Supporting Information

Ru₃(CO)₁₂-Catalyzed C-H/CO/Olefin Coupling of *N*-Pyridylindolines. Direct Carbonylation at a C-H Bond δ to the Pyridine Nitrogen

Naoto Chatani,* Shuhei Yorimitsu, Taku Asaumi, Fumitoshi Kakiuchi, and Shinji Murai

*Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Suita, Osaka 565-0871, Japan*

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General Information. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in CDCl_3 with tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, quint = quintet, m = multiplet, and 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-14A gas chromatograph, 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. *N,N*-dimethylacetamide (DMA) was distilled over BaO. Acetonitrile, 1,4-dioxane and toluene were distilled over calcium hydride. Tetrahydrofuran was distilled from sodium benzophenone ketyl. $\text{Ru}_3(\text{CO})_{12}$ was prepared according to the literature procedure¹ and used, after recrystallization from hexane. Pyridylindolines **1a**,² **1b**, **1c**, **1d**, and **5** were obtained by Pd-catalyzed amination procedure reported by Buchwald.³

1-(4-Methyl-2-pyridinyl)-2,3-dihydro-1H-indole (1b). White solid; mp 77-79 °C; R_f 0.66 (hexane/EtOAc = 1/1); ^1H NMR (CDCl_3) δ 2.31 (s, 3H, 4'-Me), 3.17 (t, J = 8.6 Hz, 2H, 3-H), 4.00 (t, J = 8.6 Hz, 2H, 2-H), 6.57 (s, 1H, 3'-H), 6.59 (d, J = 5.3 Hz, 1H, 5'-H), 6.83 (dd, J = 7.6 Hz, 7.3 Hz, 1H, 5-H), 7.14-7.16 (c, 2H, 4, 6-H), 8.17 (d, J = 7.6 Hz, 1H, 7-H), 8.19 (d, J = 5.3 Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 21.49 (4'-Me), 27.77 (3-C), 49.40 (2-C), 108.97 (3'-C), 113.19 (7-C), 115.79 (5'-C), 120.09 (5-C), 124.38 (4-C or 6-C), 127.09 (4-C or 6-C), 131.19 (3a-C), 144.94 (7a-C or 4'-C), 147.46 (6'-C), 148.00 (7a-C or 4'-C), 155.57 (2'-C); IR (KBr) 3612 w, 3008 m, 2924 m, 2878 m, 2216 w, 1939 w,

1887 w, 1845 w, 1784 w, 1734 w, 1596 s, 1558 m, 1480 s, 1459 s, 1433 s, 1375 m, 1343 m, 1330 m, 1303 s, 1249 s, 1223 m, 1194 m, 1163 m, 1092 m, 1066 m, 1017 m, 990 m, 962 m, 921 m, 863 w, 842 w, 820 m; MS, m/z (relative intensity, %) 211 ($M^+ + 1$, 17), 210 (M^+ , 100), 209 (90), 208 (20), 207 (11), 194 (26), 118 (38), 117 (18), 93 (35), 65 (11). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.01; H, 6.78; N, 13.33.

1-(5-Methyl-2-pyridinyl)-2,3-dihydro-1H-indole (1c). White solid; mp 105-106 °C; R_f 0.66 (hexane/EtOAc = 1/1); 1H NMR ($CDCl_3$) δ 2.66 (s, 3H, 5'-Me), 3.18 (t, J = 8.6 Hz, 2H, 3-H), 4.01 (t, J = 8.6 Hz, 2H, 2-H), 6.72 (d, J = 8.6 Hz, 1H, 3'-H), 6.83 (dd, J = 7.6 Hz, 7.3 Hz, 1H, 5-H), 7.13-7.25 (c, 2H, 4, 6-H), 7.40 (d, J = 8.9 Hz, 1H, 4'-H), 8.08 (d, J = 8.2 Hz, 1H, 7-H), 8.16 (s, 1H, 6'-H); ^{13}C NMR ($CDCl_3$) δ 17.65 (5'-Me), 27.82 (3-C), 49.54 (2-C), 108.31 (3'-C), 112.54 (7-C), 119.85 (5-C), 123.22 (3a-C or 7a-C), 124.42 (4-C or 6-C), 127.11 (4-C or 6-C), 131.12 (3a-C or 7a-C), 137.97 (4'-C), 145.13 (5'-C), 147.63 (6'-C), 153.49 (2'-C); IR (KBr) 3006 w, 2890 w, 1920 w, 1879 w, 1732 w, 1615 m, 1598 s, 1558 m, 1502 s, 1486 s, 1461 s, 1412 s, 1383 m, 1345 m, 1301 s, 1258 m, 1244 m, 1215 m, 1174 m, 1152 m, 1095 w, 1074 w, 1019 m, 987 w, 938 w, 910 w, 831 w, 801 m; MS, m/z (relative intensity, %) 211 (M^+ , 16), 210 (100), 209 (88), 208 (51), 207 (24), 194 (31), 118 (34), 117 (19), 93 (28), 65 (13). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.90; H, 6.65; N, 13.43.

