147)

1,3-Diphenylpropane-1,3-diamines, III[1,2]:

Synthesis of 1,3-Bis(hydroxy-halogenophenyl)-propane-1,3-diamines and their Pt(II) Complexes

Part A: Synthesis of the Ligands[*]

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The title diamines were prepared according to *von Auwer's/Arakawa's* procedures starting from appropriately substituted benzaldehydes and acetophenones *via* chalcones, addition of two moles of hydroxylamine, reduction, and separation of diastereomers as N,N'-bisacetamides. - The Pt(II) complexes of the title ligands are described in the following paper.

1,3-Diphenylpropan-1,3-diamine, 3. Mitt.[1,2]: Synthese von 1,3-Bis(hydroxy-halogenphenyl)propan-1,3-diaminen und ihren Pt(II) Komplexen

Teil A: Synthese der Liganden[*]

Die Titel-Diamine werden nach *von Auwers* bzw. *Arakawa* aus entspr. substituierten Benzaldehyden und Acetophenonen über die Chalcone hergestellt, an die 2 Mol Hydroxylamin addiert werden. Reduktion und Trennung der Diastereomeren auf der Stufe der Bisacetamide führen zu den Diaminen, die als Liganden für Pt(II) Komplexe dienen (s. nachstehende Arbeit).

During the last decade *Schönenberger et al.*[3,4] have thoroughly investigated chemical and pharmacological properties of 1,2-diphenyl*ethane*-1,2-diamine-Pt(II) complexes within the special research unit "Experimental Chemotherapy of Cancer", established by Deutsche Forschungsgemeinschaft under the leadership of *H. Schönenberger*. There are, however, only a few papers dealing with propane-1,3-diamines as ligands of Pt(II) complexes[5,5a]. In most cases the propane skeleton has been varied at C-2 (cf. spiroplatine, e.g.[6]). *Okamoto et al.*[5] have tested the cytostatic activity of the enantiomers and of the *meso*-form of unsubstituted 1,3-diphenyl*propane*-1,3-diamine-Pt(II) complex: in mice L 1210 leukemia the inefficacy was attributed to low solubility in water[5]. This compound was also tested as its dichloro-Pt- and sulfato-Pt complex[7]: here the dichloro complex revealed efficacy with T/C = 169, and the sulfato complex was nearly as effective (T/C = 158).

Here we describe the syntheses of 1,3-diphenylpropane-1,3-diamines with substitution patterns of the aromatic rings known to enhance the activity of pertinent Pt complexes as compared with the efficacy of the Pt complexes of the unsubstituted ligands, as it was found by *Schönenberger* and his group[3,3a] for 1,2-diphenylethane-1,2-diamine-Pt(II) complexes. The pertinent Pt(II) complexes with Cl^- and SO_4^{2-} as leaving ligands were prepared because we are interested in their antitumor activities and their affinities to the estrogen receptor in comparison with those of the equally substituted diphenylethane derivatives.

Schönenberger et al.[8] have correlated the estrogenic efficacy of 1,2-diphenyl*ethane*-1,2-diamines with their conformation: according to ^{1}H-NMR spectra the phenyl groups of the diastereomeric 1-(2-chloro-4-hydroxyphenyl)-2-(2,6-dichloro-4-hydroxyphenyl)ethylenediamines are oriented synclinally in the *threo*-form and in antiperiplanar conformation in the *erythro*-diastereomer. After formation of the Pt complexes the arrangement in both diastereomers is synclinal, and the estrogenic efficacy of the *erythro*-complex is increasing as compared to that of the corresponding free ligand. This is contradictional to hexestrol because for this molecule an antiperiplanar arrangement of the aromatic rings is assumed to be responsible for its interaction with the estrogen receptor[9]. - The five-membered ring of the Pt complexes of 1,2-diphenylethane-1,2-diamines can adopt λ- and δ-conformation. According to *Schönenberger's* NMR-

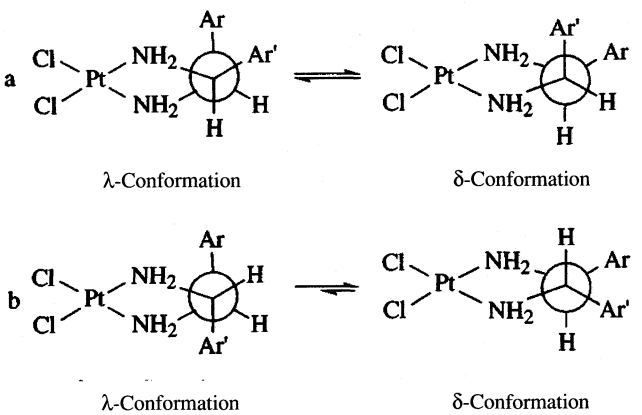

Fig. 1: Conformations of *erythro*-(*R,S*)- (**a**) and *threo*-(*S,S*)-1-(2-chloro-4-hydroxyphenyl)-2-(2,6-dichloro-4-hydroxyphenyl)ethylenediamine-dichloro-Pt(II) (**b**) complexes, according to lit.[8].
Ar: 2,6-Cl_2,4-OH-phenyl; Ar': 2-Cl,4-OH-phenyl

[*] Part B: following paper

[+] Dedicated to Prof. Dr. *B. Unterhalt*, Marburg/Germany, on the occasion of his 60th birthday.

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results there is a preference of one conformer in the *erythro*- and *threo*-diastereomer. In the *threo*-form the δ-conformation (Fig. 1), having the aromatic rings equatorially oriented, predominates. The λ-conformation is impeded probably on account of steric reasons. These results can be extended to *meso*- and *rac*-forms[10]. Also in the erythro-configuration the δ-conformation predominates. Interconversion to the λ-conformation was not observed[3a].

In contrast to the rigid 5-membered rings the 6-ring complexes are regarded to be more flexible. Therefore, we intended to prove whether cytotoxicity and affinity to the estrogen receptor (see above) are due to the 1,2-diaminoethane complexes only. If so, the additional C-atom of the 1,3-diaminopropane-Pt complexes leading to rings with less pronounced conformations should alter these pharmacological properties whilst quality and influence of the leaving ligands remain unchanged.

Here we describe the syntheses of the test compounds; the arguments for the stereochemical assignments will be given in Part V of this series.

Syntheses

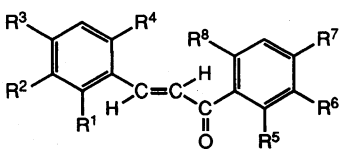
The syntheses of the 1,3-diphenylpropane-1,3-diamines is laborious, because the substituents of the phenyl rings under consideration have to be introduced in the starting materials, *i. e.* into benzaldehydes and acetophenones, respectively. These educts are not commercially available. The synthesis follows more or less the principles described by *von Auwers*[11] outlined in lit.[1]. In brief, adequately substituted benzaldehydes and acetophenones are condensed to the pertinent 1,3-diphenyl-2-propen-2-ones (chalcones) which react with two molecules of hydroxylamine forming either 1-hydroxyamino-3-hydroxyimino-1,3-diphenylpropanes or - by air induced oxidation[11] - 1,3-bis(hydroxyimino)-1,3-diphenylpropanes (cf. Scheme 2 in lit.[1]); the assignment of the hydroxyamino- and of the hydroxyimino-group, respectively, to C-1 and C-3 follows from the reaction mechanism as establshed by *von Auwers*[1,11]).

These compounds are reduced to the stereoisomeric 1,3-diphenylpropane-1,3-diamines. - These diastereomers are separated as their *N,N'*-bisacetamides, followed by hydrolysis[1]. *Denmark* and *Kim*[12] have published a diastereoselective synthesis of 1,3-diphenylpropane-1,3-diamine. This procedure, however, is not suitable for highly substituted derivatives. Moreover, high diastereoselectivity is not useful in our case because we need both diastereomers for the pharmacological tests which will be reported in a forthcoming publication.

Chalcones

The benzaldehyes and acetophenones for the formation of the chalcones are known (cf. Experim. Part). The chalcones were prepared according to *Kohler*[13]. If there is no or just one halogen substituent in the *ortho*-positions of the pertinent benzaldehydes or acetophenones, respectively, the yields of the corresponding chalcones are nearly quantitative. The synthesis of highly halogenated chalcones, however, was impeded by low solubility of the starting materials affording deteriorated products in diminished yields. Therefore, these chalcones were prepared in EtOH/water mixtures of varied composition (cf. Experim. Part). Most of the 1,3-diphenyl-2-propen-1-ones show J ≈ 16 Hz for the =C-H signals indicating *E*-configuration[14,15]. For those compounds for which the J values cannot be determined (cf. Experim. Part) we also assume *E*-configuration.

Tab. 1: 1,3-Diphenyl-2-propen-1-ones **1-16**



comp.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
1	OCH_3	H	H	H	OCH_3	H	H	H
2	H	OCH_3	H	H	H	OCH_3	H	H
3	H	H	OCH_3	H	H	H	OCH_3	H
4	H	OCH_3	OCH_3	H	H	OCH_3	OCH_3	H
5	H	H	OCH_3	H	F	H	OCH_3	H
6	H	H	OCH_3	H	Cl	H	OCH_3	H
7	H	H	OCH_3	H	Br	H	OCH_3	H
8	Cl	H	OCH_3	Cl	OCH_3	H	H	H
9	Cl	H	OCH_3	Cl	H	OCH_3	H	H
10	Cl	H	OCH_3	Cl	H	H	OCH_3	H
11	F	H	OCH_3	H	F	H	OCH_3	H
12	Cl	H	OCH_3	H	Cl	H	OCH_3	H
13	Cl	H	OCH_3	Cl	F	H	OCH_3	H
14	Cl	H	OCH_3	Cl	Cl	H	OCH_3	H
15	Cl	H	OCH_3	Cl	Cl	H	OCH_3	Cl
16	Cl	OCH_3	H	Cl	Cl	OCH_3	H	Cl

1-Hydroxyamino-3-hydroxyimino-1,3-diphenylpropanes and 1,3-bis(hydroxyimino)-1,3-diphenylpropanes

The chalcones described above were treated with two moles of $NH_2OH \cdot HCl$ in EtOH/KOH[1)2)], following *Arakawa's* modification[16)].

Tlc control of our condensation experiments indicated formation of the hydroxyamino-hydroxyimino compounds besides the bis-oximes in all cases. In the reaction of **4** both products were isolated, in all the other experiments only the main product was purified and characterized: as a rule, highly substituted educts mainly afford the hydroxyamino-hydroxyimino derivatives whilst the bis-oximes predominate in the case of starting materials not substituted in their *ortho*-positions. For the preparation of compounds **22-24** and **28-31** the standard reactions had to be modified (Experim. Part) because especially F-containing materials led to brown gums from which no defined compounds could be isolated. Some of the other crude products contained only traces of the title compounds. Here lowering the pH value to 12 afforded satisfying yields.

Hydroxyamino compounds and bis-oximes can be differentiated by the TTC-reaction[17)] (formation of red triphenylformazan from colourless 2,3,5-triphenyltetrazolium chloride): this reaction is positive with the reducing hydroxylamines, not with the bis-oximes.

1,3-Diacetamino-1,3-diphenylpropanes

A variety of methods is known for reducing hydroxylamines/oximes to amines: in our hands sodium in absol. alcohols[16,18,19)] led to poor results of highly deteriorated products. - $LiAlH_4$ may produce aziridines[20-22)] and - probably by *Beckmann*-rearrangement[23)] - sec. amines[24-26)]. $LiAlH_4$ was dismissed, however, mainly on account of elimination of aromatically bound halogen[27,28)], our experiments with the bromide **24** confirm these reports. - Hydrogenolytic elimination of halogene[29,30)] from aromatic groups excluded this procedure for the reduction of oximes[31-35)]. - Hydrosilylation[36-38)] turned out to be useless in our hands, and so did diborane[39,40)] and hydrazine/Raney-Ni[41)]. Al/Hg[42)] was not tried.

The reduction with $TiCl_4/NaBH_4$ in 1,2-dimethoxyethane as described by *Kano*[43)] proved to be optimal for our compounds. Yields were satisfying, and there was not elimination of halogen.

There are many reports concerning the active species of this reagent. Ti(IV) is reduced to Ti(III)[44)] which forms the tris-(tetrahydroborato)-(1,2-dimethoxyethane)Ti(III) complex[45)], resulting from thermal decomposition of the sodium tetra-(tetrahydroborato)-(1,2-dimethoxyethane)Ti(III) complex[46,47)] first described by *Nöth*[48)]. - We unsuccessfully tried to use terahydrofurane instead of 1,2-dimethoxyethane as a solvent.

The crude diamines were N-acetylated to the bisacetamides which were separated to the *meso-/rac-* or *threo-/erythro*-stereomers. Whilst these separations worked nicely with most compounds, it was laborious with the highly substituted bisacetamides **52-57**; compounds **58** and **59** could be separated on RP-18 silica only.

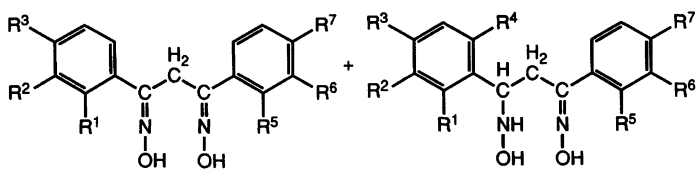
1,3-Diphenylpropane-1,3-diamines

The diamines **60-87** were obtained by heating the bisacetamides in 2N HCl/dioxane, affording the dihydrochlorides. These salts, however, could not be purified successfully. So the bases were mainly analyzed as their dipicrates.

Ether cleavage

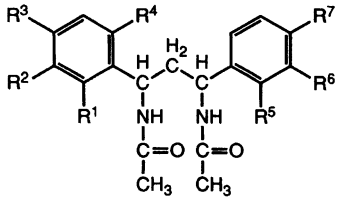
Phenolic OH-groups of a moecule in an appropriate distance seem to be a prerequiste for high affinity to the

Tab. 2: 1-Hydroxyamino-3-hydroxyimino-1,3-diphenylpropanes **19**, **20**, **22-31** and 1,3-Bis-(hydroxyimino)-1,3-diphenylpropanes **17**, **18**, and **21**



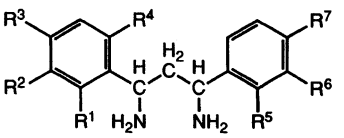
comp.	R^1	R^2	R^3	R^4	R^5	R^6	R^7
17	OCH_3	H	H	H	OCH_3	H	H
18	H	OCH_3	H	H	H	OCH_3	H
19	H	H	OCH_3	H	H	H	OCH_3
20	H	OCH_3	OCH_3	H	H	OCH_3	OCH_3
21	H	OCH_3	OCH_3	H	H	OCH_3	OCH_3
22	H	H	OCH_3	H	F	H	OCH_3
23	H	H	OCH_3	H	Cl	H	OCH_3
24	H	H	OCH_3	H	Br	H	OCH_3
25	Cl	H	OCH_3	Cl	OCH_3	H	H
26	Cl	H	OCH_3	Cl	H	OCH_3	H
27	Cl	H	OCH_3	Cl	H	H	OCH_3
28	F	H	OCH_3	H	F	H	OCH_3
29	Cl	H	OCH_3	H	Cl	H	OCH_3
30	Cl	H	OCH_3	Cl	F	H	OCH_3
31	Cl	H	OCH_3	Cl	Cl	H	OCH_3

Tab. 3: 1,3-Diacetamino-1,3-diphenylpropanes **32-59**



cop.	R^1	R^2	R^3	R^4	R^5	R^6	R^7
32, 33	OCH_3	H	H	H	OCH_3	H	H
34, 35	H	OCH_3	H	H	H	OCH_3	H
36, 37	H	H	OCH_3	H	H	H	OCH_3
38, 39	H	OCH_3	OCH_3	H	H	OCH_3	OCH_3
40, 41	H	H	OCH_3	H	F	H	OCH_3
42, 43	H	H	OCH_3	H	Cl	H	OCH_3
44, 45	H	H	OCH_3	H	Br	H	OCH_3
46, 47	Cl	H	OCH_3	Cl	OCH_3	H	H
48, 49	Cl	H	OCH_3	Cl	H	OCH_3	H
50, 51	Cl	H	OCH_3	Cl	H	H	OCH_3
52, 53	F	H	OCH_3	H	F	H	OCH_3
54, 55	Cl	H	OCH_3	H	Cl	H	OCH_3
56, 57	Cl	H	OCH_3	Cl	F	H	OCH_3
58, 59	Cl	H	OCH_3	Cl	Cl	H	OCH_3

Tab. 4: Methoxy-substituted 1,3-diphenylpropane-1,3-diamines **60-87**

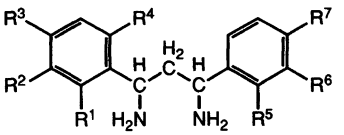


x 2 HCl

comp.	R^1	R^2	R^3	R^4	R^5	R^6	R^7
60, 61	OCH_3	H	H	H	OCH_3	H	H
62, 63	H	OCH_3	H	H	H	OCH_3	H
64, 65	H	H	OCH_3	H	H	H	OCH_3
66, 67	H	OCH_3	OCH_3	H	H	OCH_3	OCH_3
68, 69	H	H	OCH_3	H	F	H	OCH_3
70, 71	H	H	OCH_3	H	Cl	H	OCH_3
72, 73	H	H	OCH_3	H	Br	H	OCH_3
74, 75	Cl	H	OCH_3	Cl	OCH_3	H	H
76, 77	Cl	H	OCH_3	Cl	H	OCH_3	H
78, 79	Cl	H	OCH_3	Cl	H	H	OCH_3
80, 81	F	H	OCH_3	H	F	H	OCH_3
82, 83	Cl	H	OCH_3	H	Cl	H	OCH_3
84, 85	Cl	H	OCH_3	Cl	F	H	OCH_3
86, 87	Cl	H	OCH_3	Cl	Cl	H	OCH_3

estrogen receptor[49]. Therefore, the methoxy groups had to be cleaved. To this end the methoxy-diamines were refluxed with BBr_3 in dichloromethane. Even after three days the *o*-methoxy ethers **60** and **61** had not reacted, and treatment with HBr (48%) failed, too. Analogous difficulties have been observed by *Müller*[50] for *o*-methoxy-1,2-diphenylethane-1,2-diamines. This cannot, however, be generalized: contrary to **60** and **61** (*meso*, *rac*-form), *erythro*- and *threo*-1-(2,6-dichloro-4-methoxyphenyl)-3-(2-methoxyphenyl)propane-1,3-diamines **74**, **75** reacted with BBr_3 affording the pertinent phenols in good yields without problems. - The phenolic amines **88-113** were analyzed partly as dihydrobromides, partly as dipicrates.

