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A versatile method for the synthesis of heterocyclic ring-fused 1,2-oxazinones from the NHC-catalyzed reactions of 2-aroylvinylarylaldehydes with nitrosoarenes

Jing Qu, Ying Cheng *

College of Chemistry, Beijing Normal University, Beijing 100875, China

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Pyrido[3,2-*d*][1,2]oxazin-5-one

ABSTRACT

The NHC-catalyzed reactions of nitrosoarenes with 4-(2-aroylvinyl)furan-3-carbaldehydes, 4-(2-aroylvinyl) thiophene-3-carbaldehydes or 2-(2-aroylvinyl)nicotinaldehydes were studied, which produced novel furo [3,4-*d*][1,2]oxazin-4-ones, thieno[3,4-*d*][1,2]oxazin-4-ones or pyrido[3,2-*d*][1,2]oxazin-5-ones, respectively. This work developed a versatile method for the construction of different types of heterocyclic ring-fused 1,2-oxazinones that are not easy accessible by other methods.

1. Introduction

1,2-Oxazinone ring is widely present in numerous biologically active compounds with potential applications in pharmaceuticals or agrochemicals. For example, a number of 4-acyl-1,2-oxazin-3-one derivatives have been prepared as herbicides,[1,2] and some of them also were tested as acaricides and plant growth regulators.[2] 4-Aryl-1,2-oxazin-3-one derivatives were found to have herbicidal, insecticidal and acaricidal activities,[3] and *N*-carboxymethyl-1,2-oxazin-3-ones showed antibacterial activity.[4] The allosteric MEK inhibitor CH4987655, a novel 1,2-oxazin-3-one derivative, has been synthesized as an orally available anticancer agent.[5] Benzo[*d*][1,2]oxazin-4-one derivatives have been studied for their pesticidal activity,[6] or antidiabetic and hypolipidemic activities,[7] while quinoline-fused oxazinones have been evaluated for their insecticidal activity[8a,b] or for the treatment of metabolic disorders.[8c] In literature, numerous studies on the 1,2-oxazinones and benzoxazinones derivatives have been documented.[1–7,9] However, except a few work of the synthesis or bioactivities of pyrido[3,2-*d*][1,2]oxazinones having been reported,[8] the heterocyclic ring-fused 1,2-oxazinones are still largely unexplored. The development of simple, efficient, and versatile method for the construction of various heterocyclic ring-fused 1,2-oxazinones is of great importance.

A few NHC-catalyzed reactions of carbonyl compounds with nitrosoarenes have been reported, which led to the formation of *N*-arylhydroxamic acids, isoxazolidin-5-ones, isoxazol-5-ones, β-amino acid esters, benzo[*b*][1,4]oxazepin-2-ones or oxazetidinones depending on the structures of reactants and carbene catalysts.[10] Very recently, we established an efficient method for the synthesis of benzo[*d*][1,2]oxazin-4-ones from the NHC-catalyzed reactions of *ortho* electron-deficient vinyl substituted benzaldehydes with nitrosoarenes.[11] We envisioned that this reaction might be developed into a versatile strategy for the construction of various aromatic ring-fused 1,2-oxazinones by varying the structures of aromatic aldehydes. Thus, we undertook the current study on the reaction of nitrosoarenes with 4-(2-aroylvinyl)furan-3-carbaldehydes, 4-(2-aroylvinyl)thiophene-3-carbaldehydes or 2-(2-aroylvinyl)nicotinaldehydes.

2. Results and discussion

We started the work with the examination on the reaction between 4-(2-benzoylvinyl)furan-3-carbaldehyde and nitrosobenzene. Initially, the reaction of (*E*)-4-(2-benzoylvinyl)furan-3-carbaldehyde **1a** with nitrosobenzene **2a** (**1a**:**2a**=1:1.5) catalyzed by 20 mol % of different NHCs **4**, which were generated in situ from the corresponding azolium salts **3** with DBU, was examined in dry chloroform at ambient temperature. It was found that 1,4-dimethyl-

* Corresponding author. E-mail address: ycheng2@bnu.edu.cn (Y. Cheng).

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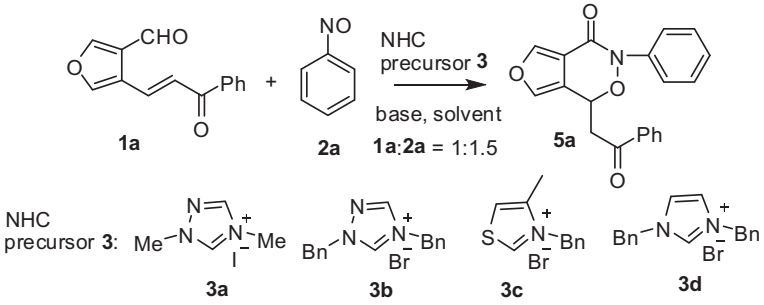
and 1,4-dibenzyltriazole carbenes **4a** and **4b** could promote the reaction to produce furo[3,4-*d*][1,2]oxazin-4-one derivative **5a** in 48% and 44% yields, respectively (Table 1, entries 1, 2). On the contrary, thiazole carbene **4c** or imidazole carbene **4d** was almost inefficient to this reaction under the same conditions. When catalyst loading of triazole carbene **4a** was increased to 30 mol %, the yield of product **5a** was improved to 59%. Under the catalysis of 30 mol % of triazole carbene **4a**, the reaction conditions were further optimized by varying reaction temperature, solvents, and bases utilizing to generate carbene catalyst. As summarized in Table 1, in dry chloroform, decreasing or elevating reaction temperature all caused the diminishing of product **5a**. Utilizing other solvents including benzene, THF, acetonitrile and acetone, and other bases, such as *t*-BuOK, NaH, and Cs_2CO_3, all decreased the yield of product **5a**.

Table 1
Optimization of the reaction conditions



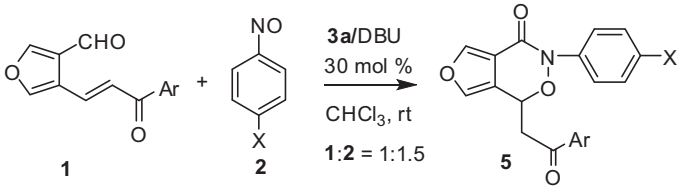
Entry	3	mol % of 3	Base	Solvent	Temp (°C)	Time (h)	Yield of 5a (%)
1	**3a**	20	DBU	$CHCl_3$	rt	15	48
2	**3b**	20	DBU	$CHCl_3$	rt	15	44
3	**3c**	20	DBU	$CHCl_3$	rt	20	Trace
4	**3d**	20	DBU	$CHCl_3$	rt	20	Trace
5	**3a**	**30**	**DBU**	$CHCl_3$	**rt**	**10**	**59**
7	**3a**	30	DBU	$CHCl_3$	−20	15	46
8	**3a**	30	DBU	$CHCl_3$	Reflux	15	29
10	**3a**	30	DBU	Benzene	rt	18	26
11	**3a**	30	DBU	THF	rt	15	43
12	**3a**	30	DBU	CH_3CN	rt	18	37
13	**3a**	30	DBU	CH_3COCH_3	rt	18	35
14	**3a**	30	NaH	$CHCl_3$	rt	15	45
15	**3a**	30	*t*-BuOK	$CHCl_3$	rt	18	26
16	**3a**	30	Cs_2CO_3	$CHCl_3$	rt	15	55

Bold values indicate the optimal condition.

