Regioselective Suzuki–Miyaura Cross-Coupling Reactions of 2,6-Dichloroquinoxaline

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Abstract: A variety of mono- and diarylated quinoxaline derivatives were prepared by site-selective Suzuki–Miyaura cross-coupling reactions of 2,6-dichloroquinoxaline. The selectivity is controlled by electronic parameters.

Key words: catalysis, palladium, Suzuki reaction, quinoxalines, regioselectivity

Quinoxalines[1] show a broad spectrum of biological activities, including antifungal,[2] antihistaminic, antioxidant and anti-inflammatory,[3] antibacterial,[4] antiamoebic,[5] antiproliferative,[6] fungicidal and algicidal,[7] antimalarial and antileishmanial,[8] cytotoxic,[9] anticancer,[10] anti-HIV and anti-HCV,[11] and antituberculosis activity.[12] In addition, quinoxalines represent potent and selective class III tyrosine kinase inhibitors[13] and potential influenza NS1A protein inhibitors.[14] Certain quinoxalines containing an octadepsipeptide substructure, such as echinomycin and triostin A, have been reported as antibacterial and antitumor agents, and as potent inhibitors of RNA synthesis.[15] Quinoxaline-derived molecules have been also studied as thermoplastics[16] and, due to their bipolar character, as potential emissive and electron-transport moieties and, hence, as potential building blocks for the synthesis of organic semiconductors.[17] In recent years, site-selective palladium-catalyzed cross-coupling reactions of polyhalogenated heterocyclic substrates have been studied.[18] Herein, we report what are, to the best of our knowledge, the first Suzuki–Miyaura cross-coupling reactions of 2,6-dichloroquinoxaline.[19] These reactions proceed with excellent site selectivity, which is controlled by electronic parameters, and provide a convenient approach to various pharmacologically relevant quinoxaline derivatives.

The reaction of commercially available 2,6-dichloroquinoxaline (**1**) with arylboronic acids **2a**–**t** (1.3 equiv) afforded the 2-aryl-6-chloroquinoxalines **3a**–**t** in 23–97% yield (Scheme 1, Table 1). The reaction conditions were systematically optimized for derivative **3c** (Table 2) in order to isolate the products in optimal yields. Both electron-poor and electron-rich arylboronic acids could be successfully employed. In the case of arylboronic acids **2d**,**l**,**r**,**t**, the yields were relatively low because of their electron-poor character and low reactivity. In the case of products **3d**,**k**,**l**,**n**,**q**,**r**,**t**, a small amount of starting material could be recovered and a small amount of the corresponding diarylated quinoxaline was formed (less than 5%). Due to the more difficult chromatographic separation, the yields were lower. The best yields were observed using tetrahydrofuran as the solvent, $Pd(PPh_3)_4$ (5 mol%) as the catalyst, and K_3PO_4 (2 equiv) as the base. The reactions were carried out at 90 °C for 8 hours (see Table 2,

Table 1 Synthesis of **3a**–**t**

2, **3**	Ar	Yield[a] (%) of **3**
a	2-Tol	77
b	3-Tol	67
c	4-Tol	75
d	2,6-$Me_2C_6H_3$	37
e	3,5-$Me_2C_6H_3$	90
f	2,4,6-$Me_3C_6H_2$	96
g	2-$MeOC_6H_4$	72
h	4-$MeOC_6H_4$	63
i	2,3-$(MeO)_2C_6H_3$	65
j	2,6-$(MeO)_2C_6H_3$	97
k	2,3,4-$(MeO)_3C_6H_2$	53
l	3-FC_6H_4	23
m	4-FC_6H_4	62
n	2-thienyl	45
o	4-EtC_6H_4	96
p	4-*t*-BuC_6H_4	77
q	4-$(F_3C)C_6H_4$	52
r	4-$(H_2C{=}CH)C_6H_4$	30
s	2-ClC_6H_4	78
t	3-ClC_6H_4	25

[a] Yield of isolated product.

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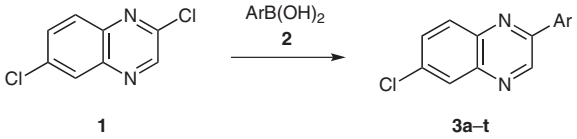
entry 6) to obtain the best yields. The reactions of (more reactive) electron-rich arylboronic acids could be successfully carried out at slightly lower temperature and for a shorter reaction time (85 °C, 4 h; Table 2, entry 3). When the reactions were carried out in toluene or 1,4-dioxane, a higher temperature was necessary and the products were isolated in lower yield than the reaction in tetrahydrofuran (Table 2, entries 2 and 5). Thus, the optimized conditions given in entry 6 allowed the preparation of the 2-aryl-6-chloroquinoxalines **3a**–**t** in optimal yields.



Scheme 1 Synthesis of **3a**–**t**. *Reagents and conditions*: **1** (1 equiv), **2** (1.3 equiv), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (2 equiv), THF, 90 °C, 8 h.

Table 2 Optimization of the Reaction Conditions for the Synthesis of **3c**

Entry	Solvent	Catalyst	Temp (°C)	Time (h)	Yield[a] (%) of **3c**
1	1,4-dioxane	$Pd(PPh_3)_4$	85	3	0
2	1,4-dioxane	$Pd(PPh_3)_4$	110	6	69
3	THF	$Pd(PPh_3)_4$	85	4	71
4	toluene	$Pd(PPh_3)_4$	85	4	29
5	toluene	$Pd(PPh_3)_4$	110	6	66
6	THF	$Pd(PPh_3)_4$	90	8	75

[a] Isolated yield; K_3PO_4 (2 equiv) was used as the base in all reactions.

The structures of all products were established by spectroscopic methods. The structure of **3g** (Figure 1) was independently confirmed by X-ray crystal structure analysis.[20]

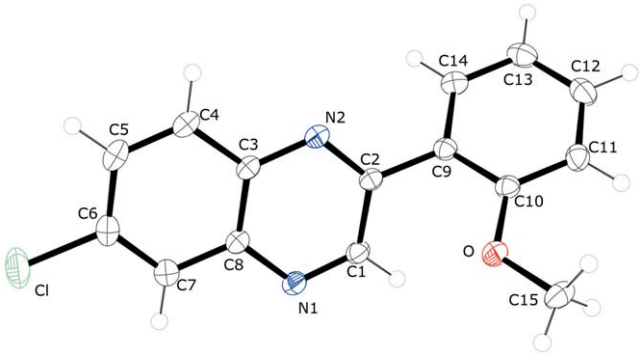
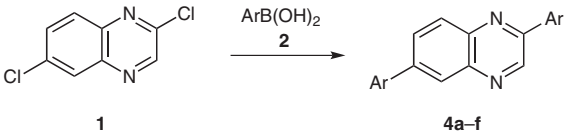


Figure 1 ORTEP view of the crystal structure of **3g**

The Suzuki–Miyaura reactions of 2,6-dichloroquinoxaline (**1**) with the arylboronic acids **2a**,**c**,**e**,**g**,**o**,**p** gave the 2,6-diarylquinoxalines **4a**–**f** in good yields (Scheme 2, Table 3). The best yields were obtained using 2.5 equivalents of the arylboronic acid, $Pd(PPh_3)_4$ (5 mol%), and a 2 M aqueous solution of K_2CO_3 (1,4-dioxane, 120 °C, 12 h).



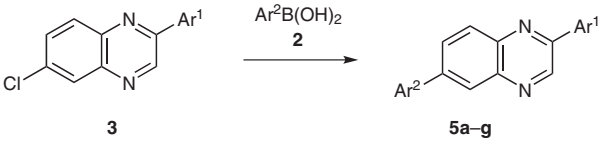
Scheme 2 Synthesis of **4a**–**f**. *Reagents and conditions*: **1** (1 equiv), **2** (2.5 equiv), $Pd(PPh_3)_4$ (5 mol%), 2 M K_2CO_3, 1,4-dioxane, 120 °C, 12 h.

Table 3 Synthesis of **4a**–**f**

2	Ar	Yield[a] (%) of **4**
a	2-Tol	**4a**: 64
c	4-Tol	**4b**: 51
e	3,5-$Me_2C_6H_3$	**4c**: 94
g	2-$MeOC_6H_4$	**4d**: 49
o	4-EtC_6H_4	**4e**: 47
p	4-*t*-BuC_6H_4	**4f**: 26

[a] Yield of isolated product.

The Suzuki–Miyaura reactions of the 2-aryl-6-chloroquinoxalines **3c**,**h**,**m**–**o** with 1.3 equivalents of the arylboronic acids **2c**,**e**,**g**,**m**,**p** afforded the disubstituted products **5a**–**g** in good yields (Scheme 3, Table 4). The reactions were carried out using $Pd(PPh_3)_4$ (5 mol%) and a 2 M aqueous solution of K_2CO_3 (1,4-dioxane, 120 °C, 8 h).



