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Asymmetric Alkynylation of Seven-Membered Cyclic Imines by Combining Chiral Phosphoric Acids and Ag(I) Catalysts: Synthesis of 11-Substituted-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine Derivatives

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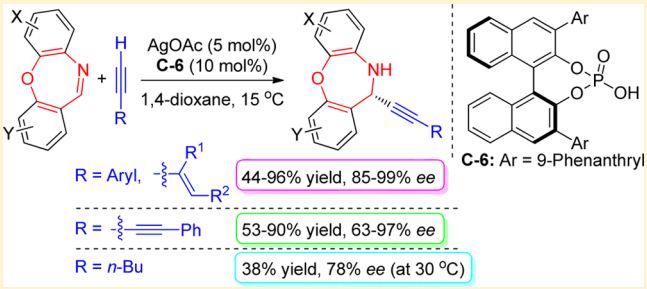
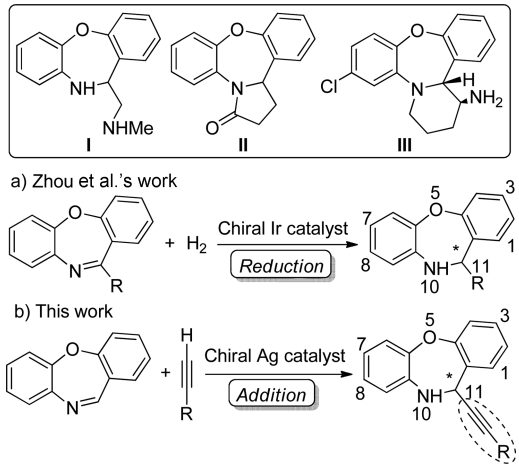
Supporting Information

ABSTRACT: Asymmetric alkynylation of seven-membered cyclic imine dibenzo[*b*,*f*][1,4]oxazepines is successfully achieved by combining chiral phosphoric acid and Ag(I) catalysts. Various arylacetylenes, conjugated enynes, and terminal 1,3-diynes are good substrates for this reaction, and aliphatic hexyne is also a suitable donor at elevated temperature. Optimization of this approach has provided a facile method to synthesize optically active 11-substituted-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine derivatives containing a carbon−carbon triple bond with 63−99% *ee*. Subsequent transformations of the carbon−carbon triple bond for the heterocyclic products have been disclosed.



Over the past decade, considerable attention has been given to 11-substituted-10,11-dihydrodibenzo[*b*,*f*][1,4]-oxazepine derivatives, which play an important role in synthetic organic chemistry and pharmaceutical science,[1,2] such as antihistaminics **I**,[1a] dibenzazepines **II** analogous to Sintamil,[1b] and progesterone receptor agonist **III** (Scheme 1).[1c] Despite the availability of several published methods for the construction of these structures,[1b,2] a catalytic method that offers high enantioselectivity is highly desired as different enantiomers or diastereomers of a molecule often have different biological activity. So far, only Ir-catalyzed asymmetric hydrogenation of the corresponding seven-membered cyclic ketimines was reported by Zhou et al.[3] Therefore, the research for other catalytic asymmetric reactions to synthesize these seven-membered cyclic optically active compounds is highly desirable.

Scheme 1. Construction of Dibenzo[*b*,*f*][1,4]oxazepine Derivatives *via* Catalytic Asymmetric Reaction



Asymmetric alkynylation of imines is one of the most efficient methods for obtaining chiral propargylamines,[4] which are important synthetic intermediates for the construction of biologically active nitrogen-containing compounds[5] and natural products.[6] While catalytic enantioselective addition to imines provides the most efficient method for the synthesis of chiral nitrogen-containing compounds,[7] the direct use of alkynes as carbon nucleophiles continues to be desired. Research more typically focuses on the use of acyclic imines and related C═N electrophiles as substrates, which are prepared prior to use[8] or generated *in situ* from aldehydes and amines.[9] However, the asymmetric alkynylation of cyclic imines is rarely reported, despite the fact that it is a potentially powerful method for the construction of optically active polyfunctional nitrogen-containing heterocycles.[10] In 2004, Jiang et al. described the highly enantioselective alkynylation of six-membered cyclic *N*-acyl trifluoromethyl-activated imine using stoichiometric Zn-$(OTf)_2$ and amino alcohol as a chiral ligand.[11] Recently, the same cyclic imines were employed for the asymmetric diynylation reaction with chloramphenicol-amine derivatives as chiral additives.[12] Two catalytic asymmetric methods used previously include the alkynylation of cyclic iminium derived from dihydroisoquinoline catalyzed by CuBr/Quinap[13] and the combined system of CuOAc/Ph-pybox with an axially chiral dicarboxylic acid.[14] To the best of our knowledge, there has

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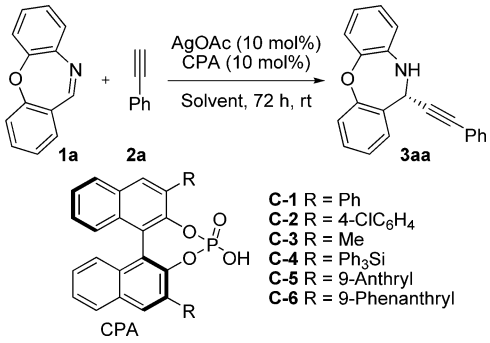
been no report of catalytic asymmetric alkynylation of seven-membered imines. In the course of our research on the catalytic enantioselective addition of cyclic imines to construct chiral *N*-heterocycles,[15] very recently, we reported organocatalyzed asymmetric direct Mannich reaction of dibenzo[*b*,*f*][1,4]-oxazepines.[15c] Inspired by those achievements, in this note, we described a highly enantioselective alkynylation of dibenzo-[*b*,*f*][1,4]oxazepines by combining chiral phosphoric acids and Ag(I) catalysts (Scheme 1). Various arylacetylenes, conjugated enynes, and terminal 1,3-diynes were tolerated in the reaction. Furthermore, the carbon−carbon triple bond introduced herein is an important functional group for further chemical transformation, and the corresponding reductions to obtain separately (*Z*)- and (*E*)-alkenes without loss of enantioselectivities were realized.

Optimization studies were performed with the alkynylation reaction of seven-membered cyclic imine **1a** and phenylacetylene **2a** as the model substrates, and the results are listed in Table 1. Cooperative catalytic models based on chiral Brønsted acids and metal catalysis[16] have been previously employed in the asymmetric alkynylation of acyclic imines.[17] In order to achieve high activity and stereoselectivity, two well-differentiated and parallel catalytic cycles were used, the addition of metallic alkynylides to imines and the use of chiral Brønsted acids as imine activators. As such, for the investigation of catalysis, we focused on the combined chiral Brønsted acids and Ag(I) catalysts.[18] Combining chiral phosphoric acid (CPA)[19] **C-1** and AgOAc catalysts in toluene at room temperature resulted in a 20% yield of the desired product **3aa** with 38% *ee* (entry 1). Further assessment of solvents revealed that 1,4-dioxane was proven to be the most favorable solvent (75% yield, 58% *ee*) (entry 5). Several silver salts were also examined, and AgOAc was yet the best choice (entries 7−11). Subsequently, a screening for CPA was undertaken (entries 12−16), resulting in the bulky substituted CPA **C-6** making a significant improvement in both reactivity and enantioselectivity (entry 16). Notably, when the AgOAc loading was reduced to 5 mol %, the product **3aa** was obtained in full conversion within a shorter time (24 h, as opposed to 72 h) (entry 17). Finally, the *ee* value was further improved to 87% by decreasing the reaction temperature to 15 °C (entry 18).[20]

Once the reaction conditions were optimized, the scope of this reaction was then evaluated, as summarized in Table 2.

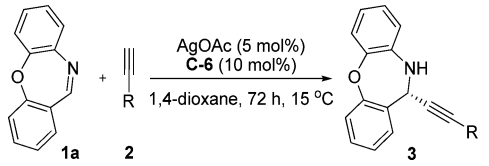
Table 1. Optimization of Reaction Conditions[a]



entry	solvent	AgX	CPA	yield [%][b]	*ee* [%][c]
1	toluene	AgOAc	**C-1**	20	38
2	benzene	AgOAc	**C-1**	40	29
3	CH_2Cl_2	AgOAc	**C-1**	11	4
4	THF	AgOAc	**C-1**	30	47
5	dioxane	AgOAc	**C-1**	75	58
6	MeOH	AgOAc	**C-1**	<5	
7	dioxane	AgO	**C-1**	65	42
8	dioxane	$AgNO_3$	**C-1**	56	27
9	dioxane	$AgBF_4$	**C-1**	49	34
10	dioxane	$AgCO_2CF_3$	**C-1**	44	34
11	dioxane	AgOTf	**C-1**	50	33
12	dioxane	AgOAc	**C-2**	30	22
13	dioxane	AgOAc	**C-3**	58	18
14	dioxane	AgOAc	**C-4**	NR	
15	dioxane	AgOAc	**C-5**	94	77
16	dioxane	AgOAc	**C-6**	91	84
17[d,e]	dioxane	AgOAc	**C-6**	92	85
18[e,f]	dioxane	AgOAc	**C-6**	88	87

[a]Reaction conditions: imine **1a** (0.1 mmol), **2a** (0.2 mmol), solvent (1.0 mL), CPA (0.01 mmol), AgOAc (10 mol %), 25 °C, 72 h. [b]Isolated yield based on imine **1a**. [c]Determined by HPLC using a chiral column. [d]24 h. [e]5 mol % AgOAc was used. [f]15 °C, 72 h.

