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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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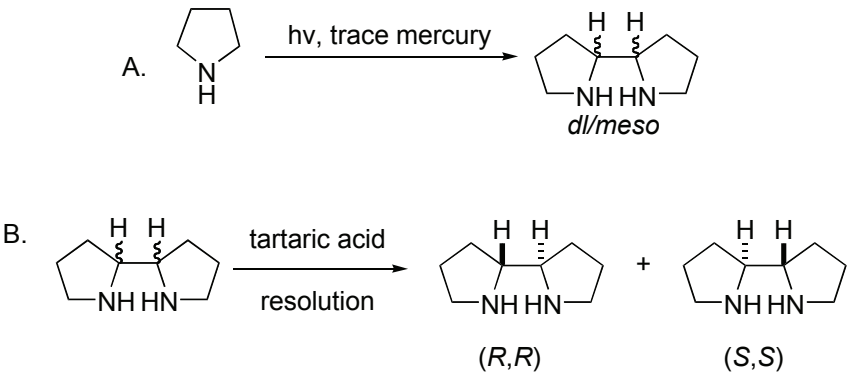
(*R*,*R*)-2,2'-BISPYRROLIDINE and (*S*,*S*)-2,2'-BISPYRROLIDINE: USEFUL LIGANDS FOR ASYMMETRIC SYNTHESIS



Submitted by Scott E. Denmark, Jiping Fu and Michael J. Lawler.[1]
Checked by Sandra Lee, Elliott Huntsman and Edward J.J. Grabowski.

Caution! This procedure should be carried out in a well-ventilated hood because of the stench of pyrrolidine and 2,2'-bispyrrolidine. The hood doors should be covered with an opaque sheet to shield the UV light.

1. Procedure

A. (R,R*) and (R*,S*)-2,2'-Bispyrrolidine.*[2,3] A three-necked, 500-mL flask equipped with three quartz refluxing columns and three water condensers (Figure 1) is charged with pyrrolidine (160 mL) and a drop of mercury (Notes 1 and 2). The water condensers are equipped with gas inlets connected to a single nitrogen source leading to an oil bubbler. The flask is placed in a Rayonet Photoreactor fitted with 14 x 8 Watt low pressure Hg lamps (254 nm). The reaction mixture is heated to reflux with a heating mantle. The lamps are turned on, after which the mixture is heated at reflux for 7 days. After the lamps are turned off, the system is allowed to cool to room temperature (Note 2). The liquid is then carefully decanted to a distillation flask and the mercury is recovered. Unreacted pyrrolidine and side products are removed by distillation at atmospheric pressure (Note 3). The residue is distilled to provide 67.6 g (50%) of a mixture of (*R**,*R**) and (*R**,*S**)-2,2'-bispyrrolidine as a clear, light yellow liquid (bp 79−81 °C at 3.0 mmHg) (Note 4). The product is of sufficient purity to be used in the resolution step (Note 5)

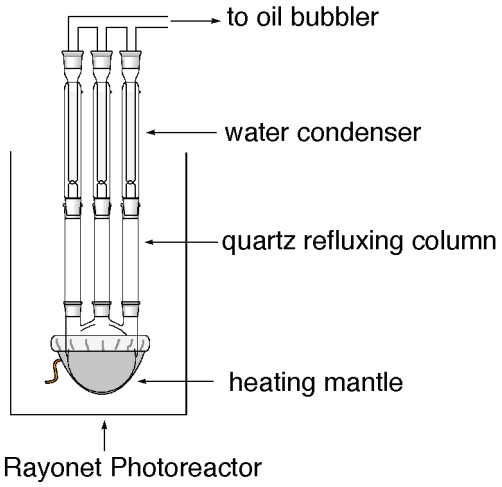


Figure 1. Apparatus for photodimerization of pyrrolidine.

B. Resolution of 2,2'-Bispyrrolidine[3,4]

1. *Preparation of (R,R)-2,2'-bispyrrolidine•(L)-tartrate.* To a solution of a 1/1 mixture of *d,l*- and *meso*-2,2'-bispyrrolidine (67.0 g, 479 mmol) in H_2O (240 mL) is added (L)-(+)-tartaric acid (36.0 g, 240 mmol, 0.5 equiv) and acetic acid (27.4 mL, 479 mmol, 1.0 equiv) (Note 6). The mixture is heated to 90 °C and the homogenous solution is allowed to cool to room temperature slowly before it is placed in an ice bath. After the solid precipitates (Note 7), the mixture is kept in an ice bath for another 2 h. The precipitate is then filtered and is washed with ice-cold water (20 mL). The mother liquor is saved for the recovery of the (*S*,*S*)-2,2'-bispyrrolidine. The collected solid is dried under high vacuum (0.5 mmHg) at 80 °C for 2 h to give 31.6 g of a light yellow powder. This solid is dissolved in hot water (90 mL) and the solution is allowed to cool slowly to room temperature before it is placed in an ice bath for 1 h. The precipitate is filtered and the solid is washed with ice-cold water (10 mL). The solid is dried under high vacuum (0.5 mmHg) at 80 °C for 2 h to give 23.0 g of white crystals. This recrystallization process is repeated using water (50 mL) to give 21.4 g (62% based on isomer content) of (*R*,*R*)-2,2'-bispyrrolidine•(L)-tartrate as white prismatic crystals (Note 8).

2. *Preparation of (R,R)-2,2'-Bispyrrolidine.* To a mixture of the tartrate salt (9.1 g) in water (15 mL) at 0 °C are added KOH (20 g) pellets (Note 9). The mixture is then stirred at 0 °C for 10 min before diethyl ether

(80 mL) is added, whereupon the solution is stirred at 0 °C for another 30 min. The aqueous layer is then separated and extracted with diethyl ether (6 x 50 mL) (Note 10). The diethyl ether extracts are combined, dried (K_2CO_3) and then are concentrated under vacuum (Note 11). The residue is transferred to a dry 25-mL, round-bottomed flask. To this is added a small piece of sodium (Note 12) and the mixture is stirred at room temperature under nitrogen for 30 min. The residue is distilled under vacuum to give 3.61 g (83%) of (*R*,*R*)-2,2'-bispyrrolidine as a clear colorless oil (bp 97−98 °C at 8.0 mmHg) (Note 13). The enantiomeric purity of product is determined by CSP-SFC and CSP-HPLC analysis of the corresponding dibenzoyl amide derivative (Note 14).

