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Note

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Pd-Catalyzed C(sp^2)−H Imidoylative Annulation: a General Approach to Construct Dibenzoox(di)azepines

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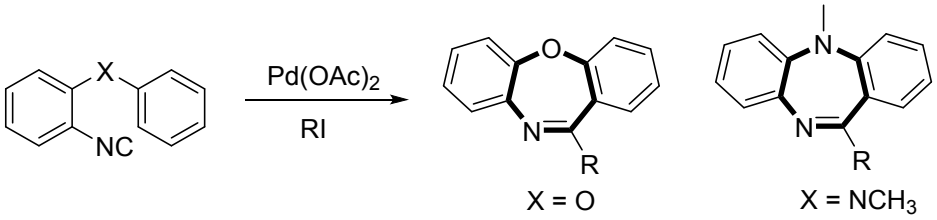
ABSTRACT



A general method to construct the scaffolds of dibenzooxazepine and dibenzodiazepine, through Pd-catalyzed isocyanide insertion and intramolecular C(sp^2)−H activation, has been developed. This is the first example of seven-membered heterocycle formation by C−H imidoylative annulation.

Dibenzooxazepine and dibenzodiazepine, both of which are seven-membered heterocycles fusing with two aromatic rings, exist as core structures of several marketed drugs including amoxapine, dibenzepin, nitroxazepine,[1] loxapine, and clozapine,[2] for the treatment of depression and schizophrenia (Figure 1). Besides, their derivatives as well as analogues exhibit diverse biological activities such as histone deacetylase inhibitors,[3] antitumor agents,[4] calcium channel antagonists,[5a] histamine H_4 receptor agonists,[5b] and lachrymatory agents[5c] (Figure 1). Meanwhile, dibenzoox(di)azepines can serve as indispensable intermediates for the preparation of secoiridoids and monoterpenoid alkaloids.[6] Therefore, much attention has been paid for their synthesis,[7] including ring-expansion,[8] Beckmann rearrangement,[9] and other multistep sequences.[10] However, the less efficiency of these synthetic routes still awaits for a straightforward and general approach applicable for both scaffolds of dibenzooxazepine and dibenzodiazepine.[11]

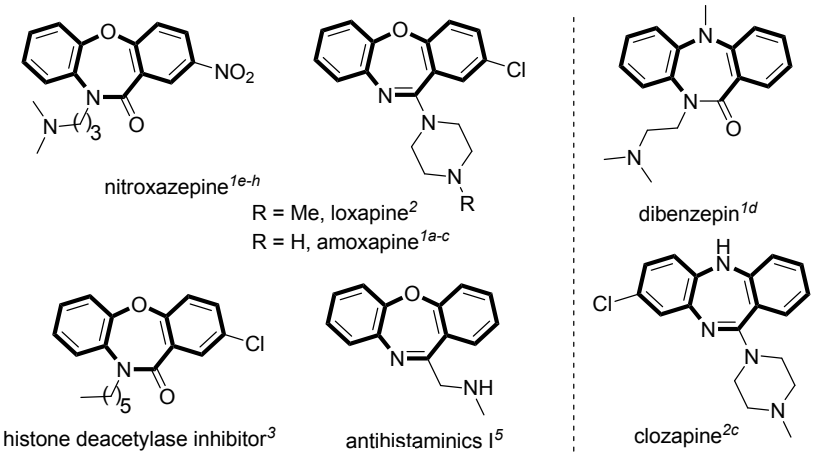
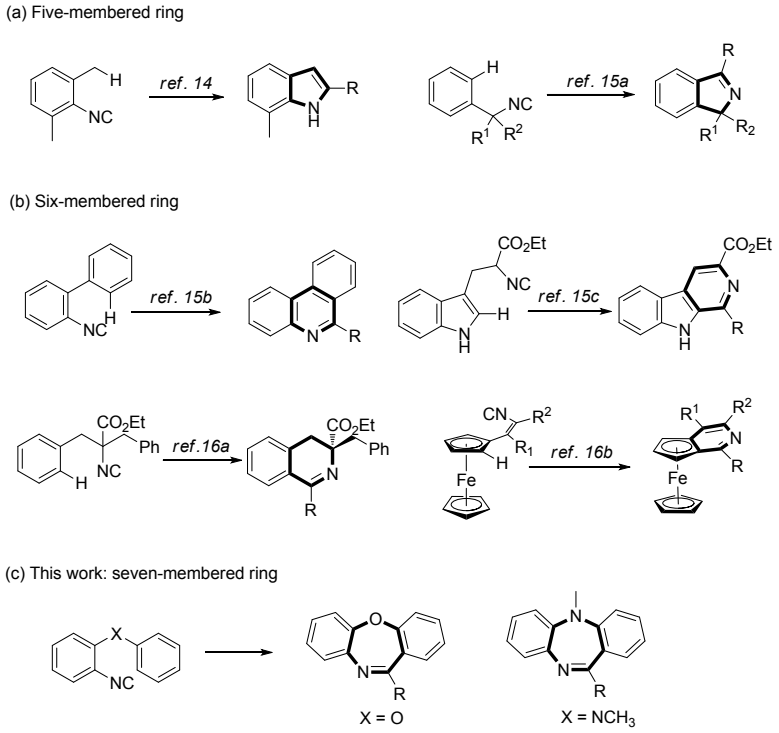


Figure 1. Dibenzoox(di)azepine containing drugs or biological active molecules.

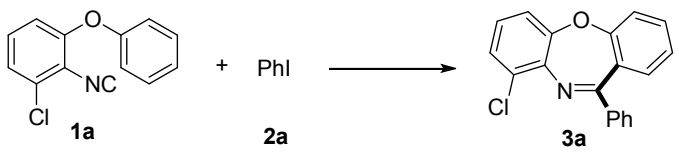
Transition metal-catalyzed annulation reaction involving C−H activation has been proven to be an efficient and atom-economical strategy for the construction of heterocycles.[12] In this context, Pd-catalyzed imidoylation of the so-called functionalized isocyanides,[13] followed by intramolecular C−H activation, has gained increasing interest for the synthesis of *N*-heterocycles in recent years. For instance, in 2003, Takemoto reported a Pd-catalyzed cascade process for the construction of indole skeleton via activation of benzylic C(sp^3)−H (a, Scheme 1).[14] Activation of aromatic C−H bond by an imidoyl palladium intermediate is more common, as exemplified by recent synthesis of 1*H*-isoindoles, phenanthridines and *β*-carbolines (a and b).[15] Enantioselective synthesis of central and planar six-membered cyclic imines was also realized by desymmetrizing imidoylation of C(sp^2)–H bond (b).[16] In spite of these achievements, the preparation of seven-membered heterocycles by C–H imidoylative annulation is still unprecedented, partly due to the energy barrier during the formation of eight-membered palladacycle intermediates.[17] Continuing our interest in isocyanide chemistry, we envision that seven-membered dibenzooxazepine and dibenzodiazepine scaffolds could be constructed using 1-isocyano-2-phenoxybenzenes and 2-isocyano-*N*-phenylanilines as functionalized isocyanides, respectively (c).



Scheme 1. Pd-catalyzed C−H cycloimidoylation

Initially, 1-isocyano-2-phenoxybenzene was chosen to react with iodobenzene **2a**. However, product generated from double isocyanide insertion product was obtained, probably due to the unfavorable reaction distance between the C(sp^2)-H bond to be activated and the Pd(II) intermediate after isocyanide insertion. [15] Thus, *ortho*-substituted functionalized isocyanide **1a** and iodobenzene **2a** were selected as model substrates in the reaction. Indeed, the desired dibenzooxazepine **3a** was formed in 15% yield catalyzed by $Pd(OAc)_2/PPh_3$ in the presence of Na_2CO_3 as a base in DMF (entry 1). Screening of bases revealed that Cs_2CO_3 could promote the reaction much more efficiently, and **3a** was isolated in 40% yield (entries 2-4). However, the yield could not be improved in other solvents, such as DMSO, 1,4-dioxane, toluene, or xylene (entries 5-8). Intriguingly, in a co-solvent of DMF/DMSO in 1:1 ratio, the annulation efficiency was increased dramatically (56%, entry 9). Acidic additives, such as CH_3COOH, CF_3COOH and PivOH were subsequently evaluated, suggesting the superiority of PivOH in the current C−H imidoylation process (entries 10-12). No positive results were observed when varying the reaction temperature or tuning the volume ratio of DMF to DMSO (entries 12-13). The yield of **3a** decreased slightly when the combination of Cs_2CO_3 and PivOH was replaced by CsOPiv, and only trace amount of **3a** was detected when Cs_2CO_3 was absent (entries 14-15). The yield decreased obviously when reducing the loading of palladium (entry 16).

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

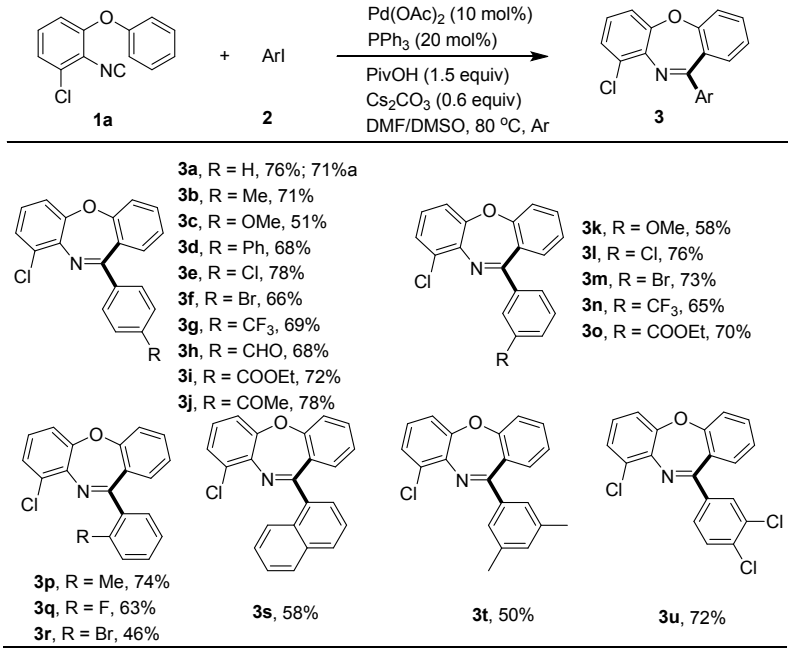


Entry	Base	Additive	Solvent	Yield[b] (%)
1	Na_2CO_3	--	DMF	15
2	Cs_2CO_3	--	DMF	40
3	KO^{t}Bu	--	DMF	<1
4	DBU	--	DMF	<1
5	Cs_2CO_3	--	DMSO	36
6	Cs_2CO_3	--	1,4-Dioxane	32
7	Cs_2CO_3	--	Toluene	29
8	Cs_2CO_3	--	Xylene	10
9	Cs_2CO_3	--	DMF/DMSO[c]	56
10	Cs_2CO_3	CH_3COOH	DMF/DMSO[c]	58
11	Cs_2CO_3	CF_3COOH	DMF/DMSO[c]	22
12	Cs_2CO_3	PivOH	DMF/DMSO[c]	76, 69[d], 75[e]
13	Cs_2CO_3	PivOH	DMF/DMSO	66[f], 72[g]
14	CsOPiv	--	DMF/DMSO[c]	59, 63[h]
15	--	PivOH	DMF/DMSO[c]	<1
16	Cs_2CO_3	PivOH	DMF/DMSO[c]	59[i], 8[j]

[a] Reaction conditions: **2a** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), base (0.6 equiv) and additive (1.5 equiv of acid) in solvent (1.0 mL) under argon atmosphere at 80 °C. A solution of **1a** (0.2 mmol, 1.0 equiv) in solvent (1 mL) was added to the reaction mixture *via* a syringe pump during 1 h. [b] Isolated yield. [c] DMF:DMSO = 1:1. [d] 70 °C. [e] 90 °C. [f] DMF:DMSO = 1:5. [g] DMF:DMSO = 5:1. [h]CsOPiv (1.2 equiv). [i]$Pd(OAc)_2$ (5%), PPh_3 (10%). [j]$Pd(OAc)_2$ (2%), PPh_3 (4%).

