Supporting Information for:

t-Bu-QuinoxP* Ligand: Applications in Asymmetric Pd-Catalyzed Allylic Substitution and Ru-Catalyzed Hydrogenation

Tsuneo Imamoto,* Miwako Nishimura, Aya Koide and Kazuhiro Yoshida

Department of Chemistry, Graduate School of Science, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Contents.

Materials. Catalyst precursors $PdCl_2(cod)$[1], $[PdCl(\eta^3\text{-}C_3H_5)]_2$[2], and $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$[3] were prepared according to the literature procedures. Chiral diphosphine ligand (*R*,*R*)-*t*-Bu-QuinoxP* (**1**) was prepared according to the method described in the literature.[4]

Conditions for determination of enantiomeric excesses of chiral products.

Pd-catalyzed asymmetric allylic alkylation

*Dimethyl 2-(1,3-diphenyl-2-propenyl)malonate (**4a**)*[5]*:* HPLC[5], Chiralpak AD-H, hexane/2-propanol = 95:5, 1.0 mL/min, 254 nm, (*R*)t_1 = 17.8 min, (*S*)t_2 = 25.5 min;

*Dimethyl 2-methyl-2-(1,3-diphenyl-2-propenyl)malonate (**4b**)*[6]*:* HPLC[6], Chiralpak AD-H, hexane/2-propanol = 199:1, 1.0 mL/min, 254 nm, (*S*)t_1 = 27.3 min, (*R*)t_2 = 44.3 min;

*Diethyl 2-butyl-2-(1,3-diphenyl-2-propenyl)malonate (**4c**)*[7]*:* HPLC, Chiralpak AD-H, hexane/2-propanol = 98:2, 0.5 mL/min, 254 nm, t_1 = 12.1 min, t_2 = 15.2 min;

*Diethyl 2-benzyl-2-(1,3-diphenyl-2-propenyl))malonate (**4d**)*[7]*:* HPLC, Chiralpak AD-H, hexane/2-propanol = 98:2, 1.0 mL/min, 254 nm, t_1 = 11.6 min, t_2 = 16.0 min;

*Diethyl 2-formamido-2-(1,3-diphenyl-2-propenyl)malonate (**4e**)*[7]*:* HPLC, Chiralpak AD-H, hexane/2-propanol = 9:1, 1.0 mL/min, 254 nm, t_1 = 15.3 min, t_2 = 22.4 min;

*Diethyl 2-acetoamido-2-(1,3-diphenyl-2-propenyl)malonate (**4f**)*[6]*:* HPLC[6], Chiralpak AD-H, hexane/2-propanol = 9:1, 1.0 mL/min, 254 nm, (*R*)t_1 = 10.5 min, (*S*)t_2 = 14.1 min;

*3-(1,3-Diphenyl-2-propenyl)-2,4-pentanedione (**4g**)*[8]*:* HPLC[9], Chiralcel OJ-H, hexane/2-propanol = 9:1, 0.5 mL/min, 254 nm, (*R*)t_1 = 36.8 min, (*S*)t_2 = 41.7 min;

Pd-catalyzed asymmetric allylic amination

*N-(1,3-Diphenyl-2-propenyl)morpholine (**4h**)*[10]*:* HPLC, Chiralcel OJ-H, hexane/2-propanol = 95:5, 0.5 mL/min, 254 nm, t_1 = 21.0 min, t_2 = 27.3 min;

*N-(1,3-Diphenyl-2-propenyl)pyrrolidine (**4i**)*[11]*:* HPLC[11], Chiralcel OD-H + OD-H, hexane/ 2-propanol = 199:1, 0.3 mL/min, 254 nm, (*R*)t_1 = 42.8 min, (*S*)t_2 = 48.3 min;

*N-(1,3-Diphenyl-2-propenyl)butylamine (**4j**)*[12]*:* HPLC, Chiralcel OD-H, hexane/2-propanol/ diisopropylamine = 400:2:1, 0.25 mL/min, 254 nm, t_1 = 36.1 min, t_2 = 40.3 min;