3. *Preparation of (S,S)-2,2'-bispyrrolidine•(D)-tartrate.* The mother liquor from initial resolution is cooled to 0 °C and KOH pellets (80 g) are added slowly. The mixture is stirred vigorously at 0 °C for 10 min (Note 15). To this solution is added diethyl ether (500 mL) and the mixture is stirred at room temperature for 20 min. The aqueous layer is separated and then is extracted with diethyl ether (4 x 500 mL). The diethyl ether extracts are combined, dried (K_2CO_3), and then are concentrated under vacuum to give 48.4 g of a yellow oil. The oil is dissolved in H_2O (150 mL), then (D)-(–)-tartaric acid (34.5 g, 230 mmol) and acetic acid (27.0 mL, 473 mmol) are added (Note 16). The mixture is heated to 90 °C and the homogenous solution is allowed to cool to room temperature slowly before it is cooled in an ice bath. After the solid precipitates, the mixture is kept in an ice bath for another 2 h. The precipitate is filtered and the solid is washed with ice-cold water (10 mL), and then is dried under high vacuum (0.5 mmHg) at 80 °C for 2 h to give 23.5 g of a light-yellow powder. The solid is dissolved in hot water (60 mL) and the solution is allowed to cool slowly to room temperature before it is placed in an ice bath for another 2 h. The precipitate is filtered, washed with 10 mL of ice-cold water, and dried under high vacuum (0.5 mmHg) at 80 °C for 2 h to give 20.16 g of white prismatic crystals. This recrystallization process is repeated using water (55 mL) to give 18.4 g (55% based on isomer content) of (*S*,*S*)-2,2'-bispyrrolidine•(D)-(–)-tartrate as white prismatic crystals (Note 17).

4. *Preparation of (S,S)-2,2'-Bispyrrolidine.* To a solution of the tartrate salt (9.3 g) in water (15 mL) at 0 °C are added KOH pellets (20 g). The mixture is stirred at 0 °C for 10 min before diethyl ether (80 mL) is added, whereupon it is stirred at 0 °C for another 30 min. The aqueous layer is separated and then is extracted with diethyl ether (6 x 50 mL). The

diethyl ether extracts are combined, dried (K_2CO_3) and then are concentrated *in vacuo* (Note 11). The residue is then transferred to a dry 25-mL, round-bottomed flask. To this is added a piece of sodium (Note 12) and the mixture is stirred at room temperature under nitrogen for 30 min. The residue is then distilled under vacuum to give 3.51 g (80%) of (*S*,*S*)-2,2′-bispyrrolidine as a clear, colorless oil (bp 97−98 °C at 8.0 mmHg) (Note 18). The enantiomeric purity of product is determined by CSP-SFC and CSP-HPLC analysis of corresponding dibenzoyl amide derivative (Note 19).

2. Notes

1. The three quartz-refluxing columns are 34 cm long and 4.0 cm in diameter. All joints are well sealed with high vacuum grease to avoid leakage. Pyrrolidine (99 %) was purchased from Aldrich Chemical Company, Inc., and was used without further purification.

Variables that are difficult to control relative to the photolysis include the age and actual power of the Hg lamps, the actual length of the quartz tubes receiving the UV light and the rate of reflux. All affect the overall rate of photolysis. The checkers found it convenient to follow the progress of the photolysis by periodically sampling the reaction and analyzing it by ^{13}C-NMR spectroscopy in $CDCl_3$. The peak heights for the methylene groups for pyrrolidine (47.1 ppm) and the bis-pyrrolidines (47.0 and 46.6) were used as measures of the relative ratios of these species. When the pyrrolidine is almost consumed in the photolysis, the reflux ceases. The submitters were able to recover ~50% of the bis-pyrrolidines after distillation following a seven-day photolysis (See Note 5). The checkers achieved the following results: 39% in seven days; 60% in nine days; 72% in 11.4 days and 60% in five days at half-scale.

2. The crude reaction mixture can be analyzed by ^1H NMR. The ratio of starting material to products can be estimated from the NMR spectrum.

3. The distillate contains 46.6 g of colorless liquid.

4. The distillation should be done carefully to avoid solidification of the diamine in the condenser.

5. The crude material (67.6 g, approximately 50% based on the pyrrolidine charged) contains a ca. 1/1 mixture of *d,l* and *meso* isomers: ^1H NMR (500 MHz, $CDCl_3$) d: 1.32−1.46 (m, 2 H), 1.61−1.92 (m, 8 H), 2.82−2.98 (m, 6 H). The checkers obtained 52.6 g from the seven-day photolysis; 81.0 g from the nine day photolysis; 97.0 g from the 11.4 day

photolysis and 41.5 g from the five day photolysis at half-scale.

6. L-(+)-Tartaric acid (99% GLC) was purchased from Aldrich Chemical Company, Inc., and was used without further purification. Acetic acid (glacial) was purchased from Fisher Scientific Company and was used without further purification. In completing the checking of this procedure, the subsequent reactions were scaled to reflect the quantity of bispyrrolidines obtained in the distillations. The reactions checked at the yields indicated.

7. The initial formation of crystals may take up to 16 h. The process can be facilitated by stirring the mixture with glass rod or by addition of small amount of seed crystals.

8. The analytical data for (*R*,*R*)-2,2'-bispyrrolidine•(L)-tartrate are as follows:[4] mp 212−216 °C; ^{1}H NMR (500 MHz, D_2O/DSS) d: 1.88−1.98 (m, 2 H), 2.08−2.28 (m, 4 H), 2.40−2.48 (m, 2 H), 3.51−3.55 (m, 4 H), 3.92−4.00 (m, 2 H), 4.43 (s, 2 H), 4.86 (br, 6 H); ^{13}C NMR (126 MHz, D_2O) d: 25.5, 31.0, 49.1, 63.2, 76.6, 181.4; IR (KBr) cm^{-1}: 3220, 2717, 2516, 1693, 1612, 1583, 1450, 1386, 1321, 1124, 1072, 709; $[\alpha]_D^{24}$ +17.9 (*c* = 1.00, H_2O); Anal. Calcd for $C_{12}H_{22}N_2O_6$: C, 49.65; H, 7.64, N, 9.65. Found: C, 49.80; H, 7.63; N, 9.65. The checkers noted slight chemical shift variations in the NMR spectra of this material, and attribute these to slight differences in concentration and apparent pH in the different samples.

9. Potassium hydroxide (87.7%) was purchased from Fisher Scientific Company and was used without further purification.

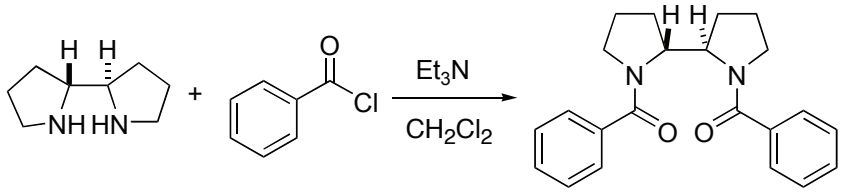
10. Diethyl ether was purchased from Mallinckrodt Inc. and was used without purification.

11. The water bath is kept at 0 °C to avoid loss of (*R*,*R*)-2,2′-bispyrrolidine.

12. The piece of sodium is about 0.5 cm^3 and it is washed with hexane before use. After distillation, the sodium was destroyed by the careful addition of isopropyl alcohol.

