

Supporting Information for:

**Transition-metal-carbene-like intermolecular insertion of a borylene into C-H bonds**

Siyuan Liu,<sup>a,b,c</sup> Marc-André Légaré<sup>b,c</sup> Alexander Hofmann,<sup>b,c</sup> Theresa Dellermann,<sup>b,c</sup> Holger  
Braunschweig<sup>\*,b,c</sup>

<sup>a</sup> *Present address: School of Materials Science and Engineering, China University of Petroleum, Qingdao, Shandong, 266580, PR China*

<sup>b</sup> *Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

<sup>c</sup> *Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

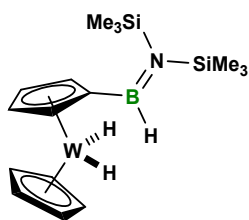
\*To whom correspondence should be addressed. E-mail: [h.braunschweig@uni-wuerzburg.de](mailto:h.braunschweig@uni-wuerzburg.de)

## Synthetic procedures

### General experimental considerations

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents.<sup>1</sup> Solvents (both deuterated and non-deuterated) were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired on a Bruker Avance 400 NMR spectrometer and a Bruker Avance 500 NMR spectrometer. Chemical shifts ( $\delta$ ) are given in ppm and internally referenced to the carbon nuclei ( $^{13}\text{C}\{^1\text{H}\}$ ) or residual protons ( $^1\text{H}$ ) of the solvent.  $^{11}\text{B}$  spectra are referenced to external standards  $[\text{BF}_3 \cdot \text{OEt}_2]$ . High-resolution mass spectrometry was obtained from a Thermo Scientific Exactive Plus spectrometer. Compound  $\text{Cp}_2\text{WH}_2$  (**2**)<sup>2</sup> and the Mo-borylene **1** were prepared as previously described.<sup>3</sup>

### Preparation of **3**



To a solid mixture of **2** (31.6 mg, 0.1 mmol) and molybdenum borylene **1** (41 mg, 0.1 mmol) was added toluene (5 mL). The mixture was stirred for 48 h at room temperature. The resulting brown solution was filtered through a cotton plug. The filtrate was evaporated under reduced pressure to afford an oil which was recrystallised in cold pentane (slow evaporation at  $-30\text{ }^\circ\text{C}$  from 5 mL to 2 mL). The mixture was again filtered through a cotton plug and the filtrate was dried by evaporation. This recrystallisation procedure was repeated two more times in order to fully remove the molybdenum-containing byproducts. Finally, the purified solution was evaporated to dryness to afford **3** as yellow crystals (13.4 mg, 27.5%).

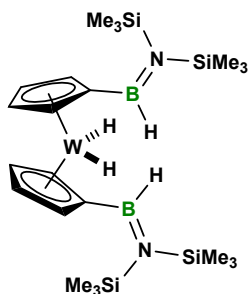
$^1\text{H}\{^{11}\text{B}\}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ : 5.13 (br, 1H, *H*-B), 4.74 (m, 2H,  $\text{C}_\text{B}\text{H}$ -Cp), 4.34 (m, 5H *CH*-Cp), 3.92 (m, 2H,  $\text{C}_\text{B}\text{H}$ -Cp), 0.32 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ),  $-11.16$  (m, 2H,  $\text{WH}_2$ )

$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$ : 39.6 (br)

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ): 82.2, 78.1, 71.6 ( $\text{C}_\text{B}\text{H}$ -Cp), 74.7 (*CH*-Cp), 4.3 ( $\text{Si}(\text{CH}_3)_3$ ). The signals from carbon atoms directly bound to boron could not be located.

HRMS ( $\text{C}_{16}\text{H}_{30}\text{BNSi}_2\text{W}$ ) calcd.:  $m/z = 487.1519$ ; found:  $m/z = 487.1524$ .

## Preparation of 4



To a solid mixture of **2** (31.6 mg, 0.1 mmol) and Mo borylene **1** (82.0 mg, 0.2 mmol) was added toluene (5 mL). The mixture was stirred at room temperature for 96 h. The resulting brown solution was filtered through a cotton plug. The filtrate was evaporated under reduced pressure to afford an oil which was recrystallised in cold pentane (slow evaporation at  $-30\text{ }^{\circ}\text{C}$  from 5 mL to 2 mL). The mixture was again filtered through a cotton plug and the filtrate was dried by evaporation. This recrystallisation procedure was repeated two more times in order to fully remove the molybdenum-containing byproducts. Finally, the purified solution was evaporated to dryness to afford **3** as yellow crystals (10.7 mg, 16.2%).

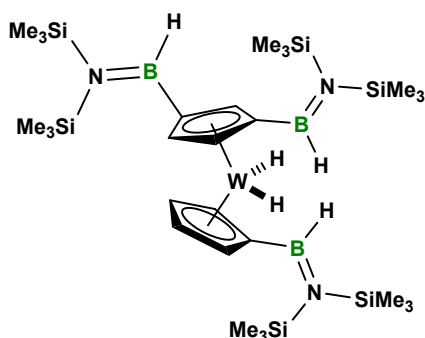
$^1\text{H}\{^{11}\text{B}\}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ : 5.13 (br, *H*-B), 4.92 (m, 4H, *CH*-Cp), 4.23 (m, 4H, *CH*-Cp), 0.30 (s, 36H,  $\text{Si}(\text{CH}_3)_3$ ),  $-10.50$  (m, 2H,  $\text{WH}_2$ )

$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$ : 41.3 (br)

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ): 84.6, 80.8 (*CH*-Cp), 4.1 ( $\text{Si}(\text{CH}_3)_3$ ). The signals from carbon atoms directly bound to boron could not be located.

HRMS ( $\text{C}_{22}\text{H}_{48}\text{B}_2\text{N}_2\text{Si}_4\text{W}$ ) calcd.:  $m/z = 658.2590$ ; found:  $m/z = 658.2600$ .

## Preparation of 5



To a solid mixture of **2** (31.6 mg, 0.1 mmol) and **1** (123.0 mg, 0.3 mmol) was added toluene (5 mL). The mixture was stirred at  $60\text{ }^{\circ}\text{C}$  for 96 h. The resulting brown solution was filtered through a cotton plug and the solvent of the filtrate was evaporated under reduced pressure to obtain a brown oil. The target compound **5** could not be separated from this crude mixture, but it could be identified by NMR and HRMS.

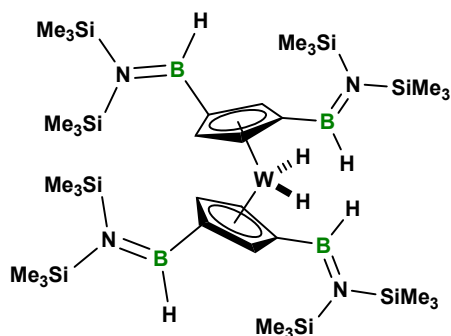
$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ : 5.31 (br, *H*-B), 4.81 (m, 4H, *CH*-Cp<sup>1</sup>), 4.78 (m, 2H, *CH*-Cp<sup>2</sup>), 4.70 (m, 2H, *CH*-Cp<sup>2</sup>),

4.37 (m, 1H, CH-Cp<sup>1</sup>), 0.35+0.32 (72H, Si(CH<sub>3</sub>)<sub>3</sub>), -10.53 (m, 2H, WH<sub>2</sub>)

<sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>): δ: 43.0 (br)

HRMS (C<sub>28</sub>H<sub>66</sub>B<sub>3</sub>N<sub>3</sub>Si<sub>6</sub>W): calcd.: *m/z* = 829.3655; found: *m/z* = 829.3627.

