

## Supporting Information

**Title : Chelation-Assisted Hydrative Dimerization of 1-Alkyne Forming  $\alpha,\beta$ -Enones by Rh(I) Catalyst**

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**General Experiments.** Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column chromatography were monitored by analytical thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60 F-254) using UV light as a visualizing agent and *p*-anisaldehyde solution, and heat as developing agent. Infrared spectra were obtained on a Nicolet Impact 400 spectrometer. Gas chromatographic analyses were performed on a Donam DS 6200 instrument with FID detector and a Hewlett-Packard HP-5 capillary column. Low- resolution mass spectra were measured on a Hewlett-Packard HP G1800A GCD system equipped with a Hewlett Packard HP-5 capillary column.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on a Bruker Advance/DPX 250 with chemical shifts reported relative to residual deuterated solvent peaks.  $^1\text{H}$  NMR spectra were referenced to tetramethylsilane ( $\delta$  0.00 ppm) as an internal standard and are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).  $^{13}\text{C}$  NMR spectra were referenced to the residual  $\text{CDCl}_3$  ( $\delta$  77.0 ppm).  $^2\text{H}$  NMR was recorded on a Varian INOVA-500 (76.71 MHz for  $^2\text{H}$ ) spectrometer with  $\text{CDCl}_3$  as an internal standard and Elementary Analysis (EA) by the Organic Chemistry Research Center, Sogang University (Seoul 121-742, Korea). High-resolution mass spectrometry was performed by the National Center for Inter-University Facilities, Seoul National University

(Seoul 151-742, Korea).

**Materials.** All alkynes are purchased from Aldrich Co. and Lancaster Co., and used as received. Deuterated 1-decyne was synthesized by the reaction of 1-decyne with *n*-BuLi followed by D<sub>2</sub>O hydrolysis. All commercially available reagent grade chemicals were purchased from Aldrich Chemical Company, TCI, and Junsei Chemical Company and used as received without further purification unless otherwise stated. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under nitrogen atmosphere prior to use. Dichloromethane was distilled from calcium hydride under nitrogen atmosphere. Chlorotris(triphenylphosphine)rhodium (**2**, (PPh<sub>3</sub>)<sub>3</sub>Rh(I)Cl) was prepared according to the literature procedure and stored in a refrigerator under N<sub>2</sub> atmosphere.<sup>1</sup>

**Typical Procedure for the Catalytic Reaction. The Reaction of 1-Octyne (1a).** (Table 1, entry 1) A screw-capped pressure vial (1 mL) was charged with 47.6 mg (0.432 mmol) of 1-octyne, 20 mg (0.0216 mmol) of (PPh<sub>3</sub>)<sub>3</sub>Rh(I)Cl (**2**), 46.7 mg (0.432 mmol) of 2-amino-3-picoline (**3**), 2.6 mg (0.0216 mmol) of benzoic acid (**4**), 7.8 mg (0.432 mmol) of H<sub>2</sub>O and the reaction mixture was dissolved in 0.22 mL of THF. It was stirred in an oil bath

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<sup>1</sup> Osborn, J. A.; Wilkinson, G. In *Reagents for Transition Metal Complex and Organometallic Syntheses*; Angelici, R., Ed.; Wiley: New York, 1989; Vol. 28, pp. 77-79.

that was preheated to 110 °C for 2h. After the reaction, the reaction mixture was purified by column chromatography (SiO<sub>2</sub>, *n*-hexane : ethyl ether = 15 : 1) to afford 42.6 mg (82%) of 7-methylenepentadecan-8-one and (*E*)-hexadec-9-en-8-one as a 4:1 mixture (determined by GC).

