

Supplementary Materials for Chemical Communications

Magnetically separable phase-transfer catalysts

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Materials

(3-Iodopropyl)trimethoxysilane was synthesized from (3-chloropropyl)trimethoxysilane according to the literature method.¹ Chloromethyl-polystyrene resin (1% cross-linked, 1.87 mmol Cl/g, 75-150 μm) was purchased from Argonaut.

Representative procedure for preparation of 1

(3-Iodopropyl)trimethoxysilane (5.80 g, 20.0 mmol) and tri-*n*-pentylamine (4.55 g, 20.0 mmol) were dissolved in toluene (10 ml). The mixture was heated at 120 °C for 36 h. After cooling to room temperature, the mixture was concentrated under reduced pressure. The residual viscous oil was washed three times with ether/hexane (1/1) and three times with hexane, and dried *in vacuo*. The ammonium salt **1c** was obtained as a pale yellow oil in 74% yield. ¹H NMR (499 MHz, CDCl₃): δ = 0.76 (t, 2H, *J* = 7.3 Hz), 0.94 (t, 9H, *J* = 7.3 Hz), 1.36-1.45 (m, 12H), 1.66-1.84(m, 8H), 3.30-3.41 (m, 8H), 3.59 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ = 5.5, 10.1, 16.3, 22.1, 22.3, 28.5, 50.9, 59.5, 60.6. MS (FAB+) 390 ([M-I]). Anal. Calc. for C₂₁H₄₈INO₃Si: C, 48.73; H, 9.35; N, 2.71. Found: C, 48.72; H, 9.34; N, 2.64.

Representative procedure for preparation of 2

(3-Iodopropyl)trimethoxysilane (2.90 g, 10.0 mmol) and triphenylphosphine (2.62 g, 10.0 mmol) were dissolved in toluene (10 ml). The mixture was heated at 80 °C for 24 h. After cooling to room temperature, the supernatant was removed, and the crude phosphonium salt was precipitated into CH₂Cl₂/hexane (1/4). The precipitation was washed with toluene and three times with ether, and dried *in vacuo*. The phosphonium salt **2g** was obtained as a white solid in 80% yield. ¹H NMR (499 MHz, CDCl₃): δ = 1.10 (t, 2H, *J* = 7.6 Hz), 1.74-1.86 (m, 2H),

3.53 (s, 9H), 3.63-3.74 (m, 2H), 7.68-7.87 (m, 15H). ^{13}C NMR (125 MHz, CDCl_3): δ = 10.1 (d, $J_{p-} = 16.6$ Hz), 16.7 (d, $J_{p-} = 3.1$ Hz), 24.9 (d, $J_{p-} = 48.5$ Hz), 50.8, 118.1 (d, $J_{p-} = 85.8$ Hz), 130.6 (d, $J_{p-} = 12.4$ Hz), 133.7 (d, $J_{p-} = 9.3$ Hz), 135.2 (d, $J_{p-} = 2.0$ Hz). ^{31}P NMR (202 MHz, CDCl_3): δ = 23.3. MS (FAB+) 425 ([M-I]). Anal. Calc. for $\text{C}_{24}\text{H}_{30}\text{IO}_3\text{PSi}$: C, 52.18; H, 5.47. Found: C, 52.24; H, 5.37.

Typical procedure for preparation of magnetically separable catalysts 3-4

A mixture of magnetite nanoparticles (11.6 g, 50.0 mmol), **1c** (5.18 g, 10.0 mmol), H_2O (0.7 ml), and EtOH (100 ml) was ultra-sonicated for 1 min and then stirred at refluxing temperature for 12 h. After cooling to room temperature, the magnetic particles were separated by magnetic decantation using an external magnet and washed five times with EtOH. After drying under reduced pressure, 10.5 g of **3c** was obtained as a dark brown powder. The catalyst loading was determined to be 0.142 mmol/g by halogen quantitative analysis.

Preparation of PS-resin supported catalyst 5c

Preparation of **5c** was performed according to the slightly modified literature method.² A mixture of 1.0 g of chloromethyl-polystyrene resin (Argonaut, 1% cross-linked, 1.87 mmol Cl/g, 75-150 μm), tri-*n*-pentylamine (1.22 g, 5.35 mmol), DMF (10 ml) was stirred at 90 $^\circ\text{C}$ for 4 days. The polymer beads were filtered and washed with EtOH, and extracted with EtOH for 12 h in a Soxhlet apparatus. After drying under reduced pressure, 503 mg of **5c** was obtained. The catalyst loading was determined to be 0.977 mmol/g by elemental microanalysis of nitrogen.

Typical procedure for *O*-alkylation reaction of sodium phenoxide

In a 5 ml sealed tube with a Teflon plug, a mixture of 3 mol% catalyst, sodium phenoxide trihydrate (128 mg, 0.750 mmol), *n*-tetradecane (20 μl), toluene (1 ml), H_2O (1 ml), and 1-bromobutane (0.12 ml, 1.13 mmol) was stirred at 100 $^\circ\text{C}$ for 12 h. After cooling to room temperature, yield was determined by GC [column: GL-SCIENCE, TC-WAX (0.25 mm \times 60 m)] using *n*-tetradecane as an internal standard.

Typical procedure for halogen exchange reaction

In a 5 ml round bottom flask, a mixture of 3 mol% catalyst, NaI (562 mg, 3.75 mmol), 1-iodooctane (145 mg, 0.750 mmol), *n*-tetradecane (20 μl), toluene (1 ml), and H_2O (1 ml) was

stirred at 100 °C for 6 h. After cooling to room temperature, yield was determined by GC [column: FRONTIER LAB, UA⁺-1 (0.25 mm × 30 m)] using *n*-tetradecane as an internal standard.

References

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