# Supporting information

## "Enantioselective construction of stereogenic quaternary centres via Rh-catalyzed asymmetric addition of alkenyl boronic acids to α,β-unsaturated pyridylsulfones"

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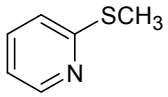
## I. Experimental section

**General.** All reagents were obtained from commercial suppliers and were used without further purification except NMO·$H_2O$ that was purified by precipitation from acetone before using. THF, $Et_2O$ and $CH_2Cl_2$ were dried over microwave-activated MS 4Å. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm Merck silica gel plates (Merck-60 230-400 mesh). Merck-60 230-400 mesh silica gel was used for flash column chromatography. NMR spectra were recorded on Bruker AC-200 or AC-300 instruments in $CDCl_3$ (calibrated at 7.26 and 77.0 ppm for $^1H$ and $^{13}C$ experiments, respectively). Mass spectra (MS) and high resolution mass spectra (HRMS) were determined on a Hewlett-Packard HP-5985 mass spectrometer at 70 eV ionising voltage (EI) or under fast atom bombardment (FAB) conditions. Melting points were determined in open-end capillary tubes on a GallemKamp apparatus. Optical rotations were measured on a Perkin-Elmer 241C polarimeter. High-Performance Liquid Chromatography (HPLC) was conducted on an Agilent 1100 instrument, using Daicel Chiralpak AD and Chiralcel OD columns. All chiral ligands were purchased from Strem Chemicals, except otherwise noted. $Rh(cod)_2BF_4$, $Rh(cod)_2PF_6$, $[Rh(cod)OMe]_2$ and $[Rh(cod)OH]_2$ were prepared according to reported procedures. $Rh(acac)(C_2H_4)_2$ was purchased from Strem Chemicals.

**Methyl 2-pyridyl thioether (I)** [18438-38-5] is available from comercial suppliers, but rather expensive. Therefore, it was prepared by us according to the following procedure.



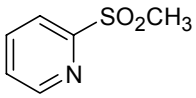

DBU (6.654 mL, 49.5 mmol) was added to a stirred solution of 2-mecaptopyridine (5.04 g, 45 mmol) in dry THF (90 mL, 0.5M), placed under nitrogen atmosphere and cooled at 0 ºC. A yellow precipitate was immediately formed, and 9 mL of $CH_3CN$ were added to improve solubility. After that, methyl iodide (3.08 mL, 49.5 mmol) was slowly added, the ice bath was removed and the suspension was allowed to stir for 4 hours. Water (40 mL) was added and the aqueous layer extracted with AcOEt (3x20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, the solvent was removed *in vacuo*, and the crude mixture was purified by column chromatography (AcOEt:hexanes, 1:2) to give methyl 2-pyridyl thioether **I** as a colorless oil (5.20 g, 41.52 mmol, 92% yield).

$^1$H NMR (200 MHz): 8.42 (m, 1H), 7.47 (m, 1H), 7.16 (m, 1H), 6.96 (m, 1H), 2.55 (s, 3H).

$^{13}$C NMR (50 MHz): 159.9, 149.3, 135.6, 121.3, 119.0, 13.1.

HRMS (FAB+, *m/z*): calcd. for $C_6H_8NS$ $[M+H]^+$, 126.0377; found, 126.0384.

**Methyl 2-pyridyl sulfone (II)**[1]




Water (6 mL) and sodium tungstate dihydrate (1.32 g, 3.99 mmol) were sequentially added to a stirred solution of methyl 2-pyridyl thioether (5.00 g, 39.95 mmol) in AcOEt (50 mL, 0.8 M). The mixture was cooled at 0 ºC and $H_2O_2$ (30% aqueous, 12.89 mL, 120 mmol) was carefully added. The yellow mixture was stirred at 0ºC for 1 hour, after which time the ice bath was removed and the reaction was allowed to stir at room temperature for another hour. The reaction was then brought back to 0 ºC, and $NaHSO_3$ was carefully added until the yellow colour completely disappeared (ca 10 mL). The organic layer was separated in an extraction funnel, and the aqueous layer was extracted with AcOEt (3x20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and the solvent was removed *in vacuo* to afford pure methyl 2-pyridyl sulfone **II** as colourless oil (6.27 mg, 39.893 mmol, quantitative yield).

[1] Giam, C. S.; Kikukawa, K.; Trujillo, D. A. *Organic Preparations and Procedures International*, 1981, **13**, 137-40.

$^1$H NMR (200 MHz): 8.77-8.70 (m, 1H), 8.12-7.89 (m, 2H), 7.62-7.49 (m, 1H), 3.21 (s, 3H).

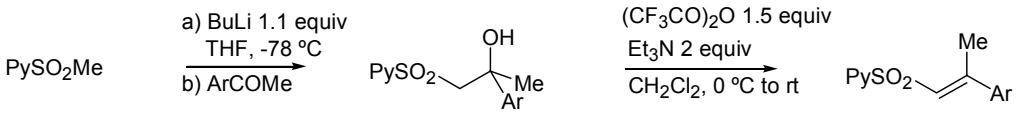
$^{13}$C NMR (50 MHz): 157.8, 149.9, 138.3, 127.4, 121.0, 39.9.

HRMS (FAB+, *m/z*): calcd. for $C_6H_8NO_2S$ $[M+H]^+$, 158.0276; found, 158.0285.

*Typical procedure for the preparation of β,β-disubstituted α,β-unsaturated pyridyl sulfones:*

**Synthesis of (E)-1-phenyl-1-((2-pyridyl)sulfonyl))-1-propene (1a)**

The procedure for the preparation of the unsaturated pyridyl sulfones consists of a two steps sequence, where the first step is a condensation of methyl pyridyl sulfone **II** with the corresponding ketone, and the second step is a dehydration of the previously obtained alcohol.




*Step one: condensation of methyl pyridyl sulfone with acetophenone*

**2-Phenyl-1-(2-pyridyl)sulfonyl))-2-propanol**

7.89 mL of BuLi (17.35 mmol, 1.1 equiv, 2.2 M in hexanes) were slowly added to a -78ºC solution of methyl pyridyl sulfone (2.48 g, 15.77 mmol) in dry THF (31 mL, 0.5 M). The yellow-orange suspension was stirred at -78 ºC for 30 min., after which time 2.03 mL of neat acetophenone (17.35 mmol, 1.1 equiv.) were slowly added. The resulting orange solution was stirred at -78 ºC until complete consumption of the starting material was observed by TLC (AcOEt, 75 min). The solution was then quenched with saturated $NH_4Cl$ (15 mL), the mixture was diluted with $CH_2Cl_2$ (20 mL) and the aqueous layer extracted with $CH_2Cl_2$ (3x20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, the solvent was removed in vacuo, and the crude mixture was purified by column chromatography (AcOEt:hexanes, 1:2) to afford 3.68 g of 2-phenyl-1-(2-pyridyl)sulfonyl))-2-propanol as a white solid (13.26 mmol, 84% yield).