## Preparation of 6



To a solid mixture of **2** (31.6 mg, 0.1 mmol) and **1** (205.0 mg, 0.5 mmol) was added toluene (5 mL). The mixture was stirred at 60 °C for 96 h. The resulting brown solution was filtered through a cotton plug. The filtrate was evaporated under reduced pressure to afford an oil which was recrystallised in cold pentane (slow evaporation at -30 °C from 5 mL to 2 mL). The mixture was again filtered through a cotton plug and the filtrate was dried by evaporation. This recrystallisation procedure was repeated two more times in order to fully remove the molybdenum-containing byproducts. Finally, the purified solution was evaporated to dryness to afford **6** as a brown oil (13.0 mg, 13.0%).

<sup>1</sup>H{<sup>11</sup>B} NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ: 5.42 (br, H-B), 4.89 (m, 2H, CH-Cp), 4.80 (m, 4H, CH-Cp), 0.36 (s, 72H, Si(CH<sub>3</sub>)<sub>3</sub>), -10.87 (m, 2H, WH<sub>2</sub>)

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>): δ: 43.0 (br)

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): 92.5, 82.5 (CH-Cp), 4.4 (Si(CH<sub>3</sub>)<sub>3</sub>)

HRMS (C<sub>34</sub>H<sub>84</sub>B<sub>4</sub>N<sub>4</sub>Si<sub>8</sub>W) calcd.: *m/z* = 1000.4731; found: *m/z* = 1000.4754

## NMR spectra of the compounds

Figure. S-1  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **3**.

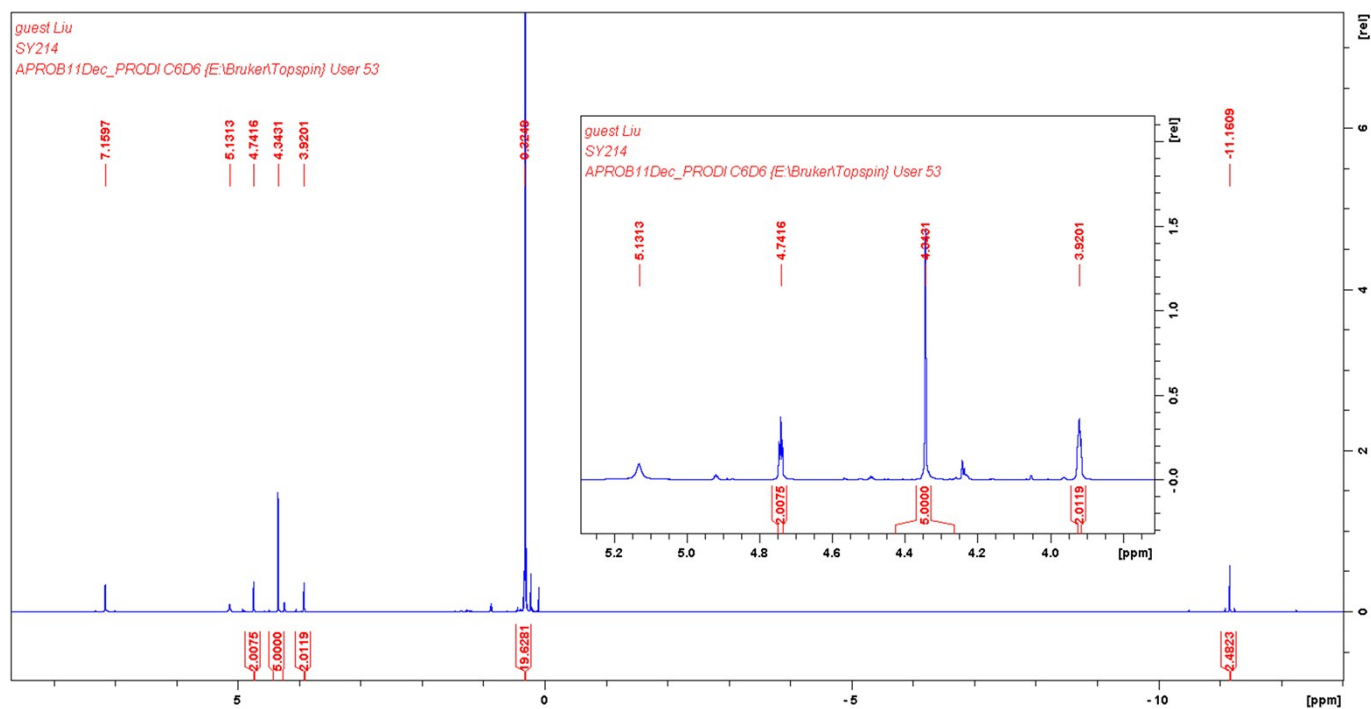


Figure. S-2  $^{11}\text{B}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **3**.

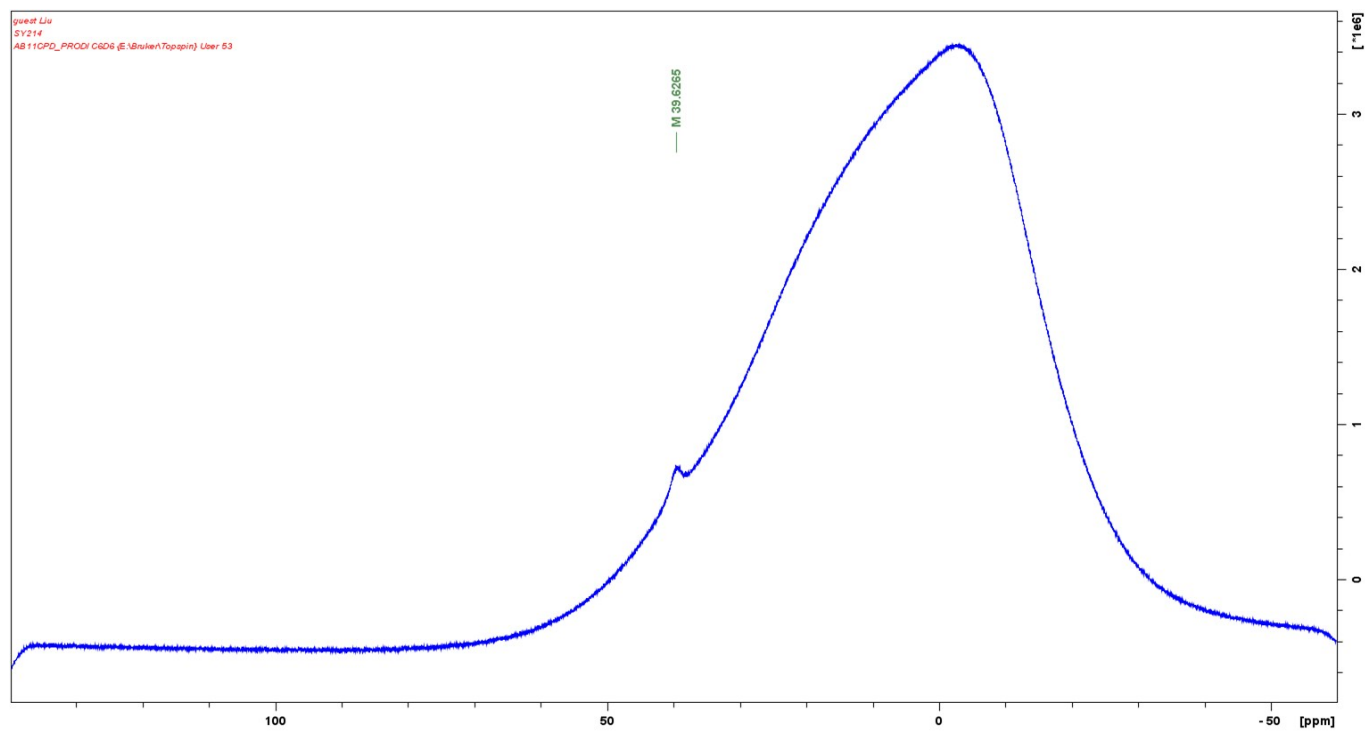


Figure. S-3  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **3**.

