Chiral Zirconium Catalysts Using Multidentate BINOL
Derivatives for Catalytic Enantioselective Mannich-Type
Reactions; Ligand Optimization and Approaches to
Elucidation of the Catalyst Structure.

Yoichi Ihori, Yasuhiro Yamashita, Haruro Ishitani, and Shū Kobayashi*

*Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo,
Bunkyo-Ku, Tokyo 113-0033, Japan*

Supporting Information

Table of Contents	Pages
General	S-2
Typical experimental procedure	S-2
Synthesis of multidentate ligands	S-6
NMR experiments of the chiral zirconium catalyst	S-15
X-ray structure of 6k	S-16
Computational data	S-17
References	S-25

Experimental Section

General

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400, JNM-LA500, ECX400, or ECX600 spectrometer in CDCl_3 , unless otherwise noted. Tetramethylsilane (TMS) served as internal standard (0 ppm) for ^1H NMR, and CDCl_3 was used as internal standard (77.0 ppm) for ^{13}C NMR. IR spectra were measured with a JASCO FT/IR-610 spectrometer. Optical rotations were measured with a JASCO P-1010 polarimeter. High-performance liquid chromatography was carried out using following apparatuses; SHIMADZU LC-10AT (liquid chromatograph), SHIMADZU SPD-10A (UV detector), and SHIMADZU C-R6A Chromatopac. EI high-resolution mass spectra (EI-HRMS) were measured with JEOL JMX-SX-102 Mass Spectrometer. ESI high-resolution mass spectra (ESI-HRMS) were measured with Bruker Daltonics BioTOF II. Column chromatography was conducted on Silica gel 60 (Merck) or Aluminium Oxide (activated, about 300 mesh, Wako) and preparative thin-layer chromatography was carried out using Wakogel B-5F. All solvents were distilled and dried over MS 4A. Zirconium *tert*-butoxide ($\text{Zr}(\text{O}^t\text{Bu})_4$) was purchased from Tri Chemical Laboratory, Inc. Aldimines of aromatic and heteroaromatic aldehydes were prepared from the corresponding aldehydes and 2-aminophenol by usual method.¹ The crude aldimines were recrystallized from ethanol to give the pure materials. Ketene silyl acetals were prepared according to the literature's methods.² All reactions were carried out under argon atmosphere in well-dried glassware.

Typical experimental procedure for asymmetric Mannich-type reactions using a chiral zirconium catalyst.

A typical procedure is described for the reaction of aldimine **1a** and silyl enol ether **2a**. To a toluene (0.25 mL) solution of ligand **4** (0.040 mmol) were added $\text{Zr}(\text{O}^t\text{Bu})_4$ (0.040 mmol) in toluene (0.5 mL) and *N*-methylimidazole (NMI, 0.048 mmol) in toluene (0.25 mL) at room temperature. The mixture

was stirred for 1 h at the same temperature, and cooled to 0 °C. **1a** (0.40 mmol) in toluene (0.5 mL) and **2a** (0.48 mmol) in toluene (0.5 mL) were successively added. The reaction mixture was stirred for 20 h, and a saturated aqueous NaHCO₃ solution was added to quench the reaction. After separation of the organic layer, the aqueous layer was extracted with CH₂Cl₂, and then the organic layers were combined and dried over anhydrous Na₂SO₄. After filtration and concentration under reduced pressure, the crude product obtained was treated with THF-1M HCl (20:1) at 0 °C for 2 h. The solution was then basicified with a saturated aqueous NaHCO₃ solution and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄. After filtration and concentration under reduced pressure, the crude product was purified by preparative thin layer chromatography to afford the desired product.³ The optical purity was determined by HPLC analysis using a chiral column (*vide infra*). In the case of **1d**, the optical purity was determined after methylation of the hydroxyl group.

Ethyl 3-phenyl-3-(2-hydroxyphenylamino)-2,2-dimethyl-propanoate (3ab): IR [cm⁻¹] (neat) 3421, 1701, 1611, 1522, 1453, 1259, 1185, 1140, 736, 705; ¹H NMR (CDCl₃) δ 1.18 (t, 3H, *J* = 7.3), 1.20 (s, 3H), 1.24 (s, 3H), 4.13 (m, 2H), 4.59 (s, 1H), 5.03 (br, 1H), 6.27 (br, 1H), 6.38 (d, 1H, *J* = 7.8 Hz), 6.47 (dd, 1H, *J* = 7.8, 7.3 Hz), 6.59 (dd, 1H, *J* = 7.8, 7.3 Hz), 6.67 (d, 1H, *J* = 7.8 Hz), 7.16-7.30 (m, 5H); ¹³C NMR (CDCl₃) δ 13.9, 19.9, 24.4, 47.2, 61.2, 64.4, 113.2, 114.2, 117.5, 120.9, 127.3, 127.8, 128.4, 135.7, 139.0, 144.0, 177.4; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 1.0 mL/min: *t*_R = 8.1 min (3*R*), *t*_R = 13.9 min (3*S*); ESI-HRMS (*m/z*) Calcd for C₁₉H₂₂NO₃ (M-H⁺) 312.1600, found 312.1597.

Methyl 3-(3-chlorophenyl)-3-(2-hydroxyphenylamino)-2,2-dimethyl-propanoate (3ca): Mp 138.5-140.5 °C; IR [cm⁻¹] (neat) 3373, 2881, 1707, 1514, 1266, 744; ¹H NMR (CDCl₃) δ 1.21 (s, 3H), 1.25 (s, 3H), 3.67 (s, 3H), 4.55 (s, 1H), 6.35 (d, 1H, *J* = 7.6 Hz), 6.52 (dd, 1H, *J* = 7.6, 7.6 Hz), 6.63 (dd, 1H, *J* = 7.6, 7.6 Hz), 6.68 (d, 1H, *J* = 7.6 Hz), 7.16-7.20 (m, 3H), 7.29 (s, 1H); ¹³C NMR (CDCl₃) δ 20.2, 24.1, 47.3, 52.3, 64.0, 113.0, 114.3, 117.8, 121.0, 126.5,

127.7, 128.3, 129.2, 134.0, 135.4, 141.5, 143.9, 177.5; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 0.8 mL/min: t_R = 10.7 min (3*R*), t_R = 11.9 min (3*S*); ESI-HRMS (m/z) Calcd for $C_{18}H_{21}ClNO_3$ ($M-H^+$) 334.1210, found 334.1200.

Methyl 3-(2'-hydroxyphenylamino)-3-(4'-methoxyphenyl)-2,2'-dimethylpropionate (3da): IR [cm^{-1}] (neat) 3420, 2979, 1715, 1612, 1510, 1252; 1H NMR ($CDCl_3$) δ 1.20 (s, 3H), 1.22 (s, 3H), 3.68 (s, 3H), 3.76 (s, 3H), 4.50 (s, 1H), 6.39 (d, 1H, J = 7.9 Hz), 6.35 (dd, 1H, J = 7.6, 7.6 Hz), 6.62 (dd, 1H, J = 7.6, 7.6 Hz), 6.68 (d, 1H, J = 7.9 Hz), 6.81 (d, 1H, J = 8.5 Hz), 7.19 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 20.1, 24.4, 47.5, 52.2, 55.2, 64.2, 113.4, 114.3, 115.3, 117.2, 118.1, 119.7, 121.1, 129.4, 131.0, 135.6, 144.4, 158.8, 177.8; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 1.0 mL/min: t_R = 11.1 min (3*R*), t_R = 28.0 min (3*S*); EI-HRMS (m/z) Calcd for $C_{19}H_{23}NO_4$ (M^+) 329.1627, found 329.1638.

Methyl 3-(2'-hydroxyphenylamino)-3-(2'-methylphenyl)-2,2'-dimethylpropionate (3ea): Mp 175-176 °C; IR [cm^{-1}] (KBr) 3413, 1711, 1521, 1194, 1143, 734; 1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.26 (s, 3H), 2.46 (s, 3H), 3.71 (s, 3H), 4.90 (s, 1H), 6.32 (d, 1H, J = 7.0 Hz), 6.55 (dd, 1H, J = 7.0, 7.3 Hz), 6.60 (dd, 1H, J = 7.0, 7.3 Hz), 6.69 (d, 1H, J = 7.3 Hz), 7.11-7.13 (m, 3H), 7.30 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 19.7, 20.4, 24.5, 48.5, 52.3, 59.5, 114.5, 114.8, 118.7, 121.0, 125.8, 127.1, 127.2, 130.5, 135.4, 136.9, 137.6, 145.1, 178.0; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 1.0 mL/min: t_R = 8.8 min (3*R*), t_R = 15.1 min (3*S*); EI-HRMS (m/z) Calcd for $C_{19}H_{23}NO_3$ (M^+) 313.1678, found 313.1701.

S-Ethyl 3-(2-hydroxyphenyl)amino-3-(2'-methylphenyl)propanethioate (3ec): IR [cm^{-1}] (neat) 3409, 1668, 1605, 1516, 1451, 1366, 1264; 1H NMR ($CDCl_3$) δ 1.22 (t, 3H, J = 7.3 Hz), 2.39 (s, 3H), 2.89 (q, 2H), 2.94 (dd, 1H, J = 4.9, 14.9 Hz), 2.99 (dd, 1H, J = 8.8, 14.9 Hz), 5.01 (dd, 1H, J = 4.9, 8.8 Hz), 6.34 (d, 1H, J = 1.5 Hz), 6.36-6.61 (m, 4H), 6.63 (d, 1H, J = 1.5 Hz), 7.14-7.39 (m, 3H), 7.39 (d, 1H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.5, 19.1, 50.1, 52.5,

114.5, 115.0, 119.2, 121.2, 125.2, 126.6, 127.3, 130.8, 135.0, 135.1, 140.0, 145.0, 198.1; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 19/1, flow rate = 1.0 mL/min: t_R = 16.7 min (3*R*), t_R = 25.8 min (3*S*); EI-HRMS (m/z) Calcd for $C_{18}H_{21}NO_2S$ (M^+) 315.1293, found 315.1303.

