Tetrahedron 69 (2013) 22–28

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Metal-free dual sp^3 C–H functionalization: I_2-promoted domino oxidative cyclization to construct 2,5-disubstituted oxazoles

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ARTICLE INFO

Article history:
Received 13 September 2012
Received in revised form 16 October 2012
Accepted 26 October 2012
Available online 2 November 2012

Keywords:
I_2-promoted
sp^3 C–H functionalization
Domino oxidative cyclization
Oxazoles

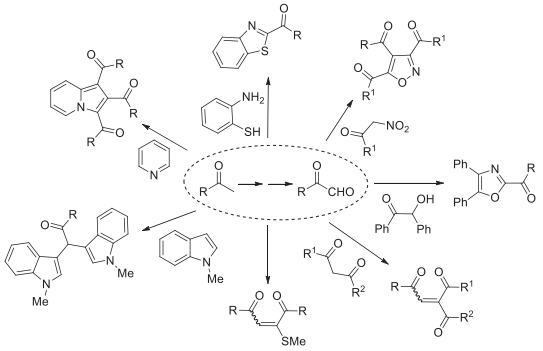
ABSTRACT

An I_2-promoted sp^3 C–H functionalization has been developed for the synthesis of 2,5-disubstituted oxazoles from easily available methyl ketones and benzylamines without any metal and peroxide catalyst. This domino oxidative cyclization process involves the cleavage of C–H bond and the formation of C–N, C–O bonds.

1. Introduction

The direct C–H bond functionalization, especially sp^3 C–H bond functionalization for the construction of carbon–carbon and carbon–heteroatom bonds has become an important synthetic strategy.[1] C–H functionalization generally makes use of the metal catalyzed activation and subsequent functionalization of sp^2 and sp^3 C–H bonds, which directly install important functional groups to enhance the structural complexity of easily-prepared substrates.[2] In recent years, many excellent results of C–H bond functionalization have been achieved based on the metal-mediated approaches.[3] On the other hand, organic reactions carried out under metal-free conditions also received much attention and great progress has been achieved in this area.[4] Nevertheless, only a few metal-free systems, such as TBHP, quaternary ammonium iodide/TBHP, $PhI(OAc)_2$, $I_2/PhI(OAc)_2$, I_2/TBHP, and I_2, focused on C–H functionalization.[5] In this paper, an I_2-promoted sp^3 C–H functionalization for accessing 2,5-disubstituted oxazoles is described.

Oxazole is an important five-membered heterocycle found in many natural products, drugs, and biologically active compounds.[6] In particular, 2,5-disubstituted oxazoles have been evaluated to show activity against diabetes, Gram-positive and Gram-negative bacterial infections, breast cancer, and pancreatic cancer.[7] Up till now, the most synthetic methodologies of oxazole derivatives are typically classified into cyclization of acyclic precursors,[8] oxidation of oxazolines,[9] and the coupling of the prefunctionalized oxazoles with other organometallic reagents.[10] However, the reports for the metal-free catalyzed approach to oxazoles are less known.[5g,11] Recently, we reported an efficient in situ trapping of unstable α-ketoaldehyde intermediates strategy to construct diverse compounds (Scheme 1),[5p,5q,11e,12] which all these methods share the same thematic concept but were quite different from each other in reactions, substrates and/or mechanistic implications. This strategy provides a new way for direct synthesis of pharmacologically interesting heterocycles from simple substrates. As a continuation of our work, we herein report a metal-free and peroxide-free I_2-promoted direct self-sequence synthesis of 2,5-disubstituted



Scheme 1. In situ trapping of unstable α-ketoaldehyde intermediates strategy to construct diverse compounds.

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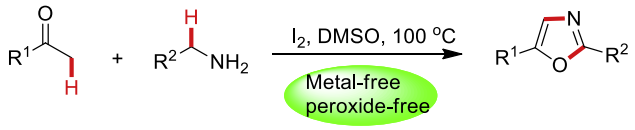
0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2012.10.072

oxazoles via dual sp^3 C–H functionalization from easily available methyl ketones and benzylamines (Scheme 2).

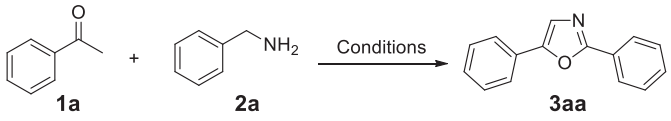


Scheme 2. I_2-promoted direct synthesis of 2,5-disubstituted oxazole via dual sp^3 C–H functionalization.

2. Results and discussion

We initiated the present study with acetophenone (**1a**) and benzylamine (**2a**) as model substrates under conditions similar to those previously reported.[11b,13] It was found that the reaction led to the desired product 2,5-diphenyloxazole (**3aa**) with a yield of 12% (Table 1, entry 1). To our surprise, the reaction could perform in moderate yield in the absence of TBHP (Table 1, entry 2). Much to our satisfaction, by increasing the CuO and I_2 loading to 1.5 equiv and 2.0 equiv, respectively, **3aa** was obtained in 70% yield (Table 1, entry 5). Then other bases employed under this condition, but none of them gave better results (Table 1, entries 6–9). It was also noted that the yield increased to 83% when the reaction was at 100 °C in the absence of base (Table 1, entry 12). Without iodine, no product was observed (Table 1, entry 13), which suggested that iodine played an important role in this reaction. Finally, the dosage of **2a** was investigated, where it was found that the addition of excess benzylamine (1.5 equiv) gave **3aa** in the highest yield (Table 1, entry 12).

Table 1
Optimization of the reaction conditions[a]

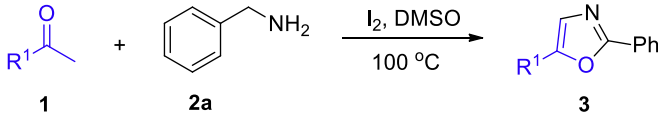


Entry	I_2 (equiv)	Base (equiv)	Oxidant	Temp (°C)	Yield (%)[b]
1	1.0	CuO (1.0)	TBHP	90	12
2	1.0	CuO (1.0)		90	65
3	1.0	CuO (1.5)		90	67
4	1.5	CuO (1.5)		90	67
5	2.0	CuO (1.5)		90	70
6	2.0	K_2CO_3 (1.5)		90	38
7	2.0	DBU (1.5)		90	30
8	2.0	DABCO (1.5)		90	18
9	2.0	Et_3N (1.5)		90	15
10	2.0			90	78
11	2.0			80	74
12	2.0			100	83
13				100	0
14[c]	2.0			100	45
15[d]	2.0			100	69

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.5 mmol) in 3 mL DMSO.
[b] Isolated yields.
[c] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol) in 3 mL DMSO.
[d] Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol) in 3 mL DMSO.