**7-Methylenepentadecan-8-one (5a):** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  5.9 (s, 1H), 5.7 (s, 1H), 2.6(t, *J* = 7.4 Hz, 2H), 2.2 (t, *J* = 7.6Hz, 2H), 1.6 (br m, 2H) 1.4-1.2 (m, 16H), 0.9 (t, *J* = 6.5, 6H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>):  $\delta$  202.7 (CO), 149.4 & 123.5 (vinyl group), 53.6, 38.1, 31.9, 31.8, 31.2, 29.5, 29.3, 29.2, 28.6, 24.9, 22.8, 14.3; MS: *m/z* (%): 238 (M<sup>+</sup>, 14.7) 223 (0.9), 209 (3.8), 195 (7.7), 181 (12.7), 167 (94.0), 139 (56.3), 125 (28.1), 111 (53.3), 97 (27.0), 84 (36.0), 69 (100), 41 (33.1), 29 (11.8), 18 (0.4); IR (neat): 2956, 2927, 2856, 1734, 1679(CO), 1626, 1465, 1377, 1264, 930, 757 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>16</sub>H<sub>30</sub>O 238.2297; found 238.2298. Anal. Calcd for C<sub>16</sub>H<sub>30</sub>O: C, 80.61; H, 12.68; O, 6.71. Found: C, 80.76; H, 12.62.

**(*E*)-hexadec-9-en-8-one (6a)<sup>2</sup>:** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  6.8 (dt, *J* = 15.8 Hz, *J* = 6.9 Hz, 1H), 6.1 (dt, *J* = 15.8 Hz, *J*=1.5 Hz 1H), 2.5 (t, *J* = 7.3 Hz, 2H), 2.2 (q, 2H), 1.6 (m,

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<sup>2</sup> a) Curci, R.; Fiorentino, M.; Fusco, C.; Mello, R.; Ballisteri, F. P.; Failla, S.; Tomaselli, G. A. *Tetrahedron Lett.* **1992**, 33, 7929-7932. b) Matsuoka, R.; Horiguchi, Y.; Kuwajima, I. *Tetrahedron Lett.* **1987**, 28, 1299-1302.

2H), 1.5-1.2 (m, 16H), 0.8 (m, 6H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.2 (CO), 147.5 & 130.5 (vinyl group), 40.3, 32.6, 31.9, 31.8, 29.5, 29.3, 29.0, 28.3, 24.5, 22.8, 22.7, 14.2; MS:  $m/z$  (%): 238 ( $\text{M}^+$ , 2.9), 223 (0.1), 209 (0.8), 195 (4.1), 181 (5.7), 154 (50.1), 153 (100), 139 (84.1), 127 (23.7), 111 (13.6), 97.1 (42.7), 81.1 (14.1), 70 (35.8), 55 (74), 41 (24.1), 29 (9.8), 18 (1.2); IR (neat): 2956, 2927, 2856, 1698, 1675(CO), 1629, 1458, 1376, 976, 723  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{30}\text{O}$  238.2297; found 238.2296.

**5-Methyleneundecan-6-one (5b)<sup>3</sup>:**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.9 (s, 1H), 5.6 (s, 1H), 2.6(t,  $J$  = 7.4 Hz, 2H), 2.2 (t,  $J$  = 6.6Hz, 2H), 1.6 (m, 2H) 1.4-1.2 (m, 8H), 0.9 (t,  $J$  = 6.5, 6H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.6 (CO), 149.3 & 123.4 (vinyl group), 40.0, 31.7, 30.8, 24.5, 22.7, 22.6, 14.1, 14.0; MS:  $m/z$  (%): 182 ( $\text{M}^+$ , 6.2) 167 (1.2), 153 (6.2), 139 (46.0), 126 (10.6), 111 (100.0), 97 (14.5), 84 (20.5), 69 (38.3), 55 (70.5); IR (neat): 2960, 2930, 2865, 1750, 1685(CO), 1463, 1375, 1242, 1051, 934, 734, 1242, 1051, 734  $\text{cm}^{-1}$

<sup>1</sup>.

**(E)-dodec-7-en-6-one (6b)<sup>4</sup>:**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.8 (dt,  $J$  = 15.9 Hz,  $J$  =

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<sup>3</sup> Jun, C.-H.; Lee, H.; Hong, J.-B.; Kown, B.-I. *Angew. Chem. Int. Ed.* 2002, 41, 2146-2147.

<sup>4</sup> (a) B, Asuncion, P, Francisco J, *Synlett*. **2001**, 6, 827-829. (b) B, Herbert C, B, Narayan G, *Tetrahedron Lett.* **1991**, 32, 3655-3658. (c) R, Noyori, I, Tomino, M, Yamada, M, Nishizawa, *J. Am. Chem. Soc.* **1984**, 106, 6717-6725.

