Highly Efficient Addition of Activated Methylene Compounds to Alkenes Catalyzed by Gold and Silver

Xiaoquan Yao and Chao-Jun Li*

Department of chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec H3A 2K6, Canada

Email: cj.li@McGill.ca

Supporting information

All experiments were carried out under an inert atmosphere of nitrogen. Dichloromethane was refluxed and distilled from CaH₂. Flash column chromatography was performed over SORBENT silica gel 30-60μm. ¹H NMR and ¹³C NMR spectra were acquired by Varian 400 MHz and 100 MHz, or 300 MHz and 75 MHz, respectively, and referenced to the internal solvent signals. IR spectra were recorded by ABB Bomem MB100 interferometer. MS data were obtained by KRATOS MS25RFA Mass Spectrometer. HRMS were made in McGill University.

Typical procedure (entry 1, Table 2): AuCl₃ (15.2mg, 0.05mmol) and AgOTf (38.5mg, 0.15mmol) were added into 2 mL of dichloromethane under N₂. The mixture was stirred at room temperature for 2 hours. 2,4-Pentanedione (103μL, 1mmol) was introduced into the solution of the catalyst prepared *in situ*. Styrene (172μL, 1.5mmol) was solved in 3mL of CH₂Cl₂ and dropped into the mixture of reaction by syringe pump in 5 hours. The mixture was stirred at room temperature overnight and removed solvent under reduced pressure. The residuum was isolated by flash chromatography with silica to give diketone alkylation product with 89% yield.

3-(1-phenylethyl)pentane-2,4-dione. CA registry Number: [5186-08-3]. IR (liquid film): $\nu_{\max}$ 3027, 2964, 1723, 1700, 1602, 1494, 1356, 1185, 1154, 955, 761, 700 cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 7.29-7.16(m, 5H), 4.05(d, J = 11.2Hz, 1H), 3.60(dq, J = 11.2, 7.2Hz, 1H), 2.26(s, 3H), 1.83(s, 3H), 1.21(d, J = 7.2Hz, 3H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 203.46, 203.40, 143.18, 129.00, 127.46, 127.17, 76.93, 40.83, 30.26, 30.18, 21.32.

3-(1-p-tolylyethyl)pentane-2,4-dione. IR (liquid film): $\nu_{\max}$ 3003, 2962, 2923, 1723, 1698, 1514, 1418, 1356, 1186, 1155, 955, 816 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 7.12-7.08(m, 4H), 4.02(d, J = 11.7Hz, 1H), 3.57(dq, J = 11.7, 6.9Hz, 1H), 2.31(s, 3H), 2.28(s, 3H), 1.86(s, 3H), 1.20(d, J = 6.9Hz, 3H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 203.68, 140.15, 136.72, 129.67, 127.31, 77.13, 40.44, 30.13, 30.09, 21.39, 21.38; MS (EI) m/z (%) 218(M^+), 200, 175(100), 161, 157, 142, 119, 91, 77; HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1306; found: 218.1296.

3-(1-(4-methoxyphenyl)ethyl)pentane-2,4-dione. IR (KBr): $\nu_{\max}$ 3008, 2965, 1719, 1696, 1518, 1363, 1291, 1251, 1182, 1037, 838, 830 cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 7.08(d, $J = 8.8\text{Hz}$, 2H), 6.81(d, $J = 8.8\text{Hz}$, 2H), 3.97(d, $J = 11.2\text{Hz}$, 1H), 3.76(s, 3H), 3.54(dq, $J = 11.2, 7.6\text{Hz}$, 1H), 2.26(s, 3H), 1.84(s, 3H), 1.18(d, $J = 7.6\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 203.75, 203.65, 158.49, 135.11, 128.42, 114.34, 77.26, 55.57, 40.14, 30.32, 30.14, 21.45; MS (EI) m/z (%) 234(M^+), 191, 173, 161, 135(100), 120, 105, 91, 77; HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$: 234.1256; found: 234.1251.

