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Supporting Information

Photocatalytic difunctionalization of arylalkenes with quinoxalinones

and dialkyl dithiophosphoric acids

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Table of Content

1. General information	S2
2. The general procedure for the photocatalysis	S2
3. The general procedure for the scale-up synthesis	S2
4. The general procedure for the control experiment	S3
5. The detection of in situ generated H ₂ O ₂ by potassium iodide-starch test paper	S3
6. The unsuccessful substrates	S4
7. The general procedure for the CV experiments	S4
8. The Stern-Volmer quenching experiments	S5
9. The characterization data	S6
10. The NMR spectra	S19

1. General information

Unless otherwise special noted, all reagents were purchased from commercial supplies and were used without further purification. Flash column chromatography was performed using silica gel (100-200 mesh). NMR spectra were obtained on a Bruker 400 MHz NMR using CDCl₃ as the solvent. Chemical shifts are given in ppm and coupling constants (*J*) in Hz. CV were performed on a CHI 600e potentiostat.

2. The general procedure for the photocatalysis

To a glass tube (8 mL) was added N-methyl quinoxalinone (0.2 mmol, 32 mg), styrene (0.4 mmol, 41 mg), diethyl dithiophosphoric acid (0.5 mmol, 94 mg), Eosin Y (0.002 mmol, 1.3 mg) and CH₃CN (2 mL) sequentially. The glass tube was then sealed with a rubber stopper and a O_2 balloon was attached. Finally, the resulting solution was irradiated by Kessil light (456 nm, 10 W) at rt for 4 h. A fan was necessary to cool down the reaction tube. After the reaction, the solvent was evaporated and the resulting crude was purified by SiO₂ (elute: petroleum ether/ethyl ether 10:1 to 4:1) to give the corresponding product 4 as a yellow oil (67 mg, 75%).

3. The general procedure for the scale-up synthesis

To a round-bottom flask (100 mL) was added N-methyl quinoxalinone (2 mmol, 320 mg), styrene (4 mmol, 410 mg), diethyl dithiophosphoric acid (5 mmol, 940 mg), Eosin Y (0.02 mmol, 13 mg) and CH₃CN (20 mL) sequentially. The glass tube was then sealed with a rubber stopper and a O_2 balloon was attached. Finally, the resulting solution was irradiated by two Kessil lights (456 nm, 10 W) at rt for 10 h. A fan was necessary to cool down the reaction tube. After the reaction, the solvent was evaporated and the resulting crude was purified by SiO₂ (elute: petroleum ether/ethyl ether 10:1 to 4:1) to give the corresponding product **4** as a yellow oil (473 mg, 53%).

4. The general procedure for the control experiment

To a glass tube (8 mL) was added N-methyl quinoxalinone (0.2 mmol, 32 mg), styrene (0.4 mmol, 41 mg), diethyl dithiophosphoric acid (0.5 mmol, 94 mg), Eosin Y (0.002 mmol, 1.3 mg) and CH₃CN (2 mL) sequentially. Then, BHT (0.4 mmol, 88 mg) was added to the reaction tube. The glass tube was then sealed with a rubber stopper and a O₂ balloon was attached. Finally, the resulting solution was irradiated by Kessil light (456 nm, 10 W) at rt for 4 h. A fan was necessary to cool down the reaction tube. After the reaction, the solvent was evaporated. The TLC analysis showed that only trace amount of product **4** was generated. However, the adduct between S-centered radical and BHT was observed by HRMS.



Fig S1. The HRMS of the radical adduct

5. The detection of in situ generated H₂O₂ by potassium iodide-starch test paper

To a glass tube (8 mL) was added N-methyl quinoxalinone (0.2 mmol, 32 mg), styrene (0.4 mmol, 41 mg), diethyl dithiophosphoric acid (0.5 mmol, 94 mg), Eosin Y (0.002 mmol, 1.3 mg) and CH₃CN (2 mL) sequentially. The glass tube was then sealed with a rubber stopper and a O_2 balloon was attached. Finally, the resulting red solution was

irradiated by Kessil light (456 nm, 10 W) at rt for 4 h. A fan was necessary to cool down the reaction tube. After the reaction, potassium iodide-starch test paper was immersed into the reaction mixture. As expected, the blue color change is clearly visible.



