Chemistry-A European Journal, **2001**.

Supporting Information

Asymmetric Reduction of Ketones with Catecholborane Using 2,6-BODOL Complexes of Titanium(IV) as Catalysts.

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(1*R*)-1-Phenylethanol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave a clear liquid 122 mg, quant. $[\alpha]_D$ +42 (c = 2, MeOH), lit.[1] $[\alpha]_D^{20}$ -45.5 (c = 5, MeOH, for the (*S*)-isomer). ^1H NMR data corresponded to those in the literature.[2] The enantiomeric purity was determined to be 96% ee by HPLC analysis (Chiralcel OD-H).

(2*R*)-Octan-2-ol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave a clear liquid 108 mg, 82%. The absolute configuration was

determined by coinjectionwith the *R*-isomer. ^{1}H NMR data corresponded to those of the literature.[3] The enantiomeric purity was determined to be 87 % ee by GC analysis (alpha-DEX) of the Mosher ester.[4]

(1*R*)-1-Phenylpropan-1-ol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave a clear liquid 68 mg, 50 %. $[\alpha]_D$ +48 (c=2, hexane), lit.[5] $[\alpha]_D^{20}$ -47 (c=2.25, hexane, for the (*S*)-isomer).^{1}H NMR data corresponded to those in the literature.[6] The enantiomeric purity was determined to be 95 % ee by HPLC analysis (Chiralcel OD-H).

(1*R*)-1, 2, 3, 4-Tetrahydronaphth-1-ol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a white solid 148 mg, quant. $[\alpha]_D$ -30 (c = 1.4, $CHCl_3$), lit.[7] $[\alpha]_D^{17}$ -32 (c=2.5, $CHCl_3$). ^{1}H NMR data corresponded to those in the literature.[8] The enantiomeric purity was determined to be 96 % ee by HPLC analysis (Chiralcel OD-H).

(1*R*)-Indan-1-ol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a slightly yellow solid 120 mg, 89%. $[\alpha]_D$ -27 (c = 1.4, $CHCl_3$), lit.[9] $[\alpha]_D^{29}$ -30 (c = 2.0, $CHCl_3$). ^{1}H NMR data corresponded to those in the literature.[10] The enantiomeric purity was determined to be 96 % ee by HPLC analysis (Chiralcel OD-H).

(1*R*)-1-(1-Naphtyl)-ethanol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a white solid 152 mg, 88%. $[\alpha]_D$ +49 (c = 2, $CHCl_3$), lit.[11] $[\alpha]_D^{25}$ -54.1 (c = 3.3, $CHCl_3$, for the (*S*)-

isomer). ^{1}H NMR data corresponded to those in the literature.[12] The enantiomeric purity was determined to be 86% ee by HPLC analysis (Chiralcel OD-H).

(1*R*)-1-(2-Methoxyphenyl)-ethanol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a clear liquid 153 mg, quant. $[\alpha]_D$ +30 (c = 2, $CHCl_3$), lit.[13] $[\alpha]_D^{10}$ +32.3 (c = 2.0, $CHCl_3$). ^{1}H NMR data corresponded to those in the literature.[14] The enantiomeric purity was determined to be 86 % ee by HPLC analysis (Chiralcel OD-H).

(1*R*)-1-(3-Methoxyphenyl)-ethanol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a clear liquid 130 mg, 85 %. $[\alpha]_D$ +36 (c = 1.2, MeOH), lit.[15] $[\alpha]_D$ +35 (c = 1, MeOH). ^{1}H NMR data corresponded to those in the literature.[16] The enantiomeric purity was determined to be 98 % ee by HPLC analysis (Chiralcel OD-H).

(1*R*)-1-(4-Methoxyphenyl)-ethanol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a clear liquid 152 mg, quant. $[\alpha]_D$ +47 (c = 1, $CHCl_3$), lit.[17] $[\alpha]_D$ +48.2 (c = 1.12, $CHCl_3$). ^{1}H NMR data corresponded to those in the literature.[18] The enantiomeric purity was determined to be 95 % ee by HPLC analysis (Chiralcel OD-H).