With the optimized conditions established for the NHC-catalyzed annulation between 4-(2-benzoylvinyl)furan-3-carbaldehyde **1a** and nitrosobenzene **2a**, we turned our attention to investigate the scope of this reaction (Table 2). A survey of different aroylvinyl substituted furanaldehydes **1** and nitrosoarenes **2** indicated that both substituents attached to the aroyl groups of **1** and the phenyls of **2** have influence on the efficiency of the reactions. For example, while 4-(2-aroylvinyl)furan-3-carbaldehydes **1a**–**e** that were attached by benzoyl, 4-methylbenzoyl, 4-methoxybenzoyl, 4-bromobenzoyl or 2-methoxybenzoyl on the vinyl group reacted with nitrosobenzene **2a** to provide furo[3,4-*d*][1,2]oxazin-4-ones **5a**–**e** in 56–63% yields, the reaction between 4-(3-methoxybenzoylvinyl)furan-3-carbaldehyde **1f** and **2a** only produced 31% yield of product **5f** (Table 2, entries 1–6). On the other hand, the electron-rich nitrosoarenes **2c** and **2d** afforded higher yields of products than the electron-deficient nitrosoarene **2b** when reacting with 4-(2-benzoylvinyl)furan-3-carbaldehyde **1a** (Table 2, entries 7–9).

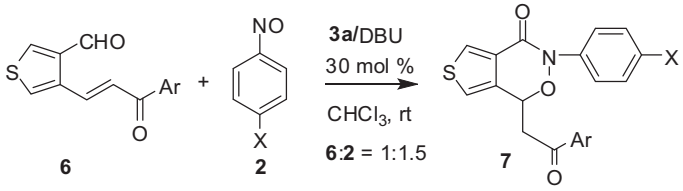
Following the reaction of 4-(2-aroylvinyl)furan-3-carbaldehydes **1** with nitrosoarenes **2**, 4-(2-aroylvinyl)thiophene-3-carbaldehydes **6** were employed to react with nitrosoarenes. Under the similar conditions for the reaction between 4-(2-aroylvinyl)furan-3-carbaldehydes **1** and nitrosoarenes **2**, 4-(2-aroylvinyl)thiophene-3-carbaldehydes **6** did undergo the annulation reaction with nitrosoarenes **2** to give the expected thieno[3,4-*d*][1,2]oxazin-4-ones **7**, albeit in lower yields than the corresponding furo[3,4-*d*][1,2]oxazin-4-ones **5** in most cases (Table 3). It was found that, the reactions between thiophene-3-carbaldehydes **6** and 1-methoxy-4-nitrosobenzene **2c** or 1-methyl-4-nitrosobenzene **2d** were efficient to produce compounds **7f**–**h** in 63–69% yields. However, when reacted with nitrosobenzene **2a** or 1-chloro-4-nitrosobenzene **2b**, thiophene-3-carbaldehydes **6** could not be totally consumed and about 30–70% of aldehydes **6** were recovered after the reactions proceeding for 15 h. The lower reactivity of 4-(2-aroylvinyl)thiophene-3-carbaldehydes **6** than 4-(2-aroylvinyl)furan-3-carbaldehydes **1** in this reaction was probably because the less electronegative sulfur than oxygen atom deactivated the aldehyde

Table 2
The NHC-catalyzed reaction of 4-(2-aroylvinyl)furan-3-carbaldehydes **1** with nitrosoarenes **2**



Entry	1	Ar	2	X	Time (h)	Yield of 5 (%)
1	**1a**	Ph	**2a**	H	15	**5a**: 59
2	**1b**	*p*-PhMe	**2a**	H	15	**5b**: 58
3	**1c**	*p*-PhOMe	**2a**	H	15	**5c**: 56
4	**1d**	*p*-PhBr	**2a**	H	15	**5d**: 63
5	**1e**	*o*-PhOMe	**2a**	H	15	**5e**: 60
6	**1f**	*m*-PhOMe	**2a**	H	20	**5f**: 31
7	**1a**	Ph	**2b**	Cl	20	**5g**: 40
8	**1a**	Ph	**2c**	OMe	10	**5h**: 67
9	**1a**	Ph	**2d**	Me	20	**5i**: 64

Table 3
The NHC-catalyzed reaction of 4-(2-aroylvinyl)thiophene-3-carbaldehydes **6** with nitrosoarenes **2**



Entry	6	Ar	2	X	Time (h)	Yield of 7 (%)
1	**6a**	Ph	**2a**	H	15	**7a**: 45[a]
2	**6b**	*p*-PhMe	**2a**	H	15	**7b**: 31[a]
3	**6c**	*p*-PhOMe	**2a**	H	15	**7c**: 24[a]
4	**6d**	*p*-PhBr	**2a**	H	15	**7d**: 36[a]
5	**6a**	Ph	**2b**	Cl	15	**7e**: 15[a]
6	**6a**	Ph	**2c**	OMe	10	**7f**: 69[b]
7	**6a**	Ph	**2d**	Me	10	**7g**: 66[b]
8	**6c**	*p*-PhOMe	**2c**	OMe	10	**7h**: 63[b]

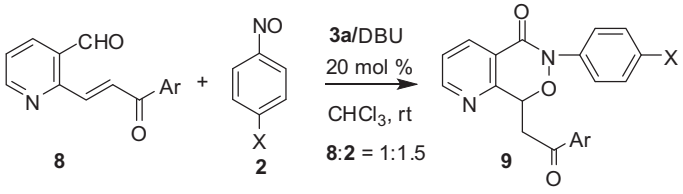
[a] Thiophene-2-carbaldehydes **6** could not be totally consumed in the reactions with **2a** or **2b**. The yields of **7a**–**e** were calculated based on the ratios of **6**:**7** in crude products detected by ^{1}H NMR. Aldehydes **6** and the corresponding products **7** have very similar polarities and were different to be separated using column chromatography, and the pure products **7** were obtained by recrystallization from the mixtures of reactants **6** and products **7**.

