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An Inverse Electron Demand Azo-Diels-Alder Reaction of *o*-Quinone Methides and Imino Ethers: Synthesis of Benzocondensed 1,3-Oxazines

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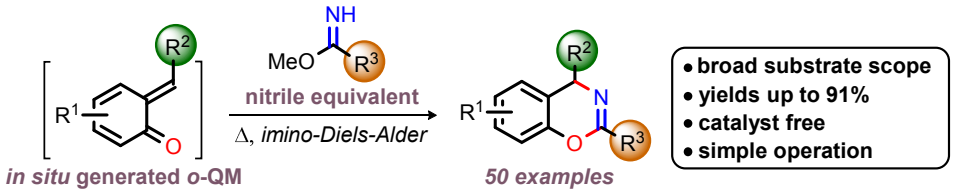


ABSTRACT: We have studied the reactions of *o*-quinone methide precursors with imino ethers. The reaction provides a versatile route to substituted 1,3-benzoxazines. The proposed reaction mechanism involves the generation of the *o*-quinone methide intermediates, imino-Diels-Alder reaction, and the elimination. This cascade process is a rare example of the participation of imino ethers as dienophiles.

INTRODUCTION

The use of hetero-substituted dienes and/or dienophiles in [4+2]-cycloaddition reactions provides rapid and economic methods for the construction of six-membered heterocycles. Preparation of nitrogen heterocycles through the imino-Diels-Alder reactions has recently received much attention.[1] As a rule, the imino dienophile is a variant of the aza-Diels-Alder reaction requires the use of imines with electron withdrawing substituents, such as N-acyl, N-sulfonyl, and C-acylimines. At the same time, there are a limited number of examples involving electron-rich (C-heteroatom-substituted) imines.

Areno-condensed 1,3-oxazine derivatives are of significant importance because of their promising biological activity.[2] In particular, they possess antibacterial, antifungal,[3a] anticancer[3b] and anti-H_5N_1[3c] activities, display DNA-dependent protein kinase inhibition.[3d] At the same time, the natural 1,3-benzoxazines are extremely rare. Among them there are two isomeric streptopyrroles isolated from *Streptomyces rimosus* and exhibiting bacterial protein histidine kinase inhibitory and antimicrobial activities,[4a] benadrostin,[4b] platensimycin B_2.[4c] Besides, 1,3-

benzoxazines have been used as precursors in the preparation of chiral bidentate (phoshinoaryl)benzoxazine ligands for asymmetric catalysis[5a,b] and as monomers for polybenzoxazines synthesis[5c] (Figure 1).

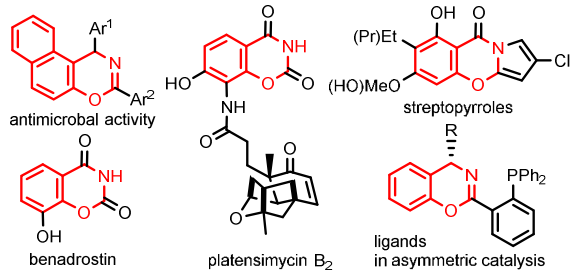


Figure 1. Selection of Relevant 1,3-Benzoxazine Derivatives.

Only a few methods for the synthesis of 1,3-benzoxazines have been reported. Main method is an acid-catalyzed interaction between *o*-hydroxybenzyl alcohols[6a,b] or amines[5b] and nitriles (Ritter reaction) as well as cyclization of N-(2-hydroxybenzyl)amides,[3c,5b,6c] thermolysis of 3-methyl-4*H*-1,2-brnzoxazine,[6d] from hydroxynitrones,[6e,f] oxydation of N-arylidene-1-(α-aminobenzyl)-2-naphtols with iodobenzene diacetate,[3a] one-pot condensation of 1,1,3,3-tetramethylguanidine, aromatic aldehydes and 2-naphthols[3a] (Figure 2) and a very recent electrochemical C-H oxygenation of *N*-benzylamides in flow.[6g] This heterocyclic system can be also considered as product of [4+2]-cycloaddition between *o*-quinone methides (*o*-QMs) and nitriles. However, non-activated nitriles are known to be poor dienophiles and unstable *o*-QMs act as heterodienes usually only with electron-rich olefins. We have proposed that the use in this reaction of stable *o*-QM precursors and imino ethers as synthetic equivalents of nitriles avoids these difficulties.

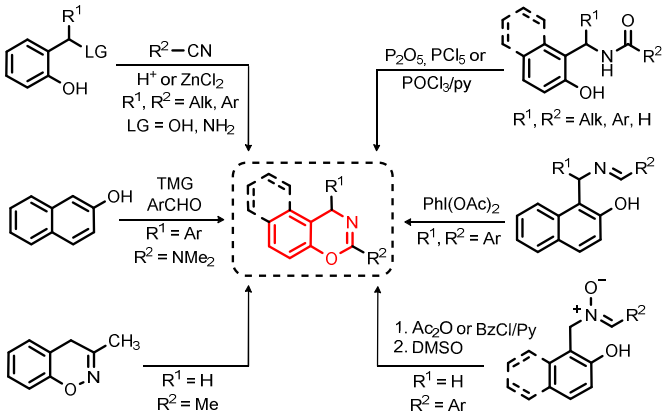


Figure 2. Known Methods for Synthesis of 4*H*-1,3-Benzoxazines and 1*H*-Naphto[1,2-*e*][1,3]oxazines.

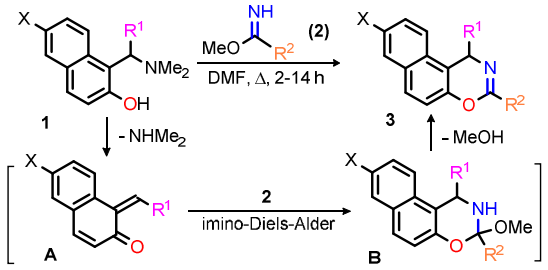
o-QMs as a heterodiene component in Diels-Alder reaction have received great attention in the construction of a wide variety of chromane skeletons.[7] It should be remarked that although *o*-QMs have been reported to undergo [4+2]-cycloadditions with different carbon dienophiles there are only a few examples of [4+2]-cycloaddition of *in situ* generated *o*-QMs to imino

compounds.[8] On the other hand, although imino ethers are widely used for the synthesis of various nitrogen-containing heterocyclic compounds,[9] they are very seldom utilized as heterodienophiles. There have been reports of several reactions of imino ethers with 1,2,4,5-tetrazines[10] and 1,2,3-triazines[11] which may be interpreted as Diels-Alder reactions. However, their use for the synthesis of 4*H*-1,3-benzoxazines has not been described in literature. As a part of our ongoing interest in developing new synthetic strategies for the construction of condensed 1,3-benzoxazines,[12] we focused our attention on the reaction of *o*-QMs derived from 2-naphthol Mannich bases with imino ethers.

RESULTS AND DISCUSSION

To the best of our knowledge, there is only one report for synthesis of 1*H*-naphtho[1,2-*e*][1,3]oxazine from imino ether. Fülöp *et al*. reported[13] the reaction of unsubstituted 1-aminomethyl-2-naphthol with ethyl benzimidate in boiling EtOH gave the described earlier 3-phenyl-1*H*-naphtho[1,2-*e*][1,3]oxazine **3aa** in 37% yield. However, in the case of 1-(α-aminobenzyl)-2-naphthol and 2-(α-aminobenzyl)-1-naphthol only decomposition of the starting aminomethylnaphthols was observed. We have shown that on heating 1-[(dimethylamino)methyl]naphthalen-2-ol **1a** and methyl benzimidate **2a** in boiling DMF, 1*H*-naphtho[1,2-*e*][1,3]oxazine **3aa** was isolated in 90% yield. When the reaction was carried out in ethanol or acetonitrile, no desired product formation was observed. The high temperature is necessary to ensure the thermal decomposition of the Mannich base. The scope and generality of this reaction were then explored. A variety of electronically divergent imino ethers and Mannich bases of the naphthalene series were examined, and the results are summarized in Table 1. The reaction proceeded without any problems for a wide range of co-reactants bearing electron-withdrawing and electron-donating substituents on the aryl rings. Products can be easily purified from impurities by single recrystallization, chromatographic purification is not usually required. Besides, imino ethers of the heterocyclic series (furan, thiophene, pyridine derivatives) were involved in this process. However, it should be noted that the reaction with ethyl nicotinimidate **2f** is completed in 13–14 hours (compounds **3af**,**gf**), although usually no more than 8 hours are required. The example of (1-adamantyl)acetimidate **2g** shows that not only arylimidates can be introduced into the reaction (compound **3ag**). The mechanism of the reaction is believed to involve initial elimination of dimethylamine from the Mannich base to afford a highly reactive 1,2-naphthoquinone-1-methide **A**, which reacts with imino ether to give unstable 2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine cycloadduct **B**. The subsequent loss of methanol leads to 1*H*-naphtho[1,2-*e*][1,3]oxazine **3**. The formation of this cyclic system may be interpreted as a result of a $LUMO_{diene}/HOMO_{dienophile}$-controlled [4+2]-cycloaddition reaction. Imino ether plays the role of heterodienophile and *o*-QM – the role of 1-oxadiene component.

Table 1. Scope of the reaction

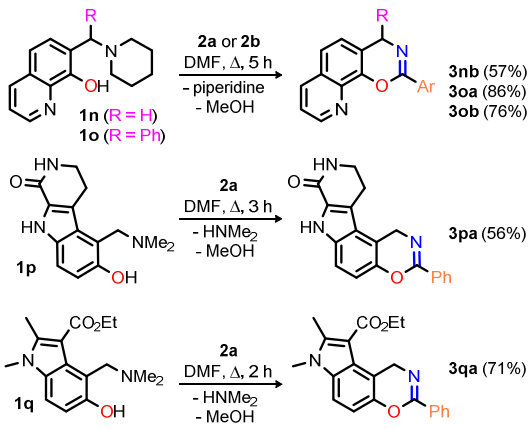


R^1 [a]	R^2	Product **3** [b]
H (**1a**)	Ph (**2a**)	**3aa**, 5h, 90%
H (**1a**)	4-BrC_6H_4 (**2b**)	**3ab**, 3h, 85%
H (**1a**)	4-$CF_3C_6H_4$ (**2c**)	**3ac**, 5h, 65%
H (**1a**)	2-furyl (**2d**)	**3ad**, 5h, 74%
H (**1a**)	2-thienyl (**2e**)	**3ae**, 5h, 77%
H (**1a**)	3-pyridyl (**2f**)	**3af**, 13h, 78%
H (**1a**)	CH_2-1-Ad (**2g**)	**3ag**, 5h, 68%
H (**1b**)	Ph (**2a**)	**3ba**, 2h, 85%
H (**1b**)	2-furyl (**2d**)	**3bd**, 2h, 68%
Ph (**1c**)	Ph (**2a**)	**3ca**, 4h, 76%
Ph (**1c**)	4-BrC_6H_4 (**2b**)	**3cb**, 4h, 80%
Ph (**1c**)	2-furyl (**2d**)	**3cd**, 6h, 78%
Ph (**1c**)	2-thienyl (**2e**)	**3ce**, 4h, 88%
4-ClC_6H_4 (**1d**)	Ph (**2a**)	**3da**, 4h, 74%
4-ClC_6H_4 (**1d**)	4-BrC_6H_4 (**2b**)	**3db**, 5h, 76%
3-ClC_6H_4 (**1e**)	Ph (**2a**)	**3ea**, 4h, 66%
4-FC_6H_4 (**1f**)	Ph (**2a**)	**3fa**, 4h, 91%
4-$MeOC_6H_4$ (**1g**)	Ph (**2a**)	**3ga**, 5h, 71%
4-$MeOC_6H_4$ (**1g**)	4-BrC_6H_4 (**2b**)	**3gb**, 5h, 88%
4-$MeOC_6H_4$ (**1g**)	3-pyridyl (**2f**)	**3gf**, 14h, 83%
2-$MeOC_6H_4$ (**1h**)	Ph (**2a**)	**3ha**, 4h, 78%
2-$MeOC_6H_4$ (**1h**)	2-furyl (**2d**)	**3hd**, 8h, 65%
2-$MeOC_6H_4$ (**1h**)	4-MeC_6H_4 (**2h**)	**3hh**, 6h, 80%
3,4-$(MeO)_2C_6H_4$ (**1i**)	4-BrC_6H_4 (**2b**)	**3ib**, 7h, 85%
3,4-$(OCH_2O)_2C_6H_4$ (**1j**)	4-BrC_6H_4 (**2b**)	**3jb**, 7h, 67%
3,4,5-$(MeO)_3C_6H_3$ (**1k**)	Ph (**2a**)	**3ka**, 5h, 85%
2-thienyl (**1l**)	Ph (**2a**)	**3la**, 2h, 83%
2-thienyl (**1l**)	2-thienyl (**2e**)	**3le**, 4h, 60%
4-pyridyl (**1m**)	Ph (**2a**)	**3ma**, 5h, 69%

[a] X = H (**1a,d-m**), X = adamantan-1-yl (**1b**). [b] Isolated yields.

