Supporting Information

A Chelation-Assisted Hydroesterification of Alkenes Catalyzed by Rhodium Complex

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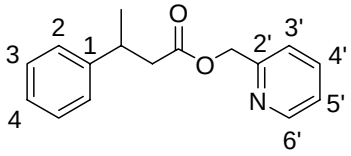
General Information. Boiling points (bp) refer to air bath temperatures for bulb- to -bulb distillation and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14B gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)). Preparative high performance liquid chromatography (HPLC) was performed on a Japan Analytical Industry LC-908 instrument, equipped with an RI absorbance detector.

Materials. Toluene and olefins were distilled over CaH_2. $Rh_4(CO)_{12}$ was purchased from Strem Chemical, Inc. and used without further purification. 2-Pyridinemethanol was distilled over CaO.

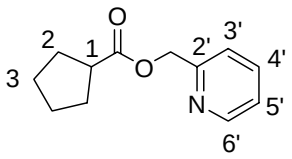
Typical procedure for Hydroesterification of Alkenes. 2-Pyridinemethanol (218mg, 2mmol), 1-hexene (505mg, 6mmol), $Rh_4(CO)_{16}$ (30mg, 0.04mmol) and toluene (1mL) were placed in a 50-mL stainless steel autoclave under N_2. The system was flushed with 10 atmosphere of CO three times. Finaly, it was pressurized to 3 atm. The autoclave was heated in an oil bath at 100 °C for 20 h, followed by cooling. CO was released. The contents were transfered to a round bottomed flask with toluene. The volatile compornents were removed in vacuo, and the residue was subjected to column chromatography on silica gel (eluent; hexane/ether = 3/1) to give a 6-heptanoic acid 2-pyridinylmethyl ester (397mg, 87 %) as a colorless oil.

Benzenepropanoic, β-Methyl-, acid 2-pyridinylmethyl ester. Colorless oil; bp 150 °C (7mmHg); ^{1}H NMR ($CDCl_3$) δ 1.34 (d, *J* = 6.9 Hz, 3H, CHC*H*$_3$), 2.68 (dd, *J* = 15.3 Hz, *J* = 8.1 Hz, 1H, COC*H*$_2$CH), 2.77 (dd, *J* = 15.2 Hz, *J* = 7.6 Hz, 1H, COC*H*$_2$CH), 3.34 (qdd, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 7.2 Hz, CH$_2$C*H*Ph), 5.16 (d, *J*= 13.5 Hz, 1H, C(O)OC*H*$_2$), 5.22 (d, *J*= 13.5 Hz, 1H, C(O)OC*H*$_2$), 7.07 (d, *J* = 7.9 Hz, 1H, 3'-H), 7.17-7.35 (c, 6H, Ar), 7.62 (•ddd, *J* = 7.7 Hz, *J* = 7.7 Hz, *J* = 1.8 Hz, 1H, 4'-H), 8.56-8.58 (m, 1H, 6'-H); ^{13}C NMR ($CDCl_3$) δ 21.99 (*C*H$_3$), 36.51 (CH$_2$*C*HPh), 42.72 (C(O)*C*H$_2$CH), 66.66 (C(O)O*C*H$_2$), 121.55 (3'-C), 122.71 (5'-C), 126.42 (4-C), 126.78 (2-C or 3-C), 128.52 (2-C or 3-C), 136.69 (4'-C), 145.47 (1-C), 149.33 (6'-C), 155.74 (2'-C), 171.98 (C=O); IR (neat) 3720 w, 3460 w, 2938 w, 2660 w, 2548 w, 2392 w,

2094 m, 1896 m, 1731 s, 1589 m, 1437 m, 1368 m, 1330 m, 1263 s, 1150 m, 1002 m, 987 m, 896 m, 752 m, 697 m, 632 m, 582 m, 402 w; MS, *m/z* (relative intensity, %) 255 (M^+, 1), 118 (19), 109 (54), 108 (28), 105 (29), 103 (10), 93 (100), 92 (21), 91 (18), 79 (15), 78 (14), 77 (15), 65 (25), 51 (15); Anal. Calcd for $C_{16}H_{11}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.08; H, 6.71; N, 5.53.