Tab. 5: Hydroxy-substituted 1,3-diphenylpropane-1,3-diamines **88-113**



x 2 HBr

comp.	R^1	R^2	R^3	R^4	R^5	R^6	R^7
88, 89	H	OH	H	H	H	OH	H
90, 91	H	H	OH	H	H	H	OH
92, 93	H	OH	OH	H	H	OH	OH
94, 95	H	H	OH	H	F	H	OH
96, 97	H	H	OH	H	Cl	H	OH
98, 99	H	H	OH	H	Br	H	OH
100, 101	Cl	H	OH	Cl	OH	H	H
102, 103	Cl	H	OH	Cl	H	OH	H
104, 105	Cl	H	OH	Cl	H	H	OH
106, 107	F	H	OH	H	F	H	OH
108, 109	Cl	H	OH	H	Cl	H	OH
110, 111	Cl	H	OH	Cl	F	H	OH
112, 113	Cl	H	OH	Cl	Cl	H	OH

Pt(II) complexes of these diamines with Cl^-, I^-, SO_4^{2-}, and water as additional ligands are described in the following paper.

Experimental Part

Devices: lit.[1].- Drying over Na_2SO_4.- Evaporation at 15 Torr.- ^{1}H-NMR-spectra at 90 MHz, if not stated otherwise.- Temp. in °C.- Compounds are colourless, if not stated otherwise.

Benzaldehydes (Formulas not shown)

2-Fluoro-4-methoxybenzaldehyde (**114**)[51]

Aldehyde **114** was prepared from 4-bromo-3-fluoroanisol: A mixture of 4-bromo-3-fluoroanisol and 2-bromo-5-fluoroanisol was prepared as follows: at -60° 15.98 g Br_2 (0.2 mole) in 25 ml of $CHCl_3$ were added drop by drop to a mixture of 12.6 g (0.1 mol) of 3-fluoroanisol (Aldrich) and 0.25 g Fe powder in 65 ml of $CHCl_3$ under stirring. Stirring was continued at -60° for 2 h. After warming up to room temp. the mixture was poured into 90 ml of water. The org. phase was separated, washed with 10% NaOH and water and dried. After evaporation the residue was distilled at 15 Torr: 76% of a mixture of the brominated anisols (*para*-/*ortho*-isomer = 4:1 - ^{1}H-NMR) which was further processed without separation.

Formation of aldehyde **114**

Under N_2 40 ml of a 2.5 molar solution of n-BuLi (0.1 mole) were diluted with 150 ml of absol. Et_2O at -70°. Then 20.5 g (0.1 mole) of the mixture of bromo-fluoroanisols (see above) in 50 ml of absol. Et_2O were added slowly keeping the temp below -55°. Stirring was continued at -55° for 15 min. Then. 11.3 g (0.1 mole) of *N*-formylpiperidine in 25 ml of absol. Et_2O were added at -55°. After warming up to room temp. the mixture was acidified by 2N HCl, the org. phase was separated, washed and dried. The isomeric aldehydes were separated by column chromatography

(cc) (silica; CH_2Cl_2/petrol ether (40°-60°) 1:1): 71% **114**, m.p. 42-44°; lit.[51]: 42.5-44°.

2-Chloro-4-methoxybenzaldehyde (**115**)[10,52]

2,6-Dichloro-4-methoxybenzaldehyde (**116**)[10,52]; Oxime: m.p. 175-177° (EtOH 50%).

2,6-Dichloro-3-methoxybenzaldehyde (**117**)[53]

Aldehydes **115-117** were prepared more or less following the procedures cited. For slight modifications see lit.[54].

Acetophenones (Formulas not shown)

2-Fluoro-4-methoxyacetophenone (**118**)[55]

2-Chloro-4-methoxyacetophenone (**119**)[56]; Oxime: 97-98° (EtOH 70%).

2-Bromo-4-methoxyacetophenone (**120**)[56,57]

2,6-Dichloro-4-methoxyacetophenone (**121**)[2]

2,6-Dichloro-3-methoxyacetophenone (**122**)[2]

1,3-Diphenyl-2-propen-1-ones

E-1,3-Bis-(2-methoxyphenyl)-2-propen-1-one (**1**)

Under vigorous stirring 15.02 g (0.1 mole) 2-methoxybenzaldehyde (Janssen) and 13.62 g (0.1 mole) 2-methoxyacetophenone (Janssen) were added to 5.07 g (0.1265 mole) NaOH in 45 ml of water and 29 ml of 96% EtOH. After stirring for 12 h at room temp. the org. phase was separated, diluted with 200 ml of dichloromethane and washed with water and satd. NaCl-solution. After drying and evaporation the viscous oil was purified by fractionating distillation: yellow, viscous oil; 96%; b.p. 198-199° (0.7 Torr).- $C_{17}H_{16}O_3$ (268.3) Calcd. C 76.1 H 6.01 Found C 75.9 H 5.90.- FT-IR (film): $\tilde{\nu}$ = 3073 m, 3046 m, 3004 m (C-H aromat.); 2965 m, 2942 m (C-H aliph.); 2838 m (OCH_3); 1657 s (C=O); 1601 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.92 (d; ^{3}J = 15.8 Hz, 1H, =CH), 7.27-6.77 (m; 9H, 8 aromat. H and 1 =CH), 3.82, 3.80 (2s; 6H, OCH_3).

E-1,3-Bis-(3-methoxyphenyl)-2-propen-1-one (**2**)

From 3-methoxybenzaldehyde (Janssen) and 3-methoxyacetophenone (Janssen) as described for **1**. Yellow, viscous oil; 95%, b.p. 184-186°, 0.1 mbar; (lit.[58]: 211-213°/0.5 Torr).- FT-IR (film, cm^{-1}): $\tilde{\nu}$ = 3073 m, 3004 m (C-H aromat.); 2961 m, 2942 m (C-H aliph.); 2836 m (OCH_3); 1684 s (C=O), 1665 s (C=C); 1597 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 8.04-6.85 (m; 10 H, 8 aromat. H and 2H, =CH), 3.94, 3.90 (2s; 6H, OCH_3).

E-1,3-Bis-(4-methoxyphenyl)-2-propen-1-one (**3**):[1]

E-1,3-Bis-(3,4-dimethoxyphenyl)-2-propen-1-one (**4**):[1]

E-1-(2-Fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)-2-propen-1-one (**5**)

From 4-methoxybenzaldehyde (Merck) and **118** as described for **1**: 90% needles, m.p. 91-92° (EtOH 70%).- $C_{17}H_{15}FO_3$ (286.3) Calcd. C 71.3 H 5.28 Found C 71.2 H 5.38.- FT-IR (KBr): $\tilde{\nu}$ = 3077 w (C-H aromat.); 2998 w, 2969 w (C-H aliph.); 2842 w (OCH_3); 1651 s (C=O and C=C); 1622 s, 1607 s, 1586 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.99-6.48 (m; 9H, 7 aromat. H and 2H, =CH), 3.85 (s; 3H, OCH_3), 3.81 (s; 3H, OCH_3).

E-1-(2-Chloro-4-methoxyphenyl)-3-(4-methoxyphenyl)-2-propen-1-one (**6**)

From 4-methoxybenzaldehyde and **119** as described for **1**: 94% needles, m.p. 81-82° (EtOH 50%).- $C_{17}H_{15}ClO_3$ (302.8) Calcd. C 67.4 H 4.99 Found C 67.2 H 4.97.- FT-IR (KBr): $\tilde{\nu}$ = 3075 w, 3029 w, 3010 w (C-H aromat.); 2946 w (C-H aliph.); 2938 w (OCH_3); 1657 s (C=O and C=C); 1591 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.68-6.79 (m; 9H, 7 aromat. H and 2H, =CH), 3.84, 3.82 (2s; 6H, OCH_3).

E-1-(2-Bromo-4-methoxyphenyl)-3-(4-methoxyphenyl)-2-propen-1-one (**7**)

From 4-methoxybenzaldehyde and **120** as described for **1**: 91% needles, m.p. 88-90° (EtOH 70%).- $C_{17}H_{15}BrO_3$ (347.2) Calcd. C 58.8 H 4.35 Found C 59.0 H 4.30.- FT-IR (KBr): $\tilde{\nu}$ = 3071 w (C-H aromat.); 2932 w (C-H aliph); 2838 w (OCH_3); 1655 s (C=O and C=C); 1593 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm/250 MHz) = 7.55-6.89 (m; 3H aromat.), 7.52, 6.91 (AA'BB'; $^3J_{AB}$ = 8.2 Hz, 4H aromat.), 7.46 (d; ^{3}J = 15.9 Hz, 1H, =CH), 7.04 (d; ^{3}J = 15.9 Hz, 1H, =CH), 3.85 (s; 3H, OCH_3), 3.84 (s; 3H, OCH_3).

1,3-Diphenyl-2-propen-1-ones **8-16**; General procedure

Under vigorous stirring 2 mmole of the pertinent benzaldehyde and 2 mmole of the suitable acetophenone were added to 0.1 g (2.5 mmole) NaOH in 20 ml of 50% EtOH at room temp. After 4 h the mixture is cooled to 0-5°C and stirred for 1 h.- The chalcone is filtered off, washed with ice cold EtOH 50%, dried and purified by crystallization from EtOH/water of suitable concentration.

E-1-(2-Methoxyphenyl)-3-(2,6-dichloro-4-methoxyphenyl)-2-propen-1-one (**8**)

From **116** and 2-methoxyacetophenone (Janssen); 88% needles, m.p. 125-127° (EtOH 99%).- $C_{17}H_{14}Cl_2O_3$ (337.2) Calcd. C 60.6 H 4.19 Found C 60.6 H 4.19.- FT-IR (KBr): $\tilde{\nu}$ = 3091 w, 3013 w (C-H aromat.); 2963 w (C-H aliph.); 2838 w (OCH_3); 1657 s (C=O); 1599 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.79 (d; ^{3}J = 16.0 Hz, 1H, =CH), 7.56 (d; ^{3}J = 16.0 Hz, 1H, =CH), 7.61-6.98 (m; 3H aromat.), 6.92 (s, 2H aromat.), 3.88 (s; 3H, OCH_3), 3.80 (s; 3H, OCH_3).

E-1-(3-Methoxyphenyl)-3-(2,6-dichloro-4-methoxyphenyl)-2-propen-1-one (**9**)

From **116** and 3-methoxyacetophenone (Janssen); 93% crystals, m.p. 105-106° (EtOH 70%).- $C_{17}H_{14}Cl_2O_3$ (337.2) Calcd. C 60.6 H 4.19 Found C 60.6 H 4.16.- FT-IR (KBr): $\tilde{\nu}$ = 3085 w (C-H aromat.); 2948 w (C-H aliph.); 2838 w (OCH_3); 1670 s (C=O); 1589 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm/250 MHz) = 7.89 (d; ^{3}J = 16.0 Hz, 1H, =CH), 7.68 (d; ^{3}J = 16.0 Hz, 1H, =CH), 7.61-7.11 (m; 3H aromat.), 7.41 (t; ^{3}J = 8.0 Hz, 1H, 5-H aromat.), 6.95 (s; 2H aromat.), 3.88 (s; 3H, OCH_3); 3.83 (s; 3H, OCH_3).

E-1-(4-Methoxyphenyl)-3-(2,6-dichloro-4-methoxyphenyl)-2-propen-1-one (**10**)

From **116** and 4-methoxyacetophenone (Merck); 96% crystals, m.p. 145-146° (EtOH 99%).- $C_{17}H_{14}Cl_2O_3$ (337.2) Calcd. C 60.6 H 4.19 Found C 60.5 H 4.26.- CW-IR (KBr): $\tilde{\nu}$ = 3090 w, 3020 w (C-H aromat.); 2970 w, 2940 w (C-H aliph.); 2850 w (OCH_3); 1670 s (C=O and C=C); 1615 s, 1605 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.90 (d, ^{3}J = 16.5 Hz, 1H, =CH), 7.67 (d; ^{3}J = 16.5 Hz, 1H, =CH), 8.04, 7.00 (AA'BB'; $^3J_{AB}$ = 9.0 Hz, 4H aromat.), 6.95 (s; 2H aromat.), 3.88 (s; 3H, OCH_3), 3.82 (s; 3H, OCH_3).- EI-MS: m/z (%) = 340; 338; 336 (5; ^{35}Cl-$M^{+\cdot}$); 303; 301 (100; $(M - {}^{\cdot}Cl)^+$); 288, 286 (9; (303, 301 - $^{\cdot}CH_3)^{+\cdot}$); 260, 258 (9; $(288, 286 - CO)^{+\cdot}$); 208, 206, 204 (6, $(C_8H_6Cl_2O_2)^+$).

E-1,3-Bis-(2-fluoro-4-methoxyphenyl)-2-propen-1-one (**11**)

From **114** and **118**; 65% crystals, m.p. 95-96° (EtOH 70%).- $C_{17}H_{14}F_2O_3$ (304.3) Calcd. C 67.1 H 4.64 Found C 66.9 H 4.77.- CW-IR (KBr): $\tilde{\nu}$ = 3100 w, 3030 w (C-H aromat.); 2990 w, 2960 w (C-H aliph.); 2850 w (OCH_3); 1665 s (C=O and C=C); 1620 s, 1595 s (C=C).- ^{1}H-NMR

($CDCl_3$): δ (ppm) = 8.03-6.55 (m; 8H, 6 aromat. H and 2H, =CH), 3.90 (s, 3H, OCH_3), 3.84 (s; 3H, OCH_3).- EI-MS: m/z (%) = 304 (100; $M^{+\bullet}$); 289 (25; M - $^{\bullet}CH_3)^{+\bullet}$); 285 (24; (M - $^{\bullet}F)^+$); 274 (71; (M - $CH_2O)^{+\bullet}$); 180 (33); 154 (59).

E-1,3-Bis-(2-chloro-4-methoxyphenyl)-2-propen-1-one (**12**)

From **115** and **119**; 80% crystals, m.p. 121-123° (EtOH 70%).- $C_{17}H_{14}Cl_2O_3$ (337.2) Calcd. C 60.6 H 4.19 Found C 60.5 H 4.36.- FT-IR (KBr): $\tilde{\nu}$ = 3108 w, 3071 w, 3013 w (C-H aromat.); 2998 w, 2986 w, 2950 w (C-H aliph.); 2842 w (OCH_3); 1655 s (C=O and C=C); 1605 s, 1584 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.89 (d; ^3J = 16.5 Hz, 1H, =CH), 7.63-6.61 (m; 7H, 6 aromat. H and 1H, =CH), 3.83; 3.81 (2s; 6H, OCH_3).

E-1-(2-Fluoro-4-methoxyphenyl)-3-(2,6-dichloro-4-methoxyphenyl)-2-propen-1-one (**13**)

From **116** and **118**; 80% needles, m.p. 156-158° (EtOH 99%).- $C_{17}H_{13}Cl_2FO_3$ (355.2) Calcd. C 57.5 H 3.69 Found C 57.5 H 3.70.- FT-IR (KBr): $\tilde{\nu}$ = 3085 w, 3010 w (C-H aromat.); 2977 w, 2942 (C-H aliph.); 2844 w (OCH_3); 1653 s (C=O and C=C); 1622 s, 1593 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 8.04-6.50 (m; 5H, 3 aromat. H and 2H, =CH), 6.92 (s; 2H aromat.), 3.86 (s; 3H, OCH_3), 3.82 (s; 3H, OCH_3).

E-1-(2-Chloro-4-methoxyphenyl)-3-(2,6-dichloro-4-methoxyphenyl)-2-propen-1-one (**14**)

From **116** and **119**; 75% crystals; m.p. 133-135° (EtOH 99%).- $C_{17}H_{13}Cl_3O_3$ (371.6) Calcd. C 54.9 H 3.53 Found C 54.8 H 3.51.- FT-IR (KBr): $\tilde{\nu}$ = 3087 w, 3010 w (C-H aromat.); 2950 w (C-H aliph.); 2836 w (OCH_3); 1665 s (C=O and C=C); 1601 s (C=C).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.90-6.30 (m; 5H, 3 aromat. H and 2H, =CH), 6.91 (s; 2H aromat.), 3.85 (s; 3H, OCH_3), 3.81 (s; 3H, OCH_3).

