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$RuCl_2(PPh_3)_3$-Catalyzed Facile One-Pot Synthesis of 1,2-Dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones and 1,2-Dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones

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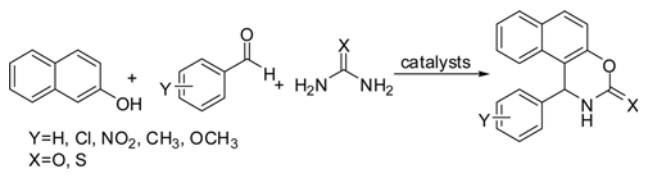
Benzoxazinones and benzthioxazinones have received considerable attention because of the attractive pharmacological properties associated with their heterocyclic scaffold.[1] Molecules bearing these skeletons have been reported to exhibit a variety of biological properties, including anti-inflammatory, antiulcer, antipyretic, antihypertensive, and antifungal activities.[2] Some of these compounds also exhibit several important biological activities such as DP receptor antagonism,[3] integrin antagonism,[4] platelet fibrinogen receptor antagonism,[5] calmodulin antagonism,[6] and inhibition of the transforming growth factor β (TGF-β) signaling pathway,[7] soybean lipoxygenase,[8] and other protein kinase.[9] Because of the importance of these compounds, several synthetic methods for 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones have been developed.[10-14] The reported methods mainly include one-pot three-component reactions of 2-naphthol, aromatic aldehydes, and urea or thiourea (Scheme 1). These reactions for the synthesis of 2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones have been studied with the use of several catalysts and reagents such as Cu-nanoparticles/PEG-400,[10] TMSCl,[11] $HClO_4/SiO_2$,[12] $H_3Mo_{12}O_{40}P$,[13] montmorillonite K10 clay,[14] and iodine.[15] Interestingly, several synthetic approaches for the synthesis of 2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones have been described, but only one example for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones has been reported through multi-component reaction.[14] The method also involves montmorillonite K10 clay-catalyzed reaction of 2-naphthol, aryl aldehydes, and thiourea.[14]

Although several methods for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones have been reported, there is still demand for simpler, less toxic, more effective, and milder catalysts. Our interest in developing mild and efficient synthetic methods that provide a variety of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones has led us to looking into more convenient and safely usable catalysts. Among these, we think tris(triphenylphosphine)-ruthenium(II) dichloride is a viable alternative, and may be a promising catalyst for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones, due to its easy availability, sustainability, and non-toxicity.[16] Recently, we have reported $RuCl_2(PPh_3)_3$-catalyzed one-pot three-component reactions for the synthesis of biologically interesting 1-amidoalkyl-2-naphthols.[17] As part of an ongoing study of the efficacy of $RuCl_2(PPh_3)_3$-catalyzed three-component reactions, we report herein an efficient and facile synthesis of biologically interesting 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones.



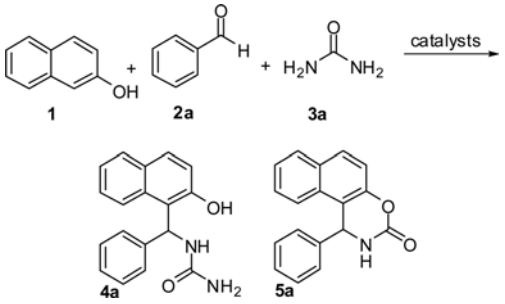
Scheme 1

Results and Discussion

Recently, it has been reported that multi-component reactions of 2-naphthol (**1**) with benzaldehyde (**2a**) and urea (**3a**) in the presence of a number of catalysts and reagents such as H_2NSO_3H,[18] $HClO_4/SiO_2$,[19] 2,4,6-trichloro-1,3,5-triazine,[20] $InCl_3$,[21] and CH_3SO_3H[22] afforded uncyclized product **4a** in good yields, without any formation of cycloadduct **5a** (Scheme 2).