With the optimal reaction conditions in hand, the scope of oxidative cyclization for the synthesis of oxazole derivatives was explored using a series of aryl methyl ketones and benzylamine as the substrates. As illustrated in Table 2, Aryl methyl ketones with both electron-rich (4-OMe, 4-OEt, 3-OMe, 2,4-OMe_2, 3,4-OCH_2O, 3,4-OCH_2CH_2O) and electron-deficient (4-NO_2, 4-Ph) methyl ketones participated in this reaction smoothly to afford the expected oxazoles in moderate to excellent yields (78–91%; **3aa**–**3ia**). Generally, an electron-donating substituent on the aromatic ring was seen to cause a considerable increase in the yield. Unprotected phenol moiety was tolerated under the reaction conditions, and **3ja** was

Table 2
Reaction scope of methyl ketones[a]



Entry	**1** (R^1)	**3**	Yields[b] (%)
1	**1a** (C_6H_5)	**3aa**	83
2	**1b** (4-$MeOC_6H_4$)	**3ba**	87
3	**1c** (4-$EtOC_6H_4$)	**3ca**	80
4	**1d** (3-$MeOC_6H_4$)	**3da**	85
5	**1e** (2,4-$OMe_2C_6H_3$)	**3ea**	82
6	**1f** (3,4-$OCH_2OC_6H_3$)	**3fa**	85
7	**1g** (3,4-$OCH_2CH_2OC_6H_3$)	**3ga**	91
8	**1h** (4-$NO_2C_6H_4$)	**3ha**	78
9	**1i** (4-PhC_6H_4)	**3ia**	79
10	**1j** (4-HOC_6H_4)	**3ja**	80
11	**1k** (2-Naphthyl)	**3ka**	82
12	**1l** (1-Naphthyl)	**3la**	84
13	**1m** (2-Benzofuryl)	**3ma**	72
14	**1n** (2-Furyl)	**3na**	76
15	**1o** (2-Thienyl)	**3oa**	74
16	**1p** (4-Morpholinyl C_6H_4)	**3pa**	94
17	**1q** ((*E*)-C_6H_5–CH=CH)	**3qa**	0

[a] Reaction conditions: **1** (1.0 mmol), **2a** (1.5 mmol), and I_2 (2.0 mmol) in DMSO (3 mL) at 100 °C for 3–5 h.
[b] Isolated yields.

obtained in 80% yield. Whereas, 2-naphthyl methyl ketone and 1-naphthyl methyl ketone also gave their corresponding products **3ka** and **3la** in 82% and 84% yields, respectively. Furthermore, heteroaryl ketones, including benzofuryl, furanyl, thienyl, and morpholinyl were also discovered to be adept in efficiently furnishing the desired products in moderate to excellent yields (72–94%; **3ma**–**3pa**). The structure of the product was further confirmed by an X-ray crystallographic study of **3ba** (Fig. 1).[14] However, the use of unsaturated methyl ketones was shown to be unsuccessful (**3qa**).

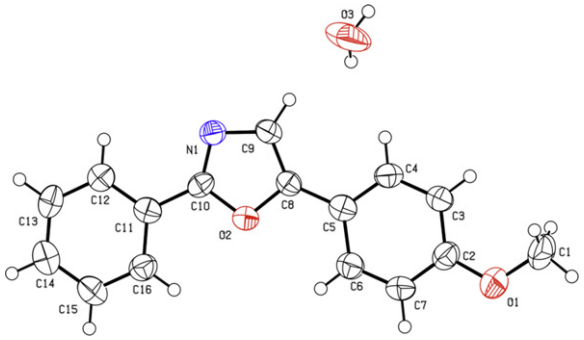
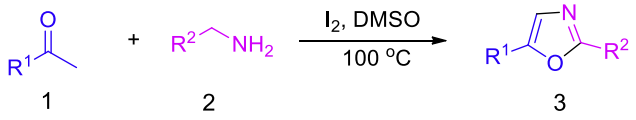


Fig. 1. X-ray crystal structure of compound **3ba**.

Subsequently, different benzylamine derivatives were investigated as summarized in Table 3. The electronic nature of the substrates was shown to strongly influence dual sp^3 C–H functionalization. Electron-deficient substituents were found to increase the product yields. On the other hand, the steric effects of substituents also had a slightly adverse influence on the reaction. For example, the reaction proceeded efficiently when *para* substituted benzylamines were employed (Table 3, entry 1, 10); however, *meta* substituents were found to have a negative effect on the transformation (Table 3, entry 4, 11). It is also worth noting that halo-substituted benzylamine were well tolerated (Table 3, entries 1, 2, 4, 5, 14, 15). Several heteroaryl amines were subsequently used in this system, affording the corresponding oxazoles in good yields (Table 3, entries 6, 7, 8). However, the desired product was not detected with *n*-$BuNH_2$ as the substrate (Table 3, entry 9).

