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Facile Synthesis of (*S*,*S*)-1,2-Diacylamides and (*S*,*S*)-1,2-Diamines with C_2-Symmetry

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Abstract: A series of chiral vicinal tertiary diacylamides with C_2-symmetry was synthesized from (*S*)-α-phenylethylamine, different aromatic aldehydes, and oxalyl chloride. The diacylamides obtained were then reduced to afford chiral vicinal diamines with C_2-symmetry. We propose that the diacylamides existed in four stable conformational isomers in solution because of the dihedral angle between acylamide bonds.

Keywords: (*S*,*S*)-1,2-Diacylamides, (*S*,*S*)-1,2-diamines, C_2-symmetry, synthesis

Chiral vicinal diamines, as important parts in organic synthesis, have been widely used in medicinal chemistry[1] and asymmetric synthesis,[2] especially as chiral ligands or chiral auxiliaries in various kinds of asymmetric reactions such as Mukaiyama aldol reactions,[3] Mannich-type reactions,[4] Michael additions,[5] Sharpless dihydroxylation,[6] chiral Lewis acid–based reactions,[7] acylation of alcohols,[8] hydrogenation of ketones,[9] protonation of enolates,[10] enantioselective addition reaction of organometallics,[11] conjugate addition,[12] desymmetrization of meso ketones,[13] epoxides,[14] asymmetric cyclopropanation of styrene,[15] and so on. Therefore, design and synthesis of new chiral ligands for the enantioselective reaction is an important goal in chemical synthesis.[16] In addition, diacylamides have industrial uses as synthetic intermediates.[17] Some of them show biological activity as pesticides.[18]

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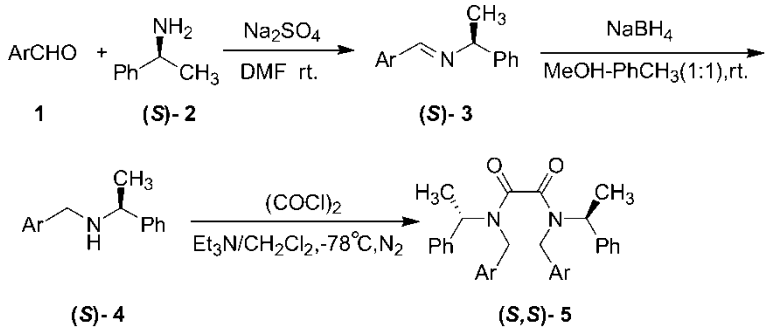


Scheme 1. Synthesis of (*S*,*S*)-1,2-diacylamides **5**.

In this article, a series of chiral diacylamides and diamines with C_2-symmetry was designed and synthesized starting from commercially available (*S*)-α-phenylethylamine, different aromatic aldehydes, and oxalyl chloride. At the same time, the possible conformations of (*S*,*S*)-1,2-diacylamides were discussed.

(*S*,*S*)-1,2-Diacylamides **5** were synthesized starting from (*S*)-α-phenylethylamine, the appropriate aromatic aldehydes, and oxalyl chloride in three steps as shown in Scheme 1.

The isolated yields and $[\alpha]_D^{25}$ data of compounds **5a**–**m** are summarized in Table 1.

Interestingly, ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of the diacylamides synthesized exhibited three or four sets of signals for the

Table 1. Yields and optical rotation data for compounds **5a**–**5m**

Entry	Compound	Ar	Yield[a] (%)	$[\alpha]_D^{25}$
1	**5a**		78	−130 (c 0.69 THF)
2	**5b**		80	−156 (c 0.59 THF)
3	**5c**	C_6H_5	81	−152 (c 0.54 THF)
4	**5d**	o-$O_2NC_6H_5$	59	−56 (c 0.69 THF)
5	**5e**	m-$O_2NC_6H_5$	77	−66 (c 0.67 THF)
6	**5f**	p-$O_2NC_6H_5$	81	−105 (c 0.67 THF)
7	**5g**	o-ClC_6H_5	72	−115 (c 0.91 THF)
8	**5h**	m-ClC_6H_5	83	−107 (c 0.82 THF)
9	**5i**	p-ClC_6H_5	76	−124 (c 0.65 THF)
10	**5j**	o-$CH_3OC_6H_5$	62	−109 (c 0.96 THF)
11	**5k**	m-$CH_3OC_6H_5$	61	−109 (c 0.85 THF)
12	**5l**	p-$CH_3OC_6H_5$	89	−140 (c 0.52 THF)
13	**5m**	$C_6H_5CH{=}CH$	47	−101 (c 0.62 THF)

[a]Isolated yields.

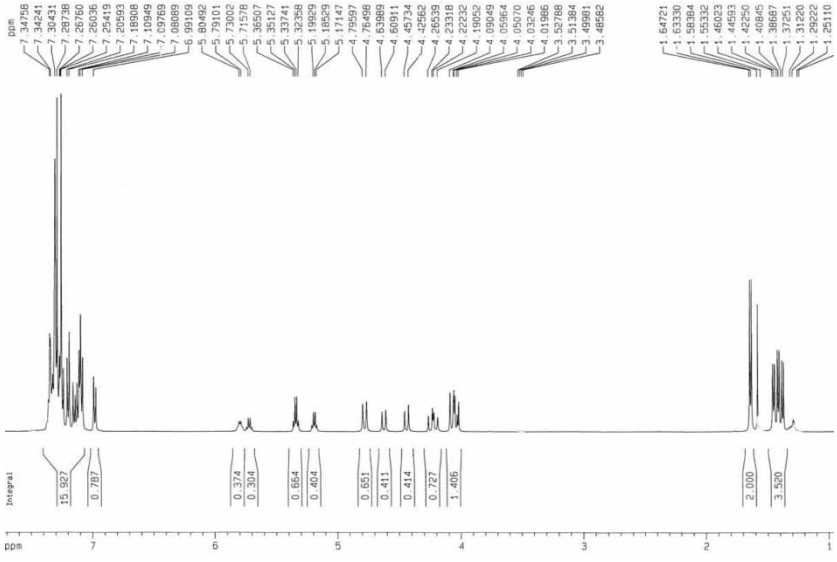


Figure 1. ^{1}H NMR (500 MHz) spectrum of chiral vicinal tertiary diacylamide **5i**.

same hydrogen atoms and carbon atoms of the methyl, methene, and methenyl groups, respectively. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra of the diacylamide **5i** are shown in Figs. 1 and 2.

Based on the elemental analysis data, mass spectral data or high-resolution mass spectral data, and melting point, each of diacylamides was

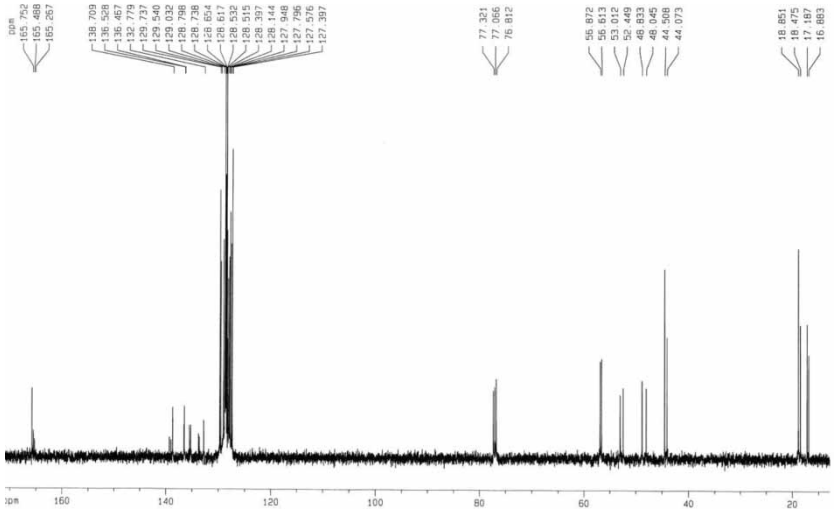


Figure 2. ^{13}C NMR (125-MHz) spectrum of chiral vicinal tertiary diacylamide **5i**.