1-(6-Methyl-2-pyridinyl)-2,3-dihydro-1H-indole (1d). White solid; mp 88-90 °C; R_f 0.69 (hexane/EtOAc = 1/1); 1H NMR ($CDCl_3$) δ 2.50 (s, 3H, 6'-Me), 3.18 (t, J = 8.6 Hz, 2H, 3-H), 3.98 (t, J = 8.6 Hz, 2H, 2-H), 6.50 (d, J = 8.2 Hz, 1H, 3'-H or 5'-H), 6.62 (d, J = 7.3 Hz, 1H, 3'-H or 5'-H), 6.84 (dd, J = 7.6 Hz, 7.3 Hz, 1H, 5-H), 7.14-7.19 (c, 2H, 4, 6-H), 7.45 (dd, J = 8.2 Hz, 7.3 Hz, 1H, 4'-H), 8.32 (d, J = 7.6 Hz, 1H, 7-H); ^{13}C NMR ($CDCl_3$) δ 24.53 (6'-Me), 27.75 (3-C), 49.25 (2-C), 105.19 (3'-C or 5'-C), 113.52 (7-C), 113.65 (3'-C or 5'-C), 120.09 (5-C), 124.28 (4-C or 6-C), 127.09 (4-C or 6-

C), 131.13 (3a-C), 137.44 (4'-C), 145.02 (7a-C), 154.91 (6'-C), 156.61 (2'-C); IR (KBr) 3054 m, 2930 m, 2884 m, 1962 w, 1931 w, 1890 w, 1836 w, 1781 w, 1720 w, 1587 s, 1486 s, 1456 s, 1394 s, 1346 s, 1320 s, 1291 m, 1264 s, 1252 s, 1212 s, 1167 s, 1124 s, 1091 m, 1082 m, 1033 m, 1021 m, 982 m, 952 m, 925 m, 866 w, 848 m; MS, m/z (relative intensity, %) 211 ($M^{+}+1$, 17), 210 (M^{+} , 100), 209 (96), 208 (16), 195 (11), 118 (41), 117 (21), 105 (10), 94 (10), 93 (39), 92 (10), 65 (12). HRMS Calcd for $C_{14}H_{14}N_2$: 210.1157. Found: 210.1149.

