

Palladium-Catalyzed Decarboxylative Selective Acylation of 4*H*-Benzo[*d*][1,3]oxazin-4-one Derivatives with α -Oxo Carboxylic acids *via* Preferential Cyclic Imine-*N*-Directed Aryl C–H Activation

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Abstract: The benzoxazine scaffolds are of much interest as they are found in a large array of natural products and pharmaceutical drugs with diverse activities. We have developed a palladium-catalyzed decarboxylative selective mono- and bis-acylation of 4*H*-benzo[*d*][1,3]oxazin-4-one derivatives with α -oxo carboxylic acids *via* preferential cyclic imine-*N*-directed C–H activation. 2-Aryl-4*H*-benzo[*d*][1,3]oxazin-4-one was acylated with a variety of substituted phenylglyoxylic acids to produce the corresponding products. It was observed that electron-donating groups (CH₃, OCH₃) at any position of the aromatic ring of phenylglyoxylic acid provided good to excellent yields, whereas phenylglyoxylic acids containing electron-withdrawing groups (COCH₃, CN, NO₂) gave the products in moderate yields. Interest-

ingly when the reaction was performed with silver triflate (AgOTf) in place of silver nitrate (AgNO₃) in the presence of 4 equivalents of glyoxylic acid, the bis-acylated product was obtained together with a small amount of mono-acylated product. This is the first report of acylation of 2-aryl-4*H*-benzo[*d*][1,3]oxazin-4-ones *via* C–H activation. The notable features of this reaction are acylation with more challenging heteroarene-oxo carboxylic acids and alkyl oxo carboxylic acids. This new protocol provides an easy and efficient access to a variety of *o*-acyl-4*H*-benzo[*d*][1,3]oxazin-4-one derivatives which are of pharmaceutical importance.

Keywords: acylation; 4*H*-benzo[*d*][1,3]oxazin-4-one; C–H activation; decarboxylation; palladium

Introduction

Transition metal-catalyzed decarboxylative coupling *via* C–H activation has received considerable attention in recent times as a powerful green tool for carbon-carbon and carbon-heteroatom bond formation as it does not require stoichiometric organometallic coupling reagents and it leaves carbon dioxide only in place of toxic metal waste.^[1] Since the pioneering work of Myers^[2] and Goossen^[3] this reaction has been used for C–H functionalization of various systems. Recently, decarboxylative acylation using α -oxo carboxylic acids has been successfully applied for *ortho*-acylation of acetanilides,^[4] *O*-phenyl carbamates,^[5] indoles,^[6] azoxybenzenes,^[7] and *O*-methyl ketoximes^[8] among others.^[9] We became interested in the functionalization of 4*H*-benzo[*d*][1,3]oxazin-4-one as benzoxazine scaffolds are of much interest. They are found in a large array of natural products and

pharmaceutical drugs with diverse activities such as chymotrypsin inhibitor,^[10] HSV-1 protease inhibitor

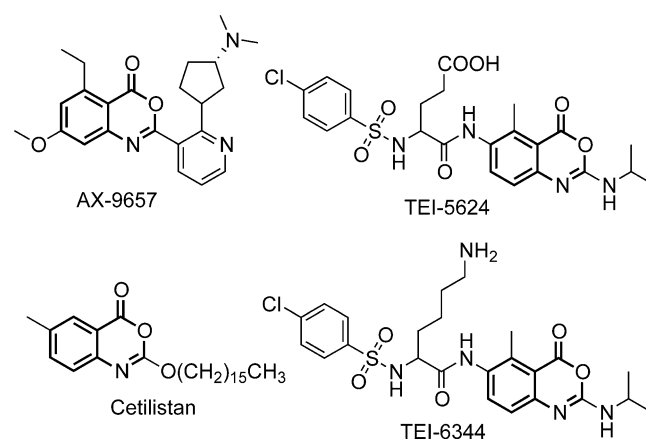
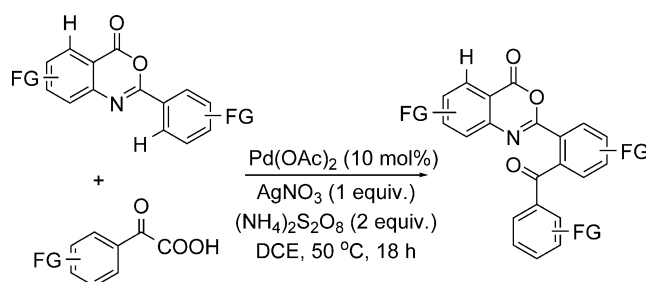


Figure 1. A few biologically active molecules containing the 4*H*-benzo[*d*][1,3]oxazin-4-one moiety.

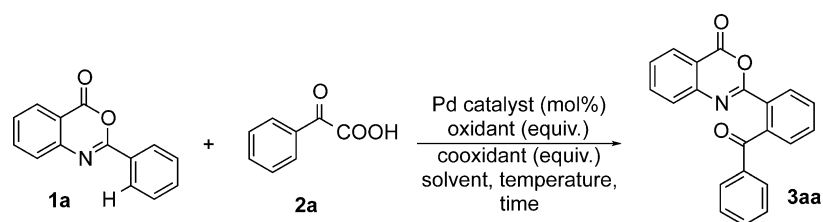
tors,^[11] serine proteases inhibitor,^[12] and inhibitors of leucocyte clatase.^[13] A few representative compounds are outlined in Figure 1.^[14] They also serve as useful building blocks in organic synthesis.^[15]

To the best of our knowledge there is no report for functionalization of this system *via* metal catalyzed C–H activation. As a part of our continuing interest in C–H functionalization by transition metal-catalyzed C–H activation^[17,18] we report here the hitherto unreported regioselective C–H acylation of benzoxazine-4-one derivatives by Pd-catalyzed cyclic imine-N-directed C–H activation (Scheme 1). Although a few procedures have been reported for their synthesis^[16] by other protocols, some of them are associated with



Scheme 1. Pd-catalyzed cyclic imine N-directed C–H acylation of benzoxazine-4-one derivatives.

Table 1. Optimization of the reaction conditions.^[a]



Entry	Pd Catalyst (mol%)	Oxidant (equiv.)	Co-oxidant (equiv.)	Solvent	Yield [%] ^[b]
1	Pd(OAc) ₂ (10)	AgOAc (1)	–	dioxane	22
2	Pd(OAc) ₂ (10)	AgOAc (1)	–	xylylene	21
3	Pd(OAc) ₂ (10)	AgOAc (1)	–	DCE	27
4	Pd(OAc) ₂ (10)	AgOAc (1)	–	DMF	–
5	Pd(OAc) ₂ (10)	AgOAc (1)	–	diglyme	–
6	Pd(OAc) ₂ (10)	AgOAc (1)	–	CH ₃ CN	–
7	Pd(OAc) ₂ (10)	Ag ₂ CO ₃ (1)	–	DCE	12
8	Pd(OAc) ₂ (10)	AgNO ₃ (1)	–	DCE	46
9	Pd(OAc) ₂ (10)	Ag ₂ O (1)	–	DCE	trace
10	Pd(OAc) ₂ (10)	AgNO ₃ (1)	K ₂ S ₂ O ₈ (1)	DCE	52
11	Pd(OAc) ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (1)	DCE	63
12	Pd(OAc) ₂ (10)	AgNO ₃ (1)	Na ₂ S ₂ O ₈ (1)	DCE	27
13	Pd(OAc) ₂ (10)	AgNO ₃ (1)	Oxone (1)	DCE	43
14	Pd(OAc) ₂ (10)	AgNO ₃ (1)	TBHP (1)	DCE	–
15	Pd(OAc)₂ (10)	AgNO₃ (1)	(NH₄)₂S₂O₈ (2)	DCE	85
16	Pd(OAc) ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (3)	DCE	83
17	Pd(CH ₃ CN) ₂ Cl ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	trace
18	Pd(acac) ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	20
19	Pd(PPh ₃) ₂ Cl ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	5
20 ^[c]	Pd(OAc) ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	69
21 ^[d]	Pd(OAc) ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	75
22 ^[e]	Pd(OAc) ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	59
23 ^[f]	Pd(OAc) ₂ (10)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	84
24	Pd(OAc) ₂ (5)	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	65
25	Pd(OAc) ₂ (10)	–	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	53
26	–	AgNO ₃ (1)	(NH ₄) ₂ S ₂ O ₈ (2)	DCE	–

^[a] Reaction conditions: 2-phenyl-4H-benzo[d][1,3]oxazin-4-one (0.5 mmol), phenylglyoxylic acid (1.5 mmol), oxidant, co-oxidant, solvent, 50 °C, 18 h.

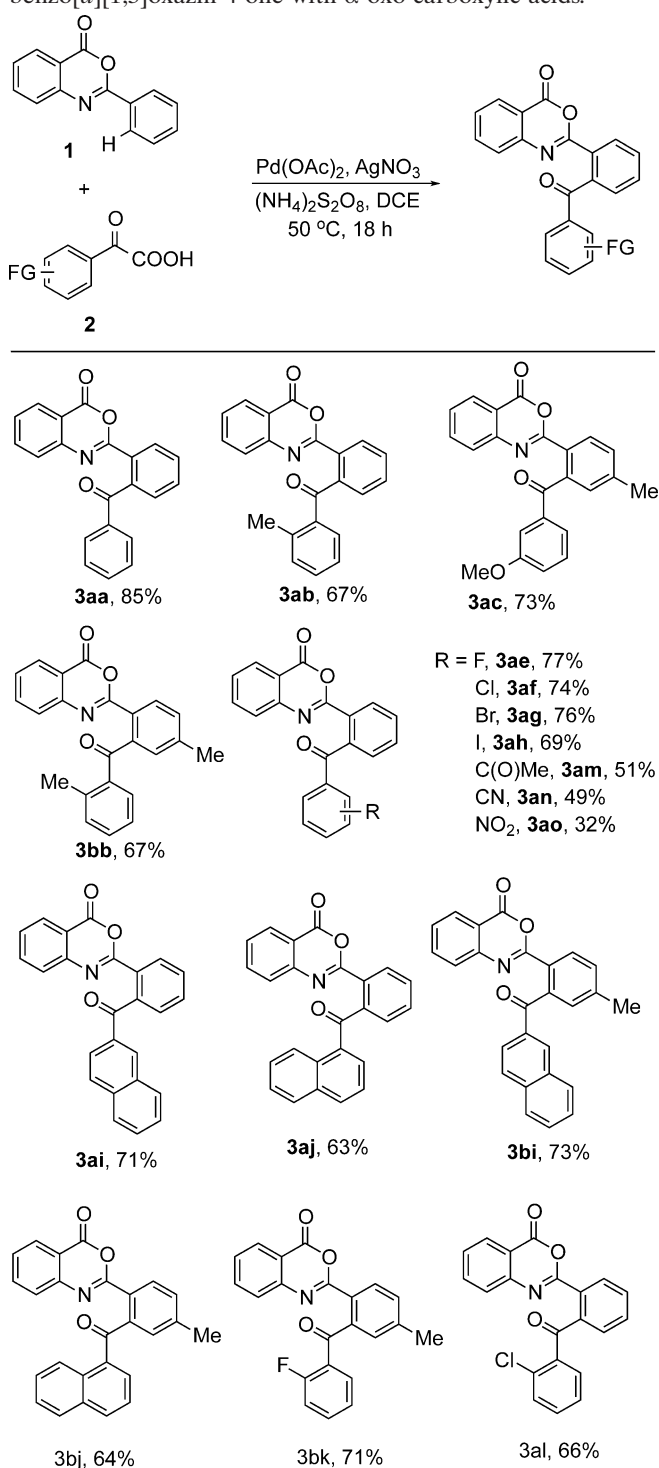
^[b] Isolated yields.