[b] Aldehydes **6** were totally consumed when reacted with 1-methoxy-4-nitrosobenzene **2c** or 1-methyl-4-nitrosobenzene **2d**.

groups of thiophene-3-carbaldehydes **6** toward nucleophilic carbene catalyst.

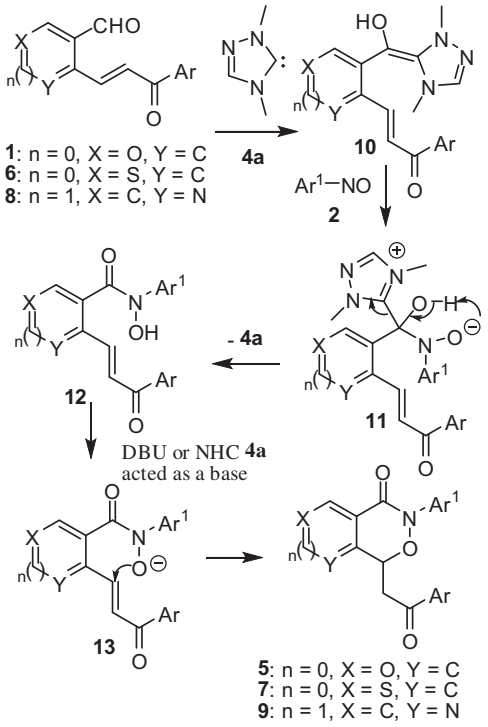
To further extend the application of the NHC-catalyzed annulation between *o*-aroylvinylarylaldehydes and nitrosoarenes **2**, the reaction of 2-(2-aroylvinyl)nicotinaldehydes **8** with nitrosoarenes **2** was also studied. It was found that nicotinaldehydes **8** were more reactive than furan-3-carbaldehydes **1** and thiophene-3-carbaldehydes **6** toward nitrosoarenes **2** under the catalysis of NHC. Thus, the catalyst loading of carbene **4a** was then decreased to 20 mol %. As shown in Table 4, all reactions between different substituted nicotinaldehydes **8** and nitrosoarenes **2** proceeded efficiently to produce pyrido[3,2-*d*][1,2]oxazin-5-ones **9** in moderated to good yields.

Table 4
The NHC-catalyzed reaction of 2-(2-aroylvinyl)nicotinaldehydes **8** with nitrosoarenes **2**



Entry	8	Ar	2	X	Time (h)	Yield of 9 (%)
1	**8a**	Ph	**2a**	H	10	**9a**: 70
2	**8b**	*p*-PhMe	**2a**	H	10	**9b**: 67
3	**8c**	*p*-PhOMe	**2a**	H	15	**9c**: 53
4	**8d**	*p*-PhBr	**2a**	H	10	**9d**: 70
5	**8a**	Ph	**2b**	Cl	10	**9e**: 65
6	**8a**	Ph	**2c**	OMe	10	**9f**: 77
7	**8a**	Ph	**2d**	Me	15	**9g**: 75

A cascade mechanism is proposed to account for the formation of heterocyclic ring-fused oxazinones **5**, **7**, and **9** (Scheme 1). The interaction of NHC with heterocyclic aldehydes **1**, **6** or **8** generates Breslow intermediates **10**. A nucleophilic addition of **10** to the nitroso group of **2** forms intermediates **11**. Intramolecular proton shifting from C–OH to N–OH accompanied by the elimination of NHC moiety from **11** produces *N*-hydroxylamides **12**. Under the



Scheme 1.

catalysis of a base like DBU or triazole carbene **4**, *N*-hydroxylamides **12** undergoes an intramolecular oxo-Michael addition to afford fused oxazinones **5**, **7** or **9**.

The multifunctional aryl-fused 1,2-oxazinones **5**, **7** or **9** are useful in the syntheses of novel furan, thiophene or pyridine derivatives. To demonstrate their synthetic utility, we conducted their reductive transformation. Under the catalysis of Pd–C in THF, hydrogenation of 1-(benzoylmethylene)-3-phenylfuro[3,4-*d*][1,2]oxazin-4-one **5a** produced 4-(1-hydroxy-3-oxo-3-phenylpropyl)-*N*-phenylfuran-3-carboxamide **14** in 50% yield. The reduction of 1-(*p*-methylbenzoylmethylene)-3-phenylthieno[3,4-*d*][1,2]oxazin-4-one **7b** using $LiAlH_4$ in THF afforded 1-(2-hydroxy-2-phenylethyl)-3-(*p*-tolyl) thieno[3,4-*d*][1,2]oxazin-4-one **15** in 61% yield (Scheme 2).

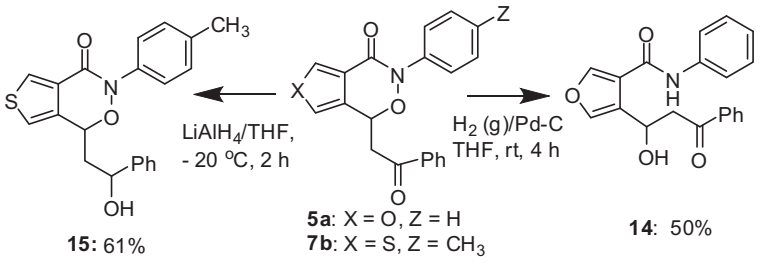
3. Conclusions

In summary, we have studied the NHC-catalyzed reactions of 4-(2-aroylvinyl)furan-3-carbaldehydes, 4-(2-aroylvinyl)thiophene-3-carbaldehydes, and 2-(2-aroylvinyl)nicotinaldehydes, with nitrosoarenes, which provided novel furo[3,4-*d*][1,2]oxazin-4-ones, thieno[3,4-*d*][1,2]oxazin-4-ones, and pyrido[3,2-*d*][1,2]oxazin-5-ones, respectively. This work developed a versatile method for the synthesis of different types of heterocyclic ring-fused 1,2-oxazinones that are not easy accessible by other methods.

4. Experimental section

4.1. General procedure for the reaction of 4-(2-aroylvinyl)furan-3-carbaldehydes 1 or 4-(2-aroylvinyl)thiophene-3-carbaldehydes 6 with nitrosoarenes 2

Under nitrogen atmosphere and at ambient temperature (about 25–30 °C), 4-(2-aroylvinyl)furan-3-carbaldehydes **1**[12] or 4-(2-aroylvinyl)thiophene-3-carbaldehydes **6**[12] (0.5 mmol), nitrosoarenes **2**[13] (0.75 mmol), and *N*,*N*-dimethyl-1,2,4-triazolium salt **3a** (0.15 mmol) were mixed in dry chloroform (10 mL), and then DBU (0.2 mmol) was added using a microsyringe. The mixture was



Scheme 2.

stirred for 10–20 h at room temperature and then the solvent was removed under vacuum. The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (15:1 to 10:1) to afford products **5** or **7**. In some cases, the crude products contained the unconsumed aldehydes reactants that could be removed from the products by recrystallization.

