

Supporting Information

Zwitterionic Salts as Mild Organocatalysts for Transesterification

Kazuaki Ishihara,* Masatoshi Niwa, and Yuji Kosugi

Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

E-mail: ishihara@cc.nagoya-u.ac.jp

Table of Contents

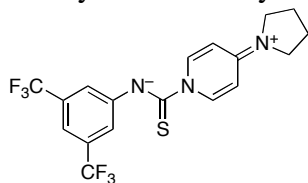
Experimental Procedures and Analytical Data	S2
--	-----------

Appendix (¹H and ¹³C NMR spectra)

Catalyst 1	S6
Ester S1	S7
Ester S2	S8
Ester S3	S9
Ester S4	S10
Ester S5	S11
Ester S6	S12
Ester S7	S13
Ester S8	S14
Ester S9	S15
Ester S10	S16
Ester S11	S17
Ester S12	S18
Ester S13	S19
Ester S14	S20

General Methods. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^1H NMR spectra were measured on Varian Gemini-2000 (300 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on Varian Gemini-2000 (75 MHz), VXR 500 (125 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuteriochloroform at 77.00 ppm). Melting points were determined using a Yanaco MP-J3. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plate (silica gel 60 GF254 0.25 mm) was used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385). Microanalyses were performed at the Graduate School of Agriculture, Nagoya University. High resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Center, Nagoya University. In experiments that required dry solvent, ether, *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from TCI or Wako as the “anhydrous” and stored over 4Å and 5Å molecular sieves. Benzene, hexane, toluene, and dichloromethane were freshly distilled from calcium hydride. Other simple chemicals were analytical-grade and obtained commercially.

Preparation of (Z)-*N*-[3,5-Bis(trifluoromethyl)phenyl]-4-(pyrrolidinium-1-ylidene)pyridine-1(4H)-carbimidothioate (1) (Scheme 1). To a solution of 3,5-Bis(trifluoromethyl)phenyl isothiocyanate (**6**) (0.92 mL, 5 mmol) in toluene (10 mL) was added PPY (0.74 g, 5 mmol) at ambient temperature. Immediately, **1** was precipitated as yellow solid. Pure **1** was obtained as yellow crystals in 92% yield by recrystallization from a hot solution of **1** in toluene.

