Electronic Supplementary Material (ESI) for Chemical Communications

Ruthenium-catalyzed Cyclization/Transfer Hydrogenation of 1,6-Diynes: Unprecedented mode of alcohol activation via Metallacyclopentatriene

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Supporting Information

1. General Considerations

Column chromatography was performed on silica gel (Cica silica gel 60N) with solvents specified below. ^{1}H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ solution at 25 °C. ^{1}H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at 7.26 ppm for chloroform. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.0 ppm for $CDCl_3$. Mass mesurements and elemental analyses were performed by the Instrumental Analysis Facility of Nagoya University. Melting points were obtained in capillary tubes. Dry solvents were purchased and used directly as received. Cp*RuCl(cod),[1] and ruthenacyclopentatriene **1**[2] were prepared according to the reports. Diynes **5a**,[3] **5b**,[4] **5c**,[5] **5c'**,[6] **5d**,[5] **5e**,[7] **5f**,[5] and **5i**,[5] and dienes **6a**,[5] **6c'**,[5] **6d**,[5] and **6f**[5] were known compounds.

2. Preparations of Substrates

Synthesis of diyne 5g: To a solution of malononitrile (0.20 g, 3.0 mmol), triethylamine (0.84 mL, 6.0 mmol) and sodium iodide (0.99 g, 6.6 mmol) in dry DMSO (9 mL) was added dropwise a solution of 3-phenylprop-2-ynyl 4-methylbenzenesulfonate (1.7 g, 6.0 mmol) in dry DMSO (3.0 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 10 h. The solution was diluted with Et_2O (20 mL) and quenched with H_2O (40 mL). The aqueous layer was extracted with Et_2O (20 mL × 2). The combined organic layer was washed with H_2O (50 mL) and brine (50 mL), and dried over $MgSO_4$. The organic layer was concentrated in vacuo to obtain dark brown solds. After short-column chromatography on silica gel, the crude product was purified by recrystallization from hexane/Et_2O to afford **5g** (0.82 g, 47% yield) as colorless crystals (mp 83.5–85.5 °C): IR (KBr) 2238 (CN) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.35 (s, 4 H), 7.30–7.42 (m, 6 H), 7.45–7.53 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 28.6, 36.9, 79.1, 87.2, 113.8, 121.3, 128.2, 128.9, 131.8; HRMS (FAB) *m/z* calcd for $C_{21}H_{15}N_2$ 295.1230, found 295.1237 $[M+H]^+$.

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Synthesis of diyne 5j: A solution of dimethyl dipropargylmalonate (6.0 g, 29 mmol), 1-bromo-4-iodobenzene (17 g, 60 mmol), $Pd(PPh_3)_4$ (70 mg, 0.060 mmol), and CuI (0.023 g, 0.12 mmol) in diisopropylamine (104 mL) was stirred at room temperature under an argon atmosphere for 5 h. The resultant mixture was diluted with AcOEt (100 mL), and quenched with H_2O (100 mL). The aqueous layer was extracted with AcOEt (100 mL). The combined organic layer was washed with H_2O (100 mL × 2) and with brine (100 mL), and dried over $MgSO_4$. The solvents were evaporated under reduced pressure to give a brown solid. After filteration through a pad of silica gel (solvent: hexne/AcOEt = 5:1), a crude product was purified by recrystallized form hot hexane/AcOEt to give **5j** (14 g, 92 %) as colorless crystals (mp 75.5–77.5 ˚C); IR (KBr): 1740 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 ˚C): δ 3.23 (s, 4 H), 3.80 (s, 6 H), 7.23 (ddd, *J* = 8.7, 2.4, 2.1 Hz, 4 H), 7.41 (ddd, *J* = 8.7, 2.4, 2.1 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C): δ 24.0, 53.3, 57.1, 82.8, 85.0, 121.7, 122.2, 131.3, 132.9, 168.9; HRMS (FAB) *m/z* calcd for $C_{25}H_{18}Br_2NaO_4$ 539.9464, found 538.9471 $[M+Na]^+$.

Synthesis of diyne 5h: **5h** was prepared from dimethyl dipropargylmalonate and *p*-iodoanisole according a similar procedure for **5j**; colorless crystals (mp 80.0–82.0 ˚C); IR (KBr): 1741 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 ˚C): δ 3.25 (s, 4 H), 3.80 (s, 12 H), 6.80 (ddd, *J* = 9.0, 2.7, 2.7 Hz, 4 H), 7.31 (ddd, *J* = 9.0, 2.7, 2.7 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C): δ 24.0, 53.1, 55.3, 57.4, 82.3, 83.5, 113.6, 115.0, 132.8, 159.0, 169.1; HRMS (FAB) *m/z* calcd for $C_{25}H_{24}NaO_6$ 443.1465, found 443.1470 $[M+Na]^+$.

Synthesis of Tetrayne 9: A solution of dimethyl 2-(3-phenylprop-2-ynyl)-2-(prop-2-ynyl)malonate (0.59 g, 2.1 mmol), 1,4-diiodobenzene (0.34 g, 1.0 mmol), $Pd(PPh_3)_4$ (1.2 mg, 0.0010 mmol), and CuI (0.66 mg, 0.0035 mmol) in degassed diisopropylamine (4.0 mL) was stirred at room temperature under an argon atmosphere for 12 h. The resultant reaction mixure was diluted with AcOEt (20 mL) and quenched with H_2O (20 mL). The aqueous layer was extracted with AcOEt (20 mL). The combined organic layer was washed with H_2O (50 mL) and then with brine (50 mL) and dried over $MgSO_4$. The solvents were removed under reduce pressure to give brown oil. The crude product was purified with column chromatography on silica gel (elution with hexane/AcOEt = 10:1–2:1) to give **8** (0.58 g, 87 % yield) as off-white solids (mp 121.5–122.5 ˚C); IR (KBr): 1741 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 ˚C): δ 3.25 (s, 4 H), 3.27 (s, 4 H), 3.81 (s, 12 H), 7.26–7.32 (m, 10 H), 7.34–7.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C): δ 24.0, 24.1, 53.2, 57.2, 83.4, 83.7, 83. 8, 85.6, 122.5, 122.8, 127.9, 128.0, 131.3, 131.4, 169.0; HRMS (FAB) *m/z* calcd for $C_{40}H_{34}O_8Na$ 665.2146, found 655.2153 $[M+Na]^+$.

3. Reactions of Ruthenacyclopentatriene 1 with MeOH.

Reaction in the absence of additives: To a stirred solution of **1** (26.0 mg, 0.050 mmol) in degassed dry THF (1.5 mL) was added degassed dry MeOH (0.1 mL, 2.5 mmol) under an argon atmosphere. The mixture was stirred at 25 ˚C for 4 h. The solvent and excess MeOH was removed under reduced pressure. The crude yield of **3** (0.025 mmol, 50%) was determined by ^{1}H NMR analysis with ethylbenzene (10.0 μL, 0.082 mmol) as internal standard. The crude material was purified with silica gel column chromatography (elution with hexane/AcOEt 10:1 ~ 5:1) to give **3** (7.90 mg, 0.015 mmol, 30%) as red micro crystals (mp. 174 ˚C decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 15 H), 3.97 (s, 2 H), 4.84 (d, *J* = 11.5 Hz, 2 H), 5.44 (d, *J* = 11.5 Hz, 2 H), 7.15–7.40 (m, 6 H), 7.52 (d, *J* = 7.2 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.3, 64.6, 71.9, 94.3, 102.6, 125.7, 126.8, 128.0, 139.5; HRMS (FAB) *m/z* calcd for $C_{28}H_{31}ClORu$ 520.1107, found 520.1107 $[M]^+$.

Reaction in the presence of a silver salt: To a stirred solution of **1** (26 mg, 0.050 mmol) and dry MeOH (0.10 mL, 2.5 mmol) in dry THF (0.5 mL) was added a solution of $AgPF_6$ (14 mg, 0.055 mmol) in dry THF (1.0 mL) under an argon atmosphere. The crude yield of **4** (0.022 mmol, 43%) was determined by ^{1}H NMR analysis with ethylbenzene (10.0 μL, 0.082 mmol) as internal standard. Purification of **4** by means of chromatography on silica gel or alumina led to extensive decomposition, and ultimately to only low-yield isolation as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (s, 3 H), 4.45 (s, 2 H), 4.81 (d, *J* = 2.4 Hz, 2 H), 7.19–7.26 (m, 2 H), 7.31–7.46 (m, 8 H), 7.57 (t, *J* = 2.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.3, 70.9, 72.5, 119.7, 123.4, 126.4, 128.0, 128.22, 128.26, 128.32, 128.5, 134.9, 137.4, 138.1, 149.6; HRMS (FAB) *m/z* calcd for $C_{19}H_{19}O_2$ 279.1385, found 279.1387 $[M+H]^+$.

