

Microwave-assisted synthesis of heterocycles from aryldiazoacetates

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Abstract: Herein we describe a rapid microwave-assisted, metal-free synthesis of substituted quinoxalinones and quinoxalines using the carbene-mediated reaction between aryldiazo esters and 1,2-diamines. The reaction can encompass a range of substituents and structural variations to afford quinoxalin-2-ones in 14-80% yield and corresponding quinoxalines in good to excellent yields upon oxidation (67-96%). The approach can be employed to generate symmetrical and unsymmetrical 2,3-diarylquinoxalines, bis-quinoxalines as well as novel quinoxaline-substituted diazo esters and should be a valuable addition to the heterocycle synthesis toolbox.

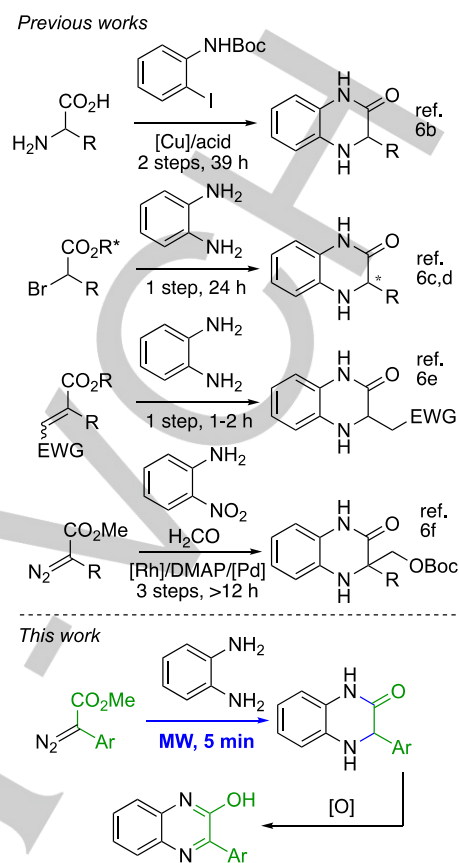
Introduction

Diazo compounds have found numerous applications in synthesis.¹ The aryldiazoacetates are particularly useful due to their stability, good reactivity and the versatility of substituents that can be employed. Despite the general notion that diazo compounds are explosive, Davies and co-workers have published studies of the thermal decomposition of aryldiazoacetates.^{2a-c} These are well-behaved at high temperatures and decompose with first-order kinetics. Moreover, they can produce free carbenes with typical carbene reactivity such as cyclopropanation, X-H insertions and C-H functionalization in synthetically useful yields.²⁻⁴

We have recently sought novel synthetic approaches to quinoxalines and dihydroquinoxalinones for synthetic and biological applications.^{5,6} Several methods exist for generating dihydroquinoxalinones starting from α -amino acids,^{6b} α -haloesters,^{6c-d} α,β -unsaturated esters^{6e} and α -diazoesters^{6f-1} (Scheme 1). These are typically characterized by long reaction times and/or use of metal catalysts such as copper or rhodium. Moreover, the metal-catalyzed processes involve more than one step to obtain the desired quinoxalinones. The shortest reaction time was reported by Kamila and Biehl using microwave irradiation with α -bromoesters and phenylenediamines in the presence of DBU (6 minutes), however, the transformation had extremely limited scope as presented.^{6d} There are other notable metal-free approaches to these heterocycles employing hypervalent iodine reagents and boron-catalysis, however, prolonged reaction times are typically required.^{6j,6k} Overall, the development of more rapid, simple, clean and practical reaction conditions is still an important synthetic goal for generating these heterocycles.

The use of microwave-assisted synthetic reactions has grown immensely over the past three decades.⁷ Employing microwave irradiation can in many instances greatly improve efficiency in terms of chemical yield, reaction times and product purity. Moreover, some reactions can be rendered more environmentally benign than conventionally heated systems and the synthesis of heterocycles for medicinal applications is one area that has benefited significantly from microwave-assisted chemistry.^{7b,c} Microwave-assisted reactions of diazocarbonyl compounds are not widely employed, however, a notable exception is the venerable Wolff-rearrangement of diazoketones.^{7d} It is clear from the literature that microwave-assisted heating can offer a number of benefits and should become a routine part of screening reaction conditions.

The metal-free N-H insertion chemistry of aryldiazoacetates became the impetus for our current study.² We envisaged that we could achieve a rapid assembly of the desired heterocyclic structures by combining aryldiazoacetates with 1,2-



Scheme 1. Previous work and current approach to quinoxalinones.

diamines in one pot without the use of metal catalysts, slow addition and with improved reaction times by conducting reactions in superheated solvent employing microwave irradiation (Scheme 1). This paper describes our efforts towards this end.

Results and Discussion

The preliminary studies on aryldiazoacetates were conducted using conditions previously reported for N-H insertion.² Although the desired product was observed using conventional heating, thus demonstrating the feasibility of the reaction, these reactions were often messy and low-yielding. The reaction between methyl phenyldiazoacetate (MPD) and two equivalents of phenylenediamine in refluxing trifluorotoluene over 6 hours, produced the desired 3-phenylquinoxaline-2-one **1** in 54% yield (by NMR, unoptimized) (Scheme 2A). The preliminary studies did not give satisfactory results in terms of reaction time, convenience and product purity. We generally aim to develop rapid and practical methods for assembling heterocycles in useful chemical yields. Thus, we hypothesized that microwave heating could be employed to increase the reaction rate since temperatures above the solvent boiling point are easily accessible and one avoids the use of sealed tubes required with conventional heating.⁷ Moreover, we wanted to mix all the reactants from the start (avoid slow addition of diazo compound)

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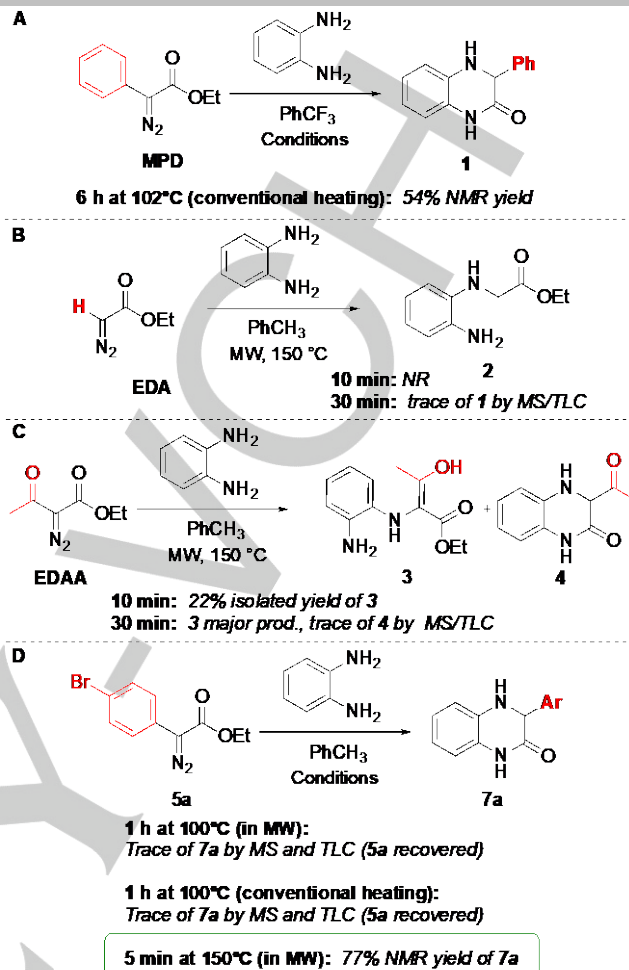
and employ a more mainstream solvent than trifluorotoluene, which is often specifically used to deter carbene reactions with the solvent. Concerned about the potential explosion hazard of diazo compounds,^{2c} the microwave reaction temperature was increased slowly starting from ca 100 °C, which was the previously reported condition for NH-insertions.² The diazo compounds were well-behaved at least up to 160 °C, where our study was stopped since we obtained satisfactorily short reaction times for the aryldiazo compounds.

The classical diazo compounds ethyl diazoacetate (EDA) and ethyl 2-diazoacetoacetate (EDAA) were subjected to microwave irradiation in the presence of phenylenediamine in toluene at 150 °C in order to compare their behaviour to that of aryldiazoacetates (Scheme 2B and 2C). EDA appeared to react very slowly and no reaction was observed after 10 minutes. After 30 min reaction time, a trace of NH-insertion product **2** was observed by TLC/MS. EDAA reacted somewhat faster, and the enol form of NH-insertion product **3** was isolated in 22% yield after 10 min reaction time. Prolonging the reaction time to 30 min showed **3** as the major product and trace of cyclized product **4** could be detected by TLC/MS. The observed slow decomposition rates are in line with previous observations.² Clearly, product formation appears feasible in the case of these diazo compounds, but only after prolonged reaction times. The reaction between methyl *p*-bromophenylacetate **5a** and phenylenediamine under the same conditions displayed 77% NMR-yield of cyclized product **7a** after only 5 minutes (Scheme 2D). This class of diazo compounds is superior in terms of reaction time under the given conditions.

In order to gauge any difference between conventional and microwave heating in this reaction, diazo compound **5a** was studied at 100 °C using both microwave irradiation and conventional heating (Scheme 2D).⁷ Only traces of cyclized product **7a** were observed in both cases after one hour of reaction time by TLC/MS. Even after 6 hrs very little conversion could be observed in both cases. There was no observable difference between the two methods. However, the microwave reactions were much more convenient to conduct and were therefore strongly preferred.

The pressure build-up in the microwave reactor did not exceed 3 bars at any point during the reactions at 150 °C, which is well below the pressure tolerance level of the reactor (ca 30 bars). Furthermore, we were pleased to observe that the reactions went smoothly at a relatively high concentration (2 mL solvent/mmol diazo compound), in contrast to conventional carbene reactions conducted often under dilute solutions.^{1,2} The reaction time required for complete consumption of the diazo compound was about 5 minutes at 150 °C and these were chosen as the standard reaction parameters. To our knowledge, this is the first example of a microwave-assisted reaction of such diazo compounds.

