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Featured Article

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Solvatochromic Fluorescent 2-Substituted 3-Ethynyl Quinoxalines: Four-Component Synthesis, Photophysical Properties, and Electronic Structure

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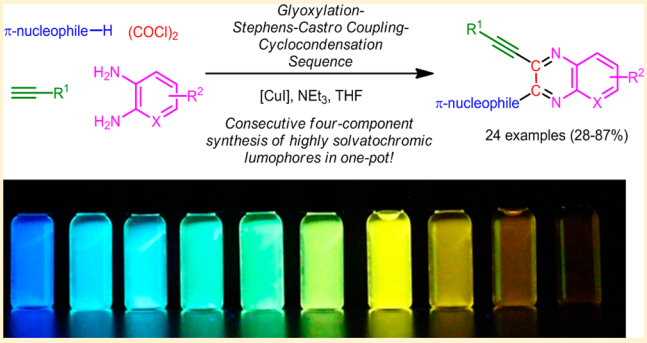
Supporting Information

ABSTRACT: 2-Substituted 3-ethynylquinoxalines can be rapidly synthesized in generally excellent yields by a consecutive four-component synthesis starting from electron-rich π-nucleophiles, oxalyl chloride, terminal alkynes, and 1,2-diaminoarenes. The title compounds are highly fluorescent with a pronounced emission solvatochromism. The photophysical properties and electronic structure were additionally corroborated by computations on the DFT level of theory.



INTRODUCTION

Over the past two decades, organic electronics have grown to an important field of interest in academia as well as in industry, providing crucial advantages over silicon-based electronics, such as low cost, flexibility, and functionality.[1] Due to the constant demand for novel tailor-made functional π-systems, new and reliable accesses toward such compounds have to be established. Diversity-oriented syntheses (DOS) are highly advantageous for synthetically exploring structural and functional characteristics because variation of the individual components leads to a heterogenic product library.[2] Among DOS, multicomponent reactions (MCRs)[3] and one-pot strategies are economically and ecologically favorable, since higher resource efficiency is combined with lower waste production in comparison to traditional multistep synthesis.[4] The concatenation of transition-metal-catalyzed reactions in one-pot processes as the liaison of their unique reactivity patterns with fundamental organic reactivity allows for convenient accesses to reactive intermediates and their in situ conversion.[5] While MCR approaches have regularly been employed in syntheses of natural products, pharmaceutically interesting compounds,[6] and in combination with high-throughput screening in medicinal chemistry, their full potential in the field of functional π-systems just has begun to be exploited.[2a,b] Most rewardingly, MCRs are ideally suited for rationally designing compound libraries for studying structure–property relationships.

Among myriad nitrogen-containing heterocycles that are ubiquitous in natural products and biological active compounds[7] as well as structural units in functional π-systems,[8] quinoxalines are particularly interesting. Many derivatives possess antitubercular,[9] antibiotic,[10] and anticancer activity,[11] and moreover, they are constantly studied due to their photophysical properties.[12] For instance, Kudo et al. reported the synthesis of a quinoxaline-based push–pull system, which was found to quantitatively screen protein binding-site polarity of bovine serum albumine as a consequence of its pronounced emission solvatochromism.[13] Lin et al. synthesized a set of chromophores based upon 2,3,5-trisubstituted quinoxaline cores, which display two-photon absorption properties.[14] Faust et al. synthesized related 2,3-bisethynylquinoxalines through the condensation of dialkynyl-1,2-diones and 1,2-diaminoarenes.[15] Their acetylenic quinoxalinoporphyrazine derivatives are potential candidates as photosensitizers in photodynamic therapy.[16]

We have recently reported a straightforward and modular one-pot approach to the densely functionalized but yet scarcely explored class of ynediones, starting from electron-rich π-nucleophiles, oxalyl chloride, and terminal alkynes (Scheme 1, path 1).[17] The sequence starts with a Lewis acid free Friedel–Crafts acylation of the π-nucleophile with oxalyl chloride. The generated glyoxyl chloride is directly converted into the ynedione by applying a Cu(I)-catalyzed Stephens–Castro alkynylation. The employment of CuI as the single catalyst is crucial for the success of the ynedione formation as the Pd/Cu-catalyzed Sonogashira protocol[18] leads to decarbonylation and eventually to the formation of ynones.[19] Furthermore, the Cu(I)-catalyzed variant[20] does not require complex ligands. An alternative route to ynediones starts from glyoxylic acids and oxalyl chloride and the subsequent transformation of the glyoxyl chloride with alkynes (Scheme 1, path 2).[21] Both methodologies allow for the introduction of a wide range of substituents to the ynedione core.

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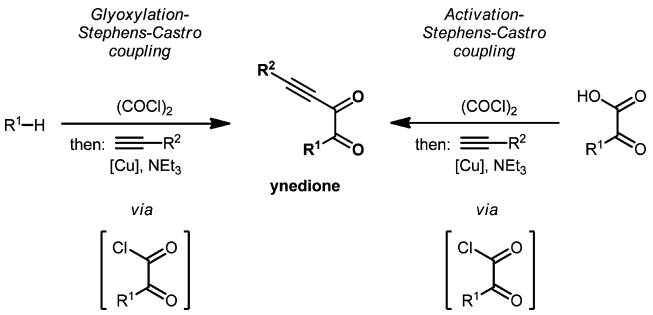
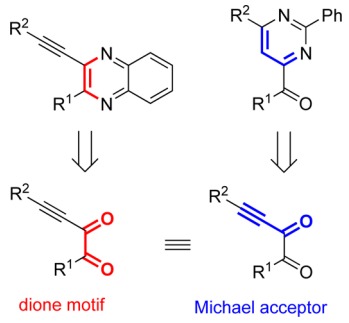
Scheme 1. Two One-Pot Routes to Ynediones via Glyoxyl Intermediates



Ynediones are highly valuable intermediates for the synthesis of various heterocyclic systems,[22] and we have illustrated that both the Michael system or the dione motif can be addressed in the final step of a consecutive one-pot sequence.[17] For instance, phenylamidine selectively reacts with the Michael acceptor furnishing a 4-acylpyrimidine, whereas 1,2-diaminobenzene exclusively addresses the dione motif to form a 2-substituted 3-ethynylquinoxaline (Scheme 2).

Scheme 2. Retrosynthetic Convergence of 4-Acylpyrimidines and 2-Substituted 3-Ethynylquinoxalines to Ynediones



Surprisingly, ethynylquinoxalines have only been scarcely studied. Ames et al. reported a Sonogashira-type reaction of 2-chloroquinoxaline with terminal alkynes to give 2-ethynylquinoxalines as precursors for the synthesis of pyrido[1,2-*a*]-quinoxalin-4-ones.[23] To our knowledge, only one ring-forming synthesis of 2-(hetero)aryl-substituted 3-ethynylquinoxalines has been reported so far,[24] where 1,2-diaminobenzene is reacted with two molecules of a terminal alkyne under Cu(I)-catalysis. However, this methodology can only generate 2-substituted 3-ethynylquinoxalines, which have identical substituents for R^1 and R^2.

Furthermore, we discovered via the naked eye that the 2-substituted 3-ethynylquinoxalines are highly fluorescent both in solution and in the solid state. In addition, test tube experiments indicated a pronounced emission solvatochromism.[25] The solvent-polarity sensitivity of solvatochromic fluorophores has found wide application in studies on protein biochemistry.[26]

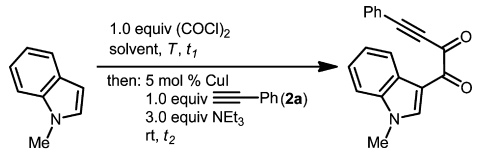
Since our multicomponent entry toward 2-(hetero)aryl-substituted 3-ethynylquinoxalines allows for a high degree of structural and functional variation due to its toolbox conception, we became intrigued to further explore this potential to luminescent derivatives. Here, we report the improved three-component synthesis of fluorescent 3-ethynylquinoxalines through a glyoxylation–Stephens–Castro coupling, as well as a study of the photophysical properties and electronic structure of this substance class.

RESULTS AND DISCUSSION

Synthesis. First optimization studies of the three-component ynedione synthesis with respect to substrate concentration, temperature, solvent, and reaction times were carried out on our previously used model system[17] consisting of *N*-methylindole (**1a**) and phenylacetylene (**2a**) furnishing the ynedione **3a** (Table 1).

The original conditions for the steps of the glyoxylation–alkynylation sequence[17] at room temperature required 4 and 24 h, respectively (Table 1, entry 1). By raising the temperature

Table 1. Optimization Study for the Synthesis of Ynedione 3a



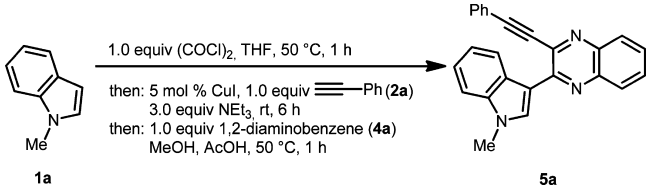
	glyoxylation				coupling		
entry[a]	c_0(**1a**) (M)	solvent	T (°C)	t_1 (h)	c_0(**2a**) (M)	t_2 (h)	ynedione **3a**[b] (%)
1	0.2	THF	rt	4	0.2	24	64
2	0.2	THF	50	1	0.2	6	63
3	**0.4**	**THF**	**50**	**1**	**0.4**	**6**	**69**
4	0.4	THF	50	1	0.4	4	61
5	0.4	1,4-dioxane	rt	1	0.4	6	67
6	0.4	CH_2Cl_2	rt	1	0.4	6	38
7	0.4	1,2-dichloroethane	rt	1	0.4	6	56

[a]All reactions were performed on a 2.00 mmol scale. [b]Yields after chromatography on silica gel.

for the glyoxylation step to 50 °C (Table 1, entry 2) and simultaneously increasing the concentration of **1a** and **2a** the reaction times of both steps were reduced to 1 and 6 h, respectively, while the yield slightly improved (Table 1, entry 3). However, further shortening of the reaction time resulted in a decreased yield (Table 1, entry 4). In addition, we found that 1,4-dioxane can be equally well used as solvent (Table 1, entry 5), whereas dichloromethane and 1,2-dichloroethane give lower yields (Table 1, entries 6 and 7).

With these optimized conditions (Table 1, entry 3) for the ynedione formation in hand and the time for the terminal cyclocondensation reduced from 3 h[17] to 1 h, the consecutive four-component synthesis of 3-ethynylquinoxaline **5a** was performed in a total reaction time of 8 h (cf. 31 h)[17] and with slightly improved yields from 72%[17] to now 80% (Scheme 3).

Scheme 3. Optimized Conditions for the Four-Component Synthesis of 3-Ethynylquinoxaline 5a



The optimized conditions were applied in the four-component synthesis of various 3-ethynylquinoxalines **5** with different substitution patterns (Scheme 4, Table 2). Much to our delight, the sequence represents a modular approach to a substance library

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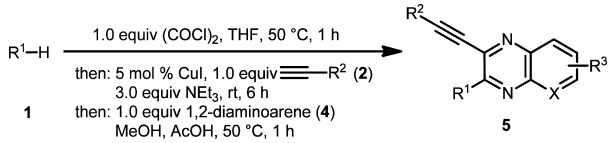
Scheme 4. Consecutive Four-Component Synthesis of 3-Ethynylquinoxalines 5 with Glyoxylation−Alkynylation−Cyclocondensation Sequence



in moderate to excellent yields. The components π-nucleophile **1**, alkyne **2**, and 1,2-diaminoarene **4** can be varied within a wide range, and it is noteworthy to mention that all four components are applied in strictly equimolar ratios.

Aryl- (**5a**, **5d−i**) as well as silyl-substituted alkynes (**5b**,**c**) can be successfully employed in the synthesis, whereas aliphatic alkynes only sluggishly undergo the Stephens−Castro coupling step. The π-nucleophile can vary from 1-methylindole (**5a**), differently *N*-substituted pyrroles (**5j−o**), and 2-methoxythiophene (**5p−r**) to azulene (**5s**). Expectedly, the initial glyoxylation, i.e., an electrophilic substitution reaction, regioselectively occurs for indoles at the 3-position for pyrroles at the 2-position with the exception of *N*-TIPS-pyrrole (**5o**) for steric reasons. Although the nucleophilicity of the substrates slightly differs according to Mayr's scale,[27] all glyoxylations reach full conversion at 50 °C. It is noteworthy to mention that a further increase of the reaction temperature does not improve the yields. In the final cyclocondensation step, the employed 1,2-diaminoarenes **4** react equally well for the 4,5-dichloro (**5t**) and 4-nitro derivative (**5u**) as well as 2,3-diaminopyridine (**5v**) giving good yields. However, 1,2-diamino-4-nitrobenzene (**4c**) and 2,3-diaminopyridine (**4d**) give mixtures of regioisomers due to the different nucleophilicities of the amino nitrogen atoms. Based upon electronic effects of the substituents on both the dione and the diamine motif the major isomer presumably arises from the attack of the more nucleophilic amino group at the alkynyl conjugated carbonyl group. Additionally, 2,3-diaminonaphthalene (**4e**) furnishes benzo[*g*]quinoxalines (**5w**,**x**) with lower yields, which can be rationalized by the poor solubility of the products, which effects a complicated work up procedure.

While the glyoxylation approach is limited to electron-rich heterocycles at the 2-position of the quinoxalines due to the initial electrophilic glyoxylation, we expanded the scope of the substitution pattern by initiating the ynedione formation through activation−Stephens−Castro coupling (see Scheme 1, path 2). This approach also enables the introduction of electroneutral substituents at position 2 of the 3-ethynylquinoxalines **7** starting from glyoxylic acids **6** in the sense of a three-component activation−Stephens−Castro coupling−cyclocondensation sequence in moderate to good yields (Scheme 5, Table 3).

The molecular structures of the 3-ethynylquinoxalines **5** and **7** were unambiguously supported by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and combustion analysis. Later, the structures were additionally corroborated by X-ray diffraction analysis of compounds **5d**, **5n**, **5q**, and **5x**.[28] Expectedly, in the solid state the quinoxaline core and the arylethynyl substituent are coplanarily alligned in all cases. However, the torsion angle between the 2-substituent and the quinoxaline core varies with the steric bulk of this substituent. For the 2-methoxythienyl derivative **5q** both moieties are almost coplanarily alligned, while for the 1-methylindole derivatives **5d** and **5x** this substituent is slightly twisted out of coplanarity by 13.2 and 16.2°, respectively. For the 1-phenylpyrrole substituent in compound **5q**, this torsion increases to 44.6° as a consequence of its bulky nature.

A closer analysis of the crystallographic data revealed the strong tendency of the molecules to build up pairs in the solid state, which are mostly caused by π−π-interactions (Figure 1, left). These pairs are arranged in columns, which resemble a herringbone pattern (Figure 1, right).

