# OPTICALLY ACTIVE AMINOMETHYLPHOSPHINES

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Optically active aminomethylphosphines IIa-IIc, which are of interest as ligands for catalysts of asymmetric reactions [2], have been synthesized for the first time after [1] according to the reaction scheme

$$(S)\text{-}(-)\text{-}MeOCH_2\underbrace{N(CH_2)_3CHCO_2Me}_{(I)} + R(R^1)PH \xrightarrow[-MeOH]{125^\circ} R(R^1)PCH_2\underbrace{N(CH_2)_3CHCO_2Me}_{(IIa\text{-}c)}$$

$R = R^1 = i\text{-}Pr$ (IIa); $R = i\text{-}Pr$, $R^1 = PhCH_2$ (IIb); $R = Me_3C$, $R^1 = Ph$ (IIc). Compound I was synthesized according to [3].

Compound IIa, 94% yield, bp 100-104°C (2 mm), m/e 245 ($M^+$), $[\alpha]_{546}^{20}$ −76.8° (c 8.5, MeOH). PMR spectrum (60 MHz, $CDCl_3$ relative to HMDS), δ, ppm (J, Hz): 1.2 ($Me_A$, $J_{HH} = 6$, $J_{HP} = 11.25$), 1.1 ($Me_B$, $J_{HH} = 6$, $J_{HP} = 9.75$), 1.72 (HCP), 1.91 and 3.3 (m, ring $CH_2$), 2.92 ($CH_2P$, $\Delta\nu = 28$ Hz, $J_{H_AP} = 2.5$, $J_{H_BP} = 4.5$, $J_{H_AH_B} = 12.5$), 3.75 (MeO).

Compound IIb, 63% yield, bp 150-152°C (1 mm), $[\alpha]_{546}^{20}$ −22.3° (c 0.5 MeOH). PMR spectrum (80 MHz, $C_6F_6$, 1:1 mixture of diastereomers): 1.06 ($Me_A$, $J_{HH} = 6$, $J_{HP} = 14$), 0.98 ($Me_B$, $J_{HH} = 6$, $J_{HP} = 12.6$), 1.81 (HCP), 1.79 and 2.69 (m, ring $CH_2$), 3.56 ($MeO^1$), 3.66 ($MeO^2$), 7.15 (Ph).

Compound IIc, 78% yield, bp 149-150° (1.5 mm), $[\alpha]_{546}^{20}$ −57.0° (c, 1.9, MeOH). PMR spectrum ($C_2Cl_4$, 1:1.2 mixture of diastereomers): 0.88 ($Me_3C^1$, $J_{HP} = 12$), 0.91 ($Me_3C^2$, $J_{HP} = 12$), 3.44 ($MeO^1$), 3.52 ($MeO^2$), 3.21 ($CH_2^1$, AB, $\Delta\nu = 66$ Hz, $J_{H_AP} = 3.5$, $J_{H_BP} = 2.5$, $J_{H_AH_B} = 13$), 3.18 ($CH_2^2$, AB, $\Delta\nu = 72$ Hz, $J_{H_AB} = 3.5$, $J_{H_BP} = 2.5$, $J_{H_AH_B} = 13$), 1.66 and 2.82 (m, ring $CH_2$), 7.0 (Ph).

The reaction of $Me_3C(Ph)PCH_2NMe_2$ (III) with 1/2 mole of (S)-(−)-$\underbrace{TsN(CH_2)_3CHCOCl}$ [4] (in ether, 0.5 h, −50°C) yielded enantiomer-enriched (−)-III. Compound III was synthesized according to [1] in a 65% yield with bp 130°C (10 mm) and m/e 233 ($M^+$). PMR spectrum ($C_6F_6$): 0.87 ($Me_3C$, $J_{HP} = 12$), 2.2 (MeN), 2.81 ($CH_2P$, AB, $\Delta\nu = 22$ Hz, $J_{H_AP} = 5.5$, $J_{H_BP} = 3.75$, $J_{H_AH_B} = 13.8$), 7.25 (Ph). $^{31}P$ NMR spectrum ($Ph_2O$): 11.5 ppm. (−)-III: $[\alpha]_{546}^{20}$ −8.2°, $[\alpha]_{404}^{20}$ −28.1° (c 1.0, $C_6H_6$), identical to III according to its constants. N-Bromobenzylated (−)-III: $[\alpha]_{546}^{20}$ −3.4°, $[\alpha]_{404}^{20}$ −5.5° (c 0.6, MeOH). PMR spectrum (60 MHz, $CD_3OD$): 1.05 ($Me_3C$, $J_{HP}$ + 13.5), 2.98 (d, MeN, $\Delta\nu = 9$ Hz), 4.2 ($CH_2P$, AB, $\Delta\nu = 36$ Hz, $J_{H_AP} = 5.0$, $J_{H_BP} = 1.5$, $J_{H_AH_B} = 15$), 4.65 ($CH_2Ph$), 7.5 (Ph).

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