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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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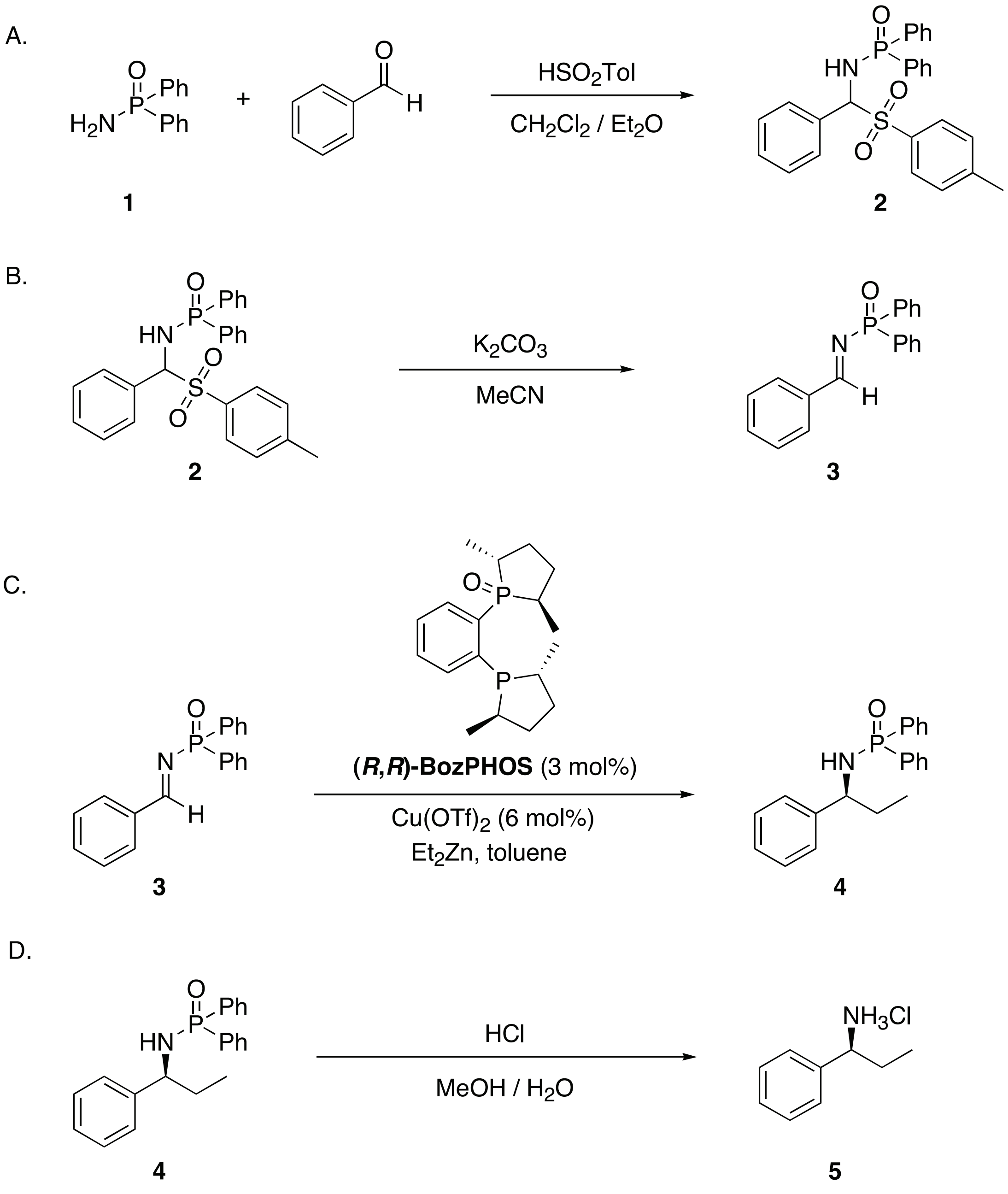
PREPARATION OF ENANTIOMERICALLY ENRICHED (1*S*)-1-PHENYLPROPAN-1-AMINE HYDROCHLORIDE BY A CATALYTIC ADDITION OF DIORGANOZINC REAGENTS TO IMINES

[Benzenemethanamine, α-ethyl-, hydrochloride, (α*S*)-]



Submitted by Jean-Nicolas Desrosiers, Alexandre Côté, Alessandro A. Boezio and André B. Charette.[1]

Checked by Scott E. Denmark and Justin I. Montgomery.

1. Procedure

A. N-[(4-Methylphenyl)sulfonyl(phenyl)methyl]-P,P-diphenylphosphinic amide (**2**). A 1-L, three-necked, round-bottomed flask equipped with a mechanical stirrer (fitted with a 7-cm Teflon paddle) and two rubber septa is charged with **1** (9.55 g, 43.97 mmol) (Notes 1, 2). Dichloromethane (75 mL) (Note 3) and diethyl ether (365 mL) (Note 4) are added successively to the flask. The resulting suspension is stirred for 5 min and benzaldehyde (6.7 mL, 65.96 mmol) (Note 5) is added via a syringe. *p*-Toluenesulfinic acid (10.3 g, 65.96 mmol) (Note 6) is then added in one portion at room temperature. The reaction mixture is capped and allowed to stir for 48 h (200 rpm), during which time a white precipitate is slowly formed. The mixture is filtered through a sintered glass funnel and the white solid is washed with diethyl ether (100 mL) and dried under vacuum (25 °C, 0.1 mmHg) to afford 18.12−18.45 g (89−91% yield) (Note 7) of the title compound.

