Supporting Information

Catalytic Cross-Coupling Reaction of Esters with Organoboron Compounds and Decarbonylative Reduction of Esters with HCOONH₄: A New Route to Acyl Transition Metal Complexes through the Cleavage of Acyl-Oxygen Bonds in

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General Information. Boiling points (bp) refer to air bath temperatures for bulb-to-bulb distillation and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded 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 and c = complex), coupling constant (Hz), integration, and interpretation. Peak assignments were made with the aid of COSY method. Infrared absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained with ionization voltages of 70 eV.

Materials. Toluene and olefins were distilled over CaH_2 under nitrogen. Dioxane was distilled over Na. $\text{Ru}_3(\text{CO})_{12}$ was prepared according to the literature procedure¹. Esters were prepared by the reactions of 2-pyridinemethanol and the corresponding acid chlorides, which were commercially available or prepared from carboxylic acids and SOCl_2 . Pentanedioic acid, ethyl 2-pyridinylmethyl ester was prepared from glutaric acid monoethyl ester which was prepared from glutaric anhydride and ethanol, with modifying the literature procedure². $\text{PhB}(\text{OH})_2$ and NaBPh_4 were purchased from Wako Pure Chemical Industries, Ltd. and Kanto Chemical Co. respectively and were used without further purification. Boronates were prepared from $\text{PhB}(\text{OH})_2$ and corresponding diol³. 9-BBN (0.5 M solution in THF) was purchased from Aldrich Chemical Co. Ammonium formate was purchased from Wako Pure Chemical Industries, Ltd.

Hexanoic acid, 2-pyridinylmethyl ester. Colorless oil; bp $114\text{ }^\circ\text{C}$ (5 mmHg); $R_f = 0.26$ (hexane/EtOAc = 3/1); ^1H NMR (CDCl_3) δ 0.89 (t, $J = 6.8$ Hz, 3H, CH_3), 1.27-1.37 (m, 4H, 4-H, 5-H), 1.62-1.73 (m, 2H, 3-H), 2.42 (t, $J = 7.6$ Hz, 2H, 2-H), 5.23 (s, 2H, OCH_2), 7.23 (dd, $J = 7.6$ Hz, $J = 4.9$ Hz, 1H, 5'-H), 7.34 (d, $J = 7.6$ Hz, 1H, 3'-H), 7.70 (td, $J = 7.7$ Hz, $J = 1.9$ Hz, 1H, 4'-H), 8.59 (d, $J = 4.0$ Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 13.9 (CH_3), 22.3 (4-C or 5-C), 24.6 (3-C), 31.2 (4-C

or 5-C), 34.1 (2-C), 66.6 (OCH₂), 121.7 (3'-C), 122.77 (5'-C), 136.7 (4'-C), 149.4 (6'-C), 155.9 (2'-C), 173.5 (C=O); IR (neat) 2924 m, 1735 s, 1588 s, 1437 s, 1376 s, 1159 s, 1095 s, 990 m, 831 m, 752 s, 597 m, 401 m; MS, *m/z* (relative intensity, %) 207 (M⁺, 0), 192 (M⁺-CH₃, 1) 164 (16), 151 (36), 110 (23), 109 (92), 108 (100), 93 (23), 92 (50), 78 (11), 65 (35), 55 (16), 51 (10). Anal. Calcd for C₁₂H₁₇NO₂: C, 69.54; H, 8.27; N, 6.76. Found C, 69.30; H, 8.17; N, 6.71.

Cyclohexanecarboxylic acid, 2-pyridinylmethyl ester. Colorless oil; bp 125 °C (3 mmHg); R_f = 0.21 (hexane/EtOAc = 4/1); ¹H NMR (CDCl₃) δ 1.15-1.38 (m, 2H, 3-H), 1.43-1.57 (m, 2H, 2-H), 1.66-1.68 (m, 2H, 4-H), 1.74-1.80 (m, 2H, 3-H), 1.94-1.99 (m, 2H, 2-H), 2.43 (tt, *J* = 11.2 Hz, *J* = 3.6 Hz, 1H, 1-H), 5.23 (s, 1H, OCH₂), 7.22 (dd, *J* = 7.3 Hz, *J* = 5.6 Hz, 1H, 5'-H), 7.33 (d, *J* = 7.6 Hz, 1H, 3'-H), 7.69 (td, *J* = 7.7 Hz, *J* = 1.9 Hz, 1H, 4'-H), 8.58-8.59 (m, 1H, 6'-H); ¹³C NMR (CDCl₃) δ 25.5 (3-C), 25.8 (4-C), 29.1 (2-C), 43.2 (1-C), 66.5 (OCH₂), 121.4 (3'-C), 122.6 (5'-C), 136.6 (4'-C), 149.3 (6'-C), 156.1 (2'-C), 175.5 (C=O); IR (neat) 3978 w, 3374 w, 2914 m, 2852 m, 2646 w, 2138 w, 1725 s, 1590 s, 1438 s, 1373 m, 1306 s, 1240 s, 1161 s, 1128 s, 1036 m, 910 w, 888 m, 750 m, 594 w, 527 w, 400 w; MS, *m/z* (relative intensity, %) 219 (M⁺, 0), 164 (11), 110 (28), 109 (100), 108 (94), 93 (23), 92 (31), 83 (21), 65 (24), 55 (70). Anal. Calcd for C₁₃H₁₇NO₂: C, 71.21; H, 7.81; N, 6.39. Found C, 70.97; H, 7.83; N, 6.42.

