Polymer supported *N*-trityl-aziridinyl(diphenyl)methanol as an effective catalyst in the enantioselective addition of diethylzinc to aldehydes

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Supporting information

Experimental procedures for polymer bound catalyst **2**. FT-IR spectrum of **2**. General procedure for the enantioselective addition of diethylzinc to aldehydes catalyzed by **2**. Chiral GC spectrum of racemic and enantiomeric 1-(4-chlorophenyl)-1-propanol. ^{19}F NMR spectrum of Mosher's ester of racemic and enantiomeric 1-cyclohexyl-1-propanol.

Polymer bound ligand 2

To a suspension of polymer bound triphenylchloromethane **4** (4.0 g, 4.4 mmol) in dichloromethane (50mL) were added aziridinylmethanol **3** (2.0 g, 8.9 mmol) and triethylamine (3.0 mL, 22.0 mmol), and the mixture was stirred at ambient temperature for three days under argon atmosphere. The resin was successively washed with dichloromethane (25 mL), water (25 mL), methanol (25 mL) and diethyl ether (25 mL) and dried *in vacuo* at 70°C for 3 h. The loading of the resin was determined to be 0.68 mmol/g (70%) by gravimetrical analysis.

Capping of the unreacted chloride moieties with methoxy groups

Dichloromethane (50 mL), methanol (50 mL) and triethylamine (3.0 mL, 22.0 mmol) were added to a sample of **2** (4 g), and the mixture was stirred for 15 min. The resin was washed with dichloromethane (25 mL), water (25 mL), methanol (25 mL) and diethyl ether (25 mL) successively, and dried *in vacuo* at 70°C for 3 h. FT-IR (KBr): ν 3455 (OH), 3052 (aryl-H), 2917 (alkyl C-H) cm^{-1}.

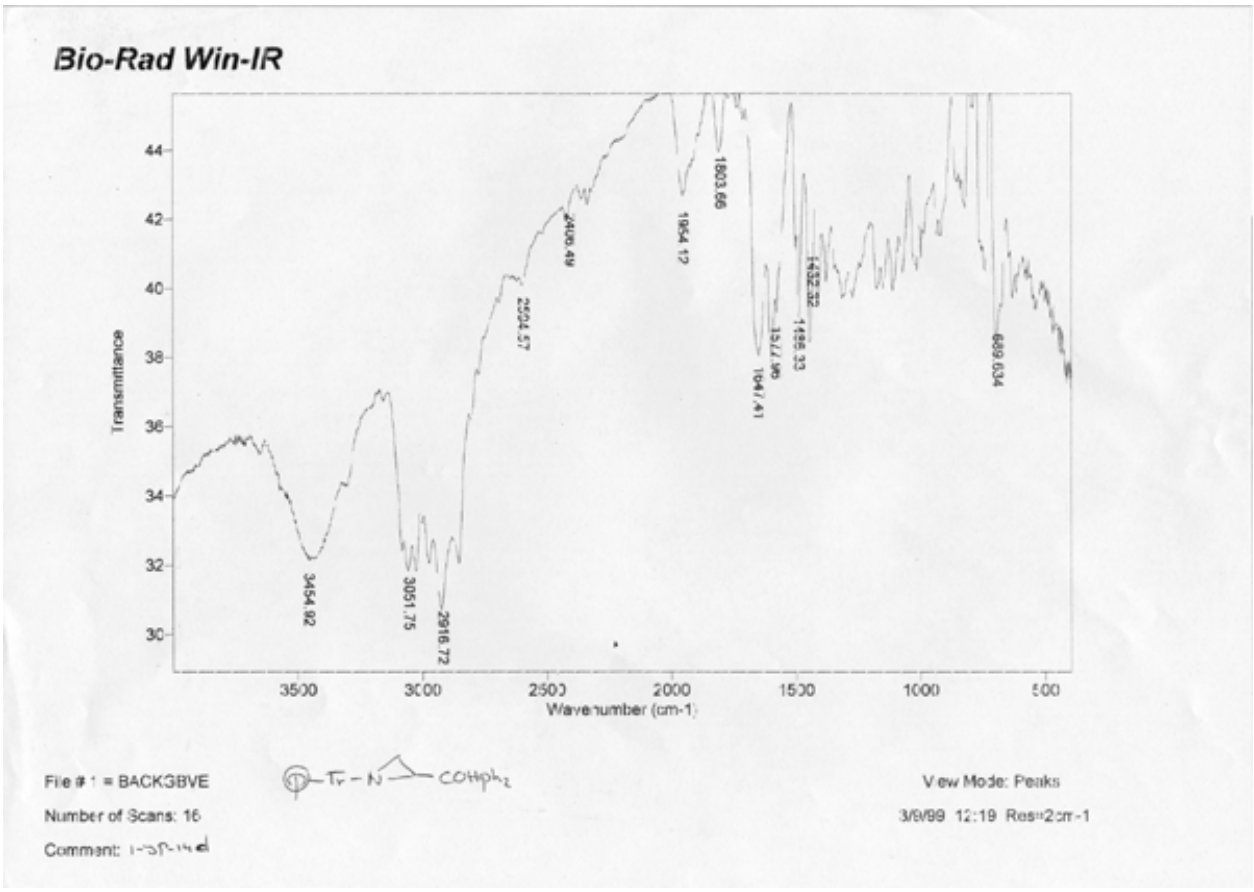
General procedure for the addition of diethylzinc to aldehydes catalyzed by polymer bound ligand 2

