Supplementary Information

Rhenium- and manganese-catalyzed insertion of acetylenes into β-keto esters: synthesis of 2-pyranones

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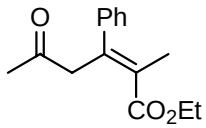
General. All reactions were carried out under an argon atmosphere. Toluene was purchased from Wako Pure Chemical Industries and was dried and degassed before use. $[ReBr(CO)_3(thf)]_2$ was prepared by heating a THF solution of $ReBr(CO)_5$ at reflux temperature for 16 h. A manganese complex, $MnBr(CO)_5$, was prepared by stirring a cyclohexane solution of $Mn_2(CO)_{10}$ (Aldrich Co.) and Br_2 at 25 ˚C for 7 h, and resulting precipitates were collected and washed with hexane.

Ethyl 2-methyl-3-oxo-3-phenylpropionate (**1d**),[1] ethyl 2-acetyloct-7-ynoate (**7**)[2], and ethyl 2-acetyl-8-phenyloct-7-ynoate (**12**)[2] were prepared according to the literature method. Other β-keto esters (**1a**, **1b, 1c**), acetylenes (**2a**-**2k**) were purchased from Wako Pure Chemical Industries, Tokyo Kasei Kogyo Co., and Aldrich Co., and used as received. Molecular sieves 4A in powder form were purchased from Nacalai tesque Inc., and used without further activation.

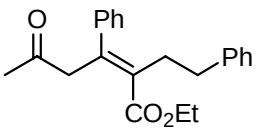
^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to Me_4Si ($CDCl_3$) at δ 0.00 ppm or residual solvent peak ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm.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

Typical Procedure for Rhenium-Catalyzed Insertion of Acetylenes into β-Keto esters. A mixture of ethyl 2-methylacetoacetate (**1a**, 72.1 mg, 0.500 mmol), phenylacetylene (**2a**, 61.2 mg, 0.600 mmol), $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), and toluene (1.0 mL) was stirred at 80 ˚C for 24 h under argon atmosphere. After purification by silica gel column chromatography, β-keto esters **3a**-**5a** were obtained in 92% (**3a** : **4a** : **5a** = 11 : 85 : 4) yield.

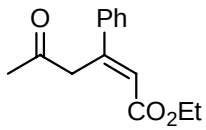
***(E)*-Ethyl 2-methyl-5-oxo-3-phenylhex-2-enoate (4a).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 1.83 (s, 3H), 2.17 (s, 3H), 3.87 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 7.16-7.18 (m, 2H), 7.25-7.27 (m, 1H), 7.33-7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 17.2, 29.7, 51.2, 60.4, 127.0, 127.3, 127.4, 127.7, 128.3, 144.7, 168.4, 204.8; IR (neat / cm^{-1}) 3057, 2982, 2926, 1717, 1701, 1491, 1356, 1259, 1129, 1027, 776, 704, 532; Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.12; H, 7.53.



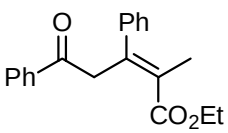
***(E)*-Ethyl 5-oxo-2-(2-phenylethyl)-3-phenylhex-2-enoate (4b) [Table 1, entry 1].** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.2 Hz, 3H), 2.15 (s, 3H), 2.49 (t, *J* = 7.8 Hz, 2H), 2.66 (t, *J* = 7.9 Hz, 2H), 3.81 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 6.96-7.33 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 29.8, 33.1, 35.6, 51.5, 60.6, 125.8, 127.1, 127.4, 128.2, 128.4, 128.5, 132.4, 141.4, 144.9, 168.4, 204.7; IR (neat / cm^{-1}) 3062, 3026, 2979, 2927, 1732, 1701, 1599, 1496, 1456, 1356, 1252, 1172, 1026, 911, 701; Anal. Calcd. for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.44; H, 7.42.



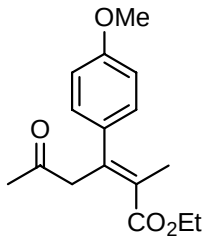
***(E)*-Ethyl 5-oxo-3-phenylhex-2-enoate (4c) [Table 1, entry 2].** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 2.28 (s, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.22 (s, 2H), 6.31 (s, 1H), 7.35-7.38 (m, 3H), 7.39-7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 29.8, 46.8, 60.1, 119.4, 126.5, 128.7, 129.2, 140.8, 152.1, 166.4, 204.7; IR (neat / cm^{-1}) 3060, 2981, 2935, 1707, 1625, 1577, 1447, 1178, 1040, 876, 767, 696, 546; Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.26; H, 7.10.