4.1.1. 1-(Benzoylmethylene)-3-phenylfuro[3,4-d][1,2]oxazin-4-one ***5a***. Yield 59%, mp 89–90 °C; IR ν (cm^{-1}) 1689, 1665, 1551; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (s, 1H), 7.96 (d, J=7.6 Hz, 2H), 7.68 (d, J=8.0 Hz, 2H), 7.61 (t, J=7.3 Hz, 1H), 7.48 (t, J=7.5 Hz, 2H), 7.37 (t, J=7.7 Hz, 2H), 7.35 (s, 1H), 7.19 (t, J=7.3 Hz, 1H), 5.94 (t, J=6.3 Hz, 1H), 3.77 (dd, J=17.4, 6.0 Hz, 1H), 3.56 (dd, J=17.4, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.8, 160.2, 145.4, 139.3, 136.4, 136.3, 133.9, 128.8, 128.7, 128.2, 125.7, 124.8, 120.8, 117.7, 73.7, 41.5; MS (EI): 105 (100), 333 (11%, M^+). Anal. Calcd for $C_{20}H_{15}NO_4$: C 72.06, H 4.54, N 4.20; found: C 71.72, H 4.92, N 4.07.

4.1.2. 1-(p-Methylbenzoylmethylene)-3-phenylfuro[3,4-d][1,2]oxazin-4-one ***5b***. Yield 58%, mp 125–127 °C; IR ν (cm^{-1}) 1681, 1600, 1552; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (d, J=0.9 Hz, 1H), 7.86 (d, J=8.2 Hz, 2H), 7.68 (d, J=8.0 Hz, 2H), 7.37 (t, J=7.9 Hz, 2H), 7.34 (s, 1H), 7.27 (d, J=8.6 Hz, 2H), 7.19 (t, J=7.4 Hz, 1H), 5.93 (t, J=6.4 Hz, 1H), 3.74 (dd, J=17.4, 6.0 Hz, 1H), 3.53 (dd, J=17.4, 7.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.4, 160.2, 145.4, 144.8, 139.3, 136.3, 133.8, 129.5, 128.6, 128.3, 125.7, 124.8, 120.8, 117.7, 73.7, 41.3, 21.7; MS (EI): 119 (100), 347 (8%, M^+). Anal. Calcd for $C_{21}H_{17}NO_4$: C 72.61, H 4.93, N 4.03; found: C 72.66, H 4.91, N 3.90.

4.1.3. 1-(p-Methoxybenzoylmethylene)-3-phenylfuro[3,4-d][1,2]oxazin-4-one ***5c***. Yield 56%, mp 110–111 °C; IR ν (cm^{-1}) 1680, 1664, 1603, 1549; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J=1.3 Hz, 1H), 7.94 (d, J=8.9 Hz, 2H), 7.68 (d, J=8.1 Hz, 2H), 7.37 (t, J=8.3 Hz, 2H), 7.33 (s, 1H), 7.18 (t, J=7.4 Hz, 1H), 6.94 (d, J=8.9 Hz, 2H), 5.92 (t, J=6.1 Hz, 1H), 3.88 (s, 3H), 3.72 (dd, J=17.2, 6.0 Hz, 1H), 3.49 (dd, J=17.2, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.2, 164.1, 160.2, 145.4, 139.3, 136.4, 130.5, 129.4, 128.6, 125.7, 124.9, 120.8, 117.7, 114.0, 73.9, 55.5, 41.1; MS (EI): 135 (100), 363 (6%, M^+). Anal. Calcd for $C_{21}H_{17}NO_5$: C 69.41, H 4.72, N 3.85; found: C 69.00, H 4.73, N 3.63.

4.1.4. 1-(p-Bromobenzoylmethylene)-3-phenylfuro[3,4-d][1,2]oxazin-4-one ***5d***. Yield 63%, mp 104–105 °C; IR ν (cm^{-1}) 1683, 1670, 1582, 1554; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (s, 1H), 7.81 (d, J=8.4 Hz, 2H), 7.65 (d, J=8.8 Hz, 2H), 7.62 (d, J=8.2 Hz, 2H), 7.37 (t, J=7.0 Hz, 2H), 7.34 (s, 1H), 7.19 (t, J=7.3 Hz, 1H), 5.92 (t, J=6.5 Hz, 1H), 3.74 (dd, J=17.5, 6.3 Hz, 1H), 3.50 (dd, J=17.5, 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.8, 160.2, 145.5, 139.2, 136.3, 135.0, 132.2, 129.6, 129.2, 128.7, 125.8, 124.6, 120.8, 117.7, 73.5, 41.4; MS (EI): 121 (100), 183/185 (64/63), 411/413 (11%, M^+). Anal. Calcd for $C_{20}H_{14}BrNO_4$: C 58.27, H 3.42, N 3.40; found: C 58.29, H 3.70, N 3.12.

4.1.5. 1-(o-Methoxybenzoylmethylene)-3-phenylfuro[3,4-d][1,2]oxazin-4-one ***5e***. Yield 60%, mp 85–87 °C; IR ν (cm^{-1}) 1673, 1617, 1595; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, J=1.3 Hz, 1H), 7.72 (dd, J=7.8, 1.7 Hz, 1H), 7.62 (d, J=7.7 Hz, 2H), 7.43 (td, J=8.5, 1.7 Hz, 2H), 7.30 (t, J=8.4 Hz, 2H), 7.26 (s, 1H), 7.11 (t, J=7.4 Hz, 1H), 6.96 (t, J=7.3 Hz, 1H), 6.90 (d, J=8.4 Hz, 1H), 5.81 (t, J=6.3 Hz, 1H), 3.80 (s, 3H), 3.71 (dd, J=18.0, 6.3 Hz, 1H), 3.54 (dd, J=17.9, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.1, 160.1, 159.0, 145.2, 139.4, 136.2, 134.5, 130.5, 128.6, 127.0, 125.6, 125.1, 120.8, 117.8, 111.7, 73.8, 55.5, 46.8; HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{18}NO_5$: 364.1185; found: 364.1193.

