Supplementary Material (ESI) for Chemical Communications

Supporting Information

Prochiral CODs in Cationic DUPHOS-Rh(I) Catalysis of Highly Enantioselective Intramolecular [4+2]Cycloaddition

Martial Vallet,[a] Hitomi Kakuno,[a] Susumu Kawauchi,[b] Kohsuke Aikawa[a] and Koichi Mikami*[a]

[a] Prof. Dr. K. Mikami, Dr. M. Vallet, Dr. K. Aikawa, H. Kakuno
Department of Applied Chemistry
Graduate School of Science and Engineering
Tokyo Institute of Technology
O-okayama, Meguro-ku, Tokyo 152-8552 (Japan)
Fax: Int. code (+81)3-5734-2776
E-mail: kmikami@o.cc.titech.ac.jp

[b] Prof. Dr. S. Kawauchi
Department of Organic and Polymeric Materials
Tokyo Institute of Technology
O-okayama, Meguro-ku, Tokyo 152-8552 (Japan)
Fax Int. Code (+81)3-5734-2888
E-mail: skawauch@polymer.titech.ac.jp

General:

All reactions involving air sensitive organometallic compounds were carried out under an atmosphere of argon using an inert gas/vacuum double manifold and standard Schlenck techniques.[1]

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were measured on Bruker AV300 (300 MHz) spectrometers.

Chemical shift of ^{1}H NMR was expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$) in $CDCl_3$. Significant ^{1}H NMR data were tabulated in following order: multiplicity (s: singlet; d: doublet; t: triplet; q: quartet; br s: broad singlet; br d: broad doublet; m: multiplet) and coupling constants (J) are reported (Hz). Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard ($\delta = 77.0$) in $CDCl_3$. Chemical shifts of ^{19}F NMR were expressed in parts per million downfield from BTF as an external standard ($\delta = -63.24$) in $CDCl_3$. Chemical shifts of ^{31}P NMR were expressed in parts per million downfield from 85% H_3PO_4 as an external standard ($\delta = 0$) in $CDCl_3$.

Analytical thin layer chromatography (TLC) were performed on a glass plates and/or aluminum sheets pre-coated with silica-gel (Merck Kieselgal 60 F_{254}, layer thickness 0.25 and 0.2 mm). Column

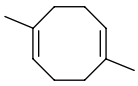
chromatography was performed on Merck Kieselgel 60 and KANTO Silica Gel 60N (spherical, neutral).

Capillary gas chromatographic analysis (GC) was conducted on Shimadzu GC-14B instrument equipped with FID detector and capillary column coated with PEG-20 M by using He as a carrier gas. Peak area was calculated by Shimadzu C-R6A as an automatic integrator. CP-Cyclodextrin-β-2,3,6-M-19 (i.d. 0.25 mm x 25 m, CHROMPACK; GL Science) was used as chiral columns. Split ratio was 100:1.

Optical rotations were measured on a JASCO P-1020.

1,5-Dibromo-1,5-cyclooctadiene and 1,5-diphenyl-1,5-cyclooctadiene (**3b**) were prepared according to the literature procedure.[2]

1,5-Dimethyl-1,5-cyclooctadiene (3a)

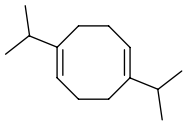


Methyl Grignard reagent (1.59 mmol) was added to a suspention of 1,5-dibromo-1,5-cyclooctadiene (280 mg, 1.05 mmol) and $NiCl_2$dppp (23 mg, 0.04 mmol) in 20 ml of dry Et_2O under argon at 0 °C.[2] The reaction mixture was stirred for 30 min at 0°C, 1 h at room temperature, and then for 2 h at reflux. H_2O (20 ml) was added and the reaction mixture was extracted three times with Et_2O. Combinated organic layer were dried over $MgSO_4$ and solvents were removed under reduced pressure. Crude product was purified by flash chromatography over sillicagel eluted with pentane to afford 128 mg (90%) of a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, J = 6.9 Hz, 12 H, Me), 2.29-2.38 (m, 10 H, CH_2, CH), 5.32 (t, J = 6.0 Hz, 2H, CH).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.3, 33.3, 122.5, 135.8.

1,5-Diisopropyl-1,5-cyclooctadiene (3c)



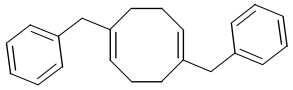
The titled compound was prepared from 1,5-dibromo-1,5-cyclooctadiene according to the procedure as discribed for 1,5-dimethyl-1,5-cyclooctadiene.[2] Colorless oil, 182 mg (90%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (s, 6 H, Me), 2.29-2.38 (m, 8 H, CH_2), 5.36 (t, , J = 6.0 Hz, 2H, CH).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.3, 33.3, 122.5, 135.8.

