Supporting Information

S1

Chiral C_2 -Symmetric Ligands with 1,4-Dioxane Backbone Derived from Tartrates: Syntheses and Applications in Asymmetric Hydrogenation

Wenge Li, Jason P. Walckirch, and Xumu Zhang*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802

(2*R*, 3*R*, 5*S*, 6*S*)-2,3-diethoxy-2,3-dimethyl-5,6-bis(((methanesulfonyl)oxy)methyl) [1,4]dioxane 12b. Bismesylate **12b** was prepared according to the procedure for making **12a** in 95% yield as a white solid: mp 78-9 °C. $[\alpha]_D^{24} = -90.3$ (*c* 1.2, CHCl₃). ¹H NMR (CDCl₃, 360 MHz) δ 4.45 (d, *J* = 12.3 Hz, 2H), 4.33 (dd, *J* = 12.3, 1.2 Hz, 2H), 4.04 (m, 2H), 3.53-3.47 (m, 4H), 3.12 (s, 6H), 1.31 (s, 6H), 1.20 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (CDCl₃, 90.56 MHz) δ 99.0, 69.0, 66.3, 56.0, 37.9, 18.0, 15.3. HRMS calcd for C₁₂H₂₂O₉S₂ (M-CH₃CH₂OH)⁺: 375.0783; found: 375.0789.

(2*S*, 3*S*, 5*R*, 6*R*)-2,3-dimethoxy-2,3-dimethyl-5,6-bis(((methanesulfonyl)oxy)methyl) [1,4]dioxane 14. Bismesylate **14** was prepared according to the procedure for making **12a**. A flash chromatography on a silica gel column eluted with hexanes/CH₂Cl₂/ethyl ether (50/35/15) gave a white solid in 97% yield: mp 87-88 °C. $[\alpha]_D^{24} = +123.6$ (*c* 1.1, CHCl₃). ¹H NMR (CDCl₃, 360 MHz) δ 4.40-4.30 (m, 4H), 4.01-3.90 (m, 2H), 3.23 (s, 6H), 3.08 (s, 6H), 1.26 (s, 6H); ¹³C NMR (CDCl₃, 90.56 MHz) δ 99.1, 68.7, 66.5, 48.1, 37.7, 17.2. HRMS calcd for C₁₁H₂₁O₉S₂ (M-OCH₃)⁺: 361.0627; found: 361.0627.

(6*R*, 7*R*, 14*S*, 15*S*)-1,8,13,16-Tetraoxa-dispiro[5,0,5,4]-14,15-(((methanesulfonyl)oxy)methyl)hexadecane (17): Bismesylate **17** was prepared according to the procedure for making **12a**. A flash chromatography on a silica gel column eluted with hexanes/CH₂Cl₂/ethyl ether (50/35/15) gave a white solid in 88% yield; mp: 102-3 °C. $[\alpha]^{24}_D = -73.2$ (*c* 0.8, CHCl₃). ¹H NMR (CDCl₃, 360 MHz) δ 4.47-4.34 (m, 4H), 4.06 (m, 2H), 3.67-3.59 (m, 4H), 3.10 (s, 6H), 1.78-1.48 (m, 12H); ¹³C NMR (CDCl₃, 90.6 MHz) δ 96.3, 68.7, 65.6, 60.7, 37.5, 27.8, 24.5, 17.7. HRMS calcd for C₁₆H₂₈O₁₀S₂Na (MNa⁺): 467.1022; found: 467.1018.

Bisphosphines **6a** and **6b** were prepared according to the similar procedure for **5** in 76% and 73% yields, respectively. Identical NMR data were obtained by comparison with the sample prepared earlier by the different route.^[8]

The **6a**•BH₃ adduct was formed by stirring the crude **6a** with 1.2 equivalent of 1M BH₃ solution in THF at rt for 12 h. Recrystallization from hexanes/ether gave a white solid in 70% yield (based on bismesylate): $[\alpha]^{24}_D = -44.3$ (*c* 1.0, CHCl₃). ¹H NMR (CDCl₃, 360 MHz) δ 7.90-7.87 (m, 4H), 7.61-7.50 (m, 4H), 7.45-7.37 (m, 12H), 4.13-4.09 (m, 2H), 2.77-2.72 (m 2H), 2.69 (s, 6H), 2.24-2.17 (m, 2H), 1.43-0.80 (br, 6H), 0.86 (s, 6H); ¹³C NMR (CDCl₃, 90.56 MHz) δ 133.4 (d, *J* = 10.0 Hz), 131.5 (d, *J* = 9.1 Hz), 131.3-130.2 (m), 128.8-127.8 (m), 98.5, 67.6 (d, *J* = 13.6 Hz), 48.2, 28.0, 27.6, 17.0; ³¹P NMR (CDCl₃) δ 15.3 (br) ppm