13. The analytical data for (*R*,*R*)-2,2'-bisyrrolidine are as follows:[3,4] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.31−1.38 (m, 2 H), 1.65−1.84 (m, 6 H), 2.06 (br, 2 H), 2.82−2.97 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 25.4, 29.0, 46.4, 63.8; IR (KBr) cm^{-1}: 3270, 2956, 2867, 1282, 1118, 1076; MS (FAB) (*m/z*): 141; HRMS (*m/z*) $C_8H_{17}N_2$ (M+H): Calc.: 141.1386; Found: 141.1375; $[\alpha]_D^{24}$ –14.91 (*c* = 1.03, MeOH); Anal. Calcd for $C_8H_{16}N$: C, 68.52; H, 11.50, N, 19.98. Found: C, 68.38; H, 11.64; N, 19.92. The free diamine is extremely hygroscopic, oxygen sensitive and absorbs CO_2 rapidly in air.

14. Procedure for derivatization is as follows (eq 1)[3,4]: To a solution of (*R*,*R*)-**2** (140 mg, 1.0 mmol) in 1.0 mL of methylene chloride (purchased from Fisher Scientific Company and distilled from P_2O_5) at 0 °C is added triethylamine (278 mL, 2.0 mmol, 2.0 equiv, purchased from Aldrich Chemical Company, Inc., and distilled from CaH_2) and benzoyl chloride (232 mL, 2.0 mmol, 2.0 equiv, purchased from Aldrich Chemical Company, Inc., and distilled before use). The mixture is stirred at room temperature for



(*R*,*R*)-**2** *(R,R)*-**3**

4 h and then EtOAc (50 mL) and H_2O (10 mL) are added. The aqueous layer is separated and then is extracted with EtOAc (3 x 15 mL). The organic layers are combined, washed with 15 mL of saturated, aqueous sodium bicarbonate solution, dried over Na_2SO_4 and then concentrated under vacuum. The residue is purified by column chromatography (SiO_2, hexane/*i*-PrOH, 6/1) to give 295 mg (85%) of (*R*,*R*)-**3** as a white solid. The analytical data for (*R*,*R*)-**3** are as follows:[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.76–2.05 (m, 6 H) 2.20–2.28 (m, 2 H), 3.19 (dt, *J* = 10.3, 7.8, 2 H), 3.79 (ddd, *J* = 10.5, 8.8, 5.1, 2 H), 4.59–4.64 (m, 2 H), 7.22–7.36 (m, 6 H), 7.38–7.42 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 24.1, 28.2, 49.1, 58.8, 127.1, 128.2, 129.5, 137.2, 164.5; IR ($CHCl_3$) cm^{-1}: 2997, 2881, 1624, 1576, 1427, 700; MS (EI, 70 eV): 348, 175, 174, 105; HRMS (*m/z*): Calc. $C_{22}H_{25}N_2O_2$ (M+H): 349.1911; Found: 349.1900; Supercritical Fluid Chromatography: t_R (*R,R*)-**3** 2.86 min (100 %); t_R (*S,S*)-**3** 3.26 min (0 %) (Chiralpak AS, 40 °C, 150 bar, 15 % MeOH in CO_2, 3.0 mL/min, 220 nm); HPLC: t_R (*S*,*S*)-**3** 8.2 min (0%); t_R (*R*,*R*)-**3** 13.2 min (100%) (Chiralpak AD, *i*-PrOH/hexane, 95/5, 0.7 mL/min)

15. The submitters initially used 40 g of KOH pellets for the neutralization. The checkers found that the use of 80 g was necessary to assure extraction of all of the diamine.

16. D-(–)-Tartaric acid (97% GLC) was purchased from Aldrich Chemical Company, Inc., and was used without further purification.

17. The analytical data for (*S*,*S*)-2,2'-bispyrrolidine•(D)-(–)-tartrate are as follows: mp 214–218 °C; ^{1}H NMR (500 MHz, D_2O/DSS) δ: 1.88–1.99

(m, 2 H), 2.08–2.29 (m, 4 H), 2.41–2.49 (br, 2 H), 3.52–3.57 (m, 4 H), 3.94–4.01 (m, 2 H), 4.44 (s, 2 H), 4.84 (br, 6 H); ^{13}C NMR (126 MHz, D_2O) δ: 25.5, 31.0, 49.1, 63.16, 76.6, 181.4; IR (KBr) cm^{-1}: 3384, 3242, 2997, 2885, 2717, 2517, 1693, 1610, 1583, 1387, 1124, 1072, 710; $[\alpha]_D^{24}$ –17.7 (*c* = 1.02, H_2O); Anal. Calcd for $C_{12}H_{22}N_2O_6$: C, 49.65; H, 7.64, N, 9.65. Found: C, 49.98; H, 7.43; N, 9.37. The checkers noted slight chemical shift variations in the NMR spectra of this material, and attribute these to slight differences in concentration and apparent pH in the different samples.

18. The analytical data for (*S*,*S*)-2,2′-bisyrrolidine are as follows: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.31-1.38 (m, 2 H), 1.65-1.84 (m, 6 H), 2.06 (br, 2 H), 2.82-2.97 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 25.4, 29.0, 46.4, 63.8; IR (KBr) cm^{-1}: 3263, 2954, 2867, 2821, 1457, 1442, 1280, 1118, 1076, 892, 869; MS (FAB) (*m/z*) 141; HRMS (*m/z*) $C_8H_{17}N_2$ (M+H): Calc: 141.1386; Found: 141.1373; $[\alpha]_D^{24}$ 14.82 (*c* = 1.01, MeOH); Anal. Calcd for $C_8H_{16}N$: C, 68.52; H, 11.50, N, 19.98. Found: C, 68.45; H, 11.64; N, 19.79.

19. For the derivatization procedure see Note 14. The analytical data for (*S*,*S*)-**3** are as follows: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.78–2.05 (m, 6 H), 2.20–2.27 (m, 2 H), 3.22 (dt, *J* = 10.4, 7.8, 2 H), 3.80 (ddd, *J* = 10.6, 8.8, 5.1, 2 H), 4.60–4.64 (m, 2 H), 7.23–7.33 (m, 6 H), 7.38–7.44 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ:. 24.3, 28.4, 49.3, 59.0, 127.4, 128.4, 129.8, 137.4, 171.2; MS (EI, 70 eV): 348, 175, 174, 105; HRMS (*m/z*) Calc. $C_{22}H_{25}N_2O_2$ (M+H): 349.1911; Found: 349.1917; Supercritical Fluid Chromatography: t_R (*R,R*)-**3** 2.86 min (0%); t_R (*S,S*)-**3** 3.26 min (100%) (Chiralpak AS, 40°C, 150 bar, 15% MeOH in CO_2, 3.0 mL/min, 220 nm); HPLC: (*S*,*S*)-**3** t_R 8.2 min (100%); (*R*,*R*)-**3** t_R 13.2 min (0%) (Chiralpak AD, *i*-PrOH/hexane, 95/5, 0.7 mL/min)

