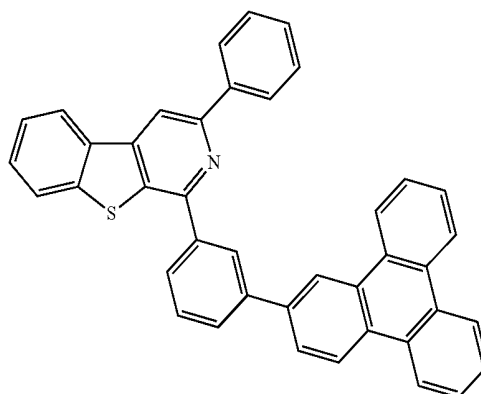
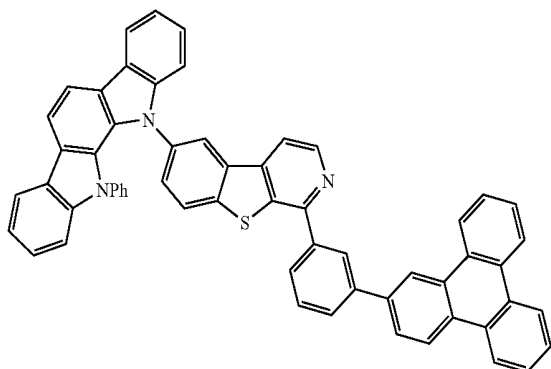


Compound 66



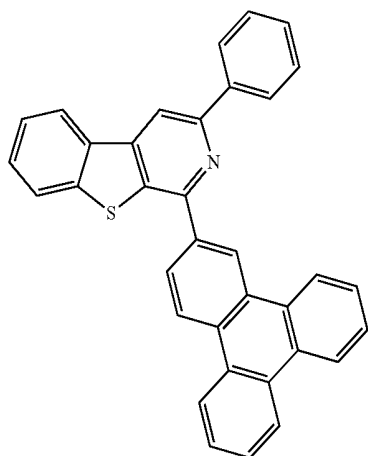
Compound 67

Compound 62



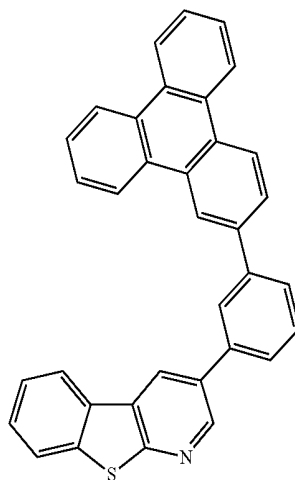
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Compound 68

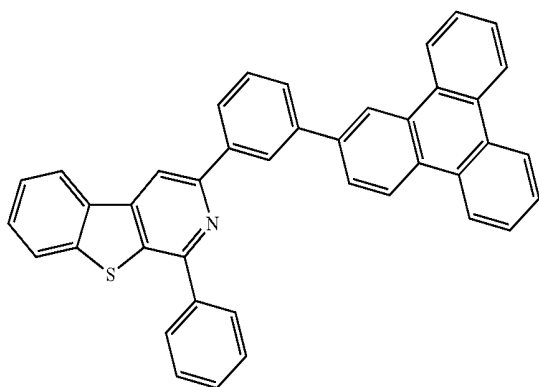


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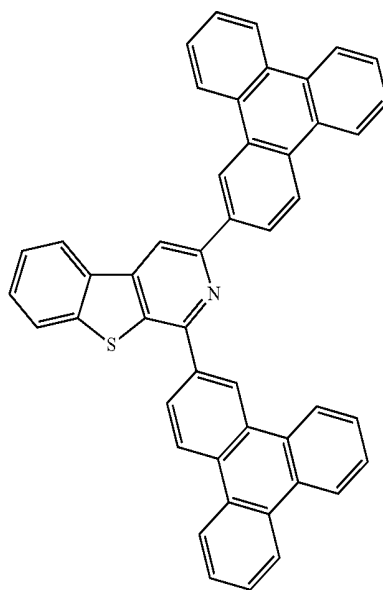
Compound 71



