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ORIGINAL PAPER

AgI nanoparticles as a remarkable catalyst in the synthesis of (amidoalkyl)naphthol and oxazine derivatives: an eco-friendly approach

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Abstract AgI nanoparticles were discovered to be an effectual heterogeneous nanocatalyst for the preparation of (amidoalkyl)naphthol and oxazine derivatives under solvent-free conditions. The advantages of the present approach are short reaction times, moderate temperature, premier yields, eco-friendly reaction conditions, simple purification and good reusability of the catalyst.

Keywords Nanoparticles · 2-Naphthol · Solvent-free conditions · Oxazine · Multicomponent reactions

Introduction

In recent years, oxazines have been considered because of their various ranges of biological properties such as antibiotic [1], antitumor agent [2], analgesic [3] and anticonvulsant [4]. In addition, benzo-1,3-oxazines are biologically active as anti-malarial [5], antianginal [6], antihypertensive [7] and potent antirheumatic agents [8]. Recently, some procedures have been reported for the preparation of naphtha-oxazine derivatives using various catalysts such as *p*-TSA [9], [bmim]Br [10], TMSCl/NaI [11], $HClO_4/SiO_2$ [12], ZnO nanoparticles [13], Cu nanoparticles [14], TMSCl [15], thiamine hydrochloride [16], I_2 [17] and montmorillonite [18]. In addition, the Vilsmeier-Haack reagent is an efficient, economical and mild reagent for the synthesis of highly functionalized oxazines [19].

Compounds containing 1,3-amino-oxygenated functional groups have been found in various important natural products and potent drugs including a number of nucleoside antibiotics and HIV protease inhibitors, such as ritonavir and lipinavir [20]. As well, 1-(amidoalkyl)-2-naphthols can be converted to 1-(aminomethyl)-2-naphthols by an amide hydrolysis reaction, which displays depressor and bradycardia effects in humans [21, 22]. Multicomponent condensation of aldehydes, 2-naphthol and acetonitrile or different amides affords 1-(amidoalkyl)-2-naphthols in the presence of Lewis or Brønsted acids such as dodecylphosphonic acid (DPA) [23], H_2NSO_3H [24], oxalic acid [25], $Fe(HSO_4)_3$ [26], $Sr(OTf)_2$ [27], I_2 [28], $K_5CoW_{12}O_{40}{\cdot}3H_2O$ [29], HPMo [30], $Yb(OTf)_3$ in ionic liquid [31], Indion-130 [32], montmorillonite K10 [33], TMSCl/NaI [34], Al_2O_3-$HClO_4$ [35], $InCl_3$ [36], 2,4,6-trichloro-1,3,5-triazine [37], CuPW and CuPMo [38], $FeCl_3/SiO_2$ [39], $H_4SiW_{12}O_{40}$ [40], CPTS [41], TrCl [42], boric acid [43] and $POCl_3/Na_2B_4O_7$ [44].

According to the above-mentioned importance of oxazines and (amidoalkyl)-2-naphthols, synthesis of oxazine and (amidoalkyl)-2-naphthol derivatives based on safety procedures is of principal interest for generating these products under mild conditions endured by sensitive functional groups from both synthetic and environmental points of view.

In modern science, one of the growing and important fields is nanotechnology. Because of different physical and chemical properties of nano-sized catalysts in comparison with bulk material, they attract interest from different researcher areas. Since the particles are in small size, the surface area exposed to the reactant is maximized, thus allowing more reactions to occur at the same time; hence,

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the process is speeded up. Among various metal nanostructures, silver nanoparticles have received significant attention owing to their unusual properties and potential applications in diverse fields [45]. In particular, advantages of silver iodide nanoparticles are available, including mild reaction conditions to produce high yields of products in short reaction times compared to traditional catalysts, and they can also be recycled [46]. Recently, catalysis by AgI nanoparticles (NPs) and related compounds as nanocatalysts has become a field of increasing importance.

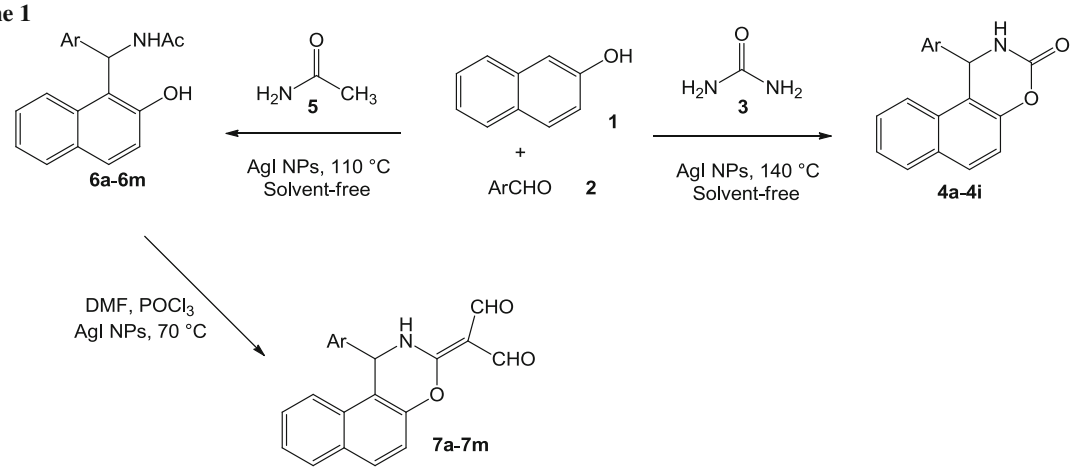
In order to achieve more efficient synthetic processes, minimize by-products and decrease the number of separate reaction steps, we have tried to develop a clean and environment-friendly approach to the synthesis of (amidoalkyl)naphthol and oxazine derivatives with high yields using AgI NPs as catalyst. The treatment of 2-naphthol, aldehyde and urea provided the synthesis of naphtho[1,2-e][1,3]oxazinones and 2-naphthol, aldehyde and acetamide resulted in 1-(amidoalkyl)-2-naphthols. Then, the prepared (amidoalkyl)naphthols were reacted with Vilsmeier reagent in the presence of AgI NPs to give highly substituted functionalized oxazine derivatives (Scheme 1).