^[c] At 40 °C.

^[d] At 60 °C.

^[e] 2 equivalents of phenylglyoxylic acid were used.

^[f] For 24 h.

Table 2. Pd-catalyzed C–H acylation of 2-phenyl-4H-benzo[d][1,3]oxazin-4-one with α -oxo carboxylic acids.^[a]

^[a] Reaction conditions: 2-aryl-4H-benzo[d][1,3]oxazin-4-one (0.5 mmol), 2-oxo-2-phenylacetic acid (1.5 mmol), $\text{Pd}(\text{OAc})_2$ (10 mol%), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1 mmol), AgNO_3 (0.5 mmol), DCE, 50 °C, 18 h.

Results and Discussion

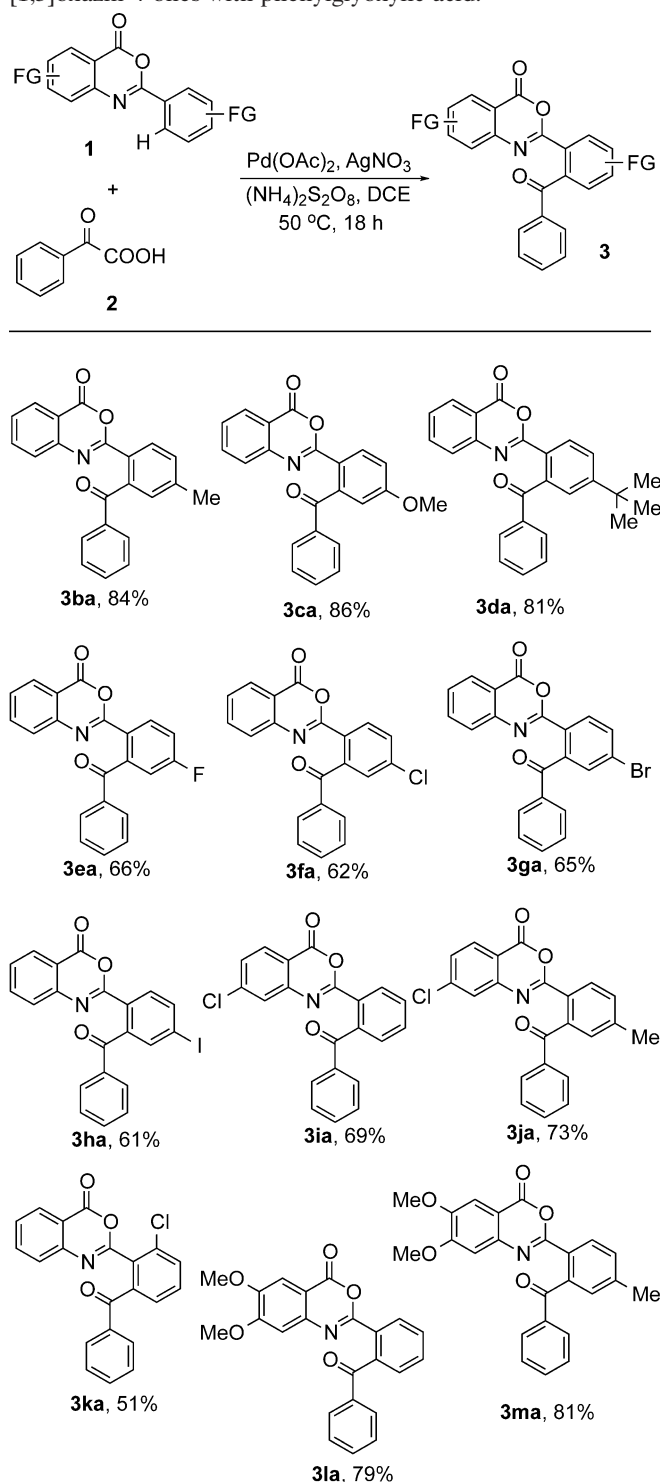
To optimize the reaction conditions a series of experiments were performed with variation of reaction parameters, such as catalyst, solvent, oxidant, temperature and time for a representative reaction of 2-phenyl-4H-benzo[d][1,3]oxazin-4-one and phenylglyoxylic acid. In the presence of $\text{Pd}(\text{OAc})_2$ (10 mol%), AgOAc (1 equiv.) as oxidant at 50 °C in 1,4-dioxane, only 22% acylated product, 2-(2-benzoylphenyl)-4H-benzo[d][1,3]oxazin-4-one was isolated (Table 1, entry 1). Dichloroethane was found to be a more effective solvent compared to 1,4-dioxane, xylene (Table 1, entries 1–3), whereas the reaction did not proceed at all in DMF, diglyme and CH_3CN (Table 1, entries 4–6). Replacement of the oxidant AgOAc by AgNO_3 improved the yield (Table 1, entry 8). However, use of Ag_2CO_3 and Ag_2O led to lower yields (Table 1, entries 7 and 9). The yield of product was further improved using $\text{K}_2\text{S}_2\text{O}_8$ as co-oxidant in combination with AgNO_3 although $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was found to be more efficient compared to $\text{K}_2\text{S}_2\text{O}_8$, $\text{Na}_2\text{S}_2\text{O}_8$, oxone and TBHP (Table 1, entries 10–14). Thus the best yield was obtained by using $\text{Pd}(\text{OAc})_2$ (10 mol%) in combination with one equivalent of AgNO_3 and two equivalents of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in dichloroethane at 50 °C for 18 h (Table 1, entry 15). An increase of the amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ beyond 2 equivalents did not improve the outcome of the reaction (Table 1, entry 16). $\text{Pd}(\text{OAc})_2$ showed better catalytic activity as compared to $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$, $\text{Pd}(\text{acac})_2$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (Table 1, entries 15 and 17–19). The reaction temperature at 50 °C is just optimum as lower and higher temperatures (40 °C and 60 °C) furnished reduced yields of product (Table 1, entries 20 and 21). The use of 2 equivalents of phenylglyoxylic acid or 5 mol% of catalyst led to a lower yield of product (Table 1, entries 22 and 24). The reaction did not proceed at all in absence of $\text{Pd}(\text{OAc})_2$ (Table 1, entry 26).

2-Aryl-4H-benzo[d][1,3]oxazin-4-one was subjected to acylation with a variety of substituted phenylglyoxylic acids under the reaction conditions to produce the corresponding products (Table 2). It was observed that electron-donating groups (CH_3 , OCH_3) at any position on the aromatic ring of phenyl glyoxylic acid provided good to excellent yields (**3ab**, **3ac** and **3bb**), whereas phenylglyoxylic acids containing electron-withdrawing groups (COCH_3 , CN , NO_2) gave the products in moderate yields (**3am**, **3an** and **3ao**).

The halogen moieties (F, Cl, Br, I) on phenylglyoxylic acids remained unaffected under the reaction conditions affording the corresponding products (**3ae**, **3af**, **3ag**, **3ah**, **3bk** and **3al**) in good yields although the Pd-catalyzed decarboxylative acylation of aryl halide was a possibility.^[19] The α - and β -naphthylglyoxylic acids

operational drawbacks such as use of high reaction temperature and generation of waste.

Table 3. Reaction of substituted 2-aryl-4*H*-benzo[*d*][1,3]oxazin-4-ones with phenylglyoxylic acid.^[a]

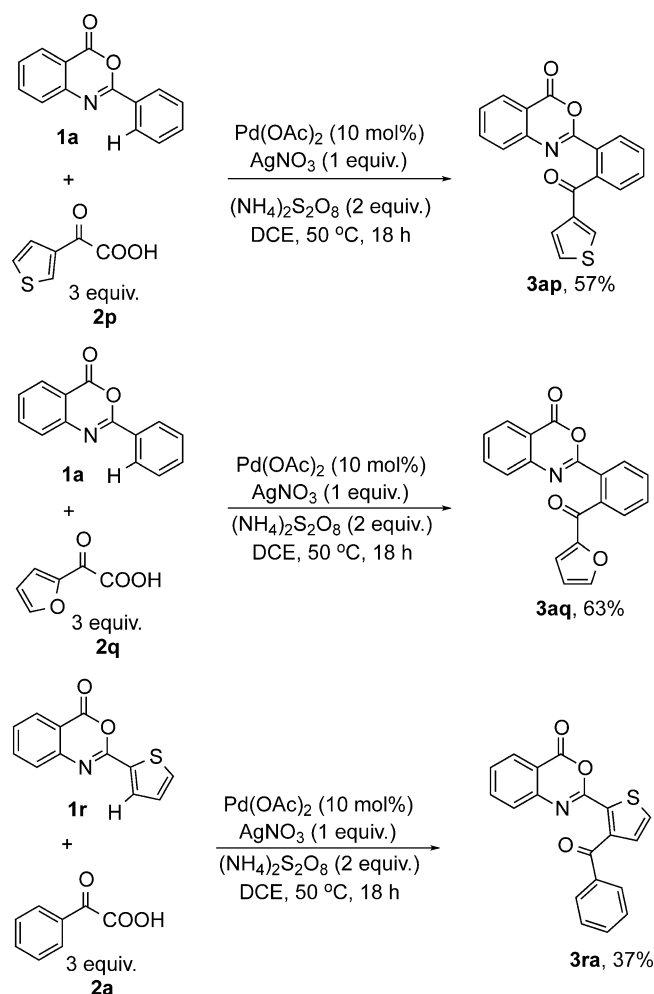


^[a] Reaction conditions: 2-aryl-4*H*-benzo[*d*][1,3]oxazin-4-one (0.5 mmol), phenylglyoxylic acid (1.5 mmol), $\text{Pd}(\text{OAc})_2$ (10 mol%), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1 mmol), AgNO_3 (0.5 mmol), DCE, 50 °C, 18 h.

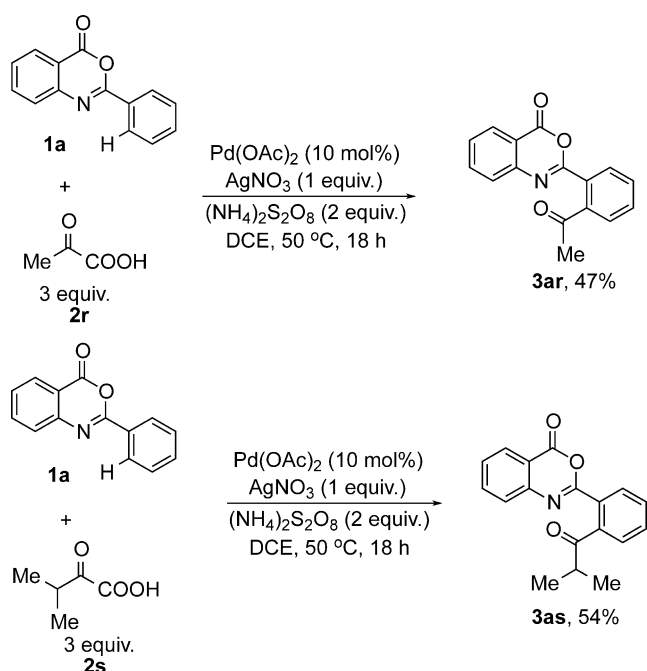
acids participated in this reaction efficiently affording good yield of products (**3ai**, **3aj**, **3bi** and **3bj**).

