Supporting Information

Tuning the Dissociation of the Fe-$PPh_2(OR)$ Bond in Chiral-at-Metal Complexes $[CpFe(Prophos)PPh_2(OR)]PF_6$, R = Me, Et, *i*Pr, *t*Bu. The Preparative Trick of N_2 Bubbling

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(R_{Fe},R_C)/(S_{Fe},R_C)-(η^5-Cyclopentadienyl)[diphenylphosphane-κP][propane-1,2-diylbis(diphenylphosphane-κP)]iron hexafluorophosphate, (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)PPh$_2$H]PF$_6$

A solution of (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)NCMe]PF$_6$ 5:95 (132 mg, 0.18 mmol) and PHPh$_2$ (0.36 mL, 2.1 mmol) in THF (15 mL) was refluxed for 20 h. The reaction mixture was passed over a short Celite column. The orange filtrate was evaporated. The residue was washed with diethyl ether/hexane to remove excess ligand. The product (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)PPh$_2$H]PF$_6$ 15:85 was obtained in 57% (90 mg) yield. Recrystallization from dichloromethane/hexane afforded a crystalline fraction of diastereomer ratio 2:98. From this sample a crystal was used to determine structure.

^{1}H NMR (CDCl$_3$, 293 K, major (S_{Fe},R_C)-diastereomer, minor (R_{Fe},R_C)-diastereomer in brackets, if distinguishable): δ 7.80-6.84 (m, 28H, Ar-H), 6.45 (br t, 2H, Ar-H) 4.54 (br s, 5H, Cp-H) [4.18 (br s, 5H, Cp-H)], 3.94-2.14 (m, 3H, CH$_2$CH), 1.13 (br s, 3H, CH$_3$).
^{31}P{^{1}H} NMR (CDCl$_3$, 293 K, major (S_{Fe},R_C)-diastereomer, minor (R_{Fe},R_C)-diastereomer in brackets): δ 100.36 (dd, 1P, $^2J_{P\text{-}P}$ = 46.5 Hz, $^2J_{P\text{-}P}$ = 37.6 Hz, PCH) [85.30 (br t, 1P, $^2J_{P\text{-}P}$ = 41.1 Hz, PCH)], 67.31 (dd, 1P, $^2J_{P\text{-}P}$ = 50.9 Hz, $^2J_{P\text{-}P}$ = 37.6 Hz, PCH$_2$) [79.32 (br t, 1P, $^2J_{P\text{-}P}$ = 43.0 Hz, PCH$_2$)], 47.97 (dd, 1P, $^2J_{P\text{-}P}$ = 50.9 Hz, $^2J_{P\text{-}P}$ = 46.5 Hz, PH) [51.14 (br t, 1P, $^2J_{P\text{-}P}$ = 48.6 Hz, PH)], -144.08 (septet, 1P, $^1J_{P\text{-}F}$ = 713.5 Hz, PF$_6$).
ES-MS: *m/z* 719 (cation, 100).
Anal. Calcd for C$_{44}$H$_{42}$F$_6$FeP$_4$ (864.2): C, 61.13; H, 4.90. Found: C, 60.85; H, 4.75.

Decomposition of (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)PPh$_2$(O*i*Pr)]PF$_6$ and spectroscopic data of (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)PPh$_2$F]PF$_6$

In C$_6$D$_5$Cl: A solution of (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)PPh$_2$(O*i*Pr)]PF$_6$ (10 mg, 1:1 ratio) in C$_6$D$_5$Cl (0.4 mL) was heated at 80 °C. The reaction was monitored by ^{31}P{^{1}H} NMR. The formation of the diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)PPh$_2$F]PF$_6$ is obvious in the time-resolved spectrum of Fig. S8.

(R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)PPh$_2$F]PF$_6$:
^{31}P{^{1}H} NMR (C$_6$D$_5$Cl, 293 K, major (S_{Fe},R_C)-diastereomer, minor (R_{Fe},R_C)-diastereomer in brackets): δ 245.00 (dt, 1P, $^1J_{P\text{-}F}$ = 914.0 Hz, $^2J_{P\text{-}P}$ = 67.1 Hz, PPh$_2$F) [245,56 (dt, 1P, $J_{P\text{-}F}$ = 900.8 Hz, $^2J_{P\text{-}P}$ = 67.4 Hz, PPh$_2$F)], 112.28 (dd, 1P, $^2J_{P\text{-}P}$ = 67.3 Hz, $^2J_{P\text{-}P}$ = 37.2 Hz, PCH) [95.27 (dd, 1P,

$^{2}J_{P\text{-}P}$ = 63.4 Hz, $^{2}J_{P\text{-}P}$ = 41.6 Hz, PCH)], 73.44 (ddd, 1P, $^{2}J_{P\text{-}P}$ = 65.9 Hz, $^{2}J_{P\text{-}P}$ = 37.2 Hz, $^{3}J_{P\text{-}F}$ = 15.4 Hz, PCH_2) [91.46 (m, 1P, PCH_2)], -142.78 (septet, 1P, $^{1}J_{P\text{-}F}$ = 712.4 Hz, PF_6).

^{19}F NMR (C_6D_5Cl, 293 K, major (S_{Fe},R_C)-diastereomer, minor (R_{Fe},R_C)-diastereomer in brackets): δ -71.90 (d, 1F, $^{1}J_{P\text{-}F}$ = 712.4 Hz, PF_6), -136.21 (d, 1F, $^{1}J_{P\text{-}F}$ = 914.0 Hz, PPh_2F) [-128.73 (d, 1F, $^{1}J_{P\text{-}F}$ = 900.8 Hz, PPh_2F)].

MS (ESI): *m/z* 737.2 (cation, 100).

HRMS (ESI): calcd for the cation $C_{44}H_{41}FFeP_3^+$ 737.1755; found *m/z* 737.1755.