Scheme 3 Synthesis of **5a**–**g**. *Reagents and conditions*: **3** (1 equiv), **2** (1.3 equiv), $Pd(PPh_3)_4$ (5 mol%), 2 M K_2CO_3, 1,4-dioxane, 120 °C, 8 h.

The structures of all products were established by spectroscopic methods. The structure of **5e** (Figure 2) was independently confirmed by X-ray crystal structure analysis.[20]

The syntheses of derivatives **3a**–**t**, **4a**–**f**, and **5a**–**g** have not, to the best of our knowledge, been previously reported, except for **3c** and **3h**.[21] Compound **3c** has been recently prepared using a copper-catalyzed condensation of a diazo ketone;[21] however, this compound could only be obtained as a 1:1 mixture of regioisomers. Thus, the method reported herein is much better suited for the synthesis of arylquinoxalines **3**. Although a variety of quinoxaline derivatives (including heterocyclic and functionalized compounds) have been successfully prepared, the use of 4-cyanophenylboronic acid, 4-formylphenylboronic acid, 4-

Table 4 Synthesis of **5a–g**

3	2	Ar^1	Ar^2	Yield[a] (%) of 5
c	**e**	4-Tol	3,5-$Me_2C_6H_3$	**5a**: 70
c	**p**	4-Tol	4-*t*-BuC_6H_4	**5b**: 78
c	**g**	4-Tol	2-$MeOC_6H_4$	**5c**: 47
h	**m**	4-$MeOC_6H_4$	4-FC_6H_4	**5d**: 76
m	**e**	4-FC_6H_4	3,5-$Me_2C_6H_3$	**5e**: 63
n	**e**	2-thienyl	3,5-$Me_2C_6H_3$	**5f**: 91
o	**c**	4-EtC_6H_4	4-Tol	**5g**: 54

[a] Yield of isolated product.

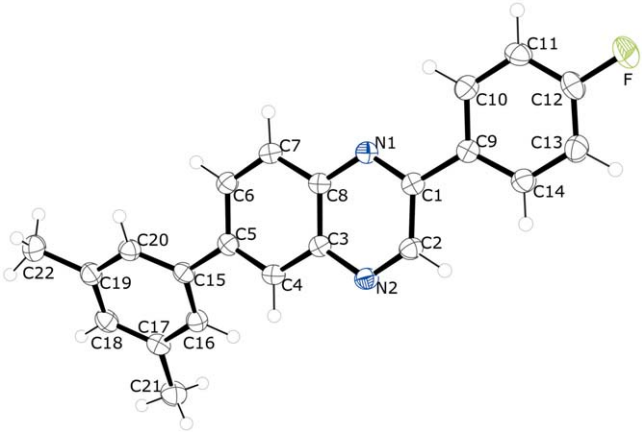


Figure 2 ORTEP view of the crystal structure of **5e**

nitrophenylboronic acid, 2-pyridylboronic acid, and 2-indolylboronic acid resulted in the formation of complex mixtures from which no pure compounds could be isolated.

The monoarylated products **3a–t** were synthesized by Suzuki–Miyaura reactions of 2,6-dichloroquinoxaline (**1**) in good yields. The site selectivity can be explained by the fact that position 2 of 2,6-dichloroquinoxaline is more electron deficient than position 6 (Figure 3).

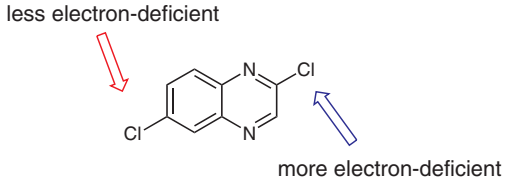


Figure 3 Possible explanation for the site selectivity in cross-coupling reactions of **1**

In conclusion, a variety of mono- and diarylated quinoxaline derivatives were prepared by site-selective Suzuki–Miyaura cross-coupling reactions of 2,6-dichloroquinoxaline.

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative-scale chromatography silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used.

Synthesis of 3a–t; General Procedure

A THF soln (8 mL) of 2,6-dichloroquinoxaline (**1**, 1.0 mmol), an arylboronic acid **2** (1.3 equiv), K_3PO_4 (2 equiv), and $Pd(PPh_3)_4$ (5 mol%) was heated at 90 °C for 8 h. The reaction mixture was cooled to r.t., then H_2O (100 mL) was added and the mixture was extracted with CH_2Cl_2 (100 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (gradient elution, *n*-heptane–EtOAc).

6-Chloro-2-(*o*-tolyl)quinoxaline (3a)

Starting with **1** (0.1 g, 0.5 mmol), **2a** (0.088 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3a** was isolated as a white solid; yield: 0.098 g (77%); mp 121–123 °C.

IR (ATR): 3074 (w), 3043 (w), 2986 (w), 2930 (w), 2746 (w), 1606 (m), 1568 (w), 1539 (m), 1445 (w), 1417 (w), 1385 (w), 1335 (w), 1268 (w), 1175 (m), 1065 (m), 1037 (s), 960 (s), 901 (s), 870 (m), 827 (s), 785 (m), 754 (s), 726 (s), 701 (m), 579 (s), 553 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 7.25–7.36 (m, 3 H, ArH), 7.44–7.48 (m, 1 H, ArH), 7.65 (dd, *J* = 9.1, 2.3 Hz, 1 H, ArH), 7.98–8.06 (m, 2 H, ArH), 8.92 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.4 (CH_3), 126.4 (CH), 128.1 (CH), 129.6 (CH), 129.9 (CH), 130.8 (CH), 131.2 (CH), 131.3 (CH), 135.5 (C), 136.6 (C), 136.7 (C), 140.5 (C), 141.3 (C), 146.7 (CH), 155.1 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 254 (35) [M^+], 253 (100).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}ClN_2$: 255.06835; found: 255.06869.

6-Chloro-2-(*m*-tolyl)quinoxaline (3b)

Starting with **1** (0.1 g, 0.5 mmol), **2b** (0.088 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3b** was isolated as a white solid; yield: 0.085 g (67%); mp 125–127 °C.

IR (ATR): 3024 (w), 2960 (w), 2856 (w), 1952 (w), 1841 (w), 1711 (w), 1606 (w), 1588 (m), 1537 (m), 1453 (m), 1330 (w), 1314 (m), 1169 (m), 1135 (m), 962 (s), 912 (s), 869 (m), 831 (s), 789 (s), 692 (s), 673 (m), 585 (s) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, CH_3), 7.26 (d, ^3J = 7.5 Hz, 1 H, ArH), 7.37 (t, *J* = 7.7 Hz, 1 H, ArH), 7.63 (dd, *J* = 8.9, 2.3 Hz, 1 H, ArH), 7.87 (d, ^3J = 7.5 Hz, 1 H, ArH), 7.92 (s, 1 H, ArH), 7.98–8.02 (m, 2 H, ArH), 9.22 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 20.5 (CH_3), 123.6 (CH), 127.0 (CH), 127.1 (CH), 128.1 (CH), 129.8 (CH), 130.22 (CH), 130.23 (CH), 134.1 (C), 135.3 (C), 138.0 (C), 139.8 (C), 140.8 (C), 143.3 (CH), 151.1 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 254 (100) [M^+], 239 (4), 227 (18), 219 (5), 192 (10), 165 (11), 75 (12).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{15}H_{11}ClN_2$: 254.06053; found: 254.06032.

6-Chloro-2-(*p*-tolyl)quinoxaline (3c)

Starting with **1** (0.1 g, 0.5 mmol), **2c** (0.088 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3c** was isolated as a white solid; yield: 0.096 g (75%); mp 136 °C.

IR (ATR): 3063 (w), 2916 (w), 2854 (w), 2722 (w), 1607 (m), 1576 (w), 1536 (m), 1476 (m), 1413 (m), 1315 (m), 1170 (s), 1064 (m),

1044 (m), 1018 (w), 958 (m), 918 (m), 890 (m), 813 (s), 712 (m), 569 (s) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 7.29 (d, ^3J = 7.9 Hz, 2 H, ArH), 7.63 (dd, J = 9.1, 2.1 Hz, 1 H, ArH), 7.97–8.02 (m, 4 H, ArH), 9.22 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.4 (CH_3), 127.4 (2 CH), 128.0 (CH), 129.9 (2 CH), 130.7 (CH), 131.2 (CH), 133.5 (C), 134.9 (C), 140.7 (C), 140.8 (C), 141.7 (C), 144.1 (CH), 151.9 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 254 (100) [M^+], 227 (20), 192 (10), 165 (9), 116 (11).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{15}H_{11}ClN_2$: 254.06053; found: 254.06064.

6-Chloro-2-(2,6-dimethylphenyl)quinoxaline (3d)
Starting with **1** (0.1 g, 0.5 mmol), **2d** (0.097 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3d** was isolated as a brownish, heavy oil; yield: 0.050 g (37%).

