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Sulfur-mediated annulation of 1,2-phenylenediamines towards benzofuro- and benzothieno-quinoxalines†

Loan T. Tran,‡[a,b] Tuan H. Ho,‡[a,b] Nhu T. A. Phan,[a,b] Tung T. Nguyen*[a,b] and Nam T. S. Phan*[a,b]

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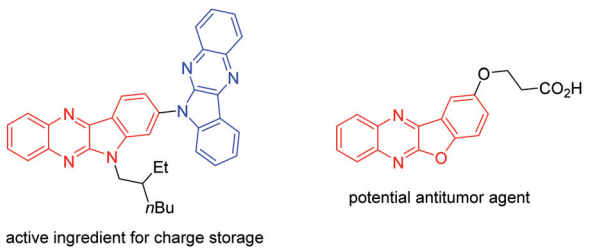
We report a method for condensation between *ortho*-phenylenediamines and *ortho*-hydroxyacetophenones to afford benzofuroquinoxalines. The reactions proceeded in the presence of an elemental sulfur mediator, DABCO base, and DMSO solvent. Functionalities such as nitrile, ester, and halogen groups were compatible. The conditions could be applicable for the synthesis of benzothienoquinoxalines from *ortho*-chloroacetophenones.

Introduction

Quinoxaline-embedded polyaromatics find uses in functional materials and bio-related studies (Scheme 1).[1] Nevertheless, synthetic methodologies for these highly condensed molecules are exceedingly rare. Most of the known examples are of indoloquinoxalines.[2] Only a few methods for the synthesis of furan- and thiophene-fused compounds were reported. Zanardi and co-workers presented a radical annulation of 2-cyanoaryl diazonium salts with isothiocyanates to afford benzothienoquinoxalines.[3a] In one example, benzofuroquinoxaline was obtained in a moderate yield after a two-step condensation/substitution of 1,2-phenylenediamine and a chloro-substituted α-ketothioester.[3b] The development of a general method for the synthesis of these furan- and thiophene-fused quinoxalines is thus in demand.

Elemental sulfur mediated annulation of *ortho*-phenylenediamines and C–H bonds has been recently used as a direct method to obtain quinoxalines and other *N*,*N*-polyaromatics.[4] Since the cheap, abundant elemental sulfur has been known for the functionalization of C–H bonds α to C=O groups,[5] the element was previously used to facilitate the coupling of cycloalkanones with diamines, affording tricyclic, substituted quinoxalines.[4a] The reactions did not require the use of any external bases and solvents. The addition of a strong acid such as trifluoroacetic acid could diversify the outcome of the reactions, furnishing tetraamination products.[4b] We envisaged that if the quinoxaline ring is formed in the presence of a proximal nucleophile such as phenoxide or thiolate, intramolecular cyclization would be viable, thus affording another fused ring. Such a design is observed in *ortho*-hydroxyacetophenones or *ortho*-haloacetophenones. It should be noted that although oxidation of α sp^3 C–H bonds in ketones with elemental sulfur is well precedented, certain problems are still unsolved. Firstly, methyl C–H bonds in acetophenones are less reactive than those in cycloalkanones.[6] Most of the known methods often suffer from the use of prefunctionalized oxime esters.[7] Secondly, sterically hindered, *ortho*-substituted acetophenones are sometimes incompetent substrates in elemental-sulfur-promoted transformations.[5b] Herein we report our attempts to obtain benzofuroquinoxalines *via* a coupling of *ortho*-phenylenediamines and *ortho*-hydroxyacetophenones. The reactions proceeded in the presence of an elemental sulfur mediator, DABCO base, and DMSO solvent. Later, the same conditions were used to annulate *ortho*-chloroacetophenones with diamines, thus furnishing benzothienoquinoxalines presumably after an S_NAr-type sulfuration.



Scheme 1 Quinoxaline-fused polyaromatics.

[a]*Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam. E-mail: tungtn@hcmut.edu.vn, ptsnam@hcmut.edu.vn*

[b]*Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam*

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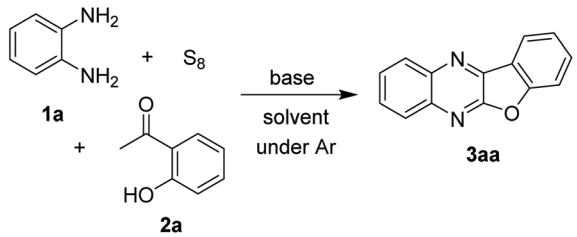
‡These authors contributed equally to this work.

Results and discussion

We started our study by focusing on the reaction of 1,2-phenylenediamine **1a** and 2′-hydroxyacetophenone **2a** in the presence of elemental sulfur. Optimization was carried out with respect to the solvent and base. The results are presented in Table 1. The annulation was tolerant of most bases, including inorganic and organic bases (entries 1–6). Similar to our previous studies,[8] DABCO was the most active base, affording 97% yield of benzofuroquinoxaline **3aa** (entry 4). Decreasing the amount of elemental sulfur resulted in significant drops of yields (entries 7–9). Meanwhile, performing the annulation in the presence of 3 equivalents of elemental sulfur furnished a quantitative yield of **3aa** (entry 10). Omitting the base had a negative impact on the reaction (entry 11). The reaction could be set up under air without a prominent loss of yield (entry 12). Solvents other than DMSO were not effective for the annulation (entries 13 and 14). A solvent-free reaction afforded **3aa** in 24% yield (entry 15). Decreasing the amount of DMSO afforded **3aa** in a quantitative yield (entry 16). Lastly, the kinetic study indicated that the annulation could be performed within 0.5 h (Scheme 2).

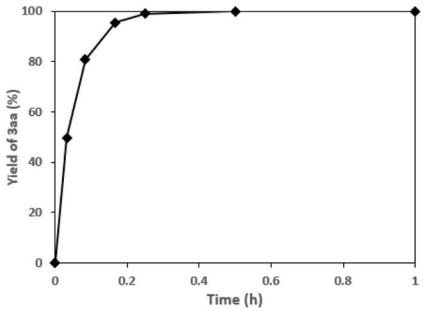
The scope of 1,2-phenylenediamines was next studied. The results are presented in Scheme 3. It should be noted that tolerance of functionalities has not been mentioned in the previous sulfur-mediated annulation of 1,2-phenylediamines.[6a,b] Using our standard conditions, the unsubstituted benzofuroquinoxaline **3aa** was isolated in 97% yield. Unsymmetrical diamines afforded the products as mixtures of isomers (at positions *x* and *y*, Scheme 3). Either electron-rich (**3ba** + **3b′a**, **3ca** + **3c′a**) or electron-poor (**3da** + **3d′a**, **3ea**, **3fa** + **3f′a**) diamines were competent substrates. Cyano (**3ea**) and ester (**3fa** + **3f′a**) groups remained intact after annulation. Reduction of the nitro functionality was observed, affording amino-substituted benzofuroquinoxaline **3ga** in a moderate yield. Its photophysical properties were somewhat different from those of other derivatives.[9] Disubstituted 1,2-phenylenediamines were