IR (neat): 2957 (s), 2931 (s), 2879 (s), 1659 (s), 1491 (m), 1603 (s), 1380 (m), 1359 (m), 1301 (w), 1255 (w), 1209 (w), 1091 (w), 1018 (w), 890 (w), 839 (w), 809 (w).

1,5-Dibenzyl-1,5-cyclooctadiene (3d)



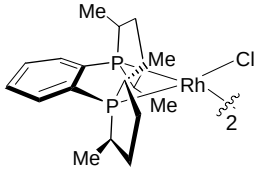
The titled compound was prepared from 1,5-dibromo-1,5-cyclooctadiene according to the procedure as discribed for 1,5-dimethyl-1,5-cyclooctadiene.[2] Colorless oil, 273 mg (90%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42-2.35 (m, 4 H, CH_2), 3.40 (s,2 H, CH_2), 5.49 (t, , *J* = 5.7 Hz, 2H, CH), 7.43-4.29 (m, 10 H, A_{arom}).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.8, 31.6, 38.3, 46.8, 125.4, 126.2, 128.4, 128.6, 129.31, 138.9, 141.0, 142.1.

IR (neat): 3082 (s), 3060 (s), 3024 (s), 2884 (s), 2830 (s) 1946 (w), 1869 (w), 1804 (w), 1743 (w), 1660 (w), 1601 (s), 1493 (s), 1453 (s), 1076 (s), 1029 (s), 908 (s), 844 (s), 743 (s), 699 (s).

[RhCl{(*R*,*R*)-DUPHOS}]$_2$ (5)[3]



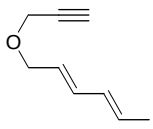
μ-Dichlorotetraethylenedirhodium (40 mg, 0.10 mmol) was added to a solution of (*R*,*R*)-DUPHOS (60 mg, 0.19 mmol) in 1 ml of dry CH_2Cl_2 at room temperature under argon. The reaction mixture was stirred 30 min at room temperature, then the complex was precipitated by addition of Et_2O. The precipitated complex was washed tree times with Et_2O, then dried *in vaccuo* to afford 80 mg (90%) of a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (dd, *J* = 6.6 Hz, *J* = 13.8 Hz, 6H, CH_3), 1.29 (dd, *J* = 7.5Hz, *J* = 15.9 Hz, 6H, CH_3), 1.72 (dq, *J* = 5.4 Hz, *J* = 13.2 Hz, 2H), 2.14 (dq, *J* = 5.7 Hz, *J* = 12.9 Hz, 2H), 2.60-2.40 (bm, 4H), 2.80-2.90 (bm, 2H), 2.97 (dq, *J* = 6.3Hz, *J* = 12.9 Hz, 2H), 7.69 (s, 2H), 7.85 (s, 2H).

^{31}P NMR (CD_2Cl_2, 121.5 MHz) δ 75.9 (d, . *J* = 131 Hz).

Anal. Calcd for $C_{36}H_{56}Cl_2P_4Rh_2/3H_2O$: C, 45.83; H, 6.62%. Found: C, 45.49; H, 6.52%.

1-Prop-2-ynyloxy-hexa-2,4-diene



To a solution of NaH (105.6 mg, 4.4 mmol) in THF (2.0 ml) was added *trans*,*trans*-2,4-hexadiene-1-ol (0.45 ml, 4.0 mmol) in THF (0.5 ml) at 0 ºC under argon atmosphere. After stirring for 45 min at room temperature, propargyl bromide (0.33 ml, 4.4 mmol) was added to the reaction mixture at 0 ºC. After stirring for 12 h, ice water was added to the solution carefully and mixture was extracted with ether twice. The organic layer was washed with brine and dried over

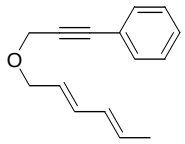
$MgSO_4$. After concentration under reduced pressure, the residue was purified by silica-gel chromatography (pentane/ether = 20/1) to give 425 mg (78%) of a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (d, *J* = 6.6Hz, 3 H), 2.41 (s, 1 H), 4.12 (s, 2 H), 4.07 (d, *J* = 6.6 Hz, 2 H), 5.59 (dt, *J* = 15.3, 6.5 Hz, 1 H), 5.72 (dq, *J* = 14.9, 6.7 Hz, 1 H), 6.05 (dd, *J* = 15.0, 15.0 Hz, 1 H), 6.23 (dd, *J* = 15.2 , 10.4Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1, 56.7, 70.0, 74.3, 79.8, 125.5, 130.5, 130.6, 134.2.

HRMS (EI), Calcd for $C_9H_{12}O$ [$M^{+\cdot}$]: 136.0888, Found: 136.0887.

