Organic Syntheses

Stereoselective Synthesis of Chiral Sulfinamide Monophosphine Ligands (Ming-Phos)(*S*, *Rs*)-M

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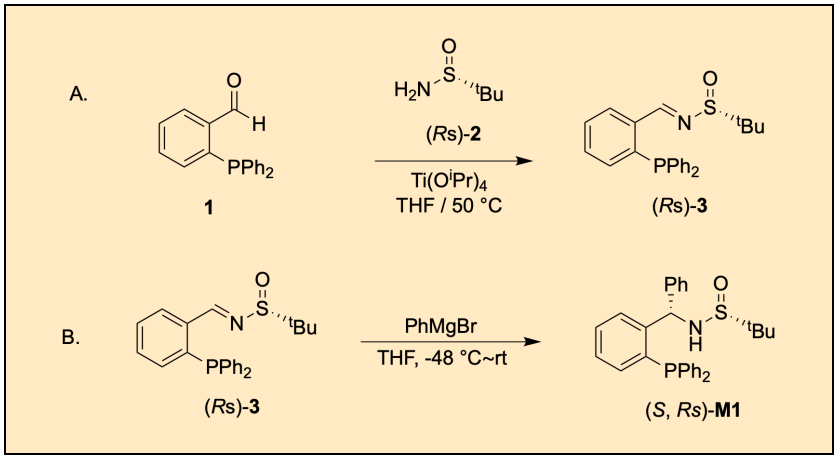

Procedure (Note 1)

A. *(R,E)-N-(2-(Diphenylphosphanyl)benzylidene)-2-methylpropane-2-sulfinamide (Rs)*-3. A 500-mL oven-dried, three-necked round-bottomed flask equipped with a teflon-coated magnetic stir bar (3.5 x 1.0 cm) is charged with 2-diphenylphosphinobenzaldehyde 1 (52.5 mmol, 15.24 g, 1 equiv) (Note 2), (*R*)-(+)-2-methylpropane-2-sulfinamide (*R*s)-2 (57.8 mmol, 7.0 g, 1.1 equiv) (Note 3). The middle neck of the flask is equipped with a reflux condenser,

DOI: 10.15227/orgsyn.097.0262
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which is connected to a gas outlet/inlet. One of the side-necks of the flask is closed with a rubber septum and the other side-neck is equipped with an internal temperature probe. The flask is evacuated and flushed three times with nitrogen before anhydrous THF (250 mL) (Note 4) is transferred into the flask via a plastic syringe through the rubber septum. The stirred mixture is heated to 50 °C in an oil bath, then titanium(IV) *iso*-propoxide (157.7 mmol, 46.6 mL, 3.0 equiv) (Note 5) is added and the resulting pale yellow mixture is stirred for 20 h at 50 °C under nitrogen atmosphere. Analysis by TLC indicates complete consumption of the aldehyde (Note 6). The yellow reaction mixture is diluted with EtOAc (100 mL) (Note 7), and vigorous stirring is continued for 0.5 h at 50 °C. The reaction mixture is then allowed to cool to room temperature (25 °C) and the reaction mixture is slowly added over a period of 5 min in three portions to a 2-L beaker that contains brine (200 mL) (Note 8) while stirring with a magnetic stir bar. In addition, the mixture is stirred using a glass rod for 5 min and the reaction mixture is filtered through a sintered funnel with Celite (Note 9) and washed with EtOAc (2 x 150 mL) to remove insoluble materials. The filtrate is transferred to a 3 L separatory funnel and water (200 mL) is added. The phases are separated, and the aqueous phase is extracted with EtOAc (3 x 50 mL). The combined organic layers are dried over anhydrous sodium sulfate (ca. 60 g) (Note 10), filtered through a filter paper into a 1.0 L round-bottomed flask and concentrated under reduced pressure (40 mmHg, 40 °C). The crude product is purified by flash column chromatography (Note 11) to afford 16.09 g (78%) as light-yellow gum (Notes 12, 13, and 14).

B. *(S,Rs)*-**M1**. A dried 250 mL three-necked, round-bottomed flask, equipped with a Teflon-coated magnetic stir bar (3.5 x 1.0 cm), is charged with *(Rs)*-**3** (20 mmol, 7.87 g, 1 equiv). The middle neck of the flask is equipped with a pressure-equalizing addition funnel (125 mL) with a rubber septum, one side-neck of the flask is connected to a Schlenk line via a gas outlet/inlet, and the other side-neck is equipped with a thermocouple (Figure 1A). The flask is evacuated and flushed with nitrogen three times before anhydrous THF (125 mL) is transferred via plastic syringe into the addition funnel through the rubber septum, and the THF is then added to the round-bottomed flask. The flask is placed in a dry ice-acetonitrile bath in order to cool the reaction mixture to -48 °C. Phenylmagnesium bromide (40.0 mmol, 1.0 M in THF, 40.0 mL, 2.0 equiv) (Note 15) is transferred into constant pressure drop funnel via plastic syringe and then added dropwise over 30 minutes to the –48 °C solution (Figure 1B). Upon completion of the addition, the solution is stirred for 2 h (Figure 2). The cooling bath is removed,

and the pale-yellow reaction mixture is allowed to warm to 25°C and stirred for additional 12 h. The reaction mixture is quenched by slow addition of saturated NH_4Cl (50 mL) and stirred for 0.5 h. The solution that contains the crude product is transferred to a 500 mL separatory funnel and water (100 mL) is added. The reaction mixture is extracted with EtOAc (3 x 50 mL), and the combined organic layers are dried over anhydrous Na_2SO_4 (ca. 20 g), filtered through filter paper into a 0.5 L round-bottomed flask, and concentrated under reduced pressure (40 mmHg, 40 °C) to give the crude product as brown oil. The crude product is placed under high vacuum (18 mmHg) for 10 min to remove the residual EtOAc.

