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Ritika Sharma, Rakesh Kumar, and Upendra Sharma

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Rh/O_2-Catalyzed C8 Olefination of Quinoline *N*-oxides with Activated and Unactivated Olefins

Ritika Sharma, Rakesh Kumar, and Upendra Sharma*

Natural Product Chemistry and Process Development Division and AcSIR, CSIR- IHBT, Palampur-176061, India

Supporting Information

ABSTRACT: The rhodium/O_2 system catalyzed distal C(sp^2)-H olefination of quinoline *N*-oxides is developed. Molecular oxygen has been explored as economic and clean oxidant, alternative to inorganic oxidants. Wide substrate scope with respect to quinoline *N*-oxides and olefins (*activated: acrylates, styrenes, and un-activated: aliphatic olefins*) demonstrates the robustness of the developed catalytic method. Interestingly, 2-substituted quinoline *N*-oxides also afforded good yields of the corresponding C8-olefinated products. Kinetic isotope studies and deuterium labeling experiments have been performed to understand the preliminary mechanistic pathway. The applicability of the developed method is demonstrated by utilizing natural product derived substrates and by converting the C8-olefinated quinoline *N*-oxides into various other useful molecules.

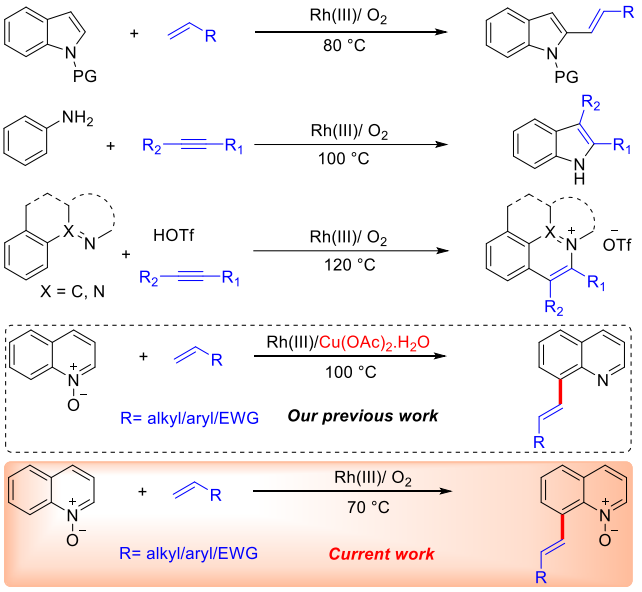
KEYWORDS: *rhodium catalyst, molecular oxygen, quinoline N-oxides, olefins, olefination.*

INTRODUCTION

In modern organic chemistry, transition metal catalyzed direct oxidative coupling *via* C-H bond functionalization has been considered as a specific step to reduce the waste generation and to achieve high selectivity.[1] Transition metal catalyzed methods involve reduction of a metal catalyst from higher oxidation state to lower oxidation state often for the completion of the catalytic cycle, a stoichiometric amount of oxidant is required which leads to the generation of unavoidable waste.[2] For replacing these stoichiometrically used metal and non-metal based oxidants, molecular O_2, the second most abundant gas in nature, is considered an appealing oxidant.[3] Low cost and H_2O as the sole byproduct further provide strong motivation to use O_2 as clean oxidant.[3b, 4] In this perspective, combining C-H activation methodology with molecular O_2 as oxidant, provide an ideal way towards green and sustainable chemical processes.[5]

Swapping the common oxidants with molecular O_2 is challenging as it can be used as an oxidant in reactions involving β-hydride elimination step but compatibility with reductive elimination is still rare.[6] The representative examples wherein O_2 is utilized as oxidant include, Rh-catalyzed method for the synthesis of acetic acid,[7] Pd-catalyzed C-H bond oxidation,[8] Cu-catalyzed Sonogashira reaction for the alkynylation of polyfluoroarenes with terminal alkynes,[9] Ru- catalyzed annulation reaction,[10] Pd-catalyzed hydroxylation of arene,[11] and Rh-catalyzed annulation etc.[12]

Synthesis and functionalization of nitrogen-containing heterocyclic scaffolds are important due to their use in organic synthesis, material science, and drugs.[13] In this regard, quinolines play a central role due to their medicinal benefits and are also an invaluable template in asymmetric synthesis.[14] Indeed, various methods have been explored already for regioselective functionalization at C2 position of quinoline,[15] but C8 position still necessitates immediate expeditious efforts.[16] Although, catalytic methods have been developed already for C-C,[17] C-N[18] and C-X (halogen)[18] bond formation at the C8 position of quinoline, use of a stoichiometric amount of metal oxidant warrant further improvement. On the other hand, Rh/O_2-catalytic system have also been explored for the functionalization and synthesis of different nitrogen-containing heterocycles,[12, 19] any such example in case of distal C8 bond functionalization of quinoline is still awaited (Scheme 1). Recently, we have reported C8 olefination of quinoline by using Rh(III)-catalyst and $Cu(OAc)_2.H_2O$ as oxidant (Scheme 1).[17f] Herein we disclose an operationally simple Rh(III)/O_2-catalyzed direct C8 olefination of quinoline *N*-oxide with acrylates, styrenes and aliphatic olefins (Scheme 1).



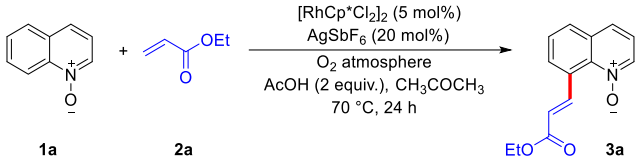
Scheme 1. Rh(III)/O_2 Catalyzed Functionalization and Synthesis of Nitrogen Containing Heterocyclic Compounds

RESULTS AND DISCUSSION

One of the major synthetic target in organic synthesis is to utilize molecular oxygen as an oxidant and henceforth we initiated to examine the reaction between quinoline *N*-oxide (**1a**) and ethyl acrylate (**2a**) in the presence of $[RhCp^*Cl_2]_2/AgSbF_6$ catalyst, acetic acid as additive and DCE as solvent, under O_2 atmosphere at 100 °C. Unfortunately, the product was not observed due to sluggish reaction (Table 1, entry 5). Optimization with various solvents gave inappropriate results at 100 °C whereas at lower temperature comparatively better results were observed. Although, good yields were observed in case of EtOH/H_2O at 70 °C, the maximum yield of 77% was obtained using acetone as solvent (Table 1, entries 6-8). Further, lowering the temperature or time of reaction resulted in a lower yield of the desired product (Table 1, entries 9-10). Increase or diminution in the catalyst loading lowers the yield of the expected product (Table 1, entries 11-12). Alteration in the Rh-catalyst or Ag-salt does not prove good for current reaction (Table 1, entries 13 and 14). To our delight, use of 2 equiv. of acetic acid at 70 °C for 24 h under O_2 atmosphere provided 86% of the desired product (Table 1, entry 1). Furthermore, the control experiments

(Table 1, entries 2-4) revealed that Rh(III)/ $AgSbF_6$, acetic acid as an additive and O_2 atmosphere are mandatory for current transformation. Other pivotal reaction conditions addressing the effect of altered parameters were also monitored for critical optimization.

Table 1. Optimization Study[a]

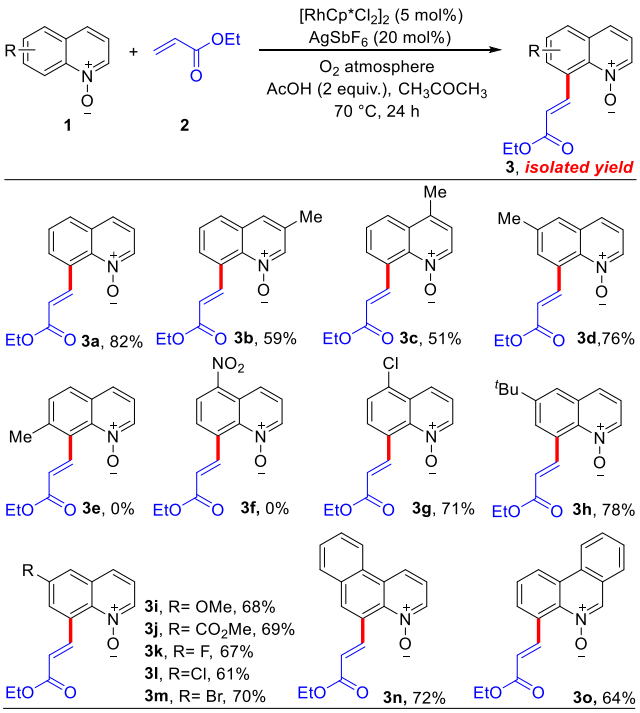


entry	variation from standard condition	**3a** yield (%)[b]
1	None	**86 (82)**[c]
2	without catalyst	n.d.
3	without AcOH	n.d.
4	N_2 atmosphere	traces
5	DCE, AcOH (1 equiv.), 100 °C	n.d.
6	EtOH, AcOH (1 equiv.)	61
7	H_2O, AcOH (1 equiv.)	56
8	$(CH_3)_2CO$, AcOH (1 equiv.)	77
9	at room temperature	55
10	12 h	51
11	$[Cp^*RhCl_2]_2$ (10 mol%)/ $AgSbF_6$ (40 mol%)	42
12	$[Cp^*RhCl_2]_2$ (2.5 mol%)/ $AgSbF_6$ (10 mol%)	17
13	[Rh(acac)(nbd)] instead of $[Cp^*RhCl_2]_2$	Traces
14	$AgBF_4$ instead of $AgSbF_6$	30
15	Without $AgSbF_6$	10

[a]reaction conditions: **1a** (0.10 mmol), **2a** (0.20 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), acetic acid (2 equiv.), acetone (0.22 M), 70 °C, 24 h. [b]Yield based on NMR analysis of crude reaction mixture using DMF as an internal standard. [c]Isolated yield in parentheses.