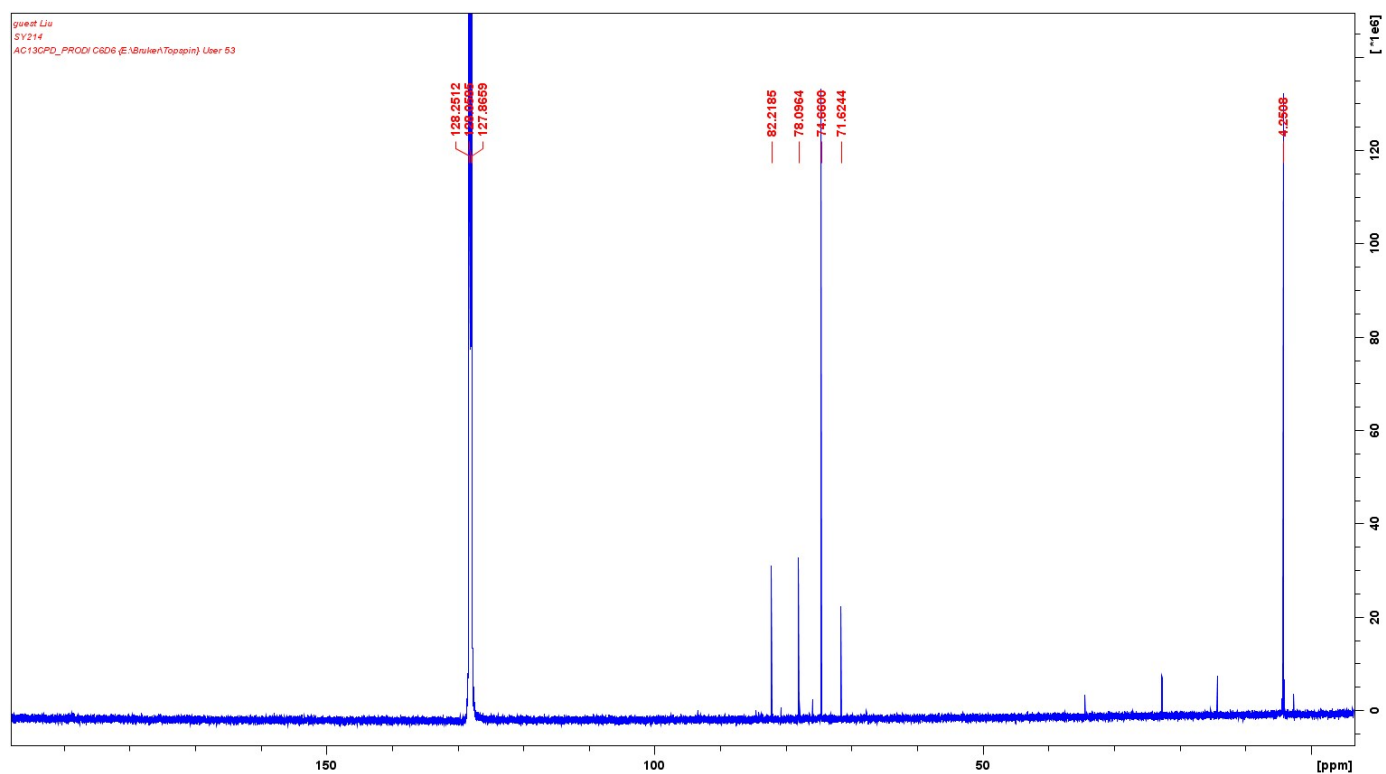


Figure. S-4  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **4**.

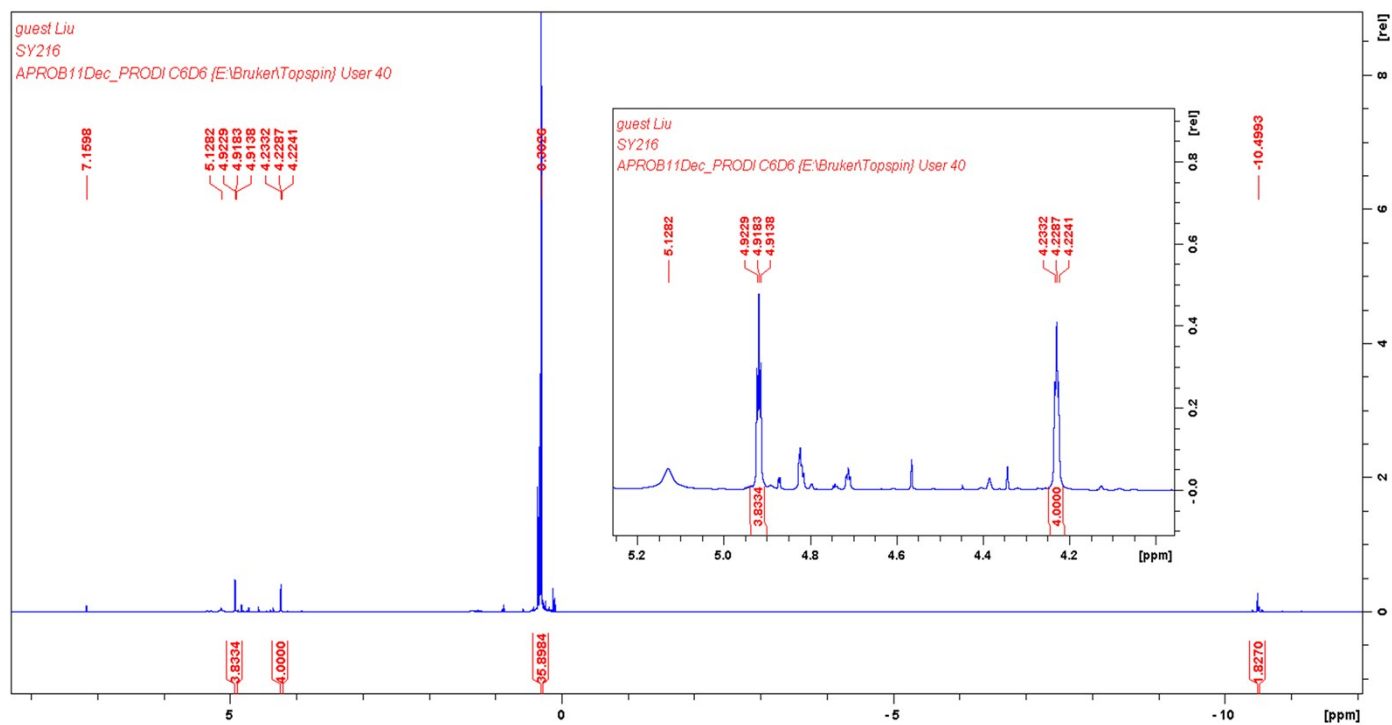


Figure. S-5  $^{11}\text{B}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **4**.