IR (ATR): 3063 (w), 3020 (w), 2919 (w), 2855 (w), 2735 (w), 2516 (w), 2392 (w), 2230 (w), 1932 (w), 1865 (w), 1748 (w), 1667 (w), 1602 (m), 1546 (m), 1505 (w), 1474 (s), 1451 (w), 1377 (w), 1293 (m), 1199 (w), 1169 (s), 1131 (w), 1091 (w), 1062 (m), 1042 (s), 1029 (w), 960 (m), 914 (w), 899 (s), 829 (s), 786 (w), 731 (m), 673 (m), 626 (m), 584 (s), 541 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.00 (s, 6 H, 2 CH_3), 7.07–7.10 (m, 2 H, ArH), 7.17–7.23 (m, 1 H, ArH), 7.65 (dd, J = 8.9, 2.3 Hz, 1 H, ArH), 7.98–8.08 (m, 2 H, ArH), 8.72 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 20.4 (2 CH_3), 128.1 (2 CH), 128.3 (CH), 129.1 (CH), 130.8 (CH), 131.3 (CH), 135.7 (C), 136.3 (2 C), 136.7 (C), 140.9 (C), 141.5 (C), 147.2 (CH), 155.7 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 268 (39) [M^+], 267 (100), 253 (6), 232 (6), 190 (2), 133 (3).

HRMS (EI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}ClN_2$: 269.08431; found: 269.08432.

6-Chloro-2-(3,5-dimethylphenyl)quinoxaline (3e)
Starting with **1** (0.1 g, 0.5 mmol), **2e** (0.097 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3e** was isolated as a white solid; yield: 0.12 g (90%); mp 178–179 °C.

IR (ATR): 3042 (w), 3010 (w), 2916 (w), 2858 (w), 2735 (w), 1936 (w), 1880 (w), 1798 (w), 1755 (w), 1606 (m), 1573 (w), 1536 (m), 1494 (w), 1453 (w), 1416 (w), 1398 (w), 1371 (w), 1312 (m), 1258 (w), 1172 (s), 1088 (m), 997 (m), 966 (m), 867 (m), 828 (s), 782 (m), 706 (s), 674 (m), 626 (m), 590 (m), 542 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.35 (s, 6 H, 2 CH_3), 7.06 (s, 1 H, ArH), 7.59 (dd, J = 8.9, 2.3 Hz, 1 H, ArH), 7.66 (s, 2 H, ArH), 7.95–7.99 (m, 2 H, ArH), 9.17 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.4 (2 CH_3), 125.3 (2 CH), 128.0 (CH), 130.7 (CH), 131.2 (CH), 132.1 (CH), 134.9 (C), 136.3 (C), 138.8 (2 C), 140.8 (C), 141.7 (C), 144.4 (CH), 152.2 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 268 (100) [M^+], 241 (13), 226 (4), 190 (6).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{13}ClN_2$: 268.07618; found: 268.07635.

6-Chloro-2-(2,4,6-trimethylphenyl)quinoxaline (3f)
Starting with **1** (0.12 g, 0.6 mmol), **2f** (0.121 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.035 g, 0.05 equiv), K_3PO_4 (0.254 g, 2 equiv), and THF (4 mL), **3f** was isolated as a yellowish solid; yield: 0.163 g (96%); mp 100 °C.

IR (ATR): 3076 (w), 3042 (m), 2964 (w), 2916 (m), 2854 (w), 1818 (w), 1727 (w), 1610 (m), 1567 (w), 1539 (m), 1470 (w), 1446 (m), 1417 (w), 1373 (m), 1330 (w), 1317 (w), 1295 (m), 1266 (w), 1163 (m), 1125 (m), 1042 (m), 964 (m), 892 (s), 846 (s), 828 (s), 788 (s), 688 (m), 588 (m), 572 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.97 (s, 6 H, 2 CH_3), 2.25 (s, 3 H, CH_3), 6.90 (s, 2 H, ArH), 7.62 (dd, J = 8.9, 2.3 Hz, 1 H, ArH), 7.96–8.06 (m, 2 H, ArH), 8.70 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 19.2 (2 CH_3), 20.1 (CH_3), 127.2 (CH), 127.8 (2 CH), 129.7 (CH), 130.1 (CH), 132.9 (C), 134.5 (C), 135.1 (2 C), 137.8 (C), 139.9 (C), 140.3 (C), 146.4 (CH), 154.8 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 282 (40) [M^+], 281 (100), 267 (9), 246 (4), 128 (2), 115 (5).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{16}ClN_2$: 283.09869; found: 283.10003.

6-Chloro-2-(2-methoxyphenyl)quinoxaline (3g)
Starting with **1** (0.1 g, 0.5 mmol), **2g** (0.099 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3g** was isolated as a white solid; yield: 0.097 g (72%); mp 143 °C.

IR (ATR): 3069 (w), 2973 (w), 2838 (w), 1939 (w), 1754 (w), 1600 (s), 1544 (w), 1493 (m), 1459 (s), 1392 (w), 1296 (w), 1239 (s), 1173 (m), 1117 (m), 1060 (s), 1020 (m), 962 (m), 930 (m), 901 (m), 876 (m), 834 (s), 741 (s), 702 (m), 641 (m), 583 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 6.98 (d, ^3J = 8.3 Hz, 1 H, ArH), 7.08 (dt, J = 7.5, 0.9 Hz, 1 H, ArH), 7.38–7.44 (m, 1 H, ArH), 7.61 (dd, J = 8.9, 2.5 Hz, 1 H, ArH), 7.81 (dd, J = 7.6, 1.7 Hz, 1 H, ArH), 7.98–8.03 (m, 2 H, ArH), 9.27 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 54.6 (OCH_3), 110.4 (CH), 120.5 (CH), 125.1 (C), 126.9 (CH), 129.7 (2 CH), 130.5 (CH), 130.7 (CH), 133.9 (C), 140.2 (C), 140.3 (C), 147.1 (CH), 151.3 (C), 156.4 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 270 (100) [M^+], 253 (55), 241 (48), 213 (17), 178 (14), 165 (27), 151 (8), 118 (11), 110 (14), 103 (9), 90 (11), 75 (24).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}ClN_2O$: 271.06327; found: 271.06367.

6-Chloro-2-(4-methoxyphenyl)quinoxaline (3h)
Starting with **1** (0.1 g, 0.5 mmol), **2h** (0.099 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3h** was isolated as a yellowish white solid; yield: 0.086 g (63%); mp 144–146 °C.

IR (ATR): 3048 (m), 3015 (w), 2930 (w), 2894 (w), 2039 (w), 1915 (w), 1882 (w), 1651 (w), 1604 (s), 1580 (w), 1519 (m), 1463 (w), 1398 (w), 1315 (s), 1269 (w), 1250 (s), 1183 (w), 1167 (s), 1114 (m), 1024 (s), 955 (m), 921 (m), 898 (m), 823 (s), 783 (m), 689 (m), 633 (m), 570 (s) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, OCH_3), 6.98 (d, ^3J = 9.1 Hz, 2 H, ArH), 7.58 (dd, J = 9.1, 2.5 Hz, 1 H, ArH), 7.92–7.98 (m, 2 H, ArH), 8.06 (d, ^3J = 8.9 Hz, 2 H, ArH), 9.18 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 114.6 (2 CH), 128.0 (CH), 128.8 (C), 128.9 (2 CH), 130.6 (CH), 131.1 (CH), 134.6 (C), 140.8 (C), 141.4 (C), 143.8 (CH), 151.5 (C), 161.6 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 270 (100) [M^+], 255 (17), 243 (10), 227 (8), 200 (7), 192 (4), 133 (11), 110 (5).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{15}H_{11}ClN_2O$: 270.05544; found: 270.05544.

6-Chloro-2-(2,3-dimethoxyphenyl)quinoxaline (3i)
Starting with **1** (0.12 g, 0.6 mmol), **2i** (0.142 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.035 g, 0.05 equiv), K_3PO_4 (0.254 g, 2 equiv), and THF (4 mL), **3i** was isolated as a white solid; yield: 0.118 g (65%); mp 124 °C.

IR (ATR): 2996 (w), 2951 (m), 2840 (m), 1582 (m), 1542 (m), 1484 (m), 1466 (s), 1428 (m), 1397 (w), 1320 (m), 1266 (s), 1234 (m), 1175 (m), 1110 (m), 1086 (m), 1041 (s), 994 (s), 934 (m), 918 (m), 850 (m), 834 (s), 783 (m), 765 (m), 741 (s), 690 (m), 679 (m), 623 (m), 597 (s), 534 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.69 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 7.00 (dd, *J* = 8.1, 1.5 Hz, 1 H, ArH), 7.15 (t, *J* = 7.9 Hz, 1 H, ArH), 7.38 (dd, *J* = 7.7, 1.5 Hz, 1 H, ArH), 7.62 (dd, *J* = 8.9, 2.3 Hz, 1 H, ArH), 7.98–8.04 (m, 2 H, ArH), 9.27 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 56.0 (OCH_3), 61.4 (OCH_3), 114.3 (CH), 122.7 (CH), 124.8 (CH), 128.0 (CH), 130.8 (CH), 130.9 (CH), 131.2 (C), 135.3 (C), 141.2 (C), 141.4 (C), 147.6 (C), 147.8 (CH), 151.9 (C), 153.1 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 300 (100) [M^+], 285 (47), 283 (91), 271 (34), 257 (23), 242 (13), 213 (11), 179 (18), 165 (26), 142 (6), 120 (7), 110 (13), 100 (7), 75 (20).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{13}ClN_2O_2$: 300.06601; found: 300.06569.