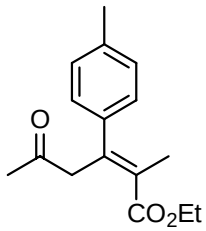
***(E)*-Ethyl 2-methyl-5-oxo-3,5-diphenylpent-2-enoate (4d) [Table 1, entry 3].** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.2 Hz, 3H), 1.88 (s, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.50 (s, 2H), 7.23-7.48 (m, 8H), 7.94 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9,



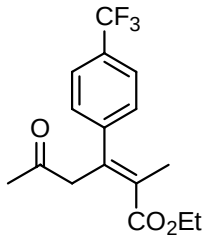
17.3, 46.6, 60.3, 127.0. 127.1, 127.4, 127.85, 127.92, 128.2, 128.3, 128.4, 132.7, 144.7, 168.4, 196.2; IR (neat / cm^{-1}) 3080, 3060, 2981, 2928, 1732, 1707, 1598, 1492, 1448, 1365, 1332, 1128, 977, 755, 704, 621; Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.91; H, 6.66.



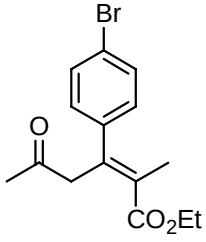
***(E)*-Ethyl 3-(4-methoxyphenyl)-2-methyl-5-oxohex-2-enoate (4e) [Table 1, entry 4].** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 1.86 (s, 3H), 2.16 (s, 3H), 3.80 (s, 3H), 3.86 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 17.3, 29.6, 51.4, 55.1, 60.3, 113.6, 128.4, 128.9, 134.7, 144.3, 158.7, 168.6, 205.1; IR (neat / cm^{-1}) 2980, 2935, 2907, 2838, 1729, 1606, 1515, 1093, 1029, 838, 770, 602, 542; Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.36; H, 7.42.



***(E)*-Ethyl 3-(4-methylphenyl)-2-methyl-5-oxohex-2-enoate (4f) [Table 1, entry 5].** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 1.84 (s, 3H), 2.16 (s, 3H), 2.34 (s, 3H), 3.86 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 17.3, 21.1, 29.7, 51.4, 60.4, 127.5, 127.6, 129.6, 137.1, 139.6, 144.7, 168.7, 205.0; IR (neat / cm^{-1}) 3022, 2982, 2926, 2871, 1728, 1623, 1512, 1447, 1042, 1021, 826, 769, 548, 519; Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.74; H, 7.91.

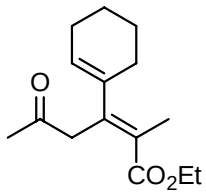


***(E)*-Ethyl 3-(4-trifluoromethylphenyl)-2-methyl-5-oxohex-2-enoate (4g) [Table 1, entry 6].** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.2 Hz, 3H), 1.82 (s, 3H), 2.19 (s, 3H), 3.89 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 17.1, 29.7, 50.7, 60.6, 125.3, 127.5, 127.9, 128.7, 129.2, 143.2, 146.4, 168.0, 204.4; IR (neat / cm^{-1}) 2988, 2926, 1716, 1653, 1616, 1559, 1325, 1259, 1164, 1128, 1068, 1018, 852; Anal. Calcd. for $C_{16}H_{17}F_3O_3$: C, 61.14; H, 5.45. Found: C, 61.13; H, 5.47.

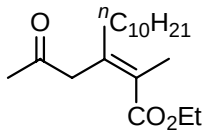


***(E)*-Ethyl 3-(4-bromophenyl)-2-methyl-5-oxohex-2-enoate (4h) [Table 1, entry 7].** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 1.82 (s, 3H), 2.17 (s, 3H), 3.85 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100

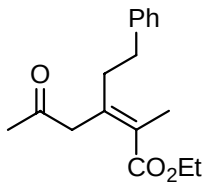
MHz, $CDCl_3$) δ 14.1, 17.1, 29.7, 50.8, 60.5, 129.0, 129.2, 131.1, 131.4, 141.4, 143.4, 168.1, 204.5; IR (neat / cm^{-1}) 2982, 2931, 1725, 1488, 1259, 1071, 1011, 834, 768, 730, 535; Anal. Calcd. for $C_{15}H_{17}BrO_3$: C, 55.40; H, 5.27. Found: C, 55.46; H, 5.16.