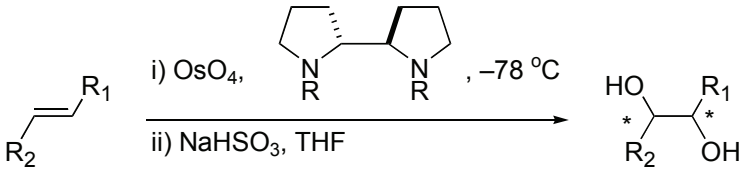
Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

C_2-Symmetric chiral diamines have found extensive application as additives, auxiliaries and catalysts in asymmetric synthesis.[5] (*R*,*R*)-2,2'-Bispyrrolidine, initially developed by Hirama, has been successfully applied

as a ligand for osmium tetraoxide in the asymmetric dihydroxylation of olefins[6] (eq 2) and as a ligand in asymmetric hydrogenation.[7]



Several syntheses of enantiopure 2,2'-bispyrrolidine have been reported.[4,8,9] The first synthesis described by Masamune and coworkers requires only two steps, but produces a *d,l/meso* mixture of isomers in a sluggish and irreproducible heterogeneous hydrogenation. This short synthesis arrives as the final product by direct resolution of the *d,l/meso* mixture of 2,2'-bispyrrolines.[4] The other routes produce enantiopure 2,2'-bispyrrolines without resolution, but they require multiple-step syntheses from chiral starting materials. For example, the synthesis developed by Kotsuki and coworkers takes 11 steps from (D)-tartaric acid.[8] Most recently, Alexakis reported a five-step synthesis of (*R*,*R*)-2,2'-bispyrrolidine by asymmetric addition to a chiral imine.[9] In the procedure described herein, the *d,l/meso* mixture of 2,2'-bispyrrolidines is easily synthesized on a large scale by the photodimerization of pyrrolidine developed by Crabtree.[2] The previously reported resolution[4] has been modified such that both enantiomers can be obtained.

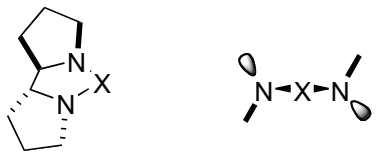


Figure 2: Stair-like structure of two pyrrolidine rings

This diamine possesses very interesting structural features that impart useful characteristics as a bidentate ligand. When the two nitrogen atoms function either in a chelate or are covalently bonded to another atom, the two pyrrolidines adopted a stair-like structure, which creates a highly asymmetric environment (Figure 2). This feature was recently exploited in the development of a highly selective catalyst for asymmetric allylations (Figure 3).[3] The addition of allylic trichlorosilanes to unsaturated aldehydes

can be catalyzed by chiral bisphosphoramide **4** derived from 2,2'-bispyrrolidine to give homoallylic alcohols with excellent diastereo- and enantioselectivities. Of particular note is the catalytic enantioselective construction of quaternary centers by the use of γ-disubstituted allylic silanes. The unique structural features of this diamine together with the ease of preparation bode well for further application in asymmetric synthesis.

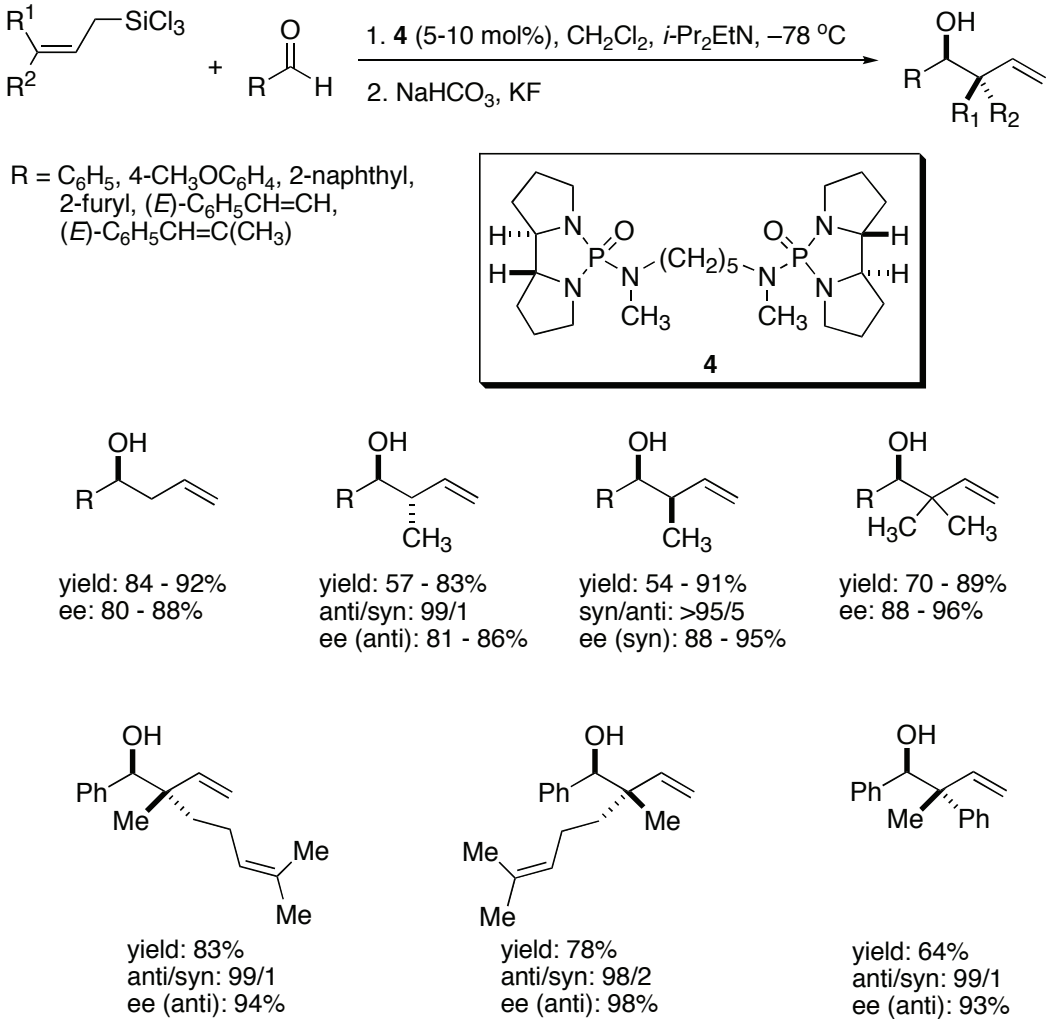


Figure 3. Enantioselective addition of allylic trichlorosilanes catalyzed by 2,2-bispyrrolidine-derived bisphosphoramide **4**.

