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External Oxidant-Dependent Reactivity Switch in Copper-Mediated Intramolecular Carboamination of Alkynes: Access to a New Class of Fluorescent Ionic Nitrogen-Doped Polycyclic Aromatic Hydrocarbons

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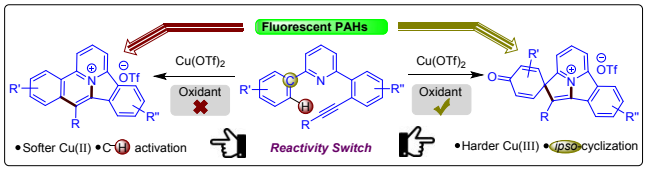
ABSTRACT:



An interesting case of external oxidant-controlled reactivity switch leading to a divergent set of ionic Nitrogen-Doped Polycyclic Aromatic Hydrocarbons (N-doped PAHs), is presented here which is quite unrecognized in copper mediated reactions. In the

current scenario, from the same pyridino-alkyne substrates, the use of external oxidant $PhI(OAc)_2$ in combination with $Cu(OTf)_2$, gave N-doped spiro-PAHs via a dearomative 1,2-carboamination process; whereas, without the use of oxidant, an alkyne/azadiene [4+2]-cycloaddition cascade occurred to exclusively afford ionic N-doped PAHs. These newly synthesized N-doped PAHs further exhibit tuneable emissions as well as excellent quantum efficiencies.

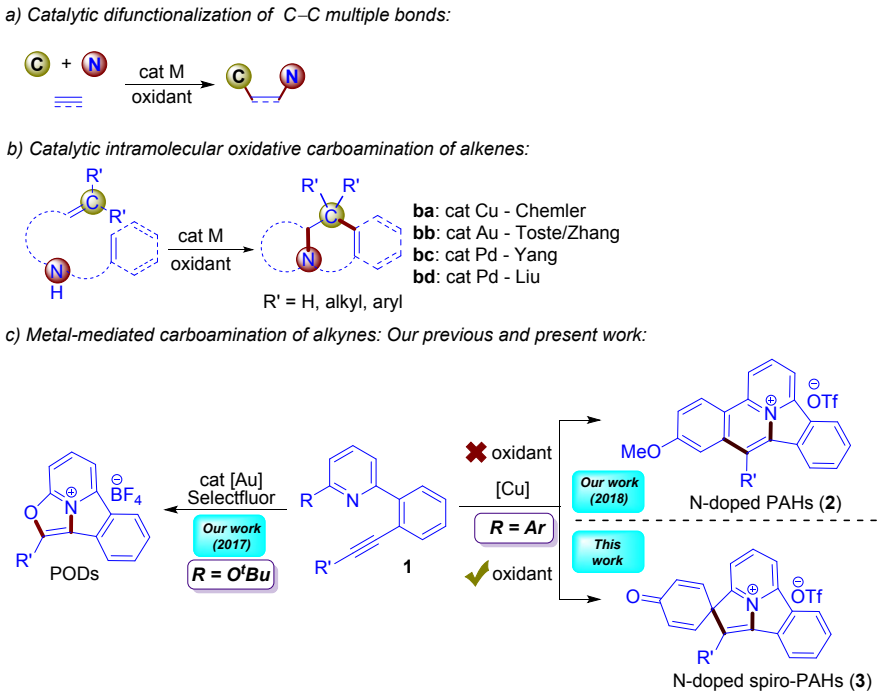
INRODUCTION

Nitrogen-doped Polycyclic Aromatic Hydrocarbons (N-doped PAHs)[1] have garnered considerable attention owing to their interesting applications in the field of optoelectronics, light emitting-diodes, supercapacitors and bio-imaging.[2,3] It was recently employed as efficient DNA intercalators as well.[4] Consequently, various methods of synthesis have been devised for these class of compounds. However, available approaches to access N-doped PAHs are confined to ring-closing metathesis reactions or Rh/Ru catalyzed aromatic C–H activation between arenes/heteroarenes.[1a,5] Considering their growing importance and multi-purpose applications, development of newer methods for expedient access to N-doped PAHs is highly desirable.

For the past decade, metal mediated carboamination reactions of C–C multiple bonds continue to be one of the most attractive strategies in synthetic organic chemistry for the incorporation of two distinct functionalities, carbon and nitrogen, across C–C multiple bonds in a single operation (Scheme 1a).[6] For instance, Chemler's group pioneered to disclose copper catalyzed/mediated oxidative carboamination reactions to construct several nitrogen-embedded heterocycles (Scheme 1ba).[7] An outstanding demonstration of external-oxidant-aided Au(I)/Au(III) catalysis strategy has been

developed by the groups of Toste and Zhang who independently reported carbohetero-functionalization reaction of alkenes (Scheme 1bb).[8] Further, Yang and co-workers elegantly demonstrated the Pd-catalyzed oxidative carboamination reactions to access indolines (Scheme 1bc).[9] Very recently, in 2017, Liu and co-workers reported a Pd-catalyzed asymmetric intramolecular oxidative carboamination reaction of alkenes to access indolines (Scheme 1bd).[10]

Based on our previous report on gold-catalyzed oxidative intramolecular 1,2-amino-oxygenation reaction of alkynes **1** to Pyridinium-Oxazole Diads **(**PODs) (Scheme 1c, R = O^{t}Bu),[11] we wondered whether ionic N-doped PAHs could be derived from substrate of type **1** (Scheme 1c, R = Ar) *via* 1,2-carboamination of alkynes in the presence of metal/oxidant conditions. Accordingly, when several metal catalysts/oxidants were screened (*vide infra*), an interesting oxidant-dependent reactivity switch was observed which led to the discovery of two new classes for N-doped PAHs, **2** and **3**, starting from the same substrate **1** through copper-mediated method. The product **2** is a result of oxidant-unaided carboamination *via* alkynes/azadienes [4+2]-cycloaddition cascade of **1**; whereas, product **3** is a result of oxidative dearomative carboamination of **1**. Of note, part of this work comprising the Cu(II)-mediated intramolecular [4+2]-cycloaddition cascade leading to PAHs **2** has been communicated by our group recently.[12] Herein, we report full details of our findings on the dearomative carboamination process leading to ionic N-doped spiro-PAHs (**1**→PAHs **3**, Scheme 1c) with due comparison to that of ionic N-doped PAHs **2**.[13]



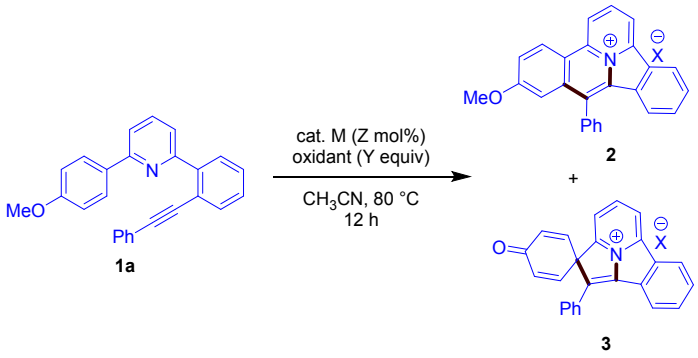
Scheme 1. Metal-mediated 1,2-carboamination reactions

RESULTS AND DISCUSSION

We initiated our study by choosing 2-(4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl) pyridine (**1a**) as a model substrate (Table 1). Based on the available literature on oxidative gold catalysis,[14] and taking our previous study[11] as a reference point, we endeavoured to investigate the proposed reaction with various gold catalysts in the presence of Selectfluor (oxidant, 1.0 equiv) in CH_3CN:MeOH[15] (99:1 v/v) at 80 °C. Accordingly, gold catalysts such as Ph_3PAuCl, $(C_6F_5)_3PAuCl$ and JohnPhosAuCl were examined; however, the desired product **3** [X = BF_4] was not observed in any of the cases (entries 1-3). On the contrary, we found that $Cu(OTf)_2$ in combination with Selectfluor can afford **2** [X = BF_4] in 62% yield (entry 4). Several other copper catalysts were also tested but to no avail; they continued to furnish **2** [X = BF_4] in varied yields (entries 5-8). When other oxidants were tried in combination with $Cu(OTf)_2$, we were encouraged to observe PAH **3a** [X = OTf]; albeit in poor yields (entries 9-11). Without oxidant,

the reaction yields **2a** [X = OTf] (entry 12) in 17% yield; such low yield was expected because now there's no entity in the reaction to provide the counter-anion X. Here, it is important to note that the contrast between entries 9-11 and entry 12 gave an early indication of an oxidant dependent selectivity of the carboamination reaction. Therefore, we decided to capitalize the opportunity by searching for two optimum orthogonal reaction conditions leading to PAH **2a** or **3a**. Not surprisingly, when catalytic loading of $Cu(OTf)_2$ was hiked, the formation of **3a** started to increase (37%, entry 13) and reached a maximum with stoichiometric amount of $Cu(OTf)_2$ (78%, entry 14). On the other hand, use of oxidant $PhI(OAc)_2$ in combination with 1.0 equiv of $Cu(OTf)_2$ completely switched the reactivity (entries 15-16) and obtained **3a** in 94% when 1.5 equiv of oxidant was used (entry 17). We further surmised that the presence of –OTf containing