Methyl 3-(2-hydroxyphenylamino)-2,2-dimethyl-3-*p*-tolylpropanoate (3fa): Mp 114.5-116.5 °C; IR [cm^{-1}] (neat) 3419, 2975, 1718, 1514, 1266, 737; 1H NMR ($CDCl_3$) δ 1.21 (s, 3H), 1.22 (s, 3H), 2.29 (s, 3H), 3.69 (s, 3H), 4.51 (s, 1H), 6.39 (d, 1H, J = 7.6 Hz), 6.53 (dd, 1H, J = 7.6, 7.6 Hz), 6.61 (dd, 1H, J = 7.6, 7.6 Hz), 6.69 (d, 1H, J = 7.6 Hz), 7.07 (d, 2H, J = 7.6 Hz), 7.15 (d, 2H, J = 7.6 Hz), 7.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.0, 21.1, 24.4, 47.4, 52.1, 64.5, 114.3, 114.6, 118.2, 121.1, 128.2, 128.7, 135.5, 135.9, 137.0, 144.5, 177.7; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 1.0 mL/min: t_R = 7.7 min (3*R*), t_R = 16.2 min (3*S*); ESI-HRMS (m/z) Calcd for $C_{19}H_{24}NO_3$ ($M-H^+$) 313.1756, found 314.1747.

Methyl 3-(2-hydroxyphenylamino)-2,2-dimethyl-3-(4-(trifluoromethyl)phenyl)propanoate (3ga): Mp 110-111 °C; IR [cm^{-1}] (neat) 3501, 1709, 1617, 1518, 1067, 740; 1H NMR ($CDCl_3$) δ 1.22 (s, 3H), 1.27 (s, 3H), 3.70 (s, 3H), 4.62 (d, 1H, J = 7.6 Hz), 6.31 (dd, 1H, J = 1.38, 7.6 Hz), 6.55 (ddd, 1H, J = 1.38, 7.6, 7.6 Hz), 6.63 (ddd, 1H, J = 1.38, 7.6, 7.6 Hz), 6.69 (dd, 1H, J = 1.38, 7.6 Hz), 7.42 (d, 2H, J = 8.2 Hz), 7.54 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 20.3, 24.3, 47.2, 52.3, 64.3, 113.5, 114.4, 118.1, 121.3, 123.2, 125.0, 128.7, 129.7 (q, J = 33 Hz), 135.2, 143.5, 143.9, 177.0; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$: 0 ppm) δ -62.8; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 1.0 mL/min: t_R = 6.4 min (3*R*), t_R = 11.3 min (3*S*); ESI-HRMS (m/z) Calcd for $C_{19}H_{21}F_3NO_3$ ($M-H^+$) 368.1473, found 368.1456.

Methyl 3-(2'-hydroxyphenylamino)-3-(2'-naphthyl)-2,2'-dimethylpropionate (3ia): Mp 165 -166 °C; IR [cm^{-1}] (KBr) 3418, 1710, 1610, 1510, 1270, 736; 1H NMR ($CDCl_3$) δ 1.26 (s, 3H), 1.29 (s, 3H), 3.70 (s, 3H), 4.71 (s, 1H), 6.40-6.70 (m, 4H) 7.41-7.46 (m, 3H), 7.75-7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.2, 24.5, 47.6, 52.3, 64.8, 114.0, 114.3, 118.0, 121.1, 125.8, 126.2,

127.5, 127.6, 127.6, 127.9, 132.9, 133.0, 135.5, 136.7, 144.3, 177.7; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 0.8 mL/min: t_R = 12.2 min (3*R*), t_R = 26.0 min (3*S*); EI-HRMS (m/z) Calcd for C₂₂H₂₃NO₃ (M⁺) 349.1678, found 349.1671.

S-Ethyl 3-(2-hydroxyphenyl)amino-3-(2'-naphthyl)propanethioate (3ic): Mp 118-119 °C; IR [cm⁻¹] (KBr) 3391, 1642, 1609, 1522, 1449, 734; ¹H NMR (CDCl₃) δ 1.19 (t, 3H, *J* = 7.3 Hz), 2.87 (q, 2H, *J* = 7.3 Hz), 3.07 (dd, 1H, *J* = 5.2, 14.9 Hz), 3.15 (dd, 1H, *J* = 8.5, 14.9 Hz), 4.95 (dd, 1H, *J* = 5.2, 8.5 Hz), 6.61-6.75 (m, 4H), 7.43-7.48 (m, 3H), 7.76-7.81 (m, 4H); ¹³C NMR (CDCl₃) δ 14.5, 23.7, 51.5, 56.6, 114.6, 115.6, 119.4, 121.2, 124.3, 125.3, 125.9, 126.2, 127.7, 127.9, 128.7, 133.0, 133.4, 139.3, 145.1, 198.0; HPLC Daicel Chiralpak AS, hexane/2-PrOH = 19/1, flow rate = 1.0 mL/min: t_R = 15.0 min (3*R*), t_R = 19.5 min (3*S*); EI-HRMS (m/z) Calcd for C₂₁H₂₁NO₂S (M⁺) 351.1293, found 351.1303.

Methyl 3-(furan-3-yl)-3-(2-hydroxyphenylamino)-2,2-dimethylpropanoate (3ka): IR [cm⁻¹] (neat) 3407, 1712, 1610, 1523, 1266, 739; ¹H NMR (CDCl₃) δ 1.25 (s, 3H), 1.28 (s, 3H), 3.71 (s, 3H), 4.52 (s, 1H), 6.31 (s, 1H), 6.57-6.74 (m, 4H), 7.27 (s, 1H), 7.32 (s, 1H); ¹³C NMR (CDCl₃) δ 20.4, 23.7, 47.3, 52.3, 57.6, 110.0, 114.6, 116.0, 119.5, 121.0, 123.7, 135.2, 140.9, 142.9, 145.6, 177.8; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 19/1, flow rate = 0.5 mL/min: t_R = 44.2 min (3*R*), t_R = 47.4 min (3*S*); ESI-HRMS (m/z) Calcd for C₁₆H₂₀NO₄ (M-H⁺) 290.1382, found 290.1385.

Methyl 3-(2'-hydroxyphenylamino)-3-(2'-thienyl)-2,2'-dimethyl-propionate (3la): Mp 120-121 °C; IR [cm⁻¹] (KBr) 3396, 1708, 1511, 1270, 1137, 736; ¹H NMR (CDCl₃) δ 1.62 (s, 3H), 1.66 (s, 3H), 4.05 (s, 3H), 5.17 (s, 1H), 6.86-7.06 (m, 4H), 7.23-7.24 (m, 2H), 7.48-7.50 (m, 1H); ¹³C NMR (CDCl₃) δ 20.6, 23.9, 47.6, 52.3, 61.2, 114.6, 115.2, 115.3, 115.3, 115.3, 115.3, 119.3, 119.4, 121.0, 124.5, 126.3, 126.4, 134.9, 143.6, 145.1, 177.5, 177.5; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 1.0 mL/min: t_R = 9.8 min (3*S*), t_R = 11.7 min (3*R*); EI-HRMS (m/z) Calcd for C₁₆H₁₉NO₃S (M⁺) 305.1086, found

305.1086.

Synthesis of Multidentate Ligands

Synthesis of (*R*)-(*R*)-Bis-BINOL-methane (**4**)

A pentane solution of *t*-BuLi (1.60 M, 22.0 mL, 35.2 mmol) was added to a THF (325 mL) solution of (*R*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (13.0 g, 34.8 mmol) dropwise over 20 min period at $-78\text{ }^{\circ}\text{C}$.⁴ After stirred for 3.5 h at $-78\text{ }^{\circ}\text{C}$, (*R*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene-3-carbaldehyde (6.95 g, 17.3 mmol) in THF (50 mL) was added to the mixture at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to warm to rt slowly, and then poured into a saturated aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water, a saturated aqueous NH_4Cl solution, and brine successively, and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography to give the coupling product (10.1 g, diastereomer mixture). A CH_2Cl_2 (20 mL) solution of the coupling product (1.69 g, 2.18 mmol) was added to the mixture of NaBH_4 (997 mg, 26.4 mmol) in CH_2Cl_2 (20 mL) and trifluoroacetic acid (20 mL) at $0\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 2 h at the same temperature, and then basicified with K_2CO_3 . The mixture was poured into water, and then extracted with CH_2Cl_2 . The organic layers were combined, and then dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to give **4** (981 mg, 78% yield).

(*R*)-(*R*)-Bis-BINOL-methane (4**):** $[\alpha]_{\text{D}}^{31} +68.4$ (c 1.37, THF); Mp $198\text{--}200\text{ }^{\circ}\text{C}$; IR $[\text{cm}^{-1}]$ (KBr) 3466, 1718, 1622, 1385, 1208, 750; ^1H NMR (CDCl_3) δ 4.47 (s, 2H), 5.09 (s, 2H), 5.44 (s, 2H), 7.11 (d, 2H, $J = 8.3\text{ Hz}$), 7.17 (d, 2H, $J = 7.8\text{ Hz}$), 7.22–7.35 (m, 10H), 7.79 (d, 2H, $J = 7.8\text{ Hz}$), 7.83 (d, 2H, $J = 7.8\text{ Hz}$), 7.86 (s, 2H), 7.88 (d, 2H, $J = 8.8\text{ Hz}$); ^{13}C NMR (CDCl_3) δ 31.6, 111.2, 111.2, 117.7, 124.0, 124.1, 124.1, 124.2, 126.8, 127.4, 127.9, 128.4, 128.8, 129.4, 129.4, 131.0, 131.3, 132.4, 133.3, 151.5, 152.7; EI-HRMS (m/z) Calcd for

C₄₁H₂₈O₄ (M⁺) 584.1988, found 584.1991.