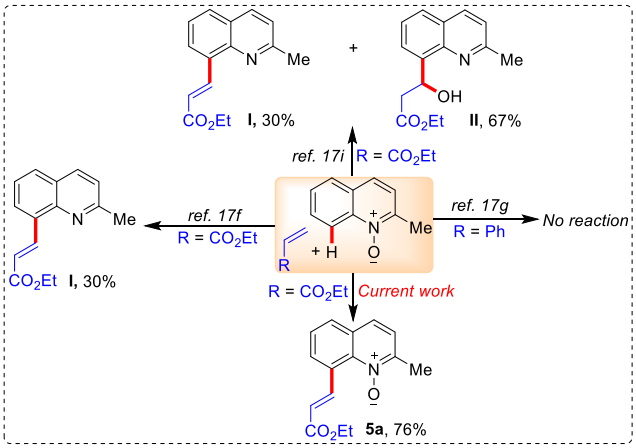
With the best optimized condition, scope of reaction was explored by reacting various substituted quinoline *N*-oxides with **2a** (Table 2). Reaction of **1a** with **2a** using $[RhCp^*Cl_2]_2$/ $AgSbF_6$ (5 mol%/ 20 mol%) catalyst and acetic acid (2 equiv.) as an additive in the presence of acetone at 70 °C under O_2 atmosphere for 24 h afforded **3a** in 82% isolated yield. The catalytic method was found to be compatible with electron donating methyl group at C3, C4, and C6 positions of quinoline *N*-oxide affording moderate to good yields of C8 olefinated product (**3b-d**, 51-76%). Unfortunately, the 7-methyl and 5-nitro quinoline *N*-oxide were not found compatible under developed reaction conditions as in both cases no product was observed **(3e-f)**. This might be due to steric hindrance in case of methyl at C7 and strong electron withdrawing effect of 5-nitro group. The 5-Cl substituted quinoline *N*-oxide was also found compatible affording product (**3g**, 71%) in good yield. Quinoline *N*-oxide with substituents such as –^{t}Bu, -OMe and –CO_2Me at C6 position reacted smoothly affording the olefinated product in 68-78% yields (**3h-j**). Notably, the halogen substituents such as –F, -Cl and –Br were well tolerated giving corresponding C8-substituted product **(3k-m)** with 61-70% yields, providing an opportunity for further functionalization. The current method is also applicable for the polycyclic quinolines including benzo[*f*]quinoline and phenanthridine affording the corresponding desired product in good yields (**3n-o**).

Table 2. Scope with Quinoline *N*-oxides[a]



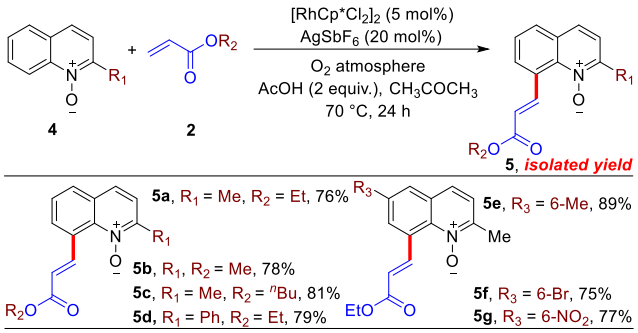
[a]reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), acetic acid (2 equiv.), acetone (0.22 M), 70 °C, 24 h.

Under our earlier developed reaction conditions for C8-olefination[17f] and alkylation[17g] either lower yield of C8-olefinated product (**I**)/no reaction or 3-hydroxyquinoline 8-yl propanoates derivatives (**II**)[17i] were observed in case of 2-substituted quinolines (Scheme 2). To our delight, 2-methyl quinoline *N*-oxide (**4a**) reacted smoothly with **2a** affording the C8 olefinated product (**5a**) in 76% yield under current reaction conditions. Various other 2-substituted quinoline *N*-oxides were reacted with different acrylates under developed reaction conditions (Table 3). Use of methyl or *n*-butyl acrylate in place of **2a** did not affect the output of the reaction and provided better yields (78-81%) of the corresponding desired product (**5b-c**). Interestingly, 2-phenyl and 2,6-disubstituted quinoline *N*-oxides also reacted well with **2a**, affording **5d-g** in 75-89% yields.



Scheme 2. Reaction of 2-Substituted Quinoline *N*-oxide with an Olefin

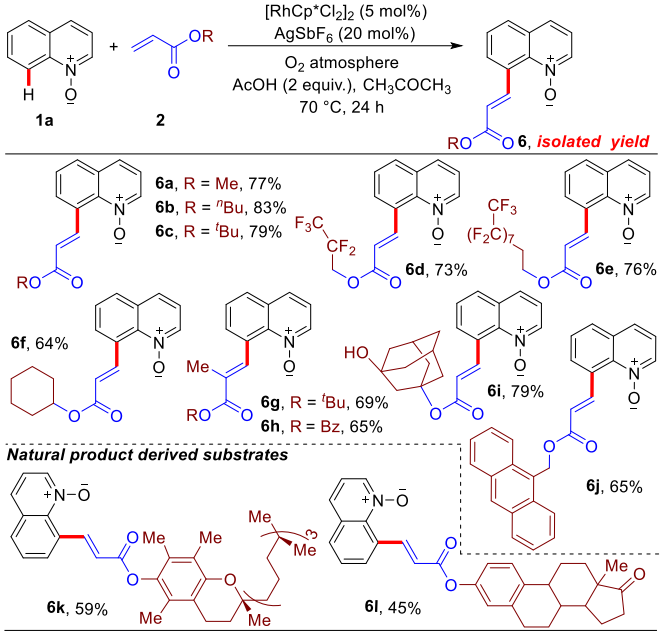
Table 3. Scope with 2-Substituted Quinoline *N*-oxides[a]



[a]reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), acetic acid (2 equiv.), acetone (0.22 M), 70 °C, 24 h.

After successfully exploring the substrate scope with various quinoline *N*-oxides, the substrate scope with acrylates was attempted (Table 4).

Table 4. Scope with Acrylates[a]

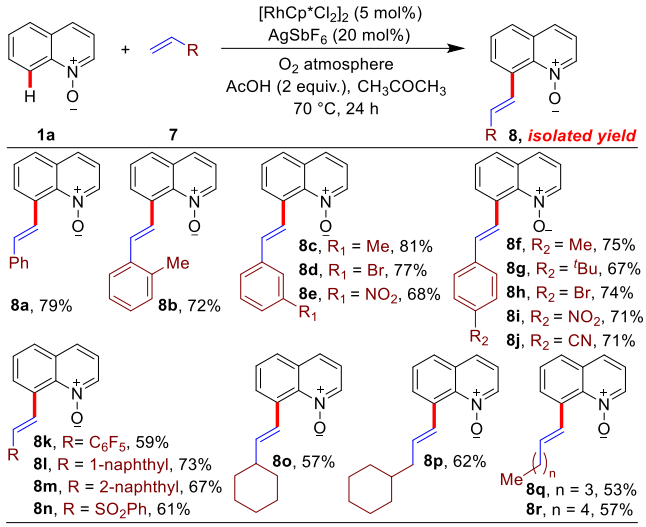


[a]reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), acetic acid (2 equiv.), acetone (0.22 M), 70 °C, 24 h.

A wide range of acrylates including methyl, *n*-butyl, *t*-butyl, cyclohexyl, and polyfluorinated acrylates reacted successfully affording the desired alkenylated product in good yields (**6a-f**). Sterically hindered *tert*-butyl methacrylate and benzyl methacrylate successfully underwent this coupling reaction, affording **6g-h** in moderate yields. Acrylate substrate derived from bulky alcohol as well as from natural products such as 3-hydroxy adamantane, 9-anthranyl methyl, vitamin E, and estrone also reacted successfully (entries **6i-l**).

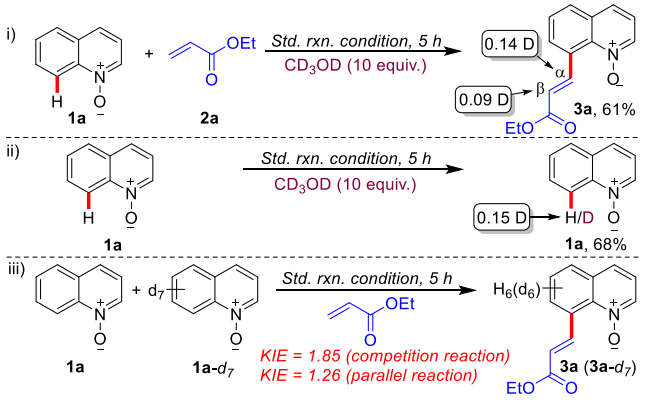
In addition to acrylates, styrenes and aliphatic olefins also worked well under developed reaction condition (Table 5). Various styrene's substituted with electron-rich as well as electron-deficient functional groups at *-ortho*, *-meta* or *-para* positions of phenyl ring were well compatible with the current Rh(III)/O_2 catalytic system, affording the desired products in 67-81% yields (**8a-j**). Other substituted olefins such as *penta*-fluoro styrene, 1-vinyl naphthalene, and 2-vinylnaphthalene also reacted smoothly to provide **8k-m** in 59-73% yields. Moreover, (vinylsulfonyl)benzene also provided the desired product (**8n**) in 61% yield under standard conditions. The abundance and unreactive nature of aliphatic olefins made them interesting and challenging substrates.[20] Reaction of **1a** with vinyl cyclohexane, allyl cyclohexane, 1-hexene and 1-heptene (**7o-r**) provided the desired products (**8o-r**) in 57-62% yields. These reactions demonstrate the generality of developed Rh(III)/O_2 catalytic system with respect to olefins.

Table 5. Scope with Styrenes and Aliphatic Olefins[a]



[a]reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), acetic acid (2 equiv.), acetone (0.22 M), 70 °C, 24 h.

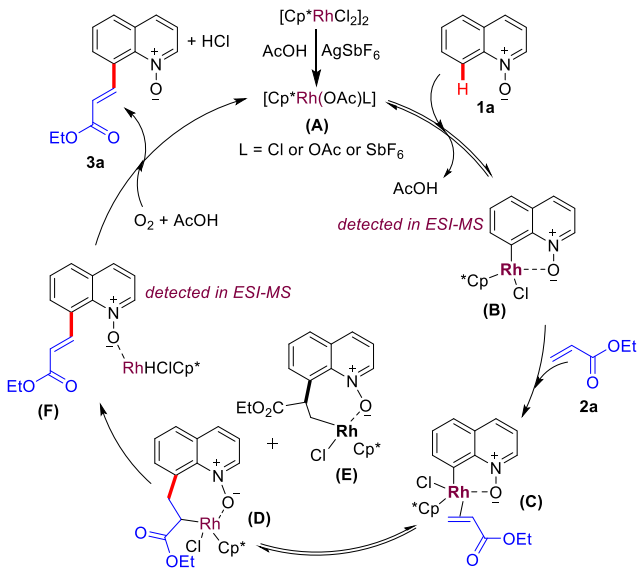
To probe the mechanism of Rh(III)/O_2 system various preliminary experiments were performed (Scheme 3). The rhodacycle complex prepared *via* earlier reported method,[17f] was found successful to catalyze the current reaction, indicating its intermediacy in the catalytic cycle. Deuterium labeling experiments were performed with methanol-*d4* and acetic acid-*d4*. In deuterium labeling experiments, deuteration was observed at C8 position of quinoline *N*-oxide in the presence or absence of acrylate (**2a**) under standard reaction conditions indicating the reversible nature of initial C-H activation step (Scheme 3). To get insight into the kinetics of the reaction, competition and two parallel experiments were carried out by reacting **1a** and **1a-d7** with **2a** under standard reaction conditions for 5 h. The K_H/K_D ratio was 1.85 and 1.26 in case of competition and parallel reactions, respectively, suggesting that C-H bond cleavage may not be the rate-determining step (Scheme 3).[21] Competitive control experiment revealed that electron rich quinoline *N*-oxides are more favorable than electron poor substrates with ethyl acrylate for the formation of product (SI).