Results and discussion

For initiating optimization of the reaction conditions, we selected model reactions. Model 1: one-pot three-component condensation of acetamide, benzaldehyde and 2-naphthol; model 2: reaction of 2-naphthol, benzaldehyde and urea; model 3: cyclization of *N*-[(phenyl)(2-hydroxynaphthalen-1-yl)methyl]acetamide (Scheme 2).

To test the efficiency of the catalytic activity, we choose to focus our initial studies on the above-mentioned model reactions in the presence of different nanocatalysts, such as AgBr, CuCl, NiO, bulk AgI and AgI NPs (Table 1). As indicated in Table 1, AgI was selected as the interesting

Scheme 1



Scheme 2

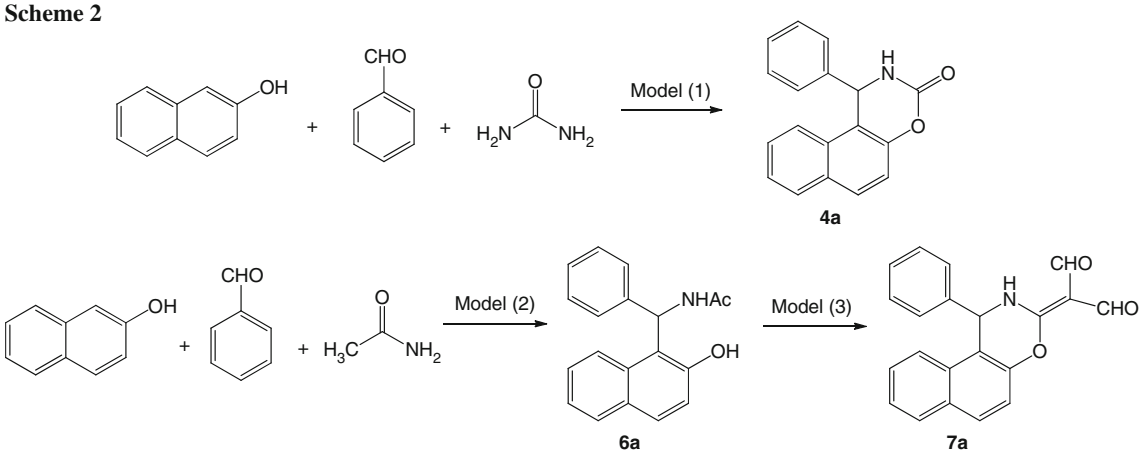
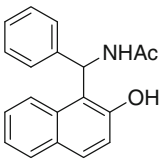
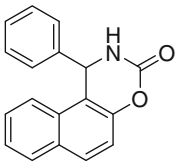
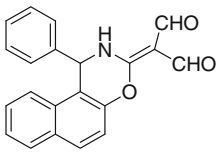


Table 1 Comparison of catalytic activity of various catalysts in model reactions

Product	Catalyst	Time/min	Yield[a]/%
 **6a**	None	120	0
	AgI	30	77
	AgBr	60	68
	NiO	75	59
	CuCl	65	62
	AgI NPs	5	89
 **4a**	None	120	0
	AgI	45	74
	AgBr	67	66
	NiO	80	55
	CuCl	74	59
	AgI NPs	8	90
 **7a**	None	180	86
	AgI	44	79
	AgBr	65	69
	NiO	59	63
	CuCl	50	73
	AgI NPs	20	88

[a] Yields refer to isolated products

catalyst because when it was used replacing bulk AgI, the yield of the desired product was maximized.

Characterization of the AgI NPs structure was gained by SEM, XRD and FT-IR spectra. The SEM images of AgI nanoparticles are depicted in Fig. 1. These results show that spherical AgI nanoparticles were obtained from $AgNO_3$ and KI with particle size in the range of 40–50 nm under ultrasound power.

The XRD pattern of AgI nanoparticles is shown in Fig. 2. All reflection peaks in Fig. 2 can be readily indexed to the pure cubic phase of AgI with the F-43 m space group (JCDPS no. 78-0641). THe Debye–Scherrer equation ($D = K\lambda/\beta\cos\theta$) is used to calculate the crystallite size diameter (D) of the AgI nanoparticles, where β (FWHM, full-width at half-maximum or half-width) is in radian and θ is the position of the maximum of diffraction peak, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the X-ray wavelength (1.5406 Å for Cu Kα). Crystallite size of AgI has been found to be 48 nm.