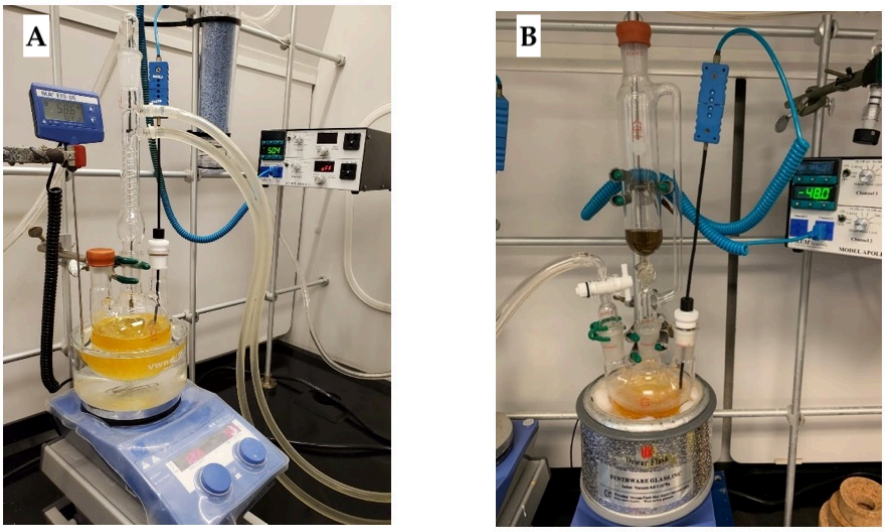

Figure 1. A) Reaction set-up; B) Grignard addition

To a –10 °C solution of the crude product in acetone (28 mL) (Note 16) is added water (20 mL) via an addition funnel and the solution stirred (150 rpm) for 3 h, resulting in the formation of a white precipitate (Note 17). The precipitate is filtered and washed with fresh cold (–10 °C) aqueous solution of acetone (H_2O/acetone = 5/7) (7.5 mL x 3). The white powder is collected and dried *in vacuo* to give 6.51 g of white product *(S,Rs)*-**M1** (Figure 2). The filtrate is concentrated and extracted with EtOAc (3 x 15 mL), the combined organic layers are dried over anhydrous Na_2SO_4 (ca. 10 g), filtered and concentrated under reduced pressure (40 mmHg, 40 °C). The residue is purified by flash column chromatography (Note 18) on silica gel to afford

1.07 g of *(S,Rs)*-**M1**. The two portions of *(S,Rs)*-**M1** are combined (7.58 g, 16.1 mmol, 80% yield) (Notes 19, 20, and 21).

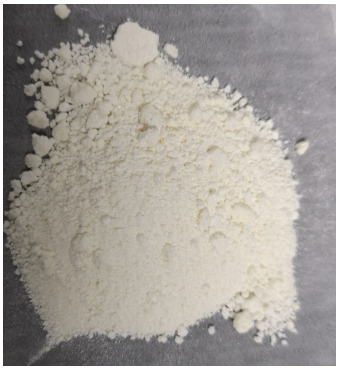

Figure 2. White solid produced in Step B (photo provided by the submitters)

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 2- diphenylphosphinobenzaldehyde, (*R*)-(+)-2-methylpropane-2-sulfin-amide, tetrahydrofuran, titanium(IV) isopropoxide, ethyl acetate, brine,

Celite, sodium sulfate, hexanes, phenylmagnesium bromide, ammonium chloride, acetone, petroleum ether, dichloromethane, silica gel, and 1,3,5-trimethylbenzene.

2. 2-(Diphenylphosphino)benzaldehyde (97 %) was purchased from Combi-Blocks.
3. (*R*)-(+)-2-methylpropane-2-sulfinamide (97 %, 99 % ee) was obtained from Combi-Blocks and used as received.
4. Tetrahydrofuran (anhydrous, >99.9%, inhibitor-free) was purchased from Sigma Aldrich.
5. Titanium(IV) isopropoxide (98+%) was purchased from Acros Organic and used as received.
6. Reaction progress was monitored by TLC analysis, using petroleum ethe/ethyl acetate (5/1) as eluent. Visualization is accomplished with 254 nm UV light. TLC analysis showed the formation of sulfinamide **3** has R_f = 0.5 (Figure 3).

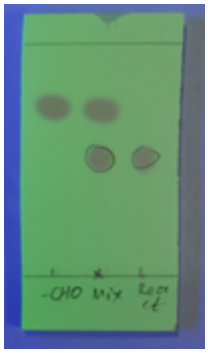

Figure 3. TLC analysis of the reaction mixture

7. Ethyl acetate (EtOAc) (ACS grade, 99.5%) was purchased from Oakwood Chemical.
8. Brine was prepared from sodium chloride, which was purchased from Oakwood Chemical.
9. Celite 545 was purchased from Acros Organics and used as received. The filtration is carried out through a sintered funnel (diameter: 10 cm), which is mounted on the top of a 2 L one-necked, round-bottomed flask and charged with 40 g celite. The funnel is connected to a vacuum source (40 mmHg).
10. Sodium sulfate (Na_2SO_4) (anhydrous, 99.5%) was purchased from Oakwood Chemical.

