Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Rhenium- and Aniline-Catalyzed One-Pot Annulation of Aromatic Ketones and α,β-Unsaturated Esters Initiated by C-H Bond Activation

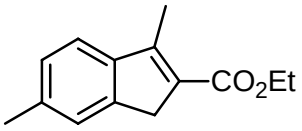
Yoichiro Kuninobu,* Yuta Nishina, Makoto Shouho, and Kazuhiko Takai*

Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan

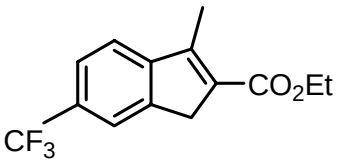
General. All reactions were carried out in dry toluene under an argon atmosphere. Toluene was purchased from Wako Pure Chemical Industries and was dried and degassed before use. $[ReBr(CO)_3(thf)]_2$ was prepared by heating a THF solution of $ReBr(CO)_5$ at reflux temperature for 16 h.[1] The resulting solution was concentrated in vacuo and was recrystallized from THF/hexane to gave $[ReBr(CO)_3(thf)]_2$ as a white solid in 75% yield.[2] Ketimine were prepared by condensation of the corresponding ketone with aniline in the presence of molecular sieves (4A) in toluene under reflux conditions for 10 h, and were used after distillation. Ketones, α,β-unsaturated carbonyl compounds and anilines were purchased from Wako Pure Chemical Industries, Tokyo Kasei Kogyo Co., Nacarai Tesque and Aldrich Co., and used after distillation.

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to Me_4Si ($CDCl_3$) at δ 0.00 ppm or residual solvent peak ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm. IR spectra were recorded on a Nicolet Protégé 460 spectrometer.

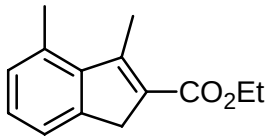
Indene derivatives **3a**, **3b** and **3h** are already known. The structures of the reaction products were determined by the comparison of the spectrum data of the products with the spectrum data of **3a**, **3b** and **3h**, which were reported in papers.[3-5]

3,6-Dimethyl-1*H*-indene-2-carboxylic acid ethyl ester (3c). 

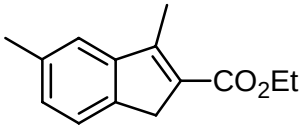
^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 2.52 (t, 3H), 3.60 (d, *J* = 2.4, 2H), 4.28 (q, *J* = 7.2, 3H),7.15 (d, *J* = 7.5, 1H), 7.28 (s, 1H), 7.37 (d, *J* = 7.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.43 (1C), 14.41 (1C), 21.62 (1C), 38.46 (1C), 59.80 (1C), 120.76 (1C), 124.70 (1C), 127.39, 1C), 128.81 (1C), 137.73 (1C), 142.78 (1C) , 143.79 (1C) , 151.42 (1C) , 166.07 (1C); IR (nujol, ν / cm^{-1}) 2923 (s), 2855 (s), 1706 (s), 1607 (m), 1574 (w), 1457 (m), 1378 (m), 1341 (w), 1324 (m), 1254 (s), 1226 (s), 1199 (s), 1135 (w), 1110 (w), 1074 (m), 1054 (m), 813 (m), 755 (w), 665 (w); Anal Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.62. Found: C, 77.88; H, 7.62.

3-Methyl-6-trifluoromethyl-1*H*-indene-2-carboxylic acid ethyl ester (3d). 

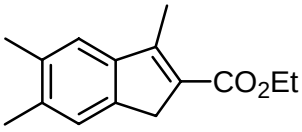
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.2 Hz, 3H), 2.56 (m, 3H), 3.70 (m, 2H), 4.32 (q, *J* = 7.2, 2H), 7.57 (d, *J* = 8.1, 1H), 7.63 (d, *J* = 8.1, 1H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.88 (1C), 15.02 (1C), 39.38 (1C), 60.78 (1C), 121.24 (1C), 121.65 (1C), 124.42 (1C), 124.99 (q, *J* = 270.1 Hz, 1C), 129.93 (q, *J* = 30.9 Hz, 1C), 133.04 (1C), 144.00 (1C) , 149.00 (1C) , 150.40 (1C) , 165.94 (1C); IR (nujol, ν / cm^{-1}) 2924 (s), 2855 (s), 1704 (s), 1653 (w), 1608 (m), 1577 (w), 1459 (m), 1377 (m), 1329 (s), 1288 (m), 1251 (m), 1210 (m), 1185 (m), 1107 (m), 1082 (w), 1064 (w), 938 (w), 902 (w), 886 (w), 831 (m), 756 (w); Anal Calcd for $C_{14}H_{13}F_3O_2$: C, 62.22; H, 4.85. Found: C, 62.32; H, 4.90.

