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Hypervalent Iodine-Mediated Oxygenation of *N,N*-Diaryl Tertiary Amines: Intramolecular Functionalization of sp^3 C−H Bonds Adjacent to Nitrogen

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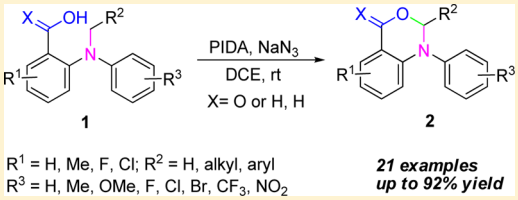
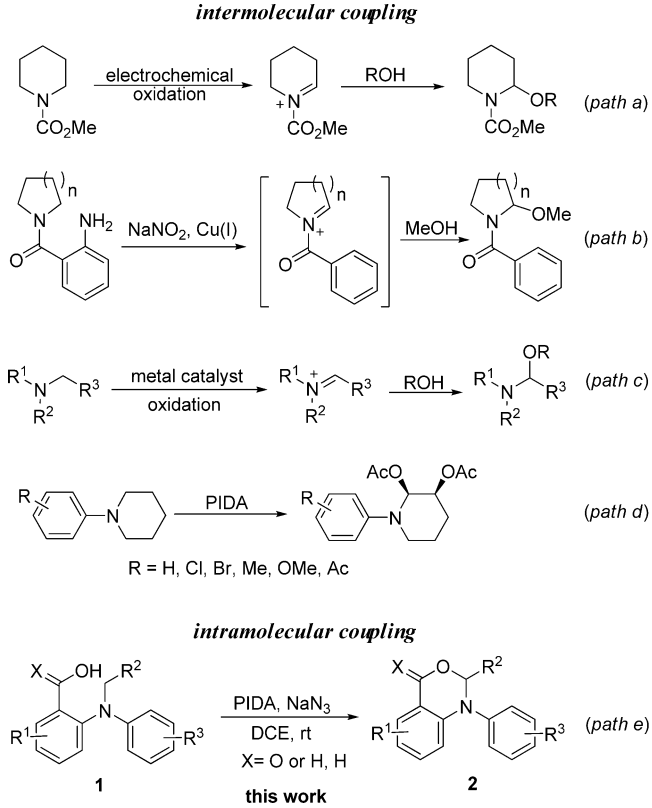
Supporting Information

ABSTRACT: An intramolecular C(sp^3)−O bond formation has been achieved via $PhI(OAc)_2/NaN_3$-mediated oxygenation of *N,N*-diaryl tertiary amines. The appealing features of this method include mild reaction conditions, absence of heavy-metal catalysts, and the direct intramolecular functionalization of sp^3 C−H bonds adjacent to nitrogen.



Direct C−H bond activation and subsequent C−C as well as C−heteroatom bond formation are of fundamental importance in the field of organic synthesis.[1] Among the many C−H bond activation approaches, catalytic cross-dehydrogenative-coupling (CDC) reactions have shown to be a class of attractive methods primarily for their step-economical property.[2] Selective functionalization of C−H bonds adjacent to a nitrogen atom in amines and amides using the CDC approach has been vastly studied for the functionalization of nitrogen-containing compounds.[3] Among them, direct formation of C−O bonds effectuated through an activated α-C−H of tertiary amines via electrochemical or transition-metal-catalyzed oxidation has been well-studied. For example, in a pioneering strategy of electrochemical oxidation developed by Shono,[4] the *N*-acyl iminium intermediate formed by electrochemical oxidation of a tertiary amine reacted with an alcohol to afford an aminal (Scheme 1, path a). Similarly, Weinreb and co-workers realized α-methoxylation of benzamides via cuprous ion-promoted decomposition of *o*-diazobenzamides, featuring a 1,5-hydrogen atom transfer process (Scheme 1, path b).[5] Transition metals, such as Ru(II), Os(III), Rh(II), or Fe(III) catalyst, have also been used in the α-functionalization of amines toward the formation of a C−O bond (Scheme 1, path c).[6] In 2009, by employing a hypervalent iodine(III) reagent, Liang and co-workers realized a direct *cis*-2,3-diacetoxylation of *N*-arylpiperidine derivates (Scheme 1, path d).[7] Most of such reactions occurred intermolecularly, and reports on applying the similar approach to intramolecularly constructing *N*-containing heterocycles are scarce.[8] In continuation of our work on applying hypervalent iodine oxidants to the construction of heterocyclic compounds,[9] we here present a novel synthesis of 1,2-dihydro-(4*H*)-3,1-benzoxazin-4-one derivatives[10] as well as 1,2-dihydro-(4*H*)-3,1-benzoxazine derivatives[11] through intramolecular functionalization of the sp^3 C−H bond adjacent to the nitrogen in an *N,N*-diaryl tertiary amine by using hypervalent iodine(III) reagents, a class of readily available oxidants[12] that have found broadened applications during recent years (Scheme 1, path e).

Scheme 1. Direct C−O Bond Formation via Activation of the C−H Bond Adjacent to N in a Tertiary Amine



