A Versatile New Method for the Synthesis of Cyclopentenones via an Unusual Rhodium-Catalyzed Intramolecular trans Hydroacylation of an Alkyne

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I. General

THF was distilled from sodium-benzophenone ketyl. CH₂Cl₂ was purified by passing through a neutral alumina column under argon. Acetone (99.9+%; Aldrich) and CH₃CN (anhydrous; Aldrich) were used as received. All other solvents and reagents were obtained from commercial sources and used as received, unless otherwise noted.

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated.
II. Preparation of 4-Alkynals

All yields are unoptimized.

\[ n-C_{16}H_{31} \equiv \text{CHO} \]

**Pentadec-4-ynal.** The title compound was prepared as a colorless oil in 55% isolated yield from 1-dodecyne and acrolein according to the procedure provided for 5-cyclohex-1-enyl-3-methylpent-4-ynal (vide infra). Acrolein (90%; Aldrich) was dried over MgSO\(_4\) prior to use.

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 9.79 (t, \(J = 1.5\) Hz, 1H), 2.60-2.64 (m, 2H), 2.46-2.50 (m, 2H), 2.09-2.13 (m, 2H), 1.42-1.48 (m, 2H), 1.23-1.37 (m, 14H), 0.88 (t, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \(\delta\) 201.8, 82.3, 78.4, 43.7, 32.6, 30.3, 30.2, 30.0, 29.8, 29.62, 29.56, 23.4, 19.4, 14.8, 12.9.

\[ n-C_{6}H_{13} \equiv \text{CHO} \]

**3-Methylundec-4-ynal.** The title compound was prepared as a colorless oil in 48% isolated yield from 1-octyne and crotonaldehyde according to the procedure provided for 5-cyclohex-1-enyl-3-methylpent-4-ynal (vide infra).

\(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 9.79 (t, \(J = 2.1\) Hz, 1H), 2.87-3.01 (m, 1H), 2.53 (ddd, \(J = 16.5, 7.5,\) and 2.1 Hz, 1H), 2.45 (ddd, \(J = 16.5, 7.5,\) and 2.1 Hz, 1H), 2.12 (dt, \(J = 6.9\) and 2.1 Hz, 2H), 1.23-1.50 (m, 8H), 1.21 (d, \(J = 6.9\) Hz, 3H), 0.88 (t, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 75MHz) \(\delta\) 202.3, 82.7, 82.1, 50.6, 31.5, 29.1, 28.7, 22.8, 21.7, 21.1, 18.9, 14.3. FTIR (neat) 2958, 2931, 2858, 2720, 2359, 1729, 1457, 1378, 1332 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{12}\)H\(_{21}\)O ([M+H]\(^+\)) 181.1587, found 181.1594.
2-Methyldodec-4-ynal. The title compound was prepared as a colorless oil in 37% isolated yield from 1-octyne and methacrolein according to the procedure provided for 5-cyclohex-1-enyl-3-methylpent-4-ynal (vide infra). Methacrolein (95+%; Alfa Aesar) was dried over MgSO₄ prior to use. 

\[ ^1H \text{NMR (CDCl}_3, 300 MHz) \delta 9.71 (d, J = 0.6 Hz, 1H), 2.31-2.56 (m, 3H), 2.13 (tt, J = 7.2 and 2.1 Hz, 2H), 1.17-1.53 (m, 8H), 1.19 (d, J = 6.9 Hz, 3H), 0.85-0.90 (m, 3H); ^{13}C \text{NMR (CDCl}_3, 75MHz) \delta 204.2, 82.9, 76.5, 45.8, 31.6, 29.1, 28.7, 22.6, 20.5, 18.9, 14.3, 13.3. \]

FTIR (neat) 2931, 2857, 2719, 2360, 2339, 1732, 1457, 1376, 1334, 1154 cm⁻¹; HRMS (ESI) calcd for C₁₂H₂₁O ([M+H]^+) 181.1587, found 181.1589.