Scheme 3. Deuterium Labeling Experiments

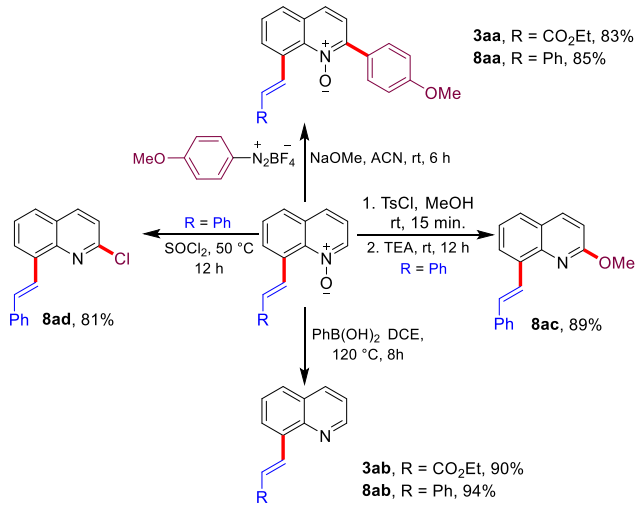
On the basis of preliminary experiments and literature, a tentative mechanistic pathway has been proposed (Scheme 4).[17] Initially, the $[RhCp^*Cl_2]_2$ precursors in the presence of $AgSbF_6$ and acetic acid give active Rh (III) species (**A**) which reacts with **1a** to form five-

membered rhodacycle (**B**). Intermediate **B** was able to catalyze the reaction and also detected in ESI-MS analysis of crude reaction mixture. Olefin interaction with rhodacycle (**B**), followed by insertion leads to the formation of intermediate **D**. The subsequent β-hydride elimination provided species **F** (detected in ESI-MS). In the presence of O_2 and AcOH, Rh(III) might be regenerated from species **F** to continue the catalytic cycle along with the formation of desired product (**3a**).



Scheme 4. Probable Reaction Pathway

Utility of current method was demonstrated by functionalization of **3a** and **8a** under various metal-free conditions (Scheme 5). Product **3a** and **8a** were successfully converted to corresponding 2-aryl-8-olefinated quinoline *N*-oxides (**3aa** and **8aa**) by following the literature procedures.[22] Reduction using phenylboronic acid afforded alkenylated product in good yields (**3ab** and **8ab**).[23] C2 chlorination[17a] and methoxylation[17a, 24] of product **8a** afforded corresponding products in 81 and 89% yields, respectively.



Scheme 5. Functionalization of C8-Olefinated Product

In summary, an operationally simple Rh(III)/O_2 based catalytic system for C8 functionalization of quinoline *N*-oxides with a wide range of substrates including 2-substituted quinolines and aliphatic olefins under milder reaction conditions has been developed. More than fifty quinoline *N*-oxide derivatives were synthesized. C8 olefinated quinoline *N*-oxide was further converted into various other valuable molecules to demonstrate the synthetic utility of the developed catalytic method. The current catalytic system found its utility by avoiding any post-work up as well as organic or inorganic oxidants.

EXPERIMENTAL SECTION

General information

All reactions were carried out in screw cap reaction vials under air atmosphere. All solvents were bought from Aldrich in sure-seal bottle and used as such. Chemicals were bought from Sigma Aldrich, Alfa-aesar and TCI. For column chromatography, silica gel (230-400 mesh) from Merck was used. A gradient elution using *n*-hexane and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel $60F_{254}$).

Analytical information: All isolated compounds are characterized by ^{1}H NMR, ^{13}C NMR, IR and LC-MS. Mass spectra were recorded on Water Q-ToF-Micro Micromass. Nuclear magnetic resonance spectra were recorded either on a Bruker-Avance 600 or 300 MHz instrument. Copies of ^{1}H and ^{13}C NMR are provided in supporting information. All ^{1}H NMR experiments are reported in units, parts per million (ppm) and were measured relative to the signals for residual chloroform (7.24), Methanol (3.31 and 4.78) and acetone (2.05) in the deuterated solvents. All ^{13}C NMR spectra were reported in ppm relative to deuterated chloroform (77.23), methanol (49.15) and acetone (29.92 and 206.68) and all were obtained with ^{1}H decoupling. The melting points were recorded on a Bronsted Electrothermal 9100.

General procedure for the preparation of Quinoline N-Oxides.[24]

All solid reactants, *m*-CPBA (4 mmol) and quinoline (2 mmol) were added in schlenk tube and put under vacuum for 2 h, then CH_2Cl_2 (4 mL) was added at 0 °C. The reaction was allowed to stirred at room temperature for 12 h. On completion, the reaction mixture was extracted with ethyl acetate and organic extract was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (230-400 mesh size) with n-hexane: EtOAc to afford desired *N*-Oxide. All synthesized *N*-oxides are known compounds [(**1b-e**, **1g**, **1k**, **1l** and **1m**),[24c] (**1f**, **1h**),[24d] **1i**,[24e] **1n**,[24f] **1o**,[24g] **4a-c**,[24h] **4d**,[15f] **4e**,[24i] **4f**,[18] **4g**[24j]].

Characterization Data. *5-Nitro quinoline 1-oxide (**1f**).*[24d] Yellow precipitates, yield = 304 mg (80%). Isolated from flash chromatography (85% EtOAc/ *n*-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.16 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 6.6 Hz, 1H), 8.60 (d, J = 9.0 Hz, 1H), 8.50 (d, J = 7.8 Hz, 1H), 7.93 – 7.90 (m, 1H), 7.62 – 7.59 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 146.0, 142.1, 136.8, 128.9, 126.9, 126.4, 124.0, 123.9, 122.4.

*6-tert-butyl quinoline 1-oxide (**1h**).*[24d] Pale Yellow liquid, yield = 290 mg (72%). Isolated from flash chromatography (92% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.66 (d, J = 9.6 Hz, 1H), 8.56 (d, J = 6.6 Hz, 1H), 7.89 – 7.87 (m, 1H), 7.80 – 7.79 (m, 2H), 7.31 (dd, J = 8.4, 6.0 Hz, 1H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 152.2, 139.7, 135.5, 130.5, 129.8, 127.3, 123.2, 120.8, 119.3, 35.1, 31.0.

General Procedure for C8 Olefination of Quinoline N-Oxides with Olefins. To an oven-dried screw cap reaction vial charged with a spinvane magnetic stir-bar, $[Cp^*RhCl_2]_2$ (5 mol%) and $AgSbF_6$ (20 mol%) were added. Depending on the physical state of the quinoline *N*-oxide (0.1 mmol) and olefin (0.2 mmol), solid compounds were weighed along with the other reagents, whereas

liquid reagents, AcOH (2 equiv.) were added by micropipette and acetone was added by laboratory syringe, respectively. The reaction vial was closed with screw cap and the reaction mixture was purged with O_2 using baloon. Then kept for vigorous stirring on a preheated heating block at 70 °C for 24 h. After completion, the reaction mixture was allowed to cool, filtered through celite and washed with DCM. Collected DCM fraction of crude reaction mixture was evaporated under reduced pressure. The residue was purified by flash chromatography using silica gel (230-400 mesh size) or using acidic alumina and *n*-hexane: EtOAc as eluent.

Characterization Data. *(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl) quinoline 1-oxide (Table 2, entry **3a**).* White transparent precipitates, yield = 20 mg (82%). mp 142-144 °C. Isolated from chromatography (90% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, CD_3OD, δ): 9.18 (d, J = 15.6 Hz, 1H), 8.61 (d, J = 6.0 Hz, 1H), 8.11 (dd, J = 19.8, 8.4 Hz, 2H), 7.83 (d, J = 7.2 Hz, 1H), 7.75 - 7.72 (m, 1H), 7.52 – 7.55 (m, 1H), 6.08 (d, J = 15.6 Hz, 1H), 4.27 (dd, J = 14.4, 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD, δ): 166.9, 146.7, 138.7, 138.3, 132.2, 132.1, 130.5, 130.3, 129.6, 128.6, 121.7, 118.4, 60.2, 13.2. IR (ZnSe) ν_{max} (cm^{-1}): 2961, 1716, 1580, 1324, 1093, 1002, 734. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{14}NO_3$, 244.0968; found, 244.0950.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-3-methylquinoline 1-oxide (Table 2, entry **3b**).* Pale yellow precipitates, yield = 15.2 mg (59%). mp 190-191 °C. Isolated from column chromatography (70% EtOAc/ n-hexane; acidic alumina). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.21 (d, J = 15.6 Hz, 1H), 8.37 (s, 1H), 7.78 (dd, J = 6.9, 3.0 Hz, 1H), 7.56 – 7.53 (m, 3H), 6.00 (d, J = 15.6 Hz, 1H), 4.32 – 4.25 (m, 2H), 2.45 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.6, 146.8, 139.0, 137.6, 131.9, 131.6, 131.2, 130.88, 130.85, 129.3, 128.5, 119.1, 60.5, 18.4, 14.4. IR (ZnSe) ν_{max} (cm^{-1}): 2954, 1721, 1610, 1338,1078, 935, 780. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{16}NO_3$, 258.1125; found, 258.1133.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-4-methylquinoline 1-oxide (Table 2, entry **3c**).* Brownish liquid, yield = 13.2 mg (51%). Isolated from column chromatography (76% EtOAc/ n-hexane; acidic alumina). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.19 (d, J = 15.6 Hz, 1H), 8.37 (d, J = 6.0 Hz, 1H), 7.97 (s, 1H), 7.63 – 7.59 (m, 2H), 7.14 (d, J = 6.0 Hz, 1H), 5.94 (d, J = 15.6 Hz, 1H), 4.28 – 4.25 (m, 2H), 2.64 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.7, 147.4, 139.2, 136.5, 134.8, 132.1, 131.4, 131.0, 128.1, 126.1, 122.1, 118.5, 60.4, 18.9, 14.4. IR (ZnSe) ν_{max} (cm^{-1}): 2922, 1706, 1623, 1305, 1179, 1096, 963, 795. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{16}NO_3$, 258.1125; found, 258.1133.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-6-methylquinoline 1-oxide (Table 2, entry **3d**).* Brown liquid, yield = 19.6 mg (76%). Isolated from column chromatography (82% EtOAc/ n-hexane; acidic alumina). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.07 (d, J = 15.6 Hz, 1H), 8.27 (s, 1H), 7.55 – 7.48 (m, 2H), 7.33 (s, 1H), 7.16 – 7.11 (m, 1H), 5.87 (d, J = 15.9 Hz, 1H), 4.19 – 4.12 (m, 2H), 2.38 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 166.6, 146.8, 138.5, 138.1, 136.8, 133.7, 132.0, 131.1, 128.7, 126.4, 121.4, 119.0, 60.3, 21.1, 14.3. IR (ZnSe) ν_{max} (cm^{-1}): 2981, 1701, 1628, 1160, 1031, 657. HRMS (ESI-TOF) m/z: calcd for $C_{15}H_{16}NO_3$ [M + H]$^+$ 258.1125; found 258.1128.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-5-chloroquinoline 1-oxide (Table 2, entry **3g**).* Brown liquid, yield = 19.7 mg (71%). Isolated from flash chromatography (84% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.08 (d, J = 16.2 Hz, 1H), 8.45 (dd, J = 6.0, 1.2 Hz, 1H), 8.02 (d, J = 2.4 Hz, 1H), 7.69 – 7.71 (m, 1H), 7.63 (dd, J = 8.4, 1.2 Hz, 1H), 7.32 (dd, J = 8.4, 6.0 Hz, 1H), 6.0 (d, J = 15.6 Hz, 1H), 4.27 – 4.30 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.1, 145.1, 138.6, 137.3, 134.1, 133.6, 132.8, 131.3, 124.8, 122.4, 122.3, 120.0, 60.5, 14.2. IR (ZnSe) ν_{max} (cm^{-1}): 3078, 2981, 1707, 1631, 1313, 1178, 1103, 1024, 939, 835, 752. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{13}ClNO_3$, 278.0578; found, 278.0565.

