Asymmetric Synthesis of β -Hydroxy sulfides controlled by remote sulfoxides.

*Yolanda Arroyo,^a J. Félix Rodríguez,^a Mercedes Santos,^{*a} M. Ascensión Sanz Tejedor^a
and José Luis García Ruano**

^aDepartamento de Química Orgánica (ETSII), Universidad de Valladolid, P^o del Cauce
s/n, 47011 Valladolid, Spain

^bDepartamento de Química Orgánica (C-I), Universidad Autónoma, Cantoblanco,
28049 Madrid, Spain

joseluis.garcia.ruano@uam.es; msantos@eis.uva.es

SUPPORTING INFORMATION

Table of contents for Supporting Information:

S3	General Experimental Methods
S3	Experimental Section
S6	X-ray structure and refinement details for compound 6'd .
S12-52	¹ H and ¹³ C-NMR spectra of compounds 4 , 6a-k , 6'c-j , 7 and 8g

Experimental Section

General method

All reactions were performed under an argon atmosphere. Dry solvents and liquid reagents were distilled just prior to use: THF and diethyl ether were distilled from sodium-benzophenone under argon. The commercially available reagents were used as received without further purification. The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230-400 mesh). ^1H -NMR (300 MHz) and ^{13}C -NMR (75.5 MHz) spectra were performed in CDCl_3 using Me_4Si as the internal standard. Mass spectra were recorded by the direct insertion technique by electronic impact (EI) at 70 eV or FAB.

General method. Synthesis of β -hydroxy sulfides. A solution of *n*-BuLi 1.6 M in hexane (0.60 mmol, 1.2 equiv) was added over $^i\text{Pr}_2\text{NH}$ (0.89 mmol, 1.8 equiv) in THF (3 mL) at -40°C . After 15 min of stirring at room temperature, the mixture was cooled at -78°C , and then a solution of (*S*)- α -Methylthio-2-(*p*-tolylsulfinyl)toluene (*S*)-**2** (0.50 mmol, 1.0 equiv) in THF (2 mL) was added. After 1 min of stirring, the electrophile **4** or **5** (1.0 mmol, 2.0 equiv) dissolved in THF (4 mL) was added at -78°C . When the reaction was completed (1 min), the mixture was quenched at that temperature with methanol (2 mL). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

[2*S*,(*S*)]-Isobutyl 2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-acetate **4:** Eluent for chromatography hexane/Et₂O 2/1; yield 56%; colorless syrup; $[\alpha_D^{20}] = -116.2$ (c 0.5, CHCl_3); ^1H -NMR: 7.92-7.89 (m, 1H), 7.74-7.71 (m, 1H), 7.52-7.48 (m, 4H), 7.24 (AA'BB' system, 2H), 5.15 (s, 1H), 3.77 (dd, 2H, $J = 6.6$ and 1.8), 2.37 (s, 3H), 2.16 (s, 3H), 1.87-1.73 (m, 1H), 0.82 and 0.80 (two d, 6H, $J = 6.8$); ^{13}C -NMR: δ 169.9, 143.6, 141.6, 134.8, 131.5, 130.0, 129.6, 129.3, 126.2, 125.7, 71.9, 47.9, 27.6, 21.4, 18.9, 15.4; HRMS calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_3\text{S}_2$ 376.1167, found 376.1149.

[2*S*,(*S*)]-1,1-Dimethyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol **6a:** Eluent for chromatography hexane/Et₂O 2/1; yield 89%; colorless syrup; $[\alpha_D^{20}] = -11.5$ (c 1.0, CHCl_3); ^1H -NMR: 7.92 (d, 1H, $J = 7.7$), 7.73 (dd, 1H, $J = 7.7$ and 1.2), 7.56 (dt, 1H, $J = 7.7$ and 1.2), 7.43-7.35 (m, 1H), 7.37 and 7.25 (AA'BB' system, 4H), 4.46 (bs, 1H), 4.43 (s, 1H), 2.36 (s, 3H), 1.43 (s, 3H), 1.16 and 1.08 (two s, 6H); ^{13}C -NMR: δ 142.9, 141.6, 141.0, 140.3, 132.3, 131.8, 129.8, 128.9, 127.3, 124.9, 72.5, 55.7, 30.7, 23.8, 21.1, 14.0; HRMS calcd. for $\text{C}_{18}\text{H}_{20}\text{OS}_2$ ($\text{M}^+ - \text{H}_2\text{O}$) 316.0956, found 316.0946.