To a cooled (0°C) suspension of polymer bound ligand **2** (0.28 g, 0.2 mmol) in a mixture of dichloromethane and toluene (1/1, v/v, 16 mL) were added aldehyde (2.0 mmol) and diethylzinc (4.1 mL of a 1 M solution of diethylzinc in *n*-hexane), and the mixture was stirred at ambient temperature overnight. A saturated, aqueous solution of ammonium chloride (25 mL) was added and the mixture was stirred for 15 min. The resin was removed by filtration, washed with dichloromethane (5 x 5 mL) and the organic layer was dried ($MgSO_4$), concentrated under reduced pressure and the product was purified by column chromatography. Enantiomeric excesses of the alcohols were determined using chiral GC (Beta-DEX^{TM}), ^{19}F NMR of the Mosher's ester or optical rotation measurements.

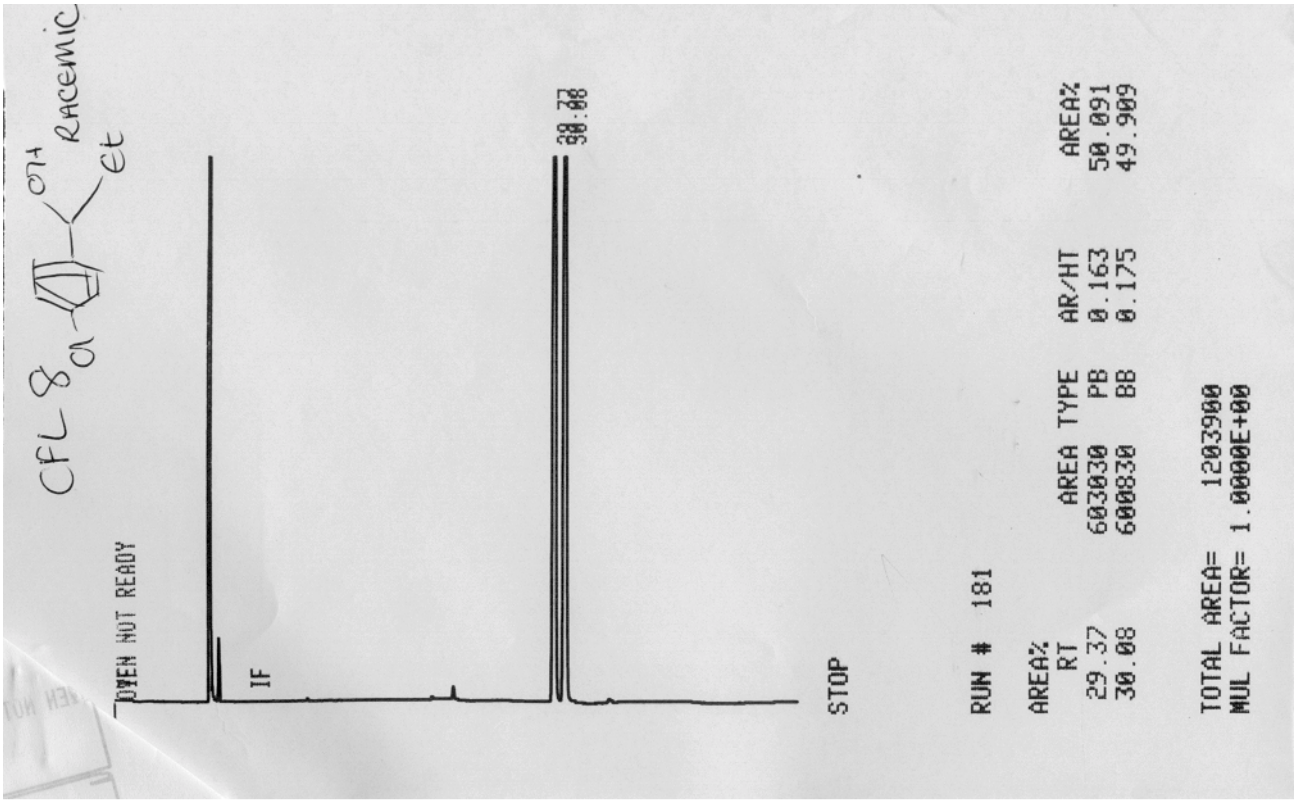
Recycling of polymer bound ligand 2

The resin (**2**) was washed successively with a saturated, aqueous solution of ammonium chloride (5 x 5 mL), water (5 x 5 mL), dichloromethane (3 x 5 mL), methanol (3 x 5 mL) and diethyl ether (3 x 5 mL) to yield polymer supported ligand **2**. FT-IR spectrometry revealed an absorption pattern identical with that of freshly prepared catalyst **2**.

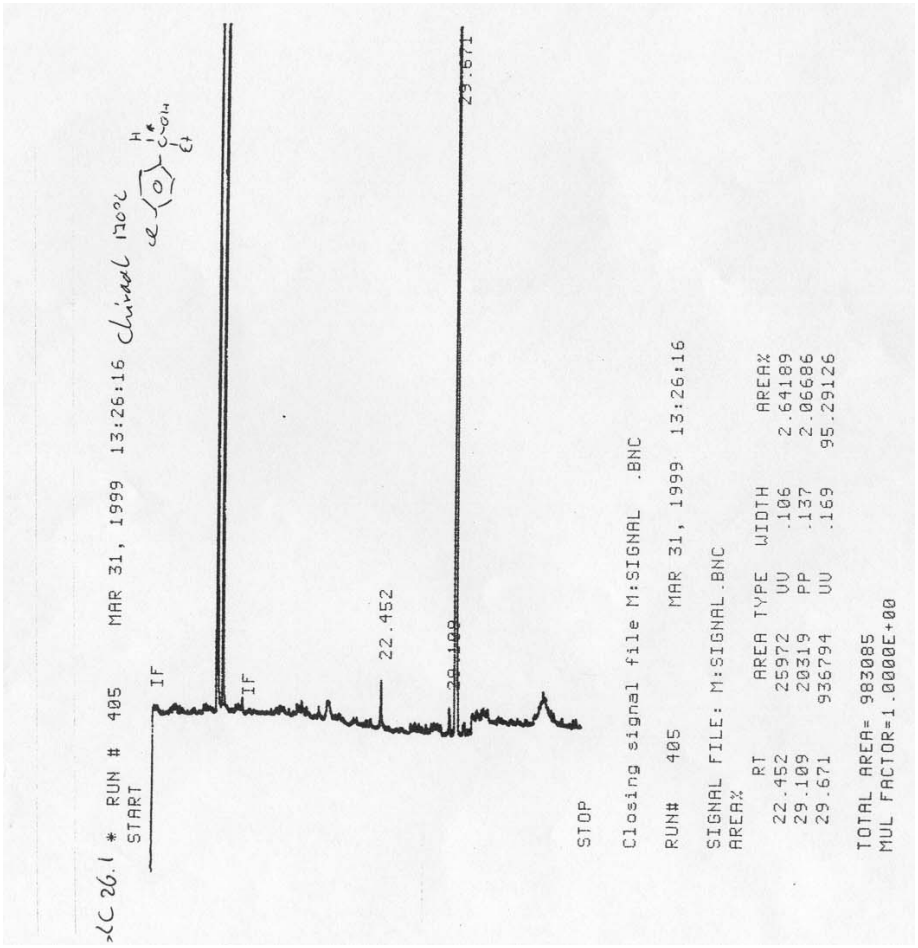
FT-IR spectrum of polymer supported ligand 2