1-(4-Methyl-2-pyridinyl)-2,3-dihydro-2-methyl-1H-indole (5). Colorless oil; bp 210 °C (0.7 mmHg); R_f 0.66 (hexane/EtOAc = 1/1); 1H NMR ($CDCl_3$) δ 1.33 (d, J = 6.3 Hz, 3H, 2-Me), 2.30 (s, 3H, 4'-Me), 2.67 (dd, J = 15.5 Hz, 2.6 Hz, 1H, 3-H), 3.40 (dd, J = 15.5 Hz, 9.2 Hz, 1H, 3-H), 4.63 (tdd, J = 6.3 Hz, 9.2 Hz, 2.6 Hz, 1H, 2-H), 6.58 (d, J = 5.3 Hz, 1H, 5'-H), 6.73 (s, 1H, 3'-H), 6.85 (t, J = 7.4 Hz, 1H, 5-H), 7.13-7.19 (c, 2H, 4, 6-H), 7.96 (d, J = 8.6 Hz, 1H, 7-H), 8.17 (d, J = 5.3 Hz, 1H, 6'-H); ^{13}C NMR ($CDCl_3$) δ 20.00 (2-Me), 21.50 (4'-Me), 36.38 (3-C), 56.46 (2-C), 109.38 (3'-C), 113.61 (7-C), 115.83 (5'-C), 120.26 (5-C), 124.82 (4-C or 6-C), 126.98 (4-C or 6-C), 130.27 (3a-C), 143.94 (7a-C or 4'-C), 147.68 (6'-C), 147.85 (7a-C or 4'-C), 155.03 (2'-C); IR (neat) 3050 m, 3010 s, 2968 s, 2924 s, 2852 m, 2320 w, 1905 w, 1675 w, 1599 s, 1556 s, 1489 s, 1430 s, 1376 m, 1354 s, 1326 m, 1303 s, 1246 m, 1223 m, 1197 m, 1164 w, 1124 m, 1094 w, 1077 m, 1058 m, 1024 m, 977 m, 951 w, 934 w, 841 w, 804 m; MS, m/z (relative intensity, %) 225 ($M^{+}+1$, 14), 224 (M^{+} , 64), 223 (23), 210 (22), 209 (100), 208 (11), 132 (28). Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.34; H, 7.24; N, 12.45.

Typical Procedure for Carbonylation at δ Position to a Pyridine Nitrogen. A 50-mL stainless autoclave was charged with 1-(2-pyridinyl)-2,3-dihydro-1H-indole (**1a**) (1 mmol, 196 mg), *N,N*-dimethylacetamide (3 mL), and $Ru_3(CO)_{12}$ (0.05 mmol, 32 mg). After the system was flushed with

10 atm of ethylene three times, it was pressurized with ethylene to 5 atm and then with carbon monoxide to an additional 10 atm. The autoclave was then immersed in an oil bath at 160 °C. After 20 hours had elapsed, it was removed from the oil bath and allowed to cool for ca. 1 h. The gases were then released. The contents were transferred to a round-bottomed flask with toluene, and the volatiles were removed in vacuo. The residue was subjected to column chromatography on silica gel (eluent; hexane/Et₂O = 5/1) to give 1-[1-(2-pyridinyl)-2,3-dihydro-7(1*H*)-indolyl]-1-propanone (**2a**) (103 mg, 41 % yield) as a pale yellow solid. Purification by HPLC afforded the analytically pure product.

1-[1-(2-Pyridinyl)-2,3-dihydro-7(1*H*)-indolyl]-1-propanone (2a). Pale yellow solid; mp 133-135 °C; *R_f* 0.029 (hexane/EtOAc = 1/1); ¹H NMR (CDCl₃) δ 0.96 (t, *J* = 7.3 Hz, 3H, CH₂CH₃), 2.66 (q, *J* = 7.3 Hz, 2H, CH₂CH₃), 3.23 (t, *J* = 8.6 Hz, 2H, 3-H), 4.17 (t, *J* = 8.6 Hz, 2H, 2-H), 6.69 (d, *J* = 8.6 Hz, 1H, 3'-H), 6.79 (dd, *J* = 7.3 Hz, 6.9 Hz, 1H, 5'-H), 6.94 (t, *J* = 7.6 Hz, 1H, 5-H), 7.25 (d, *J* = 6.6 Hz, 1H, 4-H or 6-H), 7.30 (d, *J* = 7.6 Hz, 1H, 4-H or 6-H), 7.57 (td, *J* = 7.8 Hz, 1.8 Hz, 1H, 4'-H), 8.12 (d, *J* = 5.0 Hz, 1H, 6'-H); ¹³C NMR (CDCl₃) δ 8.09 (CH₂CH₃), 28.08 (3-C), 34.27 (CH₂CH₃), 51.25 (2-C), 109.77 (3'-C), 115.73 (5'-C), 121.22 (5-C), 125.47 (4-C or 6-C), 126.20 (4-C or 6-C), 127.73 (7-C or 3a-C or 7a-C), 132.50 (7-C or 3a-C or 7a-C), 137.60 (4'-C), 140.42 (7-C or 3a-C or 7a-C), 145.55 (6'-C), 154.79 (2'-C), 198.79 (C=O); IR (KBr) 3052 w, 3006 w, 2978 w, 2938 w, 2906 w, 2876 w, 1691 s, 1645 w, 1586 s, 1568 w, 1540 w, 1464 s, 1449 s, 1430 s, 1403 m, 1373 m, 1352 m, 1334 m, 1295 s, 1232 m, 1206 w, 1183 w, 1160 w, 1147 m, 1097 w, 1077 w, 1063 w, 1052 w, 1035 m, 987 w, 872 w, 802 w; MS, *m/z* (relative intensity, %) 252 (M⁺, 5.4), 224 (24), 223 (100), 195 (17). HRMS Calcd for C₁₆H₁₆N₂O: 252.1263. Found: 252.1262.

