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PTSA-catalyzed One-pot Synthesis of Quinoxalines Using DMSO as the Oxidant

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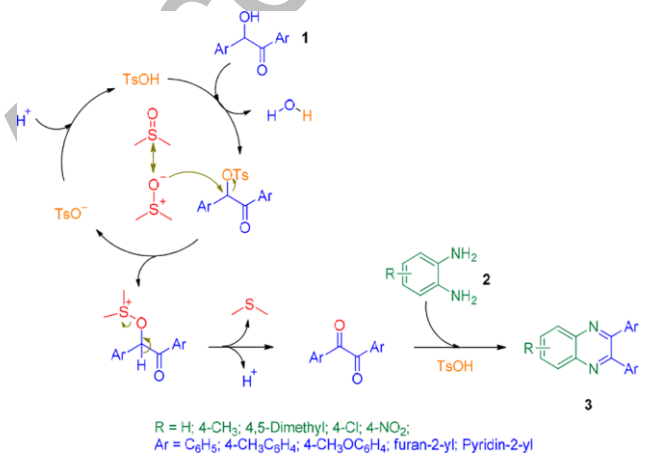
Abstract

An efficient PTSA catalyzed one-pot two-step oxidative system for cyclization of o-diaminobenzene with 1,2-diaryl-2-hydroxyethanone to quinoxalines was described. A nontoxic, readily available oxidant–DMSO was applied in this process. A broad range of substrates were applied to this method, and target compounds were obtained with good yields.

GRAPHICAL ABSTRACT



KEYWORDS: quinoxalines, PTSA-catalyzed, oxidant–DMSO, one-pot, transition metal-free, tandem process

INTRODUCTION

Quinoxaline derivatives are an important class of nitrogen-containing heterocyclic compounds and play an important role in pharmaceutical chemistry for their bioactivities, such as antiviral,[1] antibacterial,[2] anti-inflammatory,[3] anticancer and anthelmintic.[4] Furthermore, quinoxalines have been reported to be biocides,[5] dyes,[6] efficient electroluminescent materials,[7] pharmaceuticals,[8] and organic semiconductors.[9]

Many synthetic strategies have been reported for the preparation of substituted quinoxalines.[10] However, most of these methods suffer from expensive and detrimental metal precursors, harsh reaction conditions, critical product isolation procedures and unsatisfactory product yields which limit their use in green chemistry.

Since DMSO as Oxidant was first reported in 1956,[11] it has received significant attention. From previous literature, DMSO can act as an inexpensive, nontoxic, readily available oxidant for various organic transformations under mild and convenient conditions.[12] However, there is no example of quinoxaline synthesis using DMSO as oxidant.

Initially, we expected to isolate 2,4,5-triphenyloxazole from the cyclization reaction of benzoin with benzamide catalyzed by PTSA (p-toluene sulfonic acid, $TsOH \cdot H_2O$) in air atmosphere. Unexpectedly, benzil was obtained in a good yield (Scheme 1).

In the beginning, we assumed that benzil was generated by the oxidation of benzoin in air. However, benzil was still obtained in the presence of PTSA and DMSO under N_2 (Scheme 2). Kornblum reported that benzyl *p*-toluenesulfonate can be oxidized to benzaldehyde by DMSO. [11] Therefore, we eventually determined that benzil was obtained from *p*-toluenesulfonate intermediate by DMSO oxidation (Scheme 3, **a** and **b**).

Yao reported that Lewis acids catalyzed the cyclization of o-diaminobenzene with benzil to afford quinoxaline.[15a] Therefore, we carried out a one-pot two-step cyclization reaction of o-diaminobenzene with 1,2-diaryl-2-hydroxyethanone to afford the corresponding quinoxalines; 2,3-diphenylquinoxaline was obtained in a good yield (Scheme 3, **c**).

We have been focusing on the direct synthesis of heterocyclic systems using tandem reactions.[13] In this paper, we developed an efficient PTSA-catalyzed one-pot two-step oxidation reaction for the cyclization of *o*-diaminobenzene with 1,2-diaryl-2-hydroxyethanone to afford the corresponding quinoxalines.

RESULTS AND DISCUSSION

Although 2,3-diphenylquinoxaline was obtained in a good yield by the abovementioned method, the optimum condition for this reaction were determined. The results are summarized in Table 1.