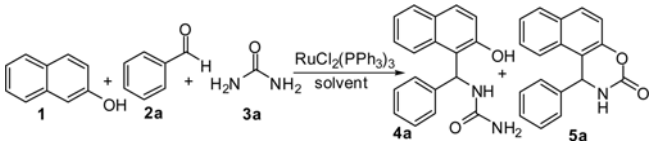
To give cycloadduct **5a**, reactions of 2-naphthol (**1**, 1.0 mmol) with benzaldehyde (**2a**, 1.2 mmol) and urea (**3a**, 1.2 mmol) were first examined in the presence of 5 mol % of $RuCl_2(PPh_3)_3$ in several solvents (Table 1). With methylene chloride and acetone in reflux for 12 h, uncyclized product **4a** was produced in 54 and 43% yields, respectively. With acetonitrile in reflux for 20 h, both **4a** (10%) and **5a** (20%) were obtained. However, when toluene was used in reflux for 15 h, cyclized product **5a** was only isolated in 93% yield. With DMF as a polar aprotic solvent, the desired product **5a** was produced in 72% yield. Compound **5a** was determined by analysis of its spectral data and by direct comparison with the reported data.[11]

In order to extend the utility of this methodology for the synthesis of a variety of 1,2-dihydro-1-arylnaphtho[1,2-



Scheme 2

Table 1. Reaction of 2-naphtol (**1**) with benzaldehyde (**2a**) and urea (**3a**) in the presence of 5 mol % of $RuCl_2(PPh_3)_3$ in several solvents

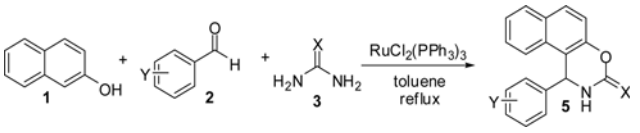


Entry	Solvent	Condition	Yield (%)	
			4a	**5a**
1	CH_2Cl_2	reflux, 12 h	54	0
2	acetone	reflux, 12h	43	0
3	CH_3CN	reflux, 20 h	10	20
4	toluene	reflux, 15 h	0	93
5	DMF	150 °C, 12 h	0	72

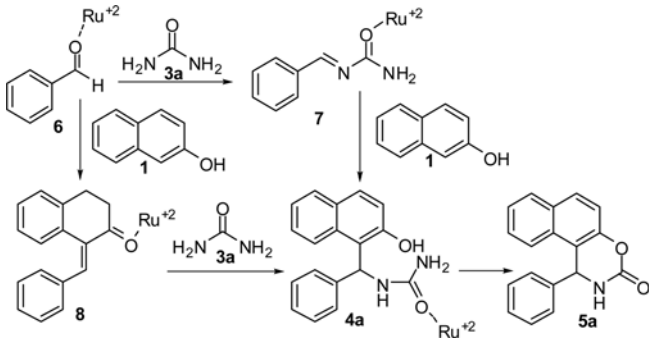
e][1,3]oxazine-3-ones and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones, further reactions of 2-naphthol with several aryl aldehydes and urea or thiourea were examined. These reactions were carried out in the presence of 5 mol % of $RuCl_2(PPh_3)_3$ in refluxing toluene for 10-20 h using the optimized conditions described above. The results are summarized in Table 2. The aromatic aldehydes bearing electron-donating as well as electron-withdrawing groups underwent reactions successfully. Treatment of 2-naphthol with 4-methylbenzaldehyde and urea in the presence of 5 mol % of $RuCl_2(PPh_3)_3$ in refluxing toluene for 15 h provided **5b** in 90% yield (entry 1, Table 2). Reactions of 3-methylbenzaldehyde, 4-methoxybenzaldehyde, and 3-methoxybenzaldehyde with urea afforded products **5c**-**5e** in 74-84% yield (entries 2-4), whereas those of 4-chlorobenzaldehyde, 4-nitrobenzaldehyde, and 2-nitrobenzaldehyde provided **5f**-**5h** in 74-85% yield (entries 5-7). When thiourea was used instead of urea, the desired products were also produced. Reaction of 2-naphthol with benzaldehyde and thiourea in refluxing toluene for 18 h gave **5i** in 74% yield (entry 8). Other aromatic aldehydes with electron-donating or withdrawing groups gave products **5j**-**5l** in 70-82% yield (entries 9-11). These reactions provided rapid synthetic approaches to various 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones **5b**–**5h** and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones **5i**-**5l** in good yields.

The formation of **5a** can be explained by the proposed mechanism through the acylimine intermediate or *ortho*-quinone methide intermediate as shown in Scheme 3. Benz-

Table 2. $RuCl_2(PPh_3)_3$-catalyzed synthesis of avariety of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones **5b**-**5h** and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones **5i**-**5l**