*N-(1,3-Diphenyl-2-propenyl)cyclohexylamine (**4k**)*[13]*:* HPLC, Chiralpak AD-H, hexane/ 2-propanol = 99:1, 0.5 mL/min, 254 nm, t_1 = 20.4 min, t_2 = 22.9 min;

Ru-catalyzed asymmetric hydrogenation

*3-Hydroxy-3-phenylpropionic acid ethyl ester (**6a**)*[14]*:* HPLC[14], Chiralcel OD-H, hexane/2-propanol = 95:5, 0.5 mL/min, 230 nm, (*S*)t_1 = 22.6 min, (*R*)t_2 = 33.0 min;

*3-Hydroxy-3-(4'-methylphenyl)propionic acid ethyl ester (**6b**)*[15]*:* HPLC[15], Chiralpak AS, hexane/2-propanol = 95:5, 0.5 mL/min, 230 nm, (*R*)t_1 = 24.5 min, (*S*)t_2 = 27.3 min;

*3-Hydroxy-3-(4'-methoxyphenyl)propionic acid ethyl ester (**6c**)*[15]*:* HPLC[15], Chiralpak AS, hexane/2-propanol = 9:1, 1.0 mL/min, 230 nm, (*R*)t_1 = 15.4 min, (*S*)t_2 = 24.7 min;

*3-Hydroxy-3-(4'-bromophenyl)propionic acid ethyl ester (**6d**)*[15]*:* HPLC[15], Chiralpak AS, hexane/2-propanol = 95:5, 0.5 mL/min, 230 nm, (*R*)t_1 = 29.0 min, (*S*)t_2 = 34.1 min;

*3-Hydroxy-3-(4'-chlorophenyl)propionic acid ethyl ester (**6e**)*[15]*:* HPLC[15], Chiralpak AS, hexane/2-propanol = 95:5, 0.5 mL/min, 230 nm, (*R*)t_1 = 23.4 min, (*S*)t_2 = 29.0 min;

*3-Hydroxy-3-(4'-fluorophenyl)propionic acid ethyl ester (**6f**)*[15]*:* HPLC, Chiralpak AS, hexane/2-propanol = 9:1, 0.3 mL/min, 254 nm, t_1 = 29.0 min, t_2 = 32.1 min;

*3-Hydroxy-3-(3',4'-dimethoxyphenyl)propionic acid ethyl ester (**6g**)*[16]*:* HPLC, Chiralpak AS-H + AS, hexane/2-propanol = 9:1, 0.8 mL/min, 235 nm, t_1 = 44.3 min, t_2 = 51.1 min;

*3-Hydroxybutyric acid methyl ester (**6h**)*[17]*:* Capillary GC[18], G-TA (30 m), 65 °C, isothermal, flow rate, 19 cm/s, (*S*)t_1 = 19.3 min, (*R*)t_2 = 19.5 min;

*4-Chloro-3-hydroxybutyric acid ethyl ester (**6i**)*[19]*:*
(benzoyl derivative): HPLC, Chiralcel OD-H, hexane/2-propanol = 95:5, 0.5 mL/min, 254 nm, t_1 = 12.8 min, t_2 = 14.0 min;

