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3-Aryl Substituted 1-Methylquinolinium Salts as Carbene Precursors

Sviatoslav Batsyts,^[a] Roman Vedmid,^[a] Jan C. Namyslo,^[a] Martin Nieger,^[b] and Andreas Schmidt^{*[a]}

Abstract: 1-Methylquinolinium salts substituted at the C3 position with phenyl, naphthalen-1-yl, phenanthren-9-yl, and pentaphenyl phenyl as well as aryl ethynyl substituents were prepared. Whereas the phenyl, naphthalen-1-yl and phenanthren-9-yl substituents are in conjugation with the quinolinium ring, the sterically crowded pentaphenyl phenyl residue causes a propeller-type molecule possessing a calculated dihedral angle between aryl substituent and the quinolinium ring of approximately 54°. The different influences of the substituents including the aryl ethynyl residues on the π -architecture is well reflected in their frontier orbital profiles, their spectroscopic properties and in their ability to form N-heterocyclic carbenes. The latter were generated from the C3-aryl substituted quinolinium salts and trapped as sulfur and selenium adducts, whereas the aryl ethynyl substituted derivatives failed to undergo the NHC generation under the conditions applied. ⁷⁷Se NMR measurements of the corresponding selenones reveal that quinolin-2-ylidenes are electron poor carbenes with strong π -acceptor character.

Scheme 1. Preparative routes for the synthesis of NHCs I from cyclic precursors.

Introduction

The first stable carbene **A** was described by Bertrand et al. in 1988^[1]. Although a strong multiple-bond character of the P-C bond stabilizes **A**, it can react as a carbene species (Scheme 1). Three years later, Arduengo et al.^[2] reported on the N-heterocyclic carbene **B** which was synthesized by deprotonation of 1,3-di-1-adamantylimidazolium chloride with sodium hydride. Meanwhile a great variety of sterically and electronically diverse carbenes have been reported.^[3] Nowadays, NHCs are used as starting materials for heterocycle synthesis,^[4] as highly efficient ligands for metal-catalyzed reactions,^[5] and as organocatalysts.^[6] Several synthetic procedures to generate NHCs **I** from cyclic precursors such as heterocumulene adducts **II**, hetarenium salts **III**, partially saturated systems **IV**, mesomeric betaines **V**, and thiones **VI** are known.^[7] In comparison to the widely applied and structurally diverse five-membered NHCs, the chemistry of six-membered NHCs is less explored. Pyridin-2-ylidene **1**, proposed as a reactive intermediate of the Hammick reaction^[8] as early as 1937, was later identified by mass spectroscopy combined with computational quantum chemistry^[9] (Scheme 2).

Palladium complexes of pyridin-2-ylidene **1** and pyridin-4-ylidene **2** as well as of their related quinolines were prepared from the corresponding chlorohetarenium salts and Pd(PPh₃)₄ by oxidative addition and, furthermore, they were screened for their catalytic activities.^[10] Other transition metal complexes such as nickel,^[11] osmium,^[12] and iridium^[13] complexes have been described as well. Several trapping reactions of these carbenes have been performed.^[14] Pyridin-4-ylidene **2** can be classified as remote NHC and can be drawn with an electron sextet structure in analogy to normal NHCs, whereas pyridin-3-ylidene, another remote NHC, can only be presented by dipolar structure **3**. The pyrazin-2-ylidene **4** was formed by decarboxylation of pyrazinium-2-carboxylate^[15] as precursor which is a pseudo-cross-conjugated mesomeric betaine (PCCMB). Mass spectrometric examinations have been performed.^[16] Phthalazine can form a carbene complex with palladium by insertion into chlorophthalazine. This enables the formation of phthalazine derivatives of **5**.^[17,18]

Scheme 2. Six-membered N-heterocyclic carbenes.

The pyridinium salt precursors of the NHCs **1**, **2**, and **3** possess a reduced electron density at position 2/6 and 4 as evidenced by the mesomeric structures of N-methylpyridinium (Scheme 3). The total electron deficiency was calculated to be +0.165 (C4) and

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FULL PAPER

+0.241 (C2/6), respectively.^[19] The lowest unoccupied molecular orbital (LUMO) resembles ψ_4^* of benzene. Its polarization, however, causes a considerably larger coefficient at C4 than at C2/6.^[20] Quinolinium salts show similar properties.

Scheme 3. Total electron deficiency, resonance structures, and the LUMO of N-methylpyridinium.

To the best of our knowledge stable quinolinium carbenes are not known, and only a few carbene complexes have been synthesized so far.^[10, 21] Some examples are given in Scheme 4.

Scheme 4. Quinoline carbene complexes.

In continuation of our interest in the different types of conjugation and their consequences for N-heterocyclic carbene formation^[7, 22] we examined the influence of substituents at C3 of quinolinium on trapping reactions of quinolin-2-ylidenes generated from them. We chose different aryl and ethynyl substituents which are in conjugation to the quinolinium ring. These are, in summary, slight electron donors in terms of Hammett's substituent constants (Ph: σ_m +0.06, σ_p -0.01; $-\text{C}\equiv\text{C}-\text{Ph}$: σ_m +0.14, σ_p +0.16).^[23] However, they cause different π -architectures of the quinolinium salts which take influence of the spectroscopic properties as well as on the chemistry of the compounds in terms of NHC generation.

Results and Discussion

Syntheses of 3-substituted quinolinium salts

To prepare the starting compounds, 3-bromoquinoline **6** was subjected to a Suzuki-Miyaura reaction with aryl boronic acids in the presence of 10% $\text{Pd}(\text{CH}_3\text{COO})_2$ as a catalyst and K_3PO_4 as a base in toluene/water solution to give 3-aryl quinolines **8a-c** (Scheme 5). Related to previous works,^[22c, 24] dimethyl sulfate was used as a convenient reagent for the quaternization of **8a-c** to give the salts **9a-c** in high yields. 50 μl of nitrobenzene were used as a catalyst in these reactions. The syntheses of the 3-alkynyl substituted quinolinium salts **9d-f** were accomplished by Sonogashira coupling reactions with the corresponding

acetylenes **7** and 3-bromoquinoline **6**, followed by methylation. Compound **8d** was converted into **8g** by a Diels-Alder reaction with pentaphenylcyclopentenone. Methylation employing the aforementioned method gave the quinolinium derivative **9g** in almost quantitative yields. Due to mutual repulsion and steric hindrance of the side wings the molecule has to adopt a propeller-type conformation.

Ar = phenyl (**a**), naphthalen-1-yl (**b**), phenanthren-9-yl (**c**)
R = H (**d**), *p*-COOMe (**e**), *o*-COOMe (**f**).

Scheme 5. Synthesis of 3-substituted quinolines **8a-f** by cross-coupling reactions and 1-methyl-3-substituted quinolinium methylsulfates **9a-g**.

Different ^{13}C NMR resonance frequencies of C3 of the quinolinium ring are observed. Whereas the 3-aryl substituted quinolinium salts **9a-c** and **9g** show chemical shifts of their C3 carbon atom between 133.4 ppm and 134.4 ppm, the 3-ethynyl substituted compounds show signals between 116.2 and 116.8 ppm. Correspondingly, the natural charges at C3 were calculated to be -0.067 (**9a**), -0.129 (**9d**) and -0.063 (**9g**) [B3LYP 6-31G(d,p)]. All other data of calculated NMR shifts as well as natural charges of the model compounds **9a**, **9d** and **9g** are presented in the supplementary material. We also calculated the most stable conformations and frontier orbitals. The dihedral angle between benzene and quinoline rings in salt **9a** was calculated to be 37.9° *in vacuo*. The corresponding angle in the propeller-type salt **9g** is larger and has a value of 54.1° . The five other phenyl rings are twisted from 66° to 68° with respect to the central phenyl ring. In the ethynyl substituted salt **9d** the two aromatics are planar with respect to each other. The calculated C3- C_{Ar} bond lengths in **9a**

and **9g** is comparable and adopt values of 148.0 pm and 149.4 pm, respectively. The calculated C3-C_{sp}α bond length of **9d** is shorter with a value of 141.2 pm. The HOMO/LUMO profiles are shown in Figure 1. The coefficients of the lowest unoccupied molecular orbital (LUMO) of **9a** and **9g** are exclusively located in the quinolinium ring. In salt **9d** a small LUMO coefficient is also located on the Cβ carbon atom of the C≡C triple bond. The HOMO of the propeller-type salt **9g** is strictly separated from the LUMO's coefficients and is located on the opposite side of the molecule. Coefficients of the HOMOs of **9a** and **9d** are distributed in the entire molecules with their highest coefficients in the substituents at C3. The calculated band gaps have values of 3.36, 2.24, and 2.67 eV for **9a**, **9g**, and **9d**, respectively.

Figure 1. HOMO (left) and LUMO (right) profiles of carbene precursors **9g** (above), **9a** (middle), and **9d** (below).

NHC formations and trapping reactions

First, deprotonations of the quinolinium salts were examined by base screenings in combination with NMR experiments. To increase the solubility of the salt **9c**, which is insoluble in toluene or benzene, the methylsulfate anion was exchanged to hexafluorophosphate by precipitation in aqueous solution. Addition of potassium *tert*-pentoxide or LiHMDS to a solution of salt **9c** in [D₆]DMSO, [D₈]THF or [D₃]MeCN at room temperature led to an upfield shift of the resonance frequencies, however, considerable amounts of decomposition products were visible in the spectra. By contrast, the base LiHMDS in [D₈]THF formed the adduct **13** of the electrophilic iminium moiety of **9cPF₆** (Scheme 6).

Scheme 6. The reaction of salt **9cPF₆** with LiHMDS in [D₈]THF and characteristic chemical shifts.

