Mannose derived hexacoordinated phosphate–a generally efficient chiral anion for asymmetric applications.

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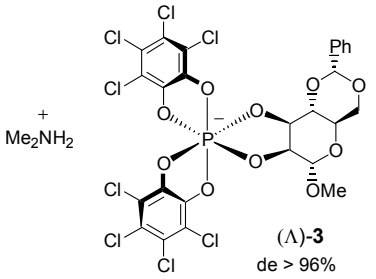
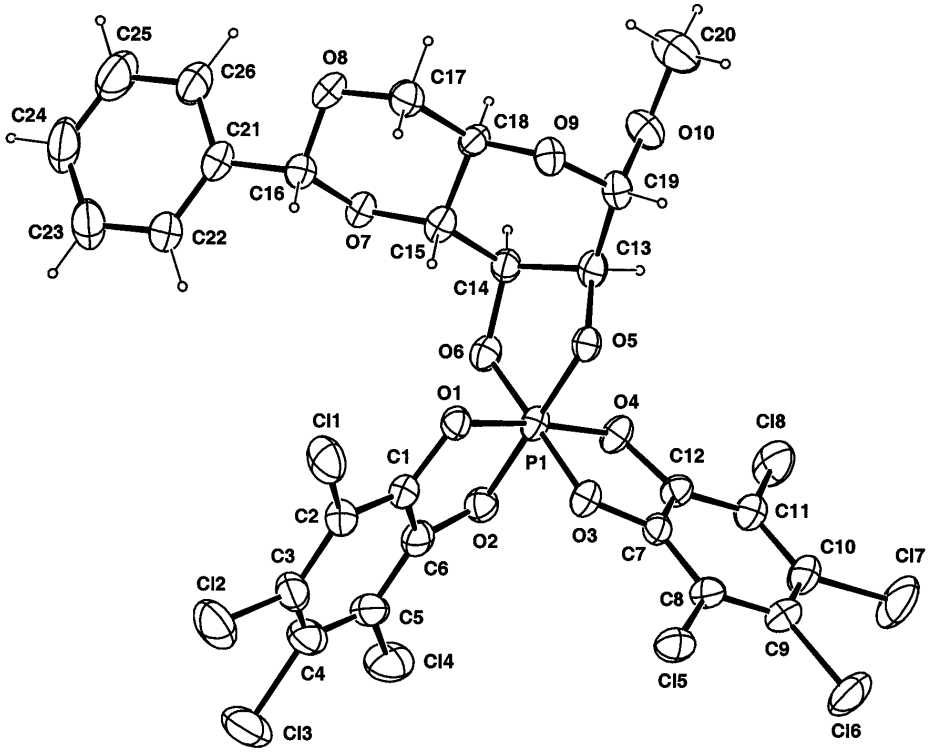
General Information. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk lines techniques with magnetic stirring, unless otherwise stated. Solvents were dried and distilled prior to use. Chloroform (Fluka) and $CDCl_3$ were filtered on basic alumina before use. Deionized water was used. Analytical thin layer chromatography was performed on Macherey-Nagel 0.25 mm silica gel plates. Visualization was accomplished with UV light. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AMX-400 spectrometer. Chemical shifts are given in ppm. ^{1}H chemical shifts were reported relative to Me_4Si. ^{31}P chemical shifts were reported relative to H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer using a diamond ATR Golden Gate sampling. The absorption is indicated in wave numbers (cm^{-1}). Optical rotations were measured on a JASCO P-1030 polarimeter in a thermostated (20 °C) 10.0 cm long microcell with high pressure lamps of sodium and are reported as follows: $[\alpha]_{\lambda}^{20}$ (c (g/100 ml), solvent). UV spectra were recorded on a CARY 1 BIO spectrophotometer in a 1 cm quartz cell; λ_{max} were given in nm and molar adsorption coefficient ε in $mol^{-1}.L.cm^{-1}$. Circular dichroism spectra were recorded on a JASCO J-715 spectropolarimeter in a 1 cm quartz cell; λ were given in nm and molar circular-dichroic absorption Δε in $mol^{-1}.L.cm^{-1}$. Electronspray mass spectra were obtained on a Finnigan SSQ 7000 spectrometer. Melting points (M.p.) were measured in open capillary tubes with a Stuart Scientific SMP3 melting point apparatus and are uncorrected.



Dimethylammonium (Λ)-Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato][D-6-Methoxy-2-phenyl-hexahydro-pyrano[3,2-d][1,3]dioxine-7,8-diolato]phosphate (salt $[Me_2NH_2][\Lambda$-**3**$]$).

297 mg (1.2 mol, 1.2 eq) of tetrachlorocatechol (recrystallized and sublimed) and a catalytic amount (usually 10 mol %) of NH_4Cl were mixed together in 5.0 mL of dry toluene under a nitrogen atmosphere. 273 μL (1.5 mmol, 1.5 eq) of freshly distilled tris(dimethylamino)phosphine (HMPA) were slowly added. Dimethylamine evolved. The mixture was refluxed for 20 minutes, then the solvent and the excess of HMPA were removed under reduced pressure and the white residue was carefully dried in vacuo. 295 mg of *o*-chloranil (1.2 mmol, 1.2 eq) were added following by 5.0 mL of CH_2Cl_2. The mixture was left for 3h30 until a precipitate was formed and the solution was turned orange. Then 282 mg (1 mmol, 1eq) of methyl-4,6-O-benzylidene-α-*D*-mannopyranoside **4** were added and 3.0 mL of CH_2Cl_2 were added. The mixture was stirred for 1 h and 1.0 mL of Et_2O were added. After 18 hours, 10 mL of Et_2O were further added. The precipitate was filtered over a Büchner funnel, washed with Et_2O and dried under high vacuum to afford the titled compound as white solid (478 mg, 56%): **M.p.** >192 °C(decomposition); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 2.54 (s, 6H, N-**Me**$_2$), 3.28 (s, 3H, O**Me**), 3.53 (td, 1H, $J_{4,5} = J_{5,6ax} = 10.1$ Hz, $J_{5,6eq} = 5.3$ Hz, **H$_5$**), 3.67 (t, 1H, $J_{6,6} = J_{56ax} = 10.4$ Hz, **H$_{6ax}$**), 3.98 (ddd,1H, $J_{H3,P} = 31.6$ Hz, $J_{2,3} = 5.3$ Hz, $J_{3,4} = 8.6$ Hz, **H$_3$**), 3.99 (m, 1H, **H$_2$**), 4.28 (dd, 1H, $J_{5,6eq} = 5.0$, $J_{6,6} = 10.1$Hz, **H$_{6eq}$**), 4.31 (dd,1H, $J_{4,5} = 9.6$ Hz, $J_{3,4} = 8.8$ Hz, **H$_4$**), 4.85 (d, 1H, $J_{1,2} = 1.5$ Hz, **H$_1$**), 5.45 (s, 1H, PhC**H**), 7.21-7.24 (m, 2H, **Ph**), 7.32-7.35 (m, 3H, **Ph**), 8.26 (broad, 2H, N**H**$_2$); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 34.3 (s, NMe), 54.3 (s, OMe), 60.1 (s, C_5), 68.4 (s, C_6), 69.5 (s, C_3), 70.9 (d, $J_{C2,P} = 4.1$ Hz, C_2), 78.0 (s, C_4), 98.3 (d, $J_{C1,P} = 21.6$Hz, C_1), 101.7 (s, Ph**C**H), 112.0 (d, $J_{C,P}$=19 Hz, $C_{catechol}$), 112.17 (d, $J_{C,P}$=19 Hz,