Table 1. Optimization studies for catalysts and oxidants[a]



Sr. No.	Cat [M] (Z mol%)	Oxidant (Y equiv)	Yield (%)[b]	
			2	**3**
1	$(C_6F_5)_3PAuCl$ (10)	Selectflour (1.0)	--	--
2	Ph_3PAuCl (10)	Selectflour (1.0)	--	--
3	JohnPhosAuCl (10)	Selectflour (1.0)	--	--
4	$Cu(OTf)_2$ (10)	Selectflour (1.0)	62[c]	--
5	$[Cu(OTf)]_2 \cdot C_6H_6$ (10)	Selectflour (1.0)	48	--

6	$CuCl_2$ (10)	Selectflour (1.0)	41	--
7	$Cu(OAc)_2$ (10)	Selectflour (1.0)	52	--
8	$Cu(ACN)_4BF_4$ (10)	Selectflour (1.0)	57	--
9	$Cu(OTf)_2$ (10)	$Ph_2I(OTf)$ (1.0)	--	09[d]
10	$Cu(OTf)_2$ (10)	$PhI(OAc)_2$ (1.0)	--	18[d]
11	$Cu(OTf)_2$ (10)	$PhI(CF_3CO_2)_2$ (1.0)	--	12[d]
12	$Cu(OTf)_2$ (10)	--	17[d]	--
13	$Cu(OTf)_2$ (50)	--	37	--
14	**$Cu(OTf)_2$ (100)**	**--**	**78**	**--**
15	$Cu(OTf)_2$ (100)	$PhI(OAc)_2$ (1.0)	--	82
16	$Cu(OTf)_2$ (100)	$PhI(OAc)_2$ (1.2)	--	85
17	**$Cu(OTf)_2$ (100)**	**$PhI(OAc)_2$ (1.5)**	**--**	**94**

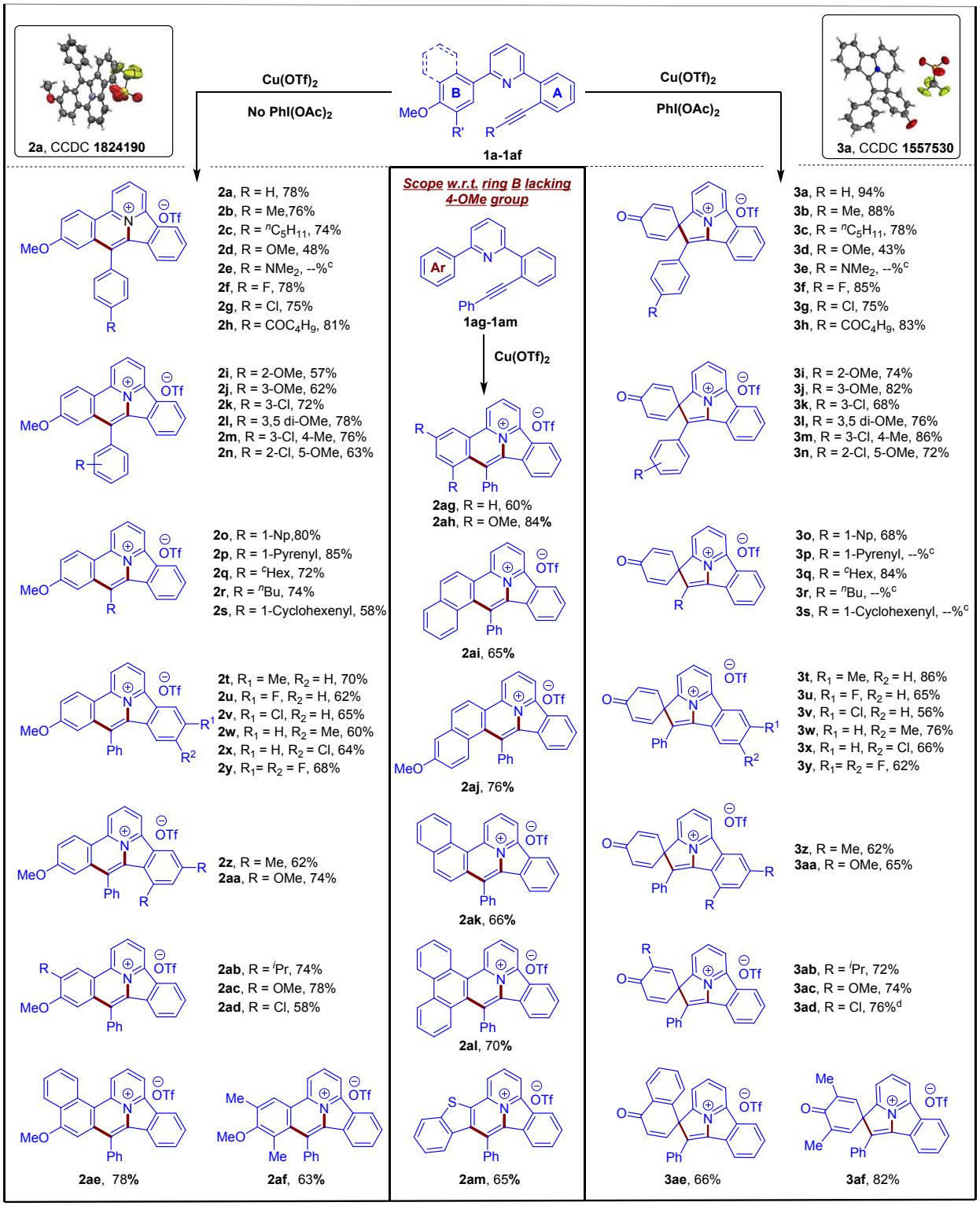
[a]Standard Reaction condition: 0.11 mmol **1a**, Z mol% catalyst [M], Y equiv of oxidant, CH_3CN (2.0 ml), 80 °C, 12 h. [b]Isolated yields. [c]Counter anion X = BF_4. [d]Counter anion X = OTf.

additives would make the reaction catalytic with respect to copper. In this regard, various additives such as $Zn(OTf)_2$, $Sc(OTf)_3$ and TfOH were examined for both the reactions leading to **2a** or **3a** (not shown here). However, they were not found to be satisfactory. The structures of product **2a** and **3a** were unambiguously confirmed by the X-ray crystallographic analysis (see Table 2).

Having optimized the reaction conditions, the scope and generality of these two divergent reactions were studied (Table 2). First, substrates with variation in aryl ring at alkyne-terminus (**1a**-**1n**) were put to test. Initially, it worked well with functional groups such as alkyl and –OMe under both the conditions (**2b**-**2d** and **3b**-**3d**). However, stronger electron donating group such as $–NMe_2$ was incompatible under the reaction conditions (**2e** or **3e**). With varying substitution

pattern (*ortho*, *meta*, *para*) on the previously mentioned aryl moiety, both the carboamination reactions were well tolerated to furnish the corresponding PAHs in good yields (**2f-2n** and **3f-3n**). Next, screening of substrates bearing bulky aromatics or long-chain/cyclic aliphatics at the alkyne terminus of the pyridino alkynes (**1o-1s**) were undertaken. The substrate with sterically encumbered pyrenyl group results only in desired PAHs **2p** (85% yield) but not the corresponding spiro-PAHs **3p**; whereas, **1o**, carrying bulky 1-Np aromatic ring, efficiently afforded both the corresponding PAHs **2o** and **3o** in 80 and 68% yields, respectively.

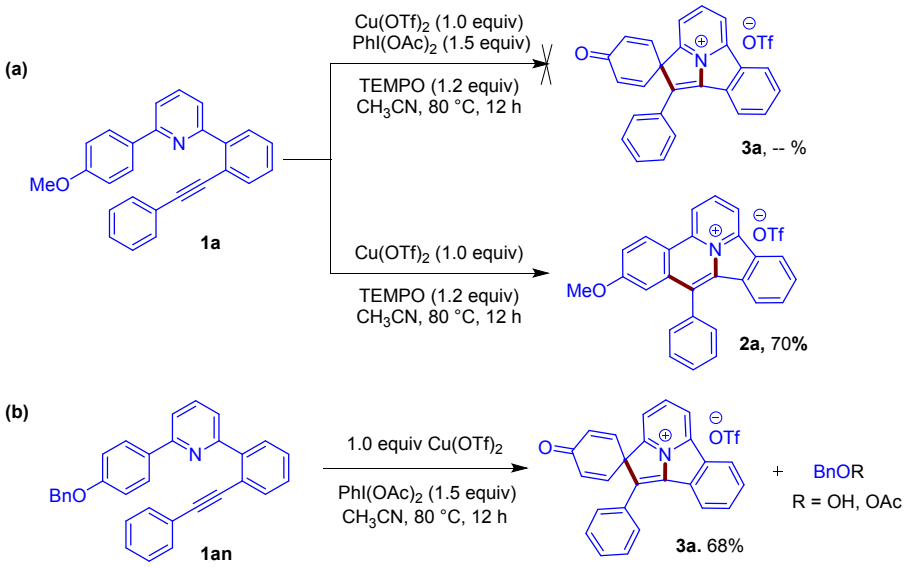
Table 2. Substrate scope of reaction[a,b]



[a]Reaction conditions: 0.25 mmol **1**, 1.0 equiv $Cu(OTf)_2$ or 1.0 equiv $Cu(OTf)_2$/1.5 equiv $PhI(OAc)_2$, CH_3CN (2 mL), 80 °C, 12 h. [b]Isolated yield. [c]Complex reaction mixture was obtained.[d] CCDC for **2aj** - 1824191 and for **3ad** –1557529.

