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TRANSITION METAL-FREE *O*-ARYLATION OF QUINOXALIN-2-ONES WITH DIARYLIODONIUM SALTS

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Abstract – The transition metal-free *O*-arylation reactions of quinoxalin-2-ones with diaryliodonium salts have been achieved, and desired 2-aryloxyquinoxalines were readily obtained in moderate to high yields. This method proved to be compatible with a series of diaryliodonium salts as well as a set of quinoxalin-2-ones.

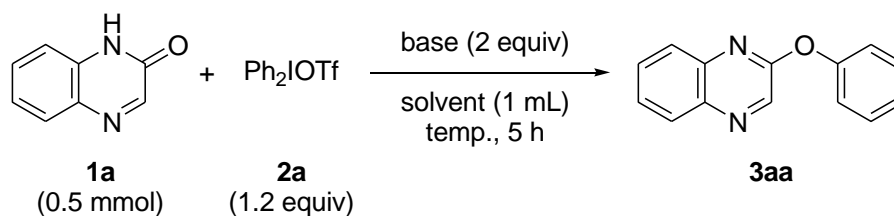
In terms of pharmaceutical research and process development, *O*-arylation reactions are a highly important transformation,^{1,2} and their catalytic and non-catalytic methods have been strenuously investigated.^{3,4} Quinoxalin-2-ones have a tautomerizable amide moiety, and their *O*-arylated structures are known as key frameworks of biologically active compounds.⁵ Although the *O*-arylation of quinoxalin-2-ones is a useful and desirable method for the synthesis of 2-aryloxyquinoxalines, this type of arylation process is quite rare. In the synthesis of a bioactive agent, the copper-catalyzed C–O coupling of quinoxalin-2-one with 4-bromo-1-methylindole was reported.⁶ The unexpected formation of 2-(*o*-tolylxy)quinoxaline as a side product in a low yield was found in a transition metal-free process with quinoxalin-2-one and an organo-bismuth compound.⁷ Recently, diaryliodonium salts have attracted much attention as mild, less-toxic, and easily accessible reagents,⁸ and transition metal-free carbon–heteroatom bond forming reactions have been actively pursued by using these arylating agents,⁹ which produced a few examples of the *O*-arylation for pyridin-2-ones or quinolin-2-ones. Herein, we report an *O*-arylation method for quinoxalin-2-ones with diaryliodonium salts under transition metal-free conditions.

At the beginning, a series of bases were screened in the *O*-phenylation of quinoxalin-2-one (**1a**) with diphenyliodonium triflate (**2a**) in *o*-xylene at 130 °C (Table 1). In the examination of alkali metal carbonates, cesium carbonate turned out to be superior, giving the desired product **3aa** in 55% yield (entries 1-3).

