Supporting Information for

## Asymmetric hydrogenation of dibenzo-fused azepines with chiral cationic ruthenium diamine catalysts

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### 1. General information

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Model Avance DMX 300 Spectrometer (<sup>1</sup>H 300 MHz and <sup>13</sup>C 75 MHz, respectively) or Bruker Model Avance DMX 400 Spectrometer (<sup>1</sup>H 400 MHz and <sup>13</sup>C 100 MHz, respectively) or Bruker Model Avance DMX 500 Spectrometer (<sup>1</sup>H 500 MHz and <sup>13</sup>C 125 MHz, respectively). Chemical shifts (δ) were given in ppm and were referenced to residual solvent or TMS peaks. Optical rotations were measured with Rudolph Autopl VI polarimeter. High resolution MS (P-ESI HRMS) were obtained on Bruker Apex IV FTMS spectrometer or Thermo Fisher Q Exactive Mass Spectrometer. HPLC analyses were performed on an Agilent 1260 liquid chromatograph. All organic solvents were dried using standard, published methods and were distilled before use. All other chemicals were used as received from Aldrich or Acros without further purification. The catalysts were prepared according to the published methods.<sup>1</sup> Seven-membered cyclic imines were synthesized according to modified literature methods.<sup>2-4</sup>

### 2. Optimization of conditions for asymmetric hydrogenation



Figure S1. Chiral ruthenium diamine catalysts used in this study

	1.0 mol % (F 1 mL solvent,	2, <i>R</i> )- <b>C1a</b> H <sub>2</sub> , 12 h	0 N H ( <i>R</i> )-2a	Ms NH2 Ph (R,R)-C1a
Entry	Solvent	H <sub>2</sub> (atm); Temp. (°C)	Conv. $(\%)^b$	$ee(\%)^c$
1	МеОН	50; 40	>99	91
2	EtOH	50; 40	>99	93
3	<i>i</i> -PrOH	50; 40	>99	96
4	<i>n</i> -BuOH	50; 40	>99	92
5	t-BuOH	50; 40	>99	96
6	<i>t</i> -AmylOH	50; 40	>99	92
7	TFE	50; 40	68	97
8	HFIP	50; 40	>99	97
9	acetone	50; 40	>99	88
10	1,4-dioxane	50; 40	>99	81
11	THF	50; 40	>99	84
12	EA	50; 40	>99	94
13	CHCl <sub>3</sub>	50; 40	>99	96
14	DCM	50; 40	>99	96
15	DCE	50; 40	>99	96
16	toluene	50; 40	>99	84
17	HFIP	50; 25	>99	97
18	HFIP	50; 70	>99	97
19	HFIP	80; 40	>99	97
20	HFIP	1;40	96	97
21 <sup>d</sup>	HFIP	1; 40	>99	97

*Table S1*: Optimization of conditions for asymmetric hydrogenation of  $\mathbf{1a}^{a}$ 

<sup>*a*</sup>Reaction conditions: **1a** (0.1 mmol) in solvent (1.0 mL), (*R*,*R*)-**C1a** catalyst (1.0 mol%), reaction for 12 h. <sup>*b*</sup>The conversions were determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. <sup>*c*</sup>The enantiomeric excesses were determined by HPLC with a chiral AD-H column. <sup>*d*</sup>Reaction for 24 h. (TFE: Trifluoroethanol, HFIP: hexafluoroisopropanol).

*Table S2*: Optimization of conditions for asymmetric hydrogenation of  $3a^{a}$ 

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S- N= 3a	<u>1.0 mol % (R</u> 1 mL solvent, 5 40 °C, 12	$\begin{array}{c} (R)\text{-cat.} \\ (R)-cat$	X = OTf SbF6	$(C1a), BF_4 (C1b) (C1d), BArF (C1f)$	, PF <sub>6</sub> ( <b>C1c</b> ) , MsO ( <b>C1g</b> )
Entry	Solvent	Catalyst	[X] <sup>-</sup>	Conv. $(\%)^b$	$ee(\%)^{c}$
1	HFIP	( <i>R</i> , <i>R</i> )-C1a	OTf	27	65
2	MeOH	( <i>R</i> , <i>R</i> )-C1a	OTf	27	82
3	EtOH	( <i>R</i> , <i>R</i> )-C1a	OTf	81	90
4	i-PrOH	( <i>R</i> , <i>R</i> )-C1a	OTf	97	93
5	THF	( <i>R</i> , <i>R</i> )-C1a	OTf	31	76
6	DCM	( <i>R</i> , <i>R</i> )-C1a	OTf	96	89
7	DCM	( <i>R</i> , <i>R</i> )-C1b	$BF_4$	28	87
8	DCM	( <i>R</i> , <i>R</i> )-C1c	PF <sub>6</sub>	89	93
9	DCM	( <i>R</i> , <i>R</i> )-C1d	SbF <sub>6</sub>	80	91
10	DCM	( <i>R</i> , <i>R</i> )-C1e	BArF	>99	99
11	DCM	( <i>R</i> , <i>R</i> )- <b>C1f</b>	OMs	32	71

<sup>*a*</sup>Reaction conditions: **3a** (0.1 mmol) in solvent (1 mL), (*R*,*R*)-**cat.** (1.0 mol%), H<sub>2</sub> (50 atm), stirred at 40 °C for 12 h. <sup>*b*</sup>The conversions were determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. <sup>*c*</sup>The enantiomeric excesses were determined by HPLC with a chiral AD-H column.

	5a	1.0 mol % ( <i>R</i> , <i>l</i> 1 mL solvent, 5 40 °C, 24	R)- <b>cat.</b> 50 atm H₂ ► 〔		
				(3)- <b>0a</b>	
Entry	Solvent	Catalyst	[X] <sup>-</sup>	Conv. $(\%)^{\nu}$	$ee(\%)^c$
1	HFIP	( <i>R</i> , <i>R</i> )- <b>C1a</b>	OTf	>99	12
2	DCM	( <i>R</i> , <i>R</i> )- <b>C1e</b>	BArF	>99	78
3	DCM	( <i>R</i> , <i>R</i> )- <b>C1a</b>	OTf	>99	72
4	DCM	( <i>R</i> , <i>R</i> )- <b>C1b</b>	$BF_4$	>99	70
5	DCM	( <i>R</i> , <i>R</i> )- <b>C1c</b>	$PF_{6}$	>99	70
6	DCM	( <i>R</i> , <i>R</i> )- <b>C1d</b>	SbF <sub>6</sub>	>99	67
7	DCM	( <i>R</i> , <i>R</i> )- <b>C1f</b>	OMs	>99	5
8	DCM	( <i>R</i> , <i>R</i> )- <b>C2e</b>	BArF	>99	48
9	DCM	( <i>R</i> , <i>R</i> )- <b>C3e</b>	BArF	>99	21
10	DCM	( <i>R</i> , <i>R</i> )- <b>C4e</b>	BArF	>99	17
11	DCM	( <i>R</i> , <i>R</i> )- <b>C5e</b>	BArF	>99	53
12	DCM	( <i>R</i> , <i>R</i> )- <b>C6e</b>	BArF	73	26
13	DCM	( <i>R</i> , <i>R</i> )- <b>C7e</b>	BArF	>99	83
14	DCM	( <i>R</i> , <i>R</i> )-C8e	BArF	>99	87
15	DCM	( <i>R</i> , <i>R</i> )- <b>C9e</b>	BArF	>99	2
16	DCM	( <i>R</i> , <i>R</i> )- <b>C10e</b>	BArF	>99	20
17	DCM	( <i>R</i> , <i>R</i> )-C11e	BArF	>99	65
18	DCM	( <i>R</i> , <i>R</i> )-C12e	BArF	>99	37

*Table S3*: Optimization of conditions for asymmetric hydrogenation of  $5a^{a}$ 

<sup>*a*</sup>Reaction conditions: **5a** (0.1 mmol) in solvent (1 mL), (*R*,*R*)-**cat**. (1.0 mol%), H<sub>2</sub> (50 atm), stirred at 40 °C for 12 h. <sup>*b*</sup>The conversions were determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. <sup>*c*</sup>The enantiomeric excesses were determined by HPLC with a chiral AD-H column.

### 3. General procedure for the synthesis of dibenzo-fused azepines<sup>2-4</sup>

**Procedure A** (for dibenzo[b,f][1,4]oxazepines)<sup>2</sup>:



### **Tipycal procedure:**

Step 1: To a reaction mixture of NaH (0.32 g, 8 mmol) and DMF (10 mL) was added dropwise a solution of phenol (0.71 g, 7.5 mmol) in DMF, it was stirred for 1 h at room temperature. Subsequently, o-fluoro nitrobenzene (0.71 g, 5 mmol) in DMF (2 mL) was dropped slowly to the mixture above and stirred for another 1 h at room temperature, then stirred for 12 h at 50 °C. After routine workup, the crude product was purified by flash chromatography on silica gel using petroleum ether and EtOAc to give the diphenyl ether derivative.

Step 2: The diphenyl ether derivative (2.0 g, 9.3 mmol) was dissolved in 5 mL of EtOH, 5% palladium on charcoal (0.10 g) and 0.25 mL of AcOH were added to the solution, the reduction was carried out with hydrogen gas at an initial pressure of 60 psi for 12 h. The catalyst was filtered off. Then concentration in vacuo and purification by flash chromatography afforded aniline derivative.

Step 3: The aniline derivative was dissolved in 20 mL of  $CH_2Cl_2$  and cooled to 0 <sup>o</sup>C, then acetyl chloride (0.70 g, 8.9 mmol) was added slowly to the solution, the temperature increased spontaneous to ambient temperature, and monitored by TLC. Then water (20 mL) was added to the mixture. The organic layers was washed by brine (1×30 mL), dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuo. The residue was purified by flash chromatography on silica gel using petroleum ether and EtOAc to give amido derivative.

Step 4: To a mixture of polyphosphoric acid (PPA) (7.0 g) and phosphorus

oxychloride (2.1 g, 13.5 mmol) was added amido derivative of diphenyl ether (0.62 g, 2.7 mmol). The reaction mixture was heated at 120 °C for 3 h and poured into ice-cold water, then treated with aqueous ammonia and extracted with  $CH_2Cl_2$  (3×50 mL), dried with anhydrous  $Na_2SO_4$ , and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel eluted by petroleum ether and EtOAc to give **dibenzo**[*b*,*f*][1,4]oxazepine.