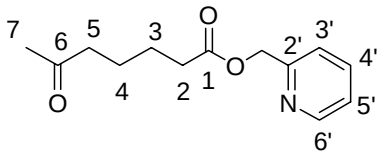


Cyclopentanecarboxylic acid, 2-pyridinylmethyl ester. Colorless oil; bp 110 °C (4 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.57-1.97 (c, 8H, 2-H, 3-H), 2.83 (tt, *J* = 8.0 Hz, *J* = 7.9 Hz, 1H, 1-H), 5.23 (s, 2H, OCH_2), 7.20-7.25 (m, 1H, 5'-H), 7.34 (d, *J* = 7.9 Hz, 1H, 3'-H), 7.70 (ddd, *J* = 7.7 Hz, *J* = 7.7 Hz, *J* = 1.9 Hz, 1H, 4'-H), 8.58-8.60 (m, 1H, 6'-H); ^{13}C NMR ($CDCl_3$) δ 25.78 (2-C or 3-C), 30.03 (2-C or 3-C), 43.68 (1-C), 66.61 (OCH_2), 121.50 (3'-C), 122.71 (5'-C), 136.70 (4'-C), 149.40 (6'-C), 156.12 (2'-C), 176.40 (C=O); IR (neat) 3784 w, 3694 w, 3600 w, 3352 w, 3194 w, 2944 m, 2716 w, 2600 w, 2458 w, 2282 w, 2136 m, 1964 m, 1875 m, 1730 s, 1589 s, 1436 s, 1347 s, 1292 s, 1254 s, 1175 s, 1144 s, 1040 m, 1001 s, 821 m, 747 s, 596 m, 488 w, 402 w, 333 w, 309 w ,288 w; MS, *m/z* (relative intensity, %) 206 (M^++1, 1), 164 (23), 110 (17), 109 (75), 108 (100), 93 (23), 92 (36), 78 (10), 69 (48), 67 (11), 65 (31), 55 (11); Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 72.12; H, 7.39; N, 6.82.

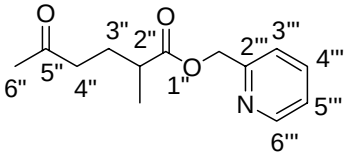


6-Oxo-heptanoic acid, 2-pyridinylmethyl ester (n) and 2-Methyl-5-oxo-hexanoic acid, 2-pyridinylmethyl ester (i).

Spectral data were obtained from a mixture of **n** and **i** :Colorless oil; bp 150 °C (6 mmHg); ^{1}H NMR ($CDCl_3$) **n**, δ 1.57-1.72 (m, 4H, 3-H, 4-H), 2.14 (s, 3H, CH_3), 2.38-49 •c, 4H, 2-H, 5-H), •5.24 (s, 2H, OCH_2), 7.24 (dd, *J* = 7.6 Hz, *J* = 5.3 Hz, 1H, 5'-H), 7.35 (d, *J* = 7.9 Hz, 1H, 3'-H), 7.71 (ddd, *J* = 7.6 Hz, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H, 4'-H), 8.59-8.61 (m, 1H, 6'-H); **i**, δ 1.23 (d, *J* = 6.9 Hz, 3H, 2"-Me), 1.70-1.98 (m, 2H, 3"-H), 2.13 (s, 3H, CH_3), 2.43-2.64 (•c, 3H, 2"-H, 4"-H), •5.24 (s, 2H, OCH_2),•other peaks were overlapped with the peaks of **n**; ^{13}C NMR ($CDCl_3$) **n**, δ 23.11 (3-C or 4-C), 24.30 (3-C or 4-C), 29.90 (CH_3), 33.90 (2-C), 43.21 (5-C), 66.75 (OCH_2), 121.83 (3'-C), 122.87 (5'-C), 136.78 (4'-C), 149.49 (6'-C), 155.76 (2'-C), 173.03 (*C*(O)O), 208.56 (*C*(O)CH_3); **i**, ^{13}C NMR ($CDCl_3$), δ 17.20, 27.31, 29.96, 38.61, 40.91 ($AcCH_2$), 66.70, 121.71,• other peaks were overlapped with the peaks of **n**; IR (neat) 3968 w, 3896 w, 3538 w, 3392 w, 2930 m, 2752 w, 2670 w, 2384 w, 2048 w, 1983 w, 1957 w, 1819 w, 1711 s, 1592 m, 1572 m, 1436 m, 1354 s, 1224 m, 1153 s, 991 m, 753 m, 646 w, 598 w, 525 w, 455 w, 403 w, 295 w; MS, *m/z* (relative intensity, %) **n**, 236 (M^+, 0), 192 (M^+-Ac, 19), 178 (15), 164 (17), 151 (39), 110 (80), 109 (92), 108 (100), 93 (31), 92 (82), 81 (15), 78 (13), 65 (48), 55 (37), 52 (13), 51 (14), **i**, 236 (M^+, 0), 192 (M^+-Ac, 8), 178 (35), 165 (68), 110 (46), 109 (78), 108 (97), 93 (33), 92 (100), 78 (13), 69 (22), 65 (51), 56 (18), 55 (26), 53 (10), 52 (13), 51 (14); Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.23; H, 7.36; N, 5.80.