4.1.6. 1-(m-Methoxybenzoylmethylene)-3-phenylfuro[3,4-d][1,2]oxazin-4-one ***5f***. Yield 31%, mp 110–111 °C; IR ν (cm^{-1}) 1686, 1659, 1613, 1594; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (d, J=1.3 Hz, 1H), 7.60 (d, J=7.7 Hz, 1H), 7.43 (t, J=7.7 Hz, 1H), 7.41 (s, 1H), 7.28–7.33 (m, 3H), 7.27 (s, 1H), 7.11 (t, J=7.4 Hz, 1H), 7.07 (dd, J=8.2, 2.0 Hz, 1H), 5.85 (t, J=6.1 Hz, 1H), 3.79 (s, 3H), 3.68 (dd, J=17.5, 6.1 Hz, 1H), 3.48 (dd, J=17.5, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.6, 160.2, 160.0, 145.4, 139.3, 137.6, 136.3, 129.8, 128.6, 125.7, 124.8, 120.81, 120.77, 120.3, 117.7, 112.4, 73.6, 55.4, 41.6; HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{18}NO_5$: 364.1185; found: 364.1193.

4.1.7. 1-(Benzoylmethylene)-3-(p-chlorophenyl)furo[3,4-d][1,2]oxazin-4-one ***5g***. Yield 40%, mp 148–150 °C; IR ν (cm^{-1}) 1679, 1654; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (s, 1H), 7.96 (d, J=7.2 Hz, 2H), 7.65 (d, J=9.0 Hz, 2H), 7.62 (t, J=7.4 Hz, 2H), 7.49 (t, J=7.9 Hz, 2H), 7.36 (s, 1H), 7.32 (d, J=9.0 Hz, 2H), 5.94 (t, J=5.6 Hz, 1H), 3.77 (dd, J=17.5, 6.5 Hz, 1H), 3.53 (dd, J=17.5, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.6, 160.0, 145.6, 137.9, 136.3, 136.2, 133.9, 130.7, 128.9, 128.7, 128.1, 124.6, 121.6, 117.5, 73.7, 41.3; HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{15}ClNO_4$: 367.0690; found: 368.0696.

4.1.8. 1-(Benzoylmethylene)-3-(p-methoxyphenyl)furo[3,4-d][1,2]oxazin-4-one ***5h***. Yield 67%, mp 139–140 °C; IR ν (cm^{-1}) 1678, 1670, 1615; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, J=1.3 Hz, 1H), 7.89 (d, J=7.2 Hz, 2H), 7.54 (t, J=7.4 Hz, 1H), 7.48 (d, J=9.1 Hz, 2H), 7.42 (t, J=7.6 Hz, 2H), 7.26 (s, 1H), 6.84 (d, J=9.1 Hz, 2H), 5.86 (t, J=6.0 Hz, 1H), 3.74 (s, 3H), 3.69 (dd, J=17.4, 6.0 Hz, 1H), 3.49 (dd, J=17.5, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.8, 160.4, 158.0, 145.1, 136.3, 133.8, 132.1, 128.8, 128.1, 124.8, 124.1, 117.6, 114.0, 73.4, 55.5, 41.5; MS (EI): 105 (100), 363 (9%, M^+). Anal. Calcd for $C_{21}H_{17}NO_5$: C 69.41, H 4.72, N 3.85; found: C 69.54, H 4.74, N 3.73.

4.1.9. 1-(Benzoylmethylene)-3-(p-tolyl)furo[3,4-d][1,2]oxazin-4-one ***5i***. Yield 64%, mp 105–106 °C; IR ν (cm^{-1}) 1678, 1555; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, J=0.9 Hz, 1H), 7.95 (d, J=7.4 Hz, 2H), 7.60 (t, J=7.4 Hz, 1H), 7.53 (d, J=8.4 Hz, 2H), 7.48 (t, J=7.7 Hz, 2H), 7.33 (s, 1H), 7.17 (d, J=8.3 Hz, 2H), 5.92 (t, J=6.4 Hz, 1H), 3.76 (dd, J=17.4, 6.0 Hz, 1H), 3.55 (dd, J=17.7, 7.1 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.8, 160.2, 145.2, 136.7, 136.4, 136.3, 135.9, 133.8, 129.2, 128.8, 128.1, 124.8, 121.4, 117.7, 73.5, 41.5, 21.0; MS (EI): 105 (100), 347 (10%, M^+). Anal. Calcd for $C_{21}H_{17}NO_4$: C 72.61, H 4.93, N 4.03; found: C 71.21, H 4.81, N 4.83.

4.1.10. 1-(Benzoylmethylene)-3-phenylthieno[3,4-d][1,2]oxazin-4-one ***7a***. Yield 45%, mp 110–112 °C; IR ν (cm^{-1}) 1687, 1657, 1594; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (d, J=2.9 Hz, 1H), 7.97 (d,

J=7.4 Hz, 2H), 7.71 (d, J=8.0 Hz, 2H), 7.61 (t, J=7.4 Hz, 1H), 7.48 (t, J=7.7 Hz, 2H), 7.36 (t, J=8.0 Hz, 2H), 7.17 (t, J=7.4 Hz, 1H), 7.13 (d, J=2.2 Hz, 1H), 6.04 (t, J=6.2 Hz, 1H), 3.80 (dd, J=17.4, 6.9 Hz, 1H), 3.59 (dd, J=17.4, 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.8, 159.9, 140.1, 139.3, 136.4, 133.8, 131.7, 131.0, 128.8, 128.6, 128.2, 125.6, 120.5, 118.9, 76.6, 41.3; HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{16}NO_3S$: 350.0851; found: 350.0852.

4.1.11. 1-(p-Methylbenzoylmethylene)-3-phenylthieno[3,4-d][1,2]oxazin-4-one ***7b***. Yield 31%, mp 138–140 °C; IR ν (cm^{-1}) 1683, 1651, 1552; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, J=2.9 Hz, 1H), 7.80 (d, J=8.2 Hz, 2H), 7.64 (d, J=8.6 Hz, 2H), 7.29 (t, J=8.4 Hz, 2H), 7.20 (d, J=8.8 Hz, 2H), 7.10 (t, J=7.4 Hz, 1H), 7.04 (d, J=2.9 Hz, 1H), 5.95 (t, J=6.0 Hz, 1H), 3.69 (dd, J=17.3, 6.8 Hz, 1H), 3.49 (dd, J=17.3, 5.9 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.4, 159.9, 144.8, 140.2, 139.3, 134.0, 131.6, 131.0, 129.5, 128.6, 128.3, 125.5, 120.5, 118.8, 76.7, 41.2, 21.7; MS (EI): 119 (100), 363 (9%, M^+). Anal. Calcd for $C_{21}H_{17}NO_3S$: C 69.40, H 4.71, N 3.85; found: C 69.53 H 4.61, N 3.72.