Further, placement of aliphatic substituents on the alkyne terminus (**1q**-**1s**), the desired PAHs **2q**-**2s** and **3q** emerged in good yields except for ^{n}Bu and cyclohexenyl group which failed to produce the desired spiro PAHs **3r** and **3s**. Next, when we focussed on examining the tolerance of the substituents on ring **A**, we were pleased to observe that introduction of –F, –Cl, and –Me substituents to the ring **A** resulted in the desired PAHs **2t**-**2x** and **3t**-**3x** in 56-86% yields. Also, both the carboamination reactions permitted di-substitutions at the ring **A** to furnish **2y**-**2aa** and **3y**-**3aa** in moderate yields.

Next, substrates **1ab-1af** were examined under both the optimized reaction conditions to investigate the tolerance of substituents at ring **B**. It was observed that the desired PAHs **2ab**-**2af** and **3ab**-**3af** were obtained in a smooth reaction from **1ab**-**1af** under both catalytic systems giving the products in good yields (58-82%). At this stage, we wanted to verify whether –OMe substituent in ring **B** is essential for the C–H activation pathway leading to PAHs **2**. If not, the substrate scope for the formation of PAHs **2** could be further extended with various substitutions on ring **B**. In this attempt, we were able to obtain PAHs **2ag** and **2ah** in good yields (60 and 84%). Moreover, replacement of phenyl group with 1-Np, 2-Np, 9-phenanthrenyl were well tolerated in the carboamination reactions to produce the desired PAHs in good yields (**2ai**-**2al**). The fact that heterocyclic moiety 1-benzothiophenyl also allowed the carboamination giving PAHs **2am** in 65% yield, increased the scope of the present carboamination reaction. Scalability of the methods was tested by employing **1a** (2.7 mmol) as a starting material to obtain **2a** in 76% and **3a** in 91%.

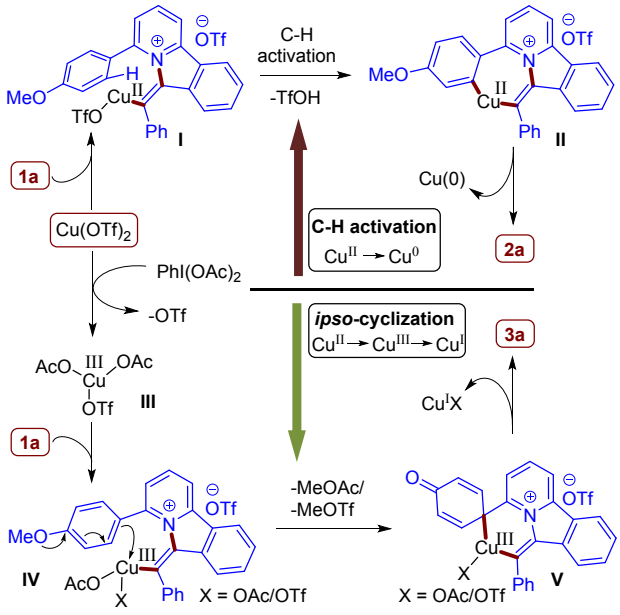


Scheme 2. Control experiments.

Next, a set of control experiments were performed to gain insight into the mechanism (Scheme 2). In the presence of radical scavengers such as 2,2,6,6-*tetra*-methylpiperidine-1-oxyl (TEMPO), the dearomative carboamination reaction yielding **3a** is completely arrested; whereas, the yield of this reaction **1a→2a** is not hampered (Scheme 2a). This implies the involvement of radical mechanism only in case of dearomative carboamination. In addition, mass spectrometry detects the formation of BnOH as well as BnOAc in the reaction mixture for **1an** which indicates that such de-alkylation (e.g. debenzylation /demethylation) steps are facile in presence of AcO and OTf anions (Scheme 2b).

A plausible mechanism based on literature reports and control experiments above is outlined in Scheme 3. At first, vinyl copper intermediate **I** is generated after activation of the alkyne by $Cu(OTf)_2$ which enabled the nucleophilic attack by the pyridyl nitrogen atom in 5-*exo*-*dig* fashion.[16] This intermediate would lead to copper(II) intermediate **II** when C–H bond of proximal aryl ring in **I** is activated followed by subsequent removal of TfOH.[17] Thereafter,

reductive elimination would take place to give product **2a**. As far as the formation of **3a** is concerned, the instantaneous generation of a highly electrophilic Cu(III) species **III** is initiated first from $Cu(OTf)_2$ and $PhI(OAc)_2$.[18] Similar to the earlier case, the electrophilic Cu(III)-species **III** would trigger *syn*-aminocupration[19] in **1a** to form vinyl copper(III) intermediate **IV**. Next, instead of regular C–H activation of proximal arene C–H bond, dearomative[20] spirocyclization *via* the intramolecular *ipso*-attack of arenes on Cu(III) centre (*cf.* **IV**) would lead to six-membered cyclic copper(III) intermediate **V** which after reductive elimination would provide **3a**. This is probably due to the inhibition of single electron transfer process between $Cu(OTf)_2$ and $PhI(OAc)_2$ which generates catalytically active Cu(III)-species **III**. The bifurcation between the two distinct mechanisms for the formation of either **2a** or **3a** from **1a** could be accounted for on the basis of Pearson's HSAB concept.[21] The softer copper Cu(II) center in **I** is likely to prefer C–H activation; whereas, the harder Cu(III) center in **IV** would prefer to act as electrophile for the *ipso* attack of aromatic ring.



Scheme 3. A plausible reaction mechanism

The photophysical properties of both the synthesized PAHs **2** and **3** were studied in CH_2Cl_2 solution which exhibited intense fluorescence (Table 3 and 4). For the study of optical properties pertaining to PAHs **2**, preference is given to those containing extended polycyclic core such as **2ag-aj**, **2al**. These fluorophores show good photoluminescence capabilities (Φ_f = 0.06 to 0.88) with the photoluminescence (PL) occuring in the visible region ranging from violet to orange (λ_{em}: 430-619 nm). In particular, the absorption and excitation maxima, the PL maxima and quantum yields (ϕ_f), as well as the excited state lifetimes (τ_f) of these compounds in CH_2Cl_2 solution are listed in Table 3 (for PAHs **2**) and 4 (for PAHs **3**), whereas the corresponding absorption and emission spectra are depicted in Figure 1 (for PAHs **2**) and 2 (for PAHs **3**). The photoluminescence spectra of fluorophores PAHs **2** show intense peaks between λ_{em}: 434-619 nm with Stokes shifts varies between (50-233 nm) which reveals violet-to-red fluorescence emissions (Table 3 and Figure 1). On the other hand, the photoluminescence spectra of PAHs **3** fluorophores, which are selected on the basis of the presence of a donor/acceptor/bulky substituent at a certain position, show intense peaks between λ_{em}: 430–540 nm with Stokes shifts varies between (50-137 nm) which reveals violet to yellow fluorescence emissions (Table 4 and Figure 2). Both of these emissions, of course, depend on the functional group present. For instance, substituents like methoxy on plain phenyl core in PAHs **2** (**2ag** and **2aa**; Figure 1) and –OMe, –F on PAHs **3** (**3j** and **3u**; Figure 2) had only modest effects on the fluorescent properties. When the core phenyl ring was replaced by bulky substituents like 1-napthyl, it had stronger effect on the fluorescent properties (**3o**, Figure 2). Extension of the π-conjugated systems leads to significant bathochromic shifts in emission (**2p**, **3i-j**; Figure 1-2). These fluorophores have good photoluminescence capabilities with Φ_f values ranging between 0.06 to 0.86 (for PAHs **2**) and 0.10 to 0.80 (for PAHs **3**). The life time τ_f values for PAHs **2** are

consistent with a doublet multiplicity; whereas, the life time τ_f values for PAHs **3** are consistent with a singlet multiplicity.

Table 3. Spectral properties of selected PAHs **2** in CH_2Cl_2 at RT (10^{-5} M)

comp	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	ΔStoke's (nm)[c]	ϕ[d]	τ_f (ns)[e]
2a	388	444	56	0.86	6.52
2p	386	619	233	0.06	10.48
2aa	417	482	65	0.38	2.38
2ag	385	434	49	0.74	0.46
2ah	454	507	53	0.88	4.89
2ai	428	470	42	0.54	2.58
2aj	346	495	149	0.73	4.37
2al	415	490	75	0.57	7.52

[a]The maximum absorption band is more than 300 nm. Excited at the longest maximum absorption band in CH_2Cl_2. [b]Excited wavelength. [c]Stokes shift = λ_{em} - λ_{abs}. [d]Quinine sulfate and fluorescein was used as the standard for calculation of quantum yield. [e]Fluorescent lifetime.