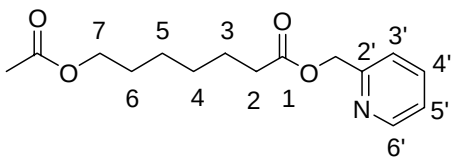
n



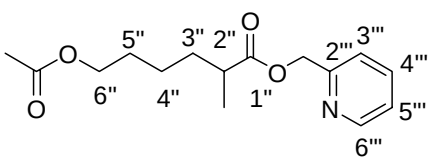
i

7-Acetoxy-heptanoic acid, 2-pyridinylmethyl ester (n) and 6-Acetoxy-2-methyl-hexanoic acid, 2-pyridinylmethyl ester (i).

Spectral data were obtained from a mixture of **n** and **i :**Colorless oil; bp 150 °C (7 mmHg); ^{1}H NMR ($CDCl_3$) **n**, δ 1.35-1.43 (c, 4H, 4-H, 5-H), 1.61-1.75 (c, 4H, 3-H, 6-H), 2.05 (s, 3H, CH_3) 2.44 (t, *J* = 7.4 Hz, 2H, 2-H), 4.05 (t, *J* = 6.6 Hz, 2H, 7-H), 5.24 (s, 2H, OCH_2), 7.22-7.27 (overlapped with $CHCl_3$, 1H, 5'-H), 7.35 (d, *J* = 7.9 Hz, 1H, 3'-H), 7.71 (•ddd, *J* = 7.8 Hz, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H, 4'-H), 8.60 (d, *J* = 4.3 Hz, 1H, 6'-H), **i**, δ 1.22 (d, *J* = 6.9 Hz, 3H, 2"-Me), 2.04 (s, 3H, CH_3), 2.51-2.59 (qt, 6.8 Hz, 6.9 Hz, 1H, 2"-H),• 4.04 (t, *J* = 6.6 Hz, 2H, 6"-H), other peaks were overlapped with the peaks of **n**; ^{13}C NMR ($CDCl_3$), **n**, δ 20.98 (CH_3), 24.72 (3-C or 6-C), 25.57 (4-C or 5-C), 28.38 (3-C or 6-C), 28.70 (4-C or 5-C), 34.02 (2-C), 64.40 (7-C), 66.69 (OCH_2) 121.78 (3'-C), 122.83 (5'-C), 136.73 (4'-C), 149.50 (6'-C), 155.86 (2'-C), 171.21 (C=O), 173.28 (C=O); **i**, δ 24.76 25.61 28.41 28.73 34.06 (2"-Me), 64.29 (6"-C), 66.72 (OCH_2), 173.33 (C=O), other peaks were overlapped with the peaks of **n**; IR (neat) 3484 w, 3342 w, 3144 w, 2926 w, 2602 w, 2432 w, 2376 w, 2284 w, 2144 w, 1917 w, 1878 w, 1728 s, 1592 m, 1572 w, 1537 w, 1435 m, 1365 m, 1235 s, 1150 s, 1094 m, 1034 m, 886 w, 756 m, 651 w, 606 w, 517 w, 427 w, 398 w, 329 w, 285 w; MS, *m/z* (relative intensity, %) **n**, 279 (M^+, 0), 236 (M^+-Ac, 2), 220 (14), 164 (14), 151 (47), 110 (54), 109 (100), 108 (99), 93 (21), 92 (53), 65 (21), 55 (51); **i**, 279 (M^+, 0), 236 (M^+-Ac, 2), 220 (11), 178 (17), 165 (49), 110 (36), 109 (69), 108 (100), 93 (25), 92 (46), 83 (13), 65 (28), 55 (67); Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.30; H, 7.49; N, 5.03.