It should be noted that good yields of 1*H*-naphtho[1,2-*e*][1,3]oxazines **3** are attained by the use of 1 equiv. of imino ethers. At the same time, for attaining reasonable yields in the reactions of *o*-QMs with many others dienophiles, a large excess of the latter is usually required[14] to prevent di- and trimerization of *o*-QMs.

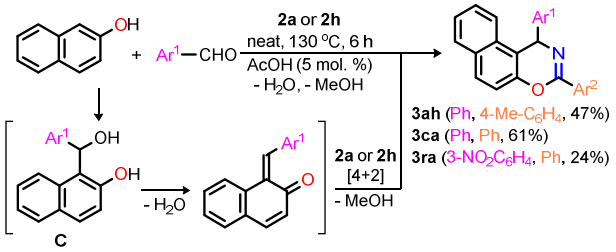
This reaction was extended to the Mannich bases of the heterocyclic series (quinoline, β-carboline and indole derivatives). It provides a facile route to the hitherto unknown heterocyclic systems 4*H*-[1,3]oxazino[5,6-*h*]quinolines **3nb,oa,ob**, 1,7,8,9,10,11-hexahydro[1,3]oxazino[5,6-*e*]pyrido[3,4-*b*]indole **3pa** and 1,7-dihydro[1,3]oxazino[5,6-*e*]indole **3qa** (Scheme 1).



Scheme 1. Extension of the Developed Methodology to Heterocyclic Precursors of *o*-Quinone Methides.

Thus, as Mannich bases can easily be synthesized from naphthols and aldehydes by the Mannich reaction and imino ethers are readily accessible from nitriles, the reaction described herein represents a convenient synthesis of 1*H*-naphtho[1,2-*e*][1,3]oxazines.

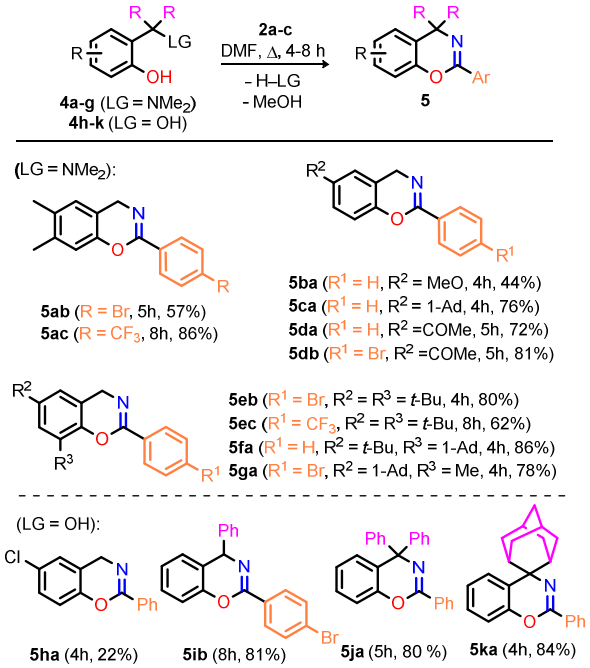
Attempts to obtain 1*H*-naphtho[1,2-*e*][1,3]oxazines by a three-component reaction from 2-naphthol, aromatic aldehyde and imino ether gave less satisfactory results. The products **3ah,ca,ra** were obtained in lower yields and required purification by column chromatography. The best results were obtained by carrying out the reaction without a solvent at 130 °C in the presence of acetic acid (5 mol. %) as a catalyst. Heating of the equimolar mixture of these reagents in DMF under reflux or at 130 °C does not result in the formation of 1*H*-naphtho[1,2-*e*][1,3]oxazines **3ah,ca,ra**. The mechanism of the three-component reaction comprise the initial hydroxyalkylation of 2-naphthols with aromatic aldehydes to yield unstable alcohols **C**, which dehydrate with generation of *o*-QMs. The further transformations lead to 1*H*-naphtho[1,2-*e*][1,3]oxazines **3ah,ca,ra** (Scheme 2). The lowest yield was found for naphthoxazine **3ra**, which has a strong electron-withdrawing nitro group in the aryl substituent. This finding is likely a result of the difficulty in generating the corresponding *o*-QM.



Scheme 2. Three-component Condensation of 2-Naphthol, Aromatic Aldehydes and Imino Ethers

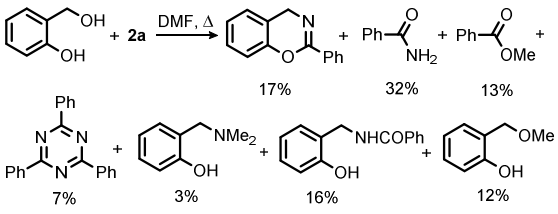
Having established a strategy for the synthesis of 1*H*-naphtho[1,2-*e*][1,3]oxazines, its applicability to the preparation of 4*H*-1,3-benzoxazines **5** was studied. It turned out that phenol Mannich bases can also be used in the reactions with imino ethers, providing 4*H*-1,3-benzoxazines **5** in moderate to good yieds. Instead of Mannich bases, 2-hydroxybenzyl alcohols

can be used as *o*-benzoquinone methide precursors (Scheme 3). The best results were also obtained in DMF under reflux. Attempts to extend this reaction to the 4-chloro-2-(hydroxymethyl)phenol, however, gave less satisfactory results to furnish the expected product **5ha**, maybe because of the relatively greater thermal stability of this hydroxybenzyl alcohol compared to the *o*-QM precursors containing electron-donating group in benzyl position and consequent difficulty in generating the *o*-QMs. The sterically hindered 4*H*-1,3-benzoxazines **5ja,ka** were obtained in excellent yields, indicating that steric hindrance had no obvious influence on the efficiency of the method.



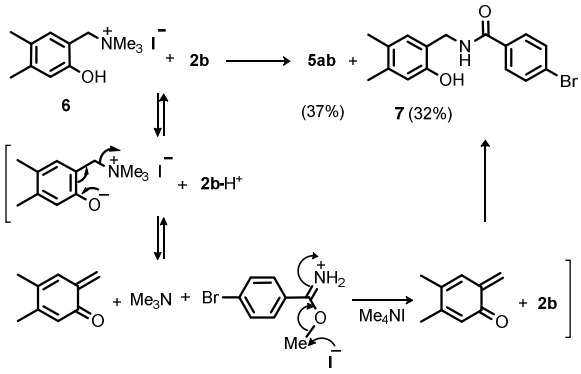
Scheme 3. Synthesis of 2-Aryl-4*H*-benzo[*e*][1,3]oxazines from Phenol Mannich Bases and 2-Hydroxybenzyl Alcohols.

In the case of unsubstituted salicyl alcohol and methyl benzimidate, the content of the desired 2-phenyl-4*H*-benzo[*e*][1,3]oxazine in the mixture did not exceed 20%. The products of decomposition and hydrolysis of imino ether, as well as products of conjugated addition of nucleophiles (methanol, dimethylamine and benzamide) to *o*-QM were identified. The composition of the reaction mixture is determined by GC-MC analysis. Dimethylamine is formed as a result of partial decomposition of DMF (Scheme 4).



Scheme 4. Reaction of Methyl Benzimidate and Salicyl alcohol

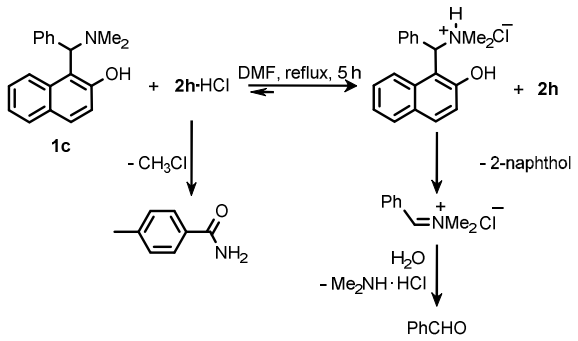
The interaction of quaternary ammonium salts with imino ethers proceeds also less unambiguously. Thus, in the reaction between quaternary ammonium salt **6** and methyl 4-bromobenzimidate **2b**, N-(2-hydroxybenzyl)benzamide **7** was isolated along with 4*H*-1,3-benzoxazine **5ab** (Scheme 5). The formation of benzamide **7** could be explained by the hydrolytic cleavage of the benzoxazine **5ab** during the treatment of the reaction mixture. However, the 1,3-benzoxazine **5ab** obtained from the Mannich base under similar conditions proves to be resistant to hydrolysis. Apparently, at first the protonated form of imino ether under the action of the iodide ion is converted to an amide (Pinner rearrangement), and then 4-bromobenzamide reacts with *o*-QM. The presence of imino ether facilitates the generation of *o*-QM from a quaternary ammonium salt **6** by partial deprotonation of phenolic hydroxyl group. It should be noted that the acidity of quaternary ammonium salts of approximately 2.6-2.7 orders of magnitude higher than the corresponding Mannich base.[15]



Scheme 5. Formation of N-(2-Hydroxybenzyl)benzamide **7**.

At the same time, the reaction between 1-[(dimethylamino)(phenyl)methyl]naphthalen-2-ol and methyl 4-benzimidate in DMF under reflux in the presence of NaI (1.5 equv.) leads only to naphtho[1,2-*e*][1,3]oxazine **3ca** in 72% yield. Thus, the presence of nucleophilic iodide ion and protonated form of imino ether is necessary for the formation of a secondary amide.

It should also be noted that in the preparation of areno-1,3-oxazines imino ethers must be used as free bases and not as salts. Indeed, the reaction of methyl 4-methylbenzimidate hydrochloride and Mannich base **1c** in boiling DMF leads to the formation of 2-naphthol and benzaldehyde due to retro-Mannich reaction as well as 4-methylbenzamide as a result of Pinner rearrangement (Scheme 6).



Scheme 6. Reaction of 2-Naphthol Mannich Base with Methyl 4-Methylbenzimidate Hydrochloride.

The structures of all products were determined on the basis of their analytical and spectral data. IR spectra of naphtho[1,2-*e*][1,3]oxazines **3** and 4*H*-1,3-benzoxazines **5** contain the band of high intensity at 1653–1694 cm^{-1} attributed to C=N bond. The ^{1}H NMR spectra of products **3**, **5** show characteristic 1-H and 2-H singlets at δ 6.34–6.97 and 4.74–5.15 ppm for methyne and methylene protons, respectively. A distinguishing resonance at 51.7–57.2 ppm for CH-1, 42.8–43.5 ppm for CH_2-1 and 145.9–147.1 ppm for C-4a are observed in the ^{13}C NMR spectra of naphtho[1,2-*e*][1,3]oxazines **3**. A signal in the region of 150.5–153.2 ppm was assigned to C-3 in 3-aryl-substituted naphtho[1,2-*e*][1,3]oxazines **3** and C-2 in 4*H*-1,3-benzoxazines **7**. The cyclic nature of the products is also confirmed by the absence of phenolic OH stretching frequencies in the IR spectra and phenolic proton signal in the ^{1}H NMR spectra. In the mass spectra of compounds **5ba, 5eb**, one of the main direction of fragmentation is retro-Diels-Alder reaction, leading to corresponding *o*-QM and nitrile.