***(2E)*-Ethyl 3-cyclohexenyl-2-methyl-5-oxohex-2-enoate (4i) [Table 1, entry 8]**. 

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 1.57-1.60 (m, 2H), 1.63-1.67 (m, 2H), 1.92 (s, 3H), 1.96-1.99 (m, 2H), 2.05-2.08 (m, 2H), 2.17 (s, 3H), 3.61 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 5.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 16.7, 21.9, 22.5, 24.8, 26.7, 29.5, 49.0, 60.2, 124.9, 125.7, 139.1, 147.2, 168.8, 205.4; IR (neat / cm^{-1}) 2982, 2931, 2858, 1725, 1707, 1355, 1265, 1118, 1028, 920, 769, 549; Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.96; H, 8.86.

***(Z)*-Ethyl 2-methyl-3-(2-oxopropyl)tridec-2-enoate (4j) [Table 1, entry 9]**. 

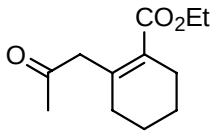
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.25-1.30 (m, 16H), 1.94 (s, 3H), 2.11 (t, *J* = 7.4 Hz, 3H), 2.19 (s, 3H), 3.58 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, **3j** + **4j**) δ 13.96, 14.03, 14.1, 15.0, 22.6, 26.9, 27.7, 29.2, 29.26, 29.32, 29.35, 29.43, 29.46, 29.54, 29.6, 31.77, 31.84, 34.4, 35.9, 41.4, 49.0, 60.1, 60.4, 123.5, 125.3, 145.7, 158.8, 168.5, 173.2, 198.1, 205.7; IR (neat / cm^{-1}, **3j** + **4j**) 2956, 2926, 2855, 1734, 1707, 1616, 1465, 1354, 1098, 862, 768; Anal. Calcd. for $C_{19}H_{34}O_3$: C, 73.50; H, 11.04. Found: C, 73.50; H, 11.28.

***(E)*-Ethyl 2-methyl-5-oxo-3-(2-phenylethyl)hex-2-enoate (4k) [Table 1, entry 10].** 

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H), 1.89 (s, 3H), 2.18 (s, 3H), 2.48 (t, *J* = 7.9 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 3.58 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 7.16-7.19 (m, 3H), 7.26-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 15.0, 29.7, 33.0, 37.8, 49.1, 60.3, 124.2, 126.0, 126.1, 128.2, 128.4, 144.2, 168.4, 205.7; IR (neat / cm^{-1}) 3086, 3062, 2981, 2937, 1721, 1617, 1496, 1454, 1356, 1190, 1103, 1029, 862, 748, 701; Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.32; H, 8.21.

Intramolecular Reaction of Ethyl 2-acetyloct-7-ynoate (7). A mixture of ethyl 2-acetyloct-7-ynoate (**7**, 105.1 mg, 0.500 mmol), 2,6-diisopropylphenylisocyanide (4.7 mg, 0.0250 mmol), powder MS4A (10.6 mg, 100wt%-Re cat.), $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), and toluene (1.0 mL) was heated at 100 ˚C for 24 h under argon

atmosphere. After purification by silica gel column chromatography, compounds **8** and **9** were obtained in 84% and 7% isolated yields, respectively.

Ethyl 2-(2-oxopropyl)cyclohex-1-enecarboxylate (8).  ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H), 1.61-1.65 (m, 4H), 2.14-2.15 (m, 2H), 2.19 (s, 3H), 2.34-2.36 (m, 2H), 3.56 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.96, 21.99, 26.1, 29.6, 33.4, 50.1, 59.9, 127.1, 143.9, 167.9, 205.7; IR (neat / cm^{-1}) 2980, 2936, 2862, 1717, 1637, 1356, 1233, 1076, 1052, 764, 684, 589; Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.27; H, 8.41.

