Supporting information

for

Visible-light-induced multicomponent cascade cycloaddition

involving N-propargyl aromatic amines, diaryliodonium salts and

sulfur dioxide: a rapid access to 3-arylsulfonylquinolines

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General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Anhydrous solvents (including MeCN, DCM, DMSO, Me₂CO, EtOH and DMF) and CDCl₃ were purchased from Energy Chemical. Materials (used as received commercially available chemicals) were obtained from Bidepharmatech Ltd., Energy Chemical, Aladdin®, Meryer (Shanghai) Chemical Technology Co., Ltd, and used as received unless otherwise stated. ¹H, ¹⁹F and ¹³C NMR spectra were recorded on a 400 MHz Bruker spectrometer (¹H 400 MHz, ¹⁹F 376 MHz, ¹³C 101 MHz). Chemical shifts (δ) for ¹H, ¹⁹F and ¹³C spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ¹H and ¹³C NMR spectra and the chemical shifts were converted to the TMS scale (CDCl₃: $\delta H = 7.26$ ppm, $\delta C = 77.16$ ppm). The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet, coupling constant in Herts (Hz) and integration. HRMS (ESI) spectra was recorded on ThermoFisher MicroTOF II. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Silica gel (200-300 mesh) and silica gel GF254 (10-40 µm) were used for column chromatography and preparative thin layer chromatography (PTLC), respectively. For irradiation with green light was performed using High Power 530 nm 5W® TaoYuan LED (5W, $\lambda = 530 \pm 10$ nm, 700mA).

Experimental section

Substrate synthesis

N-propargyl aromatic amines **1** were synthesized according to the reported methods.^[1] Diaryliodonium salts **2** were synthesized following the reported methods.^[2]

Optimization of reaction conditions

Table 1 Optimi	Table 1 Optimization of reaction conditions ²						
	Ph TsO + Ph NH 1a 2a	Eos Nał TMP + DABSO CH ₃ (green	sin Y Ph HCO ₃ CN, r.t I LEDs 3a	O II S IO Ph			
Entry	Photocatalyst	Solvent	Base (equiv.)	Yield ^b (%)			
1	Rose bengai	CH₃CN		72			
2	Eosin Y	CH₃CN		78			
3	Eosin B	CH₃CN		70			
4	Rh₅G	CH₃CN		67			
5	Fluorescein	CH₃CN		73			
6	Ru(bpy) ₃ Cl ₂ =6H ₂ O	CH₃CN		69			
7	Eosin Y	CH ₃ CN/ H ₂ O (20:1)		74			
8	Eosin Y	EtOAc		64			
9	Eosin Y	EtOH		62			
10	Eosin Y	DCM		71			
11	Eosin Y	DMSO		45			
12	Eosin Y	CH ₃ CN/ DMSO (1:1)		55			
13 ^c	Eosin Y	CH₃CN		75			
14 ^d	Eosin Y	CH₃CN		77			
15	Eosin Y	CH₃CN	TEA	60			
16	Eosin Y	CH₃CN	DIEA	58			
17	Eosin Y	CH₃CN	KOAc	81			
18	Eosin Y	CH₃CN	NaHCO ₃	83			
19	Eosin Y	CH₃CN	Na ₂ CO ₃	81			
20	Eosin Y	CH₃CN	KHCO ₃	82			
21 ^e	Eosin Y	CH₃CN	NaHCO ₃	83			
22 ^f	Eosin Y	CH₃CN	NaHCO ₃	Trace			
23 ^g	Eosin Y	CH₃CN	NaHCO ₃	38			
24	-	CH₃CN	NaHCO ₃	Trace			

 Table 1 Optimization of reaction conditions^a

^{*o*} Reaction conditions: **1a** (0.20 mmol), **2a** (0.25 mmol), DABSO (0.16 mmol), photocatalyst (5 mol %), base (0.3 mmol), solvent (4 mL), 2 X 5 W green LEDs, rt, N₂, 9 h. ^{*b*} Isolated yield of the product **3a**. ^{*c*} CH₃CN (2 mL). ^{*d*} CH₃CN (8 mL), ^{*e*} NaHCO₃ (0.4 mmol), ^{*f*} Without light irradiation. ^{*g*} Under air.