Further survey of reaction conditions was carried out with **5a** and phenylenediamine to produce **7a** as a test reaction. Prolonging the reaction time or further increase in temperature beyond the stated conditions (150 °C, 5 min) did not offer any improvements in yield. Table 1 shows parts of the reaction condition screening concerned with solvent, equivalency of diamine and concentration. Although most initial efforts were conducted in trifluorotoluene, it turned out that the yield was comparable in toluene (77% vs 81% in PhCF₃), a more common, cheap and conveniently accessible solvent. Surveying both acetonitrile and ethylene glycol dimethyl ether (EGDE), as these are both typically inert towards carbenes and good microwave solvents, gave substantially diminished yields. More polar solvents typically react with carbenes and were not tested. Therefore, toluene was chosen as a solvent for further studies. The equivalency of phenylenediamine was studied next, starting



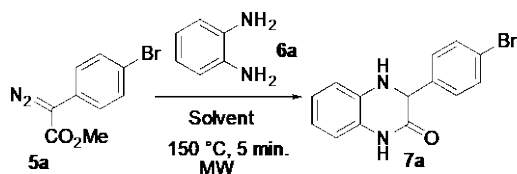
Scheme 2. Comparison with other types of diazo compounds and conventional heating.

with near equimolar amounts (1.2 equiv. of diamine) and gradually increasing. The yields increased up to 3 equivalents, which appeared to be the maximum yielding with 88% NMR-yield. As a control, isolation of the material afforded 77% yield of **7a**. Further increasing the concentration of the diazo compound did not improve the yield, so the concentration was kept at 0.5 M. In summary, our survey of reaction conditions dictates that the reaction could be generally conducted in toluene with microwave heating at 150 °C for 5 mins using 3 equivalents of diamine at a concentration of 0.5 M (with respect to diazo compound).

With good conditions in hand, we next studied the scope of the reaction. First, we employed various aryldiazoacetates **5a-f** in the reaction with phenylenediamine using the conditions identified in Table 1. *p*-Bromo and *p*-methoxy substituted diazo compounds yielded 77% and 64% yields of **7a** and **7b**, respectively (Figure 1). *p*-Trifluoromethyl substitution gave only medium 55% yield under the given conditions, but an IR-analysis of the reaction mixture revealed that the diazo compound was not fully converted. Extending the reaction time to 25 mins gave an increased yield (68% of compound **7c**), in line with the other results. 2-Naphthyl substituted diazo compound **5d** gave 68% yield of **7d**. Also heterocyclic diazo compounds were compatible, and 3-pyridyl substituted diazo compound **5e** yielded the desired

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product **7e** in 66% yield. 3,4-dichloro substituted aryldiazo compound **5f** performed similarly with 67% yield of **7f**.



Entry ^a	Solvent	Diamine (equiv.)	[5a] (M)	Yield 7a (%)
1	PhCF ₃	1.7	0.5	81
2	PhMe	1.7	0.5	77
3	MeCN	1.7	0.5	28
4	EGDE	1.7	0.5	-
5	PhMe	1.2	0.5	59
6	PhMe	2	0.5	71
7	PhMe	2	0.75	69
8	PhMe	3	0.5	88(77 ^b)
9	PhMe	4	0.5	81

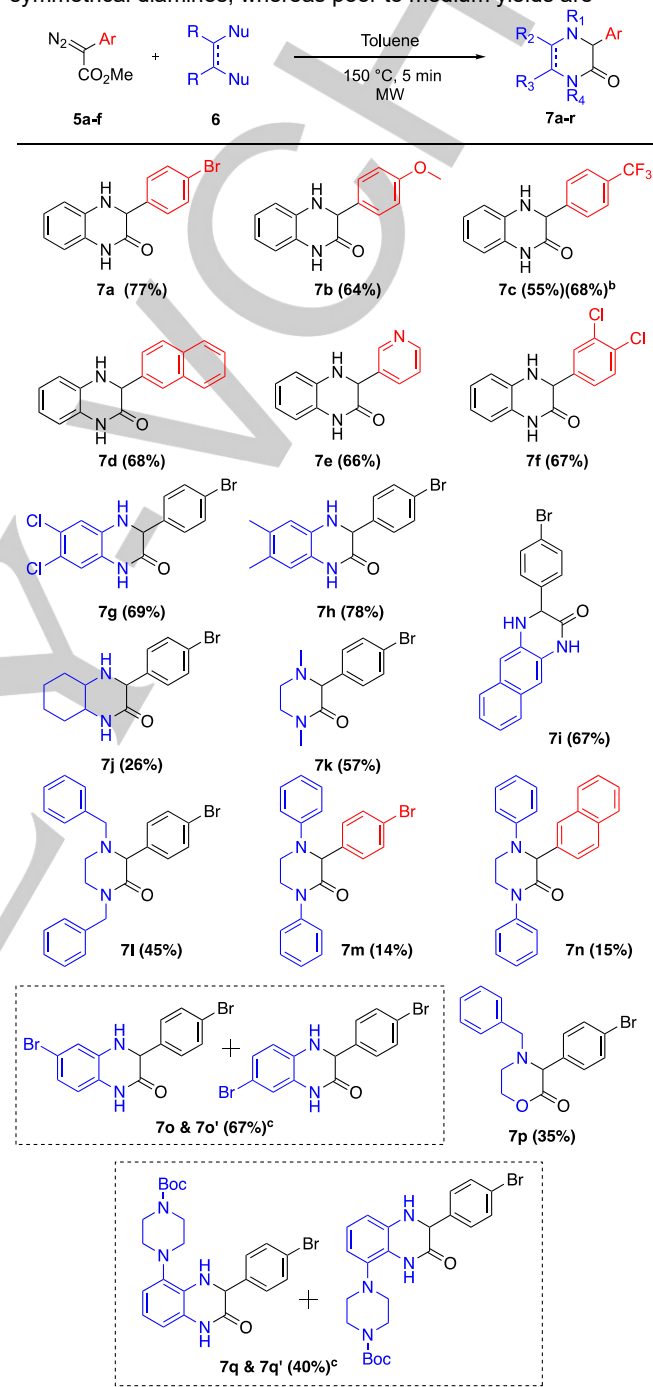
(a) Reaction conditions: In a microwave vial, diazo ester **5a** (1 mmol), diamine **6a** were mixed in toluene (2 mL). The vial was sealed and flushed with nitrogen followed by sonication for 30 s and then heated under microwave irradiation for 5 minutes at 150 °C.
(b) Isolated yield

Table 1. Screening of reaction variables

The reaction with phenylenediamine appears to work well with a range of different aryldiazoacetates and typically yields 60-70% of the expected product. It should be noted that the uncyclized N-H insertion intermediates were only observed in trace amounts in a few cases and that a lack of reactivity at the cyclization stage can not generally account for reduced yields.

Next, various diamines were employed as reaction partners. Both 4,5-dichloro- and 4,5-dimethyl-1,2-diaminobenzene gave high yields of the expected products **7g** (69%) and **7h** (78%) in the reaction with **5a**. 2,3-diaminonaphthalene also afforded similar yield of **7i** (67%). The aliphatic diamines **6j** and **6k** afforded only 26% and 57% yields of **7j** and **7k**, respectively. The latter prompted us to try other *N*-substituted systems, however, these appeared to be very sensitive to the steric environment on nitrogen. The di-*N*-benzyl system **6l** afforded 45% yield of **7l**. Attempts to improve yields by increasing reaction time and temperature were not fruitful, even after substantial optimization efforts. The problem may be related to the increased steric hindrance at nitrogen, since the *N,N*-diarylsystem **6m** gave only 14% yield of **7m**. Furthermore, this is consistent with the reaction between this diamine and the 2-naphthyl diazo compound (**7n** formed in 15% yield). The steric hindrance of the secondary amines likely deters both N-H insertion and cyclization steps. We further challenged the reaction with unsymmetrical diamines/dinucleophiles **6o-q**. With unsymmetrical phenylenediamines, near equimolar mixtures of the two possible regioisomers were formed. 4-bromo-1,2-diamine gave a good combined yield of 67% of the two isomers. Amino alcohol **6p** can also afford the product of carbene N-H insertion – cyclization, but gives a poor 35% yield of product **7p**. Here the nitrogen has selectively reacted at the carbene carbon first, which is

consistent with observations reported by Davies et al.² The complex piperazinyl substituted 1,2-diaminoarene **6q** afforded 40% overall yield of the two possible isomers **7q** and **7q'**. Overall, we can conclude that medium to high yields are common for symmetrical diamines, whereas poor to medium yields are

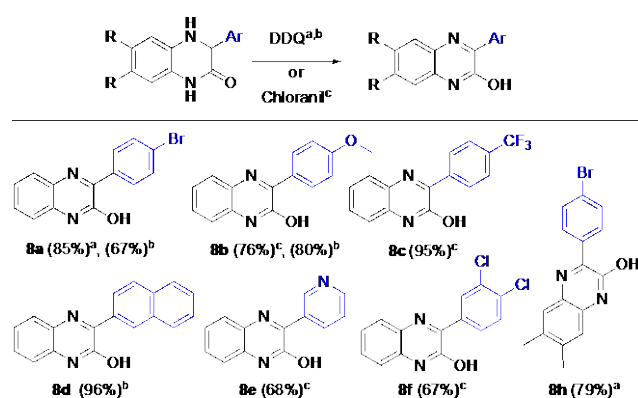


(a) Reaction conditions: In a microwave vial, diazo ester **5a**, diamine **6a** were mixed in toluene (2 mL). The vial was sealed and flushed with nitrogen followed by sonication for 30 s and heating under microwave irradiation for 5 minutes at 150 °C.
(b) The trifluoromethyl-substituted diazo compound required longer reaction times to fully convert into carbene, thus 68% yield was obtained with 25 min reaction time.
(c) Mixture of isomers were formed under the reaction conditions with no selectivity.

Figure 1. Scope of microwave-assisted heterocyclization.

