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## **Supporting Information**

## Enantioselective Synthesis of Axially Chiral Carbamates and Amides

### with Carbon Dioxide via Copper Catalysis

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#### A. General methods

All cyclic diaryliodonium salts 1 were synthesized according to previously described methods.<sup>1</sup> Ligand L1-L8 were purchased from DAICEL CHIRAL TECHNOLOGIES (CHINA) CO. LTD. Other reagents were obtained from commercial suppliers (Aldrich, TCI, Across, etc.) and used without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker AV 400 spectrometer using CDCl<sub>3</sub> or DMSO-*d6* as solvent and TMS as an internal standard. Reference values for residual solvents were taken as  $\delta = 7.26$  ppm (CDCl<sub>3</sub>), 2.50 ppm (DMSO-*d6*) for <sup>1</sup>H NMR;  $\delta = 77.00$  ppm (CDCl<sub>3</sub>),  $\delta = 40.00$  ppm (DMSO-*d6*) for <sup>13</sup>C NMR. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants were given in Hertz (Hz). IR spectra were obtained as potassium bromide pellets between two potassium bromide pellets with a spectrometer. The data of HRMS was determined on a high-resolution mass spectrometer (LCMS-IT-TOF). X-ray structural analyses were conducted on an x-ray analysis instrument. Reactions were monitored by thin-layer chromatography (TLC) using UV light. Chiral HPLC analyses were performed on an Aglient 1200 system.

#### B. General procedure for the synthesis of axially chiral carbamates

To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added 1 (0.10 mmol),  $Cu(OTf)_2$  (36.0 mg, 0.01 mmol), L6 (36.0 mg, 0.01 mmol) and  $Na_2CO_3$  (15.9 mg, 0.15 mmol) successively. The Schlenk tube was capped with a rubber septum, evacuated and backfilled with 1 atm CO<sub>2</sub>. This evacuation/backfill sequence was repeated three times. Then, a solution of 2 in anhydrous 1,4-dioxane (0.167 M, 1.5 mL, 0.25 mmol) was added to the vessel by syringe through the rubber septum cap. The mixture was then stirred at 40 °C in an oil bath for 12 h. After the reaction was completed, the reaction mixture was cooled to room temperature, filtered through a plug of celite and washed with ethyl acetate. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to give the desired product.

#### C. General procedure for the synthesis of axially chiral amides

To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added 1 (0.10 mmol),  $Cu(OTf)_2$  (36.0 mg, 0.01 mmol), L6 (36.0 mg, 0.01 mmol),  $Na_2CO_3$  (15.9 mg, 0.15 mmol) successively. The Schlenk tube was capped with a rubber septum, evacuated and backfilled with 1 atm of CO<sub>2</sub>. This evacuation/backfill sequence was repeated three times. Then, a solution of 2 in anhydrous tetrahydrofuran (0.125 M, 2.0 mL, 0.25 mmol) was added to the vessel by syringe

through the rubber septum cap. The mixture was stirred at 40 °C in an oil bath for 12 h. Then, the reaction mixture was cooled to room temperature, evacuated and backfilled with nitrogen; this evacuation/backfill sequence was also repeated three times. After the reaction mixture was cooled to 0 °C, a solution of *n*-butyl lithium in hexane (2.5 M, 0.2 mL, 0.5 mmol) was added dropwise to the above mixture by a syringe. Then, the reaction mixture was allowed to warm to room temperature and stirred for 12 h. After the reaction was completed, the reaction mixture was quenched with 2 M HCl aqueous solution (6 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to give the desired product.

#### D. Optimization of the reaction conditions

	I <sup>+</sup> ŌTf + CO <sub>2</sub> (1atm	+ HNEt <sub>2</sub> <u>Cu(OTf)<sub>2</sub>/L6</u> base, solvent			o Ph
	1a	2a	3	L0	
Entry	Catalyst	Base	Solvent	Yield (%) <sup><i>b</i></sup>	ee (%) <sup>c</sup>
1	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	95 (92)	99
2	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	THF	94	99
3	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	65	98
4	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	MeCN	86	98
5	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	Toluene	70	98
6	Cu(OTf) <sub>2</sub>	DABCO	1,4-dioxane	56	82
7	Cu(OTf) <sub>2</sub>	Et <sub>2</sub> ONa	1,4-dioxane	63	97
8	Cu(OTf) <sub>2</sub>	t-BuOK	1,4-dioxane	64	93
9	Cu(OTf) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	58	97
$10^d$	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	81	98
11 <sup>e</sup>	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	77	97
12 <sup>f</sup>	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	90	98
13 <sup>g</sup>	Cu(OTf) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	95	98
14	CuSO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	89	95
15	Cu(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	84	96

Table S1. The influence of different solvents, bases and temperatures on the reaction<sup>a</sup>

<sup>*a*</sup> Reaction conditions: **1a** (0.10 mmol), **2a** (0.25 mmol), CO<sub>2</sub> (1 atm), base (1.5 equiv), Cu(OTf)<sub>2</sub> (0.01 mmol), L6 (0.01 mmol), solvent (anhydrous, 1.5 mL), 40 °C, 12 h. <sup>*b*</sup>Yields were determined by <sup>1</sup>H NMR using dibromomethane as internal standard. The number in parentheses is isolated yield. <sup>*c*</sup>Determined by chiral HPLC. <sup>*d*</sup>60 °C. <sup>*e*</sup>100 °C. <sup>*f*</sup>Base (2 equiv). <sup>*g*</sup>Base (1 equiv).

#### E. Gram-scale synthesis of compound 3

To a 100 mL oven-dried two-necked round flask containing a magnetic stir bar was added **1a** (5.0 mmol), Cu(OTf)<sub>2</sub> (0.5 mmol), **L6** (0.5 mmol) and Na<sub>2</sub>CO<sub>3</sub> (7.5 mmol) successively. The side-neck

was capped with a rubber septum and the central neck is connected with a  $CO_2$  balloon via a 3-way value. Then, the flask was evacuated and backfilled with  $CO_2$  through the 3-way value. Subsequently, a solution of diethylamine (**2a**) in anhydrous 1,4-dioxane (0.25 M, 50 mL, 12.5 mmol) was added to the flask by syringe through the rubber septum cap on the side-neck. The mixture was stirred at 40 °C in an oil bath for 12 h. After the reaction was completed, the reaction mixture was filtered through a plug of celite and washed with ethyl acetate. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the product **3** as a light yellow oil (1.94 g, 92%, 96% ee).

#### F. Gram-scale synthesis of compound 61

To a 50 mL oven-dried two-necked round flask containing a magnetic stir bar was added **1a** (1.7 mmol), Cu(OTf)<sub>2</sub> (0.17 mmol), **L6** (0.255 mmol) and Na<sub>2</sub>CO<sub>3</sub> (1.7 mmol) successively. The side-neck was capped with a rubber septum and the central neck is connected with a CO<sub>2</sub> balloon via a 3-way value. Then, the flask was evacuated and backfilled with CO<sub>2</sub> through the 3-way value. Subsequently, a solution of Sitagliptin in anhydrous MeCN (0.213 M, 20 mL, 4.25 mmol) was added to the flask by syringe through the rubber septum cap on the side-neck. The mixture was stirred at 40 °C in an oil bath for 12 h. After the reaction was completed, the reaction mixture was filtered through a plug of celite and washed with ethyl acetate. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as the eluent to give the product **61** as a light yellow oil (0.99 g, 77%, 97% de).

#### G. Procedures for the synthesis of compounds 91-104

a) Procedure for the synthesis of compound 91<sup>ref.1a</sup>



To a solution of styrene (12.5 mg, 0.12 mmol) in AcOH (2.0 mL) was added the mixture of **3** (0.1 mmol, 99% ee),  $Pd(OAc)_2$  (1.2 mg, 0.005 mmol), AgOAc (33.4 mg, 0.2 mmol) successively. The resulting mixture was stirred at 110 °C in an oil bath for 12 h under an atmosphere of N<sub>2</sub>. After the

reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product as a light yellow oil **91** (27.2 mg, 68%, 99% ee).

#### b) Procedure for the synthesis of compound 92 ref.2



To a solution of **3** (0.1 mmol, 99% ee) and trimethylsilylacetylene (24.5 mg, 0.25 mmol) in Et<sub>2</sub>NH (2.0 mL) was added the mixture of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (7.1 mg, 0.01 mmol) and CuI (3.8 mg, 0.02 mmol) successively. The resulting mixture was stirred at room temperature for 12 h under an atmosphere of N<sub>2</sub>. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give a light yellow oil (21.2 mg). Then, the light yellow oil was treated with HOAc (0.1 mL) and TBAF (0.2 mL) in THF (2.0 mL) at room temperature for 4 h. The reaction mixture was washed with water and then extracted (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, to subject the solvent under vacuum, the crude product (0.1 mL) and TBAF (0.2 mL) in THF (2.0 mL) at room temperature for 4 h. The reaction mixture was washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **92** as a light yellow oil (15.8 mg, 54%, 99% ee).

#### c) Procedure for the synthesis of compound 93 ref.2



To a solution of phenylacetylene (12.3 mg, 0.12 mmol) in *N*,*N*-diisopropylethylamine (2.0 mL) was added the mixture of **3** (0.1 mmol, 99% ee),  $Pd(PPh_3)_2Cl_2$  (3.6 mg, 0.005 mmol) and CuI (2.0 mg, 0.01 mmol) successively. The resulting mixture was stirred at 100 °C in an oil bath for 12 h

under an atmosphere of  $N_2$ . After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous  $Na_2SO_4$ , and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **93** as a light yellow oil (19.1 mg, 48%, 99% ee).

#### d) Procedure for the synthesis of compound 94<sup>ref.1a</sup>



To a solution of **3** (0.1 mmol, 99% ee) in DMF (2.0 mL) was added the mixture of phenylboronic acid (18.3 mg, 0.15 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (11.6 mg, 0.01 mmol) and K<sub>2</sub>CO<sub>3</sub> (20.8 mg, 0.15 mmol) successively. The resulting mixture was stirred at 110 °C in an oil bath for 16 h under an atmosphere of N<sub>2</sub>. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **94** as a light yellow oil (30.6 mg, 82%, 99% ee).

#### e) Procedure for the synthesis of compound 95<sup>ref.4</sup>



To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added **3** (0.1 mmol),  $Pd(OAc)_2$  (1.2 mg, 0.005 mmol), 1,1'-ferrocenediyl-bis(diphenylphosphine) (dppf) (5.6 mg, 0.01 mmol), methanol (2.0 mL) and *N*,*N*-diisopropylethylamine (25.9 mg, 0.2 mmol) successively. The tube was then evacuated and refilled with CO (1 atm) three times. The resulting mixture was stirred at 80 °C in an oil bath for 18 h. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered.

After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as the eluent to give the desired product as a light yellow oil **95** (23.1 mg, 65%, 99% ee).

#### f) Procedure for the synthesis of compound 96<sup>ref.3</sup>



To a solution of **3** (0.1 mmol, 99% ee) in NMP (2 ml) was added CuCN (13.4mg, 0.15 mmol). The resulting mixture was heated at reflux in an oil bath for 12 h under an atmosphere of N<sub>2</sub>. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as the eluent to give the desired product **96** as a light yellow oil (28.6 mg, 89%, 99% ee).

#### g) Procedure for the synthesis of compound 97 ref.7



To a 25 mL oven-dried Schlenk tube was charged with **3** (0.1 mmol, 99% ee), phenylglyoxylic acid (19.7 mg, 0.12 mmol), Pd(OAc)<sub>2</sub> (1.2 mg, 0.005 mmol), (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (34.2 mg, 0.15 mmol), DCE (2.0 mL) and TfOH (2  $\mu$ L, 0.02 mmol) successively. The tube was then sealed and the reaction mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **97** as a white solid (47.4 mg, 90%, 98% ee).

#### h) Procedure for the synthesis of compound 98 ref.5



To a solution of **3** (0.1 mmol, 99% ee) in EtOH (2.0 mL) was added NaOH (1 mmol). The resulting mixture was heated under reflux in an oil bath for 24 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched with 2 M HCl aqueous solution and then extracted with ethyl acetate (10 mL×3). The combined organic phase was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **98** as a light yellow oil (28.8 mg, 89%, 98% ee).

#### i) Procedure for the synthesis of compound 99 ref.1a



To a solution of **98** (0.1 mmol, 98% ee) in DMSO/H<sub>2</sub>O (2 mL, v/v = 1:1) was added the mixture of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (2.0 mg, 0.01 mmol), D-glucose (3.6 mg, 0.02 mmol), KOH (33.7 mg, 0.6 mmol) successively. The resulting mixture was stirred at 110 °C in an oil bath for 12 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched with 2 M HCl aqueous solution, and then extracted with ethyl acetate (10 mL×3). The combined organic phase was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **99** as a white solid (12.8 mg, 60%, 97% ee).

#### j) Procedure for the synthesis of compound 100 ref.6



To a solution of **3** (0.1 mmol, 99% ee) in toluene (2.0 mL) was added the mixture of aniline (14  $\mu$ L, 0.15 mmol), Pd(OAc)<sub>2</sub> (1.13 mg, 0.005 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (97.7 mg, 0.30 mmol) successively. The resulting mixture was stirred at 110 °C in an oil bath for 16 h under an atmosphere of N<sub>2</sub>. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **100** as a light yellow oil (15.5 mg, 40%, 96% ee).

#### k) Procedure for the synthesis of compound 101 ref.5



To a solution of **100** (0.1 mmol) in EtOH (2.0 mL) was added NaOH (10 equiv). The resulting mixture was heated under reflux in an oil bath for 12 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched with 2 M HCl aqueous solution, and then extracted with ethyl acetate (10 mL×3). The combined organic phase was washed with water, dried over anhydrous  $Na_2SO_4$ , and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **101** as a white solid (23.1 mg, 80%, 99% ee).

#### 1) Procedure for the synthesis of compound 102



To a 25 mL oven-dried Schlenk tube containing a magnetic stir bar was added 74 (0.1 mmol, 99% ee) and THF (2 mL) successively. Then, a solution of LiAlH<sub>4</sub> in THF (2.5 M, 0.2 mL, 0.5mmol) was added dropwise to the above mixture by a syringe under an atmosphere of  $N_2$  at 0 °C. After the addition, the resulting mixture was allowed to warm to room temperature, and then heated under reflux for 12 h. After the reaction was completed, saturated NH<sub>4</sub>Cl aqueous solution was

added to quench the reaction and followed by extraction of an organic layer with EtOAc ( $3 \times 10$  mL). The combined organic phase was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as the eluent to give the desired product **102** as a colorless liquid (27.4 mg, 97%, 52% ee).

#### m) Procedure for the synthesis of compound 103



To a 25 mL oven-dried Schlenk tube containing a magnetic stir bar was added **85** (0.1 mmol, 99% ee) and THF (2 mL) successively. Then, a solution of LiAlH<sub>4</sub> in THF (2.5 M, 0.2 mL, 0.5mmol) was added dropwise to the above mixture by a syringe under an atmosphere of N<sub>2</sub> at 0 °C. After the addition, the resulting mixture was allowed to warm to room temperature, and then heated under reflux for 12 h. After the reaction was completed, saturated NH<sub>4</sub>Cl aqueous solution was added to quench the reaction and followed by extraction of an organic layer with EtOAc (3 ×10 mL). The combined organic phase was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as the eluent to give the desired product **103** as a as light yellow oil (25.3 mg, 82%, >99% ee).

#### n) Procedure for the synthesis of compound 104 ref.8



To a solution of **74** (0.1 mmol, 99% ee) in DMF (2 mL) was added the mixture of phenyl trifluoromethanesulfonate (0.15 mmol) and  $K_2CO_3$  (0.2 mmol). The reaction mixture was stirred at room temperature for 6 h. After the reaction was completed, the reaction was diluted with water, and extracted with EtOAc (3 ×10 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **104** as a white solid (21.4 mg, 50%, 99% ee).

#### H. Analytical data

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl diethylcarbamate (3)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 41.8mg, 99% yield, 99% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 2:98, flow: 0.8 mL/min,  $\lambda = 254$  nm,  $t_r = 8.351$  min (major), 8.989 min (minor).  $[\alpha]^{25}_{D} = -48.75$  (c 0.28, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.75 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 7.6 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 3.21 – 3.16 (m, 2H), 3.02 – 2.86 (m, 2H), 2.05 (s, 3H), 1.99 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H), 0.74 (t, J = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.3, 148.3, 141.6, 138.8, 137.0, 136.3, 136.2, 129.7, 129.0, 128.4, 126.5, 120.3, 101.2, 41.9, 41.5, 21.2, 19.4, 13.5, 13.1. HRMS-ESI (m/z): calcd for C<sub>19</sub>H<sub>23</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 424.0768, found 424.0763.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl dimethylcarbamate (4)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 21.7 mg, 55% yield, 95% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 3: 97, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 11.606 min (major), 11.036 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -56.71 (c 0.16, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.76 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.2 Hz, 2H), 7.15 (d, J = 7.2 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 2.81 (s, 3H), 2.54 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.0, 148.3, 141.4, 138.7, 137.0, 136.2(2), 136.1(9), 129.6, 129.0, 128.4, 126.7, 120.3, 101.1, 36.4, 35.8, 21.2, 19.3. HRMS-ESI (*m*/*z*): calcd for C<sub>17</sub>H<sub>18</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 396.0455, found 396.0456.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl dipropylcarbamate (5)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 42.8 mg, 95% yield, 98% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 1:99, flow: 0.6 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 12.278 min (major), 14.186 min (minor).  $[\alpha]^{25}_{D}$ = -59.34 (c 0.18, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.91 – 2.84 (m, 1H), 2.78 – 2.71 (m, 1H), 2.03 (s, 3H), 1.98 (s, 3H), 1.49 – 1.44 (m, 2H), 1.24 – 1.16 (m, 1H),

1.07 - 0.98 (m, 1H), 0.80 (t, J = 7.2 Hz, 3H), 0.67 (t, J = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.8, 148.3, 141.6, 138.7, 136.9, 136.3, 136.2, 129.7, 128.9, 128.3, 126.5, 120.5, 101.2, 49.3, 49.1, 21.5, 21.2, 21.1, 19.4, 11.2, 11.0. HRMS-ESI (*m/z*): calcd for C<sub>21</sub>H<sub>27</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 452.1081, found 452.1080.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl diisopropylcarbamate (6)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 22.1 mg, 49% yield, 98% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 1:99, flow: 0.6 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 29.180 min (major), 27.905 min (minor).  $[\alpha]^{25}_{D}$  = -57.63 (c 0.20,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.15 – 7.12 (m, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 3.71 (s, 2H), 2.06 (s, 3H), 1.98 (s, 3H), 1.18 – 1.07 (m, 6H), 0.86 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.5, 148.4, 141.6, 139.0, 137.0, 136.5, 136.3, 129.7, 129.0, 128.3, 126.5, 120.8, 101.5, 46.4, 45.9, 21.2, 20.7, 20.5, 20.4, 20.3, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>21</sub>H<sub>27</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 452.1081, found 452.1084.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl diallylcarbamate (7)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 38.0 mg, 85% yield, 98% ee. HPLC conditions: Chiralpak OD-H and AD-H, isopropanol/hexanes = 1:99, flow: 0.6 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 32.429 min (major), 35.268 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -56.32 (c 0.26, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.18 (d, J = 8.8 Hz, 1H), 6.95 (t, J = 8.0 Hz, 1H), 5.69 – 5.60 (m, 1H), 5.34 – 5.26 (m, 1H), 5.09 (d, J = 10.4 Hz, 1H), 5.01 – 4.90 (m, 3H), 3.78 (d, J = 4.8 Hz, 2H), 3.49 (d, J = 5.2 Hz, 2H), 2.04 (s, 3H), 2.00 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.5, 148.2, 141.4, 138.8, 137.1, 136.4, 136.3, 132.9, 129.7, 129.0, 128.4, 126.8, 120.4, 116.9, 116.6, 101.1, 48.8, 48.7, 21.2, 19.3. HRMS-ESI (m/z): calcd for C<sub>21</sub>H<sub>23</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 448.0768, found 448.0770.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl dibutylcarbamate (8)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 41.2 mg, 86% yield, 94% ee. HPLC conditions: Chiralpak RR, isopropanol/hexanes = 1:99, flow: 0.6 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 12.214 min (major), 13.438 min (minor).  $[\alpha]^{25}_{D} = -54.79$  (c 0.19, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.78 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 3.17 (td, J = 7.2, 3.2 Hz, 2H), 2.97 – 2.90 (m, 1H), 2.85 – 2.78 (m, 1H), 2.06 (s, 3H), 2.00 (s, 3H), 1.48 – 1.40 (m, 2H), 1.28 – 1.19 (m, 3H), 1.16 – 1.09 (m, 3H), 0.91 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.8, 148.3, 141.6, 138.7, 136.9, 136.3(0), 136.2(6), 129.7, 128.9, 128.4, 126.5, 120.5, 101.2, 47.2, 47.1, 30.4, 29.9, 21.2, 20.0, 19.8, 19.4, 13.8. HRMS-ESI (m/z): calcd for C<sub>23</sub>H<sub>31</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 480.1394, found 480.1394.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl dibenzylcarbamate (9)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 41.8mg, 76% yield, 99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 1:99, flow: 0.8 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 52.213 min (major), 49.923 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -40.06 (c 0.31, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.25 – 7.22 (m, 4H), 7.19 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 6.0 Hz, 2H), 6.97 – 6.93 (m, 3H), 4.38 (q, J = 14.8 Hz, 2H), 4.07 (q, J = 15.6 Hz, 2H), 2.07 (s, 3H), 2.02 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.4, 148.2, 141.3, 138.9, 137.3, 136.9, 136.5, 136.4, 129.8, 129.1, 128.6, 128.5(2), 128.4(8), 127.9, 127.8, 127.3, 127.3, 127.1, 120.5, 100.0, 49.1, 49.0, 21.3, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>29</sub>H<sub>27</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 548.8081, found 548.8082.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl methyl(propyl)carbamate (10)

Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 33.8mg, 80% yield, 98% ee. HPLC conditions: Chiralpak OJ-H, isopropanol/hexanes = 1:99, flow: 0.5 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 13.810 min (major), 16.844 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=-58.19 (c 0.18, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.2 Hz, 2H), 7.16 – 7.13 (m, 1H), 6.93 (t, J = 8.0 Hz, 1H), 3.22 – 2.50 (m, 5H), 2.04 (s, 3H), 2.00 – 1.98 (m, 3H), 1.44 – 0.97 (m, 2H), 0.77 (t, J = 7.2 Hz, 1H), 0.64 (t, J = 7.2 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.8, 148.3, 148.2, 141.6, 141.4, 138.8, 138.6, 137.0, 136.3, 136.2, 129.6, 128.9, 128.4(0), 128.3(7), 126.7, 126.5, 120.6, 120.1, 101.1(4), 101.1(1), 50.8, 50.5, 34.7, 33.7, 21.3, 21.2, 20.7, 20.3, 19.3, 10.9, 10.8. HRMS-ESI (m/z): calcd for C<sub>19</sub>H<sub>23</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 424.0768, found 424.0767.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl ethyl(propyl)carbamate (11)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 32.3 mg, 74% yield, 98% ee. HPLC conditions: Chiralpak OD-H and AD-H, isopropanol/hexanes = 1:99, flow: 0.8 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 19.120 min (major), 21.559 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -57.02 (c 0.24, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.14 (d, J = 7.6 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 3.22 – 3.08 (m, 2H), 3.02 – 2.71 (m, 2H), 2.04 (s, 3H), 1.98 (s, 3H), 1.48 – 1.43 (m, 1H), 1.24 – 1.16 (m, 1H), 1.02 (t, J = 6.8 Hz, 2H), 0.82 – 0.65 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.4, 148.3, 141.6, 138.7, 136.9, 136.3, 136.2, 129.7, 128.9, 128.4, 126.5, 120.4, 101.2, 48.7, 48.6, 42.4, 42.0, 21.6, 21.2, 19.4, 13.3, 13.0, 11.1. HRMS-ESI (m/z): calcd for C<sub>20</sub> H<sub>25</sub> INO<sub>2</sub> [M + H]<sup>+</sup>: 438.0924, found 438.0924.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl benzyl(isopropyl)carbamate (12)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 41.9 mg, 84% yield, 99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 4:96, flow: 0.8 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 10.353 min (major), 10.915 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -61.89 (c 0.31, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (t, J = 8.4 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.25 – 7.11 (m, 6H), 7.02 – 6.93 (m, 2H), 4.46 – 4.29 (m, 1H), 4.12 – 3.90 (m, 2H), 2.09 – 1.99 (m, 6H), 1.07 – 1.00 (m, 3H), 0.90 – 0.74 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.5, 148.3, 141.4, 139.2, 138.9, 137.1, 136.4, 129.7, 129.0, 128.5, 128.2, 127.1, 126.8, 126.7, 126.6, 120.6, 120.5, 101.3, 48.9, 47.0, 21.3, 20.8, 20.0, 19.4. HRMS-ESI (m/z): calcd for C<sub>25</sub>H<sub>27</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 500.1081, found 500.1080.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl ethyl(isopropyl)carbamate (13)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 30.6 mg, 70% yield, 92% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 2:98, flow: 0.5 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 11.247 min (major), 12.092 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -53.93 (c 0.28, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>): δ 7.75 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz,

2H), 7.14 (d, J = 7.6 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 4.17 – 3.84 (m, 1H), 3.20 – 3.04 (m, 1H), 2.89 – 2.70 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.02 – 0.93 (m, 6H), 0.79 – 0.76 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.4, 148.4, 141.6, 138.8, 136.9, 136.3, 129.6, 128.9, 128.4, 126.5, 120.5, 101.3, 99.9, 47.8, 37.3, 21.2, 20.7, 20.3, 19.4, 15.3. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>25</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 438.0924, found 438.0923.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl benzyl(methyl)carbamate (14)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 36.1 mg, 78% yield, >99% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 5:95, flow: 0.6 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 15.920 min (major), 16.605 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -53.14 (c 0.21, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 – 7.71 (m, 1H), 7.38 – 7.34 (m, 1H), 7.34 – 7.28 (m, 1H), 7.23 – 7.16 (m, 5H), 7.03 (d, J = 6.4 Hz, 1H), 6.95 – 6.86 (m, 2H), 4.52 – 4.06 (m, 2H), 2.77 (s, 1.4 H), 2.49 (s, 1.6 H), 2.06 (s, 3H), 2.02 – 1.99 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.4, 153.8, 148.2, 141.3(3), 141.2(6), 138.8, 138.6, 137.1(3), 137.0(8), 136.9, 136.8, 136.5, 136.4, 136.3, 136.1, 129.7, 129.1, 129.0, 128.5, 128.4(4), 128.3(8), 127.5, 127.2, 127.0, 126.7, 101.1, 52.4, 33.9, 33.4, 21.3, 21.2, 19.3(5), 19.3(3). HRMS-ESI (*m*/*z*): calcd for C<sub>23</sub>H<sub>23</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 472.0768, found 472.0771.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl cyclohexyl(methyl)carbamate (15)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 31.9 mg, 69% yield, 95% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 7:93, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 5.925 min (major), 6.443 min (minor).  $[\alpha]^{25}_{D}$ = -44.40 (c 0.25, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.15 (d, J = 7.6 Hz, 1H), 6.92 (t, J = 8.0 Hz, 1H), 3.83 – 3.45 (m, 1H), 2.70 (s, 2 H), 2.34 (s, 1 H), 2.03 (s, 3H), 1.98 (s, 3H), 1.73 – 1.56 (m, 4H), 1.49 – 1.17 (m, 4H), 1.13 – 0.95 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.6, 148.2, 141.6, 138.7, 136.9, 136.3, 129.7, 128.9, 128.4, 126.6, 120.7, 120.5, 101.1, 55.5, 55.0, 30.3, 30.0, 28.5, 25.7, 25.4, 21.3, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>22</sub> H<sub>27</sub> INO<sub>2</sub> [M + H]<sup>+</sup>: 464.1081, found 464.1080.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl methyl(naphthalen-1-ylmethyl)carbamate (16)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 44.3 mg, 85% yield, 96% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 16.709 min (major), 17.838 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -49.36 (c 0.31,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.01 (d, J = 8.0 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.80 – 7.72 (m, 2H), 7.53 – 7.28 (m, 5H), 7.21 – 7.00 (m, 3H), 6.94 – 6.65 (m, 1H), 4.94 – 4.58 (m, 2H), 2.84 (s, 1.2 H), 2.51 (s, 1.8 H), 2.07 – 1.96 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.2, 154.0, 148.3, 141.4, 141.2, 138.8, 138.4, 137.2, 136.5, 136.3, 133.8, 133.7, 132.2, 132.1, 131.6, 131.1, 129.7, 129.6, 129.0, 128.9, 128.7, 128.6, 128.5, 128.2, 127.8, 127.0, 126.7, 126.5, 126.2, 125.8, 125.7, 125.5, 125.2, 124.1, 123.5, 122.8, 120.6, 119.8, 101.2, 100.9, 50.4, 50.1, 34.5, 33.4, 21.3, 19.4. HRMS-ESI (*m*/*z*): calcd for C<sub>27</sub>H<sub>25</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 522.0924, found 522.0930.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl methyl(phenethyl)carbamate (17)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 30.1 mg, 62% yield, 95% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 12.538 min (major), 11.416 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -44.81 (c 0.24,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.79 – 7.71 (m, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.25 – 7.11 (m, 6H), 7.06 (d, J = 6.8 Hz, 1H), 6.98 – 6.85 (m, 1H), 3.45 – 3.02 (m, 2H), 2.73 – 2.27 (m, 5H), 2.08 – 2.05 (m, 3H), 2.00 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.8, 153.7, 148.2, 148.1, 141.5, 141.4, 138.9, 138.8, 138.7, 137.1, 137.0, 136.4(1), 136.3(5), 136.3, 136.2, 129.8, 129.7, 129.1, 129.0, 128.9, 128.8, 128.4(2), 128.3(5), 126.8, 126.7, 126.2, 120.5, 120.4, 101.2(2), 101.1(6), 51.2, 51.1, 35.5, 34.6, 34.2, 33.8, 21.3, 21.2, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>24</sub>H<sub>25</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 486.0924, found 486.0923.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl pyrrolidine-1-carboxylate (18)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 31.2 mg, 74% yield, 96% ee. mp: 70-71 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 7:93, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 10.574 min (major), 11.335 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -42.58 (c 0.26, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.14 (d, J = 7.6 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 3.33 – 3.20 (m, 2H), 3.04 – 2.99 (m, 1H), 2.82 – 2.76 (m, 1H), 2.05 (s, 3H), 2.00 (s, 3H), 1.76 – 1.61 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 152.3, 148.3, 141.6, 138.8, 137.0, 136.2(2), 136.1(8), 129.6, 128.9, 128.5, 126.6, 120.3, 101.2, 46.0, 45.7, 25.5, 24.8, 21.3, 19.4. HRMS-ESI (*m*/*z*): calcd for C<sub>19</sub>H<sub>21</sub> INO<sub>2</sub> [M + H]<sup>+</sup>: 422.0611, found 422.0609.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl piperidine-1-carboxylate (19)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 21.8 mg, 50% yield, >99% ee. mp: 90-91 °C. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 0.5:99.5, flow: 0.5 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 37.774 min (major), 33.173 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -33.33 (c 0.13, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.19-7.14 (m, 2H), 6.93 (t, J = 7.6 Hz, 1H), 3.41 – 3.35 (m, 1H), 3.23 – 3.11 (m, 2H), 3.05 – 2.99 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.48 – 1.42 (m, 3H), 1.33 – 1.21 (m, 2H), 1.02 – 0.89 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.8, 148.3, 141.5, 138.9, 137.0, 136.4, 136.3, 129.6, 128.9, 128.5, 126.7, 120.6, 101.2, 45.3, 45.0, 25.5, 24.2, 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>20</sub> H<sub>23</sub> INO<sub>2</sub> [M + H]<sup>+</sup>: 436.0768, found 436.0768.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl azepane-1-carboxylate (20)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 37.7 mg, 84% yield, 98% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 1:99, flow: 0.6 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 19.936 min (major), 23.159 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -39.39 (c 0.30, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.15 (d, J = 7.2 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 3.49 – 3.43 (m, 1H), 3.26 – 3.18 (m, 2H), 3.02 – 2.95 (m, 1H), 2.05 (s, 3H), 1.98 (s, 3H), 1.61 – 1.58 (m, 2H), 1.46 – 1.38 (m, 1H), 1.33 – 1.25 (m, 3H), 1.21 – 1.06 (m, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.7, 148.3, 141.6, 138.8, 137.0, 136.3(3), 136.3(1), 129.7, 129.0, 128.4, 126.6, 120.5, 101.2, 47.2, 46.9, 28.0, 27.9, 27.0, 26.5, 21.3, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>21</sub>H<sub>25</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 450.0924 , found 450.0924.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 6-azaspiro[2.5]octane-6-carboxylate (21)



Eluent: 5:1 petroleum ether / ethyl acetate; white solid, 17.5 mg, 38% yield, 98% ee. mp: 90-92 °C. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.302 min (major), 8.162 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -46.75 (c 0.15, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.15 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 8.0 Hz, 1H), 3.50 – 3.43 (m, 1H), 3.32 – 3.20 (m, 2H), 3.14 – 3.07 (m, 1H), 2.06 (s, 3H), 2.00 (s, 3H), 1.26 – 1.16 (m, 2H), 0.96 – 0.82 (m, 2H), 0.25 (s, 4H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.9, 148.3, 141.5, 138.9, 137.0, 136.4, 136.3, 129.7, 129.0, 128.5, 126.8, 120.6, 101.2, 44.3, 44.1, 34.7, 21.2, 19.3, 17.4, 11.3. HRMS-ESI (*m/z*): calcd for C<sub>22</sub>H<sub>25</sub>INO<sub>2</sub> [M+H]<sup>+</sup>: 462.0924, found 462.0921.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 3,4-dihydroisoquinoline-2(1H)-carboxylate (22)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 35.7 mg, 74% yield, 94% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 10:90, flow: 0.8 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> =

8.721 min (major), 10.127 min (minor).  $[\alpha]^{25}_{D} = -16.77$  (c 0.32,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.79 – 7.48 (m, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.24 – 7.15 (m, 4H), 7.14 – 6.62 (m, 4H), 4.53 (s, 1H), 4.24 (s, 1H), 3.70 – 3.43 (m, 1H), 3.34 (t, *J* = 4.8 Hz, 1H), 2.74 – 2.36 (m, 2H), 2.04 (s, 3H), 2.00 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.0, 152.9, 138.8, 138.7, 137.1(4), 137.1(2), 136.2(7), 136.2(6), 136.1(5), 136.1(3), 134.3, 134.2, 133.0, 132.9, 129.7, 129.5, 129.0, 128.9, 128.6(1), 128.5(5), 128.5, 126.9, 126.3(4), 126.2(9), 126.2(3), 126.2(0), 126.1, 126.0, 120.4, 45.8, 41.8, 41.5, 28.7, 28.4, 21.2(3), 21.1(7), 19.3. HRMS-ESI (*m/z*): calcd for C<sub>24</sub>H<sub>23</sub>INO<sub>2</sub> [M+H]<sup>+</sup>: 484.0768 , found 484.0765.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl morpholine-4-carboxylate (23)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 36.3 mg, 83% yield, 95% ee. mp: 109-110 °C. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 12.068 min (major), 10.957 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -40.89 (c 0.33, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.77 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.25 – 7.24 (m, 1H),

7.20 – 7.17 (m, 2H), 6.96 (t, J = 8.0 Hz, 1H), 3.62 – 3.55 (m, 1H), 3.45 – 3.31 (m, 4H), 3.11 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.7, 148.0, 141.3, 138.9, 137.2, 136.4, 136.3, 129.7, 129.2, 128.6, 127.1, 120.5, 101.1, 66.6, 66.2, 44.6, 44.1, 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>21</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 438.0561 , found 438.0562.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl thiomorpholine-4-carboxylate (24)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 38.9 mg, 86% yield, >99% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 2:98, flow: 0.6 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 15.747 min (major), 17.065 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -33.43 (c 0.36, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.78 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.93 (t, J = 8.0 Hz, 1H), 3.44 (t, J = 4.4 Hz, 4H), 2.94 – 2.89 (m, 2H), 2.77 – 2.72 (m, 2H), 2.05 (s, 3H), 1.96 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.5, 148.0, 141.3, 139.0, 137.2, 136.4, 136.3, 129.8, 129.2, 128.6, 127.1, 120.5, 101.1, 47.0, 46.5, 27.1, 26.9, 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>21</sub>INO<sub>2</sub>S [M + H]<sup>+</sup>: 454.0332, found 454.0331.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-phenylpiperazine-1-carboxylate (25)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 35.3 mg, 69% yield, 97% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 2:98, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 19.535 min (major), 20.633 min (minor).  $[\alpha]^{25}_{D}$  = -28.19 (c 0.34, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 7.21 – 7.16 (m, 3H), 6.92 – 6.84 (m, 4H), 3.59 – 3.43 (m, 2H), 3.28 (s, 2H), 3.10 (s, 1H), 2.89 – 2.83 (m, 2H), 2.52 (s, 1H), 2.04 (s, 3H), 1.99 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.6, 150.9, 148.0, 141.3, 138.9, 137.1, 136.3, 129.7, 129.2, 129.1, 128.6, 127.0, 120.5, 116.7, 101.1, 49.4, 49.1, 44.1, 43.7, 21.2, 19.3. HRMS-ESI (m/z): calcd for C<sub>25</sub>H<sub>26</sub>IN<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 513.1033, found 513.1038.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl butylcarbamate (26)



Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 30.0 mg, 71% yield, 97% ee. mp: 80-81 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 6.440

min (major), 5.965 min (minor).  $[\alpha]^{25}_{D}$  = -46.78 (c 0.30, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.76 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 8.0 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 4.62–4.52 (m, 1H), 3.10–2.83 (m, 2H), 2.05 (s, 3H), 1.98 (s, 3H), 1.39– 1.11 (m, 4H), 0.89–0.80 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.1, 147.9, 141.2, 138.8, 137.2, 136.5, 136.3, 129.7, 129.0, 128.5, 126.9, 120.5, 101.0, 40.6, 31.7, 21.2, 19.6, 19.4, 13.7. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>23</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 424.0768, found 424.0763.

#### (*R*)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl pentylcarbamate (27)



Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 29.3 mg, 67% yield, 90% ee. mp: 57-58 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 6.398 min (major), 5.916 min (minor).  $[\alpha]^{25}_{D}$  = -45.45 (c 0.29,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 7.6 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 4.63 – 4.50 (m, 1H), 3.09 – 2.81 (m, 2H), 2.05 (s, 3H), 1.98 (s, 3H), 1.41 – 1.15 (m, 6H), 0.88 (t, J = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.0, 147.9, 141.2, 138.8, 137.2, 136.5, 136.3, 129.7, 129.0, 128.5, 126.9, 120.5, 101.0, 40.9, 29.3, 28.6, 22.2, 21.2, 19.4, 13.9. HRMS-ESI (m/z): calcd for C<sub>20</sub> H<sub>25</sub> INO<sub>2</sub> [M+H]<sup>+</sup> 438.0924, found 438.0919.

#### (*R*)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl tert-butylcarbamate (28)



Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 31.3 mg, 74% yield, 97% ee. mp: 61-63 °C. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 1:99, flow: 0.6 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 14.800

min (major), 13.779 min (minor).  $[\alpha]^{25}_{D} = -51.94$  (c 0.31, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.16 – 7.11 (m, 2H), 6.94 (t, J = 7.6 Hz, 1H), 4.53 (s, 1H), 2.06 (s, 3H), 1.99 (s, 3H), 1.19 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.2, 147.9, 141.2, 138.9, 137.2, 136.7, 136.3, 129.7, 128.9, 128.4, 126.9, 120.8, 101.1, 50.4, 28.5, 21.2, 19.4. HRMS-ESI (m/z): calcd for C<sub>19</sub>H<sub>23</sub> INO<sub>2</sub> [M + H]<sup>+</sup>: 424.0768, found 424.0760.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl cyclohexylcarbamate (29)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 38.3 mg, 85% yield, 96% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 9.833 min

(major), 10.594 min (minor).  $[\alpha]^{25}_{D} = -44.65$  (c 0.38, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.23 – 7.12 (m, 3H), 6.94 (t, J = 8.0 Hz, 1H), 4.51 – 4.34 (m, 1H), 3.40 – 2.96 (m, 1H), 2.05 (s, 3H), 1.98 (s, 3H), 1.89 – 1.70 (m, 2H), 1.62-1.54 (m, 2H), 1.33-0.91 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.2, 148.0, 141.1, 138.8, 137.2, 136.5, 136.3, 129.7, 129.0, 128.5, 126.9, 120.6, 101.1, 49.8, 33.3, 32.9, 25.4, 24.9, 24.7, 21.2. HRMS-ESI (*m/z*): calcd for C<sub>21</sub>H<sub>25</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 450.0924, found 450.0917.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl pentan-3-ylcarbamate (30)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 33.2 mg, 76% yield, 96% ee. mp: 88-89 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 5.339 min

(major), 5.739 min (minor).  $[\alpha]^{25}_{D}$  = -51.86 (c 0.32, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.22 – 7.12 (m, 3H), 6.93 (t, J = 7.6 Hz, 2H), 4.33 – 4.12 (m, 1H), 3.39 – 2.98 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.50 – 1.16 (m, 4H), 0.85 (t, J = 7.6 Hz, 3H), 0.69 (t, J = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.9, 147.9, 141.2, 138.8, 137.2, 136.7, 136.3, 129.7, 129.0, 128.4, 126.9, 120.8, 101.0, 54.1, 27.6, 27.4, 21.2, 19.4, 10.1, 9.8. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>25</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 438.0924, found 438.0919.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (cyclopropylmethyl)carbamate (31)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 31.2 mg, 74% yield, 96% ee. mp: 75-77 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 7:93, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 8.367 min

(major), 7.809 min (minor).  $[\alpha]^{25}_{D}$ = -45.83 (c 0.31, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 6.8 Hz, 2H), 6.94 (t, J = 6.8 Hz, 1H), 4.75 – 4.58 (m, 1H), 2.97 – 2.65 (m, 2H), 2.05 (s, 3H), 1.98 (s, 3H), 0.87 – 0.81 (m, 1H), 0.44-0.33(m, 2H), 0.11 – 0.10 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.0, 148.0, 141.2, 138.8, 137.3, 136.4, 136.3, 129.7, 129.0, 128.5, 126.9, 120.4, 101.0, 45.8,

21.2, 19.4, 10.8, 3.1. HRMS-ESI (m/z): calcd for C<sub>19</sub>H<sub>21</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 422.0611, found 422.0606.

#### (R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl ((1R,2S,5S)-adamantan-2-yl)carbamate (32)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 42.1 mg, 84% yield, 91% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 2:98, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 13.286 min (major), 14.205 min

(minor).  $[\alpha]^{25}{}_{D}$  = -35.11 (c 0.41, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.22 – 7.12 (m, 3H), 6.93 (t, J = 7.6 Hz, 1H), 4.90 (t, J = 8.0 Hz, 1H), 3.67 – 3.31 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.81 – 1.47 (m, 14H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.7, 153.2, 148.0, 147.7, 141.3, 141.1, 138.9, 138.6, 137.2, 136.7, 136.3(4), 136.2(9), 129.7, 129.0, 128.5, 127.0, 120.7, 101.1, 55.8, 54.9, 37.4, 37.2, 37.0, 36.9, 31.9, 31.8, 31.6, 31.5, 31.3, 31.2, 27.0(3), 26.9(8), 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>25</sub>H<sub>29</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 502.1237, found 502.1230.