In $CDCl_3$: A solution of (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)PPh_2(O*i*Pr)]PF_6 (10 mg, 1:1 ratio) in $CDCl_3$ (0.4 mL) was heated at 56 ^{o}C. The reaction was monitored by $^{31}P\{^{1}H\}$ NMR and ^{19}F NMR spectroscopy. The formation of $F_2P(O)OH$ and $F_2P(O)O$*i*Pr was observed in the spectra of Figs. S9-1 and S9-2.

$F_2P(O)OH$: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -18.10 (br t, 1P, $J_{P\text{-}F}$ = 976.7Hz). ^{19}F NMR ($CDCl_3$): δ -83.41 (d, 2F, $^{1}J_{P\text{-}F}$ = 976.7 Hz).

$F_2P(O)O$*i*Pr: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -20.58 (t, 1P, $J_{P\text{-}F}$ = 1011.8 Hz). ^{19}F NMR ($CDCl_3$): δ -84.97 (d, 2F, $^{1}J_{P\text{-}F}$ = 1011.8 Hz).

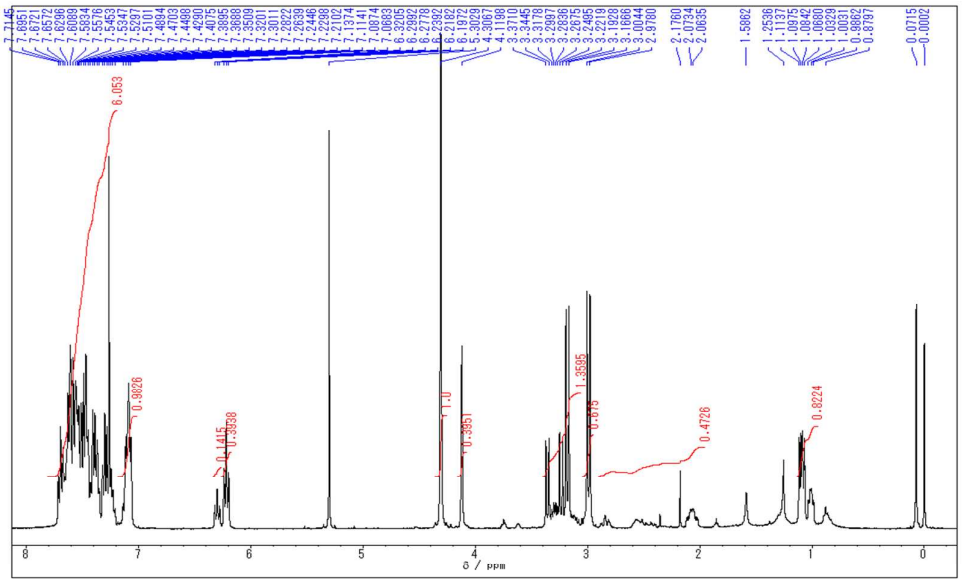

Figure S1-1. ^{1}H NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)-PPh(OMe)$_2$]PF$_6$ in CDCl$_3$ (32:68 ratio).

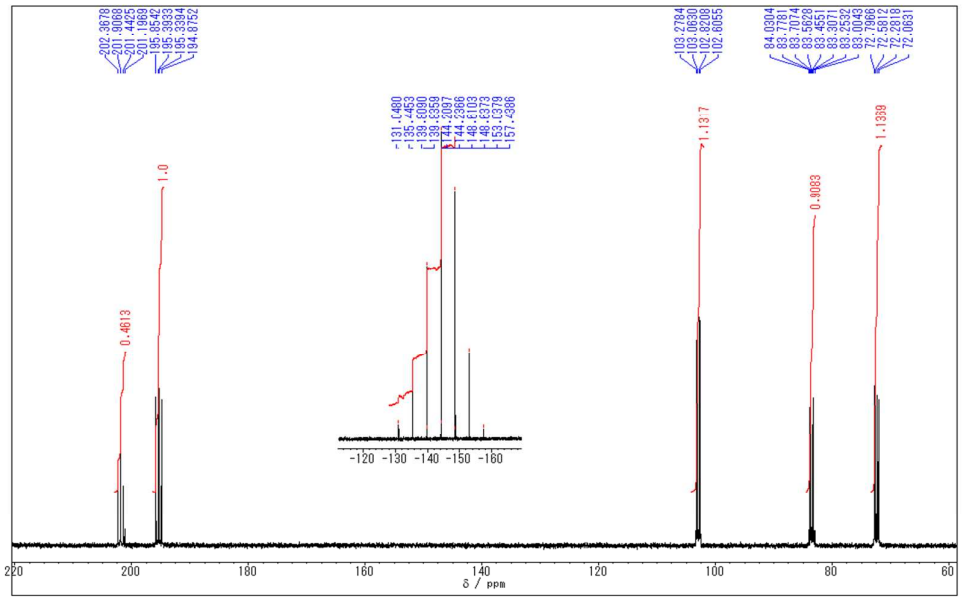

Figure S1-2. ^{31}P{^{1}H} NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe-(Prophos)PPh(OMe)$_2$]PF$_6$ in CDCl$_3$ (32:68 ratio).