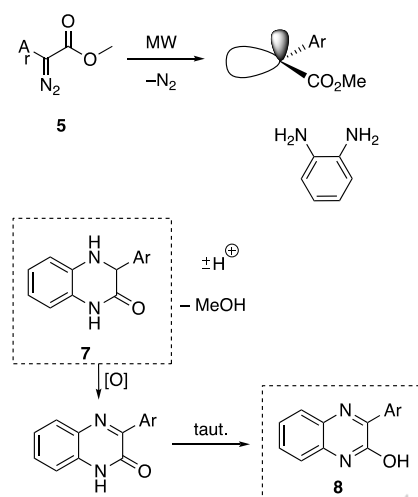
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observed with secondary amines. The reaction appears to tolerate both aromatic and aliphatic systems and different substituents on these. Unsymmetrical diamines do not display



Reaction conditions: (a) DDQ (1.1 equiv.) THF (20 mL), 1 h, rt. (b) DDQ (1.2 equiv.), DCM (20 mL), 2 h, rt. (c) Chloranil (1.1 equiv.) THF (20 mL), 1-24 h, rt.

Figure 2. Oxidation of dihydroquinoxalines to quinoxalines.



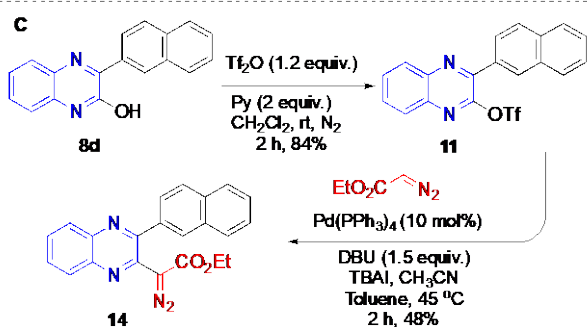
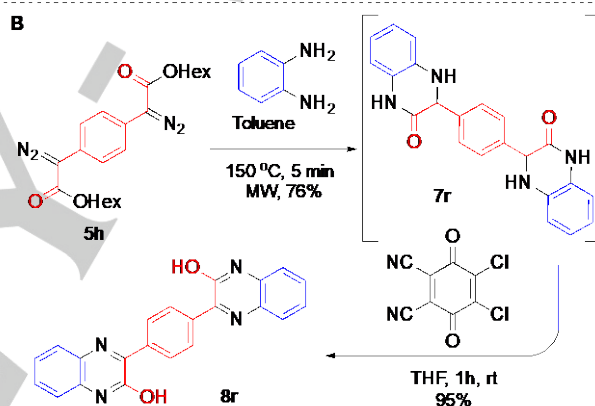
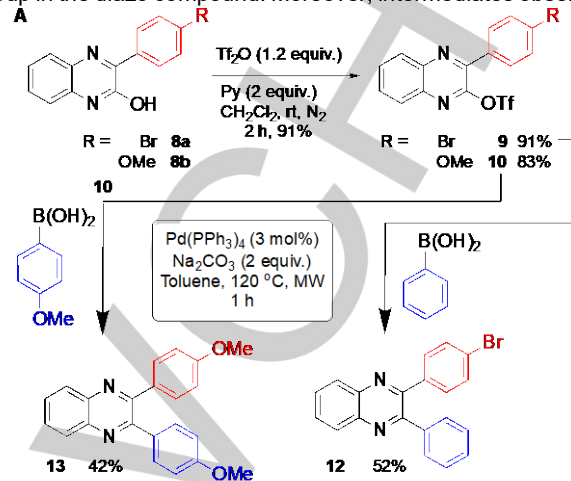
Scheme 3. Proposed mechanism for the heterocyclization.

any regioselectivity and afford equimolar amounts of isomeric products although medium to good overall yields are observed.

Oxidation of the quinoxalin-2-ones to the fully aromatic quinoxalines is possible and the sequence of heterocyclization-oxidation represents an attractive route to these heteroaromatics. Therefore, a selection of products of the microwave-assisted heterocyclization reaction were subjected to oxidations employing both DDQ and chloranil (Figure 2). All the systems proceeded smoothly to the corresponding heteroaromatic compounds **8a-h** in 67–96% isolated yields. Thus, this represents a convenient and rapid synthesis of a range of 3-arylquinoxalin-2-ols in good to excellent yields.

A mechanism of the process can be proposed based on the work of Davies and co-workers (Scheme 3).² The reaction involves thermal decomposition of the diazo compound to form the intermediate free carbene. The diamine will add to the singlet carbene LUMO to form an intermediate ylide, which undergoes rapid proton transfer and tautomerization to form an α -amino

ester. The alternative mechanism where the diamine can first form an amide, with subsequent cyclization onto the free carbene, is much less likely due to the stabilization of the ester group in the diazo compound. Moreover, intermediates observed



Scheme 4. Synthetic applications of the heterocyclization products.

in incompletely converted reactions were exclusively α -aminoesters, which supports the proposed mechanism. The ester undergoes cyclization with the second amino group with extrusion of methanol to generate the quinoxaline-2-one. The tertiary benzylic C-H bond will be prone to oxidation, with subsequent rapid tautomerization to generate the quinoxaline-system.

The aromatic hydroxyl group makes the synthesized heterocycles particularly interesting since this is a functional group capable of a variety of useful transformations. In order to

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demonstrate the synthetic utility of our generated heterocycles, the synthesis of 2,3-diarylquinoxalines can be envisioned to occur by triflation of the aromatic hydroxyl group followed by Suzuki-Miyaura couplings.⁹ Indeed, compounds **8a** (*p*-Br) and **8b** (*p*-OMe) underwent smooth triflation under standard conditions in 91% and 83% yields, respectively (Scheme 4A). The corresponding triflates were then subjected to Pd-catalyzed couplings with phenyl boronic acid and *p*-methoxyphenyl boronic acid to generate 2,3-diarylquinoxalines **12** and **13** in 52% and 42% (unoptimized) yields, respectively. This approach for the generation of unsymmetrical 2,3-diarylquinoxalines is likely of general interest. In order to demonstrate that the developed heterocyclization can be applied to generate more complex molecules, the bis-diazo ester **5h** was designed to study whether a double transformation to generate bis-heterocycles was feasible (Scheme 4B). When subjected to the standard reaction conditions, double heterocyclization occurred smoothly in ca 76% yield to generate **7r**. This molecule was prone to air oxidation and it was difficult to isolate pure material. However, it could readily be converted to the bis-quinoxaline **8r**, which was amenable to full characterization in pure form, in near quantitative 95% yield in when using DDQ. This result supports the generality of this transformation and likely even more complex systems can be accessed using our approach. A final application of the quinoxalin-2-ol series was demonstrated through triflation of 3-(2-naphthyl)-quinoxaline-2-ol **8d** followed by a palladium-catalyzed coupling of the aryl triflate with ethyl diazoacetate, as previously described by Wang and co-workers (Scheme 4C).⁹ The novel and highly unusual aryl diazo ester **14** was formed in 48% unoptimized yield in the palladium-catalyzed step. Thus, we have outlined and demonstrated a novel synthetic approach to unusual aryldiazo compounds which will likely be of interest to the broader chemical synthesis community.

In summary, we have developed a microwave-assisted, practical and rapid metal-free synthesis of substituted quinoxalinones and quinoxalines using the carbene-mediated reaction between aryldiazo esters and 1,2-diamines. The reaction can encompass a range of substituents and structural variations, although unsymmetrical diamines do not display any regioselectivity. The approach can readily be extended to generate symmetrical and unsymmetrical 2,3-diarylquinoxalines, bis-quinoxalines as well as novel quinoxaline-substituted diazo esters and should be a valuable addition to the synthesis toolbox for such heterocyclic systems.

Experimental Section

General information. Reagents used during this study were purchased from Sigma Aldrich Co, and were used as received. THF was dried on activated molecular sieve (4Å) at minimum 24 hours. Manual column chromatography was performed using Davisil (35-70 μm) silica gel. Automatic flash column chromatography was performed on Interchim PF-XS420+, or Biotage SP1, using either KP-Sil 10 g or 50 g SNAP Biotage prepacked columns (50μm silica). TLC was run on 60 F254 silica gel plates and visualized by UV and stains. Microwave reactions were performed using Anton Parr Monowave 300. ¹H and ¹³C-NMR spectra were recorded at ambient temperature at a frequency of 400 and 101 MHz, respectively. The chemical shifts are reported in ppm relative to residual CHCl₃ for proton (δ = 7.26 ppm) and CDCl₃ for carbon (δ = 77.0 ppm) and with DMSO-d₆ for proton (δ = 2.50 ppm) and for carbon (δ = 39.0 ppm) and CD₃OD for proton (δ = 3.31 ppm) and for carbon (δ = 41.0 ppm)

and with CD₃CN for proton (δ = 1.94 ppm) and for carbon (δ = 118.3 ppm) and with acetone-d₆ for proton (δ = 2.05 ppm) and for carbon (δ = 29.8, 206.3 ppm) with tetramethylsilane as an external reference. The splitting patterns were recorded as a singlet (s); doublet (d), triplet (t), quartet (q), doublet of doublet (dd), doublet of triplet (dt), doublet of doublet of doublets (ddd), multiplet (m). All NMR spectra were processed using MestreNova version 10.0.2 or 11.0. HRMS spectra were recorded on Thermo scientific LTQ Orbitrap XL using electrospray ionization (ESI). GC-MS spectra were recorded on Thermo Scientific ITQ 1100 detector. IR spectra were recorded on Agilent Cary 630 FTIR. Starting materials (**5**) were produced in accordance with literature procedures.^{1,10}

(A) General procedure for the preparation of quinoxaline-2-one derivatives (7a, 7h-r). Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) (1 mmol), dinucleophile (3 eq.), and toluene (2 ml) are mixed in a 10 ml microwave reactor. After addition, the mixture is sonicated for 2 minutes followed by degassing with N₂ gas. The microwave is set to heat as fast as possible to 150 °C, hold for five minutes, and then cool to 55 °C with 900-rpm stirring rate. Products were isolated and purified by filtration, acidic work-up, and/or flash chromatography methods.