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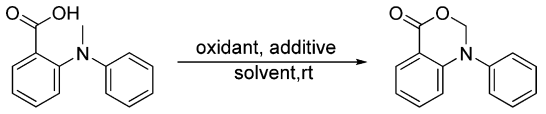
At the outset of the study, we postulated that treating *N*-methyl-*N*-phenylanthranilic acid **1a** with an appropriate hypervalent iodine reagent should generate an iminium intermediate that could be intramolecularly captured by the neighboring carboxylic acid group to yield aminal **2a**.[13] To our delight, the desired product **2a** was indeed formed after **1a** was treated with phenyliodine(III) diacetate (PIDA) in DCE at room temperature for 6 h (Table 1, entry 1). In order to improve the meager yield of 20%, the more potent phenyliodine(III) bis(trifluoroacetate) (PIFA) was employed, but only to find that it had caused the decomposition of **1a** and resulted in no desired product at all (Table 1, entry 2). Another hypervalent iodine(III) reagent, iodosobenzene (PhIO), was tested out, but the target product was obtained in an even lower yield of 12% (Table 1, entry 3). Additives known to benefit other oxidation reactions, such as $BF_3{\cdot}Et_2O$ and TFA, were found to either completely kill the reaction (Table 1, entries 4 and 6) or marginally benefit the reaction (Table 1, entry 5). Sparked by literature reports[14] on NaN_3 that it reacts with certain hypervalent iodine(III) reagents to generate a powerful iodine(III) intermediate for the oxidation reactions, we subjected 1.5 equiv of NaN_3 to the reaction and found that the desired product **2a** was obtained in a stunning yield of 90% (Table 1, entry 7). Further fine-tuning of the NaN_3 dosage as well as the solvent choice responded negatively with lower yields (Table 1, entries 8−13).[15]

Table 1. Optimization of Reaction Conditions[a]



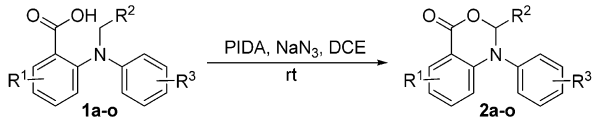
1a **2a**

entry	oxidant	additive (equiv)	solvent	time (min)	yield (%)[b]
1	PIDA		DCE	360	20
2	PIFA		DCE	5	0
3	PhIO		DCE	360	12
4	PIDA	$BF_3{\cdot}Et_2O$ (0.5)	DCE	60	0[c]
5	PIDA	TFA (0.5)	DCE	60	28[c]
6	PIDA	TFA (1.0)	DCE	60	0[c]
7	PIDA	NaN_3 (1.5)	DCE	30	90
8	PIDA	NaN_3 (2.0)	DCE	30	75
9	PIDA	NaN_3 (1.5)	DCM	30	86
10	PIDA	NaN_3 (1.5)	toluene	30	84
11	PIDA	NaN_3 (1.5)	MeOH	30	81
12	PIDA	NaN_3 (1.5)	EtOAc	30	18[d]
13	PIDA	NaN_3 (1.5)	CH_3CN	30	79

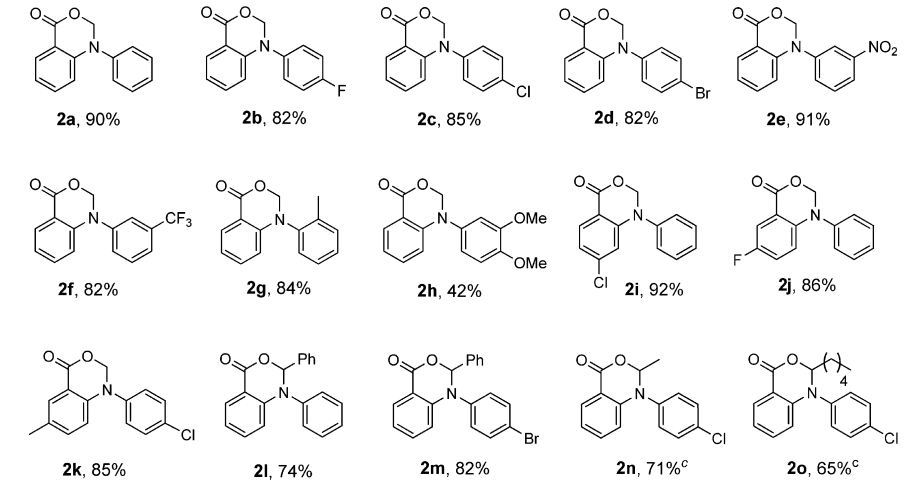
[a]Reaction conditions: **1a** (0.5 mmol), oxidant (1.5 mmol) in solvent (2.5 mL), unless otherwise stated. [b]Isolated yields. [c]A control experiment indicated that **2a** was decomposed under the acidic conditions. [d]A complex mixture.

Under the optimal reaction conditions (Table 1, entry 7), the scope of this newly established metal-free oxygenation reaction was explored. Various *N*-methyl-*N*-phenylanthranilic acid derivatives, containing either an electron-withdrawing or an electron-donating R^3 substituent were converted to the corresponding products **2b−h** in good to excellent yields. Notably, the strongly electron-donating methoxy groups negatively affected the reaction. In the case regarding the substrates bearing either a Cl, F, or a methyl R^1 group on the anthranilic ring, the desired products were also successfully achieved in good yields (Table 2, compounds **2i−k**). Importantly, when the R^2 group was extended to other substituents except H, such as an aryl or an alkyl group, the corresponding acids could also be converted into the cyclized products **2l−o** in moderate to good yields under the described conditions. The two diaryl substituents on the tertiary amine were important for this conversion, since the reaction either

Table 2. PIDA-Mediated Oxidation of *N*-Alkyl-*N*-aryl Anthranilic Acids[a,b,c]



1a-o **2a-o**



[a]Reaction conditions: **1** (0.5 mmol), PIDA (0.75 mmol), and NaN_3 (0.75 mmol) in DCE (2.5 mL) were stirred at rt for 0.5 h. [b]Isolated yields. [c]PIDA (1 mmol) and NaN_3 (1 mmol) were used.