*(E)-6-(tert-Butyl)-8-(3-ethoxy-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 2, entry **3h**).* Yellow liquid, yield = 22.3 mg (74%). Isolated from flash chromatography (79% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.13 (d, J = 15.6 Hz, 1H), 8.31 (d, J = 6.0 Hz, 1H), 7.66 – 7.57 (m, 3H), 7.17 (dd, J = 8.4, 6.0 Hz, 1H), 5.91 (d, J = 15.6 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 1.30 (s, 9H), 1.27 – 1.23 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 166.6, 151.4, 147.3, 138.1, 136.7, 131.9, 131.2, 130.5, 126.5, 125.0, 121.3, 119.0, 60.4, 34.9, 30.9, 14.3. IR (ZnSe) ν_{max} (cm^{-1}): 2985, 1715, 1628, 1161, 1043, 961, 730, 657. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{18}H_{22}NO_3$, 300.1594; found, 300.1609.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-6-methoxyquinoline (Table 2, entry **3i**).* Brown liquid, yield = 18.6 mg (68%). Isolated from flash chromatography (88% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.12 (d, J = 15.6 Hz, 1H), 8.31 (d, J = 6.0 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.09 (d, J = 3.0 Hz, 1H), 5.97 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.93 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.4, 158.3, 146.3, 135.4, 135.3, 133.3, 133.1, 125.5, 123.3, 121.7, 119.1, 107.1, 60.3, 55.7, 14.2. IR (ZnSe) ν_{max} (cm^{-1}): 2962, 1898, 1328, 1215, 1164, 840, 751. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{16}NO_4$, 274.1074; found, 274.1066.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-6-(methoxycarbonyl)quinoline 1-oxide (Table 2, entry **3j**).* Brown liquid, yield = 20.8 mg (69%). Isolated from flash chromatography (85% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.14 (d, J = 15.6 Hz, 1H), 8.57 – 8.54 (m, 2H), 8.19 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.39 – 7.37 (m, 1H), 6.07 (d, J = 15.6 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 4.01 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.7, 165.5, 146.2, 141.6, 139.3, 132.7, 132.4, 131.8, 131.1, 130.3, 127.7, 122.7, 120.4, 60.9, 53.2, 14.7. IR (ZnSe) ν_{max} (cm^{-1}): 3059, 1723, 1712, 1630, 1443, 1377, 1214, 1176, 1137, 1032, 802, 766. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{16}NO_5$, 302.1023; found, 302.1005.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-6-fluoroquinoline 1-oxide (Table 2, entry **3k**).* Brown liquid, yield = 17.5 mg (67%). Isolated from flash chromatography (82% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.10 (d, J = 15.6 Hz, 1H), 8.47 (d, J = 6.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.50 (dd, J = 7.8, 2.4 Hz, 1H), 7.41 (dd, J = 9.0, 2.4 Hz, 1H), 7.36 (dd, J = 8.4, 6.0 Hz, 1H), 6.02 (d, J = 15.6 Hz, 1H), 4.29 (dd, J = 14.4, 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.2, 160.65 (J_{CF} = 250.5 Hz), 145.4, 137.1, 136.7, 134.86 (J_{CF} = 9.0 Hz), 133.07 (J_{CF} = 10.5 Hz), 126.5, 122.6, 121.20 (J_{CF} = 27.0 Hz), 120.2, 112.87 (J_{CF} = 22.5 Hz), 60.6, 14.3. ^{19}F NMR (565 MHz, $CDCl_3$, δ): -110.2. IR (ZnSe) ν_{max} (cm^{-1}): 3079, 2981, 1707, 1619, 1573, 1383, 1270, 1175, 880, 658. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{13}FNO_3$, 262.0874; found, 262.0870.

*(E)-6-Chloro-8-(3-ethoxy-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 2, entry **3l**).* Brown precipitates, yield = 17 mg (61%). mp 111-112 °C. Isolated from flash chromatography (80% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.09 (d, J = 15.6 Hz, 1H), 8.46 (d, J = 6.0 Hz, 1H), 7.86 (d, J = 2.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 1.2 Hz, 1H), 7.35 - 7.33 (m, 1H), 6.02 (d, J = 15.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.37 – 1.35 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.2, 145.3, 138.4, 137.4, 134.4, 133.7, 132.6, 131.7, 128.0, 125.2, 122.6, 120.1, 60.6, 14.3. IR (ZnSe) ν_{max} (cm^{-1}): 3038, 2984, 2349, 1709, 1627, 1373, 1188, 1029, 827, 757, 688. HRMS (ESI-

TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}ClNO_3$, 278.0578; found, 278.0591.

*(E)-6-Bromo-8-(3-ethoxy-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 2, entry **3m**).* Yellow precipitates, yield = 22.6 mg (70%). mp 126-127 °C. Isolated from flash chromatography (80% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.09 (d, J = 15.6 Hz, 1H), 8.47 (d, J = 6 Hz, 1H), 8.03 (d, J = 1.8 Hz, 1H), 7.71 (d, J = 1.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.33 (dd, J = 8.4, 6 Hz, 1H), 6.02 (d, J = 15.6 Hz, 1H), 4.30 (dd, J = 13.8, 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$ δ): 166.2, 145.2, 138.7, 137.4, 134.2, 133.7, 132.9, 131.4, 125.0, 122.5, 122.4, 120.2, 60.6, 14.3. IR (ZnSe) ν_{max} (cm^{-1}): 3099, 3035, 2349, 1709, 1622, 1558, 1445, 1388, 1165, 1025, 755, 658. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}BrNO_3$, 322.0073; found, 322.0065.

*(E)-5-(3-Ethoxy-3-oxoprop-1-en-1-yl)benzo[f]quinoline 4-oxide (Table 2, entry **3n**).* Yellow liquid, yield = 21.1 mg (72%). Isolated from flash chromatography (72% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.16 (d, J = 16.8 Hz, 1H), 8.58 – 8.55 (m, 3H), 7.97 (d, J = 7.8 Hz, 1H), 7.93 (s, 1H), 7.79 – 7.74 (m, 2H), 7.52 – 7.49 (m, 1H), 6.09 (d, J = 15 Hz, 1H), 4.33 (dd, J = 13.8, 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.8, 147.5, 139.8, 137.6, 133.0, 131.5, 129.8, 129.24, 129.20, 129.0, 128.6, 123.3, 122.0, 120.9, 117.9, 60.4, 14.4. IR (ZnSe) ν_{max} (cm^{-1}): 2928, 1698, 1375, 1238, 1163, 1030, 748, 715, 658. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO_3$, 294.1125; found, 294.1120.

*(E)-4-(3-Ethoxy-3-oxoprop-1-en-1-yl)phenanthridine 5-oxide (Table 2, entry **3o**).* Brown liquid, yield = 18.8 mg, (64%). Isolated from flash chromatography (82% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.11 (d, J = 15.6 Hz, 1H), 8.56 – 8.50 (m, 3H), 7.91 (d, J = 7.8 Hz, 1H), 7.87 (s, 1H), 7.75 – 7.70 (m, 2H), 7.49 – 7.47 (m, 1H) 6.06 (d, J = 15.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.9, 147.5, 139.5, 137.6, 133.0, 131.4, 129.8, 129.2, 129.1, 129.0, 128.9, 128.7, 123.3, 122.0, 121.3, 117.7, 60.4, 14.4. IR (ZnSe) ν_{max} (cm^{-1}): 2990, 2349, 1715, 1693, 1305, 1175, 962, 753, 624. HRMS (ESI-TOF) m/z: $[M + H]^+$calcd for $C_{18}H_{16}NO_3$, 294.1125; found, 294.1130.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-2-methylquinoline 1-oxide (Table 3, entry **5a**).* Brown liquid, yield = 19.6 mg (76%). Isolated from flash chromatography (80% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.18 (d, J = 15.9 Hz, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.35 (d, J = 8.4 Hz, 1H), 5.93 (d, J = 14.1 Hz, 1H), 4.28 - 4.22 (m, 2H), 2.66 (s, 3H), 1.35 – 1.30 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, CD_3OD, δ): 168.3, 150.1, 148.7, 140.0, 133.3, 131.8, 131.4, 131.2, 129.7, 128.9, 124.8, 119.1, 61.5, 18.9, 14.6. IR (ZnSe) ν_{max} (cm^{-1}): 2934, 2390, 1715, 1602, 1431,1087, 784, 642. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}NO_3$, 258.1125; found, 258.1130.

*(E)-8-(3-Methoxy-3-oxoprop-1-en-1-yl)-2-methylquinoline 1-oxide (Table 3, entry **5b**).* Light yellow liquid, yield = 19.0 mg (78%). Isolated from flash chromatography to (73% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.18 (d, J = 15.9 Hz, 1H), 7.86 (dd, J = 7.8, 1.8 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.37 (d, J = 8.7 Hz, 1H), 5.92 (d, J = 15.9 Hz, 1H), 3.79 (s, 3H), 2.67 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 167.1, 147.9, 147.7, 139.7, 131.7, 131.0, 130.5, 129.9, 127.5, 126.0, 123.5, 118.1, 51.6, 19.0. IR (ZnSe) ν_{max} (cm^{-1}): 2951, 2348, 1709, 1615, 1435, 1208, 985, 824, 648. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{14}NO_3$, 244.0968; found, 244.0944.