3,4-Dimethyl-1*H*-indene-2-carboxylic acid ethyl ester (3e). 

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, *J* = 7.2 Hz, 3H), 2.65 (s, 3H), 2.77 (m, 3H), 3.62 (m, 2H), 4.28 (q, *J* = 7.2, 2H), 7.07 (d, *J* = 7.5, 1H), 7.21 (m, 1H), 7.31 (d, *J* = 7.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.41 (1C), 16.07 (1C), 20.74 (1C), 38.83 (1C), 59.82 (1C), 121.83 (1C), 127.35 (1C), 129.41 (1C), 129.57 (1C), 133.70 (1C), 140.13 (1C), 144.31 (1C), 153.42 (1C) , 166.17 (1C) ; IR (nujol, ν / cm^{-1}) 2924 (s), 2854 (s), 1709 (s), 1690 (m), 1598 (m), 1458 (s), 1375 (w), 1320 (w), 1232 (m), 1190 (s), 1078 (w), 1048 (w), 767 (w); Anal Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.48; H, 7.22.

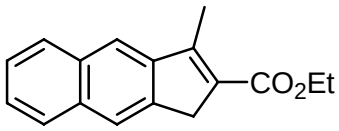
3,5-Dimethyl-1*H*-indene-2-carboxylic acid ethyl ester (3f). 

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 2.53 (m, 3H), 3.61 (m, 2H), 4.29 (q, *J* = 7.2, 2H), 7.17 (d, *J* = 7.5, 1H), 7.31 (s, 1H), 7.36 (d, *J* = 7.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.41 (1C), 14.41 (1C), 21.50 (1C), 38.33 (1C), 59.89 (1C), 121.64 (1C), 123.61 (1C), 128.55 (1C), 129.97 (1C), 136.19 (1C), 140.57 (1C) , 145.50 (1C) , 151.37 (1C) , 166.07 (1C); IR (nujol, ν / cm^{-1}) 2925 (s), 2855 (s), 1702 (s), 1600 (m), 1575 (m), 1479 (w), 1452 (m), 1367 (m), 1342 (s), 1319 (m), 1293 (m), 1248 (s), 1192 (s), 1114 (w), 1070 (w), 1056 (m), 810 (m), 756 (m), 734 (m); Anal Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.53; H, 7.34.

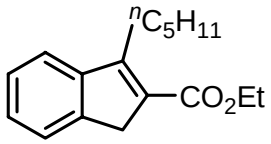
3,5-Dimethyl-1*H*-indene-2-carboxylic acid ethyl ester (3g). 

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 2.33 (s, 3H), 2.52 (m, 3H), 3.58 (m, 2H), 4.29 (q, *J* = 7.2, 2H), 7.25 (s, 1H), 7.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.49 (1C), 14.41 (1C), 20.05 (1C), 20.16 (1C), 38.21 (1C), 59.77 (1C), 122.01 (1C), 125.10 (1C), 128.75 (1C), 134.81 (1C), 136.48 (1C), 141.28 (1C) , 143.28

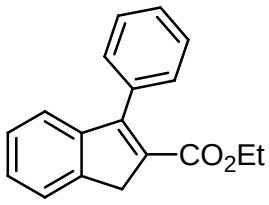
(1C) , 151.57 (1C) , 166.13 (1C); IR (nujol, ν / cm^{-1}) 2923 (s), 2854 (s), 1704 (s), 1606 (m), 1462 (s), 1376 (m), 1342 (w), 1318 (w), 1267 (w), 1253 (w), 1225 (m), 1199 (m), 1148 (w), 1061 (m); Anal Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.24; H, 7.92.

3-Methyl-1*H*-cyclopenta[b]naphthalene-2-carboxylic acid ethyl ester (3h). 