B. N-[(Phenyl)methylene]-P,P-diphenylphosphinic amide (**3**). A flame-dried 1-L, one-necked, round-bottomed flask equipped with an egg-shaped magnetic stirring bar and a rubber septum is charged with **2** (18.00 g, 39.00 mmol) and anhydrous potassium carbonate (26.95 g, 195.0 mmol) (Note 8). The flask is purged with argon and anhydrous acetonitrile (365 mL) (Note 9) is added via cannula under argon at room temperature. The resulting suspension is vigorously stirred under argon at room temperature for 12 h. The reaction mixture is filtered through a sintered glass funnel and the residue is washed with acetonitrile (50 mL). The filtrate is concentrated at 30 °C by rotary evaporation (30–50 mmHg) to afford 10.88 g (91% yield) (Note 10) of the title compound as an off-white solid.

C. N-[(1S)-1-Phenylpropyl]-P,P-diphenylphosphinic amide (**4**). A flame-dried, 500-mL, one-necked, round-bottomed flask equipped with an egg-shaped magnetic stirring bar and a rubber septum is charged with $Cu(OTf)_2$ (745 mg, 2.06 mmol) (Note 11) and ***(R,R)*-BozPHOS** (332 mg, 1.03 mmol) (Note 12) in a glove-box under argon. Anhydrous toluene (172 mL) (Note 13) is added to the flask at room temperature via cannula. The resulting dark green heterogeneous solution is stirred for 1 h at room temperature and neat diethylzinc (7.05 mL, 68.78 mmol) (Note 14) is added at room temperature under argon via a 10-mL gas-tight syringe (*CAUTION: NEAT DIETHYLZINC IS HIGHLY PYROPHORIC*). The resulting dark brown suspension is stirred for 20 min at room temperature and then is diluted by the addition of anhydrous toluene (172 mL) via cannula under argon. The mixture is cooled to 0 °C (internal temperature measured with a thermocouple probe (Note 15)) with a cryostat (Note 16) and the system is opened to add the solid **3** (10.50 g, 34.39 mmol) quickly in one portion. The flask is sealed with a septum and purged with argon over a period of 5 min. The reaction mixture is allowed to stir for 21 h at 0 °C under argon. Aqueous saturated ammonium chloride (100 mL) is added dropwise via cannula at 0 °C to quench the reaction. The mixture is poured into a 2-L separatory funnel containing aqueous saturated ammonium chloride (400 mL). The biphasic mixture is extracted with dichloromethane (3 x 500 mL). The combined extracts are dried over Na_2SO_4 (150 g), filtered and concentrated at 40 °C by rotary evaporation (100–150 mmHg) and then at 20 mmHg to afford 11.82 g of an off-white solid containing the title compound and the catalyst. This mixture is used without purification for the next step. A 200.0 mg sample of the crude product is purified by silica gel chromatography (Note 17) to afford 185.7 mg (92.9% recovery, 97% ee) (Note 18) of the title compound as a white solid.

D. (1S)-1-Phenylpropan-1-amine hydrochloride (**5**). A 1-L, one-necked, round-bottomed flask equipped with an egg-shaped magnetic stirring bar is charged with **4** (11.62 g, 92.9% purity, 32.19 mmol). A mixture of methanol (270 mL) (Note 19) and concentrated aqueous HCl (60.9 mL) (Note 21) is added to the flask. The flask is capped and the resulting clear, bright yellow solution is allowed to stir at room temperature for 16.5 h (Note 20). The reaction mixture is then concentrated at 40 °C by rotary evaporation (10 mmHg) and the residue is dissolved in 1.21 M aqueous HCl (300 mL). The precipitate (Note 22) is removed by filtration on a sintered-glass funnel. The acidic filtrate is extracted with diethyl ether (3 x 300 mL) (Note 23), then it is basified ($pH \geq 12$, Note 24) by adding 2 M NaOH (~300 mL). The resulting milky solution is extracted with dichloromethane (4 x 300 mL). The combined extracts are dried over Na_2SO_4 (160 g) and filtered. A solution of HCl in diethyl ether (1 M, 67.6 mL, 67.6 mmol) (Note 25) is added to the organic layer and the mixture is concentrated at 30 °C by rotary evaporation (200–250 mmHg), then at 50–100 mmHg. The resulting off-white to yellow solid (5.60 g) is triturated with ethyl acetate (50 mL) and filtered to afford 4.89 g (88% yield, 97% ee) (Notes 26-28) of the pure title compound as a white solid.

