All-Carbon Phosphoranes via Difluorocarbene Trapping

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Content

General Methods: All reactions were performed under an argon atmosphere. Column chromatography was carried out employing silica gel (230-400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or aq. $KMnO_4$ solution. Solvents were prepared according to standard techniques. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage –4500V) or in a negative ion mode (3200V); mass range from m/z 50 to m/z 3000.

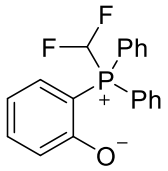
Starting materials

The following compounds were prepared according to literature procedures:

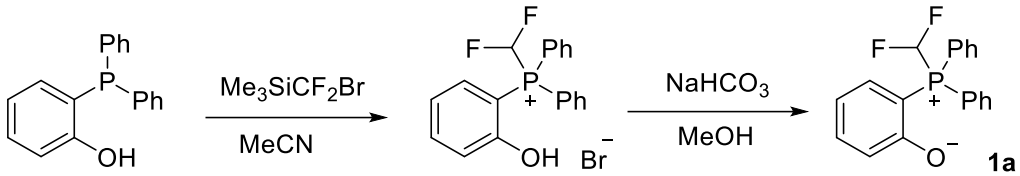
N,*N*-Dimethyl-2-(diphenylphosphino)aniline[1]
(2-Hydroxyphenyl)triphenylphosphonium bromide[2]
2-(Triphenylphosphonio)phenolate (**1e**)[3]
2-(Diphenylphosphino)phenol[4]
2-(Diphenylphosphino)thiophenol by phosphination[5] of 2-lithiothiophenolate[6]

[1] L. Horner and G. Simons, *Phosphorus, Sulfur Relat. Elem.*, 1983, **15**, 165–175.
[2] Y. Toda, S. Gomyou, S. Tanaka, Y. Komiyama, A. Kikuchi and H. Suga, *Org. Lett.*, 2017, **19**, 5786–5789.
[3] S. Guo and X. Mi, *Tetrahedron Lett.*, 2017, **58**, 2881–2884.
[4] L.-P. He, H.-L. Mu, B.-X. Li and Y.-S. Li, *J. Polym. Sci. A Polym. Chem.*, 2010, **48**, 311–319.
[5] E. Block, G. Ofori-Okai and J. Zubieta, *J. Am. Chem. Soc,*. 1989, **111**, 2327–2329.
[6] G. D. Figuly, C. K. Loop and J. C. Martin, *J. Am. Chem. Soc,*. 1989, **111**, 654–658.

2-[(Difluoromethyl)diphenylphosphonio]phenolate (1a).[7]



Originally,[7] **1a** was prepared from 2-(diphenylphosphino)phenol by treatment with pinacolborane followed by reaction with potassium bromodifluoroacetate in DMF, isolation of the reaction product (column chromatography) and its methanolysis. The procedure described below is a more convenient and cost-effective method.



(Difluoromethyl)(2-hydroxyphenyl)diphenylphosphonium bromide. To a cooled (ice/water bath) stirred suspension of 2-(diphenylphosphaneyl)phenol (1.11 g, 4.03 mmol) in MeCN (4.0 mL), $TMSCF_2Br$ (1.05 g, 5.17 mmol, 1.30 equiv) was added dropwise using a microsyringe. The reaction mixture was stirred in an ice/water bath for additional 5 minutes and then at room temperature for one hour (being a white suspension initially, the reaction mixture became a clear pale yellow solution after approximately 20 minutes of stirring at room temperature). Water (127 mg, 7.06 mmol, 1.77 equiv) was added with stirring and a copious precipitate formed within several seconds. The mixture was diluted with MeCN (8 mL), the precipitate was filtered, washed with MeCN (2×4 mL) and dried under vacuum to afford (difluoromethyl)(2-hydroxyphenyl)-diphenylphosphonium bromide (1.41 g, 3.45 mmol, 86 % yield) as off-white powder.

Mp 255-259 °C

^{1}H NMR (DMSO-d_6, 300.13 MHz): 12.26 (br.s, 1H); 8.37 (td, *J* = 47.4, 30.5 Hz, 1H); 8.07-7.97 (m, 2H); 7.95-7.70 (m, 9H); 7.36- 7.16 (m, 3H).

^{13}C{^{1}H} (DMSO-d_6, 75.47 MHz): 162.0 (d, *J* = 2.9 Hz); 139.3 (d, *J* = 2.3 Hz); 136.2 (d, *J* = 3.3 Hz); 135.4 (d, *J* = 9.0 Hz); 134.1 (d, *J* = 10.6 Hz); 130.8 (d, *J* = 13.1 Hz); 121.4 (d, *J* = 13.3 Hz); 116.9 (td, *J* = 7.2 Hz); 114.2 (td, *J* = 268.6, 87.1 Hz); 112.3 (d, *J* = 86.3 Hz); 98.3 (d, *J* = 89.9 Hz).

^{19}F NMR (DMSO-d_6, 282.4 MHz): -123.98 (dd, *J* = 81.8, 47.4 Hz).

^{31}P{^{1}H} NMR (DMSO-d_6, 121.5 MHz): 21.82 (dd, *J* = 81.8).

HRMS: for Calcd for $C_{19}H_{16}F_2OP^+$ [M-Br]: 329.0901; found: 329.0901.

A mixture of (difluoromethyl)(2-hydroxyphenyl)diphenylphosphonium bromide (1.25 g, 3.06 mmol) and $NaHCO_3$ (257 mg, 3.06 mmol, 1.00 equiv) were stirred in dry methanol (6.0 mL) at 60 °C for 40 minutes. After cooling to room temperature, the reaction mixture was evaporated, the residue was taken up in small amount of chloroform and the resulting solution was transferred to the

[7] V. O. Smirnov, A. D. Volodin, A. A. Korlyukov and A. D. Dilman, *Angew. Chem. Int. Ed.*, 2020, **59**, 12428–12431.

top of chromatography column (ca 20 g of silica gel in ethyl acetate/methanol, 8/1), followed by eluting with ethyl acetate/methanol (from 8/1 to 5/1).

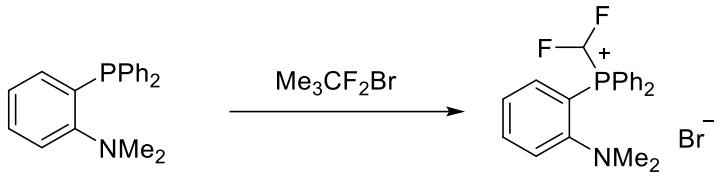
Yield 814 mg (81 %).

White solid. Mp 147-153°C (lit.[7] 144-148 °C).

R_f = 0.25 (ethyl acetate/methanol, 5/1).

Note: The column chromatography is needed to remove some impurity, presumably, (2-hydroxyphenyl)diphenylphosphine oxide, which moves higher and is developed by UV much weaker than the target product. Correspondingly, when performing column chromatography, first fractions containing the product should be carefully inspected for the presence of a higher weak UV-active spot.

(Difluoromethyl)[2-(dimethylamino)phenyl]diphenylphosphonium bromide (1c).



To a stirred mixture of *N*,*N*-dimethyl-2-(diphenylphosphino)aniline (147 mg, 0.48 mmol) and $NaHCO_3$ (103 mg, 1.23 mmol, 2.56 equiv) in ethyl acetate (2.0 mL) and methanol (0.20 mL), $TMSCF_2Br$ (196 mg, 0.97 mmol, 2.0 equiv) was added, and the resulting mixture was stirred at room temperature for 14 hours. Then, the mixture was evaporated under vacuum, the residue was taken up in CH_2Cl_2, and the resulting mixture was filtered through a small cotton plug. The plug was further washed with CH_2Cl_2, the washing was combined with the first filtrate, the combined filtrates were evaporated. The residue was dissolved in CH_2Cl_2 (2 mL) with slight heating, the solution was diluted with ethyl acetate (6 mL) to cause precipitation. The mixture was concentrated on a rotary evaporator (*ca.* 200 Torr/40 °C) to the final volume of *ca.* 4 mL. The precipitate was filtered, washed with ethyl acetate (2×3mL), and dried under vacuum to afford the product as a white crystalline powder. Yield 200 mg, 0.46 mmol, 95%.

Mp 182-198 °C.

^{1}H NMR ($CDCl_3$, 300.13 MHz): 9.04 (td, *J* = 48.1, 30.3 Hz, 1H); 7.94 (t, *J* = 7.7 Hz, 1H); 7.88-7.52 (m, 13H); 2.33 (s, 6H).

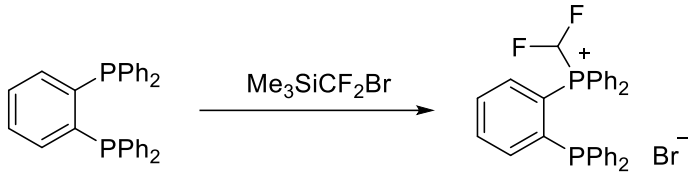
^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): 159.7 (d, *J* = 5.1 Hz); 138.7 (d, *J* = 2.6 Hz); 136.2 (d, *J* = 10.6 Hz); 135.5 (d, *J* = 3.2 Hz); 133.7 (d, *J* = 10.2 Hz); 130.4 (d, *J* = 13.0 Hz); 129.0 (d, *J* = 13.8 Hz); 125.9 (d, *J* = 8.6 Hz); 115.9 (d, *J* = 94.3 Hz); 114.3 (d, *J* = 86.6 Hz); 114.2 (dd, *J* = 271.6, 92.2 Hz); 46.14.

^{19}F NMR ($CDCl_3$, 282.4 MHz): -122.43 (dd, *J* = 86.7, 48.4 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): 20.13 (t, *J* = 86.5 Hz).

HRMS: calcd for $C_{21}H_{21}F_2NP^+$ [M-Br]: 356.1374; found: 356.1374.

(Difluoromethyl)[2-(diphenylphosphaneyl)phenyl]diphenylphosphonium bromide (1d).



To a stirred mixture of 1,2-bis(diphenylphosphino)benzene (730 mg, 1.63 mmol) and $NaHCO_3$ (367 mg, 4.37 mmol, 2.67 equiv) in dichloromethane (4.9 mL) and methanol (0.49 mL), $TMSCF_2Br$ (659 mg, 3.25 mmol, 2.0 equiv) was added, and the resulting mixture was stirred at room temperature for 7 hours until TLC analysis showed almost complete consumption of the starting diphosphine. Then, stirring was discontinued, the precipitate was allowed to settle, and the liquid phase was removed using a Pasteur pipette. The precipitate was further washed with dichloromethane (5 and 2 mL) and the combined solutions were evaporated. The residue was dissolved in dichloromethane (3 mL), and this solution was diluted with ethyl acetate (15 mL), which caused formation of white precipitate. The precipitate was filtered, washed with ethyl acetate (5 mL), and dried under vacuum to afford white crystalline powder.

Yield 900 mg, 1.55 mmol, 95 %.

Mp 227-229 °C.

^{1}H NMR ($CDCl_3$, 300.13 MHz): 9.38 (td, *J* = 47.3, 29.7 Hz, 1H); 8.57-8.45 (m, 1H); 8.10-7.00 (m, 19H); 6.85 - 6.65 (m, 4H).

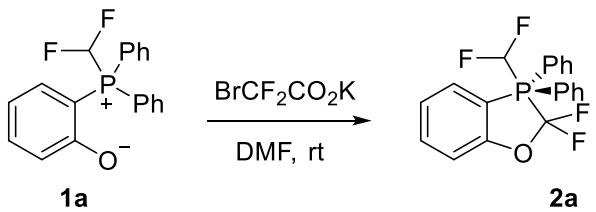
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): 143.3 (dd, *J* = 14.2, 12.1 Hz); 138.7 (d, *J* = 12.1 Hz); 138.3 (t, *J* = 11.9 Hz); 136.5 (d, *J* = 3.2 Hz); 135.6 (d, *J* = 3.2 Hz); 134.5 (dd, *J* = 10.3, 3.2 Hz); 132.8 (d, *J* = 18.4 Hz); 132.6 (d, *J* = 4.5 Hz); 132.5 (d, *J* = 12.5 Hz); 130.4 (d, *J* = 13.3 Hz); 129.7; 128.9 (d, *J* = 7.5 Hz); 121.2 (dd, *J* = 89.4, 39.6 Hz); 114.3 (ddd, *J* = 271.6, 84.4, 13.7 Hz); 114.2 (dd, *J* = 85.5, 5.5 Hz).

^{19}F NMR ($CDCl_3$, 282.4 MHz): -124.37 (ddd, *J* = 79.8, 47.3, 10.6 Hz).

$^{31}P\{^1H\}$ NMR (CDCl3, 121.5 MHz): 21.09 (td, *J* =79.7, 23.4 Hz); -11.64 (dt, *J* = 23.3, 8.9 Hz).

HRMS: calcd for $C_{31}H_{25}F_2P_2^+$ [M-Br]: 497.1394; found: 497.1405.

3-(Difluoromethyl)-2,2-difluoro-3,3-diphenyl-2,3-dihydro-3λ^5-benzo[d][1,3]oxaphosphole (2a).



1a **2a**

Compound **1a** (665 mg, 2.03 mmol) and $BrCF_2CO_2K$ (854 mg, 4.01 mmol, 2.0 equiv) were stirred in dry DMF (4.0 mL) at room temperature for 16 hours. 3-Bromobenzotrifluoride was added as a standard, and the mixture was analyzed by ^{19}F NMR providing 66 % yield of **2a**. Volatiles were removed from the reaction vessel under vacuum (*ca.* 0.4 Torr) with stirring. The residue was taken up in dichloromethane (4 mL), the solution was separated from white precipitate, diluted with

hexane (8 mL), and transferred on the top of chromatography column packed with deactivated silica gel (**Note 1**), and the product was rapidly eluted with CH_2Cl_2/hexane mixture (1/2) (**Note 2**). After evaporation on a rotary evaporator, the product was obtained as a white solid.

Note 1. For deactivation, silica gel (approx. 15 g) was suspended in CH_2Cl_2/hexane mixture (1/2) (*ca*. 40 mL) and triethylamine (3.0 mL) was added. The mixture was stirred for several minutes, transferred into chromatography column, and an excess of solvents was allowed to flow down. This column was used for purification of **2a**. Use of regular silica gel leads to significant drop in the yield or even to total loss of the product due to its decomposition.
Note 2. The eluant was collected in 12-mL test tubes and the product was detected in tubes from 3rd to 7th. The product rapidly decomposes on silica gel of TLC plate. Fractions with high content of the product may be visible on TLC under UV light as a high spot (R_f ~ 0.7, CH_2Cl_2) with a tail and a spot on the start, while fractions with low content may show starting UV-active spot only.

Yield 497 mg, 1.31 mmol (65 %).

Mp 149-152 °C.

^{1}H NMR ($CDCl_3$, 300.13 MHz): 8.18 (ddd, *J* = 10.8, 7.9, 1.5 Hz, 1H); 7.96 – 7.84 (m, 4H); 7.73 (ddt, *J* = 8.6, 7.3, 1.4 Hz, 1H); 7.65 – 7.48 (m, 6H); 7.33 (tdd, *J* = 8.1, 4.3, 1.3 Hz, 1H); 7.16 (ddd, *J* = 8.3, 5.5, 1.1 Hz, 1H); 5.96 (td, *J* = 49.1, 21.3 Hz, 1H).

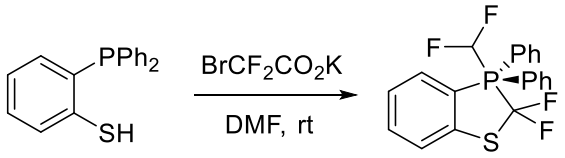
^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): 161.72 (dt, *J* = 8.5, 4.6 Hz); 136.66 (d, *J* = 2.2 Hz); 136.41 (dt, *J* = 8.5, 5.3 Hz); 130.78 (d, *J* = 3.2 Hz); 129.81 (d, *J* = 9.9 Hz); 129.23 (tq, *J* = 336.2, 3.1 Hz); 128.89 (d, *J* = 14.4 Hz); 127.92 (dp, *J* = 125.1, *J* = 3.1 Hz); 123.96 (d, *J* = 12.7 Hz); 121.92 (tdt, *J* = 280.6, 11.0, 6.5 Hz); 116.17 (d, *J* = 6.2 Hz); 111.51 (dm, *J* = 130.9 Hz)

^{19}F NMR ($CDCl_3$, 282.4 MHz): -77.23 (d, *J* = 18.6 Hz, 2F); -121.64 (dd, *J* = 48.8, 31.4 Hz, 2F).

^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): -95.26 (tt, *J* = 32.7, 18.7 Hz)

Elemental analysis:
Calcd. for $C_{20}H_{15}F_4OP$, %: C, 63.50; H, 4.00.
Found, %: C, 63.52; H, 3.93.

3-(Difluoromethyl)-2,2-difluoro-3,3-diphenyl-2,3-dihydro-3λ^5-benzo[d][1,3]thiaphosphole (2b)



2b

2-(Diphenylphosphino)thiophenol (588 mg, 2.00 mmol) and $BrCF_2CO_2K$ (1.10 g, 5.16 mmol, 2.6 equiv) were stirred in dry DMF (4.0 mL) at room temperature for 18 hours. 3-Bromobenzotrifluoride was added as a standard, and the mixture was analyzed by ^{19}F NMR providing 27 % yield of 2b. Volatiles were removed from the reaction vessel under vacuum (*ca.* 0.4 Torr) with stirring. The residue was taken up in ethyl acetate (4 mL) and water (12 mL). The organic layer was separated and dried over Na_2SO_4, the aqueous layer was diluted with water (12 mL), washed with ethyl acetate (12 mL). The combined organic phases were dried over Na_2SO_4,

concentrated under vacuum, and the residue was subjected to column chromatography on silica gel (CH_2Cl_2) to afford the product as a white solid.

Yield 216 mg, 0.55 mmol, 27 %.

R_f = 0.75 (CH_2Cl_2)

Mp 144-148 °C.

^{1}H NMR ($CDCl_3$, 300.13 MHz): 8.27 (dd, *J* = 10.7, 7.9 Hz, 1H); 8.07 – 7.84 (m, 4H); 7.69 – 7.48 (m, 7H); 7.48 – 7.32 (m, 2H); 5.87 (td, *J* = 49.6, 20.5 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): 144.0 (dt, *J* = 11.2, 3.8 Hz); 139.8 (tdt, *J* = 334.1, 16.0, 3.4 Hz); 136.9 (dt, *J* = 10.4, 4.7 Hz); 133.9 (d, *J* = 2.7 Hz); 130.5 (d, *J* = 3.1 Hz); 129.8 (d, *J* = 8.8 Hz); 128.8 (dt, *J* = 8.2, 1.8 Hz); 128.50 (d, *J* = 14.1 Hz); 126.41 (d, *J* = 12.4 Hz); 126.35 (d, *J* = 119.8 Hz); 122.14 (dp, *J* = 133.6, 4.1 Hz); 122.04 (tdt, *J* = 281.4, 11.1, 3.9 Hz).

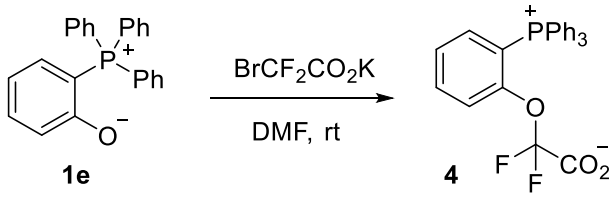
^{19}F NMR ($CDCl_3$, 282.4 MHz): -89.07 (d, *J* = 24.4 Hz, 2F); -120.57 (dd, *J* = 49.6, 31.7 Hz, 2F).

^{31}P{^{1}H} NMR (CDCl3, 121.5 MHz): -82.49 (tt, *J* = 31.7, 24.5 Hz)

Elemental analysis:

Calcd. for $C_{20}H_{15}F_4PS$, %:	C, 60.91;	H, 3.83.
Found, %:	C, 60.92;	H, 3.85.

2,2-Difluoro-2-(2-(triphenylphosphonio)phenoxy)acetate (4).



1e **4**

Compound **1e** (213 mg, 0.60 mmol) and $BrCF_2CO_2K$ (263 mg, 1.23 mmol, 2.0 equiv) were stirred in dry DMF (1.2 mL) at room temperature for 18 hours. Then, volatiles were removed from the reaction vessel under vacuum (ca. 0.4 Torr) with stirring. The residue was taken up in CH_2Cl_2 (5 mL) and precipitate was allowed to settle. The solution over the precipitate was collected and the precipitate was washed with CH_2Cl_2 (2×4 mL). The combined organic washings were evaporated, the residue was dissolved in CH_2Cl_2 (1.5 mL), ethyl acetate was added (7.5 mL) and the product was allowed to crystallize in a fridge (ca 0 °C). Mother liquor was discarded, and the residue was dried under vacuum to give white crystals, which consist of compound **4** and 0.5 equiv of ethyl acetate (this content was found to be constant during two further cycles of re-dissolving in CH_2Cl_2 and precipitation with EtOAc).

Yield 233 mg, 0.47 mmol, 79 %.

Mp 155-158 °C.

To obtain spectra without ethyl acetate, a solution of **4** in $CDCl_3$ was evaporated and the residue was re-dissolved in $CDCl_3$.

^{1}H NMR ($CDCl_3$, 300.13 MHz): 7.87 – 7.61 (m, 17H); 7.24 – 7.14 (m, 1H); 7.03 (dd, *J* = 15.1, 7.5 Hz, 1H).

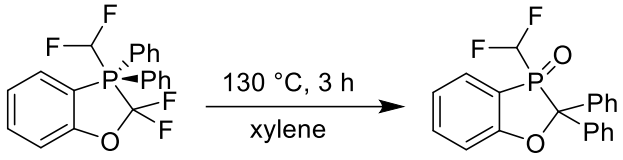
^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): 160.4 (t, *J* = 30.2 Hz), 156.4 (t, *J* = 4.2 Hz), 138.3 (d, *J* = 2.2 Hz), 135.3 (d, *J* = 8.9 Hz), 135.1 (d, *J* = 3.1 Hz), 134.5 (d, *J* = 10.7 Hz), 130.4 (d, *J* = 13.3 Hz), 123.8 (d, *J* = 12.8 Hz), 118. 9 (d, *J* = 6.2 Hz), 118.4 (d, *J* = 91.5 Hz), 117.0 (t, *J* = 286.5 Hz), 106.1 (d, *J* = 92.9 Hz).

