Pd-catalysed one-pot synthesis of 2*H*-1,4-benzoxazin-3-(4*H*)-ones from o-halophenols and 2-chloroacetamides

Fangling Yin[a], Gaofeng Feng[b], Qingbao Song[a]* and Chenze Qi[b]

[a]*College of Chemical Engineering and Material Science, Zhejiang University of Technology, Hangzhou, 310027, P. R. China*

[b]*The Institute of Applied Chemistry, Shaoxing University, Shaoxing, 312050, P. R. China*

A Pd-catalysed cascade protocol, consisting of intermolecular O-alkylation and spontaneous intramolecular amidation, has been established for efficient synthesis of 2*H*-1,4-benzoxazin-3-(4*H*)-ones from o-halophenols and 2-chloroacetamides. A varity of substrates afford the desired products in good to excellent yields. It is particularly attractive for synthesis of a library of 2*H*-1,4-benzoxazin-3-(4*H*)-ones.

Keywords: Pd catalysis, cascade reaction, 2*H*-1,4-benzoxazin-3-(4*H*)-ones, O-alkylation, amidation

2*H*-1,4-Benzoxazin-3-(4*H*)-one[1] (**1**, Fig. 1) is one of the privileged heterocyclic N derivatives skeleta in drug design. Naturally occurring and synthetic N derivatives of this heterocycle exhibit potent biological and medicinal activities (Fig. 1). For instance, the enediyne antitumour antibiotic, C-1027 **2**,[2] possesses a 2-methylene-2*H*-1,4-benzoxazin-3-(4*H*)-one subunit.

Because of their novel biological activities, a great deal of effort has been devoted to their synthesis by synthetic chemists.[3,4] Several novel strategies exist for constructing 2*H*-1,4-benzoxazin-3-(4*H*)-ones starting from different building blocks. Commonly, substituted 2-nitrophenols[5–7] and 2-aminophenols[8–10] have been employed as the starting material for accessing the heterocycle through stepwise synthetic sequences. Recently, Ugi-4CRs and subsequent cyclisation (through intramolecular O-alkylaton or Mitsunobu reaction) strategies were developed.[11–12] Alternatively, Zuo's group[13] developed one-pot efficient synthesis of 2*H*-1,4-benzoxazin-3-(4*H*)-ones from 2-chlorophenols, 2-chloroacetyl chlorides and primary amines via a Smile rearrangement. Although encouraging, this method is limited by the substrate scope. Improvements were achieved by Liu[14] and Bao's[15] groups on the basis of intermolecular O-alkylation and spontaneous Cu-catalysed amidation sequence from o-halophenols and 2-chloroacetamides. However, 2-iodophenols were necessary for achieving good yields. When 2-bromophenols were employed, only moderate yields could be obtained. Very recently, a simple Pd-catalysed intramolecular O-arylation reaction as the key annulation step for making 2*H*-1,4-benzoxazin-3-(4*H*)-ones was revealed by Kundig's group.[16] However, a three-steps sequence, consisting of condensation of N-alkyl-2-bromoaniline with 2-oxo-2-arylacetic acid, $NaBH_4$ reduction and Pd-catalysed intramolecular O-arylation, was adopted. Therefore, the development of an alternative and improved procedure towards this heterocycle is still in demand. Herein, we report an Pd-catalysed cascade process for efficient synthesis of 2*H*-1,4-benzoxazin-3-(4*H*)-ones from readily available 2-halophenols and 2-chloroacetamides.

Results and discussion

2-Bromophenol **3** and 2-chloro-N-phenylacetamide **4** were selected as the model substrates for optimising the reaction conditions in terms of catalyst, ligand, base, and molar ratio of substrates. Toluene was used as the solvent, as it is less toxic and commonly used in Pd-catalysed amidation reactions. The reaction temperature and time were set at 110 °C and 24 h, respectively. The results are summarised in Table 1. Initially, the combination of $Pd(OAc)_2$ (10 mol%), Xphos (10 mol%), and Cs_2CO_3 (2 equiv.) were selected for study, and the desired 4-phenyl-2*H*-1,4-benzoxazin-3-(4*H*)-one **1a** was isolated in 19% yield when the molar ratio of **3** and **4** is 1.2/1 (entry 1). Dppf showed no improvement (entry 2), while racemic BINAP exhibited good activity, furnishing **1a** in 64% yield (entry 3). Gratifyingly, the yield of the desired product **1a** was improved to 84% when the molar ratios of the starting material was inversed (**3/4** = 1/1.2). Further improvement of the yield (99%) was achieved by simply increasing the amount of the 2-chloro-N-phenylacetamide (**3/4** = 1/1.5). The above results indicated that the molar ratio of the building blocks was crucial for the present transformation. Other ligands, such as Xantphos and PPh_3, were then examined. Both were not as efficient as BINAP (entries 6 and 7). Further investigation showed that K_2CO_3 and *t*-BuONa were also not effective affording the product in low yields (entries 8 and 9). Other Pd(II) sources were then examined, and it was found that $PdCl_2$ and $Pd_2(dba)_3$ proved as

