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Palladium-catalyzed olefination of 4H-Benzo[d][1, 3] oxazin-4-one derivatives with activated alkenes via preferential cyclic imine-N-directed aryl C-H activation

Subir Panja,[a] Srabani Maity,[a] Biju Majhi,[a] and Brindaban C. Ranu*[a]

Abstract: A palladium-catalyzed chelation-assisted selective *ortho* C-H bond olefination of biologically active 4H-benzo[*d*][1, 3] oxazin-4-one derivatives with activated olefins has been achieved. The products are obtained in good yields with high regio- and stereoselectivities. This new protocol has been demonstrated to provide a variety of olefinated-4H-benzo[d][1,3]oxazin-4-one derivatives. The site selectivity of the reaction was explained by DFT study.

Introduction

Benzoxazinone unit is of much importance as it is present in a large number of natural products, drugs and pharmaceuticals having diverse activities. They are reported to exhibit activities such as antifungal, antibacterial, herbicidal, chymotrypsin inhibitor, HSV-1 protease inhibitor, serine proteases inhibitor, inhibitor of leucocyte elastase among others (Figure 1).[1]

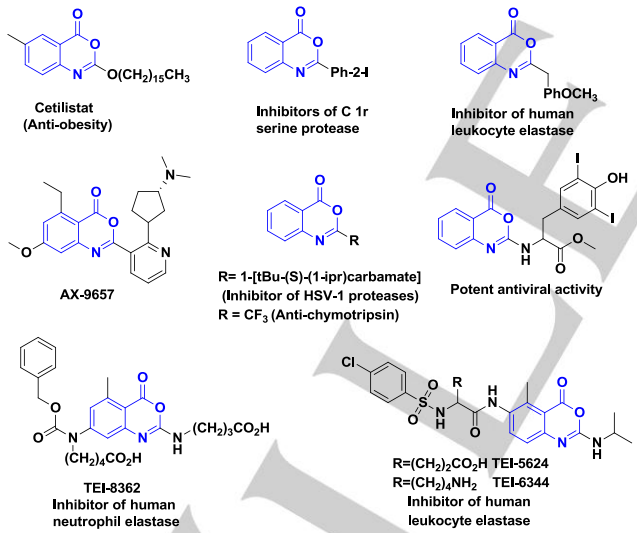

Figure 1. A few biologically active molecules containing 4H-benzo[d][1,3]oxazin-4-one moiety.

Moreover, these moieties also serve as versatile building blocks in organic synthesis. For example, they are used as synthetic intermediates for the synthesis of biologically active benzoxazinethiones, benzothiazinethiones, substituted amidobenzoates, 4-hydroxyquinolinones and quinazolinones (Figure 2).[2] Thus, the development of efficient procedure for the functionalization of benzoxazinone has received considerable attention.

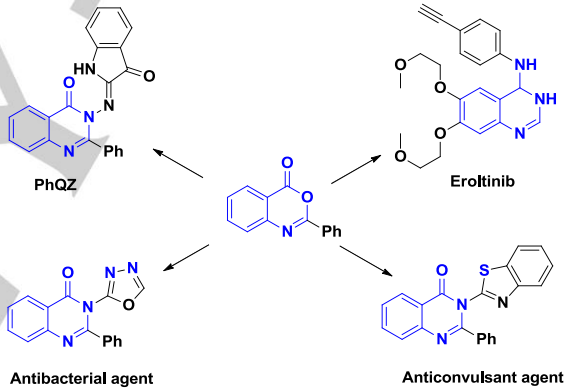

Figure 2. Application of benzoxazinone in the synthesis of bioactive quinazolin-4(3H)-ones.

The unactivated C-H bonds are abundant in organic molecules. So functionalization of unactivated C-H bonds is of much potential. One of the major advantages of this technique is elimination of prefunctionalization step and thus this strategy leads to step and atom economy and minimization of waste. During last few years tremendous development has been noticed towards the use of C-H activation tool for efficient construction of functional molecules.[3] However, functionalization at a selective C-H bond in molecules possessing more than one similar type of C-H bond is a difficult task[4] although some progress has been made in recent times.[5]

The C-H bond olefination is an important reaction as an alkene moiety can be a source of manipulation leading to various active molecules. The palladium-catalyzed coupling between aryl halide and alkenes (Mizoroki-Heck reaction) is widely used for olefination.[6] However, there are limitations of

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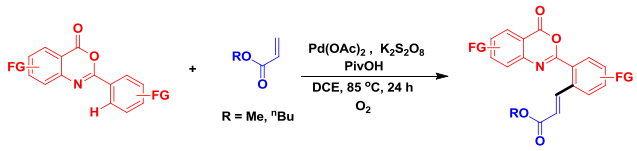
Electronic supplementary information (ESI) available: Additional experimental information, copies of ^{1}H, ^{13}CNMR spectra of all compounds

this reaction with respect to yields and cost of aryl halides.[7] Another approach involves direct olefination of C-H bonds via Fujiwara-Moritani reaction.[8] This reaction requires excess use of arene and the regioselectivity is not always satisfactory. These factors limit their application. During last few years a few elegant methods involving directing group assisted C(aryl)−H olefination were reported.[9] These include olefinations using amides,[9a] carbamates[9b] and urea[9c] as directing groups among others. Considering the importance of benzoxazinone and its derivatives we report here olefination of this unit with activated alkenes via preferential cyclic imine-N-directed aryl C-H activation (Scheme 1). The olefination of benzoxazinone was not addressed earlier.

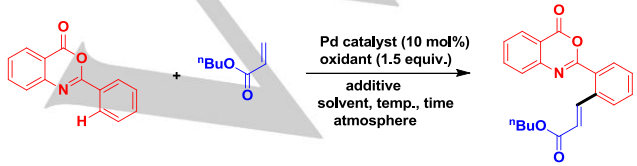


Scheme 1. Olefination of benzoxazinone unit with activated alkenes.

Results and Discussion

Initially, as a test run 2-phenyl-4H-benzo[d][1,3]oxazin-4-one was reacted with butyl acrylate in the presence of $Pd(acac)_2$ (15 mol %), $K_2S_2O_8$ (2 equivalents) as an oxidant in chlorobenzene at 110 °C under argon atmosphere for12 h. A product was isolated in 41 % yield (entry 1, Table 1) whose spectroscopic data (^1H and ^{13}C NMR) are in good agreement with the expected olefinated compound. To standardize the reaction conditions a series of experiments were performed with variation of reaction parameters such as catalyst, oxidant, additives, solvent, temperature and time (for details see supporting information). The change of solvent from chlorobenzene to dichloroethane improved the yield to some extent (entry 3, Table 1). Screening of different Pd catalysts indicated $Pd(OAc)_2$ a better choice (entry 5, Table 1). In the absence of Pd catalyst the reaction did not proceed (entry 6, Table 1). Similarly we tested various oxidizing agents. However, no one is better than $K_2S_2O_8$. It was found that the reaction provided an improved result with addition of pivalic acid (entry 9, Table 1). The best result was obtained at 85 °C (entry 10, Table 1). Screening of reaction time suggests 24 h as the optimum for a good yield (entry 13, Table 1). It was also observed that higher yield was obtained under O_2 atmosphere compared to argon (entry 14, Table 1). As acrylates are prone to polymerization at higher temperature 5 equiv. of butyl acrylate and 3 equiv. of methyl acrylate (see SI) were used. Thus, with the optimized conditions the product was obtained in 79% yield (entry 14, Table 1).

Table 1. Optimization of the reaction conditions.[a,b]



Entry	Catalyst	Oxidant	Additive	Solvent	Temp. (°C)	Time	Yields (%)
1	$Pd(acac)_2$	$K_2S_2O_8$	-	PhCl	110	12	41
2	$Pd(acac)_2$	$K_2S_2O_8$	-	THF	110	12	18
3	$Pd(acac)_2$	$K_2S_2O_8$	-	DCE	110	12	54
4	$Pd(PPh_3)_4$	$K_2S_2O_8$	-	DCE	110	12	31
5	$Pd(OAc)_2$	$K_2S_2O_8$	-	DCE	110	12	59
6	-	$K_2S_2O_8$	-	DCE	110	12	-
7	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	-	DCE	110	12	56
8	$Pd(OAc)_2$	$K_2S_2O_8$	$AdCO_2H$	DCE	110	12	33
9	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH	DCE	110	12	65
10	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH	DCE	85	12	68
11	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH	DCE	50	12	47
12	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH	DCE	85	18	65
13	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH	DCE	85	24	75
14[c]	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH	DCE	85	24	79

[a]Reaction conditions: 2-phenyl-4-H-benzo[d][1,3]oxazin-4-one (0.1 mmol), butyl acrylate (0.5 mmol), $Pd(acac)_2$ (10 mol %), $K_2S_2O_8$ (1.5 equiv.), PhCl solvent (3 ml), 110 °C, Ar atmosphere, 12 h. [b]Isolated yield. [c]O_2 atm.

