Supplementary Material (ESI) for Chemical Communications

Insertion of arynes into carbon–halogen σ-bonds: regioselective acylation of aromatic rings

Hiroto Yoshida,* Yasuhiro Mimura, Joji Ohshita and Atsutaka Kunai*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan.

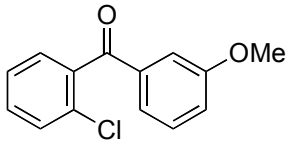
General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (^{1}H, 400 MHz; ^{13}C, 99.5 MHz) spectrometer using residual chloroform (for ^{1}H) or $CDCl_3$ (for ^{13}C) as an internal standard. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8700 spectrometer. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform as an eluent). Unless otherwise noted, commercially available reagents were used without purification. THF was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h.

Aryne Precursors. 2-(Trimethylsilyl)phenyl triflate (**1a**),[1] 3-(trimethylsilyl)-5,6,7,8-tetrahydro-2-naphthyl triflate (**1b**),[2] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**1c**),[3] 3-(trimethylsilyl)-2-naphthyl triflate (**1d**),[2] 3,6-dimethyl-2-(trimethylsilyl)phenyl triflate (**1e**),[2] 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**1f**),[3] 4-methyl-2-(trimethylsilyl)phenyl triflate (**1g**),[4] and 3-methoxy-2-(trimethylsilyl)phenyl triflate (**1h**)[5] were prepared according to literature procedures.

Reaction of Arynes with Acid Halides. ***A General Procedure.*** A Schlenk tube equipped with a magnetic stirring bar was charged with KF (0.60 mmol) and 18-crown-6 (0.60 mmol). The tube was evacuated at room temperature for 1 h with stirring before addition of THF (2 mL). To this solution was added an acid halide (0.33 mmol) and an aryne precursor (0.30 mmol), and the resulting mixture was stirred at 0 °C for the period as specified in Table 1, Table 2 or Scheme 2. The mixture was diluted with ethyl acetate, filtered through a Celite plug, washed three times with brine and dried

over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

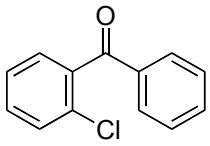
2-Chloro-3'-methoxybenzophenone (3aa).



3aa

Isolated in 70% yield as a an orange oil: ^{1}H NMR ($CDCl_3$) δ3.85 (s, 3 H), 7.14 (ddd, *J* = 8.1, 1.4, 1.2 Hz, 1 H), 7.25-7.48 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ55.4, 113.6, 120.3, 123.3, 126.6, 129.0, 129.5, 130.0, 131.8, 131.2, 137.8, 138.6, 159.8, 195.0; IR (KBr) 3059, 3003, 1663, 1593, 1485, 1462, 1436, 1327, 1292, 1259, 1231, 1144, 1059, 1036, 876, 826, 771, 749, 740, 686, 633 cm^{-1}; Anal Calcd for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.49. Found: C, 67.93; H, 4.30.

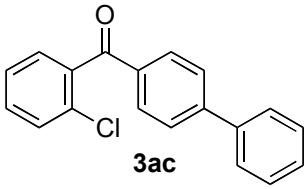
2-Chlorobenzophenone (3ab).[6]



3ab

Isolated in 68% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ7.34-7.52 (m, 6 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.81 (d, *J* = 7.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ126.6, 128.5, 129.0, 130.0, 131.0, 131.2, 133.6, 136.4, 138.5, 195.2; IR (neat) 2360, 1673, 1596, 1449, 1434, 1315, 1288, 1252, 1058, 929, 764, 744, 688, 668, 634 cm^{-1}.

2-Chloro-4'-phenylbenzophenone (3ac).

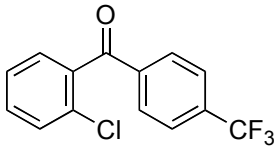


3ac

Isolated in 61% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ7.36-7.52 (m, 7 H), 7.64 (d, *J* = 7.3 Hz, 2 H), 7.69 (d, *J* = 8.3 Hz, 2 H), 7.90 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ126.6, 127.2, 127.3, 128.3, 128.9, 129.0, 130.0, 130.6, 131.0, 131.2, 135.1, 138.7, 139.7, 146.4, 194.7; IR (KBr) 3067, 3036, 1671, 1640, 1604, 1593, 1582, 1559, 1486, 1468, 1449, 1430, 1404, 1341, 1314, 1296, 1254, 1202, 1153, 1056, 933,

853, 774, 759, 744, 709, 697, 630 cm^{-1}; Anal. Calcd for $C_{19}H_{13}ClO$: C, 77.95; H, 4.48. Found: C, 77.98; H, 4.39.