[2*S*,(*S*)]-1,1-Diphenyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol, **6b:** Eluent for chromatography hexane/Et₂O 2/1; yield 40%; colorless syrup; $[\alpha_D^{20}] = +63.6$ (c 1.4, CHCl_3); ^1H -NMR: δ 7.72-7.69 (m, 1H), 7.45-7.43 (m, 1H), 7.39-7.25 (m, 13H), 7.21-7.16 (m, 3H) 5.48 (s, 1H), 5.15 (s, 1H), 2.43 (s, 3H), 1.20 (s, 3H); ^{13}C -NMR: δ 146.0, 143.9, 142.9, 141.5, 140.1, 139.8, 132.7, 131.5, 129.9, 127.9, 127.6, 127.2, 127.1, 126.7, 125.6, 79.5, 53.5, 21.3, 14.7; HRMS calcd. for $\text{C}_{26}\text{H}_{24}\text{OS}_2$ ($\text{M}^+ - \text{H}_2\text{O}$) 440.1269, found 440.1268.

2-methylthio-1-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol: Eluent for chromatography hexane/Et₂O 1/1.5; first eluted **6'c**.

[1S,2S,(S)S]-2-methylthio-1-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6'c:

colorless syrup; [α_D^{20}] = -50.5 (c 0.9, CHCl₃); ¹H-NMR: δ 7.57 (dd, 1H, *J* = 2.0 and 9.4), 7.41-7.32 (m, 3H), 7.23-7.12 (m, 7H), 7.08 (AA'BB' system, 2H, *J* = 8.3), 5.13 (dd, 1H, *J* = 2.1 and 6.9), 4.81 (d, 1H, *J* = 6.9), 4.23 (d, 1H, *J* = 2.1), 2.37 (s, 3H), 1.62 (s, 3H); ¹³C-NMR: δ 143.4, 141.0, 140.4, 140.0, 139.5, 131.6, 130.9, 129.8, 128.2, 128.0, 127.8, 127.3, 125.2, 75.2, 53.5, 21.3, 14.2; HRMS calcd. for C₂₂H₂₀OS₂ (M⁺ - H₂O) 364.0956, found 364.0965.

[1R,2S,(S)S]-2-methylthio-1-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6c:

colorless syrup; [α_D^{20}] = +31.0 (c 1.8, CHCl₃); ¹H-NMR: δ 7.94 (d, 1H, *J* = 7.2), 7.76 (dd, 1H, *J* = 7.7 and 1.2), 7.63 (dt, 1H, *J* = 7.6 and 1.1), 7.29-7.56 (m, 8H), 7.25 (part of AA'BB' system, 2H, *J* = 8.3), 4.73 (d, 1H, *J* = 8.5), 4.69 (d, 1H, *J* = 9.5), 4.56 (dd, 1H, *J* = 8.5 and 9.5), 2.35 (s, 3H), 0.99 (s, 3H); ¹³C-NMR: δ 142.8, 142.6, 142.2, 140.9, 140.6, 133.1, 130.2, 129.9, 129.0, 128.2, 127.9, 127.7, 126.9, 124.7, 78.7, 51.9, 21.2, 14.2; HRMS calcd. for C₂₂H₂₀OS₂ (M⁺ - H₂O) 364.0956, found 364.0955.

2-methylthio-1-(*p*-methoxy)phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol: Eluent for chromatography hexane/Et₂O/CH₂Cl₂ 2/1.5/1.5; first eluted compound **6d**.