11. Silica gel (230-400 mesh, purchased from SiliCycle) (270 g) is loaded in a column by wet packing with hexanes. The crude oil (27.0 g) is dissolved in dichloromethane (20 mL) with the help of sonication and then loaded onto the column. The column is eluted with a mixture of hexanes and ethyl acetate as eluent, beginning with a 10/1 ratio, and then moving to a 5/1 ratio. The desired product (TLC analysis provides R_f = 0.7 in petroleum ether/EtOAc=5/1) appears on the column as a yellow band, which can be easily observed in order to determine when the material has fully eluted.
12. A second run on the same scale provided 15.89 g (77%) of the product.
13. Spectroscopic properties of product (*R*s)-**3** are as follows: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.08 (s, 9H), 6.95–6.99 (m, 1H), 7.21–7.27 (m, 4H), 7.28–7.38 (m, 7H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.95–8.01 (m, 1H), 9.13 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 22.2, 57.3, 128.5 (*J*c.p = 7.2 Hz), 128.6 (*J*c.p = 7.0 Hz), 128.8 (*J*c.p = 4.5 Hz), 130.2 (*J*c.p = 4.0 Hz), 131.5, 134.0 (*J*c.p = 12.0 Hz), 134.1 (*J*c.p = 12.1 Hz), 136.3 (*J*c.p = 11.0 Hz), 136.4 (*J*c,p = 9.9 Hz), 137.2 (*J*c.p = 17.4 Hz), 139.8 (*J*c.p = 23.7 Hz), 161.8 (*J*c.p = 18.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ: –12.30. LC-MS [M + H]$^+$ 394.1 calcd, 394.1 found.
14. The purity was determined to be >97% wt. by quantitative ^{1}H NMR spectroscopy in 1.0 mL of $CDCl_3$ using 39.4 mg of the compound and 12 mg of 1,3,5-trimethylbenzene (98%, purchased from Sigma Aldrich and used as received) as an internal standard.
15. Phenylmagnesium bromide (1.0 M in THF) was purchased from Sigma Aldrich and used as received.
16. Acetone (99.5%) was purchased from Oakwood Chemical.
17. A sample (100 mg) of the prepared pure product was used as the seed crystal, which contributed to the formation of the white precipitate.
18. Silica gel (230-400 mesh, purchased from SiliCycle) (35 g) is loaded in a column by wet packing with hexanes. Residue (1.45 g) is dissolved in dichloromethane (5 mL) with the help of sonication and then loaded onto the column. The column is eluted with a mixture of hexanes and ethyl acetate as eluent, beginning with a 10/1 ratio, and then moving to a 4/1 ratio to obtain the desired product (TLC analysis provides R_f = 0.25 in hexanes/EtOAc=4/1).
19. A second run on the same scale provided 7.46 g (79%) of the product.
20. Spectroscopic properties of product (*S, R*s)-**M1** are as follows: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.20 (s, 9H), 3.87 (br s, 1H), 6.64 (dd, *J* = 3.5, 8.4 Hz, 1H), 7.01–7.12 (m, 6H), 7.14–7.27 (m, 8H), 7.28–7.33 (m, 3H), 7.40

(t, J = 7.5 Hz, 1H), 7.65 (dd, J = 4.2, 7.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 22.6, 55.9, 60.0 (Jc,p = 27.6 Hz), 127.3, 127.6, 127.9, 128.2, 128.3, 128.3 (Jc,p = 1.8 Hz), 128.4 (Jc,p = 8.6 Hz), 128.5 (Jc,p = 6.9 Hz), 129.3, 133.7 (Jc,p = 16.9 Hz), 133.9 (Jc,p = 17.3 Hz), 134.9, 135.8, 135.9, 136.0, 137.0 (Jc,p = 10.7 Hz), 142.0, 146.7 (Jc,p = 24.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ: –18.26. LC-MS $[M + H]^+$ 472.2 calcd, 472.1 found.

21. The purity was determined to be >97% wt. by quantitative ^{1}H NMR spectroscopy in 1.0 ml of $CDCl_3$ using 47.2 mg of the compound and 12 mg of 1,3,5-Trimethylbenzene (98%, purchased from Sigma Aldrich and used as received) as an internal standard.

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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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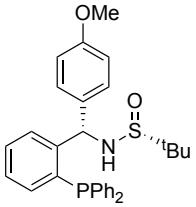
Discussion

During the course of our study on enantioselective gold catalysis,[3] we found that monocationic [LAu_2ClX] species (L = bisphosphine, X = weak counteranion), which were generated in situ from a 1:1 mixture of [LAu_2Cl_2] and a AgX activator, can give better enantioselectivity than those bicationic [LAu_2X_2] species, indicating that the second gold site might either just exert a steric influence or be involved in a second interaction with the substrate. Inspired by this interesting finding, we thus designed a new type of chiral ligand, namely Ming-Phos, which performed well in asymmetric metal catalysis.[4]

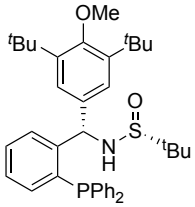
Two sets of diastereomeric (*R*, *Rs*)- and (*S*, *Rs*)-configured Ming-Phos ligands could be obtained in good yields with high diastereoselectivity from commercially available, inexpensive starting materials through a two-step procedure. The condensation reaction of 2-(diphenylphosphino) benzaldehyde **1** with (*R*s)-tert-butanesulfinamide **2** in the presence of $Ti(OPr^i)_4$ efficiently delivered Chiral sulfinyl imine (*R*s)-**3** by recrystallization (15.8 g, 76 % yield as an average of two runs) according to a modified literature procedure.[5] The stereoselective addition of PhMgBr to (*R*s)-**3** (checked above) afforded a set of Ming-Phos derivatives (*S*,*R*s)-**M1** with excellent diastereoselectivity (d.r.>15:1) (15 g, 79% yield as an average of two runs).[5b] Accordingly, the other set of Ming-Phos ligands, namely (*R*,*R*s)-**M1**, could also be obtained from the stereoselective addition of PhLi to (*R*s)-3, which will be reported in due course.

Wide structural diversity can be achieved by changing the organometallic reagents. Some representative cases from the scope study are shown in Table 1 (yields were given as an average of two runs). Compared with elaborate chiral biaryl bisphosphine ligands, such as chiral atropisomeric biaryl phosphines, spirocyclic bisphosphines, phosphoramidites and helically chiral trivalent phosphines, The salient features of these new chiral ligands, including their simple structure, air stability, the practical preparation from readily available starting materials, easy modification, and good results in enantioselective transformations, render these ligands very attractive.