6.9 Hz, 1H), 6.1 (dt,  $J$  = 15.9 Hz,  $J$  = 1.5 Hz 1H), 2.5 (t,  $J$  = 7.3 Hz, 2H), 2.2 (q, 2H), 1.6 (m, 2H), 1.5-1.2 (m, 8H), 0.9 (m, 6H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.1 (CO), 147.3 & 130.0 (vinyl group), 40.1, 32.1, 31.5, 30.2, 24.0, 22.4, 22.2, 13.9, 13.8; MS:  $m/z$  (%): 182 ( $\text{M}^+$ , 1.4) 167 (0.5), 153 (2.6), 139 (2.9), 126 (65.2), 111 (100), 97 (26.9), 83 (13.2), 70 (30), 55 (91.2); IR (neat): 2961, 2940, 2873, 1676, 1633, 1463, 1370, 1183, 984, 736  $\text{cm}^{-1}$ .

**8-Methyleneheptadecan-9-one<sup>5</sup> (5c):**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.9 (s, 1H), 5.6 (s, 1H), 2.6 (t,  $J$  = 7.2 Hz, 2H), 2.2 (t,  $J$  = 7.5 Hz, 2H), 1.6 (m, 2H) 1.4-1.2 (m, 20H), 0.9 (t,  $J$  = 6.8, 6H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.5 (CO), 149.4 & 123.4 (vinyl group), 38.0, 32.0, 31.1, 29.6, 29.5, 29.4, 29.3, 28.7, 24.8, 22.8, 14.2; MS:  $m/z$  (%): 266 ( $\text{M}^+$ , 14.3) 237 (4.8), 223 (3.3), 209 (7.5), 195 (14.1), 181 (88.9), 168 (25.2), 153 (47.8), 139 (39), 125 (17.3), 111 (52.9), 97 (35.8), 83 (47.6), 69 (100), 55 (55.3), 41 (51.3), 29 (18.6), 18 (0.4); IR (neat): 2958, 2926, 2855, 1709, 1680(CO), 1626, 1463, 1410, 1376, 1125, 1071, 930, 723  $\text{cm}^{-1}$ ; HRMS (CI) calcd for  $\text{C}_{18}\text{H}_{34}\text{O}$  266.2610; found 267.2690 [ $\text{M}+\text{H}^+$ ]. Anal. Calcd for  $\text{C}_{18}\text{H}_{34}\text{O}$ : C, 81.13; H, 12.86; O, 6.00. Found: C, 81.23; H, 12.80.

**(E)-octadec-10-en-9-one (6c):**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.8 (dt,  $J$  = 15.8 Hz,  $J$  = 6.9 Hz, 1H), 6.1 (dt,  $J$  = 15.9 Hz,  $J$  = 1.1 Hz 1H), 2.5 (t,  $J$  = 7.3 Hz, 2H), 2.2 (q, 2H), 1.6 (m,

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<sup>5</sup> Sen Gupta, A. K.; Mitchard, D. A. *Tetrahedron Lett.* **1968**, 5207-5208.

2H), 1.5-1.2 (m, 20H), 0.9 (m, 6H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.3 (CO), 147.6 & 130.5 (vinyl group), 40.3, 32.7, 32.0, 31.9, 29.6, 29.5, 29.4, 29.3, 28.3, 24.6, 22.9, 14.3; MS:  $m/z$  (%): 266 ( $\text{M}^+$ , 3.6) 251 (0.1), 223 (1.5), 209 (4.1), 195 (5.3), 169 (6.1), 167 (100), 153 (53.0), 141 (28.8), 125 (10), 110 (33.2), 97 (38.8), 83 (25.7), 69 (33.4), 55 (56.6), 41 (22.8), 28 (10.9), 18 (3); IR ( $\text{CHCl}_3$ ): 2958, 2927, 2856, 1668(CO), 1627, 1464, 1376, 1215, 975, 757, 668  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{34}\text{O}$  266.2610; found 266.2608.