E-1,3-Bis-(2,6-dichloro-4-methoxyphenyl)-2-propen-1-one (**15**):[2)]

E-1,3-Bis-(2,6-dichloro-3-methoxyphenyl)-2-propen-1-one (**16**):[2)]

1-Hydroxyamino-3-hydroxyimino-1,3-diphenylpropanes **19, 20, 22-31** *and 1,3-Bis-(hydroxyimino)-1,3-diphenylpropanes* **17, 18, 21**; *General procedure*

To a stirred solution of the chalcone (0.1 mole) in EtOH (240 ml) were added hydroxylamine-HCl (18.3 g; 0.263 mole) in water (40 ml) and KOH (24 g, 0.42 mole) in water (40 ml) at 50°. For preparation of compounds **22-24** and **28-31** KOH was added to pH 12 only. After heating to reflux for 20 min the mixture was evaporated to dryness *in vacuo*. Then 1.5 l of water were added and the mixture was stirred for 1 h.- The precipitate was dried overnight at 2-3 Torr and recrystallized from an appropriate solvent. Some products need purification by column chromatography (cc) prior to recrystallization.

1,3-Bis-(hydroxyimino)-1,3-bis-(2-methoxyphenyl)propane (**17**)

From **1**; 55% needles, m.p. 157-159° (toluene).- $C_{17}H_{18}N_2O_4$ (314.4) Calcd. C 65.0 H 5.77 N 8.9 Found C 65.5 H 5.92 N 8.5.- FT-IR (KBr): $\tilde{\nu}$ = 3237 s, br (OH); 3075 w, 3008 w (C-H aromat.); 2938 m (C-H aliph.); 2838 w (OCH_3); 1601 s, 1582 s (C=N).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 11.19 (s; 2H, =N-OH, H/D-exch.), 7.30-6.55 (m; 8H aromat.), 4.03 (s; 2H, CH_2), 3.45 (s; 6H, OCH_3).

1,3-Bis-(hydroxyimino)-1,3-bis-(3-methoxyphenyl)propane (**18**)

From **2**; 58% needles, m.p. 158-160° (EtOH 96%).- $C_{17}H_{18}N_2O_4$ (314.4) Calcd. C 65.0 H 5.77 N 8.9 Found C 65.4 H 5.75 N 8.6.- FT-IR (KBr): $\tilde{\nu}$ = 3231 s, br (OH); 3073 m, 3013 w (C-H aromat.); 2952 m, 2919 m (C-H aliph.); 2834 w (OCH_3); 1605 s, 1582 s (C=N and C=C).- ^{1}H-NMR ($CDCl_3$ + [D_6]DMSO): δ (ppm) = 11.60 (s; 2H, =N-OH, H/D-exch.), 7.23-6.73 (m; 8H aromat.), 4.30 (s; 2H, CH_2), 3.70 (s; 6H, OCH_3).- EI-MS: m/z (%) = 314 (15; $M^{+\bullet}$); 282 (74; (M - $^{\bullet}NHOH)^+$); 135 (100; (Ar-CO)$^+$); 107 (9; (135 - CO)$^+$).

1,3-Bis-(4-methoxyphenyl)-3-hydroxyamino-1-hydroxyiminopropane (**19**)

From **3**; 44% crystals, m.p. 133-134° (MeOH).- $C_{17}H_{20}N_2O_4$ (316.4) Calcd. C 64.5 H 6.37 N 8.9 Found C 64.4 H 6.40 N 8.8.- CW-IR (KBr): $\tilde{\nu}$ = 3270 m, br (NH and OH); 3080 w, 3005 w (C-H aromat.); 2960 w, 2940 w, 2900 w (C-H aliph.), 2840 w (OCH_3); 1610 s (C=N and C=C).- ^{1}H-NMR ($CDCl_3$ + [D_6]DMSO): δ (ppm) = 10.77 (s, br; 1H, =N-OH, H/D-exch.), 7.60-6.67 (m; 8H aromat.), 7.20 (s, br; 1H, OH, H/D-exch.), 5.33 (s, br; 1H, NH, H/D-exch.), 4.30-4.04 (m; 1H, CH, H/D-exch.: 4.21: ABX, $^3J_{AX}$ = 7.4 Hz, $^3J_{BX}$ = 7.4 Hz), 3.77 (s; 3H, OCH_3), 3.73 (s; 3H, OCH_3), 3.29 (ABX; $^2J_{AB}$ = 12.9 Hz, $^3J_{BX}$ = 7.4 Hz, 1H, CH_2), 2.98 (ABX; $^2J_{AB}$ = 12.9 Hz, $^3J_{AX}$ = 7.4 Hz, 1H, CH_2).- EI-MS: m/z (%) = 316 (7; $M^{+\bullet}$); 298 (7; (M - $H_2O)^{+\bullet}$); 283 (12; (298 - $^{\bullet}CH_3)^+$); 165 (23; McLafferty); 152 (100; benzylic cleavage).

1,3-Bis-(3,4-dimethoxyphenyl)-3-hydroxyamino-1-hydroxyiminopropane (**20**):[1)]

1,3-Bis-(hydroxyimino)-1,3-bis-(3,4-dimethoxyphenyl)propane (**21**):[1)]

1-(2-Fluoro-4-methoxyphenyl)-3-(hydroxyamino)-1-hydroxyimino-3-(4-methoxyphenyl)propane (**22**)

From **5**; cc prior to crystallization (SiO_2; CH_2Cl_2/EtOAc 2/1 (v/v); 26% crystals, m.p. 156-159° (toluene).- $C_{17}H_{19}FN_2O_4$ (334.4) Calcd. C 61.1 H 5.73 N 8.4 Found C 61.6 H 6.01 N 7.8.- FT-IR (KBr): $\tilde{\nu}$ = 3255 s, br (NH and OH); 3073 w, 3006 w (C-H aromat.); 2959 w, 2936 w, 2911 w (C-H aliph.); 2838 w (OCH_3); 1624 w, 1576 m (C=N).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 11.15 (s; 1H, =N-OH, H/D-exch.), 7.41 (t; ^3J = 8.5 Hz, $^4J_{HF}$ = 8.5 Hz, 1H, 6-H aromat.), 7.18 (s; 1H, OH, H/D-exch.), 7.14-6.56 (m; 6H aromat.), 5.63 (s, br; 1H, NH, H/D-exch.), 3.90 (1H, CH, overlap with OCH_3-signals), 3.86, 3.80 (2s; 6H, OCH_3), 3.35-2.82 (m; 2H, CH_2).

1-(2-Chloro-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyimino-3-(4-methoxyphenyl)propane (**23**)

From **6**; cc prior to crystallization (cf. **22**); 28% crystals, m.p. 155-158° (toluene).- $C_{17}H_{19}ClN_2O_4$ (350.8) Calcd. C 58.2 H 5.46 N 8.0 Found C 58.4 H 5.52 N 8.3.- FT-IR (KBr): $\tilde{\nu}$ = 3267 s, br (NH and OH); 3006 w (C-H aromat.); 2959 w, 2934 w (C-H aliph.); 2838 w (OCH_3); 1601 s (C=N).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 11.42 (s; 1H, =N-OH, H/D-exch.), 7.51-6.59 (m; 8H, 7 aromat. H and 1 OH, H/D-exch.), 5.61 (s, br; 1H, NH, H/D-exch.), 3.90 (1H, CH, partial overlap with OCH_3-signal), 3.77 (s; 3H, OCH_3), 3.70 (s; 3H, OCH_3), 3.21-2.69 (m; 2H, CH_2).

1-(2-Bromo-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyimino-3-(4-methoxyphenyl)propane (**24**)

From **7**; cc prior to crystallization (cf. **22**); 24% crystals, m.p. 152-155° (toluene).- $C_{17}H_{19}BrN_2O_4$ (395.3) Calcd. C 51.7 H 4.85 N 7.1 Found C 52.0 H 4.95 N 6.7.- FT-IR (KBr): $\tilde{\nu}$ = 3264 s, br (NH and OH); 3006 w (C-H aromat.); 2936 w (C-H aliph.); 2838 w (OCH_3); 1605 s (C=N).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 11.11 (s; 1H, =N-OH, H/D-exch.), 7.42-6.62 (m; 7H aromat.), 7.17 (s; 1H, OH, H/D-exch.), 5.59 (s, br; 1H, NH, H/D-exch.), 3.91 (1H, CH, partial overlap with OCH_3-signals), 3.84 (s; 3H, OCH_3), 3.77 (s; 3H, OCH_3), 3.42-2.85 (m; 2H, CH_2).

3-(2,6-Dichloro-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyimino-1-(2-methoxyphenyl)propane (**25**)

From **8**; 51% crystals, m.p. 155-157° (toluene).- $C_{17}H_{18}Cl_2N_2O_4$ (385.3) Calcd. C 53.0 H 4.71 N 7.3 Found C 53.4 H 4.76 N 7.2.- FT-IR (KBr): $\tilde{\nu}$ =

3268 s, br (NH and OH), 3079 w, 3000 w (C-H aromat.); 2942 w (C-H aliph.); 2840 w (OCH_3); 1601 s (C=N).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 11.05 (s, br; 1H, =N-OH, H/D-exch.), 7.45 (s, br; 1H, OH, H/D-exch.), 7.33-6.71 (m; 6H aromat.), 5.74 (d; ^3J = 9.0 Hz, 1H, NH, H/D-exch.), 5.10-4.75 (m; 1H, CH, H/D-exch.: 4.97; ABX, $^3J_{AX}$ = 7.0 Hz, $^3J_{BX}$ = 7.0 Hz), 3.76; 3.74 (2s; 6H, OCH_3), 3.41 (ABX; $^2J_{AB}$ = 14.4 Hz, $^3J_{BX}$ = 7.0 Hz, 1H, CH_2), 3.08 (ABX; $^2J_{AB}$ = 14.4 Hz, $^3J_{AX}$ = 7.0 Hz, 1H, CH_2).

3-(2,6-Dichloro-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyimino-1-(3-methoxyphenyl)propane (**26**)

From **9**; 53% crystals, m.p. 151-152° (toluene).- $C_{17}H_{18}Cl_2N_2O_4$ (385.3) Calcd. C 53.0 H 4.71 N 7.3 Found C 53.3 H 4.60 N 7.3.- FT-IR (KBr): $\tilde{\nu}$ = 3295 s, br (NH and OH), 3094 w, 3004 w (C-H aromat.); 2961 w, 2940 w, 2907 w (C-H aliph.); 2836 w (OCH_3); 1603 s (C=N and C=C).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 11.22 (s; 1H, =N-OH, H/D-exch.), 7.61 (d; $^3J_{HONH}$ = 1.5 Hz, 1H, OH, H/D-exch.), 7.34-6.80 (m; 4H aromat.), 6.97 (s; 2H aromat.), 5.92 (dd; $^3J_{HNOH}$ = 1.5 Hz, $^3J_{HNCH}$ = 9.0 Hz, 1H, NH, H/D-exch.), 5.17-4.81 (m; 1H, CH, H/D-exch.: 5.03; ABX, $^3J_{AX}$ = 7.5 Hz, $^3J_{BX}$ = 7.5 Hz), 3.77 (s; 6H, OCH_3), 3.47 (ABX; $^2J_{AB}$ = 12.6 Hz, $^3J_{BX}$ = 7.5 Hz, 1H, CH_2), 3.16 (ABX; $^2J_{AB}$ = 12.6 Hz, $^3J_{AX}$ = 7.5 Hz, 1H, CH_2).

3-(2,6-Dichloro-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyimino-1-(4-methoxyphenyl)propane (**27**)

From **10**; 64% crystals, m.p. 188-190° (EtOH 96%).- $C_{17}H_{18}Cl_2N_2O_4$ (385.5) Calcd. C 53.0 H 4.71 N 7.3 Found C 52.7 H 5.07 N 7.0.- CW-IR (KBr): $\tilde{\nu}$ = 3260 m, br (NH and OH); 3080 w, 3005 w (C-H aromat.); 2950 w (C-H aliph.); 2845 w (OCH_3); 1615 s (C=N).- ^{1}H-NMR ($CDCl_3$ + [D_6]DMSO): δ (ppm) = 10.80 (s; 1H, =N-OH, H/D-exch.), 7.55, 6.81 (AA'BB'; $^3J_{AB}$ = 9.0 Hz, 4H aromat.), 7.46 (d; $^3J_{HONH}$ = 1.5 Hz, 1H, OH, H/D-exch.), 6.84 (s; 2H aromat.), 5.90 (dd; $^3J_{HNOH}$ = 1.5 Hz, $^3J_{HNCH}$ = 9.0 Hz, 1H, NH, H/D-exch.), 5.15-4.88 (m; 1H, CH, H/D-exch.: 5.03; ABX, $^3J_{AX}$ = 7.6 Hz, $^3J_{BX}$ = 7.6 Hz), 3.77 (s; 3H, OCH_3), 3.73 (s; 3H, OCH_3), 3.49 (ABX; $^2J_{AB}$ = 12.9 Hz, $^3J_{BX}$ = 7.6 Hz, 1H, CH_2), 3.07 (ABX; $^2J_{AB}$ = 12.9 Hz, $^3J_{AX}$ = 7.6 Hz, 1H, CH_2).

1,3-Bis-(2-fluoro-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyiminopropane (**28**)

From **11**; cc prior to crystallization (cf. **22**); 30% crystals, m.p. 158-160° (toluene).- $C_{17}H_{18}F_2N_2O_4$ (352.3) Calcd. C 58.0 H 5.15 N 8.0 Found C 58.4 H 5.51 N 8.4.- FT-IR (KBr): $\tilde{\nu}$ = 3270 s, br (NH and OH); 3011 w (C-H aromat.); 2963 m, 2938 m, 2915 m (C-H aliph.); 2840 m (OCH_3); 1624 s, 1578 m (C=N).- ^{1}H-NMR ([D_6]DMSO): δ (ppm/250 MHz) = 11.08 (s; 1H, =N-OH, H/D-exch.), 7.87 (s; 1H, OH, H/D-exch.), 7.19 (t; ^3J = 8.4 Hz, $^4J_{HF}$ = 8.4 Hz, 1H aromat.), 6.76 (t; ^3J = 8.6 Hz, $^4J_{HF}$ = 8.6 Hz, 1H aromat.), 6.64-6.35 (m; 5H, 4 aromat. H and 1H, NH, H/D-exch.), 4.00-3.94 (m; 1H, CH, H/D-exch.: 3.85; ABX, $^3J_{AX}$ = 4.5 Hz, $^3J_{BX}$ = 4.5 Hz), 3.70 (s; 3H, OCH_3), 3.67 (s; 3H, OCH_3), 3.45 (ABX; $^2J_{AB}$ = 12.6 Hz, $^3J_{BX}$ = 4.5 Hz, 1H, CH_2), 3.03 (ABX; $^2J_{AB}$ = 12.6 Hz, $^3J_{AX}$ = 4.5 Hz, 1H, CH_2).

1,3-Bis-(2-chloro-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyiminopropane (**29**)

From **12**; cc prior to crystallization (cf. **22**); 29% crystals, m.p. 160-162° (toluene).- $C_{17}H_{18}Cl_2N_2O_4$ (385.3) Calcd. C 53.0 H 4.71 N 7.3 Found C 53.3 H 4.64 N 7.2.- FT-IR (KBr): $\tilde{\nu}$ = 3266 s, br (NH and OH); 3091 w, 3083 w, 3077 w, 3027 w, 3008 w (C-H aromat.); 2961 w, 2930 w (C-H aliph.); 2840 w (OCH_3); 1605 s, 1572 m (C=N).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 11.25 (s; 1H, =N-OH, H/D-exch.), 7.82 (d; ^3J = 9.0 Hz, 1H aromat.), 7.51 (d; ^3J = 9.0 Hz, 1H aromat.), 7.30 (s; 1H, OH, H/D-exch.), 7.23-6.69 (m; 5H, 4 aromat. H and 1H, NH, H/D-exch.), 4.62-4.31 (m; 1H, CH, H/D-exch.: 4.45; ABX, $^3J_{AX}$ = 7.5 Hz, $^3J_{BX}$ = 7.5 Hz), 3.80 (s; 3H, OCH_3), 3.76 (s; 3H OCH_3), 3.11 (ABX; $^2J_{AB}$ = 12.8 Hz, $^3J_{BX}$ = 7.5 Hz, 1H, CH_2), 2.80 (ABX; $^2J_{AB}$ = 12.8 Hz, $^3J_{AX}$ = 7.5 Hz, 1H, CH_2).