M.p.: 97-99 ºC

$^1$H NMR (200 MHz): 8.67-8.54 (m, 1H), 7.69-7.55 (m, 1H), 7.45-7.32 (m, 2H), 7.21-7.10 (m, 2H), 7.08-6.96 (m, 3H), 4.62 (bs, 1H), 4.33 (d, *J*= 16.7 Hz, 1H), 3.88 (d, *J*= 16.7 Hz, 1H), 1.63 (s, 3H).

$^{13}$C NMR (50 MHz): 149.7, 137.9, 127.8, 126.9, 124.7, 121.6, 72.5, 62.1, 30.7.

*Step two: dehydration of the alcohol*

4-Dimethylamino pyridine (81 mg, 0.66 mmol, 5 mol%) was added in one portion to a stirred solution of 1-(2-pyridyl)sulfonyl))-2-phenyl-2-propanol (3.68 g, 13.26 mmol) in 26 mL of dry $CH_2Cl_2$ (0.5 M). Air was replaced by argon and the solution was cooled at 0 ºC. Then, 3.73 mL of triethylamine (26.52 mmol, 2 equiv.) and 2.81 mL of trifluoroacetic anhydride (19.89 mmol,

1.5 equiv.) were sequentially added. After 30 min. at 0 ºC the ice bath was removed and the reaction was allowed to stir overnight. The solution was then quenched with saturated $NH_4Cl$ (20 mL), the mixture diluted with $CH_2Cl_2$ (10 mL) and the aqueous layer extracted with $CH_2Cl_2$ (3x20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, the solvent was removed in vacuo, and the crude mixture was purified by column chromatography (diethyl ether:hexanes, 1:2) to afford 2.56 g of (*E*)-1-phenyl-1-((2-pyridyl)sulfonyl))-1-propene **1a** as a white solid (9.88 mmol, 75% yield).

M.p.: 82-83 ºC

$^1$H NMR (300 MHz): 8.74 (ddd, *J*= 0.9, 1.7 and 7.7 Hz, 1H), 8.17 (dt, *J*= 0.9 and 7.7 Hz, 1H), 8.01 (dt, *J*= 1.7 and 7.7 Hz, 1H), 7.57 (ddd, *J*= 1.0, 4.6 and 7.8 Hz, 1H), 7.52-7.28 (AA'BB' system, 4H), 6.74 (q, *J*= 1.0 Hz, 1H), 2.57 (d, *J*= 1.0 Hz, 1H).

$^{13}$C NMR (75 MHz): 159.4, 155.0, 140.0, 138.0, 130.0, 128.7, 127.0, 126.3, 124.8, 121.7, 17.6.

HRMS (FAB+, *m/z*): calcd. for $C_{14}H_{14}NO_2S$ $[M+H]^+$, 260.0745; found, 260.0748.

**(*E*)-2-*p*-Chlorophenyl-1-((2-pyridyl)sulfonyl))-1-propene (1b)**

Step 1: **2-*p*-chlorophenyl-1-((2-pyridyl)sulfonyl)-2-propanol**

State: white solid

M.p.: 116-118 ºC

$^1$H NMR (300 MHz): 8.67-8.54 (m, 1H), 7.69-7.55 (m, 1H), 7.45-7.32 (m, 2H), 7.18-6.96 (AA'BB' system, 4H), 4.71 (bs, 1H), 4.49 (d, *J*= 15.2 Hz, 1H), 4.01 (d, *J*= 15.2 Hz, 1H), 1.63 (s, 3H).

$^{13}$C NMR (75 MHz): 157.1, 149.9, 142.6, 138.0, 132.9, 128.0, 127.0, 126.5, 121.8, 72.4, 62.1, 30.8.

Step 2: **(*E*)-2-*p*-chlorophenyl-1-((2-pyridyl)sulfonyl))-1-propene (1b)**

State: white solid

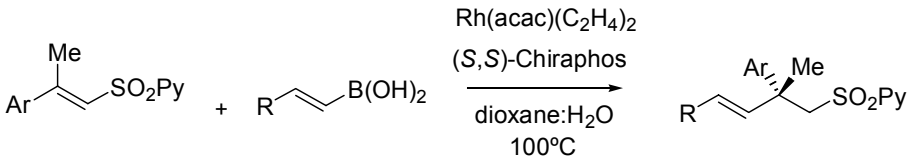
M.p.: 98-99 ºC

$^1$H NMR (300 MHz): 8.72 (ddd, *J*= 1.0, 1.8 and 7.8 Hz, 1H), 8.13 (dt, *J*= 1.0 and 7.8 Hz, 1H), 7.96 (dt, *J*= 1.8 and 7.8 Hz, 1H), 7.52 (ddd, *J*= 1.1, 4.7 and 7.8 Hz, 1H), 7.52-7.28 (AA'BB' system, 4H), 6.73 (q, *J*= 1.2 Hz, 1H), 2.54 (d, *J*= 1.2 Hz, 1H).

$^{13}$C NMR (75 MHz): 159.3, 154.6, 150.4, 138.5, 138.2, 136.1, 129.0, 127.8, 127.2, 125.3, 121.8, 17.6.

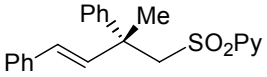
HRMS (FAB+, *m/z*): calcd. for $C_{14}H_{13}NO_2S$ $[M+H]^+$, 294.0356; found, 294.0352.

*Typical procedure for the rhodium-catalyzed enantioselective conjugate addition of organoboronic acids to β-aryl β-methyl α,β-unsaturated pyridyl sulfones:*




5 mL of anhydrous 1,4-dioxane and 500 μL of water were sequentially added to a mixture of $[Rh(acac)(C_2H_4)_2$ (6.5 mg, 0.025 mmol), (*S,S*)-chiraphos (10.7 mg, 0.025 mmol), *trans*-stiryl boronic acid (370 mg, 2.5 mmol) and the trisustituted sulfone **1a** (129.7 mg, 0.500 mmol), previously placed under inert atmosphere (argon or nitrogen) in a Schlenk tube. The solution was stirred at 100 °C for 24 h, after which time the resulting orange mixture was cooled to rt, diluted with $CH_2Cl_2$ (ca. 3 mL) and filtered through a short pad of silica gel (eluent: $CH_2Cl_2$). After concentration of the filtrate, the residue was purified by flash chromatography (AcOEt:hexanes, 1:3) to give **2a** (109 mg, 0.300 mmol, 60% yield) and unreacted **1a** (41 mg, 32% yield).

**(1*E*, 3*R*)-3-Methyl-1,3-diphenyl-4-((2-pyridyl)sulfonyl)-1-butene (2a)**




State: colourless oil

$^1$H NMR (300 MHz): 8.61 (ddd, $J$ = 0.9, 1.7 and 4.7 Hz, 1H), 7.60 (dt, $J$ = 0.9 and 7.8 Hz, 1H), 7.52 (dt, $J$ = 1.7 and 7.8 Hz, 1H), 7.31-7.07 (m, 11H), 6.40 (d, $J$ = 16.4 Hz, 1H), 6.25 (d, $J$ = 16.4 Hz, 1H), 4.16 (m, 2H), 1.85 (s, 3H).