6-Chloro-2-(2,6-dimethoxyphenyl)quinoxaline (3j)
Starting with **1** (0.12 g, 0.6 mmol), **2j** (0.142 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.035 g, 0.05 equiv), K_3PO_4 (0.254 g, 2 equiv), and THF (4 mL), **3j** was isolated as a yellow solid; yield: 0.175 g (97%); mp 135–137 °C.

IR (ATR): 3079 (w), 2985 (w), 2831 (w), 1621 (w), 1586 (m), 1538 (m), 1497 (s), 1464 (w), 1425 (m), 1394 (w), 1336 (w), 1304 (s), 1259 (m), 1225 (m), 1208 (m), 1181 (s), 1154 (m), 1060 (m), 1021 (s), 965 (m), 883 (m), 832 (s), 795 (s), 786 (m), 732 (s), 700 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.78 (s, 6 H, 2 OCH_3), 6.93–6.94 (m, 2 H, ArH), 7.40 (d, *J* = 2.8 Hz, 1 H, ArH), 7.61 (dd, *J* = 8.9, 2.3 Hz, 1 H, ArH), 7.98–8.02 (m, 2 H, ArH), 9.29 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.9 (OCH_3), 56.3 (OCH_3), 113.0 (CH), 115.9 (CH), 117.5 (CH), 126.6 (C), 127.9 (CH), 130.7 (2 CH), 135.1 (C), 141.1 (C), 141.3 (C), 148.0 (CH), 151.8 (C), 152.0 (C), 154.3 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 300 (100) [M^+], 285 (64), 283 (88), 269 (14), 257 (12), 242 (16), 214 (7), 179 (13), 165 (24), 148 (13), 120 (7), 110 (11), 100 (5), 75 (14).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{13}ClN_2O_2$: 300.06601; found: 300.06590.

6-Chloro-2-(2,3,4-trimethoxyphenyl)quinoxaline (3k)
Starting with **1** (0.12 g, 0.6 mmol), **2k** (0.165 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.035 g, 0.05 equiv), K_3PO_4 (0.254 g, 2 equiv), and THF (4 mL), **3k** was isolated as a yellowish solid; yield: 0.105 g (53%); mp 106–108 °C.

IR (ATR): 3052 (w), 2943 (m), 2848 (w), 1601 (s), 1542 (m), 1494 (w), 1460 (m), 1433 (w), 1414 (s), 1335 (w), 1309 (m), 1280 (m), 1210 (m), 1171 (m), 1133 (w), 1106 (s), 1087 (m), 1014 (s), 969 (m), 949 (w), 928 (m), 902 (m), 853 (m), 823 (m), 774 (s), 597 (m), 544 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.78 (d, ^3J = 8.7 Hz, 1 H, ArH), 7.55–7.61 (m, 2 H, ArH), 7.94–8.00 (m, 2 H, ArH), 9.24 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 56.2 (OCH_3), 61.0 (OCH_3), 61.6 (OCH_3), 108.2 (CH), 123.8 (C), 125.9 (CH), 128.0 (CH), 130.6 (CH), 130.8 (CH), 134.9 (C), 141.1 (C), 141.2 (C), 142.3 (C), 147.6 (CH), 151.7 (C), 152.5 (C), 155.7 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 330 (100) [M^+], 315 (51), 313 (40), 299 (12), 287 (14), 272 (15), 257 (13), 229 (12), 215 (15), 203 (10), 201 (26), 178 (10), 163 (14), 153 (11), 135 (8), 110 (6), 100 (7).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{15}ClN_2O_3$: 330.07657; found: 330.07637.

6-Chloro-2-(3-fluorophenyl)quinoxaline (3l)
Starting with **1** (0.1 g, 0.5 mmol), **2l** (0.09 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3l** was isolated as a white solid; yield: 0.03 g (23%); mp 172–173 °C.

IR (ATR): 3087 (w), 3065 (w), 2923 (w), 2850 (w), 1953 (w), 1815 (w), 1704 (w), 1590 (m), 1495 (w), 1435 (m), 1402 (w), 1314 (m), 1203 (m), 975 (s), 865 (s), 831 (s), 789 (s), 695 (s), 670 (s), 596 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.13–7.19 (m, 1 H, ArH), 7.43–7.50 (m, 1 H, ArH), 7.67 (dd, *J* = 8.9, 2.3 Hz, 1 H, ArH), 7.85–7.89 (m, 2 H, ArH), 8.00–8.05 (m, 2 H, ArH), 9.23 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 113.5 (d, $^2J_{CF}$ = 23.3 Hz, CH), 116.4 (d, $^2J_{CF}$ = 21.1 Hz, CH), 122.0 (d, $^4J_{CF}$ = 2.7 Hz, CH), 127.1 (CH), 129.8 (d, $^3J_{CF}$ = 8.2 Hz, CH), 129.9 (CH), 130.6 (CH), 134.7 (C), 137.6 (d, $^3J_{CF}$ = 7.8 Hz, C), 139.7 (C), 141.0 (C), 142.8 (CH), 149.5 (d, $^4J_{CF}$ = 2.7 Hz, C), 162.4 (d, $^1J_{CF}$ = 247.2 Hz, C).

^{19}F NMR (282.40 MHz, $CDCl_3$): δ = –111.56 (ArF).

GC-MS (EI, 70 eV): *m*/*z* (%) = 258 (100) [M^+], 231 (31), 196 (21), 169 (4), 129 (4), 110 (15), 100 (4), 75 (23), 63 (1), 50 (4).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_8ClFN_2$: 258.03546; found: 258.03571.

6-Chloro-2-(4-fluorophenyl)quinoxaline (3m)
Starting with **1** (0.1 g, 0.5 mmol), **2m** (0.09 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3m** was isolated as a yellowish white solid; yield: 0.08 g (62%); mp 165–168 °C.

IR (ATR): 3054 (w), 3012 (w), 2914 (w), 1600 (s), 1558 (w), 1514 (m), 1478 (m), 1305 (m), 1237 (s), 1162 (m), 1047 (m), 957 (m), 901 (m), 872 (m), 828 (s), 790 (m), 720 (m), 691 (m), 571 (s) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.13–7.21 (m, 2 H, ArH), 7.64 (dd, *J* = 9.1, 2.5 Hz, 1 H, ArH), 7.96–8.02 (m, 2 H, ArH), 8.07–8.14 (m, 2 H, ArH), 9.20 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 116.3 (d, $^2J_{CF}$ = 21.5 Hz, 2 CH), 128.1 (CH), 129.5 (d, $^3J_{CF}$ = 8.7 Hz, 2 CH), 130.7 (CH), 131.4 (CH), 132.5 (d, $^4J_{CF}$ = 3.2 Hz, C), 135.3 (C), 140.7 (C), 141.7 (C), 143.7 (CH), 150.8 (C), 164.4 (d, $^1J_{CF}$ = 251.31 Hz, C).

^{19}F NMR (282.40 MHz, $CDCl_3$): δ = –110.01 (ArF).

GC-MS (EI, 70 eV): *m*/*z* (%) = 258 (100) [M^+], 233 (11), 231 (33), 196 (20), 169 (5).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_8ClFN_2$: 258.03546; found: 258.03559.

6-Chloro-2-(2-thienyl)quinoxaline (3n)
Starting with **1** (0.1 g, 0.5 mmol), **2n** (0.082 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3n** was isolated as a yellow solid; yield: 0.056 g (45%); mp 154–156 °C.

IR (ATR): 3095 (w), 3064 (w), 3011 (w), 2007 (w), 1941 (w), 1887 (w), 1746 (w), 1693 (w), 1593 (m), 1541 (s), 1474 (m), 1433 (w), 1414 (m), 1369 (w), 1311 (m), 1269 (w), 1176 (s), 1131 (m), 1062 (s), 1002 (s), 942 (s), 872 (m), 832 (s), 789 (m), 709 (s), 588 (s), 558 (m) cm^{-1}.

^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.11–7.14 (m, 1 H, ArH), 7.48 (dd, *J* = 5.1, 1.1 Hz, 1 H, ArH), 7.59 (dd, *J* = 8.9, 2.5 Hz, 1 H, ArH), 7.77 (dd, *J* = 3.8, 1.1 Hz, 1 H, ArH), 7.89–7.96 (m, 2 H, ArH), 9.13 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 127.2 (CH), 128.1 (CH), 128.6 (CH), 130.2 (CH), 130.3 (CH), 131.4 (CH), 134.8 (C), 140.6 (C), 141.5 (C), 141.8 (C), 142.8 (CH), 147.5 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 246 (100) [M$^+$], 219 (29), 184 (12), 140 (10), 110 (11), 100 (3), 84 (2), 75 (12).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{12}H_7ClN_2S$: 246.00130; found: 246.00147.

