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Enantioselective Synthesis of 4-Substituted 4,5-Dihydro-1*H*-[1,5]benzodiazepin-2(3*H*)-ones by the Lewis Base-Catalyzed Hydrosilylation

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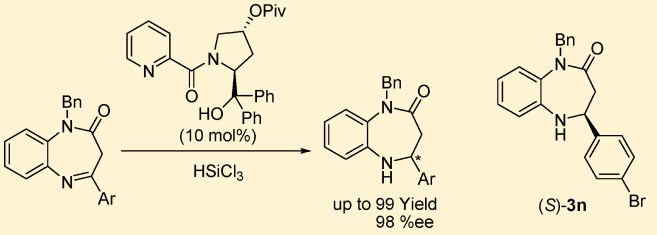
Supporting Information

ABSTRACT: Enantioselective synthesis of 4-substituted 4,5-dihydro-1*H*-[1,5]benzodiazepin-2(3*H*)-ones has been accomplished through chiral Lewis base-catalyzed hydrosilylation. The corresponding products were obtained in excellent yields (up to 99%) and enantioselectivities (up to 98%). The absolute configuration of product **3n** has been determined as *S* by X-ray crystallographic analysis.



A large number of pharmaceutical and biologically active agents incorporate heterocycles as substructural units. 1,5-Benzodiazepines belong to this family, and their derivatives are important compounds with various biological properties.[1] In this class of compounds, the 1,5-benzodiazepin-2-ones have been clinically used as antisecretory agents and anxiolytic agents, such as telenzepine,[2] arfendazam,[3] lofendazam,[4] triflubazam,[5] and clobazam.[6] In addition, some compounds of this kind have exhibited a wide range of biological activities, including interleukin-1β-converting enzyme inhibition, antiarrhythmic properties,[7] and delayed rectifier potassium current blocking.[8] Because of the aforementioned biological activities, 1,5-benzodiazepin-2-ones are considered as "privileged" scaffolds in drug development.[9]

The important biological properties of these compounds have led to considerable interest in their synthesis and biological study. Solid-phase synthetic strategies have been applied to prepare 4,5-dihydro-1*H*-[1,5]benzodiazepin-2-one derivatives.[8,10] Xiaoxia Wang and co-workers have demonstrated that *o*-phenylenediamine reacted with *N*-cinnamoylbenzotriazoles via 1,4-addition to afford 1,3,4,5-tetrahydro-1,5-benzodiazepin-2-ones.[11] In addition, several other groups also reported their studies on this subject.[12] However, to the best of our knowledge, only one example of enantioselective synthesis of these compounds has been described. Rueping and co-workers employed chiral phosphoric acids in promoting enantioselective transfer hydrogenation of 4-substituted 1,5-benzodiazepin-2-ones to afford the chiral 4-substituted 4,5-dihydro-1*H*-[1,5]benzodiazepin-2(3*H*)-ones in good yields and excellent enantioselectivities.[13] The reactions must be conducted under microwave irradiation at high temperature to achieve satisfactory yields.

Recently, asymmetric reaction involving the strategy of Lewis base activation of Lewis acids has attracted much attention.[14] Among these reactions, Lewis base-catalyzed enantioselective hydrosilylation of ketimines has become an important approach to obtaining chiral amines.[15,16] This organocatalytic methodology has many properties, including mild reaction conditions, atom economy, and operational simplicity. During our continuing research on the enantioselective Lewis base-catalyzed hydrosilylation of C=N bond compounds,[16m−o] we have developed several chiral picolinoylamide Lewis base catalysts that were appropriate for different types of substrates. Ephedrine-derived catalyst **1a** was found to succeed in promoting the enantioselective hydrosilylation of ketimines,[16p] benzoxazinones, and quinoxalinones.[16n] Proline-derived catalysts **1b** and **1c** accelerated the hydrosilylation of *N*-aryl β-enamino esters with good yields and enantioselectivities.[16m] Meanwhile, *trans*-4-hydroxy-L-proline-derived catalysts **1d** and **1e** delivered good yields and enantioselectivities in the hydrosilylation of α-ketimino esters.[16o] With these catalysts in hand, we extended their application in the hydrosilylation of 4-substituted 1,5-benzodiazepin-2-ones to prepare chiral 4,5-dihydro-1*H*-[1,5]benzodiazepin-2-ones. Herein, we describe the general, enantioselective hydrosilylation of 4-substituted 1,5-benzodiazepin-2-ones promoted by these catalysts.

First, catalysts **1a−e** (Figure 1) were evaluated in the hydrosilylation of 4-phenyl-1*H*-benzo[*b*][1,4]diazepin-2(3*H*)-

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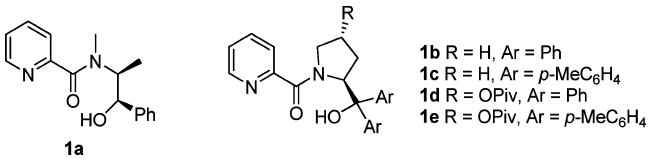
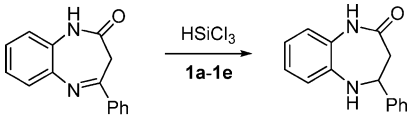


Figure 1. Chiral Lewis base organocatalysts evaluated in this study.

one (**2a**) in methylene dichloride at −10 °C. The results are summarized in Table 1. In our initial investigations, we

Table 1. Influence of Different Chiral Lewis Base Organocatalysts, Solvents, and Temperatures on the Enantioselective Hydrosilylation of 4-Phenyl-1*H*-benzo[*b*][1,4]diazepin-2(3*H*)-one 2a[a]



entry	1	solvent	*T* (°C)	*t* (h)	yield (%)[b]	ee (%)[c]
1	**1a**	DCM	−10	4	99	82
2	**1b**	DCM	−10	2	98	84
3	**1c**	DCM	−10	1	97	82
4	**1d**	DCM	−10	4	98	88
5	**1e**	DCM	−10	2.5	98	87
6	**1d**	$CHCl_3$	−10	–	NR[d]	–
7	**1d**	CH_3CCl_3	−10	–	NR[d]	–
8	**1d**	$(CH_2Cl)_2$	−10	2	98	90
9	**1d**	$(CHCl_2)_2$	−10	2	97	88
10	**1d**	THF	−10	2	97	87
11	**1d**	$(CH_2Cl)_2$	0	1.5	95	88
12	**1d**	$(CH_2Cl)_2$	−20	4	97	85

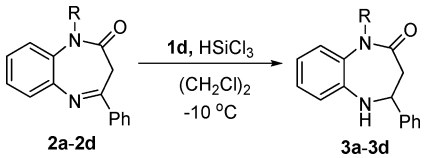
[a]Unless specified otherwise, the reaction was conducted with **2a** (0.3 mmol), trichlorosilane (0.6 mmol), and catalyst (0.03 mmol) in 3 mL of solvent. [b]Yield based on **2a**. [c]The ee value was determined by chiral-phase HPLC analysis. [d]No reaction.

observed that **2a** was rather active in this reaction system. Catalyst **1a** promoted the reaction efficiently to generate the product in excellent yield with considerably good enantioselectivity within only 4 h (Table 1, entry 1). Proline-derived catalysts **1b** and **1c** were found to result in almost the same yields and ee values (Table 1, entries 2 and 3, respectively). In addition, *trans*-4-hydroxy-L-proline-derived catalyst **1d** displayed a slightly higher enantioselectivity (Table 1, entry 4). Introduction of methyl groups at the para position of the two phenyl groups did not improve the enantioselectivity (Table 1, entry 5). Therefore, **1d** was determined to be the optimal catalyst and employed in further investigations.