CONCLUSION

A new method for the synthesis of benzocondensed 1,3-oxazines from *o*-QM precursors (Mannich bases and 2-hydroxybenzyl alcohols) and imino ethers had been developed. The reaction proceeds via electron demand imino-Diels-Alder reaction followed by elimination. The synthesis by the suggested procedure does not require an excess of any reagents, includes the use of available reagents, good functional group tolerance, simple experimental steps and product isolation, chromatographic purification is not usually required. The use of heterocyclic *o*-QM precursors permits the preparation of 1,3-benzoxazines fused to heterocyclic rings.

EXPERIMENTAL SECTION

Materials and Characterization. FTIR spectra were taken in KBr pellets. ^{1}H, ^{13}C, ^{19}F and DEPT NMR spectra were recorded using a 400 MHz NMR spectrometer in $CDCl_3$ or DMSO-d_6 solutions, relative to residual solvent signal. Chemical shifts and coupling constants were recorded in units of parts per million and hertz, respectively. Mass spectra were obtained on a Finnigan Trace DSQ instrument, energy of ionizing electrons was 70 eV. The melting points

were determined by capillary method and uncorrected. Elemental analysis was carried out on an automatic CHNS analyzer. The reaction progress was controlled by TLC on aluminum foil-backed silica gel plates, visualization under UV light and in iodine vapor, eluent CH_2Cl_2.

*1-[(Dimethylamino)(2-methoxyphenyl)methyl]naphthalen-2-ol (**1h**).* Dimethylamine (31.5 mL of a 33% aqueous solution, 0.21 mol) and 2-methoxybenzaldehyde (28.3 g, 0.21 mol) were added to a solution of naphthalen-2-ol (30 g, 0.21 mol) in ethanol (40 mL) at 25 ºC. The reaction mixture was stored at room temperature for 5 days. The precipitate formed was filtered off, washed with ice-cold methanol. Yield: 47 g (73%). Colorless solid, mp 133–135 °C. IR (KBr) υ_{max}: 3100–2400, 2958, 1624, 1600, 1512, 1458, 1415, 1373, 1350, 1246, 1188, 1153, 1138, 1026, 948, 822, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 2.56 (s, 3H), 4.03 (s, 3H), 5.78 (s, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 7.16–7.25 (m, 3H), 7.34 (t, J = 7.5 Hz, 1H), 7.54 (dd, J = 7.6, 1.6 Hz, 1H), 7.66–7.71 (m, 2H), 7.82 (d, J = 8.7 Hz, 1H), 14.21 (br. s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 41.1 (CH_3), 45.5 (CH_3), 55.7 (CH_3), 63.0 (CH), 110.6 (CH), 116.9 (C), 120.1 (CH), 121.6 (2CH), 122.4 (CH), 126.4 (CH), 128.4 (C), 128.6 (C), 128.7 (CH), 129.2 (CH), 129.3 (CH), 129.9 (CH), 132.9 (C), 156.5 (C), 156.8 (C). Anal. Calcd (%) for $C_{20}H_{21}NO_2$, %: C, 78.11; H, 6.86; N, 4.58. Found (%): C, 78.15; H, 6.89; N, 4.56.

General Experimental Procedure for the Synthesis of Areno-condensed 1,3-Oxazines. A mixture of imino ether (as the base) (2 mmol) and the corresponding precursor *o*-quinone methide (2-hydroxybenzyl alcohol, phenol or 2-naphthol Mannich base) (2 mmol) in DMF (8 mL) was heated at reflux until the release of dimethylamine ceased (control on wet indicator paper). After the indicated time period, the solution was kept at –20 °C overnight. The precipitate formed was filtered off, washed with ice-cold methanol and purified by recrystallization (method A). If no precipitate was formed, the reaction mixture was poured into brine (50 mL) to yield a solid product, which was filtered off, washed with water, dried and purified by recrystallization (method B) or column chromatography (eluent – $CHCl_3$) followed by recrystallization (method C).

*3-Phenyl-1H-naphtho[1,2-e][1,3]oxazine (**3aa**)*. Method B. Yield: 90%, 465 mg. Colorless solid, mp 161–162 °C (EtOH) (lit.[13] mp 161–162 °C). IR (KBr) υ_{max}: 1680, 1628, 1605, 1518, 1440, 1364, 1331, 1279, 1225, 1177, 1098, 1055, 1016, 806, 775, 748, 692, 671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.15 (s, 2H), 7.22 (d, J = 8.7 Hz, 1H), 7.45–7.59 (m, 5H), 7.70 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 8.12–8.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 43.4 (CH_2), 110.8 (C), 116.6 (CH), 122.2 (CH), 124.9 (CH), 127.1 (CH), 127.4 (2CH), 128.4 (2CH), 128.6 (CH), 128.7 (CH), 130.0 (C), 131.1 (CH, C), 132.4 (C), 146.5 (C), 152.3 (C). Anal. Calcd (%) for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found (%): C, 83.25; H, 4.94; N, 5.51.

*3-(4-Bromophenyl)-1H-naphtho[1,2-e][1,3]oxazine (**3ab**)*. Method A. Yield: 85%, 575 mg. Colorless solid, mp 178–179 °C (EtOH–DMF). IR (KBr) υ_{max}: 1678, 1630, 1589, 1518, 1485, 1395, 1364, 1331, 1277, 1225, 1175, 1109, 1094, 1070, 1009, 831, 806, 768, 745, 721, 706, 664. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.10 (s, 2H), 7.17 (d, J = 8.7 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.53–7.58 (m, 3H), 7.65 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 43.4 (CH_2), 110.6 (C), 116.4 (CH), 122.2 (CH), 125.0 (CH), 125.8 (C), 127.1 (CH), 128.7 (CH), 128.8 (CH), 129.0 (2CH), 130.0 (C), 131.2 (C), 131.3 (C), 131.5 (2CH), 146.3 (C), 151.5 (C). Anal. Calcd (%) for $C_{18}H_{12}BrNO$: C, 63.92; H, 3.58; N, 4.14. Found (%): C, 64.00; H, 3.62; N, 4.08.

*3-[4-(Trifluoromethyl)phenyl]-1H-naphtho[1,2-e][1,3]oxazine (**3ac**)*. Method B. Yield: 65%, 425 mg. Colorless solid, mp 175–176 °C (DMF). IR (KBr) υ_{max}: 1678, 1624, 1605, 1589, 1516, 1408, 1327, 1227, 1173, 1130, 1096, 1065, 1015, 856, 810, 748, 671 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.14 (s, 2H), 7.19 (d, J = 8.9 Hz, 1H), 7.47 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 7.56 (ddd, J = 8.2, J = 6.9, J = 1.4 Hz, 1H), 7.66–7.70 (m, 3H), 7.75 (d, J = 8.7 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 43.5 (CH_2), 110.5 (C), 116.4 (CH), 122.2 (CH), 124.0 (q, $^1J_{C–F}$ = 271.0 Hz, C), 125.1 (CH), 125.3 (q, $^3J_{C–F}$ = 3.8 Hz, 2CH), 127.2 (CH), 127.7 (2CH), 128.7 (CH), 128.9 (CH), 129.9 (C), 131.2 (C), 132.7 (q, $^2J_{C–F}$ = 32.4 Hz, C), 135.6 (C), 146.3 (C), 151.1 (C). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –62.7 (s, 3F). Anal. Calcd (%) for $C_{19}H_{12}F_3NO$: C, 69.72; H, 3.70; N, 4.28. Found (%): C, 69.87; H, 3.75; N, 3.61.

*3-(Furan-2-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3ad**)*. Method B. Yield: 74%, 370 mg. Colorless solid, mp 158–160 °C (EtOH). IR (KBr) υ_{max}: 1694, 1628, 1574, 1516, 1489, 1466, 1435, 1400, 1362, 1331, 1288, 1223, 1169, 1099, 1015, 945, 814, 741, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.15 (s, 2H), 6.52 (dd, J = 3.4, J = 1.8 Hz, 1H), 7.07 (d, J = 4.1 Hz, 1H), 7.18 (d, J = 8.9 Hz, 1H), 7.46 (ddd, J = 8.2, J = 6.9, J = 1.4 Hz, 1H), 7.54–7.58 (m, 2H), 7.70 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 42.9 (CH_2), 110.9 (C), 111.5 (CH), 113.1 (CH), 116.4 (CH), 122.2 (CH), 125.0 (CH), 127.1 (CH), 128.6 (CH), 128.8 (CH), 130.0 (C), 131.1 (C), 145.1 (CH), 145.9 (C), 146.1 (2C). Anal. Calcd (%) for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found (%): C, 77.07; H, 4.36; N, 5.49.

*3-(Thiophen-2-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3ae**)*. Method B. Yield: 77%, 408 mg. Colorless solid, mp 180–182 °C (EtOH). IR (KBr) υ_{max}: 1678, 1632, 1516, 1470, 1427, 1400, 1362, 1331, 1273, 1219, 1177, 1088, 1007, 845, 806, 768, 752, 710, 687 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.04 (s, 2H), 7.16 (dd, J = 4.6, J = 3.9 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 7.48 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.58 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.71–7.73 (m, 2H), 7.77 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.7 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 42.8 (CH_2), 111.4 (C), 116.7 (CH), 122.9 (CH), 125.5 (CH), 127.7 (CH), 128.3

(CH), 129.0 (CH), 129.3 (CH), 129.5 (CH), 130.1 (C), 131.0 (CH), 131.3 (C), 136.2 (C), 146.4 (C), 148.5 (C). Anal. Calcd (%) for $C_{16}H_{11}NOS$: C, 72.43; H, 4.18; N, 5.28; S, 12.08. Found (%): C, 72.40; H, 4.10; N, 5.37; S, 11.98.

*3-(Pyridin-3-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3af**)*. Method C. Yield: 78%, 405 mg. Colorless solid, mp 183–185 °C (EtOH). IR (KBr) υ_{max}: 1680, 1628, 1607, 1585, 1518, 1470, 1422, 1400, 1364, 1333, 1281, 1223, 1200, 1179, 1103, 1011, 818, 745, 704, 687 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.13 (s, 2H), 7.19 (d, J = 8.7 Hz, 1H), 7.37 (dd, J = 8.2, J = 5.0 Hz, 1H), 7.43–7.48 (m, 1H), 7.53–7.57 (m, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 9.1 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 8.33–8.36 (m, 1H), 8.71 (br. s, 1H), 9.31 (br. s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 43.4 (CH_2), 110.6 (C), 116.4 (CH), 122.2 (CH), 123.2 (CH), 125.1 (CH), 127.2 (CH), 128.2 (C), 128.7 (CH), 128.9 (CH), 129.9 (C), 131.2 (C), 134.8 (CH), 146.1 (C), 148.9 (CH), 150.6 (C), 151.8 (CH). Anal. Calcd (%) for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found (%): C, 78.51; H, 4.66; N, 10.65.

*3-[(Adamantan-1-yl)methyl]-1H-naphtho[1,2-e][1,3]oxazine (**3ag**)*. Method B. Yield: 68%, 450 mg. Colorless solid, mp 100–102 °C (MeOH). IR (KBr) υ_{max}: 2912, 2846, 1627, 1273, 1238, 1149, 1026, 802, 740, 516 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.62–1.75 (m, 12H), 1.97 (br.s, 3H), 2.16 (s, 2H), 4.96 (s, 2H), 7.05 (d, J = 8.7 Hz, 1H), 7.41–7.46 (m, 1H), 7.51–7.56 (m, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.8 (3CH), 33.4 (C), 36.9 ($3CH_2$), 42.8 ($3CH_2$), 42.9 (CH_2), 49.4 (CH_2), 110.8 (C), 116.5 (CH), 122.1 (CH), 124.7 (CH), 127.0 (CH), 128.5 (CH), 128.6 (CH), 130.0 (C), 131.0 (C), 146.4 (C), 155.4 (C). Anal. Calcd (%) for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found (%): C, 83.40; H, 7.58; N, 4.18.