Synthesis of (*R*)-(*R*)-Bis-BINOL-methane-monomethylether (**5**)

Monomethylether derivative **5** was also prepared by a similar procedure to the synthesis of **4** using (*R*)-2'-methoxy-2-methoxymethoxy-1,1'-binaphthalene as a starting material.⁵

(*R*)-(*R*)-3-(2-Hydroxy-2'-methoxy-1,1'-binaphthalene-3-ylmethyl)-1,1'-binaphthalene-2,2'-diol (5**):** [α]_D³¹ +71.2 (c 1.03, THF); Mp 172-174 °C; IR [cm⁻¹] (KBr) 3523, 3060, 2251, 1208, 907, 730; ¹H NMR (CDCl₃) δ 3.77 (s, 3H), 4.47 (d, 1H, *J* = 16.5 Hz), 4.52 (d, 1H, *J* = 16.5 Hz), 5.22 (s, 1H, OH), 5.29 (s, 1H, OH), 5.63 (s, 1H, OH), 7.03 (d, 1H, *J* = 8.7 Hz), 7.11 (d, 1H, *J* = 8.2 Hz), 7.18-7.37 (m, 12H), 7.46 (d, 1H, *J* = 9.2 Hz), 7.80 (dd, 1H, *J* = 8.3, 8.3 Hz), 7.84-7.89 (m, 2H), 7.94 (d, 1H, 8.7 Hz), 8.03 (d, 1H, *J* = 9.2 Hz); ¹³C NMR (CDCl₃) δ 31.7, 56.7, 111.0, 111.7, 113.8, 115.4, 115.5, 117.7, 123.4, 123.9, 124.0, 124.1, 124.2, 124.4, 124.8, 125.9, 126.7, 127.3, 127.4, 127.7, 127.9, 128.0, 128.2, 128.3, 129.2, 129.4, 129.5, 129.8, 130.7, 131.1, 131.1, 132.4, 132.9, 133.4, 134.0, 149.9, 151.7, 152.6, 156.0; ESI-HRMS (*m/z*) calcd. for C₄₂H₂₉O₄(M-H⁺): 597.2071; found: 597.2071

Syntheses of tridentate BINOL derivative (**6**)

Typical experimental procedures are described for the synthesis of **6e**, **6j** and **6k**.

Synthesis of (*R*)-3-(2-Hydroxy-3-isopropylbenzyl)-1,1'-binaphthalene-2,2'-diol (**6e**)

2-Isopropylphenol (3.00 g, 22.0 mmol) in THF (10 mL) was added dropwise to a suspension of sodium hydride (60%; 2.2 g, 55.0 mmol) in THF (25 mL) at 0 °C. After stirred for 15 min at rt and 20 min at 0 °C, chloromethyl methyl ether (3.30 mL, 43.9 mmol) was added dropwise to the reaction mixture. The reaction mixture was allowed to warm to room temperature. The reaction was carefully quenched with MeOH and water. The aqueous layer was extracted with Et₂O, and the combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. The solvent was removed under

reduced pressure. The residue was purified by silica gel column chromatography to give 1-isopropyl-2-methoxymethyloxybenzene⁶ (3.38 g, 85% yield)

1-Isopropyl-2-methoxymethyloxybenzene: ¹H NMR (CDCl₃) δ 1.27 (d, 6H, *J* = 6.9 Hz), 3.39 (sept, 1H, *J* = 6.9 Hz), 3.53 (s, 3H), 5.25 (s, 2H), 7.02 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.11 (d, 1H, *J* = 8.2 Hz), 7.17 (ddd, 1H, *J* = 8.2, 7.6, 1.4 Hz), 7.27 (dd, 1H, *J* = 7.6, 1.4 Hz); ¹³C NMR (CDCl₃) δ 22.8, 26.8, 56.0, 94.4, 113.9, 121.8, 126.1, 126.5, 137.5, 154.3.

A hexane solution of *n*-butyllithium (1.59 M; 3.2 mL, 5.1 mmol) was added to 1-isopropyl-2-methoxymethyloxybenzene (896 mg, 4.97 mmol) and TMEDA (0.83 mL, 5.5 mmol) in THF (9 mL) at -78 °C. After stirred for 30 min at -78 °C and for 30 min at 0 °C, and then the mixture was cooled at -78 °C again. This mixture was added to a THF solution (20 mL) of (*R*)-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene-3-carbaldehyde (1.00 g, 2.49 mmol) at -78 °C. The mixture was allowed to warm to room temperature slowly, and then poured into a saturated aqueous NH₄Cl solution and extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to give (*R*)-[2,2'-bis(methoxymethyloxy)-1,1'-binaphthyl-3-yl]-(3-isopropyl-2-methoxymethyloxyphenyl)methanol as a 1:1 diastereomer mixture (1.23 g, 85% yield). Saturated methanolic HCl (2 mL) was added to this alcohol (600 mg, 1.03 mmol) in CH₂Cl₂ (5 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, and poured into a saturated aqueous NaHCO₃ solution and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to give (*R*)-1-(2-hydroxynaphthalen-1-yl)-3-[2-hydroxyphenyl(methoxy)methyl]naphthalene-2-ol (425 mg, 85% yield). To this methylether derivative (162 mg, 0.348 mmol) in CH₂Cl₂ (2 mL) was added CH₂Cl₂ (1 mL) solution of Et₃SiH (134 mg, 1.15 mmol) and CH₂Cl₂ (1 mL) of BF₃•Et₂O (0.14 mL, 1.10 mmol) successively at 0 °C. The reaction mixture was

stirred for 4 h at the same temperature, and was quenched with a saturated aqueous NaHCO₃ solution at 0 °C and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to give **6e** (143 mg, 94% yield).

(R)-3-(2-Hydroxy-3-isopropylbenzyl)-1,1'-binaphthalene-2,2'-diol (6e): $[\alpha]_D^{30} +63.6$ (c 1.03, THF); Mp 205-206 °C; IR [cm⁻¹] (KBr) 3505, 3425, 1592, 1463, 820, 751; ¹H NMR (CDCl₃) δ 1.20 (d, 3H, *J* = 6.8 Hz), 1.21 (d, 3H, *J* = 6.8 Hz), 3.25 (sept, 1H, *J* = 6.8 Hz), 4.17 (d, 1H, *J* = 14.9 Hz), 4.23 (d, 1H, *J* = 14.9 Hz), 4.99 (s, 1H), 5.63 (s, 1H), 6.51 (s, 1H), 6.90 (ddd, 1H, *J* = 1.5, 7.5, 7.5 Hz), 7.08-7.11 (m, 3H), 7.22-7.39 (m, 6H), 7.82 (d, 1H, *J* = 7.9 Hz), 7.88 (d, 1H, *J* = 8.1 Hz), 7.93 (s, 1H), 7.97 (d, 1H, *J* = 9.0 Hz); ¹³C NMR (CDCl₃) δ 22.5, 22.8, 27.1, 31.5, 108.9, 110.6, 111.5, 117.8, 120.6, 124.1, 124.2, 124.5, 124.9, 125.9, 127.1, 127.6, 128.0, 128.1, 128.5, 128.8, 129.5, 129.9, 131.2, 131.7, 132.2, 133.2, 135.8, 149.8, 151.1, 152.8; HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 1.0 mL/min: *t*_R = 10.8 min (*R*), *t*_R = 15.7 min (*S*); EI-HRMS (*m/z*) Calcd for C₃₀H₂₆O₃ (*M*⁺) 434.1882, found 434.1882.

(R)-3-(2-Hydroxy-3-trifluoromethylbenzyl)-1,1'-binaphthalene-2,2'-diol (6b): $[\alpha]_D^{30} +58.9$ (c 1.02, THF); Mp 159-160 °C; IR [cm⁻¹] (KBr) 3523, 3298, 1599, 1474, 1324, 752; ¹H NMR (CDCl₃) δ 4.21 (d, 1H, *J* = 14.9 Hz), 4.24 (d, 1H, *J* = 14.9 Hz), 5.00 (s, 1H), 5.65 (s, 1H), 6.97 (dd, 1H, *J* = 7.6, 7.9 Hz), 7.08 (d, 1H, *J* = 8.5 Hz), 7.12 (d, 1H, *J* = 8.5 Hz), 7.22 (s, 1H), 7.25-7.39 (m, 4H), 7.43 (d, 1H, *J* = 7.9 Hz), 7.56 (d, 1H, *J* = 7.3 Hz), 7.84 (d, 1H, *J* = 8.2 Hz), 7.88 (d, 1H, *J* = 8.2 Hz), 7.93 (s, 1H), 7.98 (d, 1H, *J* = 9.1 Hz); ¹³C NMR (CDCl₃) δ 31.0, 110.2, 112.0, 117.9, 117.9 (q, *J* = 30 Hz), 124.0, 124.1 (q, *J* = 273 Hz), 124.2, 124.3, 124.7, 125.6 (q, *J* = 5.1 Hz), 127.3, 127.8, 127.8, 128.0, 128.5, 128.5, 129.5, 129.8, 131.2, 131.8, 132.4, 133.1, 134.5, 149.5, 152.3, 152.8; ¹⁹F NMR (283 MHz, CDCl₃, CF₃COOH: -76.5 Hz) δ -142.0; MS *m/z* 460 (*M*⁺); Anal. Calcd for C₂₈H₁₉F₃O₃: C, 73.04; H, 4.16. found: C, 72.87; H, 4.41.