Table 1 Studies of reaction conditions[a]

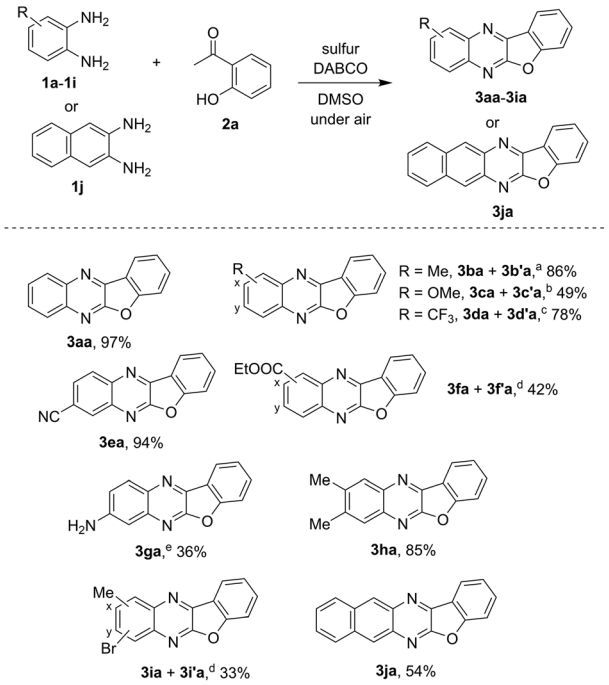


Entry	Base	Sulfur amount (equiv.)	Solvent	Yield of **3aa** (%)
1	NaOH	2	DMSO	74
2	KOH	2	DMSO	69
3	K_3PO_4	2	DMSO	69
4	DABCO	2	DMSO	97
5	MM	2	DMSO	70
6	DMPP	2	DMSO	81
7	DABCO	1	DMSO	92
8	DABCO	0.5	DMSO	86
9	DABCO	0.25	DMSO	40
10	DABCO	3	DMSO	Quant.
11	—	3	DMSO	61
12[b]	DABCO	3	DMSO	Quant.
13[b]	DABCO	3	CH_3CN	22
14[b]	DABCO	3	Dioxane	14
15[b]	DABCO	3	—	24
16[b,c]	DABCO	3	Dioxane	Quant.

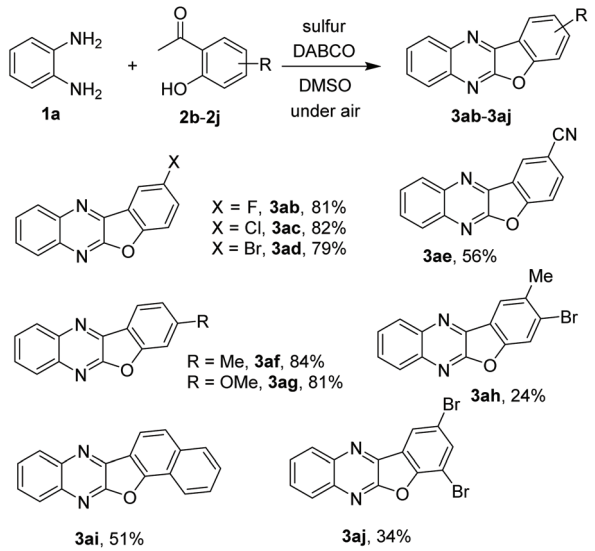
[a] **1a** (0.25 mmol), **2a** (0.5 mmol), elemental sulfur (32 g mol^{-1}), base (1.5 equiv.), solvent (0.5 mL) under argon at 120 °C for 16 h. Yields of **3aa** are GC yields using a diphenyl ether internal standard. [b] Under air. [c] DMSO (1 mmol). Abbreviations: MM = *N*-methylmorpholine, DMPP = *N*,*N*-dimethylpiperazine, quant. = quantitative.



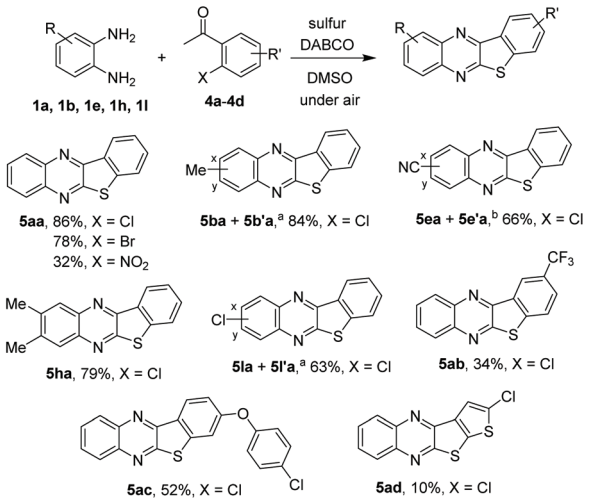
Scheme 2 Kinetic profile of the annulation of **1a** and **2a**.



Scheme 3 Scope of 1,2-phenylenediamines. Reaction conditions: Diamines (0.25 mmol), **2a** (1.05 equiv.), elemental sulfur (0.75 mmol, 32 g mol^{-1}), DABCO (1.5 equiv.), DMSO (1 mmol), 120 °C, 30 min. Yields are isolated yields. [a] Obtained as a 7 : 3 regioisomeric product. [b] Obtained as a 94 : 6 regioisomeric product. [c] Obtained as a 4 : 1 regioisomeric product. [d] Obtained as a 2 : 1 regioisomeric product. [e] The nitro group was reduced after the reaction.



Scheme 4 Scope of 2′-hydroxyacetophenones. Reaction conditions: **1a** (0.25 mmol), **2b–2j** (1.05 equiv.), elemental sulfur (0.75 mmol, 32 g mol^{-1}), DABCO (1.5 equiv.), DMSO (1 mmol), 120 °C, 30 min. Yields are isolated yields.