Thus in a general procedure, 2-phenyl-4H-benzo[d][1,3]oxazin-4-one was reacted with butyl acrylate in the presence of $K_2S_2O_8$, and 1.5 equivalent of pivalic acid in dichloroethane at 85 °C for 24 h under O_2. After the reaction was over the product was isolated by standard work-up followed by column chromatography.

After having the optimized condition in hand we investigated the scope of the reaction. A wide range of 2-aryl-4H-benzo[d][1,3]oxazin-4-ones were subjected to reaction with butyl acrylate by this procedure to produce the corresponding olefinated products in good to excellent yields (Table 2). Electron donating functional groups such as -Me**,** -Et, -^{n}Bu, -^{t}Bu, -OMe, -Ph bearing substrates provided the corresponding products **(3b, 3c, 3d**, **3e**, **3f**, **3g**) in excellent yields. Halogen-containing 2-aryl-4H-benzo[d][1, 3]oxazin-4-ones were also compatible with this reaction (**3h**, **3i**). The halogen functionalities provide scope for further manipulation. The *ortho*-substituted 2-aryl-4Hbenzo[d][1,3]oxazin-4-one was found to produce lower yields (**3k**, **3l**). This procedure is acceptable to substrates containing -CF_3 functional group (**3j**, **3l**) and usually these molecules show promising biological activities. A library of olefinated benzoxazines with substitutions at both the aromatic rings were synthesized in good yields using this protocol. The reaction of 2- aryl-4H-benzo[d][1,3]oxazin-4-one substituted at 8 position provided the product in lower yield (**3t** and **3u**). It is possibly because of the steric factors.

Table 2. Pd-catalyzed C-H olefination of benzoxazinone derivatives with butyl acrylate.[a,b]

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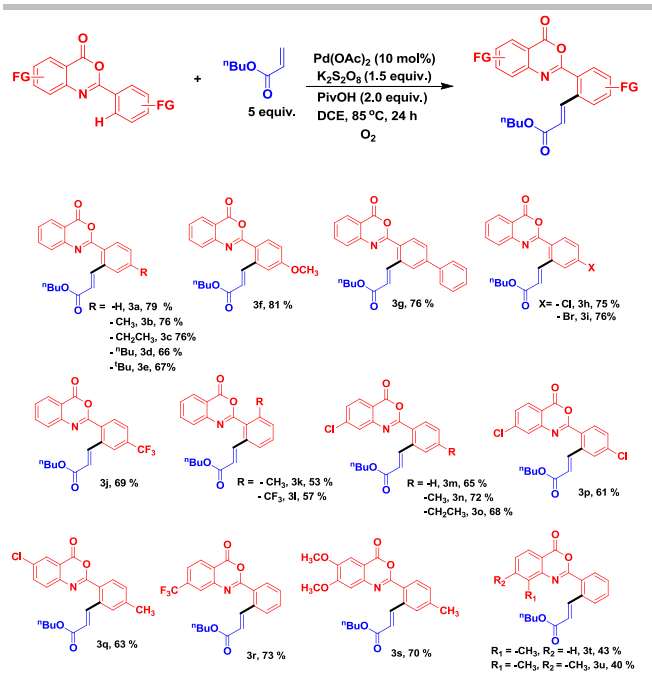
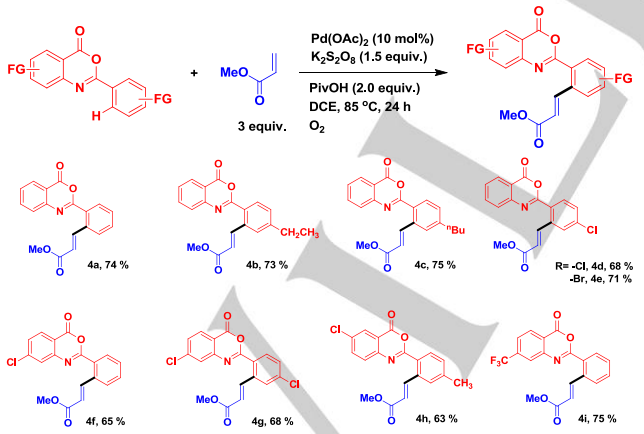


[a]Reaction conditions: benzoxazinone derivatives (0.5 mmol), butyl acrylate (2.5 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (0.75 mmol), PivOH (1 mmol), dichloroethane (3 ml), 85 °C, O_2 atmosphere, 24 h. [b]Isolated yield.

To test the generality of this procedure it was further extended to the reaction with methyl acrylate (Table 3). The 2-aryl-4H-benzo[d][1,3]oxazin-4-ones underwent reaction with methyl acrylate without any difficulty. A variety of benzoxazinones containing substituents on both the aromatic rings participated in the reaction providing good yields.

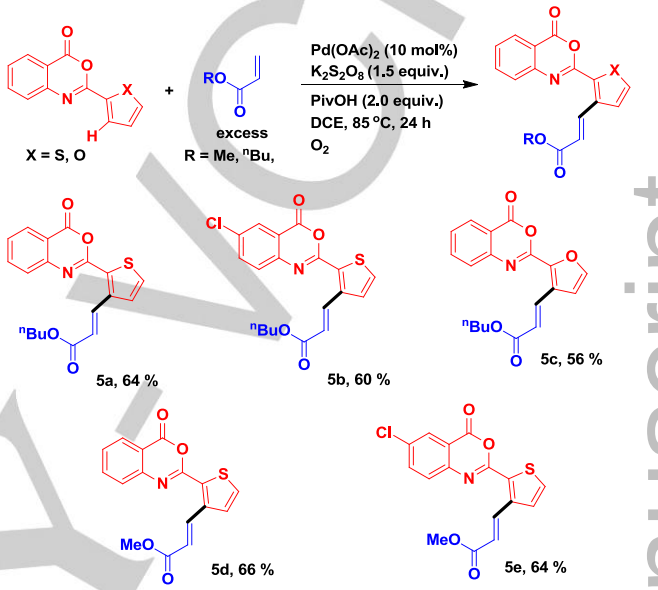
Table 3. Pd-catalyzed C-H olefination of benzoxazinone derivatives with methyl acrylate.[a,b]



[a]Reaction conditions: benzoxazinone derivatives (0.5 mmol), methyl acrylate (1.5 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (0.75 mmol), PivOH (1 mmol), dichloroethane (3 ml), 85 °C, O_2 atmosphere, 24 h. [b]Isolated yield.

Further to check the diversity of this protocol the heteroarene-substituted benzoxazinones were subjected to reaction (Table 4). The reactions of furanyl and thiophenyl ring attached benzoxazine-4-ones proceeded well although the yields are relatively low compared to other reactions. These molecules might be of potential in pharmaceutical industry. This type of C-H olefination of benzoxazinones containing a heteroarene unit was not reported.

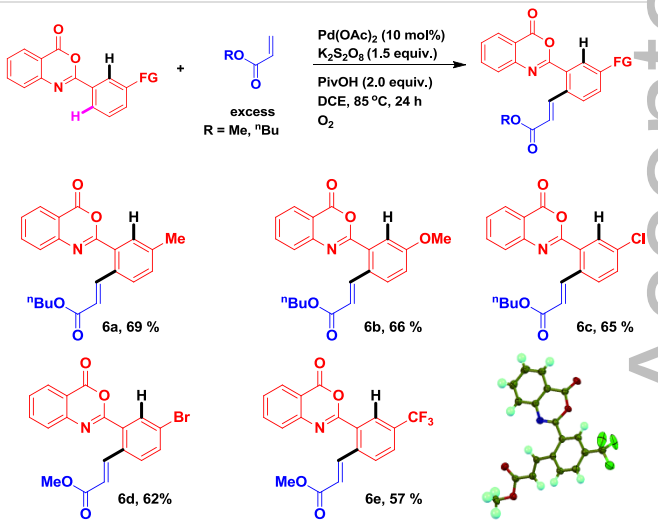
Table 4. Pd-catalyzed C-H olefination of heteroaryl benzoxazinone with butyl and methyl acrylate.[a,b]



[a]Reaction conditions: 2-heteroaryl-4H-benzo[d][1,3]oxazin-4-one (0.5 mmol), butyl acrylate (2.5 mmol), methyl acrylate (1.5 mmol), $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (0.75 mmol), PivOH (1 mmol), dichloroethane (3 ml), 85 °C O_2 atmosphere, 24 h. [b]Isolated yield.