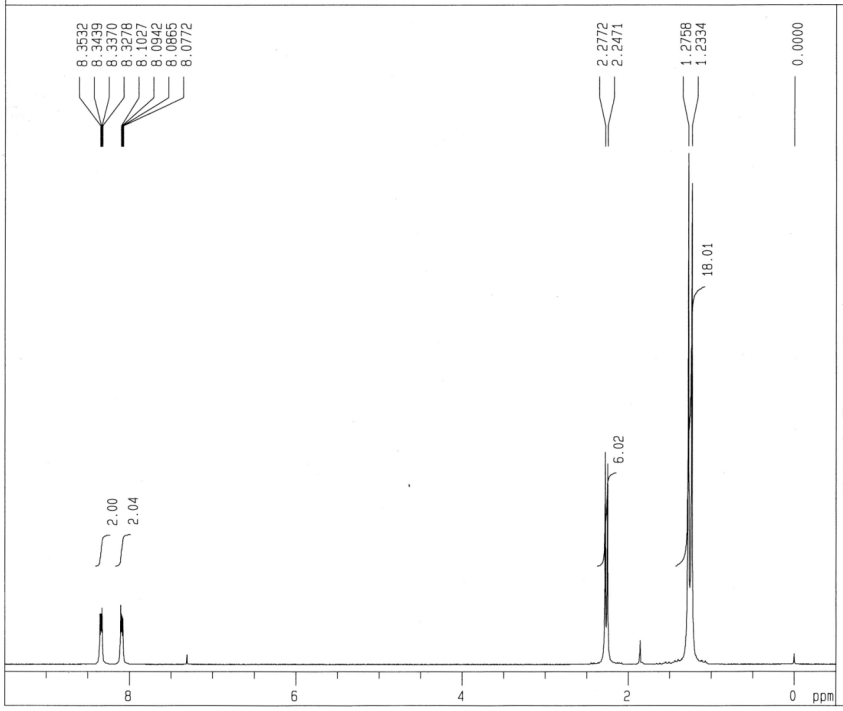
*3-Hydroxy-N,N-dimethylbutyramide (**6j**)*[20]: Capillary GC, DexCB (25m), 85 °C, isothermal, flow rate, 22 cm/s, t_1 = 50.8 min, t_2 = 51.3 min;

*5-Hydroxy-2,2-dimethyl-3-hexanone (**6k**)*[21]*:* Capillary GC, DexCB (25 m), 90°C, isothermal, flow rate, 22 cm/s, t_1 = 16.3 min, t_2 = 16.6 min;

References

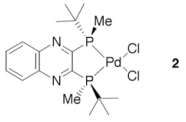
(1) Drew, D.; Doyle, J. R. *Inorg. Synth.*, **1972**, *13*, 52.
(2) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.*, **1979**, *19*, 220.
(3) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233-241.
(4) Imamoto, T.; Sugita, K.; Yoshida, K. *J. Am. Chem. Soc.* **2005**, *127*, 11934–11935.
(5) Zhang, W.; Xu, Q.; Shi, M. *Tetrahedron: Asymmetry* **2004**, *15*, 3161-3169; The absolute configuration was determined by comparing HPLC (OD-H) retention times with data in the literature.
(6) Ogasawara, M.; Ngo, H. L.; Sakamoto, T.; Takahashi, T.; Lin, W. *Org. Lett.* **2005**, *7*, 2881-2884.
(7) Chen, X.; Guo, R.; Li, Y.; Chen, G.; Yeung, C.-H.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2004**, *15*, 213-217.
(8) Ross, J.; Chen, W.; Xu, L.; Xiao, J. *Organometallics* **2001**, *20*, 138-142.
(9) Frölander, A.; Lutsenko, S.; Privalov, T.; Moberg, C. *J. Org. Chem.* **2005**, *70*, 9882-9891.
(10) Feuerstein, M.; Laurenti, D.; Doucet, H.; Santelli, M. *Journal of Molecular Catalysis A: Chemical* **2002**, *182-183*, 471-480.
(11) Smyth, D.; Tye, H.; Eldred, C.; Alcock, N. W.; Wills, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2840-2849.
(12) Ohta, T.; Sasayama, H.; Nakajima, O.; Kurahashi, N.; Fujii, T.; Fukukawa, I. *Tetrahedron: Asymmetry* **2003**, *14,* 537-542.
(13) Qian, C.; Huang, T. *Journal of Organometallic Chemistry* **1997**, *548*, 143-147.
(14) Wang, Y.-G.; Lu, S.-M.; Zhou, Y.-G. *Org. Lett.* **2005**, *7*, 3235-3238.
(15) Zhou, Y.-G.; Tang, W.; Wang, W.-B.; Li, W.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 4952-4953.
(16) Bardot, V.; Besse, P.; Gelas-Miahle, Y.; Remuson, R.; Veschambre, H. *Tetrahedron: Asymmetry* **1996**, *7*, 1077-1088.
(17) Junge, K.; Hagemann, B.; Enthaler, S.; Oehma, G.; Michaelik, M.; Monsees, A.; Riermeier, T.; Dingerdissen, U.; Beller, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 5066-5069.
(18) Nakamura, K.; Fujii, M.; Ida, Y. *Tetrahedron: Asymmetry* **2001**, *12*, 3147-3153.
(19) Ema, T.; Moriya, H.; Kofukuda, T.; Ishida, T.; Maehara, K.; Utaka, M.; Sakai, T. *J. Org. Chem.* **2001**, *66*, 8682-8684.
(20) Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1977**, *42*, 1688-1690.
(21) Chopade, P. R.; Davis, T. A.; Prasad, E.; Flowers II, R. A. *Org. Lett.* **2004**, *6*, 2685-2688.