Table 2. Addition of Different Alkynes to Imine 1a[a]



entry	R (**2**)	**3**	yield [%][b]	*ee* [%][c]
1	Ph (**2a**)	**3aa**	88	87
2	*p*-MeC_6H_4 (**2b**)	**3ab**	83	85
3	*p*-$MeOC_6H_4$ (**2c**)	**3ac**	92	88
4	*p*-FC_6H_4 (**2d**)	**3ad**	91	89
5[d]	*o*-FC_6H_4 (**2e**)	**3ae**	65	93
6	3-thienyl (**2f**)	**3af**	74	90
7[e]	*n*-butyl (**2g**)	**3ag**	38	78
8	1-cyclohexenyl (**2h**)	**3ah**	92	95
9	2-propenyl (**2i**)	**3ai**	74	91
10[f]	(*E*)-CH=CHC_6H_5 (**2j**)	**3aj**	44	90

[a]Reaction conditions: imine **1a** (0.2 mmol), **2** (0.4 mmol), solvent (2.0 mL), **C-6** (0.02 mmol), AgOAc (0.01 mmol), 15 °C, 72 h. [b]Isolated yield based on imine **1a**. [c]Determined by HPLC using a chiral column. [d]96 h. [e]30 °C. [f]24 h.

Using imine **1a** as the electrophile, a broad range of alkynes was investigated. Four different aryl acetylenes with electron-donating or electron-withdrawing groups tolerated the reaction conditions (entries 1−5). Interestingly, heteroaryl alkyne **2f** was also effective in the reaction, and the corresponding product was obtained in 74% yield with 90% *ee* (entry 6). Unfortunately, the reaction with alkyl alkynes, such as hexyne **2g**, showed very low reactivity. The desired product **3ag** could be obtained in 38% yield and 78% *ee* along with unreacted starting material **1a** remained when the temperature was raised to 30 °C (entry 7). Remarkably, conjugated enyne **2h** was an excellent nucleophile, which gave the desired product in 92% yield with 95% *ee* (entry 8). Furthermore, this reaction was also applicable to enynes **2i** and **2j**, with 91% and 90% *ee* values observed, respectively (entries 9 and 10).

Next, the scope of different substituted cyclic imines **1a−n** was examined, and generally, the reaction proceeded well enough to afford the desired products with 86−99% *ee* (Scheme 2). Only for imine **1l**, the corresponding propargylamine was obtained with relatively low enantioselectivity but

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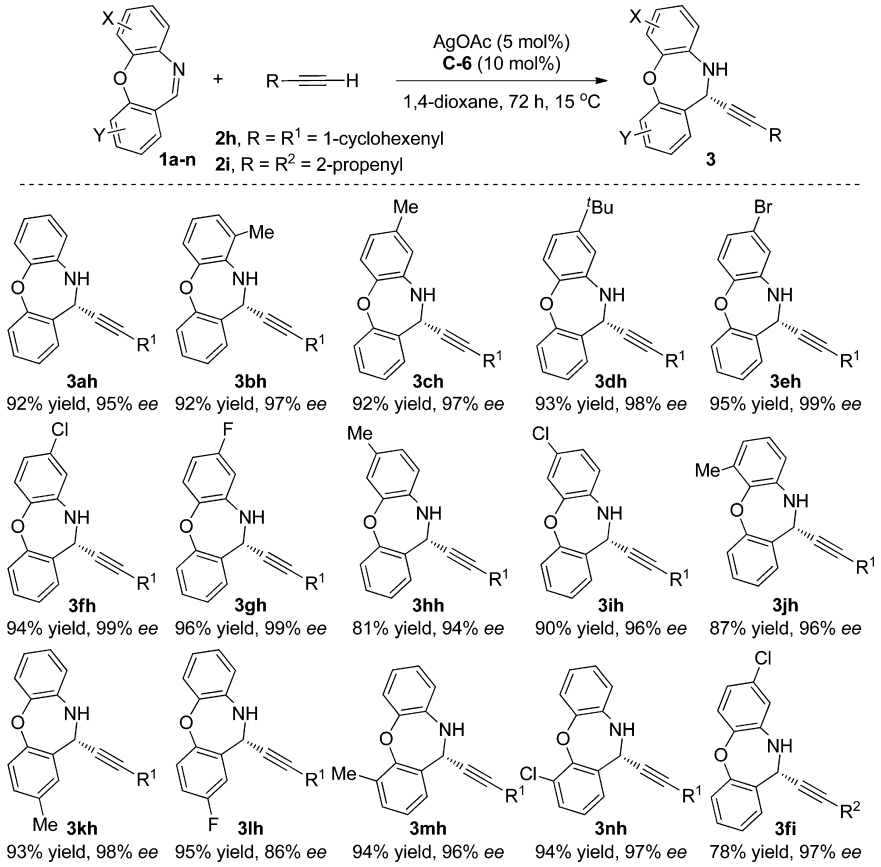
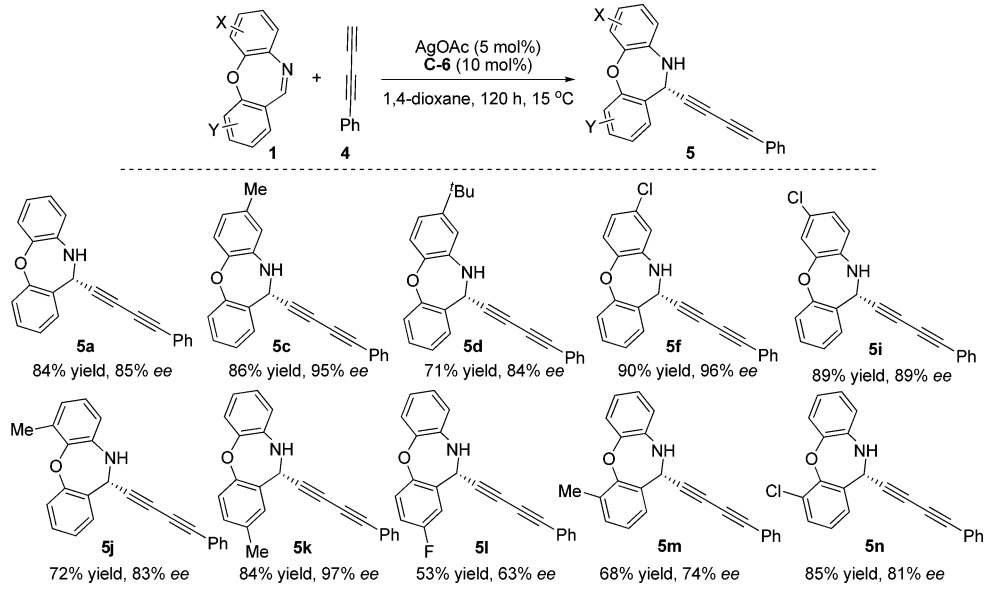
Scheme 2. Addition of Alkynes to Different Imines



Scheme 3. Reaction of Conjugated Diyne 4 with Different Imines



high yield. Additionally, the reaction of 2-methylbut-1-en-3-yne **2i** with imine **1f** proceeded smoothly, producing **3fi** in 78% yield and 97% *ee* within 4 days.

We also explored the reaction of terminal 1,3-diyne **4** with different seven-membered cyclic imines under the optimized conditions (Scheme 3). To our delight, all the imines with different substituents were tolerated in the reaction and provided moderate to high yields (53−90%) with *ee* values ranging from 63% to 97% within 5 days. It is noteworthy that the reaction of model substrate **1a** with diyne **4** could be completed within 3 days.

The absolute configuration of representative product **3eh** was determined as *R* by single-crystal X-ray analysis (see the Supporting Information).[21] The absolute configurations of all other chiral products **3** and **5** were assigned by analogy.