3-(1-(4-chlorophenyl)ethyl)pentane-2,4-dione. IR (KBr): $\nu_{\max}$ 3002, 2977, 2966, 1724, 1699, 1495, 1363, 1288, 1146, 1013, 825, 538 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 7.26(d, $J = 8.4\text{Hz}$, 2H), 7.12(d, $J = 8.4\text{Hz}$, 2H), 3.99(d, $J = 11.1\text{Hz}$, 1H), 3.59(dq, $J = 11.1, 6.9\text{Hz}$, 1H), 2.27(s, 3H), 1.87(s, 3H), 1.19(d, $J = 6.9\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 203.16, 203.08, 141.73, 132.88, 129.17, 128.85, 76.92, 40.04, 30.23, 30.03, 21.17; MS (EI) m/z (%) 238(M^+), 220, 195(100), 181, 139, 103, 101, 77; HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{ClO}_2$: 238.0761; found: 238.0754.

3-(1-(2-chlorophenyl)ethyl)pentane-2,4-dione. IR (KBr): $\nu_{\max}$ 3071, 2974, 1695, 1356, 1167, 1035, 756, 689 cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 7.35(d, J = 8.0Hz, 1H), 7.21-7.13(m, 3H), 4.20(m, 2H), 2.27(s, 3H), 1.92(s, 3H), 1.17(m, 3H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 203.17, 203.10, 140.53, 133.55, 130.37, 128.23, 128.04, 127.56, 75.38, 36.24, 31.06, 28.58, 20.26; MS (EI) m/z (%) 238(M^+), 203, 195(100), 181, 161, 159, 139, 125, 103, 101; HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{ClO}(\text{M}^+ - \text{Ac})$: 195.0577; found: 195.0570 .

3-(2,3-dihydro-1H-inden-3-yl)pentane-2,4-dione. IR (liquid film): $\nu_{\max}$ 3068, 3020, 2944, 2848, 1724, 1697, 1457, 1357, 1256, 1156, 1023, 952, 750 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 7.25-7.00(m, 4H), 4.02(m, 1H), 3.89(d, J = 10.2Hz, 1H), 3.10-2.80(m, 2H), 2.34-2.22(m, 1H), 2.20(s, 3H), 2.17(s, 3H), 1.70(m, 1H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 204.89, 203.55, 143.98, 143.60, 127.53, 126.63, 125.12, 124.29, 74.13, 44.87, 31.54, 31.23, 30.42, 29.61; MS (EI) m/z (%) 216(M^+), 173(100), 155, 129, 116, 101, 91, 43; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$: 216.1150; found: 216.1155.

2-acetyl-2-(1-phenylethyl)cyclopentanone. (The two diastereomers are difficult to be separated by flash column chromatography. But one of them can be isolated from the

mixture partly by crystallization) One of the two isomers(pure): IR (KBr): $\nu_{\max}$ 3066, 3038, 2967, 2953, 1734, 1698, 1497, 1360, 1143, 1122, 829, 763, 706 cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 7.26-7.12(m, 5H), 3.79(q, $J = 6.8\text{Hz}$, 1H), 2.76-2.71(m, 1H), 2.39-2.31(m, 1H), 2.17-2.07(m, 2H), 2.09(s, 3H), 1.88-1.70(m, 1H), 1.78-1.68(m, 1H), 1.21(d, $J = 6.8\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 215.99, 202.98, 142.32, 128.81, 127.96, 127.21, 74.83, 44.51, 39.81, 27.57, 26.57, 20.00, 19.24; MS (EI) m/z (%) 230(M^+), 212, 188, 187, 173, 159, 126, 105(100), 91, 77; HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: 230.1307; found: 230.1299.

Another diastereomer (from the mixture of two isomers, and some peaks are difficult to be distinguished): ^1H NMR (CDCl_3 , 400MHz, ppm) δ 3.94(q, $J = 7.2\text{Hz}$, 1H), 2.39(s, 3H), 1.17(d, $J = 7.2\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 215.45, 203.23, 140.88, 75.16, 43.28, 40.25, 25.96, 25.05, 19.81, 16.50.