6-Chloro-2-(4-ethylphenyl)quinoxaline (3o)
Starting with **1** (0.1 g, 0.5 mmol), **2o** (0.098 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3o** was isolated as a white solid; yield: 0.13 g (96%); mp 104 °C.

IR (ATR): 3068 (w), 3039 (w), 2955 (m), 2865 (w), 1607 (s), 1537 (s), 1504 (w), 1477 (s), 1445 (w), 1416 (m), 1334 (w), 1313 (s), 1281 (m), 1225 (w), 1173 (s), 1053 (s), 1014 (m), 957 (s), 922 (m), 908 (s), 871 (m), 825 (s), 720 (m), 689 (m), 628 (m), 582 (s), 569 (m), 540 (m) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.7 Hz, 3 H, CH_3), 2.65 (q, *J* = 7.5 Hz, 2 H, CH_2), 7.29 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.59 (dd, *J* = 9.1, 2.3 Hz, 1 H, ArH), 7.94–8.02 (m, 4 H, ArH), 9.19 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 15.4 (CH_3), 28.8 (CH_2), 127.5 (2 CH), 128.1 (CH), 128.8 (2 CH), 130.8 (CH), 131.2 (CH), 133.8 (C), 134.9 (C), 140.8 (C), 141.7 (C), 144.1 (CH), 147.1 (C), 151.9 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 268 (100) [M$^+$], 255 (26), 253 (79), 226 (4), 190 (7), 163 (2), 116 (18), 110 (8), 89 (7), 84 (1), 75 (11).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{13}ClN_2$: 268.07618; found: 268.07642.

2-(4-*tert*-Butylphenyl)-6-chloroquinoxaline (3p)
Starting with **1** (0.1 g, 0.5 mmol), **2p** (0.106 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3p** was isolated as a white solid; yield: 0.115 g (77%); mp 99–102 °C.

IR (ATR): 3093 (w), 3063 (w), 2955 (m), 2867 (w), 1601 (m), 1569 (w), 1537 (m), 1504 (w), 1474 (m), 1455 (w), 1404 (m), 1392 (w), 1360 (m), 1333 (w), 1316 (m), 1270 (m), 1200 (m), 1174 (m), 1147 (w), 1093 (m), 1045 (m), 1012 (m), 957 (s), 920 (s), 897 (s), 879 (m), 841 (s), 826 (s), 739 (m), 694 (w), 672 (m), 577 (s), 539 (m) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, 3 CH_3), 7.50 (d, ^3J = 8.7 Hz, 2 H, ArH), 7.60 (dd, *J* = 9.1, 2.5 Hz, 1 H, ArH), 7.95–8.04 (m, 4 H, ArH), 9.21 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 31.2 (3 CH_3), 34.9 (C), 126.2 (2 CH), 127.3 (2 CH), 128.1 (CH), 130.8 (CH), 131.2 (CH), 133.6 (C), 134.9 (C), 140.9 (C), 141.7 (C), 144.1 (CH), 151.9 (C), 153.9 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 296 (31) [M$^+$], 281 (100), 265 (5), 253 (11), 218 (1), 203 (1), 163 (4), 140 (2), 116 (7), 110 (4), 75 (5), 39 (1).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{17}ClN_2$: 296.10748; found: 296.10752.

6-Chloro-2-[4-(trifluoromethyl)phenyl]quinoxaline (3q)
Starting with **1** (0.1 g, 0.5 mmol), **2q** (0.123 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3q** was isolated as a white solid; yield: 0.081 g (52%); mp 128–130 °C.

IR (ATR): 3043 (w), 1928 (w), 1809 (w), 1617 (w), 1604 (m), 1538 (m), 1519 (w), 1478 (m), 1414 (m), 1326 (s), 1260 (w), 1195 (w), 1174 (w), 1157 (m), 1107 (s), 1068 (s), 1015 (m), 960 (m), 927 (m), 899 (m), 850 (m), 832 (s), 800 (w), 651 (m), 598 (s), 568 (m) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 8.9, 2.3 Hz, 1 H, ArH), 7.75 (d, ^3J = 8.1 Hz, 2 H, ArH), 8.01–8.06 (m, 2 H, ArH), 8.23 (d, ^3J = 8.1 Hz, 2 H, ArH), 9.26 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 123.9 (q, $^1J_{CF}$ = 272.35 Hz, CF_3), 126.1 (q, $^3J_{CF}$ = 3.30 Hz, 2 CH), 127.8 (2 CH), 128.2 (CH), 130.2 (q, $^2J_{CF}$ = 32.46 Hz, C), 130.9 (CH), 131.7 (CH), 136.0 (C), 139.6 (C), 140.7 (C), 142.2 (C), 143.8 (CH), 150.3 (C).

^{19}F NMR (282.40 MHz, $CDCl_3$): δ = –62.81 ($ArCF_3$).

GC-MS (EI, 70 eV): *m*/*z* (%) = 308 (100) [M$^+$], 281 (24), 246 (9), 226 (8), 212 (2), 177 (4), 152 (6), 136 (2), 110 (17), 100 (4), 75 (20), 50 (3).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{15}H_8ClF_3N_2$: 308.03226; found: 308.03178.

6-Chloro-2-(4-vinylphenyl)quinoxaline (3r)
Starting with **1** (0.1 g, 0.5 mmol), **2r** (0.096 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3r** was isolated as a yellow solid; yield: 0.04 g (30%); mp 113–115 °C.

IR (ATR): 3046 (w), 2921 (m), 2851 (w), 1606 (m), 1568 (w), 1536 (m), 1475 (m), 1445 (w), 1411 (m), 1333 (w), 1314 (m), 1210 (w), 1172 (s), 1047 (m), 957 (m), 899 (m), 825 (s), 782 (w), 731 (m), 572 (s) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 5.29 (d, *J* = 11.3 Hz, 1 H, =CH_2), 5.79 (d, *J* = 17.6 Hz, 1 H, =CH_2), 6.65–6.75 (m, 1 H, =CH), 7.49 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.61 (dd, *J* = 8.9, 2.3 Hz, 1 H, ArH), 7.95–8.00 (m, 2 H, ArH), 8.06 (d, ^3J = 8.5 Hz, 2 H, ArH), 9.21 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 114.6 (=CH_2), 125.9 (2 CH), 126.6 (2 CH), 127.0 (CH), 129.7 (CH), 130.3 (CH), 134.1 (C), 134.5 (C), 135.1 (CH), 138.6 (C), 139.8 (C), 140.7 (C), 142.9 (CH), 150.3 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 266 (100) [M$^+$], 238 (14), 204 (10), 177 (3), 129 (12).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{11}ClN_2$: 266.06053; found: 266.06088.

6-Chloro-2-(2-chlorophenyl)quinoxaline (3s)
Starting with **1** (0.12 g, 0.6 mmol), **2s** (0.121 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.035 g, 0.05 equiv), K_3PO_4 (0.254 g, 2 equiv), and THF (4 mL), **3s** was isolated as a white solid; yield: 0.129 g (78%); mp 177 °C.

IR (ATR): 3091 (w), 3047 (m), 2982 (w), 1921 (w), 1807 (w), 1621 (w), 1598 (s), 1543 (m), 1504 (w), 1476 (s), 1447 (w), 1429 (m), 1397 (w), 1356 (w), 1324 (w), 1311 (m), 1265 (w), 1248 (m), 1176 (s), 1147 (w), 1137 (m), 1093 (w), 1075 (m), 1040 (s), 961 (s), 935 (s), 921 (w), 898 (s), 833 (s), 791 (m), 748 (s), 723 (m), 686 (m), 676 (m), 579 (m), 538 (m) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.34–7.40 (m, 2 H, ArH), 7.44–7.49 (m, 1 H, ArH), 7.62–7.68 (m, 2 H, ArH), 8.00–8.07 (m, 2 H, ArH), 9.13 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 126.5 (CH), 127.2 (CH), 129.3 (CH), 129.8 (CH), 129.9 (CH), 130.3 (CH), 130.9 (CH), 131.5 (C), 134.9 (C), 135.1 (C), 139.8 (C), 140.6 (C), 145.9 (CH), 151.5 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 274 (100) [M$^+$], 247 (20), 241 (30), 239 (93), 212 (21), 177 (31), 137 (18), 110 (20), 102 (12), 100 (9).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{14}H_8Cl_2N_2$: 274.00591; found: 274.00546.

6-Chloro-2-(3-chlorophenyl)quinoxaline (3t)
Starting with **1** (0.1 g, 0.5 mmol), **2t** (0.1 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), K_3PO_4 (0.212 g, 2 equiv), and THF (4 mL), **3t** was isolated as a white solid; yield: 0.035 g (25%); mp 167 °C.

