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for the Preparation
of Organic Compounds

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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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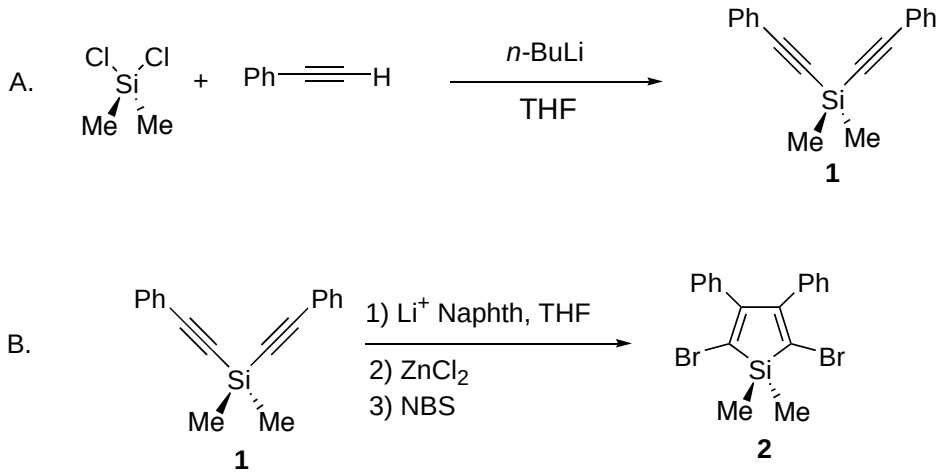
DIRECT SYNTHESIS OF 2,5-DIHALOSILOLES
(2,5-Dibromo-1,1-dimethyl-3,4-diphenyl-1*H*-silole)



Submitted by Nicholas A. Morra and Brian L. Pagenkopf.[1]
Checked by Tomita Daisuke and Tsuyoshi Mita and Maskatsu Shibasaki.

1. Procedure

A. Dimethyl-bis(phenylethynyl)silane (**1**). A 250-mL, three-necked, round-bottomed flask equipped with an internal thermometer, two rubber septa and a 3-cm egg-shaped stir bar (Note 1) is charged with phenylacetylene (6.37 mL, 58.0 mmol, 2.5 equiv) (Note 2) via syringe, 60 mL of THF (Note 3) via syringe, and the solution was cooled to an internal temperature of –70 °C or colder in a dry ice/acetone bath. *n*-Butyllithium (1.58 M, 30.8 mL, 48.7 mmol, 2.1 equiv) (Note 4) is added dropwise via syringe over 5 min directly into the stirring solution of phenylacetylene, such that the internal temperature does not exceed –50 °C. The acetone/dry ice bath is replaced with an ice/water bath. When the reaction temperature reaches approximately –5 °C, dichlorodimethylsilane (2.80 mL, 23.2 mmol) (Note 5) is added dropwise via syringe over 5 min, such that the internal temperature does not exceed 10 °C. The ice bath is removed, the solution is allowed to stir at room temperature for 10 min (Note 6), and then the reaction mixture is poured slowly through an open joint into a 1-L round bottom flask containing a rapidly stirring solution of half-saturated aqueous ammonium chloride (200 mL) (Note 7). The mixture is transferred to a 500-

mL separatory funnel and the flask is rinsed with 50 mL of ethyl acetate. The organic phase is separated and the aqueous layer is extracted with ethyl acetate (2 x 50 mL). The combined organic layers are washed with 100 mL of water and 100 mL of brine, then are dried over anhydrous $MgSO_4$ (5 g, Note 8), filtered through Celite 545 (Note 9), and concentrated by rotary evaporation (35 °C, 40 mmHg). The residue is then concentrated further at 1.5 mmHg for 4 h whereupon the residue solidifies (Note 10). The yellow-white solid is dissolved in a minimal amount of boiling hexanes (Note 11), and then is cooled in a freezer (–30 °C) for 16 h to afford the pure product as white needles that are collected by vacuum filtration (5.63 g, 93% yield) (Notes 12 and 13).

B. 2,5-Dibromo-1,1-dimethyl-3,4-diphenylsilole (**2**). *From this point forward the light sensitivity of some compounds necessitates that certain flasks be wrapped in aluminum foil to exclude light.* A 500-mL, three-necked, round-bottomed flask is equipped with two rubber septa, an internal thermometer, and 3-cm egg-shaped stir bar. Under a stream of argon (introduced through a septum with a syringe needle and balloon), lithium wire (0.53 g, 75.6 mmol, 4.5 equiv) (Note 14) is cut into (20-25) small pieces and washed with toluene (2 x 10 mL) to remove the protective oil. One septum is temporarily removed and a funnel is used to aid in the addition of the lithium pieces. The flask is then fitted with a gas adapter and evacuated (1.5 mmHg) for 10 min to ensure that all toluene is removed. The gas adapter is removed and naphthalene (10.12 g, 79.0 mmol, 4.7 equiv) (Note 15) is added with the aid of a funnel. The original septum is replaced and 50 mL of THF (Note 3) is added via syringe. The flask is sonicated for 1 h to facilitate dissolution of the lithium wire (Note 16), and the resulting dark green solution is left to stir at room temperature for 1 h. The lithium naphthalenide solution thus obtained is titrated according to a literature method[3] and found to be 1.35-1.45 M (Note 17), and the flask is wrapped in foil.

