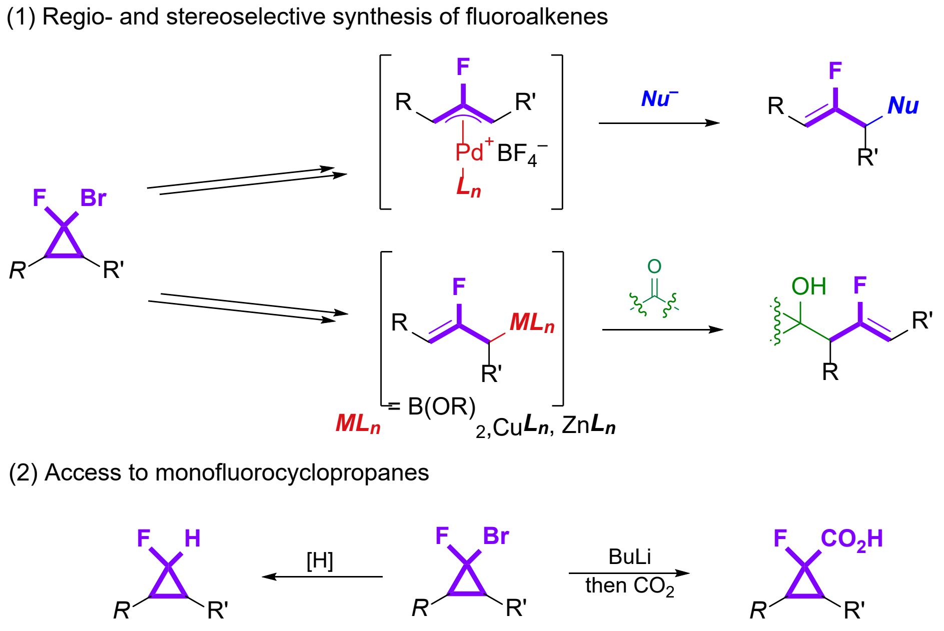
Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 698–700

(XantPhos)AgBr as a cheap and readily available catalyst for the bromofluorocyclopropanation of electron-rich alkenes

Maxim A. Novikov, Angelina Yu. Bobrova, Anton A. Servetnik, Elena I. Chernoburova,
Igor V. Zavarzin and Yury V. Tomilov

Table of content

1. General information S2
2. Experimental procedures S2
    2.1. Synthesis of phosphine silver complexes S2
    2.2. Bromofluorocyclopropanation S4
        2.2.1. Ligand optimization procedure S4
        2.2.2. Preparative synthesis S5
        2.2.3. Ozonolysis for removal of alkene impurities S8
3. Copies of ^{1}H, ^{19}F, ^{31}P{^{1}H}, ^{13}C{^{1}H}-NMR spectra S9
4. References S42



Scheme S1

1.General information

All reagents were purchased from commercial sources and used without further purification. 1,2-Dichloroethane (DCE) was distilled over CaH_2 and stored over 4Å Linde type molecular sieves. CH_2Cl_2 was distilled over KOH prior to use. AgBr was precipitated from water solution $AgNO_3$ with NaBr, filtered, washed with water and dried under high vacuum. ^{1}H, ^{19}F, ^{13}C, ^{31}P, NMR were recorded on Bruker AVANCE III HD 300 (300.1, 282.4, 75.5, 121.5 MHz, respectively), Varian Inova 400 (400.0, 376.4, 100.6, 161.9 MHz, respectively) or Bruker AC200 (81.0 MHz for ^{31}P) in $CDCl_3$. Chemical shifts in $CDCl_3$ were measured relative to TMS (δ = 0.00 ppm) for ^{1}H or $CDCl_3$ (δ = 77.1 ppm) for ^{13}C. Chemical shifts for ^{19}F were measured relative to C_6F_6 (δ = –162.2 ppm) as an internal standard. Chemical shifts for ^{31}P reported relative to 85% H_3PO_4 in water (δ = 0.0 ppm). For HRMS-ESI of silver complexes *m/z* for major ^{107}Ag-containing ions are given only.

(IPr)AgCl was prepared according to Ref.[S1] several times. However, this reaction proceeded with variable success, and in a half of cases chromatographic purification from side $(IPr)_2Ag^+X^-$ (X^- = Cl^- or $AgCl_2^-$) was required, which was achieved by column chromatography on silica eluting with CH_2Cl_2/MeOH 25/1.

2.Experimental procedures

2.1.Synthesis of phosphine silver complexes

AgBr (0.50 mmol) and appropriate Ligand (0.50 mmol (or 1.5 mmol in the case of PPh_3)) were loaded in a round-bottom flask. CH_2Cl_2 (5 mL) was added, and the mixture was stirred for 30 min until dissolution of AgBr. If small amount of solids was still persistent, then the solution was filtered through a small piece of cotton. After evaporation of solvent and drying under vacuum, silver complexes were obtained as colorless solids.

Note that detailed structures of the formed complexes could be complex and various associated may form and various crystal may be grown as was reported for example for PPh_3 complexes.[S2–S10] Therefore, the detailed structure of prepared complexes was not estimated assuming the existence of fast equilibrium between possible forms based on pure NMR spectra presented below. The stoichiometry of the complexes is given according to the Ag / ligand ratio used as no purification was required.

$(PPh_3)_3AgBr$ [S3]

^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 7.44 – 7.29 (m, 3H), 7.28 – 7.17 (m, 2H). **$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$) δ:** 3.91 (br. s). **$^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$) δ:** 134.1 (d, *J* = 16.3 Hz, CH-arom.), 132.6 (d, *J* = 23.1 Hz, C-arom.), 130.0 (d, *J* = 1.8 Hz, CH-arom.), 128.8 (d, *J* = 9.3 Hz, CH-arom.). **HRMS (ESI), *m/z*:** [(PPh$_3$)$_2$Ag]$^+$, calcd for $C_{36}H_{30}AgP_2^+$ 631.0868; found 631.0870.

(dppe)AgBr [S11]

^{1}H NMR (400.0 MHz, CDCl$_3$) δ: 7.54 – 7.44 (m, 8H), 7.35 – 7.27 (m, 4H), 7.25 – 7.14 (m, 8H), 2.59 (br. s, 4H). **^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$) δ:** 0.80 (br. d, *J* = 408.8 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ:** 133.3 (br. s, CH-arom.), 132.8 (br. s, CH-arom.), 130.0 (br. s, CH-arom.), 128.8 (br. s, CH-arom.), 22.6 (br. s, CH$_2$). **HRMS (ESI), *m/z*:** [(dppe)Ag]$^+$, calcd for $C_{26}H_{24}AgP_2^+$ 505.0399; found 505.0384.

(SPhos)AgBr

^{1}H NMR (400.0 MHz, CDCl$_3$) δ: 7.63 – 7.48 (m, 3H, arom.), 7.45 (t, *J* = 7.4 Hz, 1H, arom.), 7.23 – 7.16 (m, 1H, arom.), 6.73 (d, *J* = 8.5 Hz, 2H, arom.), 3.72 (s, 6H, 2CH$_3$), 2.13 – 2.01 (m, 2H, CH in Cy), 1.88 – 1.62 (m, 10H, CH$_2$ in Cy), 1.36 – 1.06 (m, 10H, CH$_2$ in Cy). **^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$) δ:** 21.2 (d, *J* = 602.1 Hz, ^{107}Ag), 21.2 (d, *J* = 694.8 Hz, ^{109}Ag). **^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ:** 156.7, 142.9 (d, *J* = 1.6 Hz), 142.7 (d, *J* = 1.5 Hz), 132.5 (d, *J* = 7.1 Hz), 132.2 (d, *J* = 6.1 Hz), 130.9, 130.8 (d, *J* = 2.1 Hz), 127.7, 127.3 (d, *J* = 1.8 Hz), 127.3 (d, *J* = 1.8 Hz), 117.4 (d, *J* = 9.6 Hz), 104.9, 55.6, 34.8 (d, *J* = 3.9 Hz), 34.6 (d, *J* = 3.9 Hz), 30.8, 30.7, 29.6 (d, *J* = 2.2 Hz), 29.5 (d, *J* = 2.1 Hz), 27.0, 27.0, 26.9, 26.8, 25.8, 25.8. **HRMS (ESI), *m/z*:** [(SPhos)Ag]$^+$, calcd for $C_{26}H_{35}AgO_2P^+$ 517.1420; found 517.1425.

(XPhos)AgBr

^{1}H NMR (400.0 MHz, CDCl$_3$) δ: 7.61 – 7.54 (m, 1H, arom.), 7.47 – 7.39 (m, 2H, arom.), 7.23 – 7.17 (m, 1H, arom.), 7.10 (s, 2H, arom.), 2.98 (sept, *J* = 7.0 Hz, 1H, CH in ^{i}Pr), 2.19 (sept, *J* = 6.8 Hz, 2H, CH in ^{i}Pr), 2.01 – 1.87 (m, 4H, Cy), 1.80 – 1.57 (m, 8H, Cy), 1.32 (d, *J* = 6.9 Hz, 6H, 2CH$_3$), 1.24 (d, *J* = 6.9 Hz, 6H, 2CH$_3$), 1.39 – 1.05 (m, 10H, Cy), 0.88 (d, *J* = 6.7 Hz, 6H, 2CH$_3$). **^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$) δ:** 16.6 (d, *J* = 587.3 Hz, ^{107}Ag), 16.6 (d, *J* = 677.7 Hz, ^{109}Ag). **^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ:** 150.5, 147.4, 147.2, 145.3, 134.1 (d, *J* = 8.9 Hz), 132.8 (d, *J* = 6.8 Hz), 132.3 (d, *J* = 5.9 Hz), 130.3 (d, *J* = 2.0 Hz), 128.3 (d, *J* = 5.0 Hz), 128.0 (d, *J* = 4.9 Hz), 127.5 (d, *J* = 4.6 Hz), 122.6, 35.5 (d, *J* = 4.3 Hz), 35.3 (d, *J* = 4.3 Hz), 34.2, 31.5 (d, *J* = 7.1 Hz), 30.9, 30.1 (d, *J* = 2.4 Hz), 30.1 (d, *J* = 2.3 Hz), 27.3, 27.2, 26.9, 26.8, 25.9, 25.7 (d, *J* = 1.6 Hz), 24.2, 23.5. **HRMS (ESI), *m/z*:** [(XPhos)Ag]$^+$, calcd for $C_{33}H_{49}AgP^+$ 583.2617; found 583.2609.

(Bu^{t}XPhos)AgBr

^{1}H NMR (400.0 MHz, CDCl$_3$) δ: 7.89 (t, *J* = 6.7 Hz, 1H, arom.), 7.58 – 7.43 (m, 2H, arom.), 7.35 – 7.30 (m, 1H, arom.), 7.18 (s, 2H, arom.), 3.05 (hept, *J* = 7.0 Hz, 1H, CH in ^{i}Pr), 2.37 (hept, *J* = 6.7 Hz, 2H, CH in ^{i}Pr), 1.39 (d, *J* = 6.9 Hz, 6H, CH$_3$ in ^{i}Pr), 1.36 (s, 9H, ^{t}Bu), 1.32 (s, 9H, ^{t}Bu), 1.31 (d, *J* = 7.9 Hz, 6H, CH$_3$ in ^{i}Pr), 0.93 (d, *J* = 6.6 Hz, 6H, CH$_3$ in ^{i}Pr). **^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$) δ:** 42.1 (d, *J* = 581.6 Hz, ^{107}Ag), 42.1 (d, *J* = 670.8 Hz, ^{109}Ag). **^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ:** 150.5, 148.3 (d, *J* = 1.4 Hz), 148.0 (d, *J* = 1.5 Hz), 145.4 (t, *J* = 0.9 Hz), 134.7 (d, *J* = 7.0 Hz), 134.1 (d, *J* = 1.4 Hz), 140.0 (d, *J* = 1.3 Hz), 133.9 (d, *J* = 6.8 Hz), 130.1 (d, *J* = 2.1 Hz), 129.2 (d, *J* = 3.9 Hz), 128.9 (d, *J* = 4.0 Hz), 126.9 (d, *J* = 2.0 Hz), 126.8 (d, *J* = 2.0 Hz), 123.0, 35.76 (d, *J* = 4.5 Hz), 35.7 (d, *J* = 4.5 Hz), 34.1, 31.4 (d, *J* = 1.9 Hz), 31.3 (d, *J* = 1.9 Hz), 31.0, 26.5, 24.1, 23.3. **HRMS (ESI), *m/z*:** [(^{t}BuXPhos)Ag]$^+$, calcd for $C_{29}H_{45}AgP^+$ 531.2304; found 531.2297.

(XantPhos)AgBr [S12]

^{1}H NMR (400.0 MHz, CDCl$_3$) δ: 7.55 (dd, *J* = 7.8, 1.5 Hz, 2H, arom.), 7.40 – 7.33 (m, 8H, arom.), 7.32 – 7.27 (m, 4H, arom.), 7.25 – 7.18 (m, 8H, arom.), 7.09 (t, *J* = 7.7 Hz, 2H, arom.), 6.62 – 6.56 (m, 2H, arom.), 1.67 (s, 6H, 2CH$_3$). **^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$) δ:** –8.3 (d, *J* = 364.0 Hz, ^{107}Ag), –8.3 (d, *J* = 415.7 Hz, ^{109}Ag). **^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ:** 153.4 (t, *J* = 6.8 Hz), 133.9 (t, *J* = 8.9 Hz), 132.2, 131.8, 131.5 (t, *J* = 14.2 Hz), 130.1, 128.8 (t, *J* = 5.0 Hz), 127.4, 124.7, 119.7 (t, *J* = 10.6 Hz), 35.2, 29.7. **HRMS (ESI), *m/z*:** [(XantPhos)Ag]$^+$, calcd for $C_{39}H_{32}AgOP_2^+$ 685.0974; found 685.0966.

2.2.Bromofluorocyclopropanation

2.2.1.Ligand optimization procedure

A 10 mL Schlenk tube was charged with $CFBr_2CO_2Na$ (0.5 mmol, 1 equiv.) and (L)AgX (0.01 mmol, 2 mol.%) and was dried under vacuum (0.1–0.2 Torr) for 1 hour with stirring of this solids by magnetic stirrer. Next, under argon atmosphere, a solution of styrene (1.0 mmol, 2 equiv.) and $C_{19}H_{40}$ (10–20 mg) in DCE (0.50 mL) was added, and the reaction was placed on an oil bath preheated to 80°C while keeping it open to an argon line. After heating for 5 hours, an aliquot was taken, diluted with hexane and analyzed by GC. The results are presented in the Table 1 of Main Text.

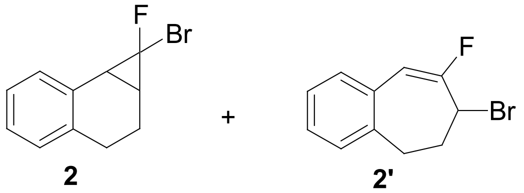
2.2.2.Preparative synthesis

Preparative syntheses were carried out in the same manner as for optimization procedure using 2–8-fold excess of $CFBr_2CO_2Na$.

A mixture $CFBr_2CO_2Na$ (2 equiv.) and (XantPhos)AgBr (2 mol.%) and was dried under vacuum (0.1–0.2 Torr) for 1 hour with stirring of these solids by magnetic stirrer. Next, under argon atmosphere, a solution of alkene (1.0 equiv.) in DCE (1 mL per mmol of alkene) was added, and the reaction was placed on an oil bath preheated to 80°C while keeping it open to an argon line. After heating for 5 hours, an aliquot was taken, diluted with hexane and analyzed by GC. If the reaction was not complete, additional $CFBr_2CO_2Na$ (2 equiv.) freshly dried under vacuum was added and heating was continued for 21 hours more. Next, the reaction mixture was analyzed by GC again, and more $CFBr_2CO_2Na$ was added with additional 24 hours of heating if complete conversion of alkene was not achieved. The last steps were repeated as many times as was necessary to achieve complete consumption of alkene.

After the reaction complete, it was evaporated with neutral Celite and the crude product was washed out with hexane/Et_2O 10:1. At this stage, the product may be pure enough by NMR to be used (as for **2**, **3**, **4**), or required chromatographic purification (as for **5**). In the cases of cyclopropanes **6** and **7**, after 8 equiv. of $CFBr_2CO_2Na$ were added and the reaction was heated for 72 hours total, still a lot of corresponding alkenes remained. Therefore, the reactions were stopped, subjected to work-up and the residue was analyzed by ^{1}H and ^{19}F NMR. The yields were determined by ^{19}F NMR with 4-fluorobenzotrifluoride as an internal standard. ^{1}H and ^{19}F NMR data of **6** and **7** are fully agreed with previously published.[13]

1-Bromo-1-fluoro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (2)



2 **2'**

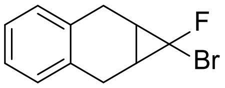
Prepared according to general procedure on 50 mmol scale using 2 equiv. of $CFBr_2CO_2Na$ and 5 hours of heating affording 12.817 g of **2** as an orange oil (*syn*/*anti* = 55/45, ratio *syn*-**2**/*anti*-**2**/**2'** = 45/37/18, 80%yield of **2**, 99% yield of overall :CFBr addition) (contained: 75 w/w % of **2**, 16 w/w % of **2'**, 2 w/w % of naphthalene, 7 w/w % of tetralin *(naphthalene and tetralin are impurities in starting 1,2-dihydronaphthalene)*). Colorless sample could be prepared by 'bulb-to-bulb' distillation (90–120°C, 0.2 Torr).

^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 7.26 – 7.08 (m, 4H), 2.85 – 2.58 (m, 3H), 2.41 – 2.15 (m, 2H), 2.00 – 1.86 (m, 1H). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –116.6 (m, *syn*-isomer), –152.6 (m, *anti*-isomer). **$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ:** 30.5 (d, J = 11.4 Hz, CH), 28.7 (d, J = 9.6 Hz, CH), 27.4 (d, J = 12.1 Hz, CH), 26.9 (d, J = 7.6 Hz, CH_2), 26.3 (d, J = 2.5 Hz, CH_2), 25.2 (d, J = 10.2 Hz, CH), 20.0 (s, CH_2), 16.7 (s, CH_2), 94.4 (d, J = 299.0 Hz, CF), 83.8 (d, J = 315.1 Hz, CF), 140.0, 139.9, 137.2, 136.5, 135.4, 133.5, 131.4, 131.4, 130.8, 130.5, 130.3, 130.1, 129.5, 129.2, 128.9, 128.7, 128.1, 128.0, 127.9, 127.2, 127.0, 126.7, 126.4, 126.3, 125.9, 125.4 (aromatic C and CH are overlapped for *syn/anti*-**2** and **8** and cannot be resolved, also it is unclear where are singlets and where are doublets).

7-Bromo-8-fluoro-6,7-dihydro-5*H*-benzo[7]annulene (2')

(Overlapped with *syn/anti*-**2**, selected signals): **^{1}H NMR (300.1 MHz, CDCl$_3$) δ:** 6.41 (d, *J* = 24.1 Hz, 1H, =CH–), 5.15 – 5.09 (m, 1H, CHBr), 3.39 (dd, *J* = 15.6, 10.9 Hz, 1H in CH$_2$), 2.90 (dd, *J* = 15.7, 8.3 Hz, 1H in CH$_2$), 2.56 – 2.46 (m, 1H in CH$_2$ (from edHSQC)), 2.28 – 2.18 (m, 1H in CH$_2$ (from edHSQC)). **^{19}F NMR (282.4 MHz, CDCl$_3$) δ:** –96.3 (dt, *J* = 24.1, 5.5 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ:** 158.0 (d, *J* = 245.6 Hz, =CF–), 113.3 (d, *J* = 30.5 Hz, =CH–), 49.5 (d, *J* = 28.6 Hz, CHBr), 31.9 (d, *J* = 7.2 Hz, CH$_2$), 31.2 (s, CH$_2$).

1-Bromo-1-fluoro-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene (3)

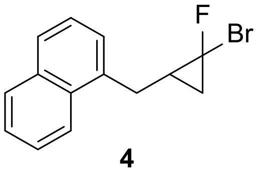


3

Prepared according to general procedure on 50 mmol scale using 4 equiv. of CFBr$_2$CO$_2$Na and 24 hours of heating affording 11.490 g of **3** as an orange oil (*syn*/*anti* = 63:37, 95% yield). Analytically pure sample was prepared by 'bulb-to-bulb' distillation (90–120°C, 0.2 Torr).