2. Notes

1. *P,P*-Diphenylphosphinic amide (**1**) was purchased from Alfa Aesar as diphenylphosphinamide (98+%).

2. *P,P*-Diphenylphosphinic amide (**1**) can be prepared by the following procedure (not attempted by the checkers): A flame-dried 2-L, one-necked, round-bottomed flask, equipped with an egg-shaped magnetic stirring bar, a rubber septum and an internal thermocouple probe is purged with argon. The flask is then charged with 1 L of anhydrous dichloromethane under argon. The septum is removed and acetone oxime (16.56 g, 227 mmol) is added quickly in one portion and the flask is sealed and purged again with argon. Freshly distilled triethylamine (31.6 mL, 227 mmol) is added via a syringe and the resulting colorless solution is cooled to –78 °C (internal temperature) with an acetone/dry ice bath (approximately 30 min are needed to reach this temperature). Freshly distilled, colorless chlorodiphenylphosphine (42 mL, 227 mmol) is added dropwise (2 mL/min) via a syringe at such a rate that the internal temperature does not exceed –70 °C. After the addition is complete, the resulting milky solution is stirred 15 min at –78 °C under argon. The cooling bath is removed, and the solution is allowed to warm to room temperature over a period of 1.5 h and stirred 1 h at that temperature. The milky solution becomes clear. The solvent is removed under reduced pressure and the resulting off-white to yellow solid is dried under vacuum for 12 h. The residue is dissolved in acetone (200 mL) and dried under reduced pressure. This last step is repeated once again. (This step makes the removal of the solid from the flask easier. Furthermore, the solid can be ground to a finer powder, which facilitates the next step. This step can be avoided but problems may occur, such as the formation of a gummy yellow solid during the addition to the aqueous ammonium hydroxide solution. This problem can be related to the presence of dichloromethane in the solid. Heating the mixture with a heat gun to dissolve everything can solve this problem, but lower yields and side-products are obtained.) The solid is removed from the flask and ground to a powder using a mortar and pestle. The powder is added in one portion into an Erlenmeyer flask containing a stirring solution (magnetic stirring bar) of concentrated aqueous ammonium hydroxide (660 mL) and distilled water (330 mL). The mixture is usually heterogeneous and the precipitate is a white solid.

Sometimes the solid added dissolves rapidly to form a clear yellow solution and, after few seconds, a white solid starts to precipitate. The heterogeneous mixture is stirred for 45 min and **1** is obtained as a white solid by filtration through a sintered glass funnel. The aqueous filtrate is extracted with dichloromethane (3 x 600 mL). The combined extracts are dried over Na_2SO_4, filtered and evaporated under reduced pressure. The white solid obtained is combined with the white precipitate obtained above after filtration. The combined solids are dissolved in benzene (300 mL) and evaporated. This step is repeated three times to remove traces of water to afford 46.31–47.87 g (94–97% yield) of **1**. The purity can be increased by crystallization in ethyl acetate.

3. Dichloromethane (ACS grade) was purchased from Fisher Scientific and was used as received.

4. Diethyl ether (ACS grade) was purchased from Fisher Scientific and was used as received.

5. Benzaldehyde was purchased from Aldrich Chemical Company, Inc. and was freshly distilled (70–72 °C, 20 mmHg) prior to use.

6. *p*-Toluenesulfinic acid was prepared according to the procedure described in *Organic Syntheses*, see ref 2.

7. The physical properties are as follows: mp 153–155 °C (sealed tube); IR (neat) cm^{-1}: 725, 748, 756, 888, 1030, 1086, 1109, 1124, 1148, 1191, 1289, 1301, 1312, 1436, 1459, 1597, 2954, 3056, 3205; ^{31}P NMR (202 MHz, DMSO) δ: 24.98. Due to the very low solubility of the compound in DMSO, clean NMR spectral data are difficult to obtain because minor impurities are much more soluble than the compound of interest.

8. Granular potassium carbonate was purchased from Aldrich Chemical Company, Inc. and was ground to a powder using a mortar and pestle then dried under vacuum (100 °C, 1 mmHg).

9. Anhydrous acetonitrile was obtained by filtration through a drying column on a GlassContour system (Irvine, CA).

10. The purity is greater than 97% according to the ^{31}P and ^{1}H NMR spectra and the only observed impurities are benzaldehyde and **1**. These impurities can be removed on a short pad of silica gel (EtOAc 100%). The physical properties of the purified material are as follows: mp 144–146 °C; R_f 0.47 (EtOAc); MS (ESI+) *m/z* 307.1 (20%), 306.1 (M^{+}+H, 100%), 233.1 (37%), 219.1 (22%), 201.2 (14%); Anal. calcd for $C_{19}H_{16}NOP$: C, 74.74; H, 5.28; N, 4.59. found: C, 74.45; H, 5.27; N, 4.71; IR (KBr) cm^{-1}: 704, 729,

752, 832, 848, 926, 998, 1074, 1110, 1127, 1199, 1311, 1368, 1443, 1577, 1597, 1626, 1663, 1698, 2881, 3024, 3056; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39−7.56 (m, 9 H), 7.90−8.02 (m, 6 H), 9.32 (d, J = 32.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CHCl_3$) δ: 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.8, 130.0, 131.4 (d, $J_{C\text{-}P}$ = 9.2 Hz), 131.7 (d, $J_{C\text{-}P}$ = 3.6 Hz), 132.8 (d, $J_{C\text{-}P}$ = 127.5 Hz), 133.5, 135.6 (d, $J_{C\text{-}P}$ = 24.2 Hz), 173.5 (dd, $J_{C\text{-}P}$ = 7.7, 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 24.78.