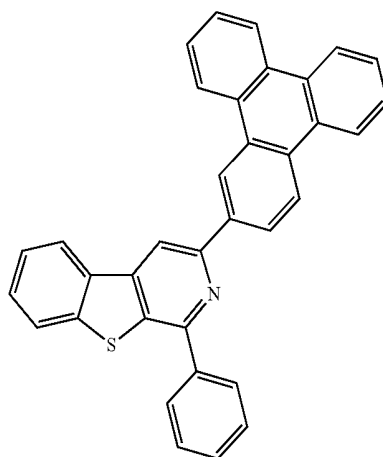
Compound 69



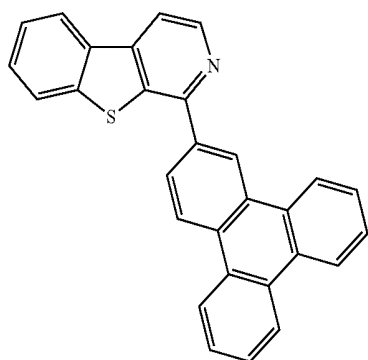
Compound 72



Compound 73



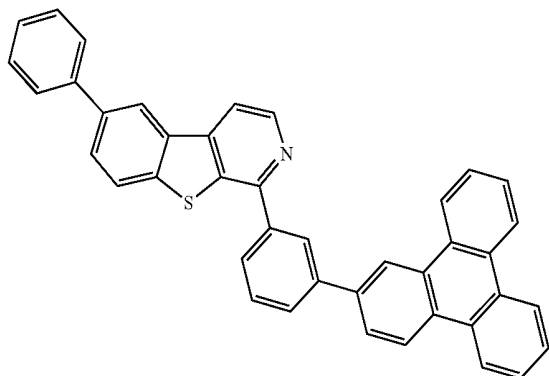
Compound 70



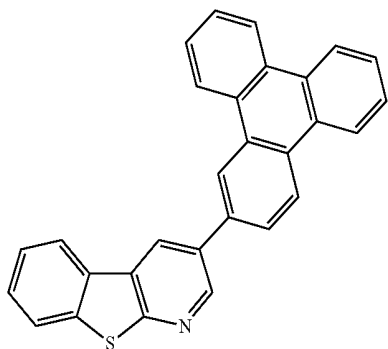


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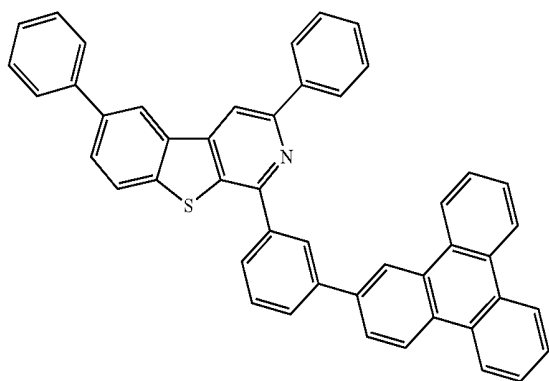
Compound 74