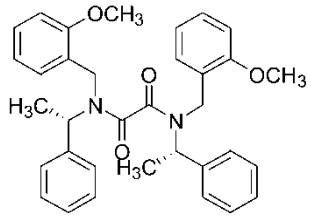


Figure 3. Structure of diacylamide **5j**.

identified as a pure component. Moreover, a series of chiral vicinal diamines were obtained in good yields by reduction of the chiral diacylamides. To verify these interesting results, simulated annealings with molecular dynamics were performed and conformations were optimized using the B3LYP[19] method at the 6-31G(d) level with the GAUSSIAN03 program for diacylamide **5j**.[20] The structure of diacylamide **5j** is shown in Fig. 3.

The four stable conformational isomers (**5j-a**, **5j-b**, **5j-c**, **5j-d**) and the corresponding energies relative to each other are shown in Fig. 4.

In addition, by careful recrystallization, the crystal of compound **5j** was obtained from *n*-hexane/ethyl ether (50/1) for the purpose of X-ray crystal structure analysis, but the crystal of other compounds in this series could not be obtained. The X-ray structure of compound **5j** confirms that it is the most stable conformational isomer in solid, and the dihedral angle between acylamide bonds was almost 90°, as shown in Fig. 5.

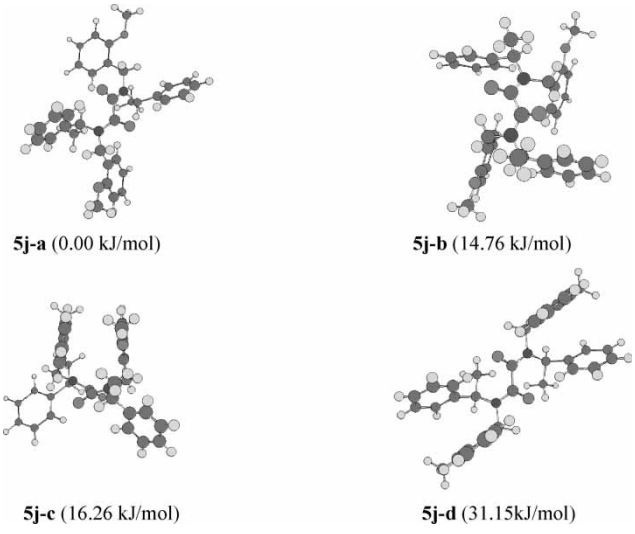


Figure 4. Four stable conformational isomers of compound **5j**.

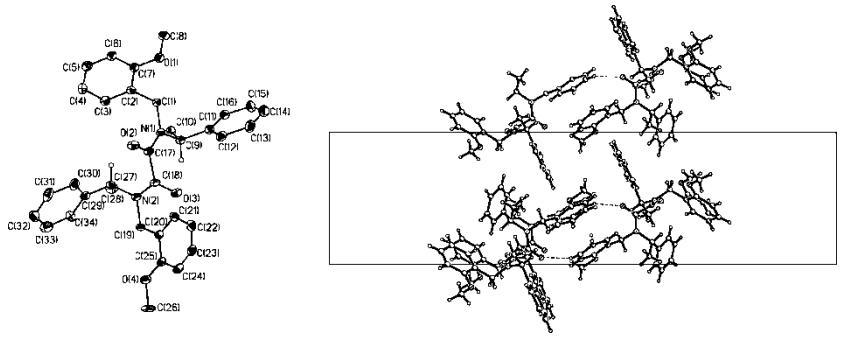


Figure 5. ORTEP and packing diagram of compound **5j**.

According to the simulated and optimized results and crystal structure analysis of vicinal diacylamide **5j**, the conformational isomer of compound **5j-a** is the most stable. The structure parameters of **5j-a** agree very well with the X-ray diffraction data of compound **5j**. The structure of conformational isomer **5j-a** is similar to the crystal structure of compound **5j** to a great extent.

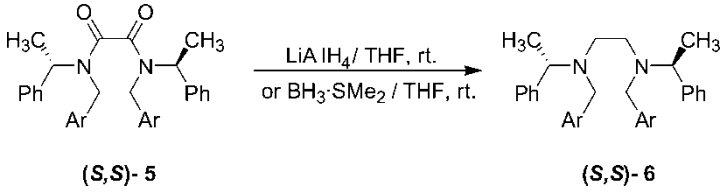
Chiral vicinal (*S*,*S*)-1,2-diamines **6** were prepared from corresponding diacylamides **5** by the following reduction procedures with $LiAlH_4$ or $BH_3 \cdot SMe_2$ in THF in good yields as shown in Scheme 2.

The isolated yields and $[\alpha]_D^{25}$ data of compounds **6a**–**m** are summarized in Table 2.

In summary, a facile synthesis has been developed to obtain chiral vicinal diamines starting from very cheap and easily available materials under mild reaction conditions. The four stable conformational isomers of (*S*,*S*)-1,2-diacylamides were described. Further investigation is in progress.

EXPERIMENTAL

Melting points were measured with a X-4 melting-point apparatus and are uncorrected. IR spectra were recorded in KBr disks with an Avatar 360 FT-IR infrared spectrometer and are expressed in centimeters^{-1}. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were measured on an Avance



Scheme 2. Synthesis of (*S*,*S*)-1,2-diamines **6**.

Table 2. Yields and optical rotation data for compounds **6a**–**6m**

Entry	Compound	Ar	Yield[a] (%)	$[\alpha]_D^{25}$
1	**6a**		82[b]	−79 (c0.66 THF)
2	**6b**		84[b]	−49 (c0.69 THF)
3	**6c**	C_6H_5	85[b]	−43 (c0.74 THF)
4	**6d**	o-$O_2NC_6H_5$	62[c]	−33 (c0.77 THF)
5	**6e**	m-$O_2NC_6H_5$	65[c]	−34 (c0.41 THF)
6	**6f**	p-$O_2NC_6H_5$	63[c]	−50 (c0.36 THF)
7	**6g**	o-ClC_6H_5	65[b]	−19 (c0.86 THF)
8	**6h**	m-ClC_6H_5	81[b]	−39 (c0.78 THF)
9	**6i**	p-ClC_6H_5	74[b]	−57 (c0.60 THF)
10	**6j**	o-$CH_3OC_6H_5$	69[b]	−27 (c0.59 THF)
11	**6k**	m-$CH_3OC_6H_5$	72[b]	−40 (c0.99 THF)
12	**6l**	p-$CH_3OC_6H_5$	63[b]	−67 (c0.36 THF)
13	**6m**	$C_6H_5CH{=}CH$	70[b]	−73 (c0.32 THF)

[a]Isolated yields; (*S*,*S*)-1,2-diamines were prepared from (*S*,*S*)-1,2-diacylamides.
[b]With $LiAlH_4$ in dry THF.
[c]With $BH_3 \cdot SMe_2$ in dry THF.

DRX 500 Bruker spectrometer with $CDCl_3$ as a solvent. Chemical shift values were given in parts per million (ppm) relative to internal tetramethylsilane (TMS) as the reference ($\delta = 0$ ppm). The multiplicities were expressed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). The elemental analyses were determined with a Vario E1 elemental analyzer. Optical rotations were measured in a Perkin-Elmer Model 343LC polarmeter using the sodium D line at 589 nm. The crystal was measured with phi and omega scans at 293(2) K on a Bruker Smart 1000 CCD area detector diffractometer. Solvents were dried using the standard procedures.