Dedicated with respect to Dr. Yasuyuki Kita on the occasion of his 77th birthday

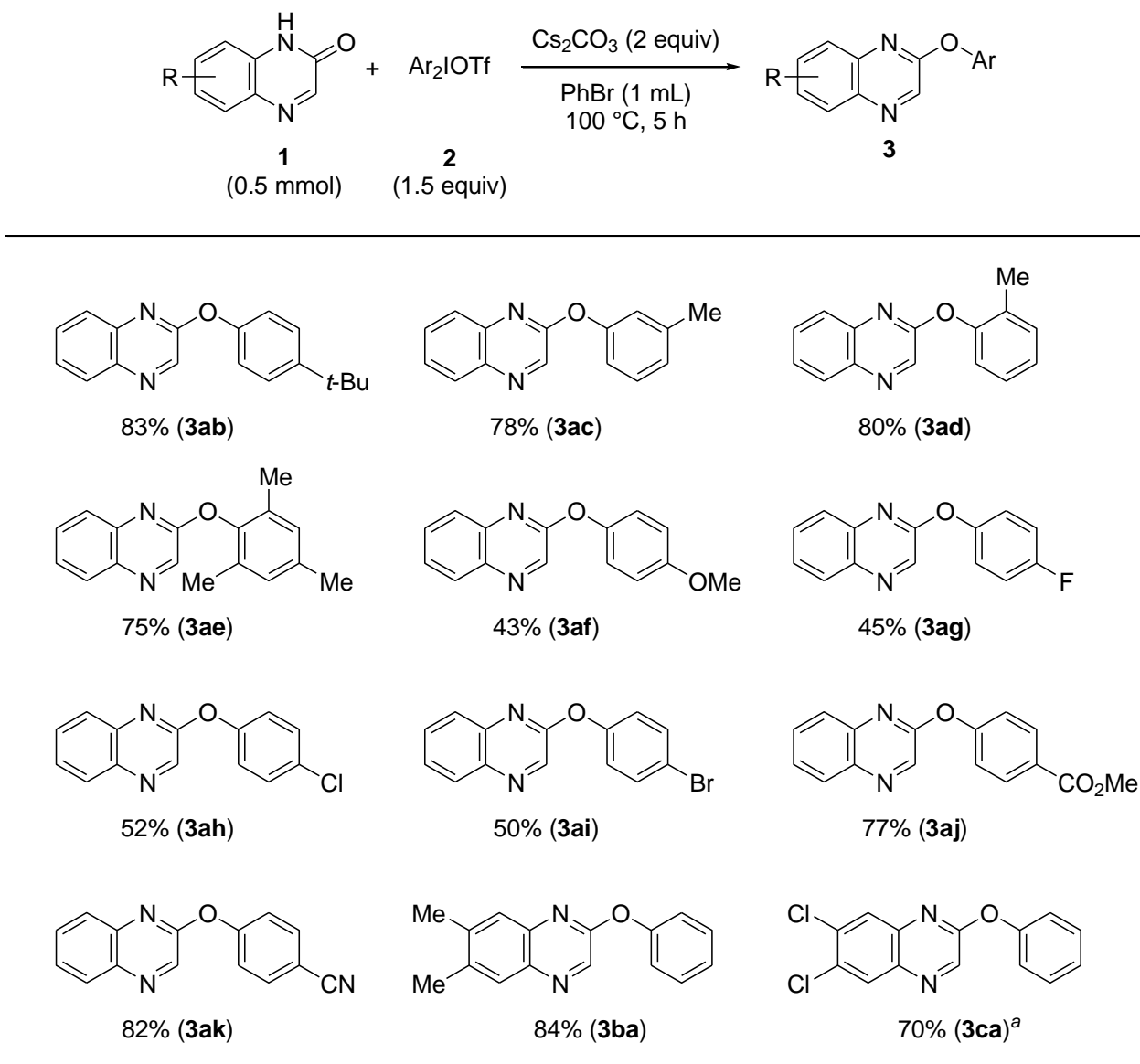
The use of potassium phosphate tribasic resulted in 61% yield (entry 4), although potassium *tert*-butoxide and potassium fluoride led to decrease in yield (entries 5-6). Subsequently, a set of organic bases were tested. In the presence of DMAP, DIPEA, and DBU, the *O*-phenylated product **3aa** was obtained in low yields, while pyridine was ineffective in this transformation (entries 7-10). At a lower temperature, better results were observed especially when using cesium carbonate (entry 11 vs. entry 12). Then, the investigation of solvents proved that less polar solvents showed a tendency to provide the desired product **3aa** in higher yields (entry 13 vs. entries 14-15). Chlorobenzene and bromobenzene were more suitable as reaction solvents (entries 16-17), and the reaction conditions with 1.5 equivalents of Ph₂IOTf (**2a**) in bromobenzene conducted to 89% yield of the *O*-phenylated product **3aa** (entry 18).

Table 1. Optimization of reaction conditions

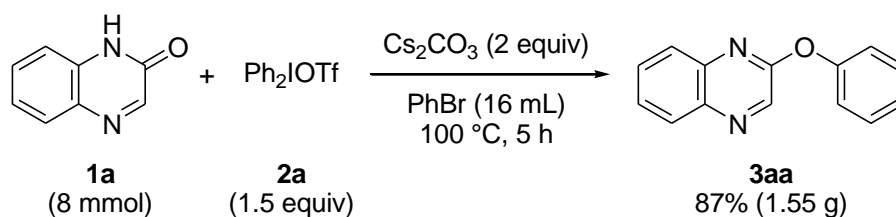


entry	base	solvent	temp. (°C)	yield (%)
1	Na ₂ CO ₃	<i>o</i> -xylene	130	43
2	K ₂ CO ₃	<i>o</i> -xylene	130	46
3	Cs ₂ CO ₃	<i>o</i> -xylene	130	55
4	K ₃ PO ₄	<i>o</i> -xylene	130	61
5	KOt-Bu	<i>o</i> -xylene	130	35
6	KF	<i>o</i> -xylene	130	34
7	pyridine	<i>o</i> -xylene	130	0
8	DMAP	<i>o</i> -xylene	130	10
9	DIPEA	<i>o</i> -xylene	130	16
10	DBU	<i>o</i> -xylene	130	26
11	Cs ₂ CO ₃	<i>o</i> -xylene	100	67
12	K ₃ PO ₄	<i>o</i> -xylene	100	62
13	Cs ₂ CO ₃	toluene	100	70
14	Cs ₂ CO ₃	dioxane	100	38
15	Cs ₂ CO ₃	DMF	100	4
16	Cs ₂ CO ₃	PhCl	100	72
17	Cs ₂ CO ₃	PhBr	100	75
18 ^a	Cs ₂ CO ₃	PhBr	100	89

^a Ph₂IOTf (1.5 equiv).