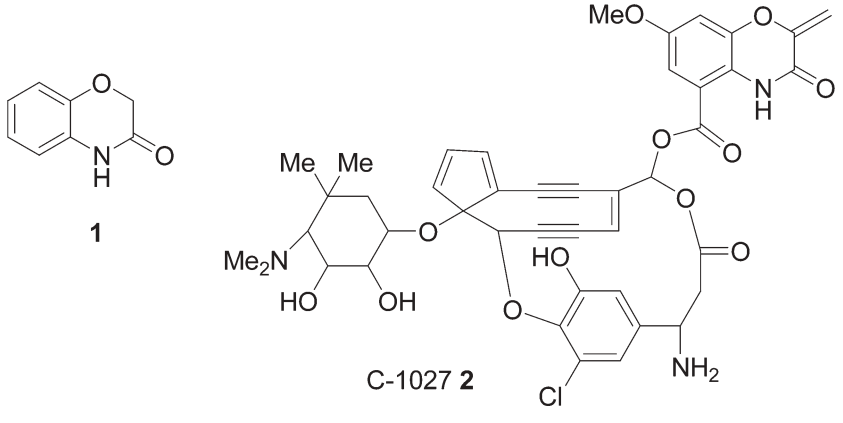
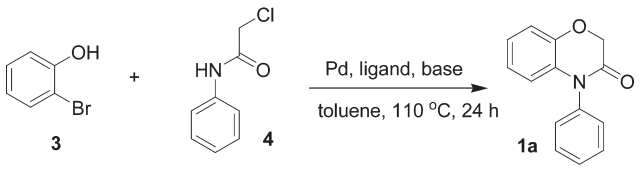


Fig. 1 Structures of 2*H*-1,4-benzoxazin-3-(4*H*)-one **1** and some biologically active derivatives.

* Correspondent. E-mail: qbsong@zjut.edu.cn; qichenze@usx.edu.cn

Table 1 Optimisation for synthesis of 4-phenyl-2H-1,4-benzoxazin-3-ones[a]



Entry	Catalyst	Ligand	Base	Ratio **3**/**4**	Yield[b] /%
1	$Pd(OAc)_2$	Xphos	Cs_2CO_3	1.2:1	19
2	$Pd(OAc)_2$	dppf	Cs_2CO_3	1.2:1	18
3	$Pd(OAc)_2$	BINAP	Cs_2CO_3	1.2:1	64
4	$Pd(OAc)_2$	BINAP	Cs_2CO_3	1:1.2	84
5	$Pd(OAc)_2$	BINAP	Cs_2CO_3	1:1.5	99
6	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	1:1.5	63
7	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	1:1.5	Trace
8	$Pd(OAc)_2$	BINAP	K_2CO_3	1:1.5	Trace
9	$Pd(OAc)_2$	BINAP	*t*-BuONa	1:1.5	32
10	$PdCl_2$	BINAP	Cs_2CO_3	1:1.5	93
11	$Pd_2(dba)_3$	BINAP	Cs_2CO_3	1:1.5	84
12[c]	$Pd(OAc)_2$	BINAP	Cs_2CO_3	1:1.5	98
13[d]	$Pd(OAc)_2$	BINAP	Cs_2CO_3	1:1.5	97
14[e]	$Pd(OAc)_2$	BINAP	Cs_2CO_3	1:1.5	38