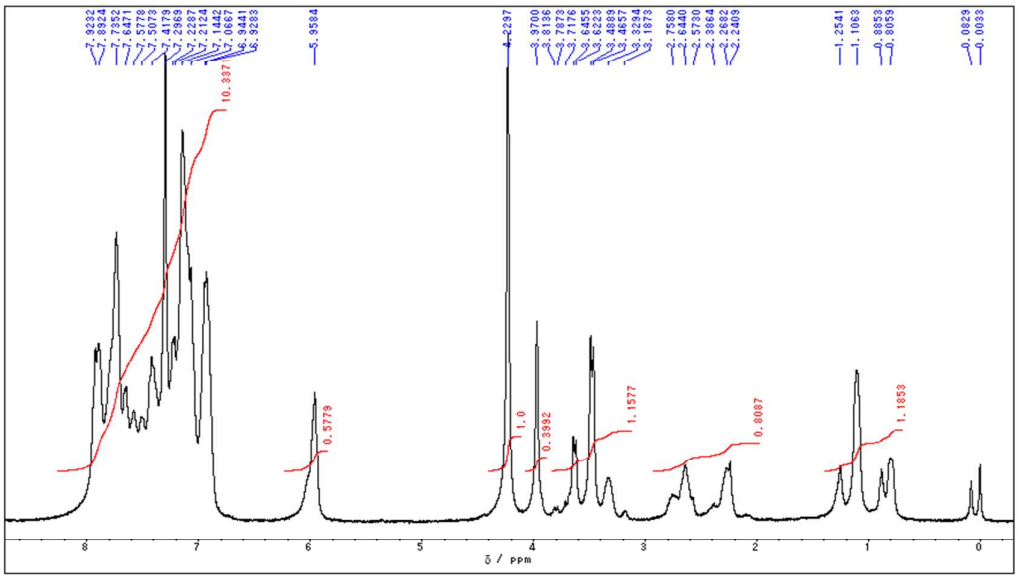

Figure S2-1. ^{1}H NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)-PPh_2(OMe)]PF_6 in $CDCl_3$ (23:77 ratio).

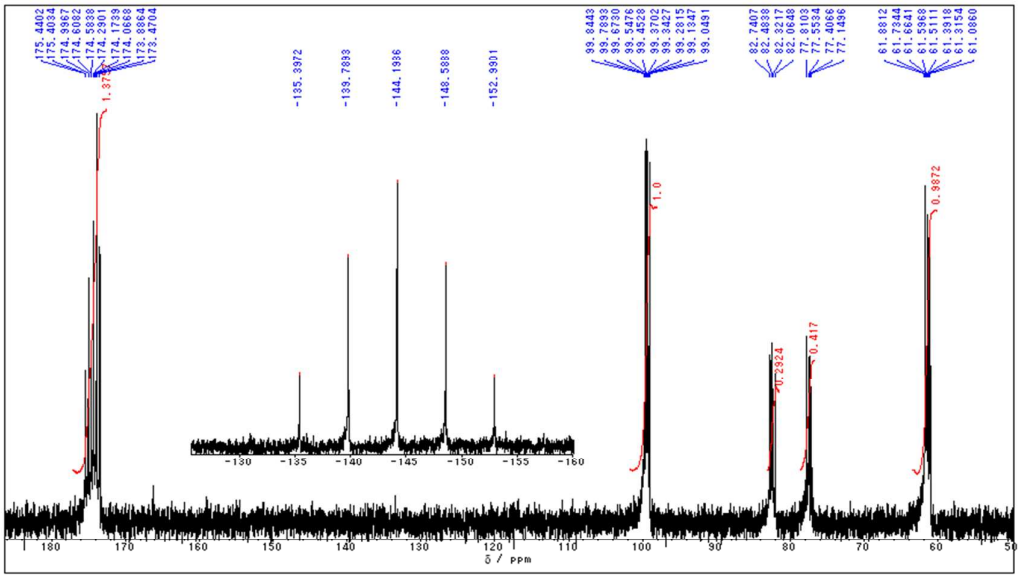

Figure S2-2. ^{31}P{^{1}H} NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe-(Prophos)PPh_2(OMe)] in $CDCl_3$ (23:77 ratio).

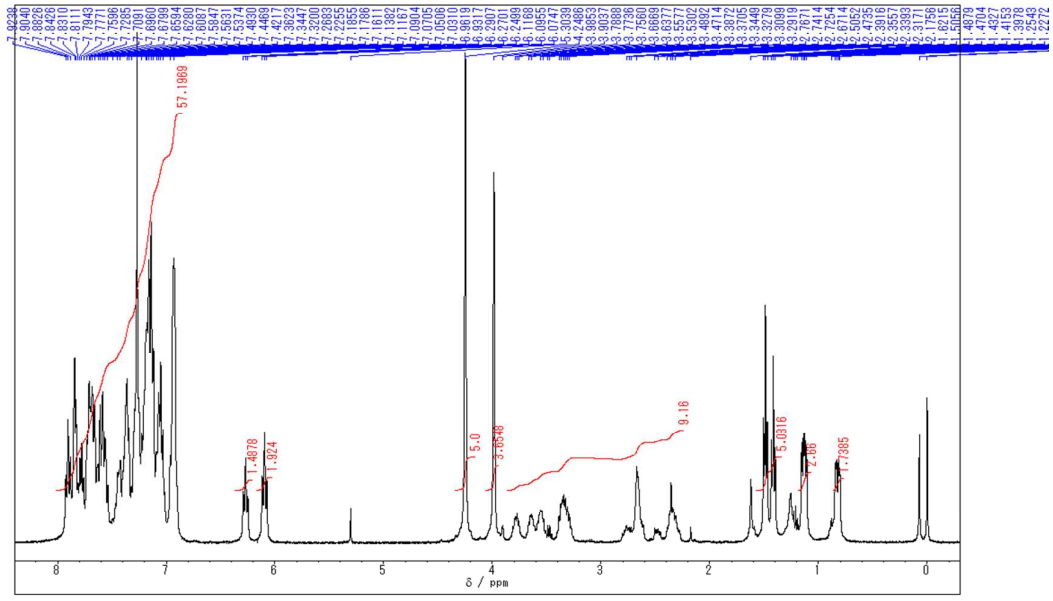

Figure S3-1. ^{1}H NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)-PPh_2(OEt)] in $CDCl_3$ (42:58 ratio).