General Procedure for Preparation of Chiral Vicinal (*S*,*S*)-1,2-Diacylamides 5

For example **5a**, (*S*)-α-phenylethylamine (1.27 g, 10.5 mmol) was added dropwise to a mixture of the furan-2-carbaldehyde (0.96 g, 10.0 mmol) and anhydrous Na_2SO_4 (1.0 g) in dry DMF (10.0 mL), and then stirred overnight at room temperature. The reaction mixture was quenched with H_2O (30 mL) and extracted with EtOAc (3 × 15 mL). After drying over anhydrous Na_2SO_4, the solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (3/1) as eluent to afford imine **3a** in good yield. $NaBH_4$ (0.81 g, 21.5 mmol) was added to a solution of compound **3a** (1.71 g, 8.6 mmol) in dry methanol–toluene (25/25 mL), and the reaction mixture was stirred for 3 h at ambient

temperature under a nitrogen atmosphere. Then the reaction mixture was quenched with saturated NH_4Cl (30 mL) and extracted with EtOAc (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and then concentrated in reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (15/1) as eluent to give product **4a**. Triethylamine (1.50 mL) and oxalyl chloride (3.4 mmol) were added dropwise to a stirred solution of amine **4a** (1.37 g, 6.8 mmol) in dichloromethane at -78°C under a nitrogen atmosphere and then stirred for 20 min at room temperature. The reaction mixture was quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was washed successively with 10% HCl (2×10 mL), saturated $NaHCO_3$ (2×10 mL), and saturated NaCl (2×10 mL), and then dried over anhydrous Na_2SO_4. The solvent was removed in reduced pressure, and the residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (8/1) as eluent to afford (*S*,*S*)-1,2-diacylamides **5a** in 78% isolated yield in the last step. The crystal of compound **5j** was obtained from *n*-hexane/ethyl ether (50/1) at ambient temperature.

Data

(*S*,*S*)-*N*,*N*′-*bis*-Furan-2-ylmethyl *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5a): Mp 136–137°C; $R_f = 0.22$ (8:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.50, 1.54, 1.65 (d, $J = 7.00$ Hz, d, $J = 7.08$ Hz, d, $J = 7.16$ Hz, 6H, $2 \times CH_3$), 3.89, 3.93, 4.23, 4.24, 4.42, 4.56, 4.72, 4.81 (d, $J = 15.90$ Hz, d, $J = 15.78$ Hz, d, $J = 16.58$ Hz, d, $J = 16.36$ Hz, d, $J = 16.58$ Hz, d, $J = 16.39$ Hz, d, $J = 15.66$ Hz, d, $J = 15.73$ Hz, 4H, $2 \times CH_2$), 5.22, 5.27, 5.80, 5.87 (q, $J = 7.09$ Hz, q, $J = 6.98$ Hz, q, $J = 7.17$ Hz, q, $J = 7.15$ Hz, 2H, $2 \times$ CH), 6.06–6.27 (m, 4H, furan-H), 7.23–7.48 (m, 12H, furan-H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.2, 17.7, 18.1, 37.7, 41.5, 41.6, 52.0, 52.2, 56.0, 56.4, 108.2, 108.4, 109.1, 109.6, 110.6, 110.7, 110.8, 127.5, 127.6, 127.7, 128.0, 128.4, 128.5, 128.6, 128.7, 138.8, 138.9, 139.3, 139.4, 141.2, 141.3, 141.9, 142.0, 150.2, 151.0, 164.7, 164.9, 165.0; IR (KBr): 3145, 3057, 2992, 1641, 1498, 1451, 1410, 1389, 1270, 1013, 757, 703 cm^{-1}; MS (m/z): 457.19 (M^+). Anal. calcd. for $C_{28}H_{28}N_2O_4$: C, 73.66; H, 6.18; N, 6.14. Found: C, 73.47; H, 6.05; N, 6.49.

(*S*,*S*)-*N*,*N*′-*bis*-(1-Phenylethyl) *N*,*N*′-*bis*-thiophen-2-ylmethyl-oxalamide (5b): Mp 136–137°C; $R_f = 0.25$ (8:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43, 1.54, 1.56, 1.67 (d, $J = 7.04$ Hz, d, $J = 8.59$ Hz, d, $J = 7.30$ Hz, d, $J = 7.02$ Hz, 6H, $2 \times CH_3$), 4.18, 4.23, 4.35, 4.45, 4.46, 4.71, 4.74, 4.88 (d, $J = 15.27$ Hz, d, $J = 15.39$ Hz, d, $J = 15.36$ Hz, d, $J = 15.41$ Hz, d, $J = 16.14$ Hz, d, $J = 16.07$ Hz, d, $J = 15.22$ Hz, d, $J = 15.37$ Hz, 4H, $2 \times CH_2$), 5.17, 5.38, 5.69, 5.86 (q, $J = 7.02$ Hz, q, $J = 6.98$ Hz, q, $J = 7.51$ Hz, q, $J = 7.27$ Hz, 2H,

2 × CH), 6.67–6.89 (m, 4H, thiophen-H), 7.12–7.53 (m, 12H, thiophen-H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.8, 16.9, 18.1, 18.8, 40.0, 40.3, 43.8, 43.9, 52.7, 52.8, 56.4, 56.5, 125.4, 125.5, 126.0, 126.1, 126.4, 126.7, 127.6, 127.7, 127.9, 128.0, 128.1, 128.4, 128.7, 138.7, 138.8, 139.8, 141.0, 165.0; IR (KBr): 3104, 3061, 2986, 1642, 1639, 1497, 1452, 1409, 1389, 1267, 1226, 1026, 854, 791, 703 cm^{-1}; MS (m/z): 489.20 (M^+). Anal. calcd. for $C_{28}H_{28}N_2O_2S_2$: C, 68.82; H, 5.78; N, 5.73. Found: C, 68.72; H, 5.86; N, 5.86.

(*S*,*S*)-*N*,*N*′-Dibenzyl *N*,*N*′-*bis*-(1-phenyl ethyl)-oxalamide (5c): Mp 40–41°C; $R_f = 0.29$ (8:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37, 1.38, 1.42, 1.62 (d, $J = 6.98$ Hz, d, $J = 7.15$ Hz, d, $J = 7.15$ Hz, d, $J = 6.97$ Hz, 6H, 2 × CH_3), 3.95, 4.02, 4.11, 4.28, 4.30, 4.55, 4.81, 4.94 (d, $J = 15.34$ Hz, d, $J = 15.51$ Hz, d, $J = 15.99$ Hz, d, $J = 15.71$ Hz, d, $J = 15.95$ Hz, d, $J = 15.77$ Hz, d, $J = 15.37$ Hz, d, $J = 15.51$ Hz, 4H, 2 × CH_2), 5.20, 5.40, 5.69, 5.74 (q, $J = 7.01$ Hz, q, $J = 6.95$ Hz, q, $J = 7.15$ Hz, q, $J = 6.75$ Hz, 2H, 2 × CH), 7.10–7.37 (m, 20H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.9, 17.2, 18.6, 19.0, 44.7, 45.1, 49.0, 49.8, 52.5, 53.3, 56.7, 56.9, 127.0, 127.3, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.7, 136.8, 138.2, 138.3, 139.0, 139.7, 165.5, 165.8, 165.9; IR (KBr): 3088, 3062, 3031, 2980, 2937, 1737, 1633, 1496, 1452, 1410, 1198, 1160, 1078, 1028, 755, 699 cm^{-1}; MS (m/z): 477.19 (M^+). Anal. calcd. for $C_{32}H_{32}N_2O_2$: C, 80.64; H, 6.77; N, 5.88. Found: C, 80.50; H, 7.23, N, 5.72.