$C_{catechol}$), 112.19 (d, $J_{C,P}$=19 Hz, $C_{catechol}$), 112.3 (d, $J_{C,P}$=19 Hz, $C_{catechol}$), 120.0 (s, $C_{catechol}$), 120.08 (s, $C_{catechol}$), 120.11 (s, $C_{catechol}$), 120.3 (s, $C_{catechol}$), 126.1 (s, C_{Ph}), 128.1 (s, C_{Ph}), 129.0 (s, C_{Ph}), 137.4 (s, C_{Ph}), 142.5 (d, $J_{C,P}$=5.8 Hz, $C_{catechol}$), 142.82 (d, $J_{C,P}$=5.8 Hz, $C_{catechol}$), 142.82 (d, $J_{C,P}$=5.8 Hz, $C_{catechol}$), 143.0 (d, $J_{C,P}$=5.8 Hz, $C_{catechol}$); **$^{31}P\{^{1}H\}$ NMR** (162 MHz, DMSO-d_6) δ -80.66 (s); **^{31}P NMR** (162 MHz, DMSO-d_6) δ -80.65 (dd, J_{H3P} = 30 Hz, J_{H2P} = 1.5 Hz), **MS (ES)** (-) m/z = 803.1 (100), 799.1 (30), 766.9 (15); **IR** (neat) 3129, 1451,1389,1302, 1237, 1095, 993, 819, 746,675, 633; **$[\alpha]_D^{20}$** = +194 (MeOH, 0.103), **CD** (MeOH, $1.67 \cdot 10^{-5}$ M, 20 °C) λ (Δε) 213 (-77), 222 (97), 248 (25).



ORTEP view of the **[Λ-3]** anion (disordered solvent molecules and **$[Me_2NH_2]$** cation omitted) with the atomic numbering. Ellipsoids are represented with 40% probability.

Table S1. Summary of crystal data, intensity measurement and structure refinement for $[Me_2NH_2][\Lambda\text{-}3](C_3H_6O)$

Formula	$(C_{26}H_{16}O_{10}PCl_8)^-$ $(C_2H_8N)^+$ (C_3H_6O)
Mol. wt.	907.2
Diffractometer	Stoe IPDS
Crystal habit	prism
Crystal dimensions	0.16 x 0.19 x 0.23
Crystal color	colourless
Temperature (K)	200
Crystal system	Monoclinic
Space Group	*C* 2
a (Å)	18.5028(13)
b (Å)	16.1920(8)
c (Å)	14.6519(9)
β (º)	110.117(7)
V ($Å^3$)	4121.9(5)
Z	4
Dc $gr.cm^{-3}$	1.462
μ(MoKα) mm^{-1}	0.64
T min.,max	0.8679 , 0.9235
2θ range (º)	5.1 – 55.7
hkl rang	-24 , 24 ; -21 , 21 ; -19 , 19
No. measured reflc.	31887
No. unique refl.	9336
No. observed reflc.	5943
Criterion for observed	$\|Fo\| > 4\sigma(Fo)$
Refinement (on F)	Full-matrix
No. parameters	511
Weighting scheme	$\omega = 1 / [\sigma^2(Fo) + 0.0002\ (Fo)^2]$
Max. Δ/σ	0.173
Max. and min. Δρ ($e.Å^{-3}$)	0.56 , -0.34
Flack parameter x	0.01(7)
S[a]	1.80(3)
R[b] , ωR[c]	0.036 , 0.036

a) $S = [\Sigma \{((Fo-Fc) / \sigma(Fo))^2\} / (N_{ref} - N_{var})]^{1/2}$
b) $R = \Sigma \ ||Fo| - |Fc|| \ / \Sigma \ |Fo|$;
c) $\omega R = [\ \Sigma\ (\omega|Fo|-|Fc|)^2 / \Sigma\ \omega|Fo|^2\ ]^{1/2}$

Table S2. Atomic coordinates and displacement parameters (Å^2) with e.s.d.'s in parenthesis for $[Me_2NH_2][\Lambda\text{-}3](C_3H_6O)$ (U_{eq} is the average of eigenvalues of *U*).

Non-Hydrogen Positional, Isotropic Displacement and Site Occupation Parameters

	x/a	y/b	z/c	U_{eq}	PP (if ≠ 1)
P(1)	0.50626(7)	0.1635(1)	0.2495(1)	0.0314	
O(1)	0.4766(2)	0.0645(2)	0.2654(3)	0.0339	
O(2)	0.5430(2)	0.1270(3)	0.1628(3)	0.0385	
O(3)	0.5914(2)	0.1372(2)	0.3432(3)	0.0353	
O(4)	0.5458(2)	0.2592(2)	0.2384(3)	0.0361	
O(5)	0.4703(2)	0.1996(2)	0.3328(3)	0.0320	
O(6)	0.4260(2)	0.1881(2)	0.1591(3)	0.0357	
O(7)	0.2622(2)	0.1312(2)	0.1053(3)	0.0378	
O(8)	0.1613(2)	0.1024(3)	0.1628(3)	0.0485	
O(9)	0.3113(2)	0.2117(2)	0.3528(3)	0.0382	
O(10)	0.3249(2)	0.3507(3)	0.3191(3)	0.0498	
Cl(1)	0.4582(1)	-0.1181(1)	0.3036(2)	0.0602	
Cl(2)	0.5354(1)	-0.2320(1)	0.1871(2)	0.0755	
Cl(3)	0.6185(1)	-0.1518(2)	0.0559(2)	0.0784	
Cl(4)	0.6217(1)	0.0435(2)	0.0378(1)	0.0663	
Cl(5)	0.75084(8)	0.1004(1)	0.4842(1)	0.0490	
Cl(6)	0.85888(9)	0.2581(1)	0.5199(2)	0.0775	
Cl(7)	0.7970(1)	0.4184(1)	0.3999(2)	0.0873	
Cl(8)	0.62963(9)	0.4226(1)	0.2449(2)	0.0577	
C(1)	0.5072(3)	0.0085(4)	0.2216(4)	0.0364	
C(2)	0.5040(3)	-0.0765(4)	0.2300(5)	0.0451	
C(3)	0.5393(4)	-0.1266(4)	0.1779(6)	0.0520	
C(4)	0.5763(4)	-0.0907(5)	0.1203(5)	0.0534	
C(5)	0.5790(3)	-0.0044(5)	0.1114(5)	0.0483	
C(6)	0.5449(3)	0.0436(4)	0.1624(5)	0.0415	
C(7)	0.6443(3)	0.1971(3)	0.3609(4)	0.0313	
C(8)	0.7182(3)	0.1922(4)	0.4252(5)	0.0389	
C(9)	0.7661(3)	0.2617(4)	0.4376(5)	0.0484	
C(10)	0.7384(3)	0.3328(4)	0.3832(5)	0.0498	
C(11)	0.6639(3)	0.3363(4)	0.3153(5)	0.0432	
C(12)	0.6178(3)	0.2677(3)	0.3038(4)	0.0350	
C(13)	0.4111(3)	0.2593(3)	0.2897(4)	0.0331	
C(14)	0.3677(3)	0.2227(3)	0.1907(4)	0.0332	
C(15)	0.3109(3)	0.1579(3)	0.1996(4)	0.0359	
C(16)	0.2097(3)	0.0694(3)	0.1161(5)	0.0407	
C(17)	0.2042(3)	0.1272(4)	0.2604(5)	0.0443	
C(18)	0.2625(3)	0.1920(3)	0.2548(5)	0.0360	
C(19)	0.3636(3)	0.2755(3)	0.3549(4)	0.0360	
C(20)	0.2796(5)	0.3805(5)	0.3733(7)	0.0696	
C(21)	0.1622(3)	0.0410(4)	0.0144(5)	0.0486	
C(22)	0.1940(3)	-0.0154(4)	-0.0308(5)	0.0531	
C(23)	0.1518(5)	-0.0408(5)	-0.1256(7)	0.0713	
C(24)	0.0779(5)	-0.0122(6)	-0.1705(6)	0.0745	
C(25)	0.0471(4)	0.0431(6)	-0.1246(7)	0.0782	
C(26)	0.0894(4)	0.0716(5)	-0.0332(6)	0.0639	
N(1a)	1/2	0.1006(4)	1/2	0.0307	
C(1a)	0.4300(3)	0.0497(4)	0.4729(5)	0.0435	
N(1b)	1/2	0.2635(6)	0	0.0989	
C(1b)	0.4220(8)	0.2766(9)	-0.028(1)	0.0748	0.50
C(2b)	0.5405(8)	0.343(1)	-0.014(1)	0.0935	0.50