3-(2,6-Dichloro-4-methoxyphenyl)-1-(2-fluoro-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyiminopropane (**30**)

From **13**; cc prior to crystallization (cf. **22**); 26% crystals, m.p. 163-165° (toluene).- $C_{17}H_{17}Cl_2FN_2O_4$ (403.2) Calcd. C 50.6 H 4.25 N 6.9 Found C 51.2 H 4.50 N 6.6.- FT-IR (KBr): $\tilde{\nu}$ = 3318 s, br (NH and OH); 3085 w, 3010 w (C-H aromat.); 2932 w (C-H aliph.); 2836 w (OCH_3); 1615 s (C=N and C=C).- ^{1}H-NMR ([D_6]DMSO): δ (ppm/250 MHz) = 11.27 (s; 1H, =N-OH, H/D-exch.), 7.50 (d; $^3J_{HONH}$ = 2.8 Hz, 1H, OH, H/D-exch.), 7.07 (t; ^3J = 8.8 Hz, $^4J_{HF}$ = 8.8 Hz, 1H aromat.), 6.94-6.63 (m; 4H aromat.), 5.79 (dd; $^3J_{HONH}$ = 2.8 Hz, $^3J_{NHCH}$ = 9.8 Hz, 1H, NH, H/D-exch.), 4.94-4.90 (m; 1H, CH, H/D-exch.: 4.92; ABX, $^3J_{AX}$ = 9.5 Hz, $^3J_{BX}$ = 6.5 Hz), 3.75 (s; 3H, OCH_3), 3.73 (s; 3H, OCH_3), 3.44 (ABX; $^2J_{AB}$ = 13.4 Hz, $^3J_{BX}$ = 6.5 Hz, 1H, CH_2), 3.07 (ABX; $^2J_{AB}$ = 13.4 Hz, $^3J_{AX}$ = 9.5 Hz, 1H, CH_2).

1-(2-Chloro-4-methoxyphenyl)-3-(2,6-dichloro-4-methoxyphenyl)-3-hydroxyamino-1-hydroxyiminopropane (**31**)

From **14**; cc prior to crystallization (cf. **22**); 32% crystals, m.p. 163-165° (toluene).- $C_{17}H_{17}Cl_3N_2O_4$ (419.7) Calcd. C 48.7 H 4.08 N 6.7 Found C 48.4 H 4.04 N 6.7.- FT-IR (KBr): $\tilde{\nu}$ = 3282 s, br (NH and OH), 3017 w (C-H aromat.); 2969 w, 2942 w (C-H aliph.); 2838 w (OCH_3); 1605 (s (C=N).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 11.19 (s; 1H, =N-OH, H/D-exch.), 7.48 (d; $^3J_{HONH}$ = 1.5 Hz, 1H, OH, H/D-exch.), 7.05-7.67 (m; 3H aromat.), 6.86 (s; 2H aromat.), 5.79 (dd; $^3J_{HNOH}$ = 1.5 Hz, $^3J_{HNCH}$ = 9.0 Hz, 1H, NH, H/D-exch.), 5.11-4.78 (m; 1H, CH, H/D-exch.: 5.01: ABX, $^3J_{AX}$ = 9.0 Hz, $^3J_{BX}$ = 7.5 Hz), 3.72 (s; 6H, OCH_3), 3.44 (ABX; $^2J_{AB}$ = 13.2 Hz, $^3J_{BX}$ = 7.5 Hz, 1H, CH_2), 3.07 (ABX; $^2J_{AB}$ = 13.2 Hz, $^3J_{AX}$ = 9.0 Hz, 1H, CH_2).

Under these general reaction conditions chalcones **15** and **16** yield 1*H*-aziridines, cf. lit.[2].

1,3-Diacetamino-1,3-diphenylpropanes

At 0° 23.4 g (0.613 mole) $NaBH_4$ were carefully added in portions to 58.2 g (0.307 mole) $TiCl_4$ in 370 ml of dry 1,2-dimethoxyethane under N_2 with stirring. The deep blue mixture was stirred for 30 min at 0°, then the suspension of 0.073 mole of 1,3-diphenyl-1-hydroxyamino-1-hydroxyiminopropane or 1,3-(bis-hydroxyimino)-1,3-diphenylpropane, respectively, in 350 ml of 1,2-dimethoxyethane was added in portions. The mixture was stirred for 24 h at 40° and then cooled to 0°. For hydrolysis 300 ml of water were added drop by drop, and the mixture was alkalized by 180 ml of conc. ammonia. The suspension so formed was mixed with 1 l of CH_2Cl_2 and 1 l of water and stirred for 1 h. Then the precipitate was filtered off by suction. The org. phase was separated, the aqueous phase was extracted 2 x with 250 ml of CH_2Cl_2 each, and the combined org. phases were washed with satd. NaCl solution, dried and evaporated *in vacuo*.- The residue was dissolved in 200 ml of CH_2Cl_2 and cooled to 0°, then 17.3 g (0.219 mole) of pyridine and 20.3 g of acetic acid anhydride were added drop by drop. The mixture was stirred for 2 h at room temp., washed with 500 ml N HCl and 500 ml satd. NaCl solution and dried. After evaporation the two diastereomers were separated by cc (silica; acetone/CH_2Cl_2/1 (v/v) for purification and separation, if not stated otherwise).

meso-1,3-Diacetamino-1,3-bis-(2-methoxyphenyl)propane (**32**)

rac-1,3-Diacetamino-1,3-bis-(2-methoxyphenyl)propane (**33**)

From **17**; **32**: 23% crystals, m.p. 201-203° (1,2-dimethoxyethane).- $C_{21}H_{26}N_2O_4$ (370.5) Calcd. C 68.1 H 7.07 N 7.6 Found C 68.1 H 6.88 N 7.6.- FT-IR (KBr): $\tilde{\nu}$ = 3305 m (NH); 3081 w (C-H aromat.); 3000 w,

2965 w, 2936 w (C-H aliph.); 2838 w (OCH_3); 1649 s (C=O); 1601 m (C=C); 1560 s (NH).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.08 (d; ^{3}J = 8.0 Hz, 2H, NH, H/D-exch.), 7.44-6.68 (m; 8H aromat.), 5.12-4.70 (m, ABX_2 and NH-coupling; $^3J_{HNCH}$ = 8.0 Hz, $^3J_{AX}$ = 6.6 Hz, $^3J_{BX}$ = 6.6 Hz, 2H, CH), 3.67 (s; 6H, OCH_3), 2.25 (ABX_2; $^2J_{AB}$ = 13.6 Hz, $^3J_{BX}$ = 6.6 Hz, 1H, CH_2), 1.98 (ABX_2; $^2J_{AB}$ = 13.6 Hz, $^3J_{AX}$ = 6.6 Hz, 1H, CH_2, partial overlap with $COCH_3$-signal), 1.84 (s; 6H $COCH_3$).

33: 13% crystals, m.p. 195-198° (toluene/n-hexane 2/1 (v/v)).- $C_{21}H_{26}N_2O_4$ (370.5) Calcd. C 68.1 H 7.07 N 7.6 Found C 67.8 H 6.87 N 7.4.- FT-IR (KBr): $\tilde{\nu}$ = 3257 s (NH); 3066 m (C-H aromat.); 2936 m (C-H aliph.); 2838 m (OCH_3); 1638 m (C=O); 1601 w (C=C); 1560 s (NH).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 7.88 (d; ^{3}J = 7.5 Hz, 2H, NH, H/D-exch.), 7.47-6.72 (m; 8H aromat.), 5.37-4.93 (m, A_2X_2 and NH-coupling; $^3J_{HNCH}$ = 7.5 Hz, $^3J_{AX}$ = 7.5 Hz, 2H, CH), 3.76 (s; 6H, OCH_3), 2.28 (A_2X_2; $^3J_{AX}$ = 7.5 Hz, 2H, CH_2, partial overlap with $COCH_3$-signal), 1.84 (s; 6H, $COCH_3$).

meso-1,3-Diacetamino-1,3-bis-(3-methoxyphenyl)propane (**34**)

rac-1,3-Diacetamino-1,3-bis-(3-methoxyphenyl)propane (**35**)

From **18**; **34**: 18% crystals, m.p. 170-171° (toluene/EtOAc 2/3 (v/v)).- $C_{21}H_{26}N_2O_4$ (370.5) Calcd. C 68.1 H 7.07 N 7.6 Found C 68.0 H 6.94 N 7.5.- CW-IR (KBr): $\tilde{\nu}$ = 3305 s (NH); 3070 m (C-H aromat.); 2970 m (C-H aliph.); 2850 m (OCH_3); 1655 s (C=O); 1605 s (C=C); 1555 s (NH).- ^{1}H-NMR ($CDCl_3$): δ (ppm/250 MHz) = 7.25-7.18 (m; 2H aromat.), 6.83-6.73 (m; 6H aromat.), 6.58 (d; ^{3}J = 7.6 Hz, 2H, NH), 4.92-4.84 (m, ABX_2 and NH-coupling; $^3J_{HNCH}$ = 7.6 Hz, $^3J_{AX}$ = 6.5 Hz, $^3J_{BX}$ = 6.5 Hz, 2H, CH), 3.76 (s; 6H, OCH_3), 2.34 (ABX_2; $^2J_{AB}$ = 13.6 Hz, $^3J_{BX}$ = 6.5 Hz, 1H, CH_2), 2.18 (ABX_2; $^2J_{AB}$ = 13.6 Hz, $^3J_{AX}$ = 6.5 Hz, 1H, CH_2), 1.93 (s; 6H, $COCH_3$).- EI-MS: m/z (%) = 370 (4, $M^{+\bullet}$); 327 (1; (M - $^\bullet COCH_3)^+$); 268 (15; (327 - $CH_3CONH_2)^+$); 192 (82; (M - $^\bullet$Ar-CH-NHAc)$^+$); 178 (26; (Ar-CH=NH-Ac)$^+$); 150 (95; (192 - CH_2=C=O)$^+$); 136 (100; (178 - CH_2=C=O)$^+$).

35: 24% crystals, m.p. 175-178° (toluene/EtOAc 2/3 (v/v)).- $C_{21}H_{26}N_2O_4$ (370.5) Calcd. C 68.1 H 7.07 N 7.6 Found C 67.9 H 6.89 N 7.5.- CW-IR (KBr): $\tilde{\nu}$ = 3305 s (NH); 3050 m, 3005 w (C-H aromat.); 2960 m, 2945 m (C-H aliph.); 2840 m (OCH_3); 1645 s (C=O); 1600 m (C=C); 1545 s (NH).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.31-7.10 (m; 2H aromat.), 6.89-6.69 (m; 6H aromat.), 6.31 (d; ^{3}J = 7.5 Hz, 2H, NH), 5.04-4.74 (m, A_2X_2 and NH-coupling; $^3J_{HNCH}$ = 7.5 Hz, $^3J_{AX}$ = 7.2 Hz, 2H, CH), 3.77 (s; 6H, OCH_3), 2.39 (A_2X_2; $^3J_{AX}$ = 7.2 Hz, 2H, CH_2), 1.92 (s; 6H, $COCH_3$).- EI-MS: m/z = 370 (4; $M^{+\bullet}$); 268 (16); 192 (89; (M - $^\bullet$Ar-CH-NHAc)$^+$); 178 (28; (Ar-CH=NH-Ac)$^+$); 150 (94; (192 - CH_2=C=O)$^+$); 136 (100; (178 - CH_2=C=O)$^+$).

meso- and rac-1,3-Diacetamino-1,3-bis-(4-methoxyphenyl)propane (**36** and **37**):[1)]

meso- and rac-1,3-Diacetamino-1,3-bis-(3,4-dimethoxyphenyl)propane (**38** and **39**):[1)]

erythro-1,3-Diacetamino-1-(2-fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane (**40**)

threo-1,3-Diacetamino-1-(2-fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane (**41**)

From **22**; **40**: 29% crystals, m.p. 245-248° (EtOH 50%).- $C_{21}H_{25}FN_2O_4$ (388.4) Calcd. C 64.9 H 6.49 N 7.2 Found C 64.9 H 6.70 N 7.3.- FT-IR (KBr): $\tilde{\nu}$ = 3311 s (NH); 3073 w (C-H aromat.); 2927 w (C-H aliph.); 2838 w (OCH_3); 1653 s (C=O); 1626 m, 1588 m (C=C), 1545 s (NH).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.37 (d; ^{3}J = 7.5 Hz, 1H, NH, H/D-exch.), 8.32 (d; ^{3}J = 9.0 Hz, 1H, NH, H/D-exch.), 7.40-6.59 (m; 7H aromat.), 4.99-4.43 (m; 2H, CH), 3.72 (s; 6H, OCH_3), 2.05-1.82 (m; 2H, CH_2, partial overlap with $COCH_3$-signals), 1.82 (s; 3H, $COCH_3$), 1.78 (s; 3H, $COCH_3$).

41: 22% crystals, m.p. 223-226° (EtOH 50%).- $C_{21}H_{25}FN_2O_4$ (388.4) Calcd. C 64.9 H 6.49 N 7.2 Found C 64.6 H 6.54 N 7.3.- FT-IR (KBr): $\tilde{\nu}$ = 3262 m (NH); 3062 w (C-H aromat.); 2942 w (C-H aliph.); 2842 w (OCH_3); 1636 s (C=O); 1588 m (C=C); 1541 s (NH).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.31 (d; ^{3}J = 8.0 Hz, 1H, NH, H/D-exch.), 8.25 (d; ^{3}J = 9.0 Hz, 1H, NH, H/D-exch.), 7.75-6.62 (m; 3H aromat.), 7.24, 6.98 (AA'BB'; $^3J_{AB}$ = 8.4 Hz, 4H aromat.), 5.13-4.67 (m; 2H, CH), 3.78; 3.77 (2s; 6H, OCH_3), 2.05-1.84 (m, 2H, CH_2, partial overlap with $COCH_3$-signal), 1.84 (s; 6H, $COCH_3$).

erythro-1,3-Diacetamino-1-(2-chloro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane (**42**)

threo-1,3-Diacetamino-1-(2-chloro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane (**43**)

From **23**; **42**: 12% crystals, m.p. 251-253° (EtOH 50%).- $C_{21}H_{25}ClN_2O_4$ (404.9) Calcd. C 62.3 H 6.22 N 6.9 Found C 62.3 H 6.23 N 7.0.- FT-IR (KBr): $\tilde{\nu}$ = 3316 s (NH); 3071 m, 3006 w (C-H aromat.); 2944 m, (C-H aliph); 2840 m (OCH_3); 1651 s (C=O); 1609 s (C=C); 1541 s (NH).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.42 (d; ^{3}J = 9.0 Hz, 1H, NH, H/D-exch.), 8.29 (d; ^{3}J = 9.0 Hz, 1H, NH, H/D-exch.), 7.32 (d; ^{3}J = 9.0 Hz, 1H aromat.), 7.14 (d, part of a AA'BB'-system; ^{3}J = 8.5 Hz, 2H aromat.), 7.00-6.75 (m; 4H aromat.), 4.94-4.49 (m; 2H, CH), 3.73 (s; 6H, OCH_3), 2.02-1.86 (m, 2H, CH_2, partial overlap with $COCH_3$-signals), 1.86 (s; 3H, $COCH_3$), 1.79 (s; 3H, $COCH_3$).

43: 17% crystals; m.p. 218-220° (EtOH 50%).- $C_{21}H_{25}ClN_2O_4$ (404.9) Calcd. C 62.3 H 6.22 N 6.9 Found C 62.1 H 6.11 N 7.0.- FT-IR (KBr): $\tilde{\nu}$ = 3262 s (NH); 3062 m, 3002 w (C-H aromat.); 2959 m, 2940 m (C-H aliph.); 2840 m (OCH_3); 1636 s (C=O); 1609 s (C=C); 1541 s (NH).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.28 (d; ^{3}J = 8.5 Hz, 1H, NH, H/D-exch.), 8.14 (d; ^{3}J = 9.0 Hz, 1H, NH, H/D-exch.), 7.46-7.10 (m; 3H aromat.), 7.10-6.67 (m; 4H aromat.), 5.23-4.72 (m; 2H, CH), 3.74 (s; 6H, OCH_3), 2.07-1.87 (m; 2H, CH_2, partial overlap with $COCH_3$-signal), 1.87 (s; 3H, $COCH_3$), 1.79 (s; 3H, $COCH_3$).

erythro-1,3-Diacetamino-1-(2-bromo-4-methoxyphenyl)-3-(4-methoxyphenyl)propane (**44**)

threo-1,3-Diacetamino-1-(2-bromo-4-methoxyphenyl)-3-(4-methoxyphenyl)propane (**45**)

From **24**; **44**: 10% crystals, m.p. 230-232° (EtOH 50%).- $C_{21}H_{25}BrN_2O_4$ (449.4) Calcd. C 56.1 H 5.61 N 6.2 Found C 55.7 H 5.71 N 6.2.- FT-IR (KBr): $\tilde{\nu}$ = 3314 m (C=O); 3069 w (C-H aromat.); 2936 w (C-H aliph.); 2838 w (OCH_3); 1653 s (C=O); 1605 m (C=C); 1543 s (NH).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm/250 MHz) = 8.36 (d; ^{3}J = 8.1 Hz, 1H, NH), 8.21 (d; ^{3}J = 8.1 Hz, 1H, NH), 7.29 (d; ^{3}J = 8.6 Hz, 1H aromat.), 7.16; 6.85 (AA'BB'; $^3J_{AB}$ = 8.7 Hz, 4H aromat.), 7.08-6.92 (m; 2H aromat.), 4.84-4.64 (m; 2H, CH), 3.73 (s; 6H, OCH_3), 1.98-1.89 (m; 2H, CH_2, partial overlap with $COCH_3$-signal), 1.86 (s; 3H, $COCH_3$), 1.78 (s; 3H, $COCH_3$).