*8-(Adamantan-1-yl)-3-phenyl-1H-naphtho[1,2-e][1,3]oxazine (**3ba**)*. Method A. Yield: 85%, 670 mg. Colorless solid, mp 221–222 °C (DMF). IR (KBr) υ_{max}: 2905, 2845, 1676, 1609, 1508, 1476, 1450, 1400, 1368, 133, 1281, 1229, 1177, 1098, 1059, 1018, 885, 806, 775, 691, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.78–1.86 (m, 6H), 2.02 (br. s, 6H), 2.15 (br. s, 3H), 5.15 (s, 2H), 7.19 (d, J = 8.7 Hz, 1H), 7.44–7.50 (m, 3H), 7.67–7.74 (m, 4H), 8.12 (d, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.0 (3CH), 36.3 (C), 36.9 ($3CH_2$), 43.2 ($3CH_2$), 43.4 (CH_2), 110.5 (C), 116.3 (CH), 121.9 (CH), 123.8 (CH), 125.3 (CH), 127.4 (2CH), 128.2 (C), 128.3 (2CH), 128.7 (CH), 131.1 (CH), 131.3 (C), 132.4 (C), 146.1 (C), 147.9 (C), 152.5 (C). Anal. Calcd (%) for $C_{28}H_{27}NO$: C, 85.46; H, 6.92; N, 3.56. Found (%): C, 85.53; H, 7.00; N, 3.49.

*8-(Adamantan-1-yl)-3-(furan-2-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3bd**)*. Method A. Yield: 68%, 522 mg. Colorless solid, mp 218–220 °C (DMF). IR (KBr) υ_{max}: 2905, 2849, 1686, 1395, 1366, 1227, 1165, 1103, 1011, 947, 883, 829, 806, 745, 708, 669 cm^{-1}. ^1H NMR (400

MHz, $CDCl_3$) δ: 1.76–1.83 (m, 6H), 1.99–2.00 (m, 6H), 2.13 (br. s, 3H), 5.11 (s, 2H), 6.51–6.52 (m, 1H), 7.07 (d, J = 3.2 Hz, 1H), 7.13 (d, J = 8.9 Hz, 1H), 7.56–7.71 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.0 (3CH), 36.3 (C), 36.9 ($3CH_2$), 42.9 (CH_2), 43.2 ($3CH_2$), 110.6 (C), 111.6 (CH), 113.2 (CH), 116.1 (CH), 122.0 (CH), 123.7 (CH), 125.4 (CH), 128.1 (C), 128.8 (CH), 131.3 (C), 145.1 (CH), 145.6 (C), 146.03 (C), 146.07 (C), 148.1 (C). Anal. Calcd (%) for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65. Found (%):C, 81.51; H, 6.51; N, 3.70.

1,3-Diphenyl-1H-naphtho[1,2-e][1,3]oxazine ***(3ca)***. Method B. Yield: 76%, 510 mg. Colorless solid, mp 164–165 °C (EtOH) (lit.[2] mp 170–171 ºC). IR (KBr) υ_{max}: 1663, 1599, 1516, 1454, 1439, 1398, 1327, 1275, 1223, 1177, 1098, 1057, 1018, 837, 818, 779, 760, 743, 698, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.48 (s, 1H), 7.18–7.23 (m, 1H), 7.25–7.31 (m, 2H), 7.38–7.51 (m, 8H), 7.72–7.75 (m, 1H), 7.82–7.87 (m, 2H), 8.13–8.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 57.1 (CH), 114.2 (C), 116.7 (CH), 123.2 (CH), 124.9 (CH), 127.2 (CH), 127.6 (CH), 127.8 (2CH), 128.0 (2CH), 128.3 (2CH), 128.7 (CH), 128.9 (2CH), 129.5 (CH), 130.3 (C), 131.2 (CH), 131.6 (C), 132.2 (C), 143.6 (C), 147.0 (C), 151.6 (C). Anal. Calcd (%) for $C_{24}H_{17}NO$: C, 85.94; H, 5.11; N, 4.18. Found (%): C, 86.02; H, 5.16; N, 4.07.

3-(4-Bromophenyl)-1-phenyl-1H-naphtho[1,2-e][1,3]oxazine ***(3cb)***. Method B. Yield: 80%, 660 mg. Colorless solid, mp 202–203 °C (EtOH) (lit.[3a] mp 201–202). IR (KBr) υ_{max}: 1670, 1589, 1485, 1450, 1393, 1315, 1227, 1096, 1072, 1007, 833, 818, 748, 725, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.42 (s, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.24–7.28 (m, 2H), 7.33–7.41 (m, 5H), 7.53 (d, J = 8.7 Hz, 2H), 7.67–7.70 (m, 1H), 7.79–7.84 (m, 2H), 7.97 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 57.2 (CH), 114.0 (C), 116.6 (CH), 123.2 (CH), 125.0 (CH), 125.9 (C), 127.2 (CH), 127.6 (CH), 128.0 (2CH), 128.7 (CH), 128.9 (2CH), 129.3 (2CH), 129.6 (CH), 130.2 (C), 131.1 (C), 131.5 (2CH), 131.6 (C), 143.4 (C), 146.7 (C), 150.8 (C). Anal. Calcd (%) for $C_{24}H_{16}BrNO$: C, 69.58; H, 3.89; N, 3.38. Found (%): C, 69.67; H, 3.94; N, 3.31.

3-(Furan-2-yl)-1-phenyl-1H-naphtho[1,2-e][1,3]oxazine ***(3cd)***. Method B. Yield: 78%, 510 mg. Colorless solid, mp 166–168 °C (EtOH). IR (KBr) υ_{max}: 1678, 1601, 1566, 1516, 1481, 1396, 1354, 1323, 1227, 1169, 1103, 1011, 945, 833, 806, 760, 741, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.44 (s, 1H), 6.50 (dd, J = 3.4, J = 1.8 Hz, 1H), 7.11 (d, J = 3.4 Hz, 1H), 7.17–7.22 (m, 1H), 7.25–7.30 (m, 2H), 7.33 (d, J = 8.9 Hz, 1H), 7.37–7.43 (m, 4H), 7.53–7.54 (m, 1H), 7.70 (dd, J = 6.9, J = 2.5 Hz, 1H), 7.80–7.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.8 (CH), 111.6 (CH), 113.7 (CH), 114.3 (C), 116.5 (CH), 123.2 (CH), 124.9 (CH), 127.2 (CH), 127.7 (CH), 128.1 (2CH), 128.7 (CH), 128.9 (2CH), 129.6 (CH), 130.2 (C), 131.6 (C), 143.2 (C), 145.0 (C), 145.2 (CH), 145.9 (C), 146.5 (C). Anal. Calcd (%) for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30. Found (%):C, 81.33; H, 4.55; N, 4.24.

*1-Phenyl-3-(thiophen-2-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3ce**)*. Method B. Yield: 88%, 600 mg. Colorless solid, mp 154–156 °C (EtOH). IR (KBr) υ_{max}: 1667, 1601, 1516, 1427, 1358, 1319, 1219, 1096, 1007, 833, 807, 748, 714, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.41 (s, 1H), 7.08 (dd, J = 5.0, J = 3.6 Hz, 1H), 7.18–7.22 (m, 1H), 7.25–7.30 (m, 2H), 7.34–7.44 (m, 6H), 7.71–7.73 (m, 1H), 7.77 (dd, J = 3.7, J = 1.2 Hz, 1H), 7.81–7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 57.0 (CH), 114.4 (C), 116.6 (CH), 123.1 (CH), 124.9 (CH), 127.2 (CH), 127.54 (CH), 127.57 (CH), 128.0 (2CH), 128.7 (CH), 128.9 (2CH), 129.3 (CH), 129.5 (CH), 129.6 (CH), 130.2 (C), 131.5 (C), 136.2 (C), 143.4 (C), 146.8 (C), 148.5 (C). Anal. Calcd (%) for $C_{22}H_{15}NOS$: C, 77.39; H, 4.43; N, 4.10; S, 9.39. Found (%):C, 77.28; H, 4.49; N, 4.22; S, 9.28.

*1-(4-Chlorophenyl)-3-phenyl-1H-naphtho[1,2-e][1,3]oxazine (**3da**)*. Method B. Yield: 74%, 615 mg. Colorless solid, mp 170–172 °C (DMF–EtOH). IR (KBr) υ_{max}: 1672, 1516, 1489, 1398, 1352, 1319, 1225, 1175, 1098, 1055, 1016, 841, 812, 775, 741, 691, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.44 (s, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.9 Hz, 1H), 7.41–7.51 (m, 5H), 7.65 (dd, J = 7.1, J = 2.1 Hz, 1H), 7.82–7.87 (m, 2H), 8.12 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.4 (CH), 113.6 (C), 116.7 (CH), 123.0 (CH), 125.0 (CH), 127.3 (CH), 127.7 (2CH), 128.4 (2CH), 128.8 (CH), 129.1 (2CH), 129.4 (2CH), 129.8 (CH), 130.1 (C), 131.4 (CH), 131.6 (C), 131.9 (C), 133.3 (C), 142.1 (C), 146.9 (C), 151.8 (C). Anal. Calcd (%) for $C_{24}H_{16}ClNO$: C, 77.94; H, 4.36; N, 3.79. Found (%): C, 78.04; H, 4.44; N, 3.71.

*3-(4-Bromophenyl)-1-(4-chlorophenyl)-1H-naphtho[1,2-e][1,3]oxazine (**3db**)*. Method B. Yield: 76%, 680 mg. Colorless solid, mp 197–198 °C (EtOH). IR (KBr) υ_{max}: 1672, 1589, 1516, 1487, 1393, 1350, 1317, 1225, 1171, 1098, 1070, 1009, 837, 826, 810, 745, 721, 662 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.41 (s, 1H), 7.24 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 9.2 Hz, 1H), 7.41–7.44 (m, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.61–7.63 (m, 1H), 7.81–7.87 (m, 2H), 7.98 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.5 (CH), 113.4 (C), 116.6 (CH), 123.0 (CH), 125.1 (CH), 126.0 (C), 127.4 (CH), 128.8 (CH), 129.1 (2CH), 129.3 (2CH), 129.3 (2CH), 129.8 (CH), 130.0 (C), 130.9 (C), 131.6 (2CH, C), 133.4 (C), 141.9 (C), 146.8 (C), 150.9 (C). Anal. Calcd (%) for $C_{24}H_{15}BrClNO$: C, 64.24; H, 3.37; N, 3.12. Found (%): C, 64.31; H, 3.34; N, 3.21.

*1-(3-Chlorophenyl)-3-phenyl-1H-naphtho[1,2-e][1,3]oxazine (**3ea**)*. Method B. Yield: 66%, 490 mg. Colorless solid, mp 150–151 °C (DMF–EtOH). IR (KBr) υ_{max}: 1663, 1591, 1518, 1468, 1432, 1425, 1400, 1323, 1223, 1167, 1101, 1059, 1016, 928, 810, 777, 743, 731, 716, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.44 (s, 1H), 7.17–7.28 (m, 3H), 7.38–7.52 (m, 7H), 7.66 (d, J = 8.7 Hz, 1H), 7.83–7.88 (m, 2H), 8.14 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.7 (CH), 113.3 (C), 116.7 (CH), 123.0 (CH), 125.0 (CH), 126.2 (CH), 127.3 (CH), 127.76

(2CH), 127.82 (CH), 128.2 (CH), 128.4 (2CH), 128.8 (CH), 129.8 (CH), 130.12 (C), 130.15 (CH), 131.4 (CH), 131.6 (C), 132.0 (C), 134.7 (C), 145.6 (C), 147.0 (C), 151.8 (C). Anal. Calcd (%) for $C_{24}H_{16}ClNO$: C, 77.94; H, 4.36; N, 3.79. Found (%): C, 77.90; H, 4.27; N, 3.68.