[1R,2S,(S)S]-2-methylthio-1-(*p*-methoxy)phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6d:

colorless syrup; [α_D^{20}] = +19.9 (c 1.0, CHCl₃); ¹H-NMR: δ 7.93 (dd, 1H, *J* = 7.8 and 0.5), 7.76 (dd, 1H, *J* = 7.7 and 1.2), 7.66-7.60 (m, 1H), 7.47-7.39 (m, 5H), 7.25 (AA'BB' system, 2H, *J* = 8.3), 6.91 (dd, 2H, *J* = 6.8 and 1.9), 4.68 (d, 1H, *J* = 9.1), 4.53 (dd, 1H, *J* = 9.0 and 9.1), 4.51 (d, 1H, *J* = 9.0), 3.82 (s, 3H), 2.35 (s, 3H) and 1.02 (s, 3H); ¹³C-NMR: δ 159.3, 142.7, 142.3, 141.0, 140.7, 133.1, 135.0, 130.2, 129.9, 128.9, 128.0, 127.7, 124.7, 113.6, 78.2, 52.1, 21.2, 14.2; HRMS calcd. for C₂₃H₂₂O₂S₂ (M⁺ - H₂O) 394.1061, found 394.1057.

[1S,2S,(S)S]-2-methylthio-1-(*p*-methoxy)phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6'd:

white solid; [α_D^{20}] = -30.2 (c 0.5, CHCl₃); ¹H-NMR: 7.59 (dd, 1H, *J* = 1.5 and 7.7), 7.45-7.32 (m, 3H), 7.19, 7.09, 7.04 and 6.70 (two AA'BB' systems, 8H), 5.09 (dd, 1H, *J* = 1.9 and 7.0), 4.78 (d, 1H, *J* = 7.0), 4.14 (d, 1H, *J* = 1.9), 3.77 (s, 3H), 2.38 (s, 3H), 1.64 (s, 3H); ¹³C-NMR: δ 159.1, 143.4, 141.0, 131.6, 132.0, 130.9, 129.7, 128.4, 128.1, 128.0, 125.3, 113.1, 74.8, 53.8, 21.3, 14.2; HRMS calcd. for C₂₃H₂₂O₂S₂ (M⁺ - H₂O) 394.1061, found 394.1070. Crystal data and structure refinement for **6'd** are at the end of the file.

2-methylthio-1-(2-naphthyl)-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol. Eluent for chromatography hexane/Et₂O/CH₂Cl₂ 2/1.25/1.25; first eluted compound **6e**.

[1R,2S,(S)S]-2-methylthio-1-(2-naphthyl)-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6e:

white syrup; [α_D^{20}] = +62.0 (c 1.0, CHCl₃); ¹H-NMR: 8.01 (d, 1H, *J* = 7.4), 7.90-7.83 (m, 4H), 7.77-7.63 (m, 3H), 7.52-7.43 (m, 3H), 7.41 and 7.20 (AA'BB' system, 4H), 4.87 (d, 1H, *J* = 7.9), 4.81 (d, 1H, *J* = 9.3), 4.76 (dd, 1H, *J* = 9.3 and 7.9), 2.32 (s, 3H), 0.98 (s, 3H); ¹³C-NMR: δ 142.6, 142.2, 141.0, 140.5, 140.1, 133.0, 133.2, 130.4, 129.9, 129.1, 128.2, 128.1, 127.8, 127.7, 126.3, 126.0, 125.8, 124.6, 124.4, 78.8, 51.7, 21.1, 14.2; HRMS calcd. for C₂₆H₂₂OS₂ (M⁺ - H₂O) 414.1112, found 414.1105.

[1S,2S,(S)S]-2-methylthio-1-(2-naphthyl)-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6'e:

yellow syrup; [α_D^{20}] = -19.2 (c 0.5, CHCl₃); ¹H-NMR: 7.78 (dd, 1H, *J* = 2.1 and 8.9), 7.71-7.62 (m, 3H), 7.54 (d, 1H, *J* = 7.6), 7.49-7.33 (m, 5H), 7.26-7.24 (m, 1H), 6.97-6.90 (m, 4H), 5.29 (d, 1H, *J* = 6.5), 4.91 (d, 1H, *J* = 6.5), 4.36 (bs, 1H), 2.29 (s, 3H), 1.26 (s, 3H); ¹³C-NMR: δ 143.3, 141.0, 140.2, 139.5, 137.5, 133.1, 132.8, 131.6, 130.9,

129.6, 128.3, 128.1, 128.0, 127.5, 127.4, 126.4, 125.9, 125.1, 125.0, 75.4, 53.6, 21.2, 14.3; HRMS calcd. for $C_{26}H_{22}OS_2$ ($M^+ - H_2O$) 414.1112, found 414.1108.

