Supplementary Material (ESI) for Chemical Communications

Transition-Metal-Catalyzed Rearrangement of 5-Alkynals to γ-Alkynylketones and 1-Cyclopentenylketones

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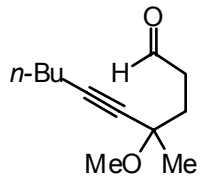
I. General

Anhydrous CH_2Cl_2 (No. 27,099-7), $(CH_2Cl)_2$ (No. 28,450-5), and CH_3CN (No. 27100-4) were obtained from Aldrich and used as received. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

II. Synthesis of 5-Alkynals

4-Methoxy-4-methyldec-5-ynal.



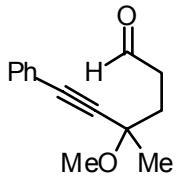
General Procedure 1: *n*-BuLi (1.58 M in *n*-hexane, 23 mL, 36 mmol) was added to a solution of 1-hexyne (5.2 mL, 46 mmol) in THF (120 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 0.5 h. 1,1-Dimethoxy-3-butanone was added at 0 °C, and stirred at rt for 0.5 h. MeI (9.4 mL, 0.15 mol) and DMSO (90 mL) were added, and the resulting mixture was stirred at 80 °C for 1 h. The reaction mixture was then diluted with water and extracted with Et_2O. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. To the residue was added water (35 mL) and AcOH (100 mL), and the resulting mixture was stirred at 80 °C for 0.5 h. The reaction mixture was diluted with water and extracted with Et_2O. The organic layer was washed with saturated aqueous Na_2CO_3, dried over Na_2SO_4, and concentrated, which afforded crude 3-methoxy-3-methylnon-4-ynal (5.1 g).

To a cooled (–10 °C) and stirred suspension of methoxymethyl triphenylphosphonium chloride (19.4 g, 56.6 mmol) in THF (61 mL) under argon atmosphere was added an lithium diisopropylamine solution consisting of *n*-BuLi (1.58 M in *n*-hexane, 34 mL, 54 mmol) and diisopropylamine (8.0 mL, 57 mmol) in THF (65 mL). To the deep red

solution was added a solution of crude 3-methoxy-3-methylnon-4-ynal (5.1 g) in THF (55 mL). The resulting solution was kept at –10 °C for 1 h and then diluted with saturated aqueous $NaHCO_3$. After extraction with Et_2O, the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. A solution of the residue in THF (375 mL) was treated with aqueous HCl (75 mL, 10%) at rt for 24 h. Saturated aqueous $NaHCO_3$ was added slowly to neutralize HCl and then extracted with Et_2O. The combined organic extracts were then washed with brine, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography (hexane:EtOAc = 15:1), which furnished 4-methoxy-4-methyldec-5-ynal (5.2 g, 26 mmol, 48% yield, unoptimized) as a pale yellow oil.

IR (neat) 3350, 2900, 1720, 1080 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 9.78 (t, J = 1.5 Hz, 1H), 3.30 (s, 3H), 2.50-2.75 (m, 2H), 2.21 (t, J = 6.9 Hz, 2H), 1.88-2.10 (m, 2H), 1.30-1.58 (m, 4H), 1.39 (s, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.4, 86.7, 79.9, 72.8, 51.2, 39.6, 34.5, 30.7, 25.8, 21.9, 18.2, 13.5; HRMS (EI) calcd for $C_{12}H_{20}O_2$ $[M]^+$ 196.1463, found 196.1426.

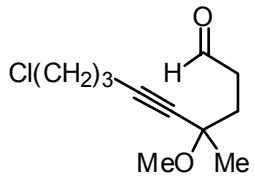
4-Methoxy-4-metyl-6-phenylhex-5-ynal.



The title compound was prepared from phenylacetylene according to the general procedure 1.

Pale yellow oil; IR (neat) 2900, 1720, 1440, 1370, 1260, 1180, 880, 760, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 9.83 (t, J = 1.5 Hz, 1H), 7.37-7.45 (m, 2H), 7.28-7.48 (m, 3H), 3.40 (s, 3H), 2.59-2.82 (m, 2H), 2.12 (dt, J = 7.5 and 1.5 Hz, 2H), 1.52 (s, 3H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.3, 131.7, 128.5, 128.3, 122.4, 89.1, 86.2, 73.2, 51.6, 39.5, 34.4, 25.6; HRMS (EI) calcd for $C_{14}H_{16}O_2$ $[M]^+$ 216.1150, found 216.1160.