^{1}H NMR (300.1 MHz, CDCl$_3$) δ: 7.14 – 7.03 (m, 4H), 3.32 – 3.04 (m, 2H), 2.83 – 2.59 (m, 2H), 2.09 – 1.86 (m, 2H). **^{19}F NMR (282.4 MHz, CDCl$_3$) δ:** –122.6 (t, *J* = 19.2 Hz, *syn*-isomer), –154.8 (br. s, *anti*-isomer). **^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$) δ:** 134.9 (s, 2C-arom.), 133.8 (d, *J* = 2.6 Hz, 2C-arom.), 128.7 (s, 2CH-arom.), 128.3 (s, 2CH-arom.), 126.2 (s, 4CH-arom.), 95.6 (d, *J* = 295.0 Hz, CF), 83.4 (d, *J* = 310.0 Hz, CF), 26.0 (d, *J* = 10.2 Hz, CH), 25.9 (s, CH$_2$), 23.2 (d, *J* = 10.9 Hz, CH), 22.9 (d, *J* = 5.6 Hz, CH$_2$). **Anal. calcd for $C_{11}H_{10}BrF$:** C, 54.80%; H, 4.18%. Found: C, 54.68%; H, 4.32%.

1-[(2-Bromo-2-fluorocyclopropyl)methyl]naphthalene (4)

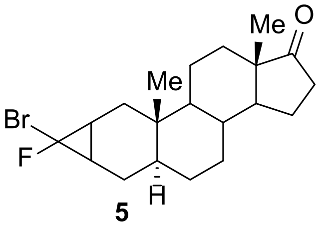


4

Prepared according to general procedure on 50 mmol scale using 8 equiv. of CFBr$_2$CO$_2$Na and 72 hours of heating affording 11.607 g of **4** as an yellow oil after filtration through a plug of silica (100 g) eluting with hexane/benzene 10/1 (*syn*/*anti* = 46/54, 83% yield). NMR data are in a full agreement with previously published.[S13]

^{1}H NMR (300.1 MHz, CDCl$_3$) δ: 8.08 – 7.95 (m, 1H), 7.91 – 7.82 (m, 1H), 7.79 – 7.66 (m, 1H), 7.56 – 7.38 (m, 4H), 3.38 (ddd, *J* = 15.7, 7.0, 2.9 Hz, 1H, both isomers), 3.19 (ddd, *J* = 15.7, 7.1, 1.2 Hz, 1H, *anti*-**4**), 3.06 (ddd, *J* = 15.7, 7.2, 2.7 Hz, 1H, *syn*-**4**), 2.07 – 1.81 (m, 1H, both isomers), 1.71 (ddd, *J* = 17.1, 11.4, 7.5 Hz, 1H, *syn*-**4**), 1.48 (dt, *J* = 10.7, 7.8 Hz, 1H, *anti*-**4**), 1.33 (dt, *J* = 17.5, 7.8 Hz, 1H, *anti*-**4**), 1.10 (q, *J* = 7.5 Hz, 1H, *syn*-**4**). **^{19}F NMR (282.4 MHz, CDCl$_3$) δ:** –127.0 (dddd, *J* = 19.7, 17.2, 7.1, 2.6 Hz, *syn*-**4**), –148.4 (dd, *J* = 17.6, 7.8 Hz, *anti*-**4**). **^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$) δ:** 135.6, 135.1, 133.9, 131.9, 129.0, 127.4, 127.4, 126.2, 125.8, 125.7, 123.4, 87.4 (d, *J* = 298.9 Hz, CF), 82.2 (d, *J* = 301.5 Hz, CF), 34.2 (s, CH$_2$), 29.9 (d, *J* = 5.7 Hz, CH$_2$), 28.8 (d, *J* = 10.6 Hz, CH), 25.6 (d, *J* = 9.6 Hz, CH), 23.1 (d, *J* = 10.8 Hz, CH$_2$), 22.7 (d, *J* = 10.2 Hz, CH$_2$).

2,3-(*gem*-Bromofluorocyclopropa)-5α-androstan-17-one (5)

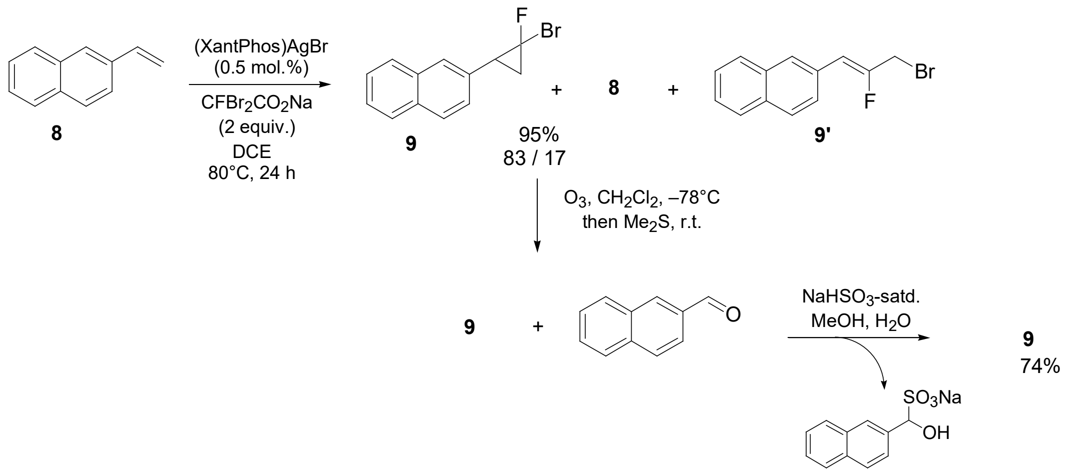


5

Prepared according to general procedure on 1 mmol scale using 8 equiv. of CFBr$_2$CO$_2$Na and 72 hours of heating affording 300.7 mg of **5** as colorless solids after filtration through a plug of silica (10 g) eluting with hexane/benzene 10:1 (*syn*-major/*syn*-minor/*anti*-major/*anti*-minor = 49/12/30/9, 78% yield).

^{1}H NMR (300.1 MHz, CDCl$_3$) δ: 2.51 – 0.58 (m). **^{19}F NMR (282.4 MHz, CDCl$_3$) δ:** –119.4 (t, *J* = 20.2 Hz, *syn*-minor), –119.7 (t, *J* = 20.4 Hz, *syn*-major), –153.7 (d, *J* = 5.5 Hz, *anti*-minor), –155.5 (br. s, *anti*-major). **^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$) δ:** 221.1 (s, C=O), 221.1 (s, C=O), 221.0 (s, C=O, 97.5 (d, *J* = 293.9 Hz, CF), 97.3 (d, *J* = 295.6 Hz, CF), 84.4 (d, *J* = 305.5 Hz, CF), 83.8 (d, *J* = 304.8 Hz, CF), 53.2, 53.1, 52.7, 52.7, 51.4, 47.8, 47.7, 47.6, 42.4, 39.3, 39.3, 38.4, 38.4, 37.7, 37.7, 35.8, 35.6, 35.5, 35.1, 35.0, 33.9, 33.8, 33.7, 33.6, 32.9, 32.8, 31.8, 31.8, 31.6, 31.6, 30.7, 30.5, 30.4, 29.7, 29.7, 29.5, 29.3, 29.1, 27.6, 27.5, 23.7, 23.4, 23.3, 23.2, 23.1, 22.6, 22.5, 22.5, 22.4, 21.8, 21.7, 21.6, 21.3, 21.1, 20.7, 20.7, 20.3, 20.3, 15.8, 14.4, 14.3, 13.9, 13.9, 13.7, 13.2, 12.4, 12.1, 12.1, 11.4, 11.3 (Aliphatic carbons are overlapped for all 4 isomers and cannot be resolved. Even it is unclear where are singlets and where are doublets). **HRMS (ESI), *m/z*:** [M+H]$^+$, calcd for C$_{20}$H$_{29}$BrFO$^+$ 383.1380; found 383.1378.

2.2.3. Ozonolysis for removal of alkene impurities



Scheme S2

Cyclopropanation of 2-vinylnaphthalene was carried out according to the general procedure described above on 50 mmole scale, but using only 0.5 mol.% of (XantPhos)AgBr. The reaction was heated for 24 hours using 2 equiv. of $CFBr_2CO_2Na$ total. After work up, 12.054 g of orange oil were obtained. This oil contained a mixture of **8** / **9** / **8'** = 17 / 81 /2 as determined by ^{1}H and ^{19}F NMR.

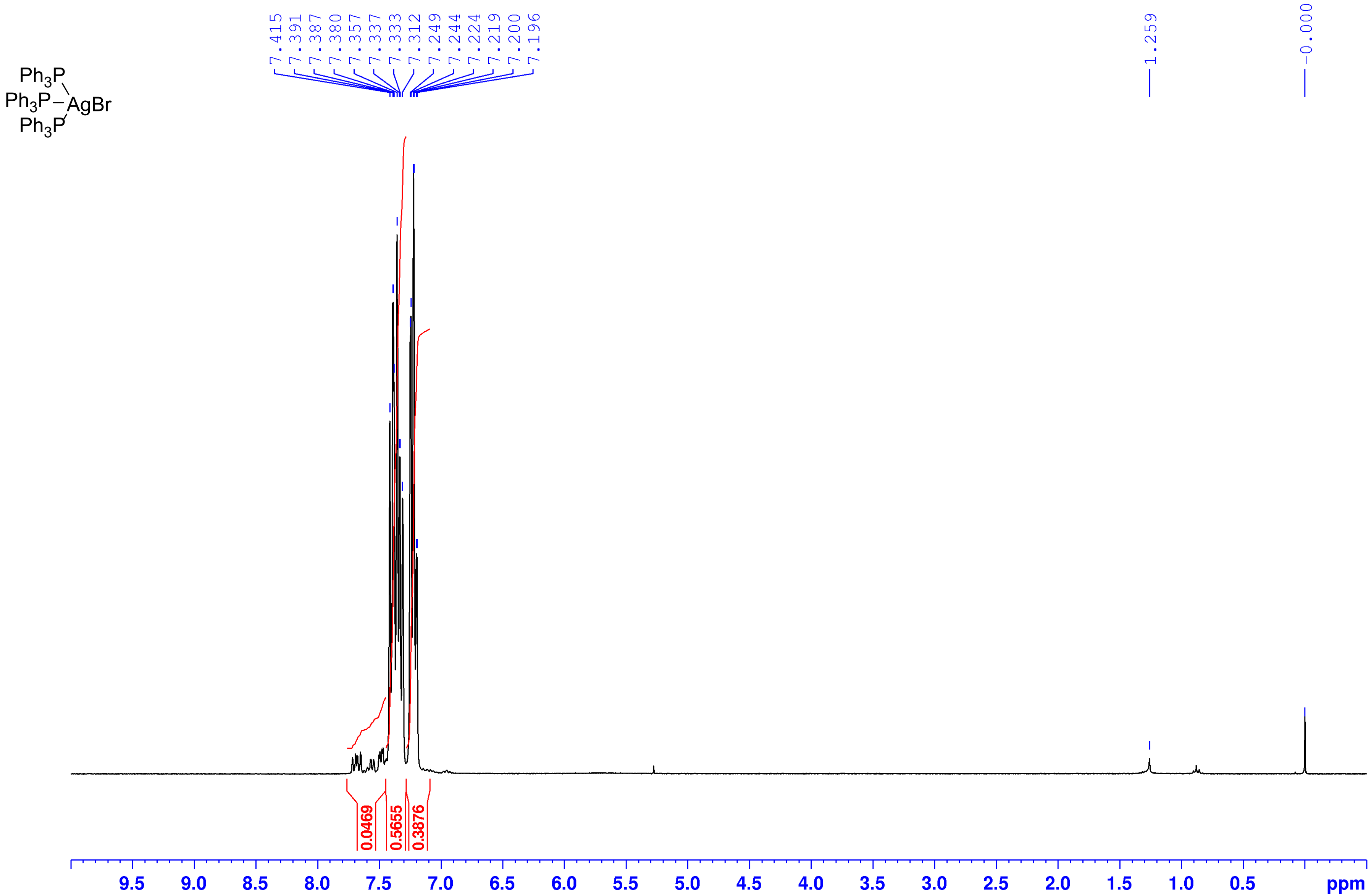
It was dissolved in 200 mL of CH_2Cl_2, cooled to –78°C (Dry Ice / light petrol bath) and O_3 was bubbled for 50 min (generated from oxygen, 18 L/h, 92–95 mg/L of O_3). Next, residual O_3 was removed by bubbling oxygen for 15 min and argon for 15 min more. Then, Me_2S (2.2 mL, 30 mmol) was added, the reaction mixture was allowed to warm to r.t., stirred for 2 hours and evaporated.

Formed aldehyde was removed by M. Boucher and C. Brindle technique.[S14] In this way, the crude product was dissolved in 50 mL of MeOH and was shaken for 1 min with 100 mL of almost conc. $NaHSO_3$ solution (prepared by dissolving of 58 g of $Na_2S_2O_5$ in water — 150 mL a total volume of the solution). This mixture was diluted with 100 mL of water and extracted twice with hexane/EtOAc 10/1. Extracts were evaporated and filtered through a plug of silica (100 g) eluting with hexane/benzene 99/1 affording pure **10** as a colorless oil that solidifies upon storage (9.788 g, 74% yield, *syn*/*anti* = 50 / 50).

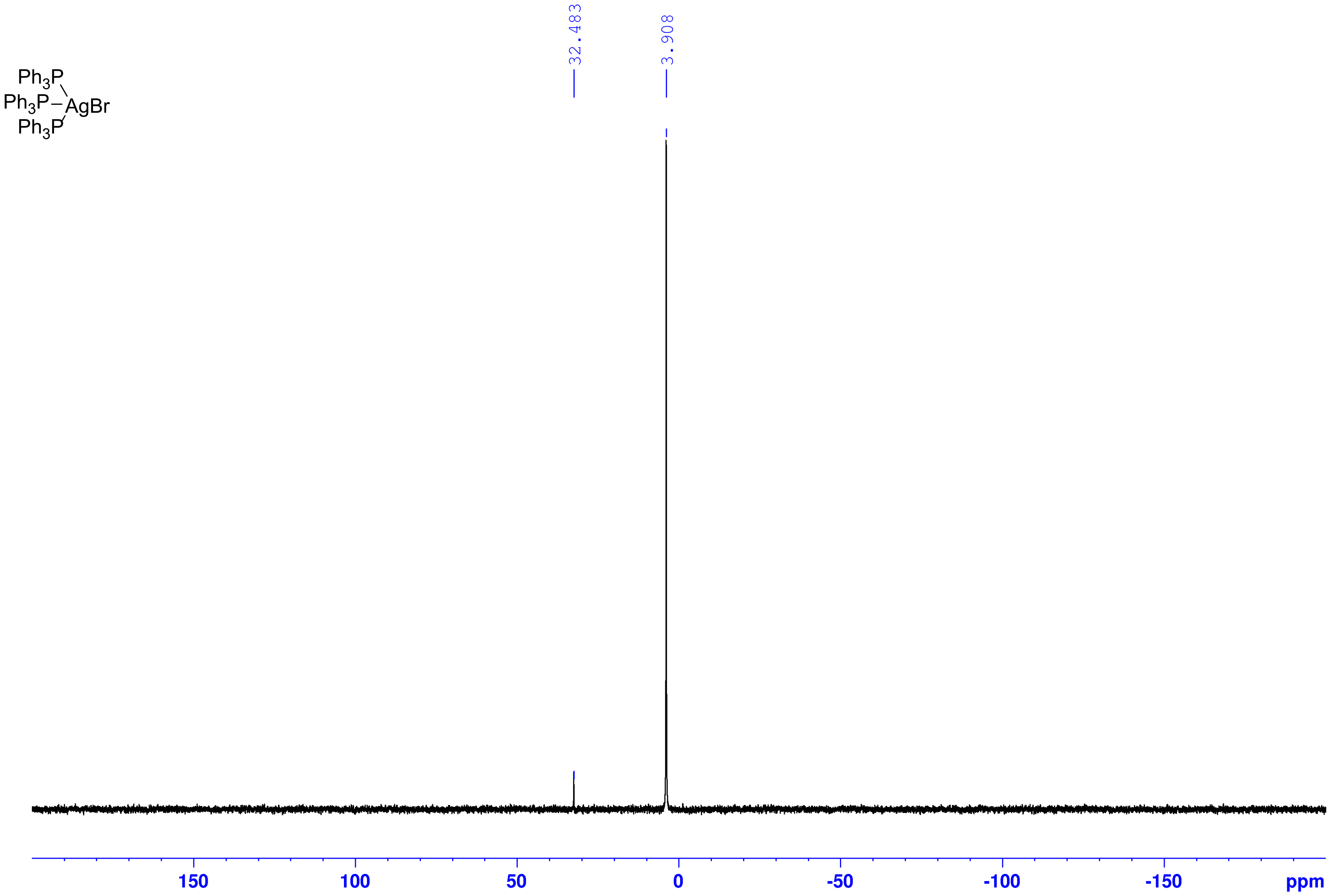
^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 7.84 – 7.75 (m, 3H, both isomers), 7.69 – 7.67 (m, 1H, only *anti*-isomer), 7.61 – 7.57 (m, 1H, only *syn*-isomer), 7.50 – 7.40 (m, 2H, both isomers), 7.37 – 7.32 (m, 1H, both isomers), 2.99 – 2.83 (m, 1H, CH, both isomers), 2.14 – 1.74 (m, 2H, CH_2, both isomers). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –125.3 (td, J = 17.5, 7.3 Hz, *syn*-isomer), –146.4 (ddd, J = 17.4, 8.7, 2.4 Hz, *anti*-isomer). **^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ:** 133.4 (s, C-arom), 133.3 (s, C-arom), 133.1 (s, C-arom), 132.8 (s, C-arom), 132.7 (s, C-arom), 131.1 (d, J = 1.9 Hz, C-arom), 128.2, 128.1, 127.8, 127.8, 127.7, 127.3, 127.3, 127.2, 126.8, 126.8, 126.4, 126.1, 126.0 (aromatic CH are overlapped for both isomers therefor it is unclear where are singlets and where are doublets), 86.1 (d, J = 301.8 Hz, CF), 80.6 (d, J = 302.2 Hz, CF), 33.5 (d, J = 10.8 Hz, CH), 30.8 (d, J = 11.0 Hz, CH), 22.8 (d, J = 10.3 Hz, CH_2), 22.0 (d, J = 10.6 Hz, CH_2). **Anal. calcd for $C_{13}H_{10}BrF$:** C, 58.89%; H, 3.80%. Found: C, 58.73%; H, 3.96%.