1-[1-(4-Methyl-2-pyridinyl)-2,3-dihydro-7(1*H*)-indolyl]-1-propanone (2b). Pale yellow solid; mp 138-139 °C; *R_f* 0.029 (hexane/EtOAc = 1/1); ¹H NMR (CDCl₃) δ 0.97 (t, *J* = 7.3 Hz, 3H, CH₂CH₃), 2.30 (s, 3H, 4'-Me), 2.67 (q, *J* = 7.3 Hz, 2H, CH₂CH₃), 3.21 (t, *J* = 8.2 Hz, 2H, 3-H), 4.17 (t, *J* = 8.2

Hz, 2H, 2-H), 6.50 (s, 1H, 3'-H), 6.61 (d, $J = 4.6$ Hz, 1H, 5'-H), 6.91 (t, $J = 7.4$ Hz, 1H, 5-H), 7.23-7.30 (c, 2H, 4, 6-H), 7.93 (d, $J = 5.0$ Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 8.33 (CH_2CH_3), 21.41 (4'-Me), 28.42 (3-C), 34.31 (CH_2CH_3), 51.81 (2-C), 110.63 (3'-C), 117.56 (5'-C), 121.14 (5-C), 125.86 (4-C or 6-C), 126.51 (4-C or 6-C), 128.20 (7-C or 3a-C or 4'-C), 132.94 (7-C or 3a-C or 4'-C), 141.23 (7-C or 3a-C or 4'-C), 146.04 (6'-C), 148.75 (7a-C), 155.90 (2'-C), 202.91 (C=O); IR (KBr) 3354 w, 3048 w, 3010 w, 2962 m, 2926 m, 2870 m, 2720 w, 2430 w, 2238 w, 1690 s, 1605 s, 1555 m, 1452 s, 1402 s, 1372 m, 1354 s, 1336 s, 1296 s, 1227 s, 1206 m, 1190 m, 1171 w, 1158 m, 1123 w, 1094 w, 1076 m, 1063 w, 1033 s, 987 m, 954 w, 870 m, 845 w, 810 s; MS, m/z (relative intensity, %) 266 (M^+ , 3.2), 238 (19), 237 (100), 209 (13). HRMS Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}$: 266.1419. Found: 266.1426.