The effect of substituents on the phenyl ring of 2-aryl-4*H*-benzo[*d*][1,3]oxazin-4-one under the reaction conditions was studied (Table 3). Both electron-donating (CH_3 , OCH_3 and *t*-Bu) and electron-withdrawing groups (F, Cl) on the aromatic ring of 2-aryl-4*H*-benzo[*d*][1,3]oxazin-4-one are compatible with the reaction conditions. The *ortho*-substituted 2-aryl-4*H*-benzo[*d*][1,3]oxazin-4-one (**1k**) was found to produce a lower yield of product (**3ka**).

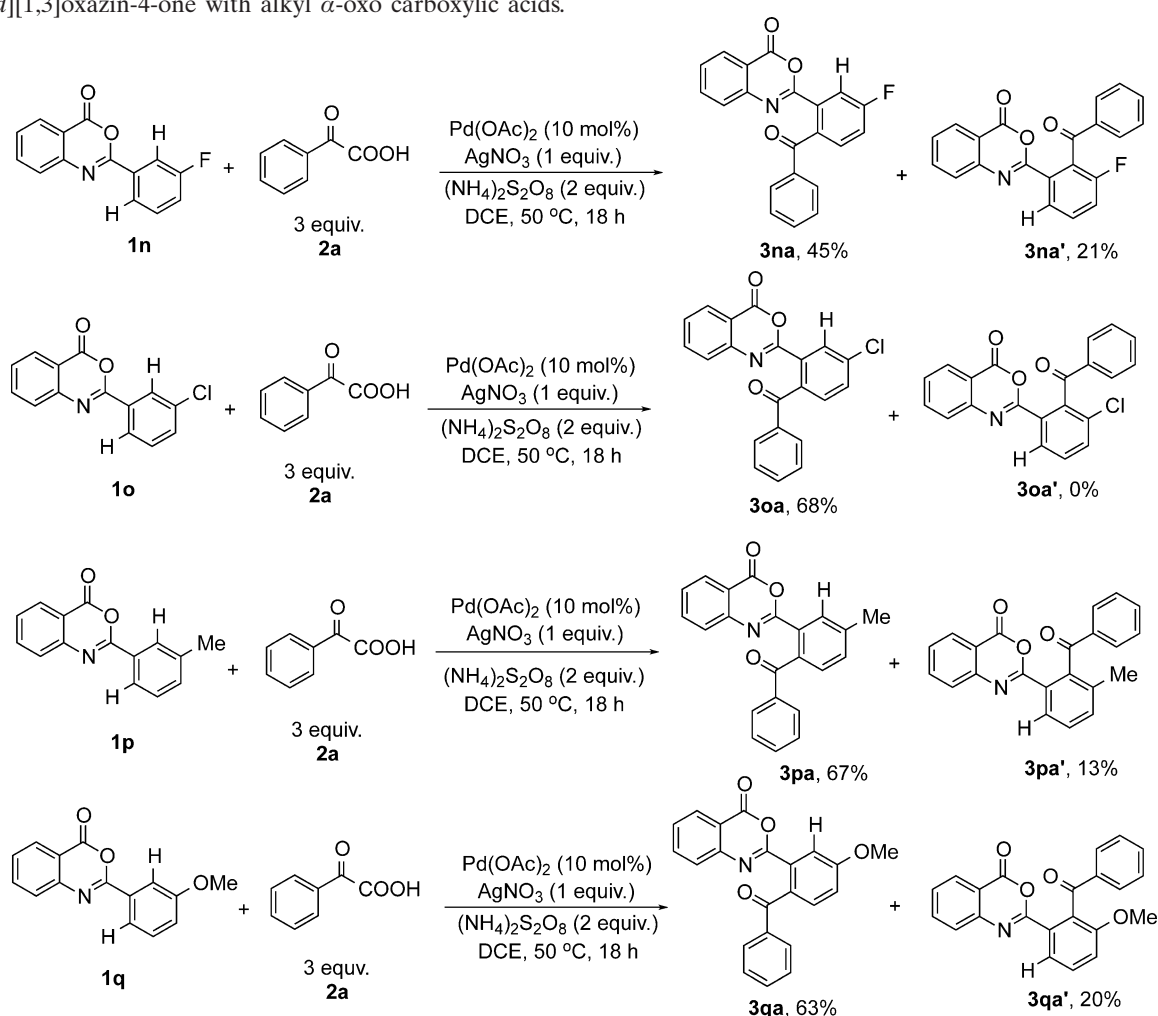
We checked this protocol of decarboxylative C–H acylation of benzoxazine-4-ones with heteroarylglyoxylic acids. Reactions with thiophenyl- (**2p**) and furanyl- (**2q**) glyoxylic acids were found to be successful producing good yields of acylated products (Scheme 2, **3ap** and **3aq**). We have also accomplished N-directed C–H acylation in the thiophenyl ring attached with the benzoxazine-4-one moiety (Scheme 2, **3ra**). This type of C–H acylation in a heteroarene unit is novel and was not been reported earlier.



Scheme 2. C–H acylation of benzoxazine-4-ones with heteroaryl glyoxylic acids.



Scheme 3. Pd-catalyzed C–H acylation of 2-phenyl-4H-benzo[d][1,3]oxazin-4-one with alkyl α -oxo carboxylic acids.



Scheme 4. C–H Acylation of *meta*-substituted 2-aryl-4H-benzo[d][1,3]oxazin-4-ones.

We have successfully performed the C–H acylations with alkylglyoxylic acids (Scheme 3) which is usually difficult to achieve.^[4,9a,k]

The 2-aryl-4H-benzo[d][1,3]oxazin-4-ones bearing *meta* substituents on the aryl ring showed excellent regioselectivity towards C–H acylation under these conditions (Scheme 4). In substrates **1n** (F), **1p** (CH₃) and **1q** (OCH₃), the acylation occurred preferentially at the N-directed positions although O-directed products are also formed in minor amounts. However, in case of *meta*-Cl substituted substrate (**1o**), acylation occurred exclusively at the N-directed position *para* to Cl (**3oa**). The structure of **3oa** was confirmed by X-ray crystallography too (Figure 2).^[20]

A suitably halo-substituted acyl 2-aryl-4H-benzo[d][1,3]oxazin-4-one may undergo further functionalization as outlined in Scheme 5. Thus, the corresponding acylated product from the reaction of **1h** and **2a** was subjected to Suzuki coupling to provide **3hax** with incorporation of a phenyl ring.

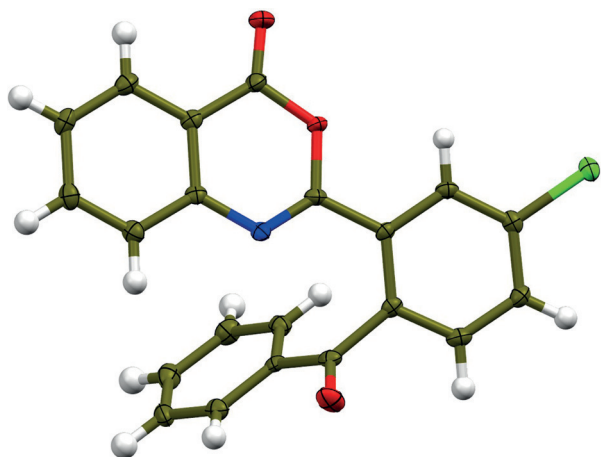
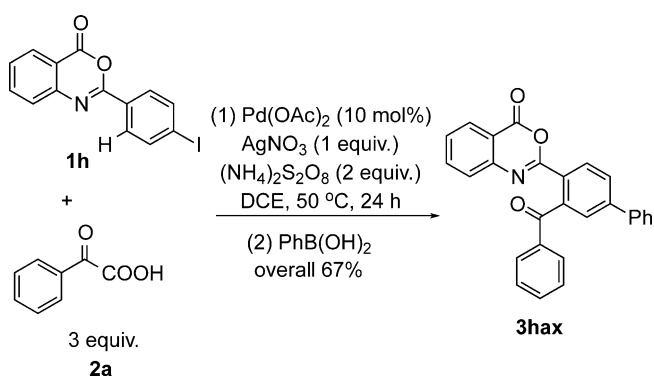


Figure 2. ORTEP diagram of 2-(2-benzoyl-5-chlorophenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 4, **30a**).

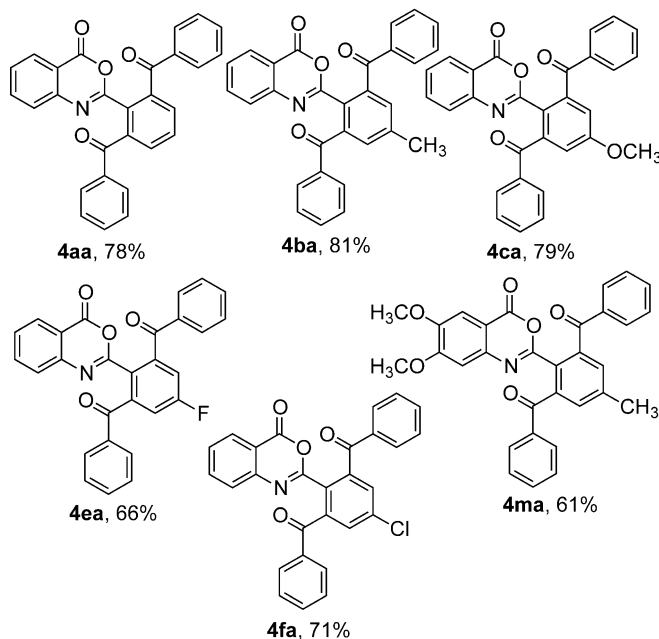
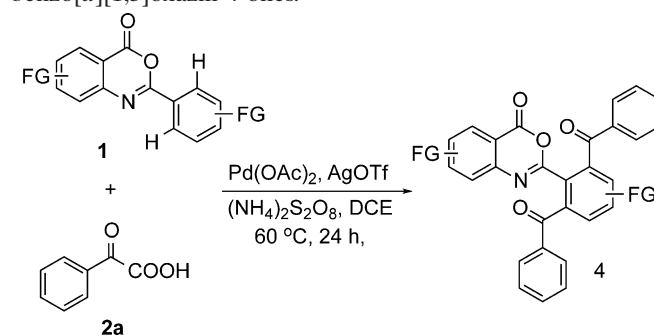


Scheme 5. Further functionalization of acylated products.

Interestingly, when the reaction was performed with AgOTf in place of AgNO₃ in the presence of 4 equivalents of glyoxylic acid, the bis-acylated product accommodating both N- and O-directed functionalization was obtained without any considerable amount (3–5%) of mono-acylated product. A series of bis-acylated products were obtained under the reaction conditions (Table 4, Table 5). The electron-donating groups, for example, OCH₃, CH₃ (**4ba**, **4ca** and **4ma**) and electron-withdrawing groups, for example, Cl, F (**4ea**, **4fa**) are compatible in this reaction. On close monitoring of the progress of the reaction it was established that the bis-acylated product was formed through the intermediacy of the mono-acylated one as depicted in Figure 3. The precise role of AgOTf in leading to bis-acylation is not very clear to us at this stage.

