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 \((R,M)-3\) (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) \(\delta\) 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, C₉H₈(CH₃)N), 3.93 (1H, d, \(J = 14.7\) Hz, C₉H₈HB), 3.72 (1H, d, \(J = 13.9\) Hz, C₉H₈HB), 3.51 (1H, d, \(J = 13.9\) Hz, C₉H₈HB), 3.44 (1H, d, \(J = 13.9\) Hz, C₉H₈HB), 1.69 (3H, d, \(J = 6.8\) Hz, CH(CH₃)N), 1.45 (9H, s, ′Bu), 1.43 (9H, s, ′Bu), 1.40 (9H, s, ′Bu), 1.31 (9H, s, ′Bu, 1.30 (9H, s, ′Bu), 1.29 (9H, s, ′Bu); ¹³C-NMR (75.5MHz, CDCl₃) \(\delta\) 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, 31.5, 29.6, 29.5, 29.5, 10.4; ¹⁹F-NMR (376.5MHz, CDCl₃) \(\delta\) -76.5 (CF₃); MS (EI) \(m/z\) (%) 879 (20, [M]+); HRMS \(m/z\) (EI) [M]+ - C₄₇H₆₈NO₆SF₃Ti requires 879.4193, found 879.4193, Elemental analysis: C₄₇H₆₈NO₆SF₃Ti requires C, 64.15, H, 7.79, N, 1.59; found C, 64.7, H, 7.38, N, 1.31.

Crystallography. C₅₀.₅H₇₂Ti₁F₃N₁O₆S₁, \(M = 926.05\), 0.25 x 0.25 x 0.15 mm³, Tetragonal, \(P4₃\), \(a = b = 14.7440(7), c = 25.1710(15)\) Å, \(V = 5471.8(5)\) Å³, \(Z = 4\), \(D_c = 1.124\) g/cm³, \(T = 173(2)\) K, \(F_{000} = 1980, 2\theta_{max} = 51.48°, 46969\) reflections collected, 11035 unique (\(R_{int} = 0.0797\)). Final \(GooF = 0.992, R₁ = 0.0675, wR₂ = 0.1750, R\) indices based on 11035 reflections with I >2sigma(I) (refinement on
$P^2_1$), 801 parameters, 39 restraints, $\mu = 0.248$ 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.
$^1$H 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 (46 mg, 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 \(^1\)H NMR spectroscopy. The crude product was purified via column chromatography (SiO\(_2\), 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 sulf oxide 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: \([\alpha]_D^{25} +42 (c \ 0.51, \text{ acetone}) \) [Lit.\(^3\) \([\alpha]_D^{14} -91 (c \ 1.0, \text{ acetone})\) for (\(S\))-8, 36% ee].
$^1$H 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