Within the pairs, the angle between the best planes of the π-systems in close contact, namely the six-membered ring of the anisole fragment and the neighboring quinoxaline fragment, is 7.4°. The distances between the atoms of the six-membered ring of the anisole fragment to the best plane of the quinoxaline fragment range from 329.3(2) to 356.9(2) pm, the center of the six-membered ring being 338.6(2) pm apart from that plane. Between the pairs, the closest π-system contact involves the above-mentioned anisole fragment and the indole fragment of a neighboring pair. The angle between the best planes of the six-membered ring of the anisole fragment and the five-membered ring of the indole fragment is 12.8°. Individual distances of the atoms of the five-membered ring to the best plane of the six-membered ring are in the range 340.1(2) to 371.5(3) pm, i.e., π−π-contacts within the pairs are significantly closer than between pairs.

Photophysical Properties. The photophysical properties of five selected 2-heteroaryl-substituted 3-ethynylquinoxalines **5** were thoroughly studied by UV/vis and fluorescence spectroscopy (Table 4). The structures were chosen as two consanguineous series to study the effects of the 2-substituent of the quinoxaline core (compounds **5a**, **5m**, **5r**) as well as the influence of the electronic nature of the aryl ethynyl group (compounds **5a**, **5d**, **5h**). Additionally, the emission solvatochromism of compound **5d** was investigated. The relative fluorescence quantum yields Φ_F were determined with coumarin 153[29] as standard according to literature procedures.[30]

In the UV/vis absorption spectra three to four distinct, broad, structureless maxima can be found, and the longest wavelength bands appear between λ_{max} = 418 and 393 nm with molar absorption coefficients ε ranging from 8000 to 14600 L/mol·cm (Figure 2).

The remote arylethynyl substituent has only a minor effect on the position of this absorption band and varies from λ_{max} = 408 (methoxy, compound **5d**) over 411 (hydrogen, compound **5a**) to 418 nm (cyano, compound **5h**). For the 2-substituent this effect is more pronounced. In the consanguineous series of compounds **5d**, **5m**, and **5r**, where the anisylethynyl substituent in 3-position is kept constant, the 1-methylindole (**5d**) and the 2-methoxythienyl (**5r**) derivative behave very similarly, whereas the more electron-rich 1-phenylpyrrolyl substituent of compound **5m** results in a blue shift of the longest wavelength absorption band to λ_{max} = 393 nm.

A similar picture emerges from the comparison of the emission spectra, where the structureless shortest wavelength emission band ranges between λ_{max} = 474 and 520 nm. By increasing the electron-withdrawing character of the remote arylethynyl substituent the emission maximum is red-shifted from λ_{max} = 506 (**5d**) over 510 (**5a**) to 520 nm (**5h**). While the position of the emission bands of **5d** and **5r** at 506 and 508 nm, respectively, are almost identical, the luminescence of the pyrrole derivative **5m** is hypsochromically shifted to 474 nm. The Stokes shifts can be found in a narrow range between 4700 and 4800 cm^{-1}, except for the 1-phenyl pyrrole derivative **5m**, which is with 4400 cm^{-1} slightly smaller. The fluorescence quantum yields Φ_F of the 1-methylindole-substituted derivatives **5a**, **5d**, and **5h** are hardly affected by the variation of the alkynyl substituent and lie between

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0.15 and 0.18. However, compounds **5m** and **5r** display with 0.24 and 0.32 higher Φ_F values. More information on the dipolar nature of the exited state was obtained by a solvatochromism study with the donor-substituted 1-methyl

Table 2. Glyoxylation–Alkynylation–Cyclocondensation Four-Component Synthesis of 2-Substituted 3-Ethynylquinoxalines 5

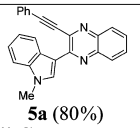
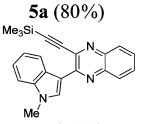
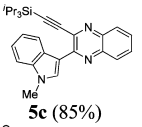
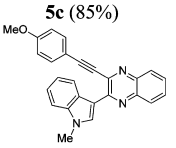
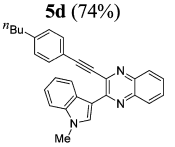
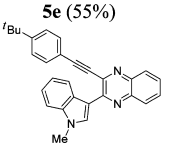
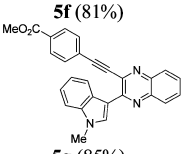
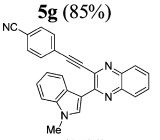
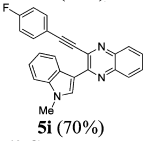
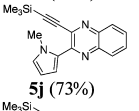
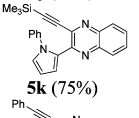
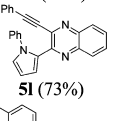
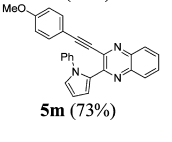
Entry[a]	R^1-H **1**	Alkyne **2**	1,2-Diaminoarene **4**	3-Ethynylquinoxaline **5** (Yield)[b]
1	*N*-methylindole (**1a**)	R^2 = Ph (**2a**)	1,2-diaminobenzene (**4a**)	 **5a** (80%)
2	**1a**	R^2 = $SiMe_3$ (**2b**)	**4a**	 **5b** (79%)
3	**1a**	R^2 = Si^iPr_3 (**2c**)	**4a**	 **5c** (85%)
4	**1a**	R^2 = 4-$MeOC_6H_4$ (**2d**)	**4a**	 **5d** (74%)
5	**1a**	R^2 = 4-$^nBuC_6H_4$ (**2e**)	**4a**	 **5e** (55%)
6	**1a**	R^2 = 4-$^tBuC_6H_4$ (**2f**)	**4a**	 **5f** (81%)
7	**1a**	R^2 = 4-$MeO_2CC_6H_4$ (**2g**)	**4a**	 **5g** (85%)
8	**1a**	R^2 = 4-NCC_6H_4 (**2h**)	**4a**	 **5h** (81%)
9	**1a**	R^2 = 4-FC_6H_4 (**2i**)	**4a**	 **5i** (70%)
10	*N*-methylpyrrole (**1b**)	**2b**	**4a**	 **5j** (73%)
11	*N*-phenylpyrrole (**1c**)	**2b**	**4a**	 **5k** (75%)
12	**1c**	**2a**	**4a**	 **5l** (73%)
13	**1c**	**2d**	**4a**	 **5m** (73%)

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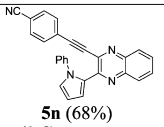
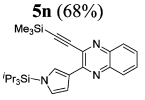
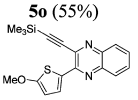
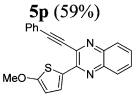
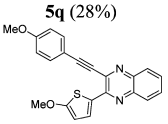
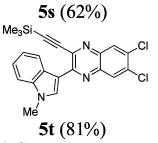
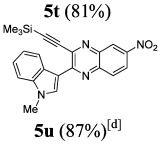
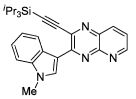
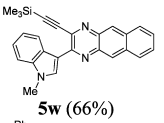
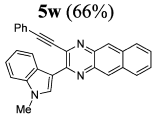
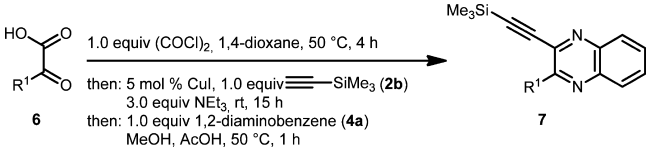
Table 2. continued

Entry[a]	R^1-H **1**	Alkyne **2**	1,2-Diaminoarene **4**	3-Ethynylquinoxaline **5** (Yield)[b]
14	**1c**	**2h**	**4a**	 **5n** (68%)
15	*N*-(triisopropylsilyl)pyrrole (**1d**)	**2b**	**4a**	 **5o** (55%)
16	2-methoxythiophene (**1e**)	**2b**	**4a**	 **5p** (59%)
17	**1e**	**2a**	**4a**	 **5q** (28%)
18	**1e**	**2d**	**4a**	 **5r** (33%)
19[c]	azulene (**1f**)	**2b**	**4a**	 **5s** (62%)
20	**1a**	**2b**	1,2-diamino-4,5-dichlorobenzene (**4b**)	 **5t** (81%)
21	**1a**	**2b**	1,2-diamino-4-nitrobenzene (**4c**)	 **5u** (87%)[d]
22	**1a**	**2c**	2,3-diaminopyridine (**4d**)	 **5v** (72%)[e]
23	**1a**	**2b**	2,3-diaminonaphthalene (**4e**)	 **5w** (66%)
24	**1a**	**2a**	**4e**	 **5x** (43%)

[a]All compounds were prepared on a 2.00 mmol scale except for compounds **5i**, **5s**, and **5v**, which were prepared on a 1.00 mmol scale. [b]Yields after chromatography on silica gel. [c]For the synthesis **5s**, the glyoxylation step was carried out for 4 h at rt and the Stephens–Castro coupling was carried out for 15 h at rt. [d]Isomer ratio: 10:1, determined according to integrals in the ^{1}H NMR spectrum. [e]Isomer ratio: 6.5:1, determined according to integrals in the ^{1}H NMR spectrum.

Scheme 5. Consecutive Three-Component Synthesis of 3-Ethynylquinoxalines 7 through Activation–Alkynylation–Cyclocondensation Sequence



indole derivative **5d** in various solvents with solvent polarity E_T^N values ranging from 0.006 to 0.762 according to Reichardt's scale (Table 5).[31]

While the UV/vis absorption spectra display only a minor positive solvatochromism in the range from 405 to 415 nm, the influence of the solvent polarity on the emission band is quite significant and positive, ranging from 468 to 525 nm, i.e., $\Delta\tilde{\nu}$ = 2300 cm^{-1} (Figure 3). This pronounced positive emission solvatochromism is additionally detectable upon eyesight, where the emission color changes from blue (cyclohexane) to orange (MeOH) (Figure 4).

The fluorescence quantum yield Φ_F increases with decreasing solvent polarity, and the highest quantum yields Φ_F were recorded in toluene (0.30). In protic solvents, such as alcohols, even lower values than for acetonitrile (0.13) were observed.

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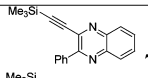
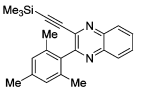
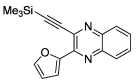
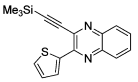
Table 3. Activation–Alkynylation–Cyclocondensation Three-Component Synthesis of 2-Substituted 3-Ethynylquinoxalines 7

Entry[a]	Glyoxylic acid **6**	3-Ethynylquinoxaline **7** (Yield)[b]
1	R^1 = Ph (**6a**)	 **7a** (85 %)
2	R^1 = mesityl (**6b**)	 **7b** (25 %)
3	R^1 = 2-furyl (**6c**)	 **7c** (30 %)
4	R^1 = 2-thienyl (**6d**)	 **7d** (69 %)

[a]All compounds were prepared on a 2.00 mmol scale. [b]Yields after chromatography on silica gel.

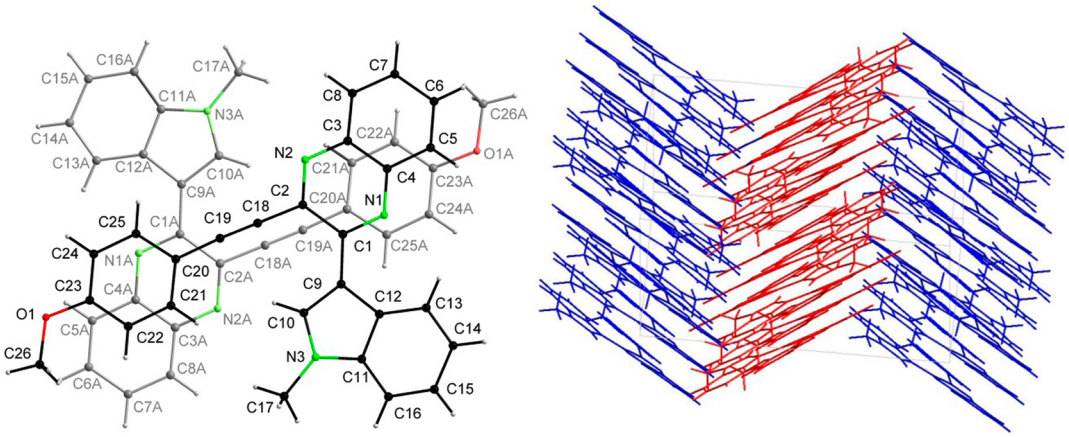


Figure 1. Solid-state pair building of compound **5d** (left) and crystal packing of compound **5d** (right).

Table 4. UV/vis Absorption and Emission Data of Selected 2-Substituted 3-Ethynylquinoxalines 5

entry	absorption $\lambda_{max,abs}$ (nm) (ε ($M^{-1}cm^{-1}$))[a]	emission $\lambda_{max,em}$/nm (Φ_F)[b,c]	Stokes shift $\Delta\tilde{\nu}$[d] (cm^{-1})
5a	273 (31600), 287 (30400), 319 (25200), 411 (9900)	510 (0.16)	4700
5d	271 (37300), 303 (33900), 323 (28400), 337 (sh), 408 (13300)	506 (0.19)	4800
5h	277 (sh), 290 (41600), 328 (27200), 418 (8000)	520 (0.15)	4700
5m	266 (31300), 303 (31400), 337 (16300), 344 (sh), 393 (14600)	474 (0.24)	4400
5r	274 (21200), 312 (28400), 327 (sh), 343 (sh), 410 (11700)	508 (0.32)	4800

[a]Recorded in CH_2Cl_2, T = 293 K, c(**5**) = 10^{-5} M. [b]Recorded in CH_2Cl_2, T = 293 K, c(**5**) = 10^{-7} M. [c]Fluorescence quantum yields were recorded relative to coumarin 153 (Φ_F = 0.45) as a standard in MeOH. [d]$\Delta\tilde{\nu} = 1/\lambda_{max,abs} - 1/\lambda_{max,em}$.

