Supporting Information

**Title : A Hydroacylation-Triggered Carbon-Carbon Triple Bond Cleavage in
Alkynes via Retro-Mannich Type Fragmentation**

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Journal : *Journal of the American Chemical Society*

General Method. NMR spectra were recorded in CDCl₃ on Bruker Avance DPX 250 spectrometer (¹H NMR, 250 MHz; ¹³C NMR, 62.5 MHz), and Bruker Avance DPX 500 spectrometer (¹H NMR, 500 MHz; ¹³C NMR, 120 MHz), and the chemical shift was expressed in ppm relative to TMS. IR spectra were recorded on Nicolet Impact 400 spectrometer. GC analyses were conducted using Donam DS 2000 Gas Chromatography. Mass spectra were obtained using G1800A GCD System. Commercially available compounds are used as received except toluene, which was purified according to the known procedure.¹ (PPh₃)₃RhCl (**3a**) and [(C₈H₁₄)₂RhCl]₂ (**3b**) was prepared as described in the literature.²

Materials. All aldehydes, alkynes are purchased from Aldrich Co. and Lancaster Co., and used as received. Cyclododecyne (**2g**) was prepared following the known procedures,^{3a} and identified by the comparison of the known spectral data.^{3b}

Cyclododecyne (2g).^{3b} ¹H NMR (250 MHz, CDCl₃): δ 2.20-2.17 (m, 4H), 1.55-1.42 (m,

¹ Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1996.

² Osborn, J. A.; Wilkinson, G. In *Reagents for Transition Metal Complex and Organometallic Synthesis*; Angelich, R., Ed.; Wiley: New York, 1989; Vol. 28, pp 77, and 90.

³ (a) Brummomd, K. M.; Gesenberg, K. D.; Kent, J. L.; kerekes, A. D. *Tetrahedron Lett.* **1998**, 39, 8613. (b) Satoh, T.; Itoh, N.; Watanabe, S.; Koike, H.; Matsuno, H.; Matsuda, K.; Yamakawa, K. *Tetrahedron* **1995**, 51, 9327.

16H). ^{13}C NMR (62.5 MHz, CDCl_3) δ 81.7, 25.9, 25.8, 25.1, 24.8, 18. MS (EI): m/z (relative intensity) 164 (M^+ , 3), 149 (3), 135 (15), 121 (46), 107 (26), 93 (50), 79 (87), 67 (100), 55 (39), 41 (48).

Typical Procedure for the Catalytic Reaction. The Reaction of Hydrocinnamaldehyde (1b) and 2-Butyne (2b). (Table 1, entry 1) A screw-capped pressure vial (1 mL) was charged with 28.6 mg (0.22 mmol) of hydrocinnamaldehyde (**1b**), 6.1 mg (0.0065 mmol) of $(\text{PPh}_3)_3\text{RhCl}$ (**3a**), 11.9 mg (0.011 mmol) of 2-amino-3-picoline (**4**), 43.6 mg (0.44 mmol) of cyclohexylamine (**5**), 2.8 mg (0.022 mmol) of aluminum chloride (**6**), 12 mg (0.22 mmol) of 2-butyne (**2b**), and the reaction mixture was dissolved in 100 mg of toluene. It was stirred in an oil bath that was preheated at 130 °C for 12h. After the reaction, the reaction mixture was hydrolyzed by 1N HCl, extracted with Et_2O and CH_2Cl_2 . The organic layers were combined, dried over MgSO_4 , and purified by column chromatography (SiO_2 , *n*-hexane : ethyl acetate = 5 : 2) to afford 32 mg (90%) of 1-phenyl-pentan-3-one (**7b**)

1-Phenyl-pentan-3-one (7b).⁴ ^1H NMR (250 MHz, CDCl_3): δ 7.30-7.16 (m, 5H), 2.90 (t,

⁴ Mattson, M. N.; Rapoport, H. J. Org. Chem. **1996**, *61*, 6071.

$J = 7.7$ Hz, 2H), 2.74 (t, $J = 7.7$ Hz, 2H), 2.40 (q, $J = 7.3$ Hz, 2H), 1.04 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (62.5MHz, CDCl_3): δ 208, 140, 0.6, 142.7, 141.8, 141.6, 135.8, 128.4, 125.9, 39.2, 30.8, 29.7, 24.8, 13.9. IR (neat): 3085, 3064, 3027, 2925, 2854, 1715, 1635, 1604, 1496, 1455 cm^{-1} .

