Organic Syntheses

(*R*)-*N*,*N*'-Dimethyl-1,1'-binaphthyldiamine

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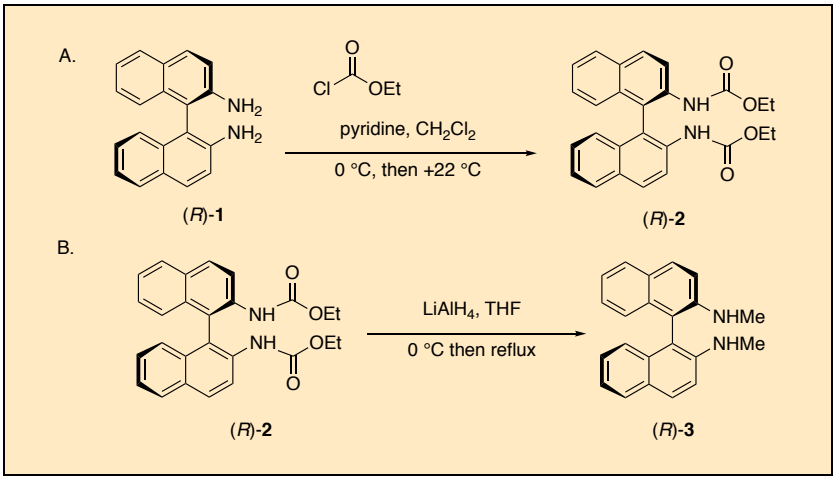
Checked by Eric R. Welin and Brian M. Stoltz



Procedure (Note 1)

A. *(1R)-[1,1'-Binaphthalene]-2,2'-diylbiscarbamic acid diethyl ester ((R)-***2***).* A 500-mL, round-bottomed, two-necked flask (24/40 joints) containing a 16 x 37 mm Teflon-coated, ellipsoid-shaped magnetic stirring bar is fitted with a rubber septum on one neck through which is inserted a thermocouple probe and with a gas inlet adapter on the other neck. The flask is flame-dried under vacuum, refilled with argon and cooled to 22 °C. The rubber septum is removed and (*R*)-(+)-1,1-binaphthyl-2,2-diamine (*R*)-**1** (5.29 g, 18.6 mmol, Note 2) is added through a plastic funnel under increased argon flow, followed by anhydrous dichloromethane (160 mL). The rubber septum is placed back into the neck and pyridine (12.0 mL, 148.8 mmol, 8.0 equiv) is

added dropwise using a 20 mL syringe (addition time of 1 min) (Note 3). The resulting yellow solution is cooled to 4 °C (internal temperature) with an ice-bath and freshly distilled ethyl chloroformate (3.91 mL, 40.92 mmol, 2.2 equiv) is added dropwise via a 5 mL syringe (addition time of 10 min) (Note 4). The reaction mixture is stirred in the ice bath for 1 h at 3–4 °C. The flask is then removed from the cooling bath and the mixture is stirred for 30 min at 22 °C (Note 5) (Figure 1).

Figure 1. Reaction mixture upon warm-up to 22 °C

The gas inlet adapter is replaced with a 125-mL, pressure-equalizing addition funnel containing a 2.0 M aq. solution of KOH (100 mL), which is added to the reaction mixture over 10 min followed by stirring for an additional 20 min at 22 °C. The resulting biphasic mixture is transferred to a 500-mL separatory funnel. The organic layer is separated and the aqueous layer is extracted with dichloromethane (3 x 50 mL). The combined organic extracts are washed with a 1 M aq. solution of HCl (2 x 150 mL) and brine (1 x 150 mL), and the extracts are dried over anhydrous $MgSO_4$ (2.5 g). The dried organic phase is vacuum-filtered (house vacuum, ~10 mmHg) through a glass funnel with glass wool into a 1-L, round-bottomed flask and the $MgSO_4$ is washed with dichloromethane (2 x 20 mL). The filtrate is concentrated by rotary evaporation (28 °C, 32 mmHg) and then dried under vacuum (1.0 mmHg, 25 °C, 12 h) to afford (*R*)-**2** as white foam (7.79 g, 98%) (Notes 6, 7 and 8) (Figure 2).

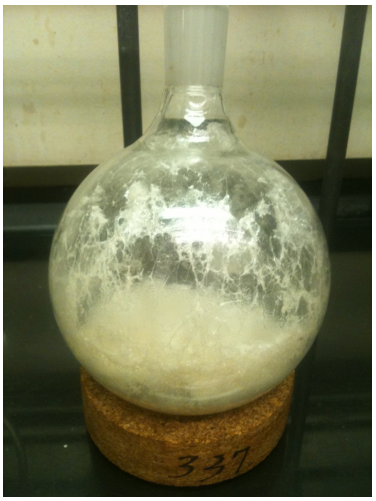


Figure 2. (*1R*)-[1,1'-Binaphthalene]-2,2'-diylbiscarbamic acid diethyl ester ((*R*)-2).

B. *(R)-N,N-Dimethyl-1,1-binaphthyldiamine ((R)-**3**).* An oven-dried, 500-mL round-bottomed, two-necked flask (24/40 joints) with a 16 x 37 mm Teflon-coated ellipsoid-shaped magnetic stirring bar is fitted with a rubber septum in one neck and a reflux condenser (length of jacket -200 mm) with a gas inlet adapter in the other neck. The flask is evacuated under vacuum, refilled with argon, placed in an ice-bath followed by the addition of anhydrous THF (75 mL) via syringe through the septum. The rubber septum is removed and under increased argon flow lithium aluminum hydride (5.06 g, 133.5 mmol, 11.0 equiv) is added through a plastic funnel in small portions (addition over 10 min) (Note 9). The resulting suspension is stirred for 10 min and a solution of (*R*)-diethyl [1,1'-binaphthalene]-2,2'-diyldicarbamate (*R*)-**2** (5.2 g, 12.14 mmol) in anhydrous THF (25 mL) is added to the reaction mixture dropwise over 12 min. The flask containing (*R*)-**2** is rinsed with THF (2 x 3 mL) and the washes are added to the reaction mixture (Figure 3).