A deactivation pathway from the excited state triggered by intermolecular solvent/solute hydrogen bonding appears to be a very likely explanation for this specific solvent effect.[32]

Furthermore, the Lippert–Mataga equation allows a more quantitative treatment of the observed emission solvatochromism.[33] Large positive emission solvatochromism correlates with a considerable increase of the dipole moment on excitation.[34] Hence, the solvent-dependent Stokes shifts were plotted against the orientation polarizability Δf, which can be calculated according to

$$\Delta f = \frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

from the relative permittivity ε_r and the optical refractive index n of the solvent. The linear correlation displays an excellent goodness of fit (r^2 = 0.92), which indicates a dominant importance of a general solvent effect (Figure 5).[34]

The change in dipole moment from the ground to the excited state can be calculated with the Lippert–Mataga equation

$$\tilde{\nu}_a - \tilde{\nu}_f = \frac{2\Delta f}{hca^3}(\mu_E - \mu_G)^2 + \text{const}$$

where $\tilde{\nu}_a$ and $\tilde{\nu}_f$ represent the absorption and emission maxima (in cm^{-1}), μ_E and μ_G are the dipole moment in the excited and ground state, h (6.6256 × 10^{-34} Js) is Planck's constant, c (2.9979 × 10^{10} cm/s) is the speed of light, and a is the radius of the solvent cavity occupied by the molecule. Upon applying the Lippert–Mataga equation on charge-transfer compounds, typically, the Onsager radius is employed for a. This assumption is reasonable in cases, where the dipole moment is extended over a sticklike molecule.[34] However, the computations on compound **5d** revealed that the charge transfer only occurs between the indolyl substituent and the

dx.doi.org/10.1021/jo4025978 | J. Org. Chem. XXXX, XXX, XXX–XXX

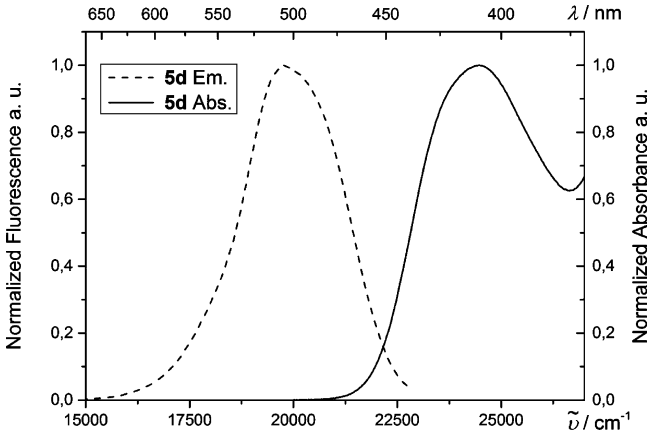


Figure 2. UV/vis absorption[a] (bold line) and emission spectrum[b] (dashed line) of compound **5d**. ([a]Recorded in CH_2Cl_2, T = 293 K, c(**5**) = 10^{-5} M. [b]Recorded in CH_2Cl_2, T = 293 K, c(**5**) = 10^{-7} M, $\lambda_{excit.}$ = 420 nm.)

Table 5. Selected UV/vis Absorption and Emission Maxima of Compound 5d, Measured in Solvents of Different Polarity

solvent	absorption $\lambda_{max,abs}$/nm (ε ($M^{-1}cm^{-1}$))[a]	emission $\lambda_{max,em}$/ nm (Φ_F)[b,c]	Stokes shift $\Delta\tilde{\nu}$[d] (cm^{-1})
toluene	407 (13300)	468 (0.30)	3200
THF	408 (13400)	490 (0.19)	4100
EtOAc	405 (14400)	491 (0.17)	4320
CH_2Cl_2	408 (13300)	506 (0.19)	4710
acetone	408 (14000)	513 (0.16)	5000
MeCN	407 (13200)	518 (0.13)	5300
^{i}PrOH	415 (11700)	519 (0.02)	4800
EtOH	415 (12000)	522 (<0.01)	4900
MeOH	415 (12300)	525 (<0.01)	5100

[a]Recorded in CH_2Cl_2, T = 293 K, c(**5**) = 10^{-5} M. [b]Recorded in CH_2Cl_2, T = 293 K, c(**5**) = 10^{-7} M. [c]Fluorescence quantum yields were recorded relative to coumarin 153 (Φ_F = 0.45) as a standard in MeOH. [d]$\Delta\tilde{\nu} = 1/\lambda_{max,abs} - 1/\lambda_{max,em}$.

(4-methoxyphenyl)ethynyl moiety, whereas the quinoxaline core, especially the benzo ring, is hardly involved. Therefore, employing the Onsager radius would not lead to reliable values for the transition dipole moment $\Delta\mu$. Nevertheless, with the computed values for $\Delta\mu$ (gas phase: 9.47 D, using Turbomole with the B3LYP functional and the def-TZVP basis set; CH_2Cl_2: relaxed 6.48 D, nonrelaxed 6.91 D, using Gaussian 09 with CAM-B3LYP functional and the 6-311G(d,p) basis set), we were able to calculate the dipole radii in the gas phase (0.51 nm) and in CH_2Cl_2 (relaxed 0.40 nm, nonrelaxed 0.42 nm). These results nicely match our estimated dipole radius (Figure 6).

Electronic Structure. A deeper rationalization of the observed photophysical behavior of the synthesized quinoxalines **5** was sought by elucidating the electronic structure by calculating UV/vis absorption spectra on the DFT level of theory, with special focus on the origin of the four longest wavelength absorption maxima of each structure. Therefore, first the geometries of the ground-state structures were optimized using Gaussian09[35] with the B3LYP functional[36] and the Pople 6-311G(d,p) basis set,[37] and the starting geometries obtained from X-ray structure analyses. Since all measurements were recorded in solution, the calculations were carried out using the polarizable continuum model (PCM) applying dichloromethane as solvent.[38] All minima structures were confirmed by analytical frequency analyses.

For the three different heteroaryl substituents in the 2-position of the quinoxaline moiety, the computations nicely match the equilibrium ground-state structures as obtained from X-ray structure analyses. For compounds **5m** and **5r**, the torsional angles between the quinoxaline plane and the heterocyclic ring in 2-position differ only slightly from the angles determined by X-ray of **5n** and **5q** (vide supra and Figure 7). In contrast, calculations suggest that the *N*-methylindole substituent of **5d** is twisted considerably more out of plane than it was found in the X-ray (θ_{calc} = 25° vs $\theta_{X\text{-}ray}$ = 13°). Accordingly, the overlap and thereby the electronic communication in the case of thienyl and indolyl substituents is more efficient than that for the *N*-phenylpyrrole substituent.

The frontier molecular orbitals of the quinoxalines **5d**, **5m**, and **5r** (Figure 8) show that for all three HOMOs the coefficient density is predominantly located on the quinoxaline and on the adjacent indolyl, pyrrolyl, and thienyl moiety, whereas the phenyl core of the pyrrole **5m** does not possess any coefficient density. For the quinoxaline derivatives **5m** (Figure 8, center) and

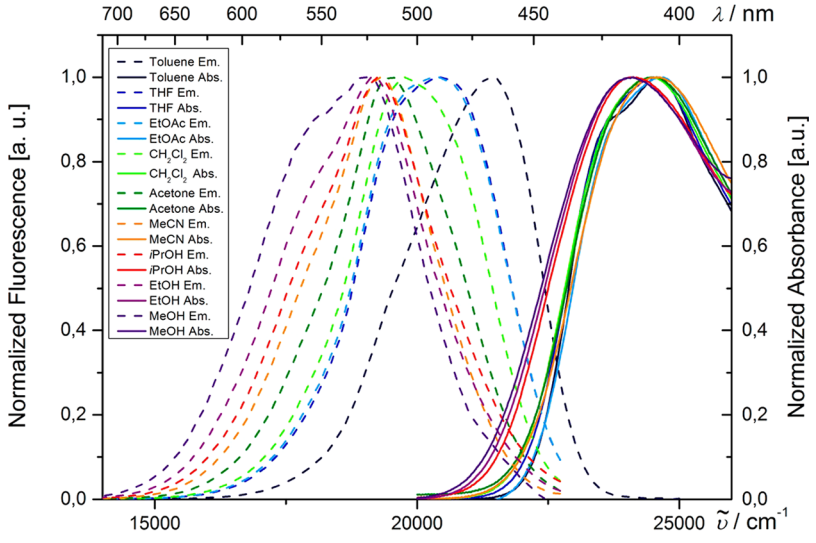


Figure 3. UV/vis absorption (solid lines) and emission spectra (dashed lines) of compound **5d**, measured in nine solvents of different polarity (recorded at T = 293 K).

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Figure 4. Emission solvatochromism of compound **5d** (recorded in cyclohexane, toluene, THF, EtOAc, acetone, CH_2Cl_2, MeCN, *i*PrOH, EtOH, MeOH (from left to right); T = 293 K; c(**5d**) = 10^{-4} M; λ_{excit} = 356 nm, hand-held UV lamp).

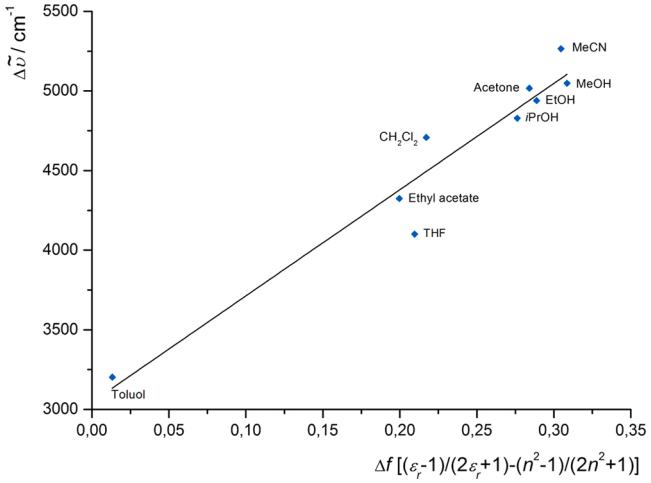

Figure 5. Lippert plot for compound **5d** (n = 9, r^2 = 0.92).

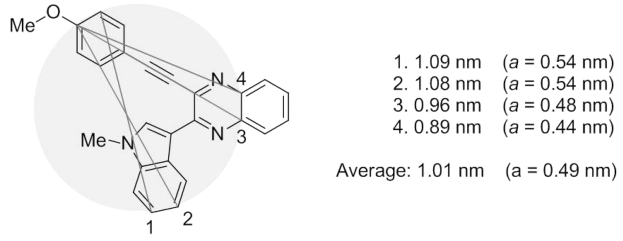

Figure 6. Estimation of the dipolar radius a of compound **5d**.

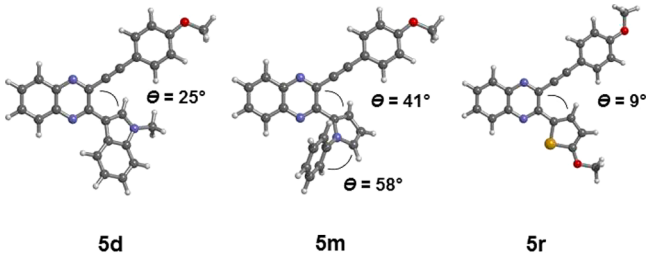

Figure 7. Optimized geometries at the B3LYP 6-311G(d,p) level for the quinoxalines **5d**, **5m**, and **5r** with different heteroaryl substituents in 2-position.

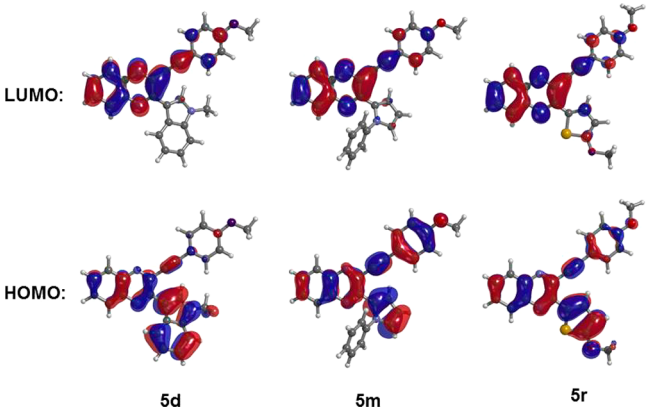

Figure 8. HOMOs (bottom) and LUMOs (top) of the quinoxalines **5d**, **5m**, and **5r**.

5r (Figure 8, right) the coefficients are also large both on the bridging triple bonds and the anisol cores, whereas only a neglectible coefficient density can be observed on the anisyl fragment of structure **5d**. In all three cases, the LUMOs do not bear any significant coefficient density on the heterocyclic substituents in 2-position of the quinoxaline. Here, the coefficients on the quinoxaline moieties are increased in comparison to the HOMOs, whereas the LUMO coefficients on the bridged triple bonds and the adjacent anisyl cores only show minor differences for structure **5d** (Figure 8, left) and a slightly diminished coefficient density for the other two structures. Already the computed ground-state structures indicate that HOMO−LUMO transitions should be accompanied with a dominant charge-transfer character from the heteroaryl substituents in 2-position to the central quinoxaline core.

The optimized structures of **5a**, **5d**, **5h**, **5m**, and **5r** were submitted to TD-DFT calculations to study the absorption characteristics (Table 6). The hybrid exchange-correlation functional CAM-B3LYP[39] was implemented and a non-equilibrium solvation[40] for the state-specific solvation of the vertical excitation was included. Expectedly, the longest wavelength absorption bands of all five computed molecules result from dominant contributions of the HOMO−LUMO transitions. The computed values are slightly hypsochromically shifted in comparison to the experimental data. The absorption maxima and shoulders appearing in the experimental UV/vis spectra at lower wavelength ranges were identified by comparing the oscillatory strength of the first 10 excitations of the first excited state. The computed values are in reasonably good agreement with the experimental data and major contributions of two more absorption maxima at lower wavelengths emanate predominantly from HOMO-1 → LUMO, HOMO-1 → LUMO+1, and HOMO → LUMO+1 transitions. Only for structures **5h** and **5r** are other molecular orbitals involved.

CONCLUSION

The improved glyoxylation−Stephens−Castro coupling−cyclo-condensation protocol represents an efficient and rapid access to 2-substituted 3-ethynylquinoxalines in the sense of a consecutive MCR. As a consequence of its diversity-oriented nature, large substance libraries are readily envisioned for

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Table 6. TD-DFT Calculations (CAM-B3LYP 6-311G(d,p)) of the UV/vis Absorption Maxima of the Quinoxalines 5a, 5d, 5h, 5m, and 5r

structure	experimental $\lambda_{max,abs}$ [a] (nm)	computed $\lambda_{max,abs}$ (nm) (most dominant contributions)
5a	273	266 (HOMO-1 → LUMO+1)
	287	298 (HOMO-1 → LUMO)
	319	323 (HOMO → LUMO+1)
	411	371 (HOMO → LUMO)
5d	271	273 (HOMO-1 → LUMO+1)
	303	299 (HOMO → LUMO+1)
	323	330 (HOMO-1→ LUMO)
	408	372 (HOMO → LUMO)
5h	277 (sh)	272 (HOMO-2 → LUMO+1)
	290	308 (HOMO-2 → LUMO)
	328	331 (HOMO → LUMO+1)
	418	383 (HOMO → LUMO)
5m	266	276 (HOMO-1 → LUMO+1)
	303	290 (HOMO → LUMO+1)
	337	327 (HOMO-1 → LUMO)
	393	364 (HOMO → LUMO)
5r	274	285 (HOMO-1 → LUMO+1)
	312	305 (HOMO-1 → LUMO)
	327 (sh)	319 (HOMO-4 → LUMO)
	343 (sh)	343 (HOMO → LUMO+1)
	410	373 (HOMO → LUMO)

[a]Recorded in CH_2Cl_2, T = 293 K, c(**5**) = 10^{-5} M.

establishing experimentally founded structure−property relationships by variation of the individual components. Most interestingly, the title compounds display substantial emission solvatochromism and high quantum yields, as revealed by detailed photophysical studies and computations to rationalize the electronic structure. In addition, the ethynyl group is well suited for incorporation of these solvatochromic lumophores into more complex systems, most favorably as sensors for protein interactions.[26] Extended pluripotent functionalizations of 2-substituted 3-ethynylquinoxalines as well as their intriguing photophysics are currently under investigation.