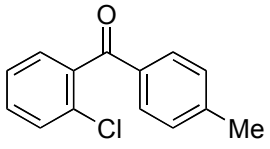
2-Chloro-4'-(trifluoromethyl)benzophenone (3ad).



3ad

Isolated in 60% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ7.37-7.53 (m, 4 H), 7.73 (d, J = 8.2 Hz, 2 H), 7.91 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ123.5 (q, J = 274.9 Hz), 125.6 (q, J = 3.7 Hz), 126.9, 129.3, 130.1, 130.2, 131.4, 131.7, 134.7 (q, J = 33.0 Hz), 137.7, 139.3, 194.2; IR (neat) 3066, 1682, 1631, 1592, 1566, 1509, 1470, 1433, 1411, 1312, 1288, 1250, 1131, 1288, 1250, 1131, 1111, 1067, 1035, 1017, 951, 932, 857, 781, 759, 741, 724, 684, 643, 595, 438, 414 cm^{-1}; Anal. Calcd for $C_{14}H_8ClF_3O$: C, 59.07; H, 2.83. Found: C, 59.05: H, 2.85.

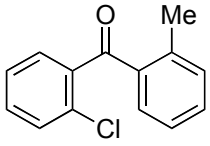
2-Chloro-4'-methylbenzophenone (3ae).



3ae

Isolated in 55% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.42 (s, 3 H), 7.30 (d, J = 8.4 Hz, 2 H), 7.33-7.50 (m, 4 H), 7.71 (d, J = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ21.7, 126.6, 128.9, 129.3, 129.9, 130.2, 130.8, 131.1, 133.9, 138.8, 144.7, 194.8; IR (KBr) 1662, 1603, 1434, 1314, 1300, 1290, 1252, 1155, 1057, 930, 839, 771, 749, 739, 714, 686, 663, 606 cm^{-1}; Anal. Calcd for $C_{14}H_{11}ClO$: C, 72.89; H, 4.81. Found: C, 72.70; H, 4.86.

2-Chloro-2'-methylbenzophenone (3af).

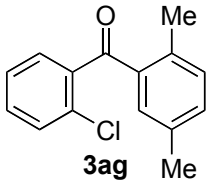


3af

Isolated in 52% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ2.58 (s, 3 H), 7.19 (t, J = 7.5 Hz, 1 H), 7.28-7.38 (m, 3 H), 7.38-7.46 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ21.1, 125.5, 126.6, 129.8, 130.2, 131.3, 131.4, 131.8, 131.9, 136.9, 139.5 139.6, 197.2; IR (neat) 3066, 1672, 1643, 1589, 1572, 1455, 1434, 1381, 1303, 1276, 1248, 1201, 1162, 1120,

1056, 1035, 927, 792, 766, 744, 716, 674, 636 cm^{-1}; Anal. Calcd for $C_{13}H_{11}ClO$: C, 72.89; H, 4.81. Found: C, 73.07; H, 4.85.

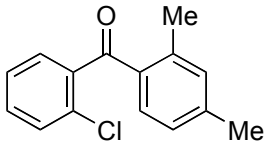
2-Chloro-2',5'-dimethylbenzophenone (3ag).



3ag

Isolated in 52% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ2.27 (s, 3 H), 2.50 (s, 3 H), 7.12 (brs, 1 H), 7.16-7.25 (m, 2 H), 7.31-7.38 (m, 1 H), 7.39-7.45 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ20.6, 20.7, 126.6, 129.9, 130.2, 131.3, 131.6, 131.7, 131.8, 132.7, 135.0, 136.3, 136.8, 139.6, 197.4; IR (neat) 3311, 3074, 2832, 1950, 1664, 1589, 1426, 1215, 1140, 996, 928, 874, 805, 771, 678 cm^{-1}; Anal. Calcd for $C_{15}H_{13}ClO$: C, 73.62; H, 5.35. Found: C, 73.49; H, 5.19.