Fig S2. Potassium iodide starch paper test

6. The unsuccessful substrates



7. The general procedure for the CV experiments

All the CV experiments were performed in a three-electrode cell at room temperature. During CV analysis, Pt disk was employed as the working electrode; Pt wire was employed as the counter electrode; SCE was employed as the reference electrode. The scan rete is 100 mV/s. The blank solution is 0.1 M LiClO₄ in CH₃CN. The concentration of the substrates is 5 mM in blank solution.

8. The Stern-Volmer quenching experiments

The UV-Vis spectrum of the cat. (eosin Y) in CH_3CN was recorded on a Shimadzu spectrophotometer. The concentration of cat. is $1*10^{-6}$ mol/L. The absorption was collected and the spectrum was shown in Fig. S3.



Fig. S3. UV-Vis spectrum of eosin Y (cat.)

The following luminescence quenching experiments were conducted in CH₃CN. The excitation wavelength was 528 nm. The concentration of cat. is $1*10^{-6}$ mol/L. We can conclude that substrate **3a** can't quench the excited state of eosin Y (Fig. S4). This result ruled out the electro- or energy transfer process thereby supported our hypothesized HAT mechanism to generate S-centered radical from **3a**.



Fig. S4. The Stern-Volmer quenching experiments

9. The characterization data

O,O-diethyl *S*-(2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl) phosphorodithioate (4)



Yellow oil (67 mg, 75%), $R_f = 0.32$ (petroleum ether/EtOAc, 4:1); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.0, 1.4 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.45 (dd, J = 5.2, 3.4 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.34 – 7.28 (m, 3H), 7.27 – 7.21 (m, 1H), 5.03 (dd, J = 9.7, 6.0 Hz, 1H), 4.26 – 4.10 (m, 4H), 3.87 (m, 1H), 3.65 (s, 3H), 3.47 (m, 1H), 1.45 – 1.34 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 154.3, 139.6, 133.3, 132.6, 130.4, 128.8, 128.6, 127.6, 123.8, 113.8, 64.0 (t, J = 5.6 Hz), 48.5 (d, J = 4.1 Hz), 36.5 (d, J = 3.8

Hz), 29.3, 16.0 (dd, J = 8.5, 4.3 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 94.6. **HRMS** (ESI) calculated for C₂₁H₂₆N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 449.1117; found: 449.1113.

O,O-diethyl *S*-(2-(4-ethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl) phosphorodithioate (5)



Yellow oil (68 mg, 74%), $R_f = 0.33$ (petroleum ether/EtOAc, 4:1); ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H), 7.35 – 7.28 (m, 3H), 7.25 (m, 1H), 5.03 (dd, J = 9.7, 6.1 Hz, 1H), 4.40 – 4.03 (m, 6H), 3.86 (m, 1H), 3.47 (m, 1H), 1.40 (dd, J = 15.6, 7.3 Hz, 6H), 1.34 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 153.8, 139.7, 132.9, 132.3, 130.6, 130.3, 128.8, 128.6, 127.5, 123.5, 113.6, 64.0 (t, J = 5.5 Hz), 48.3 (d, J = 4.1 Hz), 37.6, 36.5 (d, J = 3.8 Hz), 16.0 (dd, J = 8.5, 4.2 Hz), 12.5. ³¹P NMR (162 MHz, CDCl₃) δ 94.6. **HRMS** (ESI) calculated for C₂₂H₂₈N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 463.1273; found: 463.1269.

O,O-diethyl *S*-(2-(4-isobutyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl) phosphorodithioate (6)



Yellow oil (70.6 mg, 72%), $R_f = 0.32$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.0, 1.5 Hz, 1H), 7.54 (m, 1H), 7.47 – 7.16 (m, 7H), 5.02 (dd, J = 9.7, 6.0 Hz, 1H), 4.29 – 4.05 (m, 5H), 4.04 – 3.78 (m, 2H), 3.51 – 3.42 (m, 1H),

2.21 (m, 1H), 1.40 (m, 6H), 0.94 (dd, J = 26.7, 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 154.5, 139.7, 132.8, 132.8, 130.6, 130.1, 128.8, 128.5, 127.5, 123.5, 114.2, 64.0 (t, J = 5.6 Hz), 49.1, 48.5 (d, J = 4.0 Hz), 36.6 (d, J = 3.8 Hz), 27.3, 20.2 (d, J = 3.0 Hz), 16.0 (dd, J = 8.6, 4.3 Hz). **HRMS** (ESI) calculated for C₂₄H₃₂N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 491.1586; found: 491.1582.