EXPERIMENTAL SECTION

General Considerations. Reagents, catalysts, ligands, and solvents were purchased reagent grade and used without further purification. Anhydrous tetrahydrofuran, 1,4-dioxane, dichloromethane, and 1,2-dichloroethane were obtained from a drying system. Triethylamine was refluxed under an argon atmosphere over sodium ketyl, distilled, and stored in a Schlenk flask under nitrogen atmosphere over potassium hydroxide pellets. Column chromatography: silica gel 60, mesh 70−230. TLC: silica gel plates 60 F_{254}. All products were purified with column chromatography on silica gel 60 (0.040−0.063 mm) using flash technique under a pressure of 2 bar. The crude mixtures were absorbed on Celite 545 (0.02−0.10 mm) before chromatographic purification. The reaction progress was observed qualitatively using TLC silica gel 60 F_{254} aluminum sheets. The spots were detected with UV light at 254 and 365 nm and with aqueous potassium permanganate solution. Chemical shifts δ in the ^{1}H NMR and ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$. The assignments of quaternary C, CH, CH_2, and CH_3 signals were made by using DEPT spectra.

General Procedure for the Three-Component Synthesis of 1-(1-Methyl-1*H*-indol-3-yl)-4-phenylbut-3-yne-1,2-dione (3a). A 268 mg (2.00 mmol) portion of **1a** was placed under argon or nitrogen atmosphere in a screw-cap Schlenk tube with one of the listed solvents. The solution was degassed with argon/nitrogen. In the cases of THF, DCM, and DCE the solution was then cooled to 0 °C (water/ice, 5 min). Then, oxalyl chloride (0.18 mL, 2.00 mmol, 1.0 equiv) was added dropwise to the reaction mixture. After being warmed to room temperature (water bath, 5 min), the reaction mixture was stirred for the indicated time at the indicated temperature (water bath/oil bath). If necessary, the mixture was then cooled to room temperature (water bath, 5 min). Then, CuI (20 mg, 0.1 mmol, 5 mol %), 1 equiv of phenylacetylene **2a** (0.22 mL, 2.00 mmol, 1.0 equiv), and dry triethylamine (0.84 mL, 6.00 mmol, 3.0 equiv) were successively added to the reaction mixture, and stirring at room temperature was continued for the indicated time. 10 mL of water was added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3 × 5 mL/10 mL, monitored by TLC). The combined organic layers were dried with anhydrous sodium sulfate. After removal of the solvents in vacuo, the residue was absorbed onto Celite and purified chromatographically on silica gel with petroleum ether (boiling range 40−60 °C)/ethyl acetate (ratio 3:1) to give the ynedione **3a**. Yellow solid. Mp: 128 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.86 (s, 3 H), 7.36−7.53 (m, 6 H), 7.68−7.74 (m, 2 H), 8.33 (s, 1 H), 8.44−8.52 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.8 (CH_3), 87.7 (C_{quat}), 97.5 (C_{quat}), 105.1 (CH), 110.0 (CH), 110.8 (C_{quat}), 111.0 (CH), 119.7 (C_{quat}), 122.7 (CH), 123.6 (CH), 124.2 (CH), 127.2 (C_{quat}), 128.6 (CH), 131.2 (CH), 133.6 (CH), 137.2 (C_{quat}), 140.2 (CH), 178.6 (C_{quat}), 180.1 (C_{quat}). EI + MS (m/z): 287 (M^+, 2), 259 ($C_{18}H_{13}NO^+$, 1), 231 ($C_{17}H_{13}N^+$, 2), 158 ($[M - C_9H_5O]^+$, 100), 130 ($C_9H_8N^+$, 7), 129 ($C_9H_5O^+$), 103 (7), 97 (7), 77 ($C_6H_5^+$, 6), 57 (13). IR (solid): $\tilde{\nu}$ 3127 (w) [cm^{-1}], 2914 (w), 2853 (w), 2200 (m), 2156 (w), 1734 (w), 1643 (m), 1624 (m), 1578 (m), 1526 (m), 1464 (m), 1443 (m), 1377 (m), 1335 (w), 1281 (m), 1225 (m), 1171 (w), 1130 (m), 1074 (m), 1032 (m), 977 (m), 880 (m), 772 (m), 754 (m), 739 (s), 685 (s), 621 (m). Anal. Calcd for $C_{19}H_{13}NO_2$ (287.3): C, 79.43; H, 4.56; N, 4.88. Found: C, 79.23; H, 4.76; N, 4.78.

General Procedure for the Four-Component Synthesis of 3-Ethynylchinoxalines 5. A 2.00 mmol portion of **1** in dry THF (2.5 mL/mmol) was placed under argon or nitrogen atmosphere in a sintered screw-cap Schlenk tube, degassed with argon or nitrogen, and cooled to 0 °C (water/ice, 5 min) (for experimental details see Table 7). Then, oxalyl chloride (0.18 mL, 2.00 mmol, 1.0 equiv) was added dropwise to the reaction mixture at 0 °C. The mixture was first warmed to room temperature (water bath, 5 min) and then stirred for 1 h at 50 °C (oil bath). Thereafter, the mixture was cooled to room temperature (water bath, 5 min). Then, CuI (20 mg, 0.1 mmol, 5 mol %), 1 equiv of terminal alkyne **2**, and dry triethylamine (0.84 mL, 6.00 mmol, 3.0 equiv) were successively added to the reaction mixture, and stirring at room temperature was continued for 6 h. Then, 2 mL of methanol, 2.00 mmol of the 1,2-diaminoarene **4** (1.0 equiv), and 2 mL of acetic acid were added successively, the mixture was stirred at 50 °C for 1 h, 10 mL water was added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3 × 5 mL/10 mL, monitored by TLC). The combined organic layers were dried with anhydrous sodium sulfate. After removal of the solvents in vacuo, the residue was absorbed onto Celite and purified chromatographically on silica gel with petroleum ether (boiling range 40−60 °C)/ethyl acetate to give the 3-ethinylchinoxalines **5**.

*2-(1-Methyl-1H-indol-3-yl)-3-(phenylethynyl)quinoxaline (**5a**).* Yellow solid (574 mg, 80%). R_f = 0.15 (petroleum ether/ethyl acetate 7:1). Mp: 134 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.82 (s, 3 H), 7.22−7.29 (m, 2 H), 7.30−7.36 (m, 4 H), 7.50−7.55 (m, 2 H), 7.58 (ddd, J = 8.1 Hz, J = 4.8 Hz, J = 1.4 Hz, 1 H), 7.99 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.7 Hz, 1 H), 8.06 (dd, J = 8.2 Hz, J = 1.2 Hz, 1 H), 8.37 (s, 1 H), 8.64−8.71 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.4 (CH_3), 89.1 (C_{quat}), 94.1 (C_{quat}), 109.5 (CH), 112.4 (C_{quat}), 121.4 (CH), 122.0 (C_{quat}), 122.87 (CH), 122.93 (CH), 127.5 (C_{quat}), 128.59 (CH), 128.62 (CH), 128.7 (CH), 128.8 (CH), 129.5 (CH), 130.4 (CH), 132.0 (CH), 132.5 (CH), 137.0 (C_{quat}), 137.3 (C_{quat}) 137.4 (C_{quat}), 141.1 (C_{quat}), 151.6 (C_{quat}). EI + MS (m/z): 360 (17), 359 (74), 358 (M^+, 100), 344 ($[M - CH_3]^+$, 9), 282 ($[M - C_6H_5]^+$, 3), 180 (11), 172 (11), 158 (11), 156 ($C_{10}H_8N_2^+$, 8). IR (solid): $\tilde{\nu}$ 3055 (w), 2955 (w), 2922 (w), 2853 (w), 2210 (w), 1535 (m), 1476 (w), 1454 (m), 1425 (w), 1406 (w), 1369 (m), 1352 (w), 1337 (w), 1300 (w), 1281 (w), 1256 (w), 1236 (w), 1215 (m), 1178 (w), 1157 (w),

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Table 7. Experimental Details for the Four-Component Synthesis of 2-Substituted 3-Ethynylquinoxalines 5

entry[a]	R^1-H **1**	alkyne **2**	1,2-diaminoarene **4**	3-ethynyl-quinoxaline **5** (yield, %)[b]
1	268 mg (2.00 mmol) of **1a**	0.18 mL (2.00 mmol) of **2a**	216 mg (2.00 mmol) of **4a**	574 mg (80%) of **5a**
2	268 mg (2.00 mmol) of **1a**	0.28 mL (2.00 mmol) of **2b**	216 mg (2.00 mmol) of **4a**	564 mg (79%) of **5b**
3	268 mg (2.00 mmol) of **1a**	0.45 mL (2.00 mmol) of **2c**	216 mg (2.00 mmol) of **4a**	749 mg (85%) of **5c**
4	268 mg (2.00 mmol) of **1a**	267 mg (2.00 mmol) of **2d**	216 mg (2.00 mmol) of **4a**	573 mg (74%) of **5d**
5	268 mg (2.00 mmol) of **1a**	0.36 mL (2.00 mmol) of **2e**	216 mg (2.00 mmol) of **4a**	455 mg (55%) of **5e**
6	268 mg (2.00 mmol) of **1a**	0.38 mL (2.00 mmol) of **2f**	216 mg (2.00 mmol) of **4a**	672 mg (81%) of **5f**
7	268 mg (2.00 mmol) of **1a**	320 mg (2.00 mmol) of (**2g**)	216 mg (2.00 mmol) of **4a**	709 mg (85%) of **5g**
8	268 mg (2.00 mmol) of **1a**	262 mg (2.00 mmol) of **2h**	216 mg (2.00 mmol) of **4a**	623 mg (81%) of **5h**
9	134 mg (1.00 mmol) of **1a**	121 mg (1.00 mmol) of **2i**	108 mg (1.00 mmol) of **4a**	265 mg (70%) of **5i**
10	164 mg (2.00 mmol) of **1b**	0.28 mL (2.00 mmol) of **2b**	216 mg (2.00 mmol) of **4a**	446 mg (73%) of **5j**
11	289 mg (2.00 mmol) of **1c**	0.28 mL (2.00 mmol) of **2b**	216 mg (2.00 mmol) of **4a**	552 mg (75%) of **5k**
12	289 mg (2.00 mmol) of **1c**	0.18 mL (2.00 mmol) of **2a**	216 mg (2.00 mmol) of **4a**	544 mg (73%) of **5l**
13	289 mg (2.00 mmol) of **1c**	267 mg (2.00 mmol) of **2d**	216 mg (2.00 mmol) of **4a**	589 mg (73%) of **5m**
14	289 mg (2.00 mmol) of **1c**	262 mg (2.00 mmol) of **2h**	216 mg (2.00 mmol) of **4a**	536 mg (68%) of **5n**
15	446 mg (2.00 mmol) of **1d**	0.28 mL (2.00 mmol) of **2b**	216 mg (2.00 mmol) of **4a**	496 mg (55%) of **5o**
16	470 mg (2.00 mmol) of **1e**	0.28 mL (2.00 mmol) of **2b**	216 mg (2.00 mmol) of **4a**	398 mg (59%) of **5p**
17	470 mg (2.00 mmol) of **1e**	0.18 mL (2.00 mmol) of **2a**	216 mg (2.00 mmol) of **4a**	192 mg (28%) of **5q**
18	470 mg (2.00 mmol) of **1e**	267 mg (2.00 mmol) of **2d**	216 mg (2.00 mmol) of **4a**	243 mg (33%) of **5r**
19[c]	128 mg (1.00 mmol) of **1f**	0.14 mL (1.00 mmol) of **2b**	108 mg (1.00 mmol) of **4a**	437 mg (62%) of **5s**
20	268 mg (2.00 mmol) of **1a**	0.28 mL (2.00 mmol) of **2b**	361 mg (2.00 mmol) of (**4b**)	686 mg (81%) of **5t**
21	268 mg (2.00 mmol) of **1a**	0.28 mL (2.00 mmol) of **2b**	313 mg (2.00 mmol) of **4c**	694 mg (87%) of **5u**[d]
22	134 mg (1.00 mmol) of **1a**	0.23 mL (1.00 mmol) of **2c**	107 mg (1.00 mmol) of **4d**	358 mg (72%) of **5v**[e]
23	268 mg (2.00 mmol) of **1a**	0.28 mL (2.00 mmol) of **2b**	326 mg (2.00 mmol) of **4e**	537 mg (66%) of **5w**
24	268 mg (2.00 mmol) of **1a**	0.18 mL (2.00 mmol) of **2a**	326 mg (2.00 mmol) of **4e**	349 mg (43%) of **5x**

[a]All compounds were prepared on a 2.00 mmol scale except for compounds **5i**, **5s**, and **5v**, which were prepared on a 1.00 mmol scale. [b]Yields after chromatography on silica gel. [c]For the synthesis **5s**, the glyoxylation step was carried out for 4 h at rt and the Stephens–Castro coupling was carried out for 15 h at rt. [d]Isomer ratio: 10:1, determined according to integrals in the ^{1}H NMR spectrum. [e]Isomer ratio: 6.5:1, determined according to integrals in the ^{1}H NMR spectrum.

1128 (m), 1111 (m), 1082 (m), 1011 (w), 937 (m), 905 (w), 839 (w), 827 (w), 740 (s), 681 (s), 656 (w), 640 (w), 611 (m). Anal. Calcd for $C_{25}H_{17}N_3$ (359.4): C, 83.59; H, 4.77; N, 11.69. Found: C, 83.50; H, 4.89; N, 11.40.

*2-(1-Methyl-1H-indol-3-yl)-3-[(trimethylsilyl)ethynyl]quinoxaline (**5b**).* Yellow solid (564 mg, 79%). R_f = 0.32 (petroleum ether/ethyl acetate 7:1). Mp: 160 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.37 (s, 9 H), 3.91 (s, 3 H), 7.30–7.44 (m, 3 H), 7.65 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.4 Hz, 1 H), 7.73 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.5 Hz, 1 H), 8.04 (dd, J = 8.3 Hz, J = 1.5 Hz, 1 H), 8.12 (dd, J = 8.3 Hz, J = 1.5 Hz, 1 H), 8.58 (s, 1 H), 8.78–8.81 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.5 (CH_3), 33.3 (CH_3), 100.9 (C_{quat}), 104.4 (C_{quat}), 109.4 (CH), 112.0 (C_{quat}), 121.5 (CH), 122.9 (CH), 123.1 (CH), 127.5 (C_{quat}), 128.57 (CH), 128.63 (CH), 128.7 (CH), 130.6 (CH), 132.8 (CH), 136.3 (C_{quat}), 137.2 (C_{quat}), 139.1 (C_{quat}), 141.1 (C_{quat}), 150.4 (C_{quat}). EI + MS (m/z): 356 (29), 355 (M^+, 100), 354 (45), 341 (15), 340 ($[M - CH_3]^+$, 52), 325 ($[M - (CH_3)_2]^+$, 7), 310 ($[M - (CH_3)_3]^+$, 10), 282 ($[M - C_3H_9Si]^+$, 11), 156 ($C_{10}H_8N_2$, 10), 157 (18). IR (solid): $\tilde{\nu}$ 3065 (w), 2966 (w), 2160 (w), 1612 (w), 1531 (m), 1477 (w), 1454 (w), 1422 (w), 1369 (w), 1344 (w), 1337 (w), 1287 (m), 1248 (m), 1240 (m), 1215 (m), 1198 (w), 1161 (w), 1119 (m), 1082 (m), 1047 (w), 1013 (w), 935 (m), 914 (w), 841 (s), 758 (w), 727 (s), 700 (w), 646 (w), 633 (m), 615 (w). Anal. Calcd for $C_{22}H_{21}N_3Si$ (355.5): C, 74.33; H, 5.95; N, 11.82. Found: C, 74.13; H, 5.76; N, 11.91.