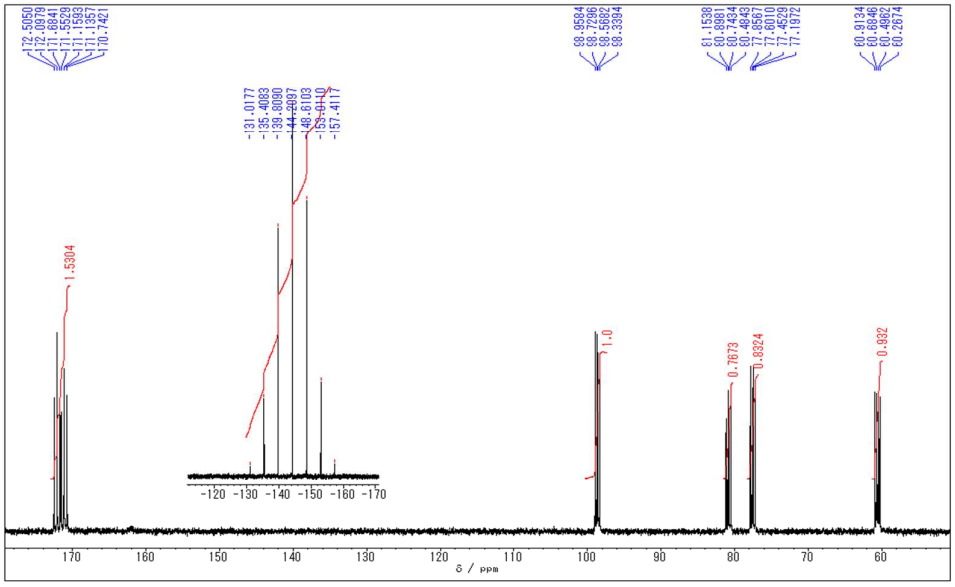

Figure S3-2. $^{31}P\{^{1}H\}$ NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe-(Prophos)PPh_2(OEt)]PF_6 in $CDCl_3$ (42:58 ratio).

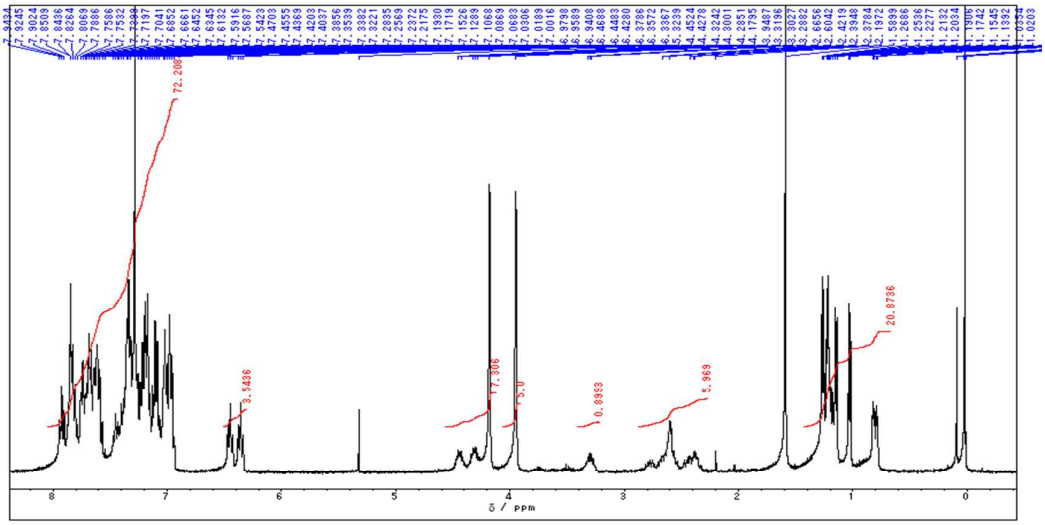

Figure S4-1. ^{1}H NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)-PPh_2(O*i*Pr)]PF_6 in $CDCl_3$ (55:45 ratio).

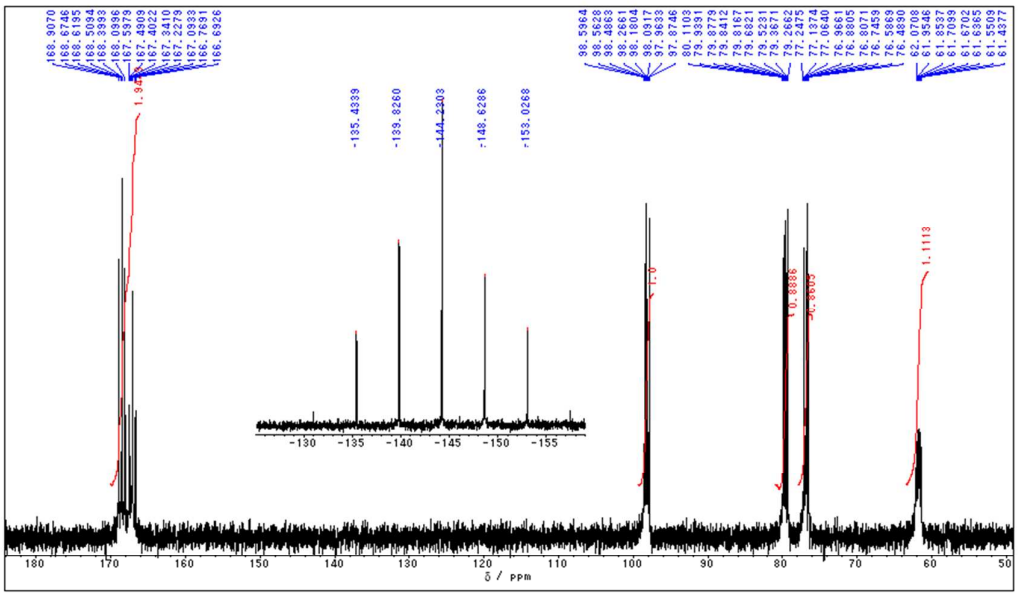

Figure S4-2. $^{31}P\{^{1}H\}$ NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe-(Prophos)PPh_2(O*i*Pr)]PF_6 in $CDCl_3$ (55:45 ratio).