^{19}F NMR ($CDCl_3$, 282.4 MHz): -77.72 (s)

^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): 23.50

HRMS: calcd. for $C_{26}H_{20}F_2O_3P$ [M+H]: 449.1113; found: 449.1108.

3-(Difluoromethyl)-2,2-diphenyl-2,3-dihydro-1,3-benzoxaphosphole 3-oxide (5).



2a **5**, 40%

Compound **2a** (227 mg, 0.60 mmol) was heated in a mixture of *p*-xylene (0.6 mL) at 130 °C for 3 hours. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (6 mL) and the resulting solution was subjected to column chromatography (silica gel, CH_2Cl_2). After evaporation of the solvent (*caution*: prone to frothing at the end of evaporation on a rotary evaporator), compound **5** was obtained as a slightly yellow oil which crystallizes on standing (85 mg, 0.24 mmol, 40% yield).

If 1,1-diphenylethylene (312 mg, 1.73 mmol, 2.9 equiv, ca 0.30 mL) was used with a half of xylene (0.3 mL) under otherwise identical conditions, 1,1-difluoro-2,2-diphenylcyclopropane (30%) was additionally observed by ^{19}F NMR (δ: -130.1 ppm, t, *J* = 7.9 Hz).[8]

R_f = 0.15 (CH_2Cl_2).

Mp 102-104 °C.

^{1}H NMR ($CDCl_3$, 300.13 MHz): 7.85-7.67 (m, 5H); 7.63 (t, *J* = 7.9 Hz, 1H); 7.44 (t, *J* = 7.5 Hz, 2H); 7.40 – 7.28 (m, 4H); 7.23 (dd, *J* = 8.4, 4.6 Hz, 1H); 7.16 (td, *J* = 7.4, 3.1 Hz, 1H); 5.80 (td, *J* = 49.1, 26.8 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): 163.4 (d, *J* = 20.4 Hz); 137.4 (d, *J* = 42.0 Hz); 136.9 (d, *J* = 34.6 Hz); 131.0 (d, *J* = 5.7 Hz); 129.1 (d, *J* = 1.7 Hz); 128.8; 128.7 (d, *J* = 2.0 Hz); 128.6; 127.4 (d, *J* = 4.2 Hz); 125.4 (d, *J* = 4.0 Hz); 123.5 (d, *J* = 10.0 Hz); 114.5 (d, *J* = 6.0 Hz); 113.3 (ddd, *J* = 268.3, 264.9, 107.9 Hz); 109.7 (d, *J* = 99.8 Hz); 86.9 (d, *J* = 68.5 Hz).

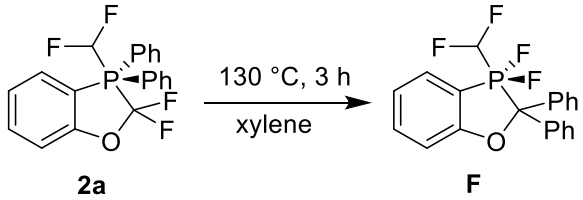
^{19}F NMR ($CDCl_3$, 282.4 MHz): -130.59 (ddd, *J* = 345.3, 72.8, 49.4 Hz); -137.40 (ddd, *J* = 345.4, 75.2, 48.7 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): 46.49 (t, *J* = 74.2 Hz)

HRMS: clacd. for $C_{20}H_{16}F_2O_2P$ [M+H]: 357.0850; found: 357.0848.

[8] L. Li, F. Wang, C. Ni and J. Hu, *Angew. Chem. Int. Ed.* **2013**, *52*, 12390–12394

Experiment in PTFE vessel



2a **F**

A magnetic stirring bar and compound **2a** (114 mg, 0.30 mmol) were placed into a PTFE thin-walled small beaker (ID 8 mm, OD 10 mm, 32 mm length). The beaker was placed into a standard 10-mL Schlenk tube. The tube was evacuated and filled with argon. Then, *p*-xylene (0.30 mL) (distilled from CaH_2 and stored over MS 3A) was added inside the beaker; additional xylene was added into the Schlenk tube *outside* the beaker to the solvent level in the beaker (*ca.* 2 mL) to serve as a heat carrier. The Schlenk tube was placed in a preheated (130 °C) bath and kept at this temperature with stirring for 3 hours.

After cooling to room temperature, 3-bromobenzotrifluoride (31.2 mg) was added to the beaker as an internal standard followed by CH_2Cl_2 (0.25 mL). The mixture was transferred to an NMR tube, and the beaker was rinsed with CH_2Cl_2 (2×0.25 mL), and the combined solution was analyzed. Complex mixture was observed, but in ^{19}F and ^{31}P NMR spectra, signals with large coupling constant were identified [^{19}F NMR (282 MHz): δ -36.29 (d, J = 659.9 Hz); $^{31}P\{^1H\}$ NMR (122 MHz): δ -51.90 (t, J = 661.2 Hz)]. These signals could be attributed to the PF_2-fragment of compound **F**.[9] However, the yield of **F** did not exceed 10%.

[9] For comparison, reported signals of Ph_3PF_2 (^{19}F NMR: -39.3 ppm, d, J = 660 Hz; ^{31}P NMR: -57.5 ppm, t, J = 660 Hz). See: S. B. Munoz, H. Dang, X. Ispizua-Rodriguez, T. Mathew and G. K. S. Prakash, *Org. Lett.*, 2019, **21**, 1659–1663.

Table S1. Crystallographic data for compounds **2a**, **2b**, **5**.

datablock	**2a**	**2b**	**5**
Brutto formula	$C_{20}H_{15}F_4OP$	$C_{20}H_{15}F_4PS$	$C_{20}H_{15}F_2O_2P$
Formula weight	378.29	394.35	356.29
Scan mode	ω scans	ω and ϕ scans	ω and ϕ scans
Anode [Wavelength, Å]	MoKα [0.71073] sealed X-ray tube	MoKα [0.71073] sealed tube	MoKα [0.71073] sealed tube
Crystal Dimensions, mm	0.23 × 0.31 × 0.36	0.11 × 0.15 × 0.16	0.32 × 0.37 × 0.46
Crystal system	monoclinic	monoclinic	triclinic
a, Å	15.0201(6)	9.0837(10)	10.1354(6)
b, Å	9.3245(4)	22.765(2)	12.5827(8)
c, Å	25.3352(11)	9.4866(11)	14.7085(9)
α, °	90	90	89.257(2)
β, °	104.9180(10)	117.427(3)	74.417(2)
γ, °	90	90	75.991(2)
Volume, Å³	3428.7(3)	1741.2(3)	1750.37(19)
Density, gcm⁻³	1.466	1.504	1.352
Temperature, K	120	120	296.15
T_{min}/T_{max}	0.7001/0.7461	0.6460/0.7461	0.6357/0.7461
μ, mm⁻¹	0.207	0.319	0.187
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Z	8	4	4
F(000)	1552	808	736
Reflections collected	74625	16693	28652
Independent reflections	10542	5301	10683
Reflections (I>2σ(I))	7197	3822	7989
Parameters	556	235	451
R_{int}	0.0741	0.0549	0.0466
$2\theta_{min}$- $2\theta_{max}$, °	3.328 - 61.160	3.578 - 61.176	4.288 - 61.214
wR_2 (all reflections)	0.1216	0.1154	0.1483
R_1(I>σ(I))	0.0552	0.0491	0.0511
GOF	1.100	1.033	1.013
ρ_{min}/ρ_{max}, eÅ⁻³	-0.399/0.396	-0.391/0.562	-0.272/0.643

Single crystal X-ray studies of **2a**, **2b** and **5** were carried out in Center for molecule composition studies of INEOS RAS. The structures were solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methyl, methylene and aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C-H bond lengths and equivalent displacement parameters (U_{eq}(H) = 1.2U_{eq}(C), C - central atom of CH_2 group; U_{eq}(H) = 1.5U_{eq}(C), C - central atom of CH_3 group. All structures were solved with the ShelXT[10] program and refined with the ShelXL[11] program. Molecular graphics was drawn using OLEX2[12] program.

CCDC-2061883 (for **2a**), CCDC-2061884 (for **2b**), CCDC-2061885 (for **5**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

[10] G. M. Sheldrick, *Acta Cryst* **2015**, *A71*, 3–8.
[11] G. M. Sheldrick, *Acta Cryst* **2015**, *C71*, 3–8.
[12] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

Calculations

Calculations were performed using ORCA program[13] version 4.2. ChemCraft graphical software[14] was used for visualization of quantum chemistry computation results, including preparation of pictures.

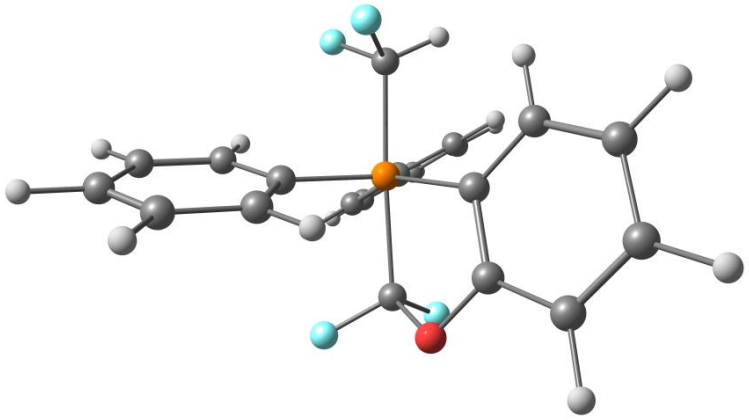
Dispersion correction D3[15] with BJ-damping[16] and gCP[17] correction were applied in all calculations.Def2-TZVP[18] basis was used throughout this work.

The nature of stationary points obtained with hybrid PBE0[19] functional (minimum or saddle point) was confirmed by Hessian calculation. IRC method[20] was used to check connectivity of saddle points and minima for gas phase.

Default parameters and presets of ORCA 4.2.0 were used, except the following: for DFT calculation, integration grid was tightened to "Grid5 NoFinalGrid" and RIJCOSX approximation was applied using GridX7.

Gas phase structures and energies were obtained using PBE0-gCP-D3(BJ)/def2-TZVP

2a



Summary of contributions to the inner energy U:
Electronic energy ... -1586.08119620 Eh
Zero point energy ... 0.30381474 Eh 190.65 kcal/mol
Thermal vibrational correction ... 0.01922850 Eh 12.07 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
---
Total thermal energy -1585.75532041 Eh

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[13] An ab *initio*, DFT and semiempirical SCF-MO package ORCA. a) Neese, F. "Software update: the ORCA program system, version 4.0" *Wiley Interdisciplinary Reviews:Computational Molecular Science*, **2017**, Vol. 8, Issue 1, p. e1327. DOI: 10.1002/wcms.1327 b) Neese, F. "The ORCA program system" *Wiley Interdisciplinary Reviews: Computational Molecular Science*, **2012**, Vol. 2, Issue 1, Pages 73-78 DOI: 10.1002/wcms.81.

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[17] H. Kruse and S. Grimme, *J. Chem. Phys.*, 2012, **136**, 154101.

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[20] I. Kazuhiro, M. Keiji and K. Andrew, *J. Chem. Phys.*, 1977, **66**, 2153–2156.

The Gibbs free energy is G = H - T*S

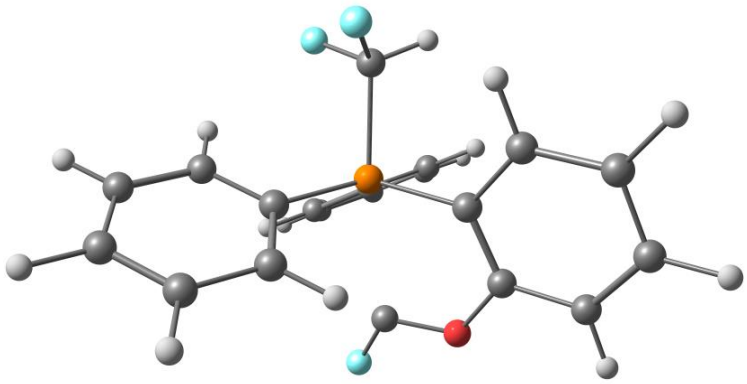
Total enthalpy ... -1585.75437620 Eh
Total entropy correction ... -0.07089063 Eh -44.48 kcal/mol

Final Gibbs free energy ... -1585.82526683 Eh

Coordinates

P	5.59430737569348	2.93806370281139	9.22828771488413
F	7.77360083351553	2.03720997035467	7.64060596467281
F	4.54366006436041	5.17268787760618	10.42958198580370
F	3.67154709049017	3.31398538562554	11.18542497313601
F	5.96390805928933	2.14441628646660	6.47204010698530
O	6.19657343363940	0.52745277059070	7.93463395544189
C	4.03370464179879	3.12182315229509	8.30046286414013
C	7.03553165221325	4.93826187150488	7.89575244970763
H	6.38478567020030	4.74519119805699	7.05041616383552
C	4.84061367522406	3.88524208468336	10.77252775282144
H	5.50116338031944	3.94571841908376	11.64666751851990
C	5.81446285799222	1.36717350201252	10.11785854866617
C	3.21480861992723	2.00610599043742	8.14595793759057
H	3.50310138194292	1.05128579443772	8.57122953524097
C	6.07399935441074	0.29313172984161	9.26420540947453
C	6.42224114661655	1.88268223936100	7.70855167659781
C	6.89859288093358	4.20282547069221	9.06959417580111
C	7.78256864840514	4.42040058602712	10.12209340195947
H	7.71151328263204	3.83171804512696	11.03040618413219
C	8.02348945937824	5.90378267139581	7.79239431046408
H	8.11690097491266	6.47961899348989	6.87830560899977
C	3.63971483088727	4.34185587677292	7.75787594954690
H	4.24947159618017	5.22623070069698	7.89130947409886
C	5.68197851361932	1.10840709053185	11.48211447542690
H	5.45930622472358	1.90623215534102	12.17669787086144
C	2.01964958631122	2.10916490973237	7.45301066875324
H	1.38684647507549	1.23541589910889	7.34369257886525
C	2.44757420410051	4.43624980112353	7.05609516136720
H	2.15060453883783	5.38988272316576	6.63368562611589
C	6.18632943894925	-1.00570050694770	9.73423764496595
H	6.38074035164333	-1.80861552074474	9.03328875484112
C	8.89978701683522	6.12187142257856	8.84605943054550
H	9.67829849450732	6.87165010993292	8.75887173641503
C	8.78613646902221	5.37008858353201	10.00552187097520
H	9.48017505713103	5.52237572511740	10.82461597982293
C	1.63623476535572	3.32260454730430	6.90142793755855
H	0.70304874289910	3.40099671417237	6.35457913517775
C	5.81665538019007	-0.17945129186542	11.96972348964611
H	5.72307664858904	-0.36610160706964	13.03286512875894
C	6.05832191019272	-1.23185521223494	11.09275651362850
H	6.15213527105389	-2.24241586215000	11.47513233375317
C	-2.30472250254596	-3.52031950135062	-1.76125369517971
F	-3.36954886415667	-4.09242993038481	-2.22859727347914
F	-2.25891457529738	-2.37191722626457	-2.36012305834115

Structure **A**



Summary of contributions to the inner energy U:
Electronic energy ... -1486.02996818 Eh
Zero point energy ... 0.30061923 Eh 188.64 kcal/mol
Thermal vibrational correction ... 0.01886713 Eh 11.84 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
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Total thermal energy -1485.70764927 Eh

The Gibbs free energy is G = H - T*S

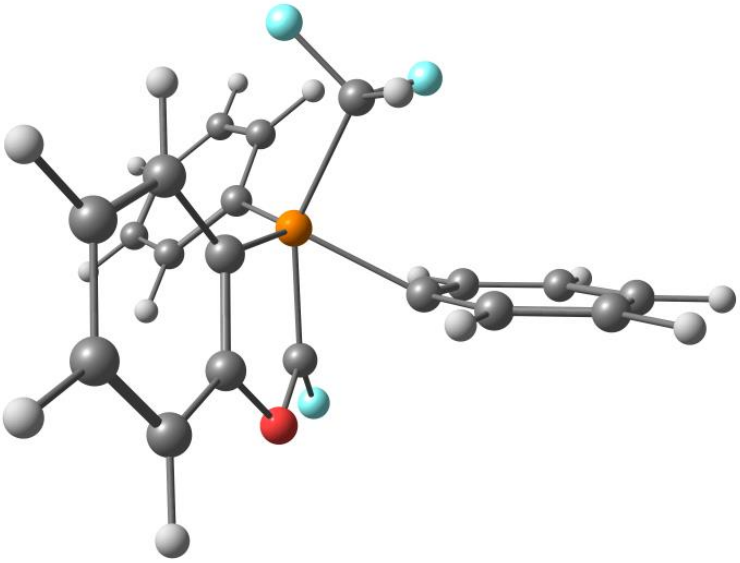
Total enthalpy ... -1485.70670507 Eh
Total entropy correction ... -0.07069123 Eh -44.36 kcal/mol

Final Gibbs free energy ... -1485.77739629 Eh

P	5.28380599786542	3.11521791764749	9.44463434897796
F	4.65368456353388	5.37100755020184	10.69190395523614
F	3.49500146933876	3.65736107607866	11.38429195541541
F	6.95304017420013	2.03788351756900	6.45406850702635
O	7.00711160053843	0.88146725777113	8.19076878750591
C	3.84581177963773	3.24112169897604	8.39394139838231
C	6.78375635686093	4.89907520191787	7.92608989201989
H	5.94930974100045	4.92410568620414	7.23438191257432
C	4.72281241322725	4.05846371938310	10.99302548288628
H	5.42457262275342	3.93025657130352	11.82585291145742
C	5.66073248121882	1.48847963472181	10.12242988786320
C	3.22055862233108	2.07459968398624	7.95761235099026
H	3.62912399535947	1.10333247293487	8.21572579687921
C	6.49944410539104	0.59138262672315	9.45598516731763
C	6.39681140756026	1.85475895279533	7.60337557819741
C	6.74388317667510	4.07933202990602	9.05306319834033
C	7.82609414522420	4.02615753382660	9.93238121064234
H	7.80288689906342	3.38188201420787	10.80573955858384
C	7.90945831066994	5.66665061259631	7.68516021011587
H	7.94513659219265	6.30614557747194	6.81103061581734
C	3.31660731702064	4.49109171200908	8.07376060411053
H	3.78143580825632	5.40325119523770	8.42652565552723
C	5.15603561893586	1.08234772980143	11.36188334681223
H	4.47255219739124	1.71674787242643	11.90960673599135
C	2.06946321341210	2.15930280364302	7.19581138873640
H	1.57811881473152	1.25342835208525	6.86078317696098
C	2.17119954110449	4.56256840150276	7.29608148952730
H	1.76188580790280	5.53199733460452	7.03731010359200
C	6.86594804151600	-0.62478844226473	9.98443073925000
H	7.52546923089536	-1.27176606312992	9.41860549845775

C	8.99128244658553	5.61217933285007	8.55491513503439
H	9.87260308982245	6.21139739967479	8.35729987502623
C	8.95153881008619	4.79104988979696	9.67329481447443
H	9.79837638968201	4.74657590331803	10.34796027667411
C	1.54864068125279	3.40261884383249	6.86013460061518
H	0.64983862884608	3.46613883996583	6.25753936650341
C	5.50144633993630	-0.14536524145764	11.90336948279721
H	5.09452338035794	-0.43627697910918	12.86417777468736
C	6.36325261532992	-0.99211865986269	11.22388471487174
H	6.64030473829172	-1.94860753114738	11.65111653212008

TS-1



Summary of contributions to the inner energy U:
Electronic energy ... -1485.99948576 Eh
Zero point energy ... 0.30040970 Eh 188.51 kcal/mol
Thermal vibrational correction ... 0.01771327 Eh 11.12 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
---
Total thermal energy -1485.67853025 Eh

The Gibbs free energy is G = H - T*S

Total enthalpy ... -1485.67758604 Eh
Total entropy correction ... -0.06799620 Eh -42.67 kcal/mol

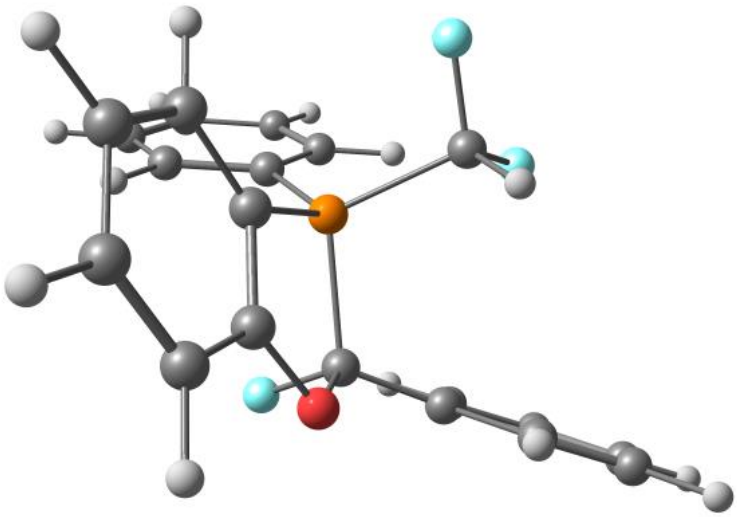
Final Gibbs free energy ... -1485.74558224 Eh

Coordinates

P	-0.25407660848286	0.03270884938321	0.07138895418516
F	-0.35789154171868	2.59023369927156	1.08665956711413
F	-1.65356002837164	1.14758662056179	2.10270799037584
F	0.92247037717981	-0.62574339759828	-2.46311446099073
O	1.47938877594413	-1.85567710198158	-0.74238286393842
C	-1.76796169688166	0.28285439929324	-0.85655554758973
C	1.41979737912777	1.87706150732948	-1.28976901180524
H	0.60915594740381	1.94588377467583	-2.00791691632206

