Supporting Information

The Ru(cod)(cot)-Catalyzed Alkenylation of Aromatic C-H Bonds with Alkenyl Acetates

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General Information

Chemical shifts in ¹H and ¹³C{¹H} NMR spectra are expressed in ppm relative to residual chloroform (δ 7.26 for ¹H, δ 77.0 for ¹³C) or tetramethylsilane (δ 0.00 for ¹H and ¹³C). ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant (Hz), and relative intensity. Gas chromatography (GC) analyses were performed using a CBP-10 capillary column (25 m × 0.22 mm, film thickness 0.25 μm). Temperature was programmed from 70 to 250 °C at 10 °C/min ramp with a final hold time of 30 min (injection temperature, 270 °C; detector temperature, 270 °C). Flash chromatography was carried out with Merck silica gel 60 (230-400 mesh ASTM).

General Procedure A for the Ru(cod)(cot)-Catalyzed Alkenylation of Aromatic Compounds with Alkenyl Acetates. In a glove box, Ru(cod)(cot) (0.05 mmol), aromatic compound (1 mmol), alkenyl acetate (3 mmol), toluene (1.5 mL) and a magnetic stirring bar were placed in a 10 mL Schlenk flask. The resulting solution was heated at 120 °C. After cooling, ca.

0.3 mL of triethylamine (ca. 20 mmol) was added to the reaction mixture. The resulting mixture was stirred for 5 minutes at room temperature and analyzed by GC. The alkenylation product was isolated by silica gel column chromatography (followed by gel permeation chromatography and/or bulb-to-bulb distillation, if necessary).

General Procedure B for the Ru(cod)(cot)-Catalyzed Alkenylation of Aromatic Compounds with Alkenyl Acetates. An apparatus consisting of a 10-mL two-necked flask equipped with a reflux condenser and a magnetic stirring bar was oven-dried. In the flask were placed Ru(cod)(cot) (0.05 mmol), aromatic compound (1 mmol), alkenyl acetate (3 mmol), and 1.5 mL of toluene. The resulting mixture was refluxed under nitrogen atmosphere. After cooling, ca. 0.3 mL of triethylamine (ca. 20 mmol) was added to the reaction mixture. The resulting mixture was stirred for 5 minutes at room temperature and analyzed by GC. The alkenylation product was isolated by silica gel column chromatography (followed by gel permeation chromatography and/or bulb-to-bulb distillation, if necessary).

2-(2-Methyl-6-vinylphenyl)pyridine (**4**).

General procedure A was followed with 2-(2-tolyl)pyridine (**1**) and vinyl butyrate (**2**), except that 5 mmol, not 3 mmol, of **2** was used. Column chromatography (6:1:0.1 hexane/EtOAc/Et₃N), followed by bulb-to-bulb distillation afforded **4** as a colorless oil in 34% yield. ¹H NMR (CDCl₃): δ 2.06 (s, 3H, CH₃), 5.07 (d, *J* = 10.8 Hz, 1H, –CH=CH₂), 5.60 (d, *J* = 16.2 Hz, 1H, –CH=CH₂), 6.32 (dd, *J* = 10.8 Hz, 16.2 Hz, 1H, –CH=CH₂), 7.11–7.30 (m, 4H, ArH), 7.49 (d, *J* = 7.5 Hz, 1H, ArH), 7.73 (t, *J* = 8.5 Hz, 1H, ArH), 8.73 (d, *J* = 5.1 Hz, 1H, ArH); ¹³C NMR (CDCl₃): δ 20.2, 114.9, 121.8, 122.8, 125.2, 128.1, 129.5, 135.3, 136.2, 136.2, 139.3, 149.6, 159.0; LRMS (EI) *m/z* (% relative intensity): 195 (M⁺, 52), 194 (100), 192 (10); IR (neat): 3079 m, 2921 w, 1585 s, 1565 m, 1473 m, 1428 m, 1407 m, 1278 w, 1147 w, 1091 w, 1056 w, 1027 w, 991 m, 912 s, 796 s, 754 s, 692 w, 667 w, 624 m, 605 w, 453 m, 408 m cm^{–1}. HRMS (ESI) calcd for [M+H]⁺ (C₁₄H₁₄N) *m/z* 196.1126. Found 196.1103.

2-[2-Methyl-6-(1-propenyl)phenyl]pyridine (6).

General procedure **A** was followed with 2-(2-tolyl)pyridine (**1**) and 1-propenyl acetate (**5**). Column chromatography (8:1 hexane/EtOAc) afforded **6** as a colorless oil in 82% yield (*E/Z* = 91/9). ¹H NMR (CDCl₃): δ 1.68 (dd, *J* = 6.2, 1.1 Hz, 3.0H, CH₃ (*E*-isomer)), 1.76 (dd, *J* = 7.1, 1.8 Hz, 0.31H, CH₃ (*Z*-isomer)), 2.03 (s, 3.0H, CH₃ (*E*-isomer)), 2.09 (s, 0.31H, CH₃ (*Z*-isomer)), 5.56 (dq, *J* = 11.5, 7.1 Hz, 0.10H, CH (*Z*-isomer)), 5.95 (d, *J* = 16.3 Hz, 1.0H, CH (*E*-isomer)), 6.00-6.15 (m, 1.1H, CH), 7.07-7.29 (m, 4.5H, ArH), 7.41 (d, *J* = 7.7 Hz, 1.0H, ArH (*E*-isomer)), 7.65-7.77 (m, 1.1H, ArH), 8.66-8.75 (m, 1.1H, ArH); ¹³C NMR (CDCl₃, *E*-isomer): δ 19.1, 20.7, 121.9, 123.1, 125.5, 127.0, 128.2, 128.7, 129.4, 136.3, 136.6, 138.9, 149.7, 159.5; LRMS (EI) *m/z* (% relative intensity): 208 (M⁺, 7), 195 (14), 194 (100); IR (neat): 3025 m, 2914 m, 1652 w, 1584 s, 1564 m, 1477 m, 1464 s, 1420 s, 1377 w, 1276 w, 1147 w, 1090 w, 1027 m, 988 m, 962 m, 793 m, 768 s, 750 s, 640 w, 619 w, 586 w, 567 w, 526 w cm⁻¹. HRMS (ESI) calcd for [M+H]⁺ (C₁₅H₁₆N) *m/z* 210.1283. Found 210.1284.