General Procedure for the Synthesis of 3:

To a clear-colored tube equipped with a stir bar was added **1a** (42 mg, 0.2 mmol), Eosin Y (5 mol%), DABSO (39 mg, 0.16 mmol) and CH₃CN (4 mL), followed by NaHCO₃ (26 mg, 0.3 mmol) and **2a** (136 mg, 0.25 mmol). The tube was deaerated by vacummn until the bubble disappeared, then cooled by liquid nitrogen and exchanged adequately by N₂ (about 3 times), and after thawing the procedure was repeated once, the mixture was warmed to room temperature. Then the mixture was illuminated with the commercially available green LEDs (2 x 5 W LED light bulbs 6 cm away from the tube) and stirred under an N₂ atmosphere for 9 h at room temperature. After the reaction was completed (monitored by TLC), water was added and the mixture was extracted with ethyl acetate (20 mL x 4). The combined organic layer was washed with water (10 mL x 4), brine (10 mL x 3), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by PTLC to afford **3a-3u** and **4a-4l**.

Gram-scale experiments

To a clear-colored glass round bottom flask equipped with a stir bar was added **1a** (1.04 g, 5 mmol), Eosin Y (5 mol%), DABSO (0.96 g, 5 mmol) and CH₃CN (50 mL), followed by NaHCO₃ (0.63 g, 7.5 mmol) and **2a** (3.39 g, 6.25 mmol). The flask was deaerated by vacummn until the bubble disappeared, then cooled by liquid nitrogen and exchanged adequately by N₂ (about 3 times), and after thawing the procedure was repeated once, the mixture was warmed to room temperature. Then the mixture was illuminated with green LEDs (2 x 5 W LED light bulbs 6 cm away from the flask) and stirred at room temperature under N₂ atmosphere. The reaction was observed by TLC. After the reaction was completed (26 h), water (30 mL) was added and the mixture was extracted with ethyl acetate (60 mL x 4). The combined organic layer was washed with water (40 mL x 4), brine (40 mL x 4), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (PE/EA= 20 to 5:1) to afford the desired product **3a** (1.33 g, 77%) and byproduct 2-iodo-1,3,5-trimethoxybenzene (1.51 g, 82%).

Control Experiment

TEMPO as radical scavenger

To a clear-colored tube equipped with a stir bar was added **1a** (42 mg, 0.2 mmol), Eosin Y (5 mol%), DABSO (39 mg, 0.16 mmol) and CH₃CN (4 mL), followed by NaHCO₃ (26 mg, 0.3 mmol), TEMPO (63 mg, 0.4 mmol) and **2a** (136 mg, 0.25 mmol). The tube was deaerated by vacummn until the bubble disappeared, then cooled by liquid nitrogen and exchanged adequately by N₂ (about 3 times), and after thawing the procedure was repeated once, the mixture was warmed to room temperature. Then the mixture was illuminated with the commercially available green LEDs (2 x 5 W LED light bulbs 6 cm away from the tube) and stirred under an N_2 atmosphere for 12 h at room temperature. The reaction was observed by TLC.

1,1-diphenylethylene (5) as radical scavenger^[3]

To a clear-colored tube equipped with a stir bar was added **1a** (42 mg, 0.2 mmol), Eosin (5 mol%), DABSO (39 mg, 0.16 mmol) and CH₃CN (4 mL), followed by NaHCO₃ (26 mg, 0.3 mmol), 1,1-diphenylethylene (2.0 equiv.) and **2a** (136 mg, 0.25 mmol). The tube was deaerated by vacummn until the bubble disappeared, then cooled by liquid nitrogen and exchanged adequately by N₂ (about 3 times), and after thawing the procedure was repeated once, the mixture was warmed to room temperature. Then the mixture was illuminated with the commercially available green LEDs (2 x 5 W LED light bulbs 6 cm away from the tube) and stirred under an N₂ atmosphere for 12 h at room temperature. After that, water was added and the mixture was extracted with ethyl acetate (20 mL x 4). The combined organic layer was washed with water (10 mL x 4), brine (10 mL x 3), dried over Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by PTLC to afford **3a** (19 mg, 28%) and **6** (31mg, 37%).

N-(3-phenylprop-2-yn-1-ylidene)aniline (7) instead of 1a^[4]

To a clear-colored tube equipped with a stir bar was added 7 (41 mg, 0.2 mmol), Eosin Y (5 mol%), DABSO (39 mg, 0.16 mmol) and CH₃CN (4 mL), followed by NaHCO₃ (26 mg, 0.3 mmol) and **2a** (136 mg, 0.25 mmol). The tube was deaerated by vacummn until the bubble disappeared, then cooled by liquid nitrogen and exchanged adequately by N₂ (about 3 times), and after thawing the procedure was repeated once, the mixture was warmed to room temperature. Then the mixture was illuminated with the commercially available green LEDs (2 x 5 W LED light bulbs 6 cm away from the tube) and stirred under an N₂ atmosphere for 12 h at room temperature. The reaction was observed by TLC.