To check the regioselectivity of the reaction a few meta substituted benzoxazinones were investigated (Table 5). There

Table 5. Pd-catalyzed C-H olefination of *meta*-substituted 2-aryl-4H-benzo [d][1,3] oxazin-4-one with butyl and methyl acrylate.[a,b]

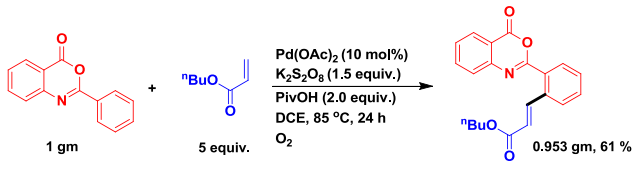


[a]Reaction conditions: *meta*-substituted 2-aryl-4H-benzo[d][1,3]oxazin-4-one (0.5 mmol), butyl acrylate (2.5 mmol), methyl acrylate (1.5 mmol), $Pd(OAc)_2$

(10 mol %), $K_2S_2O_8$ (0.75 mmol), PivOH (1 mmol), dichloroethane (3 ml), 85 ^oC, O_2 atmosphere, 24 h. [b]Isolated yield.

is a possibility of functionalization at two adjacent carbon centers. However, it was found that reaction goes through less hindered site giving only one product. The structure of one of the products, **6e** was confirmed by X-ray diffraction analysis (See SI).[10]
To check the generality of this reaction we investigated this olefination with other olefins such as acrylamide, acetophenone and styrene; however the reactions are not successful either giving very low or no yield of product.

To check the synthetic utility a gram scale reaction was performed (Scheme 2). The yield was comparable.



Scheme 2. A gram scale synthesis by our procedure.

In principle, there are possibilities of three chelating cycles directed by three different centers -N, -O, -CO (Figure 3). The energy of each possible metallocycle was calculated in its optimized structure by DFT method. From DFT calculation it was found that N- directed metallocycle (A) is more stable by 12.5 kcal/mole than O- directed metallocycle (B) and 31.4 kcal/mole

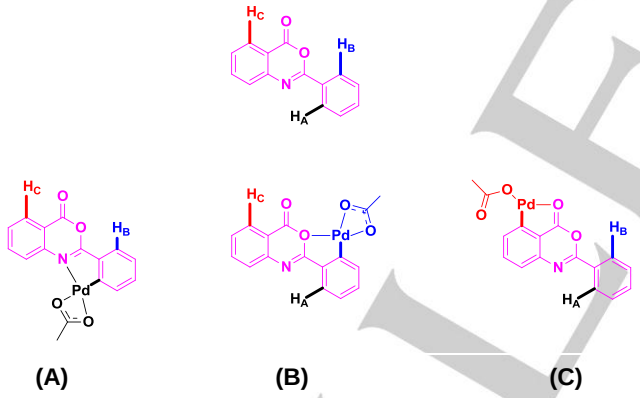
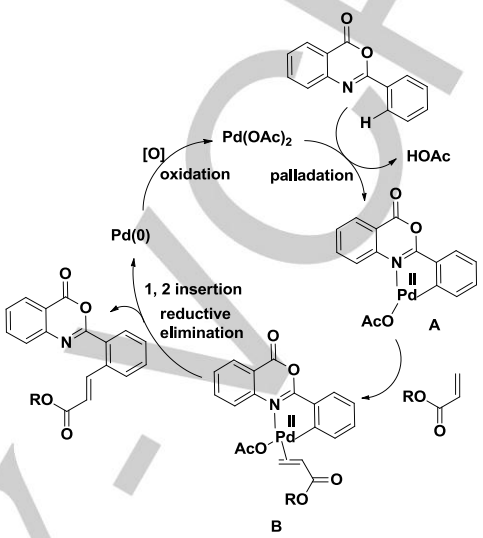


Figure 3. DFT calculation of the possible metallocycles.

more stable than C=O directed metallocycle(C). So it may be concluded that the reaction goes through preferential N-directed chelation (see SI).

Based on the previous reports[11] a possible reaction mechanism is proposed as outlined in Scheme 3. Initially in the presence of $Pd(OAc)_2$ benzoxazinone forms a 5-membered palladacycle (II) intermediate **A** which interacts with alkyl acrylate and forms the intermediate **B**. In the next step, the intermediate **B** undergoes olefin insertion, beta-hydrogen elimination, and reductive elimination of HOAc to provide the olefinated product and Pd(0) is reoxidized into Pd(II) by oxidant to restart the next cycle. It is likely that PivOH binds with the metal of metalocycle to lower the activation energy.



Scheme 3. Possible reaction pathway.

Conclusions

In conclusion, we have developed an efficient protocol for the olefination of 2-aryl-4H-benzo[d][1,3]oxazin-4-ones with activated olefins via C-H activation catalyzed by palladium. A library of olefinated-2-aryl- 4H-benzo[d][1,3]oxazin-4-ones were achieved using butyl and methyl acrylates by this simple procedure. The reaction is highly regioselective and applicable to heteroarene-benzoxazinones too. These molecules may have much potential in organic synthesis and in pharmaceutical industry. To the best of our knowledge this is the first report on the olefination of 2-aryl-4H-benzo[d][1,3]oxazin-4-ones via C-H activation.

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, 400, 500 MHz for ^1H spectra and at 75, 100, 125 MHz for ^{13}C spectra in $CDCl_3$ solutions. HRMS analysis was performed in a Qtof mass analyzer using ESI ionization method. Anthranilic acids, benzoyl chloride derivatives, n-butyl acrylate, methyl acrylate, $Pd(OAc)_2$, PivOH and $K_2S_2O_8$ were purchased from Sigma-Aldrich.

Representative experimental procedure for the preparation of 2-aryl-4H benzo[d][1,3] oxazin-4-ones following a reported one[12]

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 (20 mmol) 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 the 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 olefination of 2-phenyl-4H-benzo[d][1,3] oxazin-4-one with butyl acrylate for the synthesis of (E)-butyl3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)pheny **l)acryl ate (Table 2, 3a)**

To a solution of 2-phenyl-4H-benzo [d][1,3] oxazin-4-one (0.5 mmol, 112 mg), $K_2S_2O_8$ (0.75 mmol, 203 mg), $Pd(OAc)_2$ (5 mol %, 11 mg), PivOH (1 mmol, 102 mg) in dichloroethane (3 mL), n-butyl acrylate (5 mmol, 320 mg) was added. The resulting mixture was heated at 85 °C under O_2 atmosphere for 24 h (TLC). After the reaction was complete, the mixture was allowed to cool at room temperature and was extracted with ethyl acetate (3×20 mL) followed by washing with 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 94:6) to afford the pure product, (*E*)-butyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate as a brownish gummy liquid. This procedure was followed for all the reactions listed in Table 2, Table 3, Table 4, Table 5 and Scheme 2. All the products were obtained in high purity. All the products are unknown and characterized properly by spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, and HR-MS). All these data are provided in supporting information.

Characterization details of the starting molecules

All together 29 benzoxazinones were prepared by this procedure. Out of them 24 are known. They were identified by comparison of their spectroscopic data (^{1}H and ^{13}C NMR) with the reported ones (references are cited against each compound).