The Reaction of Acetaldehyde (1a) and 6-Dodecyne (2a). (eq 2) A screw-capped pressure vial (1 mL) was charged with 1.1 mg (0.025 mmol) of acetaldehyde (**1a**), 83.1 mg (0.50 mmol) of 6-dodecyne (**2a**), 9.0 mg (0.0125 mmol) of $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ (**3b**), 54.1 mg (0.50 mmol) of 2-amino-3-picoline (**4**), 74.2 mg (0.75 mmol) of cyclohexylamine (**5**), 6.6 mg (0.050 mmol) of aluminum chloride (**6**), 30.6 mg (0.10 mmol) of 4-diphenylphosphinobenzoic acid (**15**), and the reaction mixture was dissolved in 300 mg of toluene. It was stirred in an oil bath that was preheated at 130 °C for 12h. After the reaction, the reaction mixture was hydrolyzed by 1N HCl, extracted with Et_2O and CH_2Cl_2 . The organic layers were combined, dried over MgSO_4 , and purified by column chromatography (SiO_2 , *n*-hexane : ethyl acetate = 5 : 2) to afford 79.6 mg (87%) of dodecan-6-one (**16a**).

Dodecan-6-one (16a).⁵ ^1H NMR (250 MHz, CDCl_3): δ 2.38 (t, $J = 7.4$ Hz 4H), 1.56 (m, 4H), 1.29-1.27 (br m, 10H), 0.91-0.86 (m, 6H). IR (neat): 3065, 2958, 2931, 2861, 1716,

⁵ Molander, G. A.; Hahn, G. J. *Org. Chem.* **1986**, *51*, 1135.

1466, 1374, 1265, 834, 740, 705 cm^{-1} . MS (EI): m/z (relative intensity) 184 (M^+ , 10), 139 (30), 121, (100), 96 (94), 87 (60), 81 (35), 67 (25), 58 (76), 55 (69), 43 (76).

Among other products, commercially available compounds such as 2-octanone (**7a**), 1-phenyl-butan-2-one (**7f**), 4'-methoxypropiophenone (**7g**), 1-phenyl-propan-2-one (**7h**), 2-phenylacetophenone (**16b**), 1-phenyl-heptan-2-one (**17a**), and heptanophenone (**17b**) were identified by comparison with authentic specimens. Other ketones such as 1-phenyl-hexan-3-one (**7c**),⁶ 1-phenyl-heptan-3-one (**7d**),⁷ and 5-decanone (**7e**)⁸ have already been reported, and were identified by ^1H NMR, ^{13}C NMR, IR, and MS spectra. A new compound, 4,6,6-trimethyl-1-phenyl-hept-4-en-3-one (**14a**) is characterized as below.

4,6,6-Trimethyl-1-phenyl-hept-4-en-3-one (14a). ^1H NMR (250 MHz, CDCl_3): δ 7.30-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.58 (s, 1H), 2.96 (m, 4H), 1.89 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (62.5MHz, CDCl_3): δ 200.6, 142.7, 141.8, 141.6, 135.8, 128.4, 125.9, 39.2, 30.8, 29.7, 24.8, 13.9. IR (neat): 3411, 1657, 1265, 909 cm^{-1} . MS (EI): m/z (relative intensity) 229 (M^+ , 2), 215 (4), 173 (100), 145 (18), 125 (20), 105 (9), 91 (24), 55 (12). HRMS (EI): m/z calcd. for $\text{C}_{16}\text{H}_{22}\text{O}$ (M^+) 230.1671, found 230.1684.

⁶ Jun, C.-H.; Lee, H.; Moon, C. W.; Hong, H.-S. *J. Am. Chem. Soc.* **2001**, *123*, 8600.

⁷ Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880.

⁸ Dell'Anna, M. M.; Mastroilli, P.; Nobile, C. F.; Marchese, G.; Taurino, M. R. *J. Mol. Catal. A* **2000**, *161*, 239.