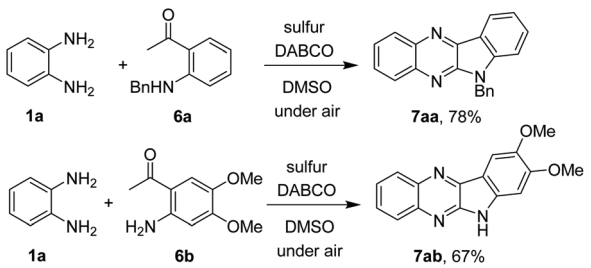


Scheme 5 Synthesis of benzothienoquinoxalines. Reaction conditions: Diamines (1.5 equiv.), 2′-haloacetophenones (0.25 mmol), elemental sulfur (0.5 mmol, 32 g mol^{-1}), DABCO (0.75 mmol), DMSO (0.5 mmol), 120 °C, 2 h. Yields are isolated yields. [a] Obtained as 8 : 1 mixtures of regioisomeric products. [b] Obtained as a 5 : 1 mixture of regioisomeric products.

also compatible with the conditions (**3ha**, **3ia** + **3i′a**, **3ja**). A hindered diamine afforded the products (**3ia** + **3i′a**) in 33% yield, implying the steric effect on annulation. Polycyclic benzofuroquinoxaline **3ja** was obtained in a moderate yield when naphthylene-1,2-diamine was used.

The reaction scope with respect to 2′-hydroxyacetophenones is presented in Scheme 4. Halo-substituted substrates were competent substrates apart from **2h**, furnishing the benzofuroquinoxalines in good yields (**3ab**, **3ac**, **3ad**). The reaction conditions were tolerant of reducing-sensitive functionalities such as the CN group (**3ae**). Uses of electron-rich 2′-hydroxyacetophenones were feasible (**3af**, **3ag**). An acetyl naphthol successfully coupled with 1,2-phenylenediamine to afford a pentacyclic furoquinoxaline in 51% yield (**3ai**). A hindered, 3′-substituted 2′-hydroxyacetophenone could also be used to afford the benzofuroquinoxaline in a moderate yield (**3aj**).

The standard conditions were suitable for the synthesis of benzothienoquinoxalines when 2′-chloroacetophenones were used to couple with 1,2-phenylenediamines. We proposed that an intramolecularly nucleophilic sulfuration would forge an annulated thiophene ring.[10] The scope of the substrates is presented in Scheme 5. A high yield of unsubstituted benzothienoquinoxaline **5aa** was obtained when 2′-chloroacetophenone was used. *ortho*-Bromo- and *ortho*-nitroacetophenones could be used, albeit affording **5aa** in lower yields. Annulation of other 1,2-phenylenediamines with 2′-chloroacetophenone was viable. Although unsymmetrical diamines afforded regioisomeric benzothienoquinoxalines, the ratios were acceptable (**5ba**, **5fa**, **5la**). The derivatives of 2′-chloroacetophenones were compatible with the reaction conditions, affording substituted benzothienoquinoxalines in moderate to good yields (**5ab**, **5ac**). A 6,6,5,5-tetracyclic heterocycle was obtained in a small quantity (**5ad**).

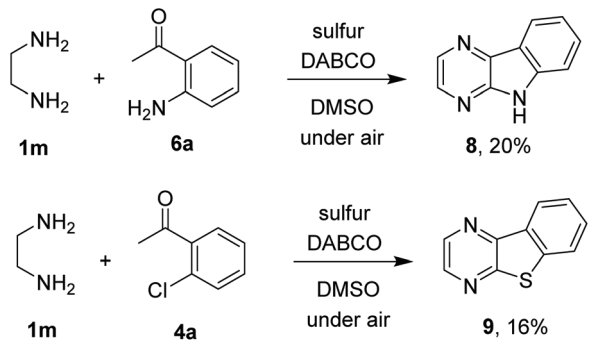


Scheme 6 Annulation of 1,2-phenylenediamine and 2′-aminoacetophenones. Reaction conditions: **1a** (0.25 mmol), **6a** or **6b** (0.5 mmol), elemental sulfur (1.05 equiv.), DABCO (1.5 equiv.), DMSO (1 mmol), 120 °C, 30 min. Yields are isolated yields.

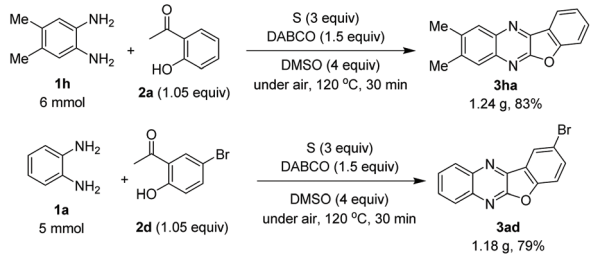
Indoloquinoxalines were the products when phenylenediamines coupled with 2′-aminoacetophenones such as **6a** and **6b**. Thus, *N*-benzyl indoloquinoxaline **7aa** was isolated in 78% yield (Scheme 6). Unprotected 2′-aminoacetophenone was also a competent substrate, affording the product **7ab** in 67% yield. Attempts to couple aliphatic diamines were also carried out (Scheme 7). Substituted piperazines (**8**, **9**) were obtained in low yields from the annulation of ethylenediamine.

The method was somewhat easy to scale up. Such examples for the synthesis of benzofuroquinoxalines are shown in Scheme 8. The yields were comparable with those obtained in small scale runs.

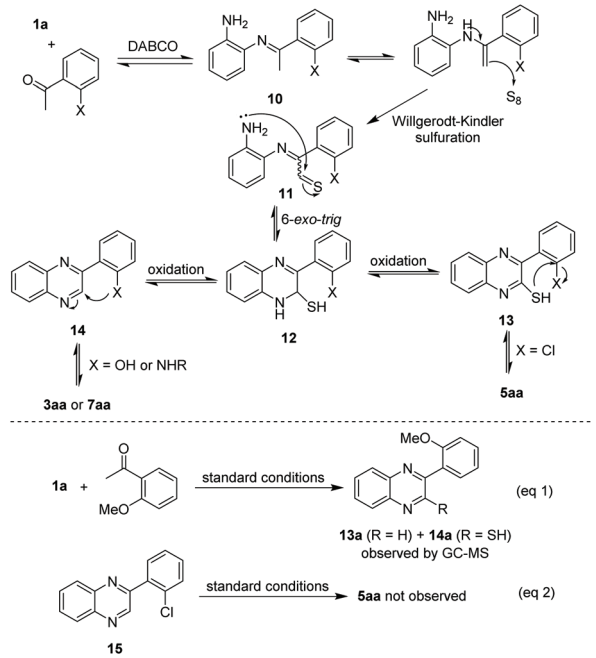
At this moment, we propose a possible mechanism as shown in Scheme 9. Condensation of diamine **1a** and the ketone functionality would afford imine **10**. The control experiment showed a significant amount of the imine when DABCO was used at elevated temperature. Tautomerization followed by sulfuration of α C–H bonds gave Willgerodt–Kindler type imi-



Scheme 7 Annulation of ethylenediamine. Reaction conditions: Ethylenediamine (0.25 mmol), **6a** or **4a** (0.5 mmol), elemental sulfur (2.5 equiv.), DABCO (1.5 equiv.), DMSO (1 mmol), 120 °C, 30 min. Yields are isolated yields.