Phosphine **6a** was liberated by stirring with two equivalents of DABCO in toluene at 50 °C for 12 h. After evaporating the solvent, the residue was passed through a short silica gel column eluted with hexanes/ether (95/5) to give the pure product.

(2*R*, 3*R*, 5*R*, 6*R*)-5,6-bis((di(3,5-dimethylphenyl)phosphanyl)methyl)-2,3-diethoxy-2,3-dimethyl[1,4]dioxane 6c. The phosphine **6c** was prepared according to the procedure for the synthesis of **5**. A

flash chromatography on a silica gel column eluted with hexanes/ethyl ether (95/5) gave a white solid in 68% yield: mp 59-61 °C. $[\alpha]_D^{24} = -92.3$ (*c* 1.0, CHCl₃). ¹H NMR (CDCl₃, 360 MHz) δ 7.46-7.23 (m, 20H), 3.68-3.64 (m, 2H), 3.33-3.29 (m, 2H), 3.21-3.17 (m, 2H), 2.28-2.24 (m, 2H), 2.11-2.08 (m, 2H), 1.17 (s, 6H), 0.92 (t, *J* = 6.0 Hz, 6H); ¹³C NMR (CDCl₃, 90.56 MHz) δ 139.2 (d, *J* = 14.2 Hz), 137.8 (d, *J* = 14.6 Hz), 137.5-137.4 (m), 131.4-129.8 (m, aromatic), 98.8, 70.3 (t, *J* = 9.9 Hz), 48.0, 30.7 (d, *J* = 12.9 Hz), 21.24, 21.19, 17.5. ³¹P NMR (CDCl₃) δ -20.7 ppm. HRMS calcd for C₄₂H₅₅O₄P₂ (MH⁺): 685.3575; found: 685.3552.

(6*R*, 7*R*, 14*R*, 15*R*)-1,8,13,16-Tetraoxa-dispiro[5,0,5,4]-14,15-bis((diphenylphosphanyl)methyl)hexadecane (7): The phosphine 7 was prepared according to the procedure for the synthesis of 5. A flash chromatography on a silica gel column eluted with hexanes/ethyl ether (95/5) gave a white solid in 53% yield: mp 105-6 °C. $[\alpha]_D^{24} = -94.3$ (*c* 0.8, CHCl₃). ¹H NMR (CDCl₃, 360 MHz) δ 7.44-7.20 (m, 20H), 3.80-3.76 (m, 2H), 3.38-3.30 (m, 4H), 2.30-2.22 (m, 4H), 1.55-1.18 (m, 12H); ¹³C NMR (CDCl₃, 90.56 MHz) δ 139.4 (d, *J* = 8.2 Hz), 138.7 (d, *J* = 9.0 Hz), 133.3 (d, *J* = 19.7 Hz), 132.4 (d, *J* = 17.9 Hz), 128.6-128.1 (m, aromatic), 96.3, 70.0 (t, *J* = 10.5 Hz), 60.6, 30.9 (d, *J* = 11.6 Hz), 28.5, 24.9, 17.7. ³¹P NMR (CDCl₃) δ -19.5 ppm. HRMS calcd for C₃₈H₄₃O₄P₂ (MH⁺): 625.2637; found: 625.2622.

(2*R*, 3*R*, 5*R*, 6*R*)-5,6-Bis((*t*-butylthio)methyl)-2,3-dimethoxy-2,3-dimethyl[1,4]dioxane (8b). Compound 8b was prepared according to the procedure for making 8a (78% yield): $[\alpha]_D^{20} = -176.5$ (*c* 0.8, CHCl₃); ¹H NMR (CDCl₃, 360 MHz): δ 3.61-3.59 (m, 2H), 3.16 (s, 6H), 2.62-2.48 (m, 4H), 1.20 (s, 18H), 1.15 (s, 6H); ¹³C NMR (CDCl₃, 90.56 MHz): 98.6, 71.7, 47.7, 41.7, 30.6, 29.5, 17.2. HRMS calcd for C₁₇H₃₃O₃S₂ (MH-MeOH): 349.1871; found: 349.1887.