Crystallographic Structural Determinations of 3: A single crystal suitable for X-ray analysis was mounted on a glass fiber, and diffraction data were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The absorption correction was made using SADABS. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 by using SHELXTL.[8] Platon SQUUEEZE was used to remove the distribution from the ill-defined solvent, which could not be modeled successfully.[9] All non-hydrogen atoms were refined with anisotropic displacement

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parameters. All hydrogen atoms were placed in calculated positions.

Table S1. Selected crystallographic data and collection parameters for **3**.

	3
Formula	$C_{28}H_{31}ClORu$
Fw	520.05
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (#19)
a [Å]	7.2976(5)
b [Å]	14.8834(11)
c [Å]	23.5529(17)
V [Å^3]	2558.2(3)
Z	4
D_{calc} [g cm^{-3}]	1.350
μ [mm^{-1}]	0.734
F(000)	1072
Crystal size [mm^3]	0.8 × 0.5 × 0.15
Reflections collected	6358
Independent reflections	6358 (R_{int} = 0.0000)
GOF on F^2	1.128
R_1 [I>2σ(I)][a]	0.0567
wR_2 (all data)[b]	0.1339
Absolute structure parameter	0.16(6)
Largest diff. peak / hole [e Å^{-3}]	0.899 / –1.439

[a] $R_1 = \Sigma|(F_o-F_c)|/\Sigma(F_o)$. [b] $wR_2 = \{\Sigma[(w(F_o^2-F_c^2)^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

4. Cp*RuCl-Catalyzed Cyclization/Transfer Hydrogenation

General procedures – Cyclization of 5a: To a solution of Cp*RuCl(cod) (23 mg, 0.060 mmol) and MeOH (0.16 mL, 4.0 mmol) in dry degassed THF (1.2 mL) was added a solution of **5a** (0.15 g, 0.60 mmol) in THF (1.2 mL) under an argon atmosphere. The reaction mixture was stirred at 70 °C for 4 h. The reaction was traced by TLC analysis. After concentration in vacuo, the crude

product was purified by column chromatography on silica gel (hexane/AcOEt = 15:1 – 8:1) to give **6a** (0.11 g, 72% yield) as colorless crystals (mp 157.5–158.5 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 4.86 (d, *J* = 2.4 Hz, 4 H), 6.98 (t, *J* = 2.4Hz, 2 H), 7.23–7.29 (m, 6 H), 7.36–7.42 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 71.1, 118.5, 127.0, 128.4, 128.5, 136.7, 138.8; HRMS (FAB) *m/z* calcd for $C_{18}H_{16}O$ 248.1201, found 248.1199 $[M]^+$.

Analytical data for 6b; colorless crystals (mp 199.5–201.0 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.43 (s, 3 H), 4.35 (d, *J* = 2.4 Hz, 4 H), 6.90 (t, *J* = 2.4 Hz, 2 H), 7.23–7.44 (m, 12 H), 7.72–7.76 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 21.8, 51.3, 120.7, 127.4, 127.5, 128.5, 128.6, 129.7, 132.8, 135.5, 136.1, 143.6; HRMS (FAB) *m/z* calcd for $C_{25}H_{23}NO_2S$ 401.1449, found 401.1448 $[M]^+$.

Analytical data for 6c; colorless crystals (mp 88.0–88.5 °C); IR (KBr): 1723 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.20 (t, *J* = 7.2 Hz, 6 H), 3.39 (d, *J* = 2.1 Hz, 4 H), 4.17 (q, *J* = 7.2 Hz, 4 H), 6.99 (t, *J* = 2.1 Hz, 2 H), 7.20–7.30 (m, 2 H), 7.30–7.46 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.2, 39.0, 59.0, 61.8, 120.4, 126.6, 128.2, 128.7, 137.2, 139.5, 170.9; HRMS (FAB) *m/z* calcd for $C_{25}H_{26}NaO_4$ 413.1723, found 413.1717 $[M+Na]^+$.

Analytical data for 6c'; colorless crystals (mp 146.5–148.0 °C); IR (KBr): 1723 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.41 (d, *J* = 2.1 Hz, 4 H), 3.72 (s, 6 H), 7.00 (t, *J* = 2.1 Hz, 2 H), 7.22–7.28 (m, 2 H), 7.33–7.44 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 39.1, 53.1, 58.9, 120.4, 126.7, 128.2, 128.8, 137.2, 139.2, 171.3; HRMS (FAB) *m/z* calcd for $C_{23}H_{22}NaO_4$ 385.1410, found 385.1414 $[M+Na]^+$.

Analytical data for 6d; colorless crystals (mp 235.5–238.0 (dec.) °C); IR (KBr): 1740 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.77 (s, 6 H), 3.48 (d, *J* = 2.1 Hz, 4 H), 7.12 (t, *J* = 2.1 Hz, 2 H), 7.23–7.28 (m, 2 H), 7.33–7.40 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 29.2, 43.2, 52.4, 105.0, 120.8, 126.9, 128.3, 128.7, 136.9, 138.5, 169.7; HRMS (FAB) *m/z* calcd for $C_{24}H_{22}NaO_4$ 397.1410, found 397.1410 $[M+Na]^+$.

Analytical data for 6e; colorless crystals (mp 132.0–133.5 °C); IR (KBr): 1702 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.13 (s, 6 H), 3.30 (d, *J* = 2.1 Hz, 4 H), 6.99 (t, *J* = 2.1 Hz, 2 H), 7.22–7.32 (m, 2 H), 7.34–7.46 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 27.0, 36.5, 73.1, 120.8, 126.9, 128.3, 128.8, 137.0, 139.3, 204.5; HRMS (FAB) *m/z* calcd for $C_{23}H_{22}O_2$ 330.1620, found 330.1616 $[M]^+$.

Analytical data for 6f; colorless crystals (mp 211.5–212.0 °C); IR (KBr): 1695 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.98 (quint, *J* = 6.6 Hz, 2 H), 2.71 (t, *J* = 6.6 Hz, 4 H), 3.25 (d, *J* = 2.4 Hz, 4 H), 6.98 (t, *J* = 2.4 Hz, 2 H), 7.20–7.30 (m, 2 H), 7.32–7.46 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 18.0, 37.6, 37.9, 71.2, 120.4, 126.7, 128.2, 128.8, 137.3, 139.6, 206.7; HRMS (FAB) *m/z* calcd for $C_{24}H_{22}O_2$ 342.1620, found 342.1617 $[M]^+$.

Analytical data for 6g; colorless crystals (mp 168.0–169.0 °C); IR (KBr): 2251 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.54 (d, *J* = 2.4 Hz, 4 H), 7.18 (t, *J* = 2.4 Hz, 2 H), 7.28–7.35 (m, 6 H), 7.38–7.46 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 33.2, 42.7, 115.5, 123.6, 127.8, 128.6, 128.7, 133.6, 135.8; HRMS (FAB) *m/z* calcd for $C_{21}H_{16}N_2$ 296.1313, found 296.1308 $[M]^+$.

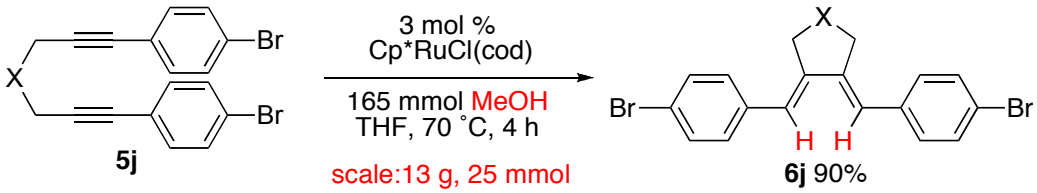
Analytical data for 6h; colorless crystals (mp 155.5–159.0 °C); IR (KBr): 1744 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.37 (d, *J* = 2.4 Hz, 4 H), 3.72 (s, 6 H), 3.84 (s, 6 H), 6.86–6.94 (m, 6 H), 7.34 (d, *J* = 8.7 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 39.1, 53.0, 55.3, 59.0, 113.7, 119.2, 130.0, 130.1, 137.3, 158.1, 171.5; HRMS (FAB) *m/z* calcd for $C_{25}H_{26}O_6$ 422.1729, found 422.1733 $[M]^+$.

