Supporting Information

Assembly State of Catalytic Modules as Chiral Switch in Asymmetric Strecker Amino Acid Synthesis

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General: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^{1}H NMR, 126.65 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported in the scale relative to $CHCl_3$ (7.26 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CDCl_3$ (77.0 ppm) as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. X-ray data were collected on a Bruker SMART CCD diffractometer. ESI-Q mass spectra were measured on Water-ZQ4000. ESI-QFT mass spectra were measured on IonSpec QFT-7 (JASCO International Co., Ltd.). FAB mass spectra were measured on JEOL MStation JMS-700. Melting points were measured on Yamato MP-21. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM). The enantiomeric excesses (ee's) were determined by HPLC. HPLC analysis was performed on JASCO HPLC systems containing of following: pump, PU-980; detector, UV-970, measured at 254 nm; column, DAICEL CHIRALPAK AD-H, AS-H, or DAICEL CHIRALCEL OD-H, OJ-H; mobile phase, 2-propanol/hexane; flow rate, 1.0 mL/min. In general, reactions were carried out in dry solvents under an argon atmosphere, unless noted otherwise. Dry solvents of tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from Kanto Chemical Co., Inc. Propionitrile was distilled from calcium hydride. Other reagents were purified by usual methods. $Gd(O^iPr)_3$ and $La(O^iPr)_3$ were purchased from Kojundo Chemical Laboratory Co., Ltd. (Fax: +81-492-84-1351, sales@kojundo.co.jp). $Gd(HMDS)_3$ was purchased from Aldrich Chemical Co., Inc.

(A) Data of Ligands

Chiral ligands were prepared by reported method.[1] Ligand **1** and **2** are commercially available from Junsei Chemical. Co., Ltd. (Fax: +81-3-3270-5461).

Ligand 1 and **2**: Known compounds.[1]

Ligand 3: white amorphous; IR (neat): 3313, 2856, 1493, 1437, 1152, 1095, 937, 742, 694, 509 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.92 (qd, J = 5.1, 12.7 Hz, 1H), 2.10 (dd, J = 5.1, 12.7 Hz, 1H), 2.69 (td, J = 9.7, 15.3 Hz, 1H), 2.84 (td, J = 2.9, 9.7 Hz, 1H), 3.23 (td, J = 1.7, 12. 7 Hz, 1H), 3.34 (ddd, J = 2.9, 8.5, 15.3 Hz, 1H), 3.48-3.56 (m, 1H), 3.70 (t, J = 8.5 Hz, 1H), 3.90 (dd, J = 5.1, 12.7 Hz, 1H), 7.02 (s, 1H), 7.03 (s, 1H), 7.46-7.61 (m, 6H), 7.68-7.80 (m, 4H); ^{13}C NMR ($CDCl_3$): δ = 31.4, 36.5 (d, J = 68.2 Hz), 65.3, 74.7, 75.9, 85.4, 118.6, 121.1, 123.6, 128.2, 128.9 (d, J = 12.4 Hz), 129.0 (d, J = 12.4 Hz), 130.1 (d, J = 101 Hz), 130.5 (d, J = 9.3 Hz), 131.0 (d, J = 10.3 Hz), 131.6 (d, J = 105 Hz), 132.5, 145.1, 149.7; MS (ESI): m/z 515 and 517 [M+Na$^+$]; HRMS (FAB): m/z calcd for $C_{24}H_{24}Cl_2O_5P$ [M+H$^+$]: 493.0738. Found: 493.0729; $[\alpha]^{25}_D$ +8.4 (c = 0.55, MeOH).

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[1] Kato, N.; Tomita, D.; Maki, K.; Kanai, M.; Shibasaki, M. *J. Org. Chem.* **2004**, *69*, 6128.

(B) Data of Substrates

Ketoimines (**4a-4e**) were prepared by reported method.[2]

***N*-(1-Thiophen-3-yl-ethylidene)diphenylphosphinamide** (**4a**): white solid; IR (neat): 1732, 1155 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 2.89 (d, J = 2.2 Hz, 3H), 7.35 (dd, J = 2.8, 5.2 Hz, 1H), 7.41-7.48 (m, 6H), 7.75 (dd, J = 1.2, 5.2 Hz, 1H), 7.93-7.97 (m, 4H), 8.01 (dd, J = 1.8, 2.8 Hz, 1H); ^{13}C NMR (CDCl$_3$): δ = 22.7 (d, J = 12.3 Hz), 126.2, 127.1 (d, J = 12.4 Hz), 130.7 (d, J = 2.1 Hz), 131.3 (d, J = 2.1 Hz), 131.5 (d, J = 9.3 Hz), 134.8 (d, J = 30.6 Hz), 144.5 (d, J = 25.6 Hz), 175.9 (d, J = 7.1 Hz); ^{31}P NMR (CDCl$_3$): δ = 19.3; MS (ESI) *m/z* 348 [M+Na$^+$]; HRMS (EI) *m/z* calcd for $C_{18}H_{17}NOPS$ [M+H$^+$]: 326.0768. Found: 326.0769; mp: 140 $^{\circ}$C.

***N*-(1-Phenylethylidene)diphenylphosphinamide** (**4b**): Known compound.[2]

***N*-(1-Methyl-3-phenylpropylidene)diphenylphosphinamide** (**4c**): Known compound.[3]

***N*-(1,2-Dimethylpropylidene)diphenylphosphinamide** (**4d**): white solid; IR (neat): 1659, 1206 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 1.18 (d, J = 7.0 Hz, 6H), 2.46 (d, J = 2.2 Hz, 3H), 2.67-2.76 (m, 1H), 7.37-7.46 (m, 6H), 7.91 (ddd, J = 1.5, 7.9, 11.6 Hz, 4H); ^{13}C NMR (CDCl$_3$): δ = 19.7, 24.7 (d, J = 13.4 Hz), 41.9 (d, J = 20.6 Hz), 128.2 (d, J = 12.4 Hz), 131.1 (d, J = 3.1 Hz), 131.4 (d, J = 8.3 Hz), 134.9 (d, J = 130.9 Hz), 196.3 (J = 11.4 Hz); ^{31}P NMR (CDCl$_3$): δ = 17.9; MS (ESI) *m/z* 308 [M+Na$^+$]; HRMS (FAB) *m/z* calcd for $C_{17}H_{21}NOP$ [M+H$^+$]: 286.1361. Found: 286.1367.

***N*-(1,2,2-Trimethylpropylidene)diphenylphosphinamide** (**4e**): white solid; IR (neat): 1662, 1200 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 1.23 (s, 9H), 2.49 (d, J = 1.8 Hz, 3H), 7.36-7.47 (m, 6H), 7.86-7.97 (m, 4H); ^{13}C NMR (CDCl$_3$): δ = 21.7, 27.6 (d, J = 11.4 Hz), 43.9 (d, J = 19.6 Hz), 128.0-128.7 (multiple peaks), 130.9-132.1 (multiple peaks), 135.0 (d, J = 130.2 Hz), 198.0 (d, J = 12.4 Hz); MS (ESI) *m/z* 322 [M+Na$^+$]; Anal. calcd for $C_{18}H_{22}NOP$: C, 72.22; H, 7.41; N, 4.68 %. Found: C, 71.73; H, 7.40; N, 4.72 %; mp; 86-87 $^{\circ}$C.