2-[2-(1-Butenyl)-6-methylphenyl]pyridine (8).

General procedure **A** was followed with 2-(2-tolyl)pyridine (**1**) and 1-butenyl acetate (**7**). Column chromatography (10:1 hexane/EtOAc) afforded **8** as a colorless oil in 91% yield (*E/Z* = 92/8). ¹H NMR (CDCl₃): δ 0.91 (t, *J* = 7.4 Hz, 3.0H, CH₃ (*E*-isomer)), 0.95 (t, *J* = 7.4 Hz, 0.26H, CH₃ (*Z*-isomer)), 1.97-2.08 (m, 5.2H, CH₂ (*E*-isomer) and CH₃), 2.14-2.25 (m, 0.18H, CH₂ (*Z*-isomer)), 5.42 (dt, *J* = 11.4, 7.4 Hz, 0.09H, CH (*Z*-isomer)), 5.93 (d, *J* = 15.8 Hz, 1.0H, CH (*E*-isomer)), 6.00-6.14 (m, 1.1H, CH), 7.10-7.27 (m, 4.5H, ArH), 7.42 (d, *J* = 7.7 Hz, 1.0H, ArH (*E*-isomer)), 7.65-7.74 (m, 1.1H, ArH), 8.67-8.72 (m, 1H, ArH); ¹³C NMR (CDCl₃, *E*-isomer): δ 13.6, 20.2, 26.1, 121.4, 122.7, 125.0, 126.9, 127.8, 128.3, 133.5, 135.7, 135.8, 136.2, 138.6, 149.2, 159.1; LRMS (EI) *m/z* (% relative intensity): 222 (M⁺, 2), 208 (19), 195(16), 194 (100); IR (neat): 2964 s, 2930 m, 1584 s, 1563 m, 1461 s, 1422 m, 1147 w, 1091 w, 1025 w, 989 w, 965 m, 788 m, 750 s, 620 w, 527 w cm⁻¹. HRMS (ESI) calcd for [M+H]⁺ (C₁₆H₁₈N) *m/z* 224.1439. Found 224.1415.

2-[2-(1-Hexenyl)-6-methylphenyl]pyridine (10).

General procedure **A** was followed with 2-(2-tolyl)pyridine (**1**) and 1-hexenyl acetate (**9**). Column chromatography (10:1 hexane/EtOAc) afforded **10** as a colorless oil in 83% yield (*E/Z* = 94:6). ¹H NMR (CDCl₃): δ 0.79-0.89 (m, 3.2H, CH₃), 1.17-1.37 (m, 4.3H, CH₂), 1.94-2.01 (m, 5.2H, CH₂ (*E*-isomer) and CH₃), 2.13-2.25 (m, 0.14H, CH₂ (*Z*-isomer)), 5.43 (dt, *J* = 11.5, 7.4 Hz, 0.07H, CH (*Z*-isomer)), 5.93 (d, *J* = 15.8 Hz, 1.0H, CH (*E*-isomer)), 5.98-6.09 (m, 1.1H, CH), 7.08-7.27 (m, 4.4H, ArH), 7.43 (d, *J* = 7.7 Hz, 1.0H, ArH (*E*-isomer)), 7.63-7.75 (m, 1.1H, ArH), 8.66-8.73 (m, 1.1H, ArH); ¹³C NMR (CDCl₃, *E*-isomer): δ 14.2, 20.6, 22.4, 31.7, 33.1, 121.8, 123.2, 125.4, 128.2, 128.4, 128.7, 132.5, 136.1, 136.2, 136.7, 138.9, 149.6, 159.5; LRMS (EI) *m/z* (% relative intensity): 250 (M⁺, 2), 208 (40), 195 (14), 194 (100), 181 (10); IR (neat): 2956 s, 2926 s, 1584 m, 1564 m, 1464 s, 1421 m, 1025 w, 968 m, 749 s, 620 w cm⁻¹. HRMS (ESI) calcd for [M+H]⁺ (C₁₈H₂₂N) *m/z* 252.1752. Found 252.1766.

2-(2-Methyl-6-styrylphenyl)pyridine (12).

