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One-pot synthesis of unsymmetrical benzils and *N*-heteroarenes through nucleophilic aroylation catalyzed by *N*-heterocyclic carbene

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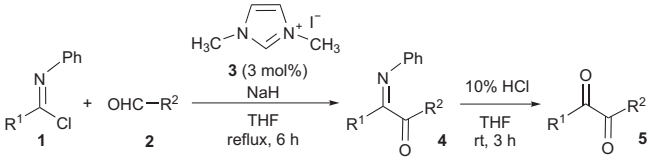
ABSTRACT

An efficient one-pot synthesis of various unsymmetrical benzils via *N*-heterocyclic carbene (NHC)-catalyzed aroylation of *N*-phenylimidoyl chlorides with aromatic aldehydes followed by acidic hydrolysis has been developed. The one-pot procedure was extended to synthesis of quinoxalines and pyrazines by condensation/annulation of unsymmetrical benzils generated in situ with diamines.

1. Introduction

Unsymmetrical benzils are not only valuable intermediates but are also key synthetic targets in organic synthesis, since they are precursors to biologically active heterocyclic compounds such as qunoxalines, pyrazines, and imidazoles[1–3] as well as inhibitors of carboxylesterase.[4] However, of the several known methods to synthesize these compounds, few can be considered environmentally friendly, versatile, and facile. For example, one of the most common methods is the oxidation of alkynes;[5] however, that the oxidation processes often require severe conditions and rare or expensive materials. An alternative method involves oxidizing unsymmetrical benzoin prepared by the addition reaction between cyanohydrin anions and aldehydes;[3,6] unfortunately, this method requires toxic cyanation reagents, which makes it problematic for commercial application. Another route is oxidation of the products of the Friedel–Crafts reaction between benzenes and 2-phenylacetyl chlorides;[6,7] in this case, the method is not always applicable owing to the directing and activating effects of the substituents.

With this motivation, we developed a new efficient synthetic method using *N*-heterocyclic carbene (NHC) catalysis.[8,9] As shown in Scheme 1, unsymmetrical benzils **5** were prepared by hydrolysis under acidic conditions from 1,2-diaryl-(2-phenyl)iminoethanone



Scheme 1. Synthesis of unsymmetrical benzils via NHC-catalyzed nucleophilic aroylation followed by hydrolysis.

4, which was synthesized from *N*-phenylbenzimidoyl chlorides **1** and aromatic aldehyde **2** by NHC-catalyzed aroylation (The mechanism of the NHC-catalyzed reaction is shown in Scheme 2.). However, although efficient, the procedure can be further simplified by performing successive hydrolysis after the first reaction without isolation of **4**.

Herein, we report one-pot synthesis of unsymmetrical benzils by NHC-catalyzed aroylation of *N*-phenylbenzimidoyl chlorides with aromatic aldehydes followed by hydrolysis of the aroylated products—i.e., α-iminoketones. We also report one-pot synthesis of *N*-heteroarenes through subsequent/simultaneous annulations of the resulting unsymmetrical benzils with diamines.

2. Results and discussion

2.1. One-pot synthesis of unsymmetrical benzils 5

Based on the procedure we previously reported,[8] NHC-catalyzed aroylation and subsequent hydrolysis were carried out using a one-

