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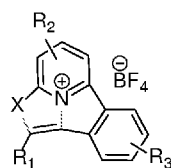
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(54) Title: PYRIDINIUM OXAZOLE DYAD SCAFFOLD AND A PROCESS FOR PREPARATION THEREOF



Formula (I)

(57) Abstract: The present invention relates to a pyridinium oxazole dyad scaffold of formula (I) and a process for the preparation thereof. The present invention further discloses a pyridine compound of formula (II) which is used for the preparation of formula (I) and a process for preparation thereof.



PYRIDINIUM OXAZOLE DYAD SCAFFOLD AND A PROCESS FOR PREPARATION THEREOF

FIELD OF THE INVENTION:

- 5 The present invention relates to a Pyridinium oxazole dyad scaffold of formula (I) and a process for the preparation thereof.

BACKGROUND AND PRIOR ART OF THE INVENTION:

10 The discovery and development of organic fluorophores is essential for progress in many areas of chemistry, biology and functional materials research. As an emerging subclass, fluorescent organic salts are gaining much attention because of their unique properties. Because of their charged nature, they impart high thermal stabilities, phase tunabilities, water-solubility and chemoselective sensing via electrostatic interactions. These unique features have inspired research in a number of areas including fundamental photophysical investigations, sensory materials, and novel materials for display applications, multiphoton excitation (MPE),
15 nanoscopic fluorescent ionic liquids, and LEC cells. In recent years, the highly photostable, less susceptible to environmental change and high specificity bearing a good photoactivatable fluoro-phore are powerful tools in biochemical and biological research such as cell lineage in development, macromolecule tracking in living cells, and super-resolved fluorescence imaging
20 such as photoactivated localization microscopy (PALM), stochastic optical reconstruction microscopy (STORM), etc. Tracking cell organelles like the dynamics of mitochondrial morphology has attracted much research interest because of its involvement in early stage apoptosis and degenerative conditions. Therefore, developing a modular approach to novel organic emissive salts with tunable photophysical properties are highly warranted.

25 Over the last decade, homogeneous gold catalysis has emerged as a powerful tool for building molecular complexity in an atom-economical fashion. Gold catalysts act as π -acid and hence they are capable of activating unsaturated carbon-carbon bonds for the addition of nucleophiles (Scheme 1, path a). While manifestation of gold-catalyzed reactions are likely to be continued
30 in the future, there is an urgent need to enable new modes of reactivities to expand gold-alkyne catalysis toolbox. In recent years, oxidative gold-catalyzed reactions have emerged as a new research field (path b). In 2007, Toste and Zhang independently reported gold(I)-catalyzed oxidative rearrangements of alkynyl sulfoxides which proceed via α -carbonyl gold-carbenoids

formed through oxygen atom transfer from the sulfoxide. On the basis of this reactivity, the research groups of Liu, Davies, Ye, Zhang and others reported a variety of oxidative gold catalyzed reactions.

5 Yet another approach in the oxidative gold catalyzed reaction feature external oxidant-poared Au(I)/Au(III) catalysis, where the metal oxidation state changes during the catalytic cycle. A historical retrospect on the progress in the field of external oxidant-poared Au(I)/Au(III) catalysis reveals that the chemistry is either based on oxidative dimerization reactions of insitu generated vinylgold species (Scheme 1, eq 1) or cross-coupling reactions between respective
10 substrates (eq 2). In recent years, gold-catalyzed aminoarylation/oxyarylation reaction of alkenes and arylboronic acids is emerging as new technique for heterocyclic synthesis (eq 3). Pioneering work from the group of Zhang and Muñiz reported the amination-arylation and diamination of alkenes via Au(I)/Au(III) catalysis (eq 4).

15 Article titled “Homogeneous Gold-Catalyzed oxidative carboheterofunctionalization of alkenes” by Guozhu Zhang et al. published in Journal of American Chemical Society, 2010, 132 (5), pp 1474–1475 reports Homogeneous carboamination, carboalkoxylation and carbolactonization of terminal alkenes are realized via oxidative gold catalysis, providing expedient access to various substituted N- or O-heterocycles. Deuterium-labeling studies
20 established the antinature of the alkene functionalization and the indispensable role of Au(I)/Au(III) catalysis. This study constitutes the first example of catalytically converting C(sp³)–Au bonds into C(sp³)–C(sp²) bonds in a cross-coupling manner and opens new opportunities to study gold alkene catalysis where alkylgold intermediates can be readily functionalized intermolecularly.

25 Article titled “Au(I)/Au(III)-catalyzed Sonogashira-type reactions of functionalized terminal alkynes with arylboronic acids under mild conditions” by Deyun Qian et al. published in Beilstein Journal of Organic Chemistry, 2011; 7: 808–812 reports a straightforward, efficient, and reliable redox catalyst system for the Au(I)/Au(III)-catalyzed Sonogashira cross-coupling
30 reaction of functionalized terminal alkynes with arylboronic acids under mild conditions has been developed.

Article titled “An efficient and recyclable magnetic-nanoparticle-supported Palladium catalyst for the Suzuki Coupling reactions of Organoboronic acids with Alkynyl Bromides” by Xiuli

Zhang et al. published in Synthesis, 2011, 2975-2983 reports a highly active, air- and moisture-stable and easily recoverable magnetic-nanoparticle-supported palladium catalyst enables the Suzuki cross-coupling reaction of alkynyl bromides with organoboron derivatives in very good yields in ethanol. The supported palladium catalyst can be recovered and reused up to 16 times without significant loss of catalytic activity.

Article titled "Gold-catalyzed intramolecular aminoarylation of alkenes: C-C bond formation through bimolecular reductive elimination." by Brenzovich WE Jr et al. published in Angewandte Chemie International Edition, 2010 Jul 26;49(32):5519-22 reports Gold-catalyzed intramolecular aminoarylation of alkenes. Article titled "Gold-catalyzed carbon-heteroatom bond-forming reactions" by A. Corma et al. published in Chemical Reviews, 2011, 111, 1657-1712 reports gold-catalyzed transformations involving any carbon-heteroatom bond formation.

There exists no report on the di-functionalization of alkynes utilising Au(I)/Au(III) catalysis.

There is need to develop tunable molecules for mitochondrial imaging and to develop intramolecular 1,2-aminoxygenation of alkynes to access pyridinium-oxazole dyad salts.

OBJECTIVES OF THE INVENTION:

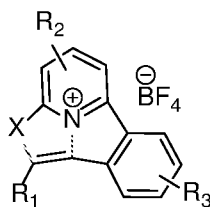
The main objective of the present invention is to provide a pyridinium oxazole dyad scaffold of formula (I) and a process for the preparation thereof.

Another objective of the present invention is to provide a pyridoalkyne compound of formula (II) and a process for the preparation thereof.

Still another objective of the present invention is to provide use of said Pyridinium oxazole dyad scaffold of formula (I).

SUMMARY OF THE INVENTION:

Accordingly, the present invention provides a Pyridinium oxazole dyad scaffold of formula (I);

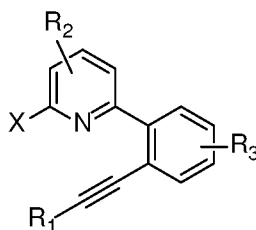


Formula (I)

Wherein; R_1 , R_2 and R_3 are same or different and each is independently selected from the group consisting of H, alkyl groups, alkenyl groups, aryl groups, heteroaryl groups, electron donating as well as electron withdrawing substituents;

- 5 X is selected from the group consisting of -CRR', O, S and -NR wherein R and R' are same or different and each is independently selected from the group consisting of H, alkyl, benzyl, and aryl; further R and R' may form a cyclic ring having 4 to 6 carbon atoms. The scaffold is used for imaging application for diagnosis of disease, wherein said imaging is mitochondrial imaging and said disease is cancer and said scaffold is used as a fluorescent agent for
10 mitochondrial imaging.

In an embodiment, the present invention provides a pyridine compound of formula (II),



Formula (II)

- 15 Wherein; R_1 , R_2 and R_3 are same or different and each is independently selected from the group consisting of H, alkyl groups, alkenyl groups, aryl groups, heteroaryl groups, electron donating as well as electron withdrawing substituents;

X is selected from the group consisting of H, alkyl, benzyl, aryl, -OR, -SR and -NR; wherein R is selected from the group consisting of H, alkyl and aryl

- 20 In an embodiment, the present invention provides a process for the preparation of said Pyridinium oxazole dyad scaffold of formula (I) as claimed in claim 1, wherein said process comprises heating the reaction mixture consisting of pyridine of formula (II), in suitable solvent system in presence of gold catalyst at the temperature ranging from 70 to 80°C for the
25 time period ranging from 6 to 8 hours.

In an embodiment, the said solvent system is selected from group consisting of acetonitrile, dichloromethane, chloroform and toluene.

In an embodiment, the said gold catalyst is selected from group consisting of Chloro(triphenylphosphine)gold(I), Triphenylphosphine Gold(I) Trifluoromethanesulfonate , Chloro[(1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I), Chloro-(2-Biphenyl)dicyclohexylphosphine gold(I), tBuCyJhonAuCl, Chloro-tris(4 fluoro-triphenylphosphine)gold(I) (4-FC6H4)3P-AuCl, Chloro-tris(4 trifluoromethyl-triphenylphosphine)gold(I) and Chloro-Tris(pentafluorophenyl)phosphine) gold (I).

In another embodiment, the present invention provides a process for the preparation of pyridine of formula (II) wherein said process comprising the steps of: degassing the reaction mixture consisting of pyridine derivative, boronic acid in suitable solvent with nitrogen; adding sodium carbonate or potassium carbonate, Palladium catalyst to the reaction mixture of step a under continuous flow of nitrogen; heating the reaction mixture of step b at the temperature ranging from 70 to 80°C for 4 to 10 hours to afford desired product of formula (II).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: Observed fluorescence under UV excitation (365 nm).

Figure 2: *In vitro* imaging in MCF-7 cells. (a1 and b1): MCF-7 cells treated with 1 μ M **3h** for 6 h; Scale bar = 64 and 100 micron. (a2): MCF-7 cells treated with 1 μ M DAPI for 6 h; Scale bar = 64 micron. (b2): MCF-7 cells treated with 1 μ M Mito Tracker Green (MG) for 1 h; Scale bar = 100 micron. (a3): merging of red (a1) and blue (a2) fluorescence images of cells. (b3): merging of red (b1), green (b2) fluorescence images of cells and fluorescence images with DAPI

Figure 3: Absorption of representative derivatives in DCM

Figure 4: Emission of representative derivatives in DCM at RT

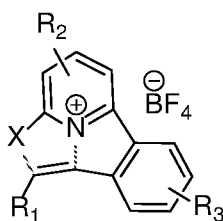
Figure 5: Excitation of representative derivatives in DCM at RT

Figure 6: MTT assay

DETAILED DESCRIPTION OF THE INVENTION

The invention will now be described in detail in connection with certain preferred and optional embodiments, so that various aspects thereof may be more fully understood and appreciated.