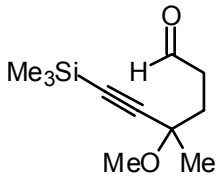
9-Chloro-4-methoxy-4-methylnon-5-ynal.



The title compound was prepared from 5-chloro-1-pentyn according to the general procedure 1.

Pale yellow oil; IR (neat) 2900, 1720, 1430, 1370, 1270, 1180, 1150, 1080 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 9.78 (t, J = 1.8 Hz, 1H), 3.65 (t, J = 6.6 Hz, 2H), 3.30 (s, 3H), 2.49-2.72 (m, 2H), 2.42 (t, J = 6.6 Hz, 2H), 1.90-2.09 (m, 4H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.1, 84.6, 81.2, 72.8, 51.4, 43.6, 39.5, 34.5, 31.3, 25.8, 16.1; HRMS (EI) calcd for $C_{10}H_{14}ClO_2$ $[M–CH_3]^+$ 201.0682, found 201.0678.

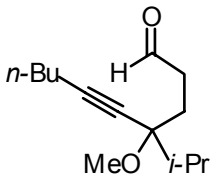
4-Methoxy-4-methyl-6-trimethylsilanylhex-5-ynal.



The title compound was prepared from (trimethylsilyl)acetylene according to the general procedure 1.

Pale yellow oil; IR (neat) 3350, 2950, 1720, 1250, 1080, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 9.79 (m, 1H), 3.32 (s, 3H), 2.50-2.75 (m, 2H), 2.01 (dt, J = 1.8 and 7.8 Hz, 2H), 1.40 (s, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.0, 105.4, 90.6, 72.9, 51.4, 39.4, 34.2, 25.5, –0.03; HRMS (EI) calcd for $C_{10}H_{17}O_2Si$ $[M–CH_3]^+$ 197.0998, found 197.0953.

4-Isopropyl-4-methoxydec-5-ynal.



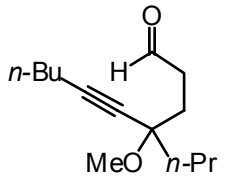
General Procedure 2: A solution of 2-(2-bromoethyl)-1,3-dioxolane (12.5 g, 69 mmol)

in THF (20 mL) was added to a stirred suspension of magnesium (3.0 g, 69 mmol) in THF (80 mL) and the reaction mixture was stirred at rt for 30 min. The solution was cooled to 0 °C, powder CuBr (9.3 g, 65 mmol) was added, and the resulting mixture was stirred at 5-15 °C for 20 min. After cooling to –70 °C, a solution of isobutyryl chloride (5.8 mL, 55 mmol) in THF (100 mL) was added over 15 min, and the reaction mixture was stirred at –70 °C for an additional 1 h. The reaction mixture was warmed to rt and stirred at rt for 18 h. The mixture was poured into an ice cold 2M solution of aqueous HCl (200 mL) and the mixture was extracted with Et_2O (3×100 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (hexane:EtOAc = 5:1) to give 1-[1,3]dioxolan-2-yl-4-methylpentan-3-one (3.0 g, 17.6 mmol, 32% yield, unoptimized) as a pale yellow oil.

n-BuLi (1.58 M in *n*-hexane, 8.4 mL, 13 mmol) was added to a solution of 1-hexyne (2.0 mL, 16.5 mmol) in THF (45 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 0.5 h. THF (10 mL) solution of 1-[1,3]dioxolan-2-yl-4-methylpentan-3-one (1.9 g, 11 mmol) was added at 0 °C, and stirred at rt for 0.5 h. MeI (3.4 mL, 55 mmol) and DMSO (34 mL) were added, and the resulting mixture was stirred at 80 °C for 1 h. The reaction mixture was then diluted with water and extracted with Et_2O. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated. To the residue was added water (5 mL) and AcOH (15 mL), and the resulting mixture was stirred at 60 °C for 1 h. The reaction mixture was diluted with water and extracted with Et_2O. The organic layer was washed with saturated aqueous Na_2CO_3, dried over Na_2SO_4, and concentrated, which afforded 4-isopropyl-4-methoxydec-5-ynal (1.1 g, 4.9 mmol, 94% yield) as a pale yellow oil.