2-Phenyl-4H-benzo[d][1,3]oxazin-4-one,[13a] 2-([1,1'-Biphenyl]-4-yl)-4H-benzo[d][1,3]oxazin-4-one,[13b] 2-(p-Tolyl)-4H-benzo[d][1,3]oxazin-4-one,[13a] 2-(4-Ethylphenyl)-4H-benzo[d][1,3]oxazin-4-one,[13c] 2-(m-Tolyl)-4H-benzo[d][1,3]oxazin-4-one,[13d] 2-(4-(tert-Butyl)phenyl)-4H-benzo[d][1,3]oxazin-4-one,[13e] 2-(4-Methoxyphenyl)-4H-benzo[d][1,3]oxazin-4-one,[13a] 2-(4-Chlorophenyl)-4H-benzo[d][1,3]oxazin-4-one,[13b] 2-(4-Bromophenyl)-4H-benzo[d][1,3]oxazin-4-one,[13b] 2-(4-(Trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazin-4-one,[13a] 2-(o-Tolyl)-4H-benzo[d][1,3]oxazin-4-one,[13f] 2-(2-(Trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazin-4-one,[13e] 7-Chloro-2-phenyl-4H-benzo[d][1,3]oxazin-4-one,[13a] 7-Chloro -2-(p-tolyl)-4H-benzo[d][1,3]oxazin-4-one,[13g] 7-Chloro-2-(4-chlorophenyl)-4H-benzo[d][1,3]oxazin-4-one,[13g] 6-Chloro-2-(p-tolyl)-4H-benzo[d] [1,3]oxazin-4-one,[13h] 2-Phenyl-7-(trifluoromethyl)-4H-benzo[d][1,3] oxazin-4-one,[13i] 6,7-Dimethoxy-2-(p-tolyl)-4H-benzo[d][1,3]oxazin-4-one,[13j] 8-Methyl-2-phenyl-4H-benzo[d][1,3]oxazin-4-one,[13a] 2-(Thiophen-2-yl)-4H-benzo[d][1,3]oxazin-4-one,[13a] 2-(Furan-2-yl)-4H-benzo[d][1,3]oxazin-4-one,[13a] 2-(3-Methoxyphenyl)-4H-benzo[d][1,3]oxazin-4-one,[13b] 2-(3-Chlorophenyl)-4H-benzo[d][1,3]oxazin-4-one,[13c] 2-(3-Bromophenyl)-4H-benzo[d][1,3]oxazin-4-one.[13k]

The new benzoxazinones were characterized by their satisfactory IR, ^{1}H NMR, ^{13}C NMR and HRMS data which are provided below.

(4-Butylphenyl)-4H-benzo[d][1,3]oxazin-4-one. yellow solid ; mp 82-87 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.34 – 8.10 (m, 2H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.63 (dd, *J* = 22.9, 8.0 Hz, 1H), 7.35 – 7.22 (m, 3H), 2.66 (dt, *J* = 10.5, 7.6 Hz, 2H), 1.65 (pd, *J* = 7.3, 2.9 Hz, 2H), 1.34 (tt, *J* = 7.6, 3.0 Hz, 2H), 0.97 – 0.79 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.76, 149.56, 147.46, 136.46, 130.25, 128.79, 128.51, 128.31, 127.93, 127.54, 127.42, 127.03, 35.95, 31.42, 22.45, 13.96; IR (KBr) 2955, 2928, 2857, 1764, 1681 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{17}NNaO_2$ 302.1157; Found 302.1157.

7-Chloro-2-(4-ethylphenyl)-4H-benzo[d][1,3]oxazin-4-one. white solid ; mp 112-116 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.22 – 7.88 (m, 4H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.37 – 7.03 (m, 2H), 2.64 (p, *J* = 8.1, 7.6 Hz, 2H), 1.23 (dt, *J* = 10.5, 7.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.47, 158.17, 149.77, 147.95, 142.54, 129.60, 128.38, 128.11, 127.47, 126.96, 126.64, 115.09, 28.85, 14.95; IR (KBr) 3039, 2966, 2932, 1757, 1614 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{13}ClNO_2$ 286.0635; Found 286.0637.

7,8-Dimethyl-2-phenyl-4H-benzo[d][1,3]oxazin-4-one. white solid ; mp 166-169 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.30 – 8.17 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.34 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 2.48 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.99, 155.36, 146.11, 144.56, 134.22, 132.13, 130.59, 129.55, 128.50, 128.03, 125.28, 114.50, 20.95, 12.92; IR (KBr) 3053, 2905, 1760, 1740, 1620 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{14}ClNO_2$ 252.1025; Found 252.1022.

6-Chloro-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazin-4-one. yellow solid ; mp 170-174 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.91 (s, 1H), 7.59 (tt, *J* = 29.4, 15.0 Hz, 3H), 7.15 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.85, 153.78, 145.50, 136.82, 133.74, 133.44, 132.76, 132.02, 128.37, 128.30, 127.99, 117.68; IR (KBr) 3077, 1753, 1616, 1598, 1470 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{12}H_7ClNO_2S$ 263.9886; Found 263.9887.

2-(3-(Trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazin-4-one. white solid ; mp 129-132 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.17 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.85 – 7.74 (m, 2H), 7.68 – 7.54 (m, 2H), 7.49 (td, *J* = 7.6, 1.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.79, 155.46, 146.34, 136.61, 131.31 (q, $^2J_{C\text{-}F}$ = 33 Hz), 131.18, 131.03, 129.26, 128.85 (q, $^4J_{C\text{-}F}$ = 3.0 Hz), 128.66, 128.56, 127.28, 125.05 (q, $^3J_{C\text{-}F}$ = 3.75 Hz), 123.61 (q, $^1J_{C\text{-}F}$ = 271.50 Hz), 116.94.; IR (KBr) 3079, 1761, 1626, 1602, 1574 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_9F_3NO_2$ 292.0585; Found 292.0583.

Analytical data of the synthesized olefinic molecules

(*E*)-butyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3a). brownish gummy liquid (eluent, hexane/ethyl acetate (94:6), (138 mg, 79%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.64 (dd, *J* = 15.9, 1.7 Hz, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.70 (dd, *J* = 11.1, 8.0 Hz, 2H), 7.60 – 7.44 (m, 3H), 6.37 (dd, *J* = 15.8, 1.8 Hz, 1H), 4.22 (td, *J* = 6.7, 1.8 Hz, 2H), 1.79 – 1.51 (m, 2H), 1.43 (hd, *J* = 7.4, 1.8 Hz, 2H), 0.94 (td, *J* = 7.4, 1.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.95, 159.43, 156.55, 146.51, 144.16, 136.80, 136.07, 132.12, 130.35, 129.79, 129.01, 128.65, 128.51, 127.69, 120.79, 116.89, 100.12, 64.61, 30.95, 19.39, 13.88; IR (KBr) 2954, 2924, 2853, 1730, 1596 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{21}H_{20}NO_4$ 350.1392; Found 350.1393.

(*E*)-Butyl 3-(5-methyl-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3b). white solid ; mp 80-85 °C. eluent, hexane/ethyl acetate (94:6), (137 mg, 76%). ^{1}H NMR (300 MHz,

Chloroform-*d*) δ 8.68 (d, *J* = 15.9 Hz, 1H), 8.24 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.77 (m, 1H), 7.69 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.57 – 7.43 (m, 2H), 7.32 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 1.70 (dq, *J* = 8.3, 6.6 Hz, 2H), 1.51 – 1.37 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 167.08, 159.57, 156.60, 146.65, 144.56, 142.78, 136.71, 136.09, 130.59, 130.36, 129.21, 128.74, 128.57, 127.58, 126.91, 120.45, 116.80, 64.58, 30.95, 21.66, 19.38, 13.87; IR (KBr) 2919, 2854, 1715, 1602 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_4$ 364.1549; Found 364.1549.

(*E*)-Butyl 3-(5-ethyl-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3c). brownish gummy liquid. eluent, hexane/ethyl acetate (94:6), (143 mg, 76%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 15.9 Hz, 1H), 8.25 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.83 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.70 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.64 – 7.44 (m, 2H), 7.36 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.70 (dq, *J* = 8.4, 6.7 Hz, 2H), 1.54 – 1.37 (m, 2H), 1.30 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.10, 159.61, 156.64, 148.96, 146.68, 144.69, 136.74, 136.20, 130.48, 129.45, 128.76, 128.60, 128.08, 127.61, 127.13, 120.44, 116.83, 64.59, 30.96, 27.13, 19.39, 15.25, 13.89; IR (KBr) 2961, 2932, 2873, 1708, 1618 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}NO_4$ 378.1705; Found 378.1702.

(*E*)-Butyl 3-(5-butyl-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3d). brownish solid ; mp 52-54 °C. eluent, hexane/ethyl acetate (94:6), (135 mg, 66%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 15.9 Hz, 1H), 8.24 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.76 (m, 1H), 7.70 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.52 (ddd, *J* = 14.4, 7.0, 1.5 Hz, 2H), 7.33 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 1.78 – 1.55 (m, 5H), 1.55 – 1.30 (m, 4H), 0.95 (td, *J* = 7.3, 1.4 Hz, 5H).^{13}C NMR (75 MHz, $CDCl_3$) δ 167.03, 159.55, 156.62, 147.71, 146.63, 144.62, 136.70, 136.06, 130.36, 129.96, 128.73, 128.57, 127.57, 127.06, 125.15, 120.39, 116.78, 64.54, 35.70, 33.29, 30.94, 22.43, 19.37, 14.01, 13.87; IR (KBr) 2957, 2929, 2871, 1763, 1602 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{28}NO_4$ 406.2018; Found 406.2018.