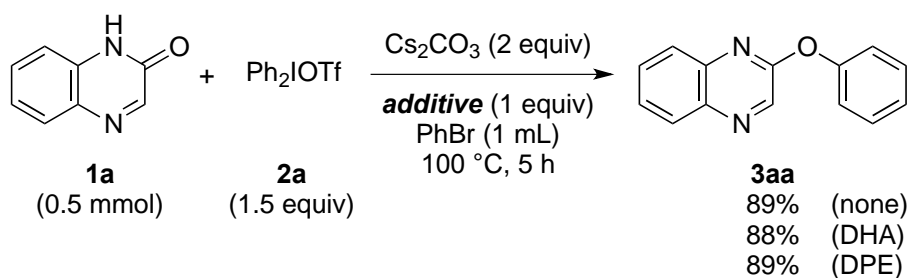
Table 2. Scope of substrates^a 90 °C.

The influence of various diaryliodonium triflates was studied (Table 2). The arylation reactions with *para*- and *meta*-alkylated arylating agents smoothly proceeded to give **3ab** and **3ac** in high yields. The steric hindrance close to a reaction site did not cause significant decrease in yield (**3ad-ae**). As well as an electron-donating group, halogen substituents in diaryliodonium salts led to moderate yields (**3af-ai**). An ester moiety in addition to a cyano group was tolerated in the reaction conditions (**3aj-ak**). Subsequently, a set of quinoxalin-2-ones were tested. The quinoxalin-2-one with methyl groups gave the desired product **3ba** in a high yield. A dichlorinated framework was also suitable in this transformation although slight decrease in yield was observed (**3ca**).



Scheme 1. Gram-scale reaction

The examination of the scalability was conducted under typical conditions (Scheme 1). Quinoxalin-2-one (**1a**) was readily converted on 8 mmol scale, and 1.55 g of the desired product **3aa** was obtained. Then, 9,10-dihydroanthracene (DHA) and 1,1-diphenylethylene (DPE) were examined as radical scavengers in order to acquire further information of this process (Scheme 2). The phenylation reactions proceeded with no problems even in the presence of these radical trapping reagents, suggesting that single electron transfer processes might not be included.



Scheme 2. *O*-Phenylation of **1a** in the presence of radical scavengers

In summary, the *O*-arylation reactions of quinoxalin-2-ones with diaryliodonium salts were developed under transition metal-free conditions. This method tolerated a series of diaryliodonium salts in addition to a set of quinoxalin-2-ones, and desired 2-aryloxyquinoxalines were synthesized in moderate to high yields. Our further efforts are focused on the investigation of reaction mechanism and application towards the synthesis of biologically active molecules.

EXPERIMENTAL

General. All melting points are not corrected. IR spectra were expressed in cm⁻¹. ¹H NMR spectra were measured at 500 MHz, and ¹³C NMR spectra were taken at 100 or 125 MHz. Chemical shift values are expressed in ppm relative to internal or external TMS. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectra (HRMS) were recorded using electron ionization (EI) or fast atom bombardment (FAB) mass spectrometry. The products were isolated by silica gel column chromatography. The quinoxalin-2-ones **1b-c**¹⁰ and diaryliodonium salts **2b-f**,¹¹ **2g**,¹²

and **2h-j**¹¹ were prepared on the basis of previous reports. All reagents and solvents were used as received without further purification.