Light/Dark Experiments^[5]

To a clear-colored tube equipped with a stir bar was added **1a** (82 mg, 0.4 mmol), Eosin (5 mol%), DABSO (77 mg , 0.32 mmol) and CD₃CN (8 mL), followed by NaHCO₃ (51 mg, 0.6 mmol) and **2a** (271 mg, 0.5 mmol). The tube was deaerated by

vacummn until the bubble disappeared, then cooled by liquid nitrogen and exchanged adequately by N_2 (about 3 times), and after thawing the procedure was repeated once, the mixture was warmed to room temperature. Then the mixture was illuminated with the commercially available green LEDs (2 x 5 W LED light bulbs 6 cm away from the tube) and stirred under an N_2 atmosphere. The lights were removed and the reaction tube was completely covered in aluminum foil during the following time increments: 2-14 h. Aliquots of 0.35 mL were taken at each of the times listed in the table below and analyzed by ¹H-NMR spectroscopy based on 1-bromo-4-methylbenzene as an internal standard.



Figure s1 "light/dark" experiments

Determination of photochemical quantum yield

The quantum yield was measured according to published procedures.^[6] The reaction was run in a standard quartz fluorescence cuvette. The cuvette was irradiated with a 530 nm LED (the power was measured to be 21 mW at a distance of 10 cm away from the light source). The quantum yield Φ was calculated from Equation 1:

$$\Phi = \frac{N_{Product}}{*N_{Photons}} = \frac{N_{A*}n_{product}}{\frac{E_{Light}}{E_{Photons}}} = \frac{N_{A*}n_{product}}{\frac{P_{absorbed*}t}{\frac{h*c}{\lambda}}} = \frac{h*c*N_{A*}n_{product}}{\lambda*P_{absorbed*t}}$$
eq1

Where Φ is the quantum yield, $N_{product}$ is the number of molecules created, $N_{photons}$ is the number of absorbed photons, N_A is Avogadro's constant in moles-1, $n_{product}$ is the molar amount of molecules created in moles, E_{Light} is the energy of light absorbed in joule, $E_{Photons}$ is the energy of a single photon in joule, $P_{absorbed}$ is the radiant power absorbed in Watt, t is the irradiation time in seconds, h is the Planck's constant in joule seconds, c is the speed of light in meter per second, λ is the wavelength of irradiation source in meter, $P_{absorbed}$ is the radiant power absorbed in Watts [$P_{absorbed} = P_{ref}^*(1-10^{-A})$].

To a standard quartz fluorescence cuvette equipped with a stir bar was added **1a** (11 mg, 0.05 mmol), Eosin Y (5 mol%), DABSO (10 mg , 0.04 mmol) and degassed CD₃CN (1 mL), followed by NaHCO₃ (6 mg, 0.075 mmol), **2a** (33 mg, 0.0625 mmol). and 1-bromo-4-methylbenzene (8 mg, 0.05mmol). After 10 min of N₂ sparging, the mixture was illuminated with 530 nm LEDs (10 cm away from the cuvette) for 2 h. The yield of the product was determined by crude ¹H-NMR spectroscopy to be 50% using 1-bromo-4-methylbenzene as an internal standard. The quantum yield was determined using eq1.

$$\Phi = \frac{h * c * N_A * n_{product}}{\lambda * P_{absorbed*t}} = \frac{6.626 * 10^{-34} J \cdot s * 2.998 * 10^8 m s^{-1} * 6.022 * 10^{23} m o l^{-1} * 2.5 * 10^{-5} m o l}{530 * 10^{-9} m * 21 * 10^{-3} J s^{-1} * 0.97 * 7200 s} = 0.020$$

0.038

Fluorescence quenching experiments^[7]

All Eosin Y solutions were irradiated at 400 nm and the emission intensity from 400 to 700 nm were recorded using an F-7000 FL Spectrophotometer. In a typical experiment, the emission spectrum of a 1×10^{-5} M solution of Eosin Y in MeCN-DMSO (1:1, degassed with N₂ for 10 min) was collected. Then, the samples were prepared by mixing Eosin Y solution (2×10^{-5} M, 1 mL) and different concentration of quenchers (1 mL). After 10 min of N₂ sparging, measurements were conducted in 10 mm quartz cuvettes. Plots are created according to the results (Fig. s2).



Characterization of Products



4-phenyl-3-(phenylsulfonyl)quinolone (3a)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 8.21 (d, J = 8.5 Hz, 1H), 7.81 (ddd, J = 8.3, 6.7, 1.4 Hz, 1H), 7.44 (t, J = 8.0 Hz, 3H), 7.36 – 7.29 (m, 5H), 7.26 – 7.20 (m, 2H), 6.96 – 6.88 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.12, 149.91, 147.78, 140.95, 133.10, 132.59, 132.45, 132.36, 130.12, 129.79, 128.78, 128.73, 127.98, 127.94, 127.82, 127.57, 127.53. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₅NNaO₂S 368.0716, found 368.0719.