Subsequently, several solvents were evaluated. Among the chlorinated solvents, 1,2-dichloroethane gave an ee value of up to 90% (Table 1, entry 8). Surprisingly, the reactions in chloroform and 1,1,1-trichloroethane failed to give any product (Table 1, entries 6 and 7, respectively). Meanwhile, THF gave the product with good yield and enantioselection (Table 1, entry 10). Then the temperature of the reaction was also investigated. When the reaction was conducted at 0 °C, the ee value dropped slightly (Table 1, entry 11). When the temperature was lowered to −20 °C, the ee value dropped even more (Table 1, entry 12).

Because of the poor solubility of substrate **2a**, sometimes the reaction suffered from poor reproducibility. To improve the solubility, several substituents were introduced at N1 of **2a** to generate substrates **2b**−**d**. Interestingly, the substituents affected the enantioselection remarkably. Both *N*-methyl substrate **2b** and *N*-allyl substrate **2c** gave very poor ee values (Table 2, entries 2 and 3, respectively). On the other hand, *N*-

Table 2. Influence of the N1 Substituents of 4-Phenyl-1*H*-benzo[*b*][1,4]diazepin-2(3*H*)-one[a]



entry	2	R	*T* (h)	yield (%)[b]	ee (%)[c]
1	**2a**	H	2	98	90
2	**2b**	Me	1	95	42
3	**2c**	allyl	1	96	55
4	**2d**	Bn	2	97	90
5[d]	**2d**	Bn	2	98	96
6[d,e]	**2d**	Bn	2	98	83
7[f]	**2d**	Bn	24	50	–

[a]Unless specified otherwise, the reaction was conducted with **2** (0.25 mmol), trichlorosilane (0.5 mmol), and **1d** (0.025 mmol) in 3 mL of $(CH_2Cl)_2$. [b]Yield based on **2**. [c]The ee value was determined by chiral-phase HPLC analysis. [d]The reaction was conducted under an inert atmosphere. [e]The catalyst loading was 5 mol %. [f]The reaction was conducted in the absence of catalyst.

benzyl substrate **2d** afforded a high enantioselectivity of 90% (Table 2, entry 4). Furthermore, we found that the ee value rose to 96% when the reaction was conducted under an inert atmosphere (Table 2, entry 5). It was suggested that the presence of water affected the enantioselectivity. Finally, we tried to lower the catalyst loading. Unfortunately, the ee value decreased (Table 2, entry 6), perhaps because of the background reaction. When the reaction was conducted in the absence of the catalyst, 50% of the product was obtained after 24 h (Table 2, entry 7).

With the optimized conditions in hand, we explored the scope of the Lewis base-catalyzed hydrosilylation of 4-substituted 1-benzyl-1*H*-benzo[b][1,4]diazepin-2(3*H*)-ones (Figure 2 and Table 3).

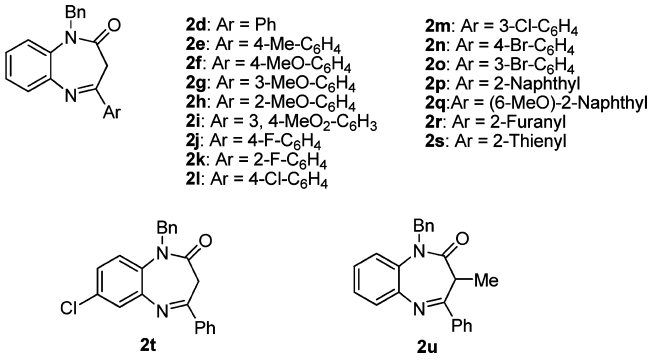


Figure 2. Various 4-substituted 1-benzyl-1*H*-benzo[b][1,4]diazepin-2(3*H*)-ones hydrosilylated in this study.

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Table 3. Enantioselective Hydrosilylation of 4-Substituted 1-Benzyl-1*H*-benzo[*b*][1,4]diazepin-2(3*H*)-ones 2d−u Catalyzed by 1d[a]

entry	2	3/yield (%)[b]	ee (%)[c]
1	**2d**	**3d**/96	96
2	**2e**	**3e**/98	96
3	**2f**	**3f**/97	94
4	**2g**	**3g**/97	94
5	**2h**	**3h**/99	5
6	**2i**	**3i**/98	98
7	**2j**	**3j**/97	91
8	**2k**	**3k**/97	54
9	**2l**	**3l**/96	92
10	**2m**	**3m**/98	93
11	**2n**	**3n**/97	94 (*S*)[d]
12	**2o**	**3o**/98	92
13	**2p**	**3p**/97	97
14	**2q**	**3q**/98	95
15	**2r**	**3r**/97	74
16	**2s**	**3s**/99	89
17	**2t**	**3t**/98	72
18	**2u**	**3u**/97 (93:7 dr)	36[e]

[a]Unless specified otherwise, the reaction was conducted with **2** (0.25 mmol), trichlorosilane (0.5 mmol), and **1d** (0.025 mmol) in 3 mL of $(CH_2Cl)_2$ at −10 °C for 2−3 h. [b]Yield based on **2**. [c]The ee value was determined by chiral-phase HPLC analysis. [d]The absolute configuration was determined by X-ray crystallographic analysis. [e]The ee value of the major diastereomer.

Generally, 4-para- or meta-substituted phenyl substrates afforded the products in excellent yields (>96%) with good enantioselectivities (91−98%), no matter whether the substituents were electron-donating or electron-withdrawing (Table 3, entries 1−4, 6, 7, 9−12). However, ortho substitution of the phenyl group decreased the degree of enantioselection dramatically. The *o*-methoxy substrate **2h** generated almost racemic product (Table 3, entry 5). Meanwhile, *o*-fluoro substrate **2k** afforded the product with a 54% ee value perhaps because of less steric hindrance of fluoride compared with the methoxy group (Table 3, entry 8). In addition, 1-benzyl-4-(naphthalen-2-yl)-1*H*-benzo[*b*][1,4]diazepin-2(3*H*)-one **2p** and 1-benzyl-4-(6-methoxynaphthalen-2-yl)-1*H*-benzo[*b*][1,4]-diazepin-2(3*H*)-one **2q** underwent the reaction smoothly to afford the corresponding product with excellent yields and ee values (Table 3, entries 13 and 14, respectively). 4-Heteroaryl substrates were also employed in this transformation to afford high yields of corresponding products with moderate to good ee values (Table 3, entries 15 and 16). With regard to the substitution of the benzene ring, the 7-chloro substrate gave the corresponding product in excellent yields, but moderate ee value (Table 3, entry 17). Finally, 3,4-disubstituted substrate **2u** was also subjected to the enantioselective hydrosilylation to provide the desired product with excellent yields and good diastereoselectivity (93:7 dr), but very poor enantioselectivity (Table 3, entry 18). Furthermore, the absolute configuration of product **3n** was determined to be *S* by X-ray crystallographic analysis (see the Supporting Information for details).