Scheme 8 Gram-scale reactions.



Scheme 9 Mechanistic consideration.

nothioaldehyde **11**. A rapid 6-*exo-trig* cyclization would afford a hemi thioaminal **12**. Oxidation of **12** furnished thiol-derived quinoxaline **13** or **14**. Since a low yield (24% for **3aa**) of the annulation product was obtained when DMSO was omitted, it was envisaged that elemental sulfur was the major oxidant. A synergistic effect of elemental sulfur and DMSO as co-oxidants is known.[4b] When 2′-methoxyacetophenone was reacted with **1a** under standard conditions, a mixture of quinoxalines (**13a**, **14a**) was obtained (eqn (1)). It should be noted that 2-halosubstituted intermediate **13** was crucial for the formation of benzothienoquinoxaline **5aa**, since intermolecular sulfuration of chloro-substituted quinoxaline **15** was not observed (eqn (2)), thus supporting the suggested mechanism. Meanwhile, benzofuroquinoxaline **5aa** or indoloquinoxaline **7aa** could be obtained by an intramolecular cyclization of phenol (X = OH) or aniline (X = NHR) functionalities in intermediates **14**.

Conclusions

In conclusion, we have developed a method for the sulfur-mediated synthesis of benzofuroquinoxalines, benzothienoquinoxalines, and indoloquinoxalines from annulation of 1,2-phenylenediamines. The use of functional groups such as halogens, esters, and nitriles was compatible with the reaction conditions. Early mechanistic studies proposed an oxidative sulfuration of α C–H bonds in *ortho*-substituted acetophenones followed by intramolecular addition of amine to afford quinoxalines. Ongoing projects include the expansion of the reaction scope.

Experimental

Materials and instrumentation

All reagents and starting materials were obtained commercially and used as received without any further purification unless otherwise noted. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). GC-MS analyses were performed on a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). ^{1}H NMR and ^{13}C NMR were performed on Bruker AV 500 spectrometers. Chemical shifts were reported in ppm and referenced to the residual peak for $CDCl_3$ (δ = 7.26 ppm for ^{1}H NMR and δ = 77.2 ppm for ^{13}C NMR) or DMSO-d_6 (δ = 2.50 ppm for ^{1}H NMR and δ = 39.5 ppm for ^{13}C NMR). Splitting was reported with the following symbols: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, td = triplet of doublets, dd = doublet of doublets, ddd = doublet of doublets of doublets, and m = multiplet. Coupling constants (J) were reported in hertz. HR-MS spectra were recorded using an Agilent HPLC 1200 Series coupled to a Bruker micrOTOF-QII. Compound **15** was synthesized following a known procedure.[11]

General procedure

In a typical experiment, a vial equipped with a magnetic stir bar was charged with *o*-phenylenediamine **1a** (0.25 mmol),

2′-hydroxyacetophenone **2a** (0.5 mmol), elemental sulfur (32 mg $mmol^{-1}$), DABCO, and DMSO. The vial was placed on a pre-heated oil bath at 120 °C, and then stirred for 30 min. Upon the completion of the reaction, ethyl acetate (5 mL) and brine (5 mL) were added to quench the reaction. The organic phase was then extracted with ethyl acetate (3 × 5 mL), dried over anhydrous Na_2SO_4, filtered, and purified by column chromatography using an eluent of hexanes/EtOAc.

Benzofuro[2,3-*b*]quinoxaline (3aa). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 53.2 mg (97%) of a yellow-white solid was obtained. R_f = 0.31 (hexanes/ethyl acetate 12 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 7.7 Hz, 1H), 8.33–8.29 (m, 1H), 8.19–8.15 (m, 1H), 7.84–7.78 (m, 2H), 7.74–7.70 (m, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.54–7.49 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 156.0, 141.3, 140.7, 139.9, 132.5, 129.9, 129.3, 128.8, 128.4, 124.6, 123.1, 121.4, 112.9. HR-MS (ESI) calcd for $C_{14}H_9N_2O^+$ $[M + H]^+$: 221.0709, found 221.0706.

9-Methylbenzofuro[2,3-*b*]quinoxaline and 8-methylbenzofuro[2,3-*b*]quinoxaline (3ba + 3b′a). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 50.4 mg (86% yield) of a yellow-white solid (as a 7 : 3 regioisomeric product) was obtained. R_f = 0.36 (major) and 0.33 (minor) (hexanes/ethyl acetate 9 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31–8.29 (overlapping of two isomers, 1H), 8.15 (minor isomer, dd, J = 8.5, 2.0 Hz, 1H), 8.04 (major isomer, s, 0.7H), 8.02 (major isomer, dd, J = 8.5, 2.0 Hz, 1H), 7.90 (minor isomer, s, 1H), 7.71–7.58 (overlapping of two isomers, 3H), 7.49–7.47 (overlapping of two isomers, 1H), 2.62 (overlapping of two isomers, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 158.5, 158.3, 156.1, 155.7, 141.3, 140.6, 140.3, 140.0, 139.76, 139.66, 138.8, 138.2, 132.1, 132.0, 130.7, 128.7, 128.23, 123.19, 127.8, 124.48, 124.45, 122.9, 122.8, 121.53, 121.49, 112.82, 112.79, 22.0, 21.8. HR-MS (ESI) calcd for $C_{15}H_{11}N_2O^+$ $[M + H]^+$: 235.0866, found 235.0866.

9-Methoxybenzofuro[2,3-*b*]quinoxaline and 8-methoxybenzofuro[2,3-*b*]quinoxaline (3ca + 3c′a). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 30.7 mg (49% yield) of a yellow-white solid (as a 96 : 4 regioisomeric product) was obtained. R_f (major) = 0.34 (hexanes/ethyl acetate 5 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (major isomer, dd, J = 7.5, 0.5 Hz, 1H), 8.29 (minor isomer, dd, J = 7.5, 0.5 Hz, 1H), 8.15 (minor isomer, d, J = 9.2 Hz, 1H), 8.03 (major isomer, d, J = 9.2 Hz, 1H), 7.72–7.67 (overlapping of two isomers, 2H), 7.59 (overlapping of two isomers, for the major isomer, d, J = 2.5 Hz, 1H), 7.50–7.45 (overlapping of two isomers, 2H), 4.00 (overlapping of two isomers, for the major isomer, s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 159.8, 158.4, 155.1, 142.8, 140.2, 135.5, 132.2, 129.5, 124.4, 122.9, 122.7, 121.5, 112.9, 107.1, 55.9. HR-MS (ESI) calcd for $C_{15}H_{11}N_2O_2^+$ $[M + H]^+$: 251.0815, found 251.0831.

