

CHEMISTRY 
A EUROPEAN JOURNAL

Supporting Information

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**Enantioselective C-C Bond Formation to Sulfonylimines Using
2-Pyridylsulfonyl Group as a Novel Stereocontroller**

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General Methods

Toluene was distilled from calcium hydride under nitrogen prior to use. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel plate (60f-254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol/heat. Column chromatography was carried out on a column packed with KANTO KAGAKU silica gel 60N 37571. Optical rotations were measured on a HORIBA SEPA-300 operating at $\lambda=589$ nm corresponding to the sodium D line. Melting points were recorded on a YANAGIMOTO micro melting point apparatus and are uncorrected. ^1H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra for solution in CDCl_3 were recorded on a Varian Mercury-200. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer. Mass spectra were recorded on a SHIMADZU QCMS-QP5050-A spectrometer (EI) and SHIMADZU LCMS-2010EV (ESI). Microanalyses were performed with a Perkin Elmer-240. HPLC analyses were performed on a JASCO PU-2080 Plus or SHIMADZU LC-2010A HT using 4.6 x 250 mm CHIRALPAK AD-H or CHIRALCEL OJ-H or CHIRALCEL OD-H or CHIRALPAK AS-H column.

Experimental Procedure

***N*-Benzylidene-2,4,6-triisopropylphenylsulfonamide (1e).**

The reaction was carried out as described in the typical procedure except for using 2,4,6-triisopropylsulfonamide (500 mg, 1.76 mmol), benzaldehyde (187 mg, 1.76 mmol), triethylamine (0.74 mL, 5.28 mmol), and titanium(IV) chloride (1.00 mol L⁻¹ in CH_2Cl_2 , 1.76 mL, 1.76 mmol). Usual work-up gave the crude product which was recrystallized with hexane/ethyl acetate to afford **1e** (459 mg, 70%); mp 128.0-130.0°C; $R_f=0.50$ (hexane/ethyl

acetate = 80/20); ^1H NMR δ 1.26 (d, J = 6.6 Hz, 12H), 1.29 (d, J = 6.6 Hz, 6H), 2.91 (sep, J = 6.6 Hz, 1H), 4.36 (sep, J = 6.6 Hz, 2H), 7.20 (s, 2H), 7.45-7.95 (m, 5H), 9.02 (s, 1H); ^{13}C NMR δ 23.8, 25.0, 30.0, 34.4, 123.7, 129.0, 130.7, 130.8, 132.5, 134.4, 150.9, 153.4, 168.4; IR (KBr) 1607, 1311, 1149, 787, 770, 674, 532 cm^{-1} ; EIMS m/z (rel. intensity) 371 (M^+ , 22), 292 (100), 229 (30), 186 (49), 160 (35), 90 (23); Anal. Calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_2\text{S}$: C, 71.12; H, 7.87; N, 3.77. Found: C, 71.22; H, 7.75; N, 3.79.

***N*-Benzylidene-8-quinolinesulfonamide (1f).**

The reaction was carried out as described in the typical procedure except for using 8-quinolinesulfonamide (500 mg, 2.40 mmol), benzaldehyde (0.25 mL, 2.40 mmol), triethylamine (1.00 mL, 7.20 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 2.40 mL, 2.40 mmol). Usual work-up gave the crude product which was recrystallized from hexane/ethyl acetate to afford **1f** (285 mg, 40%); mp 190.0-192.0 $^\circ\text{C}$; R_f = 0.37 (hexane/ethyl acetate = 60/40); ^1H NMR δ 7.41-7.76 (m, 5H), 7.96-8.23 (m, 4H) 8.72-8.76 (m, 1H), 8.91-8.94 (m, 1H), 9.59 (s, 1H); ^{13}C NMR δ 121.8, 125.4, 128.6, 128.9, 131.2, 132.5, 133.9, 134.5, 134.6, 136.3, 143.3, 151.1, 175.0; IR (KBr) 1599, 1572, 1314, 1171, 1114, 816 cm^{-1} ; EIMS m/z (rel. intensity) 298 (M^++1 , 100), 209 (10), 129 (18), 102 (40); Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 64.85; H, 4.08; N, 9.45. Found: C, 64.70; H, 4.14; N, 9.54.

***N*-Benzylidene-2-thiophenesulfonamide (1g).**

The reaction was carried out as described in the typical procedure except for using 2-thiophenesulfonamide (500 mg, 3.06 mmol), benzaldehyde (0.32 mL, 3.06 mmol), triethylamine (1.28 mL, 9.18 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 3.06 mL, 3.06 mmol). Usual work-up gave the crude product which was recrystallized from

hexane/ethyl acetate to afford **1g** (292 mg, 38%); $R_f = 0.54$ (hexane/ethyl acetate = 60/40); ^1H NMR δ 7.14 (dd, $J = 3.3, 4.9$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 7.63 (t, $J = 8.1$ Hz, 1H), 7.71 (dd, $J = 1.3, 4.9$ Hz, 1H), 7.80 (dd, $J = 1.3, 3.7$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 2H), 9.02 (s, 1H); ^{13}C NMR δ 127.7, 129.0, 131.4, 132.1, 133.8, 134.5, 135.1, 138.1, 170.2; IR (KBr) 1596, 1564, 1322, 1151, 795, 587 cm^{-1} ; EIMS m/z (rel. intensity) 251 (M^+ , 35), 187 (30), 147 (100); Anal. Calcd for $\text{C}_{11}\text{H}_9\text{NO}_2\text{S}_2$: C, 52.57; H, 3.61; N, 5.57. Found: C, 52.57; H, 3.79; N, 5.60.

***N*-Benzylidene-2-furylsulfonamide (1h).**

The reaction was carried out as described in the typical procedure except for using 2-furylsulfonamide (500 mg, 3.40 mmol), benzaldehyde (0.35 mL, 3.40 mmol), triethylamine (1.42 mL, 10.2 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 3.40 mL, 3.40 mmol). Usual work-up gave the crude product which was recrystallized from hexane/ethyl acetate to afford **1h** (511 mg, 64%); mp 127.3-128.1 $^\circ\text{C}$; $R_f = 0.60$ (hexane/ethyl acetate = 50/50); ^1H NMR δ 6.58 (s, 1H), 7.28 (d, $J = 4.0$ Hz, 1H), 7.49-7.56 (m, 2H), 7.64-7.71 (m, 2H), 7.64-7.71 (m, 2H), 7.98 (d, $J = 8.0$ Hz, 2H), 9.07 (s, 1H); ^{13}C NMR δ 111.6, 118.5, 129.0, 131.3, 131.8, 135.2, 146.4, 147.3, 171.9; IR (KBr) 1567, 1452, 1318, 1153, 1119, 811 cm^{-1} ; EIMS m/z (rel. intensity) 235 (M^+ , 60), 171 (100), 155 (85), 143 (80), 131 (63).

***N*-[(4-Methylphenyl)methylidene]-2-pyridinesulfonamide (1i).**

The reaction was carried out as described in the typical procedure except for using 2-pyridylsulfonamide (703 mg, 4.44 mmol), 4-methylbenzaldehyde (1.05 mL, 8.89 mmol), triethylamine (1.86 mL, 13.3 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 4.44 mL, 4.44 mmol). Usual work-up gave the crude product which was recrystallized from

hexane/ethyl acetate to afford **1i** (736 mg, 60%); $R_f = 0.35$ (hexane/ethyl acetate = 60/40); ^1H NMR δ 2.44 (s, 3H), 7.20-7.45 (m, 2H), 7.50-7.60 (m, 1H), 7.80-8.10 (m, 3H), 8.20-8.30 (m, 1H), 8.90-9.00 (m, 1H), 9.20 (s, 1H); ^{13}C NMR δ 22.2, 123.1, 127.0, 129.6, 129.7, 131.6, 137.8, 146.7, 150.1, 155.7, 173.7; IR (KBr) 1594, 1305, 1169, 810 cm^{-1} ; EIMS m/z (rel. intensity) 261 ($\text{M}^+ + 1$, 16), 247 (25), 195 (100), 168 (90), 154 (95); Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 59.98; H, 4.65; N, 10.76. Found: C, 60.01; H, 4.81; N, 10.56.