Next we performed a series of reactions to deprotonate the quinolinium salt **9c** at C2 in the presence of elemental sulfur and to form thiones as trapping products of the corresponding N-heterocyclic carbenes. Lithium hydroxide gave no reaction (Scheme 7, A). Potassium *tert*-butoxide^[25] in anhydrous toluene under reflux conditions gave the quinolinone **10**, presumably formed by addition of the base at C2 followed by thermal elimination of isobutene. The C2 carbon atom of **10** gives the signal at 162.0 ppm in the ¹³C NMR spectrum. Interaction of **9c** and potassium *tert*-pentoxide in acetonitrile has been examined by HRMS. The electrospray ionization mass shows the molecular peak at *m/z* = 374.0948, which corresponds to the potassium adduct **10·K⁺**. The addition of LiOH did not improve the yield (Scheme 7, B and C). However, using potassium *tert*-pentoxide led to a color change during the reaction and gave thione **11c** as an orange solid in 20% yield. Addition of 1.2 equiv of potassium *tert*-pentoxide and 10 equiv of LiOH increased the yield to 90%. Exchanging LiOH to LiBr also led to an increased yield **11c** compared to conditions without lithium compounds. However, potassium *tert*-pentoxide proved vital as LiOH alone did not give successful results as described above (Scheme 7, D-F).

Scheme 7. Trapping reaction of salt **9c** with sulfur under different conditions.

Applying the optimized reaction condition to **9a,b,g** gave the corresponding thiones **11a,b,g** as orange colored solids, however, in lower yields (Scheme 8). The same conditions for the generation of NHCs and their trapping with sulfur have been applied to the 3-ethynyl substituted quinolinium salts **9d-f**, however, without results. No reaction occurred.

Ar = phenyl (a), naphthalen-1-yl (b), phenanthren-9-yl (c), pentaphenylbenzene (d)

Scheme 8. Trapping reactions of NHCs generated from the salts **9a-c** and **9g** with sulfur by optimized conditions.

The resonance frequencies of the C=S carbon atoms in CDCl₃ are shifted downfield compared to the C=O signal of **10** and adopt values of 185.0, 185.4, and 185.3 ppm, respectively. The structure of **11b** was additionally proven by X-ray structure analysis (Figure 2). Single crystals of thione **11b** were obtained by slow evaporation of a concentrated solution in chloroform. The compound crystallized orthorhombic. The CS bond has a length of 168.39(18) pm. The typical C(sp²)=S double bond length is in the range from 159.9 to 161.1 pm, whereas the C(sp²)-S single bond length is 177 pm.^[26] The dihedral angle between the quinoline and naphthalene planes is 77.56(3)°.

Figure 2. Molecular structure of thione **11b** (displacement parameters are drawn at 50% probability level).

Reactions of the 3-substituted quinolinium salts **9a-c** with elemental selenium in the presence of potassium *tert*-pentoxide gave the selenones **12a-c** (Scheme 9). All selenones are red compounds with a specific odor. Furthermore, the bulkier the aromatic substituent, the higher the melting point in thiones and selenones. Thus, the selenone with a phenanthrenyl residue (**12c**) has a melting point of 271 °C, while the selenone with a phenyl residue (**12a**) is an oil.

Scheme 9. Trapping reactions of salts **9a-c** with selenium.

Whereas the ¹³C chemical shifts of the C2 atoms of the selenones **12a-c** are very close to the C2 carbon atoms of the thiones **11a-c**, the resonance frequencies of methyl groups differ significantly (c.f. supplementary material). The structure of **12c** was proven by X-ray structure analysis (Figure 3). Single crystals of selenone **12c** were obtained by diffusion of cyclohexane into its solution in chloroform. The compound crystallized monoclinic. The C=Se bond has a length of 183.8(2) pm. The typical C(sp²)=Se double bond length is 171 pm^[27] and the typical C(sp²)-Se single bond length is 189 pm^[26]. The dihedral angle between the quinoline and naphthalene planes is 70.08(3)°.

Figure 3. Molecular structure of selenone **12c** (displacement parameters are drawn at 50% probability level).

Quinoline selenones are rare and little information is available. Only a few compounds have been described so far.^[28] The ⁷⁷Se NMR spectra for **12a-c** were measured and the signals of Se atoms were found at 706.6, 716.8, and 720.4 ppm, respectively. These downfield shifts indicate electron poor former carbenes with strong π-acceptor character (Scheme 10).^[29] The ⁷⁷Se chemical shift of 1-methylquinoline-2(1H)-selenone has a value of 646.7 ppm.^[28c]

Scheme 10. Comparison of *Ganter's* NHC selenium adducts. ⁷⁷Se chemical shifts of **12a-c**.

Conclusions

Aryl as well as ethynyl substituents at position 3 of quinolinium salts were prepared. Whereas the former mentioned underwent trapping reactions of their N-heterocyclic carbenes with sulfur and selenium, respectively, the latter failed to undergo these reactions. This work supplements results concerning the electrophilicities vs. acidities in six-membered N-heterocyclic carbene precursors.^[30]

Experimental Section

All reactions were carried out under an atmosphere of nitrogen in flame or oven-dried glassware. All chemicals were purchased and used without further purification unless otherwise mentioned. Anhydrous solvents were dried according to standard procedures before usage. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). The ATR-IR spectra were obtained on a Bruker Alpha in the range of 400 to 4000 cm^{-1} . ^1H NMR spectra were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH , CH_3); - = down (CH_2). ^{77}Se NMR spectra were recorded at 114 MHz. The electrospray ionization mass spectra (ESIMS) were measured with a Varian 320 MS Triple Quad GC/MS/MS (EIMS) or with an Agilent LCMSD series HP 1100 with APIES at fragmentor voltages as indicated. Samples were sprayed from MeOH at 4000 V capillary voltage and fragmentor voltages of 30 V unless otherwise noted. The HR-MS spectra were obtained with a Bruker Impact II, a Bruker Daltonik Tesla-Fourier transform-ion cyclotron resonance mass spectrometer, or with a Waters Micromass LCT with the direct inlet. Chromatography: The reactions were traced by thin layer chromatography with silica gel 60 (F254, company MERCK KGAA). For the detection of substances, quenching was used at either 254 nm or 366 nm with a mercury lamp. The preparative column chromatography was conducted through silica gel 60 (230 400 mesh) of the company MERCK KGAA.

Crystal Structure Determinations of 11b and 12c

The single-crystal X-ray diffraction studies were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Direct Methods (SHELXS-97)^[31] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2)^[32]. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied. **11c** was refined as an inversion twin (see cif-file for details).

11b: yellow crystals, $\text{C}_{20}\text{H}_{15}\text{NS}$, $M_r = 301.39$, crystal size $0.20 \times 0.18 \times 0.10 \text{ mm}$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 8.3590(5) \text{ \AA}$, $b = 12.9270(7) \text{ \AA}$, $c = 13.7331(7) \text{ \AA}$, $V = 1483.95(14) \text{ \AA}^3$, $Z = 4$, $\rho = 1.349 \text{ Mg/m}^3$, $\mu(\text{Cu-K}\alpha) = 1.874 \text{ mm}^{-1}$, $F(000) = 632$, $2\theta_{\text{max}} = 144.2^\circ$, 10197 reflections, of which 2906 were independent ($R_{\text{int}} = 0.021$), 201 parameters, $R_1 = 0.026$ (for 2872 $I > 2\sigma(I)$), $wR_2 = 0.072$ (all data), $S = 1.05$, largest diff. peak / hole = $0.157 / -0.214 \text{ e \AA}^{-3}$, $x = 0.494(18)$.

12c: red crystals, $\text{C}_{24}\text{H}_{17}\text{NSe}$, $M_r = 398.34$, crystal size $0.22 \times 0.06 \times 0.02 \text{ mm}$, monoclinic, space group $P2_1/c$ (no. 14), $a = 6.1638(2) \text{ \AA}$, $b = 19.9050(6) \text{ \AA}$, $c = 14.3978(4) \text{ \AA}$, $\beta = 95.257(1)^\circ$, $V = 1759.04(9) \text{ \AA}^3$, $Z = 4$, $\rho = 1.504 \text{ Mg/m}^3$, $\mu(\text{Cu-K}\alpha) = 2.920 \text{ mm}^{-1}$, $F(000) = 808$, $2\theta_{\text{max}} = 144.2^\circ$, 16462 reflections, of which 3473 were independent ($R_{\text{int}} = 0.033$), 236 parameters, $R_1 = 0.031$ (for 3138 $I > 2\sigma(I)$), $wR_2 = 0.082$ (all data), $S = 1.05$, largest diff. peak / hole = $0.437 / -0.366 \text{ e \AA}^{-3}$.

CCDC 1874495 (**11b**), and 1874496 (**12c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculations: All density-functional theory (DFT)-calculations were carried out by using the Spartan® Software (Spartan'16, Wavefunction, Inc., Irvine, CA. Available from: <http://www.wavefun.com>) running on an

Intel® Core™ i7-6950X deca core system equipped with 64 GB RAM main memory and sufficient solid-state disc space. MMFF optimized structures were used as starting geometries. Then, the B3LYP density functional and the 6-31G(d,p) basis set was used in order to allow for comparison with previous results. All final structures were proven to be true minima by the absence of imaginary frequencies or transition states by the occurrence of a negative frequency.

General procedure for the preparation of the 3-arylquinolines

(Procedure 1; Suzuki-Miyaura coupling): Under a nitrogen atmosphere, 1.040 g (5.00 mmol) of 3-bromoquinoline **6** were dissolved in 20 mL of anhydrous toluene unless otherwise noted and treated with 10-mol-% of $\text{Pd}(\text{CH}_3\text{COO})_2$. The mixtures were then subjected to ultrasound irradiation for 5 min and then stirred at rt for additional 0.5 h. Then 6.00 mmol of the boronic acid, 40.00 mmol of potassium phosphate and 4 mL of water were added, and the mixtures were heated under reflux for 24 h. The mixtures were then allowed to cool to rt, treated with dichloromethane (50 mL) and washed with water. The organic phases were then dried over MgSO_4 and filtered, and the solvents were removed in vacuo. The resulting residues were finally purified by column chromatography (petroleum ether: ethyl acetate) to afford the products.