Current Data Parameters
 NAME Jun06-2002-Zhan
 EXPNO 110
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020606
 Time 5.13
 INSTRUM spect
 PROBHD 5 mm QNP 1H
 PULPROG zgpg30
 TO 85536
 SOLVENT CDCl3
 NS 64
 DS 4
 SWH 62500.000 Hz
 FIDRES 0.953674 Hz
 AQ 0.5243360 sec
 RG 32768
 DM 8.000 usec
 DE 11.43 usec
 TE 300.0 K
 H1 0 dB
 D1 2.0000000 sec
 CPDPRG Meltz16
 P31 106.00 usec
 S4 30 dB
 D11 0.0300000 sec
 S2 30 dB
 P1 7.50 usec
 SF01 145.7776151 MHz
 NUCLEUS 31P

F2 - Processing parameters
 SI 32768
 SF 145.7848645 MHz
 RMW 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 F1P 100.000 ppm
 F1 14578.48 Hz
 F2P -180.000 ppm
 F2 -26241.28 Hz
 PPM01 14.00000 ppm/cg
 HZ01 2040.98804 Hz/cm

31P NMR

20.108

S4

- 5 -

Current Data Parameters
 NAME JUN05-2002-Zhen
 EXPNO 111

F2 - Acquisition Parameters
 Date_ 20020906
 Time 5.16
 INSTRUM spect
 PROBHD 5 mm QNP 1H
 PULPROG zg30
 TO 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 7462.687 Hz
 FIDRES 0.113672 Hz
 AQ 4.390921 sec
 RG 128
 DW 67.000 usec
 DE 95.71 usec
 TE 300.0 K
 H1 0 dB
 D1 1.0000000 sec
 P1 12.00 usec
 SFO1 360.1361620 MHz
 NUCLEUS 1H

F2 - Processing parameters
 SI 32768
 SF 360.1340408 MHz
 EN
 MD 0
 SS 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 FIP 10.000 ppm
 F1 3601.34 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCH 0.50000 ppm/cm
 HZCH 180.06702 Hz/cm

Current Data Parameters
NAME Jun06-2002-Zhan
EXPNO 112
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020606
Time 5.20
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
F5 536
SOLVENT DMS
NS 281
DS 4
SWH 22727.273 Hz
FIDRES 0.346791 Hz
AQ 1.4418420 sec
RG 32768
DN 22,000 usec
DE 31.43 usec
TE 300.0 K
H1 0 dB
D1 2.0000000 sec
CHPRG waltz16
P31 106.00 usec
S4 30 dB
D11 0.0300000 sec
S2 30 dB
P1 7.90 usec
SF01 90.5659569 MHz
NUCLEUS 13C

F2 - Processing parameters
SI 32768
SF 90.555740 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 200.000 ppm
F1 18111.15 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCH 10.00000 ppm/cm
HZCN 905.55774 Hz/cm

5

S6

6a BH3

Current Data Parameters

NAME	MAY21-2002-Zhan
EXPNO	21
PROCNO	1

F2 - Acquisition Parameters

Date_	20020521
Time	22.24
INSTRUM	spec
PROBHD	5 mm QNP 1H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	7462.687 Hz
FIDRES	0.113872 Hz
AQ	4.3905621 sec
RG	512
DM	67.000 usec
DE	95.71 usec
TE	300.0 K
H1	0 dB
O1	1.00000000 sec
P1	12.00 usec
SFO1	360.1361620 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	32768
SF	360.1359635 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.000 ppm
F1	3601.34 Hz
F2P	0.000 ppm
F2	0.00 Hz
PRNCH	0.50000 ppm/cm
HZCM	180.06659 Hz/cm