IR (ATR): 3080 (w), 3048 (m), 1937 (w), 1822 (w), 1712 (w), 1602 (w), 1537 (m), 1475 (m), 1371 (w), 1311 (s), 1258 (w), 1175 (m), 1106 (w), 1065 (m), 1048 (w), 966 (s), 940 (m), 904 (m), 831 (m), 791 (s), 755 (m), 700 (s), 671 (m), 638 (w), 586 (m) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.41–7.43 (m, 2 H, ArH), 7.65 (dd, *J* = 8.9, 2.3 Hz, 1 H, ArH), 7.93–8.04 (m, 3 H, ArH), 8.13–8.14 (m, 1 H, ArH), 9.20 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 125.4 (CH), 127.6 (CH), 128.1 (CH), 130.4 (2 CH), 130.9 (CH), 131.6 (CH), 135.4 (C), 135.7 (C), 138.1 (C), 140.7 (C), 142.0 (C), 143.7 (CH), 150.4 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 275 (17), 274 (100) [M^+], 247 (18), 239 (26), 212 (21), 177 (23), 137 (14), 110 (18), 100 (6), 84 (2), 75 (28), 63 (2), 50 (6).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_8Cl_2N_2$: 274.00591; found: 274.00535.

Synthesis of 4a–f; General Procedure

A 1,4-dioxane soln (8 mL) of 2,6-dichloroquinoxaline (**1**, 1.0 equiv), an arylboronic acid **2** (2.5 equiv), 2 M K_2CO_3 (2 mL), and $Pd(PPh_3)_4$ (5 mol%) was heated at 120 °C for 12 h. The reaction mixture was cooled to r.t., then H_2O (100 mL) was added and the mixture was extracted with CH_2Cl_2 (100 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (gradient elution, *n*-heptane–EtOAc).

2,6-Di(*o*-tolyl)quinoxaline (4a)

Starting with **1** (0.1 g, 0.5 mmol), **2a** (0.169 g, 2.5 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **4a** was isolated as a white solid; yield: 0.1 g (64%); mp 139 °C.

IR (ATR): 3092 (w), 3019 (w), 2921 (w), 2854 (w), 2735 (w), 1954 (w), 1822 (w), 1539 (m), 1494 (w), 1481 (m), 1434 (m), 1349 (w), 1314 (m), 1268 (w), 1164 (m), 1060 (m), 1029 (m), 977 (w), 961 (m), 848 (s), 791 (w), 757 (s), 728 (s), 705 (w), 666 (m), 626 (m), 600 (w), 564 (w), 546 (w), 535 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 7.22–7.33 (m, 7 H, ArH), 7.47–7.50 (m, 1 H, ArH), 7.71 (dd, *J* = 8.7, 2.1 Hz, 1 H, ArH), 8.02–8.12 (m, 2 H, ArH), 8.95 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.4 (CH_3), 20.6 (CH_3), 126.1 (CH), 126.4 (CH), 128.0 (CH), 128.9 (CH), 129.1 (CH), 129.4 (CH), 129.9 (CH), 130.0 (CH), 130.6 (CH), 131.3 (CH), 132.2 (CH), 135.4 (C), 136.6 (C), 137.2 (C), 140.5 (C), 140.9 (C), 141.0 (C), 143.7 (C), 146.2 (CH), 154.9 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 310 (48) [M^+], 309 (100), 190 (2), 165 (8), 153 (4), 115 (10), 89 (3), 75 (1), 65 (2), 51 (1), 39 (1).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}N_2$: 311.15428; found: 311.15435.

2,6-Di(*p*-tolyl)quinoxaline (4b)

Starting with **1** (0.1 g, 0.5 mmol), **2c** (0.169 g, 2.5 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **4b** was isolated as a white solid; yield: 0.08 g (51%); mp 203–205 °C.

IR (ATR): 3020 (w), 2913 (w), 2856 (w), 2726 (w), 1614 (m), 1503 (w), 1402 (w), 1322 (w), 1275 (w), 1186 (w), 1167 (m), 1118 (w), 1054 (m), 975 (w), 931 (m), 849 (w), 816 (s), 723 (m), 691 (w), 606 (m), 587 (w), 554 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 7.25 (d, ^3J = 7.9 Hz, 2 H, ArH), 7.29 (d, ^3J = 7.9 Hz, 2 H, ArH), 7.60 (d, ^3J = 8.1 Hz, 2 H, ArH), 7.95 (dd, *J* = 8.7, 1.9 Hz, 1 H, ArH), 8.03 (d, ^3J = 8.1 Hz, 2 H, ArH), 8.08–8.21 (m, 2 H, ArH), 9.24 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.2 (CH_3), 21.5 (CH_3), 126.1 (CH), 127.3 (2 CH), 127.4 (2 CH), 129.7 (CH), 129.80 (CH), 129.83 (2 CH), 129.9 (2 CH), 134.1 (C), 136.9 (C), 137.5 (C), 138.1 (C), 140.5 (C), 141.7 (C), 142.0 (C), 143.6 (CH), 151.5 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 310 (100) [M^+], 295 (2), 268 (1), 166 (14), 139 (1), 116 (15), 91 (1), 63 (1).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{22}H_{18}N_2$: 310.14645; found: 310.14679.

2,6-Bis(3,5-dimethylphenyl)quinoxaline (4c)

Starting with **1** (0.1 g, 0.5 mmol), **2e** (0.186 g, 2.5 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **4c** was isolated as a yellow solid; yield: 0.16 g (94%); mp 190–192 °C.

IR (ATR): 3012 (w), 2913 (m), 2854 (w), 2734 (w), 1597 (m), 1538 (w), 1435 (w), 1373 (w), 1316 (m), 1286 (w), 1217 (w), 1164 (m), 1087 (m), 1037 (m), 967 (m), 938 (w), 842 (s), 788 (m), 771 (w), 711 (m), 681 (s), 628 (m), 569 (w), 544 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.33 (s, 6 H, 2 CH_3), 2.36 (s, 6 H, 2 CH_3), 6.97 (s, 1 H, ArH), 7.05 (s, 1 H, ArH), 7.29 (s, 2 H, ArH), 7.70 (s, 2 H, ArH), 7.93 (dd, *J* = 8.7, 2.1 Hz, 1 H, ArH), 8.01–8.19 (m, 2 H, ArH), 9.20 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 20.4 (4 CH_3), 124.3 (2 CH), 124.4 (2 CH), 125.4 (CH), 128.6 (CH), 128.7 (CH), 128.9 (CH), 130.8 (CH), 135.7 (C), 137.6 (2 C), 137.7 (2 C), 138.6 (C), 140.5 (C), 140.7 (C), 141.3 (C), 142.9 (CH), 150.8 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 338 (100) [M^+], 311 (2), 296 (1), 180 (7), 154 (2), 130 (8), 115 (4), 77 (1).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{24}H_{22}N_2$: 338.17775; found: 338.17749.

2,6-Bis(2-methoxyphenyl)quinoxaline (4d)

Starting with **1** (0.1 g, 0.5 mmol), **2g** (0.19 g, 2.5 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **4d** was isolated as a yellow solid; yield: 0.085 g (49%); mp 128–129 °C.

IR (ATR): 3066 (w), 3024 (w), 2938 (w), 2838 (w), 1599 (m), 1489 (m), 1440 (w), 1336 (w), 1268 (m), 1233 (s), 1163 (m), 1116 (m), 1060 (m), 1039 (w), 1016 (s), 960 (m), 904 (m), 842 (w), 828 (m), 784 (m), 741 (s), 695 (w), 666 (m), 617 (m), 576 (m), 562 (w), 541 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.75 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 6.93–6.97 (m, 2 H, ArH), 6.99–7.09 (m, 2 H, ArH), 7.26–7.40 (m, 3 H, ArH), 7.82 (dd, *J* = 7.5, 1.7 Hz, 1 H, ArH), 7.89 (dd, *J* = 8.7, 2.1 Hz, 1 H, ArH), 8.05–8.18 (m, 2 H, ArH), 9.25 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 55.6 (OCH_3), 111.4 (CH), 111.5 (CH), 121.1 (CH), 121.5 (CH), 126.7 (C), 128.6 (CH), 129.0 (CH), 129.4 (C), 129.5 (CH), 131.1 (CH), 131.3 (CH), 131.6 (CH), 132.1 (CH), 140.0 (C), 140.9 (C), 141.8 (C), 147.3 (CH), 151.8 (C), 156.6 (C), 157.4 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 342 (100) [M^+], 341 (58), 325 (48), 313 (29), 297 (10), 270 (4), 237 (19), 207 (3), 193 (4), 164 (6), 139 (15), 131 (7), 118 (8), 90 (4), 77 (3), 63 (3), 39 (1).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{22}H_{18}N_2O_2$: 342.13628; found: 342.13586.

