DABCO-Catalyzed Oxidation of Deoxybenzoins to Benzils with Air and One-Pot Synthesis of Quinoxalines

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Abstract: Aerobic oxidation of deoxybenzoins could be efficiently catalyzed by 1,4-diazabicyclo[2.2.2]octane (DABCO) with air as the sole oxidant to give the corresponding benzils in excellent yields. The effects of reaction conditions, such as different bases, temperature, time and solvent, on the yield of the product were investigated. Moreover, the process has been successfully extended to a one-pot synthesis of quinoxalines from benzyl ketones and aromatic 1,2-diamines.

Key words: deoxybenzoins, benzils, oxidation, quinoxalines, 1,2-diamines

The oxidation of a methylene group α to a ketone into a carbonyl group to form a 1,2-diketone is of great importance because 1,2-diketones are versatile synthetic intermediates.[1] This transformation can be achieved using appropriate oxidants, such as selenium dioxide,[2] potassium permanganate,[3] pyridinium chlorochromate,[4] or thallium nitrate.[5] Wasserman[6] reported a procedure that consists of the transformation of ketones into enamino ketones followed by oxidation with singlet oxygen. Bauer and Macomber[7] reported another two-step synthesis of 1,2-diketones from α-methylene ketones involving α-halogenation followed by further oxidation with dimethyl sulfoxide in the presence of sodium carbonate. The reaction of pyridine *N*-oxide with α-nosyloxy ketones formed from α-methylene ketone intermediates also afford 1,2-diketones.[8] A five-step synthesis of 1-aryl-1,2-alkanediones has also been developed by De Kimpe and co-workers.[9] However, these processes suffer from one or more drawbacks, such as the need for stoichiometric or large excess of oxidants, low product yields and tedious work-up procedures, which limit their use. Therefore, the development of an efficient and environmentally benign method for catalytic oxidation of α-methylene ketones to 1,2-diketones is still required.

Although it has been recognized for many years that, in some instances, ketones can react with molecular oxygen to form 1,2-diketones through α-hydroperoxy ketone intermediates in strongly basic media,[10] the reaction has seldom been used as a synthetically useful means of producing 1,2-diketones. As a part of our program to develop more efficient and environmentally benign methods for organic synthesis using molecular oxygen as the sole oxidant,[11] herein, we wish to report a very simple and efficient method for the preparation of benzils through the aerobic oxidation of deoxybenzoins with air as the sole oxidant, catalyzed by 1,4-diazabicyclo[2.2.2]octane (DABCO). We also wish to report the results of a study on the one-pot synthesis of substituted quinoxaline derivatives from *o*-phenylenediamines and benzyl ketones.

We first studied the oxidation of deoxybenzoin by screening the reaction conditions, including different catalysts, the reaction temperature, the reaction time, and the solvent (Table 1).

Initially, treatment of deoxybenzoin (**1a**) in *N*,*N*-dimethylformamide in the presence of 5 mol% DABCO at 90 °C for 24 hours in air, afforded benzil (**2a**) in 32% yield (Table 1, entry 1). To our delight, when the loading of DABCO was increased to 20 mol%, deoxybenzoin was quantitatively converted and gave benzil in 95% isolated yield (Table 1, entry 3). The results summarized in Table 1 show that the reaction temperature had a large impact on the reaction (Table 1, entries 3–5). Performing the reaction at lower temperature, such as 50 °C, reduced the yield to only 32%. The reaction time also had a significant effect on the yield of the product (Table 1, entries 3 and 6). The experimental results indicated that 24 hours reaction time was necessary for the reaction to reach completion. When the reaction time was shortened to 10 hours, benzil was obtained in 76% yield (Table 1, entry 6). The effect of the solvent was also evaluated (Table 1, entries 3 and 7–11). *N*,*N*-Dimethylformamide and 1,2-dimethoxyethane (DME) were found to be optimal solvents. When the reaction was performed in toluene, dimethyl sulfoxide or water, low yields of the desired product were obtained; under these conditions, benzaldehyde and benzoic acid were also formed as major byproducts from the oxidative cleavage of deoxybenzoin. Furthermore, the use of 1,4-dioxane as solvent gave no benzil but led to the formation of benzoic acid as the major product in 35% isolated yield.

Further investigations on the effects of organic bases showed that several other nitrogen- and phosphorus-base catalysts, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 4-(*N*,*N*-dimethylamino)pyridine (DMAP), *N*,*N*-diisopropylethylamine (DIPEA), and pyridine were either less effective or showed no catalytic activity in the reaction (Table 1, entries 12–16). Sodium methoxide and potassium hydroxide also gave low yields of the product,

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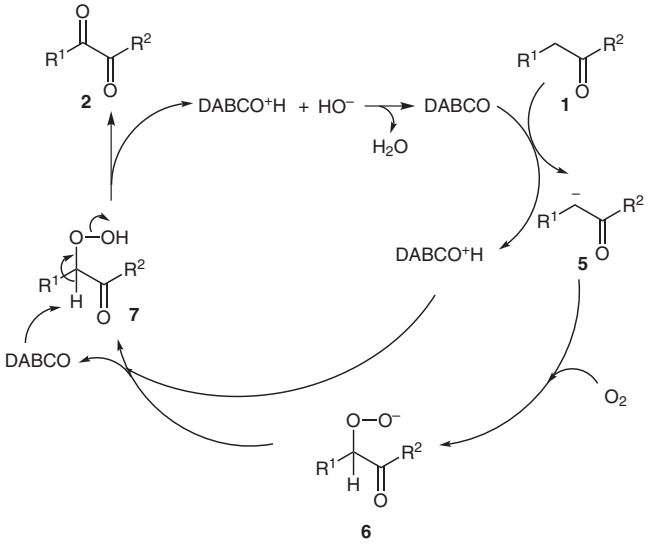
and nearly half of the starting material remained unchanged and could be recovered (Table 1, entries 17–18). A control experiment showed that the oxidation did not occur in the absence of any base (Table 1, entry 19). Thus, the optimal reaction conditions for this oxidation were established: 0.5 mmol of **1a**, 20 mol% of DABCO, and performing the reaction in *N*,*N*-dimethylformamide at 90 °C for 24 hours.