Into a 200-mL, single-necked, round-bottomed flask containing dimethyl-bis(phenylethynyl)silane (**1**) (4.37 g, 16.8 mmol) and fitted with a rubber septum (pierced with a syringe needle and argon-filled balloon) is added 120 mL of THF via syringe (Note 3). The resulting silane solution is added to the lithium naphthalenide dropwise, *over a minimum of 20 min*, via cannula (Note 18). Once the addition is complete, the solution is cooled to –10 °C using an acetone bath with a small amount of dry ice.

Meanwhile, a solution of anhydrous $ZnCl_2$ (11.45 g, 84.0 mmol, 5.0 equiv) (Note 19) in 70 mL of THF added via syringe (Notes 3 and 20) is prepared in a 100-mL single-necked, round-bottomed flask equipped with a 2-cm stir bar and rubber septum (pierced with a syringe needle and argon-filled balloon). The $ZnCl_2$ solution is added to the naphthalenide/silane mixture via cannula over a minimum of 20 min (Note 21). The acetone/dry ice bath is removed and the resulting solution is allowed to warm to room temperature (Note 22).

Meanwhile, a 1-L, three-necked, foil-wrapped, round-bottomed flask is charged with *N*-bromosuccinimide (NBS, 7.45 g, 41.9 mmol, 2.5 equiv) (Note 23) and equipped with an internal thermometer, 3-cm egg-shaped stir bar and two rubber septa (one pierced with a syringe needle and argon-filled balloon). The flask is charged with 35 mL of THF via syringe and the resulting solution is cooled to –70 °C or colder using a dry ice/acetone bath. The room temperature silane solution is added into the cold NBS solution via cannula such that the internal temperature does not exceed –50 °C. After the addition is complete the resulting mixture is stirred for a further 30 min at –70 °C or colder. One septum is removed and the cold mixture is slowly poured into a 1-L round-bottomed flask containing a 300-mL solution of rapidly stirring half-saturated aqueous ammonium chloride (Notes 7 and 24). The heterogeneous mixture is transferred to a 1-L separatory funnel and the flask is rinsed with 50 mL of ethyl acetate. The organic phase is separated and the aqueous layer is extracted with ethyl acetate (3 x 50 mL). The combined organic layers are washed successively with 100 mL of half-saturated aqueous $Na_2S_2O_3$ (Note 25), 200 mL of water, 200 mL of brine, then are dried over anhydrous $MgSO_4$ (7 g) and quickly filtered through a thin pad of silica (Note 26) into a foil wrapped 500-mL single-necked flask. The yellow solution is concentrated by rotary evaporation (35 °C, 40 mmHg) and then at 1.5 mmHg for 1 h to give approximately 17 g of crude material (quantitative mass recovery based on both naphthalene and dibromosilole **2**). ^{1}H NMR analysis of a representative sample typically shows a 1:5.2 mixture of the dibromosilole (**2**) and naphthalene (Note 27), which corresponds to a 96% yield (6.78 g) of useable dibromosilole (**2**). It is generally unnecessary to remove the naphthalene for subsequent use, such as cross coupling reactions.

If necessary, the naphthalene can be removed by sublimation in small batches. Thus, 1.7 g of the naphthalene-silole mixture is ground into powder using a mortar and pestle, and sublimed in the dark, under vacuum (1.5

mmHg) for 3–4 hours at 35 °C (Note 28). This will typically remove 99% of the naphthalene according to ^{1}H NMR analysis. If desired, further purification can be accomplished by dissolving the residual material from the combined sublimations in hot hexanes (160 mL) followed by cooling in a freezer for 16 h. The pure 2,5-dibromosilole crystallizes as white needles, which are vacuum-filtered, washed with 10 mL of ice cold hexanes and dried in vacuo to afford 6.64 g (95% yield) of **2**. (Note 29, 30 and 31). Dibromosilole **2** stored in the dark at room temperature is stable for several weeks. Even brief exposure to sunlight during processing will lead to significant decomposition (Notes 24 and 30).

2. Notes

1. All glassware was flame dried and allowed to cool completely to room temperature under a flow of argon before any reagents were introduced. All metal needles and cannula used throughout were acetone washed and oven dried for a minimum of 3 hours. The apparatuses were maintained under an inert atmosphere via an argon-filled balloon equipped with a needle. The balloon is inserted through a rubber septum for the duration of each reaction.

2. Phenylacetylene, obtained from Aldrich Chemical Company, Inc. (98%), was used as received by Checkers. The submitters distilled phenylacetylene prior to use (30 mmHg, 25−30°C) and stored it in an amber glass bottle at room temperature.

