Supplementary Information for:

# Structure-property-reactivity studies on dithiaphospholes

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Contents

## S1 Single crystal X-ray diffraction

### S1.1 Single crystal X-ray diffraction experimental

Single crystals of **1a–1c** and **2a–2c** were grown in a glovebox under a dinitrogen atmosphere. Crystals of **3b** were obtained by slow evaporation of a saturated $CH_2Cl_2$ solution under $N_2$. Crystals of **4** were grown by slow evaporation of a saturated toluene solution. Crystals of **1e** were formed by storing a saturated solution at −20 °C.

Crystallographic studies on **1a–1c** and **2a–2c** were undertaken on single crystal mounted in paratone and studied on an Agilent SuperNova Dual Atlas three-circle diffractometer using Mo- or Cu-Kα radiation and a CCD detector. Measurements were taken at 150(2) K with temperatures maintained using an Oxford Cryostream. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model within CrysAlisPro.[1] The structures were solved by direct methods and refined against $F^2$ within SHELXL-2013.[2]

Crystallographic studies on **3b**, **4** and **1e** were made on a Bruker APEX diffractometer on crystals mounted in paratone oil using Mo-Kα radiation and a CCD detector. Measurements were recorded at 153(2), 173(2) and 150(2) K respectively with temperatures maintained using an Oxford Cryostream low temperature device. Data for **3b** and **1e** were integrated using SAINT[3] and an absorption correction applied using Sadabs.[4] Data for **4** were integrated as a two component non-merohedral twin using SAINT[3] and an absorption correction applied using Twinabs.[5] The structures were solved by direct methods and refined against $F^2$ with SHELXL 2017/1.[6]

For the structure of **3b**, initial indexing afforded a monoclinic cell with $a$ = 8.0083, $b$ = 9.2891, $c$ = 37.1382, β = 96.153. An initial solution in P2(1) was achieved with DIRDIF[7] and Z' = 4. Residual light atoms were located in subsequent different maps. However refinement stalled at R1 = 18% with many Fo > Fc indicative of twinning. TWINROTMAT within PLATON[7] identified a twin (TWIN -1 0 0 0 -1 0 1 0 1) and the R value plunged to 5%. However the C atoms failed to refine anisotropically (many NPD) and further examination using ADDSYM revealed a missing inversion centre and a smaller cell. Transformation to the smaller cell setting and generation of an HKLF5 format file provided a satisfactory solution with Z' = 1 which refined to R1 < 5%.

For the structure of **1e**, the data reported were the best from multiple crystal examined which were persistently twinned. Structure initially solved in P-1 with one molecule in the asymmetric unit but large residuals. ADDSYM within PLATON[7] identified the higher symmetry P-3 space group and refinement improved but stalled at R1 = 13%. TWINROTMAT identified an inversion twin and led to a

further reduction in R1 by 4%. Although the residuals are still high the connectivity is clear and the refinement was stable and esds on geometric parameters small with molecular connectivity consistent with other analytical data.

The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers 1951113-1951115, 1951125-1951127, 1951132, 1430534 and 824860). These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**S1.2 Solid-state structures**

**Figure S1.2.1** Solid-state structure of 2-chloro-5-methylbenzo-1,3,2-dithiaphosphole (**1a**)

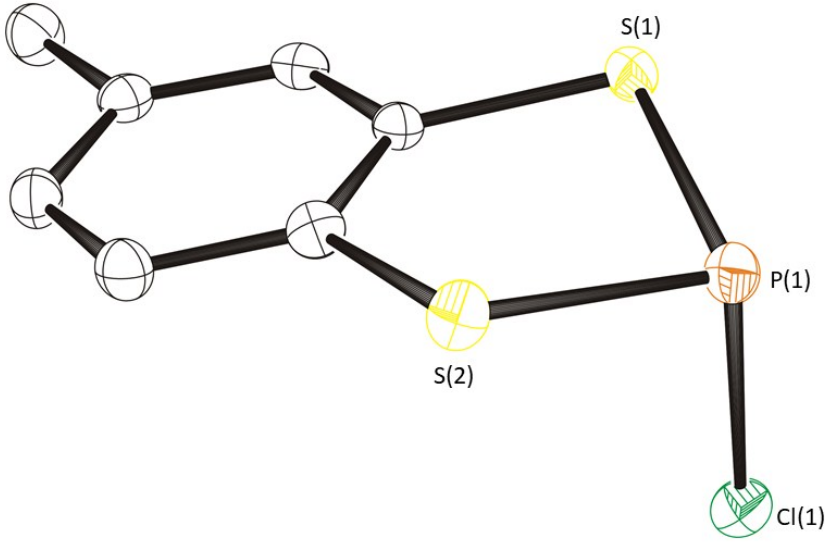


**Figure S1.2.2** Solid-state structure of 2-bromo-5-methylbenzo-1,3,2-dithiaphosphole (**1b**)

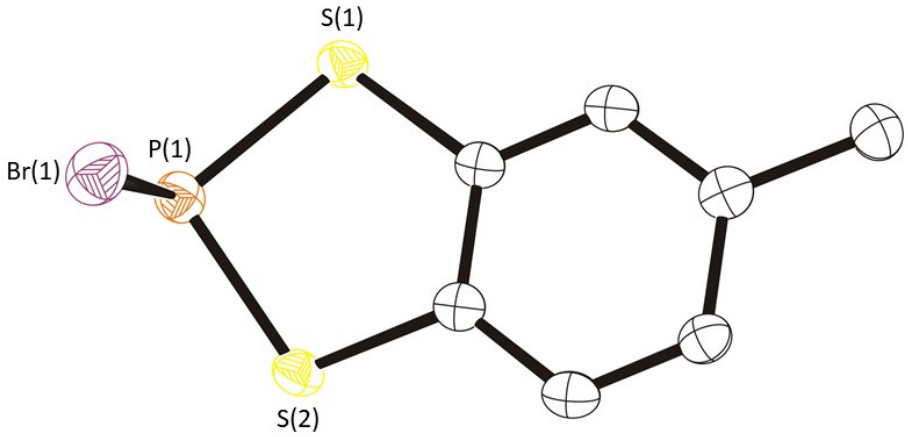


**Figure S1.2.3** Solid-state structure of 2-iodo-5-methylbenzo-1,3,2-dithiaphosphole (**1c**)

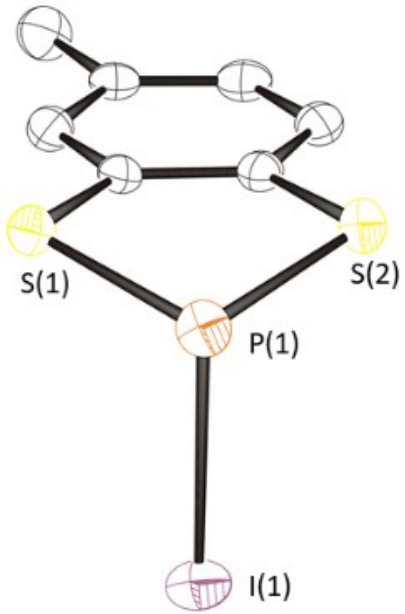


**Figure S1.2.4** Solid-state structure of 2-chlorobenzo-1,3,2-dithiaphosphole (**2a**)

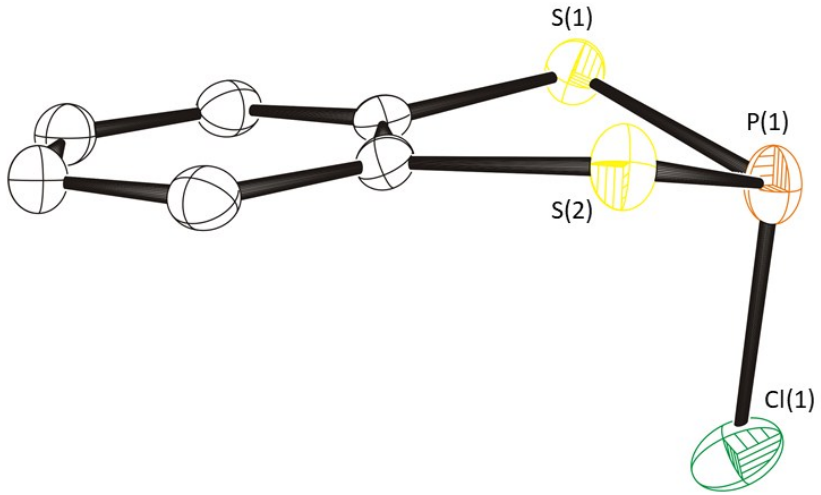


**Figure S1.2.5** Solid-state structure of 2-bromobenzo-1,3,2-dithiaphosphole (**2b**)

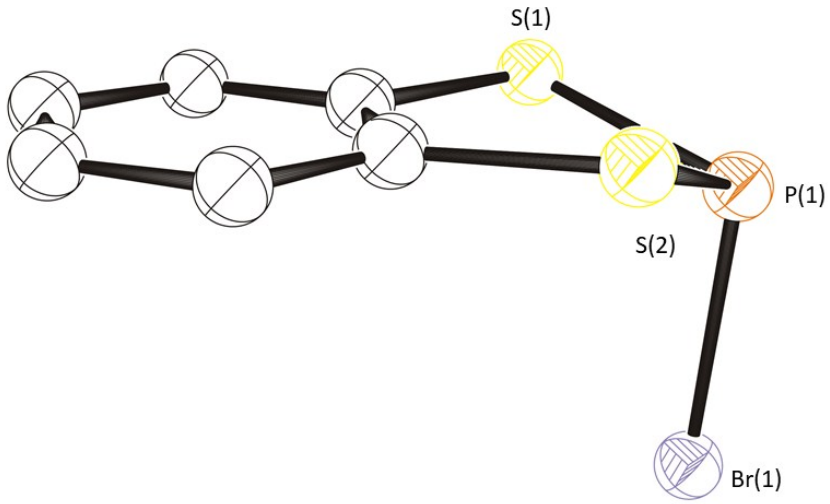


**Figure S1.2.6** Solid-state structure of 2-iodobenzo-1,3,2-dithiaphosphole (**2c**)

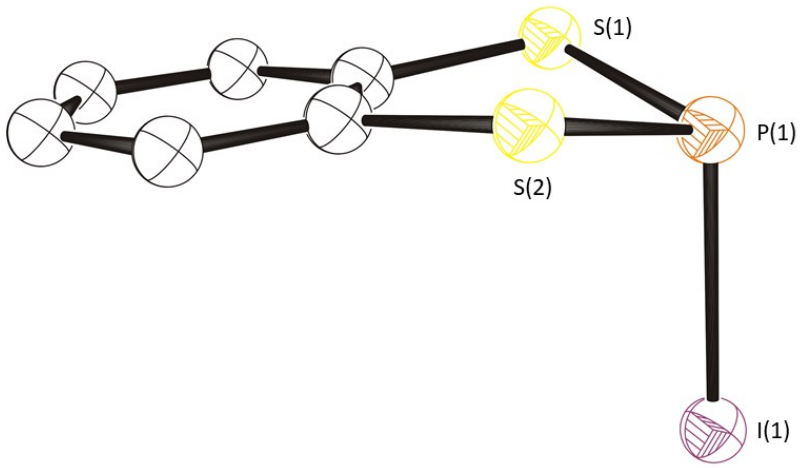


**Figure S1.2.7** Solid-state structure of paddlewheel tris(5-methylbenzo-1,3,2-dithiaphosphol-2-yl)amine $(MeC_6H_3S_2P)_3N$ (**1e**)

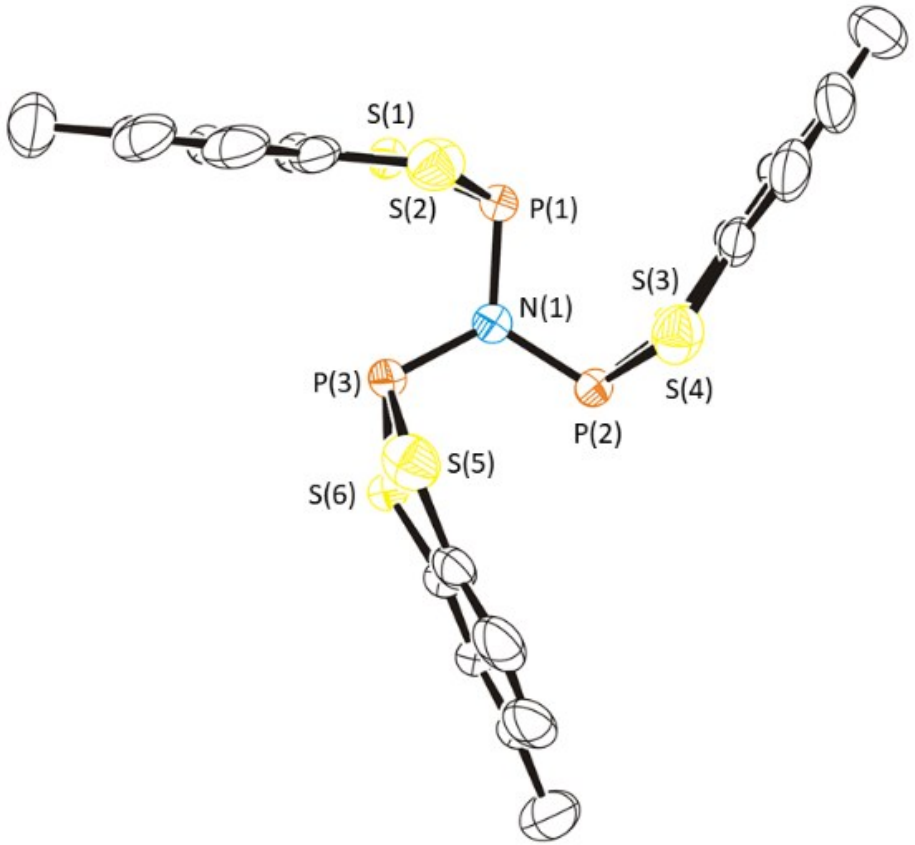


**Figure S1.2.8** Solid-state structure of 5-methylbenzo-1,3,2-dithiaphosphenium tetrachlorogallate (**3b**)

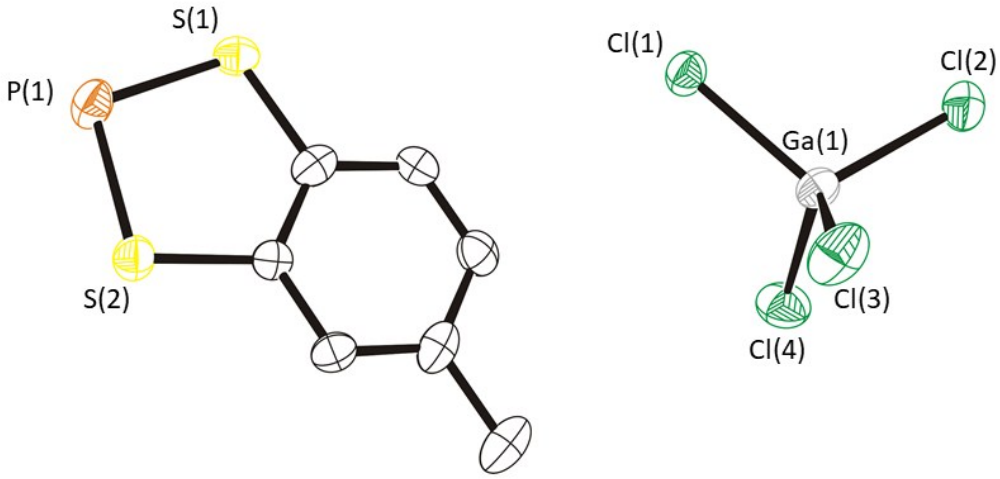
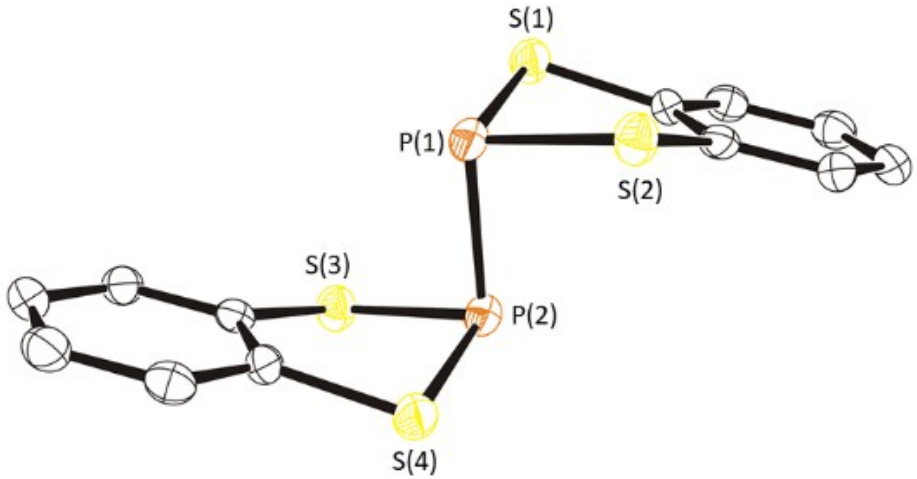


**Figure S1.2.9** Solid-state structure of 1,3,2-benzodithiaphosphoryl dimer (**4**)



**S1.3 Refinement data**

**Table S1.3.1**. Crystal data and structure refinement for compounds **1a–1c**.

| Compound | **1a** | **1b** | **1c** |
|---|---|---|---|
| Empirical formula | $C_7H_6ClPS_2$ | $C_7H_6BrPS_2$ | $C_7H_6IPS_2$ |
| Formula Weight | 220.66 | 265.12 | 312.11 |
| Temperature/ K | 150(2) | 150(2) | 150(2) |
| Wavelength /Å | 1.54178 | 0.71073 | 0.71073 |
| Crystal System | Monoclinic | Monoclinic | Monoclinic |
| Space Group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| *a*/Å | 7.9254(2) | 8.1065(5) | 9.6874(7) |
| *b*/Å | 14.9999(5) | 8.4575(5) | 12.2726(9) |
| *c*/Å | 7.5269(2) | 13.4463(8) | 8.3795(7) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 91.739(3) | 93.273(6) | 102.702(8) |
| $\gamma$/° | 90 | 90 | 90 |
| Volume/Å$^3$ | 894.38(4) | 920.39(9) | 971.85(13) |
| Z | 4 | 4 | 4 |
| Density (calc)/ g cm$^{-3}$ | 1.639 | 1.913 | 2.133 |
| Absorption coefficient/ mm$^{-1}$ | 9.255 | 5.023 | 3.823 |
| F(000) | 448 | 520 | 592 |
| Crystal size/mm$^3$ | 0.260 x 0.150 x 0.133 | 0.313 x 0.133 x 0.055 | 0.186 x 0.127 x 0.054 |
| $\theta$ range/° | 5.584 to 74.035 | 3.484 to 29.529 | 3.320 to 29.684 |
| Index ranges | $-9 \le h \le 9$ | $-11 \le h \le 7$ | $-13 \le h \le 12$ |
| | $-18 \le k \le 17$ | $-8 \le k \le 11$ | $-16 \le k \le 11$ |
| | $-9 \le l \le 9$ | $-18 \le l \le 16$ | $-11 \le l \le 8$ |
| Reflections collected | 8622 | 4305 | 5189 |
| Independent reflections | 1792 | 2191 | 2301 |
| R(int) | 0.0342 | 0.0276 | 0.0303 |
| Absorption Correction | Gaussian | Gaussian | Gaussian |
| Data / restraints / parameters | 1792/0/101 | 2191 / 0 / 101 | 2301 / 0 / 101 |
| Goodness of fit, S | 1.027 | 1.030 | 1.050 |
| Final R indices [I> 2$\sigma$(I)] | $R_1$ = 0.0329 | R1 = 0.0360 | R1 = 0.0342 |
| | wR2 = 0.0856 | wR2 = 0.0822 | wR2 = 0.0653 |
| R indices (all data) | $R_1$ = 0.0360 | R1 = 0.0486 | R1 = 0.0446 |
| | wR2 = 0.0889 | wR2 = 0.0899 | wR2 = 0.0715 |
| Max/min residual electron density/$e^-$Å$^{-3}$ | +0.533 | +0.660 | +1.536 |
| | -0.337 | -0.636 | -1.097 |

**Table S1.3.2**. Crystal data and structure refinement for compounds **2a–2c**.

| Compound | **2a** | **2b** | **2c** |
|---|---|---|---|
| Empirical formula | $C_6H_4ClPS_2$ | $C_6H_4BrPS_2$ | $C_6H_4IPS_2$ |
| Formula Weight | 206.63 | 251.09 | 298.08 |
| Temperature/ K | 150(2) | 150(2) | 150(2) |
| Wavelength /Å | 0.71073 | 0.71073 | 0.71073 |
| Crystal System | Monoclinic | Triclinic | Triclinic |
| Space Group | $P2_1/n$ | P-1 | P-1 |
| *a*/Å | 5.9973(4) | 8.9636(5) | 9.0077(6) |
| *b*/Å | 17.0236(15) | 9.1854(7) | 9.3261(7) |
| *c*/Å | 7.9817(5) | 11.3840(10) | 11.6087(7) |
| $\alpha$/° | 90 | 69.213(7) | 69.446(6) |
| $\beta$/° | 97.205(7) ° | 73.956(6) | 77.324(5) |
| $\gamma$/° | 90 | 78.555(5) | 79.406(6) |
| Volume/Å$^3$ | 808.47(11) | 836.88(12) | 884.76(11) |
| Z | 4 | 4 | 4 |
| Density (calc)/ g cm$^{-3}$ | 1.698 | 1.993 | 2.238 |
| Absorption coefficient/ mm$^{-1}$ | 1.100 | 5.518 | 4.193 |
| F(000) | 416 | 488 | 560 |
| Crystal size/mm$^3$ | 0.638 x 0.199 x 0.103 | 0.700 x 0.225 x 0.216 | 0.341 x 0.207 x 0.194 |
| $\theta$ range/° | 3.514 to 29.530 | 3.409 to 29.722 | 3.468 to 29.889 |
| Index ranges | $-6 \le h \le 8$ | $-12 \le h \le 11$ | $-12 \le h \le 12$ |
| | $-17 \le k \le 23$ | $-12 \le k \le 12$ | $-12 \le k \le 13$ |
| | $-10 \le l \le 9$ | $-12 \le l \le 14$ | $-15 \le l \le 11$ |
| Reflections collected | 4133 | 6707 | 7548 |
| Independent reflections | 1952 | 3932 | 4222 |
| R(int) | 0.0253 | 0.0262 | 0.0275 |
| Absorption Correction | Gaussian | Gaussian | Gaussian |
| Data / restraints / parameters | 1952 / 0 / 91 | 3932 / 0 / 181 | 4222 / 0 / 181 |
| Goodness of fit, S | 1.017 | 0.973 | 1.013 |
| Final R indices [I> 2$\sigma$(I)] | R1 = 0.0342 | R1 = 0.0324 | R1 = 0.0340 |
| | wR2 = 0.0653 | wR2 = 0.0527 | wR2 = 0.0652 |
| R indices (all data) | R1 = 0.0517 | R1 = 0.0468 | R1 = 0.0499 |
| | wR2 = 0.0701 | wR2 = 0.0595 | wR2 = 0.0742 |
| Max/min residual electron density/$e^-$Å$^{-3}$ | +0.385 | +0.461 | +0.660 |
| | -0.304 | -0.479 | -1.199 |

**Table S1.3.3**. Crystal data and structure refinement for compounds **3b**, **4** and **1e**.

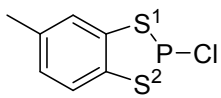
| Compound | **3b** | **4** | **1e** |
|---|---|---|---|
| Empirical formula | $C_7H_6Cl_4GaPS_2$ | $C_{12}H_8P_2S_4$ | $C_{21}H_{18}NP_3S_6$ |
| Formula Weight | 396.73 | 342.36 | 569.63 |
| Temperature/ K | 153(2) | 173(2) | 150(2) |
| Wavelength /Å | 0.71073 | 0.71073 | 0.71073 |
| Crystal System | Monoclinic | Monoclinic | Trigonal |
| Space Group | $P2_1/c$ | $P2_1/n$ | P-3 |
| *a*/Å | 8.0083(16) | 7.2588(15) | 12.134(2) |
| *b*/Å | 9.2891(19) | 6.1271(12) | 12.134(2) |
| *c*/Å | 18.572(4) | 15.846(3) | 11.246(2) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 96.23(3) | 104.17(3) | 90 |
| $\gamma$/° | 90 | 90 | 120 |
| Volume/Å$^3$ | 1373.4(5) | 683.3(3) | 1434.0(5) |
| Z | 4 | 2 | 2 |
| Density (calc)/ g cm$^{-3}$ | 1.919 | 1.664 | 1.319 |
| Absorption coefficient/ mm$^{-1}$ | 3.166 | 0.905 | 0.655 |
| F(000) | 776 | 348 | 584 |
| Crystal size/mm$^3$ | 0.30 x 0.30 x 0.30 | 0.18 x 0.16 x 0.08 | 0.14 x 0.13 x 0.04 |
| $\theta$ range/° | 2.21to 28.44 | 3.58 to 28.24 | 1.81 to 27.53 |
| Index ranges | $-10 \le h \le 10$ | $-9 \le h \le 9$ | $-15 \le h \le 15$ |
| | $-12 \le k \le 12$ | $-8 \le k \le 8$ | $-15 \le k \le 15$ |
| | $-4 \le l \le 24$ | $0 \le l \le 20$ | $0 \le l \le 14$ |
| Reflections collected | 3320 | 3308 | 6447 |
| Independent reflections | 3320 | 3347 | 2214 |
| R(int) | 0.059 | 0.0428 | 0.0353 |
| Absorption Correction | Sadabs | Twinabs | Sadabs |
| Data / restraints / parameters | 3320 / 0 / 138 | 3308/0/83 | 2214/0/96 |
| Goodness of fit, S | 1.062 | 1.072 | 1.093 |
| Final R indices [I> 2$\sigma$(I)] | R1 = 0.0464 | R1 = 0.0634 | R1 = 0.0984 |
| | wR2 = 0.1087 | wR2 = 0.1661 | wR2 = 0.2682 |
| R indices (all data) | R1 = 0.0607 | R1 = 0.0810 | R1 = 0.1047 |
| | wR2 = 0.1186 | wR2 = 0.1747 | wR2 = 0.2838 |
| Max/min residual | +0.77 | +0.71 | +1.38 |
| electron density/$e^-$Å$^{-3}$ | -0.83 | -0.47 | -0.48 |

## S2 Computational studies

### S2.1 Computational experimental

Density functional theory (DFT) calculations were performed using the graphical interface WebMO computational platform, which employed the Gaussian 09 package.[9] Compounds **1a–1c**, **3**$^{+}$, **6** analogue, **7a**–**7b**, **8a**–**8b**, **9** analogue and **10**$^{+}$ were initially geometry optimised using the meta-hybrid M06-2X functional[10] and the Pople split valence basis set 6-311+G(2d,p) on all atoms, except iodine.[11] In the case of iodine, M06-2X was again used, but the effective core potential (ECP) Def2TZVP was used as the basis set.[12] After this a vibrational frequency calculation was undertaken to ensure each structure was a minimum on the potential energy landscape. Atomic coordinates are presented in section S2.3. Natural bond orbital (NBO) analyses were then performed on the optimised geometries using the same functional and basis set described above and presented in Section S2.2.[13]

**S2.2 NBO analysis**




Natural Population Analysis **1a**

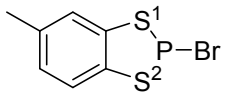
P: +0.53

$S^1$: +0.06

$S^2$: +0.06

Cl: −0.33

Wiberg bond order P–Cl: 0.86




Natural Population Analysis **1b**

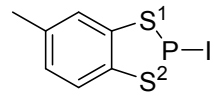
P: +0.46

$S^1$: +0.07

$S^2$: +0.07

Br: −0.27

Wiberg bond order P–Br: 0.87




Natural Population Analysis **1c**

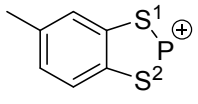
P: +0.36

$S^1$: +0.30

$S^2$: +0.30

I: −0.17

Wiberg bond order P–Br: 0.90

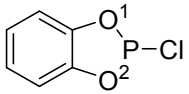



Natural Population Analysis **3** cation

P: +0.53

$S^1$: +0.30

$S^2$: +0.30




Natural Population Analysis **7a**

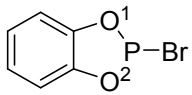
P: +1.40

$O^1$: −0.79

$O^2$: −0.79

Cl: −0.36

Wiberg bond order P–Cl: 0.87




Natural Population Analysis **7b**

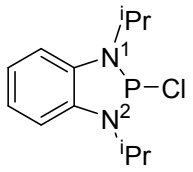
P: +1.37

$N^1$: −0.79

$N^2$: −0.79

Br: −0.33

Wiberg bond order P–Br: 0.87




Natural Population Analysis **8a**

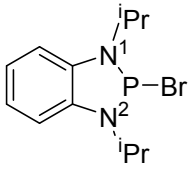
P: +1.28

$N^1$: −0.82

$N^2$: −0.82

Cl: −0.49

Wiberg bond order P–Cl: 0.66




Natural Population Analysis **8b**

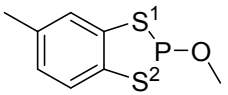
P: +1.25

$N^1$: −0.81

$N^2$: −0.81

Br: −0.49

Wiberg bond order P–Br: 0.63




Natural Population Analysis of **6** analogue

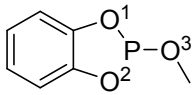
P: +0.85

$S^1$: −0.01

$S^2$: +0.03

O: −0.86

Wiberg bond order P–O: 0.70




Natural Population Analysis of **9** analogue

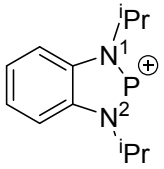
P: +1.60

$O^1$: −0.79

$O^2$: −0.79

$O^3$: −0.85

Wiberg bond order P–O: 0.73




Natural Population Analysis of **10** cation

P: +1.24

$N^1$: −0.70

$N^2$: −0.70

**S2.3 Geometry optimised coordinates**

Atom coordinates for **1a**

| | | | |
|---|---|---|---|
| C | -4.293968 | -0.841939 | 0.481257 |
| C | -2.945390 | -0.233248 | 0.207930 |
| C | -2.741913 | 1.137587 | 0.370257 |
| H | -3.569170 | 1.765314 | 0.680810 |
| C | -1.499681 | 1.709660 | 0.155768 |
| C | -0.432040 | 0.911247 | -0.240191 |
| S | 1.154636 | 1.611721 | -0.590997 |
| P | 2.321002 | -0.142416 | -0.476493 |
| S | 0.734547 | -1.448194 | -0.962386 |
| C | -0.621378 | -0.456148 | -0.408148 |
| C | -1.870943 | -1.023410 | -0.180779 |
| H | -2.003173 | -2.092293 | -0.302366 |
| Cl | 2.485242 | -0.421179 | 1.608056 |
| H | -1.353551 | 2.772834 | 0.299612 |
| H | -4.349612 | -1.863878 | 0.108111 |
| H | -5.086699 | -0.261155 | 0.007709 |
| H | -4.496985 | -0.863447 | 1.554130 |

Atom coordinates for **1b**

| | | | |
|---|---|---|---|
| C | -4.546728 | -1.205487 | -0.457416 |
| C | -3.268012 | -0.432171 | -0.283072 |
| C | -3.092887 | 0.797850 | -0.920216 |
| C | -1.917072 | 1.514703 | -0.786236 |
| C | -0.889274 | 1.012367 | 0.005141 |
| C | -1.049582 | -0.212698 | 0.643716 |
| C | -2.231843 | -0.930878 | 0.495222 |
| H | -2.339497 | -1.890518 | 0.987362 |
| S | 0.247560 | -0.809990 | 1.686686 |
| P | 1.835041 | 0.375877 | 0.962154 |
| S | 0.596812 | 1.934020 | 0.267081 |
| Br | 2.388430 | -0.698295 | -0.985894 |
| H | -1.791266 | 2.461735 | -1.295717 |
| H | -3.888718 | 1.193648 | -1.540570 |
| H | -4.670388 | -1.520378 | -1.495443 |
| H | -4.558243 | -2.096605 | 0.169170 |
| H | -5.410138 | -0.592295 | -0.193912 |

Atom coordinates for **1c**

| | | | |
|---|---|---|---|
| C | -4.684250 | -1.601994 | 0.203063 |
| C | -3.496463 | -0.712625 | -0.045170 |
| C | -3.348910 | -0.055150 | -1.267477 |
| C | -2.249225 | 0.744955 | -1.524871 |
| C | -1.273919 | 0.912017 | -0.547144 |
| C | -1.409479 | 0.263703 | 0.676633 |
| C | -2.512815 | -0.546771 | 0.921691 |
| H | -2.599787 | -1.056853 | 1.873950 |
| S | -0.189181 | 0.531193 | 1.927847 |
| P | 1.384367 | 1.227907 | 0.702029 |
| S | 0.111398 | 1.981356 | -0.804172 |
| I | 2.229290 | -0.889418 | -0.323595 |
| H | -2.141209 | 1.236209 | -2.483714 |
| H | -4.103384 | -0.183826 | -2.035110 |
| H | -4.636209 | -2.495675 | -0.422710 |
| H | -4.728284 | -1.921599 | 1.243561 |
| H | -5.614099 | -1.083309 | -0.035010 |

Atom coordinates for **$3^{+}$**

| | | | |
|---|---|---|---|
| C | 3.561613 | -1.869647 | -0.000000 |
| C | 2.371174 | -0.958010 | -0.000000 |
| C | 2.562150 | 0.440395 | 0.000000 |
| H | 3.574107 | 0.828332 | 0.000000 |
| C | 1.509787 | 1.322401 | 0.000000 |
| C | 0.206020 | 0.809477 | 0.000000 |
| S | -1.169688 | 1.860371 | 0.000000 |
| P | -2.717160 | 0.548876 | 0.000000 |
| S | -1.630214 | -1.167663 | -0.000000 |
| C | 0.000000 | -0.574166 | -0.000000 |
| C | 1.083528 | -1.458294 | -0.000000 |
| H | 0.910907 | -2.527529 | -0.000000 |
| H | 1.678843 | 2.391451 | 0.000000 |
| H | 3.266625 | -2.916926 | -0.000000 |
| H | 4.179858 | -1.682371 | 0.879855 |
| H | 4.179858 | -1.682371 | -0.879855 |

Atom coordinates for **7a**

| | | | |
|---|---|---|---|
| P | -0.811383 | 1.701515 | 0.000000 |
| Cl | 1.208153 | 2.298798 | 0.000000 |
| O | -0.754814 | 0.573727 | 1.201234 |
| C | -0.316443 | -0.630330 | 0.692571 |
| C | -0.316443 | -0.630330 | -0.692571 |
| O | -0.754814 | 0.573727 | -1.201234 |
| C | 0.056055 | -1.737619 | -1.417752 |
| C | 0.437667 | -2.867698 | -0.694729 |
| C | 0.437667 | -2.867698 | 0.694729 |
| C | 0.056055 | -1.737619 | 1.417752 |
| H | 0.050196 | -1.718927 | 2.498776 |
| H | 0.740717 | -3.758151 | 1.229396 |
| H | 0.740717 | -3.758151 | -1.229396 |
| H | 0.050196 | -1.718927 | -2.498776 |

Atom coordinates for **7b**

| | | | |
|---|---|---|---|
| P | -0.572845 | 1.577303 | -0.000000 |
| Br | 1.716801 | 1.457297 | -0.000000 |
| O | -0.899562 | 0.496704 | 1.200069 |
| C | -0.899562 | -0.784683 | 0.692574 |
| C | -0.899562 | -0.784683 | -0.692574 |
| O | -0.899562 | 0.496704 | -1.200069 |
| C | -0.925504 | -1.952491 | -1.418295 |
| C | -0.951511 | -3.144230 | -0.694953 |
| C | -0.951511 | -3.144230 | 0.694953 |
| C | -0.925504 | -1.952491 | 1.418295 |
| H | -0.923441 | -1.932803 | 2.499263 |
| H | -0.968279 | -4.084890 | 1.229085 |
| H | -0.968279 | -4.084890 | -1.229085 |
| H | -0.923441 | -1.932803 | -2.499263 |

Atom coordinates for **8a**

| | | | |
|---|---|---|---|
| C | 0.380133 | -0.485716 | 2.636707 |
| N | 0.098960 | -0.529401 | 1.195944 |
| P | 1.290160 | -0.566349 | 0.000000 |
| Cl | 2.015805 | 1.557223 | 0.000000 |
| N | 0.098960 | -0.529401 | -1.195944 |
| C | -1.170754 | -0.227326 | -0.700513 |
| C | -1.170754 | -0.227326 | 0.700513 |
| C | -2.342719 | -0.013192 | 1.407075 |
| C | -3.519415 | 0.203436 | 0.693784 |
| C | -3.519415 | 0.203436 | -0.693784 |
| C | -2.342719 | -0.013192 | -1.407075 |
| H | -2.349147 | -0.014012 | -2.488761 |
| H | -4.441987 | 0.376823 | -1.232018 |
| H | -4.441987 | 0.376823 | 1.232018 |
| H | -2.349147 | -0.014012 | 2.488761 |
| C | 0.380133 | -0.485716 | -2.636707 |
| C | 1.702620 | -1.171419 | -2.951026 |
| H | 1.841534 | -1.203389 | -4.031782 |
| H | 1.725815 | -2.191512 | -2.565950 |
| H | 2.541981 | -0.615208 | -2.525410 |
| C | 0.366322 | 0.946337 | -3.169989 |
| H | 0.440886 | 0.934190 | -4.258941 |
| H | -0.547631 | 1.470089 | -2.890323 |
| H | 1.210865 | 1.504935 | -2.765233 |
| H | -0.422702 | -1.057606 | -3.112948 |
| C | 1.702620 | -1.171419 | 2.951026 |
| H | 1.841534 | -1.203389 | 4.031782 |
| H | 1.725815 | -2.191512 | 2.565950 |
| H | 2.541981 | -0.615208 | 2.525410 |
| C | 0.366322 | 0.946337 | 3.169989 |
| H | 0.440886 | 0.934190 | 4.258941 |
| H | -0.547631 | 1.470089 | 2.890323 |
| H | 1.210865 | 1.504935 | 2.765233 |
| H | -0.422702 | -1.057606 | 3.112948 |

Atom coordinates for **8b**

| | | | |
|---|---|---|---|
| C | -0.723748 | 0.011292 | 2.637892 |
| N | -0.701559 | 0.290622 | 1.194681 |
| P | -0.965473 | -0.868501 | 0.000000 |
| Br | 1.158597 | -2.116477 | 0.000000 |
| N | -0.701559 | 0.290622 | -1.194681 |
| C | -0.185773 | 1.488194 | -0.700284 |
| C | -0.185773 | 1.488194 | 0.700284 |
| C | 0.230690 | 2.605428 | 1.407806 |
| C | 0.651735 | 3.723711 | 0.694357 |
| C | 0.651735 | 3.723711 | -0.694357 |
| C | 0.230690 | 2.605428 | -1.407806 |
| H | 0.229690 | 2.613389 | -2.489417 |
| H | 0.983991 | 4.601595 | -1.232823 |
| H | 0.983991 | 4.601595 | 1.232823 |
| H | 0.229690 | 2.613389 | 2.489417 |
| C | -0.723748 | 0.011292 | -2.637892 |
| C | -1.617535 | -1.182975 | -2.942047 |
| H | -1.687948 | -1.310562 | -4.022410 |
| H | -2.622594 | -1.044016 | -2.541791 |
| H | -1.194373 | -2.101604 | -2.527013 |
| C | 0.683888 | -0.204146 | -3.191025 |
| H | 0.642138 | -0.272526 | -4.279570 |
| H | 1.352176 | 0.612687 | -2.919769 |
| H | 1.104321 | -1.128560 | -2.794596 |
| H | -1.166429 | 0.898322 | -3.102256 |
| C | -1.617535 | -1.182975 | 2.942047 |
| H | -1.687948 | -1.310562 | 4.022410 |
| H | -2.622594 | -1.044016 | 2.541791 |
| H | -1.194373 | -2.101604 | 2.527013 |
| C | 0.683888 | -0.204146 | 3.191025 |
| H | 0.642138 | -0.272526 | 4.279570 |
| H | 1.352176 | 0.612687 | 2.919769 |
| H | 1.104321 | -1.128560 | 2.794596 |
| H | -1.166429 | 0.898322 | 3.102256 |

Atom coordinates for analogue of **6**

| | | | |
|---|---|---|---|
| C | -4.291058 | -1.113363 | 0.350949 |
| C | -2.977276 | -0.390239 | 0.222617 |
| C | -1.855028 | -1.047005 | -0.270400 |
| C | -0.647439 | -0.376555 | -0.424628 |
| S | 0.759590 | -1.189466 | -1.127597 |
| P | 2.276484 | 0.157111 | -0.457591 |
| S | 0.984672 | 1.823092 | -0.324678 |
| C | -0.545328 | 0.966573 | -0.069814 |
| C | -1.656864 | 1.627466 | 0.437623 |
| C | -2.859637 | 0.952397 | 0.576269 |
| H | -3.719353 | 1.475895 | 0.977954 |
| H | -1.577709 | 2.666906 | 0.730504 |
| O | 2.385352 | -0.183728 | 1.148109 |
| C | 3.154669 | -1.335497 | 1.485473 |
| H | 3.325075 | -1.294774 | 2.558590 |
| H | 4.116186 | -1.335646 | 0.963697 |
| H | 2.604179 | -2.245552 | 1.237346 |
| H | -1.918813 | -2.096040 | -0.536970 |
| H | -4.864510 | -1.036931 | -0.575936 |
| H | -4.139137 | -2.172416 | 0.559851 |
| H | -4.896420 | -0.688945 | 1.151821 |

Atom coordinates for **$10^+$**

| | | | |
|---|---|---|---|
| C | 0.717507 | -0.105398 | 2.647457 |
| N | 0.426488 | -0.153355 | 1.189597 |
| P | 1.580751 | -0.155310 | 0.000000 |
| N | 0.426488 | -0.153355 | -1.189597 |
| C | -0.867683 | -0.158441 | -0.700215 |
| C | -0.867683 | -0.158441 | 0.700215 |
| C | -2.066388 | -0.188927 | 1.420284 |
| C | -3.240631 | -0.215091 | 0.703176 |
| C | -3.240631 | -0.215091 | -0.703176 |
| C | -2.066388 | -0.188927 | -1.420284 |
| H | -2.074745 | -0.194512 | -2.501452 |
| H | -4.184339 | -0.239490 | -1.231678 |
| H | -4.184339 | -0.239490 | 1.231678 |
| H | -2.074745 | -0.194512 | 2.501452 |
| C | 0.717507 | -0.105398 | -2.647457 |
| C | 2.145635 | -0.543000 | -2.928404 |
| H | 2.298419 | -0.568331 | -4.006613 |
| H | 2.350366 | -1.539926 | -2.535046 |
| H | 2.869757 | 0.164714 | -2.516534 |
| C | 0.435568 | 1.295065 | -3.179000 |
| H | 0.547132 | 1.300661 | -4.263191 |
| H | -0.572250 | 1.629806 | -2.935271 |
| H | 1.148376 | 2.006578 | -2.757713 |
| H | 0.032182 | -0.826440 | -3.098533 |
| C | 2.145635 | -0.543000 | 2.928404 |
| H | 2.298419 | -0.568331 | 4.006613 |
| H | 2.350366 | -1.539926 | 2.535046 |
| H | 2.869757 | 0.164714 | 2.516534 |
| C | 0.435568 | 1.295065 | 3.179000 |
| H | 0.547132 | 1.300661 | 4.263191 |
| H | -0.572250 | 1.629806 | 2.935271 |
| H | 1.148376 | 2.006578 | 2.757713 |
| H | 0.032182 | -0.826440 | 3.098533 |

Atom coordinates for analogue of **9**

| | | | |
|---|---|---|---|
| C | -3.203102 | 0.631576 | 1.083689 |
| O | -2.040835 | -0.152777 | 0.822892 |
| P | -1.600433 | -0.341431 | -0.730676 |
| O | -0.381027 | -1.421169 | -0.441872 |
| C | 0.775633 | -0.745944 | -0.125222 |
| C | 0.677580 | 0.610658 | -0.398827 |
| O | -0.549174 | 0.940298 | -0.924067 |
| C | 1.731606 | 1.467061 | -0.179362 |
| C | 2.908931 | 0.916717 | 0.329384 |
| C | 3.006287 | -0.441148 | 0.601645 |
| C | 1.930098 | -1.300663 | 0.375363 |
| H | 1.987113 | -2.360492 | 0.582688 |
| H | 3.929622 | -0.842973 | 0.997885 |
| H | 3.757271 | 1.562408 | 0.514571 |
| H | 1.639044 | 2.521759 | -0.400224 |
| H | -3.972301 | 0.464493 | 0.324752 |
| H | -2.943898 | 1.690723 | 1.110219 |
| H | -3.584269 | 0.325194 | 2.054604 |

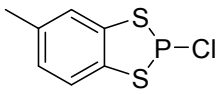
**S3 References**

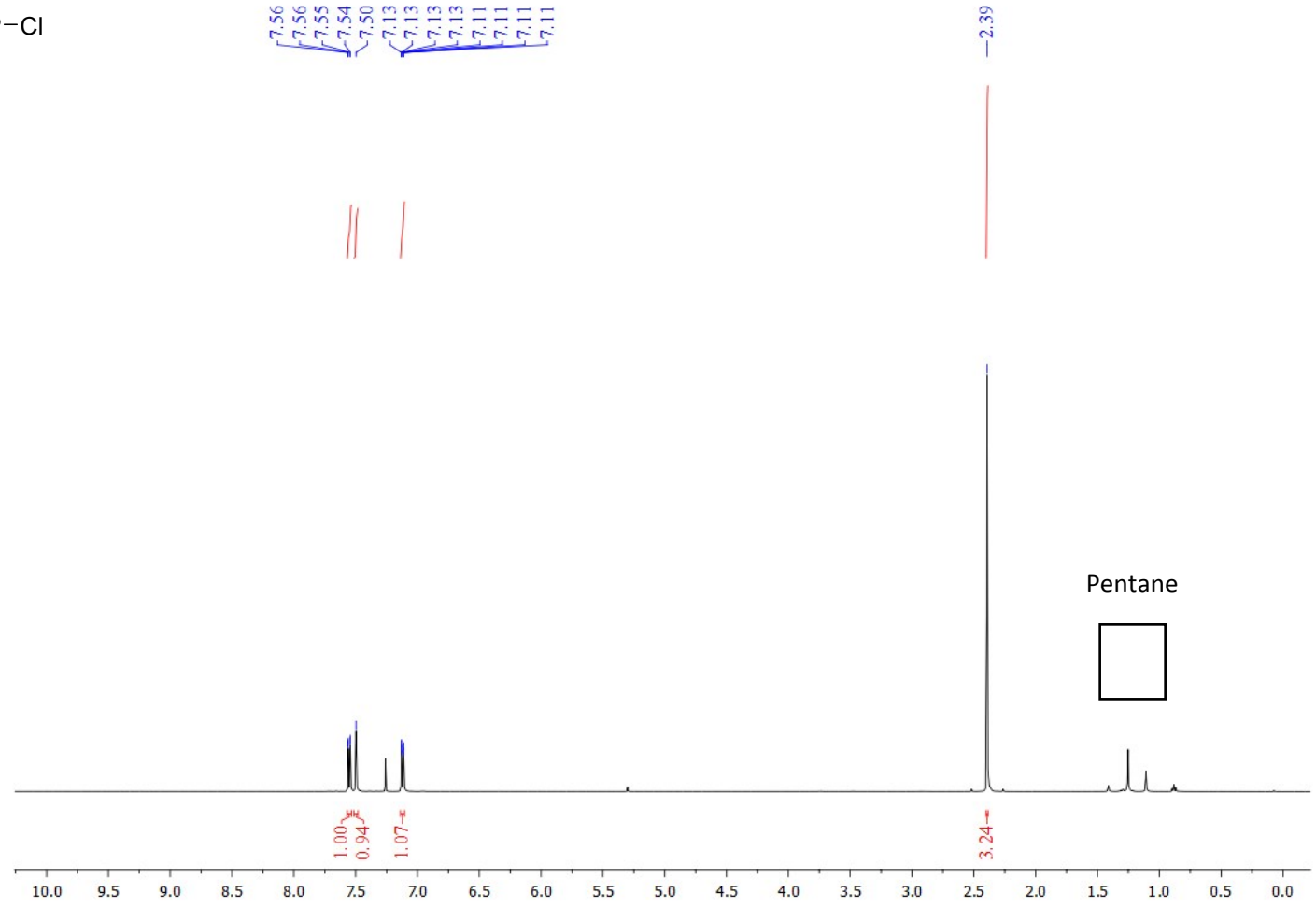

1. CrysAlisPro, Agilent Technoligies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET).
2. SHELXL-2013, G. M. Sheldrick, University of Göttingen, Germany (2013).
3. SAINT, Bruker AXS, Madison, WI, USA.
4. Sadabs, Bruker AXS, Madison, WI, USA.
5. Twinabs, Bruker AXS, Madison, WI, USA.
6. G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3–8.
7. A. L. Spek, *Acta Cryst. D*, 2009, **65**, 148 – 155.
8. DIRDIF: A Computer Program System for Crystal Structure Determination by Patterson Methods and Direct Methods Applied to Difference Structure Factors. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, Crystallography Laboratory, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands
9. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
10. Y. ZhaoDonald and G. Truhlar, *Theor. Chem. Account*, 2008, **120**, 215–241.
11. R. Ditchfield, W. J. Hehre and J.A. Pole, *J. Chem. Phys*., 1971, **54**, 724.
12. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297–3305.
13. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold.