In summary, we have developed a general, enantioselective hydrosilylation of 4-substituted 1-benzyl-1*H*-benzo[b][1,4]-diazepin-2(3*H*)-ones catalyzed by chiral Lewis base organocatalysts that are derived from *trans*-4-hydroxy-L-proline. This transformation allows a mild and efficient synthesis of various chiral tetrahydro-1,5-benzodiazepines in excellent yields (up to 99%) and enantioselectivities (up to 98%). The absolute configuration of one of the products has been determined to be *S* by X-ray crystallographic analysis.

EXPERIMENTAL SECTION

All the chlorinated solvents were distilled from CaH_2. All ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ using TMS as an internal standard. Catalysts **1a−e** were prepared according to the literature procedure.[16i,m,o,p] Compounds **2a**[17a] and **2b−t**[17b,c] were prepared according to the literature procedure.

General Procedure for the Preparation of Compounds 2b−s. A mixture of *o*-phenylenediamine (10 mmol) and *β*-keto ester (15 mmol) in toluene (70 mL) was heated to reflux for 4−8 h, while water was removed with a Dean-stark trap. Once the sample had cooled to ambient temperature, the product crystallized and was collected by filtration, washed with toluene (100 mL), dried, and used in the next step without further purification.

To a solution of the product mentioned above (2 mmol) in DMF (20 mL) were added cesium carbonate (0.78 g, 2.4 mmol) and methyl iodide, allyl bromide, or benzyl bromide (2.4 mmol). The mixture was stirred at ambient temperature for 2 h, then diluted with EtOAc (100 mL) and washed with water (100 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (10:1 petroleum ether:ethyl acetate) to give pure compounds **2b−s**.

1-Allyl-4-phenyl-1H-benzo[b][1,4]diazepin-2(3H)-one[17d] ***(2c):*** white solid; 68% yield; ^1H NMR δ 3.04 (d, J = 11.9 Hz, 1H), 4.16 (d, J = 11.8 Hz, 1H), 4.41−4.55 (m, 2H), 5.10−5.17 (m, 2H), 5.80−5.93 (m, 1H), 7.23−7.27 (m, 2H), 7.42−7.50 (m, 5H), 8.13−8.16 (m, 2H); ^{13}C NMR δ 39.7, 50.5, 116.6, 121.9, 125.3, 125.9, 127.2, 127.6, 128.6, 130.9, 133.1, 134.2, 137.3, 141.8, 160.8, 165.2; HRMS (ESI) calcd for $C_{18}H_{16}N_2OH$ 277.1335, found 277.1333.

1-Benzyl-4-p-tolyl-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2e):*** white solid; 75% yield; ^1H NMR δ 2.45 (s, 3H), 3.16 (d, J = 11.9 Hz, 1H), 4.24 (d, J = 11.8 Hz, 1H), 5.08−5.20 (m, 2H), 7.09−7.34 (m, 10H), 7.44 (dd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, 1H), 8.7(d, J = 8.1 Hz, 2H); ^{13}C NMR δ 21.3, 39.6, 51.0, 122.0, 125.3, 125.7, 126.5, 126.9, 127.1, 127.7, 128.4, 129.3, 133.9, 134.5, 137.1, 141.4, 142.1, 160.8, 165.7; HRMS (ESI) calcd for $C_{23}H_{20}N_2ONa$ 363.1468, found 363.1471.

1-Benzyl-4-(4-methoxyphenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2f):*** white solid; 68% yield; ^1H NMR δ 3.15 (d, J = 11.8 Hz, 1H), 3.90 (s, 3H), 4.22 (d, J = 11.8 Hz, 1H), 5.14 (s, 2H), 7.02 (dd, J_1 = 1.9 Hz, J_2 = 7.0 Hz, 2H), 7.09−7.33 (m, 8H), 7.43 (dd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, 1H), 8.13−8.17 (m, 2H); ^{13}C NMR δ 39.4, 51.0, 55.3, 113.9, 121.9, 125.3, 125.5, 126.5, 126.9, 127.1, 128.4, 129.5, 129.8, 133.9, 137.1, 142.2, 160.2, 162.0, 165.7; HRMS (ESI) calcd for $C_{23}H_{21}N_2O_2$ 357.1598, found 357.1586.

1-Benzyl-4-(3-methoxyphenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2g):*** white solid; 69% yield; ^1H NMR δ 3.15 (d, J = 11.9 Hz, 1H), 4.21 (d, J = 11.7 Hz, 1H), 5.12 (s, 2H), 7.04−7.10 (m, 3H), 7.12−7.27 (m, 5H), 7.31 (dd, J_1 = 1.3 Hz, J_2 = 7.9 Hz, 1H), 7.38−7.45 (m, 2H), 7.69−7.72 (m, 2H); ^{13}C NMR δ 39.9, 51.1, 55.3, 112.1, 117.6, 120.3, 122.0, 125.4, 126.0, 126.5, 127.0, 127.2, 128.5, 129.6, 134.0, 137.1, 138.7, 142.0, 159.8, 160.7, 165.6; HRMS (ESI) calcd for $C_{23}H_{20}N_2O_2Na$ 379.1417, found 379.1405.

1-Benzyl-4-(2-methoxyphenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2h):*** white solid; 59% yield; ^1H NMR δ 3.23 (d, J = 11.8 Hz, 1H), 3.88 (s, 3H), 4.22 (d, J = 11.9 Hz, 1H), 5.02 (d, J = 15.6 Hz, 1H), 5.31 (d, J = 15.6 Hz, 1H), 6.95−6.98 (m, 1H), 7.02 (dd, J_1 = 0.8 Hz, J_2 = 7.5 Hz, 1H), 7.09−7.34 (m, 8H), 7.39−7.45 (m, 2H), 7.47 (dd, J_1 = 1.6 Hz, J_2 = 7.5 Hz, 1H); ^{13}C NMR δ 42.8, 50.9, 55.2, 111.1, 120.7, 122.1, 125.2, 126.0, 126.7, 127.0, 127.4, 128.4, 130.3, 131.7, 133.5, 137.2, 141.9, 158.0, 163.9, 166.6; HRMS (ESI) calcd for $C_{23}H_{20}N_2O_2Na$ 379.1417, found 379.1407.