$^{13}$C NMR (75 MHz): 158.1, 149.7, 144.3, 137.7, 136.7, 135.5, 128.7, 128.5, 128.2, 127.6, 126.7, 126.6, 126.5, 126.4, 121.9, 61.2, 43.2, 25.5.

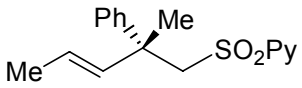
$[\alpha]_D$ = -24 (*c* 0.1, $CHCl_3$)

HPLC: 94 % *ee* [Daicel Chiralcel OD column, hexane/isopropanol 80:20, 0.6 mLmin$^{-1}$, λ = 254 nm; $t_R$/min = 31.9 (*R*) and 35.9 (*S*)].

HRMS (FAB+, *m/z*): calcd. for $C_{22}H_{22}NO_2S$ $[M+H]^+$, 364.1371; found, 364.1367.

IR (NaCl): ν (cm$^{-1}$) 1495 (C=C), 1315 ($SO_2$).

**(2*E*, 4*R*)-4-Methyl-4-phenyl-5-((2-pyridyl)sulfonyl)-2-pentene (3a)**




State: colourless oil

$^1$H NMR (300 MHz): 8.69-8.57 (m, 1H), 7.71 (dt, *J*= 1.6 and 7.5 Hz, 1H), 7.62-7.55 (m, 1H), 7.45-7.34 (ddd, *J*= 1.6, 4.8 and 7.5 Hz, 1H), 7.22-7.97 (m, 5H), 5.63-5.37 (m, 2H), 4.08 (d, *J* = 15.1 Hz, 1H), 3.92 (d, *J* = 15.1 Hz, 1H), 1.72 (s, 3H), 1.58 (d, *J* = 4.8 Hz, 3H).

$^{13}$C NMR (75 MHz): 158.2, 149.8, 144.2, 137.7, 137.2, 128.0, 126.8. 126.6, 126.4, 123.9, 121.9, 61.4, 42.8, 25.3, 18.1.

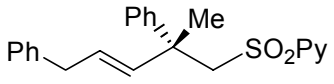
$[\alpha]_D$ = -4 (*c* 0.24, $CHCl_3$)

HPLC: 89 % *ee* [Daicel Chiralpak AD column, hexane/isopropanol 80:20, 0.4 mLmin$^{-1}$, λ = 254 nm; $t_R$/min = 24.0 (*S*) and 25.4 (*R*)].

HRMS (FAB+, *m/z*): calcd. for $C_{17}H_{20}NO_2S$ $[M+H]^+$, 302.1214; found, 302.1206.

IR (NaCl): ν (cm$^{-1}$) 1495 (C=C), 1316 ($SO_2$).

**(2*E*, 4*R*)-4-Methyl-1,4-diphenyl-5-((2-pyridyl)sulfonyl)-2-pentene (4a)**




State: white solid

M.p.: 114-115 ºC

$^1$H NMR (300 MHz): 8.67-8.58 (m, 1H), 7.71-7.63 (m, 1H), 7.62-7.54 (m, 1H), 7.43-6.99 (m, 11H), 7.22-6.97 (m, 5H), 5.81-5.60 (m, 2H), 4.13 (d, *J* = 14.9 Hz, 1H), 3.91 (d, *J* = 14.9 Hz, 1H), 3.31 (d, *J*= 6.5 Hz, 2H), 1.76 (s, 3H).

$^{13}$C NMR (75 MHz): 158.1, 149.8, 143.8, 140.1, 137.8, 137.7, 128.5, 128.4, 128.0, 127.7, 126.8, 126.6, 126.5, 126.1, 121.8, 61.4, 42.8, 39.0, 25.4.

$[\alpha]_D$ = +19 (*c* 0.1, $CHCl_3$)

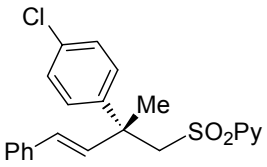
HPLC: >99 % *ee* [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.5 mLmin$^{-1}$, λ = 254 nm; $t_R$/min = 22.2 (*S*) and 25.1 (*R*)].

IR (NaCl): ν (cm$^{-1}$) 1495 (C=C), 1316 ($SO_2$).

Crystal data for $C_{23}H_{23}NO_2S$ **(4a)**: Single crystals were obtained by slow recrystallization from AcOEt. Formula weight 377.48, temperature 100(2) K, wavelength 1.54178 Å, crystal system orthorhombic, space group P2(1)2(1)2(1), unit cell dimensions a = 7.9003(2) Å α= 90°. b = 14.1271(3) Å β= 90°. c = 17.2611(5) Å γ = 90°. Volume 1926.48(8) Å$^3$. Z 4. Density

(calculated) 1.301 $Mg/m^3$, absorption coefficient 1.627 $mm^{-1}$, F(000) 800, crystal size 0.16 x 0.13 x 0.12 $mm^3$, theta range for data collection 4.04 to 70.45°. Index ranges -9<=h<=9, -17<=k<=15, -20<=l<=21, reflections collected 10238, independent reflections 3528 [R(int) = 0.0291], completeness to theta = 70.45° 97.3 %, absorption correction multiscan, refinement method full-matrix least-squares on $F^2$, data / restraints / parameters 3528 / 0 / 336, goodness-of-fit on $F^2$ 1.051, final R indices [I>2sigma(I)] R1 = 0.0285, wR2 = 0.0727, R indices (all data) R1 = 0.0296, wR2 = 0.0737, absolute structure parameter -0.010(13), largest diff. peak and hole 0.222 and -0.221 $e.Å^{-3}$

**(1*E*, 3*R*)-3-*p*-Chlorophenyl-3-methyl-1-phenyl-4-((2-pyridyl)sulfonyl)-1-butene (2b)**




State: colourless oil

$^1$H NMR (300 MHz): 8.66-8.56 (m, 1H), 7.66-7.50 (m, 2H), 7.40-7.19 (m, 6H), 7.19-7.00 (AA'BB' system, 4H), 6.39 (d, *J* = 16.3 Hz, 1H), 6.27 (d, *J* = 16.3 Hz, 1H), 4.21 (d, *J* = 14.9 Hz, 1H), 4.05 (d, *J* = 14.9 Hz, 1H), 1.84 (s, 3H).

$^{13}$C NMR (75 MHz): 157.7, 149.8, 142.2, 137.8, 136.4, 135.2, 132.7, 128.8, 128.5, 128.4, 128.1, 127.8, 126.5, 126.3, 121.8, 61.1, 42.8, 25.5.