*1-(4-Fluorophenyl)-3-phenyl-1H-naphtho[1,2-e][1,3]oxazine (**3fa**)*. Method B. Yield: 91%, 643 mg. Colorless solid, mp 151–152 °C (DMF–EtOH). IR (KBr) υ_{max}: 1668, 1603, 1501, 1468, 1449, 1398, 1352, 1319, 1217, 1190, 1177, 1155, 1101, 1090, 1057, 1016, 814, 781, 746, 694, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.46 (s, 1H), 6.94–6.99 (m, 2H), 7.34–7.51 (m, 8H), 7.66–7.69 (m, 1H), 7.82–7.87 (m, 2H), 8.12–8.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.3 (CH), 113.9 (C), 115.7 (d, $^2J_{C–F}$ = 21.0 Hz, 2CH), 116.7 (CH), 123.1 (CH), 125.0 (CH), 127.2 (CH), 127.7 (2CH), 128.4 (2CH), 128.8 (CH), 129.59 (d, $^3J_{C–F}$ = 7.6 Hz, 2CH), 129.65 (CH), 130.2 (C), 131.3 (CH), 131.6 (C), 132.1 (C), 139.5 (d, $^4J_{C–F}$ = 2.9 Hz, C), 147.0 (C), 151.6 (C), 162.1 (d, $^1J_{C–F}$ = 245.0 Hz, C). Anal. Calcd (%) for $C_{24}H_{16}FNO$: C, 81.57; H, 4.56; N, 3.96. Found (%): C, 81.42; H, 4.61; N, 3.87.

*1-(4-Methoxyphenyl)-3-phenyl-1H-naphtho[1,2-e][1,3]oxazine (**3ga**)*. Method B. Yield: 71%, 520 mg. Colorless solid, mp 205–206 °C (MeOH). IR (KBr) υ_{max}: 1663, 1582, 1508, 1460, 1441, 1325, 1244, 1229, 1177, 1098, 1034, 1018, 829, 820, 779, 752, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.72 (s, 3H), 6.42 (s, 1H), 6.80 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.36–7.50 (m, 6H), 7.72 (d, J = 7.8 Hz, 1H), 7.81–7.85 (m, 2H), 8.13 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.3 (CH_3), 56.4 (CH), 114.2 (2CH), 114.5 (C), 116.7 (CH), 123.2 (CH), 124.9 (CH), 127.1 (CH), 127.7 (2CH), 128.3 (2CH), 128.7 (CH), 129.1 (2CH), 129.4 (CH), 130.2 (C), 131.2 (CH), 131.6 (C), 132.2 (C), 136.1 (C), 146.9 (C), 151.4 (C), 158.9 (C). Anal. Calcd (%) for $C_{25}H_{19}NO_2$: C, 82.17; H, 5.24; N, 3.83. Found (%): C, 82.20; H, 5.17; N, 3.92.

*3-(4-Bromophenyl)-1-(4-methoxyphenyl)-1H-naphtho[1,2-e][1,3]oxazine (**3gb**)*. Method B. Yield: 88%, 780 mg. Colorless solid, mp 189–190 °C (EtOH). IR (KBr) υ_{max}: 1674, 1609, 1591, 1508, 1485, 1466, 1439, 1395, 1354, 1319, 1246, 1227, 1177, 1096, 1011, 839, 814 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.72 (s, 3H), 6.39 (s, 1H), 6.80 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 9.0 Hz, 1H), 7.37–7.44 (m, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 7.4 Hz, 1H), 7.80–7.84 (m, 2H), 7.99 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.3 (CH_3), 56.5 (CH), 114.3 (2CH, C), 116.6 (CH), 123.2 (CH), 124.9 (CH), 125.8 (C), 127.2 (CH), 128.7 (CH), 129.0 (2CH), 129.3 (2CH), 129.5 (CH), 130.2 (C), 131.2 (C), 131.5 (2CH), 131.6 (C), 135.9 (C), 146.7 (C), 150.5 (C), 159.0 (C). Anal. Calcd (%) for $C_{25}H_{18}BrNO_2$: C, 67.58; H, 4.08; N, 3.15. Found (%): C, 67.63; H, 4.10; N, 3.06.

*1-(4-Methoxyphenyl)-3-(pyridin-3-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3gf**)*. Method B. Yield: 83%, 610 mg. Colorless solid, mp 161–162 °C (EtOH). IR (KBr) υ_{max}: 1674, 1605, 1585,

1504, 1462, 1416, 1323, 1226, 1173, 1103, 1026, 1011, 818, 756, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.71 (s, 3H), 6.41 (s, 1H), 6.80 (d, J = 8.7 Hz, 2H), 7.28–7.45 (m, 6H), 7.67–7.70 (m, 1H), 7.79–7.84 (m, 2H), 8.37 (dt, J = 8.0, 1.8 Hz, 1H), 8.68 (d, J = 4.6 Hz, 1H), 9.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.3 (CH), 56.4 (CH), 114.2 (C), 114.3 (2CH), 116.5 (CH), 123.17 (CH), 123.23 (CH), 125.0 (CH), 127.2 (CH), 128.2 (C), 128.7 (CH), 129.1 (2CH), 129.6 (CH), 130.2 (C), 131.7 (C), 135.2 (CH), 135.7 (C), 146.6 (C), 149.0 (CH), 149.6 (C), 151.7 (CH), 159.0 (C). Anal. Calcd (%) for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found (%): C, 78.61; H, 4.90; N, 7.52.

*1-(2-Methoxyphenyl)-3-phenyl-1H-naphtho[1,2-e][1,3]oxazine (**3ha**).* Method B. Yield: 78%, 570 mg. Colorless solid, mp 132–134 °C (EtOH). IR (KBr) υ_{max}: 1667, 1582, 1489, 1465, 1439, 1400, 1327, 1227, 1180, 1096, 1049, 1015, 837, 814, 748, 725 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.03 (s, 3H), 6.79 (t, J = 7.6 Hz, 1H), 6.95–6.97 (m, 2H), 7.11 (dd, J = 7.6, J = 1.4 Hz, 1H), 7.16–7.20 (m, 1H), 7.35–7.51 (m, 6H), 7.79–7.83 (m, 3H), 8.15–8.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 50.5 (CH_3), 56.1 (CH), 111.3 (CH), 114.8 (C), 116.5 (CH), 121.3 (CH), 123.3 (CH), 124.8 (CH), 127.1 (CH), 127.8 (2CH), 128.3 (2CH), 128.6 (CH), 128.8 (CH), 129.2 (CH), 129.9 (CH), 130.3 (C), 131.2 (CH), 131.5 (C), 132.2 (2C), 147.0 (C), 152.1 (C), 156.4 (C). Anal. Calcd (%) for $C_{25}H_{19}NO_2$: C, 82.17; H, 5.24; N, 3.83. Found (%): C, 82.20; H, 5.17; N, 3.92.

*3-(Furan-2-yl)-1-(2-methoxyphenyl)-1H-naphtho[1,2-e][1,3]oxazine (**3hd**).* Method B. Yield: 65%, 460 mg. Colorless solid, mp. 163–165 °C (*i*-PrOH). IR (KBr) υ_{max}: 1682, 1624, 1597, 1585, 1477, 1462, 1396, 1327, 1258, 1231, 1169, 1115, 1011, 949, 856, 814, 779, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.99 (s, 3H), 6.49 (dd, J = 3.4, J = 1.8 Hz, 1H), 6.77–6.81 (m, 1H), 6.90 (s, 1H), 6.92 (d, J = 7.8 Hz, 1H), 7.08–7.18 (m, 3H), 7.31 (d, J = 8.9 Hz, 1H), 7.34–7.42 (m, 2H), 7.52 (d, J = 0.9 Hz, 1H), 7.76–7.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 50.1 (CH_3), 55.9 (CH), 111.1 (CH), 111.5 (CH), 113.4 (C), 115.0 (C), 116.4 (CH), 121.2 (CH), 123.3 (CH), 124.8 (CH), 127.1 (CH), 128.5 (CH), 128.9 (CH), 129.1 (CH), 129.9 (CH), 130.3 (C), 131.5 (C), 131.9 (C), 145.0 (CH), 145.4 (C), 146.2 (C), 146.6 (C), 156.3 (C). Anal. Calcd (%) for $C_{23}H_{17}NO_3$: C, 77.73; H, 4.82; N, 3.94. Found (%):C, 77.66; H, 4.80; N, 3.83.

*1-(2-Methoxyphenyl)-3-(p-tolyl)-1H-naphtho[1,2-e][1,3]oxazine (**3hh**).* Method B. Yield: 80%, 607 mg. Colorless solid, mp 154–155 °C (EtOH). IR (KBr) υ_{max}: 1634, 1288, 1226, 1091, 1014, 810, 748, 721 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 4.03 (s, 3H), 6.78 (t, J = 7.5 Hz, 1H), 6.94–6.97 (m, 2H), 7.10 (dd, J = 7.6, J = 1.1 Hz, 1H), 7.15–7.19 (m, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.35–7.43 (m, 3H), 7.78–7.83 (m, 3H), 8.05 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6 (CH_3), 50.3 (CH_3), 56.1 (CH), 111.2 (CH), 114.9 (C), 116.6 (CH), 121.3

(CH), 123.2 (CH), 124.7 (CH), 127.1 (CH), 127.7 (2CH), 128.5 (CH), 128.7 (CH), 128.9 (2CH), 129.0 (CH), 129.7 (C), 129.8 (CH), 130.4 (C), 131.4 (C), 132.5 (C), 141.3 (C), 147.1 (C), 151.9 (C), 156.3 (C). Anal. Calcd (%) for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found (%): C, 82.20; H, 5.52; N, 3.62.

3-(4-Bromophenyl)-1-(3,4-dimethoxyphenyl)-1H-naphtho[1,2-e][1,3]oxazine ***(3ib)***. Method B. Yield: 85%, 805 mg. Colorless solid, mp 156–157 °C (EtOH). IR (KBr) υ_{max}: 1669, 1589, 1512, 1485, 1464, 1450, 1439, 1418, 1396, 1356, 1329, 1275, 1252, 1223, 1175, 1152, 1138, 1096, 1069, 1059, 1030, 1007, 822, 810, 800, 748, 731, 719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.79 (s, 3H), 3.82 (s, 3H), 6.38 (s, 1H), 6.72 (d, J = 8.2 Hz, 1H), 6.78 (dd, J = 8.2, J = 2.3 Hz, 1H), 6.99 (d, J = 2.3 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 7.38–7.45 (m, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.68–7.71 (m, 1H), 7.81–7.86 (m, 2H), 7.98 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.9 (CH_3), 56.0 (CH_3), 56.8 (CH), 111.25 (CH), 111.28 (CH), 114.0 (C), 116.5 (CH), 120.1 (CH), 123.3 (CH), 125.0 (CH), 125.9 (C), 127.2 (CH), 128.7 (CH), 129.3 (2CH), 129.6 (CH), 130.2 (C), 131.2 (C), 131.5 (2CH, C), 136.2 (C), 146.8 (C), 148.5 (C), 149.2 (C), 150.6 (C). Anal. Calcd (%) for $C_{26}H_{20}BrNO_3$: C, 65.83; H, 4.25; N, 2.95. Found (%): C, 65.94; H, 4.12; N, 3.01.