Entry	Aldehyde	Amide	Time (h)	Product	Yield (%)
1	**2b** Y=4-CH_3	**3a** X=O	15	**5b** X=O,Y=4-CH_3	90
2	**2c** Y=3-CH_3	**3a** X=O	15	**5c** X=O, Y=3-CH_3	77
3	**2d** Y=4-OCH_3	**3a** X=O	15	**5d** X=O, Y=4-OCH_3	84
4	**2e** Y=3-OCH_3	**3a** X=O	14	**5e** X=O, Y=3-OCH_3	74
5	**2f** Y=4-Cl	**3a** X=O	10	**5f** X=O, Y=4-Cl	75
6	**2g** Y=4-NO_2	**3a** X=O	12	**5g** X=O, Y=4-NO_2	85
7	**2h** Y=2-NO_2	**3a** X=O	12	**5h** X=O, Y=2-NO_2	74
8	**2a** Y=H	**3b** X=S	18	**5i** X=S, Y=H	74
9	**2d** Y=4-OCH_3	**3b** X=S	20	**5j** X=S, Y=4-OCH_3	70
10	**2e** Y=3-OCH_3	**3b** X=S	20	**5k** X=S, Y=3-OCH_3	71
11	**2g** Y=4-NO_2	**3b** X=S	18	**5l** X=S, Y=4-NO_2	82



Scheme 3

aldehyde (**2a**) forms an oxygen-bonded complex in the presence of $RuCl_2(PPh_3)_3$ catalyst to give **6**, which is attacked by urea (**3a**) or by 2-naphthol (**1**) to produce the acylimine intermediate **7** or *ortho*-quinone intermediate **8**. The subsequent addition of 2-naphthol (**1**) to **7** or addition of urea (**3a**) to **8** gives another intermediate **4a**, which undergoes cyclization reaction to yield the final product **5a**.

In summary, we have developed an efficient and general synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones and 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones by $RuCl_2(PPh_3)_3$-catalyzed one-pot multi-component reactions of 2-naphthol with aromatic aldehydes and urea or thiourea. The advantages of these methodologies are easy handling, mild reaction conditions, and use of an effective and non-toxic catalyst. In particular, these methodologies provided a useful and attractive process for the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-thiones.

Experimental

[α-(2-Hydroxynaphth-1-yl)benzyl]urea (4a).[16] To a

mixture of 2-naphthol (144 mg, 1.0 mmol), benzaldehyde (126 mg, 1.2 mmol), and urea (72 mg, 1.2 mmol) in CH_2Cl_2 (10 mL) was added $RuCl_2(PPh_3)_3$ (48 mg, 0.05 mmol) under N_2. The mixture was heated under reflux for 12 h. After completion of reaction as indicated by TLC, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to give product **4a** (149 mg, 54%) as a white solid, mp 182-184 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.88 (1H, s), 7.77 (2H, d, J = 8.1 Hz), 7.71 (1H, d, J = 9.0 Hz), 7.48-7.08 (10H, m); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.0, 152.8, 144.6, 132.2, 131.0, 130.0, 129.0, 129.4, 128.6, 128.0, 126.2, 125.8, 122.3, 120.2, 118.4, 48.1; IR (KBr) 3408, 1722, 1624, 1531, 1277, 1061, 817 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{18}H_{16}N_2O_2$: 292.1213. Found: 292.1212.

General Procedure for the Synthesis of 5a-5l. To a mixture of 2-naphthol (144 mg, 1.0 mmol), aldehyde (1.2 mmol), and urea or thiourea (1.2 mmol) in toluene (10 mL) was added $RuCl_2(PPh_3)_3$ (48 mg, 0.05 mmol) under N_2. The mixture was heated under reflux for 10-12 h. After completion of reaction as indicated by TLC, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to give product.

1-Phenyl-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-one (5a):[11] Yield 93% as a white solid; mp 176-179 °C; ^{1}H NMR (300 MHz , $CDCl_3$+DMSO-d_6) δ 8.22 (1H, br), 7.79 (2H, d, J = 8.4 Hz), 7.55 (1H, d, J = 9.0 Hz), 7.34-7.20 (8H, m), 5.99 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ 149.2, 147.1, 141.7, 130.0, 129.4, 128.6, 128.2, 127.9, 127.4, 126.5, 126.4, 124.2, 122.0, 116.2, 112.7, 54.3; IR (KBr) 3452, 2371, 2281, 1727, 1399, 1223, 1170, 1113, 827 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{18}H_{13}NO_2$: 275.0945. Found: 275.0946.

1-(4-Methyphenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-one (5b):[11] Yield 90% as a white solid; mp 170-172 °C; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6) δ 8.03 (1H, s), 7.78-7.74 (2H, m), 7.53 (1H, m,), 7.36-7.31 (2H, m), 7.23 (1H, d, J = 9.0 Hz), 7.12 (2H, d, J = 8.1 Hz), 7.02 (2H, d, J = 8.1 Hz), 5.94 (1H, d, J = 3.0 Hz), 2.20 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 147.3, 138.6, 138.4, 130.8, 130.3, 129.8, 129.1, 128.6, 127.2, 126.6, 124.9, 122.6, 116.9, 112.4, 55.8, 20.9; IR (KBr) 3242, 3137, 2362, 1723, 1512, 1390, 1222, 1115, 817 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{19}H_{15}NO_2$: 289.1100. Found: 289.1103.