1-Benzyl-4-(3,4-dimethoxyphenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2i):*** white solid; 78% yield; ^1H NMR δ 3.12 (d, J = 11.8 Hz, 1H), 4.20 (d, J = 11.7 Hz, 1H), 5.11 (s, 2H), 6.95 (d, J = 8.4 Hz, 1H), 7.08−7.27 (m, 7H), 7.30 (dd, J_1 = 1.3 Hz, J_2 = 8.0 Hz, 1H), 7.42

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(dd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, 1H), 7.70 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 7.79 (d, J = 2.0 Hz, 1H); ^{13}C NMR δ 39.3, 51.1, 55.9, 109.9, 110.4, 121.7, 121.9, 125.3, 125.6, 126.5, 126.9, 127.1, 128.4, 129.9, 134.0, 137.1, 142.1, 149.0, 151.8, 160.0, 165.6; HRMS (ESI) calcd for $C_{24}H_{23}N_2O_3$ 387.1703, found 387.1693.

1-Benzyl-4-(4-fluorophenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2j):*** white solid; 73% yield; ^{1}H NMR δ 3.15 (d, J = 11.8 Hz, 1H), 4.18 (d, J = 11.8 Hz, 1H), 5.12 (s, 2H), 7.08 (d, J = 6.9 Hz, 2H), 7.14–7.26 (m, 7H), 7.32 (d, J = 8.0 Hz, 1H), 7.4 (dd, J_1 = 1.3 Hz, J_2 = 8.0 Hz, 1H), 8.14–8.18 (m, 2H); ^{13}C NMR δ 39.8, 51.1, 115.5, 115.8, 122.1, 125.5, 126.1, 126.5, 127.1, 127.2, 128.5, 129.9, 130.0, 133.5, 133.5, 134.0, 137.0, 141.9, 159.7, 163.0, 165.5, 166.3; HRMS (ESI) calcd for $C_{22}H_{18}FN_2O$ 345.1398, found 345.1394.

1-Benzyl-4-(2-fluorophenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2k):*** yellowish solid; 45% yield; ^{1}H NMR δ 3.30 (d, J = 11.9 Hz, 1H), 4.20 (d, J = 11.9 Hz, 1H), 5.04 (d, J = 15.3 Hz, 1H), 5.28 (d, J = 15.6 Hz, 1H), 7.08–7.10 (m, 2H), 7.13–7.28 (m, 7H), 7.32–7.35 (m, 1H), 7.40–7.49 (m, 2H), 7.69–7.74 (m, 1H); ^{13}C NMR δ 42.4, 42.5, 51.0, 116.3, 116.6, 122.2, 124.4, 124.4, 125.5, 126.5, 126.7, 127.1, 127.4, 128.5, 130.6, 130.7, 132.3, 132.4, 133.4, 137.0, 141.7, 159.5, 159.7, 162.9, 165.7; HRMS (ESI) calcd for $C_{22}H_{18}FN_2O$ 345.1398, found 345.1397.

1-Benzyl-4-(4-chlorophenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2l):*** white solid; 71% yield; ^{1}H NMR δ 3.14 (d, J = 11.9 Hz, 1H), 4.17 (d, J = 11.9 Hz, 1H), 5.07–5.18 (m, 2H), 7.07–7.09 (m, 2H), 7.13–7.26 (m, 5H), 7.32 (dd, J_1 = 1.3 Hz, J_2 = 7.9 Hz, 1H), 7.40–7.47 (m, 3H), 8.07–8.11 (m, 2H); ^{13}C NMR δ 39.7, 51.1, 122.1, 125.5, 126.2, 126.5, 127.1, 127.2, 128.5, 128.8, 129.0, 134.0, 135.7, 137.0, 137.3, 141.8, 159.6, 165.4; HRMS (ESI) calcd for $C_{22}H_{18}ClN_2O$ 361.1102, found 361.1098.

1-Benzyl-4-(3-chlorophenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2m):*** white solid; 68% yield; ^{1}H NMR δ 3.15 (d, J = 11.9 Hz, 1H), 4.17 (d, J = 11.9 Hz, 1H), 5.06–5.18 (m, 2H), 7.06–7.09 (m, 2H), 7.15–7.25 (m, 5H), 7.32 (dd, J_1 = 1.5 Hz, J_2 = 7.9 Hz, 1H), 7.40–7.50 (m, 3H), 9.97–8.01 (m, 1H), 8.15–8.17 (m, 1H); ^{13}C NMR δ 39.7, 51.1, 122.1, 125.5, 125.8, 126.4, 126.6, 127.1, 127.2, 127.7, 128.5, 129.9, 131.0, 134.0, 134.9, 136.9, 139.0, 141.7, 159.4, 165.4; HRMS (ESI) calcd for $C_{22}H_{18}ClN_2O$ 361.1102, found 361.1095.

1-Benzyl-4-(4-bromophenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2n):*** white solid; 65% yield; ^{1}H NMR δ 3.14 (d, J = 11.9 Hz, 1H), 4.16 (d, J = 11.8 Hz, 1H), 5.06–5.18 (m, 2H), 7.06 (d, J = 6.7 Hz, 2H), 7.17–7.26 (m, 5H), 7.30 (d, J = 1.5 Hz, 1H), 7.39 (d, J = 1.6 Hz, 1H), 7.62 (d, J = 8.6 Hz, 2H), 8.00–8.03 (m, 2H); ^{13}C NMR δ 39.6, 51.1, 122.1, 125.5, 125.9, 126.2, 126.5, 127.1, 127.2, 128.5, 129.2, 131.8, 134.0, 136.2, 137.0, 141.9, 159.7, 165.4; HRMS (ESI) calcd for $C_{22}H_{18}BrN_2O$ 405.0597, found 405.0591.

1-Benzyl-4-(3-bromophenyl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2o):*** white solid; 67% yield; ^{1}H NMR δ 3.15 (d, J = 11.9 Hz, 1H), 4.17 (d, J = 11.9 Hz, 1H), 5.07–5.18 (m, 2H), 7.07–7.09 (m, 2H), 7.17–7.27 (m, 5H), 7.31–7.43 (m, 3H), 7.62–7.65 (m, 1H), 8.02–8.05 (m, 1H), 8.33 (t, J = 1.7 Hz, 1H); ^{13}C NMR δ 39.7, 51.1, 122.1, 123.0, 125.5, 126.3, 126.4, 126.6, 127.1, 127.2, 128.5, 130.1, 130.6, 133.9, 133.9, 136.9, 139.2, 141.7, 159.3, 165.3; HRMS (ESI) calcd for $C_{22}H_{18}BrN_2O$ 405.0597, found 405.0584.

1-Benzyl-4-(naphthalen-2-yl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2p):*** white solid; 71% yield; ^{1}H NMR δ 3.24 (d, J = 11.9 Hz, 1H), 4.41 (d, J = 11.9 Hz, 1H), 5.09–5.20 (m, 2H), 7.09–7.28 (m, 7H), 7.35 (dd, J_1 = 1.3 Hz, J_2 = 8.0 Hz, 1H), 7.50 (dd, J_1 = 1.5 Hz, J_2 = 7.9 Hz, 1H), 7.54–7.59 (m, 2H), 7.87–8.03 (m, 3H), 8.36 (dd, J_1 = 1.5 Hz, J_2 = 8.6 Hz, 1H), 8.58 (s, 1H); ^{13}C NMR δ 39.7, 51.1, 122.1, 124.2, 125.5, 126.0, 126.5, 126.6, 127.0, 127.3, 127.6, 127.6, 128.4, 128.5, 128.6, 129.2, 132.9, 134.5, 134.6, 137.1, 142.2, 160.7, 165.8; HRMS (ESI) calcd for $C_{26}H_{21}N_2O$ 377.1648, found 377.1645.