Analytical data for 6i; colorless crystals (mp 161.0–163.5 °C); IR (KBr): 1735 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.35 (d, *J* = 2.1 Hz, 4 H), 3.72 (s, 6 H), 6.93 (t, *J* = 2.1 Hz, 2 H), 7.05–7.12 (m, 4 H), 7.30–7.39 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 39.0, 53.1, 58.9, 115.3 (d, *J* = 21.0 Hz), 119.3, 130.3 (d, *J* = 7.4 Hz), 133.2 (d, *J* = 3.4 Hz), 138.7, 161.3 (d, *J* = 245.3 Hz), 171.2; HRMS (FAB) *m/z* calcd for $C_{23}H_{20}F_2O_4$ 398.1330, found 398.1332 $[M]^+$.

Analytical data for 6j; off-white crystals (mp 207.5–209.5 °C); IR (KBr): 1718 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.34 (d, *J* = 1.8 Hz, 4 H), 3.72 (s, 6 H), 6.91 (t, *J* = 1.8 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 4 H), 7.49 (d, *J* = 8.4 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 39.1, 53.2, 58.8, 119.7, 120.7, 130.2, 131.4, 135.9, 139.8, 171.1; HRMS (FAB) *m/z* calcd for $C_{23}H_{20}Br_2NaO_4$ 540.9621, found 540.9616 $[M+Na]^+$.

Large-scale procedures – Cyclization of 5j: To a solution of **5j** (13.0 g, 25.0 mmol) and Cp*RuCl(cod) (0.285 g, 0.750 mmol) in dry degassed THF (100 mL) was added MeOH (6.70 mL , 165 mmol) under an argon atmosphere. The reaction mixture was stirred at 70 °C for 4 h. The reaction mixture was cooled to room temperature, filtered through a celite pad. After concentration in vacuo, the crude product was purified by recrystallization from hot AcOEt to afford **6j** (11.6 g,

90%) as pale-yellow micro crystals.



Scheme S1. Large scale synthesis of **6j** from **5j**.

Cyclization of tetrayne 9: A solution of tetrayne **9** (0.19 g, 0.30 mmol), Cp*RuCl(cod) (5.7 mg, 0.015 mmol), and MeOH (0.16 mL, 4.0 mmol) in dry degassed THF (1.8 mL) was stirred at 70 ℃ for 5 h under an argon atmosphere. After concentration in vacuo, the crude product was purified by column chromatography on silica gel ($CHCl_3$) to give **10** (0.19 g, quantitative yield) as yellow crystals (mp 243.5–247.0 °C); IR (KBr): 1734 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.42 (d, J = 2.1 Hz, 4 H), 3.44 (d, J = 2.1 Hz, 4 H), 3.74 (s, 12 H), 7.00 (t, J = 2.1 Hz, 2 H), 7.02 (t, J = 2.1 Hz, 2 H), 7.21–7.29 (m, 2 H), 7.34–7.46 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 39.1, 39.4, 53.1, 59.0, 120.1, 120.5, 126.7, 128.2, 128.8, 128.9, 135.8, 137.1, 139.3, 139.4, 171.3; HRMS (FAB) m/z calcd for $C_{40}H_{38}O_8$ 646.2567, found 646.2571 $[M]^+$.

Cyclization of 5c with CD_3OH: A solution of **5c** (0.12 g, 0.30 mmol), Cp*RuCl(cod) (11 mg, 0.030 mmol), and CD_3OH (0.080 mL, 2.0 mmol) in THF (1.2 mL) was stirred at 70 °C under an argon atmosphere for 4 h. After the concentration in vacuo, the crude product was purified by column chromatography on silica gel (elution: toluene) to give **6c**-d_1 (0.11 g, 90 % yield). In its ^1H NMR specrum, the peak areas are as follows: δ 1.21 (t, H_a, area = 6.15), 3.39 (s, H_c and H_d, area = 4.01), 4.17 (q, H_b, area = 4.00), and 6.99 (t, H_e, area = 1.00) indicating that the ratio of newly incorporated H and D in the diene moiety is H : D = 1.01 : 1.00. The product was analyzed by FAB-MS spectroscopy with the aid of NaI in NBA matrix. The peak intensity calculated for [**6c**-d_1+Na^+] was m/z: 414 (100%), 415 (27%), 416 (4%), while the observation was m/z: 414 (100%), 415 (30%), 416 (6%). This consistency shows that the product was a single isotopologue rather than a mixture with statistical H/D distribution (Fig. S1).

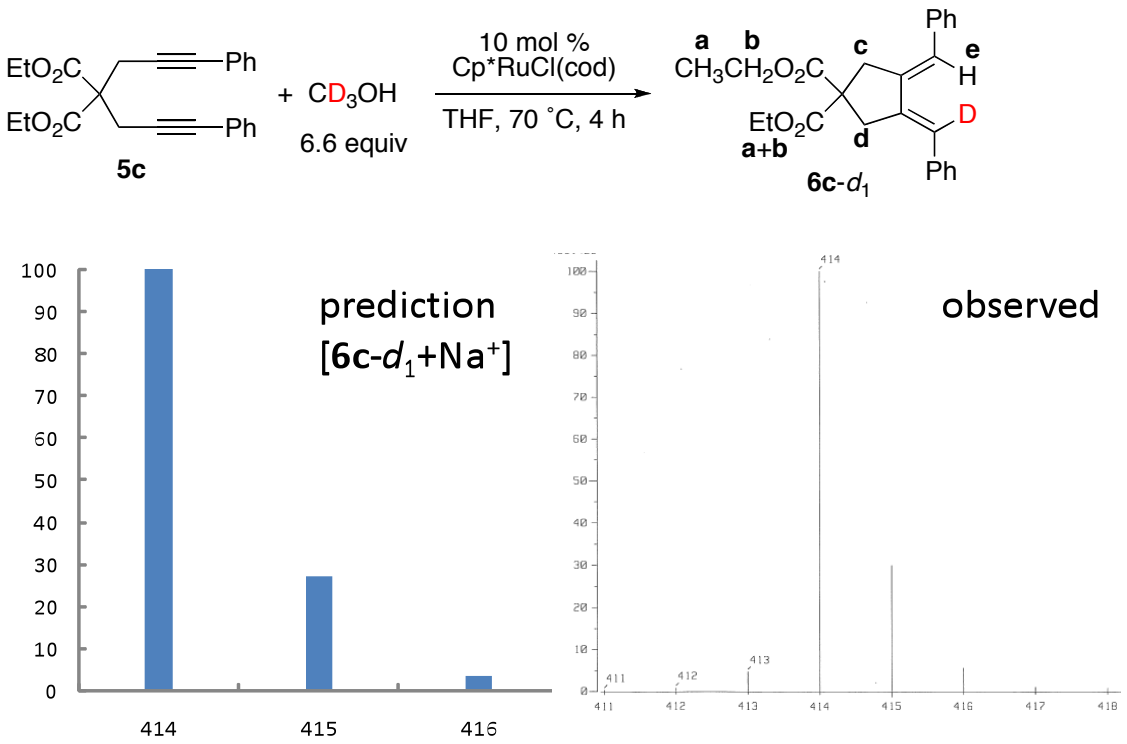


Figure S1. Cyclization of **5c** with CD_3OH and FAB-MS spectrum of **6c**-d_1.

Cyclization of 5c' with benzyl alcohol: A solution of **5c'** (0.11 g, 0.30 mmol), Cp*RuCl(cod) (11 mg, 0.030 mmol) and benzyl alcohol (0.16 mL, 1.5 mmol) in dry degassed THF (1.2 mL) was stirred at 70 ˚C under Ar atmosphere for 2 h. The reaction was traced by TLC analysis. THF was carefully removed under reduced pressure to concentrate the solution to approximately quarter of the original volume. To thus obtained crude mixture was added ethyl benzene (50.0 μL, 0.410 mmol) as a internal standard. The molar ratio of the compounds in the crude mixture was determined with ^{1}H NMR by comparing the peak area of following signals; **6c'**: δ 3.41 (d, 4 H), 7.01 (d, 2 H), benzaldehyde: δ 10.01 (s, 1 H), unreacted benzyl alcohol: δ 4.69 (s, 2 H), ethylbenzene: δ 2.66 (q, 2 H). The ratio was [**6c'**] : [benzaldehyde] : [benzyl alcohol] : [ethylbenzene] = 1.0 : 0.98 : 4.0 : 1.4. This corresponds to 0.30 mmol (99% yield) of **6c'**, 0.29 mmol (96% yield) of benzaldehyde, and 1.2 mmol of benzyl alcohol.