2-methylthio-1-(*p*-ciano)phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol. Eluent for chromatography hexane/Et₂O/CH₂Cl₂ 2/1/1; first eluted compound **6f**.

[1*S*,2*S*,(*S*)*S*]-2-methylthio-1-(*p*-ciano)phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol **6f:** colorless syrup; [α_D^{20}] = -101 (c 0.5, CHCl₃); ¹H-NMR: 7.69-7.63 (m, 1H), 7.52-7.40 (m, 3H), 7.55, 7.45, 7.36 and 7.26 (two AA'BB' systems, 8H), 5.05 (dd, 1H, *J* = 2.6 and 6.3), 4.56 (d, 1H, *J* = 6.3), 3.61 (d, 1H, *J* = 2.6), 2.39 (s, 3H), 1.60 (s, 3H); ¹³C-NMR: δ 146.6, 142.4, 141.7, 141.2, 138.7, 131.9, 131.1, 130.0, 129.5, 128.1, 127.7, 127.0, 124.9, 63.7, 56.0, 21.1, 13.9. HRMS calcd. for $C_{23}H_{19}OS_2$ ($M^+ - H_2O$) 389.0908, found 389.0902.

[1*R*,2*S*,(*S*)*S*]-2-methylthio-1-(*p*-ciano)phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol **6f:** colorless syrup; [α_D^{20}] = -72.8 (c 0.7, CHCl₃); ¹H-NMR: 7.73-7.71 (m, 1H), 7.48-7.36 (m, 3H), 7.63, 7.52 and 7.32 (two systems AA'BB' system, 8H), 4.90 (dd, 1H, *J* = 4.8 and 7.7), 4.69 (d, 1H, *J* = 7.7), 4.05 (d, 1H, *J* = 4.8), 2.41 (s, 3H) and 1.60 (s, 3H); ¹³C-NMR: δ 146.7, 143.9, 142.5, 139.2, 138.2, 111.8, 132.0, 131.8, 130.2, 129.0, 128.7, 127.7, 126.4, 125.4, 76.3, 53.1, 21.5, 15.0. HRMS calcd. for $C_{23}H_{19}OS_2$ ($M^+ - H_2O$) 389.0908, found 389.0901.

1-(2,6-dimethyl)phenyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol. Eluent for chromatography hexane/Et₂O/CH₂Cl₂ 2/1/1; first eluted compound **6g**.

[1*R*,2*S*,(*S*)*S*]-1-(2,6-dimethyl)phenyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol **6g:** colorless syrup; [α_D^{20}] = -75.9 (c 1.0, CHCl₃); ¹H-NMR: 7.96 (d, 1H, *J* = 7.1), 7.62-7.70 (m, 1H), 7.45-7.37 (m, 1H), 7.51 and 7.26 (AA'BB' system, 4H), 5.41 (da, 1H, *J* = 9.3), 5.26 (da, 1H, *J* = 9.3), 4.06 (bs, 1H), 2.62 (bs, 6H), 2.37 (s, 3H), 1.15 (s, 3H); ¹³C-NMR: δ 143.8, 142.9, 140.9, 137.1, 137.0, 133.2, 129.8, 129.5, 128.6, 128.0, 127.7, 124.6, 75.8, 48.4, 21.2, 20.9, 14.3; HRMS calcd. for $C_{24}H_{24}OS_2$ ($M^+ - H_2O$) 392.1268, found 392.1267.

[1*S*,2*S*,(*S*)*S*]-1-(2,6-dimethyl)phenyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol **6g:** colorless syrup; [α_D^{20}] = -144.0 (c 0.7, CHCl₃); ¹H-NMR: 7.94 (d, 1H, *J* = 7.7), 7.76 (d, 1H, *J* = 7.5), 7.62-7.50 (m, 1H), 7.15-7.11 (m, 1H), 7.26 and 7.06 (AA'BB' system, 4H), 5.48 (dd, 1H, *J* = 3.3 and 9.6), 4.90 (d, 1H, *J* = 9.6), 2.64 (s, 6H), 2.37 (s, 3H), 2.30 (d, 1H, *J* = 3.3), 1.14 (s, 3H); ¹³C-NMR: δ 152.0, 144.4, 142.2, 141.2, 139.2, 137.2, 136.3, 131.8, 130.1, 128.7, 128.1, 127.8, 126.6, 75.5, 49.8, 21.2, 20.9, 14.7; HRMS calcd. for $C_{24}H_{24}OS_2$ ($M^+ - H_2O$) 392.1268, found 392.1256.