#### (R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (((1S,3R)-adamantan-1-yl)methyl)carbamate (33)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 44.3 mg, 86% yield, 98% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 10.229 min (major), 9.503 min (minor).  $[\alpha]^{25}_{D}$  = -42.26 (c 0.43,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.22 – 7.10 (m, 3H), 6.94 (t, J = 7.6 Hz, 1H), 4.68 – 4.56 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.93 – 1.88 (m, 2H), 1.70 – 1.67 (m, 4H), 1.58 – 1.51 (m, 3H), 1.34 – 1.19 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.5, 147.9, 141.2, 138.9, 137.2, 136.7, 136.3, 129.7, 128.9, 128.5, 127.0, 120.7, 101.1, 52.6, 39.7, 39.5, 36.8(0), 36.7(5), 33.8, 28.1, 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>26</sub>H<sub>31</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 516.1394, found 516.1390.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (3-phenylpropyl)carbamate (34)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 31.0 mg, 64% yield, 95% ee. mp: 58-59 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.848 min (major), 9.436 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -35.83 (c 0.25, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 – 7.69 (m, 1H), 7.36 – 7.27 (m, 3H), 7.22 – 7.12 (m, 6H), 6.94 – 6.82 (m, 1H), 4.69 – 4.59 (m, 1H), 3.15 – 3.10 (m, 2H), 2.54 – 3.40 (m, 2H), 2.06 (s, 3H), 1.99 (s, 3H), 1.75 – 1.68 (m, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.1, 147.8, 141.3, 141.1, 138.8, 137.3, 136.5, 136.3, 129.7, 129.0, 128.5, 128.4, 128.3, 127.0, 125.9, 120.5, 101.0, 40.4, 32.7, 31.2, 21.2, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>24</sub>H<sub>25</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 486.0924, found 486.0917.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl benzylcarbamate (35)

Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 40.2 mg, 88% yield, 99% ee. mp: 95-96 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 7:93, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 11.666

min (major), 10.230 min (minor).  $[\alpha]^{25}_{D} = -42.18$  (c 0.40, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.76 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.24 (d, J = 7.6 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.10 – 6.94 (m, 3H), 5.01 – 4.73 (m, 1H), 4.35 – 4.00 (m, 2H), 2.04 (s, 3H), 2.00 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.2, 147.8, 141.1, 138.8, 138.1, 137.4, 136.6, 136.4, 129.7, 129.0, 128.5, 127.4, 127.2, 127.1, 120.5, 101.0, 44.8, 21.2, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>22</sub>H<sub>21</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 458.0611, found 458.0606.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (4-methylbenzyl)carbamate (36)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 37.2 mg, 79% yield, 98% ee. mp: 94-95 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 9.252

min (major), 8.522 min (minor).  $[\alpha]^{25}_{D}$  = -45.98 (c 0.36, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.76 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.10 (t, J = 7.6 Hz, 2H), 7.00 – 6.88 (m, 3H), 4.95 – 4.69 (m, 1H), 4.30 – 3.96 (m, 2H), 2.34 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.1, 147.8, 141.1, 138.8, 137.3, 137.0, 136.5, 136.3, 135.0, 129.7, 129.2, 129.0, 128.5, 127.2, 127.1, 120.5, 101.0, 44.6, 21.2, 21.1, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>23</sub>H<sub>23</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 472.0768, found 472.0764.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (4-fluorobenzyl)carbamate (37)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 34.2 mg, 72% yield, 98% ee. mp: 109-110 °C. HPLC conditions: Chiralpak INC,

isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.459 min (major), 6.821 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -41.11 (c 0.34, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.09 – 6.96 (m, 5H), 5.04 – 4.79 (m, 1H), 4.33 – 4.01 (m, 2H), 2.05 (s, 3H), 2.01 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  162.1 (d, J = 244.0 Hz), 154.2, 147.7, 141.1, 138.8, 137.4, 136.5, 136.4, 133.9 (d, J = 2.9 Hz), 129.7, 129.0, 128.9 (d, J = 8.1 Hz), 128.6, 127.2, 120.5, 115.3(d, J = 21.3 Hz), 101.0, 44.1, 21.2, 19.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -115.23 (s). HRMS-ESI (*m*/*z*): calcd for C<sub>22</sub>H<sub>20</sub>FINO<sub>2</sub> [M + H]<sup>+</sup>: 476.0517, found 476.0510.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (4-chlorobenzyl)carbamate (38)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 38.2 mg, 78% yield, 98% ee. mp: 111-112 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.548

min (major), 6.882 min (minor).  $[\alpha]^{25}_{D}$  = -45.48 (c 0.38, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.76 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.24 – 7.13 (m, 5H), 7.01 – 6.88 (m, 3H), 5.05 – 4.93 (m, 1H), 4.30 – 3.97 (m, 2H), 2.03 (s, 3H), 1.99 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 154.2, 147.7, 141.0, 138.8, 137.4, 136.7, 136.5, 136.4, 133.1, 129.7, 129.0, 128.6(0), 128.5(5), 128.5, 127.2, 120.5, 101.0, 44.1, 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>22</sub> H<sub>20</sub>ClINO<sub>2</sub> [M + H]<sup>+</sup>: 492.0222, found 492.0213.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (4-bromobenzyl)carbamate (39)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 44.9 mg, 84% yield, 98% ee. mp: 127-129 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.862 min (major), 7.122 min (minor).  $[\alpha]^{25}{}_{\rm D}$ = -40.83 (c 0.48, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.0 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.22 – 7.14 (m, 3H), 6.98 – 6.83(m, 3H), 5.01 – 4.78 (m, 1H), 4.30 – 3.92 (m, 2H), 2.02 (s, 3H), 1.99 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.2, 147.7, 141.0, 138.8, 137.4, 137.2, 136.6, 136.4, 131.6, 129.7, 129.1, 128.9, 128.6, 127.3, 121.2, 120.5, 101.0, 44.2, 21.2, 19.4. HRMS-ESI (m/z): calcd for C<sub>22</sub> H<sub>20</sub>BrINO<sub>2</sub> [M + H]<sup>+</sup>: 535.9717, found 535.9710.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (4-methoxybenzyl)carbamate (40)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 35.6 mg, 73% yield, 98% ee. mp: 108-109 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> =

12.691 min (major), 11.418 min (minor).  $[\alpha]^{25}{}_{D} = -46.11$  (c 0.35, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.04 – 6.93 (m, 3H), 4.96 – 4.70 (m, 1H), 4.27 – 3.94 (m, 2H), 3.80 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.9, 154.1, 147.8, 141.1, 138.7, 137.3, 136.5, 136.3, 130.2, 129.7, 129.0, 128.6, 128.5, 127.1, 120.5, 113.9, 101.0, 55.3, 44.4, 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>23</sub>H<sub>23</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 487.0717, found 487.0710.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (2-bromobenzyl)carbamate (41)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 39.0 mg, 73% yield, 97% ee. mp: 123-125 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$ = 254 nm, t<sub>r</sub> = 10.140

min (major), 9.243 min (minor).  $[\alpha]^{25}{}_{D}$  = -27.89 (c 0.38, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.75 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.25 (t, J = 6.8 Hz, 1H), 7.18 - 7.11(m, 5H), 6.93 (t, J = 8.4 Hz, 1H), 5.17 - 4.99 (m, 1H), 4.38 - 4.07 (m, 2H), 1.99 (s, 3H), 1.98 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.1, 147.8, 140.9, 138.7, 137.3, 137.1, 136.6, 136.3, 132.6, 129.6(9), 129.6(7), 129.0(2), 128.9(9), 128.5, 127.5, 127.2, 123.4, 120.6, 100.9, 45.2, 21.1, 19.3. HRMS-ESI (m/z): calcd for C<sub>22</sub> H<sub>20</sub>BrINO<sub>2</sub> [M + H]<sup>+</sup>: 535.9717, found 535.9714.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (2-methoxybenzyl)carbamate (42)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 29.2 mg, 60% yield, 97% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 22.637

min (major), 19.918 min (minor).  $[\alpha]^{25}_{D}$  = -27.90 (c 0.28, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.78 - 7.72 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.24 - 7.07 (m, 4H), 6.92 - 6.83 (m, 3H), 5.14 - 5.04 (m, 1H), 4.26 - 3.97 (m, 2H), 3.79 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.2, 154.2, 147.9, 141.1, 138.8, 137.2, 136.5, 136.2, 129.7, 129.1, 128.9, 128.7, 128.4, 126.9, 126.2, 120.6, 120.4, 110.0, 101.0, 55.1, 40.7, 21.1, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>23</sub>H<sub>23</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 487.0717, found 487.0711.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (3-methoxybenzyl)carbamate (43)

Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 38.0 mg, 78% yield, 98% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 12.792 min (major), 11.407 min (minor).  $[\alpha]^{25}_{D} = -43.40$  (c 0.37, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.76 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.23 – 7.17 (m, 4H), 6.94 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.70 - 6.61 (m, 2H), 5.02 - 4.79 (m, 1H), 4.30 - 3.95 (m, 2H), 3.79 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H).  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.7, 154.1, 147.8, 141.0, 139.6, 138.7, 137.3, 136.5, 136.3, 129.7, 129.6, 129.0, 128.5, 127.1, 120.4, 119.5, 112.9, 112.8, 101.0, 55.2, 44.9, 21.2, 19.3. HRMS-ESI (m/z): calcd for C<sub>23</sub>H<sub>23</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 487.0717, found 487.0712.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (2-phenylpropan-2-yl)carbamate (44)



yield, 98% ee. mp: 105-106 °C.HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 0.5 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 10.561

Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 38.8 mg, 80%

min (major), 10.237 min (minor).  $[\alpha]^{25}_{D} = -58.99$  (c 0.28, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.82 (d, J = 7.6 Hz, 1H), 7.32 – 7.28 (m, 4H), 7.23 – 7.19 (m, 3H), 7.15 – 7.09 (m, 2H), 7.02 (t, J = 7.6 Hz, 1H), 5.03 (s, 1H), 1.98 (s, 3H), 1.97 (s, 3H), 1.61 (s, 3H), 1.53 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.0, 147.7, 146.5, 141.2, 139.0, 137.2, 136.3, 129.8, 129.0, 128.4, 128.2, 127.0, 126.6, 124.7, 120.9, 101.2, 55.3, 29.6, 28.4, 21.1, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>24</sub>H<sub>25</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 486.0924, found 486.0921.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (naphthalen-1-ylmethyl)carbamate (45)



Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 44.1 mg, 87% yield, 98% ee. mp: 73-75 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 13.425

min (major), 11.861 min (minor).  $[\alpha]^{25}_{D} = -37.76$  (c 0.43, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.92 - 7.86 (m, 2H), 7.80 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.56 - 7.51 (m, 2H), 7.41 - 7.35 (m, 2H), 7.23 – 7.13 (m, 4H), 6.88 (t, J = 7.6 Hz, 1H), 5.02 – 4.90 (m, 1H), 4.38 – 4.39 (m, 2H), 2.04 (s, 3 H), 2.01 (s, 3 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.9, 147.8, 141.0, 138.6, 137.3, 136.5, 136.3, 133.7, 133.2, 131.1, 129.7, 128.9, 128.7, 128.5, 128.4, 127.1, 126.5, 125.8, 125.7, 125.3, 123.1, 120.5, 100.9, 43.0, 21.2, 19.3. HRMS-ESI (*m*/*z*): calcd for C<sub>26</sub>H<sub>23</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 508.0768, found 508.0761.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (furan-2-ylmethyl)carbamate (46)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 35.8 mg, 80% yield, 99% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 9.250 min (major), 8.492 min

(minor).  $[\alpha]^{25}{}_{D}$  = -39.38 (c 0.35, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.15 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.30 – 6.26 (m, 1H), 6.10 – 6.00 (m, 1H), 5.00 – 4.80 (m, 1H), 4.26 – 3.84 (m, 2H), 2.03 (s, 3H), 1.98 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.9, 151.2, 147.8, 142.1, 141.0, 138.7, 137.3, 136.4, 136.3, 129.7, 129.0, 128.5, 127.1, 120.4, 110.3, 107.2, 100.9, 38.0, 21.2, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>19</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 448.0404 , found 448.0398.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (thiophen-2-ylmethyl)carbamate (47)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 36.6 mg, 79%
s yield, 98% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min, λ = 254 nm, t<sub>r</sub> = 8.790 min (major), 8.008 min

(minor).  $[\alpha]^{25}_{D}$  = -44.10 (c 0.36, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.21 – 7.16 (m, 4H), 6.96 – 6.91 (m, 2H), 6.84 – 6.74 (m, 1H), 5.05 – 4.78 (m, 1H), 4.49 – 4.05 (m, 2H), 2.04 (s, 3H), 1.99 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 153.8, 147.8, 141.0, 140.8, 138.7, 137.3, 136.4, 136.3, 129.8, 129.0, 128.5, 127.1, 126.8, 125.7, 125.0, 120.4, 100.9, 39.8, 21.2, 19.4. HRMS-ESI (*m*/*z*): calcd for C<sub>20</sub>H<sub>19</sub>INO<sub>2</sub>S [M+H]<sup>+</sup>: 464.0176, found 464.0172.

#### Tert-butyl (R)-N-(((2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl)-N-methylglycinate (48)



Eluent: 10:1 petroleum ether / ethyl acetate;light yellow oil, 25.7 mg, 67% yield, 98% ee). HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 2:98, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 11.388 min (major), 12.275 min

(minor).  $[\alpha]^{25}_{D} = -45.02$  (c 0.25, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.33 (td, J = 8.0, 2.4 Hz, 1H), 7.23 (t, J = 8.4 Hz, 2H), 7.15 (m, 1H), 6.95 (t, J = 7.6 Hz, 1H), 3.79 (s, 1H), 3.56 – 3.34 (m, 1H), 2.89 (s, 1.4H), 2.60 (s, 1.6H), 2.03 (s, 3H), 1.99 (d, J = 8.4 Hz, 3H), 1.43 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.1, 153.7, 148.1, 141.2, 138.6, 137.0, 136.2, 135.9, 129.7, 129.0, 128.4, 126.7, 120.2, 101.0, 81.6, 51.4, 51.1, 35.9, 35.1, 28.0, 21.2, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>22</sub> H<sub>27</sub>INO<sub>4</sub> [M + H]<sup>+</sup>: 496.0979, found 496.0972.

#### Tert-butyl (R)-(((2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl)glycinate (49)

Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 35.1mg, 73% yield, 98% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 17.573

min (major), 21.320 min (minor).  $[\alpha]^{25}_{D} = -39.88$  (c 0.34, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.76 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 2H), 6.94 (t, J = 8.0 Hz, 1H), 5.15 – 4.92 (m, 1H), 3.83 – 3.27 (m, 2H), 2.03 (s, 3H), 1.98 (s, 3H), 1.45 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.6, 153.9, 147.8, 141.0, 138.6, 137.4, 136.4, 136.2, 129.7, 129.1, 128.5, 127.0, 120.2, 100.9, 82.2, 43.4, 28.0, 21.2, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>21</sub>H<sub>25</sub>INO<sub>4</sub> [M + H]<sup>+</sup>: 482.0823, found 482.0815.

#### Ethyl (*R*)-*N*-benzyl-*N*-(((2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl)glycinate (50)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 39.1 mg, 72% yield, >99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 2:98, flow: 0.8 mL/min,  $\lambda = 254$  nm,  $t_r = 31.458$  min (major), 33.772 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -49.36 (c 0.39, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.74 (dd, J = 10.8, 8.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 7.18 (d, J = 7.6 Hz, 1H), 7.03 (dd, J = 7.2, 2.0 Hz, 1H), 6.95 (td, J = 7.6, 3.2 Hz, 1H), 6.86 – 6.82 (m, 1H), 4.61 – 4.08 (m, 4H), 3.87 – 3.75 (m, 1H), 3.56 – 3.33 (m, 1H), 2.05 (s, 3H), 2.00 (s, 3H), 1.23 (dt, J = 7.6, 3.2 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.0, 154.0, 148.0, 141.2, 138.8, 137.2, 136.5, 136.4, 136.1, 129.8, 129.1, 128.6, 128.5, 128.0, 127.8, 127.5, 127.1, 127.0, 120.4, 100.9, 61.1, 51.3, 47.3, 21.2, 19.4, 14.2. HRMS-ESI (*m/z*): calcd for C<sub>26</sub>H<sub>27</sub>INO<sub>4</sub> [M + H]<sup>+</sup>: 544.0979, found 544.0980.

#### *Tert*-butyl ((((*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl)-L-alaninate (51)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 36.6 mg, 74% yield, >99:1 dr. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> =

6.398 min (major), 7.089 min (minor).  $[\alpha]^{25}_{D} = -55.08$  (c 0.33, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.16 (td, J = 21.6, 7.4 Hz, 3H), 6.94 (t, J = 7.6 Hz, 1H), 5.26 – 5.11 (m, 1H), 4.17 – 3.54 (m, 1H), 2.05 (s, 3H), 1.98 (s, 3H), 1.44 (s, 9H), 1.20 – 1.08 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  171.7, 153.2, 147.9, 140.9, 138.7, 137.3, 136.5, 136.4, 129.7, 129.0, 128.5, 127.1, 120.4, 101.0, 82.0, 50.1, 27.9, 21.1, 19.3, 18.6. HRMS-ESI (*m/z*): calcd for C<sub>22</sub>H<sub>27</sub>INO<sub>4</sub> [M+H]<sup>+</sup>: 496.0979, found 496.0970.

#### *Tert*-butyl ((((*R*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl)-L-tyrosinate (52)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 41.7 mg, 71% yield, 98.5:1.5 dr. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 47.311 min (major), 43.102 min (minor).  $[\alpha]^{25}_{D}$  = -50.52 (c 0.48,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 – 7.71 (m, 1H), 7.38 – 7.30 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.09 (m, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.88 – 6.60 (m, 4H), 5.26 – 5.06 (m, 1H), 4.43 – 4.12 (m, 1H), 2.98 – 2.29 (m, 2H), 2.10 (s, 1H), 2.01 (s, 3H), 1.98 (s, 3H), 1.39 (s, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.2, 154.8, 153.3, 147.6, 141.0, 138.5, 137.4, 136.5, 136.3, 130.6, 129.7, 129.1, 128.4, 127.4, 127.1, 120.3, 115.3, 100.8, 82.4, 55.3, 37.3, 27.9, 21.3, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>28</sub>H<sub>29</sub>INO<sub>5</sub> [M + H]<sup>+</sup>: 586.1096, found 586.1094.

(R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (2-(5-methoxy-1H-indol-3-yl)ethyl)carbamate (53)



Eluent: 20:1 petroleum ether / ethyl acetate; yellow oil, 30.2 mg, 56% yield, 90% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 15:85, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> =

19.509 min (major), 16.235 min (minor).  $[\alpha]^{25}_{D} = -29.07$  (c 0.29, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.96 (s, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.25 – 7.13 (m, 4H), 6.99 – 6.91 (m, 2H), 6.88 – 6.81 (m, 2H), 4.80 – 4.55 (m, 1H), 3.85 (s, 3H), 3.41 – 3.16 (m, 2H), 2.84 – 2.46 (m, 2H), 2.06 (s, 3H), 1.98 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.1, 154.0,

147.9, 141.2, 138.8, 137.3, 136.4, 136.3, 131.4, 129.7, 129.0, 128.5, 127.5, 127.0, 122.9, 120.4, 112.3, 112.2, 111.9, 101.1, 100.5, 56.0, 41.0, 25.5, 21.2, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>26</sub>H<sub>26</sub>IN<sub>2</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 541.0983, found 541.0976.

### (*R*)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl (((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)carbamate (54)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil (48.9 mg, 77% yield, 97:3 dr. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.091 min (major), 7.786 min (minor).  $[\alpha]^{25}_{D}$ =

-28.43 (c 0.49, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.64 (t, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.20 – 7.10 (m, 3H), 7.03 (t, J = 8.4 Hz, 1H), 6.90 (s, 1H), 6.82 – 6.73 (m, 2H), 4.67 – 4.51 (m, 1H), 3.18 – 3.13 (m, 1H), 2.90 – 2.73 (m, 5H), 2.28 – 2.25 (m, 1H), 1.97 (s, 3H), 1.85 (s, 3H), 1.73 – 1.63 (m, 4H), 1.35 – 1.27 (m, 2H), 1.26 (s, 3H), 1.24 (s, 3H), 1.19 (s, 3H), 1.18 – 1.08 (m, 2H), 0.87 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.3, 147.7, 147.2, 145.6, 141.0, 138.5, 137.2, 136.5, 136.1, 134.8, 129.6, 128.9, 128.4, 126.9, 123.9, 123.7, 120.6, 100.7, 51.3, 44.1, 38.1, 37.5, 37.2, 35.6, 33.5, 29.8, 25.3, 24.1, 24.0, 21.0, 19.3, 18.8, 18.7, 18.4. HRMS-ESI (*m/z*): calcd for C<sub>35</sub>H<sub>43</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 636.2333, found 636.2327.

#### (*R*)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl

#### (1R,3R,5S)-3-hydroxy-8-azabicyclo[3.2.1]octane-8-carboxylate (55)



Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 13.2 mg, 30% yield, 95:5 dr. mp: 89-90 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 23.040 min (major), 21.307 min (minor).  $[\alpha]^{25}_{D} = -28.03$  (c 0.13, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.23 – 7.12 (m, 3H), 7.21 (q, J = 7.2 Hz, 1H), 4.18 – 4.13 (m, 1H), 3.96 (s, 1H), 3.82 – 3.71 (m, 1H), 2.07 (s, 3H), 2.03 (s, 1H), 1.98 (s, 3H), 1.90 – 175 (m, 2H), 1.71 – 1.42 (m, 4H), 1.33 – 1.25 (m, 1H), 0.92 – 1.86 (dt, J = 14.8, 4.0 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.9, 150.8, 148.0, 147.9, 141.6(1), 141.5(8), 139.1, 138.9, 137.1, 136.6, 136.4, 136.3, 136.1, 129.6, 129.5, 129.0, 128.5, 128.4, 126.9, 126.7, 120.7, 120.5, 101.5, 101.0, 65.0, 53.3(5), 53.3(0), 52.8, 52.7, 38.4, 38.3, 37.9(3), 37.9(0), 28.5, 28.3, 27.5, 21.2(4), 21.1(7), 19.4, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>22</sub>H<sub>25</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 478.0874, found 478.0869.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl 4-benzhydrylpiperazine-1-carboxylate (56)



Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 30.2 mg, 50% yield, 97% ee. mp: 143-145 °C. HPLC conditions: Chiralpak AS-H, isopropanol/hexanes = 3:97, flow: 0.5 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 12.523 min (major), 15.127 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -27.14 (c 0.28,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.72 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.34 (m, 5H), 7.32 – 7.27 (m, 4H), 7.22 – 7.15 (m, 5H), 6.92 (t, *J* = 7.6 Hz, 1H), 4.14 (s, 1H), 3.44 – 3.32 (m, 2H), 3.14 (s, 2H), 2.33 (s, 1H), 2.14 – 2.09 (m, 2H), 2.03 (s, 3H), 1.99 (s, 3H), 1.80 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.6, 148.1, 142.2, 142.1, 141.3, 138.8, 137.0, 136.4, 136.3, 129.7, 129.1, 128.5(3), 128.5(0), 127.9, 127.8, 127.1, 126.9, 120.6, 101.1, 99.9, 75.9, 51.4, 51.3, 44.4, 44.0, 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>32</sub>H<sub>32</sub>IN<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 603.1503, found 603.1497.





