Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

A convenient and clean synthetic method for borasiloxanes by Pd-catalysed reaction of silanols with diborons

Aya Yoshimura,‡ Michiyo Yoshinaga, Hiroshi Yamashita,* Masayasu Igarashi, Shigeru Shimada and Kazuhiko Sato

National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1, Higashi, Tsukuba, Ibaraki 305-8565, Japan.

‡ Present address: Department of Applied Chemistry, Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan.

[*] E-mail: hiro-yamashita@aist.go.jp

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1. General comments

Unless otherwise noted, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. All reagents were purchased from commercial suppliers and used without further purification except for $PhMe_2SiOH$. $PhMe_2SiOH$ (Wako Pure Chemical Industries, Ltd., No. 328-90483, Lot ECH3187) was used after distillation to remove a contaminated disiloxane ($PhMe_2SiOSiMe_2Ph$). All solvents were dried and/or distilled by standard methods. The products were isolated by a preparative GPC instrument (Japan Analytical Industry Co., Ltd., LC-908) or a short-path distillation apparatus (Sibata Scientific Technology Ltd., Glass tube oven GTO-350RD). All the products **2a-i** were obtained in reasonably pure forms (≥95%).

As for Pd acetate catalysts, the compound obtained from Strem Chemicals Inc. (No. 46-1780, Lot 142265-SA) as $Pd(OAc)_2$ was mainly $Pd_3(OAc)_6$, while the compound purchased from Tokyo Chemical Industry Co., Ltd. as $Pd(OAc)_2$ (No. A1424, Lot TBFTE-MA) was found to be almost pure $Pd_3(OAc)_5(NO_2)$. Their ^1H NMR spectra shown in Fig. S1 (a) and (b) were in good agreement with their reported spectra.[S1]

^1H, ^{13}C, ^{29}Si, and ^{11}B NMR spectra were recorded on a Bruker AVANCE III HD 600 spectrometer equipped with a CryoProbe (600 MHz for ^1H, 150 MHz for ^{13}C, 119 MHz for ^{29}Si, and 193 MHz for ^{11}B; pulse programs: zg30 for ^1H, zgpg30 for ^{13}C, zgig30 for ^{29}Si, and zg for ^{11}B) using $CDCl_3$, C_6D_6, or THF-d_8 solvent. The chemical shifts are referenced to tetramethylsilane (0 ppm) for ^1H, ^{13}C, and ^{29}Si NMR, boron trifluoride diethyl ether complex (0 ppm) for ^{11}B NMR, or the solvent resonances for ^1H and ^{13}C NMR as internal standards (for ^1H, $CHCl_3$: 7.26 ppm, C_6D_5H: 7.15 ppm, THF-d_7 (H at 2-C): 3.58 ppm; for ^{13}C, $CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm, THF-d_8 (2-C): 67.2 ppm). The high-resolution ESI mass spectra were obtained on a Bruker micrOTOF II. Melting points were determined on Opti Melt MPA100 apparatus (TOKYO INSTRUMENT, INC.).

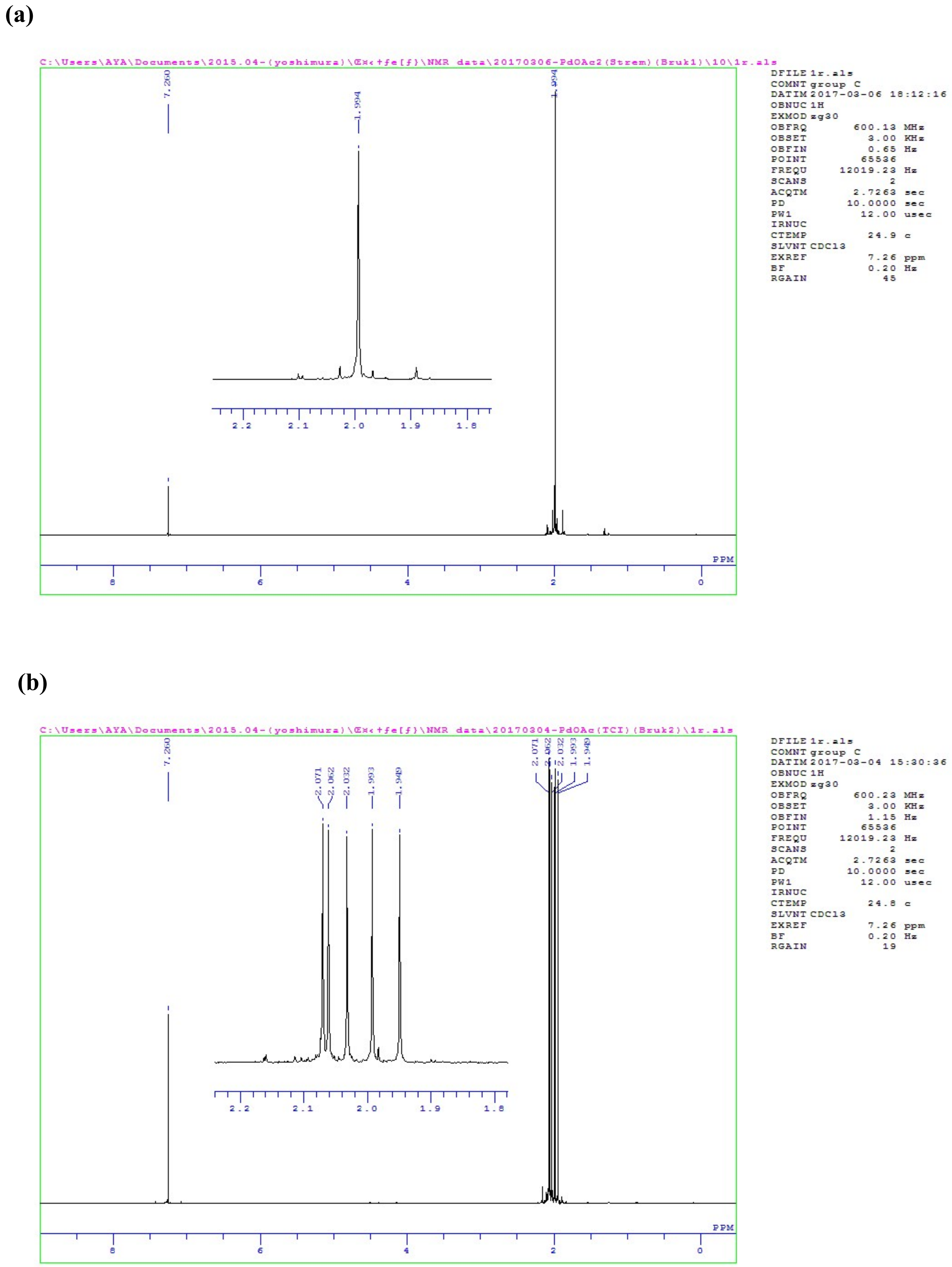

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Fig. S1 ^{1}H NMR spectra (in $CDCl_3$) of the Pd acetates, (a) $Pd_3(OAc)_6$ and (b) $Pd_3(OAc)_5(NO_2)$, which were obtained from Strem Chemicals Inc. and Tokyo Chemical Industry Co., Ltd., respectively.

2. Experimental procedures

2-1. General procedure for the synthesis of 1a by transition metal-catalysed reaction of a Et_3SiOH with a B_2pin_2 in Table 1

In a 10 mL Schlenk flask were placed bis(pinacolato)diboron (0.50 mmol), catalysts (0.5-26 mol%), and Et_3SiOH (1.0 mmol) under nitrogen. The mixture was stirred under the reaction conditions specified in Table 1. After the reaction, the yield of the product **1a** was determined by ^{29}Si NMR spectroscopy using $PhMe_3Si$ as an internal standard. In ^1H NMR, the peak separation between the starting materials and the products has not been sufficient in some cases. On the other hand, all the peaks of the starting materials and the products can be observed clearly in ^{29}Si NMR, and therefore, we have chosen ^{29}Si NMR for estimation of the yields of the products. A typical example of the ^{29}Si NMR spectrum of the reaction mixture containing $PhMe_3Si$ (10 μL) in C_6D_6 is shown in Fig. S2.

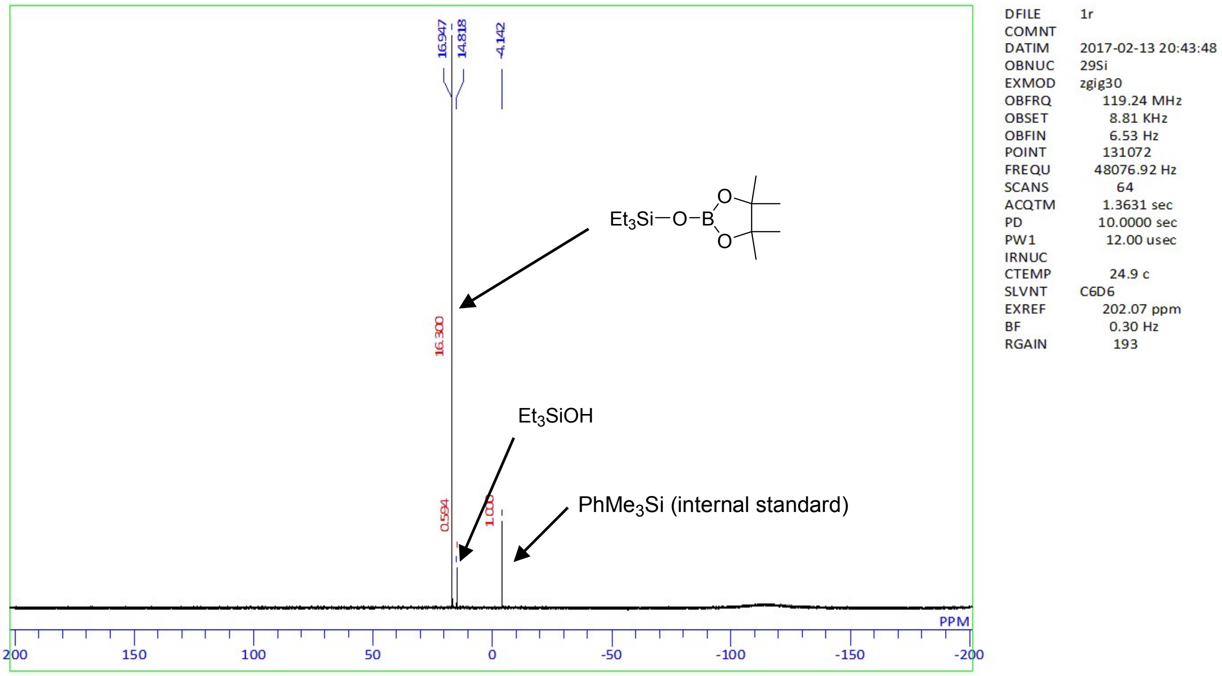

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Fig. S2 ^{29}Si NMR of the reaction mixture obtained in the reaction of Et_3SiOH with B_2pin_2 catalysed by $Pd_3(OAc)_5(NO_2)$ (Table 1, entry 1).

2-2. Preparation of 1a-1i in Table 2

In each reaction, Pd acetate ($Pd_3(OAc)_5(NO_2)$ or $Pd_3(OAc)_6$) was used. Their catalytic activities were similar to each other.

Preparation of 1a

In a 10 mL Schlenk flask were placed Pd acetate ($Pd_3(OAc)_6$, 0.5 mol% Pd), bis(pinacolato)diboron (0.55 mmol), and Et_3SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 25 °C for 3 h. After the reaction, the product **1a** was obtained in 94% NMR yield. The product was isolated in 81% yield by preparative GPC using toluene (super dehydrated) as an eluent.

Preparation of 1b

In a 10 mL Schlenk flask were placed Pd acetate ($Pd_3(OAc)_5(NO_2)$, 1 mol% Pd), bis(pinacolato)diboron (0.55 mmol), and $PhMe_2SiOH$ (1.0 mmol) under nitrogen. The mixture was stirred at 25 °C for 3 h. After the reaction, the product **1b** was obtained in 99% NMR yield. The product was isolated in 92% yield by short-path distillation under a reduced pressure (bp 150–160 °C/200 mmHg).

Preparation of 1c

In a 10 mL Schlenk flask were placed Pd acetate ($Pd_3(OAc)_5(NO_2)$, 1 mol% Pd), bis(pinacolato)diboron (0.55 mmol), Ph_3SiOH (1.0 mmol), and distilled THF (0.25 mL) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product **1c** was obtained in 95% NMR yield. The product was isolated in 84% yield by short-path distillation under a reduced pressure (bp 190–200 °C/0.9 mmHg).

Preparation of 1d

In a 10 mL Schlenk flask were placed Pd acetate ($Pd_3(OAc)_5(NO_2)$, 1 mol% Pd), bis(pincolato)diboron (1.0 mmol), $(^tBuO)_3SiOH$ (1.0 mmol), and distilled THF (0.25 mL) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product **1d** was obtained in 99% NMR yield. The product was isolated in 83% yield by short-path distillation under a reduced pressure (bp 145–155 °C/22 mmHg).

Preparation of 1e

In a 10 mL Schlenk flask were placed Pd acetate ($Pd_3(OAc)_5(NO_2)$, 1 mol% Pd), bis(pinacolato)diboron (1.0 mmol), and Me_3SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 25 °C for 4 h. After the reaction, the product **1e** was obtained in 98% NMR yield. The product was isolated in 64% yield by short-path distillation under a reduced pressure (bp 90–100 °C/245 mmHg).

Preparation of 1f

In a 10 mL Schlenk flask were placed a Pd acetate ($Pd_3(OAc)_5(NO_2)$, 1 mol% Pd), bis(pinacolato)diboron (2.0 mmol), $Ph_2Si(OH)_2$ (1.0 mmol), and distilled THF (0.25 mL) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product **1f** was obtained in 97% NMR yield. The product was isolated in 86% yield by short-path distillation under a reduced pressure (bp 190–200 °C/0.9 mmHg).

Preparation of 1g

In a 10 mL Schlenk flask were placed Pd acetate ($Pd_3(OAc)_5(NO_2)$, 1 mol% Pd), bis(neopentyl glycolato)diboron (1.0 mmol), and Et_3SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product **1g** was obtained in 94% NMR yield. The product was isolated in 77% yield by short-path distillation under a reduced pressure (bp 110–120 °C/25 mmHg).

Preparation of 1h

In a 10 mL Schlenk flask were placed Pd acetate ($Pd_3(OAc)_5(NO_2)$, 1 mol% Pd), bis(hexylene glycolato)diboron (1.0 mmol), and Et_3SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product **1h** was obtained in 98% NMR yield. The product was isolated in 85% yield by short-path distillation under a reduced pressure (bp 120–130 °C/19 mmHg).

Preparation of 1i

In a 10 mL Schlenk flask were placed Pd acetate ($Pd_3(OAc)_5(NO_2)$, 1 mol% Pd), bis(catecolato)diboron (1.0 mmol), and Et_3SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 25 °C for 3 h. After the reaction, the product **1i** was obtained in 99% NMR yield. The product was isolated in 94% yield by short-path distillation under a reduced pressure (bp 160–170 °C/50 mmHg).

2-3. Procedures for the stoichiometric reactions (eqns 1 and 2)

(1) Treatment of Pd acetate with bis(pinacolato)diboron and then with Et_3SiOH (eqn 1)

A Young NMR tube was charged with $Pd_3(OAc)_5(NO_2)$ (10.8 mg, 0.05 mmol Pd), bis(pinacolato)diboron (12.3 mg, 0.05 mmol), and THF-d_8 (30 μL) under nitrogen. The mixture was kept at 25 °C for 3 h, and then, Et_3SiOH (0.1 mmol) was added, and the resulting mixture was kept at 25 °C for additional 3 h. The ^1H and ^{29}Si NMR spectra of the reaction mixture (Fig. S3 (a) and (b), respectively) showed the formation of **1a** in 68% yield along with unreacted Et_3SiOH.