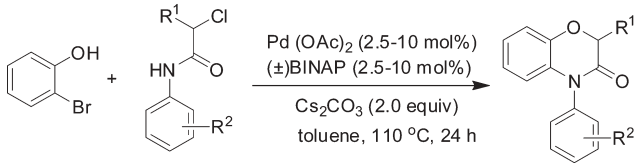
[a] Reaction conditions: catalyst (10 mol%), ligand (10 mol%), base (2.0 equiv.), toluene (0.1 M), 110 °C, 24 h.
[b] Isolated yield.
[c] The loadings of catalyst and ligand were 5 mol% and 5 mol%, respectively.
[d] The loadings of catalyst and ligand were 2.5 mol% and 2.5 mol%, respectively.
[e] The loadings of catalyst and ligand were 1 mol% and 1 mol%, respectively.
Xantphos: 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene
Xphos: 2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl

effective, although the yields were slightly lower than that of $Pd(OAc)_2$ (entry 10 and 11). Finally, an effort to reduce the catalyst loading was carried out. Gratifyingly, the yield of the desired product was not decreased (98% and 97%) when the loadings of catalyst and ligand were reduced to 5 mol% and 5 mol%, even to 2.5 mol% and 2.5 mol%, respectively (entries 12 and 13). However, when 1 mol% of catalyst and 1 mol% of ligand were employed, the yield was decreased dramatically (entry 14). On the basis of these investigations, the optimum conditions are: 2-chloroacetamide (1.5 equiv.) and 2-bromophenol (1.0 equiv.) with $Pd(OAc)_2$ (2.5 mol%), (±)BINAP (10 mol%), and Cs_2CO_3 (2.0 equiv.) in toluene at 110 °C for 24 h.

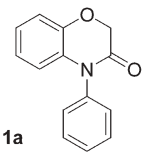
With the optimised conditions in hand, the generality of the process was then examined. As shown in Table 2, the process was compatible with various 2-chloroacetamides, providing a verity of N-substituted-2*H*-1,4-benzoxazin-3-(4*H*)-one in good to excellent yields. Acetamides possessing methyl group at *para* and *meta* positions of phenyl ring provided the corresponding products (**1b** and **1c**) in excellent yields with 2.5 mol% loadings of catalyst and ligand. A small steric effect on the amidation step was observed as *ortho* methyl substituted 2-chloroacetamide afforded the corresponding product in moderate yield (60%).

Highly bulky N-(2,6-dimethylphenyl) acetamide was also compatible, although the corresponding product **1e** was isolated in only 25% yield under the same condition. The yield could be improved to 51% by increasing the catalyst loading to 10 mol%. Moreover, the process was compatible with 2-chloroacetamides containing both electron-donating and electron-withdrawing substituents. It was observed that N-(4-methoxyphenyl) and N-(3-methoxyphenyl) acetamides provided the corresponding products **1f** and **1g** in excellent

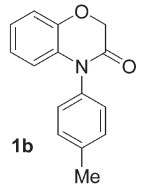
Table 2 Synthesis of 2*H*-1,4-benzoxazin-3-(4*H*)-ones via Pd-catalysed cascade process[a]



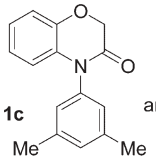
Products and yield



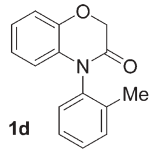
97%
96–97 °C[c]
96–98 °C[d]



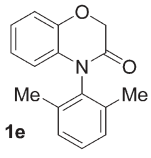
93%
128–129 °C[c]
128–130 °C[d]



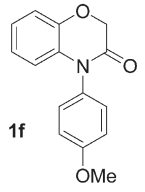
86%
amorphous solid



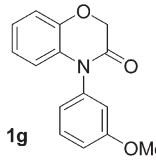
60%
100–102 °C[c]



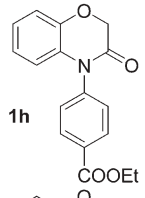
51%[b]
107–109 °C [c]



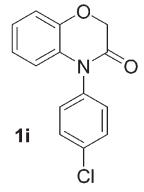
90%
117–119 °C[c]
118–120 °C[d]



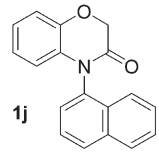
91%
85–86 °C[c]



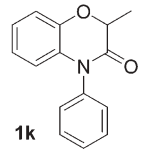
80%[b]
113–115 °C[c]



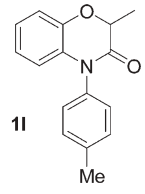
70%[b]
158–159 °C[c]



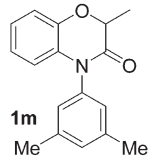
72%[b]
146–147 °C[c]