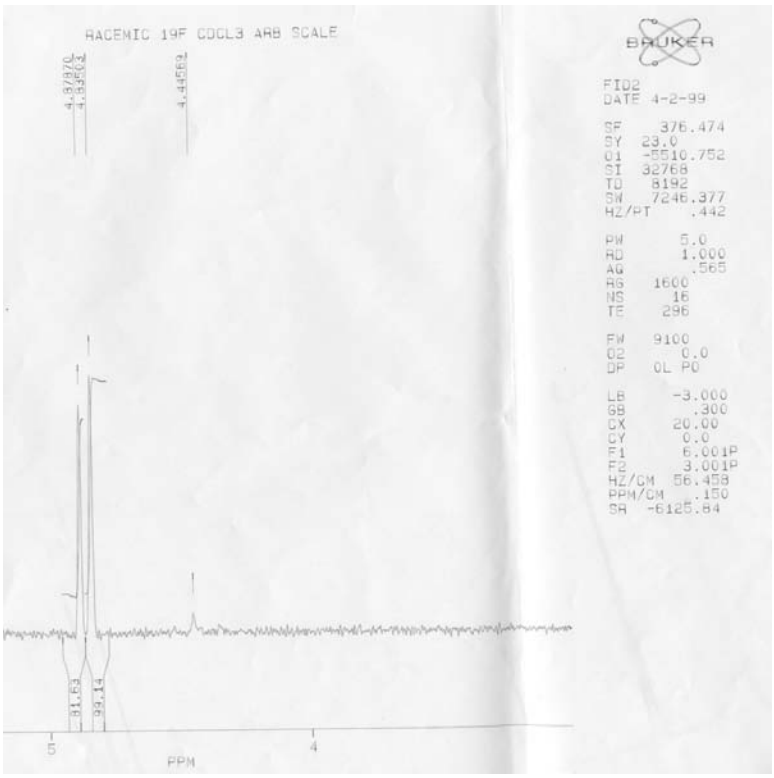
GC spectrum of racemic 1-(4-chlorophenyl)-1-propanol (Beta-DEX™, 170°C, isotherm)



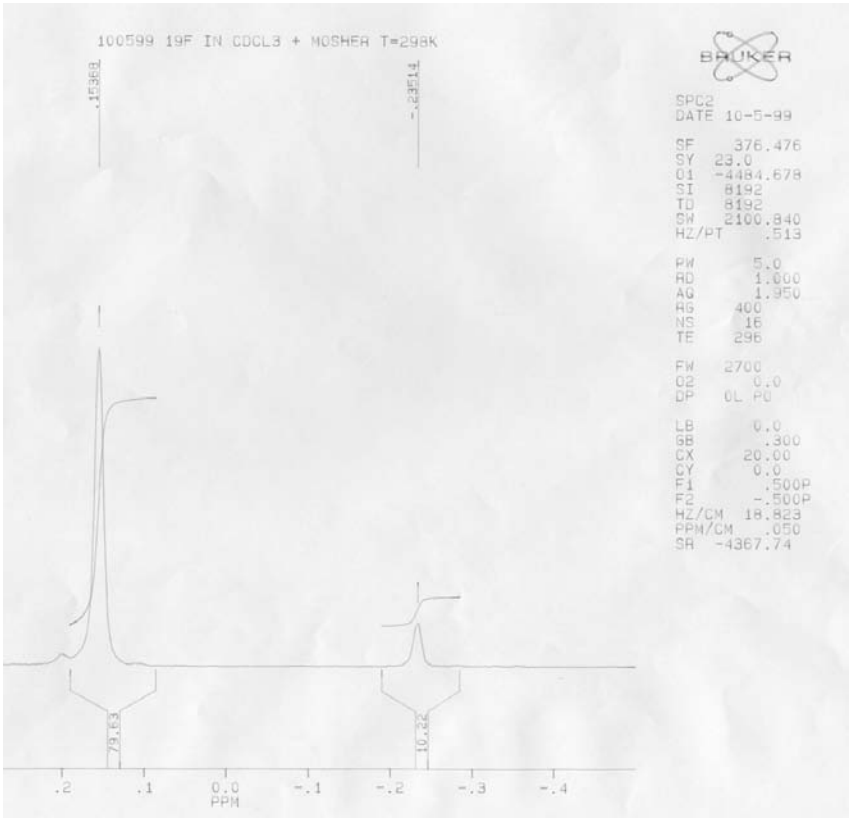
GC spectrum of enantiomeric (S)-1-(4-chlorophenyl)-1-propanol (Beta-DEX™, 170°C, isotherm), ee 96%