11. $Cu(OTf)_2$ was purchased from Strem Chemicals, Inc. It was stored under argon atmosphere in a glove-box and was used without prior purification.

12. (*R,R*)-BozPHOS was prepared according to the preceeding procedure and was stored under argon in a glove box.

13. Anhydrous toluene was obtained by filtration through a drying column on a GlassContour system (Irvine, CA).

14. Diethylzinc is a moisture sensitive and pyrophoric liquid and must be manipulated in an inert atmosphere. Neat diethylzinc was purchased from Aldrich Chemical Co. Inc. and was used without prior purification.

15. A PFA coated thermocouple probe, Type K (Omega Engineering, Inc.) was inserted through the septum after the addition of diethylzinc to monitor the internal temperature of the reaction solution.

16. Approximately 35 min are needed to reach that temperature. A Neslab, model CC-65II, cryostat was used to maintain the reaction mixture at 0 °C.

17. The mixture was dissolved in a minimum amount of dichloromethane and then was charged onto a column (diameter = 2 cm, height = 15 cm) of 200 g of UltraPure silica gel (40–63 μm) purchased from Silicycle. The column was eluted with EtOAc and 8-mL fractions were collected. Fractions 15-33 were combined and concentrated by rotary evaporation (30 °C, 50 mmHg). The desired product can be visualized on TLC with a UV lamp or by spraying with a phosphomolybdic acid solution. The R_f value of the title compound in EtOAc is 0.37.

18. The physical properties are as follows: mp 127–129 °C; MS (ESI+) *m/z*: 337.2 (M^+ + H, 21%), 336.1 (M^+, 100%), 233.2 (17%), 219.2 (18%), 218.1 (28%), 201.2 (9%). Anal. calcd. for $C_{21}H_{22}NOP$: C, 75.21; H, 6.61; N, 4.18; found: C, 74.90; H, 6.55; N, 4.35; IR (KBr) cm^{-1}: 722, 752, 904, 933, 1057, 1090, 1109, 1122, 1182, 1198, 1438, 1460, 2873, 2926, 2963, 3055, 3135; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.78 (t, J = 7.5 Hz, 3 H),

1.78−1.88 (m, 1 H), 1.96−2.06 (m, 1 H, exchanges with D_2O), 3.27 (br, 1 H), 4.09 (pent, J = 8.4 Hz, 1 H), 7.14−7.16 (m, 2 H), 7.21−7.34 (m, 5 H), 7.39−7.50 (m, 4 H), 7.75 (ddt, J = 12.0, 6.9, 1.5 Hz, 2 H), 7.86 (ddt, J = 12.0, 7.1, 1.3 Hz, 2 H); ^{13}C NMR (126 MHz, $CHCl_3$) δ: 10.5, 32.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 57.1, 126.5, 127.1, 128.3 (d, $J_{C\text{-}P}$ = 12.9 Hz), 128.4, 128.4 (d, $J_{C\text{-}P}$ = 12.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.2 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.9 (d, $J_{C\text{-}P}$ = 131.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 133.2 (d, $J_{C\text{-}P}$ = 128.0 Hz), 143.5 (d, $J_{C\text{-}P}$ = 5.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 22.74; $[\alpha]_D^{20}$ –41.6 (c = 2.14, MeOH). The enantiomeric excess of the product is determined by HPLC analysis at 254 nm [Chiralpak, AD, 85:15 hexanes: *i*-PrOH, 1mL/min: (*R*) t_r (minor) = 10.2 min, (*S*) t_r (major) = 13.4 min)].

19. Methanol (ACS grade) was purchased from Fisher Scientific and was used as received.

20. The reaction was followed by ^{31}P NMR spectroscopic analysis. The rate of disappearance of the signal at 23.2 ppm is proportional to the rate of formation of the desired product. The new signals at 34.3 ppm and at 36.6 ppm correspond, respectively, to diphenylphosphinic acid and methyl diphenylphosphinate.

21. Aqueous concentrated HCl (ACS grade) was purchased from Fisher Scientific and was used as received.

22. The precipitate is diphenylphosphinic acid.

23. This step is used to extract the methyl diphenylphosphinate.

24. An ColorpHast indicator strip purchased from EM Science, Inc. was used to measure the pH.

25. 1 M Hydrogen chloride solution in diethyl ether was purchased from Aldrich Chemical Company, Inc. and was used as received.