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11-methyldibenzo[b,f][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* 2011, 47, 7845). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm)

7.45-7.39 (m, 2H), 7.29-7.25 (m, 1H), 7.21-7.13 (m, 5H), 2.64 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 167.4, 161.0, 152.6, 140.8, 132.8, 129.2, 128.6, 127.8, 127.3, 125.7, 125.2, 120.9, 120.8, 27.7.

11-ethyldibenzo[b,f][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, Chem. Commun. 2011, 47, 7845). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.44-7.39
(m, 2H), 7.32-7.25 (m, 1H), 7.22-7.12 (m, 5H), 2.95 (q, J = 7.4 Hz, 2H), 1.30 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 171.7, 161.6, 152.7, 140.8, 132.7, 128.2, 127.8, 127.2, 125.6, 125.2, 121.0, 120.7, 33.3, 11.9.

11-propyldibenzo[b,f][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* 2011, 47, 7845). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm)

7.39-7.34 (m, 2H), 7.31-7.27 (m, 1H), 7.17-7.08 (m, 5H), 2.89 (t, J = 7.5 Hz, 2H), 1.80-1.67 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 170.8, 161.5, 152.6, 140.8, 132.5, 128.2, 127.7, 127.1, 125.5, 125.1, 120.8, 120.6, 42.1, 20.9, 13.8.



**11-butyldibenzo**[*b*,*f*][1,4]oxazepine: (Known compound, see: K. O. Lars, E. Fredrik, O. Roger, *Org. Lett.* **2006**, *8*, 1771). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.45-7.39 (m, 2H), 7.32-7.29 (m, 1H), 7.22-7.14 (m, 5H), 2.94 (t, *J* = 7.5 Hz, 2H),

1.76-1.66 (m, 2H), 1.52-1.40 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 171.2, 161.5, 152.7, 140.8, 132.6, 128.5, 128.3, 127.8, 127.2, 125.6, 125.2, 120.9, 120.7, 40.1, 29.8, 22.6, 14.1.

**11-isobutyldibenzo**[*b*,*f*][1,4]oxazepine: (New compound). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.41-7.39 (m, 2H), 7.29-7.25 (m, 1H), 7.20-7.13 (m, 5H), 2.82 (d, *J* = 7.2 Hz, 2H), 2.09-1.96 (m, 1H), 1.00 (d, *J* = 6.6 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 170.8, 161.6, 152.8, 140.8, 132.6, 128.6, 128.4, 127.8, 127.2, 125.6, 125.1, 121.0, 120.7, 49.4, 27.6, 22.6.

HRMS-ESI exact mass calcd. for  $C_{15}H_{14}NS^+([M+H]^+)$  requires m/z 252.13829, found m/z 252.13870.

11-benzyldibenzo[b,f][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* 2011, 47, 7845). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm)
7.45-7.42 (m, 1H), 7.39-7.34 (m, 4H), 7.29-7.25 (m, 2H), 7.21-7.09 (m, 6H), 4.29 (s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 168.7, 161.6, 152.6, 140.7, 137.5, 132.7, 128.9, 128.7, 128.4, 128.2, 127.9, 127.5, 126.7, 125.6, 125.0, 120.9, 120.7, 46.9.



**4,11-dimethyldibenzo**[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* **2011**, 47, 7845). Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.28-7.24 (m, 3H), 7.16-7.13 (m, 3H), 7.07-7.04 (m, 1H), 2.62 (s, 3H),

2.47 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 167.9, 158.8, 152.4, 141.1, 133.9, 130.2, 129.1, 127.7, 127.0, 126.2, 125.5, 124.7, 121.0, 27.9, 16.4.



4-bromo-11-methyldibenzo[b,f][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, Chem. Commun. **2011**, 47, 7845). Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.67 (d, J = 8.0 Hz, 2H), 7.44-7.37 (m, 2H), 7.29-7.26 (m, 1H),

7.19-7.17 (m, 2H), 7.09-7.05 (m, 1H), 2.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 166.4, 156.5, 152.0, 140.4, 135.8, 130.6, 127.7, 127.6, 127.5, 126.1, 121.7, 115.7, 27.8.

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11-methyl-4-phenyldibenzo[b,f][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, Chem. Commun. **2011**, 47, 7845). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.59-7.39 (m, 7H), 7.26-7.18 (m, 2H), 7.06-7.02 (m, 1H), 6.91-6.86

(m, 1H), 6.33 (d, J = 7.8 Hz, 1H), 2.68 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 167.5, 157.2, 152.2, 140.9, 137.1, 134.8, 133.4, 130.0, 129.8, 128.2, 127.7, 127.5, 127.3, 127.0, 125.5, 125.0, 120.8, 27.9.



2,11-dimethyldibenzo[b,f][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, Chem. Commun. **2011**, *47*, 7845). Yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.27-7.25 (m, 1H), 7.20-7.19 (m, 2H), 7.13-7.11 (m, 3H), 7.06-7.04 (m, 1H), 2.62 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 167.4, 158.9, 152.8, 140.8, 134.7, 133.4, 128.8, 128.8, 127.7, 127.2, 125.5, 120.6, 120.5, 27.6, 20.9.



2-fluoro-11-methyldibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, Chem. Commun. 2011, 47, 7845). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.29-7.26 (m, 1H), 7.18-7.09 (m, 6H), 2.62 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 165.9, 159.5 (d,  $J_{1C-F} = 243.0$  Hz), 156.8, 152.5, 140.4, 130.1 (d, J<sub>3C-F</sub> = 6.8 Hz), 127.9, 127.7, 125.9, 122.2 (d, J<sub>3C-F</sub> = 6.8 Hz), 120.6, 119.4 (d,  $J_{2C-F} = 23.3$  Hz), 114.8 (d,  $J_{2C-F} = 23.3$  Hz), 27.5.



2-chloro-11-methyldibenzo[*b*,*f*][1,4]oxazepine: (New compound). Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.38-7.34 (m, 2H), 7.29-7.26 (m, 1H), 7.19-7.08 (m, 4H), 2.61 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 165.9, 159.4, 152.2, 140.4, 132.6, 130.6,

130.3, 128.3, 127.9, 127.7, 125.9, 122.3, 120.7, 27.5.

HRMS-ESI exact mass calcd. for  $C_{15}H_{14}NS^{+}([M+H]^{+})$  requires m/z 244.05237, found m/z 244.05313.



8,11-dimethyldibenzo[*b*,*f*][1,4]oxazepine: (New compound). Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.44-7.39 (m, 2H), 7.20-7.15 (m, 1H), 7.09 (s, 1H), 7.04-7.02 (m, 1H), 6.96-6.93 (m,

1H), 2.64 (s, 3H), 2.29 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 167.3, 161.0, 150.5, 140.2, 135.3, 132.7, 129.2, 128.5, 128.1, 127.9, 125.0, 120.8, 120.3, 27.6, 20.8. HRMS-ESI exact mass calcd. for  $C_{15}H_{14}NS^{+}([M+H]^{+})$  requires m/z 224.10699, found m/z 224.10750.



8-chloro-11-methyldibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, Org. Lett. 2017, 19, 3855). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.42-7.37 (m, 2H), 7.25 (s, 1H), 7.22-7.11 (m, 2H), 7.08-7.01 (m, 2H), 2.60 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 168.6, 160.6, 151.1, 141.7, 133.0, 130.5, 128.8, 128.6, 127.4, 126.9, 125.3, 121.6, 120.7, 27.6.



7-methylbenzo[*b*]naphtho[2,1-*f*][1,4]oxazepine: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, Org. *Lett.* 2017, 19, 3855). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.57 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.64-7.54 (m,

3H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.34-7.24 (m, 2H), 7.17-7.13 (m, 2H), 2.70 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 168.1, 156.6, 152.6, 141.3, 136.0, 128.1, 127.8, 127.7, 127.5, 127.2, 126.6, 125.7, 124.9, 124.3, 123.9, 123.2, 120.9, 27.8.

11-phenyldibenzo[b,f][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* 2011, 47, 7845). Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm)
7.88-7.86 (m, 2H), 7.54-7.49 (m, 5H), 7.32-7.16 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 167.3, 162.2, 152.6, 140.8, 140.1, 133.2, 131.5, 130.6, 129.9, 128.3, 127.7, 127.5, 125.7, 124.6, 121.1, 120.8.

### **Procedure B** (for dibenzo[*b*,*f*][1,4]thiazepines)<sup>3</sup>:



### **Typical procedure:**

The diphenyl thioether derivatives were obtained by the treatment of o-fluoro nitrobenzenes with substituted thiophenols in the presence of KF/Al<sub>2</sub>O<sub>3</sub> and 18-crown-6 in acetonitrile. Then the reduction of nitro group with Fe/AcOH followed by acylation with acyl chloride afforded amide derivatives. Subsequently, amide derivatives were transformed to dibenzothiazepines via cyclization with polyphosphoric acid (PPA) and POCl<sub>3</sub> at 120 °C.



**11-methyldibenzo**[*b*,*f*][**1**,**4**]**thiazepine**: (Known compound, see: J. Wang, *Tetrahedron Lett.* **2013**, *54*, 5956). Yellow solid; <sup>1</sup>H NMR (400

<sup>3a</sup> MHz, CDCl<sub>3</sub>): δ (ppm) 7.46-7.38 (m, 3H), 7.31-7.23 (m, 3H),
7.19-7.17 (m, 1H), 7.05-7.01 (m, 1H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 169.8, 148.7, 139.9, 139.4, 132.4, 132.0, 130.7, 129.2, 128.8, 128.4, 127.9,
125.6, 125.4, 29.6.



11-ethyldibenzo[b,f][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* **2013**, *54*, 5956). Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.46-7.36 (m, 3H), 7.31-7.22 (m, 3H),

7.19-7.17 (m, 1H), 7.04-7.00 (m, 1H), 2.96-2.90 (m, 2H), 1.26 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 174.2, 148.8, 140.6, 139.0, 132.4, 131.9, 130.5, 129.1, 128.9, 128.4, 127.6, 125.3, 125.3, 35.4, 11.7.

3c

11-propyldibenzo[b,f][1,4]thiazepine: (Known compound, see: J. Wang, Tetrahedron Lett. 2013, 54, 5956). Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.45-7.36 (m, 3H), 7.30-7.22 (m, 3H), 7.19-7.17 (m, 1H), 7.04-7.00 (m, 1H), 3.02-2.95 (m, 1H), 2.85-2.78 (m, 1H),

1.74-1.65 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 173.4, 148.8, 140.6, 138.9, 132.4, 132.0, 130.5, 129.1, 128.9, 128.4, 127.8, 125.4, 44.4, 20.8, 14.0.