(B) General procedure for the preparation of quinoxaline-2-one derivatives (7b-7f, 7o). Aryldiazoacetates (1 mmol), o-phenylenediamine (**6a**) (3 eq.), and toluene (2 ml) are mixed in a 10 ml microwave reactor. After addition, the mixture is sonicated for 2 minutes followed by degassing with N₂ gas. The microwave is set to heat as fast as possible to 150 °C, hold for five minutes, and then cool to 55 °C, with 900-rpm stirring rate. The reaction solvent was evaporated under reduced pressure, and the crude material was dissolved in ethyl acetate and washed with water, hydrochloric acid solution (pH 1-2), and brine. The organic layer was dried with Na₂SO₄ and the solvent evaporated under reduced pressure. Products were purified by flash chromatography on silica gel using ethyl acetate in heptane eluent mixtures.

Ethyl-(Z)-2-((2-aminophenyl)amino)-3-hydroxybut-2-enoate (**3**)

Ethyl 2-diazo-3-oxobutanoate (**EDAA**) and o-phenylenediamine (**6a**) were used to generate **3** in accordance with general procedure **A**. The crude mixture was added into ethyl acetate and washed with water and brine. The organic layer was dried over Na₂SO₄, and the solvent was evaporated under reduced pressure. The solid residue was purified by dry loaded flash chromatography on silica gel (10-20% ethyl acetate in pentane). Yellow solid **3** was isolated in 22 % (51 mg) yield. *R*_f = 0.42 (40% EtOAc/Pentane). ¹H NMR (400 MHz, CDCl₃) δ 8.20 – 8.13 (m, 1H), 8.07 – 8.00 (m, 1H), 7.78 (dddd, *J* = 26.5, 8.3, 6.9, 1.5 Hz, 2H), 4.55 (q, *J* = 7.1 Hz, 2H), 2.94 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.7, 152.8, 144.5, 142.5, 139.9, 131.8, 129.8, 129.8, 128.5, 62.5, 23.7, 14.3. **HRMS** (ESI) *m/z*: [M+Na]⁺ Calculated for: [C₁₂H₁₆N₂NaO₃]⁺ 259.1053; found 259.1058.

3-(4-bromophenyl)-3,4-dihydroquinoxalin-2(1H)-one (7a). Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and o-phenylenediamine (**6a**) were used to generate **7a** in accordance with general procedure **A**. The crude mixture was added ethyl acetate and washed with water and brine. The organic layer was dried over Na₂SO₄, and the solvent was evaporated under reduced pressure. The solid residue was purified by dry loaded flash chromatography on silica gel (10% to 40% ethyl acetate in heptane). Yellow crystalline **7a** was isolated in 77 % (243 mg) yield. Alternative procedure: Following the microwave reaction the crude was heated quickly by heat gun and filtrated while still warm. The precipitate was washed with toluene. Yellow crystalline product **7a** was isolated in 75 % (228 mg) yield. *R*_f = 0.35 (40% EtOAc/Heptane). ¹H NMR (400 MHz, DMSO-d₆) δ 10.45 (s, 1H), 7.53 (dd, *J* = 8.4, 2.5 Hz, 2H), 7.30 (dd, *J* = 8.4,

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2.4 Hz, 2H), 6.84 – 6.70 (m, 3H), 6.67 (d, $J = 1.4$ Hz, 1H), 6.60 (ddd, $J = 8.0, 6.5, 2.2$ Hz, 1H), 4.94 (d, $J = 1.4$ Hz, 1H). $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6) δ 165.5, 139.5, 133.6, 131.2, 129.2, 125.3, 123.1, 120.8, 117.9, 114.9, 113.4, 58.7. **HRMS** (ESI) m/z : [M+Na] Calculated for: [C₁₄H₁₁BrN₂O₂Na] 324.9952; found 324.9953. **IR**: ν/cm^{-1} 3417, 3193, 3056, 2966, 2925, 2888, 1678, 1603, 1506, 1383, 1313, 1227, 1015.

3-(4-methoxyphenyl)-3,4-dihydroquinoxalin-2(1H)-one (7b). Methyl 2-diazo-2-(4-methoxyphenyl)acetate (**5b**) and o-phenylenediamine (**6b**) were used to generate **7b** in accordance with general procedure **B**. Product was purified by flash chromatography on silica gel (10 % to 60 % Ethyl acetate in Heptane) to give 64 % (161 mg) product. TLC: 40 % Ethyl acetate/Heptane. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ 10.36 (s, 1H), 7.27 – 7.18 (m, 2H), 6.92 – 6.83 (m, 2H), 6.82 – 6.69 (m, 3H), 6.62 – 6.53 (m, 2H), 4.84 (d, $J = 1.8$ Hz, 1H), 3.71 (s, 3H). $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6) δ 166.1, 158.7, 133.8, 132.3, 128.0, 125.4, 122.9, 117.6, 114.7, 113.7, 113.3, 58.7, 55.1. **HRMS** (ESI) m/z [M+Na] calculated for [C₁₅H₁₄N₂O₂Na] 277.0953; found 277.0948. **IR**: ν/cm^{-1} 3305, 3063, 3007, 2962, 2936, 2903, 2840, 1670, 1607, 1514, 1480, 1387, 1290, 1253, 1186, 1097, 1037.

3-(4-(trifluoromethyl)phenyl)-3,4-dihydroquinoxalin-2(1H)-one (7c). Methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (**5c**) and o-phenylenediamine (**6c**) were used to generate **7c** in accordance with general procedure **B**. Product was isolated and purified by flash chromatography on silica gel (20 % to 50 % Ethyl acetate in Heptane), to yield 55 % (161 mg) product. TLC: 40 % Ethyl acetate/Heptane. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ 10.51 (s, 1H), 7.72 (d, $J = 8.1$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 6.84 – 6.78 (m, 2H), 6.75 (dd, $J = 5.8, 2.1$ Hz, 2H), 6.62 (ddd, $J = 8.2, 6.2, 2.5$ Hz, 1H), 5.08 (d, $J = 1.9$ Hz, 1H). $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6) δ 165.3, 144.7, 133.6, 127.9, 125.3, 125.2, 123.1, 118.0, 114.9, 113.4, 59.0. **HRMS** (ESI) m/z [M+Na] Calculated for [C₁₅H₁₁CF₃N₂O₂Na] 315.0721; found 315.0714. **IR**: ν/cm^{-1} 3309, 3201, 3064, 2962, 2925, 2787, 1670, 1607, 1506, 1380, 1324, 1175, 1130, 1071, 1022.

3-(naphthalen-2-yl)-3,4-dihydroquinoxalin-2(1H)-one (7d). Methyl 2-diazo-2-(naphthalen-2-yl)acetate (**5d**) and o-phenylenediamine (**6d**) were used to generate **7d** in accordance with general procedure **B**. Product was isolated and purified by flash chromatography on silica gel (20 % to 100 % Ethyl acetate in Heptane) to give 68 % (186 mg) yield. TLC: 40 % Ethyl acetate/Heptane. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ 10.47 (s, 1H), 7.91 – 7.81 (m, 4H), 7.54 – 7.46 (m, 3H), 6.83 – 6.73 (m, 4H), 6.61 (dq, $J = 8.3, 4.1$ Hz, 1H), 5.11 (d, $J = 1.6$ Hz, 1H). $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6) δ 165.9, 137.7, 133.9, 132.6, 132.5, 127.9, 127.8, 127.5, 126.3, 126.1, 125.7, 125.4, 125.3, 123.1, 117.7, 114.9, 113.4, 59.5. **HRMS** (ESI) m/z [M-H]⁻ calculated for [C₁₈H₁₃N₂O] 273.1033; found 273.1033.

3-(pyridin-3-yl)-3,4-dihydroquinoxalin-2(1H)-one (7e). Ethyl 2-diazo-2-(pyridine-3-yl) acetate (**5e**) and o-phenylenediamine (**6e**) were used to generate **7e** in accordance with general procedure **B**. Precipitated product was filtrated, and filtrate was concentrated by evaporation. Isolated product and product in filtrate were purified separately by flash chromatography on silica gel (50 % to 100 % Ethyl acetate in Heptane), to yield 66 % (149 mg) product. TLC: 70 % Ethyl Acetate/ Heptane. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ 10.53 (s, 1H), 8.57 – 8.46 (m, 2H), 7.71 (dt, $J = 8.0, 2.0$ Hz, 1H), 7.37 (dd, $J = 7.9, 4.7$ Hz, 1H), 6.85 – 6.74 (m, 3H), 6.64 (ddd, $J = 14.7, 8.2, 1.9$ Hz, 2H), 5.02 (d, $J = 1.8$ Hz, 1H). $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6) δ 165.6, 148.9, 148.6, 135.4, 134.8, 133.7, 125.5, 123.5, 123.1, 118.1, 115.0, 113.6, 57.4. **HRMS** (ESI) m/z [M-H]⁻ calculated for [C₁₃H₁₀ON₃] 224.0829; found 224.0821.

3-(3,4-dichlorophenyl)-3,4-dihydroquinoxalin-2(1H)-one (7f). Methyl 2-diazo-2-(3,4-dichlorophenyl)acetate (**5f**) and o-

phenylenediamine (**6f**) were used to generate **7f** in accordance with general procedure **B**. Product was purified by flash chromatography on silica gel (20 % to 50 % Ethyl acetate in Heptane) to yield 67 % (194 mg) of product. TLC: 40 % Ethyl acetate/Heptane. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ 10.52 (s, 1H), 7.66 – 7.56 (m, 2H), 7.32 (dd, $J = 8.4, 2.1$ Hz, 1H), 6.86 – 6.70 (m, 4H), 6.62 (ddd, $J = 8.1, 6.6, 2.1$ Hz, 1H), 5.01 (d, $J = 1.9$ Hz, 1H). $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6) δ 165.2, 141.0, 133.4, 130.9, 130.6, 130.3, 129.2, 127.4, 125.3, 123.2, 118.1, 115.0, 113.5, 58.2. **HRMS** (ESI) m/z [M-H]⁻ Calculated for [C₁₄H₉BCl₂N₂O] 291.0097; found 291.0078. **IR**: ν/cm^{-1} 3305, 3186, 3096, 3063, 2966, 2892, 2806, 1663, 1603, 1506, 1473, 1387, 1313, 1134, 1033.