Figure 3 shows the FT-IR spectrum of AgI nanoparticles. The broad peak at 3,436 and 1,628 cm^{-1} can be attributed to the (OH) stretching and bending vibrations, respectively; these peaks indicate the presence of physisorbed water linked to nanoparticles. The peak corresponding to CH_2 stretching vibration of SDS (sodium dodecyl sulfonate) can be seen at 2,923 cm^{-1}. The appearance of this peak suggests that a trace amount of SDS has been coated on the surface of AgI nanoparticles.

In another effort, we have investigated the effect of different solvents and also solvent-free conditions for the preparation of products **4a** and **6a**. Afterwards, it was concluded that solvent-free conditions were the best choice for the synthesis of these organic compounds. As nanoAgI was preferred as the most suitable catalyst for these reactions under solvent-free conditions, we then tried to optimize the amount of catalyst for the model reactions. Our optimization studies disclosed that the yields increased smoothly with catalyst load up to 0.03 g and then remained unchanged to 0.05 g (Table 2). With these results, we extended our work to various aldehydes, and all of the results are shown in Tables 3 and 4.

Heterogeneous catalysts are useful because of the ability to reuse of them to reduce waste. In order to study the stability of our catalyst, the reaction was run successively with the same catalyst in the same reaction. Figure 4 shows the results of this survey in the model reaction 1 in the presence of AgI NPs. After completion of the reaction, the catalyst was washed well with chloroform and methanol

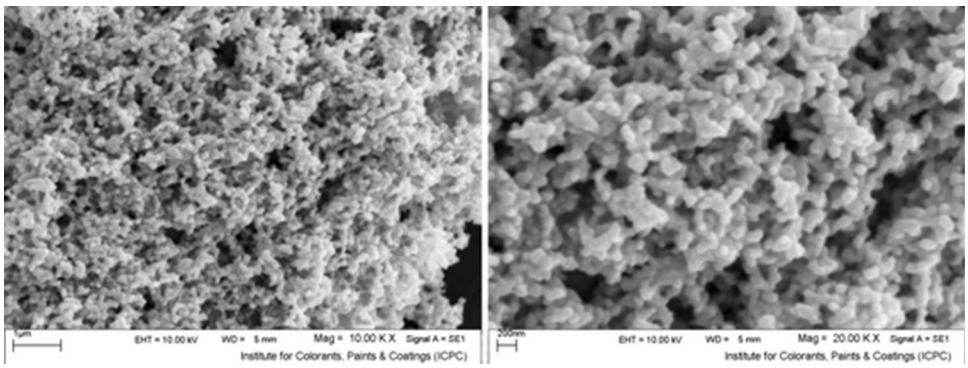


Fig. 1 SEM image of AgI nanoparticles

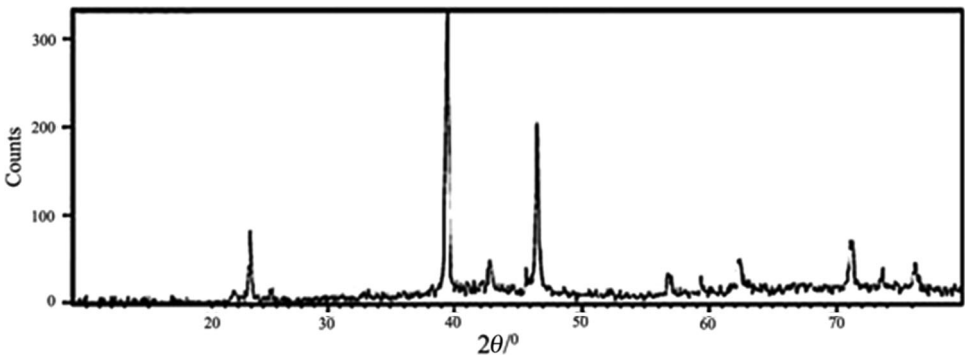


Fig. 2 The XRD pattern of silver iodide nanoparticles

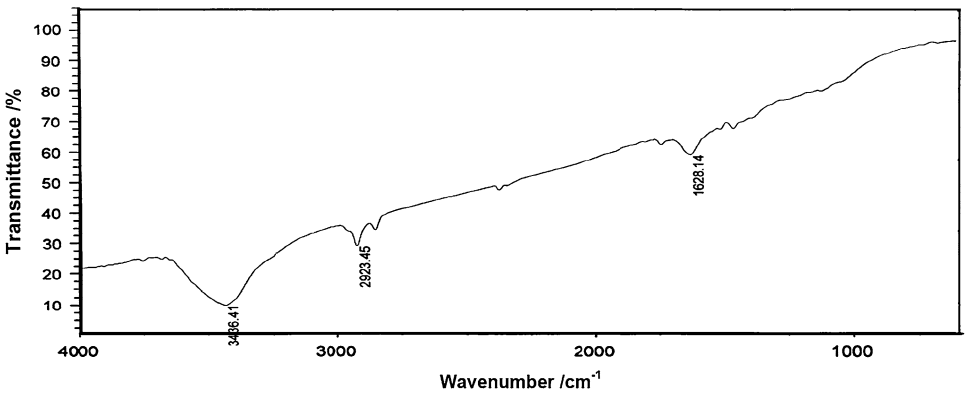


Fig. 3 FT-IR spectrum of AgI nanoparticles

and dried at 70 °C for 10 h. Then the filtered catalyst was used several times with a slightly decreased activity as shown in Fig. 4. It could thus be concluded that AgI NPs with high activity and good reusability could be a satisfying catalyst for these reactions.