26. The physical properties are as follows: mp 231–234 °C; MS (EI) *m/z*: 135.1, (4%), 106.1 (100%), 79.1 (18%), 74.1 (75%), 59.0, (100%). Anal. calcd. for $C_9H_{14}ClN$: C, 62.97; H, 8.22; N, 8.16; found: C, 62.71; H, 8.33; N, 8.18; IR (KBr) cm^{-1}: 754, 764, 1386, 1394, 1458, 1509, 1600, 2536, 2618, 2685, 2914, 2963, 3035; ^{1}H NMR (400 MHz, MeOD) δ: 0.88 (t, J = 7.3 Hz, 3 H), 1.90−2.10 (m, 2 H), 4.15 (dd, J = 9.5, 5.8 Hz, 1 H), 7.39−7.49 (m, 5 H); ^{13}C NMR (100 MHz, MeOD) δ: 10.5, 28.7, 58.3, 128.4, 130.3, 130.3, 138.1; $[\alpha]_D^{20}$ +16.2 (c = 1.03, MeOH).

27. The enantiomeric excess of the product was determined on the trifluoroacetyl derivative of the amine by GC analysis with an FID detector (Astec Chiraldex GT-A (30 m x 0.32 mm) 10 psi, 90 °C isothermal): (*R*) t_r

(minor) = 19.59 min, (*S*) t_r (major) = 20.53 min). To prepare the trifluoroacetamide derivative, 1 mL of 2 M aqueous NaOH solution was added to 10 mg of the amine hydrochloride salt in a 5 mL conical vial. The aqueous layer was extracted with 1 mL of dichloromethane. The organic layer was dried over Na_2SO_4 (0.5 g), and was decanted into a 5-mL round-bottomed flask. An egg-shaped magnetic stir bar and 250 μL of trifluoroacetic anhydride were added and the mixture was stirred at room temperature under argon for 5 min. The solvent and excess reagents were removed by rotary evaporation (80 mmHg, 25 °C, 5 min; then 5 mmHg, 25 °C, 10 min). The solid residue was dissolved in 1 mL of dichloromethane and the liquid was filtered through a syringe filter for GC analysis. For the enantioenriched compounds, the sample was concentrated to ca. 0.1 mL to observe the minor isomer.

28. The submitters were able to determine the enantiomeric excess of the free amine directly by GC analysis with an FID detector [Beta Dex^{TM} 120; 30 °C to 85 °C in 11 min and isothermal thereafter: (*R*) t_r (minor) = 43.0 min, (*S*) t_r (major) = 43.6 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.

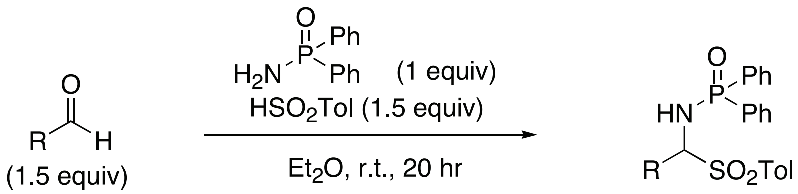
3. Discussion

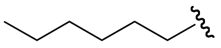
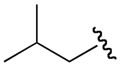
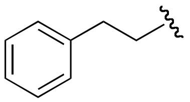
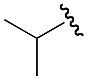
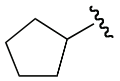
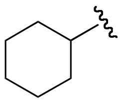
This procedure provides an attractive route to α-substituted chiral amines by using a catalytic asymmetric addition of a diorganozinc reagent. Numerous activating groups have been reported for the catalytic asymmetric additions of diorganozinc reagents to imines. Among them, *N*-tosylimines,[4] *N*-arylimines[5] and *N*-acylimines[6] have been used as precursors. Herein, we use the *N*-phosphinoyl group because of its facile cleavage under mildly acidic conditions. The other activating groups require harsh oxidizing, reducing or basic conditions for cleavage. Another advantage of using the *N*-phosphinoyl activating group is that a crystalline product is generally obtained. This product can often be recrystallized from low polarity solvents to increase enantiopurity.[7]

Earlier syntheses of *N*-diphenylphosphinoylimines involved either a condensation between an aldehyde and *N*-diphenylphosphinoyl amide promoted by $TiCl_4$ and Et_3N[8] or a radical rearrangement between an oxime and chlorodiphenylphosphine with the presence of Et_3N.[9] These methods are not useful for the synthesis of *N*-phosphinoylimines on large scale because of the low yields that result from tedious workup procedures or extensive purification. However, the present synthesis of *N*-phosphinoylimines via a stable sulfinyl adduct is very effective for production of multi-gram quantities of material.[10] The procedure, which consists of deprotonating the sulfinyl adduct **2** with K_2CO_3 to induce imine formation, is general, straightforward, inexpensive, and high yielding.