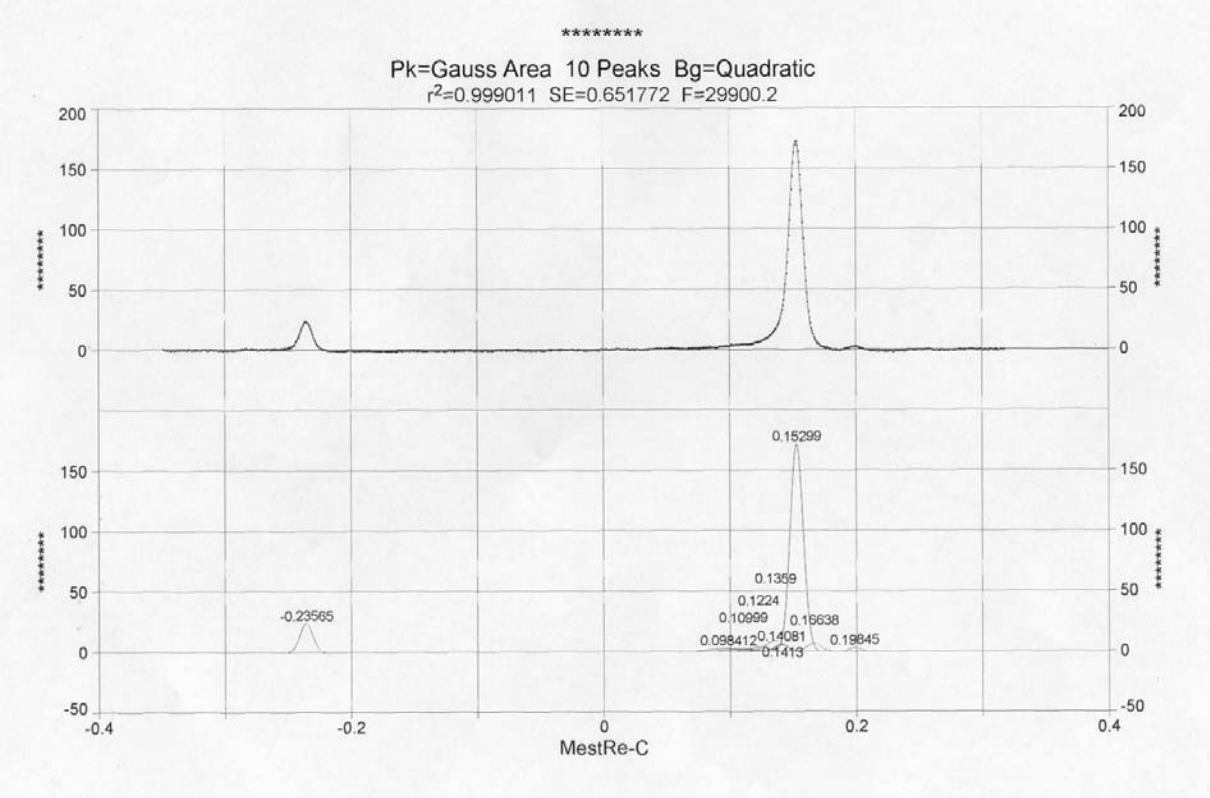
^{19}F NMR spectrum of Mosher's ester of racemic 1-cyclohexyl-1-propanol