(R)-3-(2-Hydroxy-3-methylbenzyl)-1,1'-binaphthalene-2,2'-diol (6c): $[\alpha]_D^{27}$

+54.0 (c 1.05, THF); Mp 101-102 °C; IR [cm^{-1}] (KBr) 3485, 1620, 1469, 1205, 1146, 750; ^1H NMR (CDCl_3) δ 2.20 (s, 3H), 4.13 (d, 1H, $J = 14.9$ Hz), 4.20 (d, 1H, $J = 14.9$ Hz), 5.04 (s, 1H), 5.71 (s, 1H), 6.37 (s, 1H), 6.82 (dd, 1H, $J = 7.3$, 7.6 Hz), 7.02 (d, 1H, $J = 7.3$ Hz), 7.09 (dd, 1H, $J = 7.3$, 7.3 Hz), 7.21-7.34 (m, 6H), 7.80 (d, 1H, $J = 8.1$ Hz), 7.85 (d, 1H, $J = 8.1$ Hz), 7.89 (s, 1H), 7.93 (d, 1H, $J = 9.0$ Hz); ^{13}C NMR (CDCl_3) δ 16.2, 31.3, 110.8, 111.6, 117.8, 120.5, 124.1, 124.1, 124.4, 125.2, 125.7, 127.0, 127.6, 128.0, 128.4, 128.5, 128.9, 129.4, 129.5, 129.8, 131.0, 131.5, 132.3, 133.3, 149.9, 152.1, 152.8; EI-HRMS (m/z) Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_3$ (M^+) 406.1569, found 406.1580.

(R)-3-(3-Ethyl-2-hydroxybenzyl)-1,1'-binaphthalene-2,2'-diol (6d): $[\alpha]_{\text{D}}^{30}$ +60.7 (c 1.05, THF); Mp 157-158 °C; IR [cm^{-1}] (KBr) 3433, 1618, 1593, 1505, 1466, 752; ^1H NMR (CDCl_3) δ 1.20 (t, 3H, $J = 7.5$ Hz), 2.62 (q, 2H, $J = 7.5$ Hz), 4.16 (d, 1H, $J = 15$ Hz), 4.22 (d, 1H, $J = 15$ Hz), 4.99 (s, 1H), 5.62 (s, 1H), 6.41 (s, 1H), 6.87 (dd, 1H, $J = 7.5$, 7.5 Hz), 7.04-7.11 (m, 3H), 7.25-7.38 (m, 6H), 7.82 (d, 1H, $J = 7.9$ Hz), 7.89 (d, 1H, $J = 7.9$ Hz), 7.92 (s, 1H), 7.97 (d, 1H, $J = 8.99$ Hz); ^{13}C NMR (CDCl_3) δ 14.0, 23.3, 31.3, 110.6, 111.5, 117.8, 120.6, 124.1, 124.5, 125.8, 127.0, 127.6, 127.8, 128.0, 128.4, 128.4, 128.8, 129.5, 129.8, 131.1, 131.3, 131.6, 132.2, 133.2, 149.8, 151.7, 152.8; MS m/z 420 (M^+); Anal. Calcd for $\text{C}_{29}\text{H}_{24}\text{O}_3$: C, 82.83; H, 5.75. found: C, 82.61; H, 5.92.

(R)-3-(3-tert-Butyl-2-hydroxybenzyl)-1,1'-binaphthalene-2,2'-diol (6f): $[\alpha]_{\text{D}}^{30}$ +73.2 (c 1.20, THF); Mp 248-250 °C; IR [cm^{-1}] (KBr) 3478, 1620, 1595, 1439, 1226, 751; ^1H NMR (CDCl_3) δ 1.38 (s, 9H), 4.17 (d, 1H, $J = 15$ Hz), 4.22 (d, 1H, $J = 15$ Hz), 4.99 (s, 1H), 5.59 (s, 1H), 6.71 (s, 1H), 6.87 (dd, 1H, $J = 7.5$, 7.7 Hz), 7.09-7.12 (m, 2H), 7.18-7.41 (m, 7H), 7.81 (d, 1H, $J = 7.7$ Hz), 7.90 (d, 1H, $J = 8.1$ Hz), 7.92 (s, 1H), 7.99 (d, 1H, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3) δ 29.7, 31.4, 34.8, 110.4, 111.5, 117.8, 120.1, 124.0, 124.1, 124.2, 124.5, 125.7, 126.7, 127.1, 127.7, 128.1, 128.5, 128.6, 128.6, 129.5, 129.9, 131.2, 131.7, 132.1, 133.1, 137.2, 149.6, 152.9, 152.9; MS m/z 448 (M^+); Anal. Calcd for $\text{C}_{31}\text{H}_{28}\text{O}_3$: C, 83.01; H, 6.29. found: C, 82.87; H, 6.44.

(R)-3-(2-Hydroxybiphenyl-3-ylmethyl)-1,1'-binaphthalene-2,2'-diol (6g):

$[\alpha]_D^{26} +48.2$ (c 0.13, THF); Mp 107-109 °C; IR [cm^{-1}] (KBr) 3492, 1620, 1434, 1212, 1147, 750; ^1H NMR (CDCl_3) δ 4.25 (d, 1H, $J = 15$ Hz), 4.30 (d, 1H, $J = 15$ Hz), 5.07 (s, 1H), 5.76 (s, 1H), 6.06 (s, 1H), 6.98 (dd, 1H, $J = 7.6, 7.6$ Hz), 7.08-7.48 (m, 14H), 7.80-7.93 (m, 4H); ^{13}C NMR (CDCl_3) δ 31.2, 111.4, 111.5, 117.7, 120.8, 123.9, 124.1, 124.1, 124.3, 126.6, 126.8, 127.3, 127.7, 127.9, 128.4, 128.7, 129.0, 129.1, 129.2, 129.4, 129.5, 130.4, 130.9, 131.2, 132.4, 133.3, 137.5, 150.3, 151.0, 152.5; EI-HRMS (m/z) Calcd for $\text{C}_{33}\text{H}_{24}\text{O}_3$ (M^+) 468.1725, found 468.1735.

(*R*)-3-(3-Hydroxy-4-trifluoromethylbenzyl)-1,1'-binaphthalene-2,2'-diol

(6h): $[\alpha]_D^{26} +46.9$ (c 0.095, THF); Mp 224-225 °C; IR [cm^{-1}] (KBr) 3476, 1620, 1430, 1332, 1122, 748; ^1H NMR (CDCl_3) δ 4.19 (d, 1H, $J = 15$ Hz), 4.24 (d, 1H, $J = 15$ Hz), 5.03 (s, 1H), 5.67 (s, 1H), 6.78 (s, 1H), 7.09 (d, 1H, $J = 8.2$ Hz), 7.11 (d, 1H, $J = 8.8$ Hz), 7.17 (d, 1H, $J = 7.9$ Hz), 7.27-7.39 (m, 6H), 7.47 (d, 1H, $J = 7.9$ Hz), 7.84 (d, 1H, $J = 8.2$ Hz), 7.89 (d, 1H, $J = 8.2$ Hz), 7.91 (s, 1H), 7.98 (d, 1H, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3) δ 31.2, 110.4, 111.9, 113.8 (q, $J = 4.1$ Hz), 117.6 (q, $J = 4.1$ Hz), 117.9, 123.9 (q, $J = 272$ Hz), 124.0, 124.2, 124.7, 127.3, 127.7, 127.7, 128.0, 128.5, 129.5, 129.8, 130.3, 130.5 (q, $J = 32$ Hz), 131.1, 131.3, 131.8, 132.4, 133.2, 149.7, 152.8, 154.1; ^{19}F NMR (283 MHz, CDCl_3 , CF_3COOH : -76.5 ppm) δ -142.9; EI-HRMS (m/z) Calcd for $\text{C}_{28}\text{H}_{19}\text{O}_3\text{F}_3$ (M^+) 460.1286, found 460.1300.

(*R*)-3-(4-Hydroxybiphenyl-3-ylmethyl)-1,1'-binaphthalene-2,2'-diol (6i):

$[\alpha]_D^{26} +56.8$ (c 1.35, THF); Mp 112-114 °C; IR [cm^{-1}] (KBr) 3400, 1620, 1486, 1265, 1211, 751; ^1H NMR (CDCl_3) δ 4.14 (d, 1H, $J = 15$ Hz), 4.19 (d, 1H, $J = 15$ Hz), 5.11 (s, 1H), 5.95 (s, 1H), 6.64 (s, 1H), 6.77 (d, 1H, $J = 8.3$ Hz), 7.04-7.05 (m, 2H), 7.17-7.56 (m, 12H), 7.73-7.87 (m, 4H); ^{13}C NMR (CDCl_3) δ 31.3, 111.1, 111.8, 116.8, 117.7, 124.0, 124.1, 124.1, 124.3, 126.5, 126.6, 126.7, 126.8, 126.9, 127.4, 127.9, 128.3, 128.7, 128.7, 129.3, 129.5, 129.7, 130.9, 131.3, 132.4, 133.3, 134.2, 140.8, 150.0, 152.5, 153.1; EI-HRMS (m/z) Calcd for $\text{C}_{33}\text{H}_{24}\text{O}_3$ (M^+) 468.1725, found 468.1731.

Synthesis of 6j and 6k

NaH (60% in oil, 223 mg, 5.58 mmol) was added to (*R*)-(2,2'-dimethoxymethyloxy-1,1'-binaphthalen-3-yl)-(3-isopropyl-2-methoxymethyloxyphenyl)methanol in DMF (10 mL) at 0 °C. The reaction mixture was stirred for 45 min at room temperature, and then cooled to 0 °C again. MeI (1.83 g, 12.9 mmol) was added to the mixture at the same temperature. The reaction mixture was allowed to warm to room temperature slowly, and poured into water and extracted with Et₂O. The organic layers were washed with water and brine, dried over Na₂CO₃. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to give a diastereomer mixture of 3-[(3-Isopropyl-2-methoxymethyloxyphenyl)-methoxymethyl]-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene (674 mg, 88% yield). Saturated methanolic HCl (2 mL) was added to 3-[(3-Isopropyl-2-methoxymethyloxyphenyl)-methoxymethyl]-2,2'-bis(methoxymethyloxy)-1,1'-binaphthlene (674 mg, 1.13 mmol) in CH₂Cl₂ at 0 °C. The reaction mixture was stirred for 2 h at the same temperature, and poured into a saturated aqueous NaHCO₃ solution and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to give **6j** (71.3 mg, 14% yield), **6k** (159 mg, 31% yield) and a mixture of **6j** and **6k** (138 mg, 27% yield). The stereochemistry of **6k** was confirmed by single crystal X-ray analysis.