45: 5% crystals, m.p. 204-205° (toluene/EtOAc 2/3 (v/v)).- $C_{21}H_{25}BrN_2O_4$ (449.4) Calcd. C 56.1 H 5.61 N 6.2 Found C 56.0 H 5.78 N 6.5.- FT-IR (KBr): $\tilde{\nu}$ = 3266 s (NH); 3062 m, 3000 w (C-H aromat.); 2959 m, 2940 m (C-H aliph.); 2838 m (OCH_3); 1638 s (C=O); 1605 s (C=C); 1541 s (NH).- ^{1}H-NMR ($CDCl_3$ + [D$_6$]DMSO): δ (ppm) = 7.79 (d; ^{3}J = 8.0 Hz, 1H, NH, H/D-exch.), 7.19-6.70 (m; 8H, 7 aromat. H and 1H, NH, H/D-exch.), 5.34-4.87 (m; 2H, CH), 3.76 (s; 6H, OCH_3), 2.28-1.95 (m; 2H, CH_2, partial overlap with $COCH_3$-signal), 1.95 (s; 3H, $COCH_3$), 1.91 (s; 3H, $COCH_3$).

erythro-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(2-methoxyphenyl)propane (**46**)

threo-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(2-methoxyphenyl)propane (**47**)

From **25**; **46**: 31% crystals, m.p. 167-169° (toluene).- $C_{21}H_{24}Cl_2N_2O_4$ (439.3) Calcd. C 57.4 H 5.51 N 6.4 Found C 56.9 H 5.38 N 6.4.- FT-IR (KBr): $\tilde{\nu}$ = 3291 s (NH); 3071 m (C-H aromat.); 2940 m (C-H aliph.); 2838 m (OCH_3); 1655 s (C=O); 1603 s (C=C); 1557 s (NH).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.45-6.63 (m; 6H, 4 aromat. H and 2H, NH, H/D-exch.), 6.89 (s; 2H aromat.), 5.95-5.60 (m; 1H, CH), 5.18-4.87 (m; 1H, CH), 3.79 (s; 6H, OCH_3), 2.50-2.16 (m; 2H, CH_2), 1.99 (s; 3H, $COCH_3$), 1.96 (s; 3H, $COCH_3$).

47: 19% crystals, m.p. 170-173° (toluene/n-hexane 3/1 (v/v)).- $C_{21}H_{24}Cl_2N_2O_4$ (439.3) Calcd. C 57.4 H 5.51 N 6.4 Found C 56.9 H 5.38 N 6.3.- FT-IR (KBr): $\tilde{\nu}$ = 3289 s (NH); 3067 m (C-H aromat.); 2967 m, 2938 m (C-H aliph.); 2838 m (OCH_3); 1655 s (C=O); 1603 s (C=C); 1557 s (NH).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.52-6.91 (m; 4H aromat.), 6.84 (s; 2H aromat.), 6.42 (d; ^{3}J = 7.5 Hz, 1H, NH), 6.06 (d; ^{3}J = 7.5 Hz, 1H, NH), 6.06-5.70 (m; 1H, CH, partial overlap with NH-signal), 5.49-5.03 (m; 1H, CH), 3.76 (s; 6H, OCH_3), 2.55-2.09 (m; 2H, CH_2), 1.88 (s; 3H, $COCH_3$), 1.84 (s; 3H, $COCH_3$).

erythro-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(3-methoxyphenyl)propane (**48**)

threo-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(3-methoxyphenyl)propane (**49**)

From **26**; **48**: 16% crystals, m.p. 170-173° (EtOH 25%).- $C_{21}H_{24}Cl_2N_2O_4$ (439.3) Calcd. C 57.4 H 5.51 N 6.4 Found C 57.5 H 5.47 N 6.3.- FT-IR (KBr): $\tilde{\nu}$ = 3285 s (NH); 3081 m, 3006 w (C-H aromat.); 2942 m (C-H aliph.); 2838 m (OCH_3); 1653 s (C=O); 1603 s (C=C); 1557 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.42 (d; ^{3}J = 8.0 Hz, 1H, NH, H/D-exch.), 8.32 (d; ^{3}J = 8.0 Hz, 1H, NH, H/D-exch.), 7.39-6.63 (m; 4H aromat.), 6.95 (s; 2H aromat.), 5.43-5.12 (m; 1H, CH), 4.67-4.39 (m; 1H, CH), 3.78 (s; 3H, OCH_3), 3.73 (s; 3H, OCH_3), 2.39-2.01 (m; 2H, CH_2), 1.82 (s; 6H, $COCH_3$).

49: 16% crystals, m.p. 174-176° (1,2-dimethoxyethane).- $C_{21}H_{24}Cl_2N_2O_4$ (439.3) Calcd. C 57.4 H 5.51 N 6.4 Found C 57.3 H 5.58 N 6.4.- FT-IR (KBr): $\tilde{\nu}$ = 3276 s (NH); 3067 m, 2996 w (C-H aromat.); 2954 m, 2938 m (C-H aliph.); 2836 m (OCH_3), 1653 s (C=O); 1601 s (C=C); 1557 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm/250 MHz) = 8.21 (d; ^{3}J = 6.9 Hz, 1H, NH), 8.09 (d; ^{3}J = 9.1 Hz, 1H, NH), 7.25-6.76 (m; 4H aromat.), 6.96 (s; 2H aromat.), 5.47-5.40 (m; 1H, CH), 5.05-4.95 (m; 1H, CH), 3.76 (s; 3H, OCH_3), 3.74 (s; 3H, OCH_3), 2.45-2.38 (m; 1H, CH_2), 1.91 (m; 1H, CH_2, partial overlap with $COCH_3$-signals), 1.83 (s; 3H, $COCH_3$), 1.81 (s; 3H, $COCH_3$).

erythro-1,3-Diacetamino-1-(2,6-dichoro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane (**50**)

threo-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane (**51**)

From **27**; **50**: 29% powder, m.p. 234-235° (toluene).- $C_{21}H_{24}Cl_2N_2O_4$ (439.4) Calcd. C 57.4 H 5.51 N 6.4 Found C 57.1 H 5.80 N 6.1.- CW-IR (KBr): $\tilde{\nu}$ = 3260 m (NH); 3090 w, 3030 w (C-H aromat.); 2990 w, 2970 w (C-H aliph.); 2850 m (OCH_3); 1655 s (C=O); 1610 s (C=C); 1560 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm/250 MHz) = 8.35 (d; ^{3}J = 8.0 Hz, 1H, NH), 8.30 (d; ^{3}J = 6.8 Hz, 1H, NH), 7.08; 6.84 (AA'BB', $^3J_{AB}$ = 8.7 Hz, 4H aromat.), 6.95 (s; 2H aromat.), 5.30-5.21 (m; 1H, CH), 4.54-4.45 (m; 1H, CH), 3.76 (s; 3H, OCH_3), 3.71 (s; 3H, OCH_3), 2.36-2.22 (m; 1H, CH_2), 2.20-2.08 (m; 1H, CH_2), 1.81 (s; 3H, $COCH_3$), 1.79 (s; 3H, $COCH_3$).- EI-MS: m/z (%) = 438 (5; ^{35}Cl-$M^{+\cdot}$); 395 (2; (M - $^{\cdot}COCH_3)^+$); 336 (6; (395 - $CH_3CONH_2)^+$); 246 (8; $(C_{10}H_{10}Cl_2NO_2)^+$); 204 (18; (246 - CH_2=C=O)$^+$); 192 (100; $(C_{11}H_{14}NO_2)^+$); 178 (13; $(C_{10}H_{12}NO_2)^+$); 150 (47; (192 - CH_2=C=O)$^+$); 136 (35; (178 - CH_2=C=O)$^+$).

51: 41% powder, m.p. 225-228° (toluene/n-hexane 3/1 (v/v)).- $C_{21}H_{24}Cl_2N_2O_4$ (439.4) Calcd. C 57.4 H 5.51 N 6.4 Found C 57.6 H 5.80 N 6.4.- CW-IR (KBr): $\tilde{\nu}$ = 3280 m (NH); 3070 w, 3000 w (C-H aromat.); 2960 w, 2940 w (C-H aliph.); 2840 m (OCH_3); 1660 s (C=O); 1605 s (C=C); 1560 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm/250 MHz) = 8.30 (d, ^{3}J = 6.0 Hz, 1H, NH, 8.11 (d; ^{3}J = 9.3 Hz, 1H, NH), 7.28; 6.87 (AA'BB', $^3J_{AB}$ = 8.8 Hz, 4H aromat.), 6.97 (s; 2H aromat.), 5.44-5.36 (m; 1H, CH), 5.01-4.92 (m; 1H, CH), 3.76 (s; 3H, OCH_3), 3.72 (s; 3H, OCH_3), 2.47-2.36 (m; 1H, CH_2), 1.90 (m; 1H, CH_2, partial overlap with $COCH_3$-signals), 1.81 (s; 3H, $COCH_3$), 1.80 (s; 3H, $COCH_3$).- EI-MS: m/z (%) = 438 (4; ^{35}Cl-$M^{+\cdot}$); 403 (2; (M - $^{\cdot}Cl)^+$); 395 (3; (M - $^{\cdot}COCH_3)^+$); 336 (8; (395 - $CH_3CONH_2)^+$); 246 (9; $(C_{10}H_{10}Cl_2NO_2)^+$); 204 (17; (246 - CH_2=C=O)$^+$); 192 (100; $(C_{11}H_{14}NO_2)^+$); 178 (11; $(C_{10}H_{12}NO_2)^+$); 150 (44, (192 - CH_2=C=O)$^+$); 136 (29; (178 - CH_2=C=O)$^+$).

meso-1,3-Diacetamino-1,3-bis-(2-fluoro-4-methoxyphenyl)propane (**52**)

rac-1,3-Diacetamino-1,3-bis-(2-fluoro-4-methoxyphenyl)propane (**53**)

From **28**; **52**: 16% crystals, m.p. 245-247° (Me-CO-Et).- $C_{21}H_{24}F_2N_2O_4$ (406.4) Calcd. C 62.1 H 5.95 N 6.9 Found C 61.9 H 5.91 N 6.8.- FT-IR (KBr): $\tilde{\nu}$ = 3318 s (NH); 3077 m, 3008 w (C-H aromat.); 2956 m, 2938 m (C-H aliph.); 2840 m (OCH_3); 1653 s (C=O); 1588 m (C=C); 1545 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.40 (d; ^{3}J = 8.0 Hz, 2H, NH, H/D-exch.), 7.21 (t; ^{3}J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 2H aromat.), 6.85-6.50 (m; 4H aromat.), 4.99-4.64 (m, ABX_2 and NH-coupling; $^3J_{HNCH}$ = 8.0 Hz, $^3J_{AX}$ = 7.5 Hz, $^3J_{BX}$ = 7.5 Hz, 2H, CH), 3.71 (s; 6H, OCH_3), 2.00 (ABX_2; $^2J_{AB}$ = 13.0 Hz, $^3J_{BX}$ = 7.5 Hz, 1H, CH_2), 1.88 (ABX_2; $^2J_{AB}$ = 13.0 Hz, $^3J_{AX}$ = 7.5 Hz, 1H, CH_2, partial overlap with $COCH_3$-signal), 1.78 (s; 6H, $COCH_3$).

53: 13% powder, m.p. 232-234° (EtOH 50%).- $C_{21}H_{24}F_2N_2O_4$ (406.4) Calcd. C 62.1 H 5.95 N 6.9 Found C 62.0 H 5.94 N 6.7.- FT-IR (KBr): $\tilde{\nu}$ = 3268 s (NH); 3067 m, 3013 w (C-H aromat.); 2973 m, 2944 m (C-H aliph.); 2844 m (OCH_3), 1626 s (C=O); 1588 m (C=C); 1543 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.27 (d; ^{3}J = 8.0 Hz, 2H, NH, H/D-exch.), 7.30 (t; ^{3}J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 2H aromat.), 6.94-6.61 (m; 4H aromat.), 5.19-4.80 (m, A_2X_2 and NH-coupling; $^3J_{HNCH}$ = 8.0 Hz, $^3J_{AX}$ = 8.0 Hz, 2H, CH), 3.73 (s; 6H, OCH_3), 2.09 (A_2X_2; $^3J_{AX}$ = 8.0 Hz, 2H, CH_2, partial overlap with $COCH_3$-signal), 1.78 (s; 6H, $COCH_3$).

meso-1,3-Diacetamino-1,3-bis-(2-chloro-4-methoxyphenyl)propane (**54**)

rac-(1,3-Diacetamino-1,3-bis-(2-chloro-4-methoxyphenyl)propane (**55**)

From **29**; **54**: 5% crystals, m.p. 224-226° (EtOH 25%).- $C_{21}H_{24}Cl_2N_2O_4$ (439.3) Calcd. C 57.4 H 5.51 N 6.4 Found C 57.4 H 5.54 N 6.4.- FT-IR (KBr): $\tilde{\nu}$ = 3295 s (NH); 3079 m, 3008 w (C-H aromat.); 2959 m, 2909 w (C-H aliph.); 2840 m (OCH_3), 1653 s (C=O); 1607 s (C=C); 1560 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.29 (d; ^{3}J = 7.5 Hz, 2H, NH, H/D-exch.), 7.32 (d; ^{3}J = 8.0 Hz, 2H aromat.), 7.00-6.68 (m; 4H aromat.), 5.07-4.73 (m, ABX_2 and NH-coupling; $^3J_{HNCH}$ = 8.0 Hz, $^3J_{AX}$ = 7.5 Hz, $^3J_{BX}$ = 7.5 Hz, 2H, CH), 3.70 (s; 6H, OCH_3), 2.10 (ABX_2; $^2J_{AB}$ = 13.0 Hz, $^3J_{BX}$ = 7.5 Hz, 1H, CH_2), 1.90 (ABX_2; $^2J_{AB}$ = 13.0 Hz, $^3J_{AX}$ = 7.5 Hz, 1H, CH_2, partial overlap with $COCH_3$-signal), 1.80 (s; 6H, $COCH_3$).- EI-MS: m/z (%) = 438 (1; ^{35}Cl-$M^{+\cdot}$); 403 (18; (M - $^{\cdot}Cl)^+$, *ortho*-effect); 226 (34; $(C_{11}H_{13}ClNO_2)^+$); 212 (21; $(C_{10}H_{11}ClNO_2)^+$); 184 (36; (226 - CH_2=C=O)$^+$); 170 (100).

55: 2% crystals, m.p. 240-252 (EtOH 50%).- $C_{21}H_{24}Cl_2N_2O_4$ (439.3) Calcd. C 57.4 H 5.51 N 6.4 Found C 57.6 H 5.56 N 6.4.- FT-IR (KBr): $\tilde{\nu}$ = 3266 s (NH); 3064 m, 3013 w (C-H aromat.), 2967 m, 2946 m (C-H aliph.); 2842 m (OCH_3); 1643 s (C=O), 1607 s (C=C); 1541 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm/250 MHz) = 8.13 (d; ^{3}J = 8.5 Hz, 2H, NH), 7.40 (d; ^{3}J = 8.5 Hz, 2H aromat.), 6.95-6.88 (m; 4H aromat.), 5.22-5.13 (m, A_2X_2 and NH-coupling; $^3J_{HNCH}$ = 8.5 Hz, $^3J_{AX}$ = 7.4 Hz, 2H, CH),

3.74 (s; 6H, OCH_3), 1.94 (A_2X_2; $^3J_{AX}$ = 7.4 Hz, 2H, CH_2), 1.79 (s; 6H, $COCH_3$).- EI-MS: m/z (%) = 403 (17; (M - $^{\bullet}Cl)^+$, *ortho*-effect); 226 (43; $(C_{11}H_{13}ClNO_2)^+$); 212 (34; $(C_{10}H_{11}ClNO_2)^+$); 184 (38; (226 - CH_2=C=O)$^+$); 170 (100).

erythro-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(2-fluoro-4-methoxyphenyl)propane (**56**)

threo-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(2-fluoro-4-methoxyphenyl)propane (**57**)

From **30**; **56**: 6% powder, m.p. 231-234° (toluene/n-hexane 2/1 (v/v)).- $C_{21}H_{23}Cl_2FN_2O_4$ (457.3) Calcd. C 55.2 H 5.07 N 6.1 Found C 55.6 H 5.59 N 6.0.- FT-IR (KBr): $\tilde{\nu}$ = 3450 s, 3293 s (NH); 3081 m (C-H aromat.); 2936 m (C-H aliph.); 2851 m (OCH_3); 1655 s (C=O); 1628 s, 1603 s (C=C), 1557 s (NH).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.16 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 1H aromat.), 7.31-6.62 (m; 6H, 4 aromat. H and 2H, NH), 6.25-5.84 (m; 1H, CH), 5.44-5.03 (m; 1H, CH), 3.76 (s; 6H, OCH_3), 2.55-2.17 (m; 2H, CH_2), 1.95 (s; 6H, $COCH_3$).