The present invention provides a pyridinium oxazole dyad scaffold of formula (I).



Formula (I)

Wherein; R_1 , R_2 and R_3 are selected from the group consisting of H, alkyl groups, alkenyl groups, aryl groups, heteroaryl groups, such as electron donating as well as electron withdrawing substituents; R_1 , R_2 and R_3 may be similar or different;

$X = -CRR'$, O, S, $-NR$ wherein R and R' are same or different and each is independently selected from the group consisting of H, alkyl, benzyl, or aryl; further R and R' may form a cyclic ring having 4 to 6 carbon atoms.

In preferred embodiment, said compound of formula I is tunable in UV region and Tunable emission wavelength depends upon substituents.

In an embodiment, the present invention provides pyridinium-oxazole dyad salts of formula (I) with tunable emission wavelengths.

In another embodiment of the present invention, said pyridinium-oxazole dyad salts of formula (I) can be accessed utilizing gold (I)-catalyzed oxidative intramolecular 1,2-aminoxxygenation reactions, combining gold(I)/gold(III) catalysis.

In still another embodiment, the present invention provides intramolecular 1,2-aminoxxygenation of alkynes to access pyridinium-oxazole dyad salts with tunable emission wavelengths.

In yet another embodiment, the present invention provides di-functionalization of alkynes utilising gold (I)/gold (III) catalysis.

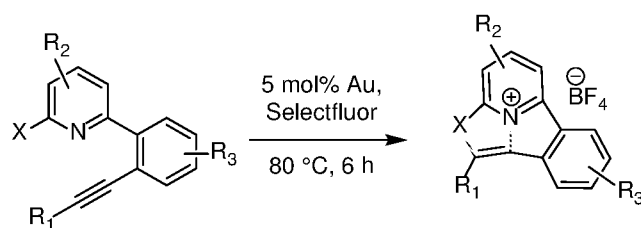
In still yet another embodiment, the present invention provides a process for the preparation of a Pyridinium oxazole dyad scaffold of formula (I) comprises heating the reaction mixture consisting of pyridine of formula (II), Selectfluor in suitable solvent in presence of gold

catalyst at the temperature ranging from 70 to 80°C for the time period ranging from 6 to 8 hours to afford Pyridinium oxazole dyad scaffold.

In preferred embodiment, said pyridinium oxazole dyad scaffold of formula (I) are selected from 1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(naphthalen-1-

- 5 yl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 1-(naphthalen-2-yl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 1-(phenanthren-9-yl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(p-tolyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-isopropylphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-pentylphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-butoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium, 1-(4-fluorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 1-(4-chlorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 1-(4-(dimethylamino)phenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 1-(4-pentanoylphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 1-(2-methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 1-(3-methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 1-(3-chlorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 6-methyl-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 7-methyl-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-iumtetrafluoroborate, 7-fluoro-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 7-chloro-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-phenyldibenzo[a,f]oxazolo[4,3,2-cd]indolizin-12-ium tetrafluoroborate.

The scheme 1 is as shown below

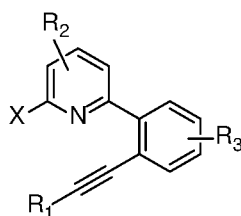


Scheme 1

In another preferred embodiment, said solvent system is selected from acetonitrile (CH₃CN), dichloromethane (CH₂Cl₂), chloroform (CHCl₃) and toluene.

In still another preferred embodiment, said gold catalyst is selected from Chloro(triphenylphosphine)gold(I) (PPh_3AuCl), Triphenylphosphine Gold(I) Trifluoromethanesulfonate (PPh_3AuOTf), Chloro[(1,1'-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) (JohnPhosAuCl), Chloro-(2-Biphenyl)dicyclohexylphosphine gold(I) (CyJohnPhosAuCl), *t*BuCyJhonAuCl, Chloro-tris(4 fluoro-triphenylphosphine)gold(I) ($4\text{-FC}_6\text{H}_4)_3\text{P-AuCl}$, Chloro-tris(4 trifluoromethyl-triphenylphosphine)gold(I) ($4\text{-CF}_3\text{C}_6\text{H}_4)_3\text{PAuCl}$, Chloro-Tris(pentafluorophenyl)phosphine) gold (I) ($\text{C}_6\text{F}_5)_3\text{P-AuCl}$.

In still yet another embodiment, the present invention provides pyridine of formula (II) which is used for the preparation of formula (I).



Formula (II)

Wherein; R_1 , R_2 and R_3 are selected from the group consisting of H, alkyl groups, alkenyl groups, aryl groups, heteroaryl groups, such as electron donating as well as electron withdrawing substituents; R_1 , R_2 and R_3 may be similar or different; $\text{X} = \text{H}$, alkyl, benzyl, aryl, -OR, -SR, -NR; wherein $\text{R} = \text{H}$, alkyl or aryl.

In a preferred embodiment, said compound of formula (II) are selected from 2-(*tert*-butoxy)-6-(2-(phenylethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-(naphthalen-1-ylethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-(naphthalen-2-ylethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-(phenanthren-9-ylethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-(hept-1-yn-1-yl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-(cyclohex-1-en-1-ylethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-(*p*-tolylethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-((4-isopropylphenyl)ethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-((4-pentylphenyl)ethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-((4-methoxyphenyl)ethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-((4-butoxyphenyl)ethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-((4-fluorophenyl)ethynyl)phenyl)pyridine, 2-(*tert*-butoxy)-6-(2-((4-chlorophenyl)ethynyl)phenyl)pyridine,

4-((2-(6-(tert-butoxy)pyridin-2-yl)phenyl)ethynyl)-N,N-dimethylaniline, 1-(4-((2-(6-(tert-butoxy)pyridin-2-yl)phenyl)ethynyl)phenyl)pentan-1-one, 2-(tert-butoxy)-6-(2-((2-methoxyphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((3-methoxyphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((3-chlorophenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-methyl-6-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(5-methyl-2-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(5-fluoro-2-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(5-chloro-2-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(4-chloro-2-(phenylethynyl)phenyl)pyridine, 1-methoxy-3-(2-(phenylethynyl)phenyl)isoquinoline, 2-(tert-butoxy)-6-(2-((2-chloro-5-methoxyphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((3-chloro-4-methylphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(3,5-dimethoxy-2-(phenylethynyl)phenyl)pyridine.

In still yet another embodiment, the present invention provides a process for the preparation of pyridine of formula (II) comprising the steps of

- a) degassing the reaction mixture consisting of pyridine derivative, boronic acid in suitable solvent with nitrogen;
- b) adding sodium carbonate or potassium carbonate, Palladium catalyst to the reaction mixture of step a under continuous flow of nitrogen;
- c) heating the reaction mixture of step b at the temperature ranging from 70 to 80°C for 4 to 10 hours to afford desired product of formula (II).

In preferred embodiment, said boronic acid of step (a) is 2-alkynyl aryl boronic acid preferably 2-alkynyl phenyl boronic acid.

In another preferred embodiment, said solvent is DMF/H₂O in ratio 1:1.

In still another preferred embodiment, said Palladium catalyst of step (b) is PdCl₂(PPh)₂.

In yet another embodiment, the present invention provides use of said compound of formula I for imaging application, particularly mitochondrial imaging for diagnosis of cancer.

In a preferred embodiment, said compound of formula I is used as a fluorescent agent for mitochondrial imaging.

In still yet another embodiment, the present invention provides cytotoxicity evaluation study of compound of formula I preferably **3n** using a 3-(4,5-dimethyl-2-thiazolyl)- 2,5-diphenyl tetrazolium bromide (MTT) assay (Fig. 6).

- 5 In still yet another embodiment, the present invention provides assessment of compound of formula I preferably **3n** for its ability to localize and stain mitochondria in living cells by fluorescence microscope.

The novel compounds of the invention are brightly fluorescent. The compounds and the salts thereof are class of fluorescent materials containing a pyridinium-oxazole functional group. The photo- physical properties of representative salts are studied in CH₂Cl₂ at RT (Fig 1). The corresponding absorption, emission and excitation, spectra are depicted in Figures 3, 4 and 5. The photoluminescence spectra of salts show intense peaks between λ_{em} : 400–560 nm (Figure 1) with Stokes shifts varies between (30-80 nm) which reveals violet-to-yellow fluorescence emissions depending on the functional group present in the salts. The compounds display good quantum yields upto 0.76.

The novel compounds of the invention may be useful as Organic light emitting diodes (OLED) materials for solution processing.

- 20 Table 1 shows Spectral properties of representative derivatives in DCM at Room temperature (RM) (10⁻⁵ M)

Table 1: Spectral properties of representative derivatives in DCM at RM (10⁻⁵ M)

Comp	λ_{abs} (nm) ^a	λ_{em} (nm) ^b	λ_{ex} (nm) ^c	Δ_{Stokes} (nm) ^d	Φ_f^e	τ_f (nm) ^f
3a	368	404	338	036	0.10	1.2
3m	370	410	339	040	0.19	1.7
3l	372	414	343	042	0.09	0.9
3q	376	455	332	079	0.20	2.0
3j	405	458	338	053	0.42	2.4
3c	410	481	364	071	0.49	5.2
3d	411	487	365	076	0.54	7.2
3n	506	555	511	049	0.76	9.1

a The maximum absorption bands more than 300nm; b Excited at the longest maximum absorption band in CH₂Cl₂; ^cExcited wavelength; ^d Stokes shift= $\lambda_{em} - \lambda_{abs}$; ^eQuinine sulfate and rhodamine 6G was used as the standard; ^f Fluorescent lifetime

5

The current invention provides compounds that display brightly fluorescence as well as a good ϕ_f . The salts are a novel class of fluorescent materials that contain a pyridinium-oxazole functional group and the photo- physical properties of representative salts are studied in CH₂Cl₂ at RT The absorption and excitation maxima, the photoluminescence (PL) maxima and
10 quantum yields (FF), as well as the excited state lifetimes (t_f) of these compounds in CH₂Cl₂ solution are listed in Tables 3, whereas the corresponding absorption, emission, excitation spectra are depicted in Figures 3, 4 and 5. The photoluminescence spectra of salts show intense peaks between λ_{em} : 400–560 nm (Table 3) with Stokes shifts varies between (30-80 nm) which reveals violet-to-yellow fluorescence emissions depending on the functional group present in
15 the salts. Substituents like chloro and fluoro on the core had only a modest effect on the fluorescent properties (3l and 3j). When phenyl ring replaced by bulky substituents like 2-naphthyl and 9-phenanthryl on the core had stronger effect on the fluorescent properties (3c and 3d). The presence of stronger donar group like -NMe₂ leads to significant bathochromic shifts in emission (4a and 4h, and Figure 1). These observations are indicative of a predominant π - π^*
20 character for the lowest excited state, and the life time t_f values are consistent with a singlet multiplicity. Most of these compounds display good quantum yields upto 0.76 (3n). The radiative rate constants are barely affected by the substitution pattern, an indication of the similar excited state character for all compounds.