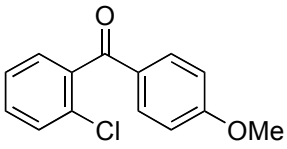
2-Chloro-2',4'-dimethylbenzophenone (3ah).[7]



3ah

Isolated in 43% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ2.40 (s, 3 H), 2.61 (s, 3 H), 7.02 (d, J = 8.0 Hz, 1 H), 7.16 (s, 1 H), 7.26 (d, J = 8.0 Hz, 1 H), 7.34-7.50 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ21.3, 21.4, 126.1, 126.6, 129.5, 130.1, 131.0, 131.5, 132.1, 132.8, 133.9 140.0, 142.8, 196.8; IR (neat) 2960, 1666, 1609, 1590, 1566, 1433, 1305, 1281, 1251, 1234, 1055, 1034, 955, 897, 828, 756, 742, 687, 662, 612 cm^{-1}.

2-Chloro-4'-methoxybenzophenone (3ai).[8]

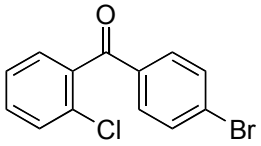


3ai

Isolated in 42% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ3.87 (s, 3 H), 6.93 (d, J = 9.0 Hz, 2 H), 7.34-7.49 (m, 4 H), 7.79 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ55.5, 113.8, 126.6, 128.8, 129.4, 129.9, 130.7, 131.0, 132.4, 139.0, 164.0, 193.8; IR (KBr) 3053, 2966, 2840, 1657, 1597, 1574, 1513, 1470, 1458, 1434, 1424, 1298, 1257, 1191,

1179, 1151, 1114, 1056, 1022, 983, 950, 930, 865, 826, 764, 741, 698, 665, 634, 609, 578, 514 cm^{-1}.

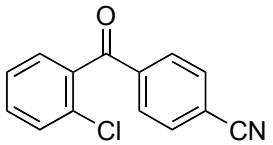
2-Chloro-4'-bromobenzophenone (3aj).



3aj

Isolated in 61% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ7.34-7.52 (m, 4 H), 7.57-7.73 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ126.8, 129.02, 129.07, 130.1, 131.2, 131.36, 131.39, 131.9, 135.2, 138.0, 194.1; IR (KBr) 3053, 1665, 1582, 1569, 1485, 1465, 1431, 1399, 1304, 1292, 1277, 1246, 1179, 1153, 1106, 1068, 1056, 1033, 1013, 982, 929, 856, 833, 773, 748, 704, 674, 643 cm^{-1}; Anal. Calcd for $C_{13}H_8BrClO$: C, 52.83; H, 2.73. Found: C, 52.84; H, 2.56.

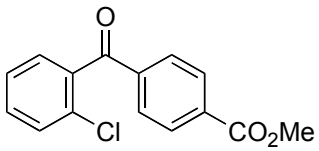
2-Chloro-4'-cyanobenzophenone (3ak).



3ak

Isolated in 54% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ7.39-7.44 (m, 2 H), 7.45-7.52 (m, 2 H), 7.76 (d, J = 8.3 Hz, 2 H), 7.88 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ116.7, 117.8, 127.0, 129.3, 130.1, 130.2, 131.3, 131.9, 132.4, 137.2, 139.6, 193.8; IR (KBr) 3334, 3092, 3043, 2233, 1672, 1607, 1590, 1560, 1472, 1432, 1409, 1319, 1260, 1152, 1118, 1060, 1022, 929, 863, 779, 758, 738, 711, 686, 653, 549 cm^{-1}; Anal. Calcd for $C_{14}H_8ClNO$: C, 69.48; H, 3.34; N, 5.80. Found: C, 69.48; H,3.17; N, 5.78.

2-Chloro-4'-(methoxycarbonyl)benzophenone (3al).

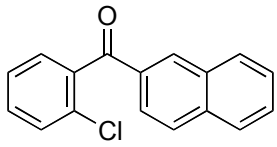


3al

Isolated in 51% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ3.94 (s, 3 H), 7.35-7.42(m, 2 H), 7.43-7.50 (m, 2 H), 7.85 (d, J = 8.3 Hz, 2 H), 8.11 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ52.4, 126.8, 129.3, 129.75, 129.77, 130.1, 131.4, 131.5, 134.2, 137.9, 139.8,

166.1, 194.7; IR (KBr) 3423, 3331, 2959, 1724, 1678, 1436, 1408, 1247, 1106, 1055, 1015, 931, 870, 827, 793, 765, 744, 730, 718, 694, 644, 582, 521 cm^{-1}; Anal. Calcd for $C_{15}H_{11}ClO_3$: C, 65.58; H, 4.04. Found: C, 65.55; H, 3.83.