(*S*,*S*)-*N*,*N*′-*bis*-(2-Nitro-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5d): Mp 82–83°C; $R_f = 0.38$ (3:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.38, 1.54, 1.55, 1.75 (d, $J = 7.15$ Hz, d, $J = 7.40$ Hz, d, $J = 7.23$ Hz, d, $J = 6.90$ Hz, 6H, 2 × CH_3), 4.68, 4.71, 4.82, 4.89, 4.99, 5.09 (d, $J = 16.30$ Hz, d, $J = 16.98$ Hz, d, $J = 17.69$ Hz, d, $J = 17.57$ Hz, d, $J = 17.73$ Hz, d, $J = 17.56$ Hz, 4H, 2 × CH_2), 5.29, 5.49, 5.73, 5.78 (q, $J = 6.95$ Hz, q, $J = 6.92$ Hz, q, $J = 7.04$ Hz, q, $J = 7.16$ Hz, 2H, 2 × CH), 7.10–7.99 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.9, 17.1, 18.6, 18.7, 41.8, 42.2, 45.2, 45.8, 53.0, 53.8, 56.9, 57.0, 124.8, 124.9, 127.0, 127.2, 127.6, 127.8, 128.2, 128.3, 128.5, 128.7, 128.8, 129.0, 130.7, 133.0, 133.5, 138.1, 138.8, 147.5, 165.9, 166.0, 166.2; IR (KBr): 2980, 1638, 1525, 1496, 1453, 1405, 1341, 1204, 1162, 1028, 728, 701 cm^{-1}; MS (m/z): 255.17 (100). Anal. calcd. for $C_{32}H_{30}N_4O_6$: C, 67.83; H, 5.34; N, 9.89. Found: C, 67.74; H, 5.22; N, 9.45.

(*S*,*S*)-*N*,*N*′-*bis*-(3-Nitro-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5e): Mp 62–63°C; $R_f = 0.31$ (3:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.38, 1.51, 1.77 (d, $J = 7.15$ Hz, d, $J = 6.91$ Hz, d, $J = 6.96$ Hz, 6H, 2 × CH_3), 4.34, 4.45, 4.47, 4.50, 4.54, 4.65 (d, $J = 15.31$ Hz, d, $J = 15.29$ Hz, d, $J = 16.18$ Hz, d, $J = 15.64$ Hz,

d, $J = 16.11$ Hz, d, $J = 15.66$ Hz, 4H, $2 \times CH_2$), 5.30, 5.43, 5.83, 5.97 (q, $J = 6.94$ Hz, q, $J = 6.91$ Hz, q, $J = 7.04$ Hz, q, $J = 7.14$ Hz, 2H, $2 \times CH$), 7.10–8.02 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.7, 16.9, 18.2, 18.6, 44.1, 44.5, 47.8, 48.3, 52.3, 52.7, 56.6, 56.8, 122.0, 122.1, 122.2, 122.8, 122.9, 127.5, 127.6, 127.8, 127.9, 128.3, 128.4, 128.6, 128.7, 128.9, 129.3, 129.4, 133.6, 134.4, 138.1, 138.8, 139.7, 165.5; IR (KBr): 3066, 2980, 2938, 1636, 1529, 1452, 1408, 1349, 1288, 1202, 1158, 1098, 1028, 793, 731, 700 cm^{-1}; MS (m/z): 566.18 (M^+). Anal. calcd. for $C_{32}H_{30}N_4O_6$: C, 67.83; H, 5.34; N, 9.89. Found: C, 68.08; H, 5.45; N, 9.33.

(*S*,*S*)-*N*,*N*′-*bis*-(4-Nitro-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5f): Mp 151–152°C; $R_f = 0.30$ (3:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.38, 1.48, 1.51, 1.72 (d, $J = 7.17$ Hz, d, $J = 7.17$ Hz, d, $J = 7.00$ Hz, d, $J = 6.94$ Hz, 6H, $2 \times CH_3$), 4.23, 4.36–4.41, 4.51, 4.57, 4.74 (d, $J = 15.28$ Hz, m, d, $J = 16.40$ Hz, d, $J = 15.89$ Hz, d, $J = 15.98$ Hz, 4H, $2 \times CH_2$), 5.30, 5.39, 5.79, 5.93 (q, $J = 6.97$ Hz, q, $J = 6.91$ Hz, q, $J = 7.10$ Hz, q, $J = 7.16$ Hz, 2H, $2 \times CH$), 7.10–7.47 (m, 14H, aromatic), 8.00–8.10 (m, 4H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.9, 17.1, 18.4, 18.7, 44.2, 44.7, 47.9, 48.6, 52.5, 52.9, 56.7, 56.9, 123.5, 123.6, 127.4, 127.5, 127.8, 127.9, 128.0, 128.3, 128.5, 128.6, 128.7, 128.9, 129.0, 138.2, 138.3, 144.1, 145.0, 147.0, 165.3, 165.6, 165.7; IR (KBr): 2974, 1630, 1601, 1520, 1410, 1344, 1155, 1110, 1030, 796, 751, 700 cm^{-1}; MS (m/z): 566.13 (M^+). Anal. calcd. for $C_{32}H_{30}N_4O_6$: C, 67.83; H, 5.34; N, 9.89. Found: C, 67.95; H, 5.31; N, 9.73.

(*S*,*S*)-*N*,*N*′-*bis*-(2-Chloro-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5g): Mp 64–65°C; $R_f = 0.26$ (8:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.39, 1.42, 1.58, 1.68 (d, $J = 7.23$ Hz, d, $J = 7.01$ Hz, d, $J = 7.23$ Hz, d, $J = 6.95$ Hz, 6H, $2 \times CH_3$), 4.33, 4.36, 4.79, 4.92 (d, $J = 16.80$ Hz, d, $J = 17.36$ Hz, s, d, $J = 16.66$ Hz, d, $J = 16.71$ Hz, 4H, $2 \times CH_2$), 5.19, 5.48, 5.68, 5.75 (q, $J = 6.99$ Hz, q, $J = 6.92$ Hz, q, $J = 7.00$ Hz, q, $J = 7.19$ Hz, 2H, $2 \times CH$), 7.16–7.65 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.9, 17.3, 18.5, 42.0, 42.6, 45.6, 46.5, 52.6, 53.9, 56.7, 57.0, 126.9, 127.2, 127.7, 127.9, 128.0, 128.1, 128.5, 128.7, 128.8, 129.1, 129.2, 130.0, 134.6, 138.8, 140.0, 165.7, 165.8, 166.0, 166.2; IR (KBr): 3064, 2979, 1638, 1496, 1444, 1407, 1278, 1200, 1164, 1050, 1049, 751, 699 cm^{-1}; MS (m/z): 545.30 (M^+). Anal. calcd. for $C_{32}H_{30}Cl_2N_2O_2$: C, 70.46; H, 5.54; N, 5.14. Found: C, 70.88; H, 5.78; N, 4.88.

(*S*,*S*)-*N*,*N*′-*bis*-(3-Chloro-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5h): Mp 127–128°C; $R_f = 0.26$ (10:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.39, 1.40, 1.51, 1.68 (d, $J = 7.11$ Hz, d, $J = 6.90$ Hz, d, $J = 7.16$ Hz, d, $J = 6.95$ Hz, 6H, $2 \times CH_3$), 4.08, 4.13, 4.17, 4.28, 4.30, 4.46, 4.59, 4.74 (d, $J = 15.45$ Hz, d, $J = 17.48$ Hz, d, $J = 15.79$ Hz, d, $J = 16.21$ Hz, d, $J = 16.06$ Hz, d, $J = 16.25$ Hz,

d, $J = 15.46$ Hz, d, $J = 15.54$ Hz, 4H, $2 \times CH_2$), 5.20, 5.36, 5.75, 5.84 (q, $J = 6.98$ Hz, q, $J = 6.86$ Hz, 2H, q, $J = 7.12$ Hz, q, $J = 7.07$ Hz, 2H, $2 \times CH$), 6.96–7.35 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.7, 17.1, 18.3, 18.8, 44.2, 44.6, 48.2, 48.8, 52.4, 53.1, 56.6, 56.8, 125.6, 127.1, 127.2, 127.5, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 129.7, 129.8, 138.6, 140.0, 165.6; IR (KBr): 3065, 3032, 2981, 2941, 1641, 1632, 1453, 1402, 1317, 1208, 1152, 946, 781, 763, 730, 701 cm^{-1}; MS (m/z): 545.19 (M^+). Anal. calcd. for $C_{32}H_{30}Cl_2N_2O_2$: C, 70.46; H, 5.54; N, 5.14. Found: C, 70.32; H, 5.63; N, 5.00.