11-butyldibenzo[b,f][1,4]thiazepine: (New compound). Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.46-7.36 (m, 3H), 7.31-7.16 (m,, 4H), 7.04-7.00 (m, 1H), 3.00-2.84 (m, 2H), 3d 1.71-1.42 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 173.6, 148.8, 140.6, 139.0, 132.4, 131.9, 130.5, 129.1, 128.9, 128.4, 127.7, 125.4, 125.4, 42.3, 29.6, 22.6, 14.1.

HRMS-ESI exact mass calcd. for  $C_{17}H_{18}NS^+([M+H]^+)$  requires m/z 268.11545, found m/z 268.11541.

11-pentyldibenzo[b,f][1,4]thiazepine: (Known compound, see: J. Wang, Tetrahedron Lett. 2013, 54, 5956). Yellow oil; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) 7.48-7.24 (m, 6H), 7.16-7.02 (m, 3e 2H), 3.02-2.81 (m, 2H), 1.71-1.64 (m, 2H), 1.48-1.36 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 173.6, 148.8, 140.6, 139.0, 132.4, 131.9, 130.5, 129.1, 128.9, 128.4, 127.7, 125.4, 42.5, 31.7, 27.1, 22.6, 14.1.



11-phenethyldibenzo[b,f][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* **2013**, *54*, 5956). Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.45-7.40 (m, 2H), 7.34-7.17 (m, 10H), 7.05-7.01 (m, 1H), 3.27-3.12 (m, 3H), 3.03-2.96 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 172.1, 148.8, 141.7, 140.7, 138.9, 132.4, 132.0, 130.6, 129.2,

128.8, 128.7, 128.5, 128.5, 127.7, 126.1, 125.5, 125.4, 43.9, 33.3.



**8,11-dimethyldibenzo**[*b*,*f*][1,4]thiazepine: (New compound). Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.44-7.37 (m, 2H), 7.30-7.24 (m, 3H), 7.01 (s, 1H), 6.85 (d, J = 7.8 Hz, 1H), 2.64 (s,

3H), 2.27 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 169.7, 148.5, 140.2, 139.5, 139.3, 132.2, 131.9, 130.7, 128.3, 127.9, 126.5, 125.9, 125.6, 29.6, 21.2.

HRMS-ESI exact mass calcd. for  $C_{15}H_{14}NS^{+}([M+H]^{+})$  requires m/z 240.08415, found m/z 240.08429.



7,11-dimethyldibenzo[b,f][1,4]thiazepine: (Known compound, see: J. Wang, Tetrahedron Lett. 2013, 54, 5956). Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.46-7.37 (m, 2H), 7.32-7.26 (m, 2H),

7.24 (s, 1H), 7.10-7.00 (m, 1H), 2.65 (s, 3H), 2.27 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 169.3, 146.4, 139.9, 139.5, 135.5, 132.8, 131.9, 130.7, 130.1, 128.4, 128.0, 125.3, 29.6, 20.7.

4,11-dimethyldibenzo[b,f][1,4]thiazepine: (Known compound, see: J. Wang, Tetrahedron Lett. 2013, 54, 5956). Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.44 (d, J = 7.2 Hz, 1H), 7.27-7.15 (m, 5H), 3i 7.05-6.99 (m, 1H), 2.64 (s, 3H), 2.53 (s, 3H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 170.6, 149.3, 140.0, 139.5, 139.4, 132.8, 131.8, 129.2, 128.6, 128.0, 125.5, 125.3, 125.1, 29.8, 21.2.



**2,11-dimethyldibenzo**[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* **2013**, *54*, 5956). Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.40-7.38 (m, 1H), 7.40-7.38 (m, 1H),

7.32 (d, *J* = 8.0 Hz, 1H), 7.04-7.00 (m, 1H), 2.64 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 169.9, 148.8, 139.2, 138.5, 136.7, 132.3, 131.8, 131.6, 129.1, 129.1, 128.5, 125.5, 125.3, 29.6, 21.3.



**2-fluoro-11-methyldibenzo**[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* **2013**, *54*, 5956). Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.44-7.39 (m, 2H),

7.30-7.25 (m, 1H), 7.19-7.16 (m, 1H), 7.11-6.99 (m, 3H), 2.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 168.2, 162.7 (d,  $J_{C-F} = 248.0$  Hz), 148.5, 140.9 (d,  $J_{C-F} = 7.0$  Hz), 135.3 (d,  $J_{C-F} = 3.0$  Hz), 133.7 (d,  $J_{C-F} = 8.0$  Hz), 132.4, 129.4, 128.6, 125.8, 125.4, 117.9 (d,  $J_{C-F} = 21.0$  Hz), 114.9 (d,  $J_{C-F} = 23.0$  Hz), 29.3.

2-chloro-11-methyldibenzo[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* 2013, 54, 5956). Yellow oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) 7.40-7.36 (m, 3H), 7.29-7.26 (m, 2H), 7.18-7.17 (m, 1H), 7.07-7.05 (m, 1H), 2.64 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 168.2, 148.6, 140.6, 138.5, 134.7, 133.2, 132.5, 130.8, 129.5, 128.3, 127.9, 125.9, 125.5, 29.4.

### **Procedure C** (for dibenzo[*b*,*e*]azepines)<sup>4</sup>:



#### Typical procedure for the synthesis of 5h:

**Step 1:** To a solution of 4-chloro-1-methyl-2-nitrobenzene (20 g, 1 eq.) in CH<sub>3</sub>CN, NBS (26 g, 1 eq.) and AIBN (2.3 g, 0.1 eq) was added under N<sub>2</sub>. The reaction was allowed to reflux overnight. Solvent was removed by distillation and the resulting mixture was filtered to remove solid particles. The residue was purified by silica gel, (PET/EA = 20 : 1) to provide 1-(bromomethyl)-4-chloro-2-nitrobenzene (yellow solid, 30 g).

**Step 2:** To a solution of 1-(bromomethyl)-4-chloro-2-nitrobenzene (5 g, 1 eq.) in toluene,  $K_2CO_3$  (6 g, 2 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.26 g, 0.01 eq.) and phenylboronic acid (1 eq.) was added under N<sub>2</sub>. After stirring at 80 °C overnight, the reaction mixture was poured into water and extracted with dichloromethane. The combined extracts were washed with brine, dried with anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 5:1) to provide 1-benzyl-4-chloro-2-nitrobenzene (yellow oil, 2.4-2.9 g).

**Step 3:** To a solution of 1-benzyl-4-chloro-2-nitrobenzene (2.4-2.9 g, 1 eq.) in EtOH and H<sub>2</sub>O, con. HCl and Fe powder (5 eq.) was added under N<sub>2</sub>. The reaction was allowed to reflux overnight. Solvent was removed by distillation and the resulting mixture was filtered to remove solid particles. The residue was neutralized with 7M NaOH aqueous solution until pH >7. The result aqueous phase was extracted with dichloromethane, dried with anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 10:1) to provide 2-benzyl-5-chloroaniline (yellow oil, 2.0-2.5 g).

**Step 4:** To a solution of 2-benzyl-5-chloroaniline (2.0-2.5 g, 1 eq.) in DCM, AcCl (1.1 eq.) and Et<sub>3</sub>N (2 eq.) was added at 0 °C under N<sub>2</sub>. After stirring at room temperature for 1 h, the reaction mixture was poured into water and extracted with dichloromethane. The combined extracts were washed with brine, dried with anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 5:1) to provide *N*-(2-benzyl-5-chlorophenyl)acetamide (yellow oil, 2.4-3.0 g).

Step 5: To a solution of N-(2-benzyl-5-chlorophenyl)acetamide (2.4-3.0 g, 1 eq.)

in PPA, POCl<sub>3</sub> (5 eq.) was added under N<sub>2</sub>. After stirring at 120 °C for 3 h, the reaction mixture was added ice water and neutralized with ammonia until pH >7. The resulting aqueous phase was extracted with dichloromethane, dried over anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA = 20:1) to provide 3-chloro-6-methyl-11*H*-dibenzo[*b*,*e*]azepine **5h** (yellow oil, 2.2-2.8 g).



**6-methyl-11***H***-dibenzo[***b,e***]azepine**: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, *Org. Lett.* **2017**, *19*, 3855). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.39 (d, *J* = 7.5

Hz, 1H), 7.28-7.24 (m, 2H), 7.17-7.12 (m, 4H), 7.06-7.01 (m, 1H), 3.52 (s, 2H), 2.63 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 167.4, 145.6, 142.4, 133.7, 132.8, 130.8, 127.2, 127.0, 126.6, 126.5, 125.9, 125.2, 39.1, 28.6.

6-methyl-11*H*-dibenzo[*b,e*]azepine: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, Org. Lett. 2017, 19, 3855). Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.45 (d, J = 7.2 Hz, 1H), 7.35-7.30 (m, 1H), 7.25-7.15 (m, 5H), 7.09-7.04 (m, 1H), 3.55 (s, 2H), 3.00-2.96 (m, 2H), 1.25 (t, J = 7.5 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 172.0, 145.7, 143.1, 133.0, 132.9, 130.7, 127.1, 127.0, 126.9, 126.6, 126.5, 125.7, 125.2, 39.1, 34.4, 12.3.



**6-methyl-11***H***-dibenzo[***b***,***e***]azepine: (New compound). Yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.43 (d,** *J* **= 7.2 Hz, 1H), 7.33-7.14 (m, 6H), 7.08-7.03 (m, 1H), 3.54 (s, 2H), 3.05-2.87 (m, 2H), 1.73-1.63** 

(m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 171.2, 145.7, 143.1, 133.0, 132.9, 130.7, 127.1, 127.0, 127.0, 126.6, 126.5, 125.7, 125.3, 43.4, 39.2, 21.4, 14.1.

HRMS-ESI exact mass calcd. for  $C_{17}H_{18}N^+([M+H]^+)$  requires m/z 236.14338, found m/z 236.14344.



1.46-1.39 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 171.4, 145.7, 143.1, 133.0, 132.9, 130.7, 127.0, 127.0, 126.6, 126.5, 125.7, 125.3, 41.3, 39.1, 30.3, 22.8, 14.1.