*2-(1-Methyl-1H-indol-3-yl)-3-[(triisopropylsilyl)ethynyl]-quinoxaline (**5c**).* Yellow solid (749 mg, 85%). R_f = 0.47 (petroleum ether/ethyl acetate 6:1). Mp: 100 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.12–1.29 (m, 21 H), 3.88 (s, 3 H), 7.30–7.43 (m, 3 H), 7.64 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 7.72 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.04 (dd, J = 8.3 Hz, J = 1.4 Hz, 1 H), 8.11 (dd, J = 8.3 Hz, J = 1.4 Hz, 1 H), 8.59 (s, 1 H), 8.73–8.80 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.4 (CH), 18.7 (CH_3), 33.2 (CH_3), 97.6 (C_{quat}), 106.4 (C_{quat}), 109.4 (CH), 112.2 (C_{quat}), 121.4 (CH), 122.9 (CH), 123.0 (CH), 127.5 (C_{quat}), 128.5 (CH), 128.6 (CH), 128.7 (CH), 130.4 (CH), 132.6 (CH), 136.7 (C_{quat}), 137.3 (C_{quat}), 139.4 (C_{quat}), 141.0 (C_{quat}), 150.4 (C_{quat}). EI + MS (m/z): 440 (35), 439 (M^+, 100), 397 (24), 396 ($[M - C_3H_7]^+$, 70), 368 (11), 354 (26), 353 ($[M - (C_3H_7)_2]^+$, 6), 339 (11), 338 (10), 326 (20), 312 (12), 311 (21), 310 ($[M - (C_3H_7)_3]^+$, 33), 296 (13), 167 (12), 162 (12), 156 (12), 155 (11), 154 (10), 149 (17). IR (solid): $\tilde{\nu}$ 2945 (w), 2864 (w), 1537 (m), 1526 (m), 1452 (m), 1423 (w), 1383 (m), 1371 (m), 1339 (w), 1310 (w), 1287 (w), 1242 (w), 1217 (m), 1200 (m), 1159 (w), 1142 (w), 1125 (w), 1084 (m), 1013 (w), 995 (w), 935 (m), 880 (m), 758 (m), 745 (s), 681 (s), 658 (m), 615 (m). Anal. Calcd for $C_{28}H_{33}N_3Si$ (439.7): C, 76.49; H, 7.57; N, 9.56. Found: C, 76.68; H, 7.69; N, 9.42.

*2-[(4-Methoxyphenyl)ethynyl]-3-(1-methyl-1H-indol-3-yl)-quinoxaline (**5d**).* Yellow solid (573 mg, 74%). R_f = 0.33 (dichloromethane). Mp: 164 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.77 (s, 3 H), 3.83 (s, 3 H), 6.79–6.93 (m, 2 H), 7.20–7.39 (m, 3 H), 7.41–7.51 (m, 2 H), 7.55–7.68 (m, 2 H), 7.99 (dd, J = 8.2 Hz, J = 1.4 Hz, 1 H), 8.05 (dd, J = 8.2 Hz, J = 1.2 Hz, 1 H), 8.38 (s, 1 H), 8.63–8.71 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.4 (CH_3), 55.4 (CH_3), 88.7 (C_{quat}), 94.9 (C_{quat}), 109.4 (CH), 112.4 (C_{quat}), 113.9 (C_{quat}), 114.3 (CH), 121.4 (CH), 123.0 (CH), 127.5 (C_{quat}), 128.4 (CH), 128.6 (CH), 128.8 (CH), 130.2 (CH), 132.6 (CH), 133.7 (CH), 137.4 (C_{quat}) 139.4 (C_{quat}), 140.8 (C_{quat}), 150.5 (C_{quat}), 160.7 (C_{quat}). EI + MS (m/z):. 390 (26), 389 (M^+, 100), 388 (94), 374 ($[M - CH_3]^+$, 21), 358 ($[M\text{-}OCH_3]^+$, 6), 346 (15), 345 (21), 282 ($C_{19}H_{12}N_3^+$, 4), 232 ($C_{16}H_{12}N_2^+$, 4), 231 (13), 195 (11), 190 (11), 173 (14), 172 (16), 156 (11), 155 (11). IR (solid): $\tilde{\nu}$ 3044 (w), 2967 (w), 2901 (w), 2197 (w), 1605 (w), 1539 (m), 1508 (m), 1454 (m), 1371 (w), 1292 (w), 1254 (m), 1236 (w), 1211 (w), 1167 (w), 1155 (w), 1125 (m), 1113 (m), 1082 (m), 1032 (m), 1011 (m), 937 (m), 822 (s), 795 (w), 756 (m), 741 (s), 625 (m). Anal. Calcd for $C_{26}H_{19}N_3O$ (389.5): C, 80.18; H, 4.92; N, 10.79. Found: C, 80.00; H, 4.88; N, 10.68.

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*2-[(4-Butylphenyl)ethynyl]-3-(1-methyl-1H-indol-3-yl)quinoxaline (**5e**).* Yellow solid (455 mg, 55%). R_f = 0.48 (dichloromethane). Mp: 129 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.95 (t, J = 7.3 Hz, 3 H), 1.38 (sext, J = 7.3 Hz, 2 H), 1.57−1.69 (m, 2 H), 2.65 (t, J = 7.7 Hz, 2 H), 3.91 (s, 3 H), 7.20−7.25 (m, 2 H), 7.30−7.44 (m, 3 H), 7.50−7.56 (m, 2 H), 7.66 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 7.73 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.7 Hz, 1 H), 8.03−8.11 (m, 1 H), 8.10−8.17 (m, 1 H), 8.48 (s, 1 H), 8.73−8.81 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9 (CH_3), 22.3 (CH_2), 33.3 (CH_2), 33.4 (CH_3), 35.7 (CH_2), 89.2 (C_{quat}), 94.7 (C_{quat}), 109.4 (CH), 112.3 (C_{quat}), 119.0 (C_{quat}), 121.4 (CH), 122.9 (CH), 127.5 (C_{quat}), 128.5 (CH), 128.6 (CH), 128.8 (CH), 130.3 (CH), 131.9 (CH), 132.6 (CH), 137.1 (C_{quat}), 137.3 (C_{quat}), 139.3 (C_{quat}), 140.9 (C_{quat}), 145.0 (C_{quat}), 150.6 (C_{quat}). MALDI-MS: m/z = 416.1 [MH^+]. IR (solid): $\tilde{\nu}$ 3100 (w), 3040 (w), 2959 (w), 2930 (w), 2899 (w), 2859 (w), 2311 (w), 2203 (w), 1528 (m), 1508 (m), 1474 (w), 1456 (w), 1423 (w), 1402 (w), 1368 (m), 1352 (w), 1339 (m), 1329 (w), 1296 (w), 1277 (w), 1256 (w), 1234 (w), 1211 (m), 1171 (w), 1153 (w), 1126 (m), 1113 (m), 1080 (m), 1047 (w), 1015 (m), 988 (w), 935 (m), 908 (w), 881 (w), 826 (m), 812 (w), 783 (w), 756 (s), 739 (s), 642 (w), 610 (m). Anal. Calcd for $C_{29}H_{25}N_3$ (415.5): C, 83.82; H, 6.06; N, 10.11. Found: C, 83.58; H, 6.28; N, 10.09.

*2-[(4-tert-Butylphenyl)ethynyl]-3-(1-methyl-1H-indol-3-yl)-quinoxaline (**5f**).* Yellow solid (672 mg, 81%). R_f = 0.24 (petroleum ether/ethyl acetate 8:1). Mp: 130 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (s, 9 H), 3.92 (s, 3 H), 7.31−7.39 (m, 2 H), 7.40−7.47 (m, 3 H), 7.54−7.59 (m, 2 H), 7.67 (ddd, J = 8.2 Hz, J = 6.8 Hz, J = 1.6 Hz, 1 H), 7.73 (ddd, J = 8.2 Hz, J = 6.8 Hz, J = 1.7 Hz, 1 H), 8.07 (dd, J = 8.1 Hz, J = 1.3 Hz, 1 H), 8.14 (dd, J = 8.2 Hz, J = 1.2 Hz, 1 H), 8.49 (s, 1 H), 8.74−8.81 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.1 (CH_3), 33.5 (CH_3), 35.0 (C_{quat}), 89.2 (C_{quat}), 94.6 (C_{quat}), 109.4 (CH), 112.4 (C_{quat}), 118.9 (C_{quat}), 121.4 (CH), 122.9 (CH), 125.7 (CH), 127.5 (C_{quat}), 128.5 (CH), 128.6 (CH), 128.7 (CH), 130.3 (CH), 131.8 (CH), 132.6 (CH), 137.2 (C_{quat}), 137.3 (C_{quat}), 139.3 (C_{quat}), 140.9 (C_{quat}), 150.6 (C_{quat}), 153.1 (C_{quat}). MALDI-MS: m/z = 416 [MH^+]. IR (solid): $\tilde{\nu}$ 3048 (w), 3030 (w), 2957 (w), 2930 (w), 2909 (w), 2866 (w), 2853 (w), 2376 (w), 2205 (w), 1533 (s), 1518 (m), 1506 (m), 1477 (w), 1452 (w), 1425 (w), 1371 (m), 1298 (w), 1236 (w), 1215 (m), 1130 (w), 1101 (m), 1082 (w), 1013 (w), 935 (m), 908 (w), 835 (w), 758 (m), 743 (s), 694 (w), 638 (w), 615 (m). Anal. Calcd for $C_{29}H_{25}N_3$ (415.5): C, 83.82; H, 6.06; N, 10.11. Found: C, 83.71; H, 5.95; N, 9.89.

*2-[(4-Methoxycarbonylphenyl)ethynyl]-3-(1-methyl-1H-indol-3-yl)quinoxaline (**5g**).* Yellow solid (709 mg, 85%). R_f = 0.14 (dichloromethane). Mp: 182 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.88 (s, 3 H), 3.94 (s, 3 H), 7.30−7.39 (m, 2 H), 7.39−7.44 (m, 1 H), 7.58−7.64 (m, 2 H), 7.67 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.5 Hz, 1 H), 7.74 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.02−8.19 (m, 3 H), 8.11−8.16 (m, 1 H), 8.35 (s, 1 H), 8.67−8.75 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.4 (CH_3), 52.3 (CH_3), 92.0 (C_{quat}), 92.7 (C_{quat}), 109.5 (CH), 112.3 (C_{quat}), 121.4 (CH), 122.8 (CH), 123.0 (CH), 126.4 (C_{quat}), 127.3 (C_{quat}), 128.6 (CH), 128.7 (CH), 128.9 (CH), 129.7 (CH), 130.6 (C_{quat}), 130.7 (CH), 131.8 (CH), 132.3 (CH), 136.5 (C_{quat}), 137.3 (C_{quat}), 139.4 (C_{quat}), 141.2 (C_{quat}), 150.6 (C_{quat}), 166.2 (C_{quat}). MALDI-MS: m/z = 418 [MH^+]. IR (solid): $\tilde{\nu}$ 3649 (w), 3127 (w), 3046 (w), 3019 (w), 2992 (w), 2945 (w), 2913 (w), 2874 (w), 2835 (w), 2313 (w), 2205 (w), 1719 (s), 1603 (w), 1539 (m), 1506 (w), 1474 (w), 1454 (w), 1429 (w), 1402 (w), 1369 (w), 1339 (w), 1271 (m), 1236 (m), 1217 (m), 1171 (m), 1132 (m), 1101 (m), 1082 (m), 1049 (w), 1015 (m), 935 (m), 907 (w), 847 (w), 816 (w), 748 (s), 687 (m), 646 (w), 615 (m). Anal. Calcd for $C_{27}H_{19}N_3O_2$ (417.5): C, 77.68; H, 4.59; N, 10.07. Found: C, 77.54; H, 4.70; N, 9.90.

*2-[(4-Cyanophenyl)ethynyl]-3-(1-methyl-1H-indol-3-yl)-quinoxaline (**5h**).* Yellow solid (623 mg, 81%). R_f = 0.12 (dichloromethane). Mp: 245 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.91 (s, 3 H), 7.35 (tdd, J = 8.4 Hz, J = 7.0 Hz, J = 1.6 Hz, 2 H), 7.41−7.46 (m, 1 H), 7.60 (m 2 H), 7.67 (m, 2 H), 7.70 (ddd, J = 8.5 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 7.78 (ddd, J = 8.4 Hz, J = 7.0 Hz, J = 1.6 Hz, 1 H), 8.07 (dd, J = 8.2 Hz, J = 1.2 Hz, 1 H), 8.15 (dd, J = 8.2 Hz, J = 1.1 Hz, 1 H), 8.25 (s, 1 H), 8.59−8.68 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.5 (CH_3), 91.5 (C_{quat}), 93.1 (C_{quat}), 109.6 (CH), 112.4 (C_{quat}), 112.8 (C_{quat}), 118.1 (C_{quat}), 121.5 (CH), 122.6 (CH), 123.1 (CH), 126.7 (C_{quat}), 127.2 (C_{quat}), 128.7 (CH), 128.8 (CH), 129.2 (CH), 131.1 (CH), 132.1 (CH), 132.2 (CH), 132.4 (CH), 136.2 (C_{quat}), 137.3 (C_{quat}), 139.5 (C_{quat}), 141.3 (C_{quat}), 150.7 (C_{quat}). MALDI-MS: m/z = 385 [MH^+]. IR (solid): $\tilde{\nu}$ 3649 (w), 3123 (w), 3046 (w), 2907 (w), 2369 (w), 2224 (w), 1601 (w), 1541 (m), 1535 (m), 1499 (w), 1476 (w), 1456 (m), 1423 (w), 1404 (w), 1371 (m), 1352 (w), 1339 (w), 1300 (w), 1256 (w), 1236 (w), 1211 (m), 1130 (m), 1111 (m), 1082 (m), 1011 (w), 937 (m), 908 (w), 837 (w), 822 (w), 768 (s), 739 (s), 646 (w), 619 (w). Anal. Calcd for $C_{26}H_{16}N_4$ (384.4): C, 81.23; H, 4.20; N, 14.57. Found: C, 81.28; H, 4.04; N, 14.33.