(*S*,*S*)-*N*,*N*′-*bis*-(4-Chloro-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5i): Mp 56–57°C; $R_f = 0.26$ (8:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.38, 1.42, 1.45, 1.64 (d, $J = 7.18$ Hz, d, $J = 7.03$ Hz, d, $J = 7.15$ Hz, d, $J = 6.96$ Hz, 6H, $2 \times CH_3$), 4.04, 4.05, 4.08, 4.21, 4.25, 4.44, 4.62, 4.78 (d, $J = 15.42$ Hz, d, $J = 13.59$ Hz, d, $J = 15.43$ Hz, d, $J = 15.90$ Hz, d, $J = 16.11$ Hz, d, $J = 15.86$ Hz, d, $J = 15.39$ Hz, d, $J = 15.50$ Hz, 4H, $2 \times CH_2$), 5.19, 5.34, 5.72, 5.80 (q, $J = 7.00$ Hz, q, $J = 6.93$ Hz, q, $J = 7.12$ Hz, q, $J = 6.96$ Hz, 2H, $2 \times CH$), 6.99–7.35 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.9, 17.2, 18.5, 18.6, 44.1, 44.5, 48.1, 48.8, 52.5, 53.0, 56.6, 56.9, 127.4, 127.6, 127.8, 128.0, 128.1, 128.4, 128.5, 128.6, 128.7, 128.8, 129.0, 129.5, 129.7, 132.8, 136.5, 138.7, 165.3, 165.5, 165.8; IR (KBr): 3063, 3031, 2980, 2937, 1636, 1492, 1405, 1199, 1159, 1091, 1015, 789, 755, 700 cm^{-1}; MS (m/z): 244.17 (100). Anal. calcd. for $C_{32}H_{30}Cl_2N_2O_2$: C, 70.46; H, 5.54; N, 5.14. Found: C, 70.25; H, 5.41; N, 5.37.

(*S*,*S*)-*N*,*N*′-*bis*-(2-Methoxy-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5j): Mp 105–106°C; $R_f = 0.23$ (5:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.36, 1.40, 1.54, 1.63 (d, $J = 6.97$ Hz, d, $J = 7.20$ Hz, d, $J = 7.20$ Hz, d, $J = 6.96$ Hz, 6H, $2 \times CH_3$), 3.67, 3.75, 3.78 (3s, 6H, $2 \times OCH_3$), 4.09, 4.19, 4.36, 4.57, 4.78, 4.88 (d, $J = 16.26$ Hz, d, $J = 16.40$ Hz, s, s, d, $J = 16.21$ Hz, d, $J = 16.40$ Hz, 4H, $2 \times CH_2$), 5.14, 5.45, 5.96–5.67 (q, $J = 7.01$ Hz, q, $J = 6.88$ Hz, m, 2H, $2 \times CH$), 6.72–7.35 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.8, 17.2, 18.0, 18.4, 39.0, 39.5, 43.3, 43.7, 52.6, 53.7, 55.0, 55.1, 55.2, 56.5, 56.7, 109.7, 109.8, 120.4, 120.5, 120.7, 127.4, 127.5, 127.6, 127.7, 127.8, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.8, 139.3, 140.2, 140.4, 156.3, 165.8, 165.9, 166.1, 166.4; IR (KBr): 3063, 3031, 2985, 2939, 2837, 1738, 1651, 1603, 1494, 1463, 1410, 1290, 1243, 1162, 1112, 754, 700 cm^{-1}; MS (m/z): 537.07 (M^+). Anal. calcd. for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22. Found: C, 76.11; H, 6.77; N, 5.20.

(*S*,*S*)-*N*,*N*′-*bis*-(3-Methoxy-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5k): Mp 133–134°C; $R_f = 0.23$ (6:1, petroleum ether/ethyl acetate); ^1H NMR

(500 MHz, $CDCl_3$); δ 1.38, 1.40, 1.47, 1.64 (d, $J = 7.11$ Hz, d, $J = 7.26$ Hz, d, $J = 7.10$ Hz, d, $J = 7.00$ Hz, 6H, $2 \times CH_3$), 3.55, 3.68, 3.78, 3.79 (4s, 6H, $2 \times OCH_3$), 3.87, 4.00, 4.08, 4.21, 4.29, 4.54, 4.83, 4.91 (d, $J = 15.37$ Hz, d, $J = 15.52$ Hz, d, $J = 15.98$ Hz, d, $J = 15.82$ Hz, d, $J = 16.02$ Hz, d, $J = 15.77$ Hz, d, $J = 15.37$ Hz, d, $J = 15.52$ Hz, 4H, $2 \times CH_2$), 5.18, 5.40, 5.73, 5.79 (q, $J = 6.97$ Hz, q, $J = 6.91$ Hz, q, $J = 7.11$ Hz, q, $J = 7.14$ Hz, 2H, $2 \times CH$), 6.69–7.40 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.9, 17.3, 18.5, 18.9, 44.6,45.0, 48.9, 49.5, 52.4, 53.1, 54.9, 55.1, 55.3, 56.7, 56.9, 112.4, 113.0, 113.3, 113.4, 114.0, 119.6, 120.6, 127.5, 127.7, 127.9, 128.1, 128.4, 128.5, 128.7, 129.3, 129.4, 129.5, 138.4, 138.6, 139.9, 140.1, 159.6, 159.7, 159.8, 165.6, 165.8, 165.9; IR (KBr): 3035, 2961, 2941, 2839, 1643, 1600, 1494, 1466, 1439, 1358, 1264, 1244, 1208, 1167, 1080, 1035, 782, 751, 699 cm^{-1}; MS (m/z): 536.25 (M^+). Anal. calcd. for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22. Found: C, 75.83; H, 6.64; N, 5.08.

(*S*,*S*)-*N*,*N*′-*bis*-(4-Methoxy-benzyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5l): Mp 51–52°C. $R_f = 0.22$ (5:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.39, 1.44, 1.61 (d, $J = 6.81$ Hz, d, $J = 6.28$ Hz, d, $J = 6.80$ Hz, 6H, $2 \times CH_3$), 3.75, 3.78, 3.83 (3s, 6H, $2 \times OCH_3$), 3.88, 3.94, 4.01, 4.16, 4.26, 4.48, 4.76, 4.87 (d, $J = 15.11$ Hz, d, $J = 15.27$ Hz, d, $J = 15.71$ Hz, d, $J = 14.43$ Hz, d, $J = 15.72$ Hz, d, $J = 15.45$ Hz, d, $J = 15.11$ Hz, d, $J = 15.22$ Hz, 4H, $2 \times CH_2$), 5.17, 5.35, 5.68–5.73 (q, $J = 6.70$ Hz, q, $J = 6.78$ Hz, m, 2H, $2 \times CH$), 6.69–7.37 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.0, 17.2, 18.6, 19.0, 44.0, 44.5, 48.4, 49.2, 52.4, 53.0, 55.2, 55.3, 56.6, 56.8, 113.7, 113.8, 113.9, 127.6, 127.7, 127.8, 128.0, 128.4, 128.5, 128.6, 128.7, 128.8, 129.1, 129.6, 129.8, 130.5, 139.1, 158.6, 159.2, 159.3, 165.5, 165.7, 165.8, 165.9; IR (KBr): 3060, 3030, 2935, 2835, 1635, 1513, 1453, 1408, 1302, 1247, 1176, 1111, 1029, 790, 754, 699 cm^{-1}; MS (m/z): 535.42 (M^+). Anal. calcd. for $C_{34}H_{36}N_2O_4$: C, 76.09; H, 6.76; N, 5.22. Found: C, 75.91; H, 6.44; N, 4.97.