6-fluoro-4-phenyl-3-(phenylsulfonyl)quinolone (3b)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 8.21 (dd, J = 9.2, 5.4 Hz, 1H), 7.57 (ddd, J = 9.6, 7.9, 2.8 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.36 – 7.20 (m, 6H), 6.95 – 6.86 (m, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -109.55. ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.22 (d, J = 250.9 Hz), 149.43 (d, J = 6.0 Hz), 147.19 (d, J = 2.8Hz), 147.14, 140.73, 133.28, 133.25, 132.44 (d, J = 9.2 Hz), 132.24, 130.00, 129.06, 128.80, 128.7, 128.01, 128.73, 122.69 (d, J = 26.1 Hz), 110.84 (d, J = 23.7 Hz). HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₄FNNaO₂S 386.0621, found 386.0621.



6-chloro-4-phenyl-3-(phenylsulfonyl)quinolone (3c)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.73 (dd,

J = 9.0, 2.3 Hz, 1H), 7.45 (qd, J = 6.6, 5.5, 3.3 Hz, 2H), 7.36 – 7.20 (m, 7H), 6.93 – 6.86 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.21, 148.36, 148.01, 140.66, 134.20, 133.42, 133.27, 133.24, 131.93, 131.43, 130.07, 129.11, 128.81, 128.43, 128.06, 127.98, 126.11. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₄ClNNaO₂S 402.0326, found 402.0336.



6-bromo-4-phenyl-3-(phenylsulfonyl)quinolone (**3d**)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.88 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.29 (ddt, *J* = 15.4, 12.4, 7.1 Hz, 6H), 6.95 – 6.88 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.12, 148.54, 148.12, 140.64, 135.79, 133.38, 133.26, 131.86, 131.47, 130.07, 129.43, 129.12, 128.83, 128.80, 128.06, 127.96, 122.44. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₂₁H₁₄BrNNaO₂S 445.9821, found 445.9829.



6-methoxy-4-phenyl-3-(phenylsulfonyl)quinolone (3e)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.65 (s, 1H), 8.09 (d, J = 9.2 Hz, 1H), 7.44 (tt, J = 7.8, 2.1 Hz, 3H), 7.35 – 7.13 (m, 6H), 6.91 (dd, J = 8.0, 1.4 Hz, 2H), 6.49 (d, J = 2.8 Hz, 1H), 3.59 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.74, 148.28, 146.30, 145.36, 141.06, 133.03, 132.91, 132.68, 131.16, 130.03, 128.91, 128.74, 128.70, 127.95, 127.92, 125.03, 104.87, 55.45. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₇NNaO₃S 398.0821, found 398.0828.



6-isocyano-4-phenyl-3-(phenylsulfonyl)quinolone (3f)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 8.31 (d, J = 8.7 Hz, 1H), 7.94 (dd, J = 8.8, 1.8 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.56 – 7.42 (m, 2H), 7.44 – 7.22 (m, 6H), 6.95 – 6.88 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.62, 150.60, 150.55, 140.26, 134.32, 133.86, 133.52, 132.55, 131.48, 131.19, 129.98, 129.57, 128.92, 128.27, 128.05, 127.38, 117.97, 111.92. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₄N₂NaO₂S 393.0668, found 393.0656.



6-(tert-butyl)-4-phenyl-3-(phenylsulfonyl)quinolone (3g)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.11 (d, J = 8.9 Hz, 1H), 7.88 (dd, J = 8.9, 2.2 Hz, 1H), 7.40 (td, J = 7.4, 5.6 Hz, 2H), 7.33 – 7.16 (m, 7H), 6.90 (dd, J = 8.2, 1.3 Hz, 2H), 1.15 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.02, 149.90, 148.57, 147.16, 141.14, 132.98, 132.76, 132.34, 131.41, 130.13, 129.26, 128.72, 128.68, 127.91, 127.73, 127.24, 122.27, 35.17, 30.91. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₅H₂₃NNaO₂S 424.1342, found 424.1342.



6-methyl-4-phenyl-3-(phenylsulfonyl)quinolone (**3h**)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 7.66 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.38 – 7.22 (m, 6H), 7.07 (s, 1H), 6.93 (dd, *J* = 7.9, 1.5 Hz, 2H), 2.37 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.30, 148.61, 146.86, 141.06, 138.25, 134.69, 133.01, 132.72, 132.40, 130.14, 129.46, 128.69, 128.67, 127.89, 127.79, 127.54, 126.05, 21.86. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₇NNaO₂S 382.0872, found 382.0876.