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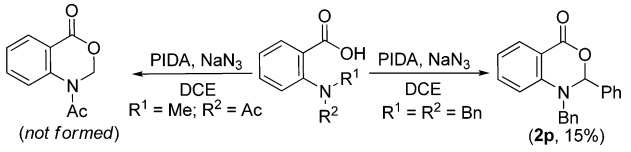
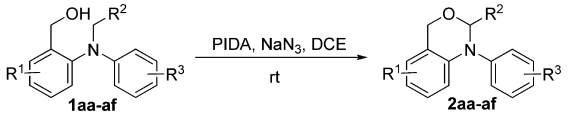
provided a trace amount of the desired product or could not occur at all when two benzyl groups or an acyl group and a methyl group were installed on the N atom in the substrates, respectively (Scheme 2).[16]

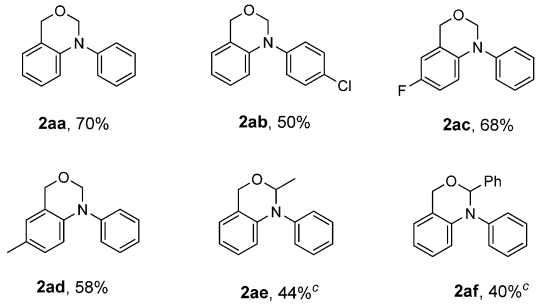
Scheme 2. Study of the Substrates Bearing an *N*-Alkylamine Substitutent



Our following study was to apply the novel method to a benzyl alcohol moiety where the carbonyl group in **1a** was replaced with a methylene group (Table 3). The yields were,

Table 3. PIDA-Mediated Oxidation of 2-(*N*-Alkyl-*N*-arylamino)benzyl Alcohol[a,b,c]





[a]Reaction conditions: **1** (0.5 mmol), PIDA (0.75 mmol), and NaN_3 (0.75 mmol) in DCE (2.5 mL) were stirred at rt for 0.5 h. [b]Isolated yields. [c]PIDA (1 mmol) and NaN_3 (1 mmol) were used, and the reaction time was 1 h.

overall, lower than the carboxylic acids series by 20−50%. Minute substituent effects were again observed, largely similar to that of the acid series, and for R^2 being a methyl or phenyl group, the reactions gave the corresponding cyclized products in acceptable yields, but again, were accompanied by lengthened reaction time.

On the basis of the above results as well as those in the literature,[3,7] we propose a possible mechanistic pathway. Shown in Scheme 3, the unstable and highly reactive azidoiodinane, $PhI(N_3)OAc$, was first generated in situ from the reaction of $PhI(OAc)_2$ with NaN_3. Then, a direct nucleophilic attack of the N center of *N*-methyl-*N*-phenylanthranilic acid **1a** onto the iodine center of $PhI(N_3)OAc$ generates the ammonium ion **A′**. In the presence of the basic N_3 anion, the ammonium **A′** is converted to iminium salt **A**, with the release of one molecule of iodobenzene, acetic acid, and hydrazoic acid. Finally, an intramolecular nucleophilic cyclization occurred in **A** and led to the formation of the aminal product **2a**. Although hydrazoic acid is known to be sensitive to shock and friction, it readily decomposed to N_2 and H_2 triggered by the stirring during the reactions. The substituent effect of R^3 observed in our study suggests that the final intramolecular nucleophilic cyclization is the more important step in the overall reaction, as the electron-withdrawing group (NO_2) would effectively increase the electrophilicity of the nitrogen in the iminium while the electron-donating group (OMe) would do the opposite. Our control experiment showed that the radical inhibitor, i.e., TEMPO, did not have any influence on the reaction rate and outcome of the product yield, which suggests that the reaction might proceed via an ionic mechanism.

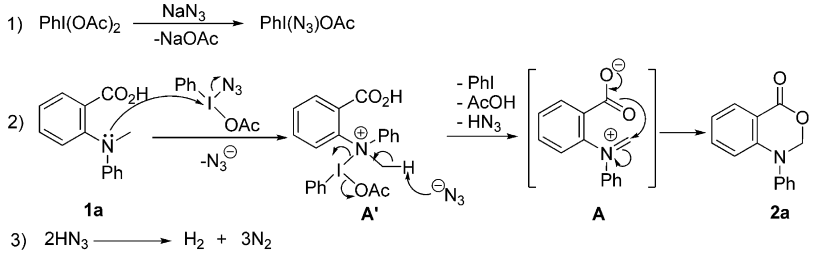
In summary, we have discovered a new PIDA-mediated oxygenation protocol of intramolecularly functionalizing sp^3 C−H bonds adjacent to the nitrogen in a tertiary amine. This method features a direct construction of an aminal skeleton through α-C−H bond activation/C−O bond formation mediated by $PhI(OAc)_2$. With this method, a series of 1,2-dihydro-(4*H*)-3,1-benzoxazin-4-one derivatives and 1,2-dihydro-(4*H*)-3,1-benzoxazine derivatives were synthesized under mild reaction conditions. Further research on elucidating the oxidative system of PIDA with NaN_3 and synthetic applications of the strategy are in progress in our lab.

EXPERIMENTAL SECTION

I. General Information. ^1H and ^{13}C NMR spectra were recorded on a 600 MHz or 400 MHz spectrometer at 25 °C. Chemical shifts values are given in ppm (parts per million) and referred to the internal standard TMS set as 0.00 ppm. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; m, multiplet; dd, doublet of doublets and td, triplet of doublets. The coupling constants, *J*, are reported in hertz (Hz). High-resolution mass spectrometry (HRMS) was obtained on a Q-TOF micro spectrometer. Melting points were determined with a MicroMelting point apparatus without corrections. TLC plates were visualized by UV fluorescence quenching. Reagents and solvents were purchased as reagent grade and were used without further purification. All reactions were performed in standard glassware, heated at 70 °C for 4 h before use. Flash column chromatography was performed over Sephadex LH-20 or silica gel (200−300 mesh), and the eluent was a mixture of EtOAc and petroleum ether (PE).

II. General Procedures for Synthesis of Substrates 1. All the known substrates **1a**,[17] **1f**,[18] **1l**,[19] **1p**,[17] **1aa**,[20] **1ac**,[21] and **1ad**[21] were prepared following literature procedures.