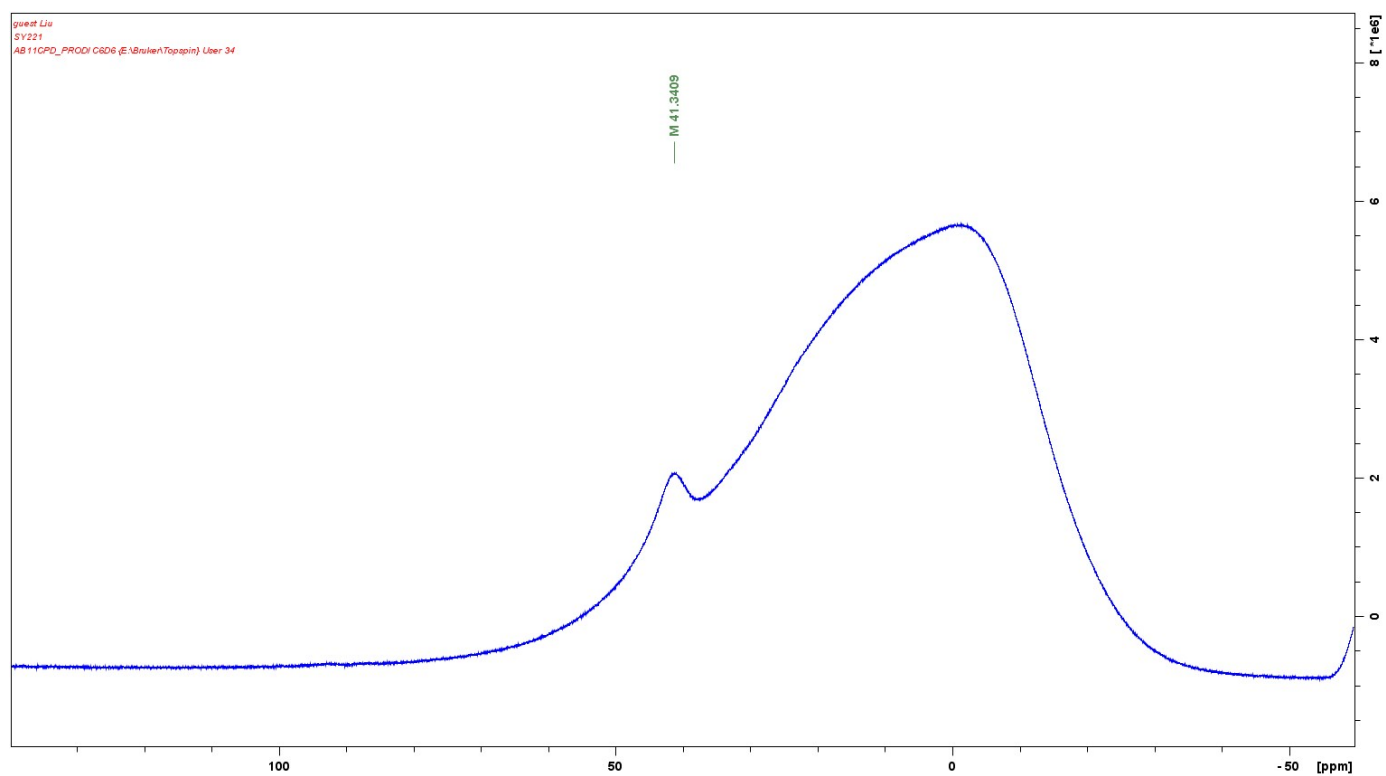


Figure. S-6  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **4**.

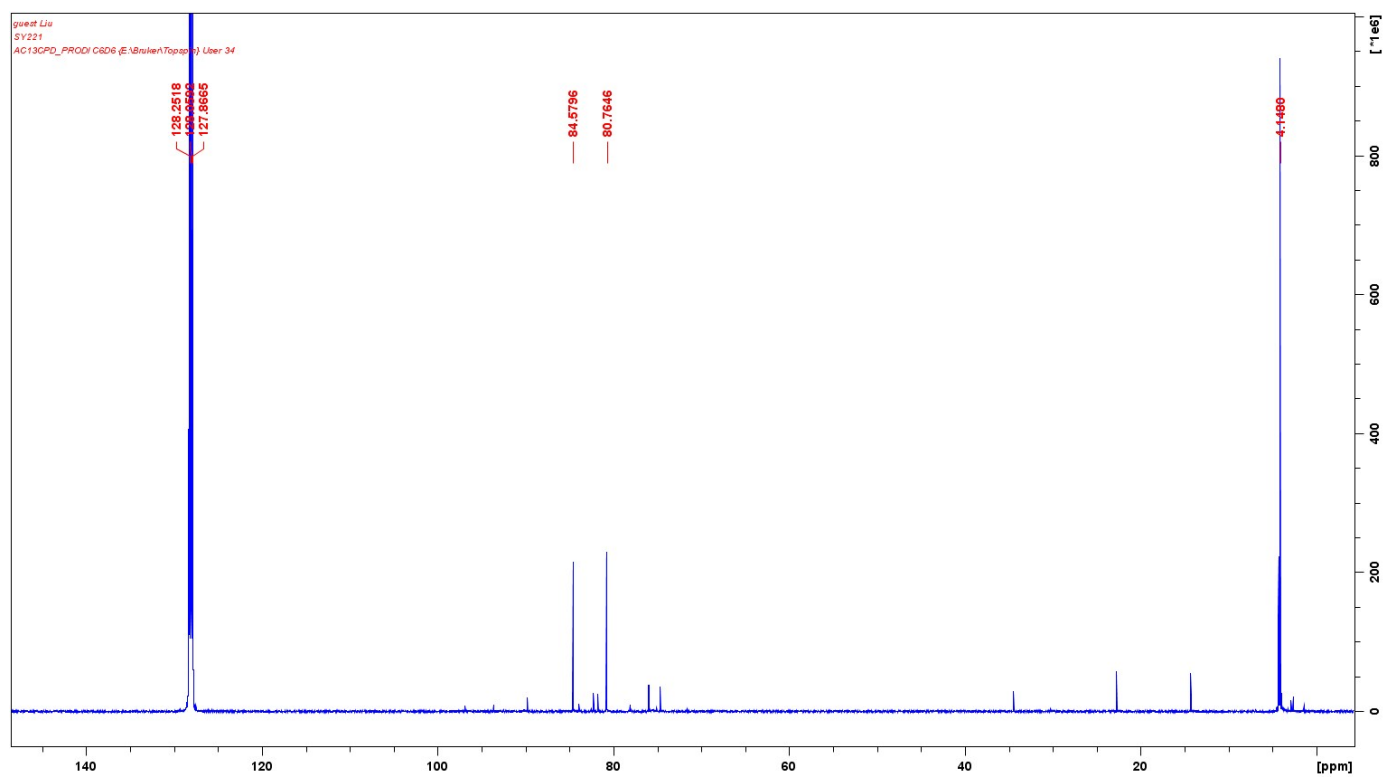


Figure. S-7  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **6**.