(2) Treatment of Pd acetate with Et_3SiOH and then with bis(pinacolato)diboron (eqn 2)

A Young NMR tube was charged with $Pd_3(OAc)_5(NO_2)$ (11.5 mg, 0.05 mmol Pd), Et_3SiOH (8 μL, 0.05 mmol), and THF-d_8 (30 μL) under nitrogen. The mixture was kept at 25 °C for 3 h, and then, bis(pinacolato)diboron (0.05 mmol) was added, and the resulting mixture was kept at 25 °C for additional 3 h. The ^1H and ^{29}Si NMR spectra of the reaction mixture (Fig. S4 (a) and (b), respectively) showed the formation of **1a** and $Et_3SiOSiEt_3$ in 73% and 26% yields, respectively

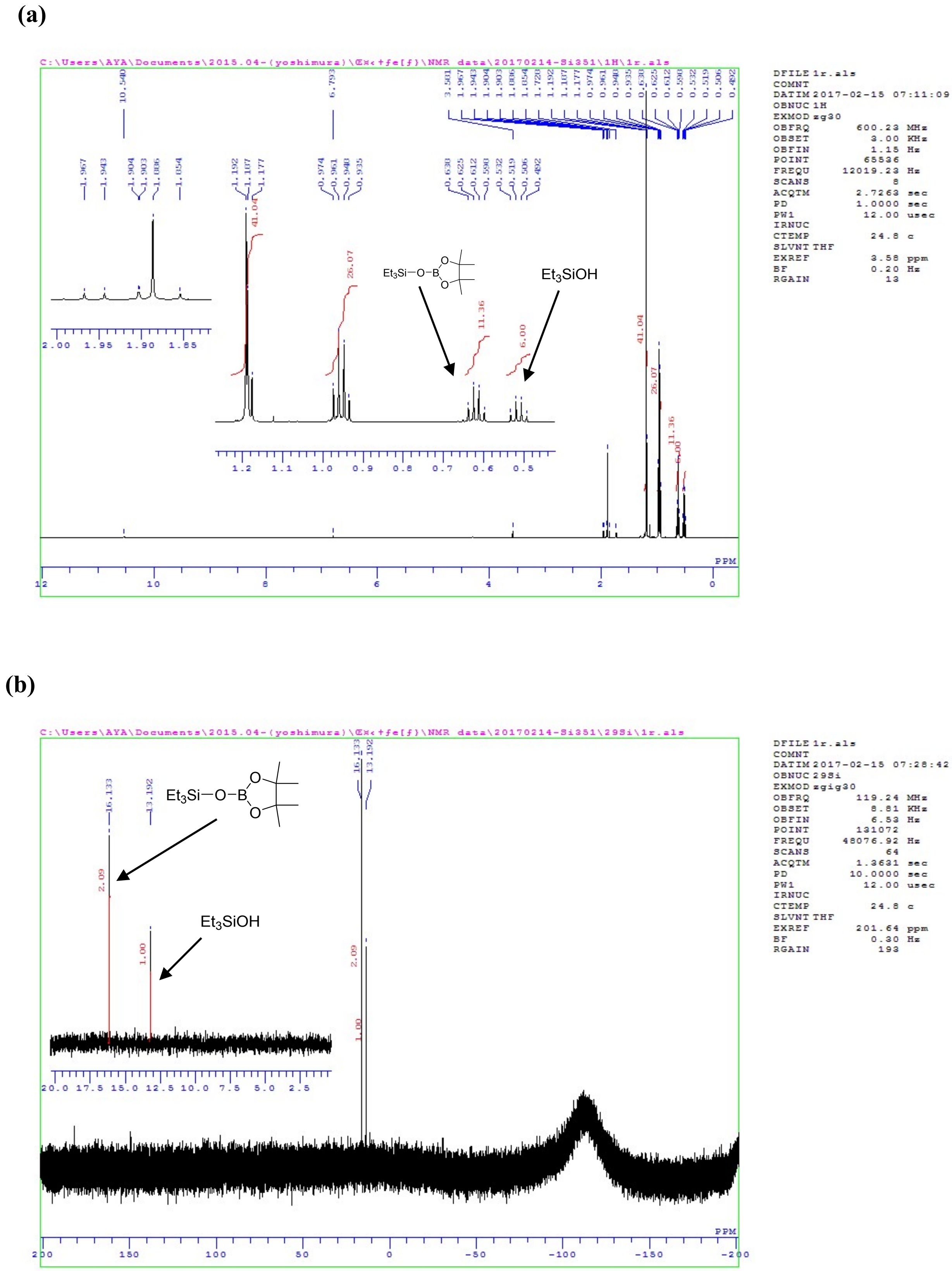
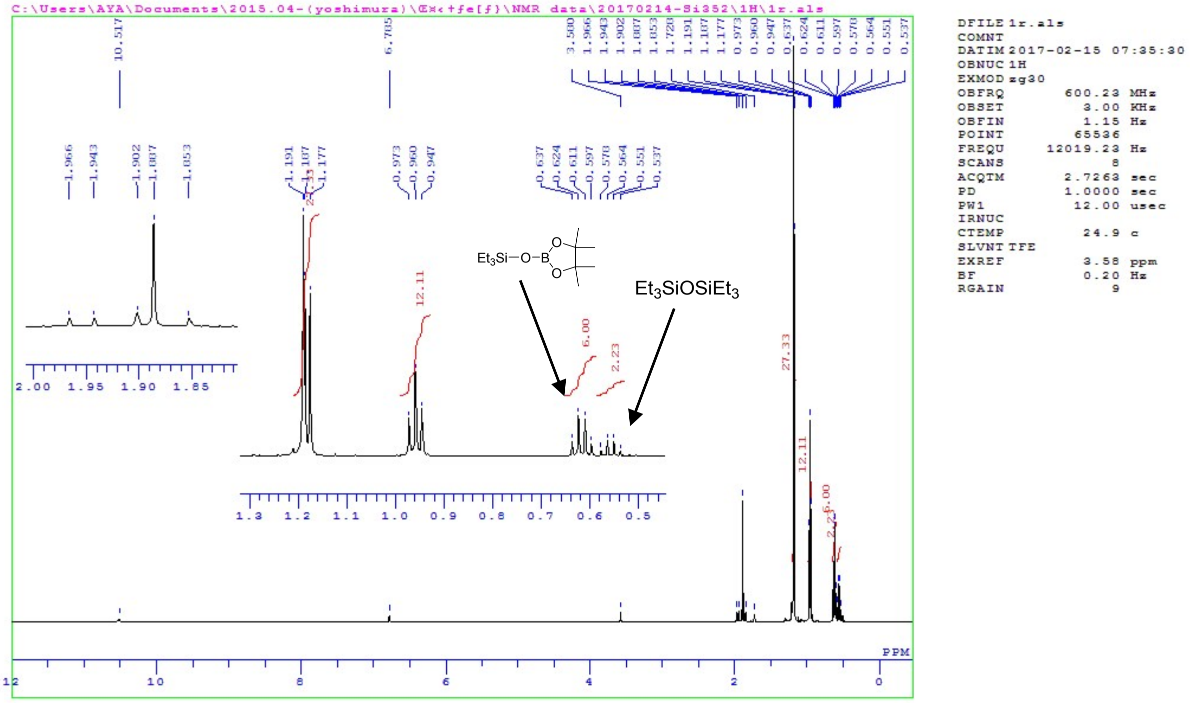


Fig. S3 (a) ^{1}H NMR and (b) ^{29}Si NMR of the reaction mixture obtained by treatment of $Pd_3(OAc)_5(NO_2)$ with bis(pinacolato)diboron and then with Et_3SiOH (eqn 1).

(a)



(b)

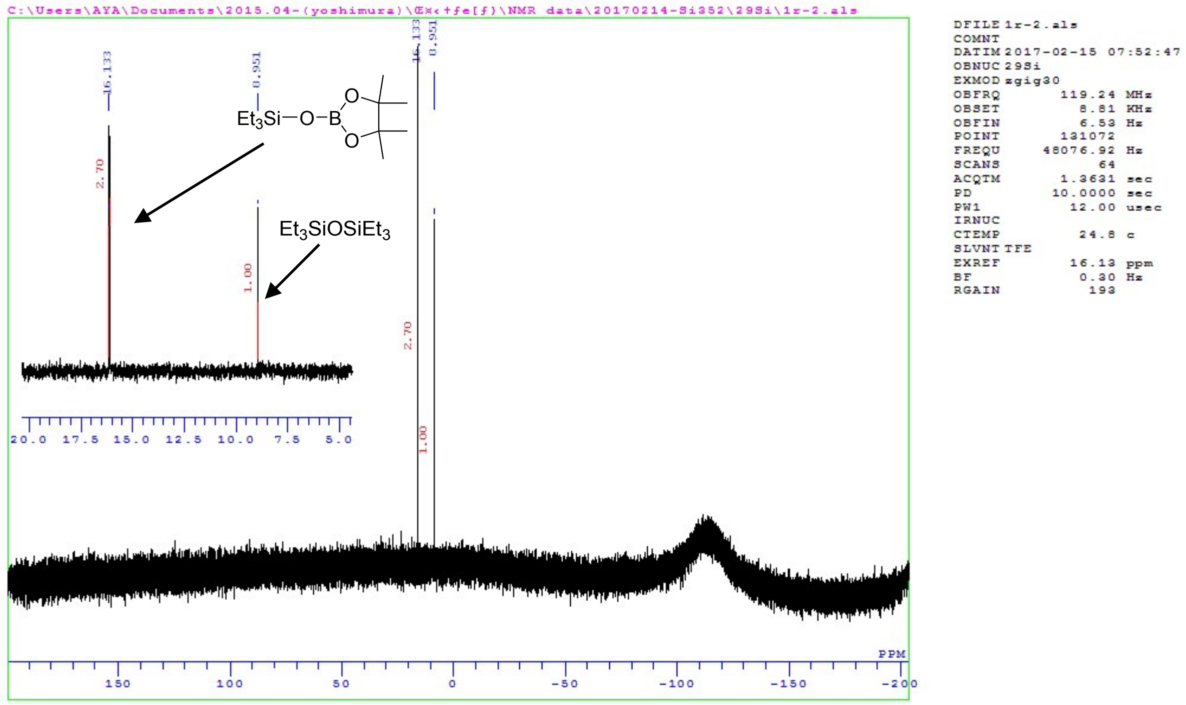
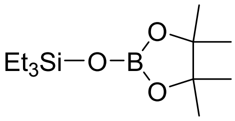


Fig. S4 (a) ^{1}H NMR and (b) ^{29}Si NMR of the reaction mixture obtained by treatment of $Pd_3(OAc)_5(NO_2)$ with Et_3SiOH and then bis(pinacolato)diboron (eqn 2).

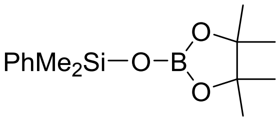
2-4. Spectral data of the products 1a-i

1a[S2]



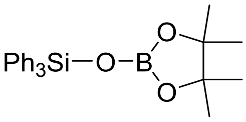
Colorless oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.62 (q, J = 8.1 Hz, 6H, $SiCH_2$), 0.97 (t, J = 8.1 Hz, 9H, $SiCCH_3$), 1.04 (s, 12H, $OCCH_3$); ^{13}C NMR (C_6D_6, 150 MHz) δ 5.9, 6.8, 24.6, 81.8; ^{29}Si NMR (C_6D_6, 119 MHz) δ 17.0; ^{11}B NMR (C_6D_6, 193 MHz) δ 20.4.

1b[S2(b), S3]



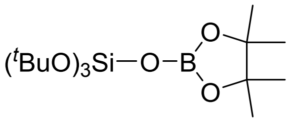
Colorless oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.45 (s, 6H, $SiCH_3$), 1.02 (s, 12H, $OCCH_3$), 7.18–7.23 (m, 3H, phenyl proton), 7.64–7.69 (m, 2H, phenyl proton); ^{13}C NMR (C_6D_6, 150 MHz) δ -0.0, 24.6, 82.1, 128.1, 129.8, 133.5, 138.6; ^{29}Si NMR (C_6D_6, 119 MHz) δ 5.1; ^{11}B NMR (C_6D_6, 193 MHz) δ 20.7.

1c [S2(b)]



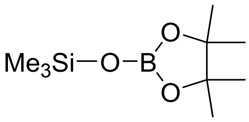
White solid; mp 96–97 °C; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.99 (s, 12H, $OCCH_3$), 7.15–7.19 (m, 9H, phenyl proton), 7.82–7.85 (m, 6H, phenyl proton); ^{13}C NMR (C_6D_6, 150 MHz) δ 24.6, 82.5, 128.1, 130.3, 135.2, 135.7; ^{29}Si NMR (C_6D_6, 119 MHz) δ -15.6; ^{11}B NMR (C_6D_6, 193 MHz) δ 21.1.

1d



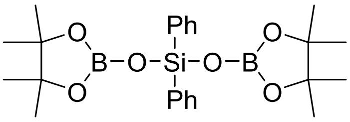
Colorless oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 1.06 (s, 12H, $OCCH_3$), 1.45 (s, 27H, $C(CH_3)_3$); ^{13}C NMR (C_6D_6, 150 MHz) δ 24.7, 31.5, 73.2, 81.9; ^{29}Si NMR (C_6D_6, 119 MHz) δ -100.8; ^{11}B NMR (C_6D_6, 193 MHz) δ 19.9; HRMS (ESI): m/z calcd for $[C_{18}H_{39}BO_6SiNa]^+$ (M+Na): 413.2501; found: 413.2492.

1e[S4]



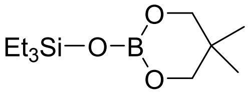
Colorless oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.21 (s, 9H, $SiCH_3$), 1.04 (s, 12H, $OCCH_3$); ^{13}C NMR (C_6D_6, 150 MHz) δ 1.0, 24.7, 81.9; ^{29}Si NMR (C_6D_6, 119 MHz) δ 15.5; ^{11}B NMR (C_6D_6, 193 MHz) δ 20.4.

1f[S5]



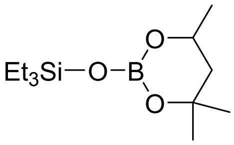
Colorless oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 1.01 (s, 24H, $OCCH_3$), 7.14–7.16 (m, 6H, phenyl proton), 7.95–7.99 (m, 4H, phenyl proton); ^{13}C NMR (C_6D_6, 150 MHz) δ 24.6, 82.5, 128.0, 130.6, 134.0, 135.0; ^{29}Si NMR (C_6D_6, 119 MHz) δ -39.8; ^{11}B NMR (C_6D_6, 193 MHz) δ 20.7.

1g



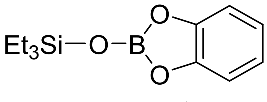
Colorless oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.57 (s, 6H, $C(CH_3)_2$), 0.75 (q, J = 7.9 Hz, 6H, $SiCH_2$), 1.09 (t, J = 7.9 Hz, 9H, $SiCCH_3$), 3.31 (s, 4H, OCH_2); ^{13}C NMR (C_6D_6, 150 MHz) δ 6.1, 7.0, 21.3, 31.4, 72.9; ^{29}Si NMR (C_6D_6, 119 MHz) δ 14.5; ^{11}B NMR (C_6D_6, 193 MHz) δ 16.2; HRMS (ESI): m/z calcd for $[C_{11}H_{25}BO_3SiNa]^+$ (M+Na): 267.1558; found: 267.1555.

1h



Colorless oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.73 (q, J = 8.0 Hz, 6H, $SiCH_2$), 1.00 (s, 3H, $C(C\underline{H}^a{}_3)(CH^b{}_3)$), 1.03 (d, J = 6.1 Hz, 3H, $OCHC\underline{H}_3$), 1.08 (d, J = 5.7 Hz, 2H, $OCCH_2$), 1.09 (t, J = 8.0 Hz, 9H, $SiCCH_3$), 1.09 (s, 3H, $C(CH^a{}_3)(C\underline{H}^b{}_3)$), 3.88–3.93 (m, 1H, OCH); ^{13}C NMR (C_6D_6, 150 MHz) δ 6.2, 7.0, 23.3, 27.7, 31.3, 45.6, 65.5, 71.2; ^{29}Si NMR (C_6D_6, 119 MHz) δ 14.3; ^{11}B NMR (C_6D_6, 193 MHz) δ 16.4; HRMS (ESI): m/z calcd for $[C_{12}H_{27}BO_3SiNa]^+$ (M+Na):281.1715; found: 281.1693.

1i[S6]



Colorless oil; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.63 (q, J = 8.1 Hz, 6H, $SiCH_2$), 0.95 (t, J = 8.1 Hz, 9H, $SiCCH_3$), 6.73 (dd, J = 5.9, 3.3 Hz, 2H, phenylene proton), 6.93 (dd, J = 5.9, 3.3 Hz, 2H, phenylene proton); ^{13}C NMR (C_6D_6, 150 MHz) δ 5.6, 6.5, 112.1, 122.4, 148.7; ^{29}Si NMR (C_6D_6, 119 MHz) δ 20.6; ^{11}B NMR (C_6D_6, 193 MHz) δ 21.0.

3. References and notes

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S2 (a) D. Frąckowiak, J. Walkowiak, G. Hreczycho and B. Marciniec, *Eur. J. Inorg. Chem.*, 2014, 3216; (b) M. Ito, M. Itazaki and H. Nakazawa, *J. Am. Chem. Soc.*, 2014, **136**, 6183.

S3 (a) C. Gryparis and M. Stratakis, *Org. Lett.* 2014, **16**, 1430; (b) C. Kleeberg, M. S. Cheung, Z. Lin and T. B. Marder, *J. Am. Chem. Soc.*, 2011, **133**, 19060.

S4 T. Ohmura, T. Torigoe and M. Suginome, *J. Am. Chem. Soc.*, 2012, **134**, 17416.