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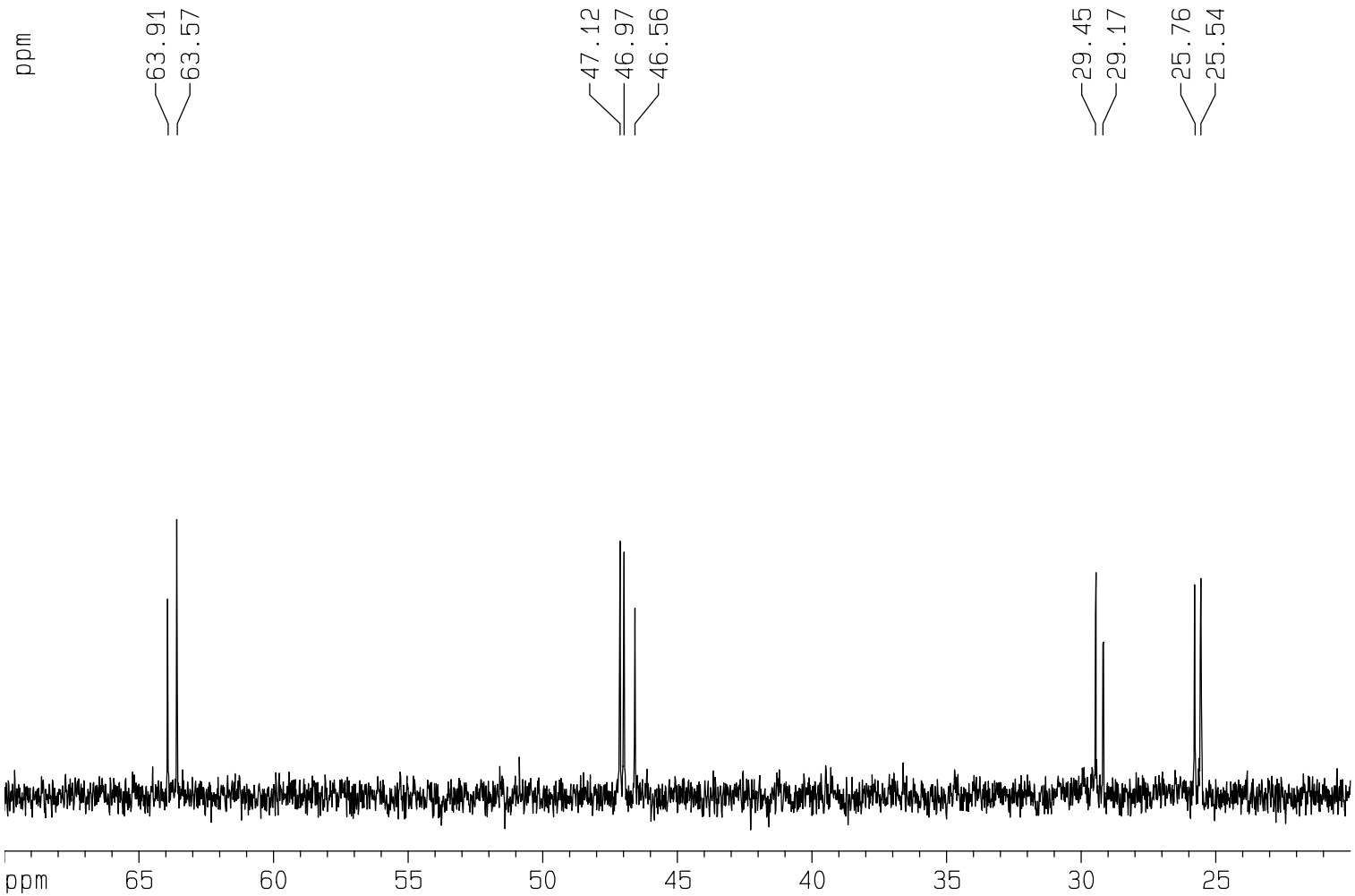
Appendix
Chemical Abstracts Nomenclature; (Registry Number)

2,2-Bispyrrolidine; 2,2-Bipyrrolidine; (74295-58-2)
(*R*,*R*)-2,2'-bispyrrolidine•(L)-tartrate: 2,2'-Bipyrrolidine, (2*R*,2'*R*)-, (2*R*,3*R*)-2,3-dihydroxybutanedioate (1:1)-; (137037-21-9)
(*S*,*S*)-2,2'-bispyrrolidine•(D)-tartrate: 2,2'-Bipyrrolidine, [*S*-(*R**,*R**)]-, [S-(*R**,*R**)]-2,3-dihydroxybutanedioate (1:1); (136937-03-6)
(*R,R*)-2,2'-Bispyrrolidine: 2,2'-Bipyrrolidine, (2*R*,2'*R*)-; (137037-20-8)
(*S,S*)-2,2'-Bispyrrolidine: 2,2'-Bipyrrolidine, (2*S*,2'*S*)-; (124779-66-4)



^{13}C-BISPYRROLIDINE PHOTOLYSIS
(NMR of photomixture in $CDCl_3$)
Pyrrolidine - 47.1 ppm
Meso-Bispyrrolidine - 47.0 ppm
(R,R & S,S)-Bispyrrolidine - 46.6 ppm
Peak heights used to calculate approx. conversion

DU=C:/Bruker/XWIN-NMR, USER=lab, NAME=72656-16-RRT, EXPNO=3, PROCNO=1
F1=8.000ppm, F2=0.000ppm, MI=0.24cm, MAXI=10000.00cm, PC=1.000