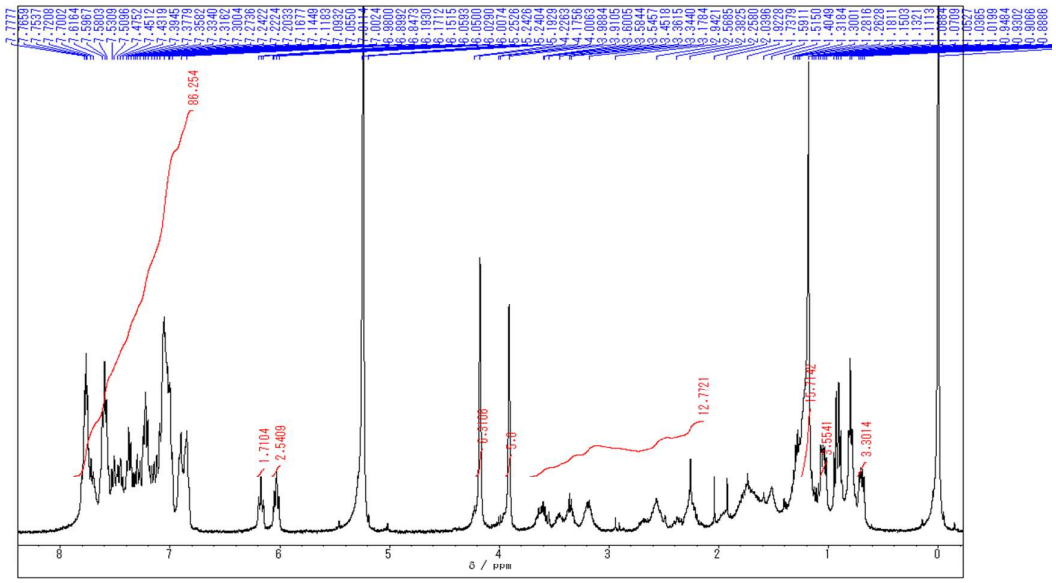

Figure S5-1. ^{1}H NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe(Prophos)-PPh_2(O*t*Bu)]PF_6 in CD_2Cl_2 (45:55 ratio).

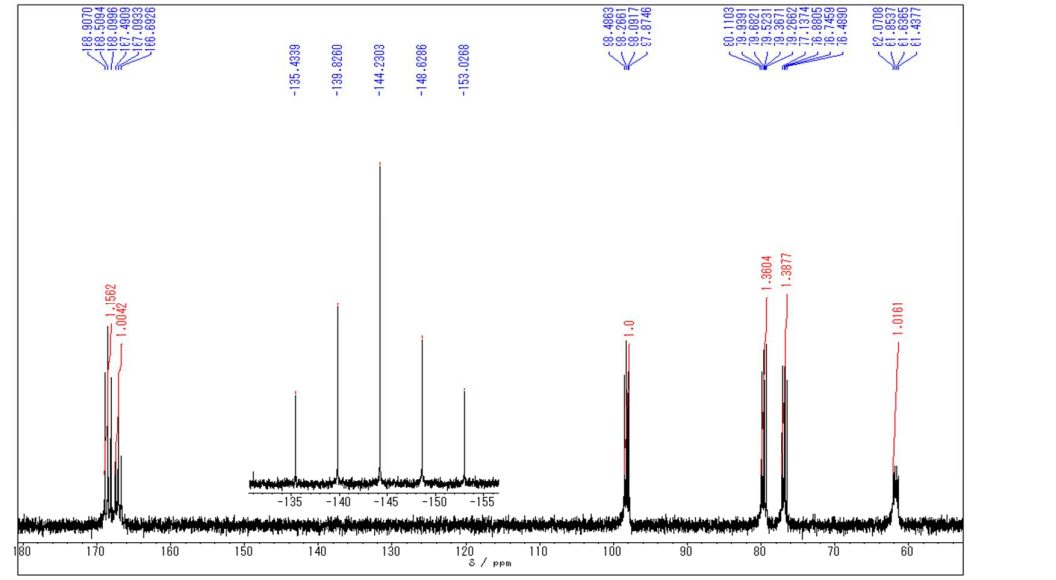

Figure S5-2. ^{31}P{^{1}H} NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe-(Prophos)PPh_2(O*t*Bu)]PF_6 in $CDCl_3$ (57:43 ratio).

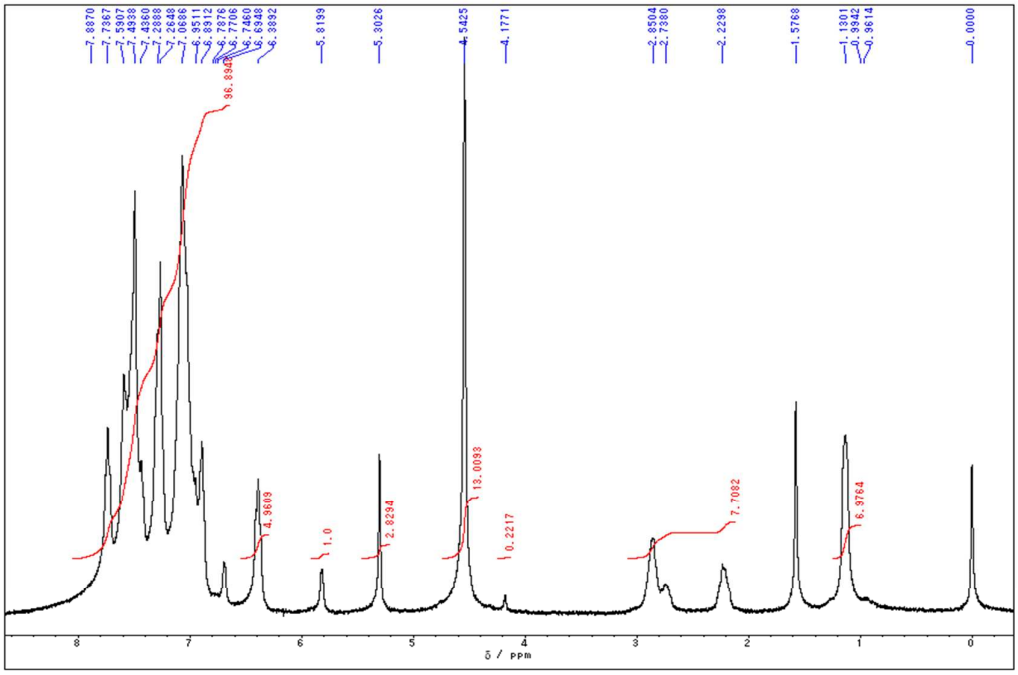

Figure S6-1. ^{1}H NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe-(Prophos)PPh_2H]PF_6 in $CDCl_3$ (2:98 ratio).