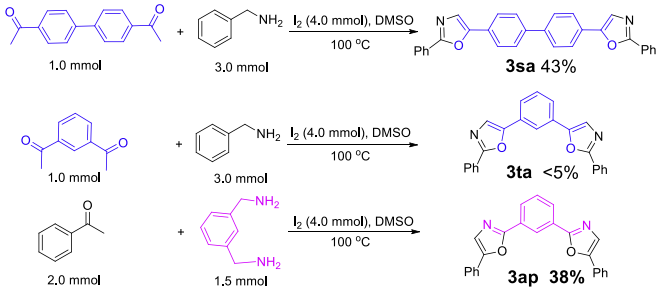
Table 3
Reaction scope of methyl ketones and benzylamine derivatives[a]



Entry	1 (R^1)	2 (R^2)	3	Yields[b] (%)
1	**1a** (C_6H_5)	**2b** (4-ClC_6H_4)	**3ab**	78
2		**2c** (4-FC_6H_4)	**3ac**	76
3		**2d** (4-$CF_3C_6H_4$)	**3ad**	78
4		**2e** (3-ClC_6H_4)	**3ae**	72
5		**2f** (2,4-$Cl_2C_6H_3$)	**3af**	88
6		**2g** (2-Furyl)	**3ag**	78
7		**2n** (4-Pyridyl)	**3ah**	87
8		**2i** (3-Pyridyl)	**3ai**	76
9		**2j** ($CH_3CH_2CH_2$)	**3aj**	0
10	**1b** (4-MeOC_6H_4)	**2k** (4-MeOC_6H_4)	**3bk**	70
11		**2l** (3-MeOC_6H_4)	**3bl**	66
12		**2m** (4-MeC_6H_4)	**3bm**	75
13		**2n** (3-$NO_2C_6H_4$)	**3bn**	72
14		**2o** (2-ClC_6H_4)	**3bo**	80
15	**1r** (4-BrC_6H_4)	**2b** (4-ClC_6H_4)	**3rb**	75

[a] Reaction conditions: **1** (1.0 mmol), **2a** (1.5 mmol), and I_2 (2.0 mmol) in DMSO (3 mL) at 100 °C for 3–5 h.
[b] Isolated yields.

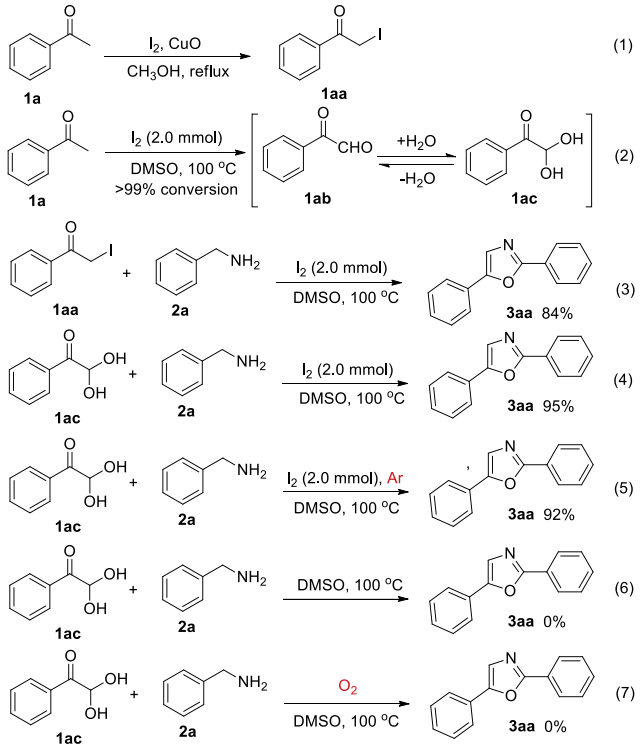
Encouraged by the established scope of this reaction, we turned our attention to the 4,4′-diacetylbiphenyl, 1,3-diacetylbenzene, and 1,3-phenylenedimethanamine. It was satisfying to find that 4,4′-diacetylbiphenyl and 1,3-phenylenedimethanamine smoothly afforded the corresponding products. Unfortunately, 1,3-diacetylbenzene could transformed into the desired products in very low yield, even with longer time (Scheme 3).



Scheme 3. Further scope of methyl ketones and benzylamine derivatives.

To gain some insights into the mechanism of the reaction, a series of control experiments were carried out. Acetophenone (**1a**) was converted into α-iodo acetophenone (**1aa**) in 96% yield using the I_2/CuO system (Scheme 4 (1)).[15] When acetophenone **1a** was heated with I_2 in DMSO at 100 °C in the absence of benzylamine (**2a**), the substrate was transformed into phenylglyoxal (**1ab**) or hydrated hemiacetal (**1ac**) in quantitative conversion (Scheme 4 (2)). Subsequently, **1aa** and **1ac** were subjected to the standard reaction conditions and **3aa** was obtained in 84% and 95% yields, respectively (Scheme 4 (3, 4, 5)). This result clearly confirmed phenacyl iodine **1aa** and phenylglyoxal **1ab** were the key intermediates for this transformation. However, when **1ac** was tested in the absence of I_2, **3aa** was not observed (Scheme 4 (6, 7)). This results indicated that iodine played an important role in the condensation/cyclization process.

To further investigate the reaction process, we monitored the reaction of **1b** (0.1 mmol), **2a** (0.12 mmol) with I_2 (0.2 mmol) in DMSO-d_6 by ^{1}H NMR spectroscopy. Through comparison with the previous report,[5p] the signal at 4.53 ppm was assigned to the $-CH_2-$ group of α-iodo aryl methyl ketone **1ba** at 5–15 min. In addition, the signals at 9.54 ppm and 5.64 ppm were assigned to the



Scheme 4. The controlled experiment to prove the mechanism.

phenylglyoxal aldehyde group (**1bb**) and the hemiacetal group (**1bc**), respectively (Fig. 2). With the consumption of **1b**, the intermediate **1bb** and **1bc** appeared and the concentration subsequently increased over time. Through comparison with an authentic sample, the signal at 4.05 ppm was assigned to the $-CH_2-$ group of benzylamine (**2a**). In addition, the signals at 3.84 ppm and 3.82 ppm were assigned to the $-OCH_3$ group of phenylglyoxal (**1bb**) or hydrated hemiacetal (**1bc**) and the $-OCH_3$ group of 2,5-diphenyloxazole (**3ba**). With the consumption of **2a**,

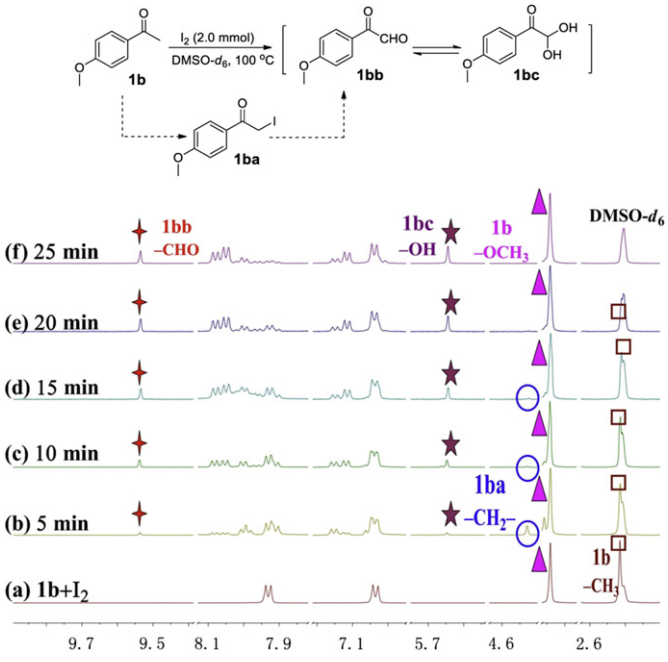


Fig. 2. The reaction process of **1b** (0.1 mmol) with I_2 (0.2 mmol) was monitored by ^{1}H NMR (600 MHz, DMSO-d_6, 298±0.5 K) over time.