3-Methyl-5-phenylpent-4-ynal. The title compound was prepared as a pale-yellow oil according to a literature procedure.²

3-Methoxy-3-methyl-5-phenylpent-4-ynal. n-BuLi (1.6 M in hexane; 17 mL, 27 mmol) was added to a stirred solution of phenylacetylene (3.0 mL, 27 mmol) in THF (30 mL) at 0 °C, and the resulting mixture was stirred at 0 °C for 15 min. Acetylacetaldelyde dimethylacetal (90+%; Aldrich; 4.0 mL, 30 mmol) was added at 0 °C, and the resulting mixture was stirred at 0 °C for 1 h. The reaction was quenched by the addition of water, and then extracted with Et₂O. The organic layer was dried
over MgSO₄, concentrated, and purified by flash chromatography (pentane:Et₂O = 4:1 → 1:1), which afforded 5,5-dimethoxy-3-methyl-1-phenylpent-1-yn-3-ol (4.7 g, 20 mmol, 77%) as a pale-yellow oil.

^1^H NMR (CDCl₃, 300 MHz) δ 7.40-7.44 (m, 2H), 7.25-7.33 (m, 3H), 4.99 (dd, J = 8.4 and 3.6 Hz, 1H), 4.28 (s, 1H), 3.48 (s, 3H), 3.38 (s, 3H), 2.09 (dd, J = 14.4 and 8.4 Hz, 1H), 2.01 (dd, J = 14.4 and 3.9 Hz, 1H), 1.56-1.60 (m, 3H).

A solution of 5,5-dimethoxy-3-methyl-1-phenylpent-1-yn-3-ol (1.0 g, 20 mmol) in THF (5 mL) was added to a stirred mixture of NaH (0.15 g, 6.3 mmol) in THF (20 mL) at rt. The resulting solution was stirred at rt for 10 min, and then MeI (0.50 mL, 8.0 mmol) was added. The mixture was stirred at rt for 1 h, and then the reaction was quenched by the addition of water and extracted with Et₂O. The organic layer was dried over MgSO₄ and concentrated. The resulting residue was dissolved in THF (30 mL), and a solution of p-toluenesulfonic acid monohydrate (0.10 g, 0.53 mmol) in water (10 mL) was added. The resulting mixture was stirred at reflux for 5 h and at rt for 12 h. The reaction was then quenched by the addition of saturated aqueous Na₂CO₃ and extracted with Et₂O. The organic layer was dried over Na₂SO₄, concentrated, and purified by flash chromatography (pentane:Et₂O = 3:1), which furnished 3-methoxy-3-methyl-5-phenylpent-4-ynal (0.75 g, 3.7 mmol, 87%) as a pale-yellow oil.

^1^H NMR (CDCl₃, 300 MHz) δ 9.94 (t, J = 2.7 Hz, 1H), 7.26-7.52 (m, 5H), 3.46 (s, 3H), 2.748 (d, J = 2.7 Hz, 1H), 2.746 (d, J = 2.7 Hz, 1H), 1.61 (s, 3H); ^1^C NMR (CDCl₃, 75 MHz) δ 201.5, 132.2, 132.0, 129.0, 128.8, 128.6, 122.2, 88.3, 87.5, 71.4, 54.4, 52.0, 26.3. FTIR (neat) 2985, 2936, 2827, 2358, 1725, 1674, 1490, 1444, 1281, 1165, 1132, 1110, 1071, 758, 691 cm⁻¹; HRMS (ESI) calcd for C₁₃H₁₄NaO₂ ([M+Na]⁺) 225.0886, found 225.0895.
5-Cyclohex-1-enyl-3-methylpent-4-ynal. $n$-BuLi (1.6 M in hexane; 15 mL, 24 mmol) was added to a stirred solution of 1-ethynylcyclohexene (2.8 mL, 24 mmol) in THF (80 mL) at −10 °C, and the resulting mixture was stirred at −10 °C for 20 min. CuI (99.999%; Aldrich; 5.0 g, 26 mmol) was added, and the mixture was stirred at −10 °C for 1 h. Then, after cooling to −78 °C, TMSI (3.8 mL, 26 mmol) was added, and the resulting solution was stirred at −78 °C for 10 min. Crotonaldehyde (99+%; Aldrich; 2.0 mL, 24 mmol) was added at −78 °C, and the mixture was stirred at −45 °C for 2 h. The reaction was quenched by the addition of saturated aqueous NH$_4$Cl and extracted with Et$_2$O. The organic layer was dried over Na$_2$SO$_4$, concentrated, and purified by flash chromatography (pentane:Et$_2$O = 20:1), which furnished 5-cyclohex-1-enyl-3-methylpent-4-ynal (2.9 g, 13 mmol, 55%) as a pale-yellow oil.

