Electronic Supplementary Material (ESI) for Chemical Science.

**Supporting Information for:**

# Synthesis of Unsymmetrical $B_2E_2$ and $B_2E_3$ Heterocycles by Borylene Insertion into Boradichalcogeniranes

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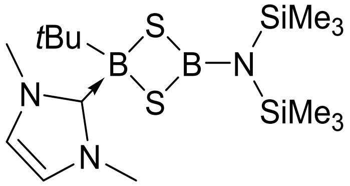
# Synthetic procedures

## General experimental considerations

All reactions were carried out in an argon-filled glovebox or using standard Schlenk techniques[1] unless otherwise specified. Compound $BS_2$ (**2b**), $BSe_2$ (**2a**), $BTe_2$ (**1**) and all borylene complexes were prepared as previously described.[2-6] All elemental chalcogens were obtained from commercial sources and used without purification. All solvents were dried by distillation over appropriate drying agents[7] and stored over molecular sieves.

Solution NMR spectra were acquired on a Bruker Avance 400 NMR spectrometer (400.130 MHz for $^1$H, 128.385 MHz for $^{11}$B) or a Bruker Avance I 500 spectrometer ($^1$H: 500 MHz, $^{11}$B: 160 MHz, $^{13}$C: 125 MHz, $^{77}$Se: 57 MHz, $^{125}$Te: 157 MHz). $^1$H NMR and $^{13}$C{$^1$H} NMR spectra were referenced to external TMS via residual protons of the solvent ($^1$H) or the solvent itself ($^{13}$C). $^{11}$B{$^1$H} NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. $^{77}$Se NMR spectra were referenced to external $(CH_3)_2Se$. Elemental analyses were performed on an Elementar Vario MICRO cube elemental analyzer. High-resolution mass spectrometry was obtained from a Thermo Scientific Exactive Plus spectrometer.

## Preparation of 7b

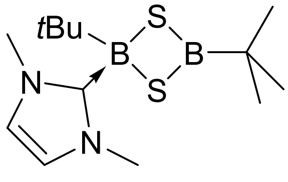


To a solid mixture of **2b** (23 mg, 0.1 mmol) and molybdenum aminoborylene **6** (41 mg, 0.1 mmol) was added toluene (5 mL). The mixture was stirred for 8 h. The resulting brown solution was filtered through a cotton plug and the filtrate was concentrated to 3 mL under reduced pressure. 5 mL pentane was the added to the toluene solution which was then cooled to –30 ºC to obtain **7b** as colourless crystals (15 mg, 38%).

$^1$H NMR (500 MHz, $C_6D_6$) δ: 5.39 (s, 2H, NCHCHN), 3.34 (s, 6H, N-$CH_3$), 1.28 (s, 9H, *t*Bu), 0.59 (s, 18H, $SiMe_3$);
$^{11}$B NMR (160 MHz, $C_6D_6$): δ: –6.1 (s, B(IMe)*t*Bu), 49.8 (s, BN($SiMe_3$)$_2$);
$^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): δ 121.0 (s, NCHCHN), 38.6 (s, N-$CH_3$), 29.5 (s, C($CH_3$)$_3$), 4.8 (s, $SiMe_3$).

HRMS ($C_{15}H_{35}N_3B_2S_2Si_2$) calcd.: *m/z* = 399.1997; calcd. [M$^+$ + H]: *m/z* = 400.2075; found: *m/z* = 400.2070 [M$^+$ + H].

## Preparation of 9b

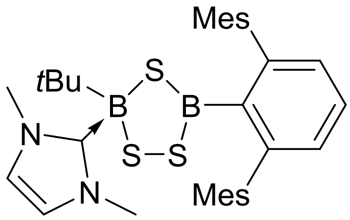


To a solid mixture of **2b** (23 mg, 0.1 mmol) and manganese *tert*-butyl borylene **8** (24 mg, 0.1 mmol) was added toluene (5 mL). The mixture was stirred for 12 h. The resulting orange solution was filtered through a cotton plug and the filtrate was concentrated to 2 mL under reduced pressure. 5 mL pentane was the added to the toluene solution which was then cooled to –30 ºC to obtain **9b** as white powder (10 mg, 34%).

$^1$H NMR (500 MHz, $C_6D_6$) δ: 5.23 (s, 2H, NCHCHN), 3.34 (s, 6H, N-$CH_3$), 1.46 (s, 9H, B-*t*Bu), 1.27 (s, 9H, B(IMe)*t*Bu); $^{11}$B NMR (160 MHz, $C_6D_6$): δ: –3.6 (s, B(IMe)*t*Bu), 72.9 (s, B-*t*Bu);
$^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): δ 121.2 (s, NCHCHN), 38.4 (s, N-$CH_3$), 29.3 (s, B(IMe)*t*Bu), 28.6 (s, B-*t*Bu).

HRMS ($C_{13}H_{26}B_2N_2S_2$) calcd.: *m/z* = 296.1723; calcd. [M$^+$ - *t*Bu]: *m/z* = 239.1014; found: *m/z* = 239.1001 [M$^+$ - *t*Bu].

## Preparation of 5b

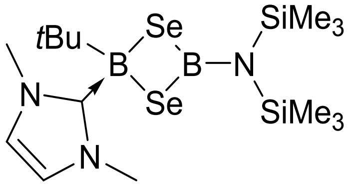


To a solid mixture of **2b** (23 mg, 0.1 mmol) and chromium Tp-borylene complex **3** (52 mg, 0.1 mmol) was added toluene (10 mL). The mixture was then stirred for 24 h. The resulting brown solution was filtered through a cotton plug and the filtrate was concentrated to 3 mL under reduced pressure. 5 mL pentane was the added to the toluene solution. The solution was then kept at room temperature for 24 h to obtain crude product **5b** as a white powder. The crude product was dissolved in 3 mL THF and 3 mL pentane was added into the solution, which was then cooled to –30 ºC to obtain **5b** as colourless crystals. (13 mg, 22%).

$^1$H NMR (400 MHz, $C_4D_8O$) δ: 7.27 (t, $^3J_{HH}$ = 8 Hz, 1H, C*H*$_{ar}$), 6.98 (s, 2H, NCHCHN), 6.83 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*$_{ar}$), 6.65 (br, 4 H, C*H*$_{ar}$), 3.83 (s, 6 H, C*H*$_3$ of IMe), 2.17 (s, 6 H, C*H*$_3$ of Mes), 1.99 (s, 6 H, Mes), 1.99 (s, 6 H, Mes), 0.65 (s, 9 H, C*H*$_3$ of *t*Bu);
$^{11}$B NMR (128 MHz, $C_4D_8O$): δ: 7.6 (s, B(IMe)*t*Bu), 66.7 (s, BTpMes);
$^{13}$C{$^1$H} NMR (100 MHz, $C_4D_8O$): δ 144.7 ($C_{ar}$), 140.9 ($C_{ar}$), 136.8 ($C_{ar}$), 136.2 ($C_{ar}$), 135.9 ($C_{ar}$), 128.5 ($CH_{ar}$), 128.0 ($CH_{ar}$), 127.7 ($CH_{ar}$), 123.6 (NCHCHN), 40.0 (N-$CH_3$), 31.1 ($C(CH_3)_3$), 21.6 ($CH_3^{ar}$), 21.5 ($CH_3^{ar}$), 21.1 ($CH_3^{ar}$).

HRMS ($C_{33}H_{42}B_2N_2S_3$) calcd.: *m/z* = 584.2696; calcd. [M$^+$ - *t*Bu]: *m/z* = 527.1986; found: *m/z* = 527.1982 [M$^+$ - *t*Bu].

## Preparation of 7a

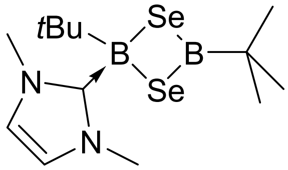


To a solid mixture of **2a** (32 mg, 0.1 mmol) and molybdenum aminoborylene **6** (41 mg, 0.1 mmol) was added toluene (5 mL). The mixture was then stirred for 8 h. The resulting brown solution was filtered through a cotton plug and the filtrate was concentrated to 2 mL under reduced pressure. 5 mL pentane was the added to the toluene solution which was then cooled down to –30 ºC to obtain **7a** as colourless crystals (26 mg, 52%).

$^1$H NMR (500 MHz, $C_6D_6$) δ: 5.36 (s, 2H, NCHCHN), 3.33 (s, 6H, N-$CH_3$), 1.37 (s, 9H, *t*Bu), 0.59 (s, 18H, 2Si$Me_3$);
$^{11}$B NMR (160 MHz, $C_6D_6$): δ: –13.4 (s, B(IMe)*t*Bu), 46.7 (s, BN(Si$Me_3$)$_2$);
$^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): δ 121.2 (s, NCHCHN), 39.3 (s, N-$CH_3$), 30.0 (s, C($CH_3$)$_3$), 5.0 (s, Si$Me_3$);
$^{77}$Se: (57 MHz, $C_6D_6$): δ 165.

HRMS ($C_{15}H_{35}B_2N_3Se_2Si_2$) calcd.: *m/z* = 495.0886; calcd. [M$^+$ - *t*Bu]: *m/z* = 438.0176; found: *m/z* = 438.0171 [M$^+$ - *t*Bu].

## Preparation of 9a

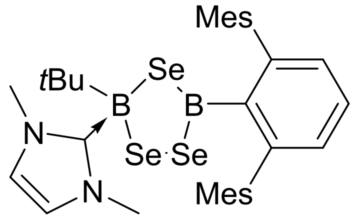


To a solid mixture of **2a** (32 mg, 0.1 mmol) and manganese *tert*-butylborylene **8** (24 mg, 0.1 mmol) was added toluene (5 mL). The mixture was stirred for 12 h. The resulting orange solution was filtered through a cotton plug and the filtrate was concentrated to 2 mL under reduced pressure. 5 mL pentane was the added to the toluene solution which was then cooled down to –30 ºC to obtain **9a** as white powder (14 mg, 36%).

$^1$H NMR (500 MHz, $C_6D_6$) δ: 5.29 (s, 2H, NCHCHN), 3.30 (s, 6H, N-$CH_3$), 1.44 (s, 9H, $CH_3$-B*t*Bu), 1.34 (s, 9H, $CH_3$-B(IMe)*t*Bu);
$^{11}$B NMR (160 MHz, $C_6D_6$): δ: –10.8 (s, B(IMe)*t*Bu), 77.5 (s, B*t*Bu);
$^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): δ 114.0 (s, NCHCHN), 31.8 (s, N-$CH_3$), 22.4 (s, B(IMe)*t*Bu), 21.2 (s, B-*t*Bu),
$^{77}$Se: (57 MHz, $C_6D_6$): δ 150.

HRMS ($C_{13}H_{26}B_2N_2Se_2$) calcd.: *m/z* = 392.0613; calcd. [M$^+$ - *t*Bu]: *m/z* = 334.9903; found: *m/z* = 334.9886 [M$^+$ - *t*Bu].

## Preparation of 5a

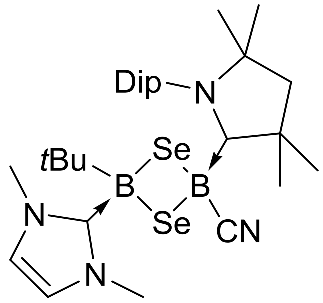


To a solid mixture of **2a** (32 mg, 0.1 mmol) and chromium Tp borylene complex **3** (52 mg, 0.1 mmol) was added toluene (10 mL). The mixture was stirred for 24 h. The resulting brown solution was filtered through a cotton plug and the filtrate was concentrated to 3 mL under reduced pressure. 5 mL pentane was the added to the toluene solution. The solution was then kept at room temperature for 24 h to obtain crude product **5a** as white powder. The crude product was dissolved in 3 mL THF and 3 mL pentane was added into the solution which was cooled down to –30 ºC to obtain **5a** as colourless crystals. (14 mg, 22%).

$^{1}$H NMR (400 MHz, $C_4D_8O$) δ: 7.32 (t, $^{3}J_{HH}$ = 8 Hz, 1H, C*H$_{ar}$*), 7.07 (s, 2H, NCHCHN), 6.85 (d, $^{3}J_{HH}$ = 8 Hz, 2H, C*H$_{ar}$*), 6.70 (d, $^{3}J_{HH}$ = 8 Hz, 4 H, C*H$_{ar}$*), 3.90 (s, 6 H, C*H*$_3$ of IMe), 2.20 (s, 6 H, C*H*$_3$ of Mes), 2.06 (s, 6 H, Mes), 2.06 (s, 6 H, Mes), 0.68 (s, 9 H, C*H*$_3$ of *t*Bu);
$^{11}$B NMR (128 MHz, $C_4D_8O$): δ: 6.4 (s, B(IMe)*t*Bu), 72.5 (s, BTpMes);
$^{13}$C{$^{1}$H} NMR (100 MHz, $C_4D_8O$): δ 143.5 (C$_{ar}$), 141.1 (C$_{ar}$), 136.6 (C$_{ar}$), 136.3 (C$_{ar}$), 136.1 (C$_{ar}$), 128.4 (CH$_{ar}$), 128.2 (CH$_{ar}$), 128.1 (CH$_{ar}$), 124.0 (NCHCHN), 40.9 (N-CH$_3$), 30.9 (C(CH$_3$)$_3$), 21.9 (CH$_3^{ar}$), 21.8 (CH$_3^{ar}$), 21.2 (CH$_3^{ar}$).

HRMS ($C_{33}H_{42}B_2N_2Se_3$) calcd.: *m/z* = 728.1030; calcd. [M$^+$ - *t*Bu]: *m/z* = 671.0325; found: *m/z* = 671.0303 [M$^+$ - *t*Bu].

## Preparation of 11



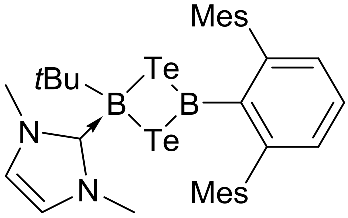
To a solid mixture of **2a** (32 mg, 0.1 mmol) and macrocyclic **10** (32 mg, 0.025 mmol) was added toluene (5 mL). The mixture was stirred for 12 h. The resulting red solution was filtered through a cotton plug and the filtrate was concentrated to 2 mL under reduced pressure. 5 mL pentane was the added to the toluene solution. The solution was then kept at room temperature to obtain **11** as red crystals (22 mg, 34%).

$^{1}$H NMR (500 MHz, $C_6D_6$) δ: 7.18 (t, $^{3}J_{HH}$ = 8 Hz, 1H, C*H$_{ar}$*), 7.07 (d, $^{3}J_{HH}$ = 8 Hz, 2H, C*H$_{ar}$*), 5.75 (s, 2H,

NCHCHN), 2.75 (sept, $^3J_{HH}$ = 7 Hz, 2H, C*H* of *i*Pr), 2.29 (s, 6 H, C*H*$_3$ of *c*AAC), 1.70 (d, $^3J_{HH}$ = 7 Hz, 6 H, C*H*$_3$ of *i*Pr), 1.53 (s, 2H, C*H*$_2$ of cAAC), 1.34 (s, 9H, C*H*$_3$ of *t*Bu), 1.12 (d, $^3J_{HH}$ = 7 Hz, 6 H, C*H*$_3$ of *i*Pr), 0.85 (s, 6H, C*H*$_3$ of *c*AAC);
$^{11}$B NMR (160 MHz, $C_6D_6$): δ: -9.5 (s, B(IMe)*t*Bu), -32.8 (s, B(*c*AAC)CN);
$^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): δ 146.3 (C*$_{ar}$*), 133.6 (C*$_{ar}$*), 130.4 (C*$_{ar}$*), 129.3 (CH$_{ar}$), 128.6 (CH$_{ar}$), 125.7 (C*$_{ar}$*), 125.4 (C*$_{ar}$*), 128.1 (CH$_{ar}$), 121.4 (NCHCHN-IMe), 76.0 (N*C*Me$_2$), 55.0 (NC*Me$_2$*), 52.2 (*C*H$_2$ of cAAC), 40.8 (N*C*H$_3$-IMe), 32.5 (*C*H$_3$-*t*Bu), 30.3 (CC(*C*H$_3$)$_2$), 29.3, 28.3 (CH-*i*Pr), 27.4, 24.8, 22.8, 21.4 (CH$_3$-*i*Pr).

HRMS ($C_{30}H_{48}B_2N_4Se_2$) calcd.: *m/z* = 646.2396; calcd. [M$^+$ - *t*Bu]: *m/z* = 589.1686; found: *m/z* = 589.1671 [M$^+$ - *t*Bu].

## Preparation of 4

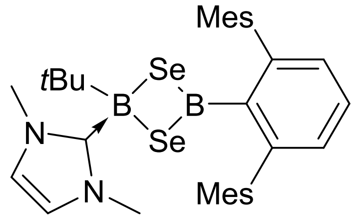


To a solid mixture of **1** (60 mg, 0.1 mmol) and chromium Tp borylene complex **3** (52 mg, 0.1 mmol) was added toluene (8 mL). The mixture was then stirred for 12 h. The resulting dark brown solution was filtered through a cotton plug and the filtrate was concentrated to 5 mL under reduced pressure. 5 mL pentane was the added to the toluene solution. The solution was cooled down to –30 ºC to obtain **4** as dark brown crystals (18 mg, 24%).