(*S*,*S*)-*N*,*N*′-*bis*-(3-Phenyl-allyl) *N*,*N*′-*bis*-(1-phenylethyl)-oxalamide (5m): Mp 143–144°C; $R_f = 0.27$ (6:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$); δ 1.62, 1.63, 1.70, 1.81 (d, $J = 6.72$ Hz, d, $J = 6.71$ Hz, d, $J = 7.07$ Hz, d, $J = 6.86$ Hz, 6H, $2 \times CH_3$), 3.72–4.10 (m, 4H, $2 \times CH_2$), 5.22, 5.31, 5.90–6.31 (q, $J = 6.84$ Hz, q, $J = 6.85$ Hz, m, 6H, $2 \times CH$, $4 \times CH{=}$), 7.17–7.40 (m, 20H, $CH{=}$, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.7, 16.9, 18.3, 18.9, 43.8, 44.1, 47.0, 47.3, 51.5, 51.7, 56.4, 124.9, 126.0, 126.5, 126.6, 127.6, 127.8, 127.9, 128.0, 128.5, 128.6, 128.7, 132.8, 136.2, 139.6, 164.8, 165.0, 165.1; IR (KBr): 3050, 3026, 2993, 2923, 1641, 1632, 1492, 1449, 1411, 1281, 1245, 969, 746, 695 cm^{-1}; MS (m/z): 527.42 (M^+). Anal. calcd. for $C_{34}H_{32}N_2O_4$: C, 81.79; H, 6.86; N, 5.30. Found: C, 81.77; H, 6.59; N, 4.93.

General Procedure for Preparation of Chiral Vicinal (*S*,*S*)-1,2-Diamines 6

For example, the compound **5a** (0.46 g, 1.0 mmol) was added to a stirred refluxing suspension of $LiAlH_4$ (0.19 g, 5.0 mmol) in THF, and the solution of reaction mixture was refluxed for 4 h with H_2O (0.5 mL). Then, 10% NaOH (2.0 mL) and H_2O (1.0 mL) were successively added to the reaction mixture, and the resulting white precipitate was filtered off. The reaction solution was extracted with EtOAc (3 × 15 mL), and the organic phase was dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The crude product was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (50/1) as eluent to give compound **6a** in 82% yield. In addition, the solution of $BH_3 \cdot SMe_2$ (2.0 mmol) in THF was dropped into a solution of (*S*,*S*)-1,2-diacylamides **5d**, **5e**, and **5f** (1.0 mmol) and then refluxed 20 h. The reaction mixture was quenched with 2.0 N HCl (20 mL) and then 10% NaOH was added to neutralize residual acid. At last, the reaction mixture was extracted with EtOAc (3 × 20 mL). After drying over anhydrous Na_2SO_4 overnight, the solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (20/1) as eluent to afford diamines **6d**, **6e**, and **6f** in 62–65% yields.

Data

(*S*,*S*)-*N*,*N*′-*bis*-Furan-2-ylmethyl *N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6a): Mp 81–82°C; $R_f = 0.14$ (50:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$); δ 1.34 (d, $J = 6.72$ Hz, 6H, 2 × CH_3), 2.48–2.57 (m, 4H, CH_2CH_2), 3.51, 3.67 (2d, $J = 14.99$ Hz, 4H, 2 × CH_2), 3.75 (q, $J = 6.70$ Hz, 2H, 2 × CH), 6.05 (d, $J = 2.98$ Hz, 2H, 3-furan-H), 6.30–6.31 (m, 2H, 4-furan-H), 7.23–7.37 (m, 12H, furan-H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.8, 47.3, 48.4, 59.8, 107.9, 110.0, 126.7, 127.7, 128.1, 141.6, 144.5, 153.7; IR (KBr): 3061, 3025, 2977, 2809, 1500, 1453, 1365, 1331, 1144, 1105, 1011, 917, 778, 733, 703 cm^{-1}; MS (m/z): 429.01 (M^+). Anal. calcd. for $C_{28}H_{32}N_2O_2$: C, 78.47; H, 7.53; N, 6.54. Found: C, 78.24; H, 7.54; N, 6.44.

(*S*,*S*)-*N*,*N*′-*bis*-(1-Phenylethyl)*N*,*N*′-*bis*-thiophen-2-ylmethylethane-1,2-diamine (6b): Mp 74–75°C; $R_f = 0.29$ (50:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (d, $J = 6.77$ Hz, 6H, 2 × CH_3), 2.51–2.66 (m, 4H, CH_2CH_2), 3.64, 3.79 (2d, $J = 14.62$ Hz, 4H, 2 × CH_2), 3.84 (q, $J = 6.73$ Hz, 2H, 2 × CH), 6.80 (d, $J = 2.70$ Hz, 2H, thiophen-H), 6.91 (m, 2H, thiophen-H), 7.20–7.35 (m, 12H, thiophen-H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.1, 48.4, 49.9, 58.5, 124.4, 124.9, 126.2, 126.8, 127.7, 128.0, 143.7,145.0; IR (KBr): 3079, 3028, 2974, 2812, 1491, 1453,

1366, 1328, 1284, 1207, 1165, 1098, 1029, 977, 898, 833, 778, 746, 700 cm^{-1}; MS (m/z): 460.97 (M^+). Anal. calcd. for $C_{28}H_{32}N_2S_2$: C, 73.00; H, 7.00; N, 6.08. Found: C, 73.11; H, 7.35; N, 6.18.

(*S*,*S*)-*N*,*N*′-Dibenzyl *N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6c): $R_f = 0.20$ (100:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.32 (d, $J = 6.54$ Hz, 6H, $2 \times CH_3$), 2.44–2.64 (m, 4H, CH_2CH_2), 3.41, 3.56 (2d, $J = 13.88$ Hz, 4H, $2 \times CH_2$), 3.78 (q, $J = 6.45$ Hz, 2H, $2 \times CH$), 7.25–7.34 (m, 20H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.7, 48.3, 55.2, 58.5, 126.6, 127.8, 128.0, 128.1, 128.8, 140.8, 143.8; IR (KBr): 3084, 3061, 3026, 2970, 2932, 2824, 1601, 1493, 1452, 1372, 1028, 745, 698 cm^{-1}; MS (m/z): 447.45 (M^+). Anal. calcd. for $C_{32}H_{36}N_2$: C, 85.67; H, 8.09; N, 6.24. Found: C, 85.70; H, 7.67; N, 6.14.

(*S*,*S*)-*N*,*N*′-*bis*-(2-Nitro-benzyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6d): Mp 113–114°C; $R_f = 0.27$ (15:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.24 (d, $J = 6.81$ Hz, 6H, $2 \times CH_3$), 2.20–2.35 (m, 4H, CH_2CH_2), 3.69 (q, $J = 6.78$ Hz, 2H, $2 \times CH$), 3.70, 3.81 (2d, $J = 15.75$ Hz, 4H, $2 \times CH_2$), 7.16–7.45 (m, 14H, aromatic), 7.57 (d, $J = 7.60$ Hz, 2H, aromatic), 7.78 (d, $J = 7.89$ Hz, 2H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.7, 49.4, 53.0, 60.0, 124.2, 126.9, 127.5, 127.6, 128.0, 130.7, 132.4, 136.1, 142.8, 149.6; IR (KBr): 2974, 2937, 2837, 1526, 1493, 1452, 1364, 1205, 1150, 1103, 779, 741, 728, 696 cm^{-1}; MS (m/z): 269.17 (100). Anal. calcd. for $C_{32}H_{34}N_4O_4$: C, 71.35; H, 6.36; N, 10.40. Found: C, 71.48; H, 6.26; N, 10.54.

(*S*,*S*)-*N*,*N*′-*bis*-(3-Nitro-benzyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6e): $R_f = 0.21$ (15:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.33 (d, $J = 6.79$ Hz, 6H, $2 \times CH_3$), 2.41–2.63 (m, 4H, CH_2CH_2), 3.47, 3.59 (2d, $J = 14.49$ Hz, 4H, $2 \times CH_2$), 3.77 (q, $J = 6.73$ Hz, 2H, $2 \times CH$), 7.24–7.32 (10H, m, aromatic), 7.38–7.41 (t, $J = 7.90$ Hz, 2H, aromatic), 7.53 (d, $J = 7.60$ Hz, 2H, aromatic), 8.05 (d, $J = 8.11$ Hz, 2H, aromatic), 8.12 (s, 2H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.6, 49.1, 54.6, 59.3, 121.9, 123.1, 127.0, 127.6, 128.2, 128.9, 134.4, 143.0, 143.2, 148.2; IR (KBr): 3062, 3028, 2968, 2929, 2838, 1529, 1492, 1451, 1349, 1202, 1087, 815, 731, 701 cm^{-1}; HRMS: calcd. for $C_{32}H_{34}N_4O_4$: M^+ 538.2562; Found: 538.2580.

