DOI: 10.1002/ejoc.200900766

Synthesis of Novel Ferrocenyl-Based P,S Ligands (ThioClickFerrophos) and Their Use in Pd-Catalyzed Asymmetric Allylic Substitutions

Minoru Kato,[a] Tatsuhito Nakamura,[a] Kenichi Ogata,[a] and Shin-ichi Fukuzawa*[a]

Keywords: Metallocenes / Asymmetric catalysis / Allylic compounds / Palladium / P,S ligands / Allylic substitution

A series of P,S ligands (ThioClickFerrophos) based on a triazoleferrocenylethyl backbone were synthesized in a four-step sequence by click chemistry methodology. The new P,S ligands were applied in allylic alkylations, etherifications, and aminations of 1,3-diphenylprop-2-enyl acetate catalyzed by Pd complexes. These reactions proceeded smoothly to give products in good yields and with good enantioselectivities of up to 90 % *ee*.

Introduction

Pd-catalyzed allylic substitution is a powerful tool for enantioselective carbon–carbon and carbon–heteroatom bond formation and has accordingly been intensively studied.[1] For highly enantioselective reactions, C_2-symmetric ligands or mixed hetero-donating ligands have typically been utilized. For mixed-donor ligands, P,N ligands have been extensively studied, and have been shown to be effective ligands for Pd-catalyzed asymmetric allylic substitution reactions.[2] Unlike in the case of P,N ligands, numerous studies have indicated potential problems with regard to the use of chiral P,S mixed donors for metal-catalyzed asymmetric reactions.[3] A sulfur atom is considered a soft atom that can form strong bonds with soft metals such as Pd and Cu.

Ferrocene-based chiral phosphanes have been employed in various important metal-catalyzed asymmetric reactions.[4] The introduction of heteroatom-based functional groups onto ferrocene systems has significantly improved the features of the ferrocene scaffold, thus extending its applicability as an industrial catalytic ligand. Although the well known ferrocenyl diphosphanes are widely used in homogeneous catalysis, due to their utility in providing highly efficient catalysts with soft metals, information relating to P,S-ferrocene systems has been sparse. Enders and co-workers have reported on the synthesis and use of ferrocenyl P,S ligands derived from ferrocenyl SAMP/RAMP hydrazones in Pd-catalyzed allylic substitutions.[5] Recently, Carretero and co-workers have successfully applied their original ferrocenyl-based P,S ligands (Fesulphos) for highly enantioselective metal-catalyzed asymmetric reactions including Pd-catalyzed allylic substitution reactions.[6] Chan and co-workers have synthesized the Bophoz-type P,S ligand FerroNPS and have shown that its Pd complexes can serve as excellent catalysts not only for the more commonly encountered asymmetric alkylation and amination but also for difficult allylic etherifications.[7a–7b] Furthermore, they have also synthesized another type of P,S ligand that was successfully applied for the allylic alkylation of indoles.[7c] The planar chirality of the ferrocene core has also been combined with other P,S ligands.[8]

We have recently reported on a ferrocenyl-1,2,3-triazole-based 1,5-diphosphane ligand (ClickFerrophos, Figure 1). This scaffold can be readily prepared by *click chemistry* methodology,[9] and possesses beneficial features such as ease of accessibility and potential for fine-tuning of the steric and electronic properties of the phosphane group. This ligand has demonstrated its effectiveness in metal-catalyzed asymmetric hydrogenations of alkenes and ketones, copper-catalyzed 1,3-dipolar cycloadditions of azomethine ylide with electron-deficient alkenes, and reductive aldol reactions of ethyl acrylate with ketones. ClickFerrophos can afford hetero-diphosphanes through the introduction of two distinct phosphane groups: firstly on its cyclopentadienyl ring and secondly on its triazole ring. Accordingly, as shown in Figure 1, a P,S ligand should be preparable either

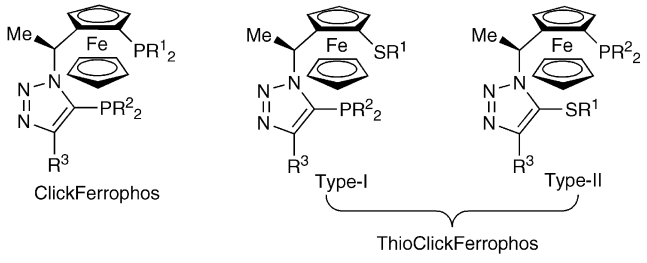


Figure 1. ClickFerrophos and ThioClickFerrophos.

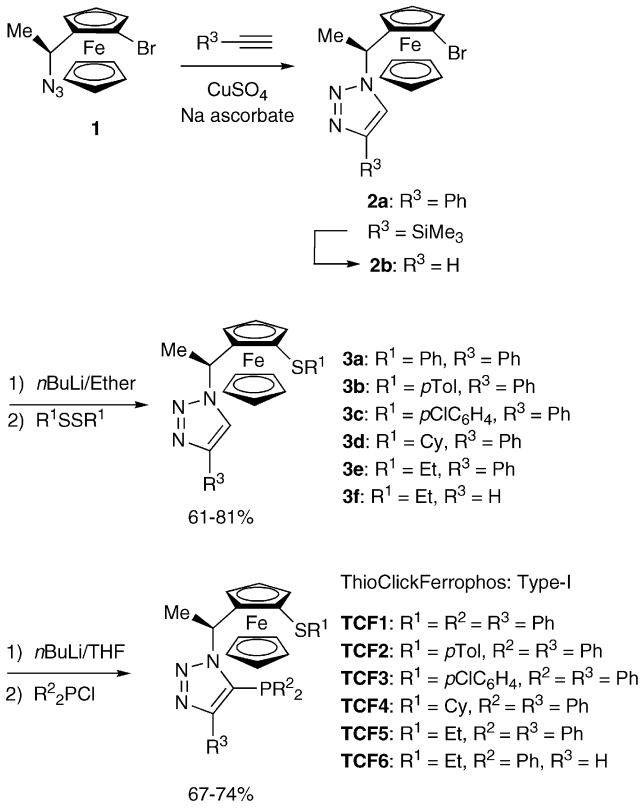
[a] Department of Applied Chemistry, Institute of Science and Engineering, Chuo University,
1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan
Fax: +81-3-3817-1895
E-mail: orgsynth@kc.chuo-u.ac.jp
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900766.