First, several solvents were investigated under N_2 atmosphere, no product was detected until DMSO was used (Table 1, entries 1-6). Based on this result, several sulfonic acids such as TsOH, MSA (methanesulfonic acid), and TfOH (trifluoromethanesulfonic acid) were screened for the reaction. MSA and TfOH showed the same catalytic activity as TsOH (Table 1, entries 6-8). However, TfOH was selected as the catalyst for its low price. Furthermore, **3a** was not obtained without adding acid (Table 1, entry 9). The amount of TsOH was also investigated; 50 mol% TsOH resulted in the highest yield of 90% (Table 1, entries 6 and 10-12). A low yield (**3a**) was obtained when **1a** and **2a** were added simultaneously (Table 1, entry 13). Further, air had no significant effect on the reaction (Table 1, entry 14).

With the optimized conditions in hand, the substrate scope of this reaction was investigated and the results are summarized in Table 2. In the presence of electron-donating substituents on the amine part, the yields of the products increased. Low yields were obtained when electron- withdrawing substituents were present on the amine except **3ae**. In

contrast, electron-donating substituents on the aromatic ring attached to hydroxy ketones decreased the product yields and reversed the trend observed with the electron-withdrawing groups. Interestingly, considerable yields were obtained when nitro substituents group were present on the amines (**3ae**, **3be**, **3ce**, **3de** and **3ee**). Previous studies either did not achieve this result[14] or attempt this reaction[15]. The presence of an electron-donating group in hydroxy ketones may hinder the nucleophilic attack on the *in situ* formed dicarbonyl, leading to a lower yield. On the other hand, an electron-withdrawing substituent on the hydroxy ketone part resulted in a shorter reaction time in the oxidation process (Table 2, entries 20-23). Over all, both the catalyst and oxidant showed exceptionally high reactivity towards this reaction.

To gain some insights into the mechanism of the reaction, several control experiments were carried out (Scheme 5). Possible intermediate **1aa** was observed to react with **2a** to generate **3aa** in good yield without TsOH. The target molecule **3aa** was also obtained from possible intermediate **1ac** reacting with **2a** in the presence of TsOH.

Based on the above experiments, the possible mechanism for this reaction can be illustrated in Scheme 6. Firstly, the dehydration of benzion **1a** and PTSA could generate sulfonic acid ester **1aa**. And secondly, sulfonic acid ester **1aa** could be oxidized to benzyl

1ac by DMSO. In the end, PTSA could catalyze the cyclization of benzyl with diamine to quinoxaline.

CONCLUSIONS

A variety of quinoxaline derivatives were synthesized by cyclization of o-diaminobenzene with 1,2-diaryl-2-hydroxyethanone using PTSA as catalyst and DMSO as oxidant. Quinoxalines were obtained in good yields and this methodology applied to a broad range of substrates. Further studies on the application of this procedure to the synthesis of pharmaceutical compounds are in progress.

EXPERIMENTAL SECTION

Reagents were commercially available and were used without further purification. All reactions were monitored by thin-layer chromatography (TLC). ^{1}H NMR spectra were recorded on a Bruker Avance 400 or 300 spectrometer at 400 or 300 MHz, using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were run in the same instrument at 100 or 75 MHz. Melting points were determined on an XD-4 digital micro melting point apparatus. HRMS spectra were determined on a Q-TOF6510 spectrograph (Agilent).

General Procedure For The Synthesis Of Compounds 3

A mixture of 1,2-diaryl-2-hydroxyethanone **1** (1.0 mmol), PTSA (0.5 mmol) in DMSO (2 mL) was heated to 100 ^{o}C (TLC monitored). Then the mixture was added in o-diaminobenzene **2** (1 mmol), and stirred for 1 h. Then the mixture was cooled to room temperature and diluted with brine (30 mL) and extracted with dichloromethane twice (2 × 30 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed in vacuo to afford a residue. The residue was purified by column chromatography to afford **3**.

2,3-Diphenylquinoxaline (3aa).

White solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.19-8.14 (2H, m), 7.95-7.81 (2H, m), 7.50-7.47 (4H, m), 7.45-7.33 (6H, m); ^{13}C NMR (75 MHz, DMSO-d_6): δ 153.04, 140.43, 138.75, 130.38, 129.66, 129.55, 129.47, 128.78, 128.73, 128.01; HRMS calcd for $C_{20}H_{14}N_2$ $(M+H)^+$ 283.1230; found: 283.1232.