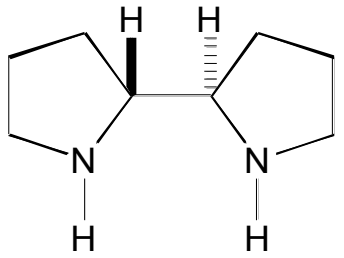
F	ADDRESS	FREQUENCY [Hz]	[PPM]	INTENSITY
1	8943.3	1959.722	4.8977	0.25
2	8992.2	1940.144	4.8488	88.31
3	9411.7	1772.130	4.4289	14.25
4	9843.9	1599.061	3.9964	0.29
5	9861.3	1592.090	3.9789	0.85
6	9867.8	1589.478	3.9724	1.46
7	9872.5	1587.598	3.9677	0.89
8	9879.1	1584.949	3.9611	1.53
9	9882.0	1583.790	3.9582	1.78
10	9885.1	1582.539	3.9551	1.57
11	9891.7	1579.916	3.9485	0.89
12	9896.2	1578.084	3.9439	1.49
13	9902.8	1575.464	3.9374	0.88
14	9920.2	1568.485	3.9199	0.30
15	10286.2	1421.923	3.5537	5.84
16	10301.1	1415.925	3.5387	3.87
17	10303.9	1414.826	3.5359	4.55
18	10307.1	1413.552	3.5327	7.88
19	10323.6	1406.924	3.5162	4.54
20	10333.1	1403.126	3.5067	0.26
21	11361.8	991.161	2.4771	0.44
22	11370.0	987.866	2.4689	0.57
23	11380.7	983.568	2.4581	0.83
24	11386.4	981.278	2.4524	0.80
25	11388.7	980.357	2.4501	0.76
26	11394.3	978.107	2.4445	0.99
27	11397.1	976.997	2.4417	0.90
28	11402.9	974.695	2.4359	0.91
29	11405.7	973.570	2.4331	1.02
30	11413.6	970.415	2.4252	0.91
31	11419.3	968.128	2.4195	0.91
32	11421.6	967.185	2.4172	0.82
33	11430.2	963.758	2.4086	0.70
34	11438.5	960.407	2.4002	0.60
35	11558.2	912.467	2.2804	0.26
36	11566.8	909.045	2.2719	0.27
37	11575.0	905.775	2.2637	0.42
38	11580.0	903.736	2.2586	0.43
39	11582.9	902.602	2.2558	0.52
40	11591.5	899.138	2.2471	0.83
41	11597.1	896.923	2.2416	0.66
42	11599.7	895.874	2.2390	0.84
43	11608.6	892.282	2.2300	0.95
44	11613.0	890.556	2.2257	1.08
45	11616.1	889.291	2.2225	0.98
46	11621.1	887.310	2.2176	0.94
47	11623.7	886.240	2.2149	0.79
48	11630.2	883.633	2.2084	1.03
49	11637.7	880.647	2.2009	0.88
50	11645.0	877.735	2.1936	1.12
51	11653.6	874.278	2.1850	0.55
52	11665.3	869.599	2.1733	1.31
53	11667.6	868.673	2.1710	1.04
54	11678.0	864.492	2.1605	0.37
55	11688.6	860.255	2.1499	1.72
56	11698.9	856.147	2.1397	0.73
57	11700.8	855.365	2.1377	0.58
58	11708.4	852.330	2.1301	1.38
59	11722.0	846.888	2.1165	0.91
60	11729.5	843.893	2.1090	0.60
61	11742.0	838.889	2.0965	0.76
62	11762.8	830.534	2.0757	0.34
63	11858.2	792.326	1.9802	0.59
64	11864.7	789.740	1.9737	0.32
65	11882.0	782.795	1.9564	1.18
66	11891.0	779.203	1.9474	0.78
67	11897.9	776.438	1.9405	0.64
68	11903.9	774.018	1.9344	1.12
69	11914.9	769.637	1.9235	1.12
70	11920.9	767.238	1.9175	0.56
71	11927.6	764.542	1.9107	0.59
72	11936.7	760.907	1.9017	0.87
73	11960.3	751.453	1.8780	0.33

Current Data Parameters
NAME 72656-16-RRT
EXPNO 3
PROCNO 1

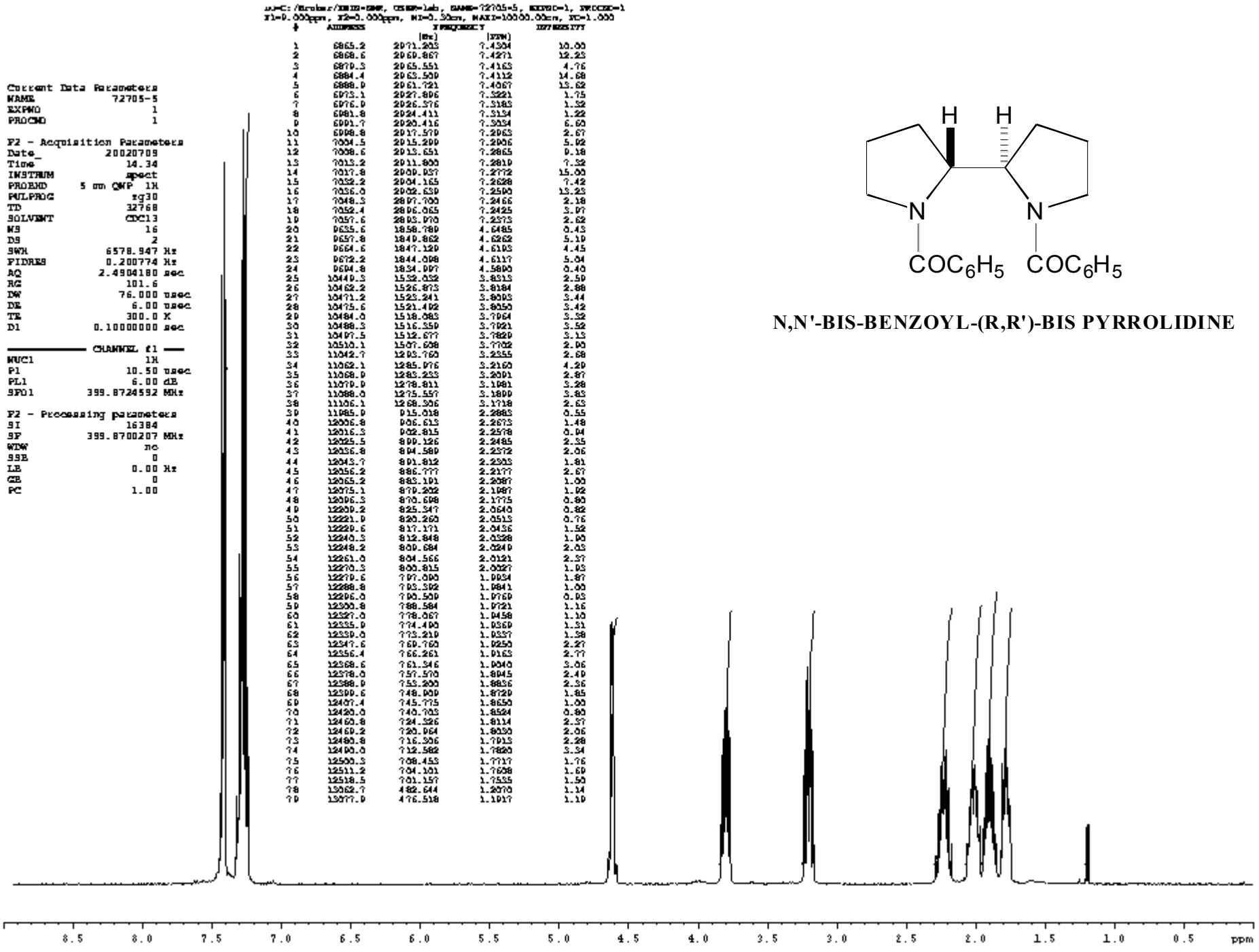
F2 - Acquisition Parameters
Date_ 20021023
Time 13.08
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT D2O
NS 32
DS 2
SWH 6561.680 Hz
FIDRES 0.200247 Hz
AQ 2.4969716 sec
RG 362
DW 76.200 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