1-[1-(5-Methyl-2-pyridinyl)-2,3-dihydro-7(1H)-indolyl]-1-propanone (2c). Yellow oil; bp 220 °C (0.7 mmHg); R_f 0.029 (hexane/EtOAc = 1/1); ^1H NMR (CDCl_3) δ 0.98 (t, $J = 7.3$ Hz, 3H, CH_2CH_3), 2.21 (s, 3H, 5'-Me), 2.67 (q, $J = 7.3$ Hz, 2H, CH_2CH_3), 3.20 (t, $J = 8.6$ Hz, 2H, 3-H), 4.14 (t, $J = 8.6$ Hz, 2H, 2-H), 6.61 (d, $J = 8.3$ Hz, 1H, 3'-H), 6.90 (dd, $J = 7.9$ Hz, 7.3 Hz, 1H, 5-H), 7.23 (dd, $J = 7.3$ Hz, 1.3 Hz, 1H, 4-H or 6-H), 7.29 (d, $J = 7.9$ Hz, 1H, 4-H or 6-H), 7.37 (dd, $J = 8.2$ Hz, 2.1 Hz, 1H, 4'-H), 7.90 (d, $J = 2.6$ Hz, 1H, 6'-H); ^{13}C NMR (CDCl_3) δ 8.42 (CH_2CH_3), 17.64 (5'-Me), 28.34 (3-C), 34.28 (CH_2CH_3), 51.96 (2-C), 109.88 (3'-C), 120.85 (5-C), 125.21 (7-C or 3a-C), 125.89 (4-C or 6-C), 126.51 (4-C or 6-C), 127.76 (7-C or 3a-C), 132.86 (7a-C or 5'-C), 138.43 (4'-C), 141.48 (7a-C or 5'-C), 146.05 (6'-C), 153.88 (2'-C), 202.93 (C=O); IR (neat) 3352 w, 2974 s, 2936 s, 2876 s, 1693 s, 1601 s, 1567 s, 1498 s, 1401 s, 1339 s, 1299 s, 1231 s, 1156 m, 1093 m, 1078 m, 1035 s, 1022 s, 980 m, 914 w, 891 m, 872 m, 815 s; MS, m/z (relative intensity, %) 266 (M^+ , 4.8), 238 (22), 237 (100), 209 (14). HRMS Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}$: 266.1419. Found: 266.1413.

1-[1-(4-Methyl-2-pyridinyl)-2,3-dihydro-7(1H)-indolyl]-1-butanone (3) and 2-Methyl-1-[1-

(4-methyl-2-pyridinyl)-2,3-dihydro-7(1H)-indolyl]-1-propanone (4). Spectral data were obtained from a mixture of linear and branched ketones. Yellow oil; bp 230 °C (0.7 mmHg); R_f 0.029 (hexane/EtOAc = 1/1); ^1H NMR (CDCl_3) δ 0.82 (t, J = 7.6 Hz, 1.20H, linear $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.87 (d, J = 6.9 Hz, 3.60H, branched $\text{CH}(\text{CH}_3)_2$), 1.50 (sextet, J = 7.6 Hz, 0.80H, linear $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.28 (s, 3H, 4'-Me), 2.61 (t, J = 7.6 Hz, 0.80H, linear $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.01 (septet, J = 6.9 Hz, 0.60H, branched $\text{CH}(\text{CH}_3)_2$), 3.19 (t, J = 8.6 Hz, 2H, 3-H), 4.17 (t, J = 8.6 Hz, 2H, 2-H), 6.51 (s, 1H, 3'-H), 6.62 (d, J = 4.6 Hz, 1H, 5'-H), [6.91 (t, J = 7.6 Hz, branched), 6.92 (t, 1H, J = 7.6 Hz, linear), 1H, 5-H], 7.24 (d, J = 7.3 Hz, 1H, 4-H or 6-H), 7.30 (d, J = 7.6 Hz, 1H, 4-H or 6-H), 7.94-7.98 (c, 1H, linear 6'-H, branched 6'-H); ^{13}C NMR (CDCl_3) δ 13.96 (branched $\text{CH}(\text{CH}_3)_2$), 17.75 (linear $\text{CH}_2\text{CH}_2\text{CH}_3$), 18.51 (linear $\text{CH}_2\text{CH}_2\text{CH}_3$), 21.29 (4'-Me), 28.33 (3-C), 38.13 (branched $\text{CH}(\text{CH}_3)_2$), 43.09 (linear $\text{CH}_2\text{CH}_2\text{CH}_3$), [51.82 (branched), 51.94 (linear), 2-C], [110.37 (branched), 110.68 (linear), 3'-C], [117.52 (branched), 117.60 (linear), 5'-C], [121.08 (linear), 121.22 (branched), 5-C], [125.92 (linear), 126.51 (branched), 4-C or 6-C], [126.55 (linear), 127.00 (branched), 4-C or 6-C], [127.20 (branched), 128.11 (linear), 7-C or 3a-C or 4'-C], [132.82 (branched), 132.96 (linear), 7-C or 3a-C or 4'-C], [141.36 (linear), 141.51 (branched), 7-C or 3a-C or 4'-C], [146.01 (linear), 146.42 (branched), 6'-C], [148.68 (linear), 148.79 (branched), 7a-C], [156.08 (linear), 156.21 (branched), 2'-C], [202.05 (linear), 205.65 (branched), C=O]; IR (neat) 3346 w, 3056 m, 2968 s, 2594 w, 1917 w, 1686 s, 1598 s, 1562 s, 1451 s, 1344 s, 1297 s, 1225 s, 1110 m, 1064 s, 1037 s, 988 m, 963 m, 907 m, 853 m, 807 s; MS, m/z (relative intensity, %) [280 (M^+ , 1.3), 238 (24), 237 (100), 209 (10), linear], [280 (M^+ , 2.7), 238 (26), 237 (100), 209 (18), branched]. HRMS Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}$: 280.1576. Found: [280.1573 (linear), 280.1577 (branched)].