by sulfination of the cyclopentadienyl moiety followed by phosphination of the triazole ring (Type I) or vice versa (Type II). Here we describe the preparation of novel P,S-ferrocenyl ligands (ThioClickFerrophos) and their applications in Pd-catalyzed asymmetric allylic substitution reactions.[10]

Results and Discussion

Preparation of ThioClickFerrophos Ligands

As shown in Scheme 1, (*S*,*Rp*)-*ortho*-bromo-(1-azidoethyl)ferrocene (**1**) was subjected to a click reaction with phenylacetylene to afford the triazole backbone **2a** in a good yield (87%). Alternatively, a click reaction with (trimethylsilyl)acetylene, followed by removal of the silyl group, afforded the 4-unsubstituted triazole **2b** in a 42% overall yield.[9c] Subsequently, the 2-*ortho*-thioferrocenes **3a**–**3f** were obtained by lithium–halogen exchange at the *ortho*-position of the cyclopentadienyl ring followed by treatment with diaryl or dialkyl disulfides (61–81% yields). Subsequent lithiation at the 5-triazole ring, followed by trapping with diphenylphosphanyl chloride, afforded ThioClickFerrophos Type I ligands (**TCF1**–**6**) in moderate to good yields. The structure of **TCF1** was confirmed by X-ray crystallography (Figure 2). Type II ligands were similarly obtained by reversal of the order of the reaction – specifically, phosphination of the cyclopentadienyl ring, followed by sulfination of the triazole ring.



Scheme 1. Preparation of ThioClickFerrophos (Type I).

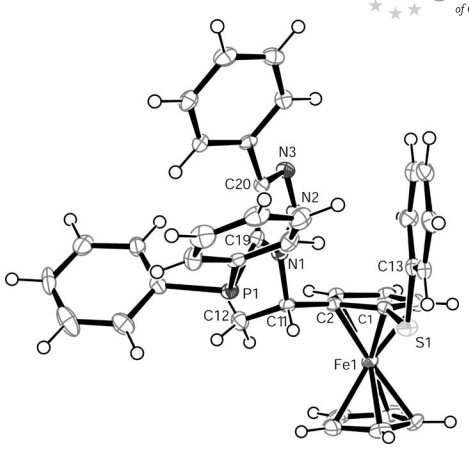
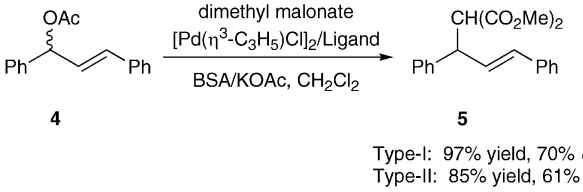


Figure 2. X-ray structure of **TCF1**.

Asymmetric Allylic Alkylation

The Type I and Type II ligands were first evaluated in the Pd-catalyzed allylic alkylation of (±)-1,3-diphenylprop-2-enyl acetate (**4**) with dimethyl malonate (Scheme 2). For the representative Type I (**TCF1**) and Type II ligands, R^1, R^2, and R^3 were all phenyl groups. The reactions were carried out at room temp. in CH_2Cl_2 for 15 h in the presence of the ligand (6 mol-%) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mol-%), along with *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc (3 mol-%) as bases. Although the Type I ligand (with **TCF1**) was effective in forming the *S*-configured product **5** in 97% yield with 70% *ee*, the Type II ligand was less effective, resulting in the *R*-configured product with a lower yield (85%) and enantioselectivity (61% *ee*; Scheme 2). Because the Type I ligand was more effective than the Type II variant, the Type I ligand derivatives (**TCF2**–**6**) were screened in the same reaction.[8e]



Scheme 2. Asymmetric allylic alkylations in the presence of Pd/ThioClickFerrophos.

The yields and enantioselectivities of the Pd-catalyzed allylic alkylations are listed in Table 1. In the cases of ligands with arylthio groups (**TCF1**–**3**, Entries 1–3, respectively), the products were obtained in high yields (97–99%) with moderate enantioselectivities (*S*, 70% *ee*). No substituent effects (methyl and chloro groups at the *para*-position) were observed in the three reactions. In the cases of ligands with alkylthio groups (**TCF4**, cyclohexyl, Entry 4 and **TCF5**, ethyl, Entry 5), improved enantioselectivities were obtained. The importance of a phenyl group at the 5-position of the triazole was demonstrated by the decreased enantioselectivity obtained with the 5-unsubstituted ligand (**TCF6**, Entry 6). The use of additives such as Cs_2CO_3 or Bu_4NCl

instead of KOAc resulted in lower enantioselectivities (75–76% *ee*, Entries 7–8). In an attempt to improve the reaction conditions, the reaction with the most effective ligand (**TCF5**) was carried out in other solvents; CH_3CN was the solvent of choice, giving the best % *ee* value (90% *ee*, Entry 9). It should be noted that the reaction in the presence of the Pd complex of *ortho*-thioferrocene **3a** afforded only a trace of the products (Entry 12), suggesting that the *P,S*-chelate complex, and not the *S,N*-chelate complex, was the active catalyst.

Table 1. Asymmetric allylic alkylation.[a]

Entry	Ligand	Solvent	Yield [%][b]	*ee* [%][c]
1	**TCF1**	CH_2Cl_2	97	70
2	**TCF2**	CH_2Cl_2	99	67
3	**TCF3**	CH_2Cl_2	98	70
4	**TCF4**	CH_2Cl_2	99	78
5	**TCF5**	CH_2Cl_2	99	84
6	**TCF6**	CH_2Cl_2	95	67
7[d]	**TCF5**	CH_2Cl_2	97	75
8[e]	**TCF5**	CH_2Cl_2	99	76
9	**TCF5**	CH_3CN	99	90
10	**TCF5**	THF	96	75
11	**TCF5**	toluene	99	75
12	**3a**	CH_2Cl_2	trace	–

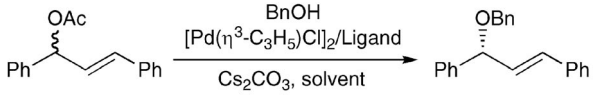
[a] Compound **4** (0.5 mmol), dimethyl malonate (1.5 mmol), BSA (1.5 mmol), KOAc (0.015 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 mmol), ligand (0.03 mmol), solvent (3 mL); room temp., 15 h. [b] Determined by ^1H NMR spectroscopy. [c] Determined by HPLC (Chiralpak AD-H). [d] Cs_2CO_3 was used in place of KOAc. [e] Bu_4NCl was used in place of KOAc.