3.Copies of ^{1}H, ^{19}F, ^{31}P{^{1}H}, ^{13}C{^{1}H}-NMR spectra

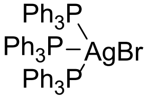
^{1}H NMR (300.1 MHz, CDCl$_3$) of (PPh$_3$)$_3$AgBr

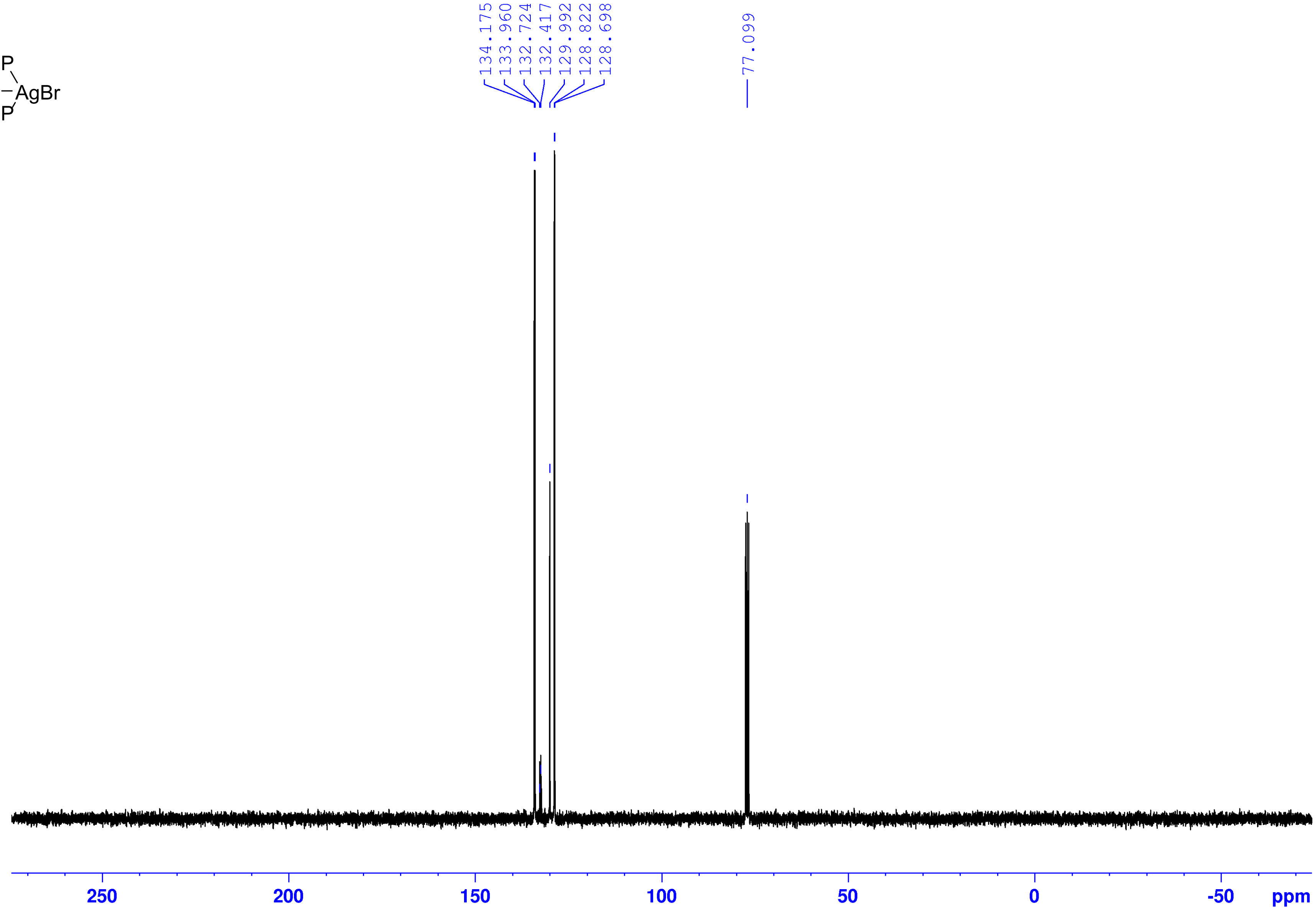


^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$) of (PPh$_3$)$_3$AgBr

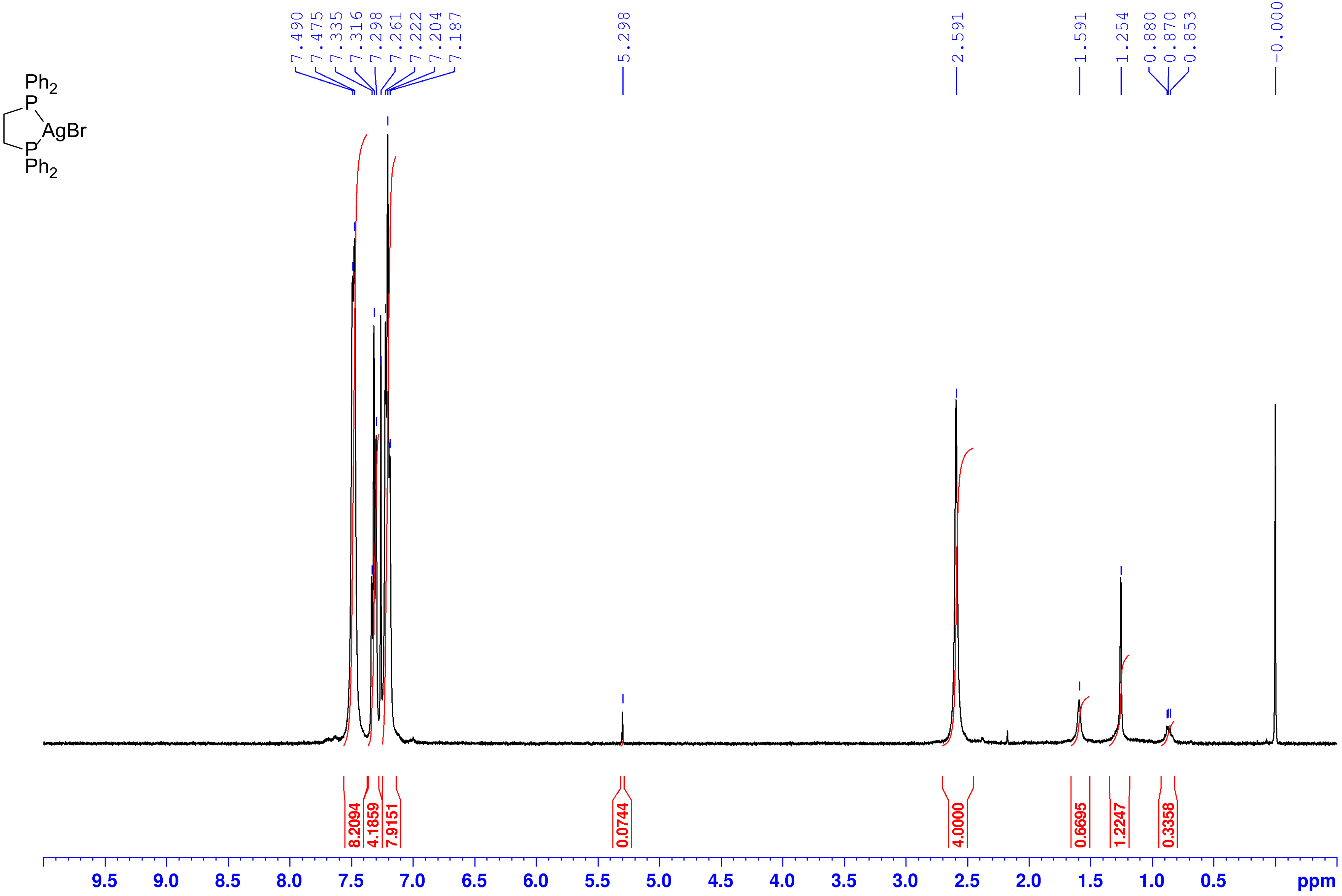


$^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$) of $(PPh_3)_3AgBr$

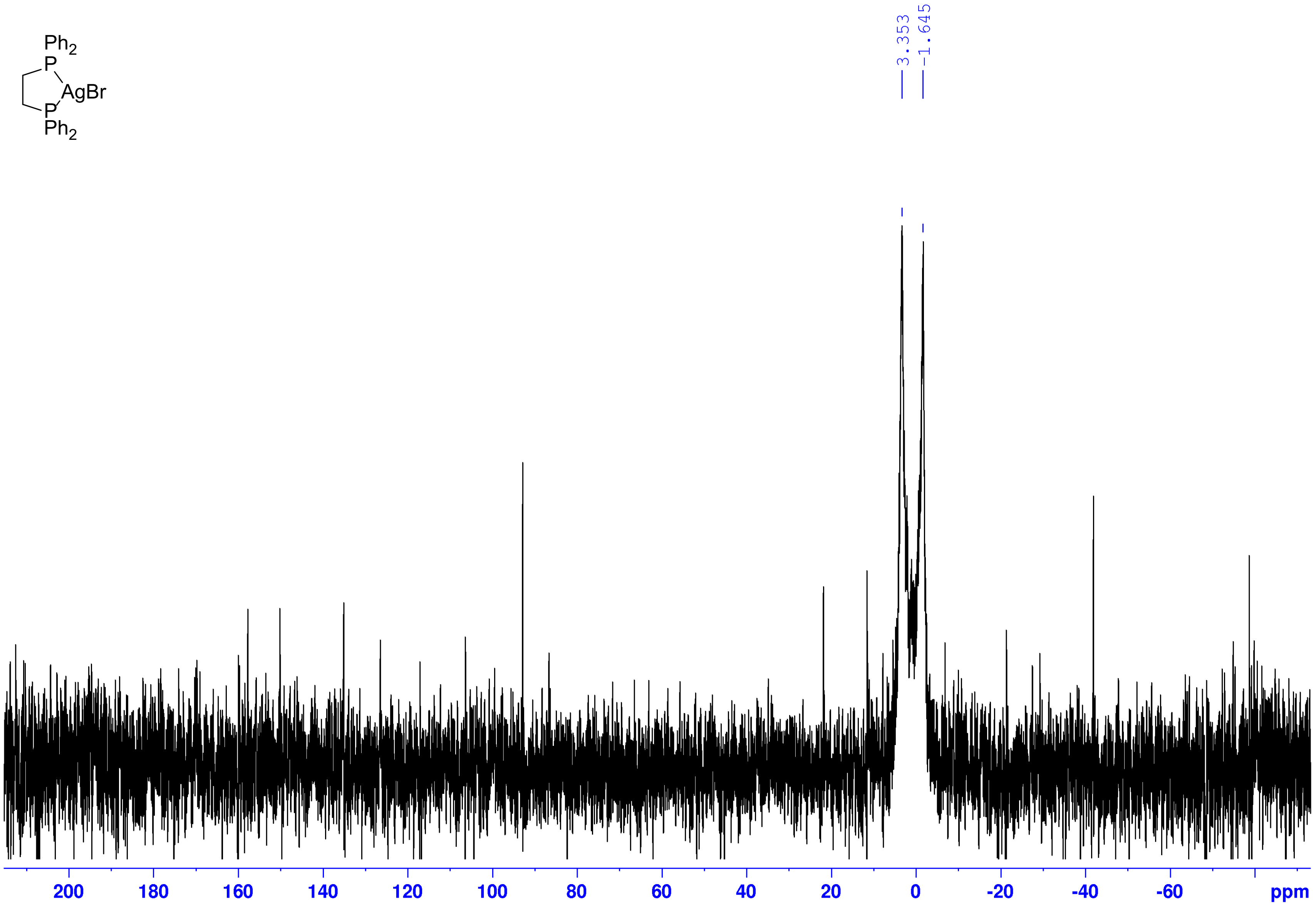




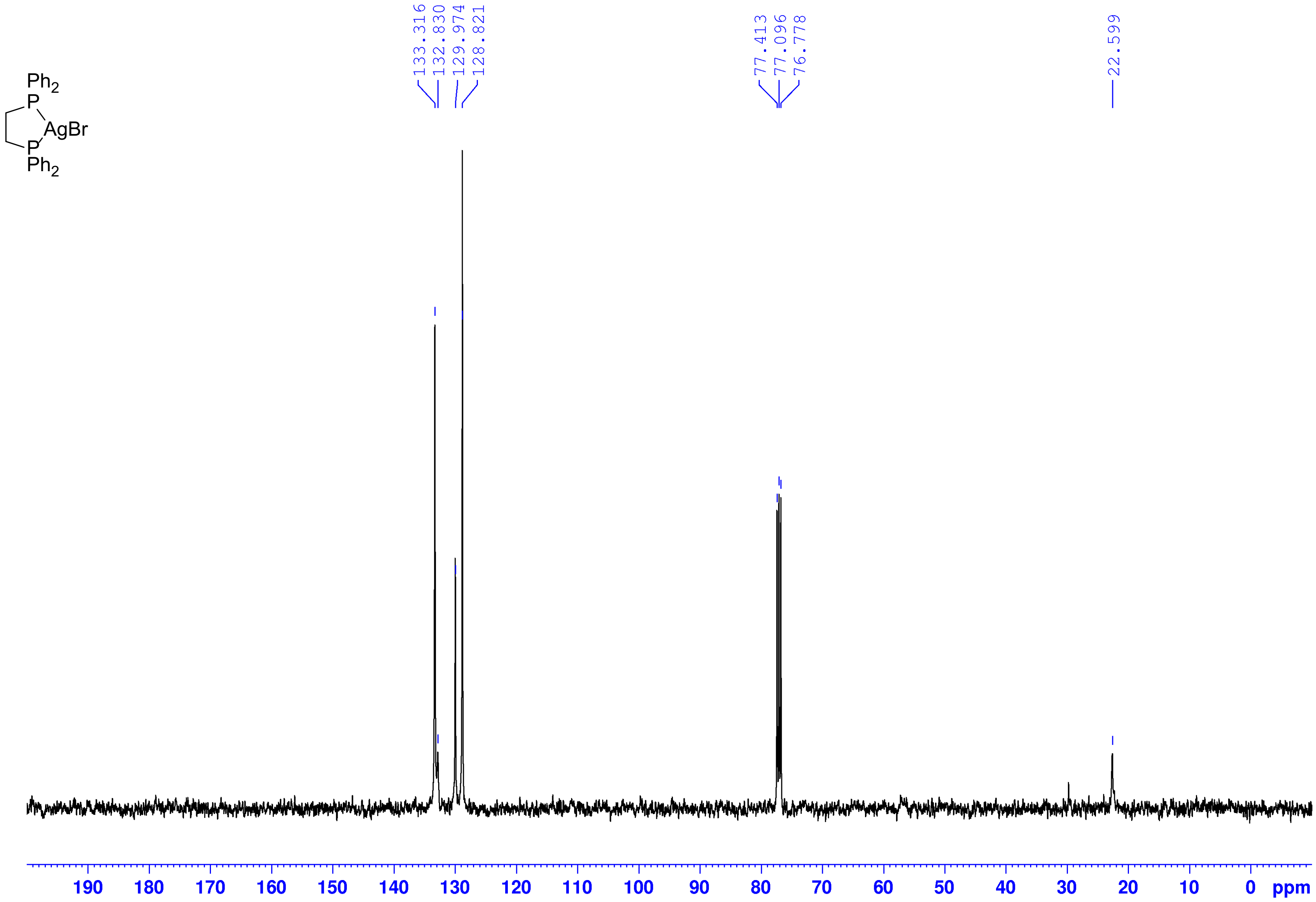
^{1}H NMR (400.0 MHz, $CDCl_3$) of (dppe)AgBr



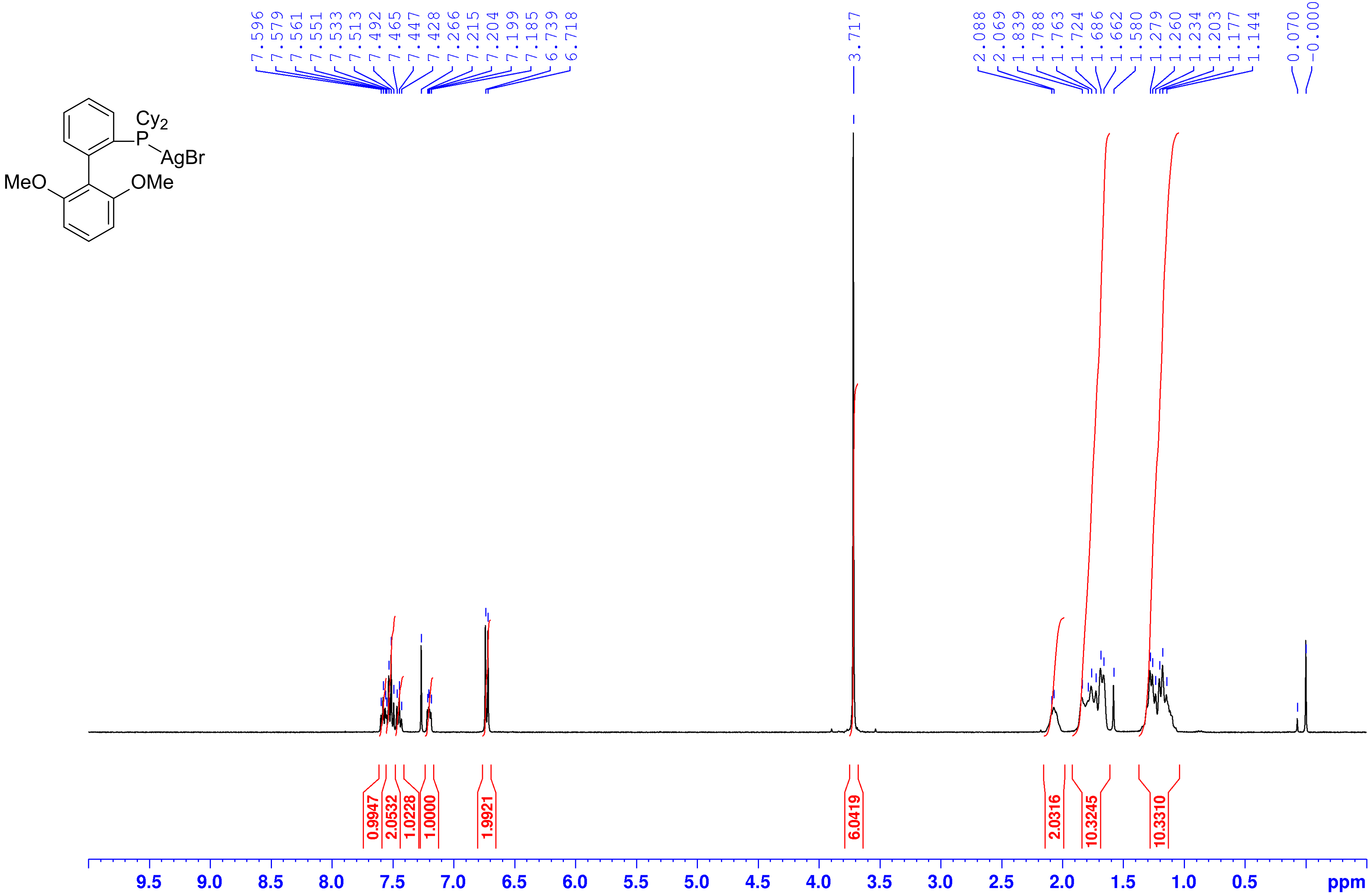
$^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$) of (dppe)AgBr



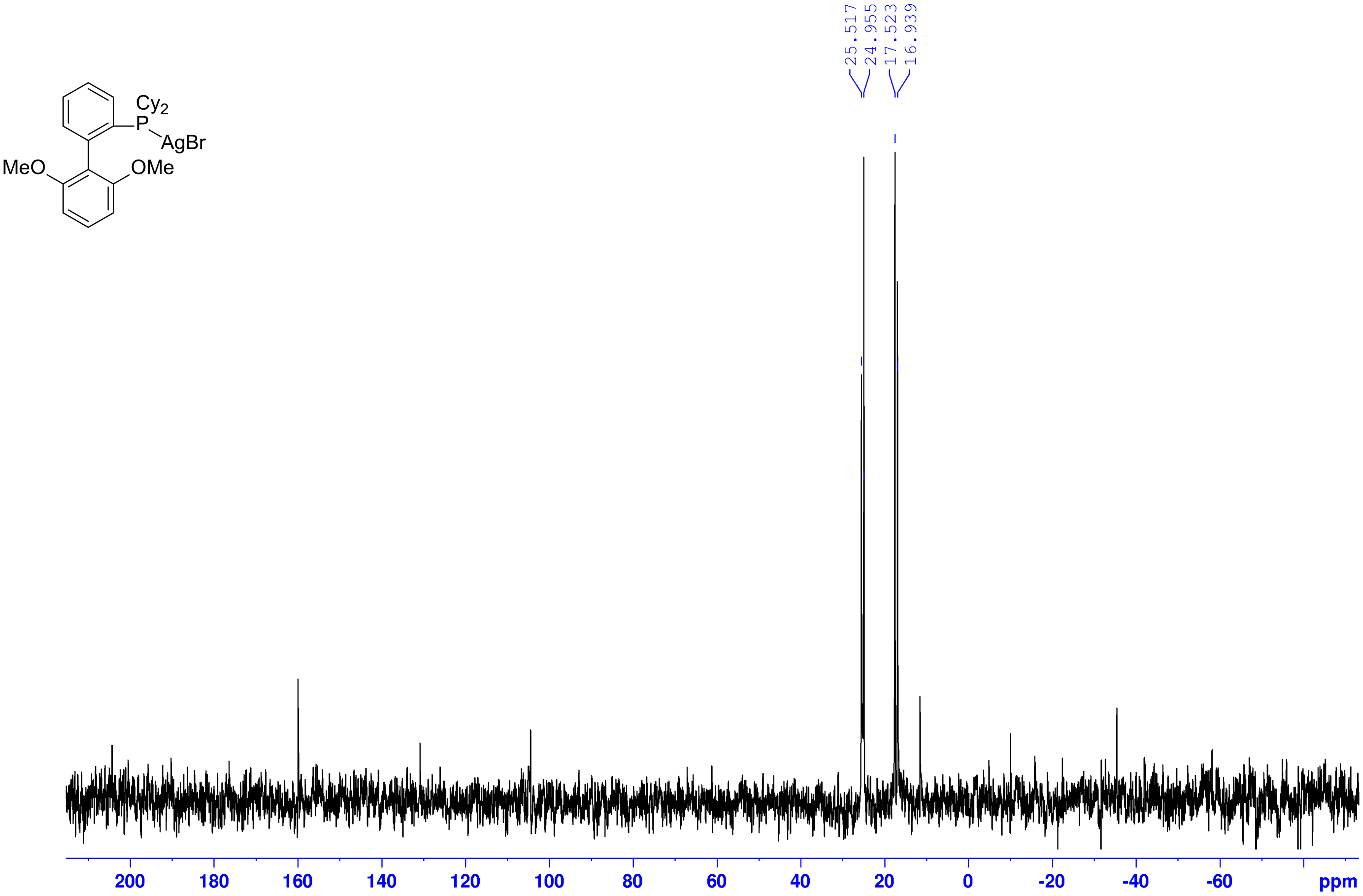
^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) of (dppe)AgBr