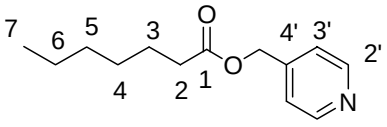
n



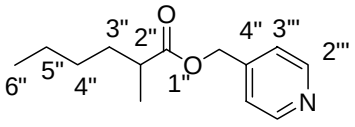
i

Heptanoic acid, 4-pyridinylmethyl ester (n) and 2-Methyl hexanoic acid, 4-pyridinylmethyl ester (i).

Spectral data were obtained from a mixture of **n** and **i** :Colorless oil; bp 130 °C (8 mmHg); ^{1}H NMR ($CDCl_3$) **n**, δ 0.89 (t, *J* = 6.6 Hz, 3H, 7-H), 1.27-1.39 (c, 6H, 4-H, 5-H, 6-H), 1.67 (•tt, *J* = 7.4 Hz, *J* = 7.3 Hz, 2H, 3-H), •2.41 (t, *J* = 7.6 Hz, 2H, 2-H), 5.13 (s, 2H, OCH_2), 7.25 (d, *J* = 5.9 Hz, 2H, 3'-H), 8.60 (d, *J* = 5.9 Hz, 2H, 2'-H); **i**, δ 1.20 (d, *J* = 6.9 Hz, 3H, 2"-Me), 2.54 (qt, *J* = 6.9 Hz, *J* = 6.9 Hz, 1H, 2"-H), other peaks were overlapped with the peaks of **n**; ^{13}C NMR ($CDCl_3$) δ 13.96 (7-C), 22.42 (4-C or 5-C or 6-C), 24.82 (3-C), 28.74 (4-C or 5-C or 6-C), 31.36 (4-C or 5-C or 6-C), 34.11 (2-C), 63.99 (OCH_2), 121.87 (3'-C), 145.14 (4'-C), 149.90 (2'-C), 173.31 (C=O); IR (neat) 3460 w, 3034 w, 2958 s, 2931 s, 2858 m, 1938, w, 1743 s, 1604 s, 1562 w, 1458 m, 1416 m, 1381 m, 1356 m, 1325 w, 1234 s, 1161 s, 1103 m, 1068 w, 993 m, 876 w, 798 m, 727 w, 581 w; MS, *m/z* (relative intensity, %) **n**, 221 (M^+, 0), 206 (M^+-Me, 1), 164 (19), 151 (13), 113 (20), 110 (12), 109 (100), 108 (19), 106 (23), 105 (14), 93 (53), 92 (65), 85 (11), 80 (11), 69 (14), 65 (34), 57 (15), 55 (29), 51 (10); **i**, 221 (M^+, 0), 178 (M^+-Pr, 11), 165 (37), 121 (12), 120 (75), 119 (16), 113 (24), 109 (48), 108 (13), 93 (62), 92 (100), 85 (72), 83 (11), 80 (14), 65 (66), 57 (44), 56 (22), 55 (46), 53 (15), 52 (20), 51 (21); HRMS (ESI-TOF): Anal. Calcd for $C_{13}H_{21}NO_2$ ($M+H^+$): 222.1494. Found 222.1466.



n



i