1-[1-(4-Methyl-2-pyridinyl)-2,3-dihydro-2-methyl-7(1H)-indolyl]-1-propanone (6). Yellow solid; mp 106-107 °C; R_f 0.029 (hexane/EtOAc = 1/1); ^1H NMR (CDCl_3) δ 0.90 (t, J = 7.3 Hz, 3H,

CH₂CH₃), 1.48 (d, J = 6.6 Hz, 3H, 2-Me), 2.29 (s, 3H, 4'-Me), 2.45 (dt, J = 17.2 Hz, 7.3 Hz, 1H, CH₂CH₃), 2.61-2.78 (c, 2H, 3-H, CH₂CH₃), 3.48 (dd, J = 15.8 Hz, 9.2 Hz, 1H, 3-H), 4.48 (m, 1H, 2-H), 6.55 (s, 1H, 3'-H), 6.60 (d, J = 5.4 Hz, 1H, 5'-H), 6.96 (dd, J = 7.9 Hz, 7.3 Hz, 1H, 5-H), 7.26 (d, J = 7.3 Hz, 1H, 4-H or 6-H), 7.33 (d, J = 7.9 Hz, 1H, 4-H or 6-H), 7.94 (d, J = 5.4 Hz, 1H, 6'-H); ¹³C NMR (CDCl₃) δ 8.28 (CH₂CH₃), 21.42 (4'-Me), 21.98 (2-Me), 34.02 (3-C), 36.62 (CH₂CH₃), 59.11 (2-C), 108.99 (3'-C), 117.42 (5'-C), 121.74 (5-C), 126.05 (4-C or 6-C), 127.07 (4-C or 6-C), 128.76 (7-C or 3a-C or 4'-C), 131.97 (7-C or 3a-C or 4'-C), 140.21 (7-C or 3a-C or 4'-C), 146.38 (6'-C), 148.84 (7a-C), 155.38 (2'-C), 201.34 (C=O); IR (KBr) 3344 w, 3068 m, 3010 w, 2956 m, 2928 m, 2868 m, 1912 w, 1859 w, 1785 w, 1762 w, 1684 s, 1595 s, 1561 s, 1486 s, 1485 s, 1436 s, 1370 s, 1344 s, 1320 s, 1299 s, 1270 s, 1238 s, 1210 s, 1200 s, 1155 m, 1124 w, 1090 s, 1067 s, 1053 m, 1023 s, 986 m, 949 m, 920 w, 898 w, 890 m, 873 w, 862 w, 831 w, 807 s; MS, m/z (relative intensity, %) 280 (M⁺, 3.1), 252 (21), 251 (100), 223 (17). HRMS Calcd for C₁₈H₂₀N₂O: 280.1576. Found: 280.1573.

References

- 1) Bruce, M. I.; Jensen, C. M.; Jones, N. L. *Inorg. Synth.* **1989**, *26*, 259.
- 2) Chatani, N.; Asaumi, T.; Yorimitsu, S.; Ikeda, T.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 10935.
- 3) Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 7240.