Experimental

All organic materials were purchased commercially from Sigma-Aldrich and Merck and were used without further purification. All melting points were determined in capillary tubes on a Boetius melting point microscope. FT-IR spectra were recorded with KBr pellets using a Magna-IR spectrometer 550 Nicolet. NMR spectra were recorded on a Bruker 400 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. CHN compositions were measured by a Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of the X'pert Company with monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å). Microscopic morphology of products was visualized by SEM (LEO 1455VP). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV.

General procedure for the preparation of silver iodide nanoparticles

A solution of 0.415 g KI (25×10^{-4} mol) in 25 cm^3 distillated water was added dropwise to a solution of 0.425 g

Table 2 Effect of solvent, temperature and catalyst load for preparation of products **4a**, **6a** and **7a**

Product	Catalyst/g	Solvent	*T*/°C	Time/min	Yield[a]/%
4a	0.05	EtOH	Reflux	150	48
	0.05	CH_3CN	Reflux	120	53
	0.05	CH_2Cl_2	Reflux	100	42
	0.05	Solvent-free	140	8	90
	0.01	Solvent-free	r.t.	240	No reaction
	0.02	Solvent-free	110	120	15
	0.03	EtOH	Reflux	140	15
	0.03	Solvent-free	110	120	23
	0.03	Solvent-free	140	8	90
	0.03	Solvent-free	140	15	90
	0.03	Solvent-free	160	8	90
6a	0.05	EtOH	Reflux	150	54
	0.05	CH_3CN	Reflux	120	66
	0.05	CH_2Cl_2	Reflux	100	44
	0.01	Solvent-free	r.t.	240	No reaction
	0.02	Solvent-free	100	120	17
	0.03	EtOH	Reflux	120	15
	0.03	Solvent-free	50	120	35
	0.03	Solvent-free	110	5	89
	0.05	Solvent-free	110	5	89
	0.03	Solvent-free	140	5	89
7a	0.05	Solvent-free	r.t.	180	No reaction
	0.05	Solvent-free	40	120	33
	0.05	Solvent-free	50	90	55
	0.01	Solvent-free	60	70	69
	0.02	Solvent-free	60	65	73
	0.03	Solvent-free	70	20	88
	0.05	Solvent-free	70	20	88
	0.03	Solvent-free	80	20	88

[a] Isolated yields

Table 3 Preparation of naphthoxazine-3-one derivatives

Products	Ar	Time/min	Yield[a]/%	M.p. [References]
4a	C_6H_5	8	90	217–219 [14]
4b	4-$MeOC_6H_4$	15	82	189–190 [13]
4c	4-MeC_6H_4	12	78	163–165 [13]
4d	4-BrC_6H_4	6	90	217–218 [14]
4e	4-ClC_6H_4	6	95	204–206 [14]
4f	3-MeC_6H_4	12	79	206–208
4g	4-*i*PrC_6H_4	15	92	171–173 [11]
4h	4-$Me_2NC_6H_4$	20	80	218–219
4i	Thiophen-2-yl	7	80	209–210 [12]

[a] Yields refer to the pure isolated products

$AgNO_3$ (25×10^{-4} mol) in 25 cm^3 distillated water under ultrasound power in the presence of 0.2 g sodium dodecyl sulfate (SDS) as surfactant. The yellow as-synthesized precipitate was separated by centrifugation and washed with distillated water and ethanol to remove impurities for several times and then dried.

*General procedure for the preparation of naphthooxazinones **4a-4i***

A mixture of β-naphthol (0.01 mol), aldehyde (0.01 mol), urea (0.012 mol) and 0.03 g AgI NPs was finely ground and heated with stirring at 140 °C in an oil bath. The reaction was monitored by TLC. After cooling, the reaction mixture was dissolved in ethyl acetate and the mixture stirred for 5 min. The suspended solution was filtered and the heterogeneous catalyst was recovered. The ethyl acetate was evaporated and the crude product crystallized from MeOH to afford the pure product.

*General procedure for the synthesis of (amidoalkyl)naphthols **6a-6m***

A mixture of 0.14 g β-naphthol (1 mmol), aldehyde (1 mmol), 0.07 g acetamide (1.2 mmol) and 0.03 g AgI NPs was finely ground and heated with stirring at 110 °C in an oil bath, and the reaction was monitored by TLC. After cooling, the reaction mixture was dissolved in hot ethanol and the mixture stirred for 5 min. The reaction mixture was filtered, and the heterogeneous catalyst was recovered. Then the crude product was crystallized from EtOH (15 %) to afford the pure product. The products were characterized by comparison of their physical data with those of known compounds unless otherwise mentioned.

*General procedure for the synthesis of 1,3-oxazines **7a-7m***

To a solution of acetamidonaphthols **6** (1 mmol) in DMF (1.2 equiv) and 0.03 g AgI NPs, $POCl_3$ (0.8 equiv) was added dropwise (15 min) at 0 °C, and the reaction mixture was allowed to reach room temperature. Then the reaction mixture was stirred at 70 °C for 20 min. After completion of the reaction, it was allowed to cool to room temperature. The reaction mixture was filtered, and the heterogeneous catalyst was recovered. The filtrate was poured into crushed ice and refrigerated overnight. The solution was neutralized with sodium acetate, and the crude compound was extracted with dichloromethane (3×10 cm^3) and washed with water (3×5 cm^3). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified through crystallization from EtOH to afford the pure product.

