

Supplementary Information

Synthesis of Phosphorus Esters by Transesterification Mediated by N-Heterocyclic Carbenes (NHCs)

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General Considerations

All reactions were carried out in an MBraun glovebox containing dry argon or using standard Schlenk techniques under an atmosphere of dry argon. Solvents for synthesis of imidazol-2-ylidenes or imidazolium salts were distilled from appropriate drying agents or were passed through an alumina column in an MBraun solvent purification system. *N*-heterocyclic carbenes (NHCs) were synthesized according to the literature procedures¹ (although carbenes IAd and I^tBu and imidazolium salts of ICy, IAd and I^tBu are commercially available – see references 24 and 29 in the ms). Solvents for NMR spectroscopy were degassed with argon and dried over molecular sieves. NMR spectra were collected on 300 MHz or 400 MHz Varian Gemini spectrometers. ³¹P-NMR spectra were recorded with 85% phosphoric acid as external standard. Flash chromatography was performed on silica gel 60 (230-400 mesh) (Natland International Corporation).

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Representative Procedure:

Under an atmosphere of argon, 1 mmol of *P*-ester was loaded to a screw-cap vial charged with the imidazol-2-ylidene or imidazolium salt (5 mol %). Molecular sieves (4 Å, 0.5 gm / mmol of alcohol) were then added to the vial. Next, alcohol (1 mmol) and THF (1 mL) were added to the vial. For reactions with carbene generated *in situ*, potassium *tert*-butoxide (0.06 mmol, 6.7 mg) was added to the reaction mixture. The vial was then sealed with cap equipped with a rubber septum. The reaction mixture was allowed to shake on a Lab-Line Orbit Shaker (set at indicated temperature (25 °C for room temperature reactions) – J-Kem Scientific, Kem-Lab Controller) or stirred over a magnetic plate at ambient temperature for the indicated time. The reactions were monitored by ³¹P-NMR of an aliquot in C₆D₆ with 85% phosphoric acid as external standard. The spectral data of the products was found to be in agreement with the literature values.

Methyl-phosphonic acid benzyl ester methyl ester²: ³¹P-NMR (161.9 MHz, C₆D₆) δ 32.90 ppm. MS (GC) *m/z* 200(M⁺)

Methyl-phosphonic acid dibenzyl ester²: ³¹P-NMR (161.9 MHz, C₆D₆) δ 32.33 ppm. MS (GC) *m/z* 276(M⁺)

Diphenyl-phosphinic acid benzyl ester³: ³¹P-NMR (161.9 MHz, C₆D₆) δ 32.92 ppm. MS (GC) *m/z* 308(M⁺)

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Screening of *N*-Heterocyclic Carbenes:

Under an atmosphere of argon, dimethylmethyl phosphonate - DMMP (1 mmol, 109 μ l) was loaded to a screw-cap vial charged with the carbene (0.05 mmol). Molecular sieves (4 Å, 0.5 gm) were then added to the vial. Next, benzyl alcohol (1 mmol, 104 μ l) and solvent – THF (1 mL) were added to the vial. The vial was then sealed with cap equipped with a rubber septum. The reaction mixture was allowed to shake on a Lab-Line Orbit Shaker (set at 25 °C – J-Kem Scientific, Kem-Lab Controller) or stirred over a magnetic plate at ambient temperature for the indicated time. The reactions were monitored by ^{31}P -NMR of an aliquot in C_6D_6 with 85% phosphoric acid as external standard.

Screening of Imidazolium Salts as Pre-catalysts:

Under an atmosphere of argon, dimethylmethyl phosphonate – DMMP (1 mmol, 109 μ l) was loaded to a screw-cap vial charged with the carbene precursor (0.05 mmol). Molecular sieves (4 Å, 0.5 gm) were then added to the vial. Next, potassium *tert*-butoxide (0.9 eq., 5.0 mg) and solvent – THF (1 mL) were added to the vial. The vial was then sealed with a cap equipped with rubber septum. The mixture was stirred for 15 minutes, allowing deprotonation of the imidazolium salt. After 15 minutes, benzyl alcohol (1 mmol, 104 μ l) was added. The reaction mixture was allowed to shake on a Lab-Line Orbit Shaker (set at 25 °C – J-Kem Scientific, Kem-Lab Controller) or stirred over a magnetic plate at ambient temperature for the indicated time. The reactions were monitored by ^{31}P -NMR of an aliquot in C_6D_6 with 85% phosphoric acid as external standard.