Tricyclo[3.3.1.1^{3,7}]decane-1-carboxylic acid, 2-pyridinylmethyl ester. White solid; mp 41-42 °C (12 mmHg); R_f = 0.34 (hexane/EtOAc = 3/1); ¹H NMR (CDCl₃) δ 1.73 (brs, 6H, 2-H), 1.96-1.97 (m, 6H, 4-H), 2.04 (brs, 3H, 3-H), 5.22 (s, 2H, OCH₂), 7.22 (dd, *J* = 6.9 Hz, *J* = 4.9 Hz, 1H, 5'-H),

7.32 (d, $J = 7.9$ Hz, 1H, 3'-H), 7.70 (td, $J = 7.7$ Hz, $J = 1.8$ Hz, 1H, 4'-H), 8.58 (d, $J = 4.6$ Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 28.0 (3-C), 36.5 (2-C or 4-C), 38.89 (2-C or 4-C), 40.8 (1-C), 66.3 (OCH_2), 121.0 (3'-C), 122.5 (5'-C), 136.6 (4'-C), 149.1 (6'-C), 156.3 (2'-C), 177.0 ($\text{C}=\text{O}$); IR (KBr) 3824 w, 3736 w, 3688 m, 3662 m, 3504 m, 3442 m, 3382 m, 3308m, 3178 m, 2902 s, 2846 s, 2572 m, 1986 m, 1908 m, 1833 m, 1723 s, 1590 s, 1475 m, 1451 s, 1360 m, 1320 m, 1261 s, 1220 s, 1178 m, 1146 m, 1099 m, 1074 s, 1044 m, 991 m, 760 m, 665 w, 591 w, 524 w, 400 w, 326 w ; MS, m/z (relative intensity, %) 271 (M^+ , 0), 215 ($\text{M}^+ - \text{C}_4\text{H}_8$, 1), 136 (17), 135 (43), 108 (100), 93 (20), 92 (15), 79 (23), 65 (14). Anal Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.17; H, 7.75; N, 5.15.

Benzeneacetic acid, 4-methoxy-, 2-pyridinylmethyl ester. Colorless oil; bp 156 °C (3 mmHg); $R_f = 0.29$ (hexane/EtOAc = 1/1); ^1H NMR (CDCl_3) δ 3.68 (s, 2H, $\text{CH}_2\text{C}(\text{O})\text{O}$), 3.80 (s, 3H, OCH_3), 5.24 (s, 2H, OCH_2), 6.85-6.89 (m, 2H, 2-H), 7.19-7.25 (m, 4H, 3-H, 3'-H, 5'-H), 7.66 (td, $J = 7.7$ Hz, $J = 1.9$ Hz, 4'-H), 8.58 (d, $J = 4.9$ Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 40.3 ($\text{CH}_2\text{C}(\text{O})\text{O}$), 55.3 (CH_3), 67.0 (OCH_2), 114.0 (3-C), 121.6 (3'-C or 5'-C), 122.8 (3'-C or 5'-C), 125.8 (1-C), 130.4 (2-C), 136.8 (4'-C), 149.4 (6'-C), 155.7 (2'-C), 158.7 (4-C), 171.5 ($\text{C}=\text{O}$); IR (neat) 2930 m, 2488 m, 1728 s, 1671 s, 1595 s, 1512 m, 1431 s, 1246 s, 1150 s, 1011 m, 816 m, 751 m, 603 w, 514 m; MS, m/z (relative intensity, %) 257 (M^+ , 3), 148 (100), 121 (42), 120 (16), 92 (16), 78 (15), 77 (12), 65 (17), 51 (11). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.73; H, 5.91; N, 5.47.

Benzeneacetic acid, 4-bromo-, 2-pyridinylmethyl ester. White solid; mp 49-52 °C (12 mmHg); $R_f = 0.16$ (hexane/EtOAc = 2/1); ^1H NMR (CDCl_3) δ 3.68 (s, 2H, $\text{CH}_2\text{C}(\text{O})\text{O}$), 5.23 (s, 2H, OCH_2),

7.16-7.25 (c, 4H, Ar, 3'-H, 5'-H), 7.44 (dt, $J = 8.6$ Hz, $J = 2.1$ Hz, 2H, Ar), 7.66 (ddd, $J = 7.8$ Hz, $J = 7.8$ Hz, $J = 1.8$ Hz, 1H, 4'-H), 8.57-8.59 (m, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 40.5 ($\text{CH}_2\text{C}(\text{O})$), 67.2 (CH_2), 121.2 (4-C), 121.7 (3'-C or 5'-C), 122.9 (3'-C or 5'-C), 131.1 (2-C or 3-C), 131.7 (2-C or 3-C), 132.6 (1-C), 136.8 (4'-C), 149.5 (6'-C), 155.4 (2'-C), 170.7 ($\text{C}=\text{O}$); IR (KBr) 3924 w, 3852 w, 3706 w, 3588 w, 3476 w, 3406 w, 2518 w, 2234 w, 2152 w, 1725 s, 1590 m, 1570 m, 1489 m, 1437 m, 1412 m, 1376 m, 1336 m, 1218 m, 1148 s, 1067 m, 1009 m, 974 m, 856 w, 799 m, 765 m, 746 m, 732 m, 670 w, 574 w, 518 w, 493 w, 399 w, 320 w; MS, m/z (relative intensity, %) 307 (M^+ for ^{81}Br , 8), 305 (M^+ for ^{79}Br , 8), 198 (98), 196 (100), 171 (37), 170 (11), 169 (72), 110 (94), 109 (14), 108 (25), 93 (18), 92 (96), 90 (65), 89 (64), 78 (14), 65 (71), 64 (14), 63 (32), 52 (17), 51 (27), 50 (14). Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{BrNO}_2$: C, 54.92; H, 3.95; N, 4.58; Br, 26.10. Found: C, 54.67; H, 3.89; N, 4.53; Br, 25.84.