IR (neat) 2900, 1690, 1070 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 9.79 (t, J = 1.5 Hz, 1H), 3.27 (s, 3H), 2.48-2.70 (m, 2H), 2.24 (t, J = 6.9 Hz, 2H), 1.83-2.10 (m, 3H), 1.33-1.58 (m, 4H), 1.01 (d, J = 6.9 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.7, 88.4, 79.5, 51.2, 39.2, 33.9, 30.9, 27.2, 22.0, 18.3, 18.0, 16.6, 13.7; HRMS (EI) calcd for $C_{10}H_{15}O_2$ $[M–C_4H_9]^+$ 167.1071, found 167.1030.

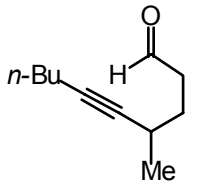
4-Propyl-4-methoxydec-5-ynal.



The title compound was prepared from 1-[1,3]dioxolan-2-yl-hexan-3-one[2] according to the general procedure 2. 1-[1,3]Dioxolan-2-yl-hexan-3-one was prepared from 2-(2-bromoethyl)-1,3-dioxolane and butyryl chloride according to the general procedure 2.

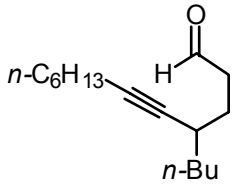
IR (neat) 3300, 2900, 1700, 1420, 1280, 1080 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 9.78 (t, J = 1.8 Hz, 1H), 3.28 (s, 3H), 2.45-2.71 (m, 2H), 2.22 (t, J = 6.9 Hz, 2H), 1.96 (t, J = 7.2 Hz, 2H), 1.30-1.72 (m, 8H), 0.93 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 202.6, 87.7, 79.5, 75.9, 51.1, 40.5, 39.4, 31.3, 30.8, 21.9, 18.3, 17.3, 14.3, 13.6; HRMS (EI) calcd for $C_{10}H_{15}O_2$ $[M–C_4H_9]^+$ 167.1071, found 167.1030.

4-Methyldec-5-ynal.[1]



The title compound was prepared according to a literature procedure.

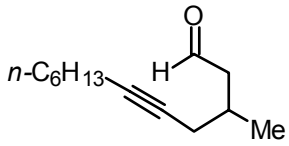
4-Butyldodec-5-ynal.



The title compound was prepared from 1-octyne and hept-2-enal by following the procedure for the synthesis of 4-methyldec-5-ynal.[1]

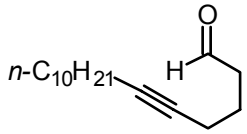
Colorless oil; IR (neat) 2850, 2720, 1715, 1390 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.81 (t, J = 1.8 Hz, 1H), 2.49-2.72 (m, 2H), 2.26-2.39 (m, 1H), 2.15 (dt, J = 7.2 and 1.8 Hz, 2H), 1.74-1.88 (m, 1H), 1.58-1.71 (m, 1H), 1.29-1.54 (m, 14H), 0.90 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.5, 82.6, 82.3 42.1, 35.2, 31.31, 31.29, 29.6, 29.0, 28.5, 27.7, 22.6, 22.5, 18.7, 14.0. HRMS (EI) calcd for $C_{16}H_{28}O$ $[M]^+$ 236.2140, found 236.2124.

3-Methyldodec-5-ynal.[1]



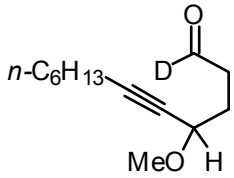
The title compound was prepared according to a literature procedure.

Hexadec-5-ynal.[1]



The title compound was prepared according to a literature procedure.

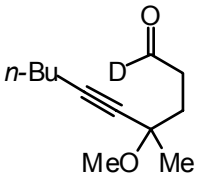
1-Deuterio-4-methoxydodec-5-ynal.