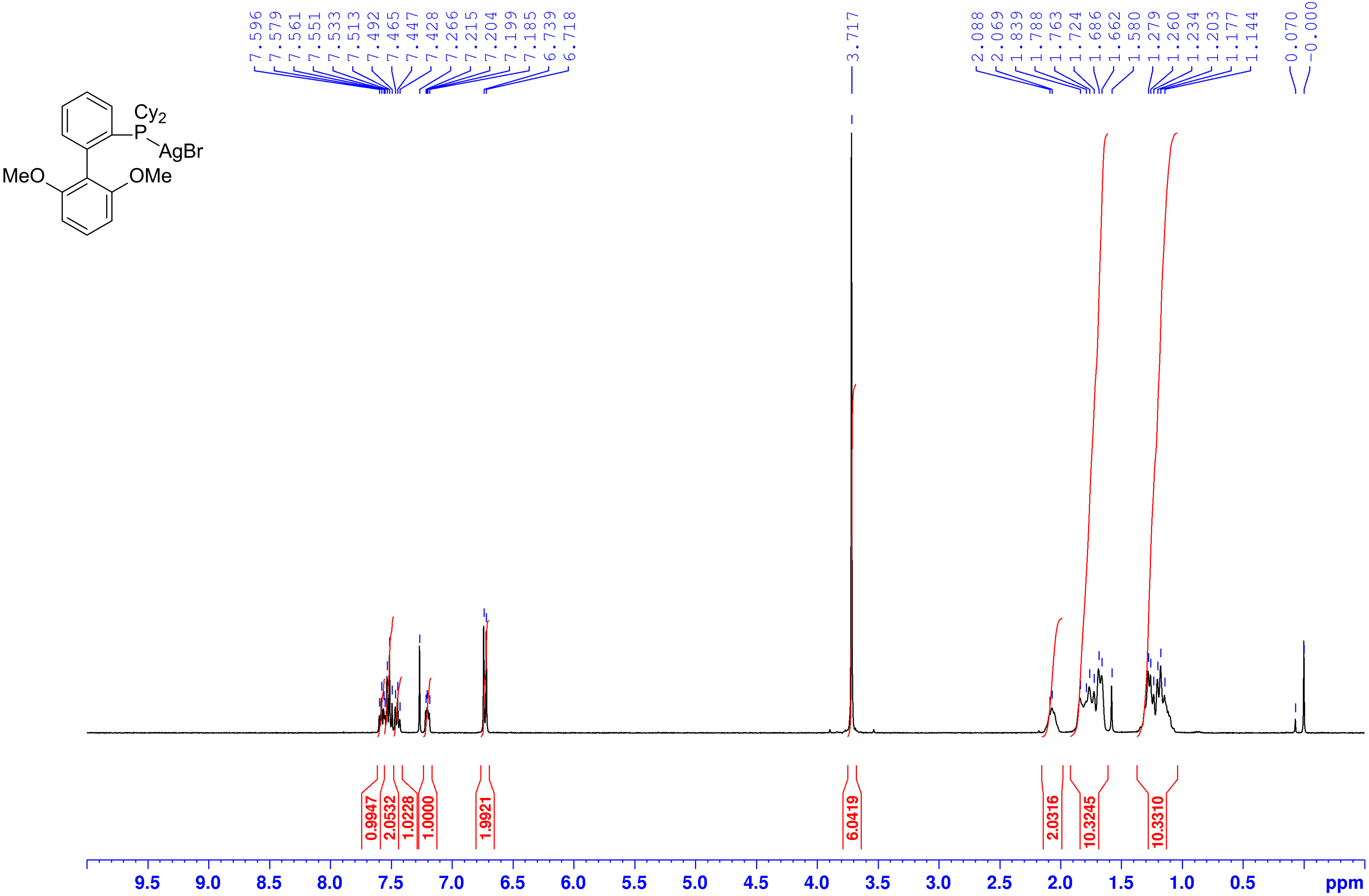
^{1}H NMR (400.0 MHz, $CDCl_3$) of (SPhos)AgBr



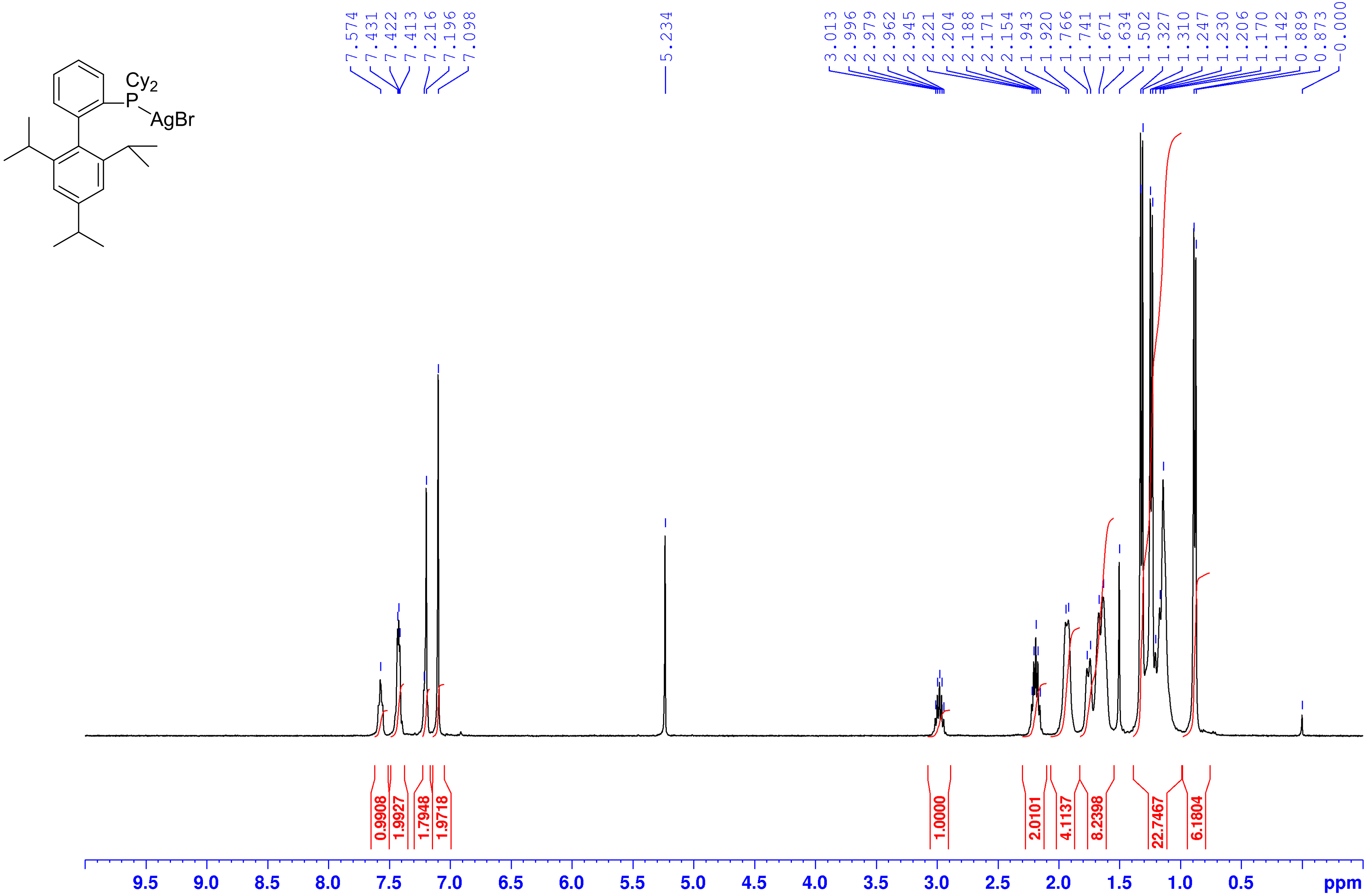
$^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$) of (SPhos)AgBr



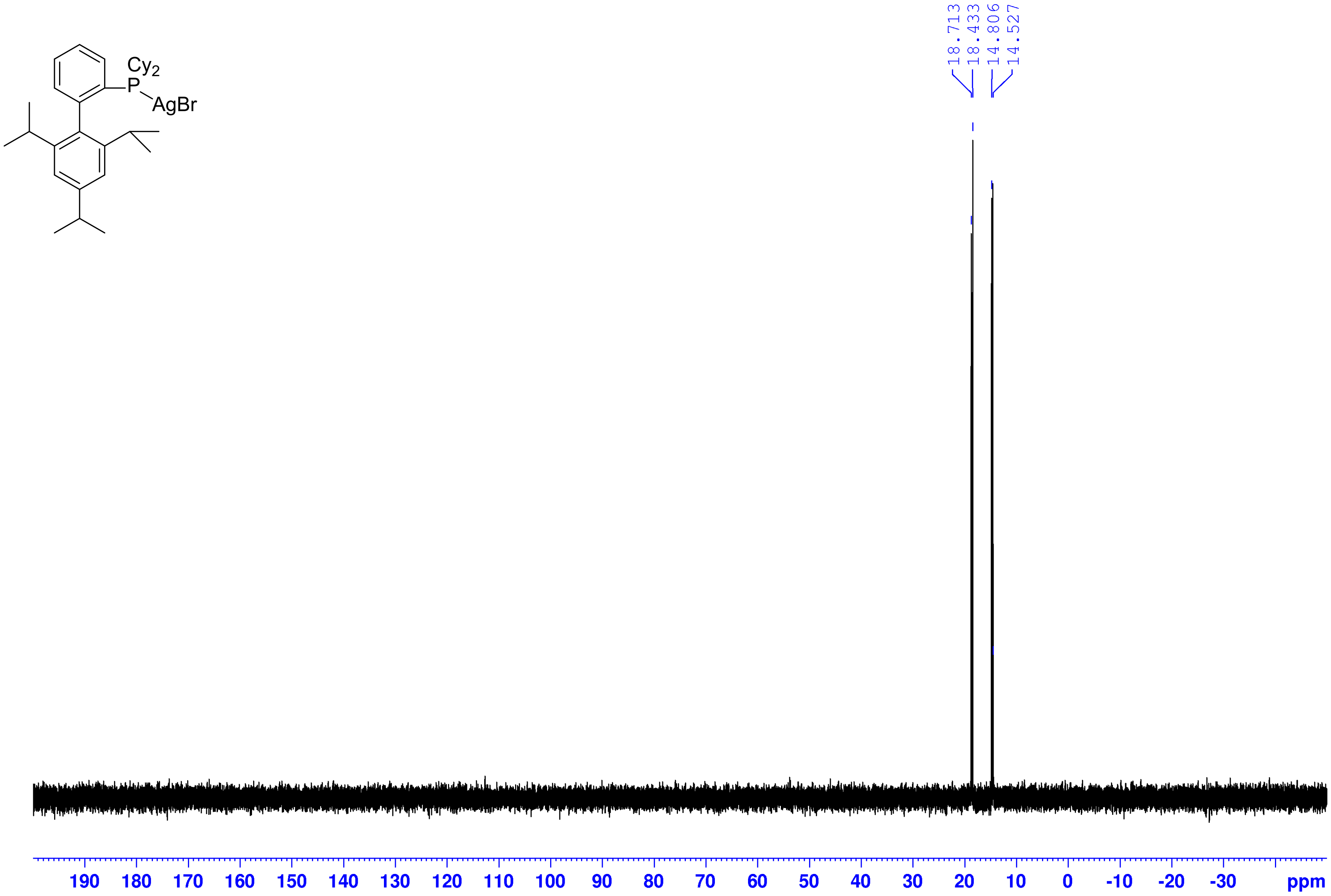
$^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) of (SPhos)AgBr



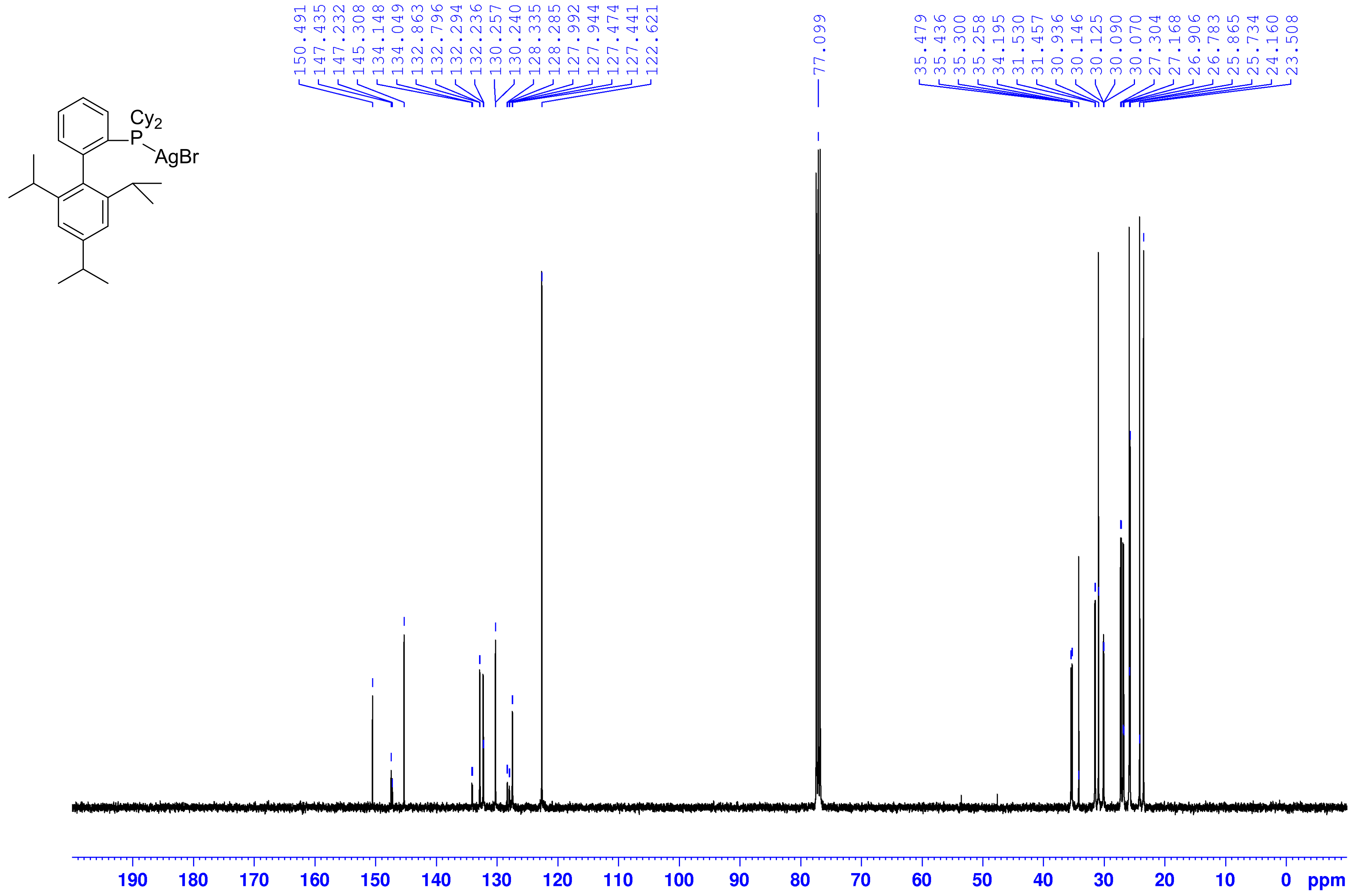
^{1}H NMR (400.0 MHz, $CDCl_3$) of (XPhos)AgBr



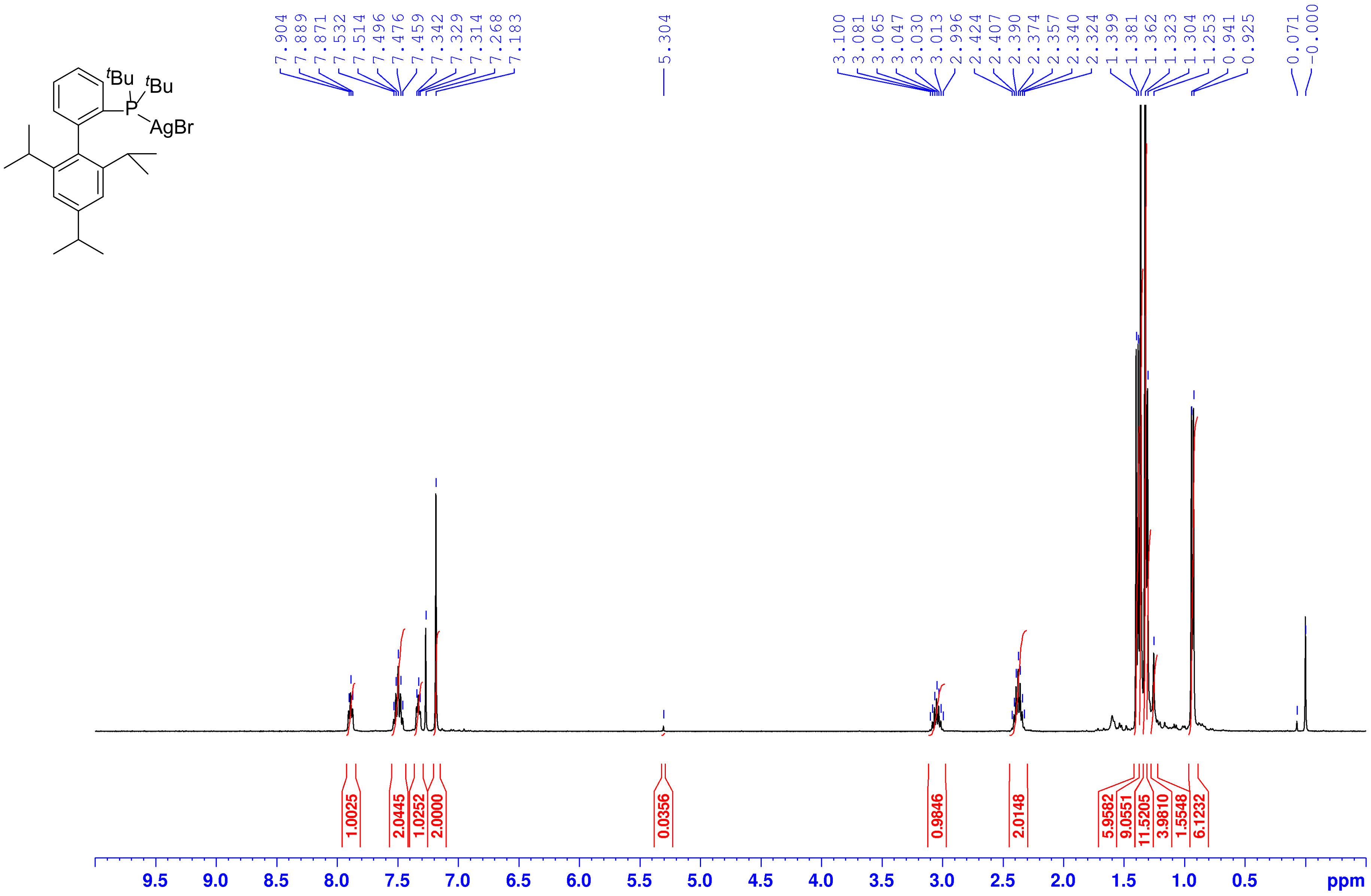
^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$) of (XPhos)AgBr