***N*-[(4-Methoxyphenyl)methylidene]-2-pyridinesulfonamide (1j).**

The reaction was carried out as described in the typical procedure except for using 2-pyridylsulfonamide (500 mg, 3.16 mmol), *p*-anisaldehyde (0.424 mL, 3.48 mmol), triethylamine (1.32 mL, 9.48 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 3.16 mL, 3.16 mmol). Usual work-up gave the crude product which was recrystallized from hexane/ethyl to afford **1j** (451 mg, 52%); $R_f = 0.35$ (hexane/ethyl acetate = 60/40); ^1H NMR δ 3.91 (s, 3H), 7.05 (d = 9.0 Hz, 2H), 7.49-7.56 (m, 1H), 7.93-8.01 (m, 3H), 8.25 (d, $J = 8.0$ Hz, 1H), 8.72-8.74 (m, 1H), 9.17 (s, 1H), ^{13}C NMR δ 55.6, 113.9, 122.6, 124.6, 126.7, 131.4, 133.6, 137.6, 149.7, 155.6, 172.5; IR (KBr) 1590, 1304, 1169, 814 cm^{-1} ; EIMS m/z (rel. intensity) 276 (M^+ , 60), 212 (100), 199 (65); Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3\text{S}$: C, 56.51; H, 4.38; N, 10.14. Found: C, 56.90; H, 4.24; N, 9.89.

***N*-[(3-Methoxyphenyl)methylidene]-2-pyridinesulfonamide (1k).**

The reaction was carried out as described in the typical procedure except for using 2-pyridylsulfonamide (500 mg, 3.16 mmol), *m*-anisaldehyde (0.424 mL, 3.48 mmol), triethylamine (1.32 mL, 9.48 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 3.16 mL, 3.16 mmol). Usual work-up gave the crude product which was recrystallized from

hexane/ethyl acetate to afford **1k** (451 mg, 52%); mp 148.0-150.0 °C; $R_f = 0.35$ (hexane/ethyl acetate = 60/40); $^1\text{H NMR}$ δ 3.83 (s, 3H), 7.15-7.56 (m, 5H), 7.93-8.26 (m, 1H), 8.24 (d, $J = 6.6$ Hz, 1H), 8.71-8.73 (m, 1H), 9.20 (s, 1H), $^{13}\text{C NMR}$ δ 56.0, 113.7, 123.0, 123.5, 126.0, 127.4, 130.3, 133.7, 138.2, 150.5, 155.5, 160.1, 174.3; IR (KBr) 1572, 1324, 1174, 828 cm^{-1} ; EIMS m/z (rel. intensity) 276 (M^+ , 56), 242 (90), 211 (100), 199 (60); Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3\text{S}$: C, 56.51; H, 4.38; N, 10.14. Found: C, 56.24; H, 4.37; N, 9.97.

***N*-[(4-Chlorophenyl)methylidene]-2-pyridinesulfonamide (1l).**

The reaction was carried out as described in the typical procedure except for using 2-pyridylsulfonamide (403 mg, 2.55 mmol), 4-chlorobenzaldehyde (716 mg, 5.10 mmol), triethylamine (1.07 mL, 7.65 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 2.55 mL, 2.55 mmol). Usual work-up gave the crude product which was recrystallized from hexane/ethyl acetate to afford **1l** (407 mg, 57%); $R_f = 0.35$ (hexane/ethyl acetate = 60/40), $^1\text{H NMR}$ δ 7.40-7.60 (m, 3H), 7.80-8.10 (m, 3H), 8.20-8.30 (m, 1H), 8.80-8.90 (m, 1H), 9.21 (s, 1H), $^{13}\text{C NMR}$ δ 123.2, 127.2, 129.5, 130.5, 132.5, 137.9, 141.7, 150.2, 155.3, 172.5; IR (KBr) 1567, 1306, 1169, 809 cm^{-1} ; EIMS m/z (rel. intensity) 281 ($\text{M}^+ + 1$, 25), 247 (58), 215 (75), 154 (100), 138 (95); Anal. Calcd for $\text{C}_{12}\text{H}_9\text{ClN}_2\text{O}_2\text{S}$: C, 51.34; H, 3.23; N, 9.98. Found: C, 51.30; H, 2.98; N, 10.09.

***N*-(1-Naphthylmethylidene)-2-pyridinesulfonamide (1m).**

The reaction was carried out as described in the typical procedure except for using 2-pyridylsulfonamide (300 mg, 1.90 mmol), 1-naphthaldehyde (296 mg, 1.90 mmol), triethylamine (0.79 mL, 5.62 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 1.9 mL, 1.90 mmol). Usual work-up gave the crude product which was recrystallized from

hexane/ethyl acetate to afford **1m** (291 mg, 39%); mp 99.0-100.0 °C; $R_f = 0.33$ (hexane/ethyl acetate = 60/40); $^1\text{H NMR } \delta$ 7.25-7.68 (m, 4H), 7.90-8.02 (m, 2H), 8.11-8.73 (m, 3H), 8.85-8.90 (m, 1H), 8.99-8.90 (m, 1H), 9.81 (s, 1H); $^{13}\text{C NMR } \delta$ 123.1, 124.2, 124.9, 126.8, 131.6, 133.5, 135.7, 136.4, 137.9, 150.1, 155.7, 173.5; IR (KBr) 1559, 1318, 1171, 758, 641, 590 cm^{-1} ; EIMS m/z (rel. intensity) 296 (M^+ , 13), 231 (42), 203 (10), 153 (100), 126 (38), 78 (96); Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 64.85; H, 4.08; N, 9.45. Found: C, 64.80; H, 4.05; N, 9.53.

***N*-(2-Naphthylmethylidene)-2-pyridinesulfonamide (1n)**

The reaction was carried out as described in the typical procedure except for using 2-pyridylsulfonamide (500 mg, 3.16 mmol), 2-naphthaldehyde (0.43 mg, 3.16 mmol), triethylamine (1.32 mL, 9.48 mmol), and titanium(IV) chloride (1.00 mol L^{-1} in CH_2Cl_2 , 3.16 mL, 3.16 mmol). Usual work-up gave the crude product which was recrystallized from hexane/ethyl acetate to afford **1n** (291 mg, 31%); mp 149.0-150.0 °C; $R_f = 0.33$ (hexane/ethyl acetate = 60/40); $^1\text{H NMR } \delta$ 7.25-7.68 (m, 3H), 7.86-8.06 (m, 5H), 8.25-8.29 (m, 1H), 8.40 (s, 1H), 8.70-8.73 (m, 1H), 9.39 (s, 1H); $^{13}\text{C NMR } \delta$ 123.4, 124.3, 126.8, 127.2, 127.3, 128.0, 129.2, 129.6, 129.7, 130.3, 132.6, 136.8, 138.1, 150.4, 160.6, 174.2; IR (KBr): 1584, 1317, 1169, 1114, 784, 605 cm^{-1} ; EIMS m/z (rel. intensity): 296 (M^+ , 5), 232 (10), 203 (5), 153 (8), 127 (24), 78 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 64.85; H, 4.08; N, 9.45. Found: C, 64.80; H, 4.05; N, 9.53.

***N*-(2-Furfurylidene)-2-pyridinesulfonamide (1o).**

The reaction was carried out as described in the typical procedure except for using 2-pyridylsulfonamide (800 mg, 5.06 mmol), furfural (0.42 mL, 5.06 mmol), triethylamine

(2.1 mL, 15.1 mmol), and titanium(IV) chloride (1.00 mol L⁻¹ in CH₂Cl₂, 5.1 mL, 5.1 mmol). Usual work-up gave the crude product which was recrystallized from hexane/ethyl acetate to afford **1o** (604 mg, 50%); mp 144.5-147.8 °C; R_f = 0.22 (hexane/ethyl acetate = 60/40); ¹H-NMR δ 6.68 (dd, *J* = 2.0, 3.7 Hz, 1H), 7.25-7.63 (m, 2H), 7.91-8.00 (m, 1H), 8.19-8.23 (m, 2H), 8.72-8.75 (m, 1H), 9.00 (s, 1H); ¹³C NMR δ 113.8, 123.2, 125.9, 127.0, 137.9, 148.8, 150.1, 150.1, 155.4, 158.8; IR (KBr) 1604, 1289, 1170, 1112, 829, 553 cm⁻¹; FABMS *m/z* (rel. intensity) 237 (M⁺+1, 100), 185 (22), 154 (8), 93 (45); Anal. Calcd for C₁₀H₈N₂O₃S: C, 50.84; H, 3.41; N, 11.86. Found: C, 50.95; H, 3.26; N, 11.89.