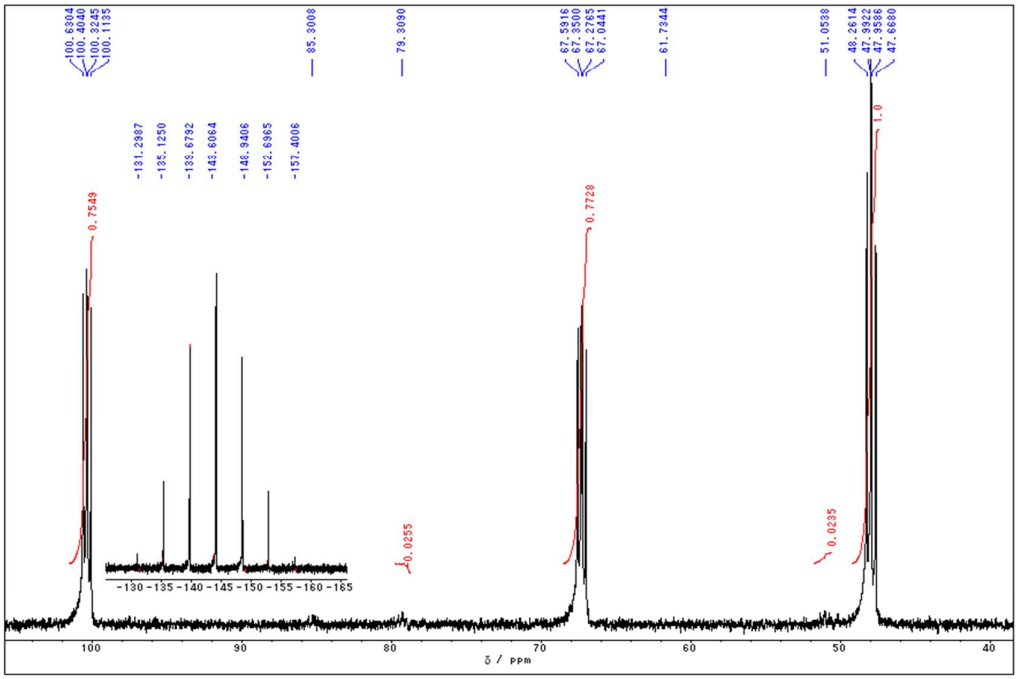

Figure S6-2. $^{31}P\{^{1}H\}$ NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe-(Prophos)PPh_2H]PF_6 in $CDCl_3$ (2:98 ratio).

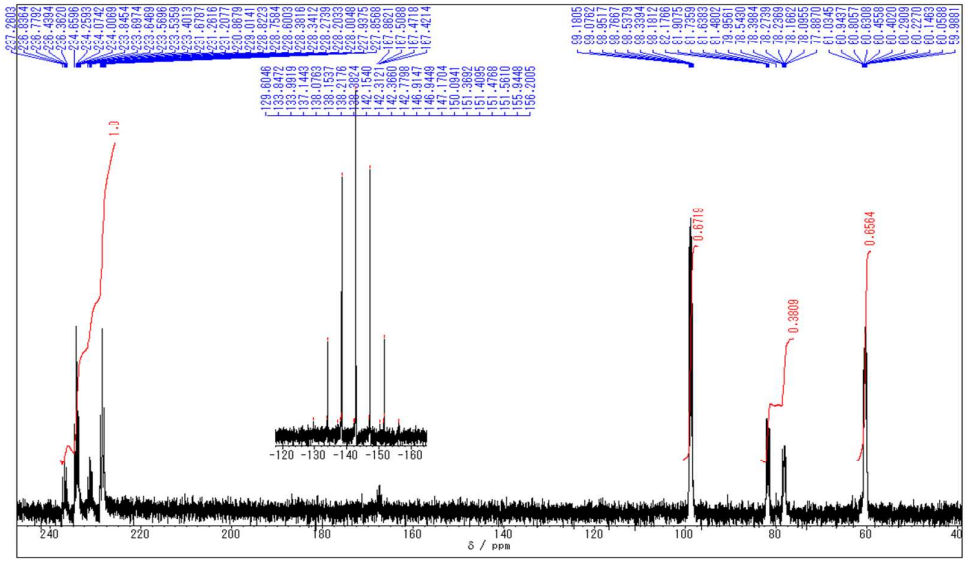

Figure S7. $^{31}P\{^{1}H\}$ NMR Spectrum of a mixture of diastereomers (R_{Fe},R_C)/(S_{Fe},R_C)-[CpFe-(Prophos)PPh_2F]PF_6 in C_6D_5Cl (15:85 ratio).