1-Benzyl-4-(6-methoxynaphthalen-2-yl)-1H-benzo[b][1,4]-diazepin-2(3H)-one ***(2q):*** white solid; 67% yield; ^{1}H NMR δ 3.20 (d, J = 11.6 Hz, 1H), 3.94 (s, 3H), 4.38 (d, J = 11.8 Hz, 1H), 5.13–5.15 (m, 2H), 7.09–7.26 (m, 9H), 7.33 (d, J = 8.0 Hz, 1H), 7.47 (dd, J_1 = 1.3 Hz, J_2 = 7.9 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 8.32 (dd, J_1 = 1.6 Hz, J_2 = 8.7 Hz, 1H), 8.51 (s, 1H); ^{13}C NMR δ 39.5, 51.1, 55.3, 105.7, 119.3, 122.1, 124.9, 125.4, 125.8, 126.6, 127.0, 127.2, 127.2, 128.3, 128.5, 128.5, 130.7, 132.5, 134.0, 136.1, 137.1, 142.3, 159.0, 160.7, 165.8; HRMS (ESI) calcd for $C_{27}H_{23}N_2O_2$ 407.1754, found 407.1750.

1-Benzyl-4-(furan-2-yl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2r):*** white solid; 66% yield; ^{1}H NMR δ 3.13 (d, J = 11.9 Hz, 1H), 4.02 (d, J = 12.0 Hz, 1H), 5.10 (s, 2H), 6.58 (q, J = 1.7 Hz, 1H), 7.08–7.29 (m, 9H), 7.44 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.65 (dd, J_1 = 0.6 Hz, J_2 = 1.6 Hz, 1H); ^{13}C NMR δ 39.2, 51.3, 112.3, 115.8, 122.2, 125.5, 126.1, 126.5, 127.0, 127.5, 128.5, 133.9, 137.0, 141.6, 146.3, 150.9, 151.2, 165.4; HRMS (ESI) calcd for $C_{20}H_{16}N_2O_2Na$ 339.1104, found 339.1107.

1-Benzyl-4-(thiophen-2-yl)-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2s):*** white solid; 64% yield; ^{1}H NMR δ 3.20 (d, J = 11.6 Hz, 1H), 4.12 (d, J = 11.3 Hz, 1H), 5.06–5.14 (m, 2H), 7.09–7.30 (m, 9H), 7.40 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 4.8 Hz, 1H), 7.74 (d, J = 3.1 Hz, 1H); ^{13}C NMR δ 40.0, 51.4, 122.1, 125.5, 126.0, 126.5, 127.0, 127.3, 128.0, 128.5, 130.6, 131.7, 134.1, 137.1, 141.5, 143.3, 155.3, 165.2; HRMS (ESI) calcd for $C_{20}H_{16}N_2OSNa$ 355.0876, found 355.0868.

1-Benzyl-7-chloro-4-phenyl-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2t).*** **2t** was prepared from 7-chloro-4-phenyl-1*H*-benzo[*b*][1,4]-diazepin-2(3*H*)-one[17e] according to the general procedure: colorless oil; 38% yield; ^{1}H NMR δ 3.13 (d, J = 11.9 Hz, 1H), 4.26 (d, J = 11.9 Hz, 1H), 5.02–5.18 (m, 2H), 7.05–7.13 (m, 3H), 7.20–7.25 (m, 4H), 7.43 (d, J = 2.4 Hz, 1H), 7.50–7.53 (m, 3H), 8.13–8.16 (m, 2H); ^{13}C NMR δ 39.9, 51.0, 123.3, 126.0, 126.6, 126.7, 127.3, 127.8, 128.6, 128.7, 130.6, 131.4, 132.6, 136.7, 137.0, 143.1, 161.9, 165.4; HRMS (ESI) calcd for $C_{22}H_{17}ClN_2ONa$ 383.0922, found 383.0922.

Synthesis of Compound 2u. To a solution of compound **2d** (0.626 g, 1.92 mmol) in THF (30 mL) was added t-BuOK (0.28 g, 2.5 mmol) at room temperature. The mixture was stirred for 10 min, and then MeI (0.14 mL) was added dropwise. The mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated NH_4Cl (100 mL), and the mixture was extracted with DCM (3 × 80 mL), washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (10:1 petroleum ether:ethyl acetate) to give a colorless oil (0.45 g, 69%).

1-Benzyl-3-methyl-4-phenyl-1H-benzo[b][1,4]diazepin-2(3H)-one ***(2u):*** colorless oil; 69% yield; ^{1}H NMR δ 1.03 (d, J = 7.5 Hz, 0.38H), 1.50 (d, J = 6.9 Hz, 2.62H), 3.33 (q, J = 6.9 Hz, 0.98H), 4.84 (q, J = 7.5 Hz, 0.12H), 5.02–5.15 (m, 1H), 5.26–5.37 (m, 1H), 7.08–7.50 (m, 12H), 7.77 (m, 2H), 8.05–8.08 (m, 0.19H); ^{13}C NMR δ 9.8, 12.4, 42.7, 47.4, 51.0, 52.3, 121.2, 121.8, 125.0, 125.3, 125.9, 125.9, 126.0, 126.1, 126.3, 126.4, 126.6, 126.8, 126.8, 126.9, 127.1, 127.3, 127.7, 127.9, 128.3, 128.3, 128.4, 129.3, 130.5, 132.2, 133.6, 136.9, 137.0, 137.5, 138.6, 141.1, 164.8, 166.7, 168.1, 168.4; HRMS (ESI) calcd for $C_{23}H_{20}N_2ONa$ 363.1468, found 363.1476.

General Procedure for the Enantioselective Hydrosilylation of Compounds 2a–u. A solution of trichlorosilane in 1,2-dichloroethane (1:4, v/v, 0.25 mL, 2.0 equiv) was added to a solution of the catalyst (10 mol %) and compound **2** (0.25 mmol) in dry 1,2-dichloroethane (3 mL) at −10 °C. The mixture was stirred at −10 °C until the reaction was completed. Then the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (1 mL). The mixture was filtered through a pad of Celite, washed with DCM (70 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (5:1 petroleum ether:ethyl acetate) to afford the pure product.

The racemates were synthesized using DMF as a catalyst.

1-Methyl-4-phenyl-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one[18] ***(3b):*** white solid; 97% yield; HPLC analysis 42% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 9.3 min, $t_{r\text{-minor}}$ = 7.9 min).