$^1$H NMR (CDCl$_3$, 500 MHz) δ 9.80 (dt, $J$ = 1.2 and 1.2 Hz, 1H), 6.02 (m, 1H), 3.08 (tq, $J$ = 4.2 and 4.2 Hz, 1H), 2.57 (ddt, $J$ = 9.9, 4.2, and 1.2 Hz, 1H), 2.51 (ddt, $J$ = 9.9, 4.2, and 1.2 Hz, 1H), 2.02-2.09 (m, 4H), 1.52-1.64 (m, 4H), 1.25 (dd, $J$ = 4.2 and 0.9 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 126 MHz) δ 202.1, 134.8, 121.2, 89.9, 84.2, 50.8, 30.1, 26.2, 23.0, 22.2, 21.91, 21.89. FTIR (neat) 2930, 2832, 2723, 2360, 1727, 1448, 1436, 1346, 1328, 1270, 1136, 1120, 1076, 919, 842, 800 cm$^{-1}$; HRMS (El) calcd for C$_{12}$H$_{16}$O (M$^+$) 176.1196, found 176.1203.

Heptadeca-4,6-diynal. A solution of 1-dodecyne (3.8 mL, 18 mmol) and 4-pentyn-
1-ol (1.7 mL, 18 mmol) in MeOH (75 mL) was added to a solution of Cu(OAc)₂ (7.0 g, 39 mmol), pyridine (75 mL), and MeOH (75 mL) at rt. The resulting mixture was stirred at rt for 16 h. This reaction solution was added to a mixture of ice and concentrated aqueous HCl (75 mL) and then extracted with Et₂O. The organic layer was washed with saturated aqueous Na₂CO₃, dried over Na₂SO₄, and concentrated. The resulting residue was purified by flash chromatography (hexanes:Et₂O = 3:1), which furnished heptadeca-4,6-diyn-1-ol (1.2 g, 5.0 mmol, 28%) as a colorless solid.

¹H NMR (CDCl₃, 300 MHz) δ 3.75 (t, J = 6.0 Hz, 2H), 2.39 (t, J = 6.9 Hz, 2H), 2.24 (t, J = 6.9 Hz, 2H), 1.73-1.82 (m, 2H), 1.18-1.60 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H).

To a solution of (COCl)₂ (0.47 mL, 5.3 mmol) in CH₂Cl₂ (15 mL) was added DMSO (0.38 mL, 5.3 mmol) at -78 °C, and the resulting mixture was stirred at -78 °C for 5 min. A solution of heptadeca-4,6-diyn-1-ol (1.20 g, 4.84 mmol) in CH₂Cl₂ (5 mL) was added at -78 °C, and the resulting mixture was stirred at -78 °C for 15 min. Triethylamine (3.4 mL, 24 mmol) was added at -78 °C, and the resulting mixture was stirred at rt for 30 min. The reaction was quenched by the addition of water and then extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, concentrated, and purified by flash chromatography (hexanes:Et₂O = 7:1), which furnished heptadeca-4,6-diynal (1.0 g, 4.1 mmol, 84%) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz) δ 9.79 (t, J = 1.2 Hz, 1H), 2.67-2.73 (m, 2H), 2.55-2.60 (m, 2H), 2.24 (t, J = 6.9 Hz, 2H), 1.21-1.56 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 200.0, 78.8, 74.9, 66.5, 65.1, 42.4, 32.1, 29.8, 29.7, 29.5, 29.3, 29.1, 28.5, 22.9, 19.4, 14.4, 12.7. FTIR (neat) 2925, 2854, 1728, 1458, 1171 cm⁻¹; HRMS (ESI) calcd for C₁₀H₂₅NaO ([M+Na]⁺) 269.1876, found 269.1871.
1-Deuterio-3-methylundec-4-ynal. To a solution of 3-methylundec-4-ynal (1.0 g, 5.6 mmol) in acetone (20 mL) at 0 °C was added Jones reagent (1.5 M; 4.1 mL, 6.1 mmol). The resulting mixture was stirred at 0 °C for 15 min, and then the reaction was quenched by the addition at 0 °C of 2-PrOH (5 mL). The mixture was stirred at rt for 10 min and then concentrated. The resulting residue was diluted with water and extracted with Et₂O. The organic layer was concentrated, and the product was purified by flash chromatography (hexanes:Et₂O = 10:1 → 1:1), which furnished 3-methylundec-4-ynoic acid (0.98 g, 5.1 mmol, 93%) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz) δ 2.85-2.95 (m, 1H), 2.56 (dd, J = 15.6 and 6.9 Hz, 1H), 2.41 (dd, J = 15.6 and 7.2 Hz, 1H), 2.12 (dt, J = 7.2 and 1.8 Hz, 2H), 1.20-1.50 (m, 8H), 1.21 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 6.6 Hz, 3H).