25 **Examples** Following examples are given by way of illustration therefore should not be construed to limit the scope of the invention.

Example 1: General procedure for sonogashira cross coupling of aryl iodides with different substituted acetylenes

30 A suspension of (un)substituted 2-bromiodobenzene (2 gm, 7.06 mmol), PdCl₂(PPh₃)₂ (99.2 mg, 0.14 mmol, 2 mol%), Cu(I) iodide (40.2 mg, 0.21 mmol, 3 mol%) in 20 mL of triethylamine was degassed three times. After 10 min a solution of (un)substituted aryl/alkyl acetylene (0.84 mL, 7.77 mmol, 1.1 eq) in Et₃N (3.6 mL) is added dropwise over 5 min via syringe and the reaction mixture is left to stir for 12 h and monitored by TLC. After total

consumption of the 2-bromoiodobenzene, the reaction mixture was filtered through celite and extracted with EtOAc (3 × 10 mL). The organic layer was washed with a saturated solution of NH₄Cl (2 × 10 mL), water (2 × 10 mL), dried over Na₂SO₄ and the solvent was removed under vacuo. The reaction mixture was purified by flash chromatography on silica gel, (eluent: pet. ether) to give the product (un)substituted bromo benzene as a yellow oil (**S1**, Yield 88%).

Example 2: General procedure for preparation of 2-alkynylphenylboronic acids

In a two-necked round bottom flask, 1.6 M solution of ⁿBuLi in ⁿhexanes (5.5 mL, 8.78 mmol, 1.5 eq) was added dropwise to a solution of 2-phenylethynyl bromobenzene (**S1**) (1.5 g, 5.85 mmol) in 45 mL of diethyl ether under nitrogen atmosphere at -78 °C. The mixture was stirred at -78 °C for 1 h and then at -40 °C for 1 h then cooled back to -78 °C and B(OⁱPr)₃ (1.65 g, 8.78 mmol, 1.5 eq) is added dropwise. The mixture was allowed to warm up gradually to room temperature, while maintaining vigorous stirring for 16 h. Then, the reaction is quenched with 40 mL of 1N HCl for 30 minutes and extracted with EtOAc (3 × 20 mL). The combined organic solution is dried over Na₂SO₄ and the solvent was removed under vacuo. The product was purified by flash chromatography on silica gel, (eluent: pet. ether/EtOAc) followed by recrystallization from pet. ether to give the product (2-(phenylethynyl)phenyl)boronic acid (**S27**) as a white solid (Yield 84%).

Example 3: General procedure for preparation of Suzuki coupling reaction between bromo-pyridines and boronic acids:

In a sealed tube 2-bromo-6-^tbutylpyridine (300 mg, 1.59 mmol) and (2-(phenylethynyl)phenyl)boronic acid (**S20**) (425 mg, 1.91 mmol, 1.2 eq) in DMF/H₂O 1:1 (2 mL) was degassed with nitrogen for 5 min followed by addition of Na₂CO₃ (507 mg, 4.78 mmol, 3 eq) under continuous flow of nitrogen, PdCl₂(PPh₃)₂ (55.8 mg, 0.079 mmol, 5 mol%) were added to the reaction mixture under a nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 12 h the solution was diluted with NaHCO₃ (5 mL), and then the product is extracted with EtOAc (3 × 05 mL). The combined organic layer was dried over Na₂SO₄ and the solvent is removed under vacuo. The crude product was purified on a silica gel column using pet. ether/EtOAc as eluent to afford 2-methoxy-6-(2 (phenylethynyl)-phenyl) pyridine (1a) as a yellow thick liquid (Yield 84%).

a) 2-(tert-butoxy)-6-(2-(phenylethynyl)phenyl)pyridine (1a):

Thick liquid, 84% yield; *R_f* = 0.80 (Pet.Ether/EtOAc = 95/05); ¹H NMR (500 MHz, CDCl₃) δ = 7.88 (d, *J* = 7.6 Hz, 1 H), 7.74 - 7.67 (m, 2 H), 7.67 - 7.61 (m, 1 H), 7.50 - 7.43 (m, 3 H),

7.42 - 7.37 (m, 1 H), 7.37 - 7.30 (m, 3 H), 6.70 (d, $J = 8.0$ Hz, 1 H), 1.69 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 163.4, 154.2, 142.2, 137.8, 133.2, 131.4, 129.7, 128.4, 128.3, 128.2, 127.7, 123.5, 121.0, 116.6, 111.8, 92.6, 89.6, 79.4, 28.8$; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{12}\text{ON}$ ($\text{M}^+ + \text{H}$) 328.1696, found 328.1694.

5 b) **2-(tert-butoxy)-6-(2-(naphthalen-1-ylethynyl)phenyl)pyridine (1b):**

Yellowish solid, 78% yield; mp = 108-109 °C; $R_f = 0.85$ (Pet.Ether/EtOAc = 95/05); ^1H NMR (500 MHz, CDCl_3) $\delta = 8.28 - 8.21$ (m, 1 H), 7.98 - 7.94 (m, 1 H), 7.92 - 7.85 (m, 3 H), 7.81 (d, $J = 7.2$ Hz, 1 H), 7.78 - 7.74 (m, 1 H), 7.69 (t, $J = 7.8$ Hz, 1 H), 7.59 - 7.53 (m, 3 H), 7.52 - 7.46 (m, 2 H), 6.82 (d, $J = 8.0$ Hz, 1 H), 1.75 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 163.6, 154.6, 142.5, 138.1, 133.3, 133.2, 133.1, 130.2, 129.7, 128.6, 128.5, 128.1, 127.8, 126.6, 126.3, 125.2, 121.3, 121.1, 116.8, 111.8, 94.3, 90.9, 79.5, 77.3, 76.7, 28.8$; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{24}\text{ON}$ ($\text{M}^+ + \text{H}$) 378.1852, found 378.1850.

c) **2-(tert-butoxy)-6-(2-(phenanthren-9-ylethynyl)phenyl)pyridine (1d):**

Yellowish solid, 68% yield; mp = 86-87 °C; $R_f = 0.85$ (Pet.Ether/EtOAc = 95/05); ^1H NMR (500 MHz, CDCl_3) $\delta = 8.66$ (d, $J = 8.4$ Hz, 1 H), 8.69 (d, $J = 8.4$ Hz, 1 H), 8.24 (d, $J = 8.4$ Hz, 1 H), 7.99 (s, 1 H), 7.90 - 7.80 (m, 3 H), 7.73 (d, $J = 7.2$ Hz, 1 H), 7.71 - 7.55 (m, 6 H), 7.53 - 7.48 (m, 1 H), 7.47 - 7.41 (m, 1 H), 6.74 (d, $J = 8.0$ Hz, 1 H), 1.66 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 163.6, 154.6, 142.6, 138.1, 133.4, 131.7, 131.2, 131.1, 130.2, 130.0, 129.8, 128.5, 127.8, 127.4, 127.1, 127.0, 126.9, 122.7, 122.6, 121.3, 119.9, 116.8, 111.9, 93.9, 91.1, 79.6, 28.9$; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{26}\text{ON}$ ($\text{M}^+ + \text{H}$) 428.2009, found 428.2007.

d) **2-(tert-butoxy)-6-(2-(hept-1-yn-1-yl)phenyl)pyridine (1e):**

Thick liquid, 56% yield; $R_f = 0.70$ (Pet.Ether/EtOAc = 95/05); ^1H NMR (500 MHz, CDCl_3) $\delta = 7.82$ (dd, $J = 1.1, 7.6$ Hz, 1 H), 7.66 (d, $J = 6.9$ Hz, 1 H), 7.60 - 7.53 (m, 2 H), 7.40 (dt, $J = 1.1, 7.6$ Hz, 1 H), 7.34 - 7.28 (m, 1 H), 6.66 (d, $J = 7.6$ Hz, 1 H), 2.40 (t, $J = 7.1$ Hz, 2 H), 1.69 (s, 9 H), 1.43 - 1.34 (m, 4 H), 0.94 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 163.3, 154.5, 141.9, 137.7, 133.4, 129.6, 127.6, 127.5, 121.8, 116.5, 111.5, 93.9, 80.5, 79.3, 31.1, 28.8, 28.1, 22.2, 19.6, 14.0$; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{28}\text{ON}$ ($\text{M}^+ + \text{H}$) 322.2165, found 322.2165.

e) **2-(tert-butoxy)-6-(2-(p-tolyethynyl)phenyl)pyridine (1g):**

Thick liquid, 82% yield; $R_f = 0.80$ (Pet.Ether/EtOAc = 95/05); ^1H NMR (500 MHz, CDCl_3) $\delta = 7.90 - 7.82$ (m, 1 H), 7.70 (d, $J = 7.2$ Hz, 1 H), 7.68 - 7.64 (m, 1 H), 7.64 - 7.59 (m, 1 H), 7.47 - 7.42 (m, 1 H), 7.39 - 7.31 (m, 3 H), 7.15 (d, $J = 8.0$ Hz, 2 H), 6.67 (d, $J = 8.0$ Hz, 1 H), 2.37 (s, 3 H), 1.66 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 163.4, 154.3, 142.1, 138.3,$

137.8, 133.2, 131.3, 129.7, 129.1, 128.2, 127.7, 121.2, 120.4, 116.6, 111.7, 92.8, 89.0, 79.4, 28.9, 21.5; **HRMS (ESI)** calcd for $C_{24}H_{24}ON$ ($M^+ + H$) 342.1852, found 342.1852.

f) **2-(tert-butoxy)-6-(2-((4-methoxyphenyl)ethynyl)phenyl)pyridine (1j):**

Thick liquid, 76% yield; $R_f = 0.70$ (Pet.Ether/EtOAc = 95/05); 1H NMR (500 MHz, $CDCl_3$) δ = 7.91 - 7.82 (m, 1 H), 7.72 (d, $J = 7.2$ Hz, 1 H), 7.69 - 7.60 (m, 2 H), 7.48 - 7.42 (m, 1 H), 7.42 - 7.34 (m, 3 H), 6.88 (d, $J = 8.8$ Hz, 2 H), 6.69 (d, $J = 8.0$ Hz, 1 H), 3.82 (s, 3 H), 1.68 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.4, 159.6, 154.3, 142.0, 137.8, 133.0, 132.8, 129.7, 128.1, 127.7, 121.3, 116.6, 115.6, 113.9, 111.7, 92.6, 88.3, 79.4, 55.2, 28.8; **HRMS (ESI)** calcd for $C_{24}H_{24}O_2N$ ($M^+ + H$) 358.1802, found 358.1801.