1-(3-Methyphenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-one (5c): Yield 77% as a white solid; mp 205-206 °C; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6) δ 8.59 (1H, br), 8.00-7.90 (2H, m), 7.81-7.75 (1H, m), 7.55-7.49 (2H, m), 7.42 (1H, d, J = 9.0 Hz), 7.30 (1H, t, J = 7.5 Hz), 7.24-7.16 (3H, m), 6.14 (1H, s), 2.37 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$+ DMSO-d_6) δ 149.5, 147.3, 142.0, 138.1, 130.2, 129.7, 128.9, 128.5, 128.4, 128.2,127.3, 126.9, 124.5, 123.8, 122.3, 116.5, 113.1, 54.5, 20.9; IR (KBr) 3144, 2960, 1746, 1388, 1221, 1114, 990, 926, 793 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{19}H_{15}NO_2$: 289.1102. Found: 289.1103.

1-(4-Methoxyphenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-one (5d):[12] Yield 84% as a white solid; mp 206-208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (2H, d, J = 8.7 Hz), 7.56-7.53 (1H, m), 7.39-7.36 (2H, m), 7.30 (1H, d, J = 9.0 Hz, $CDCl_3$), 7.17 (2H, d, J = 8.1 Hz), 6.81 (2H, d, J = 8.1 Hz), 6.17 (1H, s), 6.01 (1H, s), 3.72 (3H, s); ^{13}C NMR (75 MHz) δ 162.3, 159.8, 147.6, 134.1, 131.0, 130.5, 129.4, 128.8, 128.2, 127.4, 125.1, 122.9, 117.2, 114.7, 112.8, 55.7, 55.3; IR (KBr) 3151, 2962, 1738, 1513, 1389, 1255, 1222, 1179, 1113, 1027, 919, 834, 742 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{19}H_{15}NO_3$: 305.1050. Found: 305.1052.

1-(3-Methoxyphenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3] oxazin-3-one (5e):[11] Yield 74% as a white solid; mp 186-188 °C; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6) δ 8.17 (1H, br), 7.73-7.68 (2H, m), 7.48-7.45 (1H, m), 7.29-7.26 (2H, m), 7.17 (1H, d, J = 9.0 Hz), 7.09 (2H, d, J = 8.7 Hz), 6.68 (2H, d, J = 8.4 Hz), 5.89 (1H, d, J = 2.7 Hz), 3.60 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 159.7, 150.2, 147.6, 134.1, 131.0, 130.5, 129.4, 128.8, 128.2, 127.9, 127.4, 125.2, 122.9, 117.1, 114.7, 112.8, 55.6, 55.3; IR (KBr) 3149, 2961, 1737, 1512, 1387, 1254, 1220, 1178, 1113, 1025, 917, 833, 738 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{19}H_{15}NO_3$: 305.1054. Found: 305.1052.

1-(4-Chlorophenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-one (5f):[10] Yield 75% as a white solid; mp 216-219 °C; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6) δ 8.73 (1H, d, J = 2.1 Hz), 7.85 (2H, dd, J = 9.6, 10.2 Hz), 7.61 (1H, d, J = 7.8 Hz), 7.42-7.26 (7H, m), 6.09 (1H, d, J = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ 149.1, 147.4, 141.0, 132.9, 130.3, 130.1, 128.7, 128.6, 128.5, 128.4, 127.1, 124.7, 122.5, 116.5, 112.9, 53.4; IR (KBr) 3147, 2964, 1736, 1390, 1226, 1180, 1117, 997, 920, 831 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{18}H_{12}ClNO_2$: 309.0560. Found: 309.0557.

1-(4-Nitrophenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-one (5g):[11] Yield 85% as a white solid; mp 170-174 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.05 (1H, d, J = 2.4 Hz), 8.19 (2H, d, J = 8.7 Hz), 8.02 (1H, d, J = 9.0 Hz), 7.96 (1H, d, J = 7.2 Hz), 7.81 (1H, d, J = 7.8 Hz), 7.60 (2H, d, J = 8.4 Hz), 7.52-7.40 (3H, m), 6.42 (1H, d, J = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 148.1, 147.9, 147.8, 131.4, 131.1, 129.2, 129.0, 128.1, 127.9, 125.6, 124.7, 122.2, 117.1, 112.5, 55.2; IR (KBr) 3142, 2959, 1732, 1523, 1345, 1221, 1115, 926, 822, 757 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{18}H_{12}N_2O_4$: 320.0794. Found: 320.0797.