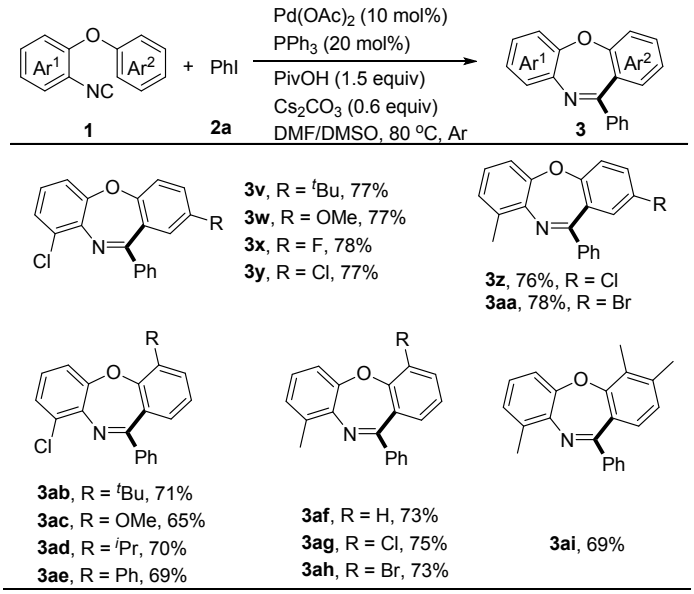
With the optimal conditions in hand, we next evaluated the scope of aryl iodide for the preparation of C11 arylated dibenzooxazepines (Scheme 2). Aryl iodides bearing electron-donating substituents in the *para*- or *meta*-position, such as methyl, methoxy and phenyl could react smoothly to provide the corresponding dibenzooxazepines **3b**, **3c** and **3k** in 71%, 51% and 58% yield, respectively. Meanwhile, aryl iodides substituted with electron-withdrawing groups were also good aryl sources for this imidoylative annulation reaction, including halides (**3e-3f**, 66-78%; **3l-3m**, 73-76%), trifluoromethyl (**3g**, 69%; **3n**, 65%), aldehyde group (**3h**, 68%), ethoxycarbonyl (**3i**, 72%; **3o**, 70%) and acetyl (**3j**, 78%). However, *ortho*-bromo substituted iodide delivered the desired product **3r** in much lower yield (46% *vs* 66% for **3f** and 73% for **3m**), suggesting that the steric effect of iodide was unneglectable. In addition, the compatibility of the functionalities in these

products, particularly for ester, aldehyde, and halide, provided facile handles for further transformations. 3,4- and 3,5-disubstituted aryl iodides as well as 1-iodonaphthalene were all compatible, giving the desired products **3s-3u** in 50-72% yields. To prove the practicality of this approach, a 2.0 mmol scale reaction was carried out, and the product **3a** was isolated in a comparable yield of 71%. Unfortunately, when PhBr, PhOTf, or MeI was used as electrophile in place of aryl iodide, no target product was formed.



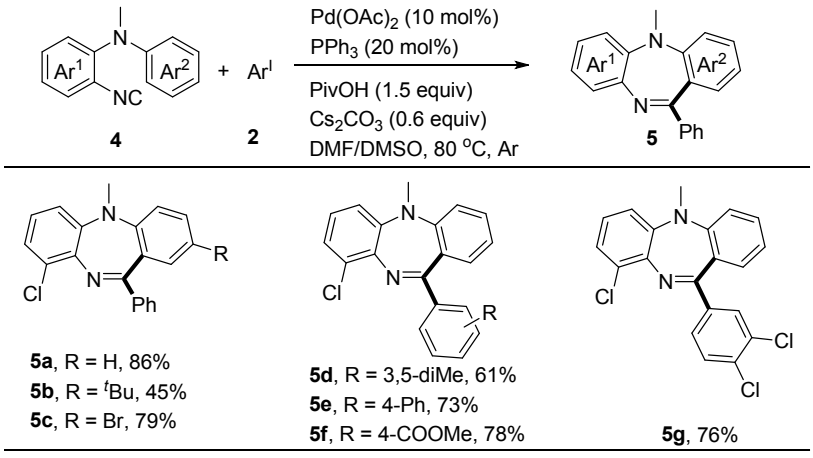
Scheme 2. The scope of aryl iodides. Reaction conditions: **2** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), PivOH (1.5 equiv) and Cs_2CO_3 (0.6 equiv) in solvent (1.0 mL) under argon atmosphere at 80 °C. A solution of **1a** (0.2 mmol, 1.0 equiv) in solvent (1 mL) was added to the reaction mixture *via* a syringe pump within 1 h, isolated yield. [a] 2.0 mmol scale.

Next, a variety of 1-isocyano-2-phenoxybenzenes **1** bearing substituents mainly on the non-isocyano aromatic ring were investigated (Scheme 3). These functionalized isocyanides were readily accessible through nucleophilic substitution of *ortho*-fluoro nitrobenzenes with various phenols followed by three steps of routine transformations. No matter the electronic nature of the *para*-substituents, these functionalized isocyanides reacted smoothly with iodobenzene **2a** to provide diversified dibenzooxazepine derivatives in similar yields (**3v-3y**, **3z**, and **3aa**, 76-78%). When the substituents were located at the *ortho*-position, even for the bulky *tert*-butyl group, the corresponding dibenzooxazepine products were formed equally well (**3ab-3ah**, 65-75%).



Scheme 3. Scope of functionalized isocyanides. Reaction conditions: **2a** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), PivOH (1.5 equiv) and Cs_2CO_3 (0.6 equiv) in solvent (1.0 mL) under argon atmosphere at 80 °C. A solution of **1** (0.2 mmol, 1.0 equiv) in solvent (1 mL) was added to the reaction mixture *via* a syringe pump within 1 h.

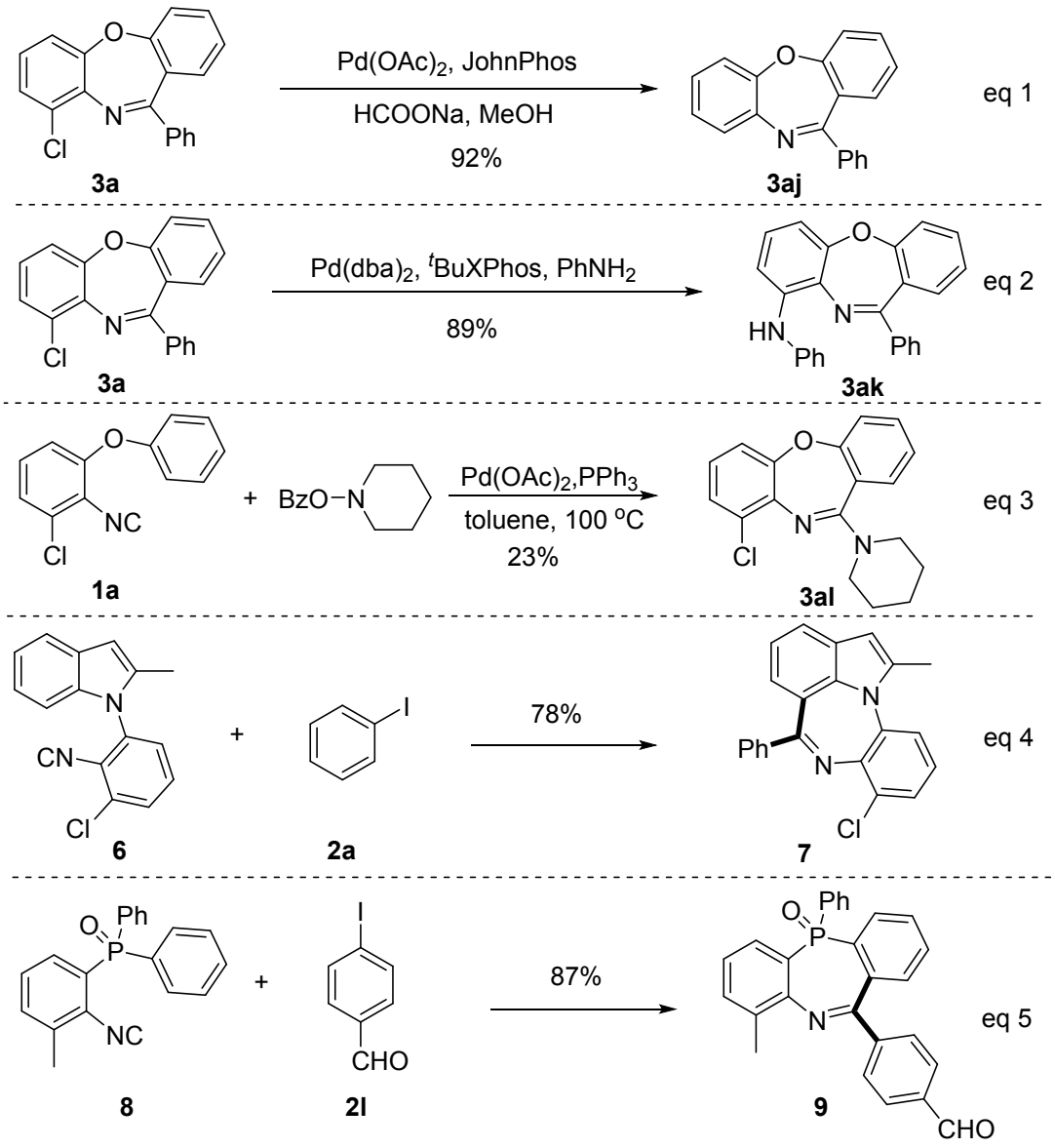
Then, The feasibility of the current Pd-catalyzed C(sp^2)−H imidoylative annulation for the construction of seven-membered heterocycles was further proven in dibenzodiazepine synthesis. As shown in Scheme 4, 2-isocyano-*N*-methyl-*N*-phenylanilines, obtained similarly as 1-isocyano-2-phenoxybenzenes, cyclized well under the slightly modified conditions. The corresponding diversified dibenzodiazepines were delivered in moderate to good yields (**5a-5g**, 45-86%).



Scheme 4. Synthesis of dibenzodiazepines. Reaction conditions: $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), PivOH (1.5 equiv) and Cs_2CO_3 (0.6 equiv) in solvent (1.0 mL) under argon atmosphere at 80 °C, after being stirred for 20 min, **2a** (0.3 mmol, 1.5 equiv) was added. Then a solution of **4** (0.2 mmol, 1.0 equiv) in solvent (1 mL) was added to the reaction mixture *via* a syringe pump within 1 h.

Although the requirement of an *ortho*-substituent in isocyanides **1** and **4** is an obvious limitation of this method, the substituent could be removed or transformed to other functionalities. For example, the C9-chloride in dibenzooxazepine **3a** could be reduced *via* Pd-catalysis in 92% yield (eq 1, Scheme 5).[18] Furthermore, amination at this position was also realized successfully through Buchwald–Hartwig cross-coupling,[19] affording C9

aminated product **3ak** in 89% yield (eq 2). Besides, replacing aryl iodide with O-benzoyl hydroxylamine also afforded corresponding amino substituted dibenzooxazepine **3al** in 23% yield using toluene as a solvent at 100 oC (eq 3). Notably, functionalized isocyanide **6**, derived from 2-methylindole, cyclized smoothly to deliver a unique indole-fused analogue **7** in 78% yield (eq 4). Besides, a seven-membered phosphine-containing analogue **9** was synthesized in good yield (eq 5). These results further demonstrated the viability of the current C(sp^2)−H imidoylative annulation in seven-membered heterocycle synthesis.