CHANNEL f1
NUC1 1H
P1 10.00 usec
PL1 -5.00 dB
SFO1 400.1322007 MHz

F2 - Processing parameters
SI 16384
SF 400.1299401 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



(R,R')-BIS-PYRROLIDINE L-TARTRATE



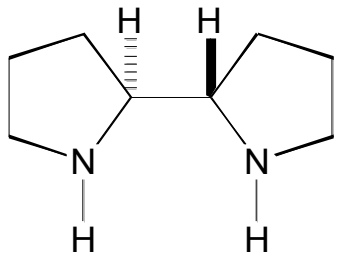
#	Address	Frequency (Hz)	Frequency (PPM)	Intensity
1	6865.2	2971.203	7.4304	10.00
2	6868.6	2969.867	7.4271	12.23
3	6879.3	2965.551	7.4163	4.76
4	6884.4	2963.509	7.4112	14.68
5	6888.9	2961.721	7.4067	13.62
6	6893.1	2959.896	7.3221	1.75
7	6896.9	2958.376	7.3183	1.52
8	6901.8	2956.411	7.3134	1.22
9	6991.7	2920.416	7.3034	6.60
10	6998.8	2917.579	7.2963	2.67
11	7004.5	2915.299	7.2906	5.02
12	7008.6	2913.651	7.2865	9.18
13	7013.2	2911.800	7.2819	7.52
14	7017.8	2909.957	7.2772	15.00
15	7032.2	2904.165	7.2628	7.42
16	7036.0	2902.639	7.2590	15.23
17	7048.3	2897.700	7.2466	2.18
18	7052.4	2896.065	7.2425	5.97
19	7057.6	2893.970	7.2373	2.62
20	9635.6	1858.789	4.6485	0.43
21	9657.8	1849.862	4.6262	5.19
22	9664.6	1847.129	4.6195	4.45
23	9672.2	1844.088	4.6117	5.04
24	9684.8	1839.097	4.5990	0.45
25	10449.3	1532.032	3.8313	2.59
26	10462.2	1526.873	3.8184	2.88
27	10471.2	1523.241	3.8093	3.44
28	10475.6	1521.402	3.8050	3.42
29	10484.0	1518.085	3.7964	3.32
30	10488.3	1516.359	3.7921	3.52
31	10497.5	1512.677	3.7829	3.13
32	10510.1	1507.608	3.7702	2.05
33	11042.7	1295.760	3.2555	2.68
34	11062.1	1285.976	3.2160	4.29
35	11068.9	1285.253	3.2091	2.87
36	11079.9	1278.811	3.1981	3.28
37	11088.0	1275.557	3.1899	3.83
38	11106.1	1268.306	3.1718	2.63
39	11985.9	915.018	2.2885	0.55
40	12006.8	906.613	2.2673	1.48
41	12016.3	902.815	2.2578	0.84
42	12025.5	899.126	2.2485	2.35
43	12036.8	894.589	2.2372	2.06
44	12043.7	891.812	2.2303	1.81
45	12056.2	886.777	2.2177	2.67
46	12065.2	883.191	2.2087	1.00
47	12075.1	879.202	2.1987	1.02
48	12096.3	870.698	2.1775	0.80
49	12259.2	825.347	2.0640	0.82
50	12221.9	820.260	2.0513	0.76
51	12229.6	817.171	2.0436	1.52
52	12240.3	812.848	2.0328	1.93
53	12248.2	809.684	2.0249	2.03
54	12261.0	804.566	2.0121	2.37
55	12270.3	800.815	2.0027	1.93
56	12279.6	797.090	1.9934	1.87
57	12288.8	793.392	1.9841	1.00
58	12296.0	790.509	1.9769	0.93
59	12300.8	788.584	1.9721	1.16
60	12327.0	778.067	1.9458	1.10
61	12335.9	774.490	1.9369	1.31
62	12339.0	773.219	1.9337	1.58
63	12347.6	769.760	1.9250	2.27
64	12356.4	766.261	1.9163	2.77
65	12368.6	761.346	1.9040	5.06
66	12378.0	757.570	1.8945	2.49
67	12388.9	753.200	1.8836	2.36
68	12399.6	748.909	1.8729	1.85
69	12407.4	745.775	1.8650	1.00
70	12420.0	740.705	1.8524	0.80
71	12460.8	724.326	1.8114	2.37
72	12469.2	720.964	1.8030	2.06
73	12480.8	716.306	1.7913	2.28
74	12495.0	712.582	1.7820	5.34
75	12500.3	708.453	1.7717	1.76
76	12511.2	704.101	1.7608	1.69
77	12518.5	701.157	1.7535	1.90
78	13062.7	482.644	1.2070	1.14
79	13077.9	476.518	1.1917	1.19

N,N'-BIS-BENZOYL-(R,R')-BIS PYRROLIDINE

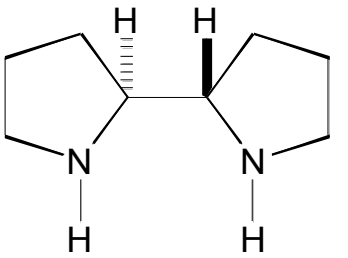
DW=C:/Bruker/XWIN-NMR, USER=lab, NAME=72705-23, EXPNO=1, PROCNO=1
F1=9.000ppm, F2=0.000ppm, MI=0.20cm, MAXI=10000.00cm, PC=1.000

