Electronic Supplementary Material (ESI) for Polymer Chemistry

Electronic Supplementary Information

Simple and efficient copper metal-mediated synthesis of alkoxyamine initiators

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Synthesis of ethyl 2-methyl-2-[*N*-tert-butyl-*N*-(1-diethoxyphosphoryl-2,2-di-methylpropyl)-aminoxy] propionate (A1) using Cu powder in DMSO. Synthesis followed the general procedure using SG1 (3.75 g, 10.8 mmol), ethyl 2-bromoisobutyrate (1.95 g, 10 mmol), Cu powder (635 mg, 10 mmol) and PMDETA (1.75 g, 10 mmol) in DMSO (20 mL). After 1 h, the reaction was dark blue and most copper had dissolved. The product was separated according to the general procedure, and purified by column chromatography on silica using 50% EtOAc/hexane as the eluent. Yield: 3.83 g (94%) as a colorless oil which crystallized on standing.

Synthesis of A1 using Cu wire in DMSO. Synthesis followed the general procedure using SG1 (1.88 g, 5.4 mmol), ethyl 2-bromoisobutyrate (0.98 g, 5 mmol), Cu wire (160mg, 2.5 mmol) and PMDETA (0.6 mL, 0.5 g, 2.9 mmol) in DMSO (10 mL). After 2 h, the mixture was diluted with 50 mL H_2O, and extracted with EtOAc (3 × 30 mL). The organic phase was washed with 10% HCl (3 × 30 mL), saturated $NaHCO_3$ (3 × 30 mL) and saturated NaCl (30 mL), then dried over $MgSO_4$. Solvent was removed on a rotary evaporator. The product was purified by column chromatography on silica using 50% EtOAc/hexane as the eluent. Yield: 1.88 g (91%) as a colorless oil which crystallized on standing.

Synthesis of A1 using Cu wire in EtOH. Synthesis and work up as in previous procedure, using EtOH (10 mL) as solvent. Yield: 1.76 g (85%) as a colorless oil which crystallized on standing.

**Synthesis of (1-[*N*-*tert*-butyl-*N*-(1-diethoxyphosphoryl-2,2-di-methylpropyl)aminoxy]-ethyl)

benzene (A2) with PMDETA as ligand. Synthesis followed the general procedure using SG1 (0.94 g, 2.7 mmol), (1-bromoethyl) benzene (0.463 g, 2.5 mmol), Cu wire (80mg, 1.25 mmol) and PMDETA (0.3 mL, 0.25 g, 1.5 mmol) in MeCN (5 mL). After 6 h, the product was separated according to the general procedure and purified by column chromatography on silica using 50% EtOAc/cyclohexane as the eluent. Yield: 0.546 g (55%) as a colorless oil containing a mixture of diastereomers.

Synthesis of 2-methyl-2-[*N*-tert-butyl-*N*-(1-diethoxyphosphoryl-2,2-di-methylpropyl)-aminoxy] propionic acid (A4) with PMDETA as ligand. Synthesis followed the general procedure using SG1 (0.94 g, 2.7 mmol), 2-bromo-2-methyl propionic acid (0.418 g, 2.5 mmol), Cu powder (160 mg, 2.5 mmol) and PMDETA (0.6 ml, 0.5 g, 3 mmol) in MeCN (5 mL). After 16 h, most copper had dissolved and a green precipitate had formed. The mixture was diluted with 50 mL 1M NaOH. The aqueous phase was washed with Et_2O (3 × 30 mL), then acidified with conc. HCl and extracted with CH_2Cl_2 (3 × 30 ml). The organic phase was dried over $MgSO_4$ and solvent was removed on a rotary evaporator. Yield: 0.522 g (55%) as a white crystalline solid.