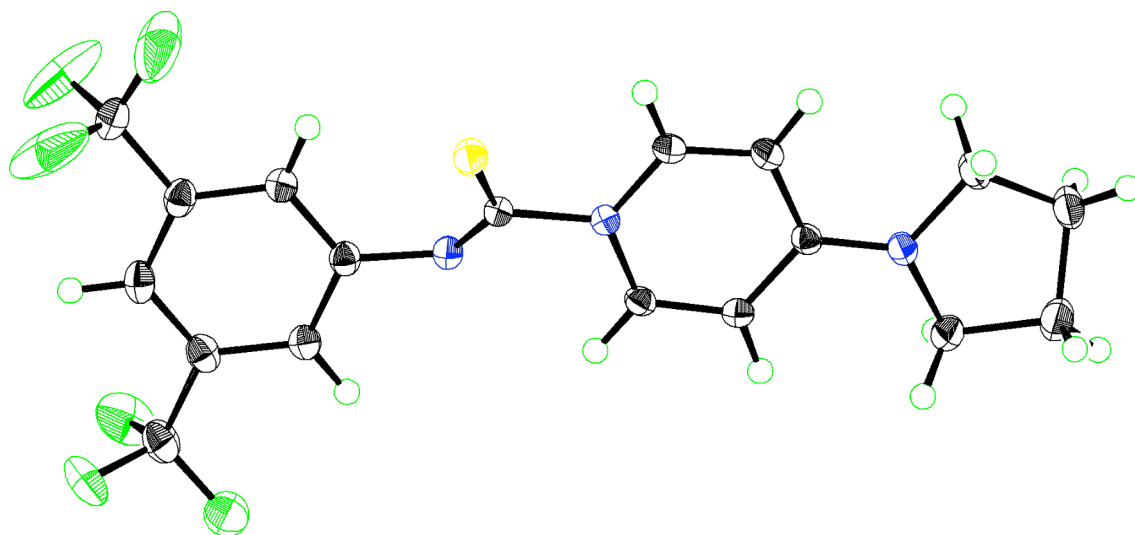


Mp. 120 °C; IR (KBr) 3448, 1641, 1567, 1541, 1508, 1376, 1164, 1119, 1082, 984 cm^{-1} ; ^1H NMR (a 3:2:2 equilibristic mixture of **1**, **6** and PPY, CD_3CN , 300 MHz) δ 2.05–2.09 (m, 4H), 3.52–3.56 (m, 4H), 6.67 (d, 2H, $J = 8.0$ Hz), 7.59 (s, 1H), 7.81 (s, 2H), 9.55 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (a 3:2:2 equilibristic mixture of **1**, **6** and PPY, CD_3CN , 75 MHz) δ 25.8 (2C), 49.7 (2C), 106.9 (2C), 116.2, 123.9 (q, 2C, $J = 270$ Hz), 124.3 (2C), 131.7 (q, 2C, $J = 32$ Hz), 139.0 (2C), 154.9, 156.1, 172.3. Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{F}_6\text{N}_3\text{S}$: C, 51.55; H, 3.61; N, 10.02; S, 7.65. Found: C, 51.41; H, 3.61; N, 9.75.

X-ray Crystallographic Analysis of 1: The yellow solid of **1** was recrystallized from toluene to obtain a yellow crystal at room temperature. Crystal data: $\text{C}_{18}\text{H}_{15}\text{F}_6\text{N}_3\text{S}$, $M = 419.39$, crystal dimensions $0.30 \times 0.30 \times 0.20 \text{ mm}^3$, monoclinic, space group $P21/c$, $a = 13.136(6)$, $b = 8.069(4)$, $c = 16.960(8) \text{ Å}$, $V = 4368(3) \text{ Å}^3$, $Z = 4$, $D_c = 1.572 \text{ g/cm}^3$, $\mu = 0.252 \text{ mm}^{-1}$, $T = 123 \text{ K}$. X-ray crystallographic analysis was performed with a Bruker SMART APEX diffractometer (graphite monochromator, $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ Å}$). The structure was solved by direct

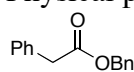
methods and expanded using Fourier techniques. 4407 reflections were independent and unique, and 253 with $I > 2\sigma(I)$ ($2\theta_{\max} = 29.21^\circ$) were used for the solution of the structure. $R = 0.0588$ and $R_w = 0.1585$.

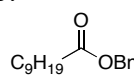
Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC-673714. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

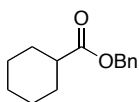


General Procedure for the Transesterification Reaction Catalyzed by 6 and PPY (Table 4). The reaction mixture of methyl carboxylate (5 mmol) and alcohol (5 mmol) in hydrocarbons (3 mL) was heated under azeotropic reflux conditions with the removal of methanol. Methanol was removed through a pressure-equalized addition funnel containing a cotton plug and 5 Å molecular sieves (pellets) and functioning as a Soxhlet extractor. After heating for 24 hours, the reaction mixture was allowed to cool to ambient temperature. And then, the resultant mixture was concentrated in vacuo, and the crude product was purified by column chromatography on silica gel with hexane–ethyl acetate as eluents.

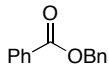
Physical properties of ester products (Tables 1–4) are as follows:

 **Benzyl 2-Phenylacetate (S1) (Tables 1 and 3, commercially available):**¹ ¹H NMR (300 MHz, CDCl₃) δ 3.67 (s, 2H), 5.13 (s, 2H), 7.25–7.40 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 40.9, 66.2, 126.8 (2C), 127.8, 127.9, 128.2 (2C), 128.3 (2C), 129.0 (2C), 133.7, 135.6, 171.0.

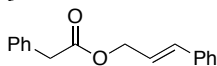
 **Benzyl Decanoate (S2) (Tables 1 and 4, commercially available):**² ¹H NMR (CDCl₃, 300 MHz) δ 0.88 (t, 3H, $J = 6.6$ Hz), 1.20–1.40 (m, 12H), 1.58–1.70 (m, 2H), 2.35 (t, 2H, $J = 7.5$ Hz), 5.11 (s, 2H), 7.28–7.39 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 13.8, 22.4, 24.6, 28.8, 29.0 (2C), 29.2, 31.6, 33.9, 65.6, 127.7, 127.8 (2C), 128.1 (2C), 136.0, 173.0.



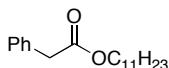
Benzyl Cyclohexanecarboxylate (S3) (Tables 1 and 4):³ ¹H NMR (CDCl₃, 300 MHz) δ 1.19–1.96 (m, 10H), 2.35 (tt, 1H, *J* = 3.6, 11.1 Hz), 5.11 (s, 2H), 7.29–7.40 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 25.0 (2C), 25.3, 28.6 (2C), 42.6, 65.3, 127.5 (2C), 127.6, 128.0 (2C), 136.0, 175.1.