***N*-(3-Phenylpropenylidene)-2-pyridinesulfonamide (1p).**

The reaction was carried out as described in the typical procedure except for using 2-pyridylsulfonamide (802 mg, 5.07 mmol), *trans*-cinnamaldehyde (0.64 mL, 5.07 mmol), triethylamine (2.1 mL, 15.1 mmol), and titanium(IV) chloride (1.00 mol L⁻¹ in CH₂Cl₂, 5.1 mL, 5.1 mmol). Usual work-up gave the crude product which was recrystallized from hexane/ethyl acetate to afford **1p** (624 mg, 45%); mp 107.5-108.2 °C; R_f = 0.26 (hexane/ethyl acetate = 60/40); ¹H-NMR δ 7.03 (dd, *J* = 9.5, 16 Hz, 1H), 7.25-7.63 (m, 7H), 7.91-8.00 (m, 1H), 8.19-8.23 (m, 1H), 8.72-8.75 (m, 1H), 9.27 (d, *J* = 9.5 Hz, 1H); ¹³C NMR δ 123.0, 124.5, 127.0, 128.6, 129.0, 131.7, 133.8, 137.8, 150.1, 155.0, 156.1, 174.5; IR (KBr) 1579, 1558, 1302, 1166, 1115, 785 cm⁻¹; EIMS *m/z* (rel. intensity) 272 (M⁺, 13), 207 (18), 129 (68), 102 (10) 78 (100); Anal. Calcd for C₁₄H₁₂N₂O₂S: C, 61.75; H, 4.44; N, 10.29. Found: C, 61.72; H, 4.37; N, 10.25.

***N*-(1-Phenylethyl)-2,4,6-triisopropylbenzenesulfonamide (2e).**

To a solution of bis(oxazoline)-Ph (30.1 mg, 0.09 mmol) and imine **1e** (22.3 mg, 0.06 mmol)

in toluene (3 mL) was added MeMgI (0.66 mol L⁻¹ in Et₂O, 0.18 mL, 0.12 mmol) at -78 °C and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO₂ 10g, benzene/ethyl acetate = 90/10) to afford **2e** (16.1 mg, 69%, 20% ee); mp. 108.0-110.0 °C; R_f = 0.48 (hexane/ethyl acetate = 80/20); ¹H NMR δ 1.17 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.45 (d, *J* = 6.8 Hz, 3H), 2.91 (sep, *J* = 6.8 Hz, 1H), 4.36 (sep, *J* = 6.8 Hz, 2H), 4.53-4.70 (m, 2H), 7.20-7.30 (m, 7H); ¹³C NMR δ 23.8, 24.8, 25.1, 29.8, 34.3, 53.5, 123.4, 125.9, 127.4, 128.3, 142.0, 132.4, 149.6, 152.3; IR (KBr) 3312, 1459, 1318, 1158, 660, 552 cm⁻¹; FABMS *m/z* (rel. intensity) 388 (M⁺+1, 46), 284 (66), 267 (28), 105 (100); Anal. Calcd for C₂₃H₃₃NO₂S: C, 71.27; H, 8.58; N, 3.61. Found: C, 71.29; H, 8.56; N, 3.60. HPLC (CHIRALPAK AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL min⁻¹), *t*_R 21 (minor), 23 (major) min.

***N*-(1-Phenylethyl)quinoline-8-sulfonamide (2f).**

To a solution of bis(oxazoline)-Ph (30.1 mg, 0.09 mmol) and imine **1f** (17.9 mg, 0.06 mmol) in toluene (3 mL) was added MeMgI (0.66 mol L⁻¹ in Et₂O, 0.18 mL, 0.12 mmol) at -78 °C and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO₂ 10g, benzene/ethyl acetate = 90/10) to afford **2f** (9.7 mg, 52%, 0% ee); mp. 190-192 °C; R_f = 0.32 (hexane/ethyl acetate = 60/40); ¹H NMR δ 1.42 (d, *J* = 7.0 Hz, 3H), 4.47 (dq, *J* = 7.0, 7.8 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.84 (m, 5H), 7.30-7.60 (m, 2H), 7.80-7.90 (m, 1H), 8.10-8.40 (m, 2H), 8.85-8.95 (m, 1H); ¹³C NMR δ 23.3, 54.6, 121.7, 125.3, 125.7, 126.9, 127.4, 128.3, 130.4, 132.6, 136.5, 140.9, 142.7, 143.4, 150.4; IR (KBr) 3293, 1321, 1141, 793, 700, 614 cm⁻¹; FABMS *m/z* (rel.intensity) 313 (M⁺+1, 100), 209 (40), 105 (42); Anal. Calcd for C₁₇H₁₆N₂O₂S: C, 65.36; H, 5.16; N, 8.97. Found: C, 65.43; H, 5.03; N, 9.03. HPLC (CHIRALCEL OD-H, hexane/*i*-PrOH = 80:20, 0.5

mL min⁻¹), *t*_R 51, 56 min.

***N*-[1-(4-Methylphenyl)ethyl]-2-pyridinesulfonamide (2i).**

To a solution of bis(oxazoline)-Ph (38.5 mg, 0.115 mmol) and imine **1i** (20.0 mg, 0.07 mmol) in toluene (4 mL) was added MeMgBr (1.44 mol L⁻¹ in Et₂O, 0.107 mL, 0.154 mmol) at -95 °C and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO₂ 10g, benzene/ethyl acetate = 90/10) to afford **2i** (14.3 mg, 67%, 83% ee); [α]_D²⁵ -44.6 (*c* 0.67, CHCl₃, 83% ee); mp. 117.5-120.3 °C; *R*_f = 0.30 (hexane/ethyl acetate = 50/50); ¹H NMR δ 1.46 (d, *J* = 7.0 Hz, 3H), 3.25 (s, 3H), 4.55 (dq, *J* = 7.0, 8.4 Hz, 1H), 5.28 (d, *J* = 8.4 Hz, 1H), 6.80-7.10 (m, 4H), 7.20-7.45 (m, 1H), 7.60-7.90 (m, 2H), 8.50-8.65 (m, 1H); ¹³C NMR δ 21.1, 23.3, 55.0, 121.9, 125.8, 126.0, 128.9, 136.7, 137.2, 138.6, 149.3, 157.5; IR (KBr) 3096, 2854, 1331, 1173, 607 cm⁻¹; EIMS *m/z* (rel. intensity) 277 (M⁺, 6) 261 (100), 212 (53), 197 (73); Anal. Calcd for C₁₄H₁₆N₂O₂S: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.76; H, 5.78; N, 10.20. HPLC (CHIRALCEL OJ-H, hexane/*i*-PrOH = 70:30, flow rate 1.5 mL min⁻¹), *t*_R 17 (major), 27 (minor) min.

***N*-[1-(4-Methoxyphenyl)ethyl]-2-pyridinesulfonamide (2j).**

To a solution of bis(oxazoline)-Ph (36.0 mg, 0.108 mmol) and imine **1j** (20.0 mg, 0.07 mmol) in toluene (4 mL) was added MeMgBr (0.78 mol L⁻¹ in Et₂O, 0.18 mL, 0.144 mmol) at -95 °C and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO₂ 10g, benzene/ethyl acetate = 90/10) to afford **2j** (20.7mg, 98%, 80% ee); [α]_D²⁵ -24.2 (*c* 0.32, CHCl₃, 80% ee); mp. 121.4-123.0 °C; *R*_f = 0.30 (hexane/ethyl acetate = 40/60); ¹H NMR δ 1.49 (d, *J* = 7.0 Hz, 3H), 3.71 (s, 3H), 4.56 (dq, *J* = 7.0, 7.8 Hz, 1H), 5.47 (d, *J* = 7.8 Hz, 1H), 6.62-6.71 (m, 3H), 7.00-7.09 (m, 1H),

7.31-7.38 (m, 1H), 7.70-7.78 (m, 2H), 8.55 (d, $J = 5.6$ Hz, 1H); ^{13}C NMR δ 23.7, 54.1, 55.7, 113.9, 122.3, 126.3, 127.7, 134.0, 137.7, 149.8, 158.0, 158.8; IR (KBr) 3244, 1511, 1331, 1299, 1179, 742 cm^{-1} ; ESIMS: m/z 315 $[\text{M}+\text{Na}^+]$. HPLC (CHIRALCEL OJ-H, hexane/*i*-PrOH = 80:20, flow rate 1.5 mL min^{-1}), t_{R} 11.7 (major), 16.7 (minor) min.

***N*-[1-(3-Methoxyphenyl)ethyl]-2-pyridinesulfonamide (2k).**

To a solution of bis(oxazoline)-Ph (36.0 mg, 0.108 mmol) and imine **1k** (20.0 mg, 0.07 mmol) in toluene (4 mL) was added MeMgBr (0.78 mol L^{-1} in Et_2O , 0.18 mL, 0.144 mmol) at -95 $^{\circ}\text{C}$ and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO_2 10g, benzene/ethyl acetate = 90/10) to afford **2k** (17.4 mg, 74%, 88% ee); $[\alpha]_{\text{D}}^{25} -38.7$ (c 0.67, CHCl_3 , 88% ee); mp. 126.2-127.1 $^{\circ}\text{C}$; $R_{\text{f}} = 0.30$ (hexane/ethyl acetate = 40/60); ^1H NMR δ 1.44 (d, $J = 6.9$ Hz, 3H), 3.72 (s, 3H), 4.55 (dq, $J = 6.8, 6.9$ Hz, 1H), 5.65 (d, $J = 6.8$ Hz, 1H), 6.63 (d, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 7.25-7.38 (m, 1H), 7.66-7.74 (m, 2H), 8.54 (d, $J = 4.6$ Hz, 1H); ^{13}C NMR δ 23.8, 54.6, 55.6, 111.9, 113.3, 118.9, 122.3, 126.3, 129.5, 137.6, 143.4, 149.7, 157.9, 159.5; IR (KBr) 3086, 2856, 1337, 1179, 614 cm^{-1} ; ESIMS: m/z 315 $[\text{M}+\text{Na}^+]$; HPLC (CHIRALCEL OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL min^{-1}), t_{R} 14.0 (minor), 15.5 (major) min.