1-(2-Nitrophenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-one (5h):[11] Yield 74% as a yellow solid; mp 104-106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (1H, d, J = 7.5 Hz), 7.93 (1H, d, J = 9.0 Hz), 7.86 (1H, d, J = 7.5 Hz), 7.49-7.30 (5H, m), 7.13 (1H, d, J = 8.1 Hz), 6.89 (1H, d, J = 7.5 Hz), 6.56 (2H, d, J = 5.7 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.8, 148.7, 148.0, 135.3, 131.5, 130.9, 130.3, 130.2, 129.3, 129.3, 128.3, 125.9, 125.7, 122.8, 117.3, 112.1, 49.7; IR (KBr) 3267, 2923, 2372, 1723, 1522, 1382, 1345, 1224, 1189, 798 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{18}H_{12}N_2O_4$: 320.0795. Found: 320.0797.

1-Phenyl-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-thione (5i): Yield 74% as a yellow solid; mp 208-210 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (1H, br), 7.87-7.80 (2H, m), 7.52-7.47 (1H, m), 7.47-7.37 (3H, m), 7.31-7.19 (5H, m), 5.99 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.4, 146.5, 140.2,

131.4, 130.9, 129.5, 129.1, 129.0, 128.9, 127.7, 127.3, 125.7, 122.7, 116.6, 56.3; IR (KBr) 3159, 3055, 2368, 1631, 1557, 1515, 1409, 1308, 1184, 828 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{18}H_{13}NOS$: 291.0721. Found: 291.0718.

1-(4-Methoxyphenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3] oxazin-3-thione (5j): Yield 70% as a white solid; mp 190-192 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (1H, br), 7.85-7.80 (2H, m), 7.53-7.49 (1H, m), 7.42-7.36 (3H, m), 7.17 (2H, d, *J* = 8.7 Hz), 6.80 (2H, d, *J* = 8.7 Hz), 5.95 (1H, d, *J* = 1.8 Hz), 3.69 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.0, 159.9, 146.4, 132.5, 131.4, 130.8, 129.0, 128.9, 128.6, 127.6, 125.6, 122.8, 116.5, 114.8, 111.9, 55.8, 55.3; IR (KBr) 3178, 3054, 1631, 1613, 1557, 1512, 1306, 1259, 1182, 1152, 1027, 922, 827, 742 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{19}H_{15}NO_2S$: 321.0821. Found: 321.0824.

1-(3-Methoxyphenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3] oxazin-3-thione (5k): Yield 71% as a yellow solid; mp 180-182 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (1H, br), 7.87-7.80 (2H, m), 7.54-7.51 (1H, m), 7.44-7.32 (3H, m), 7.21-7.18 (1H, m), 6.84 (1H, d, *J* = 7.8 Hz), 6.77 (2H, d, *J* = 6.9 Hz), 5.96 (1H, d, *J* = 2.4 Hz), 3.69 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.8, 162.4, 160.6, 146.7, 141.8, 131.5, 130.9, 130.6, 129.2, 128.9, 127.7, 125.7, 122.8, 119.5, 116.6, 114.3, 113.3, 56.4, 55.3; IR (KBr) 3178, 3052, 2947, 1714, 1598, 1544, 1316, 1259, 1157, 1040, 930, 817, 748 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{19}H_{15}NO_2S$: 321.0822. Found: 321.0824.

1-(4-Nitrophenyl)-1,2-dihydro-naphtho[1,2-*e*][1,3]oxazin-3-thione (5l): Yield 82% as a white solid; mp 135-138 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 9.13 (1H, br), 8.11 (2H, d, *J* = 8.4 Hz), 7.91 (1H, d, *J* = 9.0 Hz), 7.87-7.84 (1H, m), 7.45-7.37 (6H, m), 6.14 (1H, d, *J* = 2.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.4, 148.0, 146.5, 146.5, 131.6, 131.5, 129.2, 128.5, 128.4, 128.2, 126.1, 124.7, 122.1, 116.4, 110.6, 54.5; IR (KBr) 3070, 2943, 1607, 1521, 1343, 1160, 822, 744 cm^{-1}. HRMS *m/z* (M^+) calcd for $C_{18}H_{12}N_2O_3S$: 336.0566. Found: 336.0569.

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