Scheme 3. Proposed Reaction Pathway



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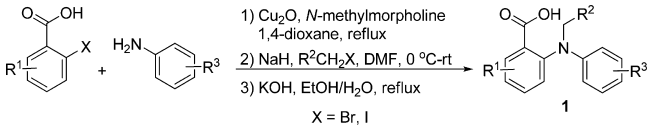

A. Synthesis of N-Alkyl-N-aryl Anthranilic Acids. To a solution of 2-iodobenzoic acid or 2-bromobenzoic acid derivative (20 mmol) in 1,4-dioxane (60 mL) were added Cu_2O (10 mmol), *N*-methylmorpholine (30 mmol), and aniline (30 mmol). The resulting mixture was refluxed under N_2 until the completion of the reaction. The mixture was then filtered and concentrated. KOH solution (0.5 N, 50 mL) was added to the residue, and the mixture was filtered. The pH value of the filtrate was adjusted to 4−5 using conc. HCl. The solid generated was filtered and dissolved into DMF (80 mL). To the solution was slowly added NaH (60 mmol) at 0 °C, and the mixture was stirred for 30 min, followed by the addition of methyl iodide (60 mmol) or haloalkane. The reaction was allowed to stir at room temperature overnight. The mixture was poured into water (150 mL) and extracted with EtOAc (3 × 80 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (PE/EtOAc) on silica gel.

To the obtained oil was added a mixture of KOH in a 5:1 mixture of MeOH/H_2O (0.6 M), and the resulting mixture was refluxed. Upon completion, the mixture was concentrated and the residue was poured into water (50 mL). The solution was acidified to pH 4−5 with conc. HCl. The solid generated was collected via filtration to give the desired product. If no precipitation, the reaction mixture was extracted with EtOAc (3 × 80 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated to give the product.

*2-((4-Fluorophenyl)(methyl)amino)benzoic Acid (**1b**).* (prepared from 2-iodobenzoic acid and methyl iodide): Yield: 2.84 g, 58% (3 steps), yellow solid, mp. 82−88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.96 (s, 1H), 8.35 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 7.9 Hz, 1H), 6.99 (t, J = 8.4 Hz, 2H), 6.89 (dd, J = 8.4, 4.2 Hz, 2H), 3.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 158.9 (d, J_{C-F} = 243.2 Hz), 150.7, 144.4, 135.0, 132.6, 127.9, 126.8, 126.1, 120.1 (d, J_{C-F} = 7.9 Hz), 116.1 (d, J_{C-F} = 22.7 Hz), 42.5. HRMS (ESI) calcd for $C_{14}H_{12}FNNaO_2^+$ [M + Na^+] 268.0744; found 268.0748.

*2-((4-Chlorophenyl)(methyl)amino)benzoic Acid (**1c**).* (prepared from 2-iodobenzoic acid and methyl iodide): Yield: 3.13 g, 60% (3 steps), yellow solid, mp. 107−108 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.66 (s, 1H), 8.36 (dd, J = 7.9, 1.5 Hz, 1H), 7.60 (td, J = 7.9, 1.6 Hz, 1H), 7.49−7.44 (m, 1H), 7.27−7.24 (m, 2H), 7.10 (dd, J = 8.0, 0.6 Hz, 1H), 6.83 (d, J = 9.0 Hz, 2H), 3.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 150.0, 147.0, 135.0, 132.7, 129.3, 127.9, 127.2, 126.4, 119.2, 116.6, 42.0. HRMS (ESI) calcd for $C_{14}H_{12}{}^{35}ClNNaO_2^+$ [M + Na^+] 284.0449; found 284.0450.

*2-((4-Bromophenyl)(methyl)amino)benzoic Acid (**1d**).* (prepared from 2-iodobenzoic acid and methyl iodide): Yield: 3.47 g, 57% (3 steps), yellow solid, mp. 113−114 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.52 (s, 1H), 8.33 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 8.3 Hz, 2H), 3.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 145.0, 147.5, 135.1, 132.7, 132.2, 128.0, 127.3, 126.3, 119.6, 115.4, 41.9. HRMS (ESI) calcd for $C_{14}H_{12}{}^{79}BrNNaO_2^+$ [M + Na^+] 327.9944; found 327.9948.

*2-(Methyl(3-nitrophenyl)amino)benzoic Acid (**1e**).* (prepared from 2-iodobenzoic acid and methyl iodide): Yield: 2.82 g, 52% (3 steps), yellow solid, mp. 124−125 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.69−7.61 (m, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 3.32 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 149.8, 149.2, 147.9, 135.2, 133.1, 129.6, 129.3, 127.7, 127.4, 120.6, 113.7, 108.6, 40.8. HRMS (ESI) calcd for $C_{14}H_{12}N_2NaO_4^+$ [M + Na^+] 295.0689; found 295.0693.

*2-(Methyl(2-tolyl)amino)benzoic Acid (**1g**).* (prepared from 2-iodobenzoic acid and methyl iodide): Yield: 2.79 g, 58% (3 steps), off-white solid, mp. 107−108 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 14.36 (s, 1H), 8.29 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.35−7.28 (m, 2H), 7.18−7.11 (m, 2H), 6.89 (d, J = 8.0 Hz, 1H), 3.20 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 151.5, 146.4, 134.4, 132.8, 132.5, 132.0, 127.0, 126.4, 125.5, 124.8, 124.5, 120.4, 45.1, 19.0. HRMS (ESI) calcd for $C_{15}H_{15}NNaO_2^+$ [M + Na^+] 264.0995; found 264.0996.