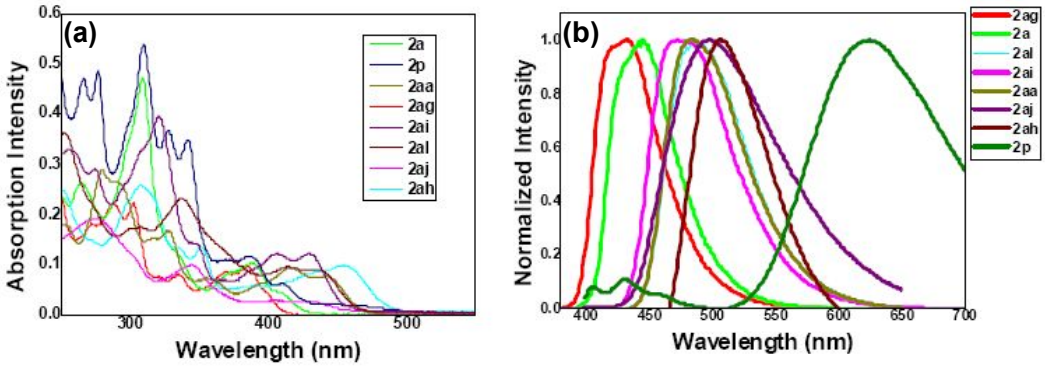


Figure 1. (a) Absorption spectra of selected PAHs **2** in CH_2Cl_2 at RT. (b) Emission spectra of selected PAHs **2** in CH_2Cl_2 at RT.

Table 4. Photophysical data of selected PAHs **3** in CH_2Cl_2 at RT

comp	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	ΔStoke's (nm)[c]	ϕ_f[d]	τ_f (ns)[e]

3a	393	453	60	0.80	2.1
3b	408	469	61	0.74	3.2
3g	395	460	65	0.57	2.4
3d	444	513	69	0.53	4.0
3h	381	437	56	0.10	3.7
3u	401	458	57	0.49	2.2
3aa	436	500	64	0.19	5.9
3j	384	521	137	0.24	4.2
3i	418	519	101	0.25	7.6
3o	426	534	108	0.15	9.7

[a]The maximum absorption bands more than 300 nm; Excited at the longest maximum absorption band in CH_2Cl_2. [b]Excited wavelength. [c]Stokes shift = λ_{em} - λ_{abs}. [d]Quinine sulfate and fluorescein was used as the standard for calculation of quantum yield. [e]Fluorescent lifetime.

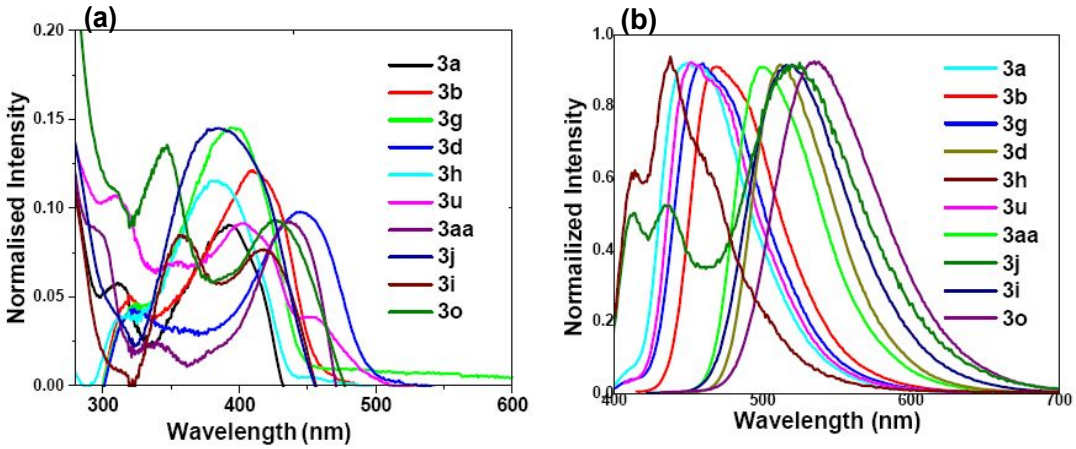


Figure 2. (a) Absorption spectra of representative spiro-PAHs **3** in CH_2Cl_2 at RT. (b) Emission spectra of representative ionic spiro-PAHs **3** in CH_2Cl_2 at RT.

CONCLUSION

To conclude, a unique example of divergent reactivity in copper-mediated intramolecular carboamination reactions of alkynes has been reported. Depending on whether the external oxidant is employed or not, two different kinds of fluorescent ionic N-doped PAHs were obtained from the same starting materials. The current phenomenon of oxidant dependent reactivity switch is quite unfamiliar[22] in copper mediated reactions and should be extendable to a

number of other copper-mediated processes. Also, this establishes the first intramolecular dearomative carboamination reaction of alkynes utilizing oxidative copper chemistry which is high-yielding and has broad functional group tolerance. Such a process would allow the direct preparation of complex "3-dimensional" molecules with a number of functional handles.[23] The presence of inherent three-dimensionality and excellent photophysical properties is supposed to make them potential candidates for further applications in material science and biology.

EXPERIMENTAL SECTION

1. General information

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Screens were performed in 2.5 mL or 5.0 mL glass vials with a PTFE-lined cap, and all other reactions were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining iodine, potassium permanganate solution and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 100-200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in petroleum ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran was distilled from Na/benzophenone under an atmosphere of dry nitrogen.

Anhydrous dichloromethane, toluene and acetonitrile were dried by using standard protocol under nitrogen. Gold and copper catalysts were purchased from Sigma-Aldrich. Deuterated solvents were used as supplied. Melting points are uncorrected and recorded using digital Büchi melting point apparatus B-540. NMR spectra were recorded on Bruker AV, 400/500 spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin(quintet), sextet (sxt), br.s. (broad signal), m (multiplet) etc. HRMS (ESI) data were recorded on an ion trap Thermo Scientific Q-Exactive, Accela 1250 pump. UV-visible absorption spectra were measured with a Perkin Elmer LAMBDA 950 UV/Vis Spectrophotometers. Fluorescence spectra were recorded by Photon Technology International, QuantaMaster™ 400 Spectrofluorometer and absolute quantum yields were determined using a calibrated integrating sphere system. Time-resolved fluorescence spectra were measured using a Horiba - Lifetime Fluorescence Spectrofluorometers system equipped with a PLP-10 picosecond light pulser (LED wavelengths: 470 or 570 nm). Single-crystal data was collected on a Super Nova Dual source X-ray diffractometer system (Agilent Technologies) equipped with CCD area detector and graphite-monochromatized (MoK_α= 0.71073Å, CuK_α= 1.54184Å) radiation.

2 Representative Procedures

2.1 Procedure for the synthesis of starting materials

The synthesis of pyridino-alkynes (**1a-z**, **1aa-an**) are in accordance with methods developed by our group.[12] Please vide ref. 12 for detailed structures of precursors of **1**, i.e, bromo-alkynes and boronic acids.

2.2 Procedure for copper-promoted intramolecular carboamination of alkynes

The corresponding synthesis of ionic PAHs **2** and spectral data thereof are reported in our previous communication.[12]

2.3 Procedure for copper-mediated intramolecular oxidative dearomative carboamination of alkynes

To a screw-cap vial containing a stir bar were added 2-(4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1a**) (40 mg, 0.11 mmol, 1.0 equiv), $PhI(OAc)_2$ (54 mg, 0.17 mmol, 1.5 equiv), $Cu(OTf)_2$ (38 mg, 0.11 mmol, 1.0 equiv) 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 12 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 the combined mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **3a** in 94% yield.

4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3a): Off white solid, 51 mg, 94% yield; mp = 268-270 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.82 (d, *J* = 8.0 Hz, 1 H), 8.64 - 8.77 (m, 2 H), 8.35 (d, *J* = 7.6 Hz, 1 H), 8.20 (d, *J* = 7.6 Hz, 1 H), 7.91 - 8.04 (m, 2 H), 7.76 - 7.85 (m, 2 H), 7.67 (d, *J* = 3.4 Hz, 3 H), 6.98 - 7.08 (d, *J* = 9.9 Hz, 2 H), 6.81 - 6.95 (d, *J* = 9.9 Hz, 2 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 183.9, 146.0, 144.9, 141.3, 140.3, 140.1, 138.1, 135.7, 134.2, 133.3, 132.3, 132.0, 129.9, 129.2, 128.2, 128.1, 125.7, 124.4, 120.1, 119.9, 65.2; ^{19}F NMR (376.5 MHz, DMSO-d_6)δ = -77.75; HRMS (ESI) calcd for $C_{25}H_{16}ON^+$ (M - OTf)$^+$ 346.1226, found 346.1226.