The title compound was prepared from 4-methoxydodec-5-ynal[1] by following the procedure for the synthesis of 1-deuterio-4-methyldec-5-ynal.[1]

Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.01 (tt, J = 6.0 and 1.8 Hz, 1H), 3.37 (s, 3H), 2.61 (t, J = 6.6 Hz, 2H), 2.22 (dt, J = 7.2 and 1.8 Hz, 2H), 2.03 (q, J = 7.2 Hz, 2H), 1.44-1.57 (m, 2H), 1.21-1.44 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H); ^{2}H NMR ($CHCl_3$, 61 MHz) δ 9.81 (s).

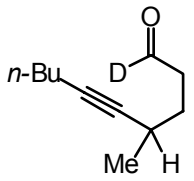
1-Deuterio-4-methoxy-4-methyldec-5-ynal.



The title compound was prepared from 4-methoy-4-methyldec-5-ynal by following the procedure for the synthesis of 1-deuterio-4-methyldec-5-ynal.[1]

Colorless oil; ^{1}H NMR ($CDCl_3$, 300MHz) δ 3.30 (s, 3H), 2.50-2.75 (m, 2H), 2.21 (t, J = 6.9 Hz, 2H), 1.88-2.10 (m, 2H), 1.41-1.58 (m, 4H), 1.39 (s, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{2}H NMR ($CHCl_3$, 61 MHz) δ 9.81 (s).

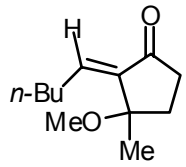
1-Deuterio-4-methyldec-5-ynal.[1]



The title compound was prepared according to a literature procedure.

III. Hydroacylation of 5-Alkynal

2-Pentyliden-3-methoxy-3-methylcyclopentanone.



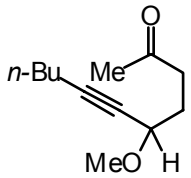
Under an Ar atmosphere, BINAP (12.5 mg, 0.020 mmol) and $[Rh(cod)_2]BF_4$ (8.1 mg, 0.020 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and the mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in Schlenk tube. After stirring for 1 h at rt, the resulting solution was concentrated to dryness. 4-Methoxy-4-methyldec-5-ynal (39.3 mg, 0.200 mmol) was added to the residue by using CH_2Cl_2 (2.0 mL). The mixture was stirred at 25 °C for 16 h. The resulting solution was concentrated and purified by silica gel preparative TLC (hexane:EtOAc = 5:1) to give 2-pentyliden-3-methoxy-3-methylcyclopentanone (30.3 mg, 0.154 mmol, 77% yield) as a colorless oil.

IR (neat) 2900, 1720, 1640, 1500, 1440, 1220, 1180, 1080, 1040, 820, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 6.78 (t, J = 7.2 Hz, 1H), 3.17 (s, 3H), 1.95-2.56 (m, 5H), 1.75-1.90 (m, 1H), 1.50 (s, 3H), 1.20-1.55 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR

($CDCl_3$, 75MHz) δ205.1, 142.6, 138.2, 81.8, 50.3, 35.9, 31.1, 30.8, 27.2, 25.6, 22.5, 13.8; HRMS (EI) calcd for $C_{12}H_{20}O_2$ $[M]^+$ 196.1463, found 196.1458.

IV. Catalytic Isomerization of 5-Alkynals

5-Methoxyundec-6-yn-2-one.

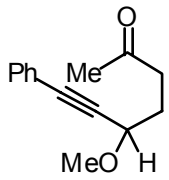


General Procedure 1 (using Rh catalyst: Table 1, entry 1). Under an Ar atmosphere, triphenylphosphite (31.0 mg, 0.10 mmol) and $[Rh(cod)_2]BF_4$ (20.3 mg, 0.050 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and the mixture was stirred at rt for 0.5 h. H_2 was introduced to the resulting solution in Schlenk tube. After stirring for 1 h at rt, the resulting solution was concentrated to dryness. 4-Methoxy-4-methyldec-5-ynal (98.1 mg, 0.500 mmol) was added to the residue by using CH_2Cl_2 (2.0 mL). The mixture was stirred at 25 °C for 16 h. The resulting solution was concentrated and purified by silica gel preparative TLC (hexane:EtOAc = 5:1) to give 5-methoxyundec-6-yn-2-one (75.5 mg, 0.385 mmol, 77% yield) as a colorless oil.