(*R*)-3-[(*R*)-(2-Hydroxy-3-isopropylphenyl)-methoxymethyl]-1,1'-

binaphthalene-2,2'-diol (6j**):** [α]_D³⁰ +26.8 (c 0.74, THF); Mp 161-162 °C; IR [cm⁻¹] (KBr) 3346, 1596, 1453, 1383, 1131, 750; ¹H NMR (CDCl₃) δ 1.28 (d, 3H, *J* = 6.8 Hz), 1.30 (d, 3H, *J* = 6.8 Hz), 3.41 (sept, 1H, *J* = 6.8 Hz), 3.57 (s, 3H), 5.09 (s, 1H), 6.01 (s, 1H), 6.30 (s, 1H), 6.87 (dd, 1H, *J* = 7.3, 7.6 Hz), 6.93 (dd, 1H, *J* = 1.7, 7.6 Hz), 7.09-7.15 (m, 2H), 7.23-7.38 (m, 5H), 7.73 (s, 1H), 7.77 (d, 1H, *J* = 8.1 Hz), 7.86-7.88 (m, 2H), 7.94 (d, 1H, *J* = 8.8 Hz); ¹³C NMR (CDCl₃) δ 22.6, 26.7, 57.5, 82.8, 112.0, 112.6, 117.7, 120.0, 122.4, 123.8, 124.2, 124.3, 124.3, 126.3, 126.5, 127.2, 127.3, 127.7, 128.4, 128.8, 129.0, 129.4, 129.8, 131.0, 133.4, 133.5, 136.6, 151.3, 152.3, 153.1; MS *m/z* 464

(M⁺); Anal. Calcd for C₃₁H₂₈O₄: C, 80.15; H, 6.08. found: C, 79.90; H, 6.12.

(R)-3-[(S)-(2-Hydroxy-3-isopropylphenyl)-methoxymethyl]-1,1'-

binaphthalene-2,2'-diol (6k): [α]_D²⁹ +138.7 (c 0.95, THF); Mp 174-176 °C; IR [cm⁻¹] (KBr) 3480, 2964, 1595, 1460, 1211, 751; ¹H NMR (CDCl₃) δ 1.28 (d, 6H, *J* = 6.8 Hz), 3.40 (sept, 1H, *J* = 6.8 Hz), 3.58 (s, 3H), 5.01 (s, 1H), 6.01 (s, 1H), 6.23 (s, 1H), 6.85 (dd, 1H, 7.5, 7.7 Hz), 6.95-6.97 (m, 1H), 7.12-7.37 (m, 7H), 7.78-7.96 (m, 5H); ¹³C NMR (CDCl₃) δ 22.8, 26.8, 57.6, 82.6, 112.1, 112.6, 117.9, 120.1, 122.9, 124.0, 124.3, 124.5, 124.5, 126.4, 126.6, 127.4, 127.7, 127.8, 128.5, 128.9, 129.2, 129.6, 129.6, 131.2, 133.5, 133.6, 136.7, 151.3, 152.5, 153.1; MS *m/z* 464 (M⁺); Anal. Calcd for C₃₁H₂₈O₄: C, 80.15; H, 6.08. found: C, 79.90; H, 6.20.

Synthesis of 6a and 7

6a and **7** were also synthesized by the similar procedure as mentioned above. In the case of **6a**, the corresponding diarylmethanol was obtained by the reaction of (R)-3-CHO-MOM-BINOL⁴ with ortho-lithiated MOM-phenol. In the case of **7**, the corresponding diarylmethanol was also obtained by the reaction of (R)-3-CHO-MOM-BINOL with phenylmagnesium bromide. Deprotection and reduction were carried out successively to afford **6a** and **7** were obtained respectively.

(R)-3-(2-Hydroxybenzyl)-1,1'-binaphthalene-2,2'-diol (6a): [α]_D²² +58.8 (c 1.02, THF); IR [cm⁻¹] (KBr) 3521, 3060, 2251, 1209, 906, 729; ¹H NMR (CDCl₃) δ 4.13 (d, 1H, *J* = 15.1 Hz), 4.19 (d, 1H, 15.1 Hz), 6.80 (d, 1H, *J* = 8.2 Hz), 6.91 (dd, 1H, *J* = 6.4, 7.4 Hz), 6.93 – 7.14 (m, 3H), 7.21–7.37 (m, 6H), 7.80 (d, 1H, *J* = 8.2 Hz), 7.84 (d, 1H, *J* = 8.2 Hz), 7.92 (s, 1H), 7.93 (d, 1H, *J* = 8.7 Hz); ¹³C NMR (CDCl₃) δ 31.1, 110.9, 111.6, 116.5, 117.8, 121.0, 124.0, 124.1, 124.4, 126.2, 127.0, 127.5, 127.9, 128.1, 128.4, 128.8, 129.4, 129.4, 129.7, 130.9, 130.9, 131.5, 132.3, 133.2150.0, 152.6, 153.6; ESI-HRMS (*m/z*) calcd. for C₂₇H₁₉O₃ (M-H⁺): 391.1340; found: 391.1347.

(R)-3-Benzyl-1,1'-binaphthalene-2,2'-diol (7): [α]_D²² +76.8 (c 1.00, THF); IR [cm⁻¹] (KBr) 3521, 3060, 1610, 1140, 909, 729; ¹H NMR (CDCl₃) δ 4.22 (d, 1H,

$J = 16.0$ Hz), 4.26 (d, 1H, $J = 16.0$ Hz), 5.03 (s, 1H, OH), 5.14 (s, 1H, OH), 7.09 (d, 1H, $J = 8.2$ Hz), 7.14 (d, 1H, $J = 8.3$ Hz), 7.22-7.39 (m, 10H), 7.71 (s, 1H), 7.79 (d, 1H, $J = 7.6$ Hz), 7.88 (d, 1H, $J = 7.8$ Hz), 7.97 (d, 1H, $J = 8.7$ Hz); ^{13}C NMR (CDCl_3) δ 36.7, 110.7, 111.0, 117.7, 124.0, 124.0, 126.2, 126.8, 127.5, 128.0, 128.4, 128.5, 129.1, 129.4, 129.5, 130.1, 130.9, 131.4, 132.3, 133.3, 140.1, 151.5, 152.8; ESI-HRMS (m/z) calcd. for $\text{C}_{27}\text{H}_{19}\text{O}_2$ (M-H^+): 375.1391; found: 375.1390.

NMR experiment for the chiral zirconium catalyst

A typical procedure is described for the preparation of the catalyst. To ligand **6e** (0.04 mmol) in benzene- d_6 (0.25 mL) were added $\text{Zr}(\text{O}^i\text{Bu})_4$ (0.04 mmol) in benzene- d_6 (0.5 mL) and *N*-methylimidazole (0.12 mmol) in benzene- d_6 (0.25 mL) at room temperature. The mixture was stirred for 1 h at the same temperature, and then ^1H and ^{13}C NMR experiments were performed.

X-ray structure of 6k

Computational data

Complex A-1

SCF Done: E = -1928.23937652302 a.u.

(B3LYP/LACVP**)

Atom	Coordinates (Angstroms)			Atom	Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
O(1)	1.333	1.833	1.301	C(43)	3.025	-0.384	-1.97
C(2)	3.427	-1.181	3.488	C(44)	3.326	2.824	-3.627
O(3)	-0.566	-0.454	1.43	H(45)	-2.675	2.469	-3.612
C(4)	-2.392	1.423	-3.524	H(46)	3.24	-3.26	2.886
C(5)	4.033	-2.526	3.062	H(47)	4.603	-2.41	2.135
O(6)	1.358	-1.941	-0.068	H(48)	4.704	-2.916	3.835
C(7)	-2.403	0.599	-4.629	H(49)	-2.698	0.987	-5.599
O(8)	2.56	-0.74	2.452	H(50)	-2.015	-1.402	-5.372
C(9)	-2.019	-0.757	-4.498	H(51)	-1.355	-2.305	-3.18
C(10)	-1.65	-1.266	-3.271	H(52)	-2.245	2.822	-1.225
C(11)	-1.636	-0.446	-2.106	H(53)	1.783	-2.068	4.597
C(12)	-2.002	0.932	-2.248	H(54)	2.129	-0.383	5.036
C(13)	-1.951	1.78	-1.112	H(55)	3.201	-1.684	5.599
C(14)	-1.513	1.334	0.115	H(56)	4.077	0.84	3.948
C(15)	-1.117	-0.043	0.25	H(57)	5.092	0.006	2.756
C(16)	-1.229	-0.943	-0.819	H(58)	5.215	-0.417	4.476
C(17)	2.584	-1.34	4.763	H(59)	-3.598	-1.99	-1.053
C(18)	4.521	-0.123	3.682	H(60)	-5.327	-3.709	-1.312
C(19)	-3.324	-3.038	-0.999	H(61)	-4.736	-6.134	-1.187
C(20)	-4.295	-4.007	-1.143	H(62)	-2.387	-6.802	-0.755
C(21)	-3.963	-5.38	-1.067	H(63)	1.706	-4.471	0.017
C(22)	-2.658	-5.75	-0.83	H(64)	-0.044	-6.21	-0.329
C(23)	-1.635	-4.778	-0.668	H(65)	2.156	6.287	1.046
C(24)	-1.959	-3.383	-0.77	H(66)	-0.261	6.802	0.947
C(25)	-0.927	-2.395	-0.622	H(67)	-1.926	4.958	1.08
C(26)	0.368	-2.814	-0.297	H(68)	-2.456	2.712	1.45
C(27)	0.678	-4.202	-0.21	H(69)	-1.243	1.678	2.204
C(28)	-0.29	-5.153	-0.398	H(70)	3.187	3.334	3.451
C(29)	-0.454	3.401	1.191	H(71)	3.698	5.002	3.149
C(30)	0.933	3.112	1.218	H(72)	4.853	3.669	2.939
C(31)	1.892	4.154	1.178	H(73)	3.503	2.775	1.061
C(32)	1.433	5.475	1.075	H(74)	4.277	5.724	0.683
C(33)	0.072	5.771	1.025	H(75)	3.994	4.58	-0.633
C(34)	-0.862	4.733	1.093	H(76)	5.327	4.317	0.505
C(35)	-1.462	2.272	1.313	H(77)	2.189	2.59	-1.048
C(36)	3.805	3.966	2.806	H(78)	3.892	0.071	-3.981
C(37)	3.375	3.829	1.332	H(79)	3.051	-1.449	-1.802
C(38)	4.29	4.66	0.419	H(80)	3.011	3.727	-3.1
N(39)	2.48	0.464	-1.022	H(81)	2.735	2.72	-4.541
C(40)	2.547	1.692	-1.529	H(82)	4.384	2.912	-3.884
N(41)	3.116	1.672	-2.755	Zr(83)	1.413	-0.178	0.995
C(42)	3.429	0.354	-3.048				

Complex A-2

SCF Done: E = -1928.23400431865 a.u.

