Supporting Information

Chiral Phosphinooxazolidine Ligands for Palladium- and Platinum-Catalyzed Asymmetric Diels-Alder Reaction

Hiroto Nakano,^{,†} Kouichi Takahashi,[†] Yuko Okuyama,[†] Chieko Senoo,[†]
Natsumi Tsugawa,[†] Yuichiro Suzuki,[†] Reiko Fujita,[†]
Kazuo Sasaki,[‡] and Chizuko Kabuto^{*,‡}*

[†]Tohoku Pharmaceutical University, 4-4-1 Komatsushima, Aoba-ku,
Sendai, 981-8558, Japan

[‡]Instrumental Analysis Center for Chemistry, Graduate School of Science,
Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan

Table of Contents

1.	General Methods	S2
2.	¹ H - and ¹³ C-NMR for 7	S3
3.	¹ H - and ¹³ C-NMR for 2a	S5
4.	¹ H - and ¹³ C-NMR for 9	S7
5.	¹ H - and ¹³ C-NMR for 9	S9
6.	¹ H - and ¹³ C-NMR for 2b	S11
7.	¹ H - and ¹³ C-NMR for 12	S13
8.	¹ H - and ¹³ C-NMR for 14a	S15
9.	¹ H - and ¹³ C-NMR for 14b	S17
10.	¹ H - and ¹³ C-NMR for 16a	S19
11.	¹ H - and ¹³ C-NMR for 16b	S21
12.	¹ H - and ¹³ C-NMR for 16c	S23
13.	¹ H - and ¹³ C-NMR for 18	S25
14.	¹ H - and ¹³ C-NMR for exo-28	S27
15.	ORTEP drawings for 12 , 14a , 14b , 16a , 16b , and 18	S29

General Methods

Melting points are uncorrected. IR spectra were recorded as KBr pellets (solids) or thin films (liquids). The ¹H- and ¹³C-NMR spectra were recorded at 270 and 67.5 MHz, and 400 and 100 MHz respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ¹H-NMR and relative to the central CDCl₃ resonance ($\delta = 77.0$) for ¹³C-NMR.

Mass spectra were obtained by EI. The enantiomeric excess (ee) of the products were determined by chiral HPLC. Optical rotations were recorded at the sodium D line with a polarimeter at room temperature. Commercially available

compounds were used without further purification. Solvents were dried according to standard procedures.
Chromatography refers to flash chromatography on silica gel (230-400 mesh), unless otherwise noted.

D:\4, @, f, \ml\ProLine\I
 COMNT Lig-025-021219
 DATIM Thu Dec 19 17:20:49 2002
 OBNUC 1H
 EXMOD NON
 OBFOQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5402.40 Hz
 SCANS 16
 ACQTM 6.0655 sec
 PD 0.9350 sec
 PW1 4.80 usec
 IRNUC 1H
 CTMP 23.6 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 Bf 0.08 Hz
 RGAIN 26

D:\4, @, f, \T-5-c.ALS
 COMNT T-5-C
 DATIM Mon Dec 22 07:46:29 2003
 OBNUC 13C
 EXMOD BCM
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.00 Hz
 POINT 32768
 FREQU 18315.00 Hz
 SCANS 42000
 ACQTM 1.7891 sec
 PD 1.2110 sec
 PW1 3.50 usec
 IRNUC 1H
 CTMP 24.3 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.30 Hz
 RGAIN 31

7

D:_h_@f_mml\PROLine\I
 LIC-041-030115
 COMNT Wed Jan 15 20:21:18 2003
 DATIM 1H
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OFFIN 5800.00 Hz
 POINT 32768
 FREQU 5402.40 Hz
 SCANS 4
 ACQTM 6.0655 sec
 PD 0.9350 sec
 PW1 4.80 usec
 IRNUC 1H
 CTMP 23.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.08 Hz
 RGAIN 16

D:\401\T-NP\NP-T-PI
 COMNT NP-T-PL-OH-C
 DATIM Mon May 12 07:04:45 2003
 OBNUC 13C
 EXMOD BCM
 OBFRO 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.00 Hz
 POINT 32768
 FREQU 18315.00 Hz
 SCANS 40000
 ACQTM 1.7891 sec
 PD 1.2110 sec
 PW1 3.50 usec
 IRNUC 1H
 CTEMP 25.5 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.30 Hz
 RGAIN 30

CCOC(=O)[C@H]1N(C(=O)O[C@@H]1C(=O)O[C@H]2C(=O)O)C(=O)O2

9

9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 PPM

D:\...f,µ\C-np\C-2-C.f
 C-2-C
 Mon Mar 08 07:07:43 2004
 13C
 BCM

EXMOD
 OBFREQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.00 Hz
 POINT 32768
 FREQ 18306.64 Hz
 SCANS 40000
 ACQTM 1.7900 sec
 PD 1.2110 sec
 PW1 3.50 usec
 IRNUC 1H
 CTMP 24.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 EF 0.30 Hz
 RGAIN 32

D:_4,6,7,8-tetrahydro-2H-pyrimidin-2-ol-5-yl
 C-5
 COMNT
 DATIM Tue Dec 16 20:44:50 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5402.40 Hz
 SCANS 32
 ACQTM 6.0655 sec
 PD 0.9350 sec
 PW1 4.80 usec
 TRNUC 1H
 CTEMP 23.7 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.08 Hz
 RGAIN 25