1bb, and **1bc**, the product **3ba** appeared, and the concentration was seen to increase over time (Fig. 3). These results disclosed that phenacyl iodine (**1ba**) and phenylglyoxal (**1bb**) were important intermediates in the whole transformation.

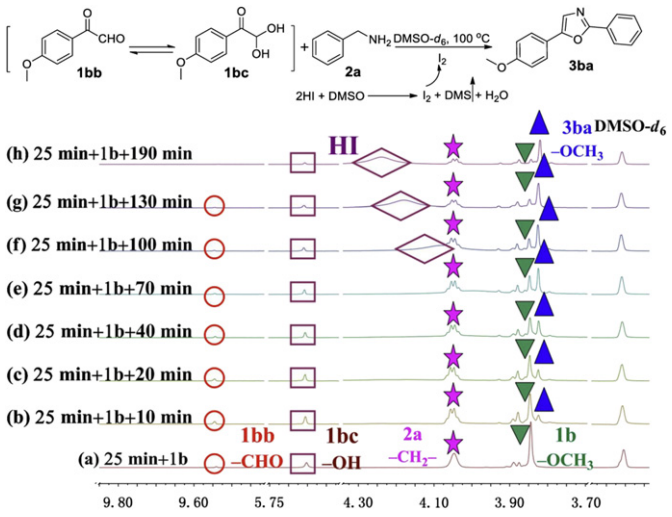
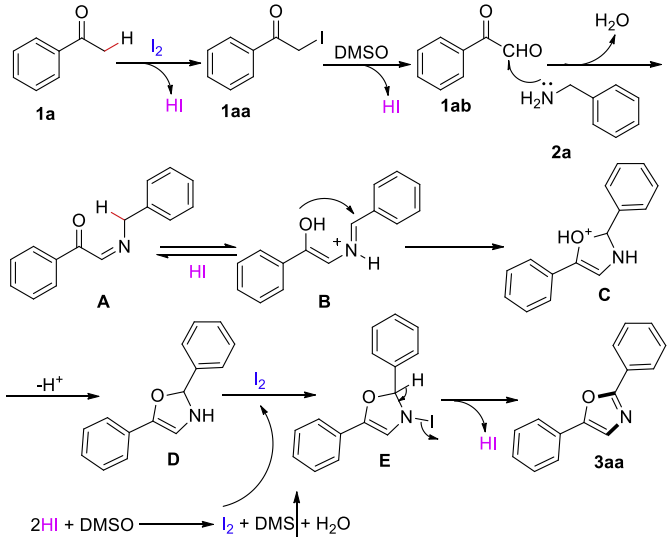


Fig. 3. The reaction process of **1b** (0.1 mmol) with I_2 (0.2 mmol) was monitored by ^1H NMR for 25 min, then **2a** (0.12 mmol) was added. This process was monitored by ^1H NMR (600 MHz, DMSO-d_6, 298±0.5 K) over time.

On the basis of the results described above and previous reports,[11a,11b,13] a plausible mechanism for I_2-promoted dual sp^3 C–H functionalization was proposed using acetophenone (**1a**) and benzylamine (**2a**) as an example (Scheme 5). Initially, the substrate **1a** was converted into the intermediate α-iodo acetophenone (**1aa**) in the presence of I_2. Subsequently, oxidation of intermediate **1aa** by DMSO could take place to yield intermediate phenylglyoxal (**1ab**). Then, benzylamine (**2a**) reacted with the aldehyde group of phenylglyoxal (**1ab**) to afford **A** or its enolizational isomer **B**, which underwent an intramolecular cyclization via an oxygen atom attacking to double bonds and providing the intermediate **C**. Consequently, intermediate **C** converted into intermediate **D** underwent deprotonation and it further furnished the desired product **3aa** in the presence of the excess or regenerated iodide.[5p,16] In the process, byproduct HI could be oxidized by DMSO to regenerate at least 0.5 equiv of iodine.[17]



Scheme 5. The plausible mechanism of the present reaction.

3. Conclusion

In conclusion, we have developed an I_2-promoted domino oxidative cyclization process to construct oxazole derivatives from easily available methyl ketones and benzylic amines. It is notable that this metal-free and peroxide-free transformation involves dual functionalization of two types of C(sp^3)–H bonds (sp^3 α-C–H of carbonyl and sp^3 α-C–H of nitrogen atom). Applications of I_2-promoted sp^3 C–H functionalization for the construction of other heterocycles are currently being investigated in our laboratory.

4. Experimental

4.1. General

All substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin–Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. ^1H spectra were recorded in $CDCl_3$ or DMSO on 400/600 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet), coupling constants (Hertz) and integration. ^{13}C spectra were recorded in $CDCl_3$ or DMSO on 100 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on a Bruker 7-T FT-ICR MS equipped with APCI. MS was carried out on a Finnigan Trace MS spectrometer (EI, 70 eV). The X-ray crystal structure determination of **3ba** was obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

4.2. General procedure for synthesis of 3 (3aa as an example)

A mixture of acetophenone **1a** (120 mg, 1.0 mmol), benzylamine **2a** (160.7 mg, 1.5 mmol), and iodine (507.6 mg, 2.0 mmol) in DMSO (3 mL) was stirred at 100 °C for 5 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc three times (3×50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc=100:1) to yield the desired product **3aa** as a white solid (183.4 mg, 83% yield).