3. Anhydrous THF, purchased from Kanto Chemical Co., Inc., was used as received by Checkers. Submitters purchased anhydrous THF from VWR, further purified (dried and degassed) by an alumina column solvent dispensing system.

4. Checkers purchased *n*-butyllithium (1.58 M in hexanes), from Kanto Chemical Co., Inc.. Submitters purchased *n*-butyllithium (2.5 M in hexanes) from Alfa Aesar and titrated according to a literature method.[2] An accurate titer is critical. Caution! *n*-Butyllithium is spontaneously flammable in air. The titrant, *N*-pivaloyl-*o*-toluidine is synthesized from *o*-toluidine and pivaloyl chloride as described by Suffert,[2] it is also commercially available from Sigma-Aldrich. To 0.373 g (1.95 mmol) of *N*-pivaloyl-*o*-toluidine in 2 mL anhydrous THF is added *n*-butyllithium slowly dropwise until the appearance of a yellow endpoint. The titration is repeated 3 times and the

closely agreeing volumes of *n*-butyllithium are averaged to calculate a concentration.

5. Dichlorodimethylsilane, purchased from Aldrich Chemical Company, Inc. (99%), was used as received by Checkers. Submitters distilled dichlorodimethylsilane over CaH_2 prior to use and stored in an amber glass bottle at room temperature.

6. The reaction takes approximately 20−30 min to warm to room temperature. Once it reaches room temperature it is stirred for an additional 10 min.

7. Ammonium chloride was purchased from Kanto Chemical Co., Inc. by Checkers (and from Caledon by Submitters), and used as received. The half saturated solution was prepared by combining equal volumes of a saturated solution and water.

8. Magnesium sulfate was purchased from Kanto Chemical Co., Inc. by Checkers (and from Caledon by Submitters), and used as received.

9. Celite 545 was obtained from Fisher Scientific and used as received. A Celite pad 6 cm in diameter and 2 cm in height was used.

10. Phenylacetylene significantly interferes with the recrystallization. Therefore it is critical that excess phenylacetylene be removed by room temperature evacuation at this point.

11. Typically 75 to 90 mL of hexanes is needed.

12. The product displayed the following physicochemical properties: mp 75 °C; R_f 0.4 (hexane/EtOAc, 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.51 (s, 6 H), 7.30-7.37 (m, 6 H), 7.52– 7.55 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 0.5, 90.6, 105.9, 122.6, 128.2, 128.8, 132.1. Anal. Calcd for $C_{18}H_{16}Si$: C, 83.02; H, 6.19. Found: C, 83.07; H, 6.23. GC: t_R (**1**), 16.53 min; t_R (naphth), 3.75 min; t_R (**2**-decomp), 7.51 min; t_R (**2**), 11.55 min (Rtx®-5 GC system; 5% diphenyl-95% dimethyl polysiloxane capillary column 30 m × 0.25 mm × 0.25 μm; (50 °C (1 min), +15 °C/min to 250 °C). ^{1}H NMR and GC showed no detectable impurities.

13. Submitters obtained the product in 85−95 % yield. Checkers obtained the product in 85% yield on a half-scale reaction.

14. Lithium wire (Na content 0.5-1%), 3.2 mm diam., 98+%, in mineral oil was obtained from Sigma Aldrich. The sodium content is critical, and lithium wire without sodium fails in this reaction.

15. Naphthalene, 99.6%, was obtained from Alfa Aesar and used as received.

16. A Branson 1510 model sonicator was used. The internal reaction temperature is not allowed to exceed 30 °C.

17. An aliquot of the lithium naphthalenide solution (1.00 mL) and 1,1-diphenylethylene (0.5 mL, 2.77 mmol) are combined in a 5-mL round-bottomed flask with a 1-cm stir bar, and a 0.5 M solution of *s*-butanol in toluene is added slowly dropwise until the appearance of a pale yellow endpoint. If the solution is found to be less than 1.35 M, all of the lithium wire has not been dissolved and the solution should be sonicated for another hour.

18. Faster addition results in a substantial decrease in yield.

19. Anhydrous zinc chloride (99.999%: ampoule), purchased from Aldrich, was used as received by Checkers. The ampoule was opened in a glove box, and zinc chloride was measured in a glove box. Submitters purchased zinc chloride (min 97.0%) from Caledon. In their case, the zinc chloride was dried, prior to use, by flame heating the flask such that the zinc chloride fully melts while under vacuum (1.5 mmHg), allowed to cool and transferred to a glove box where it was ground to a fine power using a mortar and pestle. The Checkers observed that the above procedure was not required when using anhydrous zinc chloride (99.999%: ample), purchased from Aldrich.

20. The solution is sonicated for 10 min to facilitate dissolution of the zinc chloride.

21. There is no exotherm to this reaction, so the internal reaction temperature should not exceed 0 °C.

22. Warming to room temperature takes approximately 20 min.

23. *N*-Bromosuccinimide (99%) was obtained from Alfa Aesar. Prior to use, it was dried over P_2O_5 in a vacuum desiccator. Submitters recrystallized *N*-bromosuccinimide from hot water, and dried over P_2O_5 in a vacuum desiccator, prior to use.