8-methyl-4-phenyl-3-(phenylsulfonyl)quinolone (3i)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 7.67 (d, J = 6.9 Hz, 1H), 7.44 (td, J = 7.4, 1.9 Hz, 2H), 7.38 – 7.21 (m, 7H), 7.16 (d, J = 8.6 Hz, 1H), 6.96 – 6.89 (m, 2H), 2.88 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.14, 149.03, 146.63, 141.19, 137.84, 133.13, 133.04, 132.45, 132.21, 130.22, 128.74, 128.66, 128.00, 127.76, 127.65, 125.53, 18.35. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₇NNaO₂S 382.0872, found 382.0869.



3-(phenylsulfonyl)-4-(o-tolyl)quinolone (3j)

3-(phenylsulfonyl)-4-(p-tolyl)quinoline ¹H NMR (400 MHz, Chloroform-*d*) ¹H NMR (400 MHz, Chloroform-*d*) δ 9.79 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.78 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.37 – 7.28 (m, 3H), 7.27 – 7.08 (m, 5H), 6.78 (dd, *J* = 7.5, 1.3 Hz, 1H), 1.38 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.06, 149.83, 148.13, 140.59, 137.14, 133.32, 132.43, 132.21, 132.14, 130.34, 129.95, 129.86, 129.30, 128.77, 128.37, 128.25, 127.03, 126.97, 125.37, 19.63. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₂₂H₁₇NNaO₂S 382.0872, found 382.0856.



3-(phenylsulfonyl)-4-(m-tolyl)quinolone (3k)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.74 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.74 (ddd, *J* = 8.4, 6.7, 1.5 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.32 – 7.14 (m, 7H), 6.78 (dq, *J* = 5.9, 3.0, 2.0 Hz, 1H), 6.46 (s, 1H), 2.16 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.35, 149.90, 147.74, 141.02, 137.35, 132.93, 132.49, 132.46, 132.31, 130.38, 129.74, 129.51, 128.58, 128.03, 127.90, 127.79, 127.63, 127.60, 127.42, 21.44. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₂₂H₁₇NNaO₂S 382.0872, found 382.0867.



3-(phenylsulfonyl)-4-(p-tolyl)quinolone (31)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.74 (ddd, J = 8.4, 6.7, 1.5 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.34 – 7.23 (m, 3H), 7.18 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.45, 149.90, 147.84, 141.08, 138.74, 133.06, 132.67, 132.29, 130.04, 129.78, 129.66, 128.63, 128.48, 128.00, 127.88, 127.80, 127.62, 21.53. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₇NNaO₂S 382.0872, found 382.0868.



4-(4-methoxyphenyl)-3-(phenylsulfonyl)quinolone (**3m**)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.79 (s, 1H), 8.20 (d, J = 8.5 Hz, 1H), 7.81 (ddd, J = 8.4, 6.7, 1.6 Hz, 1H), 7.50 – 7.21 (m, 7H), 6.84 (s, 4H), 3.89 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.07, 150.25, 149.91, 147.78, 141.02, 133.05, 132.86, 132.27, 131.51, 129.75, 128.64, 127.99, 127.87, 127.52, 124.56, 113.32, 55.51. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₇NNaO₃S 376.1002, found 376.0976.



4-(4-fluorophenyl)-3-(phenylsulfonyl)quinolone (**3n**)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.76 (s, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.80 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.44 (t, J = 7.9 Hz, 2H), 7.35 – 7.19 (m, 4H), 7.03 – 6.93 (m, 2H), 6.92 – 6.84 (m, 2H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -111.207. ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.07 (d, J = 249.4 Hz), 149.99, 149.07, 147.80, 141.01, 133.30, 132.77, 132.49, 132.10 (d, J = 8.4 Hz), 129.97, 128.85, 128.19, 127.85, 128.49 (d, J = 3.6 Hz). 127.60, 127.22, 115.06 (d, J = 21.7 Hz). HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₄FNNaO₂S 364.0802, found 364.0778.



4-(4-chlorophenyl)-3-(phenylsulfonyl)quinolone (30)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.83 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.40 – 7.26 (m, 7H), 6.92 – 6.84 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.92, 148.68, 147.70, 140.90, 135.18, 133.34, 132.62, 132.51, 131.50, 131.04, 129.94, 128.85, 128.24, 128.12, 127.85, 127.25, 127.14. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₂₁H₁₄ClNNaO₂S 402.0326, found 402.0314.



4-(4-bromophenyl)-3-(phenylsulfonyl)quinolone (**3p**)

1H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.84 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.54 – 7.42 (m, 4H), 7.40 – 7.24 (m, 5H), 6.85 – 6.78 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.94, 148.63, 147.72, 140.90, 133.35, 132.60, 132.53, 131.76, 131.56, 131.09, 129.98, 128.88, 128.26, 127.89, 127.16, 123.38. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₄BrNNaO₂S 445.9821, found 445.9801.