(C) General Procedure for Asymmetric Strecker Reaction of Ketoimines

(C-1) Using the catalyst derived from Gd(O^{i}Pr)$_3$ and ligand 1 (Gd-1)

To a solution of ligand **1** (6.6 mg, 15.6 μmol) in THF (150 μL), Gd(O^{i}Pr)$_3$ (0.2 M in THF, 37.5 μL, 7.5 μmol) was added at 0 $^{\circ}$C. The mixture was stirred at 45 $^{\circ}$C for 30 min, and then the solvent was evaporated at ambient temperature. After drying the resulting pre-catalyst under reduced pressure (< 5 mmHg) for 1 h, **4a** (96.5 mg, 0.30 mmol) was added as a solid in one portion. Propionitrile (400 μL) was added at -40 $^{\circ}$C, and after 20 min, TMSCN (62 μL, 0.46 mmol) was added. After 10 min, 2,6-dimethylphenol (38.7 mg, 0.32 mmol) in propionitrile (400 μL) was added to start the reaction. After 30 min, silica gel was added to the reaction mixture at -40 $^{\circ}$C. Removal of the silica gel and catalyst through the short pad silica gel column chromatography (MeOH/CHCl$_3$, 1/9) gave amidonitrile **5a**. (>99% conversion yield determined by ^{1}H NMR analysis.) This crude mixture can be purified by preparative TLC (AcOEt/hexane) to give the analytical pure **5a**.

(C-2) Using the crystal A as a catalyst

To a mixture of crystal **A** (7.6 mg, 2.5 μmol) and **4a** (48.5 mg, 0.15 mmol), propionitlile (200 μL) was added at -40 $^{\circ}$C. After 20 min, TMSCN (31 μL, 0.23 mmol) was added, and after 5 min, 2,6-dimethylphenol (18.4 mg, 0.15 mmol) in propionitrile (200 μL) was added to start the reaction.

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[2] Krzyzanowska, B.; Stec, W. J. *Synthesis* **1982**, 270.

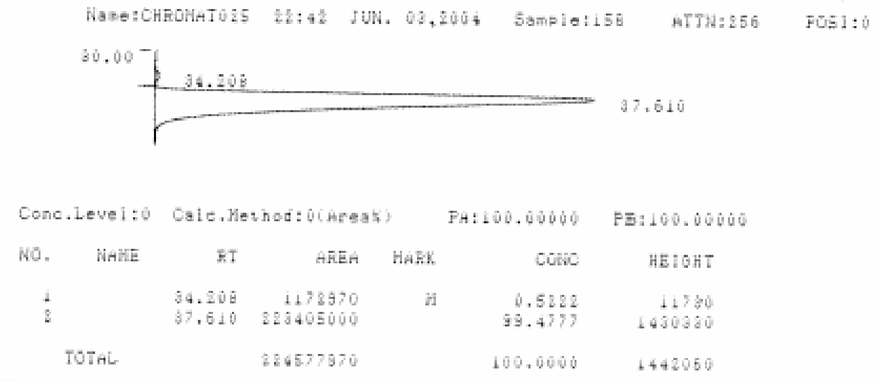
[3] Masumoto, S.; Usuda, H.; Suzuki, M.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 5634.

After 2 h, silica gel was added to the reaction mixture at -40 °C. Removal of the silica gel and catalyst through the short pad silica gel column chromatography (MeOH/$CHCl_3$, 1/9) gave amidonitrile **5a**. (>99% conversion yield determined by ^{1}H NMR analysis.)

(D) Data of Products

2-*N*-Diphenylphosphinoylamino-2-(3-thiophenyl)propionitrile (**5a**): white amorphous; IR (neat): 3112, 2867, 2210, 1192, 1123 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.84 (s, 3H), 4.54 (m, 1H), 7.14 (m, 1H), 7.18 (m, 1H), 7.26 (m, 2H), 7.32 (m, 3H), 7.39 (m, 2H), 7.66 (dd, J = 7.7, 12.2 Hz, 2H), 7.78 (dd, J = 7.4, 12.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 29.3 (d, J = 4.1 Hz), 52.5, 121.2 (d, J = 4.1 Hz), 122.6, 125.3, 127.0, 128.1, 128.3, 128.4, 131.2, 131.3, 131.56, 131.68, 131.70, 131.79, 131.83, 131.91, 132.05, 132.6, 133.1, 141.6 (d, J = 4.1 Hz); ^{31}P NMR ($CDCl_3$): δ = 20.4; MS (ESI) *m/z* 375 [M+Na$^+$]; HRMS (FAB) *m/z* calcd for $C_{19}H_{18}N_2OPS$ [M+H$^+$]: 353.0877. Found: 353.0879.

HPLC (DAICEL CHIRALPAK AS-H, hexane/2-propanol 9/1, flow 1.0 mL/min, detection at 254 nm.):
Using Gd-**1** as a catalyst (+99% ee). $[\alpha]^{23}_D$ -6.9 (c = 1.83, CH_2Cl_2).



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Name:CHROMAT025   22:42   JUN. 03,2004   Sample:158   ATTN:256   POSI:0

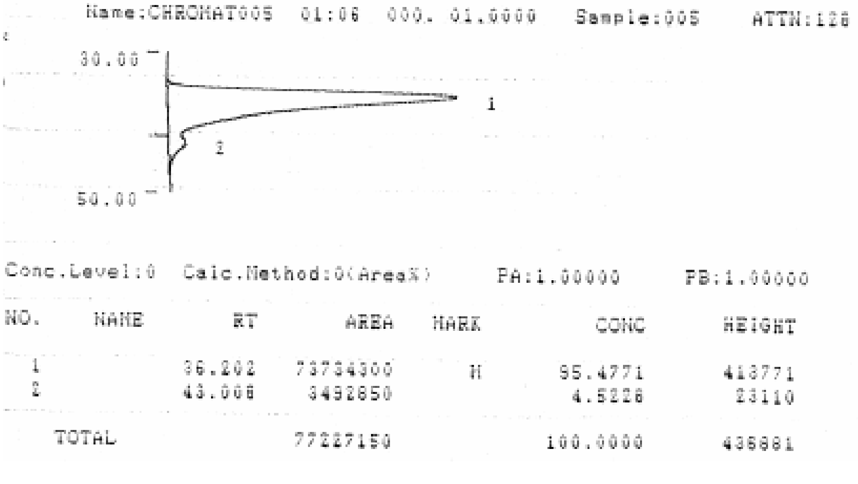
Conc.Level:0  Calc.Method:0(Area%)     PA:100.00000   PB:100.00000

NO.   NAME       RT        AREA    MARK        CONC       HEIGHT

 1             34.208     1172870     M        0.5222       11720
 2             37.610   223405000             99.4777     1430330

  TOTAL                 224577870            100.0000     1442050
```

Using crystal **A** as a catalyst (-91% ee). $[\alpha]^{23}_D$ +6.2 (c = 1.50, CH_2Cl_2).



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Conc.Level:0  Calc.Method:0(Area%)     PA:1.00000     PB:1.00000

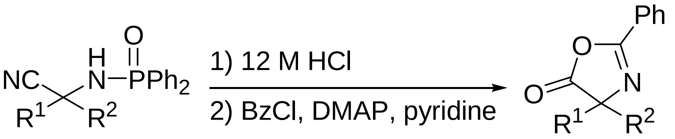
NO.    NAME        RT        AREA    MARK        CONC      HEIGHT

 1               36.202   73734300     M       95.4771     413771
 2               43.008    3492850              4.5228      23110

   TOTAL                  77227150            100.0000     436881
```

2-*N*-Diphenylphosphinoylamino-2-phenylpropionitrile (**5b**): Known compound.[3] Ee was determined after conversion to the corresponding oxazolidone following the previously reported procedures.[3] (See **Scheme S-1**.)