3-Phenylquinoline (8a): According to Procedure 1, a solution of 1.040 g (5.00 mmol) of 3-bromoquinoline **6**, 0.112 g (0.50 mmol) of $\text{Pd}(\text{CH}_3\text{COO})_2$, 0.732 g (6.00 mmol) phenylboronic acid and 8.480 g (40.00 mmol) of K_3PO_4 in 54 mL of the toluene-water mixture was heated for 24 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-phenylquinoline **8a**. Yield 0.820 g, 80%, a brownish solid, m.p. 50–51 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3): $\delta = 9.20$ (s, 1H, 2-H), 8.31 (d, $J = 1.8 \text{ Hz}$, 1H, 4-H), 8.16 (d, $J = 8.3 \text{ Hz}$, 1H, 8-H), 7.89 (d, $J = 8.1 \text{ Hz}$, 1H, 5-H), 7.74–7.71 (m, 3H, 7-H, 2'-H, 6'-H), 7.58 (t, $J = 7.4 \text{ Hz}$, 1H, 6-H), 7.54–7.52 (m, 2H, 3'-H, 5'-H), 7.44 (m, 1H, 4'-H) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 150.0$ (+, C2), 147.4 (o, C8a), 138.0 (o, C1'), 134.0 (o, C3), 133.4 (+, C4), 129.5 (+, C7), 129.3 (o, C4a), 129.3 (+, C8, C3', C5'), 128.3 (+, C4'), 128.2 (+, C5), 127.6 (+, C2', C6'), 127.2 (+, C6) ppm. IR (ATR): 3027, 1568, 1492, 1368, 1340, 1027, 952, 914, 861, 785, 773, 762, 693, 624, 612, 560, 545, 494, 479, 443 cm^{-1} . Spectroscopic data are in agreement with those reported in the literature.^[33]

3-(Naphthalen-1-yl)quinoline (8b): According to Procedure 1, a solution of 1.040 g (5.00 mmol) of 3-bromoquinoline **6**, 0.112 g (0.50 mmol) of $\text{Pd}(\text{CH}_3\text{COO})_2$, 1.032 g (6.00 mmol) naphthalene-1-boronic acid and 8.480 g (40.00 mmol) of K_3PO_4 in 54 mL of the toluene-water mixture was heated for 24 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-(naphthalen-1-yl)quinoline **8b**. Yield 1.071 g, 84%, a white solid, m.p. 57–58 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3): $\delta = 9.08$ (d, $J = 1.9 \text{ Hz}$, 1H, 2-H), 8.28 (d, $J = 1.9 \text{ Hz}$, 1H, 4-H), 8.23 (d, $J = 8.5 \text{ Hz}$, 1H, 8-H), 7.97 (m, 1H, 5'-H), 7.95 (m, 1H, 4'-H), 7.90 (d, $J = 7.9 \text{ Hz}$, 1H, 5-H), 7.87 (d, $J = 8.5 \text{ Hz}$, 1H, 8'-H), 7.79 (ddd, $J = 1.4, 7.0, 8.4 \text{ Hz}$, 1H, 7-H), 7.63 (ddd, $J = 1.0, 7.0, 8.0 \text{ Hz}$, 1H, 6-H), 7.60 (dd, $J = 7.0, 8.2 \text{ Hz}$, 1H, 3'-H), 7.54 (ddd, $J = 1.2, 6.7, 8.0 \text{ Hz}$, 1H, 6'-H), 7.53 (dd, $J = 1.2, 7.0 \text{ Hz}$, 1H, 2'-H), 7.47 (ddd, $J = 1.4, 6.9, 8.4 \text{ Hz}$, 1H, 7'-H) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 152.0$ (+, C2), 147.4 (o, C8a), 136.5 (+, C4), 136.4 (o, C1'), 134.0 (o, C4a'), 133.9 (o, C3), 131.8 (o, C8a'), 129.8 (+, C7), 129.4 (+, C8), 128.8 (+, C4'), 128.7 (+, C5'), 128.1 (+, C5), 128.0 (o, C4a), 127.9 (+, C2'), 127.2 (+, C6), 126.8 (+, C7'), 126.3 (+, C6'), 125.6 (+, C3'), 125.5 (+, C8') ppm. IR (ATR): 3034, 1811, 1566, 1508, 1490, 1396, 1364, 1332, 1125, 1017, 941, 904, 861, 774, 745, 664, 616, 566, 479, 450, 430 cm^{-1} . Spectroscopic data are in agreement with those reported in the literature.^[34]

3-(Phenanthren-9-yl)quinoline (8c): According to Procedure 1, a solution of 1.040 g (5.00 mmol) of 3-bromoquinoline **6**, 0.112 g (0.50 mmol) of

$\text{Pd}(\text{CH}_3\text{COO})_2$, 1.332 g (6.00 mmol) phenanthrene-9-boric acid and 8.480 g (40.00 mmol) of K_3PO_4 in 54 mL of the toluene-water mixture was heated for 24 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-(phenanthren-9-yl)quinoline **8c**. Yield 1.068 g, 70%, a light-yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 9.12-9.11 (m, 1H), 8.82-8.80 (m, 1H), 8.76-8.74 (m, 1H), 8.32-8.31 (m, 1H), 8.24-8.23 (m, 1H), 7.94-7.89 (m, 2H), 7.88-7.86 (m, 1H), 7.81-7.79 (m, 1H), 7.78-7.77 (m, 1H), 7.72-7.69 (m, 2H), 7.66-7.61 (m, 2H), 7.57-7.54 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 152.1, 147.6, 136.4, 135.1, 133.9, 132.4, 131.0, 130.9, 130.4, 129.8, 129.5, 128.9, 128.9, 128.1, 128.0, 127.3, 127.2, 127.2, 127.0, 127.0, 126.5, 123.3, 122.8 ppm. IR (ATR): 3058, 1732, 1618, 1566, 1489, 1449, 1337, 1239, 1123, 1044, 914, 891, 861, 787, 743, 723, 616, 537, 511, 479, 427, 411 cm^{-1} . Spectroscopic data are in agreement with those reported in the literature.^[35]

General procedure of the Sonogashira-Hagihara couplings (Procedure 2)

The reactions were carried out under a nitrogen atmosphere. A mixture of 5 mmol of 3-bromoquinoline **6**, 1 mol % of Pd(PPh₃)₂Cl₂, and 2 mol % of CuI was suspended in 7 mL of dry NEt₃ with stirring. A sample of the corresponding ethyne **7** (1.05 equiv) in dry NEt₃ was added dropwise at ambient temperature. The resulting solutions were then stirred at reflux temperature until complete conversion was monitored by TLC. The mixtures were then allowed to cool to rt. The solvents were removed in vacuo. The resulting residues were finally purified by column chromatography (petroleum ether: ethyl acetate) to afford the products.

3-(Phenylethynyl)quinoline (8d): According to Procedure 2, a solution of 2.080 g (10.00 mmol) of 3-bromoquinoline **6**, 0.070 g (0.10 mmol) of Pd(PPh₃)₂Cl₂, 0.038 g (0.20 mmol) CuI and 1.071 g (10.50 mmol) of phenylacetylene in 30 mL of anhydrous NEt₃ was heated over the period of 1.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-(phenylethynyl)quinoline **8d**. Yield 2.290 g, 100%, a white solid, m.p. 83-84 °C. ¹H NMR (600 MHz, CDCl₃): δ = 9.00 (d, *J* = 2.0 Hz, 1H, 2-H), 8.30 (d, *J* = 2.0 Hz, 1H, 4-H), 8.10 (d, *J* = 8.3 Hz, 1H, 8-H), 7.79 (d, *J* = 8.3 Hz, 1H, 5-H), 7.72 (ddd, *J* = 1.5, 6.9, 8.3 Hz, 1H, 7-H), 7.63-7.53 (m, 3H, 6-H, 2'-H, 6'-H), 7.42-7.35 (m, 3H, 3'-H, 4'-H, 5'-H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 152.1 (+, C2), 146.8 (o, C8a), 138.3 (+, C4), 131.8 (+, C2', C6'), 130.1 (+, C7), 129.4 (+, C8), 128.9 (+, C4'), 128.5 (+, C3', C5'), 127.6 (+, C6), 127.3 (+, C5), 127.3 (o, C4a), 122.6 (o, C1'), 117.5 (o, C3), 92.7 (o, Cβ), 86.7 (o, Cα) ppm. IR (ATR): 3008, 2162, 1619, 1599, 1564, 1484, 1443, 1409, 1368, 1294, 1196, 1124, 1113, 1072, 980, 905, 860, 784, 756, 691, 656, 640, 539, 515, 498, 474, 429 cm⁻¹. HRMS (ESI): *m/z* calcd for C₁₇H₁₁NNa [M+Na]⁺ 252.0789, found 252.0796.