4-oxo-1'-(p-tolyl)spiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3b): Off white solid, 48 mg, 88% yield; mp = 248-250 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.81 (d, *J* = 8.0 Hz, 1 H), 8.60 - 8.73 (m, 2 H), 8.36 (d, *J* = 7.6 Hz, 1 H), 8.17 (d, *J* = 8.0 Hz, 1 H), 7.88 - 8.05 (m, 2 H), 7.67 - 7.79 (d, *J* = 7.6 Hz, 2 H), 7.39 - 7.53 (d, *J*=7.6 Hz, 2 H), 6.95 - 7.08 (d, *J* = 9.5 Hz, 2 H), 6.79 - 6.91 (d, *J* = 9.5 Hz, 2 H), 2.42 (s, 3 H); ^{13}C{1H}NMR (125 MHz, DMSO-d_6) δ = 183.9, 145.8, 144.5, 142.6, 141.1, 140.7, 140.3, 137.5, 135.5, 134.1, 133.3, 132.1, 130.5, 128.2, 126.5, 125.6, 124.3, 120.1, 119.8, 65.1, 21.2; HRMS (ESI) calcd for $C_{26}H_{18}ON^+$ $(M - OTf)^+$ 360.1383, found 360.1382.

4-oxo-1'-(4-pentylphenyl)spiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3c): Yellowish solid, 41 mg, 78% yield; mp = 202-204 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.81 (d, *J* = 8.0 Hz, 1 H), 8.58 - 8.74 (m, 2 H), 8.39 (d, *J* = 7.2 Hz, 1 H), 8.17 (d, *J* = 7.6 Hz, 1 H), 7.93 - 8.03 (m, 2 H), 7.69 - 7.80 (t, *J* = 8.4 Hz, 2 H), 7.44 - 7.55 (t, *J* = 8.0 Hz, 2 H), 6.97 - 7.06 (t, *J* = 9.5 Hz, 2 H), 6.80 - 6.90 (d, *J* = 9.5 Hz, 2 H), 2.68 (t, *J* = 7.8 Hz, 2 H), 1.63 (quin, *J* = 7.2 Hz, 2 H), 1.33 (d, *J* = 3.1 Hz, 4 H), 0.88 (t, *J* = 6.7 Hz, 3 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 183.9, 147.4, 145.7, 144.5, 141.0, 140.7, 140.4, 137.4, 135.5, 134.0, 133.3, 132.1, 129.8, 128.2, 128.1, 126.7, 125.6, 124.4, 120.0, 119.8, 65.1, 35.1, 30.9, 30.1, 21.9, 13.8; HRMS (ESI) calcd for $C_{30}H_{26}ON^+$ $(M - OTf)^+$ 416.2009, found 416.2006.

1'-(4-methoxyphenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (**3d**): Yellow solid, 24 mg, 43% yield; mp = 198-200 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.82 (d, *J* = 7.9 Hz, 1 H), 8.63 - 8.76 (m, 2 H), 8.35 (d, *J* = 7.3 Hz, 1 H), 8.20 (d, *J* = 7.3 Hz, 1 H), 7.93 - 8.05 (m, 2 H),

7.61 (t, *J* = 7.9 Hz, 1 H), 7.41 (d, *J* = 7.3 Hz, 1 H), 7.17 - 7.31 (m, 2 H), 6.97 - 7.09 (d, *J* = 9.8 Hz, 2 H), 6.81 - 6.93 (d, *J* = 9.8 Hz, 2 H), 3.80 (s, 3 H); $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6) δ = 183.9, 159.7, 146.0, 145.0, 141.3, 140.2, 139.9, 138.3, 135.8, 134.2, 133.4, 132.4, 131.3, 130.4, 128.1, 125.7, 124.5, 120.6, 120.2, 120.0, 117.6, 113.0, 65.2, 55.3; HRMS (ESI) calcd for $C_{26}H_{18}O_2N^+$ $(M - OTf)^+$ 376.1332, found 376.1331.

1'-(4-fluorophenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3f): Off white solid, 52 mg, 85% yield; mp = 216-218 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (400 MHz, DMSO-d_6) δ = 8.82 (d, *J* = 7.9 Hz, 1 H), 8.77 - 8.64 (m, 2 H), 8.34 (d, *J* = 7.3 Hz, 1 H), 8.20 (d, *J* = 7.9 Hz, 1 H), 8.06 - 7.92 (m, 2 H), 7.88 (t, *J* = 5.5 Hz, 2 H), 7.53 (t, *J* = 7.9 Hz, 2 H), 7.10 - 6.96 (d, *J* = 9.2 Hz, 2 H), 6.93 - 6.78 (d, *J* = 9.2 Hz, 2 H); $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6) δ = 183.8, 165.0 - 162.5 (d, *J* = 252.7 Hz), 145.9, 145.0, 141.3, 139.9, 139.0, 138.1, 135.7, 135.2, 134.3, 133.3, 132.4, 131.0 - 130.9 (d, *J* = 9.2 Hz), 128.0, 125.7, 124.5, 120.2 - 120.0 (d, *J* = 20.4 Hz), 117.4 - 117.2 (d, *J* = 22.3 Hz), 65.2; HRMS (ESI) calcd for $C_{25}H_{15}ONF^+$ $(M - OTf)^+$ 364.1132, found 364.1130.

1'-(4-chlorophenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3g): Off white solid, 40 mg, 75% yield; mp = 274-276 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (400 MHz, DMSO-d_6) δ = 8.82 (d, *J* = 8.0 Hz, 1 H), 8.73 (t, *J* = 7.8 Hz, 1 H), 8.69 (d, *J* = 7.6 Hz, 1 H), 8.35 (d, *J* = 8.0 Hz, 1 H), 8.21 (d, *J* = 7.6 Hz, 1 H), 8.01 (t, *J* = 7.6 Hz, 1 H), 7.96 (t, *J* = 7.4 Hz, 1 H), 7.78 - 7.87 (d, *J* = 8.4 Hz, 2 H), 7.69 - 7.78 (d, *J* = 8.4 Hz, 2 H), 6.96 - 7.08 (d, *J* = 9.9 Hz, 2 H), 6.80 - 6.94 (d, *J* = 9.9 Hz, 2 H); $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6) δ = 183.8, 146.1, 145.2, 141.4, 139.8, 138.7, 138.5, 136.7, 135.8, 134.4, 133.3, 132.5, 130.2, 130.0, 128.0, 127.9, 125.7, 124.7, 120.2, 120.0, 65.1; HRMS (ESI) calcd for $C_{25}H_{15}ONCl^+$ $(M - OTf)^+$ 380.0837, found 380.0838.

4-oxo-1'-(4-pentanoylphenyl)spiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3h): Off white solid, 43 mg, 83% yield; mp = 246-248 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.83 (d, *J* = 8.0 Hz, 1 H), 8.75 (t, *J* = 8.0 Hz, 1 H), 8.69 (d, *J* = 7.6 Hz, 1 H), 8.36 (d, *J* = 7.6 Hz, 1 H), 8.17 - 8.26 (m, 3 H), 7.99 - 8.06 (m, 1 H), 7.88 - 7.99 (m, 3 H), 6.97 - 7.10 (d, *J* = 9.5 Hz, 2 H), 6.81 - 6.93 (d, *J* = 9.5 Hz, 2 H), 3.08 (t, *J* = 7.2 Hz, 2 H), 1.63 (quin, *J* = 7.3 Hz, 2 H), 1.30 - 1.42 (m, 2 H), 0.92 (t, *J* = 7.2 Hz, 3 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 199.4, 183.8, 146.3, 145.4, 141.5, 139.7, 139.1, 138.7, 138.6, 135.9, 134.4, 133.4, 133.1, 132.7, 129.2, 128.6, 127.9, 125.8, 124.8, 120.3, 120.1, 65.2, 37.8, 25.7, 21.7, 13.8; HRMS (ESI) calcd for $C_{30}H_{24}O_2N^+$ (M - OTf)$^+$ 430.1802, found 430.1800.

1'-(2-methoxyphenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3i): Yellow solid, 50 mg, 74% yield; mp = 214-216 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.78 (d, *J* = 7.9 Hz, 1 H), 8.69 (t, *J* = 7.6 Hz, 1 H), 8.64 (d, *J* = 7.3 Hz, 1 H), 8.16 (d, *J* = 7.3 Hz, 1 H), 7.86 - 8.00 (m, 2 H), 7.79 (d, *J* = 7.3 Hz, 1 H), 7.63 (t, *J* = 7.9 Hz, 1 H), 7.58 (d, *J* = 7.9 Hz, 1 H), 7.34 (d, *J* = 8.5 Hz, 1 H), 7.12 (t, *J* = 7.3 Hz, 1 H), 6.92 - 7.04 (d, *J* = 9.8 Hz, 2 H), 6.71 - 6.81 (d, *J* = 9.8 Hz, 2 H), 3.81 (s, 3 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 184.1, 157.0, 146.2, 144.7, 141.3, 140.2, 139.3, 135.9, 135.5, 133.6, 133.5, 132.9, 131.8, 129.0, 128.6, 126.3, 125.3, 120.8, 120.2, 120.1, 117.2, 112.5, 66.4, 55.5; HRMS (ESI) calcd for $C_{26}H_{18}O_2N^+$ (M - OTf)$^+$ 376.1332, found 376.1332.