6-Methyl-2,3-Diphenylquinoxaline (3ab).

White solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.04 (1H, J = 8.4 Hz, d), 7.94 (1H, s), 7.71 (2H, J = 8.4, 1.8 Hz, dd), 7.48-7.45 (4H, m), 7.43-7.32 (6H, m), 2.59 (3H, s); ^{13}C NMR (75 MHz, DMSO-d_6): δ 152.82, 152.08, 140.52, 140.50, 138.92, 138.85, 132.52, 129.63, 128.64, 128.57, 128.32, 127.98, 127.47, 21.32; HRMS calcd for $C_{21}H_{16}N_2$ $(M+H)^+$ 297.1386; found: 297.1391.

6,7-Dimethyl-2,3-Diphenylquinoxaline (3ac).

White solid. ^{1}H NMR (300 M, $CDCl_3$): δ 7.92 (2H, s), 7.511-7.47 (4H, m), 7.35-7.26 (6H, m), 2.52 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.50, 140.53, 140.22, 139.38, 129.86, 128.53, 128.22, 128.19, 20.42; HRMS calcd for $C_{22}H_{18}N_2$ $(M+H)^+$ 311.1543; found: 311.1550.

6-Chloro-2,3-Diphenylquinoxaline (3ad).

White solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.25 (1H, J = 2.1 Hz, d), 8.19 (1H, J =9.0 Hz), 7.92 (1H, J = 2.1, 9.0 Hz, dd), 7.50-7.35 (10H, m); ^{13}C NMR (75 MHz, DMSO-d_6): δ 154.04, 153.45, 140.76, 139.10, 138.39, 138.33, 134.60, 130.94, 129.68, 129.65, 129.00, 128.04, 127.48; HRMS calcd for $C_{20}H_{13}ClN_2$ $(M+H)^+$ 317.0840; found: 317.0851.

6-Nitro-2,3-Diphenylquinoxaline (3ae).

Yellow solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.95 (1H, J = 1.8 Hz, d), 8.57 (1H, J = 1.8, 9.0 Hz, dd), 8.38 (1H, J = 9.3 Hz, d), 7.54-7.52 (4H, m), 7.48-7.37 (6H, m); ^{13}C NMR (75 MHz, DMSO-d_6): δ 156.04, 155.38, 147.64, 142.98, 139.21, 137.97, 137.94, 130.94, 129.79, 129.71, 129.5, 129.36, 128.13, 124.83, 123.57; HRMS calcd for $C_{20}H_{13}N_3O_2$ $(M+H)^+$ 328.1081; found: 328.1083.

2,3-Di-P-Tolylquinoxaline (3ba).

White solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.16-8.10 (2H, m), 7.89-7.83 (2H, m), 7.39 (4H, J = 8.1 Hz, d), 7.18 (4H, J = 7.8 Hz, d), 2.33 (6H, s); ^{13}C NMR (75 MHz, DMSO-d_6): δ 152.93, 140.34, 138.27, 136.04, 130.14, 129.56, 128.68, 128.64, 20.81; HRMS calcd for $C_{22}H_{18}N_2(M+H)^+$ 311.1543; found: 311.1542.

6-Methyl-2,3-Di-P-Tolylquinoxaline (3bb).

White solid. ^{1}H NMR (300 M, $CDCl_3$): δ 8.04 (1H, J = 8.4 Hz, d), 7.93 (1H, s), 7.57 (1H, J = 8.4, 1.8 Hz, dd), 7.41 (4H, J = 1.2, 7.8 Hz, dd), 7.13 (4H, J = 7.8 Hz, d), 2.60 (3H, s), 2.36 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.30, 152.59, 141.14, 140.18, 139.59, 138.65, 138.57,136.47, 132.02, 129.74, 129.71, 128.94, 128.60, 127.92, 21.87, 21.83;HR MS calcd for $C_{23}H_{20}N_2$ $(M+H)^+$ 325,1699; found: 325.1699.

6,7-Dimethyl-2,3-Di-P-Tolylquinoxaline (3bc).