*(E)-8-(3-Butoxy-3-oxoprop-1-en-1-yl)-2-methylquinoline 1-oxide (Table 3, entry **5c**).* Brown liquid, yield = 23.2 mg (81%). Isolated from flash chromatography (70% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.17 (d, J = 15.6 Hz, 1H), 7.78 (dd, J = 7.8, 1.8 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.30 – 7.27 (m, 1H), 5.91 (d, J = 15.6 Hz, 1H), 4.19 – 4.15 (m, 2H), 2.61 (s, 3H), 1.70 – 1.60 (m, 2H), 1.42 – 1.35 (m, 2H), 0.93 – 0.88 (t, J = 7.5, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 166.8, 147.6, 139.7, 131.8, 131.3, 130.5, 129.8, 129.7, 127.4, 125.8, 123.4, 118.6, 64.3, 30.8, 19.2, 19.0, 13.8. IR (ZnSe) ν_{max} (cm^{-1}): 2957, 1703, 1625, 1328, 1163, 900, 825, 761, 651. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO_3$, 286.1438; found, 286.1422.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-2-phenyl 1-oxide (Table 3, entry **5d**).* Brown liquid, yield = 25.2 mg (79%). Isolated from column chromatography (25% EtOAc/ n-hexane; acidic alumina). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.19 (d, J = 15.6 Hz, 1H), 7.92 – 7.90 (m, 2H), 7.87 (dd, J = 7.8, 1.8 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.54 – 7.46 (m, 4H), 5.97 (d, J = 15 Hz, 1H), 4.28 – 4.24 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.8, 147.9, 146.5, 140.6, 133.4, 132.2, 132.1, 131.0, 129.7, 129.6, 129.5, 128.4, 128.1, 125.5, 123.9, 118.3, 60.3, 14.4. IR (ZnSe) ν_{max} (cm^{-1}): 3059, 2980, 1703, 1631, 1598, 1365, 1174, 1026, 758, 690. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO_3$, 320.1281; found, 320.1290.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-2,6-dimethylquinoline 1-oxide (Table 3, entry **5e**).* Yellow liquid, yield = 24.1 mg (89%). Isolated from flash chromatography (72% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.20 (d, J = 15.6 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.43 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 5.95 (d, J = 15.9 Hz, 1H), 4.31 – 4.24 (m, 2H), 2.65 (s, 3H), 2.50 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 166.7, 147.6, 146.7, 138.3, 137.5, 133.8, 131.1, 130.7, 128.7, 125.3, 123.4, 118.7, 60.3, 21.0, 18.9, 14.4. IR (ZnSe) ν_{max} (cm^{-1}): 2983, 1703, 1628, 1573, 1386, 1325, 1100, 1030, 854, 650. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO_3$, 272.1281; found, 272.1296.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-2-methyl-6-bromoquinoline 1-oxide (Table 3, entry **5f**).* Light yellow liquid, yield = 25.2 mg (75%). Isolated from column chromatography (50% EtOAc/ n-hexane; acidic alumina). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.10 (d, J = 15.6 Hz, 1H), 7.97 (d, J = 1.8 Hz, 1H), 7.66 (d, J = 2.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 5.97 (d, J = 15.6 Hz, 1H), 4.30 – 4.26 (m, 2H), 2.64 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.3, 147.7, 146.0, 138.7, 134.3, 133.4, 131.6, 131.3, 124.5, 124.2, 121.2, 119.6, 60.5, 19.0, 14.4. IR (ZnSe) ν_{max} (cm^{-1}): 3064, 2981, 2924, 1705, 1631, 1558, 1307, 1238, 1172, 1033, 862, 767. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO_3$, 336.0230; found, 336.0213.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-2-methyl-6-nitroquinoline 1-oxide (Table 3, entry **5g**).* Brown sticky liquid, yield = 23.3 mg (77%). Isolated from column chromatography (54% EtOAc/ n-hexane; acidic alumina). ^{1}H NMR (600 MHz, $CDCl_3$ + $(CD_3)_2CO$, δ): 9.11 (d, J = 15.6 Hz, 1H), 8.75 (d, J = 2.4 Hz, 1H), 8.33 (d, J = 2.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 6.09 (d, J = 15.6 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 2.71 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$ + $(CD_3)_2CO$, δ): 166.4, 151.1, 146.0, 145.8, 142.0, 134.5, 130.4, 126.4, 125.9, 125.6, 124.5, 120.9, 61.1, 19.6, 14.7. IR (ZnSe) ν_{max} (cm^{-1}): 2961, 1720, 1626, 1333, 1257, 1082, 1027, 794. HRMS (ESI-TOF) m/z: calcd for $C_{15}H_{15}N_2O_5$ $[M + H]^+$ 303.0975; found 303.0983.

*(E)-8-(3-Methoxy-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6a**).* Yellow sticky liquid, yield = 17.7 mg (77%). Isolated from flash chromatography (84% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, CD_3OD, δ): 9.12 (d, J = 15.6 Hz, 1H), 8.54 (d, J = 6.0, 1.2 Hz, 1H), 8.01 (d, J = 8.4, 1.2 Hz, 1H), 7.98 – 7.96 (m, 1H), 7.72 – 7.71 (m, 1H), 7.64 – 7.61 (m, 1H), 7.46 (q, J = 8.4, 6 Hz, 1H), 6.04 (d, J = 15.6 Hz, 1H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD, δ): 167.3, 146.9, 138.4, 138.2, 132.1, 131.9, 130.3, 130.2, 129.4, 128.5, 121.6, 117.9, 50.8. IR (ZnSe) ν_{max} (cm^{-1}): 2923, 1693, 1434, 1307, 1201, 1185, 819, 787.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{12}NO_3$, 230.0812; found, 230.0830.

*(E)-8-(3-(Butoxy)-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6b**).* Yellow sticky liquid, yield = 22.5 mg (83%). Isolated from flash chromatography (80% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.22 (d, J = 15.6 Hz, 1H), 8.48 (d, J = 6.0 Hz, 1H), 7.87 (dd, J = 7.8, 1.2 Hz, 1H), 7.73 (d, J = 7.8, 1H), 7.64 (d, J = 6.6, 1H), 7.59 (t, J = 7.8, 1H), 7.31 – 7.29 (m, 1H) 6.0 (d, J = 15.6 Hz, 1H), 4.24 – 4.22 (m, 2H), 1.74 – 1.69 (m, 2H), 1.48 – 1.44 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.7, 146.8, 139.8, 137.2, 131.9, 131.7, 131.5, 129.8, 128.4, 126.2, 121.4, 119.1, 64.4, 30.8, 19.2, 13.8. IR (ZnSe) ν_{max} (cm^{-1}): 3057, 2956, 2872, 1703, 1629, 1568, 1382, 1305, 1220, 1163, 1060, 962, 819, 758. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO_3$, 272.1281; found, 272.1266.

*(E)-8-(3-(tert-Butoxy)-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6c**).* Brown liquid, yield = 21.8 mg (80%). Isolated from flash chromatography (90% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.08 (d, J = 15.6 Hz, 1H), 8.46 (d, J = 6.0 Hz, 1H), 7.84 – 7.83 (m, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.61 – 7.60 (m, 1H), 7.57 – 7.54 (m, 1H), 7.29 – 7.26 (m, 1H), 5.89 (d, J = 15.6 Hz, 1H), 1.53 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 165.9, 145.7, 139.8, 137.2, 131.95, 131.86, 131.6, 129.6, 128.3, 126.2, 121.4, 121.3, 80.3, 28.2. IR (ZnSe) ν_{max} (cm^{-1}): 2978, 1694, 1625, 1308, 1220, 1143, 817, 756. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO_3$, 272.1281; found, 272.1281.

*(E)-8-(3-Oxo-3-(2,2,3,3,3-pentafluoropropoxy)prop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6d**).* Yellow liquid, yield = 24.2 mg (70%). Isolated from flash chromatography (75% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.33 (d, J = 15.6 Hz, 1H), 8.55 (d, J = 6.0 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.37 (dd, J = 8.4, 6.0 Hz, 1H), 6.05 (d, J = 15.6 Hz, 1H), 4.73 – 4.64 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 164.7, 149.5, 139.3, 137.8, 132.0, 131.8, 130.9, 130.3, 128.8, 128.6, 128.1, 127.7, 121.7, 116.6, 59.2. ^{19}F NMR (565 MHz, $CDCl_3$, δ) -83.7, -123.3. IR (ZnSe) ν_{max} (cm^{-1}): 2967, 2925, 1731, 1628, 1193, 1106, 759, 655. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{11}F_5NO_3$, 348.0654; found, 348.0634.

*(E)-8-(3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy)-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6e**).* Brown precipitates, yield = 50.2 mg (76%). mp 175-176 °C. Isolated from flash chromatography (78% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.26 (d, J = 15.6 Hz, 1H), 8.50 (d, J = 6.0 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.36 – 7.31 (m, 1H), 6.01 (d, J = 15.6 Hz, 1H), 4.54 (t, J = 6.6 Hz, 2H), 2.60 – 2.53 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 166.0, 148.0, 139.6, 137.4, 131.9, 131.6, 131.3, 130.0, 128.4, 126.6, 121.5, 117.9, 56.3, 31.0 – 30.4 (m). ^{19}F NMR (565 MHz, $CDCl_3$, δ): -80.7 – -80.8 (m), -113.5 – -113.6 (m), -121.6 – -121.7 (m), -121.8 – -122.0 (m), -122.7 – -122.8 (m), -123.46 – -123.53 (m), -126.1 – -126.2 (m). IR (ZnSe) ν_{max} (cm^{-1}): 2982, 1715, 1628, 1197, 1144, 963, 819, 654. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{13}F_{17}NO_3$, 662.0618; found, 662.0604 .

*(E)-8-(3-(Cyclohexyloxy)-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6f**).* Brown liquid, yield = 19.0 mg (64%). Isolated from flash chromatography (75% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, Acetone-d_6, δ): 9.24 (d, J = 15.6 Hz, 1H), 8.50 (d, J = 6.0 Hz, 1H), 8.07 – 8.04 (m, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.47 (dd, J = 8.4, 6.0 Hz, 1H), 6.00 (d, J = 15.6 Hz, 1H), 4.86 – 4.79 (m, 1H), 1.92 – 1.87 (m, 2H), 1.79 – 1.72 (m, 2H), 1.57 – 1.51 (m, 2H), 1.47 – 1.142 (m, 2H), 1.39 – 1.31 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, Acetone-d_6, δ): 165.5, 146.8, 139.4, 137.4, 132.2, 131.3, 130.8, 130.4, 128.4, 126.0, 122.0, 118.5, 78.3, 71.9, 31.5, 31.1, 25.3, 23.5. IR (ZnSe) ν_{max} (cm^{-1}): 2933, 2857, 1698, 1628, 1383, 1302, 1220, 1166, 1013, 818, 751, 658. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}NO_3$, 298.1438; found, 298.1450.

*(E)-8-(3-(tert-Butoxy)-2-methyl-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6g**).* Yellow liquid, yield = 19.7 mg (69%). Isolated from column chromatography (55% EtOAc/ n-hexane; acidic alumina). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.68 (s, 1H), 8.47 (d, J = 6.0 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.47 (d, J = 6.9 Hz, 1H), 7.32 – 7.27 (m, 1H), 1.86 (s, 3H), 1.58 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 167.9, 140.3, 137.1, 132.7, 131.9, 131.2, 128.5, 128.0, 126.4, 126.1, 125.8, 121.2, 80.3, 28.2, 13.6. IR (ZnSe) ν_{max} (cm^{-1}): 2977, 1695, 1658, 1387, 1223, 1183, 749, 658. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO_3$, 286.1438; found, 286.1445 .