To investigate the mechanism of the reaction, the reaction was performed in the presence of 1 equivalent of TEMPO (a radical-trapping agent) under the standardized conditions. The outcome of the reaction did not change indicating that no free radical intermediate was involved in the reaction.

Table 4. Pd-catalyzed C–H bis-acylation of 2-aryl-4H-benzo[d][1,3]oxazin-4-ones.^[a]



^[a] Reaction conditions: 2-aryl-4H-benzo[d][1,3]oxazin-4-one (0.5 mmol), phenylglyoxylic acid (2 mmol), Pd(OAc)₂ (15 mol%), (NH₄)₂S₂O₈ (1 mmol), AgOTf (1 mmol), DCE, 60 °C, 24 h.

Table 5. Mono- vs. bis-acylated products.

2-Aryl-4H-benzo[d][1,3]-oxazin-4-one	Phenylglyoxylic acid	Mono-acylated product	Bis-acylated product
1a	2a	3aa (4%)	4aa (78%)
1b	2a	3ba (3%)	4ba (81%)
1c	2a	3ca (5%)	4ca (79%)
1e	2a	3ea (4%)	4ea (66%)
1f	2a	3fa (6%)	4fa (71%)
1m	2a	3ma (3%)	4ma (61%)

In accordance with the earlier reports^[5–9] it is assumed that the reaction initiates with the *ortho*-palladation of benzoxazine in the presence of Pd(OAc)₂ forming a 5-membered palladacycle(II) intermediate **A**, which then undergoes a trans-metallation with

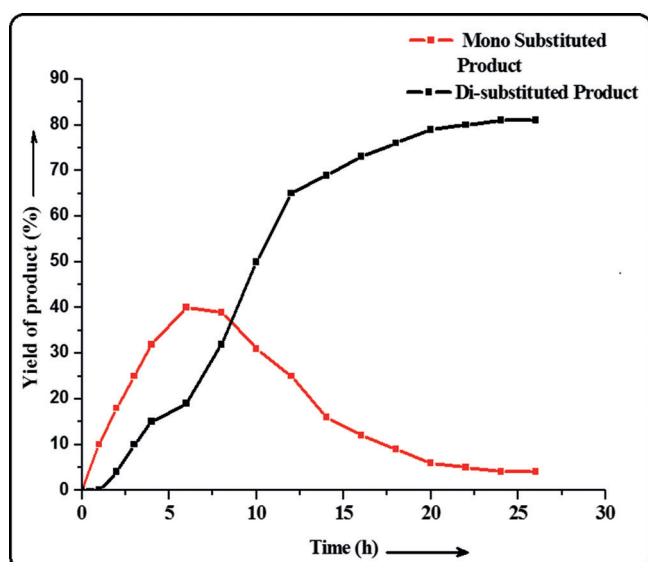
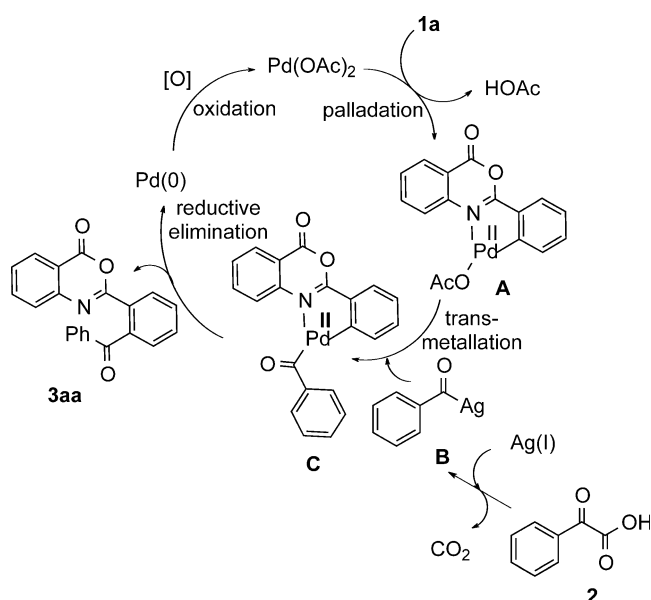


Figure 3. Monitoring the progress of the diacylated product.



Scheme 6. Plausible mechanism of the reaction.

acyl-silver species^[9f] **B** formed by the silver-mediated decarboxylation of phenylglyoxylic acid **2** to generate the intermediate **C**. In the next step, intermediate **C** undergoes a reductive elimination to provide the desired acylated product **3aa** and Pd(0) is reoxidized into Pd^{II} by AgNO₃ and (NH₄)₂S₂O₈, to start the next cycle (Scheme 6).

Conclusions

In summary, an efficient and general protocol for the decarboxylative selective acylation of 2-aryl-4H-

benzo[d][1,3]oxazin-4-ones has been developed via a palladium-catalyzed C–H activation process. To the best of our knowledge we are not aware of any earlier report on the acylation of 2-aryl-4H-benzo[d][1,3]oxazin-4-ones via C–H activation. Significantly, the mono-acylated product was obtained using AgNO₃ and (NH₄)₂S₂O₈ whereas replacement of AgNO₃ by AgOTf led to the bis-acylated compound. This is a novel and hitherto unreported observation and provides a convenient tool for an access to mono- or bis-acylated product by choice. The other notable features of this reaction are acylation with more challenging heteroarene-oxo carboxylic acids and alkyl oxo-carboxylic acids. This method provides a simple procedure for the synthesis of a library of acyl-2-aryl-4H-benzo[d][1,3]oxazin-4-ones which may have much potential in organic synthesis and the pharma industry.

Experimental Section

General Methods

IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids. NMR spectra were recorded at 300 and 500 MHz for ¹H spectra and at 75 and 125 MHz for ¹³C spectra in CDCl₃ solutions.

Representative Experimental Procedure for the Preparation of 2-aryl-4H benzo[d][1,3]oxazin-4-ones

To a solution of anthranilic acid (10 mmol, 1.37 g) in pyridine (30 mL) cooled at 0°C in an ice bath was added an acid chloride (0.02 mol) dropwise slowly and carefully with proper control. An exothermic reaction occurred. The reaction mixture was stirred for 5 min at 0°C. The ice bath was removed and the reaction mixture was allowed to warm slowly to room temperature (30°C). The reaction mixture was further stirred for 0.5 h at room temperature. After completion of the reaction (TLC) the mixture was poured into ice-cold water (200 mL) and residue was collected by filtration and washed with cold water (3 × 60 mL) and dried. The crude benzoxazin-4-one was recrystallized from ethanol as white prismatic needles.

Representative Experimental Procedure for the Mono-acylation of 2-Phenyl-4H-benzo[d][1,3]oxazin-4-one to 2-(2-Benzoylphenyl)-4H-benzo[d][1,3]oxazin-4-one

To a solution of 2-phenyl-4H-benzo[d][1,3]oxazin-4-one (0.5 mmol, 112 mg) and phenylglyoxylic acid (1.5 mmol, 226 mg) in dichloroethane (3 mL) were added AgNO₃ (0.5 mmol, 85 mg), (NH₄)₂S₂O₈ (1 mmol, 228 mg) and Pd(OAc)₂ (0.05 mmol, 11 mg). The resulting mixture was heated at 50°C under air for 18 h (TLC). After the reaction was complete, the mixture was allowed to cool to room temperature (30°C) and was extracted with ethyl acetate (3 × 20 mL). The extract was washed with water (10 mL) and

brine (10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent, the residue (crude product) was purified by column chromatography over silica gel (hexane/ethyl acetate 92:8) to afford the pure product, 2-(2-benzoylphenyl)-4H-benzo[d][1,3]oxazin-4-one (Table 2, **3aa**) as a white solid; yield: 139 mg (85%); mp 176–178 °C. ^1H NMR (300 MHz, CDCl_3): δ = 7.25 (d, J = 7.5 Hz, 1H), 7.34–7.45 (m, 4H), 7.51–7.54 (m, 1H), 7.64–7.70 (m, 3H), 7.78–7.82 (m, 2H), 8.10 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.25–8.28 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 116.6, 126.9, 128.6 (3C), 128.7 (2C), 129.0, 129.1 (2C), 129.2, 130.1, 132.3, 132.9, 136.6, 138.0, 141.3, 146.1, 155.6, 159.0, 197.1; IR (KBr): ν = 1746, 1717, 1679, 1616, 1466, 1359, 1146 cm^{-1} ; HR-MS: m/z = 328.0966, calcd. for $\text{C}_{21}\text{H}_{13}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$: 328.0968.

This procedure was followed for all the reactions listed in Table 2, Table 3, Scheme 2, Scheme 3, Scheme 4, and Scheme 5.

Representative Experimental Procedure for the Bisacylation of 2-Phenyl-4H-benzo[d][1,3]oxazin-4-one to {2-(4-Oxo-4H-benzo[d][1,3]oxazin-2-yl)-1,3-phenylene}bis(phenylmethanone)

To a solution of 2-phenyl-4H-benzo[d][1,3]oxazin-4-one (0.5 mmol, 112 mg) and phenylglyoxylic acid (2.0 mmol, 301 mg) in dichloroethane (3 mL) were added AgOTf (1.0 mmol, 257 mg), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1 mmol, 228 mg) and $\text{Pd}(\text{OAc})_2$ (0.075 mmol, 17 mg). The resulting mixture was heated at 60 °C under air for 24 h (TLC). After the reaction was complete, the mixture was allowed to cool to room temperature and was extracted with ethyl acetate (3 $\times$ 20 mL). The extract was washed with water (10 mL) and brine (10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent, the residue (crude product) was purified by column chromatography over silica gel (hexane/ethyl acetate 89:11) to afford the pure product, [2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-1,3-phenylene]bis(phenylmethanone) (Table 4, **4aa**) as a white solid; yield: 168 mg (78%); mp 258–260 °C. ^1H NMR (300 MHz, CDCl_3): δ = 7.29–7.37 (m, 2H), 7.39–7.45 (m, 2H), 7.50–7.60 (m, 5H), 7.62–7.66 (m, 2H), 7.83–7.85 (m, 1H), 7.97–8.05 (m, 4H), 8.18 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 95.5, 118.4, 123.8, 125.1, 125.3, 126.5 (2C), 128.7 (2C), 129.4 (2C), 129.9, 130.6 (2C), 130.9, 132.5, 133.0, 133.4, 134.3, 134.4, 135.8, 136.6, 136.8, 145.1, 162.0, 165.2, 193.9; IR (neat): ν = 1752, 1728, 1673, 1596, 1466, 1216 cm^{-1} ; HR-MS: m/z = 432.1231, calcd. for $\text{C}_{28}\text{H}_{18}\text{NO}_4$ [$\text{M} + \text{H}$] $^+$: 432.1230.

This procedure was followed for all the reactions listed in Table 4. All the products were obtained in high purity. All the products are unknown and characterized properly by spectroscopic data (IR, ^1H NMR, ^{13}C NMR, HR-MS and elemental analysis).