General procedure **B** was followed with 2-(2-tolyl)pyridine (**1**) and styryl acetate (**11**). Column chromatography (8:2 hexane/EtOAc) afforded **12** as a colorless oil in 98% yield. ¹H NMR (CDCl₃): δ 2.10 (s, 3H, CH₃), 6.69 (d, *J* = 16.5 Hz, 1H, VinylH), 6.95 (d, *J* = 16.5 Hz, 1H, VinylH), 7.14-7.35 (m, 9H, ArH), 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.77 (t, *J* = 7.6 Hz, 1H, ArH), 8.76 (d, *J* = 4.9 Hz, 1H, ArH); ¹³C NMR (CDCl₃): δ 20.3, 121.7, 122.8, 125.2, 126.2, 127.0, 127.2, 128.0, 128.3, 129.2, 129.5, 135.7, 136.0, 136.2, 137.3, 149.3, 158.7; LRMS (EI) *m/z* (% relative intensity): 272 (10), 271 (M⁺, 47), 270 (15), 195 (16), 194 (100), 127 (15), 51 (18); IR (neat): 3056 s, 3027 s, 2923 m, 1585 s, 1563 s, 1494 s, 1455 s, 1423 s, 1378 w, 1326 w, 1278 m, 1224 m, 1149 m, 1091 w, 1052 m, 1025 s, 985 m, 962 s, 782 s, 742 s, 692 s, 649 w, 620 m, 553 m, 522 m cm⁻¹. Anal. Calcd for C₂₀H₁₇N: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.23; H, 6.24; N, 5.06.

2-[2-Methyl-6-(2-methyl-1-propenyl)phenyl]pyridine (14).

General procedure **A** was followed with 2-(2-tolyl)pyridine (**1**) and 2-methyl-1-propenyl acetate (**13**). Column chromatography (10:1 hexane/EtOAc), followed by gel permeation chromatography (GPC) and bulb-to-bulb distillation afforded **14** as a colorless oil in 91% yield. ^1H NMR (CDCl_3): δ 1.66 (d, $J = 1.4$ Hz, 3H, CH_3), 1.72 (dt, $J = 1.4$ Hz, 3H, CH_3), 2.08 (s, 3H, CH_3), 5.80 (s, 1H, CH), 7.11-7.28 (m, 5H, ArH), 7.70 (td, $J = 7.6$ Hz, 1.9 Hz, 1H, ArH), 8.69 (dd, $J = 4.9$ Hz, 1.9 Hz, 1H, ArH); ^{13}C NMR (CDCl_3): δ 19.4, 20.2, 26.1, 121.4, 124.3, 125.2, 127.2, 127.4, 128.1, 134.9, 135.8, 135.9, 137.2, 139.8, 149.2, 159.6; LRMS (EI) m/z (% relative intensity): 223 (M^+ , 5), 209 (17), 208 (100), 90 (10), 51 (10); IR (neat): 3058 m, 2969 m, 2856 m, 1654 w, 1587 s, 1563 m, 1459 s, 1421 m, 1376 m, 1280 w, 1182 w, 1147 w, 1091 w, 1064 w, 1025 w, 987 w, 892 m, 840 m, 775 m, 752 s, 649 m, 622 m, 472 s, 441 s cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{N}$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.93; H, 7.38; N, 6.38.

2-[2-(1-Cyclohexenyl)-6-methylphenyl]pyridine (16).

General procedure **A** was followed with 2-(2-tolyl)pyridine (**1**) and 1-cyclohexenyl acetate (**15**). Column chromatography (10:1 hexane/EtOAc), followed by gel permeation chromatography (GPC) and bulb-to-bulb distillation afforded **16** as a colorless oil in 75% yield. ^1H NMR (CDCl_3): δ 1.40 (brs, 4H, CH_2), 1.79 (brs, 2H, CH_2), 1.91 (brs, 2H, CH_2), 2.13 (s, 3H, CH_3), 5.44 (brs, 1H, $\text{CH}=\text{C}$), 7.07 (d, $J = 7.3$ Hz, 1H, ArH), 7.14-7.26 (m, 5H, ArH), 7.67 (dt, $J = 1.8$, 7.6 Hz, 1H, ArH), 8.65 (d, $J = 4.6$ Hz, 1H, ArH); ^{13}C NMR (CDCl_3): δ 20.4, 21.8, 22.9, 25.5, 30.1, 121.3, 125.1, 126.1, 127.4, 127.8, 128.6, 135.5, 136.1, 138.6, 138.7, 144.1, 148.8, 160.0; LRMS (EI) m/z (% relative intensity): 249 (M^+ , 33), 248 (22), 221 (19), 220 (100), 204 (10), 194 (24), 102 (29); IR (neat) 3058 m, 3000 m, 2927 s, 2856 s, 2832 s, 1587 s, 1563 s, 1459 s, 1423 s, 1378 w, 1342 w, 1280 m, 1168 w, 1141 m, 1089 w, 1052 w, 1025 m, 991 m, 921 m, 844 w, 786 s, 750 s, 657 w, 622 w, 582 m cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{N}$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.63; H, 7.77; N, 5.60.

2-(2,6-distyrylphenyl)pyridine (**18**).

General procedure **B** was followed with 2-phenylpyridine and styryl acetate (**11**), except that 5 mmol, not 3 mmol, of **11** was used. Column chromatography (8:1:0.1 hexane/EtOAc/Et₃N) afforded **18** as a white solid in 93% yield. ¹H and ¹³C NMR spectroscopic data are in good agreement with those reported in literature; Oi, S.; Fukita, S.; Hirata, N.; Watanuki, N.; Miyano, S.; Inoue, Y. *Org. Lett.* **2001**, 3, 2579-2581.

3-Methyl-2-(2-styrylphenyl)pyridine (**19**).