1-Butyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol. Eluent for chromatography hexane/Et₂O/CH₂Cl₂ 2/1/1; first eluted compound **6i**.

[1*R*,2*S*,(*S*)*S*]-1-Butyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol **6i:** colorless syrup; [α_D^{20}] = +4.5 (c 1.0, CHCl₃); ¹H-NMR: 7.86 (d, 1H, *J* = 7.2), 7.78 (dd, 1H, *J* = 7.7 and 1.0), 7.56 (t, 1H, *J* = 7.7), 7.49-7.35 (m, 1H), 7.45 and 7.27 (AA'BB' system, 4H), 4.39 (d, 1H, *J* = 8.6), 3.62-3.54 (m, 1H), 3.22 (d, 1H, *J* = 8.4), 2.38 (s, 3H), 1.74-1.70 (m, 2H), 1.48-1.41 (m, 2H), 1.35 (s, 3H), 1.34-1.26 (m, 2H), 0.90 (t, 3H, *J* = 7.0); ¹³C-NMR: δ 143.2, 141.8, 141.2, 140.9, 132.7, 130.1, 129.9, 128.0, 127.6, 125.1, 74.5, 50.9, 35.1, 27.3, 22.6, 21.3, 14.1, 13.9; HRMS calcd. for $C_{20}H_{24}OS_2$ ($M^+ - H_2O$) 344.1269, found 344.1272.

[1S,2S,(S)S]-1-Butyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6'i:
 colorless syrup; [α_D^{20}] = -48.4 (c 0.6, CHCl₃); ¹H-NMR: 7.98-7.95 (m, 1H), 7.58-7.46 (m, 3H), 7.48 and 7.25 (AA'BB' system, 4H), 4.22 (d, 1H, *J* = 6.9), 3.73 (m, 1H), 3.17 (d, 1H, *J* = 2.7), 2.37 (s, 3H), 1.76 (s, 3H), 1.38-1.31 (m, 2H), 1.17-1.07 (m, 2H), 0.92-0.83 (m, 2H), 0.78 (t, 3H, *J* = 7.0); ¹³C-NMR: δ 142.8, 141.9, 141.1, 139.4, 131.6, 130.1, 129.6, 128.1, 126.3, 72.8, 52.5, 33.4, 28.3, 22.5, 21.4, 14.1, 13.9; HRMS calcd. for C₂₀H₂₄OS₂ (M⁺ -H₂O) 344.1269, found 344.1261.

1-Isopropyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol. Eluent for chromatography hexane/Et₂O 1/1; first eluted compound **6j**.

[1R,2S,(S)S]-1-Isopropyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6j:
 colorless syrup; [α_D^{20}] = -6.0 (c 0.5, CHCl₃); ¹H-NMR: 7.92 (d, 1H, *J* = 7.8), 7.76 (dd, 1H, *J* = 7.8 and 1.2), 7.60 (dt, 1H, *J* = 8.7 and 1.2), 7.43-7.38 (m, 1H), 7.43 and 7.28 (AA'BB' system, 4H), 4.49 (d, 1H, *J* = 10.1), 3.62 (d, 1H, *J* = 9.4), 3.46 (dd, 1H, *J* = 9.4 and 10.1), 2.38 (s, 3H), 2.20-2.15 (m, 1H), 1.08 (s, 3H), 1.00 and 0.99 (two d, 6H, *J* = 6.9); ¹³C-NMR: δ 143.3, 143.0, 141.0, 140.8, 133.1, 130.4, 129.9, 128.9, 127.4, 124.7, 79.2, 48.0, 30.50, 21.3, 20.3, 13.2, 13.9; HRMS calcd. for C₁₉H₂₂OS₂ (M⁺ -H₂O) 330.1112, found 330.1117.