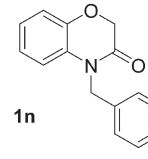
Br, 60%[b]
I, 92%[b]
78–79 °C[c]
78–89 °C[d]



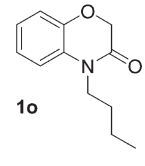
57%[b]
114–115 °C[c]



53%[b]
amorphous solid



56%
68%[b]
67–68 °C[c]
68–70 °C[d]



75%
oil

[a] Reaction conditions: catalyst (2.5 mol%), ligand (2.5 mol%), base (2.0 equiv.), toluene (0.1 M), 110 °C, 24 h.
[b] The loadings of catalyst and ligand were 10 mol% each.
[c] Melting point measured.
[d] Melting point from ref.15.

yields (90% and 91%, respectively). While N-(4-chlorophenyl) and N-(4-ethoxycarbony)phenyl acetamdie, which are sensitive to bases or acids, exhibited a little lower reactivity, providing

the corresponding products in 80% and 70% yield, respectively, although 10 mol% loading of catalyst was necessary. In addition, the reaction of 2-bromophenol and N-(1-naphthyl) acetamide proceeded smoothly, furnishing product **1j** in 72% yield using 10 mol% loading of catalyst. However, it was found that Me group at *alpha* position of 2-chloroacetamide was deleterious for achieving good yield, as **1k**, **1l**, and **1m** were isolated in only 60%, 57% and 53% yields, respectively, even when using an increased 10 mol% loading of catalyst. The lower yields were due to the incomplete amidation process, as the O-alkylated intermediates were observed in 20% yields or so as a mixture with the desired product. The observation of O-alkylated intermediate supported the idea that the present cascade protocol proceeded through a sequence of intermolecular O-alkylation and intramolecular amidation reactions. The problem could be solved by using more reactive 2-iodophenol, resulting in 92% yield. However, the significant influence of *alpha* substitution on the amidation process is puzzling and will require further investigation. Notably, reactions involving the N-alkyl groups such as *n*-butyl and benzyl also proceeded smoothly to provide the desired products **1n** and **1o** in moderate to good yield using 2.5 mol% loading of catalyst.

The scope of the process was further investigated by employing 2-chlorophenol as the building block, as aryl chloride is a challenging substrate in Pd-catalysed amidation reactions. As illustrated in Scheme 1, when N-phenyl, N-(4-methylphenyl), and N-(3-methoxyphenyl) acetamide were reacted with 2-chlorophenol, only 35–39% yields were obtained under our optimised conditions. Improvement of the yield was attempted by increasing the loading of catalyst, enhancing the reaction temperature, or prolonging the reaction time. However, the results obtained were not satisfying. These results indicated that chloride exhibited much lower reactivity than that of the bromide, which is consistent with the reported order.

In conclusion, we have established a Pd-catalysed cascade process, consisting of intermolecular O-alkylation and spontaneous intramolecular amidation, for efficient synthesis of N-substituted 2*H*-1,4-benzoxazin-3-(4*H*)-ones. This process tolerates a range of 2-chloroacetamides to assemble various products in moderate to excellent yields, which should be useful in the pharmaceutical and biochemical fields. The development of other novel cascade protocol towards 2*H*-1,4-benzoxazin-3-(4*H*)-ones is ongoing in our laboratory.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer (400 MHz for ^{1}H or 100 MHz for ^{13}C, respectively) and using $CDCl_3$ as the solvent with $CHCl_3$ as the internal reference. IR spectra (film) were recorded on a NEXUS FI/IR spectrometer. Melting points were taken on Büchi M-560. Elemental analyses and HRMS (+EI) were carried out on ThermoFinnigan EA-1112 and Bruker Daltonics FT-ICR APEX III 7.0, respectively, in Zhejiang University. Mass spectra (MS) were carried out on Thermo LCQ Fleet and measured by ESI. The reaction mixture was monitored by thin-layer chromatography on silica gel plates (60 F-254) using UV light, or 7% ethanolic phosphomolybdic acid and heating as the visualising methods. Flash column chromatography on silica gel was used for purification. Reagents were obtained commercially and used as received.