2-acetyl-2-(1-(4-chlorophenyl)ethyl)cyclopentanone. IR (KBr): $\nu_{\max}$ 3038, 2973, 1735, 1700, 1493, 1355, 1196, 1143, 1094, 1014, 835, 666 cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 7.24(d, $J = 8.0\text{Hz}$, 2H), 7.13(d, $J = 8.0\text{Hz}$, 2H), 3.90(q, $J = 6.8\text{Hz}$, 1H), 2.72-2.66(m, 1H), 2.37(s, 3H), 2.08-1.40(m, 5H), 1.14(d, $J = 6.8\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 215.32, 202.81, 139.45, 133.14, 130.71, 128.52, 75.10, 42.50, 40.11,

25.81, 25.05, 19.73, 16.45; MS (EI) m/z (%) 264(M^+), 221(100), 207, 141, 139, 115, 103, 77; HRMS calcd for $C_{15}H_{17}ClO_2$: 264.0917, found: 264.0913.

Another diastereomer: IR (KBr): $\nu_{\max}$ 3034, 2966, 1736, 1696, 1500, 1489, 1359, 1147, 1121, 1014, 840, 820 cm^{-1} ; 1H NMR ($CDCl_3$, 300MHz, ppm) δ 7.22(d, J = 8.4Hz, 2H), 7.06(d, J = 8.4Hz, 2H), 3.77(q, J = 7.2Hz, 1H), 2.75-2.68(m, 1H), 2.42-2.30(m, 1H), 2.20-2.06(m, 2H), 2.09(s, 3H), 1.95-1.64(m, 2H), 1.19(d, J = 7.2Hz, 3H); ^{13}C NMR ($CDCl_3$, 75MHz, ppm) δ 215.70, 202.71, 140.87, 133.03, 129.33, 128.99, 74.59, 43.83, 39.67, 27.43, 26.50, 19.85, 19.07; MS (EI) m/z (%) 264(M^+), 221(100), 207, 141, 139, 115, 103, 77; HRMS calcd for $C_{15}H_{17}ClO_2$: 264.0917, found: 264.0910.

2-(1-(4-chlorophenyl)ethyl)-1-phenylbutane-1,3-dione. IR (KBr): $\nu_{\max}$ 3068, 2971, 1711, 1675, 1594, 1355, 1265, 1218, 1014, 971, 826, 767 cm^{-1} ; 1H NMR ($CDCl_3$, 400MHz, ppm) δ 8.07(m, 2H), 7.64-7.48(m, 3H), 7.30-7.20(m, 4H), 4.86(d, J =10.8Hz, 1H), 3.87(dq, J = 10.8, 7.2Hz, 1H), 1.92(s, 3H), 1.20(d, J = 7.2Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz, ppm) δ 202.90, 194.94, 141.87, 137.21, 134.18, 132.90, 129.18, 129.14, 129.09, 71.01, 40.61, 28.37, 21.91; MS (EI) m/z (%) 300(M^+), 257(100), 243, 195, 179, 139, 105, 77; HRMS calcd for $C_{18}H_{17}ClO_2$: 300.0917, found: 300.0910.

Another diastereomer: IR (KBr): $\nu_{\max}$ 3066, 2972, 1713, 1670, 1596, 1494, 1360, 1218, 1176, 1098, 1012, 836, 759 cm^{-1} ; 1H NMR ($CDCl_3$, 400MHz, ppm) δ 7.81-7.78(m, 2H), 7.51(m, 1H), 7.40-7.36(m, 2H), 7.13(s, 4H), 4.77(d, J = 10.8Hz, 1H), 3.84(dq, J = 10.8,

7.2Hz, 1H), 2.24(s, 3H), 1.29(d, $J = 7.2\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 203.37, 195.00, 142.18, 136.96, 133.88, 132.49, 128.96, 128.93, 128.81, 128.69, 71.73, 39.96, 27.90, 20.62; MS (EI) m/z (%) 300(M^+), 257(100), 243, 195, 179, 139, 105, 77; HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{ClO}_2$: 300.0917, found: 300.0908.