C(1c)	0.240(1)	0.229(1)	-0.152(2)	0.0870	0.50
C(2c)	0.199(2)	0.169(1)	-0.222(2)	0.1291	0.50
C(3c)	0.1998(9)	0.260(1)	-0.099(1)	0.0650	0.50
O(1c)	0.315(1)	0.243(1)	-0.129(2)	0.1547	0.50
C(1d)	0.510(2)	0.462(1)	0.483(3)	0.1364	0.50
C(2d)	0.542(2)	0.525(2)	0.439(2)	0.1474	0.50
C(3d)	0.471(4)	0.485(2)	0.548(5)	0.2258	0.50
O(1d)	0.512(2)	0.394(1)	0.462(2)	0.1794	0.50

Hydrogen Positional, Isotropic Displacement and Site Occupation Parameters

	x/a	y/b	z/c	U	PP (if ≠ 1)
H(13)	0.4298	0.3165	0.2832	0.050	
H(14)	0.3370	0.2655	0.1441	0.050	
H(15)	0.3408	0.1125	0.2355	0.050	
H(16)	0.2382	0.0251	0.1560	0.050	
H(171)	0.1697	0.1532	0.2913	0.050	
H(172)	0.2311	0.0817	0.2985	0.050	
H(18)	0.2352	0.2428	0.2212	0.050	
H(19)	0.3962	0.2802	0.4231	0.050	
H(201)	0.2407	0.3401	0.3707	0.050	
H(202)	0.3132	0.3901	0.4411	0.050	
H(203)	0.2532	0.4343	0.3493	0.050	
H(22)	0.2452	-0.0359	0.0023	0.050	
H(23)	0.1740	-0.0774	-0.1598	0.050	
H(24)	0.0476	-0.0285	-0.2363	0.050	
H(25)	-0.0047	0.0645	-0.1567	0.050	
H(26)	0.0671	0.1147	-0.0024	0.050	
H(01a)	0.5021	0.1376	0.5554	0.050	
H(11a)	0.4265	0.0172	0.4157	0.050	
H(12a)	0.4322	0.0151	0.5273	0.050	
H(13a)	0.3845	0.0872	0.4576	0.050	
H(01b)	0.5198	0.2494	0.0682	0.050	0.50
H(02b)	0.5103	0.2208	-0.0389	0.050	0.50
H(11b)	0.4127	0.3337	-0.0070	0.050	0.50
H(12b)	0.3995	0.2744	-0.0990	0.050	0.50
H(13b)	0.3992	0.2366	0.0019	0.050	0.50
H(21b)	0.5137	0.3662	-0.0800	0.050	0.50
H(22b)	0.5386	0.3859	0.0338	0.050	0.50
H(23b)	0.5937	0.3323	-0.0067	0.050	0.50
H(21c)	0.2263	0.1583	-0.2654	0.050	0.50
H(22c)	0.1922	0.1212	-0.1886	0.050	0.50
H(23c)	0.1476	0.1935	-0.2596	0.050	0.50
H(31c)	0.2206	0.2388	-0.0337	0.050	0.50
H(32c)	0.2035	0.3203	-0.0971	0.050	0.50
H(33c)	0.1463	0.2443	-0.1284	0.050	0.50
H(21d)	0.5969	0.5348	0.4778	0.050	0.50
H(22d)	0.5383	0.5090	0.3733	0.050	0.50
H(23d)	0.5142	0.5783	0.4348	0.050	0.50
H(31d)	0.4401	0.5334	0.5254	0.050	0.50
H(32d)	0.4440	0.4395	0.5608	0.050	0.50
H(33d)	0.5136	0.5013	0.6127	0.050	0.50