1'-(3-methoxyphenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3j): Yellow solid, 56 mg, 82% yield; mp = 216-218 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.78 - 8.85 (m, 1 H), 8.62 -

8.76 (m, 2 H), 8.29 - 8.39 (m, 1 H), 8.21 (d, *J* = 7.8 Hz, 1 H), 7.93 - 8.04 (m, 2 H), 7.55 - 7.65 (m, 1 H), 7.42 (d, *J* = 7.3 Hz, 1 H), 7.20 - 7.28 (m, 2 H), 6.97 - 7.09 (m, *J* = 9.6 Hz, 2 H), 6.87 (s, 1 H), 6.89 (s, 1 H), 3.80 (s, 3 H); $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6) δ = 184.0, 159.7, 146.0, 145.0, 141.3, 140.2, 139.9, 138.3, 135.8, 134.2, 133.4, 132.4, 131.3, 130.4, 128.1, 125.7, 124.5, 120.6, 120.2, 120.0, 117.6, 113.0, 65.2, 55.4; HRMS (ESI) calcd for $C_{26}H_{18}O_2N^+$ (M - OTf)$^+$ 376.1332, found 376.1330.

1'-(3-chlorophenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3k): Off white solid, 36 mg, 68% yield; mp = 224-226 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (500 MHz, DMSO-d_6) δ = 8.83 (d, *J* = 8.0 Hz, 1 H), 8.76 (t, *J* = 8.0 Hz, 1 H), 8.69 (d, *J* = 7.6 Hz, 1 H), 8.25 (t, *J* = 8.0 Hz, 2 H), 7.92 - 8.05 (m, 2 H), 7.57 - 7.80 (m, 4 H), 6.96 - 7.09 (d, *J* = 9.5 Hz, 2 H), 6.80 - 6.94 (d, *J* = 9.9 Hz, 2 H); $^{13}C\{1H\}$ NMR (125 MHz, DMSO-d_6) δ = 183.8, 146.2, 145.5, 141.5, 139.6, 139.0, 137.8, 135.9, 134.4, 134.2, 133.5, 132.7, 132.0, 131.6, 131.0, 127.8, 127.2, 127.1, 125.8, 124.5, 120.3, 120.2, 65.3; HRMS (ESI) calcd for $C_{25}H_{15}ONCl^+$ (M - OTf)$^+$ 380.0837, found 380.0838.

1'-(3,5-dimethoxyphenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3l): Yellow solid, 40 mg, 76% yield; mp = 204-206 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (400 MHz, DMSO-d_6) δ = 8.82 (d, *J* = 7.9 Hz, 1 H), 8.62 - 8.77 (m, 2 H), 8.35 (d, *J* = 5.5 Hz, 1 H), 8.21 (d, *J* = 7.3 Hz, 1 H), 7.95 - 8.03 (m, 2 H), 7.03 (d, *J* = 9.8 Hz, 2 H), 6.86 - 6.93 (m, 4 H), 6.82 (br.s., 1 H), 3.80 (s, 6 H); $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6) δ = 184.0, 161.2, 146.0, 145.1, 141.3, 140.2, 139.7, 138.5, 135.8, 134.2, 133.5, 132.4, 130.8, 128.1, 125.8, 124.5, 120.2, 120.1, 106.0, 103.4, 65.3, 55.6; HRMS (ESI) calcd for $C_{27}H_{20}O_3N^+$ (M - OTf)$^+$ 406.1438, found 406.1435.

1'-(3-chloro-4-methylphenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3m): Off white solid, 45 mg, 86% yield; mp = 236-238 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.82 (d, *J* = 8.0 Hz, 1 H), 8.74 (t, *J* = 7.8 Hz, 1 H), 8.68 (d, *J* = 7.6 Hz, 1 H), 8.27 (d, *J* = 7.6 Hz, 1 H), 8.22 (d, *J* = 8.0 Hz, 1 H), 7.90 - 8.04 (m, 2 H), 7.73 (s, 1 H), 7.62 - 7.71 (m, 2 H), 6.94 - 7.06 (d, *J* = 9.9 Hz, 2 H), 6.79 - 6.92 (d, *J* = 9.9 Hz, 2 H), 2.45 (s, 3 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 183.8, 146.0, 145.2, 141.4, 140.0, 139.8, 138.5, 138.1, 135.8, 134.4, 134.4, 133.4, 132.8, 132.5, 128.4, 127.9, 127.7, 127.0, 125.8, 124.4, 120.3, 120.1, 65.2, 19.8; HRMS (ESI) calcd for $C_{26}H_{17}ONCl^+$ (M - OTf)$^+$ 394.0993, found 394.0989.

1'-(2-chloro-5-methoxyphenyl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3n): Yellow solid, 38 mg, 72% yield; mp = 290-292 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.72 - 8.87 (m, 2 H), 8.66 (d, *J* = 7.3 Hz, 1 H), 8.28 (d, *J* = 7.3 Hz, 1 H), 7.99 (t, *J* = 7.6 Hz, 1 H), 7.90 (t, *J* = 7.6 Hz, 1 H), 7.63 - 7.75 (m, 2 H), 7.24 (dd, *J* = 9.2, 2.4 Hz, 2 H), 7.03 (d, *J* = 2.4 Hz, 1 H), 6.91 (br.s., 2 H), 6.71 (br.s., 1 H), 3.78 (s, 3 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 183.9, 157.7, 146.8, 146.0, 142.0, 140.3, 138.5, 138.1, 136.0, 134.9, 134.1, 133.3, 132.7, 131.6, 127.6, 127.1, 125.7, 125.6, 123.6, 120.8, 120.7, 117.9, 116.2, 67.1, 55.8; HRMS (ESI) calcd for $C_{26}H_{17}O_2NCl^+$ (M - OTf)$^+$ 410.0942, found 410.0945.

1'-(naphthalen-1-yl)-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3o): Yellow solid, 36 mg, 68% yield; mp = 234-236 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.89 (d, *J* = 7.9 Hz, 1 H), 8.81 (t, *J* = 7.9 Hz, 1 H), 8.68 (d, *J* = 7.9 Hz, 1 H), 8.30 (d, *J* = 7.9 Hz, 1 H), 8.22 (d, *J* = 7.9 Hz, 1 H), 8.16 (t, *J* = 7.3 Hz, 2 H), 7.92 (t, *J* = 7.9 Hz, 1 H), 7.62 - 7.76 (m, 4 H), 7.53 (t, *J* = 7.6 Hz,

1 H), 7.38 (d, *J* = 9.2 Hz, 1 H), 6.96 (t, *J* = 7.9 Hz, 2 H), 6.89 (d, *J* = 7.9 Hz, 1 H), 6.55 (d, *J* = 9.8 Hz, 1 H); $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6) δ = 183.9, 146.9, 145.3, 141.8, 140.4, 138.8, 138.4, 137.0, 136.0, 134.8, 134.2, 133.3, 133.0, 132.2, 131.5, 130.1, 129.1, 127.8, 127.7, 127.4, 127.0, 125.6, 125.1, 125.0, 125.0, 124.6, 120.5, 120.4, 67.3; HRMS (ESI) calcd for $C_{29}H_{18}ON^+$ $(M - OTf)^+$ 396.1383, found 396.1383.

1'-cyclohexyl-4-oxospiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3q): Off white solid, 52 mg, 84% yield; mp = 212-214 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (400 MHz, DMSO-d_6) δ = 8.72 - 8.81 (m, 1 H), 8.58 - 8.71 (m, 2 H), 8.44 (d, *J* = 7.3 Hz, 1 H), 8.15 (d, *J* = 7.3 Hz, 1 H), 7.89 - 8.06 (m, 2 H), 6.70 - 6.96 (m, 4 H), 2.30 (br.s., 1 H), 1.81 - 1.89 (m, 5 H), 1.69 - 1.81 (m, 3 H), 1.51 (q, *J* = 12.4 Hz, 1 H), 1.34 (d, *J* = 11.6 Hz, 2 H); $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6) δ = 184.1, 149.7, 145.7, 144.3, 141.1, 138.5, 138.1, 135.4, 134.7, 133.1, 131.5, 127.9, 126.3, 125.4, 120.0, 119.9, 66.3, 36.0, 31.3, 25.4, 24.7; HRMS (ESI) calcd for $C_{26}H_{24}ON^+$ $(M - OTf)^+$ 366.1852, found 366.1849.

7'-methyl-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3t): Off white solid, 46 mg, 86% yield; mp = 222-224 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (500 MHz, DMSO-d_6) δ = 8.75 (d, *J* = 8.0 Hz, 1 H), 8.70 (t, *J* = 7.8 Hz, 1 H), 8.52 (s, 1 H), 8.24 (d, *J* = 8.0 Hz, 1 H), 8.17 (d, *J* = 7.6 Hz, 1 H), 7.76 - 7.85 (m, 3 H), 7.61 - 7.71 (m, 3 H), 7.01 - 7.07 (m, *J* = 9.9 Hz, 2 H), 6.85 (s, 1 H), 6.87 (s, 1 H), 2.62 (s, 3 H); $^{13}C\{1H\}$ NMR (125 MHz, DMSO-d_6) δ = 183.9, 146.0, 144.8, 143.1, 141.2, 140.3, 139.1, 138.0, 136.0, 134.1, 131.9, 129.9, 129.3, 128.1, 125.8, 125.6, 124.2, 119.9, 119.8, 65.1, 21.5; HRMS (ESI) calcd for $C_{26}H_{18}ON^+$ $(M - OTf)^+$ 360.1383, found 360.1382.