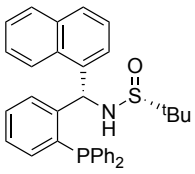
Table 1. Representative Chiral Sulfinamide Monophosphine Ligands (Ming-Phos) synthesized in the reported scope study



(*S*, *Rs*)-**M2**, 70%



(*S*, *Rs*)-**M3**, 72%



(*S*, *Rs*)-**M4**, 82%

References

1. Department of Chemistry, School of Chemistry and Molecular Engineering, East China Normal University, 500. Dongchuan Road, Shanghai, 200062, P. R. China. E-mail: yjxiao@chem.ecnu.edu.cn. ORCID : 0000-0002-0185-1961
2. Department of Chemistry, Fudan University, 220 Handan Road, Shanghai, 200433, P. R. China. E-mail: junliangzhang@fudan.edu.cn. ORCID: 0000-0002-4636-2846, We thank NSFC 21425205, 21672067, 21871093 for financial support.
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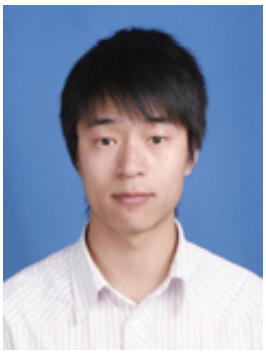
Appendix
Chemical Abstracts Nomenclature (Registry Number)

2-Diphenylphosphinobenzaldehyde; (50777-76-9)
(*R*)-2-Methylpropane-2-sulfinamide; (196929-78-9)
Titanium(IV) isopropoxide; (546-68-9)
Phenylmagnesium bromide; (100-58-3)

Anjing Hu was born in Anhui Province in 1993. He received a BSc degree from AnQing Normol University in 2015. Now, he is majoring in designing of novel chiral ligands in East China of Normal University under the supervision of Professor Yuanjing Xiao. His research interests focus on asymmetric catalysis.



Zhan-Ming Zhang was born in Shandong Province, China. He received his PhD at East China of Normal University under the supervision of Professor Junliang Zhang in 2016. Then he joined East China of Normal University as a postdoctoral researcher in 2016. He is currently a postdoctoral researcher (since 2018) at Fudan University.

Prof. Yuanjing Xiao obtained his Ph.D. from Wuhan University under the supervision of Professor Yongbing He and Professor Chengtai Wu in 2002. From 2007 to 2010, he worked with Prof. Junliang Zhang in East China Normal University as a postdoctoral fellow and then he was appointed as an associated professor. From October 2011 to October 2012, he worked in Prof. Liming Zhang's lab in University of California, Santa Barbara as a Visiting Scholar. His current research interests focus on practical process research and development for organic synthesis, asymmetric catalysis.

Prof. Junliang Zhang obtained his PhD from the Chinese Academy of Sciences in 2002 under the supervision of Prof. Shengming Ma. He worked as a postdoctoral fellow successively in University of Cologne (Humboldt Fellowship) and then University of Chicago. In 2006, he joined East China Normal University as a full professor. In 2017, he moved to Fudan University as a full professor. His research interests include developing novel synthetic methodology, design of novel chiral ligands and catalysts, asymmetric catalysis. As the corresponding authors, he has published more than 200 papers and 5 book chapters.

Dr. Anji Chen received his Ph.D. in organic chemistry at Old Dominion University, VA under the mentorship of Prof. Guijun Wang in 2018, where he made contributions on two distinct areas of research: 1) synthesis of new classes of glycoclusters and glycomimetics and their applications as soft biomaterials and 2) synthesis of novel bis-triazole linked carbohydrate-based macrocycles and their application for accelerating copper sulfate mediated click reaction. After completing his graduate studies in 2019, Anji joined TCG GreenChem, Inc. in Richmond, VA as a post-doctoral researcher.

Dr. Gopal Sirasani received his Bachelor's and Master's degrees in Hyderabad, India. He obtained his Ph.D. in synthetic organic chemistry in 2011 from Temple University, Philadelphia under the guidance of Prof. Rodrigo B. Andrade. His doctoral research was focused on developing novel methodologies, total syntheses of natural products and their analogs thereof. He got his post-doctoral training in the laboratory of Prof. Emily Balskus at Harvard University. In 2013, Gopal began his industrial career at Melinta Therapeutics, NewHaven, CT. He is currently working at TCG GreenChem, Inc. as an Associate Director in the department of process research and development.

Dr. Joseph Armstrong received his Ph.D. in organic chemistry in 1988 (with Prof. David Walba) at University of Colorado, Boulder followed by postdoctoral training in the laboratory of Prof. Robert Ireland at University of Virginia. He has over 28 years of process R&D experience. Some of the positions he held at Merck & Co include Executive Director for process R&D, Director of Formulation, Executive Director of Project Management. In 2006 he won the Presidential Green Chemistry Challenge Award. He is currently working at TCG GreenChem, Inc. as Executive Vice President, Global Head of R&D and Business Development. He is the co-author for more than 50 publications and patents.

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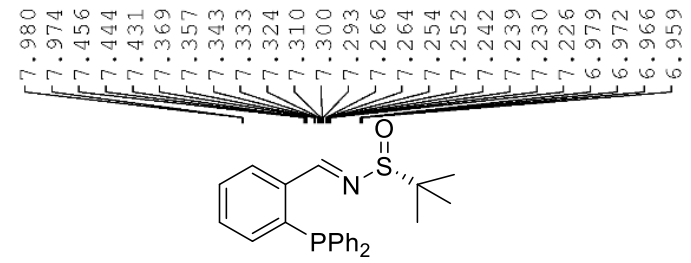