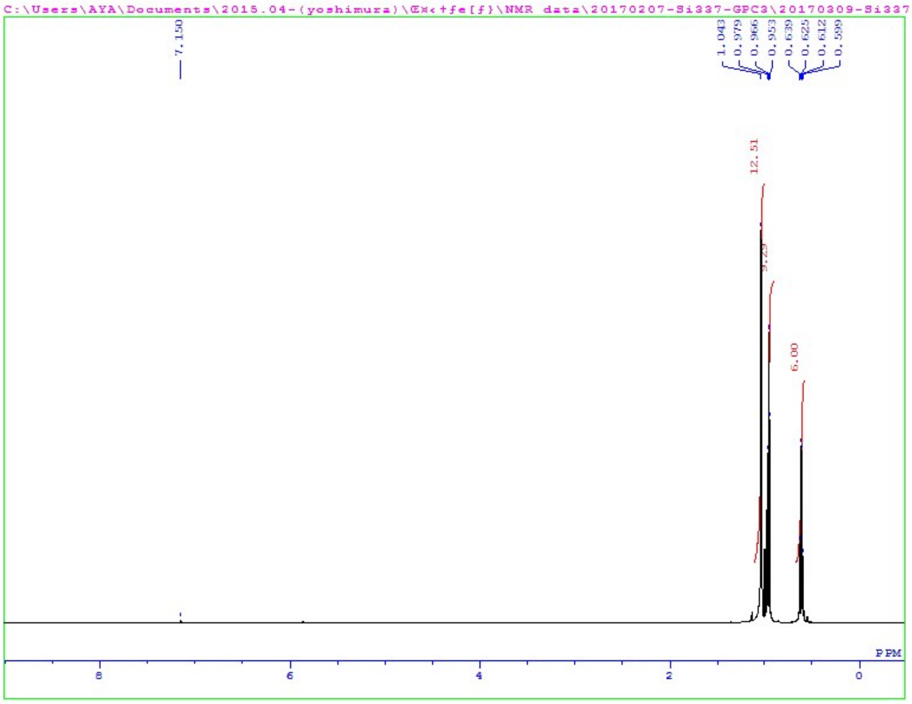
S5 B. J. O'Leary, T. R. Spalding and G. Ferguson, *Polyhedron*, 1999, **18**, 3135.

S6 In spite of repeated trials, satisfactory HRMS data of **1i** could not be obtained because of its highly hydrolysable property. However, the ^{1}H, ^{13}C, ^{29}Si and ^{11}B NMR spectral data were fully consistent with the proposed structure.

4. NMR Spectra of 1a-i (copies of the NMR charts)

1a

^{1}H NMR



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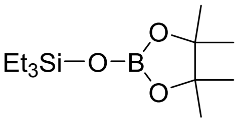
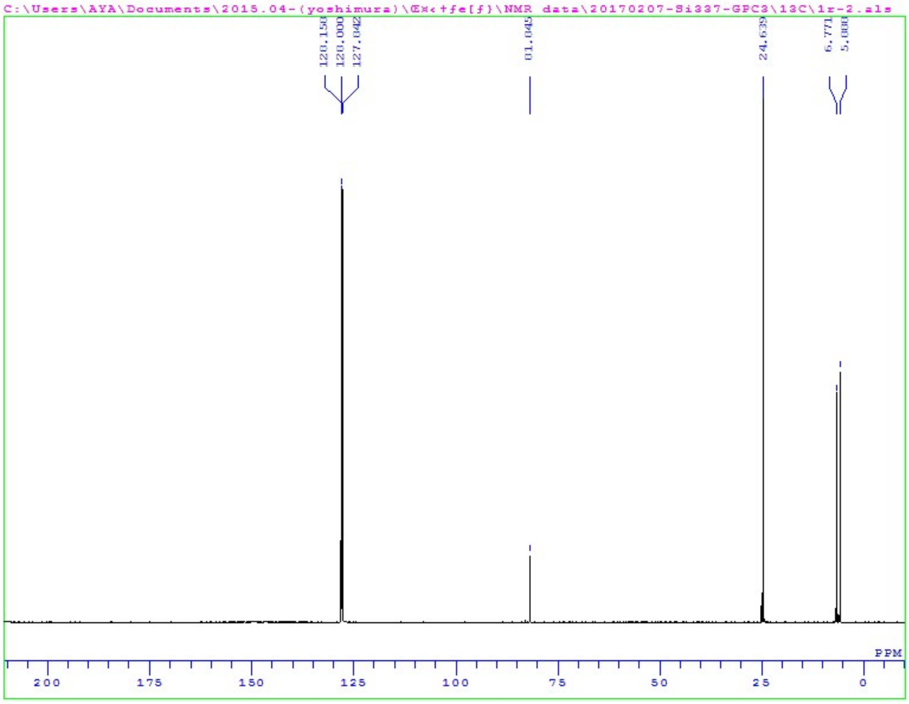


^{13}C NMR



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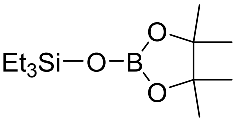
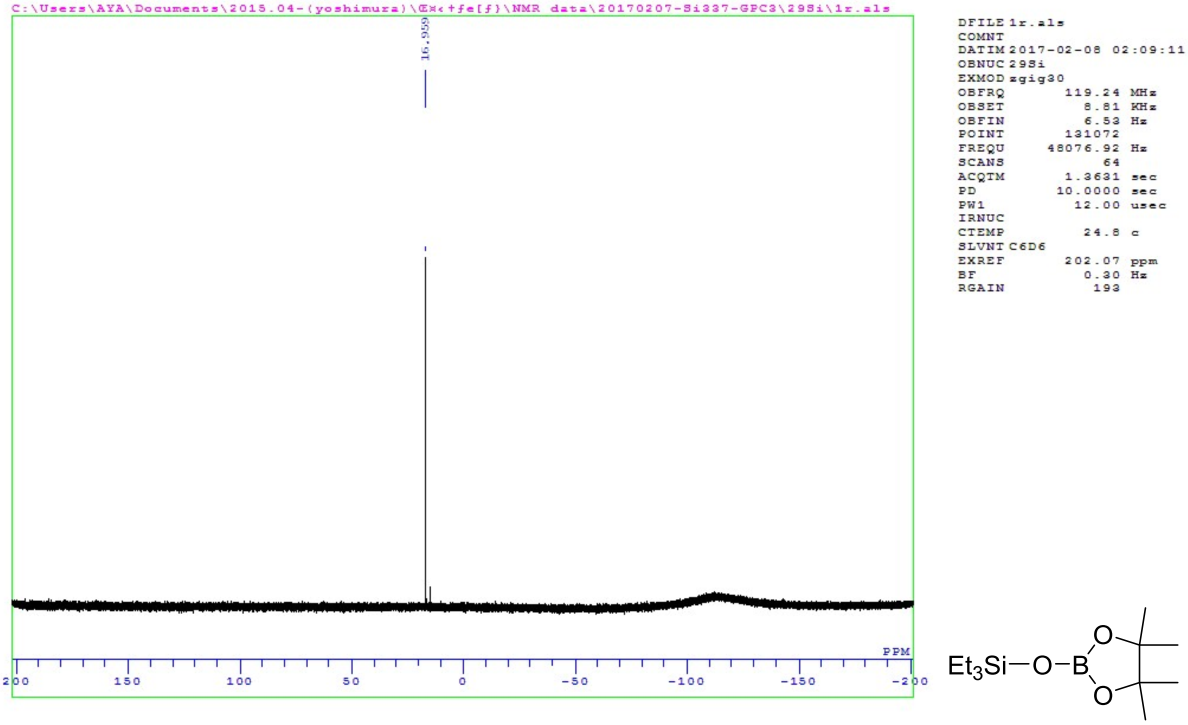
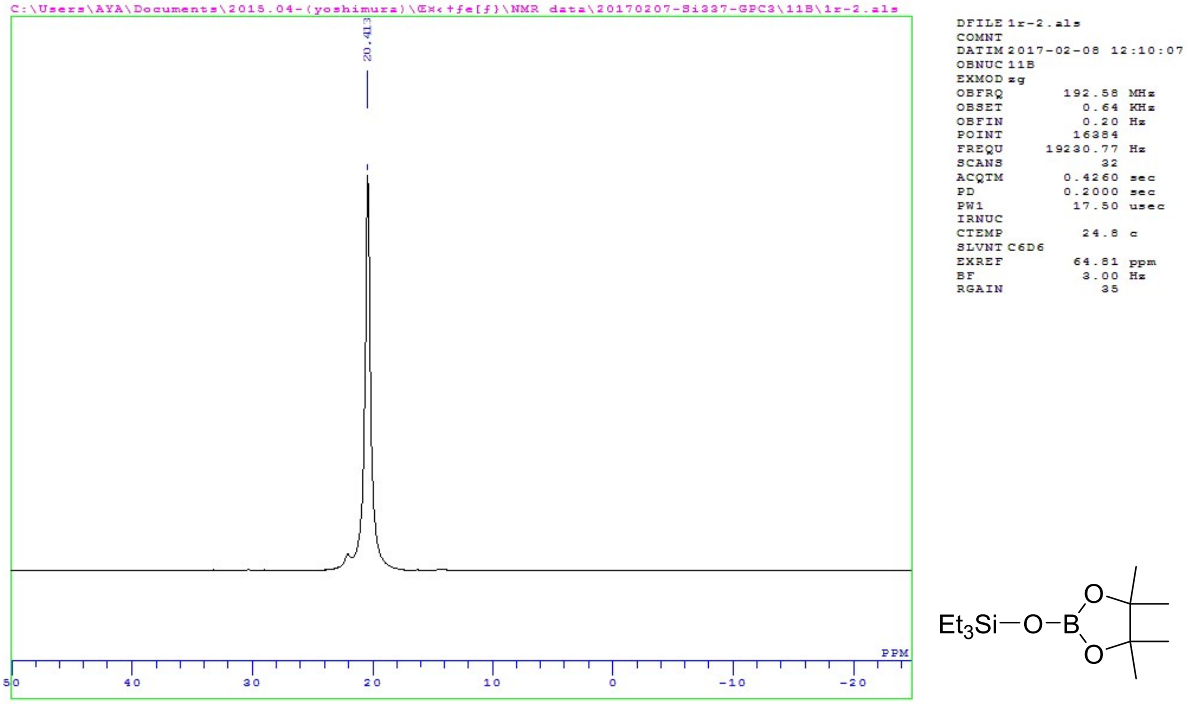
PW1             10.00 usec
IRNUC
CTEMP            24.9 c
SLVNT C6D6
EXREF          128.00 ppm
BF               1.00 Hz
RGAIN             193
```



^{29}Si NMR

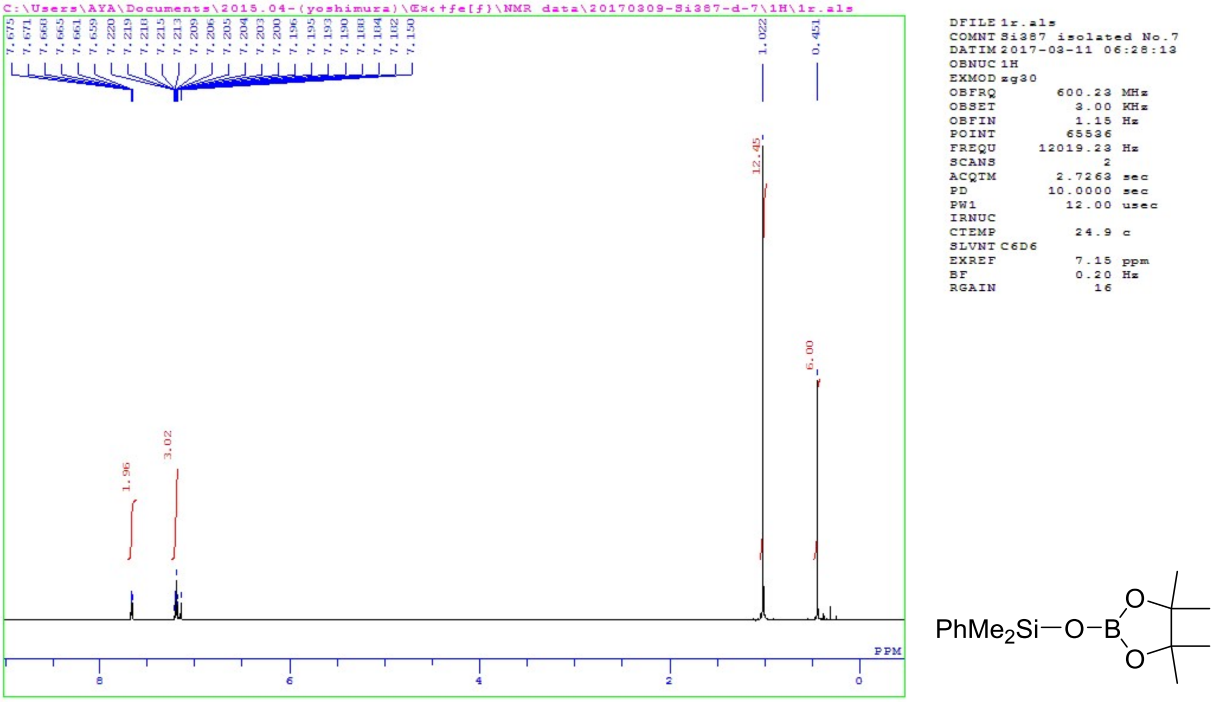


^{11}B NMR



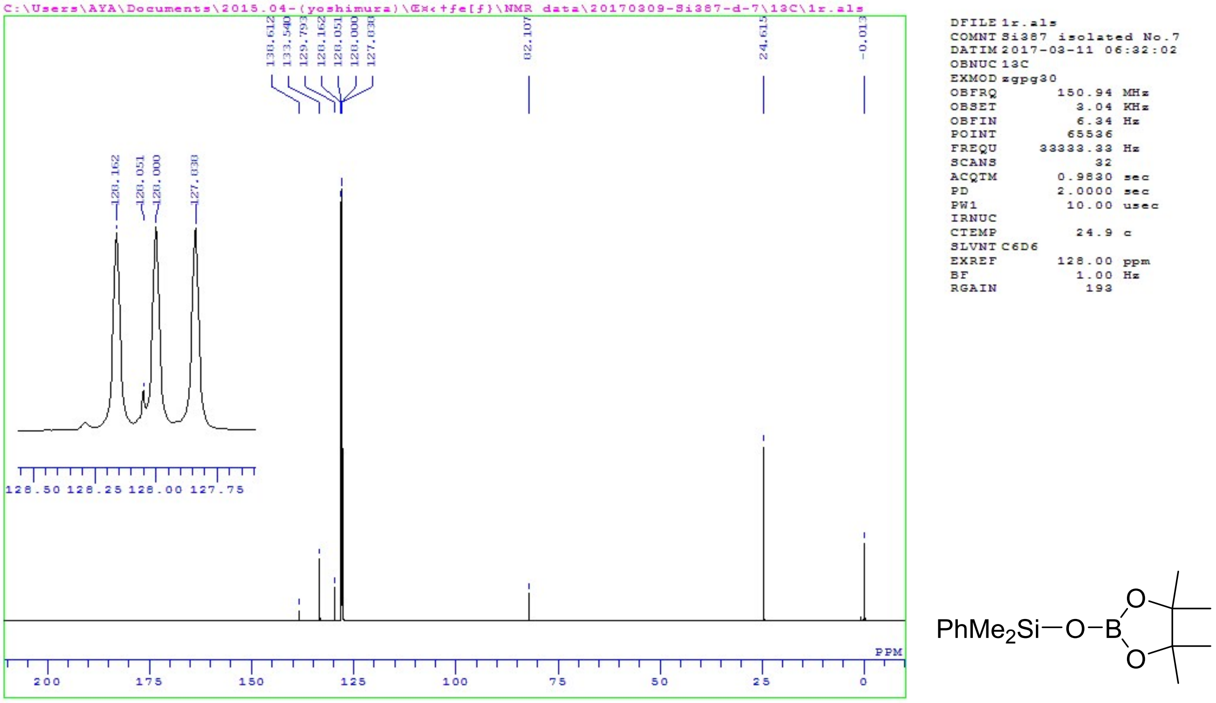
1b

^{1}H NMR



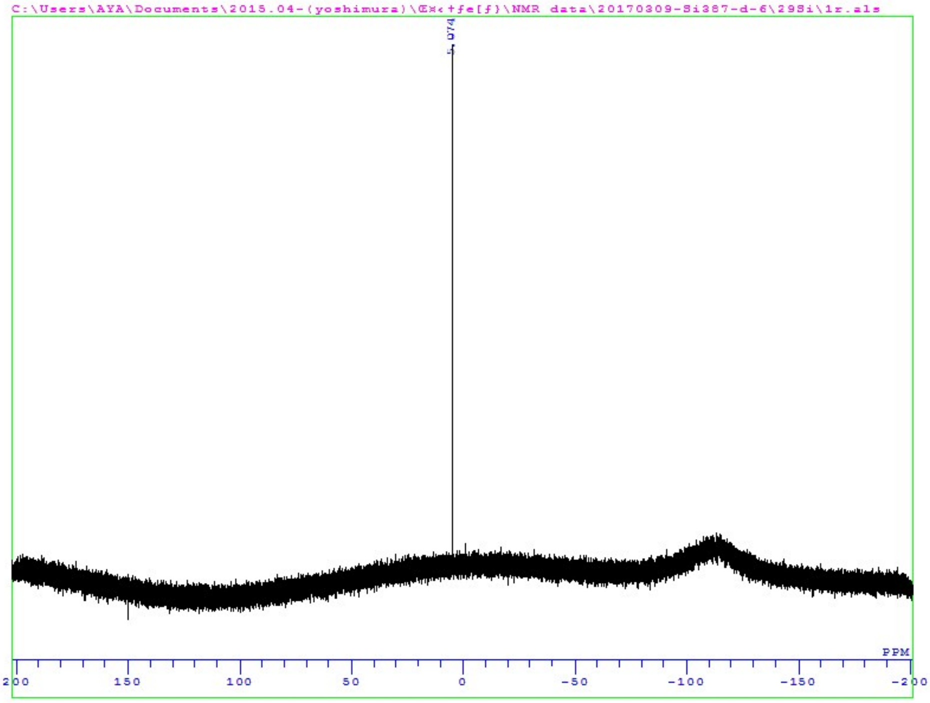
```
DFILE 1r.als
COMNT Si387 isolated No.7
DATIM 2017-03-11 06:28:13
OBNUC 1H
EXMOD zg30
OBFRQ        600.23 MHz
OBSET          3.00 KHz
OBFIN          1.15 Hz
POINT         65536
FREQU      12019.23 Hz
SCANS             2
ACQTM        2.7263 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF          7.15 ppm
BF             0.20 Hz
RGAIN            16
```

^{13}C NMR

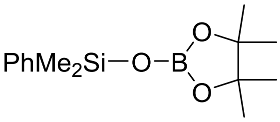