General procedure **B** was followed with 3-methyl-2-phenylpyridine and styryl acetate (**11**). Column chromatography (5:1:0.1 hexane:EtOAc:Et₃N) afforded **19** as a colorless oil in 93% yield. ¹H NMR (CDCl₃): δ 2.10 (s, 3H, CH₃), 6.76 (d, *J* = 16.2 Hz, 1H, VinylH), 7.01 (d, *J* = 16.2 Hz, 1H, VinylH), 7.18-7.44 (m, 9H, ArH), 7.58 (d, *J* = 7.2 Hz, 1H, ArH), 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 8.56 (d, *J* = 4.3 Hz, 1H, ArH); ¹³C NMR (CDCl₃): δ 19.3, 122.3, 125.2, 126.3, 126.4, 127.4, 128.1, 128.4, 129.2, 129.8, 132.1, 135.3, 137.3, 137.6, 139.5, 146.7, 158.6; LRMS (EI) *m/z* (% relative intensity): 271 (M⁺, 32), 270 (12), 195 (14), 194 (100), 134 (12), 127 (26); IR (neat) 3056 s, 3027 s, 2923 m, 1567 s, 1494 s, 1446 s, 1421 s, 1382 m, 1328 m, 1259 m, 1216 m, 1184 m, 1159 w, 1120 m, 1099 m, 1068 m, 1024 m, 964 s, 794 s, 759 s, 736 s, 692 s, 624 m, 574 w, 539 m, 520 m cm⁻¹. Anal. Calcd for C₂₀H₁₇N: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.25; H, 6.29; N, 5.13.

2-Methyl-6-(2-methyl-6-styrylphenyl)pyridine (**20**).

General procedure **B** was followed with 2-methyl-6-(2-methylphenyl)pyridine and styryl acetate (**11**). Column chromatography (15:1 hexane/EtOAc), followed by bulb-to-bulb distillation afforded **20** as a colorless oil in 19% yield. ¹H NMR (CDCl₃): δ 2.10 (s, 3H, CH₃), 2.67 (s, 3H, CH₃), 6.73 (d, *J* = 16.4 Hz, 1H, VinylH), 6.94 (d, *J* = 16.2 Hz, 1H, VinylH), 7.06 (d, *J* = 7.8 Hz, 1H, ArH), 7.11-7.33 (m, 8H, ArH), 7.60 (d, *J* = 7.6 Hz, 1H, ArH), 7.65 (t, *J* = 7.6 Hz, 1H, ArH); ¹³C NMR (CDCl₃): δ 20.4, 24.7, 121.4, 122.4, 123.0, 126.5, 127.3, 127.5, 128.0, 128.5, 129.5, 135.9, 136.4, 136.5, 137.6, 139.8, 158.2, 158.3; LRMS (EI) *m/z* (% relative intensity): 285 (M⁺, 26), 284 (12), 208 (15), 195 (14), 194 (100),

141 (16) , 134 (26), 127 (10); IR (neat): 3058 m, 3027 m, 2923 w, 1577 s, 1494 m, 1452 s, 1375 w, 1324 w, 1222 w, 1159 w, 995 m, 962 m, 800 m, 782 s, 742 s, 694 m, 644 w, 549 w, 503 w, 468 m cm^{-1} ; HRMS (FAB) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{21}\text{H}_{20}\text{N}$) m/z 286.1596. Found 286.1608.

2-(5-Methyl-2-styrylphenyl)pyridine (21).

General procedure **B** was followed with 2-(3-tolyl)pyridine and styryl acetate (**11**). Column chromatography (7:1:0.1 hexane/EtOAc/Et₃N), followed by bulb-to-bulb distillation afforded **21** as a colorless oil in 98% yield. ¹H NMR (CDCl_3): δ 2.42 (s, 3H, CH_3), 7.02 (d, $J = 16.2$ Hz, 1H, Vinyl H), 7.21-7.46 (m, 10H, Ar H , Vinyl H), 7.66 (d, $J = 7.8$ Hz, 1H, Ar H), 7.73 (t, $J = 7.8$ Hz, 1H, Ar H), 8.75 (d, $J = 4.6$ Hz, 1H, Ar H); ¹³C NMR (CDCl_3): δ 21.3, 121.7, 125.0, 126.1, 126.4, 127.3, 127.3, 128.5, 129.1, 129.4, 130.7, 132.7, 135.8, 137.5, 137.6, 139.3, 149.4, 158.7; LRMS (EI) m/z (% relative intensity): 271 (M^+ , 11), 195 (14), 194 (100), 127 (24); IR (neat): 3021 s, 2917 m, 2861 m, 1585 s, 1563 s, 1496 s, 1465 s, 1428 s, 1313 m, 1151 m, 1035 m, 964 s, 889 m, 862 w, 809 s, 786 s, 752 s, 727 m, 692 s, 649 w, 620 w, 582 m, 547 w, 520 m, 497 m cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{N}$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.24; H, 6.23; N, 5.11.

2-[2-Styryl-5-(trifluoromethyl)phenyl]pyridine (22).