C	-0.45038669693031	1.30931049647273	1.50489176416953
H	0.34039700430223	1.12806926839682	2.24496559618587
C	0.05577540941648	-1.41476131071624	1.08835941164804
C	-2.19883891034844	-0.78521992223472	-1.64932920149556
H	-1.62116034602781	-1.70307039245492	-1.69518345882102
C	0.99349069937780	-2.25247588483534	0.49074638845342
C	0.78291879269499	-0.80821507806347	-1.17819364307357
C	1.49186863647442	0.78995949735903	-0.40276545750508
C	2.56379031793659	0.68036319338774	0.49875889217873
H	2.63967243970936	-0.17610027029294	1.16081307179297
C	2.39115516924304	2.85694588595752	-1.24791009239874
H	2.33938375335291	3.70084969871575	-1.92541093494145
C	-2.51584941806519	1.46114903140341	-0.80561841017240
H	-2.19999678418693	2.30058615422446	-0.20198420233694
C	-0.47143400072045	-1.76764088052915	2.32954762863826
H	-1.21301845719886	-1.14278178784859	2.81211532902247
C	-3.37457929860256	-0.68313780900074	-2.36837760243177
H	-3.71465513293601	-1.51817992876511	-2.96938997331731
C	-3.67969037107256	1.56222188065100	-1.54980709204274
H	-4.25482015940368	2.48018341257038	-1.51996788639946
C	1.45210454363404	-3.40790701241401	1.08493293323407
H	2.19289376595799	-4.02490041008064	0.59107322527421
C	3.43961926525047	2.74990639651090	-0.34161481622951
H	4.20549592712958	3.51720619468864	-0.31679544056271
C	3.53062834953515	1.66238011530662	0.52560160849239
H	4.36481225622238	1.58425315569670	1.21292661402740
C	-4.11135154673273	0.49406329823037	-2.32314510586033
H	-5.02756998111914	0.57865093113473	-2.89660149610099
C	-0.04394436974173	-2.93873004503312	2.93177291387266
H	-0.45517963911456	-3.22859428376545	3.89112045356406
C	0.91189983984658	-3.74445844729533	2.31738993035871
H	1.23924633791624	-4.65483349831230	2.80606134174787

Structure **B**



Summary of contributions to the inner energy U:
Electronic energy ... -1486.09685279 Eh
Zero point energy ... 0.30230478 Eh 189.70 kcal/mol
Thermal vibrational correction ... 0.01815509 Eh 11.39 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
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Total thermal energy -1485.77356038 Eh

The Gibbs free energy is G = H - T*S

Total enthalpy ... -1485.77261617 Eh
Total entropy correction ... -0.06936678 Eh -43.53 kcal/mol

Final Gibbs free energy ... -1485.84198295 Eh

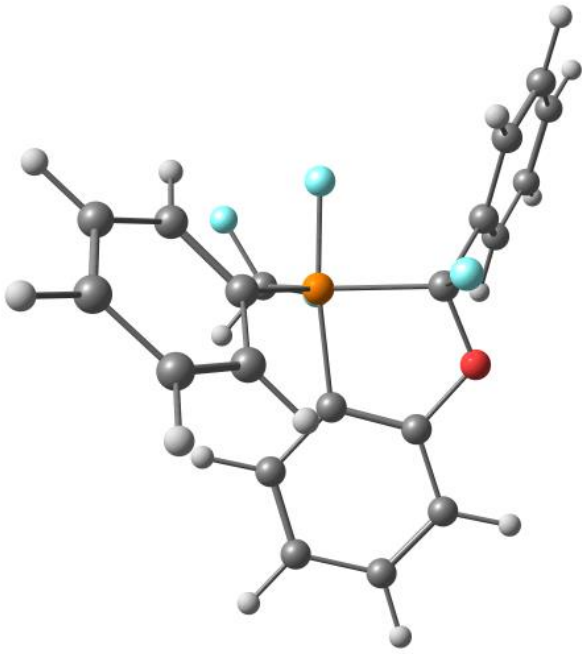
For completeness - the Gibbs free energy minus the electronic energy
G-E(el) ... 0.25486984 Eh 159.93 kcal/mol

Coordinates

P	5.36905382475724	2.49031366397199	8.90605610106383
F	6.33817847994936	4.99049152668995	8.92550934782401
F	5.47722654604453	4.27978267887404	10.80392234580761
F	5.72161641525791	1.13297787312680	6.71845250199233
O	7.14821321929323	0.65059851927741	8.37656803878870
C	3.77880044720693	2.93436626315294	8.27939114069609
C	7.16042395269037	3.39163378785614	5.96712879728466
H	6.17743011694544	3.26880352881916	5.52657067048853
C	6.22861413645531	3.93546991556091	9.74438136971505
H	7.22520221689669	3.62545825801186	10.08010855046928
C	5.44963705077897	1.09790408369822	9.96970500134672
C	2.78082588297675	1.95482035533756	8.27658719219259
H	2.97466282084721	0.96888990491551	8.68339954990083
C	6.45459923249203	0.25509462563054	9.48688633963753
C	6.55119117016981	1.67745179248271	7.65737835782315
C	7.54572360076784	2.60517459332412	7.04956308514683
C	8.81352540471814	2.74248231752420	7.60520887414417
H	9.11756573512940	2.11076065008259	8.43169489405906
C	8.05027135087654	4.31310243815033	5.44106154666000
H	7.75787071256335	4.91811094888170	4.59081768088569
C	3.54011874511636	4.20592419517361	7.74798002718417
H	4.31176361563181	4.96490605637644	7.74398224665066
C	4.73797760500622	0.76901185156473	11.12329532762182
H	3.96313044469825	1.42768577628650	11.49824115321218
C	1.53962220158538	2.25740128341247	7.74693516039022
H	0.75950996684333	1.50547146678131	7.74354482851649
C	2.29163062157106	4.48973755007065	7.22404322026898
H	2.09435043994803	5.47372270293589	6.81551920201898
C	6.76595011821221	-0.92398714261317	10.13458236977814
H	7.54263290177377	-1.57130978325657	9.74645339539076
C	9.31517777523329	4.45571966004190	5.99563767256585
H	10.00922415026873	5.17750187957056	5.58063987176657
C	9.69679297001547	3.66894405204193	7.07282626853735
H	10.69004436943770	3.76843503913459	7.49479960126573
C	1.29637913029600	3.52082935465821	7.22383256328137
H	0.32056337087470	3.75328331736838	6.81264986391150
C	5.04437269135623	-0.41004679454337	11.77339894547758
H	4.50446573602781	-0.68950284828806	12.66955840004064
C	6.04901589818728	-1.24203146107030	11.27808862526389
H	6.27657614409907	-2.16594256901447	11.79773309593003

Structure C

Diastereomer I



Summary of contributions to the inner energy U:
Electronic energy ... -1586.12557430 Eh
Zero point energy ... 0.30440216 Eh 191.01 kcal/mol
Thermal vibrational correction ... 0.01909243 Eh 11.98 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
---
Total thermal energy -1585.79924717 Eh

The Gibbs free energy is G = H - T*S

Total enthalpy ... -1585.79830296 Eh
Total entropy correction ... -0.07098628 Eh -44.54 kcal/mol

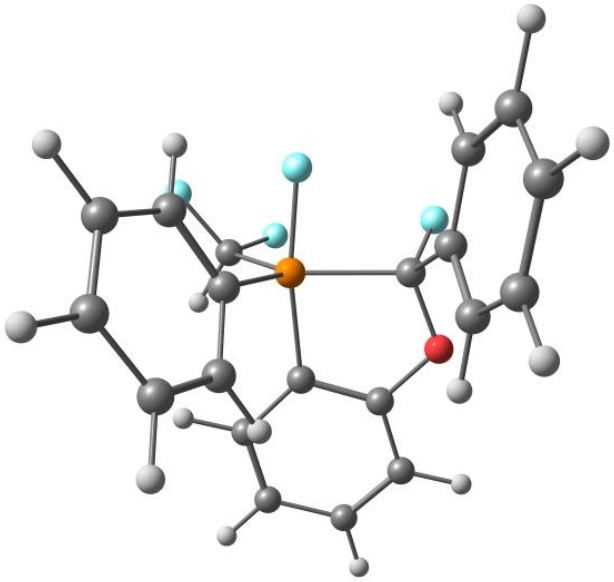
Final Gibbs free energy ... -1585.86928923 Eh

Coordinates

P	6.03249766510129	2.31828780444628	8.83814850206775
F	7.77502031880732	1.31362991610981	7.17778467273850
F	3.82929285353714	3.88771029482711	9.18072984867911
F	3.44176264838502	1.75001260449999	8.97014141596399
F	5.79742312789330	3.45670145535166	7.64301283846255
O	6.35979799700944	-0.24330651047255	7.93499123428253
C	5.63867619474780	1.14039724322711	6.17823840588367
C	7.19578908786109	4.72457961933158	9.61898307117026
H	6.33781633693244	5.18968327850953	9.15094888654198
C	4.29653499307638	2.66721142761891	9.49385733601021
H	4.28840333504880	2.56121779439639	10.58386338575713
C	6.18670920352504	0.86173044875157	9.99756562147727
C	4.43413393170448	0.45493010398815	6.07605515829852
H	4.08891900132616	-0.15387129973396	6.90272911808995

C	6.34212246936339	-0.31918454674362	9.30186448095860
C	6.43965333583320	1.04302279554524	7.43989960534706
C	7.32643303172041	3.33512780136534	9.60459757838837
C	8.45333196213212	2.74858970282234	10.17662597771013
H	8.56807236274457	1.67177513974050	10.16783822296091
C	8.16407647337267	5.50745806552057	10.22720603407379
H	8.04455229674049	6.58485900103698	10.25166325720438
C	6.08386147122378	1.91761740891870	5.11626128773514
H	7.01790170692600	2.45763252700344	5.20279675098520
C	6.14373020372216	0.80383431204175	11.38798836804777
H	6.05402871214349	1.71778506338449	11.96885318481955
C	3.68005247815018	0.54607532053966	4.91680150734026
H	2.74132743634338	0.00841969614406	4.84324592150551
C	5.33189415641374	1.99906313949676	3.95603310418484
H	5.68717528799216	2.60223703953747	3.12793412413139
C	6.45271818650979	-1.55226803908929	9.92283894623005
H	6.57678770001592	-2.45158388484605	9.33113529306278
C	9.28869122456091	4.91739858763168	10.78582728059105
H	10.05280695922357	5.53351476386156	11.24725363471888
C	9.43777113799501	3.53866040683449	10.74789963197808
H	10.32126964403921	3.07314337558847	11.17011440219889
C	4.12808227838510	1.31606819865710	3.85383567541588
H	3.53958889670479	1.38402044819521	2.94542558293519
C	6.24925716423959	-0.41322079310554	12.04275351436912
H	6.22028979921951	-0.45306013103847	13.12557535401174
C	6.40114479696539	-1.58542857846926	11.30675273232398
H	6.48665139636312	-2.53695797842538	11.81989712934713

Diastereomer II



Summary of contributions to the inner energy U:
Electronic energy ... -1586.12470918 Eh
Zero point energy ... 0.30464595 Eh 191.17 kcal/mol
Thermal vibrational correction ... 0.01905595 Eh 11.96 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
---
Total thermal energy -1585.79817473 Eh

The Gibbs free energy is G = H - T*S

Total enthalpy ... -1585.79723053 Eh

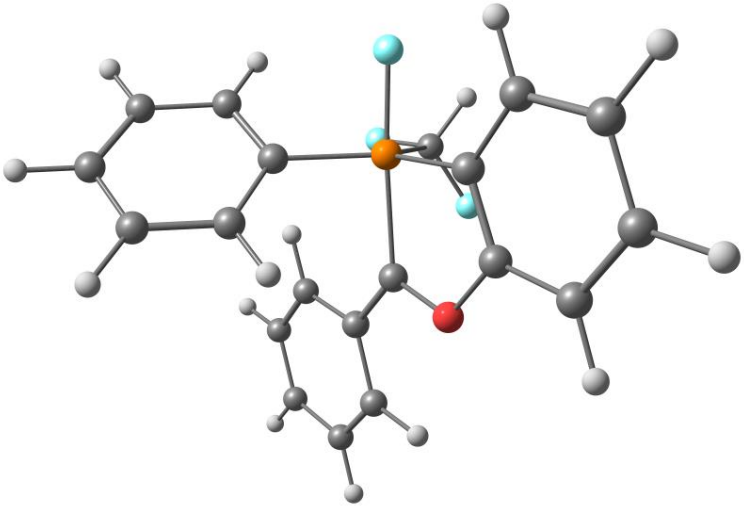
Total entropy correction ... -0.07128667 Eh -44.73 kcal/mol

Final Gibbs free energy ... -1585.86851720 Eh

Coordinates

P	6.05346081827790	2.07520359057451	9.13159692833330
F	5.59252214902996	0.62354114286116	6.91068588569115
F	4.14712150141713	3.98790667028315	9.43778221991533
F	3.40062030467001	1.99882108770239	8.92499888070417
F	5.88084019024081	3.06297799892670	7.79348478104744
O	6.63088493645084	-0.53185613076957	8.49212651866397
C	7.89423168946379	1.03324177817601	7.23280205927419
C	7.52133700782236	4.41770326699348	9.46108506158379
H	6.82900920412649	4.84569431213531	8.74934021926984
C	4.32876203979588	2.66933324252246	9.64812370178871
H	4.15149824351120	2.46521510993676	10.70802728388808
C	6.00434932165301	0.70525535527436	10.38957587119184
C	9.07082339910172	0.59233317297852	7.82808350917288
H	9.02607657863464	-0.03171115117817	8.71268626572905
C	6.28529703894284	-0.51760045059093	9.81012875606993
C	6.57090837837031	0.70504046274399	7.86321770231121
C	7.38518647479654	3.08094651944111	9.84111009279857
C	8.29683044855939	2.53652626898451	10.74473354113223
H	8.20570385828915	1.50204705786906	11.05045279861024
C	8.54068442211220	5.19228476303601	9.99034609200537
H	8.62967074401528	6.23207356945488	9.69605586610256
C	7.95307578048998	1.81939228791086	6.08767787182028
H	7.03472508888095	2.16914953888256	5.63428972711544
C	5.69372279263434	0.72895034445204	11.74889125257610
H	5.50373337952964	1.67433673832352	12.24933179925946
C	10.29800172419110	0.93682731971048	7.28348646980133
H	11.21136379752780	0.58819522690134	7.75260671819493
C	9.18132400215849	2.15354529657063	5.54102493815196
H	9.22101086364599	2.76114626560098	4.64370601513687
C	6.26313622155129	-1.70928290707697	10.51962967597358
H	6.48880587323837	-2.64298812225185	10.01807612595483
C	9.44920168006435	4.63950675608954	10.88113119686210
H	10.25281924286127	5.24596978950455	11.28476074209166
C	9.32902341171754	3.30872834189424	11.25229811574670
H	10.03929729702748	2.86758248525710	11.94262129597160
C	10.35588207285913	1.71810667346233	6.13913702331860
H	11.31586820609248	1.98571791325340	5.71133754179368
C	5.66654444490792	-0.44289879600978	12.48660108577181
H	5.43109924436145	-0.41477342951409	13.54421007115602
C	5.94603580471416	-1.65804957241821	11.86579891957253
H	5.91902352926408	-2.57663340389854	12.44163850544579

Structure **D**



Summary of contributions to the inner energy U:
Electronic energy ... -1486.09159013 Eh
Zero point energy ... 0.30258116 Eh 189.87 kcal/mol
Thermal vibrational correction ... 0.01804354 Eh 11.32 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
---
Total thermal energy -1485.76813289 Eh

The Gibbs free energy is G = H - T*S

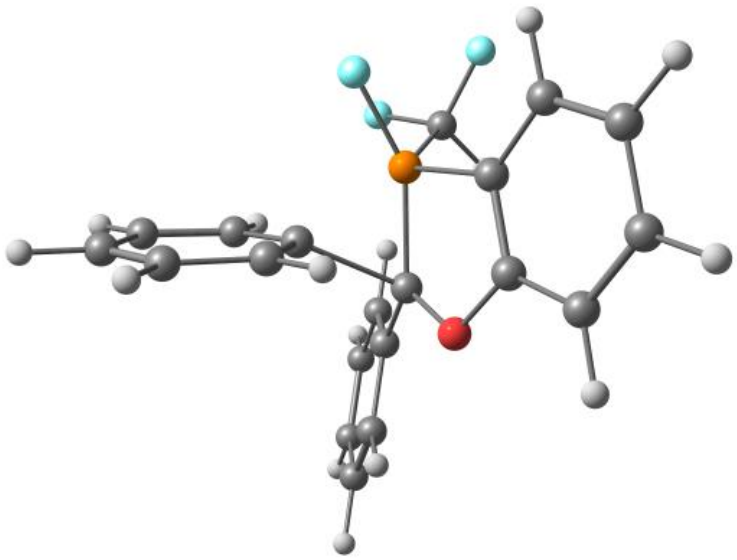
Total enthalpy ... -1485.76718868 Eh
Total entropy correction ... -0.06872219 Eh -43.12 kcal/mol

Final Gibbs free energy ... -1485.83591086 Eh

Coordinates

P	4.96982631673408	2.49343069635096	8.69034951735293
F	6.95475179841053	4.27476823396877	8.27199360057768
F	5.15627222440336	4.61607581232411	7.07720167747061
O	7.37216351549809	1.16364997180177	8.99861966785038
C	4.01399373237358	1.48558794096449	7.54229223790099
C	6.60194935019748	2.15296714459547	5.63005509881034
H	5.61451899618945	2.57818562659085	5.74839582209207
C	5.60716010879677	4.23327106975934	8.28833927684122
H	5.23744469943354	4.92516881233346	9.04962579818838
C	5.51345771974159	1.86139209205602	10.27308874460329
C	2.95623519511387	2.05235764861015	6.83285200769016
H	2.68558549352147	3.08968989842957	6.98583736636411
C	6.74642710863448	1.23671674427313	10.24571254575440
C	6.69632507940296	1.70445292144790	8.03332410193050
C	7.28942675295421	1.63711677979654	6.74468076496864
C	8.56797648836161	1.06590768308564	6.56839231877326
H	9.10310164546018	0.67357963896217	7.42396806987221
C	7.17919278108522	2.10338350235332	4.37985789201301
H	6.65008848961966	2.50054942697191	3.52222226828427
C	4.33327137502695	0.14008289361119	7.36731264014510
H	5.13668448132949	-0.32191062383514	7.93355502137947
C	4.84506079833995	1.95575603547371	11.48897101345176
H	3.87906645826783	2.44185879758791	11.53677907536679
C	2.24938068048328	1.27788103615430	5.92657485113365
H	1.43613680783942	1.72140623342205	5.36389411784330
C	3.59942693485593	-0.63503582066378	6.48571770727173
H	3.83351229617958	-1.68662440816603	6.36870801912083
C	7.35960232214304	0.69998077918377	11.34997371467646
H	8.32944167470776	0.22382700069801	11.27502576201645
C	8.43987517690829	1.53741168664420	4.22245587960003
H	8.89008242267281	1.49751284209007	3.23646179315671
C	9.13340093230350	1.01958999129185	5.31583191635650
H	10.11620093270395	0.58493824147534	5.17826669418933
C	2.56744870572802	-0.06210746110156	5.75462644376690
H	2.00163040942324	-0.66647747820882	5.05481084883544
C	5.43345617090349	1.42052120724264	12.62701342376634
H	4.91861649562836	1.48836198666763	13.57772536447099
C	6.67558913929275	0.80205486273907	12.55769831887797
H	7.12387671247142	0.39190435584965	13.45512413683932
F	3.62473205485860	3.21482701316830	9.29736698339618

TS-2



Summary of contributions to the inner energy U:
Electronic energy ... -1486.04791688 Eh
Zero point energy ... 0.30092411 Eh 188.83 kcal/mol
Thermal vibrational correction ... 0.01764009 Eh 11.07 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
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Total thermal energy -1485.72652014 Eh

The Gibbs free energy is G = H - T*S

Total enthalpy ... -1485.72557593 Eh
Total entropy correction ... -0.06800995 Eh -42.68 kcal/mol

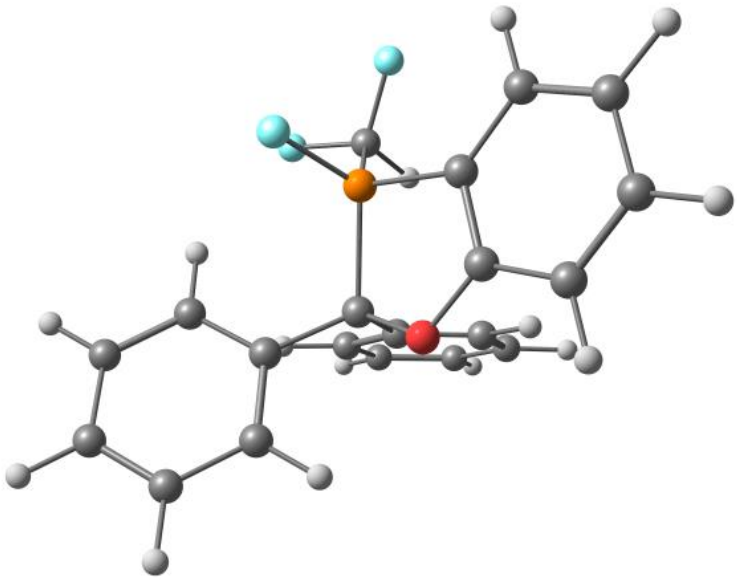
Final Gibbs free energy ... -1485.79358587 Eh

Coordinates

P	-0.75527470854413	1.04739086452398	0.78451683914183
F	-1.09896186641681	3.24860146067639	-0.69203147560082
F	-0.97228880867194	3.57732275207782	1.46113279253571
O	1.19167562769819	-0.69949570439738	0.84562393996078
C	-1.11176854497756	-0.46677325772053	-0.40497756187927
C	1.30284577305587	1.43214451932686	-2.07715130904530
H	0.74063387846920	2.30198889566716	-1.76454815220479
C	-0.46759136926793	2.87629545529452	0.43901142072218
H	0.60588656166714	3.08026402238917	0.35180440876308
C	-0.20889638578648	0.43676268709895	2.33479459730510
C	-1.51991079568398	-1.67621693499233	0.18030393736599
H	-1.10981682871748	-1.99171050638908	1.13294963362690
C	0.81351820893275	-0.48355877123411	2.13948785412348
C	0.59821207958511	0.16405016730408	-0.03295446436699
C	1.32653520023675	0.27015650013880	-1.30836547082770
C	2.06990097219101	-0.82793572312567	-1.74812942114279
H	2.09483392250807	-1.73424420446974	-1.15586288384323
C	2.00796211241596	1.49419321239798	-3.26863795919383
H	1.98781303763697	2.40495866904452	-3.85556372561505