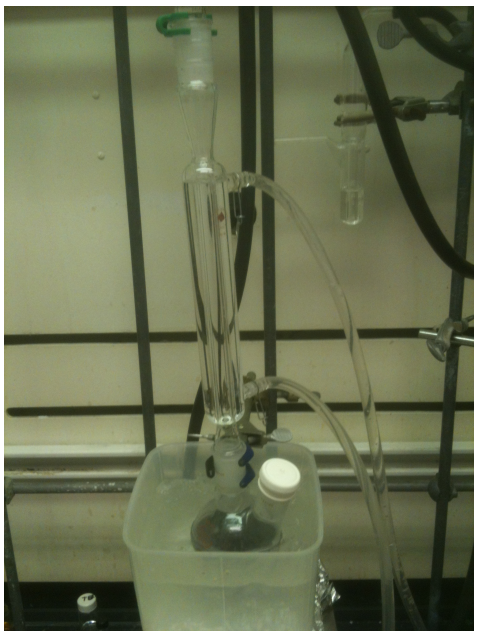


Figure 3. Reaction set up for (*R*)-2

The ice bath is replaced with an oil bath and the rubber septum is replaced with a glass stopper. The oil bath is gradually heated to 75 °C and the reaction mixture is heated to reflux for 15 h. The resulting green reaction mixture is allowed to cool to 22 °C (Note 10) and diethyl ether (400 mL) is added. The mixture is cooled in an ice-bath for 10 min. The gas inlet adapter is removed and H_2O (5.1 mL) is added dropwise to the reaction mixture through the condenser using a pipette. In a similar fashion, 3 M NaOH (5.1 mL) and H_2O (15.3 mL) are added (Note 11), and the resulting mixture is stirred for 10 min before celite (10 g) is added to the suspension through the inlet closer to the reaction solution. A medium-porosity, 15 cm diameter sintered glass funnel filled with 1 inch of celite, is pre-equilibrated with ethyl acetate. The ethyl acetate is removed by vacuum filtration into a 1 L Erlenmeyer flask and discarded before 1 inch of sand is added to the top of the now-dry celite. The reaction suspension is filtered through this pad (Figure 4) rinsing the flask with ethyl acetate (3 x 20 mL) to aid in transfer. The vacuum is removed when the solvent reaches the top of the filter cake. Ethyl acetate (50 mL) is added, and the celite filter cake is stirred with a spatula, then the supernatant solvent is filtered, again removing vacuum

when the solvent reaches the top of the filter cake. This process is repeated twice before filtering all liquid exhaustively. The filtrate is dried with Na_2SO_4 (20 g) and filtered through a plastic funnel with a cotton plug, rinsing with ethyl acetate (3 x 20 mL). The filtrate is concentrated by rotary evaporation (40 °C, 32 mmHg) and placed under high vacuum (< 1.0 mmHg, 22 °C, 36 h) to afford (*R*)-**3** as a yellow foam (3.71 g, 98%) (Notes 12, 13 and 14) (Figure 5).

Figure 4. Filtration apparatus

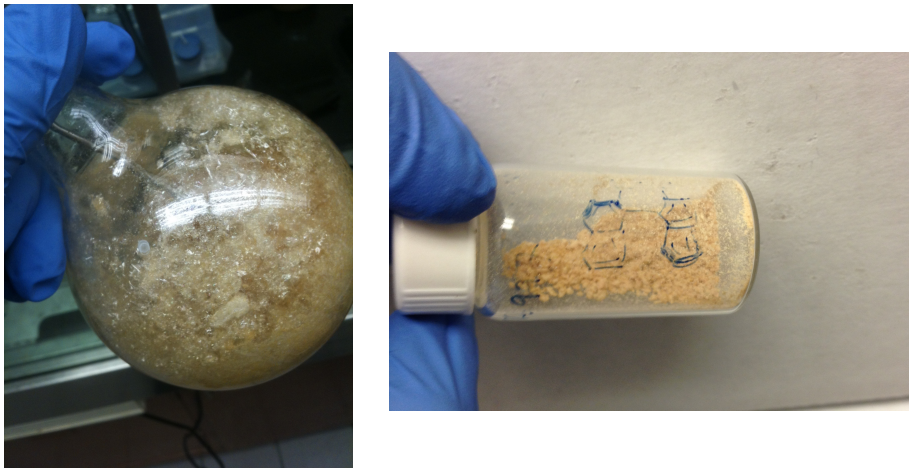


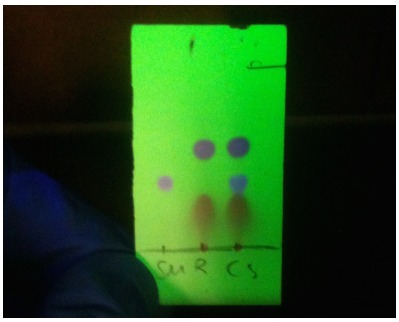
Figure 5. (*R*)-*N*,*N*-Dimethyl-1,1-binaphthyldiamine ((*R*)-3)

Notes

1. Prior to performing each reaction, a thorough hazard analysis and risk assessment should be carried out with regard to each chemical substance and experimental operation on the scale planned and in the context of the laboratory where the procedures will be carried out. Guidelines for carrying out risk assessments and for analyzing the hazards associated with chemicals can be found in references such as Chapter 4 of "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at https://www.nap.edu/catalog/12654/prudent-practices-in-the-laboratory-handling-and-management-of-chemical. See also "Identifying and Evaluating Hazards in Research Laboratories" (American Chemical Society, 2015) which is available via the associated website "Hazard Assessment in Research Laboratories" at https://www.acs.org/content/acs/en/about/governance/committees/chemicalsafety/hazard-assessment.html. In the case of this procedure, the risk assessment should include (but not necessarily be limited to) an evaluation of the potential hazards associated with argon, (*R*)-(+)-1,1-binaphthyl-2,2-diamine, dichloromethane, ethyl chloroformate, aqueous hydrochloric acid, brine, magnesium sulfate, tetrahydrofuran, lithium

aluminum hydride, diethyl ether, sodium hydroxide, celite, ethyl acetate, sodium sulfate, hexanes, calcium hydride, 1,2,4,5-tetrachlorobenzene, and ethanol.