Atomic Anisotropic Displacement Parameters

	U11	U22	U33	U12	U13	U23
P(1)	.0315	.0342	.0275	-.0082	.0088	-.0003

O(1)	.0340	.0321	.0369	-.0072	.0138	-.0042
O(2)	.0379	.0416	.0378	-.0046	.0150	-.0027
O(3)	.0336	.0364	.0331	-.0084	.0080	.0016
O(4)	.0328	.0394	.0331	-.0098	.0074	.0063
O(5)	.0342	.0334	.0256	-.0039	.0067	-.0003
O(6)	.0346	.0417	.0295	-.0070	.0092	-.0018
O(7)	.0310	.0401	.0380	-.0069	.0065	-.0051
O(8)	.0274	.0561	.0563	-.0100	.0071	-.0100
O(9)	.0448	.0335	.0363	-.0062	.0141	-.0029
O(10)	.0614	.0334	.0573	.0062	.0239	-.0020
Cl(1)	.0782	.0361	.0743	-.0113	.0364	-.0057
Cl(2)	.0932	.0449	.0831	.0157	.0234	-.0113
Cl(3)	.0786	.0892	.0693	.0312	.0276	-.0194
Cl(4)	.0594	.0964	.0537	.0047	.0330	-.0065
Cl(5)	.0376	.0497	.0544	.0101	.0090	.0045
Cl(6)	.0301	.0773	.1027	-.0070	-.0057	-.0095
Cl(7)	.0490	.0550	.1389	-.0292	.0078	-.0027
Cl(8)	.0524	.0394	.0782	-.0122	.0183	.0116
C(1)	.0318	.0374	.0363	-.0031	.0067	-.0054
C(2)	.0416	.0431	.0468	-.0017	.0103	-.0100
C(3)	.0498	.0468	.0492	.0079	.0040	-.0156
C(4)	.0482	.0685	.0414	.0119	.0128	-.0132
C(5)	.0347	.0606	.0472	.0076	.0111	-.0100
C(6)	.0340	.0548	.0306	-.0032	.0045	-.0085
C(7)	.0308	.0326	.0322	-.0054	.0131	-.0049
C(8)	.0307	.0450	.0425	.0004	.0145	-.0030
C(9)	.0281	.0534	.0571	-.0001	.0061	-.0087
C(10)	.0375	.0414	.0676	-.0140	.0140	-.0090
C(11)	.0368	.0382	.0541	-.0078	.0150	-.0056
C(12)	.0306	.0371	.0398	-.0064	.0154	-.0015
C(13)	.0376	.0249	.0332	-.0051	.0074	.0041
C(14)	.0317	.0314	.0327	-.0018	.0064	-.0026
C(15)	.0330	.0344	.0347	-.0056	.0043	.0035
C(16)	.0349	.0346	.0513	-.0052	.0133	-.0064
C(17)	.0437	.0402	.0515	-.0051	.0195	-.0044
C(18)	.0251	.0339	.0445	-.0018	.0060	-.0017
C(19)	.0435	.0314	.0301	-.0026	.0087	-.0018
C(20)	.0830	.0529	.0836	.0126	.0424	-.0043
C(21)	.0364	.0467	.0590	-.0146	.0119	-.0106
C(22)	.0443	.0471	.0662	-.0097	.0168	-.0164
C(23)	.0739	.0633	.0757	-.0222	.0242	-.0335
C(24)	.0745	.0696	.0629	-.0226	.0025	-.0273
C(25)	.0490	.0783	.0813	-.0064	-.0110	-.0087
C(26)	.0406	.0596	.0751	-.0035	-.0013	-.0161
N(1a)	.0352	.0320	.0250	0	.0103	0
C(1a)	.0378	.0540	.0421	-.0066	.0183	-.0076
N(1b)	.2139	.0546	.0138	0	.0205	0
C(1b)	.0732	.0949	.0611	-.0132	.0292	.0179
C(2b)	.0891	.0983	.0728	-.0235	.0016	-.0164
C(1c)	.1561	.0457	.1040	-.0028	.1021	.0216
C(2c)	.2349	.0860	.1349	-.0086	.1513	.0387
C(3c)	.0779	.0839	.0315	.0286	.0166	.0188
O(1c)	.1497	.0931	.2857	-.0006	.1574	.0248
C(1d)	.0448	.1264	.1931	-.0343	-.0165	.0927
C(2d)	.1206	.1781	.1422	-.0732	.0436	-.0695
O(1d)	.1239	.1448	.1927	-.0421	-.0441	.0446

Table S3. Bond lengths (Å), bond angles and torsional angles (°) for $[Me_2NH_2][\Lambda\text{-}3](C_3H_6O)$

Bond Distances (Angstroms)

P1-O1	1.736(4)	P1-O2	1.737(5)
P1-O3	1.749(3)	P1-O4	1.744(4)
P1-O5	1.683(5)	P1-O6	1.663(3)
O1-C1	1.344(8)	O2-C6	1.350(8)
O3-C7	1.338(6)	O4-C12	1.355(5)
O5-C13	1.435(6)	O6-C14	1.427(7)
O7-C15	1.432(6)	O7-C16	1.440(7)
O8-C16	1.407(9)	O8-C17	1.433(8)
O9-C18	1.445(7)	O9-C19	1.409(7)
O10-C19	1.418(7)	O10-C20	1.42(1)
Cl1-C2	1.722(8)	Cl2-C3	1.715(7)
Cl3-C4	1.729(9)	Cl4-C5	1.725(8)
Cl5-C8	1.722(6)	Cl6-C9	1.726(5)
Cl7-C10	1.724(6)	Cl8-C11	1.723(6)
C1-C2	1.385(9)	C1-C6	1.41(1)
C2-C3	1.42(1)	C3-C4	1.38(1)
C4-C5	1.40(1)	C5-C6	1.37(1)
C7-C8	1.371(7)	C7-C12	1.401(8)
C8-C9	1.405(9)	C9-C10	1.393(9)
C10-C11	1.397(7)	C11-C12	1.375(8)
C13-C14	1.516(7)	C13-C19	1.526(9)
C14-C15	1.522(8)	C15-C18	1.502(9)
C16-C21	1.518(9)	C17-C18	1.528(9)
C21-C22	1.37(1)	C21-C26	1.379(8)
C22-C23	1.40(1)	C23-C24	1.38(1)
C24-C25	1.36(1)	C25-C26	1.38(1)

Bond Angles (degrees)

O1-P1-O2	90.3(2)	O1-P1-O3	84.9(2)
O1-P1-O4	174.1(2)	O1-P1-O5	90.0(2)
O1-P1-O6	95.2(2)	O2-P1-O3	91.0(2)
O2-P1-O4	87.3(2)	O2-P1-O5	179.5(2)
O2-P1-O6	88.1(2)	O3-P1-O4	89.8(2)
O3-P1-O5	89.4(2)	O3-P1-O6	179.0(2)
O4-P1-O5	92.4(2)	O4-P1-O6	90.1(2)
O5-P1-O6	91.5(2)	P1-O1-C1	110.7(4)
P1-O2-C6	111.2(4)	P1-O3-C7	112.1(3)
P1-O4-C12	111.5(3)	P1-O5-C13	110.3(3)
P1-O6-C14	113.8(3)	C15-O7-C16	109.1(5)
C16-O8-C17	111.4(4)	C18-O9-C19	111.9(5)
C19-O10-C20	113.9(5)	O1-C1-C2	126.2(6)
O1-C1-C6	113.7(6)	C2-C1-C6	120.1(6)
Cl1-C2-C1	119.3(5)	Cl1-C2-C3	122.0(5)
C1-C2-C3	118.6(7)	Cl2-C3-C2	119.2(6)
Cl2-C3-C4	120.6(6)	C2-C3-C4	120.2(7)
Cl3-C4-C3	120.2(6)	Cl3-C4-C5	118.8(6)
C3-C4-C5	121.0(7)	Cl4-C5-C4	122.9(6)
Cl4-C5-C6	118.7(6)	C4-C5-C6	118.4(7)
O2-C6-C1	112.5(6)	O2-C6-C5	125.9(7)
C1-C6-C5	121.6(6)	O3-C7-C8	125.6(5)
O3-C7-C12	113.1(4)	C8-C7-C12	121.3(5)
Cl5-C8-C7	119.3(4)	Cl5-C8-C9	122.1(4)
C7-C8-C9	118.6(5)	Cl6-C9-C8	119.6(5)