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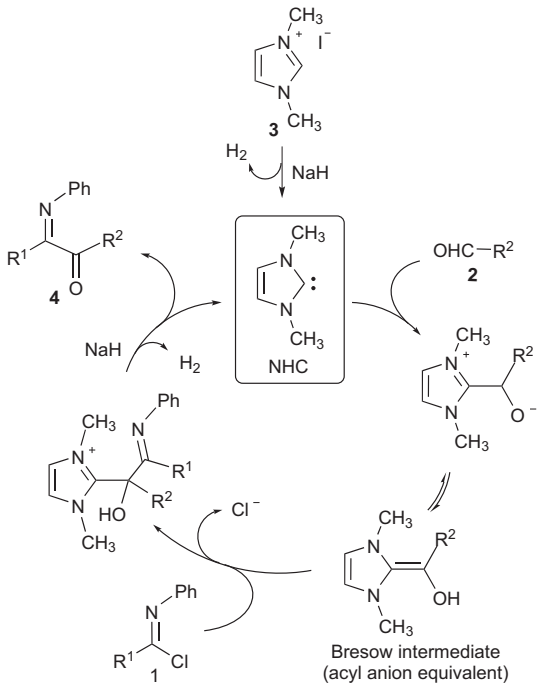
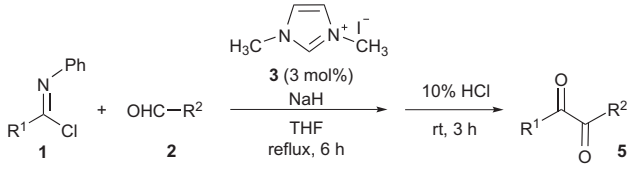


Scheme 2. Plausible mechanism for aroylation.

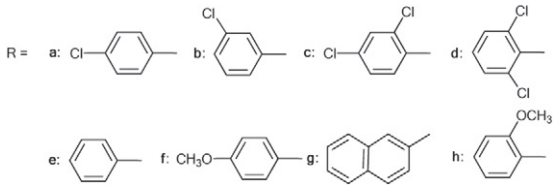
pot method. A mixture of **1a**, **2e** (1.5 equiv), NaH (1.3 equiv), and 3 mol % of 1,3-dimethylimidazolium iodide **3** in THF was refluxed for 6 h and the resulting **4ae** was confirmed by thin-layer chromatography. Although benzoin condensation can be considered to be a potential side reaction, the formation of benzoin was not observed. After cooling, 10% HCl was added: the mixture was then stirred at room temperature for 3 h to afford **5ae** in 70% yield (Table 1, entry 1).

The reaction of **1a** with aldehydes **2f**,**g** afforded benzils **5af**,**ag** in good yields, respectively (entries 2 and 3). However, the yield of **5ah**—prepared from **1a** and 2-anisaldehyde **2h**—was low (entry 4). The steric effect of chloro groups, which are versatile substituents in organic synthesis, in **1** was examined: the results showed that a 2,6-disubstituted substrate is unfavorable for aroylation (entry 9). Overall, the substrates with monochloro groups and 2,4-dichloro groups afforded benzils (entries 1–8). The advantage of this one-pot method is that benzils can be obtained efficiently without work-up and purification of the intermediates after aroylation.

Table 1
One-pot synthesis of unsymmetrical benzils **5**



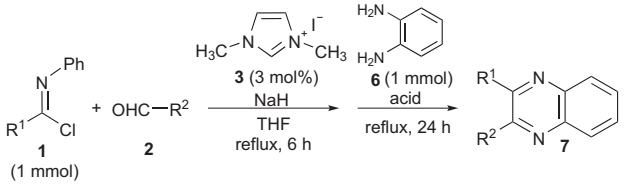
Entry	1	2	5	Yield (%)
1	**1a**	**2e**	**5ae**	70
2	**1a**	**2f**	**5af**	72
3	**1a**	**2g**	**5ag**	75
4	**1a**	**2h**	**5ah**	28
5	**1b**	**2a**	**5ab**	96
6	**1b**	**2f**	**5bf**	68
7	**1c**	**2a**	**5ac**	72
8	**1c**	**2e**	**5ce**	70
9	**1d**	**2e**	**5de**	—