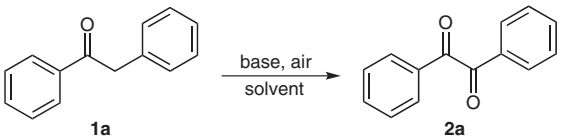
Under the optimized reaction conditions, the DABCO-catalyzed aerobic oxidation of other ketones were further examined to explore the scope and generality of the method. As seen in Table 2, all the deoxybenzoin reactions examined underwent the oxidation smoothly to give the corresponding benzils in excellent yields (Table 2, entries 1–10). The substrate 1-(4-methoxyphenyl)propan-2-one (**1k**) showed low reactivity; treatment of **1k** with 20 mol% of DABCO at 90 °C in *N*,*N*-dimethylformamide for 48 hours gave the desired 1,2-diketone in only 46% yield, along with the formation of 4-methoxybenzaldehyde as a byproduct in 13% isolated yield (Table 2, entry 11). Further attempts to increase the yield were unsuccessful. When 1-(4-fluorophenyl)propan-2-one, bearing a strong electon-withdrawing substituent in the benzyl group, was used as a substrate, no reaction occurred (Table 2, entry 12). Propiophenone also failed to undergo the oxidation and could be recovered (Table 2, entry 13).

On the basis of previous reports[10,12] and on our experimental results, a plausible mechanism for the oxidation is postulated in Scheme 1. First, carbanion **5** is formed through deprotonation of the ketone **1** in the presence of DABCO. The intermediate **5** then reacts with triplet oxygen by a radical chain process to generate the α-hydroperoxy ketone anion **6**,[10b,c] which then yields α-hydroperoxy ketone **7**. Lastly, intermediate **7** undergoes an elimination reaction in the presence of DABCO to form the product 1,2-diketone **2**.[10c]



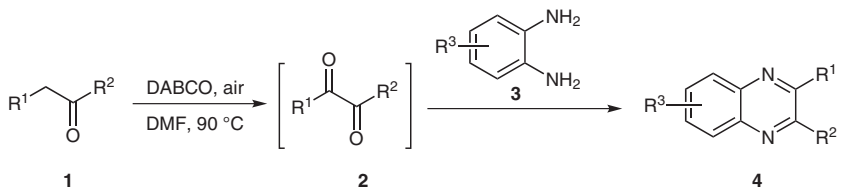
Scheme 1 Plausible mechanism for the oxidation

Table 1 Synthesis of Benzil by Aerobic Oxidation of Deoxybenzoin[a]



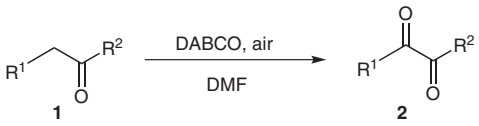
Entry	Catalyst (mol%)	Solvent	Temp (°C)	Time (h)	Conv. (%)[b]	Yield (%)[c]
1	DABCO (5)	DMF	90	24	32	32
2	DABCO (10)	DMF	90	24	65	63
3	DABCO (20)	DMF	90	24	100	98 (95)
4	DABCO (20)	DMF	70	24	81	81
5	DABCO (20)	DMF	50	24	32	32
6	DABCO (20)	DMF	90	10	77	76
7	DABCO (20)	toluene	90	24	65	44
8	DABCO (20)	DME	90	24	98	95
9	DABCO (20)	H_2O	90	24	39	31
10	DABCO (20)	1,4-dioxane	90	24	45	0
11	DABCO (20)	DMSO	90	24	68	61
12	DMAP (20)	DMF	90	24	22	14
13	DBU (20)	DMF	90	24	25	18
14	DIPEA (20)	DMF	90	24	0	0
15	pyridine (20)	DMF	90	24	20	11
16	Ph_3P (20)	DMF	90	24	12	10
17	MeONa (20)	DMF	90	24	42	38
18	KOH (20)	DMF	90	24	48	45
19	–	DMF	90	24	0	0

[a] Reaction conditions: deoxybenzoin (0.5 mmol), solvent (1.5 mL).
[b] Determined by GC analysis.
[c] Determined by GC analysis; number in parenthesis is isolated yield.



Scheme 2 One-pot synthesis of substituted quinoxaline derivatives from *o*-phenylenediamines and benzyl ketones

Table 2 Aerobic Oxidation of Various Deoxybenzoins Catalyzed by DABCO in *N*,*N*-Dimethylformamide[a]