White solid. ^{1}H NMR (300 M, $CDCl_3$): δ 7.89 (2H, s), 7.40 (4H, J = 8.1 Hz, d), 7.13 (4H, J = 8.1 Hz, d), 2.50 (6H, s), 2.360 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.49, 140.19, 140.09, 138.43, 136.63, 129.73, 128.90, 128.13, 21.32, 20.37; HRMS calcd for $C_{24}H_{22}N_2$ $(M+H)^+$ 339.1856; found: 339.1847.

6-Nitro-2,3-Di-P-Tolylquinoxaline (3be).

Yellow solid. ^{1}H NMR (300 M, $CDCl_3$): δ 9.40 (1H, J = 2.7 Hz, d), 8.49 (1H, J = 2.4, 9.0 Hz, dd), 8.25 (1H, J = 9.0 Hz, d), 7.49-7.45 (4H, m), 7.26-7.17 (4H, m), 2.39 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.32, 155.70, 147,71, 143.56, 140.02, 139.88, 139.83, 135.44, 135.38, 130.61, 129.84, 129.74, 129.18, 125.54, 123.03, 21.42; HRMS calcd for $C_{22}H_{17}N_3O_2$ $(M+H)^+$ 356.1394; found: 356.1390.

2,3-Bis(4-Methoxyphenyl)Quinoxaline (3ca).

White solid. ^{1}H NMR (300 M, $CDCl_3$): δ 8.17-8.12 (2H, m), 7.76-7.70 (2H, m), 7.52-7.48 (4H, m), 7.26-6.85 (4H, m), 3.84 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.24, 152.99, 140.96, 131.57, 131.28, 129.61, 128.94, 113.81, 55.31; HR MS calcd for $C_{22}H_{18}N_20_2$ $(M+H)^+$ 343.1441; found: 343.1442.

2,3-Bis(4-Methoxyphenyl)-6-Methylquinoxaline (3cb).

White solid. ^{1}H NMR (300 M, $CDCl_3$): δ 8.02 (1H, J = 8.4 Hz, d), 7.92 (1H, s), 7.56 (1H, J = 1.8, 8.7 Hz, dd), 7.51-7.45 (4H, m), 6.89-6.85 (4H, m), 3.83 (6H, s), 2.60 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.16, 160.09, 152.81, 152.12, 140.99, 140.11, 139.46, 131.93, 131.75, 131.70, 131.27, 131.22, 128.47, 127.78, 113.76, 55.30; HRMS calcd for $C_{23}H_{20}N_2O_2$ $(M+H)^+$ 357.1598; found: 357.1587.

2,3-Bis(4-Methoxyphenyl)-6,7-Dimethylquinoxaline (3cc).

White solid. ^{1}H NMR (300 M, $CDCl_3$): δ 7.89 (2H, s), 7.49-7.44 (4H, m), 6.89-6.84 (4H, m), 3.83 (6H, s), 2.50 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.98, 152.08, 140.06, 140.00, 132.09, 131.22, 128.10, 113.72, 55.31; HRMS calcd for $C_{24}H_{22}N_2O_2$ $(M+H)^+$ 371.1754; found: 371.1756.

6-Chloro-2,3-Bis(4-Methoxyphenyl)Quinoxaline (3cd).

White solid. ^{1}H NMR (300 M, $CDCl_3$): δ 8.13 (1H, J = 2.1 Hz, d), 8.07 (1H, J = 9.0Hz, d), 7.66 (1H, J = 2.4, 9.0 Hz, dd), 7.51-7.47 (4H, m), 6.90-6.85 (4H, m), 3.837 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.49, 160.42, 153,79,153.11,141.24, 139.42, 135.24, 131.32, 131.25, 131.20,131.13, 130.55, 130.13, 127.82, 113.86,55.33; HRMS calcd for $C_{22}H_{17}ClN_2O_2$ $(M+H)^+$ 377.1051; found: 377.1050.

2,3-Bis(4-Methoxyphenyl)-6-Nitroquinoxaline (3ce).

Yellow solid. ^{1}H NMR (300 M, $CDCl_3$): δ 9.02 (1H, J = 2.4 Hz, d), 8.48 (1H, J = 2.4, 9.0 Hz, dd), 8.24 (1H, J = 9.0Hz, d), 7.59-7.52 (4H, m), 6.92-6.89 (4H, t), 3.86 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.02, 160.87, 155.75, 155.17, 147.58, 143.46, 139.75, 131.50, 131.34, 130.64, 130.39, 125.39, 122.87, 113.98, 55.37; HRMS calcd for $C_{22}H_{17}N_3O_4$ $(M+H)^+$ 388.1292; found: 388.1393.