5. Synthesis of 8 from 6j.

Sonogashira coupling of 6j: A mixture of **6j** (0.42 g, 0.81 mmol), ethynylbenzene (0.27 mL, 2.45 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.0050 mmol), SPhos (4.1 mg, 0.010 mmol), finely ground K_2CO_3 (0.28 g, 2.0 mmol), and benzyltriethylammonium chloride (13.9 mg, 0.050 mmol)

was stirred in acetonitrile (4.0 mL) at 50 ˚C under an argon atmosphere for 24 h. After cooled to room temperature, the mixture was filtered through a pad of celite, and the solvent was removed under reduced pressure to give a yellow brown solid. The crude product was purified by column chromatography on silica gel (toluene/$CHCl_3$ = 1:1) to give **7** (0.44g, 96% yield) as light-yellow solids (mp 245.5–249.0 ˚C); IR (KBr): 1735 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 ˚C): δ 3.42 (d, *J* = 2.1 Hz, 4 H), 3.74 (s, 6 H), 7.00 (t, *J* = 2.1 Hz, 2 H), 7.32–7.44 (m, 10 H), 7.51–7.62 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C): δ 39.2, 53.2, 59.0, 89.5, 90.3, 120.4, 121.5, 123.0, 128.1, 128.2, 128.7, 131.4, 131.5, 136.9, 140.1, 171.2; HRMS (FAB) *m/z* calcd for $C_{39}H_{30}NaO_4$ 585.2036, found 585.2043 $[M+Na]^+$.

Semihydrogenation of 7: 1,3-(2,4,6-trimethylphenyl)-imidazolium chloride (10 mg, 0.030 mmol) and KO*t*Bu (7.2 mg, 0.064 mmol) were stirred in acetonitrile (3.0 mL) for 1 h at 25 ˚C under an argon atmosphere. To this solution was added a solution of Pd(1,4-(*tert*-butyl)1,4-diazabutadiene)(maleic anhydride) (11 mg, 0.030 mmol) in acetonitrile (and 3.0 mL), and the mixture was stirred for 1 h at 25 ˚C to give a catalyst stock solution. HCOOH•Et_3N stock solution was prepared by dissolving HCOOH (0.82 mL, 20 mmol) and Et_3N (2.8 mL, 20 mmol) in acetonitrile (10 mL). To the catalyst stock solution (2.0 mL, 0.0099 mmol) was added **7** (0.11 g, 0.20 mmol) and the HCOOH-Et_3N stock solution (1.4 mL, 2.1 mmol). The reaction mixture was stirred at 90 ˚C for 3 h. During that time, unsolved substrate **7** disappeared to give light yellow solution. After cooled to room temperature, the reaction mixture was diluted with $CHCl_3$ (20 mL), and washed with H_2O (50 mL). The aqueous layer was extracted with $CHCl_3$ (20 mL). The combined organic layer was washed with distilled water (50 mL × 2) and with brine (20 mL), and dried over $MgSO_4$. After concentration in vacuo, the crude product was purified by column chromatography on silica gel (elution with toluene) to afford **8** (0.11 g, 93% yield) as light yellow solids (mp 155.5–158.5 ˚C); IR (KBr): 1737 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 ˚C): δ 3.38 (d, *J* = 2.1 Hz, 4 H), 3.72 (s, 6 H), 6.57 (d, *J* = 12 Hz, 2 H), 6.63 (d, *J* = 12 Hz, 2 H), 6.92 (t, *J* = 2.1 Hz, 2 H), 7.20–7.34 (m, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C): δ 39.2, 53.1, 59.0, 120.2, 127.0, 128.1, 128.6, 128.8, 129.6, 130.2, 135.5, 136.0, 137.1, 139.3, 171.3; HRMS (FAB) *m/z* calcd for $C_{39}H_{34}NaO_4$ 589.2349, found 589.2336 $[M+Na]^+$.

6. Mechanistic Studies.

Dependence of reaction rates on [Diyne] and [MeOH]: In a Schlenk tube equipped with septum and stirring bar, diyne **5c'** (0.22 g, 0.60 mmol), methanol (0.20 mL, 4.9 mmol) and di-*n*-octyl ether as an internal standard (0.10 mL, 0.33 mmol) were dissolved in THF (1.5 mL), and the solution was heated to 50 ˚C. To this solution was added of a stock solution of Cp*RuCl(cod) in

THF (0.30 M, 1.0 mL, 0.3 mmol). Aliquots were taken out periodically, concentrated in vacuo, and analyzed as a $CDCl_3$ solution by ^1H NMR spectroscopy. The ratios of the compounds were determined by monitoring the peak areas at δ 0.89 (t, J = 6.9 Hz, 6 H, di-*n*-octyl ether), 3.72 (s, 6 H, **6c'**), and 3.81(s, 6 H, **5c'**). Since the quantitation of **5c'** is the most accurate among those of the compounds, the precise concentration of the internal standard was determined relative to that of **5c'** in the initial sampling.

The concentrations of **5c'** and **6c'** ([**5c'**] and [**6c'**], respectively) are plotted against the reaction time (t/h). The material balance was good and both plots showed good linearity within 3 h. The reaction rates were determined by referring to the linear part of the [**6c'**] vs. t plot (Fig. S2)

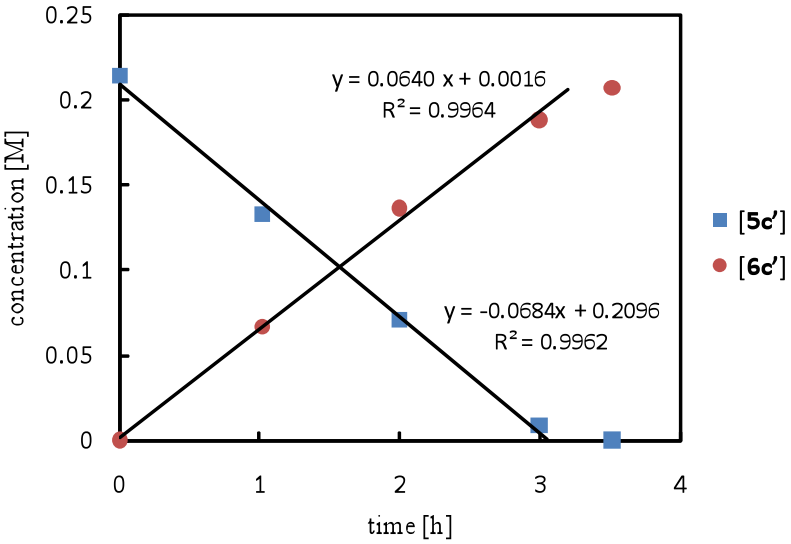


Figure S2. Representative time course of the cyclization/transfer hydrogenation of **5c'** ($[\mathbf{5c'}]_0$ = 0.21 M, $[MeOH]_0$ = 1.8 M).

The dependence of the reaction rate on the diyne concentration [**5c'**] was examined at $[\mathbf{5c'}]_0$ = 0.054, 0.11, 0.16, and 0.21 M. The plots of [**6c'**] vs. t for various $[\mathbf{5c'}]_0$ except for [**5c'**] = 0.054 M resulted in a same line, and the plots of [**5c'**] vs. t share virtually identical slope (Fig. S3). In a similar manner, the effect of MeOH was studied by performing the reactions at five methanol concentrations, $[MeOH]_0$ = 0.71, 0.89, 1.8, 3.6, and 5.4 M (Fig. S4). The obtained results are summarized in Table S2.

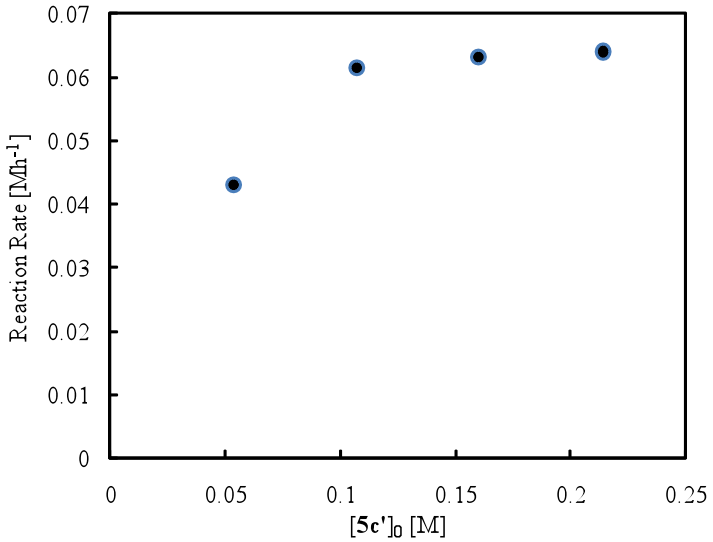


Figure S3. Dependence of the reaction rate on [**5c'**].