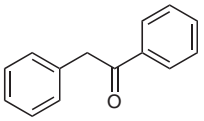
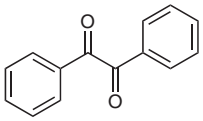
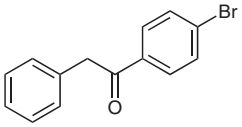
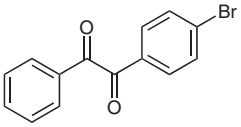
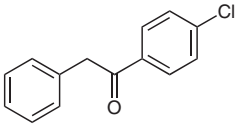
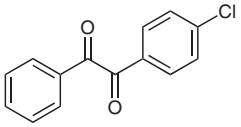
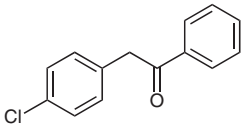
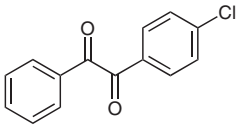
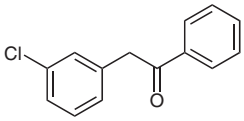
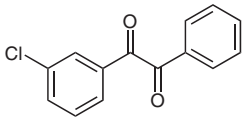
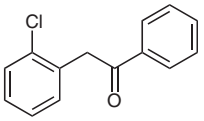
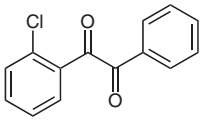
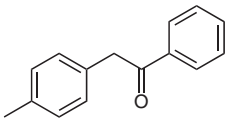
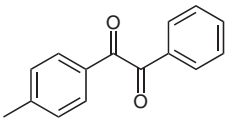
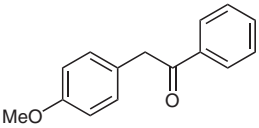
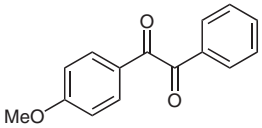
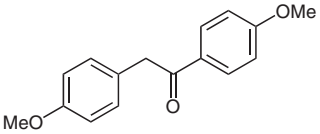
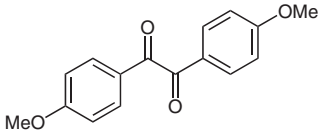
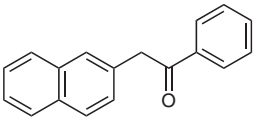
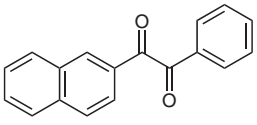
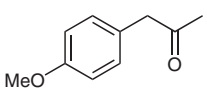
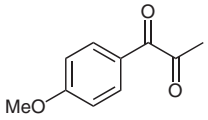
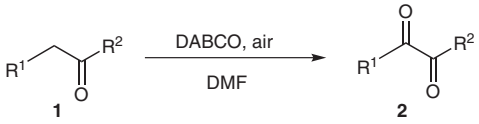
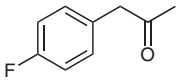
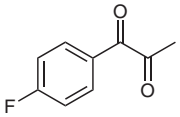
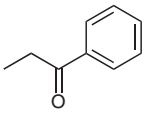
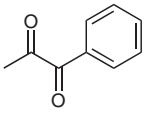
Entry	Substrate	Conv. (%)[b]	Product	Yield (%)[c]
1	**1a** 	100	**2a** 	95
2	**1b** 	100	**2b** 	99
3	**1c** 	99	**2c** 	100
4	**1d** 	100	**2c** 	93
5	**1e** 	100	**2e** 	99
6	**1f** 	100	**2f** 	95
7	**1g** 	99	**2g** 	98
8	**1h** 	100	**2h** 	97
9	**1i** 	100	**2i** 	100
10	**1j** 	100	**2j** 	95
11[d]	**1k** 	65	**2k** 	46

Table 2 Aerobic Oxidation of Various Deoxybenzoins Catalyzed by DABCO in *N*,*N*-Dimethylformamide[a] (continued)



Entry	Substrate	Conv. (%)[b]	Product	Yield (%)[c]
12	**1l** 	5	**2l** 	0
13	**1m** 	0	**2m** 	0

[a] Reaction conditions: ketone (0.5 mmol), DABCO (20 mol%), DMF (1.5 mL), 90 °C, 24 h.
[b] Determined by GC.
[c] Isolated yield.
[d] The reaction time was extended to 48 h.

In view of the success of this DABCO-catalyzed aerobic oxidation of deoxybenzoins to benzils, we envisioned that the newly developed procedure could be employed for the synthesis of substituted quinoxaline derivatives in a one-pot process (Scheme 2).

It is known that quinoxaline derivatives have shown a broad spectrum of biological activities, such as antibacterial and antiinflammatory activity.[13] In addition, they have found application in dyes,[14] efficient electroluminescent materials,[15] organic semiconductors,[16] and DNA cleaving agents.[17] The most common method for the synthesis of quinoxalines is the condensation of an aryl 1,2-diamine with 1,2-dicarbonyl compounds.[18] However, recently several alternative routes have been developed in which α-hydroxy ketones,[19] vicinal diols,[20] phenacyl bromides,[21] or even epoxides[22] were used as substitutes for 1,2-dicarbonyl compounds in the synthesis of quinoxalines.

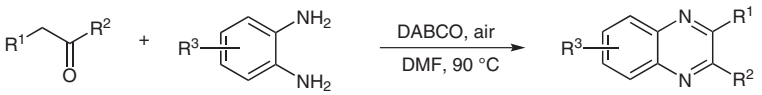
Among them, the work reported by Cho and co-workers[23] attracted our attention. They disclosed that quinoxalines could be synthesized by the reaction of *o*-phenylenediamines with ketones in PEG-400 in the presence of three equivalents of potassium hydroxide. However, the protocol suffers from low yields, long reaction time (60 h) and requires a large excess of base. In this context, we were interested in investigating the construction of quinoxalines from benzyl ketones and aromatic 1,2-diamines through a oxidation–cyclization process using DABCO as catalyst (Table 3).

We began the study by treating an equimolar amount of deoxybenzoin with *o*-phenylenediamine in DMF in the presence of 20 mol% DABCO at 90 °C under an atmosphere of air. To our surprise, the reaction was complete within three hours, affording the desired quinoxaline **4aa** in 92% isolated yield (Table 3, entry 1). Other deoxybenzoins were subjected to the reaction and all furnished the corresponding quinoxalines in good to excellent yields (Table 3, entries 2–6). The reaction of 1,2-bis(4-methoxyphenyl)ethanone also gave the desired product **4ia** in 91% isolated yield, but required a longer time (12 h) to accomplish the reaction (Table 3, entry 7). These results revealed that the presence of the electron-donating methoxy group in the benzene ring may retard the nucleophilic attack on the dicarbonyl formed in situ, leading to a lower reaction rate.

Pleasingly, the reaction of a range of alkyl benzyl ketones with *o*-phenylenediamine also proceeded smoothly to give the corresponding products in 73–89% isolated yields (Table 3, entries 8–12). Note that 1-(4-fluorophenyl)propan-2-one, which did not undergo the aerobic oxidation alone (Table 2, entry 12), could readily react with *o*-phenylenediamine to produce **4la** in 78% yield after six hours. This result indicated that the reaction may not proceed through the route shown in Scheme 2. Several other 1,2-diamines were further subjected to the reaction and all gave the corresponding quinoxalines in high yields (Table 3, entries 13–16). In the case of 4-nitrobenzene-1,2-diamine a lower reaction rate was observed, indicating that the strong electron-withdrawing nitro group in the diamine decreases its nucleophilicity (Table 3, entry 13). When 4-methylbenzene-1,2-diamine was treated with one equivalent of 1-phenylhexan-2-one, the two corresponding regioisomers were furnished in 85% overall yield (Table 3, entry 17).