57: 5% powder, m.p. 234-237° (toluene/n-hexane 2/1 (v/v)).- $C_{21}H_{23}Cl_2FN_2O_4$ (457.3) Calcd. C 55.2 H 5.07 N 6.1 Found C 55.5 H 5.32 N 6.0.- FT-IR (KBr): $\tilde{\nu}$ = 3401 s, 3297 s (NH); 3081 m (C-H aromat.); 2940 m (C-H aliph.); 2842 m (OCH_3); 1655 s (C=O), 1626 s, 1603 s (C=C); 1557 s (NH).- ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.29 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 1H aromat.), 7.12-6.79 (m; 4H aromat.), 6.68 (d; ^3J = 9.5 Hz, 1H, NH), 6.42 (d; ^3J = 9.0 Hz, 1H, NH), 6.02-5.67 (m; 1H, CH), 5.39-4.95 (m; 1H, CH), 3.76 (s; 6H, OCH_3), 2.52-2.05 (m; 2H, CH_2), 1.98 (s; 6H, $COCH_3$).

erythro-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(2-chloro-4-methoxyphenyl)propane (**58**)

threo-1,3-Diacetamino-1-(2,6-dichloro-4-methoxyphenyl)-3-(2-chloro-4-methoxyphenyl)propane (**59**)

From **31**; purification by cc as stated; separation: cc on RP-18, acetonitrile/water 97.5/2.5 (v/v).

58: 5% crystals, m.p. 232-235° (EtOH 25%).- $C_{21}H_{23}Cl_3N_2O_4$ (473.8) Calcd. C 53.2 H 4.89 N 5.9 Found C 53.5 H 5.05 N 5.6.- FT-IR (KBr): $\tilde{\nu}$ = 3434 s, 3299 s (NH); 3083 w (C-H aromat.); 2932 w (C-H aliph.), 2838 w (OCH_3); 1655 s (C=O); 1605 s (C=C); 1557 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm/250 MHz) = 8.51 (d; ^3J = 7.6 Hz, 1H, NH, H/D-exch.), 8.28 (d; ^3J = 6.6 Hz, 1H, NH, H/D-exch.), 7.23 (d; ^3J = 9.3 Hz, 1H aromat.), 6.96 (s; 2H aromat.), 6.91-6.86 (m; 2H aromat.), 5.44-5.35 (m; 1H, CH), 4.76-4.70 (m; 1H, CH), 3.77 (s, 3H, OCH_3), 3.73 (s; 3H, OCH_3), 2.40-2.22 (m; 1H, CH_2), 2.19-1.98 (m; 1H, CH_2), 1.83 (s; 3H, $COCH_3$), 1.79 (s; 3H, $COCH_3$).

59: 4% crystals, m.p. 227-230° (EtOH 25%).- $C_{21}H_{23}Cl_3N_2O_4$ (473.8) Calcd. C 53.2 H 4.89 N 5.9 Found C 53.1 H 4.64 N 5.7.- FT-IR (KBr): $\tilde{\nu}$ = 3448 m, 3293 m (NH); 3081 m, 3008 w (C-H aromat.); 2942 m (C-H aliph.); 2838 m (OCH_3); 1655 s (C=O); 1605 s (C=C); 1557 s (NH).- ^{1}H-NMR ([D_6]DMSO): δ (ppm/250 MHz) = 8.06 (d; ^3J = 8.7 Hz, 1H, NH, H/D-exch.), 7.98 (d; ^3J = 7.2 Hz, 1H, NH, H/D-exch.), 7.38 (d; ^3J = 8.7 Hz, 1H aromat.), 7.25-7.14 (m; 1H aromat.), 6.98 (s; 2H aromat.), 6.93-6.88 (m; 1H aromat.), 5.54-5.45 (m; 1H, CH), 5.22-5.15 (m; 1H, CH), 3.76 (s; 3H, OCH_3), 3.75 (s; 3H, OCH_3), 2.50-2.30 (m; 1H, CH_2, partial overlap with solvent signals), 2.18-1.98 (m; 1H, CH_2), 1.80 (s; 3H, $COCH_3$), 1.75 (s; 3H, $COCH_3$).

Methoxy-substituted 1,3-diphenylpropane-1,3-diamines

The solution of 3.24 mmole of the respective 1,3-diacetamino-1,3-diphenylpropane in 60 ml of 2N HCl and 30 ml of dioxane was heated under reflux for 12 h. After cooling to room temp. the solvents were evaporated *in vacuo* and the residue was stirred with 10 ml of acetone. The precipitated 1,3-diphenylpropane-1,3-diamine-dihydrochloride was filtered off by suction and dried at the oil pump. Because purification of these dihydrochlorides is laborious and mostly unsuccessful, the bases were liberated (cf. section: *Hydroxy-substituted 1,3-diphenylpropane-1,3-diamines*) and converted to the dipicrates by dissolving 0.2 g of the pertinent base in 5 ml of EtOH 96% and adding 5 ml of a satd. solution of picric acid in EtOH 96%. After 12 h the crystalline (yellow) dipicrates - analytically pure in most cases - are obtained. They melt under decomposition. Yields are related to the dihydrochlorides.

meso-1,3-Bis-(2-methoxyphenyl)propane-1,3-diamine dipicrate (**60**)

From **32**; 79%, m.p. 183-187°.- $C_{17}H_{22}N_2O_2$ x 2 $C_6H_3N_3O_7$ (744.6) Calcd. C 46.8 H 3.79 N 15.1 Found C 46.8 H 3.80 N 15.0.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3060 w (C-H aromat.); 2973 w, 2946 w (C-H aliph.); 2844 w (OCH_3); 1613 s (NH_3^+); 1568 s (C=C); 1539 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.60 (s; 4H aromat.), 8.23 (s, br; 6H, NH_3^+, H/D-exch.), 7.39-6.70 (m; 8H aromat.), 4.39 (s, br; 2H, CH), 3.67 (s; 6H, OCH_3), 2.56 (m; 2H, CH_2, partial overlap with solvent signals).

rac-1,3-Bis-(2-methoxyphenyl)propane-1,3-diamine dipicrate (**61**)

From **33**; 67%, m.p. 186-190°.- $C_{17}H_{22}N_2O_2$ x 2 $C_6H_3N_3O_7$ (744.6) Calcd. C 46.8 H 3.79 N 15.1 Found C 46.6 H 3.57 N 14.9.- FT-IR (KBr): $\tilde{\nu}$ = 3260-2800 m, br (NH_3^+); 3010 w (C-H aromat.); 2969 w, 2940 w (C-H aliph.); 2838 w (OCH_3); 1628 s, 1615 s (NH_3^+); 1570 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.67 (s; 4H aromat.), 8.23 (s, br; 6H, NH_3^+, H/D-exch.), 7.60-6.91 (m; 8H aromat.), 3.74 (s; 6H, OCH_3), 3.35 (m; 2H, CH, partial overlap with solvent signals), 2.56 (m; 2H, CH_2, partial overlap with solvent signals).

meso-1,3-Bis-(3-methoxyphenyl)propane-1,3-diamine dipicrate (**62**)

From **34**; 75%, m.p. 224-225° (EtOH 50%).- $C_{17}H_{22}N_2O_2$ x 2 $C_6H_3N_3O_7$ (744.6) Calcd. C 46.8 H 3.79 N 15.1 Found C 46.8 H 3.82 N 14.8.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3006 w (C-H aromat.); 2957 w, 2919 w (C-H aliph.); 2842 w (OCH_3), 1632 s, 1611 s (NH_3^+); 1568 s (C=C); 1535 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.65 (s; 4H aromat.), 8.39 (s, br; 6H, NH_3^+, H/D-exch.), 7.43-6.60 (m; 8H aromat.), 4.16 (s, br; 2H, CH), 3.73 (s; 6H, OCH_3), 2.55 (m; 2H, CH_2, partial overlap with solvent signals).

rac-1,3-Bis-(3-methoxyphenyl)propane-1,3-diamine dipicrate x 0.5 H_2O (**63**)

From **35**; 62%, m.p. 222-225° (EtOH 50%).- $C_{17}H_{22}N_2O_2$ x 2 $C_6H_3N_3O_7$ x 0.5 H_2O (753.6) Calcd. C 46.2 H 3.88 N 14.9 Found C 46.2 H 3.86 N 14.6.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+ and H_2O); 3077 w, 3004 w (C-H aromat.); 2975 w (C-H aliph.); 2844 w (OCH_3); 1638 s, 1605 s (NH_3^+); 1570 s (C=C); 1545 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.63 (s; 4H aromat.), 8.27 (s, br; 6H, NH_3^+, H/D-exch.), 7.59-6.81 (m; 8H aromat.), 3.72 (s; 6H, OCH_3); 3.42 (m; 2H, CH, partial overlap with solvent signals), 2.60 (m; 2H, CH_2, partial overlap with solvent signals).

meso-1,3-Bis-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**64**)

From **36**; 63%, m.p. 190-194°. For **64**-dihydrochloride cf. lit.[1].

rac-1,3-Bis-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**65**)

From **37**; 72%, m.p. 193-197°. For **65**-dihydrochloride cf. lit.[1].

meso-1,3-Bis-(3,4-dimethoxyphenyl)propane-1,3-diamine dipicrate (**66**):[1].

rac-1,3-Bis-(3,4-dimethoxyphenyl)propane-1,3-diamine (**67**):[1].

erythro-1-(2-Fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**68**)

From **40**; 63%, m.p. 197-202°.- $C_{17}H_{21}FN_2O_2$ x 2 $C_6H_3N_3O_7$ (762.6) Calcd. C 45.7 H 3.57 N 14.7 Found C 45.6 H 3.64 N 14.5.- FT-IR (KBr): $\tilde{\nu}$ = 3200-2800 m, br (NH_3^+); 3062 w, 3019 w (C-H aromat.); 2967 w, 2938 w (C-H aliph.); 2844 w (OCH_3); 1611 s (NH_3^+); 1588 w, 1568 s (C=C); 1541 (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.65 (s; 4H aromat.), 8.29 (s, br; 6H, NH_3^+, H/D-exch.), 7.25-6.51 (m; 7H aromat.), 4.30 (s, br; 2H, CH), 3.69 (s; 6H, OCH_3), 2.50 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2-Fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**69**)

From **41**; 55%; m.p. 205-210°.- $C_{17}H_{21}FN_2O_2$ x 2 $C_6H_3N_3O_7$ (762.6) Calcd. C 45.7 H 3.57 N 14.7 Found C 45.5 H 3.52 N 14.4.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+), 3058 w (C-H aromat.); 2938 w (C-H aliph.); 2844 w (OCH_3); 1615 s (NH_3^+); 1572 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.59 (s; 4H aromat.), 8.18 (s, br; 6H, NH_3^+, H/D-exch.), 7.45 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 1H aromat.), 7.32-6.76 (m; 6H aromat.), 3.77 (s; 3H, OCH_3), 3.74 (s; 3H, OCH_3), 3.66 (m; 2H, CH, partial overlap with solvent signals), 2.58-2.49 (m; 2H, CH_2, partial overlap with solvent signals).

erythro-1-(2-Chloro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**70**)

From **42**; 69%, m.p. 193-197°.- $C_{17}H_{21}ClN_2O_2$ x 2 $C_6H_3N_3O_7$ (778.1) Calcd. C 44.8 H 3.50 N 14.4 Found C 44.6 H 3.51 N 14.1.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3060 w (C-H aromat.); 2936 w (C-H aliph.); 2844 w (OCH_3); 1613 s (NH_3^+); 1572 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.67 (s; 4H aromat.), 8.37 (s, br; 6H, NH_3^+, H/D-exch.), 7.52-6.76 (m; 7H aromat.), 4.37 (s, br; 2H, CH), 3.70 (s; 6H, OCH_3), 2.45 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2-Chloro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**71**)

From **43**; 74%, m.p. 205-210°.- $C_{17}H_{21}ClN_2O_2$ x 2 $C_6H_3N_3O_7$ (778.1) Calcd. C 44.8 H 3.50 N 14.4 Found C 44.7 H 3.49 N 14.4.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3058 w (C-H aromat.); 2934 w (C-H aliph.); 2844 w (OCH_3); 1615 s (NH_3^+); 1572 s (C=C); 1535 s (NO_2).-^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.61 (s; 4H aromat.), 8.23 (s, br; 6H, NH_3^+, H/D-exch.), 7.63 (d; ^3J = 8.8 Hz, 1H aromat.), 7.34-6.86 (m; 6H aromat.), 4.27-3.94 (m; 2H, CH), 3.90 (s; 3H, OCH_3); 3.85 (s; 3H, OCH_3), 2.81-2.56 (m; 2H, CH_2).

erythro-1-(2-Bromo-4-methoxyphenyl)-3-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**72**)

From **44**; 61%, m.p. 189-192°.- $C_{17}H_{21}BrN_2O_2$ x 2 $C_6H_3N_3O_7$ (825.5) Calcd. C 42.2 H 3.30 N 13.6 Found C 42.2 H 3.27 N 13.6.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+), 3079 w, 3060 w, 3013 w (C-H aromat.); 2936 w (C-H aliph.); 2842 w (OCH_3); 1613 s (NH_3^+); 1572 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.69 (s; 4H aromat.), 8.32 (s, br; 6H, NH_3^+, H/D-exch.), 7.50-6.78 (m; 7H aromat.), 4.35 (s, br; 2H, CH), 3.79 (s; 6H, OCH_3); 2.42 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2-Bromo-4-methoxyphenyl)-3-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**73**)

From **45**; 54%, m.p. 191-194°.- $C_{17}H_{21}BrN_2O_2$ x 2 $C_6H_3N_3O_7$ (825.5) Calcd. C 42.2 H 3.30 N 13.6 Found C 42.1 H 3.55 N 13.5.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3058 w, 3004 (C-H aromat.); 2932 w (C-H aliph.); 2844 w (OCH_3); 1615 s (NH_3^+); 1572 s (C=C), 1535 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.69 (s; 4H aromat.), 8.28 (s, br; 6H, NH_3^+, H/D-exch.), 7.71 (d; ^3J = 8.8 Hz, 1H aromat.), 7.41-6.95 (m; 6H aromat.), 4.29-3.99 (m; 2H, CH), 3.89 (s; 3H, OCH_3), 3.85 (s; 3H, OCH_3), 2.83-2.57 (m; 2H, CH_2).

erythro-1-(2,6-Dichloro-4-methoxyphenyl)-3-(2-methoxyphenyl)propane-1,3-diamine dipicrate (**74**)

From **46**; 67%, m.p. 186-190°.- $C_{17}H_{20}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (813.5) Calcd. C 42.8 H 3.22 N 13.8 Found C 42.5 H 3.32 N 13.6.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3060 w (C-H aromat.); 2942 w (C-H aliph.), 2846 w (OCH_3); 1613 s (NH_3^+); 1568 s (C=C); 1535 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.60 (s; 4H aromat.), 8.23 (s, br; 6H, NH_3^+, H/D-exch.), 7.39-6.75 (m; 4H aromat.), 6.94 (s; 2H aromat.), 4.96-4.63 (m; 1H, CH), 4.60-4.24 (m; 1H, CH), 3.72 (s; 6H, OCH_3), 3.06-2.64 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2,6-Dichloro-4-methoxyphenyl)-3-(2-methoxyphenyl)propane-1,3-diamine dipicrate (**75**)

From **47**; 73%, m.p. 192-196°.- $C_{17}H_{20}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ x H_2O (831.5) Calcd. C 41.9 H 3.39 N 13.5 Found C 42.2 H 3.27 N 13.4.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+ and H_2O); 3081 w (C-H aromat.); 2977 w (C-H aliph.); 2844 w (OCH_3), 1615 s (NH_3^+); 1572 s (C=C); 1539 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.60 (s; 4H aromat.), 8.32 (s, br; 6H, NH_3^+, H/D-exch.), 7.30-6.65 (m; 6H aromat.), 4.61-4.23 (m; 2H, CH), 3.84 (s; 3H, OCH_3), 3.81 (s; 3H, OCH_3), 3.00-2.57 (m; 2H, CH_2, partial overlap with solvent signals).

erythro-1-(2,6-dichloro-4-methoxyphenyl)-3-(3-methoxyphenyl)propane-1,3-diamine dipicrate (**76**)

From **48**; 65%, m.p. 211-215°.- $C_{17}H_{20}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (813.5) Calcd. C 42.8 H 3.22 N 13.8 Found C 42.8 H 3.21 N 13.7.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3081 w, 3015 w (C-H aromat.); 2942 w (C-H aliph.); 2844 w (OCH_3); 1613 s (NH_3^+); 1572 s (C=C); 1535 s (NO_2).-^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.60 (s; 4H aromat.), 8.39 (s, br; 6H, NH_3^+, H/D-exch.), 7.27-6.69 (m; 4H aromat.), 6.83 (s; 2H aromat.), 4.82-4.59 (m; 1H, CH), 4.35-4.12 (m; 1H, CH), 3.69 (s; 3H, OCH_3), 3.67 (s; 3H, OCH_3), 3.06-2.59 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2,6-Dichloro-4-methoxyphenyl)-3-(3-methoxyphenyl)propane-1,3-diamine dipicrate (**77**)