24. Lengthy exposure to light during any step in part B may lead to a significant decrease in overall yield, therefore it is suggested to work in a fume hood with the lights off.

25. Sodium thiosulfate was purchased from Aldrich Chemical Company, Inc. by Checkers (and from Caledon by Submitters), and used as received. The half-saturated solution was prepared by combining equal volumes of a saturated solution and water.

26. Silica Gel was purchased from Kanto Chemical Co., Inc. by Checkers (from Silicycle by Submitters) and used as received. A silica pad 6 cm in diameter and 2 cm in height was used.

27. Naphthalene is identified by ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.54 (dd, *J* = 6.2, 3.0 Hz, 4 H), 7.87-7.91 (dd, *J* = 6.2, 3.0 Hz, 4 H). Silole is identified by ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.45 (s, 6 H), 6.93–6.96 (m, 4 H), 7.11–7.16 (m, 6 H).

28. The process was repeated ten times to purify all the naphthalene/silole mixture (1.7 g x 10 times). Submitters purified 1.0 g for each trial (1.0 g x 17 times). It is important to purify in small batches.

29. The product displays the following physicochemical properties: mp 163–164 °C; R_f 0.65 (hexane/EtOAc, 9/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.45 (s, 6 H), 6.93–6.96 (m, 4 H), 7.11–7.16 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: –6.0, 123.0, 127.6, 127.7, 129.3, 137.2, 156.2. HRMS *m/z* calcd for $C_{18}H_{17}Br_2Si$ [$M+H^+$]: 418.9466, found: 418.9461. Anal. Calcd for $C_{18}H_{17}Br_2Si$: C, 51.45; H, 3.84. Found: C, 51.22; H, 4.04.

30. Submitters obtained the product in 85−95 % yield. Checkers obtained the product in 89% yield on a half-scale reaction.

31. Photo-decomposition leads to a brown discoloration, and decomposition is indicated by a sharp singlet at 2.78 ppm in the ^{1}H NMR spectrum (see Note 13).

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

Siloles have been extensively studied for their electronic properties,[4,5] leading to their recognition as desirable π-conjugated materials for applications such as OLEDs[6] (Organic Light Emitting Diodes) and PLEDs[7] (Polymer Light Emitting Diodes). Important contributions have been made in the areas of electro and photoluminescence,[8] nitroaromatic sensors,[9] silole-copolymers,[10] and OFETs (Organic Field-Effect Transistors).[11] We have also studied the electronic properties of donor-acceptor siloles,[12] silole oligomers,[13] siloles as precursors to substituted butadienes,[14] and the

electrogenerated chemiluminescence of siloles.[15] Many of these silole chromophores have been prepared from 2,5-dihalosilole intermediates, such as that prepared here, and with the growing interest in siloles, a reliable large-scale synthesis of a 2,5-dihalosilole is becoming increasingly necessary.

In pioneering work, Tamao reported the synthesis of symmetrical 2,5-dihalo siloles via an intramolecular reductive cyclization of diethynylsilanes.[16] Yields from the original procedure ranged from 44−72%, and the reaction failed with 1,1-dimethylsiloles. The somewhat fickle and lengthy preparation of lithium naphthalenide has been shortened and now reproducibly gives essentially quantitative titers simply by using Li wire containing a small percentage of sodium and sonication of the reaction mixture. The original procedure also employed expensive *t*-$BuPh_2SiCl$ as a stoichiometric oxidant for excess lithium naphthalenide. We,[12] and others,[17] have modified the original procedure by replacing *t*-$BuPh_2SiCl$ with $ZnCl_2$. Besides the obvious cost savings, this modification simplifies product isolation, obviates the necessity for precise control over stoichiometry and gives higher yields. Another significant advantage of the modified $ZnCl_2$ procedure is that less reactive di-zinc silole intermediates can be selectively functionalized, and this allows for the direct preparation of asymmetrical siloles.[12] Specifically, replacing the NBS in part B of this procedure with *N*-chlorophthalimide followed by solid I_2, the asymmetrical chloroiodosilole is produced in a respectable 81% yield.[12] Alternatively, the di-zinc silole intermediate generated in part B before addition of NBS can be used directly in standard cross coupling reactions.[18]

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Appendix
Chemical Abstracts Nomenclature; (Registry Number)

n-Butyllithium; (109-72-8)
Phenyl acetylene: Ethynylbenzene; (536-74-3)