DFILE C:\winmr98\COMMON\C-5-c
 COMNT C-5-c
 DATIM Wed Jan 07 08:10:15 2004
 OBNUC 13C
 EXMOD BCM
 OBFREQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.00 Hz
 POINT 32768
 FREQU 18315.00 Hz
 SCANS 14000
 ACQTM 1.7891 sec
 PD 1.2110 sec
 PW1 3.50 usec
 IRNUC 1H
 CTEMP 24.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.30 Hz
 RGAIN 31

D:_4_0_1_1\1C-1p\NP-C-Of
 COMPT NP-C-OH
 DATIM Wed Dec 10 19:55:07 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5402.40 Hz
 SCANS 4
 ACQTM 6.0655 sec
 PD 0.9350 sec
 PW1 4.80 usec
 TRNUC 1H
 CTMP 23.6 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.08 Hz
 RGAIN 18

D:\4,0,f,\C-np\NP-C-Of
 COMNT NP-C-OH-C
 DATIM Mon Dec 15 20:55:31 2003
 OBNUC 13C
 EXMOD BCM
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.00 Hz
 POINT 32768
 FREQU 18315.00 Hz
 SCANS 256
 ACQTM 1.7891 sec
 PD 1.2110 sec
 PW1 3.50 usec
 IRNUC 1H
 CTEMP 24.9 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.30 Hz
 RGAIN 31

D:\YUKO\Y-03079-2-C.ALS
 Y-03079-C
 Wed Dec 24 08:05:26 2003
 13C
 BCM
 EXMOD
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OFFIN 5200.00 Hz
 POINT 32768
 FREQU 18315.00 Hz
 SCANS 41725
 ACQTM 1.7891 sec
 PD 1.2110 sec
 PW1 3.50 usec
 1H
 CDCL3
 CTMP 24.6 C
 SLVNT
 EXREF 77.00 ppm
 BF 0.30 Hz
 RGAIN 32

D:_4_0_1_1\T-NP\NP-T-PI
 NP-T-PI-OH
 Tue May 13 20:45:02 2003
 1H
 EXMOD NON
 OFFRQ 270.05 MHz
 OBSET 112.00 KHz
 OFFIN 5800.00 Hz
 POINT 32768
 FREQU 5402.40 Hz
 SCANS 16
 ACQTM 6.0655 sec
 PD 0.9350 sec
 PW1 4.80 usec
 1H
 TRNUC 1H
 CTMP 24.3 c
 CDCL3
 SLVNT
 EXREF 0.00 ppm
 BF 0.08 Hz
 RGAIN 23

DEFILE C:\winmr98\DATA\trans.f
 COMNT trans
 DATIM Wed May 21 07:08:51 2003
 OBNUC 13C
 EXMOD BCM
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.00 Hz
 POINT 32768
 FREQU 18315.00 Hz
 SCANS 14000
 ACQTM 1.7891 sec
 PD 1.2110 sec
 PW1 3.50 usec
 IRNUC 1H
 CTMP 25.5 C
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.30 Hz
 RGAIN 30

D:\4, @, t, μ C-np\NP-C-PI
 COMNT NP-C-PL-OH-Pd
 DATIM Fri May 02 19:25:16 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5402.40 Hz
 SCANS 8
 ACQTM 6.0655 sec
 PD 0.9350 sec
 PW1 4.80 usec
 IRNUC 1H
 CTEMP 24.3 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.08 Hz
 RGAIN 20

16b

D:_4_@f\h\C-np\NP-C-PI
 COMNT NP-C-PL-OH
 DATIM Fri May 09 07:34:40 2003
 OBNUC 13C
 EXMOD BCM
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OFFIN 5200.00 Hz
 POINT 32768
 FREQU 18315.00 Hz
 SCANS 12000
 ACQTM 1.7891 sec
 PD 1.2110 sec
 PW1 3.50 usec
 1H
 IIRNUC 25.3 c
 CTMP CDCL3
 SLVNT
 EXREF 0.00 ppm
 BF 0.30 Hz
 RGAIN 30

16b

DFILE UP-DOWN-OH
 COMNT Sat May 31 07:17:2.
 DATIM 13C
 OBNUC BCM
 EXMOD 67.80 MHz
 OBFRQ 135.00 KHz
 OBSET 5200.00 Hz
 OFBIN 32768
 POINT 18315.00 Hz
 FREQU 12000
 SCANS 1.7891 sec
 ACQTM 1.2110 sec
 PD 3.50 usec
 PW1 1H
 IRNUC 25.7 C
 CTEMP CDCL3
 SLVNT 0.00 ppm
 EXREF 0.30 Hz
 BF 30
 RGAIN

16c

DFILE E:\TAKAHASHI\3\3-0
 COMNT EXO
 DATIM Fri Jun 25 19:49:3
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.00 Hz
 POINT 32768
 FREQU 5401.76 Hz
 SCANS 16
 ACQTM 6.0662 sec
 PD 0.9350 sec
 PW1 4.80 usec
 IRNUC 1H
 CTEMP 24.9 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.08 Hz
 RGAIN 27

exo-28

51 Y

NOMOVE FORCED

PROBA= 50

exo-28

DFILE E:\TAKAHASHI\3\3-0:
COMNT exo-furan-1-C
DATIM Wed Jul 07 19:52:2
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18306.64 Hz
SCANS 100
ACQTM 1.7900 sec
PD 1.2110 sec
PWL 3.50 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.30 Hz
RGAIN 31

200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 PPM

ORTEP drawing of compound **12**

ORTEP drawings were output from checkcif