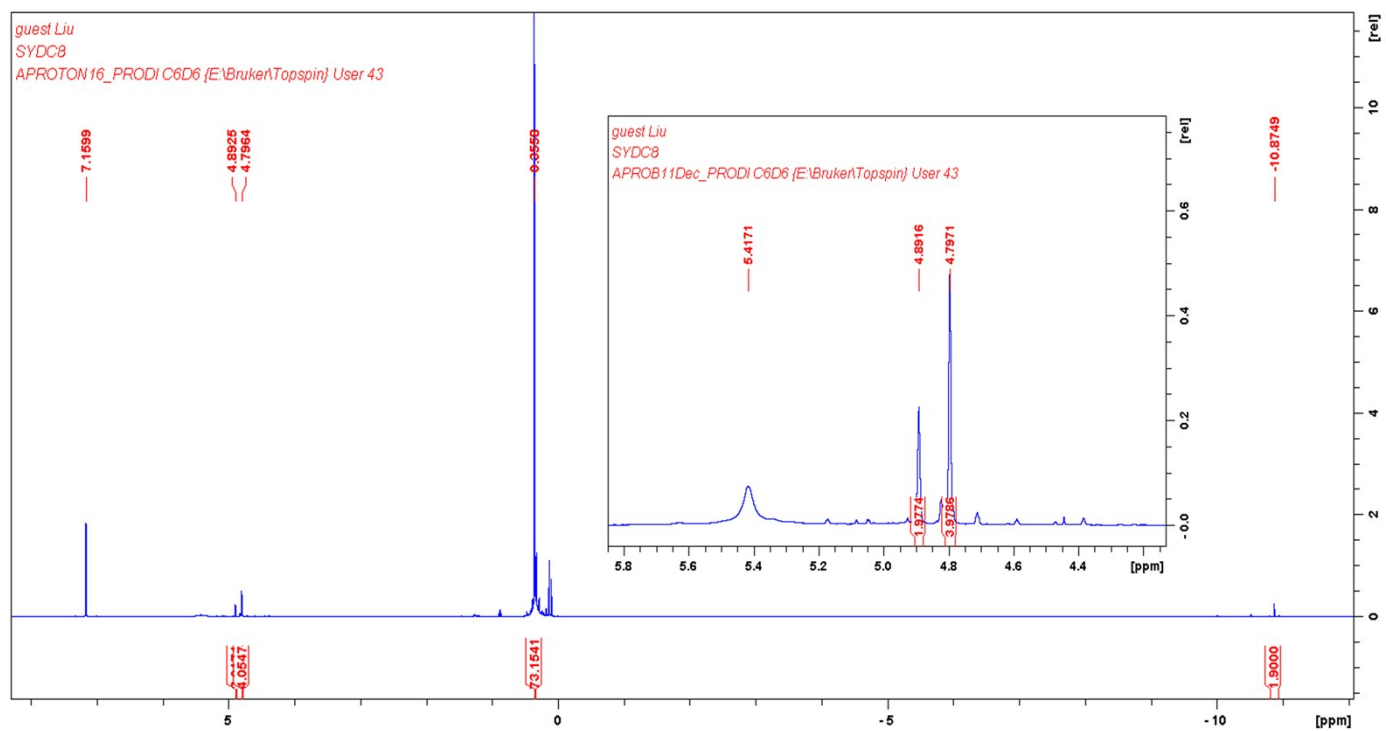


Figure. S-8  $^{11}\text{B}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **6**.

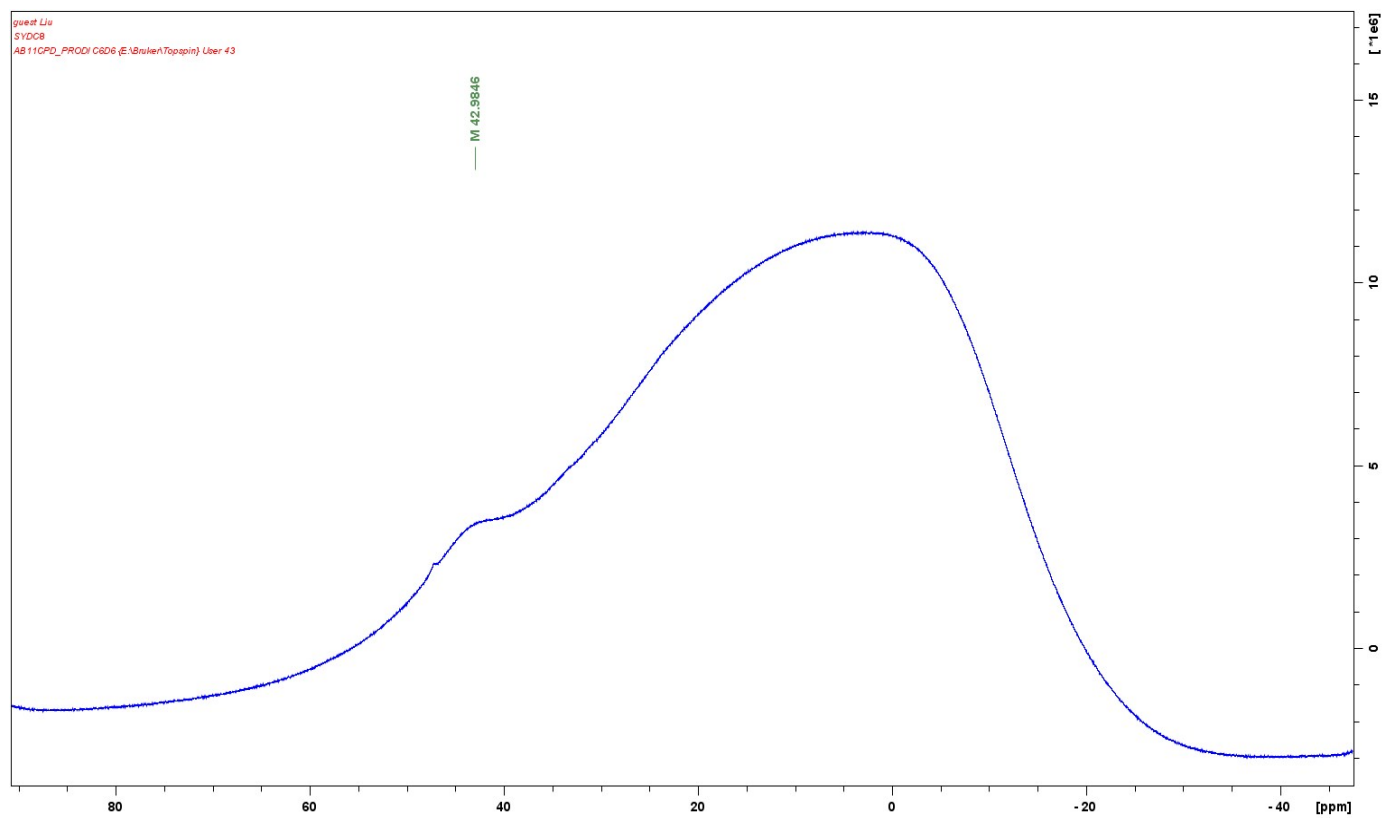




Figure. S-9  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **6**.