1-(Benzo[d][1,3]dioxol-5-yl)-3-(4-bromophenyl)-1H-naphtho[1,2-e][1,3]oxazine ***(3jb)***. Method B. Yield: 67%, 615 mg. Colorless solid, mp 174–176 °C (EtOH). IR (KBr) υ_{max}: 1670, 1591, 1516, 1501, 1487, 1443, 1395, 1319, 1254, 1223, 1173, 1098, 1040, 1009, 935, 833, 810, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.86 (d, J = 1.4 Hz, 1H), 5.88 (d, J = 1.4 Hz, 1H), 6.34 (s, 1H), 6.71 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 1.8 Hz, 1H), 6.87 (dd, J = 8.2, J = 1.8 Hz, 1H), 7.34 (d, J = 9.2 Hz, 1H), 7.38–7.46 (m, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.70 (dd, J = 7.8, J = 1.4 Hz, 1H), 7.81–7.85 (m, 2H), 7.99 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.8, 101.2, 108.5, 114.0, 116.6, 121.3, 123.2, 125.0, 125.9, 127.2, 128.7, 129.3, 129.6, 130.1, 131.1, 131.5, 131.6, 137.7, 146.7, 147.0, 148.1, 150.6. Anal. Calcd (%) for $C_{25}H_{16}BrNO_3$: C, 65.52; H, 3.52; N, 3.06. Found (%): C, 65.64; H, 3.42; N, 3.12.

3-Phenyl-1-(3,4,5-trimethoxyphenyl)-1H-naphtho[1,2-e][1,3]oxazine ***(3ka)***. Method B. Yield: 85%, 857 mg. Colorless solid, mp 231–232 °C (DMF). IR (KBr) υ_{max}: 1624, 1277, 1230, 1099, 1018, 817, 736, 709 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.75 (s, 6H), 3.79 (s, 3H), 6.39 (s, 1H), 6.62 (s, 2H), 7.38 (d, J = 9.0 Hz, 1H), 7.41–7.51 (m, 5H), 7.73 (d, J = 8.0 Hz, 1H), 7.82–7.87 (m, 2H), 8.13–8.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.2 ($2CH_3$), 57.4 (CH_3), 60.8 (CH), 105.1 (2CH), 113.9 (C), 116.6 (CH), 123.2 (CH), 124.9 (CH), 127.2 (CH), 127.7 (2CH), 128.4 (2CH), 128.7 (CH), 129.6 (CH), 130.3 (C), 131.3 (CH), 131.5 (C), 132.1 (C), 137.4 (C),

139.4 (C), 146.9 (C), 151.6 (C), 153.5 (2C). Anal. Calcd (%) for $C_{27}H_{23}NO_4$: C, 76.22; H, 5.45; N, 3.29. Found (%): C, 76.16; H, 5.40; N, 3.37.

*3-Phenyl-1-(thiophen-2-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3la**)*. Method C. Yield: 83%, 567 mg. Light-pink solid, mp 135–136 °C (DMF–EtOH). IR (KBr) υ_{max}: 1667, 1514, 1448, 1435, 1399, 1358, 1323, 1227, 1179, 1098, 1053, 822, 781, 698, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.77 (s, 1H), 6.83–6.86 (m, 2H), 7.17 (dd, J = 4.8, J = 1.6 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.43–7.54 (m, 5H), 7.84–7.87 (m, 3H), 8.18–8.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 51.7 (CH), 114.3 (C), 116.7 (CH), 123.0 (CH), 125.1 (CH), 125.1 (CH), 125.3 (CH), 126.7 (CH), 127.4 (CH), 128.0 (2CH), 128.4 (2CH), 128.8 (CH), 129.8 (CH), 130.2 (C), 131.6 (CH), 131.6 (2C), 146.7 (C), 147.4 (C), 153.2 (C). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 51.0 (CH), 115.0 (C), 117.1 (CH), 123.5 (CH), 125.61 (CH), 125.65 (CH), 126.3 (CH), 127.2 (CH), 127.8 (3CH), 129.2 (3CH), 129.9 (C), 130.3 (CH), 131.7 (2C), 132.3 (CH), 146.4 (C), 148.2 (C), 152.2 (C). Anal. Calcd (%) for $C_{22}H_{15}NOS$: C, 77.39; H, 4.43; N, 4.10; S, 9.39. Found (%): C, 77.25; H, 4.50; N, 4.01; S, 9.47.

*1,3-Di(thiophen-2-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3le**)*. Method C. Yield: 60%, 417 mg. Light-pink solid, mp 173–174 °C (DMF–MeOH). IR (KBr) υ_{max}: 1654, 1427, 1219, 1091, 813, 705 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.69 (s, 1H), 6.84 (d, J = 3.4 Hz, 2H), 7.11 (dd, J = 5.0, J = 3.7 Hz, 1H), 7.15–7.17 (m, 1H), 7.33 (d, J = 9.2 Hz, 1H), 7.42–7.53 (m, 3H), 7.80 (dd, J = 3.6, J = 1.2 Hz, 1H), 7.83–7.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 51.7 (CH), 114.5 (C), 116.6 (CH), 122.9 (CH), 125.0 (CH), 125.1 (CH), 125.2 (CH), 126.6 (CH), 127.4 (CH), 127.6 (CH), 128.8 (CH), 129.6 (CH), 129.7 (CH), 129.9 (CH), 130.2 (C), 131.5 (C), 136.0 (C), 146.6 (C), 147.4 (C), 149.8 (C). Anal. Calcd (%) for $C_{20}H_{13}NOS_2$: C, 69.14; H, 3.77; N, 4.03; S, 18.45. Found (%):C, 69.22; H, 3.80; N, 3.95; S, 18.34.

*3-Phenyl-1-(pyridin-4-yl)-1H-naphtho[1,2-e][1,3]oxazine (**3ma**)*. Method B. Yield: 69%, 465 mg. Colorless solid, mp 163–165 °C (EtOH). IR (KBr) υ_{max}: 1667, 1591, 1514, 1447, 1412, 1352, 1321, 1275, 1225, 1175, 1098, 1057, 1018, 993, 840, 820, 775, 746, 692, 665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.46 (s, 1H), 7.28 (dd, J = 4.6, 1.6 Hz, 2H), 7.39 (d, J = 9.0 Hz, 1H), 7.41–7.53 (m, 5H), 7.60–7.63 (m, 1H), 7.83–7.90 (m, 2H), 8.11–8.14 (m, 2H), 8.51 (dd, J = 4.6, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.1 (CH), 112.5 (C), 116.7 (CH), 122.8 (CH), 122.9 (2CH), 125.2 (CH), 127.5 (CH), 127.8 (2CH), 128.4 (2CH), 128.9 (CH), 130.0 (C), 130.1 (CH), 131.5 (CH), 131.7 (C), 147.1 (C), 150.4 (2CH), 151.6 (C), 152.4 (C). Anal. Calcd (%) for $C_{23}H_{16}N_2O$: C, 82.12; H, 4.79; N, 8.33. Found (%):C, 82.24; H, 4.78; N, 8.31.

*2-(4-Bromophenyl)-4H-[1,3]oxazino[5,6-h]quinoline (**3nb**).* Method C. Yield: 37%, 250 mg. Colorless solid, mp 177–178 °C (EtOH–DMF). IR (KBr) υ_{max}: 1674, 1634, 1595, 1505, 1487, 1476, 1396, 1379, 1348, 1317, 1281, 1248, 1175, 1117, 1099, 1067, 1013, 829, 792, 721, 702, 665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.92 (s, 2H), 7.18 (d, J = 8.3 Hz, 1H), 7.42 (dd, J = 8.2, J = 4.1 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 8.2 Hz, 2H), 8.10–8.14 (m, 3H), 8.98 (d, J = 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 46.1 (CH_2), 117.8 (C), 121.6 (CH), 123.9 (CH), 124.3 (CH), 125.9 (C), 128.5 (C), 129.4 (2CH), 131.2 (C), 131.6 (2CH), 136.1 (CH), 138.1 (C), 144.4 (C), 150.7 (CH), 152.6 (C). Anal. Calcd (%) for $C_{17}H_{11}BrN_2O$: C, 60.20; H, 3.27; N, 8.26. Found (%): C, 60.26; H, 3.31; N, 8.18.

*2,4-Diphenyl-4H-[1,3]oxazino[5,6-h]quinoline (**3oa**).* Method C. Yield: 86%, 580 mg. Colorless solid, mp 179–180 °C (EtOH). IR (KBr) υ_{max}: 1667, 1630, 1595, 1501, 1466, 1450, 1371, 1314, 1273, 1238, 1175, 1115, 1055, 1028, 827, 754, 731, 700, 685, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.03 (s, 1H), 7.14 (d, J = 8.5 Hz, 1H), 7.25–7.29 (m, 1H), 7.32–7.36 (m, 2H), 7.40–7.52 (m, 7H), 8.09 (dd, J = 8.2, J = 1.6 Hz, 1H), 8.34–8.37 (m, 2H), 9.04 (dd, J = 4.3, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 59.6 (CH), 121.1 (C), 121.8 (CH), 123.7 (CH), 125.3 (CH), 127.8 (CH), 128.0 (2CH), 128.2 (2CH), 128.4 (2CH), 128.5 (C), 128.9 (2CH), 131.3 (CH), 132.2 (C), 136.0 (CH), 138.4 (C), 143.7 (C), 144.0 (C), 150.7 (CH), 152.4 (C). Anal. Calcd (%) for $C_{23}H_{16}N_2O$: C, 82.12; H, 4.79; N, 8.33. Found (%): C, 82.24; H, 4.77; N, 8.25.

*2-(4-Bromophenyl)-4-phenyl-4H-[1,3]oxazino[5,6-h]quinoline (**3ob**).* Method B. Yield: 76%, 630 mg. Colorless solid, mp >300 °C (EtOH). IR (KBr) υ_{max}: 1667, 1632, 1593, 1373, 1323, 1246, 1173, 1119, 1103, 1065, 1011, 829, 760, 733, 706, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.01 (s, 1H), 7.13 (d, J = 8.5 Hz, 1H), 7.27–7.38 (m, 5H), 7.48 (dd, J = 8.2, J = 4.1 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 8.5 Hz, 2H), 8.12 (dd, J = 8.2, J = 1.6 Hz, 1H), 8.20 (d, J = 8.5 Hz, 2H), 9.04 (dd, J = 4.1, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 59.6 (CH), 120.9 (C), 121.9 (CH), 123.9 (CH), 125.3 (CH), 126.1 (C), 127.9 (CH), 128.0 (2CH), 128.5 (C), 129.0 (2CH), 129.7 (2CH), 131.1 (C), 131.6 (2CH), 136.0 (CH), 138.3 (C), 143.5 (C), 143.8 (C), 150.8 (CH), 151.6 (C). Anal. Calcd (%) for $C_{23}H_{15}BrN_2O$: C, 66.52; H, 3.64; N, 6.75. Found (%): C, 66.59; H, 3.58; N, 6.80.

*3-Phenyl-7,9,10,11-tetrahydro-[1,3]oxazino[5,6-e]pyrido[3,4-b]indol-8(1H)-one (**3pa**).* Method B. Yield: 56%, 355 mg. Colorless solid, mp 277–278 °C (EtOH). IR (KBr) υ_{max}: 3400–3100, 1676, 1661, 1535, 1503, 1433, 1337, 1306, 1292, 1219, 1169, 1128, 1098, 1065, 1024, 802, 773, 689, 671 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 3.07 (t, J = 6.9 Hz, 2H), 3.47 (td, J = 6.9, J = 2.3 Hz, 2H), 5.10 (s, 2H), 6.98 (d, J = 8.7 Hz, 1H), 7.24 (d, J = 8.7 Hz, 1H), 7.45–7.54

(m, 3H), 7.57 (s, 1H), 8.01 (d, J = 8.7 Hz, 2H), 11.68 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 22.3 (CH_2), 41.7 (CH_2), 43.5 (CH_2), 110.8 (C), 112.7 (CH), 113.9 (CH), 118.4 (C), 121.5 (C), 127.4 (2CH), 129.0 (2CH), 129.1 (C), 131.6 (CH), 132.6 (C), 135.0 (C), 142.4 (C), 151.9 (C), 162.0 (C). Anal. Calcd (%) for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found (%): C, 71.85; H, 4.82; N, 13.18.