4-(3-(phenylsulfonyl)quinolin-4-yl)benzonitrile (**3q**)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.26 (d, J = 8.5 Hz, 1H), 7.88 (t, J = 7.7 Hz, 1H), 7.65 (d, J = 7.9 Hz, 2H), 7.52 (q, J = 7.5 Hz, 2H), 7.42 – 7.30 (m, 4H), 7.20 (d, J = 8.5 Hz, 1H), 7.11 (d, J = 7.9 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.01, 147.84, 147.48, 140.95, 137.80, 133.68, 132.79, 132.31, 131.56, 131.02, 130.26, 129.12, 128.65, 127.87, 126.79, 126.60, 118.33, 113.04. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₄N₂NaO₂S 393.0668, found 393.0644.



methyl 4-(3-(phenylsulfonyl)quinolin-4-yl)benzoate (**3r**)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 8.26 (d, J = 8.5 Hz, 1H), 8.07 – 8.00 (m, 2H), 7.87 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.23 (m, 3H), 7.07 (d, J = 8.1 Hz, 2H), 4.03 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.65, 149.92, 148.84, 147.85, 140.98, 137.54, 133.45, 132.58, 132.35, 130.61, 130.28, 130.03, 129.00, 128.95, 128.31, 127.97, 127.16, 127.01, 52.56. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₂₃H₁₇NNaO₄S 426.0770, found 426.0767.



4-(4-nitrophenyl)-3-(phenylsulfonyl)quinolone (3s)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 8.24 (dd, J = 18.0, 8.6 Hz, 3H), 7.93 – 7.84 (m, 1H), 7.59 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.20 (dd, J = 8.5, 6.7 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.96, 148.23, 147.87, 147.20, 140.97, 139.73, 133.78, 132.84, 132.36, 131.28, 130.28, 129.17, 128.72, 127.88, 126.73, 126.54, 122.98. HRMS (ESI) *m/z* [M+Na]⁺ calculated for C₂₁H₁₄N₂NaO₄S 413.0566, found 413.0546.



3-(phenylsulfonyl)-4-(thiophen-2-yl)quinolone (3t)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 8.21 (d, J = 8.5 Hz, 1H), 7.84 (ddd, J = 8.4, 6.6, 1.6 Hz, 1H), 7.59 (dd, J = 8.6, 1.5 Hz, 1H), 7.56 – 7.40 (m, 5H), 7.31 (t, J = 7.8 Hz, 2H), 7.12 (dd, J = 5.1, 3.5 Hz, 1H), 7.01 (dd, J = 3.5, 1.2 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.01, 147.92, 143.38, 140.65, 134.26, 133.33, 132.64, 132.11, 131.62, 129.90, 129.06, 128.95, 128.65, 128.38, 127.99, 127.34, 126.97. HRMS (ESI) m/z [M+Na]⁺ calculated for C₁₉H₁₃NNaO₂S₂ 374.0280, found 374.0268.



2,4-diphenyl-3-(phenylsulfonyl)quinolone (**3u**)

¹H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, J = 8.4 Hz, 1H), 7.81 (dt, J = 8.4, 4.1 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.50 – 7.44 (m, 3H), 7.39 (td, J = 7.5, 5.8 Hz, 5H), 7.33 – 7.22 (m, 3H), 7.08 (d, J = 4.3 Hz, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ

157.85, 151.53, 147.76, 142.17, 140.94, 134.89, 133.04, 132.23, 132.14, 130.26, 129.62, 129.54, 128.59, 128.55, 128.34, 127.95, 127.84, 127.70, 127.46, 127.06, 126.65. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₇H₁₉NNaO₂S 444.1209, found 444.1213.



3-((4-fluorophenyl)sulfonyl)-4-phenylquinoline (4a)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.20 (d, J = 8.5 Hz, 1H), 7.82 (ddd, J = 8.4, 6.7, 1.5 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.39 – 7.22 (m, 5H), 6.98 – 6.85 (m, 4H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -103.93. ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.39 (d, J = 256.3 Hz), 150.00, 147.61, 137.00 (d, J = 3.0 Hz), 132.64, 132.47, 132.36, 130.89, 130.80, 130.22, 129.86, 128.96, 128.10, 127.92, 127.52, 127.50, 116.01 (d, J = 22.7 Hz). HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₄FNNaO₂S 386.0610, found 386.0621.