8-(Trifluoromethyl)benzofuro[2,3-*b*]quinoxaline and 9-(trifluoromethyl)benzofuro[2,3-*b*]quinoxaline (3da + 3d′a). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 56.0 mg (78% yield) of a yellow-white solid (as a 4 : 1 regioisomeric product) was obtained. Less than 5% impurity as hydroxyquinoxaline was also observed. R_f = 0.40 (major) and 0.30 (minor) (hexanes/ethyl acetate 20 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (minor isomer, s, 1H), 8.42 (major isomer, s, 1H), 8.36 (major isomer, d, J = 8.8 Hz, 1H), 8.32 (major isomer, d, J = 8 Hz, 1H), 8.31 (minor isomer, d, J = 7.5 Hz, 1H), 8.23 (minor isomer, d, J = 8.7 Hz, 1H), 7.97–7.93 (overlapping of two isomers, 1H), 7.70–7.67 (overlapping of two isomers, 1H), 7.54–7.51 (overlapping of two isomers, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 158.9, 158.8, 156.6, 156.3, 142.6, 142.3, 142.1, 141.1, 140.1, 138.8, 133.3, 133.2, 131.2 (q, J = 33.0 Hz), 130.3, 129.8, 127.1 (minor isomer, q, J = 4.4 Hz), 126.6 (major isomer, q, J = 4.4 Hz), 125.3 (minor isomer, q, J = 2.5 Hz), 124.8, 124.0 (major isomer, q, J = 3.1 Hz), 123.3, 122.7, 120.7. HR-MS (ESI) calcd for $C_{15}H_8F_3N_2O^+$ $[M + H]^+$: 289.0583, found 289.0584.

Benzofuro[2,3-*b*]quinoxaline-8-carbonitrile (3ea). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 57.4 mg (94% yield) of a yellow-brown solid was obtained. R_f = 0.34 (hexanes/ethyl acetate 3 : 1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.66 (d, J = 1.7 Hz, 1H), 8.42 (d, J = 8.6 Hz, 1H), 8.37 (d, J = 7.6 Hz, 1H), 8.13 (dd, J = 8.6, 1.8 Hz, 1H), 7.93–7.87 (m, 2H), 7.67–7.60 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.4, 155.8, 142.7, 142.0, 138.1, 133.7, 133.5, 130.1, 129.0, 124.8, 122.9, 119.9, 117.7, 112.6, 111.6. HR-MS (ESI) calcd for $C_{15}H_8N_3O^+$ $[M + H]^+$: 246.0662, found 246.0653.

Ethyl benzofuro[2,3-*b*]quinoxaline-8-carboxylate and ethyl benzofuro[2,3-*b*]quinoxaline-9-carboxylate (3fa + 3f′a). After column chromatography (2% triethylamine in hexanes/ethyl acetate 100 : 1 to 5 : 1), 30.5 mg (42% yield) of a white solid (as a 2 : 1 regioisomeric product) was obtained. R_f = 0.36 (major) and 0.33 (minor) (hexanes/ethyl acetate 9 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (minor isomer, d, J = 1.8 Hz, 1H), 8.84 (major isomer, d, J = 1.8 Hz, 1H), 8.40–8.34 (overlapping of two isomers, 1H), 8.33–8.31 (overlapping of two isomers, 1H), 8.29 (major isomer, d, J = 8.7 Hz, 1H), 8.16 (minor isomer, d, J = 8.7 Hz, 1H), 7.76–7.70 (overlapping of two isomers, 1H), 7.76–7.67 (overlapping of two isomers, 1H), 7.53–7.50 (overlapping of two isomers, 1H), 4.50–4.46 (overlapping of two isomers, 2H), 1.48–1.45 (overlapping of two isomers, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 165.98, 165.94, 159.1, 158.8, 156.7, 156.3, 143.4, 142.4, 139.1, 133.3, 133.0, 131.7, 131.3, 131.2, 130.3, 129.45, 129.38, 128.9, 128.1, 124.9, 124.8, 123.4, 123.2, 121.0, 113.0, 112.9, 61.73, 61.68, 14.5. HR-MS (ESI) calcd for $C_{17}H_{13}N_2O_3^+$ $[M + H]^+$: 293.0921, found 293.0912.

Benzofuro[2,3-*b*]quinoxalin-8-amine (3ga). After column chromatography (hexanes/toluene/ethyl acetate 1 : 1 : 1), 21.0 mg (36% yield) of a yellow-orange solid was obtained. R_f = 0.27 (hexanes/toluene/ethyl acetate 1 : 1 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 3.8 Hz, 2H), 7.48–7.43 (m, 1H), 7.21 (d, J = 2.3 Hz, 1H), 7.19 (dd, J = 8.9, 2.5 Hz, 1H), 4.25 (bs, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 156.8, 148.4, 142.3, 136.6, 136.3, 131.0, 130.4, 124.3, 122.0, 120.2, 112.6, 108.3. HR-MS (ESI) calcd for $C_{14}H_{10}N_3O^+$ $[M + H]^+$: 236.0818, found 236.0842.

8,9-Dimethylbenzofuro[2,3-*b*]quinoxaline (3ha). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 52.8 mg (85% yield) of a yellow-white solid was obtained. R_f = 0.33 (hexanes/ethyl acetate 12 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 7.7 Hz, 1H), 8.05 (s, 1H), 7.90 (s, 1H), 7.71–7.64 (m, 2H), 7.51–7.47 (m, 1H), 2.54 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 155.9, 140.7, 140.1, 139.3, 138.8, 138.7, 132.0, 128.3, 128.0, 124.4, 122.8, 121.6, 112.8, 20.6, 20.4. HR-MS (ESI) calcd for $C_{16}H_{13}N_2O^+$ $[M + H]^+$: 249.1022, found 249.1018.

8-Bromo-10-methylbenzofuro[2,3-*b*]quinoxaline and 9-bromo-7-methylbenzofuro[2,3-*b*]quinoxaline (3ia + 3i′a). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 26.1 mg (33% yield) of a yellow-white solid (as a 7 : 3 regioisomeric product) was obtained. R_f = 0.38 (for both isomers) (hexanes/ethyl acetate 20 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33–8.29 (overlapping of two isomers, 1H), 8.28 (minor isomer, dd, J = 2.2, 0.5 Hz, 1H), 8.13 (major isomer, dd, J = 2.2, 0.5 Hz, 1H), 7.75–7.68 (overlapping of two isomers, 2H), 7.68–-7.64 (overlapping of two isomers, 1H), 7.54–7.47 (overlapping of two isomers, 1H), 2.90 (major isomer, s, 3H), 2.82 (minor isomer, s, 0.9H). ^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 158.7, 156.1, 140.7, 139.7, 139.6, 139.5, 138.8, 133.2, 132.7, 132.4, 131.8, 129.4, 128.9, 124.7, 124.6, 123.6, 123.1, 123.0, 121.6, 121.2, 112.9, 17.8, 17.5. HR-MS (ESI) calcd for $C_{15}H_{10}{}^{79}BrN_2O^+$ $[M + H]^+$: 312.9971, found 312.9981.