Based on the above results, in Scheme 3 we propose a plausible mechanism for the reaction of benzyl ketones and aromatic 1,2-diamines. We suggest that the reaction involves the initial formation of imine **8** by condensation between **1** and **3**. Then, the oxidation of **8** by air, in the presence of DABCO, produces the intermediate **9**. Finally, the intermediate **9** yields the product **4** by intramolecular cyclization. Alternatively, hydrolyzation of intermediate **9** may result in the formation of diketone **2**, which can also undergo the condensation with **3** to form the product **4**.

Table 3 Synthesis of Quinoxaline Derivatives from Benzyl Ketones and *o*-Phenylenediamines[a]



1 3 4

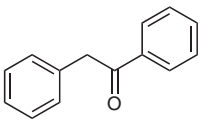
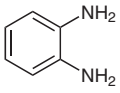
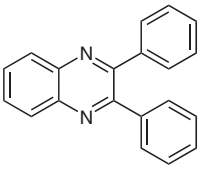
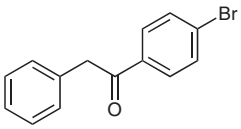
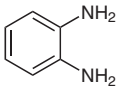
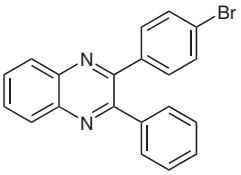
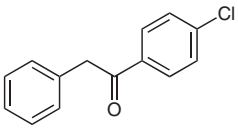
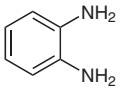
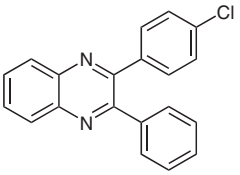
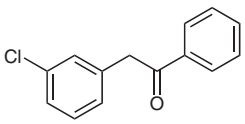
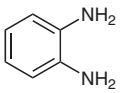
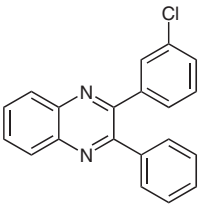
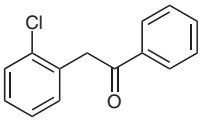
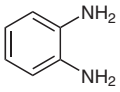
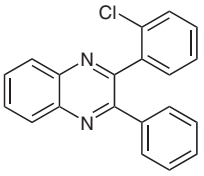
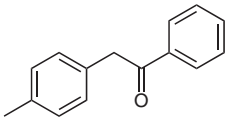
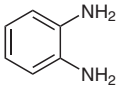
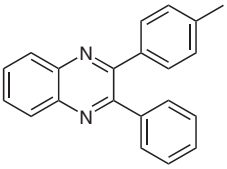
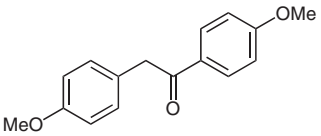
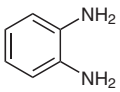
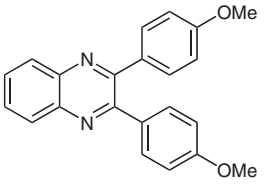
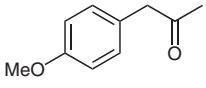
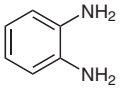
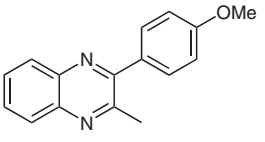
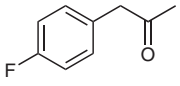
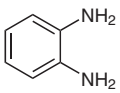
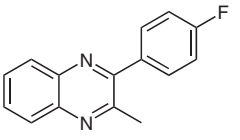
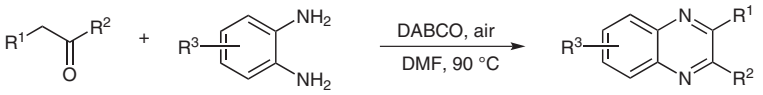
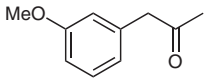
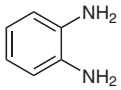
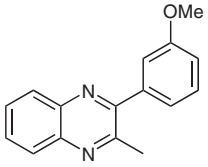
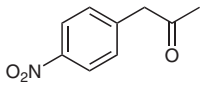
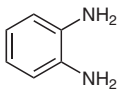
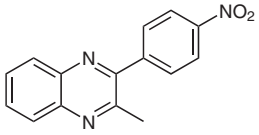
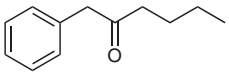
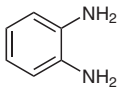
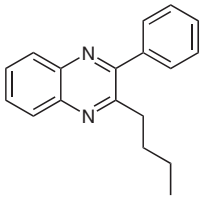
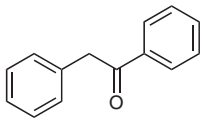
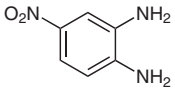
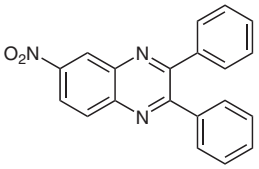
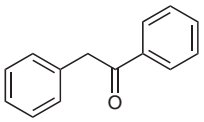
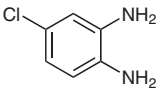
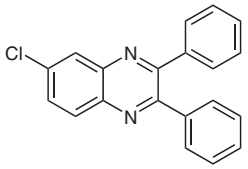
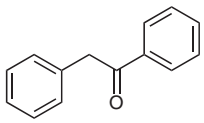
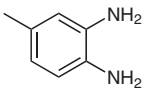
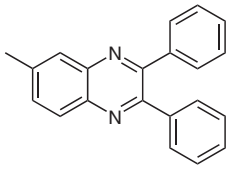
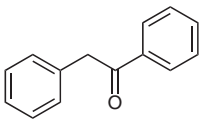
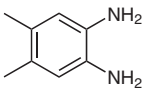
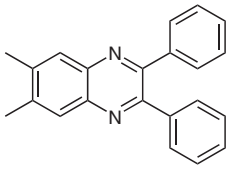
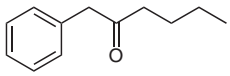
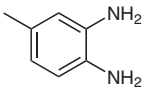
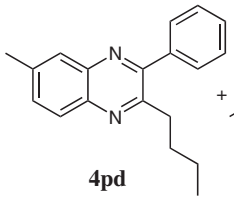
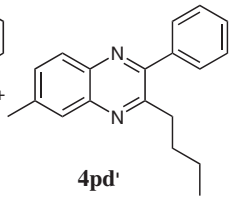
Entry	Benzyl ketone	*o*-Phenylenediamine	Product	Time (h)	Yield (%)
1	**1a** 	**3a** 	**4aa** 	3	92
2	**1b** 	**3a** 	**4ba** 	3	99
3	**1c** 	**3a** 	**4ca** 	3	96
4	**1e** 	**3a** 	**4ea** 	3	90
5	**1f** 	**3a** 	**4fa** 	3	85
6	**1g** 	**3a** 	**4ga** 	3	86
7	**1i** 	**3a** 	**4ia** 	12	86
8	**1k** 	**3a** 	**4ka** 	6	87
9	**1l** 	**3a** 	**4la** 	6	78