2,6-Bis(4-ethylphenyl)quinoxaline (4e)

Starting with **1** (0.1 g, 0.5 mmol), **2o** (0.188 g, 2.5 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **4e** was isolated as a white solid; yield: 0.08 g (47%); mp 150 °C.

IR (ATR): 3025 (w), 2931 (w), 2874 (w), 1614 (m), 1513 (w), 1452 (m), 1300 (w), 1203 (w), 1165 (m), 1121 (w), 1057 (m), 1015 (m), 960 (m), 914 (w), 829 (s), 798 (w), 684 (w), 633 (w), 609 (m), 590 (w), 553 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.24 (t, ^3J = 7.5 Hz, 3 H, CH_3), 2.65 (q, *J* = 7.5 Hz, 2 H, CH_2), 2.67 (q, *J* = 7.5 Hz, 2 H, CH_2), 7.27 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.32 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.62 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.95 (dd, *J* = 8.7, 2.1 Hz, 1 H, ArH), 8.05 (d, ^3J = 8.3 Hz, 2 H, ArH), 8.08–8.21 (m, 2 H, ArH), 9.23 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 15.4 (CH_3), 15.5 (CH_3), 28.6 (CH_2), 28.8 (CH_2), 126.1 (CH), 127.4 (2 CH), 127.5 (2 CH), 128.6 (2 CH), 128.7 (2 CH), 129.7 (CH), 129.8 (CH), 134.3 (C), 137.1 (C), 141.6 (C), 141.7 (C), 142.0 (C), 143.7 (CH), 144.4 (C), 146.7 (C), 151.5 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 338 (100) [M^+], 323 (55), 308 (13), 190 (2), 154 (13), 115 (5), 102 (1), 90 (1), 51 (1).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{24}H_{22}N_2$: 338.17775; found: 338.17782.

2,6-Bis(4-*tert*-butylphenyl)quinoxaline (4f)
Starting with **1** (0.1 g, 0.5 mmol), **2p** (0.223 g, 2.5 equiv), $Pd(PPh_3)_4$ (0.029 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **4f** was isolated as a white solid; yield: 0.052 g (26%); mp 265–267 °C.

IR (ATR): 3062 (w), 2964 (m), 2863 (w), 2707 (w), 1614 (m), 1504 (w), 1455 (m), 1361 (m), 1301 (w), 1265 (m), 1202 (w), 1138 (w), 1047 (m), 976 (w), 930 (m), 890 (m), 823 (s), 742 (w), 694 (w), 640 (w), 610 (m), 566 (s), 545 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.32 (s, 18 H, 6 CH_3), 7.47 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.52 (d, ^3J = 8.7 Hz, 2 H, ArH), 7.65 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.97 (dd, *J* = 8.7, 2.1 Hz, 1 H, ArH), 8.06 (d, ^3J = 8.5 Hz, 2 H, ArH), 8.09–8.23 (m, 2 H, ArH), 9.25 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 31.2 (3 CH_3), 31.3 (3 CH_3), 34.7 (C), 34.9 (C), 126.0 (2 CH), 126.1 (CH), 126.2 (2 CH), 127.1 (2 CH), 127.2 (2 CH), 129.7 (CH), 129.8 (CH), 134.1 (C), 136.8 (C), 141.6 (C), 141.7 (C), 141.9 (C), 143.7 (CH), 151.3 (C), 151.5 (C), 153.5 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 394 (63) [M^+], 380 (31), 379 (100), 363 (10), 335 (3), 295 (2), 182 (11), 154 (10), 102 (1), 41 (3).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{28}H_{30}N_2$: 394.24035; found: 394.24046.

Synthesis of 5a–g; General Procedure
A 1,4-dioxane soln (8 mL) of a 2-aryl-6-chloroquinoxaline **3** (1.0 equiv), an arylboronic acid **2** (1.3 equiv), 2 M K_2CO_3 (2 mL), and $Pd(PPh_3)_4$ (5 mol%) was heated at 120 °C for 8 h. The reaction mixture was cooled to r.t., then H_2O (100 mL) was added and the mixture was extracted with CH_2Cl_2 (100 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (gradient elution, *n*-heptane–EtOAc).

6-(3,5-Dimethylphenyl)-2-(*p*-tolyl)quinoxaline (5a)
Starting with **3c** (0.05 g, 0.2 mmol), **2e** (0.039 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.012 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **5a** was isolated as a light yellow solid; yield: 0.045 g (70%); mp 168 °C.

IR (ATR): 3030 (w), 2913 (m), 2727 (w), 1601 (m), 1555 (w), 1463 (w), 1427 (w), 1370 (w), 1276 (w), 1184 (w), 1164 (w), 1075 (w), 1049 (m), 960 (m), 929 (w), 881 (w), 818 (s), 776 (w), 717 (m), 682 (m), 640 (w), 624 (w), 614 (s), 569 (w), 555 (w), 536 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.34 (s, 6 H, 2 CH_3), 2.37 (s, 3 H, CH_3), 6.99 (s, 1 H, ArH), 7.28 (s, 1 H, ArH), 7.30 (s, 3 H, ArH), 7.95 (dd, *J* = 8.7, 2.1 Hz, 1 H, ArH), 8.03 (d, ^3J = 8.1 Hz, 2 H, ArH), 8.08 (d, ^3J = 8.7 Hz, 1 H, ArH), 8.20 (d, *J* = 2.1 Hz, 1 H, ArH), 9.23 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.4 (3 CH_3), 125.4 (2 CH), 126.4 (CH), 127.4 (2 CH), 129.6 (CH), 129.7 (CH), 129.8 (2 CH), 129.9 (CH), 134.0 (C), 138.6 (2 C), 139.7 (C), 140.4 (C), 141.6 (C), 141.7 (C), 142.3 (C), 143.6 (CH), 151.5 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 324 (100) [M^+], 309 (5), 297 (5), 180 (42), 162 (20), 130 (27), 115 (11), 77 (1), 65 (1), 63 (1).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{21}N_2$: 325.16993; found: 325.17059.

6-(4-*tert*-Butylphenyl)-2-(*p*-tolyl)quinoxaline (5b)
Starting with **3c** (0.05 g, 0.2 mmol), **2p** (0.046 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.012 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **5b** was isolated as a light yellow solid; yield: 0.054 g (78%); mp 185–187 °C.

IR (ATR): 3061 (w), 3032 (w), 2902 (w), 2865 (w), 1916 (w), 1614 (m), 1514 (w), 1450 (m), 1397 (w), 1362 (m), 1269 (w), 1186 (w), 1166 (m), 1143 (w), 1109 (w), 1048 (w), 1009 (w), 958 (m), 925 (m), 889 (w), 842 (w), 819 (s), 740 (w), 718 (m), 687 (w), 672 (w), 628 (w), 606 (m), 564 (w), 558 (m), 547 (m) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, 3 CH_3), 2.37 (s, 3 H, CH_3), 7.28 (d, ^3J = 7.9 Hz, 2 H, ArH), 7.46 (d, ^3J = 8.7 Hz, 2 H, ArH), 7.65 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.95 (dd, *J* = 8.9, 1.9 Hz, 1 H, ArH), 8.03 (d, ^3J = 8.3 Hz, 2 H, ArH), 8.09 (d, *J* = 8.7 Hz, 1 H, ArH), 8.22 (d, *J* = 1.5 Hz, 1 H, ArH), 9.23 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.4 (CH_3), 31.3 (3 CH_3), 34.7 (C), 126.0 (2 CH), 126.1 (CH), 127.1 (2 CH), 127.4 (2 CH), 129.7 (CH), 129.8 (CH), 129.9 (2 CH), 134.0 (C), 136.7 (2 C), 140.4 (2 C), 141.7 (C), 141.9 (C), 143.6 (CH), 151.3 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 352 (100) [M^+], 309 (25), 297 (9), 178 (10), 152 (7), 141 (15), 65 (1), 39 (1).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{25}N_2$: 353.20123; found: 353.20151.

6-(2-Methoxyphenyl)-2-(*p*-tolyl)quinoxaline (5c)
Starting with **3c** (0.05 g, 0.2 mmol), **2g** (0.04 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.012 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **5c** was isolated as a light yellow solid; yield: 0.03 g (47%); mp 125–127 °C.