1-Allyl-4-phenyl-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one ***(3c):*** white solid; 96% yield; ^{1}H NMR δ 2.65 (dd, J_1 = 4.8 Hz, J_2 = 12.7 Hz, 1H), 2.82 (dd, J_1 = 10.3 Hz, J_2 = 12.7 Hz, 1H), 3.68 (s, 1H), 4.45–4.52 (m, 2H), 5.13 (dd, J_1 = 1.4 Hz, J_2 = 10.3 Hz, 1H), 5.15–5.29 (m, 2H), 5.85–5.97 (m, 1H), 6.83–6.86 (m, 1H), 7.01–7.13 (m, 2H), 7.26–7.36 (m, 6H); ^{13}C NMR δ 41.0, 50.8, 65.4, 116.1, 122.4, 122.5, 122.9, 125.9, 126.5, 127.9, 128.7, 133.4, 135.0, 139.3, 144.3, 170.0; HPLC analysis 55% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 9.7 min, $t_{r\text{-minor}}$ = 8.5 min); HRMS (ESI) calcd for $C_{18}H_{18}N_2ONa$ 301.1397, found 301.1392.

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*1-Benzyl-4-phenyl-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3d**):* white solid; 96% yield; ^{1}H NMR δ 2.75 (dd, J_1 = 4.9 Hz, J_2 = 12.7 Hz, 1H), 2.92 (dd, J_1 = 10.1 Hz, J_2 = 12.6 Hz, 1H), 3.69 (s, 1H), 5.09 (dd, J_1 = 4.8 Hz, J_2 = 10.0 Hz, 1H), 5.16−5.22 (m, 2H), 6.85 (dd, J_1 = 1.4 Hz, J_2 = 6.8 Hz, 1H), 6.98−7.04 (m, 1H), 7.08−7.13 (m, 1H), 7.22−7.40 (m, 10H); ^{13}C NMR δ 41.0, 51.4, 65.5, 122.6, 122.6, 123.0, 125.9, 126.5, 126.8, 127.0, 127.9, 128.3, 128.8, 134.9, 137.6, 139.4, 144.3, 170.5; HPLC analysis 96% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-minor}}$ = 13.8 min, $t_{r\text{-major}}$ = 15.8 min); $[\alpha]^{20}_D$ +132.6 (*c* 0.632, $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{20}N_2ONa$ 351.1468, found 351.1463.

*1-Benzyl-4-p-tolyl-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3e**):* colorless oil; 98% yield; ^{1}H NMR δ 2.35 (s, 3H), 2.70 (dd, J_1 = 4.8 Hz, J_2 = 12.6 Hz, 1H), 2.88 (dd, J_1 = 10.2 Hz, J_2 = 12.6 Hz, 1H), 3.62 (s, 1H), 5.03 (dd, J_1 = 4.8 Hz, J_2 = 10.1 Hz, 1H), 5.13 (s, 2H), 6.81 (dd, J_1 = 1.5 Hz, J_2 = 7.7 Hz, 1H), 7.06−7.07 (m, 1H), 7.13−7.16 (m, 1H), 7.18−7.21 (m, 6H), 7.25−7.30 (m, 4H); ^{13}C NMR δ 21.1, 41.1, 51.5, 65.3, 122.6, 122.6, 123.1, 125.9, 126.6, 126.9, 127.1, 128.4, 129.5, 135.0, 137.7, 137.7, 139.6, 141.4, 170.7; HPLC analysis 96% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 15.1 min, $t_{r\text{-minor}}$ = 12.1 min); $[\alpha]^{20}_D$ +155.3 (*c* 0.656, $CHCl_3$); HRMS (ESI) calcd for $C_{23}H_{22}N_2ONa$ 365.1624, found 365.1622.

*1-Benzyl-4-(4-methoxyphenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3f**):* white solid; 97% yield; ^{1}H NMR δ 2.70 (dd, J_1 = 4.9 Hz, J_2 = 12.6 Hz, 1H), 2.85 (dd, J_1 = 10.0 Hz, J_2 = 12.6 Hz, 1H), 3.62 (s, 1H), 3.79 (s, 3H), 5.03 (dd, J_1 = 4.9 Hz, J_2 = 9.8 Hz, 1H), 5.03−5.12 (m, 2H), 6.78−6.87 (m, 3H), 6.94−7.08 (m, 2H), 7.18−7.32 (m, 8H); ^{13}C NMR δ 41.2, 51.5, 55.3, 65.0, 114.1, 122.6, 122.7, 123.1, 126.6, 126.9, 127.1, 127.2, 128.4, 135.0, 136.6, 137.7, 139.6, 159.3, 170.7; HPLC analysis 94% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 21.2 min, $t_{r\text{-minor}}$ = 16.9 min); $[\alpha]^{20}_D$ +149.2 (*c* 0.752, $CHCl_3$); HRMS (ESI) calcd for $C_{23}H_{22}N_2NaO_2$ 381.1573, found 381.1564.

*1-Benzyl-4-(3-methoxyphenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3g**):* white solid; 97% yield; ^{1}H NMR δ 2.73 (dd, J_1 = 4.9 Hz, J_2 = 12.6 Hz, 1H), 2.87 (dd, J_1 = 10.1 Hz, J_2 = 12.6 Hz, 1H), 3.69 (s, 1H), 3.75 (s, 3H), 5.02 (dd, J_1 = 4.9 Hz, J_2 = 10.0 Hz, 1H), 5.07−5.18 (m, 2H), 6.82−6.90 (m, 4H), 6.97−7.07 (m, 2H), 7.18−7.30 (m, 7H); ^{13}C NMR δ 40.9, 51.4, 55.0, 65.4, 111.4, 113.3, 118.1, 122.5, 122.6, 123.0, 126.5, 126.8, 126.9, 128.2, 129.8, 134.9, 137.6, 139.4, 145.9, 159.8, 170.5; HPLC analysis 95% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 22.2 min, $t_{r\text{-minor}}$ = 17.1 min); $[\alpha]^{20}_D$ +116.2 (*c* 1.02, $CHCl_3$); HRMS (ESI) calcd for $C_{23}H_{22}N_2O_2Na$ 381.1573, found 381.1572.

*1-Benzyl-4-(2-methoxyphenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3h**):* white solid; 99% yield; ^{1}H NMR δ 2.77 (dd, J_1 = 5.3 Hz, J_2 = 12.5 Hz, 1H), 2.91 (dd, J_1 = 8.9 Hz, J_2 = 12.5 Hz, 1H), 3.60 (brs, 1H), 3.83 (s, 3H), 5.12 (q, J = 15.6 Hz, 2H), 5.49 (dd, J_1 = 5.3 Hz, J_2 = 8.9 Hz, 1H), 6.77 (dd, J_1 = 1.5 Hz, J_2 = 7.6 Hz, 1H), 6.89−7.06 (m, 4H), 7.17−7.39 (m, 8H); ^{13}C NMR δ 38.3, 51.3, 55.1, 58.8, 110.3, 120.4, 122.3, 122.6, 122.6, 126.2, 126.3, 126.7, 127.0, 128.1, 128.6, 131.3, 135.2, 137.7, 139.9, 156.0, 171.1; HPLC analysis 5% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 26.5 min, $t_{r\text{-minor}}$ = 13.5 min); HRMS (ESI) calcd for $C_{23}H_{22}N_2O_2Na$ 381.1573, found 381.1582.