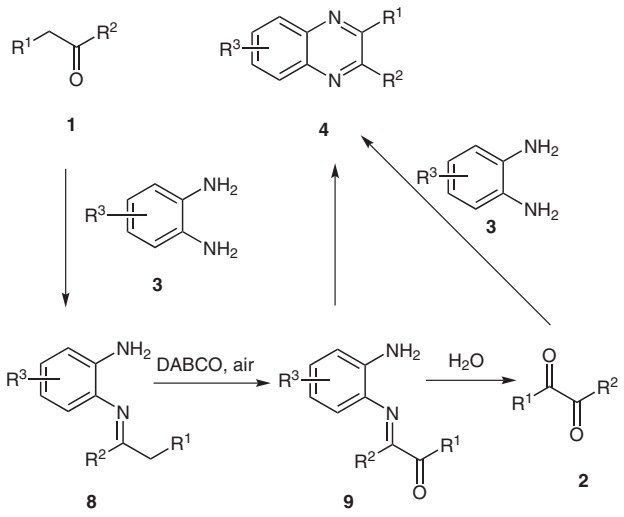
Table 3 Synthesis of Quinoxaline Derivatives from Benzyl Ketones and *o*-Phenylenediamines[a] (continued)



1 3 4

Entry	Benzyl ketone	*o*-Phenylenediamine	Product	Time (h)	Yield (%)
10	**1n** 	**3a** 	**4na** 	6	73
11	**1o** 	**3a** 	**4oa** 	6	83
12	**1p** 	**3a** 	**4pa** 	6	89
13	**1a** 	**3b** 	**4ab** 	12	83
14	**1a** 	**3c** 	**4ac** 	4	90
15	**1a** 	**3d** 	**4ad** 	4	86
16	**1a** 	**3e** 	**4ae** 	4	94
17	**1p** 	**3d** 	**4pd**  + **4pd'** 	6	85 (50:50)

[a] Reaction conditions: **1** (0.5 mmol), **3** (0.5 mmol), DABCO (20 mol%), DMF (1.5 mL), 90 °C.



Scheme 3 Proposed mechanism for the synthesis of quinoxalines from *o*-phenylenediamines and benzyl ketones

In conclusion, we have successfully demonstrated a simple and highly efficient method for the synthesis of benzils by the aerobic oxidation of deoxybenzoins using DABCO as catalyst with air as the sole oxidant. Furthermore, the procedure can be extended to the one-pot preparation of substituted quinoxaline derivatives from benzyl ketones and aromatic 1,2-diamines.

^{1}H NMR spectra were recorded with a Bruker DRX-400 spectrometer; $CDCl_3$ was used as solvent and TMS as an internal standard. GC analyses were performed on a GC-7900 chromatograph with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m). Mass spectra were recorded with a Shimadzu GCMS-QP5050A mass spectrometer at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). IR spectra were recorded with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. High resolution mass spectra were recorded with a Thermo MAT95XP (EI) mass spectrometer. Compunds **1d–f**, **1h**, and **1j** were synthesized according to the literature procedure.[24] Other chemicals were purchased from commercial sources and used without further purification.

1,2-Diketones 2; General Procedure

A mixture of ketone **1** (0.5 mmol) and DABCO (20 mol%) in DMF (1.5 mL) was stirred at 90 °C for 24 h in air. After completion of the reaction, the mixture was cooled to r.t., then poured into H_2O (20 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were then washed with brine (2 × 20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The crude mixture was then purified by column chromatography on silica gel (PE–EtOAc, 10:1) to give 1,2-diketone **2**.

Benzil (2a)[1f]

Yellow solid; mp 94–95 °C.

IR (KBr): 3066, 1665, 1590, 1448, 1320, 1210, 1172, 874, 794, 718, 685 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (t, *J* = 8.0 Hz, 4 H), 7.70 (t, *J* = 8.0 Hz, 2 H), 8.02 (d, *J* = 8.0 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.0, 129.8, 132.9, 134.8, 194.5.

MS (70 eV): *m*/*z* (%) = 210 [M]$^+$, 152, 105 (100), 77, 28.

1-(4-Bromophenyl)-2-phenylethane-1,2-dione (2b)[1f]

Yellow solid; mp 84–85 °C.