HRMS-ESI exact mass calcd. for  $C_{18}H_{20}N^+([M+H]^+)$  requires m/z 250.15903, found m/z 250.15922.



**6-pentyl-11***H***-dibenzo**[*b*,*e*]**azepine**: (New compound). Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.54-7.52 (m, 1H), 7.41-7.24 (m, 6H), 7.16-7.13 (m, 1H), 3.63 (s, 2H), 3.15-2.98 (m, 2H),

1.76-1.74 (m, 2H), 1.45 (s, 4H), 0.98-0.94 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 171.3, 145.6, 143.0, 132.9, 132.9, 130.6, 127.0, 126.9, 126.5, 126.4, 125.7, 125.2, 41.4, 39.1, 31.8, 27.7, 22.6, 14.1.

HRMS-ESI exact mass calcd. for  $C_{19}H_{22}N^+([M+H]^+)$  requires m/z 264.17468, found m/z 264.17468.



**6-isobutyl-11***H***-dibenzo**[*b,e*]**azepine**: (New compound). Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.46 (d, *J* = 7.2 Hz, 1H), 7.37-7.33 (m, 1H), 7.26-7.17 (m, 5H), 7.10-7.07 (m, 1H), 3.61-3.59 (m, 2H),

3.16-3.13 (m, 1H), 2.69-2.64 (m, 1H), 2.04-1.98 (m, 1H), 0.98-0.97 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 170.9, 145.6, 142.9, 133.0, 132.9, 130.8, 127.3, 127.1, 127.0, 126.7, 126.5, 125.9, 125.4, 50.6, 39.2, 27.5, 23.4, 22.2.

HRMS-ESI exact mass calcd. for  $C_{18}H_{20}N^+([M+H]^+)$  requires m/z 250.15903, found m/z 250.15897.



**6-methyl-11***H***-dibenzo[***b,e***]azepine: (New compound). Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): \delta (ppm) 7.51 (d, J = 7.2 Hz, 1H),**  7.31-7.05 (m, 12H), 4.40-4.21 (m, 1H), 3.43 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 169.4, 145.4, 143.2, 138.1, 132.9, 132.7, 130.8, 129.1, 128.6, 127.1, 127.1, 127.0, 126.6, 126.4, 126.1, 125.4, 48.1, 39.1.

HRMS-ESI exact mass calcd. for  $C_{21}H_{18}N^+([M+H]^+)$  requires m/z 284.14338, found m/z 284.14350.



**3-chloro-6-methyl-11***H***-dibenzo**[*b,e*]**azepine**: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, *Org. Lett.* **2017**, *19*, 3855). Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ

(ppm) 7.49 (d, J = 8.0 Hz, 1H), 7.39-7.35 (m, 1H), 7.29-7.23 (m, 3H), 7.11-7.04 (m, 2H), 3.58 (s, 2H), 2.68(s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 169.0, 146.6, 142.1, 133.6, 132.4, 131.4, 131.2, 128.1, 127.3, 126.8, 126.7, 125.8, 125.1, 38.4, 28.7.



8-isopropyl-6-methyl-11*H*-dibenzo[*b*,*e*]azepine: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, *Org. Lett.* **2017**, *19*, 3855). Yellow solid; <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>): δ (ppm) 7.31 (s, 1H), 7.25-7.11 (m, 5H), 7.08-7.04 (m, 1H), 3.55 (s, 2H), 2.89-2.82 (m, 1H), 2.69 (s, 3H), 1.20-1.18 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 167.6, 147.0, 145.7, 140.0, 133.6, 133.0, 129.0, 127.0, 126.9, 126.6, 125.7, 125.2, 125.2, 38.6, 33.9, 28.6, 24.0.

# 4. General procedure for the asymmetric hydrogenation of dibenzo-fused azepines

Procedure A (for dihydrodibenzo[b,f][1,4]oxazepines)



**General procedure**: A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate dibenzo[b,f][1,4]oxazepine (0.2 mmol), Ru-catalyst (R,R)-**C1a** (0.002 mmol) in 1 mL of HFIP under N<sub>2</sub> atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 1 atm after purging the autoclave with hydrogen gas three times. The reaction mixture was stirred at 40 °C for 24 h. Then the hydrogen gas was carefully released. The conversion was determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. The reaction mixture was filtered through a short pad of silica eluted with EA and PET to give isolated product dihydrodibenzo[b,f][1,4]oxazepine, and the enantiomeric excess of the product was determined by HPLC with a chiral column.



(*R*)-11-methyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* **2011**, *47*, 7845). Yellow oil, isolated yield 95%, 97% ee;  $[\alpha]_D^{25} = +41.4$  (*c* = 1.0, CHCl<sub>3</sub>), [Lit.<sup>2</sup>  $[\alpha]_D^{30} = -109.1$  (*c* =

1.26, CHCl<sub>3</sub>), 94% ee for *S* enantiomer]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.26-7.08 (m, 5H), 6.86-6.80 (m, 1H), 6.68-6.64 (m, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.05 (q, *J* = 6.8 Hz, 1H), 3.60 (s, br, 1H), 1.63 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>): δ (ppm) 157.7, 144.4, 138.2, 135.3, 129.0, 125.6, 124.6, 124.5, 121.9, 120.9, 119.1, 118.5, 50.1, 20.1.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 7.7 min (minor), t<sub>R2</sub> = 9.3 min (major).

(*R*)-11-ethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* 2011, 47, 7845). Yellow oil, isolated yield 98%, 95% ee; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +23.0 (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.24-7.20 (m, 1H), 7.17-7.12 (m, 2H), 7.08-7.04 (m, 2H), 6.87-6.81 (m, 1H), 6.68-6.63 (m, 1H), 6.57-6.54 (m, 1H), 4.29 (t, *J* = 7.4 Hz, 1H), 3.99 (s, br, 1H), 2.11-2.03 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H),; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 157.3, 144.1, 137.8, 134.2, 128.9, 127.3, 124.5, 124.3, 121.8, 121.2, 118.9, 118.7, 59.0, 28.0, 11.6.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 7.2 min (minor), t<sub>R2</sub> = 7.9 min (major).

(*R*)-11-propyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* 2011, *47*, 7845). Yellow solid, isolated yield 97%, 93% ee; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +28.9 (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.24-7.04 (m, 5H), 6.86-6.82 (m, 1H), 6.67-6.63 (m, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 4.44 (t, *J* = 7.2 Hz, 1H), 2.06-1.99 (m, 2H), 1.54-1.32 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 157.4, 144.0, 137.8, 134.4, 128.8, 127.1, 124.5, 124.3, 121.9, 121.2, 118.9, 118.6, 56.8, 37.0, 20.2, 14.1.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 6.9 min (minor), t<sub>R2</sub> = 7.7 min (major).



(*R*)-11-butyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (New compound). Yellow solid, isolated yield 93%, 95% ee;  $[\alpha]_D^{25} =$  -17.4 (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.25-7.03 (m, 5H), 6.87-6.82 (m, 1H), 6.69-6.64 (m, 1H), 6.57 (d, *J*)

= 7.8 Hz, 1H), 4.42 (t, J = 7.4 Hz, 1H), 3.89 (s, br, 1H), 2.11-1.96 (m, 2H), 1.47-1.26 (m, 4H), 0.90 (t, J = 6.6 Hz, 3H),; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 157.3, 144.1, 137.6, 134.3, 128.9, 127.2, 124.5, 124.3, 121.9, 121.2, 119.1, 118.8, 57.2, 34.5, 29.2, 22.7, 14.2. HRMS-ESI exact mass calcd. for C<sub>15</sub>H<sub>14</sub>NS<sup>+</sup>([M+H]<sup>+</sup>) requires m/z 254.15394, found m/z 254.15403.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 6.5 min (minor), t<sub>R2</sub> = 7.3 min (major).



(*R*)-11-isobutyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (New compound). Yellow solid, isolated yield 95%, 98% ee;  $[\alpha]_D^{25} = -17.4$  (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.25-7.03 (m, 5H), 6.87-6.82 (m, 1H), 6.69-6.64 (m, 1H), 6.52 (d, *J* = 7.8 Hz, 1H),

4.55 (t, J = 7.5 Hz, 1H), 3.76 (s, br, 1H), 1.94-1.89 (m, 2H), 1.75-1.64 (m, 1H), 0.97-0.94 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 157.5, 143.9, 137.9, 134.6, 128.8, 126.9, 124.5, 124.3, 121.9, 121.2, 118.8, 118.6, 54.6, 43.7, 25.1, 23.1, 22.5. HRMS-ESI exact mass calcd. for C<sub>15</sub>H<sub>14</sub>NS<sup>+</sup>([M+H]<sup>+</sup>) requires m/z 254.15394, found m/z 254.15466.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 5.8 min (minor), t<sub>R2</sub> = 7.2 min (major).

(*R*)-11-benzyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* **2011**, *47*, 7845). white solid, isolated yield 90%, 98% ee;  $[\alpha]_D^{25} = +70.7$  (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.31-7.10 (m,

10H), 6.86-6.81 (m, 1H), 6.72-6.67 (m, 1H), 6.45 (d, J = 7.8 Hz, 1H), 4.58-4.53 (m, 1H), 3.78 (s, br, 1H), 3.46-3.26 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 157.2, 144.1, 138.8, 137.3, 133.5, 129.5, 129.2, 128.7, 127.7, 126.7, 124.5, 124.4, 121.9, 121.3, 119.3, 119.0, 59.5, 41.6.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 7.9 min (minor), t<sub>R2</sub> = 9.5 min (major).

(*R*)-4,11-dimethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* 2011, 47, 7845). Yellow oil, isolated yield 93%, 95% ee;  $[\alpha]_D^{25} = +78.6 \ (c = 1.0, CHCl_3);$  <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.13-7.08 (m, 2H), 7.01-6.97 (m, 2H), 6.83-6.79 (m, 1H), 6.65-6.60 (m, 1H), 6.49-6.47 (m, 1H), 5.04 (q, *J* = 6.8 Hz, 1H), 3.59 (s, 3H), 2.40 (s, 3H), 1.58 (d, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 155.8, 143.6, 138.7, 135.4, 130.4, 130.2, 124.6, 124.2, 122.7, 122.1, 118.6, 118.3, 49.5, 19.8, 16.3.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 6.1 min (minor), t<sub>R2</sub> = 6.5 min (major).