(*S*,*S*)-*N*,*N*′-*bis*-(4-Nitro-benzyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6f): $R_f = 0.15$ (15:1, petroleum ether/ethyl acetate); ^1H NMR (500 MHz, $CDCl_3$): δ 1.31 (d, $J = 6.79$ Hz, 6H, $2 \times CH_3$), 2.37–2.59 (m, 4H, CH_2CH_2), 3.48, 3.59 (2d, $J = 14.87$ Hz, 4H, $2 \times CH_2$), 3.74 (q, $J = 6.66$ Hz, 2H, $2 \times CH$), 7.24–7.37 (m, 10H, aromatic), 7.39 (d, $J = 8.43$ Hz, 4H, aromatic), 8.11 (d, $J = 8.51$ Hz, 4H, aromatic); ^{13}C NMR

(125 MHz, $CDCl_3$): δ 15.7, 49.3, 54.9, 59.4, 123.4, 127.1, 127.6, 128.2, 128.9, 143.0, 147.0, 148.9; IR (KBr): 3059, 3028, 2968, 2928, 2848, 1599, 1518, 1492, 1452, 1345, 1109, 1015, 857, 738, 701 cm^{-1}; MS (m/z): 269.11 (100). Anal. calcd. for $C_{32}H_{34}N_4O_4$: C, 71.35; H, 6.36; N, 10.40. Found: C, 71.39; H, 6.49; N, 10.43.

(*S*,*S*)-*N*,*N*′-*bis*-(2-Chloro-benzyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6g): $R_f = 0.42$ (100:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (m, $J = 6.78$ Hz, 6H, $2 \times CH_3$), 2.42–2.62 (m, 4H, CH_2CH_2), 3.55, 3.69 (2d, $J = 15.23$ Hz, 4H, $2 \times CH_2$), 3.78 (q, $J = 6.66$ Hz, 2H, $2 \times$ CH), 7.14–7.53 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.5, 49.2, 52.3, 59.2, 126.5, 126.6, 127.6, 127.7, 128.0, 129.2, 130.3, 133.6, 138.2, 143.5; IR (KBr): 3061, 3027, 2971, 2933, 2828, 1738, 1493, 1443, 1373, 1241, 1202, 1143, 1119, 1048, 1036, 752, 700 cm^{-1}; MS (m/z): 517.32 (M^+). Anal. calcd. for $C_{32}H_{34}\ Cl_2N_2 \cdot 2HCl$: C, 65.09; H, 6.15; N, 4.74. Found: C, 64.62; H, 6.53; N, 4.35.

(*S*,*S*)-*N*,*N*′-*bis*-(3-Chloro-benzyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6h): $R_f = 0.26$ (100:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.33 (d, $J = 6.74$ Hz, 6H, $2 \times CH_3$), 2.42–2.62 (m, 4H, CH_2CH_2), 3.37, 3.53 (2d, $J = 14.18$ Hz, 4H, $2 \times CH_2$), 3.77 (q, $J = 6.67$ Hz, 2H, $2 \times$ CH), 7.14–7.36 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.8, 48.6, 54.8, 58.9, 126.6, 126.8, 126.9, 127.7, 128.1, 128.5, 129.4, 134.0, 143.1, 143.3; IR (KBr): 3060, 3027, 2970, 2825, 1597, 1574, 1492, 1474, 1451, 1428, 1373, 1201, 1116, 1075, 776, 734, 700 cm^{-1}; MS (m/z): 517.35 (M^+). Anal. calcd. for $C_{32}H_{34}\ Cl_2N_2 \cdot 2HCl$: C, 65.09; H, 6.15; N, 4.74. Found: C, 64.79; H, 6.32; N, 4.53.

(*S*,*S*)-*N*,*N*′-*bis*-(4-Chloro-benzyl)*N*,*N*′-*bis*-(1-phenyl-ethyl)-ethane-1,2-diamine (6i): Mp 82–83°C; $R_f = 0.20$ (100:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (d, $J = 6.80$ Hz, 6H, $2 \times CH_3$), 2.45–2.65 (m, 4H, CH_2CH_2), 3.42, 3.55 (2d, $J = 14.02$ Hz, 4H, $2 \times CH_2$), 3.83 (q, $J = 6.75$ Hz, 2H, $2 \times$ CH), 7.15–7.49 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.6, 48.6, 54.6, 58.9, 126.8, 127.7, 127.9, 128.1, 128.2, 129.8, 132.2, 139.3, 143.5; IR (KBr): 3061, 3027, 2972, 2931, 2823, 1594, 1490, 1451, 1405, 1368, 1302, 1248, 1150, 1101, 1085, 1013, 926, 850, 806, 702 cm^{-1}; MS (m/z): 516.98 (M^+). Anal. calcd. for $C_{32}H_{34}Cl_2N_2$: C, 74.26; H, 6.62; N, 5.41. Found: C, 74.11; H, 6.70; N, 5.15.

(*S*,*S*)-*N*,*N*′-*bis*-(2-Methoxy-benzyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6j): $R_f = 0.22$ (15:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (d, $J = 6.78$ Hz, 6H, $2 \times CH_3$), 2.54–2.68 (m, 4H, CH_2CH_2), 3.49, 3.66 (2d, $J = 15.12$ Hz, 4H, $2 \times CH_2$), 3.78 (s, 6H,

2 × OCH_3), 3.83 (q, $J = 6.73$ Hz, 2H, 2 × CH), 6.82 (d, $J = 8.13$ Hz, 1H, aromatic), 6.91–7.33 (m, 16H, aromatic), 7.48 ($J = 7.34$ Hz, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.7, 48.5, 49.0, 55.2, 58.8, 110.0, 120.4, 126.4, 127.2, 127.8, 127.9, 129.1, 129.6, 144.2, 157.4; IR (KBr): 3060, 3027, 2967, 2834, 1600, 1587, 1491, 1463, 1438, 1373, 1286, 1239, 1104, 1049, 1031, 754, 701 cm^{-1}; MS (m/z): 509.41 (M^+). Anal. calcd. for $C_{32}H_{40}N_2O_2$: C, 80.28; H, 7.93; N, 5.51. Found: C, 79.79; H, 8.20; N, 5.31.

(*S*,*S*)-*N*,*N*′-*bis*-(3-Methoxy-benzyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6k): $R_f = 0.36$ (15:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (d, $J = 6.79$ Hz, 6H, 2 × CH_3), 2.42–2.63 (m, 4H, CH_2CH_2), 3.38, 3.53 (2d, $J = 14.08$ Hz, 4H, 2 × CH_2), 3.76 (q, $J = 6.69$ Hz, 2H, 2 × CH), 3.79 (s, 6H, 2 × OCH_3), 6.76–7.29 (m, 18H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.8, 48.6, 55.1, 55.2, 58.6, 112.1, 113.9, 120.8, 126.6, 127.8, 128.0, 129.0, 142.7, 143.6, 159.6; IR (KBr): 3058, 3027, 2967, 2833, 1600, 1585, 1489, 1453, 1372, 1263, 1151, 1117, 1049, 778, 734, 699 cm^{-1}; MS (m/z): 509.43 (M^+). Anal. calcd. for $C_{34}H_{40}N_2O_2$: C, 80.28; H, 7.93; N, 5.51. Found: C, 80.37; H, 8.15; N, 5.22.