2. The checkers purchased (*R*)-(+)-1,1-binaphthyl-2,2-diamine (*R*)-**1** from Ark Pharm in >99% ee, which was used as received.
3. Pyridine (Alfa Aesar, 99+%) was freshly distilled from CaH_2.
4. The submitters used ethyl chloroformate (Sigma Aldrich, 97%) that was freshly distilled. The checkers used ethyl chloroformate (Sigma Aldrich, 97%) as received.
5. The reaction was monitored by TLC on Merck silica gel 60 F_{254} TLC glass plates and visualized with UV light. R_f (product) = 0.52 (hexanes/EtOAc, 3:2); R_f (starting material) = 0.34 (hexanes/EtOAc, 3:2). TLC analysis is depicted on this photograph:



6. The purity of (*R*)-**2** was determined to be 95% by Quantitative NMR analysis using 1,2,4,5-tetrachlorobenzene as the internal standard.
7. A reaction performed on half scale provided 3.92 g (98%) of the white foam.
8. An analytical sample was prepared by recrystallization of the crude product: A 25-mL Erlenmeyer flask, filled with 7 mL of ACS certified hexanes and 350 mg of (*R*)-**2** and equipped with a thermometer, was placed in a water bath and heated to 67−68 °C. The flask was occasionally stirred with a glass rod. When the internal temperature reached 58−59 °C, compound **2** was fully dissolved and clear yellowish solution was obtained. The hot solution was transferred with a Pasteur pipette and filtered through glass wool (− 1 cm thick) that was inserted in a separate pipette into a clean 20-mL scintillation vial which was placed into the same hot water bath. (**Note**: both pipettes were preheated with a

heat gun, before the transfer). The vial was covered with aluminum foil and taken out from the hot bath and cooled to 22 °C. After 20 min a white paste was obtained which was transferred to a filter paper on a Hirsh funnel (4 cm in diameter) with suction. The vial was washed with ice-cold hexanes (3 x 0.7 mL), which was transferred to the Hirsh funnel to afford 257 mg of **2** as a white solid. (mp 82−83 °C). The purified product was transferred to a 20-mL scintillation vial and recrystallized again under the same conditions from 5 mL of hexanes, upon isolation the product was washed with 0.5 x 3 mL ice-cold hexanes to afford 147 mg of white solid. The vial was loosely closed with a cap and was placed into a 30 cm tall test tube with 24/40 outer joint equipped with a gas inlet adapter and a piece of paraffin (5 x 5 cm). The sample was dried at 22 °C under vacuum for 14 h (0.1 mmHg). The test tube was slowly refilled with argon and the sample (137 mg) was recrystallized from 2 mL of hexanes and filtered to a 5-mL vial. After 20 min a white paste was obtained and the supernatant was removed using a 250-μL microliter syringe (**Note**: the paste was gently pressed with a glass rod). The product is washed with 0.5 mL of cold hexanes and excess hexanes removed in the same manner. Trace amounts of hexanes were removed azeotropically with 10 mL of THF (35 °C, 25 mmHg). The vial was fitted with a cap and dried in the tube under vacuum for 3 h (0.1 mmHg). The checkers did not observe any remaining solids upon the third recrystallization, so this material was not filtered while hot. This final iteration aids in removing the last traces of dichloromethane, which could not be removed by extended exposure to vacuum alone. Characterization data for product **2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.17 (t, J = 7.1 Hz, 6H), 4.09 (qd, J = 7.1, 2.2 Hz, 4H), 6.26 (s, 2H), 6.96 (dd, J = 8.4, 0.9 Hz, 1H), 7.26 (ddd, J = 8.4, 7.0, 1.4 Hz, 2H), 7.42 (ddd, J = 8.1, 6.8, 1.2 Hz, 2H), 7.93 (dt, J = 8.2, 0.9 Hz, 2H), 8.06 (d, J = 9.1 Hz, 2H), 8.56 (d, J = 9.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 14.5, 61.5, 117.6, 119.5, 124.9, 125.2, 127.5, 128.4, 130.4, 130.7, 132.6, 135.5, 153.8; IR (CH_2Cl_2): 3405, 3055, 2987, 1732, 1621, 1602, 1502, 1422, 1342, 1265, 1218, 1096, 1081, 1060, 1016, 956, 896, 867, 823, 737 cm^{-1}. HRMS (ESI+): m/z calcd. for $C_{26}H_{25}N_2O_4$ $[M+H]^+$ 429.1809, found 429.1817; $[\alpha]^{22}_D$ = +66.7 (c = 1.2 THF); mp = 82−83 ºC (hexanes), CSP-HPLC: CHIRALPAK ® AD-H, 50.0:50.0 hexane/*i*-PrOH, 0.5 mL/min, 220 nm, 22 °C., er > 99:1 (t_R (*R*)-**2** = 12.93 min; t_R (*S*)-**2** = 9.36 min).

9. Lithium aluminum hydride (powder, 95%) was purchased from Sigma Aldrich and used without further purification.

10. An aliquot of the reaction mixture was quenched with 1 mL of water, extracted with 1 mL of diethyl ether and checked by TLC with UV light. R_f (product) = 0.44 (hexanes/EtOAc, 5:1); R_f (starting material) = 0.34 (hexanes/EtOAc, 5:1). TLC analysis is depicted in this photograph:

11. Caution: quenching excess lithium aluminum hydride with water is a highly exothermic process that produces H_2. The quenching should be conducted in an efficient fume hood in order to safely vent the H_2 gas.
12. The purity of (*R*)-**3** was determined to be 95% by Quantitative NMR analysis using 1,2,4,5-tetrachlorobenzene as the internal standard.
13. A second reaction on slightly smaller scale provided 2.84 (99%) of the product as a yellow foam.
14. An analytical sample was prepared by recrystallization of the crude product. In a 25-mL Erlenmeyer flask were placed hexanes (1 mL), ethanol (9 mL), and (*R*)-**3** (500 mg). The flask was fitted with a thermometer and was heated in a water bath to 74–75 °C. The flask was occasionally stirred and when the internal temperature reached 68–69 °C, (*R*)-**3** was fully dissolved and a clear, yellowish solution was obtained. The hot solution was filtered through a pipette packed with glass wool (ca. 1 cm thick) into a clean 20-mL scintillation vial which was placed into the same hot water bath (**Note**: the solution was transferred with a Pasteur pipette and both pipettes were preheated with a heat gun, before the transfer). The vial was covered with aluminum foil, taken out from the hot bath and allowed to cool to 22 °C, then placed in an ice bath for 30 min. White needle-like crystals formed and were transferred to filter paper on a Hirsh funnel (4 cm in diameter) with suction. The vial was washed with ice-cold hexanes (3 x 5.0 mL) and transferred to the Hirsh funnel, giving 242 mg of (*R*)-**3** as a white solid. Characterization data for product: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.84 (s, 6H), 3.72 (br s, 2H), 6.99 (d,