Scheme 5. Derivatization of **3a** and synthesis of structural analogues

In summary, a general and practical synthesis of seven-membered heterocycles *via* C(sp^2)−H imidoylative annulation has been developed. Diversified dibenzoox(di)azepine derivatives as well as their structural analogues were synthesized in moderate to good yields. The ubiquitous existence of seven-membered heterocycles including

dibenzoox(di)azepine in drugs and biological active molecules anticipates the potential application of this methodology in medicinal chemistry.

EXPERIMENTAL SECTION

General Information: Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. ^{1}H NMR、^{13}C NMR spectra were recorded at ambient temperature on a 400 or 500 MHz NMR spectrometer (100 or 125 MHz for ^{13}C). NMR experiments were reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* were given in Hz. High-resolution mass spectra (HRMS) were obtained using a Bruker micro-TOF II focus spectrometer. IR spectra were recorded on a spectrometer using KBr discs. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All melting points were uncorrected.

Experimental Procedure:

General procedures for the Synthesis of Functionalized Isocyanides 1 (Take 1a as an example)

Procedure A: [20] To a solution of 1-chloro-3-fluoro-2-nitrobenzene **10a** (3 mmol, 1.0 equiv) and phenol **11a** (3 mmol, 1.0 equiv) in DMF (9 mL) was added K_2CO_3 (3.6 mmol, 1.2 equiv) in air. The reaction mixture was stirred at 100 °C overnight. After cooling down, the reaction mixture was quenched with water (50 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 30:1) to afford 1-chloro-2-nitro-3-phenoxybenzene **12a** in 98% yield (732 mg).

Procedure B: To a solution of **12a** (2.5 mmol, 1.0 equiv) in EtOH (25 mL) was added iron powder (9.5 mmol, 3.8 equiv) and five drops of HCl (4 M) in air. The mixture was refluxed at 80 °C for 4~12 hours (monitored by TLC). After cooling down, the reaction mixture was diluted with EtOAc (20 mL) and passed through a short celite pad. The solvent was evaporated under reduced pressure and the crude mixture was purified on a silica gel column (hexane/EtOAc, 30:1) to obtain the corresponding 2-chloro-6-phenoxyaniline **13a** in 92% yield (503 mg).

Procedure C: 2-Chloro-6-phenoxyaniline **13a** (2.3 mmol, 1.0 equiv) was dissolved in dry THF (0.6 M) in an oven-dried Schlenk flask in argon. Formic acetic anhydride, prepared by heating formic acid (2.7 equiv) and acetic anhydride (2.3 equiv) at 55 °C for 2.5 h, was added dropwise to the aniline solution at 0 °C. The combined mixture was stirred at room temperature for 2 h. Then, the reaction was quenched by adding saturated (sat.) aqueous (aq.) $NaHCO_3$ solution, and extracted with ethyl acetate (EtOAc, 3 times). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude product *N*-(2-chloro-6-phenoxyphenyl)formamide **14a** was used for the next step without purification.

Procedure D: The crude product **14a** (2.3 mmol) was dissolved in DCM (0.6 M), and Et_3N (6.7 equiv) was added in argon. The solution was cooled to 0 °C and $POCl_3$ (1.7 equiv) was added dropwise. The reaction mixture was stirred at

0 °C for 1 hour. Then, it was quenched with sat. aq. Na_2CO_3 and the resulting mixture was stirred for another 1 h. The mixture was extracted with DCM (3 times) and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The desired 1-chloro-2-isocyano-3-phenoxybenzene **1a** was purified by flash column chromatography (hexane/EtOAc, 30:1) in 61% yield (321 mg).

General procedures for the Synthesis of Functionalized Isocyanides 4 (Take 4a as an example)

3-Chloro-*N*-methyl-2-nitro-*N*-phenylaniline **17a** was prepared according to the literature.[21] The functionalized isocyanides **4** were synthesized by following the general procedures **B** to **D**.

General procedures for the Synthesis of Functionalized Isocyanides 6

Procedure E: To a solution of 1-chloro-3-fluoro-2-nitrobenzene **10a** (3 mmol, 1.0 equiv) and 2-methylindole **20** (3 mmol, 1.0 equiv) in DMSO (9 mL) was added NaOH (1.5 equiv) in air. The reaction mixture was stirred at room temperature for 4 h. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc, 30:1) to afford 1-(3-chloro-2-nitrophenyl)-2-methyl-1*H*-indole **21** in 90% yield (772 mg).

The following steps (**steps 2-4**) were the same as the general procedures **B** to **D** to get **6** in 58% overall yield (462 mg).

General procedures for the Synthesis of Functionalized Isocyanides 8

Compound (2-amino-3-methylphenyl)diphenylphosphine oxide **26** was prepared according to the reported method.[22] The following steps were the same as the general procedures **B** to **D** to get **8** in 30% overall yield (285 mg).

General Procedure for the Synthesis of Dibenzooxazepines 3

An oven-dried Schlenk tube (25 mL) charged with ArI **2** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol%), PPh_3 (10.6 mg, 20 mol%), Cs_2CO_3 (40 mg, 0.6 equiv), PivOH (35 μl, 1.5 equiv), and 1 mL of solvent (DMF : DMSO, 1:1) was vacuumed and refilled with Ar for 3 times. The tube was placed in an 80 °C oil-bath, and a solution of functionalized isocyanide **1** (0.2 mmol, 1.0 equiv) in 1.0 mL of solvent (DMF : DMSO, 1:1) was added slowly through a syringe pump during 1 h. At the end of addition, the reaction mixture was cooled to room temperature and 10 mL of water was added. Then, the mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with saturated brine and dried by anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified on a silica gel column (hexane/EtOAc, 60:1) to obtain the corresponding product **3**.

General Procedure for the Synthesis of Dibenzooxazepine 3a in a 2.0 mmol Scale

An oven-dried Schlenk tube (100 mL) charged with PhI **2a** (335 μL, 3 mmol, 1.5 equiv), $Pd(OAc)_2$ (45 mg, 10 mol%), PPh_3 (106 mg, 20 mol%), Cs_2CO_3 (400 mg, 0.6 equiv), PivOH (350 μL, 1.5 equiv), and 10 mL of solvent (DMF : DMSO, 1:1) was vacuumed and refilled with Ar for 3 times. The tube was placed in an 80 °C oil-bath, and a solution of functionalized isocyanide **1a** (2 mmol, 1.0 equiv) in 10 mL of solvent (DMF : DMSO, 1:1) was added slowly through a syringe pump during 2 h. At the end of addition, the reaction mixture was cooled to room temperature and 60 mL of water was added. Then, the mixture was extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with saturated brine and dried by anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified on a silica gel column (hexane/EtOAc, 60:1) to obtain **3a** in 71% yield (433mg).

General Procedure for the Synthesis of amino substituted dibenzooxazepine 3al

An oven-dried Schlenk tube (25 mL) charged with piperidin-1-yl benzoate (0.3 mmol, 61.5mg, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol%), PPh_3 (10.6 mg, 20 mol%), Cs_2CO_3 (40 mg, 0.6 equiv), PivOH (35 μl, 1.5 equiv), and 1 mL of toluene was vacuumed and refilled with Ar for 3 times. The tube was placed in an 100 °C oil-bath, and a solution of functionalized isocyanide **1a** (0.2 mmol, 46mg, 1.0 equiv) in 1.0 mL of toluene was added slowly through a syringe pump during 1 h. At the end of addition, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified on a silica gel column (hexane/EtOAc, 30:1) to obtain the corresponding product **3al** in 23% yield as a colorless oil (14.3 mg).

General Procedure for the Synthesis of Dibenzodiazepines 5

An oven-dried Schlenk tube (25 mL) charged with $Pd(OAc)_2$ (4.5 mg, 10 mol%), PPh_3 (10.6 mg, 20 mol%), Cs_2CO_3 (40 mg, 0.6 equiv), PivOH (35 μL, 1.5 equiv), and 1 mL of solvent (DMF : DMSO, 1:1) was vacuumed and refilled with Ar for 3 times. The tube was placed in an 80 °C oil-bath. The mixture was stirred for 20 min at this temperature. ArI **2** (0.3 mmol, 1.5 equiv) was added and a solution of functionalized isocyanide **4** (0.2 mmol, 1.0 equiv) in 1.0 mL of solvent (DMF : DMSO, 1:1) was added slowly through a syringe pump during 1 h. At the end of addition, the reaction mixture was cooled to room temperature and 10 mL of water was added. Then, the mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with saturated brine and dried by anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified on a silica gel column (hexane/EtOAc, 60:1) to obtain the corresponding product **5**.

General Procedure for the Synthesis of 7

An oven-dried Schlenk tube (25 mL) charged with $Pd(OAc)_2$ (4.5 mg, 10 mol%), PPh_3 (10.6 mg, 20 mol%), Cs_2CO_3 (40 mg, 0.6 equiv), **2a** (34 μL, 0.3 mmol, 1.5 equiv), PivOH (35 μL, 1.5 equiv), and 1 mL of 1,4-dioxane was vacuumed and refilled with Ar for 3 times. The tube was placed in an 80 °C oil-bath. A solution of **6** (0.2 mmol, 1.0 equiv) in 1.0 mL of 1,4-dioxane was added slowly through a syringe pump during 1 h. At the end of addition, the reaction mixture was cooled to room temperature and 10 mL of water was added. Then, the mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with saturated brine and dried by anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified on a silica gel column (hexane/EtOAc, 30:1) to obtain product **7** in 78% yield (53.4 mg).

General Procedure for the Synthesis of 9

An oven-dried Schlenk tube (25 mL) charged with $Pd(OAc)_2$ (4.5 mg, 10 mol%), PPh_3 (10.6 mg, 20 mol%), Cs_2CO_3 (40 mg, 0.6 equiv), PivOH (35 μL, 1.5 equiv) and 1 mL of DMF was vacuumed and refilled with Ar for 3 times. The tube was placed in an 80 °C oil-bath. The mixture was stirred for 20 min at this temperature. **2l** (0.3 mmol, 1.5 equiv) was added to the mixture and a solution of **8** (0.2 mmol, 1.0 equiv) in 1.0 mL of DMF was added slowly through a syringe pump during 1 h. At the end of addition, the reaction mixture was quenched by adding 10 mL of water and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with saturated brine and dried by anhydrous Na_2SO_4. The solvent was evaporated, and the crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc, 2:1) to obtain product **9** in 87% yield (73.3 mg).

General Procedure for the Redutive Dechlorination of 3a

An oven-dried Schlenk tube (25 mL) charged with a magnetic stirring bar, $Pd(OAc)_2$ (0.5mg, 2 mol%), 2-(di-*tert*-butylphosphino) biphenyl (1.2 mg, 4 mol%), sodium formate (13.6 mg, 2.0 equiv), and 2 mL of methanol was vacuumed and refilled with Ar for 3 times. The reaction mixture was stirred for 5 min at room temperature, then dibenzooxazepine **3a** (30.5mg, 0.1 mmol) was added. The tube was placed in an oil-bath (68 °C) and the reaction mixture was stirred for 10 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc, 60:1) to obtain product **3aj** in 92% yield (24.9 mg).

General Procedure for the Cross-coupling of 3a

An oven-dried Schlenk tube (25 mL) charged with a magnetic stirring bar, $Pd(dba)_2$ (2.9 mg, 5 mol%), ^{t}BuXPhos (4.3 mg, 10 mol%), NaO^{t}Bu (14 mg, 1.4 equiv), dibenzooxazepine **3a** (30.5 mg, 0.1 mmol) and aniline (19 μL, 2.0 equiv) was vacuumed and refilled with Ar for 3 times. The solvent-free reaction mixture was stirred at 110 °C for 24 h.

