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# Sodium tetrachloroaurate(III) dihydrate-catalyzed efficient synthesis of 1,5-benzodiazepine and quinoxaline derivatives*

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**Abstract:** Both 1,5-benzodiazepine and quinoxaline derivatives are important heterocycles in pharmaceuticals. We describe an efficient and clean method for the synthesis of 1,5-benzodiazepines from *o*-phenylenediamine and ketones catalyzed by sodium tetrachloroaurate(III) dihydrate under mild conditions. The catalyst was shown to be equally effective for the synthesis of quinoxalines from *o*-phenylenediamine and α-bromo ketones under the similar reaction conditions. This method produced good yields.

**Key words:** 1,5-benzodiaepines, *o*-phenylenediamine, Ketones, Quinoxalines, Gold catalyst
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## 1 Introduction

Benzodiazepines and quinoxalines have recently received much attention as important classes of heterocyclic compounds in pharmaceuticals. The benzodiazepine derivatives have been found to have wide applications in medical chemistry, such as anticonvulsant, anti-anxiety, analgesic, hypnotic, sedative, antidepressant and anti-inflammatory agents (Smalley, 1979; Landquist, 1984; Randall and Kappel, 1973). In addition, 1,5-benzodiazepines are intermediates used for the synthesis of other fused ring compounds such as triazolo-, oxazino- or furanobenzodiazepines (Essaber *et al*., 1998; El-snyed *et al*., 1999; Xu *et al*., 1999; Zhang *et al*., 1999; Reddy *et al*., 2000). On the other hand, quinoxaline derivatives have also shown a broad spectrum of biological activities, which has led them to be privileged structures in drug discovery (Zaragoza and Stephensen, 1999; Wu and Ede, 2001).

To date, several methods for the preparation of 1,5-benzodiazepines have been reported in the literatures, including condensation reactions of *o*-phenylenediamine with α,β-unsaturated carbonyl compounds (Ried and Stahlofen, 1957), β-haloketones (Ried and Torinus, 1959) or ketones promoted by $BF_3{\cdot}Et_2O$ (Herbert and Suschitzky, 1974), $NaBH_4$ (Morales *et al*., 1986), polyphosphoric acid or $SiO_2$, (Jung *et al*., 1999), $MgO/POCl_3$ (Balakrishna and Kaboudin, 2001), $Yb(OTf)_3$ (Curini *et al*., 2001), $Al_2O_3/P_2O_5$ or AcOH under microwave (Kaboudin and Navaee, 2001), ionic liquid (Jarikote *et al*., 2003), $SmI_2$ (Luo *et al*., 2005), $HBF_4$-$SiO_2$ (Bandgar *et al*., 2006), dodecyl sulfonic acid (Sharma *et al*., 2007), $AgNO_3$ (Kumar *et al*., 2006), $H_{14}[NaP_5W_{30}O_{110}]$ (Heravi *et al*., 2007a), polyaniline-sulfate salt (Srinivas *et al*., 2007), and 2,4,6-trichloro-1,3,5-triazine (Kuo *et al*., 2008). Meanwhile, a number of methods have also been developed for the synthesis of quinoxalines, involving condensation of 1,2-diamines with 1,2-dicarbonyl compounds (Kaupp and Naimi-Jamal, 2002; More *et al*., 2005; 2006; Bhosale *et al*., 2005; Heravi *et al*., 2007b), 1,4-addition of 1,2-diamines with 1,2-diaza-1,3-butadienes (Aparicio

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*et al*., 2006), oxidation-trapping of α-hydroxy ketones with 1,2-diamine (Raw *et al*., 2004; Kim *et al*., 2005; Robinson and Taylor, 2005), cyclization-oxidation of polymer-linked 2-nitrophenyl carbamate with α-bromo ketones (Singh *et al*., 2003), and oxidative-coupling of epoxides with *o*-phenylenediamine (Antoniotti and Duñach, 2002). However, many of these procedures for the syntheses of 1,5-benzodiazepines and quinoxalines have limitations, i.e., harsh reaction conditions, high catalyst loading, occurrence of several side products, tedious work-up procedures, use of toxic and/or hazardous transition metals, and so on. Therefore, the development of clean and efficient methods for the syntheses of these valuable compounds is desirable.