Synthesis of (2H)-1,4-benzoxazin-3-(4H)-ones (**1a–o**); *general procedure*

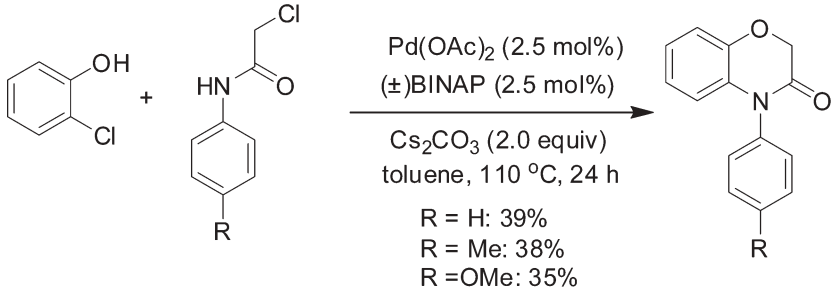
To a 10-mL pressurised process vial were added magnetic stir bar, $Pd(OAc)_2$ (1.7 mg, 7.5×10^{-3} mmol, 2.5 mol%), (±)BINAP (4.7 mg, 7.5×10^{-3} mmol, 2.5 mol%), N-phenyl-2-chloroacetamides (0.45 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol). The loaded vial was then sealed with a rubber cap. The vial was evacuated and backfilled with nitrogen through the cap (this procedure was repeated several times). The dry and degassed toluene (3 mL) and *o*-bromophenol (0.30 mmol) were added by syringe through the cap. The resultant mixture was heated at 110 °C for 24 h in an oil bath, and then filtered through celite which was washed with EtOAc. The combined filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with EtOAc and petroleum ether (60–90 °C) to afford **1a–o**. The structures and yields of the products are given in Table 2.

4-(3,5-Dimethylphenyl)-(2H)-1,4-benzoxazin-3-(4H)-one (**1c**): Yellowish amorphous solid; R_f = 0.67 (25% EtOAc/hexane); IR (film) 1707, 1376 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 7.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.98 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 6.89 (s, 1H), 6.89 (s, 1H), 6.87–6.83 (m, 1H), 6.45 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.76 (s, 2H), 2.36 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 144.8, 139.9 (×2), 135.5, 130.71, 130.66, 126.2 (×2), 124.0, 122.5, 117.0, 116.9, 68.2, 21.3 (×2); MS (+ESI) *m/z* 529 (2M+Na$^+$, 9), 702 (100); HRMS (EI) *m/z* Calcd for $C_{16}H_{15}NO_2$ (M^+) 253.1103; found 253.1104.

4-(2,6-Dimethylphenyl)-(2H)-1,4-benzoxazin-3-(4H)-one (**1e**): Yellowish crystalline solid; m.p. 107–109 °C; R_f = 0.67 (25% EtOAc/hexane); IR (film) 1688, 1370 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.00 (ddd, *J* = 8.4, 8.4, 1.2 Hz, 1H), 6.84 (ddd, *J* = 8.4, 8.4, 1.2 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 4.79 (s, 2H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 144.9, 136.6 (×2), 133.4, 129.1, 128.9 (×2), 128.8, 124.1, 122.9, 117.0, 115.5, 67.9, 17.6 (×2); MS (+ESI) *m/z* 276 (M+Na$^+$, 36), 529 (2M+Na$^+$, 21), 702 (100); HRMS (EI) *m/z* Calcd for $C_{16}H_{15}NO_2$ (M^+) 253.1103; found 253.1101.

4-(4-Chlorophenyl)-(2H)-1,4-benzoxazin-3-(4H)-one (**1i**): White crystalline solid; m.p. 158–159 °C; R_f = 0.66 (25% EtOAc/hexane); IR (film) 1677,1379 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.01 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 6.87 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 6.44 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 145.0, 134.8, 134.3, 130.3, 130.28 (×2), 130.2 (×2), 124.4, 122.7, 117.2, 116.8, 68.2; MS (+ESI) *m/z* 298 (M+K$^+$, 28), 539 (100); Anal. Calcd for $C_{14}H_{10}ClNO_2$: C, 64.75; H, 3.88; N, 5.39. Found: C, 64.89; H, 3.96; N, 5.50%.

4-Naphthanyl-(2H)-1,4-benzoxazin-3-(4H)-one (**1j**): Yellow crystalline solid; m.p. 146–147 °C; R_f = 0.55 (25% EtOAc/hexane);



Scheme 1 Investigation of the reactivity of 2-chlorophenol.