g) **2-(tert-butoxy)-6-(2-((4-fluorophenyl)ethynyl)phenyl)pyridine (1l):**

Thick liquid, 65% yield; $R_f = 0.70$ (Pet.Ether/EtOAc = 95/05); 1H NMR (500 MHz, $CDCl_3$) δ = 7.87 - 7.81 (m, 1 H), 7.68 - 7.60 (m, 3 H), 7.49 - 7.44 (m, 1 H), 7.44 - 7.34 (m, 3 H), 7.07 - 6.98 (m, 2 H), 6.68 (dd, $J = 1.9, 7.0$ Hz, 1 H), 1.66 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.5, 163.4-161.4 (d, $J = 248.91$ Hz), 154.3, 142.3, 137.8, 133.3-133.1 (d, $J = 14.31$ Hz), 133.2, 129.8, 128.5, 127.7, 120.8, 119.6-119.6 (d, $J = 2.86$ Hz), 116.5, 115.7-115.5 (d, $J = 21.94$ Hz), 111.8, 91.4, 89.3, 79.5, 28.8; **HRMS (ESI)** calcd for $C_{23}H_{21}ONF$ ($M^+ + H$) 346.1602, found 346.1600.

h) **4-((2-(6-(tert-butoxy)pyridin-2-yl)phenyl)ethynyl)-N,N-dimethylaniline (1n):**

Yellowish solid, 68% yield; mp = 116-117 °C; $R_f = 0.65$ (Pet.Ether/EtOAc = 95/05); 1H NMR (500 MHz, $CDCl_3$) δ = 7.86 (d, $J = 7.6$ Hz, 1 H), 7.77 (d, $J = 6.9$ Hz, 1 H), 7.67 - 7.59 (m, 2 H), 7.45 - 7.38 (m, 1 H), 7.37 - 7.29 (m, 3 H), 6.66 (d, $J = 9.2$ Hz, 3 H), 2.99 (s, 6 H), 1.67 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.4, 154.4, 150.0, 141.5, 137.8, 132.8, 132.5, 129.6, 127.6, 127.6, 121.9, 116.7, 111.8, 111.5, 110.3, 94.0, 87.7, 79.3, 40.2, 28.9; **HRMS (ESI)** calcd for $C_{25}H_{27}ON_2$ ($M^+ + H$) 371.2118, found 371.2117.

i) **1-(4-((2-(6-(tert-butoxy)pyridin-2-yl)phenyl)ethynyl)phenyl)pentan-1-one (1o):**

Thick liquid, 58% yield; $R_f = 0.60$ (Pet.Ether/EtOAc = 95/05); 1H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, $J = 8.3$ Hz, 2 H), 7.83 (d, $J = 7.3$ Hz, 1 H), 7.67 (d, $J = 7.8$ Hz, 1 H), 7.62 (q, $J = 7.7$ Hz, 2 H), 7.52 - 7.42 (m, 3 H), 7.42 - 7.31 (m, 1 H), 6.68 (d, $J = 7.3$ Hz, 1 H), 1.77 - 1.69 (m, 2 H), 1.65 (s, 9 H), 1.46 - 1.38 (m, 2 H), 0.97 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 199.7, 163.5, 154.1, 142.6, 137.9, 136.0, 133.3, 131.4, 129.8, 128.9, 128.1, 127.9, 127.8, 120.4, 116.5, 111.9, 92.9, 91.7, 79.5, 77.3, 76.7, 38.3, 28.8, 26.4, 22.4, 13.9; **HRMS (ESI)** calcd for $C_{28}H_{30}O_2N$ ($M^+ + H$) 412.2271, found 412.2268.

j) **2-(tert-butoxy)-6-(5-methyl-2-(phenylethynyl)phenyl)pyridine (1t):**

Thick liquid, 72% yield; R_f = 0.80 (Pet.Ether/EtOAc = 95/05); ^1H NMR (400 MHz, CDCl_3) δ = 7.70 - 7.61 (m, 3 H), 7.59 (d, J = 7.8 Hz, 1 H), 7.49 - 7.39 (m, 2 H), 7.38 - 7.29 (m, 3 H), 7.21 (d, J = 7.8 Hz, 1 H), 6.69 (d, J = 7.8 Hz, 1 H), 2.47 (s, 3 H), 1.69 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 163.4, 154.5, 142.1, 138.4, 137.8, 133.2, 131.3, 130.4, 128.6, 128.2, 128.0, 123.7, 118.1, 116.7, 111.7, 91.8, 89.8, 79.4, 77.3, 76.7, 28.9, 21.6; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{ON}$ (M^+ + H) 342.1852, found 342.1851.

k) **2-(tert-butoxy)-6-(5-fluoro-2-(phenylethynyl)phenyl)pyridine (1u):**

Thick liquid, 74% yield; mp = 65-66 °C; R_f = 0.70 (Pet.Ether/EtOAc = 95/05); ^1H NMR (400 MHz, CDCl_3) δ = 7.77 (d, J = 7.3 Hz, 1 H), 7.69 - 7.57 (m, 3 H), 7.51 - 7.41 (m, 2 H), 7.39 - 7.28 (m, 3 H), 7.09 (dt, J = 2.4, 8.2 Hz, 1 H), 6.71 (d, J = 7.9 Hz, 1 H), 1.68 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 163.7-161.3 (d, J = 248.92 Hz), 163.5, 152.8, 144.5-144.4 (d, J = 8.48 Hz), 138.0, 135.2-135.1 (d, J = 8.48 Hz), 131.3, 128.3, 128.2, 123.3, 117.0 (d, J = 3.03 Hz), 116.7-116.4 (d, J = 23.12 Hz), 116.5, , 115.2-115.0 (d, J = 21.58 Hz), 112.4, 92.3, 88.7, 79.6, 28.8; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{21}\text{ONF}$ (M^+ + H) 346.1602, found 346.1601.

l) **1-methoxy-3-(2-(phenylethynyl)phenyl)isoquinoline (1x):**

During preparation of **1x**, the 2-bromo-6-methoxyisoquinoline was used instead of 2-bromo-6-*t*-butylpyridine.

Yellowish solid, 68% yield; mp = 84-85 °C; R_f = 0.75 (Pet.Ether/EtOAc = 95/05); ^1H NMR (400 MHz, CDCl_3) δ = 8.35 (d, J = 7.6 Hz, 1 H), 8.16 (s, 1 H), 8.09 (dd, J = 1.1, 7.6 Hz, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.77 (dd, J = 1.1, 7.6 Hz, 1 H), 7.70 (dt, J = 1.3, 7.5 Hz, 1 H), 7.59 (ddd, J = 1.0, 7.0, 8.1 Hz, 1 H), 7.54 - 7.50 (m, 1 H), 7.50 - 7.45 (m, 2 H), 7.42 (dt, J = 1.3, 7.5 Hz, 1 H), 7.36 - 7.32 (m, 3 H), 4.27 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 160.2, 147.5, 141.9, 138.2, 133.5, 131.3, 130.4, 129.8, 128.5, 128.3, 128.1, 127.6, 126.6, 126.6, 124.1, 123.6, 121.1, 118.8, 115.0, 92.7, 90.0, 53.7; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{18}\text{ON}$ (M^+ + H) 336.1383, found 336.1384.

m) **2-(tert-butoxy)-6-(2-((2-chloro-5-methoxyphenyl)ethynyl)phenyl)pyridine (1y):**

Yellowish solid, 52% yield; mp = 85-86 °C; R_f = 0.60 (Pet.Ether/EtOAc = 95/05); ^1H NMR (500 MHz, CDCl_3) δ = 7.87 (dd, J = 1.1, 8.0 Hz, 1 H), 7.75 (d, J = 7.2 Hz, 1 H), 7.72 (dd, J = 1.1, 7.6 Hz, 1 H), 7.63 - 7.57 (m, 1 H), 7.48 (dt, J = 1.5, 7.6 Hz, 1 H), 7.41 - 7.35 (m, 1 H), 7.28 (d, J = 8.8 Hz, 1 H), 6.96 (d, J = 3.1 Hz, 1 H), 6.81 (dd, J = 3.1, 8.8 Hz, 1 H), 6.66 (d, J = 8.4 Hz, 1 H), 3.79 (s, 3 H), 1.65 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) δ = 163.4, 157.8, 153.9, 142.3, 138.0, 133.7, 129.9, 129.7, 128.9, 127.7, 127.4, 123.9, 120.6, 117.6, 116.9, 116.0, 111.9, 94.3, 89.5, 79.4, 55.5, 28.8; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{O}_2\text{NCl}$ (M^+ + H) 392.1412, found 392.1417.

n) **2-(tert-butoxy)-6-(2-((3-chloro-4-methylphenyl)ethynyl)phenyl)pyridine (1z):**

Yellowish solid, 52% yield; mp = 81-82 °C; R_f = 0.60 (Pet.Ether/EtOAc = 95/05); ^1H NMR (500 MHz, CDCl_3) δ = 7.67 - 7.61 (m, 3 H), 7.46 (dt, J = 1.5, 7.6 Hz, 1 H), 7.42 (d, J = 1.5 Hz, 1 H), 7.37 (dt, J = 1.1, 7.4 Hz, 1 H), 7.23 - 7.15 (m, 2 H), 6.68 (t, J = 4.4 Hz, 1 H), 2.39 (s, 3 H), 1.66 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) δ = 163.5, 154.2, 142.3, 137.9, 136.4, 134.2, 133.2, 131.6, 130.8, 129.8, 129.5, 128.6, 127.7, 122.4, 120.7, 116.5, 111.9, 91.2, 90.1, 79.5, 28.9, 20.0; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{ONCl}$ ($\text{M}^+ + \text{H}$) 376.1463, found 376.1458

o) **2-(tert-butoxy)-6-(3,5-dimethoxy-2-(phenylethynyl)phenyl)pyridine (1aa):**

Yellowish solid, 76% yield; mp = 124-125 °C; R_f = 0.55 (Pet.Ether/EtOAc = 95/05); ^1H NMR (400 MHz, CDCl_3) δ = 7.70 (d, J = 7.8 Hz, 1 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.42 (d, J = 6.4 Hz, 2 H), 7.35 - 7.25 (m, 3 H), 7.02 (d, J = 2.0 Hz, 1 H), 6.67 (d, J = 8.3 Hz, 1 H), 6.53 (d, J = 2.0 Hz, 1 H), 3.96 (s, 3 H), 3.89 (s, 3 H), 1.66 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ = 163.2, 161.8, 160.3, 154.1, 145.1, 137.8, 131.2, 128.1, 127.6, 124.1, 116.9, 111.9, 106.0, 98.3, 95.8, 85.6, 79.4, 56.2, 55.3, 28.8; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3\text{N}$ ($\text{M}^+ + \text{H}$) 388.1907, found 388.1904.