4.1.12. 1-(p-Methoxybenzoylmethylene)-3-phenylthieno[3,4-d][1,2]oxazin-4-one ***7c***. Yield 24%, mp 171–173 °C; IR ν (cm^{-1}) 1678, 1649, 1601; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23 (d, J=2.8 Hz, 1H), 7.95 (d, J=8.8 Hz, 2H), 7.71 (d, J=8.0 Hz, 2H), 7.35 (t, J=8.0 Hz, 2H), 7.17 (t, J=7.4 Hz, 1H), 7.11 (d, J=2.7 Hz, 1H), 6.94 (d, J=8.8 Hz, 2H), 6.02 (t, J=6.3 Hz, 1H), 3.87 (s, 3H), 3.74 (dd, J=17.1, 6.8 Hz, 1H), 3.53 (dd, J=17.1, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.2, 164.0, 159.9, 140.2, 139.3, 131.6, 131.0, 130.6, 129.5, 128.6, 125.5, 120.4, 118.8, 113.9, 76.7, 55.5, 40.9; HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{18}NO_4S$: 380.0957; found: 380.0963.

4.1.13. 1-(p-Bromobenzoylmethylene)-3-phenylthieno[3,4-d][1,2]oxazin-4-one ***7d***. Yield 36%, mp 126–127 °C; IR ν (cm^{-1}) 1694, 1649, 1585; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (d, J=2.9 Hz, 1H), 7.82 (d, J=8.6 Hz, 2H), 7.69 (d, J=7.9 Hz, 2H), 7.61 (d, J=8.6 Hz, 2H), 7.36 (t, J=8.0 Hz, 2H), 7.18 (t, J=7.4 Hz, 1H), 7.12 (d, J=2.1 Hz, 1H), 6.02 (t, J=6.2 Hz, 1H), 3.76 (dd, J=17.4, 7.2 Hz, 1H), 3.53 (dd, J=17.3, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.8, 159.9, 139.8, 139.2, 135.0, 132.1, 131.8, 130.9, 129.7, 129.1, 128.6, 125.6, 120.4, 118.8, 76.4, 41.2; HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{15}BrNO_3S$: 427.9956; found: 427.9957.

4.1.14. 1-(Benzoylmethylene)-3-(p-chlorophenyl)thieno[3,4-d][1,2]oxazin-4-one ***7e***. Yield 15%, mp 118–120 °C; IR ν (cm^{-1}) 1688, 1650, 1552; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.25 (d, J=2.9 Hz, 1H), 7.97 (d, J=7.8 Hz, 2H), 7.68 (d, J=9.0 Hz, 2H), 7.62 (t, J=7.4 Hz, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.31 (d, J=9.0 Hz, 2H), 7.13 (d, J=2.2 Hz, 1H), 6.03 (t, J=6.2 Hz, 1H), 3.79 (dd, J=17.4, 7.3 Hz, 1H), 3.57 (dd, J=17.4, 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.6, 159.8, 139.9, 137.8, 136.3, 133.9, 132.0, 130.7, 130.5, 128.8, 128.6, 128.2, 121.3, 118.9, 76.6, 41.1; HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{15}ClNO_3S$: 384.0461; found: 384.0468.

4.1.15. 1-(Benzoylmethylene)-3-(p-methoxyphenyl)thieno[3,4-d][1,2]oxazin-4-one ***7f***. Yield 69%, mp 160–161 °C; IR ν (cm^{-1}) 1677, 1661, 1602, 1513; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 (d, J=2.9 Hz, 1H), 7.97 (d, J=7.4 Hz, 2H), 7.61 (t, J=7.5 Hz, 1H), 7.58 (d, J=9.0 Hz, 2H), 7.48 (t, J=7.8 Hz, 2H), 7.11 (d, J=2.3 Hz, 1H), 6.89 (d, J=9.0 Hz, 2H), 6.03 (t, J=6.4 Hz, 1H), 3.80 (s, 3H), 3.78 (dd, J=17.6, 6.8 Hz, 1H), 3.59 (dd, J=17.4, 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.8, 160.1, 157.8, 140.1, 136.4, 133.8, 132.2, 131.4, 130.9, 128.8, 128.2, 123.6, 118.8, 113.9, 76.4, 55.5, 41.3; HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{18}NO_4S$: 380.0957; found: 380.0955.

4.1.16. 1-(Benzoylmethylene)-3-(p-tolyl)thieno[3,4-d][1,2]oxazin-4-one ***7g***. Yield 66%, mp 110–111 °C; IR ν (cm^{-1}) 1689, 1662, 1645; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22 (d, J=2.9 Hz, 1H), 7.97 (d, J=7.6 Hz, 2H), 7.61 (t, J=7.4 Hz, 1H), 7.57 (d, J=8.5 Hz, 2H), 7.48 (t, J=7.7 Hz, 2H), 7.17 (d, J=8.3 Hz, 2H), 7.12 (d, J=2.6 Hz, 1H), 6.03 (t, J=6.2 Hz, 1H), 3.79 (dd, J=17.4, 6.7 Hz, 1H), 3.59 (dd, J=17.4, 5.9 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.8, 159.9, 140.1, 136.7, 136.4, 135.7, 133.8, 131.5, 131.0, 129.2, 128.8, 128.2, 121.0, 118.8, 76.5, 41.3, 21.0; MS (EI): 105 (100), 363 (15%, M^+). Anal. Calcd for $C_{21}H_{17}NO_3S$: C 69.40, H 4.71, N 3.85; found: C 69.36, H 4.64, N 3.71.

4.1.17. 1-(p-Methoxybenzoylmethylene)-3-(p-methoxyphenyl)thieno[3,4-d][1,2]oxazin-4-one ***7h***. Yield 63%, mp 145–147 °C; IR ν (cm^{-1}) 1677, 1643, 1601; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 (d, J=2.9 Hz, 1H), 7.95 (d, J=8.8 Hz, 2H), 7.58 (d, J=9.1 Hz, 2H), 7.10 (d, J=2.8 Hz, 1H), 6.94 (d, J=8.9 Hz, 2H), 7.89 (d, J=9.1 Hz, 2H), 6.01 (t, J=6.4 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 3.73 (dd, J=17.2, 6.8 Hz, 1H), 3.53 (dd, J=17.2, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.2, 164.0, 160.1, 157.8, 140.3, 132.3, 131.2, 131.0, 130.5, 129.6, 123.6, 118.7, 113.9, 76.6, 55.52, 55.45, 41.0; HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{20}NO_5S$: 410.1062; found: 410.1056.

4.2. General procedure for the reaction of 2-(2-aroylvinyl) nicotinaldehydes 8 with nitrosoarenes 2

Under nitrogen atmosphere and at ambient temperature (about 25–30 °C), 2-(2-aroylvinyl)nicotinaldehydes **8**[12] (0.5 mmol), nitrosoarenes **2** (0.75 mmol), and *N*,*N*-dimethyl-1,2,4-triazolium salt **3a** (0.1 mmol) were mixed in dry chloroform (10 mL), and then DBU (0.2 mmol) was added using a microsyringe. The mixture was stirred for 10–15 h at room temperature and then the solvent was removed under vacuum. The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (10:1 to 6:1) to afford products **9**.