**S4 NMR spectra**

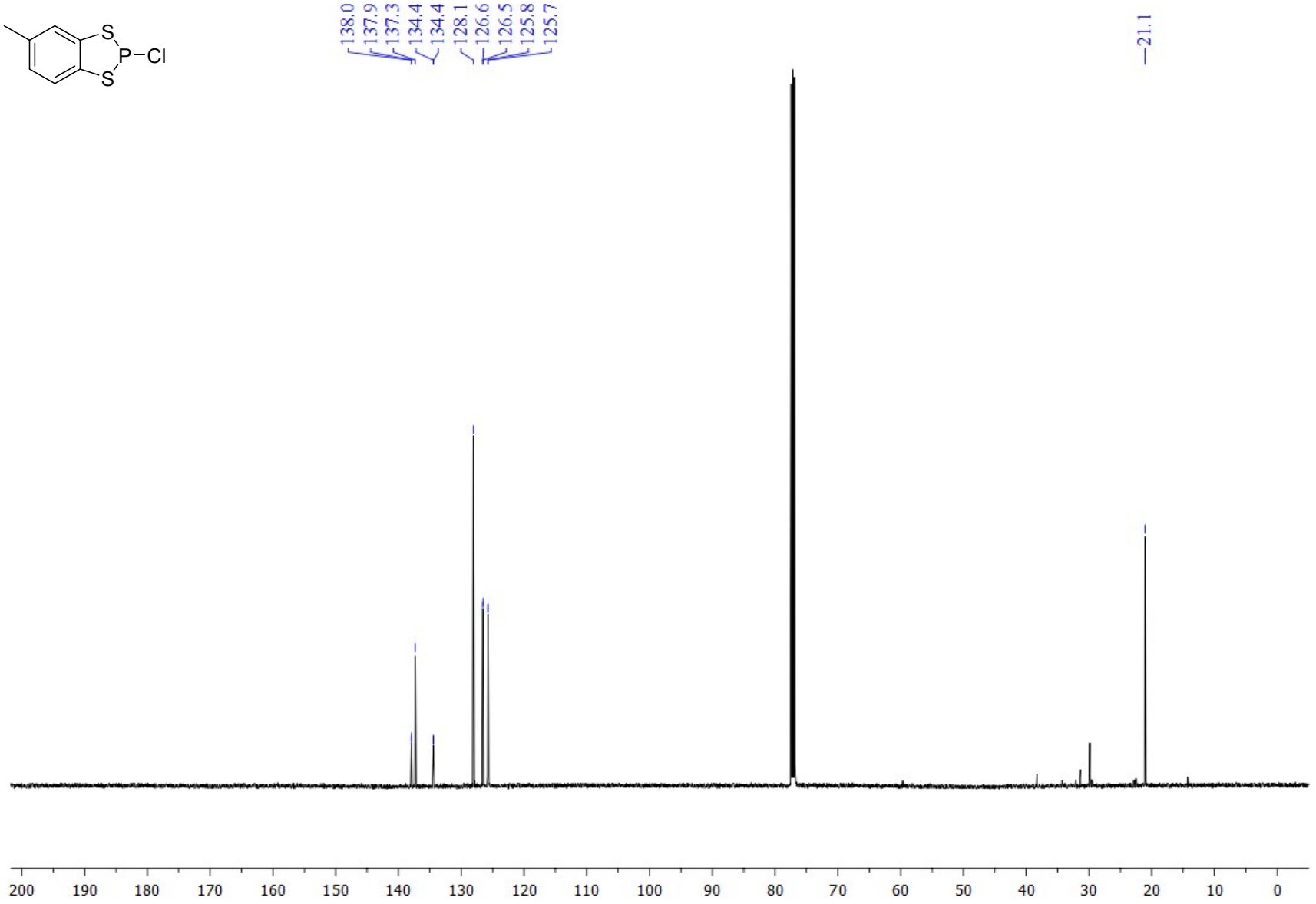
**S4.1 NMR spectra of phosphole/phosphenium compounds**

**S4.1.1** $^{1}H$ NMR (500 MHz, 295 K, $CDCl_3$) spectrum of 2-chloro-5-methylbenzo-1,3,2-dithiaphosphole (**1a**)



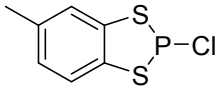



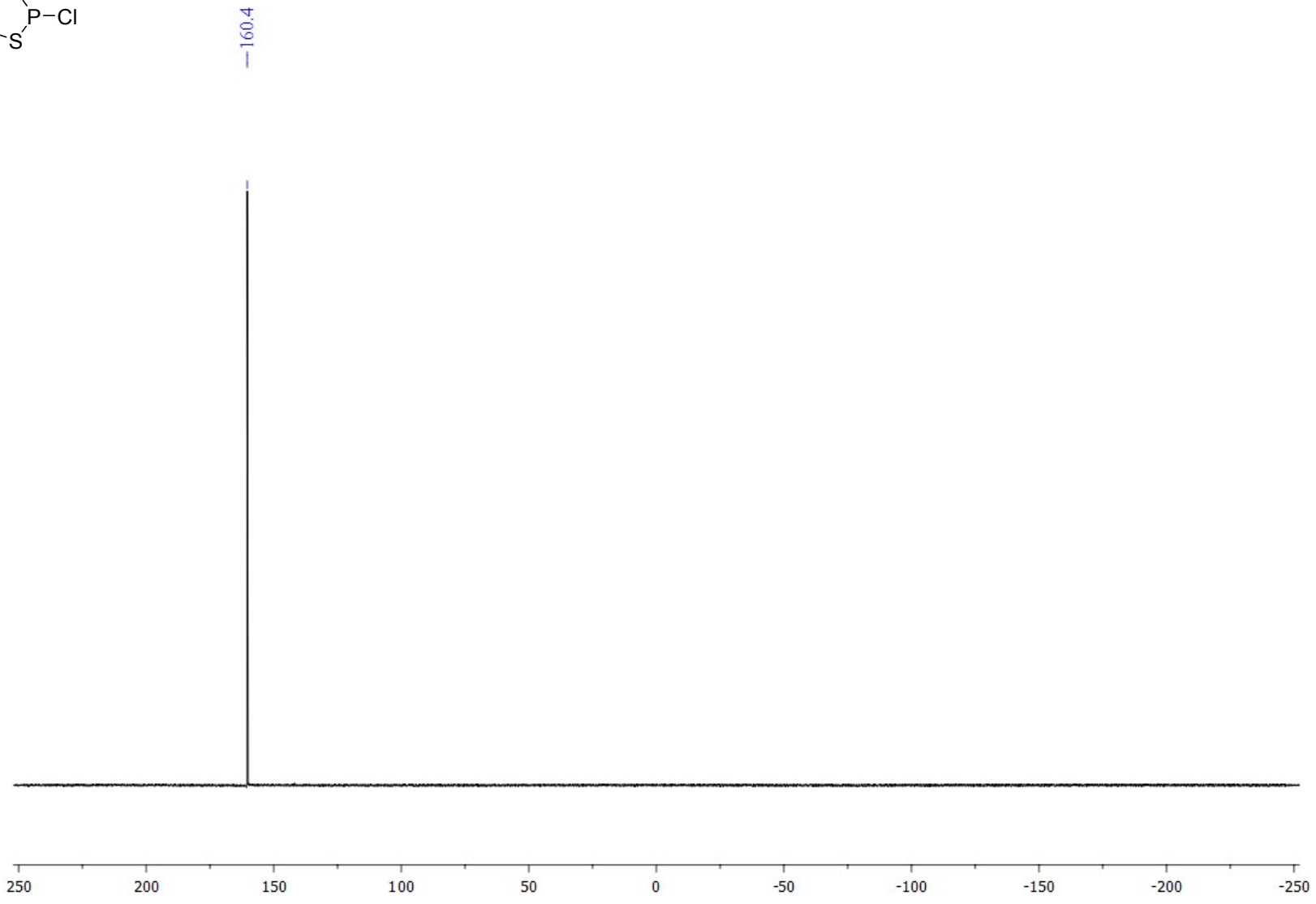
**S4.1.2** $^{13}C\{^{1}H\}$ NMR (126 MHz, 295 K, $CDCl_3$) spectrum of 2-chloro-5-methylbenzo-1,3,2-dithiaphosphole (**1a**)




**S4.1.3** $^{31}P\{^{1}H\}$ NMR (202 MHz, 295 K, $CDCl_3$) spectrum of 2-

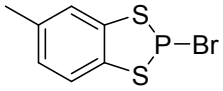
chloro-5-methylbenzo-1,3,2-dithiaphosphole (**1a**)

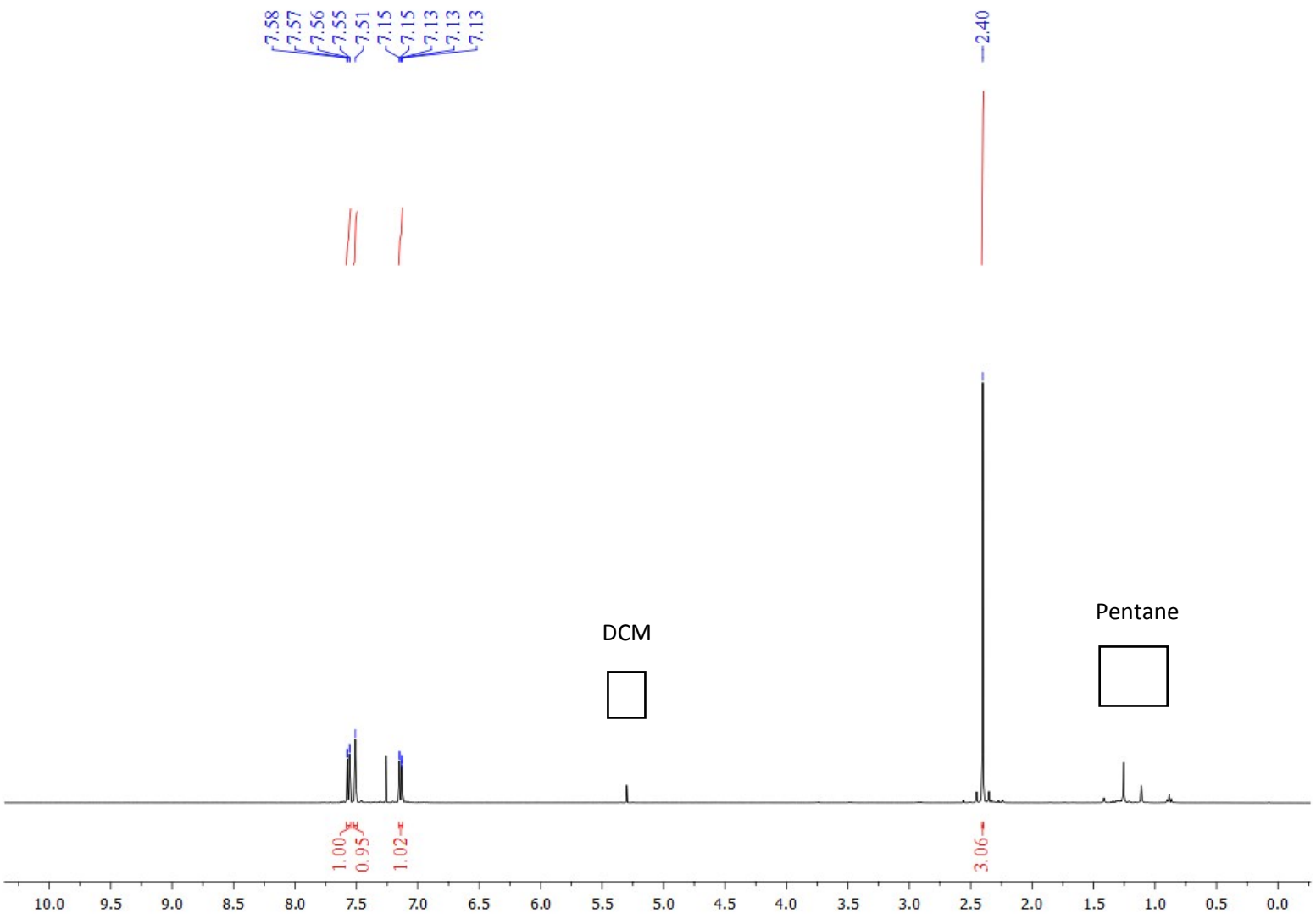


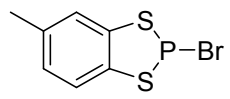

**S4.1.4** $^{1}$H NMR (400

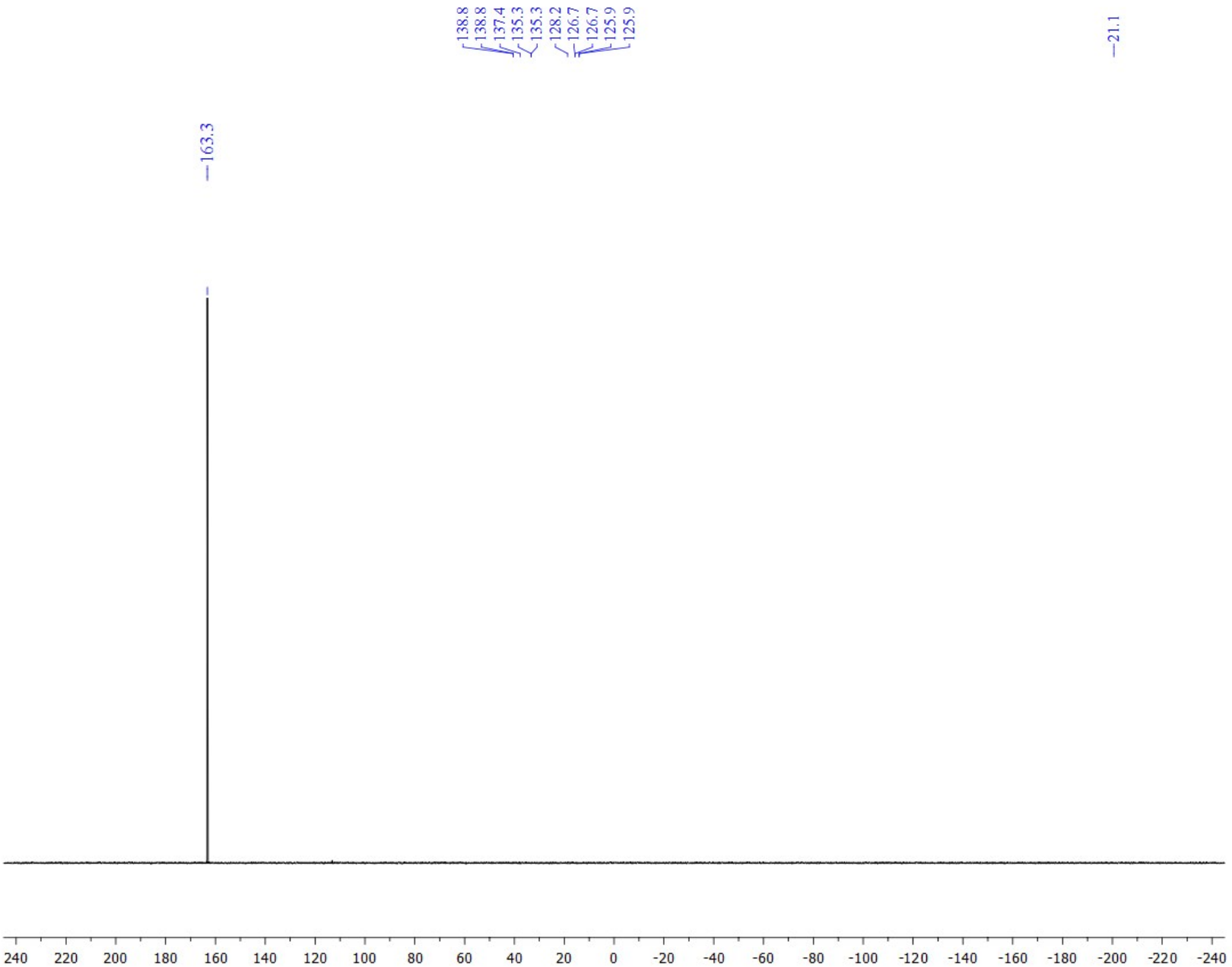
MHz, 295 K, $CDCl_3$) spectrum of 2-bromo-5-methylbenzo-1,3,2-dithiaphosphole (**1b**)





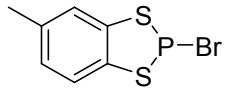

**S4.1.5** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 2-bromo-5-methylbenzo-1,3,2-dithiaphosphole (**1b**)



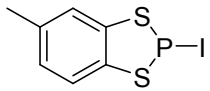




**S4.1.6** $^{31}P\{^{1}H\}$ NMR (162 MHz,

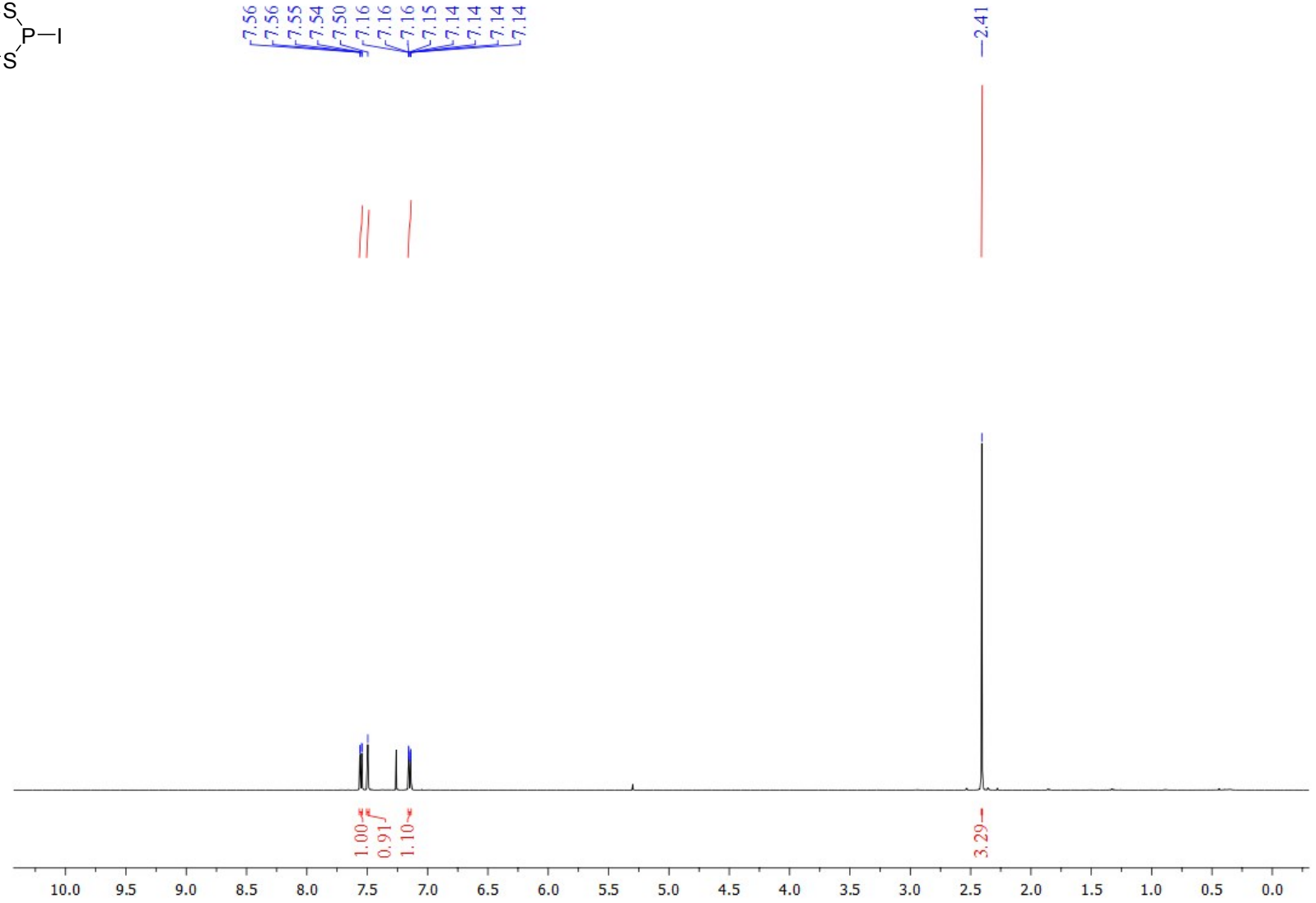
295 K, $CDCl_3$) spectrum of 2-bromo-5-methylbenzo-1,3,2-dithiaphosphole (**1b**)



**S4.1.7**



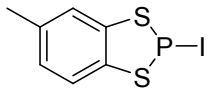

$^{1}$H NMR (500 MHz, 295 K,



$CDCl_3$) spectrum of 2-iodo-5-methylbenzo-1,3,2-dithiaphosphole (**1c**)

DCM

**S4.1.8** $^{13}C\{^{1}H\}$ NMR (126 MHz, 295 K, $CDCl_3$) spectrum of 2-iodo-5-methylbenzo-1,3,2-dithiaphosphole (**1c**)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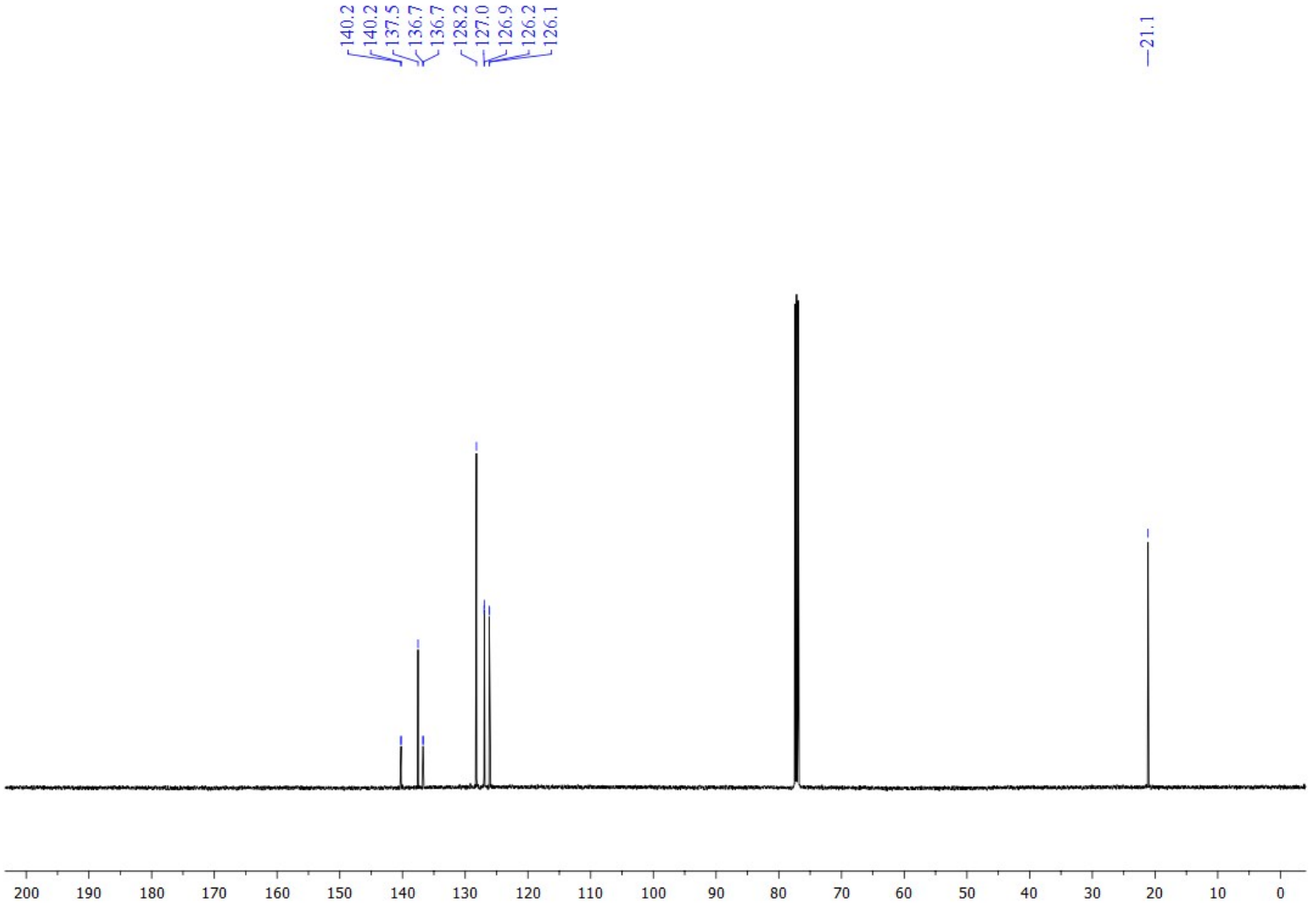
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126.9
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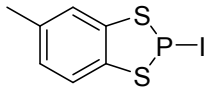
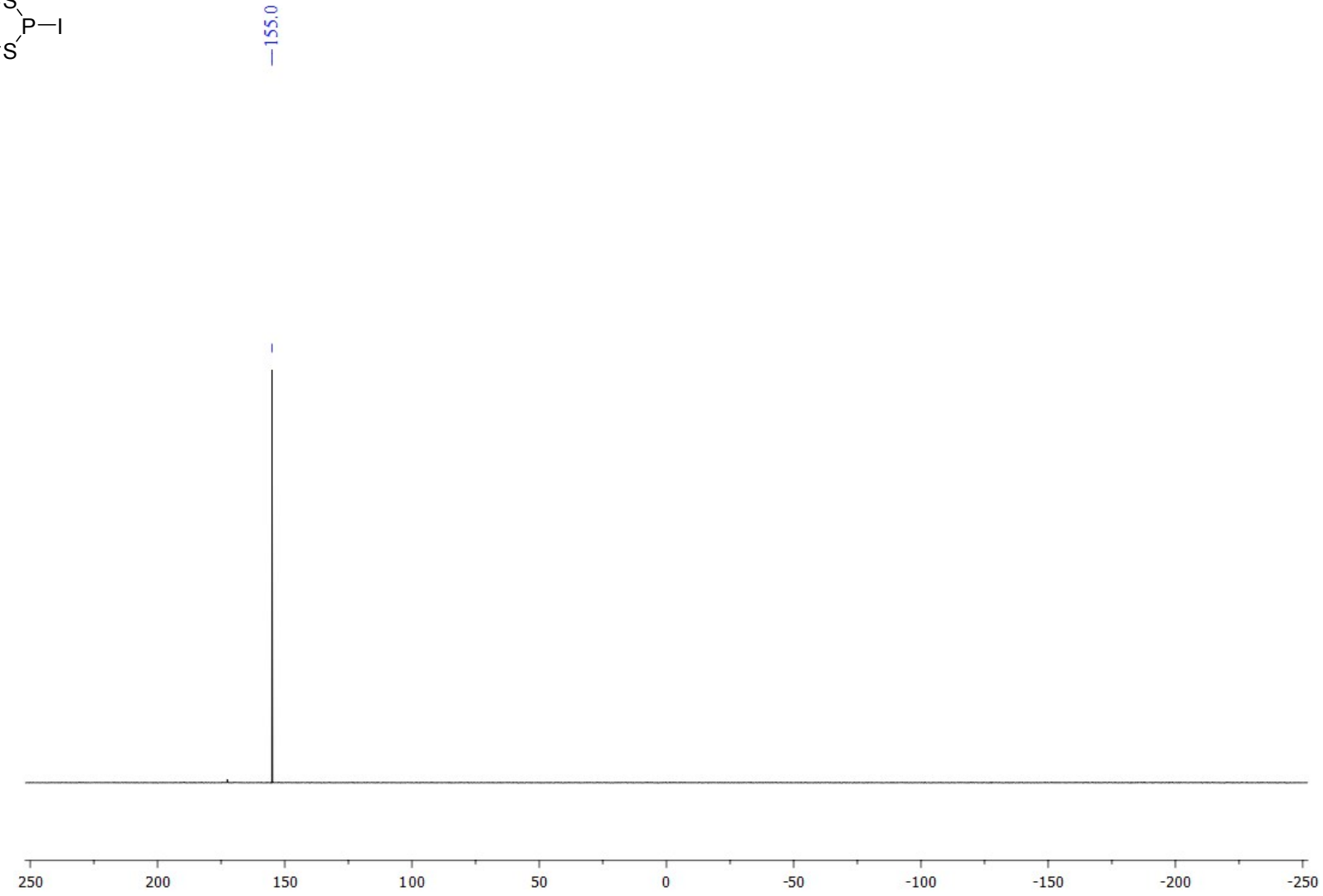


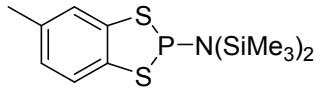

K, $CDCl_3$)
of 2-

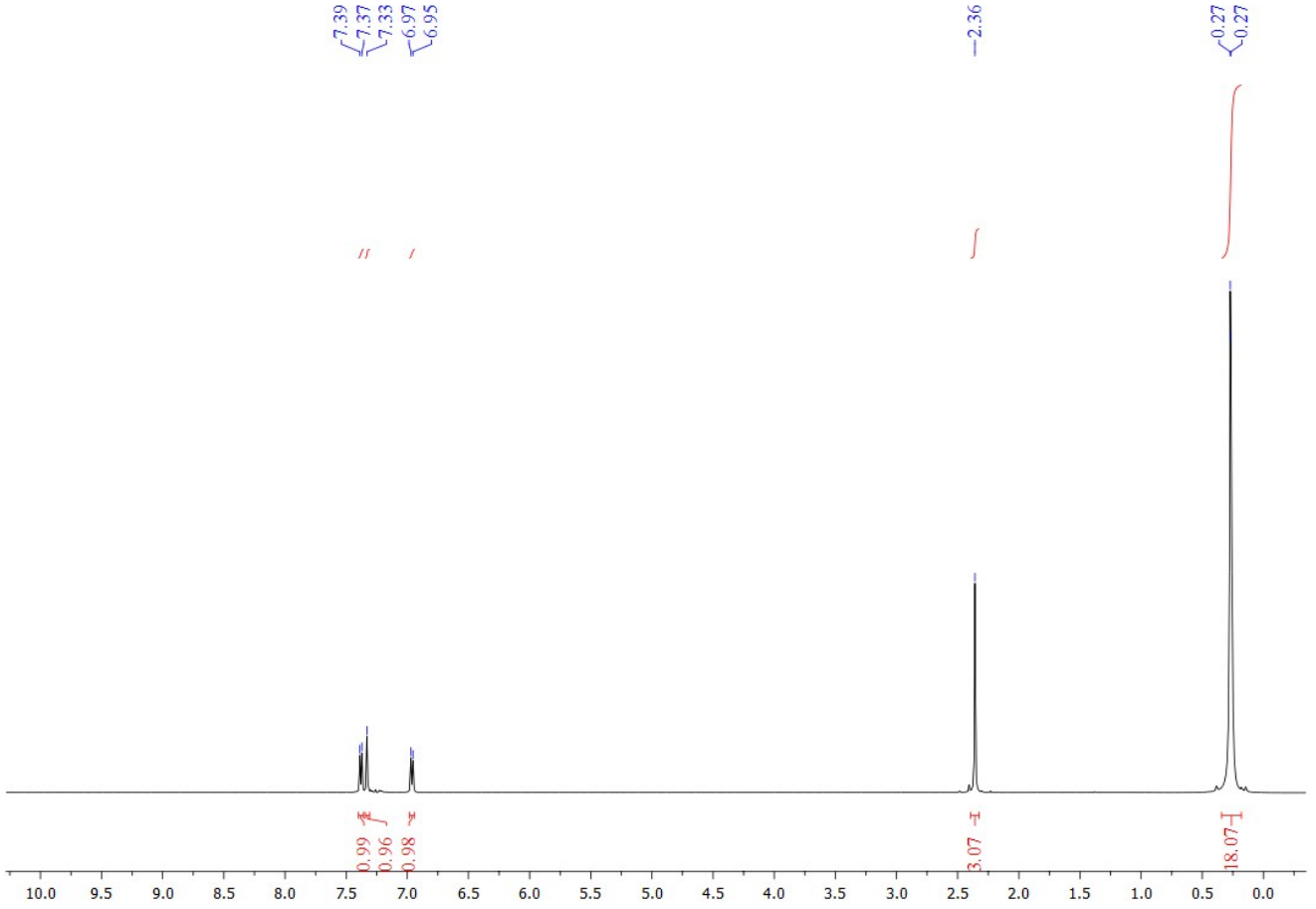
**S4.1.9**
$^{31}P\{^{1}H\}$
NMR (202
MHz, 295
spectrum



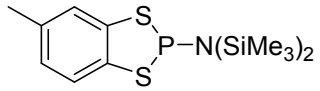
bromo-5-methylbenzo-1,3,2-dithiaphosphole (**1c**)

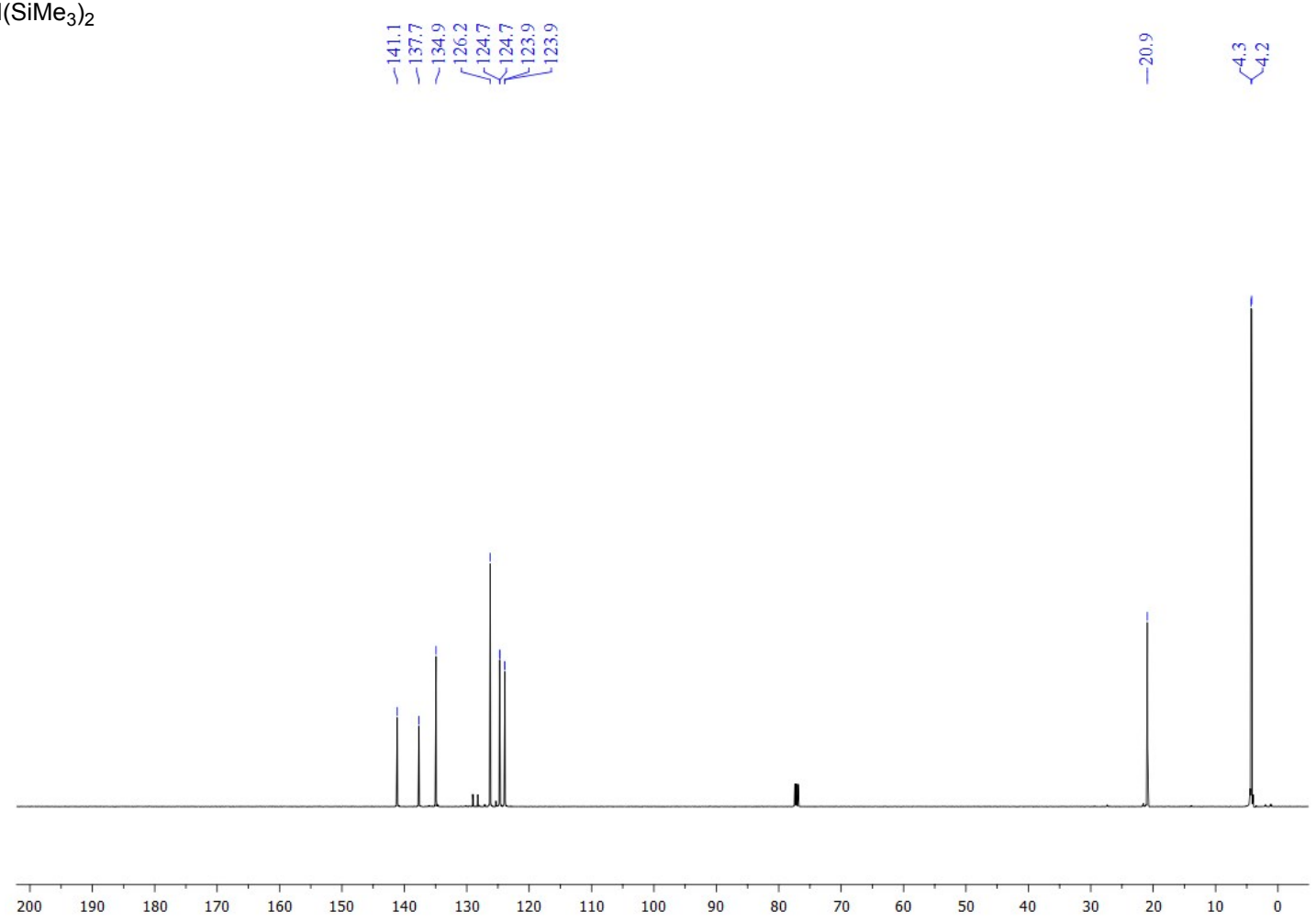
**S4.1.10** $^{1}$H NMR (500 MHz, 295 K, $CDCl_3$) spectrum of 5-methyl-N,N-bis(trimethylsilyl)benzo-1,3,2-dithiaphosphol-2-amine (**1d**)