(*E*)-Butyl 3-(5-(tert-butyl)-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3e). brownish gummy liquid. eluent, hexane/ethyl acetate (94:6), (135 mg, 67%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 15.9 Hz, 1H), 8.25 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.83 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.61 – 7.49 (m, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 1.71 (dq, *J* = 8.5, 6.7 Hz, 2H), 1.45 (q, *J* = 7.4 Hz, 2H), 1.38 (s, 9H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.05, 167.12, 159.60, 155.82, 146.66, 145.06, 136.72, 135.85, 130.23, 128.76, 128.59, 127.61, 127.02, 126.87, 125.57, 120.32, 116.83, 64.61, 38.67, 35.29, 31.17, 30.96, 27.11, 19.39, 13.89; IR (KBr) 2959, 2871, 1678, 1638, 1604 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{28}NO_4$ 406.2018; Found 406.2011.

(*E*)-Butyl 3-(5-methoxy-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3f). yellow solid ; mp 91-93 °C. eluent, hexane/ethyl acetate (93:7), (153 mg, 81%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 15.8 Hz, 1H), 8.23 (ddd, *J* = 7.9, 1.6, 0.6 Hz, 1H), 8.14 (d, *J* = 8.9 Hz, 1H), 7.81 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.67 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H), 7.52 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.14 (d, *J* = 2.6 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 3.91 (s, 3H), 1.77 – 1.60 (m, 2H), 1.53 – 1.37 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.95, 162.43, 159.66, 156.35, 146.83, 144.73, 138.39, 136.69, 132.31, 128.57, 128.48, 127.46, 121.95, 120.74, 116.67, 115.11, 113.97, 64.63, 55.75, 30.97, 19.39, 13.89; IR (KBr) 2959, 2930, 2872, 1759, 1709 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_5$ 380.1498; Found 380.1494.

(*E*)-Butyl 3-(4-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-[1,1'-biphenyl]-3-yl)acrylate (Table 2, 3g). white solid ; mp 107-109 °C. eluent, hexane/ethyl acetate (94:6), (161 mg, 76%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 15.9 Hz, 1H), 8.31 – 8.18 (m, 2H), 7.94 – 7.79 (m, 2H), 7.78 – 7.70 (m, 2H), 7.70 – 7.61 (m, 2H), 7.61 – 7.35 (m, 4H), 6.44 (d, *J* = 15.9 Hz, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.65 (m, 2H), 1.53 – 1.37 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.92, 159.41, 156.41, 146.63, 144.94, 144.57, 139.38, 136.78, 136.75, 130.90, 129.19, 128.90, 128.65, 128.22, 127.70, 127.36, 127.23, 125.32, 124.43, 120.95, 116.92, 64.63, 30.99, 19.40, 13.88; IR (KBr) 3068, 2952, 1778, 1628, 1603 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}NO_4$ 426.1705; Found 426.1707.

(*E*)-Butyl 3-(5-chloro-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3h). white solid ; mp 70-72 °C. eluent, hexane/ethyl acetate (94:6), (143 mg, 75%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 15.9 Hz, 1H), 8.31 – 8.23 (m, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.85 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.76 – 7.63 (m, 2H), 7.63 – 7.45 (m, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 1.75 – 1.64 (m, 2H), 1.52 – 1.36 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.60, 159.16, 155.68, 146.37, 143.07, 138.51, 137.94, 136.89, 131.66, 129.76, 129.18, 128.71, 128.63, 127.93, 127.73, 121.84, 116.87, 64.76, 30.93, 19.38, 13.87; IR (KBr) 2959, 2873, 1699, 1601 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}ClNO_4$ 384.1003; Found 384.1005.

(*E*)-Butyl 3-(5-bromo-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3i). white solid ; mp 66-71 °C. eluent, hexane/ethyl acetate (94:6), (162 mg, 76%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 15.9 Hz, 1H), 8.35 – 8.18 (m, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.90 – 7.79 (m, 2H), 7.68 (ddd, *J* = 16.8, 8.3, 1.6 Hz, 2H), 7.62 – 7.51 (m, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 1.76 – 1.62 (m, 2H), 1.45 (ddt, *J* = 14.5, 9.5, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.58, 159.15, 155.77, 146.35, 143.00, 138.02, 136.90, 132.73, 131.68, 131.57, 129.20, 128.72, 128.35, 127.74, 126.96, 121.85, 116.87, 64.76, 30.92, 19.38, 13.88; IR (KBr) 2959, 2929, 2872, 1766, 1714 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}BrNO_4$ 428.0497; Found 428.0497.

(*E*)-Butyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-5-(trifluoromethyl)phenyl)acrylate (Table 2, 3j). brownish liquid. eluent, hexane/ethyl acetate (94:6), (143 mg, 69%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 15.9 Hz, 1H), 8.37 – 8.20 (m, 2H), 8.04 – 7.81 (m, 2H), 7.75 (ddd, *J* = 9.4, 8.1, 1.4 Hz, 2H), 7.66 – 7.53 (m, 1H), 6.43 (d, *J* = 15.9 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 1.79 – 1.59 (m, 2H), 1.45 (dp, *J* = 9.6, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.76, 166.52, 158.94, 155.31, 146.14, 142.90, 137.00, 133.80(q, $^2J_{C\text{-}F}$ = 43.0 Hz), 132.64, 130.93, 129.57, 128.79, 127.90, 126.20 (q, $^4J_{C\text{-}F}$ = 3.75 Hz), 125.47 (q, $^3J_{C\text{-}F}$ = 4.50 Hz), 122.31, 116.99, 114.99 (q, $^1J_{C\text{-}F}$ = 234.75 Hz), 100.13, 64.86, 27.13, 19.37, 13.87. ^{19}F NMR (376 MHz, $CDCl_3$) δ -162.39; IR (KBr) 2960, 2932, 2874, 1768, 1714 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}F_3NNaO_4$ 440.1086; Found 440.1084.

(*E*)-Butyl 3-(3-methyl-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3k). yellowish gummy liquid. eluent, hexane/ethyl acetate (94:6), (96 mg, 53%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 – 8.23 (m, 1H), 7.88 (s, 1H), 7.72 (d, *J* = 3.0 Hz, 1H), 7.67 – 7.51 (m, 3H), 7.42 (s, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.40 (s, 3H), 1.58 (dd, *J* = 8.4, 6.2 Hz, 2H), 1.31 (dd, *J* = 15.1, 7.6 Hz, 2H), 0.85 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.16, 141.49, 138.76, 137.81, 136.93,

134.10, 133.39, 132.10, 130.94, 130.66, 129.37, 128.81, 127.97, 127.54, 124.42, 121.44, 120.02, 64.59, 30.78, 30.57, 19.29, 13.77; IR (KBr) 2963, 2927, 2853, 1770, 1724 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_4$ 364.1549; Found 364.1549.

(*E*)-Butyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-3-(trifluoromethyl)phenyl)acrylate (Table 2, 3l). yellowish gummy liquid. eluent, hexane/ethyl acetate (94:6), (118 mg, 57%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.30 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 2.6 Hz, 1H), 7.69 – 7.60 (m, 3H), 6.47 (d, *J* = 15.8 Hz, 1H), 4.12 (t, *J* = 6.5 Hz, 2H), 1.64 – 1.49 (m, 2H), 1.35 – 1.26 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 165.90, 158.61, 155.21, 145.77, 139.32, 137.05, 135.54, 130.99, 130.39, 130.06(q, $^2J_{C\text{-}F}$ = 6.0 Hz), 129.75, 129.54, 128.97, 127.83 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 127.64, 123.61, 123.39 (q, $^1J_{C\text{-}F}$ = 272 Hz) , 117.03, 64.86, 30.67, 19.23, 13.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -159.11. IR (KBr) 2963, 2919, 2850, 1767, 1717 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3NO_4$ 418.1266; Found 418.1262.