O,O-diethyl *S*-(2-(4-(3-methoxypropyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)-2phenylethyl) phosphorodithioate (7)



Yellow oil (69.8 mg, 69%), $R_f = 0.26$ (petroleum ether/EtOAc, 3:1), ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.0, 1.4 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.47 – 7.41 (m, 3H), 7.41 – 7.35 (m, 1H), 7.34 – 7.28 (m, 2H), 7.24 (m, 1H), 5.01 (dd, J = 9.6, 6.1 Hz, 1H), 4.41 – 4.06 (m, 6H), 3.86 (m, 1H), 3.52 – 3.45 (m, 1H), 3.43 (t, J = 5.7 Hz, 2H), 3.33 (s, 3H), 2.04 – 1.90 (m, 2H), 1.40 (dd, J = 15.5, 7.3 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 154.2, 139.7, 132.8, 132.7, 130.5, 130.4, 128.8, 128.6, 127.5, 123.6, 113.9, 69.9, 64.0 (t, J = 5.5 Hz), 58.9, 48.4 (d, J = 4.2 Hz), 40.2, 36.5 (d, J = 3.8 Hz), 27.7, 16.0 (dd, J = 8.6, 4.3 Hz). **HRMS** (ESI) calculated for C₂₄H₃₂N₂O₄PS₂⁺ Exact Mass: [M+H]⁺: 507.1536; found: 507.1530.

O,O-diethyl *S*-(2-(3-oxo-4-(3-phenoxypropyl)-3,4-dihydroquinoxalin-2-yl)-2phenylethyl) phosphorodithioate (8)



Yellow oil (72.7 mg, 64%), $R_f = 0.22$ (petroleum ether/EtOAc, 3:1), ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.46 – 7.41 (m, 4H), 7.40 – 7.37 (m, 1H), 7.34 – 7.30 (m, 3H), 7.27 – 7.25 (m, 1H), 7.00 – 6.96 (m, 1H), 6.91 – 6.88 (m, 2H), 5.02 (dd, J = 9.6, 6.1 Hz, 1H), 4.47 – 4.37 (m, 2H), 4.26 – 4.14 (m, 4H), 4.06 – 4.04 (m, 2H), 3.86 (m, 1H), 3.47 (m, 1H), 2.31 – 2.06 (m, 2H), 1.42 – 1.37 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 158.6, 154.2, 139.7, 132.8, 132.6, 130.6, 130.5, 129.7, 128.8, 128.6, 127.6, 123.7, 121.2, 114.6, 113.8, 65.2, 64.0 (d, J = 5.5 Hz), 48.4 (d, J = 4.1 Hz), 40.0, 36.5, 27.3, 16.0 (dd, J = 8.5, 3.5 Hz). **HRMS** (ESI) calculated for C₂₉H₃₄N₂O₄PS₂⁺ Exact Mass: [M+H]⁺: 569.1692; found: 569.1687.

ethyl 2-(3-(2-((diethoxyphosphorothioyl)thio)-1-phenylethyl)-2-oxoquinoxalin-1(2H)-yl)acetate (9)



Yellow oil (73.8 mg, 71%), $R_f = 0.30$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.99 (dd, J = 8.0, 1.4 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.43 – 7.38 (m, 3H), 7.33 – 7.31 (m, 2H), 7.27 – 7.21 (m, 1H), 7.13 – 7.03 (m, 1H), 5.08 – 4.95 (m, 2H), 4.89 (d, J = 17.3 Hz, 1H), 4.27 – 4.15 (m, 4H), 4.15 – 4.04 (m, 2H), 3.85 (m, 1H), 3.48 (m, 1H), 1.42 – 1.35 (m, 6H), 1.23 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 158.8, 153.9, 139.4, 132.7, 132.5, 130.8, 130.5, 128.9, 128.6, 127.6, 124.1, 113.3, 64.0 (d, J = 3.3 Hz), 62.2, 48.5 (d, J = 4.2 Hz), 43.8, 36.6, 16.0 (dd, J = 8.5, 3.6 Hz), 14.2. **HRMS** (ESI) calculated for C₂₄H₃₀N₂O₅PS₂⁺ Exact Mass: [M+H]⁺: 521.1328; found: 521.1322.

methyl 3-(3-(2-((diethoxyphosphorothioyl)thio)-1-phenylethyl)-2-oxoquinoxalin-1(2H)-yl)propanoate (10)