(B3LYP/LACVP**)

Atom	Coordinates (Angstroms)			Atom	Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
O(1)	2.632	-0.346	-1.328	C(43)	3.115	-2.986	3.513
C(2)	0.945	-4.38	-1.087	C(44)	2.766	-3.014	2.192
O(3)	1.001	0.527	1.033	C(45)	2.847	-1.268	5.365
C(4)	-0.555	5.102	-1.805	H(46)	0.217	5.795	-2.13
C(5)	0.205	-4.255	-2.43	H(47)	0.861	-3.809	-3.184
O(6)	-0.688	-0.852	-0.758	H(48)	-0.671	-3.611	-2.317
C(7)	-1.878	5.333	-2.109	H(49)	-0.124	-5.234	-2.796
O(8)	1.31	-3.076	-0.664	H(50)	-2.167	6.217	-2.671
C(9)	-2.864	4.4	-1.701	H(51)	-3.906	4.57	-1.961
C(10)	-2.515	3.276	-0.985	H(52)	-3.281	2.568	-0.687
C(11)	-1.159	3.016	-0.631	H(53)	1.954	4.337	-1.229
C(12)	-0.161	3.945	-1.078	H(54)	2.752	-5.324	-0.307
C(13)	1.203	3.657	-0.832	H(55)	2.9	-4.725	-1.969
C(14)	1.606	2.521	-0.167	H(56)	1.996	-6.217	-1.635
C(15)	0.606	1.63	0.346	H(57)	-0.877	-4.406	0.099
C(16)	-0.754	1.862	0.117	H(58)	0.538	-5.061	0.941
Zr(17)	1.23	-1.152	-0.194	H(59)	-0.272	-6.025	-0.309
C(18)	2.225	-5.214	-1.261	H(60)	-2.068	3.165	1.966
C(19)	0.027	-5.009	-0.025	H(61)	-3.813	3.667	3.625
C(20)	-2.82	2.421	2.201	H(62)	-5.56	1.969	4.177
C(21)	-3.799	2.699	3.132	H(63)	-5.51	-0.251	3.074
C(22)	-4.789	1.735	3.448	H(64)	-2.626	-2.387	-0.082
C(23)	-4.763	0.503	2.832	H(65)	-4.462	-1.837	1.509
C(24)	-3.758	0.18	1.879	H(66)	4.937	0.953	-5.008
C(25)	-2.769	1.161	1.535	H(67)	5.56	3.105	-3.953
C(26)	-1.75	0.849	0.574	H(68)	4.732	3.649	-1.673
C(27)	-1.694	-0.449	0.057	H(69)	3.638	3.047	0.311
C(28)	-2.692	-1.408	0.385	H(70)	3.225	1.365	0.649
C(29)	-3.702	-1.1	1.263	H(71)	5.165	-2.169	-3.221
C(30)	3.67	1.799	-1.424	H(72)	5.379	-1.527	-4.856
C(31)	3.355	0.559	-2.028	H(73)	4.366	-2.956	-4.596
C(32)	3.794	0.241	-3.329	H(74)	2.748	-1.604	-3.286
C(33)	4.586	1.181	-4.004	H(75)	3.284	-0.395	-6.054
C(34)	4.937	2.395	-3.415	H(76)	1.767	-0.271	-5.152
C(35)	4.474	2.698	-2.133	H(77)	2.344	-1.854	-5.711
C(36)	3.089	2.178	-0.069	H(78)	1.715	-0.089	3.026
C(37)	4.656	-1.986	-4.172	H(79)	3.605	-3.712	4.145
C(38)	3.421	-1.085	-3.976	H(80)	2.903	-3.787	1.454
C(39)	2.66	-0.887	-5.3	H(81)	3.903	-1.243	5.649
N(40)	2.154	-1.818	1.863	H(82)	2.438	-0.257	5.425
C(41)	2.134	-1.083	2.972	H(83)	2.299	-1.915	6.054
N(42)	2.704	-1.753	3.996				

Complex A-3

SCF Done: E = -1928.22984926108 a.u.

(B3LYP/LACVP**)

Atom	Coordinates (Angstroms)			Atom	Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
O(1)	1.199	1.919	0.421	C(43)	1.438	-4.3	-1.662
C(2)	4.392	-0.178	0.018	C(44)	1.957	-3.039	-1.555
O(3)	-0.225	-0.528	0.96	C(45)	-0.653	-5.413	-0.73
C(4)	-4.476	3.124	0.986	H(46)	-4.558	3.81	1.827
C(5)	5.218	-1.289	-0.648	H(47)	4.735	-2.262	-0.512
O(6)	0.037	0.327	-2.081	H(48)	6.223	-1.342	-0.219
C(7)	-5.399	3.158	-0.036	H(49)	5.309	-1.094	-1.722
O(8)	3.123	-0.115	-0.628	H(50)	-6.223	3.865	-0.01
C(9)	-5.258	2.275	-1.134	H(51)	-5.975	2.312	-1.951
C(10)	-4.218	1.37	-1.179	H(52)	-4.121	0.705	-2.03
C(11)	-3.259	1.293	-0.129	H(53)	-2.457	2.979	2.755
C(12)	-3.39	2.209	0.964	H(54)	5.135	-0.566	2.044
C(13)	-2.395	2.222	1.975	H(55)	3.595	0.306	1.988
C(14)	-1.326	1.36	1.955	H(56)	3.647	-1.439	1.63
C(15)	-1.255	0.369	0.921	H(57)	5.193	1.422	-1.212
C(16)	-2.175	0.346	-0.131	H(58)	4.496	1.969	0.324
Zr(17)	1.167	0.106	-0.403	H(59)	6.083	1.173	0.305
C(18)	4.18	-0.489	1.512	H(60)	-4.046	-1.308	0.432
C(19)	5.087	1.181	-0.15	H(61)	-5.664	-3.14	0.165
C(20)	-4.014	-1.932	-0.453	H(62)	-5.618	-4.584	-1.873
C(21)	-4.92	-2.961	-0.606	H(63)	-3.908	-4.18	-3.625
C(22)	-4.893	-3.782	-1.759	H(64)	-0.232	-1.164	-4.117
C(23)	-3.942	-3.558	-2.733	H(65)	-1.971	-2.913	-4.474
C(24)	-2.986	-2.515	-2.598	H(66)	2.499	6.08	1.643
C(25)	-3.018	-1.667	-1.44	H(67)	1.504	5.82	3.891
C(26)	-2.048	-0.616	-1.276	H(68)	0.29	3.731	4.475
C(27)	-1.022	-0.51	-2.226	H(69)	-0.544	1.645	3.942
C(28)	-1.026	-1.329	-3.393	H(70)	0.461	0.642	2.899
C(29)	-1.981	-2.294	-3.58	H(71)	4.412	5.076	0.12
C(30)	0.647	2.784	2.581	H(72)	3.27	6.314	-0.428
C(31)	1.258	2.931	1.313	H(73)	4.035	5.244	-1.603
C(32)	1.916	4.129	0.949	H(74)	2.849	3.294	-0.762
C(33)	1.991	5.155	1.897	H(75)	0.885	5.599	-1.206
C(34)	1.427	5.013	3.167	H(76)	0.52	3.877	-1.407
C(35)	0.752	3.836	3.495	H(77)	1.692	4.664	-2.48
C(36)	-0.164	1.541	2.919	H(78)	-0.656	-2.772	0.294
C(37)	3.609	5.285	-0.594	H(79)	1.764	-5.173	-2.204
C(38)	2.459	4.275	-0.467	H(80)	2.844	-2.619	-2.003
C(39)	1.32	4.623	-1.449	H(81)	-1.167	-5.605	-1.675
N(40)	1.146	-2.279	-0.731	H(82)	-0.127	-6.314	-0.405
C(41)	0.155	-3.075	-0.347	H(83)	-1.395	-5.139	0.02
N(42)	0.289	-4.308	-0.883				

Complex A-4

SCF Done: E = -1928.22441156181 a.u.