Table 4 Synthesis of (amidoalkyl)naphthols and 1,3-oxazines

Entry	Aldehyde (R)	6	Time/min	Yield[a]/%	M.p./°C [References]	7	Time/min	Yield[a]/%	M.p./°C
1	C_6H_5	**6a**	5	89	245-–246 [35]	**7a**	20	88	235–237
2	4-$NO_2C_6H_4$	**6b**	3	95	247–249 [33]	**7b**	20	92	263–264
3	2-$NO_2C_6H_4$	**6c**	4	92	178–180 [33]	**7c**	20	92	255–257
4	4-ClC_6H_4	**6d**	4	90	223–225 [33]	**7d**	20	88	232–234
5	2,4-$Cl_2C_6H_3$	**6e**	5	89	200–202 [31]	**7e**	20	80	209–210
6	4-MeC_6H_4	**6f**	10	80	222–223 [31]	**7f**	20	79	219–221
7	4-$MeOC_6H_4$	**6g**	15	84	183–185 [31]	**7g**	20	79	205–206
8	4-*i*PrC_6H_4	**6h**	20	85	220–222	**7h**	20	82	228–229
9	4-BrC_6H_4	**6j**	4	90	227–229 [27]	**7j**	20	88	237–239
10	4-OHC_6H_4	**6k**	15	80	226–227	**7k**	20	87	241–243
11	2,4-$(MeO)_2C_6H_3$	**6l**	17	85	227–229	**7l**	20	85	250–252
12	1-Naphthyl	**6m**	15	82	210–220	**7m**	20	82	245–247

[a] Yields refer to isolated products

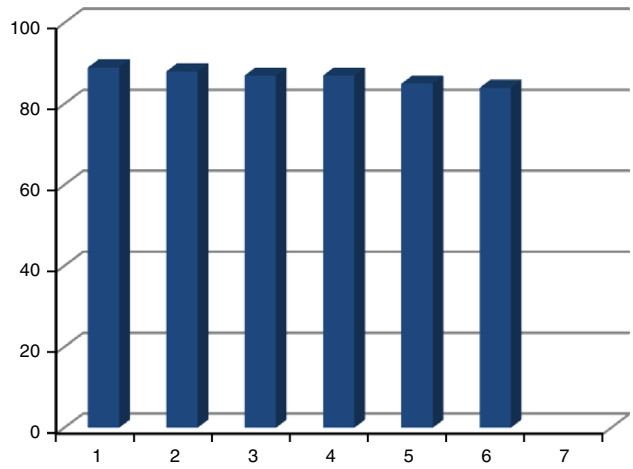


Fig. 4 Recoverability of AgI nanoparticles

1,2-Dihydro-1-(3-methylphenyl)-3H-naphtho[1,2-e]-[1,3]oxazine-3-one (**4f**, $C_{19}H_{15}NO_2$)
IR (KBr): $\bar{\nu}$ = 3,264, 1,746, 1,515, 815, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 2.21 (s, 3H, CH_3), 6.12 (s, 1H, CH), 7.04–7.12 (m, 3H, Ar–H), 7.21 (t, 1H, Ar–H), 7.35–7.48 (m, 3H, Ar–H), 7.80 (d, J = 7.6 Hz, 1H, Ar–H), 7.93 (d, J = 7.6 Hz, 1H, Ar–H), 7.98 (d, J = 7.6 Hz, 1H, Ar–H), 8.80 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.5 (CH_3), 54.3 (CH), 114.5, 115.0, 116.5, 117.3, 123.5, 124.6, 125.5, 127.8, 129.1, 129.2, 129.3, 130.7, 130.9, 138.6, 143.3, 147.9, 149.8 (CO) ppm; MS (EI): m/z = 289 (M^+).

1,2-Dihydro-1-(4-dimethylaminophenyl)-3H-naphtho-[1,2-e][1,3]oxazine-3-one (**4h**, $C_{20}H_{18}N_2O_2$)
IR (KBr): $\bar{\nu}$ = 3,224, 1,734, 1,600, 850, 730 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 2.80 (s, 6H, CH_3), 6.02 (s, 1H, CH), 6.62 (d, J = 7.8 Hz, 2H, Ar–H), 7.08 (d, J = 7.8 Hz, 2H, Ar–H), 7.35 (d, J = 7.6 Hz, 2H, Ar–H), 7.45 (t, J = 7.6 Hz, 2H, Ar–H), 7.78 (d, J = 7.6 Hz, 1H, Ar–H), 7.95 (t, J = 7.6 Hz, 1H, Ar–H), 8.68 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 31.5 (CH_3), 53.9 (CH), 112.8, 115.1, 117.3, 123.1, 125.4, 126.4, 127.7, 128.1, 129.0, 130.3, 130.8, 130.9, 147.7, 150.0, 150.4 (CO) ppm; MS (EI): m/z = 318 (M^+).