Scheme S-1. Conversion to Oxazolidone

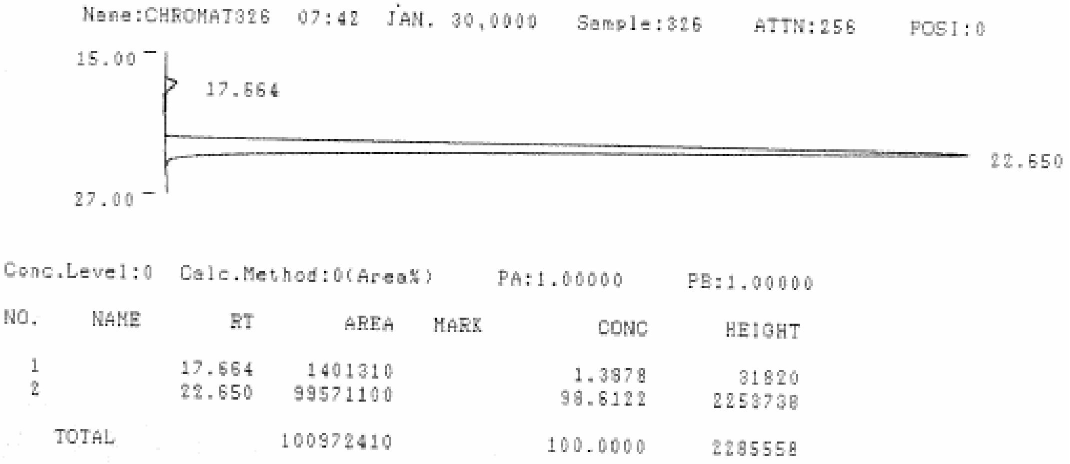


5b, **5c**, **5d** **6b**, **6c**, **6d**

4-Methyl-2,4-diphenyl-4*H*-oxazol-5-one (**6b**): Known compound.[4]

HPLC (DAICEL CHIRALCEL OD-H, hexane/2-propanol 1000/1, flow 1.0 mL/min, detection at 254 nm.):

Using Gd-**2** as a catalyst (+97% ee).



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Name:CHROMAT326  07:42  JAN. 30,0000   Sample:326   ATTN:256   POSI:0

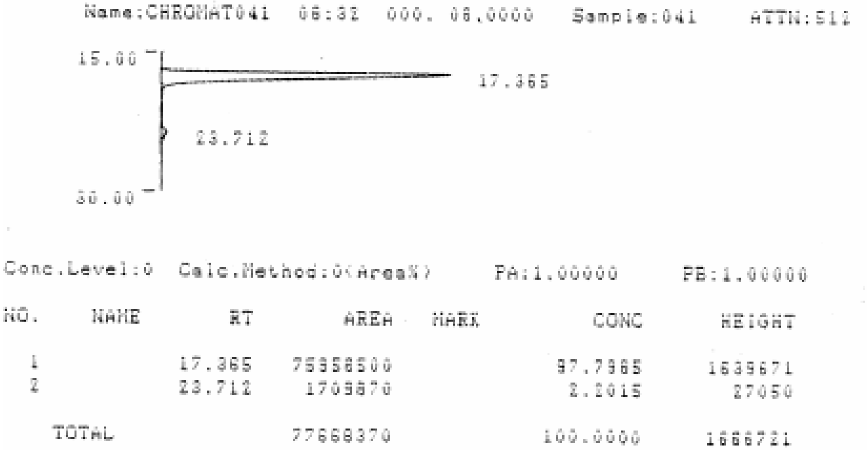
Conc.Level:0  Calc.Method:0(Area%)     PA:1.00000     PB:1.00000

NO.    NAME        RT        AREA    MARK         CONC        HEIGHT

 1               17.664    1401310               1.3878        31820
 2               22.650   99571100              98.6122      2253738

   TOTAL                 100972410             100.0000      2285558
```

Using crystal **A** as a catalyst (-96% ee).



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Name:CHROMAT041  08:32  000. 08,0000   Sample:041   ATTN:512

Conc.Level:0  Calc.Method:0(Area%)     PA:1.00000     PB:1.00000

NO.    NAME        RT        AREA    MARK         CONC        HEIGHT

 1               17.365   75958500              97.7985      1639671
 2               23.712    1709870               2.2015        27050

   TOTAL                  77668370             100.0000      1666721
```

2-*N*-Diphenylphosphinoylamino-2-methyl-4-phenylbutyronitrile (**5c**): Known compound.[3] Ee was determined after conversion to the corresponding oxazolidone following the previously reported procedures.[3] (See **Scheme 1**.)

4-Methyl-4-phenethyl-2-phenyl-4*H*-oxazol-5-one (**6c**): Known compound.[3]

HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 99/1, flow 1.0 mL/min, detection at 254 nm.):

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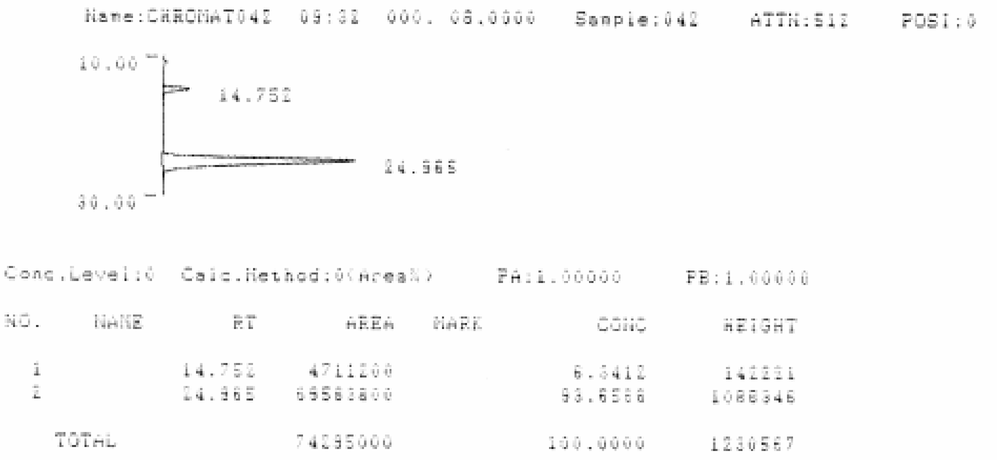
[4] Obrecht, D.; Spiegler, C; Schönholzer, P.; Müller, K.; Heimgartner, H.; Stierli, F. *Helv. Chem. Acta* **1992**, *75*, 1666.

Using Gd-**3** as a catalyst (+87% ee).



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Name:CHROMAT042  09:32  000. 06.0000   Sample:042    ATTN:512    POSI:0

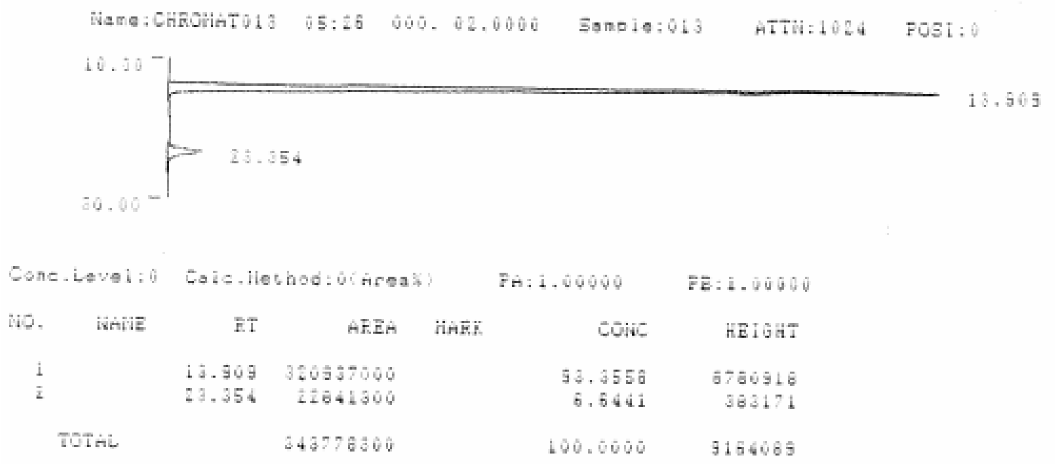
Conc.Level:0  Calc.Method:0(Area%)     FA:1.00000     FB:1.00000