Gold is a soft transition metal showing high electrophilic affinity to alkynes, alkenes, and allenes (Hashmi and Hutchings, 2006; Gorin and Toste, 2007; Hashmi, 2007; Hashmi and Rudolph, 2008; Li *et al*., 2008). It can also act as a Lewis acid for the activation of electrophiles (Arcadi *et al*., 2006). Recently, there has been growing interest in gold-catalyzed organic transformations because gold catalysts usually exhibit extraordinary reactivity and show high selectivity in the reactions. Besides, gold catalysts are quite robust, and most of the reactions tolerate both oxygen and acidic protons; thus, neither air nor humidity needs to be excluded. As part of our ongoing interest in the gold-catalyzed transformations (Liu *et al*., 2009a; 2009b), we herein described clean and efficient syntheses of 1,5-benzodiazepines and quinoxaline derivatives using sodium tetrachloroaurate(III) dihydrate as catalyst under mild reaction conditions.

## 2 Materials and methods

A representative procedure for the synthesis of 1,5-benzodiazepines **3** or quinoxalines **5** is described as follows: to a 25-ml flask, *o*-phenylenediamine **1** (0.11 g, 1.0 mmol), $NaAuCl_4{\cdot}2H_2O$ (0.008 g, 0.02 mmol), ketones **2** (2.2 mmol, for synthesis of **3**) or α-bromo ketones **4** (1.2 mmol, for synthesis of **5**), and EtOH (5 ml) were added. The mixture was stirred at room temperature for the given time in Table 2 (for **3**) or Table 3 (for **5**). Upon completion, the solvent was removed under vacuum. The residue was purified by chromatography using cyclohexane/ethyl acetate (6:1, v/v) as eluent to afford 1,5-benzodiazepines **3** or quinoxalines **5**.

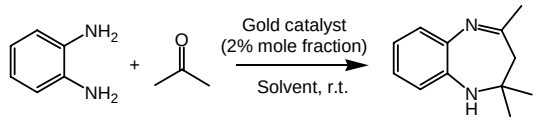
## 3 Results and discussion

Initially, the reaction of *o*-phenylenediamine **1** with acetone **2e** was tested as a model reaction for optimization of the reaction conditions (Table 1). In the absence of a gold catalyst, the reaction could hardly take place (Entry 1). The reaction proceeded smoothly to give the desired product **3e** in 80% yield when **1** and **2e** were treated with 2% (mole fraction) of $AuCl_3$ at room temperature for 5 h (Entry 2). Under the catalysis of $HAuCl_4{\cdot}4H_2O$, the yield of **3e** was increased to be 85% (Entry 3). So far, the best result was obtained by using $NaAuCl_4{\cdot}2H_2O$ as a catalyst, which gave **3e** in 95% yield (Entry 4). Solvent screening experiments showed that ethanol is the best choice for the reaction (Entries 4–8). It is noteworthy that the reaction could still proceed well even in water or solvent-free condition (Entries 9 and 10).

**Table 1 Optimization of reaction condition[a]**

| Entry | Catalyst | Solvent | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | None | EtOH | 24 | Trace |
| 2 | $AuCl_3$ | EtOH | 5 | 80 |
| 3 | $HAuCl_4{\cdot}4H_2O$ | EtOH | 5 | 85 |
| 4 | $NaAuCl_4{\cdot}2H_2O$ | EtOH | 5 | 95 |
| 5 | $NaAuCl_4{\cdot}2H_2O$ | $CH_3CN$ | 5 | 78 |
| 6 | $NaAuCl_4{\cdot}2H_2O$ | THF | 5 | 85 |
| 7 | $NaAuCl_4{\cdot}2H_2O$ | $PhCH_3$ | 5 | 90 |
| 8 | $NaAuCl_4{\cdot}2H_2O$ | $CH_2Cl_2$ | 5 | 80 |
| 9 | $NaAuCl_4{\cdot}2H_2O$ | $H_2O$ | 5 | 85 |
| 10 | $NaAuCl_4{\cdot}2H_2O$ | Neat | 6 | 80 |

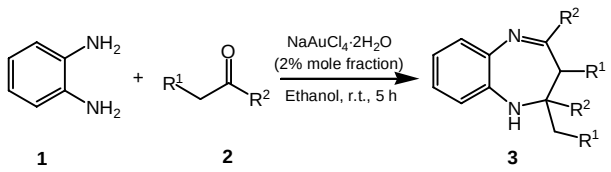
Reaction formula:




**1** **2e** **3e**

[a] Reaction conditions: *o*-phenylenediamine **1** (1.0 mmol), acetone **2e** (2.2 mmol), catalyst (0.02 mmol), solvent (5 ml), room temperature; [b] Isolated yield

With optimized conditions in hand, a variety of substrates were used in this reaction to establish the generality and efficiency (Fig. 1, Table 2). In most cases, the reaction proceeded smoothly to give **3** in




1 2 3

**Fig. 1 Synthesis of 1,5-benzodiazepines 3 using $NaAuCl_4 \cdot 2H_2O$ as catalyst**

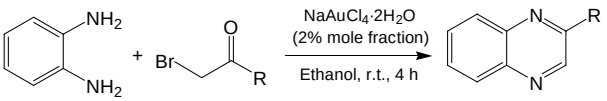
**Table 2 Synthesis of various 1,5-benzodiazepines 3 from *o*-phenylenediamine 1 and ketones 2 catalyzed by $NaAuCl_4 \cdot 2H_2O$[a]**

| Entry | Ketone (**2**) | Product (**3**) | Yield (%)[b] |
|---|---|---|---|
| 1 | **2a** | **3a** | 93 |
| 2 | **2b** | **3b** | 87 |
| 3 | **2c** | **3c** | 82 |
| 4 | **2d** | **3d** | 91 |
| 5 | **2e** | **3e** | 95 |
| 6 | **2f** | **3f** | 88 |
| | | **3f′** | <5 |
| 7 | **2g** | **3g** | 87 |
| | | **3g′** | Trace |
| 8 | **2h** | **3h** | 81 |
| 9 | **2i** | **3i** | 82 |
| 10 | **2j** | **3j** | 75 |

[a] Reaction conditions: *o*-phenylenediamine **1** (1.0 mmol), acetone **2** (2.2 mmol), $NaAuCl_4 \cdot 2H_2O$ (0.02 mmol), ethanol (5 ml), room temperature, 5 h; [b] Isolated yield

good to excellent yields under mild conditions. Reactions of *o*-phenylenediamine with acetophenones possessing electron-withdrawing groups generally gave better yield of **3** than those containing electron-donating groups (Entries 4 vs. 2, 3). Both acyclic and cyclic alkylketones were suitable substrates for the reaction (Entries 5–10). Note that lower yields were obtained from the more hindered alkylketones (Entries 5–7 vs. 8). The condensation of 2-butanone **2f** or 4-methyl 2-pentanone **2g** with *o*-phenylenediamine selectively gave **3f** or **3g**, respectively (Entries 6 and 7), along with small amount of the diastereoisomer **3f′** or **3g′**.

Encouraged by the successful application of $NaAuCl_4 \cdot 2H_2O$ as a catalyst in the synthesis of 1,5-benzodiazepines, we expected that quinoxalines **5** will be obtained if *o*-phenylenediamine **1** is allowed to react with α-bromo ketones **4** (Das *et al*., 2007). Indeed, when 1 equivalent of **1** was treated with 1.2 equivalents of **4** in ethanol under similar reaction conditions, quinoxalines **5** were produced in high yields (Fig. 2, Table 3). Control experiment showed that much lower yield of **5a** (33%) was obtained in the absence of the gold catalyst (Entry 1). A variety of aromatic ring-tethered α-bromo ketones were investigated to establish the scope and generality of the reaction, and in all cases quinoxalines **5** were produced in good to excellent yields in the presence of $NaAuCl_4 \cdot 2H_2O$ under mild reaction conditions. In the reaction, gold catalyst may act as a bifunctional catalyst; namely, it serves as a Lewis acid catalyst to help the cyclization process via activation of the carbonyl group (Yang *et al*., 2007) as well as an oxidative catalyst for the dehydrogenation of the in situ generated dihydroquinoxalines with dioxygen (Zhu and Angelici, 2007; Liu *et al*., 2009a).