2,3-Di(Furan-2-Yl)Quinoxaline (3da).

Gray solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.14-8.08 (1H, m), 7.92-7.86 (4H, m), 6.74-6.72 (4H, m); ^{13}C NMR (75 MHz, DMSO-d_6): δ 150.31, 144.91, 142.07, 139.92, 130.90, 128.68, 112.85, 112.15; HRMS calcd for $C_{16}H_{10}N_2O_2$ $(M+H)^+$ 263.0815; found: 263.0827.

2,3-Di(Furan-2-Yl)-6-Methylquinoxaline (3db).

Gray solid. ^{1}H NMR (300 M, $CDCl_3$): δ 8.05 (2H, J = 8.4 Hz, d), 7.95 (1H, s), 7.62-7.57 (3H, t), 6.67-6.55 (4H, m), 2.60 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.89, 144.18, 144.04, 142.56, 141.85, 141.20, 140.68, 139.10, 132.84, 128.62, 127.94, 112.92, 112.64, 111.90, 111.87, 21.94; HRMS calcd for $C_{17}H_{12}N_2O_2$ $(M+H)^+$ 277.0972; found: 277.0970.

2,3-Di(Furan-2-Yl)-6,7-Dimethylquinoxaline (3dc).

Yellow solid. ^{1}H NMR (300 M, $CDCl_3$): δ 7.89 (2H, s), 7.606-7.60 (2H, t), 6.61-6.54 (4H, m), 2.50 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.08, 143.88, 141.85, 141.16, 139.64, 128.17, 112.38, 111.79, 20.41; HRMS calcd for $C_{18}H_{14}N_2O_2$ $(M+H)^+$ 291.1128; found: 291.1129.

6-Chloro-2,3-Di(Furan-2-Yl)Quinoxaline (3dd).

Gray solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.19 (1H, J = 2.1 Hz, d), 8.16 (1H, J = 9.0 Hz, d), 7.94-7.87 (3H, m), 6.78-6.72 (4H, m); ^{13}C NMR (75 MHz, DMSO-d_6): δ 150.03,

149.95, 145.32, 145.15, 142.83, 140.28, 138.59, 135.12, 131.37, 130.50, 127.36, 113.58, 113.28, 112.29, 112.25; HRMS calcd for $C_{16}H_9ClN_2O_2$ $(M+H)^+$ 297.0425; found: 297.0427.

2,3-Di(Furan-2-Yl)-6-Nitroquinoxaline (3de).

Yellow solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.83 (1H, J = 2.7 Hz, d), 8.51 (1H, J = 2.4, 9.3 Hz, dd), 8.27 (1H, J = 9.0 Hz, d), 8.00-7.98 (2H, m), 6.93-6.76 (4H, m); ^{13}C NMR (75 MHz, DMSO-d_6): δ 149.74, 149.64, 147.70, 146.10, 145.66, 144.20, 143.67, 143.48, 138.58, 130.43, 124.55, 123.86, 115.10, 114.26, 112.62, 112.43; HR MS calcd for $C_{16}H_9N_3O_4$ $(M+H)^+$ 308.0666; found: 308.0677.

2,3-Di(Pyridin-2-Yl)Quinoxaline (3ea).

Yellow solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.29-8.20 (4H, m), 8.03-7.93 (6H, m), 7.38-7.34 (2H, m); ^{13}C NMR (75 MHz, DMSO-d_6): δ 158.09, 153.54, 149.20, 141.37, 137.94, 132.14, 130.08, 125.01, 124.39; HRMS calcd for $C_{18}H_{12}N_4$ $(M+H)^+$ 285.1135; found: 285.1135.

6-Methyl-2,3-Di(Pyridin-2-Yl)Quinoxaline (3eb).