N-[(2-Hydroxynaphthalen-1-yl)(4-isopropylphenyl)-methyl]acetamide (**6h**, $C_{22}H_{23}NO_2$)
IR (KBr): $\bar{\nu}$ = 3,405, 3,168, 3,058, 1,633, 1,515, 1,438, 1,370, 1,330, 1,275, 1,168, 986, 816, 744 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 1.14 (d, J = 7.0 Hz, 6H), 1.95 (s, 3H), 2.81 (m, J = 7.0 Hz, 1H), 7.06–7.11 (m, 5H), 7.19 (t, J = 7.2 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 9.96 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.1, 24.4, 33.4, 48.3, 119.0, 119.4, 122.8, 123.0, 123.6, 126.3, 126.6, 126.7, 128.0, 128.9, 129.0, 129.5, 132.8, 140.3, 146.6, 153.5, 169.5 ppm; MS (EI): m/z = 333 (M^+).

N-[(2-Hydroxynaphthalen-1-yl)(4-hydroxyphenyl)-methyl]acetamide (**6k**, $C_{19}H_{17}NO_3$)
IR (KBr): $\bar{\nu}$ = 3,406, 3,180, 3,052, 1,616, 1,514, 1,438, 1,370, 1,330, 1,275, 1,168, 986, 813, 738 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 1.97 (s, 3H), 7.04–7.09 (m, 5H), 7.19 (t, J = 7.2 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 9.20 (s, 1H), 9.87 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.4, 48.5, 119.3, 120.1, 122.8, 123.0, 123.6, 126.3, 126.6, 126.7, 128.0, 128.9, 129.0, 129.5, 132.8, 140.3, 146.8, 153.2, 168.9 ppm; MS (EI): m/z = 307 (M^+).

N-[(2,4-Dimethoxyphenyl)(2-hydroxynaphthalen-1-yl)-methyl]acetamide (**6l**, $C_{21}H_{21}NO_4$)
IR (KBr): $\bar{\nu}$ = 3,406, 3,139, 1,646, 1,521, 1,506, 1,442, 1,400, 1,374, 1,329, 1,264, 1,242, 1,091, 1,068, 818, 764,

659 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 1.90$ (s, 3H), 3.72 (s, 6H), 6.89–7.01 (m, 2H), 7.17 (d, $J = 8.4$ Hz, 1H), 7.29 (t, $J = 7.2$ Hz, 1H), 7.33–7.39 (m, 2H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.74-7.79 (m, 3H), 8.55 (d, $J = 7.6$ Hz, 1H), 9.98 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 23.3$, 48.7, 55.2, 55.9, 110.4, 118.6, 118.8, 123.2, 126.9, 128.5, 129.1, 129.5, 129.7, 130.5, 131.6, 132.8, 144.9, 149.3, 153.7, 153.9, 170.2 ppm; MS (EI): *m/z* = 351 (M^+).

N-[(1-Naphthyl)(2-hydroxynaphthalen-1-yl)methyl]-acetamide (**6m**, $C_{23}H_{19}NO_2$)
IR (KBr): $\bar{\nu} = 3{,}412$, 3,173, 3,060, 1,642, 1,572, 1,514, 1,437, 1,400, 1,374, 1,332, 1,274, 1,224, 1,172, 932, 813, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): $\delta = 1.90$ (s, 3H), 7.22–7.29 (m, 3H), 7.39–7.44 (m, 4H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.70–7.80 (m, 3H), 7.91–8.03 (d, $J = 7.6$ Hz, 3H), 8.70 (d, $J = 7.6$ Hz, 1H), 10.01 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 22.9$, 47.4, 117.6, 118.7, 119.3, 122.8, 123.5, 123.9, 125.5, 125.7, 125.9, 126.5, 126.7, 127.9, 129.0, 129.2, 129.7, 131.5, 133.3, 134.0, 137.8, 153.8, 168.9 ppm; MS (EI): *m/z* = 341 (M^+).

(1,2-Dihydro-1-phenyl-3H-naphtho[1,2-e][1,3]-oxazine-3-ylidene)malonaldehyde (**7a**, $C_{21}H_{15}NO_3$)
IR (KBr): $\bar{\nu} = 3{,}398$, 1,629, 1,515, 1,453, 1,221, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.24$ (s, 1H), 7.13–7.15 (d, $J = 7.6$ Hz, 2H), 7.17–7.21 (d, $J = 7.6$ Hz, 2H), 7.48-7.49 (t, $J = 7.6$ Hz, 3H), 7.76 (t, $J = 7.8$ Hz, 2H), 7.90 (d, $J = 7.8$ Hz, 1H), 7.97 (d, $J = 7.8$ Hz, 1H), 10.04 (br s, 2H, CHO), 12.33 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.6$, 101.1, 113.6, 118.3, 123.2, 124.7, 127.3, 128.8, 129.6, 130.4, 131.7, 132.9, 134.5, 143.6, 144.9, 148.4, 162.3, 186.9 ppm; MS (EI): *m/z* = 329 (M^+).