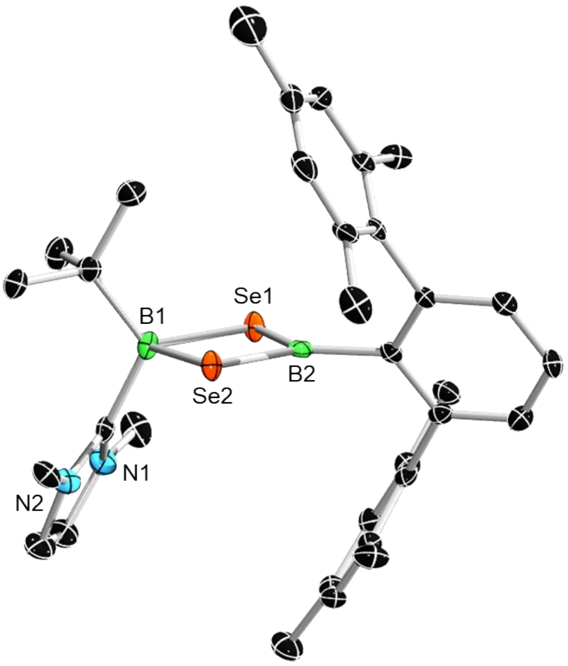
$^1$H NMR (500 MHz, $C_6D_6$) δ: 7.20 (t, $^3J_{HH}$ = 7 Hz, 1H, C*H$_{ar}$*), 6.98 (d, $^3J_{HH}$ = 7 Hz, 2H, C*H$_{ar}$*), 6.91 (s, 4H, C*H$_{ar}$*-Mes), 5.11 (s, 2H, NCHCHN), 3.01 (s, 6H, C*H*$_3$ of IMe), 2.49 (s, 12H, C*H*$_3$ of Mes), 2.17 (s, 6H, C*H*$_3$ of Mes), 1.11 (s, 9H, C*H*$_3$ of *t*Bu);
$^{11}$B NMR (160 MHz, $C_6D_6$): δ: -33.0 (s, B(IMe)*t*Bu), 61.1 (s, BTpMes);
$^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): δ 140.9 (C*$_{ar}$*), 140.3 (C*$_{ar}$*), 136.56 (C*$_{ar}$*), 136.0 (C*$_{ar}$*), 128.7 (CH*$_{ar}$*), 128.4 (CH$_{ar}$), 128.0 (C*H$_{ar}$*), 121.1 (NCHCHN), 40.0 (N-CH$_3$), 30.4 (C(CH$_3$)$_3$), 22.5 (CH$_3^{ar}$), 21.4 (CH$_3^{ar}$).
$^{125}$Te NMR (157 MHz, $C_6D_6$) δ: 337.7 (br)

HRMS ($C_{33}H_{42}B_2N_2Te_2$) calcd.: *m/z* = 748.1659; found: *m/z* = 748.1670 [M$^+$].

## Crystal structure of [*cyclo*-(*t*Bu(IMe)BSeBTpSe)] (5a')



From the reaction mixture of the synthesis of **5a** (see above) a few XRD quality crystals were obtained which correspond to a different product. The structure is given here to demonstrate the existence of [*cyclo*-(*t*Bu(IMe)BSeBTpSe)] even if it is not the major product.



## NMR spectra of the compounds

Figure S-1 $^1$H NMR (500 MHz, $C_6D_6$) spectrum of **7b.**

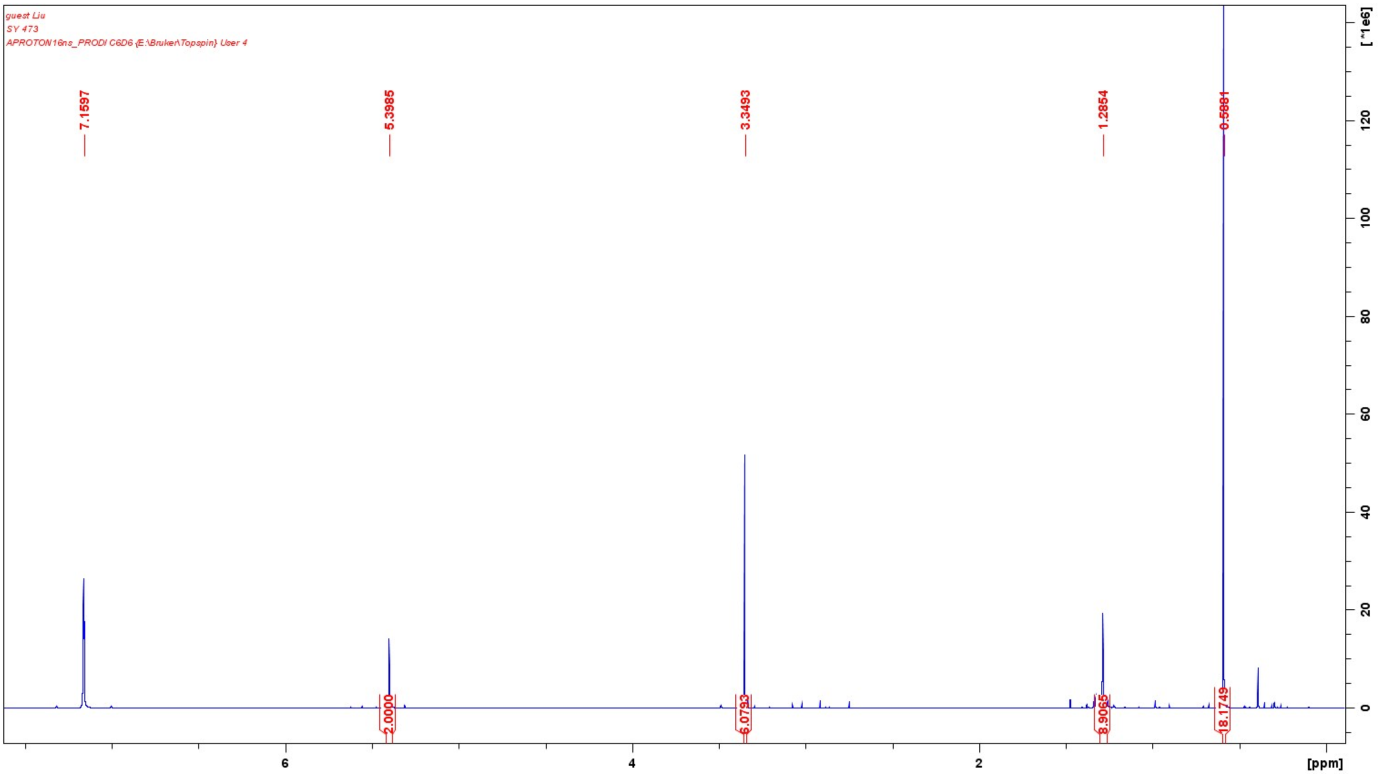


Figure S-2 $^{11}$B NMR (160 MHz, $C_6D_6$) spectrum of **7b**.

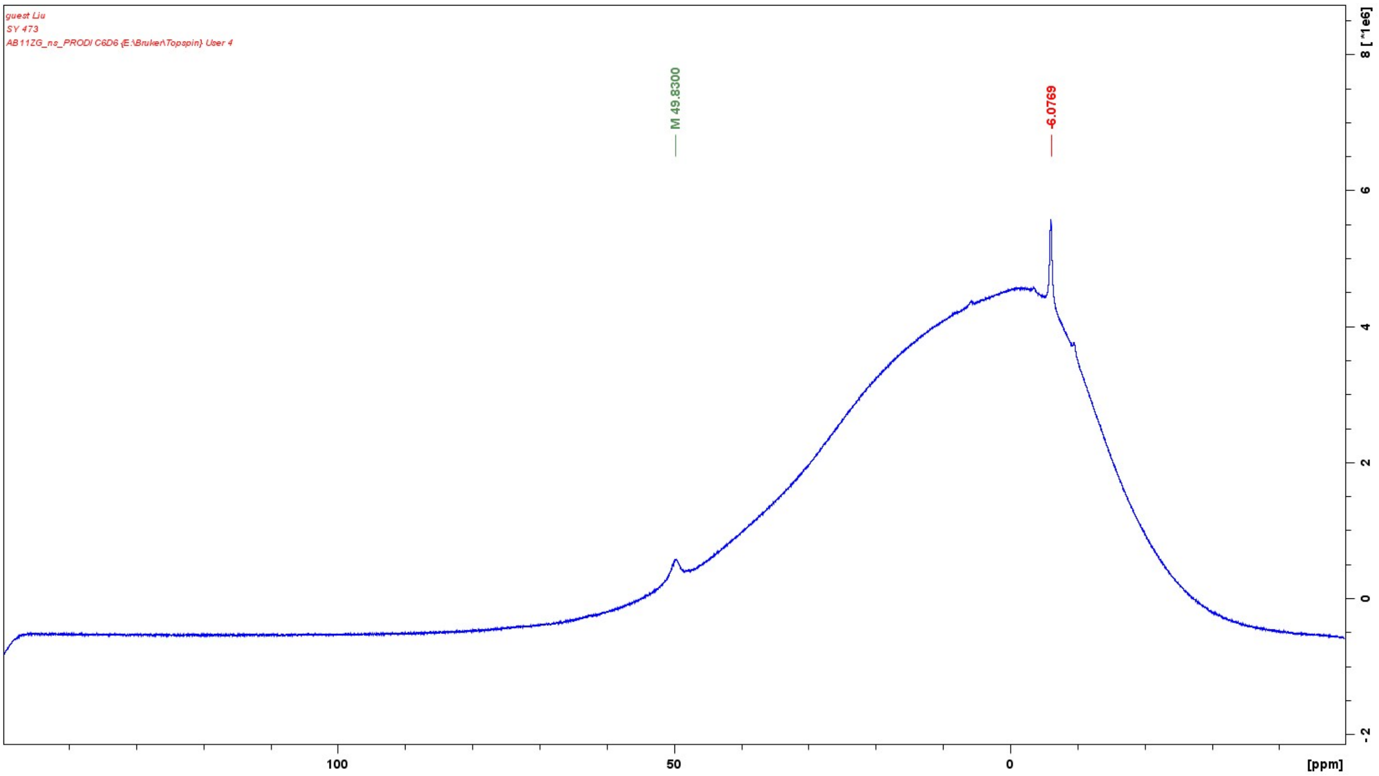


Figure S-3 $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) spectrum of **7b.**

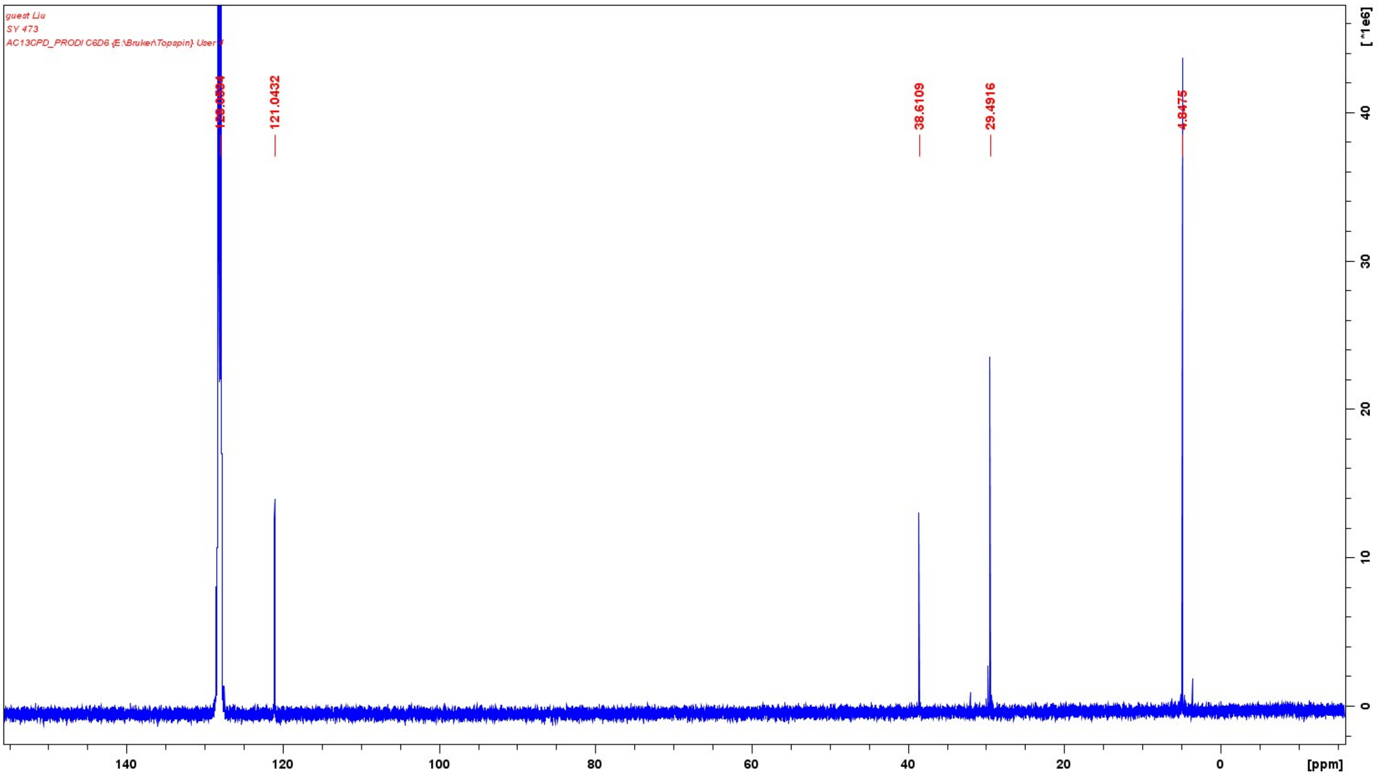


Figure. S-4 $^{1}H$ NMR (500 MHz, $C_6D_6$) spectrum of **9b.**

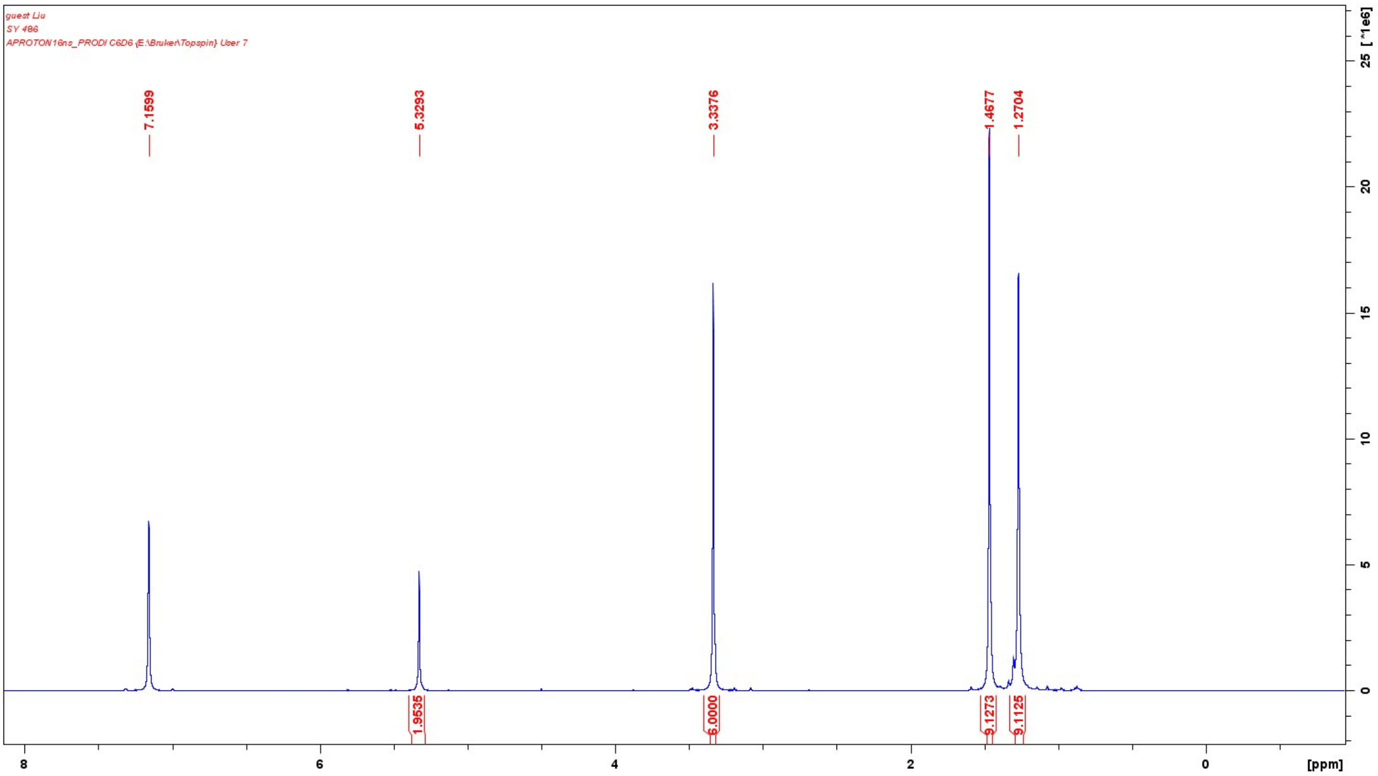


Figure S-5 $^{11}$B NMR (160 MHz, $C_6D_6$) spectrum of **9b**.