(B3LYP/LACVP**)

Atom	Coordinates (Angstroms)			Atom	Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
O(1)	0.867	1.435	0.433	C(43)	5.151	0.129	-0.065
C(2)	0.764	-3.783	-0.078	C(44)	3.869	0.523	0.208
O(3)	-0.97	-0.711	1.033	C(45)	6.156	-1.84	-1.316
C(4)	-4.68	3.475	0.718	H(46)	-4.676	4.225	1.506
C(5)	1.462	-4.562	-1.206	H(47)	2.541	-4.364	-1.211
O(6)	-0.523	-0.126	-1.916	H(48)	1.048	-4.269	-2.176
C(7)	-5.569	3.564	-0.33	H(49)	1.323	-5.642	-1.083
O(8)	0.919	-2.393	-0.338	H(50)	-6.283	4.381	-0.377
C(9)	-5.536	2.592	-1.358	H(51)	-6.224	2.671	-2.197
C(10)	-4.639	1.546	-1.311	H(52)	-4.625	0.813	-2.109
C(11)	-3.721	1.41	-0.23	H(53)	-2.728	3.18	2.544
C(12)	-3.734	2.416	0.791	H(54)	2.475	-3.811	1.268
C(13)	-2.76	2.367	1.821	H(55)	0.918	-3.535	2.074
C(14)	-1.817	1.369	1.884	H(56)	1.35	-5.164	1.514
C(15)	-1.869	0.31	0.921	H(57)	-1.241	-3.507	0.703
C(16)	-2.78	0.325	-0.14	H(58)	-1.19	-3.906	-1.02
Zr(17)	0.566	-0.447	-0.253	H(59)	-0.894	-5.177	0.188
C(18)	1.418	-4.096	1.278	H(60)	-4.932	-0.988	0.403
C(19)	-0.733	-4.118	-0.049	H(61)	-6.812	-2.544	0.112
C(20)	-4.949	-1.66	-0.446	H(62)	-6.872	-4.106	-1.835
C(21)	-6.001	-2.535	-0.611	H(63)	-5.004	-4.111	-3.466
C(22)	-6.035	-3.425	-1.713	H(64)	-0.866	-1.756	-3.858
C(23)	-4.999	-3.426	-2.62	H(65)	-2.834	-3.239	-4.232
C(24)	-3.894	-2.545	-2.471	H(66)	2.436	5.605	1.258
C(25)	-3.863	-1.626	-1.37	H(67)	1.39	5.642	3.497
C(26)	-2.754	-0.728	-1.203	H(68)	-0.025	3.734	4.232
C(27)	-1.671	-0.847	-2.083	H(69)	-1.03	1.677	3.868
C(28)	-1.719	-1.742	-3.187	H(70)	-0.144	0.494	2.909
C(29)	-2.804	-2.559	-3.384	H(71)	4.326	4.138	-0.165
C(30)	0.307	2.573	2.459	H(72)	3.382	5.521	-0.736
C(31)	0.971	2.531	1.209	H(73)	3.934	4.307	-1.887
C(32)	1.72	3.639	0.744	H(74)	2.479	2.596	-0.945
C(33)	1.86	4.747	1.592	H(75)	0.876	5.149	-1.451
C(34)	1.262	4.776	2.852	H(76)	0.263	3.492	-1.577
C(35)	0.477	3.699	3.268	H(77)	1.514	4.061	-2.699
C(36)	-0.653	1.461	2.862	H(78)	3.346	-2.218	-1.395
C(37)	3.548	4.447	-0.872	H(79)	6.106	0.568	0.178
C(38)	2.255	3.637	-0.684	H(80)	3.516	1.389	0.746
C(39)	1.16	4.112	-1.663	H(81)	6.663	-1.289	-2.114
N(40)	2.988	-0.402	-0.325	H(82)	6.872	-2.071	-0.524
C(41)	3.732	-1.337	-0.904	H(83)	5.763	-2.773	-1.722
N(42)	5.05	-1.055	-0.777				

Complex A-5

SCF Done: E = -1928.21806945302 a.u.

(B3LYP/LACVP**)

Atom	Coordinates (Angstroms)			Atom	Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
O(1)	1.505	2.402	-0.007	C(43)	3.722	-0.661	3.49
C(2)	3.337	0.391	-3.222	C(44)	3.766	-0.07	2.258
O(3)	-0.338	0.482	-0.066	C(45)	1.919	-1.909	4.781
C(4)	-3.738	-0.286	-4.417	H(46)	-4.056	0.587	-4.982
C(5)	2.163	0.861	-4.098	H(47)	1.272	0.253	-3.906
O(6)	1.193	-1.564	-0.845	H(48)	1.925	1.909	-3.886
C(7)	-4.155	-1.547	-4.786	H(49)	2.408	0.774	-5.162
O(8)	2.969	0.534	-1.85	H(50)	-4.815	-1.68	-5.64
C(9)	-3.707	-2.675	-4.056	H(51)	-4.016	-3.671	-4.36
C(10)	-2.881	-2.52	-2.964	H(52)	-2.541	-3.393	-2.417
C(11)	-2.454	-1.23	-2.535	H(53)	-2.654	2.034	-3.613
C(12)	-2.874	-0.094	-3.307	H(54)	2.775	-1.705	-3.253
C(13)	-2.37	1.195	-2.981	H(55)	4.477	-1.418	-2.849
C(14)	-1.495	1.393	-1.938	H(56)	3.93	-1.251	-4.531
C(15)	-1.16	0.267	-1.117	H(57)	5.394	0.947	-2.807
C(16)	-1.608	-1.022	-1.393	H(58)	4.345	2.315	-3.229
Zr(17)	1.664	0.406	-0.398	H(59)	4.91	1.203	-4.497
C(18)	3.65	-1.089	-3.484	H(60)	-3.832	-1.832	-0.304
C(19)	4.574	1.27	-3.456	H(61)	-5.394	-3.268	0.927
C(20)	-3.46	-2.708	0.214	H(62)	-4.571	-5.293	2.14
C(21)	-4.336	-3.515	0.909	H(63)	-2.146	-5.816	2.143
C(22)	-3.87	-4.658	1.604	H(64)	1.761	-3.711	0.378
C(23)	-2.524	-4.951	1.603	H(65)	0.161	-5.269	1.484
C(24)	-1.593	-4.127	0.913	H(66)	-0.347	5.237	3.012
C(25)	-2.063	-2.988	0.175	H(67)	-2.414	5.469	1.663
C(26)	-1.134	-2.144	-0.527	H(68)	-2.596	4.286	-0.516
C(27)	0.241	-2.382	-0.368	H(69)	-1.281	3.452	-2.421
C(28)	0.69	-3.536	0.345	H(70)	0.235	2.626	-2.164
C(29)	-0.197	-4.39	0.952	H(71)	2.837	5.577	1.713
C(30)	-0.669	3.357	-0.38	H(72)	1.974	5.816	3.238
C(31)	0.5	3.209	0.41	H(73)	3.536	4.985	3.233
C(32)	0.626	3.901	1.636	H(74)	2.572	3.114	1.916
C(33)	-0.436	4.706	2.067	H(75)	0.932	3.686	4.446
C(34)	-1.6	4.841	1.312	H(76)	1.129	2.104	3.682
C(35)	-1.701	4.173	0.091	H(77)	2.534	2.93	4.394
C(36)	-0.781	2.733	-1.762	H(78)	0.75	-1.218	2.303
C(37)	2.6	5.115	2.676	H(79)	4.46	-0.751	4.271
C(38)	1.892	3.762	2.476	H(80)	4.576	0.456	1.778
C(39)	1.605	3.08	3.827	H(81)	0.928	-2.287	4.536
N(40)	2.539	-0.234	1.638	H(82)	2.571	-2.75	5.025
C(41)	1.77	-0.912	2.489	H(83)	1.85	-1.237	5.64
N(42)	2.448	-1.192	3.622				

Complex A-6

SCF Done: E = -1928.21490067110 a.u.

(B3LYP/LACVP**)

Atom	Coordinates (Angstroms)			Atom	Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
O(1)	0.671	-0.365	-3.431	C(43)	3.526	-1.529	1.473
C(2)	0.163	-4.241	-1.757	C(44)	2.735	-1.958	0.445
O(3)	0.369	1.156	-1.081	C(45)	3.73	0.668	2.736
C(4)	-3.642	5.016	-1.436	H(46)	-3.62	5.707	-2.277
C(5)	-1.057	-4.533	-2.646	H(47)	-0.911	-4.098	-3.64
O(6)	-1.72	-0.683	-0.868	H(48)	-1.956	-4.093	-2.206
C(7)	-4.616	5.125	-0.467	H(49)	-1.215	-5.611	-2.757
O(8)	0.305	-2.834	-1.66	H(50)	-5.366	5.91	-0.527
C(9)	-4.649	4.193	0.599	H(51)	-5.431	4.262	1.35
C(10)	-3.701	3.197	0.692	H(52)	-3.744	2.488	1.511
C(11)	-2.657	3.078	-0.272	H(53)	-1.819	4.42	-3.319
C(12)	-2.657	3.995	-1.375	H(54)	1.601	-4.377	-3.382
C(13)	-1.725	3.8	-2.43	H(55)	2.314	-4.609	-1.774
C(14)	-0.776	2.801	-2.401	H(56)	1.359	-5.91	-2.51
C(15)	-0.658	2.016	-1.206	H(57)	0.801	-4.579	0.301
C(16)	-1.622	2.088	-0.198	H(58)	-0.95	-4.393	0.104
Zr(17)	0.203	-0.861	-1.525	H(59)	-0.159	-5.907	-0.379
C(18)	1.437	-4.821	-2.394	H(60)	-1.072	3.422	1.994
C(19)	-0.049	-4.817	-0.348	H(61)	-0.761	3.883	4.393
C(20)	-1.164	2.621	2.718	H(62)	-0.989	2.048	6.073
C(21)	-0.992	2.875	4.06	H(63)	-1.483	-0.259	5.314
C(22)	-1.116	1.833	5.015	H(64)	-2.028	-2.363	1.055
C(23)	-1.394	0.551	4.594	H(65)	-1.892	-1.873	3.495
C(24)	-1.558	0.251	3.213	H(66)	5.011	0.709	-4.264
C(25)	-1.463	1.307	2.245	H(67)	4.497	3.126	-4.322
C(26)	-1.617	1.023	0.847	H(68)	2.15	3.896	-4.037
C(27)	-1.745	-0.317	0.447	H(69)	-0.179	3.261	-4.389
C(28)	-1.871	-1.352	1.419	H(70)	-0.705	1.608	-4.142
C(29)	-1.793	-1.075	2.761	H(71)	1.848	-1.81	-5.52
C(30)	1.348	1.927	-3.753	H(72)	3.516	-1.567	-6.073
C(31)	1.657	0.55	-3.693	H(73)	3.055	-3.092	-5.292
C(32)	2.982	0.09	-3.891	H(74)	2.599	-1.881	-3.177
C(33)	3.988	1.04	-4.116	H(75)	5.431	-1.454	-4.27
C(34)	3.702	2.405	-4.15	H(76)	4.989	-1.334	-2.559
C(35)	2.385	2.835	-3.981	H(77)	4.799	-2.868	-3.431
C(36)	-0.089	2.408	-3.707	H(78)	1.741	1.092	0.741
C(37)	2.897	-2.006	-5.282	H(79)	4.286	-2.03	2.054
C(38)	3.265	-1.409	-3.908	H(80)	2.686	-2.923	-0.035
C(39)	4.704	-1.779	-3.518	H(81)	3.417	0.322	3.724
N(40)	1.917	-0.916	0.043	H(82)	4.82	0.676	2.68
C(41)	2.217	0.125	0.818	H(83)	3.354	1.679	2.576
N(42)	3.185	-0.204	1.699				

Complex A-7

SCF Done: E = -1928.21456868023 a.u.