4.3. Characterization data

*4.3.1. 2,5-Diphenyloxazole (**3aa**).*[11b] Yield 83%; white solid; mp 65–68 °C; IR (KBr): 3061, 1652, 1585, 1542, 1482, 1282, 1131, 1065, 1024, 949, 906, 824, 763, 704, 479 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10 (d, *J*=7.6 Hz, 2H), 7.71 (d, *J*=7.6 Hz, 2H), 7.48–7.37 (m, 6H), 7.33 (t, *J*=7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.1, 151.2, 130.3, 128.9, 128.8, 128.4, 128.0, 127.4, 126.2, 124.1, 123.4; HRMS (APCI): *m*/*z* $[M+H]^+$ calcd for $C_{15}H_{12}NO$: 222.0913; found: 222.0914.

*4.3.2. 5-(4-Methoxyphenyl)-2-phenyloxazole (**3ba**).*[11b] Yield 87%; light yellow solid; mp 73–76 °C; IR (KBr): 3057, 2969, 2840, 1656, 1607, 1498, 1252, 1173, 1021, 949, 825, 689, 613, 522 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, *J*=7.2 Hz, 2H), 7.64 (d, *J*=8.4 Hz, 2H), 7.55–7.38 (m, 3H), 7.31 (s, 1H), 6.96 (d, *J*=8.4 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.5, 159.8, 151.3, 130.1, 128.7, 127.5, 126.1, 125.7, 121.9, 120.8, 114.4, 55.3; HRMS (APCI): *m*/*z* $[M+H]^+$ calcd for $C_{16}H_{14}NO_2$: 252.1019; found: 252.1021.

*4.3.3. 5-(4-Ethoxyphenyl)-2-phenyloxazole (**3ca**).* Yield 80%; white solid; mp 89–92 °C; IR (KBr): 3104, 2973, 1612, 1568, 1542, 1500,

1389, 1289, 1248, 1174, 1111, 1044, 919, 823, 689, 523 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J=7.6 Hz, 2H), 7.63 (d, J=7.6 Hz, 2H), 7.51–7.39 (m, 3H), 7.31 (s, 1H), 6.95 (d, J=8.0 Hz, 2H), 4.05 (q, J=7.2 Hz, 2H), 1.43 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.4, 159.1, 151.3, 130.0, 128.7, 127.5, 126.1, 125.7, 121.8, 120.6, 114.8, 63.5, 14.7; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO_2$: 266.1176; found: 266.1178.

*4.3.4. 5-(3-Methoxyphenyl)-2-phenyloxazole (**3da**).*[11b] Yield 85%; light yellow solid; mp 90–92 °C; IR (KBr): 3095, 2952, 2830, 1598, 1538, 1484, 1343, 1293, 1231, 1044, 966, 837, 707, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10–8.09 (m, 2H), 7.51–7.38 (m, 4H), 7.36–7.27 (m, 2H), 7.23 (s, 1H), 6.90–6.81 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.1, 159.9, 151.0, 130.3, 130.0, 129.1, 128.8, 127.3, 126.2, 123.7, 116.7, 113.9, 109.7, 55.3; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{16}H_{14}NO_2$: 252.1019; found: 252.1021.

*4.3.5. 5-(2,4-Dimethoxyphenyl)-2-phenyloxazole (**3ea**).* Yield 82%; white solid; mp 131–134 °C; IR (KBr): 3063, 2942, 2835, 1677, 1609, 1499, 1465, 1268, 1209, 1125, 1025, 811, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11 (d, J=7.2 Hz, 2H), 7.80 (d, J=8.4 Hz, 1H), 7.52 (s, 1H), 7.50–7.36 (m, 3H), 6.61 (d, J=8.4 Hz, 1H), 6.55 (s, 1H), 3.95 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.1, 160.7, 157.0, 147.9, 129.9, 128.7, 127.7, 126.7, 126.1, 125.6, 110.6, 105.0, 98.6, 55.6, 55.5; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO_3$: 282.1125; found: 282.1126.

*4.3.6. 5-(Benzo[d][1,3]dioxol-5-yl)-2-phenyloxazole (**3fa**).*[18] Yield 85%; light yellow solid; mp 133–136 °C; IR (KBr): 3063, 2916, 1602, 1547, 1493, 1328, 1240, 1104, 1036, 963, 927, 871, 808, 705 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J=7.8 Hz, 2H), 7.50–7.42 (m, 3H), 7.32 (s, 1H), 7.24 (d, J=7.8 Hz, 1H), 7.17 (s, 1H), 6.88 (d, J=7.8 Hz, 1H), 6.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.6, 151.1, 148.2, 147.9, 130.2, 128.8, 127.4, 126.1, 122.2, 122.1, 118.3, 108.8, 104.8, 101.4; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{16}H_{12}NO_3$: 266.0812; found: 266.0814.

*4.3.7. 5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-2-phenyloxazole (**3ga**).* Yield 91%; white solid; mp 127–130 °C; IR (KBr): 3042, 2932, 1589, 868, 1500, 1316, 1278, 1119, 1060, 891, 858, 799, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11–8.03 (m, 2H), 7.52–7.39 (m, 3H), 7.30 (s, 1H), 7.25–7.16 (m, 2H), 6.92 (d, J=8.4 Hz, 1H), 4.29 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.6, 151.0, 143.9, 143.8, 130.1, 128.7, 127.4, 126.1, 122.3, 121.6, 117.8, 117.7, 113.2, 64.4, 64.3; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{14}NO_3$: 280.0968; found: 280.0970.

*4.3.8. 5-(4-Nitrophenyl)-2-phenyloxazole (**3ha**).* Yield 78%; yellow solid; mp 190–193 °C; IR (KBr): 3074, 1602, 1517, 1479, 1447, 1336, 1142, 1108, 950, 848, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.32 (d, J=8.8 Hz, 2H), 8.13 (br s, 2H), 7.87 (d, J=8.4 Hz, 2H), 7.65 (s, 1H), 7.52 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.7, 149.1, 147.0, 133.6, 131.1, 128.9, 126.9, 126.7, 126.6, 124.5, 124.4; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{15}H_{11}N_2O_3$: 267.0764; found: 267.0766.

