Supporting Information

Catalytic Asymmetric Cyclocarbonylation of *o*-Isopropenylphenols:
Enantioselective Synthesis of Six-Membered Ring Lactones

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¹H and ¹³C NMR spectra of compounds **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g** S3-S16

General experimental methods:

All NMR spectra were recorded in CDCl_3 with TMS as an internal standard on Varian XL-300 spectrometers. Infrared spectra were recorded on a Bomen MB 100-C15 Fourier transform spectrometer and are reported in wave numbers (cm^{-1}). Mass spectra were obtained on a VG 7070E spectrometer. A Fisher-Johns apparatus was used for melting point determinations. Optical rotations were measured on a Perkin-Elmer polarimeter in a 10 cm cell. Chiral chromatographic analyses were performed on a Varian 3300 gas chromatograph installed with a Supelco β -Dex 120 30-m permethylated β -cyclodextrin fused silica capillary column (0.25mm id x 0.25 μm), using helium as a carrier gas. A Waters 2996 series HPLC equipped with Chiralpak AS column was used for HPLC determination. All organic solvents were dried and distilled prior to use. $\text{Pd}(\text{OAc})_2$, $\text{Pd}_2(\text{dba})_3$, CHCl_3 , phosphine ligands were purchased from commercial sources and were used as received. The following isopropenylphenols are known compounds prepared according to literature procedures and have spectral properties in accord with literature data: **1a**, **1c**, **1e**^{8a-c}, **1b**, **1d**, **1f**, **1g**^{8d-e}.

2a

Current Data Parameters
 NAME: d81
 EXPNO: 1
 PROCNO: 1

F2 - Acquisition Parameters
 Date_: 20021116
 Time: 10.53
 INSTRUM: av300
 PROBHD: 5 mm QNP 1H/1
 PULPROG: zg30
 TD: 30720
 SOLVENT: CDCl3
 NS: 16
 DS: 0
 SMH: 5081.301 Hz
 FIDRES: 0.355407 Hz
 AQ: 3.0228980 sec
 RG: 203.2
 DW: 98.400 usec
 DE: 6.00 usec
 TE: 300.0 K
 D1: 1.00000000 sec

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 9.75 usec
 PL1: -3.00 dB
 SF01: 300.1319477 MHz

F2 - Processing parameters
 SI: 65536
 SF: 300.1300000 MHz
 WDW: EM
 SSB: 0
 LB: 0.10 Hz
 GB: 0
 PC: 1.00

1D NMR plot parameters
 CX: 20.00 cm
 CY: 10.00 cm
 F1P: 8.073 ppm
 F1: 2423.02 Hz
 F2P: 0.121 ppm
 F2: 36.24 Hz
 PPMCM: 0.39762 ppm/cm
 HZCM: 119.33875 Hz/cm

¹³C with proton decoupling

Current Data Parameters
NAME db1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20021116
Time 11.28
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1024
DS 0
SWH 17985.611 Hz
FIDRES 0.548677 Hz
AQ 0.9110004 sec
RG 1149.4
OW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

===== CHANNEL f1 =====
NUC1 ¹³C
P1 5.00 usec
PL1 -6.00 dB
SF01 75.4752653 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 14.12 dB
PL13 15.63 dB
SF02 300.1314860 MHz

F2 - Processing parameters
SI 65536
SF 75.4677500 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 177.687 ppm
F1 13409.62 Hz
F2 13.139 ppm
F2P 991.56 Hz
PPMCM 8.22740 ppm/cm
HZCM 620.90302 Hz/cm

2b

Current Data Parameters
NAME nslp
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030212
Time 17.07
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDCl3
NS 16
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 574.7
DW 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.75 usec
PL1 -3.00 dB
SF01 300.1319477 MHz

F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 8.491 ppm
F1 2548.36 Hz
F2P 0.233 ppm
F2 69.84 Hz
PRMCM 0.41291 ppm/cm
HZCM 123.92574 Hz/cm

¹³C with proton decoupling **2b**

Current Data Parameters
 NAME nslp
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20030212
 Time 17.30
 INSTRUM av300
 PROBHD 5 mm QNP 1H/1
 PULPROG zgpg30
 TO 32768
 SOLVENT CDCl3
 NS 1024
 DS 0
 SWH 17985.611 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110004 sec
 RG 1024
 DW 27.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 5.00 usec
 PL1 -6.00 dB
 SF01 75.4752653 MHz

===== CHANNEL f2 =====
 CPOPRG2 waltz16
 NUC2 ¹H
 PCPD2 70.00 usec
 PL2 -3.00 dB
 PL12 14.12 dB
 PL13 15.63 dB
 SF02 300.1314860 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677486 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 1.50 cm
 FIP 184.114 ppm
 F1 13894.70 Hz
 F2 6.344 ppm
 F2 478.80 Hz
 PPHCM 8.8850 ppm/cm
 HZCM 670.79492 Hz/cm

Current Data Parameters
 NAME cde
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20021023
 Time 10.15
 INSTRUM av300
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 30720
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 5081.301 Hz
 FIDRES 0.165407 Hz
 AQ 3.0228960 sec
 RG 228.1
 DW 98.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.75 usec
 PL1 -3.00 dB
 SF01 300.1319477 MHz

F2 - Processing parameters
 SI 65536
 SF 300.1300000 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 10.00 cm
 F1P 8.115 ppm
 F1 2435.52 Hz
 F2P 0.011 ppm
 F2 3.27 Hz
 PPMCM 0.40520 ppm/cm
 HZCM 121.61247 Hz/cm