Several *N*-phosphinoylimines derived from aromatic or aliphatic aldehydes can be generated by this sequence. For instance, acetaldehyde, heptanal, isovaleraldehyde, hydrocinnamaldehyde, isobutyraldehyde, cyclopentanecarboxaldehyde and cyclohexanecarboxaldehyde afford the desired sulfinic acid adducts of the *N*-phosphinoylimine on a small scale (Table 1).[11] These adducts are generated in diethyl ether and precipitate from the reaction mixture as white solids. In the present case, a mixture of dichloromethane and diethyl ether gives a better yield and a higher purity of the sulfinyl adduct **2**. Because of the higher solubility of its adduct, 1-naphthaldehyde gives a poor yield (30%). To avoid problems of handling unstable imines of aliphatic aldehydes, it is also possible to carry out the asymmetric addition directly on the sulfinic acid adduct.[11,12] The same reaction conditions are used except that an excess of diethylzinc (2.5 equiv) is needed to generate the imine *in situ*.

Table 1. Sulfinyl adducts synthesis[a,b]

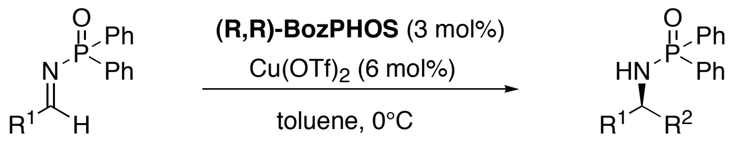


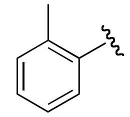
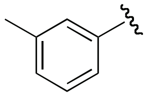
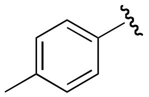
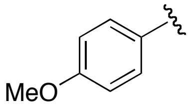
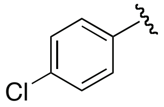
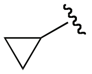
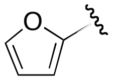
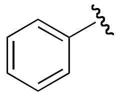
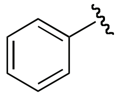
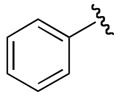
Entry	R	Yield (%)
1		91
2		87
3		84
4[c]		97
5		88
6		95
7		72

[a] See reference 11 [b] 5 mmol scale [c] 10 mmol scale.

The copper-catalyzed addition of diorganozinc reagents to alkyl- or aryl-substituted *N*-phosphinoylimines proceeds in high yields, with excellent enantioselectivities and without using a large excess of organometallic reagents. Furthermore, both enantiomers of the BozPHOS ligand synthesized from the commercially available enantiomers of Me-DuPHOS. The reaction is proceeds well with different dialkyl- (Me_2Zn, *n*-Bu_2Zn and *i*-Pr_2Zn) or functionalized zinc reagents (Table 2).[7] This system can also tolerate a wide variety of *N*-phosphinoylimines obtained from either electron-poor or electron-rich aldehydes.[7, 13]

Table 2. Enantioselective Addition of Dialkylzinc Reagents to Imines[a,b]



Entry	R^1	$R^2{}_2Zn$	Yield (%)	ee (%)
1		Et_2Zn	97	99
2		Et_2Zn	96	97
3		Et_2Zn	94	98
4		Et_2Zn	91	98
5		Et_2Zn	97	97
6		Et_2Zn	95	94
7[c]		Et_2Zn	97	96
8[d]		Me_2Zn	87	97
9		$n Bu_2Zn$	92	96
10[e]		$i Pr_2Zn$	84	95

[a] See reference 7 [b] 2 mmol scale [c] Specific conditions: 2.8 mol% $Cu(OTf)_2$ / 3.0 mol% **(R,R)-BozPHOS** at -15 °C [d] Specific conditions: 5.0 mol% $Cu(OTf)_2$• Toluene / 5.0 mol% **(R,R)-BozPHOS** at r.t. [e] 3 equiv of $i Pr_2Zn$.

1. Département de Chimie, Université de Montréal, P.O. Box 6128, Station Downtown, Montréal (Québec) Canada, H3C 3J7.
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Appendix
Chemical Abstracts Nomenclature; (Registry Number)