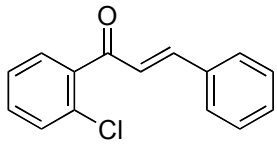
2-Chlorophenyl 2-naphthyl ketone (3am).



3am

Isolated in 50% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ7.36-7.56 (m, 5 H), 7.60 (t, J = 7.5 Hz, 1 H), 7.83-7.97 (m, 3 H), 8.02 (dd, J = 8.8, 1.7 Hz, 1 H), 8.18 (brs, 1 H); ^{13}C NMR ($CDCl_3$) δ124.6, 126.7, 126.8, 127.8, 128.6, 128.8, 129.1, 129.7, 130.1, 131.1, 131.3, 132.3, 132.8, 133.8, 135.8, 138.7, 195.2; IR (neat) 3059, 2365, 1664, 1626, 1593, 1566, 1547, 1529, 1509, 1463, 1433, 1353, 1296, 1276, 1258, 1233, 1200, 1150, 1118, 1056, 984, 933, 921, 907, 866, 852, 826, 780, 758, 740, 709, 660, 628 cm^{-1}; Anal. Calcd for $C_{17}H_{11}ClO$: C, 76.55; H, 4.16. Found: C, 76.85; H, 3.96.

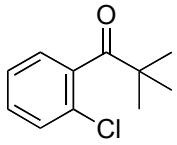
2'-Chlorochalcone (3an).



3an

Isolated in 58% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ7.12 (d, J = 16.3 Hz, 1 H), 7.32-7.50 (m, 8 H), 7.52-7.59 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ126.2, 126.8, 128.5, 128.9, 129.2, 130.2, 130.8, 131.2, 131.3, 134.3, 139.0, 146.2, 193.8; IR (neat) 3061, 2360, 1651, 1599, 1575, 1496, 1470, 1449, 1433, 1332, 1300, 1287, 1258, 1207, 1160, 1106, 1070, 1041, 1030, 1018, 1000, 979, 796, 755, 738, 720, 703, 678, 668, 646, 635, 600, 568 cm^{-1}; Anal. Calcd for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57. Found: C, 74.06; H, 4.47.

2'-Chloro-2,2-dimethylpropiophenone (3ao).

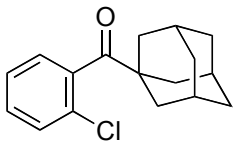


3ao

Isolated in 57% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ1.25 (s, 9 H), 7.12 (dd, J = 7.3, 2.0 Hz, 1 H), 7.25 (td, J = 7.3, 1.4 Hz, 1 H), 7.29 (td, J = 7.8, 2.0 Hz, 1 H), 7.37

(dd, J = 7.8, 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ26.8, 45.1, 126.0, 126.2, 129.3, 129.7, 129.8, 140.4, 211.5; IR (KBr) 2973, 2360, 1697, 1659, 1591, 1561, 1513, 1479, 1462, 1432, 1195, 1063, 965, 741 cm^{-1}; Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.18; H, 6.66. Found: C, 67.00; H, 6.68.

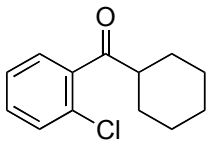
1-Adamantyl 2-chlorophenyl ketone (3ap).



3ap

Isolated in 48% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ1.64-1.76 (m, 6 H), 1.92-1.96 (m, 6 H), 2.00-2.06 (m, 3 H), 7.09 (dd, J = 7.3, 1.9 Hz, 1 H), 7.23-7.32 (m, 2 H), 7.37 (dd, J = 7.8, 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.8, 36.3, 38.1, 47.3, 126.0, 126.2, 129.4, 129.5, 129.7, 140.0, 210.8; IR (KBr) 2903, 2850, 1695, 1668, 1590, 1454, 1429, 1341, 1282, 1232, 1186, 1126, 1098, 1058, 987, 953, 942, 932, 834, 812, 757, 740, 711, 679, 636 cm^{-1}; Anal. Calcd for $C_{17}H_{19}ClO$: C, 74.31; H, 6.97. Found: C, 74.21; H, 6.89.