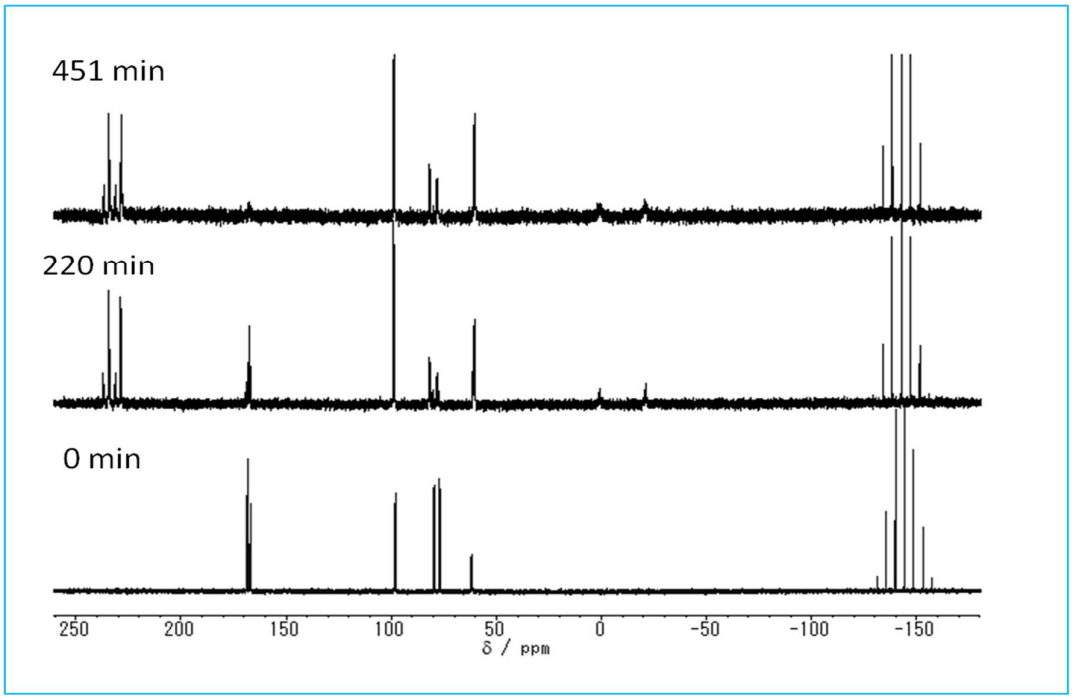

Figure S8. Time-resolved $^{31}P\{^{1}H\}$ NMR spectra of the epimerization of [CpFe(Prophos)PPh_2-(O*i*Pr)]PF_6 at 353 K in C_6D_5Cl.

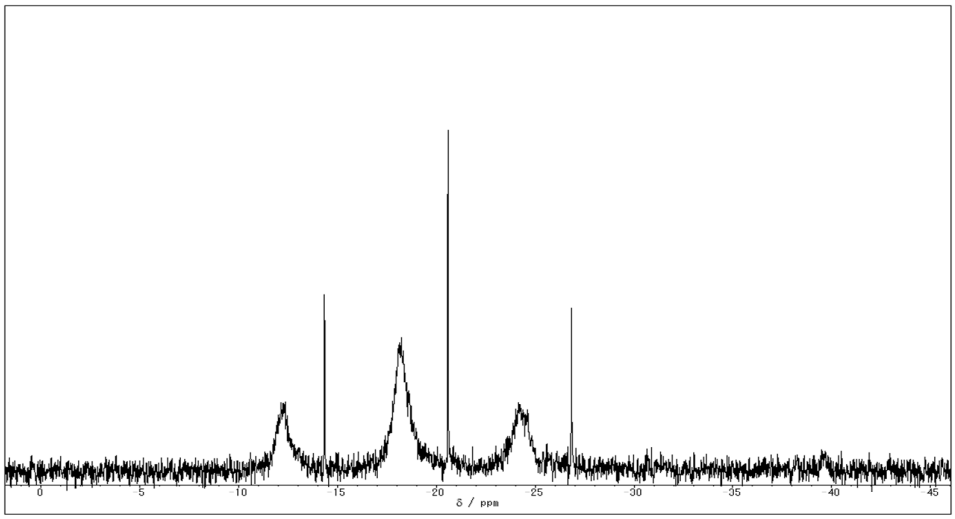

Figure S9-1. $^{31}P\{^{1}H\}$ NMR spectrum of [CpFe(Prophos)PPh_2(O*i*Pr)]PF_6, heated at 329 K in $CDCl_3$.