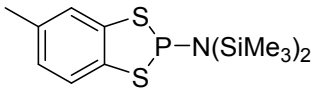



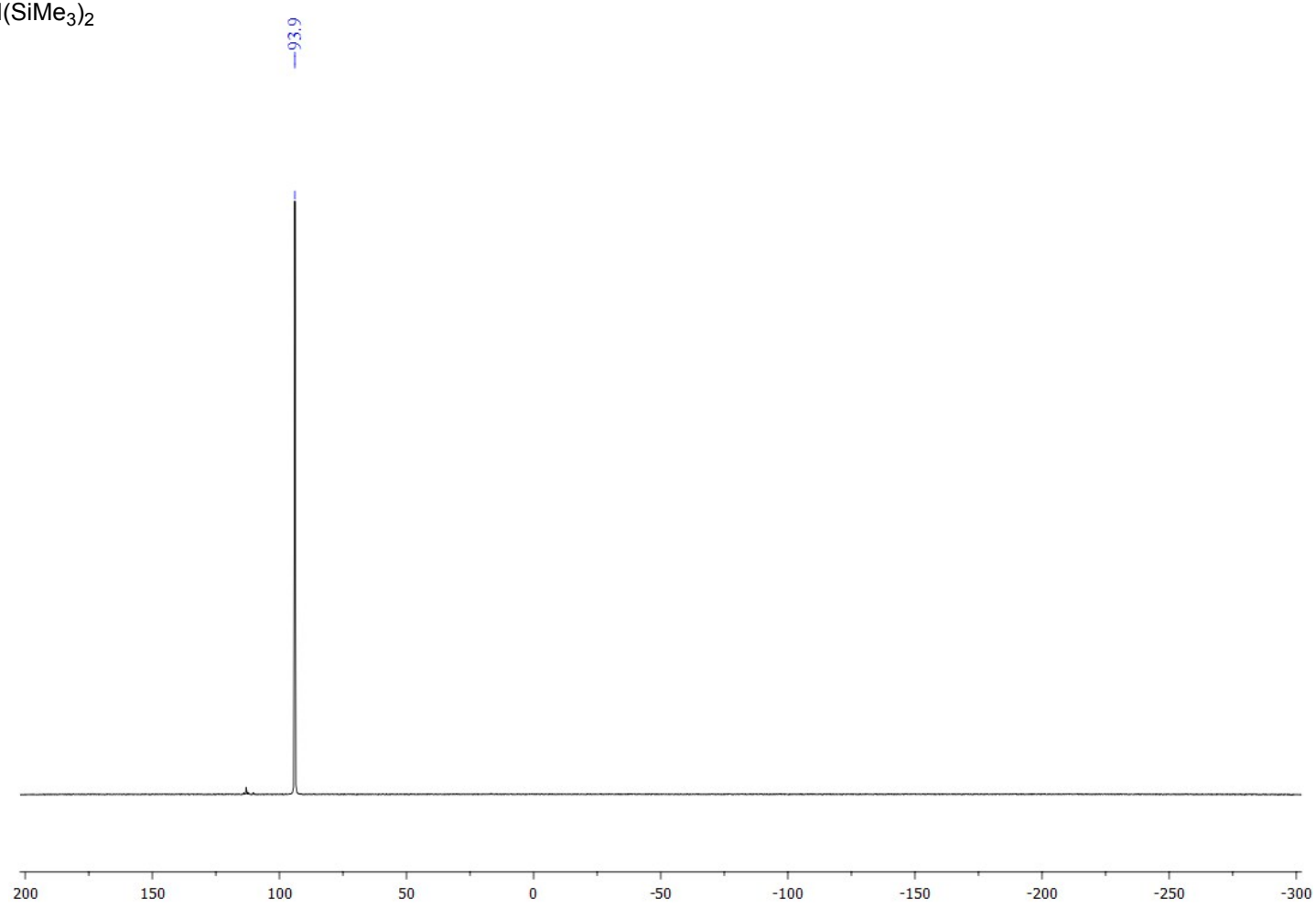
**S4.1.11** $^{13}C\{^{1}H\}$ NMR (126 MHz, 295 K, $CDCl_3$) spectrum of 5-methyl-N,N-bis(trimethylsilyl)benzo-1,3,2-dithiaphosphol-2-amine (**1d**)



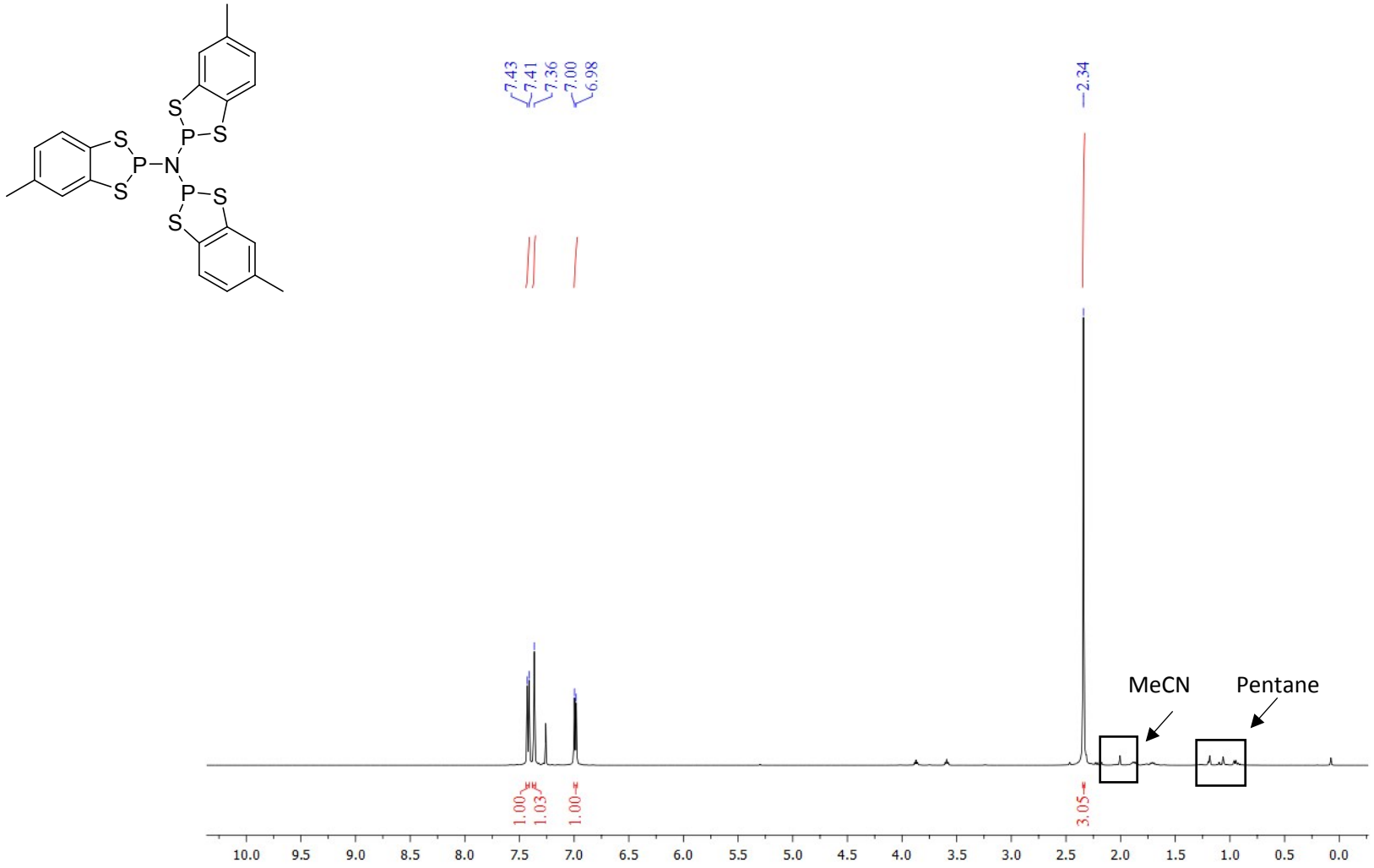



**S4.1.12** $^{31}P\{^{1}H\}$ NMR (202 MHz, 295 K, $CDCl_3$) spectrum of 5-methyl-N,N-bis(trimethylsilyl)benzo-1,3,2-dithiaphosphol-2-amine (**1d**)

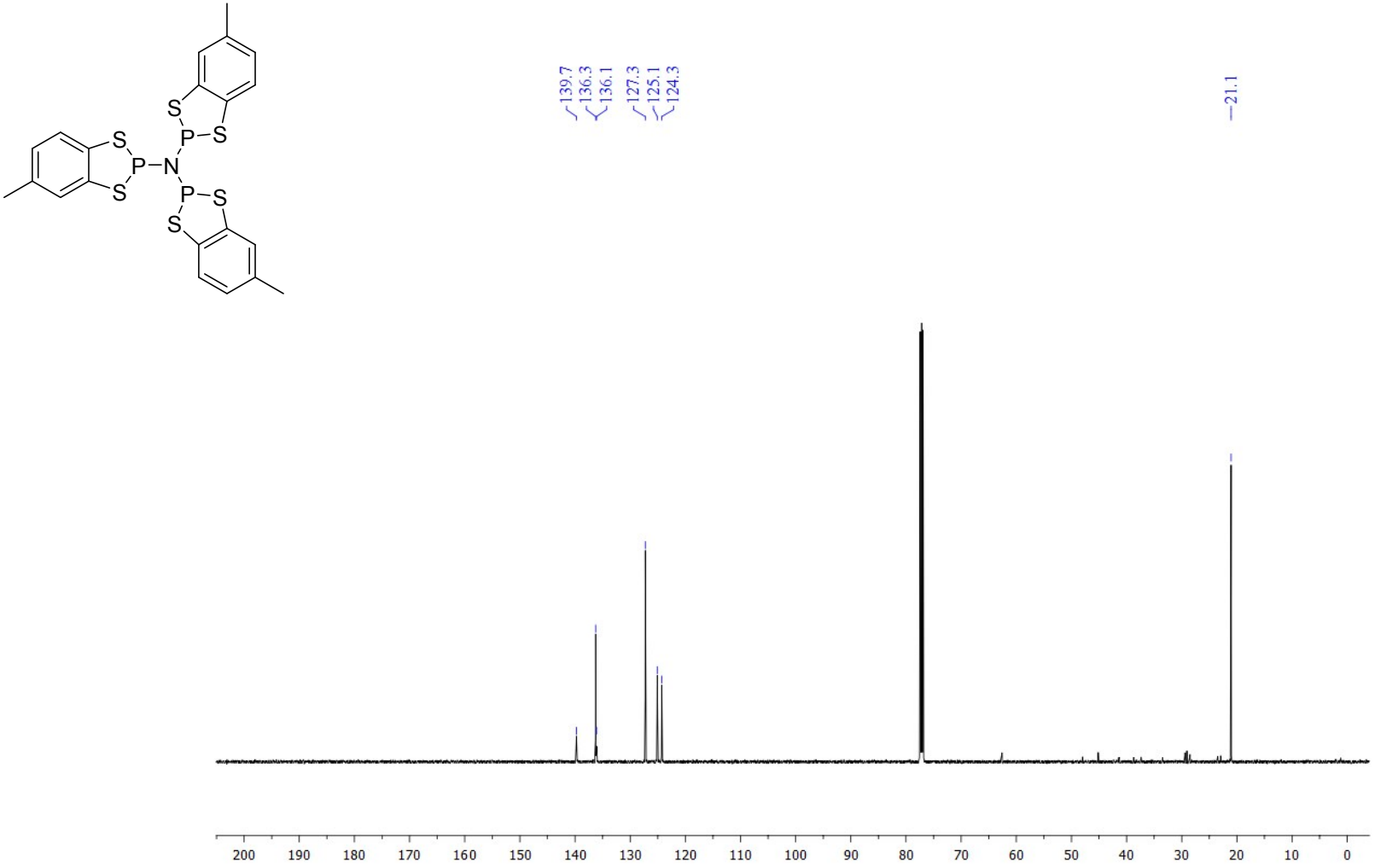


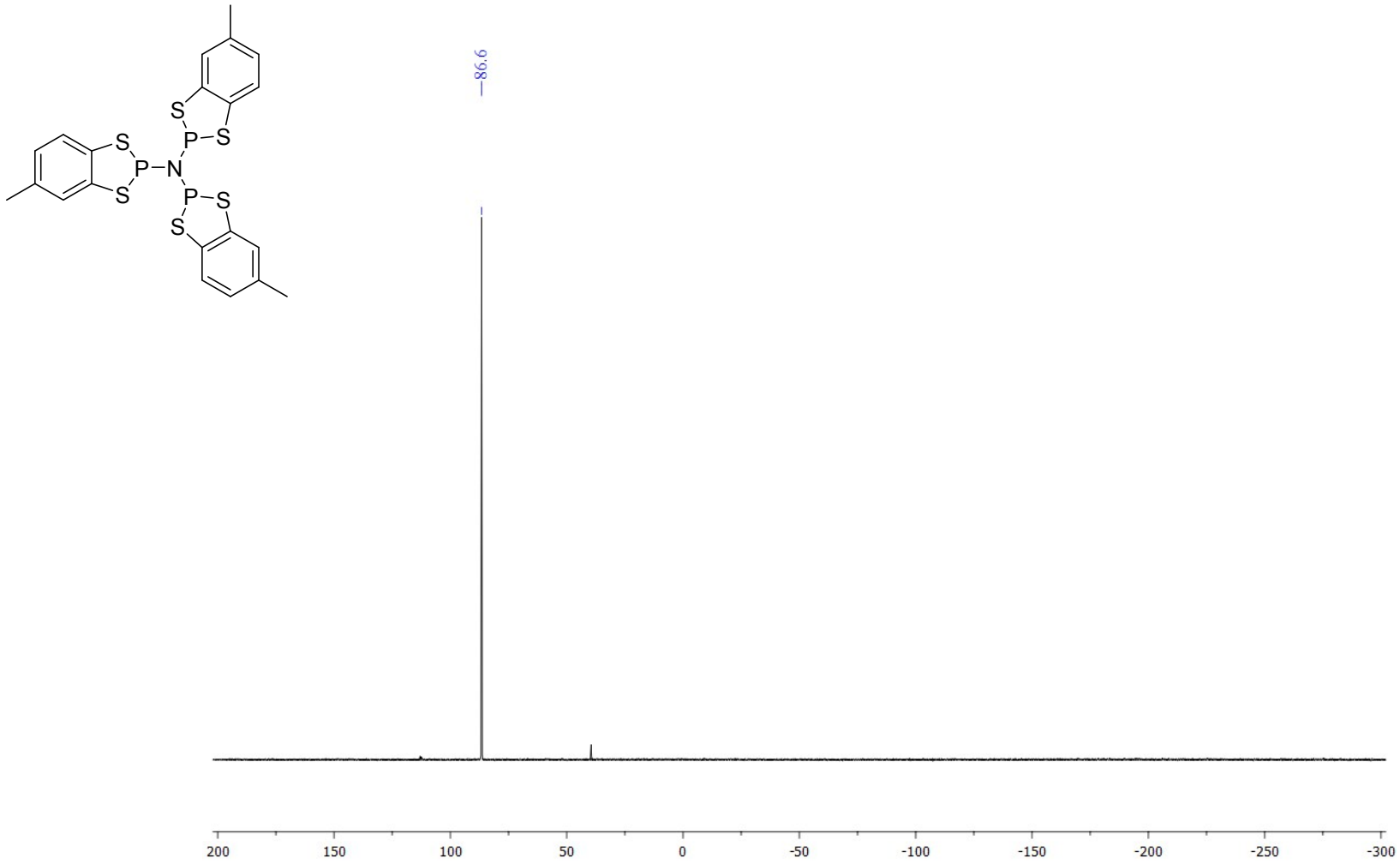
**S4.1.13** $^{1}$H NMR (500 MHz, 295 K, $CDCl_3$) spectrum of tris(5-methylbenzo-1,3,2-dithiaphosphol-2-yl)amine (**1e**)



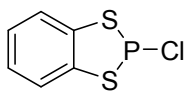
**S4.1.14** $^{13}C\{^{1}H\}$ NMR (126 MHz, 295 K, $CDCl_3$) spectrum of tris(5-methylbenzo-1,3,2-dithiaphosphol-2-yl)amine (**1e**)

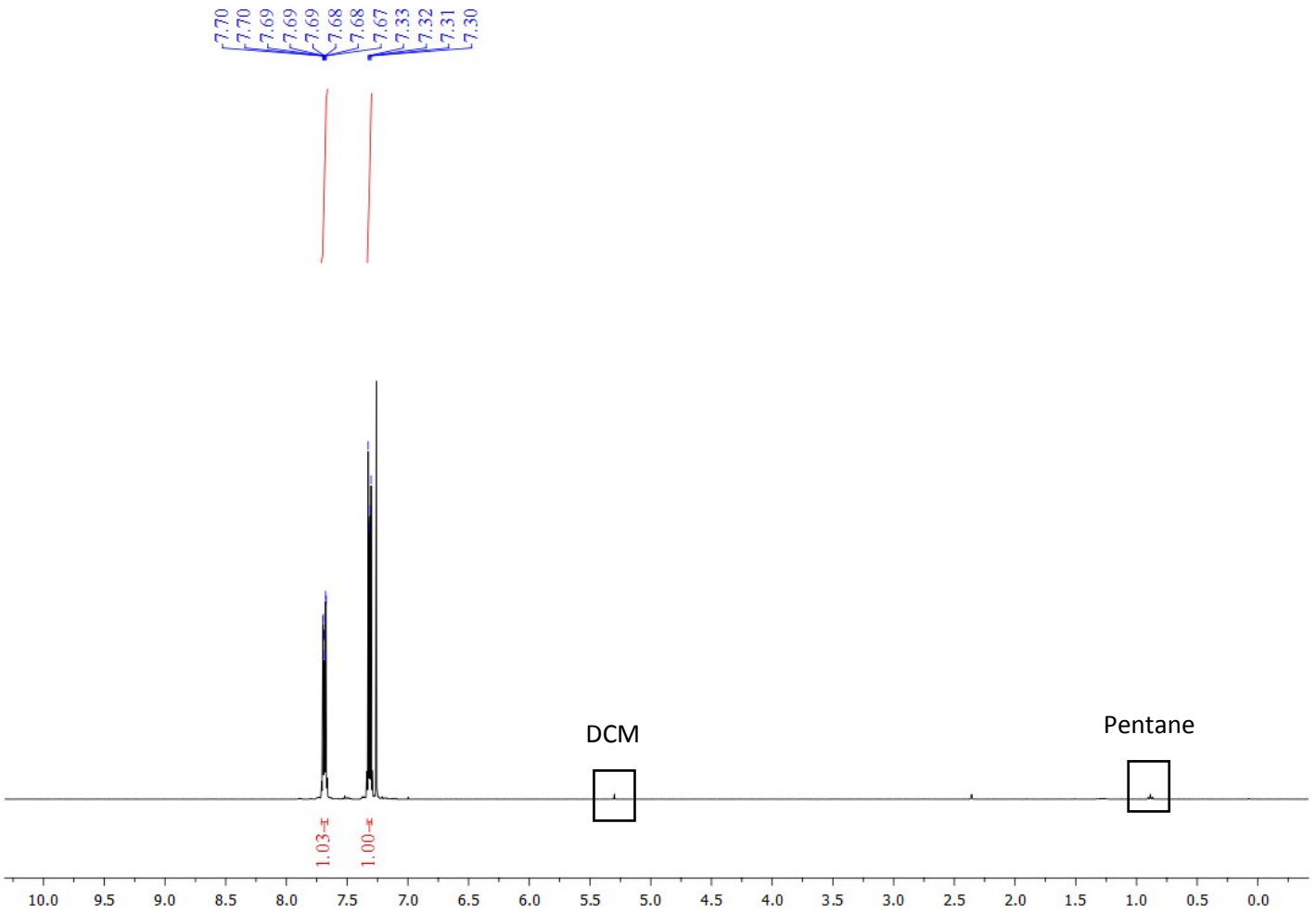


**S4.1.15** $^{31}P\{^{1}H\}$ NMR (202 MHz, 295 K, $CDCl_3$) spectrum of tris(5-methylbenzo-1,3,2-dithiaphosphol-2-yl)amine (**1e**)

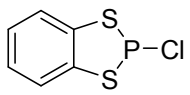


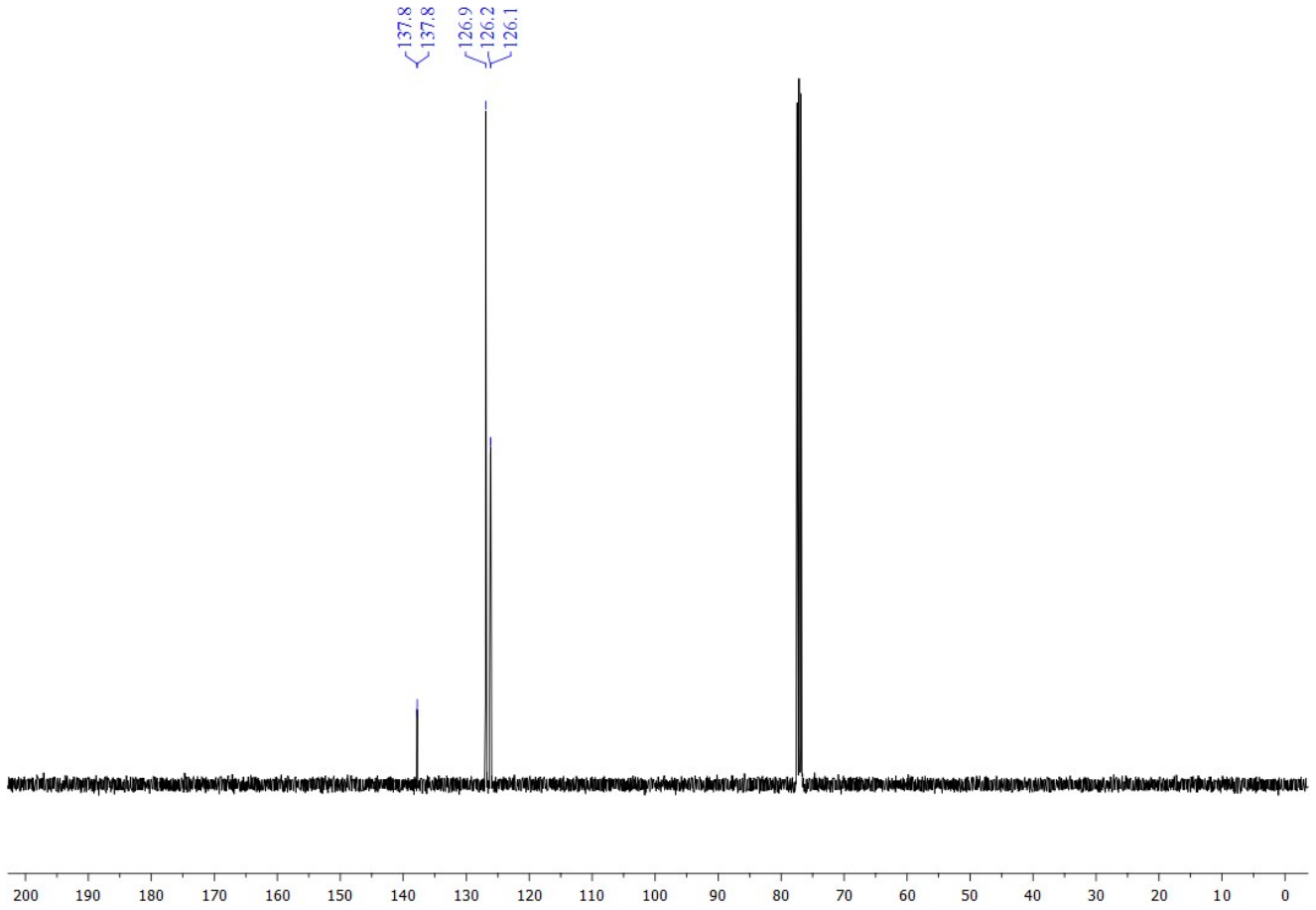
**S4.1.16** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-chlorobenzo-1,3,2-dithiaphosphole (**2a**)



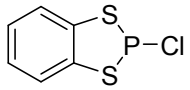



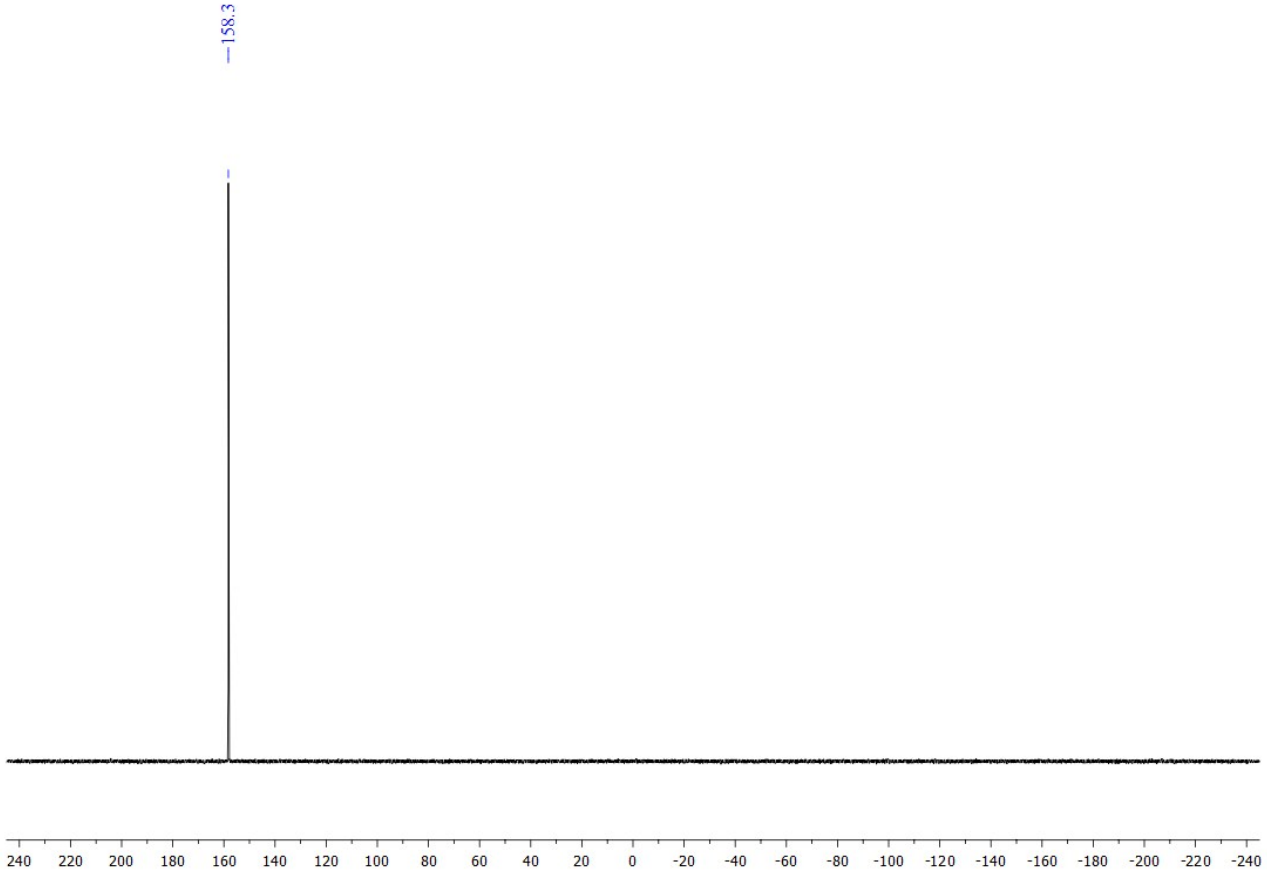
**S4.1.17** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 2-chlorobenzo-1,3,2-dithiaphosphole (**2a**)



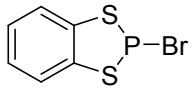



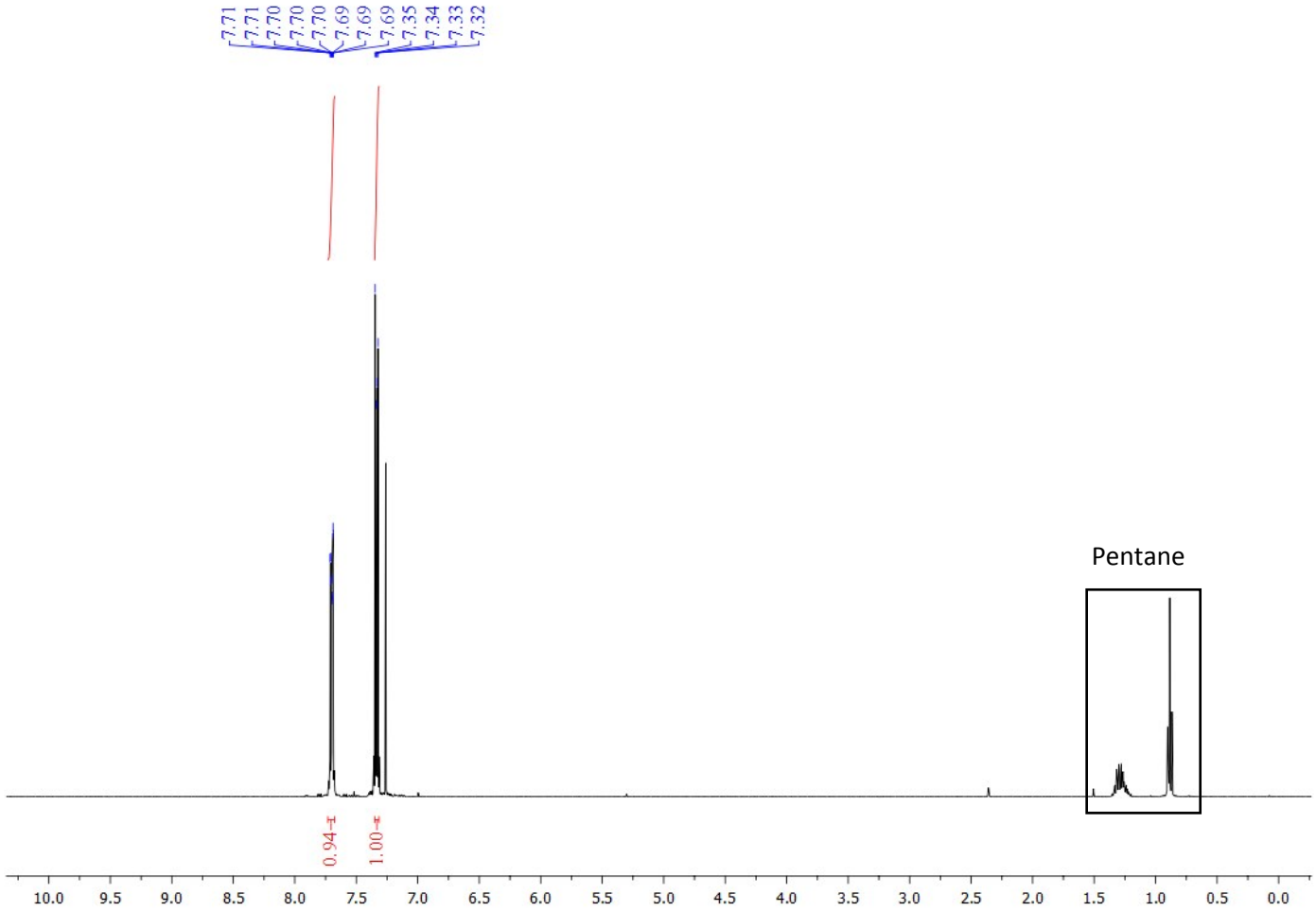
**S4.1.18** $^{31}P\{^{1}H\}$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 2-chlorobenzo-1,3,2-dithiaphosphole (**2a**)



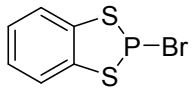



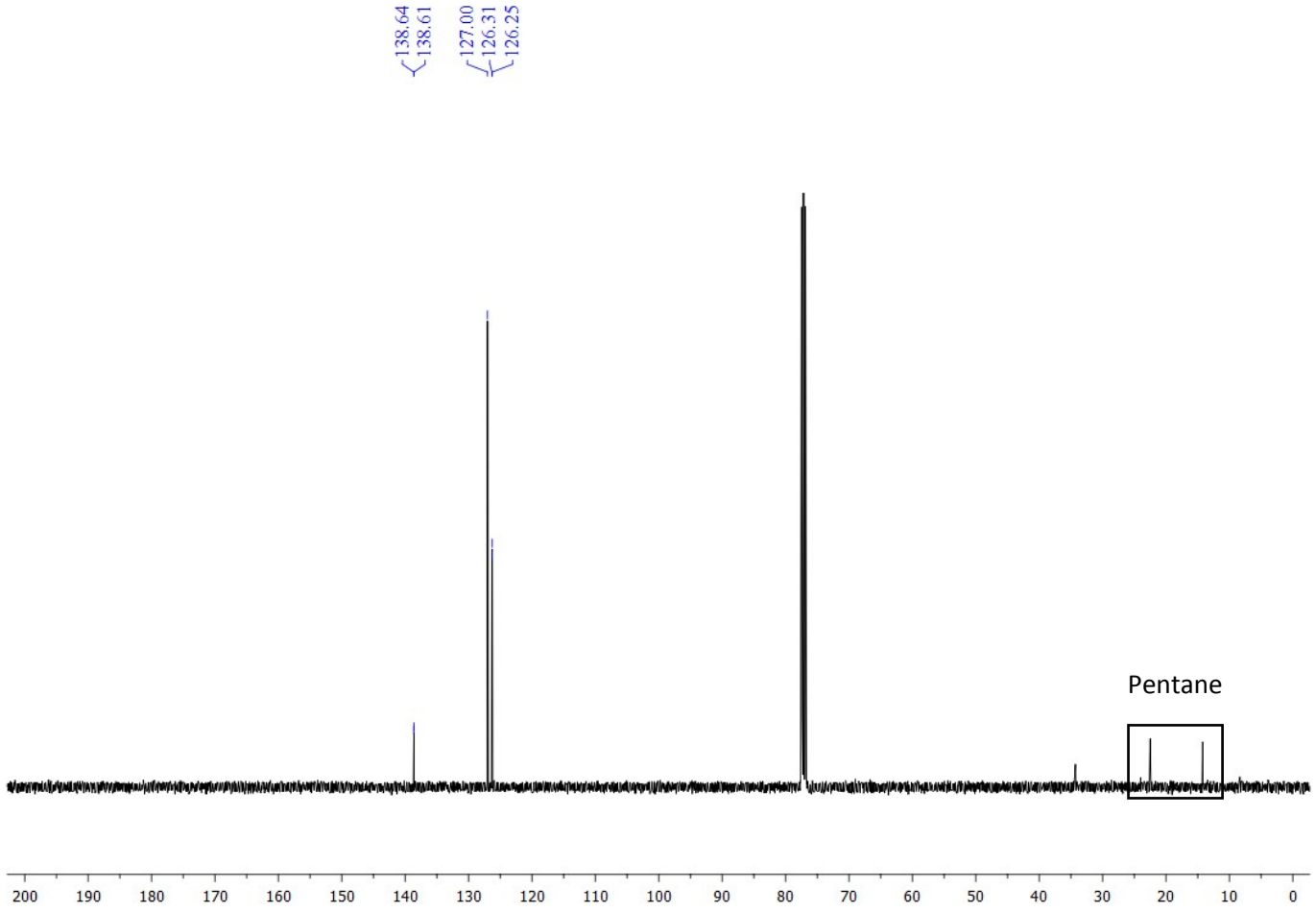
**S4.1.19** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-bromobenzo-1,3,2-dithiaphosphole (**2b**)



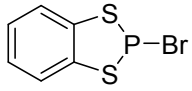



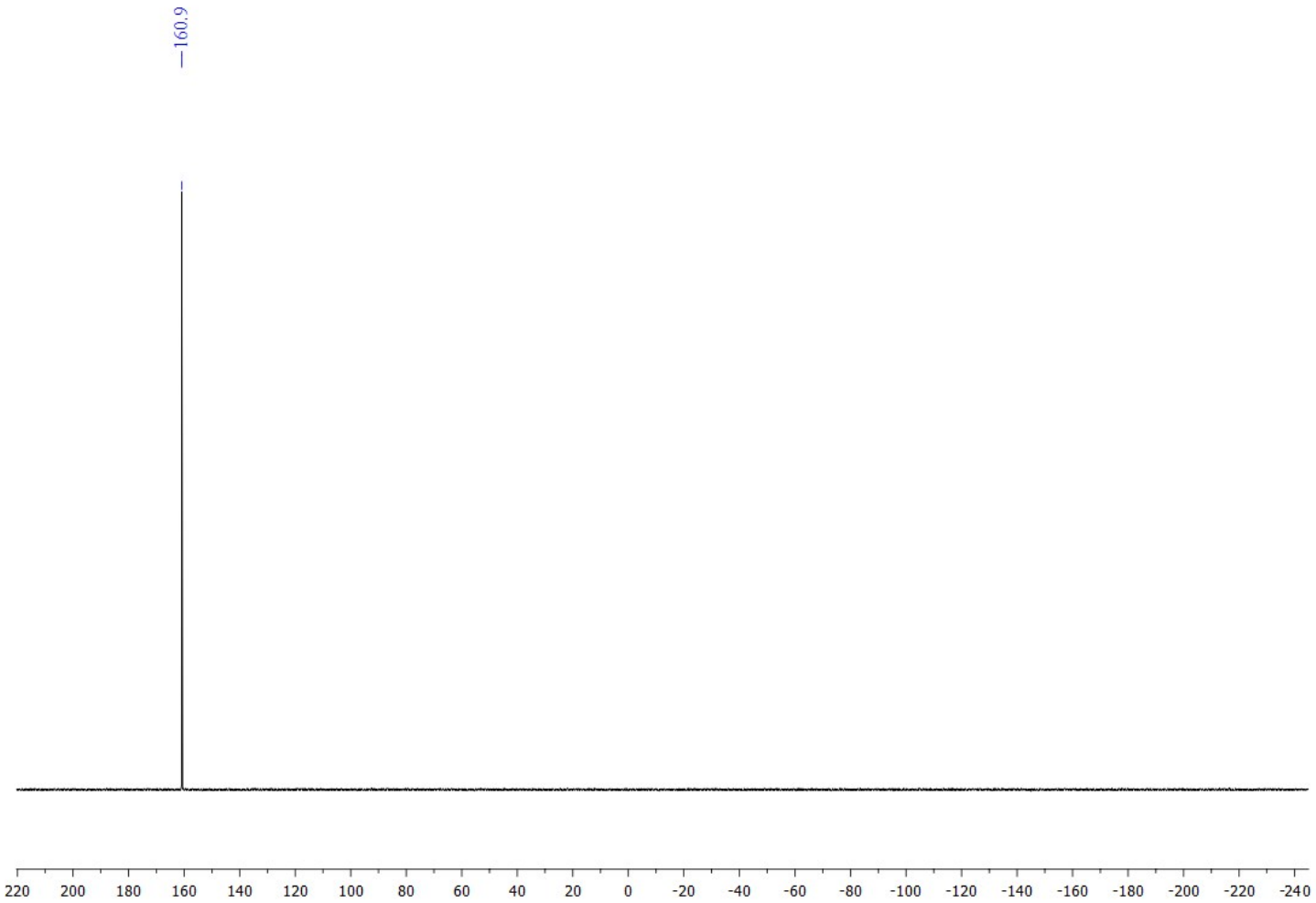
**S4.1.20** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 2-bromobenzo-1,3,2-dithiaphosphole (**2b**)



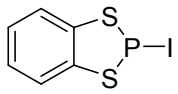



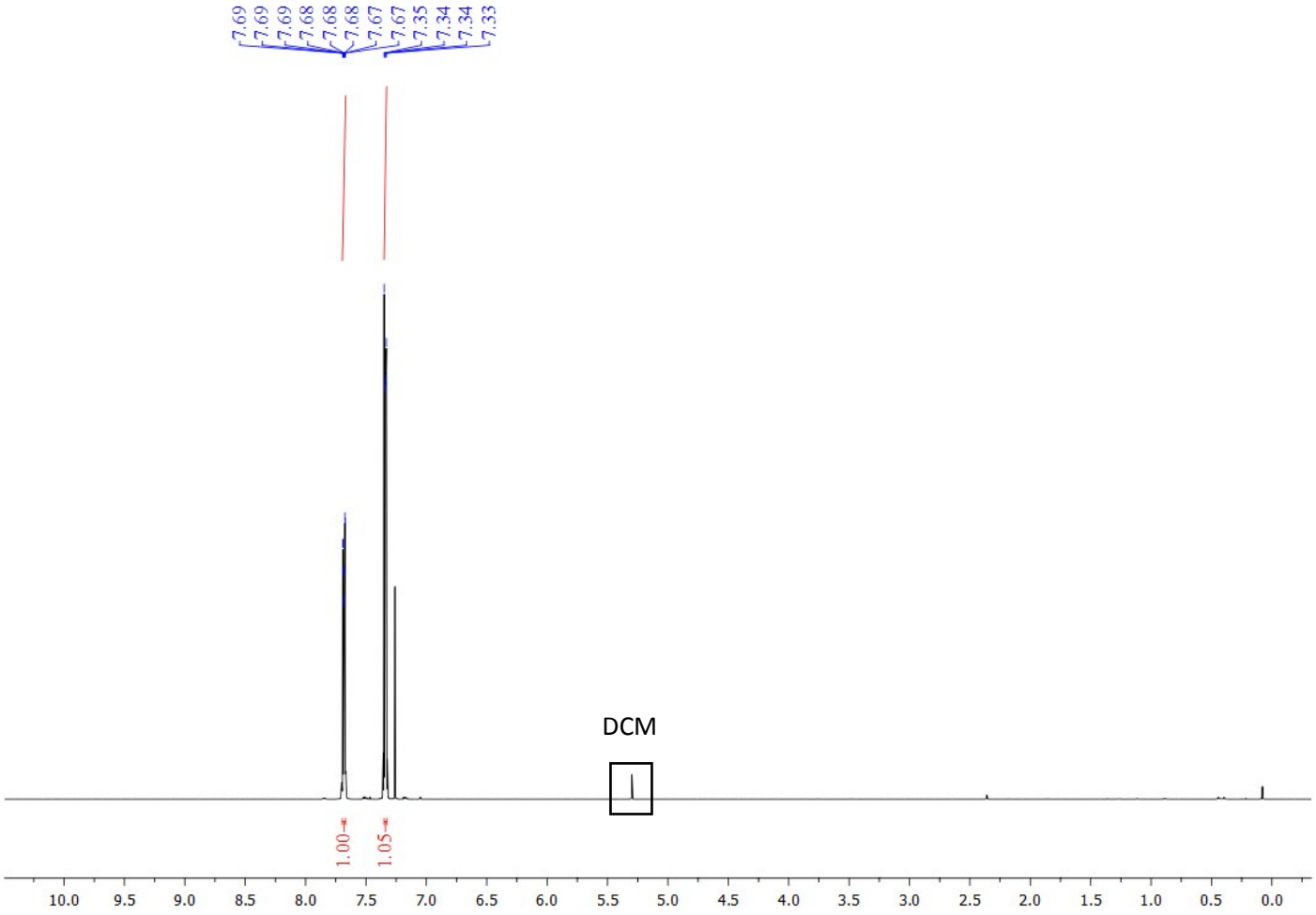
**S4.1.21** $^{31}P\{^{1}H\}$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 2-bromobenzo-1,3,2-dithiaphosphole (**2b**)