General Procedure 2 (using Cu catalyst: Table 1, entry 2). Under an Ar atmosphere, $Cu(OTf)_2$ (10.9 mg, 0.030 mmol) was dissolved in CH_3CN (1.0 mL) and the mixture was stirred at rt for 5 min. 4-Methoxy-4-methyldec-5-ynal (98.1 mg, 0.500 mmol) was added to the residue by using CH_3CN (1.0 mL). The mixture was stirred at 25 °C for 15 h. The resulting solution was concentrated and purified by silica gel preparative TLC (hexane:EtOAc = 5:1) to give 5-methoxyundec-6-yn-2-one (52.1 mg, 0.345 mmol, 69% yield) as a colorless oil.

IR (neat) 2900, 1700, 1160, 1080, 960 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ3.98 (tt, J = 1.8 and 6.3 Hz, 1H), 3.36 (s, 3H), 2.61 (t, J = 7.2 Hz, 2H), 2.22 (dt, J = 1.8 and 6.9 Hz, 2H), 2.16 (s, 3H), 1.90-2.00 (m, 2H), 1.30-1.56 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75MHz) δ208.2, 86.8, 77.9, 70.1, 56.1, 39.0, 30.6, 29.9, 29.6, 21.8, 18.2, 13.4; HRMS (EI) calcd for $C_8H_{13}O$ $[M–CH_2CH_2COMe]^+$ 125.0966, found 125.0926.

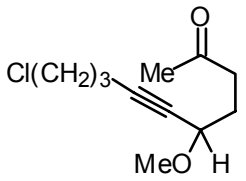
5-Methoxy-7-phenylhept-6-yn-2-one.



The title compound was prepared in 71% isolated yield from 4-methoxy-4-metyl-6-phenylhex-5-ynal according to the general procedure 1. Reaction time: 16 h.

Pale yellow oil; IR (neat) 2900, 1700, 1340, 1160, 1100, 960, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 7.41-7.47 (m, 2H), 7.29-7.34 (m, 3H), 4.24 (t, J = 6.0 Hz, 1H), 3.45 (s, 3H), 2.70 (t, J = 7.5 Hz, 2H), 2.18 (s, 3H), 2.04-2.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 75MHz) 208.2, 131.6, 128.4, 128.2, 122.4, 87.1, 86.2, 70.4, 56.5, 38.9, 30.0, 29.4; HRMS (EI) calcd for $C_{14}H_{16}O_2$ $[M]^+$ 216.1150, found 216.1072.

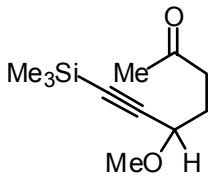
10-Chloro-5-methoxydec-6-yn-2-one.



The title compound was prepared in 74% isolated yield from 9-chloro-4-methoxy-4-methylnon-5-ynal according to the general procedure 1. Reaction time: 39 h.

Pale yellow oil; IR (neat) 2900, 1700, 1340, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 3.99 (tt, J = 1.8 and 6.1 Hz, 1H), 3.66 (t, J = 6.2 Hz, 2H), 3.37 (s, 3H), 2.61 (t, J = 7.2 Hz, 2H), 2.44 (dt, J = 1.8 and 7.0 Hz, 2H), 2.17 (s, 3H), 1.85-2.05 (m, 4H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 208.2, 84.7, 79.2, 70.1, 56.3, 43.6, 39.0, 31.2, 30.0, 29.5, 16.1; HRMS (EI) calcd for $C_{11}H_{17}ClO_2$ $[M]^+$ 216.0917, found 216.0860.

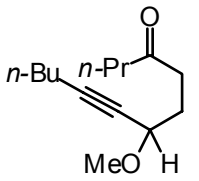
5-Methoxy-7-trimethylsilanylhept-6-yn-2-one.



The title compound was prepared in 24% isolated yield from 4-methoxy-7-trimethylsilanylhept-6-yn-2-one according to the general procedure 2. Reaction time: 110 h. Reaction temperature: 80 °C.

Colorless oil; IR (neat) 2900, 1700, 1340, 1240, 1090, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ3.98 (t, J = 6.3 Hz, 1H), 3.37 (s, 3H), 2.61 (t, J = 6.3 Hz, 2H), 2.15 (s, 3H), 1.96 (q, J = 6.3 Hz, 2H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 75MHz) δ208.1, 103.6, 91.1, 70.4, 56.4, 38.9, 30.0, 29.2, 0.1; HRMS (EI) calcd for $C_{11}H_{20}O_2Si$ $[M–CH_3]^+$ 197.0998, found 197.0939.