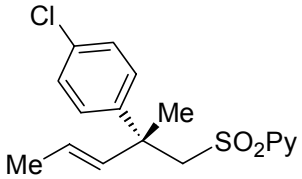
$[\alpha]_D$ = +17 (*c* 0.97, $CHCl_3$)

HPLC: 92% *ee* [Daicel Chiralpak AD column, hexane/isopropanol 80:20, 0.5 $mLmin^{-1}$, λ = 254 nm; $t_R$/min = 29.2 (*S*) and 40.2 (*R*)].

HRMS (FAB+, *m/z*): calcd. for $C_{22}H_{21}NO_2SCl$ $[M+H]^+$, 398.0981; found, 398.0975.

IR (NaCl): ν ($cm^{-1}$) 1493 (C=C), 1316 ($SO_2$).

**(2*E*, 4*R*)-4-*p*-Chlorophenyl-4-methyl-5-(2-pyridyl)sulfonyl)-2-pentene (3b)**




State: colourless oil

$^1$H NMR (300 MHz): 8.62 (ddd, *J*= 0.9, 1.7 and 4.7 Hz, 1H), 7.72 (dt, *J*= 1.7 and 7.9 Hz, 1H), 7.54 (dt, *J*= 1.1 and 7.9 Hz, 1H), 7.42 (ddd, *J*= 1.1, 4.7 and 7.9 Hz, 1H), 7.11-6.93 (AA'BB' system, 4H), 5.61-5.39 (m, 2H), 4.12 (d, *J* = 15.0 Hz, 1H), 3.82 (d, *J* = 15.0 Hz, 1H), 1.71 (s, 3H), 1.61 (d, *J* = 4.9 Hz, 3H).

$^{13}$C NMR (75 MHz): 157.9, 149.8, 142.2, 137.8, 137.1, 132.4, 128.6, 127.8, 126.6, 124.1, 121.8, 61.4, 42.4, 25.4, 18.0.

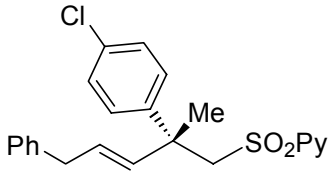
$[\alpha]_D$ = -6 (*c* 0.98, $CHCl_3$)

HPLC: 90% *ee* [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.5 mLmin$^{-1}$, λ = 254 nm; $t_R$/min = 24.0 (*S*) and 29.1 (*R*)].

HRMS (FAB+, *m/z*): calcd. for $C_{17}H_{19}NO_2SCl$ $[M+H]^+$, 336.0825; found, 336.0824.

IR (NaCl): ν (cm$^{-1}$) 1493 (C=C), 1316 ($SO_2$).

**(2*E*, 4*R*)- 4-*p*-Chlorophenyl-4-methyl-1-phenyl-5-((2-pyridyl)sulfonyl)-2-pentene (4b)**




State: colourless oil

$^1$H NMR (300 MHz): 8.66-8.55 (m, 1H), 7.76-7.64 (m, 1H), 7.60-7.50(m, 1H), 7.48-7.39 (m, 1H), 7.35-7.13 (m, 5H), 7.12-6.93 (AA'BB' system, 4H), 5.85-5.53 (m, 2H), 4.18 (d, *J* = 14.7 Hz, 1H), 3.84 (d, *J* = 14.7 Hz, 1H), 3.34 (d, *J*= 6.2 Hz, 2H), 1.75 (s, 3H).

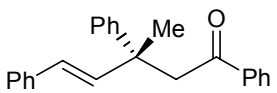
$^{13}$C NMR (75 MHz): 157.7, 149.7, 141.8, 139.8, 137.7, 137.4, 132.4, 128.5, 128.4, 128.3, 127.9, 127.8, 126.6, 126.1, 121.7, 61.3, 42.4, 38.9, 25.3.

$[\alpha]_D$ = -3 (*c* 1.31, $CHCl_3$)

HPLC: 88% *ee* [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.5 mLmin$^{-1}$, λ = 254 nm; $t_R$/min = 26.4 (*S*) and 29.4 (*R*)].

IR (NaCl): ν (cm$^{-1}$) 1494 (C=C), 1316 ($SO_2$).

**(1*E*,3*R*)-3-Methyl-1,3,5-triphenylpent-4-en-1-one (7)**




To a stirred solution of the starting chiral non racemic 2-pyridyl sulfone **2a** (160 mg, 0.43 mmol, 94% ee) dissolved in anhydrous DME (4.34 mL, 0.1 M) under argon and cooled at -78 ºC were added via syringe (1.74 mL, 0.87 mmol) of a solution of potassium hexametildisilazide (0.5 M in toluene). The resulting yellow mixture was allowed to stir at the same temperature for

30 min., and then benzoyl chloride (76 μL, 0.65 mmol) were slowly added via syringe. After 90 min. at -78ºC the reaction was quenched with saturated $NH_4Cl$ (ca. 10 mL) at the same temperature, the mixture was diluted with $CH_2Cl_2$ (5 mL) and the aqueous layer was extracted with $CH_2Cl_2$ (3x10 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, the solvent was removed *in vacuo*, and the resulting pale yellow oil was purified by column chromatography (AcOEt:hexanes 1:2.5) to give the intermediate α-sulfonyl ketone **5** as a 2:1 mixture of epimers (161 mg, 0.344 mmol, 79% yield).

Then, **5** was dissolved in THF (4.7 mL), and the solution was added to a suspension of activated Zn (powder, 700 mg) in THF (11 mL) and saturated $NH_4Cl$ (11 mL), and the reaction left to stir overnight. The mixture was then filtered through celite, washed with $CH_2Cl_2$ and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (AcOEt:hexanes 1:3) to give the desired ketone **7** as a colourless oil (140 mg, 0.430 mmol, 99% yield).

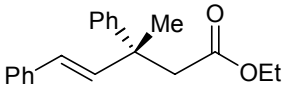
$^1$H NMR (300 MHz): 7.82-7.70 (m, 2H), 7.45-7.01 (m, 13H), 6.58 (d, $J$ = 16.2 Hz, 1H), 6.31 (d, $J$ = 16.2 Hz, 1H), 3.55 (d, $J$ = 15.5 Hz, 1H), 3.45 (d, $J$ = 15.5 Hz, 1H), 1.61 (s, 3H).

$^{13}$C NMR (75 MHz): 198.3, 147.0, 138.2, 138.1, 137.5, 132.8, 128.5, 128.4, 128.3, 128.1, 127.6, 127.2, 126.4, 126.3, 126.2, 48.9, 30.4, 26.7.

IR (NaCl): ν ($cm^{-1}$) 1692 (C=O), 1598 (C=C).