```
DFILE 1r.als
COMNT Si387 isolated No.7
DATIM 2017-03-11 06:32:02
OBNUC 13C
EXMOD zgpg30
OBFRQ        150.94 MHz
OBSET          3.04 KHz
OBFIN          6.34 Hz
POINT         65536
FREQU      33333.33 Hz
SCANS            32
ACQTM        0.9830 sec
PD           2.0000 sec
PW1           10.00 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF        128.00 ppm
BF             1.00 Hz
RGAIN           193
```

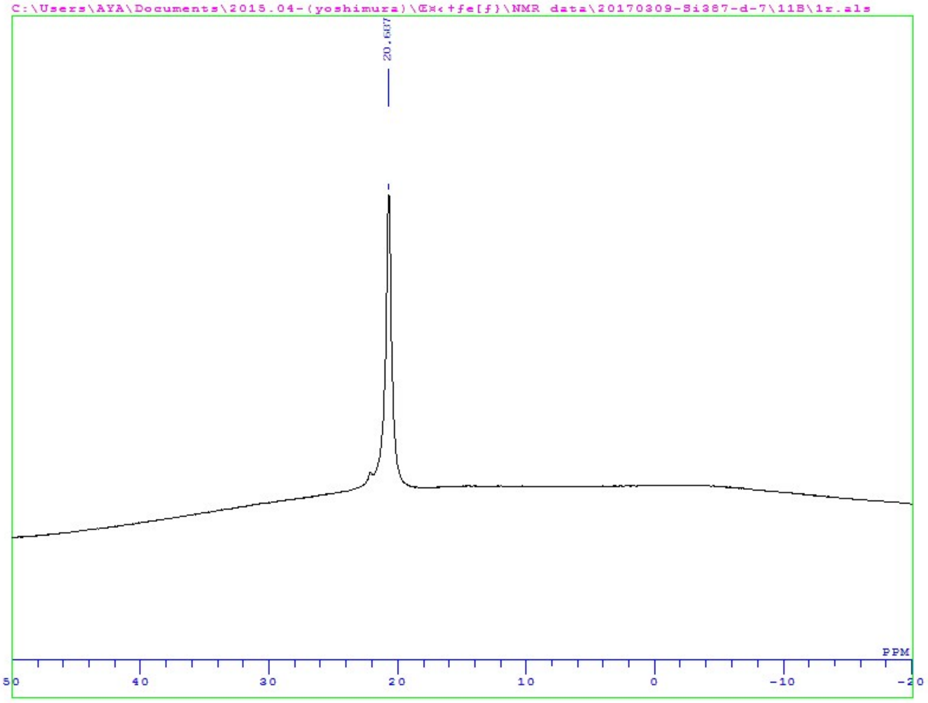
^{29}Si NMR



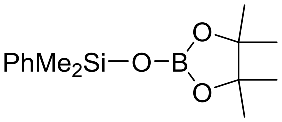
```
DFILE 1r.als
COMNT Si387 isolated No.6
DATIM 2017-03-11 06:24:12
OBNUC 29Si
EXMOD zgig30
OBFRQ        119.24 MHz
OBSET          8.81 KHz
OBFIN          6.53 Hz
POINT        131072
FREQU      48076.92 Hz
SCANS            64
ACQTM        1.3631 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF        202.07 ppm
BF             0.30 Hz
RGAIN           172
```



^{11}B NMR

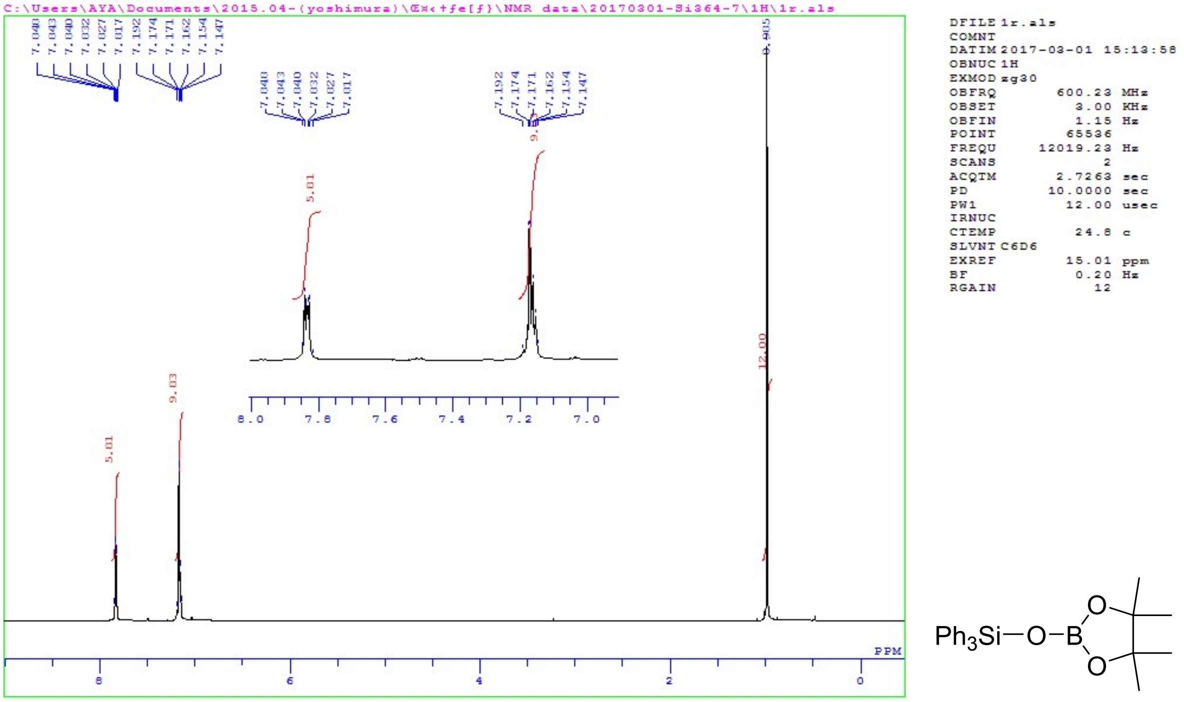


```
DFILE 1r.als
COMNT Si387 isolated No.7
DATIM 2017-03-11 06:48:53
OBNUC 11B
EXMOD zg
OBFRQ        192.58 MHz
OBSET          0.64 KHz
OBFIN          0.20 Hz
POINT         16384
FREQU      19230.77 Hz
SCANS            32
ACQTM        0.4260 sec
PD           0.2000 sec
PW1           17.50 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF         64.81 ppm
BF             3.00 Hz
RGAIN            19
```

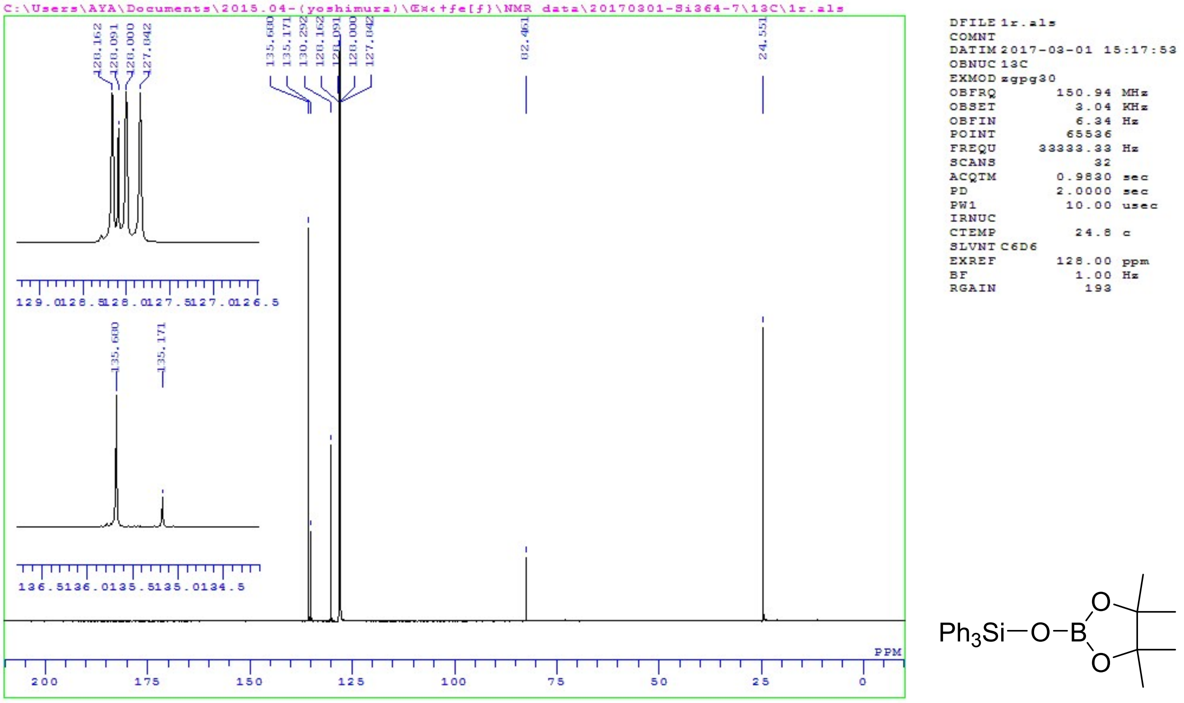


1c

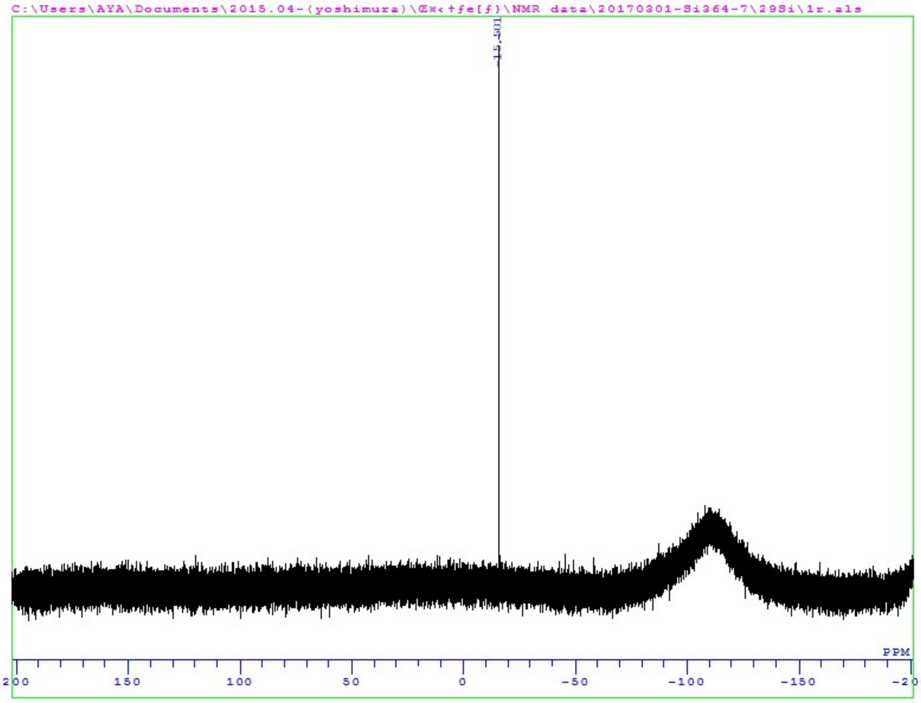
^{1}H NMR



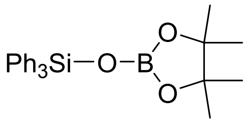
^{13}C NMR



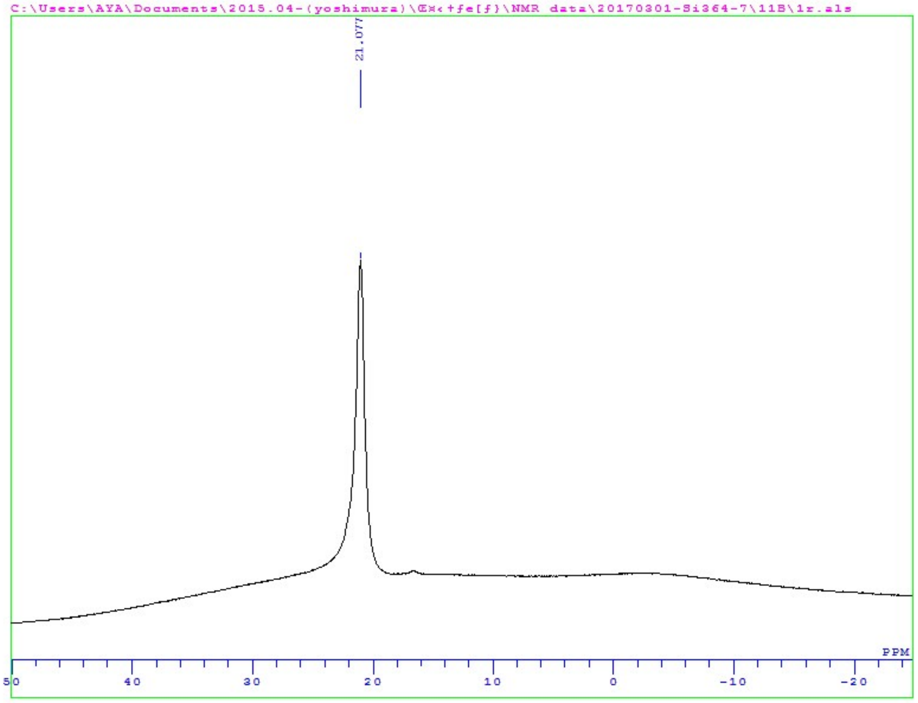
^{29}Si NMR



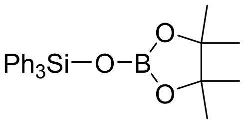
```
DFILE 1r.als
COMNT
DATIM 2017-03-01 15:32:55
OBNUC 29Si
EXMOD zgig30
OBFRQ       119.24 MHz
OBSET         8.81 KHz
OBFIN         6.53 Hz
POINT       131072
FREQU     48076.92 Hz
SCANS           64
ACQTM       1.3631 sec
PD         10.0000 sec
PW1          12.00 usec
IRNUC
CTEMP         24.9 c
SLVNT C6D6
EXREF       202.07 ppm
BF            0.30 Hz
RGAIN          193
```



^{11}B NMR

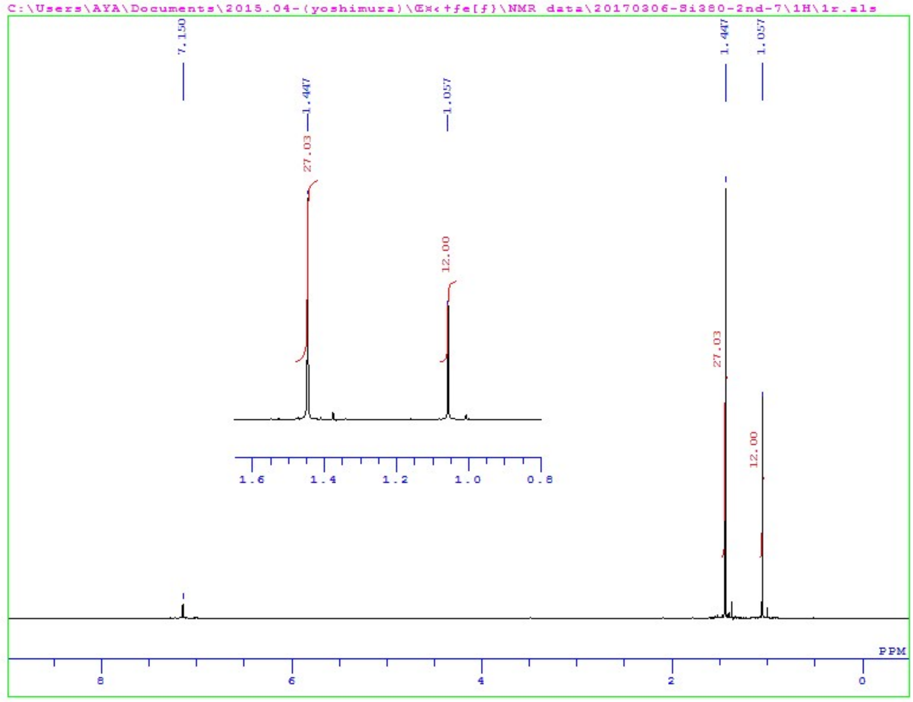