S10

6c

Current Data Parameters

NAME Jun13-2002-Zhen

EXPNO 20

PROCNO 1

F2 - Acquisition Parameters

Date_ 20020613

Time 10.28

INSTRUM spect

PROBHD 5 mm QNP 1H

PULPROG zgpg30

TD 65536

SOLVENT DMS

NS 7

DS 4

SWH 6250.000 Hz

FIDRES 0.953674 Hz

AQ 0.324380 sec

RG 32768

DM 8.000 usec

DE 11.43 usec

TE 300.0 K

HL 0 dB

D1 2.0000000 sec

CHRGPS waltz16

P31 106.00 usec

S4 30 dB

O11 0.0300000 sec

S2 30 dB

P1 7.60 usec

SFO1 145.776151 MHz

NUCLEUS 31P

F2 - Processing parameters

SI 32768

SF 145.784845 MHz

MDM EM

SSB 0

LB 1.00 Hz

GB 0

PC 1.40

10 user plot parameters

CX 20.00 cm

F1P 100.000 ppm

F1 14578.48 Hz

F2P -180.000 ppm

F2 -26241.28 Hz

PPMCH 14.00000 ppm/cm

HZCH 2040.98804 Hz/cm

6c

Current Data Parameters

NAME Jun20-2002-Zhan

EXPNO 110

PROCNO 1

F2 - Acquisition Parameters

Date_ 20020620

Time 11.10

INSTRUM spect

PROBHD 5 mm QNP 1H

PULPROG zg30

TO 65536

SOLVENT CDCl3

NS 11

DS 2

SWH 7462.697 Hz

FIDRES 0.113872 Hz

AQ 4.390821 sec

RG 64

DM 67.000 usec

DE 55.71 usec

TE 300.0 K

H1 0 dB

D1 1.00000000 sec

P1 12.00 usec

SFO1 360.1361620 MHz

NUCLEUS 1H

F2 - Processing parameters

SI 32768

SF 360.1361620 MHz

ADW EN

SSB 0

LB 0.30 Hz

GB 0

PC 1.00

1D NMR plot parameters

CX 20.00 cm

F1P 10.000 ppm

F1 360.134 Hz

F2P 0.000 ppm

F2 0.00 Hz

PPMCH 0.50000 ppm/cm

HZCH 180.06599 Hz/cm

6c

Current Data Parameters
 NAME: Jm13-2002-Zhen
 EXPNO: 22
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20020613
 Time: 10.37

CPDPRG: WALTZ16
 P31: 106.00 usec
 S4: 30 dB
 D11: 0.0300000 sec
 S2: 30 dB
 P1: 7.90 usec
 SF01: 90.5657615 MHz
 NUC1E15: ¹³C

F2 - Processing parameters
 SI: 32768
 SF: 90.5657615 MHz
 MOD: EM
 SSF: 0
 LB: 1.00 Hz
 GB: 0
 PC: 1.40

1D NMR plot parameters
 CX: 20.00 cm
 F1P: 180.000 ppm
 F1: 16300.04 Hz
 F2P: 1.500 ppm
 F2: 136.83 Hz
 PUNCH: 9.92500 pp/Hz
 HZCM: 808.21021 Hz/cm

S13

Current Data Parameters
NAME J0103-2002-Zhan
EXPNO 31
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020703
Time 4.32
INSTRUM spect
PROBHD 5 mm QNP 31H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8
DS 4
DE 6250.000 Hz
FIDRES 0.953674 Hz
AQ 0.524380 sec
RG 32768
DM 8.000 usec
DE 11.43 usec
TE 300.0 K
H1 0 dB
D1 2.0000000 sec
CPRPRG waltz16
P31 105.00 usec
S4 30 dB
D11 0.03000000 sec
S2 30 dB
P1 7.80 usec
SF01 145.775151 MHz
NUCLEUS 31P

F2 - Processing parameters
SI 32768
SF 145.7848645 MHz
KOH EN
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 100.000 ppm
F1 14578.48 Hz
F2P -180.000 ppm
F2 -26241.28 Hz
PNUC 14.00000 ppm/cm
H2O 2040.98804 Hz/cm

Current Data Parameters
NAME Jul03-2002-Zhen
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020703
Time 4:20
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
FIDRES 0.113872 Hz
AQ 4.3909621 sec
RG 128
DW 67.000 usec
DE 56.71 usec
TE 300.0 K
H1 0 dB
D1 1.00000000 sec
P1 12.00 usec
SF01 360.1361620 MHz
NUCLEUS 1H