C	-1.63554750315584	-0.06805399185383	-1.64702661347734
H	-1.29133391972907	0.84362783457088	-2.12303404790176
C	-0.69235969135921	0.69326845099163	3.61739623529711
H	-1.50190263797799	1.39711282750187	3.76908742141076
C	-2.44710487165698	-2.46321991471019	-0.46669744105898
H	-2.75998916993187	-3.40302587177901	-0.02731928070516
C	-2.58564617531040	-0.84989825256443	-2.26874659686012
H	-3.00242931557760	-0.54121016690361	-3.21990587114593
C	1.38631473649169	-1.17554220966166	3.18930941016665
H	2.17372334487598	-1.89804698794560	3.01378978798594
C	2.74393879141663	0.40127921680188	-3.69989135686668
H	3.29714970950550	0.45285376032746	-4.63056452092240
C	2.77525390500582	-0.75804740216248	-2.93476837324380
H	3.35192511057791	-1.61338520590312	-3.26710184467756
C	-2.98447668230652	-2.04688281980249	-1.68318250107967
H	-3.71615062613565	-2.67035476752627	-2.18508776523716
C	-0.10952901718535	0.03040926056728	4.67979040241954
H	-0.45410459571259	0.22118952184561	5.68871749418457
C	0.91555033541992	-0.89319657472006	4.46175376169016
H	1.35450665651423	-1.40731051061620	5.30927440807506
F	-2.31309645009927	1.29423969993095	1.06280429212144

Structure **E**



Summary of contributions to the inner energy U:
Electronic energy ... -1486.10937363 Eh
Zero point energy ... 0.30286579 Eh 190.05 kcal/mol
Thermal vibrational correction ... 0.01797023 Eh 11.28 kcal/mol
Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
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Total thermal energy -1485.78570507 Eh

The Gibbs free energy is G = H - T*S

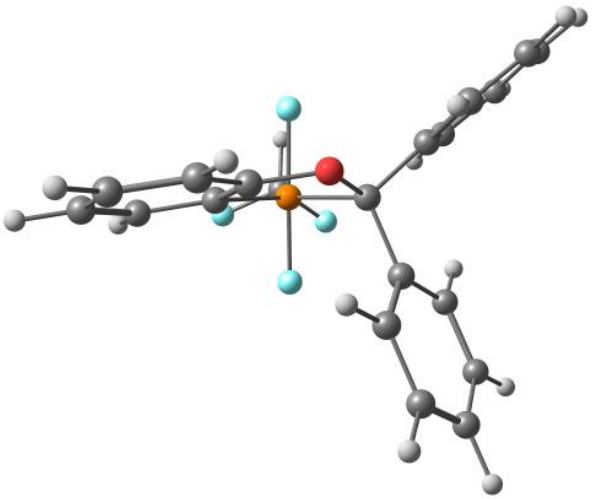
Total enthalpy ... -1485.78476086 Eh
Total entropy correction ... -0.06873557 Eh -43.13 kcal/mol

Final Gibbs free energy ... -1485.85349643 Eh

Coordinates

P	4.93355537311186	2.03286047257327	8.50510509035916
F	3.93719703019909	3.76692282355560	6.79973575561939
F	3.85176170980781	4.35648694674327	8.90344880453132
O	6.98802807123658	0.48978824113462	8.72859984139387
C	5.87198909673766	0.12050517877606	6.63330138286508
C	7.04497932425073	2.70628377990488	5.78680195611672
H	6.34590417614360	2.21068321236958	5.12491340647264
C	4.61662692743032	3.79152545103008	7.95251339586990
H	5.55267686874329	4.34601227684219	7.83604509406865
C	5.59061566372182	1.83465280873934	10.08293938885451
C	6.60775377974689	-1.05138009533316	6.49098580207067
H	7.46118893603521	-1.23863398649369	7.12990432646877
C	6.64951870673816	0.92160791494378	9.95658637774557
C	6.32185068595555	1.14422511568750	7.64397826318098
C	7.20922309187688	2.26303220453029	7.09658417155639
C	8.13875434201033	2.89188144850286	7.92357563890998
H	8.30100651129700	2.55083957108011	8.93834539152107
C	7.79951756292524	3.76867747805190	5.31358332285629
H	7.67411585565208	4.09655665673234	4.28822937628699
C	4.77843534295662	0.35407385398134	5.80494529215406
H	4.18853672111716	1.26203920315144	5.89238287981117
C	5.19456835919839	2.31943691163332	11.33825480904417
H	4.37266398681253	3.02015302936138	11.42308639803897
C	6.24649488629350	-1.97858457816347	5.52682318599263
H	6.82276616844592	-2.89038827137455	5.42143221200192
C	4.42391755938703	-0.57555678699459	4.83966843345288
H	3.56847734749356	-0.38658745689404	4.20190464188266
C	7.32513555201815	0.47492787468744	11.08291643836447
H	8.13930048218058	-0.23221163199160	10.98386300898041
C	8.71921209419277	4.39806898035863	6.14026274620191
H	9.30946716594406	5.22652246659713	5.76621283558503
C	8.89196844430208	3.95231337667861	7.44242726739666
H	9.62157724494566	4.42609718166559	8.08885055653127
C	5.15704925058020	-1.74402756498026	4.70054330661909
H	4.87686431067357	-2.47378445867104	3.94986353147086
C	5.87384740429823	1.88018507119893	12.44873950209806
H	5.59577188448800	2.23815916035255	13.43201042639628
C	6.92518837144105	0.96332670314054	12.31226247045080
H	7.44574168169989	0.62497751950431	13.20135326596544
F	3.52810341791047	1.40052460738745	8.37064860581267

Structure **F**



Summary of contributions to the inner energy U:
Electronic energy ... -1586.15122499 Eh
Zero point energy ... 0.30463047 Eh 191.16 kcal/mol
Thermal vibrational correction ... 0.01900458 Eh 11.93 kcal/mol

Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol
---
Total thermal energy -1585.82475740 Eh

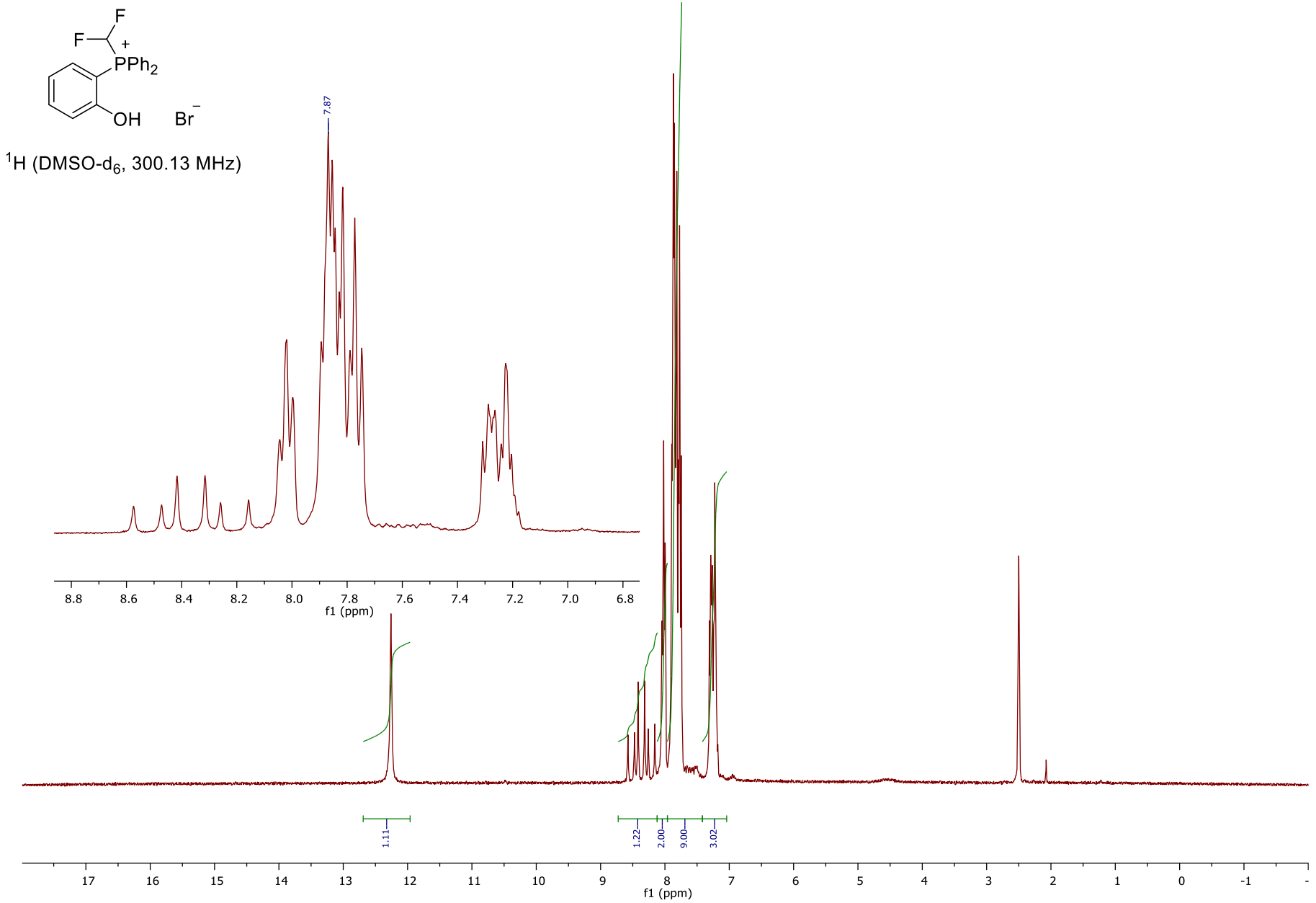
The Gibbs free energy is G = H - T*S

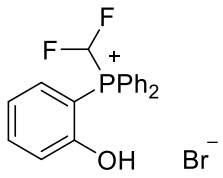
Total enthalpy ... -1585.82381319 Eh
Total entropy correction ... -0.07086736 Eh -44.47 kcal/mol

Final Gibbs free energy ... -1585.89468055 Eh

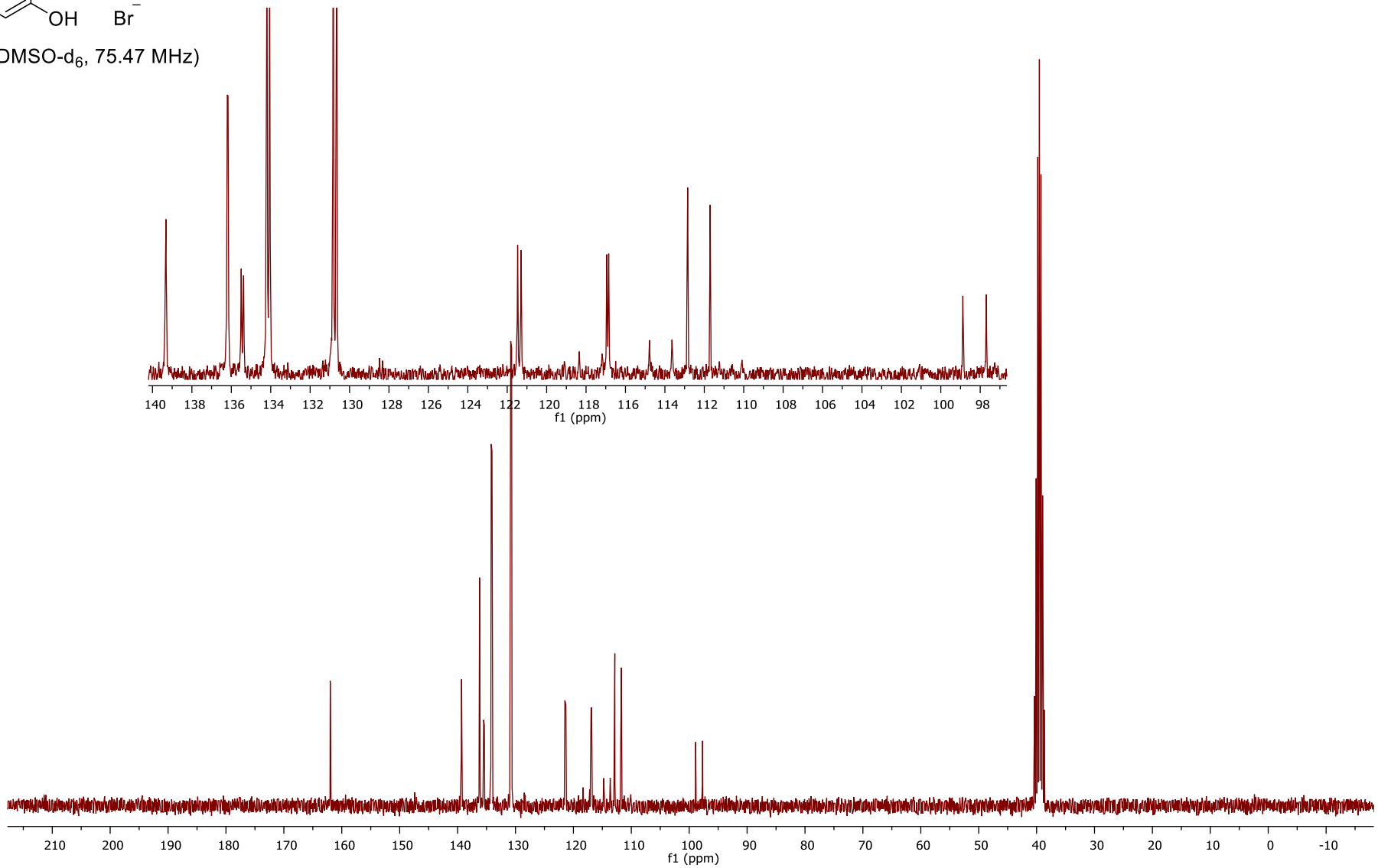
Coordinates

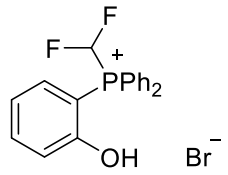
P	5.76835585194871	2.98564084463043	8.60615747989125
F	7.27719064932382	3.18698457651517	9.29980720997005
F	5.01481665502478	5.53217022318120	8.18945400275406
F	4.40936794858275	4.68820671108720	10.11153249444430
F	4.26224602393359	3.02394913184660	7.95468653689931
O	6.98350834088234	0.89301777972018	7.69599185969915
C	5.61830669947069	1.87834811148554	5.96781148315682
C	8.89102636287807	2.07395822291559	6.13195242335032
H	8.83571797874250	0.99404651681249	6.18572937447155
C	5.41541890509315	4.74657020949448	9.21031963015578
H	6.29394777868255	5.18996297273010	9.68202437812302
C	5.52969114354400	1.45321721850341	9.47933638955757
C	5.09248013315514	0.60991695707277	5.75919955342039
H	5.37186491884550	-0.20696115632041	6.41109143057722
C	6.29213120704591	0.50766256906330	8.79992200317653
C	6.58642053343784	2.14429125063036	7.10819145793615
C	7.83117368508218	2.83855073929396	6.60607162942399
C	7.91398059972790	4.22350987188891	6.53322747447706
H	7.10295300590961	4.84410474248834	6.90219829871288
C	10.01229491699827	2.68739320101288	5.59563874843570
H	10.83269717196285	2.07819458523450	5.23226812505662
C	5.24873728983441	2.90967238680902	5.10896511803525
H	5.65153004515702	3.90559909059028	5.24907931600807
C	4.80472263547986	1.10220133141905	10.60400154533563
H	4.20584365187099	1.84266074470249	11.12149665663311
C	4.21221598525358	0.37725033601827	4.71132361913930
H	3.81289796604848	-0.61991230024758	4.56166594665988
C	4.36760510873753	2.67828763959161	4.06795839994453
H	4.08968902363392	3.49488560262300	3.41082486363413
C	6.35757405875565	-0.80122965037751	9.24895295903984
H	6.95746469804854	-1.52766866661352	8.71348395425648
C	10.08680981642289	4.07035224533112	5.52042799957503
H	10.96496854385344	4.54855718679760	5.10104177003486
C	9.03243969413903	4.83774894487343	5.99146285892486
H	9.08161662797997	5.92003952783600	5.94692985172134
C	3.84475369080144	1.40856464883461	3.86346021278916
H	3.15639369328524	1.22635335748492	3.04567508208753
C	4.86287355894687	-0.20703665506419	11.05904816065824
H	4.30330287478800	-0.49895408764566	11.93960847338105
C	5.63907942469258	-1.14336286022074	10.38481782412840
H	5.68062317899764	-2.16492738602947	10.74633038932284


F
F
+
PPh2
OH
Br−
1H (DMSO-d6, 300.13 MHz)
7.87
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
1.11
1.22
2.00
9.00
3.02
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

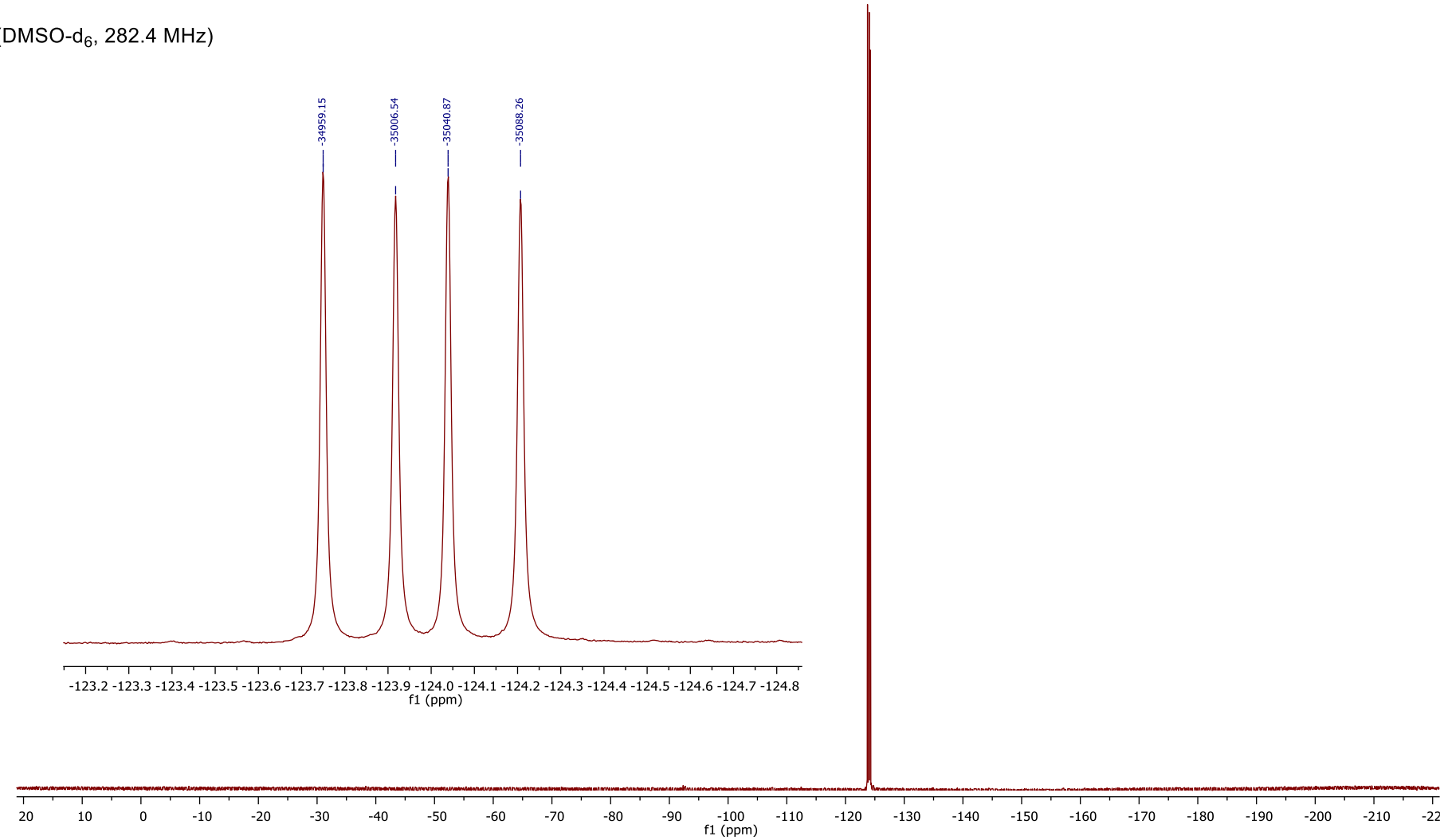


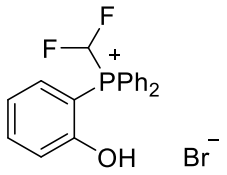
$^{13}C\{^{1}H\}$ (DMSO-d_6, 75.47 MHz)



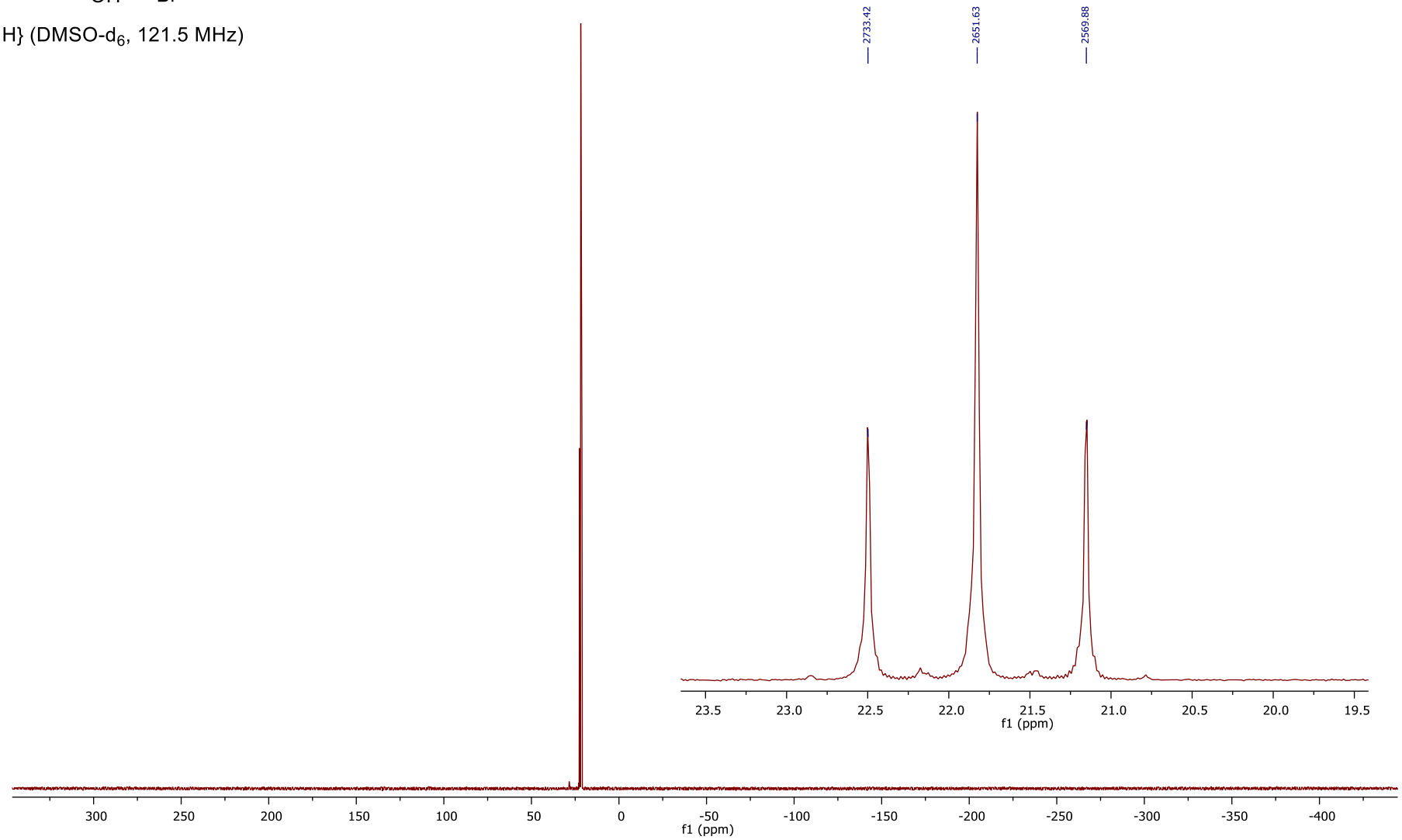


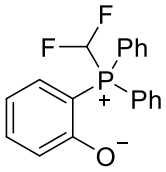
^{19}F (DMSO-d_6, 282.4 MHz)