Subsequently, the reaction mixture was transferred to a column directly for chromatography purification (hexane/EtOAc, 60:1) with minimum amount of CH_2Cl_2 to obtain product **3ak** in 89% yield (32.2 mg).

Characterization Data

Chloro-2-isocyano-3-phenoxybenzene (1a)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1a** (67% overall yield, 460 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42-7.39 (m, 2H), 7.24-7.17 (m, 3H), 7.08-7.06 (m, 2H), 6.78 (dd, J_1= 8.1 Hz, J_2 = 1.5 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.4, 155.1, 154.6, 132.1, 130.1, 129.8, 125.0, 123.6, 119.6, 116.0; HRMS (ESI) m/z calcd for $C_{13}H_9ClNO^+$ $(M+H)^+$ 230.0367, found 230.0370.

1-(4-(*Tert*-butyl)phenoxy)-3-chloro-2-isocyanobenzene (1b)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1b** (61% overall yield, 521 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42-7.40 (m, 2H), 7.21-7.14 (m, 2H), 7.01-6.99 (m, 2H), 6.78 (dd, J_1= 8.3 Hz, J_2 = 1.4 Hz, 1H), 1.34 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.3, 155.0, 152.6, 148.1, 132.1, 129.7, 127.0, 123.2, 119.3, 115.6, 34.5, 31.4; HRMS (ESI) m/z calcd for $C_{17}H_{17}ClNO^+$ $(M+H)^+$ 286.0993, found 286.0987.

1-Chloro-2-isocyano-3-(4-methoxyphenoxy)benzene (1c)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1c** (23% overall yield, 180 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19-7.10 (m, 2H), 7.03-6.99 (m, 2H), 6.94-6.90 (m, 2H), 6.68 (dd, J_1= 8.4 Hz, J_2 = 1.2 Hz, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 172.9, 156.9, 155.6, 147.9, 131.9, 129.8, 122.8, 121.39, 115.1, 114.5, 55.59; HRMS (ESI) m/z calcd for $C_{14}H_{11}ClNO_2^+$ $(M+H)^+$ 260.0473, found 260.0479.

1-Chloro-3-(4-fluorophenoxy)-2-isocyanobenzene (1d)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1d** (36% overall yield, 267 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23-7.17 (m, 2H), 7.12-7.03 (m, 4H), 6.74 (dd, J_1= 8.2 Hz, J_2 = 1.5 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.6, 159.8 (d, $J_{C\text{-}F}$ = 243.1 Hz), 154.8, 150.8 (d, $J_{C\text{-}F}$ = 2.6 Hz, 132.3, 129.9, 123.7, 121.3 (d, $J_{C\text{-}F}$ = 8.4 Hz), 116.8 (d, $J_{C\text{-}F}$ = 23.5 Hz), 115.4; HRMS (ESI) m/z calcd for $C_{13}H_8ClFNO^+$ $(M+H)^+$ 248.0273, found 248.0271.

1-Chloro-3-(4-chlorophenoxy)-2-isocyanobenzene (1e)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1e** (57% overall yield, 448 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.35 (m, 2H), 7.24-7.20 (m, 2H), 7.02-6.99 (m, 2H), 6.80 (dd, J_1= 9.6 Hz, J_2 = 1.7 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.8, 154.1, 153.8, 132.4, 130.2, 130.2, 123.0, 124.2, 120.7, 116.2; HRMS (ESI) m/z calcd for $C_{13}H_8Cl_2NO^+$ $(M+H)^+$ 263.9977, found 263.9980.

1-(4-Chlorophenoxy)-2-isocyano-3-methylbenzene (1f)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1f** (49% overall yield, 357 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33-7.31 (m, 2H), 7.21 (t, J = 8.0 Hz, 1H), 7.03-6.95 (m, 3H), 6.76 (d, J= 8.3 Hz, 1H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 170.7, 154.6, 152.5, 137.3, 129.9, 129.5, 129.3, 125.0, 120.2, 116.1, 18.6; HRMS (ESI) m/z calcd for $C_{14}H_{11}ClNO^+$ $(M+H)^+$ 244.0524, found 244.0525.

1-(4-Bromophenoxy)-2-isocyano-3-methylbenzene (1g)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1g** (45% overall yield, 387 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (d, J = 10.9 Hz, 2H), 7.21 (t, J = 10.0 Hz, 1H), 7.03-6.90 (m, 3H), 6.76 (d, J= 10.4 Hz, 1H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 170.7, 155.2, 152.4, 137.3, 132.9, 129.5, 125.0, 120.5, 116.8, 116.2, 18.63; HRMS (ESI) m/z calcd for $C_{14}H_{11}BrNO^+$ $(M+H)^+$ 288.0019, found 288.0011.

1-(2-(*tert*-butyl)phenoxy)-3-chloro-2-isocyanobenzene (1h)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1h** (30% overall yield, 256 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47-7.45 (m, 1H), 7.22-7.14 (m, 4H), 6.85 (dd, J_1 = 7.9 Hz, J_2 = 1.5 Hz, 1H), 6.73 (dd, J_1 = 8.3 Hz, J_2 = 1.3 Hz, 1H), 1.41 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.3, 155.0, 153.6, 141.6, 132.2, 129.8, 127.9, 127.4, 125.0, 123.0, 120.6, 115.3, 34.8, 30.3; HRMS (ESI) m/z calcd for $C_{17}H_{17}ClNO^+$ $(M+H)^+$ 286.0993, found 286.1003.

1-Chloro-2-isocyano-3-(2-methoxyphenoxy)benzene (1i)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1i** (20% overall yield, 156) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25-7.20 (m, 1H), 7.15-7.07 (m, 3H), 7.03-6.95 (m, 2H), 6.55 (dd, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 172.9, 155.2, 151.4, 142.7, 131.7, 129.6, 126.7, 122.6, 122.2, 121.3, 113.7, 113.2, 55.9; HRMS (ESI) m/z calcd for $C_{14}H_{11}ClNO_2^+$ $(M+H)^+$ 260.0473, found 260.0465.

1-Chloro-2-isocyano-3-(2-isopropylphenoxy)benzene (1j)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1j** (31% overall yield, 252 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.38 (m, 1H), 7.25-7.12 (m, 4H), 6.94-6.92 (m, 1H), 6.64 (dd, J_1 = 7.3 Hz, J_2 = 1.4 Hz, 1H), 3.20-3.15 (m, 1H), 1.24 (d, J = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.3, 155.3, 151.7, 140.4, 132.1, 129.8, 127.5, 127.2, 125.8, 122.8, 120.2, 116.7, 114.3, 27.3, 22.9; HRMS (ESI) m/z calcd for $C_{16}H_{15}ClNO^+$ $(M+H)^+$ 272.0837, found 272.0839.

2-(3-Chloro-2-isocyanophenoxy)-1,1'-biphenyl (1k)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1k** (35% overall yield, 320 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55-7.49 (m, 3H), 7.41-7.33 (m, 4H), 7.30-7.27 (m, 1H), 7.12 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 1H), 7.06-7.00 (m, 2H), 6.53 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.1, 154.7, 151.3, 136.7, 134.4, 131.8, 131.7, 129.5, 129.0, 128.3, 127.6, 126.0, 122.8, 121.1, 114.5; HRMS (ESI) m/z calcd for $C_{19}H_{13}ClNO^+$ $(M+H)^+$ 306.0680, found 306.0677.

2-Isocyano-1-methyl-3-phenoxybenzene (1l)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1l** (66% overall yield, 414 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.26 (m, 2H), 7.20-7.16 (m, 2H), 7.06-7.03 (m, 2H), 6.99 (d, J = 7.7 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 2.48 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 170.3, 155.9, 153.1, 137.0, 129.9, 129.4, 124.4, 124.2, 119.1, 115.8, 18.65; HRMS (ESI) m/z calcd for $C_{14}H_{12}NO^+$ $(M+H)^+$ 210.0913, found 210.0908.

1-(2-Chlorophenoxy)-2-isocyano-3-methylbenzene (1m)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1m** (59% overall yield, 430 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50 (dd, J_1= 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.31-7.28 (m, 1H), 7.21-7.17 (m, 2H), 7.07 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 5.58 (d, J = 8.4 Hz, 1H), 2.50 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 170.7, 152.6, 151.0, 137.0, 130.9, 129.3, 128.1, 126.2, 125.8, 124.4, 121.4, 117.6, 114.2, 18.57; HRMS (ESI) m/z calcd for $C_{14}H_{11}ClNO^+$ $(M+H)^+$ 244.0524, found 244.0529.

1-(2-Bromophenoxy)-2-isocyano-3-methylbenzene (1n)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1n** (49% overall yield, 421 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65 (dd, J_1= 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.33-7.30 (m, 1H), 7.17 (t, J = 8.0 Hz, 1H), 7.10 (dt, J_1 = 7.9 Hz, J_2 = 1.5 Hz, 1H), 7.03-6.98 (m, 2H), 6.57 (d, J = 8.2 Hz, 1H), 2.48 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 170.7, 152.5, 152.2, 137.1, 134.1, 129.4, 128.8 126.1, 124.5, 121.2, 115.3, 114.5, 18.6; HRMS (ESI) m/z calcd for $C_{14}H_{11}BrNO^+$ $(M+H)^+$ 288.0019, found 288.0012.

1-(2,3-Dimethylphenoxy)-2-isocyano-3-methylbenzene (1o)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **1o** (19% overall yield, 135 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.13-7.08 (m, 3H), 6.91 (d, J = 7.6 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.49 (d, J = 8.3 Hz, 1H), 3.48 (s, 3H), 3.33 (s, 3H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 169.8, 153.8, 153.0, 139.1, 136.8, 129.3, 128.7, 126.4, 126.3, 123.2, 117.7, 113.5, 20.0, 18.6, 12.1; HRMS (ESI) m/z calcd for $C_{16}H_{16}NO^+$ $(M+H)^+$ 238.1226, found 238.1228.

3-Chloro-2-isocyano-*N*-methyl-*N*-phenylaniline (4a)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **4a** (18% overall yield, 131 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32-7.24 (m, 4H), 7.20-7.18 (m, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 7.9 Hz, 2H), 3.35 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.4, 147.8, 147.4, 132.4, 130.1, 129.2, 125.5, 125.2, 120.6, 116.8, 39.9; HRMS (ESI) m/z calcd for $C_{14}H_{12}ClN_2^+$ $(M+H)^+$ 243.0684, found 243.0678.

N-(4-(*tert*-butyl)phenyl)-3-chloro-2-isocyano-*N*-methylaniline (4b)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **4b** (12% overall yield, 108 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.22 (m, 4H), 7.17 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H),6.79-6.77 (m, 2H), 3.34 (s, 3H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.0, 147.7, 145.3, 143.6, 132.3, 129.9, 125.9, 124.97, 124.7, 116.9, 40.0, 34.0, 31.4; HRMS (ESI) m/z calcd for $C_{18}H_{20}ClN_2^+$ $(M+H)^+$ 299.1310, found 299.1304.

N-(4-bromophenyl)-3-chloro-2-isocyano-*N*-methylaniline (4c)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **4c** (15% overall yield, 145 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.32 (m, 4H), 7.21-7.17 (m, 1H), 6.64 (d, J = 10.2 Hz, 2H), 3.32 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.8, 146.8, 146.7, 132.6, 132.0, 130.3, 126.3, 125.7, 117.8, 112.6, 39.8; HRMS (ESI) m/z calcd for $C_{14}H_{11}BrClN_2^+$ $(M+H)^+$ 320.9789, found 320.9795.

1-(3-Chloro-2-isocyanophenyl)-2-methyl-1*H*-indole (6)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **6** (58% overall yield, 462 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66-7.50 (m, 3H), 7.37-7.35 (m, 1H), 7.19-7.12 (m, 2H), 6.90 (d, J = 7.2 Hz, 1H), 6.51 (s, 1H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 174.3, 137.7, 136.6, 136.5, 132.4, 130.1, 129.9, 128.69, 128.7, 121.7, 120.7, 120.0, 109.4, 102.9, 12.8; HRMS (ESI) m/z calcd for $C_{16}H_{12}ClN_2^+$ $(M+H)^+$ 267.0684, found 267.0677.