Methyl 4-(quinolin-3-ylethynyl)benzoate (8e): According to Procedure 2, a solution of 2.080 g (10.00 mmol) of 3-bromoquinoline **6**, 0.070 g (0.10 mmol) of Pd(PPh₃)₂Cl₂, 0.038 g (0.20 mmol) CuI and 1.680 g (10.50 mmol) of methyl 4-ethynylbenzoate in 30 mL of anhydrous NEt₃ was heated over the period of 1.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave Yield 2.153 g, 85%, a brown solid, m.p. 138-139 °C. ¹H NMR (600 MHz, CDCl₃): δ = 9.00 (d, *J* = 2.2 Hz, 1H, 2-H), 8.33 (d, *J* = 2.2 Hz, 1H, 4-H), 8.11 (d, *J* = 8.6 Hz, 1H, 8-H), 8.06 (ddd, *J* = 1.4, 2.0, 8.3 Hz, 2H, 3'-H, 5'-H), 7.81 (d, *J* = 8.6 Hz, 1H, 5-H), 7.74 (ddd, *J* = 1.5, 6.8, 8.6 Hz, 1H, 7-H), 7.65 (ddd, *J* = 1.4, 2.0, 8.3 Hz, 2H, 2'-H, 4'-H), 7.58 (ddd, *J* = 1.5, 6.8, 8.6 Hz, 1H, 6-H), 3.94 (s, 3H, COOCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 166.5 (o, COO), 152.0 (+, C2), 147.0 (o, C8a), 138.7 (+, C4), 131.7 (+, C2', C4'), 130.4 (+, C8), 130.0 (o, C4'), 129.7 (+, C3', C5'), 129.5 (+, C7), 127.7 (+, C5), 127.5 (+, C6), 127.3 (o, C4a), 127.2 (o, C1'), 116.9 (o, C3), 91.8 (o, C8), 89.5 (o, Ca), 52.3 (+, CH₃) ppm. IR (ATR): 3017, 1716, 1276, 1098,

953, 905, 855, 767, 742, 697, 480 cm⁻¹. Spectroscopic data are in agreement with those reported in the literature.^[24]

Methyl 2-(quinolin-3-ylethynyl)benzoate (8f): According to Procedure 2, a solution of 2.080 g (10.00 mmol) of 3-bromoquinoline **6**, 0.070 g (0.10 mmol) of Pd(PPh₃)₂Cl₂, 0.038 g (0.20 mmol) CuI and 1.680 g (10.50 mmol) of methyl 2-ethynylbenzoate in 30 mL of anhydrous NEt₃ was heated over the period of 1.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave Yield 1.607 g, 56%, a light brownish solid, m.p. 64-65 °C. ¹H NMR (600 MHz, CDCl₃): δ = 9.05 (d, *J* = 2.0 Hz, 1H, 2-H), 8.36 (d, *J* = 2.0 Hz, 1H, 4-H), 8.11 (d, *J* = 8.6 Hz, 1H, 8-H), 8.02 (dd, *J* = 1.5, 7.8 Hz, 1H, 6'-H), 7.81 (d, *J* = 8.6 Hz, 1H, 5-H), 7.76-7.69 (m, 2H, 3'-H, 7-H), 7.60-7.50 (m, 2H, 4'-H, 6-H), 7.42 (td, *J* = 1.3, 7.8 Hz, 1H, 5'-H), 3.99 (s, 3H, COOCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 166.5 (o, COO), 152.2 (+, C2), 147.0 (o, C8a), 138.5 (+, C4), 134.2 (+, C5'), 131.9 (o, C2'), 131.8 (+, C3'), 130.7 (+, C4'), 130.2(+, C8), 129.5 (+, C6'), 128.5 (+, C7), 127.7 (+, C5), 127.4 (+, C6), 127.3 (C4a), 123.1 (o, C1'), 117.5 (o, C3), 91.5 (o, Cβ), 91.4 (o, Cα), 52.3 (+, CH₃) ppm. IR (ATR): 2952, 1731, 1565, 1485, 1435, 1270, 1250, 1111, 1076, 899, 746, 692, 471 cm⁻¹. Spectroscopic data are in agreement with those reported in the literature.^[24]

2,3,4,5,6-Pentaphenyl-1-(quinoline-3-yl)benzene (8g): Benzophenone (10 g) was melted in a 50 mL round-bottomed flask fitted with an air condenser. Corresponding 3-(phenylethynyl)quinoline **8d** (0.458 g, 2.00 mmol) and tetraphenylcyclopentadienone (0.961 g, 2.50 mmol) were added to the flask, which was heated for 0.5 h using a heat gun. The solution was cooled to rt and toluene (10 mL) was added to prevent the solidification of the benzophenone. After cooling, *n*-hexane (50 mL) was added, resulting in the precipitation of a product, which was collected by vacuum filtration. Yield 0.590 g, 51%, a white solid, m.p. 334-336 °C. ¹H NMR (600 MHz, CDCl₃): δ = 8.45 (d, *J* = 2 Hz, 1H, 2ⁱ-H), 7.84 (d, *J* = 8.4 Hz, 1H, 8ⁱ-H), 7.59 (d, *J* = 2 Hz, 1H, 4ⁱ-H), 7.53-7.51 (m, 1H, 7ⁱ-H), 7.43 (d, *J* = 8.0 Hz, 5ⁱ-H), 7.35-7.33 (m, 1H, 6ⁱ-H), 6.88-6.85 (m, 20H, 2ⁱⁱ-H, 6ⁱⁱ-H, 2ⁱⁱⁱ-H, 6ⁱⁱⁱ-H, 2^{iv}-H, 6^{iv}-H, 2^v-H, 6^v-H, 2^{vi}-H, 6^{vi}-H, 3ⁱⁱ-H, 5ⁱⁱ-H, 3ⁱⁱⁱ-H, 5ⁱⁱⁱ-H, 3^{iv}-H, 5^{iv}-H, 3^v-H, 5^v-H, 3^{vi}-H, 5^{vi}-H), 6.83-6.78 (m, 4H, 4ⁱⁱ-H, 4ⁱⁱⁱ-H, 4^v-H, 4^{vi}-H), 6.78-6.77 (m, 1H, 4^{iv}-H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 152.9 (+, C2ⁱ), 145.6 (o, C8aⁱ), 141.4 (o, C4), 141.07 (o, C2, C6), 140.88 (o, C3, C5), 140.44 (o, C1^{iv}), 140.34 (o, C1ⁱⁱ, C1^{vi}), 139.96 (o, C1ⁱⁱⁱ, C1^v), 137.8 (+, C4ⁱ), 136.51 (o, C1), 134.2 (o, C3ⁱ), 131.51/131.48/131.45/131.41/131.37 (+, C2ⁱⁱ, C6ⁱⁱ, C2ⁱⁱⁱ, C6ⁱⁱⁱ, C2^{iv}, C6^{iv}, C2^v, C6^v, C2^{vi}, C6^{vi}), 129.0 (+, C8ⁱ), 128.9 (+, C7ⁱ), 127.6 (+, C5ⁱ), 127.4/127.0/126.85/126.83/126.78 (+, C3ⁱⁱ, C5ⁱⁱ, C3ⁱⁱⁱ, C5ⁱⁱⁱ, C3^{iv}, C5^{iv}, C3^v, C5^v, C3^{vi}, C5^{vi}), 127.1 (o, C4aⁱ), 126.2 (+, C6ⁱ), 125.87 (+, C4ⁱⁱ, C4^{vi}), 125.54 (+, C4ⁱⁱⁱ, C4^v), 125.52 (+, C4^{iv}) ppm. IR (ATR): 3055, 3024, 1662, 1600, 1495, 1440, 1401, 1354, 1311, 1275, 1261, 1127, 1070, 1029, 966, 906, 838, 817, 779, 747, 738, 719, 695, 647, 638, 555, 544, 535, 480, 443, 413 cm⁻¹. HRMS (APCI): *m/z* calcd for C₄₅H₃₂N [M+H]⁺ 586.2529, found 586.2530.

General procedure for the preparation of the salts (Procedure 3): Samples of 0.50 mmol of the corresponding esters were dissolved in toluene containing 50 μ l of nitrobenzene. Then 0.75 mmol of dimethyl sulfate was added with stirring. Thereafter the resulting mixture was stirred under reflux temperature. After completion of the reaction (controlled by TLC), the solution was cooled, the crude product was filtered off, washed with ethyl acetate (3 $\times$ 10 mL), and dried to afford the product.

1-Methyl-3-phenylquinolinium methylsulfate (9a): According to Procedure 3, a solution of 0.513 g (2.50 mmol) of 3-phenylquinoline, 50 μ l drop of nitrobenzene and 0.284 mL (3.00 mmol) of dimethyl sulfate in 15 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 1-methyl-3-phenylquinolinium methylsulfate **9a**. Yield 0.796 g, 96%, a yellow solid, m.p. 211-212 °C. ^1H NMR (600 MHz, $[\text{D}_6]\text{DMSO}$): δ = 9.96 (d, J = 1.4 Hz, 1H, 2-H), 9.62 (d, J = 1.4 Hz, 1H, 4-H), 8.53 (d, J = 8.9 Hz, 1H,

8-H), 8.49 (d, $J = 8.9$ Hz, 1H, 5-H), 8.27 (ddd, $J = 1.5, 7.1, 8.9$ Hz, 1H, 7-H), 8.08 (ddd, $J = 1.5, 7.1, 8.9$ Hz, 1H, 6-H), 8.04–8.03 (m, 2H, 2'-H, 6'-H), 7.66 (t, 2H, $J = 7.62$ Hz, 3'-H, 5'-H), 7.60–7.58 (m, 1H, 4'-H), 4.72 (s, 3H, NCH₃), 3.37 (s, 3H, CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): $\delta = 149.3$ (+, C2), 142.9 (+, C4), 137.2 (o, C8a), 135.2 (+, C7), 133.5 (o, C3), 133.4 (o, C1'), 130.5 (+, C5), 130.2 (+, C6), 129.8 (+, C4'), 129.5 (+, C3', C5'), 129.2 (o, C4a), 127.4 (+, C2', C6'), 119.0 (+, C8), 52.8 (+, CH₃SO₄), 45.4 (+, NCH₃) ppm. IR (ATR): 3052, 1534, 1504, 1362, 1206, 1051, 1006, 859, 773, 733, 695, 607, 576, 496, 457, 427 cm⁻¹. MS (ESI): $m/z = 220.1$ [M]⁺. HRMS (ESI): m/z calcd for C₁₆H₁₄N [M]⁺ 220.1121, found 220.1126.