To a stirred mixture of LiAlD₄ (0.40 g, 9.5 mmol) in THF (20 mL) at 0 °C was added a solution of 3-methylundec-4-ynoic acid (0.97 g, 4.9 mmol) in THF (5 mL). The resulting mixture was stirred at reflux for 0.5 h and then cooled to 0 °C. The reaction was then quenched by the addition of water (0.5 mL), followed by stirring at 0 °C for 10 min. The solution was dried over MgSO₄, filtered through Celite, and concentrated to give the unpurified alcohol (0.90 g) as a colorless oil.

To a solution of (COCl)₂ (0.47 mL, 5.4 mmol) in CH₂Cl₂ (15 mL) at -78 °C was added DMSO (0.38 mL, 5.4 mmol). The resulting mixture was stirred at -78 °C for 5 min, and then a solution of the unpurified alcohol (0.90 g) in CH₂Cl₂ (5 mL) was added at -78 °C. The mixture was stirred at -78 °C for 15 min, and then Et₃N (3.4...
mL, 25 mmol) was added. After 1 h of stirring at rt, the reaction was quenched by
the addition of water and extracted with CH₂Cl₂. The organic layer was dried over
MgSO₄ and concentrated, and the residue was purified by flash chromatography
(pentane:Et₂O = 10:1), which furnished 1-deuterio-3-methylundec-4-ynal (0.68 g, 3.8
mmol, 76%) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz)  δ 2.87-2.99 (m, 1H), 2.52 (dd, J = 16.5 and 7.5 Hz, 1H),
2.44 (dd, J = 16.5 and 6.6 Hz, 1H), 2.12 (dt, J = 6.9 and 2.1 Hz, 2H), 1.18-1.50 (m, 8H), 1.20
(d, J = 7.2 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H); ²H NMR (CHCl₃)  δ 9.84 (s).
III. Rhodium-Catalyzed Synthesis of Cyclopentenones via the Intramolecular Hydroacylation of 4-Alkynals (Table 1)

**General Procedure 1 (With a glove box; Table 1, entry 4; first run).** In a N\(_2\)-filled glove box, [Rh(dppe)]\(_2\)(BF\(_4\))\(_2\) (17 mg, 0.029 mmol)\(^3\) and 3-methyl-5-phenylpent-4-yunal (50 mg, 0.29 mmol) were added to a 5-mL vial with 2.5 mL of acetone. The mixture was stirred at rt for 48 h. The reaction was then quenched by the addition of CH\(_3\)CN (1 mL). The resulting solution was concentrated, and the residue was purified by flash chromatography (pentane:Et\(_2\)O = 3:1), which furnished 4-methyl-2-phenylcyclopent-2-enone (44 mg, 0.26 mmol, 88%) as a colorless oil.

**General Procedure 2 (Without a glove box; Table 1, entry 4; second run).** In the air, [Rh(dppe)]\(_2\)(BF\(_4\))\(_2\) (34 mg, 0.058 mmol) was placed into a Schlenk tube, which was then filled with argon. Under a positive pressure of argon, 3-methyl-5-phenylpent-4-yunal (100 mg, 0.58 mmol) was added with 5 mL of acetone. The Schlenk tube was closed, and the mixture was stirred at rt for 48 h. The reaction was then quenched by the addition of CH\(_3\)CN (1 mL). The resulting solution was concentrated, and the residue was purified by flash chromatography (pentane:Et\(_2\)O = 3:1), which furnished 4-methyl-2-phenylcyclopent-2-enone (88 mg, 0.51 mmol, 88%) as a colorless oil.