Characterization Data of all Products

2-[2-(2-Methylbenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, **3ab):** white solid; mp 98–100 °C; ^1H NMR (300 MHz, CDCl_3): δ = 2.69 (s, 3H), 7.04 (t, J = 8.1 Hz, 1H), 7.15–7.25 (m, 3H), 7.39–7.46 (m, 2H), 7.57–7.74 (m, 4H), 8.07–8.12 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.9,

116.5, 125.4, 127.0, 128.6, 128.7, 129.5, 129.6, 130.0, 130.5, 131.0, 131.8, 131.9 (2C), 136.5, 136.9, 139.9, 141.9, 146.2, 156.6, 159.0, 198.2; IR (KBr): ν = 1770, 1747, 1724, 1716, 1668, 1605, 1487 cm^{-1} ; HR-MS: m/z = 342.1127, calcd. for $\text{C}_{22}\text{H}_{15}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$: 342.1125.

2-[2-(3-Methoxybenzoyl)-4-methylphenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, **3bc):** off white solid; mp 192–194 °C; ^1H NMR (300 MHz, CDCl_3): δ = 2.41 (s, 3H), 3.72 (s, 3H), 6.78–6.82 (m, 1H), 7.04 (t, J = 1.8 Hz, 1H), 7.11–7.14 (m, 1H), 7.18–7.25 (m, 2H), 7.32–7.38 (m, 2H), 7.64–7.69 (m, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.99 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 8.13–8.16 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 22.1, 55.3, 94.2, 111.7, 114.7, 116.1, 117.9, 121.1, 123.9, 124.6, 125.4, 130.4, 130.7, 131.7, 135.8, 136.8, 139.2, 145.2, 145.5, 160.2, 162.4, 165.8, 196.4; IR (neat): ν = 2926, 1740, 1724, 1691, 1606, 1487, 1365, 1215 cm^{-1} ; anal. calcd. for $\text{C}_{23}\text{H}_{17}\text{NO}_4$: C 74.38, H 4.61, N 3.77; found C 74.36, H 4.65, N 3.79%.

2-[4-Methyl-2-(2-methylbenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, **3bb):** white solid; mp 101–103 °C; ^1H NMR (300 MHz, CDCl_3): δ = 2.48 (s, 3H), 2.74 (s, 3H), 7.01–7.06 (m, 1H), 7.17–7.28 (m, 3H), 7.35–7.45 (m, 4H), 7.67–7.73 (m, 1H), 8.02–8.10 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.7, 22.0, 116.5, 125.4, 126.9, 127.0, 128.4, 128.5, 129.5, 130.1, 131.0, 131.2, 131.7, 131.9, 136.5, 136.9, 139.9, 142.1, 142.9, 146.3, 156.5, 159.1, 198.5; IR (KBr): ν = 1774, 1761, 1663, 1601, 1248, 1003 cm^{-1} ; HR-MS: m/z = 356.1283, calcd. for $\text{C}_{23}\text{H}_{17}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$: 356.1281.

2-[2-(4-Fluorobenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, **3ae):** light yellow gummy liquid; ^1H NMR (300 MHz, CDCl_3): δ = 6.97–7.03 (m, 2H), 7.24–7.29 (m, 1H), 7.49–7.54 (m, 3H), 7.59–7.65 (m, 2H), 7.67–7.73 (m, 1H), 7.98–8.02 (m, 2H), 8.15 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 116.2, 116.4, 116.7, 121.3, 123.6, 125.0, 125.8, 127.8, 127.9, 129.3, 130.9, 131.0, 134.3, 136.1, 136.5, 144.9, 161.7, 164.0 (d, J_{CF} = 255.9 Hz, 1C), 196.4; IR (neat): ν = 1726, 1691, 1676, 1605, 1485, 1367, 1217 cm^{-1} ; anal. calcd. for $\text{C}_{21}\text{H}_{12}\text{FNO}_3$: C 73.04, H 3.50, N 4.06, found C 73.06, H 3.55, N 4.05%.

2-[2-(4-Chlorobenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, **3af):** off white solid; mp 132–134 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.27–7.31 (m, 3H), 7.45–7.51 (m, 3H), 7.60–7.65 (m, 2H), 7.68–7.73 (m, 1H), 7.98–8.02 (m, 2H), 8.15 (dd, J_1 = 8.1 Hz, J_2 = 0.3 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 94.1, 116.1, 121.3, 123.6, 125.0, 125.8, 127.2 (2C), 129.3, 129.7 (2C), 130.9, 131.0, 134.4, 136.1, 136.2, 136.5, 144.7, 162.2, 165.7, 196.6; IR (neat): ν = 3020, 1724, 1693, 1678, 1606, 1485, 1367, 1217 cm^{-1} ; HR-MS: m/z = 362.0577, calcd. for $\text{C}_{21}\text{H}_{13}\text{ClNO}_3$ [$\text{M} + \text{H}$] $^+$: 362.0578.

2-[2-(4-Bromobenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, **3ag):** white solid; mp 142–144 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.22–7.26 (m, 1H), 7.45–7.53 (m, 4H), 7.65–7.70 (m, 5H), 8.13 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.26–8.29 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 116.7, 126.9, 128.1, 128.5, 128.7, 128.8, 128.9, 129.3, 130.3, 130.6 (2C), 131.9 (2C), 132.4, 136.7, 136.8, 140.8, 145.9, 155.4, 158.9, 196.0; IR (KBr): ν = 1749, 1732, 1716, 1672, 1601, 1487, 1369 cm^{-1} ; HR-MS: m/z = 406.0078, calcd. for $\text{C}_{21}\text{H}_{12}\text{BrNO}_3$ [$\text{M} + \text{H}$] $^+$: 406.0073.

2-[2-(4-Iodobenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, **3ah):** white solid; mp 186–188 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.24–7.27 (m, 3H), 7.47–7.52 (m,

2H), 7.58–7.72 (m, 5H), 7.96–8.01 (m, 1H), 8.13 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 96.0, 116.1, 121.2, 123.6, 125.0, 125.8, 127.5 (2C), 130.4, 130.9, 131.0, 134.3, 136.1, 137.4, 137.9, 138.5 (2C), 144.5, 162.1, 165.6, 196.2; IR (neat): ν = 1751, 1732, 1718, 1670, 1602, 1485, 1369 cm^{-1} ; HR-MS: m/z = 453.9937, calcd. for $\text{C}_{21}\text{H}_{12}\text{INO}_3$ $[\text{M} + \text{H}]^+$: 453.9935.

2-[2-(4-Acetylbenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, 3am): white solid; mp 212–214 °C; ^1H NMR (300 MHz, CDCl_3): δ = 2.51 (s, 3H), 7.22–7.27 (m, 1H), 7.48–7.51 (m, 1H), 7.60–7.70 (m, 5H), 7.87–7.90 (m, 2H), 7.97–8.01 (m, 2H), 8.16 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 26.7, 116.0, 121.2, 123.6, 125.1, 125.8, 126.1 (2C), 129.3 (2C), 129.4, 130.9, 131.2, 134.4, 136.1, 136.5, 138.1, 142.4, 144.3, 162.1, 165.6, 194.7, 197.1; IR (KBr): ν = 1732, 1691, 1603, 1483, 1363, 1230 cm^{-1} ; HR-MS: m/z = 370.1072, calcd. for $\text{C}_{23}\text{H}_{16}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 370.1074.

4-[2-(4-Oxo-4H-benzo[d][1,3]oxazin-2-yl)benzoyl]benzonitrile (Table 2, 3an): white solid; mp 144–146 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.25–7.31 (m, 1H), 7.48–7.50 (m, 1H), 7.62–7.73 (m, 7H), 7.99–8.03 (m, 2H), 8.16 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 93.7, 113.9, 115.8, 117.8, 121.3, 123.6, 125.2, 126.0, 126.6 (2C), 129.3, 130.9, 131.4, 133.3 (2C), 134.5, 136.3, 142.8, 143.9, 161.8, 165.5, 197.2; IR (neat): ν = 2926, 2233, 1751, 1738, 1726, 1711, 1691, 1606, 1485, 1367, 1217 cm^{-1} ; anal. calcd. for $\text{C}_{22}\text{H}_{12}\text{N}_2\text{O}_3$: C 74.99, H 3.43, N 7.95; found: C 74.95, H 3.45, N 7.93%.

2-[2-(4-Nitrobenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, 3ao): light yellow solid; mp 241–243 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.23–7.28 (m, 1H), 7.47–7.50 (m, 1H), 7.61–7.65 (m, 2H), 7.70–7.76 (m, 3H), 7.97 (m, 2H), 8.13–8.18 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 93.7, 115.7, 121.3, 123.6, 124.6 (2C), 125.3, 126.1, 127.0 (2C), 129.3, 130.9, 131.4, 134.5, 136.3, 143.7, 144.6, 148.7, 161.7, 165.4, 196.8; IR (neat): ν = 3018, 2928, 1728, 1691, 1678, 1606, 1525, 1466, 1360 cm^{-1} ; anal. calcd. for $\text{C}_{21}\text{H}_{12}\text{N}_2\text{O}_5$: C 67.74, H 3.25, N 7.52; found: C 67.77, H 3.27, N 7.49%.

2-[2-(2-Naphthoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, 3ai): off white solid; mp 222–224 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.21–7.24 (m, 1H), 7.34–7.39 (m, 1H), 7.46–7.51 (m, 1H), 7.54–7.64 (m, 3H), 7.69–7.73 (m, 2H), 7.81 (t, J = 7.2 Hz, 2H), 7.88 (d, J = 8.4 Hz, 1H), 8.04–8.12 (m, 3H), 8.30–8.34 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 116.6, 124.6, 126.8, 127.0, 127.9, 128.51, 128.54, 128.6 (2C), 128.7, 128.9, 129.3, 129.6, 130.1, 131.1, 132.3, 132.5, 135.5, 135.6, 136.5, 141.5, 146.0, 155.5, 159.0, 197.1; IR (neat): ν = 3018, 2928, 1745, 1728, 1715, 1693, 1668, 1487 cm^{-1} ; HR-MS: m/z = 378.1126, calcd. for $\text{C}_{21}\text{H}_{15}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 378.1125.

2-[2-(1-Naphthoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, 3aj): light brown solid; mp 132–134 °C; ^1H NMR (300 MHz, CDCl_3): δ = 6.99 (d, J = 8.1 Hz, 1H), 7.24–7.33 (m, 2H), 7.43–7.49 (m, 2H), 7.52–7.57 (m, 1H), 7.68–7.73 (m, 4H), 7.79 (d, J = 7.1 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.99 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 8.17–8.20 (m, 1H), 9.23 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 116.4, 124.1, 126.7, 126.8, 127.2, 128.2, 128.3, 128.4, 128.5, 129.5, 129.9, 130.0, 130.5, 130.6, 131.1, 132.0, 133.4, 134.0, 135.0, 136.3, 142.3, 145.8, 156.0, 159.0, 198.3; IR (neat): ν = 2926, 2854, 1767, 1732, 1715, 1693, 1651, 1645, 1574,

1371 cm^{-1} ; HR-MS: m/z = 400.0953, calcd. for $\text{C}_{25}\text{H}_{15}\text{NO}_3$ $[\text{M} + \text{Na}]^+$: 400.0944.