Example 3: Procedure for gold-catalyzed 1, 2 amino-oxygenation of alkyne

To a screw-cap vial containing a stir bar were added 2-(tert-butoxy)-6-(2-(phenylethynyl)phenyl)pyridine (**1a**) (80 mg, 0.10 mmol), 5 mol% $(\text{C}_6\text{F}_5)_3\text{P-AuCl}$ (7 mg, 5 mol%) and CH_3CN (2 mL). The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 80 °C for 6 h. When the reaction time was completed, the reaction mixture was allowed to cool at ambient temperature. The mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a Celite pad and the Celite pad was washed several times with CH_2Cl_2 (50 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by column chromatography on silica (DCM/MeOH; 95:5) to afford the products. **3a** as off white solid in 92% yield.

a) **1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3a):**

Off white solid, 92% yield; mp = 192-193 °C; R_f = 0.50 (DCM/MeOH = 95/05); ^1H NMR (500 MHz, DMSO-d_6) δ = 8.89 (br. s., 2 H), 8.83 (d, J = 5.9 Hz, 2 H), 8.65 (d, J = 3.9 Hz, 1 H), 8.37 (d, J = 7.3 Hz, 2 H), 8.16 - 7.99 (m, 2 H), 7.92 - 7.81 (m, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 150.4, 146.4, 142.6, 135.8, 133.9, 133.4, 132.7, 131.0, 130.5, 127.6, 127.0, 125.9, 124.6, 121.2, 117.0, 108.6; ^{11}B NMR (160 MHz, DMSO-d_6): δ -1.31; ^{19}F NMR (470 MHz, DMSO-d_6): δ -148.22, -148.28 and secondary isotopic shift (^{10}B , ^{11}B) of 0.055 ppm; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{12}\text{ON}^+$ ($\text{M}^+ - \text{BF}_4^-$) 270.0913, found 270.0910.

b) **1-(naphthalen-1-yl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3b):**

Light yellow solid, 68% yield; mp = 198-200 °C; R_f = 0.45 (DCM/MeOH = 95/05); ^1H NMR (500 MHz, DMSO- d_6) δ = 8.95 (s, 1 H), 8.84 (d, J = 7.6 Hz, 1 H), 8.73 (d, J = 7.2 Hz, 1 H), 8.49 - 8.37 (m, 3 H), 8.28 (d, J = 6.5 Hz, 1 H), 8.07 - 7.92 (m, 5 H), 7.88 - 7.77 (m, 3 H); ^{13}C NMR (125 MHz, DMSO- d_6) δ = 149.8, 147.0, 142.7, 135.9, 134.1, 133.9, 133.5, 132.5, 130.9, 129.4, 129.3, 128.9, 127.7, 127.2, 126.1, 125.9, 124.6, 124.3, 123.0, 121.4, 117.0, 109.0; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{14}\text{ON}^+$ (M^+ - BF_4^-) 320.1070, found 320.1065.

c) **1-(phenanthren-9-yl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3d):**

Light yellow solid, 63% yield; mp = 230-232 °C; R_f = 0.50 (DCM/MeOH = 95/05); ^1H NMR (400 MHz, DMSO- d_6) δ = 9.16 (d, J = 8.3 Hz, 1 H), 9.09 - 9.04 (m, 1 H), 9.01 - 8.91 (m, 2 H), 8.85 (d, J = 7.8 Hz, 1 H), 8.79 (s, 1 H), 8.75 (d, J = 7.8 Hz, 1 H), 8.50 (d, J = 7.8 Hz, 1 H), 8.39 (d, J = 7.8 Hz, 1 H), 8.13 - 7.93 (m, 5 H), 7.87 (q, J = 7.5 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 153.3, 149.6, 147.0, 142.9, 136.0, 134.2, 133.3, 132.6, 131.5, 130.9, 130.4, 130.3, 130.0, 128.6, 128.4, 128.1, 127.2, 125.9, 125.3, 124.9, 124.3, 123.5, 123.4, 123.2, 122.7, 120.6, 117.1, 115.6, 109.0; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{16}\text{ON}^+$ (M^+ - BF_4^-) 370.1225, found 370.1226.

d) **1-(p-tolyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3g):**

Off white solid, 85% yield; mp = 222-223 °C; R_f = 0.40 (DCM/MeOH = 95/05); ^1H NMR (500 MHz, DMSO- d_6) δ = 8.92 - 8.84 (m, 2 H), 8.79 (d, J = 8.0 Hz, 1 H), 8.82 (d, J = 8.0 Hz, 1 H), 8.65 - 8.56 (m, 1 H), 8.27 (d, J = 8.0 Hz, 2 H), 8.10 (t, J = 7.4 Hz, 1 H), 8.05 (t, J = 7.6 Hz, 1 H), 7.68 (d, J = 7.6 Hz, 2 H), 2.53 (s, 3 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 150.8, 146.2, 144.2, 142.2, 135.7, 133.7, 132.6, 131.0, 130.8, 127.6, 127.0, 125.8, 124.4, 121.8, 120.5, 116.9, 108.4, 21.4; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{14}\text{ON}^+$ (M^+ - BF_4^-) 284.1070, found 284.1067.

e) **1-(4-isopropylphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3h):**

Off white solid, 80% yield; mp = 214-215 °C; R_f = 0.40 (DCM/MeOH = 95/05); ^1H NMR (400 MHz, DMSO- d_6) δ = 8.88 (d, J = 3.9 Hz, 2 H), 8.79 (d, J = 7.8 Hz, 1 H), 8.82 (d, J = 7.8 Hz, 1 H), 8.63 (t, J = 3.9 Hz, 1 H), 8.36 - 8.23 (m, J = 7.3 Hz, 2 H), 8.13 - 8.02 (m, 2 H), 7.78 - 7.70 (m, J = 7.8 Hz, 2 H), 3.12 (td, J = 6.7, 13.6 Hz, 1 H), 1.32 (d, J = 7.3 Hz, 6 H); ^{13}C NMR (125 MHz, DMSO- d_6) δ = 154.5, 150.8, 146.2, 142.3, 135.7, 133.8, 132.6, 130.8, 128.5, 127.9, 127.0, 125.9, 124.4, 122.2, 120.6, 116.9, 108.5, 33.7, 23.4; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{18}\text{ON}^+$ (M^+ - BF_4^-) 312.1383, found 312.1382.

f) **1-(4-methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3j):**

Light yellow solid, 83% yield; mp = 190-192 °C; R_f = 0.30 (DCM/MeOH = 95/10); ^1H NMR (400 MHz, DMSO- d_6) δ = 8.94 - 8.70 (m, 4 H), 8.58 (d, J = 7.3 Hz, 1 H), 8.33 (d, J = 8.5 Hz, 2 H), 8.12 - 7.98 (m, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 3.97 (br. s., 3 H); ^{13}C NMR (125 MHz, DMSO- d_6) δ = 163.2, 151.1, 146.0, 141.7, 135.4, 133.5, 132.5, 130.5, 129.9, 127.1, 125.8, 124.0, 119.4, 116.7, 116.1, 108.1, 55.9; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}^+$ (M^+ - BF_4^-) 300.1019, found 300.1019.

g) **1-(4-butoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3k):**

Light yellow solid, 86% yield; mp = 183-185 °C; R_f = 0.30 (DCM/MeOH = 95/10); ^1H NMR (400 MHz, DMSO- d_6) δ = 8.95 - 8.71 (m, 4 H), 8.64 - 8.53 (m, 1 H), 8.42 - 8.22 (m, 2 H), 8.16 - 7.99 (m, 2 H), 7.42 - 7.32 (m, 2 H), 4.23 - 4.15 (m, 2 H), 1.82 - 1.74 (m, 2 H), 1.54 - 1.45 (m, 2 H), 0.98 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 162.8, 151.2, 146.1, 141.7, 135.5, 133.5, 132.6, 130.5, 130.2, 130.0, 127.1, 125.8, 124.0, 119.4, 116.8, 116.5, 108.1, 68.130.6, 18.8, 13.8; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}^+$ (M^+ - BF_4^-) 342.1489, found 342.1483.

h) **1-(4-fluorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3l):**

Off white solid, 71% yield; mp = 254-255 °C; R_f = 0.60 (DCM/MeOH = 95/10); ^1H NMR (400 MHz, DMSO- d_6) δ = 8.98 - 8.75 (m, 3 H), 8.64 (d, J = 8.3 Hz, 1 H), 8.54 - 8.37 (m, 2 H), 8.22 - 8.01 (m, 2 H), 7.85 - 7.62 (m, 3 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 166.2, 165.9- 163.4 (d, J = 254.31 Hz), 153.1, 151.3, 149.5, 146.3, 143.7, 142.7, 135.8, 133.9, 132.9, 132.6, 131.6, 131.0, 130.9-130.8 (d, J = 9.25 Hz), 130.7-130.6 (d, J = 10.02 Hz), 126.9, 126.3, 126.0, 124.7, 124.4, 121.8, 121.3, 121.0, 118.2-118.0 (d, J = 23.12 Hz), 118.1-117.9 (d, J = 22.35 Hz), 117.1, 110.4-110.3 (d, J = 6.94 Hz), 108.6; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{11}\text{ONF}^+$ (M^+ - BF_4^-) 288.0819, found 288.0815.

i) **1-(4-chlorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3m):**

Off white solid, 65% yield; mp = 274-275 °C; R_f = 0.60 (DCM/MeOH = 95/10); ^1H NMR (400 MHz, DMSO- d_6) δ = 8.99 - 8.86 (m, 2 H), 8.79 (d, J = 7.3 Hz, 1 H), 8.83 (d, J = 7.8 Hz, 1 H), 8.65 (d, J = 6.8 Hz, 1 H), 8.37 (d, J = 8.3 Hz, 2 H), 8.17 - 8.02 (m, 2 H), 7.92 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 149.3, 146.4, 142.9, 138.0, 135.9, 134.0, 132.7,

131.2, 130.7, 129.4, 126.8, 126.0, 124.6, 123.4, 121.5, 117.1, 108.8; **HRMS (ESI)** calcd for $C_{19}H_{11}ONCl^+$ ($M^+ - BF_4^-$) 304.0524, found 304.0520.

j) **1-(4-(dimethylamino)phenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3n):**