Eluent: 2:1 petroleum ether / ethyl acetate; white solid, 38.3 mg, 60% yield, 98% ee. mp: 162-165 °C. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 5:95, flow: 0.5 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 18.596 min (major), 19.822 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -28.49 (c 0.34, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.72 (d,

 $J = 7.6 \text{ Hz}, 1\text{H}, 7.36 - 7.28 \text{ (m, 5H)}, 7.21 \text{ (d, } J = 7.6 \text{ Hz}, 1\text{H}), 7.18 - 7.15 \text{ (m, 2H)}, 6.98 \text{ (t, } J = 8.4 \text{ Hz}, 4\text{H}), 6.91 \text{ (t, } J = 7.6 \text{ Hz}, 1\text{H}), 4.12 \text{ (s, 1H)}, 3.37 \text{ (s, 2H)}, 3.13 \text{ (s, 2H)}, 2.29 \text{ (s, 2H)}, 2.12 - 2.05 \text{ (m, 2H)}, 2.02 \text{ (s, 3H)}, 1.99 \text{ (s, 3H)}, 1.79 - 1.75 \text{ (m, 1H)}. {}^{13}\text{C}\{{}^{1}\text{H}\} \text{ NMR (100 MHz, CDCl}_3): \delta 161.8 \text{ (d, } J = 244.0 \text{ Hz}), 152.6, 148.1, 141.4, 138.9, 137.7, 137.6, 137.1, 136.3(1), 136.2(9), 129.7, 129.2(1) \text{ (d, } J = 7.7 \text{ Hz}), 129.2(0) \text{ (d, } J = 2.6 \text{ Hz}), 129.0, 128.5, 126.9, 120.6, 115.5 \text{ (d, } J = 21.0 \text{ Hz}), 101.1, 74.2, 51.2, 44.3, 31.6, 22.6, 21.2, 19.3. {}^{19}\text{F} \text{ NMR (376 MHz, CDCl}_3): \delta -115.27 \text{ (s)}. \text{HRMS-ESI } (m/z): \text{ calcd for } C_{32}\text{H}_{30}\text{F}_{2}\text{IN}_{2}\text{O}_{2} \text{ [M + H]}^{+}: 639.1315, \text{ found } 639.1309.$ 

#### (*R*)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl

#### methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)carbamate (58)



Eluent: 2:1 petroleum ether / ethyl acetate; light yellow oil, 51.4 mg, 78% yield, 97% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 13.629 min (major), 18.316 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>

= -20.64 (c 0.44, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 – 7.52 (m, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.27 (m, 6H), 7.16 – 7.05 (m, 3H), 6.91 – 6.67 (m, 3H), 5.12 – 5.00 (m, 1H), 3.43 – 2.97 (m, 2H), 2.83 (d, *J* = 7.2 Hz, 1.6H), 2.53 (s, 1.4H), 2.05 – 1.98 (m, 7H), 1.90 – 1.68 (m, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.2, 153.8, 148.2, 148.0, 141.4(2), 141.4(0), 138.7, 138.6, 137.1, 137.0, 136.3, 136.2, 128.7(9), 128.7(8), 128.7 (q, *J* = 48.0 Hz), 126.7 (q, *J* = 3.0 Hz), 125.9, 125.7 (d, *J* = 7.2 Hz), 123.0, 120.3 (d, *J* = 14.8 Hz), 115.7, 101.1, 78.2, 77.9, 46.3, 46.1, 36.6, 36.5, 35.3, 35.2, 21.3, 19.3(3), 19.3(2). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -61.53(s). HRMS-ESI (*m*/*z*): calcd for C<sub>32</sub>H<sub>30</sub>F<sub>3</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 660.1217, found 660.1214.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl

#### 4-(2-chlorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)piperazine-1-carboxylate (59)



Eluent: 2:1 petroleum ether / ethyl acetate; light yellow oil, 60 mg, 90% yield, 97% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 5:95, flow: 0.5 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 30.385 min (major), 28.019 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -18.50 (c 0.60,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.25 – 7.23 (m, 2H), 7.21 – 7.18 (m, 3H), 7.16 – 7.08 (m, 3H), 7.04 – 6.96 (m, 2H), 3.54 – 2.82 (m, 8H), 2.06 (s, 3H), 2.01 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.3, 158.6, 152.8, 148.0, 141.3, 139.0, 137.2, 136.4(4), 136.3(9), 132.8, 130.4, 129.8, 129.3, 128.9, 128.6, 127.2, 127.1, 125.9, 125.0, 122.8, 120.6, 120.1, 101.1, 53.9, 53.3, 44.0, 43.6, 21.2, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>32</sub>H<sub>28</sub>ClIN<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 664.0858, found 664.0857.

## 3-Ethyl 5-(2-(((((R)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl)amino)ethyl) 4-(2-chlorophenyl)-2-(methoxymethyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (60)



Eluent: 5:1 petroleum ether / ethyl acetate; light yellow oil, 65.2 mg, 86% yield, 97% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda$ = 254 nm, t<sub>r</sub> = 49.505 min (major), 43.524 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=

-26.18 (c 0.64, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (t, J = 7.6 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.24 – 7.22 (m, 3H), 7.17 – 7.11 (m, 3H), 7.06 – 7.02 (m, 1H), 6.95 – 6.91 (m, 1H), 5.41 (s, 1H), 5.06 – 4.96 (m, 1H), 4.74 – 4.59 (m, 2H), 4.07 – 4.03 (m, 2H), 3.61 (s, 3H), 3.56 – 3.25 (m, 4H), 2.29 – 2.25 (m, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.19 (t, J = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.0, 167.1, 154.6, 147.7, 145.8, 145.1, 144.4, 141.0, 138.6(8), 138.6(6), 137.4, 136.3, 132.2, 131.3(8), 131.3(7), 129.7, 129.2, 129.1, 128.4, 127.3, 127.2, 126.8(3), 126.8(1), 120.2, 103.7, 101.3, 100.9, 70.6, 68.0, 59.7, 50.7, 40.7, 37.0, 21.1, 19.3, 19.2, 14.2. HRMS-ESI (*m/z*): calcd for C<sub>35</sub>H<sub>37</sub>ClIN<sub>2</sub>O<sub>7</sub> [M + H]<sup>+</sup>: 759.1328, found 759.1323.

#### (R)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl

# ((*S*)-4-oxo-4-(3-(trifluoromethyl)-5,6-dihydro-[1,2,4]triazolo[4,3-*a*]pyrazin-7(8*H*)-yl)-1-(2,4,5-trifluorophenyl)butan-2-yl)carbamate (61)



Eluent: 2:1 petroleum ether / ethyl acetate; light yellow oil, 68.9 mg, 91% yield, 98:2 dr. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 15:85, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 36.126 min (major), 30.073 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -7.69 (c 0.66,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.68 – 7.62 (m, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.99 – 6.79 (m, 4H), 5.70 – 5.46 (m, 1H), 5.05 – 4.78 (m, 2H), 4.17 – 4.14 (m, 2H), 4.10 – 3.98 (m, 2H), 3.93 – 3.82 (m, 1H), 2.91 – 2.29 (m, 4H), 2.00 (s, 3H), 1.94 (s, 3H), 1.19 (d, J = 6.4 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.4, 169.1, 155.9 (dd, J = 243.5, 9.8 Hz), 153.4(d, J = 13.6 Hz), 150.3, 149.6, 147.4 (q, J = 14.1 Hz), 145.1 (d, J = 10.3 Hz), 144.0-142.5 (m), 140.8 (t, J = 12.4 Hz), 138.5, 138.3, 137.2, 136.1, 136.0, 129.4, 128.8, 128.2, 127.0, 121.1 (d, J = 19.5 Hz), 119.9, 119.2, 118.8 (d, J = 14.5 Hz), 118.0 (q, J = 270 Hz), 105.1 (t, J = 21.7 Hz), 100.5, 64.0, 63.8, 48.7, 48.5, 42.5, 43.0, 42.1, 41.4, 38.8, 37.7, 36.3, 32.3, 32.2, 25.0, 20.9, 19.1.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -62.95 (d, J = 52.9 Hz, 3F), -119.13 – -119.96 (m, 1F), -134.78 – -135.36 (m, 1F), -142.01 – -142.56 (m, 1F). HRMS-ESI (m/z): calcd for C<sub>31</sub> H<sub>26</sub> FIN<sub>5</sub>O<sub>3</sub> [M + e]<sup>-</sup>: 757.0985, found 757.0983.

#### (R)-2'-Iodo-3',6-dimethyl-[1,1'-biphenyl]-2-yl diethylcarbamate (62)

Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 21.1 mg, 50% yield, 84% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 2:98, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 8.410 min (major), 7.441 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>= -68.03 (c 0.12, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.32 (t, J = 8.0 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.19 – 7.17 (m, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.00 – 6.98 (m, 1H), 3.19 – 3.02 (m, 3H), 2.89 – 2.80 (m, 1H), 2.51 (s, 3H), 2.01 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H), 0.69 (t, J = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.6, 148.6, 143.2, 142.0, 138.2, 137.4, 128.3, 128.2, 127.8, 127.5, 126.7, 120.1, 107.3, 41.9, 41.5, 29.5, 19.9, 13.3, 13.2. HRMS-ESI (m/z): calcd for C<sub>19</sub>H<sub>23</sub> INO<sub>2</sub> [M + H]<sup>+</sup>: 424.0768, found 424.0768.

#### (R)-3'-Chloro-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl diethylcarbamate (63)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 39.7 mg, 87% yield, 96% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 1:99, flow: 0.6 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 15.102 min (major), 18.584 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -89.09 (c 0.22, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 8.8 Hz, 2H), 3.19 (q, J = 7.2 Hz, 2H), 3.06 – 2.99 (m, 1H), 2.91 – 2.84 (m, 1H), 2.02 (s, 3H), 1.98 (s, 3H), 1.02 (t, J = 7.2 Hz, 3H), 0.73 (t, J = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.1, 148.0, 144.4, 136.7, 136.5(9), 136.5(6), 136.3, 130.8, 128.6, 127.8, 126.6, 120.4, 105.2, 41.9, 41.5, 20.8, 19.2, 13.4, 13.2. HRMS-ESI (m/z): calcd for C<sub>19</sub>H<sub>22</sub>ClINO<sub>2</sub> [M + H]<sup>+</sup>: 458.0378, found 458.0377.

#### (R)-3'-chloro-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl thiomorpholine-4-carboxylate (64)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 39.0 mg, 80% yield, 77% ee. HPLC conditions: Chiralpak INC , isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda$  = 254 nm, tr = 7.058 min (major), 7.569 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -70.28 (c 0.35, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 (q, *J* = 8.0 Hz, 2H), 7.23 – 7.15 (m, 3H), 3.80 – 3.27 (m, 4H), 2.48 – 2.14 (m, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.92 – 1.83 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 152.4, 147.7, 144.2, 136.9, 136.8, 136.8, 136.5, 130.8, 128.9, 128.1, 127.2, 120.6, 105.3, 47.1, 46.5, 27.1, 26.8, 20.8, 19.2. HRMS (ESI) calcd for C19H20ClINO2S [M+H]<sup>+</sup>: 487.9942, found 487.9944.

Ethyl (R)-N-benzyl-N-(((3'-chloro-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl)glycinate (65)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 41.6 mg, 72% yield, >99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 5:95, flow: 0.8 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 16.126 min (major), 17.411 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -70.82 (c 0.38,

CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.39 – 7.27 (m, 4H), 7.25 – 7.24 (m, 2H), 7.19 – 7.16 (m, 2H), 7.09 – 7.06 (m, 1H), 6.84 – 6.82 (m, 1H), 4.50 (s, 1H), 4.20 – 4.18 (m, 1H), 4.15 – 4.08 (m, 2H), 3.87 – 3.78 (m, 1H), 3.46 (s, 1H), 2.02 (s, 3H), 1.98 (s, 3H), 1.23 (td, *J* = 7.2, 2.0 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.0, 168.8, 154.0, 153.9, 147.8, 147.7, 144.1, 136.9, 136.8(2), 136.7(7), 136.6(3), 136.5(9), 136.5(0), 136.4(7), 136.4, 136.3, 136.1, 130.9(4), 130.8(7), 128.8, 128.7, 128.6(1), 128.5(9), 128.1, 128.0, 127.8, 127.6(2), 127.5(7), 127.2, 127.1, 120.5, 120.3, 105.0, 104.8, 61.2, 61.1, 51.4, 51.3, 47.6, 47.2, 20.9, 20.8, 19.3, 19.2, 14.2, 14.1. HRMS-ESI (*m/z*): calcd for C<sub>26</sub>H<sub>26</sub>ClINO<sub>4</sub> [M + H]<sup>+</sup>: 578.0590, found 578.0588.

#### (R)-2'-Iodo-3',6,6'-trimethyl-[1,1'-biphenyl]-2-yl diethylcarbamate (66)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 31.5 mg, 72% yield, 98% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 1:99, flow: 0.8 mL/min,  $\lambda = 254$  nm,  $t_r = 9.432$  min (major), 10.782 min (minor).  $[\alpha]^{25}_{D} = -58.05$  (c 0.27, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.33 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.10 (s, 2H), 3.20 – 3.15 (m, 2H), 3.01 – 2.78 (m, 2H), 2.46 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H), 0.67 (t, J = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.3, 148.3, 142.1, 139.4, 137.2, 136.9, 135.4, 129.5, 128.4, 128.2, 126.5, 120.3, 108.0, 41.9, 41.5, 29.4, 20.9, 19.4, 13.3, 13.2. HRMS-ESI (m/z): calcd for C<sub>20</sub> H<sub>25</sub>INO<sub>2</sub> [M+H]<sup>+</sup>: 438.0924, found 438.0924.
#### Tert-butyl (R)-N-(((2'-iodo-3',6,6'-trimethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl)-N- methylglycinate (67)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 42.2 mg, 83% yield, 98% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 5:95, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 12.261 min (major), 11.263 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -53.55 (c 0.42, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.33 (t, J = 8.0 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.16 – 7.10 (m, 3H), 3.84 – 3.72 (m, 1H), 3.47 – 3.25 (m, 1H), 2.88 (s, 1.5H), 2.55 (s, 1.5H), 2.48 (s, 3H), 1.98 – 1.96 (m, 6H), 1.43 (d, J = 3.6 Hz, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.2, 168.1, 154.3, 153.7, 148.1, 148.0, 141.9, 141.8, 139.4, 139.3, 137.1, 137.0(4), 136.9(7), 136.9, 135.3(4), 135.2(7), 129.5(4), 129.4(9), 128.5, 128.4, 128.3, 128.2, 126.8, 126.7, 120.2, 120.0, 107.8, 107.7, 99.9, 99.7, 81.7, 81.6, 51.4, 51.1, 35.9, 35.1, 29.4, 28.1, 28.0, 20.9(2), 20.8(9), 19.4, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>23</sub> H<sub>29</sub> INO<sub>4</sub> [M+H]<sup>+</sup> 510.1136, found 510.1130.

#### (R)-2'-Iodo-3',6,6'-trimethyl-[1,1'-biphenyl]-2-yl morpholine-4-carboxylate (68)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil ( 34.7 mg, 77%, 94% ee). HPLC conditions: Chiralpak AD-H , isopropanol/hexanes = 3:97, flow: 0.5 mL/min,  $\lambda$ = 254 nm, t<sub>r</sub> = 20.669 min (major), 19.224 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>= -58.26 (c 0.32, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.35 (d, J = 7.6 Hz, 1H), 7.19 – 7.12 (m, 4H), 3.56 (s, 1H), 3.40 – 3.33 (m, 4H), 3.06 (s, 3H), 2.47 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H).  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.6, 148.0, 141.8, 139.5, 137.4, 137.1, 135.7, 129.5, 128.6, 128.4, 127.1, 120.5, 107.8, 66.6, 66.2, 44.7, 44.0, 29.4, 20.8, 19.3. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>23</sub>INO<sub>3</sub> [M+H]<sup>+</sup>: 452.0717, found 452.0712.

# (R)-2'-Iodo-3',6'-dimethyl-6-(trifluoromethyl)-[1,1'-biphenyl]-2-yl diethylcarbamate (69)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 32.9 mg, 67% yield, 92% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 2:98, flow: 1.0 mL/min,  $\lambda$ = 254 nm, t<sub>r</sub> = 5.573 min

(major), 6.438 min (minor).  $[\alpha]^{25}_{D}$  = -78.03 (c 0.31, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 – 7.62 (m, 2H), 7.57 – 7.53 (m, 1H), 7.12 (q, *J* = 7.6 Hz, 2H), 3.20 (q, *J* = 7.2 Hz, 2H), 2.97 – 2.88 (m, 1H), 2.80 – 2.71 (m, 1H), 2.46 (s, 3H), 1.99 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 0.66 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.6, 149.1, 139.5, 139.1, 136.0 (q, *J* = 2.0 Hz),

129.3, 129.2 (q, J = 29.7 Hz), 129.0, 128.8, 126.9, 123.3 (q, J = 273.0 Hz), 122.9 (q, J = 5.0 Hz), 107.9(3), 107.9(2), 42.0, 41.5, 29.3, 21.1, 13.2, 13.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -60.43 (s). HRMS-ESI (m/z): calcd for C<sub>20</sub> H<sub>22</sub> F<sub>3</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 492.0642, found 492.0643.

#### (R)-2'-Iodo-3',6'-dimethyl-6-(trifluoromethyl)-[1,1'-biphenyl]-2-yl diallylcarbamate (70)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 38.1 mg, 74% yield, 90% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 5.134 min (major), 5.696 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -92.18 (c 0.36, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.66 – 7.62 (m, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.13 (q, J = 7.6 Hz, 2H), 5.72 – 5.62 (m, 1H), 5.23 – 5.15(m, 1H), 5.14 – 5.02 (m, 2H), 4.93 – 4.88 (m, 2H), 3.84 – 3.72 (m, 2H), 3.47 – 3.28 (m, 2H), 2.46 (s, 3H), 1.99 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.9, 149.0, 139.3, 139.2, 136.0 (q, J = 2.0 Hz), 135.9, 132.6 (d, J = 1.1 Hz), 129.4, 129.2 (q, J = 30.0 Hz), 129.0, 128.8, 127.0, 123.3 (q, J = 273.0 Hz), 123.2(q, J = 5.1 Hz), 117.2, 116.7, 107.9, 49.0, 48.6, 29.3, 21.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -60.45(s). HRMS-ESI (m/z): calcd for C<sub>22</sub>H<sub>22</sub>F<sub>3</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 516.0642, found 516.0643.

# (R)-2'-Iodo-3',4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl diethylcarbamate (71)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 28.4 mg, 63% yield, 96% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 1:99, flow: 0.5 mL/min,  $\lambda = 254$  nm,  $t_r = 17.236$  min (major), 20.386 min (minor).  $[\alpha]^{25}_{D} = -50.19$  (c 0.26, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.31 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 6.99 (s, 1H), 3.17 (q, J = 6.8 Hz, 2H), 3.01 – 2.80 (m, 2H), 2.46 (s, 3H), 2.35 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H), 0.66 (t, J = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.3, 148.4, 139.9, 137.7, 137.3, 137.1, 135.8, 135.2, 131.5, 128.1, 126.4, 120.3, 109.5, 41.8, 41.4, 26.1, 21.7, 20.8, 19.4, 13.2. HRMS-ESI (m/z): calcd for C<sub>21</sub>H<sub>27</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 452.1081, found 452.1082.

# Ethyl (R)-N-benzyl-N-(((2'-iodo-3',4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl)oxy)carbonyl) glycinate (72)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 39.9 mg, 70% yield, 95% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 13.034 min (major), 12.059 min (minor).  $[\alpha]^{25}_{D}$  = -64.58 (c 0.37, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.34 (d, J = 8.0 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 7.05 – 7.01 (m, 2H), 6.75 (t, J = 7.2 Hz, 1H), 4.63 – 4.47 (m, 1H), 4.40 – 4.11 (m, 1H), 4.13 – 4.06 (m, 2H), 3.92 – 3.69 (m, 2H), 3.46 – 3.23 (m, 2H), 2.45 (s, 3H), 2.35 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.2, 169.1, 154.1, 154.0, 148.1(2), 148.0(8), 139.6, 137.5, 137.4, 136.5, 136.3, 136.0, 135.2, 135.1, 131.7, 131.6, 128.5, 128.4, 128.3, 128.2, 127.8(4), 127.7(6), 127.5, 127.3, 127.0, 126.8, 120.4, 120.0, 109.2(3), 109.1(6), 61.1, 61.0, 51.2, 51.1, 47.3, 47.1, 26.1(5), 26.1(1), 21.9, 21.8, 20.8(5), 20.7(7), 19.5, 19.4, 14.2, 14.1. HRMS-ESI (m/z): calcd for C<sub>28</sub>H<sub>31</sub>INO<sub>4</sub> [M + H]<sup>+</sup>: 572.1292, found 572.1290.