(3-Hexa-2,4-dienyloxy-prop-1-ynyl)-benzene (1a)



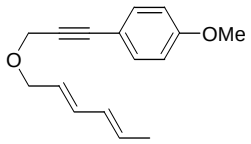
To a suspension of $PdCl_2(PPh_3)_2$ (70.2 mg, 0.10 mmol) and CuI (9.5 mg, 0.05 mmol) was added iodobenzene (1.12 ml, 10.0 mmol), diethylamine (15 ml), and 1-prop-2-ynyloxy-hexa-2,4-diene (0.68 g, 5.0 mmol) under argon atmosphere, and the mixture was refluxed for 3 h (monitored by TLC). After cooled to room temperature, the resultant mixture was added to ether, and then filtered by celite. After evaporation under reduced pressure, the resultant residue was purified by silica-gel chromatography to give 955 mg (90%) a colorless oil.

^{1}H NMR (300 MHz , $CDCl_3$) δ1.79 (dd, *J* = 6.9, 0.6 Hz, 3H), 4.17 (d, *J* = 6.3 Hz, 2H), 4.38 (s, 2H), 5.63-5.82 (m, 2H), 6.06-6.15 (m, 1H), 6.29 (dd, *J* = 15.0, 10.5 Hz, 1H), 7.31-7.36 (m, 3H), 7.46-7.49 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 18.1, 57.6, 70.1, 85.2, 86.2, 122.7, 125.8, 128.2, 128.4, 130.5, 130.7, 131.7, 134.2.

HRMS (EI), Calcd for $C_{15}H_{16}O$ [$M^{+\cdot}$]: 212.1201, Found: 212.1205.

1-(3-Hexa-2,4-dienyloxy-prop-1-ynyl)-4-methoxy-benzene (1b)



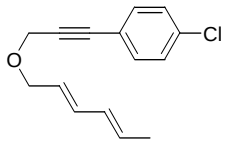
Colorless oil, 1,089 g (90%).

^{1}H NMR (300 MHz, $CDCl_3$) δ1.76 (d, *J* = 6.0 Hz, 3H), 3.81 (s, 3H), 4.13 (d, *J* = 6.6 Hz, 2H), 4.34 (s, 2H), 5.60-5.79 (m, 2H), 6.00-6.12 (m, 1H), 6.26 (dd, *J* = 14.7, 10.2 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$)δ17.8, 54.9, 57.5, 69.8, 83.6, 85.9, 113.7, 114.6, 125.8, 129.9, 130.6, 133.0, 133.7, 159.5.

HRMS (EI), Calcd for $C_{16}H_{18}O_2$ [$M^{+\cdot}$]: 242.1307, Found: 242.1313.

1-Chloro-4-(3-hexa-2,4-dienyloxy-prop-1-ynyl)-benzene (1c)



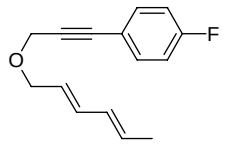
Colorless oil, 1.109 g (90%).

^{1}H NMR (300 MHz, CDCl) δ 1.73 (d, *J* = 6.6 Hz, 3H), 4.01 (d, *J* = 6.3 Hz, 2H), 4.32 (s, 2H), 5.57-5.75 (m, 2H), 6.04 (ddd, *J* = 14.7, 10.5, 1.2 Hz, 1H), 6.24 (dd, *J* = 15.3, 10.5, 1H), 7.25 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.34 (dt, *J* = 8.7, 2.1 Hz, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ17.9, 57.4, 70.0, 84.9, 86.3, 121.1, 125.6, 128.4, 130.2, 130.6, 132.8, 133.9, 134.3.

HRMS (EI), Calcd for $C_{15}H_{15}ClO$ [$M^{+\cdot}$]: 246.0811, Found: 246.0818.

1-Fluoro-4-(3-hexa-2,4-dienyloxy-prop-1-ynyl)-benzene (1d)



Pale yellow oil, 1.033 g (90%).

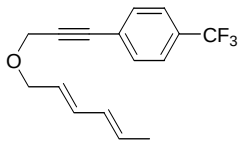
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (d, *J* = 6.6 Hz, 3H), 4.13 (d, *J* = 6.6 Hz, 2H), 4.33 (s, 2H), 5.58-5.80 (m, 2H), 6.02-6.13 (m, 1H), 6.21-6.31 (m, 1H), 6.95-7.04 (m, 2H), 7.38-7.46 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 18.0, 57.5, 70.1, 84.9, 85.0, 115.5 (d, *J*C-F = 22.0 Hz), 118.8 (d, *J*C-F = 3.7 Hz), 125.7, 130.3, 130.7, 133.6 (d, *J*C-F = 8.5 Hz), 134.0, 162.5 (d, *J*C-F = 249.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.2 (m, 1F).

HRMS (EI), Calcd for $C1_5H_{15}FO$ [M^{+}·]: 230.1107, Found: 230.1112.

1-(3-Hexa-2,4-dienyloxy-prop-1-ynyl)-4-trifluoromethyl-benzene (1e)



Colorless oil, 1.258 g (90%).