![2-n-Decylcyclopent-2-enone](image)

2-\(n\)-Decylcyclopent-2-enone (Table 1, entry 1).\(^4\) Procedure 1 was followed, using 13 mg (0.023 mmol) of [Rh(dppe)]\(_2\)(BF\(_4\))\(_2\), 50 mg (0.23 mmol) of pentadec-4-yunal, and CH\(_3\)CN (117 µL, 2.3 mmol) as an additive. Reaction temperature: 100 °C. Reaction time: 72 h. 2-\(n\)-Decylcyclopent-2-enone was obtained as a colorless oil in 67% yield.
A second run was carried out according to Procedure 2, using 26 mg (0.045 mmol) of \([\text{Rh(dppe)}]_2(\text{BF}_4)_2\), 100 mg (0.45 mmol) of pentadec-4-ynal, and CH$_3$CN (235 $\mu$L, 4.5 mmol) as an additive. Reaction temperature: 100 °C. Reaction time: 72 h. 2-n-Decylcyclopent-2-enone was obtained in 66% yield.

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.27-7.30 (m, 1H), 2.51-2.57 (m, 2H), 2.37-2.40 (m, 2H), 2.11-2.17 (m, 2H), 1.38-1.51 (m, 2H), 1.19-1.32 (m, 14H), 0.86 (t, $J = 6.6$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 210.4, 157.5, 146.8, 34.8, 32.1, 29.83, 29.80, 29.65, 29.63, 29.5, 28.0, 26.7, 25.0, 22.9, 14.3.

2-n-Hexyl-4-methylcyclopent-2-enone (Table 1, entry 2). Procedure 1 was followed, using 16 mg (0.028 mmol) of \([\text{Rh(dppe)}]_2(\text{BF}_4)_2\), 50 mg (0.28 mmol) of 3-methylundec-4-ynal, and CH$_3$CN (145 $\mu$L, 2.8 mmol) as an additive. Reaction temperature: 100 °C. Reaction time: 72 h. 2-n-Hexyl-4-methylcyclopent-2-enone was obtained as a colorless oil in 74% yield.

A second run was carried out according to Procedure 2, using 33 mg (0.056 mmol) of \([\text{Rh(dppe)}]_2(\text{BF}_4)_2\), 100 mg (0.56 mmol) of 3-methylundec-4-ynal, and CH$_3$CN (290 $\mu$L, 5.6 mmol) as an additive. Reaction temperature: 100 °C. Reaction time: 72 h. 2-n-Hexyl-4-methylcyclopent-2-enone was obtained in 76% yield.

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.15-7.17 (m, 1H), 2.80-2.92 (m, 1H), 2.62 (dd, $J = 18.9$ and 6.3 Hz, 1H), 2.10-2.16 (m, 2H), 1.95 (dd, $J = 18.9$ and 2.1 Hz, 1H), 1.40-1.52 (m, 2H), 1.20-1.38 (m, 6H), 1.15 (d, $J = 7.2$ Hz, 3H), 0.87 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 210.2, 162.8, 145.7, 43.6, 33.5, 31.8, 29.3, 27.9, 24.8, 22.8, 20.6, 14.3. FTIR (neat) 2924, 2856, 2360, 1702, 1457, 1060 cm$^{-1}$; HRMS (EI) calcd for C$_{12}$H$_{20}$O (M$^+$) 180.1509, found 180.1506.
2-n-Hexyl-5-methylcyclopent-2-enone (Table 1, entry 3). Procedure 1 was followed, using 16 mg (0.028 mmol) of [Rh(dppe)]2(BF4)2, 50 mg (0.28 mmol) of 2-methylundec-4-ynal, and CH3CN (145 µL, 2.8 mmol) as an additive. Reaction temperature: 100 °C. Reaction time: 72 h. 2-n-Hexyl-5-methylcyclopent-2-enone was obtained as a colorless oil in 68% yield.