NO.    NAME        RT         AREA    MARK          CONC       HEIGHT

 1              14.752     4711200                6.3412       142221
 2              24.965    69583800               93.6588      1088346

   TOTAL                  74295000              100.0000      1230567
```

Using crystal **A** as a catalyst (-87% ee).



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Name:CHROMAT013  05:26  000. 02.0000   Sample:013    ATTN:1024   POSI:0

Conc.Level:0  Calc.Method:0(Area%)     FA:1.00000     FB:1.00000

NO.    NAME        RT         AREA    MARK          CONC       HEIGHT

 1              13.909   320937000               93.3558      6780918
 2              23.354    22841300                6.6441       383171

   TOTAL                 343778300              100.0000      7164089
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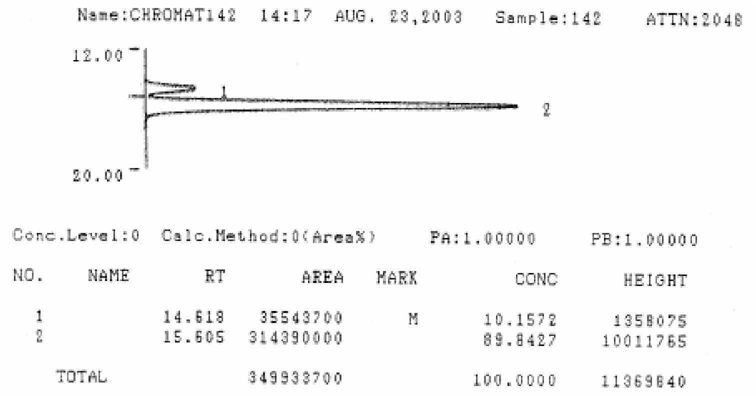
2-*N*-Diphenylphosphinoylamino-2,3-dimethylbutyronitrile (**5d**)**:** white amorphous; IR (neat) 2974, 2875, 2210, 1186, 1123 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.04 (d, J = 6.8 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H), 1.51 (s, 3H), 2.03 (quintet, J = 6.8 Hz, 1H), 3.33 (d, J = 7.5 Hz, 1H), 7.38-7.50 (m, 6H), 7.75 (dd, J = 7.6, 11.9 Hz, 2H), 7.90 (dd, J = 7.4, 12.2 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 17.1, 17.3, 22.2 (d, J = 3.8 Hz), 39.0 (d, J = 4.1 Hz), 57.2 (d, J = 2.1 Hz), 121.4 (d, J = 4.1 Hz), 128.65, 128.71, 128.75, 128.82, 131.25, 131.33, 132.0, 132.18, 132.20, 132.26, 132.28, 132.9, 133.0, 133.9 (128.65-133.9: multiple peaks); ^{31}P NMR ($CDCl_3$): δ = 21.0; MS (ESI) *m/z* 335 [M+Na$^+$]; HRMS (FAB) *m/z* calcd for $C_{18}H_{22}N_2OP$ [M+H$^+$]: 313.1470. Found 313.1462; $[\alpha]^{25}_{D}$ -12.4 (c = 1.99, CH_2Cl_2) (+80% ee).

Ee was determined after conversion to the corresponding oxazolidone following the previously reported procedures.[3] (See **Scheme 1**.)

4-Isopropyl-4-methyl-2-phenyl-4*H*-oxazol-5-one (**6d**): IR (neat): colorless oil; 1822, 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.95 (d, J = 6.7 Hz, 3H), 1.06 (d, J = 6.7 Hz, 3H), 1.50 (s, 3H), 2.12 (dq, J = 6.7, 6.7 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 16.6, 17.1, 21.7, 35.4, 72.5, 126.0, 127.9, 128.7, 132.5, 159.8, 181.0; MS (ESI) *m/z* 240 [M+Na$^+$]; HRMS (FAB) *m/z* calcd for $C_{13}H_{16}NO_2$ [M+H$^+$]: 218.1181. Found: 218.1188.

HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 499/1, flow 0.5 mL/min, detection at 254 nm.):

Using Gd-**2** as a catalyst (+80% ee).



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Name:CHROMAT142   14:17   AUG. 23,2003    Sample:142     ATTN:2048

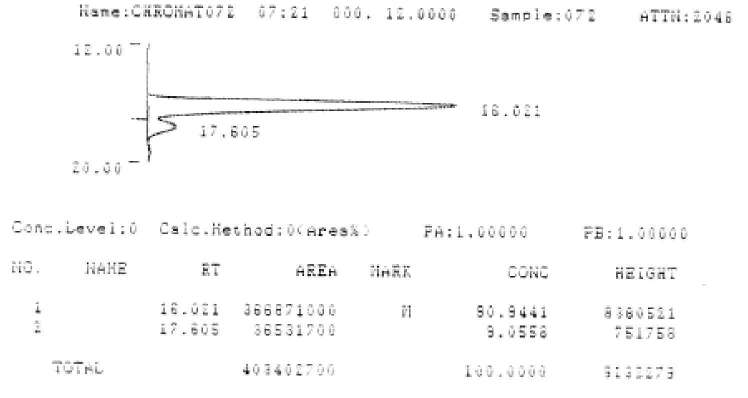
Conc.Level:0   Calc.Method:0(Area%)     PA:1.00000      PB:1.00000

NO.    NAME        RT        AREA    MARK        CONC       HEIGHT

  1             14.618    35543700     M       10.1572     1358075
  2             15.605   314390000             89.8427    10011765

    TOTAL                349933700            100.0000    11369840
```

Using crystal **A** as a catalyst (-82% ee).



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Name:CHROMAT072   07:21   000. 12.0000    Sample:072     ATTN:2048

Conc.Level:0   Calc.Method:0(Area%)     PA:1.00000      PB:1.00000

NO.    NAME        RT        AREA    MARK        CONC       HEIGHT

  1             16.021   366871000     M       90.9441     8380521
  2             17.605    36531700              9.0558      751758

    TOTAL                403402700            100.0000     9132279
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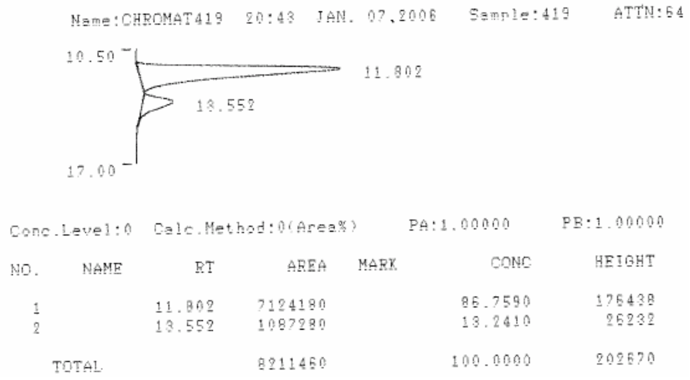
2-*N*-Diphenylphosphinoylamino-2,3,3-trimethylbutyronitrile (**5e**): white solid; mp; 128-130 ^{o}C. HPLC (DAICEL CHIRALCEL OD-H, hexane/2-propanol 20/1, flow 1.0 mL/min, detection at 254 nm.): Using Gd-**3** as a catalyst (+74% ee).