Yellow solid. ^{1}H NMR (300 M, $CDCl_3$): δ 8.39-8.37 (2H, m), 8.12 (1H, J = 8.7 Hz, d), 8.00-7.94 (3H, m), 7.85-7.78 (2H, m), 7.66 (1H, J = 8.7, 2.1 Hz, dd), 7.26-7.22 (2H, m);

^{13}C NMR (75 MHz, $CDCl_3$): δ 157.46, 152.18, 148.43, 141.27, 142.19, 139.69, 136.73, 132.90, 128.90, 124.32, 124.30, 122.95, 122.89, 21.95; HRMS calcd for $C_{19}H_{14}N_4$ $(M+H)^+$ 299.1291; found: 299.1294.

6-Chloro-2,3-Di(Pyridin-2-Yl)Quinoxaline (3ed).

Yellow solid. ^{1}H NMR (300 M, DMSO-d_6): δ 8.32-8.24 (4H, m), 8.03-7.93 (5H, m), 7.40-7.34 (2H, m); ^{13}C NMR (75 MHz, DMSO-d_6): δ 156.94, 156.90, 153.63, 153.04, 148.46, 140.95, 139.28, 137.22, 135.65, 131.94, 128.04, 124.29, 124.24, 123.82, 123.76; HRMS calcd for $C_{18}H_{11}ClN_4$ $(M+H)^+$ 319.0745; found: 319.0745.

6-Nitro-2,3-Di(Pyridin-2-Yl)Quinoxaline (3ee).

Yellow solid. ^{1}H NMR (300 M, DMSO-d_6): δ 9.04 (1H, J = 2.7 Hz, d), 8.49 (1H, J = 2.4, 9.0 Hz, dd), 8.25 (1H, J = 9.0 Hz, d), 7.49-7.45 (4H, m), 7.26-7.17 (4H, t); ^{13}C NMR (75 MHz, DMSO-d_6): δ 156.08, 154.93, 154.34, 148.18, 148.10, 142.75, 139.10, 137.01, 130.89, 124.95, 124.19, 124.08, 123.96, 123.81, 123.71; HRMS calcd for $C_{18}H_{11}N_5O_2$ $(M+H)^+$ 330.0986; found: 330.0981.

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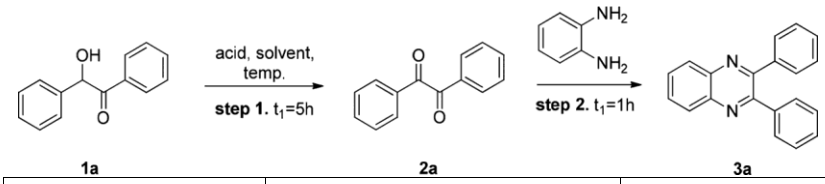
Table 1. Optimization of reaction conditions for the one-pot synthesis of 3a[a]



1a 2a 3a

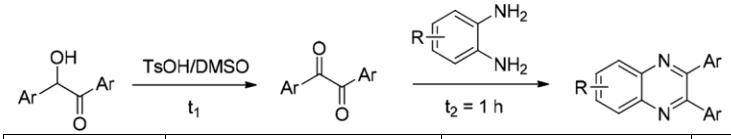
Entry	Acid	Solvent	Yield[b] (%)
1	TsOH·H_2O	DME	n.d
2	TsOH·H_2O	DCE	n.d
3	TsOH·H_2O	Toluene	n.d
4	TsOH·H_2O	PhCl	n.d
5	TsOH·H_2O	MeCN	n.d
6	TsOH·H_2O	DMSO	90
7	MSA	DMSO	91
8	TfOH	DMSO	90
9	none	DMSO	Trace
10[c]	TsOH·H_2O	DMSO	73
11[d]	TsOH·H_2O	DMSO	90
12[e]	TsOH·H_2O	DMSO	89
13[f]	TsOH·H_2O	DMSO	82
14[g]	TsOH·H_2O	DMSO	90

[a]Reaction conditions: **1a** (1 mmol), acid (50 mol%), solvent (2 mL), in a sealed tube at 100 ^oC under air atmosphere for 5h. This reaction mixture were added **2a** (1 mmol), until the disappearance of **2a**, monitored by TLC. [b] Yield of isolated product. [c] TsOH (40 mol%) was used. [d] TsOH (60 mol%) was used. [e] TsOH (80 mol%) was used. [f]

Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), acid (50 mol%), solvent (2 mL), in a sealed tube at 100 ^{o}C under air atmosphere for 5h. [g] Under air.

DME: 2-methoxyethyl ether; DCE: 1,2-dichloroethane.