2-[2-(2-Naphthoyl)-4-methylphenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, 3bi): white solid; mp 121–123 °C; ^1H NMR (300 MHz, CDCl_3): δ = 2.56 (s, 3H), 7.24 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.48–7.66 (m, 5H), 7.83–7.87 (m, 4H), 7.91–7.97 (m, 1H), 8.08 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.13–8.18 (m, 2H), 8.26 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.8, 116.6, 124.6, 125.5, 126.7, 126.8, 127.9, 128.3, 128.4, 128.5, 128.6, 129.2, 129.3, 129.6, 130.7, 131.0, 132.2, 132.5, 135.5, 136.5, 141.6, 143.3, 146.2, 155.5, 159.1, 197.4; IR (neat): ν = 2926, 1767, 1740, 1668, 1626, 1508, 1254 cm^{-1} ; HR-MS: m/z = 392.1284, calcd. for $\text{C}_{26}\text{H}_{18}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 392.1281.

2-[2-(1-Naphthoyl)-4-methylphenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, 3bj): white solid; mp 112–114 °C; ^1H NMR (300 MHz, CDCl_3): δ = 2.50 (s, 3H), 6.90–6.93 (m, 1H), 7.22–7.29 (m, 2H), 7.39–7.48 (m, 4H), 7.51–7.57 (m, 1H), 7.70–7.84 (m, 3H), 7.96 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 9.28 (d, J = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.7, 116.3, 124.1, 126.6, 126.8, 126.9, 127.1, 128.1, 128.2 (2C), 128.5, 129.4, 130.5, 130.6, 131.1 (2C), 133.3, 134.0, 135.0, 136.2, 142.5, 142.9, 145.9, 155.9, 159.1, 198.6; IR (KBr): ν = 1761, 1716, 1670, 1620, 1603, 1250 cm^{-1} ; anal. calcd. for $\text{C}_{26}\text{H}_{17}\text{NO}_3$: C 79.78, H 4.38, N 3.58; found: C 79.80, H 4.39, N 3.56%.

2-[2-(2-Fluorobenzoyl)-4-methylphenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, 3bk): colourless gummy liquid; ^1H NMR (300 MHz, CDCl_3): δ = 2.42 (s, 3H), 6.88–6.95 (m, 1H), 7.12–7.27 (m, 2H), 7.28–7.33 (m, 2H), 7.38–7.41 (m, 1H), 7.63–7.69 (m, 1H), 7.73–7.79 (m, 1H), 7.87 (d, J = 7.8 Hz, 1H), 8.00 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 8.10–8.12 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 22.1, 115.8, 117.3 (d, J_{CF} = 21.7 Hz, 1C), 121.1, 123.9, 124.5, 124.7 (d, J_{CF} = 3.7 Hz, 1C), 125.0 (d, J_{CF} = 9 Hz, 1C), 125.4, 127.6, 128.7, 130.6, 131.8 (d, J_{CF} = 8.3 Hz, 1C), 132.0, 136.0, 136.7, 143.8, 145.4, 159.4 (d, J_{CF} = 250.5 Hz, 1C), 162.5, 165.3, 196.6; IR (KBr): ν = 1775, 1730, 1672, 1622, 1598, 1242, 1151 cm^{-1} ; anal. calcd. for $\text{C}_{22}\text{H}_{14}\text{FNO}_3$: C 73.53, H 3.93, N 3.90; found: C 73.55, H 3.96, N 3.88%.

2-[2-(2-Chlorobenzoyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Table 2, 3al): white solid; mp 132–134 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.18–7.27 (m, 3H), 7.33–7.40 (m, 2H), 7.59–7.70 (m, 3H), 7.98–8.01 (m, 2H), 8.05–8.09 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 116.2, 121.4, 123.6, 124.5, 125.8, 127.6, 129.8, 130.4, 131.1, 131.2, 132.5, 133.7, 134.0, 135.9, 136.3, 142.5, 162.7, 165.9, 191.9; IR (KBr): ν = 1751, 1722, 1682, 1604, 1485, 1367 cm^{-1} ; HR-MS: m/z = 362.0577, calcd. for $\text{C}_{21}\text{H}_{13}\text{ClNO}_3$ $[\text{M} + \text{H}]^+$: 362.0578.

2-(2-Benzoyl-4-methylphenyl)-4H-benzo[d][1,3]oxazin-4-one (Table 3, 3ba): white solid; mp 191–193 °C; ^1H NMR (300 MHz, CDCl_3): δ = 2.45 (s, 3H), 7.18 (d, J = 7.8 Hz, 1H), 7.28–7.43 (m, 6H), 7.60 (t, J = 8.1 Hz, 1H), 7.77–7.80 (m, 2H), 8.03 (d, J = 7.8 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 21.6, 116.4, 125.9, 126.6, 128.30, 128.32, 128.4 (2C), 128.9 (2C), 129.0, 129.1, 130.6, 132.7, 136.4, 137.9, 141.3, 143.2, 146.0, 155.4, 158.9, 197.1; IR (KBr): ν = 1745, 1717, 1680, 1603, 1485, 1360 cm^{-1} ; HR-MS: m/z = 342.1124, calcd. for $\text{C}_{22}\text{H}_{15}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 342.1125.

2-(2-Benzoyl-4-methoxyphenyl)-4H-benzo[d][1,3]oxazin-4-one (Table 3, 3ca): white solid; mp 236–238 °C; ^1H NMR (300 MHz, CDCl_3): δ = 3.83 (s, 3H), 6.94 (s, 1H), 7.04–7.13

(m, 2H), 7.25–7.39 (m, 4H), 7.55 (t, $J=7.5$ Hz, 1H), 7.78 (d, $J=7.8$ Hz, 2H), 7.98 (d, $J=7.8$ Hz, 1H), 8.16 (d, $J=8.7$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=55.7$, 114.0, 114.9, 116.1, 120.5, 126.3, 127.9, 128.2, 128.4 (2C), 128.8 (2C), 130.9, 132.7, 136.3, 137.6, 143.3, 146.1, 155.1, 158.9, 162.6, 196.4; IR (KBr): $\nu=1720$, 1682, 1620, 1605, 1487, 1348, 1209, 1130 cm^{-1} ; anal. calcd. for $\text{C}_{22}\text{H}_{15}\text{NO}_4$: C 73.94, H 4.23, N 3.92; found: C 73.97, H 4.26, N 3.89%.

2-[2-Benzoyl-4-(*tert*-butyl)phenyl]-4H-benzo[d]

[1,3]oxazin-4-one (Table 3, 3da): light yellow solid; mp 203–205 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=1.37$ (s, 9H), 7.20–7.23 (m, 1H), 7.28–7.45 (m, 4H), 7.50–7.53 (m, 1H), 7.59–7.67 (m, 2H), 7.79–7.82 (m, 2H), 8.06 (dd, $J_1=8.1$ Hz, $J_2=1.2$ Hz, 1H), 8.18 (d, $J=8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=31.1$ (3C), 35.4, 116.4, 125.6, 126.0, 126.7, 127.0, 128.3, 128.4, 128.5 (2C), 125.7, 126.8, 128.5 (2C), 132.7, 136.4, 138.1, 141.1, 146.1, 155.5, 156.2, 159.1, 197.5; IR (neat): $\nu=2962$, 2926, 1747, 1728, 1715, 1693, 1668, 1487, 1362 cm^{-1} ; HR-MS: $m/z=384.1592$, calcd. for $\text{C}_{25}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 384.1594.

2-(2-Benzoyl-4-fluorophenyl)-4H-benzo[d][1,3]oxazin-4-one (Table 3, 3ea): white solid; mp 138–140 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=7.18$ –7.22 (m, 2H), 7.29–7.45 (m, 5H), 7.62–7.67 (m, 1H), 7.77–7.81 (m, 2H), 8.07 (dd, $J_1=7.8$ Hz, $J_2=1.2$ Hz, 1H), 8.27 (q, $J=5.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=116.2$ (d, $J_{\text{CF}}=23.3$ Hz, 1C), 116.7 (d, $J_{\text{CF}}=32.3$ Hz, 1C), 125.7, 126.8, 128.5, 128.6 (2C), 128.7, 129.1 (2C), 129.5, 131.6, 131.7, 133.2, 136.6, 137.3, 145.9, 154.6, 158.8, 164.8 (d, $J_{\text{CF}}=255.7$ Hz, 1C), 195.2; IR (KBr): $\nu=1747$, 1730, 1680, 1605, 1485, 1369, 1269 cm^{-1} ; HR-MS: $m/z=346.0877$, calcd. for $\text{C}_{21}\text{H}_{12}\text{FNO}_3$ $[\text{M}+\text{H}]^+$: 346.0874.

2-(2-Benzoyl-4-chlorophenyl)-4H-benzo[d][1,3]oxazin-4-one (Table 3, 3fa): white solid; mp 168–170 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=7.22$ (dd, $J_1=8.1$ Hz, $J_2=0.6$ Hz, 1H), 7.38–7.45 (m, 3H), 7.47–7.50 (m, 3H), 7.63–7.71 (m, 2H), 7.80–7.84 (m, 2H), 8.12 (dd, $J_1=8.1$ Hz, $J_2=1.5$ Hz, 1H), 8.23 (d, $J=8.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=116.6$, 126.9, 127.2, 128.6, 128.7 (2C), 128.8, 128.9, 129.1 (2C), 130.2, 130.5, 133.3, 136.7, 137.4, 138.9, 142.9, 145.9, 154.6, 158.7, 195.3; IR (neat): $\nu=2924$, 1728, 1695, 1678, 1605, 1487, 1365 cm^{-1} ; HR-MS: $m/z=362.0577$, calcd. for $\text{C}_{21}\text{H}_{13}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 362.057.

2-(2-Benzoyl-4-bromophenyl)-4H-benzo[d][1,3]oxazin-4-one (Table 3, 3ga): white solid; mp 242–244 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=7.18$ –7.21 (m, 1H), 7.35–7.50 (m, 4H), 7.62–7.65 (m, 2H), 7.76–7.81 (m, 3H), 8.07 (dd, $J_1=7.8$ Hz, $J_2=1.5$ Hz, 1H), 8.12 (d, $J=8.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=116.5$, 126.9, 127.3, 127.6, 128.6, 128.7 (2C), 128.9, 129.1 (2C), 130.5, 131.6, 133.1, 133.2, 136.6, 137.4, 142.8, 145.8, 154.7, 158.6, 195.2; IR (KBr): $\nu=1745$, 1718, 1676, 1603, 1483, 1360, 1246 cm^{-1} ; HR-MS: $m/z=406.0078$, calcd. for $\text{C}_{21}\text{H}_{12}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$: 406.0073.

2-(2-Benzoylphenyl)-7-chloro-4H-benzo[d][1,3]oxazin-4-one (Table 3, 3ia): white solid; mp 161–163 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=7.22$ (d, $J=1.8$ Hz, 1H), 7.35–7.41 (m, 3H), 7.46–7.52 (m, 2H), 7.65–7.70 (m, 2H), 7.78–7.81 (m, 2H), 8.01 (d, $J=8.7$ Hz, 1H), 8.23–8.26 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=114.9$, 125.6, 126.6, 128.6 (2C), 128.7, 129.1 (2C), 129.2, 129.3, 129.8, 130.1, 132.5, 133.1, 137.7, 141.5, 142.9, 147.1, 156.9, 158.1, 196.8; IR (KBr): $\nu=1761$, 1732, 1668, 1626, 1597, 1568, 1269 cm^{-1} ;

HR-MS: $m/z=362.0578$, calcd. for $\text{C}_{21}\text{H}_{13}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 362.0578.