^{1}H



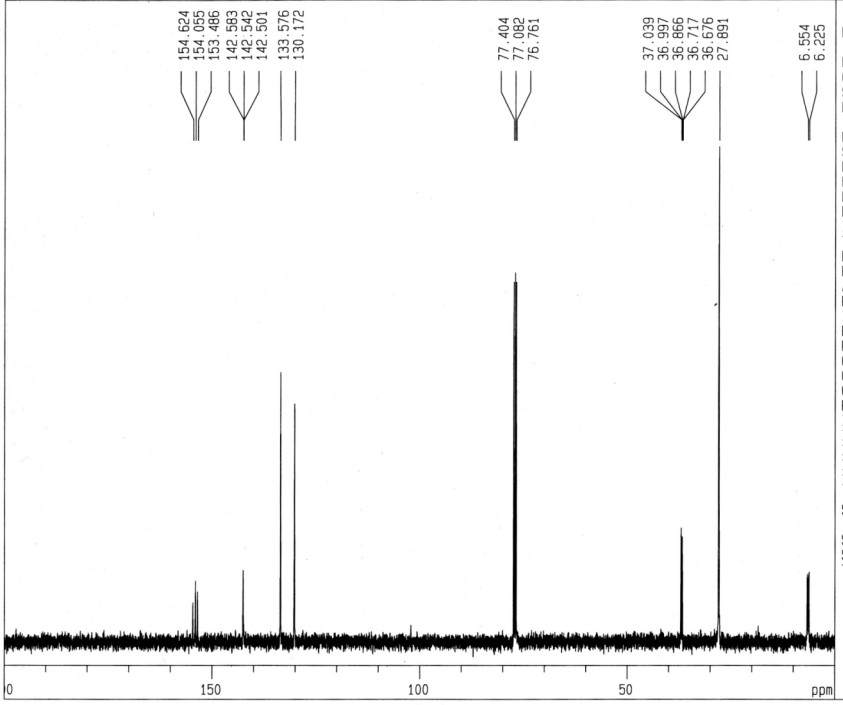
Date : Wed May 23 22:20:37 2007

FileName	:	070523mwk_m04_0371_comp
Comment	:	M04-0371 : complex_1H
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	56.9 usec
INTVL	:	100.0 usec
TIMES	:	8 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	10.00000 msec
INIWT	:	0.5000 msec
RESOL	:	0.31 Hz
PW1	:	6.25 usec
OBNUC	:	1H
OBFRQ	:	395.75 MHz
OBSET	:	136692.03 Hz
RGAIN	:	16
SCANS	:	8 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	22.2 C