# (R)-2'-Iodo-3',4',6,6'-tetramethyl-[1,1'-biphenyl]-2-yl dibenzylcarbamate (73)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 46 mg, 80% yield, 99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 2:98, flow: 1.0 mL/min,  $\lambda = 254$  nm,  $t_r = 6.956$  min (major), 6.570 min

(minor).  $[\alpha]^{25}_{D} = -73.30$  (c 0.43, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 (d, J = 8.0 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.24 (d, J = 8.4 Hz, 3H), 7.19 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 6.4 Hz, 2H), 7.01 (s, 1H), 6.90 (d, J = 7.6 Hz, 2H), 4.34 (q, J = 15.6 Hz, 2H), 4.07 (q, J = 15.6 Hz, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.4, 148.3, 139.6, 137.8, 137.5, 137.4, 137.0, 136.9, 135.9, 135.2, 131.7, 128.5, 128.4, 128.2, 128.0, 127.7, 127.3, 127.2, 126.9, 120.3, 109.3, 48.9, 48.8, 26.1, 21.9, 20.9, 19.4. HRMS-ESI (*m/z*): calcd for C<sub>31</sub>H<sub>31</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 576.1394, found 576.1393.

#### (R)-N,N-Diethyl-2'-hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-carboxamide (74)

Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 23.8 mg, 80% yield, 99% ee. mp: 133-134 °C. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 9.252 min (major), 8.695 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -114.46 (c 0.16, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d6*):  $\delta$ 9.09 (s, 1H), 7.28 – 7.24 (m, 2H), 7.07 (d, *J* = 5.6 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.68 – 6.62 (m, 2H), 3.52 – 3.48 (m, 1H), 3.34 – 3.31 (m, 1H), 2.81 – 2.72 (m, 2H), 1.94 (s, 3H), 1.89 (s, 3H), 0.91 (t, *J* = 6.4 Hz, 3H), 0.54 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  169.6, 154.8, 138.7, 138.3, 137.4, 134.9, 129.6, 128.4, 127.3, 125.3, 123.2, 120.7, 112.6, 42.3, 20.6, 19.9, 14.2, 12.1. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>24</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 298.1802, found 298.1797.

# (R)-2'-Hydroxy-6,6'-dimethyl-N,N-dipropyl-[1,1'-biphenyl]-2-carboxamide (75)

OH OH N

Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 24.3 mg, 84% yield, 97% ee. mp: 159-161 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 12.171 min (major), 15.813 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -99.25 (c 0.27, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400

MHz, DMSO-*d6*):  $\delta$  9.12 (s, 1H), 7.28 – 7.24 (m, 2H), 7.04 (d, J = 5.6 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 7.6 Hz, 1H), 3.54 – 3.48 (m, 1H), 3.31 – 3.26 (m, 1H), 2.69 – 2.60 (m, 2H), 1.93 (s, 3H), 1.88 (s, 3H), 1.47 – 1.26 (m, 2H), 1.09 – 0.88 (m, 2H), 0.65 (t, J = 7.2 Hz, 3H), 0.51 (t, J = 7.6 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  170.2, 154.8, 138.7, 138.4, 137.3, 134.8, 129.6, 128.4, 127.2, 125.4, 123.7, 120.7, 112.7, 49.7, 44.8, 21.5, 20.7, 20.0, 19.8, 11.5, 11.4. HRMS-ESI (*m*/*z*): calcd for C<sub>21</sub>H<sub>28</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 326.2115, found 326.2107. (*R*)-*N*,*N*-Dibutyl-2'-hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-carboxamide (76)



Eluent: 10:1 petroleum ether / ethyl acetate; white solid, 18.7 mg, 53% yield, >99% ee. mp: 197-199 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.888 min (major), 13.372 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -92.61 (c 0.18, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400

MHz, DMSO-*d6*):  $\delta$  9.18 (s, 1H), 7.26 (d, J = 4.4 Hz, 2H), 7.03 – 6.96 (m, 2H), 6.69 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 7.2 Hz, 1H), 3.62 (dd, J = 13.2, 7.6 Hz, 1H), 3.24 (dd, J = 14.4, 10.4 Hz, 1H), 2.60 (dd, J = 14.8, 5.2 Hz, 1H), 2.40 (dd, J = 13.2, 7.2 Hz, 1H), 1.91 (s, 3H), 1.87 (s, 3H), 1.81 – 1.72 (m, 1H), 1.56 – 1.46 (m, 1H), 0.71 (d, J = 6.8 Hz, 3H), 0.66 (d, J = 6.8 Hz, 3H), 0.52 (d, J = 6.4 Hz, 3H), 0.35 (d, J = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  171.1, 154.7, 138.5, 137.2, 134.6, 129.6, 128.6, 127.1, 125.5, 125.2, 121.0, 113.0, 55.4, 50.4, 26.3, 25.9, 20.8, 20.6(4), 20.5(7), 20.0(4), 20.0(2), 19.9. HRMS-ESI (*m*/*z*): calcd for C<sub>23</sub>H<sub>32</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 354.2428, found 354.2426.

#### (R)-N,N-Dibenzyl-2'-hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-carboxamide (77)



Eluent: 2:1 petroleum ether / ethyl acetate; white solid, 24.0 mg, 57% yield, 98% ee. mp: 138-139 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 0.8 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 22.905 min (major), 21.151 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -144.40 (c 0.23, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, DMSO-*d6*):  $\delta$  9.29 (s, 1H), 7.37 – 7.24 (m, 7H), 7.16 – 7.08 (m, 5H), 6.80 (dd, *J* = 13.6, 7.2 Hz, 2H), 6.40 (d, *J* = 7.2 Hz, 2H), 5.26 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 16.6 Hz, 1H), 3.66 (d, *J* = 16.8 Hz, 1H), 3.50 (d, *J* = 15.6 Hz, 1H), 2.00 (s, 3H), 1.96 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  171.4, 154.9, 138.8, 137.7, 137.4, 137.1, 136.8, 134.9, 130.1, 129.2, 128.9, 127.9, 127.6, 127.3(3), 127.3(0), 127.1, 125.4, 124.0, 121.3, 113.3, 51.0, 45.7, 20.7, 20.0. HRMS-ESI (*m/z*): calcd for C<sub>29</sub>H<sub>28</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 422.2115, found 422.2106.

# (R)-2'-Hydroxy-N,6,6'-trimethyl-N-propyl-[1,1'-biphenyl]-2-carboxamide (78)



Eluent: 2:1 petroleum ether / ethyl acetate; white solid, 21.7 mg, 73% yield, 98% ee. mp: 122-123 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 6.942 min (major), 10.591 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -88.63 (c 0.21, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400

MHz, DMSO-*d6*):  $\delta$  9.09 (s, 1H), 7.29 – 7.25 (m, 2H), 7.05 – 6.97 (m, 2H), 6.70 – 6.63 (m, 2H), 3.28 – 3.25 (m, 1H), 2.82 – 2.80 (m, 1H), 2.71 (s, 3H), 1.94 (s, 3H), 1.90 (s, 3H), 1.42 – 1.08 (m, 2H), 0.70 – 0.54 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  170.5, 170.2, 154.7, 154.6, 138.6, 138.4, 137.5, 137.4, 135.0, 134.9, 129.8, 128.5, 128.4, 127.4, 127.2, 125.6, 124.0, 123.7, 120.8, 112.9, 112.8, 52.2, 47.8, 36.9, 31.8, 21.3, 20.6, 20.0, 19.8, 11.4, 11.2. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>24</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 298.1802, found 298.1797.

# (R)-N-Ethyl-2'-hydroxy-6,6'-dimethyl-N-propyl-[1,1'-biphenyl]-2-carboxamide (79)



Eluent: 5:1 petroleum ether / ethyl acetate; white solid, 23.9 mg, 77% yield, 98% ee. mp: 140-142 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub>=14.339 min (major), 16.948 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -93.13 (c 0.23, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR

(400 MHz, DMSO-*d6*): δ 9.11 (s, 1H), 7.29 – 7.24 (m, 2H), 7.07 – 6.97 (m, 2H), 6.68 – 6.62 (m, 2H), 3.59 – 3.22 (m, 2H), 2.81 – 2.67 (m, 2H), 1.95 (s, 3H), 1.89 (s, 3H), 1.45 – 1.28 (m, 1H),

1.13 – 1.05 (m, 1H), 0.93 – 0.64 (m, 3H), 0.54 – 0.48 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  170.5, 170.2, 154.7, 154.6, 138.6, 138.4, 137.5, 135.0, 134.9, 129.8(2), 129.7(5), 128.5, 128.4, 127.4, 127.2, 125.6, 124.0, 123.7, 120.8, 112.9, 112.7, 52.2, 47.8, 36.9, 31.8, 21.3, 20.6, 20.0, 19.8, 11.4, 11.2. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>26</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 312.1958, found 312.1951.

#### (R)-N-Ethyl-2'-hydroxy-N-isopropyl-6,6'-dimethyl-[1,1'-biphenyl]-2-carboxamide (80)



Eluent: 5:1 petroleum ether / ethyl acetate; white solid, 20.6 mg, 66% yield, 94% ee. mp: 174-176 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 22.029 min (major), 26.795 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -58.74 (c 0.21, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400

MHz, DMSO-*d6*):  $\delta$  9.15 (s, 1H), 7.27 – 7.25 (m, 2H), 7.10 – 6.97 (m, 2H), 6.69 – 6.61 (m, 2H), 4.13 – 3.78 (m, 1H), 3.30 – 3.23 (m, 1H), 2.84 – 2.67 (m, 1H), 1.95 (s, 3H), 1.92 (d, 3H), 0.98 – 0.89 (m, 6H), 0.68 – 0.60 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  169.6, 154.7, 138.7, 138.6, 137.4, 134.5, 129.5, 128.4, 127.3, 125.3, 123.4, 120.6, 112.4, 49.0, 34.1, 21.5, 21.1, 20.7, 20.0, 14.5. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>26</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 312.1958, found 312.1951.

# (R)-N-benzyl-2'-hydroxy-N,6,6'-trimethyl-[1,1'-biphenyl]-2-carboxamide (81)



Eluent: 5:1 petroleum ether / ethyl acetate; light yellow oil, 25.2 mg, 73% yield, 97% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 17.764 min (major), 20.736 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=-103.28 (c 0.24, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d6*):

 $\delta$  9.11 (s, 1H), 7.35 – 7.31 (m, 2H), 7.17 – 7.05 (m, 5H), 6.77 – 6.70 (m, 2H), 6.63 (d, J = 6.0 Hz, 2H), 5.09 – 4.67 (m, 1H), 3.88 – 3.50 (m, 1H), 2.66 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  170.7, 155.0, 137.6, 135.0, 130.0, 129.1, 128.8, 128.6, 127.6, 127.3, 127.1, 125.5, 123.8, 121.0, 113.1, 49.3, 36.5, 20.7, 20.0. HRMS-ESI (*m/z*): calcd for C<sub>23</sub>H<sub>24</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 346.1802, found 346.1796.

# (*R*)-2'-Hydroxy-*N*,6,6'-trimethyl-*N*-(naphthalen-1-ylmethyl)-[1,1'-biphenyl]-2-carboxamide (82)



Eluent: 5:1 petroleum ether / ethyl acetate; white solid, 23.7 mg, 60% yield, 96% ee. mp: 179-181 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 20:80, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.485

min (major), 11.722 min (minor).  $[\alpha]^{25}_{D} = -103.98$  (c 0.23, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d6*):  $\delta$  9.24 (s, 1H), 7.95 – 7.82 (m, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.34 – 7.05 (m, 5H), 6.87 – 6.71 (m, 2H), 6.52 (d, J = 6.0 Hz, 1H), 5.21 – 5.17 (m, 1H), 4.68 – 4.47 (m, 1H), 2.77 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  170.8, 155.0, 137.7, 135.1, 133.7, 132.5, 131.3, 130.8, 130.1, 129.0, 128.8, 127.6, 127.5, 126.8, 126.2, 124.2, 123.9, 123.4, 121.1, 113.1, 47.7, 37.1, 20.7, 20.0. HRMS-ESI (*m/z*): calcd for C<sub>27</sub>H<sub>26</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 396.1958, found 396.1952.

# (R)-N-Benzyl-2'-hydroxy-N-isopropyl-6,6'-dimethyl-[1,1'-biphenyl]-2-carboxamide (83)



Eluent: 5:1 petroleum ether / ethyl acetate; white solid, 18.7 mg, 50% yield, >99% ee. mp: 151-152 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 18.458 min (major), 22.276 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -91.53 (c 0.18, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR

(400 MHz, DMSO-*d6*):  $\delta$  9.26 (s, 1H), 7.32 – 7.31 (m, 2H), 7.21 – 7.16 (m, 2H), 7.05 – 7.02 (m, 3H), 6.76 (t, J = 8.4 Hz, 3H), 6.46 (d, J = 6.4 Hz, 2H), 4.78 (d, J = 16.4 Hz, 1H), 4.08 – 4.01 (m, 2H), 1.98 (s, 3H), 1.95 (s, 3H), 1.03 (d, J = 6.8 Hz, 3H), 0.72 (d, J = 6.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  170.9, 155.1, 139.9, 138.9, 138.4, 137.5, 134.6, 129.7, 128.8, 128.3, 127.5, 126.3, 126.0, 125.4, 123.4, 121.0, 112.8, 49.6, 42.9, 21.5, 20.8, 20.7, 20.0. HRMS-ESI (*m/z*): calcd for C<sub>25</sub>H<sub>28</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 374.2115, found 374.2110.

#### (R)-(2'-Hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)(pyrrolidin-1-yl)methanone (84)



Eluent: 2:1 petroleum ether / ethyl acetate; light yellow oil, 11.8 mg, 40% yield, 93% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 20:80, flow: 1.0 mL/min,  $\lambda = 254$  nm,  $t_r = 17.027$  min (major), 12.501 min (minor).  $[\alpha]^{25}_{D} = -64.42$  (c 0.11, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d6*):  $\delta$ 

9.08 (s, 1H), 7.30 – 7.24 (m, 2H), 7.11 (dd, J = 6.8, 1.6 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.67 (dd, J = 16.8, 8.0 Hz, 2H), 3.48 – 3.43 (m, 1H), 3.25 – 3.19 (m, 1H), 3.02 – 2.95 (m, 2H), 1.92 (s, 3H), 1.90 (s, 3H), 1.73 – 1.65 (m, 3H), 1.60 – 1.53 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  168.7, 154.6, 139.0, 138.5, 137.4, 134.9, 130.0, 128.3, 127.4, 125.7, 123.7, 120.8, 112.8, 48.2, 45.1, 26.0, 24.4, 20.6, 20.0. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 296.1645, found 296.1639.

#### (R)-Azepan-1-yl(2'-hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)methanone (85)



Eluent: 5:1 petroleum ether / ethyl acetate; white solid, 23.6 mg, 73% yield, 96% ee. mp: 153-155 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 30.997 min (major), 25.120 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -101.75 (c 0.23, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR

(400 MHz, DMSO-*d6*):  $\delta$  9.11 (s, 1H), 7.27 – 7.24 (m, 2H), 7.05 – 6.98 (m, 2H), 6.69 – 6.63 (m, 2H), 3.35 – 3.29 (m, 2H), 3.17 – 3.08 (m, 2H), 1.91 (s, 6H), 1.54 – 1.31 (m, 8H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  170.2, 154.6, 138.7, 138.5, 137.4, 134.8, 129.7, 128.4, 127.3, 125.5, 123.9, 120.8, 112.8, 48.8, 44.5, 29.0, 28.3, 27.8, 26.1, 20.7, 20.0. HRMS-ESI (*m/z*): calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 324.1958, found 324.1953.

#### (R)-(2'-Hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)(4-phenylpiperidin-1-yl)methanone (86)



Eluent: 2:1 petroleum ether / ethyl acetate; white solid,15.4 mg, 40% yield, 95% ee. mp: 224-225 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 3:97, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 43.383 min (major), 40.196 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=-117.89 (c 0.19, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, DMSO-*d6*):  $\delta$  9.20 (s, 0.6H), 9.10 (s, 0.4H), 7.32 – 7.18 (m, 6H), 7.16 – 7.00 (m, 3H), 6.77 – 6.65 (m, 2H), 4.39 (d, J = 12.8 Hz, 1H), 3.66 (t, J = 10.8 Hz, 1H), 2.97 – 2.36 (m, 3H), 1.96 – 1.92 (m, 6H), 1.74 – 0.81 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  168.9, 168.8, 154.8, 154.6, 146.3, 146.1, 138.7, 138.5, 138.1, 137.9, 137.5, 137.4, 134.9, 134.7, 129.9, 129.7, 128.8, 128.5, 128.4, 127.4, 127.2, 127.1, 126.6(4), 126.6(0), 125.6, 125.5, 124.0, 123.8, 120.8, 112.8, 112.5, 48.0, 46.9, 42.4, 41.9, 41.7, 41.5, 33.6, 33.5, 33.2, 20.7, 20.6, 20.0, 19.9. HRMS-ESI (*m/z*): calcd for C<sub>26</sub>H<sub>28</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 386.2115, found 386.2108.

# (R)-(2'-Hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)(morpholino)methanone (87)



Eluent: 2:1 petroleum ether / ethyl acetate; white solid, 20.8 mg, 67% yield, 93% ee. mp: 154-155 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda$ = 254 nm, t<sub>r</sub> = 19.346 min (major), 17.063 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=-69.31 (c 0.20, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400

MHz, DMSO-*d6*):  $\delta$  9.16 (s, 1H), 7.28 (q, J = 7.6 Hz, 2H), 7.09 – 7.01 (m, 2H), 6.69 (dd, J = 22.8, 8.0 Hz, 2H), 3.58 – 3.48 (m, 3H), 3.25 – 3.01 (m, 5H), 1.93 (s, 3H), 1.90 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR

(100 MHz, DMSO-*d6*): δ 169.1, 154.6, 138.5, 137.6, 137.2, 135.0, 130.1, 128.6, 127.5, 125.4,
124.0, 120.9, 112.7, 66.8, 66.5, 47.2, 41.6, 20.6, 20.0. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub> [M + H]<sup>+</sup>: 312.1594, found 312.1589.

#### (*R*)-(2'-Hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)(thiomorpholino)methanone (88)



Eluent: 5:1 petroleum ether / ethyl acetate; white solid, 23.2 mg, 71% yield, 96% ee. mp: 158-160 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 21.155 min (major), 14.706 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -67.26 (c 0.22, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400

MHz, DMSO-*d6*):  $\delta$  9.15 (s, 1H), 7.31 – 7.25 (m, 2H), 7.11 (d, J = 6.8 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.68 (dd, J = 23.2, 8.0 Hz, 2H), 3.70 – 3.66 (m, 1H), 3.49 – 3.41 (m, 2H), 3.34 – 3.28 (m, 1H), 2.58 – 2.46 (m, 2H), 2.41 – 2.36 (m, 1H), 2.24 – 2.19 (m, 1H), 1.92 (s, 3H), 1.89 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  169.3, 154.5, 138.6, 137.6, 137.3, 134.9, 130.0, 128.6, 127.4, 125.4, 123.9, 120.9, 112.7, 49.5, 43.5, 27.5, 27.3, 20.5, 19.9. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>2</sub>S [M + H]<sup>+</sup>: 328.1366, found 328.1360.

#### (*R*)-(2'-Hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-yl)(4-phenylpiperazin-1-yl)methanone (89)



Eluent: 2:1 petroleum ether / ethyl acetate; white solid, 27.8 mg, 72% yield, 90% ee. mp: 209-210 °C. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 32.850 min (major), 24.301 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -116.48 (c 0.27, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H

NMR (400 MHz, DMSO-*d6*):  $\delta$  9.19 (s, 1H), 7.30 (q, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 6.0 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.80 (t, J = 7.2 Hz, 1H), 6.70 – 6.65 (m, 2H), 3.63 – 3.60 (m, 2H), 3.38 – 3.08 (m, 5H), 2.79 (t, J = 8.8 Hz, 1H), 2.59 (t, J = 8.8 Hz, 1H), 1.95 (s, 3H), 1.93 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  169.0, 154.6, 151.4, 138.6, 137.6, 137.5, 135.1, 130.1, 129.5, 128.6, 127.5, 125.5, 124.0, 120.9, 119.9, 116.6, 112.8, 49.5, 49.0, 46.6, 41.1, 20.6, 20.0. HRMS-ESI (*m*/*z*): calcd for C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 387.2067, found 387.2059.

#### Tert-Butyl (R)-N-(2'-hydroxy-6,6'-dimethyl-[1,1'-biphenyl]-2-carbonyl)-N-methylglycinate (90)



Eluent: 2:1 petroleum ether / ethyl acetate; light yellow oil, 22.9 mg, 62% yield, >99% ee. HPLC conditions: Chiralpak INC,

isopropanol/hexanes = 7:93, flow: 1 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.785 min (major), 10.382 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=-91.82 (c 0.22, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d6*):  $\delta$  9.21 (s, 0.6H), 9.05 (s, 0.4H), 7.32 – 7.21 (m, 2H), 7.11 – 6.96 (m, 2H), 6.70 – 6.63 (m, 2H), 4.20 – 4.05 (m, 2H), 3.55 (t, *J* = 16.0 Hz, 1H), 2.80 (s, 1.2H), 2.70 (s, 1.8H), 1.91 (d, *J* = 4.4 Hz, 3H), 1.88 (s, 3H), 1.39 (d, *J* = 3.2 Hz, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  171.0, 170.9, 169.3, 168.5, 154.7, 154.5, 138.5, 138.3, 137.6, 137.5, 137.3, 137.2, 135.2, 134.9, 130.3, 130.2, 128.6, 128.4, 127.4, 127.2, 125.5, 125.3, 124.0, 123.3, 120.9, 120.8, 113.0, 112.9, 81.7, 81.3, 53.3, 49.5, 38.3, 33.7, 28.2, 28.1, 20.5, 19.9. HRMS-ESI (*m*/*z*): calcd for C<sub>22</sub>H<sub>28</sub>NO<sub>4</sub> [M + H]<sup>+</sup>: 370.2013, found 370.2006.