*2-[(4-Fluorophenyl)ethynyl]-3-(1-methyl-1H-indol-3-yl)-quinoxaline (**5i**).* Yellow solid (265 mg, 70%). R_f = 0.33 (dichloromethane). Mp: 176 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.88 (s, 3 H), 7.05−7.15 (m, 2 H), 7.29−7.45 (m, 3 H), 7.52−7.60 (m, 2 H), 7.68 (dd, J = 6.9 Hz, J = 1.5 Hz, 1 H), 7.73 (dd, J = 6.8 Hz, J = 1.5 Hz, 1 H), 8.06 (dd, J = 8.2 Hz, J = 1.3 Hz, 1 H), 8.13 (dd, J = 8.3 Hz, J = 1.1 Hz, 1 H), 8.36 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.4 (CH_3), 89.4 (C_{quat}), 92.9 (C_{quat}), 109.5 (CH), 112.4 (C_{quat}), 116.0 (d, J = 22.2 Hz, CH), 118.1 (d, J = 3.5 Hz, C_{quat}), 121.4 (CH), 122.8 (CH), 122.9 (CH), 127.4 (C_{quat}), 128.6 (CH), 128.7 (CH), 128.8 (CH), 130.5 (CH), 132.3 (CH), 134.0 (d, J = 8.6 Hz, CH), 136.9 (C_{quat}), 137.3 (C_{quat}), 139.4 (C_{quat}), 141.1 (C_{quat}), 150.6 (C_{quat}) 163.2 (d, J = 251.9 Hz, C_{quat}). EI + MS (m/z):. 377 (M^+, 100), 376 (20), 159 (13), 158 (100). IR (solid): $\tilde{\nu}$ 3044 (w), 2361 (w), 2201 (w), 1599 (w), 1533 (m), 1504 (m), 1476 (w), 1452 (w), 1404 (w), 1381 (w), 1356 (m), 1339 (w), 1298 (w), 1229 (m), 1213 (m), 1177 (w), 1150 (w), 1132 (w), 1111 (m), 1078 (w), 1013 (w), 935 (w), 822 (m), 797 (w), 748 (s), 621 (w), 619 (w). Anal. Calcd for $C_{25}H_{16}FN_3$ (377.4): C, 79.56; H, 4.27; N, 11.13. Found: C, 79.37; H, 4.40; N, 10.93.

*2-(1-Methyl-1H-pyrrol-2-yl)-3-[(trimethylsilyl)ethynyl]quinoxaline (**5j**).* Brownish solid (446 mg, 73%). R_f = 0.88 (dichloromethane). Mp: 53 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.31 (s, 9 H), 4.00 (s, 3 H), 6.24 (dd, J = 4.0 Hz, J = 2.6 Hz, 1 H), 6.84−6.87 (m, 1 H), 7.38 (dd, J = 4.0 Hz, J = 1.7 Hz, 1 H), 7.62−7.68 (m, 1 H), 7.68−7.73 (m, 1 H), 7.94−7.97 (m, 1 H), 8.01−8.05 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.6 (CH_3), 37.1 (CH_3), 101.6 (CH), 103.3 (C_{quat}), 107.4 (C_{quat}), 116.3 (CH), 128.1 (CH), 128.2 (C_{quat}), 128.5 (CH), 128.8 (CH), 129.2 (CH), 130.6 (CH), 137.2 (C_{quat}), 139.3 (C_{quat}), 140.1 (C_{quat}), 147.6 (C_{quat}). MALDI-MS: m/z = 306.4 [MH^+]. IR (solid): $\tilde{\nu}$ 3067 (w), 2959 (w), 2845 (w), 2488 (w), 1541 (m), 1520 (w), 1489 (w), 1472 (w), 1450 (w), 1422 (m), 1400 (w), 1369 (w), 1337 (w), 1312 (w), 1277 (w), 1252 (w), 1227 (w), 1215 (w), 1184 (m), 1134 (w), 1123 (w), 1098 (w), 1065 (m), 980 (m), 959 (w), 912 (w), 878 (w), 843 (s), 810 (m), 760 (s), 739 (s), 692 (m), 658 (w), 631 (m), 606 (m). Anal. Calcd for $C_{18}H_{19}N_3Si$ (305.5): C, 70.78; H, 6.27; N, 13.76. Found: C, 70.89; H, 6.28; N, 13.77.

*2-(1-Phenyl-1H-pyrrol-3-yl)-3-[(trimethylsilyl)ethynyl]quinoxaline (**5k**).* Yellow resin (552 mg, 75%). R_f = 0.24 (petroleum ether/ethyl acetate 20:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.31 (s, 9 H), 6.44 (dd, J = 3.8 Hz, J = 2.8 Hz, 1 H), 7.11 (dd, J = 2.7 Hz, J = 1.7 Hz, 1 H), 7.14−7.19 (m, 2 H), 7.21−7.28 (m, 3 H), 7.32 (dd, J = 3.8 Hz, J = 1.7 Hz, 1 H), 7.50−7.65 (m, 3 H), 7.96−8.02 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.5 (CH_3), 101.8 (C_{quat}), 102.5 (C_{quat}), 109.3 (CH), 116.6 (CH), 125.4 (CH), 126.4 (CH), 127.0 (CH), 128.6 (CH), 128.66 (C_{quat}), 128.71 (CH), 129.6 (CH), 130.5 (CH), 137.6 (C_{quat}), 139.6 (C_{quat}), 140.0 (C_{quat}) 141.1 (C_{quat}), 147.5 (C_{quat}). EI + MS (m/z): 368 (14), 367 (M^+, 47), 366 (24), 353 (11), 337 ([M − CH_3]$^+$, 38), 326 (10), 294 ([M − [$Si(CH_3)_3$]$^+$, 5), 290 ([M − (C_5H_6)], 12), 243 (13), 149 (17), 101 (11), 59 (23), 58 (11); 57 (17), 56 (19), 55 (13), 43 (100), 41 (18). IR (solid): $\tilde{\nu}$ 2957 (w), 1597 (w), 1541 (w), 1520 (w), 1499 (m), 1470 (w), 1456 (w), 1425 (m), 1391 (w), 1354 (w), 1327 (w), 1306 (w), 1281 (w), 1250 (w), 1229 (w), 1207 (m), 1182 (w), 1132 (m), 1123 (m), 1074 (w), 947 (m), 910 (w), 885 (w), 841 (s), 810 (m), 797 (w), 758 (s), 725 (s), 696 (s), 663 (m), 631 (m), 613 (m). Anal. Calcd for $C_{23}H_{21}N_3Si$ (367.5): C, 75.17; H, 5.76; N, 11.43. Found: C, 75.10; H, 5.81; N, 11.32.

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*2-(1-Phenyl-1H-pyrrol-2-yl)-3-(phenylethynyl)quinoxaline (**5l**).* Yellow solid (544 mg, 73%). R_f = 0.53 (dichloromethane). Mp: 109 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.51 (dd, J = 3.8 Hz, J = 2.8 Hz, 1 H), 7.12−7.19 (m, 3 H), 7.19−7.25 (m, 2 H), 7.30 (dd, J = 3.8 Hz, J = 1.7 Hz, 1 H), 7.37−7.44 (m, 3 H), 7.57−7.64 (m, 4 H), 7.65−7.70 (m, 1 H), 7.99−8.05 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 88.0 (C_{quat}), 94.9 (C_{quat}), 109.6 (CH), 116.2 (CH), 121.8 (C_{quat}), 125.2 (CH), 126.4 (CH), 126.6 (CH), 128.45 (CH), 128.52 (CH), 128.78 (CH), 128.81 (CH), 129.1 (C_{quat}), 129.5 (CH), 129.7 (CH), 130.4 (CH), 132.3 (CH), 138.3 (C_{quat}), 139.9 (C_{quat}), 140.1 (C_{quat}), 140.9 (C_{quat}), 148.0 (C_{quat}). MALDI-MS: m/z = 372 [MH^+]. IR (solid): $\tilde{\nu}$ 3647 (w), 3057 (w), 2360 (w), 2330 (w), 2210 (w), 1989 (w), 1965 (w), 1597 (w), 1541 (m), 1491 (m), 1470 (w), 1431 (m), 1393 (w), 1360 (m), 1325 (w), 1306 (w), 1288 (w), 1252 (w), 1206 (w), 1153 (w), 1115 (m), 1105 (w), 1049 (m), 1007 (w), 945 (m), 914 (w), 870 (w), 760 (s), 727 (s), 700 (m), 687 (s), 667 (m), 650 (w), 627 (w). Anal. Calcd for $C_{26}H_{17}N_3$ (371.4): C, 84.07; H, 4.61; N, 11.31. Found: C, 83.90; H, 4.76; N, 11.39.

*2-[(4-Methoxyphenyl)ethynyl]-3-(1-phenyl-1H-pyrrol-2-yl)-quinoxaline (**5m**).* Greenish solid (589 mg, 73%). R_f = 0.39 (dichloromethane). Mp: 137 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.85 (s, 3 H), 6.50 (dd, J = 3.7 Hz, J = 2.8 Hz, 1 H), 6.88−6.96 (m, 2 H), 7.12−7.19 (m, 3 H), 7.19−7.25 (m, 3 H), 7.28 (dd, J = 3.8 Hz, J = 1.7 Hz, 1 H), 7.51−7.57 (m, 2 H), 7.57−7.68 (m, 3 H), 7.98−8.04 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.3 (CH_3), 87.3 (C_{quat}), 95.6 (C_{quat}), 109.5 (CH), 113.9 (C_{quat}), 114.2 (CH), 116.1 (CH), 125.2 (CH), 126.4 (CH), 126.5 (CH), 128.4 (CH), 128.76 (CH), 128.79 (CH), 129.2 (C_{quat}), 129.7 (CH), 130.1 (CH), 134.0 (CH), 138.7 (C_{quat}), 139.90 (C_{quat}), 139.93 (C_{quat}), 140.9 (C_{quat}), 147.9 (C_{quat}), 160.6 (C_{quat}). MALDI-MS: m/z = 402 [MH^+]. IR (solid): $\tilde{\nu}$ 3672 (w), 3055 (w), 2988 (m), 2972 (m), 2937 (m), 2901 (m), 2540 (w), 2351 (w), 2208 (w), 1599 (m), 1543 (m), 1497 (m), 1468 (m), 1429 (m), 1416 (m), 1393 (m), 1360 (m), 1287 (m), 1248 (m), 1206 (m), 1153 (m), 1115 (m), 1101 (m), 1057 (s), 1042 (s), 1028 (s), 1003 (m), 947 (m), 937 (w), 870 (w), 827 (s), 760 (s), 743 (m), 727 (s), 698 (s), 662 (m), 625 (m). Anal. Calcd for $C_{27}H_{19}N_3O$ (401.5): C, 80.78; H, 4.77; N, 10.47. Found: C, 80.57; H, 4.60; N, 10.50.

*2-[(4-Cyanophenyl)ethynyl]-3-(1-phenyl-1H-pyrrol-2-yl)-quinoxaline (**5n**).* The compound was obtained as a yellow solid (536 mg, 68%). R_f = 0.12 (dichloromethane). Mp: 214 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.50 (dd, J = 3.8 Hz, J = 2.8 Hz, 1 H), 7.11−7.18 (m, 3 H), 7.20−7.28 (m, 4 H), 7.63−7.72 (m, 7 H), 7.99−8.04 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 91.6 (C_{quat}), 92.0 (C_{quat}), 109.7 (CH), 112.7 (C_{quat}), 116.1 (CH), 118.2 (C_{quat}), 125.1 (CH), 126.56 (CH), 126.63 (C_{quat}), 126.8 (CH), 128.6 (CH), 128.8 (C_{quat}), 128.85 (CH), 128.88 (CH), 130.0 (CH), 131.0 (CH), 132.1 (CH), 132.6 (CH), 137.3 (C_{quat}), 139.9 (C_{quat}), 140.3 (C_{quat}), 140.8 (C_{quat}), 147.9 (C_{quat}). MALDI-MS: m/z = 397.3 [MH^+]. IR (solid): $\tilde{\nu}$ 3057 (w), 2222 (w), 1595 (w), 1543 (w), 1520 (w), 1495 (m), 1472 (w), 1429 (m), 1395 (w), 1358 (m), 1323 (w), 1277 (w), 1252 (w), 1221 (w), 1198 (w), 1171 (w), 1153 (w), 1115 (m), 1096 (m), 1074 (w), 1047 (m), 1036 (w), 1013 (w), 945 (m), 908 (w), 870 (w), 827 (m), 795 (w), 760 (s), 725 (s), 689 (m), 664 (m). Anal. Calcd for $C_{27}H_{16}N_4$ (396.4): C, 81.80; H, 4.07; N, 14.13. Found: C, 81.57; H, 4.08; N, 14.05.

*2-[1-(Triisopropylsilyl)-1H-pyrrol-3-yl]-3-[(trimethylsilyl)ethynyl]-quinoxaline (**5o**).* Yellow solid (496 mg, 55%. R_f = 0.26 (petroleum ether/ethyl acetate 20:1. Mp: 119 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.34 (s, 9 H), 1.16 (d, J = 7.5 Hz, 18 H), 1.54 (sept, J = 7.5 Hz, 3 H), 6.86 (dd, J = 2.8 Hz, J = 2.1 Hz, 1 H), 7.37 (dd, J = 2.9 Hz, J = 1.4 Hz, 1 H), 7.60 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.5 Hz, 1 H), 7.67 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.7 Hz, 1 H), 7.96−8.04 (m, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.4 (CH_3), 11.7 (CH), 17.8 (CH_3), 100.5 (C_{quat}), 104.3 (C_{quat}), 112.0 (CH), 124.3 (C_{quat}), 124.9 (CH), 127.5 (CH), 128.5 (CH), 128.59 (CH), 128.62 (CH), 130.4 (CH), 136.0 (C_{quat}), 139.8 (C_{quat}), 141.2 (C_{quat}), 149.7 (C_{quat}). MALDI-MS: m/z = 448 [MH^+]. IR (solid): $\tilde{\nu}$ 2945 (w), 2924 (w), 2866 (w), 2361 (w), 1539 (m), 1522 (w), 1493 (m), 1456 (w), 1319 (w), 1248 (m), 1227 (w), 1202 (m), 1128 (m), 1105 (s), 1086 (w), 1072 (w), 1034 (w), 1016 (w), 995 (w), 959 (w), 934 (w), 883 (m), 843 (s), 816 (m), 797 (m), 768 (s), 727 (m), 691 (s), 662 (s), 650 (m), 633 (m), 631 (m). Anal. Calcd for $C_{26}H_{37}N_3Si_2$ (447.8): C, 69.74; H, 8.33; N, 9.38. Found: C, 69.50; H, 8.24; N, 9.11.