Bis(4-cyanophenyl)iodonium triflate (2k). Under an argon atmosphere, MCPBA (1.1 mmol, 82% active oxidant) was charged in a reaction flask and dissolved in CH₂Cl₂ (5.0 mL). To the solution was added 4-iodobenzonitrile (229 mg, 1.0 mmol) followed by BF₃·OEt₂ (2.5 mmol) at room temperature. The mixture was stirred at room temperature for 1.5 h. Then, 4-cyanophenylboronic acid (162 mg, 1.1 mmol) was added at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was stirred at room temperature for 1 h. TFOH (0.1 mL, 1.1 mmol) was added dropwise at 0 °C, and the mixture was stirred at room temperature for 20 min. The resulting mixture was applied on an alumina plug (3 g) and eluted with CH₂Cl₂ (25 mL) and CH₂Cl₂/MeOH (20:1, 50 mL). The fraction eluted with CH₂Cl₂/MeOH was concentrated. The resulting solids were washed with Et₂O, filtered, and dried in vacuo to give 230 mg of **2k** (0.48 mmol, 48%) as yellow solids of mp 219-221 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 8.04 (d, *J* = 8.3 Hz, 4H), 8.47 (d, *J* = 8.3 Hz, 4H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 115.0 (C), 117.5 (C), 120.7 (q, *J* = 322.4 Hz, C), 121.6 (C), 135.2 (CH), 136.1 (CH). ¹⁹F NMR (470 MHz, CDCl₃): δ -73.0. IR (ATR): 820, 1220, 2230 cm⁻¹. HRMS (FAB) *m/z* Calcd for C₁₄H₈N₂I ([M-OTf]⁺): 330.9732. Found: 330.9732.

Typical procedure for *O*-arylation reactions of quinoxalin-2-ones with diaryliodonium salts. Under an argon atmosphere, a test tube was charged with quinoxalin-2-one (**1a**) (73 mg, 0.5 mmol), diphenyliodonium triflate (**2a**) (323 mg, 0.75 mmol), and Cs₂CO₃ (326 mg, 1.0 mmol). Then, bromobenzene (1.0 mL) was added. The reaction mixture was stirred at 100 °C for 5 h. After water and saturated Na₂CO₃ were added at room temperature, the resulting mixture was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄. Concentration and purification through silica gel column chromatography gave the desired product **3aa**.

2-Phenoxyquinoxaline¹³ (**3aa**). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 99 mg of the product (0.45 mmol, 89%) as white solids of mp 98-100 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.28-7.30 (m, 3H), 7.47 (t, *J* = 8.1 Hz, 2H), 7.60-7.63 (m, 1H), 7.66 (dt, *J* = 1.5, 8.1 Hz, 1H), 7.77 (dd, *J* = 1.0, 8.3 Hz, 1H), 8.07 (dd, *J* = 1.0, 8.3 Hz, 1H), 8.70 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 121.4 (CH), 125.4 (CH), 127.5 (CH), 127.8 (CH), 129.0 (CH), 129.7 (CH), 130.4 (CH), 139.3 (CH), 139.7 (C), 140.1 (C), 152.9 (C), 157.0 (C). IR (ATR): 710, 1210, 1490 cm⁻¹. HRMS (EI) *m/z* (M⁺) Calcd for C₁₄H₁₀N₂O: 222.0793. Found: 222.0793.

2-(4-*tert*-Butylphenoxy)quinoxaline¹⁴ (3ab). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 116 mg of the product (0.42 mmol, 83%) as light yellow solids of mp 62-63 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.37 (s, 9H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.59-7.68 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 8.68 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 31.5 (CH₃), 34.5 (C), 120.6 (CH), 126.5 (CH), 127.3 (CH), 127.7 (CH), 128.9 (CH), 130.3 (CH), 139.3 (CH), 139.5 (C), 140.0 (C), 148.1 (C), 150.4 (C), 157.0 (C). IR (ATR): 830, 1210, 1500 cm⁻¹. HRMS (EI) *m/z* (M⁺) Calcd for C₁₈H₁₈N₂O: 278.1419. Found: 278.1419.

2-(*m*-Tolyloxy)quinoxaline (3ac). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 92 mg of the product (0.39 mmol, 78%) as light yellow solids of mp 92-95 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.41 (s, 3H), 7.08-7.11 (m, 3H), 7.33-7.36 (m, 1H), 7.60-7.68 (m, 2H), 7.79 (dd, *J* = 0.7, 8.3 Hz, 1H), 8.05-8.07 (m, 1H), 8.68 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 21.4 (CH₃), 118.3 (CH), 121.8 (CH), 126.1 (CH), 127.3 (CH), 127.7 (CH), 128.8 (CH), 129.3 (CH), 130.2 (CH), 139.2 (CH), 139.5 (C), 139.8 (C), 140.0 (C), 152.7 (C), 156.9 (C). IR (ATR): 760, 1210, 1490 cm⁻¹. HRMS (EI) *m/z* (M⁺) Calcd for C₁₅H₁₂N₂O: 236.0950. Found: 236.0950.