5 Reddish solid, 82% yield; mp = 242-244 °C; R_f = 0.5 (DCM/MeOH = 95/10); **1H NMR (400 MHz, DMSO- d_6)** δ = 8.78 (d, J = 6.8 Hz, 2 H), 8.75 - 8.61 (m, 2 H), 8.45 (d, J = 8.3 Hz, 1 H), 8.21 - 8.10 (m, J = 8.8 Hz, 2 H), 8.05 (t, J = 7.1 Hz, 1 H), 7.97 (d, J = 7.3 Hz, 1 H), 7.13 - 6.93 (m, J = 8.3 Hz, 2 H), 3.18 - 3.13 (m, 6 H); **^{13}C NMR (125 MHz, DMSO- d_6)** δ = 153.1, 152.9, 145.5, 139.8, 134.5, 132.5, 132.1, 129.5, 129.3, 127.2, 125.5, 123.3, 116.7, 116.2, 112.7, 110.0, 106.8, 40.1; **HRMS (ESI)** calcd for $C_{21}H_{17}ON_2^+$ ($M^+ - BF_4^-$) 313.1335, found 313.1330.

k) **1-(4-pentanoylphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3o):**

Off white solid, 53% yield; mp = 202-204 °C; R_f = 0.30 (DCM/MeOH = 95/05); **1H NMR (500 MHz, DMSO- d_6)** δ = 9.00 (t, J = 9.5 Hz, 1 H), 8.93 (d, J = 7.9 Hz, 1 H), 8.81 (dd, J = 2.4, 9.2 Hz, 1 H), 8.66 (d, J = 7.9 Hz, 1 H), 8.51 (d, J = 8.5 Hz, 2 H), 8.41 - 8.35 (m, 2 H), 8.19 (t, J = 7.6 Hz, 1 H), 8.12 (t, J = 7.7 Hz, 1 H), 3.17 (t, J = 7.3 Hz, 2 H), 1.67 (quin, J = 7.4 Hz, 2 H), 1.43 - 1.37 (m, 2 H), 0.95 (t, J = 7.4 Hz, 3 H); **^{13}C NMR (125 MHz, DMSO- d_6)** δ = 199.4, 150.8, 143.9, 139.7, 133.0, 131.9, 131.8, 131.6, 129.7, 128.1, 127.8, 126.4, 126.1, 125.0, 124.1, 123.3, 110.7, 110.7, 38.1, 25.8, 21.8, 13.9; **HRMS (ESI)** calcd for $C_{24}H_{20}O_2N^+$ ($M^+ - BF_4^-$) 354.1489, found 354.1485.

l) **1-(2-methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3p):**

Light yellow solid, 72% yield; mp = 228-229 °C; R_f = 0.50 (DCM/MeOH = 95/10); **1H NMR (400 MHz, DMSO- d_6)** δ = 8.92 - 8.81 (m, 2 H), 8.78 (d, J = 7.3 Hz, 1 H), 8.59 (dd, J = 3.7, 5.5 Hz, 1 H), 8.33 (d, J = 7.9 Hz, 1 H), 8.13 (d, J = 7.9 Hz, 1 H), 8.11 - 8.03 (m, 1 H), 8.03 - 7.94 (m, 1 H), 7.84 (t, J = 7.9 Hz, 1 H), 7.53 (d, J = 8.5 Hz, 1 H), 7.38 (t, J = 7.6 Hz, 1 H), 4.14 (s, 3 H); **^{13}C NMR (100 MHz, DMSO- d_6)** δ = 157.5, 147.4, 146.3, 142.2, 135.8, 135.3, 133.9, 132.3, 130.2, 129.9, 128.4, 126.9, 125.4, 121.8, 116.5, 113.6, 112.9, 108.2, 56.5; **HRMS (ESI)** calcd for $C_{20}H_{14}O_2N^+$ ($M^+ - BF_4^-$) 300.1019, found 300.1017.

m) **1-(3-methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3q):**

Light yellow solid, 82% yield; mp = 206-208 °C; R_f = 0.60 (DCM/MeOH = 95/10); **1H NMR (400 MHz, DMSO- d_6)** δ = 8.99 - 8.69 (m, 4 H), 8.64 (br. s., 1 H), 8.23 - 8.02 (m, 2 H), 7.97 (d, J = 7.3 Hz, 1 H), 7.86 - 7.65 (m, 2 H), 7.52 - 7.28 (m, 1 H), 3.99 (br. s., 3 H); **^{13}C NMR (100**

MHz, DMSO- d_6) δ = 160.3, 150.1, 146.3, 142.7, 135.8, 134.0, 132.8, 132.0, 131.1, 126.9, 126.0, 125.8, 124.5, 120.5, 120.3, 119.9, 119.5, 117.0, 111.8, 108.7, 55.8; **HRMS (ESI)** calcd for $C_{20}H_{14}O_2N^+$ ($M^+ - BF_4^-$) 300.1019, found 300.1017.

n) **1-(3-chlorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium** tetrafluoroborate

5 (3r):

Off white solid, 58% yield; mp = 204-206 °C; R_f = 0.30 (DCM/MeOH = 95/05); **1H NMR (400 MHz, DMSO- d_6)** δ = 8.99 (t, J = 9.5 Hz, 1 H), 8.83 (d, J = 7.8 Hz, 1 H), 8.77 (d, J = 8.8 Hz, 1 H), 8.65 (d, J = 7.3 Hz, 1 H), 8.45 - 8.27 (m, 2 H), 8.18 (t, J = 7.6 Hz, 1 H), 8.11 (t, J = 7.6 Hz, 1 H), 7.93 (q, J = 7.8 Hz, 2 H); **^{13}C NMR (100 MHz, DMSO- d_6)** δ = 150.7, 150.3, 143.8, 10
135.1, 133.4, 133.0, 132.6, 131.9, 131.7, 131.5, 126.9, 126.7, 126.4, 126.2, 126.0, 125.0, 122.9, 110.7, 110.6; **HRMS (ESI)** calcd for $C_{19}H_{11}ONCl^+$ ($M^+ - BF_4^-$) 304.0524, found 304.0521.

o) **6-methyl-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium** tetrafluoroborate

(3s):

Off white solid, 85% yield; mp = 220-221 °C; R_f = 0.30 (DCM/MeOH = 95/05); **1H NMR (500 MHz, DMSO- d_6)** δ = 8.88 (t, J = 8.2 Hz, 1 H), 8.78 (d, J = 7.6 Hz, 1 H), 8.66 (d, J = 8.4 Hz, 2 H), 8.36 (d, J = 7.2 Hz, 2 H), 8.01 (t, J = 7.8 Hz, 1 H), 7.91 - 7.80 (m, 4 H), 2.99 (s, 3 H); **^{13}C NMR (125 MHz, DMSO- d_6)** δ = 150.2, 146.4, 142.5, 137.9, 135.6, 133.3, 132.7, 132.6, 132.4, 130.5, 127.6, 127.0, 124.6, 122.1, 121.3, 118.4, 108.4, 19.4; **HRMS (ESI)** calcd for $C_{20}H_{14}ON^+$ ($M^+ - BF_4^-$) 284.1070, found 284.1067.

20 p) **7-methyl-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium** tetrafluoroborate

(3t):

Off white solid, 76% yield; mp = 224-226 °C; R_f = 0.40 (DCM/MeOH = 95/05); **1H NMR (500 MHz, DMSO- d_6)** δ = 8.89 (t, J = 8.2 Hz, 1 H), 8.78 (d, J = 7.6 Hz, 1 H), 8.66 (d, J = 8.4 Hz, 2 H), 8.36 (d, J = 7.2 Hz, 2 H), 8.01 (t, J = 7.8 Hz, 1 H), 7.90 - 7.82 (m, 4 H), 2.99 (s, 3 H); **^{13}C NMR (125 MHz, DMSO- d_6)** δ = 149.8, 146.4, 142.6, 141.6, 135.8, 134.2, 133.6, 133.2, 130.5, 127.5, 126.0, 124.7, 124.6, 124.2, 121.1, 116.8, 108.5, 21.5; **HRMS (ESI)** calcd for $C_{20}H_{14}ON^+$ ($M^+ - BF_4^-$) 284.1070, found 284.1067.

q) **7-fluoro-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium** tetrafluoroborate

(3u):

30 Off white solid, 65% yield; mp = 255-256 °C; R_f = 0.60 (DCM/MeOH = 95/10); **1H NMR (400 MHz, DMSO- d_6)** δ = 9.02 - 8.84 (m, 3 H), 8.80 (dd, J = 2.1, 8.9 Hz, 1 H), 8.70 (d, J = 8.5 Hz, 1 H), 8.46 - 8.29 (m, 2 H), 7.98 (dt, J = 2.4, 8.9 Hz, 1 H), 7.92 - 7.76 (m, 3 H); **^{13}C NMR (100 MHz, DMSO- d_6)** δ = 164.2-161.7 (d, J = 250.16 Hz), 150.3, 146.3, 142.6, 135.9, 135.8, 135.1-135.1 (d, J = 3.83 Hz), 133.4, 130.5, 127.6, 126.7-126.6 (d, J = 9.59 Hz), 124.4, 123.6, 120.5,

120.5-120.2(d, $J = 23.96$ Hz), 117.7, 113.2- 112.9 (d, $J = 25.88$ Hz), 109.3; **HRMS (ESI)** calcd for $C_{19}H_{11}ONF^+$ ($M^+ - BF_4^-$) 288.0819, found 288.0815

r) 7-chloro-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3v):

5 off white solid, 56% yield; mp = 208-210 °C; $R_f = 0.35$ (DCM/MeOH = 95/05); **1H NMR (400 MHz, DMSO- d_6)** δ = 9.09 - 8.80 (m, 4 H), 8.68 (d, $J = 3.4$ Hz, 1 H), 8.39 (d, $J = 6.8$ Hz, 2 H), 8.16 (d, $J = 8.3$ Hz, 1 H), 7.87 (d, $J = 6.4$ Hz, 3 H); **^{13}C NMR (100 MHz, DMSO- d_6)** δ = 150.8, 146.3, 142.8, 140.9, 135.6, 135.3, 134.8, 133.6, 132.4, 130.5, 128.0, 127.8, 125.9, 125.6, 124.4, 120.6, 117.7, 109.4; **HRMS (ESI)** calcd for $C_{19}H_{11}ONCl^+$ ($M^+ - BF_4^-$) 304.0524, found
10 304.0517.

s) 8-chloro-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate (3w):

Off white solid, 52% yield; mp = 206-208 °C; $R_f = 0.30$ (DCM/MeOH = 95/05); **1H NMR (400 MHz, DMSO- d_6)** δ = 8.99 - 8.78 (m, 4 H), 8.68 (d, $J = 3.4$ Hz, 1 H), 8.39 (d, $J = 6.8$ Hz, 2 H),
15 8.16 (d, $J = 8.3$ Hz, 1 H), 7.87 (d, $J = 6.4$ Hz, 3 H); **^{13}C NMR (100 MHz, DMSO- d_6)** δ = 151.3, 146.3, 142.8, 137.7, 135.0, 133.7, 132.5, 131.2, 130.6, 128.4, 128.1, 127.3, 124.3, 120.4, 117.3, 108.9; **HRMS (ESI)** calcd for $C_{19}H_{11}ONCl^+$ ($M^+ - BF_4^-$) 304.0524, found 304.0533.