IR (KBr): 3088, 1668, 1581, 1450, 1313, 1209, 1173, 875, 831, 752, 708 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (t, *J* = 7.6 Hz, 2 H), 7.64–7.68 (m, 3 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 7.94 (t, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.1, 129.9, 130.5, 131.2, 131.7, 132.4, 132.7, 135.1, 193.3, 193.8.

MS (70 eV): *m*/*z* (%) = 288 [M]$^+$, 209, 183, 155, 105 (100), 77, 28.

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (2c)[25]

Yellow solid; mp 73–75 °C.

IR (KBr): 3091, 1670, 1588, 1450, 1317, 1209, 1172, 1091, 1012, 875, 835, 796, 712, 682 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.53 (m, 4 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.89–7.96 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.0, 129.4, 130.0, 131.3, 132.8, 135.1, 141.6, 193.1, 193.9.

MS (70 eV): *m*/*z* (%) = 244 [M]$^+$, 209, 139, 105 (100), 77, 28.

1-(3-Chlorophenyl)-2-phenylethane-1,2-dione (2e)[26]

Yellow solid; mp 88–89 °C.

IR (KBr): 3069, 1667, 1581, 1427, 1299, 1204, 1173, 896, 798, 756, 720, 672 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.53 (m, 3 H), 7.59–7.65 (m, 2 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.94–7.96 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.1, 129.1, 129.5, 129.9, 130.3, 132.6, 134.4, 134.8, 135.1, 135.4, 192.9, 193.6.

MS (70 eV): *m*/*z* (%) = 244 [M]$^+$, 209, 139, 105 (100), 77, 28.

1-(2-Chlorophenyl)-2-phenylethane-1,2-dione (2f)[25]

Yellow oil.

IR (KBr): 3065, 1677, 1590, 1442, 1313, 1252, 1206, 1179, 1072, 860, 789, 743, 687 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.44 (m, 2 H), 7.50–7.54 (m, 3 H), 7.65 (t, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 7.6, 1 H), 8.02 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.4, 128.9, 130.2, 130.5, 132.1, 132.4, 133.8, 134.0, 134.5, 134.6, 192.0, 193.7.

MS (70 eV): *m*/*z* (%) = 244 [M]$^+$, 209, 139, 105 (100), 77, 28.

1-Phenyl-2-*p*-tolylethane-1,2-dione (2g)[25]

Yellow oil.

IR (KBr): 3060, 2931, 1674, 1602, 1449, 1319, 1213, 1173, 1113, 881, 750, 717, 680 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.48 (t, *J* = 8.0 Hz, 2 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 2 H), 7.95 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 128.9, 129.6, 129.7, 129.9, 130.4, 132.9, 134.7, 146.1, 194.2, 194.7.

MS (70 eV): *m*/*z* (%) = 224 [M]$^+$, 119 (100), 91, 77, 28.

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (2h)[1f]

Yellow oil.

IR (KBr): 3065, 2935, 2843, 1671, 1597, 1510, 1453, 1314, 1264, 1217, 1167, 1024, 879, 842, 758, 718, 684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 7.65 (t, *J* = 8.0 Hz, 1 H), 7.95–7.99 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 114.5, 126.3, 129.0, 129.9, 132.4, 133.4, 134.6, 165.1, 193.1, 194.8.

MS (70 eV): *m*/*z* (%) = 240 $[M]^+$, 135 (100), 107, 77, 28.

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (2i)[25]
Yellow solid; mp 132–133 °C.

IR (KBr): 3051, 1652, 1598, 1508, 1423, 1312, 1261, 1162, 1014, 877, 830, 790, 746, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 6 H), 6.95 (d, *J* = 8.8 Hz, 4 H), 7.92 (d, *J* = 8.8 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 114.2, 126.2, 132.3, 164.8, 193.4.

MS (70 eV): *m*/*z* (%) = 270 $[M]^+$, 135 (100), 107, 92, 77.

1-(Naphthalen-3-yl)-2-phenylethane-1,2-dione (2j)[27]
Brown solid; mp 84–85 °C.

IR (KBr): 3061, 1671, 1594, 1453, 1370, 1245, 1174, 904, 761, 715, 674 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.66 (m, 5 H), 7.87–8.08 (m, 6 H), 8.39 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.6, 127.2, 127.9, 129.0, 129.2, 129.5, 129.9, 130.0, 130.3, 132.3, 133.1, 133.6, 134.9, 136.4, 194.6.

MS (70 eV): *m*/*z* (%) = 270 $[M]^+$, 155 (100), 127, 105, 77, 28.

1-(4-Methoxyphenyl)propane-1,2-dione (2k)[28]
White solid; mp 44–45 °C.

IR (KBr): 3049, 1679, 1601, 1463, 1425, 1247, 1169, 924, 843, 769, 674 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H), 3.88 (s, 3 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 7.99 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 55.6, 114.2, 132.3, 132.8, 164.8, 190.0, 201.2.

MS (70 eV): *m*/*z* (%) = 178 $[M]^+$, 135 (100), 107, 77, 43, 28.

Quinoxalines 4; General Procedure
A mixture of ketone **1** (0.5 mmol), *o*-phenylenediamine **4** (0.5 mmol) and DABCO (20 mol%) in DMF (1.5 mL) was stirred at 90 °C under an atmosphere of air for the given time. After completion of the reaction, as indicated by TLC, the mixture was cooled to r.t., then poured into H_2O (20 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were then washed with brine (2 × 20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The crude mixture was then purified by column chromatography on silica gel (PE–EtOAc, 10:1) to give quinoxalines **4**.

2,3-Diphenylquinoxaline (4aa)[18c]
White solid; mp 124–125 °C.

IR (KBr): 3058, 1547, 1477, 1442, 1395, 1343, 1220, 1058, 1023, 976, 766, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.35 (m, 6 H), 7.50–7.53 (m, 4 H), 7.74–7.77 (m, 2 H), 8.16–8.19 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.2, 128.8, 129.2, 129.8, 129.9, 139.1, 141.2, 153.5.

MS (70 eV): *m*/*z* (%) = 282 $[M]^+$ (100), 205, 179, 141, 103, 76.