J = 7.7 Hz, 2H), 7.18 (dddd, J = 16.6, 8.1, 6.8, 1.4 Hz, 4H), 7.28 (d, J = 8.9 Hz, 2H), 7.82 (dd, J = 7.3, 2.2 Hz, 2H), 7.94 (dd, J = 8.9, 0.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.2, 111.8, 113.6, 121.9, 123.8, 126.8, 127.7, 128.3, 129.8, 133.8, 145.7; IR (neat): 3416, 2913, 2824, 1617, 1598, 1513, 1426, 1342, 1301, 1170, 1152, 1022, 814 cm^{-1}. HRMS (ESI+): m/z calcd. for $C_{22}H_{21}N_2$ $[M+H]^+$ 313.1699, found 313.1704; $[\alpha]^{22}_D$ = +168.8 (c = 1.3 THF); mp = 144−145 °C (hexanes/ethanol, 9:1); CSP-HPLC: CHIRALPAK AD-H, 95.0 : 5.0 hexane/*i*-PrOH, 0.5 mL/min, 220 nm, 22 °C., er > 99:1 (t_R (*R*)-**3** = 9.81 min; t_R (*S*)-**3** = 9.16 min).

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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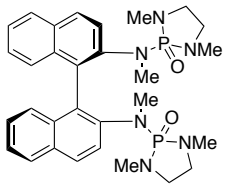
Discussion

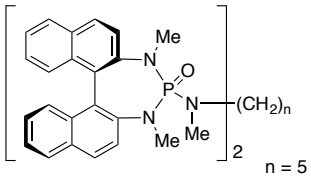
1,1′-Binaphthyl-2,2′-diamine (BINAM) based ligands represent a class of axially chiral, bidentate ligands used in asymmetric catalysis. BINAM based ligands are very useful in a variety of metal-catalyzed, enantioselective transformations including *inter alia*: conjugate addition of organozinc reagents[2a], hydroamination[2b,c], hydrogenation of carbon-carbon[2d] and carbon-oxygen[2e,f] double bonds, Diels-Alder[2g], and carbonyl-ene reactions.[2h] In addition to their utility as ligands, BINAM derivatives are often used as organocatalysts.[3] In particular, one of the BINAM derivatives - (*R*)-*N*,*N*′-dimethyl-1,1′-binaphthyldiamine ((*R*)-**5**) is widely used as a backbone for a variety of chiral ligands and organocatalysts (Table 1).[4] A number of Lewis basic catalysts developed in these laboratories, designed for the activation of Lewis acidic reagents in Groups 14 and 16, are obtained from (*R*)-*N*,*N*′ -dimethyl-1,1′-binaphthyldiamine.[5]

Because of their utility, the synthesis of BINAM derivatives has been actively investigated. Clemo and Dawson reported the use of hydrazine hydrate to convert 2-naphthol into BINAM by a Bucherer reaction, however this method requires rather harsh reaction conditions (high pressure, temperature and long reaction times).[6] A milder method for the synthesis of BINAM was reported by Luo and co-workers using 2-naphtylhydrazine and 2-naphtol; this modification allows access to BINAM at ambient pressure.[7] In addition, BINAM can be obtained by oxidative coupling of 2-naphtylamine using stoichiometric amounts of oxidants, such as Mn(IV)−, Cu(II)−, Fe(III)−based reagents and mCPBA.[8] Finally, an interesting report describes the preparation of *N*,*N*′-dialkyl-1,1′binaphthyldiamines by oxidative coupling of secondary arylamines employing heterogeneous rhodium catalysts.[9]

Table 1. Representative dimethyl BINAM-based catalysts and ligands

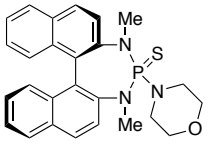


Denmark, 2000
Enantioselective Allylation of Aldehydes

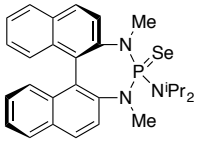


Denmark, 2001
Enantioselective Allylation and Propargylation of Aldehydes

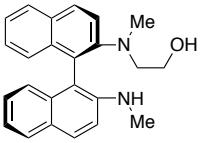
Enantioselective Crossed-Aldol Reactions of Aldehydes



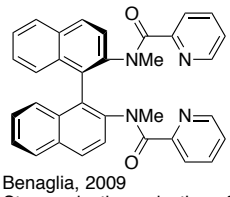
Denmark, 2010
Enantioselective Selenoetherification



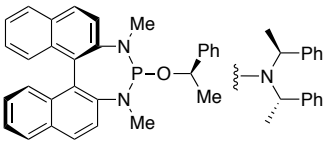
Denmark, 2013
Enantioselective Thiofunctionalization



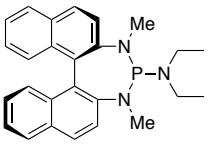
Shi, 2002
Asymmetric Additions to Aldehydes (Zn)



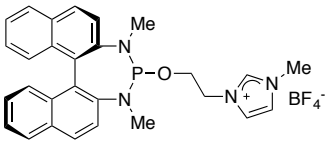
Benaglia, 2009
Stereoselective reduction of imines ($SiCl_4$)



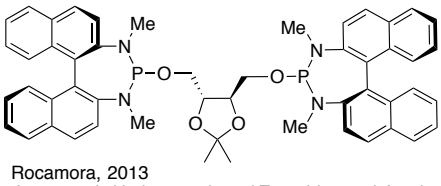
Rocamora, 2010
Asymmetric Hydrovinylation of Styrene (Pd)