(1*R*)-1-(4-Ethylphenyl)-ethanol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a clear liquid 140 mg, 93%. $[\alpha]_D$ +40 (c = 0.6, $CHCl_3$), lit.[19] $[\alpha]_D^{21}$ +48.2 (c = 1.12 $CHCl_3$, for the (*S*)-

isomer). ^{1}H NMR data corresponded to those in the literature.[20] The enantiomeric purity was determined to be 96 % ee by HPLC analysis (Chiralcel OD-H).

(2*R*)-Hexan-2-ol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave a clear liquid 82 mg, 80%. The absolute configuration was determined by coinjectionwith the *R*-isomer. ^{1}H NMR data corresponded to those of the literature.[21] The enantiomeric purity was determined to be 85 % ee by GC analysis (alpha-DEX) of the Mosher ester.[4]

(3*R*)-Octan-3-ol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a clear liquid 120 mg, 91 %. $[\alpha]_D$ -4.3 (c = 5.7, $CHCl_3$), lit.[22] $[\alpha]_D^{23}$ -9.5 (c = 0.96, $CHCl_3$). ^{1}H NMR data corresponded to those in the literature.[22] The enantiomeric purity was determined to be 55 % ee by GC analysis (beta-DEX).

(1*R*)-1-(Cyclohex-1-en-1-yl)-ethan-1-ol

Chromatography (SiO_2, diethyl ether:pentane 30:70) gave the title compound as a clear liquid 124 mg, 97 %. $[\alpha]_D$ 8.0 (c = 2.5, $CHCl_3$), lit.[23] $[\alpha]_D^{20}$ -7.58 (c = 3, $CHCl_3$, for the (*S*)-isomer). ^{1}H NMR data corresponded to those in the literature.[24] The enantiomeric purity was determined to be 96 % ee by GC analysis (beta-DEX).

(2*R*)-4-Phenylbutan-2-ol

Chromatography (SiO_2, diethyl ether:pentane 40:60) gave the title compound as a clear liquid 150 mg, quant. $[\alpha]_D$ -10 (c = 0.5, $CHCl_3$), lit.[25] $[\alpha]_D^{20}$ 17.45 (c = 2.04, $CHCl_3$, for the (*S*)-isomer). ^{1}H NMR data corresponded to those in the

literature.[25] The enantiomeric purity was determined to be 56 % ee by HPLC analysis (Chiralcel OD-H).

Deterioration of 5 and 6, table 5.
Concentrated HCl (5 µl, 70 µmol) was added to [D_4]MeOH (0.7 ml) in a NMR tube and this was shaken to assure proper mixing of the acid, thereafter the ligand **5** (15 mg, 60 µmol) was added and the NMR tube was again shaken. The ^{1}H NMR data were collected within 3 min of addition of the ligand. The rate of deteroriation was measured by integration of the H_C signal. This procedure was applied throughout table 5.