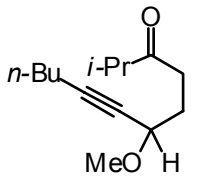
6-Methoxy-2-methyldodec-7-yn-3one.



The title compound was prepared in 43% isolated yield from 4-propyl-4-methoxydec-5-ynal according to the general procedure 1. Reaction time: 109 h.

Colorless oil; IR (neat) 2900, 1700, 1320, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ3.98 (tt, J = 1.8 and 6.3 Hz, 1H), 3.36 (s, 3H), 2.58 (t, J = 7.5 Hz, 2H), 2.40 (t, J = 7.2 Hz, 2H), 2.22 (dt, J = 1.8 and 6.9 Hz, 2H), 1.95 (q, J = 7.5 Hz, 2H), 1.61 (sextet, J = 7.2 Hz, 2H), 1.32-1.53 (m, 4H), 0.91 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75MHz) δ210.5, 86.9, 78.0, 70.3, 56.1, 44.8, 38.0, 30.7, 29.6, 21.8, 18.3, 17.2, 13.7, 13.5; HRMS (EI) calcd for $C_{14}H_{24}O_2$ $[M]^+$ 224.1776, found 224.1721.

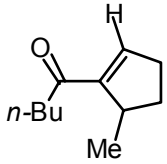
6-Methoxy-2-methyldodec-7-yn-3one.



The title compound was prepared in 57% isolated yield from 4-isopropyl-4-methoxydec-5-ynal according to the general procedure 1. Reaction time: 16 h.

Pale yellow oil; IR (neat) 2900, 1700, 1440, 1320, 1180, 1100, 1020, 960 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 3.98 (tt, J = 1.8 and 6.0 Hz, 1H), 3.37 (s, 3H), 2.51-2.69 (m, 3H), 2.23 (dt, J = 1.8 and 6.9 Hz, 2H), 1.89-2.00 (m, 2H), 1.33-1.54 (m, 4H), 1.10 (d, J = 7.2 Hz, 6H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 214.2, 78.1, 70.4, 56.2, 40.9, 35.7, 30.7, 29.7, 21.9, 18.32, 18.25, 18.2, 13.6; HRMS (EI) calcd for $C_{14}H_{24}O_2$ $[M]^+$ 224.1776, found 224.1755.

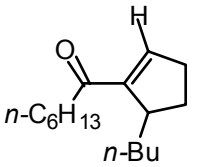
1-(5-Methylcyclopent-1-enyl)pentan-1-one.



The title compound was prepared in 62% isolated yield from 4-methyldec-5-ynal according to the general procedure 1. Reaction time: 72 h. Reaction temperature: 50 °C.

Pale yellow oil; IR (neat) 2890, 1660, 1440, 1360 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.63-6.69 (m, 1H), 2.97-3.11 (m, 1H), 2.50-2.72 (m, 3H), 2.32-2.50 (m, 1H), 2.04-2.21 (m, 1H), 1.46-1.67 (m, 3H), 1.23-1.41 (m, 2H), 1.07 (d, J = 6.9 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.4, 150.0, 142.5, 38.9, 38.2, 31.9, 31.7, 26.9, 22.4, 19.6, 13.8. HRMS (EI) calcd for $C_{11}H_{18}O$ $[M]^+$ 166.1358, found 166.1393.

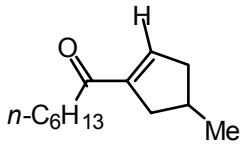
1-(5-Butylcyclopent-1-enyl)heptan-1-one.



The title compound was prepared in 71% isolated yield from 4-butyldodec-5-ynal according to the general procedure 1. Reaction time: 40 h. Reaction temperature: 50 °C.

Pale yellow oil; IR (neat) 2880, 1660, 1455, 1375 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.64-6.70 (m, 1H), 2.90-3.03 (m, 1H), 2.31-2.69 (m, 3H), 1.95-2.11 (m, 1H), 1.53-1.73 (m, 4H), 1.15-1.42 (m, 12H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.6, 149.0, 142.9, 43.5, 39.3, 33.1, 32.1, 31.7, 29.7, 29.0, 28.9, 24.7, 22.9, 22.5, 14.12, 14.05. HRMS (EI) calcd for $C_{16}H_{28}O$ $[M]^+$ 236.2140, found 236.2119.