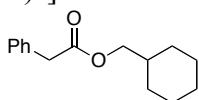
Benzyl Benzoate (S4) (Tables 1 and 4, commercially available):^{1,3,4} ¹H NMR (300 MHz, CDCl₃) δ 5.37 (s, 2H), 7.31–7.59 (m, 8H), 8.05–8.12 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 66.5, 128.0 (2C), 128.1, 128.2 (2C), 128.4 (2C), 129.5 (2C), 129.9, 132.9, 135.9, 166.2.



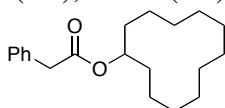
Cinnamyl 2-Phenylacetate (S5) (Tables 2 and 4, commercially available):⁵ ¹H NMR (CDCl₃, 300 MHz) δ 3.67 (s, 2H), 4.74 (dd, 2H, *J* = 1.2, 6.3 Hz), 6.24 (dt, 1H, *J* = 6.3, 15.9 Hz), 6.56 (d, 1H, *J* = 15.9 Hz), 7.22–7.38 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 40.9, 64.9, 122.7, 126.3 (2C), 126.8, 127.7, 128.2 (4C), 129.0 (2C), 133.6, 133.7, 135.8, 170.8.



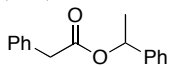
Undecyl 2-Phenylacetate (S6) (Tables 2 and 4): IR (film) 2925, 2854, 1738, 1496, 1455, 1254, 1158 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, 3H, *J* = 6.2 Hz), 1.18–1.40 (m, 16H), 1.60 (quintet, 2H, *J* = 6.6 Hz), 3.61 (s, 2H), 4.08 (t, 2H, *J* = 6.6 Hz), 7.20–7.38 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 13.8, 22.4, 25.5, 28.3, 28.9, 29.1, 29.2, 29.3, 29.4, 31.6, 41.0, 64.4, 126.6, 128.1 (2C), 128.9 (2C), 133.9, 170.9. HRMS(FAB) calcd for C₁₉H₃₁O₂ [(M+H)⁺] 291.2324. Found: 291.2335.



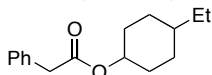
Cyclohexylmethyl 2-Phenylacetate (S7) (Tables 2 and 4):⁶ ¹H NMR (300 MHz, CDCl₃) δ 0.86–0.92 (m, 2H), 1.11–1.29 (m, 3H), 1.55–1.73 (m, 6H), 3.62 (s, 2H), 3.90 (d, 2H, *J* = 6.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 25.5 (2C), 26.2, 29.4 (2C), 36.9, 41.3, 69.9, 126.9, 128.4 (2C), 129.1 (2C), 134.1, 171.6.



Cyclododecyl 2-Phenylacetate (S8) (Table 2):⁷ ¹H NMR (300 MHz, CDCl₃) δ 1.32–1.53 (m, 20H), 1.65–1.74 (m, 2H), 3.57 (s, 2H), 5.01 (tt, 1H, *J* = 4.8, 7.2 Hz), 7.20–7.33 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 20.6 (2C), 23.0 (2C), 23.2 (2C), 23.6, 23.8 (2C), 28.8 (2C), 41.5, 72.4, 126.7, 128.3 (2C), 129.0 (2C), 134.2, 171.1.

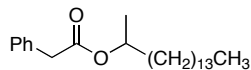


1-Phenylethyl 2-Phenylacetate (S9) (Table 4):⁸ ¹H NMR (300 MHz, CDCl₃) δ 1.51 (d, 3H, *J* = 6.6 Hz), 3.64 (s, 2H), 5.89 (q, 1H, *J* = 6.6 Hz), 7.24–7.34 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 22.1, 41.5, 72.6, 125.9 (2C), 126.9, 127.7, 128.3 (2C), 128.4 (2C), 129.2 (2C), 133.9, 141.4, 170.6.