General procedure **B** was followed with 2-[3-(trifluoromethyl)phenyl]pyridine and styryl acetate (**11**). Column chromatography (5:1:0.1 hexane/EtOAc/Et₃N) afforded **22** as a colorless oil in 93% yield. ¹H NMR (CDCl_3): δ 7.13 (d, $J = 16.5$ Hz, 1H, Vinyl H), 7.20-7.42 (m, 7H, Vinyl H , Ar H), 7.47 (d, $J = 8.1$ Hz, 1H, Ar H), 7.66 (d, $J = 8.3$ Hz, 1H, Ar H), 7.77 (td, $J = 7.6$ Hz, 1.6 Hz, 1H, Ar H), 7.80-7.87 (m, 2H, Ar H), 8.77 (d, $J = 5.6$ Hz, 1H, Ar H); ¹³C NMR (CDCl_3): δ 122.5, 124.1 (q, $J = 271.6$ Hz), 125.0, 125.2 (q, $J = 3.9$ Hz), 126.1, 126.7, 126.8, 127.3 (q, $J = 3.9$ Hz), 128.2, 128.7, 129.2 (q, $J = 32.4$ Hz), 132.3, 136.3, 136.9, 139.2, 139.8, 149.8, 157.5; LRMS (EI) m/z (% relative intensity): 325 (M^+ , 10), 249 (15), 248 (100), 127 (15), 51 (14); IR (neat): 3058 s, 3021 m, 1614 s, 1585 s, 1569 s, 1494 m, 1467 s, 1409 s, 1340 s, 1270 s, 1170 s, 1130 s, 1116 s, 1078 s, 1035 s, 989 m, 964 s, 910 s, 856 m, 825 s, 796 s, 754 s, 734 s, 692 s, 657 s, 615 m, 520 m cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{F}_3\text{N}$: C, 73.84; H, 4.34; F, 17.52; N, 4.31. Found: C, 74.04; H,

4.30; F, 17.25; N, 4.33.

2-(2-Methoxy-6-styrylphenyl)pyridine (**23**).

General procedure **B** was followed with 2-(2-methoxyphenyl)pyridine and styryl acetate (**11**). Column chromatography (3:1:0.1 hexane/EtOAc/Et₃N), followed by bulb-to-bulb distillation afforded **23** as a colorless oil in 88% yield. ¹H NMR (CDCl₃): δ 3.75 (s, 3H, CH₃), 6.75 (d, *J* = 15.9 Hz, 1H, Vinyl*H*), 6.92 (dd, *J* = 7.0 Hz, 2.1 Hz, 1H, Ar*H*), 6.99 (d, *J* = 15.9 Hz, 1H, Vinyl*H*), 7.16-7.42 (m, 9H, Ar*H*), 7.75 (t, *J* = 7.6 Hz, 1H, Ar*H*), 8.76 (d, *J* = 4.6 Hz, 1H, Ar*H*); ¹³C NMR (CDCl₃): δ 55.9, 109.9, 117.8, 121.8, 126.3, 126.4, 126.7, 127.4, 128.4, 129.0, 129.1, 130.1, 135.7, 137.3, 137.4, 149.2, 156.1, 157.0; LRMS (EI) *m/z* (% relative intensity): 287 (M⁺, 23), 211 (15), 210 (100), 195 (36), 167 (20), 127 (23), 120 (14), 51 (12); IR (neat): 3077 s, 3002 s, 2935 s, 2834 s, 1631 m, 1594 s, 1563 s, 1490 s, 1427 s, 1247 s, 1182 m, 1149 m, 1024 m, 962 s, 931 m, 850 w, 782 s, 750 s, 732 s, 694 s, 605 m, 561 m, 539 w, 501 m cm⁻¹. Anal. Calcd for C₂₀H₁₇NO: C, 83.59; H, 5.96; N, 4.87; O, 5.57. Found: C, 83.35; H, 5.94; N, 4.84.

2-(2-Styryl-6-trifluoromethylphenyl)pyridine (**24**).

General procedure **B** was followed with 2-[2-(trifluoromethyl)phenyl]pyridine and styryl acetate (**11**). Column chromatography (10:1:0.1 hexane/EtOAc/Et₃N) afforded **24** as a colorless oil in 93% yield. ¹H NMR (CDCl₃): δ 6.57 (d, *J* = 16.2 Hz, 1H, vinyl*H*), 6.99 (d, *J* = 16.2 Hz, 1H, Vinyl*H*), 7.15-7.40 (m, 7H, Ar*H*), 7.53 (t, *J* = 8.1 Hz, 1H, Ar*H*), 7.68 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.78 (td, *J* = 7.6 Hz, 4.3 Hz, 1H, Ar*H*), 7.94 (d, *J* = 8.1 Hz, 1H, Ar*H*), 8.75 (d, *J* = 4.6 Hz, 1H, Ar*H*); ¹³C NMR (CDCl₃): δ 122.5, 123.9 (q, *J* = 279.5 Hz), 124.9 (q, *J* = 5.0 Hz), 125.3, 125.4, 126.5, 127.8, 128.3, 128.5, 128.7, 129.1 (q, *J* = 29.9 Hz), 131.4, 135.8, 136.7, 137.9, 138.1, 149.1, 156.1; LRMS (EI) *m/z* (% relative intensity): 326(12), 325(62), 324(M⁺, 18), 249(13), 248(100), 228(19); IR (neat): 3079 s, 3006 s, 1953 w, 1812 w, 1635 m, 1567 s, 1492 m, 1479 m, 1450 s, 1425 s, 1332 s, 1280 m, 1245 m, 1211 m, 1054 m, 1024 m, 985 m, 960 m, 900 m, 852 w, 804 m, 692 m, 669 m, 619 w, 503 w cm⁻¹. Anal. Calcd for C₂₀H₁₄F₃N: C, 73.84; H, 4.34; F, 17.52; N, 4.31. Found: C, 73.64; H, 4.22; F, 17.66; N, 4.36.

1-[2-(2-Pyridinyl)-3-styrylphenyl]ethanone (25).

