Supporting Information

NMR and X-ray crystallographic studies of unsymmetrical 25,26;27,28-dibridged \( p\text{-}terr \)-butyl calix[4]arene bisphosphites with a large “through–space” P-P coupling

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Synthesis of phosphorodichloridites
\( ^{31} \text{P} \) NMR spectra of compounds 5, 6 and 7……………………………Fig. S1
Homonuclear \( ^{31} \text{P} \) COSY NMR spectrum of achiral unsymmetrical \( p\text{-}terr \)-butyl-calix[4]arene bisphosphite 5………………………Fig. S2
Synthesis of phosphorodichloridites

**Synthesis of 2,6-Bu$_2$-4-Me-C$_6$H$_2$-phosphorodichloridite**

Phosphorus trichloride (11.8 ml, 135 x 10$^{-3}$ mol) was added to a mixture of 2,6-Bu$_2$-4-Me-C$_6$H$_2$-OH (10 gm, 45 x 10$^{-3}$ mol) and triethylamine (7.5 ml, 54 x 10$^{-3}$ mol) at 0ºC and heated under reflux at 90 ºC for 6h. The reaction mixture was cooled to room temperature and filtered through a frit to remove the precipitate of triethylamine hydrochloride. The precipitate was washed with petrol and the washings were combined with the filtrate. The solution was evaporated and the excess of phosphorus trichloride and triethyl amine were removed by distillation under vacuum to obtain 2,6-Bu$_2$-4-Me-C$_6$H$_2$-phosphorodichloridite. Yield: 11.1 gm (76%); $^{31}$P NMR (CDCl$_3$, 161.9 MHz) δ = 201.5 ppm (s).

**Synthesis of 2,4-Bu$_2$-C$_6$H$_2$- and 2,6-Pr$_2$-C$_6$H$_3$-phosphorodichloridites**

A mixture of phosphorus trichloride (11.9 ml, 136 x 10$^{-3}$ mol; 13.7 ml, 156.8 x 10$^{-3}$ mol respectively) and the respective phenol (2,4-Bu$_2$-C$_6$H$_3$-OH 3.5 gm, 17 x 10$^{-3}$ mol; 2,6-Pr$_2$-C$_6$H$_3$-OH 3.5 gm, 19.6 x 10$^{-3}$ mol) was heated under reflux at 90 ºC for 4h. The reaction mixture was evaporated and the excess phosphorus trichloride was removed by distillation under vacuum to obtain the respective phosphorodichloridite. Yield ~70-75%. $^{31}$P NMR (CDCl$_3$, 161.9 MHz); δ = 184.9 ppm (s) for 2,4-Bu$_2$-C$_6$H$_2$-phosphorodichloridite and δ = 200.2 ppm (s) for 2,6-Pr$_2$-C$_6$H$_3$-Phosphorodichloridite.
Figure S2: The $^{31}$P NMR spectra of unsymmetrically substituted $p$-tert-butyl-calix[4]arene bisphosphites 5-7 respectively.

Figure S3. Homonuclear $^{31}$P COSY NMR spectrum of achiral unsymmetrical $p$-tert-butyl-calix[4]arene bisphosphite 5.