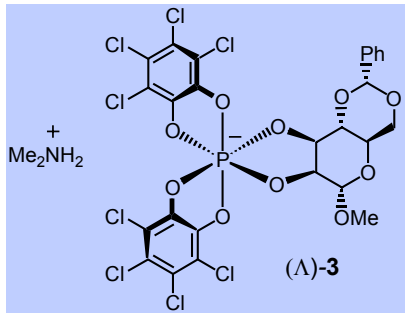
Cl6-C9-C10	120.7(5)	C8-C9-C10	119.7(5)
Cl7-C10-C9	119.5(4)	Cl7-C10-C11	119.1(5)
C9-C10-C11	121.3(5)	Cl8-C11-C10	121.9(5)
Cl8-C11-C12	119.8(4)	C10-C11-C12	118.2(5)
O4-C12-C7	113.4(5)	O4-C12-C11	125.9(5)
C7-C12-C11	120.7(4)	O5-C13-C14	103.3(4)
O5-C13-C19	110.9(5)	C14-C13-C19	115.9(4)
O6-C14-C13	104.6(4)	O6-C14-C15	112.3(4)
C13-C14-C15	110.0(5)	O7-C15-C14	110.4(5)
O7-C15-C18	109.7(4)	C14-C15-C18	110.5(5)
O7-C16-O8	110.9(5)	O7-C16-C21	106.7(5)
O8-C16-C21	110.0(4)	O8-C17-C18	107.3(6)
O9-C18-C15	109.4(4)	O9-C18-C17	108.0(5)
C15-C18-C17	109.8(5)	O9-C19-O10	111.4(4)
O9-C19-C13	113.6(5)	O10-C19-C13	104.0(5)
C16-C21-C22	118.4(5)	C16-C21-C26	121.5(7)
C22-C21-C26	120.1(6)	C21-C22-C23	119.2(6)
C22-C23-C24	119.9(8)	C23-C24-C25	120.1(8)
C24-C25-C26	120.5(7)	C21-C26-C25	120.1(8)

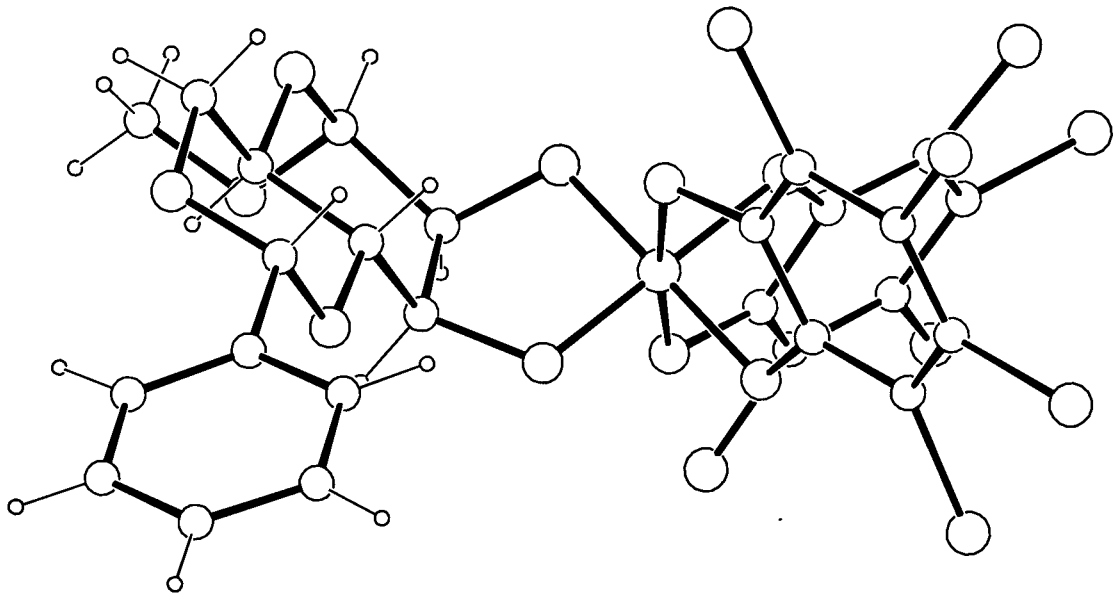
Dihedral Angles (degrees)

O2-P1-O1-C1	11.6(3)	O3-P1-O1-C1	-79.4(3)
O5-P1-O1-C1	-168.8(3)	O6-P1-O1-C1	99.7(3)
O1-P1-O2-C6	-11.4(3)	O3-P1-O2-C6	73.5(3)
O4-P1-O2-C6	163.3(3)	O6-P1-O2-C6	-106.6(3)
O1-P1-O3-C7	176.4(4)	O2-P1-O3-C7	86.2(4)
O4-P1-O3-C7	-1.1(4)	O5-P1-O3-C7	-93.5(4)
O2-P1-O4-C12	-91.9(4)	O3-P1-O4-C12	-.9(4)
O5-P1-O4-C12	88.5(4)	O6-P1-O4-C12	-180.0(4)
O1-P1-O5-C13	-118.8(3)	O3-P1-O5-C13	156.3(3)
O4-P1-O5-C13	66.5(3)	O6-P1-O5-C13	-23.6(3)
O1-P1-O6-C14	88.2(4)	O2-P1-O6-C14	178.3(4)
O4-P1-O6-C14	-94.3(4)	O5-P1-O6-C14	-1.9(4)
P1-O1-C1-C2	171.1(4)	P1-O1-C1-C6	-9.2(5)
P1-O2-C6-C1	8.4(5)	P1-O2-C6-C5	-171.6(4)
P1-O3-C7-C8	-175.2(6)	P1-O3-C7-C12	2.8(7)
P1-O4-C12-C7	2.7(7)	P1-O4-C12-C11	-178.5(6)
P1-O5-C13-C14	40.1(5)	P1-O5-C13-C19	164.9(3)
P1-O6-C14-C13	24.7(5)	P1-O6-C14-C15	-94.6(4)
C16-O7-C15-C14	179.4(4)	C16-O7-C15-C18	-58.7(5)
C15-O7-C16-O8	62.6(5)	C15-O7-C16-C21	-177.6(4)
C17-O8-C16-O7	-64.3(6)	C17-O8-C16-C21	178.0(5)
C16-O8-C17-C18	59.3(6)	C19-O9-C18-C15	64.6(6)
C19-O9-C18-C17	-175.9(5)	C18-O9-C19-O10	64.1(6)
C18-O9-C19-C13	-52.9(5)	C20-O10-C19-O9	60.5(6)
C20-O10-C19-C13	-176.8(5)	O1-C1-C2-Cl1	-.8(7)
O1-C1-C2-C3	179.7(5)	C6-C1-C2-Cl1	179.5(4)
C6-C1-C2-C3	-.1(7)	O1-C1-C6-O2	.5(6)
O1-C1-C6-C5	-179.4(4)	C2-C1-C6-O2	-179.7(4)
C2-C1-C6-C5	.3(7)	Cl1-C2-C3-Cl2	.8(7)
Cl1-C2-C3-C4	-179.3(4)	C1-C2-C3-Cl2	-179.7(4)
C1-C2-C3-C4	.2(8)	Cl2-C3-C4-Cl3	.5(7)
Cl2-C3-C4-C5	179.3(4)	C2-C3-C4-Cl3	-179.4(4)
C2-C3-C4-C5	-.6(9)	Cl3-C4-C5-Cl4	.8(7)
Cl3-C4-C5-C6	179.6(4)	C3-C4-C5-Cl4	-178.0(4)
C3-C4-C5-C6	.9(8)	Cl4-C5-C6-O2	-1.8(7)
Cl4-C5-C6-C1	178.2(4)	C4-C5-C6-O2	179.3(5)
C4-C5-C6-C1	-.7(7)	O3-C7-C8-Cl5	5(1)
O3-C7-C8-C9	-178.1(6)	C12-C7-C8-Cl5	-173.3(5)