Reetz, 2003
Enantioselective Hydroformylation (Rh)



Rocamora, Gomez, 2014
Asymmetric Allylic Substitution (Pd)



Rocamora, 2013
Asymmetric Hydrogenation of Enamides and Acrylates (Rh)

Montazeri and co-workers reported an efficient method to access enantioenriched BINAM from 2-naphthylamine in the presence of stoichiometric amounts of $FeCl_3$ $6H_2O$ and L-2-phenylglycine as a chiral ligand.[10] In addition, catalytic, stereoselective oxidative coupling of arylamines have been described, but these methods suffer from low yields and poor selectivities.[11]

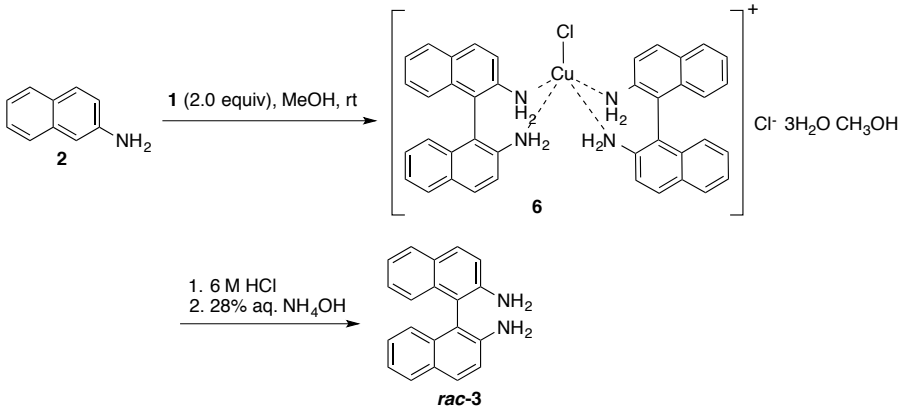
Another strategy to access BINAM derivatives involves thermal or acid-mediated [3,3]-sigmatropic rearrangement of *N*,*N*′-binaphthyl hydrazines.[12] A highly enantioselective [3,3]-sigmatropic rearrangement using chiral phosphoric acids as catalysts was independently reported by Kürti[13] and List[14]. This method provides highly enantioenriched BINAMs in good to excellent yields, moreover, the reaction can be scaled to 10 mmol without loss in selectivity or yield. Even though this method provides enantioenriched BINAM derivatives on a gram scale, it is limited to the accessibility of expensive, chiral phosphoric acids. In a related protocol, Chen and co-workers reported a synthesis of BINAM derivatives by diastereoselective [3,3]-rearrangement of N-(–)-menthoxycarbonyldiaryl hydrazines.[15] The preparation of the BINAM precursor requires four steps and the rearrangement proceeds with only marginal selectivity (dr's up to 2:1). The diastereomers are separated and require an additional step to remove chiral auxiliary.

A highly efficient kinetic resolution of BINAM derivatives involving chiral Bronsted acid-catalyzed imine formation and transfer hydrogenation was reported by Tan and co-workers.[16] This approach to enantioenriched BINAMs is illustrated for racemic BINAMs possessing a bulky substituent on one of the amino groups. Installation of this substituent results in an increased barrier to rotation greater steric interaction with the chiral phosphoric acid catalyst. Separation of functionalized product and unreacted starting material followed by deprotection affords enantiomerically pure BINAM.

Although catalytic, enantioselective methods for the synthesis of BINAM derivatives exist, they require expensive catalysts and employ substrates that are not commercially available. Current synthetic routes for BINAM derivatives typically rely on classical resolution of BINAM, followed by functionalization of the enantioenriched diamine.[17]

In view of the importance of BINAMs as important motifs in catalysis we have developed a practical, detailed procedure for the synthesis of BINAM and (*R*)-*N*,*N*′-dimethyl-1,1′-binaphthyldiamine. Racemic BINAM is obtained by oxidative coupling of 2-naphtylamine using a copper(II) oxidizing agent,

developed by Zi and co-workers.[18] The reagent is prepared from copper(II) chloride dihydrate and benzylamine; the structure of the complex has been confirmed by single-crystal X-ray analysis. Treatment of 2-naphtylamine with two equivalents of copper(II) complex **1** in methanol results in the formation of copper(II) complex **6**, which has been isolated and fully characterized by Zi and co-workers (Scheme 1). The authors report that carrying out the reaction under air or inert atmosphere has no effect on the conversion of 2-naphtylamine. Dissolution of **6** in 6 M aq. HCl, followed by addition of 28% aq. NH_4OH produces racemic BINAM (***rac*-3**).



Scheme 1. Oxidative coupling of 2-naphtylamine with Cu(II) complex 1

Resolution of the racemic diamine is accomplished with (+)-camphor-10-sulfonic acid in a mixture of dichloromethane, ethanol, and water.[17] It is important to note that the solvent ratio is critical for successful resolution. The initially formed (+)-camphor-10-sulfonate diamine salt contains BINAM with 96:4 er which can be enantioenriched to >99.5: 0.5 by refluxing the suspended salt in a mixture of dichloromethane, ethanol and, water. The free amine is recovered by treatment of the sulfonate salt with 1 M aq. NaOH/diethyl ether. Enantioenriched (*R*)-BINAM contains ~1% of diethyl ether by weight; heating under high vacuum (< 1.0 mmHg, 110 °C, 12 h) did not remove the solvent and the (*R*)-BINAM can be used as is in the next step without further purification.