1-Methyl-3-(naphthalen-1-yl)quinolinium methylsulfate (9b):

According to Procedure 3, a solution of 0.638 g (2.50 mmol) of 3-(naphthalen-1-yl)quinoline, 50 μ L drop of nitrobenzene and 0.284 mL (3.00 mmol) of dimethyl sulfate in 15 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 1-methyl-3-(naphthalen-1-yl)quinolinium methylsulfate **9b**. Yield 0.916 g, 96%, a yellow solid, m.p. 219–220 °C. ¹H NMR (600 MHz, [D₆]DMSO): $\delta = 9.82$ (d, $J = 1.3$ Hz, 1H, 2-H), 9.47 (s, 1H, 4-H), 8.61 (d, $J = 8.9$ Hz, 1H, 8-H), 8.54 (d, $J = 8.2$ Hz, 1H, 5-H), 8.35 (ddd, $J = 1.5, 7.2, 8.8$ Hz, 1H, 7-H), 8.19 (t, $J = 4.7$ Hz, 1H, 3'-H), 8.15–8.12 (m, 2H, 6-H, 5'-H), 7.95 (d, $J = 8.4$ Hz, 1H, 8'-H), 7.76–7.75 (m, 2H, 2'-H, 4'-H), 7.67 (ddd, $J = 1.2, 6.9, 8.1$ Hz, 1H, 6'-H), 7.62 (ddd, $J = 1.2, 6.9, 8.1$ Hz, 1H, 7'-H), 4.73 (s, 1H, NCH₃), 3.36 (s, 3H, CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): $\delta = 151.1$ (+, C2), 146.6 (+, C4), 137.5 (o, C8a), 135.4 (+, C7), 133.4 (o, C3), 132.3 (o, C1'), 130.6 (o, C8a'), 130.5 (+, C5), 130.2 (+, C6), 129.9 (+, C3'), 129.2 (+, C4a), 128.9 (+, C4'), 128.6 (+, C5'), 127.5 (+, C7'), 126.7 (+, C6'), 125.7 (+, C2'), 124.7 (+, C8'), 119.0 (+, C8), 52.8 (+, CH₃SO₄), 45.3 (+, NCH₃) ppm. IR (ATR): 3041, 2935, 2829, 1524, 1383, 1247, 1215, 1060, 1011, 807, 774, 738, 650, 609, 579, 576, 551, 483, 433 cm⁻¹. MS (ESI): $m/z = 270.1$ [M]⁺. HRMS (ESI): m/z calcd for C₂₀H₁₆N [M]⁺ 270.1283, found 270.1285.

1-Methyl-3-(phenanthren-9-yl)quinolinium methylsulfate (9c):

According to Procedure 3, a solution of 0.638 g (2.50 mmol) of 3-(phenanthren-9-yl)quinoline, 50 μ L of nitrobenzene and 0.284 mL (3.00 mmol) of dimethyl sulfate in 15 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 1-methyl-3-(phenanthren-9-yl)quinolinium methylsulfate **9c**. Yield 1.046 g, 97%, a yellow solid, m.p. 209–210 °C. ¹H NMR (600 MHz, [D₆]DMSO): $\delta = 9.89$ (d, $J = 1.1$ Hz, 1H, 2-H), 9.54 (s, 1H, 4-H), 9.05 (d, $J = 8.3$ Hz, 1H, 5'-H), 8.98 (d, $J = 8.2$ Hz, 1H, 4'-H), 8.63 (d, $J = 9.2$ Hz, 1H, 8-H), 8.56 (d, $J = 8.2$ Hz, 1H, 5-H), 8.37 (ddd, $J = 1.5, 7.2, 8.8$ Hz, 1H, 7-H), 8.16–8.11 (m, 3H, 6-H, 1'-H, 10'-H), 7.98 (d, $J = 7.6$ Hz, 1H, 8'-H), 7.86–7.83 (m, 2H, 3'-H, 6'-H), 7.78 (m, 1H, 2'-H), 7.71 (ddd, $J = 0.9, 7.2, 8.0$ Hz, 1H, 7'-H), 4.74 (s, 3H, NCH₃), 3.36 (s, 3H, CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): $\delta = 151.1$ (+, C2), 146.7 (+, C4), 137.7 (o, C8a), 135.5 (+, C7), 133.5 (o, C3), 131.1 (o, C9'), 130.6 (o, C10a'), 130.5 (+, C5), 130.2 (+, C6), 130.2 (o, C4b'), 130.1 (o, C4a'), 130.0 (+, C10'), 129.5 (o, C8a'), 129.2 (o, C4a), 129.1 (+, C1'), 128.2 (+, C3'), 127.7 (+, C2'), 127.6 (+, C7'), 127.6 (+, C6'), 125.9 (+, C8'), 123.7 (+, C5), 123.1 (+, C4'), 119.0 (+, C8), 52.8 (+, CH₃SO₄), 45.3 (+, NCH₃) ppm. IR (ATR): 3042, 2944, 1627, 1607, 1578, 1525, 1495, 1447, 1378, 1316, 1217, 1059, 1010, 900, 825, 726, 657, 608, 577, 426 cm⁻¹. HRMS (ESI): m/z calcd for C₂₄H₁₈N [M]⁺ 320.1434, found 320.1435.

1-Methyl-3-(phenanthren-9-yl)quinolinium hexafluorophosphate (9cPF₆):

Methylsulfate salt **9c** (0.431 g, 1.00 mmol) was dissolved in water, then NH₄PF₆ (1.05 equiv) in water was added to the prepared solution. Hexafluorophosphate salt precipitated immediately. After 0.5 h the crude product was filtered off and washed with water (3 $\times$ 30 mL) and ethyl acetate (3 $\times$ 30 mL), dried in vacuo to give **9cPF₆**. Yield 0.460 g, 99%, a yellow solid, m.p. 223–225 °C (decomp.). ¹H NMR (600 MHz, CD₃CN): $\delta = 9.38$ (d, $J = 1.1$ Hz, 1H), 9.23 (s, 1H), 8.90 (d, $J = 8.5$ Hz, 1H), 8.83 (d, $J = 8.3$ Hz, 1H), 8.45–8.43 (m, 1H), 8.40–8.38 (m, 1H), 8.28 (ddd, $J = 1.5, 7.2, 8.9$ Hz, 1H), 8.07–8.03 (m, 2H), 7.99 (s, 1H), 7.90–7.88 (m, 1H), 7.82–7.79

(m, 2H), 7.72 (ddd, $J = 1.0, 7.0, 7.9$ Hz, 1H), 7.67 (ddd, $J = 1.2, 6.9, 8.2$ Hz, 1H) 4.65 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CD₃CN): $\delta = 151.7$ (+), 148.3 (+), 139.0 (o), 136.9 (+), 135.2 (o), 131.9 (o), 131.8 (o), 131.62 (+), 131.60 (o), 131.58 (+), 131.5 (+), 131.3 (+), 130.64 (o), 130.63 (o), 130.2 (+), 129.2 (+), 128.65 (+), 128.61 (+), 128.60 (+), 126.7 (+), 124.6 (+), 124.6 (+), 123.9 (+), 119.6 (+), 46.6 (+) ppm. IR (ATR): 3053, 1525, 1447, 1378, 1354, 1247, 1214, 1172, 1060, 1012, 901, 825, 746, 724, 658, 608, 577, 551, 490, 427 cm⁻¹. HRMS (ESI): m/z calcd for C₂₄H₁₈N [M]⁺ 320.1434, found 320.1440.

1-Methyl-3-(phenylethynyl)quinolinium methylsulfate (9d):

According to Procedure 3, a solution of 1.145 g (5.00 mmol) of 3-(phenylethynyl)quinoline **8d**, 1 drop of nitrobenzene and 0.711 mL (7.50 mmol) of dimethyl sulfate in 25 mL of anhydrous toluene was heated over the period of 1.5 h under reflux temperature to give 1-methyl-3-(phenylethynyl)quinolinium methylsulfate **9d**. Yield 1.757 g, 99%, a yellow solid, m.p. 224–225 °C (decomp.). ¹H NMR (600 MHz, [D₆]DMSO): $\delta = 9.87$ (s, 1H, 2-H), 9.50 (s, 1H, 4-H), 8.54 (d, $J = 8.8$ Hz, 1H, 8-H), 8.45 (d, $J = 8.8$ Hz, 1H, 5-H), 8.31 (ddd, $J = 1.3, 7.1, 8.8$ Hz, 1H, 7-H), 8.10 (t, $J = 8.8$ Hz, 1H, 6-H), 7.74–7.66 (m, 2H, 2'-H, 6'-H), 7.60–7.50 (m, 3H, 3'-H, 4'-H, 5'-H), 4.66 (s, 3H, NCH₃), 3.38 (s, 3H, CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): $\delta = 153.1$ (+, C2), 147.9 (+, C4), 137.3 (o, C8a), 136.0 (+, C7), 131.7 (+, C2', C6'), 130.6 (+, C4'), 130.3 (+, C6), 130.2 (+, C5), 129.1 (+, C3', C5'), 128.7 (o, C4a), 120.5 (o, C1'), 119.2 (+, C8), 116.7 (o, C3), 94.8 (o, C β), 83.3 (o, C α), 52.8 (+, CH₃SO₄), 45.4 (+, NCH₃) ppm. IR (ATR): 3043, 2941, 2223, 1631, 1606, 1578, 1520, 1493, 1494, 1444, 1365, 1227, 1210, 1173, 1140, 1059, 1010, 929, 910, 878, 766, 737, 695, 607, 577, 552, 524, 501, 479, 429 cm⁻¹. MS (ESI): $m/z = 244.1$ [M]⁺. HRMS (ESI): m/z calcd for C₁₈H₁₄N [M]⁺ 244.1121, found 244.1126.