7'-fluoro-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3u): Off white solid, 35 mg, 65% yield; mp = 216-218 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.80 (d, *J* = 8.0 Hz, 1 H), 8.76 (t, *J* = 7.8 Hz, 1 H), 8.68 (dd, *J* = 8.4, 1.9 Hz, 1 H), 8.38 (dd, *J* = 8.8, 4.6 Hz, 1 H), 8.26 (d, *J* = 7.6 Hz, 1 H), 7.76 - 7.88 (m, 3 H), 7.59 - 7.72 (m, 3 H), 6.97 - 7.07 (d, *J* = 9.5 Hz, 2 H), 6.80 - 6.92 (d, *J* = 9.9 Hz, 2 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 183.9, 164.6 - 162.6 (d, *J* = 251.7 Hz), 146.2, 145.0, 140.5, 140.1, 139.9, 137.9 - 137.8 (d, *J* = 10.5 Hz), 137.2, 134.3, 132.1, 130.0, 129.1, 128.2, 126.7, 126.7, 124.7, 120.8 - 120.7 (d, *J* = 23.8 Hz), 120.6, 120.5, 113.1 - 112.9 (d, *J* = 26.7 Hz), 65.1; HRMS (ESI) calcd for $C_{25}H_{15}ONF^+$ (M - OTf)$^+$ 364.1132, found 364.1129.

7'-chloro-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3v): Off white solid, 30 mg, 56% yield; mp = 262-264 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.93 (d, *J* = 1.5 Hz, 1 H), 8.82 (d, *J* = 8.0 Hz, 1 H), 8.76 (t, *J* = 7.8 Hz, 1 H), 8.34 (d, *J* = 8.4 Hz, 1 H), 8.26 (d, *J* = 8.0 Hz, 1 H), 8.02 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.81 (dd, *J* = 6.1, 3.1 Hz, 2 H), 7.64 - 7.70 (m, 3 H), 7.02 (d, *J* = 9.9 Hz, 2 H), 6.88 (d, *J* = 9.9 Hz, 2 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 183.8, 146.1, 145.1, 141.0, 140.2, 139.8, 137.2, 136.7, 134.3, 133.1, 132.2, 130.0, 129.0, 128.2, 126.7, 125.8, 125.7, 120.6, 120.6, 65.2; HRMS (ESI) calcd for $C_{25}H_{15}OClN^+$ (M - OTf)$^+$ 380.0837, found 380.0837.

8'-methyl-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3w): Off white solid, 41 mg, 76% yield; mp = 202-204 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.74 (d, *J* = 8.0 Hz, 1 H), 8.68 (t, *J* = 7.8 Hz, 1 H), 8.56 (d, *J* = 8.0 Hz, 1 H), 8.04 - 8.17 (m, 2 H), 7.75 - 7.87 (m, 3 H),

7.60 - 7.73 (m, 3 H), 6.98 - 7.08 (m, *J* = 9.9 Hz, 2 H), 6.79 - 6.90 (d, *J* = 9.9 Hz, 2 H), 2.59 (s, 3 H); $^{13}C\{1H\}$ NMR (125 MHz, DMSO-d_6) δ = 183.9, 145.9, 144.8, 144.2, 141.4, 140.2, 140.1, 137.9, 134.1, 133.3, 133.2, 131.9, 129.9, 129.2, 128.4, 128.2, 125.4, 124.5, 119.7, 119.4, 65.2, 21.7; HRMS (ESI) calcd for $C_{26}H_{18}ON^+$ (M - OTf)$^+$ 360.1383, found 360.1382.

8'-chloro-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3x): Off white solid, 34 mg, 66% yield; mp = 246-248 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (500 MHz, DMSO-d_6) δ = 8.83 (d, *J* = 8.0 Hz, 1 H), 8.67 - 8.78 (m, 2 H), 8.17 - 8.29 (m, 2 H), 8.12 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.77 - 7.86 (m, 2 H), 7.64 - 7.73 (m, 3 H), 6.96 - 7.06 (d, *J* = 9.9 Hz, 2 H), 6.81 - 6.92 (d, *J* = 9.9 Hz, 2 H); $^{13}C\{1H\}$ NMR (125 MHz, DMSO-d_6) δ = 183.8, 146.0, 145.0, 142.0, 140.5, 139.7, 138.0, 137.0, 134.4, 134.3, 132.4, 130.1, 129.6, 128.9, 128.3, 127.2, 123.9, 120.3, 120.2, 65.3; HRMS (ESI) calcd for $C_{25}H_{15}ONCl^+$ (M - OTf)$^+$ 380.0837, found 380.0833.

7',8'-difluoro-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3y): Yellowish solid, 32 mg, 62% yield; mp = 224-226 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (500 MHz, DMSO-d_6) δ = 8.94 (dd, *J* = 9.5, 7.2 Hz, 1 H), 8.69 - 8.79 (m, 2 H), 8.39 (dd, *J* = 9.3, 7.1 Hz, 1 H), 8.24 (dd, *J* = 6.3, 2.1 Hz, 1 H), 7.82 (dd, *J* = 6.5, 3.1 Hz, 2 H), 7.64 - 7.73 (m, 3 H), 6.95 - 7.06 (d, *J* = 9.9 Hz, 2 H), 6.87 (s, 1 H), 6.89 (s, 1 H); $^{13}C\{1H\}$ NMR (125 MHz, DMSO-d_6) δ = 183.8, 153.4 - 151.3 (dd, *J* = 254.6 Hz, 14.3 Hz), 152.7 - 150.6 (dd, *J* = 253.6 Hz, 13.3 Hz), 146.1, 145.1, 141.7, 140.0, 139.7, 136.7, 134.3, 132.7-132.6 (d, *J* = 10.4 Hz), 132.4, 130.1, 128.8, 128.3, 125.2 - 125.1 (d, *J* = 9.5 Hz), 121.9, 120.3, 120.1, 115.1 - 115.0 (d, *J* = 20.9 Hz), 114.1 - 114.0 (d, *J* = 20.9 Hz), 65.2; HRMS (ESI) calcd for $C_{25}H_{14}ONF_2^+$ (M - OTf)$^+$ 382.1038, found 382.1038.

7',9'-dimethyl-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3z): Off white solid, 33 mg, 62% yield; mp = 228-230 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.67 - 8.82 (m, 2 H), 8.33 (s, 1 H), 8.21 (d, *J* = 6.9 Hz, 1 H), 7.48 - 7.64 (m, 4 H), 7.44 (d, *J* = 6.9 Hz, 2 H), 6.94 - 7.11 (d, *J* = 9.9 Hz, 2 H), 6.63 - 6.76 (d, *J* = 9.9 Hz, 2 H), 2.55 (s, 3 H), 1.92 (s, 3 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 183.9, 146.4, 145.3, 142.9, 141.8, 139.4, 139.3, 139.1, 136.3, 135.7, 134.2, 130.5, 129.9, 129.1, 128.0, 125.3, 123.2, 120.0, 119.9, 66.6, 21.2, 20.8; HRMS (ESI) calcd for $C_{27}H_{20}ON^+$ (M - OTf)$^+$ 374.1539, found 374.1539.

7',9'-dimethoxy-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3aa): Yellow solid, 34 mg, 65% yield; mp = 184-186 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.76 (d, *J* = 8.0 Hz, 1 H), 8.71 (t, *J* = 7.8 Hz, 1 H), 8.17 (d, *J* = 7.6 Hz, 1 H), 7.92 (d, *J* = 1.9 Hz, 1 H), 7.55 (d, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.2 Hz, 2 H), 7.39 - 7.47 (m, 2 H), 7.04 - 7.10 (m, 1 H), 7.02 (d, *J* = 9.9 Hz, 2 H), 6.77 (d, *J* = 9.9 Hz, 2 H), 4.03 (s, 3 H), 3.71 (s, 3 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 184.0, 164.6, 157.5, 146.2, 144.7, 141.3, 140.3, 137.9, 136.8, 136.6, 133.9, 130.4, 130.0, 129.5, 127.6, 120.2, 120.0, 110.0, 102.8, 102.6, 65.6, 56.7, 55.8; HRMS (ESI) calcd for $C_{27}H_{20}O_3N^+$ (M - OTf)$^+$ 406.1438, found 406.1438.