Dichlorodimethylsilane; (75-78-5)
Dimethyl-bis-phenylethynyl silane: Benzene, 1,1'-[(dimethylsilylene)di-2,1-ethynediyl]bis-; (2170-08-3)
Naphthalene; (91-20-3)
Lithium; (7439-93-2)
Zinc chloride; (7646-85-7)
N-Bromosuccinimide: 1-Bromo-2,5-pyrrolidinedione; (128-08-5)
2,5-Dibromo-1,1-dimethyl-3,4-diphenylsilole: Silacyclopenta-2,4-diene, 2,5-dibromo-1,1-dimethyl-3,4-diphenyl-; (686290-22-2)

Brian Pagenkopf was born in 1967 in Wausau, Wisconsin. He completed his undergraduate studies at the University of Minnesota, Twin Cities, and while there worked with Takashi Okagaki (OB/GYN), Terry Davis (3M, Encapsulation) and Gary Gray (Chemistry). His graduate studies were conducted at Montana State University (Bozeman) under the direction of Tom Livinghouse. Following his graduate research, he was a NIH Postdoctoral Fellow with Erick Carreira at Caltech in 1997, and was briefly at the ETH in Zürich after the group moved there in 1998, before beginning his independent career at the University of Texas at Austin. In 2005, he moved to the University of Western Ontario. His research interests include natural product synthesis, synthetic methods, symmetric catalysis and organic materials based on siloles.

Nicholas Morra was born in 1984 in Toronto, Canada. He graduated from the University of Western Ontario in 2007 where he spent the last two years working for Prof. Brian Pagenkopf, primarily on silole based materials. He is currently working towards a PhD with his research focused on Lewis Acid catalyzed methodologies and total synthesis of natural products.

Daisuke Tomita was born in 1980 in Tokyo, Japan. He received B.S. in 2004 from the University of Chiba and M.S. in 2006 from The University of Tokyo. Presently, he is pursuing Ph.D. degree at the Graduate School of Pharmaceutical Sciences, The University of Tokyo, under the guidance of Professor Masakatsu Shibasaki. His research interests are in the area of catalytic asymmetric reaction using copper catalyst.

Tsuyoshi Mita was born in 1976 in Tokyo, Japan, and received his M.S. degree from Keio University in 2002 under the direction of Professor Tohru Yamada. In the following years, he worked as a process chemist in the pharmaceutical research laboratory of Ajinomoto Co., INC. (Kawasaki, Japan). He left his job in 2004 and entered the University of Tokyo as a Ph.D. student. After receiving his Ph.D. degree under the guidance of Professor Masakatsu Shibasaki in 2007, he joined Professor Eric N. Jacobsen's group at Harvard University as a JSPS research fellow. His current interests are the development of new asymmetric catalysis as well as the search for drug candidates based on medicinal chemistry.

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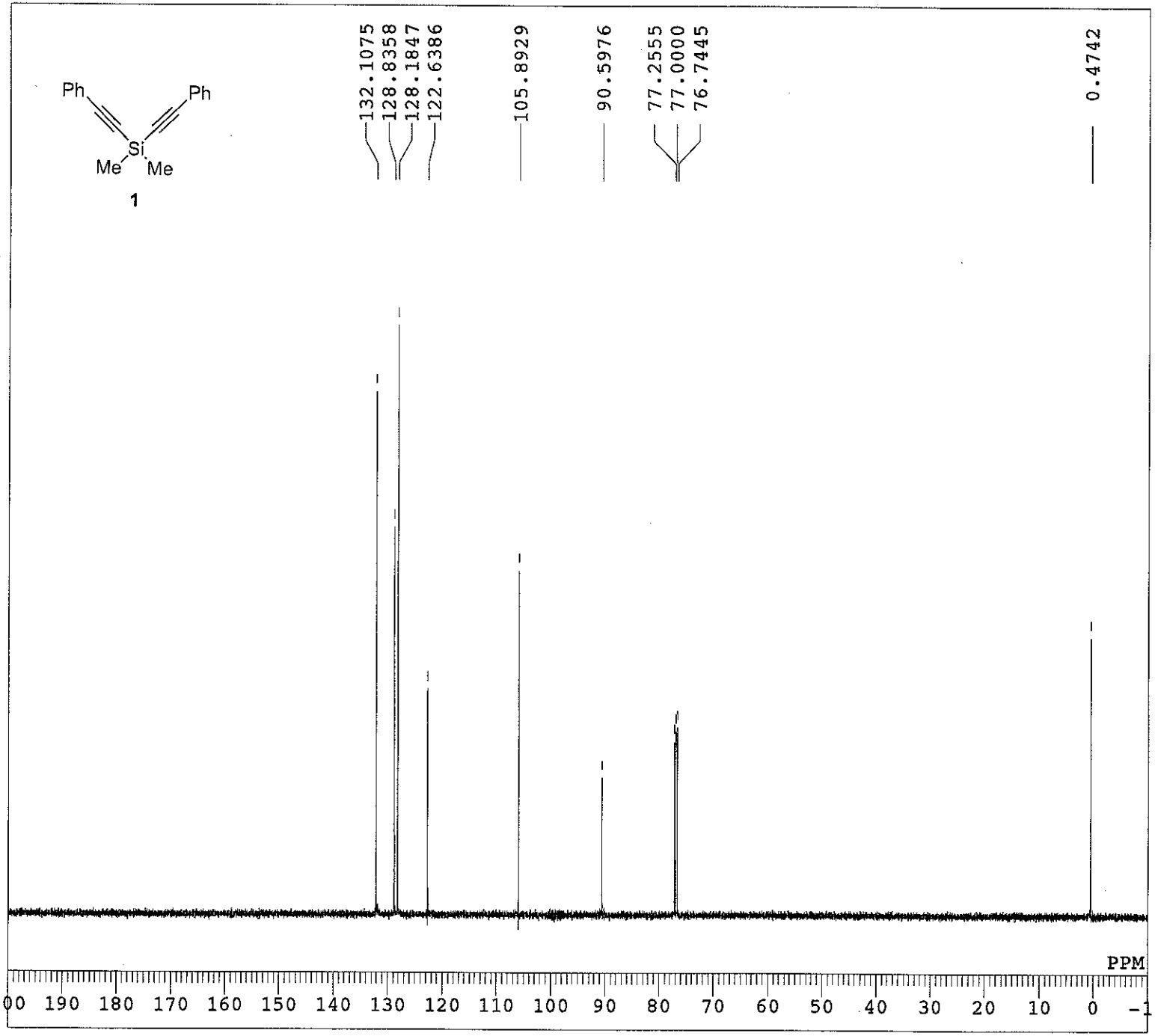

