

An enantiopure *pseudo*-C₃-symmetric titanium triflate with propeller-like chirality as a catalyst for asymmetric sulfoxidation reactions

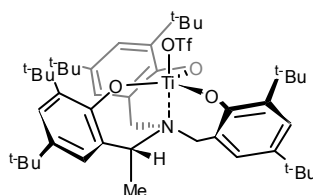
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Supplementary Data



Titanium tris-(phenolate) triflate (*R,M*)-5: Titanium isopropoxide (*R,M*)-**3**¹ (500 mg, 0.63 mmol) in toluene (7 mL) was treated with trimethylsilyl triflate (0.11 mL, 0.63 mmol) under an argon atmosphere. The resulting suspension was heated to reflux for 5 minutes and then concentrated under vacuum to yield the title product as a red solid (551 mg, 0.63 mmol, 99% yield): ¹H-NMR (300 MHz, CDCl₃) δ 7.31 (1H, d, *J* = 2.3 Hz, Ar-*H*), 7.29 (1H, d, *J* = 2.3 Hz, Ar-*H*), 7.25 (1H, d, *J* = 2.3 Hz, Ar-*H*), 7.20 (1H, d, *J* = 2.3 Hz, Ar-*H*), 7.16 (1H, d, *J* = 2.3 Hz, Ar-*H*), 7.05 (1H, d, *J* = 2.3 Hz, Ar-*H*), 4.13 (1H, q, *J* = 6.8 Hz, 1H, CH(CH₃)N), 3.93 (1H, d, *J* = 14.7 Hz, CH_AH_BN), 3.72 (1H, d, *J* = 13.9 Hz, CH_CH_DN), 3.51 (1H, d, *J* = 14.7 Hz, CH_AH_BN), 3.44 (1H, d, *J* = 13.9 Hz, CH_CH_DN), 1.69 (3H, d, *J* = 6.8 Hz, CH(CH₃)N), 1.45 (9H, s, *t*-Bu), 1.43 (9H, s, *t*-Bu), 1.40 (9H, s, *t*-Bu), 1.31 (9H, s, *t*-Bu), 1.30 (9H, s, *t*-Bu), 1.29 (9H, s, *t*-Bu); ¹³C-NMR (75.5MHz, CDCl₃) δ 161.9, 161.6, 161.2, 145.3, 145.0, 135.9, 135.8, 135.7, 126.3, 124.6, 124.0, 123.9, 123.8, 123.6, 123.1, 121.9, 55.3, 54.7, 51.8, 35.0, 34.9, 34.8, 34.8, 34.6, 31.6, 31.5, 29.6, 29.5, 29.5, 10.4; ¹⁹F-NMR (376.5MHz, CDCl₃) δ -76.5 (CF₃); MS (EI) *m/z* (%) 879 (20, [M]⁺); HRMS *m/z* (EI) [M]⁺ - C₄₇H₆₈NO₆SF₃Ti requires 879.4193, found 879.4188; Elemental analysis: C₄₇H₆₈NO₆SF₃Ti requires C, 64.15, H, 7.79, N, 1.59; found C, 64.7, H, 7.38, N, 1.31.