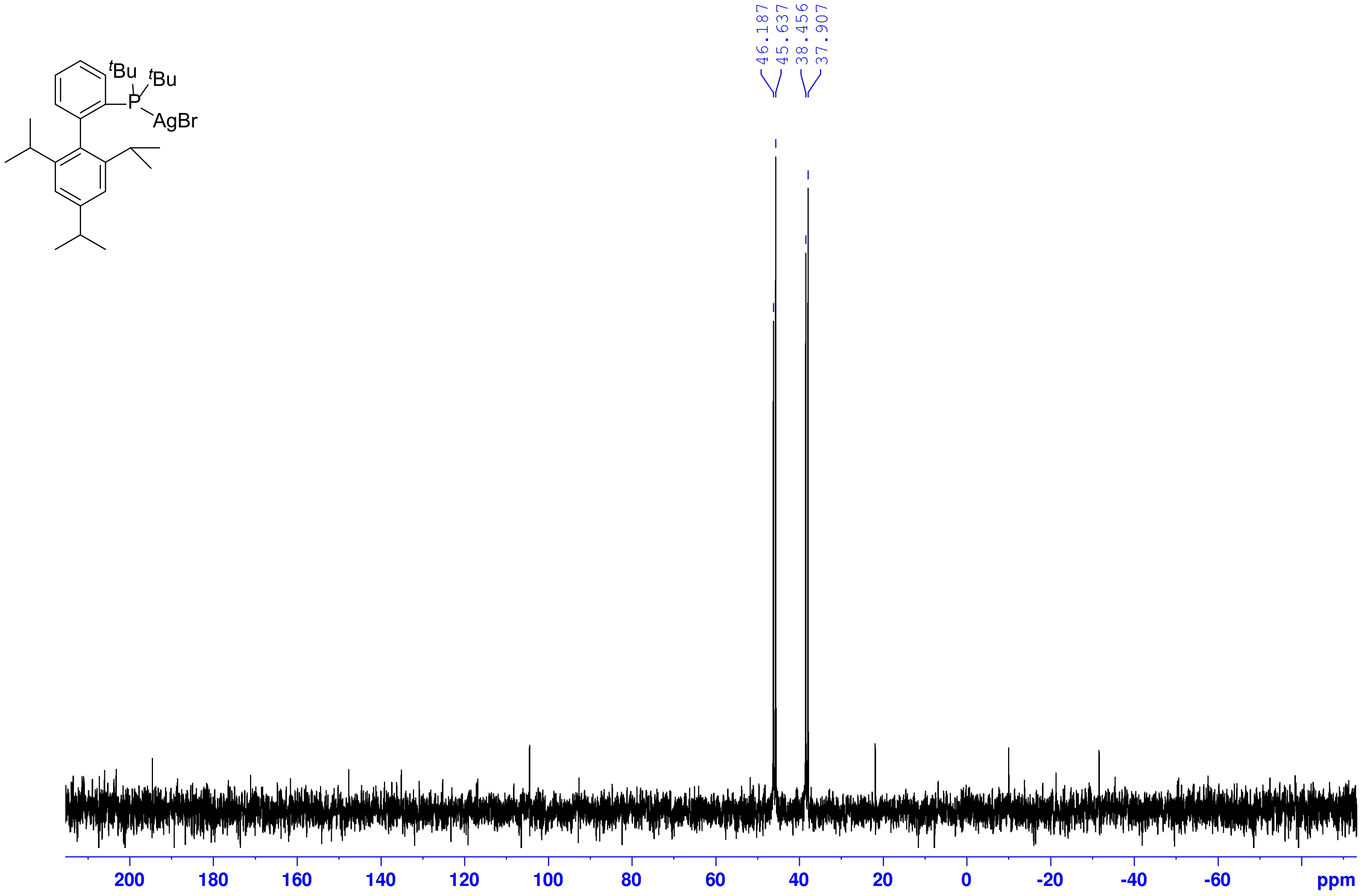
^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) of (XPhos)AgBr



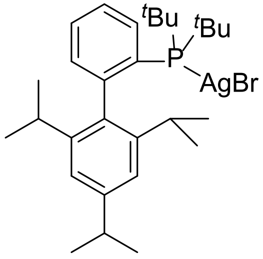
^{1}H NMR (400.0 MHz, CDCl$_3$) of (Bu^{t}XPhos)AgBr

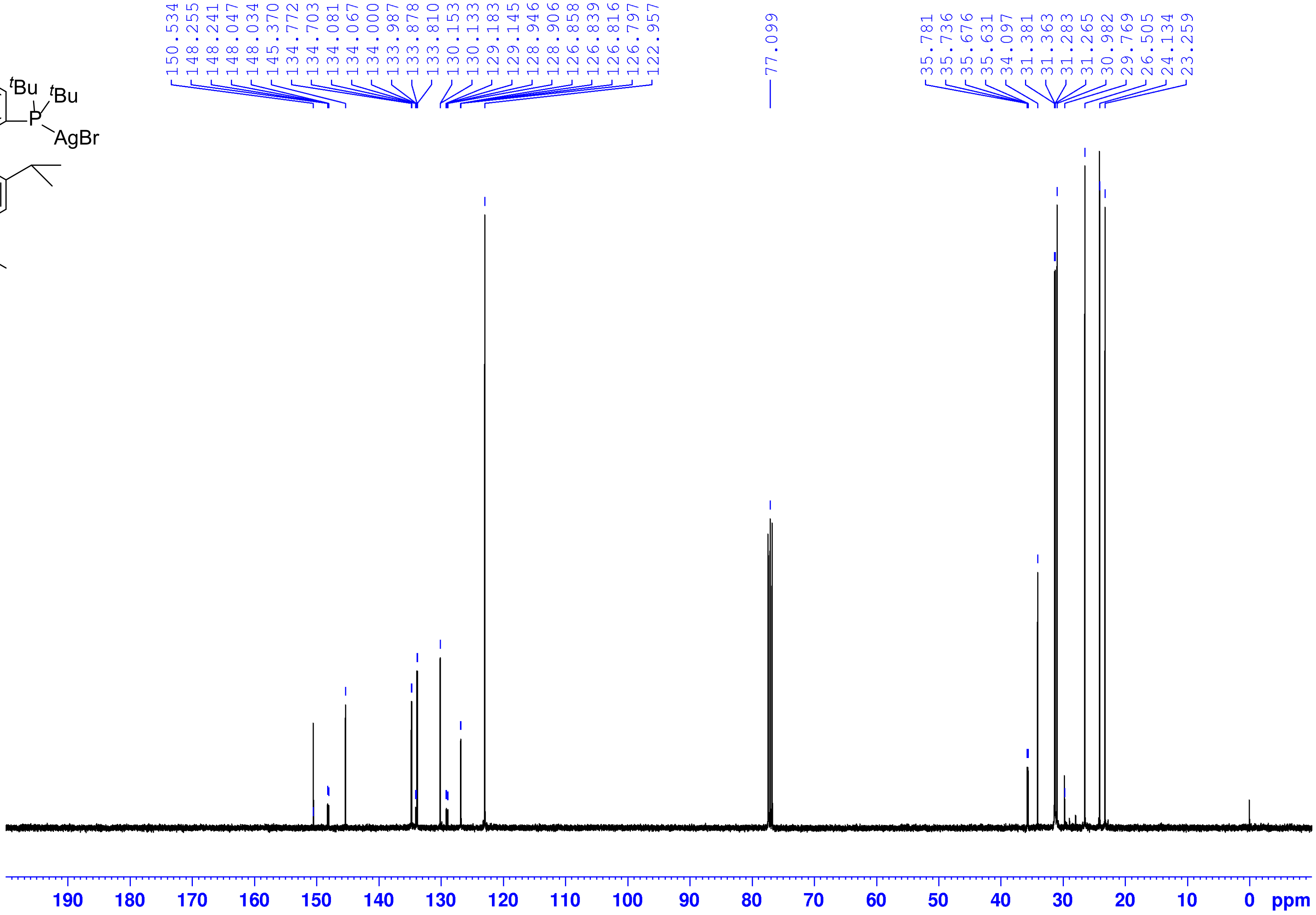


^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$) of (Bu^{t}XPhos)AgBr

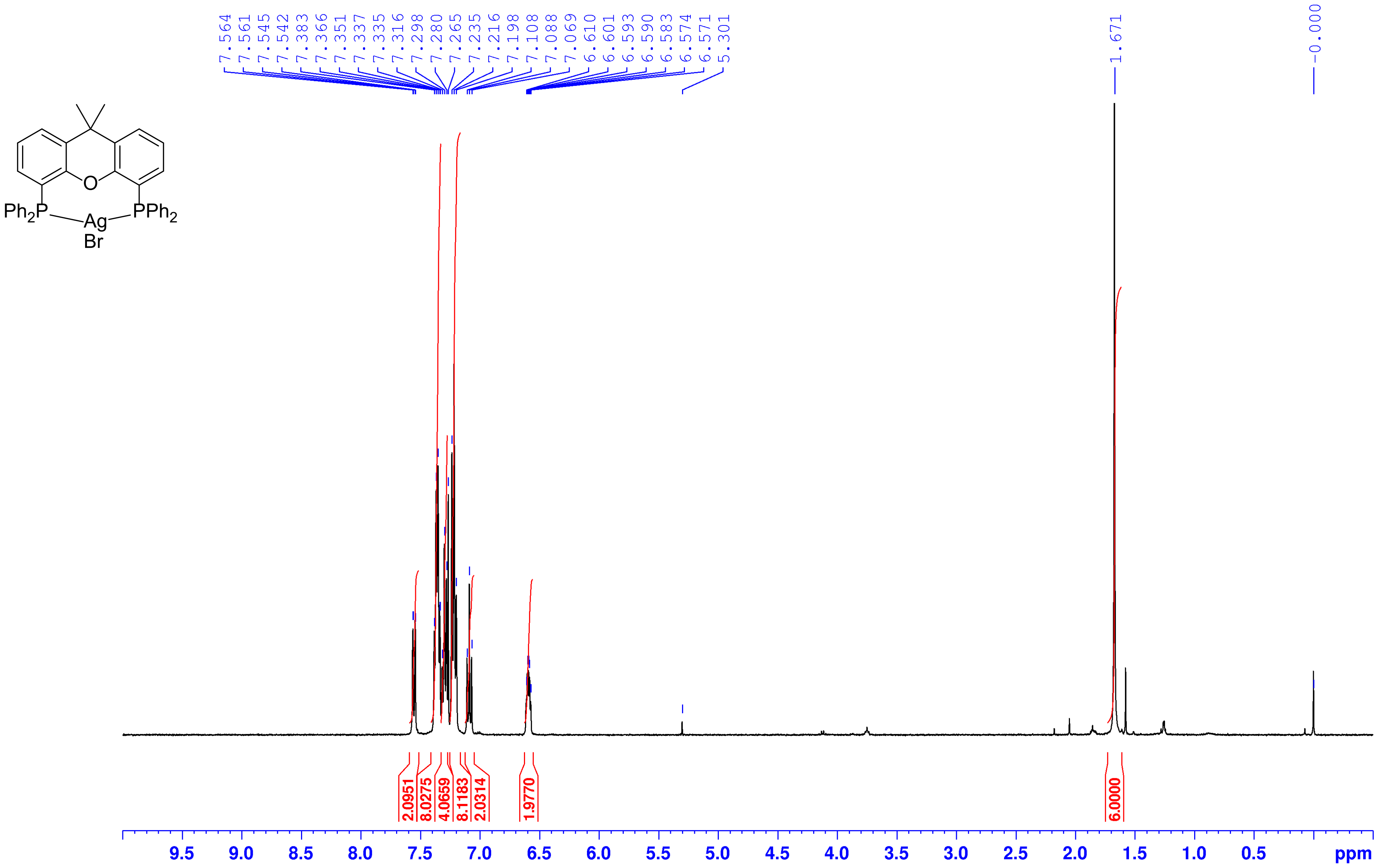


^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) of (Bu^{t}XPhos)AgBr

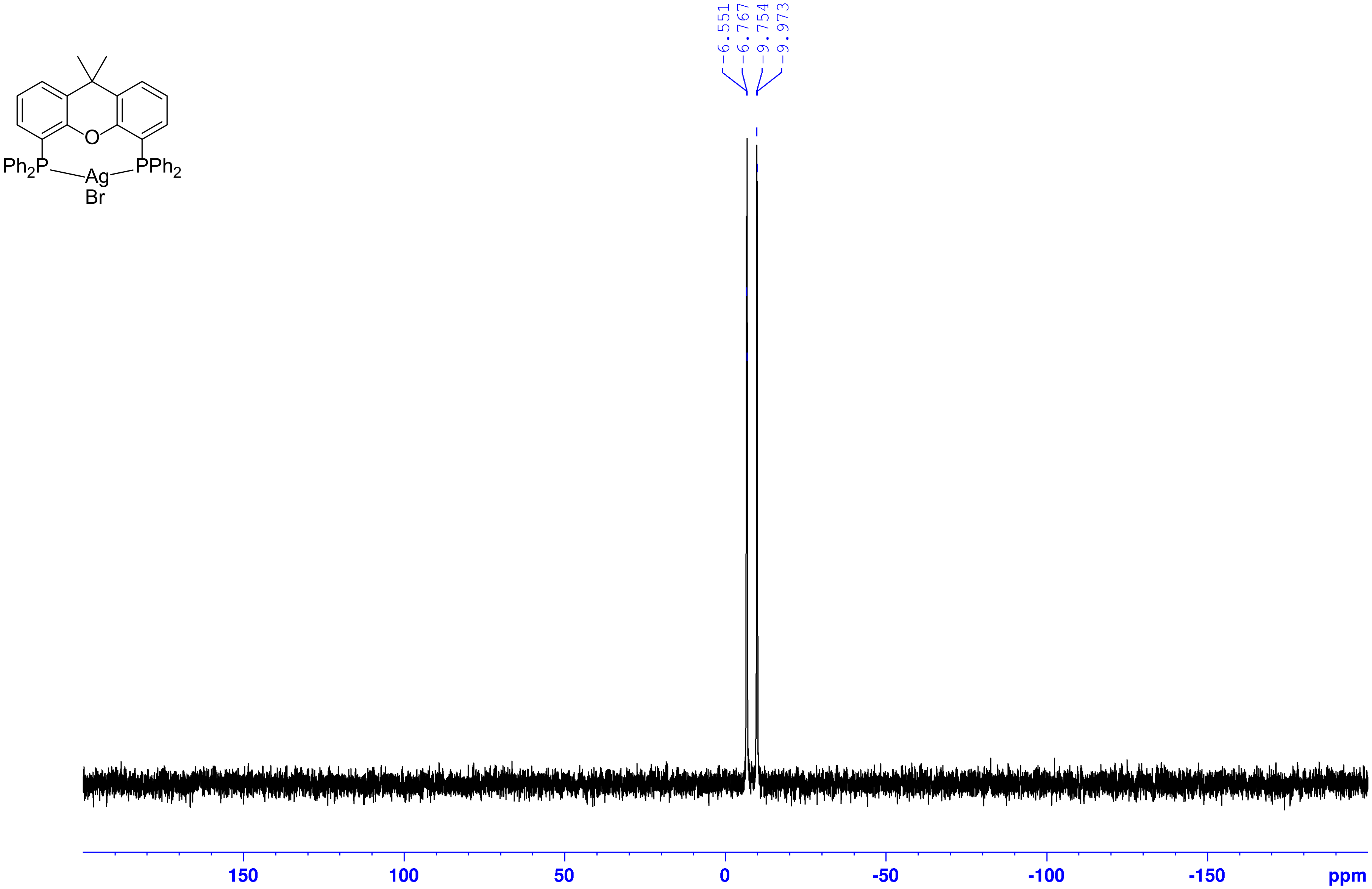




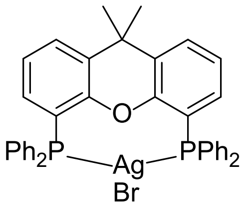
^{1}H NMR (400.0 MHz, CDCl$_3$) of (XantPhos)AgBr