Current Data Parameters	
NAME	72705-23
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20020719
Time	19.00
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	4
SWH	6578.947 Hz
FIDRES	0.200774 Hz
AQ	2.4904180 sec
RG	645.1
DW	76.000 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec
CHANNEL f1	
NUC1	1H
P1	10.50 usec
PL1	-3.00 dB
SFO1	400.2522014 MHz
F2 - Processing parameters	
SI	16384
SF	400.2499939 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F	ADDRESS	FREQUENCY [Hz]	[PPM]	INTENSITY
1	8855.1	1941.164	4.8499	55.89
2	9260.1	1778.547	4.4436	13.39
3	9689.4	1606.170	4.0129	0.27
4	9707.1	1599.056	3.9951	0.78
5	9713.5	1596.466	3.9887	1.50
6	9727.7	1590.795	3.9745	1.91
7	9741.8	1585.129	3.9603	1.55
8	9748.1	1582.596	3.9540	0.82
9	9765.9	1575.464	3.9362	0.30
10	10135.0	1427.221	3.5658	5.02
11	10155.8	1418.896	3.5450	6.50
12	10172.5	1412.194	3.5283	4.40
13	10181.6	1408.506	3.5191	0.25
14	11210.8	995.230	2.4865	0.40
15	11218.9	991.982	2.4784	0.56
16	11229.1	987.891	2.4682	0.84
17	11235.4	985.382	2.4619	0.85
18	11243.4	982.146	2.4538	1.02
19	11253.8	977.983	2.4434	1.05
20	11262.0	974.694	2.4352	0.95
21	11268.2	972.195	2.4290	0.95
22	11278.6	968.023	2.4185	0.69
23	11286.9	964.691	2.4102	0.56
24	11407.3	916.351	2.2894	0.23
25	11415.7	912.956	2.2810	0.22
26	11424.0	909.638	2.2727	0.41
27	11431.2	906.766	2.2655	0.52
28	11440.5	903.026	2.2562	0.80
29	11448.1	899.947	2.2485	0.82
30	11456.8	896.466	2.2398	0.97
31	11462.4	894.215	2.2341	1.11
32	11470.0	891.149	2.2265	0.94
33	11479.0	887.558	2.2175	1.08
34	11486.2	884.663	2.2103	0.86
35	11493.9	881.578	2.2026	0.98
36	11502.1	878.282	2.1943	0.49
37	11514.8	873.178	2.1816	1.32
38	11527.1	868.259	2.1693	0.31
39	11536.5	864.469	2.1598	1.78
40	11548.1	859.802	2.1482	0.70
41	11557.5	856.032	2.1387	1.35
42	11570.6	850.776	2.1256	0.92
43	11578.3	847.680	2.1179	0.52
44	11590.9	842.619	2.1052	0.73
45	11611.5	834.367	2.0846	0.27
46	11705.4	796.637	1.9903	0.53
47	11711.6	794.156	1.9841	0.33
48	11728.9	787.188	1.9667	1.16
49	11737.9	783.587	1.9577	0.75
50	11751.1	778.292	1.9445	1.13
51	11761.7	774.034	1.9339	1.13
52	11774.6	768.874	1.9210	0.58
53	11783.7	765.190	1.9118	0.88
54	11807.1	755.809	1.8883	0.32



(S,S')-BIS-PYRROLIDINE D-TARTRATE



(S,S')-BIS-PYRROLIDINE

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Current Data Parameters
NAME                 72705-03
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20020705
Time                   16.01
INSTRUM                spect
PROBHD     5 mm QNP  1H
PULPROG                zg30
TD                     32768
SOLVENT                CDCl3
NS                        32
DS                         2
SWH                6561.680 Hz
FIDRES             0.200247 Hz
AQ                 2.4969716 sec
RG                       128
DW                    76.200 usec
DE                     6.00 usec
TE                   300.0 K
D1                 0.10000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    10.00 usec
PL1                   -5.00 dB
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                       16384
SF            400.1300056 MHz
WDW                         no
SSB                          0
LB                        0.00 Hz
GB                           0
PC                        1.00
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IN=C:/Bruker/XWIN-NMR, USER=lab, NAME=72705-03, EXPNO=1, PROCNO=1
F1=9.000ppm, F2=0.000ppm, MI=0.84cm, MAXI=10000.00cm, PC=1.000

F	ADDRESS	FREQUENCY [Hz]	[PPM]	INTENSITY
1	6409.7	2908.911	7.2699	3.41
2	10705.8	1188.358	2.9699	4.44
3	10720.0	1182.664	2.9557	4.09
4	10724.0	1181.067	2.9517	5.11
5	10731.1	1178.192	2.9445	8.02
6	10737.7	1175.546	2.9379	4.11
7	10745.1	1172.592	2.9305	7.05
8	10749.2	1170.957	2.9264	7.60
9	10762.9	1165.452	2.9127	5.81
10	10782.1	1153.777	2.8835	1.14
11	10809.1	1146.981	2.8665	8.46
12	10820.2	1142.527	2.8554	4.46
13	10824.8	1140.671	2.8508	15.00
14	10827.9	1139.425	2.8476	11.23
15	10836.7	1135.920	2.8389	8.10
16	10844.5	1132.785	2.8310	6.69
17	10850.4	1130.447	2.8252	4.80
18	10853.3	1129.261	2.8222	4.90
19	10870.0	1122.583	2.8055	3.67
20	11284.9	956.422	2.3903	2.09
21	11833.4	736.737	1.8412	1.32
22	11838.0	734.889	1.8366	0.84
23	11845.6	731.864	1.8291	2.16
24	11850.4	729.942	1.8243	2.16
25	11855.0	728.081	1.8196	2.05
26	11859.3	726.358	1.8153	1.82
27	11862.9	724.923	1.8117	2.86
28	11867.1	723.246	1.8075	3.56
29	11872.1	721.249	1.8025	3.30
30	11874.8	720.157	1.7998	3.23
31	11879.5	718.269	1.7951	2.95
32	11884.9	716.122	1.7897	4.34
33	11890.9	713.730	1.7837	2.45
34	11896.0	711.681	1.7786	4.67
35	11898.8	710.554	1.7758	4.31
36	11903.3	708.739	1.7713	3.57
37	11907.6	707.045	1.7670	4.01
38	11911.1	705.641	1.7635	3.45
39	11915.0	704.048	1.7595	3.27
40	11923.4	700.688	1.7512	4.28
41	11924.7	700.189	1.7499	4.27
42	11929.0	698.471	1.7456	4.18
43	11934.5	696.254	1.7401	2.81
44	11941.2	693.577	1.7334	7.04
45	11946.1	691.614	1.7285	4.65
46	11953.2	688.781	1.7214	2.48
47	11954.9	688.084	1.7197	2.32
48	11959.1	686.391	1.7154	4.82
49	11960.8	685.704	1.7137	5.41
50	11964.1	684.410	1.7105	4.37
51	11975.8	679.710	1.6987	5.68
52	11980.8	677.718	1.6937	4.43
53	11982.8	676.921	1.6918	3.29
54	11984.7	676.133	1.6898	2.76
55	11987.8	674.923	1.6868	1.67
56	11994.9	672.055	1.6796	3.91
57	11996.9	671.246	1.6776	3.37
58	12002.3	669.093	1.6722	2.49
59	12006.5	667.413	1.6680	1.87
60	12012.1	665.165	1.6624	1.85
61	12016.2	663.551	1.6583	2.46
62	12026.3	659.494	1.6482	1.32
63	12027.7	658.930	1.6468	1.34
64	12033.1	656.782	1.6414	1.07
65	12047.0	651.186	1.6274	0.93
66	12295.7	551.580	1.3785	1.84
67	12300.5	549.656	1.3737	1.06
68	12314.2	544.206	1.3601	2.98
69	12318.6	542.442	1.3557	2.48
70	12325.4	539.695	1.3488	3.07
71	12331.0	537.469	1.3432	2.85
72	12337.1	534.997	1.3371	3.46
73	12343.9	532.281	1.3303	3.93
74	12348.4	530.470	1.3257	2.95
75	12354.9	527.869	1.3192	2.50
76	12362.2	524.943	1.3119	2.42
77	12366.1	523.412	1.3081	2.65
78	12385.9	515.465	1.2882	0.98