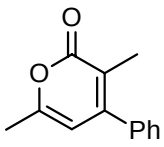
Typical Procedure for the Synthesis of 2-Pyranone Derivatives from β-Keto Esters and Acetylenes [Table 2]

Rhenium-Catalyzed Reaction of β-Keto Esters with Terminal Acetylenes. A mixture of ethyl 2-methylacetoacetate (**1a**, 72.1 mg, 0.500 mmol), phenylacetylene (**2a**, 61.2 mg, 0.600 mmol), $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), powdered MS4A (21.2 mg, 200wt%-Re cat.), and toluene (1.0 mL) was heated at 80 ˚C under argon atmosphere. After 24 h, tetrabutylammonium fluoride (1.0 M in THF, 50 μL, 0.0500 mmol) was added. The reaction mixture was stirred at 25 ˚C for 8 h. After purification by silica gel column chromatography, 3,6-dimethyl-4-phenylpyran-2-one (**6a**) was obtained in 95% isolated yield.

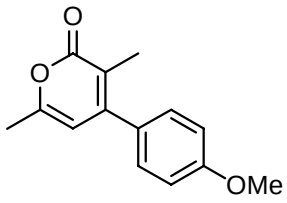
Rhenium-Catalyzed Reaction of β-keto Esters with Internal Acetylenes. A mixture of ethyl 2-methylacetoacetate (**1a**, 72.1 mg, 0.500 mmol), diphenylacetylene (**2i**, 106.9 mg, 0.600 mmol), $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), powdered MS4A (21.2 mg, 200wt%-Re cat.), and toluene (1.0 mL) was heated at 150 ˚C under argon atmosphere for 24 h. After purification by silica gel column chromatography, 3,6-dimethyl-4,5-diphenylpyran-2-one (**6g**) was obtained in 98% isolated yield.

Manganese-Catalyzed Reaction of β-keto Esters with Terminal Acetylenes. A mixture of ethyl 2-methylacetoacetate (**1a,** 72.1 mg, 0.500 mmol), phenylacetylene (**1a**, 61.2 mg, 0.600 mmol), and $MnBr(CO)_5$ (6.9 mg, 0.0250 mmol) was heated at 80 ˚C under argon atmosphere. After 24 h, tetrabutylammonium fluoride (1.0 M in THF, 50 μL, 0.050 mmol) was added. The reaction mixture was stirred at 50 ˚C for 2 h. After purification by silica gel column chromatography, 3,6-dimethyl-4-phenylpyran-2-one

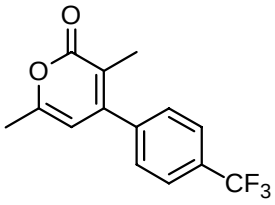
(**6a**) was obtained in 96% isolated yield.

3,6-Dimethyl-4-phenylpyran-2-one (6a) [Table 2, entry 1]. 

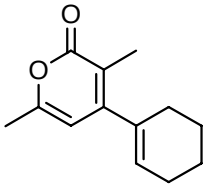
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.26 (s, 3H), 5.98 (s, 1H), 7.26-7.30 (m, 2H), 7.40-7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.68, 19.47, 106.56, 118.01, 127.77, 128.46, 128.66, 137.64, 152.08, 157.73, 164.82; IR (Nujol / cm^{-1}) 3086, 3062, 3027, 2921, 2859, 1733, 1718, 1653, 1457, 1379, 1041, 896; Anal. Calcd. For $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.86; H, 5.93.

4-(4-Methoxyphenyl)-3,6-dimethylpyran-2-one (6b) [Table 2, entry 2]. 

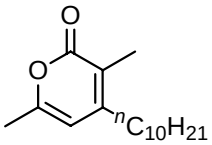
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 3H), 2.24 (s, 3H), 3.85 (s, 3H), 5.98 (s, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.81, 19.47, 55.26, 106.61, 113.83, 117.39, 129.39, 129.84, 151.62, 157.48, 159.88, 164.89; IR (Nujol / cm^{-1}) 3060, 2999, 2924, 2854, 1706, 1606, 1336, 1253, 1175, 955, 765, 600; Anal. Calcd. For $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.31; H, 6.39.

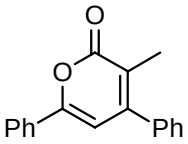
3,6-Dimethyl-4-(4-trifluoromethylphenyl)pyran-2-one (6c) [Table 2, entry 3]. 

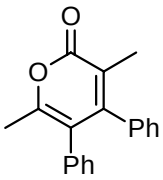
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.27 (s, 3H), 5.93 (s, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.70, 19.59, 105.89, 118.79, 122.41, 125.57 (CF3), 128.26, 130.95, 141.28, 150.50, 158.35, 164.31; IR (Nujol / cm^{-1}) 3074, 3049, 2853, 1709, 1647, 1410, 1159, 1017, 956, 842, 762, 677, 617, 570; Anal. Calcd. For $C_{14}H_{11}F_3O_2$: C, 62.69; H, 4.13. Found: C, 62.55; H, 4.03.