^{1}H NMR (300 MHz, CDCl) δ 1.76 (d, *J* = 6.6 Hz, 3H), 4.12 (d, *J* = 6.6 Hz, 2H), 4.37 (s, 2H),

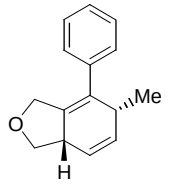
5.61-5.80 (m, 2H), 6.08 (dd, *J* = 14.1, 10.5 Hz, 1H), 6.27 (dd, *J* = 15.3, 10.5, 1H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ18.09, 57.43, 70.34, 84.78, 87.80, 123.85 (q, J_{C-F} = 271.7 Hz), 125.20 (q, J_{C-F} = 3.8 Hz), 125.52, 126.48, 130.12 (q, J_{C-F} = 33.2 Hz), 130.63, 130.67, 131.96, 134.37.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4 (s, 3F).
HRMS (ESI), Calcd for $C_{16}H_{15}F_3O$ [$M^{+\cdot}$]: 280.1075, Found: 280.1068.

Typical experimental procedure (Table 2, Entry 1)

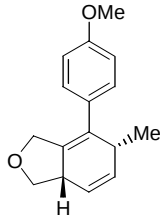
$AgBF_4$ (4.6 mg, 0.024 mmol) was added to a solution of [RhCl{(*R*,*R*)-DUPHOS)}]$_2$ (10 mg, 0.01 mmol) and 1,5-diphenyl-1,5-cyclooctadiene (**3b**) (5.7 mg, 0.022 mmol) in dry deuterated dichloromethane (1.0 mL) under argon atmosphere. After the mixture was stirred for 30 min at room temperature, dieneyne **1a** (32 mg, 0.2 mmol) was added and the reaction mixture was stirred at room temperature. The reaction was monitored by NMR. After the reaction was complete, the reaction mixture directly loaded onto a silica-gel column eluted with EtOAc/hexane (1/20) to give the corresponding cycloaddition product **2a** as a colorless oil (isolated yield 90%).

6-Methyl-7-phenyl-1,3,3a,6-tetrahydroisobenzofuran (2a)



Colorless oil, 39 mg (90%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (d, *J* = 7.5 Hz, 3H), 3.10-3.30 (m, 2H), 3.39 (dd, *J* = 11.4, 7.5, 1H), 4.13 (d, *J* = 13.5 Hz, 1H), 4.24 (d, *J* = 7.5 Hz, 1H), 4.30 (d, *J* = 13.5 Hz, 1H), 5.80 (s, 2H), 7.09-7.13 (m, 2H), 7.21-7.27 (m, 1H), 7.30-7.36 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 20.19, 34.57, 41.04, 68.25, 72.15, 121.76, 126.60, 128.02, 128.28, 132.10, 134.62, 134.94, 140.30.
HRMS (EI), Calcd for $C_{15}H_{16}O$ [$M^{+\cdot}$]: 212.1201, Found: 212.1202.
$[\alpha]_D^{24}$ = +85.3 (c = 2.71 in $CHCl_3$) (88% *ee*).[4]
GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 150 °C; injection temp, 180 °C), t_R of minor-isomer 48.8 min, t_R of major-isomer 50.7 min.

7-(4-Methoxy-phenyl)-6-methyl-1,3,3a,6-tetrahydroisobenzofuran (2b)



Colorless oil, 90% conv (NMR).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, *J* = 7.5 Hz, 3H), 3.08-3.28 (m, 2H), 3.38 (dd, *J* = 11.4, 7.5, 1H), 3.81 (s, 3H), 4.14 (d, *J* = 14.4 Hz, 1H), 4.23 (d, *J* = 7.5 Hz, 1H), 4.28 (d, *J* = 14.4 Hz, 1H), 5.79 (s, 2H), 6.87 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H).

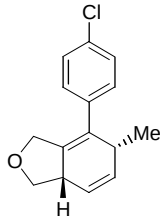
^{13}C NMR (75 MHz, $CDCl_3$) δ 20.24, 34.78, 41.10, 55.19, 68.36, 72.20, 113.74, 121.76, 129.14, 131.73, 132.62, 134.72, 135.04, 158.27.

HRMS (EI), Calcd for $C_{16}H_{18}O_2$ [$M^{+\cdot}$]: 242.1307, Found: 242.1305.

$[\alpha]_D^{23}$ = +59.8 (c = 1.01 in $CHCl_3$) (81% *ee*).[4]

GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 180 °C; injection temp, 180 °C), t_R of minor-isomer 49.4 min, t_R of major-isomer 50.9 min.

7-(4-Chloro-phenyl)-6-methyl-1,3,3a,6-tetrahydroisobenzofuran (2c)



Colorless oil, 95% conv. (NMR).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (d, *J* = 6.9 Hz, 3H), 3.07-3.28 (m, 2H), 3.38 (dd, *J* = 11.4, 7.2, 1H), 4.12 (d, *J* = 13.5 Hz, 1H), 4.24 (d, *J* = 13.5 Hz, 1H), 4.26 (d, *J* = 7.2 Hz, 1H), 5.79 (s, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H).