*(E)-8-(3-(Benzyloxy)-2-methyl-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6h**).* Brown liquid, yield = 20.7 mg (65%). Isolated from column chromatography (62% EtOAc/ n-hexane; acidic alumina). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.83 (s, 1H), 8.48 (dd, J = 6.0, 1.2 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.49 – 7.45 (m, 3H), 7.41 – 7.29 (m, 4H), 5.30 (s, 2H), 1.93 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 168.4, 145.0, 141.8, 136.9, 136.6, 132.5, 131.9, 130.8, 128.7, 128.5, 128.1, 128.0, 127.9, 126.1, 123.8, 121.3, 66.4, 13.7. IR (ZnSe) ν_{max} (cm^{-1}): 2966, 2923, 2953, 1702, 1698, 1588, 1453, 1379, 1245, 1108, 745, 688. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO_3$, 320.1281; found, 320.1300.

*8-((E)-3-(((1s,5R,7S)-3-hydroxyadamantan-1-yl)oxy)-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6i**).* Brown liquid, yield = 28.8 mg (79%). Isolated from flash chromatography (80% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.09 (d, J = 15.6 Hz, 1H), 8.48 (d, J = 5.4 Hz, 1H), 7.84 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.30 (d, J = 6.6 Hz, 1H), 5.89 (d, J = 15.6 Hz, 1H), 2.33 (s, 2H), 2.20 – 2.03 (m, 6H), 1.77 – 1.66 (m, 3H), 1.62 – 1.48 (m, 2H), 1.27 – 1.23 (m, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 165.6, 146.2, 139.8, 137.5, 132.0, 131.9, 131.8, 129.8, 128.5, 126.7, 121.5, 121.0, 81.3, 70.4, 49.4, 44.2, 40.1, 34.9, 31.4. IR (ZnSe) ν_{max} (cm^{-1}): 2913, 2855, 1698, 1285, 1108, 908, 750, 620. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{24}NO_4$, 366.1700; found, 366.1708.

*(E)-8-(3-(Anthracen-9-ylmethoxy)-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6j**).* Brown precipitates, yield = 26.3 mg (65%). mp 194-195 °C. Isolated from flash chromatography (85% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.25 (d, J = 15.6 Hz, 1H), 8.52 (s, 1H), 8.48 – 8.41 (m, 3H), 8.05 (d, J = 8.4 Hz, 2H), 7.80 (dd, J = 7.8, 1.8 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.54 – 7.50 (m, 4H), 7.25 (dd, J = 8.4, 6.0, 1H), 6.32 (s, 2H), 6.01 (d, J = 15.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 166.8, 147.7, 139.7, 137.2, 134.6, 131.7, 131.6, 131.5, 131.4, 131.2, 129.8, 129.1, 129.0, 128.3, 126.7, 126.5, 125.1, 124.2, 121.4, 118.5, 58.9. IR (ZnSe) ν_{max} (cm^{-1}): 2982, 2857, 1715, 1628, 1303, 1158, 733, 657. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{20}NO_3$, 406.1438; found, 406.1415

*(E)-8-(3-Oxo-3-((5,7,8-trimethyl-2-(5,8,12-trimethyltridecan-2-yl)chroman-6-yl)oxy)prop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6k**).* Brown liquid, yield = 36.2 mg (59%). Isolated from flash chromatography (80% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.40 (d, J = 15.6 Hz, 1H), 8.43 (d, J = 6.3 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.16 (d, J = 15.6 Hz, 1H), 2.56 – 2.51 (m, 2H), 2.10 (s, 2H), 2.03 (s, 6H), 1.99 (s, 3H), 1.75 – 1.67 (m, 2H), 1.49 – 1.42 (m, 2H), 1.33 – 1.30 (m, 2H), 1.17 (s, 13H), 1.09 – 1.01 (m, 3H), 0.80 - 0.76 (m, 12H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 165.2, 149.3, 148.4, 140.6, 139.8, 137.4, 131.9, 131.8, 131.5, 130.0, 128.4, 127.0, 126.4, 125.3, 122.9, 121.5, 118.0, 117.3, 75.0, 39.4, 37.5, 37.4, 37.3, 32.8, 32.7, 31.2, 30.9, 28.0, 24.8, 24.5, 22.7, 22.6, 21.1, 20.6, 19.8, 19.7,

19.6, 13.1, 12.3, 11.9. IR (ZnSe) ν_{max} (cm^{-1}): 2945, 1728, 1627, 1481, 1379, 1220, 1140, 981, 757. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{40}H_{56}NO_4$, 614.4204; found, 614.4220.

*(E)-8-(3-((13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)-3-oxoprop-1-en-1-yl)quinoline 1-oxide (Table 4, entry **6l**).* Brown liquid, yield = 21.0 mg (45%). Isolated from column chromatography (75% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 9.38 (d, J = 15.6 Hz, 1H), 8.60 (d, J = 6.0 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.40 (dd, J = 8.4, 6.0 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.20 (d, J = 15.6 Hz, 1H), 2.97 – 2.92 (m, 2H), 2.58 – 2.43 (m, 2H), 2.09 – 2.04 (m, 2H), 1.61 – 1.54 (m, 3H), 1.27 (s, 6H), 0.94 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 165.2, 148.8, 148.5, 139.3, 137.92, 137.87, 137.2, 132.1, 131.9, 131.1, 130.2, 128.6, 126.3, 121.73, 121.65, 118.9, 118.3, 50.5, 48.0, 44.2, 38.0, 35.9, 31.9, 31.6, 29.7, 26.4, 25.8, 22.7, 21.6, 13.9. IR (ZnSe) ν_{max} (cm^{-1}): 2933, 2924, 1728, 1627, 1492, 1382, 1305, 1219, 1139, 1053, 1008, 819, 746, 665. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{30}H_{30}NO_4$, 468.2169; found, 468.2187.

*(E)-8-Styrylquinoline 1-oxide (Table 5, entry **8a**).* Orange liquid, yield = 19.5 mg (79%). Isolated from flash chromatography (75% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.87 (d, J = 16.2 Hz, 1H), 8.48 (dd, J = 6.0, 1.2 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.72 (dd, J = 8.4, 1.2 Hz, 1H), 7.63 – 7.57 (m, 3H), 7.41 – 7.35 (m, 2H), 7.30 – 7.26 (m, 2H), 6.72 (d, J = 15.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 140.0, 137.9, 137.4, 134.4, 132.2, 130.7, 130.6, 129.8, 128.5, 128.4, 128.1, 127.4, 126.9, 126.3, 120.9. IR (ZnSe) ν_{max} (cm^{-1}): 3057, 3023, 1702, 1580, 1219, 951, 813, 741, 691, 550. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}NO$, 248.1070; found, 248.1060.

*(E)-8-(2-Methylstyryl)quinoline 1-oxide(Table 5, entry **8b**).* Brown sticky, yield = 18.8 mg (72%). Isolated from flash chromatography (72% EtOAc/ n-hexane; silica gel 230-400 mesh size) ^1H NMR (300 MHz, $CDCl_3$, δ): 8.61 (d, J = 15.9 Hz, 1H), 8.48 (d, J = 5.7 Hz, 1H), 7.73 – 7.67 (m, 4H), 7.54 – 7.45 (m, 1H), 7.20 – 7.15 (m, 2H), 7.13 – 7.07 (m, 2H), 6.80 (d, J = 15.9 Hz, 1H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 139.7, 137.9, 136.7, 135.6, 134.6, 132.1, 131.9, 131.2, 130.2, 128.5, 128.1, 127.6, 127.4, 126.3, 120.9, 20.0. IR (ZnSe) ν_{max} (cm^{-1}): 3088, 3016, 2973, 1557, 1333, 1219, 1166, 963, 744, 544. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO$, 262.1226; found, 262.1233.

*(E)-8-(3-Methylstyryl)quinoline 1-oxide (Table 5, entry **8c**).* Yellow liquid, yield = 21.2 mg (81%). Isolated from flash chromatography (77% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (600 MHz, $CDCl_3$, δ): 8.82 (d, J = 16.2 Hz, 1H), 8.51 (dd, J = 6.0, 1.2 Hz, 1H), 7.81 – 7.75 (m, 3H), 7.59 (t, J = 7.8 Hz, 1H), 7.44 (s, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.09 (d, J = 7.8 Hz, 1H), 6.68 (d, J = 16.2 Hz, 1H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 139.7, 138.1, 137.8, 137.7, 134.2, 132.1, 130.8, 130.3, 130.0, 128.5, 128.4, 128.33, 128.30, 128.1, 127.4, 124.3, 120.9, 21.5. IR (ZnSe) ν_{max} (cm^{-1}): 3053, 2917, 1693, 1588, 1379, 1218, 952, 814, 746, 655. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO$, 262.1226; found, 262.1230.

*(E)-8-(3-Bromostyryl)quinoline 1-oxide (Table 5, entry **8d**).* Brown liquid, yield = 25.1 mg (77%). Isolated from flash chromatography (75% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.63 (d, J = 15.9 Hz, 1H), 8.44 (d, J = 6.3 Hz, 1H), 7.71 – 7.64 (m, 3H), 7.55 – 7.47 (m, 2H), 7.34 (d, J = 7.8 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.12 – 7.06 (m, 1H), 6.44 (d, J = 15.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 139.9, 137.9, 133.6, 132.1, 132.0, 131.1, 130.3, 130.1, 129.6, 128.6, 128.5, 128.1, 127.6, 127.7, 125.4, 122.8, 121.1. IR (ZnSe) ν_{max} (cm^{-1}): 3058, 2349, 1693, 1588, 1472, 1303, 1218, 950, 751, 658. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}BrNO$, 326.0175; found, 326.0161.

*(E)-8-(3-Nitrostyryl)quinoline 1-oxide (Table 5, entry **8e**).* Yellow precipitates, yield = 19.9 mg (68%). mp 164-166 °C. Isolated from flash chromatography (79% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (600 MHz, $CDCl_3$, δ): 8.96 (d, J = 15.6 Hz, 1H), 8.53 (d, J = 6.0 Hz, 1H), 8.39 (s, 1H), 8.13 – 8.11 (m, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.87 – 7.86 (m, 1H), 7.81 – 7.78 (m, 2H), 7.65 (t, J = 7.8 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.32 (dd, J = 8.4, 6.0 Hz, 1H), 6.72 (d, J = 15.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 148.7, 139.8, 139.7, 137.6, 133.9, 133.3, 132.2, 132.1, 131.0, 129.4, 128.8, 128.5, 127.0, 126.9, 121.9, 121.7, 121.2. IR (ZnSe) ν_{max} (cm^{-1}): 3150, 2341, 1573, 1528, 1345, 1220, 945, 842, 721. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}N_2O_3$, 293.0921; found, 293.0923.