$[\alpha]_D$ = -13 (*c* 0.1, $CHCl_3$)

**Ethyl (1*E*,3R)-3-methyl-3,5-diphenylpent-4-enoate (8)**




To a stirred solution of the starting chiral non racemic 2-pyridyl sulfone **2a** (160 mg, 0.43 mmol, 94% ee) dissolved in anhydrous DME (4.34 mL, 0.1 M) under argon and cooled at -78 ºC were added via syringe (1.74 μL, 0.87 mmol) of a solution of potassium hexametildisilazide (0.5 M in toluene). The resulting yellow mixture was allowed to stir at the same temperature for 30 min., and then benzoyl chloride (76 μL, 0.652 mmol) were slowly added via syringe. After 90 min. at -78ºC the reaction was quenched with saturated $NH_4Cl$ (ca. 10 mL) at the same temperature, the mixture was diluted with $CH_2Cl_2$ (5 mL) and the aqueous layer was extracted with $CH_2Cl_2$ (3x10 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, the solvent was removed *in vacuo*, and the resulting pale yellow oil was purified by column chromatography (AcOEt:hexanes 1:2.5) to give the intermediate α-sulfonyl ester **6** as a 2:1 mixture of epimers (161 mg, 0.344 mmol, 82% yield).

Then, **6** was dissolved in THF (4.7 mL), and the solution was added to a suspension of activated Zn (powder, 700 mg) in THF (11 mL) and saturated $NH_4Cl$ (11 mL), and the reaction left to stir

overnight. The mixture was then filtered through celite, washed with $CH_2Cl_2$ and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (AcOEt:hexanes 1:3) to give the desired ester **8** as a colourless oil (140 mg, 0.430 mmol, 92% yield).

$^1$H NMR (300 MHz): 7.61-7.08 (m, 10H), 6.58 (d, *J* = 16.5 Hz, 1H), 6.40 (d, *J* = 16.5 Hz, 1H), 4.02 (q, *J*= 7.3 Hz, 2H), 2.88 (s, 2H), 1.67 (s, 3H), 1.09 (t, *J*= 7.3 Hz, 3H).

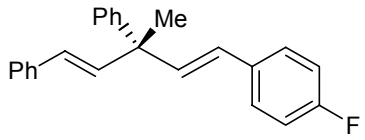
$^{13}$C NMR (75 MHz): 171.2, 146.4, 137.5, 128.5, 128.4, 128.2, 127.5, 127.3, 127.2, 126.4, 126.3, 60.1, 46.2, 43.1, 26.1, 14.1.

IR (NaCl): ν ($cm^{-1}$) 1729 (C=O), 1599 (C=C).

$[\alpha]_D$ = -4 (*c* 0.98, $CHCl_3$)

Julia-Kocienski olefination of **2a**:

**1-*p*-Fluorophenyl-3-methyl-3,5-diphenyl-1,4-pentadiene (9)**




To a stirred solution of the starting chiral non racemic 2-pyridyl sulfone **2a** (160 mg, 0.43 mmol, 94% ee) dissolved in anhydrous DME (13 mL, 0.033 M) under argon and cooled at -78 ºC were added via syringe (1.74 mL, 0.87 mmol) of a solution of potassium hexametildisilazide (0.5 M in toluene). The pale orange solution was stirred for 3 min., and then *p*-fluorobenzaldehyde (70 μL, 0.65 mmol) was added and the mixture was stirred at -78 ºC for 2 h. The pale yellow solution was quenched with saturated $NH_4Cl$ at the same temperature, the mixture was diluted with $CH_2Cl_2$ (5 mL) and the aqueous layer was extracted with $CH_2Cl_2$ (3x10 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, the solvent was removed *in vacuo*, and the resulting pale yellow oil was purified by column chromatography (hexanes) to give **9** as a colourless oil (127 mg, 0.386 mmol, 89% yield).

$^1$H NMR (300 MHz): 7.38-7.10 (m, 12H), 6.98-6.86 (m, 2H), 6.46 (d, *J*= 16.2 Hz, 1H), 6.38 (d, *J*= 16.2 Hz, 1H), 6.32 (d, *J*= 16.2 Hz, 1H), 6.28 (d, *J*= 16.2 Hz, 1H), 1.64 (s, 3H).

$^{13}$C NMR (75 MHz): 164.5, 146.4, 137.4, 137.1, 136.9, 133.5, 128.6, 128.3, 127.8, 127.7, 127.3, 127.1, 126.3, 115.6, 115.2, 47.4, 26.1.

IR (NaCl): ν ($cm^{-1}$) 1601 (C=C), 1266 (C=C).

$[\alpha]_D$ = +2 (*c* 0.5, $CHCl_3$)

## III. X-Ray crystallographic data for 4a

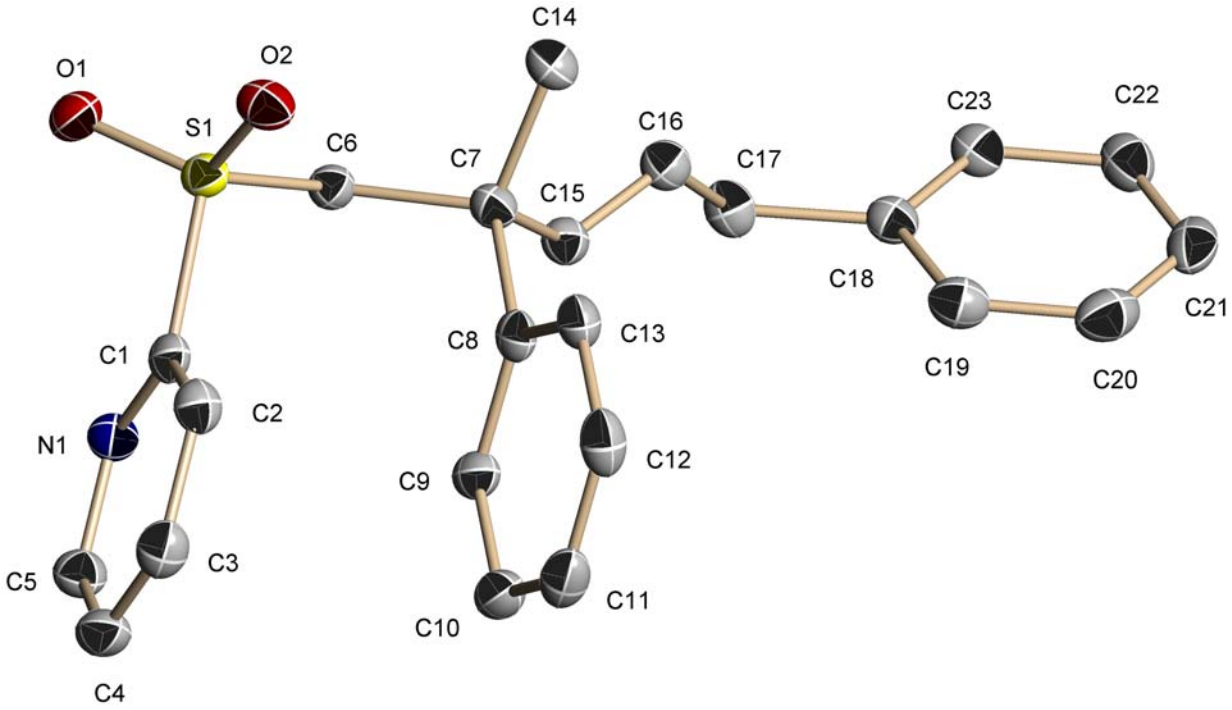



**Figure 1.** ORTEP drawing of compound **4a**

Table 1. Crystal data and structure refinement for A1_m.