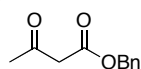


4-Ethylcyclohexyl 2-Phenylacetate (S10) (Table 4): IR (film) 2936, 2857, 1733, 1496, 1454, 1259, 1164, 1019 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.84–1.97 (m, 14H), 3.58 and 3.61 (s, 2H, trans and cis isomers), 4.67 and 4.96–5.02 (tt and m, 1H, *J* = 4.5, 11.1 Hz, trans and cis isomers), 7.23–7.34 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 11.1 and 11.3 (cis and

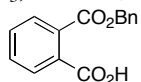
trans isomers), 26.6 and 30.2 (2C, cis and trans isomers), 28.8, 29.2 and 31.2 (2C, cis and trans isomers), 37.7 and 38.0 (cis and trans isomers), 41.3 and 41.6 (trans and cis isomers), 70.2 and 73.7 (cis and trans isomers), 126.6, 128.1 (2C), 128.8 and 128.9 (2C, trans and cis isomers), 134.1 and 134.2 (trans and cis isomers), 170.6. HRMS(FAB) calcd for C₁₆H₂₃O₂ [(M+H)⁺] 247.1698. Found: 247.1696.



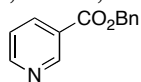
Hexadecan-2-yl 2-Phenylacetate (S11) (Table 4): IR (film) 2925, 2853, 1735, 1496, 1455, 1258, 1123 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, 3H, *J* = 6.8 Hz), 1.13–1.59 (m, 29H), 3.59 (2, 2H), 4.90 (sextet, 1H, *J* = 6.3 Hz), 7.22–7.35 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 14.0, 19.8, 22.6, 25.2, 29.3–29.6 (9C), 31.8, 35.8, 41.6, 71.2, 126.8, 128.3 (2C), 129.0 (2C), 134.2, 171.0. HRMS(FAB) calcd for C₂₄H₄₁O₂ [(M+H)⁺] 361.3107. Found: 361.3122.



Benzyl 3-Oxobutanoate (S12) (Table 4, commercially available):⁹ ¹H NMR (CDCl₃, 300 MHz) δ 2.25 (s, 3H), 3.50 (s, 2H), 5.28 (s, 2H), 7.30–7.40 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 29.4, 49.2, 66.3, 127.7 (2C), 127.8 (2C), 128.0, 135.0, 166.5, 200.0.



2-(Benzyloxycarbonyl)benzoic Acid (S13) (Table 4, commercially available):¹⁰ ¹H NMR (CDCl₃, 300 MHz) δ 5.35 (s, 2H), 7.22–7.36 (m, 3H), 7.38–7.43 (m, 2H), 7.51–7.62 (m, 2H), 7.68–7.72 (m, 1H), 7.87–7.92 (m, 1H), a proton of CO₂H was not assigned; ¹³C NMR (75 MHz, CDCl₃) δ 68.4, 129.2 (2C), 129.37 (2C), 129.40, 130.0, 131.9, 132.3, 133.0, 133.6, 136.7, 169.5, 170.3.



Benzyl Nicotinate (S14) (Table 4, commercially available):^{4,11} ¹H NMR (300 MHz, CDCl₃) δ 5.49 (s, 2H), 7.36–7.47 (m, 6H), 8.32 (dm, 1H, *J* = 7.8 Hz); 8.78 (dd, 1H, *J* = 1.5, 4.5 Hz); 9.27 (dd, *J* = 0.9, 2.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 66.8, 123.0, 125.7, 128.0 (2C), 128.2, 128.4 (2C), 135.2, 136.8, 150.7, 153.2, 164.7.

References

- (1) *Dictionary of Organic Compounds*, 4th Ed., Eyre and Spottiswoode Ltd., London, 1965.
- (2) Eliel, E.; Anderson, R. P. *J. Am. Chem. Soc.* **1952**, 74, 547–549.
- (3) Ishihara, K.; Nakayama, M.; Ohara, S.; Yamamoto, H. *Tetrahedron* **2002**, 58, 8179–8188.
- (4) Khan, K. M.; Maharvi, G. M.; Hayat, S.; Zia-Ullah, Choudhary, M. I.; Atta-ur-Rahman *Tetrahedron* **2003**, 59, 5549–5554.
- (5) Mukaiyama, T.; Toda, H.; Kobayashi, S. *Chem. Lett.* **1976**, 13–14.
- (6) Corina, D. L.; Isaac, K. *J. Chromatogr.* **1983**, 260, 51–62.
- (7) Yarchak, M. L.; Dalton, J. C.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1973**, 95, 5228–5233.
- (8) Saigo, K.; Usui, M.; Kikuchi, K.; Shimada, E.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, 50, 1863–1866.
- (9) Manz, O. *Justus Liebigs Ann. Chem.* **1974**, 345.
- (10) Node, M.; Nishide, K.; Sai, M.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1981**, 46, 1991–1993.
- (11) Barry, J.; Bram, G.; Petit, A. *Heterocycles* **1985**, 23, 875–880.