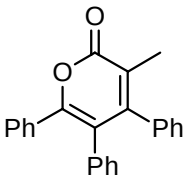
4-Cyclohex-1-enyl-3,6-dimethylpyran-2-one (6d) [Table 2, entry 4]. 

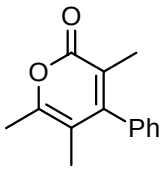
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64-1.68 (m, 2H), 1.73-1.77 (m, 2H), 2.01 (s, 3H), 2.08-2.12 (m, 2H), 2.14-2.18 (m, 2H), 2.20 (s, 3H), 5.65 (m, 1H), 5.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.16, 19.19, 21.48, 22.21, 24.74, 27.39, 105.07, 116.39, 127.81, 135.01, 154.71, 157. 31, 164.78; IR (neat / cm^{-1}) 3028, 2991, 2927, 2858, 1716, 1650, 1558, 1447, 1368, 1330, 1184, 1052, 929, 766, 708, 672; HRMS (ESI) Calcd for $C_{13}H_{16}O_2Na$ ($[M+Na]^+$): 227.1048, Found: 227.1062.

4-Decyl-3,6-dimethylpyran-2-one (6e) [Table 2, entry 5].  ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2Hz, 3H), 1.23-1.37 (m, 14H), 1.45-1.54 (m, 2H), 2.02 (s, 3H), 2.19 (s, 3H), 2.38 (t, *J* = 7.5Hz, 2H), 5.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.68, 13.92, 19.30, 22.50, 28.34, 29.14, 29.24, 29.28, 29.34, 29.39, 31.72, 32.83, 106.10, 117.30, 154.06, 157.39, 164.51; IR (neat / cm^{-1}) 2953, 2924, 2854, 1717, 1653, 1575, 1465, 1370, 1181, 1052, 982, 765; Anal. Calcd. For $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.13; H, 10.86.

3-Methyl-4,6-diphenylpyran-2-one (6f) [Table 2, entry 6].  ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 3H), 6.63 (s, 1H), 7.33-7.49 (m, 8H), 7.78-7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.90, 104.27, 119.52, 125.05, 127.74, 128.48, 128.65, 128.70, 130.12, 131.30, 137.64, 151.91, 156.13, 163.71; IR (Nujol / cm^{-1}) 3083, 3023, 2921, 2859, 1710, 1718, 1151, 1049, 923, 833, 687, 634; HRMS (ESI) Calcd for $C_{18}H_{14}O_2Na$ ($[M+Na]^+$): 285.0891, Found: 285.0914.

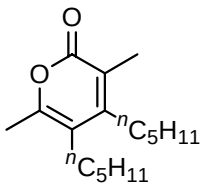
3,6-Dimethyl-4,5-diphenylpyran-2-one (6g) [Table 2, entry 7].  ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (s, 3H), 2.12 (s, 3H), 6.86-6.90 (m, 4H), 7.12-7.17 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.30, 18.45, 119.23, 119.39, 127.06, 127.48, 127.81, 127.92, 128.17, 130.43, 135.23, 136.50, 154.00, 155.64, 163.95; IR (nujol / cm^{-1}) 3086, 3062, 3027, 2921, 2859, 1718, 1653, 1258, 1073, 1002, 923, 769, 701; Anal. Calcd. For $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.46; H, 5.90.

3-methyl-4,5,6-triphenylpyran-2-one (6h) [Table 2, entry 8].  ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 6.81-6.84 (m, 2H), 6.90-6.92 (m, 2H), 7.01-7.06 (m, 3H), 7.15-7.22 (m, 6H), 7.23-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.63, 119.36, 121.10, 127.05, 127.52, 127.81, 127.90, 127.99, 128.26, 129.11, 131.15, 132.68, 135.12, 136.53, 154.59, 163.48 (two signals are overlapped); IR (Nujol / cm^{-1}) 3059, 2924, 2853, 1706, 1612, 1338, 1168, 1066, 915, 847, 775, 760, 702, 591; HRMS (ESI) Calcd for $C_{24}H_{18}O_2Na$ ($[M+Na]^+$): 361.1205, Found: 361.1170.