F2 - Processing parameters
SI 32768
SF 360.1340337 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 3601.34 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.50000 ppm/cm
HZCM 180.06702 Hz/cm

Current Data Parameters
NAME: Jn103-2002-Zhen
EXPNO: 32
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20020703
Time: 4.36
INSTRUM: spect
PROBHD: 5 mm QNP 1H
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 200
DS: 4
SWH: 22727.273 Hz
FIDRES: 0.346791 Hz
AQ: 1.4418420 sec
RG: 32768
DM: 22.000 usec
DE: 31.43 usec
TE: 300.0 K
NUC1: 13C
D1: 2.0000000 sec
waitz16
CPOPRG: 106.00 usec
P31: 30.00
S4: 30.00
D11: 0.0300000 sec
S2: 30.00
P1: 7.90 usec
SF01: 90.563968 MHz
NUC1US: 13C

F2 - Processing parameters
SI: 32768
SF: 90.557791 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40

10 MHz plot parameters
CX: 20.00 cm
F1P: 200.000 ppm
F1: 18111.15 Hz
F2P: 0.000 ppm
F2: 0.00 Hz
PPMCM: 10.00000 ppm/cm
HZCM: 905.55774 Hz/cm

Current Data Parameters

NAME: May31-2002-Zinn

EXPNO: 50

PROCNO: 1

F2 - Acquisition Parameters

Date_: 20020531

Time: 15.26

INSTRUM: spect

PROBHD: 5 mm QNP 1H

PULPROG: zg30

TD: 65536

SOLVENT: CDCl3

NS: 16

DS: 2

SWH: 7462.687 Hz

FIDRES: 0.113872 Hz

AQ: 4.390821 sec

RG: 512

DM: 87.000 usec

DE: 95.71 usec

TE: 300.0 K

HL1: 0 dB

P1: 1.0000000 sec

P2: 12.00 usec

SF01: 360.1301620 MHz

NUCLEUS: 1H

F2 - Processing parameters

SI: 32768

SF: 360.1340112 MHz

WDW: EM

SSB: 0

LB: 0.30 Hz

GB: 0

PC: 1.00

1D NMR plot parameters

CX: 20.00 cm

F1P: 11.000 ppm

F1: 3981.47 Hz

F2P: -1.000 ppm

F2: -360.13 Hz

PRICK: 0.60000 ppm/cm

NUC1: 216.08040 Hz/cm

Name	Date	Date Parameters
EXPNO	May21-2002-Zdm	
PROCNO	61	
PROCNO	1	
F2 - Acquisition Parameters		
Date_	20020531	
Time	15.35	
INSTRUM	spect	
PROBHD	5 mm QNP 1H	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	8630	
DS	4	
SWH	22727.273 Hz	
FIDRES	0.346791 Hz	
AQ	1.4418420 sec	
RG	32768	
DM	22.000 usec	
DE	31.43 usec	
TE	300.0 K	
HL	0 dB	
D1	2.00000000 sec	
CPDPRG	hell16	
P31	106.00 usec	
S4	30 dB	
D11	0.03000000 sec	
S2	30 dB	
P1	7.50 usec	
SFO1	50.565869 MHz	
NUC1E15	13C	
F2 - Processing parameters		
S1	32768	
SF	50.5657615 MHz	
WDW	EM	
SSB	0	
LB	1.00 Hz	
GB	0	
PC	1.40	
10 non plot parameters		
CX	20.00 cm	
F1P	215.000 ppm	
F1	19469.48 Hz	
F2P	-5.000 ppm	
F2	-462.78 Hz	
PRICH	11.00000 ppm/cm	
WDW	956.11340 Hz/cm