3-((4-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium

methylsulfate (9e): According to Procedure 3, a solution of 1.435 g (5.00 mmol) of methyl 4-(quinolin-3-ylethynyl)benzoate **8e**, 50 μ L of nitrobenzene and 0.711 mL (7.50 mmol) of dimethyl sulfate in 25 mL of anhydrous toluene was heated for 1.5 h under reflux temperature to give 3-((4-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **9e**. Yield 2.044 g, 99%, a brownish solid, m.p. 219–220 °C. ¹H NMR (600 MHz, [D₆]DMSO): $\delta = 9.91$ (d, $J = 1.2$ Hz, 1H, 2-H), 9.54 (d, $J = 1.2$ Hz, 1H, 4-H), 8.55 (d, $J = 9.0$ Hz, 1H, 8-H), 8.46 (d, $J = 9.0$ Hz, 1H, 5-H), 8.33 (ddd, $J = 1.3, 7.0, 9.0$ Hz, 1H, 6-H), 8.14–8.07 (m, 3H, 7-H, 2'-H, 6'-H), 7.83 (ddd, $J = 1.5, 1.9, 8.2$ Hz, 2H, 3'-H, 5'-H), 4.66 (s, 3H, NCH₃), 3.90 (s, 3H, COOCH₃), 3.37 (s, 3H, CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): $\delta = 165.5$ (o, COO), 152.2 (+, C2), 148.3 (+, C4), 137.5 (o, C8a), 136.3 (+, C7), 132.1 (+, C2', C6'), 130.7 (+, C6), 130.5 (o, C4a), 130.4 (+, C5), 129.7 (+, C3', C5'), 128.7 (o, C4'), 125.2 (C1'), 119.3 (+, C8), 116.2 (o, C3), 93.5 (o, C α), 85.9 (o, C β), 52.8 (+, CH₃SO₄), 52.5 (+, COOCH₃), 45.5 (+, NCH₃) ppm. IR (ATR): 1721, 1278, 1240, 1215, 1170, 1097, 1057, 1005, 866, 766, 729, 696, 607, 574 cm⁻¹. Spectroscopic data are in agreement with those reported in the literature.^[24]

3-((2-(Methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium

methylsulfate (9f): According to Procedure 3, a solution of 1.435 g (5.00 mmol) of methyl 2-(quinolin-3-ylethynyl)benzoate **8f**, 50 μ L of nitrobenzene and 0.711 mL (7.50 mmol) of dimethyl sulfate in 25 mL of anhydrous toluene was heated for 1.5 h under reflux temperature to give 3-((2-(methoxycarbonyl)phenyl)ethynyl)-1-methylquinolinium methylsulfate **9f**. Yield 2.044 g, 99%, a yellow solid, m.p. 217–218 °C. ¹H NMR (600 MHz, [D₆]DMSO): $\delta = 9.80$ (d, $J = 1.0$ Hz, 1H, 2-H), 9.47 (d, $J = 1.0$ Hz, 1H, 4-H), 8.54 (d, $J = 9.1$ Hz, 1H, 8-H), 8.50 (d, $J = 9.1$ Hz, 1H, 5-H), 8.32 (ddd, $J = 1.5, 7.1, 9.1$ Hz, 1H, 6-H), 8.11 (ddd, $J = 1.5, 7.1, 9.1$ Hz, 1H, 7-H), 8.04 (dd, $J = 1.0, 8.0$ Hz, 1H, 6'-H), 7.85 (dd, $J = 1.0, 8.0$ Hz, 1H, 3'-H), 7.76 (td, $J = 1.5, 7.6$ Hz, 1H, 4'-H), 7.66 (td, $J = 1.5, 7.6$ Hz, 1H, 5'-H), 4.66 (s, 3H, NCH₃), 3.96 (s, 3H, COOCH₃), 3.36 (s, CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): $\delta = 165.5$ (o, COO), 151.9 (+, C2), 148.0 (+, C4),

137.4 (o, C8a), 136.1 (+, C7), 134.3 (+, C5'), 132.7 (+, C6'), 131.8 (o, C2'), 130.6 (+, C6), 130.5 (+, C4'), 130.4 (+, C5), 130.2 (+, C3'), 128.8 (o, C4a), 120.7 (o, C1'), 119.2 (+, C8), 116.8 (o, C3), 93.4 (o, Cα), 87.4 (o, Cβ), 52.8 (+, CH₃SO₄), 52.5 (+, COOCH₃), 45.5 (+, NCH₃) ppm. IR (ATR): 2923, 2219, 1737, 1272, 1258, 1133, 1082, 832, 765, 761, 698, 556, 434 cm⁻¹. Spectroscopic data are in agreement with those reported in the literature.^[24]

1-Methyl-3-(4',5',6'-triphenyl-[1,1':2',1''-terphenyl]-3'-yl)quinolinium

methylsulfate (9g): According to Procedure 3, a solution of 0.100 g (0.171 mmol) of 2,3,4,5,6-pentaphenyl-1-(quinoline-3-yl)benzene, 50 μl of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 1-methyl-3-(4',5',6'-triphenyl-[1,1':2',1''-terphenyl]-3'-yl)quinolinium methylsulfate **9g**. Yield 0.122 g, 99%, a light green solid, m.p. 321–323 °C (decomp.). ¹H NMR (600 MHz, [D₆]DMSO): δ = 9.35 (d, *J* = 1.4 Hz, 1H, 2-H), 8.84 (s, 1H, 4-H), 8.24 (d, *J* = 8.1 Hz, 1H, 8-H), 8.14 (ddd, *J* = 1.5, 7.1, 8.8 Hz, 1H, 7-H), 8.06 (dd, *J* = 1.1, 8.4 Hz, 1H, 5-H), 7.92–7.90 (m, 1H, 6-H), 7.05 (d, *J* = 7.7 Hz, 2H, Ph), 7.02 (d, *J* = 7.7 Hz, 2H, Ph), 6.96–6.82 (m, 21H, Ph), 4.34 (s, 3H, NCH₃), 3.37 (s, 3H, CH₃SO₄) ppm. ¹³C NMR (150 MHz, [D₆]DMSO): δ = 150.6 (+, C2), 147.5 (+, C4), 142.3 (o), 140.7 (o), 140.5 (o), 139.3 (o), 139.0 (o), 138.4 (o), 135.53 (o, C8a), 135.48 (+, C7), 134.4 (o, C3), 132.8 (o, C1'), 131.0 (+), 130.7 (+), 130.64 (+), 130.60 (+), 130.54 (+), 130.5 (+, C6), 129.9 (+, C5), 127.7 (o, C4a), 127.4 (o), 126.89 (+), 126.87 (+), 126.80 (+), 126.77 (+), 126.4 (+), 125.92 (+), 125.85 (+), 118.9 (+, C8), 52.8 (+, CH₃SO₄), 44.8 (+, NCH₃) ppm. IR (ATR): 3051, 3023, 2961, 1600, 1524, 1496, 1442, 1378, 1254, 1215, 1063, 1012, 760, 697, 618, 577, 558, 441 cm⁻¹. HRMS (ESI): *m/z* calcd for C₄₆H₃₄N [M]⁺ 600.2686, found 600.2687.

1-Methyl-3-(phenanthren-9-yl)quinolin-2(1H)-one (10): Under a nitrogen atmosphere, 1-methyl-3-(phenanthren-9-yl)quinolinium methylsulfate (0.431 g, 1.00 mmol), sulfur (0.128 g, 4.00 mmol) and LiOH (0.192 g, 8.00 mmol) were suspended in absolute toluene (10 mL), and then potassium *tert* butoxide (0.896 g, 8.00 mmol) was added slowly with stirring. The resulting mixture was stirred for 6 h under reflux at 120 °C. After that, the mixture was concentrated in vacuo, and the crude product was purified by column chromatography with PE-EE as an eluent to give 1-methyl-3-(phenanthren-9-yl)quinolin-2(1H)-one **10**. Yield 0.184 g, 55%, a white solid, m.p. 56–57 °C (55–58 °C).^[35] ¹H NMR (600 MHz, CDCl₃): δ = 8.77 (d, *J* = 8.3 Hz, 1H, 5'-H), 8.72 (d, *J* = 8.0 Hz, 1H, 4'-H), 7.90 (s, 1H, 4-H), 7.88 (dd, *J* = 1.4, 7.8 Hz, 1H, 1'-H), 7.77–7.76 (m, 2H, 5'-H, 10-H), 7.68 (ddd, *J* = 1.4, 6.9, 8.3 Hz, 1H, 3'-H), 7.66–7.64 (m, 2H, 5-H, 7-H), 7.60 (ddd, *J* = 1.0, 6.9, 7.8 Hz, 1H, 2'-H), 7.53 (ddd, *J* = 1.2, 6.9, 8.2 Hz, 1H, 7'-H), 7.49 (d, *J* = 9.0 Hz, 1H, 8-H), 7.32–7.30 (m, 1H, 6-H), 3.86 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 162.0 (+, C2), 140.3 (o, C8a), 139.2 (+, C4), 134.3 (o, C9'), 133.3 (o, C3), 131.7 (o, C10a'), 130.8 (o, C4a'), 130.7 (+, C7), 130.6 (o, C4b'), 129.1 (+, C5), 128.9 (+, C1'), 128.4 (+, C10'), 127.0 (+, C3'), 126.79 (+, C8'), 126.77 (+, C2'), 126.73 (+, C7'), 126.68 (+, C6'), 123.1 (+, C5'), 122.7 (+, C4'), 122.5 (+, C6), 120.8 (o, C4a), 114.4 (+, C8), 30.2 (+, NCH₃) ppm. IR (ATR): 3059, 1638, 1590, 1570, 1528, 1495, 1463, 1448, 1432, 1416, 1383, 1364, 1343, 1329, 1317, 1295, 1275, 1242, 1211, 1164, 1146, 1127, 1105, 1085, 1040, 1018, 1001, 979, 951, 927, 918, 899, 884, 861, 853, 805, 788, 769, 753, 748, 732, 721, 710, 660, 620, 615, 578, 558, 543, 509, 496, 482, 463, 454, 426, 416, 412, 407 cm⁻¹. MS (ESI): *m/z* = 336.0 [M+H]⁺.