Yellow oil (76 mg, 73%), $R_f = 0.30$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.66 – 7.55 (m, 1H), 7.47 – 7.15 (m, 8H), 5.00 (dd, J = 9.7, 6.1 Hz, 1H), 4.49 (dd, J = 9.5, 6.0 Hz, 2H), 4.33 – 4.05 (m, 4H), 3.90 – 3.80 (m, 1H), 3.65 (s, 3H), 3.50 – 3.42 (m, 1H), 2.80 – 2.65 (m, 2H), 1.45 – 1.35 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 158.8, 154.0, 139.5, 132.9, 132.2, 130.8, 130.6, 128.8, 128.6, 127.6, 123.9, 113.4, 64.0 (t, J = 5.5 Hz), 52.1, 48.4 (d, J = 4.1 Hz), 38.4, 36.5, 31.7, 16.0 (dd, J = 8.5, 4.2 Hz). **HRMS** (ESI) calculated for C₂₄H₃₀N₂O₅PS₂⁺ Exact Mass: [M+H]⁺: 521.1328; found: 521.1323.

tert-butyl (3-(3-((diethoxyphosphorothioyl)thio)-1-phenylethyl)-2oxoquinoxalin-1(2H)-yl)propyl)carbamate (11)



Yellow oil (61.5 mg, 52%), $R_f = 0.21$ (petroleum ether/EtOAc, 2:1), ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.62 – 7.51 (m, 1H), 7.43 – 7.40 (m, 3H), 7.34 – 7.29 (m, 3H), 7.26 – 7.22 (m, 1H), 5.25 (s, 1H), 5.03 (dd, J = 9.7, 6.0 Hz, 1H), 4.35 (dd, J = 13.4, 6.6 Hz, 1H), 4.29 – 4.05 (m, 5H), 3.94 – 3.75 (m, 1H), 3.46 (m, 1H), 3.19 – 2.92 (m, 2H), 1.94 – 1.88 (m, 2H), 1.46 (s, 9H), 1.42 – 1.34 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 156.2, 154.5, 139.6, 133.0, 132.2, 130.7, 130.5, 128.8, 128.5, 127.6), 123.9, 113.7, 79.4, 64.0 (t, J = 5.6 Hz), 48.4 (d, J = 4.0 Hz), 39.8, 37.3,

36.6, 28.6, 27.7, 16.0 (dd, J = 8.5, 3.6 Hz). **HRMS** (ESI) calculated for C₂₈H₃₉N₃O₅PS₂⁺ Exact Mass: [M+H]⁺: 592.2063; found: 592.2059.

O,O-diethyl *S*-(2-(4-(2-hydroxyethyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)-2phenylethyl) phosphorodithioate (12)



Yellow oil (37.3 mg, 39%), $R_f = 0.32$ (petroleum ether/EtOAc, 1:1), ¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, J = 8.0, 1.4 Hz, 1H), 7.62 – 7.52 (m, 1H), 7.47 – 7.37 (m, 5H), 7.31 (dd, J = 10.1, 4.7 Hz, 2H), 7.25 (d, J = 7.3 Hz, 1H), 5.01 (dd, J = 9.6, 6.1 Hz, 1H), 4.51 – 4.30 (m, 2H), 4.29 – 4.05 (m, 4H), 3.99 (t, J = 5.5 Hz, 2H), 3.90 – 3.81 (m, 1H), 3.51-3.43 (m, 1H), 1.44 – 1.33 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 155.2, 139.5, 132.9, 132.8, 130.7, 130.4, 128.8, 128.6, 127.6, 124.0, 114.0, 64.0 (t, J = 5.2 Hz), 60.6, 48.4 (d, J = 4.0 Hz), 45.2, 36.6 (d, J = 3.8 Hz), 16.0 (dd, J = 8.5, 4.0 Hz). **HRMS** (ESI) calculated for C₂₂H₂₈N₂O₄PS₂⁺ Exact Mass: [M+H]⁺: 479.1223; found: 479.1217.