3-isopropyl-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3ab): Off white solid, 38 mg, 72% yield; mp = 248-250 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.80 (d, *J* = 8.0 Hz, 1 H), 8.61 - 8.73 (m, 2 H), 8.33 (d, *J* = 7.6 Hz, 1 H), 8.12 (d, *J* = 7.6 Hz, 1 H), 7.89 - 8.04 (m, 2 H), 7.77 (d, *J* = 3.4 Hz, 2 H), 7.51 - 7.70 (m, 3 H), 6.99 (dd, *J* = 9.7, 2.5 Hz, 1 H), 6.84 (d, *J* = 9.5 Hz, 1 H), 6.72 - 6.80 (m, 1 H), 3.02 (dt, *J* = 13.6, 6.7 Hz, 1 H), 1.02 (d, *J* = 6.9 Hz, 3 H), 0.97

(d, J = 6.9 Hz, 3 H); $^{13}C\{1H\}$ NMR (125 MHz, DMSO-d_6) δ = 183.5, 149.9, 146.7, 144.9, 141.2, 140.7, 138.9, 137.8, 135.7, 134.3, 133.3, 132.2, 131.9, 129.8, 129.2, 128.1, 128.1, 125.6, 124.4, 119.9, 119.7, 65.6, 26.6, 21.3, 21.0; HRMS (ESI) calcd for $C_{28}H_{22}ON^+$ $(M - OTf)^+$ 388.1696, found 388.1696.

3-methoxy-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3ac): Yellow solid, 39 mg, 74% yield; mp = 230-232 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (500 MHz, DMSO-d_6) δ = 8.78 (d, J = 8.0 Hz, 1 H), 8.60 - 8.73 (m, 2 H), 8.30 (d, J = 7.6 Hz, 1 H), 8.19 (d, J = 7.6 Hz, 1 H), 7.90 - 8.03 (m, 2 H), 7.75 - 7.86 (m, 2 H), 7.58 - 7.72 (m, 3 H), 6.98 - 7.05 (m, 1 H), 6.85 (d, J = 9.5 Hz, 1 H), 6.09 (d, J = 2.3 Hz, 1 H), 3.57 (s, 3 H); $^{13}C\{1H\}$ NMR (125 MHz, DMSO-d_6) δ = 178.9, 154.6, 147.6, 144.9, 141.2, 141.1, 139.5, 137.3, 135.6, 134.4, 133.3, 132.2, 132.0, 129.8, 129.2, 128.1, 125.6, 124.3, 119.9, 119.7, 106.3, 66.3, 55.2; HRMS (ESI) calcd for $C_{26}H_{18}O_2N^+$ $(M - OTf)^+$ 376.1332, found 376.1332.

3-chloro-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3ad): Off white solid, 40 mg, 76% yield; mp = 258-260 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^1H NMR (500 MHz, DMSO-d_6) δ = 8.84 (d, J = 8.0 Hz, 1 H), 8.76 (t, J = 8.0 Hz, 1 H), 8.69 (d, J = 7.6 Hz, 1 H), 8.37 (d, J = 7.6 Hz, 1 H), 8.34 (d, J = 8.0 Hz, 1 H), 8.02 (t, J = 7.4 Hz, 1 H), 7.97 (t, J = 7.4 Hz, 1 H), 7.72 - 7.82 (m, 2 H), 7.62 - 7.72 (m, 4 H), 7.36 (d, J = 2.7 Hz, 1 H), 7.11 (dd, J = 9.7, 2.5 Hz, 1 H), 7.02 (d, J = 9.9 Hz, 1 H); $^{13}C\{1H\}$ NMR (125 MHz, DMSO-d_6) δ = 177.0, 145.2, 145.0, 141.3, 140.3, 139.3, 138.2, 137.1, 135.8, 135.7, 133.6, 133.4, 132.5, 132.2, 130.1, 128.8, 128.1, 127.9, 125.8, 124.6, 120.4, 66.7; HRMS (ESI) calcd for $C_{25}H_{15}ONCl^+$ $(M - OTf)^+$ 380.0837, found 380.0838.

4'-oxo-1-phenyl-4'H-spiro[indolizino[3,4,5-*ab*]isoindole-2,1'-naphthalen]-10-ium trifluoromethanesulfonate (3ae): Yellowish solid, 35 mg, 66% yield; mp = 236-238 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.81 (d, *J* = 7.9 Hz, 1 H), 8.70 (d, *J* = 7.3 Hz, 1 H), 8.65 (t, *J* = 7.9 Hz, 1 H), 8.35 (d, *J* = 7.9 Hz, 1 H), 8.22 (d, *J* = 7.9 Hz, 1 H), 7.90 - 8.07 (m, 3 H), 7.59 - 7.69 (m, 1 H), 7.52 (dd, *J* = 9.2, 4.9 Hz, 6 H), 7.44 (d, *J* = 7.9 Hz, 1 H), 7.14 (d, *J* = 9.8 Hz, 1 H), 7.04 (d, *J* = 9.8 Hz, 1 H); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ = 182.8, 149.4, 145.2, 142.2, 140.2, 138.0, 136.3, 134.1, 133.6, 133.3, 133.2, 132.3, 131.9, 131.8, 130.4, 129.9, 128.9, 128.4, 128.1, 127.4, 127.2, 125.6, 124.5, 120.1, 119.6, 66.5; HRMS (ESI) calcd for $C_{29}H_{18}ON^+$ (M - OTf)$^+$ 396.1383, found 396.1382.

3,5-dimethyl-4-oxo-1'-phenylspiro[cyclohexane-1,2'-indolizino[3,4,5-*ab*]isoindole]-2,5-dien-10'-ium trifluoromethanesulfonate (3af): Off white solid, 43 mg, 82% yield; mp = 234-236 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 95/05); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 8.76 (d, *J* = 6.9 Hz, 1 H), 8.59 - 8.71 (m, 2 H), 8.34 (d, *J* = 7.2 Hz, 1 H), 8.13 (d, *J* = 6.9 Hz, 1 H), 7.90 - 8.04 (m, 2 H), 7.79 (br.s., 2 H), 7.66 (br.s., 3 H), 6.76 (br.s., 2 H), 1.96 (br.s., 7 H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ = 184.9, 147.0, 144.7, 141.1, 140.4, 137.4, 135.7, 133.6, 133.2, 132.2, 132.0, 129.9, 129.3, 128.1, 125.6, 124.4, 119.8, 119.7, 65.5, 16.4; HRMS (ESI) calcd for $C_{27}H_{20}ON^+$ (M - - OTf)$^+$ 376.1539, found 376.1539.

Gram Scale Synthesis of 3a: In a round bottom flask, equipped with magnetic stir bar, were added 2-(4-methoxyphenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1a**) (1g, 2.7 mmol, 1.0 equiv), $PhI(OAc)_2$ (1.3g, 4.05 mmol, 1.5 equiv), $Cu(OTf)_2$ (997 mg, 2.7 mmol, 1.0 equiv) and CH_3CN (40 mL) under inert atmosphere. The reaction mixture was heated at 80 °C for 12 h. The mixture was diluted with CH_2Cl_2 (10 mL) and the reaction mixture was concentrated in vacuo. The

resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **3a** (1.22 gm) in 91% yield.

3. Control experiments

3.1 Reaction of 1a with TEMPO under standard reaction conditions:

To a stirred solution of **1a** (20 mg, 0.055 mmol) in CH_3CN (1 ml) was added $Cu(OTf)_2$, (20 mg, 0.055 mmol) and TEMPO (11 mg, 0.066 mmol) at RT. The resulting mixture was stirred at 80 °C for 12 h. The mixture was diluted with CH_2Cl_2 and the reaction mixture was concentrated in vacuo. The resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **2a** (18 mg) in 70% yield.

To a stirred solution of **1a** (20 mg, 0.055 mmol) in CH_3CN (1 ml) was added $Cu(OTf)_2$, (20 mg, 0.055 mmol), TEMPO (11 mg, 0.066 mmol) and $PhI(OAc)_2$ (26 mg, 0.0825 mmol) at RT. The resulting mixture was stirred at 80 °C for 12 h. In this case, there is no formation of desired product **3a** was observed.

3.2 Reaction of 2-(4-(benzyloxy)phenyl)-6-(2-(phenylethynyl)phenyl)pyridine: To a screw-cap vial containing a stir bar were added 2-(4-(benzyloxy)phenyl)-6-(2-(phenylethynyl)phenyl)pyridine (**1an**) (40 mg, 0.11 mmol, 1.0 equiv), $PhI(OAc)_2$ (61 mg, 0.17 mmol, 1.5 equiv), $Cu(OTf)_2$ (38 mg, 0.11 mmol, 1.0 equiv) and CH_3CN (2 mL). The reaction vial was fitted with a cap and heated at 80 °C for 12 h. The mixture was diluted with CH_2Cl_2 (10 mL) and the reaction mixture was concentrated in vacuo. The resulting residue was purified by column chromatography on silica (CH_2Cl_2/MeOH; 95:05) to afford the product **3a** in 68% yield along with the detection of BnOH and BnOAc by Mass Spectrometry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:10.1021/acs.joc.XXXXXXX.

X-ray data for compound **3a** and **3ad** (CIF)

Copies of ^{1}H and ^{13}C NMR spectra of all new compounds **3** and ^{19}F spectrum for **3a** (PDF)

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Notes

The authors declare no competing financial interest.

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