(2-Isocyano-3-methylphenyl)diphenylphosphine oxide (8)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **8** (30% overall yield, 285 mg) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78-7.73 (m, 4H), 7.61-7.48 (m, 8H), 7.37 (dt, J_1 = 7.7 Hz, J_2 = 1.9 Hz, 1H), 3.41 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 173.2, 137.2 (d, $J_{c\text{-}p}$ = 6 Hz), 134.4 (d, $J_{c\text{-}p}$ = 2 Hz), 132.4 (d, $J_{c\text{-}p}$ = 3 Hz), 132.1 (d, $J_{c\text{-}p}$ = 10 Hz), 13.8 (d, $J_{c\text{-}p}$ = 107 Hz), 129.39 (d, $J_{c\text{-}p}$ = 96 Hz), 128.8, 128.7, 128.6, 19.08; HRMS (ESI) m/z calcd for $C_{20}H_{17}NOP^+$ $(M+H)^+$ 318.1042, found 318.1042.

9-Chloro-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3a)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3a** (46.4 mg, 76% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 7.0 Hz, 2H), 7.54-7.45 (m, 4H), 7.30-7.25 (m, 3H), 7.21-7.17 (m, 1H), 7.13-7.07 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 167.4, 161.7, 153.6, 139.7, 138.2, 133.2, 131.9, 131.2, 130.8, 130.0, 128.2, 127.1, 126.7, 124.8, 121.0, 119.1; HRMS (ESI) m/z calcd for $C_{19}H_{13}ClNO$ $(M+H)^+$ 306.0680, found 306.0684; IR (KBr) 3059, 3021, 1610, 1563, 1487, 1440, 1412, 1374, 1315, 1285, 1240, 1220, 1189, 1146, 1108, 1034 cm^{-1}.

9-Chloro-11-(*p*-tolyl)dibenzo[*b*,*f*][1,4]oxazepine (3b)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3b** (45.3 mg, 71% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, J = 8.1 Hz, 2H), 7.50-7.46 (m, 1H), 7.26-7.23 (m, 5H), 7.16 (dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.10-7.03 (m, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 167.3, 161.7, 153.7, 141.2, 138.3, 137.0, 133.1, 131.9, 131.3, 130.0, 129.0, 127.2, 126.9, 126.6, 124.8, 120.9, 119.1, 21.5; HRMS (ESI) m/z calcd for $C_{20}H_{15}ClNO$ $(M+H)^+$ 320.0837, found 320.0841; IR (KBr) 3066, 3028, 2914, 1595, 1561, 1477, 1446, 1432, 1406, 1374, 1315, 1285, 1260, 1240, 1225, 1194, 1182, 1143, 1101, 1035 cm^{-1}.

9-Chloro-11-(4-methoxyphenyl)dibenzo[*b*,*f*][1,4]oxazepine (3c)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3c** (33.5 mg, 51% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82-7.78 (m, 2H), 7.44-7.40 (m, 1H), 7.21-7.10 (m, 4H), 7.03-6.88 (m, 4H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 166.6, 162.0, 161.7, 153.6, 138.4, 133.1, 132.3, 131.7, 131.3, 127.1, 126.7, 126.6, 124.7, 120.9, 119.0, 113.6, 55.4; HRMS (ESI) m/z calcd for $C_{20}H_{15}ClNO_2$ $(M+H)^+$ 336.0786, found 336.0783; IR (KBr) 3061, 3028, 2939, 1602, 1590, 1583, 1569, 1490, 1458, 1443, 1369, 1328, 1280, 1222, 1205, 1187, 1182, 1146, 1035 cm^{-1}.

11-([1,1'-Biphenyl]-4-yl)-9-chlorodibenzo[*b*,*f*][1,4]oxazepine (3d)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3d** (51.8 mg, 68% yield) as a yellow solid. m.p. 135-136 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, J = 8.2 Hz, 2H), 7.62-7.57 (m, 4H), 7.45-7.37 (m, 3H), 7.30 (t, J = 7.2 Hz, 1H), 7.24-7.10 (m, 4H), 7.04-6.98 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 167.0, 161.8, 153.6, 143.6, 140.4, 138.6, 138.3, 133.3, 132.0, 131.2, 130.5, 128.9, 127.8, 127.2, 127.1, 126.9, 126.7, 124.8, 121.0, 119.2; HRMS (ESI) m/z calcd for $C_{25}H_{17}ClNO$ $(M+H)^+$ 382.0993, found 382.0992; IR (KBr) 3077, 3056, 3027, 1686, 1592, 1566, 1556, 1481, 1446, 1432, 1400, 1316, 1282, 1240, 1226, 1163, 1067, 1035. cm^{-1}.

9-Chloro-11-(4-chlorophenyl)dibenzo[*b*,*f*][1,4]oxazepine (3e)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3e** (52.9 mg, 78% yield) as a yellow solid. m.p. 130-131 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, J = 8.4 Hz, 2H), 7.43-7.39 (m, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.18-6.97 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 166.1, 161.7, 153.5, 138.1, 138.0, 137.1, 133.4, 132.0, 131.3, 130. 9, 128.5, 127.4, 126.7, 126.7, 124.9, 121.1, 119.2; HRMS (ESI) m/z calcd for $C_{19}H_{12}Cl_2NO$ $(M+H)^+$ 340.0290, found 340.0293; IR (KBr) 3065, 1644, 1596, 1562, 1480, 1443, 1397, 1371, 1315, 1268, 1239, 1171, 1141, 1088, 1035 cm^{-1}.

11-(4-Bromophenyl)-9-chlorodibenzo[*b*,*f*][1,4]oxazepine (3f)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3f** (55.6 mg, 66% yield) as a yellow solid. m.p. 131-132 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.45-7.41 (m, 1 H), 7.20-7.08 (m, 4H), 7.03-7.01 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 166.2, 161.8, 153. 6, 138.6, 138.0, 133.4, 132.0, 131.5, 131.5, 130.9, 129.8, 127.4, 126.7, 125.6, 124.9, 121.1, 119.2; HRMS (ESI) m/z calcd for $C_{19}H_{12}BrClNO$ $(M+H)^+$ 383.9785, found 383.9782; IR (KBr) 3064, 3020, 1644, 1597, 1587, 1560, 1479, 1443, 1391, 1377, 1313, 1286, 1275, 1265, 1221, 1204, 1171, 1140, 1034 cm^{-1}.

9-Chloro-11-(4-(trifluoromethyl)phenyl)dibenzo[*b*,*f*][1,4]oxazepine (3g)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate =: 60:1) gave **3g** (51.5 mg, 69% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.48-7.44 (m, 1H), 7.22-7.19 (m, 2H), 7.17-7.03 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 166.0, 161.8, 153.5, 143.0, 137.9, 133.7, 132.4

(q, J_{C-F} = 32.5 Hz), 132.2, 130.8, 130.3, 127.8, 126.8, 126.7, 125.2 (q, J_{C-F} = 3.8 Hz), 125.0, 124.0 (q, J_{C-F} = 273.8 Hz), 121.2, 119.3; HRMS (ESI) m/z calcd for $C_{20}H_{12}ClF_3NO$ $(M+H)^+$ 374.0554, found 374.0552; IR (KBr) 3064, 3012, 1602, 1569, 1514, 1484, 1448, 1434, 1408, 1326, 1315, 1243, 1205, 1126, 1109, 1016 cm^{-1}.

4-(9-Chlorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)benzaldehyde (3h)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3h** (45.3 mg, 68% yield) as a yellow solid. m.p. 173-174 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.02 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.48-7.43 (m, 1H), 7.22-7.02 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 191. 8, 166.2, 161.9, 153.5, 145.09, 137.9, 137.7, 133.7, 132.3, 130.8, 130.6, 129.5, 127.9, 126.9, 126.8, 125.1, 121.2, 119.3; HRMS (ESI) m/z calcd for $C_{20}H_{13}ClNO_2$ $(M+H)^+$ 334.0629, found 334.0631; IR (KBr) 3059, 2836, 2739, 1735, 1604, 1594, 1561, 1500, 1484, 1448, 1434, 1414, 1388, 1316, 1285, 1242, 1202, 1159, 1106, 1015 cm^{-1}.

Ethyl 4-(9-chlorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)benzoate (3i)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3i** (52.3 mg, 72% yield) as a yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.13 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 7.54-7.50 (m, 1H), 7.30-7.25 (m, 2H), 7.21-7.09 (m, 4H), 4.42 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 166.5, 166.1, 161.8, 153.5, 143.6, 137.9, 133.5, 132.3, 132.2, 130.9, 129.9, 129.4, 127.7, 126.8, 126.8, 125.0, 121.1, 119.2, 61.2, 14.3; HRMS (ESI) m/z calcd for $C_{22}H_{17}ClNO_3$ $(M+H)^+$ 378.0891, found 378.0885; IR (KBr) 3061, 2979, 2932, 2903, 1717, 1599, 1563, 1505, 1482, 1447, 1434, 1405, 1366, 1308, 1274, 1204, 1145, 1102, 1020 cm^{-1}.

1-(4-(9-Chlorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)phenyl)ethanone (3j)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3j** (54.1 mg, 78% yield) as a yellow solid. m.p. 124-125 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04-7.98 (m, 4H), 7.5-7.51 (m, 1H), 7.30-7.25 (m, 2H), 7.22-7.10 (m, 4H), 2.65 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 197.6, 166.3, 161.8, 153.5, 143.7, 138.6, 137.9, 133.5, 132.2, 130.8, 130.2, 128.1, 127.7, 126.8, 125.0, 121.1, 119.2, 26.7; HRMS (ESI) m/z calcd for $C_{21}H_{15}ClNO_2$ $(M+H)^+$ 348.0786, found 348.0780; IR (KBr) 3066, 2994, 2920, 1675, 1596, 1561, 1499, 1480, 1445, 1433, 1402, 1376, 1312, 1269, 1243, 1203, 1142, 1104, 1036 cm^{-1}.

9-Chloro-11-(3-methoxyphenyl)dibenzo[*b*,*f*][1,4]oxazepine (3k)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3k** (38.9 mg, 58% yield) as a yellow oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.46-7.40 (m, 2H), 7.33-7.25 (m, 2H), 7.19-7.16 (m, 3H), 7.10 (t, J = 7.5 Hz, 1H), 7.03-6.96 (m, 3H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 167.1, 161.7, 159.5, 153.6, 141.1, 138.1, 133.2, 132.0, 131.3, 129.1, 127.2, 127.1, 126.6, 124.8, 122.8, 120.9, 119.1, 117.0, 114.9, 55.3; HRMS (ESI) m/z calcd for $C_{20}H_{15}ClNO_2$ $(M+H)^+$ 336.0786, found 336.0780; IR (KBr) 3067, 3029, 3001, 2937, 1612, 1596, 1581, 1566, 1481, 1462, 1446, 1433, 1376, 1323, 1283, 1222, 1200, 1183, 1172, 1140, 1039 cm^{-1}.

9-Chloro-11-(3-chlorophenyl)dibenzo[*b*,*f*][1,4]oxazepine (3l)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3l** (51.5 mg, 76% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82-7.81 (m, 1H), 7.69-7.66 (m, 1H), 7.46-7.38 (m, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.21-7.17 (m, 2H), 7.14-7.12 (m, 2H), 7.03-7.02 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 166.0, 161.7, 153.6, 141.5, 137.9, 134.4, 133.5, 132.1, 130.9, 130.8, 129.9, 129.5, 128.2, 127.6, 126.8, 126.7, 125.0, 121.1, 119.2; HRMS (ESI) m/z calcd for $C_{19}H_{12}Cl_2NO$ $(M+H)^+$ 340.0290, found 340.0292; IR (KBr) 3065, 3023, 1604, 1561, 1482, 1467, 1446, 1434, 1406, 1372, 1315, 1286, 1271, 1258, 1243, 1203, 1160, 1108, 1034 cm^{-1}.