[1S,2S,(S)S]-1-Isopropyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6'j:
 colorless syrup; [α_D^{20}] = -47.4 (c 0.5, CHCl₃); ¹H-NMR: 7.82 (dd, 1H, *J* = 7.6 and 1.5), 7.61 (dd, 1H, *J* = 7.6 and 1.3), 7.52-7.42 (m, 2H), 7.46 and 7.27 (AA'BB' system, 4H), 4.38 (d, 1H, *J* = 6.5), 3.61 (dd, 1H, *J* = 4.4 and 6.5), 2.45 (d, 1H, *J* = 4.4), 2.39 (s, 3H), 1.86 (s, 3H), 1.70-1.58 (m, 1H), 0.95 and 0.71 (two d, 6H, *J* = 6.7); ¹³C-NMR: δ 143.1, 141.8, 141.0, 139.8, 131.4, 130.0, 129.5, 128.4, 127.1, 126.2, 77.0, 51.0, 31.1, 21.4, 20.3, 16.4, 13.8; HRMS calcd. for C₁₉H₂₂OS₂ (M⁺ -H₂O) 330.1112, found 330.1117.

[1R,2S,(S)S]-1-t-Butyl-2-methylthio-2-[2-(*p*-tolylsulfinyl)phenyl]-1-ethanol 6k:
 Eluent for chromatography hexane/Et₂O/CH₂Cl₂ 2/1.5/1.5; colorless syrup; [α_D^{20}] = -119.4 (c 1.0, CHCl₃); ¹H-NMR: 7.89 (dd, 1H, *J* = 7.7 and 1.4), 7.71 (d, 1H, *J* = 7.7), 7.59-7.39 (m, 2H), 7.43 and 7.27 (AA'BB' system, 4H), 4.52 (d, 1H, *J* = 5.0), 3.65 (bs, 1H), 2.89 (t, 1H, *J* = 5.0), 2.38 (s, 3H), 1.82 (s, 3H), 0.81 (s, 9H); ¹³C-NMR: δ 141.8, 141.1, 140.9, 131.4, 130.0, 129.6, 128.3, 126.4, 79.6, 49.0, 36.2, 26.5, 21.3, 14.5, 13.2; HRMS calcd. for C₂₀H₂₄OS₂ (M⁺ -H₂O) 344.1269, found 344.1274.

X-Ray structure and refinement details for compound 6'd.

Crystal data and structure refinement for 6'd

Identification code	compound 6'd	
Empirical formula	C ₂₃ H ₂₄ O ₃ S ₂	
Formula weight	412.54	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.257(5) Å	α = 90°.
	b = 15.255(10) Å	β = 90°.
	c = 16.790(11) Å	γ = 90°.
Volume	2115(2) Å ³	
Z	4	
Density (calculated)	1.296 Mg/m ³	
Absorption coefficient	0.273 mm ⁻¹	
F(000)	872	
Crystal size	0.26 x 0.20 x 0.18 mm ³	
Theta range for data collection	1.80 to 23.34°.	
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	
Reflections collected	13583	
Independent reflections	3053 [R(int) = 0.0285]	
Completeness to theta = 23.34°	99.5 %	
Absorption correction	SADABS	
Max. and min. transmission	1.000000 and 0.798085	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3053 / 0 / 257	

Goodness-of-fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0326$, $wR2 = 0.0842$
R indices (all data)	$R1 = 0.0377$, $wR2 = 0.0867$
Absolute structure parameter	0.00
Largest diff. peak and hole	0.275 and -0.197 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for meo17am. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
S(1)	1619(1)	8761(1)	6642(1)	47(1)
S(2)	-1016(1)	7041(1)	8371(1)	87(1)
O(1)	299(2)	9426(1)	6617(1)	67(1)
O(2)	504(3)	5694(2)	7287(1)	95(1)
O(3)	6795(3)	6701(2)	5451(1)	76(1)
C(1)	2277(3)	8642(2)	7658(1)	43(1)
C(2)	3188(3)	9300(2)	8015(2)	55(1)
C(3)	3752(4)	9201(2)	8780(2)	61(1)
C(4)	3398(4)	8446(2)	9191(2)	61(1)
C(5)	2455(4)	7814(2)	8849(2)	60(1)
C(6)	1850(3)	7893(2)	8076(1)	45(1)
C(7)	752(3)	7193(2)	7745(2)	55(1)
C(8)	1611(4)	6299(2)	7617(2)	63(1)
C(9)	-1916(5)	8083(3)	8256(3)	124(2)
C(11)	3028(4)	6402(2)	7064(2)	54(1)
C(12)	4606(4)	6445(2)	7332(2)	59(1)
C(13)	5885(4)	6543(2)	6819(2)	59(1)
C(14)	5627(4)	6599(2)	6016(2)	56(1)
C(15)	4047(4)	6564(2)	5735(2)	64(1)
C(16)	2788(4)	6466(2)	6251(2)	61(1)
C(17)	8432(4)	6690(3)	5716(2)	84(1)
C(18)	3392(3)	9281(2)	6248(1)	45(1)
C(19)	3204(4)	10031(2)	5805(2)	60(1)
C(20)	4562(4)	10401(2)	5452(2)	66(1)
C(21)	6068(4)	10038(2)	5535(2)	56(1)
C(22)	6224(3)	9291(2)	5992(2)	57(1)
C(23)	4895(3)	8902(2)	6340(2)	53(1)