2-(4-Bromophenyl)-3-phenylquinoxaline (4ba)
White solid; mp 147–148 °C.

IR (KBr): 3057, 1539, 1481, 1392, 1340, 1242, 1066, 836, 801, 761, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.41 (m, 5 H), 7.45–7.52 (m, 4 H), 7.76–7.79 (m, 2 H), 8.14–8.18 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.5, 128.4, 129.0, 129.2, 129.8, 130.1, 130.2, 138.0, 138.8, 141.2, 141.3, 152.2, 153.2.

MS (70 eV): *m*/*z* (%) = 360 $[M]^+$ (100), 281, 257, 205, 178, 140, 77.

HRMS: *m*/*z* calcd for $C_{20}H_{13}BrN_2$: 360.0262; found: 360.0248.

2-(4-Chlorophenyl)-3-phenylquinoxaline (4ca)
White solid; mp 142–143 °C.

IR (KBr): 3060, 1593, 1552, 1485, 1396, 1342, 1242, 1221, 1092, 1054, 1017, 838, 805, 764, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.38 (m, 5 H), 7.46–7.52 (m, 4 H), 7.75–7.79 (m, 2 H), 8.15–8.19 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.4, 128.5, 129.0, 129.2, 129.8, 130.1, 131.2, 135.1, 137.5, 138.8, 141.2, 141.3, 152.1, 153.2.

MS (70 eV): *m*/*z* (%) = 316 $[M]^+$ (100), 281, 213, 178, 140, 76.

HRMS: *m*/*z* calcd for $C_{20}H_{13}ClN_2$: 316.0767; found: 316.0755.

2-(3-Chlorophenyl)-3-phenylquinoxaline (4ea)
White solid; mp 112–113 °C.

IR (KBr): 3061, 1564, 1477, 1341, 1221, 1178, 1059, 984, 762, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.37 (m, 6 H), 7.50–7.52 (m, 2 H), 7.65 (s, 1 H),7.76–7.79 (m, 2 H), 8.16–8.18 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.2, 128.4, 128.9, 129.0, 129.2, 129.3, 129.8, 129.9, 130.2, 130.3, 134.4, 138.7, 140.8, 141.1, 141.4, 151.8, 153.2.

MS (70 eV): *m*/*z* (%) = 316 $[M]^+$ (100), 281, 213, 178, 140, 76.

HRMS: *m*/*z* calcd for $C_{20}H_{13}ClN_2$: 316.0767; found: 316.0764.

2-(2-Chlorophenyl)-3-phenylquinoxaline (4fa)
White solid; mp 123–124 °C.

IR (KBr): 3060, 1561, 1479, 1437, 1344, 1242, 1077, 1042, 978, 764, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.37 (m, 6 H), 7.50–7.52 (m, 3 H), 7.77–7.84 (m, 2 H), 8.18–8.24 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.0, 128.0, 128.8, 129.2, 129.4, 129.8, 130.0, 130.1, 130.4, 131.4, 133.0, 138.4, 138.5, 140.8, 141.8, 152.1, 153.8.

MS (70 eV): *m*/*z* (%) = 316 $[M]^+$, 281 (100), 213, 178, 140, 76.

HRMS: *m*/*z* calcd for $C_{20}H_{13}ClN_2$: 316.0767; found: 316.0764.

2-Phenyl-3-*p*-tolylquinoxaline (4ga)
White solid; mp 115–116 °C.

IR (KBr): 3058, 2921, 1548, 1476, 1448, 1343, 1242, 1053, 1022, 977, 831, 804, 764, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.31–7.36 (m, 3 H), 7.41 (d, *J* = 8.0 Hz, 2 H), 7.52–7.54 (m, 2 H), 7.73–7.75 (m, 2 H), 8.15–8.18 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 128.2, 128.7, 129.0, 129.2, 129.7, 129.8, 136.2, 138.8, 139.3, 141.1, 141.3, 153.5.

MS (70 eV): *m*/*z* (%) = 296 $[M]^+$ (100), 281, 193, 178, 147, 76.

HRMS: *m*/*z* calcd for $C_{21}H_{10}N_2$: 296.1313; found: 296.1310.

2,3-Bis(4-methoxyphenyl)quinoxaline (4ia)[18e]
White solid; mp 149–150 °C.

IR (KBr): 3060, 2934, 2836, 1607, 1512, 1463, 1342, 1296, 1250, 1176, 1029, 834, 764 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 6 H), 6.87 (d, *J* = 8.8 Hz, 4 H), 7.49 (d, *J* = 8.8 Hz, 4 H), 7.70–7.72 (m, 2 H), 8.11–8.13 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 113.8, 129.0, 129.5, 131.2, 131.7, 141.1, 153.0, 160.2.

MS (70 eV): *m*/*z* (%) = 342 $[M]^+$ (100), 311, 255, 209, 166, 133, 103, 76.

2-(4-Methoxyphenyl)-3-methylquinoxaline (4ka)
White solid; mp 99–100 °C.

IR (KBr): 3060, 2999, 2959, 2837, 1608, 1513, 1478, 1395, 1341, 1292, 1250, 1178, 1031, 998, 840, 764 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.80 (s, 3 H), 3.88 (s, 3 H), 7.03–7.06 (m, 2 H), 7.63–7.65 (m, 2 H), 7.68–7.71 (m, 2 H), 8.04–8.12 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 55.4, 114.0, 128.2, 129.1, 129.4, 130.5, 131.4, 141.0, 141.1, 152.6, 154.5, 160.3.

MS (70 eV): *m*/*z* (%) = 250 $[M]^+$, 249 (100), 219, 166, 117, 90, 76.

HRMS: *m*/*z* calcd for $C_{16}H_{14}N_2O$: 250.1106; found: 250.1089.

2-(4-Fluorophenyl)-3-methylquinoxaline (4la)[29]
White solid; mp 78–79 °C.