4.2.1. 8-(Benzoylmethylene)-6-phenylpyrido[3,2-d][1,2]oxazin-5-one ***9a***. Yield 70%, mp 101–103 °C; IR ν (cm^{-1}) 1683, 1494; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.70 (dd, J=4.8, 1.3 Hz, 1H), 8.51 (dd, J=7.8, 1.4 Hz, 1H), 8.05 (d, J=7.3 Hz, 2H), 7.83 (d, J=7.8 Hz, 2H), 7.61 (t, J=7.4 Hz, 2H), 7.48–7.52 (m, 3H), 7.39 (t, J=7.8 Hz, 2H), 7.20 (t, J=7.4 Hz, 1H), 6.22 (dd, J=8.8, 2.6 Hz, 1H), 4.18 (dd, J=18.0, 2.8 Hz, 1H), 3.70 (dd, J=18.0, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ (ppm) 195.7, 160.9, 158.2, 152.3, 138.9, 136.6, 136.1, 133.6, 128.7, 128.3, 125.9, 123.8, 123.7, 120.3, 78.5, 38.8; HRMS (ESI): 345.1244 (M+1). Anal. Calcd for $C_{21}H_{17}N_2O_3$: 345.1239 (M+1).

4.2.2. 8-(p-Methylbenzoylmethylene)-6-phenylpyrido[3,2-d][1,2]oxazin-5-one ***9b***. Yield 67%, mp 108–110 °C; IR ν (cm^{-1}) 1680, 1494; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.70 (dd, J=4.8, 1.3 Hz, 1H), 8.48 (dd, J=7.8, 1.4 Hz, 1H), 7.94 (d, J=8.2 Hz, 2H), 7.83 (d, J=8.0 Hz, 2H), 7.48 (dd, J=7.7, 5.0 Hz, 1H), 7.39 (t, J=8.0 Hz, 2H), 7.29 (d, J=8.0 Hz, 2H), 7.20 (t, J=7.4 Hz, 1H), 6.21 (dd, J=8.9, 2.6 Hz, 1H), 4.12 (dd, J=18.0, 2.8 Hz, 1H), 3.65 (dd, J=18.0, 9.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.3, 160.9, 158.3, 152.4, 144.5, 138.9, 136.0, 134.1, 129.4, 128.7, 128.4, 125.9, 123.7, 123.6, 120.2, 78.6, 38.7, 21.7; MS (EI): 119 (100), 358 (2%, M^+). Anal. Calcd for $C_{22}H_{18}N_2O_3$: C 73.73, H 5.06, N 7.82; found: C 73.73, H 5.52, N 7.64.

4.2.3. 8-(p-Methoxybenzoylmethylene)-6-phenylpyrido[3,2-d][1,2]oxazin-5-one ***9c***. Yield 53%, mp 80–81 °C; IR ν (cm^{-1}) 1674, 1600; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm), 8.69 (dd, J=4.8, 1.4 Hz, 1H), 8.46 (dd, J=7.8, 1.4 Hz, 1H), 8.02 (d, J=8.8 Hz, 2H), 7.84 (d, J=8.0 Hz, 2H), 7.46 (dd, J=7.7, 4.9 Hz, 1H), 7.38 (t, J=8.2 Hz, 2H), 7.19 (t, J=7.4 Hz, 1H), 6.93 (d, J=8.8 Hz, 2H), 6.19 (dd, J=8.9, 2.7 Hz, 1H), 4.06 (dd, J=17.8, 2.8 Hz, 1H), 3.88 (s, 3H), 3.62 (dd, J=17.8, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.1, 163.9, 160.9, 158.4, 152.4, 139.0, 136.0, 130.6, 129.7, 128.7, 125.8, 123.7, 123.6, 120.2, 113.9, 78.7, 55.5, 38.4; HRMS (ESI): 375.1347 (M+1). Anal. Calcd for $C_{22}H_{20}N_2O_4$: 375.1345 (M+1).

4.2.4. 8-(p-Bromobenzoylmethylene)-6-phenylpyrido[3,2-d][1,2]oxazin-5-one ***9d***. Yield 70%, mp 145–146 °C; IR ν (cm^{-1}) 1691, 1664,

1585; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.70 (dd, J=4.8, 1.4 Hz, 1H), 8.49 (d, J=7.6 Hz, 1H), 7.91 (d, J=8.6 Hz, 2H), 7.82 (d, J=7.8 Hz, 2H), 7.64 (d, J=8.6 Hz, 2H), 7.49–7.52 (m, 1H), 7.40 (t, J=8.3 Hz, 2H), 7.22 (t, J=7.4 Hz, 1H), 6.19 (dd, J=8.7, 2.7 Hz, 1H), 4.13 (dd, J=18.0, 2.8 Hz, 1H), 3.63 (dd, J=18.0, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.7, 160.9, 158.0, 152.4, 138.9, 136.1, 135.3, 132.1, 129.8, 128.8, 128.7, 126.0, 123.9, 123.6, 120.3, 78.5, 38.8; HRMS (ESI): 423.0342 (M+1). Anal. Calcd for $C_{21}H_{16}BrN_2O_3$: 423.0344 (M+1).

4.2.5. 8-(Benzoylmethylene)-6-(p-chlorophenyl)pyrido[3,2-d][1,2]oxazin-5-one ***9e***. Yield 65%, mp 167–168 °C; IR ν (cm^{-1}) 1693, 1676, 1489; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.71 (dd, J=4.8, 1.4 Hz, 1H), 8.46 (dd, J=7.8, 1.4 Hz, 1H), 8.05 (d, J=7.3 Hz, 2H), 7.82 (d, J=9.0 Hz, 2H), 7.62 (t, J=7.4 Hz, 1H), 7.51 (t, J=7.8 Hz, 2H), 7.48 (dd, J=8.0, 5.0 Hz, 1H), 7.35 (d, J=9.0 Hz, 2H), 6.18 (dd, J=9.2, 2.3 Hz, 1H), 4.15 (dd, J=18.2, 2.6 Hz, 1H), 3.64 (dd, J=18.2, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.7, 160.9, 158.1, 152.6, 137.5, 136.5, 136.1, 133.7, 130.9, 128.8, 128.3, 123.8, 123.4, 121.2, 78.6, 38.7; HRMS (ESI): 379.0846 (M+1). Anal. Calcd for $C_{21}H_{16}ClN_2O_3$: 379.0849 (M+1).