(*R*)-*N*,*N*′-dimethyl-1,1′-binaphthyldiamine (*R*)-**5** is prepared in two steps from R-BINAM.[19] Carbamate (*R*)-**4** is obtained by acylation with ethyl chloroformate in the presence of pyridine and is then reduced with $LiAlH_4$, to produce (*R*)-*N*,*N*′-dimethyl-1,1′-binaphthyldiamine (*R*)-**5.**

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Appendix
Chemical Abstracts Nomenclature (Registry Number)

(*R*)-(+)-1,1′-Binaphthyl-2,2′-diamine: (*R*)-[1,1'-binaphthalene]-2,2'-diamine (18741-85-0)

Pyridine: Pyridine; (110-86-1)

Ethyl chloroformate: Chloroformic ethyl ester; (541-41-3)

Lithium aluminum hydride: Luminate(1-), tetrahydro-, lithium (1:1) , (T-4)-; (16853-85-3)

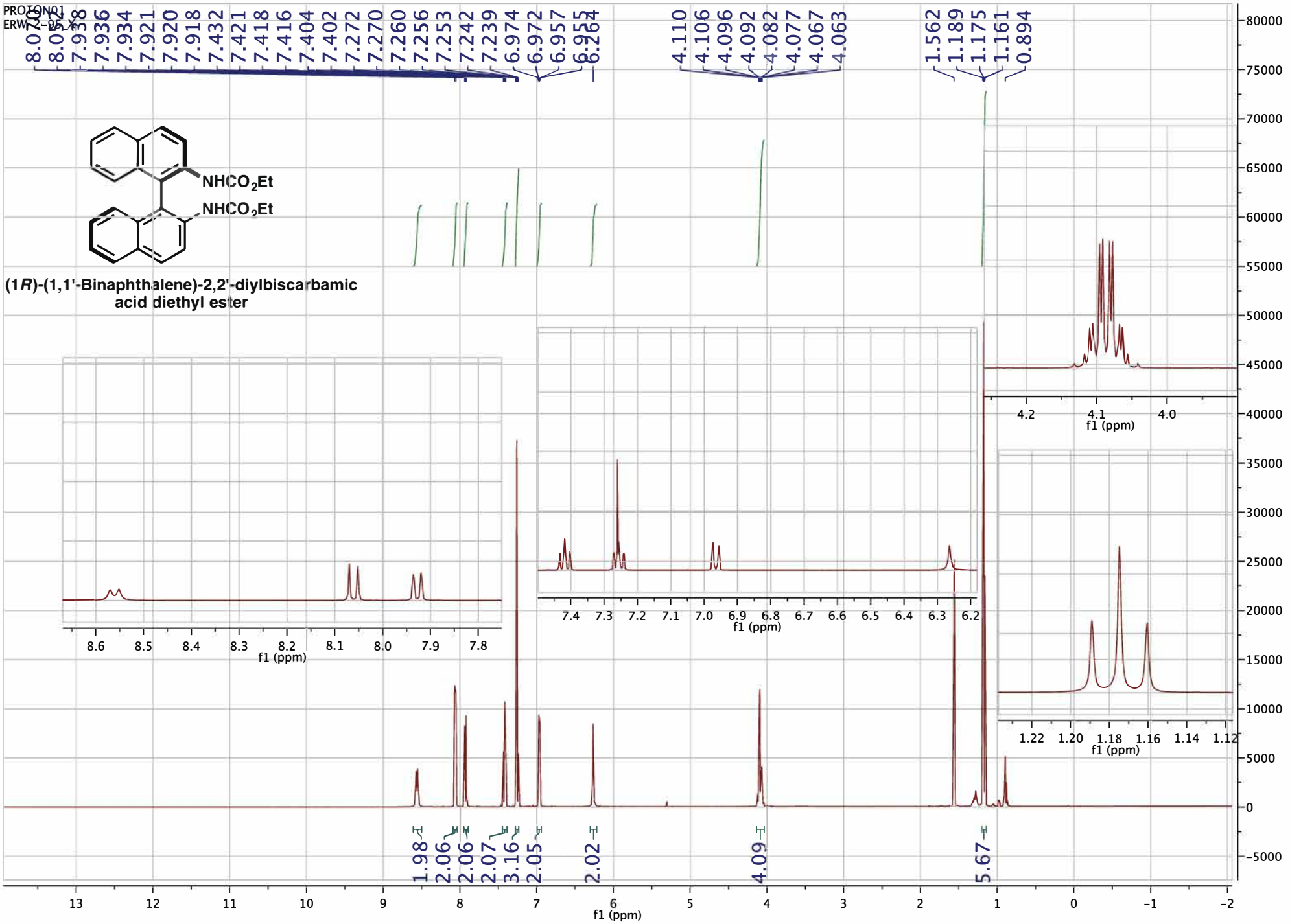
(*R*)-Diethyl [1,1'-binaphthalene]-2,2'-diyldicarbamate: Carbamic acid (1R)-[1,1'-binaphthalene]-2,2'-diylbisdiethyl ester; (93713-29-2)

(*R*)-*N*,*N*″ -Dimethyl-1,1′-binaphthyl-2,2′-diamine: [1,1'-Binaphthalene]-2,2'-diamine, N2,N2'-dimethyl-, (1R)-; (93713-30-5)

Scott E. Denmark was born in Lynbrook, New York on 17 June 1953. He obtained an S.B. degree from MIT in 1975 and his D.Sc.Tech. (with Albert Eschenmoser) from the ETH Zürich in 1980. That same year he began his career at the University of Illinois. He was promoted to associate professor in 1986, to full professor in 1987 and since 1991 he has been the Reynold C. Fuson Professor of Chemistry. His research interests include the invention of new synthetic reactions, exploratory organoelement chemistry and the origin of stereocontrol in fundamental carbon-carbon bond forming processes.

Pavel Ryabchuk was born in Moscow, Russia in 1986. He received his Diploma in Chemistry from Moscow State University, where he conducted undergraduate research in the lab of Professor Nikolay V. Zyk. He obtained his Ph.D. in chemistry in 2013 at the University of Kansas under the guidance of Professor Michael Rubin involving the development of methods for the diastereoselective synthesis of substituted cyclopropanes. In January 2014 he joined the group of Professor Scott E. Denmark, working on enantioselective dichlorination and chlorofunctionalization reactions. Since April 2016 he is a postdoctoral researcher at the Leibniz Institute for Catalysis, Rostock, Germany under Professor Matthias Beller. His current research interests are focused on the development of new heterogeneous catalysts based on non-noble Earth abundant metals.