2-(1-(2-chlorophenyl)ethyl)-1-phenylbutane-1,3-dione. IR (KBr): ν_{max} 3071, 2969, 1715, 1665, 1579, 1479, 1356, 1264, 1210, 1172, 1033, 970, 761, 689 cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 8.05(d, $J = 8.4\text{Hz}$, 2H), 7.59-7.14(m, 7H), 5.04(d, $J = 9.6\text{Hz}$, 1H), 4.49(dq, $J = 9.6, 6.8\text{Hz}$, 1H), 1.97(s, 3H), 1.19(d, $J = 6.8\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 203.36, 195.16, 140.51, 137.29, 134.08, 133.55, 130.33, 129.15, 129.06, 128.26, 127.54, 69.47, 36.99, 27.46, 20.45; MS (EI) m/z (%) 265($\text{M}^+ - \text{Cl}$), 257, 243, 223, 195, 139, 105(100), 77; HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2(\text{M}^+ - \text{Cl})$: 265.1229, found: 265.1225.

Another diastereoisomer: IR (KBr): ν_{max} 3057, 2971, 1713, 1670, 1595, 1475, 1436, 1215, 1173, 1035, 975, 770, 697 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 7.89(d, $J = 7.5\text{Hz}$, 2H), 7.60-7.03(m, 7H), 5.05(d, $J = 10.5$, 1H), 4.36(dq, $J = 10.5, 7.2\text{Hz}$, 1H), 2.26(s, 3H), 1.30(d, $J = 7.2\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 203.69, 194.87, 141.12, 136.87, 133.81, 130.28, 128.94, 128.75, 127.89, 127.22, 69.74, 36.71, 28.23, 19.62; MS (EI) m/z (%) 265($\text{M}^+ - \text{Cl}$), 257, 243, 223, 195, 139, 105(100), 77, HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2(\text{M}^+ - \text{Cl})$: 265.1229, found: 265.1225.

1,3-diphenyl-2-(1-phenylethyl)propane-1,3-dione. CA registry Number: [116140-58-0]. IR (KBr): $\nu_{\max}$ 3070, 3001, 2972, 1687, 1650, 1594, 1447, 1275, 1213, 1213, 1000, 972, 769 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 8.04(d, $J = 7.5\text{Hz}$, 2H), 7.74(d, $J = 7.5\text{Hz}$, 2H), 7.60-7.07(m, 11H), 5.61(d, $J = 9.9\text{Hz}$, 1H), 4.09(dq, $J = 9.9, 6.9\text{Hz}$, 1H), 1.36(d, $J = 6.9\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 195.04, 194.69, 143.99, 137.34, 137.09, 133.74, 133.23, 129.05, 129.02, 128.70, 128.65, 128.60, 127.94, 126.81, 65.22, 41.53, 20.63; MS (EI) m/z (%) 327($\text{M}^+ - \text{H}$), 259, 241, 223(100), 147, 129, 105, 77.

2-(1-(4-chlorophenyl)ethyl)-1,3-diphenylpropane-1,3-dione. IR (KBr): $\nu_{\max}$ 3057, 2971, 1689, 1663, 1594, 1577, 1447, 1284, 1284, 1099, 970, 762 cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 8.04(d, $J = 8.0\text{Hz}$, 2H), 7.75(d, $J = 8.0\text{Hz}$, 2H), 7.58-7.12(m, 10H), 5.57(d, $J = 10.4\text{Hz}$, 1H), 4.07(dq, $J = 10.4, 6.8\text{Hz}$, 1H), 1.32(d, $J = 6.8\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 100MHz, ppm) δ 194.74, 194.39, 142.52, 137.10, 136.83, 133.90, 133.49, 132.43, 129.32, 129.13, 129.02, 128.78, 128.71, 128.69, 65.03, 40.96, 20.74; MS (EI) m/z

(%) 362($M^+ - H$), 327, 257(100), 223, 147, 139, 105, 77; HRMS calcd for $C_{16}H_{14}ClO$ ($M^+ - CPh$): 257.0733, found: 257.0731.