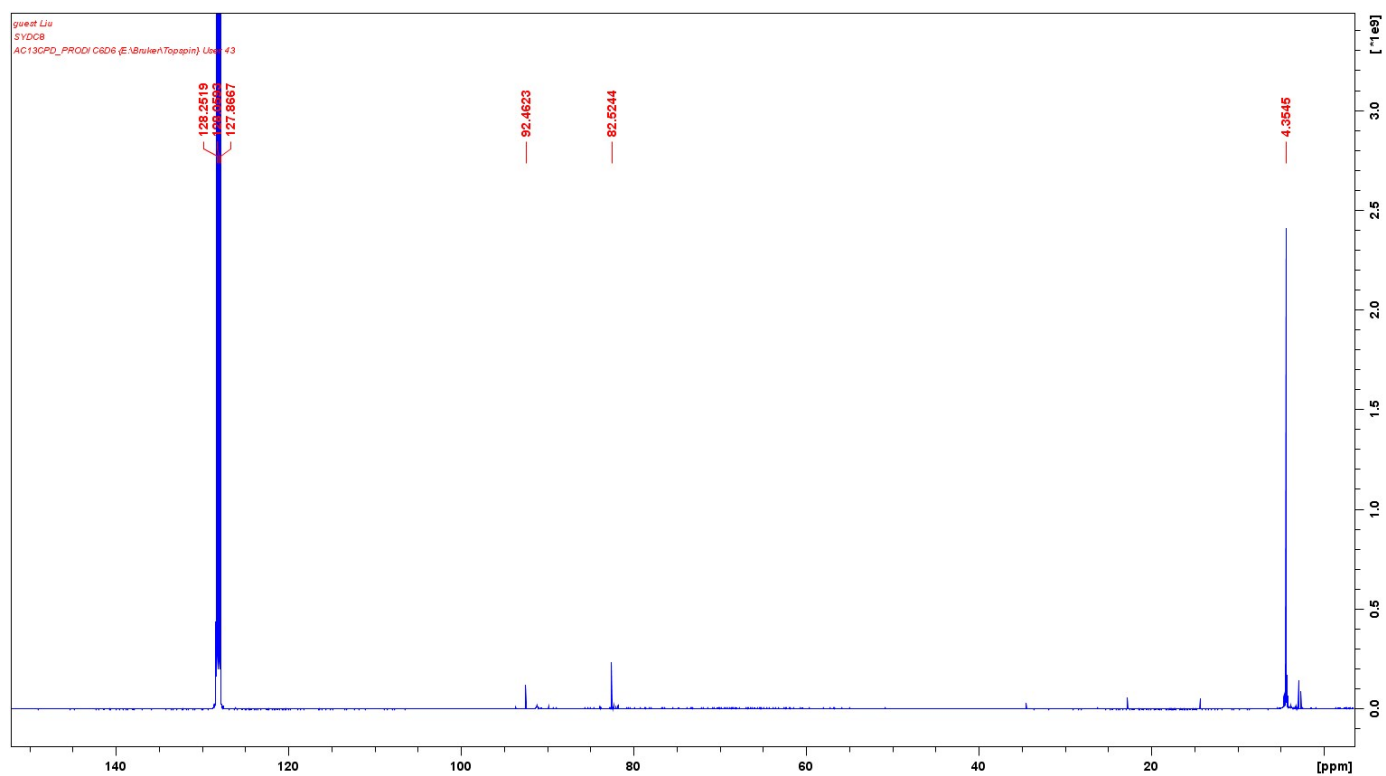
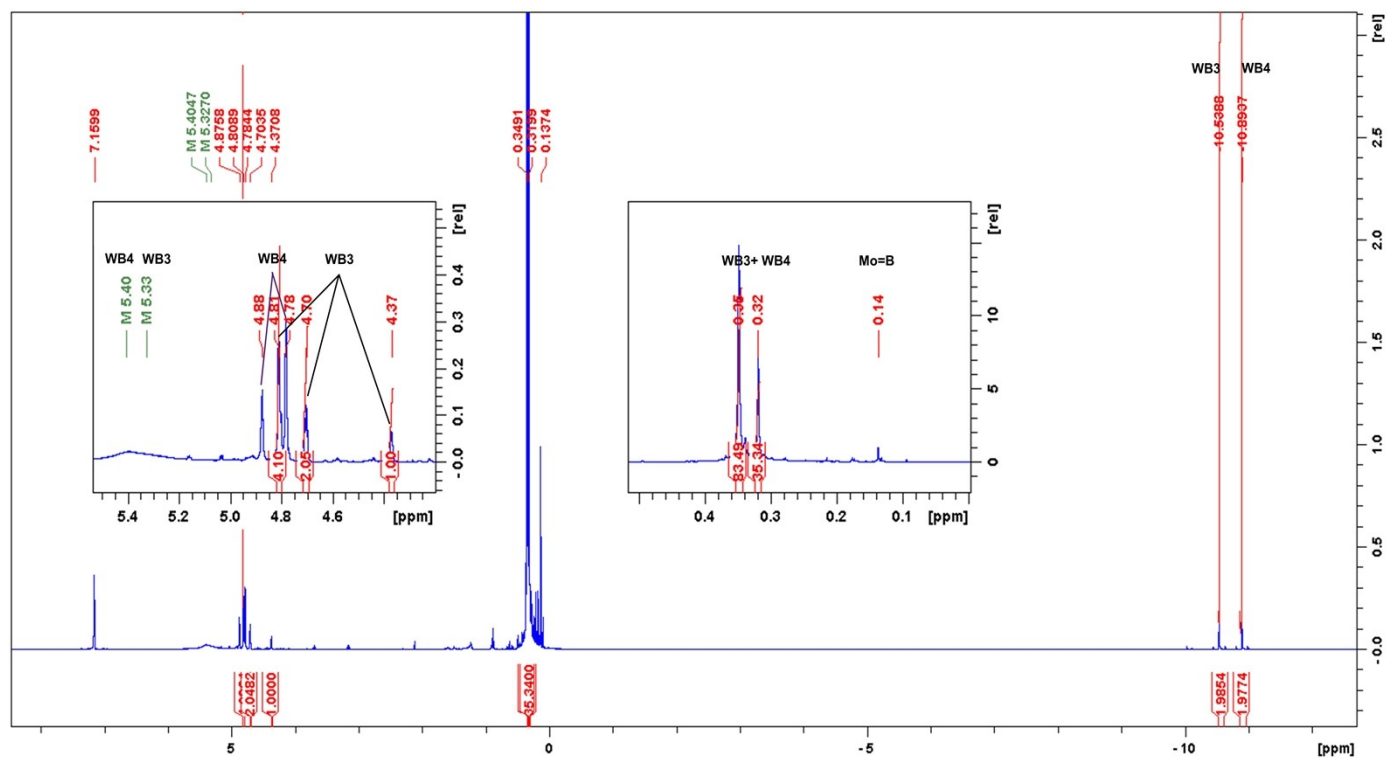


Figure. S-10  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ) spectrum of **5**.