Butanoic acid, 3, 3, -dimethyl-, 2-pyridinylmethyl ester. Colorless oil; bp 99 °C (5 mmHg); $R_f = 0.34$ (hexane/EtOAc = 3/2); ^1H NMR (CDCl_3) δ 1.05 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.32 (s, 2H, $^t\text{BuCH}_2$), 5.22 (s, 2H, OCH_2), 7.23 (dd, $J = 7.4$ Hz, $J = 4.8$ Hz, 1H, 5'-H), 7.37 (d, $J = 7.9$ Hz, 1H, 3'-H), 7.70 (td, $J = 7.7$ Hz, $J = 1.8$ Hz, 1H, 4'-H), 8.59 (d, $J = 4.6$ Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 29.7 ($\text{C}(\text{CH}_3)_3$), 30.9 ($\text{C}(\text{CH}_3)_3$), 47.8 ($^t\text{BuCH}_2$), 66.5 (OCH_2), 121.8 (3'-C), 122.7 (5'-C), 136.6 (4'-C), 149.3 (6'-C), 155.9 (2'-C), 171.7 ($\text{C}=\text{O}$); IR (neat) 3344 w, 2932 m, 1727 s, 1590 s, 1434 s, 1364 s, 1320 s, 1218 s, 1122 s, 991 m, 748 m, 597 w, 513 w, 400 w; MS, m/z (relative intensity, %) 207 (M^+ , 0), 192 ($\text{M}^+ - \text{Me}$, 3), 151 (62), 110 (47), 109 (94), 108 (100), 93 (23), 92 (57), 83 (11), 78 (10), 65 (43), 57 (60), 55 (19), 52 (12), 51 (13). Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{NO}_2$: C, 69.54; H, 8.21; N, 6.81. Found: C, 69.30; H, 8.21; N, 6.81.

Pentanedioic acid, ethyl 2-pyridinylmethyl ester. Colorless oil; bp 128 °C (3 mmHg); R_f = 0.21 (hexane/EtOAc = 1/1); ^1H NMR (CDCl_3) δ 1.23 (t, J = 7.1 Hz, 3H, CH_3), 1.98 (td, J = 7.4 Hz, J = 7.3 Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.37 (t, J = 7.4 Hz, 2H, $\text{CH}_2\text{C}(\text{O})$), 2.48 (t, J = 7.4 Hz, 2H, $\text{CH}_2\text{C}(\text{O})$), 4.11 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.21 (s, 2H, OCH_2), 7.21 (overlapped with CHCl_3 , 1H, 5'-H), 7.32 (d, J = 7.6 Hz, 1H, 3'-H), 7.68 (ddd, J = 7.7 Hz, J = 7.7 Hz, J = 1.5 Hz, 1H, 4'-H), 8.57 (d, J = 4.6 Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 14.2 (CH_3), 20.1 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 33.1 ($\text{CH}_2\text{C}(\text{O})$), 33.3 ($\text{CH}_2\text{C}(\text{O})$), 60.4 (OCH_2), 66.8 (OCH_2), 121.8 (3'-C), 122.9 (5'-C), 136.8 (4'-C), 149.5 (6'-C), 155.7 (2'-C), 172.6 ($\text{C}=\text{O}$), 172.9 ($\text{C}=\text{O}$); IR (neat) 2940 m, 2260 w, 1729 s, 1590 m, 1573 m, 1439 s, 1371 s, 1163 s, 1022 s, 839 w, 751 s, 587 w, 400 w; MS, m/z (relative intensity, %) 251 (M^+ , 0), 206 ($\text{M}^+ - \text{OEt}$, 20), 151 (48), 115 (11), 110 (25), 109 (99), 108 (100), 93 (23), 92 (83), 87 (24), 78 (11), 65 (41), 55 (26), 52 (10), 51 (10). Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 61.87; H, 6.76; N, 5.59.

Pentanoic acid, 4-oxo, 2-pyridinylmethyl ester. Colorless oil; bp 130 °C (3 mmHg); R_f = 0.33 (EtOAc); ^1H NMR (CDCl_3) δ 2.20 (s, 3H, CH_3), 2.70 (m, 2 H, $\text{CH}_2\text{C}(\text{O})$), 2.81 (m, 2H, $\text{CH}_2\text{C}(\text{O})$), 5.24 (s, 2H, OCH_2), 7.21-7.26 (m, 1H, 5'-H), 7.37 (d, J = 7.9 Hz, 1H, 3'-H), 7.71 (td, J = 7.7 Hz, J = 1.8 Hz, 1H, 4'-H), 8.57-8.60 (m, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 27.9 (CH_2), 29.8 (CH_3), 37.9 (CH_2), 66.9 (OCH_2), 121.7 (3'-C), 122.8 (5'-C), 136.8 (4'-C), 149.3 (6'-C), 155.7 (2'-C), 172.4 ($\text{C}(\text{O})\text{O}$), 206.5 ($\text{C}(\text{O})\text{CH}_3$); IR (neat) 3382 m, 2924 m, 1969 w, 1708 s, 1591 s, 1573 m, 1476 m, 1435 s, 1351 s, 1306 s, 1255 s, 1197 s, 1149 s, 1045 m, 991 m, 899 m, 757 m, 591 w, 508 w, 456 w,

401 w, 326 w, 291 w; MS, m/z (relative intensity, %) 207 (M^+ , 1), 164 (13), 110 (20), 109 (91), 108 (100), 99 (17), 93 (30), 92 (65), 78 (11), 65 (32), 55 (11), 52 (11), 51 (12). HRMS (ESI-TOF): Anal. Calcd for $C_{11}H_{13}NO_3Na$ ($M + Na^+$): 230.0793. Found: 230.0780.

2-Oxazolemethanol,4,5-dihydro-4,4-dimethyl-, benzeneacetate (14). Colorless oil; bp 141 °C (4 mmHg); R_f = 0.26 (hexane/EtOAc = 2/1); 1H NMR ($CDCl_3$) δ 1.29 (s, 6H, Me_2), 3.73 (s, 2H, CH_2), 3.98 (s, 2H, CH_2), 4.73 (s, 2H, CH), 7.28-7.33 (c, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ 28.2 (CH_3), 40.7 ($PhCH_2$), 58.5 ($C(O)OCH_2$), 67.4 (CMe_3), 79.4 (OCH_2), 127.1 (4-C), 128.4 (2 or 3-C), 129.2 (2 or 3-C), 133.3 (1-C), 160.3 ($C=N$), 170.7 ($C=O$); IR (neat) 3380 m, 3064 m, 3031 m, 2971 s, 2931 s, 2900 s, 2871 m, 1743 s, 1679 s, 1604 m, 1531 s, 1496 s, 1455 s, 1432 s, 1363 s, 1301 s, 1141 s, 1074 m, 1054 s, 1029 m, 983 s, 941 m, 881 w, 817 w, 761 m, 728 s, 705 s, 565 w, 532 w, 497 w, 472 w, 418 w; MS, m/z (relative intensity, %) 247 (M^+ , 30), 130 (52), 129 (69), 128 (17), 119 (15), 118 (100), 114 (26), 113 (13), 99 (34), 96 (27), 92 (18), 91 (80), 90 (14), 89 (12), 84 (17), 71 (10), 65 (37), 58 (16), 57 (21), 56 (13), 55 (15), 43 (18), 42 (36), 41 (44). HRMS: Anal. Calcd for $C_{14}H_{17}NO_3$: 247.1209 Found: 247.1202.