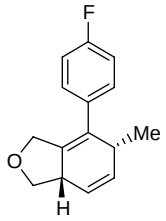
^{13}C NMR (75 MHz, $CDCl_3$) δ 20.12, 34.47, 41.10, 68.17, 72.13, 121.79, 128.59, 129.46, 131.00, 132.52, 134.43, 135.80, 138.68.

HRMS (EI), Calcd for $C_{15}H_{15}ClO$ [$M^{+\cdot}$]: 246.0811, Found: 246.0805.

$[\alpha]_D^{24}$ = +83.3 (c = 2.19 in $CHCl_3$) (86% *ee*).[4]

GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 180 °C; injection temp, 180 °C), t_R of minor-isomer 39.9 min, t_R of major-isomer 41.0 min.

7-(4-Fluoro-phenyl)-6-methyl-1,3,3a,6-tetrahydroisobenzofuran (2d)



Colorless oil, 42 mg (92%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (d, *J* = 7.2 Hz, 3H), 3.08-3.28 (m, 2H), 3.38 (dd, *J* = 10.8, 6.9, 1H), 4.12 (d, *J* = 13.2 Hz, 1H), 4.24 (d, *J* = 13.2 Hz, 1H), 4.26 (d, *J* = 6.9 Hz, 1H), 5.79 (s, 2H), 6.99-7.11 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 20.12, 34.65, 41.10, 68.22, 72.16, 115.25 (d, *J*C-F = 20.8 Hz), 121.81, 129.65 (d, *J*C-F = 8.53 Hz), 131.19, 134.51, 135.69, 136.10 (d, *J*C-F = 3.6 Hz), 161.65 (d, *J*C-F = 245.4 Hz).

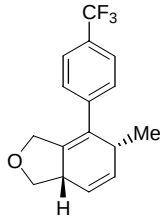
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.4 (m, 1F).

HRMS (EI), Calcd for $C_{15}H_{15}FO$ [M^{+}·]: 230.1107, Found: 230.1108.

[α]D22 = +95.7 (c = 1.90 in CHCl3) (93% *ee*).[4]

GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 180 °C; injection temp, 180 °C), tR of minor-isomer 18.6 min, tR of major-isomer 19.0 min.

6-Methyl-7-(4-trifluoromethyl-phenyl)-1,3,3a,6-tetrahydro-isobenzofuran (2e)



Colorless oil, 48 mg (86%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, *J* = 7.2 Hz, 3H), 3.16-3.33 (m, 2H), 3.41 (dd, *J* = 11.1, 7.2, 1H), 4.14 (ddd, *J* = 13.5, 3.0, 1.2 Hz, 1H), 4.27 (d, *J* = 13.5 Hz, 1H), 4.30 (d, *J* = 7.2 Hz, 1H), 5.82 (s, 2H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 20.10, 34.32, 41.07, 68.06, 72.06, 121.78, 124.17 (q, $J_{C\text{-}F}$ = 272.4 Hz), 125.37 (q, $J_{C\text{-}F}$ = 3.8 Hz), 128.41, 129.13 (q, $J_{C\text{-}F}$ = 32.5 Hz), 130.93, 134.28, 136.14, 144.07.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s, 3F).

HRMS (ESI), Calcd for $C_{16}H_{15}F_3O$ [M^{+}·]: 280.1075, Found: 280.1074.

$[\alpha]_D^{25}$ = +97.5 (c = 2.80 in $CHCl_3$) (98% *ee*).[4]

GC (column, CP-Cyclodextrin-β-2,3,6-M-19, i.d. 0.25 mm x 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 170 °C; injection temp, 180 °C), t_R of minor-isomer 25.1 min, t_R of major-isomer 26.0 min.

Cartesian matrix (Gaussian output) for the most stable diastereomer (*S*/*S*,*S*)-Me-COD (3a)-Rh-DUPHOS complex (Rh) calculated at B3LYP/6-31G(d)-SDD[5,6]

