Novel Use of *N*-Benzoyl-*N,O*-Acetals as*N*-Acylimine Equivalents in Asymmetric Heterocycloaddition :
an Extended Enantioselective Way to β -Benzamidoaldehydes.

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Supporting Information

Crystal Structure of Amido Acetal 9 :¹ Table gathers the crystallographic data of 9 ($\text{Cl}_2\text{O}_5\text{NC}_{35}\text{H}_{35}$). A small needle single crystal, selected using an optical microscope, was mounted on a glass fiber. The crystal cell parameters were obtained from a random reflection search and X-ray diffraction data were collected with a Siemens AED2 four-circle diffractometer equipped with a graphite monochromatized $\text{MoK}\alpha_1$ ($\lambda = 0.71073 \text{ \AA}$). The intensities of the reflections were corrected for Lorentz and polarization effects. The scattering factors and the anomalous dispersions corrections for all atoms were taken from "International Tables for X-ray Crystallography".² Absorption effects were corrected by the Gauss method. The space group was deduced from the observed systematic extinctions. The structure was solved by direct methods; successive refinements and difference Fourier maps using SHELXS-86³ and SHELXL-97⁴ programs. The location of the hydrogen atoms was performed by applying of geometrical constraints using AFIX option in SHELXL-97. All non-hydrogen atom displacement parameters were refined anisotropically. Full Crystallographic data of $\text{Cl}_2\text{O}_5\text{NC}_{35}\text{H}_{35}$ have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication n°CCDC 183561.

- (1) Performed by Dr. V. Maisonneuve, Laboratoire des Fluorures, Université du Maine, France.
- (2) International Tables for X-ray Crystallography; Vol. IV, The Kynoch Press: Birmingham, England, 1974.
- (3) Sheldrick, G. M., SHELXS-86. Crystallographic computing 3; Eds Sheldrick, Krüger, G.M.; , Goddard, C., R. Oxford University Press, 1985, 175.
- (4) Sheldrick G. M., SHELXL-97, a program for crystal structure determination, Göttingen University, Germany, 1997.

Table : Crystal data of amido acetal 9

Empirical formula	Cl ₂ O ₅ NC ₃₅ H ₃₅
Molar mass (g mol ⁻¹)	620.57
Crystal system, Space group	Orthorhombic, <i>P212121</i>
Unit cell dimensions	a = 5.494 (1) Å
	b = 17.050 (3) Å
	c = 34.15 (1) Å
Volume, Z	3198 (1) Å ³ , 4
Calculated density (g cm ⁻³)	1.29
Temperature (K), scan method	293, ω
Crystal dimensions (mm ³)	0.08 x 0.14 x 0.84
Radiation, λ (Å)	Mo K α , 0.71069
2 θ range for data collection (°)	2-45
(hkl) _{min} , (hkl) _{max}	-3 -18 -36, 5 18 36
Absorption correction, coefficient (mm ⁻¹)	Gaussian, 0.25
T _{min} , T _{max}	0.966, 0.991
Number of unique reflections	3620
Number of used reflections (I > 2 σ (I))	1496
Number of refined parameters	390
Difference Fourier residues (e Å ⁻³)	0.25, -0.26
Refinement on F ² : R ₁ /wR ₂	0.081/0.157
Goodness of fit	1.05
Flack parameter ⁵	-0.1(2)
Secondary extinction coefficient	0.17(5) 10 ⁻⁵

(5) Flack H. D. *Acta Cryst.* **1983**, A39, 876.

Figure : X-Ray crystal structure analysis of amido acetal 9

Copies of ^1H NMR spectra (Figures S-1 to S-16):

Figure S-1: (**4b**); Figure S-2: (**2b-endo- β**); Figure S-3: (**2c-endo- β**) and minor (**2c-exo**); Figure S-4: (**2c-exo- α**); Figure S-5: (*R*)-**1b**; Figure S-6: (*R*)-**1c**; Figure S-7: (*R*)-**1d**; Figure S-8: (*S*)-**1e**; Figure S-9: (*R*)-**1f**; Figure S-10: (*R*)-**1b** with (+)-Eu(tfc)₃; Figure S-11: crude (**2b-exo- β**); Figure S-12: purified sample of (**2c-exo- β**) (with minor *endo- β* isomer); Figure S-13: purified sample of (**2d-exo- β**); Figure S-14: purified sample of (**2e-exo- β**) (with minor *endo- β* isomer); Figure S-15: purified sample of (**2f-exo- β**) (with minor *endo- β* isomer); Figure S-16: (**9**).

N^o 6

JU1105.101
AU PROG:
X00.AU
DATE 11-12-98

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SF0 400.130
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T0 32758
SW 8064.516
HZ/P1 .492

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AQ 2.032
RG 100
NS 15
TE 297

FW 10100
D2 4171.003
DP 63L P0

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GB 0.0
CX 35.00
CY 19.00
F1 9.200
F2 .800
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PPM/CM .286
SR 4392.66

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R0 4.30
RGA 0.0
RD 0.0
PW 0.0
DE 77.50
NS 16
DS 2

Figure S-1

N² 24

BRUKER

FE080S.107
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PW 77.50
DE 32
DS 2

Figure S-2

(2b-endo-β) (4R,6S): ¹H NMR (400 MHz, CDCl₃)

N³ 5591

OC190S 120
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 O1 32768
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 PPW/CM .286
 SR 4397.58
 D1 1.0000000
 P0 4.30
 RGA
 RD 0.0
 PW 0.0
 DE 77.50
 NS 48
 DS 2

(2c-endo-β) (4R,6S) and minor (2c-exo):
¹H NMR (400 MHz, CDCl₃)

Figure S-3

Nº 860.