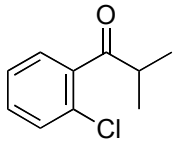
2-Chlorophenyl cyclohexyl ketone (3aq).



3aq

Isolated in 59% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ1.15-1.55 (m, 5 H), 1.60-2.00 (m, 5 H), 3.04 (tt, J = 11.2, 3.4 Hz, 1 H), 7.25-7.42 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ25.6, 25.8, 28.3, 49.9, 126.6, 128.2, 130.1, 130.4, 130.9, 139.9, 207.4; IR (neat) 2932, 2854, 1698, 1589, 1469, 1449, 1433, 1366, 1311, 1269, 1243, 1204, 1137, 1066, 1039, 974, 948, 894, 856, 817, 764, 741, 703, 644 cm^{-1}; Anal. Calcd for $C_{13}H_{15}ClO$: C, 70.11; H, 6.79. Found: C, 69.83; H, 6.80.

2'-Chloro-2-methylpropiophenone (3ar).[9]

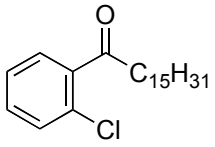


3ar

Isolated in 46% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ1.18 (d, J = 6.7 Hz, 6 H), 3.33 (septet, J = 6.8 Hz, 1 H), 7.27-7.42 (m. 4 H); ^{13}C NMR ($CDCl_3$) δ18.1, 40.2,

126.7, 128.3, 130.2, 130.5, 131.0, 139.8, 208.1; IR (neat) 2973, 2934, 2874, 1703, 1590, 1466, 1433, 1383, 1346, 1268, 1216, 1162, 1061, 1035, 980, 744, 636 cm^{-1}.

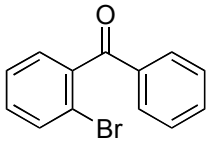
2-Chlorophenyl pentadecyl ketone (3as).



3as

Isolated in 39% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ0.87 (t, *J* = 6.7 Hz, 3 H), 1.29 (m, 24 H), 1.69 (quintet, *J* = 7.5 Hz, 2 H), 2.92 (t, *J* = 7.3 Hz, 2 H), 7.30 (td, *J* = 7.3, 1.7 Hz, 1 H), 7.33-7.44 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ14.1, 22.6, 24.1, 29.1, 29.35, 29.39, 29.4, 29.5, 29.63, 29.64, 29.66, 29.68, 31.9, 43.0, 126.8, 128.6, 130.4, 130.7, 131.3, 139.8, 203.9; IR (neat) 2924, 2853, 1693, 1591, 1467, 1433, 1274, 1070, 1038, 756, 722 cm^{-1}; Anal. Calcd for $C_{22}H_{35}ClO$: C, 75.29; H, 10.05. Found: C, 75.22; H, 10.24.

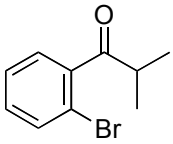
2-Bromobenzophenone (3at).



3at

Isolated in 54% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ7.33-7.55 (m, 5 H), 7.60 (tt, *J* = 7.3, 1.1 Hz, 1 H), 7.65 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.81(dd, *J* = 8.4, 1.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ119.3, 127.0, 128.4, 128.8, 130.0, 131.0, 133.0, 133.5, 136.0, 140.5, 195.7; IR (neat) 3059, 1672, 1581, 1565, 1467, 1448, 1431, 1315, 1287, 1250, 1153, 1046, 1024, 1000, 928, 800, 763, 738, 722, 702, 686, 664, 633 cm^{-1}; Anal. Calcd for $C_{13}H_9BrO$: C, 74.31; H, 6.97. Found: C, 74.12; H, 6.97.

2'-Bromo-2-methylpropiophenone (3au).[10]

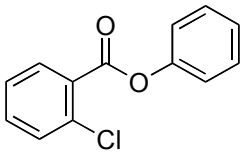


3au

Isolated in 43% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ1.18 (d, *J* = 7.0 Hz, 6 H), 3.31 (septet, *J* = 6.8 Hz, 1 H), 7.24-7.32 (m, 2 H), 7.32-7.38 (m, 1 H), 7.56-7.62 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ18.0, 18.1, 40.1, 118.5, 127.2, 128.0, 131.0, 133.3, 141.9,

208.7; IR (neat) 2972, 2932, 2873, 1703, 1587, 1564, 1468, 1428, 1384, 1217, 1079, 1052, 1029, 978, 739, 555 cm^{-1}.