# HRMS spectra of the compounds

Figure S-10 HRMS spectrum of 3

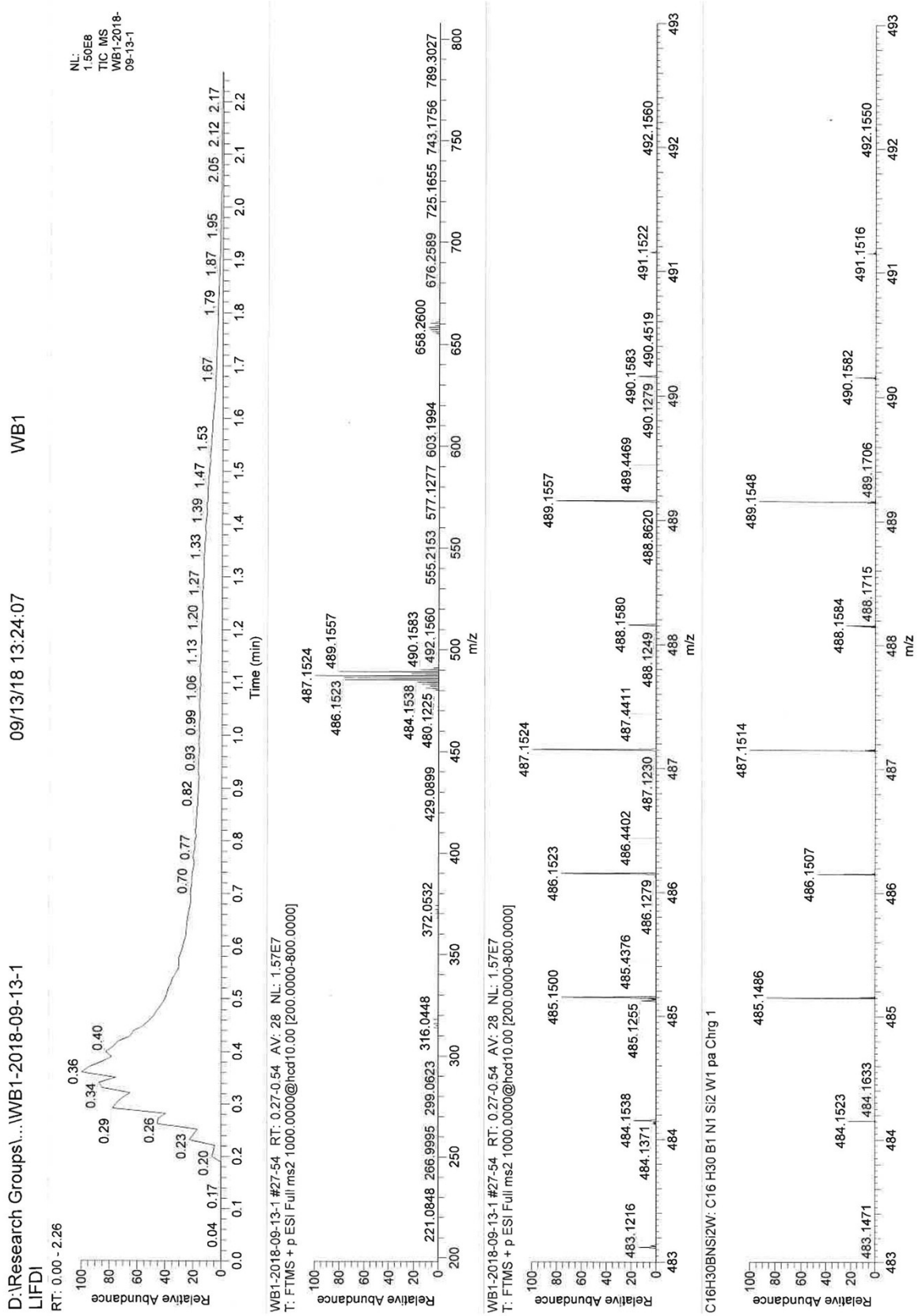


Figure S-11 HRMS spectrum of 4

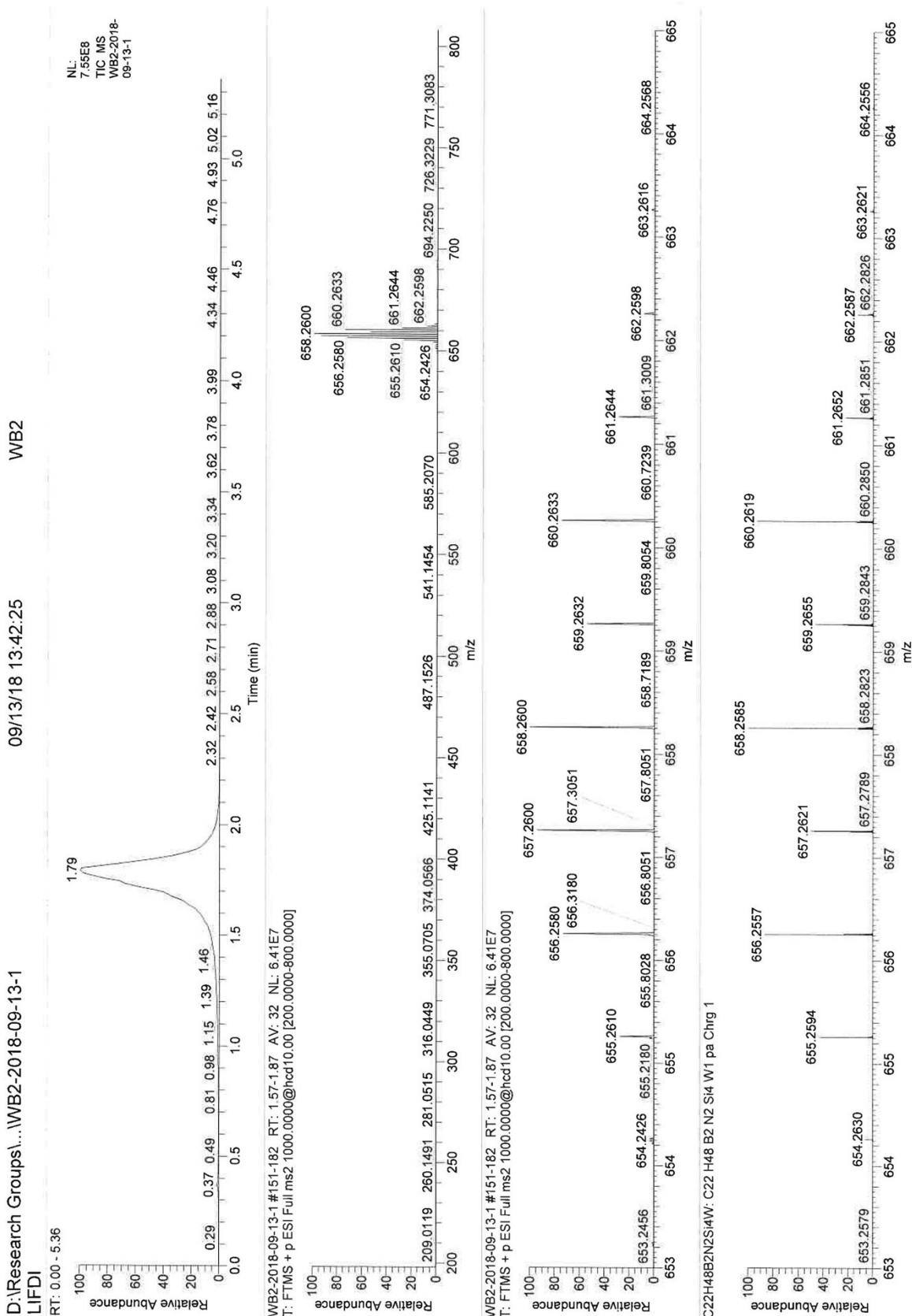


Figure S-12 HRMS spectrum of 5

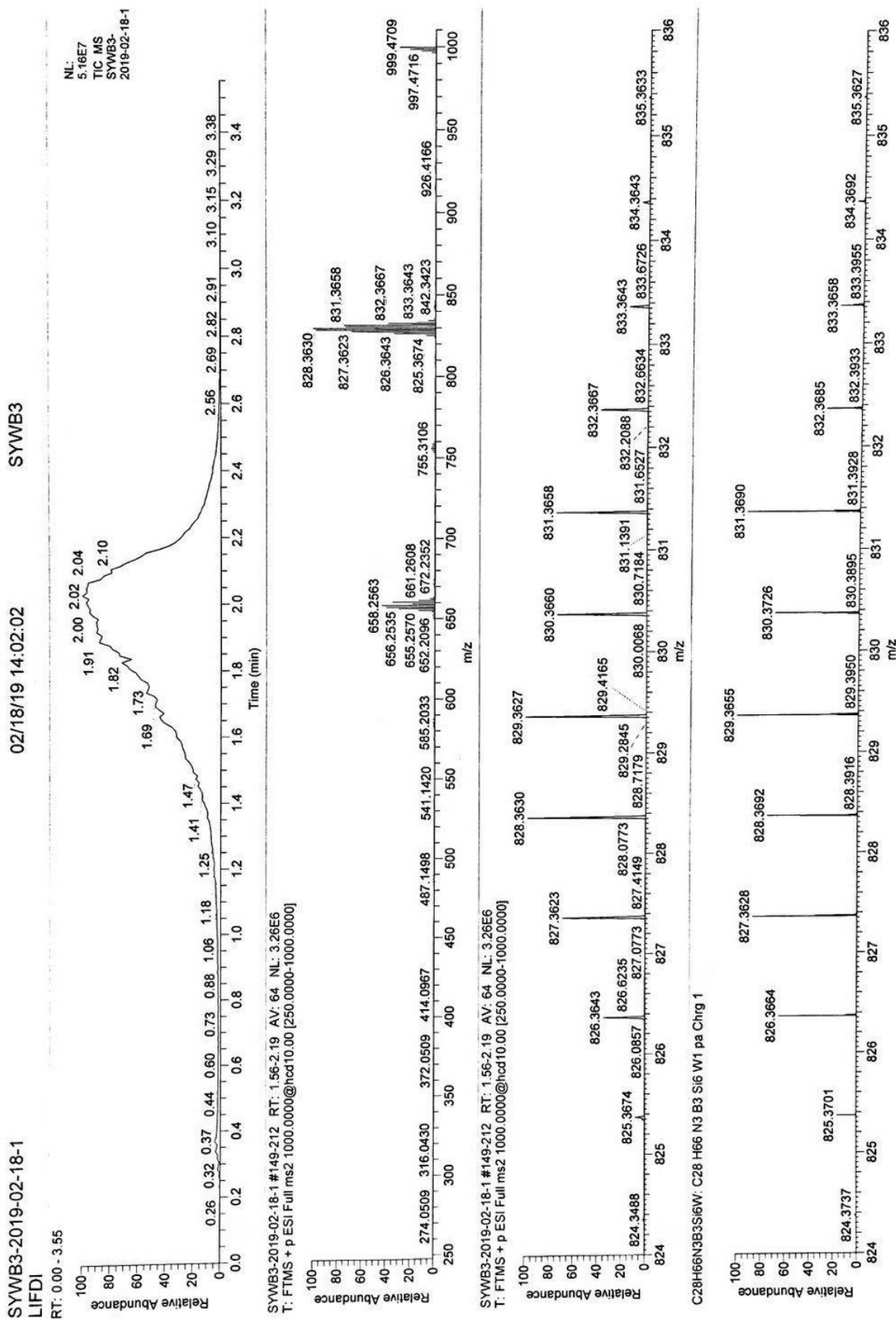
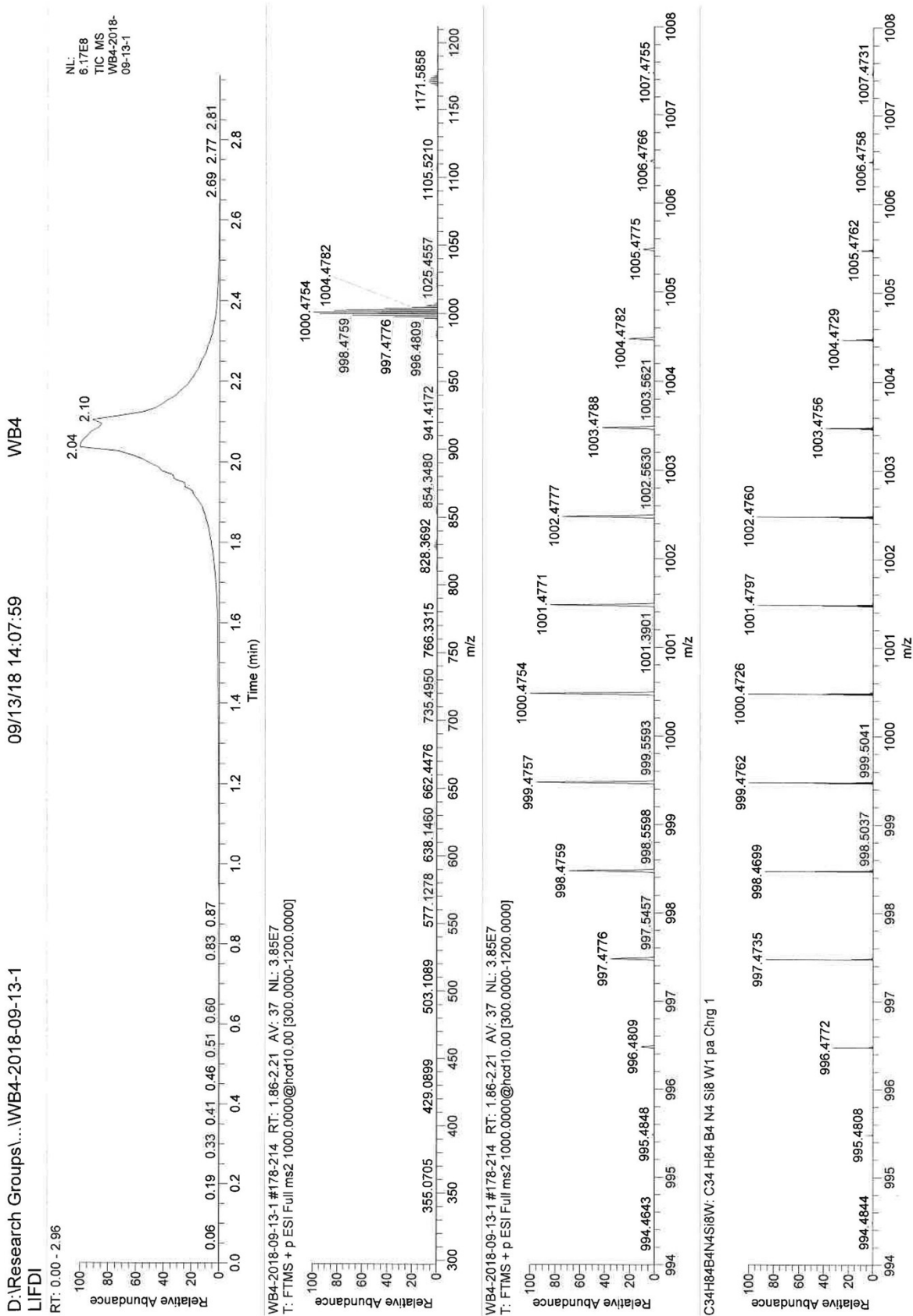


Figure S-13 HRMS spectrum of **6. 7** can be seen with a mass of 1171.5858.



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### X-ray Structure Determination:

The crystal data of **3**, **4** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated  $\text{Mo}_{K\alpha}$  radiation. The structure was solved using the intrinsic phasing method,<sup>4</sup> refined with the ShelXL program<sup>5</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except in H1 and H2 in structure **4** were assigned to idealised positions. The coordinates of H1 and H2 were refined freely.

For structure **4**: The displacement parameters of atoms C1 to C5 of residue 5 were restrained to the same value with similarity restraint SIMU. The distances between atoms C1 and C2, C2 and C3, C3 and C4 and C4 and C5 were restrained during refinement to the same value with SADI restraint. The atomic displacement parameters of atoms C1\_5 to C5\_5 were restrained with RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.004 for both parameters s1 and s2 were used).