| | | |
|---|---|---|
| Empirical formula | C23 H23 N O2 S | |
| Formula weight | 377.48 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 7.9003(2) Å | α= 90°. |
| | b = 14.1271(3) Å | β= 90°. |
| | c = 17.2611(5) Å | γ = 90°. |
| Volume | 1926.48(8) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.301 $Mg/m^3$ | |
| Absorption coefficient | 1.627 $mm^{-1}$ | |
| F(000) | 800 | |
| Crystal size | 0.16 x 0.13 x 0.12 $mm^3$ | |
| Theta range for data collection | 4.04 to 70.45°. | |
| Index ranges | -9<=h<=9, -17<=k<=15, -20<=l<=21 | |
| Reflections collected | 10238 | |
| Independent reflections | 3528 [R(int) = 0.0291] | |
| Completeness to theta = 70.45° | 97.3 % | |
| Absorption correction | multiscan | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3528 / 0 / 336 | |
| Goodness-of-fit on $F^2$ | 1.051 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0285, wR2 = 0.0727 | |
| R indices (all data) | R1 = 0.0296, wR2 = 0.0737 | |
| Absolute structure parameter | -0.010(13) | |
| Largest diff. peak and hole | 0.222 and -0.221 $e.Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for A1_m. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 1414(1) | 1985(1) | 3864(1) | 21(1) |
| N(1) | -1865(2) | 1712(1) | 3779(1) | 22(1) |
| O(1) | 1575(2) | 1166(1) | 4357(1) | 28(1) |
| O(2) | 2737(2) | 2169(1) | 3310(1) | 27(1) |
| C(1) | -522(2) | 1882(1) | 3335(1) | 20(1) |
| C(2) | -539(2) | 1959(1) | 2536(1) | 23(1) |
| C(3) | -2096(2) | 1839(1) | 2171(1) | 27(1) |
| C(4) | -3502(3) | 1657(1) | 2613(1) | 27(1) |
| C(5) | -3342(2) | 1599(1) | 3413(1) | 25(1) |
| C(6) | 1100(2) | 2968(1) | 4500(1) | 20(1) |
| C(7) | 1372(2) | 3985(1) | 4184(1) | 20(1) |
| C(8) | 316(2) | 4147(1) | 3448(1) | 20(1) |
| C(9) | -1454(2) | 4078(1) | 3477(1) | 22(1) |
| C(10) | -2437(2) | 4249(1) | 2824(1) | 27(1) |
| C(11) | -1672(3) | 4504(1) | 2133(1) | 30(1) |
| C(12) | 67(3) | 4564(1) | 2090(1) | 28(1) |
| C(13) | 1057(2) | 4387(1) | 2741(1) | 24(1) |
| C(14) | 3273(2) | 4152(1) | 4062(1) | 25(1) |
| C(15) | 680(2) | 4637(1) | 4814(1) | 21(1) |
| C(16) | 1527(2) | 5281(1) | 5212(1) | 23(1) |
| C(17) | 728(2) | 5891(1) | 5824(1) | 25(1) |
| C(18) | 985(2) | 6940(1) | 5683(1) | 23(1) |
| C(19) | 564(2) | 7333(1) | 4969(1) | 29(1) |
| C(20) | 778(2) | 8292(2) | 4833(1) | 34(1) |
| C(21) | 1414(2) | 8878(1) | 5407(1) | 31(1) |
| C(22) | 1840(2) | 8496(1) | 6119(1) | 30(1) |
| C(23) | 1622(2) | 7530(1) | 6255(1) | 24(1) |

Table 3. Bond lengths [Å] and angles [°] for A1_m.

| | |
|---|---|
| S(1)-O(2) | 1.4392(13) |
| S(1)-O(1) | 1.4426(12) |
| S(1)-C(1) | 1.7872(17) |
| S(1)-C(6) | 1.7883(16) |
| N(1)-C(1) | 1.330(2) |
| N(1)-C(5) | 1.337(2) |
| C(1)-C(2) | 1.383(2) |
| C(2)-C(3) | 1.393(2) |
| C(2)-H(2) | 0.905(18) |
| C(3)-C(4) | 1.372(3) |
| C(3)-H(3) | 0.96(2) |
| C(4)-C(5) | 1.389(2) |
| C(4)-H(4) | 0.95(2) |
| C(5)-H(5) | 0.97(2) |
| C(6)-C(7) | 1.552(2) |
| C(6)-H(6A) | 0.967(19) |
| C(6)-H(6B) | 0.99(2) |
| C(7)-C(15) | 1.528(2) |
| C(7)-C(14) | 1.535(2) |
| C(7)-C(8) | 1.537(2) |
| C(8)-C(13) | 1.395(2) |
| C(8)-C(9) | 1.403(2) |
| C(9)-C(10) | 1.390(2) |
| C(9)-H(9) | 0.99(2) |
| C(10)-C(11) | 1.385(3) |
| C(10)-H(10) | 0.97(2) |
| C(11)-C(12) | 1.378(3) |
| C(11)-H(11) | 0.97(3) |
| C(12)-C(13) | 1.392(3) |
| C(12)-H(12) | 0.93(2) |
| C(13)-H(13) | 0.93(2) |
| C(14)-H(14A) | 0.94(2) |
| C(14)-H(14B) | 0.963(19) |
| C(14)-H(14C) | 0.97(2) |
| C(15)-C(16) | 1.321(2) |
| C(15)-H(15) | 0.97(2) |

| | |
|---|---|
| C(16)-C(17) | 1.503(2) |
| C(16)-H(16) | 0.98(2) |
| C(17)-C(18) | 1.515(2) |
| C(17)-H(17A) | 0.98(2) |
| C(17)-H(17B) | 1.024(19) |
| C(18)-C(23) | 1.386(2) |
| C(18)-C(19) | 1.393(2) |
| C(19)-C(20) | 1.385(3) |
| C(19)-H(19) | 0.97(2) |
| C(20)-C(21) | 1.385(3) |
| C(20)-H(20) | 0.88(2) |
| C(21)-C(22) | 1.383(3) |
| C(21)-H(21) | 0.99(2) |
| C(22)-C(23) | 1.396(2) |
| C(22)-H(22) | 0.94(2) |
| C(23)-H(23) | 0.964(19) |