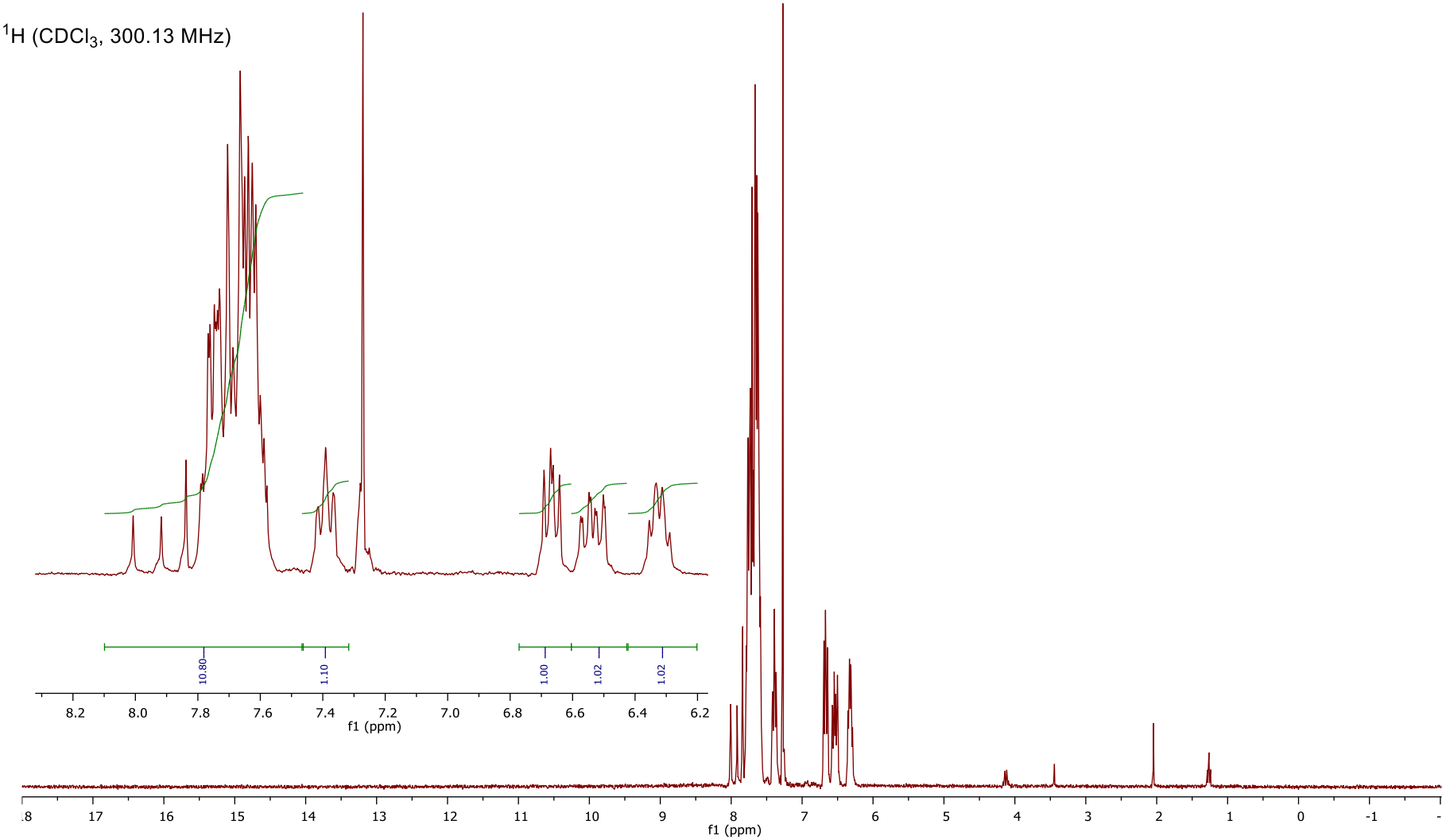
$^{31}P\{^{1}H\}$ (DMSO-d_6, 121.5 MHz)

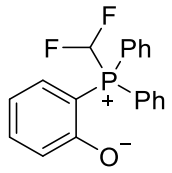




1a

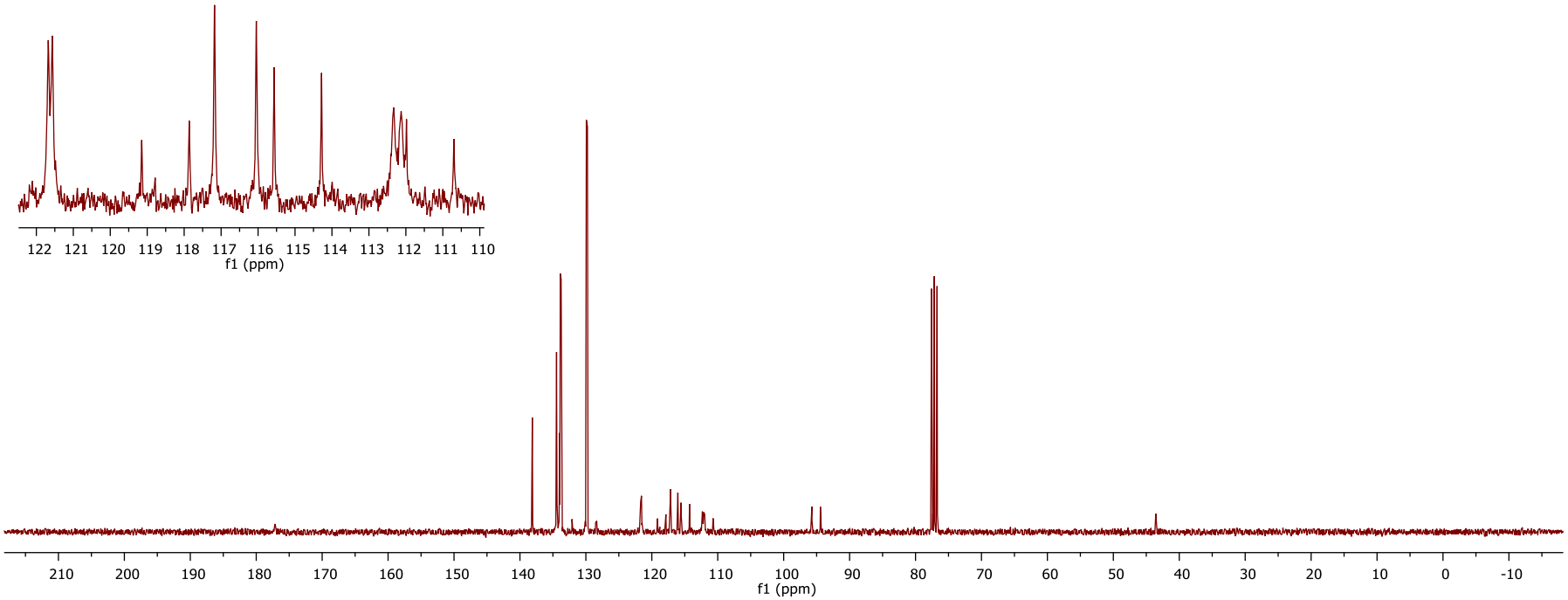
^{1}H ($CDCl_3$, 300.13 MHz)

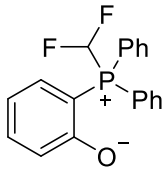




1a

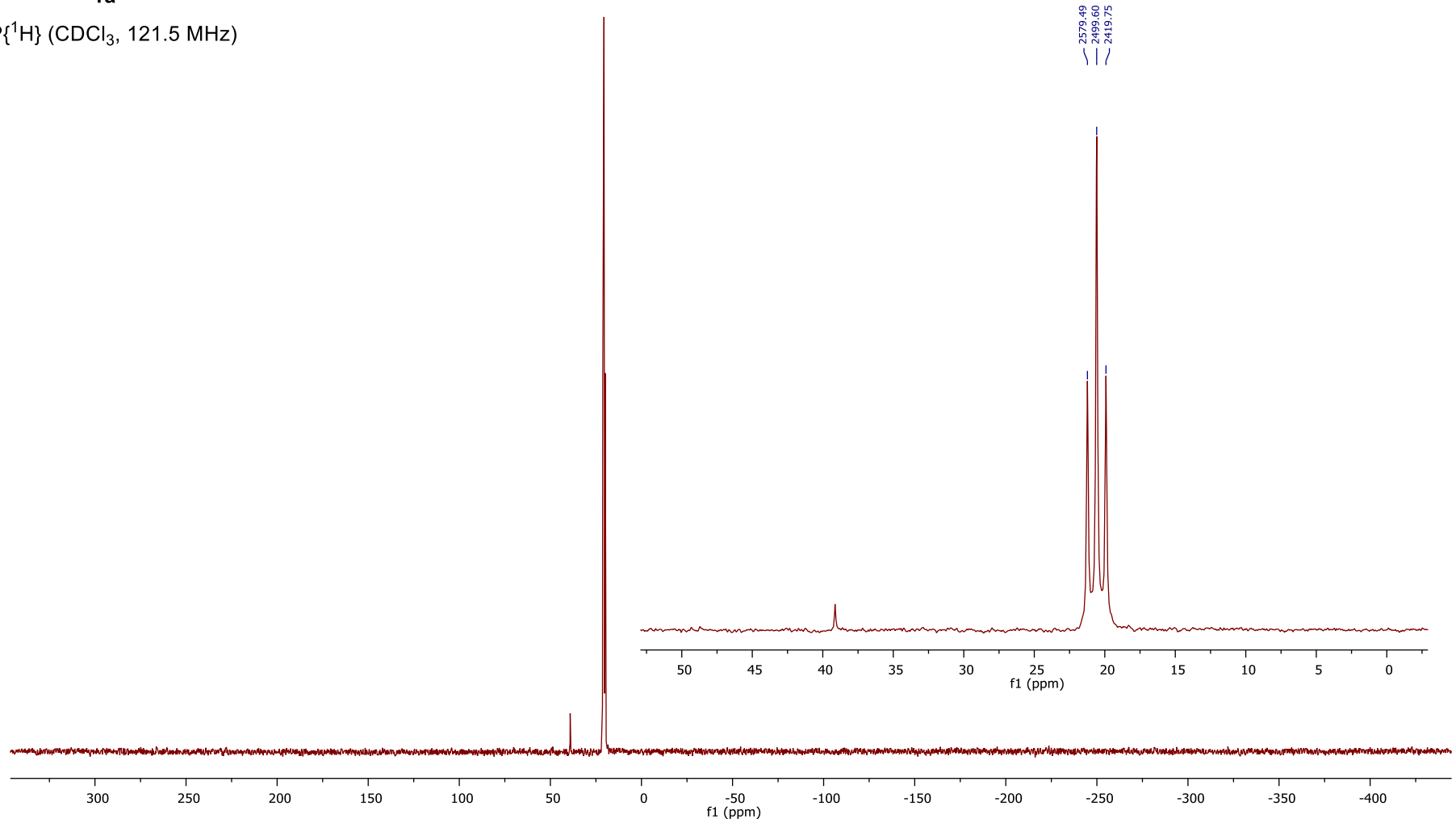
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75.47 MHz)

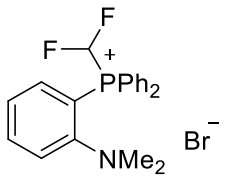




1a

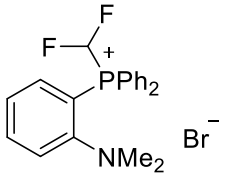
$^{31}P\{^{1}H\}$ ($CDCl_3$, 121.5 MHz)





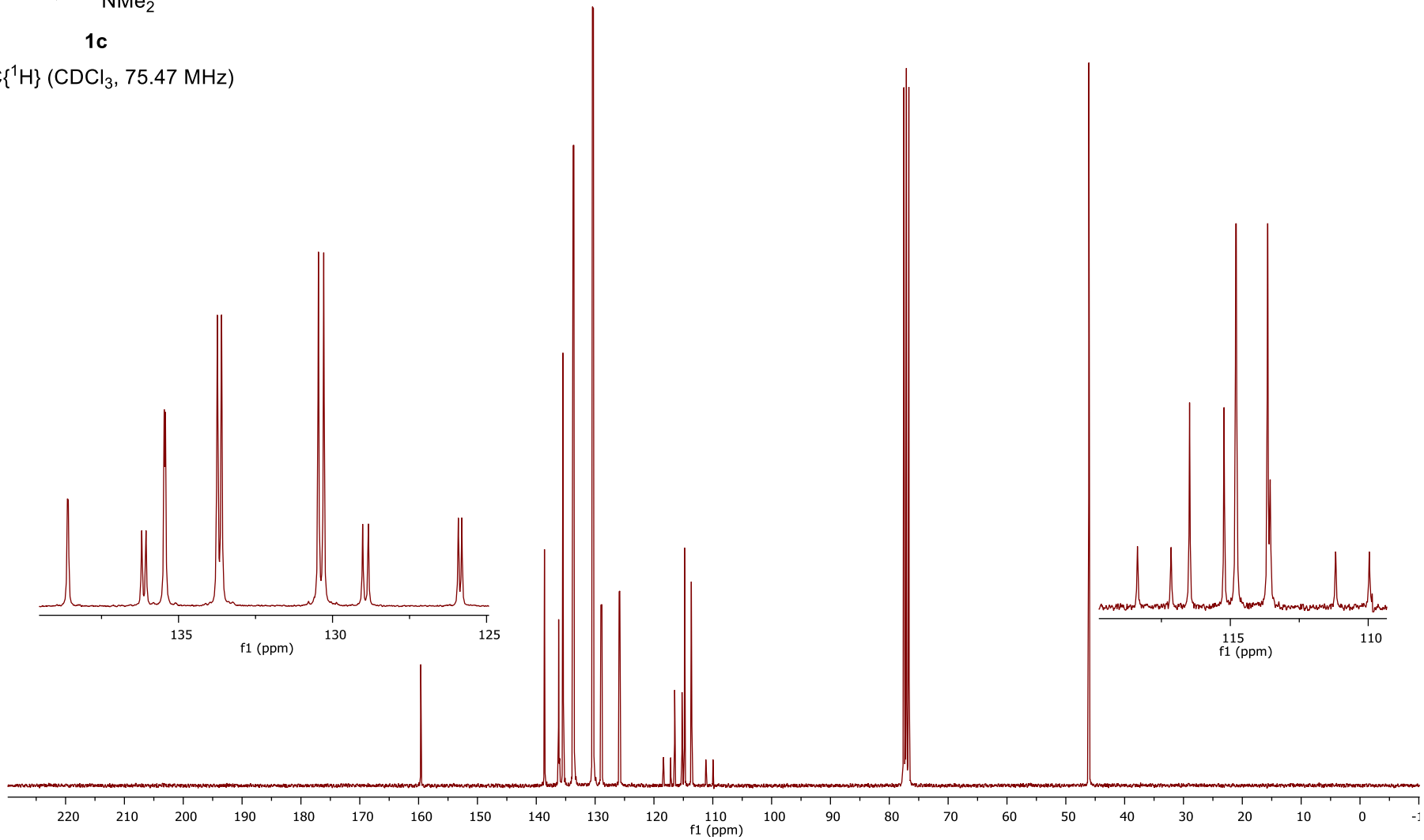
1c

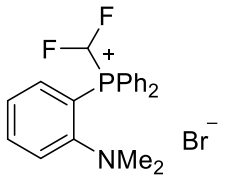
^{1}H ($CDCl_3$, 300.13 MHz)



1c

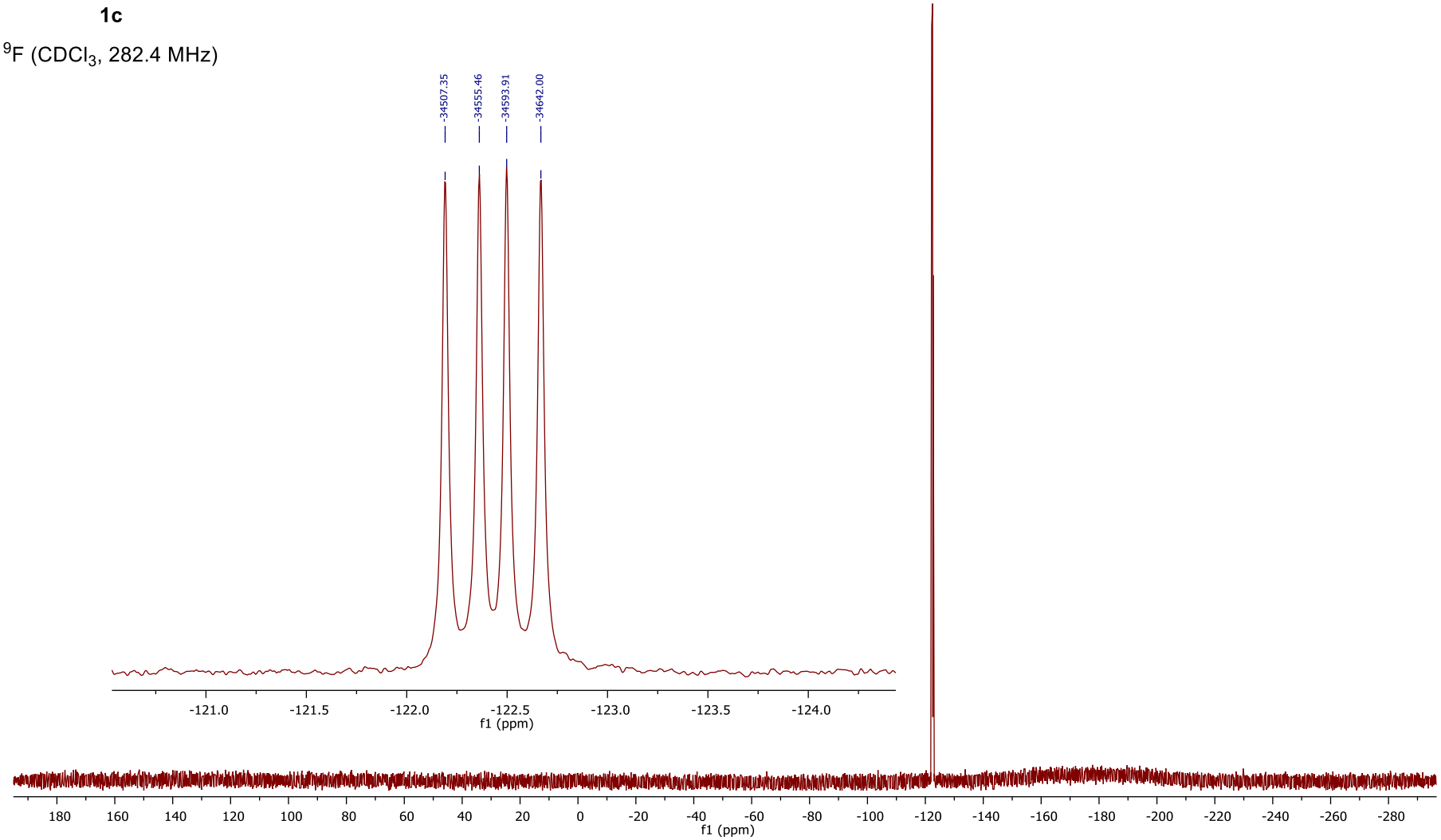
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75.47 MHz)