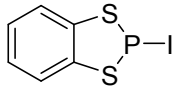



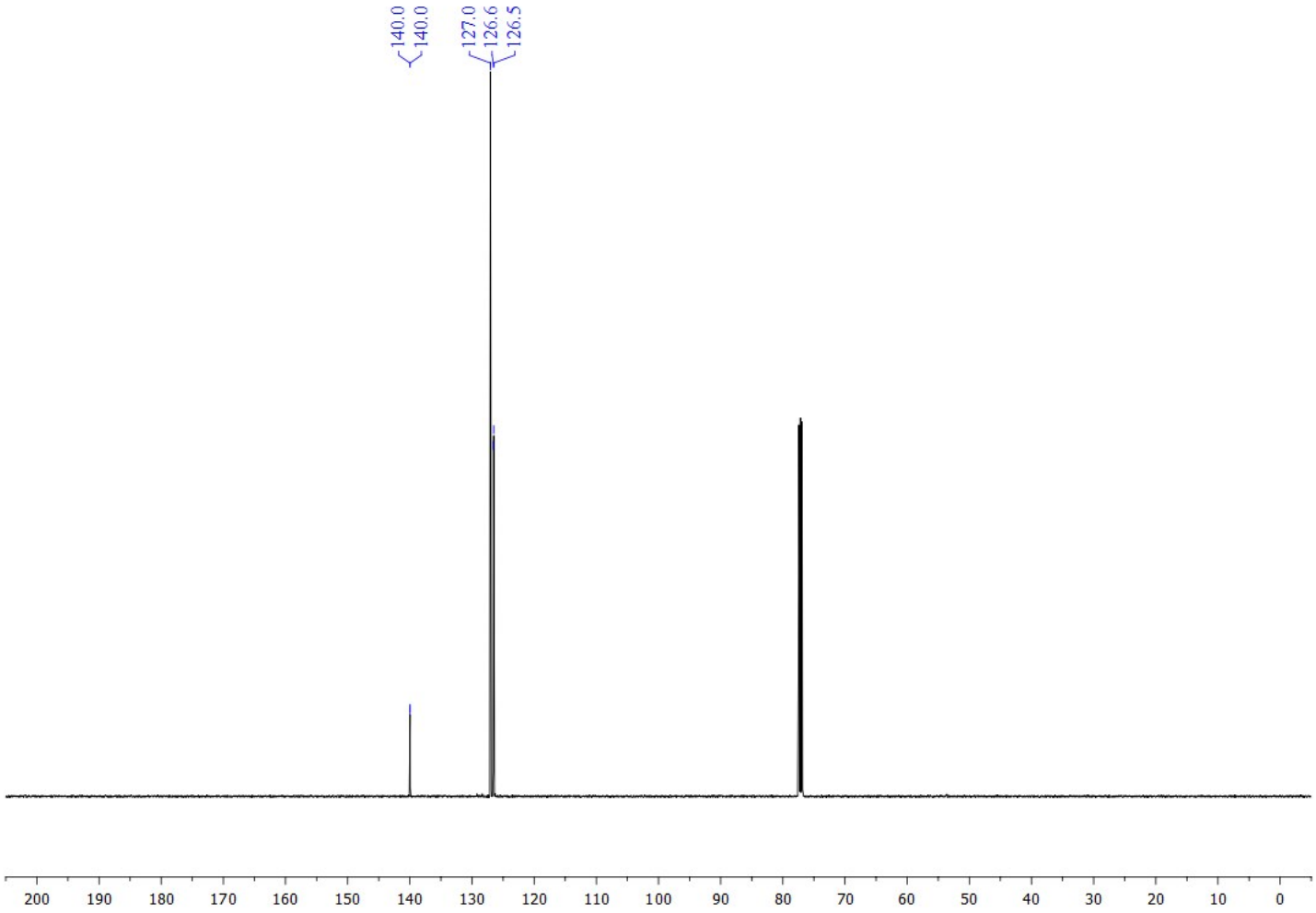
**S4.1.22** $^{1}$H NMR (500 MHz, 295 K, $CDCl_3$) spectrum of 2-iodobenzo-1,3,2-dithiaphosphole (**2c**)



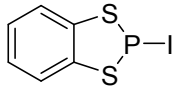



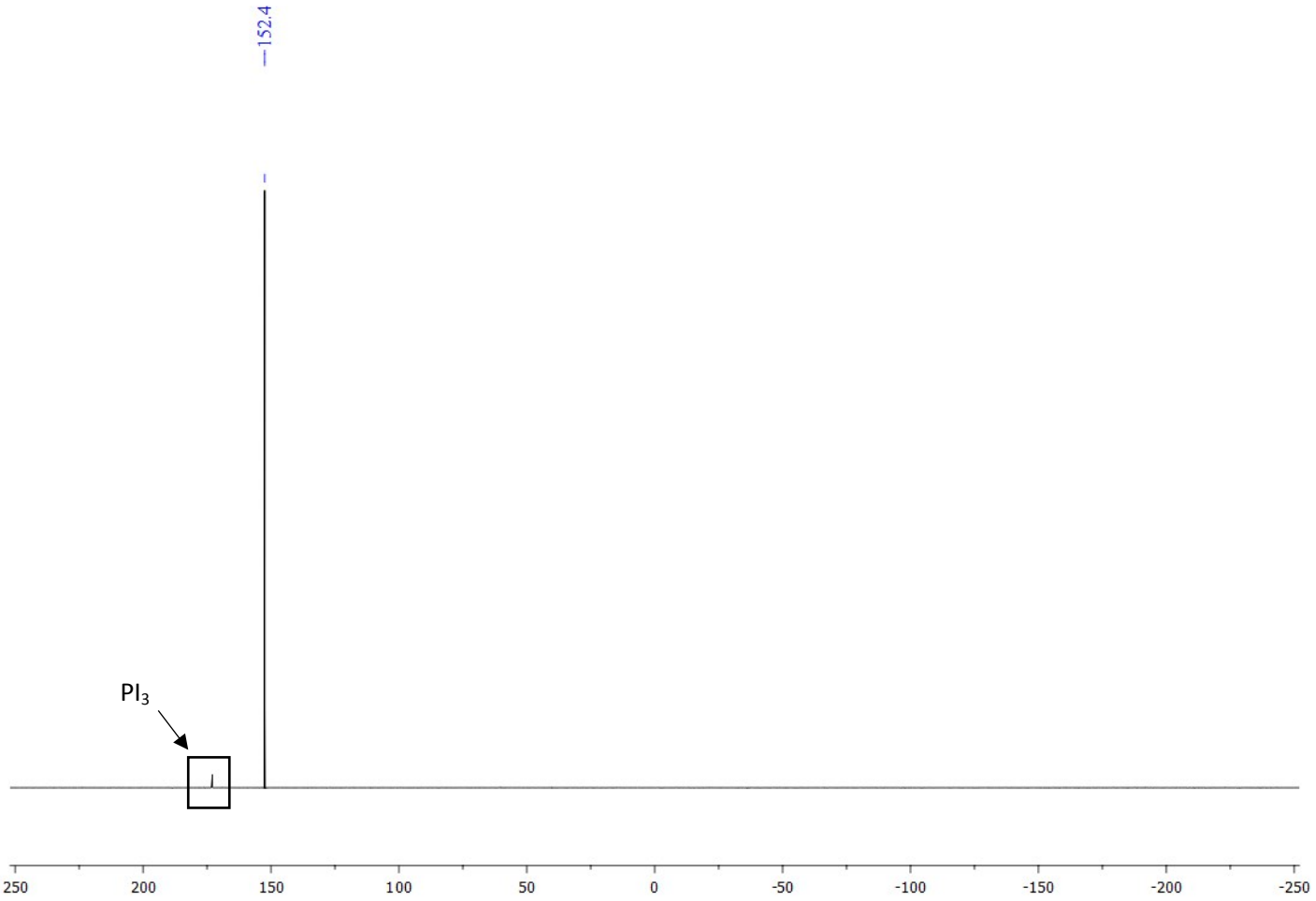
**S4.1.23** $^{13}C\{^{1}H\}$ NMR (126 MHz, 295 K, $CDCl_3$) spectrum of 2-iodobenzo-1,3,2-dithiaphosphole (**2c**)



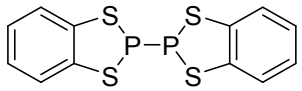



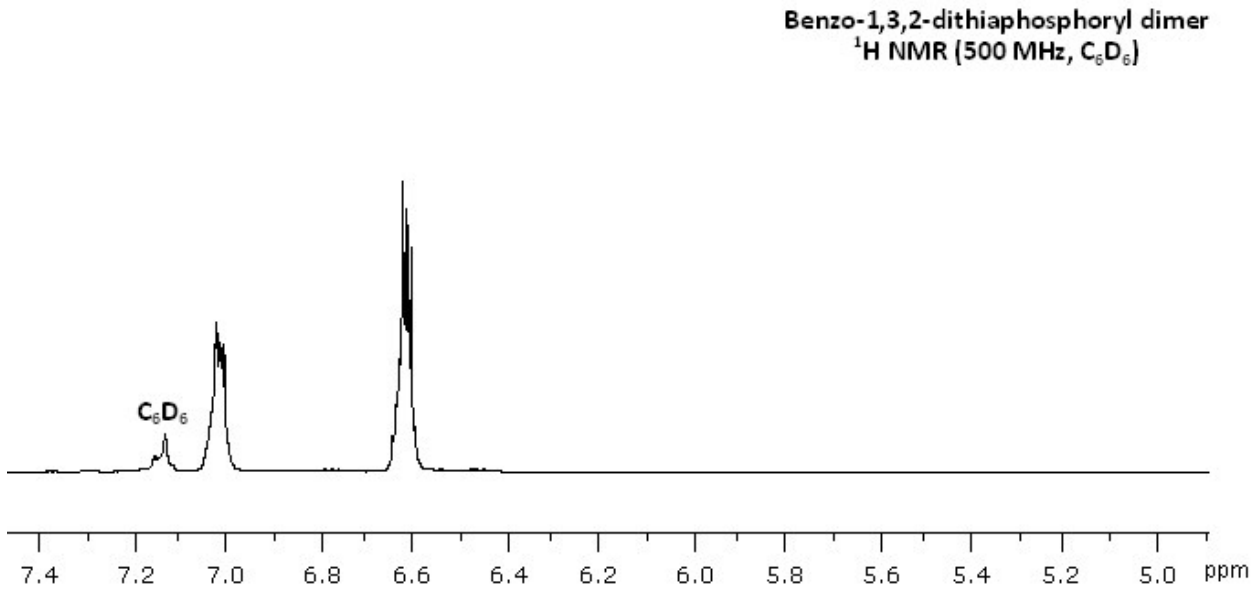
**S4.1.24** $^{31}P\{^{1}H\}$ NMR (202 MHz, 295 K, $CDCl_3$) spectrum of 2-iodobenzo-1,3,2-dithiaphosphole (**2c**)



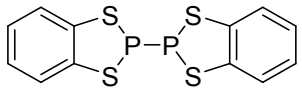



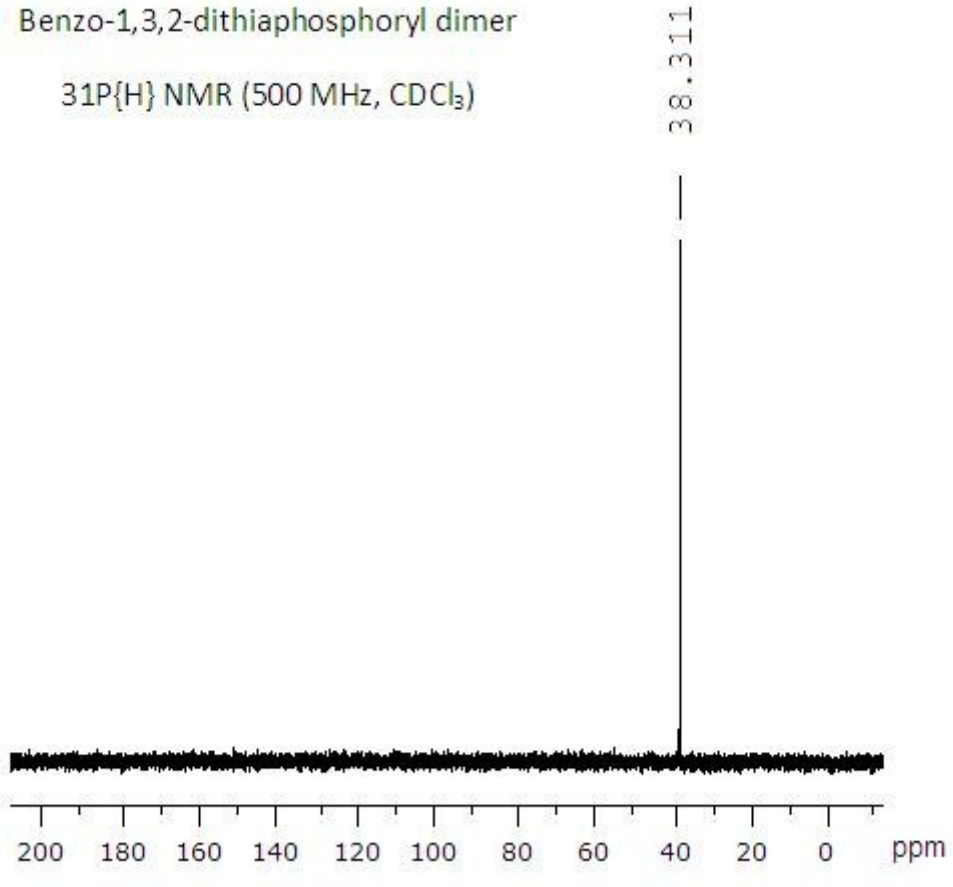

**S4.1.25** $^{1}H$ NMR (500 MHz, 295 K, $C_6D_6$) spectrum of 1,3,2-benzodithiaphosphoryl dimer (**4**)



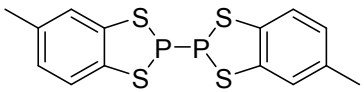


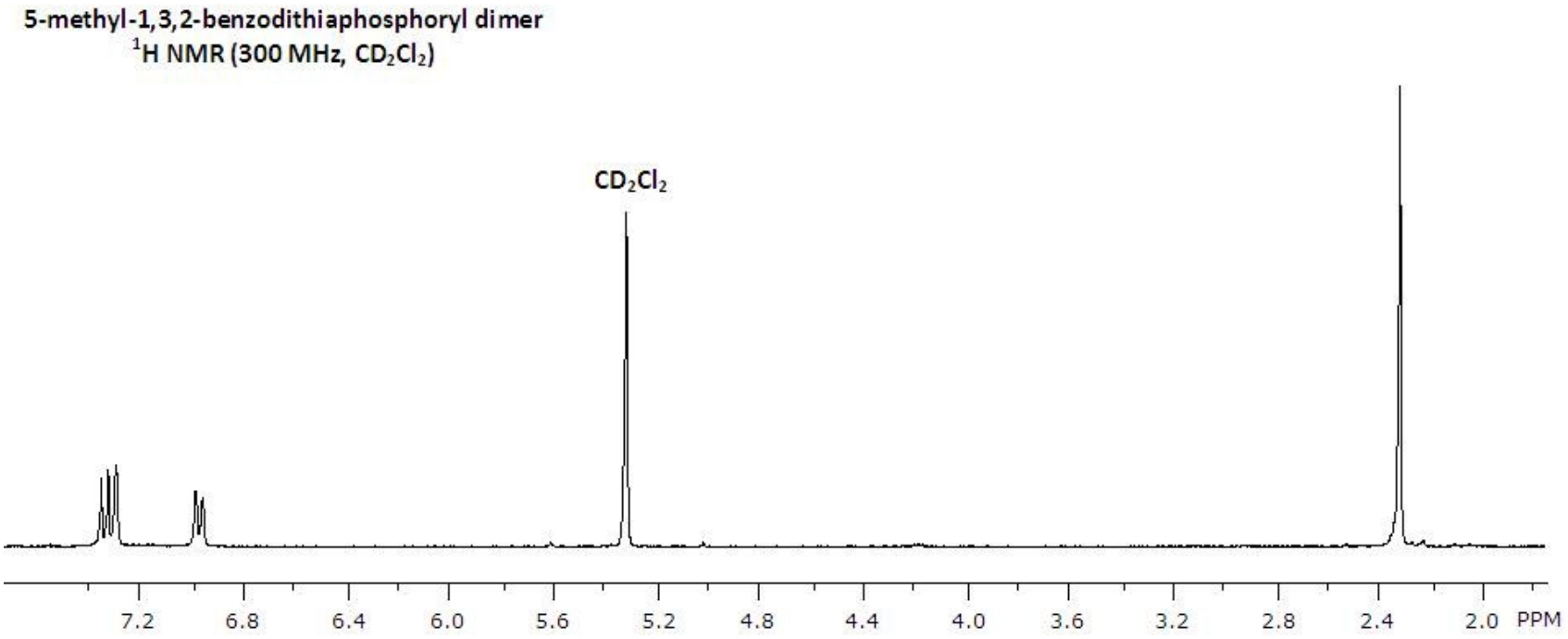

**S4.1.26** $^{31}P\{^{1}H\}$ NMR (202 MHz, 295 K, $CDCl_3$) spectrum of 1,3,2-benzodithiaphosphoryl dimer (**4**)



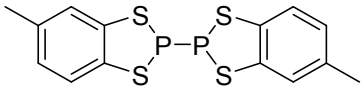


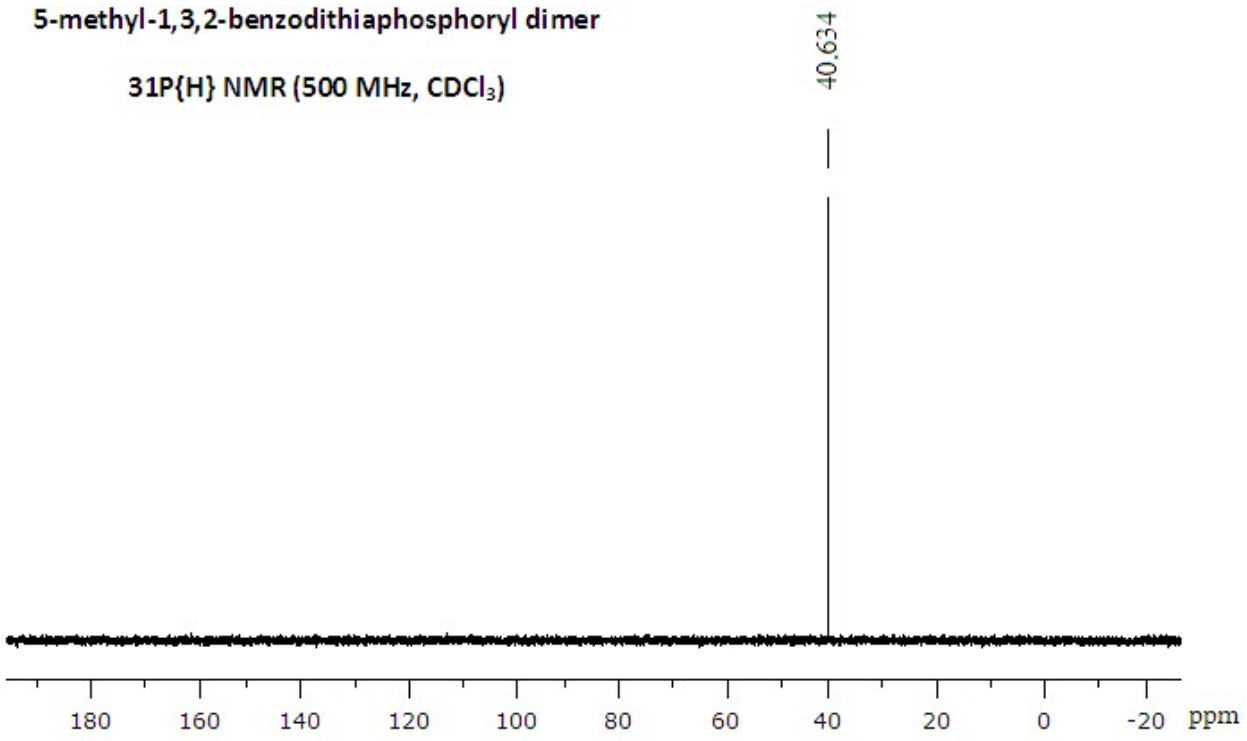

**S4.1.27** $^{1}$H NMR (300 MHz, 295 K, $CD_2Cl_2$) spectrum of 5-methyl-1,3,2-benzodithiaphosphoryl dimer (**5**)



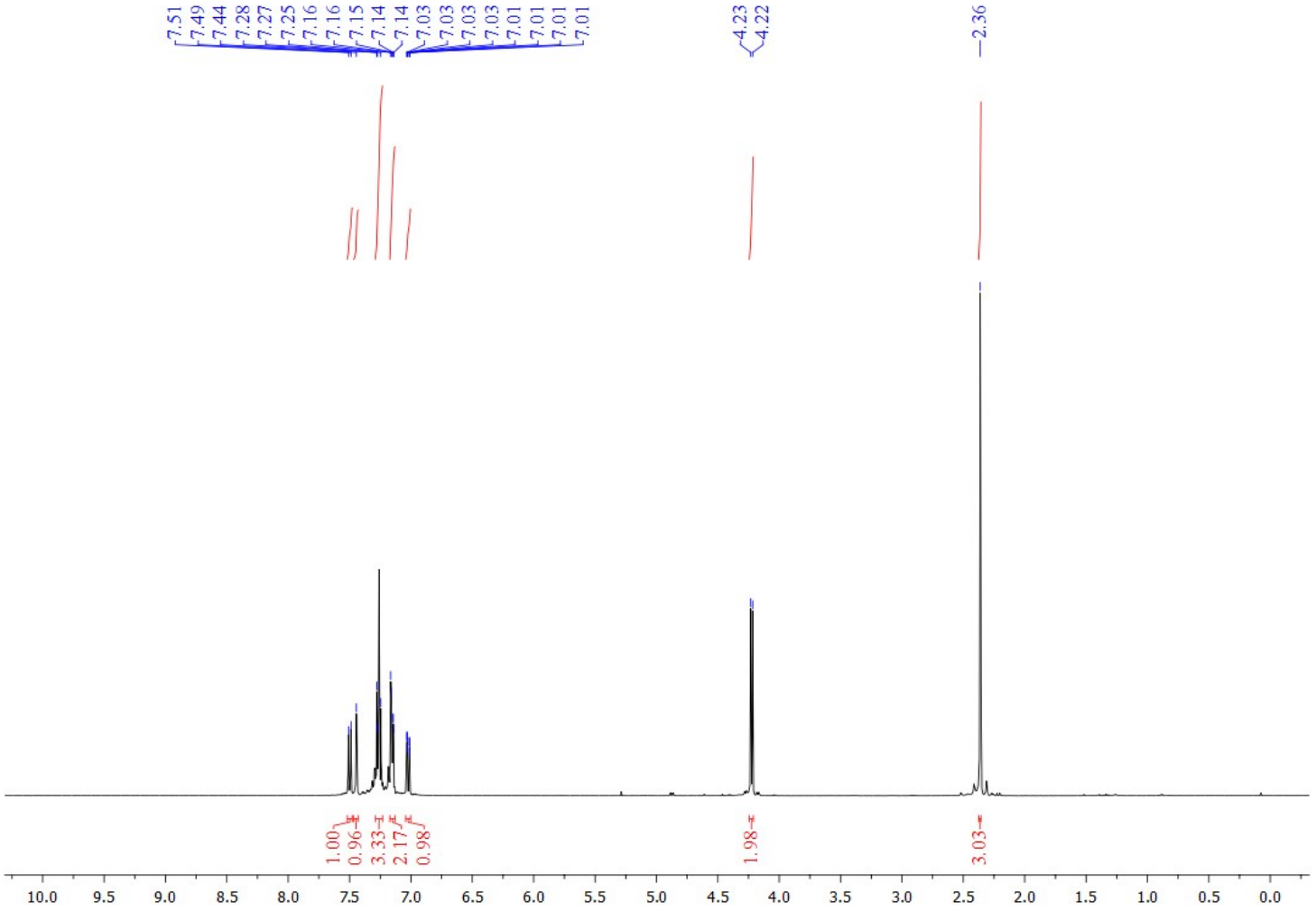



**S4.1.28** $^{31}P\{^{1}H\}$ NMR (121 MHz, 295 K, $CDCl_3$) spectrum of 5-methyl-1,3,2-benzodithiaphosphoryl dimer (**5**)






**S4.1.29** $^{1}$H NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-(benzyloxy)-5-methylbenzo-1,3,2-dithiaphosphole (**6a**)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7.03
7.01
7.01
7.01
7.01
4.23
4.22
2.36
1.00
0.96
3.33
2.17
0.98
1.98
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
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1.5
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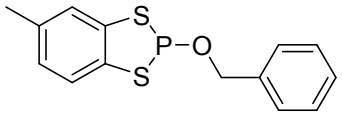
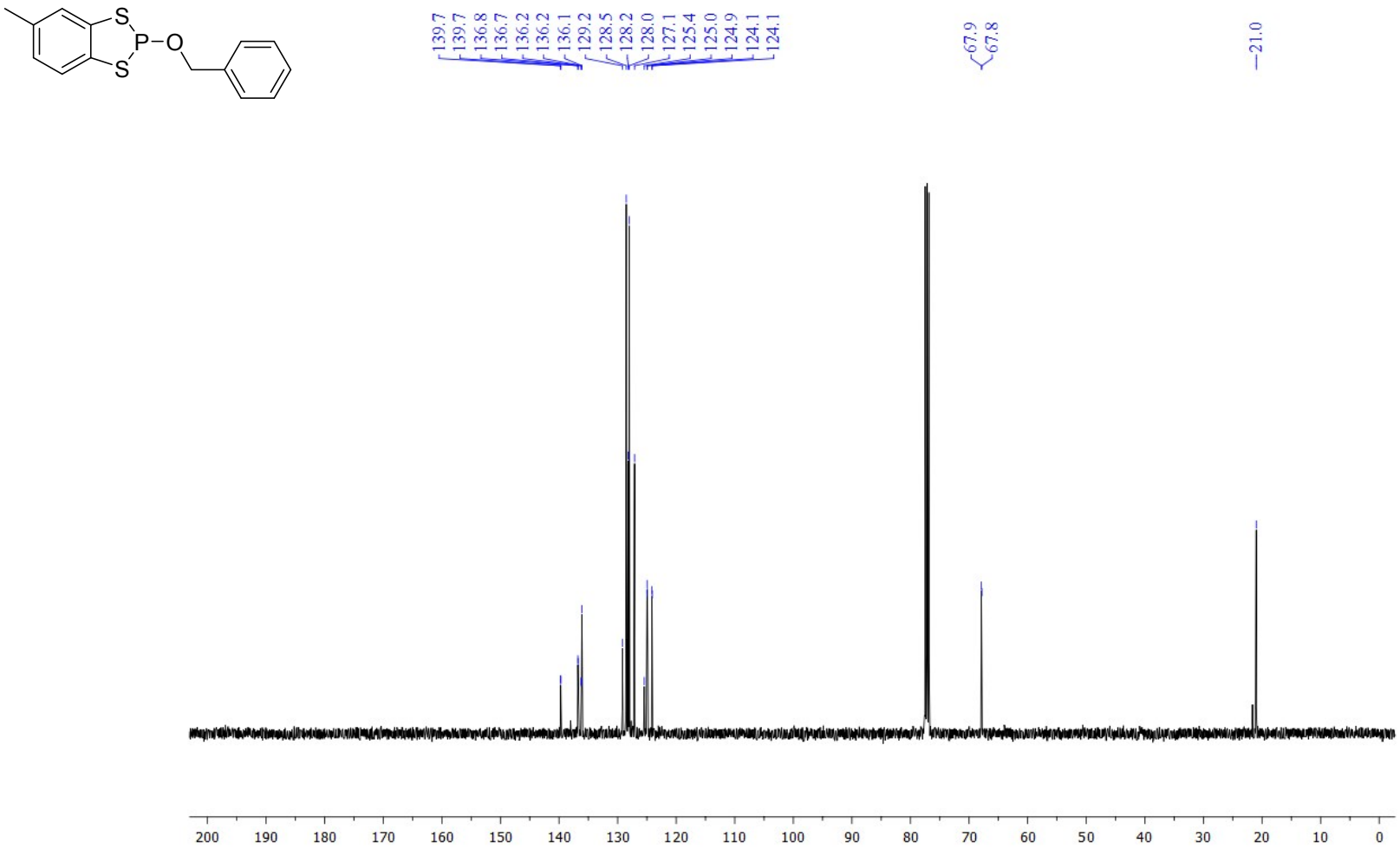
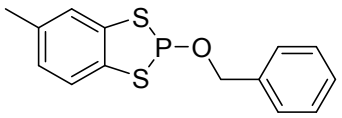
0.0


S
P
O
S

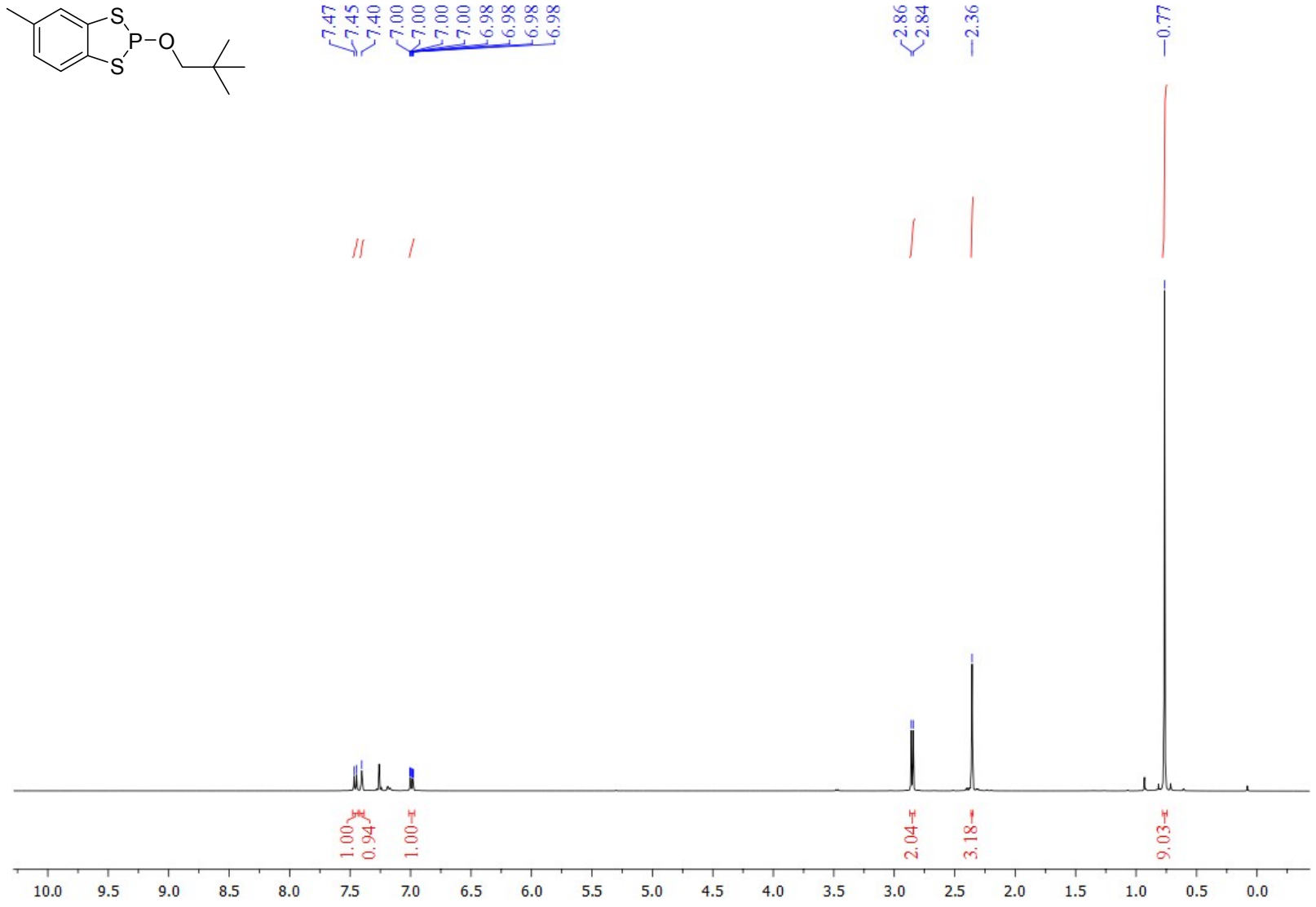
**S4.1.30** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 2-(benzyloxy)-5-methylbenzo-1,3,2-dithiaphosphole (**6a**)



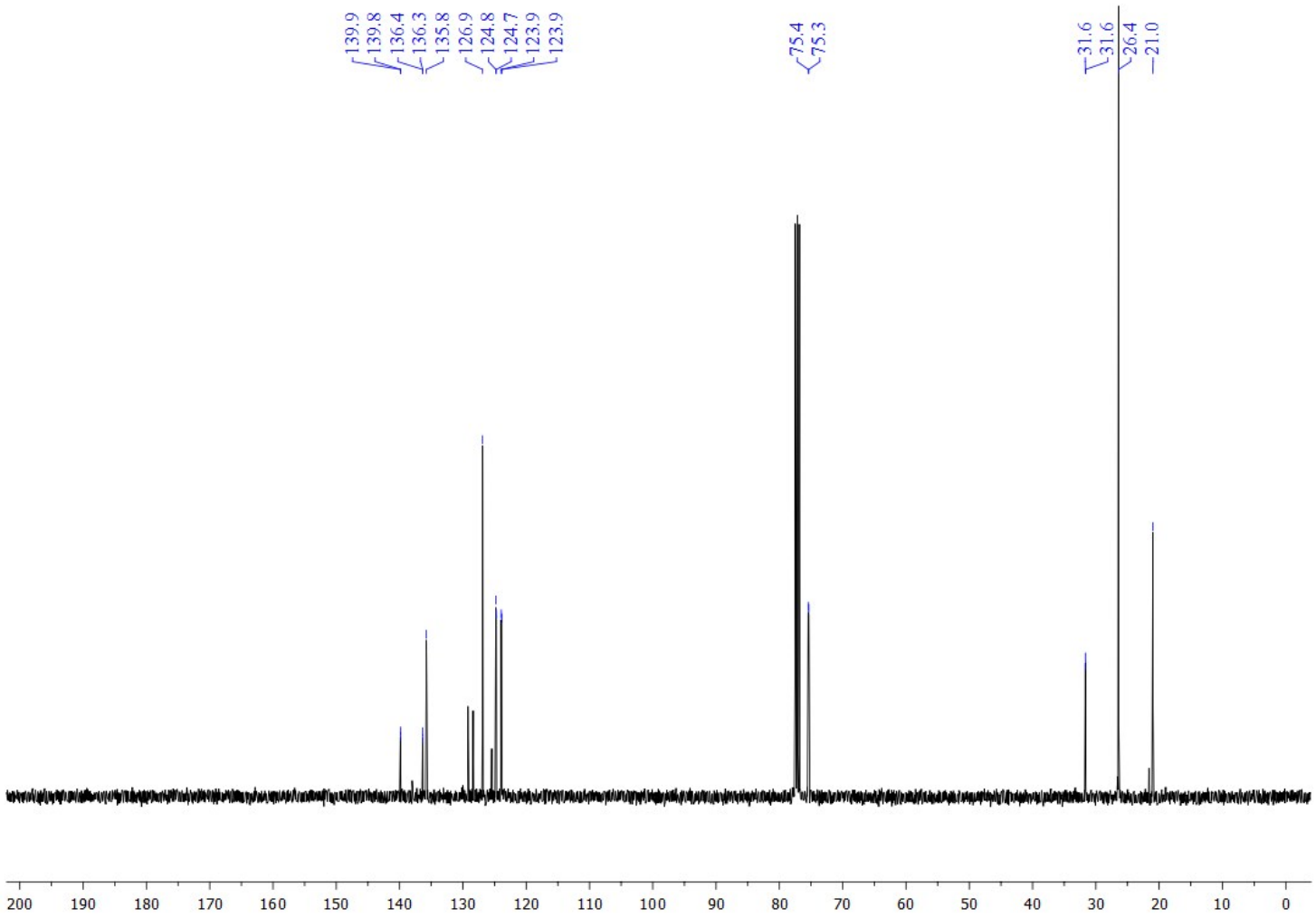
**S4.1.31** $^{31}P$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 2-(benzyloxy)-5-methylbenzo-1,3,2-dithiaphosphole (**6a**)



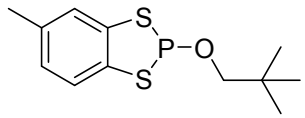
**S4.1.32** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 5-methyl-2-(neopentyloxy)benzo-1,3,2-dithiaphosphole (**6b**)



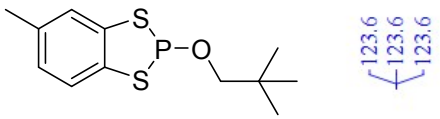
**S4.1.33** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 5-



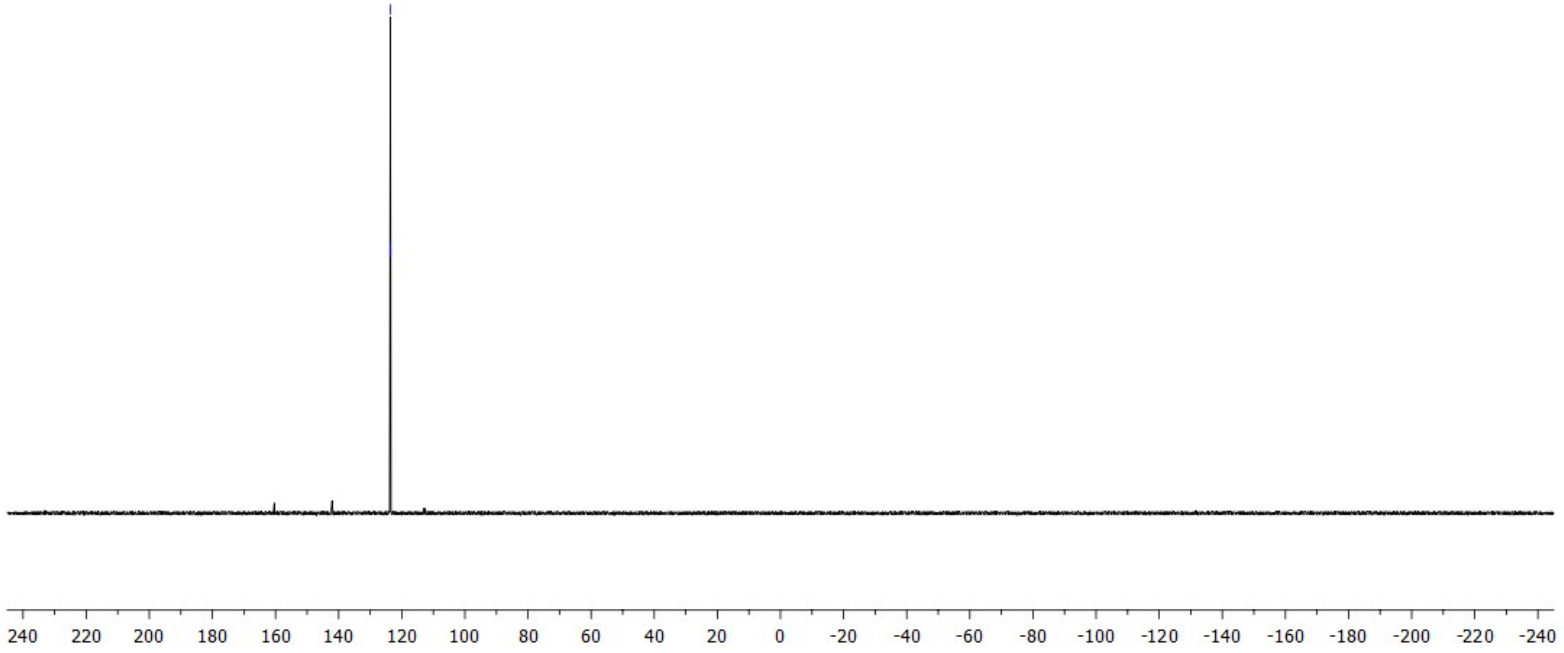
methyl-2-(neopentyloxy)benzo-1,3,2-dithiaphosphole (**6b**)



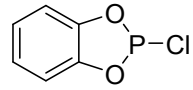
**S4.1.34** $^{31}P$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 5-methyl-2-(neopentyloxy)benzo-1,3,2-dithiaphosphole (**6b**)