***N*-[1-(4-Chlorophenyl)ethyl]-2-pyridinesulfonamide (2l).**

To a solution of bis(oxazoline)-Ph (35.7 mg, 0.107 mmol) and imine **1l** (20.0 mg, 0.07 mmol) in toluene (4 mL) was added MeMgBr (1.44 mol L^{-1} in Et_2O , 0.09 mL, 0.142 mmol) at -95 $^{\circ}\text{C}$ and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO_2 10g, benzene/ethyl acetate = 90/10) to afford **2l** (16.2 mg, 77%, 76% ee); $[\alpha]_{\text{D}}^{24} -39.4$ (c 0.54, CHCl_3 , 76% ee); mp. 146.5-148.0 $^{\circ}\text{C}$; $R_{\text{f}} =$

0.33 (hexane/ethyl acetate = 50/50); ^1H NMR δ 1.45 (d, J = 6.8 Hz, 3H), 4.58 (dq, J = 6.8, 8.2 Hz, 1H), 5.40-5.60 (br, 1H), 6.90-7.10 (m, 4H), 7.30-7.50 (m, 1H), 7.70-7.80 (m, 2H), 8.50-8.70 (m, 1H); ^{13}C NMR δ 23.0, 53.2, 121.9, 126.0, 127.4, 127.9, 132.5, 137.5, 140.3, 149.1, 157.2; IR (KBr) 3122, 1336, 1177, 604 cm^{-1} ; EIMS m/z (rel. intensity) 297 (M^+ , 2.5), 247 (25), 217 (30), 154 (100); Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{N}_2\text{O}_2\text{S}$: C, 52.61; H, 4.42; N, 9.44. Found: C, 52.40; H, 4.03; N, 9.56. HPLC (CHIRALCEL OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL min^{-1}), t_{R} 19 (minor), 23 (major) min.

***N*-[1-(1-Naphthyl)ethyl]-2-pyridinesulfonamide (2m).**

To a solution of bis(oxazoline)-Ph (40.0 mg, 0.120 mmol) and imine **1m** (17.8 mg, 0.06 mmol) in toluene (4 mL) was added MeMgBr (1.00 mol L^{-1} in Et_2O , 0.12 mL, 0.120 mmol) at -95 $^\circ\text{C}$ and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO_2 10g, benzene/ethyl acetate = 90/10) to afford **2m** (13.9 mg, 74%, 76% ee); Recrystallization from hexane/ CH_2Cl_2 afforded **2m** with 95% ee; $[\alpha]_{\text{D}}^{25}$ +49.0 (c 0.55, CHCl_3 , 95% ee); mp. 140.0-145.0 $^\circ\text{C}$; R_{f} = 0.27 (hexane/ethyl acetate = 60/40); ^1H NMR δ 1.60 (d, J = 6.8 Hz, 3H), 5.30-5.60 (br, 2H), 7.19-7.78 (m, 9H), 7.97-8.02 (m, 1H), 8.41-8.43 (m, 1H); ^{13}C NMR δ 23.3, 50.1, 121.7, 122.6, 123.5, 124.9, 125.4, 125.9, 126.0, 127.8, 128.5, 129.9, 133.4, 137.0, 137.2, 149.2, 157.2; IR (KBr) 3098, 1333, 1172, 1112, 779, 593 cm^{-1} ; FABMS m/z (rel. intensity) 313 (M^++1 , 50), 170 (70), 155 (100); Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$: C, 65.36; H, 5.16; N, 8.97. Found: C, 65.36; H, 5.43; N, 8.70. HPLC (CHIRALCEL OD-H, hexane/*i*-PrOH = 80:20, 1.0 mL min^{-1}), t_{R} 12 (minor), 15 (major) min.

***N*-[1-(2-Furyl)ethyl]-2-pyridinesulfonamide (2o).**

To a solution of bis(oxazoline)-Ph (226 mg, 0.677 mmol) and imine **1o** (80.0 mg, 0.339 mmol) in toluene (12 mL) was added MeMgBr (1.44 mol L⁻¹ in Et₂O, 0.47 mL, 0.677 mmol) at -95 °C and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO₂ 10g, benzene/ethyl acetate = 90/10) to afford **2o** (32.3 mg, 38%, 87% ee); [α]_D²⁷ -60.8 (*c* 0.70, CHCl₃, 87% ee); mp.110.0-111.0 °C; R_f = 0.27 (hexane/ethyl acetate = 60/40); ¹H NMR δ 1.50 (d, *J* = 7.0 Hz, 3H), 4.68 (dq, *J* = 7.0, 8.4 Hz, 1H), 5.47 (d, *J* = 8.4 Hz, 1H), 5.94-5.96 (m, 1H), 6.06-6.09 (m, 1H), 7.06-7.08 (m, 1H), 7.26-7.43 (m, 1H), 7.78-7.93 (m, 2H), 8.55-8.59 (m, 1H); ¹³C NMR δ 20.9, 47.9, 106.0, 109.8, 121.7, 126.1, 137.5, 141.6, 149.6, 153.4, 157.4; IR (KBr) 3087, 2877, 1337, 1149, 769, 597 cm⁻¹; FABMS *m/z* (rel. intensity) 253 (M⁺+1, 40), 110 (22), 95 (100), 93 (20); Anal. Calcd for C₁₁H₁₂N₂O₃S: C, 52.37; H, 4.79; N, 11.10. Found: C, 52.32; H, 4.99; N, 10.95. HPLC (CHIRALCEL OJ-H, hexane/*i*-PrOH = 80:20, 1.5 mL min⁻¹), *t*_R 18 (major), 21 (minor) min.

***N*-[2-(4-Phenyl-3-butenyl)]-2-pyridinesulfonamide (2p).**

To a solution of bis(oxazoline)-Ph (36.8 mg, 0.588 mmol) and imine **1p** (20.0 mg, 0.07 mmol) in toluene (12 mL) was added MeMgBr (1.44 mol L⁻¹ in Et₂O, 0.102 mL, 0.147 mmol) at -95 °C and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO₂ 10g, benzene/ethyl acetate = 90/10) to afford **2p** (20.8 mg, 98%, 82% ee); [α]_D²⁵ -90.8 (*c* 0.69, CHCl₃, 82% ee); mp. 102.0-104.5 °C; R_f = 0.30 (hexane/ethyl acetate = 60/40); ¹H NMR δ 1.33 (d, *J* = 7.0 Hz, 3H), 4.15-4.25 (m, 1H), 5.50-5.70 (m, 1H), 5.82 (dd, *J* = 7.0, 15.8 Hz, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 7.07-7.35 (m, 6H), 7.68-7.80 (m, 1H), 7.90-8.10 (m, 1H), 8.66-8.80 (m, 1H); ¹³C NMR δ 22.0, 52.5, 122.2, 126.1, 126.2, 127.5, 128.2, 129.6, 130.4, 135.8, 137.6, 149.5, 157.8; IR

(KBr) 3173, 1333, 1174, 1120, 701, 599 cm^{-1} ; FABMS m/z (rel. intensity) 289 ($M^{+}+1$, 21), 159 (5), 131 (100); Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$: C, 62.48; H, 5.59; N, 9.71. Found: C, 62.32; H, 5.54; N, 9.66. HPLC (CHIRALCEL OJ-H, hexane/*i*-PrOH = 70:30, 1.2 mL min^{-1}), t_R 14 (minor), 17 (major) min.