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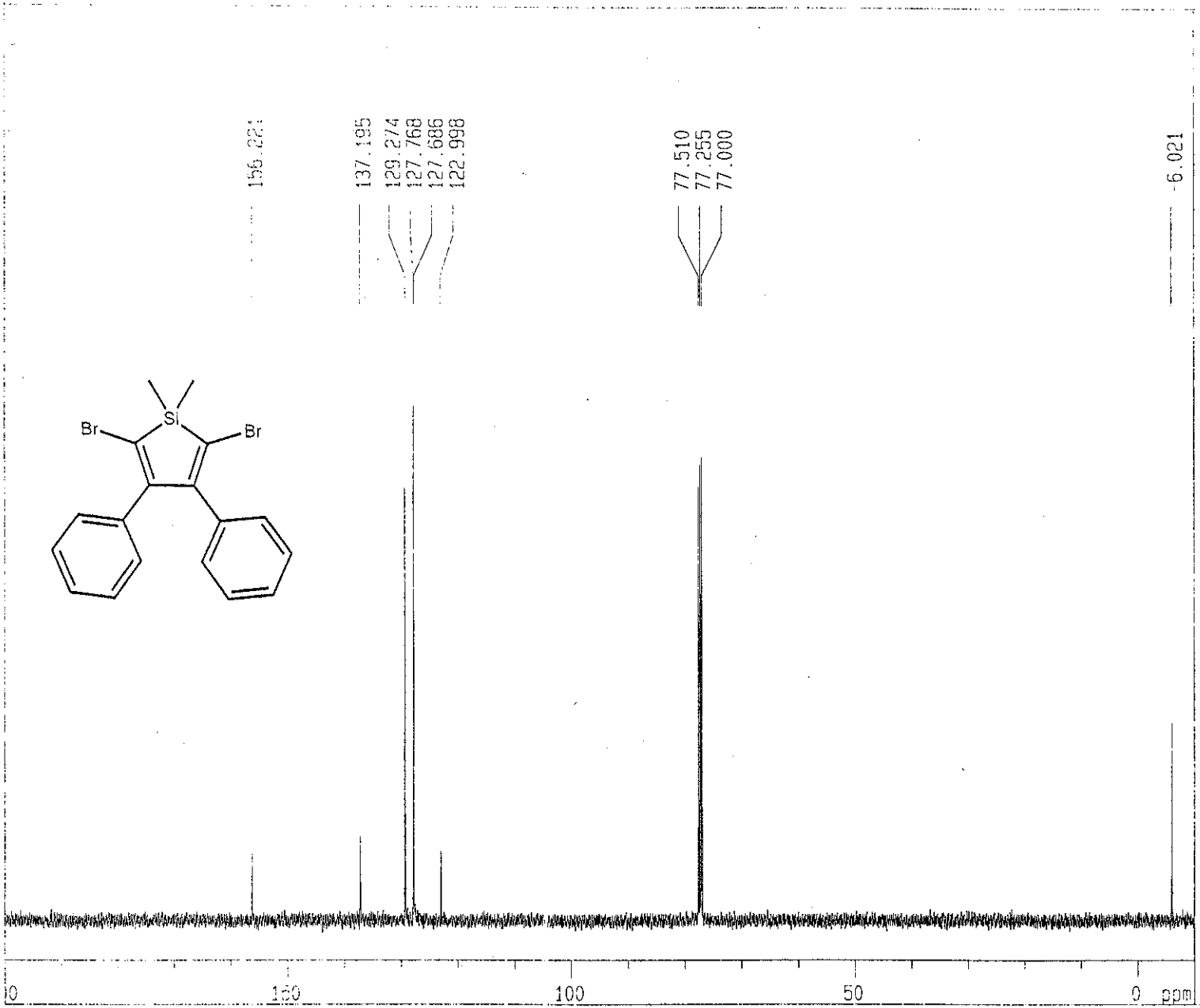