# (*R*, *E*)-2',6-Dimethyl-6'-styryl-[1,1'-biphenyl]-2-yl diethylcarbamate (91)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 27.2 mg, 68% yield, 99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 4.053 min (major), 3.661 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -64.17 (c 0.24, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.59 (d, J = 8.0 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.24 (d, J = 7.6 Hz, 2H), 7.21 – 7.13 (m, 4H), 6.95 (d, J = 16.4 Hz, 1H), 6.76 (d, J = 16.4 Hz, 1H), 3.13 (q, J = 6.8 Hz, 1H), 2.88 (q, J = 6.8 Hz, 1H), 2.00 (s, 3H), 1.94 (s, 3H), 0.95 (t, J = 6.8 Hz, 3H), 0.70 (t, J = 6.8 Hz, 3H).  $^{13}C{^{1}H}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.6, 148.9, 138.0, 137.7, 137.1, 136.3, 135.7, 132.1, 129.0, 128.9, 128.5, 128.0, 127.4(4), 127.4(3), 127.2, 126.7, 126.6, 122.4, 120.5, 41.8, 41.4, 20.0, 19.6, 13.4, 13.0. HRMS-ESI (*m*/*z*): calcd for C<sub>27</sub> H<sub>30</sub> NO<sub>2</sub> [M + H]<sup>+</sup>: 400.2271, found 400.2272.

#### (*R*)-2'-Ethynyl-6,6'-dimethyl-[1,1'-biphenyl]-2-yl diethylcarbamate (92)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 15.8 mg, 54% yield, 99% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 2:98, flow: 0.5 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 13.932 min (major), 14.745 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=-13.43 (c 0.07, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.41 (d, J = 7.6 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.14 (d, J = 7.2 Hz, 1H), 3.22 – 3.11 (m, 2H), 2.98 – 2.87 (m, 2H), 2.82 (s, 1H), 2.02 (s, 6H), 0.99 (t, J = 6.0 Hz, 3H), 0.73 (t, J = 6.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.4, 148.8, 139.7, 137.5, 132.1, 130.3, 130.1, 128.0, 127.1, 126.3, 122.4, 120.0, 100.0, 82.3, 79.1, 41.7, 41.4, 19.8, 19.4, 13.4, 13.1. HRMS-ESI (*m/z*): calcd for  $C_{21}H_{24}NO_2$  [M + H]<sup>+</sup>: 322.1802, found 322.1801.

# (R)-2',6-Dimethyl-6'-(phenylethynyl)-[1,1'-biphenyl]-2-yl diethylcarbamate (93)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 19.1 mg, 48% yield, 99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 2:98, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 7.438 min (major), 6.911 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -131.07 (c 0.10, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>):  $\delta$  7.43 (t, J = 5.2 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.24 – 7.19 (m, 6H), 7.15 (d, J = 7.6 Hz, 1H), 7.09 – 7.06 (m, 2H), 3.23 – 3.10 (m, 2H), 2.97 – 2.87 (m, 2H), 2.08 (s, 3H), 2.05 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H), 0.72 (t, J = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.5, 149.1, 139.6, 137.8, 137.4, 132.5, 131.4, 129.8, 128.8, 128.0, 127.8(3), 127.7(6), 127.2, 126.2, 123.6, 123.5, 119.9, 91.8, 88.5, 41.7, 41.4, 19.9, 19.5, 13.4, 13.1. HRMS-ESI (*m/z*): calcd for C<sub>27</sub>H<sub>28</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 398.2115, found 398.2111.

# (*R*)-6,6'-Dimethyl-[1,1':2',1''-terphenyl]-2-yl diethylcarbamate (94)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 30.6 mg, 82% yield, 99% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 2:98, flow: 0.5 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 12.144 min (major), 13.904 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -92.31 (c 0.23, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.34 – 7.28 (m, 1H), 7.26 – 7.21 (m, 2H), 7.17 – 7.12 (m, 6H), 7.10 – 7.08 (m, 1H), 6.91 – 6.89 (m, 1H), 3.27 – 3.19 (m, 2H), 3.05 – 2.91 (m, 2H), 2.04 (s, 3H), 1.84 (s, 3H), 1.07 (t, J = 6.8 Hz, 3H), 0.73 (t, J = 6.8 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.5, 149.2, 141.7, 138.8, 137.3, 137.2, 137.0, 136.3, 135.0, 132.3, 129.7, 128.8(4), 128.7(9), 128.4, 127.5, 127.4(5), 127.4(1), 127.3(7), 126.4, 126.1, 119.9, 101.2, 42.0, 41.5, 20.2, 19.7, 13.4, 13.2. HRMS-ESI (*m/z*): calcd for C<sub>25</sub> H<sub>28</sub> NO<sub>2</sub> [M + H]<sup>+</sup>: 374.2115 found 374.2113.

# Methyl (R)-2'-((diethylcarbamoyl)oxy)-6,6'-dimethyl-[1,1'-biphenyl]-2-carboxylate (95)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 23.1 mg, 65% yield, 99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 4.611 min (major), 4.295 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -70.37 (c 0.11, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 3.57 (s, 3H), 3.16 – 3.11 (m, 2H), 2.88 – 2.83 (m, 2H), 2.01 (s, 3H), 2.00 (s, 3H), 0.97 (t, J = 6.4 Hz, 3H), 0.68 (t, J = 6.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 167.8, 153.5, 148.1, 138.1, 137.4, 137.0, 133.3, 132.6, 131.2, 127.6, 127.4, 127.2, 126.1, 119.9, 51.8, 41.8, 41.3, 19.8, 19.6, 13.4, 13.1. HRMS-ESI (m/z): calcd for C<sub>21</sub>H<sub>26</sub>NO<sub>4</sub> [M + H]<sup>+</sup>: 356.1856, found 356.1855.

# (R)-2'-Cyano-6,6'-dimethyl-[1,1'-biphenyl]-2-yl diethylcarbamate (96)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 28.6 mg, 89% yield, 99% ee). HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 14.323 min (major), 16.822 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = -62.87 (c 0.24, CH2Cl2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.57 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.34 (q, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 3.18 – 3.10 (m, 2H), 3.08 – 2.88 (m, 2H), 2.09 (s, 3H), 2.03 (s, 3H), 0.96 (t, J = 6.8 Hz, 3H), 0.76 (t, J = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.2, 148.8, 140.4, 139.1, 137.2, 134.2, 130.1, 129.3, 127.9, 126.9, 120.4, 117.9, 113.8, 41.8, 41.5, 19.6, 19.4, 13.5, 13.1. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 323.1754, found 323.1752.

# (R)-3-Benzoyl-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-yl diethylcarbamate (97)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 47.4 mg, 90% yield, 98% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 50.045 min (major), 46.525 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=-16.25 (c 0.16, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 

7.86 – 7.84 (m, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 2.98 – 2.85 (m, 2H), 2.71 – 2.62 (m, 1H) 2.54 – 2.45 (m, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 0.78 (t, J = 6.8 Hz, 3H), 0.45 (t, J = 6.8 Hz, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  194.6, 152.2, 146.2, 140.9, 140.9, 138.8, 138.0, 137.3, 136.4, 132.3, 130.9, 130.0, 129.8, 129.2, 128.0, 126.6, 101.0, 41.9, 41.2, 21.3, 19.7, 13.1, 13.0. HRMS-ESI (*m*/*z*): calcd for C<sub>26</sub>H<sub>27</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 528.1030, found 528.1025.

#### (*R*)-2'-Iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-ol (98)

С

Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 28.8 mg, 89% yield, 98% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 1:99, flow: 1 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 25.976 min (major), 23.645 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = +8.79

(c 0.39, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.85 (d, J = 8.0 Hz, 1H), 7.33 (d,

J = 7.6 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.88 (dd, J = 14.8, 7.2 Hz, 2H), 4.45 (s, 1H), 2.09 (s, 3H), 1.95 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  151.8, 139.7, 139.6, 137.3, 136.7, 130.4, 130.2, 130.1, 129.1, 122.2, 113.0, 102.4, 21.2, 19.5. HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>12</sub>IO [M-H]<sup>-</sup>: 322.9938, found 322.9938.

#### (*R*)-6,6'-Dimethyl-[1,1'-biphenyl]-2,2'-diol (99)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 12.8 mg, 60% yield, 97% ee. HPLC conditions: Chiralpak OD-H, isopropanol/hexanes = 15:85, flow: 1 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 5.868 min (major), 9.122 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = +50 (c 0.06, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.23 (t, *J* = 8.0 Hz, 2H), 6.89 (t, *J* =

8.8 Hz, 2H), 4.74 (s, 2H), 1.99 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 153.8, 138.9, 130.1, 122.5, 119.6, 113.2, 19.5. HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>13</sub>O<sub>2</sub> [M - H]<sup>-</sup>: 213.0921, found 213.0917.

#### (R)-2',6-Dimethyl-6'-(phenylamino)-[1,1'-biphenyl]-2-yl diethylcarbamate (100)



Eluent: 20:1 petroleum ether / ethyl acetate; light yellow oil, 15.5 mg, 40% yield, 96% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda$  = 254 nm, t<sub>r</sub> = 4.384 min

(major), 4.141 min (minor).  $[\alpha]^{25}_{D} = -51.67$  (c 0.06, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR

(400 MHz, DMSO-*d6*):  $\delta$  7.32 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 7.18 – 7.10 (m, 4H), 7.09 (d, J = 8.0 Hz, 1H), 6.89 – 6.84 (m, 3H), 6.77 (t, J = 7.6 Hz, 1H), 6.11 (s, 1H), 3.20 – 2.92 (m, 4H), 1.93 (s, 3H), 1.86 (s, 3H), 0.86 (t, J = 6.8 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  154.5, 149.9, 144.1, 141.8, 138.6, 137.6, 131.5, 129.6, 128.8, 128.5, 127.8, 126.9, 123.0, 121.2, 120.2, 117.4, 115.2, 42.1, 41.8, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 20.2, 19.6, 13.8, 13.4. HRMS-ESI (*m/z*): calcd for C<sub>25</sub>H<sub>29</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 389.2224, found 389.2219.

#### (*R*)-2',6-Dimethyl-6'-(phenylamino)-[1,1'-biphenyl]-2-ol (101)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 23.1 mg, 80% yield, 99% ee. HPLC conditions: Chiralpak AD-H, isopropanol/hexanes = 10:90, flow: 1 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 5.614 min (major), 6.549 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub> = +7.14 (c 0.04, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d6*):  $\delta$  9.09 (s, 1H), 7.14

- 7.10 (m, 4H), 7.07 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H), 6.87 (dd, J = 6.0, 2.4 Hz, 1H), 6.79 - 6.74 (m, 3H), 5.93 (s, 1H), 1.89 (s, 3H), 1.85 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  155.4, 144.8, 141.3, 138.0, 137.9, 129.4, 129.0, 128.6, 127.6, 124.1, 123.0, 121.2, 119.9, 117.3, 116.2, 113.6, 20.3, 19.9. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>20</sub>NO [M + H]<sup>+</sup>: 290.1539, found 290.1535.

# (R)-2'-((Diethylamino)methyl)-6,6'-dimethyl-[1,1'-biphenyl]-2-ol (102)



Eluent: 10:1 petroleum ether / ethyl acetate; colorless liquid, 27.4 mg, 97% yield, 52% ee. HPLC conditions: Chiralpak OJ-H, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda = 254$  nm,  $t_r = 3.344$  min (major), 3.752 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=-23.37 (c 0.47, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d6*):  $\delta$ 

9.32 (s, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.76 (t, J = 7.2 Hz, 2H), 3.12 (s, 2H), 2.32 (q, J = 7.2 Hz, 4H), 1.86 (s, 3H), 1.78 (s, 3H), 0.80 (t, J = 7.2 Hz, 6H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*):  $\delta$  154.6, 137.9, 137.2, 136.3, 128.6, 128.3, 127.3, 127.0, 126.9, 121.2, 114.3, 55.5, 46.5, 20.1, 20.0, 11.7. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>26</sub>NO [M + H]<sup>+</sup>: 284.2009, found 284.2005.

# (*R*)-2'-(Azepan-1-ylmethyl)-6,6'-dimethyl-[1,1'-biphenyl]-2-ol (103)



Eluent: 10:1 petroleum ether / ethyl acetate; light yellow oil, 25.3 mg, 82% yield, >99% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 3:97, flow: 1.0 mL/min,  $\lambda = 254$  nm,  $t_r = 5.281$  min (major), 4.862 min (minor).  $[\alpha]^{25}_{D} = -34.92$  (c 0.13, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d6*):

 $\delta$  9.29 (s, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.77 – 6.75 (m, 2H), 3.21 (q, *J* = 14.4 Hz, 2H), 2.45 (s, 4H), 1.86 (s, 3H), 1.77 (s, 3H), 1.51 (s, 8H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*): δ 154.5, 137.8, 137.1, 136.4, 128.6,

128.3, 127.0, 126.5, 121.2, 114.1, 60.2, 55.6, 27.7, 26.8, 20.1, 20.0. HRMS-ESI (*m/z*): calcd for C<sub>21</sub>H<sub>28</sub>NO [M + H]<sup>+</sup>: 310.2165, found 310.2156.

# (R)-2'-(Diethylcarbamoyl)-6,6'-dimethyl-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (104)



Eluent: 20:1 petroleum ether / ethyl acetate; white solid, 21.4 mg, 50% yield, 99% ee. HPLC conditions: Chiralpak INC, isopropanol/hexanes = 2:98, flow: 1.0 mL/min,  $\lambda = 254$  nm, t<sub>r</sub> = 10.279 min (major), 9.05 min (minor). [ $\alpha$ ]<sup>25</sup><sub>D</sub>=

-60.0 (c 0.08, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.36 – 7.33 (m, 2H),

7.29 (d, J = 7.6 Hz, 2H), 7.18 – 7.15 (m, 1H), 7.10 (d, J = 7.6 Hz, 1H), 3.66 – 3.56 (m, 1H), 3.44 – 3.36 (m, 1H), 3.08 – 2.92 (m, 2H), 2.15 (s, 3H), 2.09 (s, 3H), 1.13 (t, J = 6.8 Hz, 3H), 0.78 (t, J = 6.8 Hz, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.2, 147.1, 138.1, 137.0, 132.0, 131.5, 130.6, 129.5, 129.0, 128.0, 122.8, 119.8, 117.5, 116.7, 42.7, 37.9, 20.1, 19.5, 13.9, 11.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -74.77 (s). HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>23</sub>F<sub>3</sub>NO<sub>4</sub>S [M + H]<sup>+</sup>: 430.1294, found 430.1293.

# I. Crystal data and structure refinement





X-ray stucture of 23

Table S2.	Crystal	data and	1 structure	refinements	for	23
	2					

Compound	23		
Empirical formula	C <sub>19</sub> H <sub>20</sub> INO <sub>3</sub>		
Formula weight	437.26		
Temperature/K	170.0		
Crystal system	Monoclinic		
Space group	P21		
a/Å	7.9482(3)		
b/Å	8.5150(3)		
c/Å	14.1656(6)		
$\alpha/^{\circ}$	90		
β/°	105.8200(10)		
$\gamma^{/\circ}$	90		
Volume/Å <sup>3</sup>	922.40(6)		
Z	2		
Density (calculated)/g•cm <sup>-3</sup>	1.574		
$\mu/mm^{-1}$	1.752		
F(000)	436.0		
Crystal size/mm <sup>3</sup>	$0.08\times0.05\times0.04$		
Radiation	MoKa ( $\lambda = 0.71073$ )		
$2\Theta$ range for data collection/°	5.328 to 52.806		
Index ranges	$-9 \le h \le 9, -10 \le k \le 10, -16 \le l \le 17$		
Reflections collected	10652		
Independent reflections	$3631 [R_{int} = 0.0344, R_{sigma} = 0.0420]$		
Data/restraints/parameters	3631/1/219		
Goodness-of-fit on F <sup>2</sup>	1.099		
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0283, wR_2 = 0.0515$		
Final R indexes [all data]	$R_1 = 0.0376, wR_2 = 0.0574$		
Largest diff. peak/hole/e Å <sup>-3</sup>	0.44/-0.73		
Flack parameter	-0.047(13)		



39



X-ray stucture of 39

Table S3. Crystal data and structure refinements for 39

Compound	39		
Empirical formula	$C_{22}H_{19}BrINO_2$		
Formula weight	536.19		
Temperature/K	150		
Crystal system	monoclinic		
Space group	P21		
a/Å	12.4830(18)		
b/Å	8.0886(9)		
c/Å	21.009(3)		
$\alpha ^{\prime \circ }$	90		
$\beta^{\prime\circ}$	93.942(4)		
$\gamma^{/\circ}$	90		
Volume/Å <sup>3</sup>	2116.3(5)		
Z	4		
Density (calculated)/g•cm <sup>-3</sup>	1.683		
µ/mm <sup>-1</sup>	3.417		
F(000)	1048.0		
Crystal size/mm <sup>3</sup>	0.09  imes 0.05  imes 0.04		
Radiation	MoKa ( $\lambda = 0.71073$ )		
$2\Theta$ range for data collection/°	3.918 to 50.684		
Index ranges	$-14 \le h \le 14, -9 \le k \le 9, -25 \le l \le 25$		
Reflections collected	16502		
Independent reflections	$6454 \; [R_{int} = 0.0843,  R_{sigma} = 0.0970]$		
Data/restraints/parameters	6454/1/491		
Goodness-of-fit on F <sup>2</sup>	1.032		
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0546, wR_2 = 0.1246$		
Final R indexes [all data]	$R_1 = 0.0790, wR_2 = 0.1418$		
Largest diff. peak/hole/e Å <sup>-3</sup>	1.38/-0.94		
Flack parameter	0.028(16)		





X-ray stucture of 55

Table S4. Crystal data and structure refinements for 55

Compound	55		
Empirical formula	C <sub>22</sub> H <sub>24</sub> INO <sub>3</sub>		
Formula weight	477.32		
Temperature/K	150		
Crystal system	monoclinic		
Space group	P2 <sub>1</sub> /c		
a/Å	18.1680(6)		
b/Å	14.5103(5)		
c/Å	15.8483(5)		
$\alpha/^{\circ}$	90		
β/°	99.0800(10)		
γ/°	90		
Volume/Å <sup>3</sup>	4125.6(2)		
Ζ	8		
Density (calculated)/g•cm <sup>-3</sup>	1.537		
$\mu/mm^{-1}$	1.574		
F(000)	1920.0		
Crystal size/mm <sup>3</sup>	0.16  imes 0.08  imes 0.04		
Radiation	MoKa ( $\lambda = 0.71073$ )		
$2\Theta$ range for data collection/°	3.828 to 52.798		
Index ranges	$-22 \le h \le 22, -18 \le k \le 16, -19 \le l \le 19$		
Reflections collected	30574		
Independent reflections	8338 [ $R_{int} = 0.0505, R_{sigma} = 0.0472$ ]		
Data/restraints/parameters	8338/579/531		
Goodness-of-fit on F <sup>2</sup>	1.084		
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0446, wR_2 = 0.0947$		
Final R indexes [all data]	$R_1 = 0.0624, wR_2 = 0.1034$		
Largest diff. peak/hole/e Å <sup>-3</sup>	0.45/-0.34		





Table 5.	Crystal	data and	structure	refinements	for ( <i>R</i>	)-64
					•	

Compound	64		
Empirical formula	C <sub>19</sub> H <sub>19</sub> ClINO <sub>2</sub> S		
Formula weight	487.76		
Temperature/K	170.0		
Crystal system	monoclinic		
Space group	P21		
a/Å	8.7600(3)		
b/Å	10.9737(3)		
c/Å	10.8434(4)		
$\alpha /^{\circ}$	90		
β/°	105.8870(10)		
$\gamma/^{\circ}$	90		
Volume/Å <sup>3</sup>	1002.56(6)		
Z	2		
Density (calculated)/g•cm <sup>-3</sup>	1.616		
$\mu/\text{mm}^{-1}$	1.846		
F(000)	484.0		
Crystal size/mm <sup>3</sup>	0.25  imes 0.15  imes 0.08		
Radiation	MoKa ( $\lambda = 0.71073$ )		
$2\Theta$ range for data collection/°	5.32 to 52.792		
Index ranges	$-8 \le h \le 10, -13 \le k \le 11, -13 \le l \le 13$		
Reflections collected	7712		
Independent reflections	$3621 \ [R_{int} = 0.0245, R_{sigma} = 0.0371]$		
Data/restraints/parameters	3621/1/228		
Goodness-of-fit on F <sup>2</sup>	1.063		
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0242, wR_2 = 0.0459$		
Final R indexes [all data]	$R_1 = 0.0276, wR_2 = 0.0482$		
Largest diff. peak/hole/e Å <sup>-3</sup>	0.38/-0.61		
Flack parameter	0.032(12)		





X-ray stucture of 80

Table S5. Crystal data and structure refinements for 80

Compound	80		
Empirical formula	C <sub>20</sub> H <sub>25</sub> NO <sub>2</sub>		
Formula weight	311.41		
Temperature/K	150.0		
Crystal system	trigonal		
Space group	P3 <sub>2</sub>		
a/Å	24.3390(16)		
b/Å	24.3390(16)		
c/Å	7.9076(6)		
α/°	90		
β/°	90		
$\gamma^{/\circ}$	120		
Volume/Å <sup>3</sup>	4056.8(6)		
Z	9		
$ ho_{ m calc}g/cm^3$	1.147		
µ/mm <sup>-1</sup>	0.073		
F(000)	1512.0		
Crystal size/mm <sup>3</sup>	$0.12\times0.07\times0.04$		
Radiation	MoKa ( $\lambda = 0.71073$ )		
$2\Theta$ range for data collection/°	3.864 to 52.722		
Index ranges	$-13 \le h \le 29, -30 \le k \le 28, -9 \le l \le 8$		
Reflections collected	11341		
Independent reflections	8498 [ $R_{int} = 0.0664, R_{sigma} = 0.1321$ ]		
Data/restraints/parameters	8498/1129/641		
Goodness-of-fit on F <sup>2</sup>	1.101		
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0722, wR_2 = 0.1285$		
Final R indexes [all data]	$R_1 = 0.1366, wR_2 = 0.1671$		
Largest diff. peak/hole / e Å <sup>-3</sup>	0.26/-0.28		

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# J. Copies of NMR spectroscopies



Figure S2. <sup>13</sup>C NMR Spectrum of 3



Figure S4. <sup>13</sup>C NMR Spectrum of 4



Figure S6. <sup>13</sup>C NMR Spectrum of 5



Figure S8. <sup>13</sup>C NMR Spectrum of 6



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Figure S10. <sup>13</sup>C NMR Spectrum of 7



Figure S12. <sup>13</sup>C NMR Spectrum of 8



Figure S14. <sup>13</sup>C NMR Spectrum of 9



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Figure S16. <sup>13</sup>C NMR Spectrum of 10







Figure S18. <sup>13</sup>C NMR Spectrum of 11





Figure S20. <sup>13</sup>C NMR Spectrum of 12



Figure S22. <sup>13</sup>C NMR Spectrum of 13



Figure S24. <sup>13</sup>C NMR Spectrum of 14



Figure S26. <sup>13</sup>C NMR Spectrum of 15



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Figure S28. <sup>13</sup>C NMR Spectrum of 16



Figure S30. <sup>13</sup>C NMR Spectrum of 17


Figure S32. <sup>13</sup>C NMR Spectrum of 18



Figure S34. <sup>13</sup>C NMR Spectrum of 19



Figure S36. <sup>13</sup>C NMR Spectrum of 20







Figure S38. <sup>13</sup>C NMR Spectrum of 21



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Figure S40. <sup>13</sup>C NMR Spectrum of 22



Figure S42. <sup>13</sup>C NMR Spectrum of 23



Figure S44. <sup>13</sup>C NMR Spectrum of 24







Figure S48. <sup>13</sup>C NMR Spectrum of 26







S83



Figure S54. <sup>13</sup>C NMR Spectrum of 29



Figure S56. <sup>13</sup>C NMR Spectrum of 30







Figure S60. <sup>13</sup>C NMR Spectrum of 32











Figure S64. <sup>13</sup>C NMR Spectrum of 34



Figure S66. <sup>13</sup>C NMR Spectrum of 35



Figure S68. <sup>13</sup>C NMR Spectrum of 36



Figure S70. <sup>13</sup>C NMR Spectrum of 37



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2.