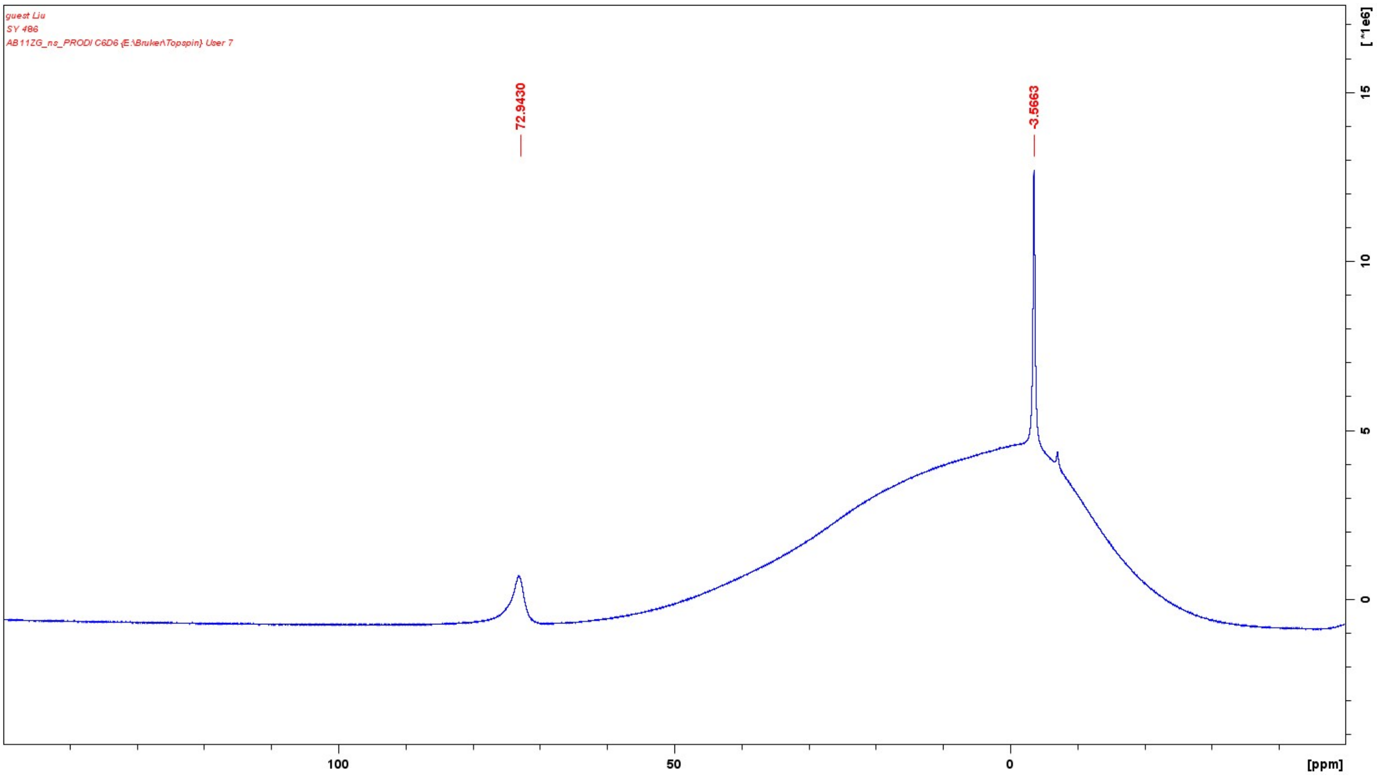


Figure S-6 $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$) spectrum of **9b**

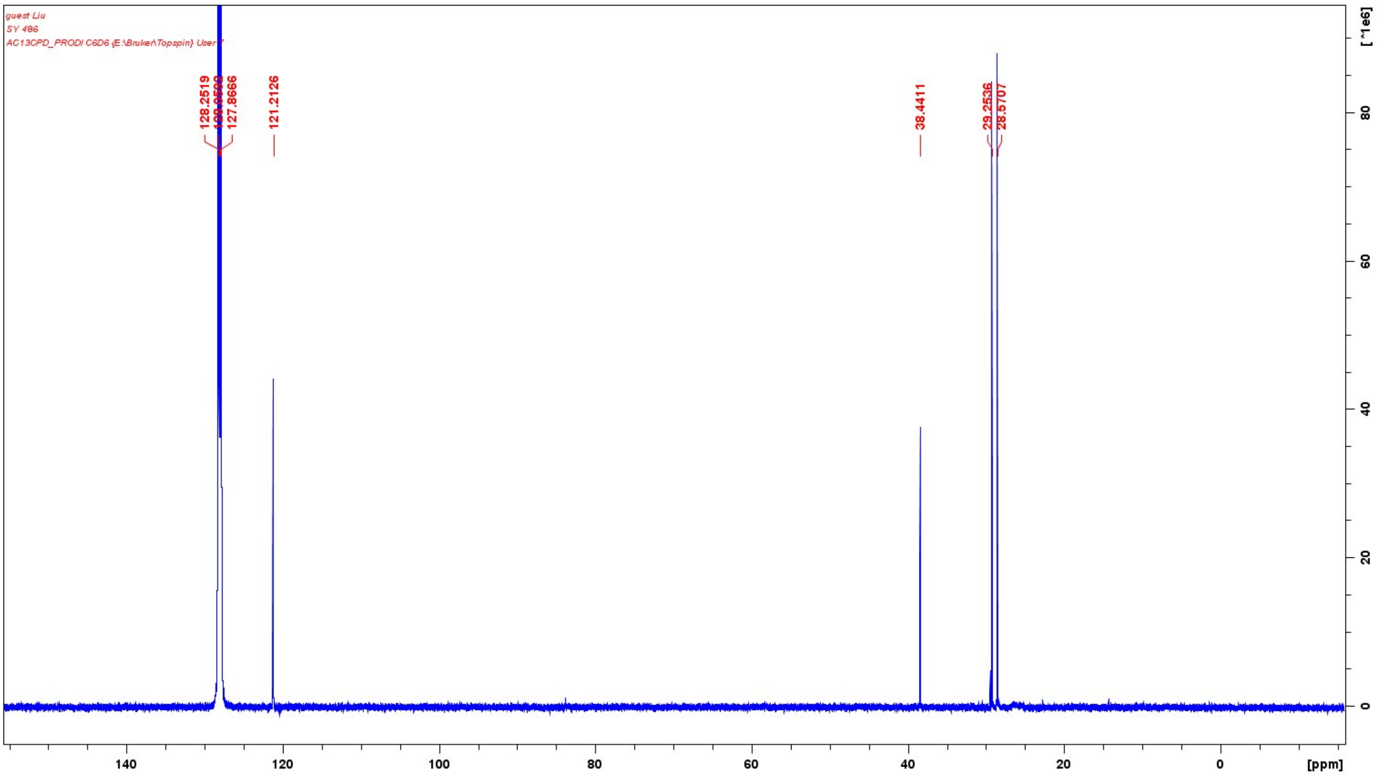


Figure. S-7 $^1$H NMR (400 MHz, $C_4D_8O$) spectrum of **5b.**

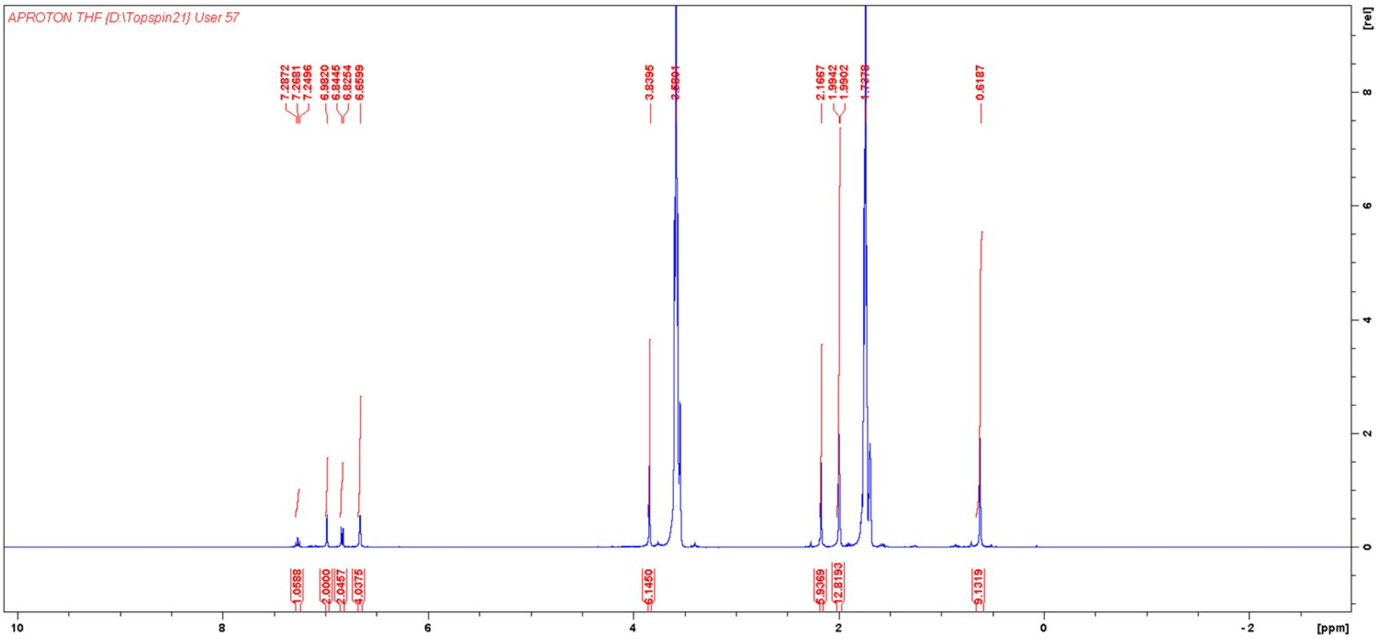


Figure S-8 $^{11}$B NMR (128 MHz, $C_4D_8O$) spectrum of **5b**.

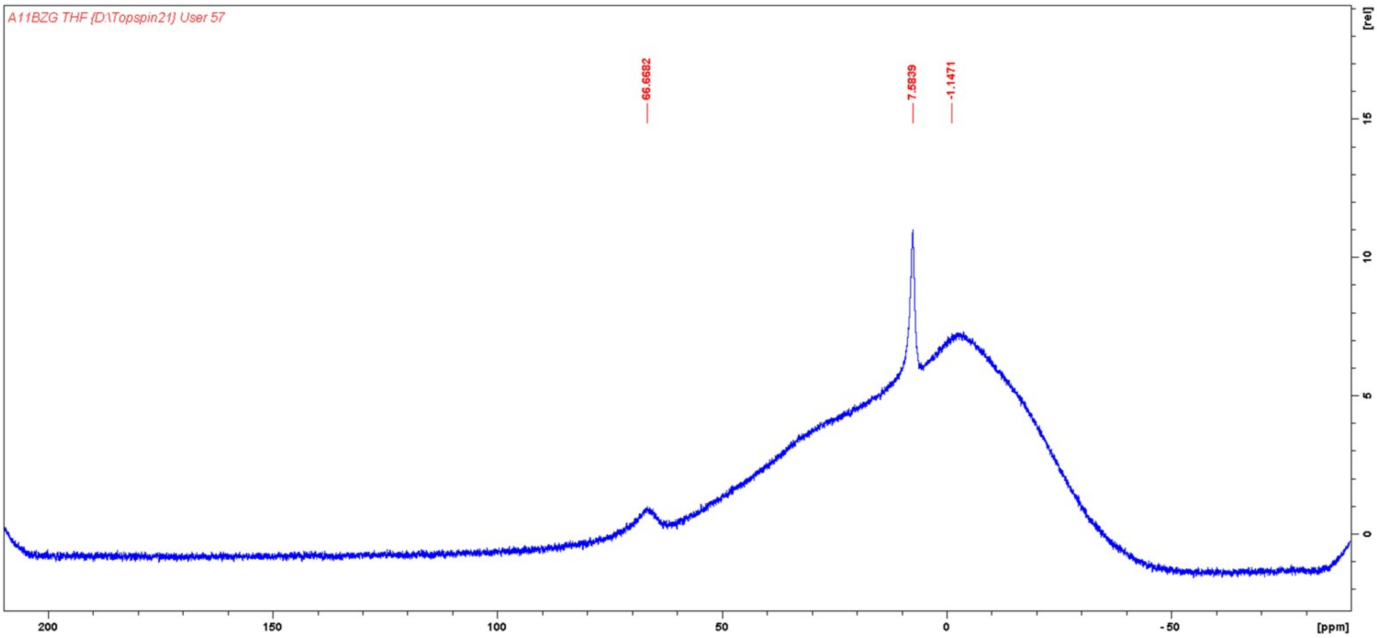


Figure S-9 $^{13}C\{^1H\}$ NMR (100 MHz, $C_4D_8O$) spectrum of **5b**

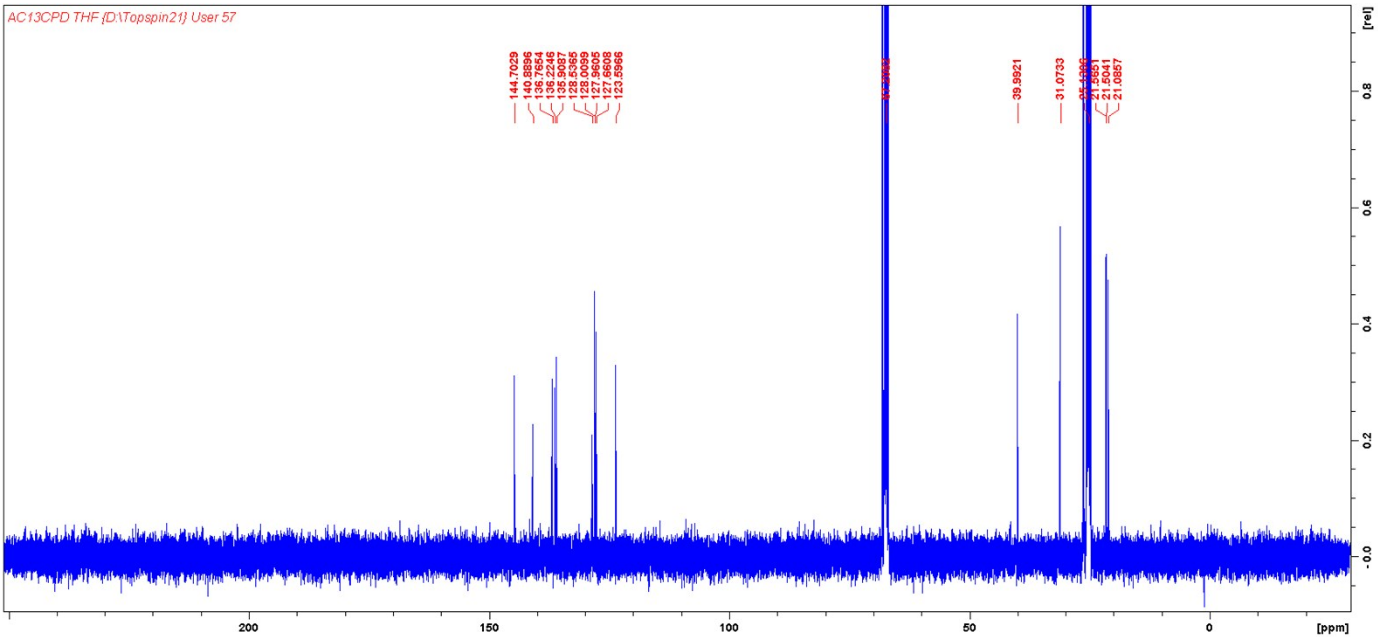


Figure. S-10 $^1H$ NMR (500 MHz, $C_6D_6$) spectrum of **7a.**

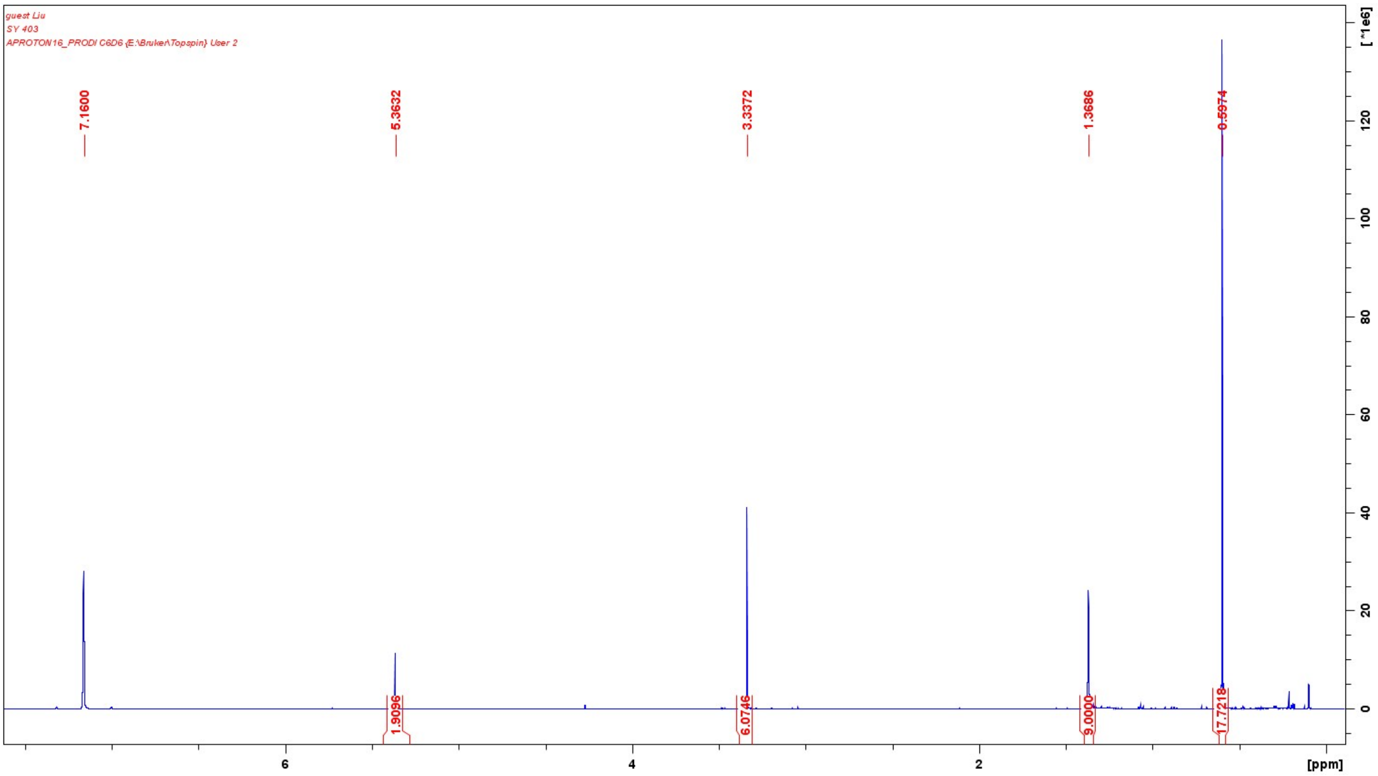


Figure S-11 $^{11}$B NMR (160 MHz, $C_6D_6$) spectrum of **7a**.