Asymmetric Allylic Etherification

Unlike allylic alkylation, allylic etherification remains a challenge for synthetic chemists, and accordingly has yet to be widely reported. In view of the encouraging results obtained with the $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/**TCF5** complex, we undertook the asymmetric allylic etherification between benzyl alcohol and **4** (chosen as a model substrate) in the presence of the catalyst (4 mol-%) and Cs_2CO_3 as the base, as shown in Table 2. In CH_2Cl_2, the reaction was complete within 2 h at room temp., the *R*-configured benzyl ether **6** being obtained quantitatively with 69% *ee*. Subsequently, the benzyl ether was obtained with 82% *ee* under optimized reaction conditions with toluene as the solvent and Cs_2CO_3 as the base (Table 2, Entries 1–6). Unlike in the allylic alkylation, the other ThioClickFerrophos ligands (Entries 9–12; *R*, 45–59% *ee*) were not as effective as **TCF5** (Entry 8) for the allylic etherifications.

As shown in Table 3, the asymmetric allylic etherification reaction was further evaluated with a substituted benzyl alcohol. Under optimized reaction conditions, the etherifications proceeded smoothly to give the corresponding benzylic ethers **6a**–**e** in high yields and with moderate to good enantioselectivities. The effects of the substituents on the enantioselectivities were similar to those seen in Chan's studies on allylic etherification in the presence of the FerroNPS ligand – benzylic alcohols bearing electron-withdrawing groups correspond to lower % *ee* values.[7a]

Table 2. Optimization of allylic etherification.[a]

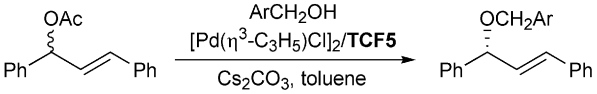


4 **6**

Entry	Ligand	Solvent	Yield [%][b]	*ee* [%][c]
1	**TCF5**	CH_2Cl_2	95	69
2	**TCF5**	toluene	95	82
3	**TCF5**	CH_3CN	90	74
4	**TCF5**	THF	27	62
5	**TCF5**	Et_2O	41	64
6[d]	**TCF5**	toluene	15	66
7[e]	**TCF5**	toluene	36	75
8	**TCF1**	toluene	95	45
9	**TCF2**	toluene	91	50
10	**TCF3**	toluene	82	55
11	**TCF4**	toluene	90	59
12	**TCF6**	toluene	88	51

[a] Compound **4** (0.5 mmol), benzyl alcohol (1.5 mmol), Cs_2CO_3 (1.5 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 mmol), ligand (0.02 mmol), solvent (3 mL); room temp., 2 h. [b] Isolated yield. [c] Determined by HPLC (Chiralcel OJ-H). [d] KOAc was used in place of Cs_2CO_3. [e] K_2CO_3 was used in place of Cs_2CO_3.

Table 3. Asymmetric allylic etherification.[a]

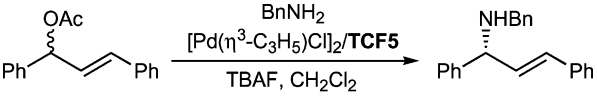


4 **6a–e**

Entry	Ar in Alcohol	Yield [%][b]	*ee* [%][c]
1	Ph	99	82
2	$pMeC_6H_4$	99	80
3	$pMeOC_6H_4$	99	80
4	$pClC_6H_4$	85	74
5	pFC_6H_4	91	74

[a] Compound **4** (0.5 mmol), benzyl alcohol (1.5 mmol), Cs_2CO_3 (1.5 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.01 mmol), **TCF5** (0.02 mmol), toluene (3 mL); room temp., 5 h. [b] Determined by ^1H NMR spectroscopy. [c] Determined by HPLC (Chiralcel OJ-H, OD-H).

The Pd/**TCF5** complex was also applied to the allylic amination of **4** with benzylamine (Scheme 3). The reaction proceeded in CH_2Cl_2 at room temp. over 72 h in the presence of tetrabutylammonium fluoride (TBAF) to give the benzylic amine **7** in 91% yield with 66% *ee* (*R*).



4 **7**

Scheme 3. Asymmetric allylic amination by Pd/**TCF5**.

Conclusions

In conclusion, we have successfully synthesized novel ferrocenyl P,S ligands with a triazole backbone (ThioClick-Ferrophos), which allows the fine-tuning of various steric and electronic properties of the donor atoms. The Pd complexes of the ThioClickFerrophos ligands were effectively employed in asymmetric allylic alkylation, etherification, and amination of (±)-1,3-diphenylprop-2-enyl acetate (**4**). Our results demonstrate that the novel ligand is highly effective for the reactions, especially for asymmetric allylic etherifications, and should, with continued fine-tuning of the framework's electronic and steric factors, be a promising ligand.

Experimental Section

General: The ^{1}H and ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ with a Varian Mercury 300 NMR (300 MHz) spectrometer. The chemical shifts are reported in δ units downfield from the Me_4Si internal reference. The optical rotations were determined with a JASCO P-2200 instrument. The HPLC analyses were carried out on chiral columns (Chiralcel AD-H, OJ-H) with a JASCO PU-1580 apparatus fitted with a multi-wavelength detector (MD 2010). Preparative TLC was conducted with a 20 × 20 cm glass sheet coated with a 2 mm thick layer of Merck Kieselgel 60 PF_{254}. All products of asymmetric reactions were reported compounds and were characterized by spectroscopic methods by reference to the literature.

Crystallography: The diffraction data were collected at –150 °C with a Mercury CCD area detector with use of graphite monochromated Mo-K_α radiation and the ω-2θ scan technique to a maximum 2θ value of 55°. The structure solution and refinements were carried out with the aid of the Crystal Structure crystallographic software packages. The structure was solved by direct methods (SHELX97) and expanded by Fourier techniques (DIRDIF99). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by use of the riding model.