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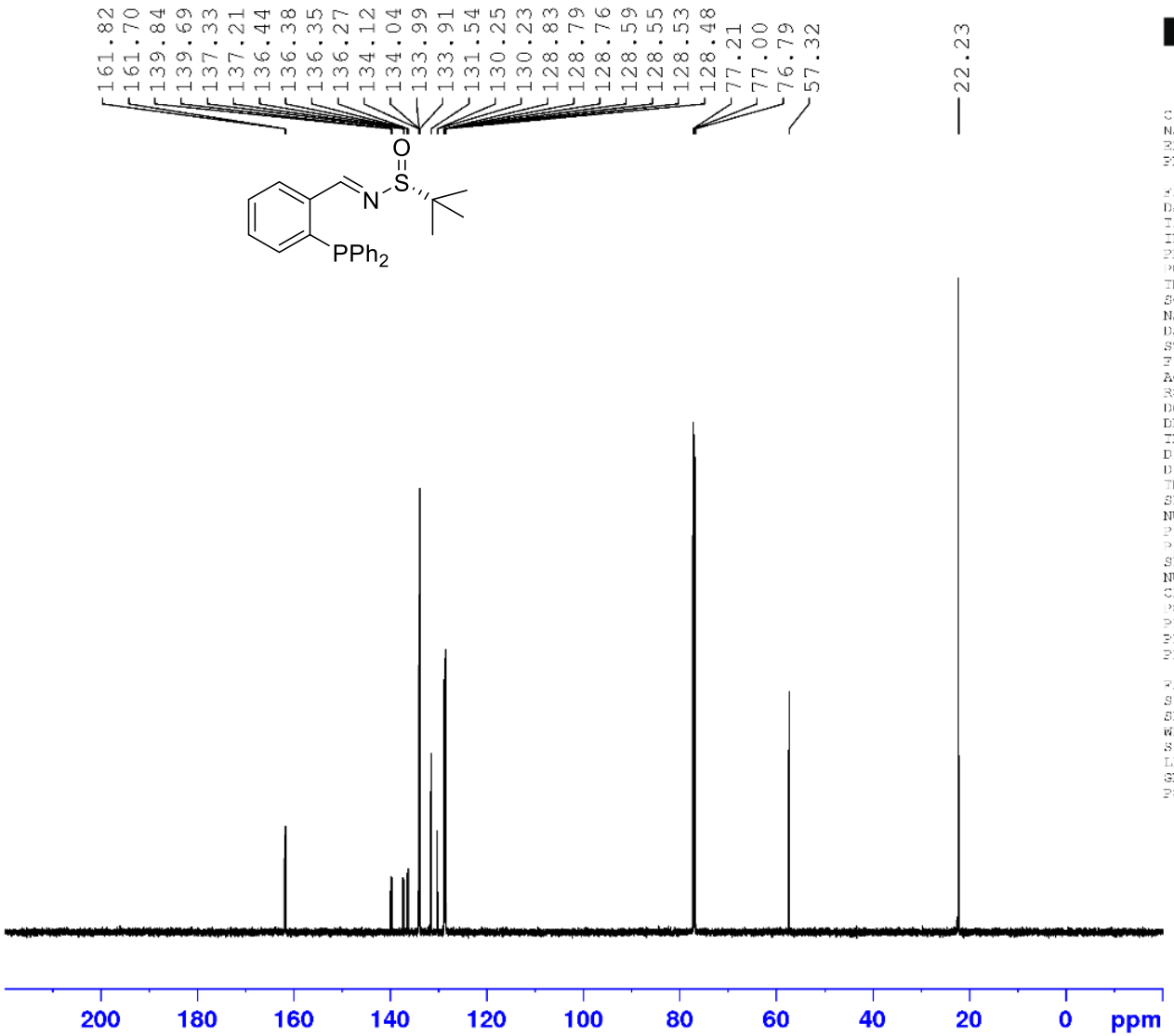

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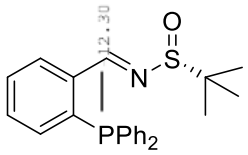
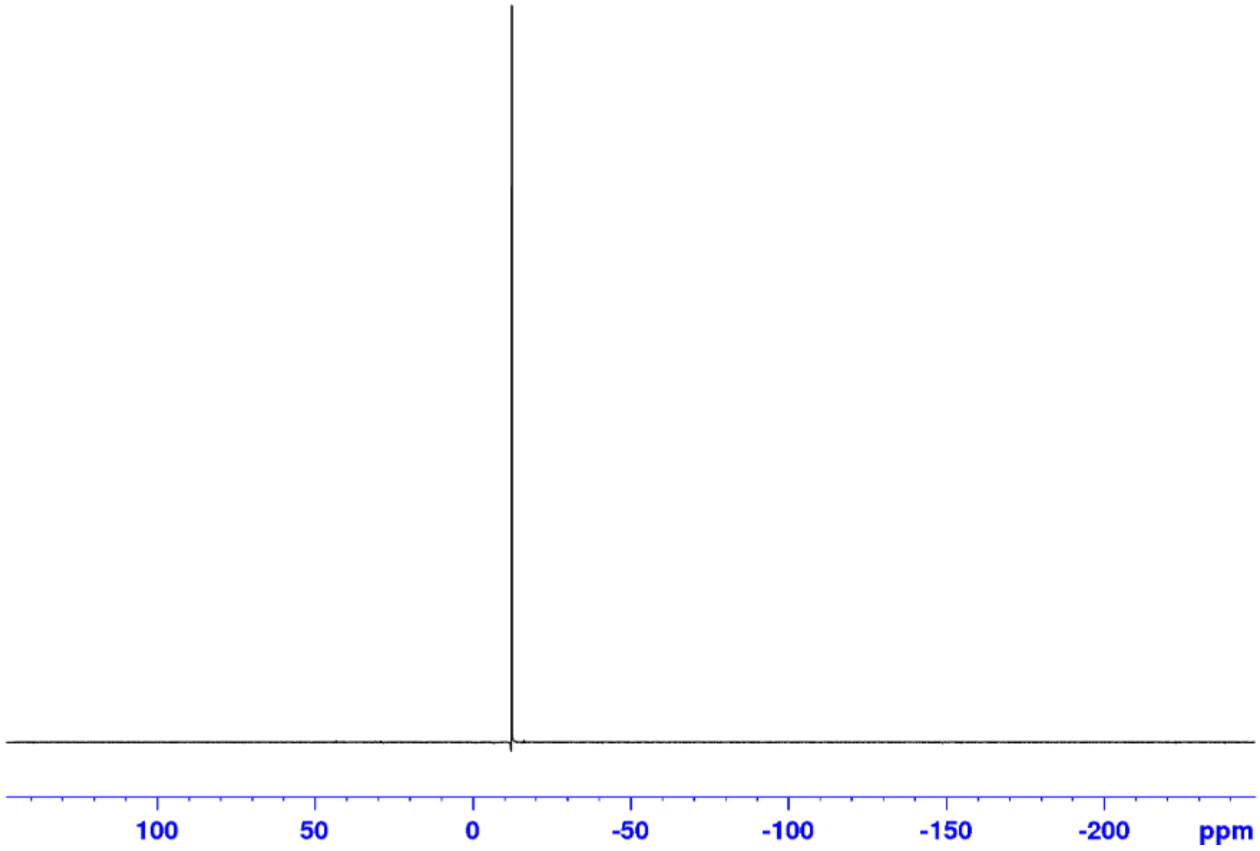
```

Imine-31P



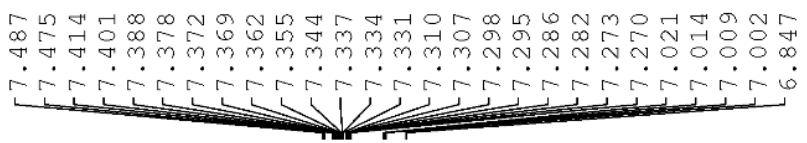


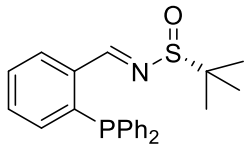