Current Data Parameters

NAME Jun20-2002-Zhan

EXPNO 60

PROCNO 1

F2 - Acquisition Parameters

Date_ 20020620

Time 8.33

INSTRUM spect

PROBHD 5 mm QNP 1H

PULPROG zg30

TD 65536

SOLVENT CDCl3

NS 16

DS 2

SWH 7462.687 Hz

FIDRES 0.113872 Hz

AQ 4.3909621 sec

RG 32

DW 67.000 usec

DE 50.71 usec

TE 300.0 K

H1 0 dB

O1 1.00000000 sec

P1 12.00 usec

SFO1 360.1361620 MHz

NUCLEUS 1H

F2 - Processing parameters

SI 32768

SF 360.1338828 MHz

MDN EM

SSB 0

LB 0.30 Hz

GB 0

PC 1.00

1D FID plot parameters

CX 20.00 cm

F1P 10.000 ppm

F1 3601.34 Hz

F2P 0.000 ppm

F2 0.00 Hz

PRMCM 0.30000 ppm/cm

HZCM 180.06659 Hz/cm

Current Data Parameters
NAME Jun20-2002-Zhen
EXPNO 61
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020520
Time 8:30
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 22727.273 Hz
FIDRES 0.346791 Hz
AQ 1.4418420 sec
RG 32768
DM 22.000 usec
DE 31.43 usec
TE 300.0 K
H1 0 dB
D1 2.00000000 sec
CPDPRG waltz16
P31 106.00 usec
S4 30 dB
D11 0.03000000 sec
S2 30 dB
P1 7.90 usec
SF01 90.5658959 MHz
NUCLEUS 13C

F2 - Processing parameters
SI 32768
SF 90.555781 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 19469.48 Hz
F2P -5.000 ppm
F2 -62.78 Hz
FREQM 11.00000 ppm/cm
HZCM 996.11359 Hz/cm

Current Data Parameters

NAME May29-2002-Zhan

EXPNO 30

PROCNO 1

F2 - Acquisition Parameters

Date_ 20020529

Time 11:57

INSTRUM spect

PROBHD 5 mm QNP 1H

PULPROG zg30

TD 65536

SOLVENT CDCl3

NS 16

DS 2

SWH 7462.887 Hz

FIDRES 0.113872 Hz

AQ 4.3909621 sec

RG 128

OW 87.000 usec

DE 95.77 usec

TE 300.0 K

HL1 0 dB

D1 1.00000000 sec

P1 12.00 usec

SFO1 360.1361620 MHz

NUCLE1 1H

F2 - Processing parameters

SF 360.1361620 MHz

SI 32768

WDW EM

SSB 0

LB 0.30 Hz

GB 0

PC 1.00

1D NMR plot parameters

CX 20.00 cm

F1P 11.000 ppm

F1 3961.47 Hz

F2P -1.000 ppm

F2 -360.13 Hz

PPMCK 0.00000 ppm/cm

HZCK 216.00036 Hz/cm

Current Data Parameters
 NAME J0103-2002-Zhen
 EXPNO 41
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020703
 Time 5:47
 INSTRUM spect
 PROBRD 5 mm QNP 1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 98
 DS 4
 SWH 22727.273 Hz
 FIDRES 0.346791 Hz
 AQ 1.4419420 sec
 RG 32768
 DM 22.000 usec
 DE 31.43 usec
 TE 300.0 K
 H1 0 dB
 D1 2.0000000 sec
 CHPRG Waltz16
 P31 106.00 usec
 S4 30 dB
 D11 0.0300000 sec
 S2 30 dB
 P1 7.90 usec
 SFO1 90.565969 MHz
 NUC1 13C

F2 - Processing parameters
 SI 32768
 SF 90.5657698 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 F1P 200.000 ppm
 F1 18111.15 Hz
 F2P 0.000 ppm
 F2 10.000000 ppm/cm
 FREQM 905.56574 Hz/cm