(*R*)-4-bromo-11-methyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine:
 (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* 2011, 47, 7845). Yellow oil, isolated yield

92%, 97% ee;  $[\alpha]_D^{25} = -29.9$  (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  (ppm) 7.49 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.98 (t, J = 7.8 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.68 (t, J = 7.6 Hz, 1H), 6.53 (d, J = 8.0 Hz, 1H), 5.12 (q, J = 6.8 Hz, 1H), 3.73 (s, br, 1H), 1.64 (d, J = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 154.3, 143.2, 138.2, 137.4, 132.5, 125.6, 125.2, 124.4, 122.9, 118.9, 118.1, 115.7, 49.7, 19.8.

(R)-2h

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column

(*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 254 nm), t<sub>R1</sub> = 9.1 min (major), t<sub>R2</sub> = 10.1 min (minor).

(*R*)-11-methyl-4-phenyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* **2011**, *47*, 7845). Yellow oil, isolated yield 97%, 96% ee;  $[\alpha]_D^{25} = -89.7$  (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  (ppm) 7.54-7.52 (m, 2H), 7.47-7.37 (m, 3H), 7.31-7.30 (m, 1H), 7.25-7.15 (m, 2H), 6.80-6.76 (m, 1H), 6.50-6.49 (m, 3H), 5.17 (q, J = 6.8 Hz, 1H), 3.72 (s, br, 1H), 1.68 (d, J = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 154.6, 144.0, 138.7, 138.1, 136.4, 135.0, 130.3, 130.1, 128.0, 127.4, 124.6, 124.5, 124.4, 122.2, 118.8, 118.1, 49.8, 19.8.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 6.5 min (major), t<sub>R2</sub> = 7.7 min (minor).

### (*R*)-2,11-dimethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine:



(R)-2i

(Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* **2011**, *47*, 7845). Yellow oil, isolated yield 96%, 95% ee;  $[\alpha]_D^{25} = +49.2$  (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  (ppm) 7.09-7.01 (m, 4H), 6.86-6.82 (m, 1H), 6.68-6.64 (m, 1H), 6.54-6.52 (m, 1H), 5.03 (q, *J* = 6.8 Hz, 1H), 3.72 (s, 1H), 2.32 (s, 3H), 1.64 (d, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 155.5, 144.6, 138.3, 134.8, 134.0, 129.3, 125.9, 124.5, 121.8, 120.6, 119.0, 118.5, 50.0, 21.1, 20.1.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 5.5 min (major), t<sub>R2</sub> = 6.1 min (minor).



(Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* **2011**, *47*, 7845). Yellow solid, isolated yield 94%, 95% ee;  $[\alpha]_D^{25} = +60.1$  (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.14-7.07 (m, 2H), 6.94-6.84 (m, 3H), 6.69-6.65 (m, 1H), 6.55-6.53 (m, 1H), 5.07 (q, *J* = 6.8 Hz, 1H), 3.69 (s, br, 1H), 1.62 (d, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 159.4 (d, *J*<sub>1C-F</sub> = 241.0 Hz), 153.7, 144.3, 138.1, 137.1 (d, *J*<sub>3C-F</sub> = 7.0 Hz), 124.9, 122.1 (d, *J*<sub>3C-F</sub> = 8.0 Hz), 121.8, 119.2, 118.5, 115.0 (d, *J*<sub>2C-F</sub> = 23.0 Hz), 112.1 (d, *J*<sub>2C-F</sub> = 24.0 Hz), 49.3, 19.6.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 0.8 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 6.2 min (major), t<sub>R2</sub> = 7.2 min (minor).

(R)-2I

(*R*)-2-chloro-11-methyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (New compound). Yellow oil, isolated yield 95%, 96% ee;  $[\alpha]_D^{25} =$  +77.5 (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm)

7.22-7.18 (m, 2H), 7.11-7.07 (m, 2H), 6.89-6.85 (m, 1H), 6.70-6.66 (m, 1H), 6.54 (d, J = 8.0 Hz, 1H), 5.03 (q, J = 6.8 Hz, 1H), 3.70 (s, br, 1H), 1.62 (d, J = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 156.1, 144.1, 137.9, 136.9, 129.5, 128.7, 125.6, 124.9, 122.4, 121.8, 119.3, 118.6, 49.7, 19.8. HRMS-ESI exact mass calcd. for C<sub>15</sub>H<sub>14</sub>NS<sup>+</sup>([M+H]<sup>+</sup>) requires m/z 246.06802, found m/z 246.06845.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 0.8 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 7.8 min (major), t<sub>R2</sub> = 9.3 min (minor).



(*R*)-8,11-dimethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (New compound). Yellow oil, isolated yield 93%, 96% ee;  $[\alpha]_D^{25} = +14.6$  (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.25-7.07 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H),

5.03 (q, J = 6.8 Hz, 1H), 2.17 (s, 3H), 1.63 (d, J = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 157.9, 142.5, 137.7, 135.3, 134.2, 128.9, 125.4, 124.5, 121.6, 120.8,

119.8, 118.9, 50.0, 20.8, 20.1. HRMS-ESI exact mass calcd. for  $C_{15}H_{14}NS^+([M+H]^+)$  requires m/z 226.12264, found m/z 226.12300.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 0.8 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 9.7 min (minor), t<sub>R2</sub> = 11.2 min (major).

(*R*)-8-chloro-11-methyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, *Org. Lett.* **2017**, *19*, 3855). Yellow solid, isolated yield 96%, 97% ee;  $[\alpha]_D^{25} = +23.5$  (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.28-7.24 (m, 1H), 7.20-7.18 (m, 1H), 7.15-7.10 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.59-6.56 (m, 1H), 6.49 (s, 1H), 5.03 (q, *J* = 6.8 Hz, 1H), 3.79 (s, 1H), 1.63 (d, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 157.5, 142.8, 139.4, 135.0, 129.5, 129.2, 125.4, 124.8, 123.0, 120.8, 118.4, 117.5, 49.8, 20.0.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 7.7 min (minor), t<sub>R2</sub> = 11.6 min (major).





(Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, *Org. Lett.* **2017**, *19*, 3855). Yellow oil, isolated yield 97%, 95% ee;  $[\alpha]_D^{25} = -89.7$  (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.47 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H),

7.63-7.47 (m, 3H), 7.36-7.34 (m, 2H), 6.89-6.86 (m, 1H), 6.74-6.70 (m, 1H), 6.60-6.58 (m, 1H), 5.21 (q, J = 6.8 Hz, 1H), 3.76 (s, br, 1H), 1.74 (d, J = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 152.6, 144.4, 138.8, 134.3, 130.2, 127.8, 127.4, 126.4, 126.3, 124.8, 124.0, 123.4, 122.2, 122.0, 119.2, 118.9, 50.5, 20.6.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 0.8 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 12.9 min (major), t<sub>R2</sub> = 18.9 min (minor).



(*R*)-11-phenyl-10,11-dihydrodibenzo[*b*,*f*][1,4]oxazepine: (Known compound, see: K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, *Chem. Commun.* **2011**, *47*, 7845). Yellow oil, isolated yield 95%, 62% ee;  $[\alpha]_D^{25} = -15.7 \ (c = 1.0, CHCl_3); {}^{1}H NMR \ (400 \text{ MHz}, CDCl_3): \delta (ppm)$ 

7.47-7.35 (m, 5H), 7.31-7.27 (m, 1H), 7.24-7.22 (m, 1H), 7.16-7.13 (m, 1H), 7.09-7.05 (m, 1H), 6.95-6.91 (m, 2H), 6.77-6.73 (m, 1H), 6.69-6.66 (m, 1H), 5.94 (s, 1H), 4.12 (s, br, 1H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 157.6, 144.9, 141.2, 138.3, 134.4, 129.3, 128.8, 128.6, 127.8, 127.4, 124.8, 124.3, 122.0, 121.3, 119.6, 118.8, 60.5.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 0.8 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 7.0 min (minor), t<sub>R2</sub> = 9.2 min (major).

### Procedure B (for dihydrodibenzo[b,f][1,4]thiazepines)



**General procedure**: A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate dibenzo[b,f][1,4]thiazepine (0.2 mmol), Ru-catalyst (R,R)-**C1e** (0.002 mmol) in 1 mL of DCM under N<sub>2</sub> atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas three times. The reaction mixture was stirred at room temperature for 24 h. Then the hydrogen gas was carefully released. The conversion was determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. The reaction mixture was filtered through a short pad of silica eluted with EA and PET to give isolated product dihydrodibenzo[b,f][1,4]thiazepine, and the enantiomeric excess of the product was determined by HPLC with a chiral

column.

(*R*)-11-methyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* 2013, *54*, 5956). Colorless oil; isolated yield 98%, 99% ee;  $[\alpha]_D^{25} = -102.4$  (*c* = 0.5, CH<sub>2</sub>Cl<sub>2</sub>), [Lit.<sup>5</sup>  $[\alpha]_D^{20} = -87.1$  (c 0.48, CHCl<sub>3</sub>), 92% ee for *R* enantiomer]; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 7.54 (d, *J* = 7.6 Hz, 1H), 7.38-7.31 (m, 2H), 7.29-7.25 (m, 1H), 7.14-7.12 (m, 1H), 6.92-6.87 (m, 1H), 6.54-6.51 (m, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 6.15-6.12 (m, 1H), 3.74 (s, br, 1H), 1.62-1.60 (m, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 147.1, 146.2, 136.7, 132.5, 132.1, 129.2, 128.7, 128.5, 124.5, 118.3, 117.8, 116.0, 50.4, 19.7.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 8.6 min (minor), t<sub>R2</sub> = 9.3 min (major).

(*R*)-4b (*R*)-11-ethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* 2013, *54*, 5956). Colorless oil; isolated yield 97%, 95% ee;  $[\alpha]_D^{25} = -40.2$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 7.54 (d, J = 7.6 Hz, 1H), 7.37-7.33 (m, 1H), 7.27-7.24 (m, 2H), 7.13 (d, J = 7.6 Hz, 1H), 6.92-6.88 (m, 1H), 6.53 (t, J = 7.6 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 5.73 (t, J = 7.2 Hz, 1H), 3.68 (s, br, 1H), 2.15-2.04 (m, 1H), 1.99-1.88 (m, 1H), 1.13 (t, J = 7.2 Hz, 3H) ; <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 147.2, 145.4, 136.7, 132.4, 132.2, 129.1, 128.6, 128.3, 125.2, 118.3, 118.0, 116.3, 57.3, 26.9, 11.7.