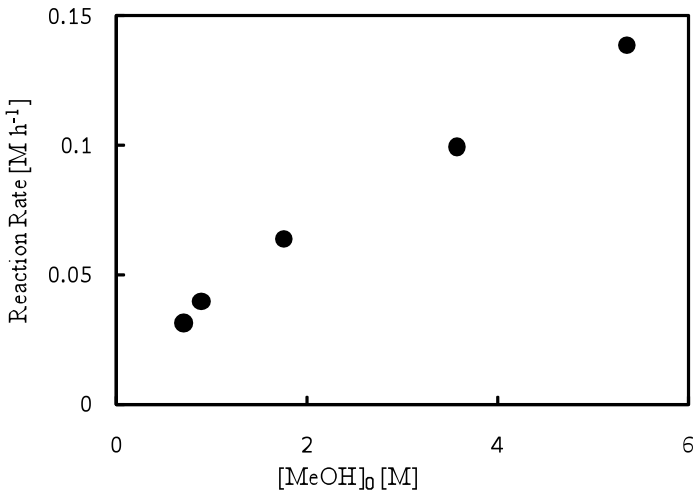


Figure S4. Dependance of the reaction rate on [MeOH].

Table S2. Summary of kinetic studies.

No.	[**5c'**]$_0$/M	[MeOH]$_0$/M	Numbers of points	Decision coeffocoent R^2		–d[**5c'**]/dt /Mh^{-1}	d[**6c'**]/dt /Mh^{-1}
				[**5c'**] vs. *t*	[**6c'**] vs. *t*		
1	0.0536	1.76	3	0.968	0.976	0.0449	0.0431
2	0.107	1.76	4	0.991	0.997	0.0589	0.0614
3	0.16	1.76	5	0.999	0.998	0.0639	0.0631
4	0.214	1.76	4	0.996	0.996	0.0684	0.0640
5	0.214	0.705	6	0.986	0.993	0.0341	0.0314
6	0.214	0.89	7	0.991	0.999	0.0407	0.0399
7	0.214	3.57	5	0.984	0.998	0.1050	0.0996
8	0.214	5.36	4	0.998	0.998	0.1450	0.1390

Kinetic isotope effects: By employing 1.8 M of CH_3OH, CD_3OH or CH_3OD as a hydrogen surrogates, the rates of the cyclization/transfer hydrogenation of diyne **5c'** ([**5c'**]$_0$ = 0.21 M) was measured in a similar manner as described above. To cancel the experimental error, the measurements were repeated 3 times for each alcohol. The concentrations of **6c'** or **6c'**-d_1 in each experiment are shown in Figs S5–S7. The obtained results are summarized in Table S3.

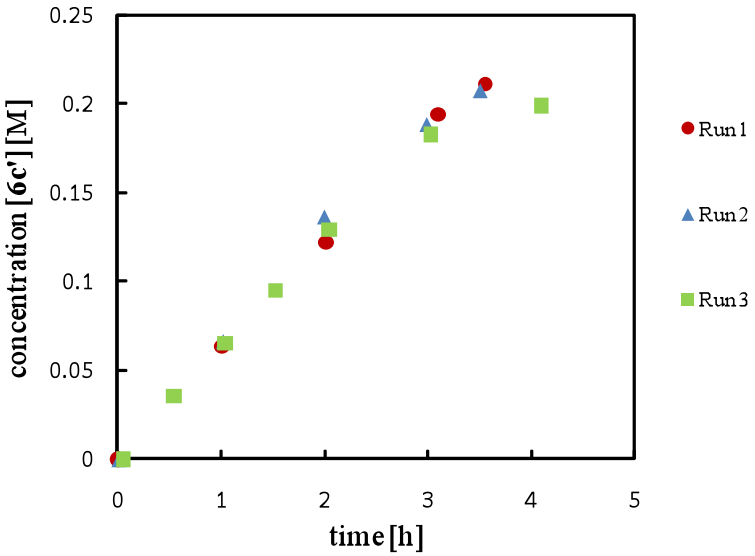


Figure S5. Time course of the cyclization/transfer hydrogenation of **5c'** with CH_3OH.

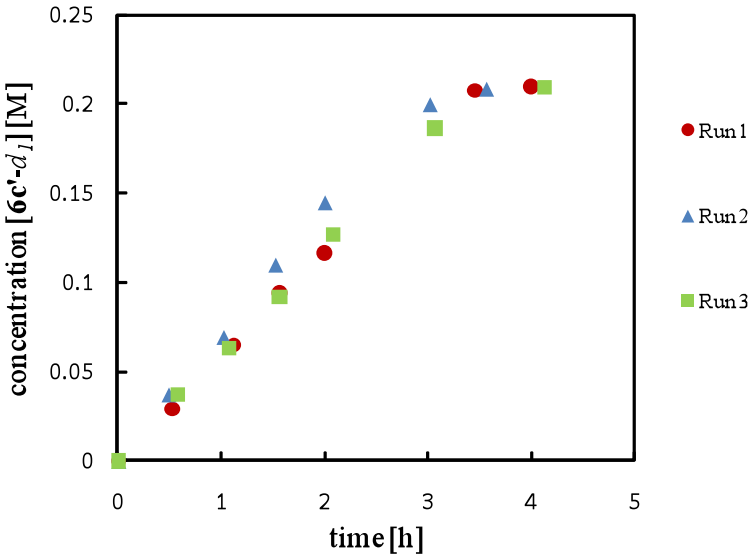


Figure S6. Time course of the cyclization/transfer hydrogenation of **5c'** with CD_3OH.

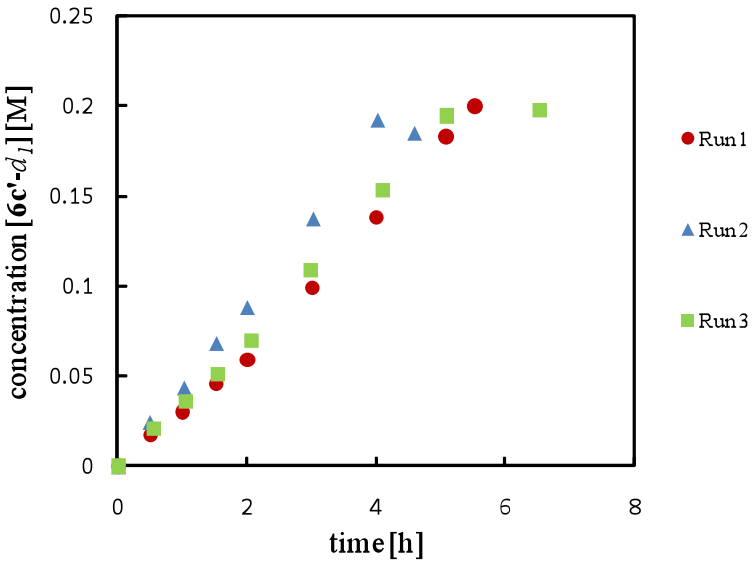
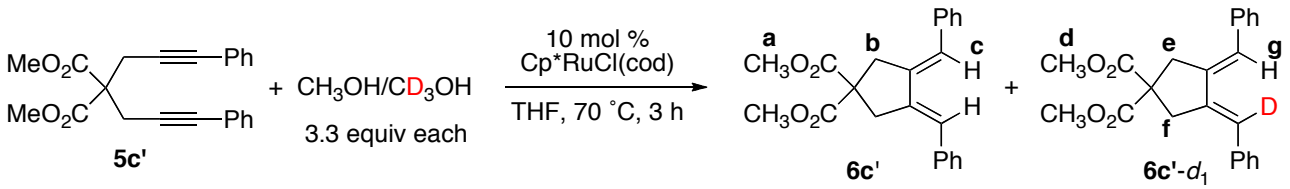


Figure S7. Time course of the cyclization/transfer hydrogenation of **5c'** with CH_3OD.

Table S3. Summary of initial rates (Mh^{-1}) of reactions using CH_3OH, CD_3OH, and CH_3OD.