4.2.6. 8-(Benzoylmethylene)-6-(p-methoxyphenyl)pyrido[3,2-d][1,2]oxazin-5-one ***9f***. Yield 77%, mp 136–137 °C; IR ν (cm^{-1}) 1686, 1659, 1504; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.69 (dd, J=4.8, 1.4 Hz, 1H), 8.47 (dd, J=7.8, 1.4 Hz, 1H), 8.05 (d, J=7.3 Hz, 2H), 7.72 (d, J=9 Hz, 2H), 7.61 (t, J=7.4 Hz, 1H), 7.46–7.52 (m, 3H), 6.92 (d, J=9.1 Hz, 2H), 6.22 (dd, J=8.8, 2.7 Hz, 1H), 4.15 (dd, J=18.0, 2.8 Hz, 1H), 3.82 (s, 3H), 3.66 (dd, J=18.0, 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.7, 160.8, 158.2, 157.9, 152.3, 136.6, 135.9, 133.5, 131.9, 128.7, 128.3, 123.7, 123.6, 123.2, 114.0, 78.5, 55.5, 38.8; MS (EI): 105 (67), 121 (100), 374 (27%, M^+). Anal. Calcd for $C_{22}H_{18}N_2O_4$: C 70.58, H 4.85, N 7.48; found: C 70.59, H 5.04, N 7.47.

4.2.7. 8-(Benzoylmethylene)-6-(p-tolyl)pyrido[3,2-d][1,2]oxazin-5-one ***9g***. Yield 75%, mp 115–117 °C; IR ν (cm^{-1}) 1692, 1669, 1509; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.68 (dd, J=4.8, 1.4 Hz, 1H), 8.46 (dd, J=7.8, 1.4 Hz, 1H), 8.04 (d, J=7.3 Hz, 2H), 7.69 (d, J=8.5 Hz, 2H), 7.60 (t, J=7.3 Hz, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.46 (dd, J=7.8, 4.9 Hz, 1H), 7.19 (d, J=8.4 Hz, 2H), 6.20 (dd, J=8.8, 2.8 Hz, 1H), 4.12 (dd, J=18.0, 3.0 Hz, 1H), 3.65 (dd, J=18.0, 8.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.7, 159.8, 157.2, 151.3, 135.6, 135.4, 134.9, 132.5, 128.3, 127.7, 122.7, 122.6, 119.7, 77.5, 37.7, 20.0; HRMS (ESI): 359.1400 (M+1). Anal. Calcd for $C_{22}H_{19}N_2O_3$: 359.1396 (M+1).

4.2.8. Pd-catalyzed hydrogenation of 1-(benzoylmethylene)-3-phenylfuro[3,4-d][1,2]oxazin-4-one ***5a***. At ambient temperature, furo[3,4-*d*][1,2]oxazin-4-one **5a** (0.3 mmol) was mixed with Pd–C (10 mg, 10% w/w) in THF (20 mL). The air in flask was sucked by an oil pump and hydrogen gas was then bubbled into the reaction mixture. The reaction mixture was stirred at room temperature for about 4 h until reactant **5a** was consumed. After filtrating Pd–C and removal of THF under vacuum, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (5:1) to give the product **14** in 50% yield.

4.2.9. 4-(1-Hydroxy-3-oxo-3-phenylpropyl)-N-phenylfuran-3-carboxamide ***14***. Yield 50%, mp 145–146 °C; IR ν (cm^{-1}) 3292, 3137, 1686, 1636, 1601, 1556; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 10.16 (s, 1H), 8.24 (d, J=1.6 Hz, 1H), 8.04 (d, J=7.2 Hz, 2H), 7.74 (d, J=7.6 Hz, 2H), 7.72 (d, J=1.4 Hz, 1H), 7.62 (t, J=7.4 Hz, 1H), 7.50 (t, J=7.4 Hz, 2H), 7.35 (t, J=7.6 Hz, 2H), 7.11 (t, J=7.4 Hz, 1H), 5.53–5.58 (m, 2H), 3.68 (dd, J=16.3, 8.2 Hz, 1H), 3.52 (dd, J=16.2, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 198.6, 162.5, 148.3, 142.3, 139.9, 138.2, 133.9, 129.6, 129.5, 129.0, 128.0, 124.7, 123.3, 120.8, 63.7, 46.2; HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{18}NO_4$: 336.1236; found: 336.1241.

4.2.10. Reduction of 1-(p-methylbenzoylmethylene)-3-phenylthieno[3,4-d][1,2]oxazin-4-one ***7b*** *using $LiAlH_4$.* At −20 °C, the solution of thieno[3,4-*d*][1,2]oxazin-4-one **7b** (0.3 mmol) in dry THF (10 mL) was added dropwise to $LiAlH_4$ (0.66 mmol) in dry THF (10 mL) with stirring. The reaction mixture was stirred for 2 h at −20 °C, and then the reaction was quenched by the addition of aqueous HCl (2 M) until no hydrogen gas releasing. After removal of THF, the residue was extracted with ethyl acetate (50×3 mL), and the combined extraction was dried and evaporated. The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (5:1) to give product **15** in 61% yield.

4.2.11. 1-(2-Hydroxy-2-phenylethyl)-3-(p-tolyl)thieno[3,4-d][1,2]oxazin-4-one ***15***. Yield 61%, mp 120–121 °C; IR ν (cm^{-1}) 3373, 1641, 1552, 1507, 1466; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 8.30 (d, J=2.9 Hz, 1H), 7.59 (d, J=8.5 Hz, 2H), 7.51 (dd, J=2.8, 1.0 Hz, 1H), 7.43 (d, J=7.2 Hz, 2H), 7.32 (t, J=7.5 Hz, 2H), 7.25 (t, J=7.2 Hz, 1H), 7.23 (d, J=8.3 Hz, 2H), 5.29 (t, J=6.2 Hz, 1H), 4.98–5.01 (m, 1H), 4.59 (d, J=4.0 Hz, 1H), 2.47–2.51 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 160.5, 145.6, 141.8, 138.3, 135.8, 132.1, 132.0, 129.8, 129.2, 128.2, 127.0, 121.6, 120.0, 79.3, 71.3, 42.5, 20.9; HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{20}NO_3S$: 366.1164; found: 366.1173.

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Supplementary data

Electronic Supplementary data (ESI): the methods for the syntheses of 4-(2-aroylvinyl)furan-3-carbaldehydes **1**, 4-(2-aroylvinyl) thiophene-3-carbaldehydes **6** and 2-(2-aroylvinyl)nicotinaldehydes **8**, and the copies of ^{1}H NMR and ^{13}C NMR spectra of products **5**, **7**, **9**, **14**, and **15** are available. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.10.089. These data include MOL files and InChiKeys of the most important compounds described in this article.

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