3-(4-bromophenyl)-6,7-dichloro-3,4-dihydroquinoxalin-2(1H)-one (7g). Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and 4,5-Dichloro-1,2-phenylenediamine (**6g**) were used to generate **7g** in accordance with general procedure **A**. The product was isolated and purified by automatic flash chromatography (0 % to 50 % Ethyl acetate in Heptane). Impure product fractions were collected and purified in a second column, to yield a total of 69 % (259 mg) orange crystalline **7g** product. $R_f = 0.36$ (40 % EtOAc/Heptane). $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 10.70 (s, 1H), 7.56 (dd, $J = 8.4, 2.5$ Hz, 2H), 7.28 (dd, $J = 8.4, 2.4$ Hz, 2H), 7.09 (d, $J = 1.6$ Hz, 1H), 6.93 (s, 1H), 6.88 (s, 1H), 5.06 (d, $J = 1.6$ Hz, 1H). $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6) δ 165.0, 139.0, 133.9, 131.4, 129.1, 125.5, 124.2, 121.1, 118.3, 115.6, 113.7, 58.1. **HRMS** (ESI) m/z : [M+Na] Calculated for: [C₁₄H₉BrCl₂N₂O₂Na] 392.9173; found 392.9168. **IR**: ν/cm^{-1} 3413, 3178, 3059, 2936, 1681, 1618, 1506, 1380, 1231, 1130, 1074, 1011.

3-(4-bromophenyl)-6,7-dimethyl-3,4-dihydroquinoxalin-2(1H)-one (7h). Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and 4,5-Dimethyl-1,2-phenylenediamine (**6h**) were used to generate **7i** in accordance with general procedure **A**. Following the microwave reaction, product precipitate was filtrated and washed with THF to isolate 171 mg (52 %) product. Product residue in the filtrate was collected and purified by automated flash column (0 % to 100 % Ethyl acetate in Heptane) to obtain additional 26 % yield. The yellow crystalline product was isolated in 78 % (257 mg) yield total. $R_f = 0.32$ (40 % EtOAc/Heptane). $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 10.31 (s, 1H), 7.52 (dd, $J = 8.4, 2.5$ Hz, 2H), 7.28 (dd, $J = 8.4, 2.4$ Hz, 2H), 6.55 (s, 1H), 6.50 (s, 1H), 6.43 (d, $J = 1.7$ Hz, 1H), 4.85 (d, $J = 1.6$ Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H). $^{13}\text{C-NMR}$ (101 MHz, DMSO- d_6) δ 165.5, 139.7, 131.2, 131.2, 130.3, 129.1, 125.1, 123.1, 120.7, 116.0, 114.8, 58.9, 19.1, 18.6. **HRMS** (ESI) m/z : [M+Na]⁺ Calculated for [C₁₆H₁₅BrN₂O₂Na] 353.0265 found 353.0265. **IR**: ν/cm^{-1} 3305, 3182, 3063, 2966, 2940, 2918, 2862, 1663, 1596, 1518, 1488, 1415, 1402, 1275, 1071, 1011.

3-(4-bromophenyl)-3,4-dihydrobenzo[g]quinoxalin-2(1H)-one (7i). Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and 2,3-Diaminonaphthalene (**6i**) were used to generate **7i** in accordance with general procedure **A**. The crude mixture was added Ethyl acetate and washed with water, hydrochloric acid solution (pH 1-2) and brine. The organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The solid residue was purified by automatic flash chromatography (5 % to 30 % Ethyl acetate in Heptane), isolating 58 % product. The contents of the used column were flushed out with ethyl acetate, concentrated and purified by an additional manual flash chromatography on silica gel (5 % to 30 % Ethyl acetate in Heptane), isolating additional 10 % product. Product **7i** was isolated as a yellow solid in 67 % (239 mg) yield total. $R_f = 0.35$ (40% EtOAc/Heptane). $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 10.87 (s, 1H), 7.63 – 7.49 (m, 4H), 7.32 (dd, $J = 8.4, 2.3$ Hz, 2H), 7.26 – 7.20 (m, 1H), 7.19 – 7.07 (m, 4H), 5.08 (d, J

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= 1.6 Hz, 1H). ¹³C-NMR (101 MHz, DMSO-*d*₆) δ 166.3, 139.6, 134.0, 131.3, 130.9, 129.1, 127.4, 126.5, 125.3, 124.5, 122.5, 121.0, 110.6, 107.1, 58.6. HRMS (ESI) *m/z* [M+Na]⁺ calculated for [C₁₈H₁₃BrN₂O₂Na]⁺ 375.0109; found 375.0110. IR: *v*/cm⁻¹ 3298, 3175, 3052, 2959, 2791, 1670, 1644, 1592, 1536, 1488, 1398, 1335, 1272, 1190, 1074, 1015.

3-(4-bromophenyl)octahydroquinoxalin-2(1H)-one (7j)

Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and 1,2-Diaminocyclohexane (**6j**) were used to generate **7j** in accordance with general procedure **A**. Precipitate from the reaction was filtrated and washed with Toluene, to give 107 mg (26 %) product **7j** as a white solid. *R*_f = 0.3 (EtOAc). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.33 (dd, *J* = 8.3, 2.0 Hz, 2H), 6.02 (s, 1H), 4.61 (s, 1H), 3.21 (t, *J* = 9.7 Hz, 1H), 2.70 (td, *J* = 9.7, 9.1, 3.4 Hz, 1H), 2.17 (s, 1H), 1.87 – 1.75 (m, 4H), 1.45 – 1.26 (m, 4H). ¹³C-NMR (101 MHz, Chloroform-*d*) δ 170.2, 138.7, 131.7, 130.5, 122.1, 64.7, 59.1, 58.4, 31.5, 30.7, 24.6, 23.9. HRMS (ESI) *m/z*: [M+H]⁺ Calculated for [C₁₄H₁₈BrN₂O] 309.0603; found 309.0597. IR: *v*/cm⁻¹ 3283, 3208, 3082, 2933, 2854, 1659, 1592, 1488, 1402, 1354, 1316, 1246, 1074, 1015.

3-(4-bromophenyl)-1,4-dimethylpiperazin-2-one (7k)

Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and *N,N'*-Dimethylethylenediamine (**6k**) were used to generate **7k** in accordance with general procedure **A**. The product was purified by automated flash chromatography (80 % to 100 % Ethyl acetate in Heptane). Product **7k** was isolated in 57 % (162 mg) yield as a white solid. *R*_f = 0.17 (EtOAc). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.3, 2.3 Hz, 2H), 7.28 (dd, *J* = 8.1, 2.3 Hz, 2H), 3.71 (td, *J* = 11.4, 4.3 Hz, 1H), 3.66 (s, 1H), 3.19 (ddd, *J* = 11.8, 3.8, 2.4 Hz, 1H), 3.00 (ddd, *J* = 12.0, 4.3, 2.3 Hz, 1H), 2.96 (s, 3H), 2.67 (td, *J* = 11.6, 3.8 Hz, 1H), 2.16 (s, 3H). ¹³C-NMR (101 MHz, Chloroform-*d*) δ 167.6, 138.3, 131.5, 130.8, 121.8, 72.6, 51.1, 48.4, 44.0, 34.8. HRMS (ESI) *m/z* [M+Na]⁺ calculated for [C₁₂H₁₅BrN₂O₂Na]⁺ 305.0265; found 305.0265. IR: *v*/cm⁻¹ 2951, 2847, 2873, 2799, 1640, 1596, 1491, 1458, 1406, 1346, 1257, 1238, 1156, 1071, 1011.

1,4-dibenzyl-3-(4-bromophenyl)piperazin-2-one (7l)

Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and *N,N'*-Dibenzylethylenediamine (**6l**) were used to generate **7l** in accordance with general procedure **A**. The product was isolated and purified by automated flash chromatography (10 % to 30% Ethyl acetate in Heptane), to yield 45 % (198 mg) **7m**. *R*_f = 0.35 (EtOAc/Heptane). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.57 (dd, *J* = 8.4, 2.2 Hz, 2H), 7.45 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.37 – 7.20 (m, 10H), 4.51 (s, 2H), 4.14 (s, 1H), 3.53 (d, *J* = 13.6 Hz, 1H), 3.40 (ddd, *J* = 11.8, 10.4, 4.0 Hz, 1H), 3.22 (d, *J* = 13.6 Hz, 1H), 3.17 (dt, *J* = 12.0, 3.4 Hz, 1H), 2.86 (dt, *J* = 12.0, 3.6 Hz, 1H), 2.54 – 2.44 (m, 1H). ¹³C-NMR (101 MHz, DMSO-*d*₆) δ 166.8, 139.4, 137.5, 137.0, 131.1, 131.1, 128.6, 128.4, 128.3, 127.4, 127.2, 127.1, 120.6, 69.4, 57.8, 49.2, 46.1, 45.6. HRMS (ESI) *m/z* [M+H]⁺ calculated for [C₂₄H₂₄BrN₂O] 435.1067; found 435.1073. IR: *v*/cm⁻¹ 3283, 3063, 3029, 2921, 2806, 2724, 1715, 1648, 1488, 1454, 1357, 1238, 1145, 1074, 1015.

3-(4-bromophenyl)-1,4-diphenylpiperazin-2-one (7m)

Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and *N,N'*-Diphenylethylenediamine (**6m**) were used to generate **7n** in accordance with general procedure **A**. The reaction mixture was diluted with Ethyl acetate (20 ml) and washed with water, brine and dried over Na₂SO₄. The solvent was evaporated under reduced pressure and gave the product (**7m**) as a yellow solid (55 mg, 14%). *R*_f = 0.40 [(EtOAc:Heptane, 20:80)]. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.41 (m, 4H), 7.41 – 7.32 (m, 2H), 7.29 – 7.19 (m, 5H), 6.82 (td, *J* = 7.3, 1.1 Hz, 1H), 6.73 – 6.64 (m, 2H), 5.46 (s, 1H), 3.99 – 3.85 (m, 1H), 3.85 – 3.74 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 167.3, 147.6, 141.6, 137.0,

132.1, 129.6, 129.5, 129.3, 128.4, 127.0, 125.0, 122.2, 118.8, 113.7, 112.9, 65.4, 47.3, 44.8. HRMS (ESI) *m/z* [M+Na]⁺ calculated for [C₂₂H₁₉⁷⁹BrN₂NaO⁺] 429.0573; found 429.0589. calculated for [C₂₂H₁₉⁸¹BrN₂NaO⁺] 431.0553; found 431.0567. IR: *v*/cm⁻¹ 1670, 1599, 1503, 1473, 1402, 1313, 1208, 1011, 911, 750, 732, 695.