2.2. One-pot synthesis of 2,3-diarylquinoxalines 7

Next, we attempted to extend this procedure to one-pot synthesis of 2,3-diarylquinoxalines. As mentioned above, unsymmetrical benzils are an important precursor to heterocyclic compounds. For example, condensation of benzils with *o*-phenylenediamine **6** and ethylenediamine **8** affords 2,3-diarylquinoxalines **7** and 2,3-diaryl-5,6-dihydropyradines, respectively. Derivatives of these diarylheterocyclic compounds have been reported to have useful bioactivities such as anti-inflammatory effects.[7,9] Huang and co-workers reported the synthesis of α-phenyl-3-trifluoromethylquinoxaline **7** (R^1=CF_3, R^2=phenyl) by reacting α-iminoketone **4** (R^1=CF_3, R^2=phenyl) with **6** under acidic conditions (6 N HCl in methanol).[10] Following their work, we constructed a quinoxaline framework in a one-pot method by adding concd HCl and **6** after aroylation of **1a**,**b** with **2a**,**e** to afford the corresponding **7** (Table 2, entries 1, 2, and 4). The use of concd H_2SO_4 instead of HCl increased the reaction yield (entries 3 and 5). Note that annulation also proceeded without acids, although the yield was lower (entry 6). Moreover, a large excess of **6** slightly increased the product yield (entries 7 and 8) (Table 2).

Table 2
One-pot synthesis of 2,3-diarylquinoxalines **7**



Entry	1	2	Acid	7	Yield (%)
1	**1a**	**2e**	Concd HCl 2 mL	**7ae**	65
2	**1b**	**2e**	Concd HCl 2 mL	**7be**	48
3	**1b**	**2e**	Concd H_2SO_4 0.6 mL	**7be**	63
4	**1b**	**2a**	Concd HCl 2 mL	**7ab**	65
5	**1b**	**2a**	Concd H_2SO_4 0.6 mL	**7ab**	75
6	**1b**	**2a**	None	**7ab**	40
7[a,b]	**1b**	**2a**	Concd H_2SO_4 0.6 mL	**7ab**	73
8[a,c]	**1b**	**2a**	concd H_2SO_4 0.6 mL	**7ab**	80

[a] The reaction mixture was refluxed for 9 h for aroylation.
[b] 2 mmol of **6** was used.
[c] 10 mmol of **6** was used.

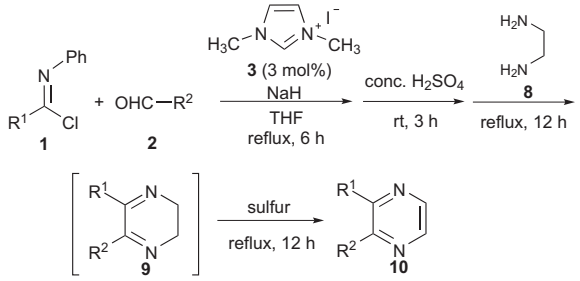
2.3. One-pot synthesis of 2,3-diarylpyrazines 10

Next, the feasibility of completing four successive reactions with this one-pot method to synthesize 2,3-diarylpyrazines **10** was examined (Table 3). After aroylation and acidic hydrolysis, the reaction mixture containing **5** was refluxed with **8** (12 equiv) to promote condensation/annulation. Oxidation of the resulting **9** using sulfur powder (2 equiv) as an oxidant was carried out at reflux temperature. The reaction sequence was started with aroylation of **1a**,**b** with **2a**,**f**,**g**,**i** to afford the corresponding **10** in good-to-moderate yields.

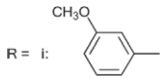
3. Summary

We described the one-pot synthesis of benzils, 2,3-diarylquinoxalines, and 2,3-diarylpyrazines in sequences of 2–4

Table 3
One-pot synthesis of 2,3-diarypyrazines **10**



Entry	1	2	10	Yield (%)
1	**1a**	**2f**	**10af**	56
2	**1a**	**2g**	**10ag**	61
3	**1a**	**2i**	**10ai**	57
4	**1b**	**2a**	**10ab**	75
5	**1b**	**2f**	**10bf**	55



reactions starting with NHC-catalyzed aroylation of *N*-phenylbenzimidoyl chlorides with aromatic aldehydes. The substrates of the catalytic reaction—*N*-phenylbenzimidoyl chlorides—are easily obtained by chlorination of benzanilides. By combining *N*-phenylarenecarboxamides and aldehydes appropriately, our method makes it possible to prepare various unsymmetrical benzils, 2,3-diarylquinoxalines, and 2,3-diarylpyrazines. The products of the catalytic reaction—α-iminoketones—are versatile intermediates. The development of novel synthetic routes to other heterocyclic compounds such as imidazoles, thiazoles, pyrroles, and pyridines via these α-iminoketones is currently underway in our laboratory.