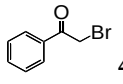
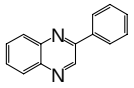
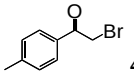
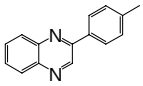
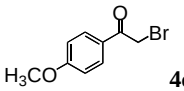
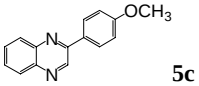
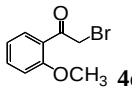
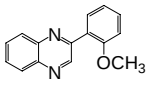
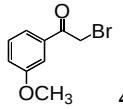
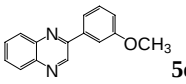
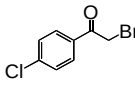
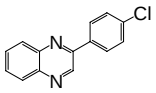
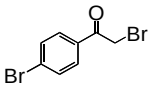
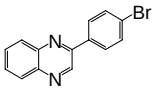
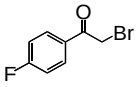
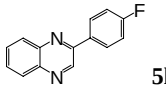
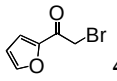
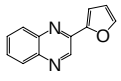
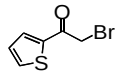
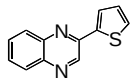

1 4 5

**Fig. 2 Synthesis of quinoxalines 5 using $NaAuCl_4 \cdot 2H_2O$ as catalyst**

## 4 Conclusion

In summary, we described a clean and efficient protocol for syntheses of 1,5-benzodiazepines and quinoxalines. The advantages of the present method

**Table 3 Synthesis of various quinoxalines 5 from *o*-phenylenediamine 1 and α-bromo ketones 4 catalyzed by $NaAuCl_4·2H_2O$[a]**

| Entry | α-bromo ketone (**4**) | Product (**5**) | Yield (%)[b] |
|---|---|---|---|
| 1 |  **4a** |  **5a** | 90 (33[c]) |
| 2 |  **4b** |  **5b** | 92 |
| 3 |  **4c** |  **5c** | 89 |
| 4 |  **4d** |  **5d** | 84 |
| 5 |  **4e** |  **5e** | 87 |
| 6 |  **4f** |  **5f** | 92 |
| 7 |  **4g** |  **5g** | 92 |
| 8 |  **4h** |  **5h** | 90 |
| 9 |  **4i** |  **5i** | 86 |
| 10 |  **4j** |  **5j** | 83 |

[a] Reaction conditions: *o*-phenylenediamine **1** (1.0 mmol), α-bromo ketones **4** (1.2 mmol), $NaAuCl_4·2H_2O$ (0.02 mmol), ethanol (5 ml), room temperature, 4 h; [b] Isolated yield; [c] In the absence of $NaAuCl_4·2H_2O$

lie in relatively low catalyst loading, mild reaction conditions, simple operation, and good yields.

## 5 Experimental details

All the starting chemicals were commercial products (Aldrich or J & K Chemica). Melting points were measured on a Büchi B-545 and uncorrected. Infrared (IR) spectra were recorded on a Bruker EQUINOX 55 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were obtained on a Bruker AVANCE III 500 (500 MHz) instrument in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Chemical shifts ($\delta$) are expressed in $\times10^{-6}$ and coupling constants ($J$) are given in Hz. Mass spectra were obtained on an HP 5989B mass spectrometer. Gas chromatograph-mass spectrometer (GC-MS) experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector.

2-methyl-2,4-diphenyl-2,3-dihydro-1H-1,5-benzodiazepine (**3a**): yellow solid, m.p. 151–152 °C [152–153 °C (Mahajan *et al*., 2008)]; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 1.77 (s, 3H, $CH_3$), 2.98 (d, $J$=12.8 Hz, 1H, $CH^a$), 3.15 (d, $J$=12.8 Hz, 1H, $CH^b$), 3.55 (br s, 1H, NH), 6.85–7.60 (m, 14H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3325, 1632, 1595; MS (70 eV): $m/z$ (%)=312 (18%) [$M^+$].

2-methyl-2,4-di(4-methylphenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**3b**): yellow solid, m.p. 141–143 °C [142–144 °C (Kuo *et al*., 2006)]; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 2.25–2.31 (m, 9H, $CH_3$), 2.95 (d, $J$=13.2 Hz, 1H, $CH^a$), 3.06 (d, $J$=13.2 Hz, 1H, $CH^b$), 3.52 (br s, 1H, NH), 6.81–7.56 (m, 12H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3270, 1644, 1601; MS (70 eV): $m/z$ (%)=340 (14%) [$M^+$].