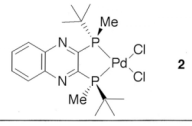
2

^{13}C

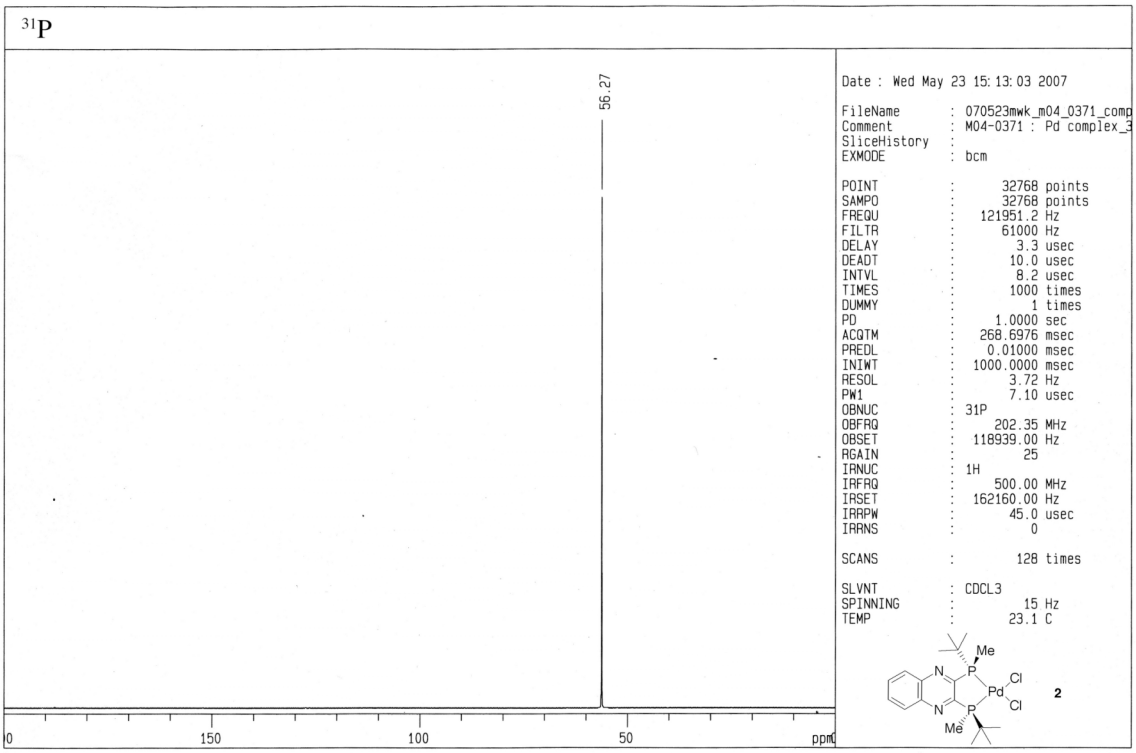


Date : Wed May 23 22:18:12 2007

FileName	:	070523mwk_m04_0371_comp
Comment	:	M04-0371 : Pd-complex_1
SliceHistory	:	
EXMODE	:	bcm
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	26881.7 Hz
FILTR	:	13450 Hz
DELAY	:	14.9 usec
DEADT	:	19.8 usec
INTVL	:	37.2 usec
TIMES	:	256 times
DUMMY	:	1 times
PD	:	1.7810 sec
ACQTM	:	1218.9696 msec
PREDL	:	10.00000 msec
INIWT	:	10.0000 msec
RESOL	:	0.82 Hz
PW1	:	5.00 usec
OBNUC	:	13C
OBFRQ	:	99.45 MHz
OBSET	:	104750.00 Hz
RGAIN	:	30
IRNUC	:	1H
IRFRQ	:	395.75 MHz
IRSET	:	134498.00 Hz
IRPW	:	40.0 usec
IRNS	:	0
SCANS	:	256 times
SLVNT	:	CDCL3
SPINNING	:	11 Hz
TEMP	:	22.3 C



2


31P
56.27
150
100
50
ppm
Date : Wed May 23 15:13:03 2007
FileName : 070523mwk_m04_0371_comp
Comment : M04-0371 : Pd complex_3
SliceHistory :
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 121951.2 Hz
FILTR : 61000 Hz
DELAY : 3.3 usec
DEADT : 10.0 usec
INTVL : 8.2 usec
TIMES : 1000 times
DUMMY : 1 times
PD : 1.0000 sec
ACQTM : 268.6976 msec
PREDL : 0.01000 msec
INIWT : 1000.0000 msec
RESOL : 3.72 Hz
PW1 : 7.10 usec
OBNUC : 31P
OBFRQ : 202.35 MHz
OBSET : 118939.00 Hz
RGAIN : 25
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRRPW : 45.0 usec
IRRNS : 0
SCANS : 128 times
SLVNT : CDCL3
SPINNING : 15 Hz
TEMP : 23.1 C
Me
N
P
Pd
Cl
Cl
N
P
Me
2