C12-C7-C8-C9	4(1)	O3-C7-C12-O4	-3.6(8)
O3-C7-C12-C11	177.5(6)	C8-C7-C12-O4	174.6(6)
C8-C7-C12-C11	-4(1)	Cl5-C8-C9-Cl6	-4.2(9)
Cl5-C8-C9-C10	175.7(6)	C7-C8-C9-Cl6	178.6(6)
C7-C8-C9-C10	-1(1)	Cl6-C9-C10-Cl7	-1(1)
Cl6-C9-C10-C11	179.2(6)	C8-C9-C10-Cl7	179.1(6)
C8-C9-C10-C11	0(1)	Cl7-C10-C11-Cl8	2(1)
Cl7-C10-C11-C12	-179.4(6)	C9-C10-C11-Cl8	-178.0(6)
C9-C10-C11-C12	0(1)	Cl8-C11-C12-O4	2(1)
Cl8-C11-C12-C7	-179.5(5)	C10-C11-C12-O4	-176.7(7)
C10-C11-C12-C7	2(1)	O5-C13-C14-O6	-39.4(5)
O5-C13-C14-C15	81.5(5)	C19-C13-C14-O6	-160.9(4)
C19-C13-C14-C15	-40.0(6)	O5-C13-C19-O9	-75.7(5)
O5-C13-C19-O10	163.1(4)	C14-C13-C19-O9	41.7(6)
C14-C13-C19-O10	-79.6(5)	O6-C14-C15-O7	-71.9(5)
O6-C14-C15-C18	166.6(4)	C13-C14-C15-O7	172.0(4)
C13-C14-C15-C18	50.5(5)	O7-C15-C18-O9	174.7(4)
O7-C15-C18-C17	56.3(6)	C14-C15-C18-O9	-63.3(5)
C14-C15-C18-C17	178.3(4)	O7-C16-C21-C22	80.1(7)
O7-C16-C21-C26	-98.7(8)	O8-C16-C21-C22	-159.5(6)
O8-C16-C21-C26	21.6(9)	O8-C17-C18-O9	-174.4(4)
O8-C17-C18-C15	-55.2(6)	C16-C21-C22-C23	-178.4(7)
C26-C21-C22-C23	0(1)	C16-C21-C26-C25	-178.6(7)
C22-C21-C26-C25	3(1)	C21-C22-C23-C24	-3(1)
C22-C23-C24-C25	3(1)	C23-C24-C25-C26	0(1)
C24-C25-C26-C21	-3(1)		

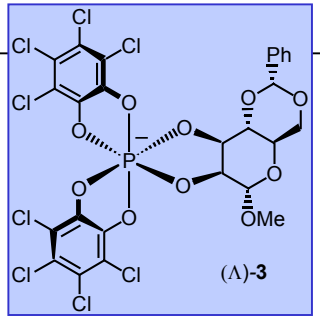
*[Me_2NH_2][Λ-**3**] – X-ray diffraction analysis*



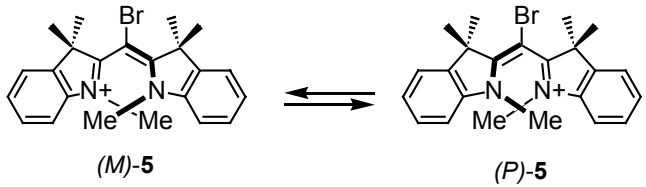


Cation omitted for clarity

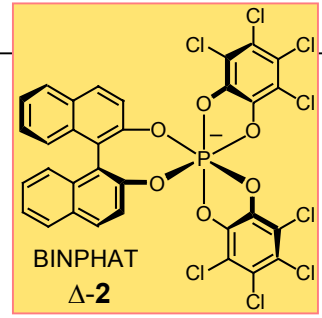
[5][Λ-3] and [5][Δ-2] - Stereoselective Induction – CD