2-(*o*-Tolyloxy)quinoxaline⁷ (3ad). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 95 mg of the product (0.40 mmol, 80%) as light yellow solids of mp 87-89 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.22 (s, 3H), 7.17-7.24 (m, 2H), 7.26-7.34 (m, 2H), 7.58-7.62 (m, 1H), 7.64 (dt, *J* = 1.2, 8.3 Hz, 1H), 7.74 (dd, *J* = 1.0, 8.3 Hz, 1H), 8.06 (dd, *J* = 1.0, 8.3 Hz, 1H), 8.71 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 16.4 (CH₃), 121.9 (CH), 125.8 (CH), 127.1 (CH), 127.3 (CH), 127.8 (CH), 128.9 (CH), 130.4 (CH), 130.7 (C), 131.5 (CH), 138.9 (CH), 139.6 (C), 140.3 (C), 151.3 (C), 156.9 (C). IR (ATR): 760, 1210, 1490 cm⁻¹. HRMS (EI) *m/z* (M⁺) Calcd for C₁₅H₁₂N₂O: 236.0950. Found: 236.0950.

2-(Mesityloxy)quinoxaline¹⁴ (3ae). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 99 mg of the product (0.37 mmol, 75%) as light brown solids of mp 69-72 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.11 (s, 6H), 2.35 (s, 3H), 6.96 (s, 2H), 7.57-7.65 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.71 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 16.6 (CH₃), 20.9 (CH₃), 127.0 (CH), 127.7 (CH), 128.8 (CH), 129.3 (CH), 130.1 (CH), 130.3 (C), 135.0 (C), 138.5 (CH), 139.4 (C), 140.4 (C), 147.4 (C), 156.3 (C). IR (ATR): 750, 1300, 1570 cm⁻¹. HRMS (EI) *m/z* (M⁺) Calcd for C₁₇H₁₆N₂O: 234.1263. Found: 234.1262.

2-(4-Methoxyphenoxy)quinoxaline¹⁴ (3af). Silica gel column chromatography (hexane/EtOAc = 5/1) gave 54 mg of the product (0.21 mmol, 43%) as light yellow solids of mp 146-148 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.86 (s, 3H), 6.98 (d, *J* = 9.1 Hz, 2H), 7.21 (d, *J* = 9.1 Hz, 2H), 7.59-7.67 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.68 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 55.6 (CH₃), 114.6 (CH), 122.3 (CH), 127.2 (CH), 127.7 (CH), 128.8 (CH), 130.3 (CH), 139.2 (CH), 139.5 (C), 140.0

(C), 146.1 (C), 156.9 (C), 157.2 (C). IR (ATR): 760, 1180, 1240, 1500 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2$: 252.0899. Found: 252.0899.

2-(4-Fluorophenoxy)quinoxaline¹⁴ (3ag). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 54 mg of the product (0.23 mmol, 45%) as light brown solids of mp 103-105 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.15 (t, J = 8.3 Hz, 2H), 7.25-7.27 (m, 2H), 7.60-7.64 (m, 1H), 7.67 (dt, J = 1.2, 8.3 Hz, 1H), 7.75-7.76 (m, 1H), 8.07 (d, J = 8.1 Hz, 1H), 8.70 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 116.3 (d, J = 24.0 Hz, CH), 123.0 (d, J = 8.3 Hz, CH), 127.6 (CH), 127.7 (CH), 129.0 (CH), 130.5 (CH), 139.1 (CH), 139.7 (C), 139.9 (C), 148.5 (C), 156.9 (C), 160.1 (d, J = 244.2 Hz, C). ^{19}F NMR (470 MHz, CDCl_3): δ -117.4. IR (ATR): 760, 1220, 1500 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{14}\text{H}_9\text{FN}_2\text{O}$: 240.0699. Found: 240.0698.

2-(4-Chlorophenoxy)quinoxaline (3ah). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 67 mg of the product (0.26 mmol, 52%) as white solids of mp 102-104 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.24-7.26 (m, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.61-7.65 (m, 1H), 7.68 (dt, J = 1.2, 8.3 Hz, 1H), 7.76 (dd, J = 1.0, 8.3 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 8.70 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 122.9 (CH), 127.67 (CH), 127.71 (CH), 129.0 (CH), 129.7 (CH), 130.6 (CH), 130.7 (C), 139.1 (CH), 139.79 (C), 139.84 (C), 151.2 (C), 156.6 (C). IR (ATR): 760, 1210, 1490 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{14}\text{H}_9^{35}\text{ClN}_2\text{O}$: 256.0403. Found: 256.0401.