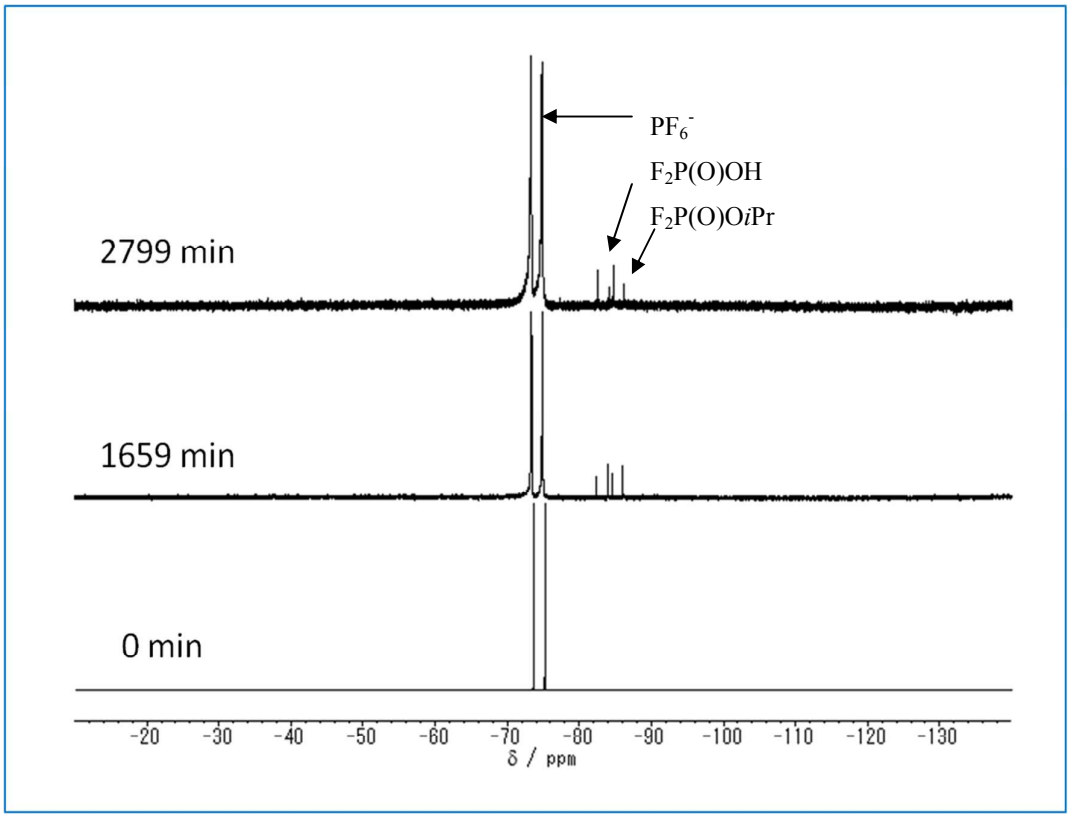

Figure S9-2. Time-resolved ^{19}F NMR spectra of [CpFe(Prophos)PPh_2(O*i*Pr)]PF_6, heated at 329 K in $CDCl_3$.

Table S1. Crystallographic Data for [CpFe(Prophos)L]PF_6 complexes

	(S_{Fe},R_C)-[CpFe(Prophos)PPh-(OMe)$_2$]PF_6	**(R_{Fe},R_C)-[CpFe(Prophos)-PPh_2(OMe)]PF_6 × EtOAc**	**(R_{Fe},R_C)-[CpFe(Prophos)-PPh_2(OEt)]PF_6**	**(R_{Fe},R_C)-[CpFe(Prophos)-PPh_2(O*i*Pr)]PF_6**	**(S_{Fe},R_C)-CpFe(Prophos)-PPh_2H]PF_6**
Empirical formula	$C_{40}H_{42}F_6FeO_2P_4$	$C_{49}H_{52}F_6FeO_3P_4$	$C_{46}H_{46}F_6FeO_3P_4$	$C_{47}H_{48}F_6FeOP_4$	$C_{44}H_{42}F_6FeP_4$
Crystal size [mm^3]	0.19 × 0.04 × 0.01	0.27 × 0.21 × 0.07	0.39 × 0.32 × 0.19	0.10 × 0.05 × 0.03	0.31 × 0.09 × 0.05
Colour and shape	yellow rod	orange prism	orange block	orange rod	orange rod
Formula weight [g mol^{-1}]	848.47	982.64	908.56	922.58	864.51
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Absorption correction	multi-scan	multi-scan	analytical	analytical	multi-scan
Transmission min/max	0.626 / 1.000	0.665 / 1.000	0.741 / 0.857	0.892 / 0.956	0.537 / 1.000
a [Å]	14.8881(4)	11.360(4)	9.71600	9.8728(2)	10.594(5)
b [Å]	12.2420(4)	18.091(5)	16.0141(1)	14.7452(3)	19.124(5)
c [Å]	20.6738(6)	11.767(3)	29.1646(2)	31.4174(5)	20.771(5)
α[°]	90	90	90	90	90
β [°]	94.951(2)	107.386(10)	90	90	90
γ[°]	90	90	90	90	90
V [Å^3]	3753.95(19)	2307.8(12)	4537.81(4)	4573.63(15)	4208(2)
Z	4	2	4	4	4
T [K]	123(1)	173(2)	123(1)	123(1)	173(2)
λ(Å)	1.54178	0.71073	1.54178	1.54178	0.71073
ρ_{calc} [[g/cm^3]	1.501	1.414	1.330	1.340	1.365
μ (mm^{-1})	5.407	0.531	4.493	4.466	0.568
Theta range [°]	3.82/73.59	3.14 / 27.52	3.03/ 77.23	3.31/ 70.65	3.04 / 27.55
Reflections collected to θ_{full}	31163	17484	133311	18941	39858
Unique reflections (R_{int})	14673 (0.0536)	7241 (0.0633)	9607 (0.0372)	8225 (0.0316)	9502 (0.1704)
Refl. obs. [*I*	13553	6331	9596	7103	5301

$>2\sigma(I)$]					
Parameters	961	568	586	595	500
Completeness to θ	0.984	0.981	0.999	0.974	0.991
R-values [$I >$ $2\sigma(I)$]	0.0487 / 0.1276	0.0476 / 0.0935	0.0260 / 0.0660	0.0356 / 0.0794	0.0769 / 0.1142
R-values (all data)	0.0527 / 0.1329	0.0600 / 0.1063	0.0260 / 0.0661	0.0449 / 0.0831	0.1508 / 0.1409
GOF on F^2	1.014	1.066	1.043	1.015	1.043
Residual density [eÅ^{-3}]	–0.611 / 0.708	–0.328 / 0.416	–0.270 / 0.253	–0.269 / 0.221	–0.712 / 0.562
Flack-Parameter	–0.012(3)	0.027(19)	0.006(2)	–0.004(4)	0.00(3)
CCDC-No.	946921	946922	946923	946924	946925

Table S2. Thermodynamic parameters of the complexes (R_{Fe},R_C)- and (S_{Fe},R_C)-[CpFe(Prophos)(L)]PF_6 (U = Total thermal energy)

Confi-guration	L	U (kcal·mol^{-1})	H (kcal·mol^{-1})	$T{\cdot}S$ (kcal·mol^{-1})
(R_{Fe},R_C)	MeCN	-2079631.29	-2079630.70	62.76
(R_{Fe},R_C)	PPh_2(OMe)	-2572910.72	-2572910.13	74.33
(S_{Fe},R_C)	MeCN	-2079629.09	-2079628.50	62.39
(S_{Fe},R_C)	PPh_2(OMe)	-2572910.33	-2572909.74	72.63