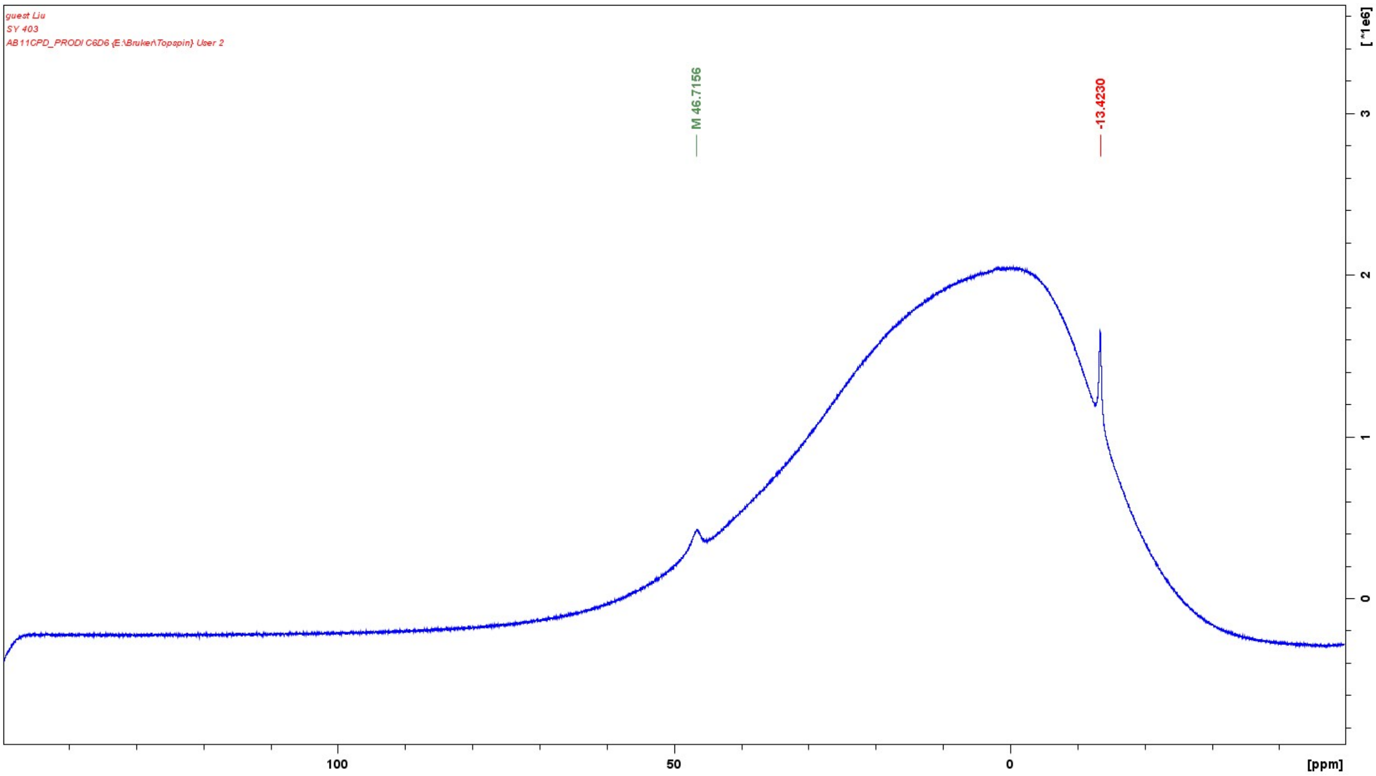


Figure S-12 $^{13}C\{^1H\}$ NMR (125 MHz, $C_6D_6$) spectrum of **7a**

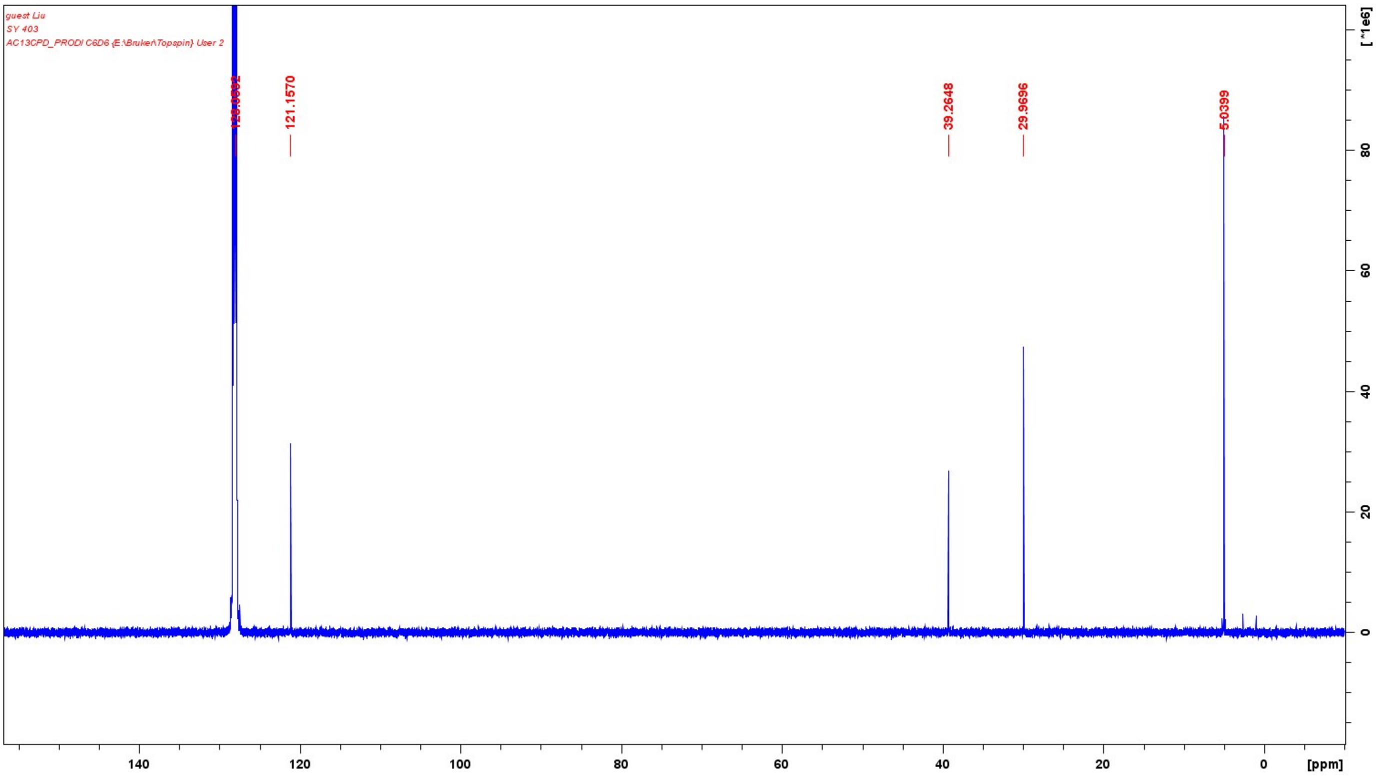


Figure S-13 $^{77}$Se NMR (57 MHz, $C_6D_6$) spectrum of **7a.**

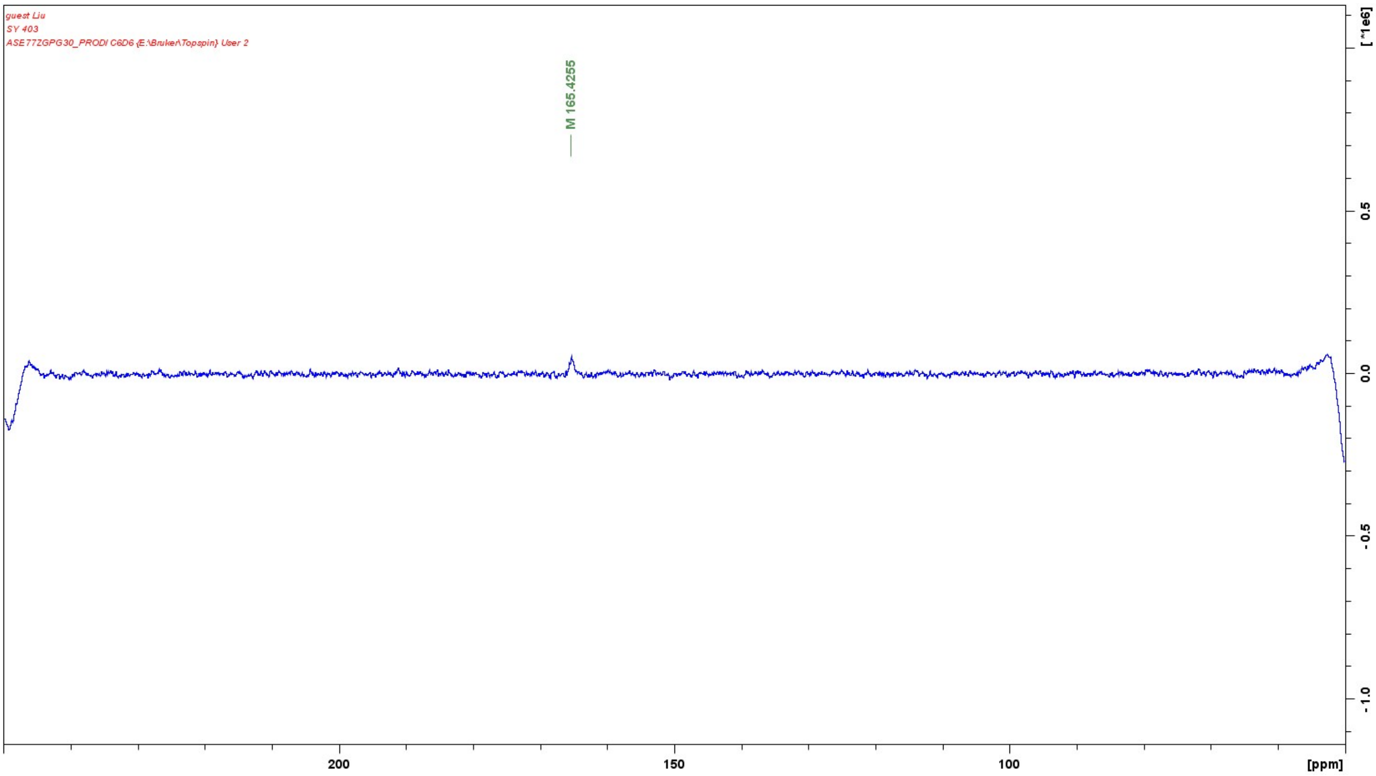


Figure S-14 $^{1}$H NMR (500 MHz, $C_6D_6$) spectrum of **9a.**

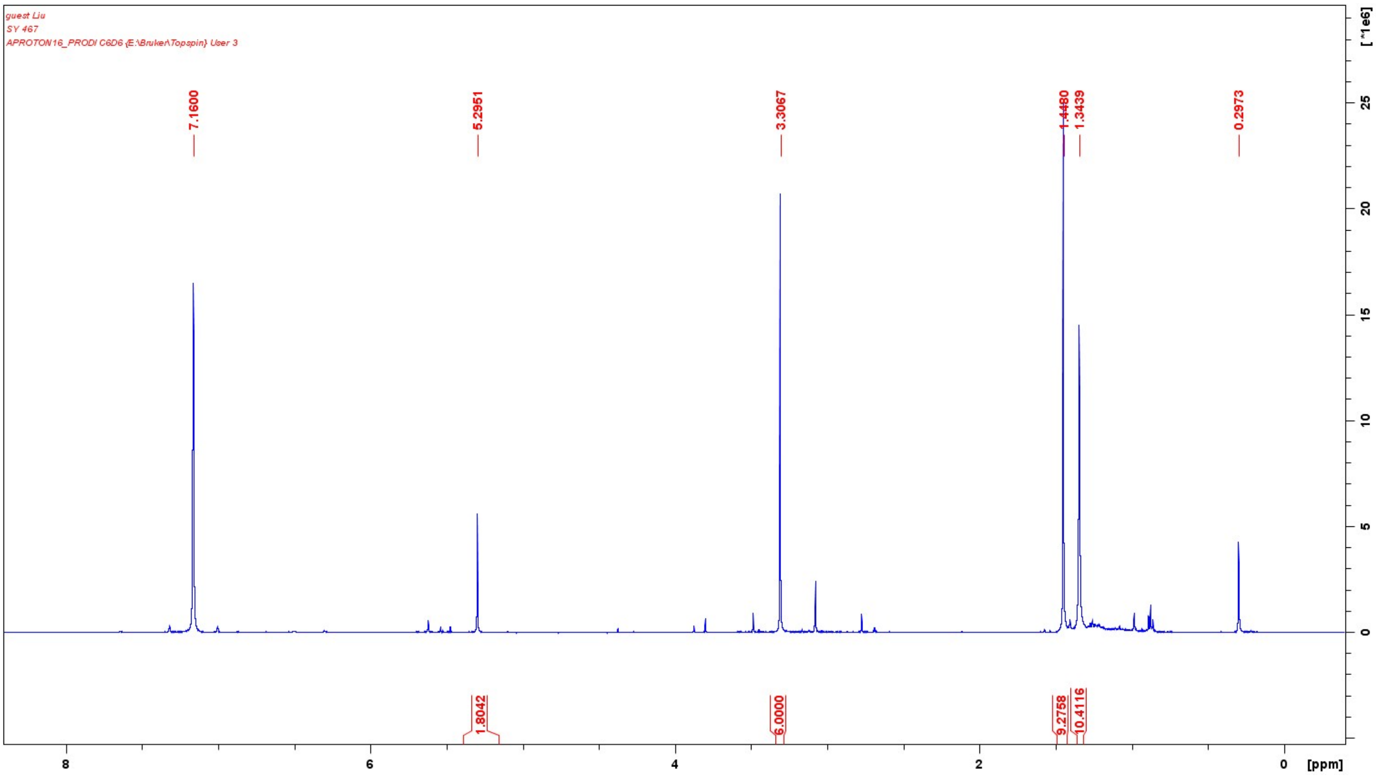


Figure S-15 $^{11}$B NMR (160 MHz, $C_6D_6$) spectrum of **9a**.

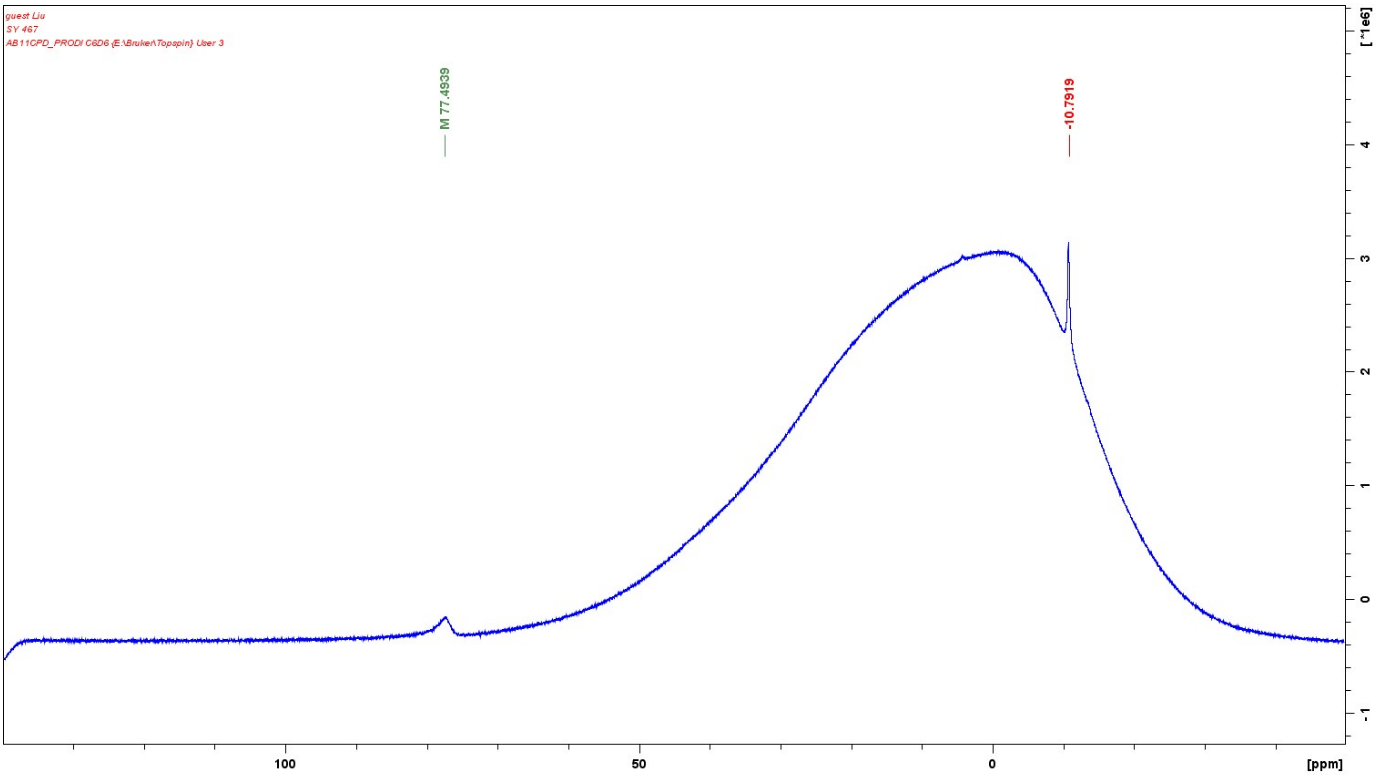


Figure S-16 $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$) spectrum of **9a**