11-(3-Bromophenyl)-9-chlorodibenzo[*b*,*f*][1,4]oxazepine (3m)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate =: 60:1) gave **3m** (55.9 mg, 73% yield) as a yellow solid. m.p. 138-139 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.56-7.53 (m, 1H), 7.46-7.42 (m, 1H), 7.24-7.12 (m, 5H),7.02 (d, J = 4.9 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 165.8, 161.7, 153.5, 141.7, 137.8, 133.7, 133.5, 132.8, 132.1, 130.9, 129.8, 128.7, 127.6, 126.8, 126.7, 125.0, 122.5, 121.1, 119.2; HRMS (ESI) m/z calcd for $C_{19}H_{12}BrClNO$ $(M+H)^+$ 383.9785, found 383.9786; IR (KBr) 3074, 3051, 1681, 1644, 1603, 1559, 1483, 1464, 1447, 1434, 1402, 1314, 1282, 1269, 1258, 1246, 1228, 1203, 1176, 1144, 1067, 1035 cm^{-1}.

9-Chloro-11-(3-(trifluoromethyl)phenyl)dibenzo[*b*,*f*][1,4]oxazepine (3n)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3n** (48.5 mg, 65% yield) as a yellow solid. m.p. 127-129 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08-8.03 (m, 2H), 7.69 (d, J = 6.2 Hz, 1H), 7.53-7.45 (m, 2H), 7.23-7.03 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 165.9, 161.8, 153.6, 140.5, 137.8, 133.7, 133.2, 132.2, 130.9 (q, $J_{C\text{-}F}$ = 32.5 Hz), 130.7, 128.9, 127.7, 127.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 126.8, 126.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 126.6, 125.1, 123.9 (q, $J_{C\text{-}F}$ = 270 Hz), 121.3,119.3; HRMS (ESI) m/z calcd for $C_{20}H_{12}ClF_3NO$ $(M+H)^+$ 374.0554, found 374.0551; IR (KBr) 3084, 3069, 1601, 1561, 1479, 1449, 1436, 1384, 1341, 1301, 1263, 1245, 1203, 1167, 1144, 1106, 1035 cm^{-1}.

Ethyl 3-(9-chlorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)benzoate (3o)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3o** (50.8 mg, 70% yield) as a yellow solid. m.p. 128-129 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (s, 1H), 8.18-8.15 (m, 2H), 7.56-7.48 (m, 2H), 7.28-7.08 (m, 6H),4.37 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 166.5, 166.1, 161.7, 153.6, 140.1, 137.9, 134.1, 133.5, 132.0, 131.7, 131.1, 130.9, 130.7, 128.5, 127.5, 126.8, 126.7, 125.0, 121.1, 119.2, 61.2, 14.2; HRMS (ESI) m/z calcd for $C_{22}H_{17}ClNO_3$ $(M+H)^+$ 378.0891, found 378.0886; IR (KBr) 3063, 3036, 2982, 2962, 2940, 2900, 1718, 1600, 1579, 1563, 1462, 1435, 1390, 1325, 1252, 1159, 1108, 1108, 1019 cm^{-1}.

9-Chloro-11-(*o*-tolyl)dibenzo[*b*,*f*][1,4]oxazepine (3p)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3p** (47.2 mg, 74% yield) as a yellow solid. m.p. 128-129 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54-7.52 (m, 1H), 7.47-7.43 (m, 1H), 7.37-7.33 (m, 1H), 7.29-7.21 (m, 4H), 7.13-7.07 (m, 3H), 6.96-6.94 (m, 1H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 169.7, 160.8, 153.8, 140.4, 138.0, 136.8, 133.2, 132.3, 130.8, 130.4, 130.3, 129.6, 129.2, 127.5, 126.8, 125.8, 125.2, 120.6, 119.3, 20.5; HRMS (ESI) m/z calcd for $C_{20}H_{15}ClNO$ $(M+H)^+$ 320.0837, found 320.0833; IR (KBr) 3061, 3013, 2957, 2922, 1593, 1563, 1477, 1445, 1433, 1376, 1314, 1265, 1241, 1225, 1200, 1173, 1141, 1100, 1030 cm^{-1}.

9-Chloro-11-(2-fluorophenyl)dibenzo[*b*,f][1,4]oxazepine (3q)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3q** (40.7 mg, 63% yield) as a yellow solid. m.p. 123-124 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.91-7.88 (m, 1H), 7.41-7.37 (m, 2H), 7.23-7.16 (m, 2H), 7.15 (d, J =8.2 Hz, 1H), 7.08-6.99 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 164.3, 160.9 (d, $J_{C\text{-}F}$ = 251.3 Hz), 160.3, 153.8, 137.7, 133,4, 132.34, 132.27 (d, $J_{C\text{-}F}$ = 2.5 Hz), 132.1 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.8 (d, $J_{C\text{-}F}$ = 1.3 Hz), 128.4 (d, $J_{C\text{-}F}$ = 1.3 Hz), 128.2 (d, $J_{C\text{-}F}$ = 11.3 Hz), 127.8, 126.7, 125.2, 124.5 (d, $J_{C\text{-}F}$ = 2.5 Hz), 120.8, 119.3, 116.2 (d, $J_{C\text{-}F}$ = 22.5 Hz); HRMS (ESI) m/z calcd for $C_{19}H_{12}ClFNO$ $(M+H)^+$ 324.0586, found 324.0585; IR (KBr) 3057, 3021, 1601, 1577, 1505, 1481, 1446, 1370, 1320, 1285, 1269, 1246, 1223, 1205, 1176, 1140, 1095, 1031 cm^{-1}.

11-(2-Bromophenyl)-9-chlorodibenzo[*b*,*f*][1,4]oxazepine (3r)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3r** (35.2 mg, 46% yield) as a yellow solid. m.p. 178-180 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1 H), 7.40 (t, J = 7.4 Hz, 2H), 7.27-7.15 (m, 3H), 7.09-7.02 (m, 3H), 6.86 (d, J = 7.7 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 168.3, 161.1, 153.8, 141.5, 137.6, 133.4, 133.3, 132.4, 131.9, 131.0, 129.8, 128.5, 128.1, 127.6, 126.8, 125.3, 122.4, 120.8, 119.5; HRMS (ESI) m/z calcd for $C_{19}H_{12}BrClNO$ $(M+H)^+$ 383.9785, found 383.9786; IR (KBr) 3060, 3009, 1593, 1562, 1479, 1464, 1445, 1433, 1375, 1316, 1290, 1277, 1242, 1199, 1176, 1142, 1107, 1023 cm^{-1}.

9-Chloro-11-(naphthalen-1-yl)dibenzo[*b*,*f*][1,4]oxazepine (3s)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3s** (41.2 mg, 58% yield) as a yellow solid. m.p. 164-165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (d, J = 5.6 Hz, 1H), 7.91-7.88 (m, 2H), 7.73-7.71 (m, 1H), 7.55-7.44 (m, 4H), 7.33-7.27 (m, 2H), 7.18-7.12 (m, 2H), 7.04-7.00 (m, 1H), 6.93-6.90 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 168.9, 160.8, 153.9, 138.2, 138.2, 133.9, 133.3, 132.4, 131.3, 131.0, 130.5, 129.8, 129.2, 128.3, 127.7, 126.9, 126.7, 126.1, 126.1, 125.3, 124.9, 120.7, 119.4; HRMS (ESI) m/z calcd for $C_{23}H_{15}ClNO$ $(M+H)^+$ 356.0837, found 356.0839; IR (KBr) 3062, 1605, 1561, 1508, 1483, 1446, 1432, 1393, 1341, 1312, 1275, 1242, 1201, 1162, 1141, 1118, 1075, 1034 cm^{-1}.

9-Chloro-11-(3,5-dimethylphenyl)dibenzo[*b*,*f*][1,4]oxazepine (3t)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3t** (33.3 mg, 50% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56-7.50 (m, 3H), 7.31-7.20 (m, 3H), 7.21 (dt, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H), 7.17-7.08 (m, 3H), 2.40 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 167.9, 161.7, 153.7, 139.8, 138.3, 137.8, 133.1, 132.6, 131.9, 131.4, 127.8, 127.4, 127.0, 126.6, 124.8, 120.9, 119.1, 21.34; HRMS (ESI) m/z calcd for $C_{21}H_{17}ClNO$ $(M+H)^+$ 334.0993, found 334.0998; IR (KBr) 3051, 3013, 2912, 2853, 1601, 1569, 1485, 1445, 1435, 1379, 1330, 1277, 1235, 1206, 1165, 1109, 1031 cm^{-1}.

9-Chloro-11-(3,4-dichlorophenyl)dibenzo[*b*,*f*][1,4]oxazepine (3u)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3u** (53.7 mg, 72% yield) as a yellow solid. m.p. 137-138 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 2.0 Hz, 1H), 7.67-7.64 (m, 1H), 7.48-7.44 (m, 2H), 7.23-7.17 (m, 2H), 7.15-7.12 (m, 2H), 7.06-7.02 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 164.9, 161.8, 153.5, 139.5, 137.8, 135.2, 133.7, 132.7, 132.1, 131.7, 130.6, 130.3, 129.1, 127.8, 126.8, 126.4, 125.1, 121.3, 119.3; HRMS (ESI) m/z calcd for $C_{19}H_{11}Cl_3NO$ $(M+H)^+$ 373.9901, found 373.9901; IR (KBr) 3058, 1659, 1599, 1569, 1552, 1481, 1465, 1445, 1433, 1374, 1314, 1277, 1267, 1239, 1203, 1172, 1130, 1031 cm^{-1}.

2-(*Tert*-butyl)-9-chloro-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3v)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3v** (55.6 mg, 77% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94-7.91 (m, 2H), 7.52-7.44 (m, 4H), 7.27-7.23 (m, 2H), 7.17 (d, J = 8.6 Hz, 1H), 7.10-7.04 (m, 2H), 1.22 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 167.7, 159.7, 153.8, 147.7, 139.8, 138.3, 131.9, 130.8, 130.1, 130.1, 128.3, 128.2, 127.0, 126.5, 126.3, 120.2, 119.1, 34.5, 31.2; HRMS (ESI) m/z calcd for $C_{23}H_{21}ClNO$ $(M+H)^+$ 362.1306, found 362.1299; IR (KBr) 3061, 2962, 2904, 1602, 1569, 1488, 1447, 1435, 1395, 1363, 1321, 1283, 1242, 1174, 1157, 1120, 1098, 1028 cm^{-1}.

9-Chloro-2-methoxy-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3w)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3w** (51.6 mg, 77% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (d, J = 6.9 Hz, 2H), 7.43-7.35 (m, 3H), 7.18-7.16 (m, 1H), 7.08 (d, J = 8.9 Hz, 1H), 7.00-6.96 (m, 2H), 6.93 (dd, J_1 = 8.9 Hz, J_2 = 3.1 Hz, 1H), 6.62 (d, J = 3.1 Hz, 1H), 3.58 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 167.0, 156.2, 155.5, 153.9, 139.5, 138.1, 131.9, 130.8, 130.0, 128.2, 127.4, 127.1, 126.5, 121.6, 118.9, 115.3, 114.9, 55.7; HRMS (ESI) m/z calcd for $C_{20}H_{15}ClNO_2$ $(M+H)^+$ 336.0786, found 336.0778; IR (KBr) 3060, 3006, 3000, 2935, 1063, 1568, 1486, 1447, 1412, 1377, 1333, 1320, 1293, 1268, 1247, 1232, 1198, 1136, 1108, 1036 cm^{-1}.