2-methyl-2,4-di(4-methoxylphenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**3c**): yellow solid, m.p. 119–120 °C [(120–121 °C (Reddy *et al*., 2007)]; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 1.76 (s, 3H, $CH_3$), 2.95 (d, $J$=13.2 Hz, 1H, $CH^a$), 3.01 (d, $J$=13.2 Hz, 1H, $CH^b$), 3.78 (s, 3H, $OCH_3$), 3.88 (s, 3H, $OCH_3$), 6.77–7.51 (m, 12H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3350, 1631, 1596; MS (70 eV): $m/z$ (%)=372 (16%) [$M^+$].

2-methyl-2,4-di(4-chlorophenyl)-2,3-dihydro-1H-1,5-benzodiazepine (**3d**): yellow solid, m.p. 159–160 °C [162–163 °C (Mahajan *et al*., 2008)]; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 1.75 (s, 3H, $CH_3$), 2.90 (d, $J$=13.2 Hz, 1H, $CH^a$), 3.10 (d, $J$=13.2 Hz, 1H, $CH^b$), 3.47 (br s, 1H, NH), 6.84–7.53 (m, 12H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3328, 1632, 1593; MS (70 eV): $m/z$ (%)=380 (22%) [$M^+$].

2,2,4-trimethyl-2,3-dihydro-1H-1,5-benzodiazepine (**3e**): yellow solid, m.p. 137–139 °C [136–137 °C (Mahajan *et al*., 2008)]; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 1.34 (s, 6H, $CH_3$), 2.25 (s, 2H, $CH_2$), 2.39 (s, 3H, $CH_3$), 2.96 (br s, 1H, NH), 6.70–7.18 (m, 4H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3335, 1642, 1593; MS (70 eV): $m/z$ (%)=188 (28%) [$M^+$].

2.4-diethyl-2-methyl-2,3-dihydro-1H-1,5-benzodiazepine (**3f**): yellow solid, m.p. 139–140 °C [140–142 °C (Mahajan *et al*., 2008)]; $^1$H NMR

($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 0.94 (t, $J$=7.6 Hz, 3H, $CH_3$), 1.25 (m, 6H, $CH_3$), 1.62 (m, 2H, $CH_2$), 2.14 (d, $J$=12.8 Hz, 1H, $CH^a$), 2.23 (d, $J$=12.8 Hz, 1H, $CH^b$), 2.59 (q, $J$=7.2 Hz, 2H, $CH_2$), 3.08 (br s, 1H, NH), 6.69–7.26 (m, 4H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3328, 1636, 1605; MS (70 eV): $m/z$ (%)=216 (15%) [$M^+$].

2-methyl-2,4-diisobutyl-2,3-dihydro-1H-1,5-benzodiazepine (**3g**): yellow solid, m.p. 115–116 °C [117–119 °C (Mahajan *et al*., 2008)]; $^1$H NMR ($CDCl_3$, 500 Hz): $\delta$ ($\times10^{-6}$) 0.96–1.02 (m, 12H), 1.33 (s, 3H), 1.50–1.54 (m, 2H), 1.72–1.76 (m, 1H), 2.13–2.24 (m, 3H), 2.46 (d, $J$=6.4 Hz, 2H), 3.14 (br s, 1H, NH), 6.68–7.26 (m, 4H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3320, 1650, 1600; MS (70 eV): $m/z$ (%)=272 (12%) [$M^+$].

2,2,4-triethyl-3-methyl-2,3-dihydro-1H-1,5-benzodiazepine (**3h**): yellow solid, m.p. 139–140 °C [142–143 °C (Mahajan *et al*., 2008)]; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 0.75–1.60 (m, 15H), 2.51 (s, 3H, $CH_3$), 2.82 (q, $J$=6.8 Hz, 1H, CH), 3.84 (br s, 1H, NH), 6.61–7.34 (m, 4H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3322, 1639, 1595; MS (70 eV): $m/z$ (%)= 244 (26%) [$M^+$].

1′,2′,3′,4′,10′,11a′-hexahydrospiro[cyclohexane-1,11′-dibenzo[b,e][1,4]diazepine] (**3i**): yellow solid, m.p. 133–134 °C [135–136 °C (Mahajan *et al*., 2008)]; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 1.12–1.89 (m, 16H), 2.27–2.38 (m, 3H), 3.82 (br s, 1H, NH), 6.76–7.29 (m, 4H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3290, 1640, 1600; MS (70 eV): $m/z$ (%)=268 (23%) [$M^+$].