2-(1-(2-chlorophenyl)ethyl)-1,3-diphenylpropane-1,3-dione. IR (KBr): ν_{max} 3064, 2984, 1695, 1657, 1594, 1447, 1290, 1198, 1035, 988, 751, 688 cm^{-1} ; 1H NMR ($CDCl_3$, 400MHz, ppm) δ 7.95(m, 2H), 7.86(m, 2H), 7.54-7.22(m, 8H), 7.07-7.04(m, 2H), 5.87(d, $J = 8.4Hz$, 1H), 4.48(dq, $J = 8.4, 7.2Hz$, 1H), 1.37(d, $J = 7.2Hz$, 3H); ^{13}C NMR ($CDCl_3$, 100MHz, ppm) δ 195.42, 194.66, 141.24, 137.17, 136.69, 133.76, 133.72, 133.40, 130.15, 129.01, 128.79, 128.68, 127.93, 127.05, 62.00, 32.03, 18.69; MS (CI) m/z (%) 363($M^+ + H$), 327, 257, 225, 207, 139, 105(100), 77; HRMS calcd for $C_{23}H_{19}O_2(M^+ - Cl)$: 327.1385, found: 327.1380.

1,3-diphenyl-2-(1-phenylpropyl)propane-1,3-dione. IR (KBr): ν_{max} 3060, 2979, 1685, 1661, 1594, 1447, 1277, 1196, 986, 963, 759, 701 cm^{-1} ; 1H NMR ($CDCl_3$, 400MHz, ppm) δ 8.07(d, $J = 6.8Hz$, 2H), 7.72(d, $J = 7.2Hz$, 2H), 7.56-7.06(m, 11H), 5.69(d, $J = 10.0$, 1H), 3.84(m, 1H), 1.79-1.66(m, 2H), 0.72(dd, $J = 7.2, 7.4Hz$, 3H); ^{13}C NMR

(CDCl₃, 100MHz, ppm) δ 195.13, 194.44, 141.35, 137.40, 137.16, 133.79, 133.18, 129.08, 129.03, 128.87, 128.69, 128.60, 128.46, 126.79, 64.74, 49.16, 27.47, 12.54; MS (EI) m/z (%) 342(M⁺), 313, 257, 237(100), 223, 195, 147, 129, 105, 77; HRMS calcd for C₂₄H₂₂O₂: 342.1620, found: 342.1607.

2-(bicyclo[2.2.1]heptan-2-yl)-1,3-diphenylpropane-1,3-dione. IR (KBr): $\nu_{\max}$ 3068, 2652, 2906, 2861, 1694, 1656, 1448, 1287, 1200, 985, 758, 699cm⁻¹; ¹H NMR (CDCl₃, 400MHz, ppm) δ 8.03(d, J = 7.2Hz, 2H), 7.93(d, J = 6.8Hz, 2H), 7.57-7.37(m, 6H), 5.03(d, J = 10.8, 1H), 2.74(m, 1H), 2.24(s, 1H), 1.96(s, 1H), 1.62(m, 1H), 1.51-1.48(m, 3H), 1.30(m, 1H), 1.22-1.19(m, 2H), 1.13-1.10(m, 1H); ¹³C NMR (CDCl₃, 100MHz, ppm) δ 195.87, 195.26, 137.34, 137.25, 133.66, 133.45, 129.07, 129.05, 128.93, 128.89, 64.73, 44.03, 40.02, 37.63, 37.11, 36.43, 30.46, 28.94; MS (EI) m/z (%) 318(M⁺), 300, 224, 213, 196, 167, 143, 105, 77; HRMS calcd for C₂₂H₂₂O₂: 318.1620, found: 318.1614.

The configuration of the product was determined by NOE.