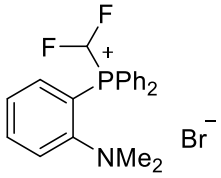




1c

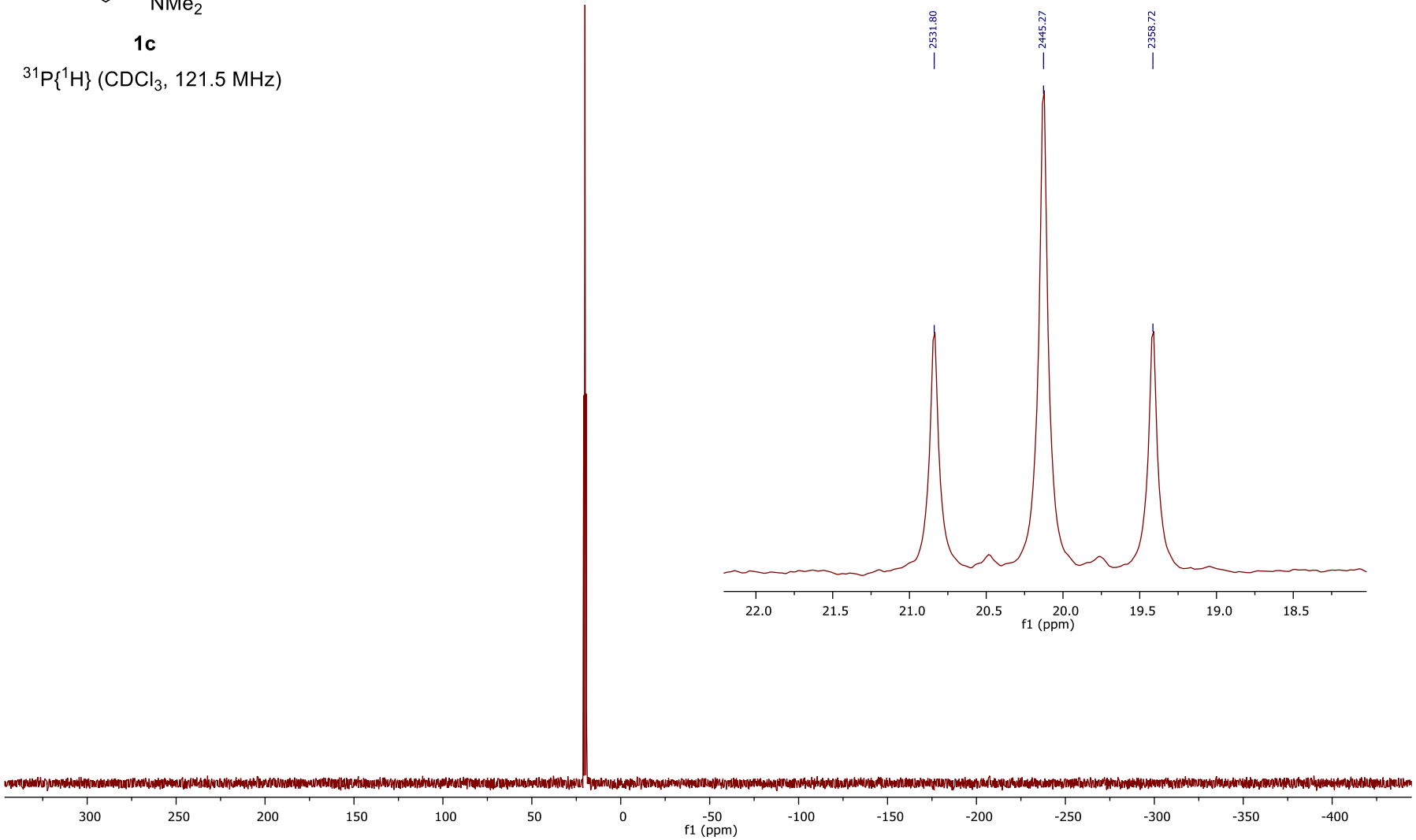
^{19}F ($CDCl_3$, 282.4 MHz)

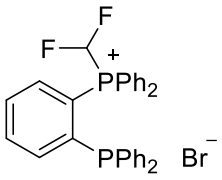




1c

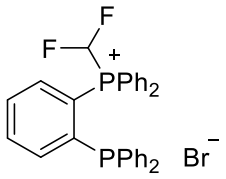
$^{31}P\{^{1}H\}$ ($CDCl_3$, 121.5 MHz)





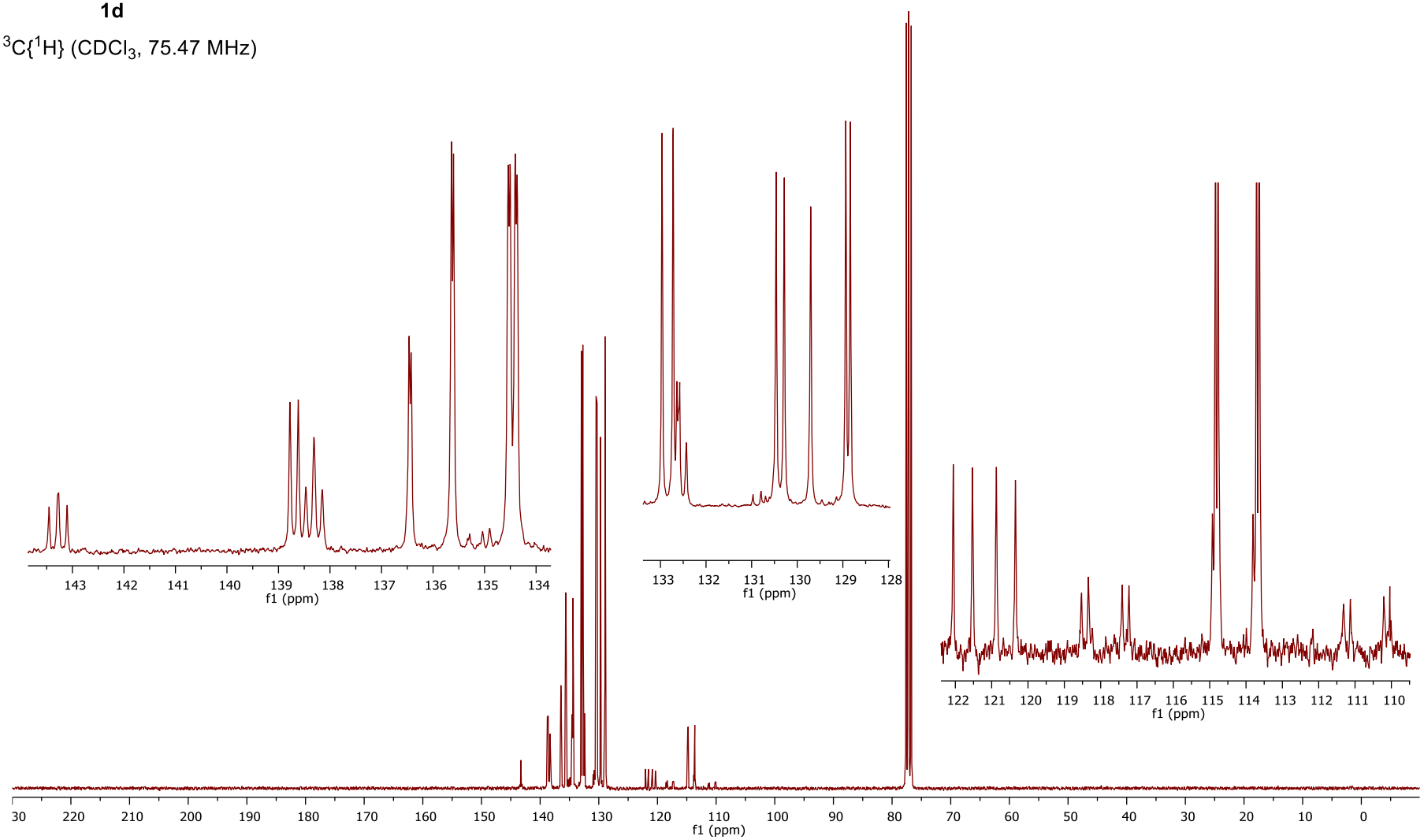
1d

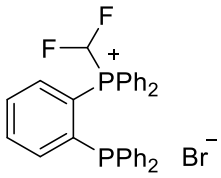
^{1}H ($CDCl_3$, 300.13 MHz)



1d

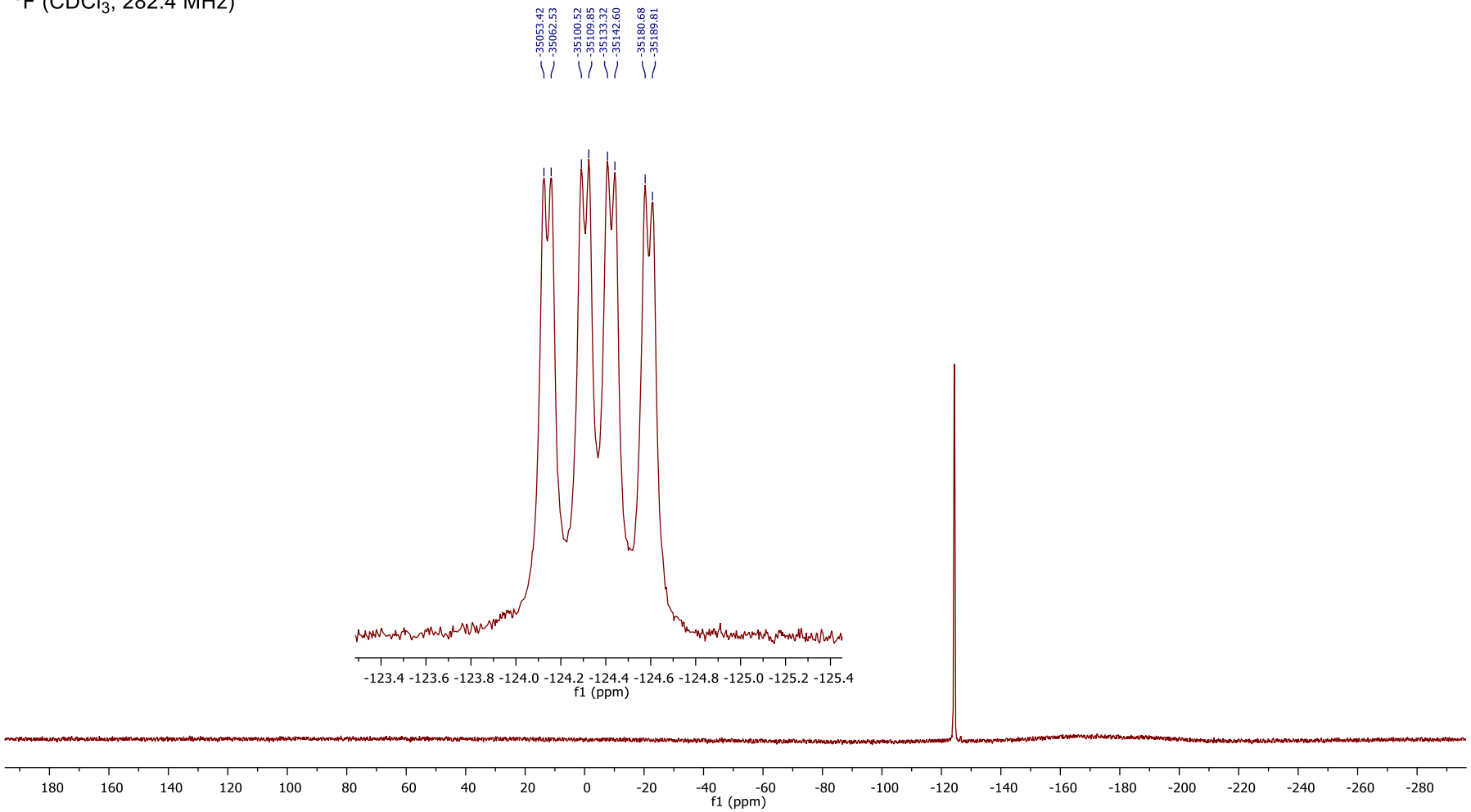
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75.47 MHz)

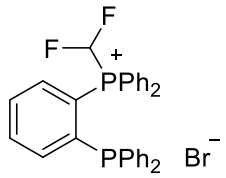




1d

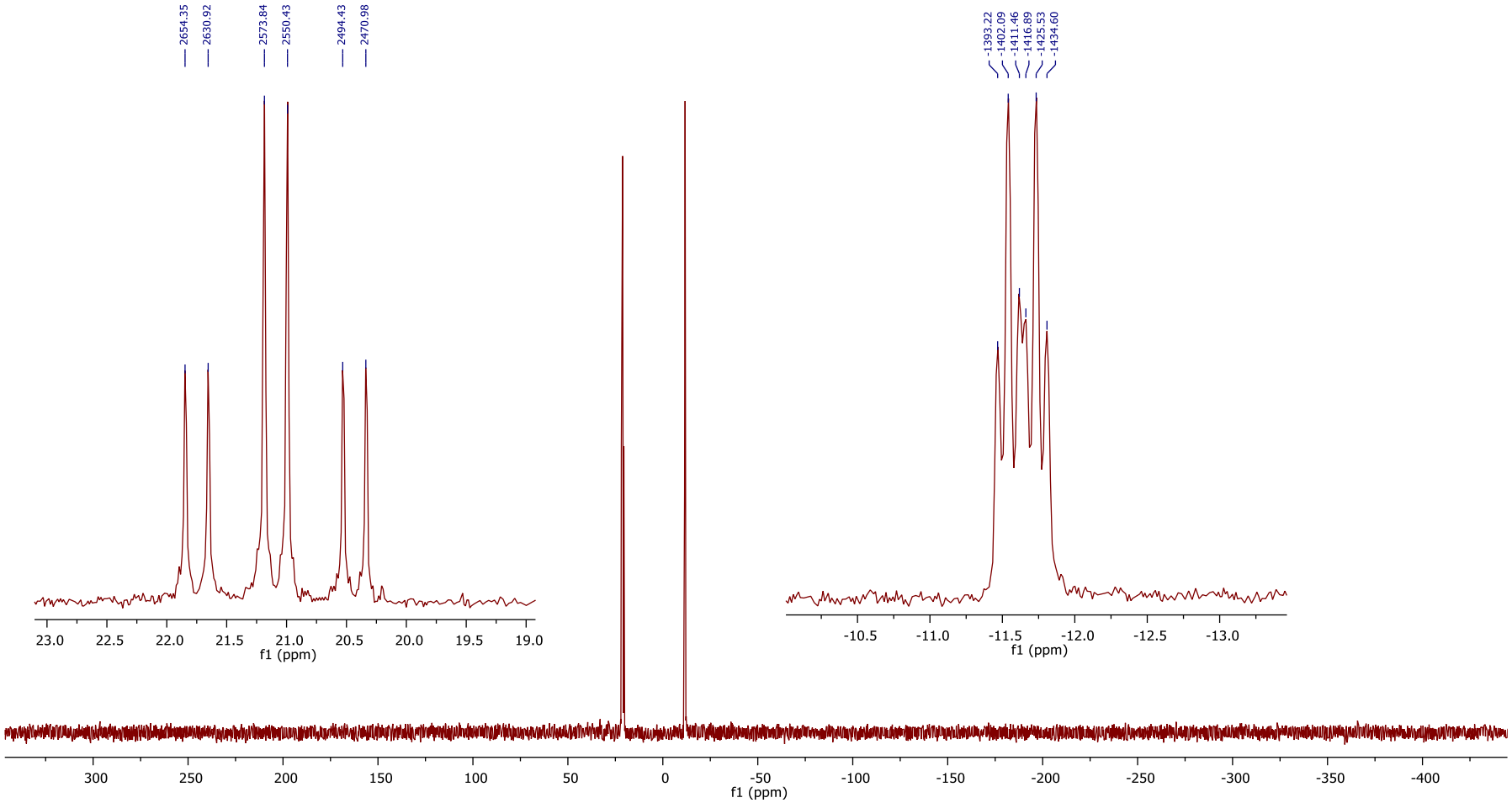
^{19}F ($CDCl_3$, 282.4 MHz)

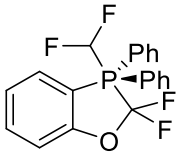




1d

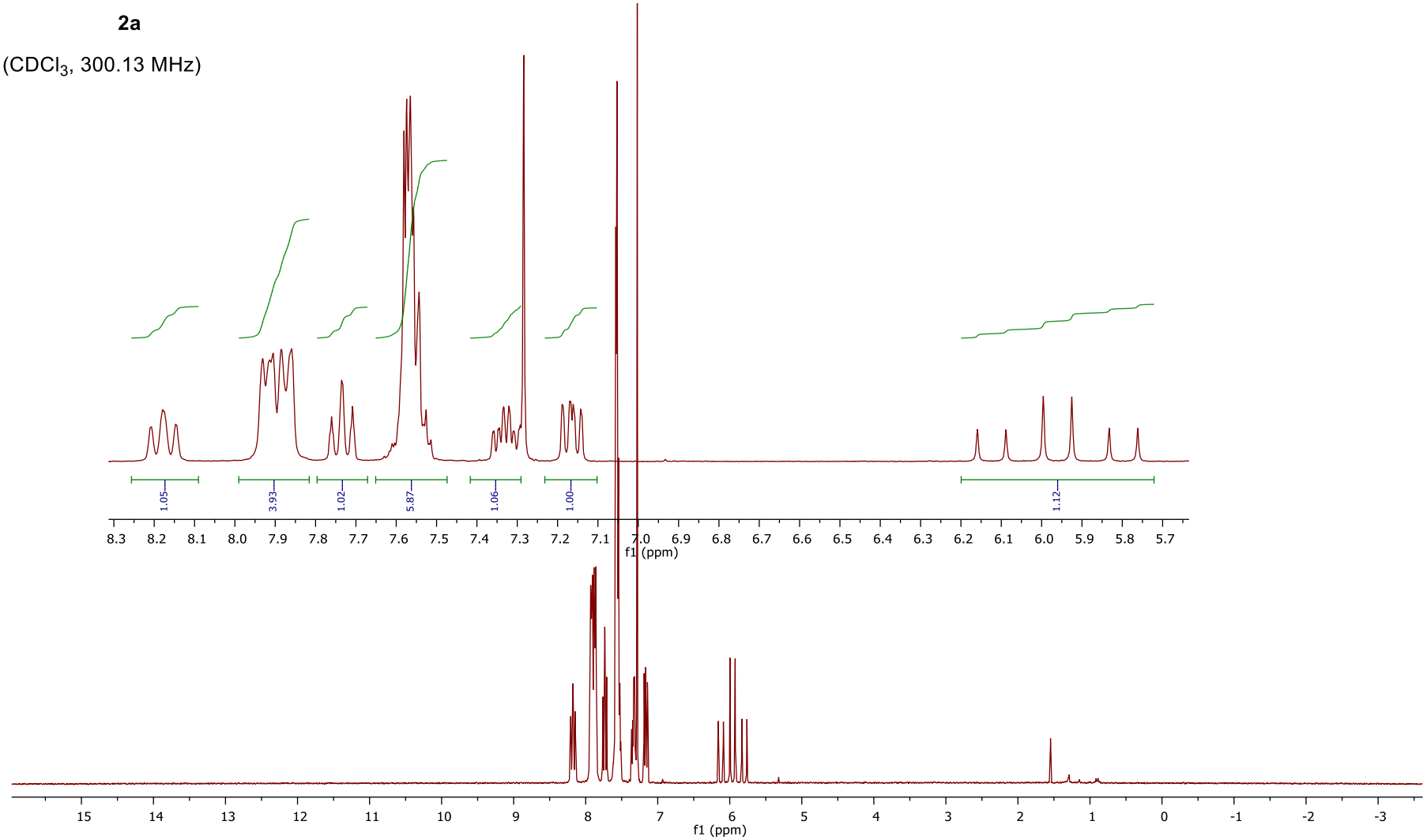
$^{31}P\{^{1}H\}$ ($CDCl_3$, 121.5 MHz)

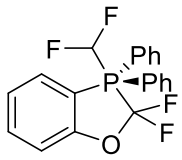




2a

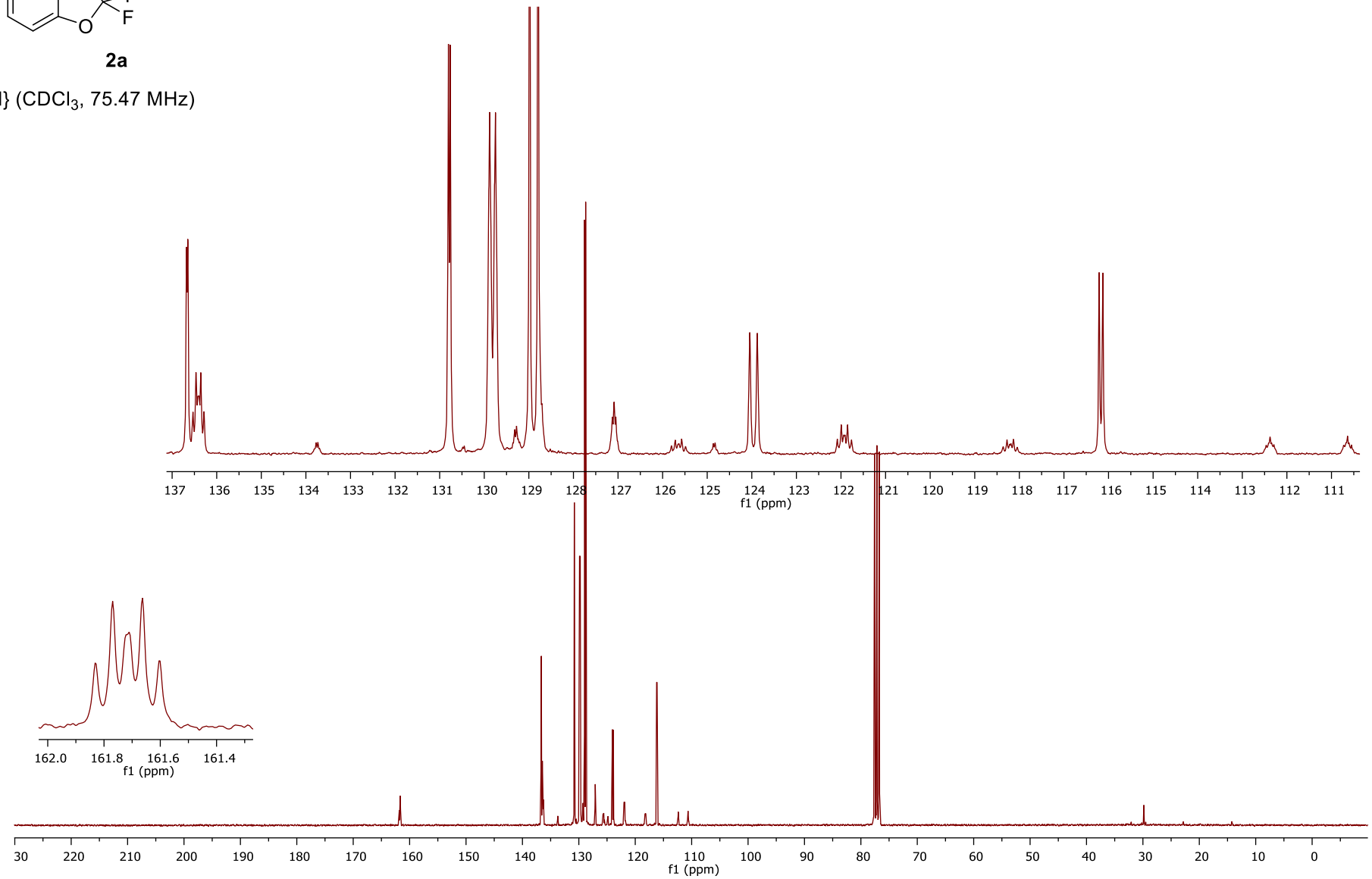
^{1}H ($CDCl_3$, 300.13 MHz)