IR (film) 1682, 1370 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.61–7.55 (m, 2H), 7.49–7.39 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 8.4, 8.4 Hz, 1H), 6.70 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 4.91 & 4.84 (AB q, *J* = 15.6, 15.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 144.8, 134.9, 132.3, 130.7, 130.1, 129.8, 128.8, 127.55, 127.52, 126.8, 126.0, 124.2, 122.9, 122.4, 117.1, 116.9, 68.3; MS (+ESI) *m/z* 298 ($M+Na^+$, 53), 572 ($2M+Na^+$, 100); Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.56; H, 4.79; N, 4.98%.

2-Methyl-4-(3,5-dimethylphenyl)-(2H)-1,4-benzoxazin-3-(4H)-one (**1m**): Yellowish amorphous solid; R_f = 0.72 (25% EtOAc/hexane); IR (film) 1693, 1372 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.15 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 7.06 (s, 1H), 7.06 (s, 1H), 7.03 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 6.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.97 (q, *J* = 6.8 Hz, 1H), 2.54 (s, 3H), 2.54 (s, 3H), 1.83 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 144.1, 139.8 (×2), 136.1, 131.0, 130.5, 126.2 (×2), 123.9, 122.4, 117.2, 116.8, 74.0, 21.3 (×2), 16.4; MS (+ESI) *m/z* 290 ($M+Na^+$, 22), 557 ($2M+Na^+$, 100); HRMS (EI) *m/z* Calcd for $C_{17}H_{17}NO_2$ (M^+) 267.1259; found 267.1257.

Financial support by the University of Shaoxing is acknowledged with thanks.

Received 23 November 2011; accepted 7 January 2012
Paper 1101000 doi: 10.3184/174751912X13263685422317
Published online: 31 January 2012

References

1 M. Sainsbury, *Comprehensive heterocyclic chemistry*, A.R. Katritzky and C.W. Rees (eds), Pergamon, Oxford, 1984, Vol. 3, pp. 995–1038.
2 Y. Minami, K. Yoshida, R. Azuma, M. Saeki and T. Otani, *Tetrahedron Lett*., 1993, **34**, 2633.
3 J. Ilaš, P.S. Anderluh, M.S. Dolenc and D. Kikelj, *Tetrahedron*, 2005, **61**, 7325.
4 B. Achari, S.B. Mandal, P.K. Dutta and C. Chowdhury, *Synlett*, 2004, 2449.
5 A. Arrault, F. Touzeau, G. Guillaumet, J.-M. Léger, C. Jarry and J.-Y. Mérour, *Tetrahedron*, 2002, **58**, 8145.
6 C. Ramesh, B.R. Raju, V. Kavala, C.-W. Kuo and C.-F. Yao, *Tetrahedron*, 2011, **67**, 1187.
7 F. Touzeau, A. Arrault, G. Guillaumet, E. Scalbert, B. Pfeiffer, M. Rettori, P. Renard and J.-Y. Mérour, *J. Med. Chem*., 2003, **46**, 1962.
8 G. Feng, J. Wu and W.-M. Dai, *Tetrahedron*, 2006, **62**, 4635.
9 G. Caliendo, E. Perissutti, V. Santagada, F. Fiorino, B. Severino, D. Cirillo, R. d'Emmanuele di Villa Bianca, L. Lippolis, A. Pinto and R. Sorrentino, *Eur. J. Med. Chem*., 2004, **39**, 815.
10 Dai, W.-M., Wang, X. and Ma, C. *Tetrahedron*, 2005, **61**, 6879.
11 L. Banfi, A. Basso, L. Giardini, R. Riva, V. Rocca and G. Guanti, *Eur. J. Org. Chem.*, 2011, 100.
12 X. Xing, J. Wu, G. Feng and W.-M. Dai, *Tetrahedron*, 2006, **62**, 6774.
13 H. Zuo, L. Meng, M. Ghate, K.-H. Hwang, Y.K. Cho, S. Chandrasekhar, C.R. Reddy and D.-S. Shi, *Tetrahedron Lett*., 2008, **49**, 3827.
14 E. Feng, H. Huang, Y. Zhou, D. Ye, H. Jiang and H. Liu, *J. Org. Chem*., 2009, **74**, 2846.
15 D. Chen, G. Shen and W. Bao, *Org. Biomol. Chem*., 2009, **7**, 4067.
16 K.E.O. Ylijoki and E.P. Kundig, *Chem. Commun*., 2011, **47**, 10608.