```
Current Data Parameters
NAME      TCG-GS-1-62-Pure-3-10-20
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_          20200310
Time             16.51 h
INSTRUM            spect
PROBHD   Z148658_0003 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    4
SWH           96153.844 Hz
FIDRES         2.934382 Hz
AQ             0.3407872 sec
RG                199.73
DW                5.200 usec
DE                6.50 usec
TE                297.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1        242.8743317 MHz
NUC1                31P
P1                15.00 usec
PLW1        24.74699974 W
SFO2        600.0074000 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        13.23200035 W
PLW12        0.64876997 W
PLW13        0.32633001 W

F2 - Processing parameters
SI                32768
SF          242.8864760 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Imine Q study





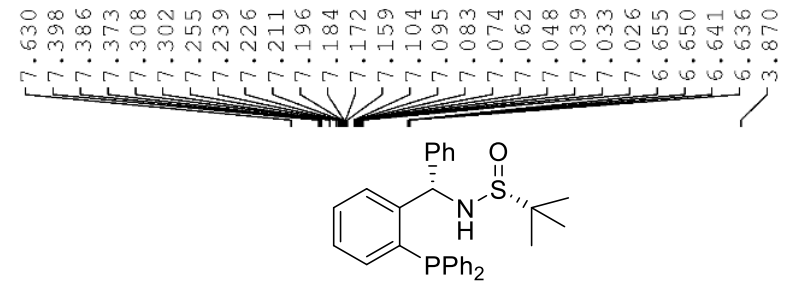
1,3,5-trimethylbenzene
Purity: 97%


```
Current Data Parameters
NAME      TCG GS 1 66 Q studies 6 19 20
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200619
Time              21.34 h
INSTRUM           spect
PROBHD   Z148658_0003 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12019.230 Hz
FIDRES          0.366798 Hz
AQ              2.7262976 sec
RG                 68.55
DW                41.600 usec
DE                 6.50 usec
TE                296.1 K
D1             1.00000000 sec
TD0                    1
SFO1         600.0387050 MHz
NUC1                  1H
P1                 15.50 usec
PLW1         13.23200035 W

F2 - Processing parameters
SI                 65536
SF           600.0050000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

PhMgBr addition-1H



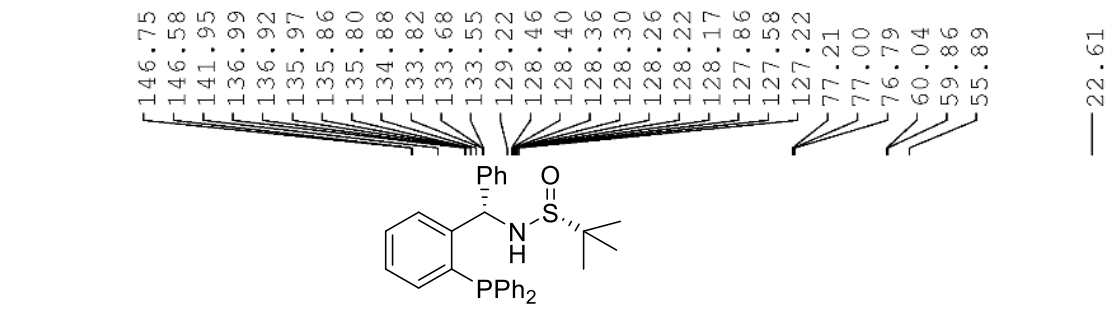
BRUKER

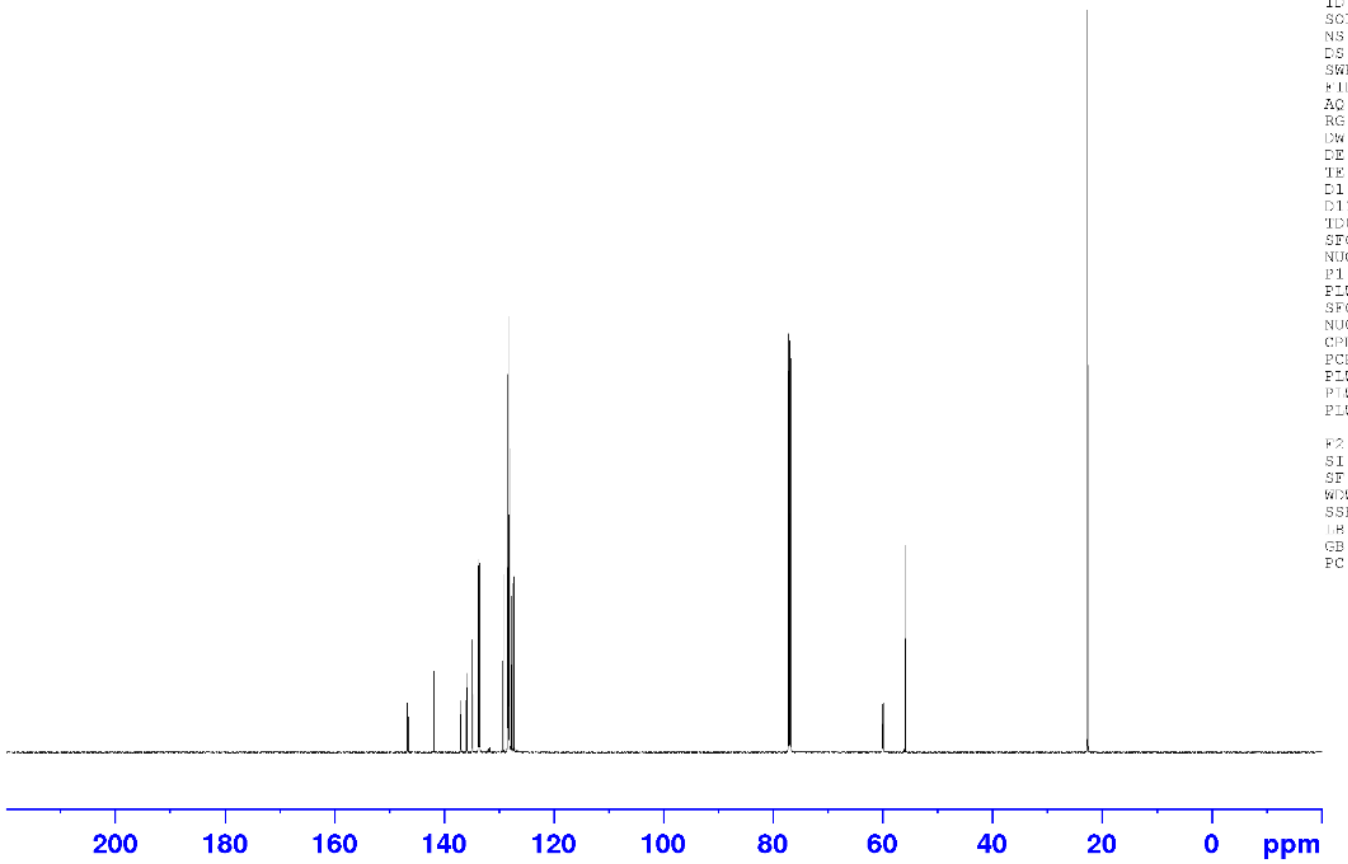
```
Current Data Parameters
NAME      TCG-AC-1-138-pure-3-11-20
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200311
Time              15.12 h
INSTRUM           spect
PROBHD    Z855801_0104 (
PULPROG           zg30
TD               65536
SOLVENT           CDCl3
NS                  32
DS                   2
SWH           12019.230 Hz
FIDRES        0.366798 Hz
AQ            2.7262976 sec
RG                71.27
DW               41.600 usec
DE                6.50 usec
TE              296.0 K
D1           1.00000000 sec
TD0                  1
SFO1        599.9587047 MHz
NUC1                1H
P1                7.75 usec
PLW1         11.99499989 W