(*S*,*S*)-*N*,*N*′-*bis*-(4-Methoxy-benzyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6l): $R_f = 0.40$ (10:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (d, $J = 7.11$ Hz, 6H, 2 × CH_3), 2.39–2.59 (m, 4H, CH_2CH_2), 3.32, 3.46 (2d, $J = 13.66$ Hz, 4H, 2 × CH_2), 3.75 (q, $J = 6.81$ Hz, 2H, 2 × CH), 3.82 (s, 6H, 2 × OCH_3), 6.82 (d, $J = 8.56$ Hz, 4H, aromatic), 7.16 (d, $J = 8.51$ Hz, 4H, aromatic), 7.23–7.31 (m, 10H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.6, 48.1, 54.4, 55.2, 58.4, 113.4, 126.6, 127.8, 128.0, 129.7, 132.8, 143.9, 158.4; IR (KBr): 3060, 3027, 2967, 2832, 1611, 1511, 1452, 1372, 1301, 1248, 1170, 1104, 1037, 734, 701 cm^{-1}; MS (m/z): 507.35 (M^+). Anal. calcd. for $C_{34}H_{40}N_2O_2$: C, 80.28; H, 7.93; N, 5.51. Found: C, 80.55; H, 8.03; N, 5.26.

(*S*,*S*)-*N*,*N*′-*bis*-(3-Phenyl-allyl)*N*,*N*′-*bis*-(1-phenylethyl)-ethane-1,2-diamine (6m): $R_f = 0.28$ (10:1, petroleum ether/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (d, $J = 6.67$ Hz, 6H, 2 × CH_3), 2.57–2.66 (m, 4H, CH_2CH_2), 3.13–3.18 (m, 4H, 2 × CH_2), 3.85 (q, $J = 6.68$ Hz, 2H, 2 × CH), 6.18–6.24 (m, 2H, 2 × CH═), 6.43 (d, $J = 15.87$ Hz, 2H, 2 × CH═), 7.22–7.34 (m, 20H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.1, 48.7, 53.8, 59.6, 126.3, 126.7, 127.2, 127.7, 128.0, 128.4, 128.7, 131.7, 137.3, 144.2; IR (KBr): 3059, 3025, 2968, 1600, 1493, 1449, 1370, 1118, 1075, 1030, 966, 742, 699 cm^{-1}; MS (m/z): 499.19 (M^+). Anal. calcd. for $C_{34}H_{36}N_2$: C, 86.35; H, 8.05; N, 5.59. Found: C, 85.90; H, 8.35; N, 5.61.

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REFERENCES

1. (a) Michalson, E. T.; Szmuszkovicz, J. *Prog. Drug. Res.* **1989**, *33*, 135–149; (b) Chang, A.-C.; Takemori, A.-E.; Ojala, W. H.; Gleason, W. B.; Portoghese, P. S. *J. Med. Chem.* **1994**, *37*, 4490–4498; (c) Weerawara, S. A.; Davis, R. D.; Nelsn, W. L. *J. Med. Chem.* **1994**, *37*, 2856–2864.
2. (a) Whitsell, J. K. *Chem. Rev.* **1989**, *89*, 1581–1590; (b) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*; VCH: New York, 1993; (c) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497–526; (d) Tomioka, K. *Synthesis* **1990**, 541–549.
3. (a) Uragami, M.; Tomioka, K.; Koga, K. *Tetrahedron: Asymmetry* **1995**, *6*, 701–704; (b) Kobayashi, S.; Hayashi, T. *J. Org. Chem.* **1995**, *60*, 1098–1099.
4. Hamada, T.; Manabe, K.; Kobayashi, S. *J. Am. Chem. Soc.* **2004**, *126*, 7768–7769.
5. (a) Yasuda, K.; Shindo, M.; Koga, K. *Tetrahedron Lett.* **1996**, *37*, 6343–6346; (b) Andrey, O.; Alexakis, A.; Bernardinelli, G. *Org. Lett.* **2003**, *5*, 2559–2562.
6. (a) Corey, E. J.; DaSilva Jardine, P.; Virgil, S.; Yuen, P.-W. *J. Am. Chem. Soc.* **1989**, *111*, 9243–9244; (b) Kubota, H.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1993**, *34*, 8135–8138; (c) Hanessian, S.; Meffre, P.; Girard, M.; Beaudoin, S.; Sancéau, Y.-J. *J. Org. Chem.* **1993**, *58*, 1991–1993.
7. Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493–5495.
8. Kubota, H.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1993**, *34*, 8135–8138.
9. (a) Halle, R.; Bréhéret, A.; Schulz, E.; Pinel, C.; Lemaire, M. *Tetrahedron: Asymmetry* **1997**, *8*, 2101–2108; (b) Sato, S.; Watanabe, H.; Asami, M. *Tetrahedron: Asymmetry* **2000**, *11*, 4329–4340; (c) Kim, G. J.; Kim, S. H.; Chong, P. H.; Kwon, M. A. *Tetrahedron Lett.* **2002**, *43*, 8059–8062; (d) Ma, Y. P.; Liu, H.; Chen, L.; Cui, X.; Zhu, J.; Deng, J. G. *Org. Lett.* **2003**, *5*, 2103–2106; (e) Itsuno, S.; Tsuji, A.; Takahashi, M. *Tetrahedron Lett.* **2003**, *44*, 3825–3828.
10. Martin, J.; Lanse, M.-C.; Plaquevent, J.-C.; Duhamel, L. *Tetrahedron Lett.* **1997**, *38*, 7181–7182.
11. Nakajima, M.; Tomioka, K.; Koga, K. *Tetrahedron* **1993**, *49*, 9735–9750.
12. (a) Rossiter, B. E.; Eguchi, M.; Miao, G.; Swingle, N. M.; Hernandez, A. E.; Vickers, D.; Fluckiger, E.; Patterson, R. G.; Reddy, K. V. *Tetrahedron* **1993**, *49*, 965–986; (b) Miao, G.; Rossiter, B. E. *J. Org. Chem.* **1995**, *60*, 8424–8427; (c) Pàmies, O.; Net, G.; Ruiz, A.; Claver, C.; Woodward, S. *Tetrahedron: Asymmetry* **2000**, *11*, 871–877.
13. (a) Shirai, R.; Tanaka, M.; Koga, K. *J. Am. Chem. Soc.* **1986**, *108*, 543–545; (b) Imai, M.; Hagihara, A.; Kawasaki, H.; Manabe, K.; Koga, K. *J. Am. Chem. Soc.* **1994**, *116*, 8829–8830; (c) Yamashita, T.; Sato, D.; Kiyoto, T.; Kumar, A.; Koga, K. *Tetrahedron Lett.* **1996**, *37*, 8195–8198; (d) Shirai, K.; Sato, D.; Aoki, K.; Tanaka, M.; Kawasaki, H.; Koga, K. *Tetrahedron* **1997**, *53*, 5963–5972; (e) Magnus, P.; Sebhat, I. K. *J. Am. Chem. Soc.* **1998**, *120*, 5341–5342.

14. (a) Asami, M.; Inoue, S. *Tetrahedron* **1995**, *51*, 11725–11730; (b) Leonard, J.; Bennett, L.; Mahmood, A. *Tetrahedron Lett.* **1999**, *40*, 3965–3968.
15. Shepperson, I.; Quici, S.; Pozzi, G.; Nicoletti, M.; O'Hagan, D. *Eur. J. Org. Chem.* **2004**, 4545–4551.
16. (a) Kagan, H. B. Chiral ligands for asymmetric catalysts. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, pp. 1–39; (b) Saravanan, P.; Bisai, A.; Baktharaman, S.; Chandrasekhar, M.; Singh, V. K. *Tetrahedron* **2002**, *58*, 4693–4706.
17. (a) Murata, S. *Chem. Lett.* **1983**, 1819–1820; (b) Kitagawa, T.; Kuroda, H.; Sasaki, H.; Kawasaki, K. *Chem. Pharm. Bull.* **1987**, *35*, 4294–4301.
18. (a) Boger, M.; Drabek, J.; Neumann, R. BP 2,145,716 (1985); *Chem. Abstr.* **1985**, *103*, 141636u; (b) Lunkenheimer, W.; Brandes, W. *Ger. Offen.* 2,836,158; *Chem. Abstr.* **1980**, *93*, 168596t.
19. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652; (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
20. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003.