O,O-diethyl *S*-(2-(3-oxo-4-((trimethylsilyl)methyl)-3,4-dihydroquinoxalin-2-yl)-2phenylethyl) phosphorodithioate (13)



Yellow oil (76 mg, 73%), $R_f = 0.41$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.0, 1.5 Hz, 1H), 7.55 (m, 1H), 7.47 – 7.17 (m, 7H), 5.02 (dd, J = 9.8, 5.9 Hz, 1H), 4.33 – 4.05 (m, 4H), 3.98 – 3.81 (m, 2H), 3.75 (d, J = 14.9 Hz, 1H), 3.51 – 3.43 (m, 1H), 1.49 – 1.34 (m, 6H), 0.07 – -0.05 (m, 9H). ¹³C NMR (100 MHz, 100 MHz)

CDCl₃) δ 158.4, 153.9, 139.8, 133.2, 132.9, 130.5, 129.9, 128.7, 128.5, 127.4, 123.4, 114.5, 63.9 (t, *J* = 5.8 Hz), 48.6 (d, *J* = 4.1 Hz), 36.5 (d, *J* = 3.9 Hz), 34.2, 16.0 (dd, *J* = 8.6, 4.1 Hz), -1.3. **HRMS** (ESI) calculated for C₂₄H₃₄N₂O₃PS₂Si⁺ Exact Mass: [M+H]⁺: 521.1512; found: 521.1506.

S-(2-(4-allyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl) *O*,*O*-diethyl phosphorodithioate (14)



Yellow oil (62.5 mg, 66%), $R_f = 0.36$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.0, 1.4 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.47 – 7.41 (m, 2H), 7.41 – 7.35 (m, 1H), 7.33 – 7.23 (m, 4H), 5.89 (m, 1H), 5.24 (m, 1H), 5.14 (dd, J = 17.3, 0.6 Hz, 1H), 5.03 (dd, J = 9.7, 6.1 Hz, 1H), 4.95 – 4.89 (m, 1H), 4.82 – 4.71 (m, 1H), 4.28 – 4.04 (m, 4H), 3.91 – 3.81 (m, 1H), 3.51 – 3.43 (m, 1H), 1.40 (dd, J = 14.9, 7.5 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 153.9, 139.6, 132.8, 132.6, 130.7, 130.5, 130.3, 128.8, 128.6, 127.6, 123.7, 118.3, 114.3, 64.0 (t, J = 5.2 Hz), 48.4 (d, J = 4.2 Hz), 44.8, 36.6, 16.0 (dd, J = 8.6, 3.8 Hz). **HRMS** (ESI) calculated for C_{23H28}N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 475.1273; found: 475.1269.

S-(2-(4-(but-3-en-1-yl)-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl) *O*,*O*diethyl phosphorodithioate (15)



Yellow oil (66.4 mg, 68%), $R_f = 0.36$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.57 – 7.55 (m, 1H), 7.44 – 7.37 (m, 3H), 7.35 – 7.27 (m, 3H), 7.27 – 7.21 (m, 1H), 5.82 (m, 1H), 5.12 – 4.95 (m, 3H), 4.36 – 4.08 (m, 6H), 3.85 (m, 1H), 3.46 m, 1H), 2.46 (dd, J = 14.8, 7.4 Hz, 2H), 1.47 – 1.34 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 154.0, 139.6, 133.9, 132.8, 132.4, 130.7, 130.3, 128.8, 128.6, 127.5, 123.6, 117.8, 113.7, 64.0 (t, J = 5.6 Hz), 48.4 (d, J = 4.2 Hz), 41.8, 36.5, 31.5, 16.0 (dd, J = 8.6, 4.1 Hz). **HRMS** (ESI) calculated for C₂₄H₃₀N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 489.1430; found: 489.1425.

O,O-diethyl *S*-(2-phenyl-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2yl)ethyl) phosphorodithioate (16)



Yellow oil (67.6 mg, 71%), $R_f = 0.35$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H), 7.44 – 7.40 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.19 (m, 1H), 7.06 (s, 1H), 4.99 (dd, J = 9.7, 6.1 Hz, 1H), 4.26 – 4.10 (m, 4H), 3.84 (m, 1H), 3.62 (s, 3H), 3.44 (m, 1H), 2.44 (s, 3H), 2.40 (s, 3H), 1.43 – 1.37 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 157.6, 154.4, 140.2, 139.9, 132.7, 131.4, 131.0, 130.5, 128.8, 128.6, 127.5, 114.3, 64.0 (t, J = 5.7 Hz), 48.4 (d, J = 4.2 Hz), 36.6, 29.2, 20.7, 19.3, 16.0 (dd, J = 8.5, 4.3 Hz). **HRMS** (ESI) calculated for C₂₃H₃₀N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 477.1430; found: 477.1425.