A second run was carried out according to Procedure 2, using 33 mg (0.056 mmol) of [Rh(dppe)]2(BF4)2, 100 mg (0.56 mmol) of 2-methylundec-4-ynal, and CH3CN (290 µL, 5.6 mmol) as an additive. Reaction temperature: 100 °C. Reaction time: 72 h. 2-n-Hexyl-5-methylcyclopent-2-enone was obtained in 65% yield.

1H NMR (CDCl3, 300 MHz) δ 7.18-7.22 (m, 1H), 2.73-2.85 (m, 1H), 2.30-2.40 (m, 1H), 2.07-2.17 (m, 3H), 1.40-1.50 (m, 2H), 1.21-1.36 (m, 6H), 1.15 (d, J = 7.5 Hz, 3H), 0.86 (t, J = 6.6 Hz, 3H); 13C NMR (CDCl3, 75 MHz) δ 212.8, 155.7, 145.5, 40.2, 35.8, 31.8, 29.3, 27.9, 25.1, 22.8, 16.7, 14.3.

4-Methyl-2-phenylcyclopent-2-enone (Table 1, entry 4). Procedures 1 and 2 were followed.

1H NMR (CDCl3) δ 7.26-7.71 (m, 6H), 2.95-3.06 (m, 1H), 2.81 (dd, J = 18.9 and 6.3 Hz, 1H), 2.16 (dd, J = 18.9 and 2.4 Hz, 1H), 1.25 (d, J = 6.9 Hz, 3H); 13C NMR (CDCl3) δ 207.7, 164.3, 142.5, 131.7, 128.7, 128.6, 127.4, 44.7, 33.2, 20.4.
4-Methoxy-4-methyl-2-phenylcyclopent-2-enone (Table 1, entry 5). Procedure 1
was followed, using 15 mg (0.025 mmol) of [Rh(dppe)]2(BF4)2 and 50 mg (0.25 mmol)
of 3-methoxy-3-methyl-5-phenylpent-4-ynal. Reaction time: 72 h. 4-Methoxy-4-
methyl-2-phenylcyclopent-2-enone was obtained as a yellow oil in 71% yield.

A second run was carried out according to Procedure 2, using 29 mg (0.049 mmol)
of [Rh(dppe)]2(BF4)2 and 100 mg (0.49 mmol) of 3-methoxy-3-methyl-5-phenylpent-4-
ynal. Reaction time: 62 h. 4-Methoxy-4-methyl-2-phenylcyclopent-2-enone was
obtained in 79% yield.

1H NMR (CDCl3) δ 7.36-7.74 (m, 6H), 3.26 (s, 3H), 2.87 (d, J = 18.6 Hz, 1H), 2.52 (d, J =
18.6 Hz, 1H), 1.56 (s, 3H); 13C NMR (CDCl3) δ 202.3, 159.3, 143.8, 130.6, 129.3, 128.8,
127.8, 78.5, 51.5, 47.0, 25.7. FTIR (neat) 2929, 2362, 1716, 1653, 1558, 1540, 1506, 1491,
1457, 1305, 1195, 1147, 1076, 767, 694 cm⁻¹; HRMS (EI) calcd for C13H14O2 (M⁺) 202.0988,
found 202.0996.

2-Cyclohex-1-enyl-4-methylcyclopent-2-enone (Table 1, entry 6). Procedure 1 was
followed, using 17 mg (0.028 mmol) of [Rh(dppe)]2(BF4)2 and 50 mg (0.28 mmol) of 5-
cyclohex-1-enyl-3-methylpent-4-ynal. Reaction time: 48 h. 2-Cyclohex-1-enyl-4-
methylcyclopent-2-enone was obtained as a colorless oil in 85% yield.

A second run was carried out according to Procedure 2, using 33 mg (0.057 mmol)
of [Rh(dppe)]2(BF4)2 and 100 mg (0.57 mmol) of 5-cyclohex-1-enyl-3-methylpent-4-
ynal. Reaction time: 44 h. 2-Cyclohex-1-enyl-4-methylcyclopent-2-enone was obtained in 83% yield.