4. Experimental section

4.1. General procedure for the one-pot synthesis of unsymmetrical benzils

To a mixture of the *N*-phenylbenzimidoyl chlorides **1** (1.0 mmol), aromatic aldehyde **2** (1.5 mmol), and 1,3-dimethylimidazolium iodide **3** (6.7 mg, 0.03 mol) in THF (20 mL), NaH (60% in oil, 52 mg, 1.3 mmol) was added with stirring under an argon atmosphere. After refluxing for an appropriate time, the reaction mixture was cooled and 10% HCl (2 mL) was added. The reaction mixture was then stirred at room temperature for 3 h and poured into water. The products were extracted with diethyl ether, washed with brine, and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate) to obtain benzils **5**.

*4.1.1. 1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (**5ae**).*[8,9] Yellowish solid, 70%; ^{1}H NMR (500 MHz) $CDCl_3$ δ: 7.51 (2H, d, J=8.5 Hz), 7.53 (2H, d, J=8.5 Hz), 7.68 (1H, t, J=8.3 Hz), 7.93 (2H, td, J=8.3, 1.5 Hz), 7.98 (2H, dd, J=8.3, 1.5 Hz).

*4.1.2. 1-(4-Chlorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (**5af**).*[8,9] Yellowish solid, 2%; ^{1}H NMR (500 MHz) $CDCl_3$ δ: 3.89 (3H, s), 6.98 (2H, d, J=8.5 Hz), 7.48 (2H, d, J=8.5 Hz), 7.93–7.98 (4H, m).

*4.1.3. 1-(4-Chlorophenyl)-2-(naphthalen-2-yl)ethane-1, 2-dione (**5ag**).*[8] Yellowish solid, 75%; ^{1}H NMR (500 MHz) $CDCl_3$ δ: 7.46 (1H, t, J=8.0 Hz), 7.56–7.67 (3H, m), 7.89–8.01 (4H, m), 8.03 (1H, t, J=2.0 Hz), 8.09 (1H, dd, J=8.0, 2.0 Hz), 8.40 (1H, s).

*4.1.4. 1-(4-Chlorophenyl)-2-(2-methoxyphenyl)ethane-1,2-dione (**5ah**).* Yellowish solid, 28%; mp 108–110 °C; IR (ATR, cm^{-1}): 1585 (C=O), 1662 (C=O); HRMS (FAB) calcd for $C_{15}H_{12}O_3Cl$ $(M+1)^+$: 275.0475, found: 275.0447; ^{1}H NMR (500 MHz) $CDCl_3$ δ: 3.90 (3H, s), 6.88 (1H, d, J=8.8 Hz), 7.08 (1H, t, J=8.8 Hz), 7.41 (2H, d, J=8.5 Hz), 7.54 (1H, t, J=8.8 Hz), 7.81 (2H, d, J=8.5 Hz), 7.94 (1H, d, J=8.8 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 55.5, 112.3, 121.6, 123.6, 129.1, 130.5, 130.6, 131.2, 136.6, 140.2, 160.3, 192.1, 194.2.

*4.1.5. 1-(4-Chlorophenyl)-2-(3-chlorophenyl)ethane-1,2-dione (**5ab**).* Yellowish solid, 96%; mp 111–113 °C; IR (ATR, cm^{-1}): 1585 (C=O), 1662 (C=O); HRMS (ESI) calcd for $C_{14}H_9O_2Cl_2$ $(M+1)^+$: 278.9980, found: 279.0018; ^{1}H NMR (400 MHz) $CDCl_3$ δ: 7.47 (1H, t, J=7.8 Hz), 7.51 (2H, d, 7.8 Hz), 7.64 (1H, ddd, J=7.8, 1.7, 1.1 Hz), 7.84 (1H, dt, J=7.8, 1.7 Hz), 7.92 (2H, d, J=7.8 Hz), 7.97 (1H, t, J=1.7 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 128.8, 129.6, 130.4, 131.0, 131.2, 134.2, 134.5, 134.9, 135.4, 141.8, 192.0, 192.2.