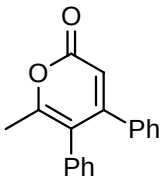
3,5,6-Trimethyl-4-phenylpyran-2-one (6i) [Table 2, entry 9].  ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 3H), 1.81 (s, 3H), 2.28 (s, 3H), 7.05-7.08 (m, 2H), 7.37-7.41 (m, 1H), 7.44-7.48 (m, 2H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 14.03, 14.27, 17.56, 110.76, 119.52, 127.12, 127.88, 128.63, 137.12, 154.02, 155.37, 164.17; IR (neat / cm^{-1}) 3058, 3023, 2924, 2872, 1716, 1642, 1557, 1444, 1385, 1311, 1176, 1144, 1058, 862, 763, 704; Anal. Calcd. For $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.62; H, 6.64.

3,6-Dimethyl-4,5-dipentylpyran-2-one (6j) [Table 2, entry 10]. ^1H NMR (400 MHz, $CDCl_3$) δ 0.90-0.94 (m, 6H), 1.33-1.40 (m, 12H), 2.06 (s, 3H), 2.22 (s, 3H), 2.27 (t, *J* = 8.0 Hz, 2H), 2.41 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.43, 13.83, 13.88, 17.23, 22.45, 22.30, 27.03, 28.46, 29.70, 29.95, 31.75, 32.06, 115.81, 118.47, 154.19, 154.97, 164.07; IR (neat / cm^{-1}) 2957, 2928, 2859, 1709, 1636, 1555, 1465, 1380, 1318, 1185, 1060, 917, 768, 733; Anal. Calcd. For $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.36; H, 10.89.

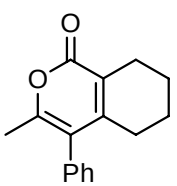


6-Methyl-4,5-diphenylpyran-2-one (6k) [Table 2, entry 11]. ^1H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 3H), 6.24 (s, 1H), 6.97-7.00 (m, 4H), 7.14-7.17 (m, 2H), 7.20-7.24 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.81, 111.88, 118.22, 127.46, 127.86, 128.22, 128.59, 130.55, 134.52, 136.77, 158.42, 159.77, 162.24 (one signal is overlapped); IR (Nujol / cm^{-1}) 3056, 2922, 2853, 1719, 1254, 1147, 1073, 1002, 924, 896, 859, 769, 702; HRMS (ESI) Calcd for $C_{18}H_{14}O_2Na$ ($[M+Na]^+$): 285.0891, Found: 285.0903.



Intramolecular Reaction of Ethyl 2-acetyl-8-phenyloct-7-ynoate (12). A mixture of ethyl 2-acetyl-8-phenyloct-7-ynoate (**12**, 143.2 mg, 0.500 mmol), $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), powdered MS4A (10.6 mg, 100wt%-Re cat.), and toluene (2.0 mL) was heated at 150 ˚C for 24 h under argon atmosphere. After purification by silica gel column chromatography, 3-Methyl-4-phenyl-5,6,7,8-tetrahydro-1*H*-2-benzopyran-1-one (**13**) was obtained in 95% isolated yield.

3-Methyl-4-phenyl-5,6,7,8-tetrahydro-1*H*-2-benzopyran-1-one (13). ^1H NMR (400 MHz, $CDCl_3$) δ 1.59-1.63 (m, 2H), 1.67-1.72 (m, 2H), 2.00 (s, 3H), 2.06 (t, *J* = 6.1 Hz, 2H), 2.51 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.96, 21.41, 21.57, 23.45, 28.34, 119.36, 119.83, 127.79, 128.66, 129.94, 134.90, 151.55, 154.60, 163.35; IR (Nujol / cm^{-1}) 3086, 3053, 3028, 2948, 2857, 1716, 1495, 1285, 1153, 1038, 948, 855, 770, 728,



694; HRMS (ESI) Calcd for $C_{16}H_{16}O_2Na$ ($[M+Na]^+$): 263.1048, Found: 263.1035.

References

1. Wierenga, W.; Skulnick, H. I.; Stringfellow, D. A.; Weed, S. D.; Renis, H. E.; Eidson, E. E. *J. Med. Chem.* **1980**, *23*, 237.
2. Cruciani, P.; Stammler, R. Aubert, C.; Malacria, M. *J. Org. Chem.* **1996**, *61*, 2699.