(*E*)-Butyl 3-(2-(7-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3m). brownish solid ; mp 104-107 °C. eluent, hexane/ethyl acetate (94:6), (124 mg, 65%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 15.9 Hz, 1H), 8.23 – 8.09 (m, 2H), 7.70 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.65 – 7.44 (m, 3H), 6.37 (d, *J* = 15.8 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 1.79 – 1.64 (m, 2H), 1.53 – 1.33 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.86, 158.60, 157.82, 147.62, 143.99, 143.31, 136.41, 132.49, 130.49, 129.96, 129.80, 129.55, 129.30, 128.66, 127.43, 121.10, 115.31, 64.69, 31.00, 19.40, 13.86; IR (KBr) 2959, 2929, 2867, 1766, 1712 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}ClNO_4$ 384.1003; Found 384.1003.

(E)-butyl 3-(2-(7-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-5-methylphenyl)acrylate (Table 2, 3n). white solid ; mp 111-114 °C. eluent, hexane/ethyl acetate (94:6), (143 mg, 72%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 15.9 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.36 – 7.30 (m, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 2.46 (s, 3H), 1.79 – 1.63 (m, 2H), 1.54 – 1.35 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.91, 158.71, 157.95, 147.83, 144.35, 143.29, 143.22, 136.54, 130.59, 130.55, 129.92, 129.40, 129.28, 127.35, 126.53, 120.86, 115.31, 64.64, 31.05, 21.69, 19.42, 13.86; IR (KBr) 2959, 2926, 2854, 1779, 1715 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}ClNO_4$ 398.1159; Found 398.1147.

(*E*)-Butyl 3-(2-(7-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-5-ethylphenyl)acrylate (Table 2, 3o). white solid ; mp 77-80 °C. eluent, hexane/ethyl acetate (94:6), (139 mg, 68%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 15.8 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.34 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.78 – 1.65 (m, 2H), 1.46 (dp, *J* = 9.5, 7.3 Hz, 2H), 1.34 – 1.19 (m, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.91, 158.71, 157.78, 149.40, 147.70, 144.45, 143.13, 136.47, 130.58, 129.86, 129.41, 129.24, 128.20, 127.27, 126.55, 120.65, 115.18, 64.60, 30.96, 28.97, 19.38, 15.17, 13.86; IR (KBr) 2961, 2930, 2873, 1763, 1711 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}ClNO_4$ 412.1316; Found 412.1312.

(*E*)-Butyl 3-(5-chloro-2-(7-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3p). white solid ; mp 139-141 °C. eluent, hexane/ethyl acetate (94:6), (127 mg, 61%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 15.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.67 (dd, *J* = 16.1, 2.1 Hz, 2H), 7.51 (ddd, *J* = 10.1, 8.5, 2.1 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 1.72 (dd, *J* = 8.5, 6.2 Hz, 2H), 1.46 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.47, 158.30, 156.91, 147.42, 143.39, 142.84, 138.95, 138.20, 131.77, 129.98, 129.77, 129.69, 128.77, 127.43, 122.09, 115.24, 64.82, 30.95, 19.38, 13.85; IR (KBr) 3082, 2960, 2929, 2873, 1773 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{19}Cl_2NO_4$ 440.0432; Found 440.0431.

(*E*)-Butyl 3-(2-(6-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-5-methylphenyl)acrylate (Table 2, 3q). yellowish liquid. eluent, hexane/ethyl acetate (94:6), (125 mg, 63%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 15.9 Hz, 1H), 8.21 (d, *J* = 2.4 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.49 (t, *J* = 1.3 Hz, 1H), 7.39 – 7.29 (m, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 2.46 (s, 3H), 1.80 – 1.58 (m, 2H), 1.54 – 1.34 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.99, 158.46, 156.85, 145.21, 144.49, 143.16, 137.01, 136.36, 134.42, 130.63, 130.44, 129.38, 129.17, 127.99, 126.51, 120.69, 117.97, 64.60, 31.00, 21.70, 19.40, 13.89; IR (KBr) 2958, 2928, 2872, 1761, 1711 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}ClNO_4$ 398.1159; Found 398.1152.

(*E*)-Butyl 3-(2-(4-oxo-7-(trifluoromethyl)-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3r). brownish gummy liquid. eluent, hexane/ethyl acetate (94:6), (152 mg, 73%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 15.9 Hz, 1H), 8.39 (d, *J* = 8.2 Hz, 1H), 8.20 – 8.13 (m, 1H), 7.97 (d, *J* = 1.7 Hz, 1H), 7.79 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.58 (ddd, *J* = 10.9, 7.5, 1.6 Hz, 2H), 6.38 (d, *J* = 15.9 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 1.77 – 1.64 (m, 2H), 1.50 – 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.76, 158.25, 157.90, 146.90, 143.79, 138.35 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 136.54, 132.69, 130.55, 129.84, 129.73, 129.06, 128.75, 125.15 (q, $^4J_{C\text{-}F}$ = 3.0 Hz), 124.99 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 123.11(q, $^1J_{C\text{-}F}$ = 273 Hz), 121.35, 119.50, 64.74, 30.96, 19.34, 13.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -163.41; IR (KBr) 2960, 2928, 2870, 1773, 1713 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3NO_4$ 418.1266; Found 418.1268.

(*E*)-Butyl 3-(2-(6,7-dimethoxy-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-5-methylphenyl)acrylate (Table 2, 3s). yellowish liquid. eluent, hexane/ethyl acetate (90:10), (148 mg, 70%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 15.9 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.57 (s, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.33 (dt, *J* = 8.3, 1.2 Hz, 1H), 7.10 (s, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 4.03 (s, 3H), 4.01 (s, 3H), 2.45 (s, 3H), 1.70 (tt, *J* = 8.5, 6.5 Hz, 2H), 1.52 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.03, 159.52, 156.80, 156.33, 150.31, 144.45, 143.17, 142.39, 135.78, 130.62, 130.32, 129.11, 127.51, 120.55, 109.58, 108.56, 107.79, 64.55, 56.67, 31.06, 29.86, 21.64, 19.41, 13.86; IR (KBr) 2961, 2925, 2854, 1752, 1711 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}NO_6$ 424.1760; Found 424.1761.

(*E*)-Butyl 3-(2-(8-methyl-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3t). brownish solid ; mp 66 - 68 °C. eluent, hexane/ethyl acetate (94:6), (78 mg, 43%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 16.0 Hz, 1H), 8.25 – 8.17 (m, 1H), 8.11 (ddd, *J* = 7.9, 1.6, 0.7 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.61 – 7.50 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 2.61 (s, 3H), 1.73 – 1.65 (m, 2H), 1.51 – 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.94, 159.96, 155.04, 145.19, 137.60, 137.10, 136.63, 132.03, 130.25, 129.83, 129.74 128.93, 128.41, 127.81, 126.20, 120.53, 116.94, 64.59, 31.03, 29.85, 22.83, 19.36, 17.49, 13.85; IR (KBr) 2958, 2926, 2872, 1760, 1710 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_4$ 364.1549; Found 364.1549.

(*E*)-Butyl 3-(2-(7,8-dimethyl-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 2, 3u). brownish gummy liquid. eluent, hexane/ethyl acetate (94:6), (75 mg, 40%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 15.9 Hz, 1H), 8.27 – 8.13 (m, 1H), 8.02 (d,

J = 8.0 Hz, 1H), 7.75 – 7.62 (m, 1H), 7.62 – 7.46 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 2.53 (s, 3H), 2.46 (s, 3H), 1.81 – 1.64 (m, 2H), 1.50 – 1.34 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.94, 160.17, 154.87, 146.60, 145.28, 144.83, 136.50, 135.27, 131.88, 130.47, 130.23, 130.14, 129.72, 128.88, 125.55, 120.44, 114.70, 64.56, 31.05, 21.22, 19.36, 13.85, 13.47; IR (KBr) 2958, 2929, 2872, 1751, 1711 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}NO_4$ 378.1705; Found 378.1706.

(*E*)-Methyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 3, 4a). white solid ; mp 133-136 °C. eluent, hexane/ethyl acetate (94:6), (113 mg, 74%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 15.9 Hz, 1H), 8.26 (ddd, *J* = 7.9, 1.6, 0.6 Hz, 1H), 8.19 – 8.08 (m, 1H), 7.85 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 7.77 – 7.64 (m, 2H), 7.62 – 7.50 (m, 3H), 6.38 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.33, 159.43, 156.55, 146.55, 144.65, 136.86, 136.05, 132.14, 130.38, 129.86, 129.82, 129.02, 128.67, 128.55, 127.74, 120.27, 116.91, 51.91; IR (KBr) 2951, 2924, 2850, 1781, 1766 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}NO_4$ 308.0923; Found 308.0923.