Run	CH_3OH	CD_3OH	CH_3OD
1	0.0603	0.0603	0.0365
2	0.0640	0.0670	0.0432
3	0.0613	0.0606	0.0383
average	0.062 ± 0.002	0.063 ± 0.002	0.039 ± 0.005

A competition experiment using a 1:1 mixture of CH_3OH and CD_3OH was carried out as follows (Scheme S2). A solution of **5c'** (0.108 g, 0.300 mmol), Cp*RuCl(cod) (11 mg, 0.030 mmol), and a 1:1 mixture of CH_3OH/CD_3OH (0.080 mL, 0.99 mmol each) in THF. (1.2 mL) was stirred at 70 ˚C under an argon atmosphere for 3 h. After concentration in vacuo, the crude mixture was purified by column chromatography on silica gel (elution by toluene) to yield the cyclized product (0.101 g, 93 % yield). The ratio of the isotopomers was determined by comparing the peak areas in ^1H NMR analysis. The peak areas were as follows; δ 3.38–3.43 (overlapped singlet and doublet, H_b, H_e and H_f, area = 4.00), 3.72 (two overlapped singlets, H_a and H_d, area = 5.98), 7.00 (two overlapped triplets, H_c and H_g, area = 1.65). From these data, isotopomer ratio is determined as **6c'** : **6c'**-d_1 = 0.65 : 0.35, and, hence, KIE = 1.9.



Scheme S2. Competition experiment using a mixture of CH_3OH and CD_3OH.

8. Theoretical Calculations.

The Gaussian 03 program package was used for all geometry optimizations.[10] The geometries

[10] Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.;

of stationary points and transition states were fully optimized by means of the Becke's three-parameter hybrid density functional method (B3LYP)[11] with the basis set, consisting of a double-ζ basis set with the relativistic effective core potential of Hay and Wadt (LanL2DZ)[12] for Ru and the 6-31G(d)[13] basis sets for other elements (BS-I). The vibrational frequencies, zero-point energy (ZPE) and thermal correction to Gibbs free energy (TCGFE) were calculated at the same level of theory. The obtained structures were characterized by the number of imaginary frequencies (one or zero for transition or ground states, respectively). The connectivity of each step was further confirmed by IRC calculation[14] from the transition states followed by optimization of the resulted geometries. The obtained geometry of η^4-diene complex **s7** was in good agreement with those of an X-ray structure of **3** (Table S4).

Single-point energies for geometries obtained by the above method were calculated at the same level using the basis sets consisting of a [6*s*5*p*3*d*2*f*1*g*] contracted valence basis set with the Stuttgart-Dresden-Bonn energy-consistent pseudopotential (SDD)[15, 16] for Ru and the 6-311++G(2d,p) basis sets[17] for other elements. Relative energies were corrected with unscaled ZPE obtained at the B3LYP/BS-I level. The obtained results are summarized in Table S5.

Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.

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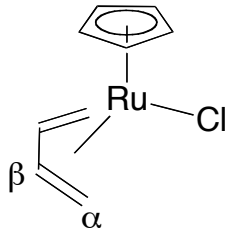
Table S4. Comparison of selected bond distances of **3** and **s7**.



	3 (X-ray)	**s7**
Ru–Cl [Å]	2.4544(14)	2.48
Ru–Cα [Å]	2.240(5), 2.249(6)	2.25, 2.26
Ru–Cβ [Å]	2.216(6)	2.21
Cα–Cβ [Å]	1.422(8), 1.403(8)	1.41
Cβ–Cβ [Å]	1.424(9)	1.44
Cα–Cβ–Cβ [°]	122.9(5), 123.3(5)	121.7, 121.9

Table S5. Summary of theoretical calculations.

Model	Energy/au	ZPE/au	TCGFE/au	IF/cm^{-1}
s1	–558.49947218	0.190611	0.151864	
TS-II	–558.45898596	0.185968	0.148335	1112.2089i
s2	–558.48422448	0.187941	0.146837	
s3	–1019.33675981	0.198689	0.152940	
TS-III	–1019.31293919	0.200114	0.158994	102.1790i
s4	–1019.34270237	0.203641	0.162531	
TS-IV	–1019.31109623	0.200116	0.159954	1032.2411i
s5	–1019.35214680	0.203265	0.161244	
s6	–904.80630105	0.171998	0.133942	
TS-V	–904.79961402	0.170452	0.132214	338.3980i
s7	–904.86077935	0.174389	0.136356	
HCHO	–114.54178832	0.026841	0.005177	

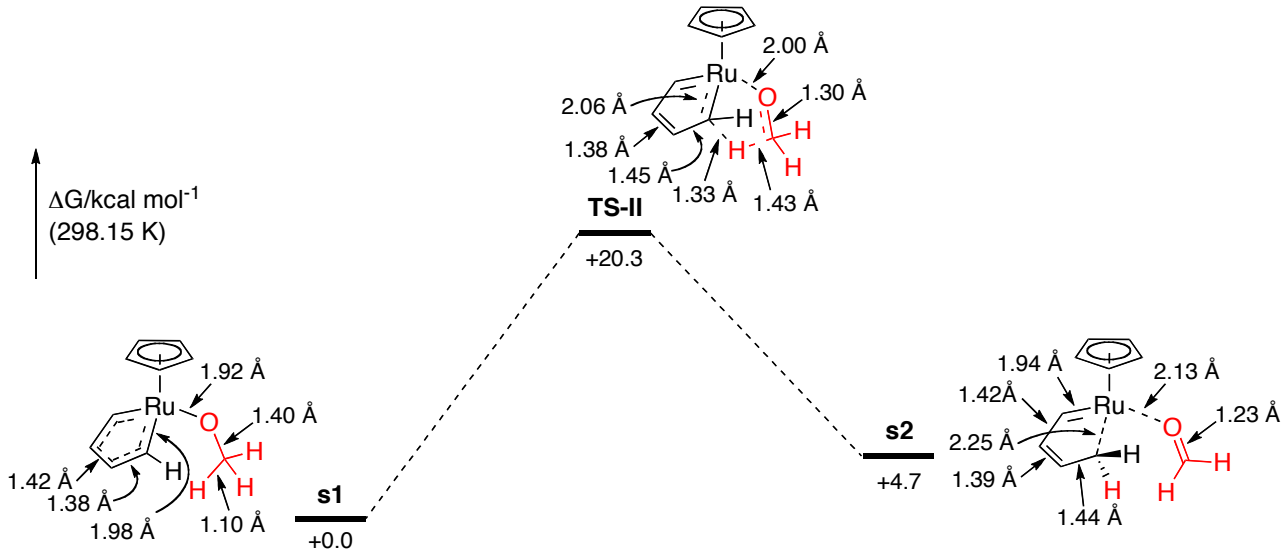


Figure S8. Reaction profile for hydride transfer via TS-II.