***N*-(1-Phenylpropyl)-2-pyridinesulfonamide (2q).**

To a solution of bis(oxazoline)-Ph (30.1 mg, 0.09 mmol) and imine **1a** (14.8 mg, 0.06 mmol) in toluene (3 mL) was added EtMgBr (1.83 mol L^{-1} in Et_2O , 0.07 mL, 0.12 mmol) at $-95\text{ }^\circ\text{C}$ and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO_2 10g, benzene/ethyl acetate = 90/10) to afford **2q** (12.3 mg, 74%, 50% ee); $[\alpha]_D^{25} -10.8$ (c 0.31, CHCl_3 , 50% ee); mp. $92.0\text{-}93.0\text{ }^\circ\text{C}$, $R_f = 0.32$ (hexane/ethyl acetate = 60/40); $^1\text{H NMR}$ δ 0.83 (t, $J = 7.4$ Hz, 3H), 1.69-1.96 (m, 2H), 4.31 (ddd, $J = 7.4, 7.6, 8.0$ Hz, 1H), 5.24 (br, 1H), 6.96-7.10 (m, 5H), 7.28-8.51 (m, 4H); $^{13}\text{C NMR}$ δ 10.8, 30.5, 60.4, 121.8, 125.8, 126.5, 127.0, 128.0, 137.2, 139.9, 149.4, 157.4; IR (KBr) 3173, 1333, 1174, 1120, 701, 599 cm^{-1} ; FABMS m/z (rel. intensity) 277 ($M^{+}+1$, 85), 159 (95), 134 (15), 119 (100), 91 (52); Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.88; H, 5.72; N, 10.23. HPLC (CHIRALCEL OJ-H, hexane/*i*-PrOH = 70:30, 1.0 mL min^{-1}), t_R 11 (major), 23 (minor) min.

***N*-(1-Phenylpentyl)-2-pyridinesulfonamide (2r).**

To a solution of bis(oxazoline)-Ph (30.1 mg, 0.09 mmol) and imine **1a** (14.8 mg, 0.06 mmol) in toluene (3 mL) was added BuMgBr (0.68 mol L^{-1} in Et_2O , 0.18 mL, 0.12 mmol) at $-95\text{ }^\circ\text{C}$ and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO_2 10g, benzene/ethyl acetate = 90/10) to afford **2r**

(12.7 mg, 69%, 51% ee); $[\alpha]_D^{26} -4.8$ (c 0.36, CHCl₃, 51% ee); mp. 101.0-102.3 °C; $R_f = 0.20$ (hexane/ethyl acetate = 90/10); ¹H-NMR δ 0.79-1.00 (m, 3H), 1.01-1.24 (m, 4H), 1.25-2.00 (m, 2H), 4.30-4.45 (m, 1H), 5.55 (d, $J = 8.0$ Hz, 1H), 6.99-7.05 (m, 5H), 7.24-7.31 (m, 1H), 7.56-7.63 (m, 2H), 8.45-8.78 (m, 1H); ¹³C NMR δ 14.1, 22.4, 37.2, 58.9, 121.8, 125.8, 126.4, 127.0, 128.0, 137.1, 140.3, 149.4, 157.4; IR (KBr) 3084, 2866, 1334, 1177, 768, 614 cm⁻¹; Anal. Calcd C₁₆H₂₀N₂O₂S: C, 63.13; H, 6.62; N, 9.20. Found: C, 63.05; H, 6.58; N, 9.41. EIMS m/z (rel. intensity) 305 (M⁺, 1), 279 8 (50), 252 (52), 167 (95), 149 (100); HPLC (CHIRALCEL OJ-H, = hexane/*i*-PrOH 80:20, 1.0 ml/min), t_R 15 (minor), 20 (major) min.

***N*-(1,4-Diphenylpropynyl)-2-pyridinesulfonamide (2s).**

To a solution of Diethyl-bis(oxazoline)-Ph (44.0 mg, 0.122 mmol) and imine **1a** (20.0mg, 0.081 mmol) in toluene (1 mL) was added PhC≡CMgBr (0.96 mol L⁻¹ in Et₂O, 0.13 mL, 0.12 mmol) and Phenylacetylene (0.0178ml, 0.162mmol) at -78 °C and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO₂ 10g, benzene/ethyl acetate = 90/10) to afford **2s** (16.8 mg, 60%, 78% ee); mp. 152.4-153.8 °C; $R_f = 0.35$ (hexane/ethyl acetate = 90/10); ¹H NMR δ 5.63 (d, $J = 9.2$ Hz, 1H), 6.33 (br, 1H), 7.08-7.33 (m, 9H), 7.50-7.55 (m, 2H), 7.69-7.74 (m, 1H), 7.93-7.98 (m, 1H), 8.48 (d, $J = 5.6$ Hz, 1H); ¹³C NMR δ 50.7, 85.8, 87.0, 122.1, 122.5, 126.6, 127.7, 128.3, 128.5, 128.6, 128.8, 131.7, 137.4, 137.8, 149.9, 157.52; IR (KBr) 3080, 1338, 1177, 1124, 609 cm⁻¹; ESIMS: m/z 347 [M-H]; HPLC (CHIRALPAK AS, hexane/*i*-PrOH = 85:15, 2.0 mL min⁻¹), t_R 17 (minor), 26 (major) min.

***N*-(Phenyl-4-methylphenyl-methyl)-2-pyridinesulfonamide (2t).**

To a solution of bis(oxazoline)-Ph (45.3 mg, 0.09 mmol) and imine **1i** (20.0 mg, 0.07 mmol)

in toluene (3 mL) was added PhMgBr (1.07 mol L⁻¹ in Et₂O, 0.14 mL, 0.153 mmol) at -78 °C and the reaction mixture was stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (SiO₂ 10g, benzene/ethyl acetate = 90/10) to afford **2t** (19.7 mg, 72%, 61% ee); [α]_D²⁵ +4.97 (*c* 0.62, CHCl₃, 61% ee); mp.170-172 °C; ¹H NMR 2.26 (s, 3H), 4.21 (d, *J* =8.0 Hz, 1H), 5.80-5.90 (m, 1H), 6.85-7.20 (m, 9H), 7.21-7.90 (m, 3H), 8.40-8.55 (m, 1H); ¹³C NMR δ 21.2, 61.51, 121.9, 125.9, 127.2, 128.1, 128.8, 137.0, 137.1, 137.2, 140.1, 149.4, 157.2; IR (KBr) 3068, 1334, 1174, 735 cm⁻¹; EIMS *m/z* (rel. intensity) 339 (M⁺+1, 1), 196 (100), 165 (17); Anal. Calcd for C₁₉H₁₈N₂O₂S: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.41; H, 5.27; N, 8.38; HPLC (CHIRALCEL OJ-H, hexane/*i*-PrOH = 70:30, 1.0 mL min⁻¹), *t*_R 11 (major):14 (minor) min.

2-(2-Pyridylsulfonyl)amino-2-(4-methylphenyl)acetonitrile (3i)

The reaction was carried out as described in the typical procedure except for using imine **1i** (20.0 mg, 0.077 mmol), bis(oxazoline)-Ph (2.8 mg, 11 mol%), Mg(OTf)₂ (2.5 mg, 10 mol%), and trimethylsilyl cyanide (12 μ l, 0.10 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **3i** (22.0 mg, 99%, 72% ee) as a white solid; mp 164-165 °C; [α]_D²⁷ +36 (*c* 0.03, CHCl₃, 72% ee); *R*_f = 0.30 (benzene/ethyl acetate = 80/20); ¹H NMR (DMSO-*D*₆) δ 2.27 (s, 3H), 5.83 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.63-7.70 (m, 1H), 7.91-7.95 (m, 1H), 8.03-8.11 (m, 1H), 8.70-8.73 (m, 1H), 9.52 (d, *J* = 8.0 Hz, 1H); IR (KBr) 3096, 1354, 1183, 614 cm⁻¹; EIMS *m/z* (rel. intensity) 287 (M⁺, 1), 223 (5), 145 (25), 91 (38), 79 (100); Anal. Calcd for C₁₄H₁₃N₃O₂S: C, 58.52; H, 4.56; N, 14.62. Found: C: 58.29, H: 4.67, N: 14.30. HPLC (Daicel CHIRALPAK IA, hexane/*i*-PrOH = 90/10; 0.5 mL/min; *t*_R = 12.9 min (major),

$t_R = 15.4$ min (minor)).

2-(2-Pyridylsulfonyl)amino-2-(4-methoxyphenyl)acetonitrile (3j)

The reaction was carried out as described in the typical procedure except for using imine **1j** (20.0 mg, 0.072 mmol), bis(oxazoline)-Ph (2.6 mg, 11 mol%), Mg(OTf)₂ (2.3 mg, 10 mol%), and trimethylsilyl cyanide (12 μ l, 0.094 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **3j** (21.7 mg, 99%, 84% ee) as a white solid; mp 140.0-141.0 °C; $[\alpha]_D^{26} +35$ (*c* 0.03, CHCl₃, 84% ee); $R_f = 0.32$ (benzene/ethyl acetate = 80/20); ¹H NMR (DMSO-*D*₆) δ 3.72 (s, 3H), 5.80 (d, *J* = 9.0 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.63-7.66 (m, 1H), 7.90-7.94 (m, 1H), 8.06-8.10 (m, 1H), 8.69 (m, 1H), 9.46-9.51 (d, *J* = 9.0 Hz, 1H); IR (KBr) 3292, 3116, 1514, 1349, 1182, 770, 614 cm⁻¹; EIMS *m/z* (rel. intensity) 303 (M⁺, 1), 272 (2), 239 (4), 161 (47), 146 (12), 134 (8), 79 (100); Anal. Calcd for C₁₄H₁₃N₃O₃S: C, 55.43; H, 4.32; N, 13.85. Found: C: 55.32, H: 4.36, N: 13.16. HPLC (Daicel CHIRALPAK IA, hexane/*i*-PrOH = 90/10, 0.5 mL/min, $t_R = 19.6$ min(major), $t_R = 24.2$ min (minor)).