2-(4-Bromophenoxy)quinoxaline (3ai). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 75 mg of the product (0.25 mmol, 50%) as light yellow solids of mp 121-124 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.20 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.62-7.70 (m, 2H), 7.76 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 8.70 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 118.3 (C), 123.3 (CH), 127.6 (CH), 127.7 (CH), 128.9 (CH), 130.5 (CH), 132.6 (CH), 139.0 (CH), 139.7 (C), 139.8 (C), 151.7 (C), 156.5 (C). IR (ATR): 760, 1210, 1480 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{14}\text{H}_9^{79}\text{BrN}_2\text{O}$: 299.9898. Found: 299.9898.

Methyl 4-(quinoxalin-2-yloxy)benzoate (3aj). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 108 mg of the product (0.39 mmol, 77%) as white solids of mp 146-148 °C. ^1H NMR (500 MHz, CDCl_3): δ 3.95 (s, 3H), 7.38 (d, J = 8.8 Hz, 2H), 7.63-7.67 (m, 1H), 7.69 (dt, J = 1.2, 8.3 Hz, 1H), 7.77 (dd, J = 1.2, 8.6 Hz, 1H), 8.08-8.10 (m, 1H), 8.16 (d, J = 8.8 Hz, 2H), 8.73 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 52.1 (CH_3), 121.1 (CH), 127.1 (C), 127.7 (CH), 127.8 (CH), 129.0 (CH), 130.6 (CH), 131.4 (CH), 139.1 (CH), 139.8 (C), 139.9 (C), 156.3 (C), 156.6 (C), 166.4 (C). IR (ATR): 760, 1220, 1500, 1710 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_3$: 280.0848. Found: 280.0849.

2-(4-Cyanophenoxy)quinoxaline (3ak). Silica gel column chromatography (hexane/EtOAc = 3/1) gave 101 mg of the product (0.41 mmol, 82%) as light brown solids of mp 185-187 °C. ^1H NMR (500 MHz,

CDCl₃): δ 7.46 (d, J = 8.6 Hz, 2H), 7.66-7.73 (m, 2H), 7.77-7.78 (m, 3H), 8.10-8.11 (m, 1H), 8.75 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 109.0 (C), 118.4 (C), 122.2 (CH), 127.6 (CH), 128.1 (CH), 129.0 (CH), 130.8 (CH), 133.9 (CH), 138.9 (CH), 139.5 (C), 140.0 (C), 155.7 (C), 156.1 (C). IR (ATR): 770, 1220, 1500, 2230 cm⁻¹. HRMS (EI) m/z (M⁺) Calcd for C₁₅H₉N₃O: 247.0746. Found: 247.0746.

6,7-Dimethyl-2-phenoxyquinoxaline (3ba). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 105 mg of the product (0.42 mmol, 84%) as white solids of mp 127-129 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.41 (s, 3H), 2.45 (s, 3H), 7.26-7.28 (m, 3H), 7.45 (t, J = 7.8 Hz, 2H), 7.54 (s, 1H), 7.80 (s, 1H), 8.59 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 20.0 (CH₃), 20.2 (CH₃), 121.3 (CH), 125.1 (CH), 127.1 (CH), 128.1 (CH), 129.6 (CH), 137.5 (C), 137.9 (CH), 138.5 (C), 138.6 (C), 140.8 (C), 153.0 (C), 156.7 (C). IR (ATR): 790, 1210, 1490 cm⁻¹. HRMS (EI) m/z (M⁺) Calcd for C₁₆H₁₄N₂O: 250.1106. Found: 250.1106.

6,7-Dichloro-2-phenoxyquinoxaline (3ca). Silica gel column chromatography (hexane/EtOAc = 20/1) gave 102 mg of the product (0.35 mmol, 70%) as white solids of mp 128-130 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.26 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.88 (s, 1H), 8.17 (s, 1H), 8.69 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 121.4 (CH), 125.8 (CH), 128.3 (CH), 129.5 (CH), 129.7 (CH), 131.5 (C), 134.8 (C), 138.2 (C), 138.8 (C), 140.4 (CH), 152.2 (C), 157.4 (C). IR (ATR): 680, 770, 1210, 1490 cm⁻¹. HRMS (EI) m/z (M⁺) Calcd for C₁₄H₈³⁵Cl₂N₂O: 290.0014. Found: 290.0014.

ACKNOWLEDGEMENTS

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