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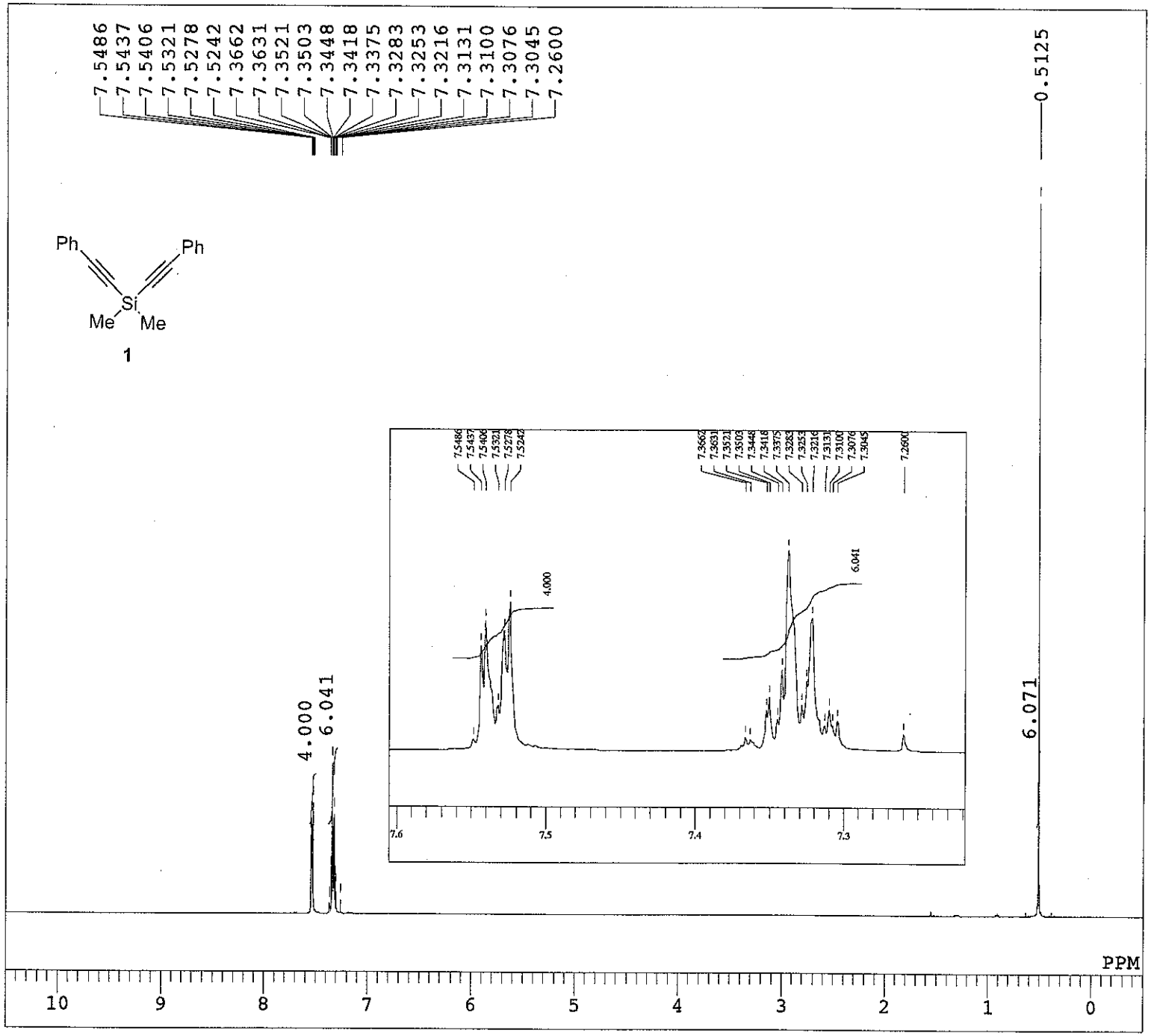
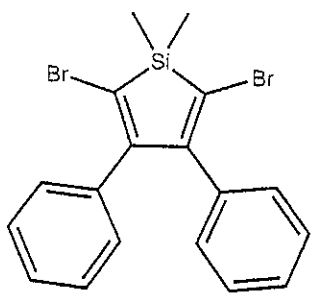
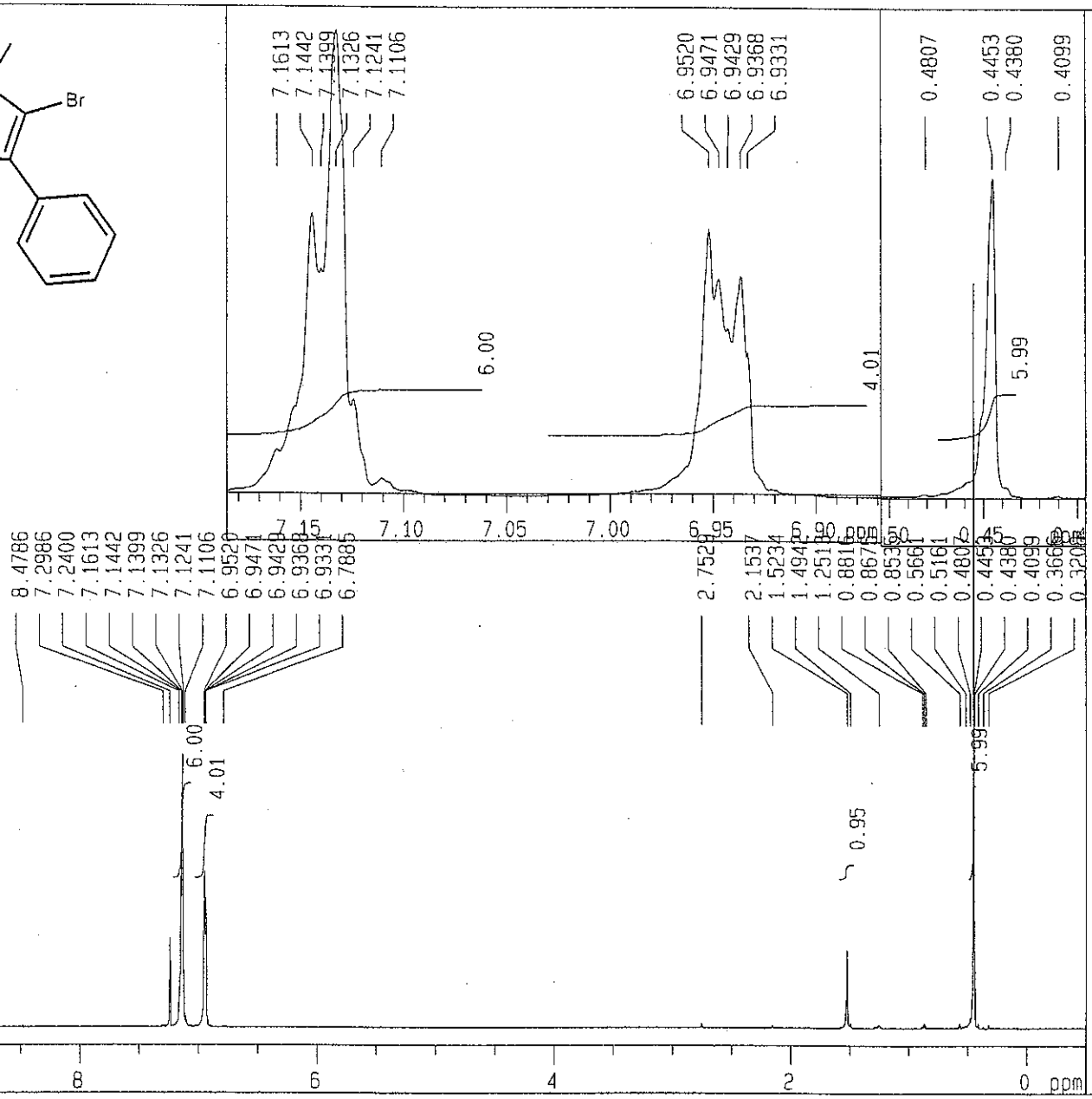
C:\My Documents\PGousei\MITA Tsuyoshi\OS\Step 1 1H.als
1H Line