CCDC-734593 (for **TCF1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of the (*S*,*Rp*)-*ortho*-Thioferrocene: The following provides a typical experimental procedure for preparation of the *ortho*-thioferrocenes. The (*S*,*Rp*)-*ortho*-bromotriazole ferrocene **2a** (300 mg, 0.69 mmol)[9] and dry diethyl ether (30 mL) were placed under a slight pressure of nitrogen in a 50 mL Schlenk tube containing a magnetic stirring bar. The flask was cooled to –78 °C, and a hexane solution of *n*BuLi (0.5 mL, 0.8 mmol, 1.6 M) was then added by syringe through a septum with magnetic stirring. After 2 h, diethyl disulfide (120 μL, 0.96 mmol) was injected into the mixture at –78 °C. When the addition was complete, the mixture was stirred at the same temperature for 10 min, and was then allowed to warm to room temp. and stirred for 24 h. The reaction was quenched with saturated NH_4Cl, and the solution was then extracted with diethyl ether (3 × 30 mL). The combined extracts were washed (brine), dried ($MgSO_4$), and filtered, and the solvent was removed on a rotary evaporator to leave an orange solid. The crude product was purified by PTLC (hexane/diethyl ether/dichloromethane 4:2:1) to give pure **3e** (R^1 = Et, R^3 = Ph). Yield 232 mg, 0.56 mmol, 81%, orange solid, m.p. 52–54 °C. $[\alpha]_D^{25}$ = +137 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 3 H, C*H*$_3$CH$_2$), 1.90 (dq, *J* = 7.2, 12.5 Hz, 1 H, one of CH$_2$), 2.00 (d, *J* = 7.0 Hz, 3 H, C*H*$_3$CH), 2.0–2.1 (m, 1 H), 4.23 (s, 5 H, Cp), 4.38 (t, *J* = 2.4 Hz, 1 H), 4.49 (m, 1 H), 4.57 (m, 1 H), 6.13 (q, *J* = 7.0 Hz, 1 H, CH$_3$C*H*), 7.27–7.39 (m, 3 H), 7.51 (s, 1 H, TzH), 7.74 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (CH$_3$), 21.5 (CH$_3$), 30.8 (CH$_2$), 54.8 (CH), 67.5, 68.7, 70.5 (Cp), 76.3, 79.1, 89.0, 117.5, 125.5, 127.9, 128.7, 130.7, 146.9 ppm. HRMS: calcd. for $C_{22}H_{23}FeN_3S$ [M + Na$^+$] 440.0860; found 440.0980.

Compound 3a (R^1 = R^3 = Ph): Yield 259 mg, 77%, yellow solid, m.p. 168–170 °C. $[\alpha]_D^{25}$ = +77.4 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04 (d, *J* = 7.0 Hz, 3 H, CH$_3$), 4.31 (s, 5 H, Cp), 4.50 (t, *J* = 1.3 Hz, 1 H), 4.60 (m, 1 H), 4.73 (m, 1 H), 5.95 (q, *J* = 7.0 Hz, 1 H, CH), 6.68–6.87 (m, 5 H, Ph), 7.03 (s, 1 H, TzH), 7.24–7.40 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (CH$_3$), 54.4 (CH), 68.7, 69.6, 70.7 (Cp), 75.9, 76.7, 90.0, 118.5, 125.3, 125.5, 125.7, 127.5, 128.3, 128.4, 130.7, 138.4, 146.3 ppm. HRMS: calcd. for $C_{26}H_{23}FeN_3S$ [M + Na$^+$] 488.0860; found 488.0862.

Compound 3b (R^1 = *p*Tol, R^3 = Ph): Yield 218 mg, 63%, yellow solid, m.p. 184–185 °C. $[\alpha]_D^{25}$ = +74.6 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, CH$_3$), 2.02 (d, *J* = 7.0 Hz, 3 H, C*H*$_3$CH), 4.30 (s, 5 H, Cp), 4.48 (t, *J* = 2.6 Hz, 1 H), 4.61 (m, 1 H), 4.69 (m, 1 H), 5.96 (q, *J* = 7.0 Hz, 1 H, CH$_3$C*H*$_2$), 6.62 (s, 4 H), 6.89 (s, 1 H, TzH), 7.18–7.41 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3 (CH$_3$), 21.1 (CH$_3$), 54.5 (CH), 68.6, 69.4, 70.7 (Cp), 76.8, 76.9, 89.8, 118.4, 125.3, 126.3, 127.4, 128.3, 129.2, 130.7, 134.5, 135.5, 146.0 ppm. HRMS: calcd. for $C_{27}H_{25}FeN_3S$ [M + Na$^+$] 502.1016; found 502.1006.

Compound 3c (R^1 = *p*-ClC_6H_4, R^3 = Ph): Yield 219 mg, 61%, yellow solid, m.p. 194–195 °C. $[\alpha]_D^{25}$ = +89.0 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (d, *J* = 7.0 Hz, 3 H, CH$_3$), 4.31 (s, 5 H, Cp), 4.50 (t, *J* = 2.5 Hz, 1 H), 4.58 (m, 1 H), 4.75 (m, 1 H), 5.96 (q, *J* = 6.8 Hz, 1 H, CH), 6.58 (d, *J* = 8.2 Hz, 2 H), 6.79 (d, *J* = 8.2 Hz, 2 H), 7.05 (s, 1 H, TzH), 7.28–7.42 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (CH$_3$), 54.5 (CH), 68.8, 69.7, 70.7 (Cp), 75.4, 76.7, 89.9, 118.1, 125.4, 126.8, 127.6, 128.5, 130.3, 131.2, 137.0, 146.5 ppm. HRMS: calcd. for $C_{26}H_{22}ClFeN_3S$ [M + Na$^+$] 522.0470; found 522.0467.

Compound 3d (R^1 = Cy, R^3 = Ph): This compound could not be isolated in pure form and so was used for the synthesis of **TCF4** in the crude state. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.6–1.55 (m, 11 H), 1.97 (d, *J* = 7.0 Hz, 3 H, CH$_3$), 4.22 (s, 5 H, Cp), 4.38 (m, 1 H), 4.45 (m, 1 H), 4.58 (m, 1 H), 6.15 (q, *J* = 7.0 Hz, 1 H, CH), 7.28–7.38 (m, 3 H), 7.48 (s, 1 H, TzH), 7.73 (d, *J* = 7.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH$_3$), 25.4, 25.5, 25.9, 32.6, 33.6, 47.7, 54.9, 67.5, 68.6, 70.4 (Cp), 77.2, 78.0, 89.2, 111.5, 125.5, 127.8, 128.6, 130.7, 146.9 ppm. HRMS: calcd. for $C_{26}H_{29}FeN_3S$ [M + Na$^+$] 494.1329; found 494.1369.