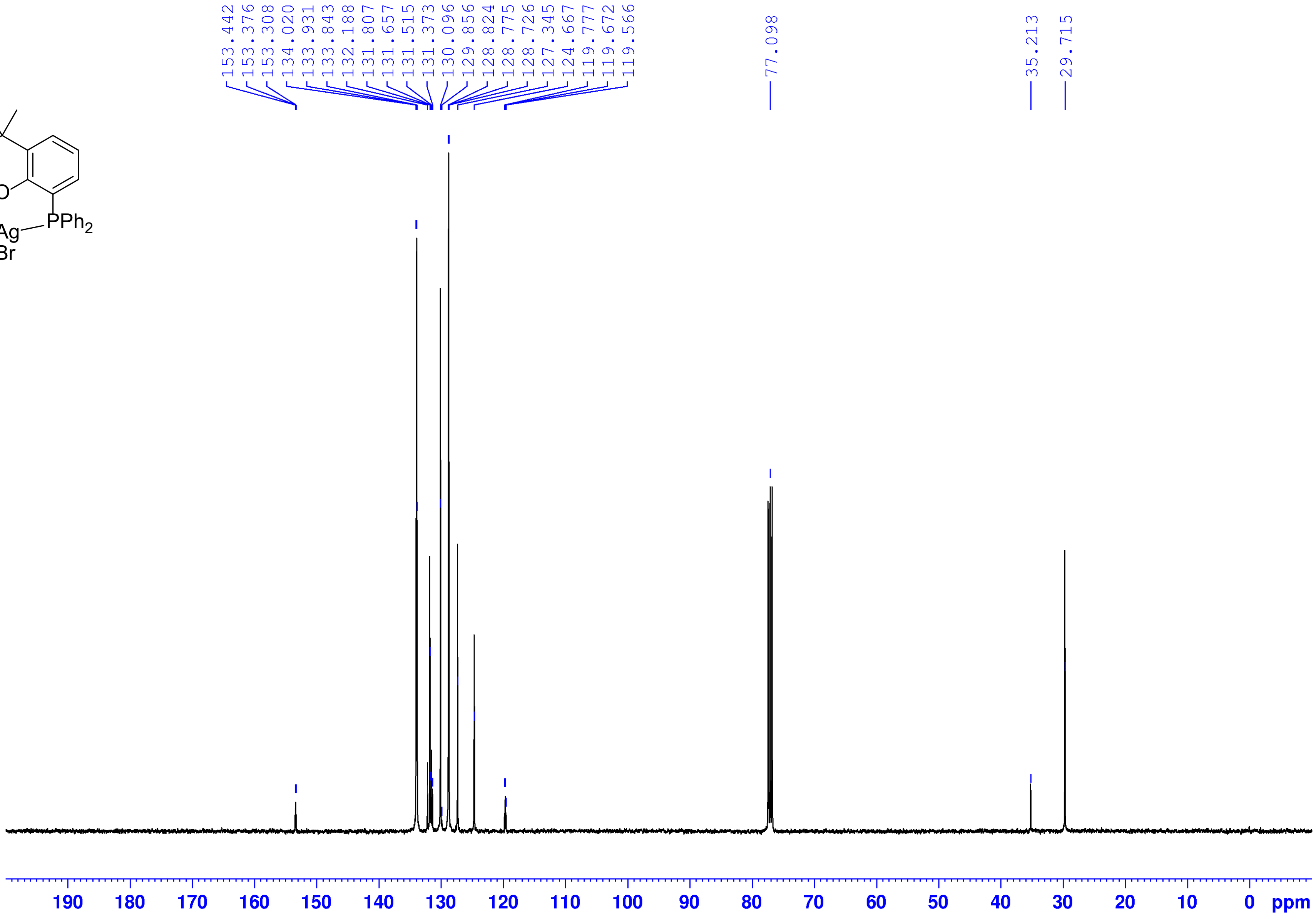


^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$) of (XantPhos)AgBr

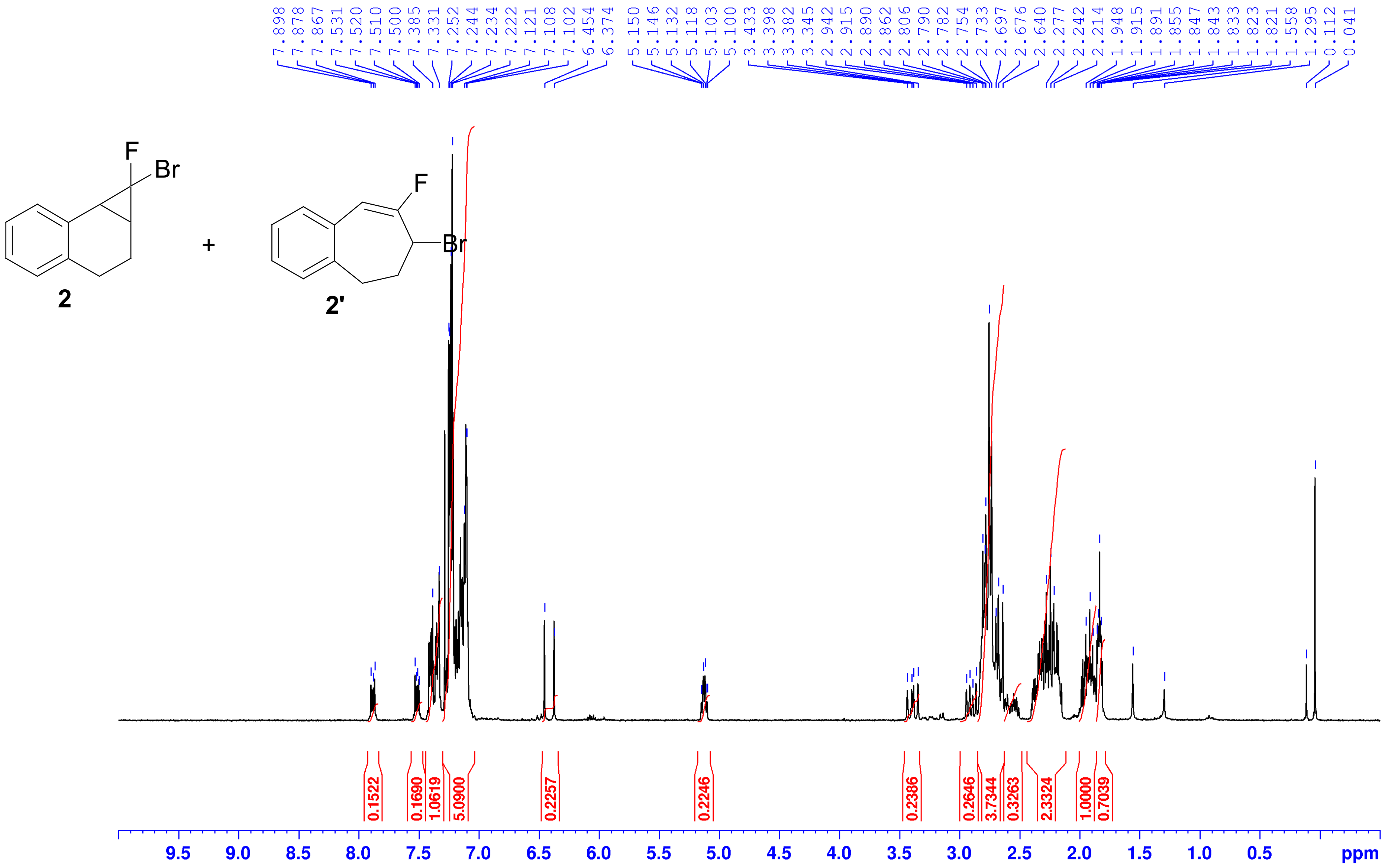


^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) of (XantPhos)AgBr

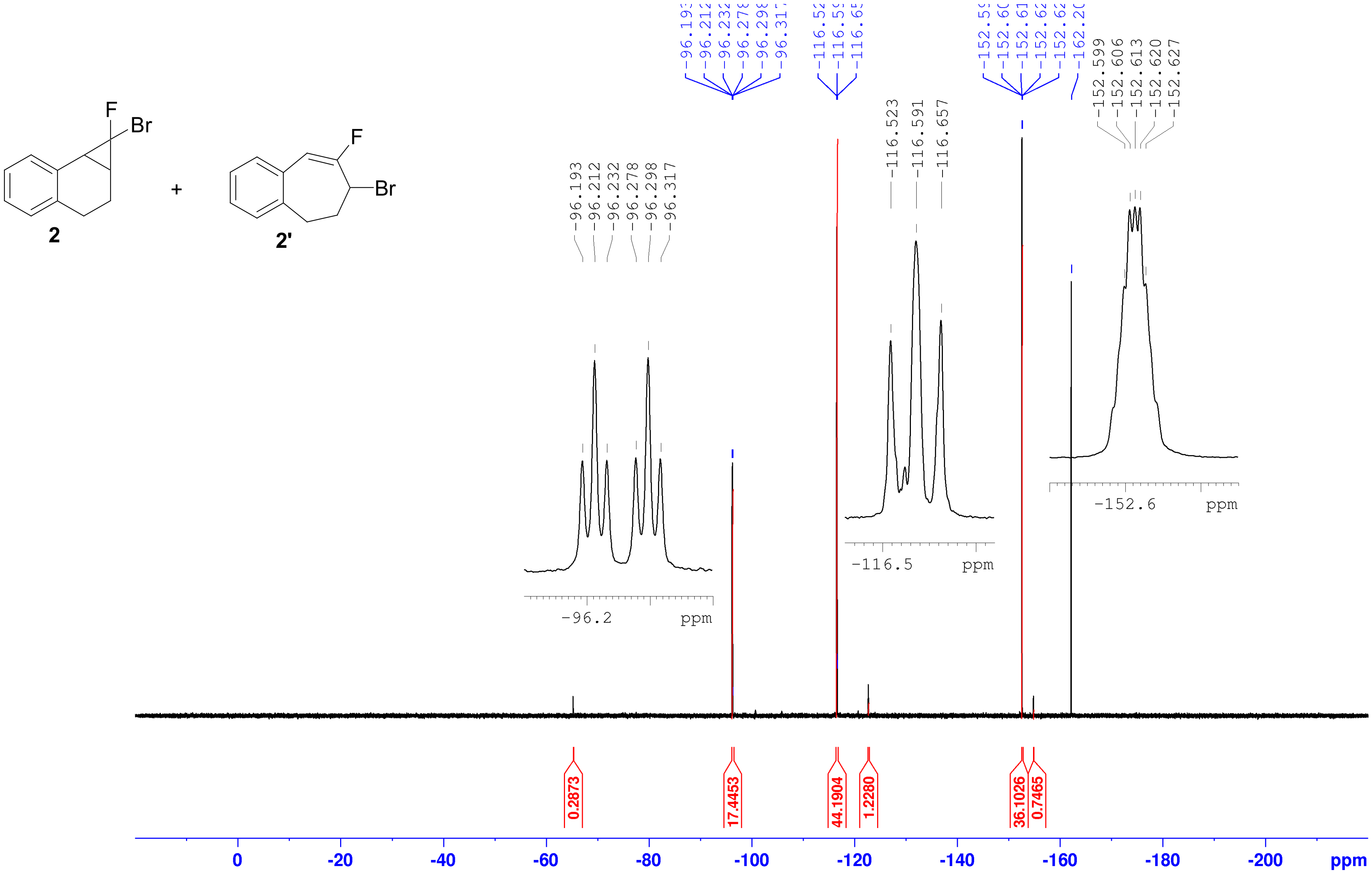




^{1}H NMR (300.1 MHz, $CDCl_3$) of 2



^{19}F NMR (282.4 MHz, CDCl$_3$) of 2

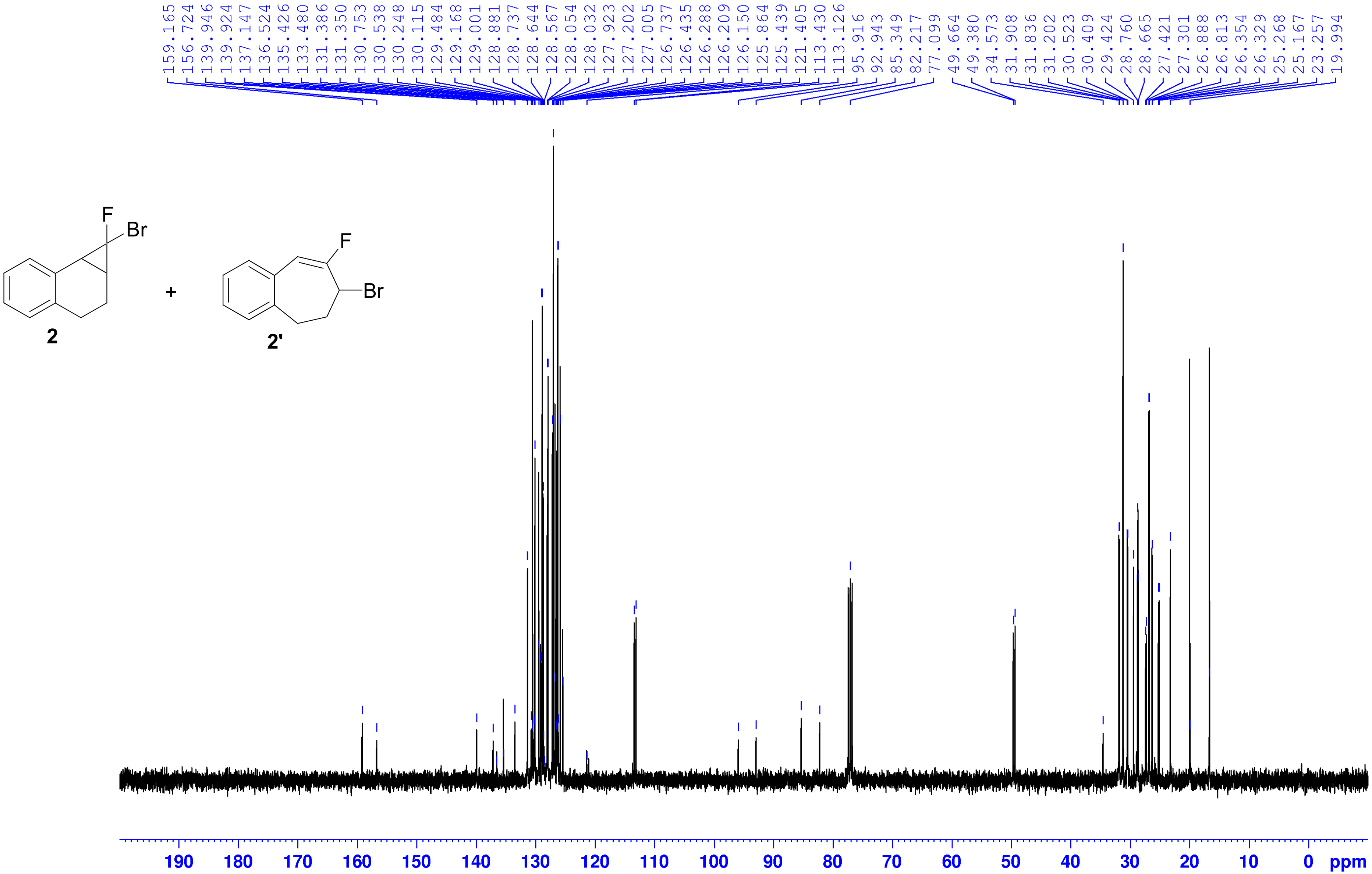


2

+

2'

$^{13}C\{^{1}H\}$ NMR (75.4 MHz, CDCl$_3$) of 2

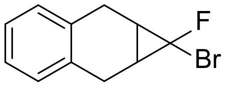


2

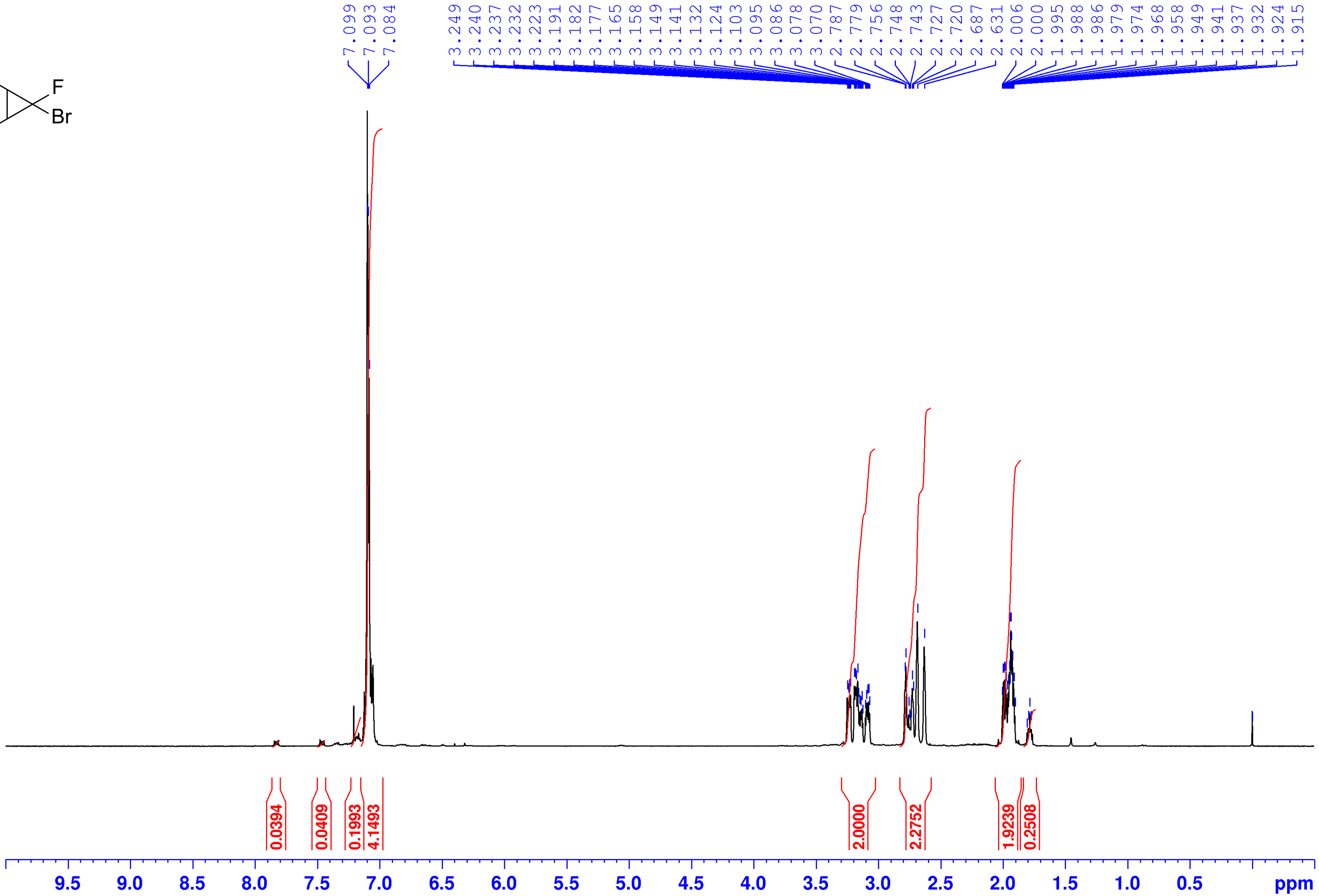
+

2'