Benzeneacetic acid, α -2-propenyl-, 2-pyridinylmethyl ester (25). Colorless oil; bp = 130 °C (3 mmHg); R_f = 1H NMR ($CDCl_3$) δ 2.52-2.62 (m, 1H, $CHCH_2$), 2.83- 2.94 (m, 1H, $CHCH_2$), 3.77 (dd, J = 8.2 Hz, J = 6.9 Hz, 1H, $PhCH$), 4.93 (d, J = 10.2 Hz, 1H, H_c), 5.08 (dd, J = 17.1 Hz, J = 1.6 Hz, 1H, H_b), 5.74 (ddt, J = 16.8 Hz, J = 10.2 Hz, J = 6.9 Hz, 1H, H_a), 7.08 (d, J = 7.9 Hz, 1H, 3'-H), 7.18 (dd, J = 6.9 Hz, J = 4.9 Hz, 1H, 5'-H), 7.27-7.35 (c, 5 H, Ar), 7.60 (ddd, J = 7.6 Hz, J = 7.6 Hz, J = 1.6 Hz, 1H, 4'-H), 8.54 (d, J = 4.6 Hz, 1H, 6'-H); ^{13}C NMR ($CDCl_3$) δ 37.3 (CH_2CH), 51.3

(CH), 66.9 (OCH₂), 117.1 (=CH₂), 121.2 (3'-C), 122.6 (5'-C), 127.4 (4-C), 128.0 (2 or 3-C), 128.6 (2 or 3-C), 135.0 (CH=), 136.6 (4'-C), 138.2 (1-C), 149.2 (6'-C), 155.8 (2'-C), 172.9 (C=O); IR neat 3895 w, 3853 w, 3650 w, 3565 w, 3066 w, 3025 w, 2925 m, 2854 w, 1739 s, 1644 w, 1594 w, 1573 w, 1494 w, 1475 w, 1438 m, 1375 m, 1344 m, 1268 m, 1226 m, 1193 m, 1159 s, 1049 w, 995 m, 919 m, 754 m, 730 m, 700s, 551 w, 505 m, 468 m; MS, *m/z* (relative intensity, %) 267 (M⁺, 24), 226 (13), 158 (17), 148 (24), 132 (13), 131 (57), 130 (48), 129 (38), 128 (14), 118 (13), 116 (27), 115 (23), 110 (23), 109 (54), 108 (49), 103 (10), 93 (58), 92 (100), 91 (91), 90 (15), 89 (10), 78 (13), 77 (16), 65 (54), 53 (16), 52 (10), 51 (21), 41 (11); HRMS: Anal. Calcd for C₁₇H₁₇NO₂: 267.1259 Found: 267.1261.

2-Naphthalenecarboxylic acid, 2-pyridinediyl ester (37). White solid; mp 117-118 °C (5 mmHg); R_f = 0.24 (hexane/EtOAc = 4/1); ¹H NMR (CDCl₃) δ 7.18-7.23 (m, 2H, Ar), 7.46-7.58 (m, 2H, Ar), 7.78-7.93 (m, 4H, Ar), 8.13 (dd, *J* = 8.6 Hz, *J* = 1.6 Hz, 1H, Ar), 8.39-8.8.42 (m, 1H, 6'-H), 8.75 (s, 1H, Ar); ¹³C NMR (CDCl₃) δ 116.7 (Ar), 122.1 (Ar), 125.4 (Ar), 126.2 (Ar), 126.8 (Ar), 127.8 (Ar), 128.4 (Ar), 128.7 (Ar), 129.5 (Ar), 132.3(Ar), 132.4 (Ar), 135.9 (Ar), 139.5 (4'-C), 148.7 (6'-C), 158.2 (2'-C), 164.9 (C=O); IR (KBr) 3451 w, 3056 w, 1735 s, 1627 w, 1589 m, 1504 w, 1473 m, 1428 m, 1351 w, 1263 m, 1211 s, 1184 s, 1126 m, 1072 s, 1045 m, 993 w, 950 m, 921 w, 892 w, 858 w, 827 w, 802 w, 761 m, 563 w, 476 m, 414 w; MS, *m/z* (relative intensity, %) 249 (M⁺, 12), 156 (100), 127 (49); HRMS: Anal. Calcd for C₁₆H₁₁NO₂: 249.0790. Found: 249.9787.

Benzoic acid, 4-chloro-, 2-pyridinylmethyl ester (38m). White solid; mp 41-42 °C (5 mmHg); R_f = 0.34 (hexane/EtOAc = 2/1); ¹H NMR (CDCl₃) δ 5.45 (s, 2H, CH₂), 7.23 (dd, *J* = 6.6 Hz, *J* = 4.9

Hz, 1H, 5'-H), 7.38-7.43 (c, 3H, 3-H and 3'-H), 7.70 (ddd, $J=7.6$ Hz, $J=7.6$ Hz, $J=1.6$ Hz, 1H, 4'-H), 8.02 (dt, $J=8.6$ Hz, 2.3 Hz, 2H, 2-H), 8.60 (d, $J=4.0$ Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 67.4 (CH_2), 121.8 (3'-C), 123.0 (5'-C), 128.3 (1-C), 128.8 (3-C), 131.2 (2-C), 136.8 (4'-C), 139.7 (4-C), 149.6 (6'-C), 155.7 (2'-C), 165.4 (C=O); IR (KBr) 3149 w, 3060 w, 3008 w, 1727 s, 1594 s, 1481 m, 1452 m, 1432 m, 1400 m, 1373 m, 1282 s, 1249 s, 1174 s, 1124 s, 1091 s, 1047 m, 1010 s, 983 m, 885 m, 852 m, 754 s, 680 m, 626 w, 592 w, 526 m, 476 w; MS, m/z (relative intensity, %) 247 (M^+ , 0), 141 (11), 139 (35), 111 (22), 109 (11), 108 (100), 92 (11), 75 (14), 65 (13); Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{ClNO}_2$: C, 63.04; H, 4.07; N, 5.66. Found: C, 62.93; H, 4.19; N, 5.79.