2-(2-Pyridylsulfonyl)amino-2-(3-methoxyphenyl)acetonitrile (3k)

The reaction was carried out as described in the typical procedure except for using imine **1k** (20.0 mg, 0.072 mmol), bis(oxazoline)-Ph (2.6 mg, 11 mol%), Mg(OTf)₂ (2.3 mg, 10 mol%), and trimethylsilyl cyanide (12 μ l, 0.094 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **3k** (21.0 mg, 93%, 78% ee) as a white solid; mp 156.2-158.3 °C; $[\alpha]_D^{25} +28$ (*c* 0.06, CHCl₃, 78% ee); $R_f = 0.30$ (benzene/ethyl acetate = 80/20); ¹H NMR (DMSO-*D*₆) δ 3.73 (s, 3H), 5.82-5.89 (m, 1H), 6.90-7.02 (m, 3H), 7.26-7.34 (m, 1H), 7.64-7.71 (m, 1H), 7.89-8.13 (m, 2H), 8.71-8.74 (m,

1H), 8.59 (d, $J = 7.8$ Hz, 1H); IR (KBr) 3292, 3094, 1347, 1184, 1047, 620 cm^{-1} ; ESIMS : m/z 326 $[\text{M}+\text{Na}^+]$; HPLC (Daicel CHIRALPAK AD-H, hexane/*i*-PrOH = 80/20, 1.0 mL/min, $t_R = 14.9$ min(minor), $t_R = 18.3$ min (major)).

2-(2-Pyridylsulfonyl)amino-2-(4-chlorophenyl)acetonitrile (3l)

The reaction was carried out as described in the typical procedure except for using imine **1l** (20.0 mg, 0.071 mmol), bis(oxazoline)-Ph (2.6 mg, 11 mol%), $\text{Mg}(\text{OTf})_2$ (2.3 mg, 10 mol%), and trimethylsilyl cyanide (12 μl , 0.094 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **3l** (21.7 mg, 99%, 72% ee) as a white solid; mp 162-163 $^\circ\text{C}$; $[\alpha]_D^{27} +21$ (c 0.03, CHCl_3 , 72% ee); $R_f = 0.35$ (benzene/ethyl acetate = 80/20); ^1H NMR ($\text{DMSO-}D_6$) δ 5.96 (d, $J = 9.2$ Hz, 1H), 7.38-7.48 (m, 4H), 7.65-7.71 (m, 1H), 7.91-7.95 (m, 1H), 8.04-8.11 (m, 1H), 8.70-8.72 (m, 1H), 9.62 (d, $J = 9.2$ Hz, 1H); IR (KBr) 3312, 3098, 1348, 1185, 612 cm^{-1} ; EIMS m/z (rel. intensity) 308 (M^+ , 2) 243 (9), 165 (19), 111 (17), 78 (100); Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{ClN}_3\text{O}_2\text{S}$: C, 50.73; H, 3.28; N, 13.65. Found: C: 51.17, H: 3.58, N: 13.31. HPLC (Daicel CHIRALCEL OJ-H, hexane/*i*-PrOH = 70/30; 1.0 mL/min; $t_R = 17.9$ min (minor), $t_R = 21.2$ min (major)).

2-(2-Pyridylsulfonyl)amino-2-(1-naphthyl)acetonitrile (3m)

The reaction was carried out as described in the typical procedure except for using imine **1m** (20.0 mg, 0.067 mmol), bis(oxazoline)-Ph (2.5 mg, 11 mol%), $\text{Mg}(\text{OTf})_2$ (2.2 mg, 10 mol%), and trimethylsilyl cyanide (11 μl , 0.087 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **3m** (22.1 mg, 99%, 75% ee) as a white solid; mp 166.0-167.0 $^\circ\text{C}$; $[\alpha]_D^{27} +43$ (c 0.03, CHCl_3 , 75% ee); $R_f = 0.32$ (benzene/ethyl acetate = 80/20); ^1H NMR ($\text{DMSO-}D_6$) δ 6.50 (d, $J = 8.8$ Hz, 1H),

7.48-7.70 (m, 5H), 7.89-8.14 (m, 5H), 8.64 (m, 1H), 9.57 (d, $J = 8.8$ Hz, 1H); IR (KBr) 3230, 3090, 1348, 1185, 777, 610 cm^{-1} ; EIMS m/z (rel. intensity) 323 (M^+ , 2), 259 (5), 232 (13), 181 (20), 154 (56), 127 (28), 79 (100); HPLC (Daicel CHIRALPAK AD-H, hexane/*i*-PrOH = 80/20, 1.5 mL/min, $t_R = 15.0$ min (minor), $t_R = 45.1$ min (major)).

2-(2-Pyridylsulfonyl)amino-2-(2-naphthyl)acetonitrile (3n)

The reaction was carried out as described in the typical procedure except for using imine **1n** (20.0 mg, 0.067 mmol), bis(oxazoline)-Ph (2.5 mg, 11 mol%), $\text{Mg}(\text{OTf})_2$ (2.2 mg, 10 mol%), and trimethylsilyl cyanide (11 μl , 0.087 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **3n** (21.5 mg, 99%, 73% ee) as a white solid; mp 170.0-171.0 $^\circ\text{C}$; $[\alpha]_D^{27} +31$ (c 0.029, CHCl_3 , 75% ee); $R_f = 0.31$ (benzene/ethyl acetate = 80/20); ^1H NMR ($\text{DMSO-}D_6$) δ 6.09 (d, $J = 9.0$ Hz, 1H), 7.46-7.68 (m, 4H), 7.88-8.06 (m, 6H), 8.70-8.73 (m, 1H), 9.67 (d, $J = 9.0$ Hz, 1H); IR (KBr) 3095, 1348, 1184, 735, 608 cm^{-1} ; EIMS m/z (rel. intensity) 323 (M^+ , 1), 296 (15), 232 (30), 181 (54), 153 (31), 127 (85), 78 (100); HPLC (Daicel CHIRALPAK AD-H, hexane/*i*-PrOH = 80/20, 1.5 mL/min, $t_R = 18.7$ min (minor), $t_R = 22.6$ min (major)).

(R)-Methyl 2,2-dimethyl-3-phenyl-3-[(8-quinolylsulfonyl)amino]propionate (4f)

The reaction was carried out as described in the typical procedure except for using imine **1f** (20.0 mg, 0.067 mmol), bis(oxazoline)-Ph (2.5 mg, 0.0074 mmol), $\text{Cu}(\text{OTf})_2$ (2.5 mg, 0.0067 mmol), and silylketene acetal (18 μl , 0.087 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **4f** (5.2 mg, 19%, 1% ee) as a white solid; mp 91.5-92.5 $^\circ\text{C}$; $[\alpha]_D^{20} +0.081$ (c 1, CHCl_3 , 1.0% ee); $R_f = 0.68$ (benzene/ethyl acetate = 70/30); ^1H NMR δ 1.11 (s, 3H), 1.36 (s, 3H), 3.60 (s, 3H),

4.49 (d, $J = 10$ Hz, 1H), 6.53-6.67 (m, 4H), 6.66 (d, $J = 6$ Hz, 1H), 7.23-7.31 (m, 2H), 7.44-7.54 (m, 1H), 7.72-7.76 (m, 1H), 7.99-8.09 (m, 2H), 9.06 (d, $J = 4$ Hz, 1H); ^{13}C NMR δ 22.9, 23.2, 47.8, 52.2, 58.9, 115.9, 120.2, 121.3, 122.1, 126.6, 127.3, 127.4, 127.5, 127.7, 131.1, 141.0, 177.3; IR (KBr) 3244, 1740, 1491, 1323, 1136, 1048, 720 cm^{-1} ; EIMS m/z (rel. intensity) 399 ($\text{M}^+ + 1$, 26), 247 (100), 209 (36), 128 (90); Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$: C, 63.30; H, 5.56; N, 7.03. Found: C, 63.55; H, 5.26; N, 6.89. HPLC (CHIRALCEL AS-H, hexane/ i PrOH=80:20, 1.0 ml/min) t_R 14.6 (major), 18.1 (minor) min.