*4.3.9. 5-([1,1′-Biphenyl]-4-yl)-2-phenyloxazole (**3ia**).* Yield 79%; light yellow solid; mp 140–143 °C; IR (KBr): 3060, 2924, 1671, 1541, 1478, 1134, 1060, 949, 835, 764, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14 (d, J=6.4 Hz, 2H), 7.80 (d, J=8.4 Hz, 2H), 7.69 (d, J=8.0 Hz, 2H), 7.64 (d, J=7.2 Hz, 2H), 7.55–7.43 (m, 6H), 7.38 (d, J=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.1, 151.0, 141.1, 140.2, 130.3, 128.8(2), 128.7(7), 127.6, 127.5, 127.3, 126.9, 126.8, 126.2, 124.5, 123.5; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{21}H_{16}NO$: 298.1226; found: 298.1228.

*4.3.10. 4-(2-Phenyloxazol-5-yl)phenol (**3ja**).*[11b] Yield 80%; yellow solid; mp 197–202 °C; IR (KBr): 3124, 1666, 1609, 1541, 1504, 1479, 1443, 1274, 1171, 1133, 948, 842, 805, 707, 618, 524 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.86 (s, 1H), 8.05 (br s, 2H), 7.77–7.62 (m, 2H), 7.58 (s, 1H), 7.56–7.42 (m, 3H), 6.99 (d, J=7.2 Hz, 1H), 6.89 (d, J=6.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 158.0, 157.1, 151.3, 149.7, 134.4, 130.2, 129.1, 127.0, 125.8, 121.8, 120.6, 118.6, 115.9; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{15}H_{12}NO_2$: 238.0863; found: 238.0865.

*4.3.11. 5-(Naphthalen-2-yl)-2-phenyloxazole (**3ka**).*[11b] Yield 82%; light yellow solid; mp 93–96 °C; IR (KBr): 3091, 2926, 1728, 1480, 1130, 970, 857, 817, 743, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.18–8.12 (m, 3H), 7.90–7.84 (m, 2H), 7.82 (d, J=8.0 Hz, 1H), 7.76–7.73 (m, 1H), 7.54–7.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.3, 151.3, 133.3, 133.0, 130.3, 128.8, 128.7, 128.2, 127.8, 127.4, 126.8, 126.5, 126.3, 125.2, 123.9, 122.9, 122.0; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{19}H_{14}NO$: 272.1070; found: 272.1072.

*4.3.12. 5-(Naphthalen-1-yl)-2-phenyloxazole (**3la**).*[11b] Yield 84%; light yellow solid; mp 110–114 °C; IR (KBr): 3052, 1554, 1481, 1444, 1393, 1152, 1116, 1066, 1025, 990, 920, 838, 793, 767, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.35 (d, J=8.0 Hz, 1H), 8.15 (d, J=7.6 Hz, 2H), 7.88 (t, J=8.0 Hz, 2H), 7.80 (d, J=7.2 Hz, 1H), 7.59–7.43 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.4, 150.5, 133.8, 130.4, 130.0, 129.5, 128.8, 128.7, 127.4, 127.1, 126.7, 126.3, 126.3, 126.2, 125.2 (×2), 124.8; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{19}H_{14}NO$: 272.1070; found: 272.1072.

*4.3.13. 5-(Benzofuran-2-yl)-2-phenyloxazole (**3ma**).*[11b] Yield 72%; White solid; mp 140–143 °C; IR (KBr): 3063, 2924, 1545, 1445, 1254, 1161, 1128, 1062, 879, 838, 789, 745, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15–8.08 (m, 2H), 7.61 (d, J=7.6 Hz, 1H), 7.57 (s, 1H), 7.54–7.45 (m, 4H), 7.33 (t, J=7.6 Hz, 1H), 7.29–7.22 (m, 1H), 7.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.7, 154.8, 145.2, 143.4, 130.7, 128.9, 128.3, 126.9, 126.5, 125.6, 125.1, 123.4, 121.2, 111.2, 103.2; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{12}NO_2$: 262.0863; found: 262.0865.

*4.3.14. 5-(Furan-2-yl)-2-phenyloxazole (**3na**).*[11b] Yield 76%; White solid; mp 71–74 °C; IR (KBr): 3318, 2962, 1639, 1547, 1482, 1449, 1261, 1159, 1005, 882, 801, 744, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.13–8.04 (m, 2H), 7.53–7.43 (m, 4H), 7.35 (s, 1H), 6.70 (d, J=3.2 Hz, 1H), 6.54–6.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.6, 143.6(4), 143.5(9), 142.8, 130.4, 128.7, 127.0, 126.3, 123.3, 111.5, 107.2; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{13}H_{10}NO_2$: 212.0707; found: 212.0706.

*4.3.15. 2-Phenyl-5-(thiophen-2-yl)oxazole (**3oa**).* Yield 74%; light green solid; mp 71–74 °C; IR (KBr): 3098, 1583, 1475, 1443, 1256, 1127, 1019, 908, 814, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10–8.02 (m, 2H), 7.51–7.40 (m, 3H), 7.37–7.35 (m, 1H), 7.33 (d, J=4.8 Hz, 1H), 7.30 (s, 1H), 7.10–7.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.6, 146.7, 130.3, 129.8, 128.8, 127.8, 127.1, 126.2, 125.6, 124.2, 123.1; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{13}H_{10}NOS$: 228.0478; found: 228.0479.

*4.3.16. 4-(4-(2-Phenyloxazol-5-yl)phenyl)morpholine (**3pa**).* Yield 94%; light yellow solid; mp 179–182 °C; IR (KBr): 3122, 2962, 2852, 1612, 1546, 1505, 1447, 1382, 1350, 1268, 1240, 1122, 1068, 928, 817, 778, 705, 659, 529 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J=7.6 Hz, 2H), 7.62 (d, J=7.6 Hz, 2H), 7.50–7.39 (m, 3H), 7.30 (s, 1H), 6.95 (d, J=8.0 Hz, 2H), 3.87 (t, J=4.6 Hz, 4H), 3.21 (t, J=4.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.3, 151.4, 151.1, 130.9, 130.0, 128.7, 127.6, 126.0, 125.3, 121.6, 115.3, 66.7, 48.6; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_2$: 307.1441; found: 307.1443.