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Name:CHROMAT419   20:43   JAN. 07,2006    Sample:419     ATTN:64

Conc.Level:0   Calc.Method:0(Area%)     PA:1.00000      PB:1.00000

NO.    NAME        RT        AREA    MARK        CONC       HEIGHT

  1             11.802     7124180             86.7590      176438
  2             13.552     1087280             13.2410       26232

    TOTAL                  8211460            100.0000      202670
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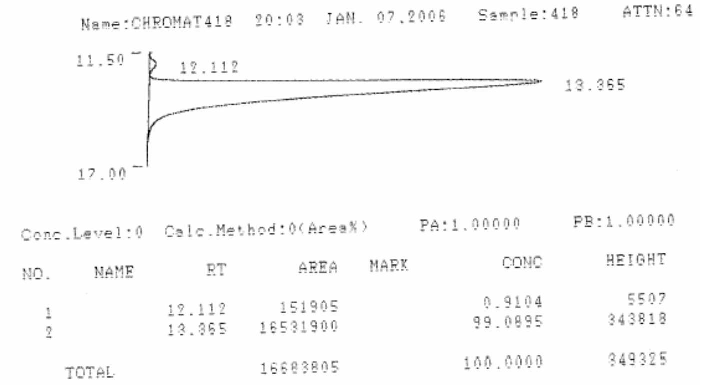
Using crystal **A** as a catalyst (-98% ee).



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Name:CHROMAT418   20:03   JAN. 07,2006    Sample:418     ATTN:64

Conc.Level:0   Calc.Method:0(Area%)     PA:1.00000      PB:1.00000

NO.    NAME        RT        AREA    MARK        CONC       HEIGHT

  1             12.112      151905              0.9104        5507
  2             13.365    16531900             99.0895      343818