*4.1.6. 1-(3-Chlorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (**5bf**).* Yellowish solid, 68%; mp 78–80 °C; IR (ATR, cm^{-1}): 1593 (C=O), 1654 (C=O); HRMS (FAB) calcd for $C_{15}H_{12}O_3Cl$ $(M+1)^+$: 275.0475, found: 275.0511; ^{1}H NMR (400 MHz) $CDCl_3$ δ: 3.83 (3H, s), 6.98 (2H, d, J=8.4 Hz), 7.44 (1H, t, J=8.0 Hz), 7.60 (1H, ddd, J=8.0, 1.5, 1.1 Hz), 7.83 (1H, dt, J=8.0, 1.5 Hz), 7.92 (2H, d, J=8.4 Hz), 7.96 (1H, t, J=1.5 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 55.6, 114.4, 125.6, 128.0, 129.4, 130.2, 132.4, 134.5, 134.6, 135.2, 165.1, 192.1, 193.2.

*4.1.7. 1-(2,4-Dichlorophenyl)-2-(3-chlorophenyl)ethane-1,2-dione (**5ac**).* Yellowish solid, 72%; mp 82–85 °C; IR (ATR, cm^{-1}): 1625 (C=O), 1682 (C=O); HRMS (FAB) calcd for $C_{14}H_8O_2Cl_3$ $(M+1)^+$: 312.9590, found: 312.9613; ^{1}H NMR (500 MHz) $CDCl_3$ δ: 7.38 (1H, dd, J=8.5, 2.0 Hz), 7.41 (1H, d, J=2.0 Hz), 7.47 (2H, d, J=8.7 Hz), 7.87 (1H, d, J=8.5 Hz), 7.92 (1H, d, J=8.7 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 127.9, 129.3, 129.5, 130.3, 131.6, 132.2, 132.9, 134.7, 140.6, 141.3, 190.2, 192.2.

*4.1.8. 1-(2,4-Dichlorophenyl)-2-phenylethane-1,2-dione (**5ce**).*- Yellowish solid, 70%; mp 69–72 °C; IR (ATR, cm^{-1}): 1573 (C=O), 1666 (C=O); HRMS (FAB) calcd for $C_{14}H_9O_2Cl_2$ $(M+1)^+$: 278.9980, found: 278.9993; ^{1}H NMR (500 MHz) $CDCl_3$ δ: 7.43 (1H, dd, J=8.2, 1.8 Hz), 7.51 (1H, d, J=1.8 Hz), 7.54 (2H, t, J=7.4 Hz), 7.67 (1H, t, J=7.4 Hz), 7.86 (1H, d, J=8.2 Hz), 8.01 (2H, d, J=7.4 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 128.2, 129.1, 130.3, 130.5, 130.7, 132.2, 132.8, 134.5, 134.8, 140.5, 191.4, 192.3.

4.2. General procedure for the one-pot synthesis of quinoxalines

To a mixture of the *N*-phenylbenzimidoyl chlorides **1** (1.0 mmol), aromatic aldehyde **2** (1.5 mmol), and 1,3-dimethylimidazolium iodide **3** (6.7 mg, 0.03 mol) in THF (20 mL), NaH (60% in oil, 52 mg, 1.3 mmol) was added with stirring under an argon atmosphere. After refluxing for the indicated time, the reaction mixture was cooled and concd HCl (2.0 mL) or concd H_2SO_4 (0.6 mL), and *o*-phenylenediamine (104 mg, 1.0 mmol) were added. The reaction mixture was then stirred at reflux temperature for 24 h and poured into water. The products were extracted with diethyl ether, washed with brine, and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate) to obtain quinoxalines **7**.