A Ring-Opening Oligomerization of Cyclododecyne (2g). (Scheme 4) A screw-capped pressure vial (1 mL) was charged with 263.0 mg (1.600 mmol) of cyclododecyne (**2g**), 39.1 mg (0.320 mmol) of phenylacetaldehyde (**1d**), 6 mmol) of 29.6 mg (0.032 mmol) of (PPh₃)₃RhCl (**3a**), 34.6 mg (0.32 mmol) of 2-amino-3-picoline (**4**), 158.7 mg (1.600 mmol) of cyclohexylamine (**5**), 19.6 mg (0.064 mmol) of 4-diphenylphosphinobenzoic acid (**15**), and the reaction mixture was dissolved by 50 mg of toluene. It was stirred in an oil bath that was preheated at 100 °C for 72h. After the reaction, the reaction mixture was hydrolyzed by 1N HCl, and purified by column chromatography (SiO₂, *n*-hexane : diethyl ether = 10 : 1) to afford 88.6 mg of a mixture of polyketones **18** (30% based on total amount of all starting materials, **1d** and **2g**). The degree of oligomerization was determined by ¹H NMR (Figure S1) and ESI-MS (Figure 1), which showed that **18a** (*n*=0) and polyketone **18b-e** (*n*=0-4) were formed in this one-pot reaction. The ratio of **18a** : **18b-e** was determined as 21 : 79 by ¹H NMR. Among polyketones **18a-e**, 1-cyclododec-1-enyl-2-phenyl-ethanone (**18a**) and 1-cyclododec-1-enyl-14-phenyl-tetradecane-1,13-dione (**18b**) were isolated and characterized as below.

1-Cyclododec-1-enyl-2-phenyl-ethanone (18a). ¹H NMR (500 MHz, CDCl₃): 7.30-7.27

(m, 2H), 7.22-7.18 (m, 3H), 6.67 (t, $J = 7.7$ Hz, 1H), 3.96 (s, 2H), 2.34 (t, $J = 6.4$ Hz, 2H), 2.27 (q, $J = 7.3$ Hz, 2H), 1.55-1.29 (m, 20H). ^{13}C NMR (120 MHz, CDCl_3): δ 200.0, 144.3, 141.5, 135.8, 129.5, 128.7, 126.7, 45.3, 26.5, 26.4, 26.2, 25.3, 25.2, 25.1, 23.9, 23.2, 23.1, 22.4. IR (neat): 3018, 2931, 2859, 2360, 2340, 1707, 1663, 1216, 758, 668 cm^{-1} . MS (EI): m/z (relative intensity) 284(1), 193(100), 165(1), 141 (1), 109(6), 83(24), 69(10), 55(22), 41(12). HRMS (EI): m/z calcd. for $\text{C}_{20}\text{H}_{28}\text{O}$ (M^+) 284.21401, found 284.21400.

1-Cyclododec-1-enyl-14-phenyl-tetradecane-1,13-dione (18b). ^1H NMR (250 MHz, CDCl_3): δ 7.33-7.31 (m, 2H), 7.22-7.19 (m, 3H), 6.56 (t, $J = 7.9$ Hz, 1H), 3.67 (s, 2H), 2.62 (t, $J = 7.4$ Hz, 2H), 2.43 (t, $J = 7.3$ Hz, 2H), 2.35 (t, $J = 6.6$ Hz, 2H), 2.27 (q, $J = 7.3$ Hz, 2H), 1.58-1.22 (m, 38H). ^{13}C NMR (62.5MHz, CDCl_3): δ 208.9, 203.1, 142.8, 142.0, 134.7, 129.7, 128.9, 127.1, 50.4, 42.3, 38.0, 29.7, 29.7, 29.6, 29.4, 26.6, 26.5, 26.3, 25.4, 25.2, 24.0, 23.9, 23.2, 23.0, 22.4. IR (neat): 3016, 2927, 2850, 2401, 1709, 1658, 1425, 1221, 932, 775 cm^{-1} . FAB MS (EI): m/z calcd. for $\text{C}_{32}\text{H}_{51}\text{O}_2$ ($\text{M}+\text{H}^+$) 467.3889, found 467.3878.

Figure S1. ^1H NMR spectrum of polyketones **18**