Benzo[*g*]benzofuro[2,3-*b*]quinoxaline (3ja). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 36.7 mg (54% yield) of a yellow-orange solid was obtained. R_f = 0.33 (hexanes/ethyl acetate 7 : 1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.91 (s, 1H), 8.71 (s, 1H), 8.33 (d, J = 7.7 Hz, 1H), 8.28–8.21 (m, 2H), 7.87–7.81 (m, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.67–7.63 (m, 2H), 7.61–7.56 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.4, 155.1, 141.9, 137.6, 135.8, 133.2, 132.8, 131.9, 127.8, 127.4, 126.9, 126.5, 125.9, 125.4, 124.4, 122.6, 120.3, 112.3. HR-MS (ESI) calcd for $C_{18}H_{11}N_2O^+$ $[M + H]^+$: 271.0856, found 271.0851.

2-Fluorobenzofuro[2,3-*b*]quinoxaline (3ab). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 47.9 mg (81% yield) of a yellow-white solid was obtained. This compound is known.[3c] R_f = 0.35 (hexanes/ethyl acetate 15 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 8.01 (dd, J = 7.1, 2.0 Hz, 1H), 7.86–7.78 (m, 2H), 7.64 (dd, J = 9.0, 3.8 Hz, 1H), 7.43 (td, J = 8.9, 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6 (d, J = 244.3 Hz), 156.5, 154.3, 141.2, 140.0, 130.2, 129.3, 128.7, 128.5, 122.3 (d, J = 9.6 Hz), 119.7 (d, J = 25.9 Hz), 113.8 (d, J = 8.6 Hz), 109.0 (d, J = 25.4 Hz). One carbon signal could not be located.

2-Chlorobenzofuro[2,3-*b*]quinoxaline (3ac). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 52.3 mg (82% yield) of a yellow-white solid was obtained. R_f = 0.38 (hexanes/ethyl acetate 10 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 2.0 Hz, 1H), 8.32–8.29 (m, 1H), 8.20–8.17 (m, 1H), 7.87–7.80 (m, 2H), 7.68 (dd, J = 8.7, 2.0 Hz, 1H), 7.63 (d, J = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 156.2, 141.6, 140.2, 139.6, 132.4, 130.4, 129.5, 128.9, 128.7, 122.83, 122.78, 114.1. HR-MS (ESI) calcd for $C_{14}H_8{}^{35}ClN_2O^+$ $[M + H]^+$: 255.0320, found 255.0320.

2-Bromobenzofuro[2,3-*b*]quinoxaline (3ad). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 58.9 mg (79% yield) of a yellow-white solid was obtained. R_f = 0.32 (hexanes/ethyl acetate 10 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 2.0 Hz, 1H), 8.29 (dd, J = 8.1, 1.5 Hz, 1H), 8.17 (dd, J = 8.2, 1.4 Hz, 1H), 7.85–7.79 (m, 3H), 7.57 (d, J = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 156.0, 141.5, 140.2, 139.3, 135.2, 130.4, 129.5, 128.8, 128.7, 125.8, 123.3, 117.6, 114.5. HR-MS (ESI) calcd for $C_{14}H_8{}^{79}BrN_2O^+$ $[M + H]^+$: 298.9815, found 298.9817.

Benzofuro[2,3-*b*]quinoxaline-2-carbonitrile (3ae). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 34.3 mg (56% yield) of a yellow-white solid was obtained. R_f = 0.35 (hexanes/ethyl acetate 2 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, J = 1.3 Hz, 1H), 8.35–8.31 (m, 1H), 8.22–8.18 (m, 1H), 7.99 (dd, J = 8.6, 1.7 Hz, 1H), 7.91–7.85 (m, 2H), 7.81 (d, J = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 156.0, 141.9, 140.4, 138.6, 135.6, 131.0, 129.7, 129.2, 129.0, 127.5, 122.7, 118.2, 114.2, 108.9. HR-MS (ESI) calcd for $C_{15}H_8N_3O^+$ $[M + H]^+$: 246.0662, found 246.0667.

3-Methylbenzofuro[2,3-*b*]quinoxaline (3af). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 49.3 mg (84% yield) of a yellow-white solid was obtained. R_f = 0.25 (hexanes/ethyl acetate 10 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, J = 6.5, 3.0 Hz, 1H), 8.18 (d, J = 7.9 Hz, 1H), 8.13 (dd, J = 6.6, 2.9 Hz, 1H), 7.80–7.73 (m, 2H), 7.46 (s, 1H), 7.29 (d, J = 7.8 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 156.1, 144.1, 141.2, 140.8, 139.6, 129.5, 129.1, 128.7, 128.3, 125.9, 122.6, 118.7, 113.1, 22.6. HR-MS (ESI) calcd for $C_{15}H_{11}N_2O^+$ $[M + H]^+$: 235.0866, found 235.0897.

3-Methoxybenzofuro[2,3-*b*]quinoxaline (3ag). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 50.7 mg (81% yield) of a yellow-white solid was obtained. This compound is known.[12] R_f = 0.33 (hexanes/ethyl acetate 2 : 1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24–8.20 (m, 1H), 8.18 (d, J = 8.6 Hz, 1H), 8.10–8.06 (m, 1H), 7.84–7.80 (m, 2H), 7.42 (d, J = 2.2 Hz, 1H), 7.14 (dd, J = 8.6, 2.2 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.5, 159.6, 155.3, 140.4, 140.0, 137.9, 128.7, 128.2, 127.77, 127.72, 123.1, 112.9, 112.7, 97.5, 55.9.

3-Bromo-2-methylbenzofuro[2,3-*b*]quinoxaline (3ah). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 19.1 mg (24% yield) of a yellow-white solid was obtained. R_f = 0.33 (hexanes/ethyl acetate 8 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28–8.24 (m, 1H), 8.17 (s, 1H), 8.16–8.12 (m, 1H), 7.89 (s, 1H), 7.83–7.76 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 156.1, 141.5, 140.0, 139.9, 134.6, 130.0, 129.3, 128.8, 128.6, 123.7, 120.7, 116.8, 23.2. HR-MS (ESI) calcd for $C_{15}H_{10}{}^{79}BrN_2O^+$ $[M + H]^+$: 312.9952, found 312.9971.