P,P-Diphenylphosphinic amide; (5994-87-6)
Benzaldehyde; (100-52-7)
p-Toluenesulfinic acid: Benzenesulfinic acid, 4-methyl-; (536-57-2)
N-[(4-Methylphenyl)sulfonyl(phenyl)methyl] *P,P*-diphenylphosphinic amide; (701291-86-3)
N-[(Phenyl)methylene]-*P,P*-diphenylphosphinic amide: Phosphinic amide, *P*,*P*-diphenyl-*N*-(phenylmethylene)-; (67764-52-7)
$Cu(OTf)_2$: Methanesulfonic acid, trifluoro-, copper(2+) salt; (34946-82-2)
(*R,R*)-BozPHOS: Phospholane, 1-[2-[(2*R*,5*R*)-2,5-dimethyl-1-oxido-1-phospholanyl]phenyl]-2,5-dimethyl-, (2*R*,5*R*)-; (38132-66-8)
Diethylzinc; (557-20-0)
N-[(*1S*)-1-Phenylpropyl]-*P,P*-diphenylphosphinic amide: Phosphinic amide, *P,P*-diphenyl-*N*-[(*1S*)-1-phenylpropyl]-; (106651-15-4)
(1*S*)-1-Phenylpropan-1-amine hydrochloride: Benzenemethanamine, α-ethyl-, hydrochloride, (α*S*)-: (19146-52-2)

```
JIM-XV-15F1_1Hprint

exp1  std1h

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solvent    CDCl3  dof           0
file        exp  dm           nnn
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sfrq    399.951  dmf          200
tn           H1  dpwr          20
at        4.096    PROCESSING
np        65536  lb          0.30
sw       8000.0  wtfile
fb         4400  proc          ft
bs           16  fn      not used
tpwr         63  math           f
pw          8.9
d1            0  werr
tof      -425.7  wexp
nt            4  wbs
ct            4  wnt
alock         n     DISPLAY
gain   not used  sp        -200.0
    FLAGS        wp        4399.3
il            n  vs            54
in            n  sc             0
dp            y  wc           250
hs           nn  hzmm       17.60
                 is        620.99
                 rfl       4902.5
                 rfp       2903.6
                 th            20
                 ins        6.000
                 nm    ph
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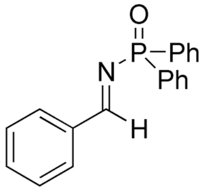