General procedure **B** was followed with 1-[2-(2-pyridinyl)phenyl]ethanone and styryl acetate (**11**). Column chromatography (1:1 hexane/EtOAc) afforded **25** as a colorless oil in 64% yield. ^1H NMR (CDCl_3): δ 2.14 (s, 3H, Me), 6.89 (d, J = 16.2 Hz, 1H, Vinyl H), 7.03 (d, J = 16.2 Hz, 1H, Vinyl H), 7.20-7.40 (m, 7H, Ar H), 7.45-7.56 (m, 2H, Ar H), 7.76 (t, J = 7.8 Hz, 1H, Ar H), 7.86 (d, J = 7.3 Hz, 1H, Ar H), 8.71 (d, J = 4.3 Hz, 1H, Ar H); ^{13}C NMR (CDCl_3): δ 30.0, 122.3, 125.7, 126.1, 126.5, 126.8, 127.7, 128.3, 128.3, 128.5, 131.1, 135.9, 136.7, 136.9, 137.5, 141.5, 149.3, 157.3, 202.9; LRMS (EI) m/z (% relative intensity): 299 (M^+ , 43), 298 (17), 284 (20), 254 (15), 223 (18), 222 (100), 179 (17), 178 (11), 141 (14), 127 (38), 51 (14); IR (neat): 3050 s, 3002 s, 1697 s, 1679 s, 1590 s, 1563 s, 1492 s, 1475 s, 1421 s, 1353 s, 1272 s, 1240 s, 1178 m, 1151 m, 1114 s, 1022 m, 962 s, 852 w, 802 s, 748 s, 694 s, 651 w, 622 m, 568 m, 538 m, 503 m cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{NO}$: C, 84.25; H, 5.72; N, 4.68. Found: C, 83.97; H, 5.72; N, 4.71.

4-(3-Methyl-2-pyridinyl)-3-styrylbenzonitrile (26).

General procedure **B** was followed with 4-(3-methyl-2-pyridinyl)benzonitrile and styryl acetate (**11**). Column chromatography (3:1 hexane/EtOAc), followed by bulb-to-bulb distillation afforded **26** as a white solid in 86% yield. Mp 108.9-109.8 $^{\circ}\text{C}$; ^1H NMR (CDCl_3): δ 2.10 (s, 3H, CH_3), 6.68 (d, J = 16.2 Hz, 1H, Vinyl H), 7.06 (d, J = 16.2 Hz, 1H, Vinyl H), 7.23-7.33 (m, 6H, Ar H), 7.39 (d, J = 8.1 Hz, 1H, Ar H), 7.61-7.65 (m, 2H, Ar H), 8.06 (s, 1H, Ar H), 8.58 (d, J = 4.6 Hz, 1H, Ar H); ^{13}C NMR (CDCl_3): δ 19.1, 112.4, 118.7, 123.1, 123.9, 126.7, 128.3, 128.6, 129.2, 130.3, 130.4, 131.9, 132.4, 136.3, 136.9, 138.2, 143.4, 147.0, 156.6; LRMS (EI) m/z (% relative intensity): 296 (M^+ , 29), 295 (12), 220 (18), 219 (100), 65 (10), 51 (15); IR (KBr): 3034 m, 2225 s, 1636 w, 1603 w, 1570 s, 1495 m, 1449 s, 1423 s, 1328 w, 1260 w, 1224 w, 1185 w, 1122 w, 1107 w, 1066 w, 1022 m, 990 w, 957 s, 889 m, 851 w, 825 m, 788 s, 761 m, 735 s, 690 w, 671 w, 609 w, 570 w, 550 w, 536 w, 511 m cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 84.91; H, 5.51; N, 9.45.

2-(2,5-Distyryl-1H-pyrrol-1-yl)pyridine (**27**).

General procedure **B** was followed with 2-(1H-pyrrol-1-yl)pyridine and styryl acetate (**11**). Column chromatography (10:1:0.1 hexane/EtOAc/Et₃N) afforded **27** as a yellow solid in 92% yield. Mp 147.4-148.4 °C; ¹H NMR (CDCl₃): δ 6.71 (d, *J* = 16.4 Hz, 2H, Vinyl*H*), 6.71 (s, 2H, Ar*H*), 6.84 (d, *J* = 16.5 Hz, 2H, Vinyl*H*), 7.12-7.35 (m, 11H, Ar*H*), 7.42-7.47 (m, 1H, Ar*H*), 7.91 (td, *J* = 8.1 Hz, 1.9 Hz, 1H, Ar*H*), 8.76 (d, *J* = 4.8 Hz, 1H, Ar*H*); ¹³C NMR (CDCl₃): δ 108.7, 117.7, 123.2, 123.5, 126.0, 126.6, 127.0, 128.5, 134.2, 137.7, 138.3, 149.7, 150.9; LRMS (EI) *m/z* (% relative intensity): 349 (27), 348 (M⁺, 100), 347 (31), 272 (10), 271 (37), 256 (12), 173 (20), 173 (15), 134 (26), 115 (10), 78 (27), 51 (14); IR (KBr): 3021 w, 1621 m, 1585 m, 1571 m, 1492 w, 1469 s, 1436 s, 1407 m, 1342 w, 1328 w, 1249 w, 1022 w, 950 m, 796 m, 767 m, 746 m, 692 s, 555 m, 507 w cm⁻¹. Anal. Calcd for C₂₅H₂₀N₂: C, 86.17; H, 5.79; N, 8.04. Found: C, 85.89; H, 5.75; N, 7.96.