^{19}F NMR spectrum of Mosher's ester of enantiomeric (S)-1-cyclohexyl-1-propanol



Curve fitting (Jandel Peak Fit) of ^{19}F NMR spectrum of Mosher's ester of (S)-1-cyclohexyl-1-propanol, ee 97%



Peak Summary Jul 15, 1999 Page 1

Description: ********
X Variable: MestRe-C
Y Variable: ********
File Source: c:\windows\desktop\oc1999.txt

Fitted Parameters

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.99901123	0.99897674	0.65177213	29900.2424

Peak	Type	a_0	a_1	a_2
1	Gauss Area	0.28999198	-0.2356458	0.00491815
2	Gauss Area	0.07011182	0.09841221	0.01182428
3	Gauss Area	0.05227798	0.10999458	0.00983889
4	Gauss Area	0.06454344	0.12240279	0.00777993
5	Gauss Area	0.16368656	0.13589848	0.00754140
6	Gauss Area	0.07768226	0.14080603	0.00519300
7	Gauss Area	0.06768724	0.14130190	0.00483721
8	Gauss Area	2.19073104	0.15299041	0.00509435
9	Gauss Area	0.08851534	0.16638172	0.00547984
10	Gauss Area	0.03222733	0.19845354	0.00415823
B	Quadratic Bg	-0.3017288	-0.5196136	1.89009827

Measured Values

Peak	Type	Amplitude	Center	FWHM	Asym50	FW Base	As
1	Gauss Area	23.5230873	-0.2356458	0.01158136	0.99999984	0.02318250	0.9
2	Gauss Area	2.36552041	0.09841221	0.02784405	0.99999998	0.05573566	1.0
3	Gauss Area	2.11974037	0.10999458	0.02316882	1.00000018	0.04637721	1.0
4	Gauss Area	3.30968335	0.12240279	0.01832034	1.00000000	0.03667197	1.0
5	Gauss Area	8.65907046	0.13589848	0.01775863	1.00000014	0.03554760	1.0
6	Gauss Area	5.96778758	0.14080603	0.01222859	1.00000015	0.02447806	0.9
7	Gauss Area	5.58241249	0.14130190	0.01139076	0.99999998	0.02280097	1.0
8	Gauss Area	171.557696	0.15299041	0.01199628	1.00000024	0.02401305	1.0
9	Gauss Area	6.44408167	0.16638172	0.01290403	1.00000023	0.02583010	0.9
10	Gauss Area	3.09190689	0.19845354	0.00979187	1.00000000	0.01960047	1.0

Peak	Type	Anlytc Area	% Area	Int Area	% Area	Centroid	Mo
1	Gauss Area	0.28999198	9.36226604	0.28999198	9.36226604	-0.2356458	2.41
2	Gauss Area	0.07011182	2.26353002	0.07011182	2.26353002	0.09841221	0.0
3	Gauss Area	0.05227798	1.68777196	0.05227798	1.68777196	0.10999458	9.6
4	Gauss Area	0.06454344	2.08375712	0.06454344	2.08375712	0.12240279	6.0
5	Gauss Area	0.16368656	5.28455004	0.16368656	5.28455004	0.13589848	5.6
6	Gauss Area	0.07768226	2.50793830	0.07768226	2.50793830	0.14080603	2.6
7	Gauss Area	0.06768724	2.18525327	0.06768724	2.18525327	0.14130190	2.3
8	Gauss Area	2.19073104	70.7268081	2.19073104	70.7268081	0.15299041	2.5
9	Gauss Area	0.08851534	2.85767963	0.08851534	2.85767963	0.16638172	3.0
10	Gauss Area	0.03222733	1.04044548	0.03222733	1.04044548	0.19845354	1.7
	Total	3.09745498	100.000000	3.09745498	100.000000		

Parameter Statistics

Peak 1 Gauss Area

Parm	Value	Std Error	t-value	95% Confidence Limits	
Area	0.28999198	0.00153648	188.737923	0.28697997	0.29300398
Ctr	-0.2356458	2.8428e-05	-8289.3208	-0.2357015	-0.2355900
Wid	0.00491815	2.9083e-05	169.107887	0.00486114	0.00497516

Peak 2 Gauss Area