*2-(5-Methoxythiophene-2-yl)-3-[(trimethylsilyl)ethynyl]-quinoxaline (**5p**).* Yellow solid (398 mg, 59%). R_f = 0.24 (petroleum ether/ethyl acetate 20:1). Mp: 148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.37 (s, 9 H), 3.99 (s, 3 H), 6.28 (d, J = 4.3 Hz, 1 H), 7.62 (ddd, J = 8.2 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 7.68 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.7 Hz, 1 H), 7.94 (ddd, J = 8.3 Hz, J = 1.7 Hz, J = 0.7 Hz, 1 H), 7.99 (ddd, J = 8.3 Hz, J = 1.7 Hz, J = 0.7 Hz, 1 H), 8.35 (d, J = 4.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.6 (CH_3), 60.1 (CH_3), 102.2 (C_{quat}),103.4 (C_{quat}), 105.2 (CH), 128.1 (C_{quat}), 128.3 (CH), 128.6 (CH), 129.1 (CH), 129.9 (CH), 130.9 (CH), 134.1 (C_{quat}), 139.7 (C_{quat}), 140.6 (C_{quat}) 147.5 (C_{quat}), 171.3 (C_{quat}). EI + MS (m/z): 340 (11), 339 (26), 338 (M^+, 100), 323 ([M − CH_3]$^+$, 9), 308 ([M − $(CH_3)_2$], 6), 307 ([M-OCH_3], 4), 295 (11), 293 ([M − $(CH_3)_3$]$^+$, 4), 280 (13), 279 (10), 265 ([M-$Si(CH_3)_3$]$^+$, 7), 205 (21), 140 (11), 43 (25). IR (solid): $\tilde{\nu}$ 2953 (w), 2897 (w), 2154 (w), 1551 (w), 1479 (s), 1452 (m), 1418 (s), 1395 (m), 1358 (w), 1339 (m), 1310 (w), 1250 (m), 1215 (s), 1180 (m), 1134 (m), 1125 (w), 1067 (s), 986 (m), 939 (w), 845 (s), 810 (w), 750 (s), 737 (m), 725 (w), 702 (w), 640 (w), 625 (w). Anal. Calcd for $C_{18}H_{18}N_2OSSi$ (338.5): C, 63.87; H, 5.36; N, 8.28. Found: C, 63.64; H, 5.64; N, 8.00.

*2-(5-Methoxythiophene-2-yl)-3-(phenylethynyl)quinoxaline (**5q**).* Yellow crystals (192 mg, 28%). R_f = 0.16 (petroleum ether/ethyl acetate 10:1). Mp: 164 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.99 (s, 3 H), 6.31 (d, J = 4.3 Hz, 1 H), 7.40−7.47 (m, 3 H), 7.60−7.73 (m, 4 H), 7.91−7.98 (m, 1 H), 8.01 (dd, J = 8.1 Hz, J = 1.3 Hz, 1 H), 8.31 (d, J = 4.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 60.1 (CH_3), 88.6 (C_{quat}), 94.9 (C_{quat}), 105.5 (CH), 121.7 (C_{quat}), 128.2 (C_{quat}), 128.4 (CH), 128.55 (CH), 128.59 (CH), 129.1 (CH), 129.5 (CH), 129.7 (CH), 130.8 (CH), 132.1 (CH), 134.7 (C_{quat}), 139.9 (C_{quat}), 140.6 (C_{quat}), 147.5 (C_{quat}), 171.2 (C_{quat}). EI + MS (m/z): 343 (24), 342 (M^+, 100), 328 (10), 327 ([M − CH_3]$^+$, 46), 300 (17), 299 (72), 298 (30), 267 (13), 156 (17), 155 (11), 149 (16), 128 (21), 127 (21). IR (solid): $\tilde{\nu}$ 3065 (w), 2933 (w), 2210 (w), 1543 (w), 1477 (s), 1452 (w), 1416 (s), 1396 (m), 1285 (w), 1258 (w), 1209 (m), 1150 (w), 1132 (m), 1111 (m), 1059 (m), 1024 (w), 995 (m), 953 (w), 934 (m), 908 (w), 874 (w), 847 (w), 824 (w), 777 (m), 760 (m), 754 (s), 737 (m), 723 (m), 690 (s), 664 (m), 622 (m), 611 (m). Anal. Calcd for $C_{21}H_{14}N_2OS$ (342.4): C, 73.66; H, 4.12; N, 8.18, S 9.36. Found: C, 73.89; H, 4.18; N, 8.10, S 9.32.

*2-[(4-Methoxyphenyl)ethynyl]-3-(5-methoxythiophene-2-yl)-quinoxaline (**5r**).* Yellow crystals (243 mg, 33%). R_f = 0.15 (petroleum ether/ethyl acetate 5:1). Mp: 120 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.85 (s, 3 H), 3.99 (s, 3 H), 6.31 (d, J = 4.3 Hz, 1 H), 6.94 (d, J = 8.6 Hz, 2 H), 7.56−7.75 (m, 4 H), 7.87−8.08 (m, 2 H), 8.32 (dd, J = 4.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.4 (CH_3), 60.1 (CH_3), 87.8 (C_{quat}), 95.5 (C_{quat}), 105.4 (CH), 113.7 (C_{quat}), 114.3 (CH), 128.26 (C_{quat}), 128.33 (CH), 128.5 (CH), 129.1 (CH), 129.5 (CH), 130.5 (CH), 133.7 (CH), 135.0 (C_{quat}), 140.0 (C_{quat}), 140.4 (C_{quat}), 147.5 (C_{quat}), 160.76 (C_{quat}), 171.1 (C_{quat}). EI + MS (m/z): 373 (24), 372 (M^+, 100), 357 ([M − CH_3]$^+$, 12), 342 ([M − $(CH_3)_2$]$^+$, 9), 330 (17), 329 (76), 314 (39), 298 (15), 286 (34), 285 (17), 165 (25), 157 ($C_{10}H_7NO^+$, 10), 149 (10), 143.4 (15), 142.6 (29). IR (solid): $\tilde{\nu}$ 3059 (w), 3046 (w), 2933 (w), 2830 (w), 2207 (m), 1603 (m), 1551 (w), 1510 (m), 1489 (s), 1474 (m), 1454 (m), 1423 (m), 1398 (m), 1352 (m), 1292 (m), 1246 (s), 1204 (s), 1182 (m), 1132 (m), 1113 (m), 1061 (s), 1034 (s), 995 (m), 935 (m), 910 (w), 841 (m), 808 (m), 779 (s), 758 (s), 723 (m), 646 (w), 608 (m). Anal. Calcd for $C_{22}H_{16}N_2O_2S$ (372.4): C, 70.95; H, 4.33; N, 7.52. Found: C, 70.69; H, 4.47; N, 7.31.

*2-(Azulen-1-yl)-3-[(trimethylsilyl)ethynyl]quinoxaline (**5s**).* Dark green solid (437 mg, 62%). R_f = 0.28 (petroleum ether/ethyl acetate 10:1). Mp: 105 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.19 (s, 9 H), 7.30−7.43 (m, 2 H), 7.46 (d, J = 4.1 Hz, 1 H), 7.64−7.83 (m, 3 H), 8.10−8.15 (m, 2 H), 8.46 (d, J = 9.5 Hz, 1 H), 8.75 (d, J = 4.1 Hz, 1 H), 9.15 (d, J = 9.7 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.7 (CH_3), 101.6 (C_{quat}), 103.5 (C_{quat}), 117.1 (CH), 124.3 (C_{quat}), 125.1 (CH), 125.9 (CH), 128.78 (CH), 128.83 (CH), 129.4 (CH),

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130.7 (CH), 137.1 (CH), 137.5 (CH), 138.5 (C_{quat}), 138.6 (CH), 139.1 (C_{quat}), 139.4 (CH), 139.8 (C_{quat}) 140.8 (C_{quat}) 143.4 (C_{quat}), 152.3 (C_{quat}). EI + MS (*m*/*z*): 353 (29), 352 (M^+, 100), 351 (82), 337 ($[M - CH_3]^+$, 15), 307 ($[M - (CH_3)_2]^+$, 9), 293 (16), 280 (10), 279 ($[M\text{-}Si(CH_3)_3]^+$, 26), 228 (26), 227 (10), 153 ($C_{11}H_7N$, 18). IR (solid): $\tilde{\nu}$ 3053 (w), 2958 (w), 1524 (w), 1504 (w), 1472 (w), 1422 (w), 1396 (m), 1310 (w), 1296 (w), 1250 (w), 1207 (m), 1190 (w), 1136 (w), 1123 (w), 1088 (w), 1051 (w), 1003 (w), 957 (w), 924 (w), 912 (w), 872 (w), 843 (s), 800 (w), 781 (s), 758 (s), 733 (m), 706 (w), 631 (w), 613 (m). Anal. Calcd for $C_{23}H_{20}N_2Si$ (352.5): C, 78.37; H, 5.72; N, 7.95. Found: C, 78.28; H, 5.48; N, 7.94.

*6,7-Dichloro-2-(1-methyl-1H-indol-3-yl)-3-[(trimethylsilyl)-ethynyl]quinoxaline (**5t**).* Yellow solid (686 mg, 81%). R_f = 0.90 (dichloromethane). Mp: 237 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.39 (s, 9 H), 3.89 (s, 3 H), 7.30−7.41 (m, 3 H), 8.07 (d, *J* = 0.4 Hz, 1 H), 8.15 (d, *J* = 0.4 Hz, 1 H), 8.63 (s, 1 H), 8.71−8.77 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.5 (CH_3), 33.4 (CH_3), 102.3 (C_{quat}), 104.0 (C_{quat}), 109.5 (CH), 111.6 (C_{quat}), 121.8 (CH), 123.2 (CH), 123.2 (CH), 127.3 (C_{quat}), 129.0 (CH), 130.9 (CH), 132.6 (C_{quat}), 133.4 (CH), 134.8 (C_{quat}), 136.9 (C_{quat}), 137.2 (C_{quat}), 137.5 (C_{quat}), 139.8 (C_{quat}), 151.1 (C_{quat}). MALDI-MS: *m*/*z* = 424.0 [MH^+]. IR (solid): $\tilde{\nu}$ 3138 (w), 2957 (w), 2928 (w), 2895 (w), 1946 (w), 1867 (w), 1587 (w), 1516 (m), 1462 (w), 1443 (m), 1406 (w), 1400 (w), 1362 (m), 1337 (w), 1312 (w), 1285 (w), 1246 (m), 1238 (m), 1225 (w), 1198 (m), 1179 (m), 1157 (m), 1126 (w), 1099 (m), 1084 (m), 1051 (w), 1018 (w), 974 (w), 935 (m), 880 (m), 860 (m), 835 (s), 797 (w), 745 (s), 727 (m), 702 (m), 664 (m), 644 (m), 623 (m). Anal. Calcd for $C_{22}H_{19}Cl_2N_3Si$ (424.4): C, 62.26; H, 4.51; N, 9.90. Found: C, 62.12; H, 4.35; N, 9.79.

*2-(1-Methyl-1H-indol-3-yl)-6-nitro-3-[(trimethylsilyl)ethynyl]-quinoxalines and 2-(1-Methyl-1H-indol-3-yl)-7-nitro-3-[(trimethylsilyl)ethynyl]quinoxaline (**5u**).* Red solid (694 mg, 87%). R_f = 0.58 (dichloromethane). Mp: 232 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): isomer ratio =10:1; δ 0.41 (s, 9 H), 3.92 (s, 3 H), 7.34−7.45 (m, 3 H), 8.08 (dd, *J* = 9.1 Hz, *J* = 0.5 Hz, 1 H), 8.34 (dd, *J* = 9.1 Hz, *J* = 2.5 Hz, 1 H), 8.71 (s, 1 H), 8.78−8.86 (m, 1 H), 8.91 (dd, *J* = 2.5 Hz, *J* = 0.5 Hz, 1 H); additional signals for the minor isomer: δ 8.12 (dd, *J* = 9.2 Hz, *J* = 0.5 Hz, 1 H), 8.43 (dd, *J* = 9.2 Hz, *J* = 2.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.6 (CH_3), 33.5 (CH_3), 103.91 (C_{quat}), 103.94 (C_{quat}), 109.6 (CH), 111.4 (C_{quat}), 121.7 (CH), 122.1 (CH), 123.3 (CH), 123.5 (CH), 124.6 (CH), 127.3 (C_{quat}), 130.0 (CH), 133.8 (CH), 137.3 (C_{quat}), 138.8 (C_{quat}), 140.0 (C_{quat}), 141.2 (C_{quat}), 148.2 (C_{quat}), 151.9 (C_{quat}). MALDI-MS: *m*/*z* = 401.1 [MH^+]. IR (solid): $\tilde{\nu}$ 3686 (w), 2970 (w), 2959 (w), 2901 (w), 2357 (w), 2330 (w), 1614 (w), 1516 (s), 1476 (m), 1458 (w), 1418 (w), 1408 (w), 1371 (m), 1337 (s), 1317 (w), 1287 (m), 1242 (m), 1215 (m), 1194 (m), 1159 (w), 1121 (w), 1090 (m), 1070 (m), 1057 (m), 1018 (w), 959 (w), 901 (m), 868 (m), 839 (s), 818 (m), 793 (m), 748 (s), 729 (s), 702 (m), 658 (m), 638 (m), 619 (m). Anal. Calcd for $C_{22}H_{20}N_4O_2Si$ (400.5): C, 65.98; H, 5.03; N, 13.99. Found: C, 65.76; H, 5.15; N, 14.08.

*3-(1-Methyl-1H-indol-3-yl)-2-[(triisopropylsilyl)ethynyl]pyrido-[2,3-b]pyrazine and 2-(1-Methyl-1H-indol-3-yl)-3-[(triisopropylsilyl)-ethynyl]pyrido[2,3-b]pyrazine (**5v**).* Orange resin (358 mg, 72%). R_f = 0.32 (petroleum ether/ethyl acetate 3:1). Mp: 99 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): isomer ratio =6.5:1; δ 1.17−1.27 (m, 21 H), 3.88 (s, 3 H), 7.27−7.47 (m, 4 H), 7.61 (dd, *J* = 8.3 Hz, *J* = 4.2 Hz, 1 H), 8.42 (dd, *J* = 8.3 Hz, *J* = 1.9 Hz, 1 H), 8.77 (s, 1 H), 8.77−8.82 (m, 1 H), 9.02 (dd, *J* = 4.2 Hz, *J* = 1.9 Hz, 1 H); additional signals for the minor isomer: δ 3.84 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.3 (CH), 18.7 (CH_3), 33.3 (CH_3), 100.1 (C_{quat}), 106.0 (C_{quat}), 109.5 (CH), 111.7 (C_{quat}), 121.7 (CH), 123.0 (CH), 123.1 (CH), 125.3 (CH), 127.4 (C_{quat}), 133.5 (CH), 136.5 (C_{quat}), 137.1 (CH), 137.3 (C_{quat}), 139.2 (C_{quat}), 148.1 (C_{quat}), 151.3 (C_{quat}), 151.4 (CH). Additional signals for the minor isomer: δ 33.6 (CH_3), 109.8 (CH), 122.6 (CH), 123.7 (CH), 140.2 (CH). EI + MS (*m*/*z*): 441 (36), 440 (M^+, 100), 398 (13), 397 ($[M - C_3H_7]^+$, 41), 356 (13), 355 (41), 354 ($[M - (C_3H_7)_2]^+$, 8), 327 (28), 318 (19), 325 (12), 311 ($[M - (C_3H_7)_3]^+$, 47), 163 (12), 158 (21), 156 (15), 155 (12), 135 (13). IR (solid): $\tilde{\nu}$ 2941 (w), 2887 (w), 2862 (w), 1609 (w), 1591 (w), 1533 (s), 1522 (s), 1480 (w), 1464 (m), 1452 (m), 1435 (m), 1373 (s), 1339 (w), 1304 (w), 1279 (m), 1240 (s), 1207 (m), 1186 (w), 1159 (m), 1142 (w), 1117 (m), 1086 (m), 1015 (w), 997 (w), 935 (m), 883 (m), 839 (m), 824 (w), 791 (w), 761 (s), 741 (s), 681 (s), 654 (s), 611 (s). Anal. Calcd for $C_{27}H_{32}N_4Si$ (440.6): C, 73.59; H, 7.32; N, 12.71. Found: C, 73.74; H, 7.28; N, 12.54.