2-(2-Benzoyl-4-methylphenyl)-7-chloro-4H-benzo[d]

[1,3]oxazin-4-one (Table 3, 3ja): white solid; mp 173–175 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=2.47$ (s, 3H), 7.16 (s, 1H), 7.29–7.46 (m, 6H), 7.77–7.80 (m, 2H), 7.97 (dd, $J_1=8.4$ Hz, $J_2=1.2$ Hz, 1H), 8.12 (d, $J=8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=21.7$, 114.8, 125.5, 126.4, 128.5 (2C), 128.9, 129.0 (2C), 129.2, 129.3, 129.7, 130.6, 132.9, 137.8, 141.5, 142.8, 143.7, 147.1, 156.8, 158.2, 196.9; IR (KBr): $\nu=1755$, 1724, 1670, 1595, 1211, 1011 cm^{-1} ; HR-MS: $m/z=376.0732$, calcd. for $\text{C}_{22}\text{H}_{15}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 376.0735.

2-(2-Benzoyl-6-chlorophenyl)-4H-benzo[d][1,3]oxazin-4-one (Table 3, 3ak): white solid; mp 156–158 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=7.24$ (d, $J=8.7$ Hz, 1H), 7.36–7.45 (m, 3H), 7.50–7.53 (m, 1H), 7.63–7.69 (m, 3H), 7.78–7.81 (m, 2H), 8.09 (dd, $J_1=8.1$ Hz, $J_2=1.5$ Hz, 1H), 8.24–8.27 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=116.6$, 126.9, 128.5 (2C), 128.7 (2C), 128.9, 129.1 (2C), 129.2, 129.4, 130.1, 132.2, 132.9, 136.5, 137.9, 141.3, 146.0, 155.5, 159.0, 197.0; IR (KBr): $\nu=1749$, 1732, 1699, 1659, 1487, 1360 cm^{-1} ; HR-MS: $m/z=362.0577$, calcd. for $\text{C}_{21}\text{H}_{13}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 362.0578.

2-(2-Benzoylphenyl)-6,7-dimethoxy-4H-benzo[d]

[1,3]oxazin-4-one (Table 3, 3la): white solid; mp 189–191 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=3.90$ (s, 3H), 3.91 (s, 3H), 6.62 (s, 1H), 7.31–7.43 (m, 4H), 7.51–7.53 (m, 1H), 7.64–7.67 (m, 2H), 7.76–7.79 (m, 2H), 8.20–8.23 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=56.4$, 56.5, 107.5, 107.6, 109.2, 128.5 (2C), 128.7, 128.8, 128.9 (2C), 129.2, 130.1, 131.9, 132.8, 138.1, 140.9, 142.4, 150.0, 154.9, 156.3, 158.9, 197.1; IR (KBr): $\nu=1751$, 1715, 1668, 1603, 1510, 1288 cm^{-1} ; anal. calcd. for $\text{C}_{23}\text{H}_{17}\text{NO}_5$: C 71.31, H 4.42, N 3.62; found: C 71.35, H 4.45, N 3.60%.

2-(2-Benzoyl-4-methylphenyl)-6,7-dimethoxy-4H-benzo[d][1,3]oxazin-4-one (Table 3, 3la): light yellow solid; mp 203–205 °C; ^1H NMR (300 MHz, CDCl_3): $\delta=2.46$ (s, 3H), 3.87 (s, 3H), 3.89 (s, 3H), 6.58 (s, 1H), 7.30–7.37 (m, 4H), 7.39–7.44 (m, 2H), 7.76–7.79 (m, 2H), 8.10 (d, $J=8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=21.6$, 55.4, 56.4, 107.4, 107.5, 109.0, 126.2, 128.4 (2C), 128.7, 128.9 (2C), 129.2, 130.7, 132.7, 138.1, 140.9, 142.5, 142.9, 149.7, 154.9, 156.2, 159.0, 197.3; IR (KBr): $\nu=1747$, 1666, 1618, 1603, 1502, 1290, 1248, 1026 cm^{-1} ; HR-MS: $m/z=402.1335$, calcd. for $\text{C}_{24}\text{H}_{20}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 402.1336.

2-[2-(Thiophene-3-carbonyl)phenyl]-4H-benzo[d]

[1,3]oxazin-4-one (Scheme 2, 3ap): off white gummy liquid; ^1H NMR (300 MHz, CDCl_3): $\delta=6.91$ (dd, $J_1=4.8$ Hz, $J_2=1.2$ Hz, 1H), 7.21–7.29 (m, 2H), 7.55–7.72 (m, 5H), 7.97–8.05 (m, 2H), 8.12–8.15 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=93.0$, 116.1, 121.1, 123.6, 124.9, 125.1, 125.7, 128.0, 129.4, 130.8, 131.0, 134.2, 135.9, 136.6, 139.1, 144.3, 162.5, 165.4, 191.5; IR (neat): $\nu=2959$, 1726, 1680, 1607, 1487, 1364, 1253 cm^{-1} ; HR-MS: $m/z=334.0532$, calcd. for $\text{C}_{19}\text{H}_{12}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 334.0532.

2-[2-(Furan-2-carbonyl)phenyl]-4H-benzo[d][1,3]oxazin-4-one (Scheme 2, 3aq): light yellow gummy liquid; ^1H NMR (300 MHz, CDCl_3): $\delta=6.43$ (q, $J=1.8$ Hz, 1H), 6.99–7.00 (m, 1H), 7.40 (d, $J=8.1$ Hz, 1H), 7.44–7.51 (m, 2H), 7.57–7.60 (m, 1H), 7.65–7.75 (m, 3H), 8.15 (dd, $J_1=7.8$ Hz, $J_2=1.2$ Hz, 1H), 8.21–8.24 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=112.4$, 116.6, 118.4, 127.2, 128.6, 128.7, 128.8, 129.3, 129.4, 130.6, 132.1, 136.7, 139.9, 146.2, 146.8, 153.2,

155.9, 159.1, 184.3; IR (neat): ν =1771, 1723, 1670, 1601, 1486, 1247 cm^{-1} ; anal. calcd. for $\text{C}_{19}\text{H}_{11}\text{NO}_4$: C 71.92, H 3.49, N 4.41, found: C 71.93, H 3.51, N 4.38%.

2-(3-Benzoylthiophen-2-yl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 2, 3ra): colourless gummy liquid; ^1H NMR (300 MHz, CDCl_3): δ =7.25–7.32 (m, 2H), 7.38–7.45 (m, 3H), 7.50–7.56 (m, 1H), 7.66–7.69 (m, 2H), 7.87–7.90 (m, 2H), 8.06–8.09 (dd, J_1 =7.8 Hz, J_2 =1.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ =116.5, 127.0, 128.4, 128.6, 128.7 (2C), 128.8, 129.4 (3C), 131.4, 133.5, 136.6, 137.6, 144.5, 146.5, 152.5, 158.2, 193.3; IR (KBr): ν =1761, 1670, 1601, 1416, 1267, 1038 cm^{-1} ; HR-MS: m/z =334.0534, calcd. for $\text{C}_{19}\text{H}_{12}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 334.0532.

2-(2-Acetylphenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 3, 3ar): white solid; mp 142–144 °C; ^1H NMR (300 MHz, CDCl_3): δ =1.95 (s, 3H), 7.34–7.39 (m, 1H), 7.62–7.67 (m, 1H), 7.72–7.79 (m, 3H), 7.95–7.97 (m, 1H), 8.10–8.17 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ =24.5, 92.7, 115.7, 121.5, 122.7, 124.8, 125.7, 130.8, 131.1, 134.1, 135.9, 136.3, 144.3, 162.1, 164.9, 203.2; IR (KBr): ν =1736, 1726, 1678, 1605, 1489, 1373, 1240 cm^{-1} ; anal. calcd. for $\text{C}_{16}\text{H}_{11}\text{NO}_3$: C 72.45, H 4.18, N 5.28; found: C 72.42, H 4.20, N 5.30%.

2-(2-Isobutyrylphenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 3, 3as): colourless gummy liquid; ^1H NMR (300 MHz, CDCl_3): δ =0.56 (d, J =6.6 Hz, 3H), 1.32 (d, J =6.9 Hz, 3H), 2.64–2.73 (m, 1H), 7.29–7.34 (m, 1H), 7.59–7.76 (m, 4H), 7.95 (d, J =7.2 Hz, 1H), 8.09–8.16 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ =16.4, 17.2, 35.0, 97.5, 116.0, 120.9, 123.9, 124.7, 125.5, 130.6, 130.9, 133.4, 135.9, 136.4, 141.3, 161.9, 165.1, 201.3; IR (neat): ν =2925, 1725, 1670, 1601, 1449, 1357 cm^{-1} ; anal. calcd. for $\text{C}_{18}\text{H}_{15}\text{NO}_3$: C 73.71, H 5.15, N 4.78, found: C 73.69, H 5.16, N 4.79%.

2-(2-Benzoyl-5-fluorophenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 4, 3na): off white solid; mp 192–194 °C; ^1H NMR (300 MHz, CDCl_3): δ =7.27 (d, J =8.1 Hz, 1H), 7.33–7.39 (m, 3H), 7.41–7.46 (m, 2H), 7.49–7.54 (m, 1H), 7.65–7.71 (m, 1H), 7.76–7.79 (m, 2H), 7.93 (dd, J_1 =9.3 Hz, J_2 =2.7 Hz, 1H), 8.07–8.10 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ =94.2, 111.8 (d, J_{CF} =24 Hz, 1C), 116.2, 121.2, 121.7 (d, J_{CF} =24 Hz, 1C), 125.61 (2C), 125.62 (d, J_{CF} =8.3 Hz, 1C), 129.5 (2C), 129.8, 130.8, 131.8 (d, J_{CF} =33 Hz, 1C), 136.0, 136.4, 137.2, 140.7 (d, J_{CF} =2.3 Hz, 1C), 162.2, 164.2 (d, J_{CF} =250.5, 1C), 164.5 (d, J_{CF} =3.8 Hz, 1C), 196.2; IR (KBr): ν =1746, 1729, 1679, 1606, 1484, 1269 cm^{-1} ; HR-MS: m/z =346.0877, calcd. for $\text{C}_{21}\text{H}_{12}\text{FNO}_3$ $[\text{M}+\text{H}]^+$: 346.0874.

2-(2-Benzoyl-3-fluorophenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 4, 3na'): light yellow solid; mp 186–188 °C; ^1H NMR (300 MHz, CDCl_3): δ =7.11–7.14 (m, 1H), 7.39–7.48 (m, 4H), 7.52–7.61 (m, 1H), 7.63–7.69 (m, 2H), 7.89–7.91 (m, 2H), 8.11–8.15 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ =116.8, 120.1 (d, J_{CF} =21.7 Hz, 1C), 125.0 (d, J_{CF} =3 Hz, 1C), 126.9, 128.7, 128.8 (2C), 128.9 (2C), 129.0, 129.1, 130.4 (d, J_{CF} =4.5 Hz, 1C), 131.0 (d, J_{CF} =8.3 Hz, 1C), 133.4, 136.7, 137.9, 145.8, 154.2, 158.7, 159.8 (d, J_{CF} =246 Hz, 1C), 192.6; IR (KBr): ν =2924, 1776, 1734, 1668, 1630, 1603, 1454, 1259 cm^{-1} ; HR-MS: m/z =346.0877, calcd. for $\text{C}_{21}\text{H}_{12}\text{FNO}_3$ $[\text{M}+\text{H}]^+$: 346.0874.