References

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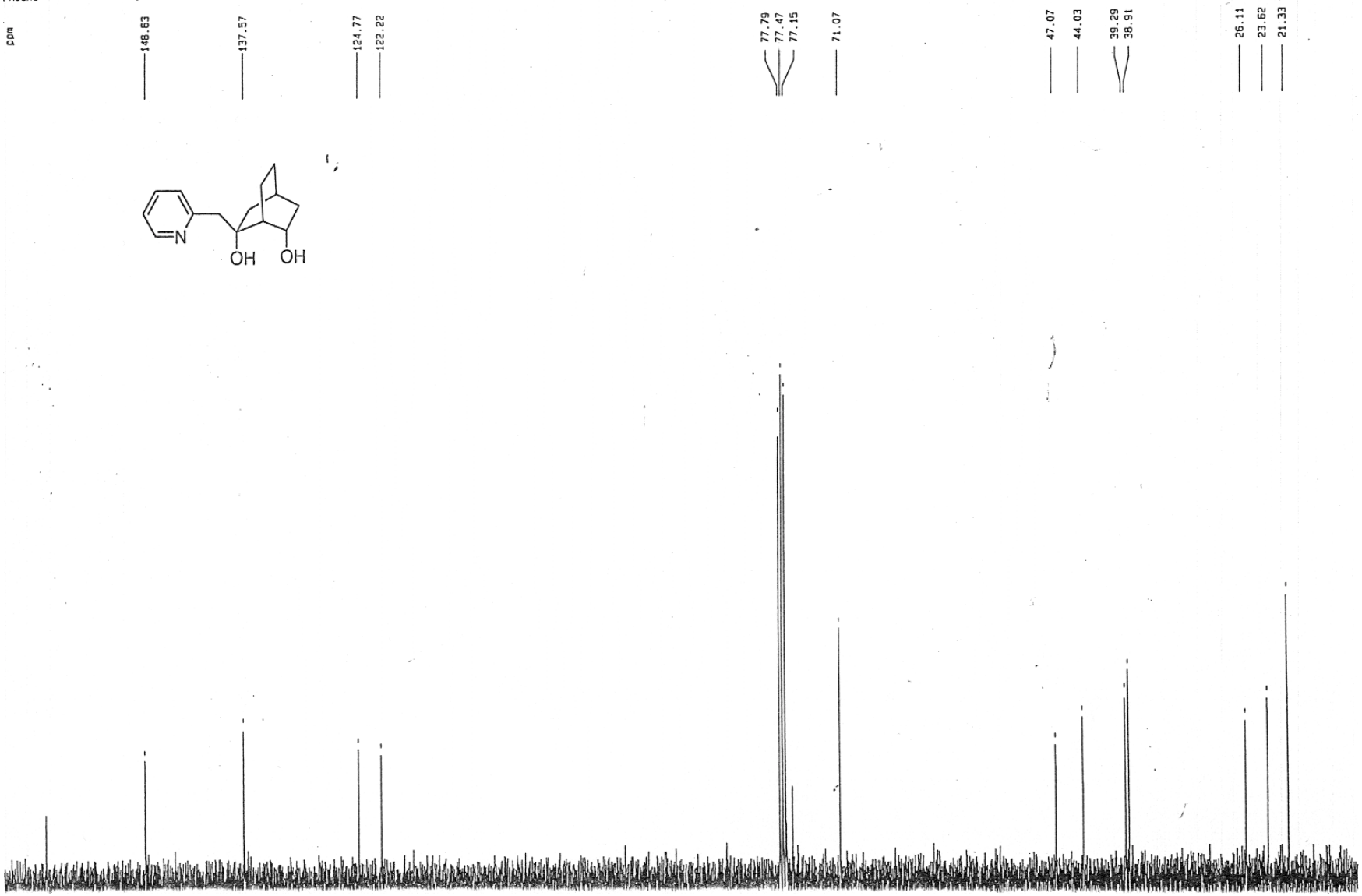