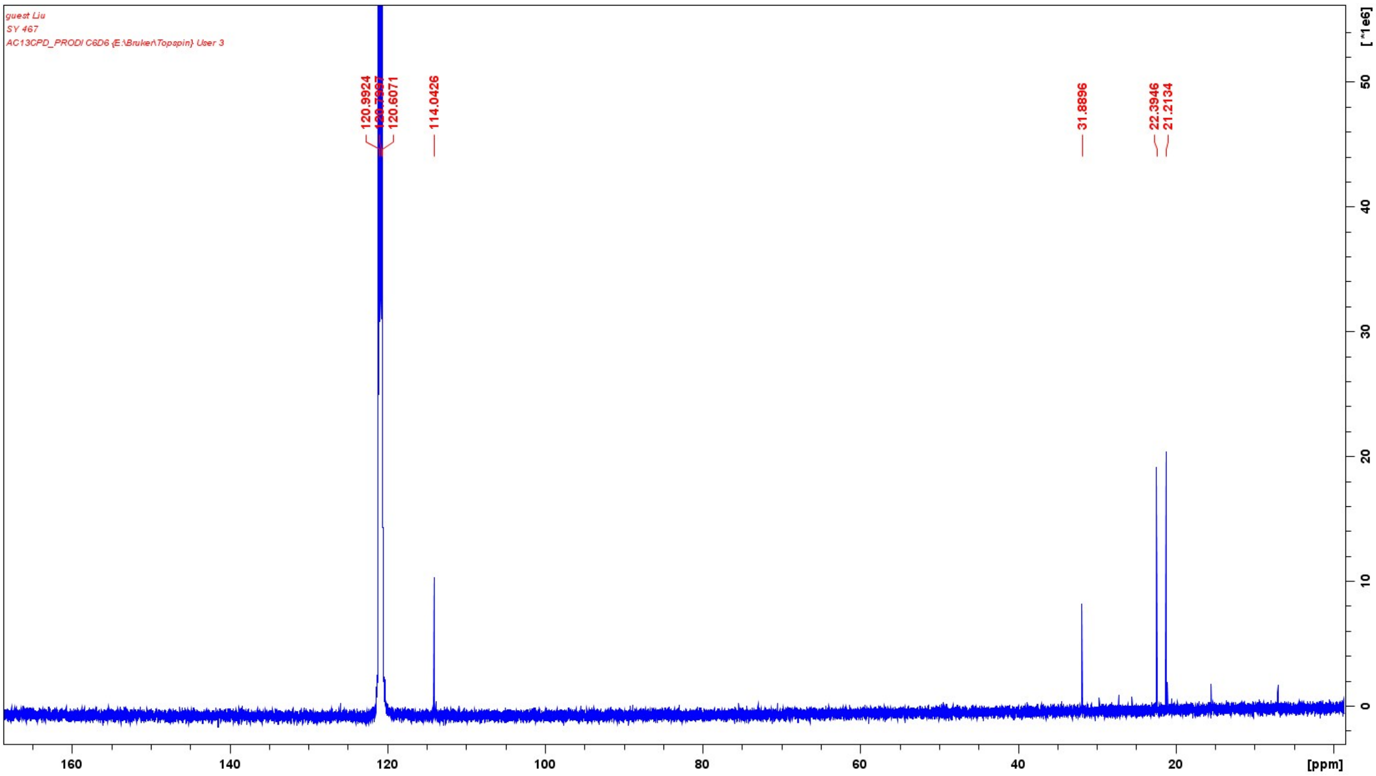


Figure S-17 $^{77}$Se NMR (57 MHz, $C_6D_6$) spectrum of **9a**

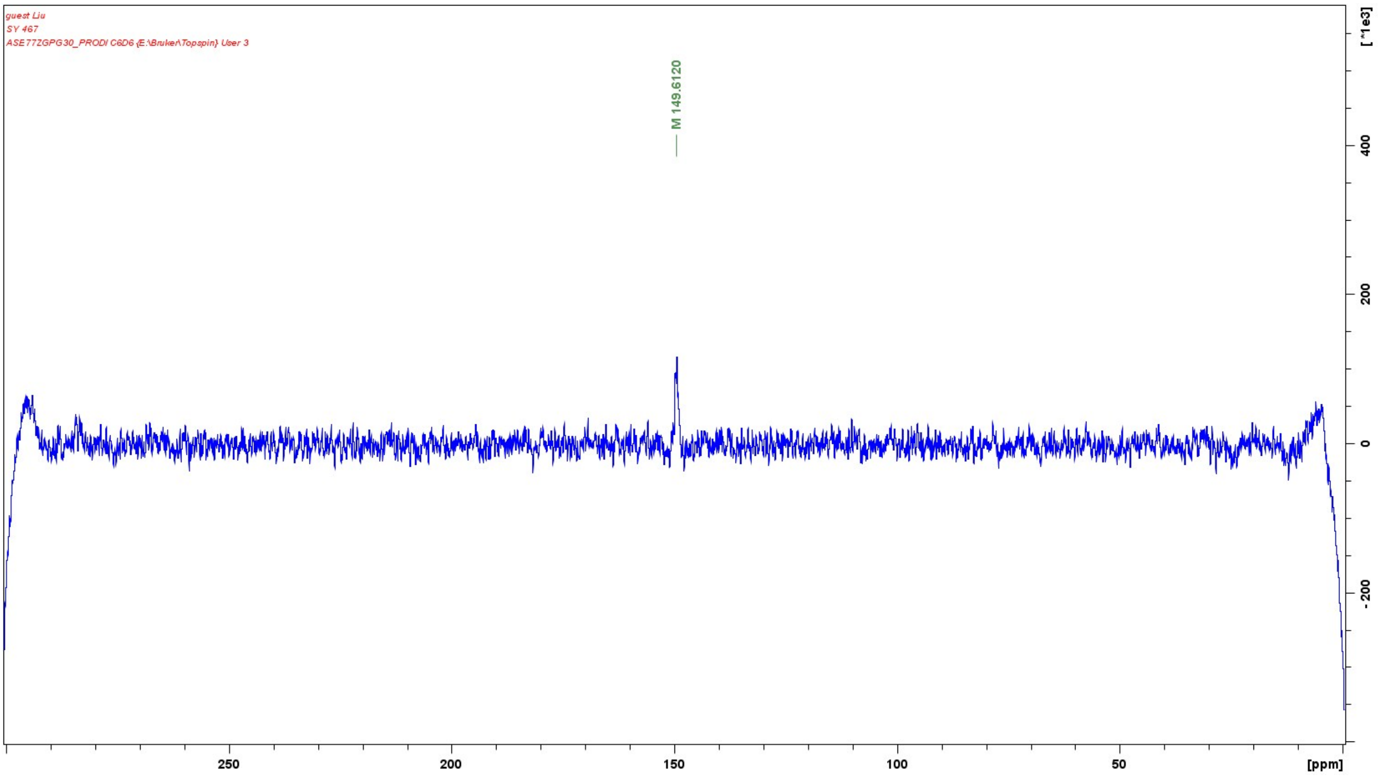


Figure S-18 $^1$H NMR (400 MHz, $C_4D_8O$) spectrum of **5a.**

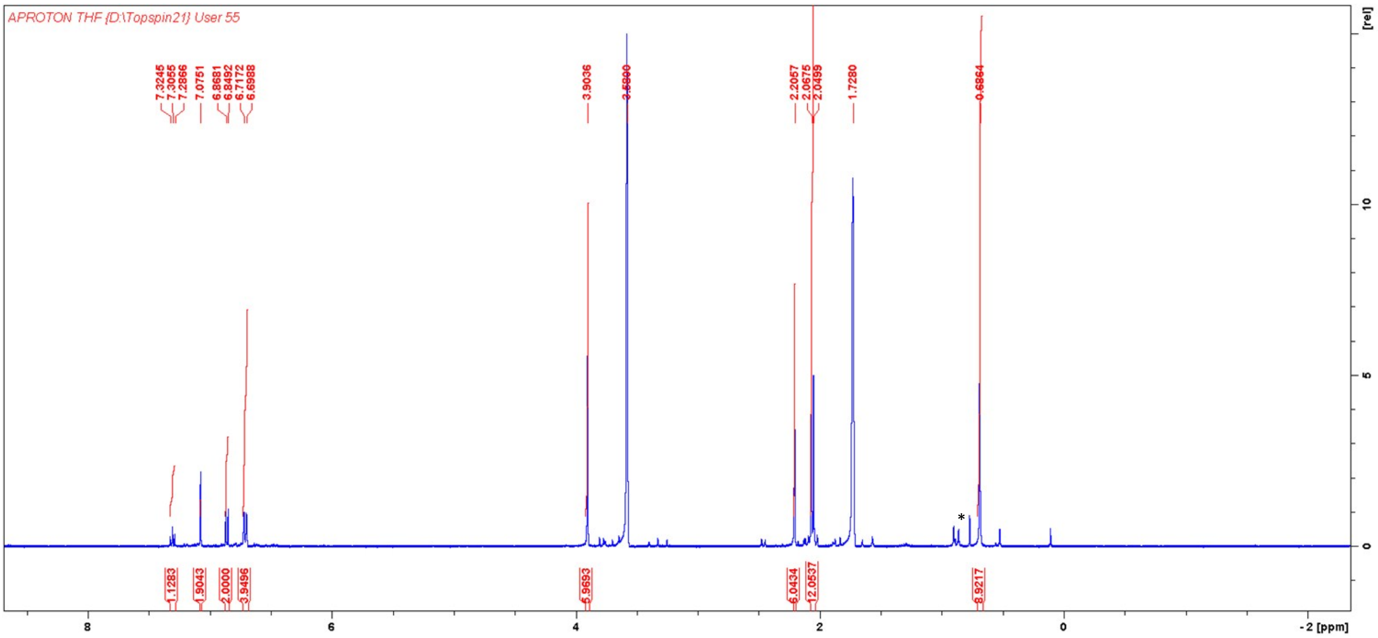


Figure S-19 $^{11}$B NMR (128 MHz, $C_4D_8O$) spectrum of **5a** (*: pentane).

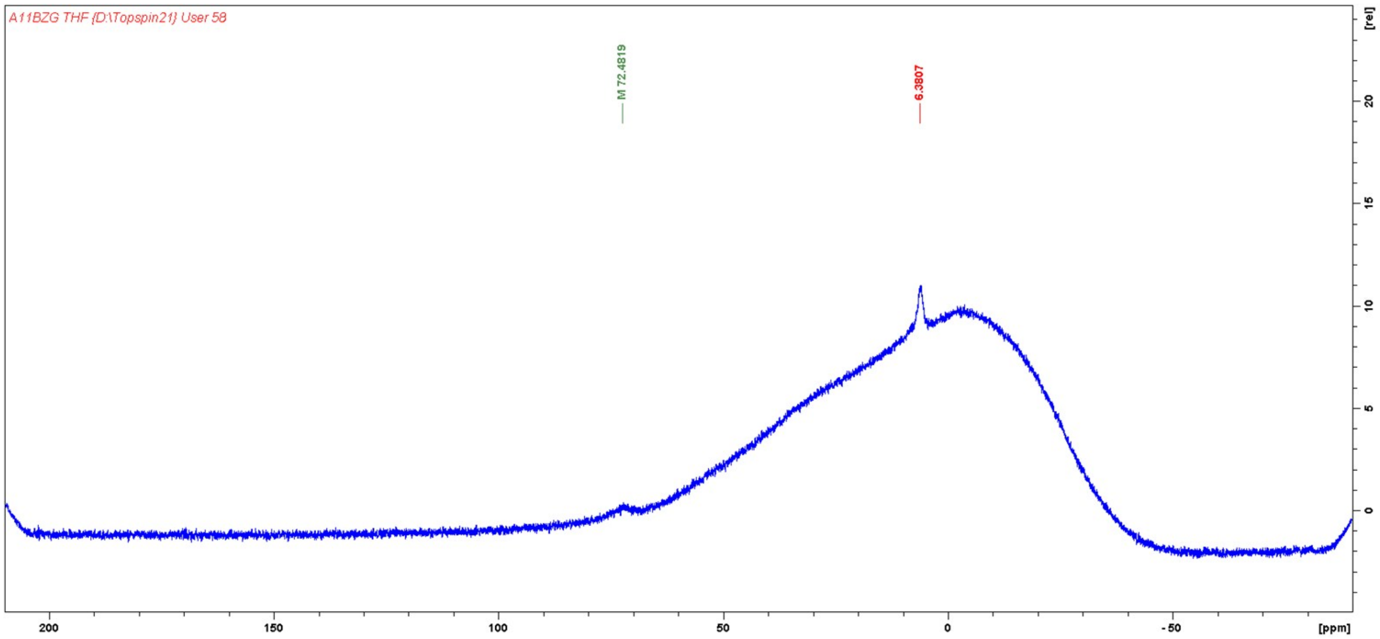


Figure S-20 $^{13}C\{^{1}H\}$ NMR (100 MHz, $C_4D_8O$) spectrum of **5a**

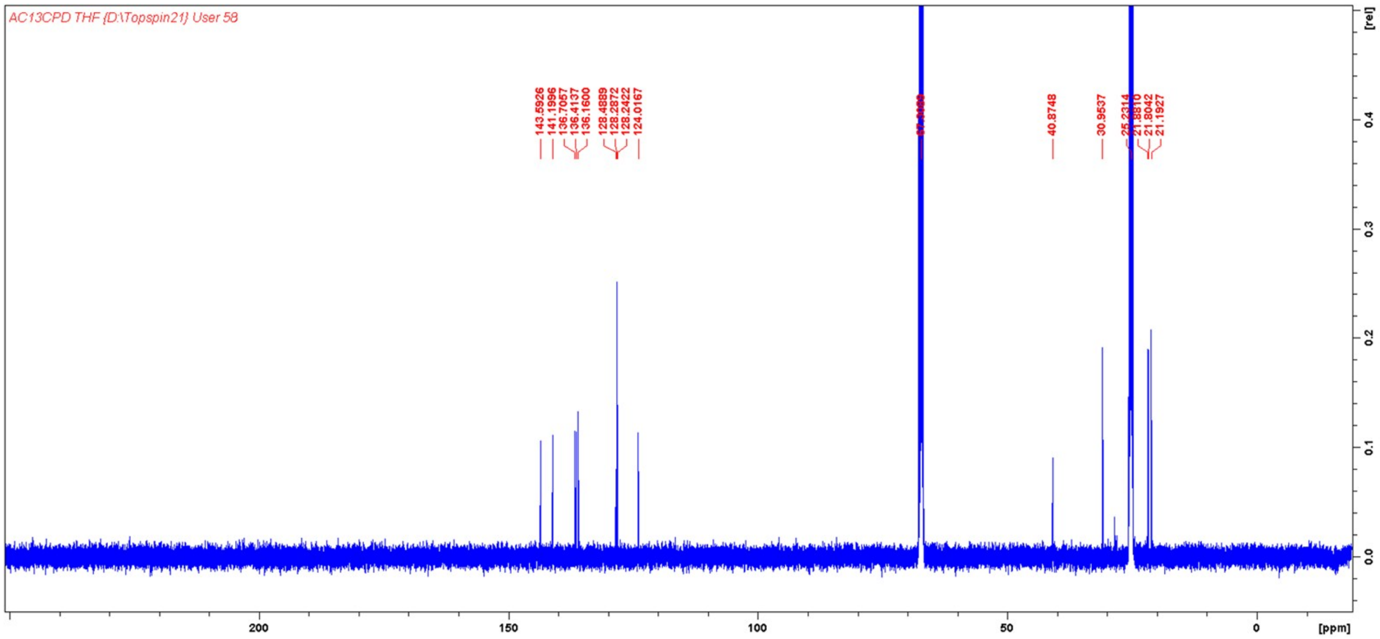


Figure S-21 $^{1}H$ NMR (500 MHz, $C_6D_6$) spectrum of **11.**

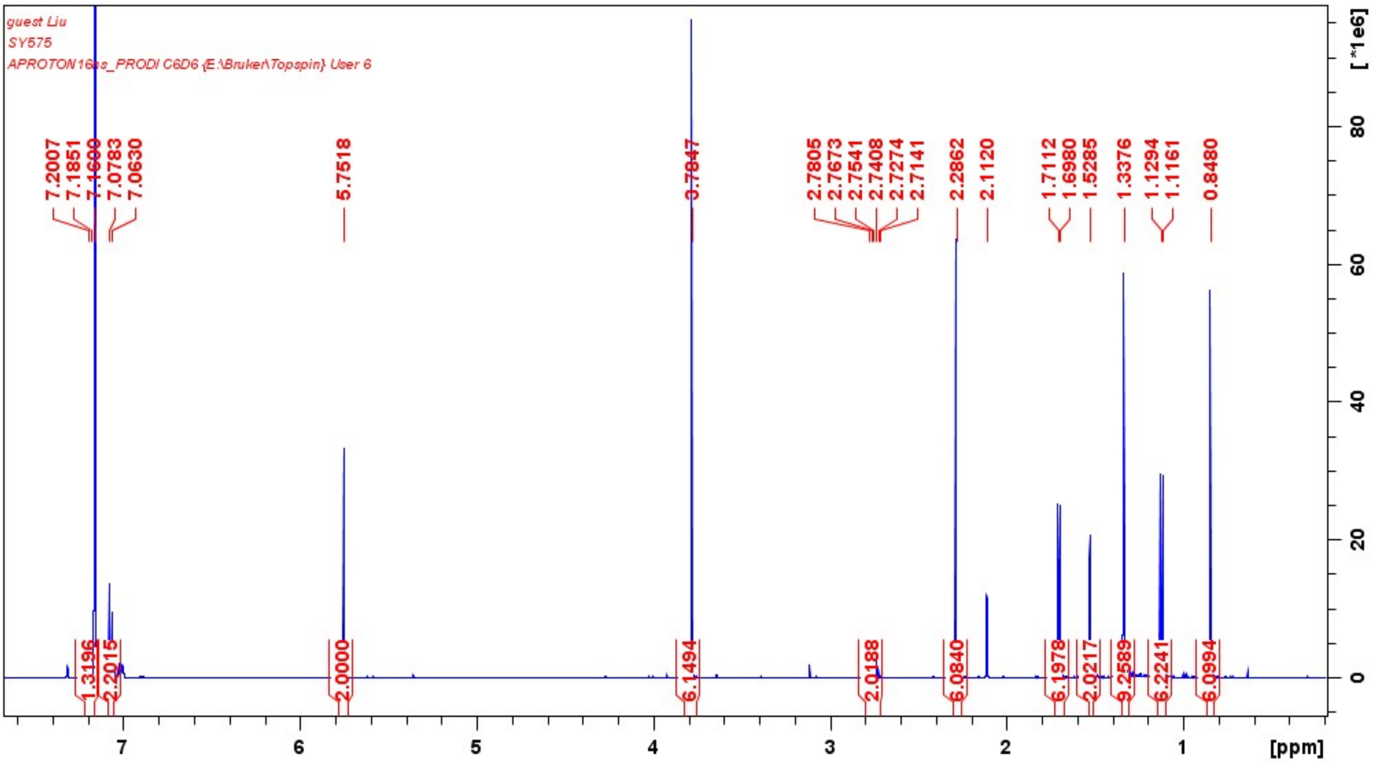


Figure S-22 $^{11}$B NMR (160 MHz, $C_6D_6$) spectrum of **11**.