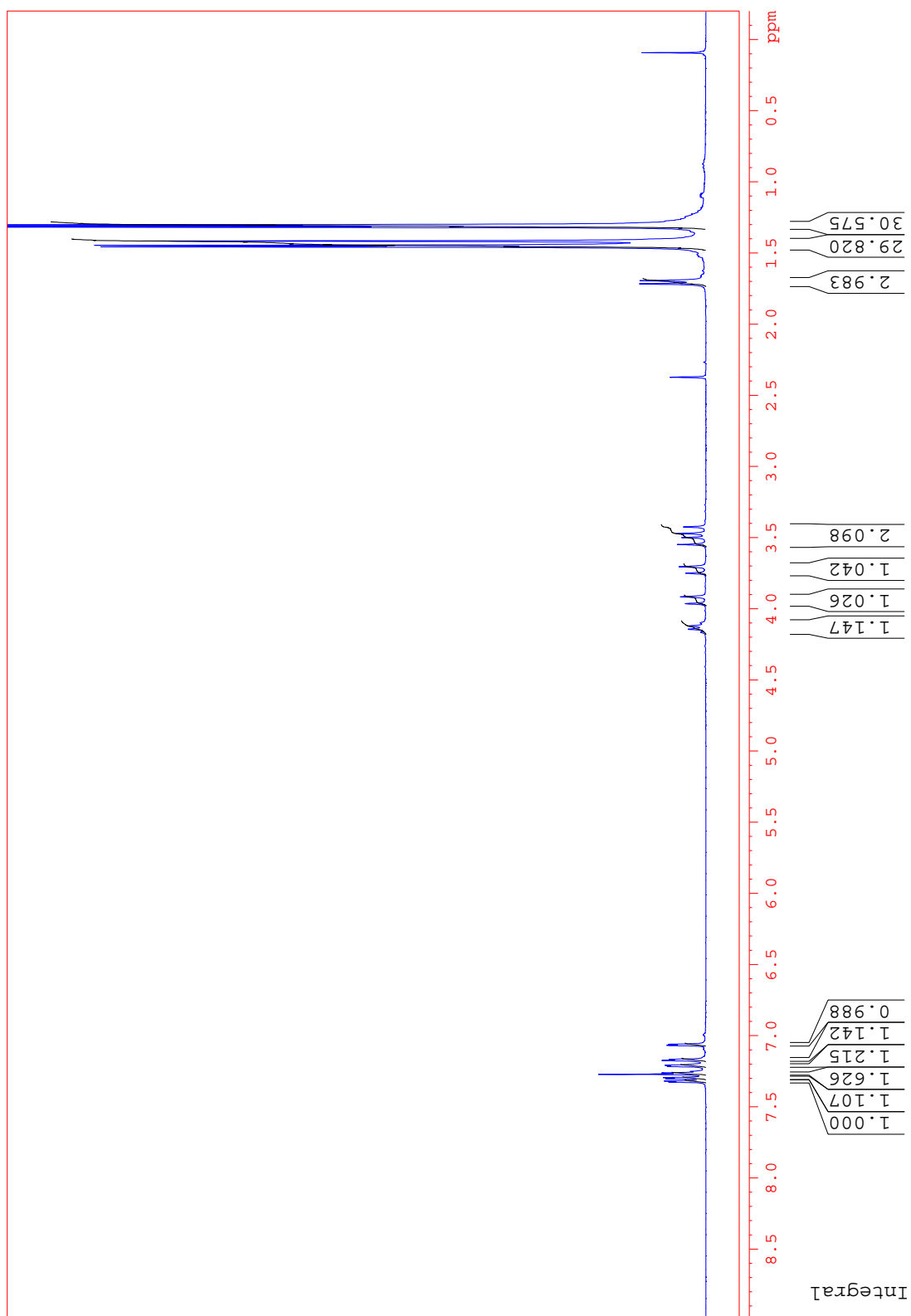
Crystallography. C_{50.5}H₇₂TiF₃N₁O₆S₁, *M* = 926.05, 0.25 x 0.25 x 0.15 mm³, Tetragonal, *P*4₃, *a* = *b* = 14.7440(7), *c* = 25.1710(15) Å, *V* = 5471.8(5) Å³, *Z* = 4, *D*_c = 1.124 g/cm³, *T* = 173(2) K, *F*₀₀₀ = 1980, 2θ_{max} = 51.48°, 46969 reflections collected, 11035 unique (*R*_{int} = 0.0797). Final *GooF* = 0.992, *R*_I = 0.0675, *wR*₂ = 0.1750, *R* indices based on 11035 reflections with *I* > 2σ(*I*) (refinement on

F^2), 801 parameters, 39 restraints, $\mu = 0.248 \text{ mm}^{-1}$. Absolute structure parameter = 0.06(13). CCDC No 737968.

Added notes on refinement:

The absolute structure was determined by refinement of the Flack parameter. The structure exhibited severe disorder; this is due to both the *P* and *M* form of the pseudo C_3 symmetric ligand being present in the crystal structure, the phenoxide oxygen and three carbon atoms of the phenyl ring are modelled over two positions around a 3-fold molecular axis. This was modelled using PART 1 and PART 2 terms, hence certain bond lengths {C(23a)-C(24)} are not ideal. The tBu groups also exhibited severe disorder hence certain bond lengths {C(17)-C(42a)} are again not ideal. The sulphur and non-coordinating oxygen groups of the triflate moiety were also modelled over two positions using the PART 1 and PART 2 instructions. The solvent of crystallisation was refined with half occupancy.