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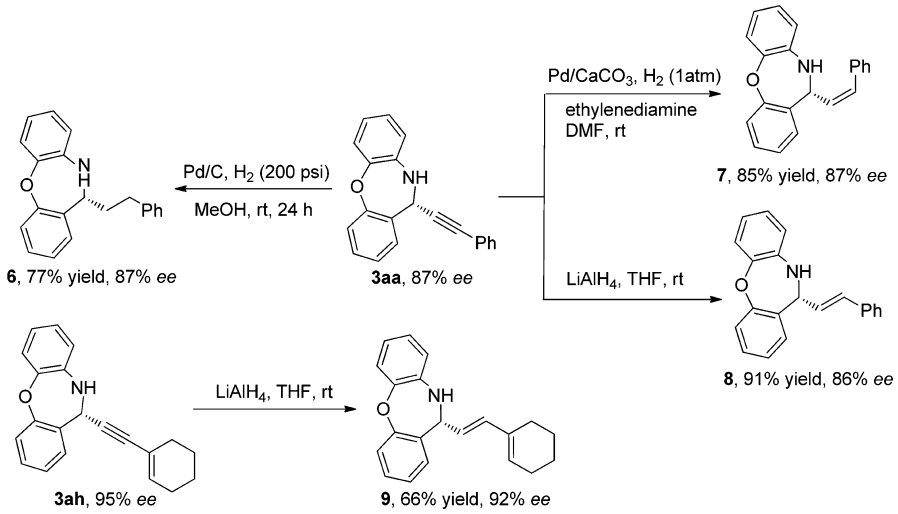
Scheme 4. Reduction of Propargylamine 3



The C≡C bond in the chiral propargylamine **3** presents an attractive site for further modifications. For example, reduction of **3aa** gave **6** in 77% without loss of optical purity (Scheme 4). (*Z*)-alkene **7** and (*E*)-alkene **8** were obtained in 85% and 91% yield when $Pd/CaCO_3$ and $LiAlH_4$ were used, respectively. Conjugated diene **9** was obtained in 66% yield with slightly decreased enantioselectivity when **3ah** was treated with $LiAlH_4$.

In summary, we have demonstrated the asymmetric alkynylation of seven-membered cyclic imines catalyzed by combining chiral phosphoric acids and silver salts as chiral catalysts. This approach has provided a new method to synthesize optically active 11-substituted-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine derivatives containing a carbon−carbon triple bond with excellent enantioselectivities. The reaction shows the wide substrate scope for different imines and terminal alkynes. Typically, various arylacetylenes, conjugated enynes, and 1,3-diynes all can be employed for this reaction as good donors. When the temperature was increased, aliphatic hexyne is also a suitable donor. The present study also significantly extends the scope of the catalytic asymmetric alkynylation for other challenging and unexplored substrates.

EXPERIMENTAL SECTION

General. All commercially available compounds were used as provided without further purification unless otherwise noted. Imines **1a**−**j**,[22] **1k**−**n**,[23] enyne **2j**[24], and **4**[25] were prepared according to the procedures reported in the literature. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$ on a 400 MHz instrument with tetramethylsilane (TMS) as internal standard. High-resolution mass spectra (HRMS) were recorded using ESI-TOF (electrospray ionization-time-of-flight) mass spectrometry. Enantiomeric excess was determined by HPLC analysis, using a chiral column described below in detail. Optical rotations were measured by a polarimeter. Flash column chromatography was performed on silica gel (200−300 mesh).

General Procedure for the Asymmetric Alkynylation of Imines. To the mixture of imine (0.2 mmol), AgOAc (5 mol %, 0.01 mmol), and **C-6** (10 mol %, 0.02 mmol) in dioxane (2.0 mL) was added alkyne (0.4 mmol). This reaction mixture was stirred at 15 °C in the showed reaction time. Direct purification of the reaction mixture by column chromatography on a silica gel (petroleum ether/EtOAc: 40/1 to 20/1) gave the desired product. Racemic adducts were obtained from racemic 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate.

*(R)-11-(Phenylethynyl)-10,11-dihydrodibenzo[b,f][1,4]oxazepine (**3aa**).* Colorless oil, 52.3 mg, 88% yield, R_f = 0.50 (Petroleum ether:EtOAc = 10:1); 87% *ee*, $[\alpha]_D^{20}$ = +48.2 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.49 (dd, *J* = 6.5, 3.0, 2H), 7.40−7.25 (m, 4H), 7.21−7.07 (m, 3H), 6.93−6.82 (m, 1H), 6.74 (td, *J* = 7.9, 1.4 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.09 (s, 1H), 4.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 144.9, 137.2, 131.9, 131.4, 129.7, 128.7, 128.4, 127.0, 124.6, 124.5, 122.4, 121.9, 120.9, 120.3, 119.2, 86.8, 86.5, 48.6; HRMS (ESI): *m*/*z* calculated for $C_{21}H_{16}NO$ $[M + H]^+$ 298.1226, found: 298.1226; HPLC (Chiralcel IC column, hexane/*i*PrOH = 95/5, 0.7 mL/min, 254 nm): t_1 = 9.9 min (major), t_2 = 10.8 min.

*(R)-11-(p-Tolylethynyl)-10,11-dihydrodibenzo[b,f][1,4]oxazepine (**3ab**).* Pale yellow oil, 51.4 mg, 83% yield, R_f = 0.43 (Petroleum ether:EtOAc = 10:1); 85% *ee*, $[\alpha]_D^{20}$ = +46.7 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.28 (td, *J* = 7.9, 1.5 Hz, 1H), 7.20−7.09 (m, 5H), 6.87 (td, *J* = 7.8, 1.4 Hz, 1H), 6.73 (td, *J* = 7.9, 1.4 Hz, 1H), 6.61 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.11 (s, 1H), 4.22 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 144.9, 138.9, 137.3, 131.8, 131.6, 129.6, 129.2, 127.0, 124.54, 124.49, 121.8, 120.8, 120.2, 119.3, 119.2, 87.0, 85.7, 48.6, 21.5; HRMS (ESI): *m*/*z* calculated for $C_{22}H_{18}NO$ $[M + H]^+$ 312.1383, found: 312.1394; HPLC (Chiralcel IC column, hexane/*i*PrOH = 95/5, 0.7 mL/min, 254 nm): t_1 = 10.0 min (major, *R*), t_2 = 10.6 min.

*(R)-11-((4-Methoxyphenyl)ethynyl)-10,11-dihydrodibenzo[b,f][1,4]oxazepine (**3ac**).* Pale yellow oil, 60.4 mg, 92% yield, R_f = 0.35 (Petroleum ether:EtOAc = 10:1); 88% *ee*, $[\alpha]_D^{20}$ = +45.7 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.45−7.39 (m, 2H), 7.28 (td, *J* = 7.9, 1.6 Hz, 1H), 7.19−7.09 (m, 3H), 6.91−6.80 (m, 3H), 6.77−6.67 (m, 1H), 6.61 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.10 (s, 1H), 4.17 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 157.2, 144.9, 137.3, 133.4, 131.7, 129.6, 127.0, 124.53, 124.47, 121.8, 120.8, 120.1, 119.2, 114.5, 114.1, 86.8, 85.0, 55.3, 48.6; HRMS (ESI): *m*/*z* calculated for $C_{22}H_{18}NO_2$ $[M + H]^+$ 328.1332, found: 328.1337; HPLC (Chiralcel IC column, hexane/*i*PrOH = 95/5, 0.7 mL/min, 254 nm): t_1 = 14.0 min (major, *R*), t_2 = 15.0 min.

*(R)-11-((4-Fluorophenyl)ethynyl)-10,11-dihydrodibenzo[b,f][1,4]-oxazepine (**3ad**).* Yellow oil, 57.2 mg, 91% yield, R_f = 0.36 (Petroleum ether:EtOAc = 10:1); 89% *ee*, $[\alpha]_D^{20}$ = +36.5 (*c* 0.52 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.50−7.41 (m, 2H), 7.30 (td, *J* = 7.8, 1.6 Hz, 1H), 7.22−7.10 (m, 3H), 7.06−6.98 (m, 2H), 6.89 (ddd, *J* = 8.9, 7.6, 1.5 Hz, 1H), 6.75 (ddd, *J* = 10.9, 6.5, 2.5 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.05 (s, 1H), 4.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, $^1J_{C-F}$ = 250.0 Hz), 157.1, 144.9, 137.1, 133.8 (d, $^3J_{C-F}$ = 8.4 Hz), 131.3, 129.7, 126.9, 124.5, 121.8, 120.9, 120.3, 119.2, 118.4 (d, $^4J_{C-F}$ = 3.5 Hz),

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115.7 (d, $^2J_{C-F}$ = 22.1 Hz), 86.2, 85.6, 48.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −110.2; HRMS (ESI): m/z calculated for $C_{21}H_{15}FNO$ $[M + H]^+$ 316.1132, found: 316.1138; HPLC (Chiralcel IC column, hexane/*i*PrOH = 95/5, 0.7 mL/min, 254 nm): t_1 = 10.0 min (major, *R*), t_2 = 11.0 min.