```
DFILE 1r.als
COMNT
DATIM 2017-03-01 15:34:46
OBNUC 11B
EXMOD zg
OBFRQ       192.58 MHz
OBSET         0.64 KHz
OBFIN         0.20 Hz
POINT        16384
FREQU     19230.77 Hz
SCANS           32
ACQTM       0.4260 sec
PD          0.2000 sec
PW1          17.50 usec
IRNUC
CTEMP         24.9 c
SLVNT C6D6
EXREF        64.81 ppm
BF            3.00 Hz
RGAIN           16
```

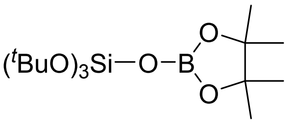


1d

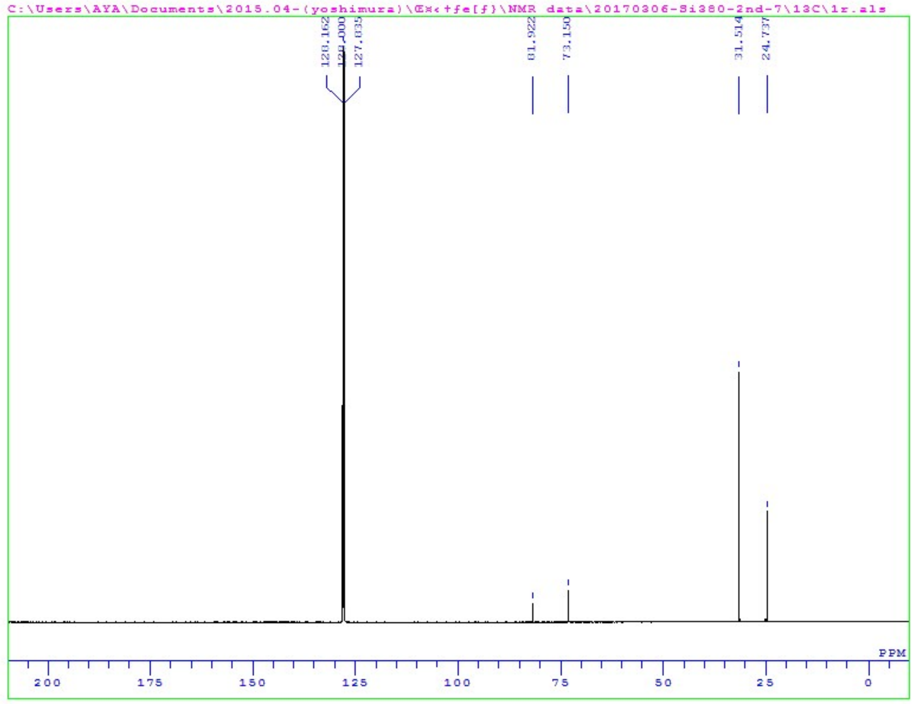
^{1}H NMR



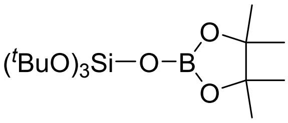
```
DFILE 1r.als
COMNT Si380-2nd-7
DATIM 2017-03-06 15:35:14
OBNUC 1H
EXMOD zg30
OBFRQ        600.23 MHz
OBSET          3.00 KHz
OBFIN          1.15 Hz
POINT         65536
FREQU      12019.23 Hz
SCANS             2
ACQTM        2.7263 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF          7.15 ppm
BF             0.20 Hz
RGAIN            13
```



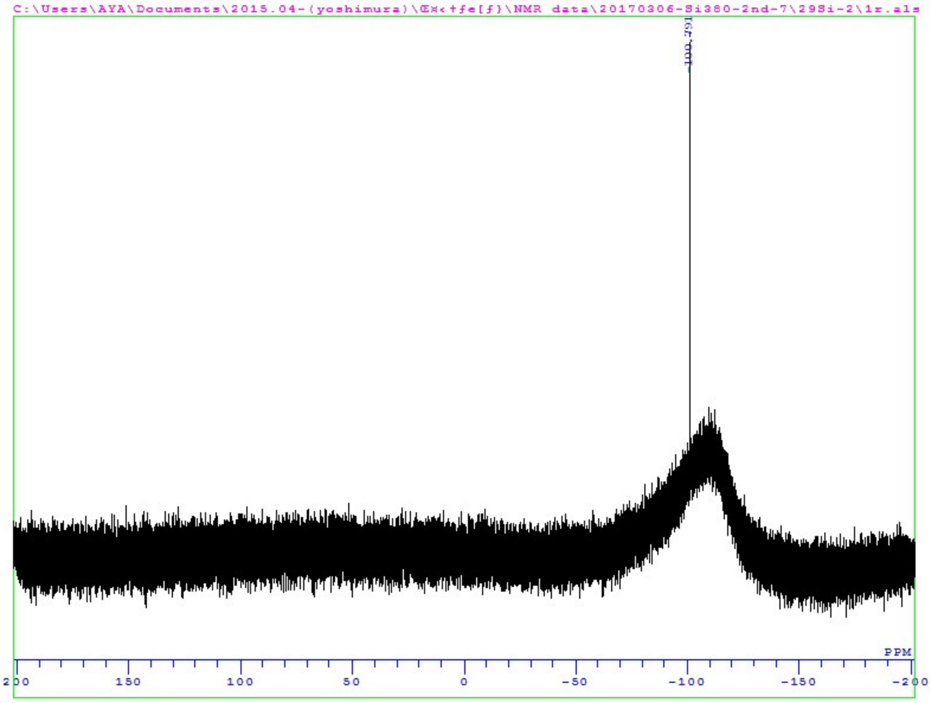
^{13}C NMR



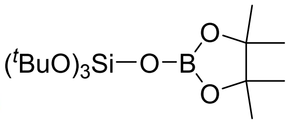
```
DFILE 1r.als
COMNT Si380-2nd-7
DATIM 2017-03-06 15:39:17
OBNUC 13C
EXMOD zgpg30
OBFRQ        150.94 MHz
OBSET          3.04 KHz
OBFIN          6.34 Hz
POINT         65536
FREQU      33333.33 Hz
SCANS            32
ACQTM        0.9830 sec
PD           2.0000 sec
PW1           10.00 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF        128.00 ppm
BF             1.00 Hz
RGAIN           193
```



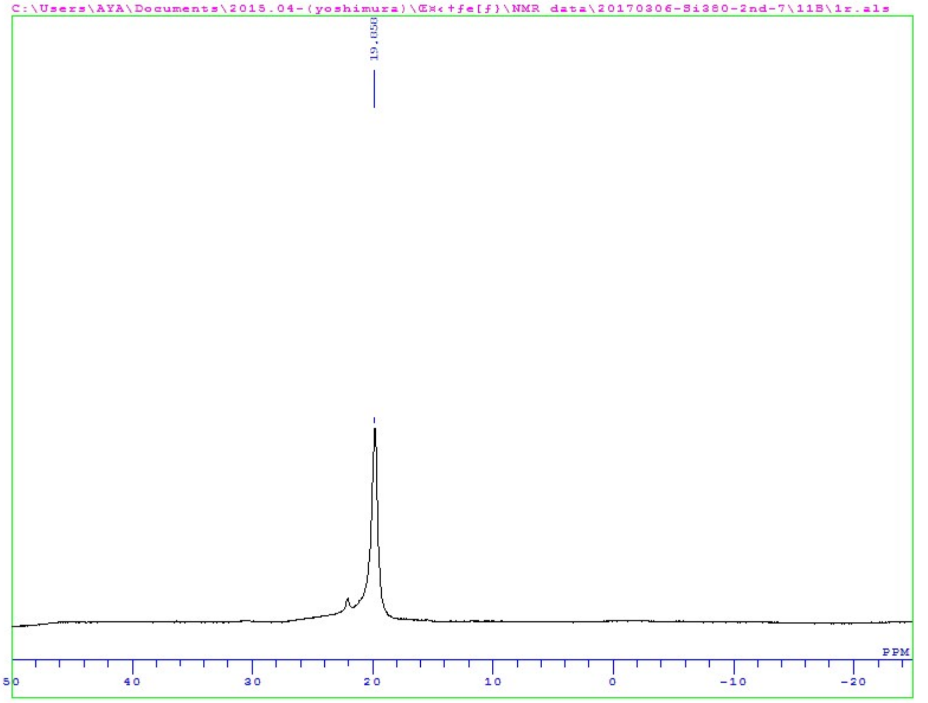
^{29}Si NMR



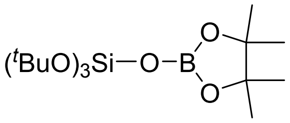
```
DFILE 1r.als
COMNT group Cgroup
DATIM 2017-03-07 04:09:03
OBNUC 29Si
EXMOD zgig30
OBFRQ        119.24 MHz
OBSET          8.81 KHz
OBFIN          6.53 Hz
POINT        131072
FREQU      48076.92 Hz
SCANS           128
ACQTM        1.3631 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF        201.58 ppm
BF             0.30 Hz
RGAIN           193
```



^{11}B NMR

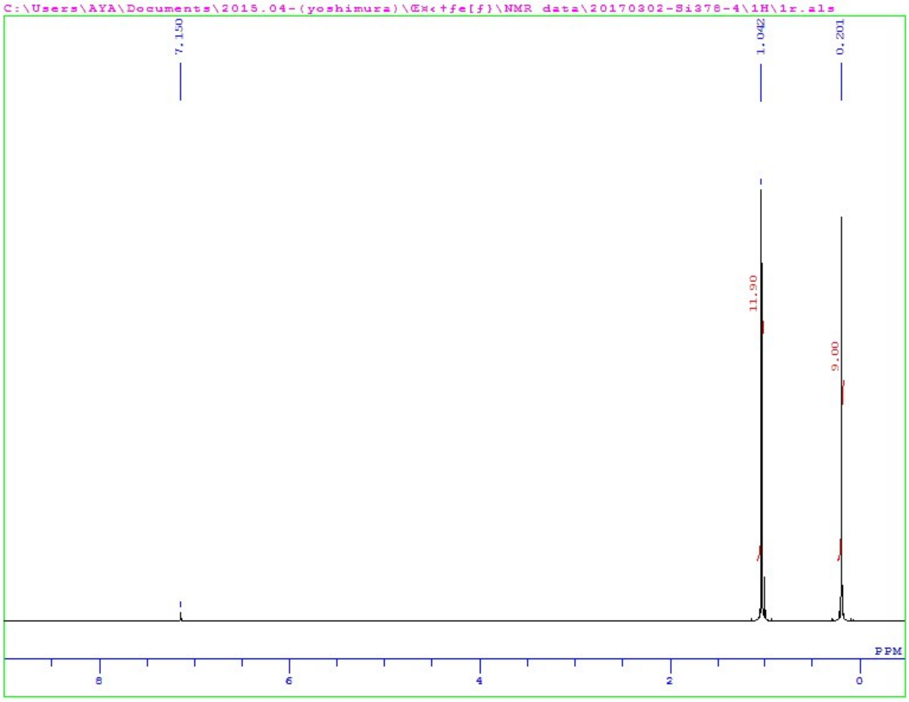