*Ethyl 7,8-dimethyl-3-phenyl-1,7-dihydro-[1,3]oxazino[5,6-e]indole-9-carboxylate (**3qa**).* Method A. Yield: 71%, 495 mg. Colorless solid, mp 208–209 °C (EtOH–DMF). IR (KBr) υ_{max}: 1686, 1674, 1489, 1435, 1412, 1379, 1360, 1323, 1283, 1225, 1204, 1169, 1152, 1109, 1084, 1069, 1028, 924, 800, 775, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (t, J = 7.3 Hz, 3H), 2.64 (s, 3H), 3.63 (s, 3H), 4.39 (q, J = 7.3 Hz, 2H), 5.20 (s, 2H), 6.93 (d, J = 8.7 Hz, 1H), 7.12 (d, J = 8.7 Hz, 1H), 7.40–7.48 (m, 3H), 8.08 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.3 (CH_3), 14.7 (CH_3), 29.9 (CH_3), 46.0 (CH_2), 60.1 (CH_2), 105.7 (C), 108.6 (CH), 111.0 (C), 111.4 (CH), 122.2 (C), 127.3 (2CH), 128.2 (2CH), 130.8 (CH), 132.7 (C), 134.2 (C), 144.8 (2C), 152.5 (C), 165.8 (C). Anal. Calcd (%) for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found (%): C, 72.43; H, 5.84; N, 7.96.

*2-(4-Bromophenyl)-6,7-dimethyl-4H-benzo[e][1,3]oxazine (**5ab**).* Method B (from Mannich base). Yield: 57%, 360 mg. Colorless solid, mp 127–128 °C (EtOH). IR (KBr) υ_{max}: 1667, 1589, 1501, 1458, 1396, 1339, 1269, 1204, 1173, 1119, 1099, 1072, 1003, 868, 837 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.20 (s, 3H), 2.23 (s, 3H), 4.69 (s, 2H), 6.79 (s, 2H), 7.54 (d, J = 8.7 Hz, 2H), 7.90 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.2 (CH_3), 19.7 (CH_3), 45.2 (CH_2), 116.0 (C), 116.4 (CH), 125.6 (C), 126.8 (CH), 128.9 (2CH), 131.5 (2CH), 131.6 (C), 133.2 (C), 136.7 (C), 147.2 (C), 152.2 (C). Anal. Calcd (%) for $C_{16}H_{14}BrNO$: C, 60.78; H, 4.46; N, 4.43. Found (%): C, 60.75; H, 4.52; N, 4.38.

Method C (from quaternary ammonium salt **6**). Yield: 37%, 235 mg. Along with **5ab**, amide **7** was isolated.

*4-Bromo-N-(2-hydroxy-4,5-dimethylbenzyl)benzamide (**7**).* Yield: 32%, 215 mg. Colorless solid, mp 207–208 °C ($CHCl_3$). IR (KBr) υ_{max}: 3318, 3100–2600, 1628, 1589, 1560, 1501, 1483, 1439, 1389, 1317, 1296, 1238, 1072, 1011, 835, 760 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.03 (s, 3H), 2.07 (s, 3H), 4.31 (d, J = 5.5 Hz, 2H), 6.56 (s, 1H), 6.84 (s, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 8.91 (t, J = 5.5 Hz, 1H), 9.16 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 19.0 (CH_3), 19.7 (CH_3), 38.5 (CH_2), 117.1 (CH), 122.5 (C), 125.5 (C), 126.4 (C), 130.0 (2CH), 130.2 (CH), 131.9 (2CH), 133.9 (C), 136.0 (C), 153.2 (C), 166.1 (C).

Anal. Calcd (%) for $C_{16}H_{16}BrNO_2$: C, 57.50; H, 4.83; N, 4.19. Found (%): C, 57.58; H, 4.90; N, 4.15.

*6,7-Dimethyl-2-[4-(trifluoromethyl)phenyl]-4H-benzo[e][1,3]oxazine (**5ac**).* Method B. Yield: 56%, 342 mg. Colorless solid, mp 145–146 °C (EtOH). IR (KBr) υ_{max}: 1667, 1620, 1582, 1501, 1458, 1408, 1327, 1269, 1246, 1169, 1123, 1099, 1069, 1018, 853, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 2.24 (s, 3H), 4.74 (s, 2H), 6.80 (s, 1H), 6.82 (s, 1H), 7.67 (d, J = 7.8 Hz, 2H), 8.15 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.2 (CH_3), 19.7 (CH_3), 45.3 (CH_2), 115.8 (C), 116.4 (CH), 124.0 (q, $^1J_{C–F}$ =271.0 Hz, C), 125.2 (q, $^3J_{C–F}$ =3.8 Hz, 2CH), 126.8 (CH), 127.7 (2CH), 132.5 (q, $^2J_{C–F}$ =31.5 Hz, C), 133.4 (C), 135.9 (C), 136.8 (C), 147.1 (C), 151.7 (C). Anal. Calcd (%) for $C_{17}H_{14}F_3NO$: C, 66.88; H, 4.62; N, 4.59. Found (%): C, 66.98; H, 4.51; N, 4.65.

*6-Methoxy-2-phenyl-4H-benzo[e][1,3]oxazine (**5ba**).* After completion of the reaction, the solvent was distilled off in vacuo, the residue was recrystallized from aqueous methanol and then again from methanol. Yield: 44%, 280 mg. Colorless solid, mp 56–57 °C (MeOH). IR (KBr) υ_{max}: 1678, 1612, 1501, 1462, 1447, 1427, 1354, 1319, 1285, 1254, 1319, 1285, 1254, 1204, 1088, 1065, 1030, 1003, 930, 841, 826, 795, 779, 694, 671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.78 (s, 3H), 4.77 (s, 2H), 6.57 (d, J = 3.0 Hz, 1H), 6.76 (dd, J = 8.7, J = 3.0 Hz, 1H), 6.95 (d, J = 8.7 Hz, 1H), 7.40–7.49 (m, 3H), 8.03–8.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 45.8 (CH_2), 55.7 (CH_3), 110.5 (CH), 113.7 (CH), 116.5 (CH), 120.0 (C), 127.4 (2CH), 128.3 (2CH), 131.0 (CH), 132.5 (C), 143.4 (C), 153.1 (C), 156.6 (C). MS (EI, 70 eV): *m/z* (%)=239 (M^+, 20), 136 (M^+–PhCN, 100), 108 (M^+–PhCN–CO, 43), 103 (6), 78 (21), 65 (42). Anal. Calcd (%) for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found (%): C, 75.42; H, 5.39; N, 5.93.

*6-(Adamantan-1-yl)-2-phenyl-4H-benzo[e][1,3]oxazine (**5ca**).* Method A. Yield: 76%, 522 mg. Colorless solid, mp 135–136 °C (DMF). IR (KBr) υ_{max}: 2899, 2845, 1674, 1503, 1449, 1341, 1250, 1217, 1175, 1155, 1125, 1090, 1063, 806, 773, 691, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.72–1.81 (m, 6H), 1.86–1.90 (m, 6H), 2.10 (br. s, 3H), 4.79 (s, 2H), 6.96 (d, J = 8.5 Hz, 1H), 7.03 (d, J = 2.1 Hz, 1H), 7.22 (dd, J = 8.5, J = 2.1 Hz, 1H), 7.39–7.49 (m, 3H), 8.03–8.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.0 (3CH), 36.0 (C), 36.8 ($3CH_2$), 43.4 ($3CH_2$), 45.8 (CH_2), 115.1 (CH), 118.6 (C), 122.5 (CH), 124.6 (CH), 127.4 (2CH), 128.3 (2CH), 131.0 (CH), 132.5 (C), 147.3 (C), 148.3 (C), 153.0 (C). Anal. Calcd (%) for $C_{24}H_{25}NO$: C, 83.93; H, 7.34; N, 4.08. Found (%): C, 84.05; H, 7.31; N, 3.99.

*1-[2-Phenyl-4H-benzo[e][1,3]oxazin-6-yl]ethan-1-one (**5da**).* Method B. Yield: 72%, 360 mg. Colorless solid, mp 135–137 °C (EtOH). IR (KBr) υ_{max}: 1674, 1587, 1495, 1423, 1283,

1250, 1229, 1169, 1117, 1076, 1057, 1030, 961, 887, 839, 777, 692, 671, 662 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.57 (s, 3H), 4.82 (s, 2H), 7.06 (d, J = 8.2 Hz, 1H), 7.41–7.51 (m, 3H), 7.69 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.5 (CH_3), 45.3 (CH_2), 115.8 (CH), 119.5 (C), 126.9 (CH), 127.4 (2CH), 128.4 (2CH), 129.1 (CH), 131.4 (CH), 131.7 (C), 134.0 (C), 152.1 (C), 153.2 (C), 196.7 (C). Anal. Calcd (%) for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found (%): C, 76.59; H, 5.16; N, 5.39.

*1-[2-(4-Bromophenyl)-4H-benzo[e][1,3]oxazin-6-yl]ethan-1-one (**5db**).* Method B. Yield: 81%, 535 mg. Colorless solid, mp 187–188 °C (EtOH). IR (KBr) υ_{max}: 1674, 1612, 1589, 1501, 1423, 1396, 1362, 1281, 1250, 1231, 1173, 1130, 1115, 1084, 1015, 999, 826, 721, 664 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.57 (s, 3H), 4.80 (s, 2H), 7.05 (d, J = 8.5 Hz, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.69 (s, 1H), 7.84 (dd, J = 8.5, J = 1.4 Hz, 1H), 7.91 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.5 (CH_3), 45.2 (CH_2), 115.8 (CH), 119.3 (C), 126.1 (C), 126.9 (CH), 129.0 (2CH), 129.1 (CH), 130.6 (C), 131.7 (2CH), 134.2 (C), 151.4 (C), 152.9 (C), 196.6 (C). Anal. Calcd (%) for $C_{16}H_{12}BrNO_2$: C, 58.20; H, 3.66; N, 4.24. Found (%): C, 58.22; H, 3.49; N, 4.16.

*2-(4-Bromophenyl)-6,8-di-tert-butyl-4H-benzo[e][1,3]oxazine (**5eb**).* Method B. Yield: 80%, 640 mg. Colorless solid, mp 185–187 °C (*i*-PrOH). IR (KBr) υ_{max}: 2967, 2909, 2866, 1678, 1589, 1481, 1393, 1362, 1346, 1277, 1223, 1200, 1169, 1123, 1088, 1069, 999, 837, 721, 664 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.31 (s, 9H), 1.48 (s, 9H), 4.77 (s, 2H), 6.91 (d, J = 2.3 Hz, 1H), 7.24 (d, J = 2.3 Hz, 1H), 7.58 (d, J = 8.7 Hz, 2H), 7.96 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.2 ($3CH_3$), 31.6 ($3CH_3$), 34.7 (C), 34.9 (C), 46.2 (CH_2), 118.4 (C), 120.8 (CH), 122.7 (CH), 125.5 (C), 129.0 (2CH), 131.6 (2CH), 131.7 (C), 136.0 (C), 145.8 (C), 147.1 (C), 152.4 (C). MS (EI, 70 eV): *m/z* (%)=399 (M^+, 7), 218 (M^+–BrC_6H_4CN, 35), 203 (M^+–BrC_6H_4CN–CH_3, 100), 161 (M^+–BrC_6H_4CN–C_4H_9, 36), 57 (C_4H_9, 8). Anal. Calcd (%) for $C_{22}H_{26}BrNO$: C, 66.00; H, 6.55; N, 3.50. Found (%): C, 65.89; H, 6.64; N, 3.40.