(R)-11-((2-Fluorophenyl)ethynyl)-10,11-dihydrodibenzo[b,f][1,4]-oxazepine (**3ae**). Yellow oil, 40.9 mg, 65% *ee*, R_f = 0.45 (Petroleum ether:EtOAc = 10:1); 93% *ee*, $[\alpha]_D^{20}$ = +53.6 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68−7.60 (m, 1H), 7.52−7.42 (m, 1H), 7.37−7.26 (m, 2H), 7.22−7.04 (m, 5H), 6.93−6.83 (m, 1H), 6.79−6.70 (m, 1H), 6.63 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.14 (s, 1H), 4.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1 (d, $^1J_{C-F}$ = 252.0 Hz), 157.2, 145.0, 137.1, 133.7, 131.2, 130.5 (d, $^3J_{C-F}$ = 8.0 Hz), 129.7, 127.0, 124.6 (d, $^5J_{C-F}$ = 0.9 Hz), 124.0 (d, $^4J_{C-F}$ = 3.7 Hz), 121.8, 120.8, 120.3, 119.3, 115.6 (d, $^2J_{C-F}$ = 20.8 Hz), 111.1, 110.9, 91.7 (d, $^4J_{C-F}$ =3.3 Hz), 80.2, 48.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −109.6; HRMS (ESI): m/z calculated for $C_{21}H_{15}FNO$ $[M + H]^+$ 316.1132, found: 316.1143; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 90/10, 0.7 mL/min, 254 nm): t_1 = 18.5 min (major, *R*), t_2 = 20.5 min.

(R)-11-(Thiophen-3-ylethynyl)-10,11-dihydrodibenzo[b,f][1,4]-oxazepine (**3af**). Pale yellow oil, 45.2 mg, 74% yield, R_f = 0.34 (Petroleum ether:EtOAc = 10:1); 90% *ee*, $[\alpha]_D^{20}$ = +45.2 (*c* 0.61 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.33−7.24 (m, 2H), 7.21−7.09 (m, 4H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.80−6.68 (m, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.07 (s, 1H), 4.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 144.9, 137.2, 131.4, 130.0, 129.7, 129.4, 127.0, 125.5, 124.6, 124.5, 121.9, 121.4, 120.9, 120.3, 119.2, 86.1, 81.9, 48.6; HRMS (ESI): m/z calculated for $C_{19}H_{14}NOS$ $[M + H]^+$ 304.0791, found: 304.0806; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 20.5 min (major, *R*), t_2 = 28.9 min.

(R)-11-(Hex-1-ynyl)-10,11-dihydrodibenzo[b,f][1,4]oxazepine (**3ag**). Pale yellow oil, 20.9 mg, 38% yield, R_f = 0.53 (Petroleum ether:EtOAc = 20:1); 78% *ee*, $[\alpha]_D^{20}$ = +41.9 (*c* 0.42 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62−7.52 (m, 1H), 7.31−7.23 (m, 1H), 7.18−7.05 (m, 3H), 6.85 (td, *J* = 7.8, 1.4 Hz, 1H), 6.70 (td, *J* = 7.9, 1.5 Hz, 1H), 6.58 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.93 (t, *J* = 1.9 Hz, 1H), 4.06 (s, 1H), 2.40−2.26 (m, 2H), 1.63−1.51 (m, 2H), 1.51−1.38 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 144.7, 137.4, 132.0, 129.4, 126.8, 124.4, 124.4, 121.7, 120.6, 119.9, 118.9, 87.7, 77.2, 47.9, 30.7, 22.0, 18.5, 13.6. HRMS (ESI): m/z calculated for $C_{19}H_{20}NO$ $[M + H]^+$ 278.1539, found: 278.1541; HPLC (Chiralcel IA column, hexane/*i*PrOH = 95/5, 0.7 mL/min, 254 nm): t_1 = 11.3 min (major, *R*), t_2 = 13.9 min.

(R)-11-(Cyclohexenylethynyl)-10,11-dihydrodibenzo[b,f][1,4]-oxazepine (**3ah**). Colorless oil, 55.5 mg, 92% yield, R_f = 0.40 (Petroleum ether:EtOAc = 10:1); 95% *ee*, $[\alpha]_D^{20}$ = +61.0 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61−7.49 (m, 1H), 7.26 (td, *J* = 7.8, 3.8 Hz, 1H), 7.20−7.04 (m, 3H), 6.91−6.79 (m, 1H), 6.76−6.66 (m, 1H), 6.57 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.24−6.16 (m, 1H), 6.03 (s, 1H), 4.10 (s, 1H), 2.23−2.01 (m, 4H), 1.77−1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 144.7, 137.4, 135.9, 131.8, 129.5, 126.9, 124.5, 124.4, 121.8, 120.7, 120.1, 120.0, 119.0, 88.7, 83.6, 48.3, 29.2, 25.7, 22.3, 21.5; HRMS (ESI): m/z calculated for $C_{21}H_{20}NO$ $[M + H]^+$ 302.1539, found: 302.1550; HPLC (Chiralcel IC column, hexane/*i*PrOH = 95/5, 0.7 mL/min, 254 nm): t_1 = 8.9 min (major, *R*), t_2 = 9.5 min.

(R)-11-(3-Methylbut-3-en-1-ynyl)-10,11-dihydrodibenzo[b,f][1,4]-oxazepine (**3ai**). Colorless oil, 38.7 mg, 74% yield, R_f = 0.62 (Petroleum ether:EtOAc = 10:1); 91% *ee*, $[\alpha]_D^{20}$ = +50.9 (*c* 0.69 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.28 (td, *J* = 7.9, 1.6 Hz, 1H), 7.21−7.05 (m, 3H), 6.86 (td, *J* = 7.8, 1.5 Hz, 1H), 6.72 (td, *J* = 7.9, 1.5 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.02 (s, 1H), 5.39 (s, 1H), 5.33−5.27 (m, 1H), 4.03 (s, 1H), 2.08−1.80 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 144.8, 137.2, 131.5, 129.6, 126.8, 126.1, 124.52, 124.46, 122.8, 121.8, 120.8, 120.2, 119.1, 88.0, 85.4, 48.3, 23.4; HRMS (ESI): m/z calculated for $C_{18}H_{16}NO$ $[M + H]^+$ 262.1226, found: 262.1244; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 97/3, 0.6 mL/min, 254 nm): t_1 = 20.2 min (major, *R*), t_2 = 22.0 min.

(R)-(E)-11-(4-Phenylbut-3-en-1-ynyl)-10,11-dihydrodibenzo[b,f]-[1,4]oxazepine (**3aj**). Yellow oil, 28.4 mg, 44% yield, R_f = 0.35 (Petroleum ether:EtOAc = 10:1); 90% *ee*, $[\alpha]_D^{20}$ = +42.5 (*c* 0.40 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.43−7.25 (m, 6H), 7.20−7.09 (m, 3H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.92−6.84 (m, 1H), 6.74 (ddd, *J* = 7.9, 7.4, 1.6 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.24 (dd, *J* = 16.3, 2.1 Hz, 1H), 6.03 (d, *J* = 1.8 Hz, 1H), 4.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 144.8, 142.3, 137.1, 136.0, 131.4, 129.6, 128.8, 128.7, 126.9, 126.3, 124.51, 124.45, 121.8, 120.8, 120.2, 119.1, 107.2, 88.5, 85.8, 48.7; HRMS (ESI): m/z calculated for $C_{23}H_{18}NO$ $[M + H]^+$ 324.1383, found: 324.1386; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 25.9 min, t_2 = 29.3 min (major, *R*).

(R)-11-(Cyclohexenylethynyl)-9-methyl-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3bh**). Pale yellow oil, 58.2 mg, 92% yield, R_f = 0.71 (Petroleum ether:EtOAc = 10:1); 99% *ee*, $[\alpha]_D^{20}$ = +37.2 (*c* 0.50 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.7 Hz, 1H), 7.31−7.24 (m, 1H), 7.20−7.10 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.3 Hz, 1H), 6.62 (t, *J* = 7.7 Hz, 1H), 6.26−6.21 (m, 1H), 6.18 (s, 1H), 3.75 (s, 1H), 2.24−2.18 (m, 2H), 2.16−2.08 (m, 5H), 1.73−1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 144.7, 136.0, 135.7, 132.3, 129.5, 126.6, 126.1, 125.9, 124.5, 120.5, 120.1, 119.7, 119.0, 88.5, 83.7, 48.0, 29.3, 25.7, 22.3, 21.5, 17.9; HRMS (ESI): m/z calculated for $C_{22}H_{22}NO$ $[M + H]^+$ 316.1696, found: 316.1697; HPLC (Chiralcel OD-H column, hexane/*i*PrOH = 99/1, 0.6 mL/min, 254 nm): t_1 = 9.1 min (major, *R*), t_2 = 12.2 min.