2-(2-Benzoyl-5-chlorophenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 4, 3oa): white solid; mp 171–173 °C; ^1H NMR (300 MHz, CDCl_3): δ =7.22–7.26 (m, 1H), 7.36 (t, J =

6.9 Hz, 2H), 7.43–7.46 (m, 3H), 7.61–7.66 (m, 2H), 7.75–7.78 (m, 2H), 8.07 (d, J =7.8 Hz, 1H), 8.22 (d, J =1.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ =116.5, 126.9, 128.6 (2C), 129.0 (3C), 129.1, 130.0, 130.6, 132.1, 133.1, 136.3, 136.6, 138.6, 139.4, 145.7, 154.3, 158.5, 195.8; IR (KBr): ν =1774, 1672, 1622, 1599, 1261 cm^{-1} ; HR-MS: m/z =362.0578, calcd. for $\text{C}_{21}\text{H}_{13}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 362.0578.

2-(2-Benzoyl-5-methylphenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 4, 3pa): white solid; mp 198–200 °C; ^1H NMR (300 MHz, CDCl_3): δ =2.47 (s, 3H), 7.23–7.31 (m, 4H), 7.39–7.41 (m, 2H), 7.49–7.52 (m, 2H), 7.65–7.71 (m, 1H), 7.78 (d, J =0.9 Hz, 1H), 7.99 (dd, J_1 =7.8 Hz, J_2 =1.5 Hz, 1H), 8.14–8.17 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ =21.6, 94.5, 116.3, 121.2, 123.4, 125.1, 125.5, 125.7 (2C), 129.3 (2C), 129.6, 130.8, 135.1, 135.9, 136.8, 137.8, 141.4, 142.6, 162.7, 166.0, 196.2; IR (neat): ν =3020, 2399, 1755, 1724, 1709, 1676, 1661, 1597, 1217 cm^{-1} ; HR-MS: m/z =342.1125, calcd. for $\text{C}_{22}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 342.1125.

2-(2-Benzoyl-5-methoxyphenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 4, 3qa): white solid; mp 168–170 °C; ^1H NMR (300 MHz, CDCl_3): δ =3.95 (s, 3H), 7.17 (dd, J_1 =8.4 Hz, J_2 =2.7 Hz, 1H), 7.29–7.34 (m, 3H), 7.37–7.45 (m, 2H), 7.51 (d, J =8.4 Hz, 1H), 7.65–7.68 (m, 2H), 7.75–7.78 (m, 2H), 8.08 (dd, J_1 =7.5 Hz, J_2 =1.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ =55.9, 114.1, 116.5, 117.7, 127.0, 128.4 (2C), 128.5, 128.7, 129.1 (2C), 130.9, 131.4, 132.6, 133.3, 136.5, 138.4, 146.0, 155.9, 158.9, 161.0, 196.5; IR (KBr): ν =1757, 1676, 1595, 1448, 1274, 1215 cm^{-1} ; anal. calcd. for $\text{C}_{22}\text{H}_{15}\text{NO}_4$: C 73.94, H 4.23, N 3.92; found: C 73.96, H 4.20, N 3.95%.

2-(2-Benzoyl-3-methoxyphenyl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 4, 3qa'): white solid; mp 171–173 °C; ^1H NMR (300 MHz, CDCl_3): δ =3.79 (s, 3H), 7.09 (d, J =7.8 Hz, 1H), 7.23 (d, J =8.1 Hz, 1H), 7.38–7.45 (m, 3H), 7.49–7.64 (m, 3H), 7.87–7.94 (m, 3H), 8.11 (dd, J_1 =7.5 Hz, J_2 =1.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ =55.4, 115.5, 116.9, 121.3, 126.9, 128.54, 128.57 (2C), 128.6, 128.7 (2C), 129.3, 130.4, 130.5, 132.8, 136.5, 138.5, 146.1, 155.0, 157.5, 159.1, 195.7; IR (KBr): ν =2924, 2854, 1759, 1747, 1678, 1603, 1462, 1265 cm^{-1} ; anal. calcd. for $\text{C}_{22}\text{H}_{15}\text{NO}_4$: C 73.94, H 4.23, N 3.92; found: C 73.97, H 4.20, N 3.96%.

2-(3-Benzoyl-[1,1'-biphenyl]-4-yl)-4H-benzo[d][1,3]oxazin-4-one (Scheme 5, 3hax): white solid; mp 155–157 °C; ^1H NMR (300 MHz, CDCl_3): δ =7.24 (d, J =8.4 Hz, 1H), 7.37–7.49 (m, 8H), 7.67 (d, J =7.2 Hz, 3H), 7.74 (d, J =1.8 Hz, 1H), 7.85–7.89 (m, 3H), 8.33 (d, J =8.4 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ =116.5, 125.7, 126.8, 127.0, 127.3 (2C), 128.2, 128.4, 128.5 (2C), 128.7, 129.0 (2C), 129.1 (2C), 129.4, 129.6, 132.9, 136.4, 137.9, 138.9, 141.9, 145.0, 146.0, 155.3, 158.9, 196.9; IR (KBr): ν =1772, 1720, 1670, 1603, 1487, 1366, 1248 cm^{-1} ; anal. calcd. for $\text{C}_{27}\text{H}_{17}\text{NO}_3$: C 80.38, H 4.25, N 3.47, found: C 80.41, H 4.27, N 3.44%.

[5-Methyl-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-1,3-phenylene]bis(phenylmethanone) (Table 4, 4ba): white solid; mp 260–262 °C; ^1H NMR (300 MHz, CDCl_3): δ =2.39 (s, 3H), 7.27–7.36 (m, 4H), 7.42 (t, J =7.8 Hz, 2H), 7.54 (t, J =7.2 Hz, 2H), 7.63 (t, J =7.2 Hz, 2H), 7.71 (d, J =8.1 Hz, 1H), 7.97–8.04 (m, 4H), 8.17 (d, J =7.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ =22.2, 95.3, 118.3, 124.2, 124.9, 125.1, 126.2, 126.5 (2C), 128.6 (2C), 129.4 (2C), 129.8, 130.6 (2C), 131.8, 132.4, 132.9, 133.4, 134.4, 135.7, 136.6, 136.9, 145.4, 145.6, 162.0, 165.3, 193.9; IR (neat): ν =1728, 1672, 1452,

1360, 1215 cm^{-1} ; HR-MS: m/z = 468.1214, calcd. for $\text{C}_{29}\text{H}_{19}\text{NO}_4$ $[\text{M} + \text{Na}]^+$: 468.1206.

[5-Methoxy-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-1,3-phenylene]bis(phenylmethanone) (Table 4, 4ca): white solid; mp = 251–253 °C; ^1H NMR (300 MHz, CDCl_3): δ = 3.82 (s, 3H), 6.94–7.02 (m, 2H), 7.27–7.37 (m, 2H), 7.40–7.45 (m, 2H), 7.52–7.57 (m, 2H), 7.60–7.65 (m, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.95–7.99 (m, 2H), 8.01–8.04 (m, 2H), 8.17 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 56.0, 94.9, 108.5, 117.5, 118.3, 121.0, 124.9, 126.5 (2C), 129.4 (2C), 129.9 (2C), 130.6 (2C), 132.5, 132.9, 133.3, 134.6, 135.7, 136.7, 137.0, 147.6, 162.1, 164.8, 193.9; IR (neat): 2926, 1727, 1670, 1492, 1356, 1263 cm^{-1} ; anal. Calcd. for $\text{C}_{29}\text{H}_{19}\text{NO}_5$: C 75.48, H 4.15, N 3.04, found: C 75.46, H 4.16, N 3.07 %.

(5-Fluoro-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-1,3-phenylene)bis(phenylmethanone) (Table 4, 4ea): white solid; mp 264–266 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.17–7.23 (m, 2H), 7.30–7.44 (m, 4H), 7.53–7.58 (m, 2H), 7.62–7.66 (m, 2H), 7.81–7.85 (m, 1H), 7.97–8.04 (m, 4H), 8.18 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 94.6, 111.6 (d, J_{CF} = 24.7 Hz, 1C), 118.3, 118.7 (d, J_{CF} = 23.3 Hz, 1C), 124.8 (d, J_{CF} = 2.3 Hz, 1C), 125.4, 126.4 (2C), 127.4 (d, J_{CF} = 9.7 Hz, 1C), 128.7 (2C), 129.5 (2C), 130.2, 130.6 (2C), 132.4, 133.0, 133.5, 134.2, 135.8, 136.4 (d, J_{CF} = 20.2 Hz, 1C), 147.6 (d, J_{CF} = 9.7 Hz, 1C), 161.6, 164.1, 166.4 (d, J_{CF} = 255.7 Hz, 1C), 193.8; IR (neat): ν = 2926, 1726, 1670, 1602, 1450, 1358 cm^{-1} , anal. calcd. for $\text{C}_{28}\text{H}_{16}\text{FNO}_4$: C 74.83, H 3.59, N 3.12; found: C 74.86, H 3.62, N 3.09 %.

[5-Chloro-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-1,3-phenylene]bis(phenylmethanone) (Table 4, 4fa): off white solid; mp 274–276 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.34–7.50 (m, 6H), 7.56 (t, J = 7.5 Hz, 2H), 7.64–7.69 (m, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.96–8.04 (m, 4H), 8.17–8.20 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 94.8, 118.4, 124.4, 125.5, 126.3, 126.5 (2C), 127.3, 128.7 (2C), 129.6 (2C), 130.2, 130.6 (2C), 131.5, 132.5, 133.0, 133.5, 134.2, 135.8, 136.2, 136.5, 140.8, 146.6, 161.6, 164.2, 193.8; IR (neat): ν = 3020, 2928, 1751, 1728, 1672, 1597, 1477, 1215 cm^{-1} ; anal. calcd. for $\text{C}_{28}\text{H}_{16}\text{ClNO}_4$: C 72.19, H 3.46, N 3.01; found: C 72.17, H 3.45, N 3.05 %.

[2-(6,7-Dimethoxy-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-5-methyl-1,3-phenylene]bis(phenylmethanone) (Table 4, 4ma): light yellow solid; mp 268–270 °C; ^1H NMR (300 MHz, CDCl_3): δ = 2.45 (s, 3H), 3.81 (s, 3H), 3.92 (s, 3H), 7.31–7.37 (m, 5H), 7.41–7.42 (m, 1H), 7.45–7.60 (m, 6H), 7.87–7.90 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 22.1, 56.2, 56.7, 94.4, 103.6, 107.9, 111.1, 125.3, 125.7 (2C), 128.8 (2C), 129.4 (2C), 129.8, 130.0, 130.1 (2C), 132.1, 134.1, 136.5, 137.4, 138.5, 145.3, 146.0, 147.0, 155.6, 162.4, 164.2, 195.0; IR (neat): ν = 2926, 2854, 1713, 1693, 1666, 1610, 1514, 1427, 1275, 1215 cm^{-1} ; HR-MS: m/z = 506.1595, calcd. for $\text{C}_{31}\text{H}_{24}\text{NO}_6$ $[\text{M} + \text{H}]^+$: 506.1598.

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