C(24)	7536(4)	10430(2)	5130(2)	81(1)
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Table 3. Bond lengths [Å] and angles [°] for meo17am.

S(1)-O(1)	1.4898(19)
S(1)-C(18)	1.791(3)
S(1)-C(1)	1.800(3)
S(2)-C(9)	1.765(5)
S(2)-C(7)	1.815(3)
O(2)-C(8)	1.412(3)
O(3)-C(14)	1.361(3)
O(3)-C(17)	1.423(4)
C(1)-C(6)	1.387(3)
C(1)-C(2)	1.391(4)
C(2)-C(3)	1.374(4)
C(3)-C(4)	1.374(4)
C(4)-C(5)	1.365(4)
C(5)-C(6)	1.396(4)
C(6)-C(7)	1.508(4)
C(7)-C(8)	1.551(4)
C(8)-C(11)	1.503(4)
C(11)-C(12)	1.380(4)
C(11)-C(16)	1.383(4)
C(12)-C(13)	1.371(4)
C(13)-C(14)	1.368(4)
C(14)-C(15)	1.388(4)
C(15)-C(16)	1.361(4)
C(18)-C(19)	1.374(4)
C(18)-C(23)	1.377(4)
C(19)-C(20)	1.388(4)
C(20)-C(21)	1.368(4)
C(21)-C(22)	1.380(4)
C(21)-C(24)	1.512(4)
C(22)-C(23)	1.378(4)
O(1)-S(1)-C(18)	106.68(12)
O(1)-S(1)-C(1)	108.39(11)

C(18)-S(1)-C(1)	98.51(12)
C(9)-S(2)-C(7)	99.28(17)
C(14)-O(3)-C(17)	117.0(2)
C(6)-C(1)-C(2)	120.9(2)
C(6)-C(1)-S(1)	119.11(18)
C(2)-C(1)-S(1)	119.95(19)
C(3)-C(2)-C(1)	120.4(3)
C(2)-C(3)-C(4)	119.3(3)
C(5)-C(4)-C(3)	120.2(3)
C(4)-C(5)-C(6)	122.2(3)
C(1)-C(6)-C(5)	116.8(2)
C(1)-C(6)-C(7)	123.4(2)
C(5)-C(6)-C(7)	119.8(2)
C(6)-C(7)-C(8)	113.5(2)
C(6)-C(7)-S(2)	111.09(19)
C(8)-C(7)-S(2)	109.65(19)
O(2)-C(8)-C(11)	109.2(2)
O(2)-C(8)-C(7)	109.4(3)
C(11)-C(8)-C(7)	110.5(2)
C(12)-C(11)-C(16)	117.0(3)
C(12)-C(11)-C(8)	122.6(2)
C(16)-C(11)-C(8)	120.4(3)
C(13)-C(12)-C(11)	121.8(3)
C(14)-C(13)-C(12)	120.4(3)
O(3)-C(14)-C(13)	125.7(3)
O(3)-C(14)-C(15)	115.7(2)
C(13)-C(14)-C(15)	118.6(3)
C(16)-C(15)-C(14)	120.4(3)
C(15)-C(16)-C(11)	121.7(3)
C(19)-C(18)-C(23)	120.8(3)
C(19)-C(18)-S(1)	118.4(2)
C(23)-C(18)-S(1)	120.62(19)
C(18)-C(19)-C(20)	118.6(3)
C(21)-C(20)-C(19)	121.7(3)
C(20)-C(21)-C(22)	118.4(3)
C(20)-C(21)-C(24)	121.5(3)
C(22)-C(21)-C(24)	120.1(3)
C(23)-C(22)-C(21)	121.2(3)