2,3,9,10a-tetrahydro-1H-spiro[benzo[b]cyclopenta [e][1,4]diazepine-10,1′-cyclopentane] (**3j**): yellow solid, m.p. 135–136 °C [136–137 °C (Mahajan *et al*., 2008)]; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 1.25–1.96 (m, 12H), 2.27–2.36 (m, 3H), 4.0 (br s, 1H, NH), 6.60–7.26 (m, 4H, ArH); IR (KBr): $\nu_{max}$ ($cm^{-1}$) 3338, 1660, 1598; MS (70 eV): $m/z$ (%)=240 (28%) [$M^+$].

2-phenyl quinoxaline (**5a**) (Das *et al*., 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 7.51–7.58 (m, 3H), 7.74–7.82 (m, 2H), 8.12–8.21 (m, 4H), 9.34 (s, 1H); MS (70 eV): $m/z$ (%)=206 (100%) [$M^+$].

2-(4-methylphenyl)quinoxaline (**5b**) (Das *et al*., 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 2.44 (s, 3H), 7.31 (d, $J$=8.0 Hz, 2H), 7.70–7.78 (m, 2H), 8.09–8.15 (m, 4H), 9.30 (s, 1H); MS (70 eV): $m/z$ (%)=220 (100%) [$M^+$].

2-(4-methoxylphenyl)quinoxaline (**5c**) (Das *et al*., 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 3.91 (s, 3H), 7.09 (d, $J$=8.5 Hz, 2H), 7.70–7.79 (m, 2H), 8.09–8.19 (m, 4H), 9.30 (s, 1H); MS (70 eV): $m/z$ (%)=236 (100%) [$M^+$].

2-(2-methoxylphenyl)quinoxaline (**5d**) (Cho and Oh, 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 3.91 (s, 3H), 7.07 (d, $J$=8.0 Hz, 2H), 7.17 (t, $J$=7.0 Hz, 1H), 7.47–7.51 (m, 1H), 7.74–7.79 (m, 2H), 7.89–7.91 (m, 1H), 8.12–8.18 (m, 2H), 9.34 (s, 1H); MS (70 eV): $m/z$ (%)=236 (100%) [$M^+$].

2-(3-methoxylphenyl)quinoxaline (**5e**) (Cho and Oh, 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 3.95 (s, 3H), 7.08 (d, $J$=8.0 Hz, 2H), 7.47 (t, $J$=8.0 Hz, 1H), 7.74–7.81 (m, 4H), 8.12–8.18 (m, 2H), 9.32 (s, 1H); MS (70 eV): $m/z$ (%)=236 (100%) [$M^+$].

2-(4-chlorophenyl)quinoxaline (**5f**) (Das *et al*., 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 7.54 (d, $J$=8.5 Hz, 2H), 7.75–7.82 (m, 2H), 8.11–8.16 (m, 4H), 9.30 (s, 1H); MS (70 eV): $m/z$ (%)=240 (100%) [$M^+$].

2-(4-bromophenyl)quinoxaline (**5g**) (Das *et al*., 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 7.70 (d, $J$=8.5 Hz, 2H), 7.70–7.81 (m, 2H), 8.08–8.15 (m, 4H), 9.30 (s, 1H); MS (70 eV): $m/z$ (%)=284 (100%) [$M^+$].

2-(4-fluorophenyl)quinoxaline (**5h**) (Das *et al*., 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 7.23–7.28 (m, 2H), 7.74–7.81 (m, 2H), 8.08–8.15 (m, 4H), 9.30 (s, 1H); MS (70 eV): $m/z$ (%)=224 (100%) [$M^+$].

2-(2-furyl)quinoxaline (**5i**) (Das *et al*., 2007): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 6.64 (d, $J$=1.5 Hz, 1H), 7.33 (t, $J$=3.0 Hz, 1H), 7.69–7.78 (m, 3H), 8.07–8.12 (m, 2H), 9.26 (s,1H); MS (70 eV): $m/z$ (%)=196 (100%) [$M^+$].

2-(2-thienyl)quinoxaline (**5j**) (Peter *et al*., 2004): $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ ($\times10^{-6}$) 7.21 (t, $J$=3.5 Hz, 1H), 7.55 (d, $J$=4.0 Hz, 1H), 7.68–7.77 (m, 2H), 7.86 (t, $J$=3.0 Hz, 1H), 8.06–8.09 (m, 2H), 9.24 (s, 1H); MS (70 eV): $m/z$ (%)=212 (100%) [$M^+$].

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