(R)-11-(Cyclohexenylethynyl)-8-methyl-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3ch**). Pale yellow oil, 57.9 mg, 92% yield, R_f = 0.63 (Petroleum ether:EtOAc = 10:1); 97% *ee*, $[\alpha]_D^{20}$ = +44.9 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.5 Hz, 1H), 7.29−7.21 (m, 1H), 7.15−7.08 (m, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 6.37 (s, 1H), 6.20 (s, 1H), 6.01 (s, 1H), 3.99 (s, 1H), 2.22−2.15 (m, 5H), 2.14−2.07 (m, 2H), 1.71−1.53 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 142.7, 136.9, 135.8, 134.1, 131.9, 129.5, 126.8, 124.4, 121.5, 120.6, 120.1, 119.4, 88.6, 83.7, 48.2, 29.2, 25.7, 22.3, 21.5, 20.6; HRMS (ESI): m/z calculated for $C_{22}H_{22}NO$ $[M + H]^+$ 316.1696, found: 316.1702; HPLC (Chiralcel IA column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 9.2 min (major, *R*), t_2 = 10.1 min.

(R)-8-tert-Butyl-11-(cyclohexenylethynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3dh**). Pale yellow oil, 66.2 mg, 93% yield, R_f = 0.62 (Petroleum ether:EtOAc = 10:1); 99% *ee*, $[\alpha]_D^{20}$ = +22.9 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60−7.53 (m, 1H), 7.29−7.21 (m, 1H), 7.17−7.08 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.73 (dd, *J* = 8.4 Hz, 2.3, 1H), 6.60 (d, *J* = 2.3 Hz, 1H), 6.25−6.16 (m, 1H), 6.06 (s, 1H), 4.04 (s, 1H), 2.23−2.04 (m, 4H), 1.78−1.49 (m, 4H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 147.4, 142.6, 136.3, 135.8, 131.8, 129.4, 126.8, 124.3, 121.2, 120.6, 120.0, 117.1, 116.2, 88.6, 83.6, 48.1, 34.1, 31.3, 29.2, 25.6, 22.2, 21.4; HRMS (ESI): m/z calculated for $C_{25}H_{28}NO$ $[M + H]^+$ 358.2165, found: 358.2166; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 6.7 min (major, *R*), t_2 = 10.3 min.

(R)-8-Bromo-11-(cyclohexenylethynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3eh**). White solid, 72.0 mg, 95% yield, R_f = 0.65 (Petroleum ether:EtOAc = 10:1); 99% *ee*, mp = 116−117 °C (from dichloromethane and hexane), $[\alpha]_D^{20}$ = +15.6 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.20−7.10 (m, 2H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.70 (d, *J* = 2.2 Hz, 1H), 6.25−6.15 (m, 1H), 6.02 (s, 1H), 4.02 (s, 1H), 2.25−2.05 (m, 4H), 1.75−1.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 143.6, 138.8, 136.2, 131.6, 129.7, 126.9, 124.7, 123.2, 122.3, 121.0, 120.6, 119.9, 116.8, 89.0, 83.0, 48.0, 29.2, 25.7, 22.3, 21.4; HRMS (ESI): m/z calculated for $C_{21}H_{19}BrNO$ $[M + H]^+$ 380.0645, found: 380.0645; HPLC (Chiralcel IC column, hexane/*i*PrOH = 95/5, 0.7 mL/min, 254 nm): t_1 = 7.4 min (major, *R*), t_2 = 8.5 min.

(R)-8-Chloro-11-(cyclohexenylethynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3fh**). Pale yellow oil, 63.0 mg, 94% yield, R_f = 0.65 (Petroleum ether:EtOAc = 10:1); 99% *ee*, $[\alpha]_D^{20}$ = +33.3 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.8 Hz, 1H),

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7.31−7.21 (m, 1H), 7.14 (t, J = 7.8 Hz, 2H), 6.99 (d, J = 8.5 Hz, 1H), 6.62 (dd, J = 8.5, 2.4 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 6.21 (s, 1H), 6.01 (s, 1H), 4.11 (s, 1H), 2.24−2.03 (m, 4H), 1.75−1.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 143.1, 138.4, 136.2, 131.6, 129.7, 129.3, 126.9, 124.7, 122.9, 120.6, 119.9, 119.3, 118.1, 89.0, 83.0, 48.0, 29.2, 25.7, 22.3, 21.5; HRMS (ESI): m/z calculated for $C_{21}H_{19}ClNO$ $[M + H]^+$ 336.1150, found: 336.1149; HPLC (Chiralcel OD-H column, hexane/*i*PrOH = 97/3, 0.6 mL/min, 254 nm): t_1 = 12.4 min (major, *R*), t_2 = 13.2 min.

*(R)-11-(Cyclohexenylethynyl)-8-fluoro-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3gh**).* White solid, 61.2 mg, 96% yield, mp = 76−77 °C, R_f = 0.63 (Petroleum ether:EtOAc = 10:1); 99% *ee*, $[\alpha]_D^{20}$ = +62.4 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61−7.51 (m, 1H), 7.29 (td, J = 7.7, 1.6 Hz, 1H), 7.15 (t, J = 7.9 Hz, 2H), 7.02 (dd, J = 8.8, 5.6 Hz, 1H), 6.41−6.31 (m, 1H), 6.30−6.20 (m, 2H), 6.08 (s, 1H), 4.11 (s, 1H), 2.29−2.03 (m, 4H), 1.79−1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5 (d, $^1J_{C-F}$ = 240.6 Hz), 157.3, 140.6, 138.4 (d, $^3J_{C-F}$ =10.8 Hz), 136.2, 131.7, 129.7, 126.8, 124.7, 122.7 (d, $^3J_{C-F}$ = 10.0 Hz), 120.5, 119.9, 105.7 (d, $^2J_{C-F}$ = 23.1 Hz), 105.7 (d, $^2J_{C-F}$ = 26.6 Hz), 89.0, 83.0, 47.7, 29.2, 25.7, 22.2, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −119.0; HRMS (ESI): m/z calculated for $C_{21}H_{19}FNO$ $[M + H]^+$ 320.1445, found: 320.1468; HPLC (Chiralcel AS-H column, hexane/*i*PrOH = 98/2, 0.5 mL/min, 254 nm): t_1 = 20.5 min (major, *R*), t_2 = 22.2 min.

*(R)-11-(Cyclohexenylethynyl)-7-methyl-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3hh**).* Pale yellow oil, 51.3 mg, 81% yield, R_f = 0.61 (Petroleum ether:EtOAc = 10:1); 94% *ee*, $[\alpha]_D^{20}$ = +92.6 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (dd, J = 7.5, 1.1 Hz, 1H), 7.30−7.21 (m, 1H), 7.16−7.08 (m, 2H), 6.92 (d, J = 1.0 Hz, 1H), 6.71−6.63 (m, 1H), 6.50 (d, J = 8.0 Hz, 1H), 6.22−6.15 (m, 1H), 5.96 (s, 1H), 3.95 (s, 1H), 2.21 (s, 3H), 2.20−2.06 (m, 4H), 1.70−1.55 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 144.8, 135.8, 134.6, 131.8, 130.0, 129.4, 127.0, 125.0, 124.3, 122.1, 120.7, 120.1, 119.3, 88.6, 83.8, 48.5, 29.2, 25.7, 22.3, 21.5, 20.3; HRMS (ESI): m/z calculated for $C_{22}H_{22}NO$ $[M + H]^+$ 316.1696, found: 316.1721; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 10.6 min (major, *R*), t_2 = 18.7 min.

*(R)-7-Chloro-11-(cyclohexenylethynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3ih**).* Pale yellow oil, 60.6 mg, 90% yield, R_f = 0.52 (Petroleum ether:EtOAc = 10:1); 96% *ee*, $[\alpha]_D^{20}$ = +124.5 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.4 Hz, 1H), 7.31−7.22 (m, 1H), 7.18−7.07 (m, 3H), 6.80 (dd, J = 8.5, 2.3 Hz, 1H), 6.47 (d, J = 8.5 Hz, 1H), 6.19 (s, 1H), 5.96 (s, 1H), 4.05 (s, 1H), 2.23−2.03 (m, 4H), 1.72−1.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 144.7, 136.1, 131.6, 129.7, 126.9, 124.8, 124.4, 123.8, 121.9, 120.7, 119.9, 119.7, 88.9, 83.2, 48.2, 29.2, 25.7, 22.3, 21.5; HRMS (ESI): m/z calculated for $C_{21}H_{19}ClNO$ $[M + H]^+$ 336.1150, found: 336.1170; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 10.2 min (major, *R*), t_2 = 14.8 min.