C(18)-C(23)-C(22)

119.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for meo17am. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	47(1)	48(1)	46(1)	-1(1)	-4(1)	2(1)
S(2)	70(1)	124(1)	65(1)	0(1)	10(1)	-36(1)
O(1)	51(1)	76(1)	75(1)	5(1)	-6(1)	20(1)
O(2)	125(2)	75(1)	85(2)	3(1)	-18(2)	-47(2)
O(3)	70(1)	99(2)	60(1)	-14(1)	-5(1)	14(1)
C(1)	42(1)	41(1)	45(1)	-7(1)	2(1)	5(1)
C(2)	63(2)	47(1)	54(2)	-8(1)	1(1)	-7(1)
C(3)	62(2)	61(2)	59(2)	-20(1)	-8(1)	-8(2)
C(4)	66(2)	72(2)	44(1)	-11(1)	-9(1)	0(2)
C(5)	75(2)	59(2)	44(2)	4(1)	-9(1)	-7(2)
C(6)	45(1)	49(1)	42(1)	-4(1)	1(1)	-3(1)
C(7)	59(2)	63(2)	43(1)	2(1)	-4(1)	-17(1)
C(8)	88(2)	42(1)	58(2)	3(1)	-16(2)	-21(2)
C(9)	78(3)	157(4)	138(4)	-56(3)	32(3)	-14(3)
C(11)	77(2)	33(1)	51(2)	-1(1)	-12(1)	-2(1)
C(12)	84(2)	44(2)	49(2)	1(1)	-18(2)	4(2)
C(13)	67(2)	49(2)	60(2)	-7(1)	-18(2)	9(1)
C(14)	69(2)	48(2)	50(2)	-10(1)	-12(2)	12(1)
C(15)	72(2)	75(2)	44(2)	-12(1)	-16(2)	10(2)
C(16)	62(2)	62(2)	59(2)	-9(1)	-16(2)	2(1)
C(17)	65(2)	111(3)	76(2)	-8(2)	-6(2)	4(2)
C(18)	52(1)	41(1)	41(1)	1(1)	-4(1)	5(1)
C(19)	63(2)	55(2)	64(2)	11(1)	-3(2)	10(2)
C(20)	86(2)	53(2)	60(2)	17(1)	2(2)	0(2)
C(21)	65(2)	55(2)	46(2)	-6(1)	4(1)	-8(2)
C(22)	52(2)	62(2)	58(2)	-1(1)	5(1)	5(1)
C(23)	58(2)	48(2)	53(2)	5(1)	1(1)	10(1)
C(24)	94(2)	78(2)	72(2)	-3(2)	24(2)	-26(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for meo17am.

	x	y	z	U(eq)
H(2)	250	5332	7626	142
H(2A)	3416	9811	7735	66
H(3)	4367	9640	9017	73
H(4)	3802	8365	9702	73
H(5)	2208	7313	9142	72
H(7)	372	7395	7223	66
H(8)	1994	6078	8132	75
H(9A)	-1191	8526	8450	187
H(9B)	-2910	8104	8553	187
H(9C)	-2139	8186	7703	187
H(12)	4808	6406	7876	71
H(13)	6934	6571	7018	71
H(15)	3848	6607	5191	76
H(16)	1738	6442	6051	73
H(17A)	8642	7203	6030	126
H(17B)	9142	6684	5263	126
H(17C)	8617	6175	6032	126
H(19)	2189	10285	5742	72
H(20)	4446	10910	5151	80
H(22)	7244	9046	6066	69
H(23)	5011	8389	6633	63
H(24A)	7685	10158	4619	122
H(24B)	8477	10332	5453	122
H(24C)	7376	11048	5060	122

^1H and ^{13}C -NMR spectra of compounds 4, 6a-k, 6'c-j, 7 and 8g

6d

6e

6j