    TOTAL                 16683805            100.0000      349325
```

(E) Synthesis of Crystals

Crystal A

To a solution of ligand **3** (116.4 mg, 0.24 mmol) in THF (300 μL), Gd(O^{i}Pr)$_3$ (0.2 M in THF, 750 μL, 0.15 mmol) was added at 0 °C. The mixture was stirred at 45 °C for 40 min, and then the solvent was evaporated at ambient temperature. After drying the residue under reduced pressure (< 5 mmHg) over night, propionitrile-hexane (2:1) solution (600 μL) was added. After 2 days, colorless prisms appeared and were washed with propionitrile three times and dried under vacuum (80% yield). Anal. calcd for $C_{120}H_{109}Cl_{10}Gd_4O_{28}P_5$: C, 45.94; H, 3.50 %. Found: C, 46.21; H, 3.75 %.

Crystal B

To a solution of ligand **1** (100.9 mg, 0.24 mmol) in THF (1.5 mL), La(O^{i}Pr)$_3$ (0.2 M in THF, 750 μL, 0.15 mmol) was added at room temperature. The mixture was stirred at 45 °C for 1 h, and then the solvent was evaporated at ambient temperature. After drying the residue under reduced pressure (< 5 mmHg) for 2 h, THF (1 mL) was added. After 1 day, colorless prisms appeared and were washed with THF three times and dried under vacuum (49.4 mg, 47% yield). Anal. calcd for $C_{200}H_{202}La_6O_{44}P_8$ (+2THF): C, 54.71; H, 4.64 %. Found: C, 54.76; H, 4.69 %.

(F) ESI-MS Studies

Figure S-1. Spectrum of Crystal **A** (analyzed by ESI-Q-MS: ZQ4000)

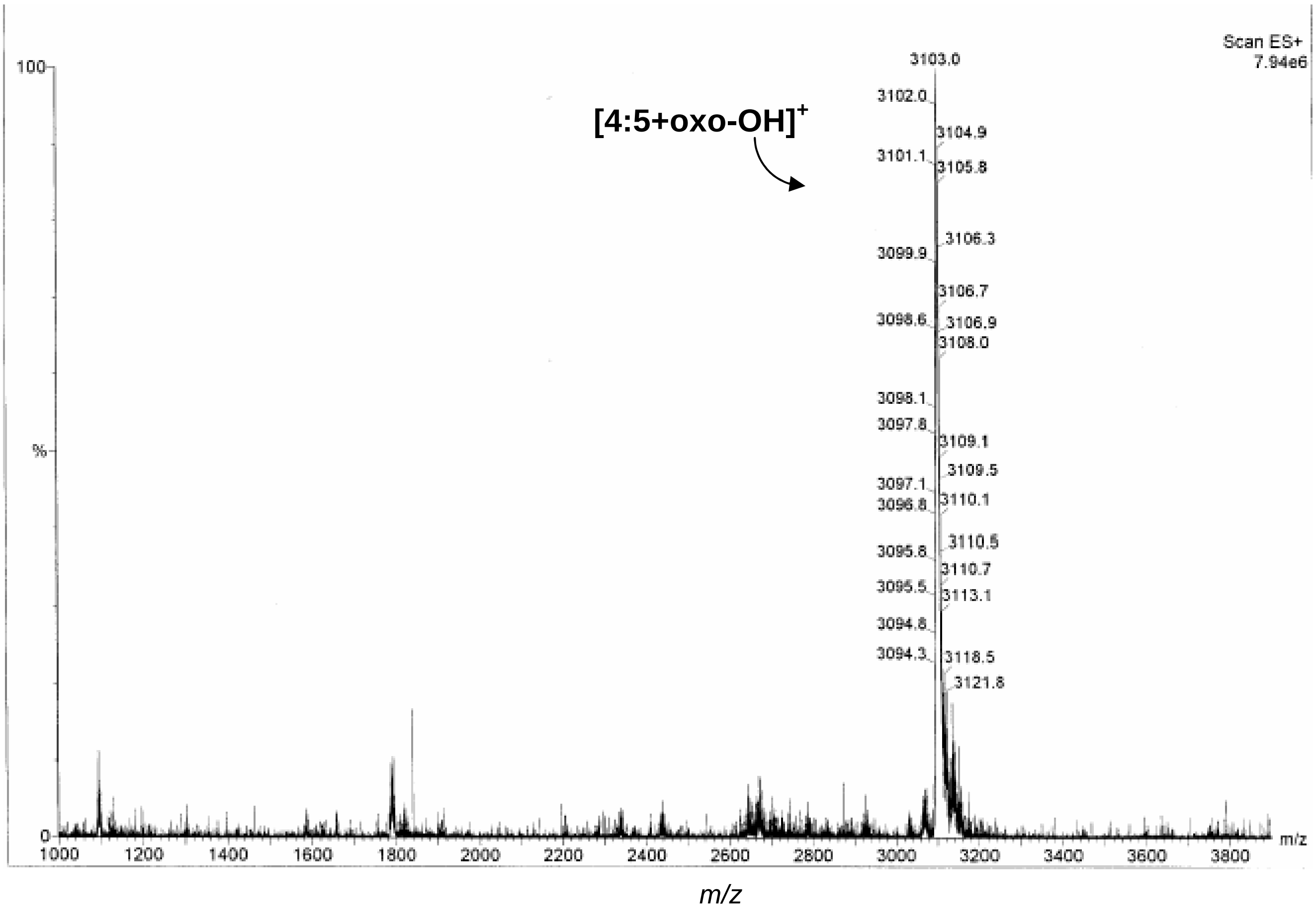


Figure S-2. Spectrum of Crystal **B** (analyzed by ESI-QFT-MS[5]: QFT-7)

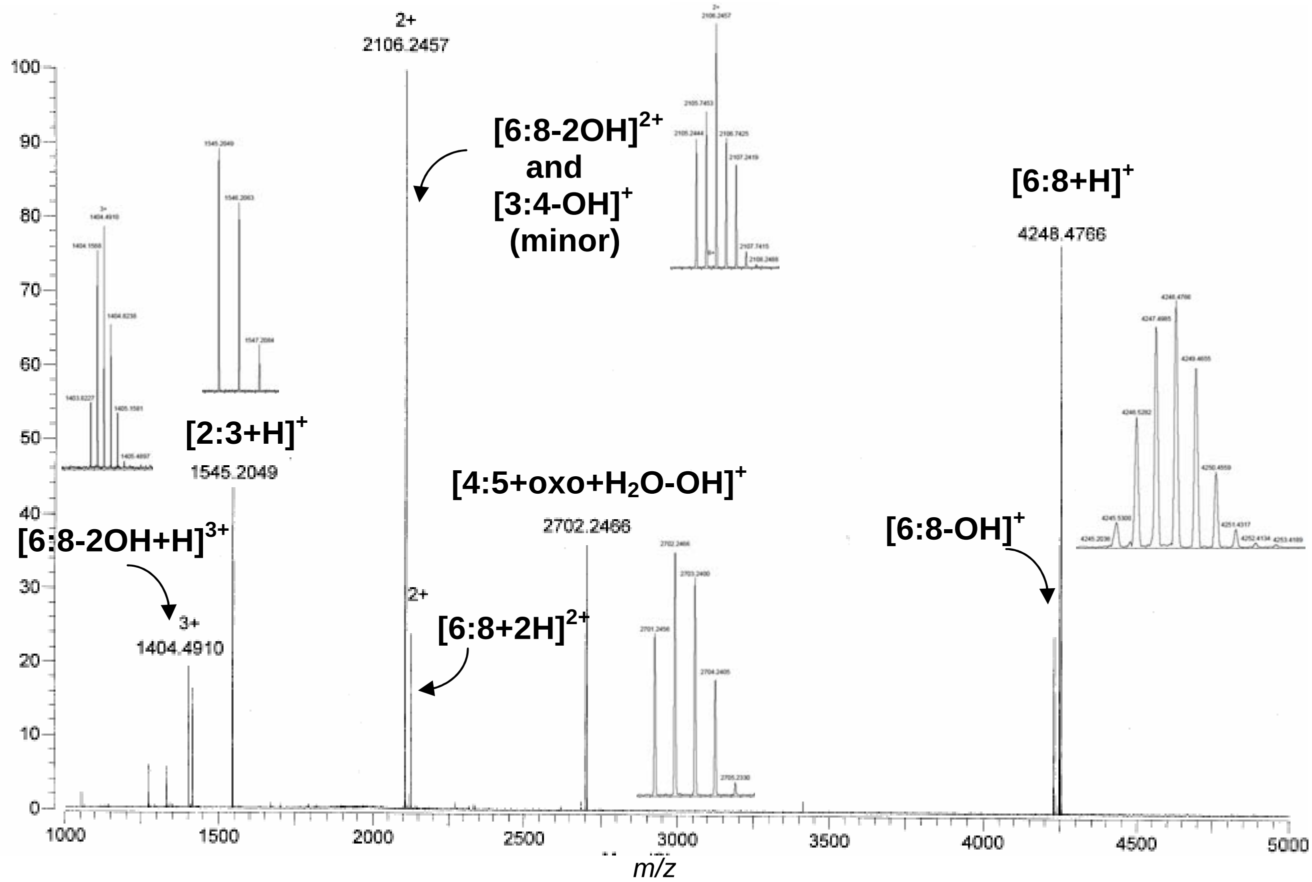
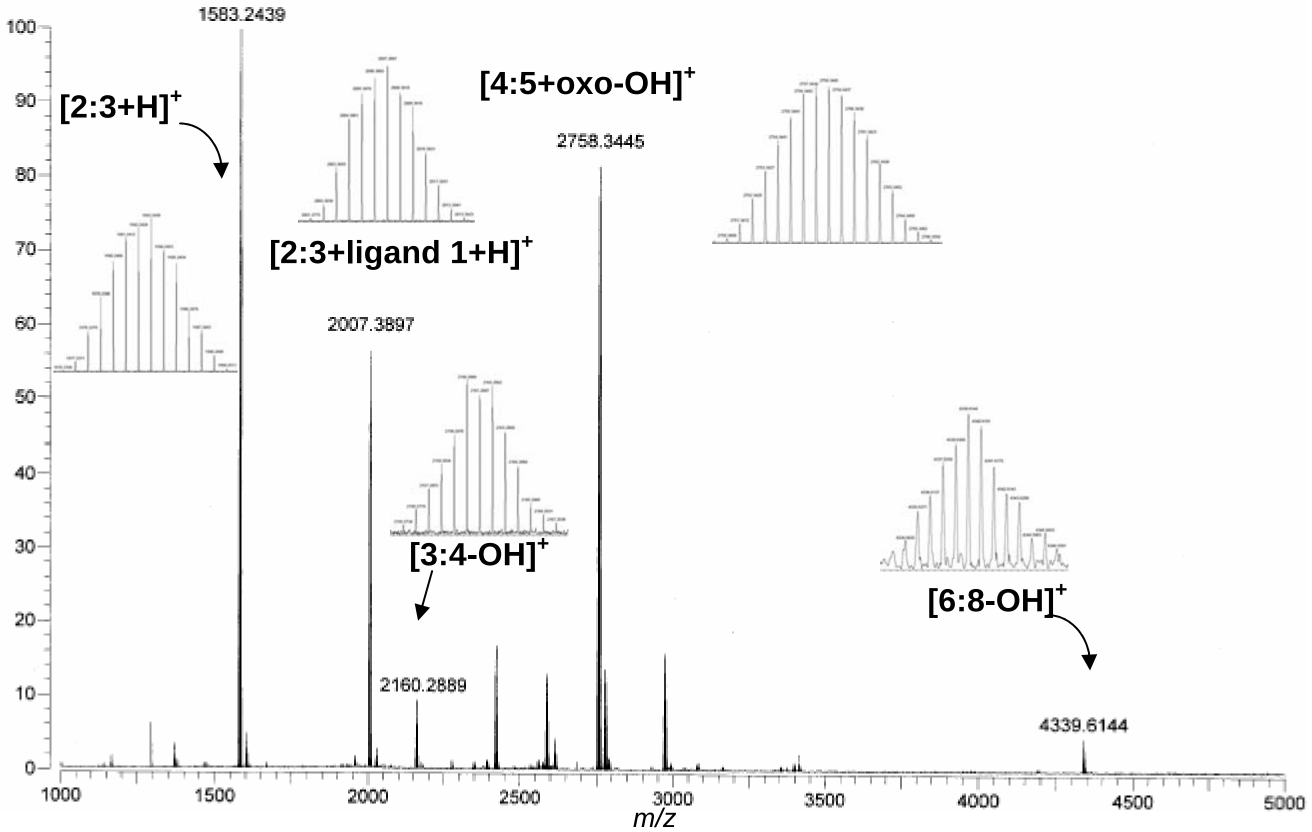


Figure S-3. Spectrum of Gd-**1** (analyzed by ESI-QFT-MS: QFT-7)



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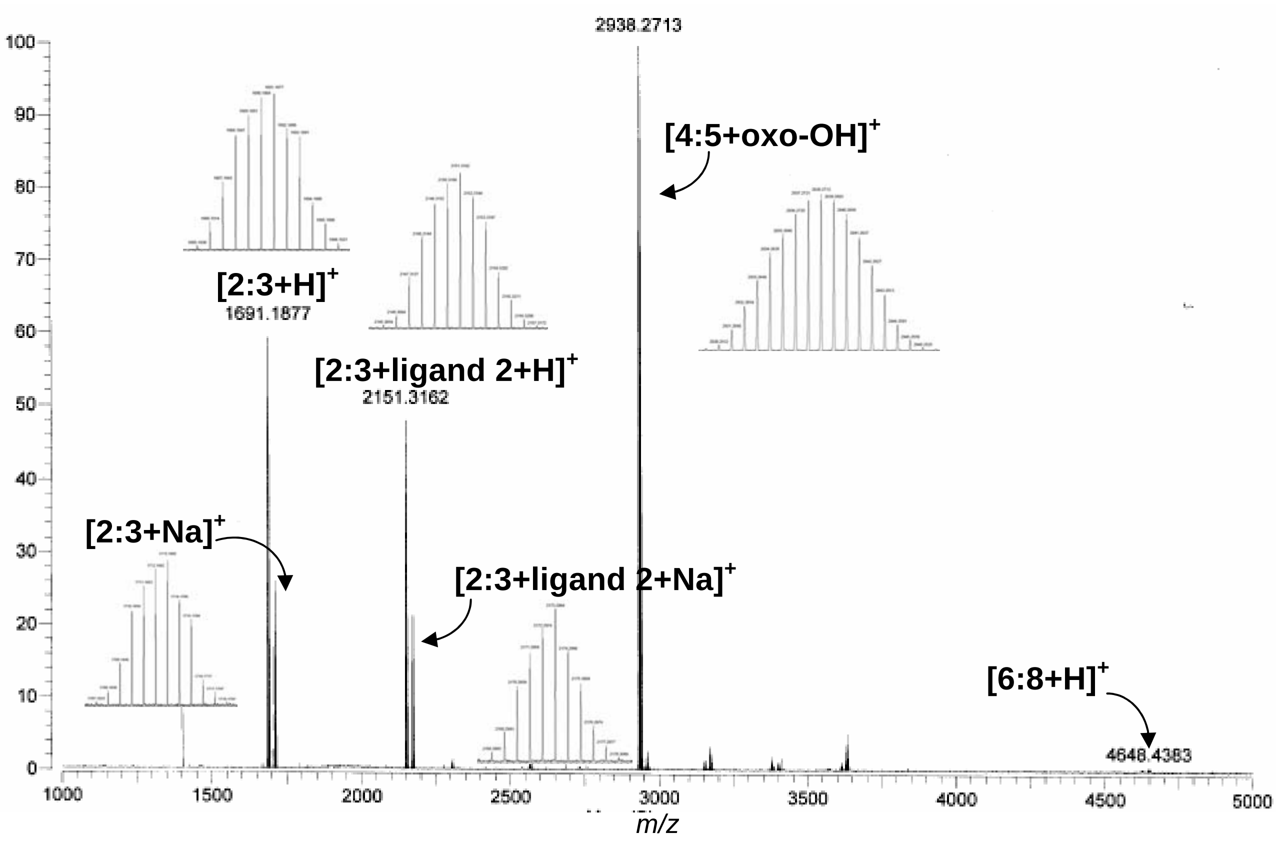
[5] Gross, M. L.; Rempel, D. L. *Science* **1984**, *226*, 261.

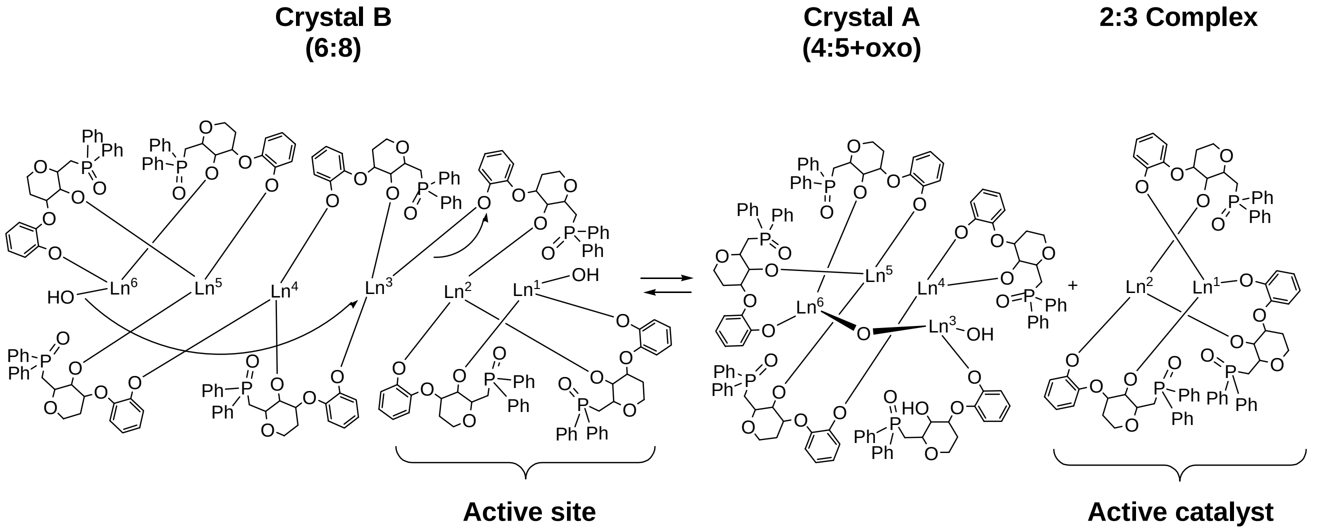
Figure S-4. Spectrum of Gd-**2** (analyzed by ESI-QFT-MS: QFT-7)



The isotope distribution patterns of fragment ion peaks completely matched with calculated patterns.