(*R*)-Methyl 2,2-dimethyl-3-phenyl-3-[(2-thienylsulfonyl)amino]propionate (4g)

The reaction was carried out as described in the typical procedure except for using imine **1g** (25.0 mg, 0.098 mmol), bis(oxazoline)-Ph (3.7 mg, 0.0108 mmol), $\text{Cu}(\text{OTf})_2$ (3.6 mg, 0.0098 mmol), and silylketene acetal (26 μl , 0.128 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 95/5) to afford **4g** (17.4 mg, 47%, 0.5% ee) as a white solid; mp 106.1-108.5 $^\circ\text{C}$; $[\alpha]_D^{20} -0.024$ (c 1, CHCl_3 , 0.5% ee); $R_f = 0.50$ (benzene/ethyl acetate = 90/10); ^1H NMR δ 1.11 (s, 3H), 1.38 (s, 3H), 3.65 (s, 3H), 4.40 (d, $J = 10$ Hz, 1H), 6.31 (d, $J = 8$ Hz, 1H), 6.69-6.74 (m, 1H), 6.96-7.01 (m, 2H), 7.06-7.15 (m, 3H), 7.27-7.28 (s, 2H); ^{13}C NMR δ 22.7, 24.9, 47.2, 52.2, 65.1, 126.6, 127.4, 127.6, 127.8, 131.1, 131.7, 136.7, 141.5, 176.0; IR (KBr) 3283, 1734, 1457, 1331, 1157, 1134, 706 cm^{-1} ; EIMS m/z (rel. intensity) 353 (M^+ , 14), 313 (38), 252 (60), 236 (100); Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_4\text{S}_2$: C, 54.37; H, 5.42; N, 3.96. Found: C, 54.45; H, 5.47; N, 3.41. HPLC (CHIRALPAK AD-H, hexane/ i PrOH=90:10, 1.0 ml/min) t_R 21.2 (major), 24.2 (minor) min.

(*R*)-Methyl 2,2-dimethyl-3-phenyl-3-[(2-furylsulfonyl)amino]propionate (4h)

The reaction was carried out as described in the typical procedure except for using imine **1h** (25.0 mg, 0.0106 mmol), bis(oxazoline)-Ph (4.0 mg, 0.012 mmol), Cu(OTf)₂ (3.6 mg, 0.011 mmol), and silylketene acetal (28 μ l, 0.138 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **4h** (21.0 mg, 59%, 8% ee) as a white solid; mp 89.6-90.5 °C; $[\alpha]_D^{20}$ +3.06 (*c* 1, CHCl₃, 8.0% ee); R_f = 0.53 (benzene/ethyl acetate = 90/10); ¹H NMR δ 1.08 (s, 3H), 1.37 (s, 3H), 3.65 (s, 3H), 4.32 (d, *J* = 10 Hz, 1H), 6.09-6.12 (m, 1H), 6.42 (d, *J* = 10 Hz, 1H), 6.59-6.61 (m, 1H), 6.97-7.14 (m, 6H); ¹³C NMR δ 22.7, 25.0, 47.0, 52.3, 65.0, 110.6, 115.8, 127.4, 127.8, 136.8, 145.1, 145.2, 148.0, 176.0; IR (KBr) 3283, 1733, 1457, 1350, 1162, 1131, 636 cm⁻¹; EIMS *m/z* (rel. intensity) 337 (M⁺, 40), 281 (100), 236 (80); Anal. Calcd for C₁₆H₁₉NO₅S : C, 56.96; H, 5.68; N, 4.15. Found: C, 56.72; H, 5.65; N, 3.99. HPLC (CHIRALPAK AD-H, hexane/ⁱPrOH=80:20, 1.0 ml/min) *t_R* 10.3 (major), 12.6 (minor) min.

(R)-Methyl 2,2-dimethyl-3-(4-methylphenyl)-3-[(2-pyridylsulfonyl)amino]propionate (4i)

The reaction was carried out as described in the typical procedure except for using imine **1i** (25.0 mg, 0.0096 mmol), bis(oxazoline)-Ph (3.7 mg, 0.011 mmol), Cu(OTf)₂ (3.5 mg, 0.011 mmol), and silylketene acetal (25 μ l, 0.096 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 85/15) to afford **4i** (13.9 mg, 40%, 70% ee) as a white solid; mp 118.3-119.0 °C; $[\alpha]_D^{20}$ -10.4 (*c* 1, CHCl₃, 70% ee); R_f = 0.59 (benzene/ethyl acetate = 70/30); ¹H NMR δ 1.09 (s, 3H), 1.38 (s, 3H), 2.18 (s, 3H), 3.66 (s, 3H), 4.40 (d, *J* = 10 Hz, 1H), 6.46 (d, *J* = 10 Hz, 1H), 6.77 (s, 3H), 7.14-7.23 (m, 2H), 7.50-7.52 (m, 2H), 8.42-8.44 (s, 1H); ¹³C NMR δ 21.0, 22.6, 24.8, 47.0, 52.1, 64.9, 121.6, 125.4, 127.6, 128.0, 133.5, 136.4, 136.8, 149.2, 157.0, 175.9; IR (KBr) 2933, 1734, 1573,

1429, 1341, 1178, 779 cm^{-1} ; EIMS m/z (rel. intensity) 362 (M^+ , 15), 279 (32), 261 (100), 220 (73); Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$: C, 59.65; H, 6.12; N, 7.73. Found: C, 59.55; H, 6.24; N, 7.60. HPLC (CHIRALPAK AD-H, hexane/ i PrOH=80:20, 1.0 ml/min) t_R 11.7 (major), 17.2 (minor) min.

(R)-Methyl 2,2-dimethyl-3-(4-methoxyphenyl)-3-[(2-pyridylsulfonyl)amino]propionate (4j)

The reaction was carried out as described in the typical procedure except for using imine **1j** (25.0 mg, 0.0092 mmol), bis(oxazoline)-Ph (3.5 mg, 0.010 mmol), $\text{Cu}(\text{OTf})_2$ (3.4 mg, 0.0092 mmol), and silylketene acetal (24 μl , 0.118 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **4j** (16.6 mg, 49%, 40% ee) as a white solid; mp 111.3-120.0 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{20}$ -36.3 (c 1.0, CHCl_3 , 40% ee); R_f = 0.45 (benzene/ethyl acetate = 70/30); ^1H NMR δ 1.09 (s, 3H), 1.38 (s, 3H), 3.66 (s, 3H), 3.70 (s, 3H), 4.40 (d, J = 10 Hz, 1H), 6.47 (d, J = 2 Hz, 1H), 6.52 (d, J = 2 Hz, 1H), 6.79 (d, J = 8 Hz, 2H), 7.20-7.30 (m, 2H), 7.52-7.54 (m, 2H), 8.44-8.46 (m, 1H); ^{13}C NMR δ 22.7, 24.6, 47.2, 52.2, 55.2, 64.6, 112.9, 121.6, 125.6, 128.4, 128.7, 128.9, 136.9, 149.3, 158.3, 175.9; IR (KBr) 2955, 1736, 1516, 1431, 1178, 1120, 607 cm^{-1} ; EIMS m/z (rel. intensity) 378 (M^+ , 28), 277 (100), 236 (72); Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_5\text{S}$: C, 57.13; H, 5.86; N, 7.40. Found: C, 57.36; H, 6.08; N, 7.48. HPLC (CHIRALPAK AD-H, hexane/ i PrOH=80:20, 1.0 ml/min) t_R 12.1 (minor), 17.3 (major) min.

(R)-Methyl 2,2-dimethyl-3-(4-chlorophenyl)-3-[(2-pyridylsulfonyl)amino]propionate (4k)

The reaction was carried out as described in the typical procedure except for using imine **1l**

(25.0 mg, 0.0091 mmol), bis(oxazoline)-Ph (3.4 mg, 0.010 mmol), Cu(OTf)₂ (3.3 mg, 0.009 mmol), and silylketene acetal (24 μ l, 0.118 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 85/15) to afford **4l** (29.5 mg, 52%, 75% ee) as a white solid; mp 141.3-142.0 °C; $[\alpha]_D^{20}$ -17.2 (*c* 1, CHCl₃, 62% ee); R_f = 0.53 (benzene/ethyl acetate = 70/30); ¹H NMR δ 1.09 (s, 3H), 1.41 (s, 3H), 3.66 (s, 3H), 4.42 (d, *J* = 10 Hz, 1H), 6.58 (d, *J* = 10 Hz, 1H), 6.87 (d, *J* = 14 Hz, 1H), 6.98 (d, *J* = 9 Hz, 1H), 7.30 (s, 1H), 7.56-7.59 (m, 4H), 8.46 (d, *J* = 4 Hz, 1H); ¹³C NMR δ 22.7, 24.8, 47.0, 52.3, 64.5, 121.6, 125.7, 127.5, 129.2, 133.0, 135.4, 137.0, 149.4, 157.0, 175.7; IR (KBr) 3343, 1737, 1425, 1341, 1179, 1119, 779 cm⁻¹; EIMS *m/z* (rel. intensity) 382 (M⁺, 7), 351 (100), 318 (60); Anal. Calcd for C₁₇H₁₉ClN₂O₄S: C, 53.33; H, 5.00; N, 7.32. Found: C, 53.55; H, 5.03; N, 7.21. HPLC (CHIRALPAK AD-H, hexane/*i*PrOH=80:20, 1.0 ml/min) *t*_R 15.7 (major), 24.7 (minor) min.