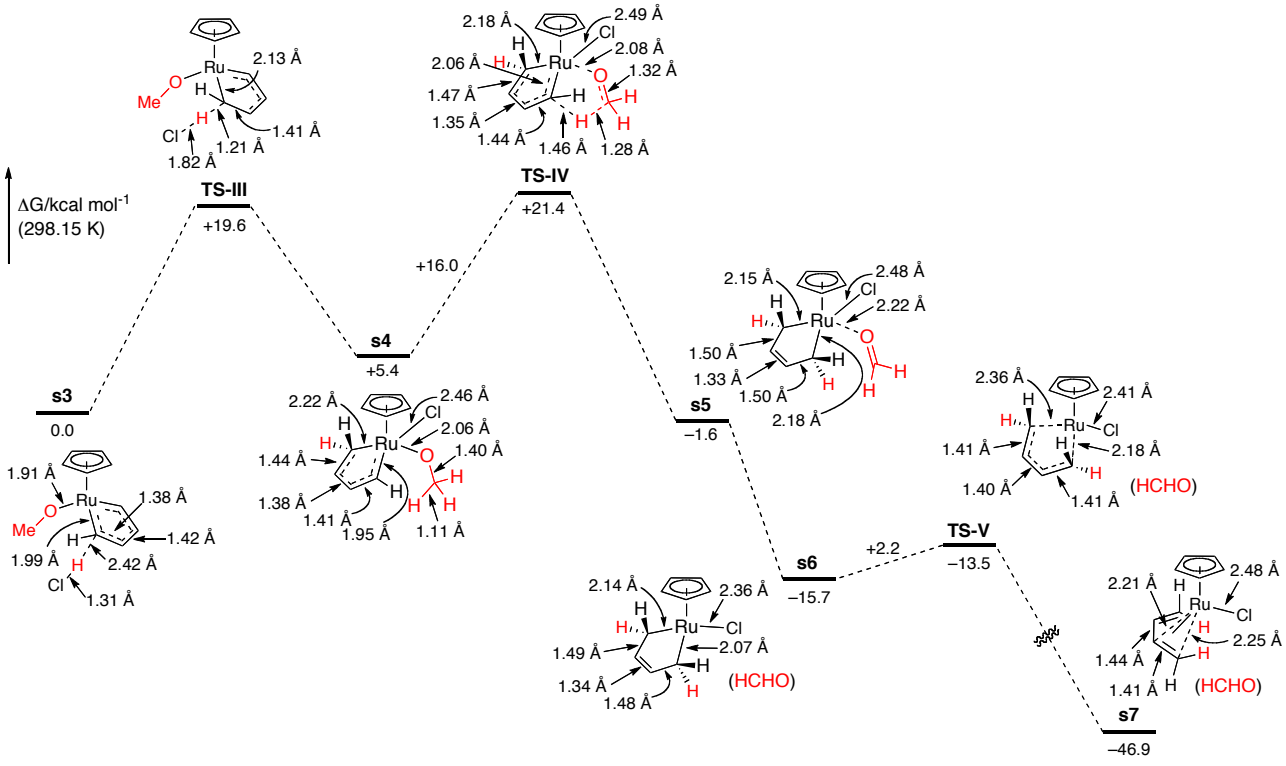


Figure S9. Reaction profile for protonation/hydride transfer/isomerization via TS-III, TS-IV, and TS-V.

Standard Orientations for Models.

Standard orientations for **s1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.058547	0.164697	-0.000003
2	6	0	-1.724105	-1.410694	-0.000406
3	1	0	-1.437618	-2.453108	-0.000757
4	6	0	-1.963306	-0.594390	-1.148401
5	1	0	-1.866091	-0.911177	-2.178874
6	6	0	-2.418275	0.685905	-0.704612
7	1	0	-2.664394	1.525075	-1.342737
8	6	0	-2.418230	0.685398	0.705312
9	1	0	-2.664356	1.524094	1.344066
10	6	0	-1.963277	-0.595229	1.148161
11	1	0	-1.866098	-0.912762	2.178405
12	6	0	1.152239	-0.766761	1.252705
13	1	0	0.960829	-0.777071	2.329008
14	6	0	2.221718	-1.452522	0.709949
15	1	0	2.980881	-1.961338	1.304148
16	6	0	2.221574	-1.452763	-0.709788
17	1	0	2.980569	-1.961870	-1.303962
18	6	0	1.151969	-0.767246	-1.252617
19	1	0	0.960376	-0.778054	-2.328880
20	8	0	0.822791	1.867310	-0.000137
21	6	0	2.212056	2.044275	-0.000105
22	1	0	2.667584	1.573561	0.886168
23	1	0	2.667731	1.572959	-0.886023
24	1	0	2.440147	3.118720	-0.000501

Standard orientations for **TS-II**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.081255	0.091163	-0.167777
2	6	0	1.616391	-1.145875	0.914555
3	1	0	1.308029	-1.977667	1.533737
4	6	0	1.881372	0.196668	1.366583
5	1	0	1.711657	0.574744	2.366096
6	6	0	2.368609	0.929876	0.265149
7	1	0	2.595404	1.988811	0.261530
8	6	0	2.465953	0.057772	-0.865561
9	1	0	2.809010	0.334133	-1.853989
10	6	0	2.019002	-1.220835	-0.462287
11	1	0	1.971679	-2.106220	-1.083222
12	6	0	-1.017141	-1.218024	-1.037003
13	1	0	-0.702717	-1.735390	-1.950913
14	6	0	-2.228983	-1.640000	-0.415156
15	1	0	-2.904059	-2.372069	-0.859877
16	6	0	-2.462319	-1.049757	0.804700
17	1	0	-3.331410	-1.282399	1.420876
18	6	0	-1.486454	-0.037470	1.155701
19	1	0	-1.333634	0.160777	2.223891
20	8	0	-0.706604	1.908500	-0.465926
21	6	0	-1.978391	2.046205	-0.230176
22	1	0	-2.696113	1.488294	-0.848463
23	1	0	-2.103980	1.094289	0.832383
24	1	0	-2.314504	3.042185	0.088499

Standard orientations for **s2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.130492	-0.023662	0.032907
2	6	0	-1.951196	-1.264475	-0.169275
3	1	0	-1.904358	-2.331620	-0.345758
4	6	0	-2.198486	-0.253172	-1.173413
5	1	0	-2.254156	-0.423540	-2.240584
6	6	0	-2.284083	0.984423	-0.524679
7	1	0	-2.394964	1.947429	-1.008253
8	6	0	-2.111013	0.780962	0.892094
9	1	0	-2.181274	1.545645	1.654653
10	6	0	-1.962376	-0.621789	1.114847
11	1	0	-1.885930	-1.114552	2.075508
12	6	0	1.171892	-0.703179	1.295462
13	1	0	0.994682	-0.873217	2.365705
14	6	0	2.465960	-0.974148	0.785537
15	1	0	3.343736	-1.149022	1.411713
16	6	0	2.539627	-1.004424	-0.600764
17	1	0	3.496865	-0.902596	-1.118990
18	6	0	1.300573	-1.102102	-1.329502
19	1	0	0.775000	-2.045364	-1.166867
20	8	0	1.020578	1.696874	-0.469962
21	6	0	1.947148	2.259860	0.103683
22	1	0	2.405467	1.837570	1.006522
23	1	0	1.338819	-0.844610	-2.390146
24	1	0	2.334843	3.208276	-0.295634

Standard orientations for **s3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.633777	-0.005691	0.185710
2	6	0	2.270529	0.273358	-1.382701
3	1	0	2.136520	1.047202	-2.125511
4	6	0	1.872073	-1.091450	-1.494507
5	1	0	1.357427	-1.531368	-2.339002
6	6	0	2.330360	-1.795287	-0.334880
7	1	0	2.165838	-2.845061	-0.127803
8	6	0	2.959802	-0.868104	0.517119
9	1	0	3.364674	-1.075403	1.499419
10	6	0	2.898446	0.420154	-0.105394
11	1	0	3.317466	1.336455	0.290207
12	6	0	0.230189	1.928041	0.398375
13	1	0	0.882561	2.575163	0.990471
14	6	0	-0.864469	2.430007	-0.267565
15	1	0	-1.200936	3.463777	-0.195572
16	6	0	-1.496379	1.465570	-1.102539
17	1	0	-2.352388	1.702775	-1.735326
18	6	0	-0.892685	0.223746	-1.063738
19	1	0	-1.181443	-0.564367	-1.764747
20	1	0	-3.142085	-0.471256	-0.510640
21	17	0	-4.326662	-1.008859	-0.528922
22	8	0	-0.243140	-0.566879	1.788178
23	6	0	-1.403675	-0.007882	2.344242
24	1	0	-1.304909	1.085148	2.438009
25	1	0	-2.280085	-0.206679	1.710503
26	1	0	-1.575620	-0.449276	3.334508

Standard orientations for **TS-III**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.267770	-0.086778	0.139770
2	6	0	2.236412	0.846531	-0.439441
3	1	0	2.319163	1.923956	-0.461333
4	6	0	1.967981	-0.006665	-1.542433
5	1	0	1.762107	0.315431	-2.554116
6	6	0	2.028140	-1.366830	-1.104139
7	1	0	1.823913	-2.235604	-1.716189
8	6	0	2.274236	-1.366599	0.279402
9	1	0	2.293281	-2.235426	0.923785
10	6	0	2.375659	0.002057	0.721748
11	1	0	2.636479	0.330156	1.719422
12	6	0	-0.259743	1.429899	1.309964
13	1	0	-0.020239	1.393884	2.376109
14	6	0	-0.836782	2.558215	0.761926
15	1	0	-1.108426	3.439294	1.340402
16	6	0	-1.005093	2.471593	-0.628661
17	1	0	-1.291123	3.333057	-1.233094
18	6	0	-0.755852	1.211475	-1.208750
19	1	0	-0.554116	1.177218	-2.279746
20	1	0	-1.637904	0.395987	-1.071876
21	17	0	-2.637922	-1.099786	-1.325038
22	8	0	-0.595767	-1.306086	1.336397
23	6	0	-1.736269	-1.079131	2.124273
24	1	0	-1.688095	-0.115517	2.657975
25	1	0	-2.624129	-1.073720	1.478057
26	1	0	-1.814116	-1.888691	2.861853