Compound 3f (R^1 = Et, R^3 = H): Yield 195 mg, 78%, orange oil. $[\alpha]_D^{25}$ = +132 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.6 Hz, 3 H, C*H*$_3$CH$_2$), 1.78 (dq, *J* = 7.3, 12.6 Hz, 1 H, CH$_3$C*H*$_2$), 1.95 (d, *J* = 7.0 Hz, 1 H, C*H*$_3$CH), 1.9–2.03 (m, 1 H), 4.22 (s, 5 H), 4.36 (t, *J* = 2.6 Hz, 1 H), 4.47 (m, 1 H), 4.56 (m, 1 H), 6.12 (q, *J* = 7.0 Hz, 1 H, CH$_3$C*H*), 7.33 (s, 1 H), 7.55 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (CH$_3$), 21.5 (CH$_3$), 30.6 (CH$_2$), 54.6 (CH), 67.4, 68.6, 70.4 (Cp), 76.2, 79.0, 88.9, 121.3 (Tz), 133.0 (Tz) ppm. HRMS: calcd. for $C_{16}H_{19}FeN_3S$ [M + Na$^+$] 364.0547; found 364.0520.

Preparation of ThioClickFerrophos: The following provides a typical experimental procedure for the preparation of ThioClickFer-

rophos. Compound **3e** (150 mg, 0.36 mmol) and dry THF (3.0 mL) were placed under a slight pressure of nitrogen in a 20 mL Schlenk tube containing a magnetic stirring bar. The flask was cooled to –78 °C and a hexane solution of *n*BuLi (0.24 mL, 0.40 mmol, 1.6 M) was then added by syringe through the septum with magnetic stirring. After 10 min, Ph_2PCl (77 μL, 0.43 mmol) was injected into the mixture at –78 °C and the mixture was stirred for 10 min. The mixture was allowed to warm to room temp. and was then stirred for an additional 3 h. The reaction was quenched with saturated NH_4Cl, and the solution was then extracted with diethyl ether (10 mL × 3). The combined extracts were washed (brine), dried ($MgSO_4$), and filtered, and the solvent was removed on a rotary evaporator to leave a yellow residue. The crude product was purified by PTLC (hexane/diethyl ether/dichloromethane 4:2:1) to give pure **TCF5**. Yield 168 mg, 0.28 mmol, 75%, yellow solid, m.p. 111–113 °C. $[a]_D^{25}$ = +155 (*c* = 0.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3 H, CH_3CH_2), 1.72 (dq, *J* = 7.0, 12.5 Hz, 1 H, one of CH_3CH_2), 1.83 (d, *J* = 6.7 Hz, 3 H, CH_3CH), 1.95 (dq, *J* = 7.3, 12.5 Hz, 1 H, one of CH_3CH_2), 4.17 (s, 5 H, Cp), 4.30 (t, *J* = 2.5 Hz, 1 H), 4.42 (m, 1 H), 4.63 (m, 1 H), 6.35 (quint, *J* = 7.0 Hz, 1 H, CH_3CH), 6.92–7.16 (m, 10 H, Ph), 7.32–7.34 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6 (CH_3), 21.5 (CH_3), 30.7 (CH_2), 54.5 (d, *J* = 14.4 Hz, CH), 68.4, 69.2, 70.2 (Cp), 75.9, 78.9, 89.4, 126.6, 127.0, 127.4, 127.5, 128.2 (d, *J* = 7.1 Hz), 128.7 (d, *J* = 6.7 Hz), 128.8, 129.2, 131.4, 132.3 (d, *J* = 6.1 Hz), 132.5 (d, *J* = 19.6 Hz), 132.7 (d, *J* = 6.4 Hz), 133.0 (d, *J* = 19.8 Hz), 152.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –34.2 (s) ppm. HRMS: calcd. for $C_{34}H_{32}FeN_3PS$ [M + Na^+] 624.1302; found 624.1309.

Compound TCF1: Yield 95 mg, 39%, yellow solid, m.p. 202–204 °C. $[a]_D^{25}$ = +97.7 (*c* = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.74 (d, *J* = 7.3 Hz, 3 H, CH_3), 4.28 (s, 5 H, Cp), 4.51–4.52 (m, 2 H), 4.89 (m, 1 H), 6.35 (quint, *J* = 7.1 Hz, 1 H, CH), 6.36–6.55 (m, 4 H, Ph), 6.71–7.02 (m, 11 H, Ph), 7.32–7.38 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7 (CH_3), 53.4 (d, *J* = 16.5 Hz, CH), 70.0, 70.3, 70.5 (Cp), 74.3, 76.4, 90.9, 124.2, 127.0, 127.1, 127.8 (d, *J* = 6.5 Hz), 128.1, 128.5, 128.8 (d, *J* = 7.2 Hz), 129.0, 129.3, 131.2, 131.6 (d, *J* = 4.9 Hz), 131.9 (d, *J* = 18.9 Hz), 132.7 (d, *J* = 6.9 Hz), 133.3 (d, *J* = 20.3 Hz), 140.1, 151.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –34.1 (s) ppm. HRMS: calcd. for $C_{38}H_{32}FeN_3PS$ [M + Na^+] 672.1302; found 672.1303. Crystals suitable for X-ray analysis was obtained by recrystallization from $CHCl_3$/hexane (CCDC-734593).

Compound TCF2: Yield 165 mg, 67%, yellow solid, m.p. 80–82 °C. $[a]_D^{25}$ = +74.2 (*c* = 0.3, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.71 (d, *J* = 7.0 Hz, 3 H, CH_3CH), 2.15 (s, 3 H, CH_3), 4.26 (s, 5 H, Cp), 4.50 (m, 2 H), 4.88 (m, 1 H), 6.34 (quint, *J* = 7.0 Hz, 1 H, CH_3CH), 6.39–6.44 (m, 4 H, tolyl), 6.70–6.98 (m, 10 H, Ph), 7.34–7.40 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6 (CH_3), 21.6 (CH_3), 53.4 (d, *J* = 16.1 Hz, CH), 69.9, 70.2, 70.5 (Cp), 74.5, 76.4, 91.0, 124.1, 126.9, 127.0, 127.7 (d, *J* = 6.7 Hz), 128.1, 128.9 (d, *J* = 7.2 Hz), 129.0, 129.2, 129.4, 131.2, 131.5 (d, *J* = 5.2 Hz), 132.0 (d, *J* = 19.0 Hz), 132.8 (d, *J* = 7.8 Hz), 133.6 (d, *J* = 20.3 Hz), 133.8, 136.5, 151.8 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –34.1 (s) ppm. HRMS: calcd. for $C_{39}H_{34}FeN_3OPS$ [M + Na^+] 686.1458; found 686.1428.

