Transesterification/Acylation of Secondary Alcohols Mediated by *N*-Heterocyclic Carbene Catalysts

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Supporting information

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General Information

- All esters and alcohols were degassed prior to use or used as recieved. THF (anhydrous) was distilled under argon from sodium benzophenone ketyl. Potassium *tert* butoxide and sodium hydride were stored under argon in a glovebox. Flash chromatography was performed on silica gel 60 (230-400 mesh) 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.; Kraftczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375-3382.
- ^{1}H and ^{13}C NMR and spectra were recorded on a 400 MHz spectrometer at ambient temperature in $CDCl_3$.
- 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:

  Table 1 – entries 3[1],4[1],5[1],7[2],8[3]

  Table 2 – entries 1[4], 2[5]

  Table 3 – entries 2[6],3[7],4[8]

  Table 5[9]

  Scheme 1[10]

Transesterification of Esters with Alcohols.

Procedure A. *Esterification of Alcohols with Methyl/Ethyl acetate.* Under an atmosphere of argon 1 mmol alcohol and 1 ml methylacetate or ethyl acetate was added sequentially to a screw cap vial loaded with 5 mol% N,N-dicyclohexyl imidazole-2-ylidene (ICy) and 0.5 g of 4Å molecular sieves (5 Å for ethyl acetate). The resulting mixture was stirred at room temperature for the indicated time; the solvent (methyl acetate) excess was evaporated and the residue was purified by flash chromatography using ethylacetate/hexanes mixtures.

Procedure B. *Esterification of Alcohols with in situ Generation of Catalyst.* Same procedure is followed for both catalyst precursors. Under an atmosphere of argon, 1 ml of methyl acetate was added to a screw cap vial loaded with indicated amounts of imidazolium salt and base. The mixture is stirred for 15 minutes. 1 mmol alcohol and 0.5 g of 4Å molecular sieves were then added. The resulting mixture was stirred at room temperature for the indicated time; the solvent (methyl acetate) excess was evaporated and the residue was purified by flash chromatography using ethylacetate/hexanes mixtures.

Procedure C. *Esterification of Diol with Vinyl Benzoate.* Under an atmosphere of argon 1 mmol diol and 0.9 mmol of vinyl benzoate were added sequentially to a screw cap vial loaded with 5 mol% N,N-dicyclohexyl imidazole-2-ylidene and THF. The resulting mixture was stirred at room temperature for the indicated time; the solvent (methyl acetate) excess was evaporated and the residue was purified by flash chromatography using ethylacetate/hexanes mixtures.

Acetic acid 1-(4-fluoro-phenyl)-ethyl ester (Table 1, entry 6) $C_{10}H_{11}FO_2$, MW = 182.19 g mol^{-1}

^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 1.52 (d, *J=5.86 Hz.* 3H); 2.06 (s, 3H); 5.86 (q, *J=6.84 Hz.* 1H); 7.03 (t, *J=8.79 Hz.* 2H); 7.33 (t, J=8.79 Hz. 2H).

^{13}C NMR: (400 MHz, $CDCl_3$, ppm) δ 21.2, 22.1, 71.5, 115.2, 115.4, 127.9, 135.2, 171.2.
MS (ESI) *m/z* 182(M^+)

Acetic acid indan-1-yl ester (Table 3, entry 1) $C_{11}H_{12}O_2$,MW = 176.21 g mol^{-1}

^{1}H NMR: (400 MHz, $CDCl_3$, ppm) δ 2.06 (s, 3H); 2.11(m, *J=8.79 Hz.* 1H); 2.51 (m, *J=8.79 Hz.* 3H); 2.88 (m, *J=8.79 Hz.* 1H); 3.11 (m, *J=8.79 Hz.* 1H); 6.205 (t, *J=3.91 Hz.* 1H); 7.24 (m, 4H).

^{13}C NMR: (400 MHz, $CDCl_3$, ppm) δ 21.2, 30.1, 32.2, 78.3, 124.8, 125.5, 126.7, 171.1.

MS (ESI) *m/z* 176(M^+)

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