F2 - Processing parameters
SI               65536
SF          599.9550188 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

PhMgBr addition-13C





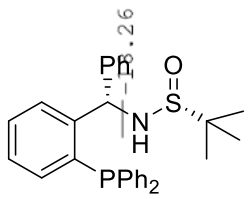
BRUKER

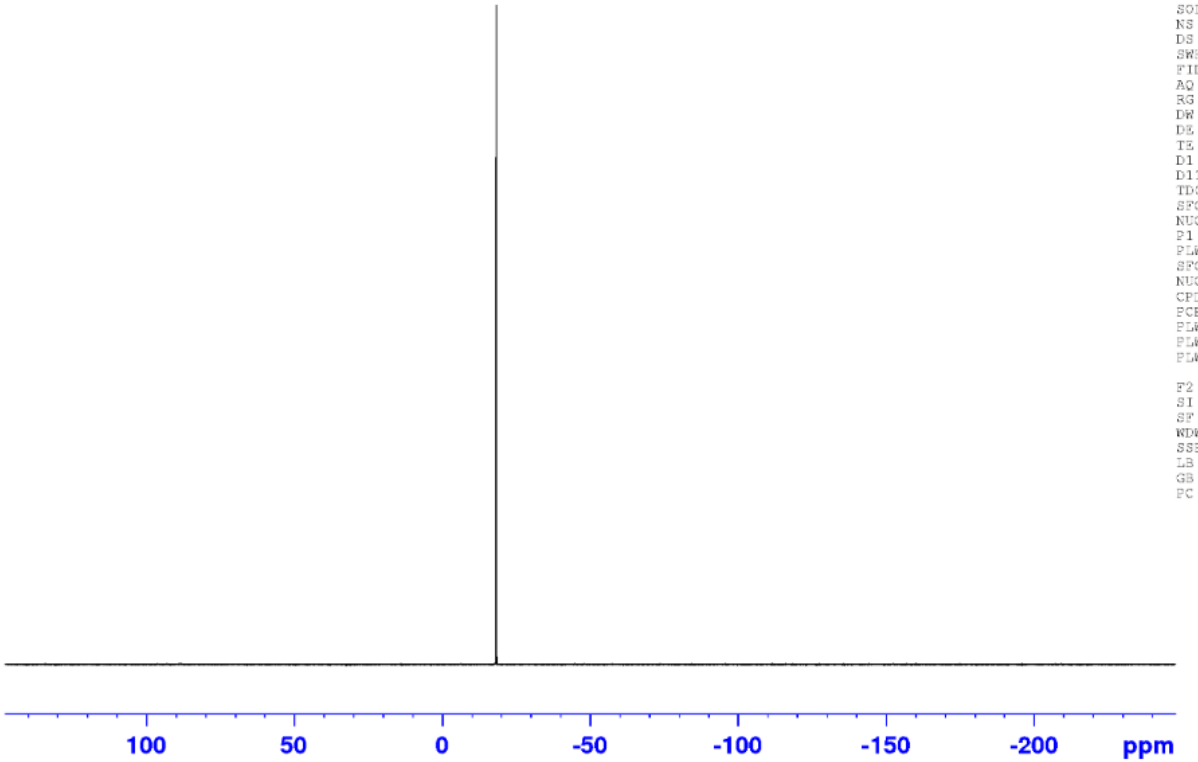
```
Current Data Parameters
NAME      TCG-AC-1-158-pure-3-12-20
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20200313
Time              4.02 h
INSTRUM           spect
PROBHD   Z148658_0003 (
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 5000
DS                    4
SWH           36231.883 Hz
FIDRES         1.105709 Hz
AQ            0.9043968 sec
RG               199.73
DW               13.800 usec
DE                6.50 usec
TE                298.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        150.8864644 MHz
NUC1                13C
P1                12.00 usec
PLW1        77.65699768 W
SFO2       600.0074000 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             70.00 usec
PLW2        13.23200035 W
PLW12        0.64876997 W
PLW13        0.32633001 W

F2 - Processing parameters
SI                32768
SF          150.8713940 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

PhMgBr addition-31P



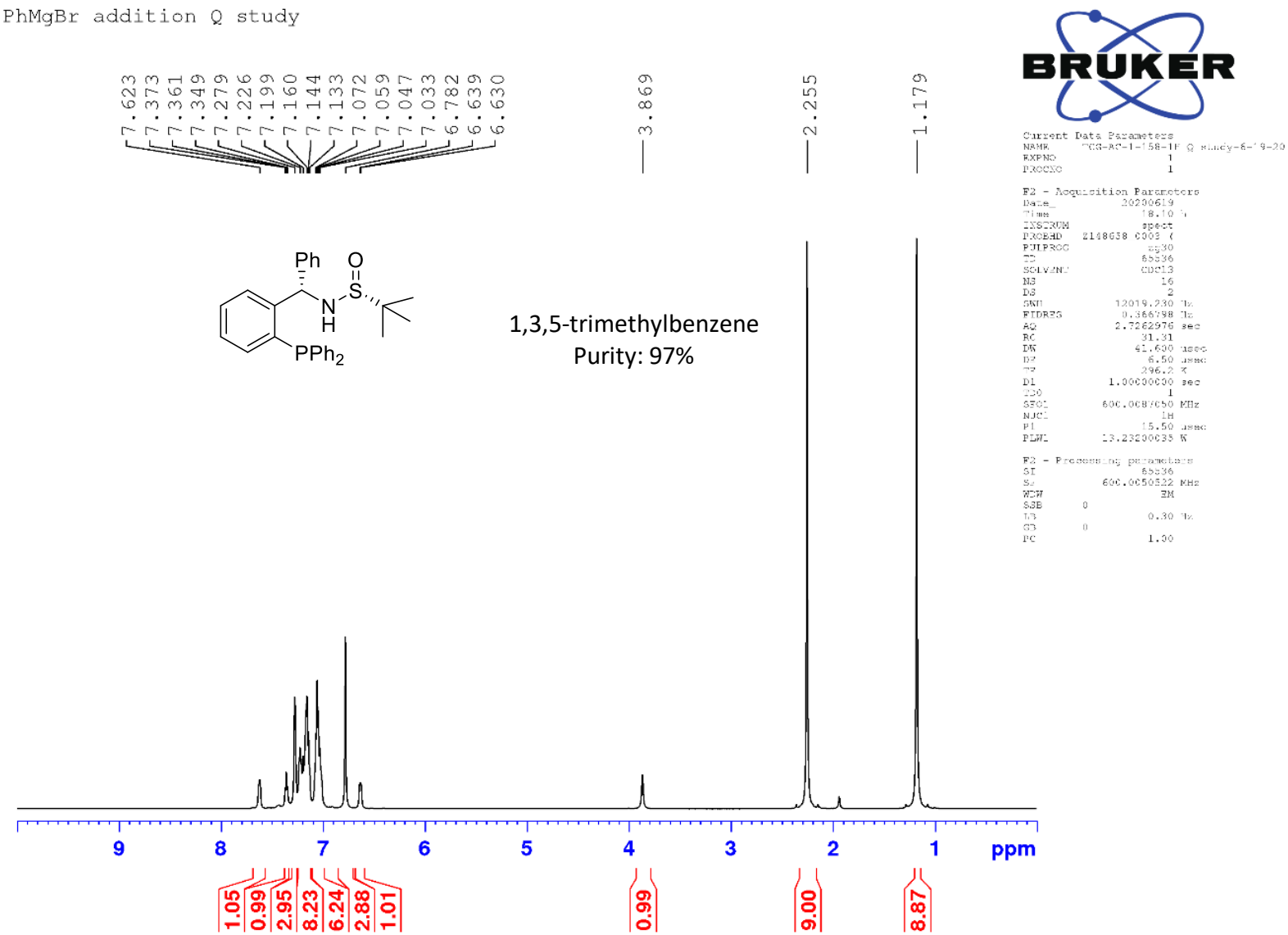



```
Current Data Parameters
NAME      TCG-AC-1-158-pure-3-12-20
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_           20200312
Time              17.30 h
INSTRUM           spect
PROBHD   Z148658_0003 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    4
SWH            96153.844 Hz
FIDRES          2.934382 Hz
AQ              0.3407872 sec
RG                199.73
DW                5.200 usec
DE                6.50 usec
TE                297.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1
SFO1          242.8743317 MHz
NUC1                 31P
P1                15.00 usec
PLW1          24.74699974 W
SFO2          600.0074000 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             70.00 usec
PLW2          13.23200035 W
PLW12          0.64876997 W
PLW13          0.32633001 W

F2 - Processing parameters
SI                32768
SF            242.8864760 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

PhMgBr addition Q study



Current Data Parameters
NAME TCG-AC-1-158-1H Q study-8-19-20
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200619
Time 18.10 h
INSTRUM spect
PROBHD 2148638 0003 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 2.7262976 sec
RG 31.31
DW 41.600 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
D20 1
SFO1 600.0087050 MHz
NUC1 1H
P1 15.50 usec
PLW1 13.23200035 W

F2 - Processing parameters
SI 65536
SF 600.0050522 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00