JL0705.116
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SFO 400.130
SY 230.0
O1 6897.559
SI 32768
TD 32768
SW 8064.515
HZ/PT 492
PW 0.0
RD 0.0
AG 2.032
NS 16
TE 297
FW 10100
O2 4171.003
DP 63L PO
LB 0.300
GB 0.0
CX 35.00
CY 19.00
F1 9.201P
F2 1.798P
HZ/CM 114.321
PBW/CM 286
SR 4393.64
D1 1.0000000
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RGA 0.0
RD 0.0
PW 0.0
DE 77.50
NS 16
DS 2

Figure S-4

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TD 32768
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PW 0.0
RD 0.0
AQ 2.032
RG 80
NS 80
TE 297
FW 10100
O2 4171.003
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CY 19.00
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PPM/CM .314
SR 4393.64
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P0 4.30
RG 0.0
RD 0.0
PW 77.50
DE 80
NS 2

Figure S-5

(R)-1b: ¹H NMR (400 MHz, CDCl₃)

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Q1 32768
T0 32768
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HZ/PT 492
PW 0.0
RD 0.0
AG 2.032
RG 10
NS 15
YE 297
FW 10100
Q2 4171.003
DP 63L PD
LB 0.300
GB 0.0
CX 35.00
CY 19.00
F1 9.201P
F2 7.798P
HZ/CM 114.321
PPM/CM 286
SR 4394.13
D1 1.0000000
P0 4.30
RGA 0.0
RD 0.0
PW 0.0
DE 77.50
NS 16
DS 2

Figure S-6

N^o 5868

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 TO 32768
 SM 6064.516
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 PH 0.0
 RD 0.0
 AG 2.032
 RG 100
 NS 48
 TE 297
 FM 10100
 O2 4171.003
 DP 63L PD
 LB 300
 GB 0.0
 CX 35.00
 CY 15.00
 F1 9.201
 F2 7.953
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 PPM/CM 286
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 RW 77.50
 DE 48
 NS 2
 DS

Figure S-7

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 SM 8064.516
 HZ/PT 492
 PW 0.0
 RD 0.0
 AG 2.032
 RG 10
 NS 16
 TE 297
 FW 10100
 O2 4171.003
 DP 63L P0
 LB 300
 GB 0.0
 CX 35.00
 CY 19.00
 F1 9.201P
 F2 7.798P
 HZ/CM 114.321
 DBM/CM 286
 SR 4393.64
 D1 1.0000000
 P0 4.30
 RGA 0.0
 RD 0.0
 PW 0.0
 DE 77.50
 NS 16
 DS 2

Figure S-8

Figure S-10

(*R*)-1b: ^1H NMR (400 MHz, CDCl_3 , (+)- $\text{Eu}(\text{tfc})_3$ 55 % mol)
 CHO : $\delta(R)$ 10.15 (98 %), $\delta(S)$ 10.06 (2 %)
 cc = 96 %

FE0905:09
AU PROG:
X00.AU
DATE 31-8-99

SF	400.134
SFO	400.130
SY	230.0
01	6897.559
SI	32768
TD	32768
SW	8064.516
HZ/PT	.492

PW	0.0
RD	0.0
AG	2.032
RG	10
NS	16
TE	297

FW 10100
02 4171.003
DP 63L PO

135 0.300

[illegible]

HZ/CM 114.321
 PPM/CM .286
 SR 4394.63

01 1.0000000
20 4.30

0.0
0.0
0.0

1650

Figure S-11

Figure S-12

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 SW 8064.516
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 PW 0.0
 RD 0.0
 AG 2.032
 RG 30
 NS 32
 TE 297
 FW 10100
 O2 4171.003
 DP 63L PD
 LB 300
 GB 0.0
 CX 35.00
 CY 19.00
 F1 10.000F
 F2 10.000F
 HZ/CM 125.755
 PPM/CM 314
 SR 4394.13
 D1 1.000000C
 P0 4.30
 RGA 0.0
 RD 0.0
 PW 77.50
 DE 32
 NS 2
 DS

Figure S-13

~~BIOMER~~
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 RG 80
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 O2 4171.003
 DP 63L PO
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 CY 19.00
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Figure S-14

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 TE:297
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 NS:16
 DS:2

BIOKOR

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 RG 16
 NS 297
 TE
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 O2 4171.003
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 GB 0.0
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 CY 19.00
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 PPM/CM 286
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 D1 1.0000000
 P0 4.30
 RGA
 RD 0.0
 PW 0.0
 DE 77.50
 NS 16
 DS 2

Figure S-15

purified sample of (2f-exo-β)(4R,6R)
 (with minor *endo*-β isomer):
¹H NMR (400 MHz, CDCl₃)

Figure S-16