3-(naphthalen-2-yl)-3,4-dihydroquinoxalin-2(1H)-one (7n)

Methyl 2-diazo-2-(naphthalen-2-yl)acetate (**5d**) (226 mg, 1.0 mmol), *N,N'*-Diphenylethylenediamine (**6n**) (637 mg, 1.18 mmol, 3 eq.), and Toluene (2 ml), is mixed in a 10 ml microwave reactor. After addition, the mixture is sonicated for 2 minutes followed by degassed with N₂ gas. The microwave is set to heat to 150 °C for 5 minutes, and then cool to 55 °C, with 900-rpm stirring rate. The reaction mixture was diluted with Ethyl acetate (20 ml), washed with water, brine, and dried over Na₂SO₄. The solvent was evaporated under reduced pressure and gave the product (**7g**) as a white solid (55 mg, 15%). *R*_f = 0.33 [(EtOAc:Heptane, 20:80)]. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.92 – 7.69 (m, 4H), 7.54 – 7.44 (m, 2H), 7.43 – 7.33 (m, 2H), 7.32 – 7.19 (m, 5H), 6.89 – 6.82 (m, 1H), 6.82 – 6.76 (m, 2H), 5.72 (s, 1H), 4.12 – 3.99 (m, 1H), 3.98 – 3.80 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 167.6, 147.8, 135.4, 133.5, 133.3, 129.6, 129.3, 128.9, 128.3, 127.8, 126.9, 126.4, 126.3, 125.5, 125.1, 124.6, 118.6, 112.9, 66.2, 47.3, 45.0. HRMS (ESI) *m/z* [M+Na]⁺ calculated for [C₂₆H₂₂N₂NaO⁺] 401.1624; found 401.1624. IR: *v*/cm⁻¹ 1675, 1560, 1416, 1392, 1258, 1146, 763, 699.

6-bromo-3-(4-bromophenyl)-3,4-dihydroquinoxalin-2(1H)-one (7o) & 7-bromo-3-(4-bromophenyl)-3,4-dihydroquinoxalin-2(1H)-one (7o')

Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and 4-Bromo-1,2-diaminobenzene (**6o**) were used to generate **7o** and **7o'** in accordance with general procedure **B**. The product was isolated and purified by dry-loaded flash chromatography (10% to 40% Ethyl acetate in Heptane), to yield 245 mg (67 %) orange crystalline product as isomer mixtures. Characterisation obtained from isolated isomer fraction. *R*_f = 0.47 (40 % EtOAc/Heptane). ¹H-NMR (400 MHz, DMSO-*d*₆) δ 10.59 (s, 1H), 7.61 – 7.49 (m, 2H), 7.32 – 7.23 (m, 2H), 6.94 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 2.3 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.99 (d, *J* = 1.9 Hz, 1H). ¹³C-NMR (101 MHz, DMSO-*d*₆) δ 165.3, 139.2, 133.0, 131.3, 129.2, 126.9, 125.3, 121.0, 117.0, 114.9, 108.2, 58.4. HRMS (ESI) *m/z*: [M+Na]⁺ Calculated for: [C₁₄H₁₀Br₂N₂O₂Na]⁺ 402.9058; found 402.9055. IR: *v*/cm⁻¹ 3420, 3059, 2955, 2877, 1681, 1599, 1506, 1376, 1231, 1074, 1011

4-benzyl-3-(4-bromophenyl)morpholin-2-one (7p)

Methyl 2-(4-bromophenyl)-2-diazoacetate (**5a**) and 2-Benzylaminoethanol (**6p**) were used to generate **7p** in accordance with general procedure **A**. The crude mixture was purified by automated flash chromatography (3 % to 20 % Ethyl acetate in Heptane). Product **7p** was obtained as a clear oil in 35 % (122 mg) yield. *R*_f = 0.5 (40 % EtOAc/Heptane). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.47 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.41 – 7.27 (m, 3H), 7.27 – 7.19 (m, 2H), 4.55 (td, *J* = 11.1, 3.1 Hz, 1H), 4.37 (ddd, *J* = 10.9, 3.3, 2.1 Hz, 1H), 4.23 (s, 1H), 3.76 (d, *J* = 13.3 Hz, 1H), 3.19 (d, *J* = 13.3 Hz, 1H), 3.01 (ddd, *J* = 12.8, 3.1, 2.1 Hz, 1H), 2.66 (ddd, *J* = 12.9, 11.3, 3.3 Hz, 1H). ¹³C-NMR (101 MHz, Chloroform-*d*) δ 168.2, 136.5, 136.5, 132.0, 130.7, 129.0, 128.7, 127.9, 122.7, 69.9, 68.7, 59.0, 47.0. HRMS (ESI) *m/z* [M+Na]⁺ calculated for [C₁₇H₁₆BrNO₂Na]⁺ 368.0262; found 368.0263. IR: *v*/cm⁻¹ 3029, 2959, 2813, 1741, 1491, 1458, 1410, 1302, 1205, 1063, 1015.

tert-butyl 4-(3-(4-bromophenyl)-2-oxo-1,2,3,4-tetrahydroquinoxalin-5-yl)piperazine-1-carboxylate (7q) & tert-butyl 4-(2-(4-bromophenyl)-3-oxo-1,2,3,4-tetrahydroquinoxalin-5-yl)piperazine-1-carboxylate (7q')

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Bromo-diazoacetate (**5a**) (77 mg, 0.3 mmol), tert-butyl 4-(2,3-diaminophenyl)piperazine-1-carboxylate (**6q**) (88 mg, 0.3 mmol, 1 equiv.), and toluene (2 ml), is mixed in a 10 ml microwave reactor. After addition, the mixture is sonicated for 2 minutes followed by degassed with N₂ gas. The microwave is set to heat to 150 °C for 5 minutes, and then cool to 55 °C, with 900 rpm stirring rate. The reaction mixture was diluted with ethyl acetate (20 ml) and washed with water, brine and dried over Na₂SO₄. The solvent was evaporated under reduced pressure and gave the mixture of isomers (**7q** & **7q'**) as a yellow liquid (55 mg, 40%). **¹H NMR** (400 MHz, Methanol-*d*₄) δ 7.52 – 7.37 (m, 4H), 7.36 – 7.20 (m, 4H), 6.96 – 6.75 (m, 2H), 6.69 (t, *J* = 7.9 Hz, 1H), 6.66 – 6.52 (m, 3H), 2.93 – 2.66 (m, 8H), 1.47 (d, *J* = 1.4 Hz, 18H). **¹³C NMR** (101 MHz, Methanol-*d*₄) δ 168.7, 168.0, 156.4, 141.2, 140.6, 140.0, 139.9, 135.9, 132.7, 132.6, 132.3, 130.0, 129.6, 125.4, 122.9, 120.2, 119.9, 116.7, 113.0, 111.4, 111.4, 81.3, 60.8, 60.7, 52.7, 28.7. **HRMS** (ESI) *m/z* [M-H]⁻ calculated for [C₂₃H₂₆⁷⁹BrN₄O₃] 485.1194; found 485.1144. calculated for [C₂₃H₂₆⁸¹BrN₄O₃] 487.1173; found 487.1124. **IR**: *v*/cm⁻¹ 3421, 3008, 2975, 2926, 1716, 1425, 1366, 1224.

(C) General procedure for the oxidation of dihydroquinoxalin-2-one using Chloranil (8b-8e,8). 7b-e, 7i was added THF (20 ml), and Chloranil (1.1 eq.) and set to stir at room temperature. Reactions was monitored by TLC. Following the reaction solvent was removed and the crude residue was purified by flash chromatography on silica gel using Ethyl acetate in Heptane mixtures to yield corresponding oxidized products.

3-(4-bromophenyl)quinoxalin-2-ol (8a). All glassware were oven dried prior to use, and the reaction was carried out under a drying tube (CaCl₂). **7a** (65.2 mg, 0.215 mmol) was added DDQ (54 mg, 0.237 mmol, 1.1 eq.), dissolved in dry THF (20 ml) and set to stir at room temperature. The reaction was monitored by TLC. After 1 hour the crude reaction mixture was added water which led to product precipitation. Product was isolated by filtration, and washed with Ethyl acetate to yield 85 % (55 mg) **8a** product. *R_f* = 0.43 (40 % EtOAc/heptane). **¹H-NMR** (400 MHz, DMSO-*d*₆) δ 12.63 (s, 1H), 8.35 – 8.26 (m, 2H), 7.84 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.56 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38 – 7.29 (m, 2H). **¹³C-NMR** (101 MHz, DMSO-*d*₆) δ 154.5, 152.8, 134.7, 132.1, 131.9, 131.2, 130.9, 130.6, 128.8, 124.0, 123.5, 115.2. **HRMS** (ESI) *m/z* [M+Na]⁺ Calculated for [C₁₄H₉BrN₂O₂Na] 322.9796; found 322.9798. **IR**: *v*/cm⁻¹ 3301, 3096, 2944, 2880, 2828, 2732, 1655, 1588, 1536, 1477, 1436, 1398, 1283, 1182, 1071, 1004.