*2-((3,4-Dimethoxyphenyl)(methyl)amino)benzoic Acid (**1h**).* (prepared from 2-iodobenzoic acid and methyl iodide): Yield: 3.55 g, 62% (3 steps), light yellow solid, mp. 95−96 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 14.59 (s, 1H), 8.36 (dd, J = 7.9, 1.4 Hz, 1H), 7.57 (td, J = 7.9, 1.5 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 6.59 (dd, J = 8.7, 2.7 Hz, 1H), 6.41 (d, J = 2.6 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 151.2, 149.7, 145.9, 141.9, 134.8, 132.4, 127.7, 126.5, 125.8, 111.7, 110.5, 104.5, 56.2, 56.0, 42.7. HRMS (ESI) calcd for $C_{16}H_{17}NNaO_4^+$ [M + Na^+] 310.1050; found 310.1057.

*4-Chloro-2-(methyl(phenyl)amino)benzoic Acid (**1i**).* (prepared from 2-bromo-4-chlorobenzoic acid and methyl iodide): Yield: 2.35 g, 45% (3 steps), yellow solid, mp. 90−91 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.76 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.31 (t, J = 6.9 Hz, 2H), 7.09 (m, 2H), 6.91 (d, J = 7.4 Hz, 2H), 3.22 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 151.6, 147.7, 140.5, 133.7, 129.5, 128.2, 127.5, 124.8, 123.4, 118.5, 42.0. HRMS (ESI) calcd for $C_{14}H_{12}{}^{35}ClNNaO_2^+$ [M + Na^+] 284.0449; found 284.0450.

*5-Fluoro-2-(methyl(phenyl)amino)benzoic Acid (**1j**).* (prepared from 2-bromo-5-fluorobenzoic acid and methyl iodide): Yield: 2.59 g, 53% (3 steps), yellow solid, mp. 71−72 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.78 (s, 1H), 8.02 (dd, J = 8.8, 3.1 Hz, 1H), 7.33−7.26 (m, 3H), 7.13 (dd, J = 8.8, 4.7 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 7.9 Hz, 2H), 3.21 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 161.1 (d, J_{C-F} = 249.6 Hz), 148.1, 146.6, 129.5, 129.1 (d, J_{C-F} = 8.1 Hz), 128.4 (d, J_{C-F} = 7.8 Hz), 123.3, 122.2 (d, J_{C-F} = 23.2 Hz), 118.6 (d, J_{C-F} = 24.2 Hz), 118.4, 42.1. HRMS (ESI) calcd for $C_{14}H_{12}FNNaO_2^+$ [M + Na^+] 268.0744; found 268.0746.

*2-((4-Chlorophenyl)(methyl)amino)-5-methylbenzoic Acid (**1k**).* (prepared from 2-bromo-5-methylbenzoic acid and methyl iodide): Yield: 2.97 g, 54% (3 steps), off-white solid, mp. 98−99 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.75 (s, 1H), 8.15 (s, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.23 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.1 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 3.19 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 147.5, 147.2, 138.3, 135.8, 132.8, 129.2, 128.0, 126.8, 125.9, 119.3, 42.0, 20.9. HRMS (ESI) calcd for $C_{15}H_{14}{}^{35}ClNNaO_2^+$ [M + Na^+] 298.0605; found 298.0610.

*2-(Benzyl(4-bromophenyl)amino)benzoic Acid (**1m**).* (prepared from 2-iodobenzoic acid and benzyl bromide): Yield: 4.72 g, 62% (3 steps), yellow solid, mp. 122−123 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (dd, J = 7.9, 1.4 Hz, 1H), 7.58 (td, J = 7.9, 1.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 9.0 Hz, 2H), 7.26−7.18 (m, 6H), 6.76 (d, J = 8.9 Hz, 2H), 4.74 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 147.7, 147.5, 136.5, 134.2, 132.6, 131.9, 129.3, 128.7, 128.3, 127.9, 127.6, 127.1, 118.5, 112.8, 57.9. HRMS (ESI) calcd for $C_{20}H_{16}{}^{79}BrNNaO_2^+$ [M + Na^+] 404.0257; found 404.0260.

*2-((4-Chlorophenyl)(ethyl)amino)benzoic Acid (**1n**).* (prepared from 2-iodobenzoic acid and ethyl bromide): Yield: 3.02 g, 55% (3 steps), yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 14.33 (s, 1H), 8.36 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 8.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 3.62 (d, J = 6.9 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 148.0, 146.3, 135.0, 132.4, 129.4, 128.5, 128.1, 127.7, 127.4, 120.6, 48.4, 12.2. HRMS (ESI) calcd for $C_{15}H_{14}{}^{35}ClNNaO_2^+$ [M + Na^+] 298.0605; found 298.0608.

*2-((4-Chlorophenyl)(hexyl)amino)benzoic Acid (**1o**).* (prepared from 2-iodobenzoic acid and hexyl bromide): Yield: 3.31 g, 50% (3 steps), yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 14.03 (s, 1H), 8.35 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 7.1 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 7.9 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 3.56−3.45 (m, 2H), 1.62−1.51 (m, 2H), 1.36−1.22 (m, 6H), 0.86 (t, J = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 148.6, 146.4, 134.8, 132.5, 129.4, 128.5, 127.9, 127.6, 127.2, 120.6, 54.6, 31.4,

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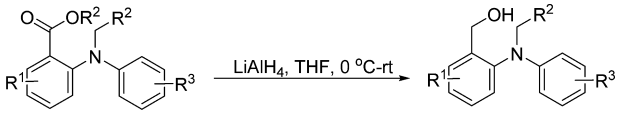
26.9, 26.8, 22.5, 13.9. HRMS (ESI) calcd for $C_{19}H_{22}{}^{35}ClNNaO_2{}^+$ [M + Na^+] 354.1231; found 354.1238.

B. Synthesis of 2-(N-Alkyl-N-arylamino)benzyl Alcohol. The starting material used in this section was prepared by the method



described above: To a solution of the ester (10 mmol) in THF (30 mL) was slowly added $LiAlH_4$ (15 mmol) portionwise at 0 °C, and then the mixture was stirred at room temperature until the completion of the reaction. Then, the reaction was quenched by diluted HCl (2 N, 10 mL), followed by the adding of water (30 mL). The mixture was extracted with EtOAc (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (PE/EtOAc) on silica gel to give the desired product.