The enantiomeric excess was determined by HPLC on a Chiralpak AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220nm), t<sub>R1</sub> = 7.4 min (major), t<sub>R2</sub> = 8.5 min (minor).



compound, see: J. Wang, *Tetrahedron Lett.* **2013**, *54*, 5956). Colorless oil; isolated yield 99%, 93% ee;  $[\alpha]_D^{25} = -34.4$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.54-7.51 (m, 1H), 7.30-7.28 (m, 1H), 7.23-7.19 (m, 2H), 7.14-7.12 (m, 1H), 6.89-6.85 (m, 1H), 6.54-6.50 (m, 1H), 6.34-6.32 (m, 1H), 5.87-5.84 (m, 1H), 3.59 (s, br, 1H), 2.00-1.84 (m, 2H), 1.58-1.52 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 146.8, 145.3, 136.4, 132.2, 132.1, 128.8, 128.2, 128.1, 124.7, 118.2, 117.8, 116.1, 54.7, 35.8, 20.1, 14.2.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 6.2 min (major), t<sub>R2</sub> = 7.7 min (minor).

(R)-4d

(*R*)-11-butyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine: (New compound). Colorless oil; isolated yield 97%, 91% ee;  $[\alpha]_D^{25} = -30.2$  (*c* = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 7.54-7.52

(m, 1H), 7.37-7.23 (m, 3H), 7.13-7.10 (m, 1H), 6.91-6.87 (m, 1H), 6.54-6.50 (m, 1H), 6.38-6.35 (m, 1H), 5.85-5.82 (m, 1H), 3.72 (s, br, 1H), 2.08-201 (m, 1H), 1.93-1.88 (m, 1H), 1.58-1.42 (m, 4H), 0.98-0.95 (m, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 147.2, 145.7, 136.7, 132.4, 132.2, 129.1, 128.6, 128.3, 125.2, 118.3, 117.9, 116.2, 55.4, 33.6, 29.4, 23.1, 14.2. HRMS-ESI exact mass calcd. for C<sub>17</sub>H<sub>20</sub>NS<sup>+</sup>([M+H]<sup>+</sup>) requires m/z 270.13110, found m/z 270.13125.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 6.8 min (major), t<sub>R2</sub> = 7.8 min (minor).



(*R*)-11-pentyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* 2013, *54*, 5956). Colorless oil; isolated yield 98%, 90% ee;  $[\alpha]_D^{25} = -29.5$  (*c* = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.55-7.52 (m, 1H),

7.38-7.23 (m, 3H), 7.13-7.10 (m, 1H), 6.92-6.87 (m, 1H), 6.55-6.50 (m, 2H), 6.38-6.35 (m, 1H), 5.86-5.83 (m, 1H), 3.72 (d, J = 4.8 Hz, 1H), 2.06-1.88 (m, 2H),

1.59-1.35 (m, 6H), 0.93 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 146.8, 145.4, 136.5, 132.2, 132.1, 128.8, 128.2, 128.0, 124.7, 118.3, 117.8, 116.3, 55.2, 33.8, 32.0, 26.7, 22.7, 14.2.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 5.5 min (major), t<sub>R2</sub> = 6.2 min (minor).



## (*R*)-11-phenethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, *Tetrahedron Lett.* 2013, *54*, 5956). Colorless oil; isolated yield 97%, 85% ee; $[\alpha]_D^{25} = -14.6$ (*c* = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): $\delta$ (ppm)

7.54-7.51 (m, 1H), 7.32-7.27 (m, 3H), 7.23-7.19 (m, 5H), 7.15-7.13 (m, 1H), 6.90-6.86 (m, 1H), 6.56-6.52 (m, 1H), 6.32-6.30 (m, 1H), 5.83-5.79 (m, 1H), 3.62 (s, 1H), 2.90-2.78 (m, 2H), 2.41-2.31 (m, 1H), 2.26-2.17 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 146.5, 144.9, 141.6, 136.3, 132.2, 132.2, 128.8, 128.7, 128.6, 128.2, 128.2, 126.3, 124.9, 118.4, 118.1, 116.4, 55.1, 35.6, 33.3.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 9.1 min (major), t<sub>R2</sub> = 9.9 min (minor).

(R)-4g

(*R*)-8,11-dimethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine: (New compound). Light yellow oil; isolated yield 98%, 99% ee;  $[\alpha]_D^{25} = -127.3 \ (c = 0.5, CH_2Cl_2); {}^{1}H \ NMR \ (400 \ MHz, CD_2Cl_2): \delta$ 

(ppm) 7.52 (d, *J* =7.6 Hz, 1H), 7.37-7.30 (m, 2H), 7.27-7.23 (m, 1H), 7.01 (d, *J* =8.0 Hz, 1H), 6.36 (d, *J* =7.6 Hz, 1H), 6.18 (s, 1H), 6.11 (q, *J* =6.6 Hz, 1H), 3.67 (s, 1H), 2.12 (s, 3H), 1.60 (d, *J* =6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 146.8, 146.2, 138.8, 137.0, 132.5, 132.0, 129.1, 128.4, 124.5, 119.4, 118.3, 112.8, 50.3, 21.0, 19.8. HRMS-ESI exact mass calcd. for C<sub>15</sub>H<sub>16</sub>NS<sup>+</sup>([M+H]<sup>+</sup>) requires m/z 242.09980, found m/z 242.09985.

The enantiomeric excess was determined by HPLC on a Chiralcel OJ-H column

(*n*-hexane : isopropanol = 70 : 30, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 220$  nm), t<sub>R1</sub> = 19.5 min (major), t<sub>R2</sub> = 23.2 min (minor).

(*R*)-7,11-dimethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, Tetrahedron Lett. 2013, 54, 5956). Light yellow oil; isolated yield 97%, 99% ee;  $[\alpha]_D^{25} = -17.4$ (*R*)-**4h**  $(c = 0.5, CH_2Cl_2)$ ; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 7.52 (d, J = 7.6 Hz, 1H), 7.36-7.23 (m, 3H), 6.96 (s, 1H), 6.72 (d, J = 8.4 Hz, 1H), 6.29 (d, J = 8.0 Hz, 1H), 6.03 (q, J = 6.8 Hz, 1H), 3.64 (s, 1H), 2.13 (s, 3H), 1.59 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) 146.2, 144.6, 136.6, 132.6, 132.0, 129.4, 129.1, 128.4, 128.0, 124.7, 118.1, 116.2, 50.6, 20.1, 19.9.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$ = 220 nm),  $t_{R1} = 10.1$  min (major),  $t_{R2} = 11.9$  min (minor).



(*R*)-4,11-dimethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine: (Known compound, see: J. Wang, Tetrahedron Lett. 2013, 54, 5956). Light yellow oil; isolated yield 99%, 98% ee;  $[\alpha]_D^{25} = -295.4$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.23-7.11 (m,

4H), 6.89-6.85 (m, 1H), 6.49 (t, J = 7.4 Hz, 1H), 6.32-6.28 (m, 2H), 3.58 (s, 1H), 2.53 (s, 3H), 1.57 (d, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 147.1, 146.0, 139.9, 136.4, 133.3, 129.9, 128.6, 128.2, 121.6, 117.9, 117.3, 115.4, 50.0, 21.6, 20.0. The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column (*n*-hexane : isopropanol = 70 : 30, flowing rate = 0.7 mL/min, 25 °C, UV detection at  $\lambda = 220 \text{ nm}$ ),  $t_{R1} = 6.5 \text{ min (minor)}$ ,  $t_{R2} = 7.7 \text{ min (major)}$ .



### (*R*)-2,11-dimethyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepine:

(Known compound, see: J. Wang, Tetrahedron Lett. 2013, 54, 5956). Light yellow oil; isolated yield 97%, 99% ee;  $\left[\alpha\right]_{D}^{25} = -54.2$ (R)-**4**j  $(c = 0.5, CH_2Cl_2)$ ; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 7.41 (d, J = 7.6 Hz, 1H), 7.14-7.07 (m, 3H), 6.88 (t, J =7.6 Hz, 1H), 6.50 (t, J =7.4 Hz, 1H), 6.33 (d, J =8.4 Hz, 1H), 6.13 (q, J = 6.6 Hz, 1H), 3.70 (s, 1H), 2.36 (s, 3H), 1.59 (d, J =6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 147.1, 145.9, 136.4, 133.2, 132.4, 132.0, 129.0, 128.6, 125.3, 118.2, 117.7, 116.3, 50.2, 21.6, 16.7.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 7.6 min (minor), t<sub>R2</sub> = 8.0 min (major).



## (*R*)-2-fluoro-11-methyl-10,11-dihydrodibenzo[*b*,*f*][1,4]thiazepi ne: (Known compound, see: J. Wang, *Tetrahedron Lett.* 2013, 54,

<sup>A</sup> (R)-4k 5956). Yellow oil; isolated yield 97%, 95% ee;  $[\alpha]_D^{25} = -75.2$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 7.56-7.52 (m, 1H), 7.14-7.12 (m, 1H), 7.07-7.04 (m, 1H), 7.00-6.95 (m, 1H), 6.93-6.89 (m, 1H), 6.53 (t, J = 7.4 Hz, 1H), 6.35 (d, J = 8.0 Hz, 1H), 6.15 (q, J = 6.8 Hz, 1H), 3.69 (s, 1H), 1.58 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 163.5 (d,  $J_{C-F} = 246.0$  Hz), 148.6 (d,  $J_{C-F} = 7.0$  Hz), 146.8, 134.5 (d,  $J_{C-F} = 8.0$  Hz), 132.5, 131.8 (d,  $J_{C-F} = 3.0$  Hz), 128.9, 118.4, 117.7, 115.7, 115.1 (d,  $J_{C-F} = 22.0$  Hz), 112.0 (d,  $J_{C-F} = 22.0$  Hz), 50.1 (d,  $J_{C-F} = 1.0$  Hz), 19.5.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 6.7 min (major), t<sub>R2</sub> = 8.7 min (minor).