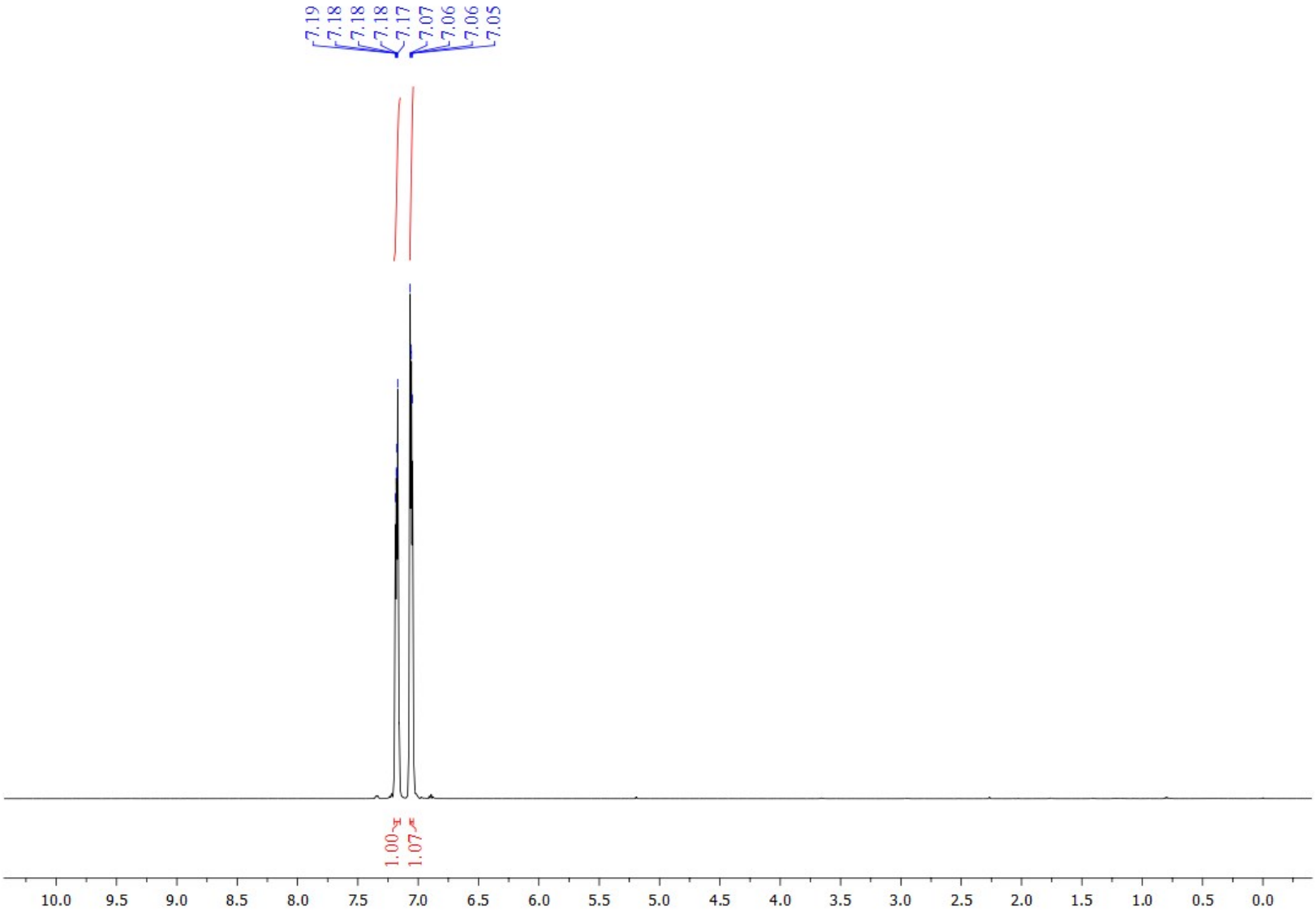



123.6
123.6
123.6

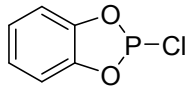


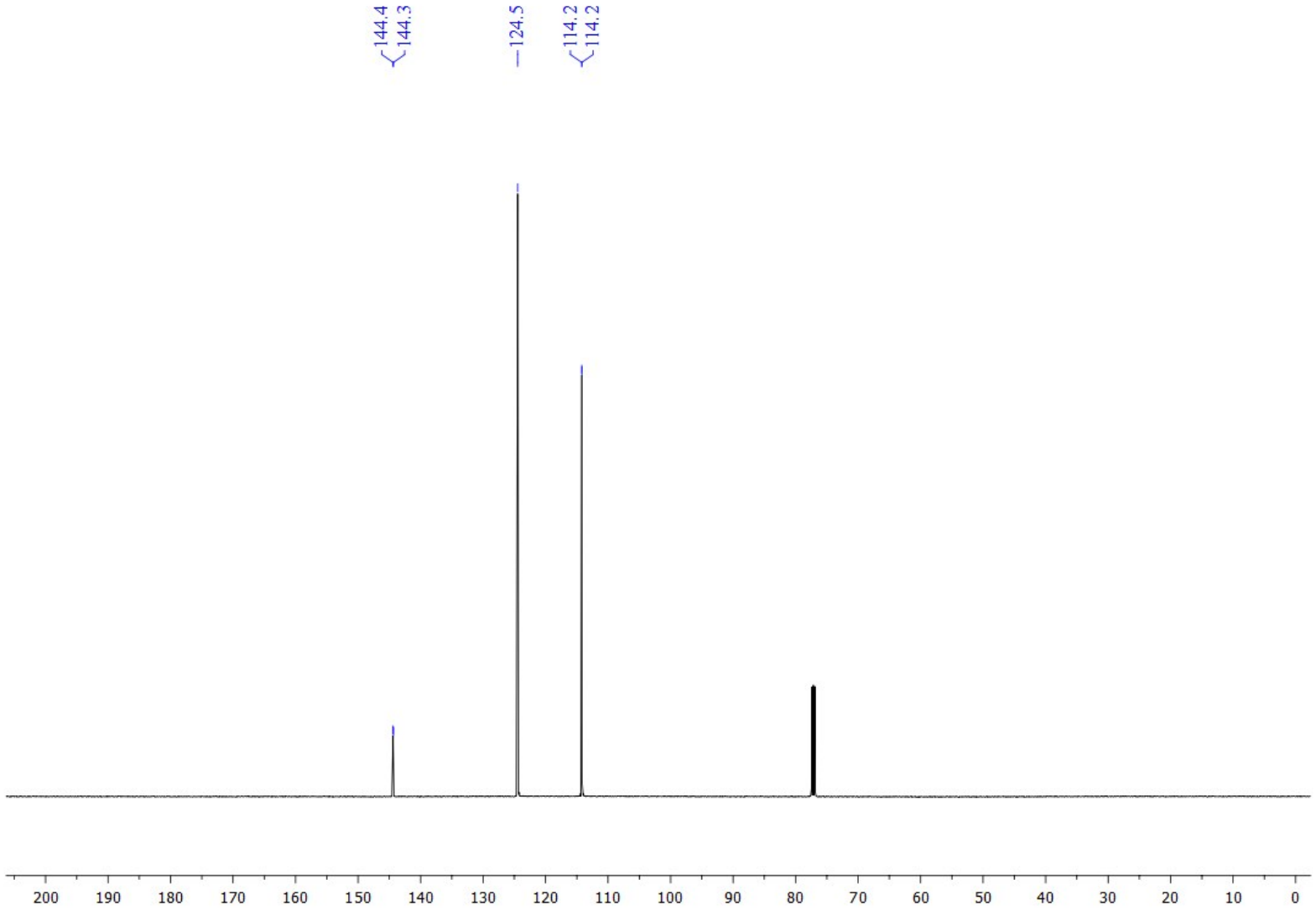
**S4.1.35** $^{1}H$ NMR (500 MHz, 295 K, $CDCl_3$) spectrum of 2-chlorobenzo-1,3,2-dioxaphosphole (**7a**)



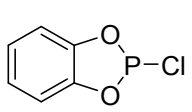



**S4.1.36** $^{13}C\{^{1}H\}$ NMR (126 MHz, 295 K, $CDCl_3$) spectrum of 2-chlorobenzo-1,3,2-dioxaphosphole (**7a**)

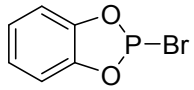


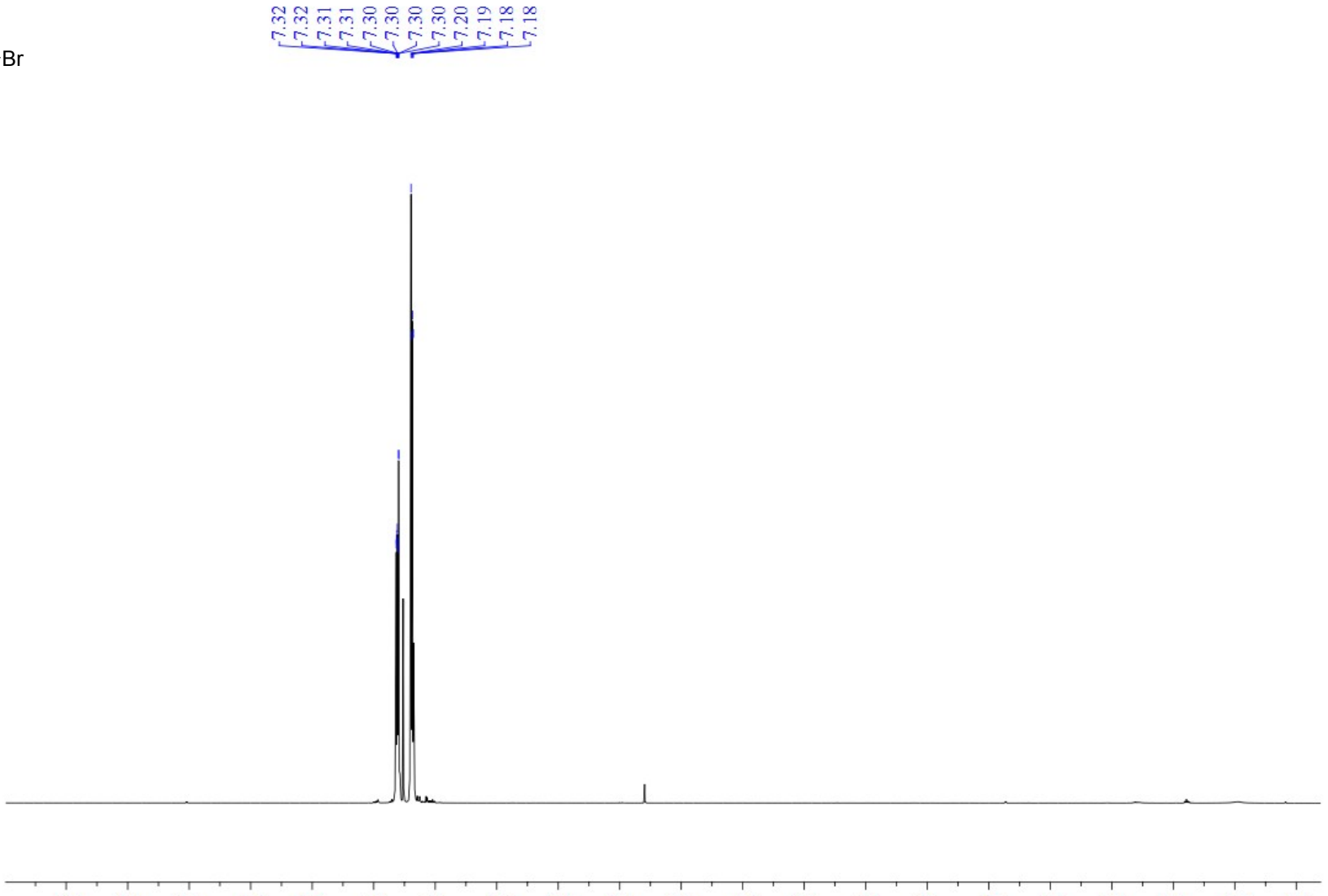
**S4.1.37** $^{31}P\{^{1}H\}$ NMR (202 MHz, 295 K, $CDCl_3$) spectrum of 2-chlorobenzo-1,3,2-dioxaphosphole (**7a**)



**S4.1. 38**



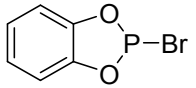

NMR (500 MHz, 295 $CDCl_3$) spectrum of $^1H$

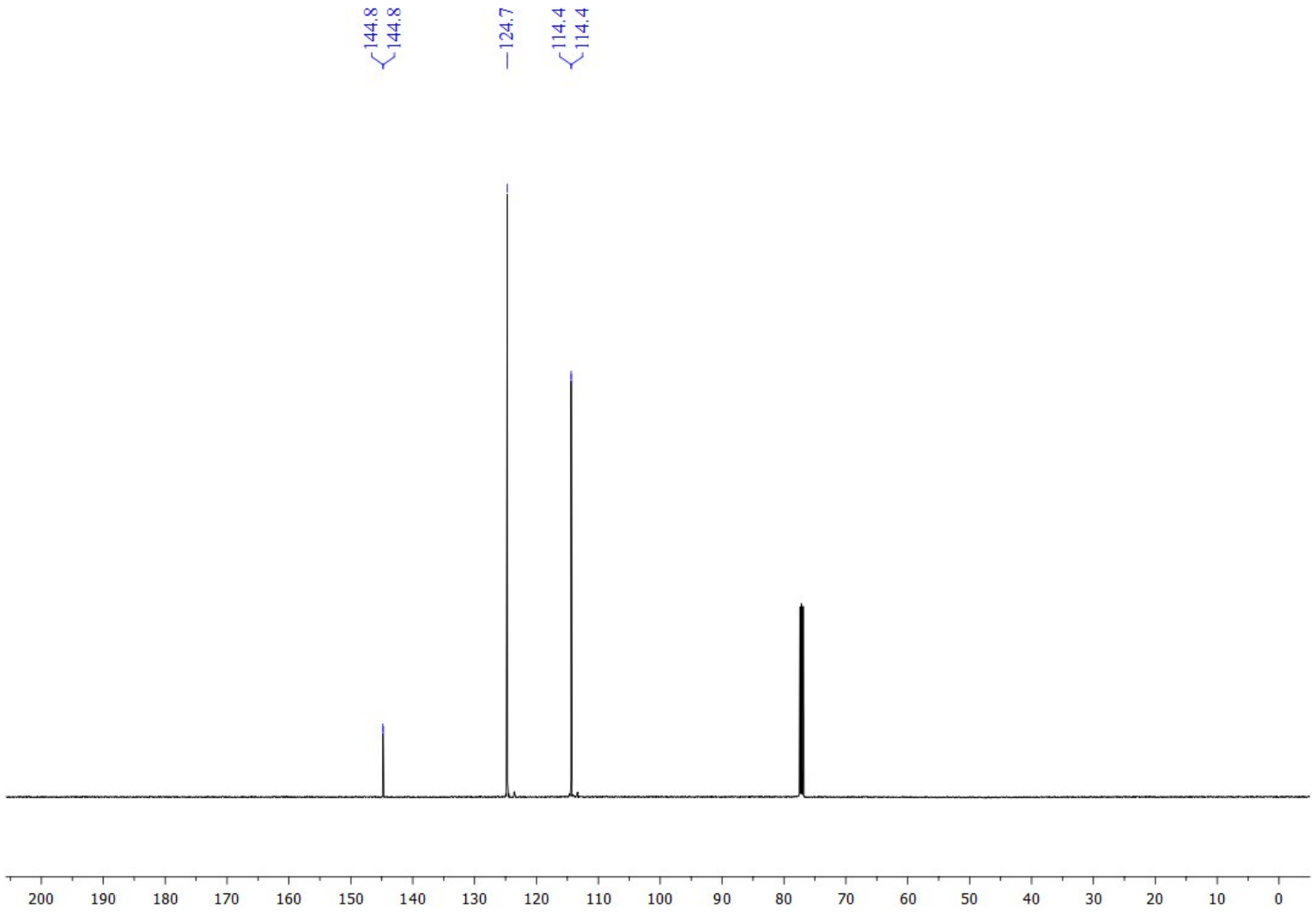


2-bromobenzo-1,3,2-dioxaphosphole (**7b**)

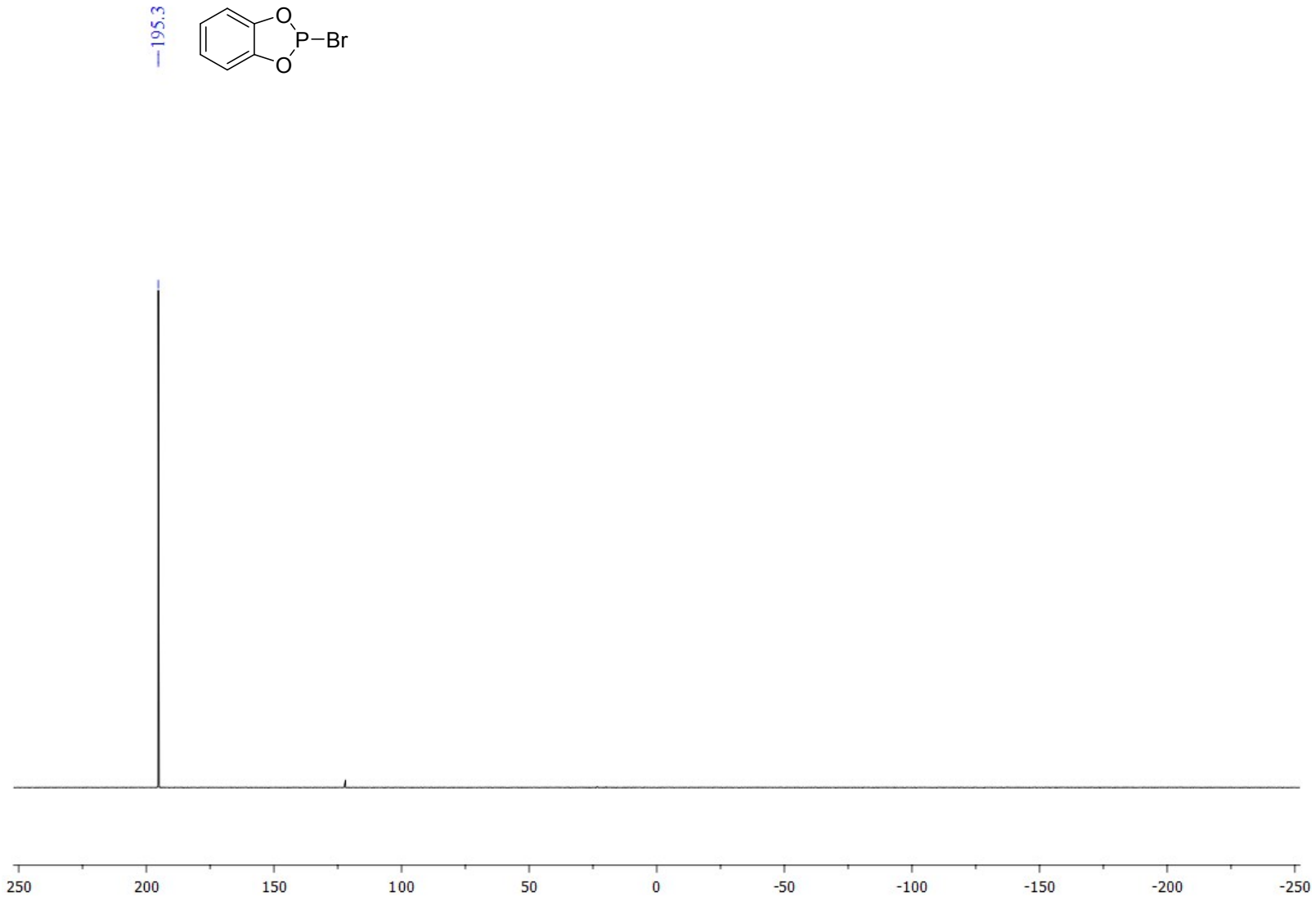
DCM

**S4.1.39** $^{13}C\{^{1}H\}$ NMR (126 MHz, 295 K, $CDCl_3$) spectrum of 2-bromobenzo-1,3,2-dioxaphosphole (**7b**)

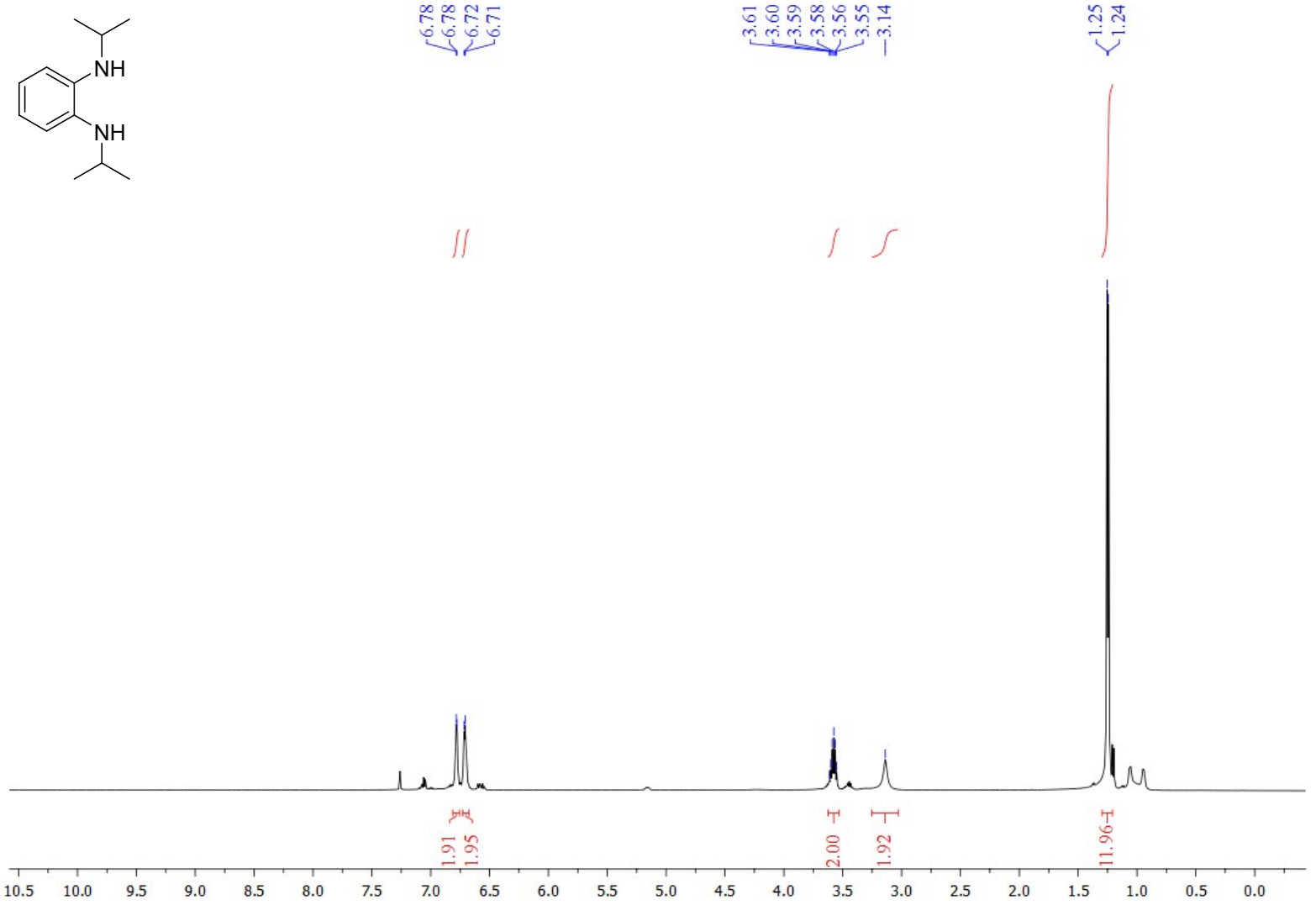




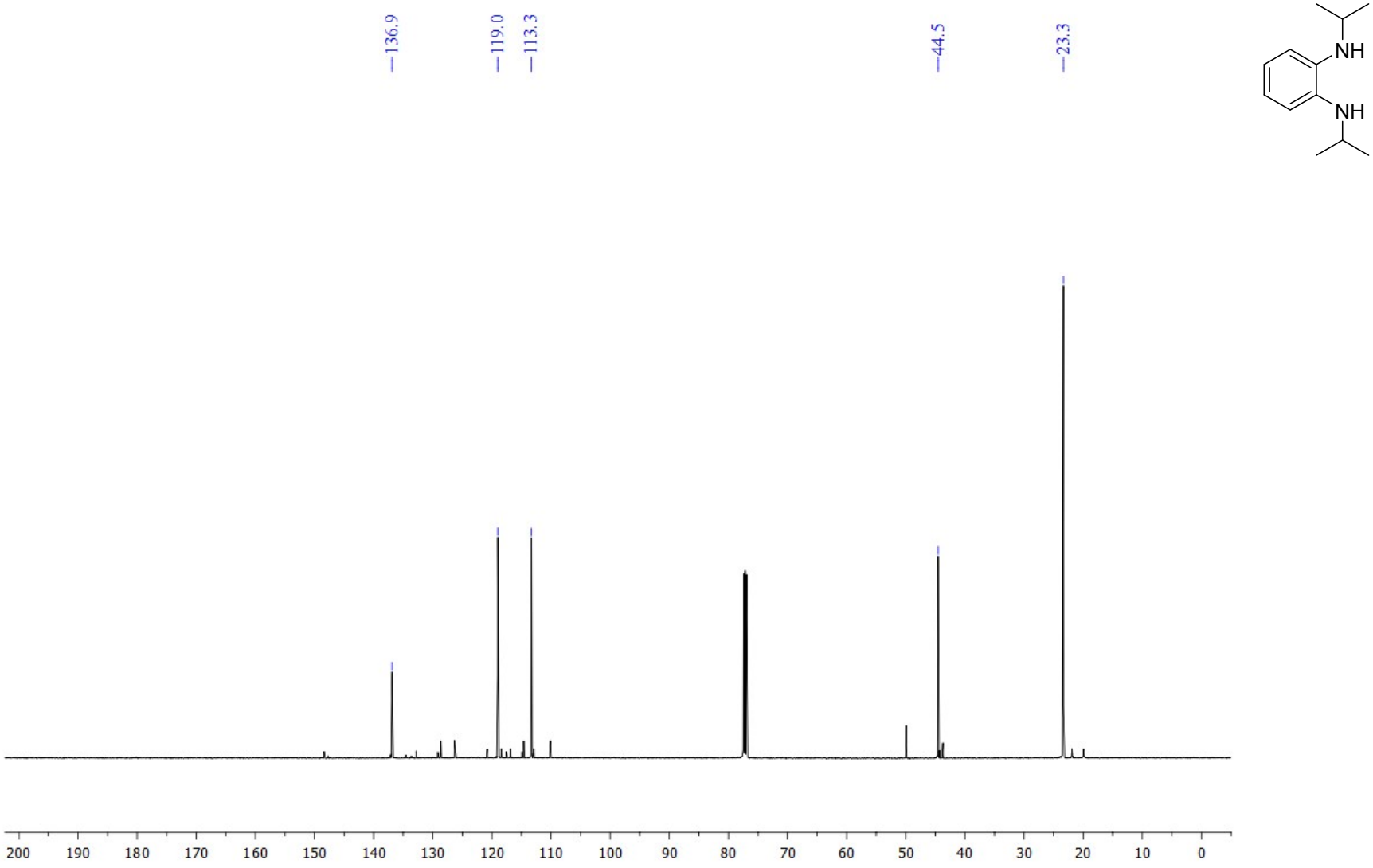

**S4.1.40** $^{31}P\{^{1}H\}$ NMR (202 MHz, 295 K, $CDCl_3$) spectrum of 2-bromobenzo-1,3,2-dioxaphosphole (**7b**)



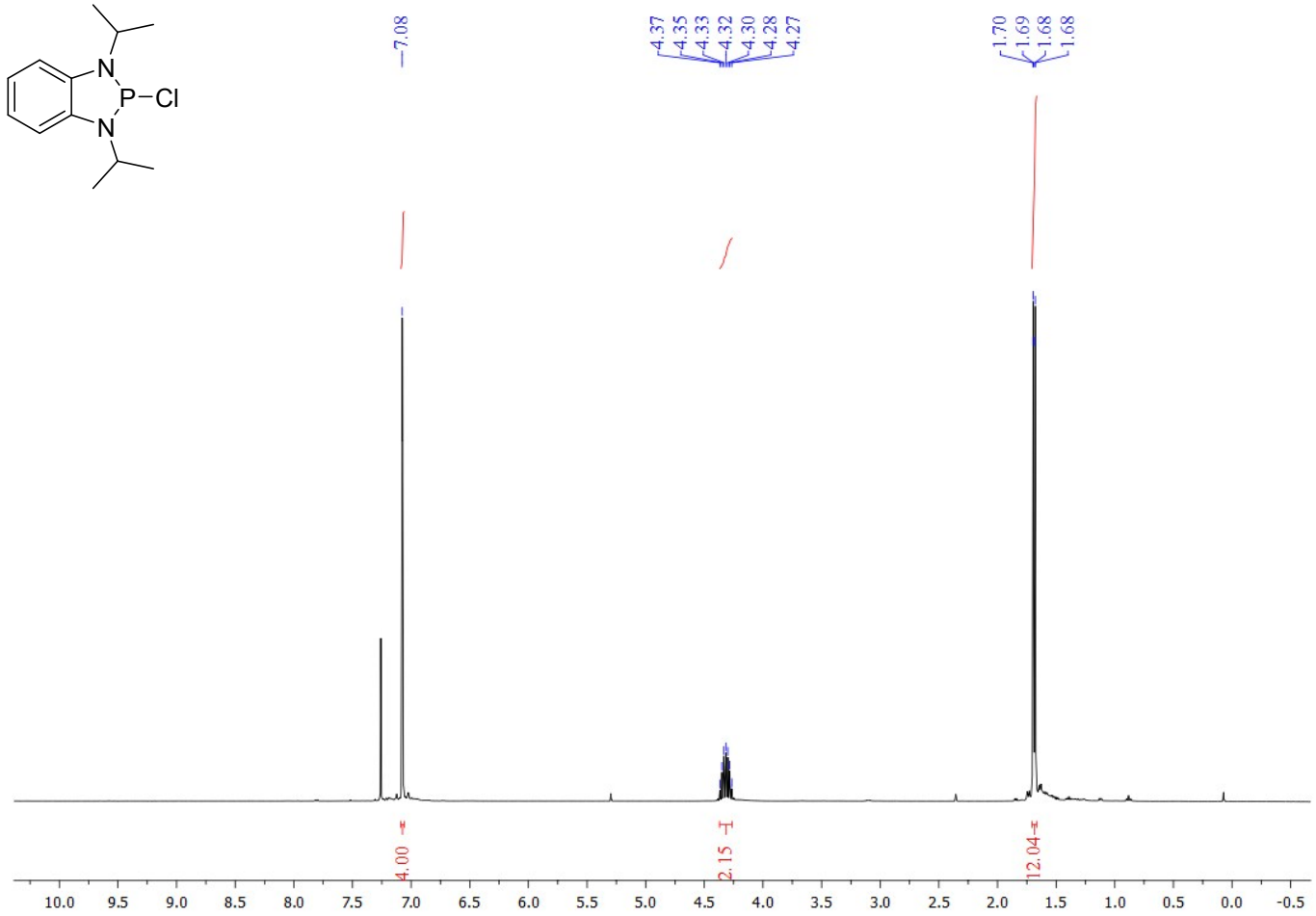

**S4.1.41** $^{1}$H NMR (500 MHz, 295 K, $CDCl_3$) spectrum of N,N'-diisopropylbenzene-1,2-diamine


NH
NH
6.78
6.78
6.72
6.71
3.61
3.60
3.59
3.58
3.56
3.55
3.14
1.25
1.24
1.91
1.95
2.00
1.92
11.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

**S4.1.42** $^{13}C\{^{1}H\}$ NMR (126 MHz, 295 K, $CDCl_3$) spectrum of N,N'-diisopropylbenzene-1,2-diamine

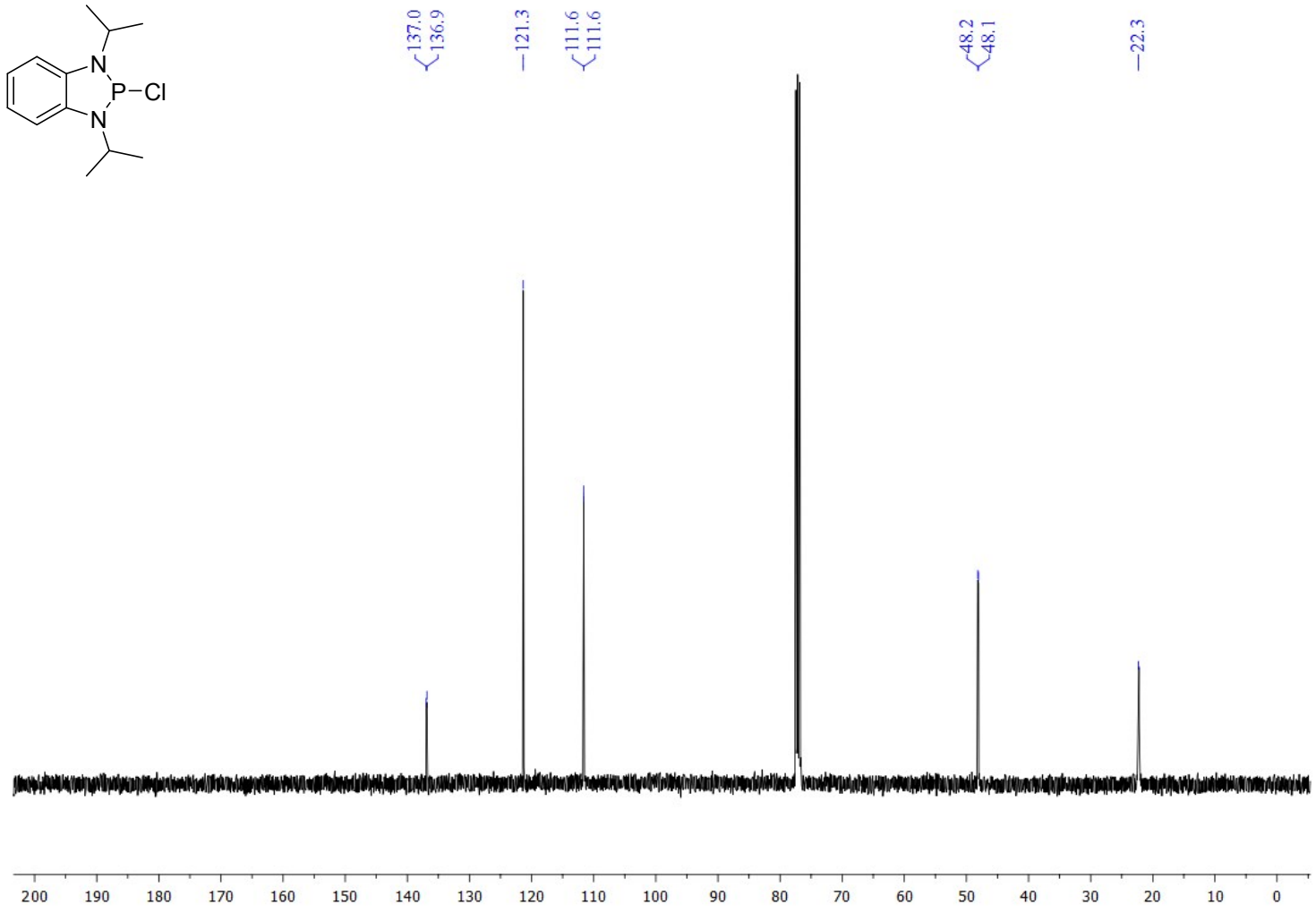


**S4.1.43** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-chloro-1,3-diisopropyl-benzodiazaphosphole (**8a**)

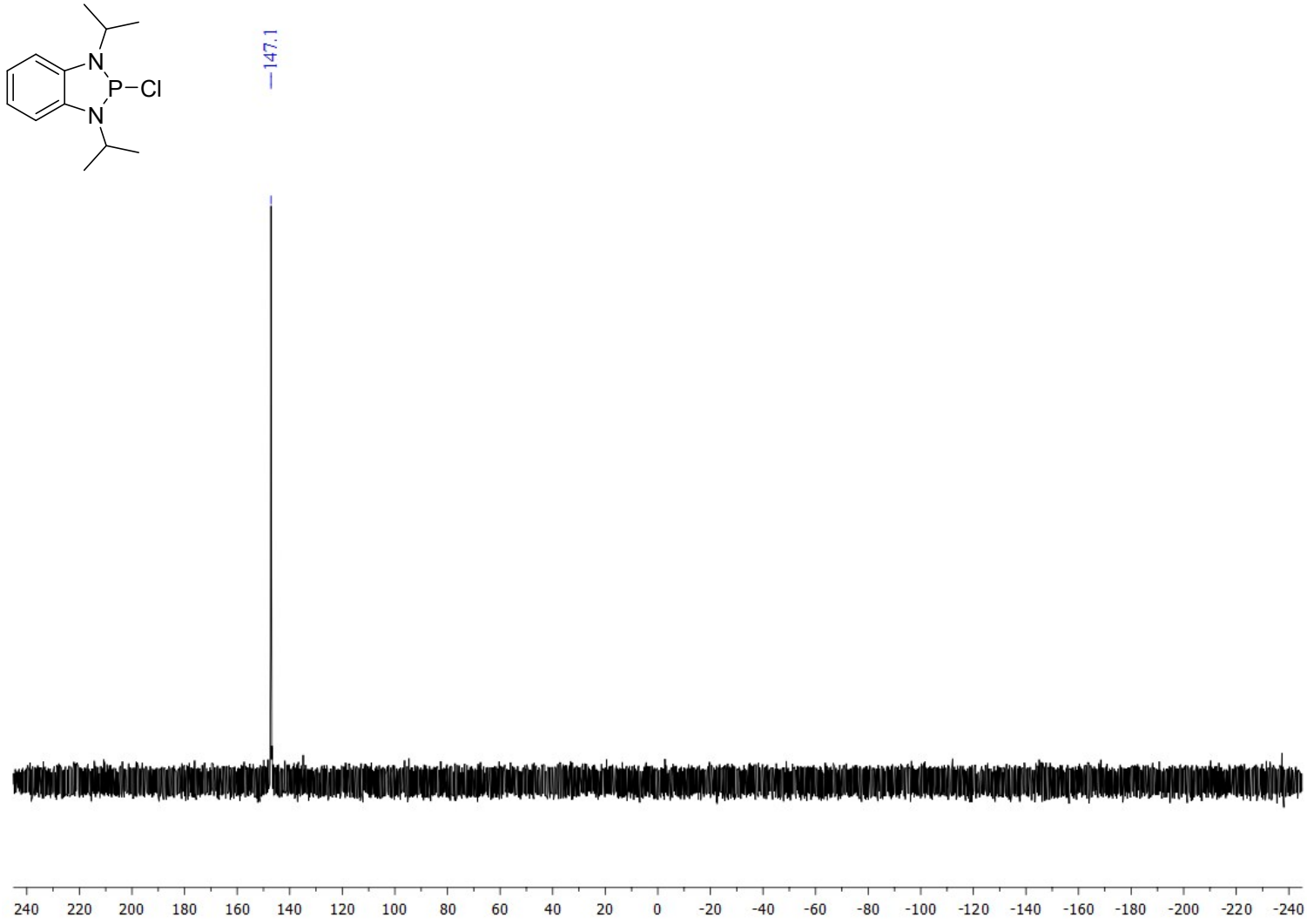



DCM

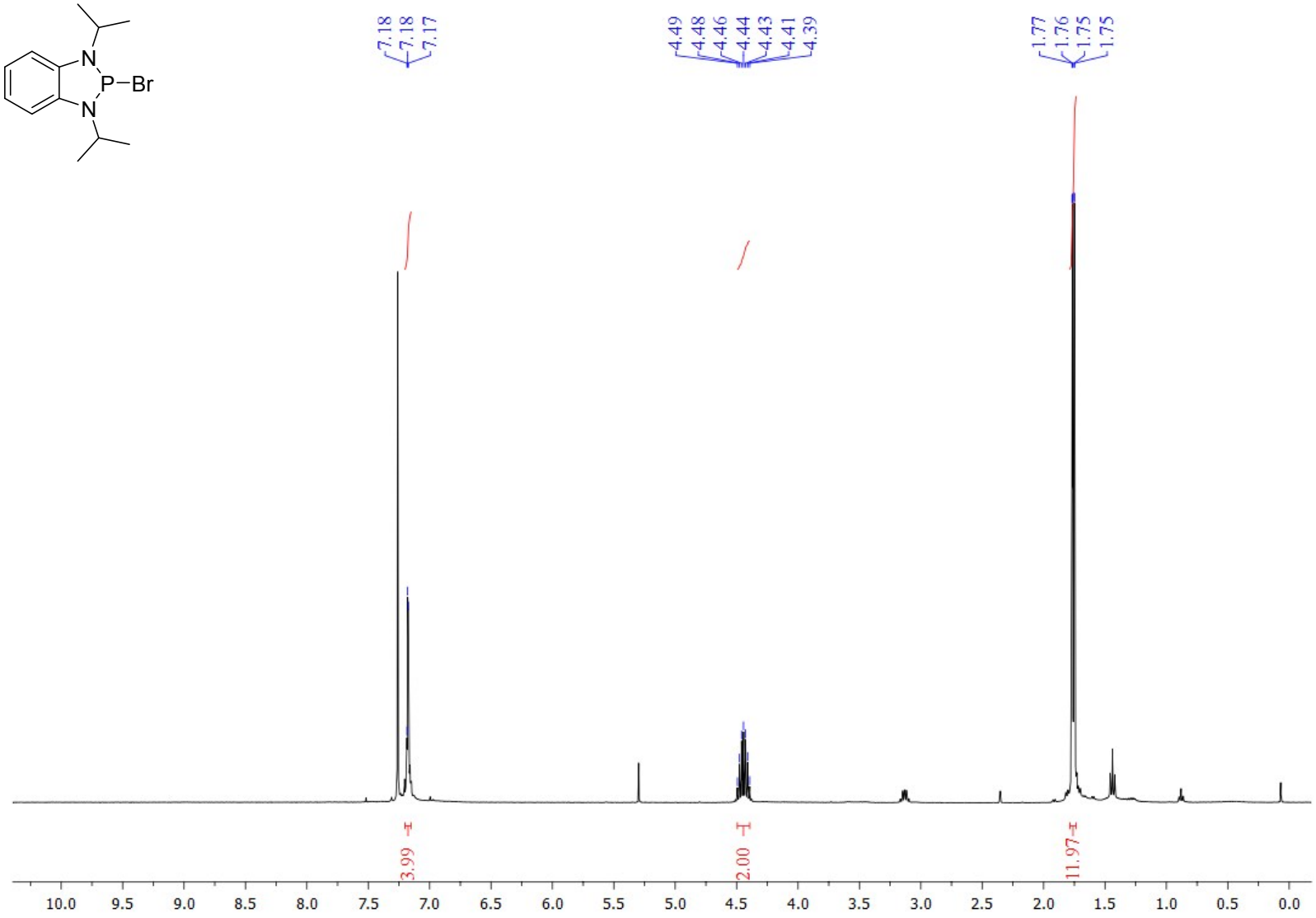
**S4.1.44** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 2-chloro-1,3-diisopropyl-benzodiazaphosphole (**8a**)



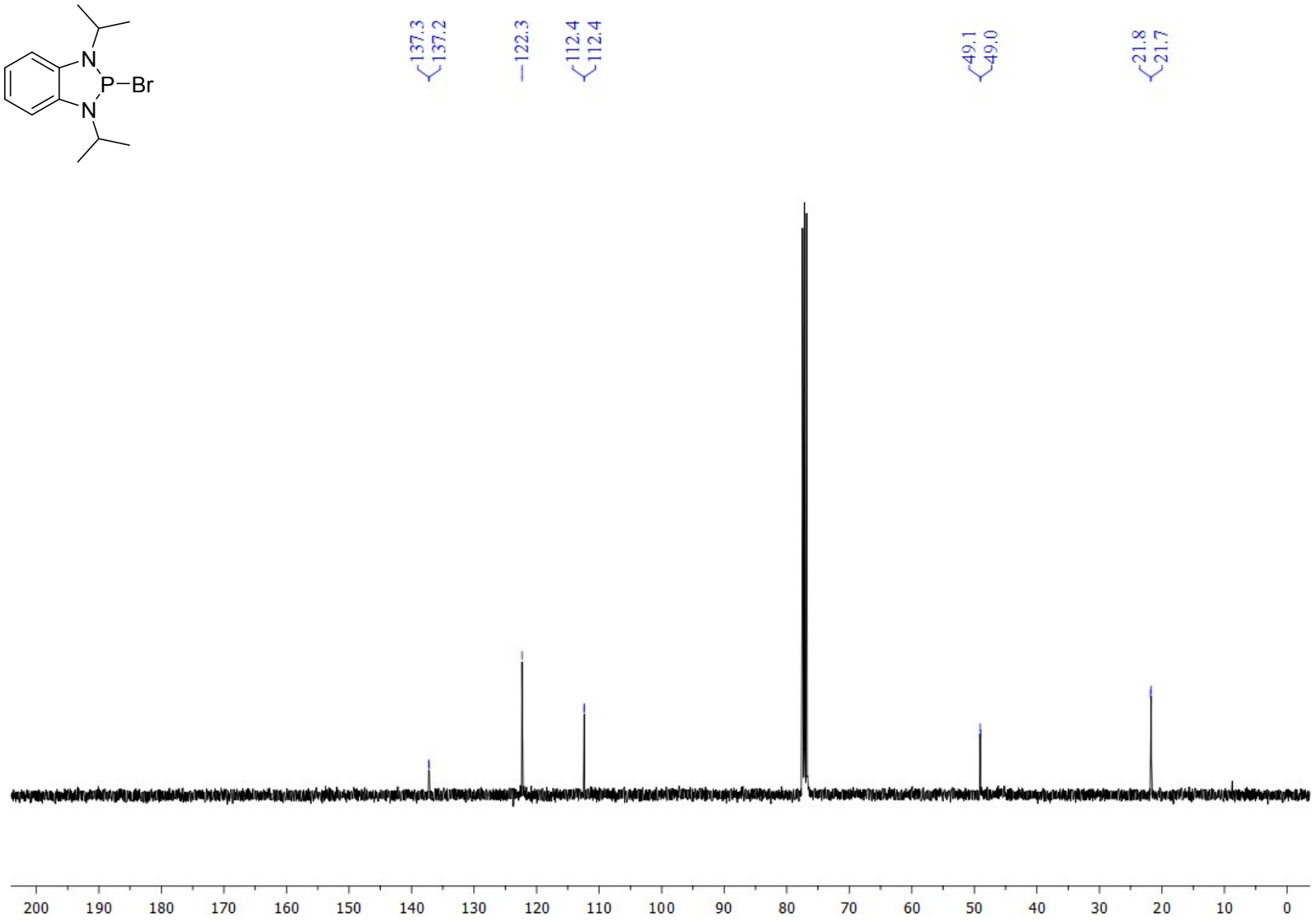
**S4.1.45** $^{31}P\{^{1}H\}$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 2-chlorobenzo-1,3,2-dioxaphosphole (**8a**)