From **49**; 70%, m.p. 215-219°.- $C_{17}H_{20}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (813.5) Calcd. C 42.8 H 3.22 N 13.8 Found C 43.0 H 3.26 N 13.8.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3064 w (C-H aromat.); 2963 w, 2944 w (C-H aliph.); 2842 w (OCH_3); 1616 s (NH_3^+); 1572 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.61 (s; 4H aromat.), 8.32 (s, br; 6H, NH_3^+, H/D-exch.), 7.49-6.80 (m; 4H aromat.), 6.93 (s; 2H, aromat.), 4.66-4.18 (m; 2H, CH), 3.81 (s; 3H, OCH_3), 3.74 (s; 3H, OCH_3), 3.11-2.60 (m; 2H, CH_2, partial overlap with solvent signals).

erythro-1-(2,6-Dichloro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**78**)

From **50**; 67%, m.p. 163-166°.- $C_{17}H_{20}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (813.5) Calcd. C 42.8 H 3.22 N 13.8 Found C 42.4 H 3.24 N 13.6.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3079 w (C-H aromat.); 2936 w (C-H aliph.), 2842 w (OCH_3); 1613 s (NH_3^+); 1572 s (C=C); 1535 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.67 (s; 4H aromat.), 8.31 (s, br; 6H, NH_3^+, H/D-exch.), 7.29, 6.80 (AA'BB', $^3J_{AB}$ = 8.0 Hz, 4H aromat.), 6.89 (s; 2H aromat.), 4.90-4.60 (m; 1H, CH), 4.48-4.10 (m; 1H, CH), 3.73 (s; 3H, OCH_3), 3.70 (s; 3H, OCH_3), 3.09-2.64 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2,6-Dichloro-4-methoxyphenyl)-3-(4-methoxyphenyl)propane-1,3-diamine dipicrate (**79**)

From **51**; 70%, m.p. 168-170°.- $C_{17}H_{20}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (813.5) Calcd. C 42.8 H 3.22 N 13.8 Found C 42.5 H 3.30 N 13.5.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3083 w, 3035 w, 3008 w (C-H aromat.); 2957 w, 2936 w (C-H aliph.); 2844 w (OCH_3); 1613 s (NH_3^+); 1572 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.65 (s; 4H aromat.), 8.23 (s, br; 6H, NH_3^+, H/D-exch.), 7.31, 6.97 (AA'BB', $^3J_{AB}$ = 8.0 Hz, 4H aromat.), 7.05 (s; 2H aromat.), 4.68-4.25 (m; 2H, CH), 3.83 (s; 3H, OCH_3), 3.77 (s; 3H, OCH_3), 3.12-2.62 (m; 2H, CH_2, partial overlap with solvent signals).

meso-1,3-Bis-(2-fluoro-4-methoxyphenyl)propane-1,3-diamine dipicrate (**80**)

From **52**; 71%, m.p. 190-193°.- $C_{17}H_{20}F_2N_2O_2$ x 2 $C_6H_3N_3O_7$ x H_2O (798.6) Calcd. C 43.6 H 3.53 N 14.0 Found C 43.7 H 3.60 N 13.9.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+ and H_2O); 3079 w (C-H aromat.); 2940 w (C-H aliph.); 2844 w (OCH_3); 1630 s, 1615 s (NH_3^+), 1572 s (C=C), 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.66 (s; 4H aromat.), 8.33 (s, br; 6H, NH_3^+, H/D-exch.), 7.26 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 2H aromat.), 6.80-6.42 (m; 4H aromat.), 4.43 (s, br; 2H, CH), 3.66 (s; 6H, OCH_3), 2.60 (m; 2H, CH_2, partial overlap with solvent signals).

rac-1,3-Bis-(2-fluoro-4-methoxyphenyl)propane-1,3-diamine dipicrate x H_2O (**81**)

From **53**; 81%, m.p. 193-197°.- $C_{17}H_{20}F_2N_2O_2$ x 2 $C_6H_3N_3O_7$ x H_2O (798.6) Calcd. C 43.6 H 3.53 N 14.0 Found C 43.6 H 3.36 N 13.7.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+ and H_2O); 3058 w (C-H aromat.); 2938 w (C-H aliph.), 2846 w (OCH_3); 1626 s, 1615 s (NH_3^+); 1574 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.68 (s; 4H aromat.), 8.27 (s, br; 6H, NH_3^+, H/D-exch.), 7.43 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 2H aromat.), 7.18-6.83 (m; 4H aromat.), 3.81 (s; 6H, OCH_3), 3.49 (m; 2H, CH, overlap with solvent signals), 2.62 (m; 2H, CH_2, overlap with solvent signals).

meso-1,3-Bis-(2-chloro-4-methoxyphenyl)propane-1,3-diamine dipicrate (**82**)

From **54**; 64%, m.p. 175-179°.- $C_{17}H_{20}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (813.5) Calcd. C 42.8 H 3.22 N 13.8 Found C 42.5 H 3.20 N 13.8.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+), 3058 w (C-H aromat.); 2934 w (C-H aliph.); 2842 w (OCH_3); 1613 s (NH_3^+); 1574 s (C=C); 1535 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.62 (s; 4H aromat.), 8.37 (s, br; 6H, NH_3^+, H/D-exch.), 7.30 (d; ^3J = 9.0 Hz, 2H aromat.), 6.94-6.69 (m; 4H aromat.), 4.63 (s, br; 2H, CH), 3.73 (s; 6H, OCH_3), 2.58 (m; 2H, CH_2, partial overlap with solvent signals).

rac-1,3-Bis-(2-chloro-4-methoxyphenyl)propane-1,3-diamine dipicrate (**83**)

From **55**; 65%, m.p. 179-183°.- $C_{17}H_{20}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (813.5) Calcd. C 42.8 H 3.22 N 13.8 Found C 43.1 H 3.32 N 13.7.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3058 w (C-H aromat.); 2930 w (C-H aliph.); 2846 w (OCH_3); 1613 s (NH_3^+); 1572 s (C=C); 1533 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.58 (s; 4H aromat.), 8.23 (s, br; 6H, NH_3^+, H/D-exch.), 7.22 (d; ^3J = 9.0 Hz, 2H aromat.), 7.11-6.88 (m; 4H aromat.), 3.81 (s; 6H, OCH_3), 3.20 (m; 2H, CH, overlap with solvent signals), 2.58 (m; 2H, CH_2, overlap with solvent signals).

erythro-1-(2,6-Dichloro-4-methoxyphenyl)-3-(2-fluoro-4-methoxyphenyl)propane-1,3-diamine dipicrate (**84**)

From **56**; 72%, m.p. 202-205°.- $C_{17}H_{19}Cl_2FN_2O_2$ x 2 $C_6H_3N_3O_7$ (831.5) Calcd. C 41.9 H 3.03 N 13.5 Found C 41.9 H 2.92 N 14.2.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3081 w (C-H aromat.); 2938 w (C-H aliph.); 2844 w (OCH_3); 1613 s (NH_3^+); 1572 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.65 (s; 4H aromat.), 8.34 (s, br; 6H, NH_3^+, H/D-exch.), 7.35 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 1H aromat.), 7.00-6.47 (m; 4H aromat.), 5.01-4.72 (m; 1H, CH), 4.69-4.39 (m; 1H, CH), 3.75 (s; 6H, OCH_3), 3.17-2.61 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2,6-Dichloro-4-methoxyphenyl)-3-(2-fluoro-4-methoxyphenyl)propane-1,3-diamine dipicrate (**85**)

From **57**; 61%, m.p. 206-210°.- $C_{17}H_{19}Cl_2FN_2O_2$ x $C_6H_3N_3O_7$ (831.5) Calcd. C 41.9 H 3.03 N 13.5 Found C 42.0 H 2.96 N 13.3.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3087 w (C-H aromat.); 2940 w (C-H aliph.); 2844 w (OCH_3); 1628 s, 1613 s (NH_3^+); 1574 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.70 (s; 4H aromat.), 8.43 (s, br; 6H, NH_3^+, H/D-exch.), 7.54 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 1H aromat.), 7.32-6.74 (m; 4H aromat.), 4.71-4.39 (m; 2H, CH), 3.80 (s, 6H, OCH_3), 3.21-2.68 (m; 2H, CH_2, partial overlap with solvent signals).

erythro-1-(2,6-Dichloro-4-methoxyphenyl)-3-(2-chloro-4-methoxyphenyl)propane-1,3-diamine dipicrate (**86**)

From **58**; 67%, m.p. 200-203°.- $C_{17}H_{19}Cl_3N_2O_2$ x 2 $C_6H_3N_3O_7$ (847.9) Calcd. C 41.1 H 2.97 N 13.2 Found C 41.1 H 2.89 N 13.1.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3085 w (C-H aromat.); 2936 w (C-H aliph.); 2844 w (OCH_3); 1611 s (NH_3^+); 1574 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.63 (s; 4H aromat.), 8.39 (s, br; 6H, NH_3^+, H/D-exch.), 7.34 (d; ^3J = 7.5 Hz, 1H aromat.), 7.01-6.68 (m; 2H aromat.), 6.92 (s; 2H aromat.), 5.00-4.76 (m; 1H, CH), 4.76-4.55 (m; 1H, CH), 3.72 (s; 6H, OCH_3), 3.15-2.62 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2,6-Dichloro-4-methoxyphenyl)-3-(2-chloro-4-methoxyphenyl)propane-1,3-diamine dipicrate (**87**)

From **59**; 76%, m.p. 205-208°.- $C_{17}H_{19}Cl_3N_2O_2$ x 2 $C_6H_3N_3O_7$ (847.9) Calcd. C 41.1 H 2.97 N 13.2 Found C 40.8 H 2.94 N 13.2.- FT-IR (KBr): $\tilde{\nu}$ = 3250-2800 m, br (NH_3^+); 3083 w (C-H aromat.); 2942 w (C-H aliph.); 2849 w (OCH_3); 1611 s (NH_3^+); 1572 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.61 (s; 4H aromat.), 8.39 (s, br; 6H, NH_3^+, H/D-exch.), 7.59 (d; ^3J = 9.0 Hz, 1H aromat.), 7.27-7.11 (m; 3H aromat.), 7.05 (s; 2H aromat.), 4.62-4.21 (m; 2H, CH), 3.80 (s; 6H, OCH_3), 3.25-2.71 (m; 2H, CH_2, partial overlap with solvent signals).

Hydroxy-substituted 1,3-diphenylpropane-1,3-diamines

To 2.8 mmole of the pertinent methoxy-substituted 1,3-diphenylpropane-1,3-diamine dihydrochloride, dissolved in 10 ml of water, were added 5 ml of 2N NaOH and the corresponding base was separated by threefold extraction with 30 ml CH_2Cl_2 each. After washing with 50 ml of water and 50 ml of satd. NaCl solution, drying and evaporation the base was obtained as a colourless oil.- To 1.75 mmole of base in 50 ml of absol. CH_2Cl_2 were added 3.51 g (14.0 mmole) BBr_3 in 5 ml of absol. CH_2Cl_2 at -70° under vigorous stirring. Then the mixture was allowed to warm up to room temp., heated to reflux for 6 h and stirred for 12 h at room temp. Within 30 min 30 ml of absol. MeOH were added drop by drop under ice cooling, then the mixture was evaporated to dryness *in vacuo*. After addition of 20 ml of acetone the crystalline dihydrobromides were filtered by suction. Because only some of these salts can be purified, the bases of the other compounds were liberated by filtration over silica using the solvent mentioned for the preparation of the corresponding Pt(II)-complex (cf. following paper). Liberation of the bases as described for the dihydrochlorides (see above) is unsuccessful in most cases!- The bases are characterized as dipicrates by dissolving 0.1 g of base in 2.5 ml of EtOH, adding 2.5 ml of a satd. solution of picric acid, careful evaporation of EtOH on the

steam bath, dissolving the residue in boiling water and filtration whilst hot. After standing overnight the analytically pure (yellow) dipicrates can be filtered and dried at 60° at the oil pump. They melt under decomposition.

meso-1,3-Bis-(3-hydroxyphenyl)propane-1,3-diamine dipicrate (**88**)

From **62** x 2 HCl; 91 % dihydrobromide; dipicrate m.p. 172-175°.- $C_{15}H_{18}N_2O_2$ x 2 $C_6H_3N_3O_7$ (716.6) Calcd. C 45.3 H 3.38 N 15.6 Found C 45.3 H 3.44 N 15.3.- FT-IR (KBr): $\tilde{\nu}$ = 3422 m, br (OH); 3300-2700 m, br (NH_3^+); 3089 w (C-H aromat); 2927 w (C-H aliph.); 1634 s, 1613 s (NH_3^+); 1564 s (C=C); 1516 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.65 (s; 4H aromat.), 8.42 (s, br; 6H, NH_3^+, H/D-exch.), 7.39-6.69 (m; 8H aromat.), 4.23-3.92 (m; 2H, CH), 2.35 (m; 2H, CH_2, partial overlap with solvent signals).

rac-1,3-Bis-(3-hydroxyphenyl)propane-1,3-diamine dipicrate (**89**)

From **63** x 2 HCl; 88% dihydrobromide; dipicrate m.p. 185-188°.- $C_{15}H_{18}N_2O_2$ x 2 $C_6H_3N_3O_7$ (716.6) Calcd. C 45.3 H 3.38 N 15.6 Found C 44.9 H 3.63 N 15.4.- FT-IR (KBr): $\tilde{\nu}$ = 3484 m, br (OH); 3300-2700 m, br (NH_3^+); 3067 w (C-H aromat.); 2930 w (C-H aliph.); 1618 s (NH_3^+); 1595 s, 1576 s (C=C); 1545 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.63 (s; 4H aromat.), 8.39 (s, br; 6H, NH_3^+, H/D-exch.), 7.43-6.69 (m; 8H aromat.), 3.86-3.54 (m; 2H, CH), 2.32 (m; 2H, CH_2, partial overlap with solvent signals).

meso-1,3-Bis-(4-hydroxyphenyl)propane-1,3-diamine dihydrobromide (**90**):[1].

rac-1,3-Bis-(4-hydroxyphenyl)propane-1,3-diamine dihydrobromide (**91**):[1].

meso-1,3-Bis-(3,4-dihydroxyphenyl)propane-1,3-diamine dihydrobromide (**92**):[1].

rac-1,3-Bis-(3,4-dihydroxyphenyl)propane-1,3-diamine dihydrobromide (**93**):[1].

erythro-1-(2-Fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamine dihydrobromide (**94**)

From **68** x 2 HCl; recrystallization from HBr 62%/water (2/1; v/v), 65%, m.p. 167-169°.- $C_{15}H_{17}FN_2O_2$ x 2 HBr (438.2) Calcd. C 41.1 H 4.37 N 6.4 Found C 41.2 H 4.37 N 6.2.- FT-IR (KBr): $\tilde{\nu}$ = 3600-2600 s, br (OH and NH_3^+); 3021 w (C-H aromat.); 2921 w (C-H aliph.); 1630 s (NH_3^+); 1599 s (C=C).- ^{1}H-NMR (D_2O): δ (ppm) = 7.10-6.15 (m; 7H aromat.), 4.52-4.19 (m; 2H, CH), 3.00-2.43 (m; 2H, CH_2).

threo-1-(2-Fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamine dihydrobromide (**95**)

From **69** x 2 HCl; purification by dissolving in EtOH 96% and reprecipitation by Et_2O: 71% powder, m.p. 168-170°.- $C_{15}H_{17}FN_2O_2$ x 2 HBr x 2.5 H_2O (483.2) Calcd. C 37.3 H 5.01 N 5.8 Found C 37.1 H 4.86 N 5.6.- FT-IR (KBr): $\tilde{\nu}$ = 3600-2700 m, br (H_2O, OH and NH_3^+); 3025 w (C-H aromat.); 2961 w (C-H aliph.); 1630 s, 1618 s (NH_3^+); 1599 s, 1568 m (C=C).- ^{1}H-NMR (D_2O): δ (ppm) = 7.02-6.29 (m; 7H aromat.), 3.97-3.49 (m; 2H, CH), 2.68-2.34 (m; 2H, CH_2).

erythro-1-(2-Chloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamine dipicrate (**96**)

From **70** x 2 HCl; 61% dihydrobromide; m.p. dipicrate 158-161°.- $C_{15}H_{17}ClN_2O_2$ x 2 $C_6H_3N_3O_7$ (751.0) Calcd. C 43.2 H 3.09 N 14.9 Found C 42.9 H 3.47 N 14.5.- FT-IR (KBr): $\tilde{\nu}$ = 3424 m, br (OH); 3300-2700 m, br (NH_3^+); 3089 w (C-H aromat.); 2927 w (C-H aliph.); 1630 s, 1611 s (NH_3^+); 1560 s (C=C); 1531 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.65 (s; 4H aromat.), 8.23 (s, br; 6H, NH_3^+, H/D-exch.), 7.35 (d; ^{3}J = 9.0 Hz, 1H aromat.), 7.25-6.65 (m; 6H aromat.), 4.36-4.10 (m; 2H, CH), 2.40 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2-Chloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamine dipicrate (**97**)

From **71** x 2 HCl; 69% dihydrobromide; m.p. dipicrate 155-159°.- $C_{15}H_{17}ClN_2O_2$ x 2 $C_6H_3N_3O_7$ (751.0) Calcd. C 43.2 H 3.09 N 14.9 Found C 43.1 H 3.30 N 14.6.- FT-IR (KBr): $\tilde{\nu}$ = 3450 m, br (OH); 3300-2700 m, br (NH_3^+); 3098 w (C-H aromat.); 2927 w (C-H aliph.); 1632 s, 1611 s (NH_3^+); 1560 s (C=C); 1528 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.63 (s; 4H aromat.), 8.39 (s, br; 6H, NH_3^+, H/D-exch.), 7.27-6.67 (m; 7H aromat.), 3.84-3.52 (m; 2H, CH), 2.58 (m; 2H, CH_2, overlap with solvent signals).