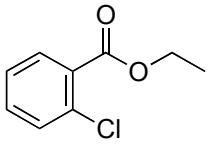
Phenyl 2-chlorobenzoate (3av).



3av

Isolated in 64% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ7.23-7.33 (m, 3 H), 7.37-7.56 (m, 5 H), 8.05 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ121.5, 126.0, 126.7, 129.3, 129.5, 131.2, 131.8, 133.1, 134.3, 150.6, 164.0; IR (neat) 3073, 1746, 1591, 1491, 1473, 1434, 1285, 1271, 1244, 1193, 1162, 1138, 1097, 1071, 1037, 1003, 914, 854, 745, 718, 688, 653 cm^{-1}; Anal. Calcd for $C_{13}H_9ClO_2$: C, 67.11; H, 3.90. Found: C, 67.28; H, 3.80.

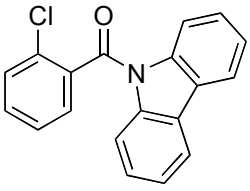
Ethyl 2-chlorobenzoate (3aw).



3aw

Isolated in 56% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ1.38 (t, *J* = 7.2 Hz, 3 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 7.29 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.36-7.45 (m, 2 H), 7.79 (dd, *J* = 8.0, 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ14.6, 61.5, 126.5, 130.4, 130.9, 131.2, 132.3, 133.5, 165.7; IR (neat) 3072, 2983, 2938, 2905, 2873, 1710, 1681, 1659, 1593, 1571, 1547, 1529, 1513, 1474, 1437, 1390, 1366, 1252, 1215, 1115, 1041, 1016, 956, 853, 829, 748, 718, 693, 650, 609 cm^{-1}; Anal. Calcd for $C_9H_9ClO_2$: C, 58.55; H, 4.91. Found: C, 58.35; H, 4.93.

9-(2-Chlorobenzoyl)carbazole (3ax).

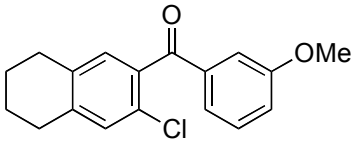


3ax

Isolated in 53% yield as a colorless solid: ^{1}H NMR ($CDCl_3$) 7.28-7.60(m, 10 H), 7.98 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ115.7, 119.7, 124.1, 126.5, 127.2, 127.6, 128.7, 130.4, 131.2, 131.8, 136.2, 138.4, 166.4; IR (KBr) 1679, 1592, 1446, 1439,

1364, 1334, 1325, 1213, 1089, 1048, 948, 765, 626 cm^{-1}; Anal. Calcd for $C_{19}H_{12}ClON$: C, 74.64; H, 3.96; N, 4.58. Found: C, 74.58; H, 3.93; N, 4.55.

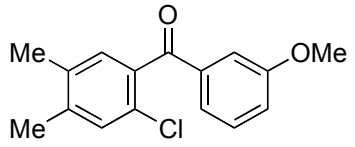
5,6,7,8-Tetrahydro-3-chloro-2-naphthyl 3-methoxyphenyl ketone (3ba).



3ba

Isolated in 62% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ1.71-1.85 (m, 4 H), 2.62-2.82 (m, 4 H), 3.84 (s, 3 H), 7.06 (s, 1 H), 7.09-7.16 (m, 2 H), 7.28-7.36 (m, 2 H), 7.40-7.45 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ22.5, 22.7, 28.7, 29.1, 55.4, 113.5, 120.0, 123.3, 127.8, 129.4, 129.8, 130.1, 135.5, 135.8, 138.2, 141.0, 159.7, 195.4; IR (neat) 3378, 2937, 2861, 2836, 1736, 1667, 1597, 1582, 1484, 1449, 1432, 1393, 1372, 1312, 1281, 1242, 1200, 1162, 1137, 1030, 994, 969, 921, 867, 799, 763, 732, 682, 653, 613 cm^{-1}; Anal. Calcd for $C_{18}H_{13}ClO_2$: C, 71.88; H, 5.70. Found: C, 71.72; H, 5.50.