(*E*)-Methyl 3-(5-ethyl-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 3, 4b). blakish solid ; mp 122-126 °C. eluent, hexane/ethyl acetate (94:6), (122 mg, 73%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 15.9 Hz, 1H), 8.25 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.83 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.75 – 7.63 (m, 1H), 7.63 – 7.43 (m, 2H), 7.36 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.38 – 1.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.40, 159.56, 156.62, 148.98, 146.69, 145.12, 136.77, 136.17, 130.49, 129.48, 128.76, 128.59, 128.10, 127.65, 127.17, 119.92, 116.84, 51.86, 28.97, 15.22.; IR (KBr) 2963, 2928, 2853, 1763, 1719 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{17}NNaO_4$ 358.1055; Found 358.1057.

(*E*)-methyl 3-(5-butyl-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 3, 4c). yellow gummy liquid. eluent, hexane/ethyl acetate (94:6), (136 mg, 75%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 15.9 Hz, 1H), 8.24 (ddd, *J* = 7.9, 1.6, 0.6 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.82 (ddd, *J* = 8.1, 7.2, 1.5 Hz, 1H), 7.69 (ddd, *J* = 8.1, 1.2, 0.5 Hz, 1H), 7.53 (ddd, *J* = 7.9, 7.2, 1.2 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.33 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.64 (tt, *J* = 9.0, 7.5 Hz, 2H), 1.46 – 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.52, 167.40, 159.54, 156.62, 147.74, 146.67, 145.11, 136.75, 136.05, 130.38, 130.00, 128.73, 128.57, 127.62, 127.12, 119.88, 116.80, 51.85, 35.69, 27.11, 22.43, 14.00; IR (KBr) 2955, 2934, 2866, 1763, 1719 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_4$ 364.1549; Found 364.1549.

(*E*)-Methyl 3-(5-chloro-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 3, 4d). yellow solid ; mp 167-172 °C. eluent, hexane/ethyl acetate (94:6), (115 mg, 68%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 15.8 Hz, 1H), 8.24 (ddd, *J* = 7.9, 1.6, 0.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.84 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.70 (ddd, *J* = 8.1, 1.3, 0.5 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.56 (ddd, *J* = 7.9, 7.3, 1.2 Hz, 1H), 7.49 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.94, 159.10, 155.62, 146.35, 143.52, 138.50, 137.87, 136.91, 131.65, 129.79, 129.16, 128.69, 128.64, 127.93, 127.75, 121.25, 116.85, 52.00; IR (KBr) 2950, 2925, 2847, 1767, 1724 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}ClNO_4$ 342.0533; Found 342.0531.

(*E*)-Methyl 3-(5-bromo-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 3, 4e). white solid ; mp 170-173 °C. eluent, hexane/ethyl acetate (94:6), (136 mg, 71%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 15.8 Hz, 1H), 8.26 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.90 – 7.76 (m, 2H), 7.69 (ddd, *J* = 15.7, 8.4, 1.7 Hz, 2H), 7.58 (ddd, *J* = 8.1, 7.4, 1.3 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.96, 159.12, 155.79, 146.39, 143.47, 138.00, 136.94, 132.80, 131.70, 131.62, 129.21, 128.73, 128.43, 127.79, 126.98, 121.33, 116.91, 52.01; IR (KBr) 2923, 2852, 1776, 1621, 1602 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}BrNO_4$ 386.0028; Found 386.0024.

(*E*)-Methyl 3-(2-(7-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 3, 4f). blackish gummy liquid. eluent, hexane/ethyl acetate (94:6), (110 mg, 65%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 15.9 Hz, 1H), 8.24 – 8.08 (m, 2H), 7.75 – 7.64 (m, 2H), 7.64 – 7.44 (m, 3H), 6.37 (d, *J* = 15.8 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.24, 158.62, 157.79, 147.60, 144.43, 143.33, 136.26, 132.50, 130.50, 129.95, 129.88, 129.58, 129.37, 128.69, 127.46, 120.51, 115.27, 51.97; IR (KBr) 2918, 2853, 1766, 1719, 1598 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{12}ClNaO_4$ 364.0353; Found 364.0353.

(*E*)-Methyl 3-(5-chloro-2-(7-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 3, 4g). white solid ; mp 172-175 °C. eluent, hexane/ethyl acetate (94:6), (127 mg, 68%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 15.8 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 16.3, 2.0 Hz, 2H), 7.51 (ddd, *J* = 8.4, 6.1, 2.1 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 158.31, 156.89, 147.41, 143.42, 143.30, 138.94, 138.08, 131.79, 129.98, 129.84, 129.72, 128.79, 127.50, 127.47, 121.51, 115.21, 52.07; IR (KBr) 3089, 2922, 2852, 1774, 1723 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{12}Cl_2NO_4$ 376.0143; Found 376.0143.

(*E*)-Methyl 3-(2-(6-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-5-methylphenyl)acrylate (Table 3, 4h). brownish gummy liquid. eluent, hexane/ethyl acetate (94:6), (111 mg, 63%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 15.8 Hz, 1H), 8.20 (dd, *J* = 2.4, 0.5 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.76 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.65 (dd, *J* = 8.6, 0.5 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.40 – 7.29 (m, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.38, 158.48, 156.75, 145.16, 144.97, 143.18, 137.07, 136.24, 134.40, 130.69, 130.41, 129.40, 129.20, 127.96, 126.48, 120.06, 117.91, 51.91, 21.71; IR (KBr) 2919, 2850, 1777, 1723, 1621 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{14}ClNNaO_4$ 378.0509; Found 378.0508.

(*E*)-Methyl 3-(2-(4-oxo-7-(trifluoromethyl)-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 3, 4i). brownish solid ; mp 131-134 °C. eluent, hexane/ethyl acetate (94:6), (140 mg, 75%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 15.9 Hz, 1H), 8.45 – 8.32 (m, 1H), 8.15 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.96 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.77 (ddd, *J* = 8.2, 1.7, 0.7 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.64 – 7.48 (m, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 3.84 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.11, 158.21, 157.86, 146.86, 144.21, 138.31 (q, $^2J_{C-F}$ = 33.0 Hz), 136.39, 132.66, 130.54, 129.87, 129.69, 129.12, 128.72, 125.15 (q, $^4J_{C-F}$ = 3.0 Hz), 125.0 (q, $^3J_{C-F}$ = 4.0 Hz), 123.08 (q, $^1J_{C-F}$ = 272.0 Hz), 120.72, 119.45, 51.92. ^{19}F NMR (376 MHz, $CDCl_3$) δ -163.62. IR (KBr) 2950, 2918, 2853, 1772, 1718 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{13}F_3NO_4$ 376.0797; Found 376.0799.

(*E*)-Butyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)thiophen-3-yl)acrylate (Table 4, 5a). yellow solid ; mp 62-64 °C. eluent, hexane/ethyl acetate (93:7), (113 mg, 64%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.90 (dd, *J* = 16.1, 0.7 Hz, 1H), 8.21 (ddt, *J* = 7.9, 1.5, 0.7 Hz, 1H), 7.81 (dddd, *J* = 8.0, 7.2, 1.5, 0.6 Hz, 1H), 7.73 – 7.63 (m, 1H), 7.59 – 7.45 (m, 2H), 7.42 (dt, *J* = 5.3, 0.6 Hz, 1H), 6.42 (dd, *J* = 16.2, 0.7 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 1.84 – 1.62 (m, 2H), 1.62 – 1.38 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ

167.11, 158.60, 153.37, 146.71, 140.58, 137.37, 136.82, 131.82, 130.72, 128.83, 128.59, 127.56, 127.45, 122.04, 116.79, 64.77, 30.92, 19.42, 13.91; IR (KBr) 3107, 2958, 2932, 2872, 1765 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NO_4S$ 356.0957; Found 356.0959.

(*E*)-Butyl 3-(2-(6-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)thiophen-3-yl)acrylate (Table 4, 5b). yellow solid ; mp 72-75 °C. eluent, hexane/ethyl acetate (93:7), (116 mg, 60 %). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.88 (dt, *J* = 16.1, 0.6 Hz, 1H), 8.19 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.65 (dd, *J* = 8.7, 0.5 Hz, 1H), 7.56 (dd, *J* = 5.3, 0.7 Hz, 1H), 7.43 (dd, *J* = 5.3, 0.5 Hz, 1H), 6.44 (d, *J* = 16.1 Hz, 1H), 4.30 – 4.21 (m, 2H), 1.80 – 1.67 (m, 2H), 1.54 – 1.39 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.98, 157.47, 153.71, 145.35, 140.84, 137.22, 137.11, 134.29, 131.09, 128.98, 128.56, 128.25, 127.74, 122.44, 117.96, 64.80, 31.01, 19.43, 13.87; IR (KBr) 2958, 2927, 2872, 1768, 1710 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}ClNO_4S$ 390.0567; Found 390.0569.