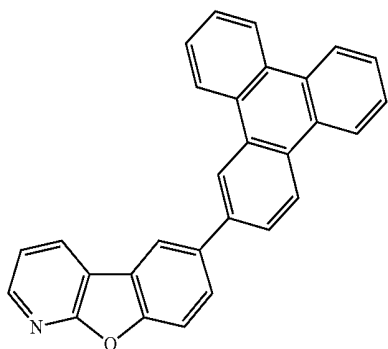
Compound 75



Compound 76

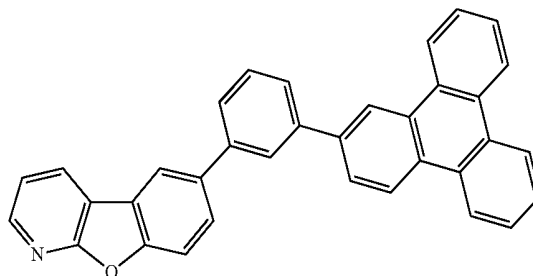


Compound 77

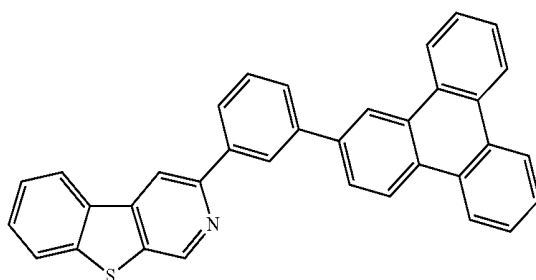


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Compound 78



Compound 79



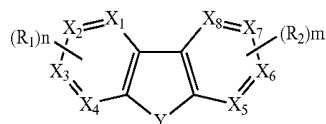
5. A first device comprising an organic light emitting device, further comprising:

an anode;

a cathode;

an organic layer disposed between the anode and the cathode, the organic layer further comprising a compound having the formula:

FORMULA I



wherein m and n are 0, 1, 2, 3, or 4;

wherein X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, X<sub>5</sub>, X<sub>6</sub>, X<sub>7</sub>, and X<sub>8</sub> are independently selected from the group consisting of a carbon atom and a nitrogen atom;

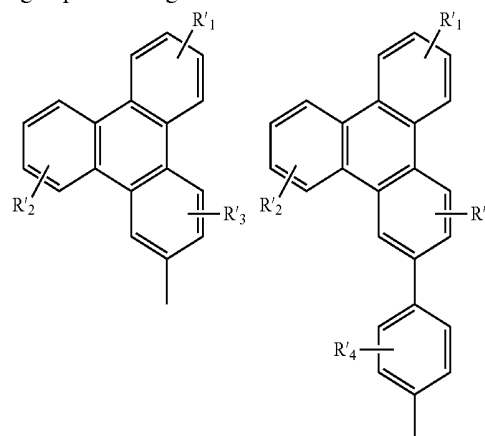
wherein at least one of X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, X<sub>5</sub>, X<sub>6</sub>, X<sub>7</sub>, and X<sub>8</sub> is a nitrogen atom;

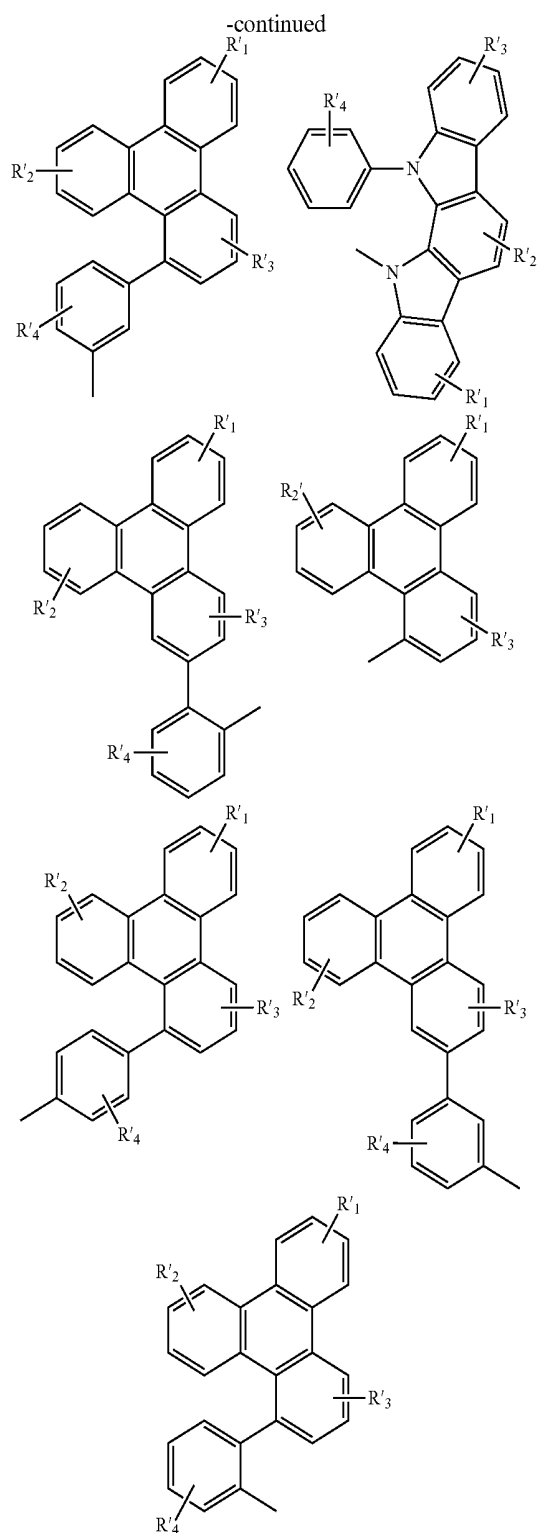
wherein Y is S or O;