Compound TCF3: Yield 173 mg, 68%, yellow solid, m.p. 78–80 °C. $[a]_D^{25}$ = +55.7 (*c* = 0.3, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.71 (d, *J* = 7.0 Hz, 3 H, CH_3CH), 4.27 (s, 5 H, Cp), 4.49 (m, 1 H), 4.54 (t, *J* = 2.6 Hz, 1 H), 4.90 (m, 1 H), 6.30 (quint, *J* = 7.0 Hz, 1 H, CH_3CH), 6.44–6.46 (m, 4 H, *p*ClC_6H_4), 6.78–6.97 (m, 10 H, Ph), 7.33–7.41 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 53.3 (d, *J* = 16.1 Hz, CH), 70.1, 70.51, 70.52 (Cp), 73.4, 76.2, 90.0, 125.2, 126.4, 126.7, 127.1, 127.8 (d, *J* = 6.8 Hz), 128.3, 128.4, 128.8 (d, *J* = 7.9 Hz), 128.9, 129.4, 130.0, 130.9, 131.3 (d, *J* = 5.0 Hz), 131.8 (d, *J* = 19.2 Hz), 132.7 (d, *J* = 7.2 Hz), 133.3 (d, *J* = 20.3 Hz), 138.6, 151.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –33.6 (s) ppm. HRMS: calcd. for $C_{38}H_{31}ClFeN_3PS$ [M + Na^+] 706.0912; found 706.0953.

Compound TCF4: Yield 88 mg, 36%, yellow solid, m.p. 62–63 °C. $[a]_D^{25}$ = +118 (*c* = 0.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91–1.60 (m, 11 H, Cy), 1.79 (d, *J* = 7.0 Hz, 3 H, CH_3CH), 4.13 (s, 5 H, Cp), 4.27 (t, *J* = 2.6 Hz, 1 H), 4.40 (m, 1 H), 4.59 (m, 1 H), 6.32 (quint, *J* = 6.4 Hz, 1 H, CH_3CH), 6.94–7.16 (m, 10 H, Ph), 7.34–7.36 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7 (CH_3), 25.6, 25.8, 26.1, 32.8, 33.4, 47.3, 54.6 (d, *J* = 12.7 Hz, CH), 68.4, 69.5, 70.3 (Cp), 76.7, 89.5, 126.4, 126.8, 127.4, 128.1 (d, *J* = 6.9 Hz), 128.7, 128.8 (d, *J* = 6.3 Hz), 129.1, 129.2, 131.5, 132.3 (d, *J* = 5.5 Hz), 132.6 (d, *J* = 20.7 Hz), 132.7 (d, *J* = 7.0 Hz), 133.2 (d, *J* = 19.8 Hz), 152.8 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –34.1 (s) ppm. HRMS: calcd. for $C_{38}H_{38}FeN_3PS$ [M + Na^+] 678.1771; found 678.1773.

Compound TCF6: Yield 146 mg, 74%, yellow solid, m.p. 40–42 °C. $[a]_D^{25}$ = +106 (*c* = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.3 Hz, 3 H, CH_3CH_2), 1.54 (dq, *J* = 7.3, 12.6 Hz, 1 H, one of CH_3CH_2), 1.74 (d, *J* = 7.0 Hz, 3 H, CH_3CH), 1.83 (dq, *J* = 7.3, 12.5 Hz, 1 H, one of CH_3CH_2), 4.19 (s, 5 H, Cp), 4.28 (t, *J* = 2.7 Hz, 1 H), 4.39 (m, 1 H), 4.64 (m, 1 H), 6.29 (dq, *J* = 2.5, 7.0 Hz, 1 H, CH_3CH), 7.16–6.93 (m, 10 H, Ph), 7.36 (s, 1 H, Tz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (CH_3), 21.1 (CH_3), 30.7 (CH_2), 54.4 (d, *J* = 10.3 Hz, CH), 68.4, 69.2, 70.3 (Cp), 76.0, 78.9, 89.0, 128.7 (d, *J* = 6.4 Hz), 128.8, 128.9, 129.6 (d, *J* = 7.3 Hz), 133.1, 133.3 (d, *J* = 16.2 Hz), 133.4, 133.7, 133.8 (d, *J* = 6.5 Hz), 139.8 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –40.3 (s) ppm. HRMS: calcd. for $C_{28}H_{28}FeN_3PS$ [M + Na^+] 548.0989; found 548.1082.

Type II (R^1 = R^2 = R^3 = Ph): Yield 176 mg, 73%, yellow solid, m.p. 218–221 °C. $[a]_D^{25}$ = +224 (*c* = 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.70 (d, *J* = 6.8 Hz, 3 H, CH_3CH), 3.68 (m, 1 H), 4.14 (s, 5 H, Cp), 4.41 (m, 1 H), 4.90 (m, 1 H), 6.26 (dq, *J* = 3.0, 6.8 Hz, 1 H, CH_3CH), 6.70–6.97 (m, 7 H), 7.13–7.47 (m, 11 H), 7.70–7.73 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 52.0 (d, *J* = 8.1 Hz, CH), 69.8, 69.9 (Cp), 71.0 (d, *J* = 2.9 Hz), 71.9 (d, *J* = 4.0 Hz), 76.1 (d, *J* = 6.3 Hz), 91.8 (d, *J* = 24.2 Hz), 121.3, 126.4, 126.7, 127.0, 127.8 (d, *J* = 6.9 Hz), 127.9, 128.0 (d, *J* = 5.2 Hz), 128.1, 129.1, 129.3, 130.1, 131.7 (d, *J* = 19.0 Hz), 134.6, 134.8 (d, *J* = 20.7 Hz), 136.3 (d, *J* = 8.6 Hz), 137.3 (d, *J* = 8.1 Hz), 148.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –25.6 (s) ppm. HRMS: calcd. for $C_{38}H_{32}FeN_3NaPS$ [M + Na^+] 672.1302; found 672.1332.