*4.2.1. 2-(4-Chlorophenyl)-3-phenylquinoxaline (**7ae**).* Colorless powder, 65%; mp 142–143 °C; HRMS (FAB) calcd for $C_{20}H_{14}N_2Cl$ $(M+1)^+$: 317.0846, found: 317.0862; ^1H NMR (400 MHz) $CDCl_3$ δ: 7.30–7.38 (5H, m), 7.46–7.52 (4H, m), 7.75–7.79 (2H, m), 8.15–8.19 (2H, m); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 128.5, 128.6, 129.0, 129.1, 129.8, 129.9, 130.1, 130.2, 131.3, 135.1, 137.7, 138.8, 141.2, 141.3, 152.1, 153.2.

*4.2.2. 2-(3-Chlorophenyl)-3-phenylquinoxaline (**7be**).* Colorless powder, 48%; mp 112–113 °C; HRMS (FAB) calcd for $C_{20}H_{14}N_2Cl$ $(M+1)^+$: 317.0846, found: 317.0872; ^1H NMR (500 MHz) $CDCl_3$ δ: 7.17–7.37 (6H, m), 7.50–7.52 (2H, m), 7.32 (1H, s), 7.76–7.79 (2H, m), 8.16–8.18 (2H, m); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 128.0, 128.6, 128.8, 129.0, 129.1, 129.2, 129.5, 129.7, 130.1, 130.4, 131.1, 134.6, 135.3, 137.0, 140.5, 141.1, 151.4, 151.6.

*4.2.3. 2-(3-Chlorophenyl)-3-(4-chlorophenyl)quinoxaline (**7ab**).* Colorless powder, 65%; mp 95–97 °C; HRMS (FAB) calcd for $C_{20}H_{13}N_2Cl_2$ $(M+1)^+$: 351.0456, found: 351.0455; ^1H NMR (500 MHz) $CDCl_3$ δ: 7.09–7.48 (5H, m), 7.47–7.49 (2H, m), 7.62 (1H, s), 7.75–7.79 (2H, m), 8.14–8.22 (2H, m); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 128.0, 128.3, 128.4, 128.8, 128.9, 129.0, 129.1, 129.2, 129.6, 129.7, 129.8, 130.1, 130.2, 134.3, 138.5, 140.7, 140.9, 141.2, 151.7, 153.1.

4.3. General procedure for the one-pot synthesis of pyrazines

To a mixture of the *N*-phenylbenzimidoyl chlorides **1** (1.0 mmol), aromatic aldehyde **2** (1.5 mmol), and 1,3-dimethylimidazolium iodide **3** (6.7 mg, 0.03 mol) in THF (20 mL), NaH (60% in oil, 52 mg, 1.3 mmol) was added with stirring under an argon atmosphere. The reaction mixture was refluxed for 6 h, and cooled. After the addition of concd H_2SO_4 (0.6 mL), the reaction mixture was stirred at room temperature for 3 h, and then ethylenediamine (104 mg, 1.0 mmol) was added. The reaction mixture was refluxed for 12 h, and then sulfur (63 mg, 2.0 mmol) was added. The reaction mixture was refluxed for another 12 h, and then poured into water. The products were extracted with diethyl ether, washed with brine, and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate) to obtain pyrazines **10**.

*4.3.1. 2-(4-Chlorophenyl)-3-(4-methoxyphenyl)pyrazine (**10af**).* Brown oil, 56%; HRMS (FAB) *m/z* calcd for $C_{17}H_{14}OClN_2$ $(M+1)^+$: 297.0795, found: 297.0779; ^1H NMR (500 MHz) $CDCl_3$ δ: 3.81 (3H, s), 6.84 (2H, d, *J*=8.5 Hz), 7.28 (2H, d, *J*=8.3 Hz), 7.37 (2H, d, *J*=8.5 Hz), 7.40 (2H, d, *J*=8.3 Hz), 8.57 (1H, d, *J*=2.2 Hz), 8.62 (1H, d, *J*=2.2 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 55.4, 114.0, 128.7, 130.6, 131.0, 131.2, 134.9, 137.4, 141.7, 142.4, 151.3, 152.5, 160.3.