IR (KBr): 3061, 2966, 2926, 1602, 1559, 1511, 1481, 1341, 1229, 1160, 1004, 845, 763 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.77 (s, 3 H), 7.20 (t, *J* = 8.4 Hz, 2 H), 7.64–7.67 (m, 2 H), 7.70–7.76 (m, 2 H), 8.04–8.10 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 115.6, 128.3, 129.2, 129.8, 130.9, 135.1, 140.9, 141.2, 152.3, 153.8, 163.3.

MS (70 eV): *m*/*z* (%) = 238 $[M]^+$, 237 (100), 197, 170, 117, 76.

2-(3-Methoxyphenyl)-3-methylquinoxaline (4na)
Yellow oil.

IR (KBr): 3061, 2931, 2837, 1590, 1484, 1460, 1341, 1254, 1171, 1125, 1049, 1020, 857, 763 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.78 (s, 3 H), 3.88 (s, 3 H), 7.02–7.05 (m, 1 H), 7.18–7.22 (m, 2 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.70–7.76 (m, 2 H), 8.05–8.13 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.3, 55.4, 114.5, 114.8, 121.2, 128.3, 129.2, 129.6, 129.7, 140.3, 140.9, 141.2, 152.5, 154.5, 159.7.

MS (70 eV): *m*/*z* (%) = 250 $[M]^+$, 249 (100), 219, 166, 117, 90, 76.

HRMS: *m*/*z* calcd for $C_{16}H_{14}N_2O$: 250.1106; found: 250.1097.

2-Methyl-3-(4-nitrophenyl)quinoxaline (4oa)
Yellow solid; mp 137–138 °C.

IR (KBr): 3070, 2967, 2852, 1598, 1518, 1480, 1345, 1112, 1001, 858, 759, 714 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.79 (s, 3 H), 7.75–7.82 (m, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 8.10 (t, *J* = 9.6 Hz, 2 H), 8.39 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 123.7, 128.5, 129.3, 129.7, 130.2, 130.6, 140.8, 141.6, 145.3, 148.1, 151.6, 152.4.

MS (70 eV): *m*/*z* (%) = 265 $[M]^+$, 218 (100), 178, 151, 117, 90, 76.

HRMS: *m*/*z* calcd for $C_{15}H_{11}N_3O_2$: 265.0851; found: 265.0843.

2-Butyl-3-phenylquinoxaline (4pa)[19g]
Yellow oil.

IR (KBr): 3060, 2958, 2930, 2866, 1558, 1476, 1453, 1344, 1217, 1174, 1078, 1009, 763, 701 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.6 Hz, 3 H), 1.26–1.36 (m, 2 H), 1.68–1.76 (m, 2 H), 3.04 (t, *J* = 8.0 Hz, 2 H), 7.46–7.54 (m, 3 H), 7.60–7.62 (m, 2 H), 7.67–7.73 (m, 2 H), 8.08–8.12 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 22.6, 31.1, 35.8, 128.5, 128.8, 129.1, 129.2, 129.6, 139.2, 140.7, 141.5, 155.0, 156.3.

MS (70 eV): *m*/*z* (%) = 262 $[M]^+$, 219 (100), 178, 109, 77.

6-Nitro-2,3-diphenylquinoxaline (4ab)[18d]
Yellow solid; mp 188–189 °C.

IR (KBr): 3062, 1564, 1482, 1434, 1341, 1219, 1126, 1069, 816, 762 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.47 (m, 6 H), 7.57–7.60 (m, 4 H), 8.32 (d, *J* = 9.2 Hz, 1 H), 8.53–8.56 (m, 1 H), 9.10 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.3, 125.6, 128.4, 129.6, 129.7, 129.8, 129.9, 130.7, 138.0, 138.1, 140.0, 143.6, 147.9, 155.7, 156.3.

MS (70 eV): *m*/*z* (%) = 327 $[M]^+$, 281, 178, 141, 104, 75 (100).

6-Chloro-2,3-diphenylquinoxaline (4ac)[18d]
White solid; mp 122–123 °C.

IR (KBr): 3059, 1600, 1546, 1470, 1445, 1341, 1243, 1189, 1069, 1026, 977, 922, 833, 766, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.37 (m, 6 H), 7.50 (d, *J* = 6.8 Hz, 4 H), 7.67–7.70 (m, 1 H), 8.09 (d, *J* = 8.8 Hz, 1 H), 8.16 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.1, 128.3, 129.0, 129.1, 129.8, 130.4, 130.9, 135.6, 138.7, 139.7, 141.5, 153.6, 154.3.

MS (70 eV): *m*/*z* (%) = 316 $[M]^+$ (100), 280, 239, 213, 178, 151, 110, 75.

6-Methyl-2,3-diphenylquinoxaline (4ad)[18d]
White solid; mp 116–117 °C.

IR (KBr): 3057, 2092, 1550, 1487, 1344, 1246, 1060, 1025, 829, 770, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.64 (s, 3 H), 7.34–7.38 (m, 6 H), 7.52–7.55 (m, 4 H), 7.62–7.64 (m, 1 H), 7.98 (s, 1 H), 8.09 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 128.0, 128.2, 128.6, 128.7, 129.8, 132.3, 139.3, 139.7, 140.4, 141.3, 152.6, 153.3.

MS (70 eV): *m*/*z* (%) = 296 $[M]^+$ (100), 281, 219, 192, 165, 140, 89.

6,7-Dimethyl-2,3-diphenylquinoxaline (4ae)[18f]
White solid; mp 174–175 °C.

IR (KBr): 3058, 2921, 1560, 1446, 1341, 1200, 1094, 1021, 802, 766, 695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.51 (s, 3 H), 2.78 (s, 3 H), 7.30–7.32 (m, 6 H), 7.51–7.58 (m, 5 H), 7.90 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 20.6, 125.9, 128.1, 128.2, 128.5, 129.8, 130.2, 132.9, 134.6, 137.7, 139.5, 139.6, 139.7, 140.2, 151.5, 151.7.

MS (70 eV): *m*/*z* (%) = 310 $[M]^+$ (100), 295, 233, 206, 165, 103, 77.

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