Rh,0,-0.0763730583,0.0920721976,0.1441721874
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C,0,1.0593543177,-0.3177141101,2.1579919992
C,0,-0.3885115535,2.2924028107,0.8856253513
C,0,0.9196570943,2.0978728205,0.4400605127
P,0,0.0629436944,0.2901582989,-2.2263525981
P,0,-1.0361970856,-2.0192786551,-0.4015831043
C,0,-0.9751980183,-1.0153440921,-3.0264041507
C,0,-2.4570870291,-3.130144327,-4.1433476213
C,0,-1.4385985119,-2.0611904355,-2.206211493
C,0,-1.2766521496,-1.0407162303,-4.3995859378
C,0,-2.0143984854,-2.0846096625,-4.9540600085
C,0,-2.1680526522,-3.1160609671,-2.7808661691
H,0,-0.9439784944,-0.2415000908,-5.0496943564
H,0,-2.2412975074,-2.0803254313,-6.016073131
H,0,-2.5177927205,-3.939483258,-2.1667831817
H,0,-3.0272860783,-3.9510290156,-4.5680392187
C,0,-2.6616841266,-2.5791354975,0.4112772534
C,0,-0.1452075695,-3.6476504969,-0.0294772867
C,0,-2.2593108361,-3.7865999742,1.2825432375
H,0,-3.1444954091,-4.3766541106,1.5483525034
H,0,-1.8151282806,-3.4393958683,2.2258847584
C,0,-1.232624292,-4.6107879765,0.4945755251
H,0,-0.7775110492,-5.3939327531,1.1122002387
C,0,1.7766538867,-0.0440528771,-2.9542441537
C,0,-0.1589492986,1.869026277,-3.2282075733
C,0,0.8591667512,1.8114726154,-4.4124606064
H,0,0.3286352664,1.9113289814,-5.3660777581
H,0,1.5288290191,2.6757257336,-4.3469148666
C,0,1.6819334325,0.4980146508,-4.3963959192
H,0,1.2082629639,-0.2526267523,-5.0353292539
H,0,2.686288551,0.6577734846,-4.8059995499
C,0,-0.7246725406,2.2792449976,2.3845002292
H,0,-1.5608931882,2.960918705,2.5594544692

H,0,0.123088743,2.7064214461,2.9284293082
C,0,-1.0924048855,0.8972995992,2.9520455831
H,0,-0.9686308968,0.9059706254,4.0470058678
H,0,-2.1575699642,0.7184314395,2.7749414418
C,0,2.1344425033,1.907211088,1.324549932
H,0,2.4392500186,2.8764599484,1.7506827887
H,0,2.9645187951,1.5926352518,0.684822366
C,0,1.9704693805,0.8813715228,2.464802491
H,0,1.5883739896,1.3684704151,3.3676695322
H,0,2.9605059292,0.5042829965,2.7333993339
H,0,-1.7263011899,-5.1193092559,-0.3444639814
H,0,0.1653556822,2.6482805657,-2.5305410094
H,0,1.9312498658,-1.1291723663,-2.9558712093
H,0,-3.2549316227,-2.9581827559,-0.4289531542
H,0,0.5064082381,-3.3927160005,0.8096967337
C,0,-1.5972233268,2.2214120521,-3.6318689763
H,0,-1.6106944887,3.213013473,-4.0973007247
H,0,-2.2617598485,2.2564151038,-2.7650170822
H,0,-2.014457809,1.5127069713,-4.3515576683
C,0,2.9115472597,0.6163891662,-2.1608295777
H,0,2.8164812402,1.7080903527,-2.132639839
H,0,3.8726406641,0.3863845362,-2.6354686877
H,0,2.9440592036,0.2525421612,-1.1312193945
C,0,-3.503992888,-1.5186493815,1.1202190783
H,0,-3.7308241568,-0.6747904992,0.4601999619
H,0,-3.0086682945,-1.1305465348,2.0134366462
H,0,-4.4574078847,-1.9579825988,1.4372238884
C,0,0.7295483334,-4.2123180018,-1.1518475716
H,0,1.504282874,-3.500683435,-1.4577105672
H,0,0.1444407589,-4.4805664432,-2.0369889028
H,0,1.2380664965,-5.1164912492,-0.7980316585
H,0,-0.8236151987,-1.2213990512,2.4782041946
H,0,1.1597262029,2.4797032953,-0.5494696497
C,0,-1.3997228636,3.0159094872,0.052727401
C,0,-1.040871083,4.181137861,-0.6464798952
C,0,-2.7590468252,2.6512205299,0.0850872482
C,0,-2.0071094874,4.953378551,-1.2959092916
H,0,-0.0061311723,4.5129932379,-0.6409616385