General procedure for the preparation of thiones (Procedure 4):

Under a nitrogen atmosphere the corresponding salt (1.00 mmol), sulfur (4.00 mmol) and LiOH (8.00 mmol) were suspended in absolute toluene (10 mL), and then potassium *tert*-pentoxide (1.20 mmol, 1.7 M solution in toluene) was added slowly with stirring. The resulting mixture was stirred for 6 h under reflux at 120 °C. After the mixture was concentrated in vacuo,

the crude product was purified by column chromatography with petrol ether-ethyl acetate as an eluent.

1-Methyl-3-phenylquinoline-2(1H)-thione (11a): According to Procedure 4, a solution of 0.331 g (1.00 mmol) of 1-methyl-3-phenylquinolinium methylsulfate, 0.128 g (4.00 mmol) of sulfur, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-phenylquinoline-2(1H)-thione **11a**. Yield 0.050 g, 20%, an orange solid, m.p. 118–119 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.67–7.65 (m, 2H, 5-H, 7-H), 7.63–7.60 (m, 2H, 4-H, 8-H), 7.50–7.49 (m, 2H, 2'-H, 6'-H), 7.44–7.41 (m, 2H, 3'-H, 5'-H), 7.40–7.35 (m, 2H, 6-H, 4'-H), 4.41 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 185.0 (o, C2), 143.0 (o, C3), 141.3 (o, C8a), 140.9 (o, C1'), 132.1 (+, C4), 131.2 (+, C7), 129.6 (+, C2', C6'), 129.1 (+, C5), 128.0 (+, C3', C5'), 127.9 (+, C4'), 124.3 (+, C6), 123.8 (o, C4a), 115.8 (+, C8), 39.1 (+, NCH₃) ppm. IR (ATR): 1612, 1595, 1563, 1493, 1443, 1414, 1372, 1346, 1324, 1299, 1233, 1215, 1180, 1146, 1121, 1091, 1054, 1028, 1000, 973, 964, 947, 911, 876, 852, 782, 757, 746, 740, 692, 646, 618, 595, 576, 551, 500, 481, 466, 452, 447 cm⁻¹. MS (ESI): *m/z* = 252.1 [M+H]⁺. HRMS (ESI): *m/z* calcd for C₁₆H₁₄NS [M+H]⁺ 252.0847, found 252.0848.

1-Methyl-3-(naphthalen-1-yl)quinoline-2(1H)-thione (11b): According to Procedure 4, a solution of 0.381 g (1.00 mmol) of 1-methyl-3-(naphthalen-1-yl)quinolinium methylsulfate, 0.128 g (4.00 mmol) of sulfur, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(naphthalen-1-yl)quinoline-2(1H)-thione **11b**. Yield 0.115 g, 38%, an orange solid, m.p. 216–218 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.90 (d, *J* = 4.6 Hz, 1H, 4'-H), 7.89 (d, *J* = 4.6 Hz, 1H, 5'-H), 7.73 (s, 1H, 4-H), 7.71–7.65 (m, 3H, 5-H, 7-H, 8-H), 7.62 (d, *J* = 8.4 Hz, 1H, 8'-H), 7.55 (m, 1H, 3'-H), 7.46 (m, 1H, 6'-H), 7.42–7.36 (m, 3H, 6-H, 2'-H, 7'-H), 4.45 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 185.4 (o, C2), 142.2 (o, C3), 141.2 (o, C8a), 139.0 (o, C1'), 133.7 (o, C4a), 133.4 (+, C4), 131.9 (o, C8a'), 131.4 (+, C7), 129.2 (+, C5), 128.6 (+, C4'), 128.4 (+, C5'), 126.8 (+, C2'), 126.2 (+, C1'), 126.0 (+, C8), 125.9 (+, C6'), 125.6 (+, C3'), 124.3 (+, C6), 123.7 (o, C4a), 115.9 (+, C8), 38.9 (+, NCH₃) ppm. IR (ATR): 1615, 1602, 1594, 1563, 1505, 1494, 1464, 1446, 1410, 1376, 1347, 1338, 1322, 1291, 1239, 1222, 1176, 1146, 1096, 1086, 1054, 1034, 1022, 1008, 970, 954, 943, 904, 879, 851, 796, 773, 761, 747, 731, 711, 664, 649, 637, 594, 581, 563, 511, 491, 474, 461, 452, 447, 425, 413 cm⁻¹. MS (ESI): *m/z* = 302.1 [M+H]⁺. HRMS (ESI): *m/z* calcd for C₂₀H₁₆NS [M+H]⁺ 302.1003, found 302.1003.

1-Methyl-3-(phenanthren-9-yl)quinoline-2(1H)-thione (11c): According to Procedure 4, a solution of 0.431 g (1.00 mmol) of 1-methyl-3-(phenanthren-9-yl)quinolinium methylsulfate, 0.128 g (4.00 mmol) of sulfur, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(phenanthren-9-yl)quinoline-2(1H)-thione **11c**. Yield 0.316 g, 90%, an orange solid, m.p. 227–228 °C. ¹H NMR (600 MHz, CDCl₃): δ = 8.75 (d, *J* = 8.3 Hz, 1H, 5'-H), 8.73 (d, *J* = 8.3 Hz, 1H, 4'-H), 7.88 (d, *J* = 7.9 Hz, 1H, 1'-H), 7.81 (s, 1H, 4-H), 7.74–7.66 (m, 6H, 4-H, 7-H, 8-H, 3'-H, 8'-H, 10'-H), 7.63 (ddd, *J* = 1.2, 7.1, 8.2 Hz, 1H, 6'-H), 7.60 (ddd, *J* = 0.8, 7.1, 7.7 Hz, 1H, 2'-H), 7.49 (ddd, *J* = 1.1, 7.0, 8.1 Hz, 1H, 7'-H), 7.40 (ddd, *J* = 1.2, 7.0, 8.0 Hz, 1H, 6-H), 4.47 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 185.3 (o, C2), 142.5 (o, C3), 141.2 (o, C8a), 137.9 (o, C9'), 133.6 (+, C4), 131.9 (o, C10a), 131.4 (+, C7), 131.1 (o, C8a'), 130.6 (o, C4a'), 130.5 (o, C4b'), 129.2 (+, C5), 128.9 (+, C1'), 127.3 (+, C10'), 127.0 (+, C8'), 126.9 (+, C3'), 126.8 (+, C2'), 126.6 (+, C7'), 126.6 (+, C6'), 124.3 (+, C6), 123.7 (o, C4a), 123.1 (+, C5), 122.8 (+, C4'), 115.9 (+, C8), 38.8 (+, NCH₃) ppm. IR (ATR): 1611, 1595, 1563, 1525, 1494, 1456, 1449, 1424, 1386, 1369, 1347, 1328, 1309, 1271, 1244, 1233, 1210, 1185, 1166, 1144, 1110, 1097, 1088, 1038, 1009, 951, 945, 915, 909, 892,

874, 857, 846, 783, 759, 749, 739, 721, 701, 658, 636, 617, 611, 582, 557, 529, 506, 499, 486, 428 cm⁻¹. MS (ESI): *m/z* = 352.1 [M+H]⁺. HRMS (ESI): *m/z* calcd for C₂₄H₁₈NS [M+H]⁺ 352.1160, found 352.1155.

1-Methyl-3-(4',5',6'-triphenyl-[1,1':2',1''-terphenyl]-3'-yl)quinoline-2(1H)-thione (11g):

According to Procedure 4, a solution of 0.154 g (0.22 mmol) of 2,3,4,5,6-phenyl-1-(1-methylquinolinium-3-yl)benzene methylsulfate, 0.055 g (1.72 mmol) of sulfur, 0.042 g (1.82 mmol) of LiOH, potassium *tert*-pentoxide (0.26 mmol, 1.7 M solution in toluene) in 5 mL of toluene was stirred for 6 h under reflux temperature to give thione **11g**. Yield 0.050 g, 38%, a yellow solid, m.p. >330 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.46 (ddd, *J* = 1.6, 7.1, 8.7 Hz, 1H, 7-H), 7.41 (s, 1H, 4-H), 7.39 (dd, *J* = 1.5, 7.8 Hz, 1H, 5-H), 7.37–7.36 (m, 2H, Ph), 7.30 (d, *J* = 8.6 Hz, 1H, 8-H), 7.17 (ddd, *J* = 0.7, 7.2, 8.1 Hz, 1H, 6-H), 6.93–6.76 (m, 23H, Ph), 4.00 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 184.7 (o, C2), 142.4 (o, C3), 140.8 (o), 140.65 (o), 140.61 (o), 140.5 (o), 140.03 (o), 139.99 (o, C8a), 138.8 (o), 135.3 (+, C4), 131.9 (+), 131.8 (+), 131.6 (+), 131.4 (+), 131.1 (+), 130.9 (+), 130.5 (+, C7), 128.6 (+, C5), 126.80 (+), 126.76 (+), 126.54 (+), 126.47 (+), 126.0 (+), 125.7 (+), 125.2 (+), 123.5 (+, C6), 122.9 (o, C4a), 115.4 (+, C8), 38.4 (+, NCH₃) ppm. IR (ATR): 3055, 3022, 2922, 2850, 1733, 1616, 1568, 1495, 1441, 1372, 1315, 1235, 1184, 1148, 1095, 1072, 1043, 1027, 909, 792, 740, 695, 644, 552, 502, 481 cm⁻¹. HRMS (ESI): *m/z* calcd for C₄₆H₃₃NNaS [M+Na]⁺ 654.2220, found 654.2200.