t) 1-phenyldibenzo[a,f]oxazolo[4,3,2-cd]indolizin-12-ium tetrafluoroborate (3x):

20 White solid, 72% yield; mp = 258-259 °C; $R_f = 0.5$ (DCM/MeOH = 95/10); **1H NMR (500 MHz, DMSO- d_6)** δ = 9.30 (s, 1 H), 9.06 (d, $J = 8.0$ Hz, 1 H), 8.81 - 8.77 (m, 1 H), 8.77 - 8.73 (m, 1 H), 8.69 (d, $J = 8.4$ Hz, 1 H), 8.45 - 8.42 (m, 2 H), 8.35 - 8.30 (m, 1 H), 8.30 - 8.24 (m, 1 H), 8.09 - 8.01 (m, 2 H), 7.90 - 7.86 (m, 2 H), 7.82 (d, $J = 7.2$ Hz, 1 H); **^{13}C NMR (125 MHz, DMSO- d_6)** δ = 148.3, 145.7, 138.1, 134.4, 134.1, 132.6, 132.1, 131.4, 130.6, 130.4, 129.7,
25 127.1, 127.0, 126.9, 125.3, 124.8, 124.8, 123.6, 122.0, 116.7, 113.9; **HRMS (ESI)** calcd for $C_{23}H_{14}ON^+$ ($M^+ - BF_4^-$) 320.1070, found 320.1071.

u) 6-(2-chloro-5-methoxyphenyl)-4H-pyrido[2,1-a]isoquinolin-4-one (3y'')

Yellow solid, 62% yield; mp = 186-187 °C; $R_f = 0.40$ (Pet. Ether /EtOAc = 70/30); **1H NMR (500 MHz, $CDCl_3$)** δ = 7.89 (d, $J = 7.6$ Hz, 1 H), 7.76 (d, $J = 7.2$ Hz, 1 H), 7.56 - 7.47 (m, 2 H), 7.41 (dd, $J = 6.9, 8.8$ Hz, 1 H), 7.34 - 7.28 (m, 2 H), 6.83 (dd, $J = 3.1, 8.8$ Hz, 1 H), 6.74 (d, $J = 6.5$ Hz, 1 H), 6.60 (d, $J = 2.7$ Hz, 1 H), 6.49 (d, $J = 9.2$ Hz, 1 H), 3.75 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 159.7, 156.4, 145.0, 137.7, 136.4, 135.6, 134.8, 130.5, 130.0, 129.2, 128.5, 125.5, 120.5, 120.3, 119.7, 116.5, 114.7, 112.2, 99.0, 55.4; **HRMS (ESI)** calcd for $C_{20}H_{15}O_2NCl$ ($M^+ + H$) 336.0784, found 336.0779.

v) **(E)-6-(3-chloro-4-methylbenzylidene)pyrido[2,1-a]isoindol-4(6H)-one (3z'')**:

Yellow solid, 23% yield; mp = 194-195 °C; R_f = 0.35 (Pet. Ether /EtOAc = 60/20); ^1H NMR (500 MHz, CDCl_3) δ = 9.34 (s, 1 H), 7.54 (s, 1 H), 7.51 - 7.42 (m, 6 H), 7.40 (d, J = 7.2 Hz, 1 H), 7.14 (d, J = 8.4 Hz, 1 H), 7.02 (d, J = 8.0 Hz, 1 H), 6.76 (d, J = 6.5 Hz, 1 H), 6.64 (d, J = 9.2 Hz, 1 H), 2.42 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ = 163.0, 143.9, 139.5, 137.9, 137.6, 135.9, 131.9, 131.0, 130.0, 129.1, 128.7, 127.9, 123.8, 123.2, 120.5, 120.1, 98.5, 21.6; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{14}\text{ONCl}$ ($\text{M}^+ + \text{H}$) 319.0680, found 319.0675.

Example 4: Bioimaging studies of pyridinium-oxazole dyad salt 3n in MCF-7 cells:

Materials: MCF-7 cells are obtained from National Centre for Cell Science, Pune, India. Dulbecco's modified eagle medium (DMEM), Dulbecco's phosphate buffered saline (DPBS), fetal bovine serum (FBS), MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) and DAPI are purchased from Sigma-Aldrich, USA.

Sample preparation for *in vitro* studies: The stock solutions (5 mM) of the organic molecules are prepared in DMSO solvent. Each time, the freshly prepared stock solutions are used for all the cell culture experiments.

Cell culture: MCF-7 cells were obtained from National Centre for Cell Science, Pune, India. For bio imaging purpose, the cells were seeded in a 6 well plate at a density of 10^5 cells/mL in Dulbecco's Modified Eagle's Medium + Ham's F12 containing 10% fetal bovine serum and a 0.1% antibiotic solution for 24h at 37°C and 5% CO_2 for adherence

Cell viability assay: Cell viability assay was performed in MCF-7 cells using MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) reagent. Compounds at concentration of 1, 5, 10 and 20 μM dissolved in DMSO were added to the cells in media without FBS. DMSO was used as a control. MTT assay was carried out after 24h incubation. A MTT solution (20 μl , 5mg/mL) was prepared in PBS pH 7.4 then added to each well and incubated for 3h. The purple formazan crystals formed were dissolved by addition of 150 μl of DMSO for 5min absorbance was measured using Biotek SYNERGY HT, microplate reader. IC_{50} was determined by using ED50V10 excel add-on software. Finally, the absorbance of solution was measured using a multimode reader (Biotek Synergy) at 570 nm.

***In vitro* imaging:** MCF-7 cells (1×10^4 cells/mL/well) were seeded in a 6-well tissue culture plate for 48 h. The cells were then treated with 1 μM concentration of different organic

molecules for 30 minutes. After thorough washing with 1X PBS (P^H 7.4), the cells are fixed used paraformaldehyde (4% in PBS) for 15 minutes. Then cells were washed using 1X PBS twice. Further cells are permeated using 0.4 % triton X in PBS for 30 seconds followed by treatemt with 1 μ g/mL of DAPI solution for 15 minutes. The cells are again ished twice with
5 1X PBS (P^H 7.4). Finally, a confocal fluorescence microscope (Nikon Eclipse: TE 2000-E, Japan). Bioimaging studies are carried out using red and green filters. (Figure 2)

Example 5: Co-staining experiment with standard mitotracker green (MG):

Cells are cultured and maintained as described above. Cells were treated with 1 μ M compound
10 for 30 min followed by washing with PBS. Further cells were treated with 50 nm MG for 10 min and then washed with PBS. Cells were fixed and treated with DAPI as described above.

Example 6: Assessment of 3n for its ability to localize and stain mitochondria in living cells:

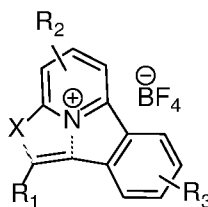
15 MCF-7 cells were incubated with 1 μ M of 3n for 1 h, and excess dyes were washed away by buffer solution. As shown in Figure 2 (a1 and b1), 3n stains specifically the mitochondrial region in MCF-7 cells. The costaining experiment with MitoTracker green MG (MT), a commercially available mitochondria imaging agent, suggests that the observed fluorescence from 3n is localized in the mitochondria of the living MCF-7 cells (Figure 2). This study
20 suggests that the 3n can successfully be exploited as an imaging agent for mitochondrial targeting.

Advantages of the invention:

1. This is first method for preparation of pyridinium-oxazole dyad salts.
- 25 2. These are new class of fluorescent molecules.
3. These class of molecules can be used as mitochondria tracker in live cells.
4. These ionic salts can be used as dopants in organic light emitting diods cells.

WE CLAIM:

1. A Pyridinium oxazole dyad scaffold of formula (I);



Formula (I)

Wherein; R_1 , R_2 and R_3 are same or different and each is independently selected from the group consisting of H, alkyl groups, alkenyl groups, aryl groups, heteroaryl groups, electron donating as well as electron withdrawing substituents;

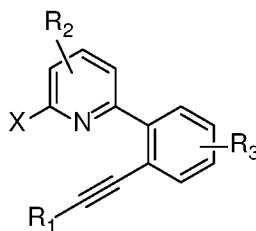
X is selected from the group consisting of $-CRR'$, O, S and $-NR$ wherein R and R' are same or different and each is independently selected from the group consisting of H, alkyl, benzyl, and aryl; further R and R' may form a cyclic ring having 4 to 6 carbon atoms.

2. The dyad scaffold as claimed in claim 1, wherein said scaffold is selected from group consisting of 1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(naphthalen-1-yl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(naphthalen-2-yl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(phenanthren-9-yl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(p-tolyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-isopropylphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-pentylphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-butoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium, 1-(4-fluorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-chlorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-(dimethylamino)phenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(4-pentanoylphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(2-methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(3-

methoxyphenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 1-(3-chlorophenyl)benzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 6-methyl-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 7-methyl-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 7-fluoro-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate, 7-chloro-1-phenylbenzo[a]oxazolo[4,3,2-cd]indolizin-10-ium tetrafluoroborate and 1-phenyldibenzo[a,f]oxazolo[4,3,2-cd]indolizin-12-ium tetrafluoroborate.

3. The dyad scaffold as claimed in claim 1, wherein said scaffold is used for imaging application for diagnosis of disease, wherein said imaging is mitochondrial imaging and said disease is cancer and said scaffold is used as a fluorescent agent for mitochondrial imaging.

4. A pyridine compound of formula (II),

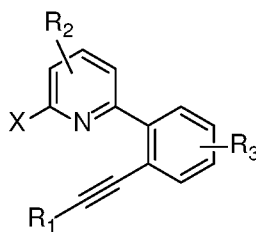


Formula (II)

wherein; R₁, R₂ and R₃ are same or different and each is independently selected from the group consisting of H, alkyl groups, alkenyl groups, aryl groups, heteroaryl groups, electron donating as well as electron withdrawing substituents;

X is selected from the group consisting of H, alkyl, benzyl, aryl, -OR, -SR and -NR; wherein R is selected from the group consisting of H, alkyl and aryl.

5. A process for the preparation of said Pyridinium oxazole dyad scaffold of formula (I) as claimed in claim 1, wherein said process comprises heating the reaction mixture consisting of pyridine of formula (II),



Formula (II)

wherein; R₁, R₂ and R₃ are same or different and each is independently selected from the group consisting of H, alkyl groups, alkenyl groups, aryl groups, heteroaryl groups, electron donating as well as electron withdrawing substituents;

X is selected from the group consisting of H, alkyl, benzyl, aryl, -OR, -SR and -NR; wherein R is selected from the group consisting of H, alkyl and aryl in suitable solvent system in presence of gold catalyst at the temperature ranging from 70 to 80°C for the time period ranging from 6 to 8 hours.