**9-Methylenenonadecan-10-one (5d):**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.9 (s, 1H), 5.7 (s, 1H), 2.6(t,  $J$  = 7.3 Hz, 2H), 2.2 (t,  $J$  = 6.7 Hz, 2H), 1.6 (m, 2H) 1.4-1.2 (m, 24H), 0.9 (t,  $J$  = 6.8, 6H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.7 (CO), 149.4 & 123.4 (vinyl group), 38.1, 32.1, 31.2, 29.7, 29.6, 29.5, 28.7, 24.9, 22.8, 14.3; MS:  $m/z$  (%): 294 ( $\text{M}^+$ , 18.1) 266 (0.9), 251 (5), 237 (3.1), 209 (18.7), 195 (100), 182 (27.5), 167 (45.6), 153 (37.7), 139 (18.4), 124 (28.2), 111 (55.9), 97 (46.3), 83 (53.4), 69 (86.3), 55 (54.4), 43 (55.3), 18 (1.4); IR (neat): 2958, 2925, 2854, 1680(CO), 1622, 1464, 1401, 1376, 927, 707  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{38}\text{O}$  294.2923; found 294.2924. Anal. Calcd for  $\text{C}_{20}\text{H}_{38}\text{O}$ : C, 81.56; H, 13.01; O, 5.43. Found: C, 81.67; H, 12.97.

**(E)-icos-11-en-10-one (6d):**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.8 (dt,  $J$  = 15.9 Hz,  $J$  = 6.9 Hz, 1H), 6.1 (dt,  $J$  = 15.9 Hz,  $J$  = 1.6 Hz 1H), 2.5 (t,  $J$  = 7.3 Hz, 2H), 2.2 (q, 2H), 1.6 (m,

2H), 1.5-1.2 (m, 24H), 0.9 (m, 6H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.3 (CO), 147.6 & 130.5 (vinyl group), 40.3, 32.7, 32.1, 32.0, 31.1, 29.6, 29.5, 29.4, 28.3, 24.6, 22.9, 14.3; MS:  $m/z$  (%): 294 ( $\text{M}^+$ , 3.0) 251 (1), 237 (0.8), 209 (5), 195 (4.3), 181 (100), 155 (30.8), 124 (25.6), 111 (10.1), 97 (45), 83 (34), 69 (26), 55 (54.7), 43 (27.3), 18 (2.8); IR ( $\text{CHCl}_3$ ): 2958, 2925, 2854, 1697, 1676(CO), 1630, 1464, 1369, 975, 708  $\text{cm}^{-1}$ ; HRMS (CI) calcd for  $\text{C}_{20}\text{H}_{38}\text{O}$  294.2923; found 295.3000 [ $\text{M}+\text{H}^+$ ].

**1,3-dicyclohexylbut-3-en-2-one (5e):**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.9 (s, 1H), 5.6 (s, 1H), 2.6-2.5(m, 3H), 1.8-1.6 (m, 10H), 1.4-0.9 (m, 11H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.6 (CO), 155.2 & 121.5 (vinyl group), 46.0, 37.7, 35.0, 33.5, 33.4, 33.3, 32.8, 26.8, 26.5, 26.4, 26.38, 26.31; MS:  $m/z$  (%): 234 ( $\text{M}^+$ , 36.8) 216 (3.5), 205 (0.6), 191 (22.7), 165 (4.5), 152 (76.2), 137 (100), 123 (13.7), 109 (99), 95 (14.4), 81 (24.3), 67 (52.6), 55 (41.5), 41 (24.9) 29 (4.7), 18 (0.5); IR (neat): 2924, 2851, 1677(CO), 1615, 1448, 1288, 1027, 927  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{26}\text{O}$  234.1984; found 234.1983. Anal. Calcd for  $\text{C}_{16}\text{H}_{26}\text{O}$ : C, 81.99; H, 11.18; O, 6.83. Found: C, 82.12; H, 11.14.

**(E)-1,4-dicyclohexylbut-3-en-2-one (6e):**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.7 (dd,  $J=16$  Hz,  $J=6.7$  Hz, 1H), 6.1 (dd,  $J=16$  Hz,  $J=1.1$  Hz 1H), 2.4 (d,  $J=6.8$  Hz, 2H), 2.2 (br, 1H), 1.8-1.6 (m, 10H), 1.4-0.8 (m, 11H);  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.3 (CO),

152.4 & 128.5 (vinyl group), 48.0, 40.7, 34.7, 33.5, 32.0, 26.4, 26.3, 26.1, 25.9; MS: *m/z* (%): 234 (M<sup>+</sup>, 1.6) 206 (0.1), 191 (0.3), 152 (100), 137 (22.1), 119 (5.0), 109 (27.0), 94 (48.3), 71 (22.7), 55 (52.9), 41 (14.9), 28 (6.5), 18 (1.0); IR (neat): 2924, 2851, 1694, 1672(CO), 1625, 1447, 1351, 1287, 1216, 1184, 981 cm<sup>-1</sup>; HRMS (CI) calcd for C<sub>16</sub>H<sub>26</sub>O 234.1984; found 235.2061 [M+H<sup>+</sup>].