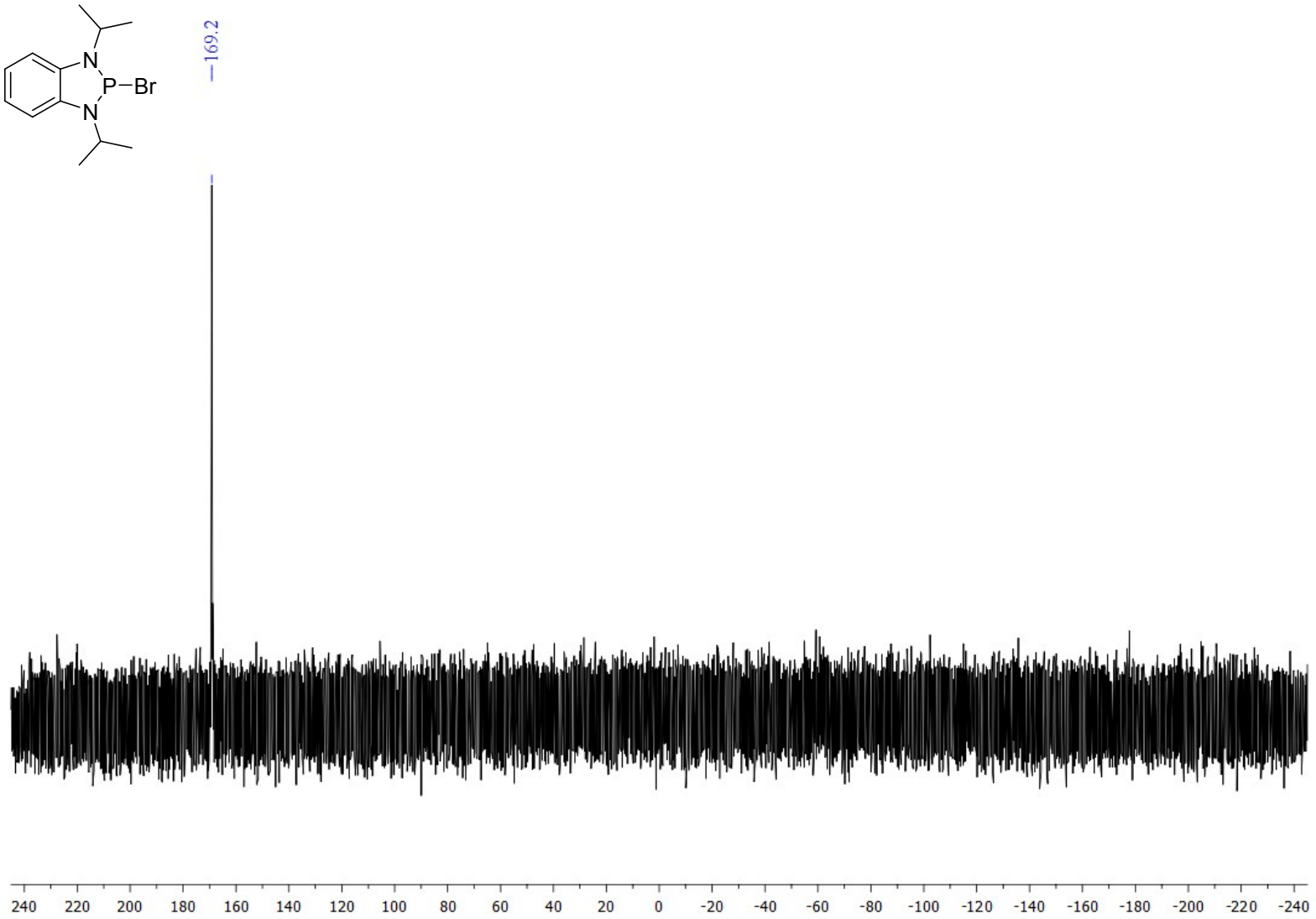
**S4.1. 46** $^{1}$H NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-bromo-1,3-diisopropyl-benzodiazaphosphole (**8b**)



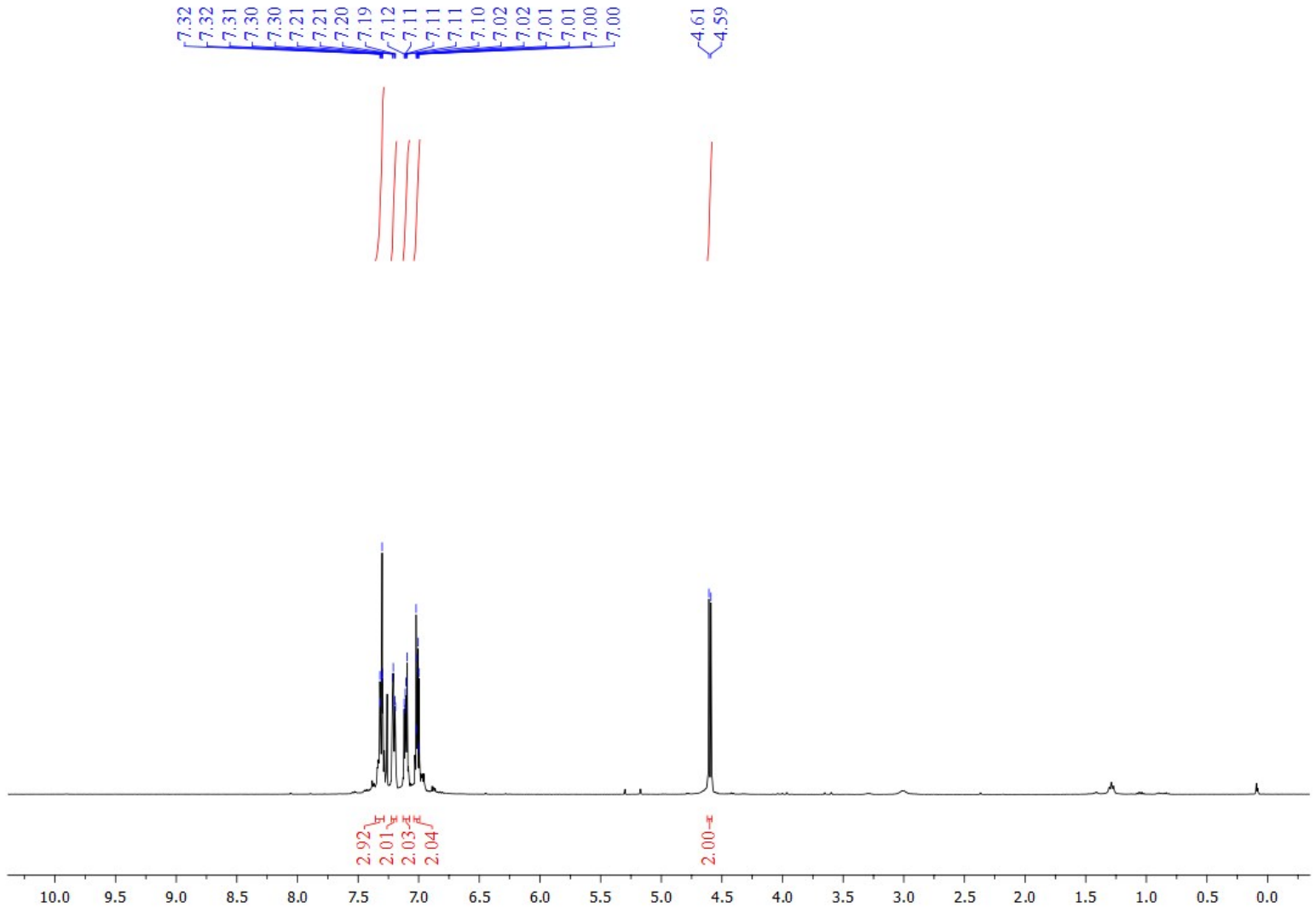
**S4.1.47** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 2-bromo-1,3-diisopropyl-benzodiazaphosphole (**8b**)

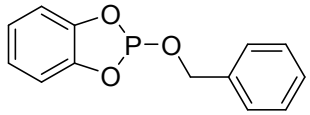


**S4.1.48** $^{31}P\{^{1}H\}$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 2-chlorobenzo-1,3,2-dioxaphosphole (**8b**)

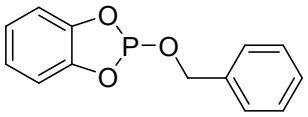


**S4.1.49** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-(benzyloxy)benzo-1,3,2-dioxaphosphole (**9a**)

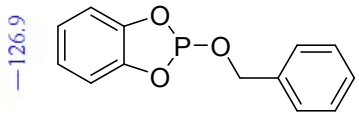


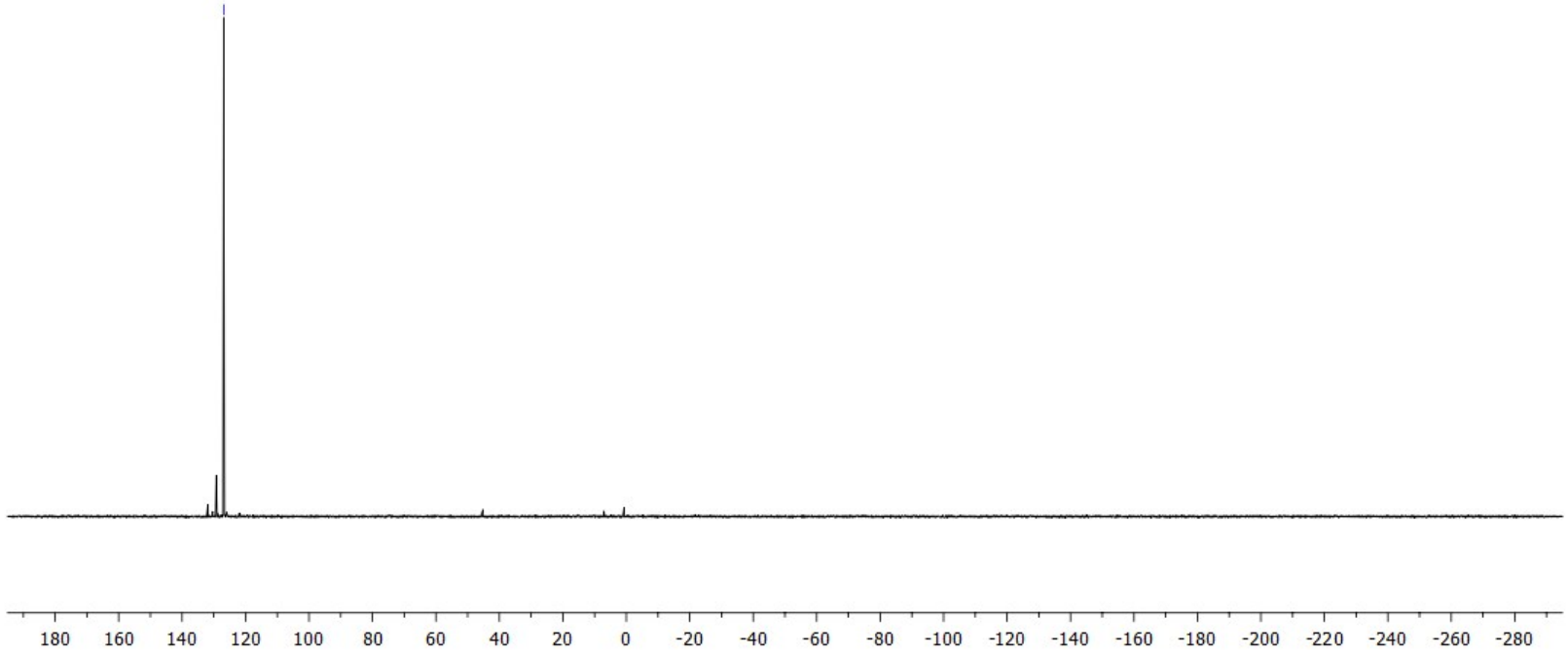



**S4.1.50** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 2-(benzyloxy)benzo-1,3,2-dioxaphosphole (**9a**)

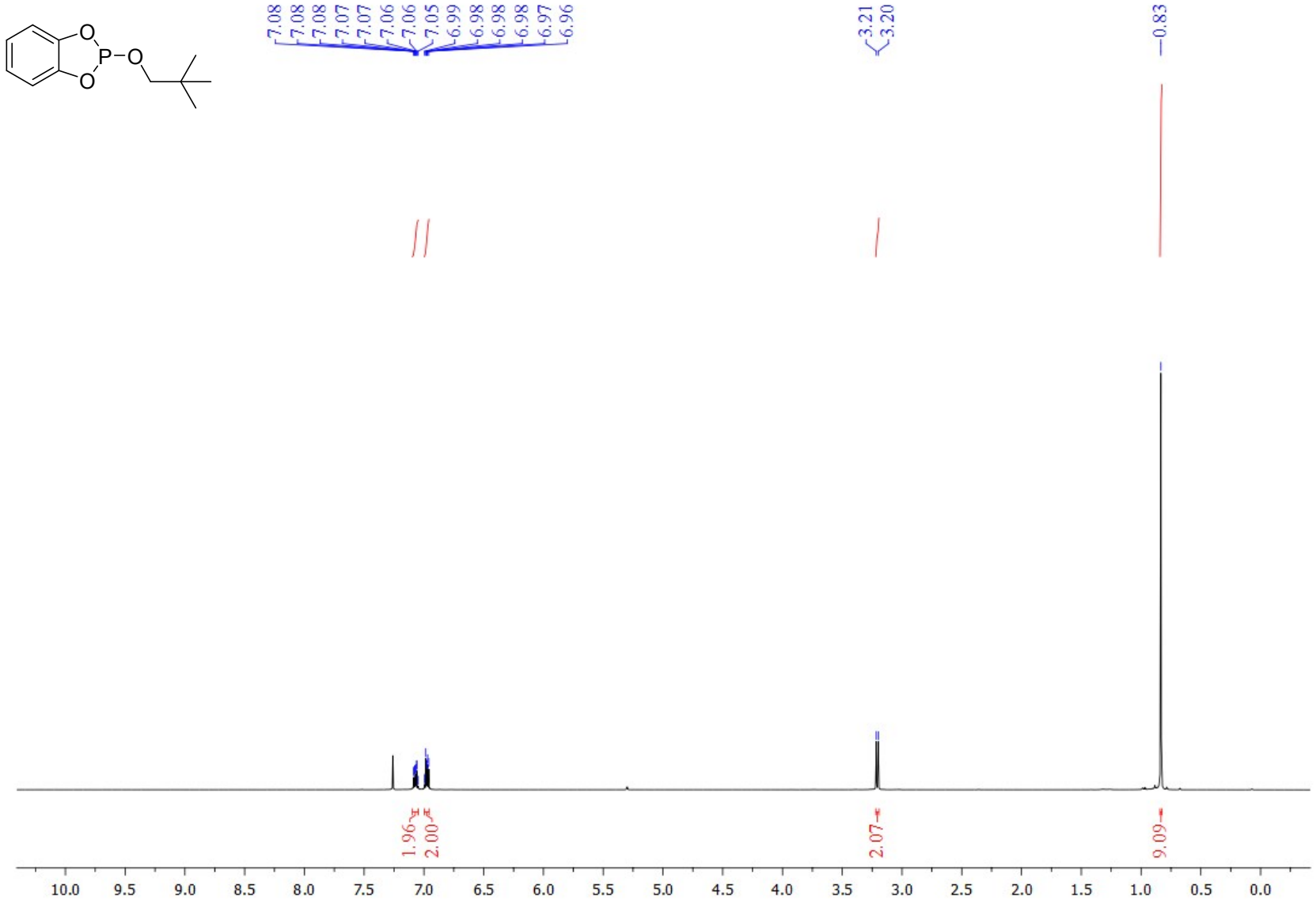


**S4.1.51** $^{31}P\{^{1}H\}$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 2-(benzyloxy)benzo-1,3,2-dioxaphosphole (**9a**)

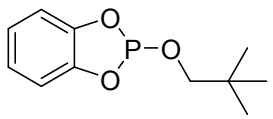


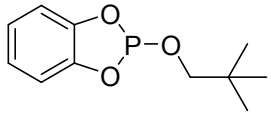
**S4.1.52** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-(neopentyloxy)benzo-1,3,2-dioxaphosphole (**9b**)



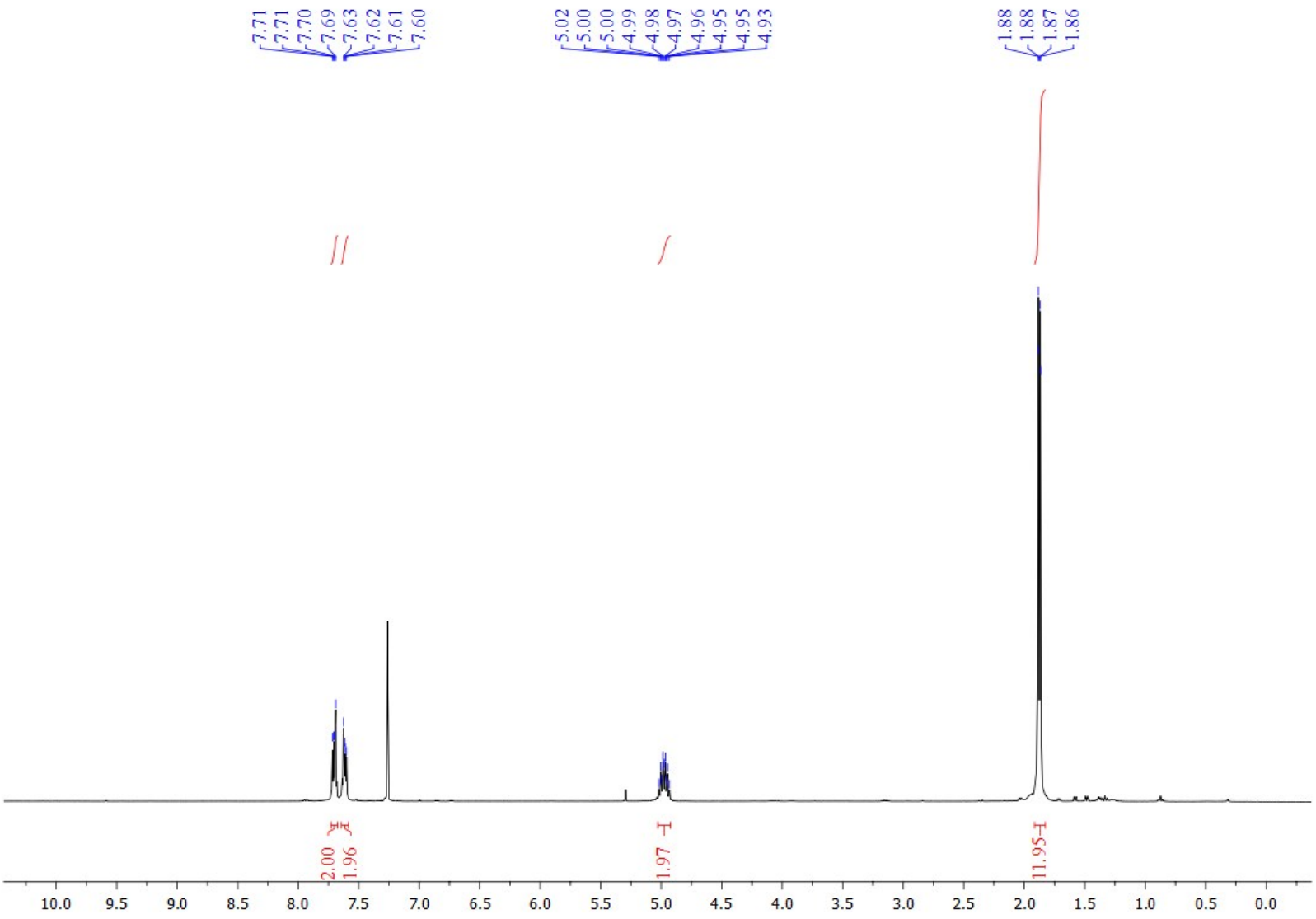
**S4.1.53** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 2-(neopentyloxy)benzo-1,3,2-dioxaphosphole (**9b**)

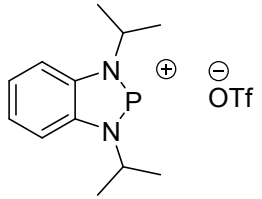


**S4.1.54** $^{31}P$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 2-(neopentyloxy)benzo-1,3,2-dioxaphosphole (**9b**)

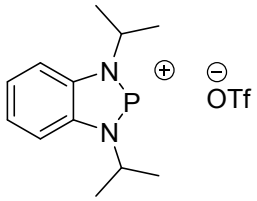


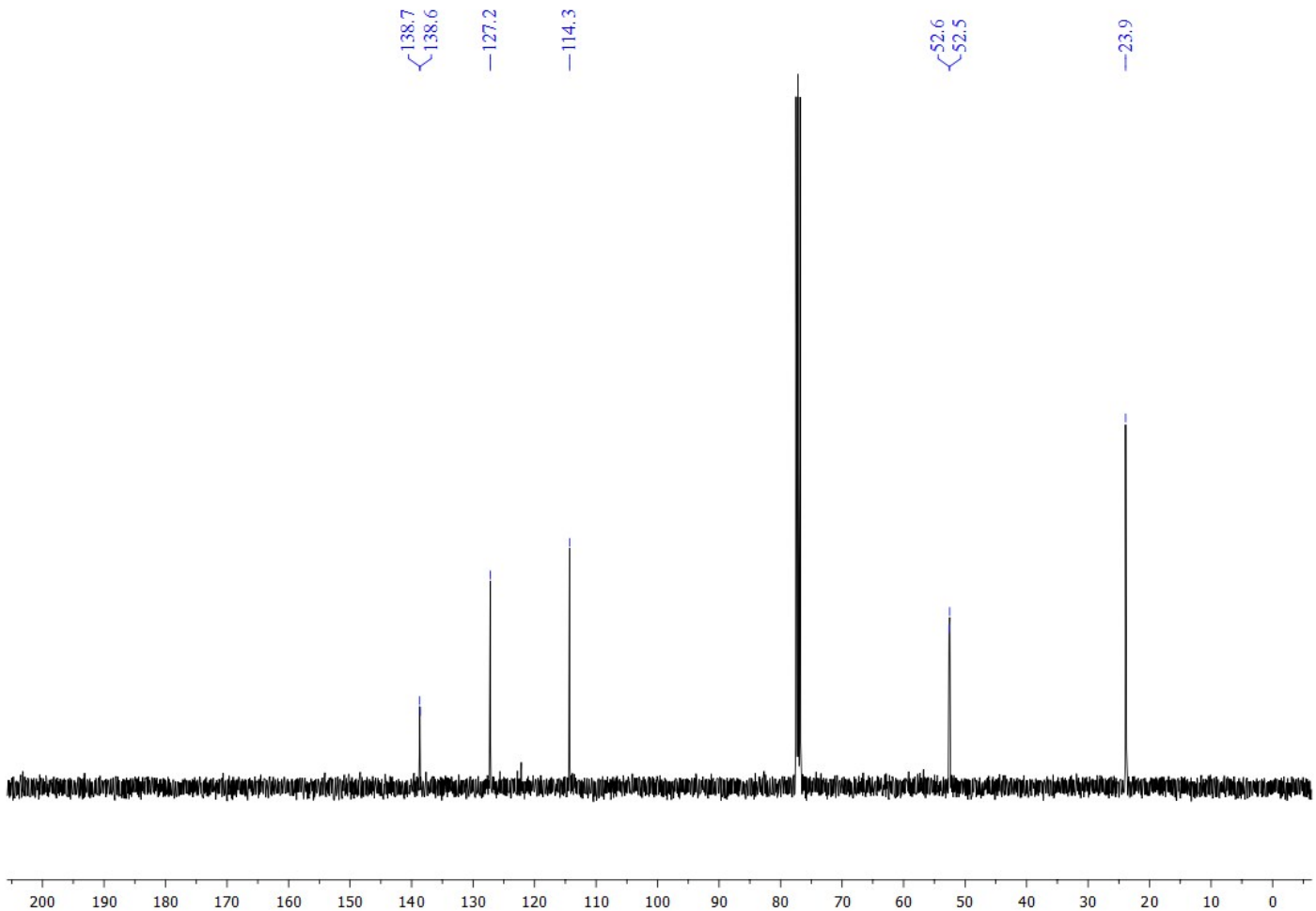
**S4.1.55** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 1,3-diisopropyl-benzodiphosphenium triflate (**10**)

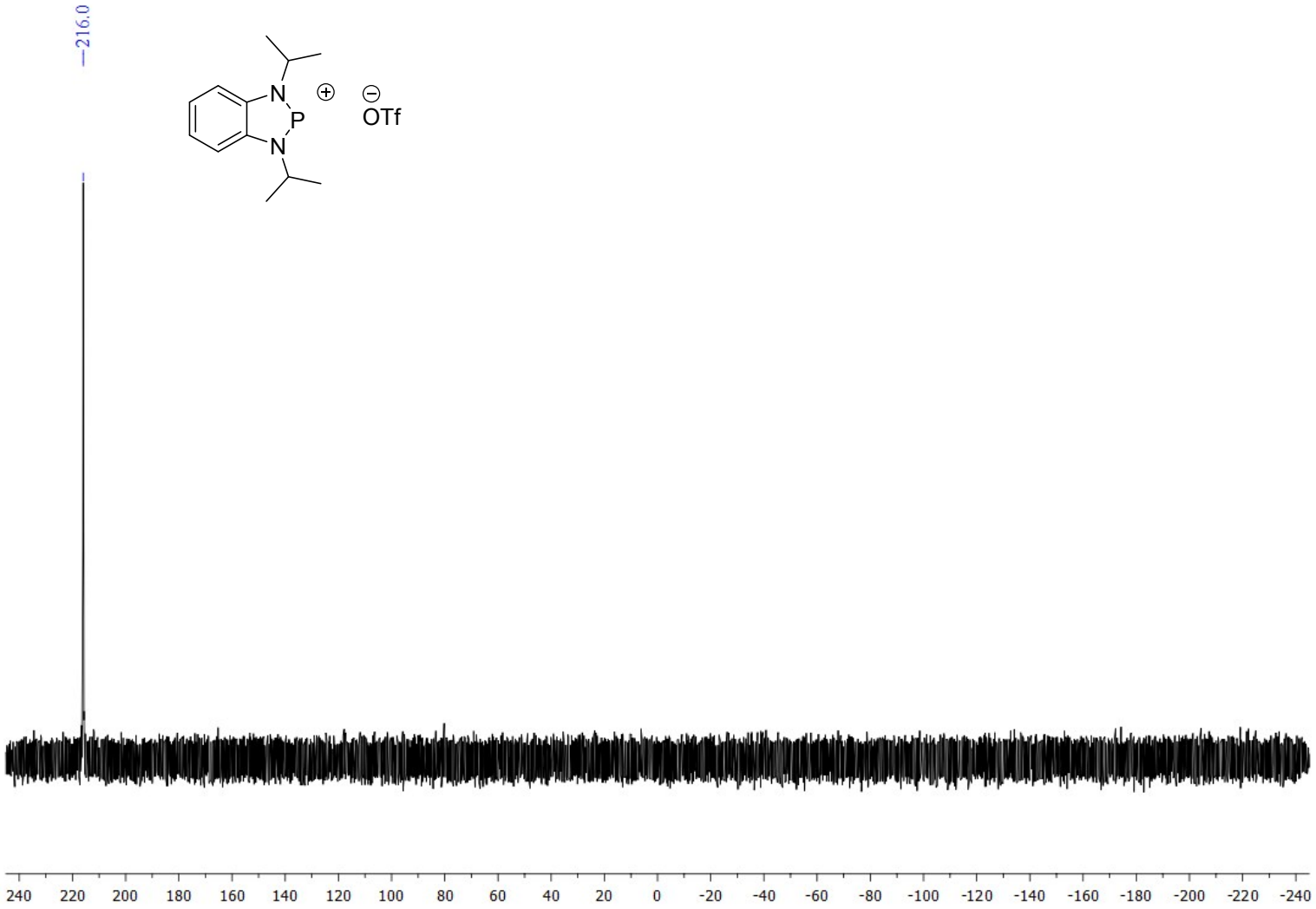


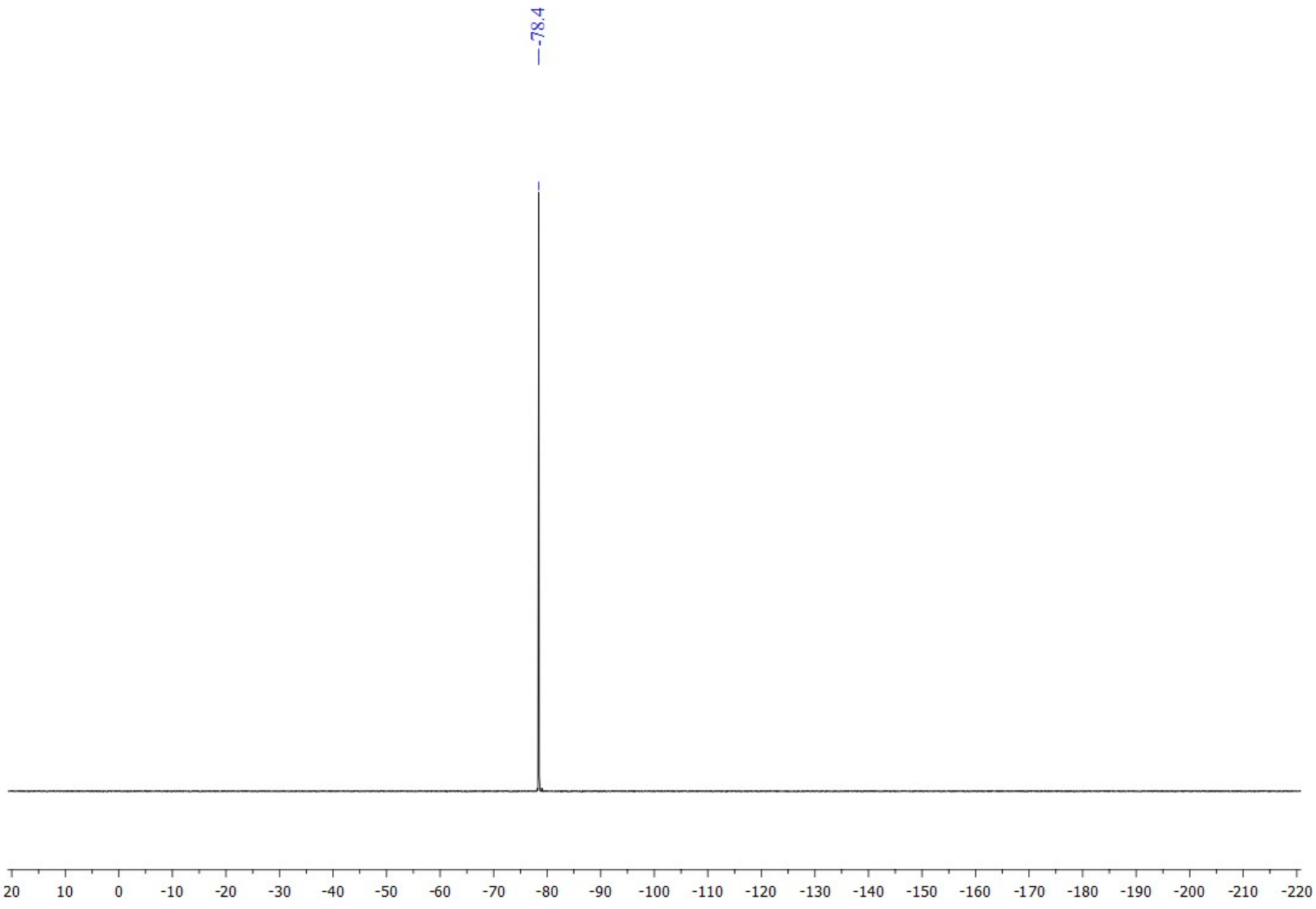
**S4.1.56** $^{13}C\{^{1}H\}$ NMR (101 MHz, 295 K, $CDCl_3$) spectrum of 1,3-diisopropyl-benzodiphosphenium triflate (**10**)



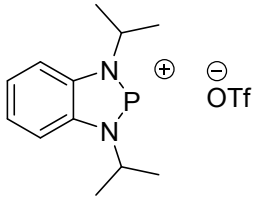



**S4.1.57** $^{31}P$ NMR (162 MHz, 295 K, $CDCl_3$) spectrum of 1,3-diisopropyl-benzodiphosphenium triflate (**10**)

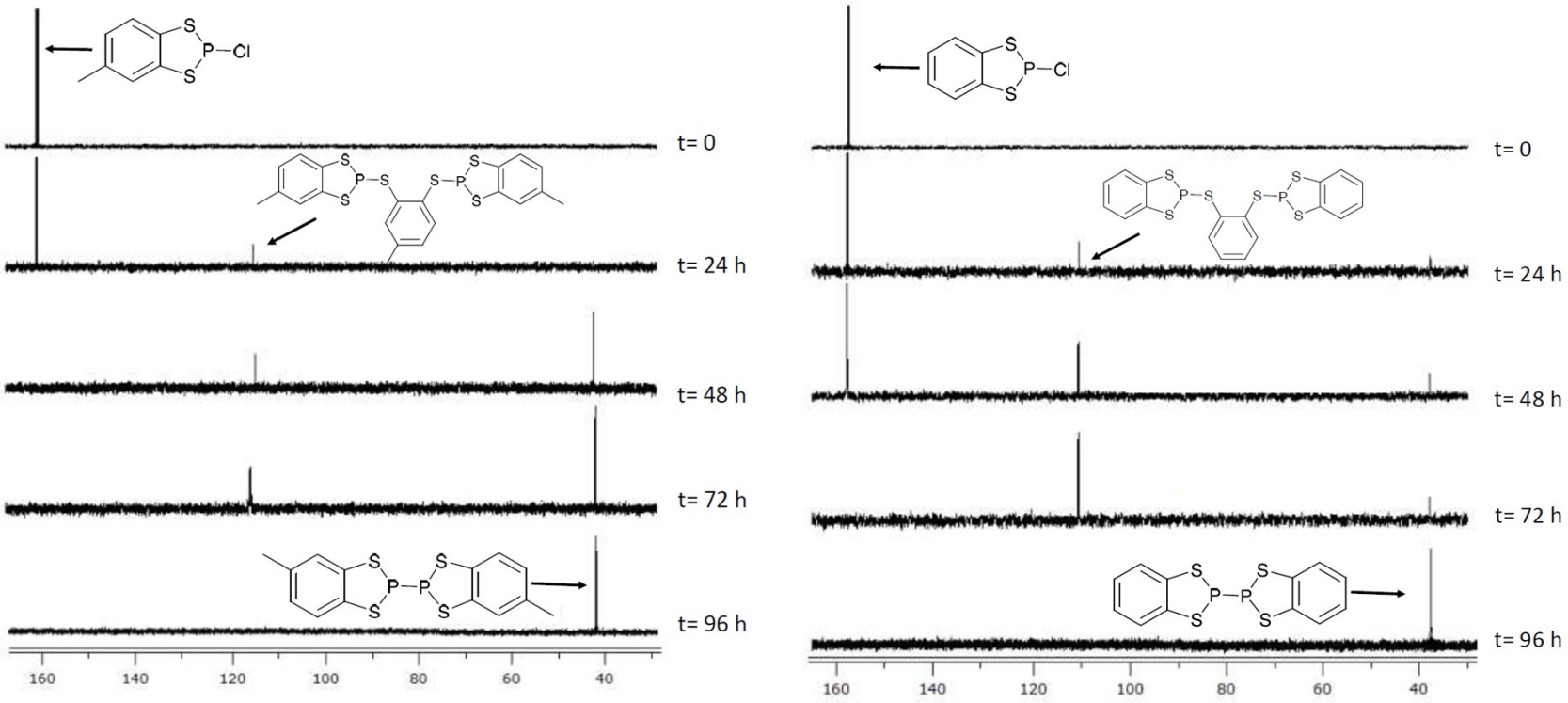



**S4.1.58** $^{19}F$ NMR (376 MHz, 295 K, $CDCl_3$) spectrum of

1,3-diisopropyl-benzodiphosphenium triflate (**10**)



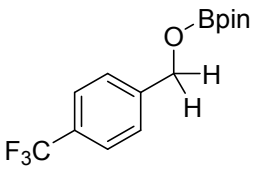
**S4.1.59** Stack-plot of $^{31}P\{^{1}H\}$ NMR (202.5 MHz, 295 K, $d_8$-toluene) spectra of the reduction of **1a** and **2a** to form **5** and **4** respectively

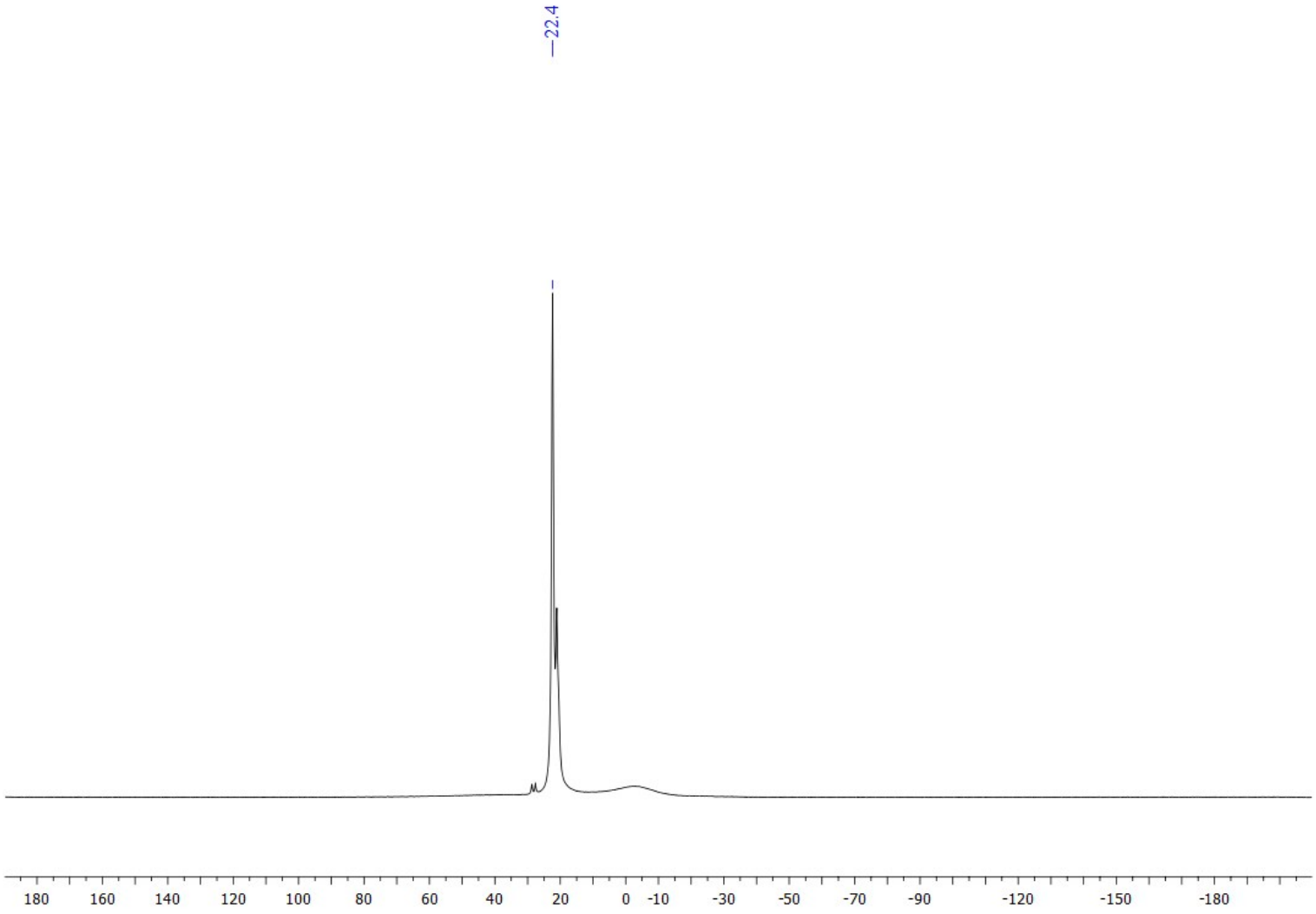


**S4.2 NMR spectra of hydroborated aldehydes**

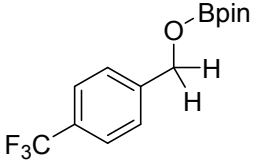
**S4.2.1.** $^{1}H$ NMR (500 MHz, 295 K, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)benzyl)oxy)-1,3,2-dioxaborolane (**11a**)