```
DFILE 1r.als
COMNT Si380-2nd-7
DATIM 2017-03-06 15:56:20
OBNUC 11B
EXMOD zg
OBFRQ        192.58 MHz
OBSET          0.64 KHz
OBFIN          0.20 Hz
POINT         16384
FREQU      19230.77 Hz
SCANS            32
ACQTM        0.4260 sec
PD           0.2000 sec
PW1           17.50 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF         64.81 ppm
BF             3.00 Hz
RGAIN            16
```

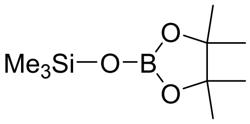


1e

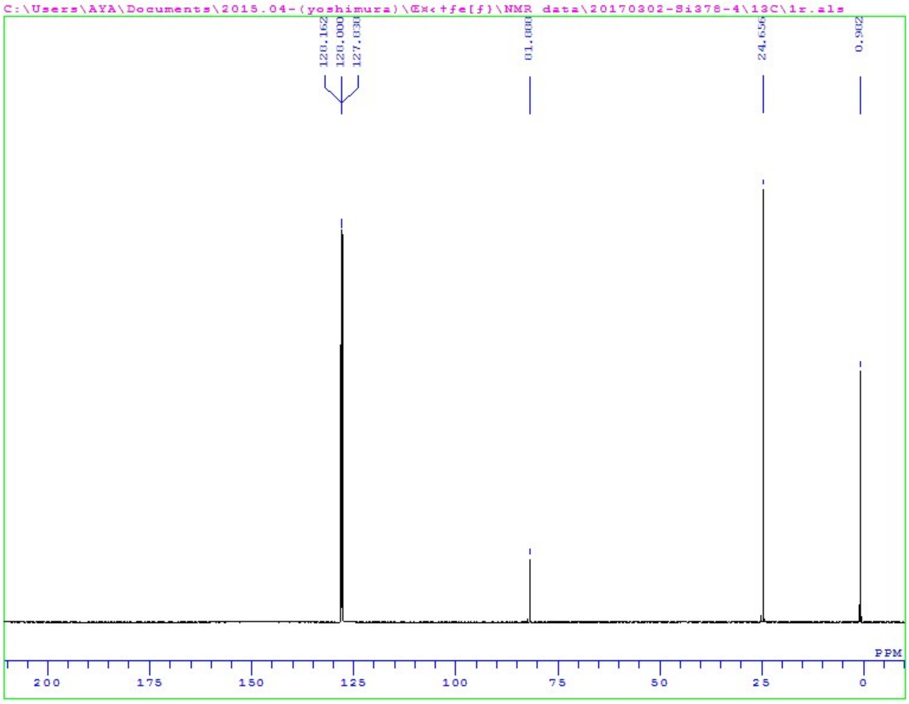
^{1}H NMR



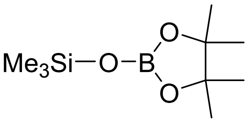
```
DFILE 1r.als
COMNT Si378-isolated No.4
DATIM 2017-03-02 13:06:38
OBNUC 1H
EXMOD zg30
OBFRQ        600.23 MHz
OBSET          3.00 KHz
OBFIN          1.15 Hz
POINT         65536
FREQU      12019.23 Hz
SCANS             2
ACQTM        2.7263 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF          7.15 ppm
BF             0.20 Hz
RGAIN             9
```



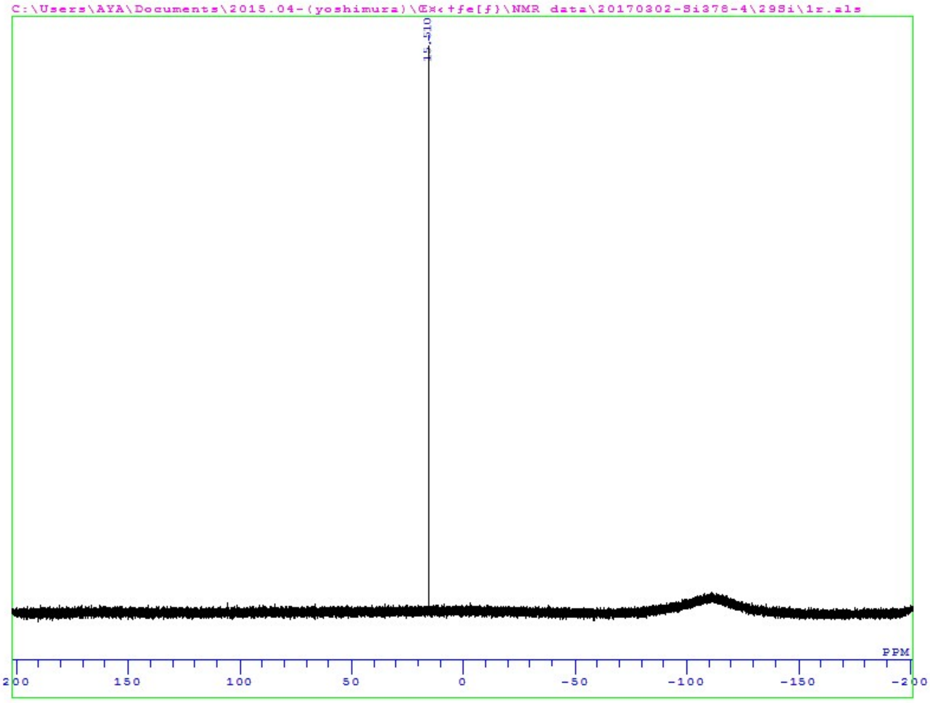
^{13}C NMR



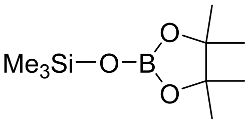
```
DFILE 1r.als
COMNT Si378-isolated No.4
DATIM 2017-03-02 13:10:16
OBNUC 13C
EXMOD zgpg30
OBFRQ        150.94 MHz
OBSET          3.04 KHz
OBFIN          6.34 Hz
POINT         65536
FREQU      33333.33 Hz
SCANS            32
ACQTM        0.9830 sec
PD           2.0000 sec
PW1           10.00 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF        128.00 ppm
BF             1.00 Hz
RGAIN           193
```



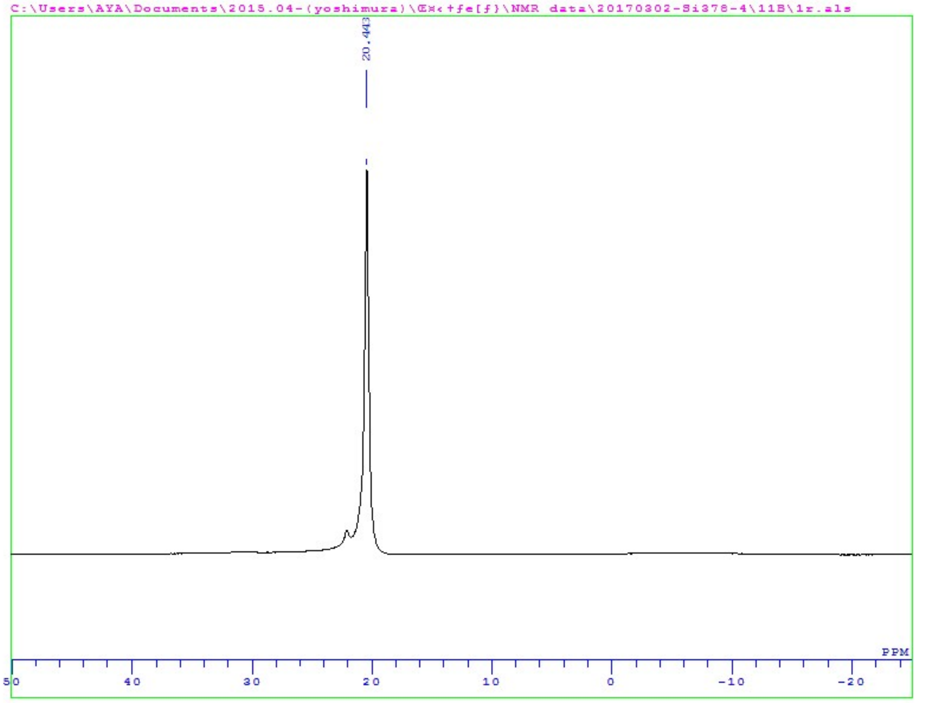
^{29}Si NMR



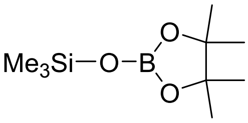
```
DFILE 1r.als
COMNT Si378-isolated No.4
DATIM 2017-03-02 13:25:05
OBNUC 29Si
EXMOD zgig30
OBFRQ         119.24 MHz
OBSET           8.81 KHz
OBFIN           6.53 Hz
POINT         131072
FREQU       48076.92 Hz
SCANS             64
ACQTM         1.3631 sec
PD           10.0000 sec
PW1            12.00 usec
IRNUC
CTEMP           24.9 c
SLVNT C6D6
EXREF         202.07 ppm
BF              0.30 Hz
RGAIN            193
```



^{11}B NMR

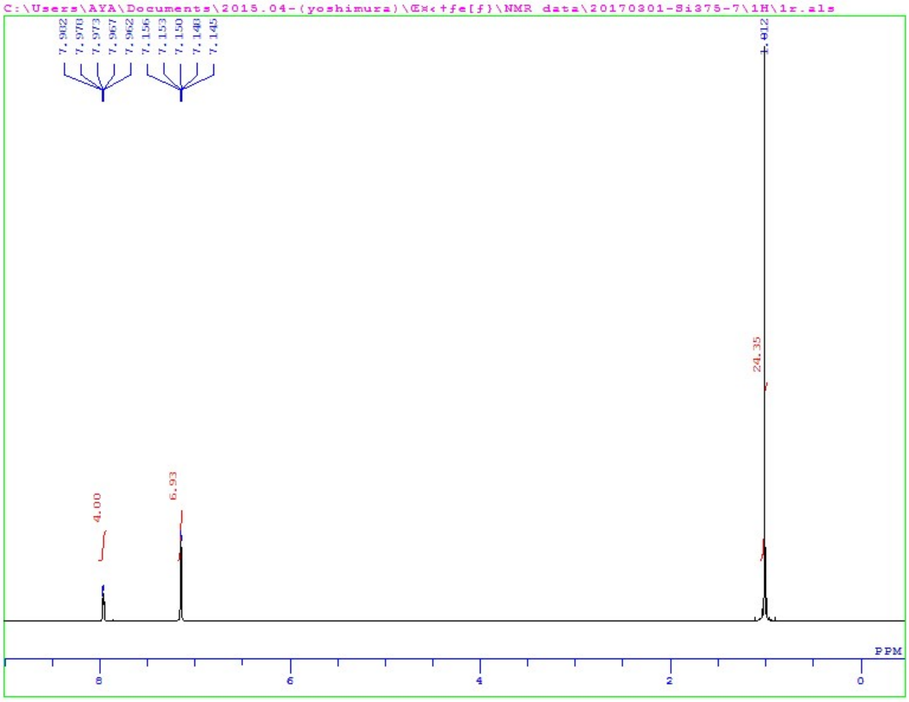


```
DFILE 1r.als
COMNT Si378-isolated No.4
DATIM 2017-03-02 13:27:04
OBNUC 11B
EXMOD zg
OBFRQ         192.58 MHz
OBSET           0.64 KHz
OBFIN           0.20 Hz
POINT          16384
FREQU       19230.77 Hz
SCANS             32
ACQTM         0.4260 sec
PD            0.2000 sec
PW1            17.50 usec
IRNUC
CTEMP           24.9 c
SLVNT C6D6
EXREF          64.81 ppm
BF              3.00 Hz
RGAIN             24
```

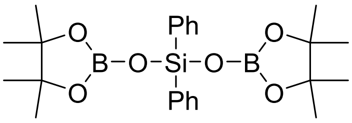


1f

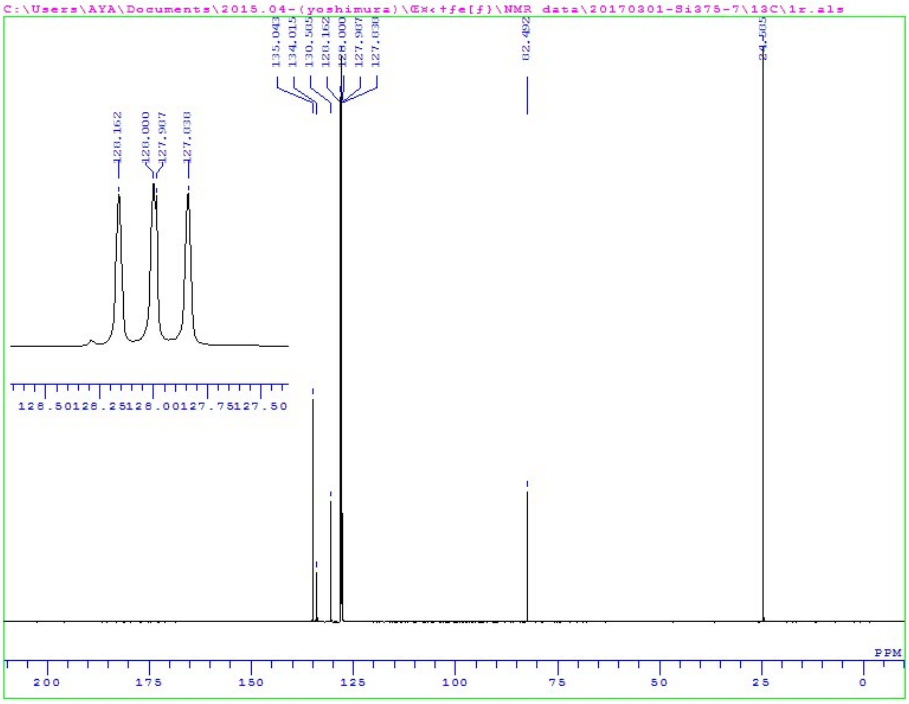
^{1}H NMR



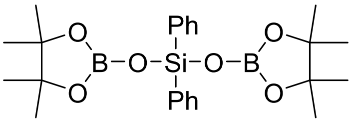
```
DFILE 1r.als
COMNT
DATIM 2017-03-01 21:09:21
OBNUC 1H
EXMOD zg30
OBFRQ        600.23 MHz
OBSET          3.00 KHz
OBFIN          1.15 Hz
POINT         65536
FREQU      12019.23 Hz
SCANS             2
ACQTM        2.7263 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF         15.01 ppm
BF             0.20 Hz
RGAIN             9
```



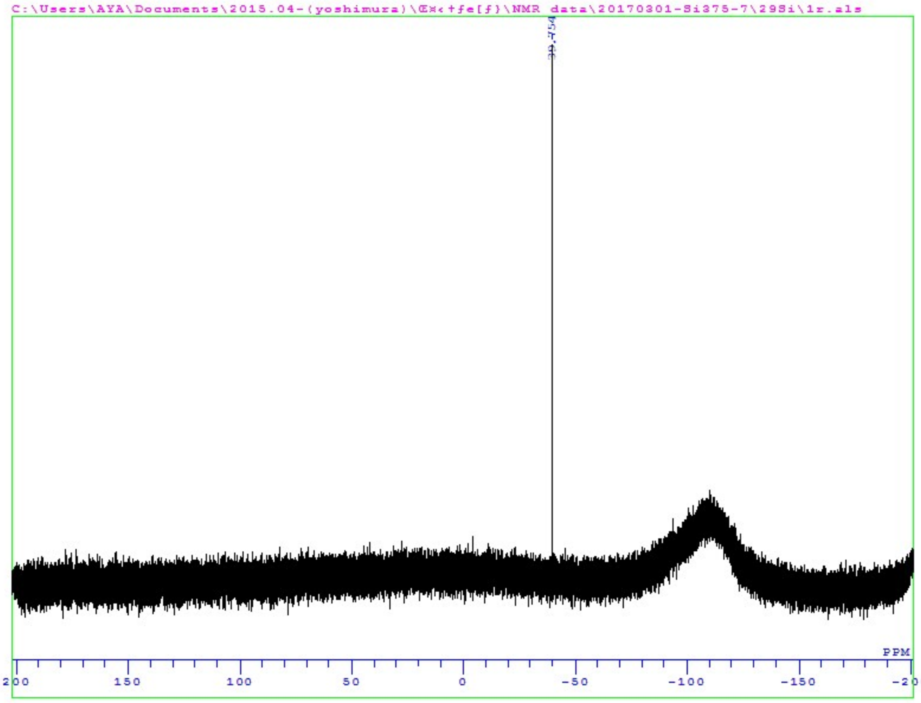
^{13}C NMR



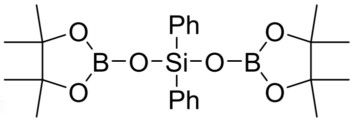
```
DFILE 1r.als
COMNT
DATIM 2017-03-01 21:13:19
OBNUC 13C
EXMOD zgpg30
OBFRQ        150.94 MHz
OBSET          3.04 KHz
OBFIN          6.34 Hz
POINT         65536
FREQU      33333.33 Hz
SCANS            32
ACQTM        0.9830 sec
PD           2.0000 sec
PW1           10.00 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF        128.00 ppm
BF             1.00 Hz
RGAIN           193
```



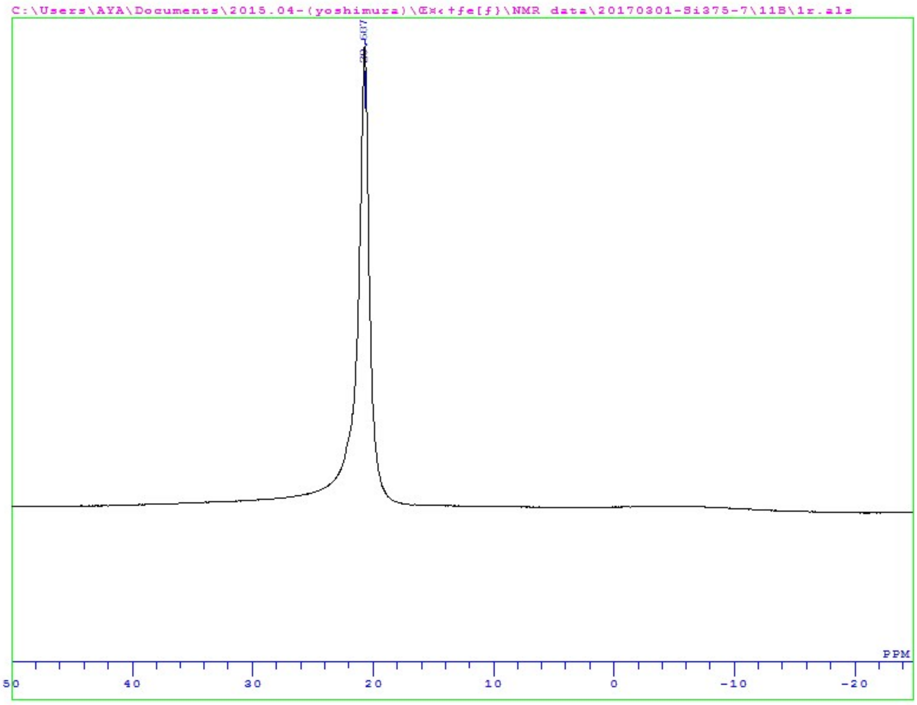
^{29}Si NMR



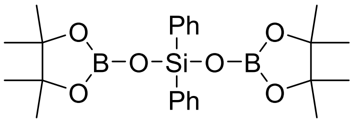
```
DFILE 1r.als
COMNT
DATIM 2017-03-01 21:28:05
OBNUC 29Si
EXMOD zgig30
OBFRQ        119.24 MHz
OBSET          8.81 KHz
OBFIN          6.53 Hz
POINT        131072
FREQU      48076.92 Hz
SCANS            64
ACQTM        1.3631 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF        202.07 ppm
BF             0.30 Hz
RGAIN           193
```



^{11}B NMR

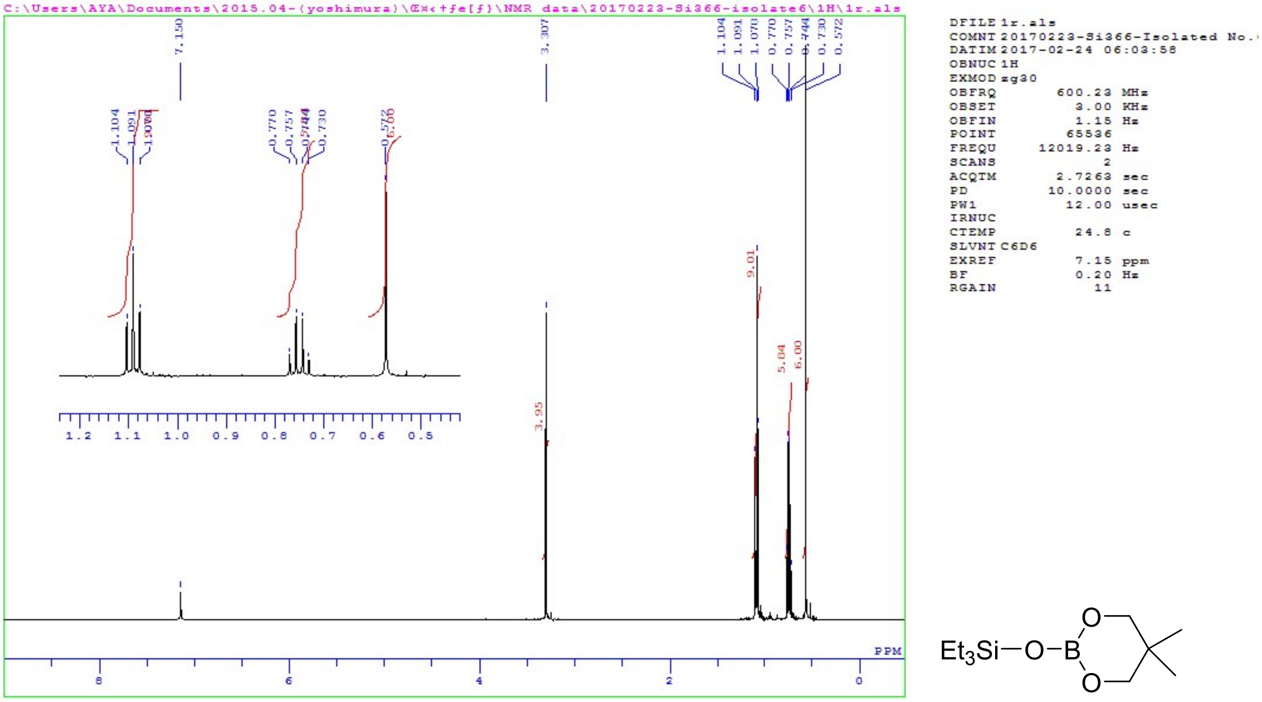