4,5-Dihydro-4,4-dimethyl-2-(2-methyl-6-styrylphenyl)oxazole (**28**)

General procedure **B** was followed with 4,5-dihydro-4,4-dimethyl-2-(2-methylphenyl)oxazole and styryl acetate (**11**), except that 2 mmol of 2,6-lutidine was also added. Column chromatography (10:1 hexane/EtOAc) afforded **28** as a white solid in 69% yield. Mp 86.0-87.1 °C; ¹H NMR (CDCl₃): δ 1.47 (s, 6H, CH₃), 2.37 (s, 3H, CH₃), 4.41 (s, 2H, CH₂), 7.04 (d, *J* = 16.2 Hz, 1H, Vinyl*H*), 7.12 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.24-7.37 (m, 5H, Ar*H*, Vinyl*H*), 7.44-7.47 (m, 2H, Ar*H*), 7.53 (d, *J* = 7.8 Hz, 1H, Ar*H*); ¹³C NMR (CDCl₃): δ 19.7, 28.6, 68.2, 79.0, 122.6, 126.0, 126.4, 127.6, 128.6, 128.9, 129.4, 130.5, 136.6, 137.2, 137.3, 161.6; LRMS (EI) *m/z* (% relative intensity): 291 (M⁺, 6), 215 (16), 214 (100), 142 (12), 55 (24); IR (KBr): 3064 m, 2967 s, 2925 m, 2869 m, 1656 s, 1592 m, 1494 m, 1461 s, 1359 m, 1292 s, 1211 m, 1187 m, 1103 m, 1043 s, 958 s, 919 m, 869 w, 821 w, 781 m, 742 s, 709 s, 692 m, 619 w, 557 w, 512 w, 491 w cm⁻¹. Anal. Calcd for C₂₀H₂₁NO: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.20; H, 7.19; N, 4.74.

1-Methyl-5-(2-styrylphenyl)-1H-tetrazole (29).

General procedure **B** was followed with 1-methyl-5-phenyl-1H-tetrazole and styryl acetate (**11**). Column chromatography (1:1 hexane/EtOAc) afforded **29** as a white solid in 52% yield. Mp 122.8-123.4 °C; ¹H NMR (CDCl₃): δ 3.90 (s, 3H, Me), 6.80 (d, *J* = 16.2 Hz, 1H, Ar*H*), 7.06 (d, *J* = 16.2 Hz, 1H, Ar*H*), 7.29-7.47 (m, 7H, Ar*H*), 7.57-7.63 (m, 1H, Ar*H*), 7.84 (d, *J* = 7.83 Hz, 1H, Ar*H*); ¹³C NMR (CDCl₃): δ 34.2, 122.0, 123.9, 126.2, 126.5, 127.6, 128.3, 128.6, 130.2, 131.3, 132.7, 136.0, 137.3, 154.2; LRMS (EI) *m/z* (% relative intensity): 262 (*M*⁺, 44), 233 (19), 218 (11), 208 (10), 207 (53), 204 (20), 192 (20), 190 (10), 189 (14), 186 (11), 185 (78), 165 (20), 158 (12), 157 (100), 128 (21), 116 (25), 102 (11), 89 (28), 77 (23), 76 (14), 75 (10), 63 (25), 51 (33), 50 (15); IR (KBr): 3048 w, 3021 w, 2952 w, 2362 w, 1631 w, 1598 m, 1573 w, 1535 m, 1490 m, 1471 m, 1446 m, 1400 m, 1288 m, 1261 m, 1211 w, 1120 m, 1091 m, 1033 m, 968 s, 763 s, 740 m, 694 s, 549 w, 526 m cm⁻¹. Anal. Calcd for C₁₆H₁₄N₄: C, 73.26; H, 5.38; N, 21.36. Found: C, 73.26; H, 5.47; N, 21.24.

4-(2,6-Distyrylphenyl)-2-methylthiazole (30).

General procedure **B** was followed with 2-methyl-4-phenylthiazole and styryl acetate (**11**). Column chromatography (10:1:0.1 hexane/EtOAc/Et₃N), followed by gel permeation chromatography (GPC) and bulb-to-bulb distillation afforded **30** as a white solid in 60% yield. Mp 134.2-135.0 °C; ¹H NMR (CDCl₃): δ 2.84 (s, 3H, CH₃), 6.91 (d, *J* = 16.2 Hz, 2H, Vinyl*H*), 7.01 (d, *J* = 16.4 Hz, 2H, Vinyl*H*), 7.05 (s, 1H, Ar*H*), 7.18-7.36 (m, 10H, Ar*H*), 7.42 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.68 (d, *J* = 7.8 Hz, 2H, Ar*H*); ¹³C NMR (CDCl₃): δ 19.3, 118.4, 124.5, 126.3, 127.2, 127.3, 128.3, 129.7, 133.0, 137.3, 137.5, 151.7, 164.9; LRMS (EI) *m/z* (% relative intensity): 380 (10), 379 (*M*⁺, 32), 302 (26), 289 (27), 288 (100), 243 (10), 242 (10), 150 (29), 59 (24); IR (KBr): 3052 m, 3025 m, 1594 m, 1569 m, 1490 s, 1444 s, 1326 w, 1282 m, 1191 m, 1162 s, 1072 w, 1051 w, 958 s, 844 w, 788 s, 736 s, 690 s, 649 m, 551 w, 532 m, 501 m cm⁻¹. Anal. Calcd for C₂₆H₂₁NS: C, 82.28; H, 5.58; N, 3.69; S, 8.45. Found: C, 82.17; H, 5.57; N, 3.58; S, 8.45.