Naphtho[2′,1′:4,5]furo[2,3-*b*]quinoxaline (3ai). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 34.4 mg (51% yield) of a yellow solid was obtained. R_f = 0.31 (hexanes/ethyl acetate 6 : 1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.49 (d, J = 7.9 Hz, 1H), 8.35–8.31 (m, 1H), 8.29 (d, J = 8.5 Hz, 1H), 8.21

(d, J = 7.6 Hz, 1H), 8.20–8.16 (m, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.93–7.88 (m, 2H), 7.86–7.79 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.2, 154.8, 140.8, 140.1, 138.5, 134.9, 129.2, 128.52, 128.49, 128.47, 128.1, 128.0, 127.4, 124.8, 120.5, 119.9, 117.8, 115.7. HR-MS (ESI) calcd for $C_{18}H_{11}N_2O^+$ $[M + H]^+$: 271.0856, found 271.0866.

2,4-Dibromobenzofuro[2,3-*b*]quinoxaline (3aj). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 32.5 mg (34% yield) of a yellow-white solid was obtained. R_f = 0.37 (hexanes/ethyl acetate 15 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, J = 1.9 Hz, 1H), 8.31–8.27 (m, 1H), 8.20–8.16 (m, 1H), 7.99 (d, J = 1.9 Hz, 1H), 7.89–7.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 154.7, 141.8, 140.4, 139.1, 137.3, 130.9, 129.6, 129.1, 129.0, 124.6, 124.5, 117.8, 106.7. HR-MS (ESI) calcd for $C_{14}H_7{}^{79}Br_2N_2O^+$ $[M + H]^+$: 376.8920, found 376.8910.

Benzo[4,5]thieno[2,3-*b*]quinoxaline (5aa). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 51.0 mg (86% yield) of a yellow-white solid was obtained. This compound is known.[3a] When 2′-bromoacetophenone (0.25 mmol, 49.8 mg) was used, 46.0 mg (78% yield) of the desired product was obtained. When 2′-nitroacetophenone (0.25 mmol, 41.3 mg) was used, 19.0 mg (32% yield) of the desired product was obtained. R_f = 0.35 (hexanes/ethyl acetate 10 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 7.8, 0.6 Hz, 1H), 8.27–8.23 (m, 1H), 8.15–8.11 (m, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.81–7.75 (m, 2H), 7.65–7.60 (m, 1H), 7.57–7.52 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 147.9, 141.5, 140.5, 140.1, 131.5, 131.0, 129.8, 129.6, 129.1, 128.4, 125.8, 124.5, 123.6.

9-Methylbenzo[4,5]thieno[2,3-*b*]quinoxaline and 8-methylbenzo[4,5]thieno[2,3-*b*]quinoxaline (5ba + 5b′a). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 52.6 mg (84% yield) of a yellow-white solid (as an 8 : 1 regioisomeric product) was obtained. The major isomer is known.[3a] R_f = 0.30 (for both isomers) (hexanes/ethyl acetate 8 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (major isomer, d, J = 7.8 Hz, 1H), 8.56 (minor isomer, d, J = 7.8 Hz, 1H), 8.17 (minor isomer, d, J = 8.6 Hz, 0.11H), 8.06–8.03 (major isomer, m, 2H), 7.92 (minor isomer, s, 1H), 7.87–7.75 (overlapping of two isomers, 1H), 7.68–7.62 (overlapping of two isomers, 2H), 7.59–7.56 (overlapping of two isomers, 1H), 2.64 (overlapping of two isomers, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 156.5, 147.6, 141.6, 140.7, 140.5, 140.15, 140.11, 139.8, 132.3, 131.66, 131.59, 131.0, 130.8, 129.1, 128.3, 128.0, 127.3, 125.8, 124.5, 124.3, 123.7, 22.1, 22.0.

Benzo[4,5]thieno[2,3-*b*]quinoxaline-8-carbonitrile and benzo[4,5]thieno[2,3-*b*]quinoxaline-9-carbonitrile (5ea + 5e′a). After column chromatography (toluene/ethyl acetate 100 : 1 to 20 : 1), 42.9 mg (66% yield) of a yellow solid (as a 5 : 1 regioisomeric product) was obtained. R_f = 0.33 (for both isomers) (toluene/ethyl acetate 40 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (minor isomer, d, J = 1.7 Hz, 1H), 8.59–8.57 (overlapping of two isomers, 1H), 8.51 (major isomer, d, J = 1.7 Hz, 1H), 8.34 (major isomer, d, J = 8.7 Hz, 1H), 8.22 (minor isomer, d, J = 8.7 Hz, 1H), 7.93–7.89 (overlapping of two isomers, 2H), 7.75–7.72 (overlapping of two isomers, 1H), 7.64–7.61 (overlapping of two isomers, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 150.1, 142.0, 140.9, 140.3, 135.7, 134.4, 132.4, 132.2, 131.2, 130.8, 130.3, 130.1, 129.7, 126.44, 126.36, 125.3, 123.9, 118.3, 113.0. HR-MS (ESI) calcd for $C_{15}H_7N_3NaS^+$ $[M + Na]^+$: 284.0253, found 284.0259.

8,9-Dimethylbenzo[4,5]thieno[2,3-*b*]quinoxaline (5ha). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 52.4 mg (79% yield) of a yellow-white solid was obtained. R_f = 0.34 (hexanes/ethyl acetate 7 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, J = 7.7 Hz, 1H), 7.99 (s, 1H), 7.87 (s, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 2.52 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 139.8, 139.7, 131.9, 130.6, 128.6, 127.5, 125.7, 124.2, 123.6, 20.6, 20.5. HR-MS (ESI) calcd for $C_{16}H_{13}N_2S^+$ $[M + H]^+$: 265.0794, found 265.0791.

9-Chlorobenzo[4,5]thieno[2,3-*b*]quinoxaline and 8-chlorobenzo[4,5]thieno[2,3-*b*]quinoxaline (5la + 5l′a). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 42.8 mg (63% yield) of a white-yellow solid (as an 8 : 1 regioisomeric product) was obtained. This compound is known.[3a] R_f = 0.36 (major) and 0.30 (minor) (hexanes/ethyl acetate 12 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56–8.54 (overlapping of two isomers, 1H), 8.26 (major isomer, d, J = 2.2 Hz, 1H), 8.20 (minor isomer, d, J = 9.0 Hz, 1H), 8.14 (minor isomer, d, J = 2.2 Hz, 1H), 8.08 (major isomer, d, J = 9.0 Hz, 1H), 7.88–7.86 (overlapping of two isomers, 1H), 7.75–7.73 (overlapping of two isomers, 1H), 7.70–7.66 (overlapping of two isomers, 1H), 7.60–7.57 (overlapping of two isomers, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 157.6, 148.6, 140.9, 140.4, 140.0, 134.9, 131.5, 131.2, 130.8, 129.6, 128.5, 126.0, 124.8, 123.7.