*(2-((4-Chlorophenyl)(methyl)amino)phenyl)methanol (**1ab**).* Yield: 1.35 g, 55% (3 steps), light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, J = 7.3 Hz, 1H), 7.34 (dt, J = 7.5, 3.7 Hz, 1H), 7.30 (t, J = 7.0 Hz, 1H), 7.13−7.06 (m, 3H), 6.47 (d, J = 9.0 Hz, 2H), 4.54 (s, 2H), 3.18 (s, 3H), 2.30 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 145.9, 138.9, 129.5, 129.0, 128.9, 128.0, 127.2, 122.7, 114.8, 61.9, 40.1. HRMS (ESI) calcd for $C_{14}H_{14}{}^{35}ClNNaO^+$ [M + Na^+] 270.0656; found 270.0660.

*(2-(Ethyl(phenyl)amino)phenyl)methanol (**1ae**).* Yield: 1.31 g, 58% (3 steps), yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 7.13 (t, J = 7.7 Hz, 3H), 6.70 (t, J = 7.2 Hz, 1H), 6.53 (d, J = 8.1 Hz, 2H), 4.52 (s, 2H), 3.63 (q, J = 7.2 Hz, 2H), 2.40 (s, 1H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.5, 144.3, 139.6, 129.5, 129.3, 129.2, 129.0, 127.0, 117.5, 113.7, 62.0, 46.3, 12.8. HRMS (ESI) calcd for $C_{15}H_{17}NNaO^+$ [M + Na^+] 250.1202; found 250.1208.

*(2-(Benzyl(phenyl)amino)phenyl)methanol (**1af**).* Yield: 1.73 g, 60% (3 steps), yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, J = 7.2 Hz, 1H), 7.34−7.28 (m, 6H), 7.23 (m, 2H), 7.12 (t, J = 7.9 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 8.3 Hz, 2H), 4.83 (s, 2H), 4.49 (s, 2H), 1.80 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.0, 145.1, 139.4, 138.7, 129.4, 129.3, 129.2, 129.0, 128.7, 127.2, 127.1, 127.1, 118.1, 114.2, 61.8, 56.8. HRMS (ESI) calcd for $C_{20}H_{19}NNaO^+$ [M + Na^+] 312.1359; found 312.1360.

III. General Procedure for PIDA/NaN_3-Mediated Oxygenation of Substrates 1. To a solution of substrate **1** (0.5 mmol) in DCE (2.5 mL) was added PIDA (1.5 equiv) and NaN_3 (1.5 equiv). The mixture was stirred at room temperature until the total consumption of the substrate. Then, saturated $NaHCO_3$ (20 mL) was added to quench the reaction, followed by extraction with EtOAc (2 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (PE/EtOAc) on sephadex LH-20 (for **2a**−**p**) or silica gel (for **2aa**−**af**) to afford the desired product.

*1-Phenyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2a**).*[10h] Yield: 103 mg, 92%, light brown solid, mp. 66−67 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, J = 7.9, 1.1 Hz, 1H), 7.49−7.43 (m, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.7 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 5.57 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.1, 146.7, 143.7, 134.9, 131.0, 129.8, 125.5, 123.1, 122.5, 118.2, 116.7, 80.7.

*1-(4-Fluorophenyl)-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2b**).* Yield: 99 mg, 82%, light yellow solid, mp. 77−78 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.9, 1.3 Hz, 1H), 7.47−7.43 (m, 1H), 7.15−7.07 (m, 5H), 6.91 (d, J = 8.3 Hz, 1H), 5.50 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 160.5 (d, J_{C-F} = 246.2 Hz), 147.1, 139.9, 134.9, 131.1, 125.7 (d, J_{C-F} = 8.4 Hz), 122.5, 117.8, 116.7 (d, J_{C-F} = 22.8 Hz), 116.6, 80.9. HRMS (ESI) calcd for $C_{14}H_{10}FNNaO_2{}^+$ [M + Na^+] 266.0588; found 266.0590.

*1-(4-Chlorophenyl)-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2c**).*[10h] Yield: 110 mg, 85%, light brown solid, mp. 108−109 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 7.9 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 8.7 Hz, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.3 Hz, 1H), 5.53 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 146.2, 142.5, 135.0, 131.1, 130.7, 129.9, 124.2, 123.0, 118.4, 117.1, 80.7.

*1-(4-Bromophenyl)-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2d**).*[10h] Yield: 124 mg, 82%, light brown solid, mp. 110−111 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, J = 7.7 Hz, 1H), 7.49 (dd, J = 12.6, 8.4 Hz, 3H), 7.15 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.1 Hz, 3H), 5.54 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 146.1, 143.0, 135.0, 132.9, 131.1, 124.5, 123.1, 118.4, 118.3, 117.2, 80.6.

*1-(3-Nitrophenyl)-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2e**).* Yield: 122 mg, 91%, yellow solid, mp. 132−133 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.7 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.99 (s, 1H), 7.57 (t, J = 8.0 Hz, 2H), 7.48 (d, J = 7.5 Hz, 1H), 7.30−7.26 (m, 1H), 7.13 (d, J = 8.1 Hz, 1H), 5.66 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 149.2, 145.5, 144.9, 135.2, 131.4, 130.7, 127.6, 124.4, 119.4, 119.2, 118.2, 116.6, 80.5. HRMS (ESI) calcd for $C_{14}H_{10}N_2NaO_4{}^+$ [M + Na^+] 293.0533; found 293.0535.