6. The process as claimed in claim 5, wherein said solvent system is selected from group consisting of acetonitrile, dichloromethane, chloroform and toluene.
7. The process as claimed in claim 5, wherein said gold catalyst is selected from group consisting of Chloro(triphenylphosphine)gold(I), Triphenylphosphine Gold(I) Trifluoromethanesulfonate, Chloro[(1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I), Chloro-(2-Biphenyl)dicyclohexylphosphine gold(I), tBuCyJhonAuCl, Chloro-tris(4-fluoro-triphenylphosphine)gold(I) (4-FC₆H₄)₃P-AuCl, Chloro-tris(4-trifluoromethyl-triphenylphosphine)gold(I) and Chloro-Tris(pentafluorophenyl)phosphine gold (I).
8. The process as claimed in claim 5, wherein said pyridine compound of formula (II) is selected from group consisting of 2-(tert-butoxy)-6-(2-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-(naphthalen-1-ylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-(naphthalen-2-ylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-(phenanthren-9-ylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-(hept-1-yn-1-yl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-(cyclohex-1-en-1-ylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-(p-tolylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((4-isopropylphenyl)ethynyl)

phenyl)pyridine, 2-(tert-butoxy)-6-(2-((4-pentylphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((4-methoxyphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((4-butoxyphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((4-fluorophenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((4-chlorophenyl)ethynyl)phenyl)pyridine, 4-((2-(6-(tert-butoxy)pyridin-2-yl)phenyl)ethynyl)-N,N-dimethylaniline, 1-(4-((2-(6-(tert-butoxy)pyridin-2-yl)phenyl)ethynyl)phenyl)pentan-1-one, 2-(tert-butoxy)-6-(2-((2-methoxyphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((3-methoxyphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((3-chlorophenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-methyl-6-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(5-methyl-2-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(5-fluoro-2-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(5-chloro-2-(phenylethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(4-chloro-2-(phenylethynyl)phenyl)pyridine, 1-methoxy-3-(2-(phenylethynyl)phenyl)isoquinoline, 2-(tert-butoxy)-6-(2-((2-chloro-5-methoxyphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(2-((3-chloro-4-methylphenyl)ethynyl)phenyl)pyridine, 2-(tert-butoxy)-6-(3,5-dimethoxy-2-(phenylethynyl)phenyl)pyridine.

9. A process for the preparation of pyridine compound of formula (II) as claimed in claim 4, wherein said process comprising the steps of:

- a) degassing the reaction mixture consisting of pyridine derivative, boronic acid in suitable solvent with nitrogen;
- b) adding sodium carbonate or potassium carbonate, Palladium catalyst to the reaction mixture of step a under continuous flow of nitrogen;
- c) heating the reaction mixture of step b at the temperature ranging from 70 to 80°C for 4 to 10 hours to afford desired product of formula (II).

10. The process as claimed in claim 9, wherein said boronic acid of step (a) is 2-alkynyl phenyl boronic acid and said solvent of step (a) is DMF/H₂O in a ratio of 1:1 and the said catalyst of step (b) is PdCl₂(PPh₃)₂.

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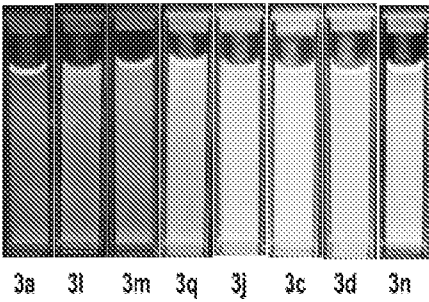


Fig. 1

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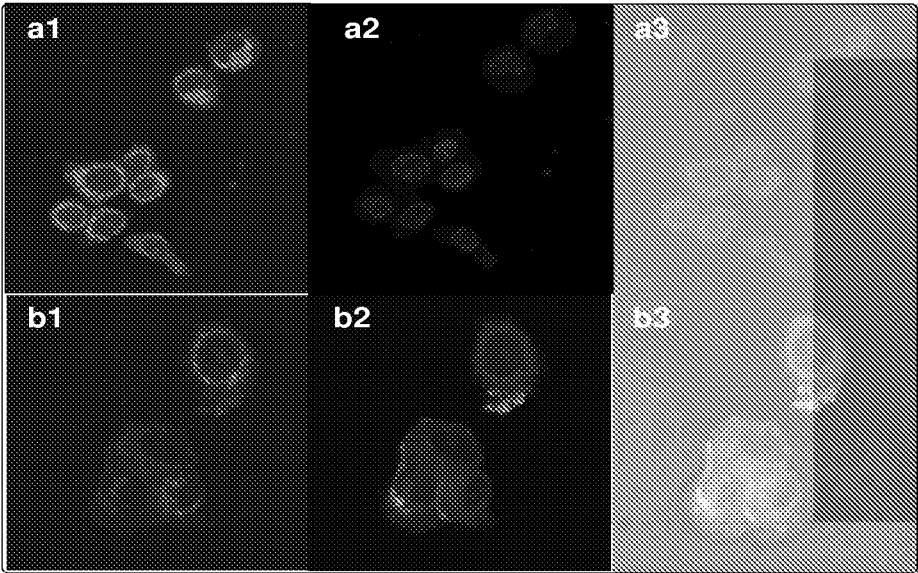


Fig. 2

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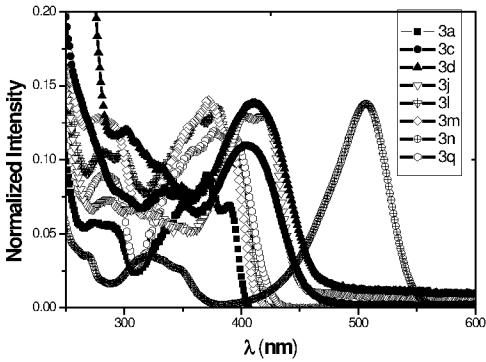


Fig. 3

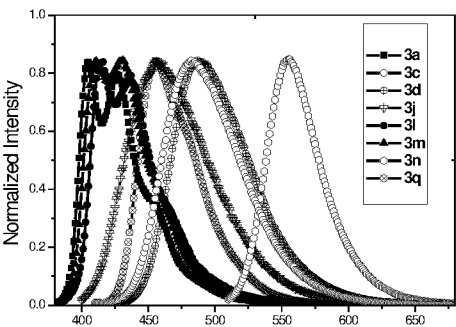


Fig. 4

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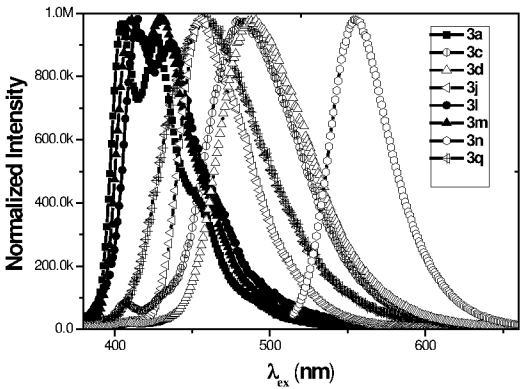


Fig. 5

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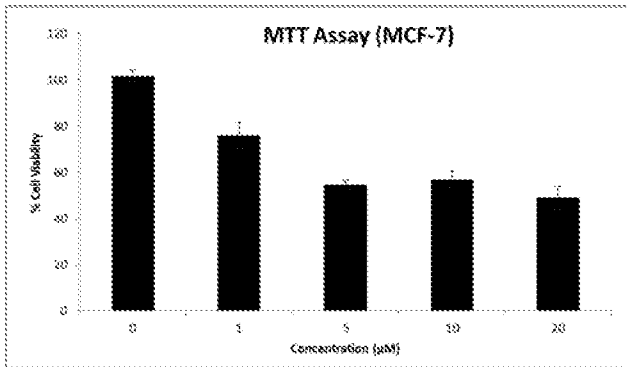


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2017/050480

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D471/06 C07D498/06 C07D513/06 A61K49/0015
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/136201 A1 (MAO FEI [US] ET AL) 9 June 2011 (2011-06-09) claims; examples	1-3,5-8
A	WO 2007/009101 A2 (UNIV LOUISIANA STATE [US]; HAMMER ROBERT P [US]; SOPER STEVEN A [US];) 18 January 2007 (2007-01-18) claims; examples	1-3,5-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 December 2017

Date of mailing of the international search report

19/03/2018

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Authorized officer

Gavriliu, Daniela

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2017/050480

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FORTAGE, JEROME ET AL: "Molecular Dyads of Ruthenium(II)- or Osmium(II)-Bis(terpyridine) Chromophores and Expanded Pyridinium Acceptors: Equilibration between MLCT and Charge-Separated Excited States", INORGANIC CHEMISTRY, vol. 52, no. 20, 2013, pages 11944-11955, XP002776219, ISSN: 0020-1669, DOI: 10.1021/IC401639G the whole document	1-3,5-8
A	SHINDE, POPAT S. ET AL: "Efficient access to alkynylated quinalizines via the gold(I)-catalyzed aminoalkynylation of alkynes", CHEMICAL COMMUNICATIONS, vol. 52, no. 52, 4 July 2016 (2016-07-04), pages 8152-8155, XP002776220, (CAMBRIDGE, UNITED KINGDOM) ISSN: 1359-7345, DOI: 10.1039/C6CC03414D the whole document table 1	1-3,5-8
X,P	SHAIKH, ASLAM C. ET AL: "Oxidative Intramolecular 1,2-Amino-Oxygenation of Alkynes under AuI/AuIII-Catalysis: Discovery of Pyridinium-Oxazole Dyad as an Ionic Fluorophore", ANGEWANDTE CHEMIE, INTERNATIONAL EDITION, vol. 56, no. 3, 16 January 2017 (2017-01-16), pages 757-761, XP002776221, ISSN: 1433-7851, DOI: 10.1002/ANIE.201609335 the whole document	1-3,5-8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2017/050480

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of Item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-3, 5-8

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-3, 5-8

Compounds of formula (I) and their preparation and uses for
mitochondrial imaging

2. claims: 4, 9, 10

Compounds of formula (II) and their preparation

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IN2017/050480

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011136201 A1	09-06-2011	CN 102712614 A	03-10-2012
		EP 2507220 A1	10-10-2012
		US 2011136201 A1	09-06-2011
		US 2017247402 A1	31-08-2017
		WO 2011068569 A1	09-06-2011

WO 2007009101 A2	18-01-2007	EP 1912921 A2	23-04-2008
		US 2009215105 A1	27-08-2009
		WO 2007009101 A2	18-01-2007