*4.3.2. 2-(4-Chlorophenyl)-3-(2-naphthyl)prazine (**10ag**).* Yellow oil, 61%; HRMS (ESI) calcd for $C_{20}H_{14}ClN_2$ $(M+1)^+$: 317.0846, found: 317.0871; ^1H NMR (500 MHz) $CDCl_3$ δ: 7.25 (2H, d, *J*=8.9 Hz), 7.40–7.52 (6H, m), 7.76 (1H, d, *J*=8.9 Hz), 7.78–7.80 (2H, m), 8.10 (1H, s), 8.61 (1H, d, *J*=2.3 Hz), 8.64 (1H, d, *J*=2.3 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 126.5, 126.8, 127.0, 127.1, 127.7, 128.1, 128.7, 128.8, 129.6, 131.1, 133.4, 135.1, 135.8, 137.0, 142.2, 142.6, 151.7, 152.7.

*4.3.3. 2-(4-Chlorophenyl)-3-(3-methoxyphenyl)pyrazine (**10ai**).* Yellow oil, 57%; HRMS (FAB) *m/z* calcd for $C_{17}H_{14}OClN_2$ $(M+1)^+$: 297.0795, found: 297.0791; ^1H NMR (400 MHz) $CDCl_3$ δ: 3.73 (3H, s), 6.90 (1H, dd, *J*=8.3, 2.2 Hz), 6.96 (1H, d, *J*=8.3 Hz), 7.02 (1H, t, *J*=2.2 Hz), 7.20 (1H, t, *J*=8.3 Hz), 7.28(2H, d, *J*=8.3 Hz), 7.41 (2H, d, *J*=8.3 Hz), 8.59 (1H, d, *J*=2.4 Hz), 8.60 (1H, d, *J*=2.2 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 55.3, 114.7, 115.2, 122.2, 128.7, 129.6, 130.1, 131.1, 135.0, 137.0, 139.6, 142.3, 151.6, 152.7, 159.7.

*4.3.4. 2-(4-Chlorophenyl)-3-(3-chlorophenyl)pyrazine (**10ab**).* Yellow oil, 75%; HRMS (FAB) calcd for $C_{16}H_{11}Cl_2N_2$ $(M+1)^+$: 301.0299, found: 301.0325; ^1H NMR (400 MHz) $CDCl_3$ δ: 7.18–7.23 (2H, m), 7.27–7.34 (3H, m), 7.40 (2H, d, *J*=8.8 Hz), 7.58 (1H, t, *J*=1.2 Hz), 8.60 (1H, d, *J*=2.4 Hz), 8.61 (1H, d, *J*=2.4 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 127.9, 128.7, 129.1, 129.6, 129.7, 131.0, 134.7, 135.3, 136.6, 140.1, 142.4, 142.6, 151.3, 151.7.

*4.3.5. 2-(3-Chlorophenyl)-3-(4-methoxyphenyl)pyrazine (**10bf**).* Yellow oil, 55%; HRMS (ESI) calcd for $C_{17}H_{14}OClN_2$ $(M+1)^+$: 297.0795, found: 297.0799; ^1H NMR (400 MHz) $CDCl_3$ δ: 3.80 (3H, s), 6.84 (2H, d, *J*=8.8 Hz), 7.16–7.32 (3H, m), 7.39 (2H, d, *J*=8.8 Hz), 7.58 (1H, t, *J*=1.7 Hz), 8.54 (1H, d, *J*=2.4 Hz), 8.57 (1H, d, *J*=2.4 Hz); ^{13}C NMR (125 MHz) $CDCl_3$ δ: 55.8, 113.8, 128.8, 129.5, 129.6, 130.4, 131.0, 131.1, 134.5, 140.8, 141.6, 142.6, 151.0, 125.6, 160.3.

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