^{1}H NMR (300.1 MHz, $CDCl_3$) of 3

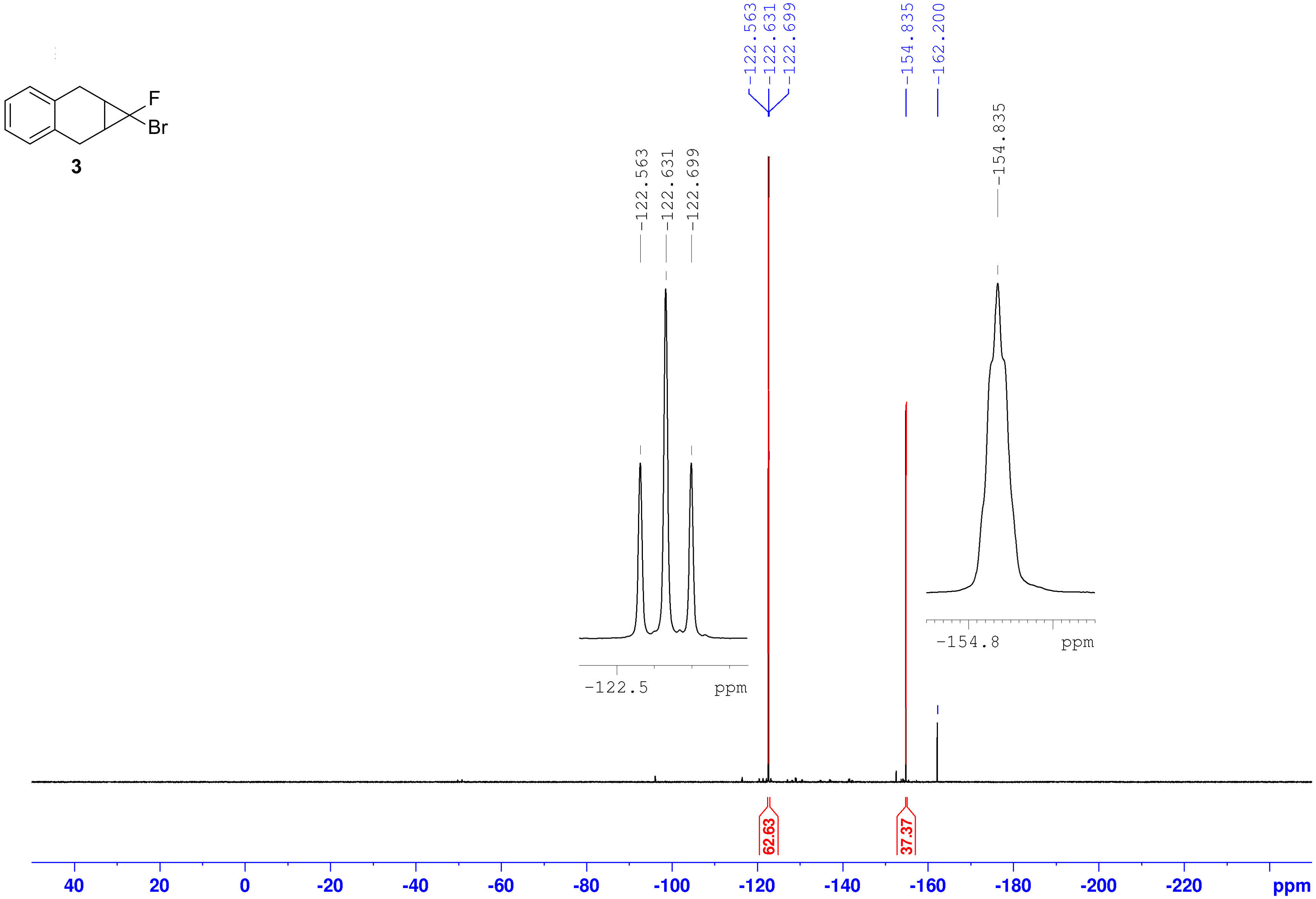


3

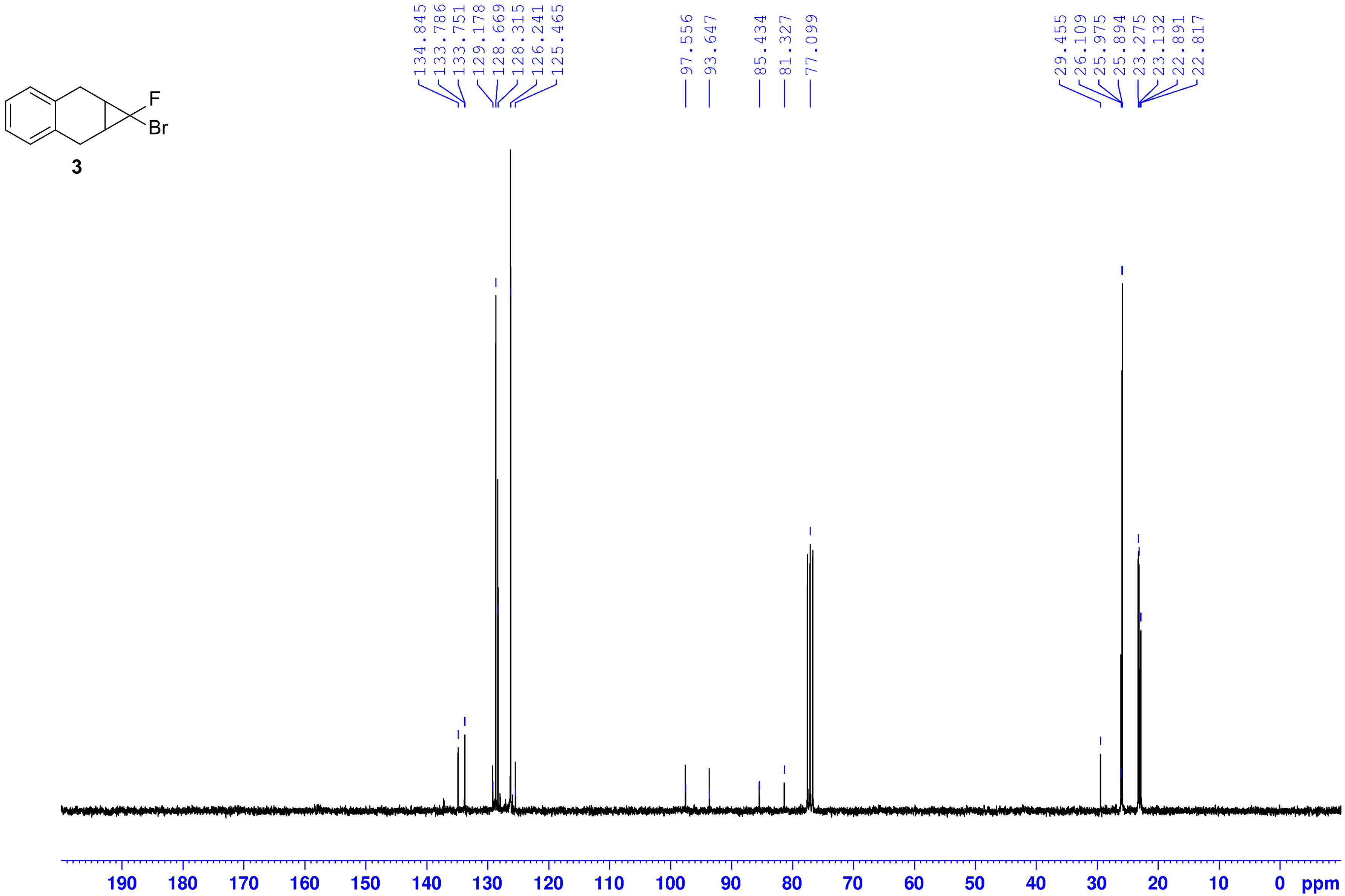


^{19}F NMR (282.4 MHz, CDCl$_3$) of 3

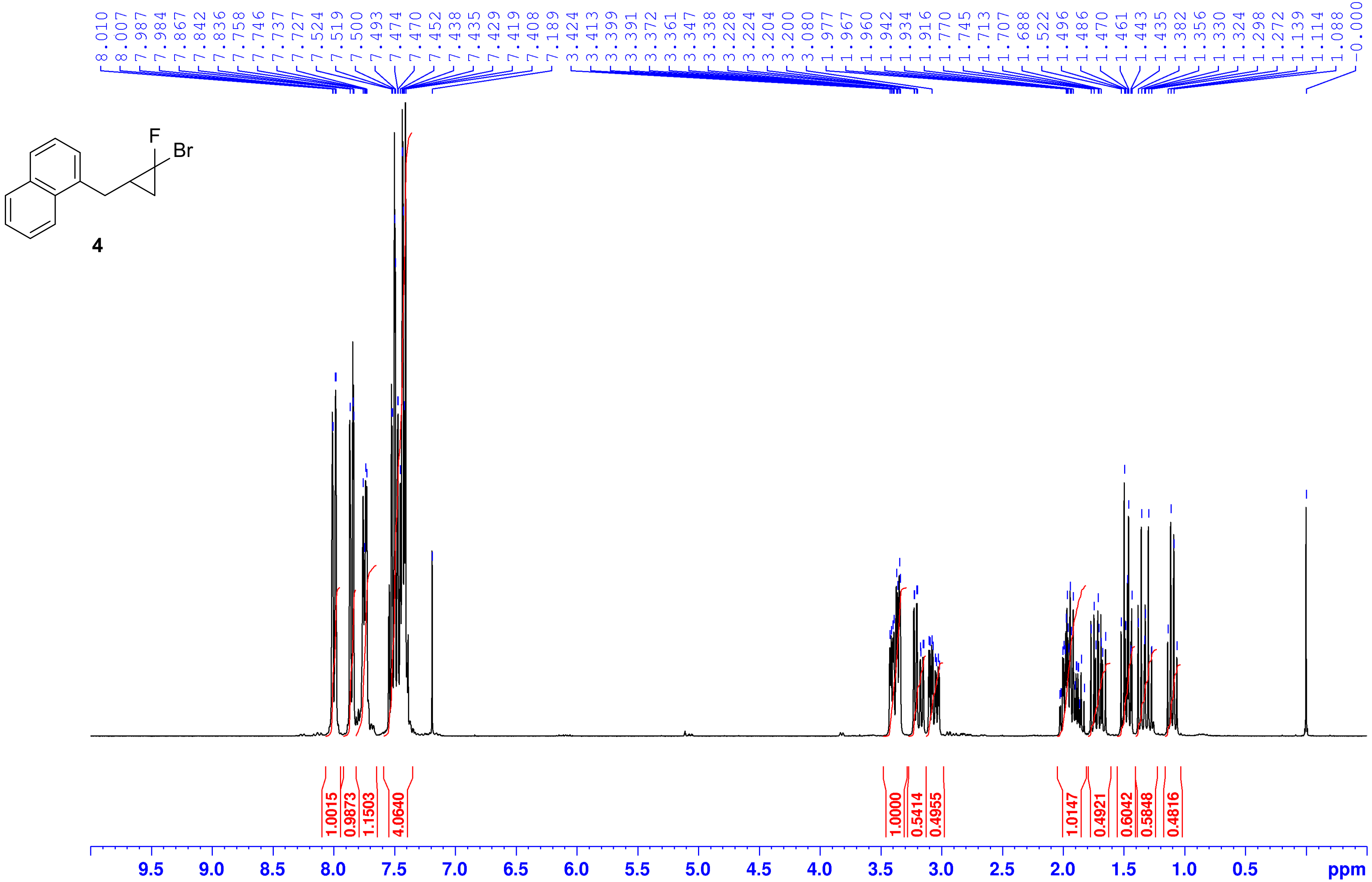
3



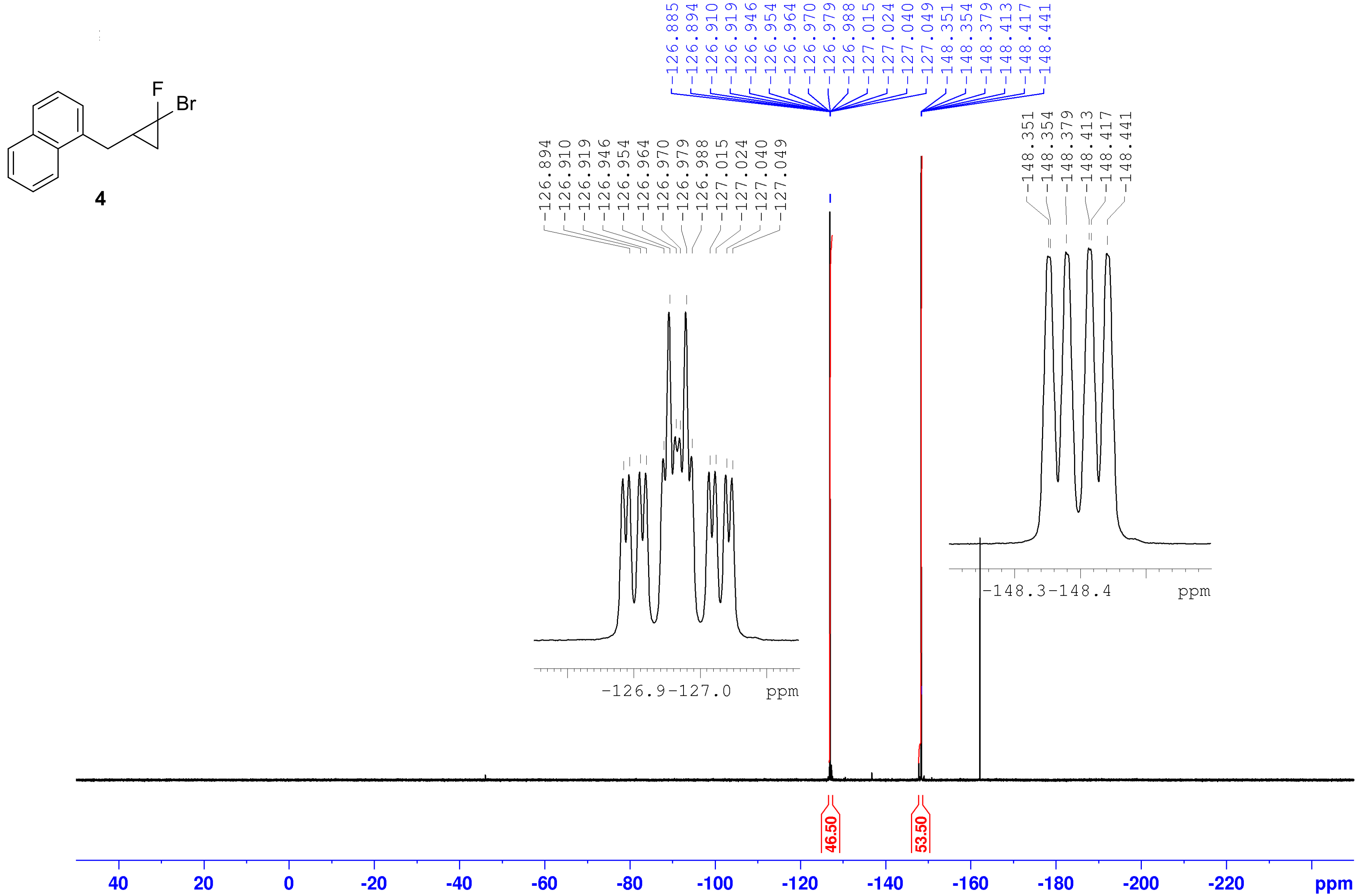
$^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) of 3



^{1}H NMR (300.1 MHz, CDCl$_3$) of 4

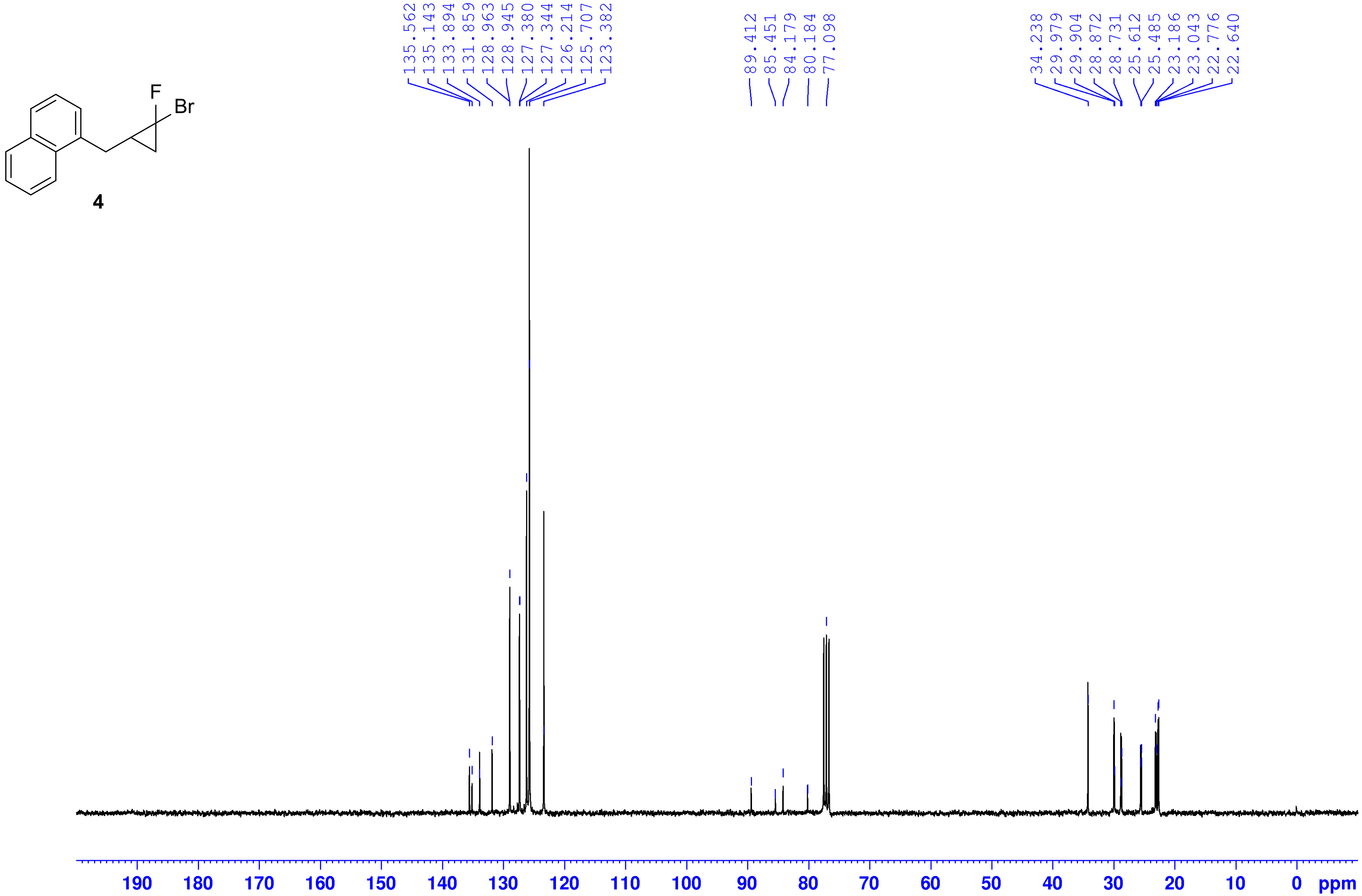


^{19}F NMR (282.4 MHz, CDCl$_3$) of 4



4

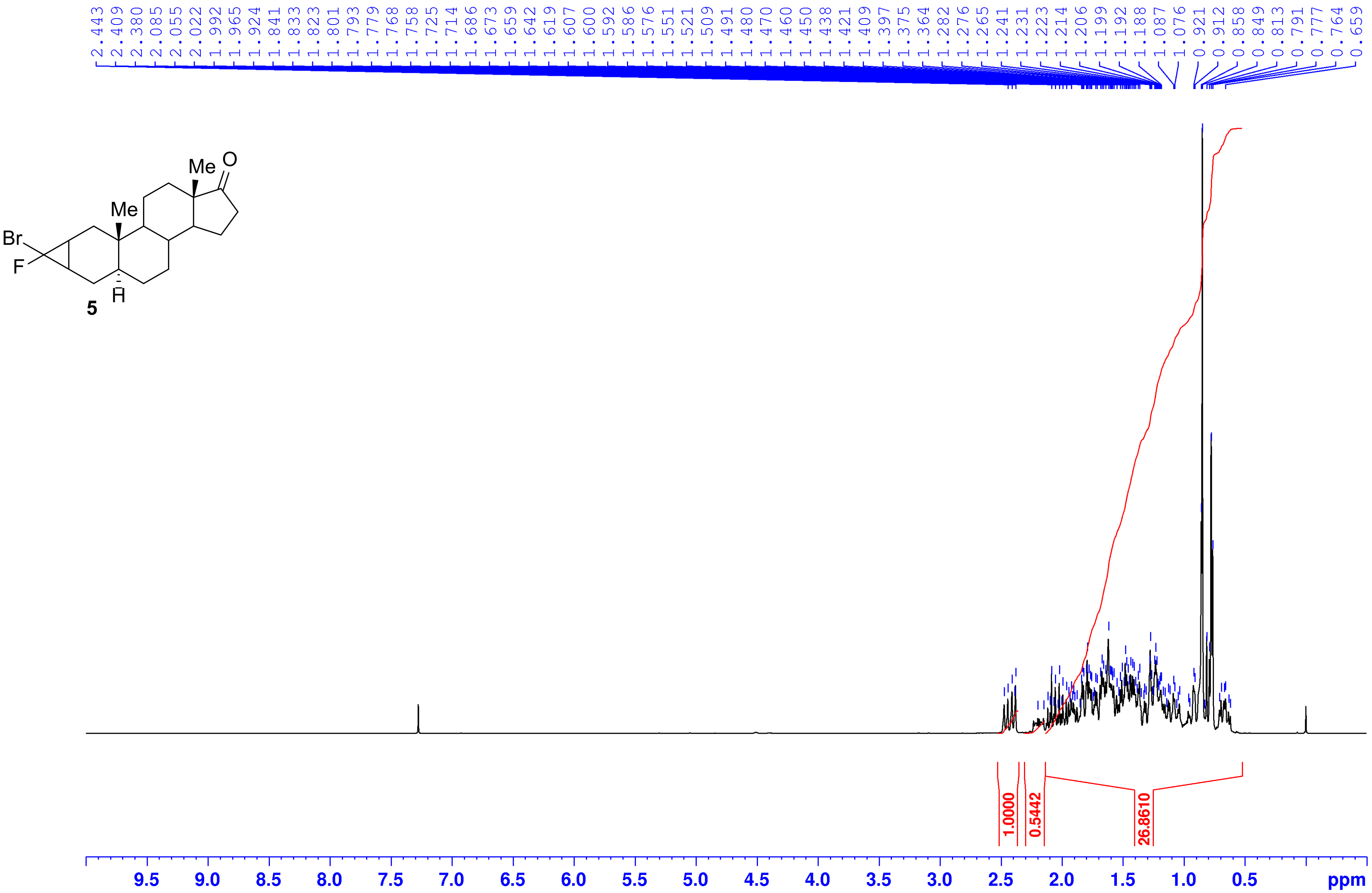
$^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$) of 4