¹³C with proton decoupling

2d

Current Data Parameters
NAME 2d
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030224
Time 10:22
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDCl3
VS 16
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 287.4
DQ 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.75 usec
PL1 -3.00 dB
SF01 300.1319477 MHz

F2 - Processing parameters
SI 65936
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

10 NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 7.893 ppm
F1 2368.85 Hz
F2P 0.026 ppm
F2 7.71 Hz
PPMCM 0.39335 ppm/cm
HZCM 116.05739 Hz/cm

13C with proton decoupling

Current Data Parameters
 NAME 5-bromone
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20030224
 Time 10:56
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zgpg30
 TO 32768
 SOLVENT CDCl3
 NS 1024
 DS 8
 SWH 17985.611 Hz
 FIDRES 0.948877 Hz
 AQ 0.9110004 sec
 RG 1024
 DM 27.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 d12 0.00002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 5.00 usec
 PL1 -6.00 dB
 SF01 75.4752653 MHz

===== CHANNEL f2 =====
 CPOPRG2 waltz16
 NUC2 1H
 PCPO2 70.00 usec
 PL2 -3.00 dB
 PL12 14.12 dB
 PL13 15.63 dB
 SF02 300.1314860 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677503 MHz
 WDW EM
 SSB 0
 GB 1.00 Hz
 GC 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 3.00 cm
 F1P 179.236 ppm
 F1 13526.50 Hz
 F2P 7.942 ppm
 F2 599.34 Hz
 PPMCM 8.56469 ppm/cm
 HZCM 646.35791 Hz/cm

2e

Current Data Parameters
NAME me
EXPNO 1
PROCNO 1

F2 -- Acquisition Parameters
Date_ 20021205
Time 15.48
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDCl3
NS 16
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 203.2
DW 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.75 usec
PL1 -3.00 dB
SFO1 300.1319477 MHz

F2 -- Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 7.709 ppm
F1 231.162117
F2P 0.072 ppm
F2 21.51 Hz
FIDRES 0.38185 ppm/cm
HZCH 114.60542 Hz/cm

¹³C with proton decoupling

Current Data Parameters

NAME	me
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20021205
Time	16.32
INSTRUM	av300
PROBHD	5 mm QNP 1H/1
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	1024
DS	0
SWH	17985.611 Hz
FIDRES	0.548877 Hz
AQ	0.9110004 sec
RG	1148.4
DW	27.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
d11	0.03000000 sec
d12	0.0002000 sec

===== CHANNEL f1 =====

NUC1	13C
P1	5.00 usec
PL1	-6.00 dB
SFO1	75.4752653 MHz

===== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	1H
PCPD2	70.00 usec
PL2	-3.00 dB
PL12	14.12 dB
PL13	15.63 dB
SFO2	300.1314860 MHz

F2 - Processing parameters

SF	65536
SF	75.4677486 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

F0 NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	10.00000 ppm/cm
HZCM	754.67749 Hz/cm

2f

Current Data Parameters
NAME brone
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030209
Time 11.43
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDCl3
NS 16
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 406.4
DW 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.75 usec
PL1 -3.00 dB
SF01 300.1319477 MHz

F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
-B 0.10 Hz
GB 0
PC 1.00
ID NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm

13C with proton decoupling

2f

Current Data Parameters
NAME brOne
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030209
Time 13.02
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 936
DS 0
SWH 17985.611 Hz
FIDRES 0.546877 Hz
AQ 0.9110004 sec
RG 1290.2
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SF01 75.4752653 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 14.12 dB
PL13 15.63 dB
SF02 300.1314860 MHz

F2 - Processing parameters
SI 65536
SF 75.4677489 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 3.00 cm
FIP 176.987 ppm
F1 13356.81 Hz
F2 7.636 ppm
F2 576.28 Hz
PPMCM 8.46755 ppm/cm
HZCM 639.02686 Hz/cm

2g

Current Data Parameters
NAME clone
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030209
Time 11:50
INSTRUM av300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 30720
SOLVENT CDCl3
NS 16
DS 0
SWH 5081.301 Hz
FIDRES 0.165407 Hz
AQ 3.0228980 sec
RG 512
DW 98.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.75 usec
PL1 -3.00 dB
SF01 300.1319477 MHz

F2 - Processing parameters
SI 65536
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 7.594 ppm
F1 2279.10 Hz
F2P 0.486 ppm
F2 145.78 Hz
PPMCM 0.35540 ppm/cm
HZCM 106.66590 Hz/cm

13C with proton decoupling

Current Data Parameters
 NAME clone
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030209
 Time 12.26
 INSTRUM av300
 PROBD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 1024
 DS 0
 SWH 17985.611 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110004 sec
 RG 1149.4
 DW 27.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 d12 0.0000200 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 5.00 usec
 PL1 -6.00 dB
 SF01 75.4752653 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 P2 70.00 usec
 PL2 -3.00 dB
 PL12 14.12 dB
 PL13 15.63 dB
 SF02 300.1314860 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677489 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D HMQ plot parameters
 CX 20.00 cm
 CY 3.00 cm
 F1P 176.987 ppm
 F1 13356.81 Hz
 F2P 12.169 ppm
 F2 918.39 Hz
 PRGCM 8.24058 mm/cm
 -27CM 621.9406 mm/cm