Standard orientations for **s4**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.043091	0.024040	-0.044007
2	6	0	1.252642	1.769608	-0.565072
3	1	0	2.311375	1.611897	-0.718463
4	6	0	0.630020	2.212786	0.647845
5	1	0	1.131828	2.401364	1.586560
6	6	0	-0.761069	2.367752	0.405112
7	1	0	-1.507000	2.603893	1.151144
8	6	0	-1.023593	1.983453	-0.926331
9	1	0	-1.999679	1.885609	-1.380137
10	6	0	0.219529	1.617069	-1.549131
11	1	0	0.349125	1.330449	-2.583285
12	6	0	1.072738	-1.256142	-0.998544
13	1	0	0.696630	-1.644072	-1.945523
14	6	0	2.372661	-1.564473	-0.554720
15	1	0	3.087698	-2.135065	-1.145250
16	6	0	2.641844	-1.075911	0.705642
17	1	0	3.647738	-1.047781	1.126514
18	6	0	1.493433	-0.586526	1.431780
19	1	0	1.674250	0.084932	2.270000
20	1	0	0.830729	-1.399294	1.745230
21	17	0	-1.582291	-0.594619	1.770078
22	8	0	-1.410021	-0.868473	-1.299450
23	6	0	-1.898965	-2.155519	-1.061360
24	1	0	-1.109838	-2.932444	-1.111391
25	1	0	-2.414982	-2.257583	-0.098938
26	1	0	-2.618188	-2.375942	-1.867221

Standard orientations for **TS-IV**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.133666	0.048963	-0.045261
2	6	0	1.328434	-1.822529	-0.208167
3	1	0	0.833789	-2.783770	-0.171983
4	6	0	1.910573	-1.126544	0.904227
5	1	0	1.892974	-1.449562	1.935747
6	6	0	2.540013	0.053399	0.417515
7	1	0	3.002695	0.818261	1.025826
8	6	0	2.311715	0.127080	-0.972916
9	1	0	2.583653	0.953407	-1.616355
10	6	0	1.561533	-1.028762	-1.377794
11	1	0	1.275379	-1.276746	-2.391015
12	6	0	-1.520191	-0.714324	-1.009862
13	1	0	-1.379129	-0.887525	-2.083296
14	6	0	-2.416713	-1.600003	-0.306575
15	1	0	-3.234300	-2.122898	-0.800448
16	6	0	-2.100961	-1.754601	0.998644
17	1	0	-2.605302	-2.483032	1.636422
18	6	0	-1.035724	-0.889792	1.543378
19	1	0	-0.421351	-1.382946	2.301761
20	1	0	-1.464145	0.006491	2.002389
21	17	0	-0.153005	2.014875	1.454288
22	8	0	-0.365393	1.466198	-1.481222
23	6	0	-1.662506	1.700122	-1.420341
24	1	0	-2.197357	0.534584	-1.359384
25	1	0	-2.063076	2.067371	-0.463685
26	1	0	-2.077930	2.205254	-2.306257

Standard orientations for **s5**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.075172	0.046803	0.075740
2	6	0	-0.603031	2.099047	-0.220113
3	1	0	-1.634615	2.253298	-0.503386
4	6	0	0.494428	1.852917	-1.097879
5	1	0	0.457797	1.798677	-2.176986
6	6	0	1.697958	1.797793	-0.293982
7	1	0	2.685296	1.576524	-0.675135
8	6	0	1.349942	1.982309	1.050175
9	1	0	2.021310	1.930988	1.897606
10	6	0	-0.072459	2.097963	1.118619
11	1	0	-0.644448	2.251946	2.023042
12	6	0	-1.811351	-0.263848	1.129246
13	1	0	-1.942583	0.506320	1.895600
14	6	0	-2.967368	-0.347510	0.184806
15	1	0	-3.988622	-0.267010	0.562330
16	6	0	-2.678761	-0.587198	-1.091997
17	1	0	-3.445985	-0.729699	-1.856034
18	6	0	-1.232570	-0.729556	-1.447624
19	1	0	-0.963690	-0.195812	-2.367267
20	1	0	-0.961784	-1.780265	-1.609785
21	17	0	1.691605	-1.254402	-1.275453
22	8	0	0.640175	-1.491290	1.573353
23	6	0	0.942235	-2.660809	1.383545
24	1	0	-1.661171	-1.210458	1.662582
25	1	0	0.898982	-3.114112	0.386393
26	1	0	1.279128	-3.271227	2.235559

Standard orientations for **s6**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	0.079320	0.110947	-0.170334
2	6	0	0.911347	-1.573843	0.929148
3	1	0	0.247030	-2.221097	1.484982
4	6	0	1.498036	-0.342752	1.391434
5	1	0	1.374283	0.094866	2.372882
6	6	0	2.409409	0.120917	0.365597
7	1	0	2.976157	1.041605	0.408148
8	6	0	2.356573	-0.768671	-0.715047
9	1	0	2.880332	-0.663702	-1.656185
10	6	0	1.385611	-1.777605	-0.402636
11	1	0	1.108367	-2.601434	-1.046778
12	6	0	-1.384155	-0.962276	-1.174171
13	1	0	-1.069963	-1.809614	-1.789816
14	6	0	-2.662151	-1.139445	-0.454714
15	1	0	-3.444878	-1.782026	-0.857113
16	6	0	-2.781608	-0.447166	0.684609
17	1	0	-3.709381	-0.422814	1.259459
18	6	0	-1.580336	0.295773	1.168996
19	1	0	-1.217062	-0.135362	2.114216
20	1	0	-1.796745	1.352505	1.363632
21	17	0	-0.023278	2.463444	-0.299917
22	1	0	-1.358844	-0.042739	-1.819434

Standard orientations for **TS-V**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	0.144164	0.008497	-0.096883
2	6	0	1.470935	-1.379201	0.958093
3	1	0	1.111833	-2.155710	1.620620
4	6	0	1.796658	-0.019837	1.331538
5	1	0	1.714284	0.406854	2.321986
6	6	0	2.307395	0.640142	0.171327
7	1	0	2.579419	1.685001	0.110312
8	6	0	2.255531	-0.265599	-0.921664
9	1	0	2.537489	-0.044896	-1.942416
10	6	0	1.736214	-1.515426	-0.437652
11	1	0	1.583527	-2.408739	-1.028243
12	6	0	-1.360595	-1.226453	-1.073147
13	1	0	-1.082448	-1.999427	-1.790301
14	6	0	-2.620274	-1.312570	-0.450590
15	1	0	-3.373807	-2.028173	-0.778233
16	6	0	-2.848252	-0.415179	0.593353
17	1	0	-3.851367	-0.049616	0.817608
18	6	0	-1.735163	0.038690	1.329297
19	1	0	-1.104679	-0.751337	1.739706
20	1	0	-1.839192	0.909101	1.971497
21	17	0	-0.558784	2.293777	-0.368377
22	1	0	-1.133643	-0.198537	-1.520609

Standard orientations for **s7**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	44	0	-0.027967	-0.074851	-0.000495
2	6	0	1.868028	-1.130643	0.584891
3	1	0	1.876752	-2.080879	1.103290
4	6	0	1.922162	0.161468	1.199108
5	1	0	1.940423	0.370214	2.259628
6	6	0	1.906053	1.124861	0.154321
7	1	0	1.857416	2.195973	0.289830
8	6	0	1.876929	0.451722	-1.111454
9	1	0	1.875480	0.924073	-2.083323
10	6	0	1.858128	-0.950417	-0.840425
11	1	0	1.846739	-1.742204	-1.578311
12	6	0	-1.685257	-0.501202	-1.458501
13	1	0	-1.462751	-0.504664	-2.521525
14	6	0	-1.391948	-1.657568	-0.712906
15	1	0	-0.947692	-2.522514	-1.200545
16	6	0	-1.402055	-1.653184	0.724091
17	1	0	-0.962216	-2.514312	1.222244
18	6	0	-1.703578	-0.495288	1.461023
19	1	0	-2.439800	0.228020	1.131643
20	1	0	-1.492260	-0.492724	2.526229
21	17	0	-1.054073	2.183309	0.001003
22	1	0	-2.433092	0.217735	-1.145299

Standard orientations for **HCHO**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.529154	0.000000	0.000003
2	8	0	0.677464	0.000000	-0.000006
3	1	0	-1.122395	0.938191	-0.000006
4	1	0	-1.122395	-0.938191	0.000033