erythro-1-(2-Bromo-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamine dipicrate (**98**)

From **72** x 2 HCl; 83% dihydrobromide; m.p. dipicrate 159-162°.- $C_{15}H_{17}BrN_2O_2$ x 2 $C_6H_3N_3O_7$ (795.5) Calcd. C 40.8 H 2.91 N 14.1 Found C 40.8 H 3.17 N 14.0.- FT-IR (KBr): $\tilde{\nu}$ = 3450 m, br (OH); 3300-2700 m, br (NH_3^+); 3094 w, 3067 w (C-H aromat.); 2925 w (C-H aliph.); 1609 s (NH_3^+); 1570 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.64 (s; 4H aromat.), 8.25 (s, br; 6H, NH_3^+, H/D-exch.), 7.40 (d, ^{3}J = 9.0 Hz, 1H aromat.), 7.29-6.66 (m; 6H aromat.), 4.41-4.07 (m; 2H, CH), 2.45 (m; 2H, CH_2, partial overlap with solvent signals).

threo-1-(2-Bromo-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamine dipicrate (**99**)

From **73** x 2 HCl; 44% dihydrobromide; m.p. dipicrate 158-161°.- $C_{15}H_{17}BrN_2O_2$ x 2 $C_6H_3N_3O_7$ (795.5) Calcd. C 40.8 H 2.91 N 14.1 Found C 41.0 H 3.41 N 13.8.- FT-IR (KBr): $\tilde{\nu}$ = 3450 m, br (OH); 3300-2700 m, br (NH_3^+); 3089 w (C-H aromat.); 2929 w (C-H aliph.); 1630 s, 1618 s, 1611 s (NH_3^+); 1560 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.65 (s; 4H aromat.), 8.20 (s, br; 6H, NH_3^+, H/D-exch.), 7.55 (d; ^{3}J = 9.0 Hz, 1H aromat.), 7.28-6.73 (m; 6H aromat.), 3.82-3.43 (m; 2H, CH), 2.58 (m; 2H, CH_2, overlap with solvent signals).

erythro-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(2-hydroxyphenyl)propane-1,3-diamine dipicrate (**100**)

From **74** x 2 HCl; 81% dihydrobromide; m.p. dipicrate 158-160°.- $C_{15}H_{16}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ x H_2O (803.5) Calcd. C 40.4 H 3.01 N 13.9 Found C 40.4 H 2.82 N 13.8.- FT-IR (KBr): $\tilde{\nu}$ = 3422 m, br (OH); 3300-2700 m, br (H_2O and NH_3^+); 3079 w (C-H aromat.); 2965 w, 2930 w (C-H aliph); 1613 s (NH_3^+); 1570 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.66 (s; 4H aromat.), 8.35 (s, br; 6H, NH_3^+, H/D-exch.), 7.33-6.55 (m; 4H aromat.), 6.73 (s; 2H aromat.), 4.87-4.14 (m; 2H, CH), 2.99-2.64 (m; 2H, CH_2).

threo-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(2-hydroxyphenyl)propane-1,3-diamine dipicrate (**101**)

From **75** x 2 HCl; 75% dihydrobromide; m.p. dipicrate 160-164°.- $C_{15}H_{16}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (785.5) Calcd. C 41.3 H 2.82 N 14.3 Found C 41.3 H 3.23 N 14.1.- FT-IR (KBr): $\tilde{\nu}$ = 3422 m, br (OH); 3300-2700 m, br (NH_3^+); 3089 w (C-H aromat.); 2965 w, 2936 w (C-H aliph.); 1615 s (NH_3^+); 1568 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.64 (s; 4H aromat.), 8.34 (s, br; 6H, NH_3^+, H/D-exch.), 7.47-6.60 (m; 4H aromat.), 6.85 (s; 2H aromat.), 4.65-4.32 (m; 1H, CH), 3.70-3.39 (m; 1H, CH), 2.91-2.60 (m; 2H, CH_2).

erythro-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamine dipicrate (**102**)

From **76** x 2 HCl; 71% dihydrobromide; m.p. dipicrate 155-158°.- $C_{15}H_{16}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (785.5) Calcd. C 41.3 H 2.82 N 14.3 Found

C 41.1 H 2.80 N 14.0.- FT-IR (KBr): $\tilde{\nu}$ = 3438 m, br (OH); 3300-2700 m, br (NH_3^+); 3087 w (C-H aromat.); 2965 w, 2927 w (C-H aliph.); 1618 s (NH_3^+); 1576 s, 1560 s (C=C); 1543 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.62 (s; 4H aromat.), 8.52 (s, br; 3H, NH_3^+, H/D-exch.), 8.33 (s, br; 3H, NH_3^+, H/D-exch.), 7.21-6.60 (m; 4H aromat.), 6.69 (s; 2H aromat.), 4.86-4.50 (m; 1H, CH), 4.43-4.03 (m; 1H, CH), 2.85-2.58 (m; 2H, CH_2).

threo-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamine dipicrate (**103**)

From **77** x 2 HCl; 74% dihydrobromide; m.p. dipicrate 189-192° (dec.).- $C_{15}H_{16}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (785.5) Calcd. C 41.3 H 2.82 N 14.3 Found C 41.4 H 2.77 N 14.1.- FT-IR (KBr): $\tilde{\nu}$ = 3428 m, br (OH); 3300-2700 m, br (NH_3^+); 3075 w (C-H aromat.); 2981 w (C-H aliph.); 1628 s, 1615 s (NH_3^+); 1570 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.63 (s; 4H aromat.), 8.42 (s, br; 3H, NH_3^+, H/D-exch.), 8.21 (s, br; 3H, NH_3^+, H/D-exch.), 7.35-6.71 (m; 6H aromat.), 4.62-4.25 (m; 1H, CH), 3.86-3.53 (m; 1H, CH), 3.10-2.83 (m; 2H, CH_2).

erythro-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamine dipicrate (**104**)

From **78** x 2 HCl; 88% dihydrobromide; m.p. dipicrate 179-182°.- $C_{15}H_{16}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (785.5) Calcd. C 41.3 H 2.82 N 14.3 Found C 41.2 H 3.11 N 14.1.- FT-IR (KBr): $\tilde{\nu}$ = 3505 m, br (OH); 3300-2700 m, br (NH_3^+); 3075 w (C-H aromat.); 2965 w, 2929 w (C-H aliph.); 1615 s (NH_3^+); 1568 s (C=C); 1537 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.67 (s; 4H aromat.), 8.56 (s, br; 3H, NH_3^+, H/D-exch.), 8.35 (s, br; 3H, NH_3^+, H/D-exch.), 7.21, 6.67 (AA'BB', $^3J_{AB}$ = 8.0 Hz, 4H aromat.), 6.76 (s; 2H aromat.), 4.88-4.49 (m; 1H, CH), 4.40-3.98 (m; 1H, CH), 2.90-2.59 (m; 2H, CH_2).

threo-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamine dipicrate (**105**)

From **79** x 2 HCl; 94% dihydrobromide; m.p. dipicrate 165-168°.- $C_{15}H_{16}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ x H_2O (803.5) Calcd. C 40.4 H 3.01 N 13.9 Found C 40.6 H 3.01 N 13.5.- FT-IR (KBr): $\tilde{\nu}$ = 3415 m, br (OH); 3300-2700 m, br (H_2O and NH_3^+); 3087 w (C-H aromat.); 2965 w, 2927 w (C-H aliph.); 1630 s, 1615 s (NH_3^+); 1568 s (C=C); 1539 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.62 (s; 4H aromat.), 8.53 (s, br; 3H, NH_3^+, H/D-exch.), 8.24 (s, br; 3H, NH_3^+, H/D-exch.), 7.15; 6.65 (AA'BB', $^3J_{AB}$ = 8.0 Hz, 4H aromat.), 6.73 (s; 2H aromat.), 4.63-4.29 (m; 1H, CH), 3.92-3.57 (m; 1H, CH), 3.09-2.65 (m; 2H, CH_2).

meso-1,3-Bis-(2-fluoro-4-hydroxyphenyl)propane-1,3-diamine dipicrate (**106**)

From **80** x 2 HCl; 84% dihydrobromide; m.p. dipicrate 155-159° (dec.).- $C_{15}H_{16}F_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (734.6) Calcd. C 43.1 H 2.95 N 14.9 Found C 43.0 H 3.01 N 14.6.- FT-IR (KBr): $\tilde{\nu}$ = 3428 m, br (OH); 3300-2700 m, br (NH_3^+); 3081 w (C-H aromat.); 2925 w (C-H aliph.); 1632 s, 1611 s (NH_3^+); 1568 s (C=C); 1528 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.60 (s; 4H aromat.), 8.26 (s, br; 6H, NH_3^+, H/D-exch.), 7.19 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 2H aromat.), 6.66-6.30 (m; 4H aromat.), 4.59-4.27 (m; 2H, CH), 2.65 (m; 2H, CH_2, partial overlap with solvent signals).

rac-1,3-Bis-(2-fluoro-4-hydroxyphenyl)propane-1,3-diamine dipicrate (**107**)

From **81** x 2 HCl; 89% dihydrobromide; m.p. dipicrate 153-157°.- $C_{15}H_{16}F_2N_2O_2$ x 2 $C_6H_3N_3O_7$ x H_2O (770.6) Calcd. C 42.1 H 3.14 N 14.5 Found C 42.3 H 2.95 N 14.4.- FT-IR (KBr): $\tilde{\nu}$ = 3425 m, br (OH); 3300-2700 m, br (H_2O and NH_3^+); 3089 w (C-H aromat.); 2981 w, 2929 w (C-H aliph.); 1630 s, 1611 s (NH_3^+); 1568 s (C=C); 1535 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm/250 MHz) = 10.26 (s, br; 2H, OH, H/D-exch.), 8.59 (s; 4H aromat.), 8.18 (s, br; 6H, NH_3^+, H/D-exch.), 7.36 (t; ^3J = 8.6 Hz, $^4J_{HF}$ = 8.6 Hz, 2H aromat.), 6.77-6.73 (m; 2H aromat.), 6.63-6.58 (m; 2H aromat.), 3.97-3.83 (m; 2H, CH), 2.60 (m; 2H, CH_2, partial overlap with solvent signals).

meso-1,3-Bis-(2-chloro-4-hydroxyphenyl)propane-1,3-diamine dipicrate (**108**)

From **82** x 2 HCl; 90% dihydrobromide; m.p. dipicrate 152-156°.- $C_{15}H_{16}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (785.5) Calcd. C 41.3 H 2.82 N 14.3 Found C 41.3 H 2.89 N 13.8.- FT-IR (KBr): $\tilde{\nu}$ = 3247 m, br (OH); 3300-2700 m, br (NH_3^+); 3089 w (C-H aromat.); 2921 w (C-H aliph.); 1615 s (NH_3^+); 1568 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.69 (s; 4H aromat.), 8.37 (s, br; 6H, NH_3^+, H/D-exch.), 7.26 (d; ^3J = 8.5 Hz, 2H aromat.), 6.77-6.47 (m; 4H aromat.), 4.75-4.36 (m; 2H, CH), 2.60 (m; 2H, CH_2, partial overlap with solvent signals).

rac-1,3-Bis-(2-chloro-4-hydroxyphenyl)propane-1,3-diamine dipicrate (**109**)

From **83** x 2 HCl; 81% dihydrobromide; m.p. dipicrate 151-155°.- $C_{15}H_{16}Cl_2N_2O_2$ x 2 $C_6H_3N_3O_7$ (785.5) Calcd. C 41.3 H 2.82 N 14.3 Found C 41.0 H 2.87 N 13.9.- FT-IR (KBr): $\tilde{\nu}$ = 3430 m, br (OH); 3300-2700 m, br (NH_3^+); 3106 w (C-H aromat.); 2979 w, 2927 w (C-H aliph.); 1632 s, 1611 s (NH_3^+); 1560 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.66 (s; 4H aromat.), 8.30 (s, br; 6H, NH_3^+, H/D-exch.), 7.46 (d; ^3J = 8.5 Hz, 2H aromat.), 6.84-6.48 (m; 4H aromat.), 4.05-3.68 (m; 2H, CH), 2.63 (m; 2H, CH_2, partial overlap with solvent signals).

erythro-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(2-fluoro-4-hydroxyphenyl)propane-1,3-diamine dipicrate (**110**)

From **84** x 2 HCl; 72% dihydrobromide; m.p. dipicrate 152-154°.- $C_{15}H_{15}Cl_2FN_2O_2$ x 2 $C_6H_3N_3O_7$ (803.4) Calcd. C 40.4 H 2.63 N 13.9 Found C 40.6 H 3.09 N 13.7.- FT-IR (KBr): $\tilde{\nu}$ = 3505 m, br (OH); 3300-2700 m, br (NH_3^+); 3079 w (C-H aromat.); 2965 w, 2929 w (C-H aliph.); 1628 m, 1613 s (NH_3^+); 1568 s (C=C); 1535 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.68 (s; 4H aromat.), 8.40 (s, br; 6H, NH_3^+, H/D-exch.), 7.25 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 1H aromat.), 6.79-6.30 (m; 4H aromat.), 4.95-4.63 (m; 1H, CH), 4.60-4.27 (m; 1H, CH), 3.06-2.67 (m; 2H, CH_2).

threo-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(2-fluoro-4-hydroxyphenyl)propane-1,3-diamine dipicrate (**111**)

From **85** x 2 HCl; 59% dihydrobromide; m.p. dipicrate 145-147°.- $C_{15}H_{15}Cl_2FN_2O_2$ x 2 $C_6H_3N_3O_7$ (803.4) Calcd. C 40.4 H 2.63 N 13.9 Found C 40.2 H 2.79 N 13.8.- FT-IR (KBr): $\tilde{\nu}$ = 3450 m, br (OH); 3300-2700 m, br (NH_3^+); 3089 w (C-H aromat.); 2925 w (C-H aliph.); 1630 s, 1611 s (NH_3^+); 1560 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.61 (s; 4H aromat.), 8.34 (s, br; 6H, NH_3^+, H/D-exch.), 7.46 (t; ^3J = 9.0 Hz, $^4J_{HF}$ = 9.0 Hz, 1H aromat.), 6.98-6.41 (m; 4H aromat.), 4.75-4.35 (m; 1H, CH), 4.18-3.76 (m; 1H, CH), 3.15-2.75 (m; 2H, CH_2).

erythro-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(2-chloro-4-hydroxyphenyl)propane-1,3-diamine dipicrate (**112**)

From **86** x 2 HCl; 73% dihydrobromide; m.p. dipicrate 156-158°.- $C_{15}H_{15}Cl_3N_2O_2$ x 2 $C_6H_3N_3O_7$ (819.9) Calcd. C 39.6 H 2.58 N 13.7 Found C 39.7 H 2.79 N 13.3.- FT-IR (KBr): $\tilde{\nu}$ = 3428 m, br (OH); 3300-2700 m, br (NH_3^+); 3104 w (C-H aromat.); 2929 w (C-H aliph.); 1630 s, 1609 s (NH_3^+); 1560 s (C=C); 1532 s (NO_2).- ^{1}H-NMR ([D$_6$]DMSO): δ (ppm) = 8.62 (s; 4H aromat.), 8.37 (s, br; 6H, NH_3^+, H/D-exch.), 7.30 (d; ^3J = 9.0 Hz, 1H aromat.), 6.94-6.48 (m; 2H aromat.), 6.78 (s; 2H aromat.), 4.94-4.62 (m; 1H, CH), 4.50-4.15 (m; 1H, CH), 3.16-2.71 (m; 2H, CH_2).

threo-1-(2,6-Dichloro-4-hydroxyphenyl)-3-(2-chloro-4-hydroxyphenyl)propane-1,3-diamine dipicrate (**113**)

From **87** x 2 HCl; 89% dihydrobromide; m.p. dipicrate 152-155°.- $C_{15}H_{15}Cl_3N_2O_2$ x 2 $C_6H_3N_3O_7$ x 0.5 H_2O (828.9) Calcd. C 39.1 H 2.68 N 13.5 Found C 39.4 H 2.88 N 13.1.- FT-IR (KBr): $\tilde{\nu}$ = 3422 m, br (OH); 3300-2700 m, br (H_2O and NH_3^+); 3087 w (C-H aromat.); 2969 w, 2938 w (C-H aliph.); 1611 s (NH_3^+), 1570 s (C=C); 1541 s (NO_2).- ^{1}H-NMR ([D_6]DMSO): δ (ppm) = 8.57 (s; 4H aromat.), 8.32 (s, br; 6H, NH_3^+, H/D-exch.), 7.51 (d; ^{3}J = 9.0 Hz, 1H aromat.), 6.94-6.51 (m; 2H aromat.), 6.69 (s; 2H aromat.), 4.62-4.29 (m; 1H, CH), 4.29-3.90 (m; 1H, CH), 3.04-2.63 (m; 2H, CH_2).

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