## (R)-2-chloro-11-methyl-10,11-dihydrodibenzo[b,f][1,4]thiazepi

ne: (Known compound, see: J. Wang, *Tetrahedron Lett.* 2013, 54, 5956). Light yellow oil; isolated yield 96%, 96% ee;  $[\alpha]_D^{25} = -50.4$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 7.48 (d,

J = 8.4 Hz, 1H), 7.30 (d, J = 2.4 Hz, 1H), 7.26-7.23 (m, 1H), 7.12-7.10 (m, 1H), 6.93-6.88 (m, 1H), 6.55-6.51 (m, 1H), 6.37-6.35 (m, 1H), 6.11 (q, J = 7.0 Hz, 1H), 3.77 (s, 1H), 1.59 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 147.8, 146.8, 135.0, 134.9, 133.4, 132.5, 128.9, 128.4, 125.0, 118.6, 117.8, 115.4, 50.3, 19.6.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 6.9 min (major), t<sub>R2</sub> = 8.8 min (minor).

#### **Procedure C** (for dihydrodibenzo[b,e]azepines)



**General procedure**: A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrate dibenzo[b,e]azepine (0.2 mmol), Ru-catalyst (R,R)-**C8e** (0.002 mmol) in 1 mL of DCM under N<sub>2</sub> atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas three times. The reaction mixture was stirred at room temperature for 24 h. Then the hydrogen gas was carefully released. The conversion was determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. The reaction mixture was filtered through a short pad of silica eluted with EA and PET to give isolated product dihydrodibenzo[b,e]azepine, and the enantiomeric excess of the product was determined by HPLC with a chiral column.

(S)-6-methyl-6,11-dihydro-5H-dibenzo[b,e]azepine: (Known



compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, Org.

<sup>H</sup> (S)-6a *Lett.* **2017**, *19*, 3855). Yellow oil, isolated yield 93%, 87% ee;  $[\alpha]_D^{25} = -36.3 \ (c = 1.0, \text{CHCl}_3)$ , [Lit.<sup>4</sup>  $[\alpha]_D^{25} = -30.0 \ (c = 0.4, \text{CHCl}_3)$ , 97% ee for *S* enantiomer]; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.22-7.21 (m, 4H), 6.98-6.90 (m, 2H), 6.62-6.57 (m, 1H), 6.40 (d, *J* = 8.1 Hz, 1H), 5.20 (q, *J* = 6.6 Hz, 1H), 4.81 (d, *J* = 15.0 Hz, 1H), 3.57-3.52 (m, 2H), 1.60 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 145.7, 140.4, 139.7, 130.5, 128.2, 127.7, 127.6, 127.1, 123.7, 123.1, 118.2, 117.3, 49.8, 40.0, 20.2. The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 6.8 min (minor), t<sub>R2</sub> = 8.9 min (major).

(S)-6-ethyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, *Org. Lett.* **2017**, *19*, 3855). Yellow oil, isolated yield 95%, 88% ee;  $[\alpha]_D^{25} =$ -116.6 (*c* =1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.25-7.16 (m, 4H), 7.01-6.92 (m, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 4.81-4.77 (m, 1H), 4.63 (d, *J* = 15.2 Hz, 1H), 3.71 (d, *J* = 15.2 Hz, 1H), 3.64 (s, 1H), 2.12-2.03 (m, 1H), 1.96-1.85 (m, 1H), 1.14 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 145.8, 139.7, 139.7, 130.4, 128.4, 127.6, 127.6, 127.0, 124.7, 123.8, 118.3, 117.6, 57.1, 40.1, 27.7, 11.5.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 6.2 min (minor), t<sub>R2</sub> = 7.6 min (major).

(*S*)-6-propyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine: (New compound). Yellow solid, isolated yield 96%, 90% ee;  $[\alpha]_D^{25} = -108.4$  (*s*)-6c (*c* =1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.24-7.16 (m, 4H), 7.01-6.91 (m, 2H), 6.60 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 4.91-4.88 (m, 1H), 4.66 (d, *J* = 15.2 Hz, 1H), 3.68 (d, *J* = 15.2 Hz, 1H), 3.62 (s, 1H), 2.01-1.98 (m, 1H), 1.89-1.86 (m, 1H), 1.62-1.54 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 145.8, 139.9, 139.7, 130.5, 128.4, 127.6, 127.6, 127.0, 124.5, 123.5, 118.2, 117.5, 54.9, 40.1, 36.8, 20.0, 14.3. HRMS-ESI exact mass calcd. for C<sub>17</sub>H<sub>20</sub>N<sup>+</sup>([M+H]<sup>+</sup>) requires m/z 238.15903, found m/z 238.15904.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 6.6 min (minor), t<sub>R2</sub> = 7.9 min (major).

(*S*)-6-butyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine: (New compound). Yellow oil, isolated yield 95%, 88% ee;  $[\alpha]_D^{25} = -94.6$  (*c* =1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.23-7.16 (m, 4H), 7.00-6.91 (m, 2H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 4.89-4.86 (m, 1H), 4.66 (d, *J* = 15.2 Hz, 1H), 3.68 (d, *J* = 14.8 Hz, 1H), 3.63 (s, 1H), 2.04-2.01 (m, 1H), 1.90-1.86 (m, 1H), 1.56-1.40 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 145.8, 139.9, 139.7, 130.4, 128.4, 127.6, 127.5, 127.0, 124.5, 123.5, 118.2, 117.5, 55.2, 40.1, 34.3, 29.0, 22.9, 14.2. HRMS-ESI exact mass calcd. for C<sub>18</sub>H<sub>22</sub>N<sup>+</sup>([M+H]<sup>+</sup>) requires m/z 252.17468, found m/z 252.17474. The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 220 nm), t<sub>R1</sub> = 6.0 min (minor), t<sub>R2</sub> = 7.2 min (major).



(*S*)-6-pentyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine: (New compound). Yellow oil, isolated yield 98%, 92% ee;  $[\alpha]_D^{25} =$  -76.0 (*c* = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.23-7.16 (m, 4H), 7.00-6.91 (m, 2H), 6.62-6.58 (m, 1H), 6.43 (d,

J = 7.6 Hz, 1H), 4.89-4.86 (m, 1H), 4.66 (d, J = 14.8 Hz, 1H), 3.68 (d, J = 14.8 Hz, 1H), 2.03-1.82 (m, 2H), 1.56-1.37 (m, 6H), 0.91 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 145.8, 139.9, 139.7, 130.4, 128.4, 127.6, 127.5, 127.0, 124.5, 123.5, 118.2, 117.5, 55.2, 40.1, 34.6, 32.0, 26.6, 22.8, 14.2. HRMS-ESI exact mass calcd. for C<sub>19</sub>H<sub>24</sub>N<sup>+</sup>([M+H]<sup>+</sup>) requires m/z 266.19033, found m/z 266.19040.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 6.3 min (minor), t<sub>R2</sub> = 7.0 min (major).

(S)-6-isobutyl-6,11-dihydro-5H-dibenzo[b,e]azepine: (New compound). Yellow oil, isolated yield 94%, 94% ee;  $[\alpha]_D^{25} = -122.7$ (S)-6f ( $c = 1.0, CHCl_3$ ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.22-7.16 (m, 4H), 7.00 (d, J = 7.6 Hz, 1H), 6.95-6.91 (m, 1H), 6.62-6.59 (m, 1H), 6.43 (d, J = 7.6 Hz, 1H), 5.01-4.98 (m, 1H), 4.73 (d, J = 15.2 Hz, 1H), 3.66 (d, J = 15.2 Hz, 1H), 1.93-1.78 (m, 3H), 1.03-1.01 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 145.5, 140.0, 139.7, 130.6, 128.4, 127.6, 127.0, 124.3, 123.2, 118.3, 117.6, 52.6, 43.5, 40.2, 24.9, 23.5, 22.4. HRMS-ESI exact mass calcd. for  $C_{18}H_{22}N^+([M+H]^+)$  requires m/z 252.17468, found m/z 252.17479.

The enantiomeric excess was determined by HPLC on a Chiralcel OD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 4.9 min (minor), t<sub>R2</sub> = 5.3 min (major).

(S)-6-benzyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine: (New compound). Yellow oil, isolated yield 98%, 91% ee;  $\left[\alpha\right]_{D}^{25} = -105.2$  (c ́Вп =1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.37-7.19 (m, (S)-**6g** 9H), 7.01 (d, J = 7.2 Hz, 1H), 6.90-6.88 (m, 2H), 6.65-6.63 (m, 1H), 6.36 (d, J = 8.0 Hz, 1H), 5.14 (dd,  $J_1 = 22.2$  Hz,  $J_2 = 4.0$  Hz, 1H), 4.50 (d, J = 15.2 Hz, 1H), 3.87 (d, J= 14.8 Hz, 1H), 3.36-3.32 (m, 1H), 3.18-3.12 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 145.7, 139.5, 139.5, 138.6, 130.1, 129.4, 128.9, 128.7, 127.8, 127.5, 127.1, 126.9, 125.7, 125.3, 119.0, 118.2, 57.4, 42.0, 40.1. HRMS-ESI exact mass calcd. for  $C_{21}H_{20}N^{+}([M+H]^{+})$  requires m/z 286.15903, found m/z 286.15917.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$ = 220 nm), t<sub>R1</sub> = 7.2 min (minor), t<sub>R2</sub> = 8.3 min (major).

### (S)-3-chloro-6-methyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine:

(Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, Org. Lett. 2017, 19, 3855). Yellow solid, isolated yield (S)-**6h** 98%, 84% ee;  $[\alpha]_D^{25} = -16.2$  (*c* =1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.27-7.20 (m, 4H), 6.88 (d, J = 8.0 Hz, 1H), 6.53 (d, J = 8.0 Hz, 1H), 6.36 (S, 1H), 5.20 (d, J = 6.8 Hz, 1H), 4.75 (d, J = 14.8, Hz, 1H), 3.48 (d, J = 15.2 Hz, 1H), 1.60 (d, J = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>);  $\delta$  (ppm) 146.6, 139.9, 139.3, 132.8, 131.5, 128.1, 128.0, 127.3, 127.1, 123.6, 121.1, 117.8, 116.5, 49.5, 39.4, 19.9.

The enantiomeric excess was determined by HPLC on a Chiralcel AS-H column (*n*-hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda$  = 254 nm), t<sub>R1</sub> = 9.7 min (major), t<sub>R2</sub> = 10.8 min (minor).