2-(Trifluoromethyl)benzo[4,5]thieno[2,3-*b*]quinoxaline (5ab). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 26.1 mg (34% yield) of a pink solid was obtained. R_f = 0.32 (hexanes/ethyl acetate 12 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87–8.84 (m, 1H), 8.33–8.28 (m, 1H), 8.21–8.16 (m, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.90 (dd, J = 8.3, 1.3 Hz, 1H), 7.89–7.83 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 157.1, 146.8, 143.7, 143.7, 141.9, 140.8, 131.9, 130.6, 129.8, 129.7, 128.6, 127.2 (q, J = 3.5 Hz), 124.2, 121.5 (q, J = 4.1 Hz). HR-MS (ESI) calcd for $C_{15}H_8F_3N_2S^+$ $[M + H]^+$: 305.0355, found 305.0353.

3-(4-Chlorophenoxy)benzo[4,5]thieno[2,3-*b*]quinoxaline (5ac). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 47.4 mg (52% yield) of a yellow-white solid was obtained. R_f = 0.32 (hexanes/ethyl acetate 7 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, J = 8.6 Hz, 1H), 8.26–8.22 (m, 1H), 8.15–8.11 (m, 1H), 7.82–7.76 (m, 2H), 7.41–7.37 (m, 2H), 7.37 (d, J = 2.3 Hz, 1H), 7.20 (dd, J = 8.6, 2.2 Hz, 1H), 7.10–7.06 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 157.3, 154.6, 147.4, 142.0, 141.0, 140.6, 130.3, 130.0, 129.6, 129.5, 129.3, 128.5, 126.7, 125.9, 121.5, 116.9, 112.2. HR-MS (ESI) calcd for $C_{20}H_{12}{}^{35}ClN_2OS^+$ $[M + H]^+$: 363.0353, found 363.0348.

2-Chlorothieno[3′,2′:4,5]thieno[2,3-*b*]quinoxaline (5ad). After column chromatography (hexanes/ethyl acetate 100 : 1 to 10 : 1), 7.2 mg (10% yield) of a yellow solid was obtained. R_f = 0.36 (hexanes/ethyl acetate 12 : 1). ^{1}H NMR (500 MHz, $CDCl_3$)

δ 8.23–8.20 (m, 1H), 8.15–8.12 (m, 1H), 7.85–7.77 (m, 2H), 7.72 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 144.1, 141.1, 140.5, 139.8, 135.3, 132.1, 129.8, 129.6, 129.4, 128.7, 120.3. HR-MS (ESI) calcd for $C_{12}H_6ClN_2S_2^+$ $[M + H]^+$: 276.9655, found 276.9705.

6-Benzyl-6*H*-indolo[2,3-*b*]quinoxaline (7aa). After column chromatography (toluene/ethyl acetate 100 : 1 to 50 : 1), 60.1 mg (78% yield) of a yellow solid was obtained. This compound is known.[3d] R_f = 0.35 (toluene/ethyl acetate 100 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 7.6 Hz, 1H), 8.33 (dd, J = 8.3, 1.2 Hz, 1H), 8.15 (dd, J = 8.4, 1.2 Hz, 1H), 7.76 (ddd, J = 8.3, 6.9, 1.5 Hz, 1H), 7.69 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.63–7.57 (m, 1H), 7.39–7.31 (m, 4H), 7.31–7.23 (m, 3H), 5.72 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 144.5, 140.8, 140.2, 139.7, 136.7, 131.2, 129.5, 128.97, 128.94, 128.0, 127.8, 127.4, 126.3, 122.9, 121.3, 119.8, 110.3, 45.2.

8,9-Dimethoxy-6*H*-indolo[2,3-*b*]quinoxaline (7ab). After column chromatography (gradient 0% to 5% methanol in ethyl acetate), 46.5 mg (67% yield) of a yellow-orange solid was obtained. R_f = 0.29 (hexanes/ethyl acetate 1 : 1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.76 (s, 1H), 8.17 (dd, J = 8.2, 1.3 Hz, 1H), 8.02 (dd, J = 8.3, 1.2 Hz, 1H), 7.79 (s, 1H), 7.73 (ddd, J = 8.3, 6.9, 1.5 Hz, 1H), 7.67 (ddd, J = 8.2, 6.9, 1.5 Hz, 1H), 7.10 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.4, 145.9, 144.9, 140.0, 139.8, 139.1, 138.5, 128.6, 127.7, 127.4, 125.7, 110.0, 104.1, 95.4, 56.1, 55.9. HR-MS (ESI) calcd for $C_{16}H_{14}N_3O_2^+$ $[M + H]^+$: 280.1081, found 280.1094.

5*H*-Pyrazino[2,3-*b*]indole (8). After column chromatography (chloroform/ethyl acetate 100 : 1 to 1 : 1), 8.4 mg (20% yield) of a brown solid was obtained. This compound is known.[13] R_f = 0.38 (hexanes/ethyl acetate 3 : 1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.12 (s, 1H), 8.49 (d, J = 2.7 Hz, 1H), 8.44 (d, J = 2.7 Hz, 1H), 8.23 (d, J = 7.8 Hz, 1H), 7.64–7.57 (m, 2H), 7.36–7.31 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 145.5, 140.2, 139.9, 136.4, 135.2, 129.0, 120.9, 120.5, 119.3, 112.1.

Benzo[4,5]thieno[2,3-*b*]pyrazine (9). After column chromatography (hexanes/ethyl acetate 100 : 1 to 5 : 1), 7.5 mg (16% yield) of an ivory yellow solid was obtained. R_f = 0.37 (hexanes/ethyl acetate 5 : 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, J = 2.5 Hz, 1H), 8.56 (d, J = 2.5 Hz, 1H), 8.47 (ddd, J = 7.7, 1.4, 0.7 Hz, 1H), 7.92–7.88 (m, 1H), 7.63 (td, J = 7.6, 1.4 Hz, 1H), 7.58 (td, J = 7.6, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 147.0, 142.0, 141.0, 139.0, 132.0, 129.8, 125.7, 123.7, 123.4. HR-MS (ESI) calcd for $C_{10}H_7N_2S^+$ $[M + H]^+$: 187.0324, found 187.0357.

Conflicts of interest

There are no conflicts to declare.

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