S-(2-(6,7-dichloro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl) *O*,*O*-diethyl phosphorodithioate (17)



Yellow oil (64 mg, 62%), $R_f = 0.30$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 1H), 7.43 – 7.38 (m, 3H), 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 5.01 (dd, J = 9.7, 6.0 Hz, 1H), 4.27 – 4.09 (m, 4H), 3.86 – 3.72 (m, 1H), 3.63 (s, 3H), 3.48 – 3.39 (m, 1H), 1.43 – 1.37 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 153.8, 139.0, 134.5, 132.8, 131.6, 131.1, 128.9, 128.6, 127.8, 127.6, 115.3, 64.1 (t, J = 5.8 Hz), 48.7 (d, J = 3.8 Hz), 36.4 (d, J = 3.6 Hz), 29.5, 16.0 (dd, J = 8.4, 4.6 Hz). **HRMS** (ESI) calculated for C₂₁H₂₄Cl₂N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 517.0338; found: 517.0333.

O,O-dimethyl *S*-(2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl) phosphorodithioate (18)



Yellow oil (64 mg, 76%), $R_f = 0.33$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.60 – 7.58 (m, 1H), 7.46 – 7.38 (m, 3H), 7.35 – 7.29 (m, 3H), 7.27 – 7.21 (m, 1H), 5.01 (dd, J = 9.6, 6.1 Hz, 1H), 3.93 – 3.82 (m, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.65 (s, 3H), 3.45 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 154.4, 139.4, 133.3, 132.6, 130.4, 130.4, 128.8, 128.6, 127.6, 123.8, 113.8, 54.1 (t, J = 5.1 Hz), 48.4 (d, J = 4.0 Hz), 36.6 (d, J = 3.8 Hz), 29.3. **HRMS** (ESI) calculated for C₁₉H₂₂N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 421.0804; found: 421.0801.

O,O-diethyl *S*-(2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-(p-tolyl)ethyl) phosphorodithioate (19)



Yellow oil (68.4 mg, 74%), $R_f = 0.33$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, J = 8.0, 1.4 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.42 – 7.36 (m, 1H), 7.31 (dd, J = 11.3, 8.8 Hz, 3H), 7.12 (d, J = 7.9 Hz, 2H), 4.98 (dd, J = 9.7, 6.1 Hz, 1H), 4.30 – 4.08 (m, 4H), 3.85 (m, 1H), 3.64 (s, 3H), 3.45 (m, 1H), 2.31 (s, 3H), 1.47 – 1.35 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 154.3, 137.3, 136.5, 133.3, 132.6, 130.3, 130.3, 129.5, 128.4, 123.7, 113.7, 64.0 (t, J = 5.7 Hz), 48.1 (d, J = 4.0 Hz), 36.4 (d, J = 3.7 Hz), 29.2, 21.2, 16.0 (dd, J = 8.6, 4.4 Hz). **HRMS** (ESI) calculated for C₂₂H₂₈N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 463.1273; found: 463.1267.

S-(2-(4-chlorophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)ethyl) *O*,*O*diethyl phosphorodithioate (20)



Yellow oil (73.2 mg, 73%), $R_f = 0.30$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, J = 8.0, 1.4 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.44 – 7.36 (m, 3H), 7.33 – 7.26 (m, 3H), 5.00 (dd, J = 9.4, 6.3 Hz, 1H), 4.24 – 4.12 (m, 4H), 3.83 (m, 1H), 3.65 (s, 3H), 3.44 (m, 1H), 1.43 – 1.37 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.5, 154.3, 138.1, 133.5, 133.3, 132.5, 130.6, 130.4, 130.0, 129.0, 123.9, 113.8, 64.1 (dd, J = 5.7, 4.0 Hz), 47.9 (d, J = 4.0 Hz), 36.5 (d, J = 3.7 Hz), 29.3, 16.0 (dd, J = 8.5, 4.5 Hz). HRMS (ESI) calculated for C₂₁H₂₅ClN₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 483.0727; found: 483.0724.