Eric R. Welin was born in Columbus, Ohio, in 1987. He obtained his B.S. degree in Chemistry in 2010 from the Ohio State University, where he conducted undergraduate research in the laboratory of Professor James P. Stambuli. In the same year, he began his graduate studies at Princeton University under the supervision of Professor David W. C. MacMillan. At Princeton his research focused on developing new methods utilizing photoredox catalysis. He earned his Ph.D. in 2015, and later that year he joined the laboratory of Professor Brian M. Stoltz as an American Cancer Society postdoctoral fellow. His current research focuses on the total synthesis of bioactive natural products.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NHCO2Et
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8.2
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f1 (ppm)

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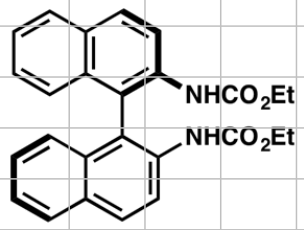

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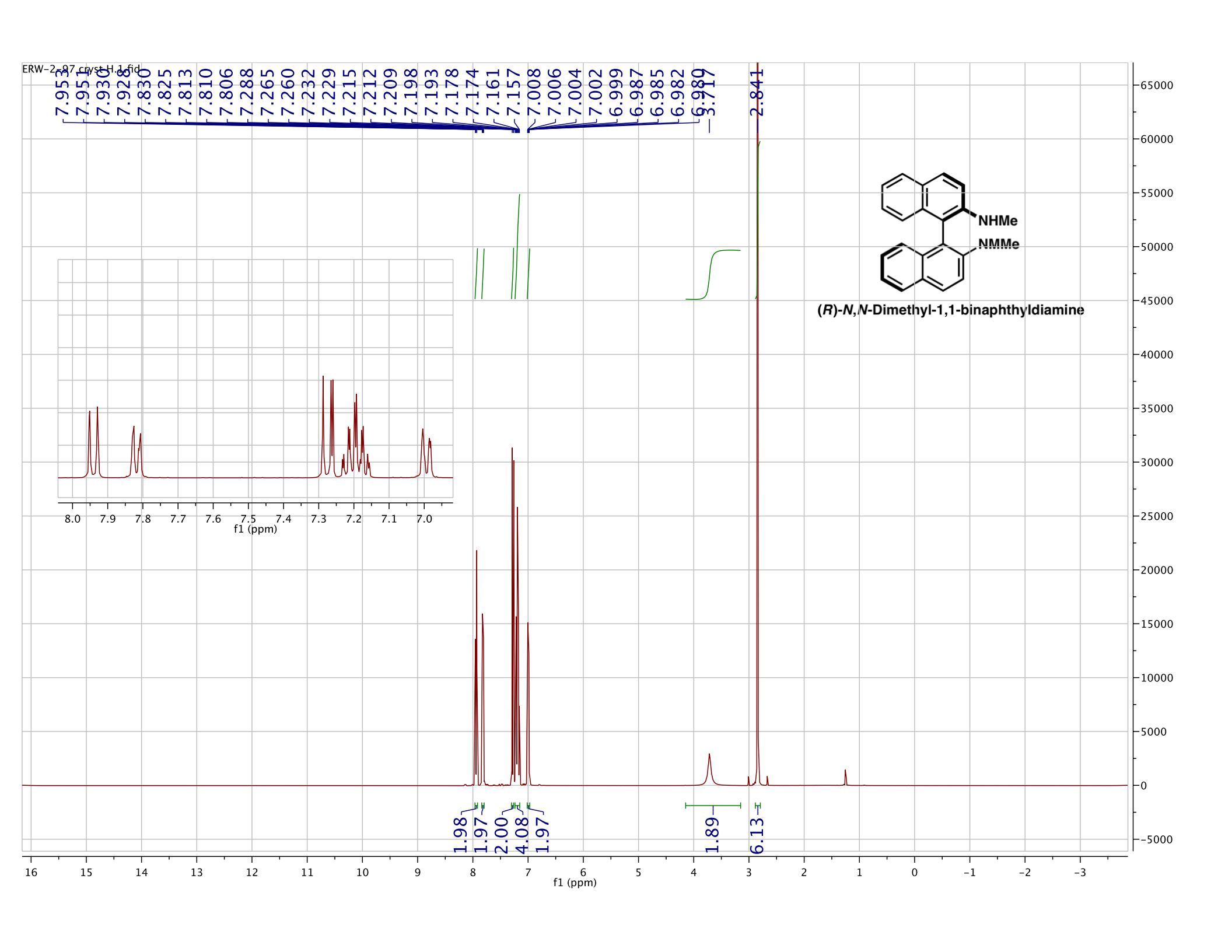
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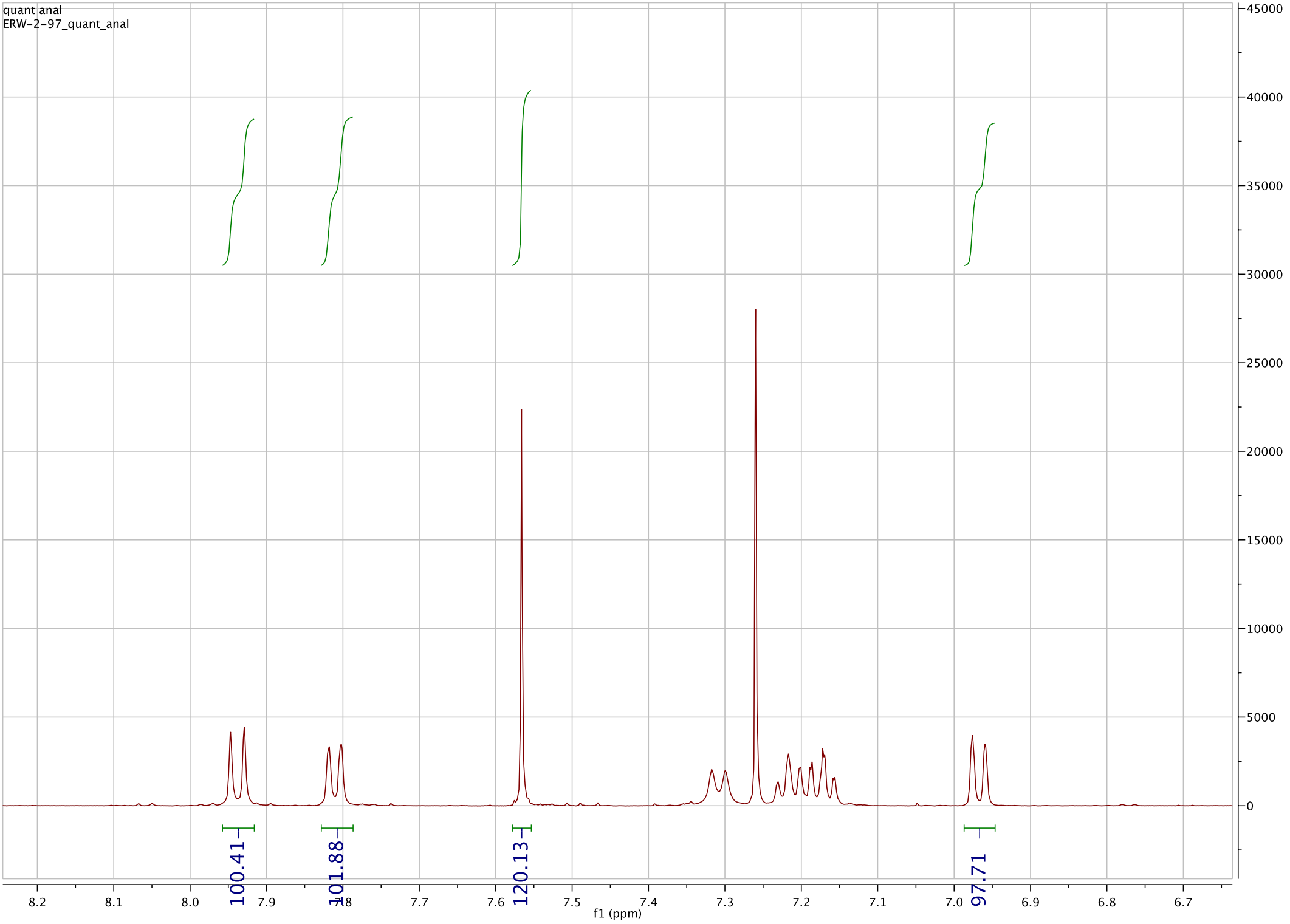
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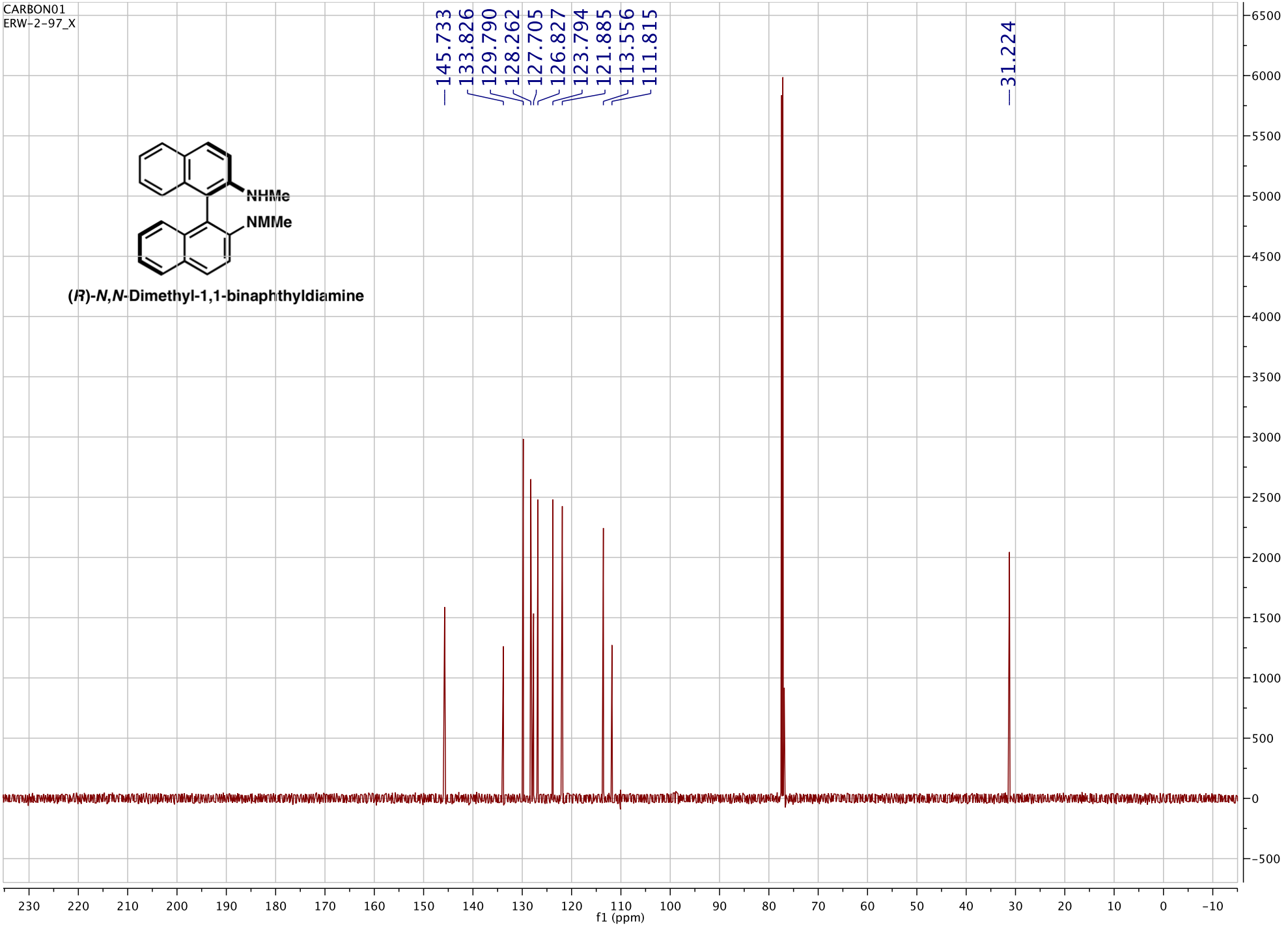
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