Allylic Alkylation of (±)-1,3-Diphenylprop-2-enyl Acetate (4) Catalyzed by a Palladium/TCF Complex: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.8 mg, 0.01 mmol, 2 mol-%) and ligand **TCF5** (18 mg, 0.03 mmol, 6 mol-%) dissolved in CH_3CN (3.0 mL) were placed in a Schlenk tube containing a stirring bar. The mixture was stirred under nitrogen at room temp. for 30 min. Compound **4** (126 mg, 0.5 mmol), dimethyl malonate (170 μL,1.5 mmol), BSA (370 μL,1.5 mmol), and KOAc (1.5 mg, 0.015 mmol) were successively added to this solution. The mixture was stirred at room temp. and monitored by TLC. After completion (15 h), the mixture was diluted with CH_2Cl_2 (20 mL), washed with saturated aqueous NH_4Cl, dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure, and the brown residue was subjected to PTLC (hexane/ethyl acetate 40:3) to give pure **5** (160 mg, 0.49 mmol, 97% yield). ^1H NMR (300 MHz,

$CDCl_3$): δ = 3.51 (s, 3 H, CH_3), 3.70 (s, 3 H, CH_3), 3.96 (d, J = 10.9 Hz, 1 H, CHCO), 4.26 (dd, J = 8.7, 10.9 Hz, 1 H, CHPh), 6.33 (dd, J = 8.7, 15.7 Hz, 1 H, =CHCH), 6.46 (d, J = 15.7 Hz, 1 H, PhCH=), 7.2–7.3 (m, 10 H) ppm. ^{13}C NMR (7MHz, $CDCl_3$): δ = 49.0 (CHPh), 52.3 (CH_3), 52.5 (CH_3), 57.5 (CHCO), 126.3, 127.1, 127.5, 127.6, 127.7, 127.8, 128.1, 128.4, 128.5, 128.6, 129.0, 131.7, 136.7, 140.0, 167.5 (CO), 168.1 (CO) ppm. The enantiomeric excess of the product (90% *ee*) was determined by HPLC [Chiralpack AD-H, 25 cm, hexane/*i*PrOH 90:10, 1.0 mL min^{-1}, t_R (*R*) = 12.9 min, t_R (*S*) = 14.1 min].

Allylic Etherification Catalyzed by Palladium/TCF Complex: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.8 mg, 0.01 mmol, 2 mol-%) and **TCF5** (12 mg, 0.02 mmol, 4 mol-%) dissolved in dry toluene (5.0 mL) were placed in a Schlenk tube containing a stirring bar, and the mixture was stirred under nitrogen at room temp. for 30 min. Compound **4** (126 mg, 0.5 mmol), (*p*-methoxyphenyl)methanol (210 μL, 1.5 mmol), and Cs_2CO_3 (488 mg, 1.5 mmol) were successively added to this solution. The mixture was stirred at room temp. and monitored by TLC. After completion (5 h), the mixture was diluted with ethyl acetate (20 mL), washed with saturated aqueous NH_4Cl, dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure. The brown residue was subjected to PTLC (hexane/ethyl acetate 95:5) to give pure product **6c** (165 mg, 0.50 mmol, >99% yield). The enantiomeric excess of the product (80% *ee*) was determined by HPLC [Chiralcel OJ-H, 25 cm, hexane/*i*PrOH 86:14, 0.75 mL min^{-1}, t_R (*S*) = 13.3 min, t_R (*R*) = 15.4 min]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OCH_3), 4.50 (s, 2 H, $ArCH_2$), 4.99 (d, J = 7.0 Hz, 1 H, CHO), 6.33 (dd, J = 7.0, 15.9 Hz, 1 H, =CH), 6.61 (d, J = 15.9 Hz, 1 H, PhCH=), 6.89 (d, J = 8.5 Hz, 2 H), 7.15–7.42 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2, 69.7, 81.2, 113.8, 126.5, 127.0, 127.7, 128.5, 129.3, 130.3, 130.4, 131.4, 136.5, 141.1, 159.1 ppm.

Compound 6a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.54 (d, J = 12.5 Hz, 1 H, one of $PhCH_2$), 4.60 (d, J = 12.5 Hz, 1 H, one of $PhCH_2$), 5.00 (d, J = 7.0 Hz, 1 H, CHO), 6.32 (dd, J = 7.6, 15.8 Hz, 1 H, =CH), 6.61 (d, J = 15.8 Hz, 1 H, PhCH=), 7.21–7.44 (m, 15 H) ppm. The enantiomeric excess of the product (81% *ee*) was determined by HPLC [Chiralcel OJ-H, 25 cm, hexane/*i*PrOH 98:2, 0.75 mL min^{-1}, t_R (*R*) = 17.2 min, t_R (*S*) = 19.6 min].

Compound 6b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 4.53 (s, 2 H, $PhCH_2$), 5.00 (d, J = 7.0 Hz, 1 H, CHO), 6.33 (dd, J = 7.0, 15.9 Hz, 1 H, =CH), 6.61 (d, J = 15.9 Hz, 1 H, PhCH=), 7.17–7.44 (m, 15 H) ppm. The enantiomeric excess of the product (80% *ee*) was determined by HPLC [Chiralcel OJ-H, 25 cm, hexane/*i*PrOH 98:2, 0.75 mL min^{-1}, t_R (*S*) = 16.6 min, t_R (*R*) = 22.8 min].

Compound 6d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.50 (d, J = 12.4 Hz, 1 H, one of $ArCH_2$), 4.56 (d, J = 12.4 Hz, 1 H, one of $ArCH_2$), 4.99 (d, J = 7.0 Hz, 1 H, CHO), 6.32 (dd, J = 7.0, 15.9 Hz, 1 H, =CHCH), 6.63 (d, J = 15.9 Hz, 1 H, PhCH=), 7.23–7.43 (m, 15 H) ppm. The enantiomeric excess of the product (74% *ee*) was determined by HPLC [Chiralcel OJ-H, 25 cm, hexane/*i*PrOH 96:4, 0.4 mL min^{-1}, t_R (*S*) = 17.2 min, t_R (*R*) = 19.6 min].

Compound 6e: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.50 (d, J = 12.6 Hz, 1 H, one of $ArCH_2$), 4.56 (d, J = 12.6 Hz, 1 H, one of $ArCH_2$), 5.00 (d, J = 7.0 Hz, 1 H, CHO), 6.33 (dd, J = 7.0, 15.9 Hz, 1 H, =CH), 6.61 (d, J = 15.9 Hz, 1 H, PhCH=), 7.04 (t, J = 8.6 Hz, 2 H), 7.20–7.43 (m, 12 H) ppm. The enantiomeric excess of the product (74% *ee*) was determined by HPLC [Chiralcel OD-H, 25 cm, hexane/*i*PrOH 98:2, 0.2 mL min^{-1}, t_R (*S*) = 21.1 min, t_R (*R*) = 29.2 min].