9-Chloro-2-fluoro-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3x)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3x** (50.4 mg, 78% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (d, J = 7.1 Hz, 2H), 7.55-7.47 (m, 3H), 7.31-7.28 (m, 1H), 7.25-7.18 (m, 2H), 7.13-7.09 (m, 2H), 6.96-6.94 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 166.0, 159.0 (d, $J_{C\text{-}F}$ = 244 Hz),

157.5 (d, J_{C-F} = 1.3 Hz), 153.5, 139.1, 137.9, 132.1, 131.1, 129.9, 128.4, 128.2 (d, J_{C-F} = 6.3 Hz), 127.4, 126.8, 122.3 (d, J_{C-F} = 7.5 Hz), 119.9 (d, J_{C-F} = 24 Hz), 119.0, 117.3 (d, J_{C-F} = 25 Hz); HRMS (ESI) m/z calcd for $C_{19}H_{12}ClFNO$ $(M+H)^+$ 324.0586, found 324.0585; IR (KBr) 3075, 3054, 3022, 1613, 1603, 1590, 1569, 1480, 1447, 1406, 1375, 1319, 1272, 1244, 1213, 1154, 1233, 1097, 1027 cm^{-1}.

2,9-Dichloro-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3y)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3y** (52.2 mg, 77% yield) as a yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91-7,89 (m, 2H), 7.56-7.45 (m, 4H), 7.31-7.29 (m, 1H), 7.22-7.19 (m, 2H), 7.13-7.08 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 165.9, 160.1, 153.3, 139.1, 137.9, 133.1, 132.1, 131.1, 130.6, 130.4, 129.9, 128.5, 128.3, 127.4, 126.9, 122.4, 119.0; HRMS (ESI) m/z calcd for $C_{19}H_{12}Cl_2NO$ $(M+H)^+$ 340.0290, found 340.0285; IR (KBr) 3060, 3051, 1600, 1562, 1474, 1447, 1435, 1390, 1318, 1307, 1269, 1252, 1204, 1174, 1150, 1086, 1028 cm^{-1}.

2-Chloro-9-methyl-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3z)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3z** (48.5 mg, 76% yield) as a yellow solid. m.p 122-123 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.87-7.85 (m, 2H), 7.52-7.427 (m, 3H), 7.43 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H), 7.22-7.20 (m, 2H), 7.12-7.02 (m, 3H), 2.55 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 163.9, 160.4, 152.3, 139.7, 138. 8, 136.6, 132.6, 130.6, 130.3, 129.9, 129.5, 128.7, 128.4, 127.3, 127.3, 122.3, 118.0, 18.28; HRMS (ESI) m/z calcd for $C_{20}H_{15}ClNO$ $(M+H)^+$ 320.0837, found 320.0831; IR (KBr) 3060, 3021, 2957, 2922, 1607, 1593, 1573, 1561, 1466, 1444, 1390, 1379, 1318, 1309, 1292, 1251, 1201, 1156, 1080, 1022 cm^{-1}.

2-Bromo-9-methyl-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3aa)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3aa** (56.6 mg, 78% yield) as a yellow solid. m.p 141-143 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, J = 6.7 Hz, 2H), 7.58 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1H), 7.54-7.47 (m, 3H), 7.35 (d, J = 2.4 Hz, 1H), 7.16-7.02 (m, 4H), 2.55 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 163., 160.9, 152.3, 139.6, 138.8, 136.5, 135.6, 133.2, 130.7, 129.5, 129.1, 128.4, 127.3, 127.3, 122.7, 118.0, 117.4, 18.28; HRMS (ESI) m/z calcd for $C_{20}H_{15}BrNO$ $(M+H)^+$ 364.0332, found 364.0333; IR (KBr) 3076, 3059, 3020, 2960, 2850, 1606, 1591, 1573, 1557, 1491, 1476, 1466, 1444, 1379, 1318, 1306, 1289, 1270, 1251, 1176, 1114, 1023 cm^{-1}.

4-(*Tert*-butyl)-9-chloro-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3ab)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3ab** (51.3 mg, 71% yield) as a yellow solid. m.p. 139-140 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.80 (d, J = 7.1 Hz, 2H), 7.57-7.41 (m, 4H), 7.30-7.27 (m, 2H), 7.09-7.02 (m, 3H), 1.59 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 168.9, 162.2, 154.1, 142.3, 140.7, 139.2, 132.3, 131.0, 130.6, 130.2, 123.0, 128.6, 128.1, 126.4, 126.3, 123.8, 120.1, 35.2, 31.6; HRMS (ESI) m/z calcd for

$C_{23}H_{21}ClNO$ $(M+H)^+$ 362.1306, found 362.1308; IR (KBr) 3077, 3055, 3015, 2998, 2953, 2911, 1607, 1585, 1572, 1563, 1481, 1423, 1377, 1361, 1316, 1278, 1255, 1213, 1174, 1136, 1076 cm^{-1}.

9-Chloro-4-methoxy-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3ac)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3ac** (43.6 mg, 65% yield) as a yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 8.1 Hz, 2H), 7.55-7.46 (m, 3H), 7.31-7.25 (m, 2H), 7.16-7.10 (m, 3H), 6.84-6.81 (m, 1H), 3.98 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 167.2, 153.5, 151.4, 149.9, 139.6, 138.5, 131.7, 130.8, 130.0, 128.3, 128.2, 127.0, 126.6, 124.8, 122.2, 119.6, 115.2, 56.33; HRMS (ESI) m/z calcd for $C_{20}H_{15}ClNO_2$ $(M+H)^+$ 336.0786, found 336.0790; IR (KBr) 3068, 3025, 3004, 2972, 2941, 1591, 1567, 1473, 1458, 1445, 1432, 1372, 1295, 1232, 1202, 1176, 1140, 1080, 1029 cm^{-1}.

9-Chloro-4-isopropyl-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3ad)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3ad** (48.9 mg, 70% yield) as a yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.94-7.92 (m, 2H), 7.51-7.44 (m, 4H), 7.29 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.17-7.06 (m, 4H), 3.85-3.78 (m, 1H), 1.34 (d, J = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 168.0, 158.5, 153.6, 140.9, 140.1, 138.6, 132.0, 130.7, 130.04, 130.01, 128.7, 128.1, 127.2, 126.8, 126.5, 124.7, 119.3, 26.2, 23.5; HRMS (ESI) m/z calcd for $C_{22}H_{19}ClNO$ $(M+H)^+$ 348.1150, found 348.1147; IR (KBr) 3061, 3027, 2963, 2927, 1606, 1592, 1570, 1488, 1447, 1432, 1384, 1363, 1304, 1272, 1246, 1197, 1148, 1096, 1031 cm^{-1}.

9-Chloro-4,11-diphenyldibenzo[*b*,*f*][1,4]oxazepine (3ae)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3ae** (52.6 mg, 69% yield) as a yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 7.0 Hz, 2H), 7.67 (d, J = 7.0 Hz, 2H), 7.61-7.49 (m, 7H), 7.28-7.20 (m, 3H), 6.87 (t, J = 8.1 Hz, 1H), 6.26 (d, J = 8.1 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 167.5, 158.0, 153.2, 139.9, 138.4, 136.7, 135.1, 133.8, 131.6, 130.9, 130.3, 130.1, 130.0, 128.3, 128.2, 127.9, 127.8, 126.9, 126.5, 124.8, 119.2; HRMS (ESI) m/z calcd for $C_{25}H_{17}ClNO$ $(M+H)^+$ 382.0993, found 382.0992; IR (KBr) 3053, 3033, 1683, 1604, 1592, 1569, 1495, 1446, 1424, 1377, 1318, 1293, 1278, 1265, 1206, 1176, 1161, 1111, 1073, 1024 cm^{-1}.

9-Methyl-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3af)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3af** (41.6 mg, 73% yield) as a yellow solid. m.p 120-121 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.88 (d, J = 6.9 Hz, 2H), 7.52-7.45 (m, 4H), 7.30-7.24 (m, 2H), 7.16 (dt, J_1= 7.5 Hz, J_2 = 1.0 Hz, 1H), 7.12-7.06 (m, 3H), 2.56 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 165.4, 162.1, 152.7, 140.3, 139.1, 136.4, 132.8, 130.9, 130.3, 129.7, 128.2, 127.5, 126.99, 126.98, 124.4, 120.9, 118.1,

18.31; HRMS (ESI) m/z calcd for $C_{20}H_{16}NO$ $(M+H)^+$ 286.1226, found 286.1228; IR (KBr) 3053, 3026, 2979, 2953, 1604, 1575, 1480, 1463, 1445, 1427, 1373, 1319, 1282, 1252, 1200, 1175, 1105, 1030 cm^{-1}.

4-Chloro-9-methyl-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3ag)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3ag** (47.9 mg, 75% yield) as a yellow solid. m.p 118-119 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, J = 6.8 Hz, 2H), 7.56-7.45 (m, 4H), 7.29 (d, J = 7.7 Hz, 1H), 7.14-7.07 (m, 4H), 2.56 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 164.4, 156.5, 152.0, 139.9, 138.9, 136.3, 132.7, 130.5, 129.5, 129.2, 129.0, 128.2, 127.3, 127.1, 126.7, 124.8, 118.9, 18.25; HRMS (ESI) m/z calcd for $C_{20}H_{15}ClNO$ $(M+H)^+$ 320.0837, found 320.0839; IR (KBr) 3062, 3024, 2918, 2851, 1603, 1588, 1573, 1489, 1466, 1440, 1374, 1316, 1298, 1222, 1177, 1135, 1078, 1022 cm^{-1}.

4-Bromo-9-methyl-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3ah)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3ah** (53.0 mg, 73% yield) as a yellow solid. m.p 236-238 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, J = 7.1 Hz, 2H), 7.72 (dd, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 1H), 7.53-7.45 (m, 3H), 7.38 (d, J = 7.7 Hz, 1H), 7.19-7.09 (m, 3H), 7.02 (t, J = 7.9 Hz, 1H), 2.57 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 164.3, 157.5, 152.0, 139.9, 138.7, 136.3, 135.7, 130.5, 130.0, 129.5, 128.9, 128.2, 127.3, 127.1, 125.2, 119.0, 115.7, 18.25; HRMS (ESI) m/z calcd for $C_{20}H_{15}BrNO$ $(M+H)^+$ 364.0332, found 364.0332; IR (KBr) 3061, 2925, 2947, 2916, 1603, 1588, 1572, 1555, 1490, 1465, 1434, 1373, 1316, 1272, 1233, 1221, 1195, 1157, 1078, 1023 cm^{-1}.

3,4,9-Trimethyl-11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3ai)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3ai** (43.2 mg, 69% yield) as a yellow solid. m.p 128-130 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.88 (d, J = 7.4 Hz, 2H), 7.50-7.44 (m, 3H), 7.14-7.06 (m, 3H), 6.96 (s, 2H), 2.57 (s, 3H), 2.50 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 165.9, 159.8, 152.6, 142.2, 140. 7, 139.6, 136.3, 130.2, 129.7, 128.7, 128.0, 127.7, 126.8, 126.5, 125.5, 125.1, 118.3, 20.23, 18.28, 12.33; HRMS (ESI) m/z calcd for $C_{22}H_{20}NO$ $(M+H)^+$ 314.1539, found 314.1534; IR (KBr) 3060, 3023, 2942, 2917, 1602, 1587, 1573, 1466, 1446, 1440, 1410, 1381, 1317, 1276, 1256, 1236, 1203, 1189, 1156, 1080, 1040 cm^{-1}.

11-phenyldibenzo[*b*,*f*][1,4]oxazepine (3aj)[7b]

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3aj** (24.9 mg, 92% yield) as a pale yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.84-7.81 (m, 2H), 7.51-7.42 (m, 5H), 7.28 (d, J = 9.1 Hz, 1H), 7.21-7.15 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 167.1, 162.0, 152.4, 140.9, 140.1, 133.0, 131.2, 130.4, 129.7, 128.19, 128.16, 127.5, 127.4, 125.6, 124.5, 120.9, 120.7.