[1,2-Dihydro-1-(4-nitrophenyl)-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7b**, $C_{21}H_{14}N_2O_5$)
IR (KBr): $\bar{\nu} = 3{,}408$, 1,632, 1,515, 1,453, 1,221, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.23$ (s, 1H), 7.10–7.14 (d, $J = 7.6$ Hz, 2H), 7.17–7.21 (d, $J = 7.6$ Hz, 2H), 7.46–7.49 (t, $J = 7.6$ Hz, 3H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.96 (d, $J = 7.7$ Hz, 1H), 10.02 (br s, 2H, CHO), 12.25 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.3$, 101.3, 113.4, 117.9, 123.3, 125.7, 127.3, 128.5, 128.9, 129.6, 130.4, 131.7, 131.8, 132.9, 134.5, 143.6, 144.9, 148.4, 162.6, 187.0 ppm; MS (EI): *m/z* = 374 (M^+).

[1,2-Dihydro-1-(2-nitrophenyl)-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7c**, $C_{21}H_{14}N_2O_5$)
IR (KBr): $\bar{\nu} = 3{,}399$, 1,630, 1,515, 1,453, 1,221, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.23$ (s, 1H), 7.10–7.14 (d, $J = 7.6$ Hz, 2H), 7.17–7.21 (t, $J = 7.6$ Hz, 2H), 7.46–7.49 (t, $J = 7.7$ Hz, 3H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.96 (d, $J = 7.8$ Hz, 1H), 10.01 (br s, 2H, CHO), 12.26 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 48.9$, 101.1, 113.7, 118.4, 123.3, 125.7, 127.3, 128.5, 128.9, 129.6, 130.4, 131.7, 131.8, 132.9, 134.5, 143.2, 144.5, 148.2, 162.3, 186.8 ppm; MS (EI): *m/z* = 374 (M^+).

[1-(4-Chlorophenyl)-1,2-dihydro-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7d**, $C_{21}H_{14}ClNO_3$)
IR (KBr): $\bar{\nu} = 3{,}406$, 1,627, 1,515, 1,453, 1,221, 831 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.21$ (s, 1H), 7.12–7.14 (d, $J = 7.6$ Hz, 2H), 7.19–7.25 (d, $J = 7.6$ Hz, 2H), 7.46–7.49 (t, $J = 7.7$ Hz, 3H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.88 (d, $J = 7.7$ Hz, 1H), 7.96 (d, $J = 7.7$ Hz, 1H), 10.01 (br s, 2H, CHO), 12.28 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.4$, 101.1, 113.4, 117.9, 123.3, 125.7, 127.3, 128.5, 128.9, 129.6, 130.4, 131.7, 131.8, 132.9, 134.5, 143.6, 144.9, 148.4, 163.1, 186.7 ppm; MS (EI): *m/z* = 363 (M^+).

[1-(2,4-Dichlorophenyl)-1,2-dihydro-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7e**, $C_{21}H_{13}Cl_2NO_3$)
IR (KBr): $\bar{\nu} = 3{,}409$, 1,620, 1,510, 1,449, 1,220, 826 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.22$ (s, 1H), 7.19–7.25 (d, $J = 7.6$ Hz, 2H), 7.49–7.62 (d, $J = 7.7$ Hz, 2H), 7.65–7.70 (d, $J = 7.7$ Hz, 2H), 7.89–7.93 (d, $J = 7.8$ Hz, 2H), 8.11 (s, 1H), 10.03 (br s, 2H, CHO), 12.28 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.3$, 101.3, 113.4, 117.2, 123.1, 124.3, 126.8, 128.8, 128.9, 129.6, 130.1, 131.7, 131.8, 131.9, 134.5, 143.0, 144.8, 148.6, 162.1, 186.7 ppm; MS (EI): *m/z* = 397 (M^+).

[1,2-Dihydro-1-(4-methylphenyl)-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7f**, $C_{22}H_{17}NO_3$)
IR (KBr): $\bar{\nu} = 3{,}408$, 1,628, 1,515, 1,453, 1,219, 821 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.30$ (s, 3H), 6.20 (s, 1H), 7.10–7.13 (d, $J = 7.6$ Hz, 2H), 7.15–7.20 (d, $J = 7.6$ Hz, 2H), 7.42–7.48 (t, $J = 7.7$ Hz, 3H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 7.7$ Hz, 1H), 7.97 (d, $J = 7.7$ Hz, 1H), 10.03 (br s, 2H, CHO), 12.26 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 23.3$, 50.2, 101.1, 113.4, 117.9, 123.3, 125.7, 127.3, 128.5, 128.9, 129.6, 130.4, 131.7, 131.8, 132.9, 134.5, 142.9, 144.4, 147.8, 162.2, 186.8 ppm; MS (EI): *m/z* = 343 (M^+).

[1,2-Dihydro-1-(4-methoxyphenyl)-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7g**, $C_{22}H_{17}NO_4$)
IR (KBr): $\bar{\nu} = 3{,}403$, 1,624, 1,513, 1,449, 1,220, 819 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.48$ (s, 3H), 6.21 (s, 1H), 7.18–7.26 (d, $J = 7.6$ Hz, 2H), 7.45–7.60 (d, $J = 7.7$ Hz, 2H), 7.63–7.72 (d, $J = 7.8$ Hz, 2H), 7.87–7.91 (d,

$J = 7.8$ Hz, 2H), 8.08 (s, 1H), 10.02 (br s, 2H, CHO), 12.24 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 33.5, 50.1, 101.1, 113.4, 117.2, 123.1, 124.3, 126.8, 128.8, 128.9, 129.6, 130.4, 131.7, 131.8, 131.9, 134.2, 143.5, 145.4, 148.4, 162.2, 187.2$ ppm; MS (EI): $m/z = 359$ (M^+).