| | |
|---|---|
| O(2)-S(1)-O(1) | 118.26(8) |
| O(2)-S(1)-C(1) | 107.32(7) |
| O(1)-S(1)-C(1) | 108.12(7) |
| O(2)-S(1)-C(6) | 111.60(7) |
| O(1)-S(1)-C(6) | 105.79(7) |
| C(1)-S(1)-C(6) | 104.95(7) |
| C(1)-N(1)-C(5) | 116.47(14) |
| N(1)-C(1)-C(2) | 125.50(16) |
| N(1)-C(1)-S(1) | 113.80(11) |
| C(2)-C(1)-S(1) | 120.68(13) |
| C(1)-C(2)-C(3) | 116.76(16) |
| C(1)-C(2)-H(2) | 120.6(11) |
| C(3)-C(2)-H(2) | 122.6(11) |
| C(4)-C(3)-C(2) | 119.04(16) |
| C(4)-C(3)-H(3) | 121.9(14) |
| C(2)-C(3)-H(3) | 119.0(14) |
| C(3)-C(4)-C(5) | 119.42(18) |
| C(3)-C(4)-H(4) | 121.3(14) |
| C(5)-C(4)-H(4) | 119.3(14) |
| N(1)-C(5)-C(4) | 122.81(17) |
| N(1)-C(5)-H(5) | 116.4(12) |

| | |
|---|---|
| C(4)-C(5)-H(5) | 120.8(12) |
| C(7)-C(6)-S(1) | 118.89(11) |
| C(7)-C(6)-H(6A) | 111.6(10) |
| S(1)-C(6)-H(6A) | 105.0(10) |
| C(7)-C(6)-H(6B) | 110.1(11) |
| S(1)-C(6)-H(6B) | 105.3(11) |
| H(6A)-C(6)-H(6B) | 104.9(15) |
| C(15)-C(7)-C(14) | 110.78(14) |
| C(15)-C(7)-C(8) | 107.76(13) |
| C(14)-C(7)-C(8) | 113.26(13) |
| C(15)-C(7)-C(6) | 104.94(12) |
| C(14)-C(7)-C(6) | 109.08(14) |
| C(8)-C(7)-C(6) | 110.70(13) |
| C(13)-C(8)-C(9) | 117.83(16) |
| C(13)-C(8)-C(7) | 122.10(15) |
| C(9)-C(8)-C(7) | 120.05(15) |
| C(10)-C(9)-C(8) | 121.01(17) |
| C(10)-C(9)-H(9) | 120.8(11) |
| C(8)-C(9)-H(9) | 118.2(11) |
| C(11)-C(10)-C(9) | 120.02(18) |
| C(11)-C(10)-H(10) | 120.8(12) |
| C(9)-C(10)-H(10) | 119.2(12) |
| C(12)-C(11)-C(10) | 119.86(17) |
| C(12)-C(11)-H(11) | 121.7(15) |
| C(10)-C(11)-H(11) | 118.4(15) |
| C(11)-C(12)-C(13) | 120.32(18) |
| C(11)-C(12)-H(12) | 121.3(15) |
| C(13)-C(12)-H(12) | 118.4(15) |
| C(12)-C(13)-C(8) | 120.94(17) |
| C(12)-C(13)-H(13) | 121.7(13) |
| C(8)-C(13)-H(13) | 117.4(13) |
| C(7)-C(14)-H(14A) | 107.9(14) |
| C(7)-C(14)-H(14B) | 111.1(11) |
| H(14A)-C(14)-H(14B) | 108.4(18) |
| C(7)-C(14)-H(14C) | 110.0(13) |
| H(14A)-C(14)-H(14C) | 109.1(17) |
| H(14B)-C(14)-H(14C) | 110.2(15) |
| C(16)-C(15)-C(7) | 127.17(17) |

| | |
|---|---|
| C(16)-C(15)-H(15) | 117.8(12) |
| C(7)-C(15)-H(15) | 115.0(12) |
| C(15)-C(16)-C(17) | 123.18(17) |
| C(15)-C(16)-H(16) | 120.9(12) |
| C(17)-C(16)-H(16) | 115.9(12) |
| C(16)-C(17)-C(18) | 113.10(14) |
| C(16)-C(17)-H(17A) | 108.0(12) |
| C(18)-C(17)-H(17A) | 108.7(12) |
| C(16)-C(17)-H(17B) | 107.6(11) |
| C(18)-C(17)-H(17B) | 109.3(11) |
| H(17A)-C(17)-H(17B) | 110.2(16) |
| C(23)-C(18)-C(19) | 118.50(16) |
| C(23)-C(18)-C(17) | 121.49(14) |
| C(19)-C(18)-C(17) | 120.01(15) |
| C(20)-C(19)-C(18) | 120.70(18) |
| C(20)-C(19)-H(19) | 122.3(12) |
| C(18)-C(19)-H(19) | 117.0(12) |
| C(19)-C(20)-C(21) | 120.55(18) |
| C(19)-C(20)-H(20) | 122.8(16) |
| C(21)-C(20)-H(20) | 116.6(16) |
| C(22)-C(21)-C(20) | 119.30(17) |
| C(22)-C(21)-H(21) | 116.8(12) |
| C(20)-C(21)-H(21) | 123.9(12) |
| C(21)-C(22)-C(23) | 120.08(18) |
| C(21)-C(22)-H(22) | 121.5(13) |
| C(23)-C(22)-H(22) | 118.4(13) |
| C(18)-C(23)-C(22) | 120.87(17) |
| C(18)-C(23)-H(23) | 117.7(11) |
| C(22)-C(23)-H(23) | 121.3(11) |