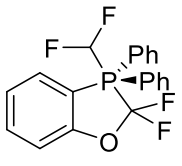




2a

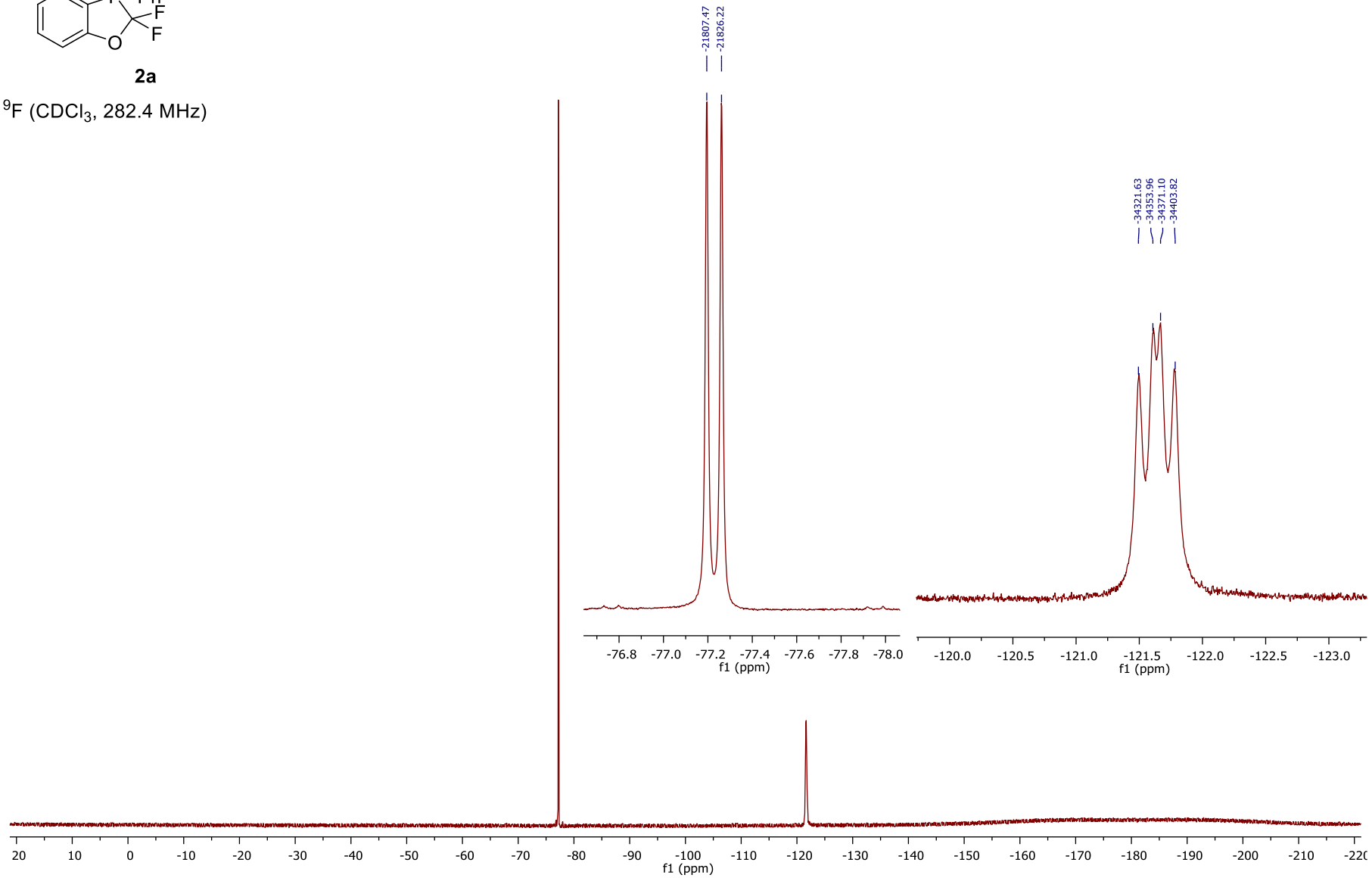
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75.47 MHz)

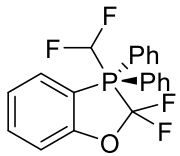




2a

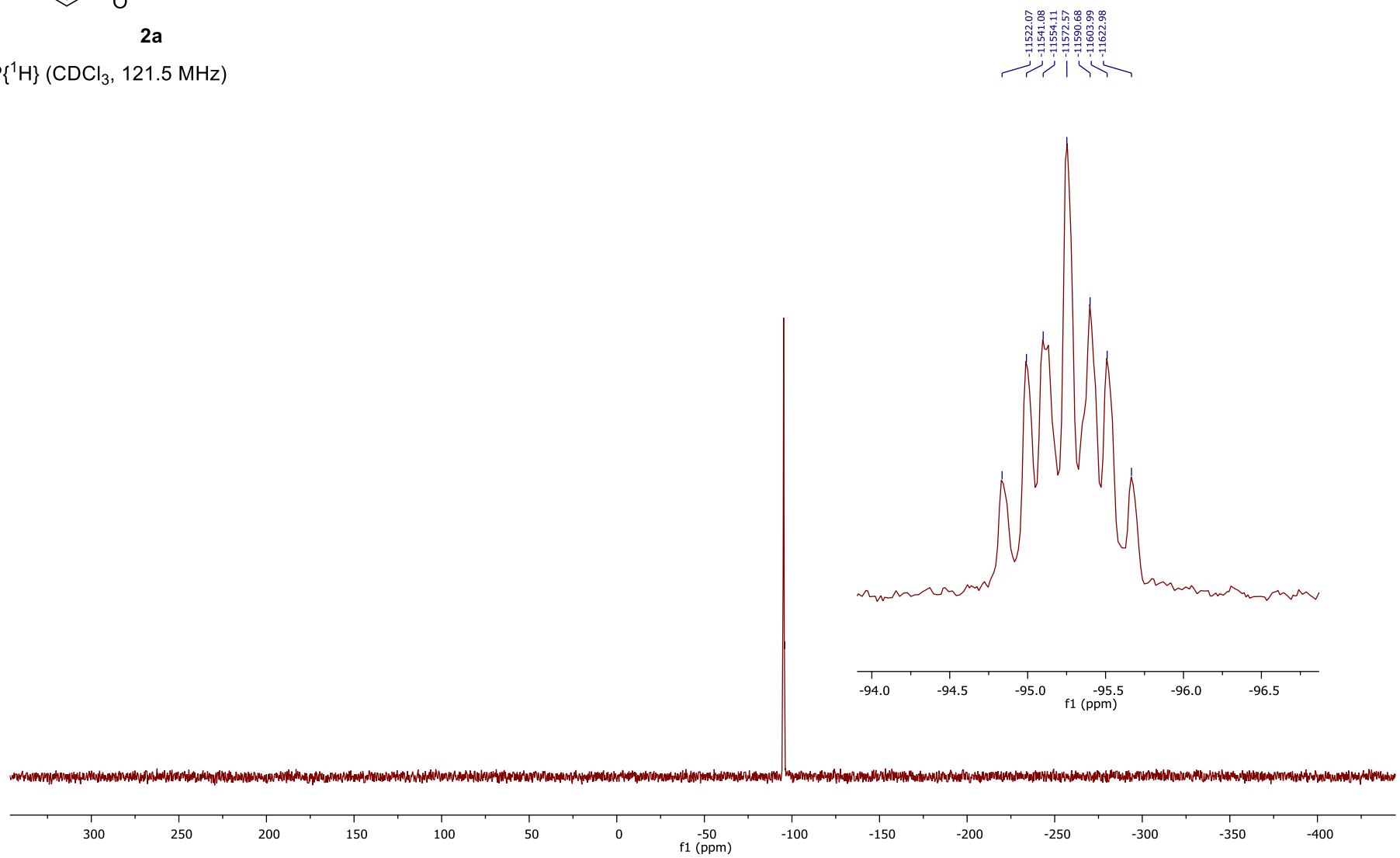
^{19}F ($CDCl_3$, 282.4 MHz)

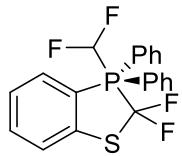




2a

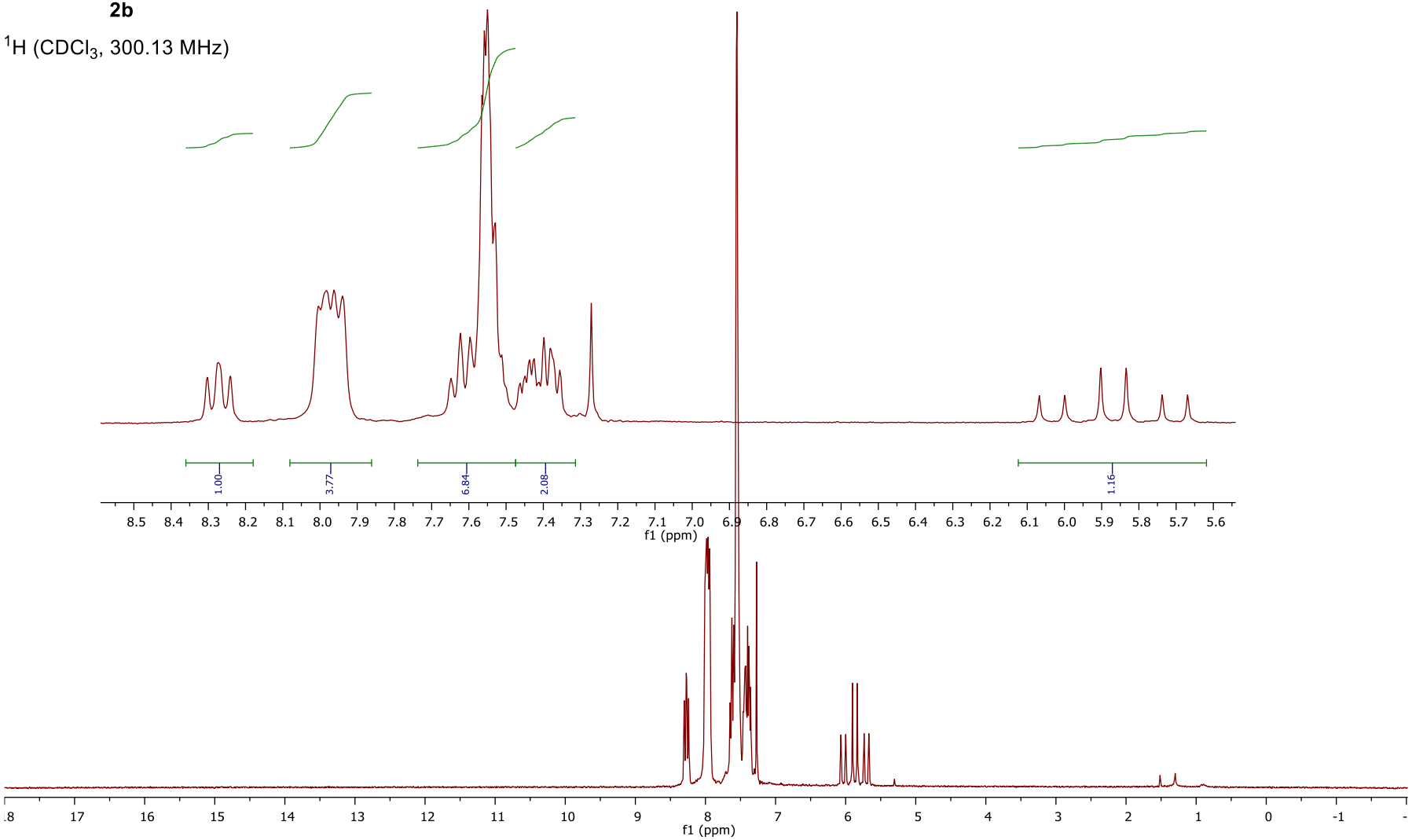
$^{31}P\{^{1}H\}$ ($CDCl_3$, 121.5 MHz)

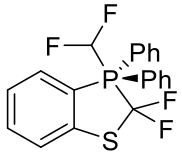




2b

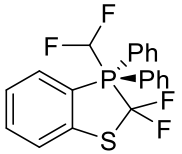
^{1}H ($CDCl_3$, 300.13 MHz)





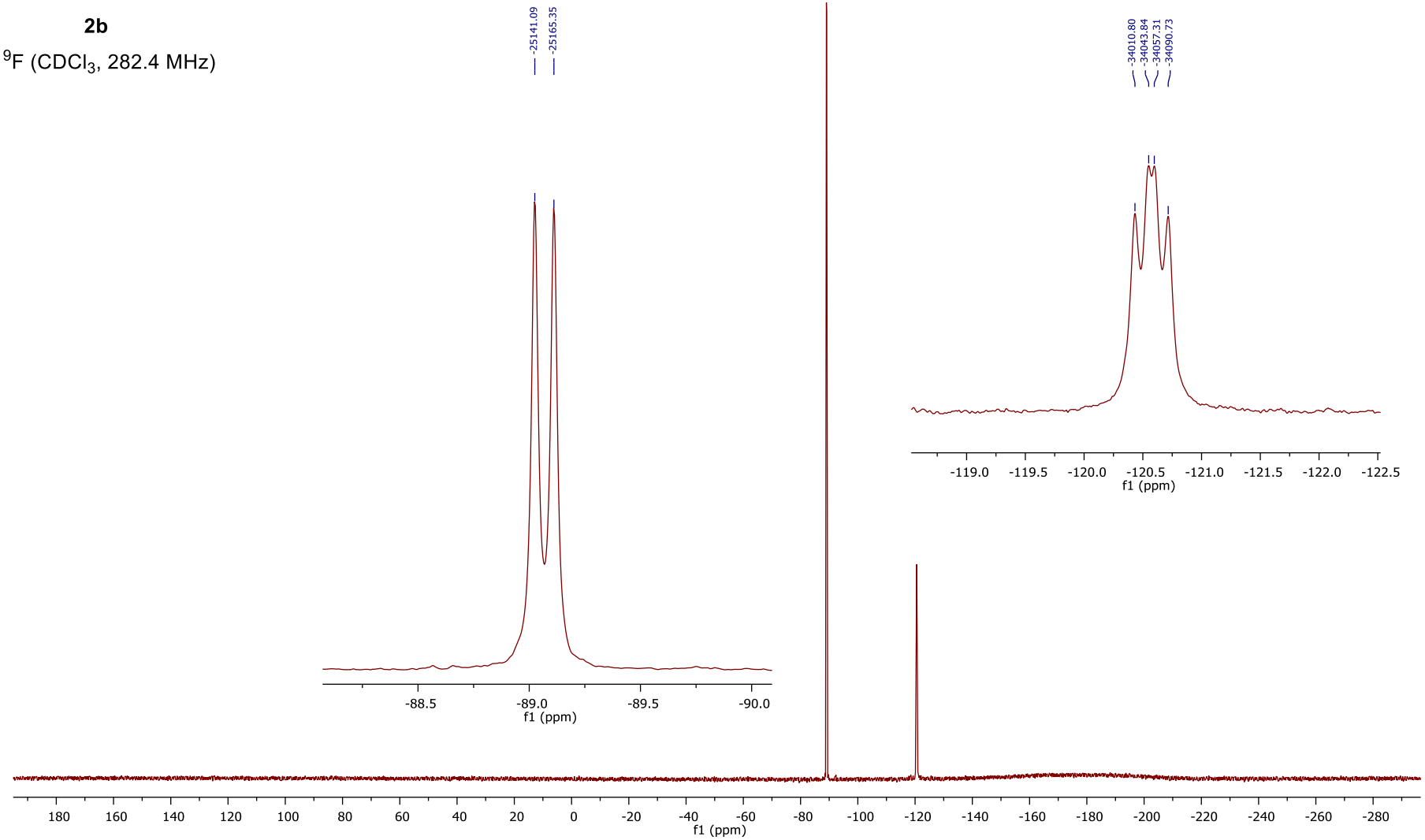
2b

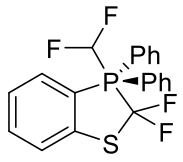
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75.47 MHz)



2b

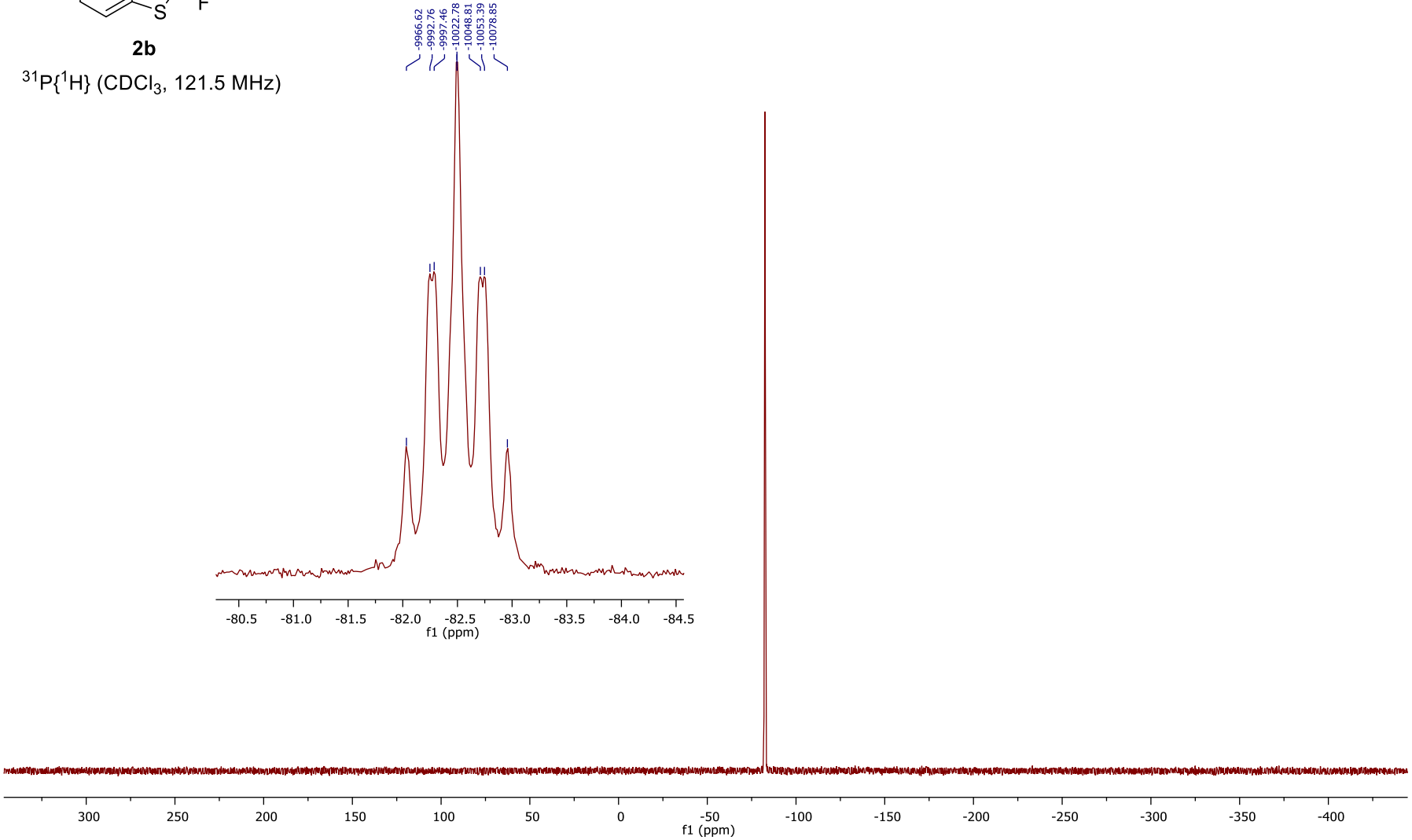
^{19}F ($CDCl_3$, 282.4 MHz)

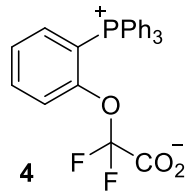




2b

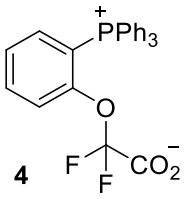
$^{31}P\{^{1}H\}$ ($CDCl_3$, 121.5 MHz)





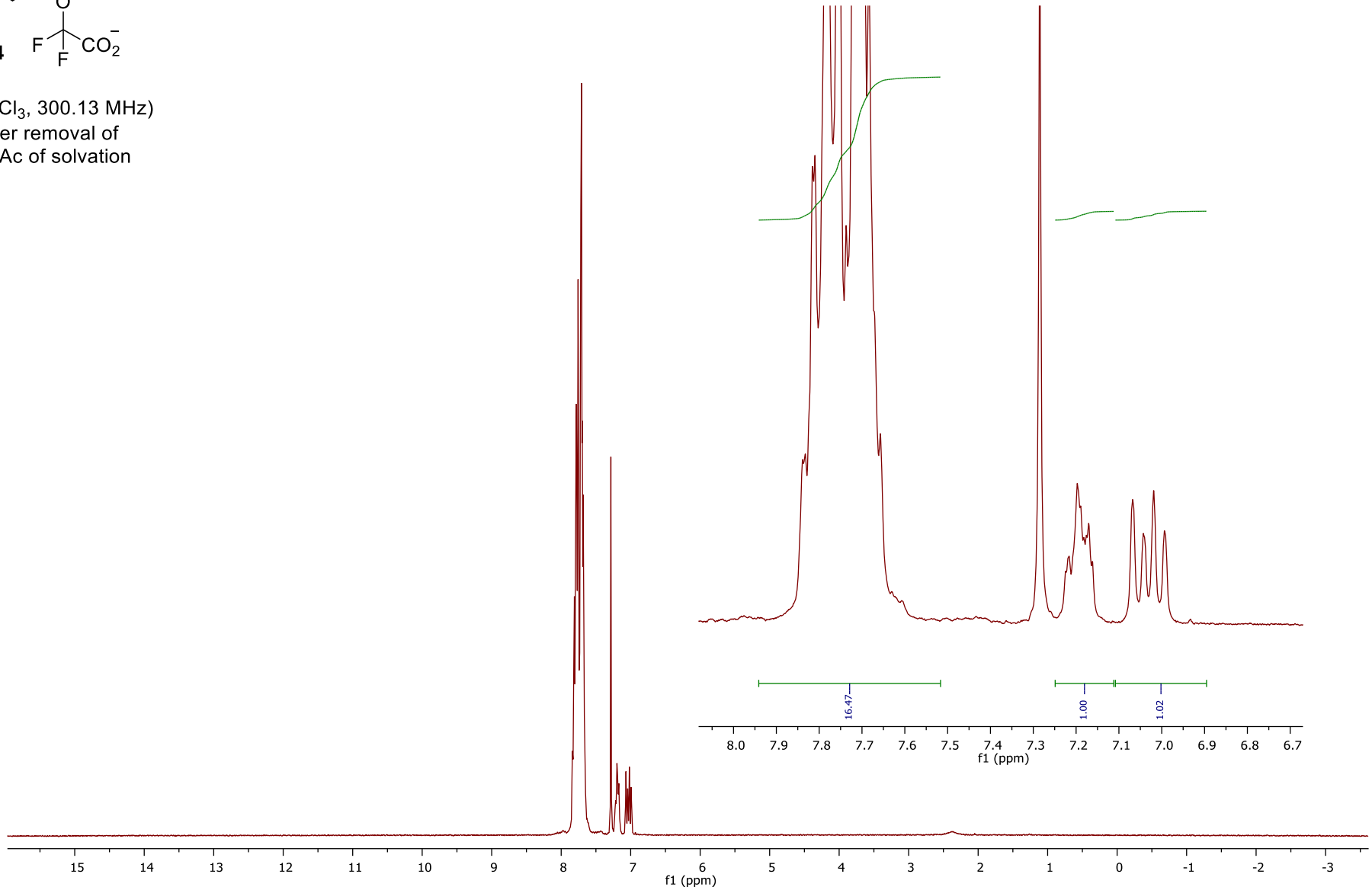
4

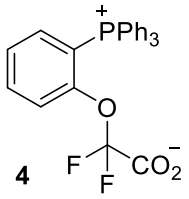
^{1}H ($CDCl_3$, 300.13 MHz)
contains EtOAc of solvation