Table 2. Scope of 4-substituted benzene-1,2-diamines and 2-hydroxy-1,2-diarylethanones[a]



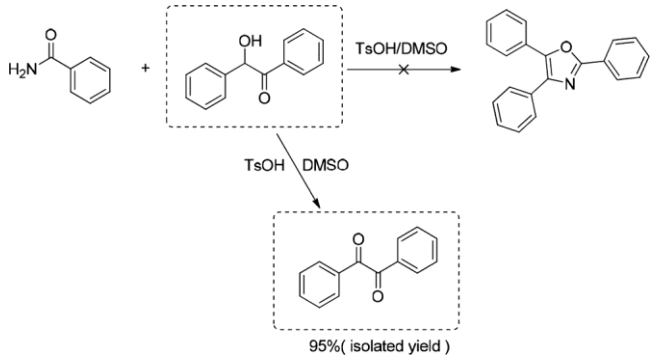
Entry	Ar	R	t_1 (h)	Product	Yield (%)b
1	C_6H_5	H	5	**3aa**	90
2	C_6H_5	4-CH_3	5	**3ab**	93
3	C_6H_5	4,5-Dimethyl	5	**3ac**	92
4	C_6H_5	4-Cl	5	**3ad**	85
5	C_6H_5	4-NO_2	5	**3ae**	92
6	4-$CH_3C_6H_4$	H	5	**3ba**	89
7	4-$CH_3C_6H_4$	4-CH_3	5	**3bb**	88
8	4-$CH_3C_6H_4$	4,5-Dimethyl	5	**3bc**	87
9	4-$CH_3C_6H_4$	4-NO_2	5	**3be**	84
10	4-$CH_3OC_6H_4$	H	6	**3ca**	85
11	4-$CH_3OC_6H_4$	4-CH_3	6	**3cb**	86
12	4-$CH_3OC_6H_4$	4,5-Dimethyl	6	**3cc**	85
13	4-$CH_3OC_6H_4$	4-Cl	6	**3cd**	81
14	4-$CH_3OC_6H_4$	4-NO_2	6	**3ce**	78
15	Furan-2-yl	H	5	**3da**	83
16	Furan-2-yl	4-CH_3	5	**3db**	85
17	Furan-2-yl	4,5-Dimethyl	5	**3dc**	87

18	Furan-2-yl	4-Cl	5	**3dd**	82
19	Furan-2-yl	4-NO_2	5	**3de**	80
20	Pyridin-2-yl	H	1	**3ea**	92
21	Pyridin-2-yl	4-CH_3	1	**3eb**	89
22	Pyridin-2-yl	4-Cl	1	**3ed**	88
23	Pyridin-2-yl	4-NO_2	1	**3ee**	87

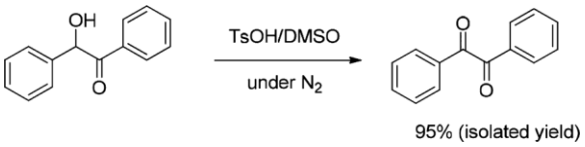
[a]Reaction conditions: 1,2-diaryl-2-hydroxyethanone **1** (1.0 mmol), PTSA (0.5 mmol) in DMSO (2 mL) was heated to 100 ^{o}C (TLC monitored), then o-diaminobenzene (1 mmol)was added.

[b]Isolated yield

Scheme 1. A serendipity.

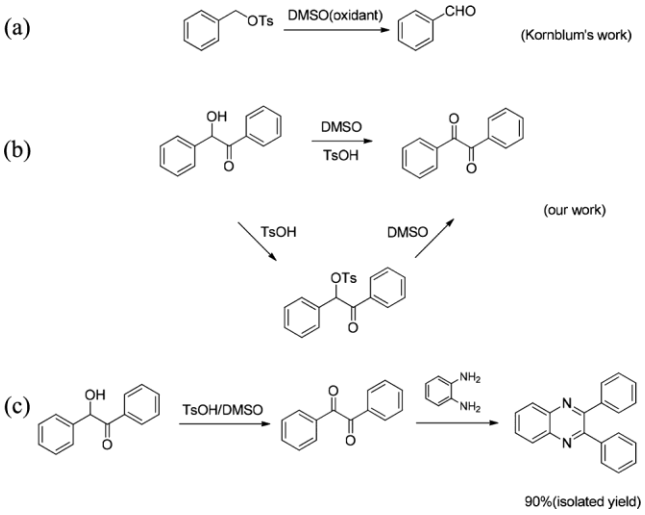


Scheme 2. Repeated test under N_2.