1-Methyl-1H-indole-3-carboxylic acid 2-pyridinylmethyl ester (38u). White solid; mp 84 °C (5 mmHg); R_f = 0.43 (EtOAc); ^1H NMR (CDCl_3) δ 3.83 (s, 3H, CH_3), 5.51 (s, 2H, CH_2), 7.20-7.38 (m, 3H, Ar), 7.47 (d, $J=7.9$ Hz, 1H, 3'-H), 7.70 (ddd, $J=7.6$ Hz, $J=7.6$ Hz, $J=1.6$ Hz, 1H, 4'-H), 7.86 (s, 1H, 2-H), 8.18-8.24 (m, 1H, Ar), 8.61 (dd, $J=4.9$ Hz, $J=0.7$ Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 33.5 (CH_3), 66.0 (CH_2), 106.4 (Ar), 109.8 (Ar), 121.5 (Ar), 121.6 (Ar), 122.0 (Ar), 122.6 (Ar), 122.9 (Ar), 126.6 (Ar), 135.6 (2-C), 136.7 (4'-C), 137.2 (Ar), 149.3 (6'-C), 156.9 (2'), 164.4 (C=O). IR (KBr) 3417 w, 3112 w, 3054 w, 2931 w, 1698 s, 1590 m, 1535 s, 1469 m, 1428 m, 1394 w, 1369 w, 1338 m, 1267 m, 1222 s, 1149 s, 1103 s, 1031 m, 991 w, 794 w, 769 m, 744 s, 609 w, 566 w, 539 w, 476 w, 428 w; MS, m/z (relative intensity, %) 266 (M^+ , 24), 159 (12), 158 (100), 130 (10), 77 (11); HRMS: Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$: 266.1055. Found: 266.1060.

Benzeneacetic acid, α , α -dimethyl-, 2-pyridinylmethyl ester (40e). Colorless oil; bp 124 °C (4 mmHg); R_f = 0.31; ^1H NMR (CDCl_3) δ 1.64 (s, 6H, Me_2), 5.21 (s, 2H, CH_2), 6.97 (d, J = 7.9 Hz, 1H, 3'-H), 7.14 (ddd, J = 7.6 Hz, J = 4.9 Hz, J = 0.7 Hz, 1H, 5'-H), 7.23-7.39 (c, 5H, Ar), 7.55 (ddd, J = 7.9 Hz, J = 7.9 Hz, J = 2.0 Hz, 1H, 4'-H), 8.50 (d, J = 4.0 Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 26.4 (Me_2), 46.5 (PhMe_2C), 66.8 (CH_2), 120.9 (3'-C), 122.6 (5'-C), 125.8 (2 or 3-C), 126.8 (4-C), 128.4 (2 or 3-C), 136.6 (4'-C), 144.3 (1-C), 149.2 (6'-C), 156.2 (2'-C), 176.2 ($\text{C}=\text{O}$); IR (neat) 3897 w, 3473 w, 3060 m, 2975 m, 2927 m, 2854 m, 1735 s, 1594 m, 1573 w, 1496 w, 1473 m, 1440 m, 1390 m, 1369 m, 1261 m, 1247 m, 1145 s, 1101 m, 1078 m, 1049 w, 1025 m, 993 w, 933 m, 896 m, 838 w, 761 s, 732 m, 701 m, 592 s, 433 m; MS, m/z (relative intensity, %) 255 (M^+ , 4), 136 (21), 120 (16), 119 (100), 109 (21), 108 (26), 103 (11), 93 (33), 92 (53), 91 (75), 79 (16), 78 (12), 77 (16), 65 (32), 51 (15), 41 (48); HRMS: Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_2$: 255.1259. Found: 255.1260.

Benzoic acid, 4-(trifluoromethyl)-, 2-pyridinylmethyl ester. White solid; mp 41-43 °C (12 mmHg); R_f = 0.16 (hexane/EtOAc = 4/1); ^1H NMR (CDCl_3) δ 5.51 (s, 2H, OCH_2), 7.25-7.29 (m, 1H, 5'-H), 7.44 (d, J = 7.9 Hz, 1H, 3'-H), 7.71-7.77 (c, 3H, 2-H, 4'-H), 8.23 (d, J = 7.9 Hz, 2H, 3-H), 8.62-8.64 (m, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 67.7 (OCH_2), 121.9 (3'-C), 123.1 (5'-C), 123.6 (q, J = 273 Hz, CF_3), 125.5 (q, J = 3.7 Hz, 4-C), 130.2 (2-C), 133.0 (1-C), 134.6 (q, J = 32.9 Hz, 4-C), 136.9 (4'-C), 149.6 (6'-C), 155.4 (2'-C), 165.0 ($\text{C}=\text{O}$); IR (KBr) 3580 w, 3404 w, 3060 w, 2010 w, 1710 s, 1596 m, 1514 w, 1476 m, 1451 m, 1440 m, 1412 m, 1375 m, 1327 s, 1311 s, 1291 s, 1166 s, 1122 s, 1063 s, 1010 m, 986 m, 863 m, 775 m, 750 m, 700 w, 590 w, 535 w, 480 w, 341 w; MS, m/z (relative intensity, %) 281 (M^+ , 0), 262 ($\text{M}^+ - \text{F}$, 1), 173 (14), 145 (20), 108 (100), 65 (11). Anal. Calcd for $\text{C}_{14}\text{H}_9\text{F}_3\text{NO}_2$ ($\text{M} + \text{Na}^+$): 304.0547. Found: 304.0561.