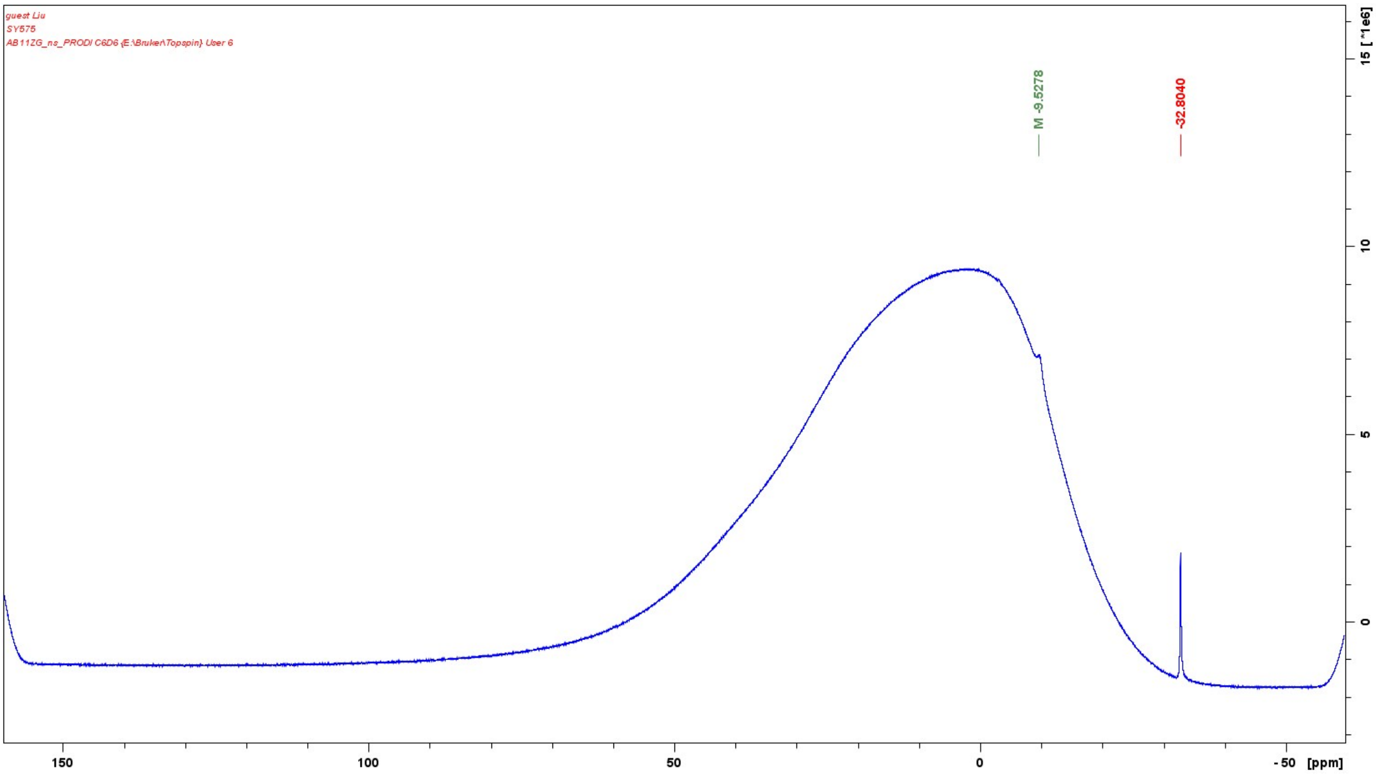


Figure S-23 $^{13}$C{$^{1}$H} NMR (125 MHz, $C_6D_6$) spectrum of **11**

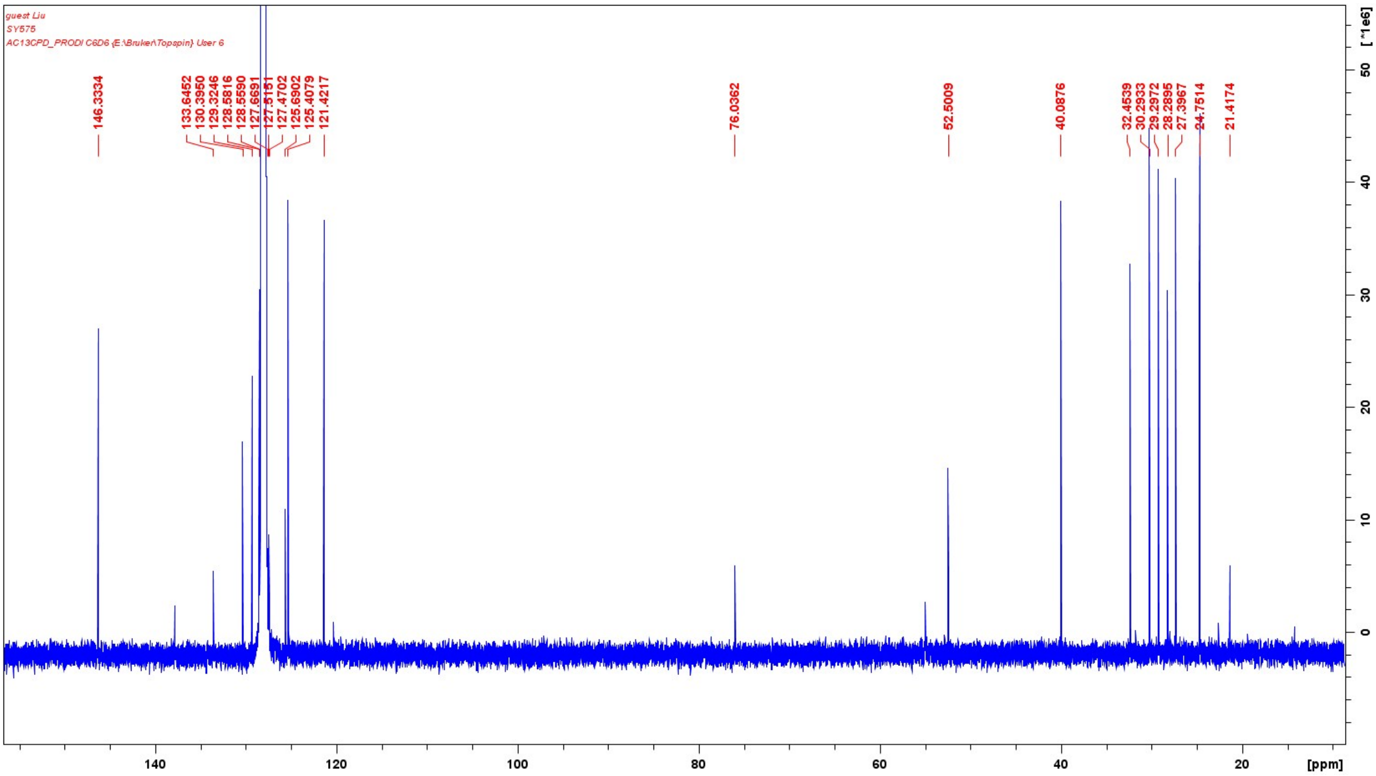


Figure S-24 $^1$H NMR (500 MHz, $C_6D_6$) spectrum of **4**

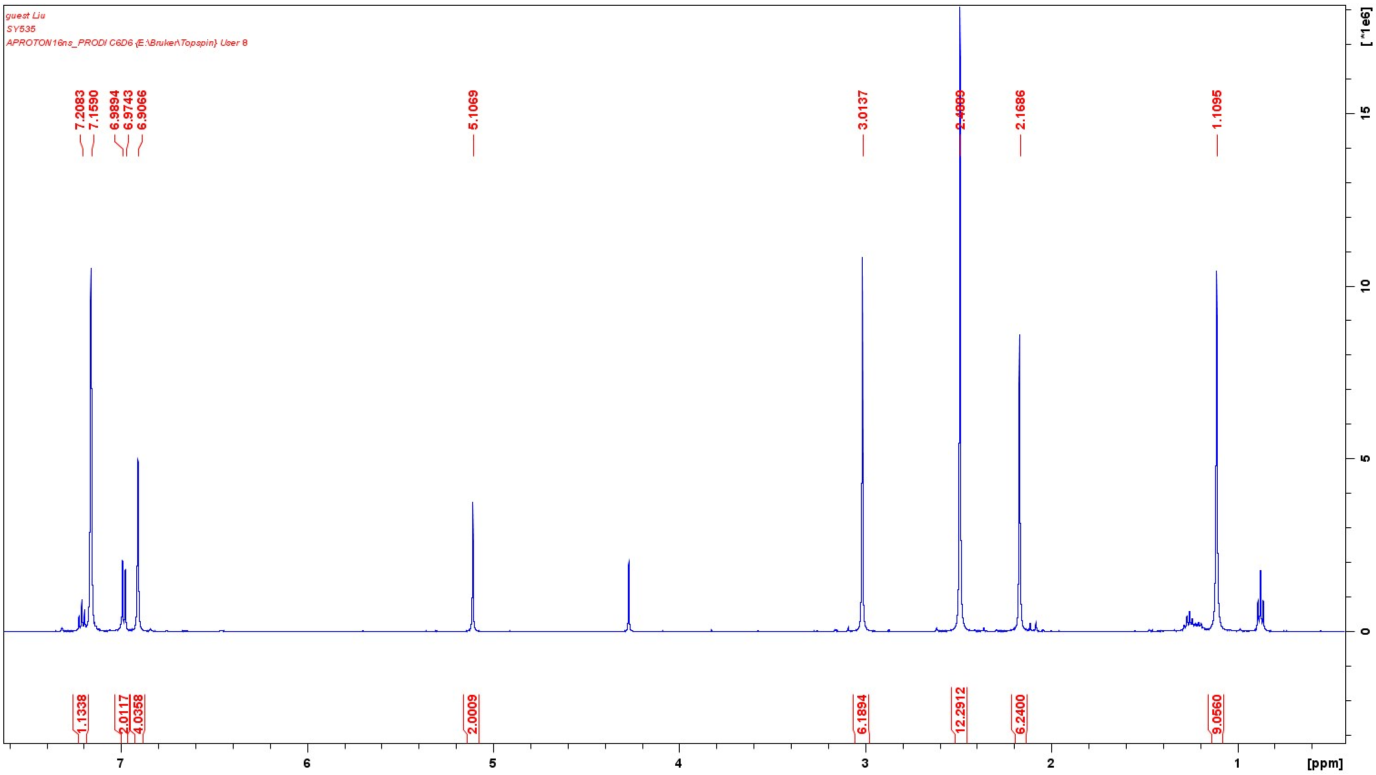


Figure S-25 $^{11}$B NMR (160 MHz, $C_6D_6$) spectrum of **4**.

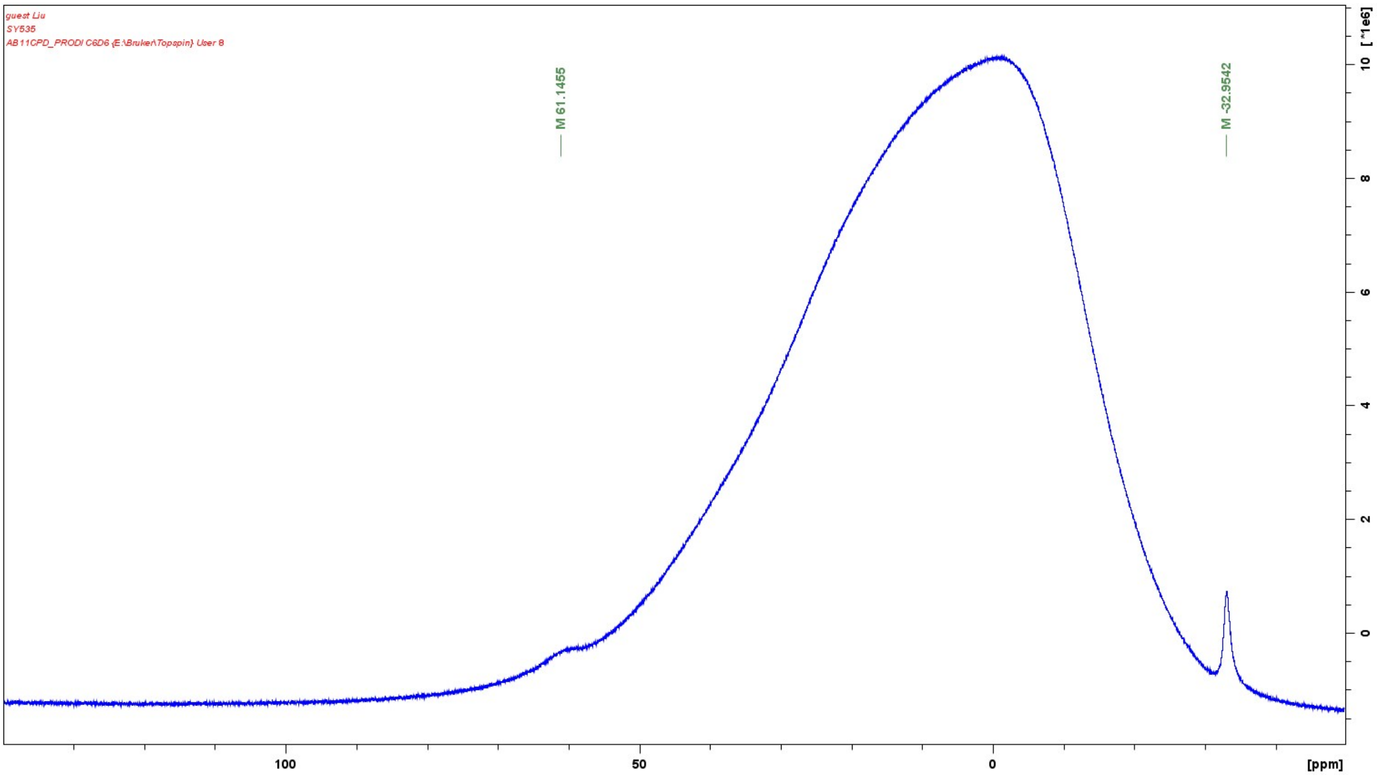


Figure S-23 $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) spectrum of **4**

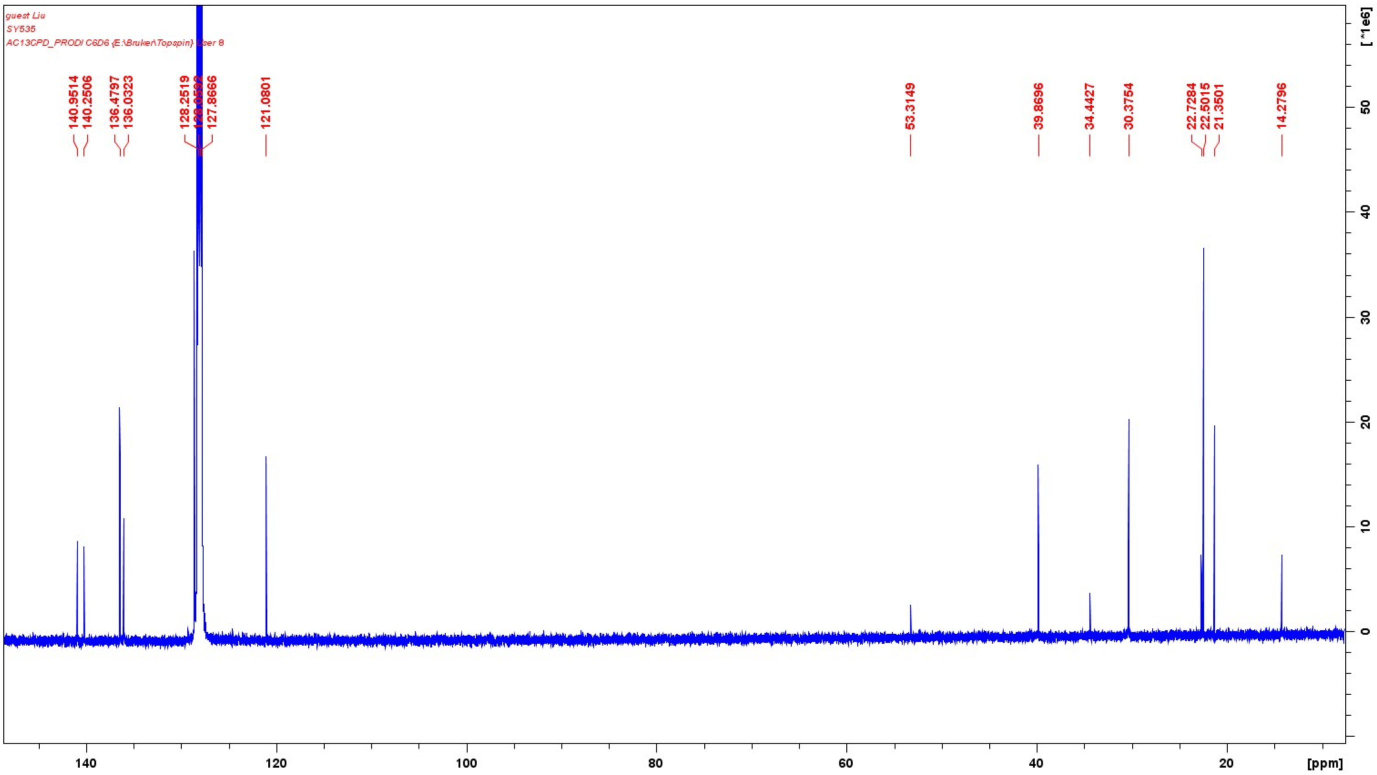
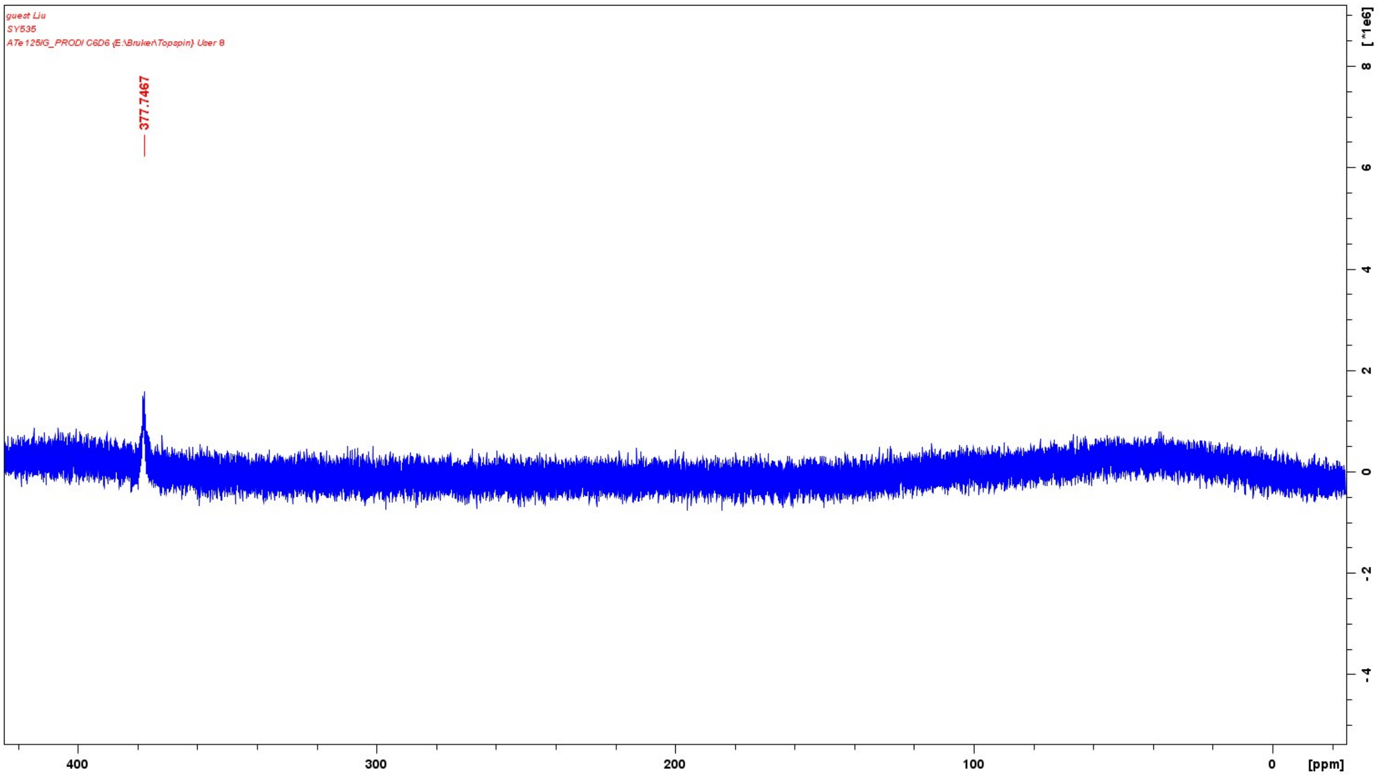