3-((4-chlorophenyl)sulfonyl)-4-phenylquinoline (4b)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.83 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.40 - 7.30 (m, 3H), 7.24 -7.19 (m, 4H), 6.99 – 6.92 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.09, 150.02, 147.58, 139.86, 139.42, 132.57, 132.55, 130.21, 132.18, 129.85, 129.43, 129.00, 128.13, 127.92, 127.51, 127.49. HRMS (ESI) *m*/*z* [M+Na]⁺ calculated for C₂₁H₁₄ClNNaO₂S 402.0326, found 402.0326.



3-((4-bromophenyl)sulfonyl)-4-phenylquinoline (4c)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.83 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.47 (qd, J = 6.3, 3.0 Hz, 2H), 7.41 – 7.31 (m, 5H), 7.19 – 7.10 (m, 2H), 6.99 – 6.92 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.07, 150.00, 147.53, 139.95, 132.54, 132.12, 131.97, 130.19, 129.83, 129.46, 128.98, 128.41, 128.12, 127.91, 127.50, 127.47. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₄BrNNaO₂S 445.9821, found 445.9833.



4-phenyl-3-tosylquinoline (4d)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.23 – 8.17 (m, 1H), 7.81 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.45 (dtd, J = 6.8, 5.3, 2.5 Hz, 2H), 7.33 (td, J = 7.4, 6.6, 3.1 Hz, 3H), 7.19 (d, J = 2.0 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.98 – 6.93 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.95, 149.83, 147.90, 144.15, 138.12, 132.77, 132.25, 130.15, 129.78, 129.36, 128.77, 128.06, 127.93, 127.76, 127.64, 127.55, 21.68. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₇NNaO₂S 382.0872, found 382.0874.



4-phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)quinolone (**4e**) ¹H NMR (400 MHz, Chloroform-*d*) δ 9.81 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.85 (ddd, *J* = 8.3, 6.7, 1.4 Hz, 1H), 7.53 – 7.39 (m, 6H), 7.32 (q, *J* = 7.9 Hz, 3H), 6.96 – 6.89 (m, 2H). ¹⁹F (376 MHz, Chloroform-*d*) -63.27). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.26, 150.18, 147.45, 144.42, 134.68 (q, J = 33.1 Hz),132.73, 132.45, 131.81, 130.24, 129.93, 129.06, 128.50, 128.25, 127.97, 127.52, 127.42, 125.81, 125.79 (q, J = 3.7 Hz), 124.54, 123.18 (d, J = 273.1 Hz). HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₄NF₃NaO₂S 436.0590, found 436.0595.



(4-((4-phenylquinolin-3-yl)sulfonyl)phenyl)methanol (4f)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.71 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.79 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.43 (dtd, J = 6.9, 3.6, 1.7 Hz, 2H), 7.30 (ddd, J = 7.6, 4.2, 2.8 Hz, 3H), 7.22 (s, 4H), 6.95 – 6.87 (m, 2H), 4.70 (s, 2H), 3.12 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.24, 149.68, 147.66, 147.15, 139.52, 132.54, 132.49, 132.45, 130.07, 129.54, 128.88, 128.09, 128.06, 127.81, 127.60, 127.56, 126.52, 63.96. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₇NNaO₃S 398.0821, found 398.0818.



methyl 4-((4-phenylquinolin-3-yl)sulfonyl)benzoate (4g)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.92 – 7.79 (m, 3H), 7.51 – 7.42 (m, 2H), 7.40 – 7.26 (m, 5H), 6.95 – 6.88 (m, 2H), 3.92 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.54, 150.33, 150.07, 147.59, 144.78, 134.08, 132.62, 132.40, 131.88, 130.18, 129.85, 129.79, 129.02, 128.15, 127.98, 127.90, 127.52, 127.46, 52.78. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₇NNaO₃S 426.0770, found 426.0774.



4-((4-phenylquinolin-3-yl)sulfonyl)benzonitrile (4h)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.79 (s, 1H), 8.23 (d, J = 8.5 Hz, 1H), 7.86 (ddd, J = 8.4, 6.7, 1.5 Hz, 1H), 7.56 – 7.44 (m, 4H), 7.43 – 7.30 (m, 5H), 6.97 – 6.90 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.35, 150.24, 147.36, 145.02, 132.89, 132.37, 132.34, 131.39, 130.28, 129.95, 129.20, 128.55, 128.36, 128.03, 127.50, 127.35, 117.21, 116.68. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₄N₂NaO₂S 393.0668, found 393.0677.