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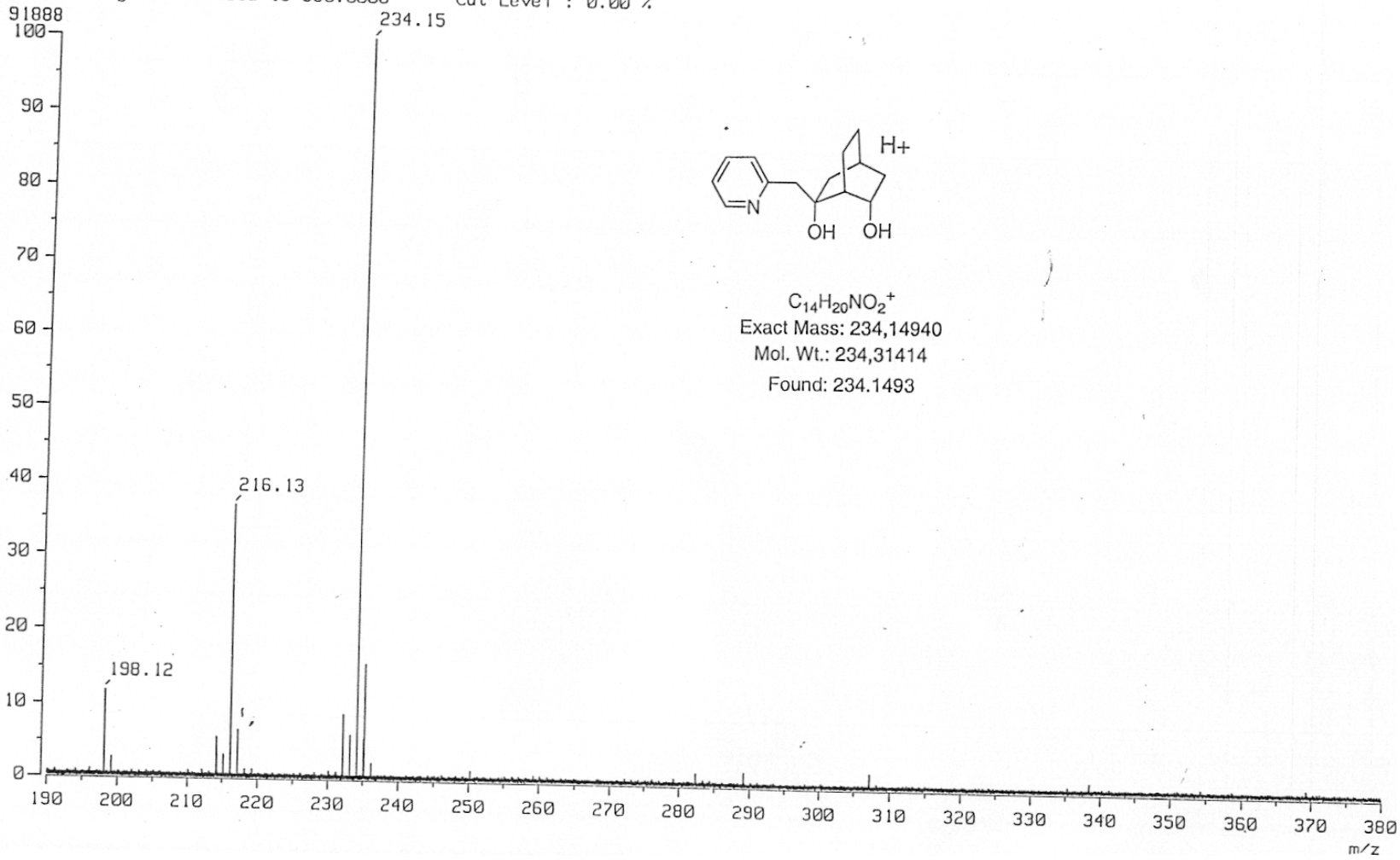

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Mass Tolerance : 10ppm, 5mmu if m/z < 500, 200mmu if m/z > 20000
Unsaturation (U.S.) : -0.5 - 100.0

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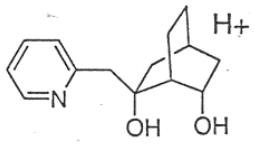
		-0.7 / -0.2	5.5	C 14 1H 20 O 2 N
		+16.4 / +3.8	1.5	C 9 1H 20 O 4 N 3



$C_{14}H_{20}NO_2^+$
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Mol. Wt.: 234,31414
Found: 234.1493

[Elemental Composition]

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Unsaturation (U.S.) : -0.5 - 100.0

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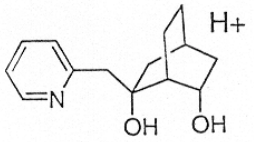

$C_{14}H_{20}NO_2^+$
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Mol. Wt.: 234,31414
Found: 234.1493

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Unsaturation (U.S.) : -0.5 - 100.0

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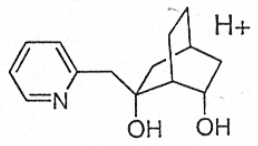

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Exact Mass: 234,14940
Mol. Wt.: 234,31414
Found: 234.1493

[Elemental Composition]

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Unsaturation (U.S.) : -0.5 - 100.0

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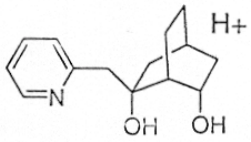
		+10.4 / +2.4	1.5	C 9 1H 20 O 4 N 3



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