*(R)-11-(Cyclohexenylethynyl)-6-methyl-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3jh**).* Pale yellow oil, 55.1 mg, 87% yield, R_f = 0.61 (Petroleum ether:EtOAc = 10:1); 97% *ee*, $[\alpha]_D^{20}$ = +104.3 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, J = 7.6, 1.6 Hz, 1H), 7.31−7.25 (m, 1H), 7.20−7.10 (m, 2H), 6.75 (t, J = 7.7, 1H), 6.61 (dd, J = 7.4, 0.8 Hz, 1H), 6.45 (dd, J = 7.9, 1.2 Hz, 1H), 6.23−6.17 (m, 1H), 6.06 (s, 1H), 3.98 (s, 1H), 2.42 (s, 3H), 2.22−2.07 (m, 4H), 1.71−1.55 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 143.6, 137.5, 135.8, 131.9, 130.6, 129.3, 126.9, 124.3, 123.9, 121.8, 121.0, 120.0, 117.0, 88.5, 83.8, 48.3, 29.2, 25.6, 22.2, 21.4, 17.1; HRMS (ESI): m/z calculated for $C_{22}H_{22}NO$ $[M + H]^+$ 316.1696, found: 316.1725; HPLC (Chiralcel IA column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 7.4 min (major, *R*), t_2 = 8.4 min.

*(R)-11-(Cyclohexenylethynyl)-2-methyl-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3kh**).* Pale yellow oil, 58.6 mg, 93% yield, R_f = 0.62 (Petroleum ether:EtOAc = 10:1); 98% *ee*, $[\alpha]_D^{20}$ = +76.9 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1H), 7.11−6.99 (m, 3H), 6.89−6.79 (m, 1H), 6.69 (td, J = 8.0, 1.4 Hz, 1H), 6.56 (dd, J = 7.9, 1.3 Hz, 1H), 6.24−6.15 (m, 1H), 5.99 (s, 1H), 4.04 (s, 1H), 2.32 (s, 3H), 2.22−2.07 (m, 4H), 1.76−1.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 144.9, 137.3, 135.8, 134.0, 131.3, 130.0, 127.3, 124.4, 121.7, 120.4, 120.1, 119.9, 119.0, 88.6, 83.7, 48.2, 29.2, 25.7, 22.3, 21.5, 21.0; HRMS (ESI): m/z calculated for $C_{22}H_{22}NO$ $[M + H]^+$ 316.1696, found: 316.1716; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 9.0 min (major, *R*), t_2 = 10.9 min.

*(R)-11-(Cyclohexenylethynyl)-2-fluoro-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3lh**).* Pale yellow oil, 60.5 mg, 95% yield, R_f = 0.57 (Petroleum ether:EtOAc = 10:1); 86% *ee*, $[\alpha]_D^{20}$ = +61.6 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (dd, J = 8.7, 3.1 Hz, 1H), 7.09 (ddd, J = 9.4, 8.4, 3.1 Hz, 2H), 6.94 (td, J = 8.4, 3.1 Hz, 1H), 6.87 (td, J = 7.8, 1.4 Hz, 1H), 6.71 (td, J = 7.8, 1.5 Hz, 1H), 6.57 (dd, J = 7.9, 1.5 Hz, 1H), 6.27−6.20 (m, 1H), 6.07 (s, 1H), 4.02 (s, 1H), 2.28−2.04 (m, 4H), 1.77−1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1 (d, $^1J_{C-F}$ = 243.2 Hz), 153.0 (d, $^4J_{C-F}$ = 2.8 Hz), 144.5, 137.1, 136.4, 133.7 (d, $^3J_{C-F}$ =7.3 Hz), 124.7, 121.9 (d, $^3J_{C-F}$ =8.3 Hz), 121.7, 120.0, 119.8, 118.9, 115.6 (d, $^2J_{C-F}$ = 23.3 Hz), 113.6 (d, $^2J_{C-F}$ = 25.0 Hz), 89.1, 82.6, 47.7, 29.1, 25.7, 22.2, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −117.4; HRMS (ESI): m/z calculated for $C_{21}H_{19}FNO$ $[M + H]^+$ 320.1445, found: 320.1463; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 8.8 min (major, *R*), t_2 = 10.8 min.

*(R)-11-(Cyclohexenylethynyl)-4-methyl-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3mh**).* Pale yellow oil, 59.0 mg, 94% yield, R_f = 0.57 (Petroleum ether:EtOAc = 10:1); 97% *ee*, $[\alpha]_D^{20}$ = +41.9 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.4 Hz, 1H), 7.18−7.08 (m, 2H), 7.02 (t, J = 7.5 Hz, 1H), 6.84 (t, J = 7.6 Hz, 1H), 6.73−6.65 (m, 1H), 6.54 (d, J = 7.9 Hz, 1H), 6.25−6.17 (m, 1H), 6.09 (s, 1H), 4.07 (s, 1H), 2.39 (s, 3H), 2.23−2.05 (m, 4H), 1.76−1.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 144.0, 137.8, 135.9, 132.1, 131.1, 130.1, 124.5, 124.2, 122.1, 120.1, 119.5, 118.8, 88.5, 83.7, 47.8, 29.3, 25.7, 22.3, 21.5, 16.2; HRMS (ESI): m/z calculated for $C_{22}H_{22}NO$ $[M + H]^+$ 316.1696, found: 316.1704; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 8.0 min (major, *R*), t_2 = 9.9 min.

*(R)-4-Chloro-11-(cyclohexenylethynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**3nh**).* Pale yellow oil, 63.2 mg, 94% yield, R_f = 0.52 (Petroleum ether:EtOAc = 10:1); 97% *ee*, $[\alpha]_D^{20}$ = −15.8 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, J = 7.6, 0.7 Hz, 1H), 7.34 (dd, J = 8.0, 1.1 Hz, 1H), 7.29−7.22 (m, 1H), 7.06 (t, J = 7.9 Hz, 1H), 6.87 (td, J = 7.7, 1.0 Hz, 1H), 6.70 (dd, J = 11.0, 4.3 Hz, 1H), 6.55 (dd, J = 8.0, 1.2 Hz, 1H), 6.25−6.19 (m, 1H), 6.11 (s, 1H), 4.05 (s, 1H), 2.24−2.02 (m, 4H), 1.78−1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 143.5, 137.3, 136.3, 134.1, 130.1, 126.1, 125.1, 125.0, 122.6, 119.9, 119.7, 118.6, 89.0, 83.0, 47.8, 29.2, 25.7, 22.3, 21.5; HRMS (ESI): m/z calculated for $C_{21}H_{19}ClNO$ $[M + H]^+$ 336.1150, found: 336.1155; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 8.4 min (major, *R*), t_2 = 9.8 min.

*(R)-8-Chloro-11-(3-methylbut-3-en-1-ynyl)-10,11-dihydrodibenzo[b,f][1,4]oxazepine (**3fi**).* White solid, 46.0 mg, 78% yield, mp = 77−78 °C, R_f = 0.55 (Petroleum ether:EtOAc = 10:1); 97% *ee*, $[\alpha]_D^{20}$ = +26.8 (*c* 0.80 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.5 Hz, 1H), 7.37−7.25 (m, 1H), 7.15 (t, J = 7.6 Hz, 2H), 7.00 (d, J = 8.5 Hz, 1H), 6.64 (dd, J = 8.5, 2.4 Hz, 1H), 6.55 (d, J = 2.4 Hz, 1H), 5.99 (s, 1H), 5.40 (s, 1H), 5.31 (s, 1H), 4.10 (s, 1H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 143.2, 138.3, 131.3, 129.8, 129.4, 126.8, 126.0, 124.8, 123.1, 122.9, 120.7, 119.5, 118.2, 88.3, 84.8, 48.0, 23.4; HRMS (ESI): m/z calculated for $C_{18}H_{15}ClNO$ $[M + H]^+$ 296.0837, found: 296.0873; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 97/3, 0.6 mL/min, 254 nm): t_1 = 27.2 min, t_2 = 29.9 min (major, *R*).