General Procedure for the Cross-Coupling Reaction of Pyridinylmethyl Esters with Phenylboronate. 9-mL pressure tube equipped with a magnetic stirring bar and a rubber septum was flame dried under a flow of nitrogen and cooled to room temperature. Pyridinylmethyl ester (1 mmol), phenylboronate (1.5 mmol), $\text{Ru}_3(\text{CO})_{12}$ (0.03 mmol) and toluene (Method A and B: 3 mL, Method C: 1 mL) were placed in the tube under N_2 . The vessel was heated in an oil bath (Method A: at 140 °C for 20 h, Method B: at 140 °C for 40 h, Method C: at 120 °C for 40 h) followed by cooling. The resulting mixture was analyzed by GC, then the volatile components were removed *in vacuo* and the residue was subjected to column chromatography on silica gel to give a phenyl ketone.

General Procedure for the Cross-Coupling Reaction of Pyridinylmethyl Esters with alkyl-9-BBN. 9-mL pressure tube equipped with a magnetic stirring bar and a rubber septum was flame dried under a flow of nitrogen and cooled to room temperature. Olefin (2.5 mmol) and 9-BBN solution (2 mmol, 4 mL) were placed in the tube and the resulting mixture was stirred at room temperature for 3 h. THF and excess olefin were removed *in vacuo*, and pyridinylmethyl ester (1 mmol), $\text{Ru}_3(\text{CO})_{12}$ (0.03 mmol) and toluene (Method A: 3 mL, Method C: 1 mL) were added to the mixture. The vessel was heated in an oil bath (Method A: at 140 °C for 20 h, Method C: at 120 °C for 40 h), followed by cooling. The resulting mixture was analyzed by GC, then the volatile components were removed *in vacuo* and the residue was subjected to column chromatography on silica gel to give a dialkyl ketone.

1-Propanone, 1-(4-dimethylaminophenyl)-3-phenyl-. White solid; mp 88-89 °C (5 mmHg); R_f = 0.19 (hexane/EtOAc = 10/1); ^1H NMR (CDCl_3) δ 3.01-3.07 (overlapped with peak (δ = 3.05), 2H, CH_2), 3.05 (s, 6H, Me_2), 3.19-3.24 (m, 2H, CH_2), 6.64 (dt, J = 8.9 Hz, J = 2.5 Hz, 2H, 3-H), 7.16-

7.32 (m, 5H, Ar), 7.88 (dt, $J = 2.5$ Hz, $J = 2.5$ Hz, 2H, 2-H); ^{13}C NMR (CDCl_3) δ 30.7 (CH_2), 39.8 (CH_2), 40.0 (Me_2), 110.6 (3-C), 124.8 (1-C), 125.9 (4'-C), 128.4 (2' and 3'-C), 130.2 (2-C), 141.9 (1'-C), 153.3 (4-C), 197.4 ($\text{C}=\text{O}$); IR (KBr) 3448 w, 3025 w, 2815 w, 1648 s, 1606 s, 1554 m, 1525 m, 1481 m, 1448 m, 1369 s, 1295 m, 1230 m, 1187 s, 1066 m, 1002 w, 975 m, 944 w, 817 m, 781 m, 752 m, 725 w, 700 m, 597 w, 565 w, 522 w, 491 w; MS, m/z (relative intensity, %) 253 (M^+ , 0), 247 (22), 130 (41), 129 (54), 128 (13), 119 (11), 118 (74), 114 (20), 113 (10), 99 (24), 96 (19), 92 (13), 91 (100), 90 (10), 84 (12), 65 (24), 58 (11), 57 (14), 55 (10), 43 (11), 42 (23), 41 (27); HRMS: Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$: 253.1466. Found: 253.1462.

Benzoic acid, 4-(1-oxo-3-phenylpropyl)-, methyl ester (n), Benzoic acid, 4-(1-oxo-2-phenylpropyl)-, methyl ester (i). Spectral data were obtained from a mixture of n and i: White solid; mp 78-82 °C (5 mmHg); $R_f = 0.17$ (hexane/EtOAc = 10/1); ^1H NMR (CDCl_3) **n**, δ 3.07 (t, $J = 7.6$ Hz, 2H, CH_2), 3.33 (t, $J = 7.7$ Hz, 2H, CH_2), 3.95 (s, 3H, CH_3), 7.18-7.34 (c, 9H, Ar), 7.99 (d, $J = 8.6$ Hz, 2H,), 8.11 (d, $J = 8.6$ Hz, 2H,); **i**, 3.91 (s, 3H, CH_3), 4.66 (q, $J = 6.7$ Hz, 1H, CHCH_3); ^{13}C NMR (CDCl_3) **n**, δ 29.9 (3'-C), 40.8 (2'-C), 52.5 (CH_3), 127.7 (Ar), 127.9 (3-C), 128.5 (2'' or 3''-C), 128.6 (2'' or 3''-C), 128.6 (Ar), 129.1 (Ar), 129.7 (Ar), 129.8 (2-C), 166.2 ($\text{C}(\text{O})\text{O}$), 198.7 ($\text{C}=\text{O}$); **i**, 19.3, 48.4, 126.2, 127.1; IR (KBr) 3423 w, 3058 w, 3027 w, 2956 w, 2360 w, 1722 s, 1675 s, 1604 w, 1571 w, 1498 w, 1434 m, 1405 w, 1373 w, 1282 s, 1189 w, 1108 s, 1012 w, 987 w, 954 w, 867 w, 829 w, 759 m, 700 m, 561 w, 534 w, 464 w; MS, m/z (relative intensity, %) 268 (M^+ , 0), 247 (31), 130 (55), 129 (73), 128 (18), 119 (16), 118 (100), 114 (27), 113 (14), 99 (32), 96 (25), 92 (17), 91 (72), 90 (13), 89 (11), 84 (15), 65 (32), 58 (14), 57 (18), 56 (11), 55 (13), 43 (14), 42 (29), 41 (35); HRMS: **n**, Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$: 268.1099. Found: 268.1101; **i**, Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$: 268.1100. Found: 268.1125.