(S)-8-isopropyl-6-methyl-6,11-dihydro-5*H*-dibenzo[*b*,*e*]azepine: (Known compound, see: P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, *Org. Lett.* **2017**, *19*, 3855). Yellow oil, isolated yield 98%, 76% ee;  $[\alpha]_D^{25} = -69.2$  (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.15-7.13 (m, 1H), 7.07-7.06 (m, 2H), 6.99 (d, J = 7.2 Hz, 1H), 6.94-6.91 (m, 1H), 6.62-6.58 (m, 1H), 6.43 (d, J = 8.0 Hz, 1H), 5.18 (d, J = 6.4 Hz, 1H), 4.76 (d, J = 11.2Hz, 1H), 3.55 (d, J = 11.2 Hz, 1H), 2.89-2.84 (m, 1H), 1.62 (d, J = 6.4 Hz, 3H), 1.23-1.22 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 147.6, 145.6, 140.2, 137.0, 130.4, 128.3, 127.5, 125.4, 123.7, 122.1, 118.4, 117.5, 118.2, 50.1, 39.6, 34.2, 24.3, 24.2, 20.3.

The enantiomeric excess was determined by HPLC on a Chiralcel AD-H column (*n*-hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at  $\lambda = 254$  nm), t<sub>R1</sub> = 6.9 min (minor), t<sub>R2</sub> = 7.4 min (major).
## 5. References

- (a) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem., Int. Ed.* **1997**, *36*, 285; (b) F. Chen, T. Wang, Z. Ding, Y. He, Z. Li, L. Xu, Q.-H. Fan, *Chem. Eur. J.* **2011**, *17*, 1109.
- 2. K. Gao, C.-B. Yu, W. Li, Y.-G. Zhou, X. Zhang, Chem. Commun. 2011, 47, 7845.
- R.-N. Guo, K. Gao, Z.-S. Ye, L. Shi, Y. Li, Y.-G. Zhou, Pure Appl. Chem. 2013, 85, 843.
- 4. P. Li, Y. Huang, X. Hu, X.-Q. Dong, X. Zhang, Org. Lett. 2017, 19, 3855.
- 5. J. Wang, Tetrahedron Lett. 2013, 54, 5956.

## 6. Copy of NMR spectra























































































































































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## 7. Copy of HPLC spectra









峌	保留时间	奀型	峰苋	峰囬枳	峰尚	峰田枳
#	[min]		[min]	[mAU*s]	[mAU]	Ŷ
1	6.604	MM	0.1627	4864.12891	498.13934	50.4540
2	7.639	MM	0.2014	4776.58398	395.33887	49.5460









峰	保留时间	奀型	哞苋	峰田积	峰尚	峰囬积
#	[min]		[min]	[mAU*s]	[mAU]	olo
	-					
1	5.824	MM	0.1642	3956.76465	401.62625	49.9313
2	2 7.165	MM	0.2260	3967.65991	292.63208	50.0687









峰	保留时间	奀型	峰苋	峰囬枳	峰局	峰囬枳
#	[min]		[min]	[mAU*s]	[mAU]	olo Olo
	-					
1	6.103	MM	0.1443	2829.76099	326.81302	49.1095
2	6.514	MM	0.1428	2932.38916	342.15329	50.8905









#	[min]		[min]	[mAU*s]	[mAU]	olo
1	6.556	VB R	0.1480	1735.50037	182.43024	50.8752
2	7.660	BB	0.1624	1675.78918	159.72038	49.1248





п	["""]		[m±n]	[10210 0]	[mri0]	0
·						
1	5.532	BV	0.1341	656.26013	74.26038	49.9608
2	6.109	VB	0.1468	657.28894	67.97305	50.0392





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#	[min]		[min]	[mAU*s]	[mAU]	ojo
	-					
1	6.219	BB	0.1205	1712.26758	220.83284	49.8881
2	2 7.221	BB	0.1650	1719.95007	161.82474	50.1119



1	6.219 MM	0.1343	1535.47925	190.55466	97.6928
2	7.238 MM	0.2002	36.26373	3.01918	2.3072



2 9.353 MM 0.2971 1670.71606 93.71886 49.9391





2 10.989 MM 0.3030 1.55930e4 857.83191 50.3339



2 11.178 MM 0.2868 1.13665e4 660.55127 97.9893



#	[min]		[min]	[mAU*s]	[mAU]	8
1	7.678	BB	0.1777	3211.87427	270.16354	50.0868
2	11.534	BB	0.2695	3200.73779	178.20679	49.9132



1	7.690	BB	0.1735	38.71240	3.35792	1.3029
2	11.566	BB	0.2716	2932.63623	162.49332	98.6971











信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
8.605	MM m	0.83	1787.60	146. 32	50. 31
9.323	MM m	0.90	1765.74	135.72	49.69
		总和	3553.35		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
8.607	MM m	0.34	22.50	2.47	0.24
9.326	MM m	1.06	9430.28	711.50	99.76
		总和	9452.77		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
7.373	MM m	0.90	1942.98	184. 50	49.92
8.452	MM m	1.13	1949.37	160.47	50.08
		总和	3892.36		



信号:	VWD1A, Wave	length=220 nm				
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	
7.367	MM m	1.10	8795.64	817.10	97.26	
8.454	MM m	0.59	247.92	21.19	2.74	
		总和	9043.56			



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
6.167	MM m	0.67	7770. 11	745.23	49.86
7.680	MM m	1.03	7813.31	635.68	50.14
		总和	15583.42		



信号:	VWD1A, Wave	VWD1A,Wavelength=220 nm						
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%			
6.166	MM m	0.85	11324.71	1079.29	96.28			
7.679	MM m	0.45	438.04	38.92	3.72			
		总和	11762.75					



信号:	VWD1A, Wave	length=220 nm				
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	
6.776	MM m	0.77	1497.09	151.66	49.69	
7.751	MM m	1.09	1515.85	134.38	50.31	
		总和	3012.93			



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
6.772	MM m	1.01	11417.29	1143.13	95.49
7.754	MM m	0.84	539.56	47.05	4.51
		总和	11956.85		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
5. 502	MM m	0.75	1702.73	151.64	50.39
6.159	MM m	0.78	1676.67	136.88	49.61
		总和	3379.41		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
5.498	MM m	0.86	28379.11	2509.57	95.18
6.158	MM m	0.83	1436.04	120. 51	4.82
		总和	29815.15		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
9.008	MM m	0.80	11732.21	799.54	49.96
9.816	MM m	0. 98	11748.67	786.66	50.04
		总和	23480.88		



信号:	VWD1A, Wave	length=220 nm				
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	
9.058	MM m	1.09	29551.95	1994. 70	92.46	
9.896	MM m	0.82	2409.56	159.24	7.54	
		总和	31961.51			



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
19.631	MM m	3.26	2282.56	53.31	49.91
23.051	MM m	3.91	2290.77	46.00	50.09
		总和	4573.33		



信号:	VWD1A,Wavelength=220 nm					
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	
19.474	MM m	3.98	6865.43	157.02	99.44	
23.234	MM m	2.02	38.64	0.83	0.56	
		总和	6904.07			



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
10.097	MM m	1.42	1277.72	88.44	50.06
11.938	MM m	1.73	1274.80	70.35	49.94
		总和	2552. 52		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
10.080	MM m	1.50	9074.34	615.58	99.51
11.922	MM m	0.97	44.27	2.46	0.49
		总和	9118. 61		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
6.532	MM m	1.03	26507.74	2234.98	50.43
7.737	MM m	1.13	26054.62	2177.64	49.57
		总和	52562.35		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
6.516	MM m	0.73	546.81	24.88	1.03
7.725	MM m	1.44	52777.68	4094.50	98.97
		总和	53324.49		



信号: VWD1A,Wavelength=220 nm					
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
7.652	MM m	0.54	1062.70	99. 07	49.49
8.063	MM m	0.61	1084.51	92.75	50.51
		总和	2147.21		



信号:	VWD1A, Wave	length=220 nm				
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	
7.627	MM m	0.32	55. 03	5.66	0.39	
8.032	MM m	1.18	13916.96	1187.39	99.61	
		总和	13971.99			



信号:	VWD1A, Wavelength=220 nm						
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%		
6.763	MM m	0.96	659.93	59.15	49.13		
8.648	MM m	1.12	683.23	50. 99	50.87		
		总和	1343. 16				



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
6.730	MM m	1.30	2947.21	285. 28	97.44
8.709	MM m	0.80	77.49	5. 30	2.56
		总和	3024.70		



信号:	VWD1A,Wavelength=220 nm						
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%		
6.897	MM m	0.67	625.58	55.68	49.68		
8.674	MM m	0.83	633. 53	48.13	50.32		
		总和	1259.10				



信号:	VWD1A, Wave	length=220 nm				
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	
6.897	MM m	1.07	13633.63	1216.81	98.04	
8.772	MM m	0.64	272.32	19.29	1.96	
		总和	13905.95			



峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	8
	·					
1	6.776	BB	0.1647	1312.09070	120.80309	50.2006
2	8.917	BB	0.1952	1301.60254	101.07877	49.7994



						-
1	6.760	MM	0.1678	603.81342	59.95949	6.6007
2	8.882	MM	0.2185	8543.84766	651.67072	93.3993



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
6.229	MM m	0.78	2270.95	242.56	49.46
7.570	MM m	1.11	2320.49	202.48	50.54
		总和	4591.43		



信号:	VWD1A, Wave	length=220 nm				
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	
6.237	MM m	0.52	1600.81	167.31	6.21	
7.581	MM m	2.51	24190.00	1891.09	93.79	
		总和	25790.81			



信号:	VWD1A,Wavelength=220 nm					
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	
6.554	BB	0.64	946.60	94.36	49.19	
7.882	MM m	0.95	977.67	81.23	50.81	
		总和	1924. 27			



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
6.557	MM m	0.48	1167.79	119.44	5.16
7.884	MM m	1.09	21443.56	1635.35	94.84
		总和	22611.35		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
5.989	MM m	0.77	1551.51	163.24	49.33
7.158	MM m	0.95	1593.52	142.19	50.67
		总和	3145.04		



信号:	VWD1A,Wavelength=220 nm				
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
5.996	MM m	0.39	1903.51	209.31	6.22
7.167	MM m	1.41	28676.92	2247.64	93.78
		总和	30580.43		



峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	90
	-					
1	6.397	MM	0.1453	1628.86328	186.80881	49.4538
	2 7.070	MM	0.1623	1664.84094	170.94958	50.5462






信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
7.199	MM m	1.07	14528.85	1046.43	49.77
8.328	MM m	1.12	14664.29	957.81	50.23
		总和	29193.14		



信号:	VWD1A, Wave	length=220 nm			
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%
7.225	MM m	0.51	689.75	62.38	4.72
8.347	MM m	1.80	13930.67	1021.18	95.28
		总和	14620.42		





