Synthesis, Reaction, and Recycle of Fluorous Palladium Catalysts for an Asymmetric Allylic Alkylation without Using Fluorous Solvents

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Table of Contents

Figure S1	S3
Figure S2	S4
^1H , ^{13}C , and ^{31}P NMR of 3	S5-7
^1H , ^{13}C , and ^{31}P NMR of 4c	S8-10
^1H , ^{13}C , and ^{31}P NMR of 4d	S11-13
Chiral phase HPLC chart of 9a	S14
Chiral phase HPLC chart of 9b	S14
Chiral phase HPLC chart of 9c	S15

Figure S1. Photographs of Fluorous Palladium Complex (entry 6, Table 3): (A) room temperature at start of reaction; (B) 30 °C at start of reaction; (C) after 1 h; (D) after 2 h; (E) room temperature after reaction; (F) after addition of hexane at 0 °C; (G) recovered catalyst; (H) recovered catalyst in diethyl ether.

A

B

Figure S2. The FAB-MS spectrum of palladium complexes: (A) palladium catalyst prepared from $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ and ligand **4c**; (B) recovered palladium catalyst.

¹H NMR of 3

¹³C NMR of 3

³¹P NMR of 3

Current Data Parameters
 NAME 12038p
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20031002
 Time 21.59
 INSTRUM spect
 PROBHD 5 mm BBO BB-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 1
 SWH 75187.969 Hz
 FIDRES 1.147277 Hz
 AQ 0.4358644 sec
 RG 3251
 DW 6.650 usec
 DE 6.00 usec
 TE 300.0 K
 d11 0.03000000 sec
 d12 0.00002000 sec
 PL13 25.00 dB
 D1 8.00000000 sec
 waltz16
 CPDPRG2 100.00 usec
 PCPD2 300.2312009 MHz
 SFO2 1H
 NUC2 2.00 dB
 PL2 25.00 dB
 F1 8.00 usec
 SFO1 121.5351820 MHz
 NUC1 31P
 PL1 3.00 dB

F2 - Processing parameters
 SI 32768
 SF 121.5352715 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 FLP 200.000 ppm
 F1 24307.05 Hz
 F2P -200.000 ppm
 F2 -24307.05 Hz
 PPMCM 20.00000 ppm/cm
 HZCM 2430.70532 Hz/cm

¹H NMR of 4c

¹³C NMR of **4c**

³¹P NMR of 4c

Current Data Parameters
NAME 11553p
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030408
Time 20.14
INSTRUM spect
PROBHD 5 mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8
DS 1
SWH 75187.969 Hz
FIDRES 1.147277 Hz
AQ 0.4358644 sec
RG 3251
DW 6.650 usec
DE 6.00 usec
TE 300.0 K
d11 0.03000000 sec
d12 0.0002000 sec
PL13 25.00 dB
D1 8.0000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.2312009 MHz
NUC2 1H
PL2 2.00 dB
PL12 25.00 dB
P1 8.00 usec
SFO1 121.5351820 MHz
NUC1 31P
PL1 3.00 dB

F2 - Processing parameters
SI 32768
SF 121.5352715 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
FIP 200.000 ppm
F1 24307.05 Hz
F2P -200.000 ppm
F2 -24307.05 Hz
PPhCM 20.00000 ppm/cm
HzCM 2430.70532 Hz/cm

—14.885

wdw

¹H NMR of 4d

¹³C NMR of 4d

³¹P NMR of 4d

Chiral phase HPLC chart of **9a** (Table 1, entry 14); 95%ee

Daicel CHIRALCEL OD-H; Hexane : *i*-PrOH = 99 : 1; Flow : 0.3 mL/min

Chiral phase HPLC chart of **9b** (Table 2, entry 5); 97%ee

-- % CALCULATION RESULT --

TEST-DATA

WINDOW = 0 %		SCALE FACTOR = 1.0000		PEAK AREA	
PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	16.425	5354	231		1.6837
2	22.487	312633	9608		98.3163
TOTAL		317987	9839		100.0000

Daicel CHIRALPAK AD-H; Hexane : *i*-PrOH = 95 : 5; Flow : 1.0 mL/min

Chiral phase HPLC chart of **9c** (Table 2, entry 3); 81%ee

Daicel CHIRALCEL OD-H+OD at 0 °C; Hexane : *i*-PrOH = 199 : 1; Flow : 0.3 mL/min