2-Propanone, 1-(2-chlorophenyl)-3-phenyl- (14). White solid; mp 46 °C (12 mmHg); R_f = 0.10 (hexane/EtOAc = 10/1); ^1H NMR (CDCl_3) δ 3.70 (s, 2H, 1-H or 3-H), 3.79 (s, 2H, 1-H or 3-H), 7.04-7.31 (c, 9H, Ar); ^{13}C NMR (CDCl_3) δ 46.8 (CH_2), 49.6 (CH_2), 126.9 (Ar), 127.1 (Ar), 128.7 (Ar), 128.7 (Ar), 129.5 (2C,Ar), 131.8 (Ar), 132.7 (Ar), 133.8 (Ar), 134.4 (Ar), 204.5 ($\text{C}=\text{O}$); IR (KBr) 3814 w, 3022 w, 1713 s, 1596 m, 1473 s, 1444 s, 1322 s, 1201 m, 1049 s, 934 m, 741 s, 694 s, 542 w, 472 w; MS, m/z (relative intensity, %) 244 (M^+ , 2), 127 (14), 125 (43), 91 (100), 89 (14), 65 (19), 63 (10). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{ClO}$: C, 73.62; H, 5.35; Cl, 14.49. Found: C, 73.33; H, 5.47; Cl, 14.79.

2-Octanone, 1-(2-chlorophenyl)- (15-n) and 2-Heptanone, 3-methyl-1-(2-chlorophenyl)- (15-i). Spectral data were obtained from a mixture of **15-n** and **15-i**: Colorless oil; bp 100 °C (3 mmHg); R_f = 0.11 (hexane/EtOAc = 10/1); ^1H NMR (CDCl_3), **15-n**: δ 0.87 (t, J = 6.8 Hz, 3H, 8-H), 1.25-1.30 (c, 6H, 5-H, 6-H, 7-H), 1.57-1.62 (c, 2H, 4-H), 2.48 (t, J = 7.4 Hz, 2H, 3-H), 3.83 (s, 2H, 1-H), 7.13-7.24 (c, 3H, Ar), 7.36-7.40 (c, 1H, Ar); **15-i**: δ 1.13 (d, J = 6.9 Hz, 3H, 3'-Me), 2.61-2.66 (m, 1H, 3'-H), 3.88 (s, 2H, 1'-H) (other peaks were overlapped with the peaks of **15-n**); ^{13}C NMR (CDCl_3), **15-n**: δ 14.0 (8-C), 22.5 (5-C or 6-C or 7-C), 23.7 (4-C), 28.8 (5-C or 6-C or 7-C), 31.6 (5-C or 6-C or 7-C), 42.5 (3-C), 47.5 (1-C), 126.9 (Ar), 128.5 (Ar), 129.5 (Ar), 131.7 (Ar), 133.0 (Ar), 134.4 (Ar), 207.4 ($\text{C}=\text{O}$); **15-i**: δ 13.9, 16.5, 22.7, 29.4, 32.7, 45.9, 46.0, 126.8, 128.5, 129.5, 131.8 (other peaks were overlapped with the peaks of **15-n**); IR (neat) 3372 w, 3286 w, 2906 s, 1711 s, 1557 m, 1443 s, 1355 s, 1124 s, 1050 s, 743 s, 441w; MS, m/z (relative intensity, %) **15-n**:

239 (M^+ , 0), 127 (14), 126 (12), 125 (M^+ -HexC(O), 41), 113 (100), 89 (31), 85 (36), 63 (16), 57 (51), 55 (27); **15-i**: 239 (M^+ , 0), 125 (M^+ -HexC(O), 24), 113 (29), 89 (19), 85 (100), 63 (12), 57 (36), 55 (14). Anal. Calcd for $C_{14}H_{19}ClO$: C, 70.43; H, 8.02; Cl, 14.85. Found: C, 70.18; H, 7.84; Cl, 14.61.

2-Butanone, 1-(2-chlorophenyl)-4-cyclohexyl (16). Colorless oil; bp 152 °C (5 mmHg); R_f = 0.13 (hexane/EtOAc = 30/1); 1H NMR ($CDCl_3$) δ 0.79-0.92 (c, 2H, Cy), 1.09-1.26 (c, 4H, Cy), 1.49 (td, J = 7.5 Hz, J = 7.4 Hz, 2H, 4-H), 1.64-1.68 (c, 5H, Cy), 2.50 (t, J = 7.7 Hz, 2H, 3-H), 3.84 (s, 2H, 1-H), 7.20-7.26 (c, 3H, Ar), 7.37-7.40 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$) δ 26.2 (3'-C), 26.5 (4'-C), 31.1 (4-C), 33.1 (2'-C), 37.1 (1'-C), 40.0 (3-C), 47.5 (1-C), 126.9 (Ar), 128.5 (Ar), 129.5 (Ar), 131.7 (Ar), 133.0 (Ar), 134.4 (Ar), 207.6 (C=O); IR (neat) 2894 s, 2842 s, 2654 w, 1709 s, 1572 m, 1471 s, 1444 s, 1410 s, 1317 s, 1046 s, 743 s, 680 m, 546 w, 441 w; MS, m/z (relative intensity, %) 264 (M^+ , 3), 139 (34), 125 (22), 121 (70), 95 (38), 93 (29), 89 (26), 83 (22), 79 (26), 69 (51), 67 (21), 56 (12), 55 (100), 53 (10). Anal. Calcd for $C_{16}H_{21}ClO$: C, 72.57; H, 7.99; Cl, 13.39. Found: C, 72.49; H, 7.87; Cl, 13.30.