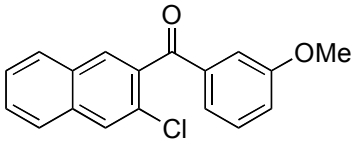
2-Chloro-4,5-dimethyl-3'-methoxybenzophenone (3ca).



3ca

Isolated in 50% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ2.24 (s, 3 H), 2.28 (s, 3 H), 3.83 (s, 3 H), 7.10-7.14 (m, 1 H), 7.13 (s, 1 H), 7.20 (s, 1 H), 7.27-7.35 (m, 2 H), 7.41 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ19.1, 19.6, 55.4, 113.5, 120.0, 123.2, 128.2, 129.4, 130.2, 130.7, 135.2, 135.7, 138.1, 140.5, 159.7, 195.3; IR (KBr) 2997, 2831, 1664, 1593, 1486, 1451, 1426, 1382, 1365, 1336, 1318, 1248, 1215, 1158, 1140, 1079, 1028, 995, 928, 903, 888, 874, 805, 771, 738, 726, 690, 678, 648, 638, 563, 550 cm^{-1}; Anal. Calcd for $C_{16}H_{15}ClO_2$: C, 69.95; H, 5.50. Found: C, 69.91; H, 5.44.

3-Chloro-2-naphthyl 3-methoxyphenyl ketone (3da).

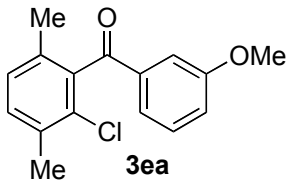


3da

Isolated in 47% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ3.85 (s, 3 H), 7.13-7.20 (m, 1 H), 7.28-7.38 (m, 2 H), 7.45-7.50 (m, 1 H), 7.51-7.62 (m, 2 H), 7.79-7.88 (m, 2 H), 7.88(s, 1 H), 7.94(s, 1 H); ^{13}C NMR ($CDCl_3$) δ55.4, 113.5, 120.4, 123.4, 126.9, 127.0,

128.2, 128.3, 128.4, 129.3, 129.5, 130.9, 134.3, 136.2, 138.1, 159.8, 194.9; IR (KBr) 3059, 2845, 1663, 1626, 1603, 1581, 1482, 1448, 1437, 1322, 1265, 1237, 1220, 1198, 1141, 1122, 1052, 1021, 948, 902, 897, 881, 801, 777, 744, 679, 641, 602, 576 cm^{-1}; Anal. Calcd for $C_{18}H_{13}ClO_2$: C, 72.85; H, 4.42. Found: C, 72.98; H, 4.42.

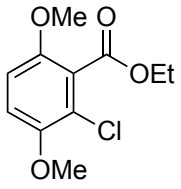
2-Chloro-3,6-dimethyl-3'-methoxybenzophenone (3ea).



3ea

Isolated in 69% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ2.11 (s, 3 H), 2.35 (s, 3 H), 3.84 (s, 3 H), 7.05 (d, *J* = 7.7 Hz, 1 H), 7.13 (d, *J* = 8.0, 1 H), 7.19 (d, *J* = 7.7 Hz, 1 H), 7.26 (dt, *J* = 7.7, 0.7 Hz, 1 H), 7.32 (t, *J* = 7.7 Hz, 1 H), 7.44-7.50 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ31.5, 55.3, 55.4, 112.8, 120.4, 122.6, 128.3, 129.8, 130.0, 130.9, 133.8, 133.9, 137.5, 138.6, 159.9, 196.5; IR (KBr) 2831, 1676, 1595, 1565, 1485, 1464, 1427, 1388, 1324, 1283, 1248, 1204, 1181, 1154, 1124, 1083, 1045, 1034, 994, 980, 954, 900, 848, 825, 810, 785, 749, 722, 709, 683, 661, 612, 551, 534 cm^{-1}; Anal. Calcd for $C_{16}H_{15}ClO_2$: C, 69.95; H, 5.50. Found: C, 69.65; H, 5.22.

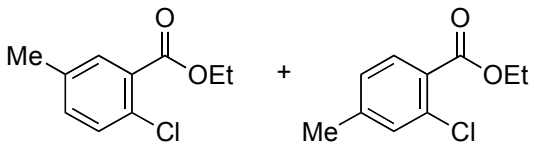
Ethyl 2-chloro-3,6-dimethoxybenzoate (3fw).



