Supporting Information

Acetals from Primary Alcohols with the Use of Tridentate Proton Responsive Phosphinepyridonate Iridium Catalysts

A. R. Sahoo[a], F. Jiang[a], C. Bruneau[a], G. V. M. Sharma[b], S. Suresh[b] and M. Achard[a,*]

[a]*UMR 6226, Institut des Sciences Chimiques de Rennes, Université de Rennes 1, OMC : Organometallics : Materials and Catalysis, Campus de Beaulieu-35042, Rennes Cedex (France)*

[b]*Organic and Biomolecular chemistry Division, CSIR-IICT-Hyderabad-500007-India*

mathieu.achard@univ-rennes1.fr

List of Contents

A. General method S1

B. Synthesis of the ligand..S1

C. Synthesis of the Complex...S3

D. Optimization of the reaction conditions S5

E.1. General procedure for the direct synthesis of acetals from primary alcohols.....S6

E.2. Analytical data S7

F. Procedure for cross acetal formation...S11

G.1. General procedure of dehydrogenation of secondary alcohols........................S12

G.2. Analytical data...S12

H. NMR spectra S14

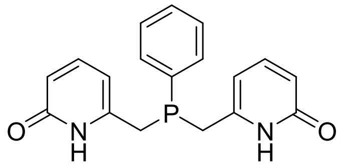
A. General Experimental Methods

All reactions were carried out under an inert argon atmosphere with standard schlenk techniques. Solvents were degassed and stored in argon atmosphere before use. Reagents were used as received without further purification, unless otherwise stated. ^{1}H NMR spectra were recorded using a Bruker GPX 400 MHz NMR spectrometer. All ^{1}H-NMR data are reported in δ units, parts per million (ppm) and were calibrated relative to the reported residual solvent signals in the corresponding deuterated solvents. All ^{13}C-NMR and ^{31}P-NMR data are reported in ppm and were recorded with ^{1}H decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, q = quartet, quint = quintet, br = broad, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Bruker microTOF mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

B. Synthesis of the ligands:

6,6'-(phenylphosphinediyl)bis(methylene)dipyridin-2(1H)-one [P(NOH)$_2$] L2-H:

6-methylpyridin-2-ol **L1-H** (1.0 g, 9.16 mmol, 1.0 equiv.) was dissolved in 10.0 mL THF, cooled at 0 °C followed by the slow addition of *n*-BuLi (12 mL, 19.2 mmol, 2.1equiv.). This solution was stirred for an hour. Then it was cooled to -78°C and was added to another solution containing dichloro(phenyl)phosphine (0.6 mL, 4.58 mmol, 0.5 equiv.) in 2.5 mL of THF at -78 °C. This solution was stirred at -78 °C for one hour and was allowed to warm up naturally to room temperature and was stirred at room temperature for 16 hours. After the completion of reaction, solvent was evaporated followed by addition of 15 mL degassed water. This solution was acidified slowly with 5% HCl solution (degassed) till the pH was around 2. Off-white solid gradually appeared with acidification. This solution was allowed to stir for 5 minutes. Removal of the water layer yielded off-white solid which was further washed with degassed acetone (3×10 mL) to afford the desired product with 74 % yield (1.1g) as off-white powder.



^{1}H NMR (400 MHz, CD_3OD): δ 7.56 (dt, J_1 = 8.0 Hz, J_2 = 1.6 Hz, ArC*H*, 2H), 7.43-7.34 (m, ArC*H*, 5H), 6.29 (d, J = 8.8 Hz, ArC*H*, 2H), 6.01 (d, J = 7.2 Hz, ArC*H*, 2H), 3.16 (s, CH_2, 4H);

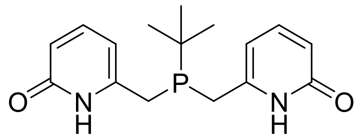
^{31}P {^{1}H} NMR (162 MHz, CD_3OD): δ -14.17;

^{13}C {^{1}H} NMR (100 MHz, CD_3OD): δ 166.5, 147.2 (d, $J_{P–C}$ = 7.2 Hz), 143.7, 135.8 (d, $J_{P–C}$ = 17.3 Hz), 134.4 (d, $J_{P–C}$ = 22.1 Hz), 131.7, 130.0 (d, $J_{P–C}$ = 7.7 Hz), 117.6 (d, $J_{P–C}$ = 1.7 Hz), 108.7 (d, $J_{P–C}$ = 6.8 Hz), 33.8 (d, $J_{P–C}$ = 21.6 Hz).