*(E)-8-(4-Methylstyryl)quinoline 1-oxide(Table 5, entry **8f**).* Pale yellow precipitates, yield = 19.6 mg (75%). mp 94-95 °C. Isolated from flash chromatography (82% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (600 MHz, $CDCl_3$, δ): 8.83 (d, J = 16.2 Hz, 1H), 8.48 (dd, J = 6.0, 1.2 Hz, 1H), 7.81 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 7.8 Hz, 2H), 7.26 (dd, J = 8.4, 6.0 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 6.71 (d, J = 15.6 Hz, 1H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 139.9, 137.5, 137.3, 135.1, 134.5, 132.2, 130.5, 129.8, 129.6, 129.3, 128.4, 127.9, 126.8, 126.5, 120.9, 21.3. IR (ZnSe) ν_{max} (cm^{-1}): 3152, 2917, 2349, 1584, 1507, 1379, 1214, 987, 815, 753. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO$, 262.1226; found, 262.1241.

*(E)-8-(4-(tert-Butyl)styryl)quinoline 1-oxide (Table 5, entry **8g**).* Yellow precipitates, yield = 20.3 mg (67%). mp 178-180 °C. Isolated from flash chromatography (80% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.83 (d, J = 15.9 Hz, 1H), 8.48 (d, J = 1.8 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.56 (d, J = 8.1 Hz, 3H), 7.40 (d, J = 8.1, 2H), 7.28 – 7.25 (m, 1H), 6.72 (d, J = 15.9 Hz, 1H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 150.6, 139.9, 137.5, 135.1, 134.5, 132.2, 130.5, 129.9, 129.7, 128.4, 127.9, 126.6, 126.5, 125.4, 120.9, 34.6, 31.3. IR (ZnSe) ν_{max} (cm^{-1}): 2962, 2888, 2349, 1698, 1379, 1220, 822, 759, 648. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO$, 304.1696; found, 304.1701.

*(E)-8-(4-Bromostyryl)quinoline 1-oxide (Table 5, entry **8h**).* Yellow liquid, yield = 24.1 mg (74%). Isolated from flash chromatography (74% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (600 MHz, $CDCl_3$, δ): 8.78 (d, J = 16.2 Hz, 1H), 8.48 (d, J = 6.0 Hz, 1H), 7.79 – 7.74 (m, 3H), 7.57 (t, J = 7.8 Hz, 1H), 7.42 (dd, J = 18.0, 8.4 Hz, 4H), 7.28 – 7.25 (m, 1H), 6.59 (d, J = 16.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 139.5, 137.8, 136.8, 133.7, 132.1, 131.7, 131.3, 130.9, 128.5, 128.42, 128.37, 128.3, 127.5, 121.2, 121.1. IR (ZnSe) ν_{max} (cm^{-1}): 3067, 2344, 1643, 1597, 1488, 1219, 817, 752, 655. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}BrNO$, 326.0175; found, 326.0171.

*(E)-8-(4-Nitrostyryl)quinoline 1-oxide (Table 5, entry **8i**).* Yellow precipitates, yield = 20.7 mg (71%). mp 205-207 °C. Isolated from flash chromatography (78% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.92 (d, J = 15.9 Hz, 1H), 8.43 (d, J = 6.0 Hz, 1H), 8.15 – 8.11 (m, 2H), 7.79 – 7.52 (m, 6H), 7.26 – 7.18 (m, 1H), 6.63 (d, J = 15.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 146.7, 144.4, 139.8, 137.6, 135.4, 133.2, 132.1, 130.9, 129.0, 128.5, 127.2, 127.0, 126.8, 124.0, 121.3. IR (ZnSe) ν_{max} (cm^{-1}): 2923, 2851, 1711, 1587, 1503, 1334, 949, 814, 743, 578. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}N_2O_3$, 293.0921; found, 293.0903.

*(E)-8-(4-Cyanostyryl)quinoline 1-oxide (Table 5, entry **8j**).* Yellow precipitates, yield = 19.3 mg (71%). mp 265-267 °C. Isolated from flash chromatography (74% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (600 MHz, $CDCl_3$, δ): 8.97 (d, J = 16.2 Hz, 1H), 8.51 (d, J = 6.0 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.80 – 7.78 (m, 2H), 7.68 – 7.64 (m, 5H), 7.34 – 7.29 (m, 1H), 6.68 (d, J = 16.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 142.4, 137.7, 134.5, 133.3, 133.2, 132.9, 132.4, 132.1, 131.0, 128.9, 128.5,

127.5, 127.2, 126.9, 121.3, 110.4. IR (ZnSe) ν_{max} (cm^{-1}): 2958, 2923, 2224, 1652, 1593, 1223, 1184, 810, 743. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}N_2O$, 273.1022; found, 273.1015.

*(E)-8-(2-(Perfluorophenyl)vinyl)quinoline 1-oxide (Table 5, entry **8k**).* Yellow precipitates, yield = 19.9 mg (59%). mp 140-142 °C. Isolated from flash chromatography (70% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 9.08 (d, J = 16.5 Hz, 1H), 8.45 (d, J = 6.0 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.67 – 7.62 (m, 1H), 7.42 – 7.36 (m, 1H), 6.49 (d, J = 15.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 146.9 – 143.5 (m), 140.65 – 140.37 (m), 140.0, 137.8, 133.4, 132.62, 132.56, 131.2, 130.0, 128.9, 126.5, 122.2, 112.67 – 112.53 (m). ^{19}F NMR (565 MHz, $CDCl_3$, δ): -138.57 – -138.64 (m), -153.4 – -153.5 (m), -159.3 – -159.4 (m). IR (ZnSe) ν_{max} (cm^{-1}): 2924, 1701, 1150, 900, 733, 658. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_9F_5NO$, 338.0599; found, 338.0585.

*(E)-8-(2-(Naphthalen-1-yl)vinyl)quinoline 1-oxide (Table 5, entry **8l**).* Brown liquid, yield = 21.7 mg (73%). Isolated from flash chromatography (75% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.88 (d, J = 15.6 Hz, 1H), 8.51 (dd, J = 6.0, 1.5 Hz, 1H), 8.35 – 8.32 (m, 1H), 7.89 – 7.88 (m, 3H), 7.84 – 7.81 (m, 2H), 7.75 (dd, J = 8.4, 1.5 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.57 – 7.51 (m, 2H), 7.45 (d, J = 15.9 Hz, 1H), 7.31 – 7.26 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 140.1, 137.5, 135.2, 134.6, 133.8, 133.6, 132.2, 131.4, 131.0, 128.6, 128.5, 128.2, 127.8, 126.5, 126.4, 125.90, 125.86, 125.6, 124.5, 123.9, 121.0. IR (ZnSe) ν_{max} (cm^{-1}): 2923, 2851, 1711, 1587, 1334, 949, 814, 743, 578. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}NO$, 298.1226; found, 298.1230 .

*(E)-8-(2-(Naphthalen-2-yl)vinyl)quinoline 1-oxide (Table 5, entry **8m**).* Yellow liquid, yield = 19.9 mg (67%). Isolated from flash chromatography (73% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 9.02 (d, J = 15.9 Hz, 1H), 8.50 (dd, J = 6.3, 1.2 Hz, 1H), 7.94 (s, 1H), 7.89 – 7.82 (m, 5H), 7.80 – 7.73 (m, 2H), 7.62 (t, J = 7.8 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.30 – 7.26 (m, 1H), 6.90 (d, J = 15.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 139.9, 137.5, 135.5, 134.3, 133.7, 133.0, 132.2, 131.0, 130.6, 129.9, 128.4, 128.2, 128.1, 128.0, 127.7, 126.5, 126.1, 125.7, 124.4, 121.0. IR (ZnSe) ν_{max} (cm^{-1}): 2931, 2820, 1702, 1457, 1208, 849, 780, 678, 523. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}NO$, 298.1226; found, 298.1215.

*(E)-8-(2-(Phenylsulfonyl)vinyl)quinoline 1-oxide (Table 5, entry **8n**).* Orange liquid, yield = 18.9 mg (61%). Isolated from column chromatography (65% EtOAc/ n-hexane; acidic alumina). ^1H NMR (300 MHz, $CDCl_3$, δ): 9.20 (d, J = 15.0 Hz, 1H), 8.49 – 8.45 (m, 1H), 8.10 – 8.07 (m, 2H), 7.91 – 7.88 (m, 1H), 7.76 – 7.73 (m, 1H), 7.61 – 7.56 (m, 5H), 7.33 (dd, J = 8.4, 6.0 Hz, 1H), 6.44 (d, J = 15.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 146.1, 140.9, 139.7, 137.2, 133.2, 131.8, 131.6, 130.5, 129.4, 129.3, 128.4, 127.8, 126.4, 126.3, 121.8. IR (ZnSe) ν_{max} (cm^{-1}): 3101, 2925, 1825, 1588, 1445, 1140, 1028, 680, 558. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}NO_3S$, 312.0689; found, 312.0672.

*(E)-8-(2-Cyclohexylvinyl)quinoline 1-oxide (Table 5, entry **8o**).* Brown liquid, yield = 14.4 mg (57%). Isolated from flash chromatography (70% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.44 (dd, J = 6.0, 1.2 Hz, 1H), 8.02 (d, J = 15.9 Hz, 1H), 7.73 – 7.62 (m, 3H), 7.55 – 7.49 (m, 1H), 7.24 – 7.19 (m, 1H), 5.78 (dd, J = 15.6, 6.6 Hz, 1H), 2.31 – 2.22 (m, 1H), 1.96 – 1.92 (m, 2H), 1.83 – 1.68 (m, 4H), 1.43 – 1.30 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 139.9, 137.7, 137.4, 135.1, 132.1, 130.9, 129.3, 128.3, 127.4, 126.3, 120.7, 41.0, 32.9, 26.3, 26.1. IR (ZnSe) ν_{max} (cm^{-1}): 2928, 2852, 1620, 1590, 752. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO$, 254.1539; found, 254.1530.

*(E)-8-(3-Cyclohexylprop-1-en-1-yl)quinoline 1-oxide (Table 5, entry **8p**).* Yellow liquid, yield = 16.6 mg (62%). Isolated from flash chromatography (62% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.45 – 8.42 (m, 1H), 8.00 (d, J = 15.6 Hz, 1H), 7.73 – 7.63 (m, 3H), 7.55 – 7.49 (m, 1H), 7.24 – 7.18 (m, 1H), 5.87 – 5.78 (m, 1H), 2.23 – 2.19 (m, 2H), 1.86 – 1.82 (m, 3H), 1.76 – 1.65 (m, 4H), 1.30 – 1.22 (m, 3H), 1.08 – 1.04 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 139.8, 137.3, 134.9, 132.4, 132.1, 131.0, 130.6, 128.3, 127.5, 126.2, 120.7, 41.0, 38.3, 33.3, 26.6, 26.4. IR (ZnSe) ν_{max} (cm^{-1}): 2919, 2844, 1692, 1419, 966, 819, 756. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}NO$, 268.1696; found, 268.1686.