C,0,-3.7215523522,3.4150889846,-0.5724995439
H,0,-3.0600927245,1.762843197,0.6332018775
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H,0,-4.7650954228,3.1148321569,-0.536852088
H,0,-4.1014749881,5.1780403538,-1.7600110266
C,0,1.7681269781,-1.6357715328,2.1580963699
C,0,1.4017914453,-2.6393452551,3.0727695208
C,0,2.8853514486,-1.8656135527,1.3343327505
C,0,2.1115921342,-3.8406230319,3.1429690105
H,0,0.5764960659,-2.4667117598,3.7575683122
C,0,3.5856819931,-3.0687973521,1.3939916598
H,0,3.2015327112,-1.0957280186,0.6366263343
C,0,3.1999485676,-4.0632983484,2.2983544623
H,0,1.8209908879,-4.5946904299,3.8690609828
H,0,4.4403823159,-3.2280650655,0.7424675131
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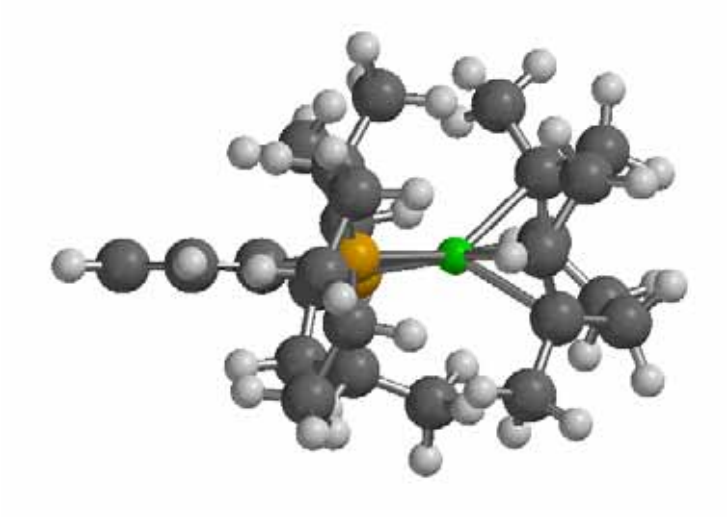
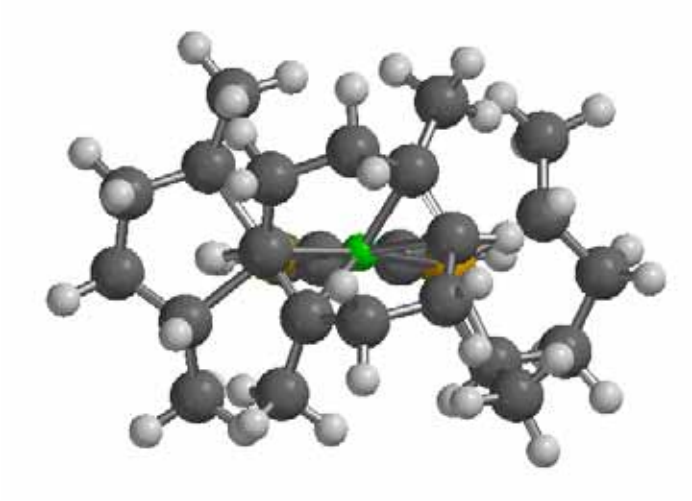
Total energy = -1886.634681 au

Zero-point energy = 418.2058 kcal/mol



side wiew



front view

Cartesian matrix (Gaussian output) and side and front view for the unstable diastereomer (*R*/*S*,*S*)-Me-COD (3a)-Rh-DUPHOS complex (Rh') calculated at B3LYP/6-31G(d)-SDD

Rh,0,-0.2057326457,-0.062744772,-0.0247881486
C,0,0.1331693154,0.1188483002,2.2373072984
C,0,1.3877794391,-0.0278754195,1.6565447713
C,0,-0.3195579422,2.1492568476,0.1846013086
C,0,0.8298619144,1.815382716,-0.5629005979
P,0,0.4846028393,-2.2011372874,-0.9204337887
P,0,-1.9688621472,-0.3282234652,-1.5372624739
C,0,-0.4690655398,-2.4709749037,-2.4937035993
C,0,-1.9391755295,-2.8290444584,-4.865911691
C,0,-1.5387191266,-1.6008317374,-2.8026974086
C,0,-0.1885756209,-3.5356843002,-3.3646620559
C,0,-0.9103351334,-3.7133090593,-4.5441743518
C,0,-2.2568164307,-1.7884588352,-3.9937871926
H,0,0.6058441016,-4.2362346499,-3.1321756117
H,0,-0.6651779893,-4.5356939504,-5.2096772076
H,0,-3.0781409585,-1.1304966519,-4.2553076456
H,0,-2.5028330721,-2.9537768238,-5.7856772267
C,0,-3.1741189362,0.8937904496,-2.3336353587
C,0,-3.3192681788,-1.0817712,-0.4075146592
C,0,-4.2315866305,1.097834985,-1.2312755383
H,0,-5.0969675077,1.6380692844,-1.6323189516
H,0,-3.8218184079,1.7097194449,-0.4152596556

C,0,-4.6132198817,-0.2965355918,-0.7239872471
H,0,-5.2597524025,-0.2537359125,0.159635353
C,0,0.68508802,-3.9901182105,-0.27571402
C,0,2.332368854,-1.9976980914,-1.3629712834
C,0,3.0218579372,-3.1623920598,-0.613752971
H,0,4.0155163057,-3.356611657,-1.0340235807
H,0,3.1731835526,-2.89043447,0.438980221
C,0,2.1181193089,-4.4005941417,-0.6960072237
H,0,2.1201514227,-4.7880038942,-1.7217005261
H,0,2.48787004,-5.2108003851,-0.0567451577
C,0,-0.283831843,2.6104518823,1.6378479589
H,0,-1.0860209069,3.3392727384,1.7955744149
H,0,0.6466233264,3.1519157738,1.8372641276
C,0,-0.4748251696,1.4576815455,2.6387093459
H,0,-0.0809856424,1.7335436213,3.6299375805
H,0,-1.5494611518,1.2944470237,2.7839896709
C,0,2.2317429705,1.7731665357,0.0372290704
H,0,2.623662685,2.8023179684,0.0687465884
H,0,2.8744369345,1.240113135,-0.6730452152
C,0,2.3650246147,1.114334822,1.4244591807
H,0,2.2522170135,1.8591080087,2.2181979191
H,0,3.3843529502,0.727225623,1.5276216978
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H,0,2.6271124153,-1.0442613834,-0.9179272122
H,0,-0.0611803597,-4.591097505,-0.8053774302
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H,0,2.1014415829,-1.1751165291,-3.3850659251
H,0,2.4939196979,-2.8963484357,-3.3665572494
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H,0,0.5395066007,-5.2235514731,1.4927172854
H,0,-0.5485617207,-3.8309379152,1.5275239175
C,0,-2.6563671608,2.1829482379,-2.9726030565
H,0,-1.9209973506,1.988257919,-3.7598164992
H,0,-2.2095478404,2.8609914704,-2.2400442113

