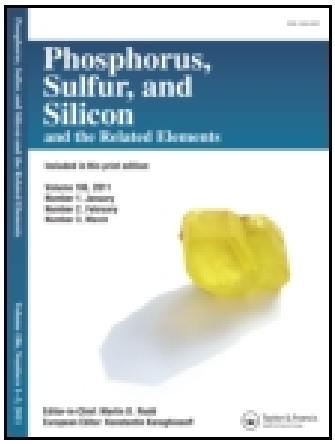

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SYNTHESIS AND STRUCTURE OF A NOVEL SYMMETRICALLY SUBSTITUTED PHOSPHATRIPTYCENE OXIDE

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SYNTHESIS AND STRUCTURE OF A NOVEL SYMMETRICALLY SUBSTITUTED PHOSPHATRIPTYCENE OXIDE

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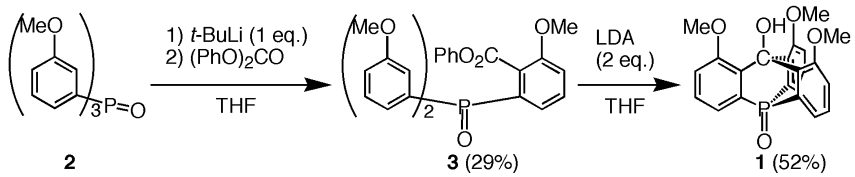
Heterotriptycenes bearing one or two heteroatoms at bridgehead positions have been widely investigated, and phosphatriptycenes are one of attractive targets because electronic and structural properties of the bridgehead can be studied by ^{31}P NMR. Since the first synthesis of a phosphatriptycene in 1974,[1] there have been two other examples reported.[2] However, their synthetic routes were complicated and not suitable in the case of multifunctionalized substrates. Here we report the synthesis of phosphatriptycene oxide **1** from tris(3-methoxyphenyl)phosphine oxide **2** in moderate yield by two steps.

Direct lithiation of **2** with *t*-BuLi, followed by the reaction with diphenyl carbonate gave the corresponding phenoxycarbonyl derivative **3** in 29% yield. Phosphatriptycene oxide **1** was synthesized in 52% yield via intramolecular cyclization by treatment of **3** with 2 equivalents of lithium diisopropylamide.



2 **3** (29%) **1** (52%)

SCHEME 1

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^{31}P NMR signal of **1** was observed at δ_P 2.0, which is 28 ppm upfield shifted compared to that of **2** (δ_P 30.3). Such an upfield shift attributable to the distortion around the phosphorus atom was also observed in the reported phosphatriptycenes. Its crystal structure was determined by x-ray crystallographic analysis.

Phosphatriptycene oxide **1** easily was converted to the corresponding phosphatripticene and other chalcogenides in good yields.

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