2-Hexanone, 5,5-dimethyl-1-(2-chlorophenyl) (17). Colorless oil; bp 144 °C (5 mmHg); R_f = 0.19 (hexane/EtOAc = 20/1); 1H NMR ($CDCl_3$) δ 0.85 (s, 9H, t Bu), 1.46-1.52 (m, 2H, 4-H), 2.42-2.48 (m, 2H, 3-H), 3.84 (s, 2H, 1-H), 7.16-7.23 (m, 3H, Ar), 7.34-7.39 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$) δ 29.2 (CMe_3), 30.0 (CMe_3), 37.4 (4-C), 38.3 (3-C), 47.5 (1-C), 126.9 (Ar), 128.5 (Ar), 129.4 (Ar), 131.6 (Ar), 132.9 (Ar), 134.3 (Ar), 207.4 (C=O); IR (neat) 3524 w, 2904 s, 1710 s, 1571 m, 1468 s, 1444 s, 1408 s, 1360 s, 1314 s, 1242 m, 1178 m, 1081 s, 1034 s, 940 m, 742 s, 678 m, 576 w, 441 m; MS, m/z (relative intensity, %) 238 (M^+ , 0), 223 (M^+ - CH_3 , 3), 127 (14), 125 (43), 113 (70), 89

(16), 85 (20), 57 (100), 55 (12). Anal. Calcd for C₁₄H₁₉ClO: C, 70.43; H, 8.02; Cl, 14.85; Found: C, 70.43; H, 8.02; Cl, 14.65.

2-Butanone, 1-(2-chlorophenyl)-4-(trimethylsilyl) (18). Colorless oil; bp 92 °C (3 mmHg); R_f = 0.34 (hexane/EtOAc = 10/1); ¹H NMR (CDCl₃) δ -0.01 (s, 9H, Si(CH₃)₃), 0.76-0.82 (c, 2H, 4-H), 2.44-2.50 (c, 2H, 3-H), 3.86 (s, 2H, 1-H), 7.20-7.25 (m, 3H, Ar), 7.35-7.40 (m, 1H, Ar); ¹³C NMR (CDCl₃) δ -1.9 (Si(CH₃)₃), 10.3 (4-C), 37.1 (3-C), 46.8 (1-C), 126.9 (Ar), 128.5 (Ar), 129.5 (Ar), 131.7 (Ar), 133.1 (Ar), 134.3 (Ar), 208.0 (C=O); IR (neat) 2896 m, 1716 s, 1476 s, 1412 s, 1318 m, 1244 s, 1178 m, 1050 m, 842 s, 744 s, 686 m, 568 w, 444 w; MS, m/z (relative intensity, %) 254 (M⁺, 0), 239 (M⁺-Me), 101 (12), 93 (16), 75 (17), 73 (100). HRMS (ESI-TOF): Anal. Calcd for C₁₃H₁₉ClOSiNa (M + Na⁺): 277.0791. Found: 277.0779.

2-Butanone, 1-(2-chlorophenyl)-4-phenyl (19-n). White solid; mp 57-59 °C (12 mmHg); R_f = 0.26 (hexane/EtOAc = 10/1); ¹H NMR (CDCl₃) δ 2.78-2.84 (m, 2H, 3-H), 2.89-2.95 (m, 2H, 4-H), 3.82 (s, 2H, 1-H), 7.14-7.30 (c, 8H, Ar), 7.35-7.41 (m, 1H, Ar); ¹³C NMR (CDCl₃) δ 29.7 (3-C), 43.9 (4-C), 47.8 (1-C), 126.1 (4'-C), 127.0 (Ar), 128.3 (2'-C or 3'-C), 128.5 (2'-C or 3'-C), 128.7 (Ar), 129.6 (Ar), 131.7 (Ar), 132.7 (Ar), 134.4 (Ar), 140.9 (1'-C), 206.2 (C=O); IR (KBr) 3920 w, 3022 w, 2060 w, 1710 s, 1477 m, 1446 m, 1410 m, 1358 m, 1323 m, 1281 w, 1156 w, 1076 m, 1051 m, 1011 m, 753 m, 727 m, 696 m, 553 w, 504 w, 302 w; MS, m/z (relative intensity, %) 259 (M⁺, 0), 133 (41), 125 (11), 105 (100), 91 (86), 89 (12), 77 (15), 65 (12), 51 (10). HRMS (ESI-TOF): Anal. Calcd for C₁₆H₁₅ClONa (M + Na⁺): 281.0709. Found: 281.0708.

2-Butanone, 1-(2-chlorophenyl)-3-phenyl (19-i). Colorless oil; bp 124 °C (4 mmHg); R_f = 0.34 (hexane/EtOAc = 10/1); ^1H NMR (CDCl_3) δ 1.42 (d, J = 6.9 Hz, 3H, CH_3), 3.71 (d, J = 16.8 Hz, 1H, 1-H), 3.83 (d, J = 16.8 Hz, 1H, 1-H), 3.89 (q, J = 6.9 Hz, 1H, 3-H), 7.01-7.04 (m, 1H, Ar), 7.13-7.38 (c, 8H, Ar); ^{13}C NMR (CDCl_3) δ 17.7 (CH_3), 45.9 (1-C), 52.6 (3-C), 126.8 (Ar), 127.3 (Ar), 128.1 (2'-C or 3'-C), 128.5 (Ar), 129.0 (2'-C or 3'-C), 129.4 (Ar), 131.8 (Ar), 132.9 (Ar), 134.4 (Ar), 140.2 (Ar), 206.9 (C=O); IR (neat) 3474 w, 2918 m, 2400 m, 1705 s, 1597 m, 1445 s, 1408 s, 1370 s, 1322 s, 1114 s, 1025 s, 743 s, 696 s, 540 m, 439m; MS, m/z (relative intensity, %) 258 (M^+ , 1), 127 (10), 125 (30), 105 (100), 79 (14), 77 (18). HRMS (ESI-TOF): Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{ClONa}$ ($\text{M} + \text{Na}^+$): 281.0709. Found: 281.0701.

Typical procedure for Decarbonylative Reduction of Esters. 3,4,5-Trimethoxybenzoic acid 2-pyridinylmethyl ester (**38i**) (60.7mg, 0.2mmol), ammonium formate (37.8 mg, 0.6 mmol), $\text{Ru}_3(\text{CO})_{12}$ (6.4mg, 0.01 mmol) and 1,4-dioxane (0.6mL) were placed in a 8-mL screw capped vial under N_2 . The vessel was heated in an oil bath at 160 °C for 20 h, followed by cooling. The mixture was analysed by GC and yield was determined using $n\text{-C}_{14}\text{H}_{30}$ as an internal standard (88% GC yield). The solvent was removed in vacuo, and the residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 4/1) to give a 1,2,3-trimethoxybenzene(**39i**) (22mg, 65%).

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