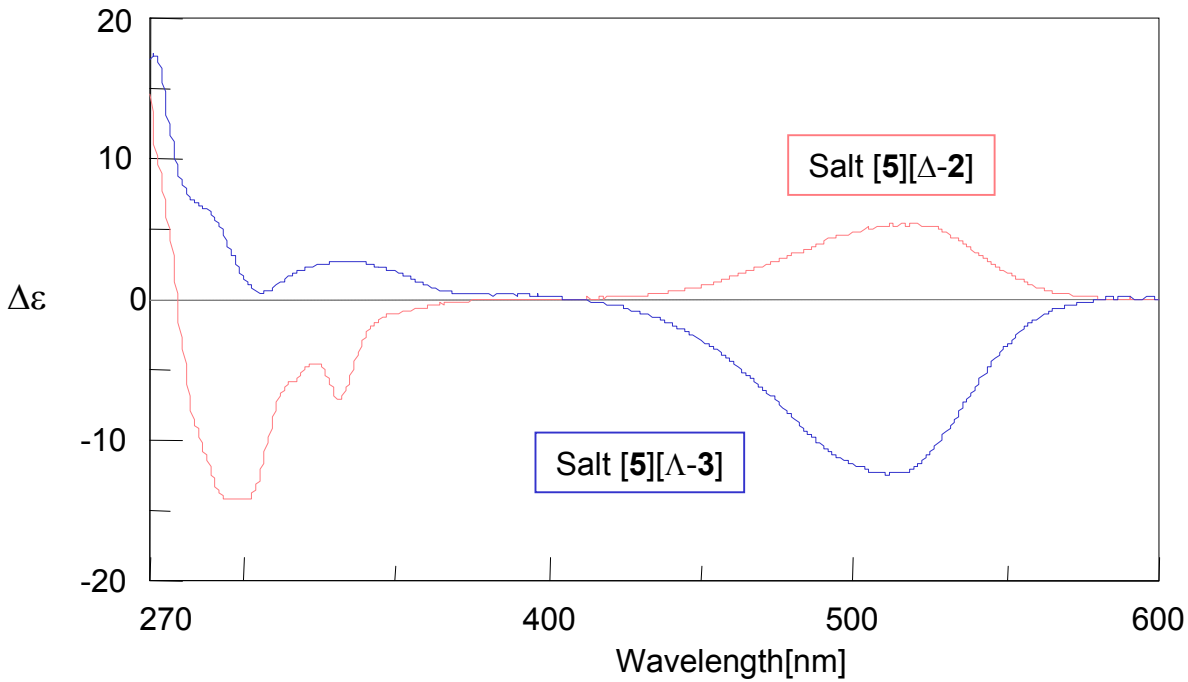
$CHCl_3$, $4.40 \cdot 10^{-5}$ *M*



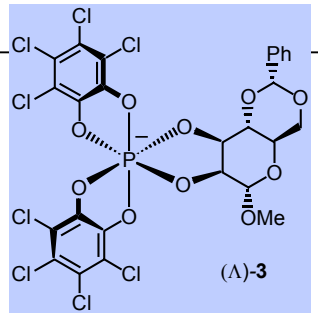
(M)-**5** ⇌ *(P)*-**5**

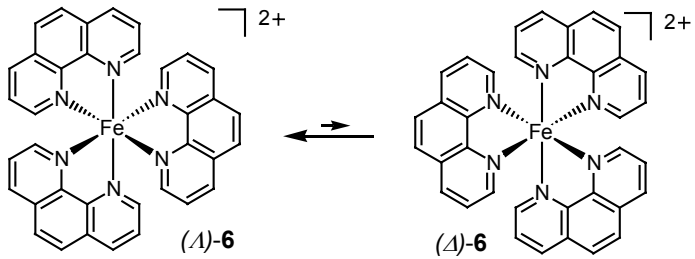


$CHCl_3$, $4.40 \cdot 10^{-5}$ *M*



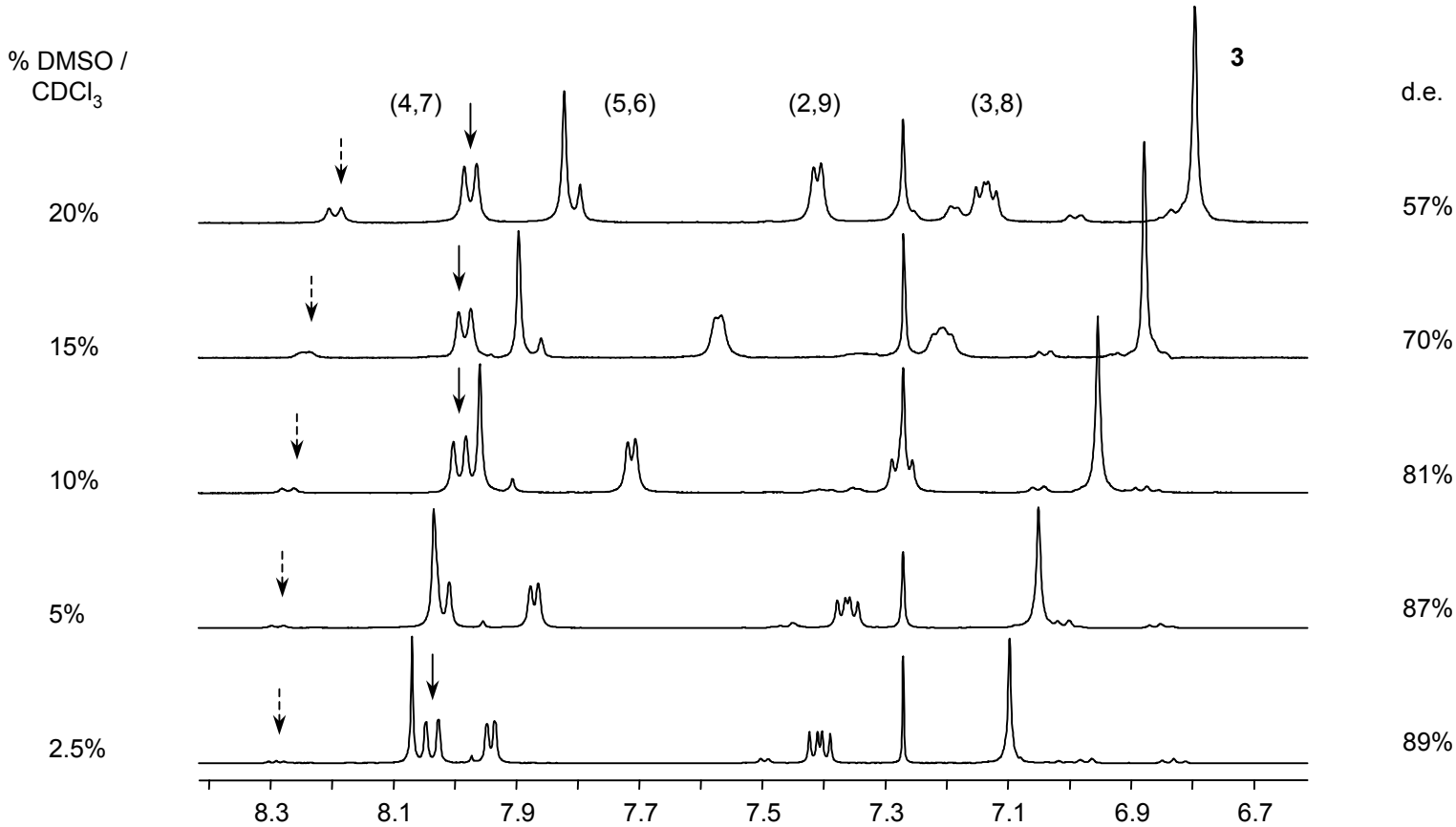
[6][Λ-3] - Stereoselective Induction – Solvent dependence



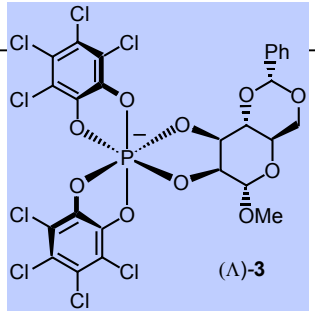


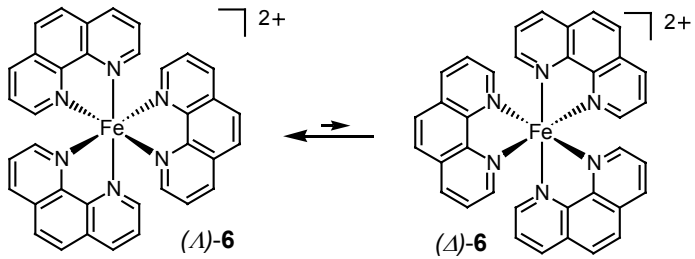
↓ Major diastereomer

↓ Minor diastereomer



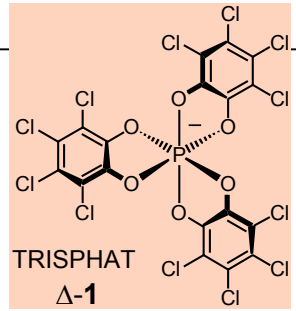
[6][Λ-3] - Stereoselective Induction – Combined NMR data





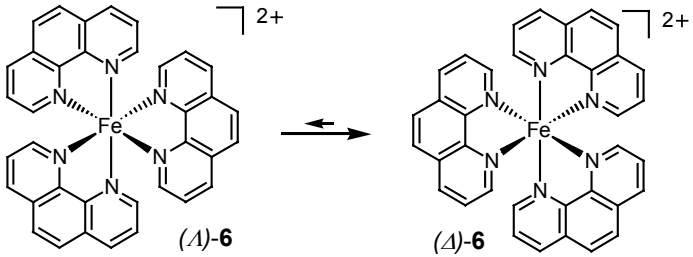
δ	in ppm						
% DMSO	2.5	5	7.5	10	12.5	15	20
H2,9 Maj	7.941	7.870	7.799	7.712	7.651	7.571	7.410
H2,9 min	7.496	7.450	7.400	7.380	7.350	7.340	7.190
H3,8 Maj	7.406	7.361	7.319	7.272	7.243	7.206	7.135
H3,8 min	7.496	7.450	7.400	7.380	7.350	7.340	7.190
H4,7 Maj	8.036	8.019	8.005	7.992	7.990	7.984	7.975
H4,7 min	8.290	8.289	8.282	8.271	8.256	8.242	8.195
H5,6 Maj	8.069	8.034	7.999	7.959	7.932	7.896	7.822
H5,6 min	7.973	7.954	7.934	7.906	7.889	7.860	7.796
% DMSO	2.5	5	7.5	10	12.5	15	20
d.e.	89%	87%	86%	81%	74%	70%	57%
Δδ							
% DMSO	2.5	5	7.5	10	12.5	15	20
H2,9	0.445	0.420	0.398	0.332	0.301	0.231	0.220
H3,8	-0.090	-0.089	-0.081	-0.108	-0.107	-0.134	-0.055
H4,7	-0.254	-0.270	-0.277	-0.279	-0.266	-0.258	-0.220
H5,6	0.097	0.080	0.064	0.053	0.044	0.037	0.026