S-(2-(4-bromophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)ethyl) *O*,*O*diethyl phosphorodithioate (21)



Yellow oil (74.2 mg, 71%), $R_f = 0.30$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, J = 8.0, 1.2 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.46 – 7.37 (m, 3H), 7.32 (d, J = 8.5 Hz, 3H), 4.99 (dd, J = 9.3, 6.3 Hz, 1H), 4.32 – 4.04 (m, 4H), 3.83 (m, 1H), 3.65 (s, 3H), 3.44 (m, 1H), 1.42 – 1.36 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.5, 154.3, 138.6, 133.3, 132.5, 131.9, 130.6, 130.5, 130.4, 123.9, 121.7, 113.8, 64.1 (dd, J = 5.7, 4.0 Hz), 48.0 (d, J = 4.0 Hz), 36.4 (d, J = 3.6 Hz), 29.3, 16.0 (dd, J = 8.4, 4.5 Hz). **HRMS** (ESI) calculated for C₂₁H₂₅BrN₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 527.0222; found: 527.0219.

methyl 4-(2-((diethoxyphosphorothioyl)thio)-1-(4-methyl-3-oxo-3,4dihydroquinoxalin-2-yl)ethyl)benzoate (22)



Yellow oil (67.8 mg, 67%), $R_f = 0.29$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.94 (m, 3H), 7.62 – 7.57 (m, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.45 – 7.37 (m, 1H), 7.32 (dd, J = 8.4, 0.8 Hz, 1H), 5.08 (dd, J = 9.4, 6.3 Hz, 1H), 4.27 – 4.07 (m, 4H), 3.95 – 3.80 (m, 4H), 3.65 (s, 3H), 3.47 (m, 1H), 1.44 – 1.34 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 158.3, 154.3, 144.8, 133.4, 132.6, 130.6, 130.5, 130.1, 129.5, 128.7, 123.9, 113.8, 64.1 (t, J = 5 Hz), 52.2, 48.5 (d, J = 3.9 Hz), 36.3 (d, J = 3.6 Hz), 29.3, 16.0 (dd, J = 8.4, 4.9 Hz). **HRMS** (ESI) calculated for C₂₃H₂₈N₂O₅PS₂⁺ Exact Mass: [M+H]⁺: 507.1172; found: 507.1166.

O,O-diethyl *S*-(2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-(m-tolyl)ethyl) phosphorodithioate (23)



Yellow oil (65.6 mg, 71%), $R_f = 0.31$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.44 – 7.36 (m, 1H), 7.31 (dd, J = 8.4, 0.8 Hz, 1H), 7.20 (dd, J = 13.4, 6.3 Hz, 3H), 7.06 (d, J = 7.0 Hz, 1H), 4.98 (dd, J = 9.8, 5.9 Hz, 1H), 4.26 – 4.12 (m, 4H), 3.85 (m, 1H), 3.65 (s, 3H), 3.44 (m, 1H), 2.33 (s, 3H), 1.44 – 1.37 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 154.4, 139.5, 138.4, 133.4, 132.6, 130.4, 130.3, 129.3, 128.7, 128.4, 125.6, 123.7, 113.7, 64.0 (t, J = 5.9 Hz), 48.5 (d, J = 4.1 Hz), 36.5 (d, J = 3.7 Hz), 29.3, 21.6, 16.0 (dd, J = 8.5, 4.4 Hz). HRMS (ESI) calculated for C₂₂H₂₈N₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 463.1273; found: 463.1270.

S-(2-(3-chlorophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)ethyl) *O*,*O*diethyl phosphorodithioate (24)



Yellow oil (67.5 mg, 70%), $R_f = 0.31$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.45 – 7.31 (m, 4H), 7.28 – 7.20 (m, 2H), 5.00 (dd, J = 9.5, 6.2 Hz, 1H), 4.30 – 4.07 (m, 4H), 3.83 (m, 1H), 3.66 (s, 3H), 3.44 (m, 1H), 1.43 – 1.37 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 154.3, 141.6, 134.6, 133.4, 132.6, 130.6, 130.5, 130.1, 128.4, 127.9 127.2, 123.9, 113.8, 64.1 (t, J = 5.5 Hz), 48.2 (d, J = 4.0 Hz), 36.5, 29.3, 16.0 (dd, J = 8.4, 4.9 Hz). **HRMS** (ESI) calculated for C₂₁H₂₅ClN₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 483.0727; found: 483.0723.

S-(2-(2-chlorophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)ethyl) *O*,*O*diethyl phosphorodithioate (25)



Yellow oil (60.7 mg, 63%), $R_f = 0.30$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, J = 8.0, 1.4 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.48 – 7.39 (m, 2H), 7.34 (dd, J = 8.4, 0.9 Hz, 1H), 7.22 – 7.10 (m, 3H), 5.51 (dd, J = 10.0, 5.4 Hz, 1H), 4.27 – 4.12 (m, 4H), 3.82 – 3.68 (m, 1H), 3.66 (d, J = 2.7 Hz, 3H), 3.40 (m, 1H), 1.43 – 1.37 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 154.2, 137.4, 135.0, 133.4, 132.4, 130.7, 130.5, 130.3, 128.7, 128.5, 127.0, 123.8, 113.8, 64.0 (dd, J = 15.7, 5.5 Hz), 45.0 (d, J = 4.4 Hz), 35.3 (d, J = 4.1 Hz), 29.3, 16.0 (dd, J = 8.4, 5.2 Hz). **HRMS** (ESI) calculated for C₂₁H₂₅ClN₂O₃PS₂⁺ Exact Mass: [M+H]⁺: 483.0727; found: 483.0722.