3-(4-methoxyphenyl)quinoxalin-2-ol (8b). **7b** (135 mg, 0.53 mmol) was oxidized using general procedure (C). The reaction was complete after 55 minutes. Flash chromatography on silica gel was performed (20 % to 40 % Ethyl acetate in Heptane) to yield 76 % (103 mg) product. TLC: 40 % EtOAc/Heptane. **¹H-NMR** (400 MHz, DMSO-*d*₆) δ 12.50 (s, 1H), 8.44 – 8.35 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.51 (td, *J* = 7.7, 7.1, 1.4 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.09 – 7.00 (m, 2H), 3.84 (s, 3H). **¹³C-NMR** (101 MHz, DMSO-*d*₆) δ 161.0, 154.7, 153.1, 132.1, 131.8, 131.0, 129.7, 128.5, 128.1, 123.3, 115.0, 113.3, 55.3. **HRMS** (ESI) *m/z* [M+Na]⁺ calculated for [C₁₅H₁₂N₂O₂Na] 275.0796; found 275.0791. **IR**: *v*/cm⁻¹ 3316, 3093, 3007, 2940, 2888, 2840, 1663, 1599, 1510, 1469, 1436, 1290, 1257, 1175, 1030.

3-(4-(trifluoromethyl)phenyl)quinoxalin-2-ol (8c). **7c** (152 mg, 0.52 mmol) was oxidized using general procedure (C). The reaction was not complete after 6 hours and was left to stir over night. The product was isolated by flash chromatography on silica gel (10 % to 40 % Ethyl acetate in Heptane) to yield 95% (141 mg) product. TLC: 40 % EtOAc/Heptane. **¹H-NMR** (400 MHz, DMSO-*d*₆) δ 12.70 (s, 1H), 8.51 (d, *J* = 8.2 Hz, 2H), 7.86 (dd, *J* = 8.5, 2.8 Hz, 3H), 7.58 (td, *J* = 7.6, 1.4 Hz, 1H), 7.35 (dd, *J* = 8.1, 6.7 Hz, 2H). **¹³C-NMR** (101 MHz, DMSO-*d*₆) δ 154.5,

152.8, 139.3, 132.3, 131.9, 131.0, 129.9 (q, *J* = 31.8 Hz), 129.9 (s, 2C), 129.0, 124.7 (q, *J* = 3.7 Hz, 2C), 124.2 (q, *J* = 272.3 Hz), 123.6, 115.2. **HRMS** (ESI) *m/z* [M+H]⁺ Calculated for [C₁₅H₁₀F₃N₂O] 291.0740; found 291.0755. **IR**: *v*/cm⁻¹ 3316, 3104, 2951, 2888, 2836, 1663, 1611, 1536, 1413, 1331, 1156, 1112, 1074, 1007.

3-(naphthalen-2-yl)quinoxalin-2-ol (8d). **7d** (153 mg, 0.56 mmol) was oxidized using general procedure (C). The reaction was complete after 4,5 hours. Product was purified by flash chromatography on silica gel (15 % to 100 % ethyl acetate in heptane) to yield 96 % (145 mg) product. TLC: 40 % Ethyl acetate/Heptane. **¹H-NMR** (400 MHz, DMSO-*d*₆) δ 12.65 (s, 1H), 9.11 (d, *J* = 1.6 Hz, 1H), 8.39 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.10 – 7.92 (m, 3H), 7.89 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.65 – 7.51 (m, 3H), 7.41 – 7.29 (m, 2H). **¹³C-NMR** (101 MHz, DMSO-*d*₆) δ 154.8, 153.5, 133.6, 133.0, 132.3, 132.1, 132.0, 130.4, 129.8, 129.1, 128.8, 127.5, 127.4, 127.3, 126.5, 125.9, 123.5, 115.1. **HRMS** (ESI) *m/z* [M+H]⁺ Calculated for [C₁₈H₁₁N₂O] 271.0877 found; 271.0876. **IR**: *v*/cm⁻¹ 3316, 3100, 3059, 2977, 2884, 2843, 2724, 1663, 1611, 1596, 1532, 1484, 1436, 1361, 1267, 1186, 1130.

3-(pyridin-3-yl)quinoxalin-2-ol (8e). **7e** (142 mg, 0.63 mmol) was oxidized using general procedure (C). The reaction was complete after 4 hours. The product was purified by flash chromatography on silica gel using (60% to 100% Ethyl acetate in Heptane), followed by 5 % Methanol in Ethyl acetate to yield 68% (95,8 mg) product **8b**. TLC: 70 % EtOAc/Heptane. **¹H-NMR** (400 MHz, DMSO-*d*₆) δ 12.67 (s, 1H), 9.41 (d, *J* = 2.1 Hz, 1H), 8.68 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.61 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.47 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 2H). **¹³C-NMR** (101 MHz, DMSO-*d*₆) δ 154.5, 152.5, 150.5, 149.8, 136.5, 132.2, 132.0, 131.4, 130.8, 128.9, 123.6, 123.1, 115.3. **HRMS** (ESI) *m/z* [M+H]⁺ calculated for [C₁₃H₁₀N₃O] 224.0818; found 224.0823. **IR**: *v*/cm⁻¹ 3320, 3100, 3003, 2951, 2888, 2840, 2735, 1666, 1614, 1596, 1395, 1305, 1194, 1011.

3-(3,4-dichlorophenyl)quinoxalin-2-ol (8f). **7f** (175 mg, 0.62 mmol) was oxidized general procedure (C). The reaction was complete after 3.5 hours. Product was isolated and purified by flash chromatography on silica gel (10 % to 30 % ethyl acetate in heptane) to yield 67 % product. TLC: 40 % EtOAc/Heptane. **¹H-NMR** (400 MHz, DMSO-*d*₆) δ 12.71 (s, 1H), 8.62 (d, *J* = 2.0 Hz, 1H), 8.35 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.87 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.58 (td, *J* = 7.6, 7.1, 1.4 Hz, 1H), 7.35 (ddd, *J* = 7.0, 3.7, 2.4 Hz, 2H). **¹³C-NMR** (101 MHz, DMSO-*d*₆) δ 154.5, 151.2, 136.0, 132.9, 132.3, 131.8, 131.0, 130.8, 130.7, 130.3, 129.2, 129.0, 123.6, 115.2. **HRMS** (ESI) *m/z* [M-H]⁻ Calculated for [C₁₄H₇Cl₂N₂O] 288.9941; found 288.9936. **IR**: *v*/cm⁻¹ 3111, 2933, 2880, 2847, 1666, 1614, 1529, 1469, 1436, 1383, 1033.

3-(4-bromophenyl)-6,7-dimethylquinoxalin-2-ol (8h). All glassware were oven dried prior to use, and the reaction was carried out under a drying tube (CaCl₂). **7h** (235 mg, 0.71 mmol) was added DDQ (161 mg, 0.71 mmol, 1 eq.), dissolved in dry THF (20 ml), and set to stir. for 1 hour. The reaction was monitored by TLC. After 1 hour, the reaction solvent was removed, and Ethyl acetate was added. Following addition of water, the product was observed in both phases and the water phase was extracted several times with Ethyl acetate. The combined organic phases was washed with brine and dried over Na₂SO₄, and the solvent was evaporated under reduced pressure. The residue was purified by automated flash chromatography (5% to 100% Ethyl acetate in Heptane). Pure product was obtained in 38 % yield from the column. Most solvent was removed from mixed fractions and added Methanol to induce product precipitation. Precipitated product was filtered and washed with Methanol. In total 79% (185 mg) product was collected. *R_f* = 0.42 (40 % EtOAc/Heptane). **¹H-NMR** (400 MHz,

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DMSO- d_6) δ 12.50 (s, 1H), 8.31 – 8.25 (m, 2H), 7.72 – 7.63 (m, 2H), 7.59 (s, 1H), 7.07 (s, 1H), 2.31 (s, 3H), 2.29 (s, 3H). ^{13}C -NMR (101 MHz, DMSO- d_6) δ 154.6, 151.3, 140.4, 134.9, 132.2, 131.0, 130.9, 130.5, 130.2, 128.6, 123.7, 115.1, 19.9, 19.0. HRMS (ESI) m/z [M+Na] Calculated for $[\text{C}_{16}\text{H}_{13}\text{BrN}_2\text{O}_2\text{Na}]$ 351.0109; found 351.0110. IR: ν/cm^{-1} 3301, 2914, 2854, 2828, 1655, 1585, 1529, 1491, 1402, 1261, 1074, 1011.

3,3'-(1,4-phenylene)bis(quinoxalin-2-ol) (8r). **7r** (1 equiv.) was oxidized using general chloranil oxidation procedure (C). The reaction was completed after 1 hour. The solvent was removed and diluted with ethylacetate and water. The aqueous layer was extracted with ethyl acetate and dried over Na_2SO_4 . The solvent was evaporated under reduced pressure to obtain the compound (**8s**) as a yellow solid in 95% yield. $R_f = 0.1$ [(EtOAc: 100)]. ^1H NMR (400 MHz, DMSO- d_6) δ 12.67 (s, 2H), 8.45 (s, 3H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.57 (t, $J = 7.7$ Hz, 3H), 7.42 – 7.31 (m, 4H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 154.6, 153.5, 150.9, 137.1, 132.2, 132.1, 130.6, 129.3, 128.9, 128.7, 123.5, 115.2, 113.8, 101.6. HRMS (ESI) m/z [M+H] $^+$ Calculated for $[\text{C}_{22}\text{H}_{14}\text{N}_4\text{NaO}_2]^+$ 389.1009 found; 389.1018. IR: ν/cm^{-1} 3183, 3004, 2960, 2889, 2848, 2256, 1667, 1455, 1280, 1191, 893, 750.

(D) General procedure for preparation of organotriflates. A solution of trifluoromethanesulfonic anhydride (1.2 equiv.) in CH_2Cl_2 (5 mL) was added dropwise to a solution of pyridine (2 equiv.) and quinoxaline-2-ol (**8**) in anhydrous CH_2Cl_2 (10 mL) at 0 °C. After complete addition, the mixture was warmed to room temperature and allowed to stir for 2 hours. The mixture was then diluted with DCM, quenched with 10 % aq HCl, washed with brine, and dried over Na_2SO_4 . The solvent was removed under reduced pressure to yield the corresponding organotriflate.