Figure S-23 $^{125}Te$ NMR (157 MHz, $C_6D_6$) spectrum of **4**


guest Liu
SY535
ATe125IG_PRODI C6D6 {E:\Bruker\Topspin} User 8
377.7467
[*1e6]
8
6
4
2
0
-2
-4
400
300
200
100
0
[ppm]

## HRMS spectra of the compounds

Figure S-24 HRMS spectrum of **7b**

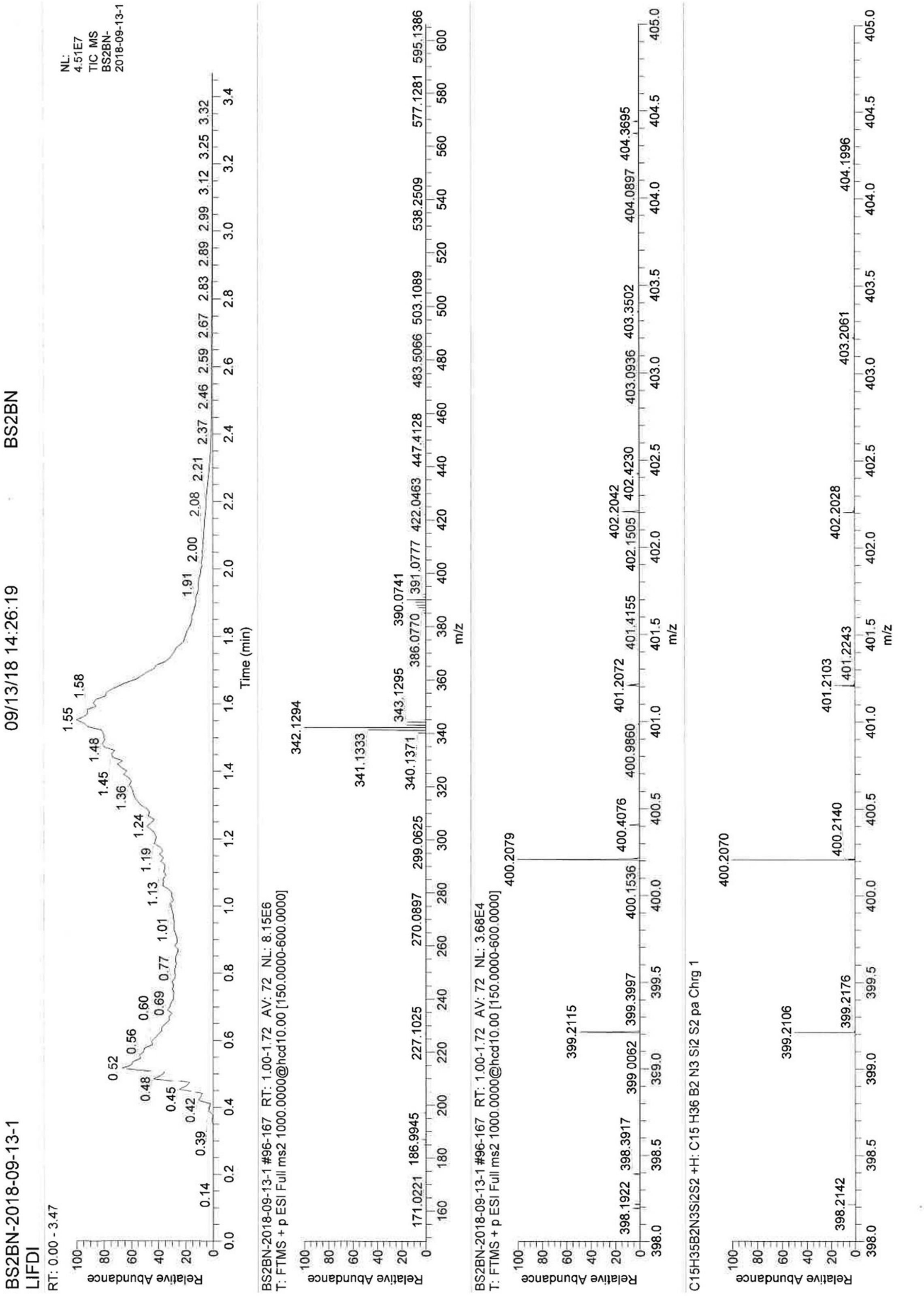


Figure S-25 HRMS spectrum of **9b**

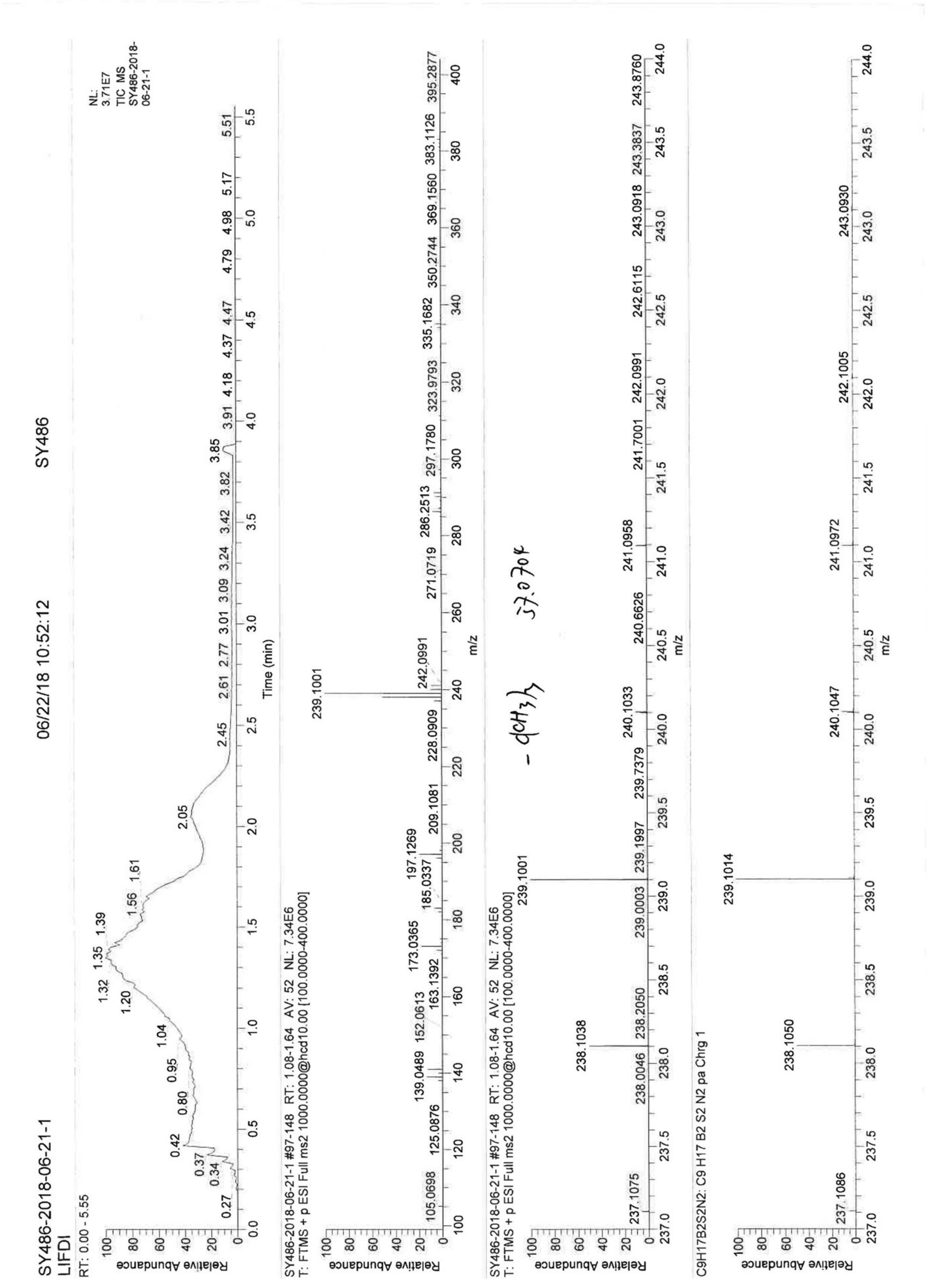


Figure S-26 HRMS spectrum of **5b**

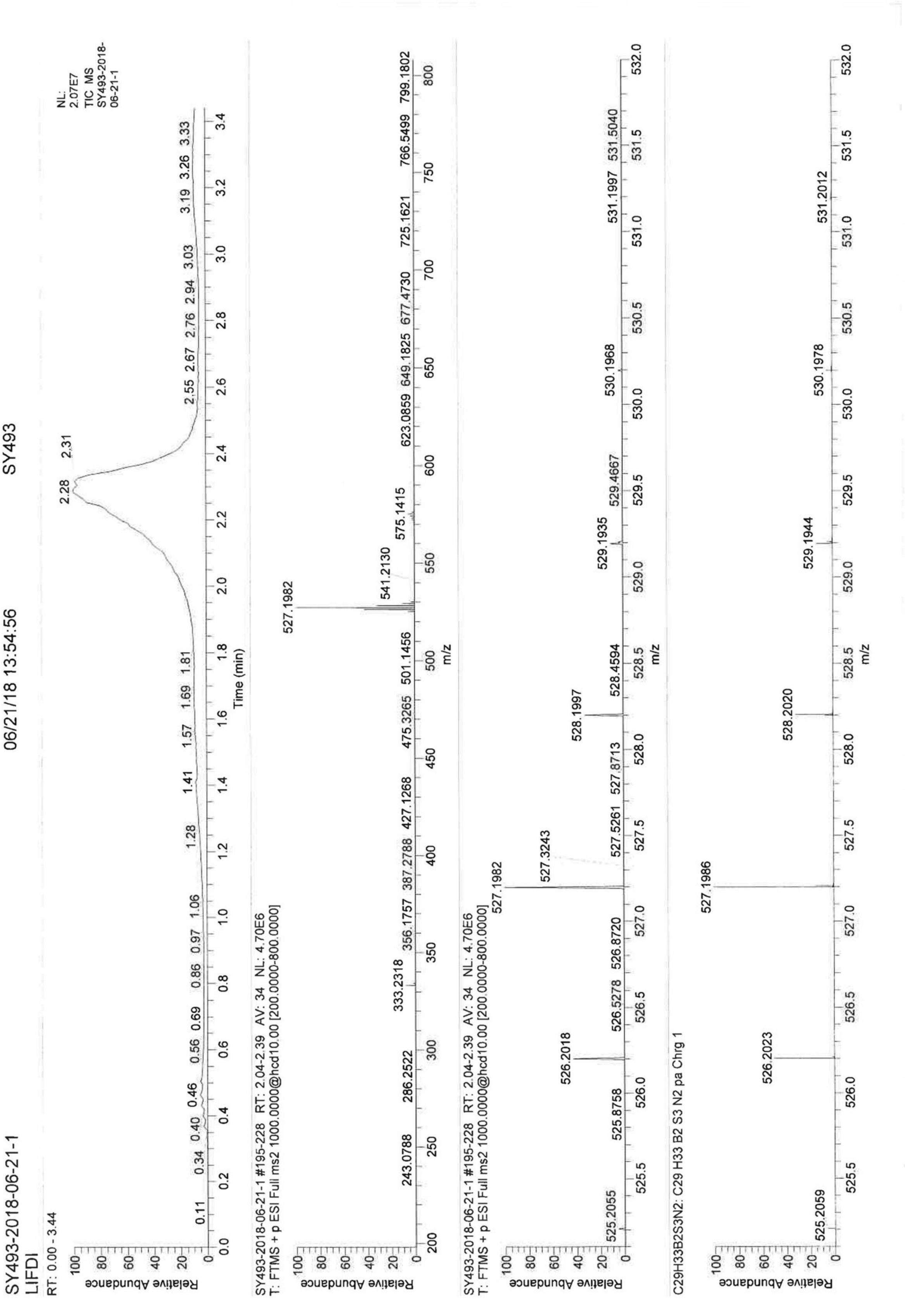


Figure S-27 HRMS spectrum of **7a**

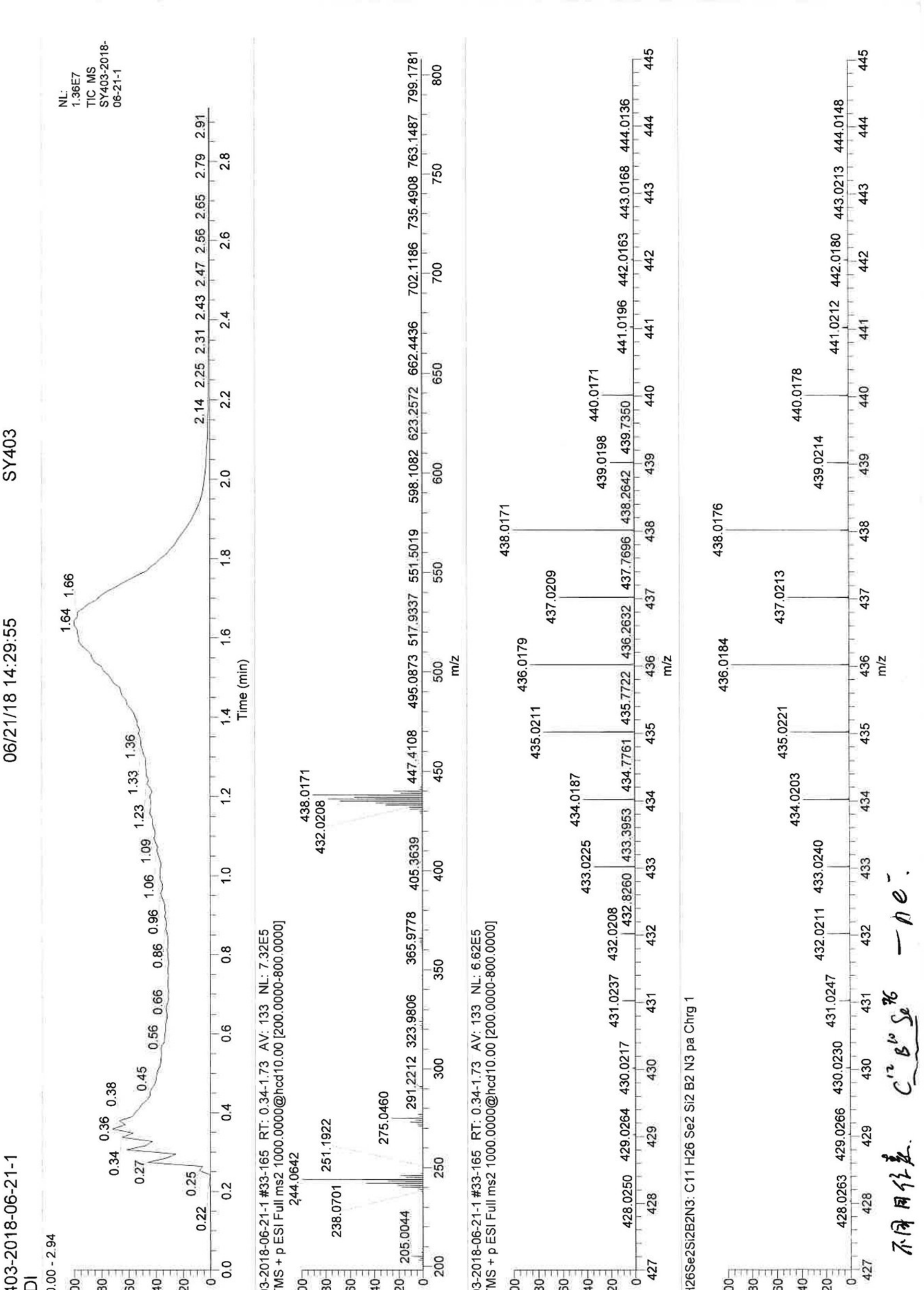


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Figure S-28 HRMS spectrum of **9a**