O,O-diethyl *S*-(2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl) phosphorothioate (27)



Yellow oil (26.8 mg, 31%), $R_f = 0.25$ (petroleum ether/EtOAc, 4:1), ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.0, 1.4 Hz, 1H), 7.57 (ddd, J = 8.6, 7.5, 1.5 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.34 – 7.15 (m, 5H), 5.01 (dd, J = 9.3, 6.4 Hz, 1H), 4.27 – 4.05 (m, 4H), 3.90 – 3.81 (m, 1H), 3.65 (s, 3H), 3.49 – 3.41 (m, 1H), 1.46 – 1.33 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 154.3, 139.4, 133.3, 132.6, 130.4, 128.8, 128.7, 127.6, 123.8, 113.8, 63.6 (t, J = 5.3 Hz), 48.7 (d, J = 5.0 Hz), 34.1 (d, J = 3.6 Hz), 29.3, 16.2 (dd, J = 7.3, 2.2 Hz). **HRMS** (ESI) calculated for C₂₁H₂₆N₂O₄PS⁺ Exact Mass: [M+H]⁺: 433.1345; found: 433.1341.

10. The NMR spectra



¹H NMR of 4

¹³C NMR of 4





¹³C NMR of **5**







7.97 7.95 7.56 -7.56 -7.56 -7.55 -7.54 -7.52 -7.52 -7.54 -7.52 -7.53 -7.34 -7.39 -7.39 -7.35 -7.35 -7.35 -7.35 -7.35 -7.35 -7.32 -7.30 -7.30 -7.30 -7.30 -7.30 -7.30 -7.30 -7.32 -7.25 -7.25 -7.25 -7.25 -7.25 -7.25 -7.25 -7.25 -7.25 -7.25 -7.25 -7.25 -7.25 -7.23 -7.25 -7.25 -7.23 -7.25 -7.23 -7.25 -7.23 -7.25 -7.23 -7.25 -7.23 -7.23 -7.25 -7.23 -7.24 -7.23 -7.24 -7.23 -7.24 -7.

¹³C NMR of **6**



S24

¹H NMR of **7**



¹³C NMR of **7**



 1 H NMR of **8**



¹³C NMR of 8





¹³C NMR of **9**





S31

¹³C NMR of **10**



¹H NMR of **11**



¹³C NMR of **11**









 1 H NMR of **13**



¹³C NMR of **13**







¹³C NMR of **14**





 $\begin{array}{c} 7.98\\ 7.98\\ 7.96\\ 7.96\\ 7.96\\ 7.59\\ 7.56\\ 7.55\\ 7.55\\ 7.55\\ 7.55\\ 7.55\\ 7.57\\ 7.26\\ 7.26\\ 5.83\\ 5.79\\ 7.26\\ 5.83\\ 5.79\\ 7.26\\ 5.83\\ 5.79\\ 7.26\\ 5.83\\ 5.79\\ 5.00\\$

¹³C NMR of **15**





¹³C NMR of **16**





¹³C NMR of **17**



¹H NMR of **18**



¹³C NMR of **18**



¹H NMR of **19**





 1 H NMR of **20**



¹³C NMR of **20**



¹H NMR of **21**





¹³C NMR of **21**



¹H NMR of **22**



¹³C NMR of **22**



 1 H NMR of **23**







S57

¹³C NMR of **23**





¹³C NMR of **24**



¹H NMR of **25**





¹³C NMR of **25**



¹H NMR of **27**



180 170 160 Ś P_OEt 150140-139.44 133.31 132.57 130.36 128.77 128.65 127.59 123.76 130 120 -113.75 110 100 90 f1 -1 (ppm) √
77.48
√
77.16
√
76.84
 70 63.66 63.61 63.55 60 <48.69 48.64 $\overline{0}$ 40 <34.13 34.09 30 -29.26 (16.26 16.24 16.19 16.16 20 10 0

-10