```
DFILE 1r.als
COMNT
DATIM 2017-03-01 21:29:50
OBNUC 11B
EXMOD zg
OBFRQ        192.58 MHz
OBSET          0.64 KHz
OBFIN          0.20 Hz
POINT         16384
FREQU      19230.77 Hz
SCANS            32
ACQTM        0.4260 sec
PD           0.2000 sec
PW1           17.50 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF         64.81 ppm
BF             3.00 Hz
RGAIN            35
```



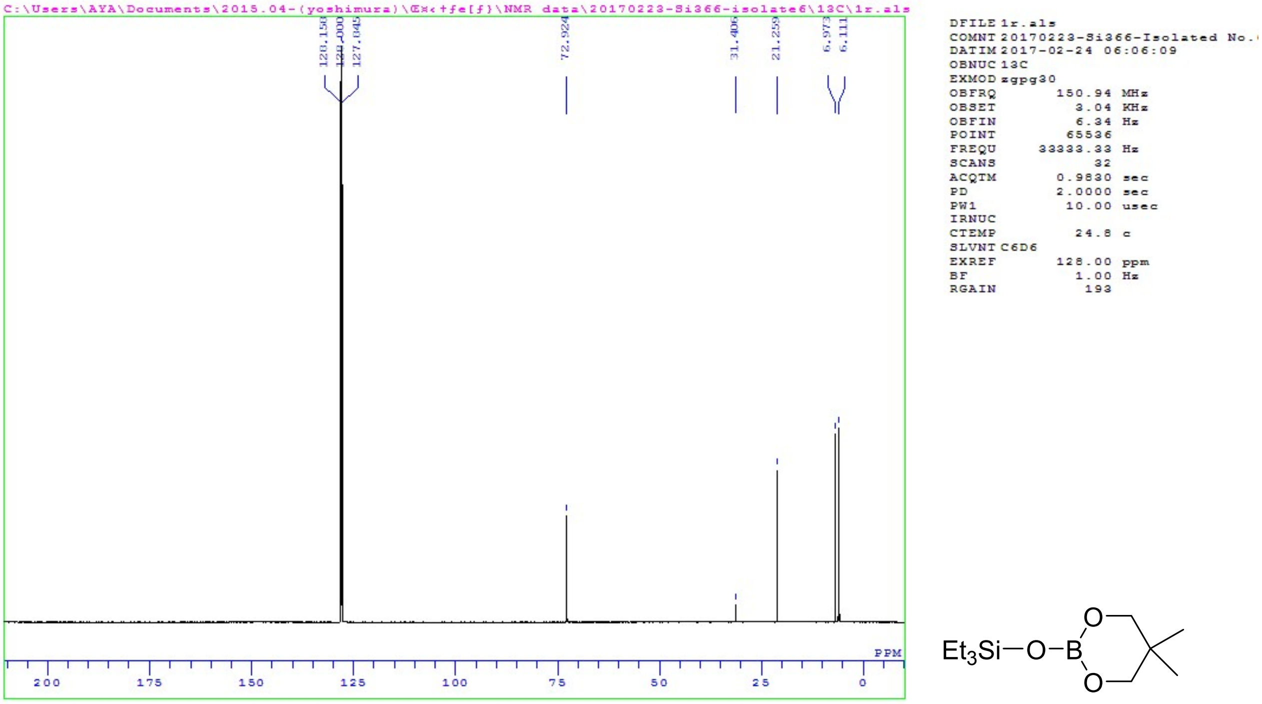
1g

^{1}H NMR



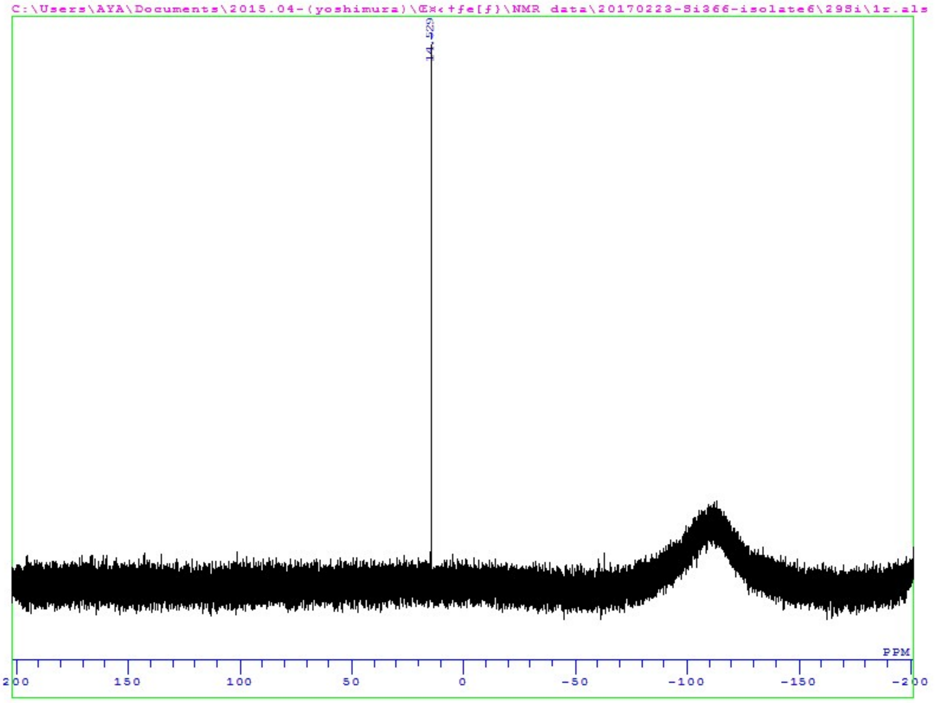
```
DFILE 1r.als
COMNT 20170223-Si366-Isolated No.
DATIM 2017-02-24 06:03:58
OBNUC 1H
EXMOD zg30
OBFRQ        600.23 MHz
OBSET          3.00 KHz
OBFIN          1.15 Hz
POINT         65536
FREQU      12019.23 Hz
SCANS             2
ACQTM        2.7263 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF          7.15 ppm
BF             0.20 Hz
RGAIN            11
```

^{13}C NMR

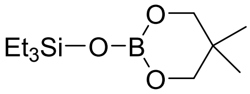


```
DFILE 1r.als
COMNT 20170223-Si366-Isolated No.
DATIM 2017-02-24 06:06:09
OBNUC 13C
EXMOD zgpg30
OBFRQ        150.94 MHz
OBSET          3.04 KHz
OBFIN          6.34 Hz
POINT         65536
FREQU      33333.33 Hz
SCANS            32
ACQTM        0.9830 sec
PD           2.0000 sec
PW1           10.00 usec
IRNUC
CTEMP          24.8 c
SLVNT C6D6
EXREF        128.00 ppm
BF             1.00 Hz
RGAIN           193
```

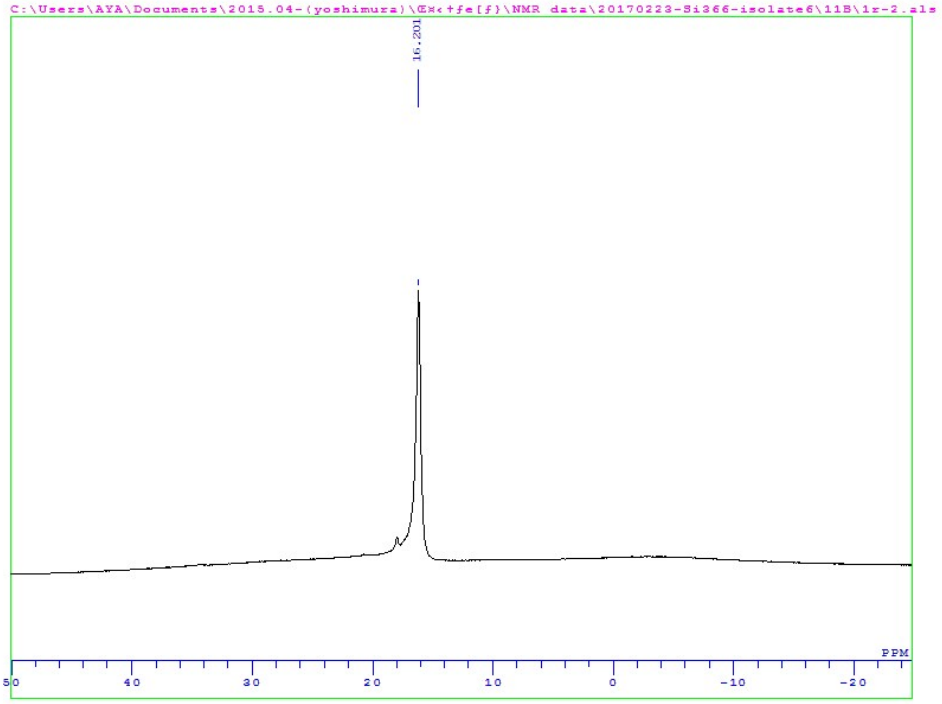
^{29}Si NMR



```
DFILE 1r.als
COMNT 20170223-Si366-Isolated No.
DATIM 2017-02-24 06:21:08
OBNUC 29Si
EXMOD zgig30
OBFRQ        119.24 MHz
OBSET          8.81 KHz
OBFIN          6.53 Hz
POINT        131072
FREQU      48076.92 Hz
SCANS            64
ACQTM        1.3631 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF        202.07 ppm
BF             0.30 Hz
RGAIN           193
```



^{11}B NMR



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DFILE 1r-2.als
COMNT 20170223-Si366-Isolated No.
DATIM 2017-02-24 06:22:52
OBNUC 11B
EXMOD zg
OBFRQ        192.58 MHz
OBSET          0.64 KHz
OBFIN          0.20 Hz
POINT         16384
FREQU      19230.77 Hz
SCANS            32
ACQTM        0.4260 sec
PD           0.2000 sec
PW1           17.50 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF         64.81 ppm
BF             3.00 Hz
RGAIN            19
```
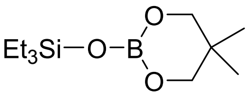
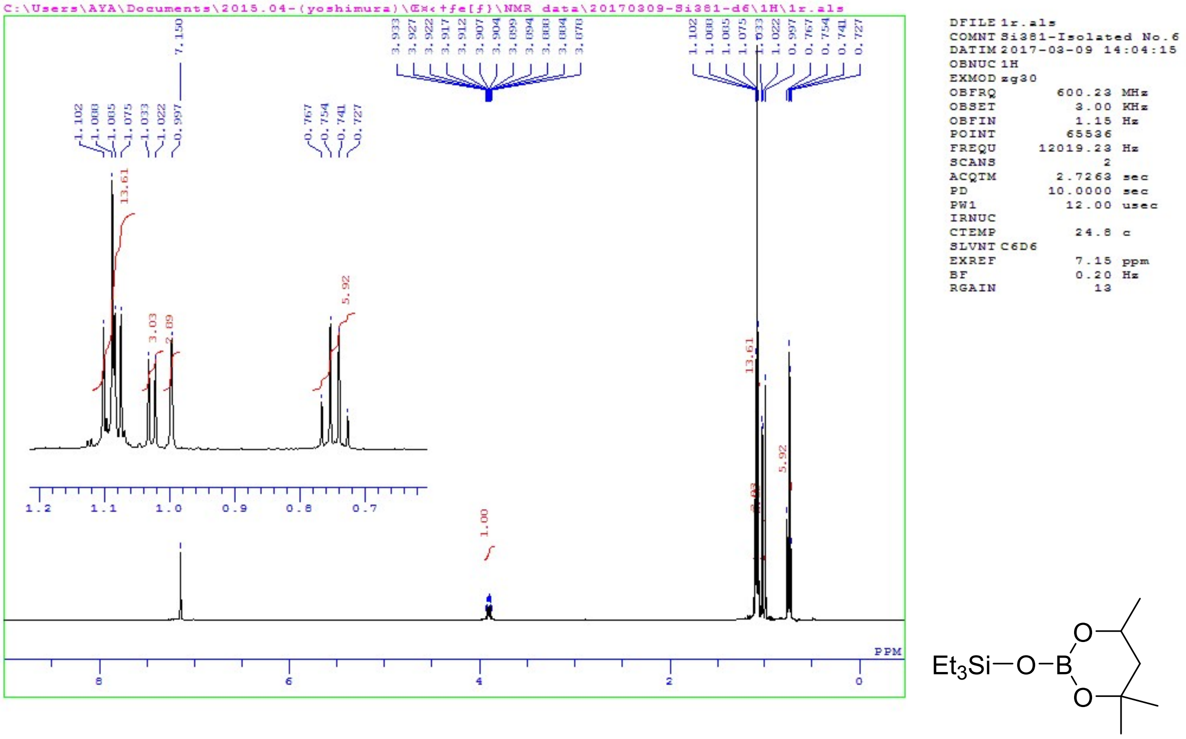
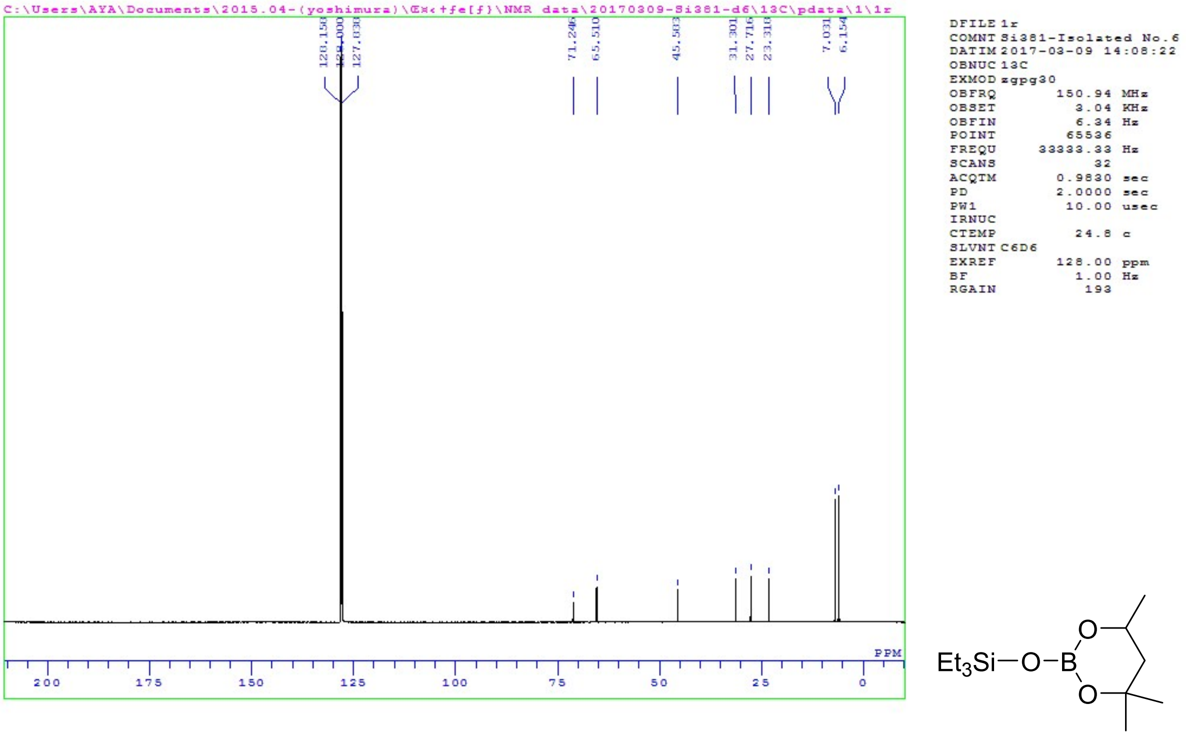