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for A1_m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 19(1) | 20(1) | 22(1) | -2(1) | -1(1) | 2(1) |
| N(1) | 21(1) | 24(1) | 21(1) | -1(1) | 1(1) | 0(1) |
| O(1) | 28(1) | 23(1) | 31(1) | -1(1) | -7(1) | 5(1) |
| O(2) | 21(1) | 30(1) | 30(1) | -7(1) | 2(1) | 1(1) |
| C(1) | 23(1) | 15(1) | 22(1) | -3(1) | 0(1) | 1(1) |
| C(2) | 25(1) | 22(1) | 22(1) | 0(1) | 3(1) | -2(1) |
| C(3) | 35(1) | 25(1) | 21(1) | -1(1) | -3(1) | 1(1) |
| C(4) | 24(1) | 27(1) | 28(1) | -3(1) | -6(1) | 1(1) |
| C(5) | 21(1) | 28(1) | 26(1) | 1(1) | 0(1) | 0(1) |
| C(6) | 20(1) | 21(1) | 19(1) | -1(1) | -2(1) | 0(1) |
| C(7) | 19(1) | 21(1) | 21(1) | -2(1) | -1(1) | -1(1) |
| C(8) | 25(1) | 14(1) | 21(1) | -4(1) | 0(1) | -1(1) |
| C(9) | 23(1) | 20(1) | 24(1) | -4(1) | -2(1) | 2(1) |
| C(10) | 28(1) | 22(1) | 31(1) | -3(1) | -7(1) | 2(1) |
| C(11) | 42(1) | 22(1) | 25(1) | -1(1) | -12(1) | 0(1) |
| C(12) | 44(1) | 22(1) | 20(1) | 0(1) | 0(1) | -7(1) |
| C(13) | 28(1) | 19(1) | 24(1) | -1(1) | 0(1) | -3(1) |
| C(14) | 23(1) | 27(1) | 24(1) | -1(1) | 0(1) | -4(1) |
| C(15) | 21(1) | 22(1) | 21(1) | 2(1) | 1(1) | -1(1) |
| C(16) | 24(1) | 24(1) | 22(1) | -1(1) | 0(1) | -1(1) |
| C(17) | 30(1) | 26(1) | 20(1) | -3(1) | 1(1) | -4(1) |
| C(18) | 20(1) | 26(1) | 22(1) | -2(1) | 3(1) | 0(1) |
| C(19) | 26(1) | 35(1) | 24(1) | -1(1) | -3(1) | -1(1) |
| C(20) | 28(1) | 41(1) | 33(1) | 11(1) | 0(1) | 4(1) |
| C(21) | 24(1) | 24(1) | 47(1) | 3(1) | 10(1) | 4(1) |
| C(22) | 28(1) | 26(1) | 35(1) | -7(1) | 4(1) | -1(1) |
| C(23) | 25(1) | 26(1) | 22(1) | -4(1) | 2(1) | -1(1) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for A1_m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 430(20) | 2078(12) | 2272(10) | 12(4) |
| H(3) | -2160(30) | 1907(16) | 1615(13) | 37(6) |
| H(4) | -4580(30) | 1581(15) | 2385(13) | 36(6) |
| H(5) | -4320(30) | 1461(15) | 3737(12) | 31(5) |
| H(6A) | -30(20) | 2885(12) | 4704(10) | 15(4) |
| H(6B) | 1860(30) | 2851(13) | 4944(12) | 27(5) |
| H(9) | -1990(20) | 3909(13) | 3979(11) | 21(5) |
| H(10) | -3660(30) | 4186(14) | 2860(11) | 25(5) |
| H(11) | -2390(30) | 4635(17) | 1689(15) | 46(7) |
| H(12) | 610(30) | 4731(16) | 1629(13) | 38(6) |
| H(13) | 2240(30) | 4424(14) | 2723(12) | 25(5) |
| H(14A) | 3820(30) | 4047(16) | 4535(13) | 38(6) |
| H(14B) | 3490(20) | 4794(13) | 3902(10) | 16(4) |
| H(14C) | 3710(30) | 3711(14) | 3678(11) | 25(5) |
| H(15) | -510(30) | 4560(14) | 4927(11) | 26(5) |
| H(16) | 2730(30) | 5396(13) | 5111(12) | 25(5) |
| H(17A) | -490(30) | 5759(14) | 5829(11) | 28(5) |
| H(17B) | 1260(30) | 5710(14) | 6345(11) | 24(5) |
| H(19) | 120(30) | 6906(15) | 4579(12) | 32(5) |
| H(20) | 560(30) | 8557(17) | 4381(14) | 41(6) |
| H(21) | 1590(30) | 9564(16) | 5342(12) | 34(5) |
| H(22) | 2280(30) | 8874(15) | 6521(12) | 30(5) |
| H(23) | 1850(20) | 7257(13) | 6756(11) | 20(5) |

Table 6. Torsion angles [°] for A1_m.

| | |
|---|---|
| C(5)-N(1)-C(1)-C(2) | 0.7(2) |
| C(5)-N(1)-C(1)-S(1) | -178.02(12) |
| O(2)-S(1)-C(1)-N(1) | -179.83(11) |
| O(1)-S(1)-C(1)-N(1) | 51.58(13) |
| C(6)-S(1)-C(1)-N(1) | -60.98(13) |
| O(2)-S(1)-C(1)-C(2) | 1.38(16) |
| O(1)-S(1)-C(1)-C(2) | -127.21(14) |
| C(6)-S(1)-C(1)-C(2) | 120.23(14) |
| N(1)-C(1)-C(2)-C(3) | -0.7(3) |
| S(1)-C(1)-C(2)-C(3) | 177.99(12) |
| C(1)-C(2)-C(3)-C(4) | 0.2(3) |
| C(2)-C(3)-C(4)-C(5) | 0.1(3) |
| C(1)-N(1)-C(5)-C(4) | -0.3(2) |
| C(3)-C(4)-C(5)-N(1) | -0.1(3) |
| O(2)-S(1)-C(6)-C(7) | 33.39(15) |
| O(1)-S(1)-C(6)-C(7) | 163.27(12) |
| C(1)-S(1)-C(6)-C(7) | -82.52(14) |
| S(1)-C(6)-C(7)-C(15) | 169.44(11) |
| S(1)-C(6)-C(7)-C(14) | -71.81(16) |
| S(1)-C(6)-C(7)-C(8) | 53.45(18) |
| C(15)-C(7)-C(8)-C(13) | 125.18(16) |
| C(14)-C(7)-C(8)-C(13) | 2.3(2) |
| C(6)-C(7)-C(8)-C(13) | -120.59(16) |
| C(15)-C(7)-C(8)-C(9) | -53.22(19) |
| C(14)-C(7)-C(8)-C(9) | -176.12(15) |
| C(6)-C(7)-C(8)-C(9) | 61.02(19) |
| C(13)-C(8)-C(9)-C(10) | -0.4(2) |
| C(7)-C(8)-C(9)-C(10) | 178.02(15) |
| C(8)-C(9)-C(10)-C(11) | -0.8(3) |
| C(9)-C(10)-C(11)-C(12) | 1.6(3) |
| C(10)-C(11)-C(12)-C(13) | -1.2(3) |
| C(11)-C(12)-C(13)-C(8) | -0.1(3) |
| C(9)-C(8)-C(13)-C(12) | 0.9(2) |
| C(7)-C(8)-C(13)-C(12) | -177.55(15) |
| C(14)-C(7)-C(15)-C(16) | 1.0(2) |
| C(8)-C(7)-C(15)-C(16) | -123.44(18) |

| | |
|---|---|
| C(6)-C(7)-C(15)-C(16) | 118.55(18) |
| C(7)-C(15)-C(16)-C(17) | 179.96(15) |
| C(15)-C(16)-C(17)-C(18) | -125.06(18) |
| C(16)-C(17)-C(18)-C(23) | -128.44(18) |
| C(16)-C(17)-C(18)-C(19) | 52.1(2) |
| C(23)-C(18)-C(19)-C(20) | 0.0(3) |
| C(17)-C(18)-C(19)-C(20) | 179.46(17) |
| C(18)-C(19)-C(20)-C(21) | 0.0(3) |
| C(19)-C(20)-C(21)-C(22) | 0.1(3) |
| C(20)-C(21)-C(22)-C(23) | -0.2(3) |
| C(19)-C(18)-C(23)-C(22) | -0.1(3) |
| C(17)-C(18)-C(23)-C(22) | -179.52(16) |
| C(21)-C(22)-C(23)-C(18) | 0.2(3) |

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for A1_m [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|