wherein R<sub>1</sub> and R<sub>2</sub> represent mono, di, tri, or tetra substitutions;

wherein R<sub>1</sub> and R<sub>2</sub> are independently selected from the group consisting of hydrogen, alkyl, aryl and halide; and

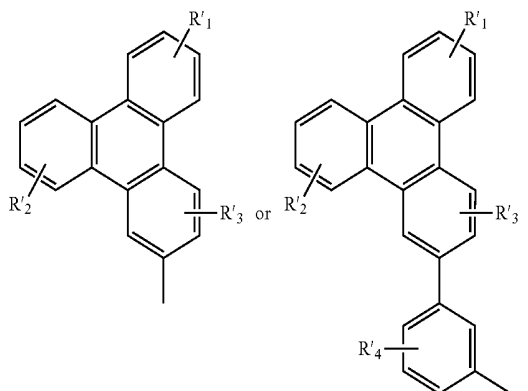
wherein at least one of R<sub>1</sub> and R<sub>2</sub> is selected from the group consisting of:





wherein  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are independently selected from the group consisting of hydrogen, alkyl, heteroalkyl, aryl and heteroaryl.

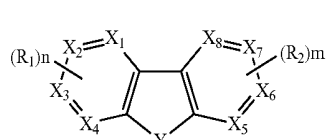
6. The device of claim 5, wherein at least one of  $R_1$  and  $R_2$ , is



7. The device of claim 5, wherein  $m+n$  is equal to or greater than 2 and  $m+n$  is equal to or less than 6.

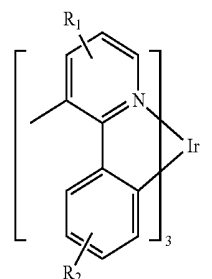
8. The device of claim 5, wherein the first device is a consumer product.

9. The device of claim 5, wherein the organic layer is an emissive layer and the compound having the formula



is a host.

10. The device of claim 5, wherein the organic layer further comprises an emissive dopant and the emissive dopant has the formula:



wherein  $R_1$  and  $R_2$  are each independently selected from the group consisting of hydrogen, alkyl, and aryl.

\* \* \* \* \*

专利名称(译)	有机电致发光材料和器件		
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申请(专利权)人(译)	通用显示器公司		
当前申请(专利权)人(译)	通用显示器公司		
[标]发明人	LIN CHUN MA BIN KWONG RAYMOND DYATKIN ALEXEY BORISOVICH WU YONGGANG ELSHENAWY ZEINAB M		
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#### 摘要(译)

提供了一类含有氮杂 - 二苯并噻吩或氮杂 - 二苯并呋喃的新化合物。该化合物可用于有机发光器件中，从而提供改善的稳定性，改进的效率，长寿命和低操作电压。特别地，该化合物可用作具有主体和发光掺杂剂的发光层的主体材料，或用作增强层中的材料。