(*E*)-Butyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)furan-3-yl)acrylate (Table 4, 5c). brownish gummy liquid. eluent, hexane/ethyl acetate (93:7), (94 mg, 56%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.58 (dt, *J* = 16.1, 0.7 Hz, 1H), 8.24 (ddd, *J* = 7.9, 1.6, 0.6 Hz, 1H), 7.84 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1H), 7.73 (ddd, *J* = 8.1, 1.3, 0.6 Hz, 1H), 7.63 (dd, *J* = 1.9, 0.7 Hz, 1H), 7.54 (ddd, *J* = 7.9, 7.3, 1.3 Hz, 1H), 6.82 (dd, *J* = 1.9, 0.6 Hz, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 1.73 (dd, *J* = 8.5, 5.9 Hz, 2H), 1.56 – 1.44 (m, 2H), 1.03 – 0.96 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.58, 158.19, 150.13, 147.21, 146.69, 146.27, 136.90, 134.32, 128.96, 128.83, 128.12, 127.53, 122.90, 117.14, 110.58, 64.80, 30.93, 19.41, 13.91. IR (KBr) 2964, 2931, 2873, 1770, 1712 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NO_5$ 340.1185; Found 340.1185.

(*E*)-Methyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)thiophen-3-yl)acrylate (Table 4, 5d). yellow solid ; mp 159-162 °C. eluent, hexane/ethyl acetate (93:7), (103 mg, 66%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.89 (dt, *J* = 16.1, 0.7 Hz, 1H), 8.21 (ddd, *J* = 7.9, 1.6, 0.6 Hz, 1H), 7.81 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.69 (ddd, *J* = 8.1, 1.3, 0.6 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.41 (dd, *J* = 5.3, 0.6 Hz, 1H), 6.42 (d, *J* = 16.1 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.38, 158.51, 153.42, 146.76, 140.51, 137.68, 136.78, 132.04, 130.68, 128.81, 128.58, 127.59, 127.53, 121.61, 116.86, 51.96; IR (KBr) 3020, 2924, 2852, 1758, 1745 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}NO_2S$ 314.0487; Found 314.0488.

(*E*)-Methyl 3-(2-(6-chloro-4-oxo-4H-benzo[d][1,3]oxazin-2-yl)thiophen-3-yl)acrylate (Table 4, 5e). yellow solid ; mp 172-177 °C. eluent, hexane/ethyl acetate (93:7), (111 mg, 64%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.84 (d, *J* = 16.1 Hz, 1H), 8.16 (d, *J* = 2.4 Hz, 1H), 7.75 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.55 (dd, *J* = 5.2, 0.7 Hz, 1H), 7.41 (dd, *J* = 5.3, 0.5 Hz, 1H), 6.42 (d, *J* = 16.1 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.34, 157.48, 153.53, 145.20, 140.81, 137.48, 137.11, 134.24, 131.50, 131.12, 129.02, 128.17, 127.71, 121.80, 117.83, 52.05; IR (KBr) 2960, 2954, 2850, 1767, 1718 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{11}ClNO_4S$ 348.0097; Found 348.0097.

(*E*)-Butyl 3-(4-methyl-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 5, 6a). brownish gummy liquid. eluent, hexane/ethyl acetate (94:6), (125 mg, 69%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 15.9 Hz, 1H), 8.25 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.85 – 7.79 (m, 1H), 7.75 – 7.68 (m, 1H), 7.63 – 7.51 (m, 2H), 7.43 – 7.32 (m, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 4.27 – 4.18 (m, 2H), 2.45 (s, 3H), 1.75 – 1.58 (m, 2H), 1.42 (ddq, *J* = 16.7, 9.4, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.09, 159.53, 156.68, 146.55, 143.94, 140.24, 136.77, 133.17, 132.92, 130.85, 129.62, 128.92, 128.61, 128.36, 127.65, 119.96, 116.85, 64.51, 30.95, 21.38, 19.37, 13.87; IR (KBr) 2960, 2938, 2876, 1723, 1601 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_4$ 364.1549; Found 364.1544.

(*E*)-Butyl 3-(4-methoxy-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 5, 6b). yellow solid ; mp 90-91 °C. eluent, hexane/ethyl acetate (94:6), (125 mg, 66%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 15.8 Hz, 1H), 8.25 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.72 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.09 (ddd, *J* = 8.7, 2.8, 0.6 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.90 (s, 3H), 1.72 – 1.59 (m, 2H), 1.54 – 1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.21, 160.80, 159.35, 156.43, 146.46, 143.42, 136.79, 131.27, 129.81, 129.04, 128.65, 128.33, 127.73, 118.96, 118.52, 116.94, 114.82, 64.46, 55.86, 30.98, 19.38, 13.86; IR (KBr) 2958, 2932, 2873, 1760, 1707 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_5$ 380.1498; Found 380.1496.

(*E*)-Butyl 3-(4-chloro-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 5, 6c). white solid ; mp 63-68 °C. eluent, hexane/ethyl acetate (94:6), (124 mg, 68%).^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.60 (dt, *J* = 15.8, 0.6 Hz, 1H), 8.26 (ddd, *J* = 7.9, 1.6, 0.6 Hz, 1H), 8.13 (d, *J* = 2.2 Hz, 1H), 7.85 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.72 (ddd, *J* = 8.1, 1.3, 0.6 Hz, 1H), 7.67 – 7.47 (m, 3H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 2H), 1.77 – 1.62 (m, 2H), 1.51 – 1.35 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.72, 158.98, 155.36, 146.24, 142.97, 136.91, 135.98, 134.49, 132.14, 131.02, 130.28, 129.79, 129.35, 128.75, 127.79, 121.29, 116.93, 64.72, 30.93, 19.37, 13.85; IR (KBr) 2958, 2926, 2851, 1766, 1716 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}ClNO_4$ 384.1003; Found 384.1005.

(*E*)-Methyl 3-(4-bromo-2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)phenyl)acrylate (Table 5, 6d). white solid ; mp > 200 °C. eluent, hexane/ethyl acetate (94:6), (119 mg, 62%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 15.9 Hz, 1H), 8.37 – 8.17 (m, 2H), 7.86 (d, *J* = 1.3 Hz, 1H), 7.79 – 7.64 (m, 2H), 7.64 – 7.46 (m, 2H), 6.36 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05, 158.95, 155.22, 146.24, 143.51, 136.95, 135.11, 134.88, 133.17, 131.20, 129.93, 129.35, 128.74, 127.83, 123.99, 120.76, 116.92, 51.96; IR (KBr) 3064, 2951, 1773, 1727, 1629 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}BrNO_4$ 386.0028; Found 386.0021.

(*E*)-Methyl 3-(2-(4-oxo-4H-benzo[d][1,3]oxazin-2-yl)-4-(trifluoromethyl)phenyl)acrylate (Table 5, 6e). brownish solid; mp 90-94 °C. eluent, hexane/ethyl acetate (94:6), (106 mg, 57%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 15.9 Hz, 1H), 8.41 (dd, *J* = 1.8, 0.9 Hz, 1H), 8.27 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.83 – 7.76 (m, 2H), 7.73 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.60 (td, *J* = 7.6, 1.2 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.83, 158.88, 155.32, 146.20, 143.39, 139.51, 137.03, 131.98 (q, $^2J_{C-F}$ = 34.0 Hz), 130.35, 129.51, 129.31, 128.83, 128.56 (q, $^4J_{C-F}$ = 3.0 Hz), 127.87, 127.37 (q, $^3J_{C-F}$ = 4.0 Hz), 122.21, 121.96 (q, $^1J_{C-F}$ = 265.0 Hz), 116.98, 52.09.; IR (KBr) 2925, 2354, 1766, 1722, 1628 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{13}F_3NO_4$ 376.0797; Found 376.0794.

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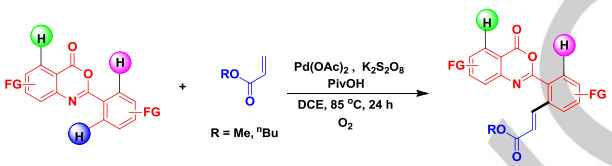

An efficient procedure for the Pd-catalyzed olefination of 4H-benzo[d][1,3]oxazin-4-ones with activated alkenes has been achieved via C-H activation.

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