*2-(1-Methyl-1H-indol-3-yl)-3-[(trimethylsilyl)ethynyl]benzo[g]-quinoxaline (**5w**).* Orange solid (537 mg, 66%). R_f = 0.65 (dichloromethane). Mp: 251 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.39 (s, 9 H), 3.92 (s, 3 H), 7.35−7.45 (m, 3 H), 7.48−7.58 (m, 2 H), 8.02−8.12 (m, 2 H), 8.59 (s, 1 H), 8.64 (s, 2 H), 8.87−8.95 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.5 (CH_3), 33.4 (CH_3), 101.4 (C_{quat}), 104.7 (C_{quat}), 109.4 (CH), 112.3 (C_{quat}), 121.6 (CH), 123.1 (CH), 123.3 (CH), 126.16 (CH), 126.19 (CH), 127.0 (CH), 127.1 (CH), 127.6 (C_{quat}), 128.3 (CH), 128.8 (CH), 133.2 (C_{quat}), 133.3 (CH), 134.6 (C_{quat}), 136.2 (C_{quat}), 137.3 (C_{quat}), 137.6 (C_{quat}), 137.7 (C_{quat}), 149.8 (C_{quat}). MALDI-MS: *m*/*z* = 406 [MH^+]. IR (solid): $\tilde{\nu}$ 3046 (w), 2951 (w), 2891 (w), 1528 (s), 1474 (w), 1464 (w), 1447 (w), 1420 (w), 1369 (m), 1339 (w), 1296 (w), 1260 (w), 1248 (m), 1229 (m), 1215 (w), 1177 (w), 1159 (w), 1130 (w), 1088 (m), 1053 (w), 1016 (w), 937 (w), 870 (m), 843 (s), 793 (w), 770 (w), 748 (s), 737 (s), 702 (w), 691 (w), 642 (w), 627 (m), 605 (w). Anal. Calcd for $C_{26}H_{23}N_3Si$ (405.6): C, 77.00; H, 5.72; N, 10.36. Found: C, 76.78; H, 5.87; N, 10.32.

*2-(1-Methyl-1H-indol-3-yl)-3-(phenylethynyl)benzo[g]-quinoxaline (**5x**).* Orange solid (349 mg, 43%). R_f = 0.87 (dichloromethane). Mp: 249 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.92 (s, 3 H), 7.36−7.49 (m, 6 H), 7.50−7.59 (m, 2 H), 7.63−7.66 (m, 2 H), 8.08 (d, *J* = 9.6 Hz, 2 H) 8.53 (s, 1 H), 8.61 (s, 1 H), 8.67 (s, 1 H), 8.85−8.91 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.5 (CH_3), 90.1 (C_{quat}), 94.5 (C_{quat}), 109.5 (CH), 112.6 (C_{quat}), 121.6 (CH), 121.9 (C_{quat}), 123.1 (CH), 123.2 (CH), 126.2 (CH), 126.3 (CH), 126.9 (CH), 127.0 (CH), 127.6 (C_{quat}), 128.3 (CH), 128.68 (CH), 128.73 (CH), 129.7 (CH), 132.0 (CH), 133.0 (CH), 133.3 (C_{quat}), 134.6 (C_{quat}), 136.5 (C_{quat}), 137.4 (C_{quat}) 137.6 (C_{quat}), 138.3 (C_{quat}), 150.1 (C_{quat}). EI + MS (*m*/*z*): 410 (23), 409 (M^+, 88), 408 (100), 394 ($[M - CH_3]^+$, 11), 332 ($[M - Ph]^+$, 3), 282 ($C_{20}H_{14}N_2^+$, 5), 281 (12), 204.4 (20), 203.5 (18), 197 (13), 156 (17), 155 (12), 126 (24). IR (solid): $\tilde{\nu}$ 2207 (w), 1520 (m), 1489 (w), 1441 (w), 1423 (w), 1371 (m), 1341 (w), 1306 (w), 1285 (w), 1148 (w), 1117 (m), 1084 (m), 1013 (w), 997 (w), 937 (w), 908 (w), 874 (m), 837 (w), 773 (m), 741 (s), 683 (s), 658 (w), 624 (m), 611 (w). Anal. Calcd for $C_{29}H_{19}N_3$ (409.5): C, 85.06; H, 4.68; N, 10.26. Found: C, 84.93; H, 4.49; N, 10.38.

General Procedure for the Three-Component Synthesis of 3-Ethynylquinoxalines 7. A 2.00 mmol portion of glyoxylic acid **7** in dry 1,4-dioxane (2.5 mL/mmol) was placed under argon or nitrogen atmosphere in a screw-cap Schlenk tube and degassed with argon or nitrogen (for experimental details, see Table 8). Then, oxalyl chloride (0.18 mL, 2.00 mmol, 1.0 equiv) was added dropwise to the reaction mixture. The mixture was stirred at room temperature (water bath) for 5 min and then at 50 °C for 4 h. Thereafter, the mixture was cooled to room temperature (water bath, 5 min). Then, CuI (20 mg, 0.1 mmol, 5 mol %), trimethylsilylacetylene (**2b**) (0.28 mL, 2.00 mmol, 1 equiv), and dry triethylamine (0.84 mL, 6.00 mmol, 3.0 equiv) were successively added to the reaction mixture, and stirring at room temperature was continued for 15 h. Then, 2 mL of methanol, 216 mg of 1,2-diaminobenzene (**4a**) (2.00 mmol, 1.0 equiv), and 2 mL of acetic acid were added successively, and the mixture was stirred at

Table 8. Experimental Details for the Three-Component Synthesis of 2-Substituted 3-Ethynylquinoxalines 7

entry[a]	glyoxylic acid **6**	3-ethynylquinoxaline **7** (yield, %)[b]
1	300 mg (2.00 mmol) of **6a**	515 mg (85%) of **7a**
2	384 mg (2.00 mmol) of **6b**	178 mg (26%) of **7b**
3	280 mg (2.00 mmol) of **6c**	178 mg (30%) of **7c**
4	312 mg (2.00 mmol) of **6d**	427 mg (69%) of **7d**

[a]All compounds were prepared on a 2.00 mmol scale. [b]Yields after chromatography on silica gel.

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50 °C for 3 h. Then, 10 mL of water was added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3 × 5 mL/10 mL, monitored by TLC). The combined organic layers were dried with anhydrous sodium sulfate. The reaction mixture was absorbed onto Celite in vacuo and purified chromatographically on silica gel with solvent mixtures of petroleum ether (boiling range 40−60 °C) and ethyl acetate or dichloromethane to give the 3-ethynylquinoxalines **7**.

*2-Phenyl-3-[(trimethylsilyl)ethynyl]quinoxaline (**7a**).* Colorless oil (515 mg, 85%). R_f = 0.28 (petroleum ether/ethyl acetate 20:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.22 (s, 9 H), 7.47−7.54 (m, 3 H), 7.72−7.79 (m, 2 H), 8.03−8.15 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.71 (CH_3), 102.1 (C_{quat}), 102.7 (C_{quat}), 127.9 (CH), 128.8 (CH), 129.2 (CH), 129.6 (CH), 129.7 (CH), 130.2 (CH), 130.8 (CH), 137.3 (C_{quat}), 137.5 (C_{quat}), 140.75 (C_{quat}), 140.76 (C_{quat}), 154.9 (C_{quat}). EI + MS (*m*/*z*): 303 (12), 302 (M^+, 47), 301 (61), 288 (25), 287 ($[M - CH_3]^+$, 100), 272 ($[M - (CH_3)_2]^+$, 6), 271 (11), 257 (22). IR (solid): $\tilde{\nu}$ 3061 (w), 2959 (w), 2897 (w), 2160 (w), 1609 (w), 1557 (m), 1530 (w), 1477 (w), 1393 (w), 1335 (m), 1308 (m), 1285 (w), 1250 (m), 1217 (w), 1188 (w), 1130 (m), 1123 (w), 1076 (w), 1036 (w), 997 (w), 912 (w), 839 (2), 820 (m), 758 (s), 729 (m), 692 (s), 635 (m), 606 (m). HR-MS: mass calcd for $C_{19}H_{18}N_2Si^-H^+$ 303.13175, found 303.13120.

*2-Mesityl-3-[(trimethylsilyl)ethynyl]quinoxaline (**7b**).* Colorless solid (178 mg, 26%). R_f = 0.32 (petroleum ether/ethyl acetate 20:1). Mp: 101 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.03 (s, 9 H), 2.01 (s, 6 H), 2.34 (s, 3H), 6.95 (s, 2 H), 7.74−7.81 (m, 2 H), 8.08−8.16 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.9 (CH_3), 19.7 (CH_3), 21.1 (CH_3), 101.3 (C_{quat}), 102.0 (C_{quat}), 128.1 (CH), 129.0 (CH), 129.3 (CH), 130.2 (CH), 130.5 (CH), 134.3 (C_{quat}), 135.8 (C_{quat}), 138.3 (C_{quat}) 139.8 (C_{quat}) 140.78 (C_{quat}), 140.83 (C_{quat}), 158.1 (C_{quat}). EI + MS (*m*/*z*): 345 (30), 344 (M^+, 100), 343 (38), 330 (13), 329 ($[M - CH_3]^+$, 47), 157 (14), 147 (58), 119 ($C_9H_{11}^+$, 13). IR (solid): $\tilde{\nu}$ 2959 (w), 2918 (w), 2853 (w), 2162 (w), 1652 (w), 1613 (m), 1589 (w), 1556 (w), 1539 (m), 1456 (w), 1433 (w), 1379 (w), 1329 (m), 1314 (w), 1192 (m), 1157 (w), 1130 (m), 1119 (m), 1065 (w), 1036 (w), 1013 (w), 1001 (w), 986 (w), 949 (w), 912 (w), 839 (s), 812 (m), 766 (s), 739 (m), 700 (w), 669 (m), 650 (m), 631 (m), 608 (m). Anal. Calcd for $C_{22}H_{24}N_2Si$ (344.5): C, 76.70; H, 7.02; N, 8.13. Found: C, 76.69; H, 6.80; N, 7.83.

*2-(Furan-2-yl)-3-[(trimethylsilyl)ethynyl]quinoxaline (**7c**).* Beige solid (178 mg, 30%). R_f = 0.26 (petroleum ether/ethyl acetate 10:1). Mp: 78 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.37 (s, 9 H), 6.62 (dd, *J* = 3.6 Hz, *J* = 1.8 Hz, 1 H), 7.66−7.79 (m, 3 H), 7.88 (dd, *J* = 3.6 Hz, *J* = 0.7 Hz, 1 H), 8.02−8.08 (m, 1 H), 8.10−8.16 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.6 (CH_3), 102.6 (C_{quat}), 102.7 (C_{quat}), 111.9 (CH), 115.6 (CH), 128.9 (CH), 129.1 (CH), 130.1 (CH), 131.2 (CH), 134.8 (C_{quat}), 140.2 (C_{quat}), 140.5 (C_{quat}), 143.9 (C_{quat}), 145.4 (CH), 149.8 (C_{quat}). EI + MS (*m*/*z*): 293 (19), 292 (M^+, 80), 278 (24), 277 ($[M - (CH_3)]^+$, 100), 262 ($(M - (CH_3)_2)^+$, 4), 247 ($(M - (CH_3)_3)^+$, 19). IR (solid): $\tilde{\nu}$ 3142 (w), 3123 (w), 2955 (w), 2924 (w), 2899 (w), 2853 (w), 2164 (w), 1611 (w), 1574 (w), 1522 (w), 1472 (w), 1451 (w), 1404 (w), 1335 (m), 1314 (w), 1252 (w), 1225 (w), 1196 (m), 1163 (w), 1132 (m), 1123 (w), 1083 (w), 1040 (w), 1007 (w), 962 (w), 923 (w), 885 (w), 841 (s), 800 (w), 760 (s), 739 (m), 700 (w), 664 (w), 633 (m) 621 (m). Anal. Calcd for $C_{17}H_{16}N_2OSi$ (292.4): C, 69.83; H, 5.52; N, 9.58. Found: C, 69.58; H, 5.48; N, 9.36.

*2-(Thiophene-2-yl)-3-[(trimethylsilyl)ethynyl]quinoxaline (**7d**).* Light yellow solid (427 mg, 69%). R_f = 0.30 (petroleum ether/ethyl acetate 25:1). Mp: 81 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.37 (s, 9 H), 7.18 (dd, *J* = 5.1 Hz, *J* = 3.9 Hz, 1 H), 7.56 (dd, *J* = 5.1 Hz, *J* = 1.0 Hz, 1 H), 7.65−7.76 (m, 2 H), 8.00−8.07 (m, 2 H), 8.55 (dd, *J* = 3.8 Hz, *J* = 1.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.6 (CH_3), 102.6 (C_{quat}), 103.1 (C_{quat}), 127.8 (CH), 128.7 (CH), 128.8 (CH), 129.9 (CH), 130.2 (CH), 130.4 (CH), 131.0 (CH), 134.8 (C_{quat}), 140.3 (C_{quat}), 140.6 (C_{quat}) 141.8 (C_{quat}) 147.6 (C_{quat}). EI + MS (*m*/*z*): 309 (15), 308 (M^+, 54), 307 (26), 293 ($[M - (CH_3)]^+$, 100), 263 (20). IR (solid): $\tilde{\nu}$ 2957 (w), 1526 (w), 1474 (w), 1427 (w), 1335 (m), 1248 (m), 1230 (w), 1217 (w), 1180 (w), 1134 (w), 1082 (w), 1058 (w), 947 (w), 912 (w), 843 (s), 810 (m), 759 (s), 739 (m), 716 (s), 708 (s), 662 (w), 631 (m), 617 (m). Anal. Calcd for $C_{17}H_{16}N_2SSi$ (308.5): C, 66.19; H, 5.23; N, 9.08. Found: C, 65.97; H, 5.43; N, 8.90.

■ ASSOCIATED CONTENT

Supporting Information

Experimental data on the optimization study for the synthesis of ynediones **3**. Selected ^{1}H and ^{13}C NMR spectra of compounds **5a−x** and **7a−d**, selected absorption and emission spectra of compounds **5a**, **5d**, **5h**, **5m**, and **5r**. Crystallographic data of the X-ray structure analyses of compounds **5d**, **5n**, **5q**, and **5x**. Computational data and TD-DFT computed UV/vis spectra of the quinoxalines **5a**, **5d**, **5h**, **5m**, and **5r**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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