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.21 (d, $J = 3.0$ Hz, 1H), 6.84-6.91 (m, 1H), 2.79-2.91 (m, 1H), 2.67 (dd, $J = 18.6$ and 6.6 Hz, 1H), 2.10-2.20 (m, 4H), 2.02 (dd, $J = 18.6$ and 2.1 Hz, 1H), 1.53-1.74 (m, 4H), 1.16 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 208.6, 160.4, 142.3, 129.3, 128.5, 45.1, 32.4, 26.8, 25.8, 22.8, 22.2, 20.6. FTIR (neat) 2926, 2359, 1702, 1448, 1408, 1386, 1320, 1295, 1106, 926, 843 cm$^{-1}$; HRMS (EI) calcd for C$_{12}$H$_{16}$O (M$^+$) 176.1196, found 176.1188.

![n-C$_{10}$H$_{24}$](image)

2-Dodec-1-ynylcyclopent-2-enone (Table 1, entry 7). Procedure 1 was followed, using 12 mg (0.020 mmol) of [Rh(dppe)$_2$(BF$_4$)$_2$] and 50 mg (0.20 mmol) of heptadeca-4,6-diynal. Reaction temperature: 100 °C. Reaction time: 48 h. 2-Dodec-1-ynylcyclopent-2-enone was obtained as a colorless oil in 77% yield.

A second run was carried out according to Procedure 2, using 24 mg (0.041 mmol) of [Rh(dppe)$_2$(BF$_4$)$_2$] and 100 mg (0.41 mmol) of heptadeca-4,6-diynal. Reaction temperature: 100 °C. Reaction time: 48 h. 2-Dodec-1-ynylcyclopent-2-enone was obtained in 75% yield.

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.68 (t, $J = 2.7$ Hz, 1H), 2.66-2.70 (m, 2H), 2.43-2.46 (m, 2H), 2.38 (t, $J = 7.2$ Hz, 2H), 1.51-1.60 (m, 2H), 1.20-1.44 (m, 14H), 0.87 (t, $J = 6.6$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 300 MHz) $\delta$ 206.7, 164.3, 130.1, 97.9, 71.3, 34.1, 32.1, 29.8, 29.7, 29.6, 29.4, 29.2, 28.7, 27.3, 22.9, 19.8, 14.4. FTIR (neat) 2925, 2854, 2235, 1719, 1466, 1297, 1101, 1011, 927, 784 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{26}$NaO ([M+Na]$^+$) 269.1876, found 269.1886.
IV. Mechanistic Studies

Eq 5. Procedure 1 was followed, using 16 mg (0.028 mmol) of [Rh(dppe)]$_2$(BF$_4$)$_2$, 50 mg (0.28 mmol) of 1-deuterio-3-methylundec-4-ynal, and CH$_3$CN (145 µL, 2.8 mmol) as an additive. Reaction temperature: 100 °C. Reaction time: 72 h. 3-Deuterio-2-n-hexyl-4-methylcyclopent-2-enone was obtained in 70% yield.

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 2.80-2.90 (m, 1H), 2.61 (dd, $J = 18.9$ and 6.3 Hz, 1H), 2.09-2.15 (m, 2H), 1.94 (dd, $J = 18.9$ and 2.1 Hz, 1H), 1.38-1.50 (m, 2H), 1.20-1.37 (m, 6H), 1.14 (d, $J = 6.9$ Hz, 3H), 0.86 (t, $J = 6.6$ Hz, 3H); $^2$H NMR (CHCl$_3$) $\delta$ 7.29 (s).

Eq 6. In a N$_2$-filled glove box, [Rh(dppe)]$_2$(BF$_4$)$_2$ (6.5 mg, 0.011 mmol), 2-methylundec-4-ynal (20 mg, 0.11 mmol), 1-deuterio-3-methylundec-4-ynal (20 mg, 0.11 mmol), and CH$_3$CN (57 µL, 1.1 mmol) were added to a Schlenk tube with 2 mL of acetone. The mixture was stirred at 100 °C for 72 h. The reaction was then quenched by the addition of CH$_3$CN (1 mL). The resulting solution was concentrated, and the residue was purified by flash chromatography (pentane:Et$_2$O = 20:1), which furnished 2-n-hexyl-5-methylcyclopent-2-enone (first fraction; 4 mg), 3-deuterio-2-n-hexyl-4-methylcyclopent-2-enone (third fraction; 5 mg), and a mixture of the two compounds (second fraction; 14 mg). The structures of the products were determined by $^1$H and $^2$H NMR analysis.
V. References


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