*1-Benzyl-4-(3,4-dimethoxyphenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3i**):* white solid; 98% yield; ^{1}H NMR δ 2.73 (dd, J_1 = 5.2 Hz, J_2 = 12.7 Hz, 1H), 2.83 (dd, J_1 = 9.5 Hz, J_2 = 12.7 Hz, 1H), 3.60 (s, 1H), 3.79 (s, 3H), 3.86 (s, 3H), 5.00 (dd, J_1 = 5.2 Hz, J_2 = 9.4 Hz, 1H), 5.06−5.20 (m, 2H), 6.82 (m, 4H), 6.98−6.70 (m, 1H), 7.06−7.07 (m, 1H), 7.19 (m, 7H); ^{13}C NMR δ 29.5, 41.1, 51.3, 55.6, 55.8, 65.3, 109.1, 111.1, 118.0, 122.5, 122.6, 122.9, 126.4, 126.7, 126.9, 128.2, 135.0, 136.9, 137.6, 139.6, 148.5, 149.0, 170.5; HPLC analysis 98% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-minor}}$ = 34.0 min, $t_{r\text{-major}}$ = 19.6 min); $[\alpha]^{20}_D$ +63.7 (*c* 0.43, $CHCl_3$); HRMS (ESI) calcd for $C_{24}H_{24}N_2O_3Na$ 411.1679, found 411.1679.

*1-Benzyl-4-(4-fluorophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3j**):* colorless oil; ^{1}H NMR δ 2.71−2.83 (m, 2H), 3.63 (s, 1H), 5.00−5.05 (m, 2H), 5.12−5.17 (m, 1H), 6.83 (d, J = 1.5 Hz, 1H), 6.98−7.04 (m, 4H), 7.19−7.29 (m, 8H); ^{13}C NMR δ 41.0, 51.4, 64.8, 115.4, 115.6, 122.5, 122.8, 123.0, 126.6, 126.9, 127.0, 127.6, 127.7, 128.2, 135.1, 137.6, 139.4, 139.8, 139.8, 160.6, 163.9, 170.2; HPLC analysis 91% ee, Chiralcel OD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 8.3 min, $t_{r\text{-minor}}$ = 18.6 min); $[\alpha]^{20}_D$ +82.5 (*c* 0.86, $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{19}FN_2ONa$ 369.1374, found 369.1366.

*1-Benzyl-4-(2-fluorophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3k**):* colorless oil; 97% yield; ^{1}H NMR δ 2.80−2.89 (m, 2H), 3.57 (s, 1H), 5.03−5.19 (m, 2H), 5.40−5.44 (m, 1H), 6.82 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H), 6.96−7.12 (m, 4H), 7.18−7.32 (m, 7H), 7.41−7.47 (m, 1H).; ^{13}C NMR δ 39.0, 51.4, 58.1, 58.1, 115.3, 115.6, 122.7, 122.9, 124.2, 124.3, 126.5, 126.8, 127.1, 127.5, 127.5, 128.2, 129.1, 129.3, 130.1, 130.3, 135.3, 137.6, 139.6, 157.9, 161.1, 170.3; HPLC analysis 55% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 10.9 min, $t_{r\text{-minor}}$ = 22.1 min); $[\alpha]^{20}_D$ +26.1 (*c* 1.072, $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{19}FN_2ONa$ 369.1374, found 369.1374.

*1-Benzyl-4-(4-chlorophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3l**):* white solid; 96% yield; ^{1}H NMR δ 2.74−2.76 (m, 2H), 3.66 (s, 1H), 4.98−5.03 (m, 1H), 5.08−5.17 (m, 2H), 6.83−7.00 (m, 1H), 7.00−7.08 (m, 2H), 7.19−7.30 (m, 10H); ^{13}C NMR δ 40.8, 51.4, 64.8, 122.5, 122.9, 123.0, 126.6, 126.8, 127.0, 127.4, 128.2, 128.8, 133.5, 135.1, 137.5, 139.3, 142.3, 170.1; HPLC analysis 92% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 14.5 min, $t_{r\text{-minor}}$ = 16.9 min); $[\alpha]^{20}_D$ +100.6 (*c* 0.596, $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{19}ClN_2ONa$ 385.1078, found 385.1075.

*1-Benzyl-4-(3-chlorophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3m**):* white solid; 98% yield; ^{1}H NMR δ 2.72−2.84 (m, 2H), 3.63 (s, 1H), 4.98−5.18 (m, 3H), 6.82−6.85 (m, 1H), 7.00−7.08 (m, 2H), 7.18−7.31 (m, 10H); ^{13}C NMR δ 40.7, 51.4, 64.9, 122.6, 122.9, 123.1, 124.2, 126.3, 126.6, 126.9, 127.1, 128.0, 128.3, 130.0, 134.5, 135.0, 137.5, 139.3, 145.9, 170.0; HPLC analysis 93% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 14.0 min, $t_{r\text{-minor}}$ = 15.8 min); $[\alpha]^{20}_D$ +133.2 (*c* 0.6, $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{19}ClN_2ONa$ 385.1078, found 385.1078.

*(S)-1-Benzyl-4-(4-bromophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3n**):* white solid; 97% yield; ^{1}H NMR δ 2.74−2.76 (m, 2H), 3.63 (s, 1H), 4.96−5.03 (m, 1H), 5.08−5.17 (m, 2H), 6.08−6.82 (m, 1H), 6.83−7.08 (m, 2H), 7.15−7.29 (m, 8H), 7.43−7.45 (m, 2H); ^{13}C NMR δ 40.7, 51.4, 64.8, 121.7, 122.5, 122.9, 123.1, 126.6, 126.9, 127.1, 127.8, 128.2, 131.8, 135.1, 137.5, 139.3, 142.8, 170.1; HPLC analysis 94% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 15.3 min, $t_{r\text{-minor}}$ = 18.6 min).; $[\alpha]^{20}_D$ +98.6 (*c* 0.596, $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{19}BrN_2ONa$ 429.0573, found 429.0562.

*1-Benzyl-4-(3-bromophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3o**):* white solid; 98% yield; ^{1}H NMR δ 2.72−2.82 (m, 2H), 3.66 (s, 1H), 4.95−5.02 (m, 1H), 5.07 (m, 2H), 6.82−6.84 (m, 1H), 7.08−7.19 (m, 2H), 7.20−7.29 (m, 8H), 7.40−7.47 (m, 1H); ^{13}C NMR δ 40.7, 51.4, 64.8, 122.6, 122.6, 122.9, 123.1, 124.6, 126.6, 126.9, 127.0, 128.3, 129.2, 130.3, 130.9, 135.0, 137.5, 139.2, 146.1, 170.0; HPLC analysis 92% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 15.3 min, $t_{r\text{-minor}}$ = 16.7 min); $[\alpha]^{20}_D$ +62.9 (*c* 1.888, $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{19}BrN_2ONa$ 429.0573, found 429.0562.