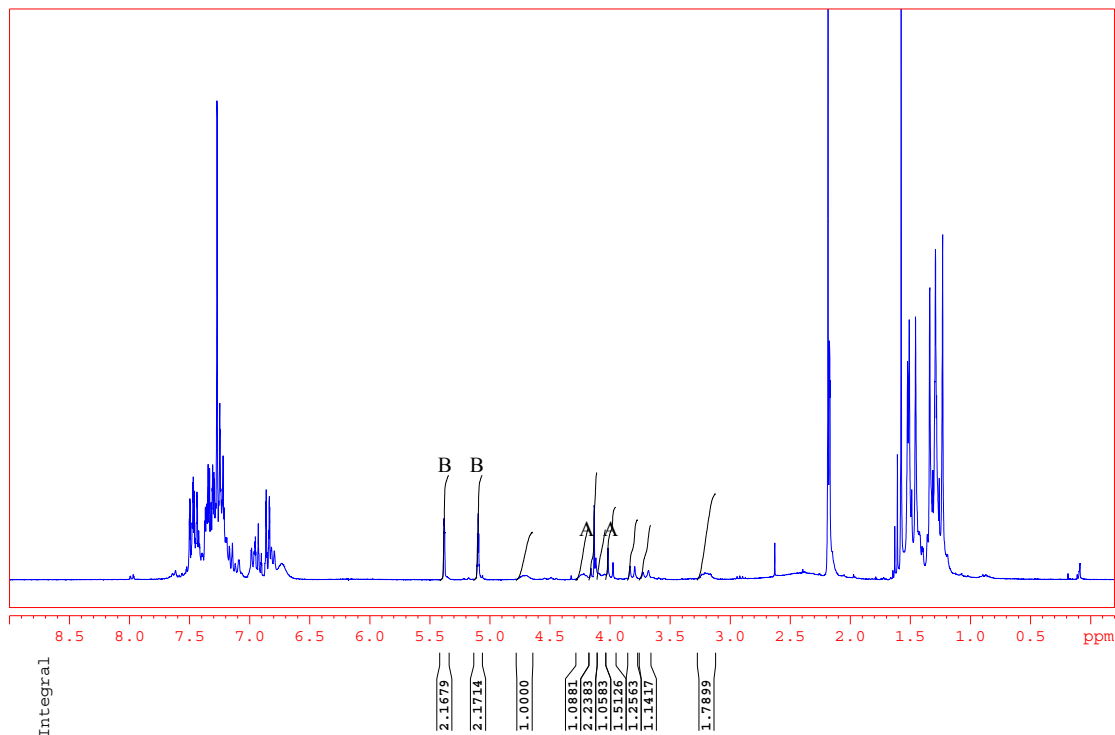
^1H NMR spectrum of titanium triflate (*R,M*)-5.



Representative protocol for titanium triflate (*R,M*)-**5** catalysed asymmetric sulfoxidation reactions of sulphide **7**

A solution of titanium triflate ((*R,M*)-**5** (20 mg, 0.025 mmol) and benzyl(phenyl)sulfide **7** (46mg, 0.25 mmol) in dichloromethane (3 mL) was stirred under nitrogen at -30 °C before cumene hydroperoxide (88% in cumene) was added. The reaction was stirred for 24 hours before being quenched via addition of saturated aqueous sodium sulfite (8 mL), extracted with dichloromethane (3 x 10 mL) and the combined organic layers dried over magnesium sulfate. After evaporation of the solvent under reduced pressure the crude product was analysed by ¹H NMR spectroscopy. The crude product was purified via column chromatography (SiO₂, 70:30 to 50:50 Petrol:EtOAc) to yield benzyl phenyl sulfoxide **8** as an off-white solid. The enantiomeric excess of sulfoxide **8** was determined via chiral HPLC analysis through a Diacel Chiralcel OD-H column using a mixed *n*-hexane/*i*-PrOH (9:1) solvent system at a flow rate of 1 mL/min with the (*R*)- enantiomer having a retention time of 13 min and with the (*S*)- enantiomer having a retention time of 15 min. The configuration of the sulfoxide was determined by the order of elution of the enantiomers compared with that previously reported in the literature,² and by comparison of the sign of its optical rotation with literature values. For example, (*R*)-benzyl phenyl sulfoxide **8**, 23% ee: $[\alpha]_D^{25} +42$ (*c* 0.51, acetone) [Lit.³ $[\alpha]_D^{24} -91$ (*c* 1.0, acetone) for (*S*)-**8**, 36% ee].

¹H NMR spectrum of the crude reaction product arising from a mixture of one equivalent of titanium triflate (*R,M*)-5 with two equivalents of sulfide 7 and four equivalents of cumene hydroperoxide.



A - Resonances corresponding to sulfoxide **8**.

B - Resonances corresponding to α -methylstyrene arising from decomposition of cumene hydroperoxide.

References

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- 3) G. Glahsl and R. Hermann, *J. Chem. Soc. Perkin Trans. I* 1988, 1753.