Current Data Parameters

NAME: May23-2002-21m

EXPNO: 80

PROCNO: 1

F2 - Acquisition Parameters

Date_: 20020523

Time: 9.10

INSTRUM: spect

PROBHD: 5 mm QNP 1H

PULPROG: zg30

TD: 65536

SOLVENT: CDCl3

NS: 16

DS: 2

SWH: 7462.687 Hz

FIDRES: 0.113872 Hz

AQ: 4.390821 sec

RG: 512

DE: 67.000 usec

TE: 300.0 K

HL1: 0 dB

D1: 1.00000000 sec

P1: 12.00 usec

SFO1: 360.1361820 MHz

NUC1: 1H

F2 - Processing parameters

SI: 32768

SF: 360.1359835 MHz

WDW: EM

SSB: 0

LB: 0.30 Hz

GB: 0

PC: 1.00

1D NMR plot parameters

CX: 20.00 cm

F1P: 10.000 ppm

F1: 3601.34 Hz

F2P: 0.000 ppm

F2: 0.00 Hz

PH000: 0.58000 ppm/cm

HZ000: 180.06599 Hz/cm

Current Data Parameters

NAME: May23-2002-Zhan

EXPNO: 91

PROCNO: 1

F2 - Acquisition Parameters

Date_: 20020523

Time: 9.18

INSTRUM: spect

PROBHD: 5 mm QNP 3H

PULPROG: zgpg30

TD: 65536

SOLVENT: CDCl3

NS: 365

DS: 4

SWH: 22727.273 Hz

FIDRES: 0.346791 Hz

AQ: 1.4418420 sec

RG: 32768

OW: 22.000 usec

DE: 31.43 usec

TE: 300.0 K

FL1: 0 dB

OTPROG: 2.00000000 sec

wait45

P31: 106.00 usec

S4: 30 dB

D11: 0.03000000 sec

S2: 30 dB

P1: 7.90 usec

SF01: 90.5638999 MHz

NUC1EUS: 13C

F2 - Processing parameters

SI: 32768

SF: 90.5637664 MHz

WDW: EM

SSB: 0

LB: 1.00 Hz

GB: 0

PC: 1.40

1D NMR plot parameters

CA: 20.00 cm

F1P: 200.000 ppm

F1: 18111.15 Hz

F2P: 0.000 ppm

F2: 0.00 Hz

PPMCH: 10.00000 ppm/cm

HZCH: 905.56774 Hz/cm

Current Data Parameters
NAME May23-2002-Zhan
EXPNO 111
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020623
Time 11.30
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
FIDRES 0.113672 Hz
AQ 4.300621 sec
RG 128
DM 67.000 usec
DE 95.71 usec
TE 300.0 K
H1 0 dB
D1 1.00000000 sec
P1 12.00 usec
SFO1 360.1361620 MHz
NUCLEI 1H

F2 - Processing parameters
SI 32768
SF 360.1361620 MHz
MDX EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 360.134 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPM/CM 0.50000 ppm/cm
HZ/CM 180.06639 Hz/cm

Current Data Parameters
NAME: May23-2002-Zhan
EXPNO: 110
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20020523
Time: 10.53
INSTRUM: spect
PROBHD: 5 mm QNP 1H
PULPROG: zgpg30
TO: 65536
SOLVENT: CDCl3
NS: 611
DS: 4
SWH: 22727.273 Hz
FIDRES: 0.346791 Hz
AQ: 1.4418420 sec
RG: 32766
DM: 22.000 usec
DE: 31.43 usec
TE: 300.0 K
HL1: 0 dB
D1: 2.00000000 sec
wait18
COPRG: 106.00 usec
P31: 30 dB
S4: 0.03000000 sec
DS: 30 dB
SF: 7.50 usec
P1: 90.5658869 MHz
NUCLEUS: 13C

F2 - Processing parameters
SI: 32768
SF: 90.5657670 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40

10 MHz plot parameters
CX: 20.00 cm
F1P: 200.000 ppm
F1: 16111.15 Hz
F2P: 0.000 ppm
F2: 0.00 Hz
PPMCH: 10.0000 ppm/cm
HZCM: 905.150762 Hz/cm

16

Current Data Parameters
NAME Jun26-2002-Zhan
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020626
Time 2.50
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 2630
FIDRES 4.309621 sec
AQ 256
RG 67.000 usec
DE 55.71 usec
TE 300.0 K
H1 0 dB
D1 1.00000000 sec
P1 12.00 usec
SFO1 360.1361620 MHz
NUCLEUS 1H

F2 - Processing parameters
SI 32768
SF 360.1339628 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 3601.34 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCH 0.50000 ppm/cm
HZCH 180.05658 Hz/cm