*6,8-Di-tert-butyl-2-[4-(trifluoromethyl)phenyl]-4H-benzo[e][1,3]oxazine (**5ec**).* Method B. Yield: 60%, 467 mg. Colorless solid, mp 90–91 °C (EtOH). IR (KBr) υ_{max}: 2957, 2901, 2847, 1672, 1601, 1479, 1447, 1408, 1364, 1321, 1277, 1229, 1219, 1200, 1163, 1123, 1088, 1064, 1016, 1005, 851, 671 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.32 (s, 9H), 1.50 (s, 9H), 4.81 (s, 2H), 6.92 (d, J = 2.5 Hz, 1H), 7.26 (d, J = 2.5 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 8.22 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.2 ($3CH_3$), 31.5 ($3CH_3$), 34.7 (C), 34.9 (C), 46.3 (CH_2), 118.3 (C), 120.9 (CH), 122.9 (CH), 124.0 (q, $^1J_{C–F}$ = 270.8 Hz, C), 125.4 (q, $^3J_{C–F}$ = 3.8 Hz, 2CH), 127.7 (3CH), 132.6 (q, $^2J_{C–F}$ = 32.4 Hz, C), 136.0 (C), 145.7 (C), 147.3 (C), 152.1

(C). Anal. Calcd (%) for $C_{23}H_{26}F_3NO$: C, 70.93; H, 6.73; N, 3.60. Found (%):C, 71.02; H, 6.70; N, 3.54.

*8-(Adamantan-1-yl)-6-(tert-butyl)-2-phenyl-4H-benzo[e][1,3]oxazine (**5fa**).* Method B. Yield: 86%, 823 mg. Colorless solid, mp 164–166 °C (*i*-PrOH). IR (KBr) υ_{max}: 2959, 2909, 2847, 1678, 1605, 1474, 1450, 1346, 1319, 1277, 1250, 1188, 1123, 1107, 1088, 1065, 868, 772, 687 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.32 (s, 9H), 1.83–1.91 (m, 6H), 2.16 (br. s, 3H), 2.20 (br. s, 6H), 4.79 (s, 2H), 6.91 (d, J = 2.3 Hz, 1H), 7.21 (d, J = 2.3 Hz, 1H), 7.44–7.52 (m, 3H), 8.17–8.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.1 (3CH), 31.6 ($3CH_3$), 34.7 (C), 37.1 ($3CH_2$), 37.2 (C), 41.0 ($3CH_2$), 46.3 (CH_2), 118.5 (C), 120.7 (CH), 122.7 (CH), 127.5 (2CH), 128.3 (2CH), 130.9 (CH), 132.9 (C), 136.4 (C), 146.2 (C), 147.0 (C), 153.2 (C). Anal. Calcd (%) for $C_{28}H_{33}NO$: C, 84.17; H, 8.32; N, 3.51. Found (%): C, 84.25; H, 8.24; N, 3.61.

*8-(Adamantan-1-yl)-6-methyl-2-phenyl-4H-benzo[e][1,3]oxazine (**5ga**).* Method B. Yield: 78%, 680 mg. Colorless solid, mp 135–136 °C (DMF–MeOH). IR (KBr) υ_{max}: 2905, 2874, 2847, 1678, 1607, 1470, 1449, 1346, 1277, 1236, 1200, 1150, 1105, 1092, 1063, 1013, 851, 773, 685, 673 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.81–1.89 (m, 6H), 2.14 (br. s, 3H), 2.17–2.20 (m, 6H), 2.30 (s, 3H), 4.75 (s, 2H), 6.71 (d, J = 1.4 Hz, 1H), 6.96 (d, J = 1.4 Hz, 1H), 7.43–7.51 (m, 3H), 8.15–8.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.2 (CH_3), 29.1 (3CH), 36.8 (C), 37.1 ($3CH_2$), 40.9 ($3CH_2$), 46.0 (CH_2), 119.1 (C), 124.3 (CH), 126.4 (CH), 127.5 (2CH), 128.3 (2CH), 130.9 (CH), 132.8 (C), 133.7 (C), 136.9 (C), 146.3 (C), 153.3 (C). Anal. Calcd (%) for $C_{25}H_{27}NO$: C, 83.99; H, 7.61; N, 3.92. Found (%): C, 84.09; H, 7.53; N, 3.80.

*6-Chloro-2-phenyl-4H-benzo[e][1,3]oxazine (**5ha**).* After completion of the reaction, the solvent was distilled off in vacuo, the residue was dissolved in methanol, water was added until the solution became cloudy and allowed to stand for 2 days at room temperature and then for 12 hours at –20 °C. The precipitated product was filtered off and recrystallized from methanol. Yield: 22%, 107 mg. Colorless solid, mp 80–82 °C (MeOH). IR (KBr) υ_{max}: 1678, 1585, 1489, 1447, 1420, 1342, 1277, 1238, 1184, 1119, 1088, 1061, 868, 810, 775, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.75 (s, 2H), 6.95 (d, J = 8.7 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 7.18 (dd, J = 8.7, J = 2.3 Hz, 1H), 7.41–7.51 (m, 3H), 8.03 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 45.2 (CH), 117.0 (CH), 120.9 (C), 126.0 (CH), 127.4 (2CH), 128.2 (CH), 128.4 (2CH), 129.6 (C), 131.3 (CH), 131.9 (C), 148.1 (C), 152.6 (C). Anal. Calcd (%) for $C_{14}H_{10}ClNO$: C, 69.00; H, 4.14; N, 5.75. Found (%): C, 68.89; H, 4.10; N, 5.71.

*2-(4-Bromophenyl)-4-phenyl-4H-benzo[e][1,3]oxazine (**5ib**).* Method B. Yield: 81%, 590 mg. Colorless solid, mp 133–135 °C (EtOH). IR (KBr) υ_{max}: 1667, 1585, 1489, 1454, 1396,

1323, 1300, 1242, 1219, 1180, 1111, 1088, 1011, 845, 752, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.84 (s, 1H), 6.95 (d, J = 7.6 Hz, 1H), 7.06 (dd, J = 7.4, J = 1.2 Hz, 1H), 7.10 (dd, J = 8.2, J = 0.9 Hz, 1H), 7.23–7.30 (m, 2H), 7.32–7.38 (m, 4H), 7.56 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 58.9 (CH), 115.7 (CH), 122.6 (C), 125.2 (CH), 125.9 (C), 127.5 (CH), 127.6 (CH), 127.8 (2CH), 128.4 (CH), 128.8 (2CH), 129.3 (2CH), 131.2 (C), 131.6 (2CH), 144.0 (C), 148.5 (C), 151.4 (C). Anal. Calcd (%) for $C_{20}H_{14}BrNO$: C, 65.95; H, 3.87; N, 3.85. Found (%): C, 66.08; H, 3.78; N, 3.93.

*2,4,4-Triphenyl-4H-benzo[e][1,3]oxazin (**5ja**)*. Method B. Yield: 80%, 578 mg. Colorless solid, mp 192–193 °C (DMF–MeOH). IR (KBr) υ_{max}: 1659, 1584, 1491, 1483, 1445, 1315, 1296, 1277, 1227, 1215, 1179, 1113, 1096, 1067, 1024, 1005, 928, 781, 756, 702, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.92 (dd, J = 7.8, J = 1.4 Hz, 1H), 7.09–7.13 (m, 1H), 7.19–7.34 (m, 12H), 7.42–7.52 (m, 3H), 8.21–8.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 65.4 (C), 115.8 (CH), 124.5 (CH), 125.7 (C), 126.9 (2CH), 127.9 (5CH), 128.3 (2CH), 128.5 (CH), 128.6 (4CH), 129.4 (CH), 131.2 (CH), 132.3 (C), 147.4 (2C), 149.1 (C), 151.9 (C). Anal. Calcd (%) for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88. Found (%): C, 86.31; H, 5.37; N, 3.77.

*2'-Phenylspiro[adamantane-2,4'-benzo[e][1,3]oxazine] (**5ka**)*. Method A. Yield: 84%, 553 mg. Colorless solid, mp 138–139 °C (DMF). IR (KBr) υ_{max}: 2893, 2847, 1653, 1580, 1493, 1479, 1470, 1449, 1315, 1285, 1267, 1206, 1175, 1101, 1057, 1024, 881, 779, 746, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.59 (d, J = 12.8 Hz, 2H), 1.81 (br. s, 4H), 1.96 (br. s, 2H), 2.17–2.23 (m, 4H), 2.82 (d, J = 12.4 Hz, 2H), 7.15–7.21 (m, 2H), 7.25–7.29 (m, 1H), 7.42–7.50 (m, 3H), 7.80 (dd, J = 7.8, 1.4 Hz, 1H), 8.15–8.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.4 (CH), 27.6 (CH), 33.9 ($2CH_2$), 34.9 ($2CH_2$), 37.4 (2CH), 38.9 (CH_2), 60.4 (C), 116.3 (CH), 123.9 (CH), 126.9 (CH), 127.0 (CH), 127.9 (2CH), 128.4 (2CH), 131.0 (CH, C), 132.3 (C), 151.4 (C), 152.3 (C). Anal. Calcd (%) for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25. Found (%): C, 83.80; H, 6.94; N, 4.13.

Three-component Synthesis of 1*H*-Naphtho[1,2-*e*][1,3]oxazines 3ah, 3ca, 3ra. A mixture of imino ether (7 mmol), 2-naphthol (7 mmol) and aromatic aldehyde (7 mmol) was heated at 130 °C for 6 h without a solvent in the presence of a catalytic amount of acetic acid (0.02 g, 0.35 mmol). The mixture was cooled, suspended in methanol (5 mL), the precipitate was filtered off and purified by recrystallization.

*1-Phenyl-3-(p-tolyl)-1H-naphtho[1,2-e][1,3]oxazine (**3ah**)*. Yield: 47%, 1.15 g. Colorless solid, mp 156–158 °C (EtOH). (lit.[12] mp 194–195 °C). IR (KBr) υ_{max}: 1667, 1626, 1599, 1516, 1493, 1454, 1398, 1356, 1327, 1223, 1194, 1179, 1098, 1072, 1057, 1018, 837, 816, 779, 762,

745, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 6.45 (s, 1H), 7.17–7.29 (m, 5H), 7.37–7.44 (m, 5H), 7.72–7.74 (m, 1H), 7.81–7.85 (m, 2H), 8.02 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6 (CH_3), 57.1 (CH), 114.3 (C), 116.7 (CH), 123.2 (CH), 124.8 (CH), 127.1 (CH), 127.5 (CH), 127.7 (2CH), 128.0 (2CH), 128.7 (CH), 128.8 (2CH), 129.0 (2CH), 129.4 (CH, C), 130.3 (C), 131.5 (C), 141.5 (C), 143.7 (C), 147.0 (C), 151.7 (C). Anal. Calcd (%) for $C_{25}H_{19}NO$: C, 85.93; H, 5.48; N, 4.01. Found (%): C, 85.88; H, 5.54; N, 3.93.

1,3-Diphenyl-1H-naphtho[1,2-e][1,3]oxazine ***(3ca)***. Yield: 61%, 1.43 g. Product was identical in spectral characteristics to a sample prepared previously.

1-(3-Nitrophenyl)-3-phenyl-1H-naphtho[1,2-e][1,3]oxazine ***(3ra)***. Yield: 24%, 0.64 g. Colorless solid, mp 172–173 °C (DMF). IR (KBr) υ_{max}: 1670, 1628, 1528, 1474, 1443, 1400, 1346, 1323, 1277, 1223, 1177, 1103, 1057, 1018, 829, 806, 779, 733, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.57 (s, 1H), 7.40–7.52 (m, 7H), 7.58–7.61 (m, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.84–7.87 (m, 1H), 7.90 (d, J = 8.9 Hz, 1H), 8.07 (dd, J = 8.0, J = 0.9 Hz, 1H), 8.14 (d, J = 7.1 Hz, 2H), 8.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.5 (CH), 112.5 (C), 116.8 (CH), 122.7 (2CH), 123.1 (CH), 125.2 (CH), 127.6 (CH), 127.8 (2CH), 128.5 (2CH), 129.0 (CH), 129.9 (C, CH), 130.3 (CH), 131.6 (CH), 131.6 (C), 131.7 (C), 134.1 (CH), 145.6 (C), 147.1 (C), 148.7 (C), 152.1 (C). Anal. Calcd (%) for $C_{24}H_{16}N_2O_3$: C, 75.78; H, 4.24; N, 7.36. Found (%): C, 75.71; H, 4.19; N, 7.30.

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Supporting Information

Copies of ^1H, ^{13}C, and ^{19}F NMR spectra for new synthesized compounds.

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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