Similar ESI-MS patterns were observed from crystal **B**, Gd-**1**, and Gd-**2**. Peak intensity of the 6:8 Gd-complex depended on ligand structure. This fact indicates that the major components (2:3, 4:5+oxo, and 6:8 complex) in those catalyst solutions are the same and that equilibrium among the three compounds may exist. Perhaps, crystal **A** derived from the 4:5+oxo subunit of the Gd:**3** = 6:8 complex corresponding to crystal **B** through conformational change, attack of the terminal La^6-OH group at La^3, and eliminating the 2:3 subunit (**Scheme S-2**). In fact, the coordination number of La^3 (and La^4) was less than those of La^1 and La^2 (or La^5 and La^6), which indicated that La^3 (and La^4) is sterically and electronically more accessible by a donor atom. Conversion from the pure 2:3 complex generated from $Gd(HMDS)_3$ to the 4:5+oxo complex in solution is intrinsically very slow, based on ESI-MS studies. Interestingly, however, this process is autocatalytic. Seeding of crystal **A** in a pure 2:3 complex solution (Gd*-**3**) significantly facilitated the generation of the 4:5+oxo complex in solution. Commercially available Gd(O-*i*-Pr)$_3$ possibly contains gadolinium oxo species as impurities, which can facilitate the formation of crystal **A**.

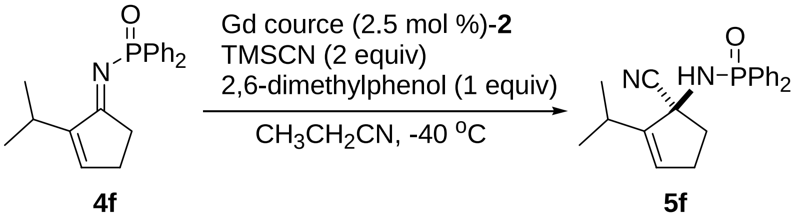
Scheme S-2. Proposed Equilibrium in Catalyst Solution



(G) Experimental Support for the Hypothesis that a sGd:Ligand = 2:3 Complex is the Actual Catalyst in Solution

Comparison of the results using catalysts prepared from Gd(O^{i}Pr)$_3$ and Gd(HMDS)$_3$ in the catalytic Strecker reaction of ketoimine **4f**[6] (**Scheme S-3**) demonstrated that the reactivity and enantioselectivity depend on the purity of the 2:3 complex observed in ESI-MS. A catalyst solution prepared from Gd(O^{i}Pr)$_3$ and **2** in a 1:2 ratio contains two species (2:3 complex and 4:5+oxo complex) (Gd-**2**, **Figure S-4**). On the other hand, a catalyst solution prepared form Gd(HMDS)$_3$ and **2** in a 1:1.5 ratio contains pure 2:3 complex (Gd*-**2**, **Figure S-5**). The reactivity and enantioselectivity of the catalyst prepared under the latter conditions were slightly higher than the former catalyst (**Scheme S-3**). The similar tendency was observed in the catalytic enantioselective cyanosilylation of ketones promoted by the related catalyst.[7]