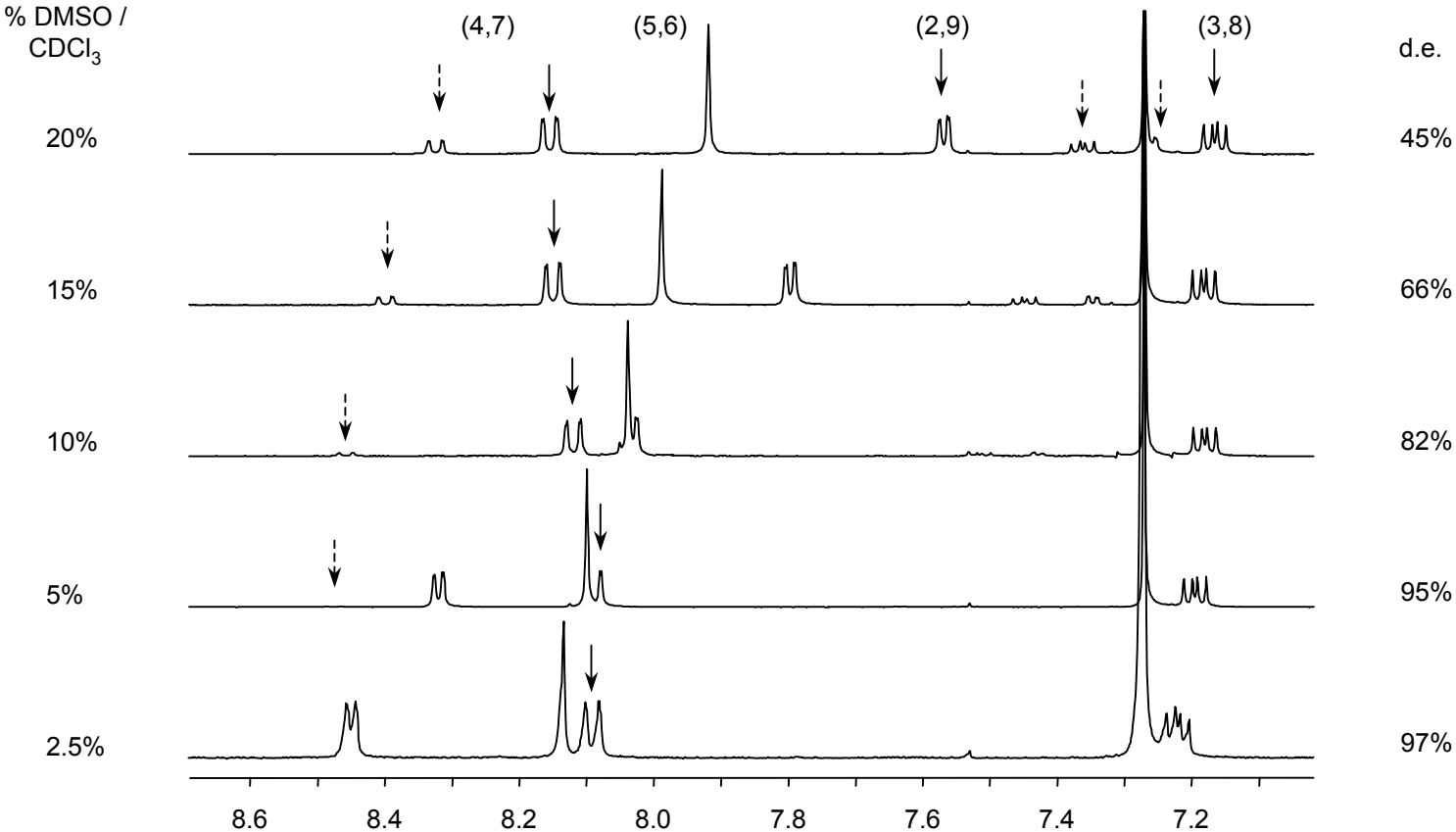
[6][Δ-1] - Stereoselective Induction – Solvent dependence



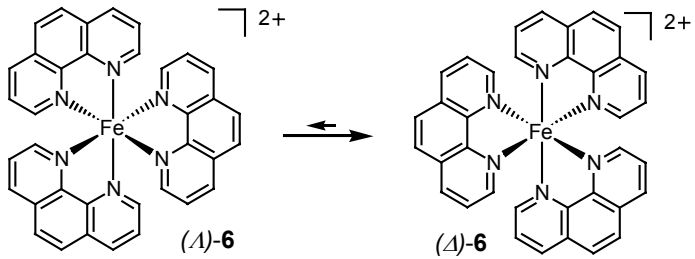
↓ Major diastereomer

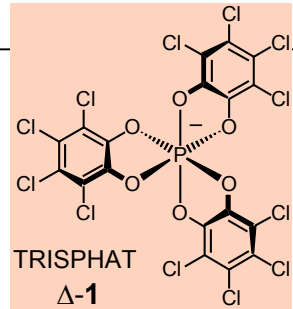
↓ Minor diastereomer





[6][Δ-1] - Stereoselective Induction – Combined NMR data





δ							
% DMSO	2.5	5	7.5	10	12.5	15	20
H2,9 Maj	8.450	8.321	8.188	8.032	7.889	7.797	7.568
H2,9 min			7.480	7.427	7.379	7.347	7.260
H3,8 Maj	7.221	7.201	7.183	7.180	7.180	7.182	7.165
H3,8 min			7.555	7.521	7.476	7.449	7.362
H4,7 Maj	8.092	8.089	8.100	8.121	8.139	8.150	8.154
H4,7 min		8.474	8.496	8.456	8.424	8.399	8.324
H5,6 Maj	8.134	8.099	8.069	8.038	8.008	7.988	7.919
H5,6 min		8.124		8.050	8.013	7.988	7.919
d.e.							
% DMSO	2.5	5	7.5	10	12.5	15	20
de phen	97%	95%	91%	82%	73%	66%	45%
Δδ							
% DMSO	2.5	5	7.5	10	12.5		
H2,9			0.708	0.605	0.511	0.450	0.308
H3,8			-0.372	-0.341	-0.296	-0.267	-0.197
H4,7		-0.385	-0.395	-0.335	-0.285	-0.249	-0.170
H5,6		-0.025		-0.012	-0.006	0.000	0.000

[6][Λ-3] and [6][Δ-1] - Stereoselective Induction – CD