3-((2-bromophenyl)sulfonyl)-4-phenylquinoline (4i)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.88 (s, 1H), 8.26 (d, J = 8.5 Hz, 1H), 7.90 – 7.81 (m, 1H), 7.54 – 7.44 (m, 2H), 7.36 – 7.24 (m, 2H), 7.17 (t, J = 7.6 Hz, 4H), 7.06 (t, J = 7.7 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.76, 149.38, 149.09, 139.75, 134.67, 134.17, 132.39, 132.22, 131.49, 131.38, 129.91, 129.80, 128.74, 127.99, 127.68, 127.50, 127.26, 120.19. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₄BrNNaO₂S 445.9821, found 445.9822.



3-((3-bromophenyl)sulfonyl)-4-phenylquinoline (**4j**)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.81 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.57 – 7.41 (m, 3H), 7.36 – 7.22 (m, 5H), 7.11 (t, J = 7.8 Hz, 1H), 6.94 – 6.88 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.31, 150.05,

147.49, 142.66, 136.25, 132.62, 132.15, 132.01, 131.08, 130.28, 130.13, 129.85, 129.27, 128.15, 127.92, 127.55, 127.48, 126.47, 122.72. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₁H₁₄BrNNaO₂S 445.9821, found 445.9834.



3-((4-phenylquinolin-3-yl)sulfonyl)benzonitrile (4k)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.86 (ddd, J = 8.3, 6.7, 1.3 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.66 – 7.53 (m, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.47 – 7.31 (m, 5H), 6.98 – 6.91 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.31, 150.26, 147.29, 142.44, 136.13, 132.89, 132.14, 131.94, 131.78, 131.53, 130.33, 129.97, 129.82, 129.57, 128.35, 128.13, 127.49, 127.33, 116.82, 113.37. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₄N₂NaO₂S 393.0668, found 393.0660.



3-((6-chloropyridin-3-yl)sulfonyl)-4-phenylquinoline (41)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.79 (s, 1H), 8.24 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 2.6 Hz, 1H), 7.87 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.50 (ddt, J = 12.8, 10.1, 7.5 Hz, 3H), 7.45 – 7.33 (m, 3H), 7.20 (d, J = 8.4 Hz, 1H), 7.03 – 6.96 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.99, 150.26, 150.24, 149.37, 147.25, 137.88, 136.51, 132.95, 132.22, 131.63, 130.26, 129.99, 129.59, 128.41, 128.22, 127.52, 127.33, 124.22. HRMS (ESI) m/z [M+Na]⁺ calculated for C₂₂H₁₃ClN₂NaO₂S 403.0278, found 403.0279.



 $(2-(phenylsulfonyl)ethene-1, 1-diyl)dibenzene (6)^{[8]}$

¹H NMR (400 MHz, Chloroform-*d*) δ ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.35 (ddd, *J* = 20.5, 14.4, 5.4 Hz, 8H), 7.23 (d, *J* = 13.0 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.07 (s, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.35, 141.65, 139.26, 135.61, 132.96, 130.46, 129.91, 129.02, 128.92, 128.81, 128.73, 128.35, 128.00, 127.78.

References

- [1] B. X. Yuan, F. M. Zhang, Z. M. Li, S. H. Yang and R. L. Yan, Org. Lett., 2016, 18, 5928.
- [2] T. L. Seidl, S. K. Sundalam, B. McCullough and D. R. Stuart, J. Org. Chem., 2016, 81, 1998.
- [3] T. Liu, D. Zheng and J. Wu, Org. Chem. Front., 2017, 4, 1079.
- [4] L. Zhang, S. Chen, Y. Gao, P. Zhang, Y. Wu, G. Tang and Y. Zhao, Org. Lett., 2016, 18, 1286.
- [5] H. Jiang, Y. Cheng, R. Wang, Y. Zhang and S. Yu, Chem. Commun., 2014, 50, 6164.
- [6] (a) U. Megerle, R. Lechner, B. König and E. Riedle, *Photochem. Photobiol. Sci.*, 2010, 9, 1400; (b) R. Zhou, Y. Y. Goh, H. W. Liu, H. R. Tao, L. H Li and J. Wu, *Angew. Chem.*, 2017, 129, 16848; (c) A. U. Meyer, T. Slanina, C-J. Yao, and B. König, *ACS Catal.*, 2016, 6, 369.
- [7] (a)Y. Yasu, Y. Arai, R. Tomita, T. Koike and M. Akita, *Org. Lett.*, 2014, **16**, 780; (b) H. C. Huang, G. J. Zhang, L. Gong, S. Y. Zhang and Y. Y. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 2280.
- [8] R. Mao, Z. Yuan, R. Zhang, Y. Ding, X. Fan and J. Wu, Org. Chem. Front., 2016, 3, 1498.

Copies of NMR spectra







90 80 f1 (ppm)

































10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0 f1 (ppm)





90 80 f1 (ppm)





90 80 fl (ppm)





90 80 fl (ppm)

















90 80 fl (ppm)











10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)











---63.27

