IR (ATR): 3063 (w), 3002 (w), 1916 (w), 2834 (w), 1613 (w), 1567 (w), 1518 (w), 1464 (m), 1415 (w), 1322 (w), 1283 (w), 1243 (m), 1182 (w), 1119 (m), 1059 (w), 1025 (m), 977 (w), 932 (m), 900 (m), 833 (s), 823 (s), 754 (s), 716 (w), 636 (w), 616 (w), 609 (m), 576 (w), 543 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 3.77 (s, 3 H, OCH_3), 6.94–7.04 (m, 2 H, ArH), 7.26–7.33 (m, 3 H, ArH), 7.39 (dd, *J* = 7.5, 1.7 Hz, 1 H, ArH), 7.91 (dd, *J* = 8.7, 1.9 Hz, 1 H, ArH), 8.01–8.17 (m, 4 H, ArH), 9.21 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.4 (CH_3), 55.6 (OCH_3), 111.4 (CH), 121.1 (CH), 127.4 (2 CH), 128.6 (CH), 129.0 (CH), 129.3 (C), 129.5 (CH), 129.9 (2 CH), 131.1 (CH), 132.6 (CH), 134.1 (C), 139.9 (C), 140.4 (C), 141.4 (C), 141.5 (C), 143.3 (CH), 151.5 (C), 156.6 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 326 (100) [M^+], 311 (20), 284 (20), 182 (9), 163 (12), 139 (12), 131 (5), 115 (2), 102 (1), 63 (1), 39 (1).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}N_2O$: 327.14919; found: 327.15004.

6-(4-Fluorophenyl)-2-(4-methoxyphenyl)quinoxaline (5d)
Starting with **3h** (0.08 g, 0.3 mmol), **2m** (0.054 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.017 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **5d** was isolated as a white solid; yield: 0.074 g (76%); mp 187–189 °C.

IR (ATR): 3062 (w), 3014 (w), 2970 (w), 2843 (w), 1600 (m), 1545 (w), 1510 (m), 1454 (w), 1401 (w), 1306 (w), 1253 (m), 1226 (m), 1178 (w), 1115 (w), 1100 (w), 1027 (m), 960 (m), 902 (w), 890 (w), 826 (s), 785 (w), 720 (w), 696 (w), 640 (m), 631 (w), 589 (m), 554 (w), 534 (m) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 7.02 (d, ^3J = 9.1 Hz, 2 H, ArH), 7.13 (t, *J* = 8.7 Hz, 2 H, ArH), 7.62–7.69 (m, 2 H, ArH), 7.90 (dd, *J* = 8.7, 2.1 Hz, 1 H, ArH), 8.07–8.16 (m, 4 H, ArH), 9.23 (s, 1 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 114.6 (2 CH), 116.0 (d, $^2J_{CF}$ = 22.0 Hz, 2 CH), 126.4 (CH), 128.9 (2 CH), 129.1 (d, $^3J_{CF}$ = 8.3 Hz, 2 CH), 129.3 (C), 129.6 (CH), 129.8 (CH), 135.9 (d, $^4J_{CF}$ = 3.3 Hz, C), 140.8 (C), 141.4 (C), 141.6 (C), 143.6 (CH), 151.3 (C), 161.5 (C), 163.0 (d, $^1J_{CF}$ = 247.59 Hz, C).

^{19}F NMR (282.40 MHz, $CDCl_3$): δ = –114.27 (ArF).

GC-MS (EI, 70 eV): *m*/*z* (%) = 330 (100) [M^+], 315 (14), 287 (10), 260 (2), 195 (2), 170 (12), 120 (20), 103 (1), 90 (1), 75 (1), 65 (1), 63 (1).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{21}H_{15}FN_2O$: 330.11629; found: 330.11615.

6-(3,5-Dimethylphenyl)-2-(4-fluorophenyl)quinoxaline (5e)

Starting with **3m** (0.07 g, 0.3 mmol), **2e** (0.058 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.017 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **5e** was isolated as a white solid; yield: 0.055 g (63%); mp 163–165 °C.

IR (ATR): 3339 (s), 2919 (w), 2859 (w), 2735 (w), 1599 (m), 1538 (w), 1469 (w), 1410 (w), 1343 (w), 1298 (w), 1264 (w), 1225 (m), 1142 (w), 1048 (m), 960 (m), 911 (w), 839 (m), 827 (s), 789 (w), 722 (m), 684 (m), 634 (w), 612 (s), 573 (w), 552 (w), 541 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.34 (s, 6 H, 2 CH_3), 6.99 (s, 1 H, ArH), 7.16 (t, *J* = 8.7 Hz, 2 H, ArH), 7.29 (s, 2 H, ArH), 7.95 (dd, *J* = 8.7, 1.9 Hz, 1 H, ArH), 8.04–8.20 (m, 4 H, ArH), 9.19 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.4 (2 CH_3), 115.2 (d, $^2J_{CF}$ = 21.97 Hz, 2 CH), 124.4 (2 CH), 125.4 (CH), 128.3 (CH), 128.5 (d, $^3J_{CF}$ = 8.2 Hz, 2 CH), 128.8 (CH), 129.2 (CH), 131.9 (d, $^4J_{CF}$ = 3.2 Hz, C), 137.6 (2 C), 138.6 (C), 140.5 (C), 140.7 (C), 141.6 (C), 142.2 (CH), 149.3 (C), 163.2 (d, $^1J_{CF}$ = 250.8 Hz, C).

^{19}F NMR (282.40 MHz, $CDCl_3$): δ = –110.61 (ArF).

GC-MS (EI, 70 eV): *m*/*z* (%) = 328 (100) [M^+], 313 (3), 180 (13), 164 (3), 130 (9), 115 (5), 94 (1), 75 (1).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{22}H_{17}FN_2$: 328.13703; found: 328.13668.

6-(3,5-Dimethylphenyl)-2-(2-thienyl)quinoxaline (5f)

Starting with **3n** (0.05 g, 0.2 mmol), **2e** (0.039 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.012 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **5f** was isolated as a yellow solid; yield: 0.058 g (91%); mp 152 °C.

IR (ATR): 3106 (w), 3012 (w), 2913 (m), 2858 (w), 2722 (w), 1602 (m), 1573 (w), 1539 (m), 1454 (w), 1417 (m), 1371 (w), 1321 (m), 1238 (w), 1161 (w), 1132 (m), 1064 (w), 1006 (m), 935 (w), 919 (m), 891 (w), 819 (s), 786 (w), 775 (m), 750 (w), 703 (m), 682 (s), 625 (w), 615 (s), 606 (w), 561 (w), 537 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 6.98 (s, 1 H, ArH), 7.10–7.13 (m, 1 H, ArH), 7.29 (s, 2 H, ArH), 7.46 (dd, *J* = 5.1, 1.1 Hz, 1 H, ArH), 7.77 (dd, *J* = 3.8, 1.1 Hz, 1 H, ArH), 7.90–8.16 (m, 3 H, ArH), 9.15 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.4 (2 CH_3), 125.3 (2 CH), 126.4 (CH), 126.8 (CH), 128.5 (CH), 129.2 (CH), 129.7 (CH), 129.8 (CH), 130.2 (CH), 138.6 (3 C), 139.6 (C), 141.4 (C), 141.6 (C), 142.2 (C), 142.4 (CH), 147.0 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 316 (100) [M^+], 301 (4), 180 (19), 158 (7), 130 (14), 115 (5), 69 (1), 63 (1), 57 (1).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}N_2S$: 317.11070; found: 317.11119.

2-(4-Ethylphenyl)-6-(*p*-tolyl)quinoxaline (5g)

Starting with **3o** (0.07 g, 0.3 mmol), **2c** (0.053 g, 1.3 equiv), $Pd(PPh_3)_4$ (0.017 g, 0.05 equiv), 2 M K_2CO_3 (1 mL), and 1,4-dioxane (4 mL), **5g** was isolated as a yellowish solid; yield: 0.046 g (54%); mp 152–154 °C.

IR (ATR): 3021 (w), 2962 (m), 2854 (w), 2729 (w), 1915 (w), 1822 (w), 1727 (w), 1613 (m), 1513 (w), 1452 (m), 1336 (w), 1276 (w), 1209 (w), 1165 (m), 1080 (w), 1015 (w), 960 (m), 932 (m), 894 (w), 835 (m), 817 (s), 788 (w), 722 (w), 665 (w), 608 (m), 588 (w), 554 (w), 542 (w) cm^{-1}.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.5 Hz, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.65 (q, *J* = 7.7 Hz, 2 H, CH_2), 7.22 (d, ^3J = 7.7 Hz, 2 H, ArH), 7.29 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.57 (d, ^3J = 8.1 Hz, 2 H, ArH), 7.92 (dd, *J* = 8.7, 2.1 Hz, 1 H, ArH), 8.02–8.18 (m, 4 H, ArH), 9.21 (s, 1 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 15.4 (CH_3), 21.2 (CH_3), 28.8 (CH_2), 126.1 (CH), 127.3 (2 CH), 127.5 (2 CH), 128.7 (2 CH), 129.7 (2 CH), 129.8 (2 CH), 134.3 (C), 136.8 (C), 138.1 (C), 141.6 (C), 141.7 (C), 141.9 (C), 143.7 (CH), 146.7 (C), 151.5 (C).

GC-MS (EI, 70 eV): *m*/*z* (%) = 324 (100) [M^+], 309 (36), 254 (1), 166 (8), 154 (7), 116 (11), 103 (1), 91 (2), 77 (1), 51 (1).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{23}H_{20}N_2$: 324.16210; found: 324.16206.

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