Allylic Amination Catalyzed by Palladium/TCF Complex: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.8 mg, 0.01 mmol, 2 mol-%) and **TCF5** (18 mg, 0.03 mmol, 6 mol-%) dissolved in dry CH_2Cl_2 (2.0 mL) were placed in a Schlenk tube containing a stirring bar, and the mixture was stirred under nitrogen at room temp. for 30 min. Compound **4** (126 mg,0.5 mmol), benzylamine (0.43 g,4.0 mmol), and TBAF (1 M in THF, 1.0 mL, 1.0 mmol) were successively added to this solution. The mixture was stirred at room temp. and monitored by TLC. After completion (72 h), the mixture was diluted with diethyl ether (20 mL), washed with saturated aqueous NH_4Cl, dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure. The brown residue was subjected to PTLC (hexane/ethyl acetate 40:3) to give pure product (135 mg, 0.45 mmol, 91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74 (br. s, 1 H), 3.74 (d, J = 13.3 Hz, 1 H, one of $PhCH_2$), 3.78 (d, J = 13.3 Hz, 1 H, one of $PhCH_2$), 4.37 (d, J = 7.4 Hz, 1 H, CHN), 6.30 (dd, J = 7.4, 15.9 Hz, 1 H, =CH), 6.56 (d, J = 15.9 Hz, 1 H, PhCH=), 7.2–7.4 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.3 (CH_2), 64.5 (CH), 126.4, 126.9, 127.3, 127.4, 128.1, 128.4, 128.5, 128.6, 130.3, 132.5, 136.8, 140.3, 142.8 ppm. The *ee* of the product (66%) was determined by HPLC [Chiracel OJ-H, 25 cm, hexane/*i*PrOH/diethylamine 90:10:1, 0.60 mL min^{-1}, t_R (*S*) = 14.5 min, t_R (*R*) = 17.6 min].

Supporting Information (see also the footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra of ferrocenyl sulfide **3a**–**3f**, ThioClickFerrophos **TCF1**–**TCF6**, and Type II P,S ligand, products of allylic substitutions, **5**, **6a**–**6d**, **7**, and copies of their chiral HPLC chart.

Acknowledgments

This study was financially supported by Chuo University (grant for Special Research).

[1] a) J. Tsuji, in: *Palladium Reagents and Catalysts*, Wiley, Chichester, **2004**, pp. 439–466; b) A. Pfalz, M. Lautens, in: *Comprehensive Asymmetric Synthesis* (Eds.: E. N. Jacobsen, A. Pfalz, H. Yamamoto), Springer, Berlin, **2000**; c) B. M. Trost, C. Lee, in: *Catalytic Asymmetric Synthesis*, 2nd ed. (Ed.: I. Ojima), Wiley-VCH, New York, **2000**, pp. 593–649.

[2] a) H. A. McManus, D. Cusack, P. J. Guiry, in: *Phosphorus Ligands in Asymmetric Catalysis*, vol. 2 (Ed.: A. Börner), Wiley-VCH, Weinheim, **2008**, pp. 549–632; b) P. J. Guiry, C. P. Saunders, *Adv. Synth. Catal.* **2004**, *346*, 497–537.

[3] R. Malacea, E. Manoury, in: *Phosphorus Ligands in Asymmetric Catalysis* (Ed.: A. Börner), Wiley-VCH, Weinheim, **2008**, vol. 2, pp. 749–784.

[4] a) P. Štěpnička, in: *Ferrocenes: Ligands, Materials and Biomolecules*, John Wiley & Sons, West Sussex, **2008**; b) W. Cheng, H.-U. Blaser, in: *Phosphorus Ligands in Asymmetric Catalysis* (Ed.: A. Börner), Wiley-VCH, Weinheim, **2008**, vol. 1, pp. 345–349; c) R. G. Arrayás, J. Adrio, J. C. Carretero, *Angew. Chem. Int. Ed.* **2006**, *45*, 7674–7715.

[5] a) D. Enders, R. Peters, R. Lochtman, G. Raabe, J. Runsink, J. W. Bats, *Eur. J. Org. Chem.* **2000**, 3399–3426; b) D. Enders, R. Peters, J. Runsink, J. W. Bats, *Org. Lett.* **1999**, *1*, 1863–1866.

[6] O. G. Mancheño, J. Priego, S. Cabrera, R. G. Arrayás, T. Liamas, J. C. Carretero, *J. Org. Chem.* **2003**, *68*, 3679–3686.

[7] a) F. L. Lam, T. T.-L. Au-Yeung, F. Y. Kwong, Z. Zhou, K. Y. Wong, A. S. C. Chan, *Angew. Chem. Int. Ed.* **2008**, *47*, 1280–1283; b) F. L. Lam, T. T.-L. Au-Yeung, H. Y. Cheung, S. H. L. Kok, W. S. Lam, K. Y. Wong, A. S. C. Chan, *Tetrahedron: Asymmetry* **2006**, *17*, 497–499; c) H. Y. Cheung, W.-Y. Yu, F. L. Lam, T. T.-L. Au-Yeung, Z. Zhou, T. H. Chan, A. S. C. Chan, *Org. Lett.* **2007**, *9*, 4295–4298.

[8] a) B. F. Binini, M. Fochi, A. Ricci, *Synlett* **2007**, 360–373; b) L. Routaboul, S. Vincendeau, J.-C. Daran, E. Manoury, *Tetrahedron: Asymmetry* **2005**, *16*, 2685–2690; c) S. Nakamura, T. Fukuzumi, T. Toru, *Chirality* **2004**, *16*, 10–12; d) J. Kang, J. H. Lee, K. S. Im, *J. Mol. Catal.* **2003**, *196*, 55–63; e) T. Tu, Y.-G. Zhou, X.-L. Hou, L.-X. Dai, X.-C. Dong, Y.-H. Yu, J. Sun, *Organometallics* **2003**, *22*, 1255–1265.

[9] a) M. Kato, H. Oki, K. Ogata, S.-i. Fukuzawa, *Synlett* **2009**, 1299–1302; b) S.-i. Fukuzawa, H. Oki, *Org. Lett.* **2008**, *10*, 1747–1750; c) S.-i. Fukuzawa, H. Oki, M. Hosaka, J. Sugasawa, S. Kikuchi, *Org. Lett.* **2007**, *9*, 5557–5560.

[10] A chiral ferrocenyl P,S ligand bearing a 1,2,4-triazole group has been reported during the preparation of this manuscript: H. Y. Cheung, W.-Y. Yu, T. T. L. Au-Yeung, A. Zhou, A. S. C. Chan, *Adv. Synth. Catal.* **2009**, *351*, 1412–1422.

Received: July 10, 2009
Published Online: September 8, 2009