1-[2-(2-Pyridinyl)-3-styrylphenyl]ethyl acetate (**32**)

General procedure **B** was followed with 1-[2-(2-pyridinyl)phenyl]ethyl acetate and styryl acetate (**11**). Column chromatography (gradient elution 6:1-4:1 hexane/EtOAc) afforded **32** as a yellow oil in 76% yield. ^1H NMR (CDCl_3): δ 1.44 (d, $J = 6.5$ Hz, 3H, Me), 1.99 (s, 3H, Ac), 5.53 (brs, 1H, CH), 6.63 (d, $J = 15.9$ Hz, 1H, Vinyl H), 6.94 (d, $J = 15.9$ Hz, 1H, Vinyl H), 7.15-7.65 (m, 9H, Ar H), 7.70 (d, $J = 8.9$ Hz, 1H, Ar H), 7.79 (t, $J = 8.5$ Hz, 1H, Ar H), 8.75 (d, $J = 6.7$ Hz, 1H, Ar H); ^{13}C NMR (CDCl_3): δ 21.2, 22.1, 70.0, 122.3, 124.7, 124.9, 125.8, 126.5, 126.8, 127.6, 128.5, 128.8, 130.3, 136.2, 137.3, 138.0, 149.5, 157.6, 170.1; LRMS (EI) m/z (% relative intensity): 344 (34), 343 (M^+ , 100), 342 (11), 322 (14), 310 (12), 300 (22), 284 (33), 283 (60), 282 (58), 268 (12), 267 (18), 266 (65), 255 (10), 253 (11), 223 (10), 209 (47), 208 (25), 207 (29), 206 (63), 204 (14); IR (neat): 3027 s, 2983 s, 2931 m, 1743 s, 1727 s, 1585 s, 1563 m, 1494 m, 1475 m, 1448 s, 1425 s, 1371 s, 1286 s, 1151 m, 1070 s, 1022 s, 960 s, 850 w, 796 s, 748 s, 727 s, 694 s, 619 w, 541 m, 503 m cm^{-1} . HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{23}\text{H}_{21}\text{NNaO}_2$) m/z 366.1700. Found 366.1476.

Examination on the Effect of Trifurylphosphine on Vinylation Reaction. Reactions of 2-(2-tolyl)pyridine (**1**) with vinyl acetate and vinyl butyrate (**2**) were examined in the presence of trifurylphosphine under the reaction conditions shown in footnote f of Table 1. The corresponding vinylation product **4** was obtained in 18% and 10% yields, respectively (eq s1). In order to compare these results using the same catalyst loading, we also examined the reaction of **1** with **2** using 10 mol% of Ru(cod)(cot) (**3**) under the reaction conditions shown in eq 1. The yield of **4** was slightly improved from 34% to 37% (eq s2). Thus, for the reaction of vinyl ester, trifurylphosphine lowered the activity of the ruthenium catalyst.

Preliminary Results on the Reaction Mechanisms

To obtain information with respect to the reaction pathway, several control experiments have been examined (eq s3-s7). If the alkenylation takes place through the addition of a C-H bond to an alkenyl acetate followed by the elimination of acetic acid from the product, the reaction of arylpyridine **31** with **11** should give 2-{2-(styryl)-6-vinylphenyl}pyridine **33**. However, only the alkenylation at the C-H bond proceeded and formation of **33** was not observed (s3). This suggests that the present coupling reaction does not involve hydroarylation at the alkenyl acetate step.

When a toluene-*d*₈ solution of (η^1 -C₂H₃)(η^2 -OAc)Ru(PEt₃)₃ (**A**) and **1** was heated at 120 °C for 1 h, the ¹H NMR spectrum showed that *ortho*-ruthenated tolylpyridine complex **C** and free ethylene were formed (eq s4, Figure S1). Any hydride or vinyl group was not observed. This seems to indicate reductive elimination from Ru(IV) intermediate **B** selectively occurred with the hydride and the vinyl group. (Overall conversion of **A** to **C** may not proceed through **B**, but via σ -bond metathesis). However, because the reaction of **1** with **2** was not efficiently catalyzed by complex **A** (equation s5), effect of phosphine ligands on the observed selectivity of reductive elimination is unclear.

Reaction of **3** with **1** (3 equiv) and **2** (1 equiv) at 120 °C for 3 h afforded signals assignable to an *ortho*-ruthenated tolylpyridine complex on the ¹H NMR spectrum (eq 6, Figure s2). After addition of 8 equiv of **2**, the reaction mixture was heated for another 9 h, and the product (**4**) was obtained in 66% yield. On the other hand, reactions of **3** with **1** resulted only in isomerization of **3** to Ru(cyclooctadienyl)₂. These results suggest that both alkenyl acetate and arylpyridine are essential to accomplish the efficient C-H bond cleavage by ruthenium.

Very recently, Oi *et al.* reported that the $[\text{RuCl}_2(\text{cod})]_n/\text{PPh}_3$ -catalyzed reaction of arylpyridines with allyl acetates gave a mixture of ortho allylation and alkenylation products. Their catalyst system was applied to our alkenylation reaction (eq s7). We carried out the following two control experiments using 2-phenylpyridine and **11** in the presence of $[\text{RuCl}_2(\text{cod})]_n/\text{PPh}_3$ as a catalyst. One reaction was conducted under reaction condition A (in toluene at 120 °C) and the other reaction was examined under reaction condition B used in their study. In both cases, the ortho alkenylation product was obtained in less than 4% yield. From these observations, our reaction described here is different from their reaction.