N-Heterocyclic Carbenes as Versatile Nucleophilic Catalysts for Transesterification/Acylation Reactions

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Supporting Information

General Information

- All esters and alcohols (Aldrich) were degassed or used as received. THF (anhydrous, Aldrich) was distilled under argon from sodium benzophenone ketyl. Potassium *tert* butoxide and sodium hydride (Aldrich) were stored under argon in a MBraun glovebox. Flash chromatography was performed on silica gel 60 (230-400 mesh) (Natlant International Corporation) using hexanes or 10% ethyl acetate/hexanes.
- *N*-heterocyclic carbenes were synthesized according to literature procedures: Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, A.; Hugh, A.; Goerlich, J. R.; William, J. M.; Unverzagt, M. *Tetrahedron*, **1999**, 55, 14523-14534; Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, 361-363; Arnold, P. L.; Cloke, F. G. N.; Geldbach, T.; Hitchcock, P. B. *Organometallics* **1999**, 18, 3228-3233; Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. J. *J. Am. Chem. Soc.* **1994**, 116, 4391-4393; Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, 17, 3375-3382.
- ¹H and ¹³C NMR spectra were recorded on a Varian-300 or Varian-400 MHz spectrometer at ambient temperature in CDCl₃ (Cambridge Isotope Laboratories, Inc.).
- All reactions were carried out under an atmosphere of argon in screw cap vials with magnetic stirring, unless otherwise indicated.
- The identity of every product was confirmed by comparison with literature spectroscopic data: **3**,¹ **6**,² **8**,³ **10**,⁴ **14**,⁵ **16**,⁵ **18**.⁵

Transesterification of Esters with Alcohols.

Procedure A. *Esterification of Vinyl acetate with Alcohols.* Under an atmosphere of argon, 1 mL of THF, 1 mmol of alcohol and 1.2 mmol of vinylacetate was added sequentially to a screw cap vial loaded with 0.5 mol% catalyst. The resulting mixture was stirred at room temperature for the indicated time; the solvent and ester excess were evaporated and the residue was purified flash chromatography using 10% ethylacetate/hexanes.

Procedure B. *Esterification of Methyl acetate/Ethyl acetate with Alcohols.* Under an atmosphere of argon, 1 mL of methyl acetate (ethyl acetate) and 1 mmol of alcohol was added sequentially to a screw cap vial loaded with 2.5 mol% catalyst and 0.5 g 4 Å (5 Å for ethyl acetate) molecular sieves. The resulting mixture was stirred at room temperature for the indicated time; the acetate was evaporated and the residue was purified flash chromatography using 10% ethyl acetate/hexanes.

Procedure C. *Esterification of Methyl Esters with Benzyl Alcohol.* Under an atmosphere of argon, 1 mL of THF and 2 mmol of benzyl alcohol was added sequentially to a screw cap vial loaded with 2.5 mol% catalyst and 0.5 g molecular sieves. The resulting mixture was stirred at room temperature for the indicated time; the solvent was evaporated and the residue was purified flash chromatography using 10% ethyl acetate/hexanes.

Benzyl dimethoxyacetate (12) (Table 2, entry 6): ^1H NMR: (400 MHz, CDCl_3) 3.41 (s, 6H), 4.84 (s, 1H), 5.24 (s, 2H), 7.34-7.4 (m, 5H). ^{13}C NMR: (400 MHz, CDCl_3) 167, 135.4, 128.8, 128.6, 99, 67.2, 54. Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_4$: C, 64.13; H, 6.71; O, 30.44. Found: C, 62.8; H, 6.62; O, 30.58.

Benzyl acrylate (21) (Table 2, entry 12): ^1H NMR: (300 MHz, CDCl_3) 5.21 (s, 2H), 5.84 (d, 1H, $J_{\text{H-H}} = 9$ Hz), 6.18 (q, 1H, $J_{\text{H-H}} = 9$ Hz), 6.46 (d, 1H, $J_{\text{H-H}} = 18$ Hz), 7.37 (m, 5H). ^{13}C NMR: (300 MHz, CDCl_3) 166.1, 136, 131.2, 128.7, 128.4 (br), 128.39, 128.36, 66.44.

11-bromo-undecenyl methacrylate (26) (Scheme 4) (300 MHz, CDCl₃) 1.26 (m, 11H), 3.37 (t, 2H, J_{H-H} = 9 Hz), 4.11 (t, 2H, J_{H-H} = 6 Hz), 5.51 (s, 1H), 6.07 (s, 1H). ¹³C NMR: (300 MHz, CDCl₃) 168, 137, 125.3, 65, 34.1, 33, 29.6, 29.4, 28.8, 28.3, 26.1, 18.5.

¹ Aldrich Library, **1** (2), 1201B.

² Aldrich Library, **1** (1), 998B.

³ Aldrich Library, **1** (2), 1201B.

⁴ D'Sa, B.; Verkade, J. G. *J. Org. Chem.* **1996**, *61*, 2963-2966.

⁵ Kissling, R. M.; Gagné, M. R. *Org. Lett.* **2000**, *2*, 4209-4212.