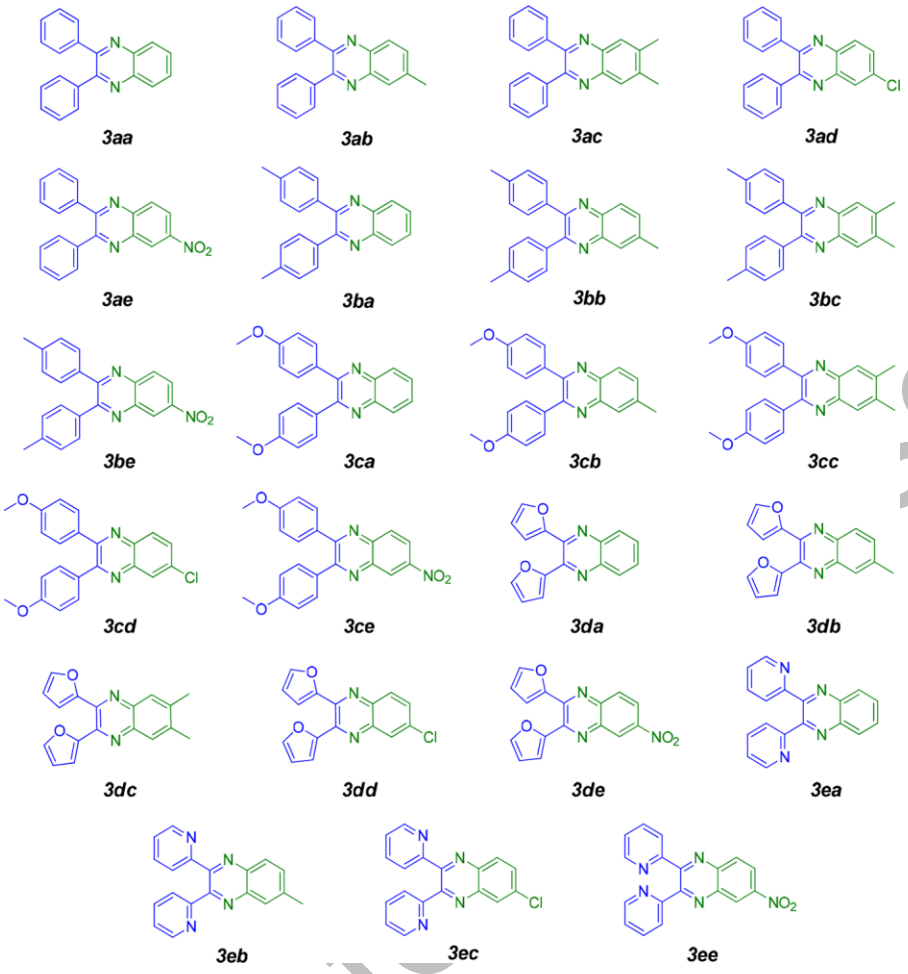


95% (isolated yield)

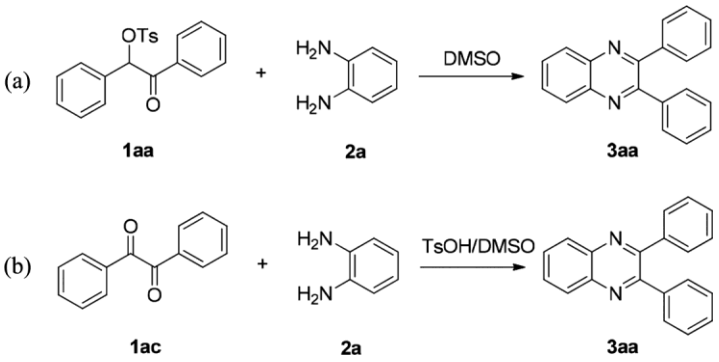
Scheme 3. Previous work and our idea.



Scheme 4. Structures of the desired compounds 3aa–ee.



Scheme 5. Control Experiments.



Scheme 6. Proposed mechanism.