H,0,-3.4954671144,2.7149128592,-3.4361087077
C,0,-3.4879228266,-2.6013323005,-0.4803774451
H,0,-2.5731609736,-3.1320995768,-0.1964356835
H,0,-3.7706607935,-2.929257368,-1.4860489921
H,0,-4.280026417,-2.9158254951,0.2095952916
H,0,1.8253813488,-1.0229511482,1.692844708
C,0,-0.5417676641,-1.0519815101,2.9178896862
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H,0,-1.5986591776,-1.1387048087,2.6388986438
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C,0,0.8743988611,2.0203935586,-2.0632585116
H,0,1.4033322414,1.2050017084,-2.5693461484
H,0,1.4331996264,2.9438166486,-2.2790866839
H,0,-0.114468844,2.1227182624,-2.505040275
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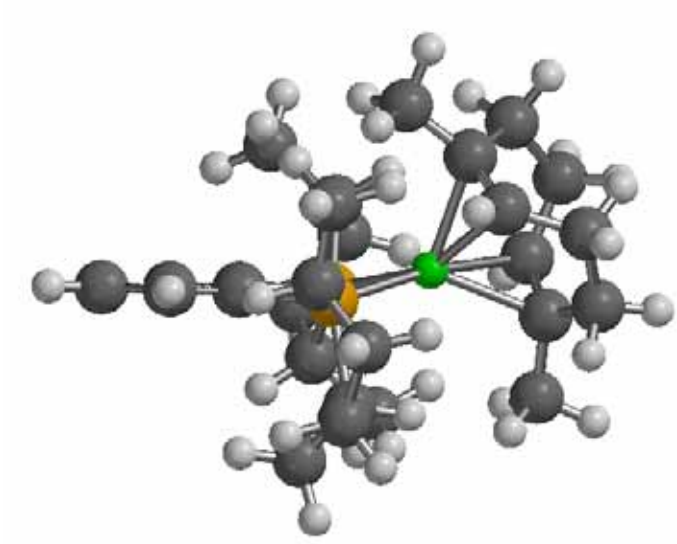
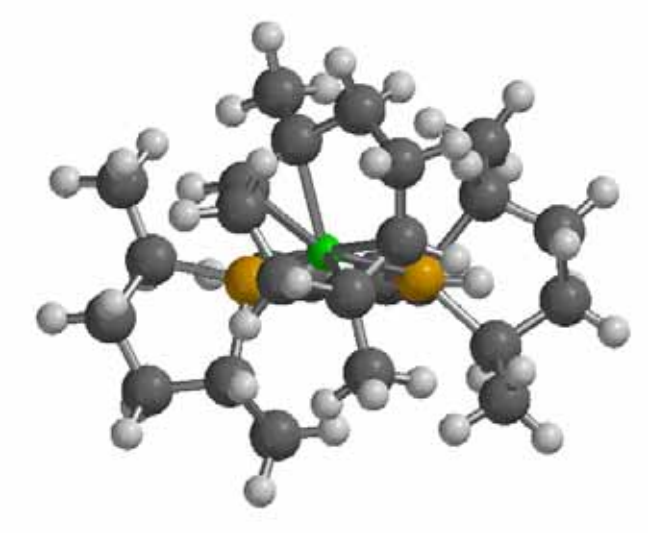
Total energy = -1886. 626167 au

Zero-point energy = 417.92299 kcal/mol



side view



front view

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[2] Kina, A.; Ueyama, K.; Hayashi, T. *Org. Lett.* **2005**, *7*, 5889-5892.

[3] Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am.Chem. Soc.* **2002,** *124*, 5052.

[4] Aikawa, K.; Akutagawa, S.; Mikami, K. *J. Am. Chem. Soc.* **2006,** *128*, 12648-12649.

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[6] For recent excellent review of *ab initio* molecular orbital theory, see F. Jensen, *Introduction to Computational Chemistry 2nd Ed*., Wiley, England, 2007.