(R)-Methyl 2,2-dimethyl-3-(1-naphthyl)-3-[(2-pyridylsulfonyl)amino]propionate (4m)

The reaction was carried out as described in the typical procedure except for using imine **1m** (25.0 mg, 0.0084 mmol), bis(oxazoline)-Ph (3.2 mg, 0.0092 mmol), Cu(OTf)₂ (3.1 mg, 0.0084 mmol), and silylketene acetal (22 μ l, 0.109 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **4m** (18.0 mg, 50%, 71% ee) as a white solid; mp 115.1-116.0 °C; $[\alpha]_D^{20}$ + 63.4 (*c* 1, CHCl₃, 71% ee); R_f = 0.63 (benzene/ethyl acetate = 70/30); ¹H NMR δ 1.08 (s, 3H), 1.48 (s, 3H), 3.68 (s, 3H), 5.46 (d, *J* = 10 Hz, 1H), 6.56 (d, *J* = 10 Hz, 1H), 6.83-6.89 (m, 1H), 6.98-7.25 (m, 4H), 7.40-7.48 (m, 3H), 7.64-7.68 (m, 1H), 8.03-8.13 (m, 2H); ¹³C NMR δ 22.1, 25.4, 48.1, 52.3, 57.7, 121.4, 122.7, 124.5, 125.2, 126.0, 126.4, 127.8, 128.2, 128.4, 131.4, 132.8, 133.5, 136.1, 148.8, 156.4, 176.0; IR(KBr) 3297, 1732, 1431, 1337, 1172, 1120, 775 cm⁻¹; EIMS *m/z* (rel.

intensity) 398 (M^+ , 26), 297 (100), 256 (76), 217 (60); Anal. Calcd for $C_{21}H_{22}N_2O_4S$: C, 63.30; H, 5.56; N, 7.03. Found: C, 63.00; H, 5.54; N, 6.85. HPLC (CHIRALPAK AD-H, hexane/ i PrOH=80:20, 0.30 ml/min) t_R 68.4 (major), 72.7 (minor) min.

(*R*)-Methyl 2,2-dimethyl-3-(2-naphthyl)-3-[(2-pyridylsulfonyl)amino]propionate (4n)

The reaction was carried out as described in the typical procedure except for using imine **1n** (25.0 mg, 0.0084 mmol), bis(oxazoline)-Ph (3.2 mg, 0.0092 mmol), $Cu(OTf)_2$ (3.1 mg, 0.0084 mmol), and silylketene acetal (22 μ l, 0.011 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **4n** (20.6 mg, 62%, 64% ee) as a white solid; mp 109.8-110.5 °C; $[\alpha]_D^{20}$ -23.6 (c 1, $CHCl_3$, 64% ee); R_f = 0.63 (benzene/ethyl acetate = 70/30); 1H NMR δ 1.15 (s, 3H), 1.47 (s, 3H), 3.68 (s, 3H), 4.60 (d, J = 10 Hz, 1H), 6.68 (d, J = 10 Hz, 1H), 6.81-6.88 (m, 1H), 7.03 (d, J = 8 Hz, 1H), 7.15-7.23 (m, 1H), 7.36-7.48 (m, 5H), 7.59-7.68 (m, 2H), 8.26 (d, J = 4 Hz, 1H); ^{13}C NMR δ 22.7, 24.9, 47.1, 52.2, 65.3, 121.5, 125.2, 125.3, 125.8, 127.0, 127.1, 127.4, 127.5, 132.0, 132.1, 133.8, 136.4, 149.1, 156.8, 175.9; IR (KBr) 2952, 1733, 1433, 1336, 1176, 1122, 746 cm^{-1} ; EIMS m/z (rel. intensity) 398 (M^+ , 15), 367 (19), 344 (55), 256 (100); Anal. Calcd for $C_{21}H_{22}N_2O_4S$: C, 63.30; H, 5.56; N, 7.03. Found: C, 63.34; H, 5.69; N, 6.86. HPLC (CHIRALPAK AD-H, hexane/ i PrOH=80:20, 1.0 ml/min) t_R 14.3 (major), 22.4 (minor) min.

(*R*)-Methyl 2,2-dimethyl-3-(2-furyl)-3-[(2-pyridylsulfonyl)amino]propionate (4o)

The reaction was carried out as described in the typical procedure except for using imine **1o** (25.0 mg, 0.108 mmol), bis(oxazoline)-Ph (4.1 mg, 0.0119 mmol), $Cu(OTf)_2$ (4.0 mg, 0.0108 mmol), and silylketene acetal (28 μ l, 0.014 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 75/25) to afford **4o** (19.1 mg,

52%, 73% ee) as a white solid; mp 108.0-109.2 °C; $[\alpha]_D^{20}$ -19.1 (*c* 1, CHCl₃, 73% ee); R_f = 0.48 (benzene/ethyl acetate = 70/30); ¹H NMR δ 1.19 (s, 3H), 1.33 (s, 3H), 3.70 (s, 3H), 4.55 (d, *J* =10 Hz, 1H), 6.19 (d, *J* =12 Hz, 1H), 7.01-7.02 (m, 1H), 7.27-7.36 (m, 3H), 7.72-7.81 (m, 2H), 8.47 (d, *J* = 6 Hz, 1H); ¹³C NMR δ 22.6, 23.6, 46.9, 52.2, 58.3, 108.1, 109.7, 121.5, 125.8, 137.2, 141.4, 149.4, 150.0, 156.8, 175.5; IR (KBr) 2921, 1737, 1436, 1342, 1181, 1121, 752 cm⁻¹; EIMS *m/z* (rel. intensity) 338 (M⁺, 35), 277 (69), 261 (100), 175 (57); Anal. Calcd for C₁₅H₁₈N₂O₅S: C, 53.24; H, 5.36; N, 8.28. Found: C, 53.38; H, 5.27; N, 8.17. HPLC (CHIRALPAK AD-H, hexane/^{*i*}PrOH=80:20, 0.60 ml/min) *t_R* 35.0 (major), *t_S* 38.1 (minor) min.

(*R*)-(*E*)-Methyl 2,2-dimethyl-5-phenyl-3-[(2-pyridylsulfonyl)amino]pent-4-enoate (4p**)**

The reaction was carried out as described in the typical procedure except for using imine **1p** (25.0 mg, 0.094 mmol), bis(oxazoline)-Ph (3.5 mg, 0.0103 mmol), Cu(OTf)₂ (3.4 mg, 0.0094 mmol), and silylketene acetal (25 μl, 0.0122 mmol). Usual work-up gave the crude product which was purified by chromatography (benzene/ethyl acetate = 90/10) to afford **4p** (14.9 mg, 43%, 71% ee) as a white solid; mp 97.5-98.9 °C; $[\alpha]_D^{20}$ -51.8 (*c* 1, CHCl₃, 71% ee); R_f = 0.65 (benzene/ethyl acetate = 70/30); ¹H NMR δ 1.19 (s, 3H), 1.38 (s, 3H), 3.70 (s, 3H), 3.93 (dd, *J* =9, 10 Hz, 1H), 5.71 (dd, *J* =10, 10 Hz, 1H), 5.96 (d, *J* =14 Hz, 1H), 6.95-6.98 (m, 2H), 7.09-7.20 (m, 4H), 7.57-7.65 (m, 2H), 7.87 (d, *J* =8 Hz, 1H), 8.54 (d, *J* =1 Hz, 1H); ¹³C NMR δ 23.1, 23.7, 46.6, 52.1, 64.0, 121.9, 124.2, 125.2, 125.9, 127.6, 128.0, 133.4, 135.4, 137.2, 149.6, 157.4, 175.9; IR (KBr) 3245, 1733, 1429, 1339, 1120, 1179, 600 cm⁻¹; EIMS *m/z* (rel. intensity) 374 (M⁺, 20), 367 (45), 343 (100), 281 (60); Anal. Calcd for C₁₉H₂₂N₂O₄S: C, 60.94; H, 5.92; N, 7.48. Found: C, 61.02; H, 5.78; N, 7.31. HPLC

(CHIRALPAK AD-H, hexane/*i*PrOH=80:20, 1.0 ml/min) t_R 11.6 (major), t_S 17.0 (minor) min.