*(E)-8-(Hex-1-en-1-yl)quinoline 1-oxide (Table 5, entry **8q**).* Yellow liquid, yield = 12.0 mg (53%). Isolated from flash chromatography (65% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.45 – 8.43 (m, 1H), 8.03 (d, J = 15.3 Hz, 1H), 7.73 – 7.61 (m, 3H), 7.54 – 7.49 (m, 1H), 7.24 – 7.18 (m, 1H), 5.88 – 5.78 (m, 1H), 2.36 – 2.28 (m, 2H), 1.58 – 1.50 (m, 2H), 1.47 – 1.40 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 139.8, 137.3, 134.9, 132.09, 132.06, 131.4, 130.9, 128.3, 127.5, 126.3, 120.7, 32.7, 31.5, 22.4, 14.0. IR (ZnSe) ν_{max} (cm^{-1}): 3102, 2929, 1692, 1225, 854, 793, 622. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}NO$, 228.1383; found, 228.1400.

*(E)-8-(Hept-1-en-1-yl)quinoline 1-oxide (Table 5, entry **8r**).* Brown liquid, yield = 13.7 mg (57%). Isolated from flash chromatography (60% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (600 MHz, $CDCl_3$, δ): 8.45 (dd, J = 6.0, 1.2 Hz, 1H), 8.03 (d, J = 15.6 Hz, 1H), 7.73 – 7.71 (m, 1H), 7.69 (dd, J = 8.4, 1.2 Hz, 1H), 7.63 (dt, J = 7.2, 1.2 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.22 (dd, J = 8.4, 6.0 Hz, 1H), 5.84 (dt, J = 15.6, 6.6 Hz, 1H), 2.33 – 2.29 (m, 2H), 1.59 – 1.54 (m, 2H), 1.41 - 1.37 (m, 4H), 0.94 - 0.92 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 139.7, 137.4, 134.9, 132.3, 132.1, 131.3, 131.1, 128.3, 127.5, 126.5, 120.7, 33.0, 31.6, 29.1, 22.6, 14.1. IR (ZnSe) ν_{max} (cm^{-1}): 3075, 2926, 2854, 1692, 1455, 945, 821, 780. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO$, 242.1539; found, 242.1556.

*(E)-8-(3-Ethoxy-3-oxoprop-1-en-1-yl)-2-(4-methoxyphenyl)quinoline 1-oxide (Scheme 5, **3aa**).* To an oven-dried screw cap reaction vial charged with a spinvane magnetic stir-bar, aryldiazonium tetrafluoroborate salt (0.1 mmol), 8-substituted quinoline *N*-oxide (**3a**, 3 equiv.) and sodium acetate (2 equiv.) were added in MeCN (5 ml) and stir for 6 h at room temperature. After completion, reaction mixture was diluted with ethyl acetate and washed with brine solution three time. Organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Brownish liquid, yield = 29.0 mg (90%). Isolated from flash chromatography (35% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 9.20 (d, J = 15.6 Hz, 1H), 7.95 (d, J = 8.7 Hz, 2H), 7.85 (dd, J = 7.8, 1.8 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.51 (d, J = 8.7 Hz, 1H), 7.04 (d, J = 8.7 Hz, 2H), 5.96 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.89 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 166.8, 160.6, 148.0, 146.3, 140.6, 132.0, 131.1, 130.6, 129.6, 127.9, 125.5, 123.7, 118.0, 113.8, 60.3, 55.4, 14.4. IR (ZnSe) ν_{max} (cm^{-1}): 2998, 2845, 1712, 1653, 1595, 1435, 1250, 1136, 834, 768. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}NO_4$, 350.1387; found, 350.1400.

*(E)-Ethyl-3-(quinolin-8-yl)acrylate (Scheme 5, **3ab**).*[17f] To an oven-dried screw cap reaction vial charged with a spinvane magnetic stir-bar, 8-substituted quinoline *N*-oxide (**3a**, 0.1 mmol), phenylboronic acid (1.5 equiv.) and 0.5 ml DCE were added. The reaction mixture was allowed to stir at 120 °C for 12 h. After completion the reaction mixture was diluted with DCM and washed with water three times. Combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Brown sticky liquid, yield = 20.4 mg (90%). Isolated from flash chromatography (15% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 9.01 (dd, J = 4.2, 1.8 Hz, 1H), 8.92 (d, J = 16.2 Hz, 1H), 8.19 (dd, J = 8.4, 1.8 Hz, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.48 (dd, J = 8.4, 4.2 Hz, 1H), 6.85 (d, J = 16.2 Hz, 1H), 4.34 (q, J

= 7.2 Hz, 2H), 1.42 – 1.37 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 167.1, 150.2, 146.2, 140.9, 136.3, 133.2, 130.0, 128.5, 128.0, 126.3, 121.6, 120.8, 60.5, 14.4. IR (ZnSe) ν_{max} (cm^{-1}) 2922, 2852, 1716, 1651, 1606, 1452, 1259, 1170, 1132, 840, 736.

2-(4-Methoxyphenyl)-8-styrylquinoline 1-oxide (Scheme 5, ***8aa****).* To an oven-dried screw cap reaction vial charged with a spinvane magnetic stir-bar, 8-substituted quinoline *N*-oxide (**8a**, 0.1 mmol), phenylboronic acid (1.5 equiv.) and 0.5 ml DCE were added. The reaction mixture was allowed to stir at 120 °C for 12 h. After completion the reaction mixture was diluted with DCM and washed with water three times. Combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Brown liquid, yield = 21.5 mg (85%). Isolated from flash chromatography (40% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.69 (d, J = 15.9 Hz, 1H), 7.91 – 7.79 (m, 4H), 7.63 (d, J = 7.8 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.36 – 7.33 (m, 2H), 7.31 – 7.21 (m, 1H), 7.03 (d, J = 9.0 Hz, 2H), 6.67 (d, J = 15.9 Hz, 1H), 3.87 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 160.8, 137.9, 135.3, 134.5, 132.2, 31.4, 131.3, 130.8, 129.6, 128.7, 128.5, 128.2, 128.1, 127.4, 126.9, 123.3, 114.3, 113.9, 55.4. IR (ZnSe) ν_{max} (cm^{-1}): 3057, 2927, 2837, 1691, 1602, 1500, 1440, 1249, 1178, 1028, 829, 750. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{20}NO_2$, 354.1489; found, 354.1490.

(E)-8-Styrylquinoline (Scheme 5, ***8ab****).*[17f] To an oven-dried screw cap reaction vial charged with a spinvane magnetic stir-bar, 8-substituted quinoline *N*-oxide (**8a**, 0.1 mmol), phenylboronic acid (1.5 equiv.) and 0.5 ml DCE were added. The reaction mixture was allowed to stir at 120 °C for 12 h. After completion the reaction mixture was diluted with DCM and washed with water three times. Combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Pale yellow precipitates, yield = 21.7 mg (94%). mp 96-98 °C. Isolated from flash chromatography (12% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.99 – 8.97 (m, 1H), 8.50 (d, J = 16.5 Hz, 1H), 8.18 – 8.15 (m, 1H), 8.07 (d, J = 7.5 Hz, 1H), 7.77 – 7.74 (m, 1H), 7.71 – 7.69 (m, 2H), 7.61 – 7.54 (m, 1H), 7.45 – 7.34 (m, 4H), 7.31 – 7.25 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 149.5, 146.0, 137.8, 136.3, 136.1, 130.6, 129.1, 128.6, 127.7, 127.3, 127.0, 126.5, 125.2, 124.7, 121.2. IR (ZnSe) ν_{max} (cm^{-1}): 3053, 1597, 1496, 1263, 1135, 968, 821, 790, 736, 692.

2-Methoxy-8-styrylquinoline (Scheme 5, ***8ac****).* To an oven-dried screw cap reaction vial charged with a spinvane magnetic stir-bar, 8-substituted quinoline *N*-oxide (**8a**, 0.1 mmol) and *p*-toluenesulfonic chloride (0.15 mmol) in 2 ml methanol were added. The reaction mixture was allowed to stir at room temperature for 15 min., then triethyl amine (2 equiv.) was added and reaction continued at room temperature for 12 h. After completion, the reaction mixture was diluted with 1M HCl and DCM. Collected DCM fraction of crude reaction mixture washed with saturated sodium bicarbonate solution three times. Combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Transparent sticky liquid, yield = 23.2 mg (89%). Isolated from flash chromatography (20% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.37 (d, J = 16.5 Hz, 1H), 8.03 – 7.99 (m, 2H), 7.79 – 7.64 (m, 3H), 7.49 – 7.39 (m, 4H), 7.33 – 7.40 (m, 1H), 6.97 (d, J = 8.7 Hz, 1H), 4.16 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 161.6, 144.0, 139.1, 138.2, 133.8, 129.7, 128.76, 127.5, 127.0, 126.7, 125.8, 125.4, 125.2, 123.8, 112.9, 53.4. IR (ZnSe) ν_{max} (cm^{-1}): 3047, 2943, 2845, 1614, 1573, 1483, 1330, 1269, 1128, 1020, 968, 827, 746, 688. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO$, 262.1226; found, 262.1230.

2-Chloro-8-styrylquinoline (Scheme 5, ***8ad****).* To an oven-dried screw cap reaction vial charged with a spinvane magnetic stir-bar, 8-substituted quinoline *N*-oxide (**8a**, 0.1 mmol) and thionyl chloride (2 ml) were added. The reaction mixture was allowed to stir at 50 °C for 12 h. After completion, the reaction mixture was collected in round bottom flask and reaction vial was washed with DCM. Collected DCM fraction of crude reaction mixture was evaporated under reduced pressure. Pale yellow sticky liquid, yield = 21.5 mg (81%). Isolated from flash chromatography (15% EtOAc/ n-hexane; silica gel 230-400 mesh size). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.38 (d, J = 16.8 Hz, 1H), 8.13 – 8.09 (m, 2H), 7.77 – 7.67 (m, 3H), 7.62 – 7.57 (m, 1H), 7.45 – 7.32 (m, 5H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 149.9, 145.5, 139.0, 137.6, 135.4, 131.0, 128.6, 127.8, 127.2, 127.1, 126.9, 126.8, 126.1, 124.0, 122.5. IR (ZnSe) ν_{max} (cm^{-1}): 3055, 2924, 2850, 1726, 1587, 1489, 1419, 1315, 1116, 964, 829, 750, 692. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}ClN$, 266.0731; found, 266.0745.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, details of optimization studies, characterization data for all synthesized compounds including ^1H and ^{13}C NMR spectra. This material is available at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author: *upendra@ihbt.res.in; upendraihbt@gmail.com

Web address: http://www.ihbt.res.in/en/staff/scientific-staff?chronoform=sctdetail&task=detail&id=41

Notes

The authors declare no competing financial interests.

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