# Crystal structure of enantiomerically pure, P-stereogenic bisphosphine – (*S,S*)-Ethylenebis[(2-methylphenyl)-phenylphosphine] (*o*-tolyl DiPAMP)

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## Supporting information

**Table S1** Angles between phenyl rings in *o*-tolyl DiPAMP (º)

| | **Ph1** | **MePh1** | **Ph2** | **MePh2** |
|---|---|---|---|---|
| **Ph1** | --- | 85.96 (6) | 53.04 (8) | 59.44 (6) |
| **MePh1** | 85.96 (6) | --- | 60.42 (6) | 66.96 (6) |
| **Ph2** | 53.04 (8) | 60.42 (6) | --- | 87.16 (6) |
| **MePh2** | 59.44 (6) | 66.96 (6) | 87.16 (6) | --- |

**Table S2** Relative orientation of the phenyl rings as described by a set of pseudotorsion angles $C_{ortho}$-$C_{ipso}$...$C_{ipso}$-$C_{ortho}$ (º). Of the four possible values always the smallest absolute value has been chosen.

| | Ph1 | MePh1 | Ph2 | MePh2 |
|---|---|---|---|---|
| **Ph1** | --- | 41.0(2) | 37.8(2) | 45.1(2) |
| **MePh1** | 41.0(2) | --- | -5.7(2) | -5.4(2) |
| **Ph2** | 37.8(2) | -5.7(2) | --- | 51.2(2) |
| **MePh2** | 45.1(2) | -5.4(2) | 51.2(2) | --- |

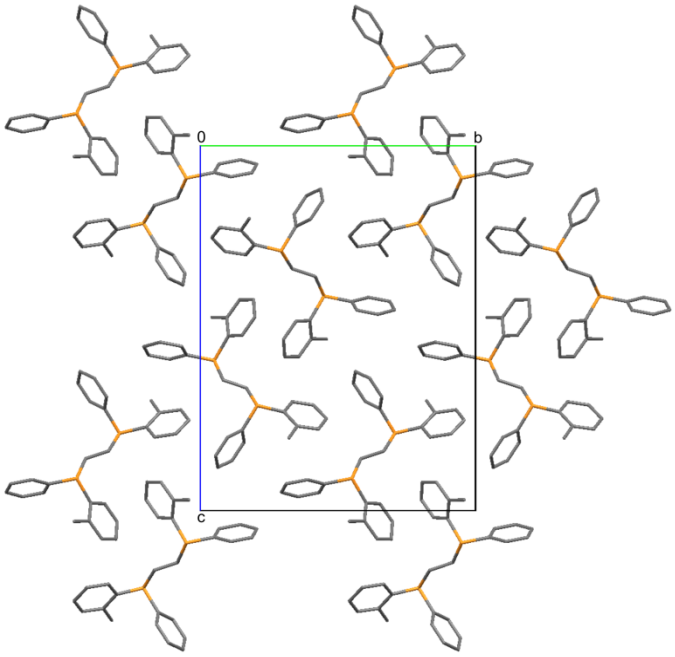


**Figure S1** Packing of molecules in the crystal structure of *o*-tolyl DiPAMP, as viewed along the *a*-direction.

**Experimental details for the synthesis of (*S*,*S*)-Ethylenebis[(2-methylphenyl)-phenylphosphine] (*o*-tolyl DiPAMP)**

(*S*,*S*)-Ethylenebis[(2-methylphenyl)-phenylphosphine oxide] (*o*-tolyl DiPAMPO)

The procedure of Knowles ($_{\text{Vineyard}}$, *et al*., 1977) for the preparation of *o*-tolyl DiPAMPO was followed. (S)-methylphenyl-*o*-tolylphosphine oxide (1.46 g, 6.36 mmol) was dissolved in anhydrous THF (20 ml) in a Schlenk flask. The solution was cooled to 0°C, and LDA (3.90 ml of a 2.0 M solution in THF/heptane/ethylbenzene, 7.80 mmol) was added over 10 minutes. The reaction mixture turned yellow/orange in colour. The mixture was stirred for 30 minutes, while the temperature was maintained at 0°C. Solid anhydrous copper (II) chloride (0.94 g, 7.02 mmol, hygroscopic) was added quickly to the vessel, giving a dark green coloured solution. The reaction was allowed to warm to room temperature and stirred overnight. Concentrated hydrochloric acid (6 ml) was added slowly giving rise to fuming. The mixture was transferred to a separatory funnel and pentane (15 ml) was added. The mixture now consisted of three layers. The upper layer (pentane, heptane) was removed. The aqueous layer was removed and extracted with chloroform (50 ml). The middle layer was combined with the organic washes, and washed with ammonia solution (4 × 40 ml; the first wash being green, the next two violet and the final one clear in colour) and then water (3 × 40 ml; the final wash was clear). The solvent was removed *in vacuo* to give a brown residue which was recrystallised from THF to give the target compound as a white solid (1.38 g, 95% yield).

(*S,S*)-Ethylenebis[(2-methylphenyl)-phenylphosphine] (*o*-tolyl DiPAMP)

The procedure of Knowles (Vineyard, *et al*., 1977) for the preparation of *o*-tolyl DiPAMP was followed, with minor changes. All operations were handled under an inert atmosphere of nitrogen gas. To a stirred solution of (S,S)-*o*-tolyl DiPAMPO (1.0 g, 2.18 mmol) in anhydrous toluene (25 ml) in a Schlenk flask was added $Bu_3N$ (2.60 ml, 10.90 mmol). The reaction was heated to 70°C and trichlorosilane (2.20 ml, 21.80 mmol) dropwise over 15 minutes with rapid stirring. The reaction was heated for a further 2 hrs at 70°C and then allowed to cool to ambient temperature. The reaction mixture was added via a large bore cannula to rapidly stirred 25% w/v NaOH aqueous solution (50 ml), stirred for 10 minutes and the layers separated. The aqueous layer was extracted further with toluene (3 x 25 ml). Organic layers were pooled, dried (anh. $Na_2SO_4$), filtered and the solvent evaporated to give the target compound as a white solid which was recrystallised from THF to give pure (*S,S*)-*o*-tolyl DiPAMP (0.93 g, 65% yield). A suitable crystal for X-ray analysis was grown by the slow evaporation method in THF under a gentle stream of nitrogen gas.

Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachmann, G. L.; Weinkauff, D. J. (1977) *J. Am. Chem. Soc*. **99**, 5946-5952