3fw

Isolated in 41% yield as an orange solid: ^{1}H NMR ($CDCl_3$) δ1.37 (t, *J* = 7.1 Hz, 3 H), 3.77 (s, 3 H), 3.83 (s, 3 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 6.76 (d, *J* = 9.0 Hz, 1 H), 6.88 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ14.1, 56.5, 56.8, 61.8, 110.1, 113.1, 120.3, 125.4, 149.3, 150.5, 165.2; IR (KBr) 2982, 2833, 1726, 1585, 1488, 1477, 1441, 1427, 1361, 1286, 1264, 1246, 1188, 1159, 1130, 1113, 1050, 1020, 930, 874, 857, 795, 745, 730, 592 cm^{-1}; Anal. Calcd for $C_{11}H_{13}ClO_4$: C, 54.00; H, 5.36. Found: C, 53.88; H, 5.38.

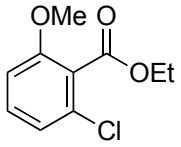
A mixture of ethyl 2-chloro-5-methylbenzoate (3gw) and ethyl 2-chloro-4-methylbenzoate (3'gw).



3gw **3'gw**

Isolated in 55% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ1.37 (t, *J* = 7.1 Hz, 3 H), 1.39 (t, *J* = 7.1 Hz, 3 H), 2.33 (s, 3 H), 2.34 (s, 3 H), 4.36 (q, *J* = 7.1, 2 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 7.08 (dd, *J* = 8.0, 0.7 Hz, 1 H), 7.18 (dd, *J* = 8.2, 2.1 Hz, 1 H), 7.25 (s, 1 H), 7.29 (d, *J* = 8.2 Hz, 1 H), 7.59 (d, *J* = 1.9 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ14.2, 20.6, 21.1, 61.3, 61.4, 127.2, 127.3, 130.0, 130.4, 130.6, 131.3, 131.5, 131.6, 133.1, 133.6, 136.5, 143.4, 165.6, 165.9; IR (neat) 2982, 1732, 1607, 1477, 1446, 1389, 1366, 1296, 1276, 1253, 1204, 1119, 1096, 1050, 1020, 896, 866, 822, 771, 688 cm^{-1}; Anal. Calcd for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.58. Found: C, 60.40; H, 5.54.

Ethyl 2-chloro-6-methoxybenzoate (3hw).



3hw

Isolated in 52% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ1.37 (t, *J* = 7.1 Hz, 3 H), 3.82 (s, 3 H), 4.41 (q, *J* = 7.1 Hz, 2 H), 6.81 (d, *J* = 8.5 Hz, 1 H), 6.97 (d, *J* = 8.2 Hz, 1 H), 7.25 (t, *J* = 8.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ14.1, 56.1, 61.7, 109.3, 121.4, 123.9, 130.8, 131.4, 157.1, 165.5; IR (neat) 2982, 2941, 2906, 2841, 1732, 1654, 1593, 1579, 1463, 1435, 1387, 1366, 1268, 1192, 1161, 1106, 1067, 1043, 1018, 860, 780, 759, 733, 702, 606 cm^{-1}; Anal. Calcd for $C_{10}H_{11}ClO_3$: C, 55.96; H, 5.17. Found: C, 56.23; H, 5.07.

1 Y. Himeshima, T. Sonoda and H. Kobayashi, *Chem. Lett.*, 1983, 1211.

2 H. Yoshida, T. Terayama, J. Ohshita and A. Kunai, *Chem. Commun.*, 2004, 1980.

3 H. Yoshida, S. Sugiura and A. Kunai, *Org. Lett.*, 2002, **4**, 2767.

4 E. Yoshikawa, K. V. Radhakrishnan and Y. Yamamoto, *J. Am. Chem. Soc.*, 2000, **122**, 7280.

5 D. Peña, D. Pérez, E. Guitián and L. Castedo, *J. Am. Chem. Soc.*, 1999, **121**, 5827.

6 This compound is commercially available.

7 H. Sharghi and H. Eshghi, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 135.

8 M. H. Sarrari and H. Sharghi, *J. Org. Chem.*, 2004, **69**, 6953.

9 J. Cámpora, C. M. Maya, P. Palma, E. Carmona, E. Guitiérrez, C. Ruiz, C. Graiff and A. Tiripicchio, *Chem. Eur. J.*, 2005, **11**, 6889.

10 K. Sato, M. Aoki, J. Takagi, K. Zimmermann and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 2287.