[1,2-Dihydro-1-(4-isopropylphenyl)-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7h**, $C_{24}H_{21}NO_3$)
IR (KBr): $\bar{\nu} = 3{,}407, 1{,}619, 1{,}513, 1{,}454, 1{,}220, 834$ cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.19$ (d, $J = 7.0$ Hz, 6H), 2.84 (m, $J = 7.0$ Hz, 1H), 6.20 (s, 1H), 7.19–7.25 (d, $J = 7.6$ Hz, 3H), 7.49–7.62 (t, $J = 7.7$ Hz, 3H), 7.89–7.93 (t, $J = 7.6$ Hz, 2H), 8.12 (m, 2H), 10.02 (br s, 2H, CHO), 12.26 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 23.2, 33.5, 50.3, 101.3, 113.4, 117.2, 123.1, 124.3, 126.8, 128.8, 128.9, 129.6, 130.1, 131.7, 131.8, 131.9, 134.5, 143.0, 144.8, 148.6, 162.1, 186.7$ ppm; MS (EI): $m/z = 371$ (M^+).

[1-(4-Bromophenyl)-1,2-dihydro-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7j**, $C_{21}H_{14}BrNO_3$)
IR (KBr): $\bar{\nu} = 3{,}410, 1{,}620, 1{,}513, 1{,}446, 1{,}220, 815$ cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.20$ (s, 1H), 7.13–7.15 (d, $J = 7.6$ Hz, 2H), 7.18–7.20 (d, $J = 7.6$ Hz, 2H), 7.46–7.49 (t, $J = 7.7$ Hz, 3H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.96 (d, $J = 7.7$ Hz, 1H), 10.01 (br s, 2H, CHO), 12.27 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.5, 101.1, 113.3, 118.2, 123.5, 124.4, 127.3, 128.8, 128.9, 129.6, 130.2, 131.7, 131.8, 131.9, 134.5, 143.6, 145.4, 148.6, 162.4, 186.8$ ppm; MS (EI): $m/z = 406$ (M^+).

[1,2-Dihydro-1-(4-hydroxyphenyl)-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7k**, $C_{21}H_{15}NO_4$)
IR (KBr): $\bar{\nu} = 3{,}405, 1{,}626, 1{,}514, 1{,}449, 1{,}220, 822$ cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.23$ (s, 1H), 7.18–7.24 (d, $J = 7.6$ Hz, 2H), 7.47–7.63 (d, $J = 7.6$ Hz, 2H), 7.63–7.71 (d, $J = 7.7$ Hz, 2H), 7.89–7.93 (d, $J = 7.8$ Hz, 2H), 8.11 (s, 1H), 9.45 (s, 1H), 10.01 (br s, 2H, CHO), 12.29 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.3, 101.3, 113.4, 117.2, 123.1, 124.3, 126.8, 128.8, 128.9, 129.6, 130.1, 131.7, 131.8, 131.9, 134.5, 143.0, 144.8, 148.6, 162.1, 186.7$ ppm; MS (EI): $m/z = 345$ (M^+).

[1,2-Dihydro-1-(2,4-dimethoxyphenyl)-3H-naphtho-[1,2-e]-[1,3]oxazine-3-ylidene]malonaldehyde
(**7l**, $C_{23}H_{19}NO_5$)
IR (KBr): $\bar{\nu} = 3{,}397, 1{,}628, 1{,}515, 1{,}449, 1{,}220, 821$ cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.72$ (s, 6H), 6.22 (s, 1H), 7.19–7.25 (d, $J = 7.6$ Hz, 2H), 7.49–7.62 (d, $J = 7.7$ Hz, 2H), 7.65–7.70 (d, $J = 7.7$ Hz, 2H), 7.89–7.93 (d, $J = 7.8$ Hz, 2H), 8.11 (s, 1H), 10.03 (br s, 2H, CHO), 12.28 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.1, 53.5, 53.6, 101.2, 113.4, 117.2, 123.1, 124.3, 126.8, 128.8, 128.9, 129.6, 130.2, 131.7, 131.8, 131.9, 134.5, 143.0, 144.8, 148.4, 163.6, 186.9$ ppm; MS (EI): $m/z = 389$ (M^+).

[1,2-Dihydro-1-(naphthalen-1-yl)-3H-naphtho-[1,2-e][1,3]oxazine-3-ylidene]malonaldehyde
(**7m**, $C_{25}H_{17}NO_3$)
IR (KBr): $\bar{\nu} = 3{,}404, 1{,}623, 1{,}510, 1{,}449, 1{,}220, 826$ cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.20$-7.27 (m, 3H), 7.36–7.42 (m, 4H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.70–7.82 (m, 3H), 7.89–8.01 (d, $J = 7.6$ Hz, 3H), 8.77 (d, $J = 7.6$ Hz, 1H), 10.01 (br s, 2H, CHO), 12.27 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 53.4, 101.1, 118.7, 119.3, 122.8, 123.5, 123.9, 125.5, 125.7, 125.9, 126.5, 126.7, 127.9, 129.0, 129.2, 129.7, 131.5, 133.3, 134.0, 137.8, 144.8, 148.4, 163.6, 186.9$ ppm; MS (EI): $m/z = 379$ (M^+).

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