*1-(3-(Trifluoromethyl)phenyl)-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (**2f**).*[22] Yield: 120 mg, 82%, off-white solid, mp. 68−69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.2 Hz, 1H), 7.53 (t, J = 8.3 Hz, 2H), 7.47 (d, J = 7.7 Hz, 1H), 7.40 (s, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.3 Hz, 1H), 5.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 145.7, 144.7, 135.0, 132.4 (q, J_{C-F} = 32.4 Hz), 131.2, 130.4, 125.7, 123.6 (q, J_{C-F} = 272.1 Hz), 123.6, 121.7 (q, J_{C-F} = 3.7 Hz), 119.2 (q, J_{C-F} = 3.7 Hz), 118.7, 117.7, 80.6.

*1-(2-Tolyl)-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2g**).*[10h] Yield: 100 mg, 84%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H), 7.40−7.33 (m, 2H), 7.29−7.25 (m, 2H), 7.09 (dd, J = 6.6, 1.8 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.47 (d, J = 8.3 Hz, 1H), 5.42 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 148.2, 140.8, 135.9, 135.2, 131.8, 131.2, 127.9, 127.6, 127.3, 120.8, 115.8, 114.3, 80.2, 18.3.

*1-(3,4-Dimethoxyphenyl)-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2h**).* Yield: 60 mg, 42%, light brown solid, mp. 129−130 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 5.49 (s, 2H), 3.91 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.1, 149.8, 147.8, 147.5, 136.6, 134.9, 131.0, 121.7, 117.3, 116.7, 115.6, 111.7, 108.5, 80.9, 56.2, 56.1. HRMS (ESI) calcd for $C_{16}H_{15}NNaO_4{}^+$ [M + Na^+] 308.0893; found 308.0898.

*7-Chloro-1-phenyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2i**).*[10h] Yield: 119 mg, 92%, light brown solid, mp. 94−95 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 7.2 Hz, 1H), 7.44 (s, 2H), 7.27 (d, J = 6.2 Hz, 1H), 7.17 (d, J = 5.3 Hz, 2H), 7.04 (d, J = 6.8 Hz, 1H), 6.96 (s, 1H), 5.54 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 147.8, 142.6, 141.4, 132.5, 130.1, 126.3, 123.7, 122.7, 117.2, 114.2, 80.5.

*6-Fluoro-1-phenyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2j**).* Yield: 104 mg, 86%, light brown solid, mp. 76−77 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.2, 2.9 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.24−7.18 (m, 2H), 7.11 (d, J = 7.7 Hz, 2H), 7.05 (dd, J = 8.8, 4.3 Hz, 1H), 5.57 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 158.0 (d, J_{C-F} = 243.7 Hz), 144.2, 143.0, 129.9, 125.4, 122.9 (d, J_{C-F} = 24.0 Hz), 122.8 (s), 121.1 (d, J_{C-F} = 7.7 Hz), 118.3 (d, J_{C-F} = 7.7 Hz), 116.2 (d, J_{C-F} = 23.7 Hz), 81.2. HRMS (ESI) calcd for $C_{14}H_{10}FNNaO_2{}^+$ [M + Na^+] 266.0588; found 266.0589.

*1-(4-Chlorophenyl)-6-methyl-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (**2k**).* Yield: 107 mg, 90%, off-white solid, mp. 110−111 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.32 (t, J = 7.1 Hz, 3H), 7.04 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.5 Hz, 1H), 5.52 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 143.7, 143.2, 136.1, 133.3, 130.7, 130.2, 129.8, 123.8, 119.1, 117.5, 80.9, 20.8. HRMS (ESI) calcd for $C_{15}H_{12}{}^{33}ClNNaO_2{}^+$ [M + Na^+] 296.0449; found 296.0449.

*1,2-Diphenyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2l**).* Yield: 111 mg, 74%, off-white solid, mp. 103−104 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, J = 6.9 Hz, 1H), 7.59−7.06 (m, 12H),

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6.98 (d, J = 7.3 Hz, 1H), 6.78 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 144.9, 144.7, 137.5, 135.2, 130.6, 129.8, 129.1, 128.8, 127.3, 125.3, 122.9, 122.1, 119.1, 117.4, 91.0. HRMS (ESI) calcd for $C_{20}H_{15}NNaO_2^+$ [M + Na^+] 324.0995; found 324.0998.

1-(4-Bromophenyl)-2-phenyl-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (**2m**). Yield: 155 mg, 82%, light brown solid, mp. 102−103 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 1H), 7.48−7.44 (m, 5H), 7.32 (d, J = 5.4 Hz, 3H), 7.09 (d, J = 8.3 Hz, 1H), 7.06 (d, J = 8.1 Hz, 2H), 7.02 (t, J = 7.2 Hz, 1H), 6.73 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 144.5, 143.8, 137.0, 135.3, 132.8, 130.7, 129.3, 128.9, 127.3, 124.6, 122.6, 119.1, 118.2, 117.7, 90.9. HRMS (ESI) calcd for $C_{20}H_{14}{}^{79}BrNNaO_2^+$ [M + Na^+] 402.0100; found 402.0104.

1-(4-Chlorophenyl)-2-methyl-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (**2n**). Yield: 97 mg, 71%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 10.1 Hz, 3H), 7.12 (d, J = 7.7 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 6.69 (d, J = 8.3 Hz, 1H), 5.76 (q, J = 5.5 Hz, 1H), 1.57 (d, J = 5.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 147.1, 141.0, 135.1, 132.5, 130.7, 130.1, 128.3, 121.8, 118.2, 115.9, 87.3, 19.9. HRMS (ESI) calcd for $C_{15}H_{12}{}^{35}ClNNaO_2^+$ [M + Na^+] 296.0449; found 296.0450.