Figure S71. <sup>19</sup>F NMR Spectrum of 37



Figure S73. <sup>13</sup>C NMR Spectrum of 38



S95



Figure S77. <sup>13</sup>C NMR Spectrum of 40







Figure S79. <sup>13</sup>C NMR Spectrum of 41



Figure S81. <sup>13</sup>C NMR Spectrum of 42



Figure S83. <sup>13</sup>C NMR Spectrum of 43



Figure S85. <sup>13</sup>C NMR Spectrum of 44











210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Figure S91. <sup>13</sup>C NMR Spectrum of 47



Figure S93. <sup>13</sup>C NMR Spectrum of 48







Figure S97. <sup>13</sup>C NMR Spectrum of 50










Figure S103. <sup>13</sup>C NMR Spectrum of 53







Figure S107. <sup>13</sup>C NMR Spectrum of 55





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Figure S109. <sup>13</sup>C NMR Spectrum of 56



Figure S111. <sup>13</sup>C NMR Spectrum of 57



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2. fl (ppm)



 $\begin{array}{c} 7.7.75\\ 7.727\\ 7.727\\ 7.727\\ 7.727\\ 7.724\\ 7.727\\ 7.724\\ 7.724\\ 7.724\\ 7.724\\ 7.727\\ 7.724\\ 7.726\\ 7.725\\ 7$ 







Figure S114. <sup>13</sup>C NMR Spectrum of 58



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2. fl (ppm)





Figure S117. <sup>13</sup>C NMR Spectrum of 59



Figure S119. <sup>13</sup>C NMR Spectrum of 60



Figure S121. <sup>13</sup>C NMR Spectrum of 61



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: Supplementary Figure 122. <sup>19</sup>F NMR Spectrum of 61



Figure S124. <sup>13</sup>C NMR Spectrum of 62











210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

Figure S128. <sup>13</sup>C NMR Spectrum of 64



Figure S130. <sup>13</sup>C NMR Spectrum of 65



Figure S132. <sup>13</sup>C NMR Spectrum of 66





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)









Figure S136. <sup>13</sup>C NMR Spectrum of 68



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)

Figure S138. <sup>13</sup>C NMR Spectrum of 69



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2. fl (ppm)





Figure S141. <sup>13</sup>C NMR Spectrum of 70



-36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 fl (ppm)





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)





Figure 146. <sup>13</sup>C NMR Spectrum of 72



Figure S148. <sup>13</sup>C NMR Spectrum of 73







Figure S152. <sup>13</sup>C NMR Spectrum of 75







Figure S156. <sup>13</sup>C NMR Spectrum of 77



Figure S158. <sup>13</sup>C NMR Spectrum of 78



S140





Figure S162. <sup>13</sup>C NMR Spectrum of 80



Figure S164. <sup>13</sup>C NMR Spectrum of 81



Figure S166. <sup>13</sup>C NMR Spectrum of 82




## -9.078 -9.078 -9.078 -9.078 -7.121 -7







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)





Figure S172. <sup>13</sup>C NMR Spectrum of 85



Figure S174. <sup>13</sup>C NMR Spectrum of 86



S148



Figure S178. <sup>13</sup>C NMR Spectrum of 88



S150









Figure S184. <sup>13</sup>C NMR Spectrum of 91











Figure S188. <sup>13</sup>C NMR Spectrum of 93



Figure S190. <sup>13</sup>C NMR Spectrum of 94



Figure S191. <sup>13</sup>C NMR Spectrum of 95





Figure S193. <sup>13</sup>C NMR Spectrum of 96

## $\begin{array}{c} 7,857\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7559\\ 7,7529\\ 7,7592\\$



Figure S195. <sup>13</sup>C NMR Spectrum of 97



Figure S197. <sup>13</sup>C NMR Spectrum of 98



Figure S199. <sup>13</sup>C NMR Spectrum of 99



Figure S201. <sup>13</sup>C NMR Spectrum of 100



Figure S203. <sup>13</sup>C NMR Spectrum of 101



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 Figure S205. <sup>13</sup>C NMR Spectrum of 102





7.358 7.347 7.338 7.347 7.338 7.7.338 7.7.174 7.7.121 7.7.151 7.7.151 7.7.151 7.7.151 7.7.151 7.7.151 7.7.151 7.7.151 7.7.151 7.7.151 7.7.055 3.640 3.656 3.640 3.656 7.2054 7.2054 7.2054 7.2055 7.2056 7.2055 7.2057



Figure S209. <sup>13</sup>C NMR Spectrum of 104



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2

## Figure S210. <sup>19</sup>F NMR Spectrum of 104

## K. Copies of HPLC traces



P	eak	RetTime	Area	Height	Width	Symmetry	Area
_	#	[min]	[mAU*s]	[mAU]	[min]		[%]
Г	1	8.325	1593.8	138.2	0.1765	0.747	49.112
	2	8.873	1651.5	126.1	0.2008	0.706	50.888

Figure S211. HPLC Spectra of racemic 3a



]	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
[	1	8.351	4564.8	383.2	0.1985	0.7	99.618
	2	8.989	17.5	1.4	0.2154	0.265	0.382

Figure S212. HPLC Spectra of 3a





]	Peak	RetTime	Area	Height	Width	Symmetry	Area
_	#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	1	11.155	573.7	39.5	0.2419	0.964	49.889
	2	11.786	576.2	36.9	0.2604	0.909	50.111

Figure S213. HPLC Spectra of racemic 4



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
-		· — · — · — ·					
	1	11.036	77.3	5.8	0.2224	1.085	2.602
	2	11.606	2892.7	181.5	0.2657	0.757	97.398

Figure S214. HPLC Spectra of 4





	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	12.378	3337.6	177.8	0.291	0.915	50.142
[	2	14.842	3318.7	141.1	0.3625	0.755	49.858

Figure S215. HPLC Spectra of racemic 5



1	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
-	- · - ·				<u> </u>	<u> </u>	
ſ	1	12.278	20679.9	1471.2	0.2343	1.33	99.146
[	2	14.186	178.1	10.7	0.2778	0.624	0.854

Figure S216. HPLC Spectra of 5



#	[min]	[mAU*s]	[mAU]	[min]	Symmetry	[%]
1	27.596	9783.3	257.8	0.5828	0.579	50.009
2	29.347	9779.7	223.1	0.6634	0.504	49.991

Figure S217. HPLC Spectra of racemic 6



Figure S218. HPLC Spectra of 6





0.000	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
	1	33.637 36.442	2775.7 2781.6	94.2 87.5	0.4597	0.875	49.946 50.054

Figure S219. HPLC Spectra of racemic 7



	Реак. #	[min]	[mAU*s]	[mAU]	[min]	Symmetry	[%]
1	1	32.429	1102.9	38.2	0.4808	0.87	98.752
	2	35.268	13.9	6E-1	0.3902	0.947	1.248

Figure S220. HPLC Spectra of 7





Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	12.44	2173	126.1	0.2871	0.8	52.304

Figure S221. HPLC Spectra of racemic 8



	Peak #	RetTime [min]	e Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
	1	12.214	6532.9	394	0.2763	0.647	97.064
	2	13.438	197.6	13.3	0.2481	0.995	2.936

Figure S222. HPLC Spectra of 8



1	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Г	1	49.975	2072.3	30	1.1506	0.911	50.133
	2	53.006	2061.4	29.6	1.1625	0.903	49.867

Figure S223. HPLC Spectra of racemic 9



Ρ	eak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
_							
Г	1	49.923	34.6	5.5E-1	1.0442	0.557	0.465
	2	52.213	7412.7	100.8	1.1022	0.615	99.535

Figure S224. HPLC Spectra of 9



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1 2	12.907 16.064	815.7 805.4	13.3 9.8	1.0246	0.836	50.318 49.682

Figure S225. HPLC Spectra of racemic 10



г	#	[min]	[mAU*s]	[mAU]	[min]	Symmetry	[%]
Ē	1	13.81	2004.9	30.2	1.1054	0.925	98.927
L	2	16.844	21.8	3E-1	1.2074	0.508	1.073

Figure S226. HPLC Spectra of 10



ł	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
I	1	18.662	524.6	20.7	0.3934	0.981	50.199
	2	21.214	520.4	18.6	0.4348	0.968	49.801

Figure S227. HPLC Spectra of racemic 11



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
-		· — · — · — ·				<u> </u>	<u> </u>
	1	19.12	4302.8	168.2	0.4004	1.062	99.246
	2	21.559	32.7	1.6	0.3388	0.989	0.754

Figure S228. HPLC Spectra of 11





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	10.296	1153.9	82.2	0.2178	0.901	49.836
2	10.874	1161.5	76.9	0.2342	0.895	50.164

Figure S229. HPLC Spectra of racemic 12



Figure S230. HPLC Spectra of 12





	Peak #	RetTime [min]	e Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	1	11.187	681.7	30.9	0.3434	0.923	49.965
	2	12.161	682.7	28.4	0.3724	0.897	50.035

Figure S231. HPLC Spectra of racemic 13



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
	· — · — · — ·				<u> </u>	
1	11.247	14875.6	1049.9	0.2362	0.676	96.096
2	12.092	604.3	38.8	0.2596	0.621	3.904

Figure S232. HPLC Spectra of 13



I	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
C	1	15.984	507.1	25.9	0.3042	0.946	49.733
	2	16.595	512.5	25.1	0.314	0.941	50.267

Figure S233. HPLC Spectra of racemic 14



Figure S234. HPLC Spectra of 14





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	5.923	1136.4	147.5	0.1199	0.937	50.000
2	6.427	1136.4	134.9	0.1303	0.931	50.000

Figure S235. HPLC Spectra of racemic 15



Figure S236. HPLC Spectra of 15





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	16.89	3610.8	146	0.3866	0.993	49.902
2	18.055	3625	135.1	0.4189	1.035	50.098

Figure S237. HPLC Spectra of racemic 16



#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	16.709	2264.3	93	0.406	0.979	98.228
2	17.838	40.9	1.8	0.3801	0.951	1.772

Figure S238. HPLC Spectra of 16


	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	11.359	839.3	50.5	0.26	0.883	50.030
l	2	12.662	838.3	44.2	0.2934	0.871	49.970

Figure 239. HPLC Spectra of racemic 17



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	11.416	180.6	13	0.2318	0.97	2.526
2	12.538	6968.9	345.8	0.3358	0.571	97.474

Figure S240. HPLC Spectra of 17



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	10.571	524.4	38.7	0.2122	0.933	50.204
2	11.279	520.1	35.9	0.2271	0.933	49.796

Figure S241. HPLC Spectra of racemic 18



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1 2	10.574 11.335	1877.7 38.3	136.5 2.8	0.2125	0.822	97.999 2.001

Figure S242. HPLC Spectra of 18





Pea #	k RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	32.429	1902.3	21.5	1.4725	0.831	49.964
2	37.254	1905.1	18.3	1.736	0.728	50.036

Figure S243. HPLC Spectra of racemic 19



Figure S244. HPLC Spectra of 19





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	20.485	7409.6	118.5	0.9936	0.867	50.013
2	23.293	7405.8	100.6	1.127	0.728	49.987

Figure S245. HPLC Spectra of racemic 20



Figure S246. HPLC Spectra of 20





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	7.321	451.8	51.4	0.1366	0.919	50.101
2	8.133	450	45.2	0.1541	0.919	49.899

Figure S247. HPLC Spectra of racemic 21



#	[min]	[mAU*s]	[mAU]	[min]	Symmetry	[%]
	7.302	2171.5	239	0.14	0.831	98.978
2	8.162	22.4	2.4	0.1551	0.733	1.022

Figure S248. HPLC Spectra of 21



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	8.487	1247.1	109.1	0.1774	0.737	50.172
2	9.819	1238.6	94.7	0.2026	0.924	49.828

Figure S249. HPLC Spectra of racemic 22



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
I	1	8.721	7265.1	679.7	0.1667	0.91	96.904
I	2	10.127	232.1	18.2	0.2122	1.091	3.096

Figure S250 HPLC Spectra of 22





]	Peak	RetTime	Area	Height	Width	Symmetry	Area
-	#	[min]	[mAU*s]	[mAU]	[min]		[%]
	1	11.22	580.2	37.4	0.2584	0.902	49.976
[	2	12.259	580.8	34.5	0.2809	0.889	50.024

Figure S251. HPLC Spectra of racemic 23



Peak #	[min]	Area [mAU*s]	[mAU]	[min]	Symmetry	Area [%]
1	10.957	11.2	7.5E-1	0.2483	1.057	2.431
2	12.068	448.3	29.3	0.2383	0.909	97.569

Figure S252. HPLC Spectra of 23





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	15.648	141.8	7.7	0.2897	0.917	49.888
2	16.938	142.5	7.1	0.3077	0.936	50.112

Figure S253. HPLC Spectra of racemic 24



Figure S254. HPLC Spectra of 24



]	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Ī	1	19.199	2731	102.6	0.4145	0.814	50.020
	2	20.514	2728.8	87.3	0.4845	0.64	49.980

Figure S255. HPLC Spectra of racemic 25



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	19.535	272.2	11.1	0.4099	0.823	1.536
2	20.633	17453.9	553.5	0.4819	0.563	98.464

Figure S256. HPLC Spectra of 25





0.00	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
	1	5.97	1817.4	246.2	0.1141	0.891	49.898
	2	6.449	1824.9	227.8	0.1235	0.893	50.102

Figure S257. HPLC Spectra of racemic 26



Peak #	[min]	Area [mAU*s]	[mAU]	[min]	Symmetry	Area [%]
	5.965	12.7	1.7	0.1223	1.535	1.321
2	6.44	952.6	119.6	0.1249	0.917	98.679

Figure S258. HPLC Spectra of 26





	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
2							
	1	5.913	802.3	109.2	0.1137	0.918	49.871
	2	6.412	806.5	99.7	0.1244	0.916	50.129

Figure S259. HPLC Spectra of racemic 27



Figure S260 HPLC Spectra of 27



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
I	1	13.319	2302.2	107	0.3311	0.682	49.824
I	2	14.383	2318.5	99.6	0.3576	0.701	50.176

Figure S261. HPLC Spectra of racemic 28



Figure S262. HPLC Spectra of 28





	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	1	9.906	291.4	21.5	0.2103	0.907	49.961
l	2	10.625	291.8	19.5	0.2303	0.893	50.039

Figure S263. HPLC Spectra of racemic 29



]	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
ſ	1	9.833	2277	165.1	0.2129	0.767	98.202
l	2	10.594	41.7	2.9	0.2396	0.772	1.798

Figure S264. HPLC Spectra of 29



	Peak	RetTime	Area	Height	Width	Symmetry	Area	
	#	[min]	[mAU*s]	[mAU]	[min]		[%]	
ſ	1	5.353	1646.8	247.5	0.1036	0.905	50.000	-
t	2	5.733	1646.8	219.9	0.1154	0.888	50.000	

Figure S265. HPLC Spectra of racemic 30



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	5.339	3830	566.9	0.1048	0.859	97.992
2	5.739	78.5	9.8	0.1214	0.974	2.008

Figure S266. HPLC Spectra of 30





1	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
ſ	1	7.851	138	14	0.1527	0.942	50.279
l	2	8.434	136.5	13	0.1747	0.959	49.721

Figure S267. HPLC Spectra of racemic 31



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
í	1	7.809	51.5	57	0.1504	1 118	1.890
	2	8.367	2674.6	250	0.1648	0.818	98.110

Figure S268. HPLC Spectra of 31



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	1	13.733	723.9	38.5	0.2913	0.81	49.883
	2	14.544	727.3	37	0.3054	0.81	50.117

Figure S269. HPLC Spectra of racemic 32



Figure S270 HPLC Spectra of 32





0.000	Peal #	k RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
ſ	1	9.517	992.3	63.3	0.2613	0.923	50.006
l	2	10.276	992.1	59.8	0.2575	0.918	49.994

Figure S271. HPLC Spectra of racemic 33



Figure S272. HPLC Spectra of 33



1	Peal #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Ē	1	7.858	382	35.3	0.1683	0.943	50.697
L	2	9.536	371.5	73.7	0.0768	0.917	49.303

Figure S273. HPLC Spectra of racemic 34



	Peak	RetTime	Area	Height	Width	Symmetry	Area	
	#	[min]	[mAU*s]	[mAU]	[min]		[%]	
1	1	7.848	34.1	3.1	0.1837	1.153	2.589	-
	2	9.436	1282	280	0.0763	0.94	97.411	

Figure S274. HPLC Spectra of 34





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	10.223	463.9	34.7	0.2082	0.897	49.993
2	11.699	464	29.5	0.2435	0.899	50.007

Figure S275. HPLC Spectra of racemic 35



Figure S276. HPLC Spectra of 35





]	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
ſ	1	8.514	1090.5	98.6	0.173	0.877	49.915
l	2	9.275	1094.2	88	0.193	0.88	50.085

Figure S277. HPLC Spectra of racemic 36



Figure S278. HPLC Spectra of 36



	Peal #	k RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	6.805	293.2	32.2	0.1422	0.891	49.978
	2	7.494	293.5	29.1	0.1678	0.947	50.022

Figure S279. HPLC Spectra of racemic 37



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	6.821	53.1	5.5	0.1598	0.792	0.821
2	7.459	6420.5	633	0.1563	0.736	99.179

Figure S280 HPLC Spectra of 37



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	6.892	77.3	8.7	0.138	0.883	50.544
2	7.585	75.6	7.8	0.1489	0.94	49.456

Figure S281. HPLC Spectra of racemic 38



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	6.882	22	1.6	0.1921	0.405	1.151
l	2	7.548	1887	193.3	0.1519	0.849	98.849

Figure S282. HPLC Spectra of 38



	Peal #	c RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Ì	1	7.063	1374.6	141.1	0.1516	0.869	50.260
	2	7.834	1360.3	125.6	0.1683	0.868	49.740

Figure S283. HPLC Spectra of racemic 39



#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	7.122	15.6	1.5	0.172	0.726	1.008
2	7.862	1533	142.4	0.1676	0.859	98.992

Figure S284. HPLC Spectra of 39



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	1	11.42	633.8	39.7	0.2659	0.919	48.614
	2	12.735	670	37.5	0.2978	0.924	51.386

Figure S285. HPLC Spectra of racemic 40



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
	11.418	10.6	6.9E-1	0.2541	1.425	0.782
2	12.691	1341	75.2	0.2781	0.865	99.218

Supplementary Figure 286. HPLC Spectra of 40





	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
í	1	0.201	1252.0		0.1007	0.001	E0 249
ł	2	10.276	1233.0	81.7	0.2333	0.001	49.751

Figure S287. HPLC Spectra of racemic 41



#	[mm]	[mAU*s]	[mAU]	[mm]		[%]
1	9.243	38.7	2.7	0.2128	1.055	1.581
2	10.14	2408.3	153	0.2376	0.65	98.419

Figure S288. HPLC Spectra of 41



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	19.766	279.1	9	0.4613	0.907	50.253
2	22.524	276.2	7.5	0.5137	0.844	49.747

Figure S289. HPLC Spectra of racemic 42



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
i	1	19.918	14.6	5.2E-1	0.4719	0.902	1.470
	2	22.637	979.6	26.2	0.582	0.861	98.530

Figure S290 HPLC Spectra of 42





	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
I	1	11.522	340.8	22.2	0.2388	0.924	49.996
Į	2	12.917	340.9	19.4	0.2708	0.916	50.004

Figure S291. HPLC Spectra of racemic 43



	Peak #	[min]	[mAU*s]	[mAU]	[min]	Symmetry	Area [%]
Ì	1	11.407	7.5	4.9E-1	0.2552	1.088	0.863
ļ	2	12.792	866.7	49	0.2765	0.894	99.137

Figure S292. HPLC Spectra of 43



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	10.304	1699.1	150.9	0.1733	0.912	49.572
Ī	2	10.669	1728.5	145	0.1851	0.896	50.428

Figure S293. HPLC Spectra of racemic 44



	Peal #	k RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Ì	1	10.237	102.4	11	0.1451	1.349	0.910
l	2	10.561	11151.2	921.4	0.1872	0.775	99.090