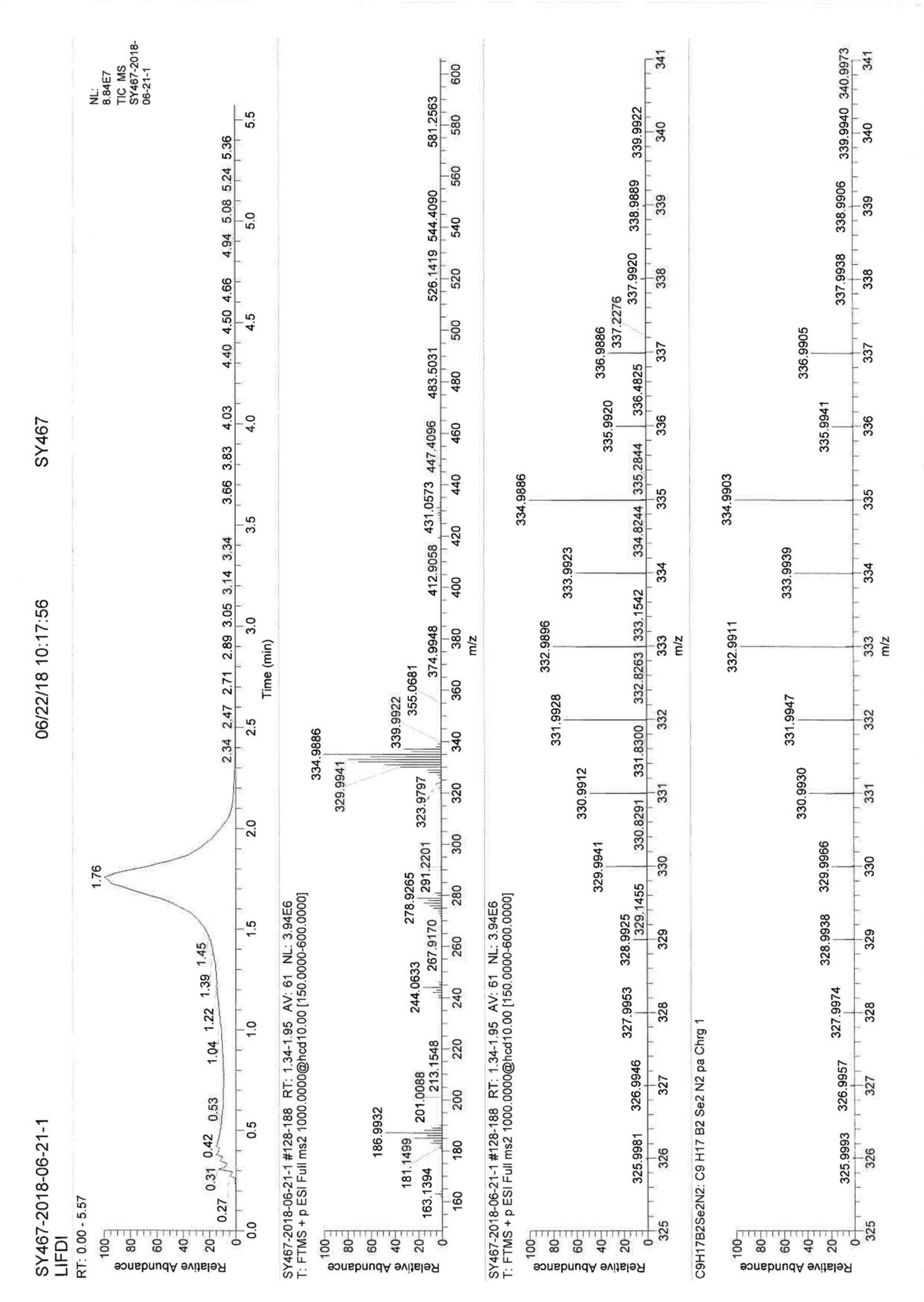


Figure S-29 HRMS spectrum of **5a**

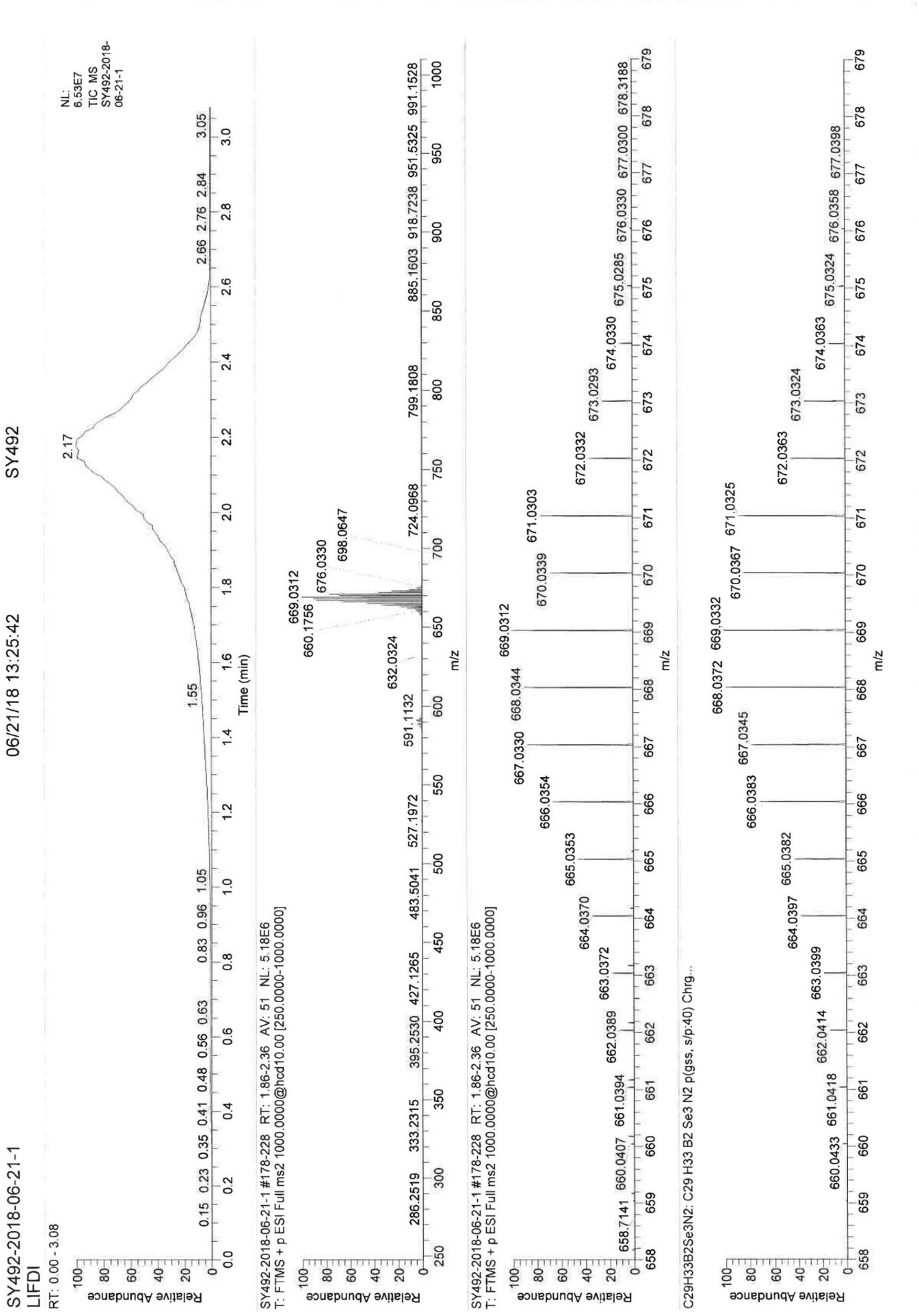


Figure S-30 HRMS spectrum of **11**

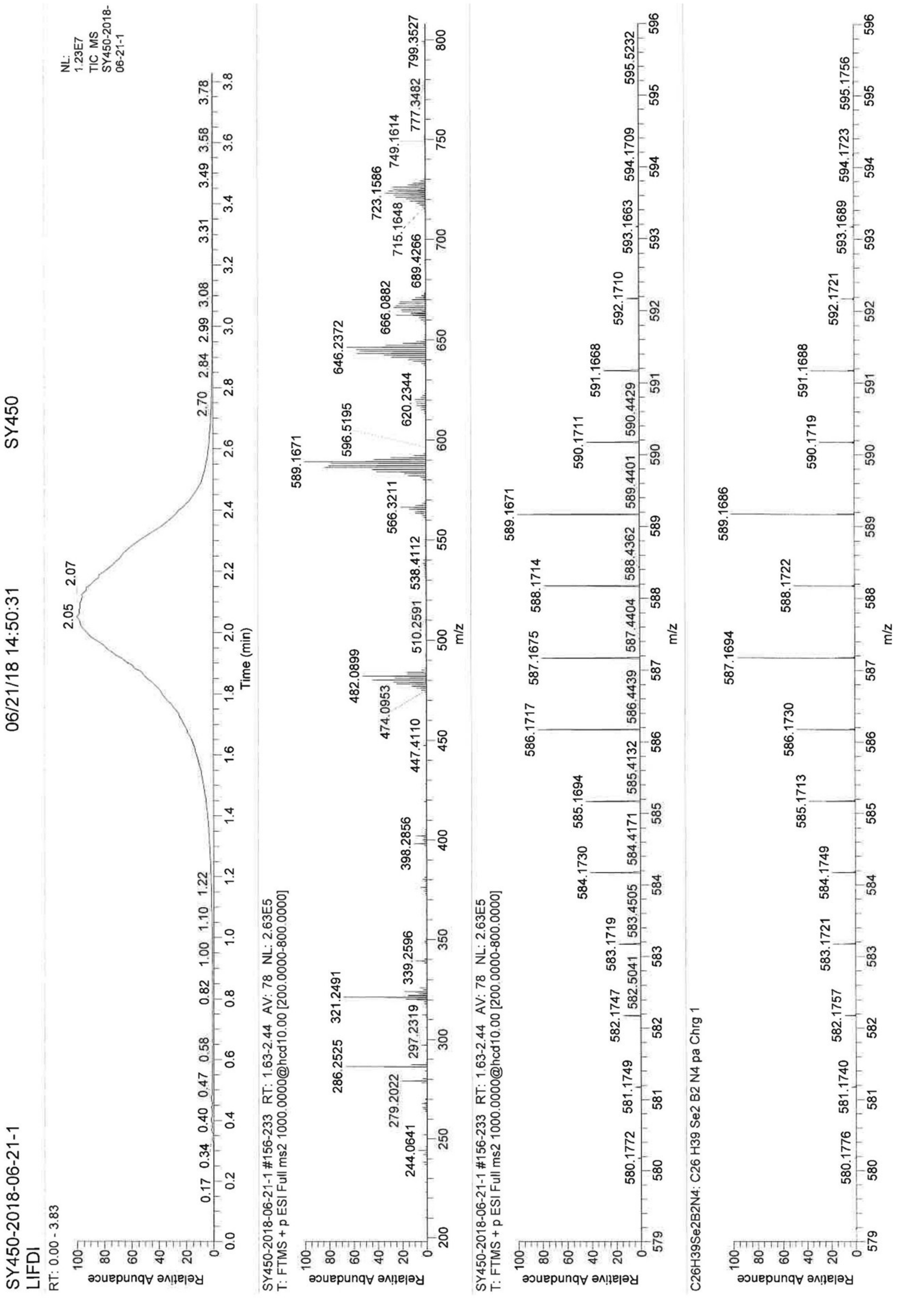
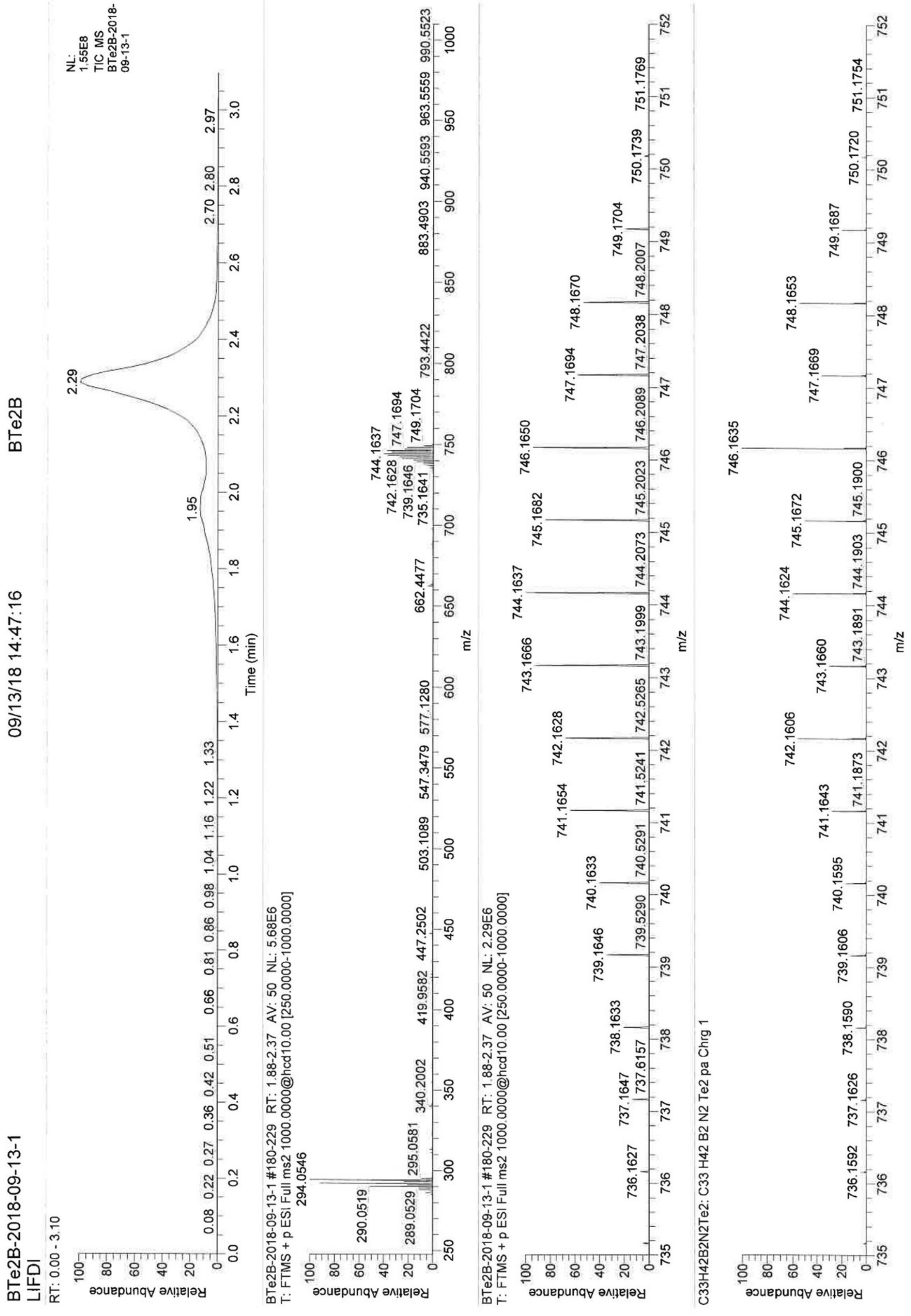


Figure S-31 HRMS spectrum of **4**



## X-ray Structure Determination:

The crystal data of **4, 5-a, 5-b,7-a, 7-b, 11 and 5-a'** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using intrinsic phasing methods,[8] refined with the ShelXL program[9] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for **7-a**: $C_{15}H_{35}B_2N_3Se_2Si_2$, $M_r$ = 493.18, colourless plate, 0.412×0.388×0.146 mm3, monoclinic space group $P2_1/n$, a = 11.500(5) Å, b = 12.544(6) Å, c = 16.944(7) Å, β = 109.60(2)°, V = 2302.8(18) Å3, Z = 4, ρcalcd = 1.423 g·cm–3, μ = 3.319 mm–1, F(000) = 1008, T = 100(2) K, R1 = 0.0668, wR2 = 0.0956, 4531 independent reflections [2θ≤52.034°] and 228 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1886448**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **7-b**: $C_{35}H_{82}B_4N_6S_4Si_4$, $M_r$ = 870.90, yellow block, 0.375×0.258×0.167 $mm^3$, triclinic space group $P\bar{1}$, $a$ = 9.1005(10) Å, $b$ = 11.8019(13) Å, $c$ = 12.4035(13) Å, α = 80.466(3)°, β = 84.795(3)°, γ = 86.977(4)°, $V$ = 1307.4(2) $Å^3$, $Z$ = 1, $\rho_{calcd}$ = 1.106 $g\cdot cm^{-3}$, μ = 0.303 $mm^{-1}$, $F$(000) = 474, $T$ = 100(2) K, $R_1$ = 0.0701, $wR^2$ = 0.1725, 5150 independent reflections [2θ≤52.038°] and 266 parameters.

The displacement parameters of atoms C1_4 > C5_4 were restrained to the same value with similarity restraint SIMU. The atomic displacement parameters of atoms C1_4 > C5_4 were were restrained with RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.001 for both parameters s1 and s2 were used).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1886454**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **5-a**: $C_{33}H_{42}B_2N_2Se_{2.96}$, $M_r$ = 722.39, colourless plate, 0.19×0.185×0.175 $mm^3$, triclinic space group $P\bar{1}$, $a$ = 8.6416(7) Å, $b$ = 13.4779(11) Å, $c$ = 14.6575(12) Å, α = 75.409(3)°, β = 77.096(3)°, γ = 85.540(3)°, $V$ = 1610.0(2) $Å^3$, $Z$ = 2, $\rho_{calcd}$ = 1.490 $g\cdot cm^{-3}$, μ = 3.412 $mm^{-1}$, $F$(000) = 730, $T$ = 100(2) K, $R_1$ = 0.0549, $wR^2$ = 0.0905, 6330 independent reflections [2θ≤52.044°] and 397 parameters.

The displacement parameters of atoms B1_4 and B1_44 as well as B2_4 and B2_44 were constrained to the same value. The displacement parameters of atoms B1_4 > Se3_44 were restrained to the same value with similarity restraint SIMU. The distances between atoms C1_1 B1_4 and C1_1 B1_44 as well as C1_2 B2_4 and C1_2 B2_44 were restrained during refinement to the same value with SADI restraint. The atomic displacement parameters of atoms B1_4 > Se3_44 were restrained with RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.001 for both parameters s1 and s2 were used).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1886449**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **5-b**: $C_{33}H_{42}B_2N_2S_3$, $M_r$ = 584.48, ? needle, 0.488×0.379×0.11 mm$^3$, triclinic space group $P\bar{1}$, $a$ = 8.4766(11) Å, $b$ = 13.3667(19) Å, $c$ = 14.6143(19) Å, $\alpha$ = 75.204(4)°, $\beta$ = 77.352(4)°, $\gamma$ = 85.490(4)°, $V$ = 1561.7(4) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.243 g·cm$^{-3}$, $\mu$ = 0.263 mm$^{-1}$, $F$(000) = 624, $T$ = 100(2) K, $R_1$ = 0.2750, $wR^2$ = 0.4813, 6136 independent reflections [$2\theta \le 52.038°$] and 373 parameters.

The low quality of the obtained data allows only a proof of connectivity.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1886451**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **4**: $C_{33}H_{42}B_2N_2Te_2$, $M_r$ = 743.50, colourless needle, 0.397×0.288×0.108 mm$^3$, triclinic space group $P\bar{1}$, $a$ = 8.8783(8) Å, $b$ = 13.1076(11) Å, $c$ = 14.7911(13) Å, $\alpha$ = 73.716(2)°, $\beta$ = 75.160(3)°, $\gamma$ = 83.313(2)°, $V$ = 1595.3(2) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.548 g·cm$^{-3}$, $\mu$ = 1.853 mm$^{-1}$, $F$(000) = 736, $T$ = 100(2) K, $R_1$ = 0.0239, $wR^2$ = 0.0559, 6279 independent reflections [$2\theta \le 52.044°$] and 363 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1886452**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **11**: $C_{30}H_{48}B_2N_4Se_2$, $M_r$ = 644.26, red block, 0.555×0.41×0.242 mm$^3$, triclinic space group $P\bar{1}$, $a$ = 9.2253(4) Å, $b$ = 13.3449(5) Å, $c$ = 14.4581(6) Å, $\alpha$ = 107.0150(10)°, $\beta$ = 93.8670(10)°, $\gamma$ = 90.0350(10)°, $V$ = 1697.77(12) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.260 g·cm$^{-3}$, $\mu$ = 2.201 mm$^{-1}$, $F$(000) = 668, $T$ = 100(2) K, $R_1$ = 0.0202, $wR^2$ = 0.0455, 6448 independent reflections [$2\theta \le 51.364°$] and 357 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1886450**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **5-a'**: $C_{33}H_{42}B_2N_2Se_2$, $M_r$ = 646.22, colourless plate, 0.296×0.134×0.129 mm$^3$, monoclinic space group $P2_1/n$, $a$ = 12.9542(7) Å, $b$ = 12.1291(7) Å, $c$ = 20.4231(10) Å, $\beta$ = 90.590(2)°, $V$ = 3208.8(3) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.338 g·cm$^{-3}$, $\mu$ = 2.328 mm$^{-1}$, $F$(000) = 1328, $T$ = 100(2) K, $R_1$ = 0.0792, $wR^2$ = 0.0858, 6084 independent reflections [$2\theta \le 51.362°$] and 363 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**1886453**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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