Current Data Parameters

NAME Jun26-2002-27m

EXPNO 40

PROCNO 1

F2 - Acquisition Parameters

Date_ 20020626

Time 3.11

INSTRUM spect

PROBHD 5 mm QNP 1H

PULPROG zgpg30

TD 65536

SOLVENT CDCl3

NS 1024

DS 4

SWH 22727.273 Hz

FIDRES 0.346791 Hz

AQ 1.4418420 sec

RG 32768

DM 22.000 usec

DE 31.43 usec

TE 300.0 K

HL 1 0 dB

D1 2.00000000 sec

CPDPRG waitz16

P31 105.00 usec

S4 30 dB

D11 0.03000000 sec

S2 30 dB

P1 7.90 usec

SFO1 90.5659669 MHz

NUCLEUS 13C

F2 - Processing parameters

SI 32768

SF 90.5657622 MHz

WDW EM

SSB 0

LB 1.00 Hz

GB 0

PC 1.40

1D NMR plot parameters

CX 20.00 cm

F1P 200.000 ppm

F1 18111.15 Hz

F2P 0.000 ppm

F2 0.00 Hz

PPMCM 10.00000 ppm/cm

HZCM 905.55762 Hz/cm

17

Current Data Parameters

NAME: Jun28-2002-zhan

EXPNO: 30

PROCNO: 1

F2 - Acquisition Parameters

Date_: 20020628

Time: 2.41

INSTRUM: spect

PROBHD: 5 mm QNP 1H

PULPROG: zgpg30

TD: 65536

SOLVENT: CDCl3

NS: 16

DS: 2

SWH: 7462.687 Hz

FIDRES: 0.113072 Hz

AQ: 4.3908621 sec

RG: 256

DM: 87.000 usec

DE: 96.71 usec

TE: 300.0 K

H41: 0 dB

D1: 1.00000000 sec

P1: 12.00 usec

SFO1: 360.1361620 MHz

NUCLEUS: 1H

F2 - Processing parameters

SI: 32768

SF: 360.1309649 MHz

WDW: EM

SSB: 0

LB: 0.30 Hz

GB: 0

PC: 1.00

1D NMR plot parameters

CX: 20.00 cm

F1P: 10.000 ppm

F1: 3601.34 Hz

F2P: 0.000 ppm

F2: 0.00 Hz

PRNCH: 0.50000 ppm/cm

HZCH: 180.06569 Hz/cm

S29

Current Data Parameters

NAME Jun28-2002-zhan

EXPNO 21

PROCNO 1

F2 - Acquisition Parameters

Date_ 20020628

Time 2.21

INSTRUM spect

PROBHD 5 mm DNP 1H

PULPROG zgpg30

TD 65536

SOLVENT CDCl3

NS 281

DS 4

SWH 22727.273 Hz

FIDRES 0.346791 Hz

AQ 1.4418420 sec

RG 32768

DM 22.000 usec

DE 31.43 usec

TE 300.0 K

HL1 0 dB

D1 2.0000000 sec

OPPRG wait16

P31 105.00 usec

S4 30 dB

D11 0.0300000 sec

S2 30 dB

P1 7.90 usec

SFO1 90.565899 MHz

NUCLEUS 13C

F2 - Processing parameters

SF 32768

SI 90.5657802 MHz

WDW EM

SSB 0

LB 1.00 Hz

GB 0

PC 1.40

1D NMR plot parameters

CX 20.00 cm

FAP 200.000 ppm

F1 18111.16 Hz

F2 0.000 ppm

F2 0.00 Hz

PRICH 10.00000 ppm/cm

HZCM 905.56780 Hz/cm

S30

Results of Rh/1,4-bisphosphine Catalyzed Asymmetric Hydrogenation of Enamides

3 (*R,R*)-DIOP

4 (*R,S,S,R*)-DIOP*

25 (*R,R*)-Py*-DIOP
Ar = 2,6-dimethoxypyridyl

26 (*S,S*)-bdpmi

27

28

29 (*R,R*)-BICP

30 (*2R,3S*)-MOCBP

31 (-)-CDP

20
78% ee by **29** (*R,R*)-BICP
81% ee by **30** (*2R,3S*)-MOCBP

32
85% ee by **31** (-)-CDP

19a

68% ee by **3** (*R,R*)-DIOP
98% ee by **4** (*R,S,S,R*)-DIOP*
98.5% ee by **26** (*S,S*)-bdpmi
91% ee by **27**
95% ee by **28**
86% ee by **29** (*R,R*)-BICP
76% ee by **31** (-)-CDP

19b

87% ee by **3** (*R,R*)-DIOP
97% ee by **4** (*R,S,S,R*)-DIOP*
84% ee by **25** (*R,R*)-Py*-DIOP
>99% ee by **26** (*S,S*)-bdpmi
96% ee by **27**
77% ee by **28**
95% ee by **29** (*R,R*)-BICP