**(E)-2,2,7,7-tetramethyloct-5-en-4-one<sup>6</sup> (6f):** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  6.8 (d, *J* = 16Hz, 1H), 6.0 (d, *J* = 16Hz, 1H), 2.4(s, 2H), 1.1 (s, 9H), 1.0 (s, 9H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>):  $\delta$  201.2 (CO), 157.0 & 127.1 (vinyl group), 53.1, 33.8, 31.4, 30.2, 28.9; MS: *m/z* (%): 182 (M<sup>+</sup>, 0.08) 167 (2.1), 125 (31.3), 111 (100), 93 (4.2), 83 (16.4), 69 (4.2), 57 (15.6), 55 (13.7), 43 (11.9), 41 (14.6), 29 (5), 15 (0.3); IR (neat): 2958, 2904, 2868, 1738, 1686(CO), 1622, 1465, 1363, 1317, 1249, 1231, 1084, 1026, 985, 925, 757 cm<sup>-1</sup>; HRMS (CI) calcd for C<sub>12</sub>H<sub>22</sub>O 182.1671; found 183.1747 [M+H<sup>+</sup>].

**(E)-3-methyl-N-((E)-2,2,7,7-tetramethyloct-5-en-4-ylidene)pyridine-2-amine (6f'):** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  8.2 (d, *J* = 4.2 Hz, 1H), 7.4 (d, *J* = 7.4 Hz, 1H), 6.8 (dd, *J* = 7.4 Hz, *J* = 4.2 Hz, 1H), 6.3 (d, *J* = 16.2 Hz, 1H), 5.7 (d, *J* = 16.2 Hz, 1H), 2.6 (s, 2H), 2.1 (s, 3H), 1.1 (s, 9H), 0.9 (s, 9H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>):  $\delta$  168.9, 162.2, 153.0,

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<sup>6</sup> **6f** was isolated as a mixture of hydrolyzed enone and ketimine form (**6f'**).

146.2, 138.3, 123.2, 121.4, 118.8, 47.7, 34.0, 32.0, 30.8, 29.5, 29.3, 29.0, 18.0; MS: *m/z* (%): 272 (M<sup>+</sup>, 0.4) 257 (9.9), 215 (100), 201 (10.2), 185 (3.9), 159 (52.7), 145 (1.7), 118 (1), 109 (3.4), 92 (10.9), 57 (2.5), 28 (14.4), 18 (5.4); IR (neat): 2956, 2898, 2866, 1638, 1610, 1583, 1463, 1441, 1412, 1364, 1252, 1233, 1109, 975, 752 cm<sup>-1</sup>; HRMS (CI) calcd for C<sub>18</sub>H<sub>28</sub>N<sub>2</sub> 272.2252; found 273.2330 [M+H<sup>+</sup>].

**The Reaction of D-substituted 1-Decyne under (PPh<sub>3</sub>)<sub>3</sub>Rh(I)Cl (2) and 2-*N*-methylaminopyridine (23).** (Eq 2) A screw-capped pressure vial (1 mL) was charged with 60.1 mg (0.432 mmol) of D-substituted 1-decyne, 20 mg (0.0216 mmol) of (PPh<sub>3</sub>)<sub>3</sub>Rh(I)Cl (2), 46.7 mg (0.432 mmol) of 2-*N*-methylaminopyridine (23) and the reaction mixture was dissolved in 0.22 mL of THF. It was stirred in an oil bath that was preheated to 110 °C for 2h. After the reaction, the reaction mixture was purified by column chromatography (SiO<sub>2</sub>, *n*-hexane : ethyl acetate = 10 : 1) to afford 20.6 mg (ca. 33%) of deuterium containing 1-decanal.

**Figure S1.**  $^1\text{H}$  and  $^2\text{H}$  NMR of **24**