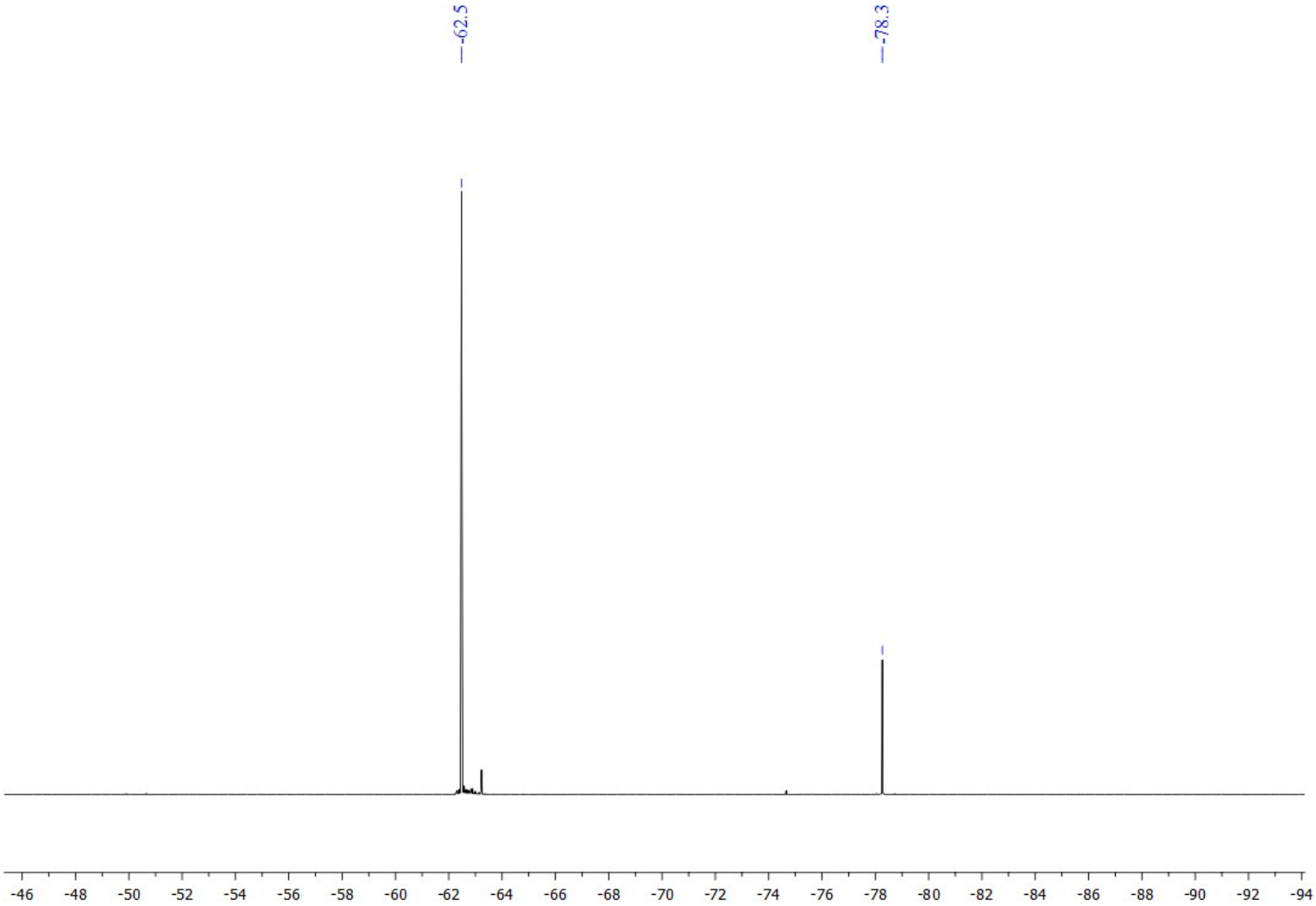
**S4.2.2.** $^{11}B$ NMR (160 MHz, 295 K, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)benzyl)oxy)-1,3,2-dioxaborolane (**11a**)



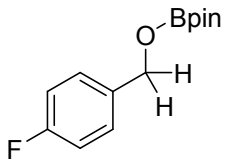



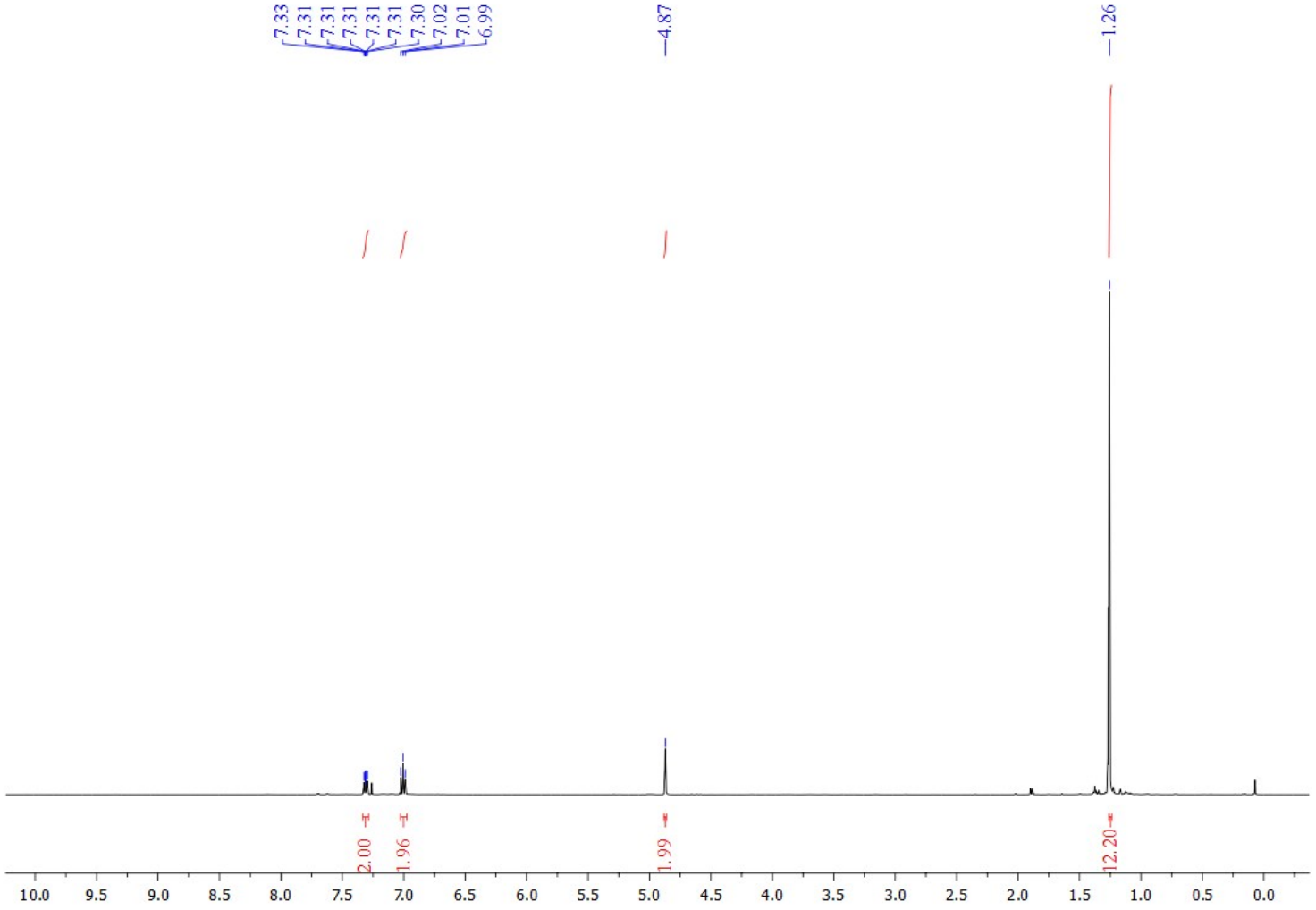
**S4.2.3.** $^{19}F\{^{1}H\}$ NMR (471 MHz, 295 K, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)benzyl)oxy)-1,3,2-dioxaborolane (**11a**)



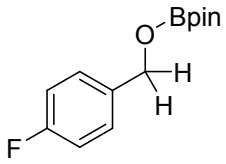



**S4.2.4.** $^{1}H$ NMR (500 MHz, 295 K, $CDCl_3$) spectrum of 2-((4-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11b**)

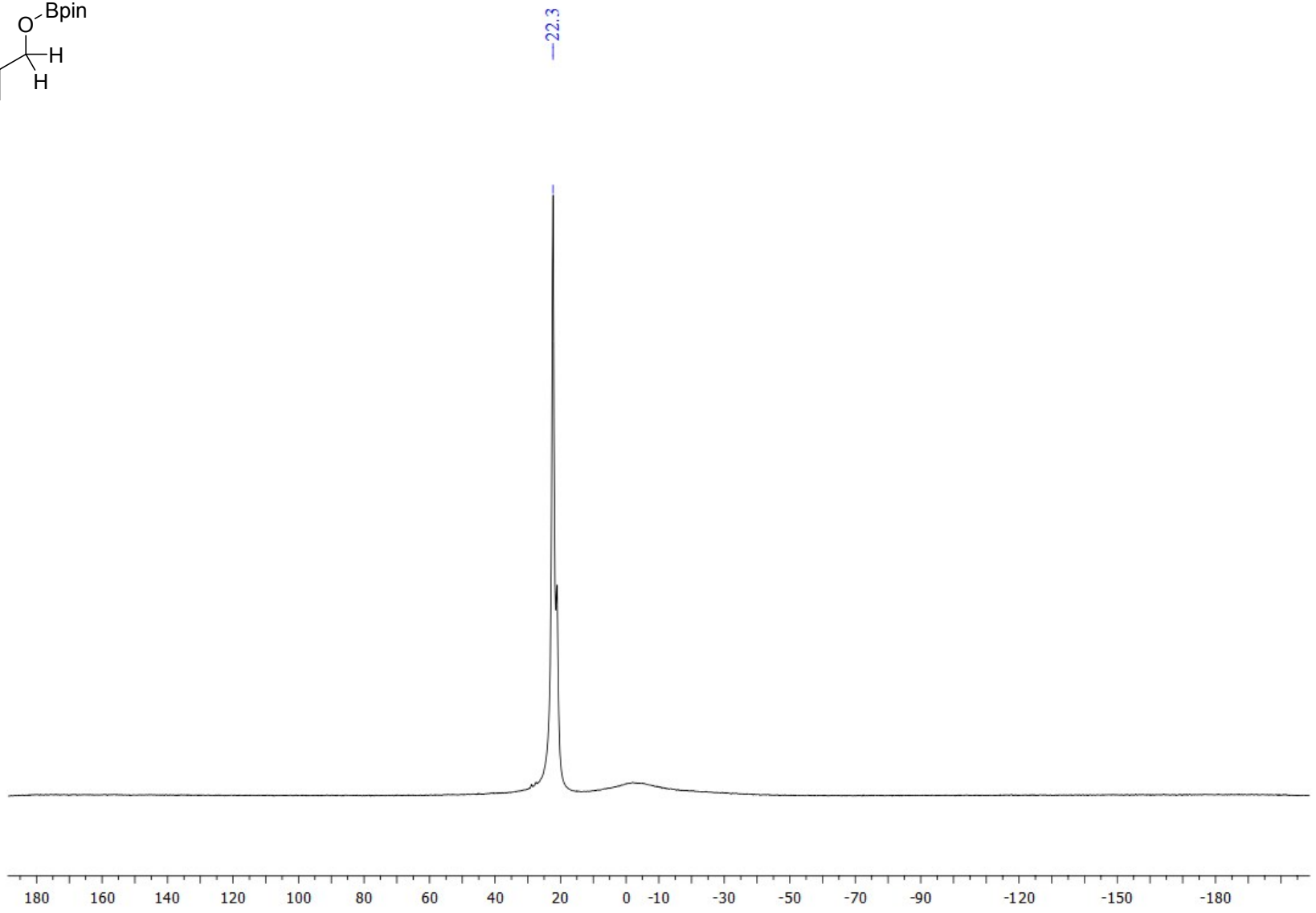


**S4.2.5.**

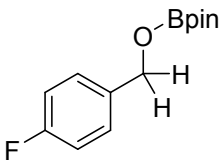



$^{11}B$ NMR (128 MHz, 295 K,

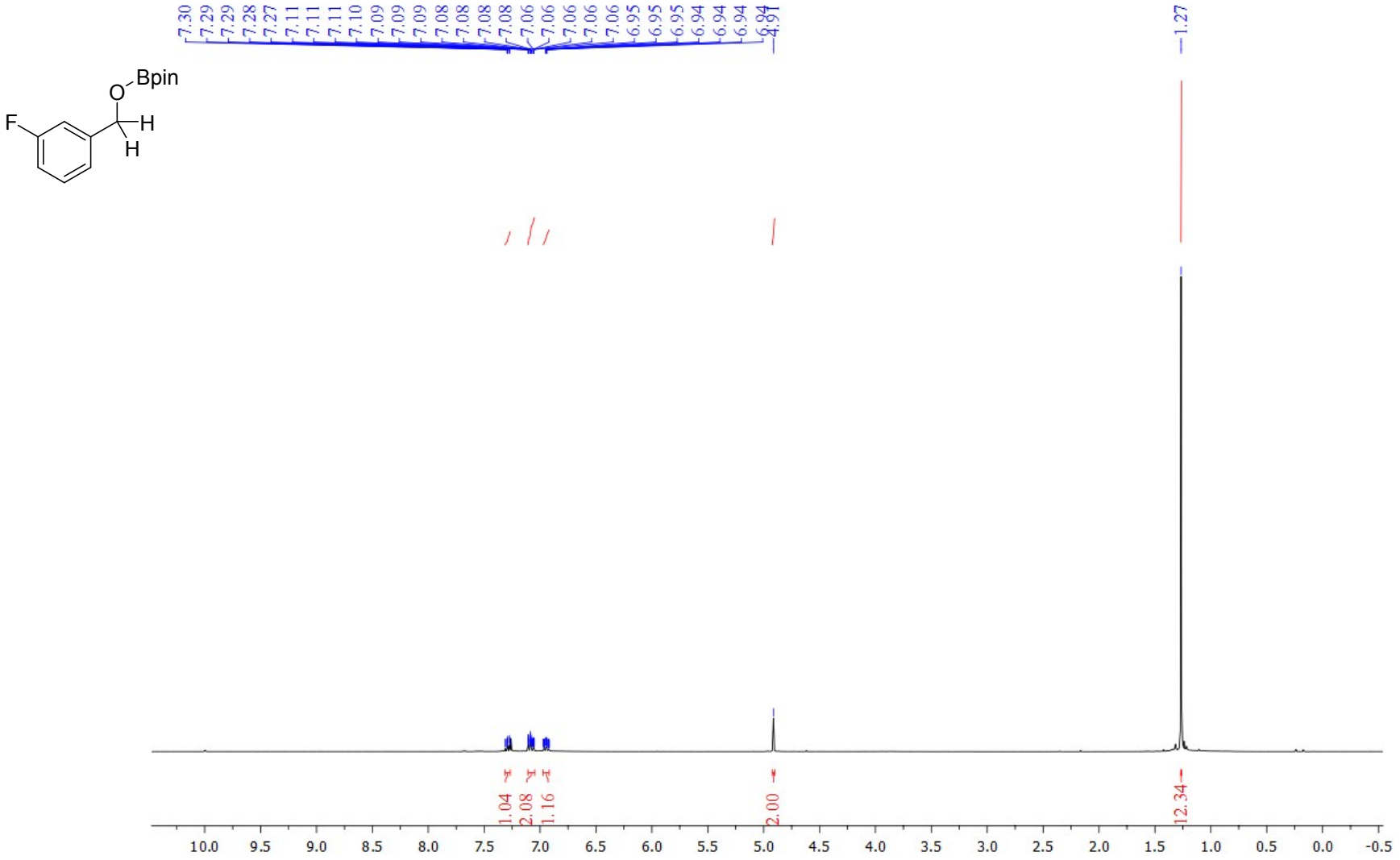


$CDCl_3$) spectrum of 2-((4-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11b**)

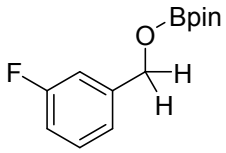
**S4.2.6.** $^{19}F\{^{1}H\}$ NMR (376 MHz, 295 K, $CDCl_3$) spectrum of 2-((4-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11b**)

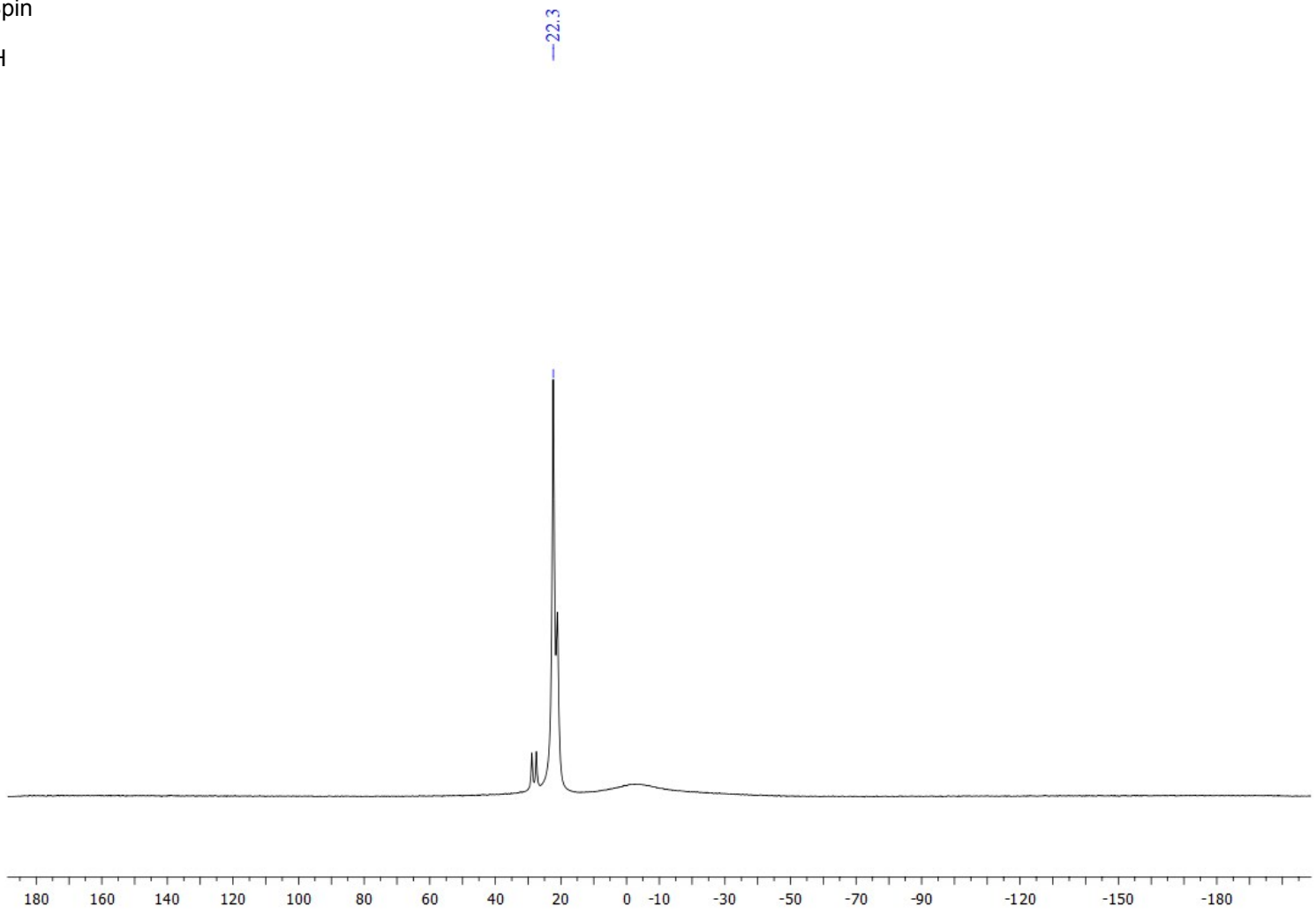


**S4.2.7.** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-((3-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11c**)

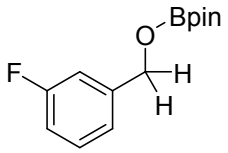


**S4.2.8.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of 2-((3-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11c**)

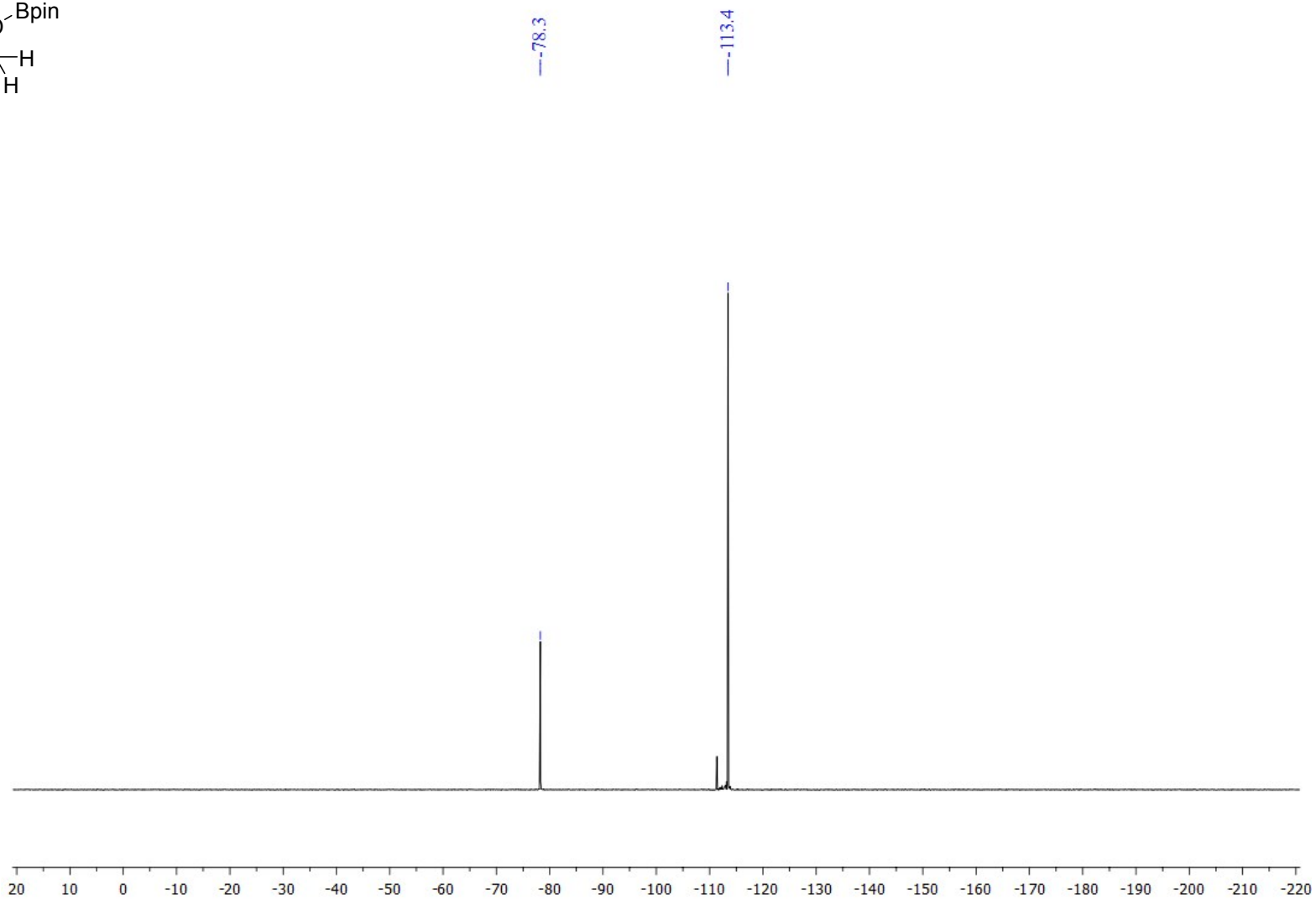


**S4.2.9.**

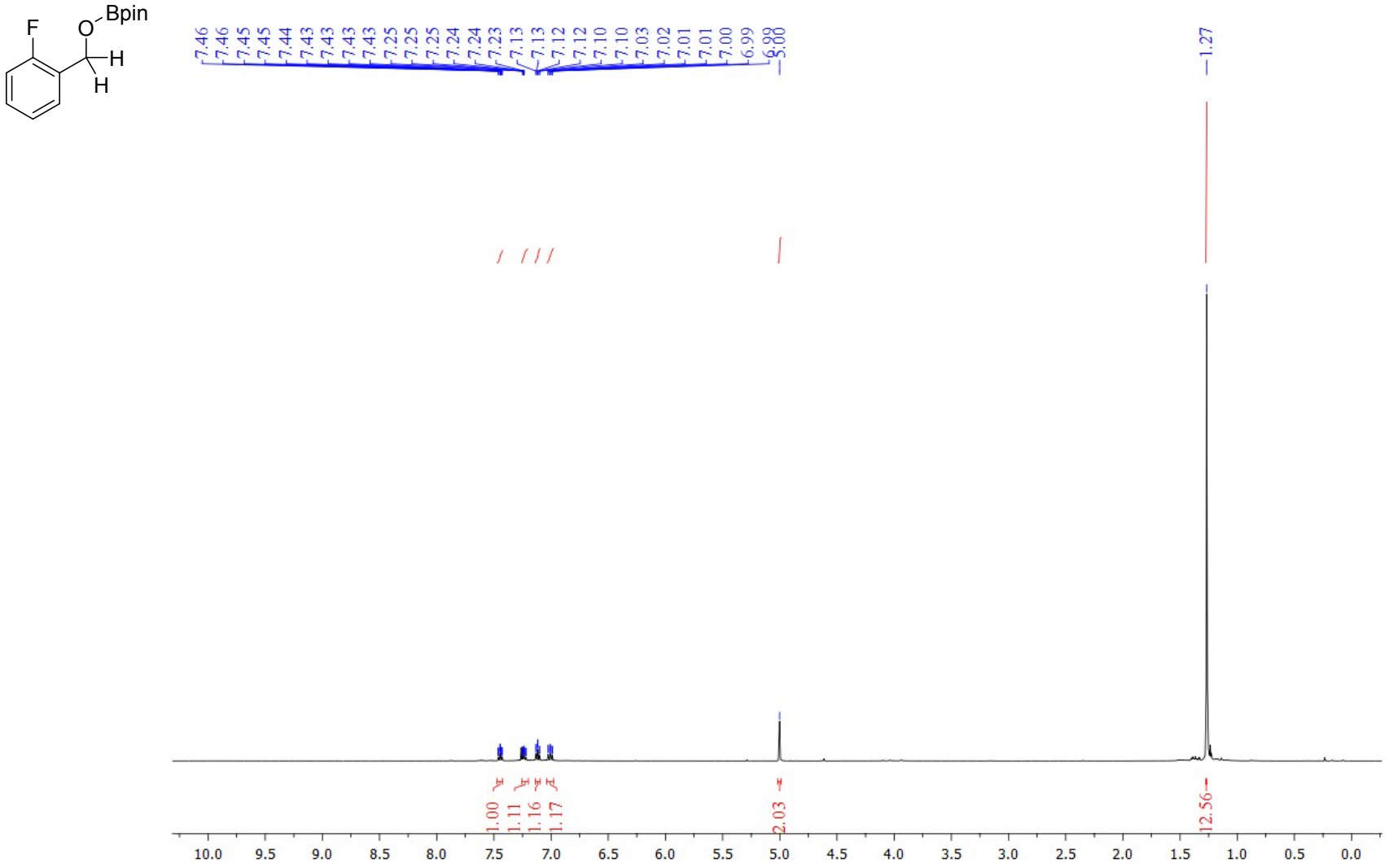



$^{19}F\{^{1}H\}$ NMR (376 MHz, 295 K, $CDCl_3$) spectrum

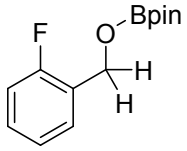


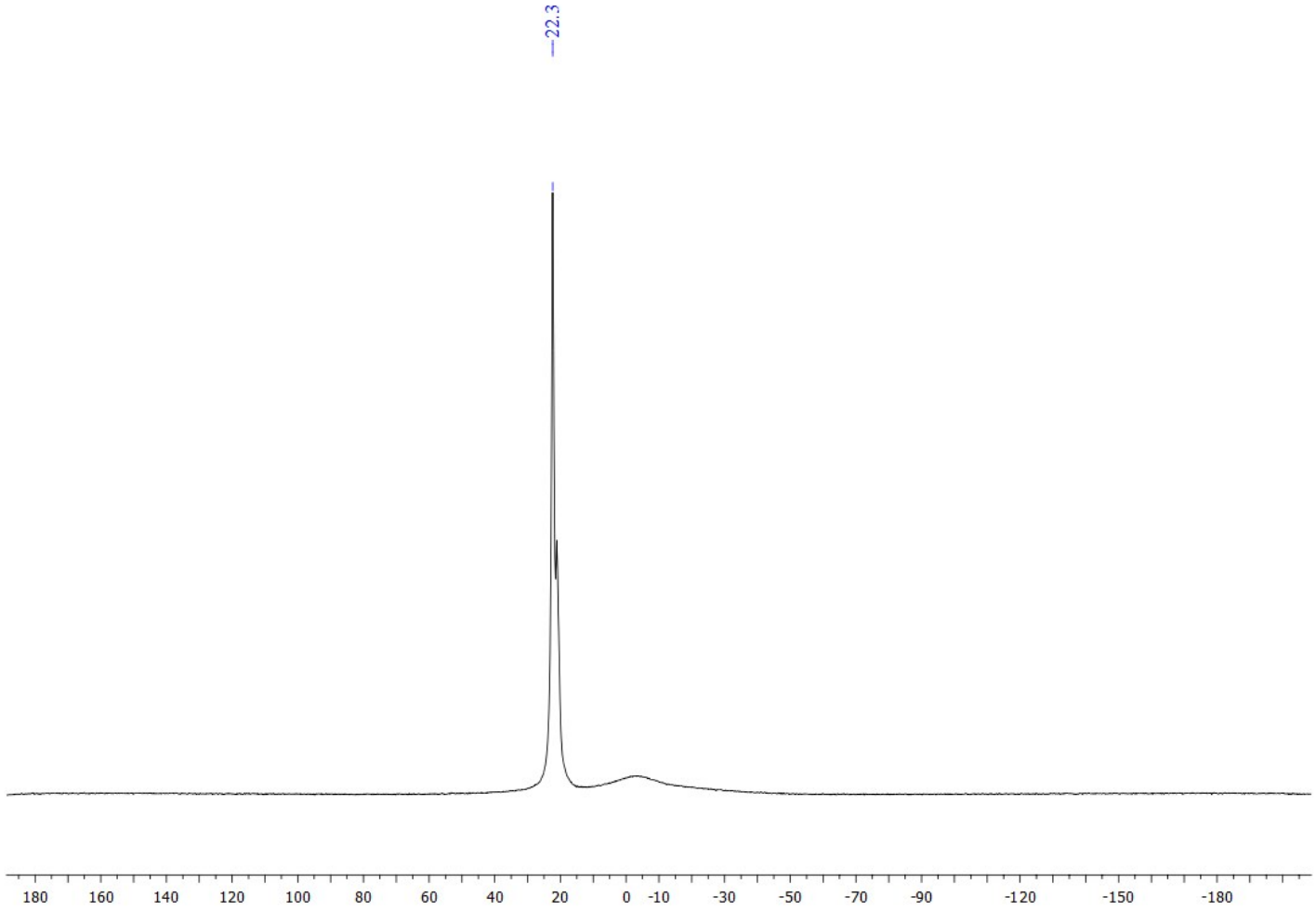
of 2-((3-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11c**)

**S4.2.10.** $^{1}H$ NMR (500 MHz, 295 K, $CDCl_3$) spectrum of 2-((2-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11d**)

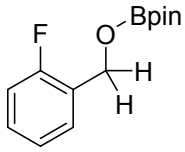


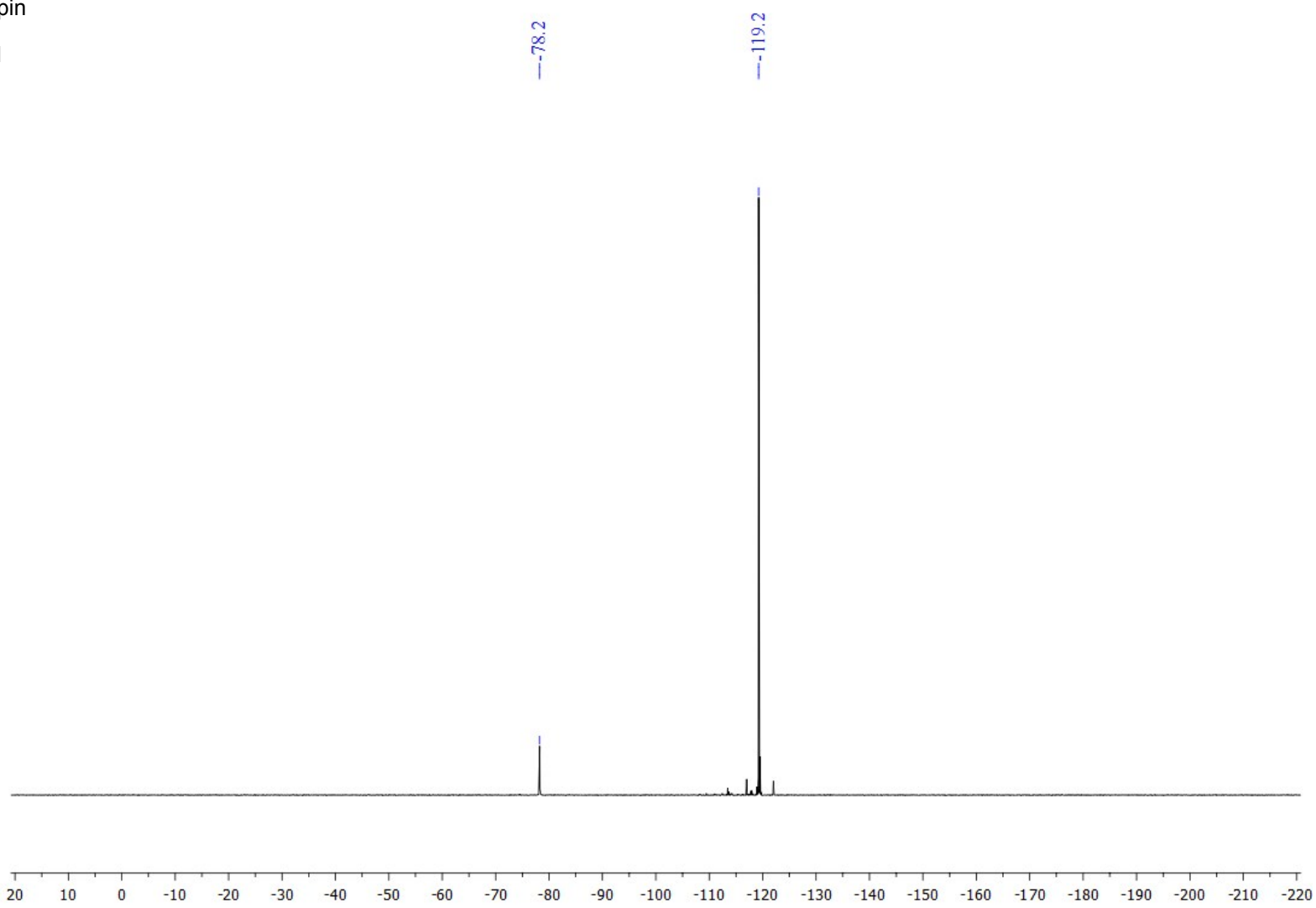
**S4.2.11.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of 2-((2-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11d**)



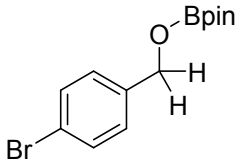



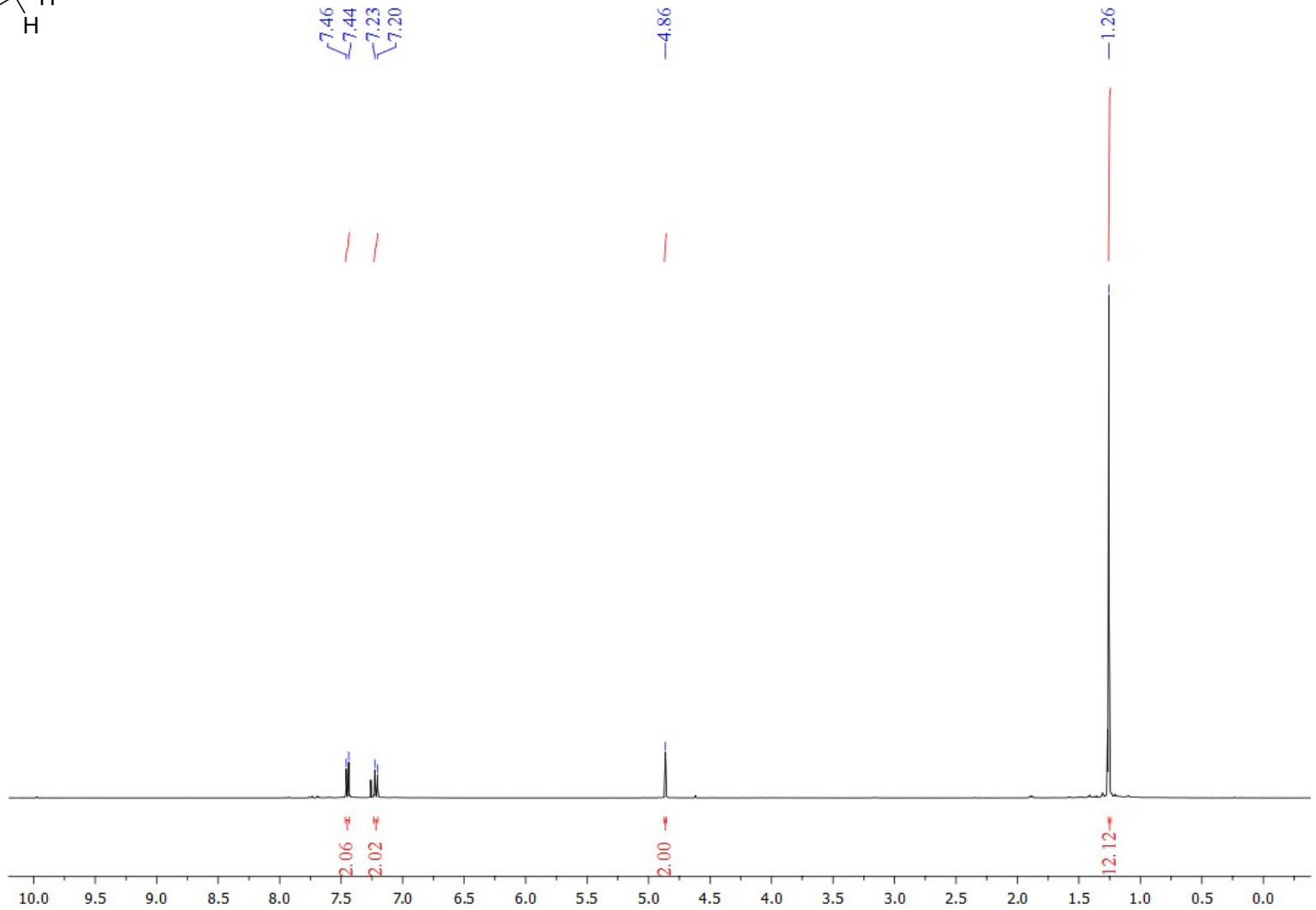
**S4.2.12.** $^{19}F\{^{1}H\}$ NMR (376 MHz, 295 K, $CDCl_3$) spectrum of 2-((2-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11d**)



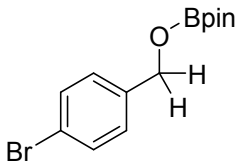



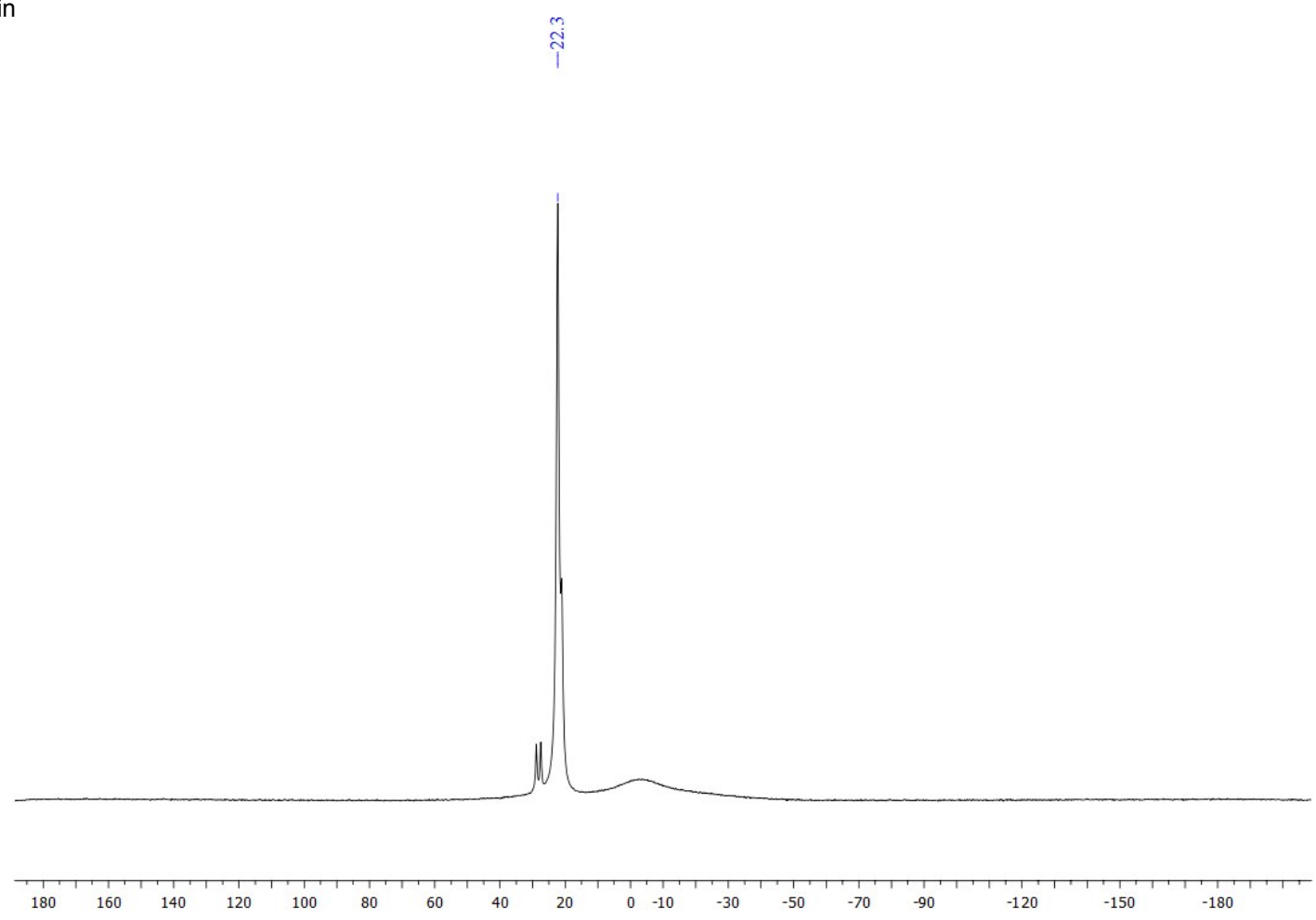
**S4.2.13.** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 2-((4-bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11e**)