1-(4-Chlorophenyl)-2-pentyl-1,2-dihydro-4H-benzo[d][1,3]-oxazin-4-one (**2o**). Yield: 107 mg, 65%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 7.7 Hz, 2H), 7.09 (d, J = 7.9 Hz, 3H), 6.82 (d, J = 8.2 Hz, 1H), 5.60 (t, J = 6.5 Hz, 1H), 1.99−1.78 (m, 2H), 1.61−1.43 (m, 2H), 1.31−1.24 (m, 4H), 0.87 (t, J = 5.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 145.8, 142.9, 135.0, 131.5, 130.5, 129.9, 126.5, 122.4, 119.6, 117.1, 91.7, 33.3, 31.2, 24.6, 22.5, 14.0. HRMS (ESI) calcd for $C_{19}H_{20}{}^{35}ClNNaO_2^+$ [M + Na^+] 352.1075; found 352.1075.

1-Benzyl-2-phenyl-1,2-dihydro-4H-benzo[d][1,3]oxazin-4-one (**2p**). Yield: 23 mg, 15%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 1H), 7.48−7.40 (m, 3H), 7.36−7.26 (m, 8H), 6.95 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.33 (s, 1H), 4.63 (d, J = 16.1 Hz, 1H), 4.41 (d, J = 16.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.89 (s), 148.32 (s), 136.89 (s), 136.00 (s), 135.44 (s), 130.93 (s), 129.42 (s), 128.84 (s), 128.67 (s), 127.68 (s), 127.48 (s), 127.20 (s), 120.81 (s), 116.36 (s), 115.97 (s), 90.45 (s), 53.35 (s). HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2^+$ [M + Na^+] 338.1151; found 338.1157.

1-Phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazine (**2aa**). Yield: 74 mg, 70%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, J = 7.7 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 7.08 (dd, J = 12.7, 6.5 Hz, 2H), 7.01 (d, J = 7.5 Hz, 1H), 6.98−6.91 (m, 2H), 5.03 (s, 2H), 4.97 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.8, 141.6, 129.3, 127.0, 125.2, 125.1, 123.8, 123.5, 121.5, 120.1, 82.1, 67.7. HRMS (ESI) calcd for $C_{14}H_{13}NNaO^+$ [M + Na^+] 234.0889; found 234.0893.

1-(4-Chlorophenyl)-1,4-dihydro-2H-benzo[d][1,3]oxazine (**2ab**). Yield: 61 mg, 50%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, J = 8.8 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 7.06−7.03 (m, 2H), 7.00 (d, J = 7.3 Hz, 1H), 6.97−6.90 (m, 2H), 4.98 (s, 2H), 4.95 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.6, 141.3, 129.4, 128.9, 127.1, 125.4, 125.3, 124.6, 121.9, 120.4, 82.1, 67.6. HRMS (ESI) calcd for $C_{14}H_{12}{}^{35}ClNNaO^+$ [M + Na^+] 268.0500; found 268.0508.

6-Fluoro-1-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazine (**2ac**). Yield: 77 mg, 68%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, J = 7.8 Hz, 2H), 7.11−7.05 (m, 3H), 6.94 (dd, J = 8.9, 5.0 Hz, 1H), 6.83 (td, J = 8.6, 2.6 Hz, 1H), 6.73 (dd, J = 8.6, 2.5 Hz, 1H), 5.00 (s, 2H), 4.93 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1 (d, J_{C-F} = 241.5 Hz), 148.46 (s), 137.60 (s), 129.37 (s), 127.22 (d, J = 6.8 Hz), 123.71 (s), 123.08 (s), 122.81 (d, J = 7.7 Hz), 114.31 (d, J = 22.6 Hz), 111.41 (d, J = 23.1 Hz), 82.31 (s), 67.27 (s). HRMS (ESI) calcd for $C_{14}H_{12}FNNaO^+$ [M + Na^+] 252.0795; found 252.0798.

6-Methyl-1-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazine (**2ad**). Yield: 65 mg, 58%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, J = 7.8 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 7.04 (t, J = 7.3 Hz, 1H), 6.91 (q, J = 8.3 Hz, 2H), 6.83 (s, 1H), 5.02 (s, 2H), 4.93 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.4, 139.0, 131.4, 129.3, 127.8, 125.6, 125.5, 123.4, 123.0, 121.0, 82.2, 67.6, 20.9. HRMS (ESI) calcd for $C_{15}H_{15}NNaO^+$ [M + Na^+] 248.1046; found 248.1048.

2-Methyl-1-phenyl-1,4-dihydro-2H-benzo[d][1,3]oxazine (**2ae**). Yield: 49 mg, 44%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, J = 7.8 Hz, 2H), 7.24−7.17 (m, 3H), 7.03−6.96 (m, 2H), 6.83 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H), 5.15 (q, J = 5.8 Hz, 1H), 5.04 (d, J = 14.9 Hz, 1H), 4.96 (d, J = 14.9 Hz, 1H), 1.33 (d, J = 5.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.7, 143.1, 129.5, 128.0, 127.2, 125.8, 124.6, 123.0, 119.8, 118.8, 85.6, 65.5, 19.9. HRMS (ESI) calcd for $C_{15}H_{15}NNaO^+$ [M + Na^+] 248.1046; found 248.1050.

1,2-Diphenyl-1,4-dihydro-2H-benzo[d][1,3]oxazine (**2af**). Yield: 57 mg, 40%, light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 7.3 Hz, 2H), 7.26 (t, J = 7.2 Hz, 2H), 7.24−7.19 (m, 3H), 7.09 (d, J = 7.7 Hz, 2H), 7.03−6.98 (m, 3H), 6.78−6.74 (m, 2H), 6.10 (s, 1H), 4.75 (d, J = 15.1 Hz, 1H), 4.56 (d, J = 14.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.5, 140.2, 138.6, 129.3, 128.7, 128.3, 127.8, 127.1, 124.8, 123.9, 123.7, 123.6, 120.3, 118.8, 89.5, 62.3. HRMS (ESI) calcd for $C_{20}H_{17}NNaO^+$ [M + Na^+] 310.1202; found 310.1203.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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