*4.3.17. 2-(4-Chlorophenyl)-5-phenyloxazole (**3ab**).*[11b] Yield 78%; light yellow solid; mp 117–120 °C; IR (KBr): 3064, 2926, 1728, 1601,

1476, 1399, 1276, 1129, 1086, 947, 826, 760, 729, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02 (d, J=8.4 Hz, 2H), 7.69 (d, J=7.6 Hz, 2H), 7.46–7.37 (m, 5H), 7.34 (t, J=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.1, 151.4, 136.3, 129.1, 128.9, 128.5, 127.7, 127.5, 125.8, 124.2, 123.5; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{15}H_{11}ClNO$: 256.0524; found: 256.0526.

*4.3.18. 2-(4-Fluorophenyl)-5-phenyloxazole (**3ac**).*[11b] Yield 76%; light yellow solid; mp 78–81 °C; IR (KBr): 3052, 2924, 1652, 1604, 1491, 1410, 1225, 1129, 1092, 949, 905, 837, 758, 731, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12–8.04 (m, 2H), 7.69 (d, J=7.6 Hz, 2H), 7.49–7.37 (m, 3H), 7.33 (t, J=7.2 Hz, 1H), 7.16 (t, J=8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.2, 162.7, 151.3, 128.9, 128.4(3), 128.3(5), 128.3, 127.8, 124.1, 123.8, 123.3, 116.1, 115.8; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{15}H_{11}FNO$: 240.0819; found: 240.0821.

*4.3.19. 5-Phenyl-2-(4-(trifluoromethyl)phenyl)oxazole (**3ad**).*[11b] Yield 78%; light yellow solid; mp 108–112 °C; IR (KBr): 3082, 2925, 1549, 1483, 1413, 1329, 1126, 948, 845, 760, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.20 (d, J=8.0 Hz, 2H), 7.80–7.70 (m, 4H), 7.46 (t, J=7.4 Hz, 3H), 7.37 (t, J=7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.6, 152.1, 131.6, 130.5, 129.0, 128.8, 127.6, 126.4, 125.8(3), 125.8(0), 124.3, 123.8, 123.7; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{16}H_{11}F_3NO$: 290.0787; found: 290.0789.

*4.3.20. 2-(3-Chlorophenyl)-5-phenyloxazole (**3ae**).*[11b] Yield 72%; white solid; mp 100–103 °C; IR (KBr): 3060, 1578, 1538, 1459, 1302, 1130, 1075, 950, 884, 822, 792, 761, 720, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07 (s, 1H), 8.01–7.95 (m, 1H), 7.70 (d, J=7.2 Hz, 2H), 7.49–7.39 (m, 5H), 7.34 (t, J=7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.7, 151.7, 134.9, 130.2, 130.1, 129.0, 128.9, 128.6, 127.7, 126.2, 124.3, 124.2, 123.5; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{15}H_{11}ClNO$: 256.0524; found: 256.0526.

*4.3.21. 2-(2,4-Dichlorophenyl)-5-phenyloxazole (**3af**).* Yield 88%; white solid; mp 111–115 °C; IR (KBr): 3070, 2927, 1729, 1554, 1481, 1450, 1387, 1260, 1132, 1101, 1031, 953, 869, 829, 757, 731, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.04 (d, J=8.4 Hz, 1H), 7.71 (d, J=7.6 Hz, 2H), 7.53 (s, 1H), 7.50 (s, 1H), 7.44 (t, J=7.6 Hz, 2H), 7.38–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.1, 151.9, 136.3, 132.9, 131.3, 131.1, 128.9, 128.7, 127.5, 127.3, 124.6, 124.3, 123.2; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{15}H_{10}Cl_2NO$: 290.0134; found: 290.0137.

*4.3.22. 2-(Furan-2-yl)-5-phenyloxazole (**3ag**).*[11a] Yield 78%; white solid; mp 67–70 °C; IR (KBr): 3137, 3058, 2924, 1625, 1516, 1449, 1260, 1167, 1132, 1007, 936, 883, 830, 759, 717, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, J=7.2 Hz, 2H), 7.56 (s, 1H), 7.40 (t, J=7.6 Hz, 3H), 7.31 (t, J=7.4 Hz, 1H), 7.06 (d, J=3.2 Hz, 1H), 6.56–6.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.8, 150.7, 144.3, 142.8, 128.8, 128.4, 127.5, 124.0, 123.1, 111.8, 111.3; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{13}H_{10}NO_2$: 212.0706; found: 212.0708.

*4.3.23. 5-Phenyl-2-(pyridin-4-yl)oxazole (**3ah**).* Yield 87%; white solid; mp 98–102 °C; IR (KBr): 3373, 3102, 3050, 1606, 1533, 1480, 1414, 1214, 1134, 996, 954, 870, 831, 758, 706, 683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.75 (d, J=4.8 Hz, 2H), 7.93 (d, J=5.2 Hz, 2H), 7.5 (d, J=7.6 Hz, 2H), 7.50 (s, 1H), 7.49–7.42 (m, 2H), 7.41–7.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.6, 152.5, 150.4, 134.1, 129.0(2), 128.9(7), 127.2, 124.4, 123.9, 119.7; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{14}H_{11}N_2O$: 223.087; found: 223.0864.

*4.3.24. 5-Phenyl-2-(pyridin-3-yl)oxazole (**3ai**).*[11a] Yield 76%; white solid; mp 85–87 °C; IR (KBr): 3052, 1567, 1480, 1404, 1185, 1112, 1057, 1021, 948, 814, 763, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.33 (s, 1H), 8.70–8.66 (m, 1H), 8.33 (d, J=8.0 Hz, 1H), 7.71 (t, J=4.0 Hz, 2H), 7.47–7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.6, 151.9, 150.8, 147.4, 133.2, 129.0, 128.9, 128.7, 127.4, 124.3, 124.2, 123.5; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{14}H_{11}N_2O$: 223.0866; found: 223.0864.

*4.3.25. 2,5-Bis(4-methoxyphenyl)oxazole (**3bk**).* Yield 70%; light yellow solid; mp 123–126 °C; IR (KBr): 3010, 2929, 1611, 1302, 1251, 1171, 1055, 1021, 948, 832, 737, 701, 632 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02 (d, J=8.0 Hz, 2H), 7.63 (d, J=8.0 Hz, 2H), 7.28 (s, 1H) 6.97 (t, J=8.4 Hz, 4H), 3.87 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.2, 160.6, 159.6, 150.7, 127.8, 125.6, 121.7, 121.0, 120.4, 114.3, 114.2, 55.5, 55.4; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO_3$: 282.1125; found: 282.1127.