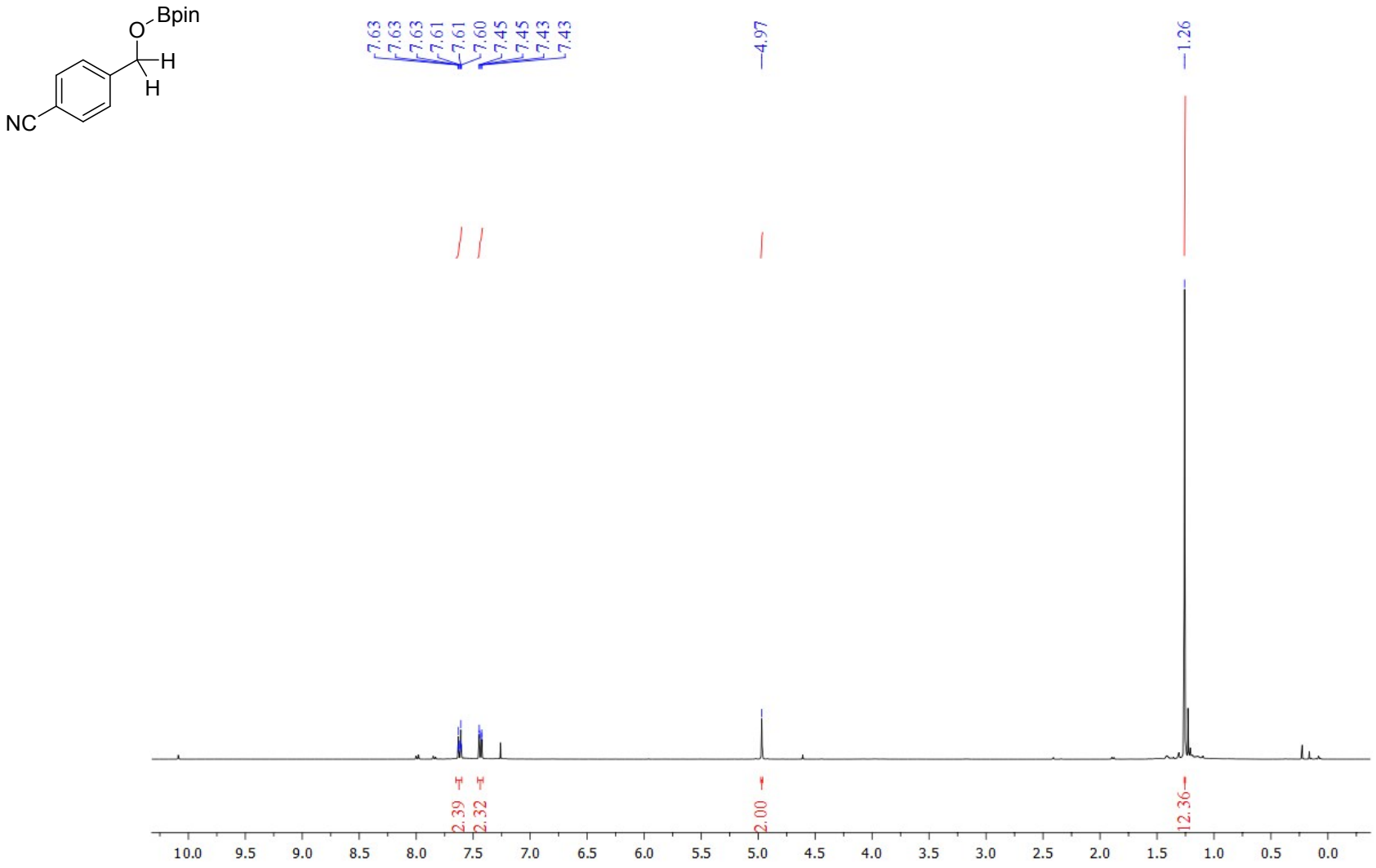


**S4.2.14.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of 2-((4-bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11e**)



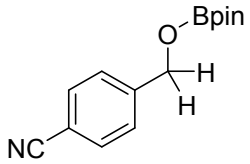



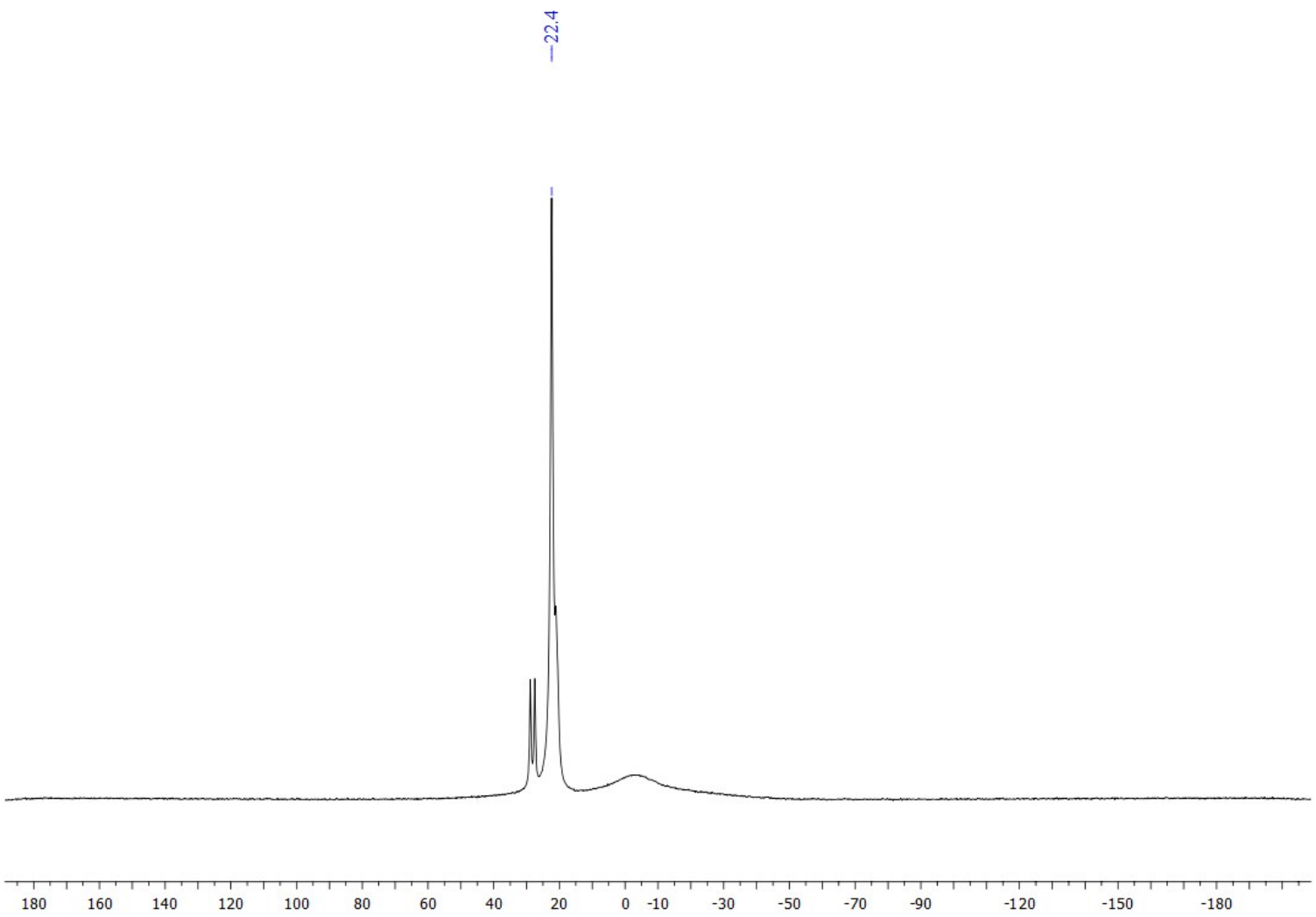



**S4.2.15.** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of

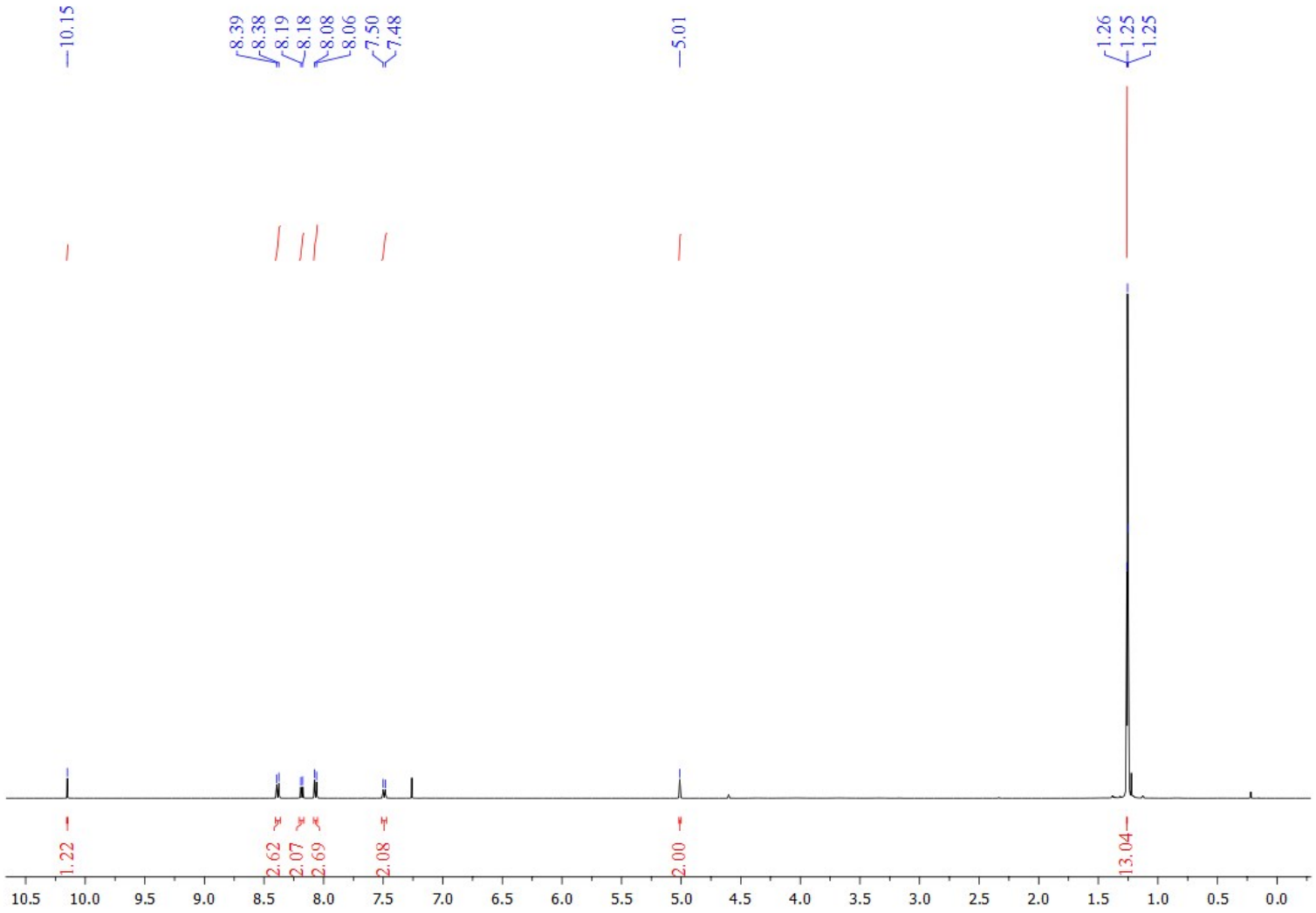
4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (**11f**)

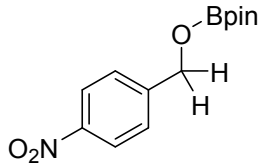
**S4.2.16.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of 4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (**11f**)





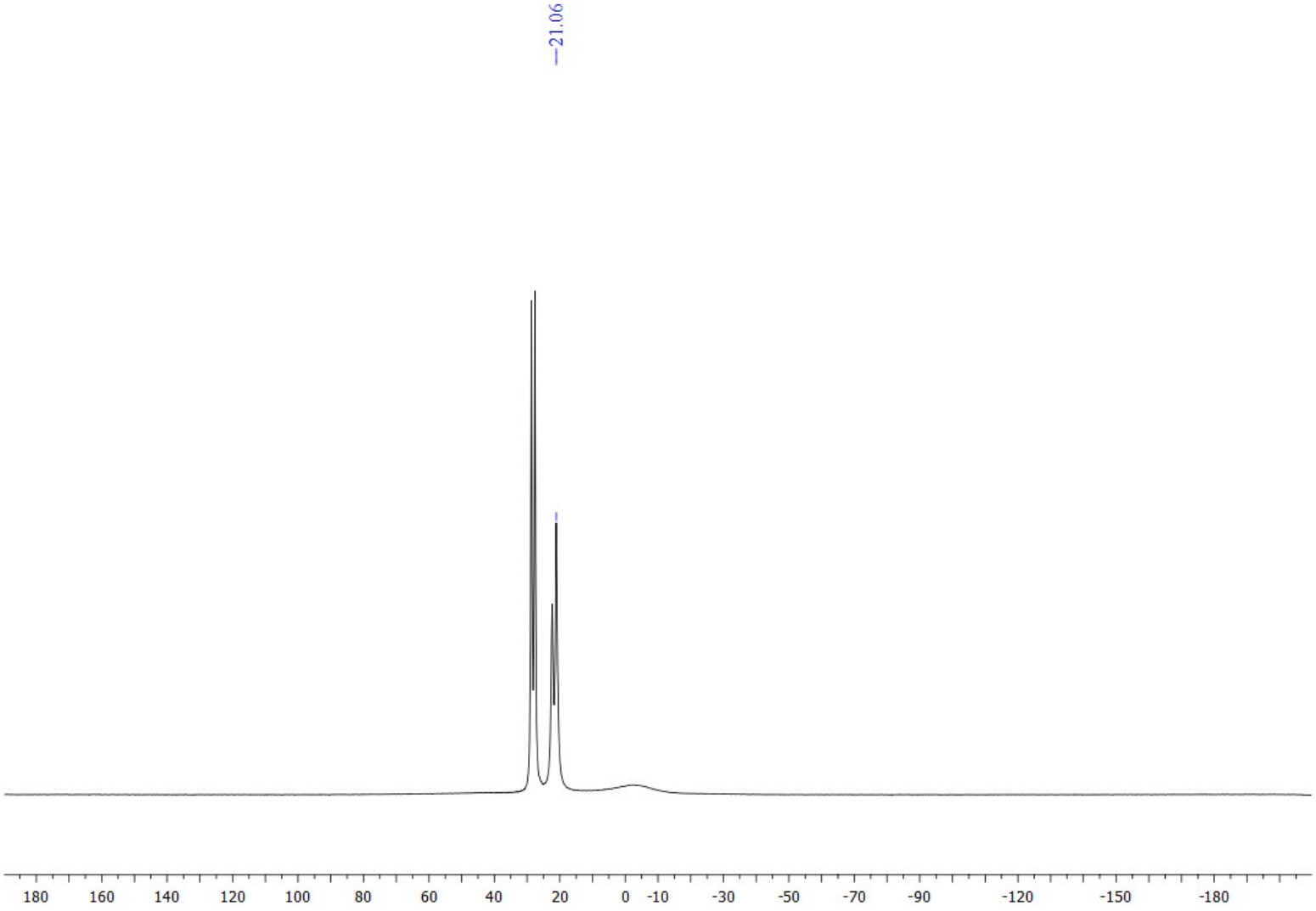

**S4.2.17.** $^{1}$H NMR (500 MHz, 295 K, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (**11g**)


10.15
8.39
8.38
8.19
8.18
8.08
8.06
7.50
7.48
5.01
1.26
1.25
1.25
1.22
2.62
2.07
2.69
2.08
2.00
13.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

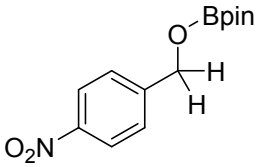

Bpin
O
H
H
O2N

**S4.2.18.**
(160 MHz, $CDCl_3$)

$^{11}B$ NMR
295 K,
spectrum



of 4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (**11g**)

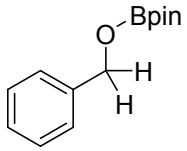


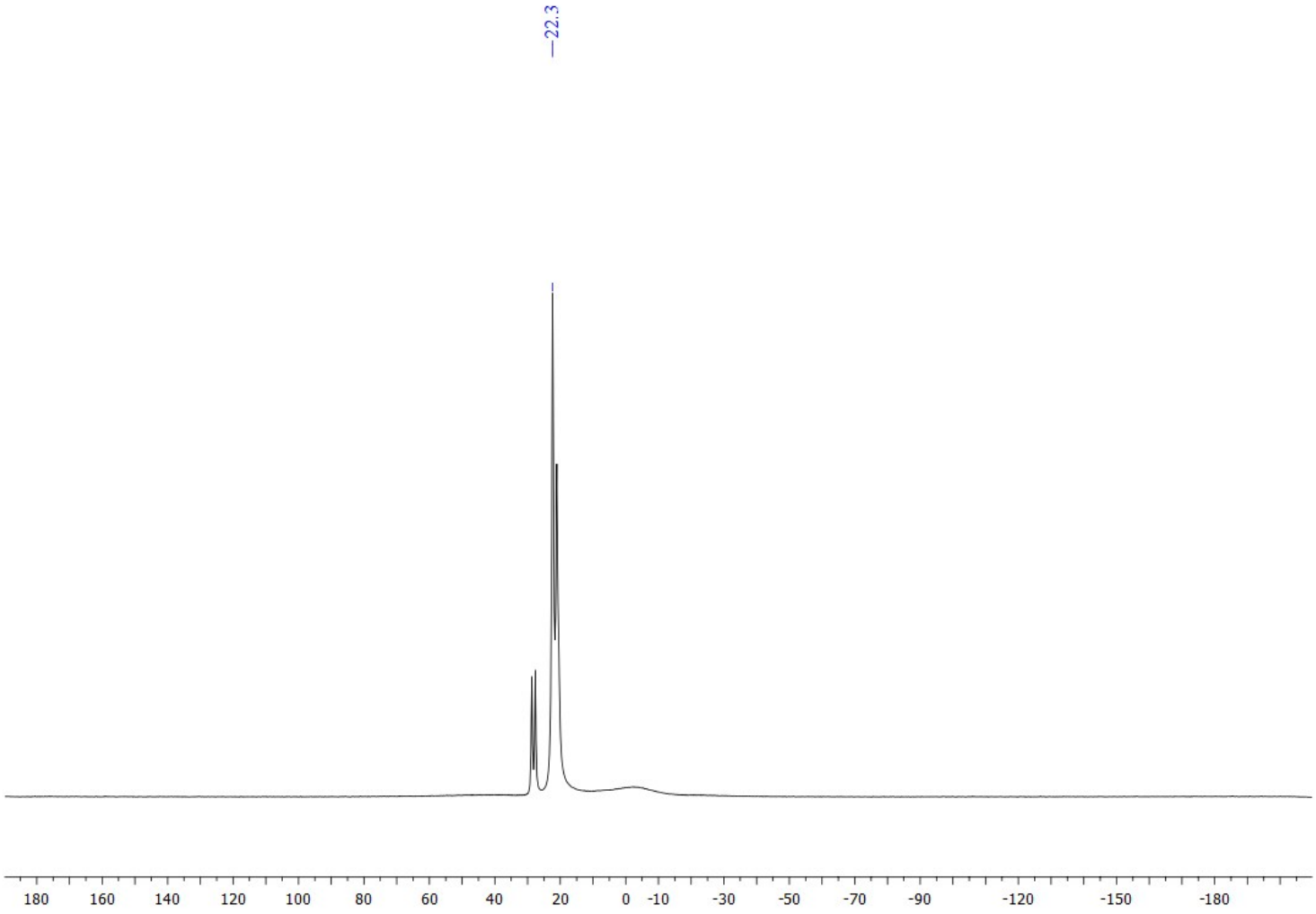

**S4.2.19**

. $^1$H NMR (400 MHz, 295 K,

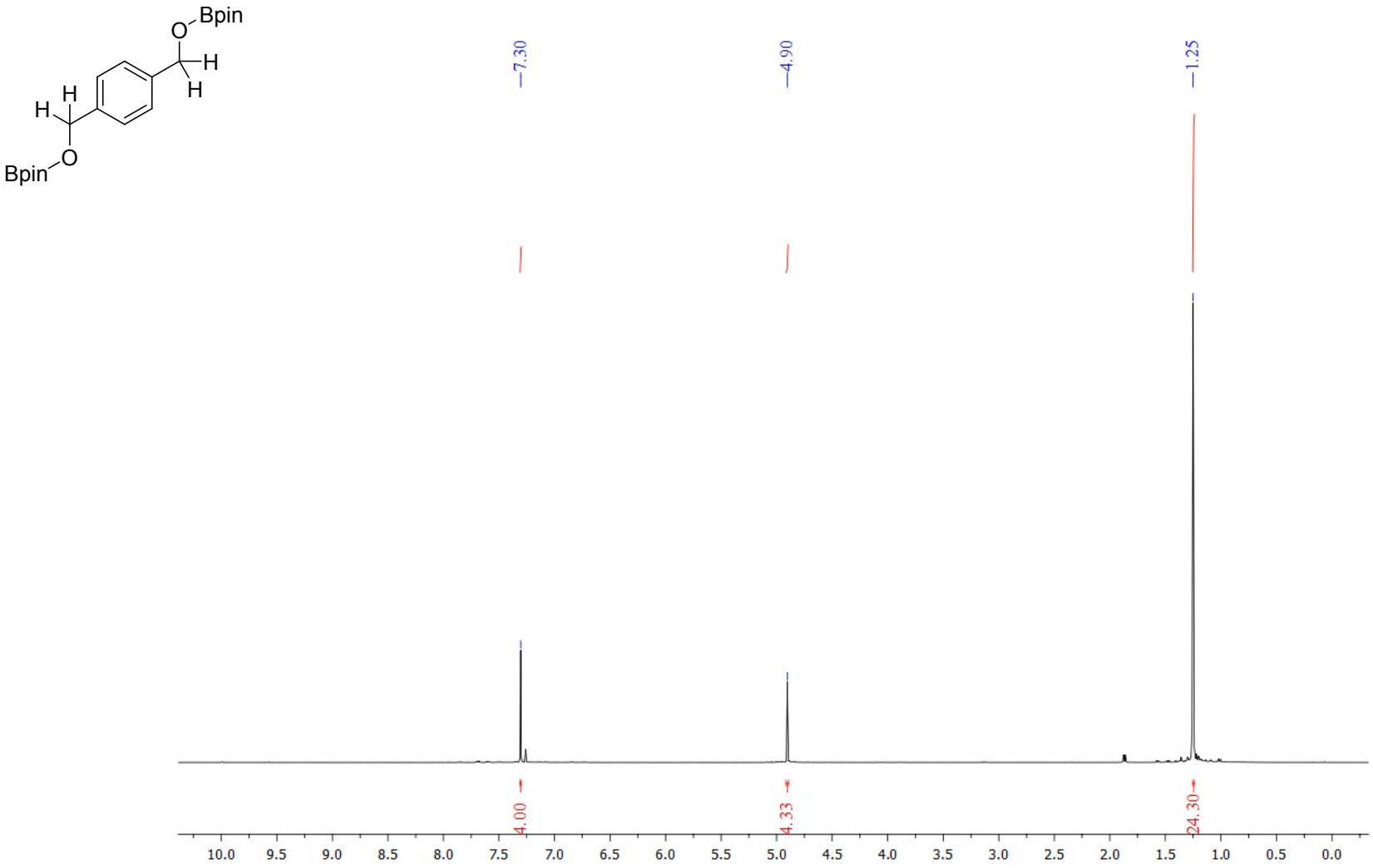
$CDCl_3$) spectrum of 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11h**)

**S4.2.20.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11h**)

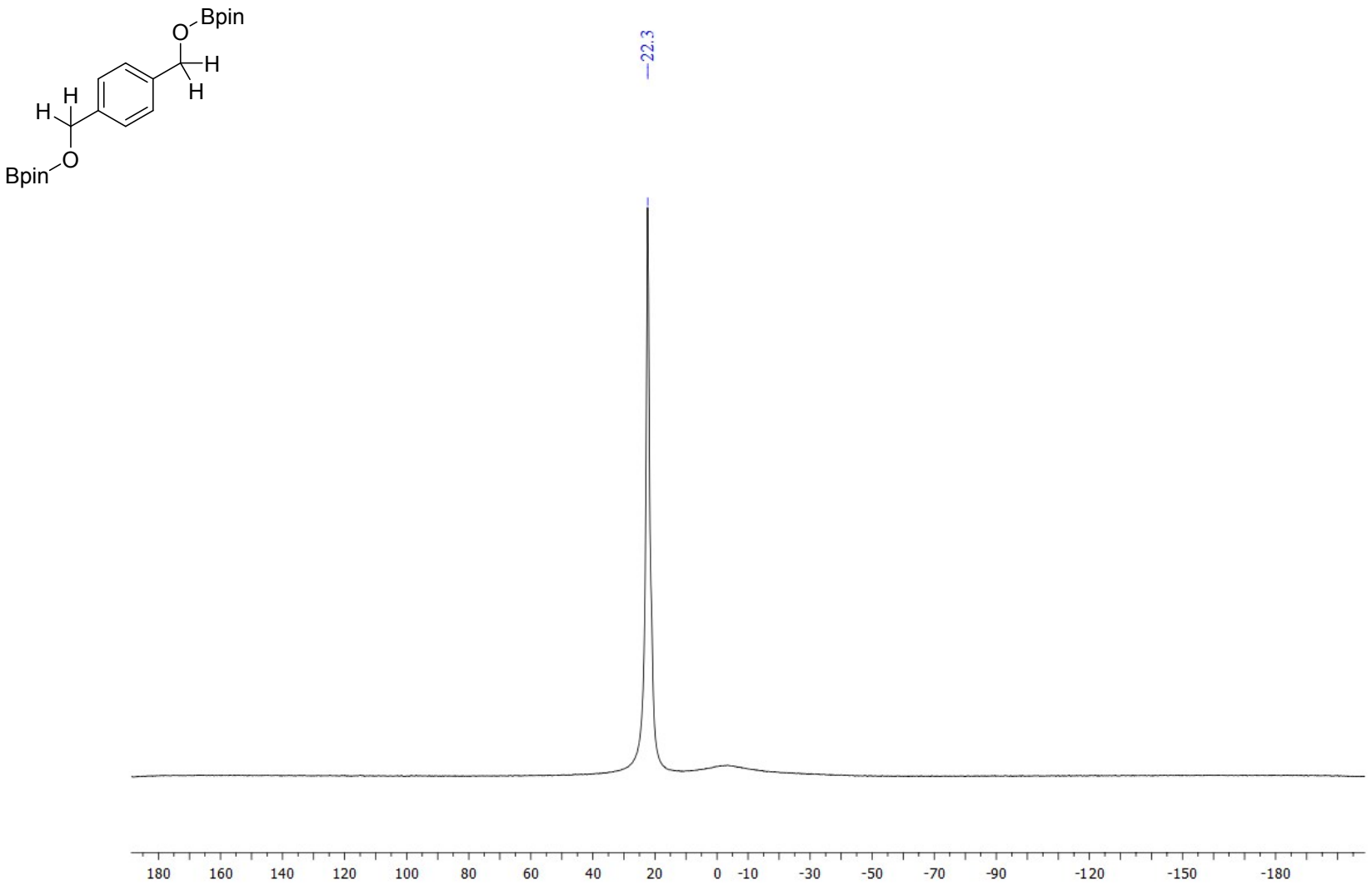


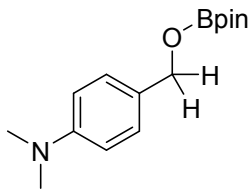
**S4.2.21.** $^{1}$H NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 1,4-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (**11i**)

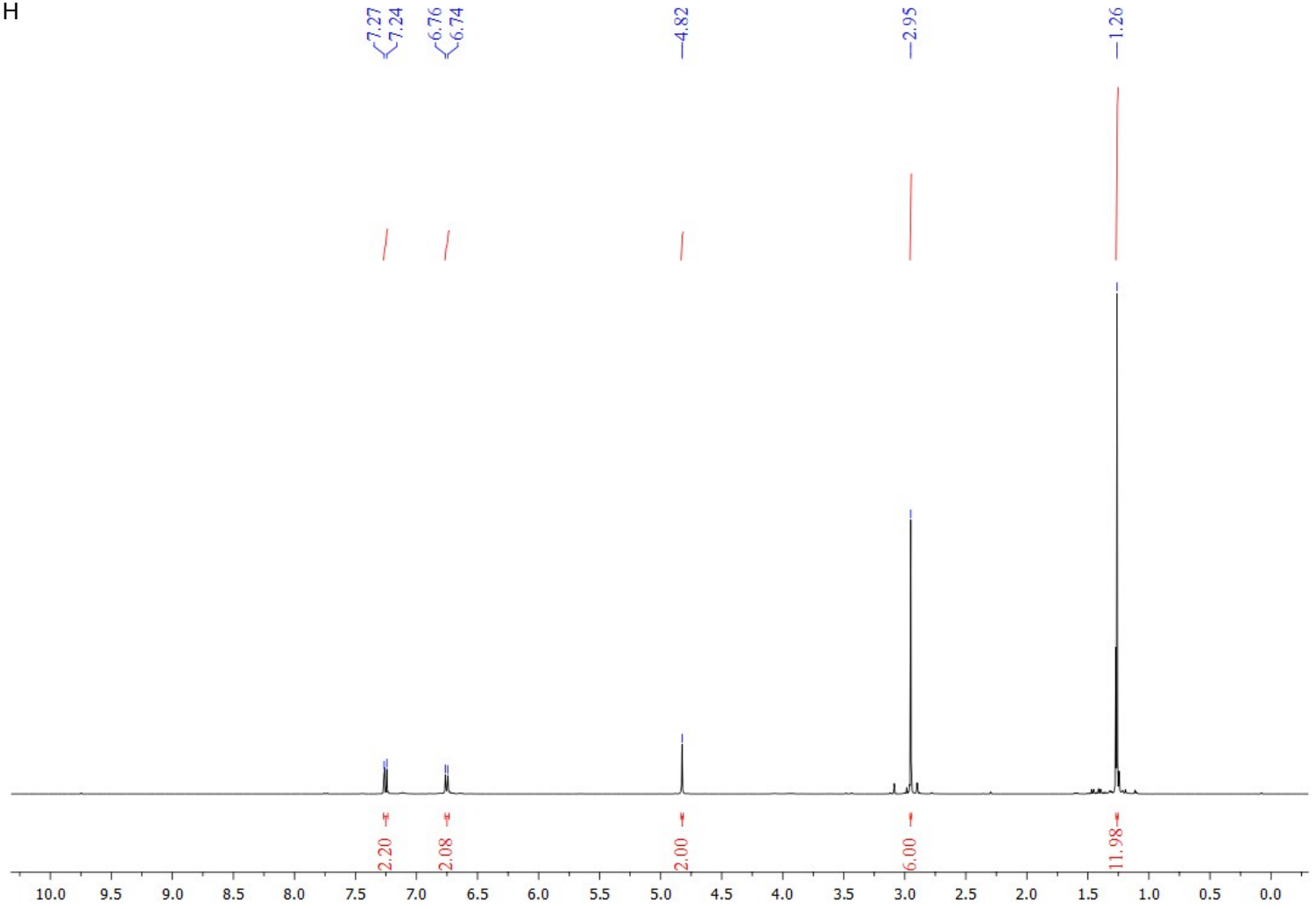


**S4.2.22.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of 1,4-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (**11i**)

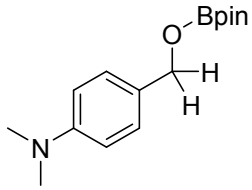


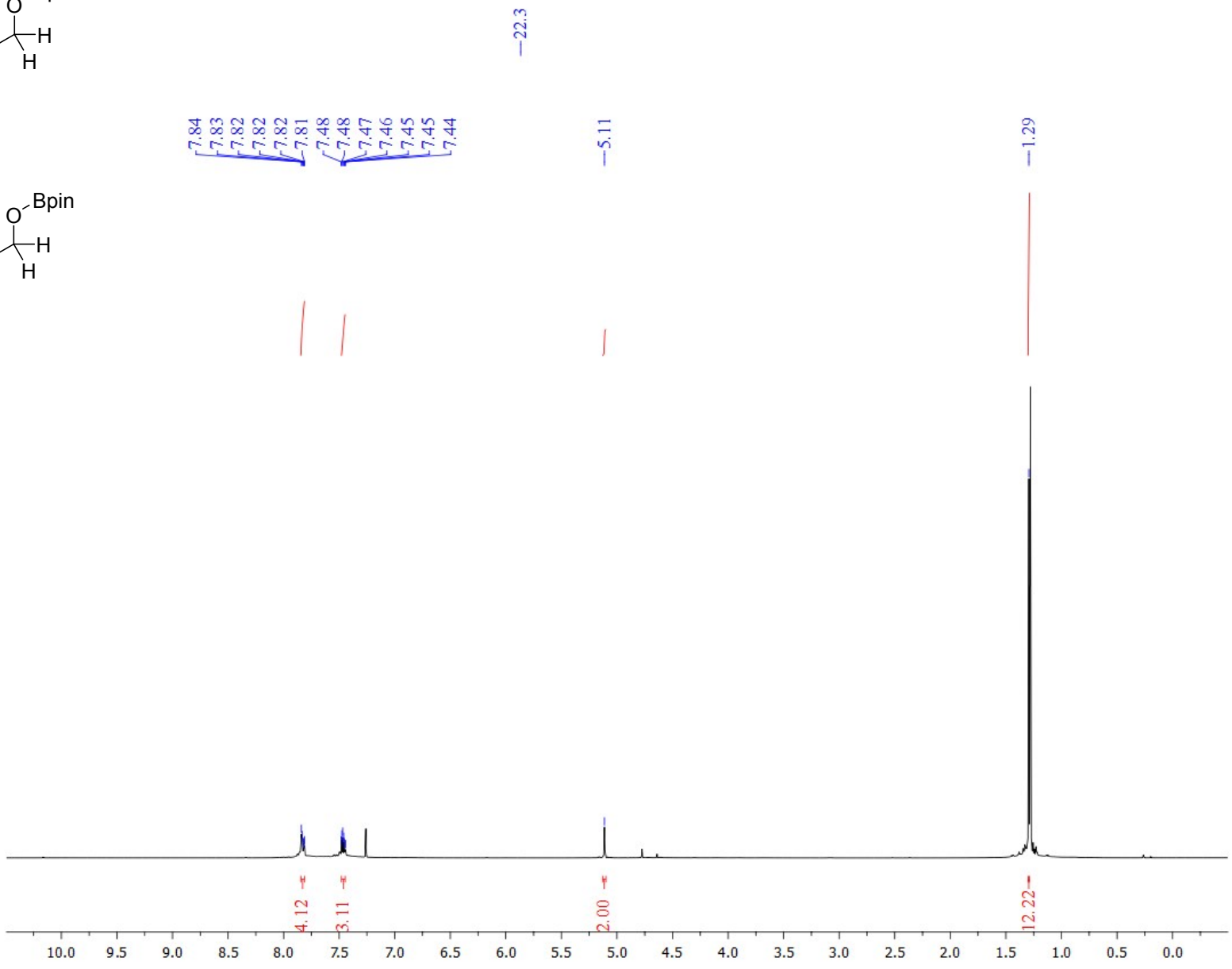
**S4.2.23.** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of N,N-dimethyl-4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)aniline (**11j**)



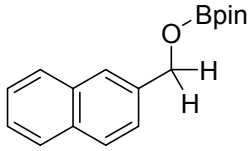



**S4.2.24.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of N,N-dimethyl-4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)aniline (**11j**)



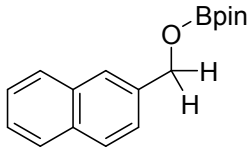

**S4.2.25.**

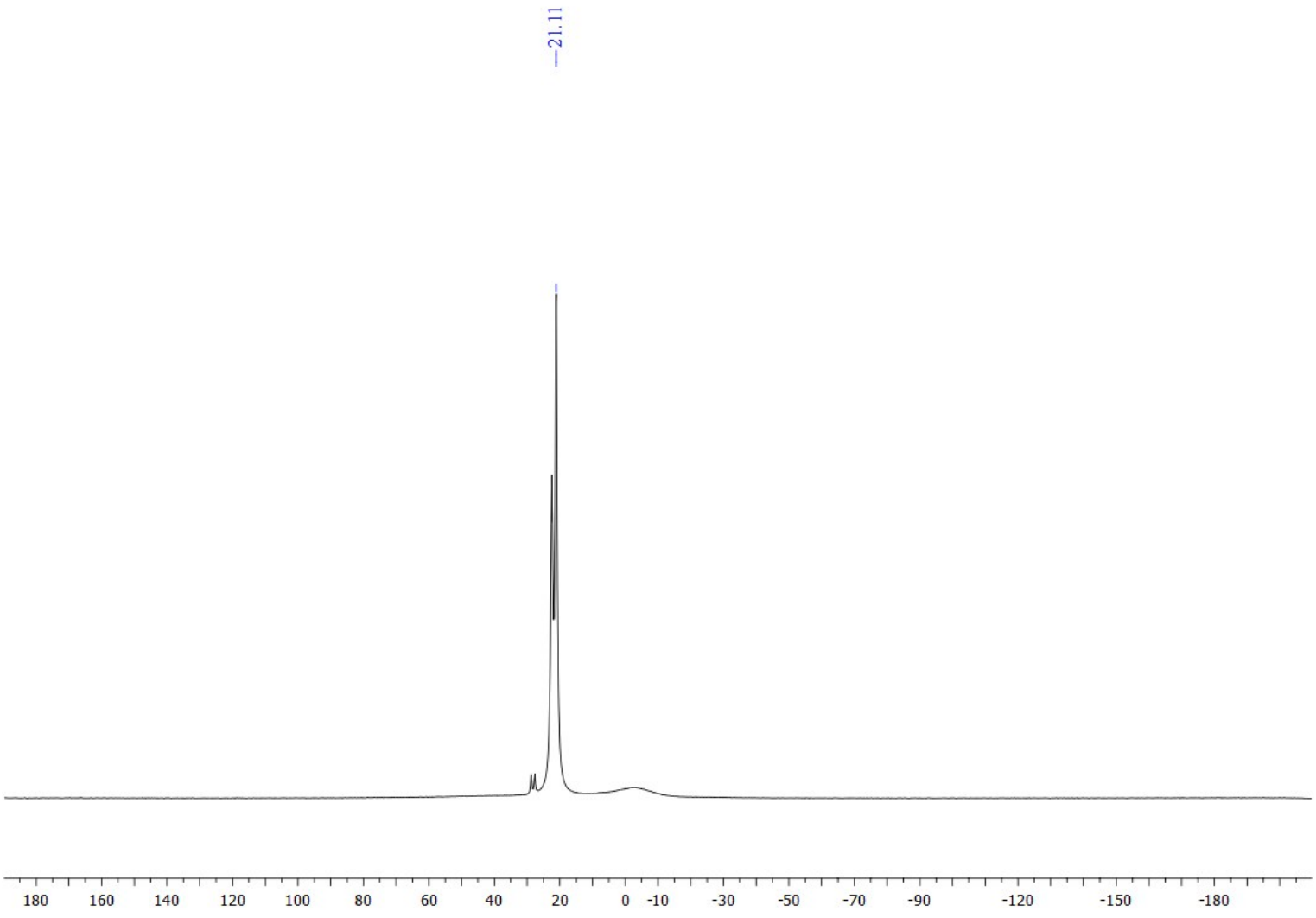



$^1H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum

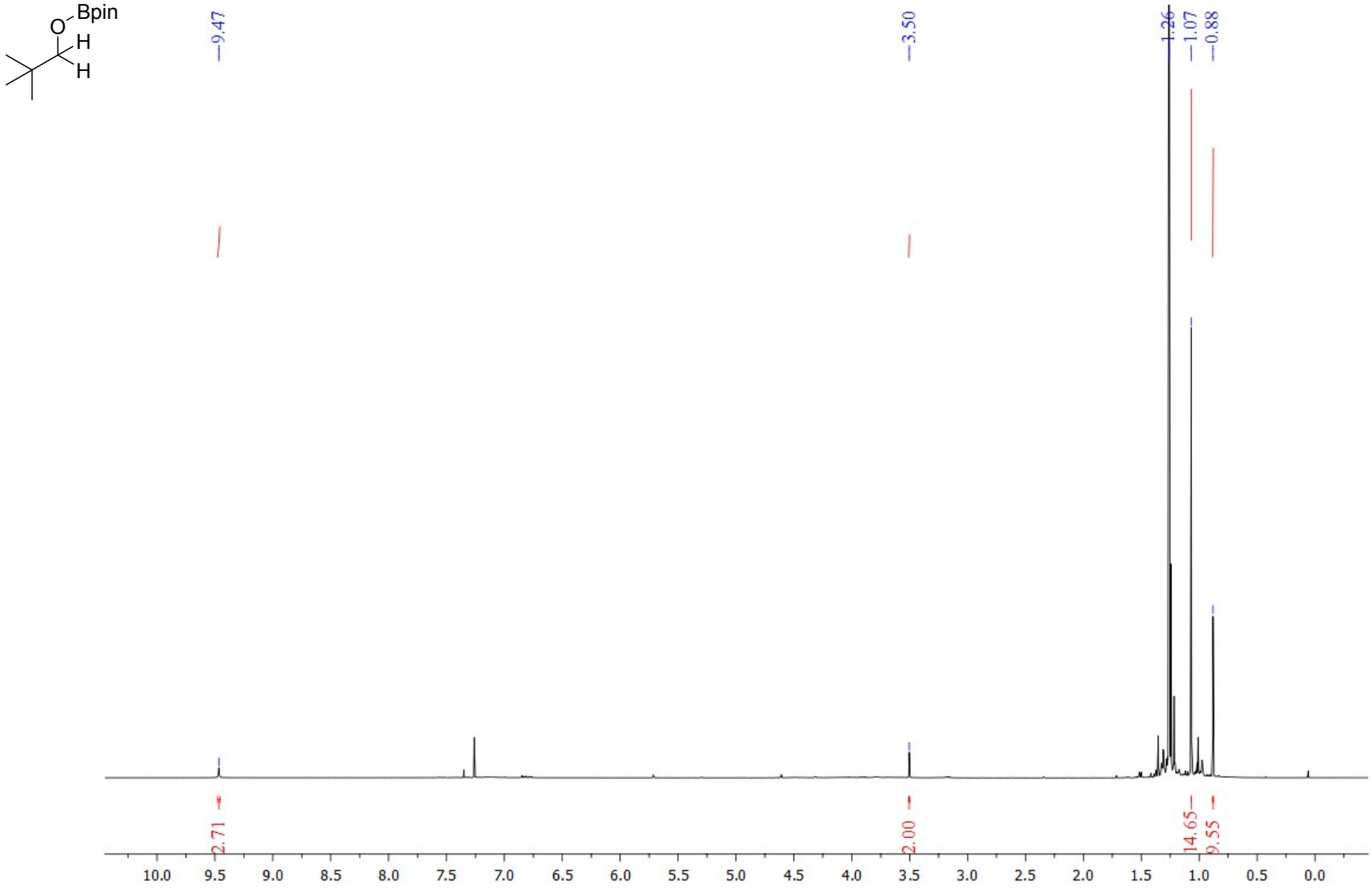
of 4,4,5,5-tetramethyl-2-(naphthalen-2-ylmethoxy)-1,3,2-dioxaborolane (**11k**)

**S4.2.26.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(naphthalen-2-ylmethoxy)-1,3,2-dioxaborolane (**11k**)



**S4.2.27.** $^{1}H$ NMR (400 MHz, 295 K, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(neopentyloxy)-1,3,2-dioxaborolane (**11l**)



**S4.2.28.** $^{11}B$ NMR (128 MHz, 295 K, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(neopentyloxy)-1,3,2-dioxaborolane (**11l**)