*(R)-11-(Phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo[b,f][1,4]-oxazepine (**5a**).* Yellow solid, 53.8 mg, 84% yield, mp = 114−115 °C, R_f = 0.42 (Petroleum ether:EtOAc = 10:1); 85% *ee*, $[\alpha]_D^{20}$ = −56.4 (*c* 1.08 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52−7.44 (m, 3H), 7.40−7.26 (m, 4H), 7.21−7.09 (m, 3H), 6.89 (t, J = 7.5 Hz, 1H), 6.76 (t, J = 7.6 Hz, 1H), 6.62 (d, J = 7.9 Hz, 1H), 5.84 (s, 1H), 4.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.0, 144.9, 136.7, 132.6, 130.4, 129.9, 129.4, 128.5, 127.2, 124.6, 124.5, 121.9, 121.4, 121.1, 120.7, 119.4, 80.1, 78.8, 73.4, 70.9, 49.3; HRMS (ESI): m/z calculated

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for $C_{23}H_{16}NO$ $[M + H]^+$ 322.1226, found: 322.1219; HPLC (Chiralcel IC column, hexane/*i*PrOH = 90/10, 0.7 mL/min, 254 nm): t_1 = 8.6 min (major, *R*), t_2 = 9.4 min.

*(R)-8-Methyl-11-(phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**5c**).* Yellow oil, 57.9 mg, 86% yield, R_f = 0.34 (Petroleum ether:EtOAc = 20:1); 95% *ee*, $[\alpha]_D^{20}$ = +21.4 (*c* 1.16 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52−7.42 (m, 3H), 7.38−7.25 (m, 4H), 7.19−7.09 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 6.41 (s, 1H), 5.80 (s, 1H), 4.06 (s, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.2, 142.9, 136.1, 134.3, 132.7, 130.5, 129.9, 129.4, 128.5, 127.2, 124.5, 121.7, 121.4, 121.3, 121.0, 119.7, 80.3, 78.7, 73.5, 70.8, 49.2, 20.7; HRMS (ESI): *m*/*z* calculated for $C_{24}H_{18}NO$ $[M + H]^+$ 336.1383, found: 336.1378; HPLC (Chiralcel IA column, hexane/*i*PrOH = 80/20, 0.8 mL/min, 254 nm): t_1 = 11.0 min (major, *R*), t_2 = 12.4 min.

*(R)-8-tert-Butyl-11-(phenylbuta-1,3-diynyl)-10,11-dihydro-dibenzo[b,f][1,4]oxazepine (**5d**).* Yellow oil, 53.3 mg, 71% yield, R_f = 0.51 (Petroleum ether:EtOAc = 10:1); 84% *ee*, $[\alpha]_D^{20}$ = 3.5 (*c* 1.07 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53−7.46 (m, 3H), 7.39−7.26 (m, 4H), 7.20−7.10 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H), 5.87 (s, 1H), 4.12 (s, 1H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.2, 147.7, 142.8, 135.7, 132.6, 130.6, 129.9, 129.4, 128.5, 127.1, 124.5, 121.4, 121.0, 117.8, 116.5, 100.0, 80.2, 78.7, 73.4, 70.8, 49.2, 34.2, 31.3; HRMS (ESI): *m*/*z* calculated for $C_{27}H_{24}NO$ $[M + H]^+$ 378.1852, found: 378.1847; HPLC (Chiralcel IC column, hexane/*i*PrOH = 90/10, 0.7 mL/min, 254 nm): t_1 = 6.2 min, t_2 = 7.2 min (major, *R*).

*(R)-8-Chloro-11-(phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**5f**).* White solid, 64.1 mg, 90% yield, mp = 141−142 °C, R_f = 0.36 (Petroleum ether:EtOAc = 20:1); 96% *ee*, $[\alpha]_D^{20}$ = −6.6 (*c* 1.28 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53−7.42 (m, 3H), 7.39−7.27 (m, 4H), 7.19−7.11 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.56 (d, *J* = 2.3 Hz, 1H), 5.80 (s, 1H), 4.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.8, 143.2, 137.7, 132.7, 130.4, 130.2, 129.50, 129.45, 128.5, 127.2, 124.9, 123.1, 121.3, 121.0, 120.0, 118.4, 79.5, 79.0, 73.2, 71.2, 48.9; HRMS (ESI): *m*/*z* calculated for $C_{23}H_{15}ClNO$ $[M + H]^+$ 356.0837, found: 356.0833; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 22.4 min, t_2 = 25.3 min (major, *R*).

*(R)-7-Chloro-11-(phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**5i**).* White solid, 63.3 mg, 89% yield, mp = 152−153 °C, R_f = 0.24 (Petroleum ether:EtOAc = 20:1); 89% *ee*, $[\alpha]_D^{20}$ = +107.7 (*c* 0.91 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53−7.42 (m, 3H), 7.40−7.27 (m, 4H), 7.20−7.10 (m, 3H), 6.85 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 5.77 (s, 1H), 4.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.5, 144.9, 135.4, 132.7, 130.2, 130.1, 129.5, 128.5, 127.3, 124.9, 124.6, 122.1, 121.3, 121.1, 120.1, 79.6, 79.0, 73.2, 71.1, 49.2; HRMS (ESI): *m*/*z* calculated for $C_{23}H_{15}ClNO$ $[M + H]^+$ 356.0837, found: 356.0833; HPLC (Chiralcel IC column, hexane/*i*PrOH = 90/10, 0.7 mL/min, 254 nm): t_1 = 7.3 min (major, *R*), t_2 = 7.9 min.

*(R)-6-Methyl-11-(phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**5j**).* Yellow oil, 48.1 mg, 72% yield, R_f = 0.32 (Petroleum ether:EtOAc = 20:1); 83% *ee*, $[\alpha]_D^{20}$ = +96.7 (*c* 0.96 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52−7.44 (m, 3H), 7.39−7.25 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 5.84 (s, 1H), 4.04 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.7, 144.0, 136.8, 132.6, 130.8, 130.3, 129.7, 129.3, 128.4, 127.4, 124.3, 124.0, 122.6, 121.3, 121.3, 117.5, 80.4, 78.6, 73.4, 70.6, 49.4, 17.1; HRMS (ESI): *m*/*z* calculated for $C_{24}H_{18}NO$ $[M + H]^+$ 336.1383, found: 336.1382; HPLC (Chiralcel IC column, hexane/*i*PrOH = 90/10, 0.7 mL/min, 254 nm): t_1 = 9.2 min (major, *R*), t_2 = 11.8 min.

*(R)-2-Methyl-11-(phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**5k**).* Yellow oil, 56.5 mg, 84% yield, R_f = 0.28 (Petroleum ether:EtOAc = 20:1); 97% *ee*, $[\alpha]_D^{20}$ = +97.4 (*c* 1.21 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53−7.46 (m, 2H), 7.39−7.27 (m, 3H), 7.24 (s, 1H), 7.14−7.04 (m, 3H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.79 (s, 1H), 4.10 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.8, 145.0, 136.6, 134.2, 132.6, 130.3, 129.9, 129.4, 128.4, 127.5, 124.5, 121.8, 121.4, 120.7, 120.5, 119.3, 80.2, 78.7, 73.4, 70.7, 49.1, 20.9; HRMS (ESI): *m*/*z* calculated for $C_{24}H_{18}NO$ $[M + H]^+$ 336.1383, found: 336.1382; HPLC (Chiralcel IC column, hexane/*i*PrOH = 90/10, 0.7 mL/min, 254 nm): t_1 = 9.3 min (major, *R*), t_2 = 10.4 min.

*(R)-2-Fluoro-11-(phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**5l**).* Yellow oil, 36.2 mg, 53% yield, R_f = 0.29 (Petroleum ether:EtOAc = 20:1); 63% *ee*, $[\alpha]_D^{20}$ = +44.4 (*c* 0.72 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55−7.47 (m, 2H), 7.42−7.28 (m, 3H), 7.27−7.21 (m, 1H), 7.19−7.05 (m, 2H), 6.98 (td, *J* = 8.4, 2.8 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.90 (s, 1H), 4.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0 (d, $^1J_{C-F}$ = 243.9 Hz), 153.0 (d, $^4J_{C-F}$ = 2.9 Hz), 144.7, 136.5, 132.7, 132.2 (d, $^3J_{C-F}$ = 7.4 Hz), 129.5, 128.5, 124.9, 122.3 (d, $^3J_{C-F}$ = 8.4 Hz), 121.8, 121.2, 120.6, 119.3, 116.1 (d, $^2J_{C-F}$ = 23.1 Hz), 113.8 (d, $^2J_{C-F}$ = 24.9 Hz), 79.02, 78.98, 73.0, 71.3, 48.6; 19F NMR (376 MHz, $CDCl_3$) δ = −117.15; HRMS (ESI): *m*/*z* calculated for $C_{23}H_{15}FNO$ $[M + H]^+$ 340.1132, found: 340.1127; HPLC (Chiralcel IC column, hexane/*i*PrOH = 90/10, 0.7 mL/min, 254 nm): t_1 = 7.5 min (major, *R*), t_2 = 8.4 min.