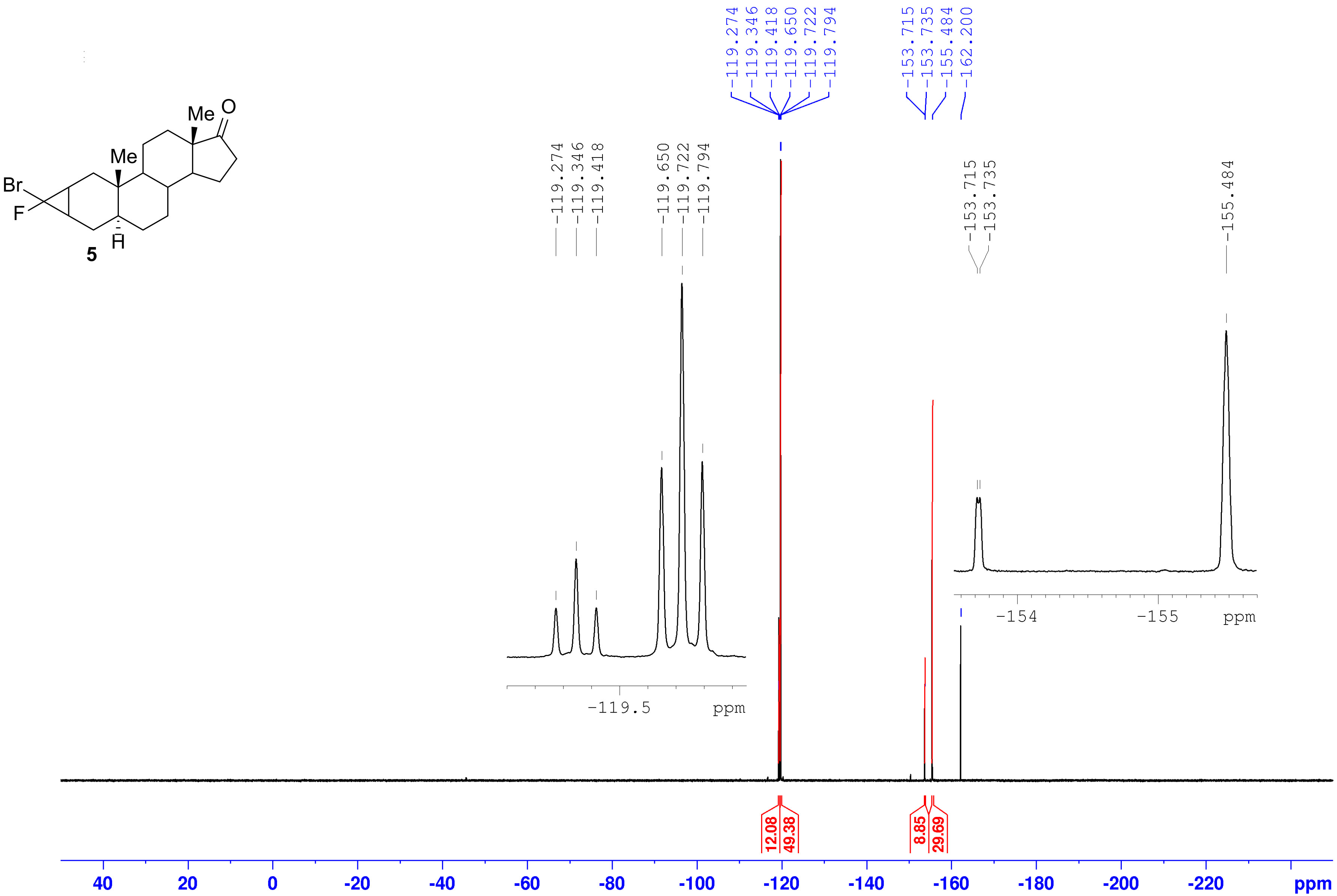
4

^{1}H NMR (300.1 MHz, CDCl$_3$) of 5

5



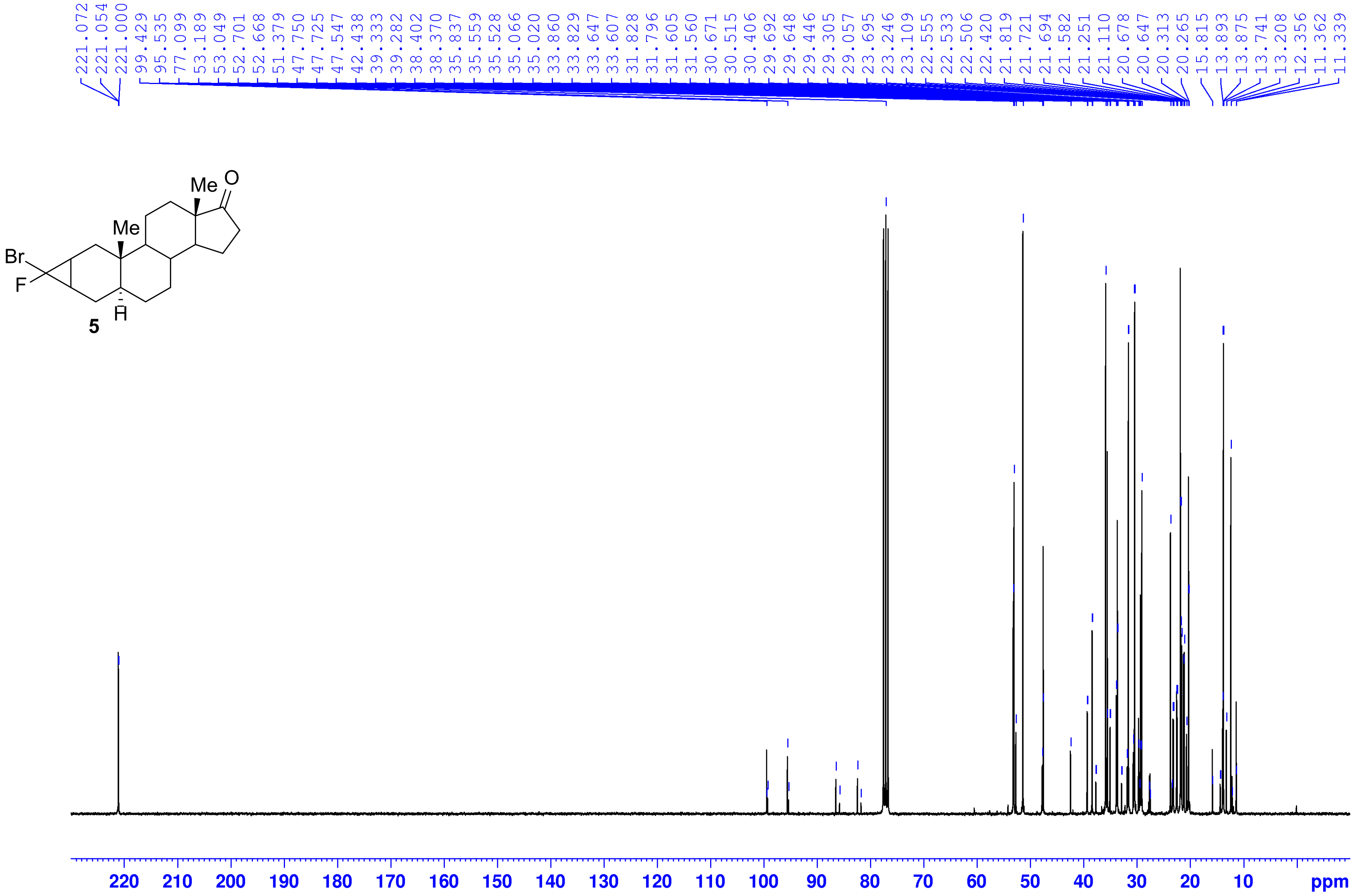
^{19}F NMR (282.4 MHz, CDCl$_3$) of 5



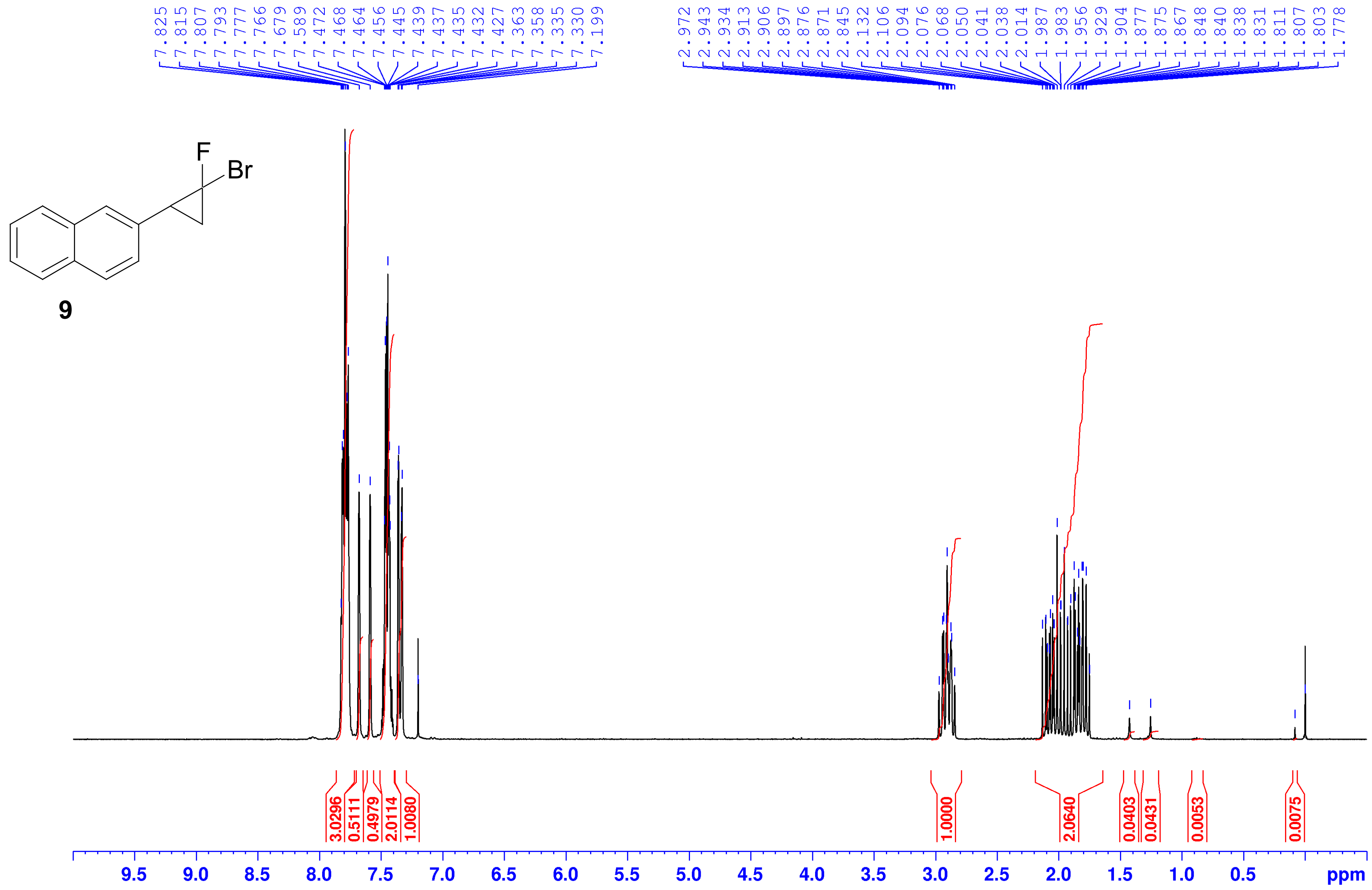
5

$^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) of 5

5

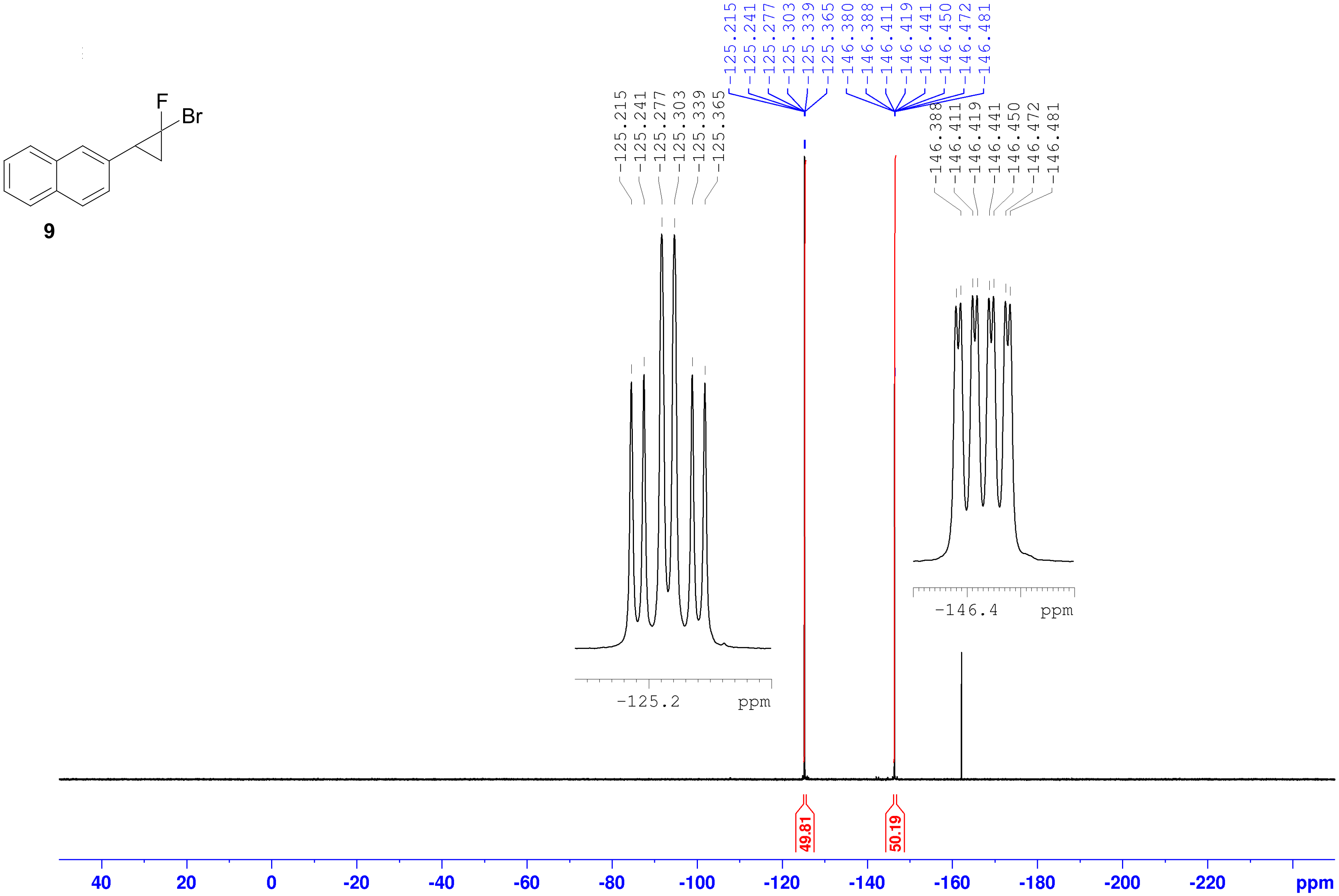


^{1}H NMR (300.1 MHz, CDCl$_3$) of 9

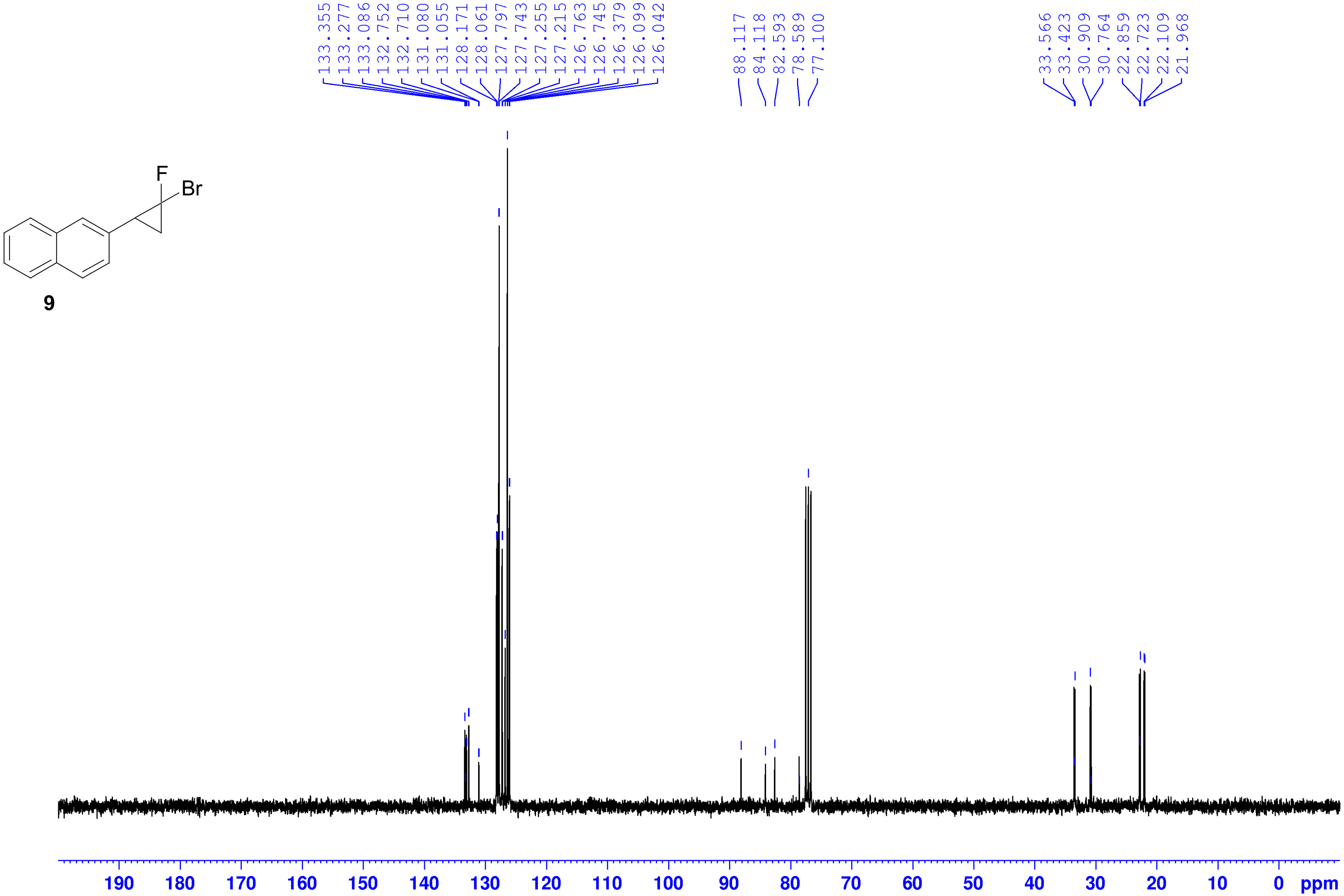


^{19}F NMR (282.4 MHz, CDCl$_3$) of 9

9



$^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) of 9



9

4.References

S1 C. A. Citadelle, E. L. Nouy, F. Bisaro, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans.*, 2010, 39, 4489.
S2 B.-K. Teo and J. C. Calabrese, *J Chem. Soc. Chem. Commun.*, 1976, 185.
S3 L. Engelhardt, P. Healy, V. Patrick and A. White, *Aust. J. Chem.*, 1987, 40, 1873.
S4 G. A. Bowmaker, E. Effendy, J. V. Hanna, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 1387.
S5 G. A. Bowmaker, Effendy, R. D. Hart, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1997, 50, 653.
S6 M. M. Olmstead, M. Sheffrin and F. Jiang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, 60, m1142.
S7 W. Gao, Y. Zhou and H. Zhang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2009, 65, m441.
S8 S. Zartilas, S. K. Hadjikakou, N. Hadjiliadis, N. Kourkoumelis, L. Kyros, M. Kubicki, M. Baril, I. S. Butler, S. Karkabounas and J. Balzarini, *Inorg. Chim. Acta*, 2009, 362, 1003.
S9 A. M. Owczarzak, L. Kyros, S. K. Hadjikakou and M. Kubicki, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2011, 67, m1507.
S10 S.-L. Zhang and W.-F. Bie, *RSC Adv.*, 2016, 6, 70902.
S11 S. S. Sandhu and R. S. Sandhu, *Ind. J. Chem.*, 1971, 9, 482.
S12 A. Kaltzoglou, P. J. Cox and P. Aslanidis, *Polyhedron*, 2007, 26, 1634.
S13 A. A. Andrianova, Y. D. Maslova, M. A. Novikov, S. E. Semenov and O. M. Nefedov, *J. Fluorine Chem.*, 2018, 209, 49.
S14 M. M. Boucher, M. H. Furigay, P. K. Quach and C. S. Brindle, *Org. Process Res. Dev.*, 2017, 21, 1394.