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BF 0.12 Hz
RGAIN 14

C:\WINDOWS\AIP\%A_T\181TA-1004-1 (pure) 13C.als
2a

DFILE C:\WINDOWS\AIP\%A_T\181TA-1004-1
COMINT 2a
DATIM Fri Apr 12 10:32:04 2002
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 926
ACQTM 1.789 sec
PD 1.211 sec
PWI 3.9 us
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 27

DFILE C:\WINDOWS\AIP\½ Å T1817A-1066-1
 COMINT 2b
 DATIM Thu Mar 22 14:51:22 2001
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.0 Hz
 POINT 16384
 FREQU 5402.4 Hz
 SCANS 8
 ACQTM 3.033 sec
 PD 3.967 sec
 PWM 5.3 us
 IRNUC 1H
 CTEMP 23.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

C:\WINDOWS\A\p\2\A\181TA-1066-1 (pure) 13C.als
2b

DFILE C:\WINDOWS\A\p\2\A\181TA-1066-1
 COMNT 2b
 DATIM Thu Mar 22 15:12:42 2001
 13C
 OBNUC 13C
 EXMOD BCM
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.0 Hz
 POINT 32768
 FREQU 18315.0 Hz
 SCANS 331
 ACQTM 1.789 sec
 PD 1.211 sec
 PWM 3.9 us
 IRNUC 1H
 CTEMP 23.9 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 26

C:\WINDOWS\AIP\½ Å T1817A-1068-1 (pure).als
2c

DFILE C:\WINDOWS\AIP\½ Å T1817A-1068-1 (pure).als
COMINT 2c
DATIM Fri Apr 06 16:52:05 2001
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 16384
FREQU 5402.4 Hz
SCANS 8
ACQTM 3.033 sec
PD 3.967 sec
PWI 5.3 us
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14

C:\WINDOWS\AIP\%A\T181TA-1068-1 (pure) 13C.als
2c

DFILE C:\WINDOWS\AIP\%A\T181TA-1068-1(
COMNT 2c
DATIM Fri Apr 06 17:04:05 2001
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 140
ACQTM 1.789 sec
PD 1.211 sec
PWI 3.9 us
IRNUC 1H
CTEMP 23.4 c
SOLVT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 26

C:\WINDOWS\AP\%A\T181TA-1379-1 (116-35).als
a mixture of 3 and 4

DFILE C:\WINDOWS\AP\%A\T181TA-1379-1(116-35).als
COMNT a mixture of 3 and 4
DATIM Thu May 16 10:39:08 2002
1H
NON
EXMOD 270.05 MHz
OBFRQ 112.00 KHz
OBSET 5800.0 Hz
OBFIN 16384
POINT 5402.4 Hz
FREQU 8
SCANS 3.033 sec
ACQTM 3.967 sec
PD 5.3 us
PWI 1H
IRNUC 23.0 c
CTEMP CDCL3
SLVNT 0.00 ppm
EXREF 0.12 Hz
BF 13
RGAIN

C:\WINDOWS\AP\%A\18\ITA-1379-1 (116-35) 13C.als
a mixture of 3 and 4

DFILE C:\WINDOWS\AP\%A\18\ITA-1379-1 (116-35) 13C.als
COMNT a mixture of 3 and 4
DATIM Thu May 16 11:35:55 2002
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 1000
ACQTM 1.789 sec
PD 1.211 sec
PW1 3.9 us
IRNUC 1H
CTEMP 23.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 26

DFILE C:\WINDOWS\AIP\A\T\181TA-1070-1.a1s

COMNT 6

DATIM Wed Apr 11 11:30:10 2001

OBNUC 1H

EXMOD NON

OBFRQ 270.05 MHz

OBSET 112.00 KHz

OBFIN 5800.0 Hz

POINT 16384

FREQU 5402.4 Hz

SCANS 8

ACQTM 3.033 sec

PD 3.967 sec

PWM 5.3 us

IRNUC 1H

CTEMP 22.4 c

CDCL3

SLVNT 0.00 ppm

EXREF 0.12 Hz

BF 15

RGAIN

C:\WINDOWS\p1\p1\181TA-1070-1 13C.als

6

DFILE C:\WINDOWS\p1\p1\181TA-1070-1
 COMINT 6
 DATIM Wed Apr 11 12:25:49 2001
 OBNUC 13C
 EXMOD BCM
 OBFREQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.0 Hz
 POINT 32768
 FREQU 18315.0 Hz
 SCANS 1000
 ACQTM 1.789 sec
 PD 1.211 sec
 PWT 3.9 us
 IRNUC 1H
 CTEMP 22.8 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 26