*(R)-4-Methyl-11-(phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**5m**).* Yellow oil, 45.9 mg, 68% yield, R_f = 0.30 (Petroleum ether:EtOAc = 20:1); 74% *ee*, $[\alpha]_D^{20}$ = +38.4 (*c* 0.92 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52−7.44 (m, 2H), 7.39−7.26 (m, 4H), 7.19−7.13 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 5.86 (s, 1H), 4.12 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.3, 144.1, 137.0, 132.7, 131.5, 130.9, 130.5, 129.4, 128.5, 124.7, 124.5, 124.3, 122.2, 121.4, 120.1, 119.0, 80.3, 78.7, 73.46, 70.7, 48.8, 16.2; HRMS (ESI): *m*/*z* calculated for $C_{24}H_{18}NO$ $[M + H]^+$ 336.1383, found: 336.1377; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 13.6 min, t_2 = 14.6 min (major, *R*).

*(R)-4-Chloro-11-(phenylbuta-1,3-diynyl)-10,11-dihydrodibenzo-[b,f][1,4]oxazepine (**5n**).* Pale yellow oil, 60.8 mg, 85% yield, R_f = 0.22 (Petroleum ether:EtOAc = 20:1); 81% *ee*, $[\alpha]_D^{20}$ = +2.1 (*c* 1.09 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54−7.47 (m, 2H), 7.44−7.27 (m, 6H), 7.07 (t, *J* = 7.9 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 5.93 (s, 1H), 4.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 143.6, 136.6, 132.8, 132.7, 130.5, 129.5, 128.5, 126.5, 125.3, 125.2, 125.2, 122.7, 121.2, 120.3, 118.9, 79.3, 79.0, 73.2, 71.3, 48.7; HRMS (ESI): *m*/*z* calculated for $C_{23}H_{15}ClNO$ $[M + H]^+$ 356.0837, found: 356.0838; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 85/15, 0.7 mL/min, 254 nm): t_1 = 15.4 min, t_2 = 17.6 min (major, *R*).

Transformation of Product 3. *(R)-11-Phenethyl-10,11-dihydro-dibenzo[b,f][1,4]oxazepine (**6**).* To a solution of **3aa** (35.0 mg, 0.12 mmol) in methanol (2.0 mL) was added 5% palladium on charcoal (7.0 mg). The reaction was carried out with hydrogen gas at an initial pressure of 200 psi at 25 °C for 24 h. The catalyst was filtered off, and the filtrate was concentrated by rotary evaporation. The crude product was purified by flash chromatography to afford **6** as a pale yellow oil (28.0 mg, 77%). R_f = 0.30 (Petroleum ether:EtOAc = 20:1); 87% *ee*, $[\alpha]_D^{20}$ = +36.5 (*c* 0.52 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31−7.13 (m, 7H), 7.12−7.02 (m, 3H), 6.84 (ddd, *J* = 7.9, 7.4, 1.5, 1H), 6.66 (ddd, *J* = 7.9, 7.4, 1.6, 1H), 6.52 (dd, *J* = 7.9, 1.5, 1H), 4.38−4.31 (m, 1H), 3.58 (s, 1H), 2.85−2.58 (m, 2H), 2.53−2.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.2, 143.9, 141.4, 137.4, 133.9, 128.9, 128.5, 128.4, 127.3, 126.0, 124.4, 124.2, 121.7, 121.1, 118.9, 118.6, 56.7, 36.4, 33.0; HRMS (ESI): *m*/*z* calculated for $C_{21}H_{20}NO$ $[M + H]^+$ 302.1539, found: 302.1552; HPLC (Chiralcel IA column, hexane/*i*PrOH = 95/5, 0.6 mL/min, 254 nm): t_1 = 18.8 min, t_2 = 19.9 min (major, *R*).

*(R,Z)-11-Styryl-10,11-dihydrodibenzo[b,f][1,4]oxazepine (**7**).*[26] To a solution of **3aa** (45.7 mg, 0.15 mmol) in DMF (1.0 mL) was added ethylenediamine (10.8 mg, 0.18 mmol) and 5% palladium on calcium carbonate (4.6 mg). The reaction flask was evacuated, purged with hydrogen five times, and then stirred under a hydrogen atmosphere for 1 h. The catalyst was filtered off, and the filtrate was

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diluted with ethyl acetate. The resulting solution was washed with 2 wt % NH_4Cl and brine and dried over anhydrous Na_2SO_4. The organic solution was concentrated to afford **7** as a pale yellow oil (38.2 mg, 85%). R_f = 0.21 (Petroleum ether:EtOAc = 20:1); 87% *ee*, $[\alpha]_D^{20}$ = −53.9 (*c* 0.66 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.36−7.16 (m, 8H), 7.13−7.05 (m, 2H), 6.86−6.75 (m, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 6.27−6.15 (m, 1H), 5.82 (d, *J* = 9.5 Hz, 1H), 3.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.5, 144.4, 137.8, 136.3, 133.6, 132.1, 130.4, 129.2, 128.7, 128.5, 127.6, 126.9, 124.5, 121.7, 121.2, 119.4, 118.8, 53.5; HRMS (ESI): *m*/*z* calculated for $C_{21}H_{18}NO$ $[M + H]^+$ 300.1383, found: 300.1394; HPLC (Chiralcel AD-H column, hexane/*i*PrOH = 80/20, 0.7 mL/min, 254 nm): t_1 = 11.3 min, t_2 = 17.6 min (major, *R*).

*(R,E)-11-(4-Methyl)-10,11-dihydrodibenzo[b,f][1,4]oxazepine (**8**).* To a solution of **3aa** (41.6 mg, 0.14 mmol) in THF (2.0 mL) was added $LiAlH_4$ (26.6 mg, 0.70 mmol) at room temperature. The reaction mixture was stirred for additional 1 h, and then quenched by the addition of water, and extracted with with CH_2Cl_2. The combined organic extracts were washed with brine and concentrated under reduced pressure to afford **8** as a yellow oil (38.2 mg, 91%). R_f = 0.23 (Petroleum ether:EtOAc = 20:1); 86% *ee*, $[\alpha]_D^{20}$ = +59.8 (*c* 0.82 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.42−7.36 (m, 2H), 7.34−7.26 (m, 2H), 7.26−7.16 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.75−6.66 (m, 3H), 6.65−6.59 (m, 1H), 5.25 (d, *J* = 6.0 Hz, 1H), 4.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 144.8, 137.7, 136.5, 133.0, 131.9, 129.5, 129.1, 128.6, 127.8, 127.6, 126.6, 124.6, 124.3, 121.8, 121.1, 119.6, 119.0, 59.5; HRMS (ESI): *m*/*z* calculated for $C_{21}H_{18}NO$ $[M + H]^+$ 300.1383, found: 300.1390; HPLC (Chiralcel IA column, hexane/*i*PrOH = 90/10, 0.7 mL/min, 254 nm): t_1 = 17.4 min, t_2 = 18.4 min (major, *R*).

*(R,E)-11-(2-Cyclohexenylvinyl)-10,11-dihydrodibenzo[b,f][1,4]-oxazepine (**9**).* To a solution of **3ah** (38.0 mg, 0.13 mmol) in THF (2.0 mL) was added $LiAlH_4$ (24.7 mg, 0.65 mmol) at room temperature. The reaction mixture was stirred for additional 5 h, and then quenched by the addition of water, and extracted with with CH_2Cl_2. The combined organic extracts were washed with brine and concentrated under reduced pressure. Purification by column chromatography on silica gel afforded **9** as a pale yellow oil (26.1 mg, 66%). R_f = 0.27 (Petroleum ether:EtOAc = 20:1); 92% *ee*, $[\alpha]_D^{20}$ = +54.3 (*c* 0.30 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.30−7.00 (m, 5H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.73−6.66 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.32 (d, *J* = 15.7 Hz, 1H), 6.02 (dd, *J* = 15.6, 7.9 Hz, 1H), 5.78 (s, 1H), 5.21 (d, *J* = 7.9 Hz, 1H), 3.92 (s, 1H), 2.25−2.00 (m, 4H), 1.72−1.51 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 144.8, 138.0, 135.9, 135.1, 133.5, 130.6, 128.9, 127.5, 125.1, 124.5, 124.2, 121.8, 121.0, 119.4, 118.9, 59.33, 25.91, 24.7, 22.5, 22.4. HRMS (ESI): *m*/*z* calculated for $C_{21}H_{22}NO$ $[M + H]^+$ 304.1696, found: 304.1705; HPLC (Chiralcel IC column, hexane/*i*PrOH = 95/5, 0.7 mL/min, 254 nm): t_1 = 10.5 min (major, *R*), t_2 = 12.9 min.

■ ASSOCIATED CONTENT

Supporting Information

^1H, ^{13}C, and ^{19}F NMR spectra, HPLC copy, and the single crystal X-ray diffraction structure data of **3eh** (CIF) are available. 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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