1h

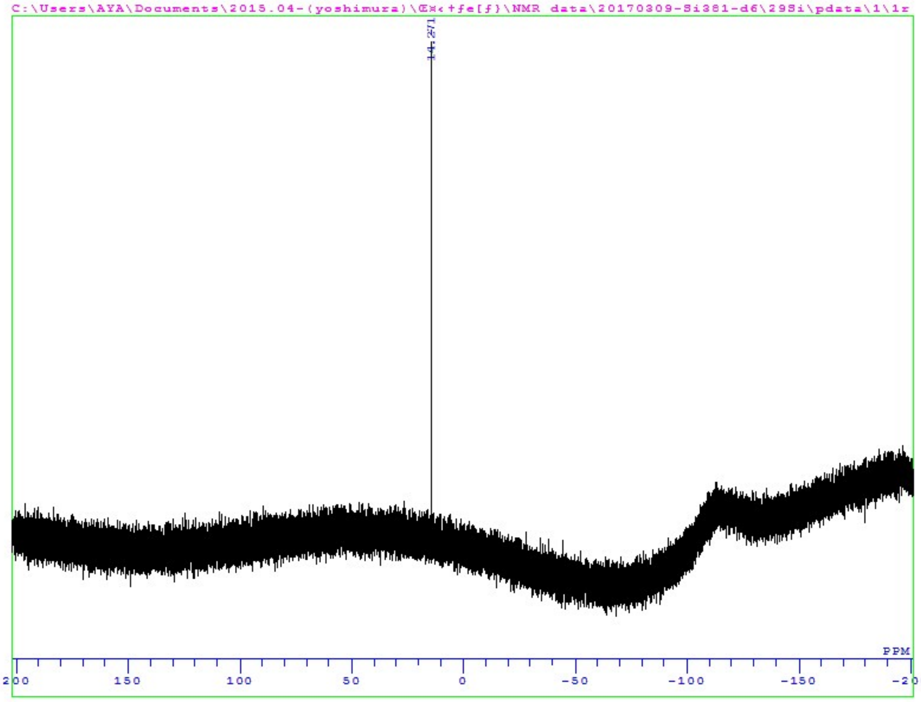
^{1}H NMR



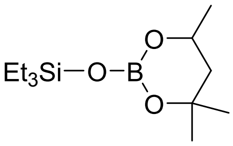
^{13}C NMR



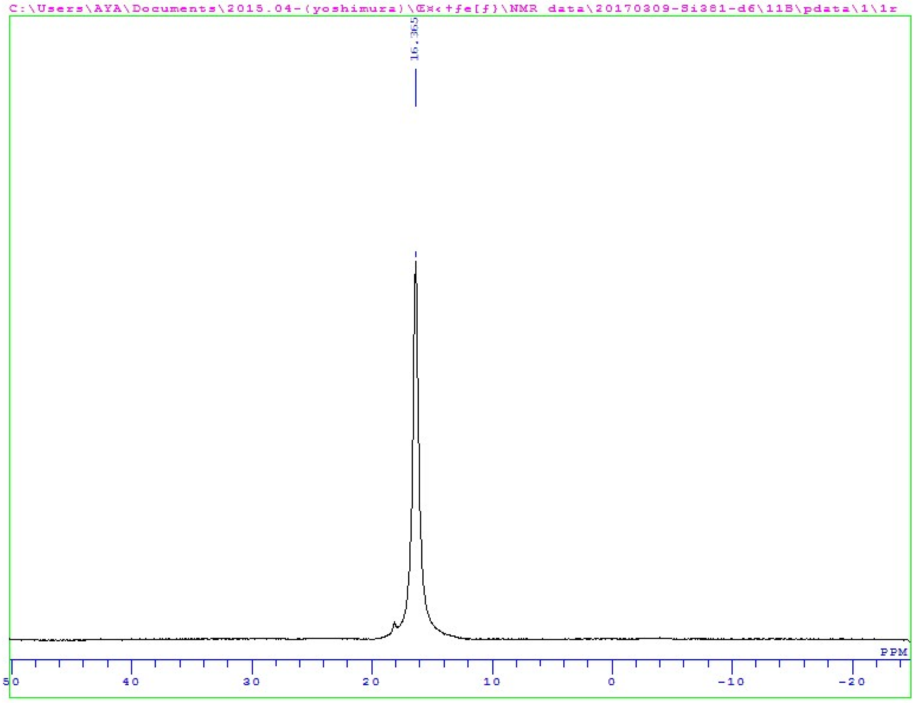
^{29}Si NMR



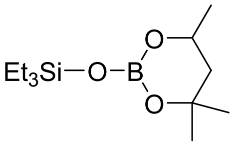
```
DFILE 1r
COMNT Si381-Isolated No.6
DATIM 2017-03-09 14:23:31
OBNUC 29Si
EXMOD zgig30
OBFRQ          119.24 MHz
OBSET            8.81 KHz
OBFIN            6.53 Hz
POINT          131072
FREQU        48076.92 Hz
SCANS              64
ACQTM          1.3631 sec
PD            10.0000 sec
PW1             12.00 usec
IRNUC
CTEMP            24.9 c
SLVNT C6D6
EXREF          202.07 ppm
BF               0.30 Hz
RGAIN             193
```



^{11}B NMR

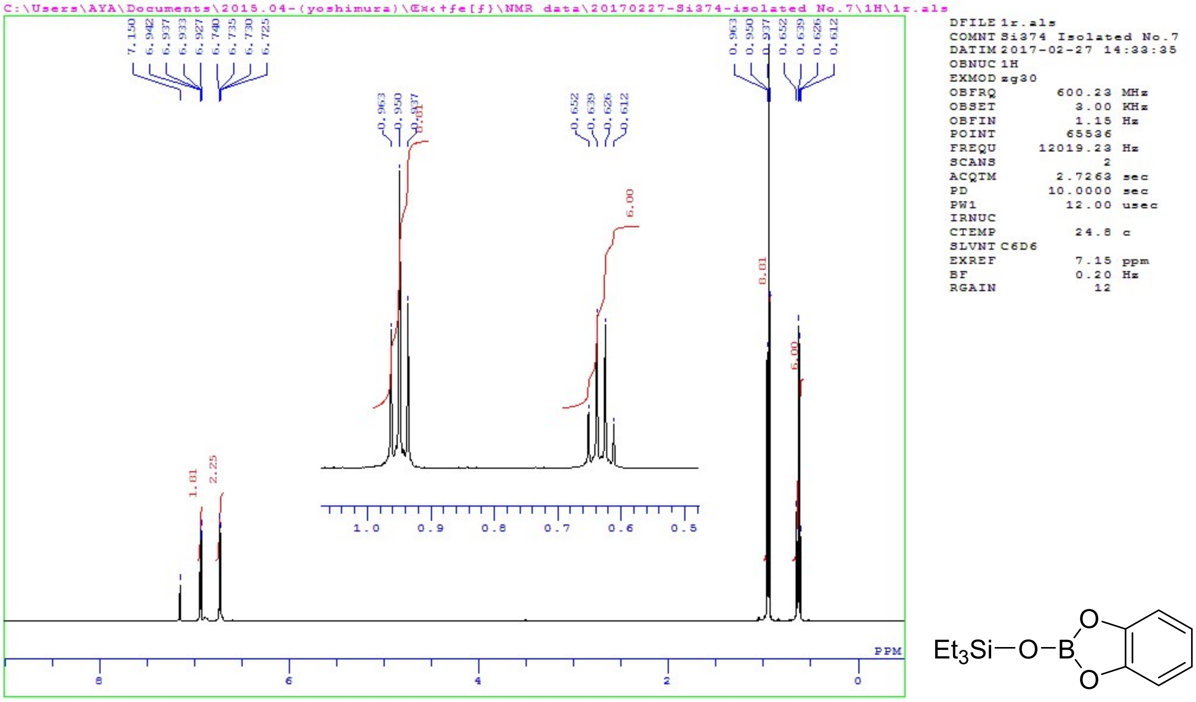


```
DFILE 1r
COMNT Si381-Isolated No.6
DATIM 2017-03-09 14:25:21
OBNUC 11B
EXMOD zg
OBFRQ          192.58 MHz
OBSET            0.64 KHz
OBFIN            0.20 Hz
POINT           16384
FREQU        19230.77 Hz
SCANS              32
ACQTM          0.4260 sec
PD             0.2000 sec
PW1             17.50 usec
IRNUC
CTEMP            24.8 c
SLVNT C6D6
EXREF           64.81 ppm
BF               3.00 Hz
RGAIN              16
```

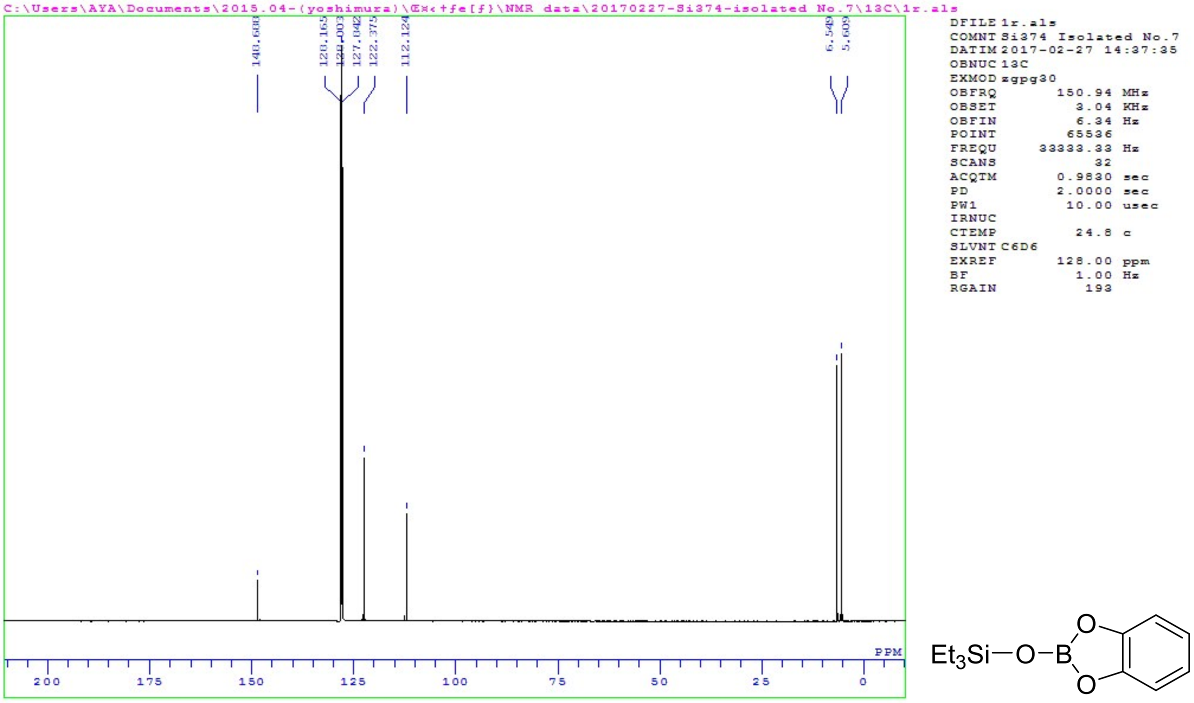


1i

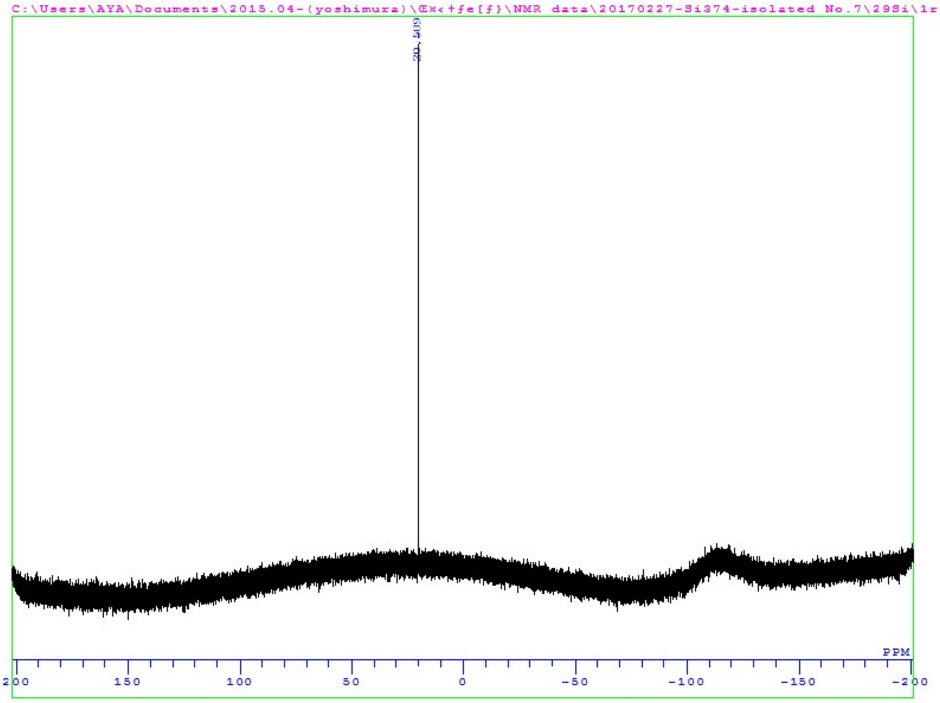
^{1}H NMR



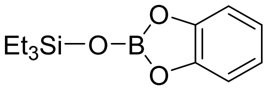
^{13}C NMR



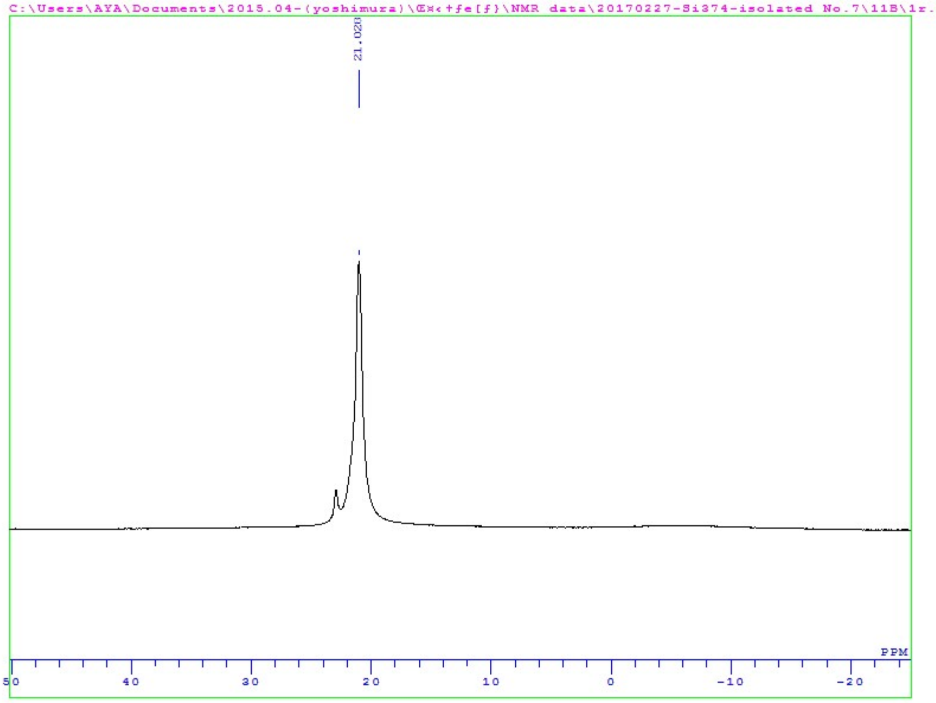
^{29}Si NMR



```
DFILE 1r-3.als
COMNT Si374 Isolated No.7
DATIM 2017-02-27 14:52:29
OBNUC 29Si
EXMOD zgig30
OBFRQ        119.24 MHz
OBSET          8.81 KHz
OBFIN          6.53 Hz
POINT        131072
FREQU      48076.92 Hz
SCANS            64
ACQTM        1.3631 sec
PD          10.0000 sec
PW1           12.00 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF        202.07 ppm
BF             0.30 Hz
RGAIN           193
```



^{11}B NMR



```
DFILE 1r.als
COMNT group
DATIM 2017-02-27 14:54:35
OBNUC 11B
EXMOD zg
OBFRQ        192.58 MHz
OBSET          0.64 KHz
OBFIN          0.20 Hz
POINT         16384
FREQU      19230.77 Hz
SCANS            32
ACQTM        0.4260 sec
PD           0.2000 sec
PW1           17.50 usec
IRNUC
CTEMP          24.9 c
SLVNT C6D6
EXREF         64.81 ppm
BF             3.00 Hz
RGAIN            24
```