3-(4-bromophenyl)quinoxalin-2-yl trifluoromethanesulfonate (9). **8a** (100 mg, 0.334 mmol) was converted to the corresponding organotriflate using general procedure (D). **9** was obtained as a brown solid in 91% (120 mg) yield. $R_f = 0.74$ [(EtOAc: 100)]. ^1H NMR (400 MHz, Chloroform- d) δ 8.25 – 8.17 (m, 1H), 8.11 – 8.02 (m, 1H), 7.94 – 7.81 (m, 4H), 7.75 – 7.67 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 147.9, 145.3, 142.2, 138.9, 132.8, 132.2, 131.8, 131.4, 131.1, 129.4, 128.5, 125.7, 120.1, 117.0. HRMS (ESI) m/z [M+H] $^+$ Calculated for $[\text{C}_{15}\text{H}_9^{79}\text{BrF}_3\text{N}_2\text{O}_3\text{S}^+]$ 432.9464 found; 432.9469. Calculated for $[\text{C}_{15}\text{H}_9^{81}\text{BrF}_3\text{N}_2\text{O}_3\text{S}^+]$ 434.9443 found; 434.9428. IR: ν/cm^{-1} 2926, 2855, 1424, 1171, 1119, 1074, 918, 829, 799.

3-(4-methoxyphenyl)quinoxalin-2-yl trifluoromethanesulfonate (10). **8b** (85 mg, 0.334 mmol) was converted to the corresponding organotriflate using general procedure (D). **10** was obtained as a pale yellow solid in 83% (117 mg) yield. $R_f = 0.74$ [(EtOAc: 100)]. ^1H NMR (400 MHz, Chloroform- d) δ 8.23 – 8.13 (m, 1H), 8.09 – 7.96 (m, 3H), 7.82 (pd, $J = 7.0, 1.7$ Hz, 2H), 7.13 – 7.04 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 161.9, 148.1, 146.0, 142.3, 138.5, 131.3, 131.1, 131.0, 129.2, 128.4, 126.3, 120.2, 117.0, 114.4, 55.6. HRMS (ESI) m/z [M+H] $^+$ Calculated for $[\text{C}_{16}\text{H}_{12}\text{F}_3\text{N}_2\text{O}_4\text{S}^+]$ 385.0464 found; 385.0460. IR: ν/cm^{-1} 2937, 2848, 1612, 1422, 1347, 1182, 1165, 1138, 997, 840, 769.

3-(naphthalen-2-yl)quinoxalin-2-yl trifluoromethanesulfonate (11). **8f** (68 mg, 0.250 mmol) was converted to the corresponding organotriflate using general procedure (D). **11** was obtained as a yellow solid in 84% (85 mg) yield. $R_f = 0.89$ [(EtOAc: Pentane, 20:80)]. ^1H NMR (400 MHz, Chloroform- d) δ 8.53 (d, $J = 1.8$ Hz, 1H), 8.32 – 8.20 (m, 1H), 8.11 (ddd, $J = 9.3, 7.6, 2.2$ Hz, 2H), 8.09 – 7.95 (m, 2H), 7.96 – 7.90 (m, 1H), 7.92 – 7.80 (m, 2H), 7.66 – 7.52 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 148.3, 146.3, 142.2, 138.7, 134.3, 133.1, 131.5, 131.2, 131.2, 130.3, 129.4, 129.2, 128.8, 128.5, 127.9, 127.0, 126.0, 120.1, 116.9. HRMS (ESI) m/z [M+Na] $^+$

Calculated for $[\text{C}_{19}\text{H}_{11}\text{F}_3\text{N}_2\text{NaO}_3\text{S}^+]$ 427.0335 found; 427.0350. IR: ν/cm^{-1} 1418, 1213, 1160, 1116, 1011, 825, 769.

2-(4-bromophenyl)-3-phenylquinoxaline (12). Aryl triflate (**9**) (80 mg, 0.185 mmol), Phenylboronic acid (34 mg, 0.278 mmol), Na_2CO_3 (39 mg, 0.368 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (6 mg, 0.005 mmol, 3 mol-%) were added to a 10 ml microwave reactor vial. The vial was sealed and flushed with N_2 before Toluene (2.5 mL) was added. The solution was stirred for 10 s under ultra-sonication before being subjected into microwave heating for 60 min at 120 °C. After the reaction, the solvent was removed under reduced pressure. The reaction crude was diluted with ethyl acetate (40 mL) and washed with water (30 mL). The water layer was extracted with ethyl acetate (2 \times 30 mL). The organic layers were combined and dried over Na_2SO_4 . The crude product was purified by silica-gel flash column chromatography using 5% EtOAc/pentane eluent system and obtained the product **13** as a pale-yellow solid (34 mg, 52%). $R_f = 0.63$ [(EtOAc: Pentane, 20:80)]. ^1H NMR (400 MHz, Chloroform- d) δ 8.17 (ddd, $J = 6.8, 5.7, 3.4$ Hz, 2H), 7.82 – 7.75 (m, 2H), 7.55 – 7.49 (m, 2H), 7.47 (m, 2H), 7.44 – 7.33 (m, 5H). ^{13}C NMR (101 MHz, Chloroform- d) δ 153.3, 152.1, 141.4, 141.3, 138.9, 138.1, 131.6, 130.4, 130.3, 130, 129.4, 129.3, 129.2, 128.6, 123.6. HRMS (ESI) m/z [M+H] $^+$ Calculated for $[\text{C}_{20}\text{H}_{14}^{79}\text{BrN}_2]^+$ 361.0335 found; 361.0329. Calculated for $[\text{C}_{20}\text{H}_{14}^{81}\text{BrN}_2]^+$ 363.0314 found; 363.0307. IR: ν/cm^{-1} 3060, 2925, 2854, 1588, 1480, 1346, 1074, 981, 844, 806, 765.

2,3-bis(4-methoxyphenyl)quinoxaline (13). Aryl triflate (**10**) (80 mg, 0.208 mmol), 4-methoxyphenylboronic acid (48 mg, 0.316 mmol), Na_2CO_3 (44 mg, 0.415 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (7 mg, 0.006 mmol, 3 mol-%) were added to a 10 ml microwave reactor vial. The vial was sealed and flushed with N_2 before Toluene (2.5 mL) was added. The solution was stirred for 10 s under ultra-sonication before being subjected into microwave heating for 60 min at 120 °C. After the reaction time, the solvent was removed under reduced pressure. The reaction crude was diluted with ethyl acetate (40 mL) and washed with water (30 mL). The water layer was extracted with ethyl acetate (2 \times 30 mL). The organic layers were combined and dried over Na_2SO_4 . The crude product was purified by silica-gel flash column chromatography using 10% EtOAc/pentane eluent system and obtained the product **13** as a yellow solid (30 mg, 42%). $R_f = 0.43$ [(EtOAc: Pentane, 20:80)]. ^1H NMR (400 MHz, Chloroform- d) δ 8.13 (dd, $J = 6.4, 3.4$ Hz, 2H), 7.72 (dd, $J = 6.4, 3.4$ Hz, 2H), 7.54 – 7.46 (m, 4H), 6.92 – 6.84 (m, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 160.3, 153.2, 141.2, 131.8, 131.4, 129.7, 129.1, 113.9, 55.5. HRMS (ESI) m/z [M+Na] $^+$ Calculated for $[\text{C}_{22}\text{H}_{18}\text{N}_2\text{NaO}_2]^+$ 365.1260 found; 365.1273. IR: ν/cm^{-1} 2963, 2930, 2841, 1608, 1518, 1463, 1249, 1175, 1030, 832, 769.

Ethyl 2-diazo-2-(3-(naphthalen-2-yl)quinoxalin-2-yl)acetate (14). To a mixture of aryl triflate (**11**) (80 mg, 0.20 mmol), EDA (56 mg, 0.05 mL, 0.49 mmol), DBU (45 mg, 0.04 mL, 0.30 mmol), $n\text{-Bu}_4\text{NI}$ (73 mg, 0.20 mmol) in CH_3CN (10 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 0.02 mmol). The mixture was stirred at 45 °C for 2 hours under N_2 until **11** disappeared. The solvent was evaporated in vacuo. Purification by column chromatography using [20% EtOAc/Pentane] eluent gave pure **14** as pale-brown solid (35 mg, 48%). $R_f = 0.35$ [(EtOAc: Pentane, 20:80)]. ^1H NMR (400 MHz, Chloroform- d) δ 8.88 – 8.79 (m, 1H), 8.34 – 8.26 (m, 1H), 8.24 (d, $J = 1.8$ Hz, 1H), 8.02 (d, $J = 8.5$ Hz, 1H), 7.98 – 7.90 (m, 2H), 7.93 – 7.79 (m, 3H), 7.64 – 7.50 (m, 2H), 3.89 (q, $J = 7.1$ Hz, 2H), 0.75 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 161.2, 153.1, 137.0, 135.5, 135.0, 134.4, 132.9, 130.8, 130.4, 129.8, 128.8, 128.7, 128.5, 128.0, 127.7, 127.04, 125.3, 125.1, 124.6, 116.1, 62.1, 13.5. HRMS (ESI) m/z [M+Na] $^+$ Calculated for $[\text{C}_{22}\text{H}_{16}\text{N}_4\text{NaO}_2]^+$ 391.1165

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found; 391.1153. IR: $\nu_{\text{cm}^{-1}}$ 3053, 2975, 2926, 2126, 1727, 1526, 1384, 1236, 1187, 822, 763, 742.

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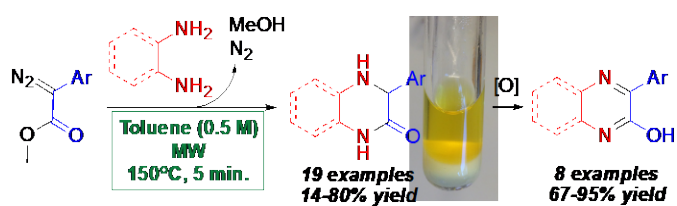
Keywords: microwave • diazoacetates • N-H insertion • dihydroquinoxalinones • quinoxalines

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Microwave-superheated solutions of aryldiazoacetates and 1,2-diamines mixed in toluene yield rapid access to quinoxalinones and quinoxalines without the use of catalysts, additives or otherwise complicated reaction conditions.