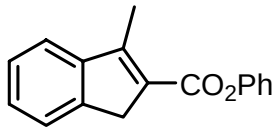
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.2 Hz, 3H), 2.62 (s, 3H), 3.76 (s, 2H), 4.32 (q, *J* = 7.2, 3H),7.45-7.47 (m, 2H), 7.83-7.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.43 (1C), 14.43 (1C), 37.86 (1C), 60.09 (1C), 119.83 (1C), 122.30 (1C), 125.37 (1C), 125.90, 1C), 127.79 (1C), 128.43 (1C), 131.13 (1C) , 132.64 (1C) , 133.41 (1C) , 140.31 (1C) , 144.37 (1C), 150.80 (1C), 166.00, 1C); IR (nujol, ν / cm^{-1}) 2923 (s), 2854 (s), 1702 (s), 1611 (w), 1598 (w), 1461 (s), 1376 (m), 1331 (w), 1247 (s), 1228 (s), 1209 (w), 1170 (w), 1135 (w), 1095 (w), 1061 (m), 869 (m), 749 (m), 665 (w); Anal Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.81; H, 6.22.

3-Pentyl-1*H*-indene-2-carboxylic acid ethyl ester (3i). 

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.34-1.48 (m, 7H), 1.66 (m, 2H), 3.05 (t, *J* = 7.8, 2H), 3.68 (s, 2H), 4.31 (q, *J* = 6.9, 1H), 7.34-7.37 (m, 2H) , 7.48-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.03 (1C), 15.27 (1C), 22.56 (1C), 26.65 (1C) , 28.94 (1C), 32.21 (1C), 38.86 (1C), 59.89 (1C), 121.26 (1C), 124.06 (1C), 126.46 (1C), 127.45 (1C), 129.43 (1C), 143.81 (1C), 144.68 (1C) , 156.04 (1C), 165.77 (1C); IR (nujol, ν / cm^{-1}) 2925 (s), 2855 (s), 1707 (s), 1652 (w), 1603 (m), 1576 (w), 1559 (w), 1459 (m), 1374 (m), 1322 (w), 1242 (m), 1189 (m), 1096 (w), 1078 (w), 1020 (w), 7586 (w); Anal Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.79; H, 8.59.

3-Phenyl-1*H*-indene-2-carboxylic acid ethyl ester (3j). 

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, *J* = 6.9 Hz, 3H), 3.81 (s, 2H), 4.10 (q, *J* = 6.9, 3H),7.24-7.51 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.96 (1C), 39.35 (1C), 60.02 (1C), 122.74 (1C), 124.06 (1C), 126.67 (1C), 127.24, 1C), 127.60 (1C), 127.97 (1C), 128.42 (1C) , 128.83 (1C) , 131.08 (1C) , 134.44 (1C) , 141.26 (1C), 143.46 (1C), 144.91, 1C) , 153.04 (1C), 165.06 (1C); IR (nujol, ν / cm^{-1}) 2924 (s), 2854 (s), 1701 (s), 1574 (w), 1463 (m), 1374 (s), 1349 (m), 1263 (m), 1237 (s), 1191 (w), 1152 (m), 1111 (s), 1094 (s), 757 (s), 745 (m), 719 (m), 698 (w); Anal Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.53; H, 6.07.

3-Methyl-1*H*-indene-2-carboxylic acid phenyl ester (3l). 

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (t, *J* = 2.4 Hz, 3H), 3.84 (q, *J* = 2.4 Hz, 2H), 7.19-7.28 (m, 3H), 7.39-7.45 (m, 4H), 7.53-7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.61(1C), 38.79 (1C), 121.32 (1C), 121.79 (2C), 124.03 (1C), 125.05 (1C), 126.68 (1C), 128.12 (1C), 129.34 (2C) , 143.66 (1C), 144.95 (1C), 150.68 (1C), 154.17 (1C) , 164.04 (1C); IR (nujol, ν / cm^{-1}) 2924 (s), 2854 (s), 1725 (w), 1706 (w), 1489 (w), 1458 (m), 1377 (m), 1356 (w), 1198 (w), 1182 (m), 1161 (w), 1152 (w), 1030 (w), 757 (w), 732 (w), 666 (w); Anal Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.35; H, 5.79.

[1] S. Du, J. A. Kautz, T. D. McGrath, F. G. A. Stone, *Organometallics* **2003**, *22*, 2842-2850.

[2] D. Vitali, F. Calderazzo, *Gazz. Chim. Ital.* **1972**, *102*, 587-596.

[3] L. Jalander, *Synth. Commun.* **1988**, *18*, 343-349.

[4] P. N. Ghoshal, B. Pathak, *J. Ind. Chem. Soc.* **1976**, *53*, 1126-1130.

[5] K.-J. Chang, D. K. Rayabarapu, C.-H. Cheng, *J. Org. Chem.* **2004**, *69*, 4781-4787.