(B3LYP/LACVP**)

Atom	Coordinates (Angstroms)			Atom	Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
O(1)	1.789	0.472	-3.032	C(43)	0.141	-4.196	-2.324
C(2)	2.768	0.396	1.446	C(44)	-0.147	-2.864	-2.436
O(3)	0.619	2.204	-1.102	C(45)	1.867	-5.514	-1.005
C(4)	-3.611	5.415	-2.779	H(46)	-3.479	5.996	-3.688
C(5)	3.758	1.502	1.053	H(47)	3.229	2.324	0.564
O(6)	-1.156	0.114	-0.887	H(48)	4.513	1.117	0.363
C(7)	-4.777	5.511	-2.05	H(49)	4.267	1.896	1.94
O(8)	2.112	-0.065	0.256	H(50)	-5.573	6.178	-2.37
C(9)	-4.943	4.715	-0.892	H(51)	-5.873	4.767	-0.331
C(10)	-3.937	3.873	-0.466	H(52)	-4.085	3.27	0.422
C(11)	-2.7	3.783	-1.167	H(53)	-1.4	4.811	-4.176
C(12)	-2.562	4.547	-2.374	H(54)	1.175	1.783	1.959
C(13)	-1.421	4.339	-3.195	H(55)	0.974	0.168	2.657
C(14)	-0.407	3.483	-2.831	H(56)	2.172	1.288	3.341
C(15)	-0.458	2.898	-1.526	H(57)	2.782	-1.594	2.316
C(16)	-1.603	2.958	-0.735	H(58)	4.227	-1.213	1.346
Zr(17)	0.871	0.226	-1.229	H(59)	4.033	-0.518	2.968
C(18)	1.707	0.941	2.412	H(60)	-1.701	4.649	1.272
C(19)	3.498	-0.808	2.057	H(61)	-2.134	5.487	3.544
C(20)	-1.943	3.953	2.069	H(62)	-2.692	3.903	5.393
C(21)	-2.185	4.42	3.343	H(63)	-2.752	1.464	4.947
C(22)	-2.495	3.522	4.394	H(64)	-1.851	-1.285	1.142
C(23)	-2.531	2.167	4.146	H(65)	-2.487	-0.433	3.396
C(24)	-2.266	1.654	2.847	H(66)	5.873	2.231	-3.993
C(25)	-1.987	2.559	1.77	H(67)	4.929	4.511	-4.256
C(26)	-1.72	2.057	0.45	H(68)	2.457	4.82	-4.187
C(27)	-1.592	0.67	0.278	H(69)	0.408	3.591	-4.782
C(28)	-1.902	-0.219	1.347	H(70)	0.141	1.97	-4.188
C(29)	-2.249	0.256	2.589	H(71)	5.518	0.145	-1.527
C(30)	2.038	2.773	-3.706	H(72)	3.964	-0.692	-1.522
C(31)	2.599	1.498	-3.434	H(73)	5.423	-1.537	-2.075
C(32)	3.989	1.281	-3.598	H(74)	5.652	0.047	-3.965
C(33)	4.801	2.389	-3.885	H(75)	2.97	-1.417	-3.953
C(34)	4.275	3.67	-4.044	H(76)	3.812	-0.833	-5.393
C(35)	2.894	3.843	-3.988	H(77)	4.56	-2.086	-4.386
C(36)	0.541	2.952	-3.902	H(78)	2.308	-2.788	-0.358
C(37)	4.898	-0.573	-2.075	H(79)	-0.3	-5.069	-2.778
C(38)	4.657	-0.093	-3.52	H(80)	-0.916	-2.376	-3.016
C(39)	3.953	-1.174	-4.361	H(81)	2.314	-6.027	-1.86
N(40)	0.722	-2.142	-1.64	H(82)	1.15	-6.178	-0.515
C(41)	1.518	-3.029	-1.054	H(83)	2.654	-5.256	-0.295
N(42)	1.205	-4.287	-1.44				

Complex E

SCF Done: E = -1662.66716098996 a.u.

(B3LYP/LACVP**)

Atom	Coordinates (Angstroms)			Atom	Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
O(1)	0.97	1.183	-2.1	C(37)	2.508	3.384	-2.932
C(2)	-3.593	1.323	-2.164	C(38)	3.755	4.281	-2.9
O(3)	-0.687	-1.17	-0.896	Zr(39)	-0.555	0.819	-0.894
C(4)	4.367	-2.601	1.071	H(40)	5.128	-2.906	0.357
C(5)	-3.851	2.673	-2.843	H(41)	-3.108	2.854	-3.625
O(6)	-0.239	1.253	1.055	H(42)	-3.789	3.486	-2.113
C(7)	4.64	-2.576	2.421	H(43)	-4.846	2.694	-3.3
O(8)	-2.282	1.365	-1.591	H(44)	5.619	-2.87	2.788
C(9)	3.643	-2.151	3.332	H(45)	3.866	-2.115	4.395
C(10)	2.394	-1.778	2.884	H(46)	1.641	-1.451	3.592
C(11)	2.069	-1.816	1.498	H(47)	3.638	-2.396	-1.507
C(12)	3.09	-2.219	0.577	H(48)	-3.392	-0.775	-2.697
C(13)	2.827	-2.171	-0.817	H(49)	-4.612	0.095	-3.651
C(14)	1.603	-1.794	-1.315	H(50)	-2.886	0.352	-3.976
C(15)	0.552	-1.499	-0.383	H(51)	-4.529	1.87	-0.282
C(16)	0.769	-1.457	0.997	H(52)	-5.619	1.037	-1.411
C(17)	-3.624	0.176	-3.186	H(53)	-4.377	0.119	-0.534
C(18)	-4.593	1.072	-1.027	H(54)	0.037	-3.693	2.086
C(19)	-0.646	-3.307	2.835	H(55)	-1.036	-5.232	3.673
C(20)	-1.251	-4.169	3.725	H(56)	-2.617	-4.371	5.401
C(21)	-2.15	-3.682	4.703	H(57)	-3.132	-1.947	5.499
C(22)	-2.436	-2.335	4.758	H(58)	-1.836	1.884	2.958
C(23)	-1.838	-1.422	3.849	H(59)	-2.835	0.336	4.634
C(24)	-0.912	-1.908	2.868	H(60)	4.429	2.476	-4.716
C(25)	-0.299	-0.994	1.943	H(61)	4.816	0.164	-5.499
C(26)	-0.693	0.349	1.974	H(62)	3.419	-1.691	-4.619
C(27)	-1.597	0.826	2.962	H(63)	1.7	-2.502	-3.342
C(28)	-2.145	-0.034	3.88	H(64)	0.331	-1.456	-3.014
C(29)	2.21	-0.43	-3.37	H(65)	0.471	3.437	-3.738
C(30)	1.98	0.905	-2.966	H(66)	1.685	4.167	-4.799
C(31)	2.783	1.97	-3.428	H(67)	1.137	5.037	-3.355
C(32)	3.8	1.674	-4.344	H(68)	2.147	3.289	-1.9
C(33)	4.025	0.37	-4.783	H(69)	4.116	4.516	-3.908
C(34)	3.238	-0.67	-4.29	H(70)	4.574	3.81	-2.347
C(35)	1.398	-1.593	-2.812	H(71)	3.52	5.232	-2.412
C(36)	1.381	4.045	-3.753				

References and Notes

- (1) Astudillo, H. E. A.; Chokotho, N. C. J.; Jarvis, T. C.; Johnson, C. D.; Lewis, C. C.; McDonnell, P. D. *Tetrahedron* **1985**, *41*, 5919.
- (2) (a) Kobayashi, S.; Manabe, K.; Ishitani, H.; Matsuo, J. "Silyl Enol Ethers", in *Science of Synthesis, Houben-Weyl Methods of Molecular Transformations*; Bellus, D.; Ley, S. V.; Noyori, R.; Regitz, M.; Schaumann, E.; Shinkai, I.; Thomas, E. J.; Trost, B. M., Eds.; Georg Thieme Verlag: Stuttgart, 2002; vol. 4, p. 317. (b) Ireland, R. E.; Wipf, P.; Armstrong III, J. D. *J. Org. Chem.* **1991**, *56*, 650. (c) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.
- (3) Except for new compounds, all Mannich-type adducts were identified by previous report: (a) Ishitani, H.; Ueno, M.; Kobayashi, S. *J. Am. Chem. Soc.* **2000**, *122*, 8180. (b) Kobayashi, S.; Arai, K.; Shimizu, H.; Ihori, Y.; Ishitani, H.; Yamashita, Y. *Angew. Chem. Int. Ed.* **2005**, *44*, 761.
- (4) Cox, P. J.; Wang, W.; Snieckus, V. *Tetrahedron Lett.* **1992**, *33*, 2253.
- (5) Nakamura, H.; Ishihara, K.; Yamamoto, H. *J. Org. Chem.* **2002**, *67*, 5124.
- (6) Dan, Y.; Xiang-Yang, Y.; Ming, X.; Kwan-Wah, P.; Kung-Kai, C. *J. Am. Chem. Soc.* **2000**, *122*, 1658.