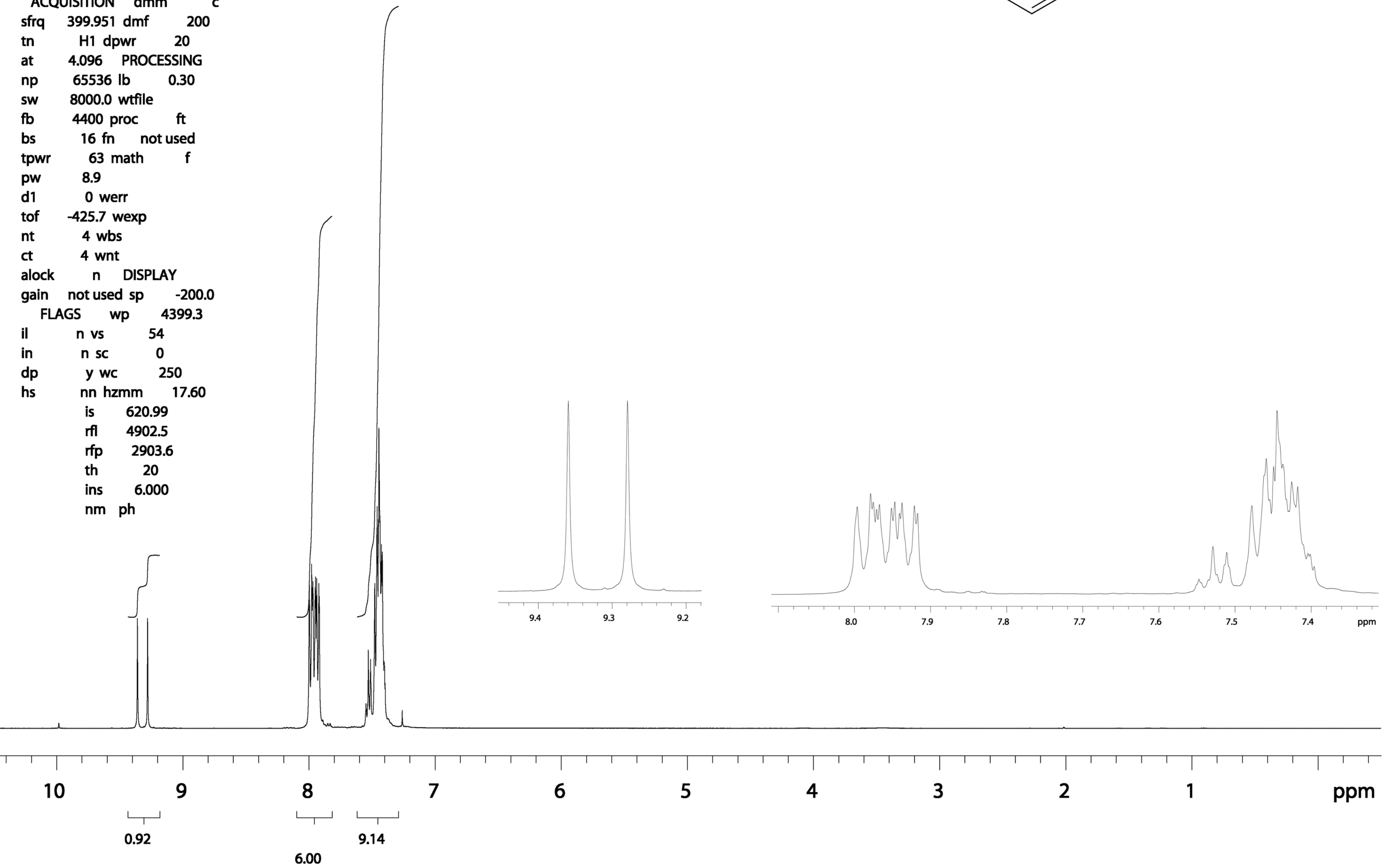

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tn           H1    dmm             c
at        4.665    dmf           200
np        65536    dseq
sw       7024.9    dres          1.0
fb         4000    homo            n
bs            4    PROCESSING
tpwr         63    wtfile
pw          5.8    proc           ft
d1            0    fn       not used
tof         2.0    math            f
nt            4
ct            4    werr
alock         n    wexp
gain   not used    wbs
   FLAGS           wnt
il            n
in            n
dp            y
hs           nn
   DISPLAY
sp       -249.9
wp       5496.5
vs           31
sc            0
wc          250
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is      1472.39
rfl      4643.9
rfp      3627.8
th            7
ins       2.000
ai   ph
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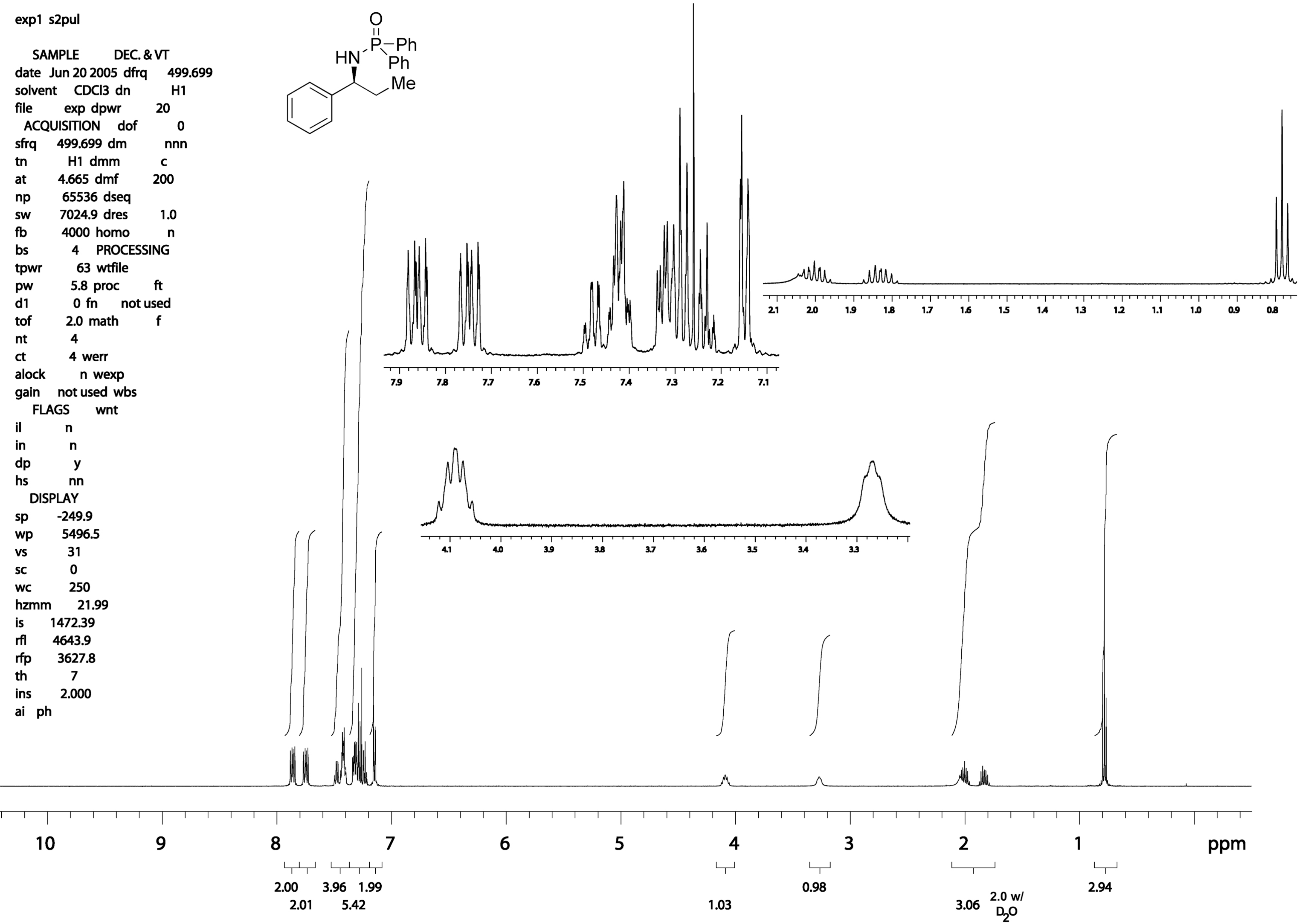

JIM-XV-19R

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file        exp  dm           nnn
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tn            H1  dpwr         20
at         4.096     PROCESSING
np         65536  lb         0.30
sw        8000.0  wtfile
fb          4400  proc         ft
bs            16  fn     not used
tpwr          63  math          f
pw           8.9
d1             0  werr
tof       -425.7  wexp
nt             4  wbs
ct             4  wnt
alock          n     DISPLAY
gain    not used  sp       -200.0
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il             n  vs           50
in             n  sc            0
dp             y  wc          250
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                  is       803.64
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                  th            4
                  ins       1.000
                  nm   ph
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