DFILE	C:\My Documents\PGousei\MIT	
COMNT	1H Line	
DATIM	Wed Feb 21 10:04:11 2007	
OBNUC	1H	
EXMOD	non	
OBFRQ	499.10	MHz
OBSET	120.00	KHz
OBFIN	8250.00	Hz
POINT	32768	
FREQU	9980.04	Hz
SCANS	32	
ACQTM	3.2834	sec
PD	3.7166	sec
PW1	6.25	usec
IRNUC	1H	
CTEMP	23.8	c
SLVNT	CDCL3	
EXREF	7.26	ppm
BF	0.12	Hz
RGAIN	14	

OS Final Check





Date : Wed Jun 6 20:50:56 2007

FileName	:	.LoadingFID.nmdata
Comment	:	OS Final Check
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	10000.0 Hz
FILTR	:	5000 Hz
DELAY	:	40.0 usec
DEADT	:	57.1 usec
INTVL	:	100.0 usec
TIMES	:	32 times
DUMMY	:	1 times
PD	:	3.7232 sec
ACQTM	:	3276.7998 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.31 Hz
PW1	:	5.70 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162160.00 Hz
RGAIN	:	21
SCANS	:	13 times
SLVNT	:	CDCL3
SPINNING	:	17 Hz
TEMP	:	25.2 C