*1-Benzyl-4-(naphthalen-2-yl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3p**):* white solid; 97% yield; ^{1}H NMR δ 2.82 (dd, J_1 = 4.8 Hz, J_2 = 12.6 Hz, 1H), 3.00 (dd, J_1 = 10.0 Hz, J_2 = 12.6 Hz, 1H), 3.73 (s, 1H), 5.09−5.20 (m, 2H), 5.23 (dd, J_1 = 4.9 Hz, J_2 = 9.8 Hz, 1H), 6.86 (dd, J_1 = 1.5 Hz, J_2 = 7.6 Hz, 1H), 6.99−7.13 (m, 2H), 7.22−7.53 (m, 9H), 7.76−7.85 (m, 4H); ^{13}C NMR δ 40.8, 51.5, 65.5, 122.6, 123.0, 123.9, 124.7, 126.0, 126.2, 126.6, 126.8, 127.0, 127.6, 127.9, 128.3, 128.7, 133.0, 133.2, 134.9, 137.6, 139.5, 141.4, 170.4; HPLC analysis 97% ee, Chiralcel OD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 19.2 min, $t_{r\text{-minor}}$ = 27.8 min); $[\alpha]^{20}_D$ +187.8 (*c* 0.86, $CHCl_3$); HRMS (ESI) calcd for $C_{26}H_{22}N_2ONa$ 401.1608, found 401.1614.

*1-Benzyl-4-(6-methoxynaphthalen-2-yl)-4,5-dihydro-1H-benzo-[b][1,4]diazepin-2(3H)-one (**3q**):* white solid; 98% yield; ^{1}H NMR δ 2.78 (dd, J_1 = 4.8 Hz, J_2 = 12.8 Hz, 1H), 2.99 (dd, J_1 = 10.2 Hz, J_2 = 12.7 Hz, 1H), 3.69 (s, 1H), 3.91 (s, 3H), 5.08−5.21 (m, 3H), 6.84 (dd, J_1 = 1.4 Hz, J_2 = 7.7 Hz, 1H), 6.96−7.37 (m, 11H), 7.67−7.71 (m,

3H); ^{13}C NMR δ 41.0, 51.6, 55.3, 65.6, 105.7, 119.2, 122.6, 122.7, 123.1, 124.5, 124.6, 126.7, 126.9, 127.1, 127.6, 128.4, 128.7, 129.5, 134.2, 135.0, 137.8, 139.4, 139.6, 157.9, 170.6; HPLC analysis 95% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 29.3 min, $t_{r\text{-minor}}$ = 24.0 min); $[\alpha]^{20}_D$ +182.9 (c 0.886, $CHCl_3$); HRMS (ESI) calcd for $C_{27}H_{24}N_2O_2Na$ 431.1730, found 431.1723.

*1-Benzyl-4-(furan-2-yl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3r**):* white solid; 97% yield; ^{1}H NMR δ 2.77 (dd, J_1 = 5.4 Hz, J_2 = 12.6 Hz, 1H), 2.90 (dd, J_1 = 10.5 Hz, J_2 = 12.6 Hz, 1H), 3.69 (s, 1H), 5.09−5.14 (m, 3H), 6.14 (d, J = 3.2 Hz, 1H), 6.29−6.31 (m, 1H), 6.75−6.76 (m, 1H), 6.98−7.00 (m, 2H), 7.15−7.36 (m, 7H); ^{13}C NMR δ 37.6, 51.4, 58.6, 105.4, 110.2, 122.7, 123.4, 123.5, 126.5, 126.9, 127.0, 128.3, 136.0, 137.6, 138.6, 142.0, 155.7, 170.5; HPLC analysis 75% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 19.3 min, $t_{r\text{-minor}}$ = 12.9 min); $[\alpha]^{20}_D$ +187.5 (c 0.778, $CHCl_3$); HRMS (ESI) calcd for $C_{20}H_{18}N_2O_2Na$ 341.1260, found 341.1254.

*1-Benzyl-4-(thiophen-2-yl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3s**):* white solid; 99% yield; ^{1}H NMR δ 2.79−2.91 (m, 2H), 3.66 (s, 1H), 5.06−5.18 (m, 2H), 5.38 (dd, J_1 = 6.1 Hz, J_2 = 9.2 Hz, 1H), 6.81−6.83 (m, 1H), 6.95−7.04 (m, 4H), 7.18−7.30 (m, 7H); ^{13}C NMR δ 41.6, 51.4, 61.0, 122.9, 123.4, 123.6, 123.6, 124.5, 126.6, 126.8, 126.9, 127.1, 128.1, 128.4, 135.7, 137.6, 138.3, 147.5, 170.2; HPLC analysis 90% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min. $t_{r\text{-major}}$ = 20.2 min, $t_{r\text{-minor}}$ = 16.5 min); $[\alpha]^{20}_D$ +174.5 (c 0.638, $CHCl_3$); HRMS (ESI) calcd for $C_{20}H_{18}N_2OSNa$ 357.1022, found 357.1032.

*1-Benzyl-7-chloro-4-phenyl-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3t**).* colorless oil; 98% yield; ^{1}H NMR δ 2.72 (dd, J_1 = 4.6 Hz, J_2 = 12.8 Hz, 1H), 2.88 (dd, J_1 = 10.2 Hz, J_2 = 12.8 Hz, 1H), 3.72 (s, 1H), 5.02−5.15 (m, 3H), 6.82 (d, J = 2.3 Hz, 1H), 6.91−6.95 (m, 1H), 7.12 (d, J = 8.6 Hz, 1H), 7.22−7.36 (m, 10H); ^{13}C NMR δ 40.8, 51.4, 65.2, 121.9, 122.3, 124.1, 125.8, 127.0, 128.1, 128.4, 128.9, 131.3, 133.2, 137.2, 140.7, 143.8, 170.2; HPLC analysis 73% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, $t_{r\text{-major}}$ = 17.0 min, $t_{r\text{-minor}}$ = 14.2 min).; $[\alpha]^{20}_D$ +75.3 (c 0.96, $CHCl_3$); HRMS (ESI) calcd for $C_{22}H_{19}ClN_2ONa$ 385.1078, found 385.1071.

*1-Benzyl-3-methyl-4-phenyl-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (**3u**):* white solid; 97% yield; ^{1}H NMR δ 0.82 (d, J_1 = 6.8 Hz, 3H), 3.13−3.22 (m, 1H), 3.66 (s, 1H), 4.72 (d, J = 6.4 Hz, 1H), 5.00 (d, J = 15.3 Hz, 1H), 5.32 (d, J = 15.3 Hz, 1H), 6.94−6.98 (m, 1H), 7.04−7.11 (m, 2H), 7.22−7.37 (m, 10H); ^{13}C NMR δ 12.8, 38.9, 51.6, 72.7, 122.1, 122.7, 123.3, 126.3, 126.8, 127.5, 128.0, 128.2, 128.4, 136.5, 137.9, 139.6, 140.9, 172.7; HPLC analysis 93:7 dr, 36% ee, Chiralcel AD-H (80:20 hexane:iPrOH, 1.0 mL/min, t = 5.3, 7.0, 8.0, 8.6 min); HRMS (ESI) calcd for $C_{23}H_{23}N_2O$ 343.1805, found 343.1800.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds and chiral HPLC analysis spectra and single-crystal X-ray diffraction data of compound **3n**. This material is available free of charge via the Internet at http://pubs.acs.org.

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