General procedure for the preparation of selenones (Procedure 5):

Under a nitrogen atmosphere, the corresponding salt (1.00 mmol), selenium (4.00 mmol) and LiOH (8.00 mmol) were suspended in absolute toluene (10 mL), then potassium *tert*-pentoxide (1.20 mmol, 1.7 M solution in toluene) was added slowly with stirring. The resulting mixture was stirred for 6 h under reflux at 120 °C. Afterward, the mixture was concentrated in vacuo and the crude product was purified by column chromatography with petrol ether-ethyl acetate as eluent.

1-Methyl-3-phenylquinoline-2(1H)-selenone (12a): According to Procedure 5, a solution of 0.331 g (1.00 mmol) of 1-methyl-3-phenylquinolinium methylsulfate, 0.316 g (4.00 mmol) of selenium, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-phenylquinoline-2(1H)-selenone **12a**. Yield 0.059 g, 20%, a red oil. ¹H NMR (600 MHz, CDCl₃): δ = 7.74–7.69 (m, 4H, 4-H, 5-H, 7-H, 8-H), 7.47–7.37 (m, 6H, 6-H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H), 4.56 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 186.4 (o, C2), 146.7 (o, C3), 142.7 (o, C1'), 141.5 (o, C8a), 131.4 (+, C7), 130.4 (+, C4), 129.7 (+, C2', C6'), 129.3 (+, C5), 127.9 (+, C3', C4', C5'), 125.0 (+, C6), 125.0 (o, C4a), 116.4 (+, C8), 43.9 (+, NCH₃) ppm. ⁷⁷Se NMR (114 MHz, CDCl₃) δ = 706.6 ppm. IR (ATR): 1639, 1591, 1559, 1493, 1443, 1371, 1321, 1234, 1142, 1070, 907, 790, 743, 694, 638, 590, 576, 480 cm⁻¹. HRMS (APCI): *m/z* calcd for C₁₆H₁₄NSe [M+H]⁺ 300.0286, found 300.0275.

1-Methyl-3-(naphthalen-1-yl)quinoline-2(1H)-selenone (12b):

According to Procedure 5, a solution of 0.381 g (1.00 mmol) of 1-methyl-3-(naphthalen-1-yl)quinolinium methylsulfate, 0.316 g (4.00 mmol) of selenium, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(naphthalen-1-yl)quinoline-2(1H)-selenone **12b**. Yield 0.220 g, 63%, a red solid, m.p. 196–198 °C (decomp.). ¹H NMR (600 MHz, CDCl₃): 7.90 (m, 2H, 4'-H, 5'-H), 7.82 (s, 1H, 4-H), 7.80 (d, *J* = 8.7 Hz, 1H, 8-H), 7.75 (ddd, *J* = 1.5, 7.1, 8.7 Hz, 1H, 7-H), 7.70 (dd, *J* = 1.5, 7.8 Hz, 1H, 5-H) 7.61 (d, *J* = 8.4 Hz, 1H, 8'-H), 7.56 (dd, *J* = 6.9, 8.2 Hz, 1H, 3'-H), 7.47–4.43 (m, 2H, 6-H, 6'-H) 7.42 (dd, *J* = 1.1, 7.0 Hz, 1H, 2'-H), 7.38 (ddd, *J* = 1.4, 6.9, 8.4 Hz, 1H, 7'-H), 4.59 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 186.8 (o, C2), 145.9 (o, C3), 141.8 (o, 8a), 140.3 (o, C1'), 133.6 (o, C4a'), 132.0 (o, C8a'), 131.8 (+,

C4), 131.7 (+, C7), 129.4 (+, C5), 128.5 (+, C5'), 128.3 (+, C4'), 127.0 (+, C2'), 126.1 (+, C7'), 126.0 (+, C8'), 125.9 (+, C6), 125.6 (+, C3'), 125.0 (+, C6'), 124.9 (o, C4a), 116.4 (+, C8), 43.7 (+, NCH₃) ppm. ⁷⁷Se NMR (114 MHz, CDCl₃) δ = 716.8 ppm. IR (ATR): 3051, 3017, 2919, 2849, 2185, 1967, 1733, 1610, 1560, 1373, 1238, 1145, 1096, 1067, 795, 773, 761, 581, 491, 423 cm⁻¹. HRMS (APCI): *m/z* calcd for C₂₀H₁₆NSe [M+H]⁺ 350.0443, found 350.0441.

1-Methyl-3-(phenanthren-9-yl)quinoline-2(1H)-selenone (12c):

According to Procedure 5, a solution of 0.431 g (1.00 mmol) of 1-methyl-3-(phenanthren-9-yl)quinolinium methylsulfate, 0.316 g (4.00 mmol) of selenium, 0.192 g (8.00 mmol) of LiOH, potassium *tert*-pentoxide (1.2 mmol, 1.7 M solution in toluene) in 10 mL of toluene was stirred for 6 h under reflux temperature to give 1-methyl-3-(phenanthren-9-yl)quinoline-2(1H)-selenone **12c**. Yield 0.080 g, 20%, a red solid, m.p. 271–272 °C. ¹H NMR (600 MHz, CDCl₃): δ = 8.75 (d, *J* = 8.3 Hz, 1H, 5'-H), 8.73 (d, *J* = 8.0 Hz, 1H, 4'-H), 7.90 (s, 1H, 4-H), 7.87 (d, *J* = 7.8 Hz, 1H, 1'-H), 7.83 (d, *J* = 8.6 Hz, 1H, 8-H), 7.77 (ddd, *J* = 1.6, 7.1, 8.8 Hz, 1H, 7-H), 7.72 (dd, *J* = 1.5, 7.8 Hz, 1H, 5-H), 7.69–7.65 (m, 3H, 3'-H, 8'-H, 10'-H), 7.63 (ddd, *J* = 1.3, 6.9, 8.3 Hz, 1H, 6'-H), 7.60 (ddd, *J* = 1.0, 7.0, 7.9 Hz, 1H, 2'-H), 7.49–7.45 (m, 2H, 6-H, 7'-H), 4.61 (s, 3H, NCH₃) ppm. ¹³C NMR (150 MHz, CDCl₃(deptq)): δ = 186.8 (-, C2), 146.2 (-, C3), 141.9 (-, C8a), 139.0 (-, C9'), 132.1 (+, C4), 131.9 (-, C10a'), 131.7 (+, C7), 131.3 (-, C8a'), 130.5 (-, C4a'), 130.5 (-, C4b'), 129.5 (+, C5), 129.0 (+, C1'), 127.5 (+, C9'), 127.1 (+, C8'), 126.9 (+, C3'), 126.8 (+, C2'), 126.6 (+, C6', C7'), 125.1 (+, C6), 125.0 (-, C4a), 123.1 (+, C5'), 122.9 (+, C4'), 116.5 (+, C8), 43.6 (+, NCH₃) ppm. ⁷⁷Se NMR (114 MHz, CDCl₃) δ = 720.4 ppm. IR (ATR): 1591, 1561, 1449, 1367, 1211, 1135, 1065, 908, 890, 759, 749, 740, 721, 611, 556, 488, 428 cm⁻¹. HRMS (ESI): *m/z* calcd for C₂₄H₁₇NNaSe [M+Na]⁺ 422.0413, found 422.0411.

1-Methyl-3-(phenanthren-9-yl)-N,N-bis(trimethylsilyl)-1,2-dihydroquinolin-2-amine (13):

1-Methyl-3-(phenanthren-9-yl)quinolinium hexafluorophosphate (0.015 g, 0.032 mmol) and 2 M solution of LiHMDS in THF (0.02 mL, 0.380 mmol) were used for the NMR experiment. ¹H NMR (600 MHz, [D₈]THF): δ = 8.76 (d, *J* = 8.3 Hz, 1H, 5'-H), 8.71 (d, *J* = 8.1 Hz, 1H, 4'-H), 8.18 (d, *J* = 8.1 Hz, 1H, 1'-H), 7.89 (s, 1H, 10'-H), 7.85 (d, *J* = 7.9 Hz, 1H, 8'-H), 7.60–7.56 (m, 2H, 3'-H, 6'-H), 7.53–7.49 (m, 2H, 2'-H, 7'-H), 7.17 (t, *J* = 7.8 Hz, 1H, 7-H), 7.13 (d, *J* = 7.1 Hz, 1H, 5-H), 6.81 (d, *J* = 8.1 Hz, 1H, 8-H), 6.76 (s, 1H, 4-H), 6.71 (t, *J* = 7.3 Hz, 1H, 6-H), 5.58 (s, 1H, 2-H), 3.19 (s, 3H, NCH₃), 0.00 (s, 18H, NSi₂(CH₃)₆) ppm. ¹³C NMR (150 MHz, [D₈]THF): δ = 141.5 (o, C8a), 136.9 (o, C9'), 133.1 (o, C3), 131.8 (o, C10a'), 131.0 (o, C8a'), 130.8 (o, C4a'), 130.0 (o, C4b'), 128.6 (+, C7), 128.4 (+, C8'), 127.4 (+, C10'), 126.51 (+, C1'), 126.46 (+, C7'), 126.42 (+, C4), 126.3 (+, C6'), 126.2 (+, C2'), 126.1 (+, C3'), 122.9 (+, C5), 122.4 (+, C4'), 121.1 (o, C4a), 116.9 (+, C6), 111.2 (+, C8), 83.6 (+, C2), 35.4 (+, NCH₃), 1.7 (+, NSi₂(CH₃)₆) ppm.

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Keywords: quinoline • carbene • selenones • heterocycle synthesis • quinolin-2-ylidene

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Entry for the Table of Contents

FULL PAPER

Series of substituted quinolinium salts were prepared which possess aryl groups or ethynyl groups in position 3. For R = aryl N-heterocyclic carbene trapping reactions were performed with sulfur and selenium in the presence of potassium *tert*-pentoxide and lithium hydroxide.

N-Heterocyclic Carbenes

*Sviatoslav Batsyts, Roman Vedmid, Jan C. Namyslo, Martin Nieger, and Andreas Schmidt**

Page No. – Page No.

3-Aryl Substituted 1-Methylquinolinium Salts as Carbene Precursors