Crystal data for **3**:  $\text{C}_{16}\text{H}_{30}\text{BNSi}_2\text{W}$ ,  $M_r = 487.25$ , colourless plate,  $0.118 \times 0.061 \times 0.052 \text{ mm}^3$ , triclinic space group  $P\bar{1}$ ,  $a = 9.1544(9) \text{ \AA}$ ,  $b = 13.250(2) \text{ \AA}$ ,  $c = 17.443(3) \text{ \AA}$ ,  $\alpha = 99.524(8)^\circ$ ,  $\beta = 102.213(5)^\circ$ ,  $\gamma = 106.236(4)^\circ$ ,  $V = 1927.7(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.679 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu = 6.111 \text{ mm}^{-1}$ ,  $F(000) = 960$ ,  $T = 100(2) \text{ K}$ ,  $R_1 = 0.0495$ ,  $wR^2 = 0.0577$ , 7942 independent reflections [ $2\theta \leq 52.742^\circ$ ] and 406 parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1999138**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

Crystal data for **4**:  $\text{C}_{49}\text{H}_{108}\text{B}_4\text{N}_4\text{Si}_8\text{W}_2$ ,  $M_r = 1389.05$ , colourless needle,  $0.274 \times 0.15 \times 0.097 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ ,  $a = 12.0424(6) \text{ \AA}$ ,  $b = 8.8836(5) \text{ \AA}$ ,  $c = 31.4360(15) \text{ \AA}$ ,  $\alpha = 90.468(3)^\circ$ ,  $V = 3362.9(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.372 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu = 3.593 \text{ mm}^{-1}$ ,  $F(000) = 1420$ ,  $T = 100(2) \text{ K}$ ,  $R_1 = 0.0265$ ,  $wR^2 = 0.0479$ , 6624 independent reflections [ $2\theta \leq 52.042^\circ$ ] and 354 parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1999139**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

## References:

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