*4.3.26. 2-(3-Methoxyphenyl)-5-(4-methoxyphenyl)oxazole (**3bl**).* Yield 66%; yellow solid; mp 73–76 °C; IR (KBr): 3018, 2961, 1602, 1541, 1500, 1457, 1322, 1297, 1250, 1177, 1024, 826, 727, 682, 612 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, J=7.6 Hz, 1H), 7.62 (d, J=8.8 Hz, 3H), 7.36 (t, J=7.8 Hz, 1H), 7.30 (s, 1H), 7.06–6.91 (m, 3H), 3.87 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.3, 159.8, 151.3, 129.7, 128.7, 125.8, 125.7, 121.8, 120.7, 118.5, 116.5, 114.3, 110.7, 55.4, 55.3; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO_3$: 282.1125; found: 282.1122.

*4.3.27. 5-(4-Methoxyphenyl)-2-(p-tolyl)oxazole (**3bm**).* Yield 75%; light green solid; mp 115–120 °C; IR (KBr): 3123, 2925, 1656, 1611, 1584, 1499, 1293, 1254, 1175, 1110, 1056, 1025, 949, 827, 727, 630, 498 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (d, J=8.0 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H), 7.36–7.27 (m, 3H), 6.97 (d, J=8.4 Hz, 2H), 3.86 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.7, 159.7, 150.9, 140.3, 129.4, 126.1, 125.6, 124.8, 121.7, 120.9, 114.3, 55.3, 21.5; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO_2$: 266.1176; found: 266.1178.

*4.3.28. 5-(4-Methoxyphenyl)-2-(3-nitrophenyl)oxazole (**3bn**).* Yield 72%; yellow solid; mp 155–158 °C; IR (KBr): 3102, 2925, 1611, 1521, 1351, 1296, 1256, 1179, 1104, 1021, 900, 819, 740, 706, 614, 513 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.88 (s, 1H), 8.40 (d, J=7.6 Hz, 1H), 8.28 (d, J=8.0 Hz, 1H), 7.66 (t, J=8.0 Hz, 3H), 7.37 (s, 1H), 6.99 (d, J=8.4 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.2, 158.1, 152.4, 131.6, 130.7, 129.9, 129.1, 126.0, 124.3, 122.3, 120.8, 120.1, 114.5, 55.4; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{16}H_{13}N_2O_4$: 297.0870; found: 297.0872.

*4.3.29. 2-(2-Chlorophenyl)-5-(4-methoxyphenyl)oxazole (**3bo**).* Yield 80%; light yellow solid; mp 98–102 °C; IR (KBr): 3121, 3048, 2926, 1690, 1613, 1573, 1498, 1453, 1345, 1291, 1252, 1176, 1028, 954, 836, 810, 764, 730, 650, 610, 525 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12–8.03 (m, 1H), 7.64 (d, J=8.8 Hz, 2H), 7.53–7.45 (m, 1H), 7.38 (s, 1H), 7.36–7.31 (m, 2H), 6.94 (d, J=8.4 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.8, 158.2, 151.6, 132.0, 131.2, 130.6, 130.5, 126.7, 126.1, 125.8, 121.6, 120.5, 114.3, 55.2; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{16}H_{13}ClNO_2$: 286.0629; found: 286.0631.

*4.3.30. 5-(4-Bromophenyl)-2-(4-chlorophenyl)oxazole (**3rb**).* Yield 75%; yellow solid; mp 145–149 °C; IR (KBr): 3083, 1602, 1476, 1404, 1133, 1096, 1008, 948, 826, 733, 495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00 (d, J=6.4 Hz, 2H), 7.55 (s, 4H), 7.43 (d, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.4, 150.4, 136.8, 136.6, 132.1, 129.1, 127.5, 126.6, 125.6, 124.0, 122.4; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{15}H_{10}BrClNO$: 333.9629; found: 333.9631.

*4.3.31. 4,4′-Bis(2-phenyloxazol-5-yl)-1,1′-biphenyl (**3sa**).* Yield 43%; yellow solid; mp 167–171 °C; IR (KBr): 3039, 2925, 2854, 1728, 1672, 1604, 1538, 1472, 1263, 1134, 1060, 950, 821, 710, 686, 487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14 (d, J=7.6 Hz,

4H), 7.81 (d, J=8.4 Hz, 4H), 7.72 (d, J=8.0 Hz, 4H), 7.50 (d, J=7.2 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.3, 151.0, 140.1, 130.9, 130.4, 128.9, 127.4, 126.3, 124.7, 123.8, 109.9; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{30}H_{21}N_2O_2$: 441.1598; found: 441.1595.

*4.3.32. 1,3-Bis(5-phenyloxazol-2-yl)benzene (**3ap**).* Yield 38%; white solid; mp 176–179 °C; IR (KBr): 3108, 3063, 1586, 1537, 1478, 1425, 1309, 1134, 1059, 1025, 939, 908, 824, 761, 709, 683, 492 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.82 (s, 1H), 8.21 (d, J=7.2 Hz, 2H), 7.77 (d, J=6.8 Hz, 4H), 7.62 (t, J=7.6 Hz, 1H), 7.47 (t, J=8.4 Hz, 6H), 7.37 (t, J=6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.4, 151.7, 129.4, 129.0, 128.6, 128.2, 127.9, 127.8, 124.4, 123.8, 123.6; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{24}H_{17}N_2O_2$: 365.1285; found: 365.1288.

Acknowledgements

We thank the National Natural Science Foundation of China (Grant 20902035, 21032001 and 21272085). We also thank Dr. Xianggao Meng for his help with X-ray diffraction analysis and Dr. Chuanqi Zhou, Hebei University, for analytical support.

Supplementary data

The general experimental methods and the ^{1}H NMR titration experiments of **3ba** with HI. The reaction process of **1b** (0.1 mmol), **2a** (0.12 mmol) with I_2 (0.2 mmol) was monitored by ^{1}H NMR (600 MHz, DMSO-d_6, 298±0.5 K) and X-ray crystal structures of compound **3ba** are available in Supplementary data. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.10.072.

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