_N_,11-diphenyldibenzo[_b,f_][1,4]oxazepin-9-amine (3ak)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3ak** (32.2 mg, 89% yield) as a dark yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (dd, J_1 = 7.7 Hz, J_2 = 1.3 Hz, 2H), 7.54-7.45 (m, 4H), 7.38-7.34 (m, 2H), 7.30-7.28 (m, 3H), 7.23-7.15 (m, 3H), 7.12-7.04 (m, 3H), 6.68 (dd, J_1 = 7.3 Hz, J_2 = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 165.6, 161.4, 153.3, 142.0, 141.3, 140.0, 133.1, 131.0, 130.4, 129.5, 129.3, 128.3, 128.3, 127.9, 127.7, 124.5, 122.4, 121.2, 120.6, 110.6, 109.6; HRMS (ESI) m/z calcd for $C_{25}H_{19}N_2O$ $(M+H)^+$ 363.1492, found 363.1488.

9-Chloro-11-(piperidin-1-yl)dibenzo[_b,f_][1,4]oxazepine (3a1)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60:1) gave **3a1** (14.3 mg, 23% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.41 (m, 1H), 7.36 (J_1 = 7.7 Hz, J_2 = 1.6 Hz, 1H), 7.24-7.14 (m, 3H), 7.02 (J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1H), 6.84 (t, J = 8.1 Hz, 1H), 3.53 (brs, 4H), 1.75-1.63 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 160.4, 160.1, 153.1, 138.7, 132.6, 130.5, 129.5, 126.3, 124.9, 123.8, 123.0, 121.2, 118.5, 48.40, 25.95, 24.93.

9-Chloro-5-methyl-11-phenyl-5_H_-dibenzo[_b,e_][1,4]diazepine (5a)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) gave **5a** (54.7 mg, 86% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, J = 8.0 Hz, 2H), 7.47-7.40 (m, 4H), 7.17-7.02 (m, 5H), 6.87 (d, J = 8.1 Hz, 1H), 3.26 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 169.6, 157.5, 148.5, 140.5, 139.6, 131.7, 131.3, 131.1, 130.5, 129.9, 128.9, 128.0, 126.3, 124.9, 123.1, 117.7, 115.8, 37.0; HRMS (ESI) m/z calcd for $C_{20}H_{16}ClN_2$ $(M+H)^+$ 319.0997, found 319.0993; IR (KBr) 3059, 3046, 2951, 2920, 1612, 1594, 1580, 1481, 1449, 1432, 1377, 1319, 1301, 1264, 1226, 1150, 1119, 1028 cm^{-1}.

2-(_Tert-butyl_)-9-chloro-5-methyl-11-phenyl-5_H_-dibenzo[_b,e_][1,4]diazepine (5b)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) gave **5b** (33.7 mg, 45% yield) as a yellow solid. m.p 122-123 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, J = 6.9 Hz, 2H), 7.47-7.40 (m, 4H), 7.15-7.11 (m, 2H), 7.04-6.98 (m, 2H), 6.85 (d, J = 8.1 Hz, 1H), 3.23 (s, 3H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 169.9, 155.0, 148.7, 145.7, 140.5, 139.7, 131.3, 130.5, 123.0, 128.5, 128.4, 128.2, 128.0, 126.2, 124.8, 117.1, 115.6, 37.0, 34.2, 31.2; HRMS (ESI) m/z calcd for $C_{24}H_{24}ClN_2$ $(M+H)^+$ 375.1623, found 375.1623; IR (KBr) 3055, 3027, 2960, 2920, 1626, 1605, 1593, 1575, 1513, 1498, 1480, 1467, 1450, 1431, 1394, 1362, 1301, 1281, 1253, 1201, 1159, 1108, 1026 cm^{-1}.

2-Bromo-9-chloro-5-methyl-11-phenyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (5c)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) gave **5c** (62.6 mg, 79% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, J = 6.9 Hz, 2H), 7.52-7.43 (m, 4H), 7.22 (d, J = 2.3 Hz, 1H), 7.19-7.16 (m, 1H),7.05 (t, J = 8.1 Hz, 1H), 6.94 (d, J = 8.7 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H),3.22 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 168.0, 156.5, 147.9, 139.9, 139.3, 134.4, 133.4, 131.5, 130.8, 130.6, 129.8, 128.3, 126.6, 125.2, 119.4, 116.1, 115.8, 37.04; HRMS (ESI) m/z calcd for $C_{20}H_{15}BrClN_2$ $(M+H)^+$ 397.0102, found 397.0095; IR (KBr) 3059, 2989, 2952, 2921, 1612, 1577, 1561, 1478, 1450, 1433, 1386, 1317, 1302, 1249, 1222, 1176, 1126, 1075, 1028 cm^{-1}.

9-Chloro-11-(3,5-dimethylphenyl)-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (5d)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) gave **5d** (42.2 mg, 61% yield) as a yellow solid. m.p 127-128 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.39 (m, 3H),7.15 (d, J = 7.9 Hz, 1H), 7.10-7.00 (m, 5H), 6.86 (d, J = 8.1 Hz, 1H), 3.25 (s, 3H), 2.36 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 170.0, 157.4, 148.5, 140.6, 139.6, 137.5, 132.2, 131.6, 131.2, 131.2, 129.2, 127.7, 126.1, 124.9, 123.0, 117.6, 115.6, 37.0, 21.3; HRMS (ESI) m/z calcd for $C_{22}H_{20}ClN_2$ $(M+H)^+$ 347.1310, found 347.1308; IR (KBr) 3055, 3009, 2985, 2953, 2917, 1611, 1594, 1561, 1486, 1451, 1434, 1376, 1329, 1305, 1261, 1234, 1121, 1038 cm^{-1}.

11-([1,1'-Biphenyl]-4-yl)-9-chloro-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (5e)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) gave **5e** (57.5mg, 73% yield) as a yellow solid. m.p 137-138 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.2 Hz, 4H), 7.49-7.27 (m, 4H), 7.19-7.03 (m, 5H), 6.88 (d, J = 8.2 Hz, 1H), 3.27 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 169.2, 157.6, 148.5, 143.2, 140.5, 139.7, 139.4, 131.7, 131.4, 131.1, 130.4, 128.8, 127.7, 127.2, 126.8, 126.3, 125.0, 123.1, 117.8, 115.8, 37.1; HRMS (ESI) m/z calcd for $C_{26}H_{20}ClN_2$ $(M+H)^+$ 395.1310, found 395.1308; IR (KBr) 3057, 3028, 1613, 1599, 1581, 1556, 1489, 1449, 1431, 1403, 1378, 1317, 1276, 1249, 1266, 1188, 1150, 1079, 1042 cm^{-1}.

Methyl 4-(9-chloro-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepin-11-yl)benzoate (5f)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) gave **5f** (58.7 mg, 78% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.1 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.48-7.44 (m, 1H), 7.19 (d, J = 7.1 Hz, 1H), 7.11-7.06 (m, 4H), 6.90 (d, J = 7.5 Hz, 1H), 3.97 (s, 3H), 3.28 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 168.8, 166.8, 157. 7, 148.4, 144.6, 139.3, 132.0, 131.6, 130.8, 129.8, 129.3, 128.6, 126.8, 125.0, 123.3, 118.0, 115.9, 52.3, 37.1; HRMS (ESI) m/z calcd for $C_{22}H_{18}ClN_2O_2$ $(M+H)^+$ 377.1051, found 377.1050; IR (KBr) 3060, 3022, 2992, 2920, 1615, 1583, 1564, 1482, 1433, 1405, 1306, 1276, 1191, 1177, 1104, 1066 cm^{-1}.

9-Chloro-11-(3,4-dichlorophenyl)-5-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (5g)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) gave **5g** (58.7 mg, 76% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 1.7 Hz, 1H), 7.71 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.47-7.42 (m, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.09-7.04 (m, 4H), 6.87 (d, J = 8.1 Hz, 1H), 3.25 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 167.2, 157.7, 148.3, 140.4, 139.1, 134.7, 132.4, 132.2, 131.5, 131.5, 130.6, 130.1, 129.0, 128.1, 126.9, 125.1, 123.4, 118.1, 116.0, 37.03; HRMS (ESI) m/z calcd for $C_{20}H_{14}Cl_3N_2$ $(M+H)^+$ 387.0217, found 387.0219; IR (KBr) 3062, 2952, 2920, 1613, 1583, 1553, 1491, 1465, 1450, 1432, 1380, 1312, 1279, 1263, 1245, 1198, 1130, 1079, 1029 cm^{-1}.

6-Chloro-11-methyl-4-phenylbenzo[2,3][1,4]diazepino[6,7,1-*hi*]indole (7)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) gave **7** (53.4 mg,78% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 7.2 Hz, 2H), 7.49-7.40 (m, 4H), 7.27 (d, J = 8.4 Hz, 1H), 7.10-6.95 (m, 3H), 6.60 (d, J = 8.0 Hz, 1H), 6.57 (s, 1H), 2.61 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 171.4, 153.3, 141.2, 140.2, 138.5, 138.4, 132.8, 131.1, 130.4, 130.3, 127.9, 126.9, 126.4, 125.9, 122.3, 122.1, 121.9, 121.1, 110.5, 14.8; HRMS (ESI) m/z calcd for $C_{22}H_{16}ClN_2$ $(M+H)^+$ 343.0997, found 343.1002; IR (KBr) 3057, 3026, 2920, 1615, 1592, 1561, 1476, 1454, 1446, 1415, 1383, 1364, 1295, 1266, 1227, 1179, 1148, 1026 cm^{-1}.

4-(9-Methyl-5-oxido-5-phenyl-5*H*-dibenzo[*b*,*e*][1,4]azaphosphepin-11-yl)benzaldehyde (9)

Flash column chromatography on silica gel (petroleum ether : ethyl acetate = 2:1) gave **9** (73.3 mg, 87% yield) as a yellow solid. m.p 239-241 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.99 (s, 1H), 8.45-8.40 (m, 1H), 8.12-8.07 (m, 1H), 7.73 (d, J = 8.1 Hz, 3H), 7.59-7.33 (m, 7H), 7.23-7.15 (m, 4H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 191.7, 163.4, 145.3, 137.15 (d, $J_{C\text{-}P}$ = 99 Hz), 137.12, 134.5 (d, $J_{C\text{-}P}$ = 2 Hz), 133.3 (d, $J_{C\text{-}P}$ = 9 Hz), 133.0 (d, $J_{C\text{-}P}$ = 11 Hz), 132.0 (d, $J_{C\text{-}P}$ = 3 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2 Hz), 130.82 (d, $J_{C\text{-}P}$ = 10 Hz), 130.77 (d, $J_{C\text{-}P}$ = 12 Hz), 130.3 (d, $J_{C\text{-}P}$ = 6 Hz), 129.59 (d, $J_{C\text{-}P}$ = 20 Hz), 129.61, 129.2 (d, $J_{C\text{-}P}$ = 5 Hz), 129.0, 128.13 (d, $J_{C\text{-}P}$ = 13 Hz), 126.3 (d, $J_{C\text{-}P}$ = 12 Hz), 123.7, 122.7, 18.6; HRMS (ESI) m/z calcd for $C_{27}H_{21}NO_2P$ $(M+H)^+$ 422.1304, found 422.1300; IR (KBr) 3052, 2971, 2922, 1608, 1578, 1562, 1501, 1485, 1440, 1407, 1375, 1301, 1270, 1248, 1206, 1179, 1140, 1112, 1038 cm^{-1}.

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Supporting Information:

Schemes for the synthesis of functionalized isocyanides along with copies of ^{1}H, ^{13}C NMR spectra for all isolated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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