4

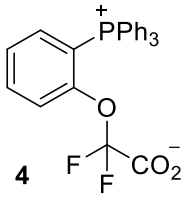
^{1}H ($CDCl_3$, 300.13 MHz)
after removal of
EtOAc of solvation





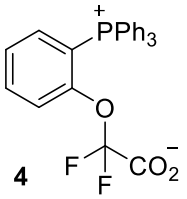
4

$^{13}C\{^{1}H\}$ ($CDCl_3$, 75.47 MHz)
contains EtOAc of solvation



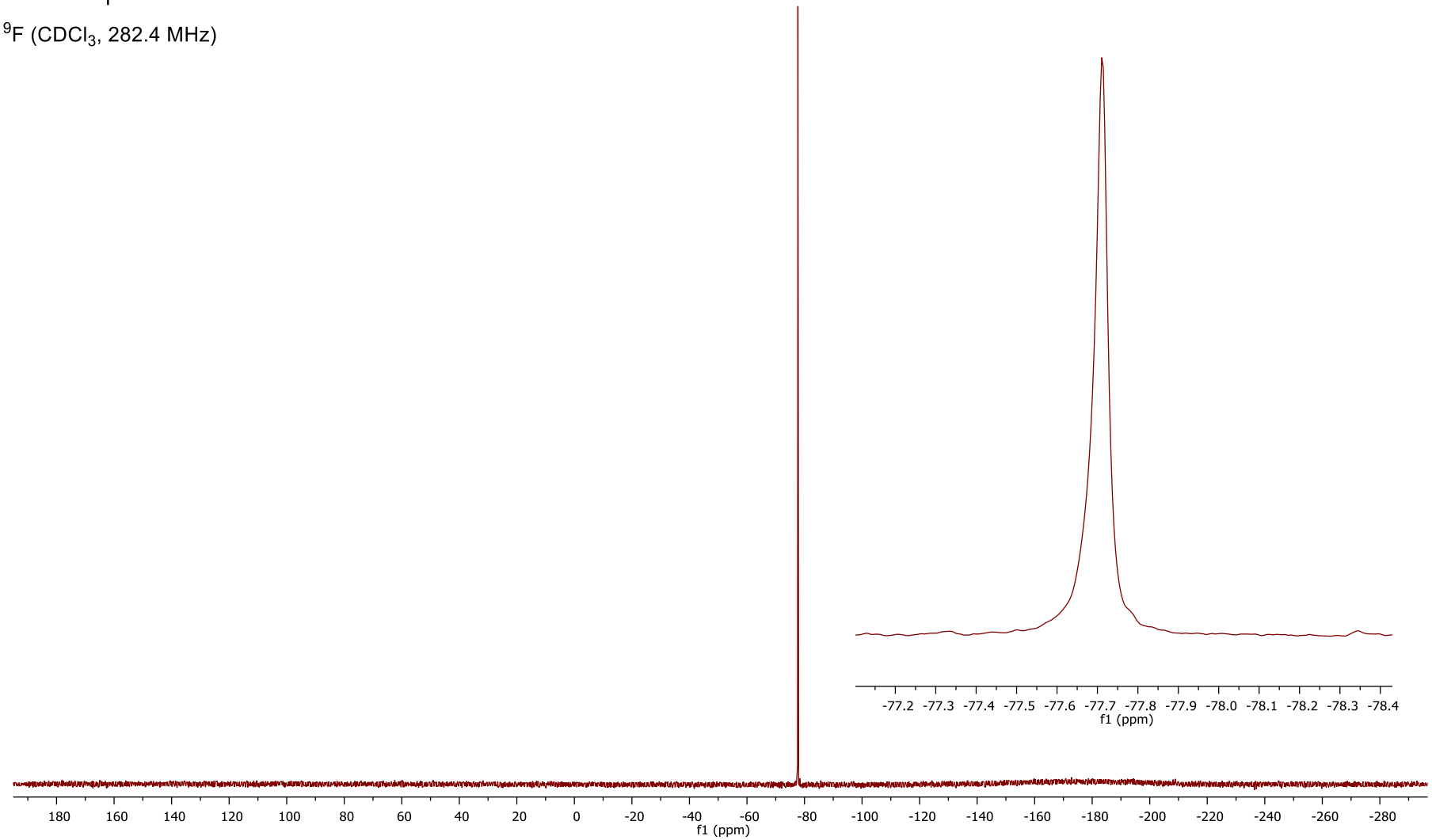
4

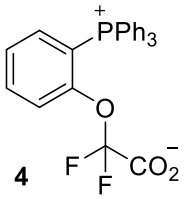
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75.47 MHz)
after removal of
EtOAc of solvation



4

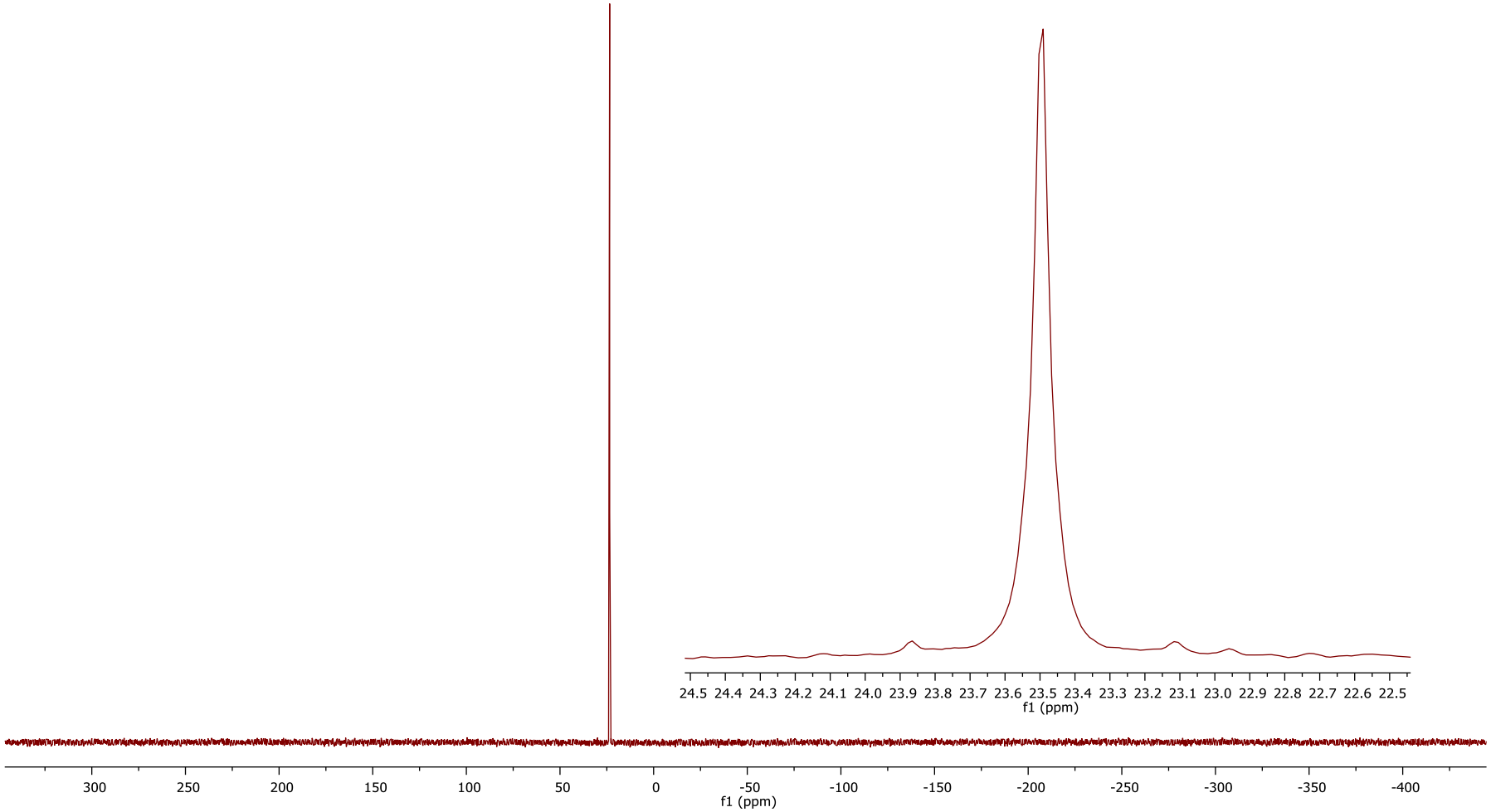
^{19}F ($CDCl_3$, 282.4 MHz)

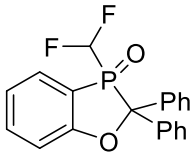




4

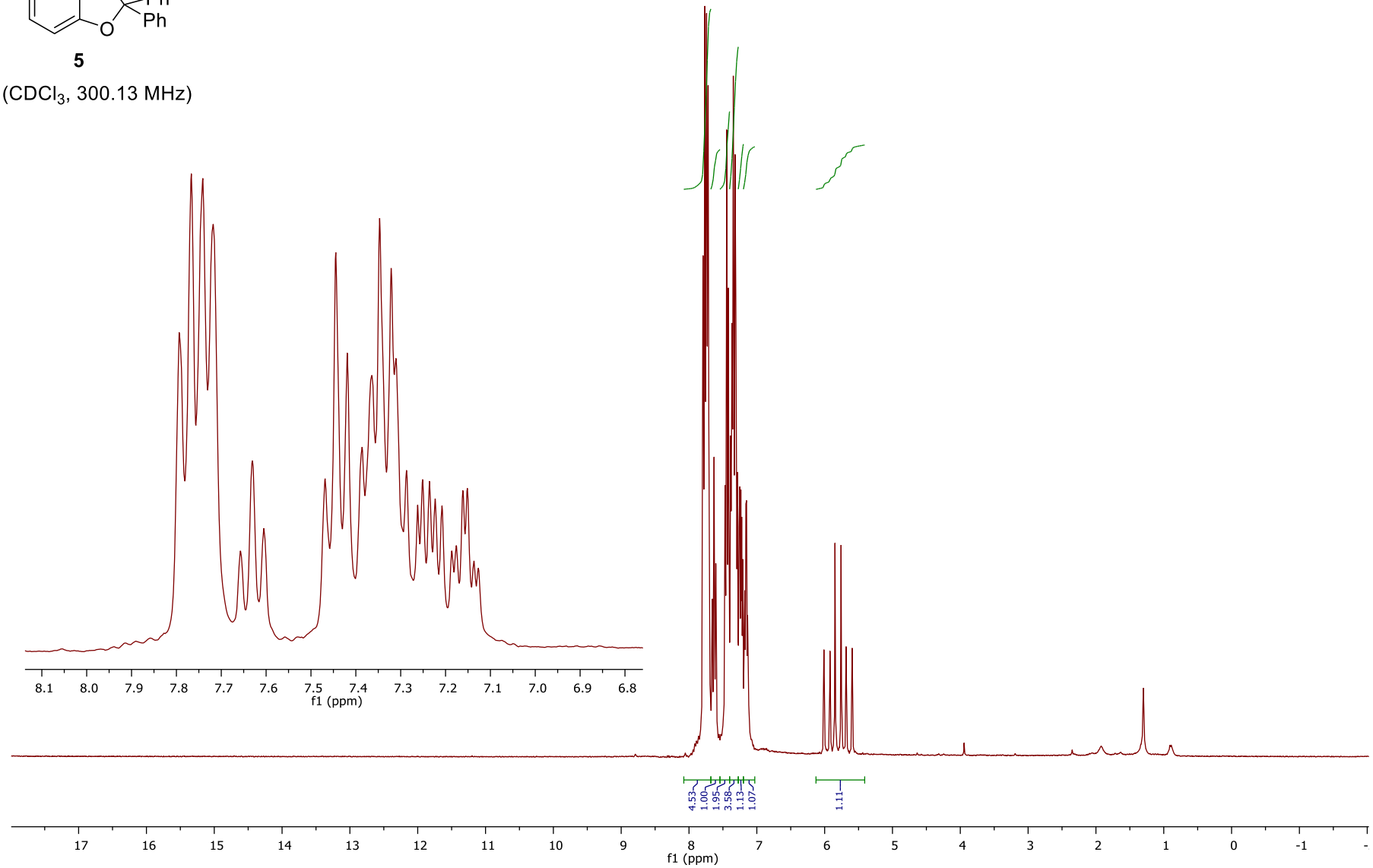
$^{31}P\{^{1}H\}$ ($CDCl_3$, 121.5 MHz)

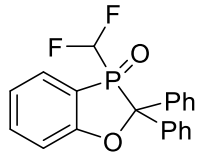




5

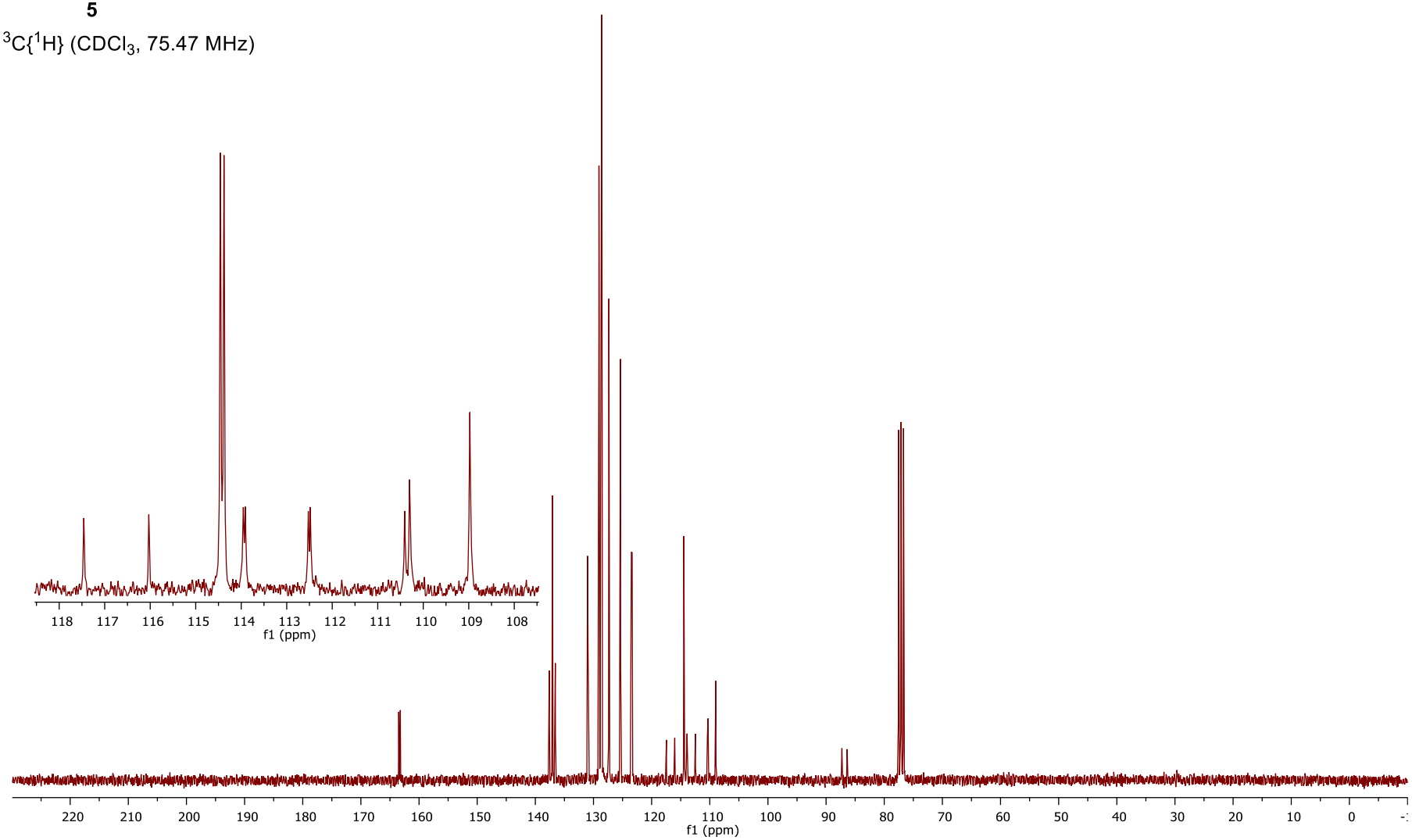
^{1}H ($CDCl_3$, 300.13 MHz)

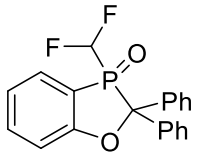




5

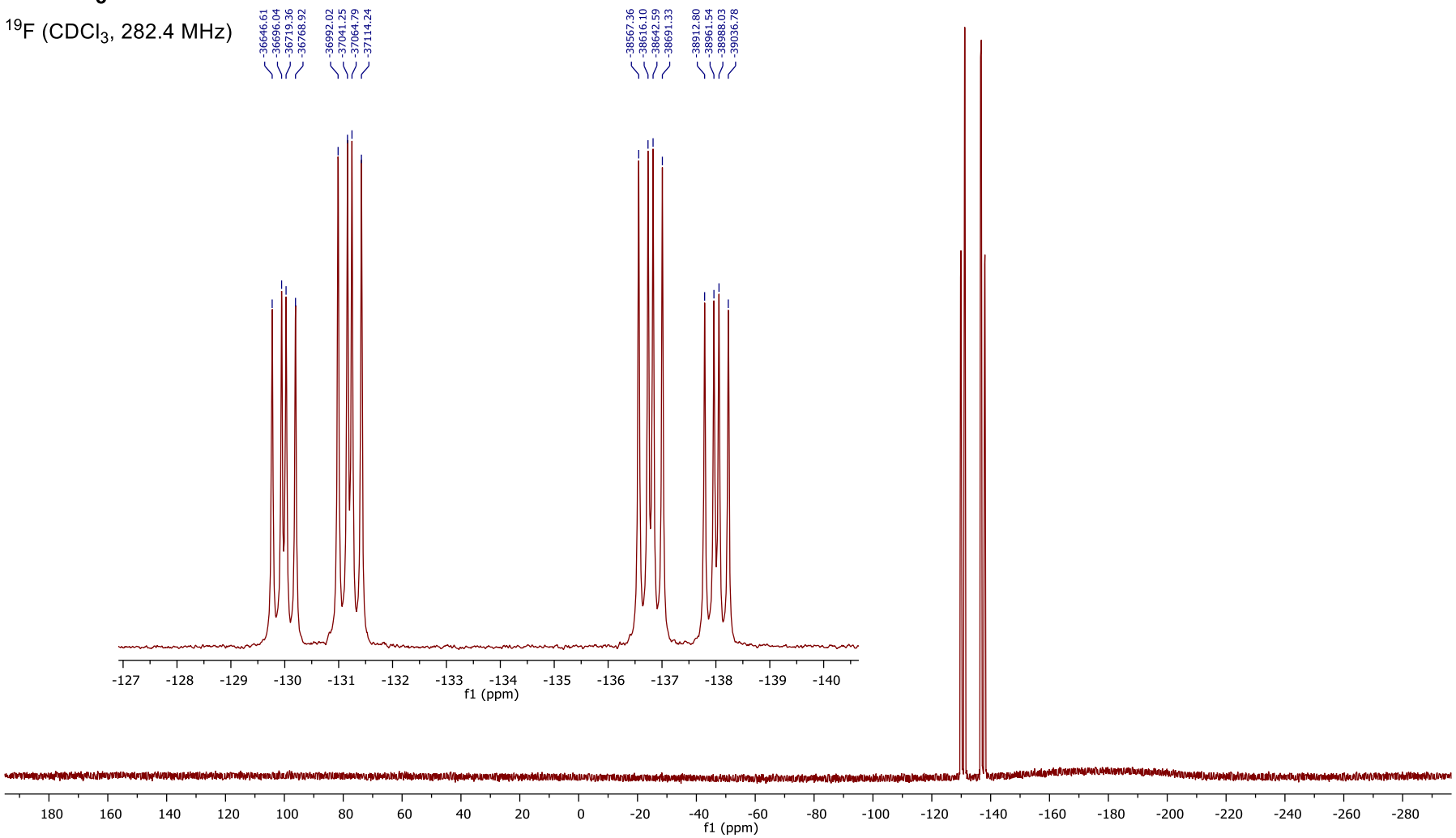
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75.47 MHz)

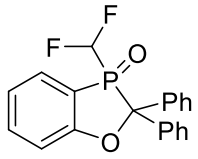




5

^{19}F ($CDCl_3$, 282.4 MHz)





5

$^{31}P\{^{1}H\}$ ($CDCl_3$, 121.5 MHz)