Figure S294. HPLC Spectra of 44



1	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Γ	1	11.744	2398.4	86.8	0.4365	1.069	50.077
E	2	13.478	2391	99.5	0.3742	0.858	49.923

Figure S295. HPLC Spectra of racemic 45







Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	8.502	44.2	4.2	0.1656	0.948	50.409
2	9.28	43.5	3.7	0.1845	0.966	49.591

Figure S297. HPLC Spectra of racemic 46



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1 2	8.492 9.25	6.8 1325.2	7.8E-1 111.8	0.1448	0.879	0.507 99.493

Figure S298. HPLC Spectra of 46





	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
Ī	1	8.053	605.3	59.4	0.159	0.918	50.008
l	2	8.861	605.1	53.4	0.1783	0.916	49.992

Figure S299. HPLC Spectra of racemic 47



P	eak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Γ	1	8.008	10.3	1.1	0.1539	1.018	0.799
Г	2	8.79	1274.7	112.6	0.1781	0.894	99.201

Figure S300 HPLC Spectra of 47





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1 2	11.244 12.144	963 962.3	58.5 53.2	0.2559	0.926	50.019 49.981

Figure S301. HPLC Spectra of racemic 48



Peak	RetTime	Area	Height	Width	Symmetry	Area
	[mm]	[mAU*s]	[mAU]	[min]		[ %]
1	11.388	27.6	1.8	0.258	1.065	1.103
2	12.275	2477.9	137.5	0.2823	0.918	98.897

Figure S302. HPLC Spectra of 48







F	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
Ē		17 411				1.007	
H	+	17.411	8864	203.3	0.5858	1.267	0.000
L	2	21.025	8844.6	191.1	0.7239	0.847	49.945

Figure S303. HPLC Spectra of racemic 49



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	17.573	546.7	17.7	0.4749	0.961	99.033
2	21.32	5.3	1.7E-1	0.5362	1.341	0.967

Figure S304. HPLC Spectra of 49





Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	30.568	2865	59.3	0.7554	0.782	49.951
2	32.624	2870.6	48.2	0.9129	0.761	50.049

Figure S305. HPLC Spectra of racemic 50



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
	1	31.458	3728.6	75.3	0.7618	0.744	99.624
1	2	33.772	14.1	3.6E-1	0.6445	1.218	0.376

Figure S306. HPLC Spectra of 50



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
[	1	6.464	1305	150.3	0.1353	0.859	49.575
[	2	7.131	1327.4	134.3	0.1647	0.888	50.425

Figure S307. HPLC Spectra of racemic 51



Peal #	k RetTime [min]	e Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	6.398	4036.6	462.5	0.1358	0.772	99.117
2	7.089	36	3.8	0.1592	0.859	0.883

Figure S308. HPLC Spectra of 51





	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
I	1	42.381	1985.5	23.7	1.3965	0.814	47.296
	2	47.161	2212.6	23.2	1.5909	0.628	52.704

Figure S309. HPLC Spectra of racemic 52



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	43.102	60.2	7.7E-1	1.3036	1.253	1.523
2	47.311	3890.7	37.7	1.7218	0.492	98.477

Figure S310 HPLC Spectra of 52






Pe	eak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
_	· — ·						-·-·-
	1	16.298	460.3	15.6	0.4922	0.864	49.996
	2	19.685	460.3	12.7	0.6048	0.895	50.004

Figure S311. HPLC Spectra of racemic 53



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	16.235	260.5	9	0.4456	0.876	4.693
2	19.509	5290.3	143	0.6166	0.765	95.307

Figure S312. HPLC Spectra of 53





	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
	1	7.117	1898.6	149.3	0.2119	0.916	45.763
1	2	7.792	2250.1	152.7	0.2455	0.885	54.237

Figure S313. HPLC Spectra of racemic 54



1	7.091	2354.1	186.5	0.1952	0.887	96.996
2	7.786	72.9	4.9	0.2304	0.967	3.004

Figure S314. HPLC Spectra of 54





	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	1	21.129	1901.4	47.7	0.6155	0.811	49.890
	2	23.044	1909.8	40.4	0.7277	0.835	50.110

Figure S315. HPLC Spectra of racemic 55



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	21.307	126	3.7	0.4121	0.874	4.592
2	23.04	2618	55.4	0.7271	0.794	95.408

Figure S316. HPLC Spectra of 55



I	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
Г	1	12.683	7871.5	196.5	0.6115	0.718	50.925
E	2	15.482	7585.6	128.7	0.8857	0.75	49.075

Figure S317. HPLC Spectra of racemic 56



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	12.523	8785.8	208.4	0.6458	0.645	98.508
2	15.127	133.1	2.3	0.9475	1.673	1.492

Figure S318. HPLC Spectra of 56





Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	18.467	2366.5	72.5	0.507	0.743	49.865
2	19.842	2379.3	65.8	0.5536	0.773	50.135

Figure S319. HPLC Spectra of racemic 57



1	Peak	RetTime	Area	Height	Width	Symmetry	Area
22	#	[min]	[mAU*s]	[mAU]	[min]		[%]
ſ	1	18.596	25.4	9.5E-1	0.3274	1.169	0.900
t	2	19.822	2791.8	80.2	0.5401	0.743	99.100

Figure S320 HPLC Spectra of 57





Pe #	ak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
_							
1		12.298	818.8	45.5	0.3	0.903	24.102
2		13.507	880.4	43.5	0.3374	0.885	25.915
3		18.004	878.6	31.3	0.4677	0.912	25.864
4		21.902	819.3	23	0.5938	0.967	24.119

Figure S321. HPLC Spectra of racemic 58



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	12.481	47.1	2.8	0.2775	1.123	0.743
2	13.629	3315.8	157.9	0.3499	0.742	52.251
3	18.316	33.3	1.5	0.3749	1.136	0.525
4	22.248	2949.6	81.8	0.6007	0.914	46.480

Figure S322. HPLC Spectra of 58



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	27.765	5300.1	84.4	0.959	0.66	49.721
[	2	30.272	5359.5	79.1	1.0101	0.734	50.279

Figure S323. HPLC Spectra of racemic 59



Figure S324. HPLC Spectra of 59





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
	30.778	1707	28.6	0.9956	0.866	24.779
2	33.037	1747.2	27	1.0795	0.86	25.361
3	43.647	1716.6	20.6	1.3896	0.916	24.918
4	49.967	1718.2	17.9	1.604	0.975	24.942

Figure S325. HPLC Spectra of racemic 60



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	30.386	6817.4	112.5	1.0098	0.721	51.062
2	32.819	91.9	1.4	1.0726	0.88	0.688
3	43.517	95.9	1.2	1.3501	1.102	0.719
4	49.505	6345.9	64.8	1.6315	0.869	47.531

Figure S326. HPLC Spectra of 60



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Ì	1	29.112	9784.7	130.1	1.2536	0.6	48.933
	2	35.374	10211.4	116	1.4669	0.625	51.067

Figure S327. HPLC Spectra of racemic 61



0000	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
I	1	30.073	57.2	8.3E-1	1.1557	0.788	2.077
	2	36.126	2697.8	29.1	1.545	0.681	97.923

Figure S328. HPLC Spectra of 61



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1 2	7.35 8.33	2320.7 2302.7	154.2 137.4	0.2356	0.727	50.195 49.805

Figure S329. HPLC Spectra of racemic 62



	#	[min]	[mAU*s]	[mAU]	[min]	Symmetry	[%]
Γ	1	7.441	185.9	12.2	0.2396	0.919	8.183
Ľ	2	8.41	2085.9	122	0.2675	0.71	91.817

Figure S330 HPLC Spectra of 62



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
i	1	15.135	6317.5	272.4	0.3546	0.622	50.029
	2	18.873	6310.2	210.9	0.455	0.591	49.971

Figure S331. HPLC Spectra of racemic 63



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
I	1	15.102	17223.4	872.3	0.3291	0.595	97.957
ļ	2	18.584	359.2	12.6	0.4742	1.053	2.043

Figure S332. HPLC Spectra of 63





	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	1	7.013	489.6	56.1	0.1359	0.886	49.932
	2	7.502	491	51.7	0.1488	0.898	50.068

Figure S333. HPLC Spectra of racemic 64



Figure S334. HPLC Spectra of 64





	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	16.27	3244.6	127.7	0.3945	0.865	50.076
	2	17.467	3234.7	107.9	0.4676	0.89	49.924

Figure S335. HPLC Spectra of racemic 65



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	16.126	6763.1	261.7	0.4015	0.751	99.666
2	17.411	22.7	1.2	0.3203	0.979	0.334

Figure S336. HPLC Spectra of 65



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	9.02	1683.9	50.5	0.5289	0.88	50.017
2	10.333	1682.7	49.4	0.5437	0.867	49.983

Figure S337. HPLC Spectra of racemic 66



Figure S338. HPLC Spectra of 66





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area
1	11.242	508.9	28.7	0.2748	0.907	50.070
2	12.379	507.4	23.3	0.3396	0.903	49.930

Figure S339. HPLC Spectra of racemic 67



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	11.263	47.9	2.8	0.2832	0.95	1.092
I	2	12.261	4341.4	195.5	0.3431	0.667	98.908

Figure S340. HPLC Spectra of 67



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
ſ	1	18.728	3427.9	142.7	0.3762	0.865	49.986
Ľ	2	20.141	3429.8	134.9	0.3986	0.856	50.014

Figure S341. HPLC Spectra of racemic 68



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	19.224	92.3	4.6	0.3052	0.904	3.258
2	20.669	2741	122.8	0.3485	0.83	96.742

Figure S342. HPLC Spectra of 68





Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1 2	5.643	256.6 257.8	38.6 33.1	0.1036	0.916	49.884 50.116

Figure S343. HPLC Spectra of racemic 69



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	5.573	4019.2	632.7	0.0981	1.047	95.995
2	6.438	167.7	21.9	0.1175	0.891	4.005

Figure S344. HPLC Spectra of 69





]	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	5.125	1354.1	220.3	0.0957	0.912	50.035
Ľ	2	5.678	1352.2	197.2	0.106	0.863	49.965

Figure S345. HPLC Spectra of racemic 70



Figure S346. HPLC Spectra of 70



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	17.115	5615.8	64.2	1.3147	0.788	50.542
[	2	20.139	5495.4	56.7	1.3907	0.767	49.458

Supplementary Figure 347. HPLC Spectra of racemic 71



Figure S348. HPLC Spectra of 71





Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1 2	12.166	1011.2 961.3	55.4 47.2	0.2848	0.861	51.267 48.733

Figure S349. HPLC Spectra of racemic 72



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	12.059	120.8	7.5	0.2698	0.936	2.401
	2	13.034	4910.5	239.9	0.3168	0.662	97.599

Figure S350. HPLC Spectra of 72



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
11	6.286	2070.5	219.8	0.1479	0.859	50.115
2	6.88	2061	187.5	0.1682	0.952	49.885

Figure S351. HPLC Spectra of racemic 73



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[mm]	[mAU*s]	[mAU]	[mm]		[%]
[	1	6.57	5.4	8.8E-1	0.1015	0.977	0.479
[	2	6.956	1118.9	109.4	0.1593	0.892	99.521

Figure \$352. HPLC Spectra of 73



Peak		RetTime	Area	Height	Width	Symmetry	Area
2	#	[min]	[mAU*s]	[mAU]	[min]		[%]
[	1	8.641	1132.1	96	0.1836	0.704	49.670
ĺ	2	9.308	1147.1	83.3	0.2127	0.688	50.330

Figure S353. HPLC Spectra of racemic 74



Figure S354. HPLC Spectra of 74



]	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Г	1	12.33	951.7	50.4	0.2944	0.86	50.014
	2	15.718	951.2	37.4	0.3926	0.828	49.986

Figure S355. HPLC Spectra of racemic 75



Figure S356. HPLC Spectra of 75





]	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Ē	1	7.834	1618.2	100.7	0.2455	1.079	50.555
	2	13.303	1582.7	20.8	1.2712	1.747	49.445

Figure S357. HPLC Spectra of racemic 76



Figure S358. HPLC Spectra of 76



Pe	ak	RetTime	Area	Height	Width	Symmetry	Area
#	£	[min]	[mAU*s]	[mAU]	[min]		[%]
1		20.942	1125	17.9	1.0031	1.17	49.512
2		22.999	1147.1	19.2	0.9411	0.955	50.488

Figure S359. HPLC Spectra of racemic 77



Figure S360. HPLC Spectra of 77



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	6.924	1625	58.5	0.4299	1.497	50.296
2	10.442	1605.9	24.5	1.0918	0.609	49.704

Figure S361. HPLC Spectra of racemic 78



Peal	k RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	6.942	7530.7	441.1	0.2652	0.663	98.828
2	10.591	89.3	2.7	0.4725	0.866	1.172

Figure S362. HPLC Spectra of 78





Pea	k RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	14.371	1496.2	45.2	0.5164	0.91	49.929
2	16.849	1500.5	40.2	0.5879	0.897	50.071

Figure S363. HPLC Spectra of racemic 79



Peal #	k RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	14.339	2835.3	87.5	0.5059	0.836	99.231
2	16.948	22	6.7E-1	0.5485	1.15	0.769

Figure S364. HPLC Spectra of 79





Figure S365. HPLC Spectra of racemic 80



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	22.029	3728.1	30.1	2.0669	1.277	96.827
2	26.795	122.2	1.6	1.2674	0.578	3.173

Figure S366. HPLC Spectra of 80





	Peak	c RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
ſ	1	17.86	5663.7	1123	0.8165	0.945	49.920
ł	2	20.511	5681.8	94.8	0.9691	0.952	50.080





Figure S368. HPLC Spectra of 81





P	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
Ē	1	7.755	14191.1	625	0.3449	0.576	49.971
	2	11.748	14207.2	371.2	0.5926	0.748	50.029

Figure S369. HPLC Spectra of racemic 82



Figure S370. HPLC Spectra of 82



1 18679 2229 29.2 12722 0.978	#	[min]	[mAU*s]	[mAU]	[min]	Symmetry	[%]
	1	18.679	2229	29.2	1.2722	0.978	50.245

Figure S371. HPLC Spectra of racemic 83



Figure S372. HPLC Spectra of 83



	Peal	c RetTime	Area	Height	Width	Symmetry	Area	
	#	[min]	[mAU*s]	[mAU]	[min]		[%]	
1								•
ſ	1	12.342	5339	201.2	0.4256	0.761	49.991	
ĺ	2	16.885	5340.9	170.3	0.494	0.768	50.009	

Figure S373. HPLC Spectra of racemic 84



	Peak	RetTime	Area	Height	Width	Symmetry	Area	
	#	[min]	[mAU*s]	[mAU]	[min]		[%]	
Ì	1	12.501	186.3	9	0.3224	0.934	3.558	ì
ĺ	2	17.027	5051.3	179.6	0.4382	0.736	96.442	1

Figure S374. HPLC Spectra of 84





	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
•							
ſ	1	24.552	6763.7	129.3	0.8719	0.463	50.022
[	2	31.086	6757.9	115.9	0.912	0.784	49.978

Figure S375. HPLC Spectra of racemic 85



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	25.12	107.1	2.2	0.8031	0.957	1.687
2	30.997	6242.4	121.7	0.8025	0.741	98.313

Figure S376. HPLC Spectra of 85





P	eak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
Ē	1	39.824	1816.3	22.6	1.3422	0.796	50.084
	2	43.158	1810.2	18.7	1.6148	0.831	49.916

Figure S377. HPLC Spectra of racemic 86



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	40.196	58.7	8E-1	1.2254	0.961	2.477
2	43.383	2310.6	22.7	1.6985	0.79	97.523

Figure S378. HPLC Spectra of 86



	Peal	k RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
2							
L	1	16.822	3337.8	82.9	0.6398	0.825	50.145
E	2	19.345	3318.5	68.4	0.8087	0.823	49.855

Figure S379. HPLC Spectra of racemic 87



100	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	1	17.063	165.7	5.3	0.4775	0.891	3.403
	2	19.346	4701.9	108.3	0.7235	0.731	96.597

Figure S380 HPLC Spectra of 87



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	14.555	2396.1	47	0.8494	1.157	49.995
2	21.137	2396.6	38.6	1.0358	0.956	50.005

Figure S381. HPLC Spectra of racemic 88



]	Peal #	k RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Ľ	1	14.706	90.6	2.7	0.5635	0.964	2.038
L	2	21.155	4357.3	76	0.9551	0.945	97.962

Figure S382. HPLC Spectra of 88


Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
	23.811	5994.3	116.1	0.8086	0.891	50.358
2	32.446	5909.1	73.4	1.3426	0.933	49.642

Figure S383. HPLC Spectra of racemic 89



Figure S384. HPLC Spectra of 89



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
i	1	7 770	10047	45	0.4210	1.024	
	-	1.113	1264.7	45	0.4316	1.034	00.343
	2	10.326	1247.5	2b.1	0.7311	0.896	49.657

Figure S385. HPLC Spectra of racemic 90



#	[min]	[mAU*s]	[mAU]	[min]	Symmetry	[%]
1	7.785	4185.5	203.3	0.3142	0.647	99.627
2	10.382	15.7	8.7E-1	0.2137	0	0.373

Figure S386. HPLC Spectra of 90



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	1	3.676	4361.7	837.9	0.0767	1.004	49.763
	2	4.07	4403.1	806.3	0.0837	0.978	50.237

Figure S387. HPLC Spectra of racemic 91



#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	3.661	20.4	3.3	0.1032	0.573	0.623
2	4.053	3251.2	510.7	0.0923	1.199	99.377

Figure S388. HPLC Spectra of 91



	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	13.8	6243.5	350.8	0.2736	0.725	48.929
[	2	14.55	6516.9	312.9	0.317	0.616	51.071

Figure S389. HPLC Spectra of racemic 92



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
	13.932	2936.6	162	0.3021	0.806	99.343
2	14.745	19.4	9.7E-1	0.3349	0.401	0.657

Figure S390. HPLC Spectra of 92



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
	6.939	7670.1	890	0.1345	0.933	36.476
2	7.452	13357.6	1405.7	0.1489	0.903	63.524

Figure S391. HPLC Spectra of racemic 93



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	6.911	47.6	5.6	0.133	0.95	0.416
2	7.438	11384.1	1218.6	0.145	0.903	99.584

Figure S392. HPLC Spectra of 93



P	eak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
Г	1	12.684	3876.2	118.9	0.4904	1.206	50.395
Г	2	14.467	3815.4	100.9	0.5832	1.114	49.605

Figure S393. HPLC Spectra of racemic 94



Figure S394. HPLC Spectra of 94



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1 2	4.291 4.611	245.8 247.2	39.7 37.6	0.0963	0.875	49.856 50.144

Figure S395. HPLC Spectra of racemic 95



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	4.295	25.2	4.7	0.0889	0.668	0.778
2	4.611	3214.7	495.9	0.108	0.867	99.222

Figure S396. HPLC Spectra of 95





10000	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
I	1	14.692	1583.9	55.2	0.4607	0.805	49.968
	2	16.832	1585.9	47.4	0.5384	0.733	50.032

Figure S397. HPLC Spectra of racemic 96



Figure S398. HPLC Spectra of 96



]	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
F	1 2	46.682	4440.8 4420.5	63.7 57.5	1.0776	0.892	50.115 49.885

Figure S399. HPLC Spectra of racemic 97



Figure S400. HPLC Spectra of 97





Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1 2	23.63 26.104	1934.9 1946.5	35.4 32.8	0.852	0.904 0.852	49.851 50.149

Figure S401. HPLC Spectra of racemic 98



Peak #	[min]	Area [mAU*s]	[mAU]	Width [min]	Symmetry	Area [%]
1	23.645	50.5	9.3E-1	0.9066	1.199	1.124
2	25.976	4446.8	75.2	0.9321	0.682	98.876

Figure S402. HPLC Spectra of 98



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
	6.396	723.1	39.3	0.3064	1.173	49.712
2	9.421	731.4	28.4	0.4048	0.816	50.288

Figure S403. HPLC Spectra of racemic 99



	Peak	RetTime	Area	Height	Width	Symmetry	Area
1	#	[min]	[mAU*s]	[mAU]	[min]		[%]
[	1	5.868	39.9	1.3	0.5122	0.312	1.524
	2	9.122	2577.5	81.2	0.5043	0.737	98.476

Figure S404. HPLC Spectra of 99



	Peak	RetTime	Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
1	1	3.975	1534.9	297.1	0.0803	0.912	49.881
1	2	4.31	1542.2	277.6	0.0868	0.91	50.119

Figure S405. HPLC Spectra of racemic 100



Figure S406. HPLC Spectra of 100



No. of the second secon	Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
[	1	5.599	2293	256.1	0.1492	1.065	50.813
[	2	6.528	2219.6	233.5	0.1584	0.907	49.187

Figure S407. HPLC Spectra of racemic 101



Figure S408. HPLC Spectra of 101



Figure S409. HPLC Spectra of racemic 102



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
1 2	3.752 4.344	617.6 1945.7	45 72.3	0.2002	1.479	24.093 75.907

Figure S410. HPLC Spectra of 102



P	eal	c RetTime	e Area	Height	Width	Symmetry	Area
	#	[min]	[mAU*s]	[mAU]	[min]		[%]
Ē	1	4.862	217.7	31.8	0.106	0.852	50.080
	2	5.219	217	29.4	0.1142	0.851	49.920

Figure S411. HPLC Spectra of racemic 103



Peak #	RetTime	Area [mAU*s]	Height [mAU]	Width	Symmetry	Area
	5.281	176.9	24.2	0.1133	0.837	100.000

Figure S412. HPLC Spectra of 103



Peak	RetTime	Area	Height	Width	Symmetry	Area
#	[min]	[mAU*s]	[mAU]	[min]		[%]
				<u> </u>		
1	9.045	985.1	41.7	0.3754	1.09	49.907
2	10.244	988.7	39.6	0.3975	1.017	50.093

Figure S413. HPLC Spectra of racemic 104



Peak #	RetTime [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry	Area [%]
1	9.05	6.4	3.4E-1	0.3123	1.227	0.441
2	10.279	1444.3	56.6	0.4079	0.98	99.559

Figure S414. HPLC Spectra of 104