Scheme S-3. Catalytic Asymmetric Strecker Reaction of **4f**



Gd-2: Gd(O^{i}Pr)$_3$ (2.5 mol %)-**2** (5 mol %): 99% / 4 days, 96% ee
Gd*-2: Gd(HMDS)$_3$ (2.5 mol %)-**2** (3.75 mol %): 99% / 2 days, 98% ee

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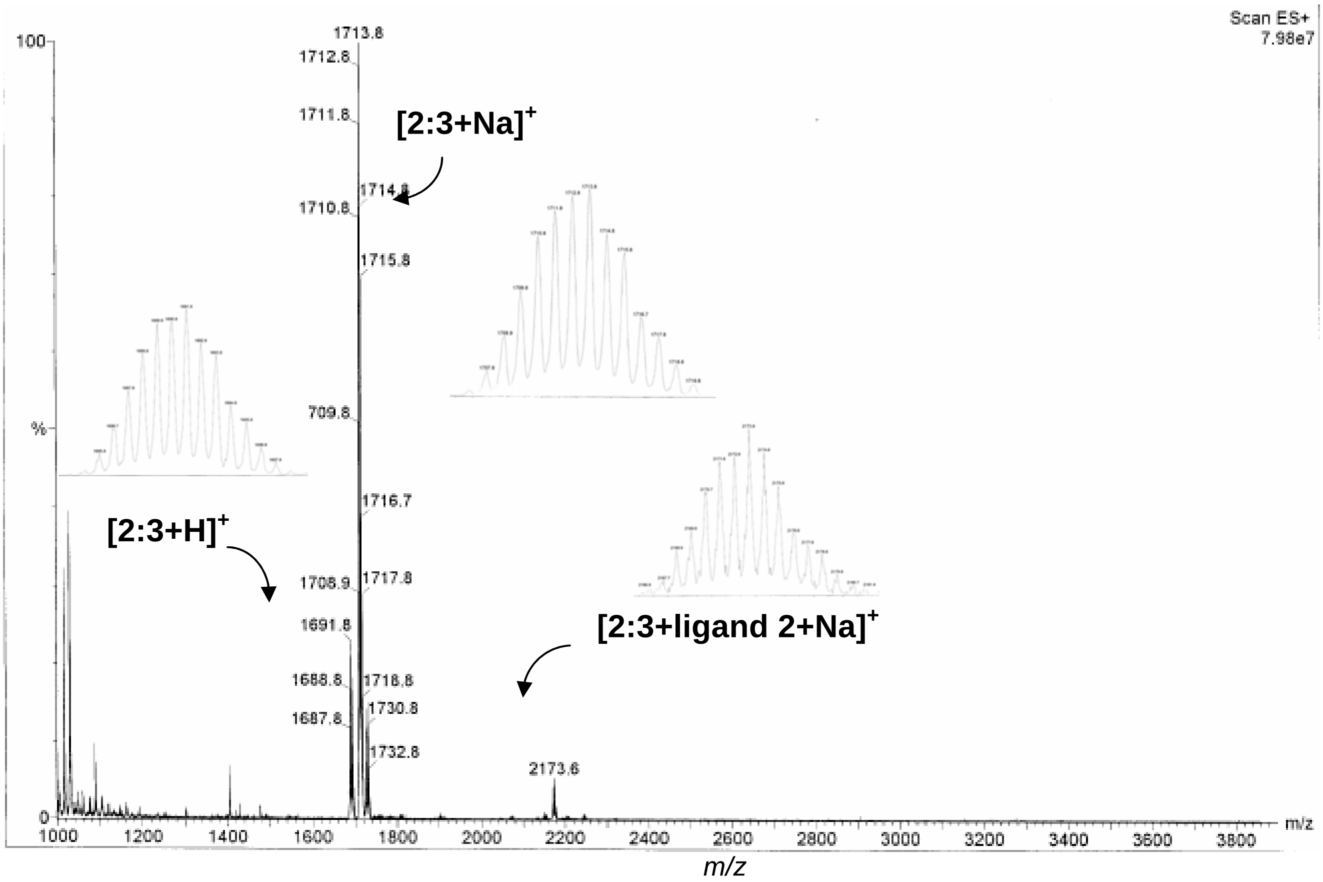
[6] Fukuda, N.; Sasaki, K.; Sastry, T. V. R. S.; Kanai, M.; Shibasaki, M. *J. Org. Chem.* **2006**, *71*, 1220.

[7] Suzuki, M.; Kato, N.; Kanai, M.; Shibasaki, M. *Org. Lett.* **2005**, *7*, 2527.

Figure S-5. Spectrum of Gd*-**2** (analyzed by ESI-Q-MS: ZQ4000)



(H) X-ray Analysis

Table S1. Crystallographic and selected experimental data for crystal **A** and **B**.

	Crystal **A**	Crystal **B**
Chemical formula	$C_{120}H_{109}Cl_{10}Gd_4O_{28}P_5$	$C_{232}H_{243}La_6O_{51}P_9$
Formula weight	3137.53	4959.58
Crystal system	Orthorhombic	Monoclinic
Space group	I 222	P 2_1
Crystal color & shape	Colorless rod	Colorless block
Crystal size	0.33 x 0.29 x 0.10	0.23 x 0.18 x 0.12
a (Å)	30.666(8)	21.547(4)
b (Å)	35.228(9)	29.449(6)
c (Å)	37.646(10)	27.169(6)
β (°)		113.260(4)
V (Å^3)	40668 (18)	15839(6)
Z	8	2
T (K)	80(2)	100(2)

D_c (g·cm^{-3})	1.024	1.028
μ (mm^{-1})	1.503	0.890
Scan range (°)	$2.16 < 2\theta < 57.38$	$2.76 < 2\theta < 57.50$
Unique reflections	48164	74623
Refl. used [$I>2\sigma(I)$]	11684	24661
R_{int}	0.3638	0.2200
Final R indices [$I>2\sigma(I)$]	0.1665, wR_2 0.3261	0.1192, wR_2 0.2729
R indices (all data)	0.4326, wR_2 0.4336	0.2838, wR_2 0.3405
Goodness-of-fit	1.153	0.953
Max, Min $\Delta\rho$/e (Å^{-3})	2.367, -1.677	1.609, -1.043
λ (Mo Kα) (Å)	0.71073	0.71073

The structure was solved by direct method (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 1305 parameters for crystal **A** and 1651 parameters for crystal **B**. The resolution has shown that the solvent molecules were highly disordered and not well defined. However, the metal clusters were found without ambiguity from Fourier difference maps and show only minor disorder at the periphery. The high R1 value is mainly due to the disorder around the cluster molecules, and therefore, we believed that it does not reflect the real quality of the data.