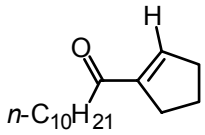
1-(4-Methylcyclopent-1-enyl)heptan-1-one.



The title compound was prepared in 47% isolated yield from 3-methyldodec-5-ynal according to the general procedure 1. Reaction time: 72 h. Reaction temperature: 50 °C.

Pale yellow oil; IR (neat) 2940, 1660, 1425, 1375 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.59-6.68 (m, 1H), 2.67-2.77 (m, 2H), 2.63 (t, J = 7.6 Hz, 2H), 2.35-2.49 (m, 1H), 2.09-2.20 (m, 2H), 1.54-1.65 (m, 2H), 1.20-1.38 (m, 6H), 1.05 (d, J = 6.8 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.5, 144.7, 142.0, 42.0, 38.9, 38.8, 31.8, 31.7, 29.1, 24.7, 22.6, 21.5, 14.1. HRMS (EI) calcd for $C_{13}H_{22}O$ $[M]^+$ 194.1671, found 194.1643.

1-Cyclopent-1-enyldodecan-1-one.



The title compound was prepared in 43% isolated yield from hexadec-5-ynal according to the general procedure 1. Reaction time: 72 h. Reaction temperature: 50 °C.

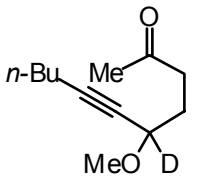
Pale yellow oil; IR (neat) 2870, 1660, 1440, 1360 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.67-6.77 (m, 1H), 2.64 (t, J = 7.5 Hz, 2H), 2.49-2.60 (m, 4H), 1.92 (quint, J = 7.5 Hz, 2H), 1.53-1.67 (m, 2H), 1.16-1.38 (m, 14H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.5, 145.7, 143.0, 39.0, 33.8, 31.8, 30.6, 29.52, 29.46, 29.42, 29.37, 29.3,

24.7, 22.7, 22.6, 14.1. HRMS (EI) calcd for $C_{16}H_{28}O$ $[M]^+$ 236.2140, found 236.2093.

V. Deuterium Labelling Studies

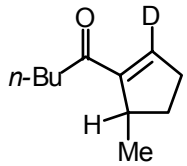
The reactions of deuterium labelled 5-alkynals (eq 2, 3, and 4) were conducted according to the general procedure 1. The ratio of X = H/Y = H (58/42, 88 h, eq 2) was determined by ^{1}H NMR integration of 9.78 ppm/4.00 ppm. The ratio of X = D/Y = D (45/55, 88 h, eq 2) was determined by ^{2}H NMR integration of 9.80 ppm/3.98 ppm.

5-Dueterio-5-methoxyundec-6-yn-2-one.



^{1}H NMR ($CDCl_3$, 300MHz) δ 3.36 (s, 3H), 2.61 (t, J = 7.2 Hz, 2H), 2.22 (t, J = 6.6 Hz, 2H), 2.16 (s, 3H), 1.94 (t, J = 7.2 Hz, 2H), 1.30-1.59 (m, 4H), 0.91 (t, J = 6.6 Hz, 3H); ^{2}H NMR ($CHCl_3$, 61 MHz) δ 3.96 (s).

1-(2-Deuterio-5-Methylcyclopent-1-enyl)pentan-1-one.



^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.97-3.12 (m, 1H), 2.51-2.69 (m, 3H), 2.35-2.49 (m, 1H), 2.04-2.20 (m, 1H), 1.47-1.66 (m, 3H), 1.33 (sextet, J = 7.2 Hz, 2H), 1.07 (d, J = 6.6 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); ^{2}H NMR ($CHCl_3$, 61 MHz) δ 6.70 (s).

VI. References

(1) K. Takeishi, K. Sugishima, K. Sasaki, K. Tanaka, *Chem. Eur. J.*, 2004, **10**, 5681. S.Dang, B. P. Roberts, *J. Chem. Soc., Perkin Trans. 1*, 1998, 67.