HRMS(ESI-TOF) : calc'd for $C_{18}H_{17}N_2O_2PNa$ $[M+Na]^+$ 347.0925; found 347.0928.

6,6'-(tert-butylphosphinediyl)bis(methylene)dipyridin-2(1H)-one [^{t}BuP(NOH)$_2$] L3-H:

6-methylpyridin-2-ol **L1-H** (1.0 g, 9.16 mmol, 1.0 equiv.) was dissolved in 10.0 mL THF, cooled at 0 °C followed by the slow addition of *n*-BuLi (12 mL, 19.2 mmol, 2.1equiv.). This solution was stirred for an hour. Then it was cooled to -78°C and was added to another solution containing *tert*-butyldichlorophosphine (0.95 mL, 4.58 mmol, 0.5 equiv.) in 2.5 mL of THF at -78 °C. This solution was stirred at -78 °C for one hour and was allowed to warm up naturally to room temperature and was stirred at room temperature for 16 hours. After the completion of reaction, solvent was evaporated followed by addition of 10 mL degassed water. This solution was acidified slowly with 5% HCl solution (degassed) till the pH was around 2. This solution was extracted with degassed DCM (3×5 mL). The collected organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent yielded a solid which was further washed by 1:1 mixture of diethyl ether and acetone at -30 °C to get the desired product with 65% yield (900mg) as yellowish white powder.



^{1}H NMR (400 MHz, $CDCl_3$): δ 13.41 (br, N*H*, 2H), 7.17 (t, J = 8.0 Hz, ArC*H*, 2H), 6.24 (d, J = 9.0 Hz, ArC*H*, 2H), 6.17 (d, J = 6.9 Hz, ArC*H*, 2H), 3.06 (dd, J_1 = 14.7 Hz, J_2 = 4.0 Hz, 2H), 2.87 (dd, J_1 = 14.8 Hz, J_2 = 3.9 Hz, 2H), 1.20 (d, J = 12.0 Hz, CH_3, 9H);

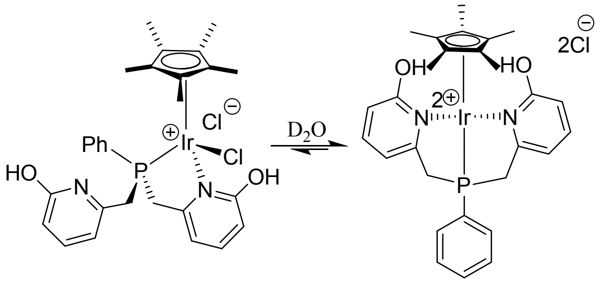
^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 6.5;

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.7, 147.4 (d, $J_{P–C}$ = 8.7 Hz), 141.4, 116.3, 106.7 (d, $J_{P–C}$ = 9.8 Hz), 28.9 (d, $J_{P–C}$ = 13.1 Hz), 27.2 (d, $J_{P–C}$ = 13.5 Hz), 24.8.

C. 1. Synthesis of the complex Ir-1

The ligand **L2-H** (81 mg, 0.25 mmol, 1.0 equiv.) was dissolved in well degassed methanol (5 mL) under argon atmosphere at room temperature. After stirring the solution for 5 minutes, $[Cp^*IrCl_2]_2$ (100 mg, 0.13 mmol, 0.5 equiv.) was added to the solution. The solution became clear yellow after 16 h of stirring. Disappearance of the peak at -14 ppm in the ^{31}P NMR indicated the completion of the reaction. Then solvent was evaporated using vacuum. The solid was washed with degassed diethylether (3×0.5 mL) to afford the desired Ir-complex with 95% yield (163 mg) as yellow solid. The complex was crystallized from methanol and diethyl ether to obtain crystals suitable for x-ray diffraction studies.

^{1}H and ^{31}P NMR analyses in CD_3OD showed the presence of two species in dynamic equilibrium. Use of D_2O as NMR solvent shifted the equilibrium completely towards a single species. VT NMR analyses (25 °C to 60 °C) conducted in CD_3OD demonstrated that the Ir-1/Ir-1' remained unaltered.



Ir-1
(major)

Ir-1'
(minor)

^{31}P(MeOD) : 30.2 ppm (minor)
13.5 ppm (major)

$^{31}P(D_2O+MeOD)$: 30.2 ppm

(Dynamic behaviour of well-defined Ir-complex)

^{1}H NMR (400 MHz, CD_3OD): (mixture where the half open form is major) δ 8.03-7.98 (m, 2H, *minor*), 7.83-7.79 (m, 3H, *minor*), 7.72-7.70 (m, 5H, *major*), 7.70 (t, J = 8.4 Hz, 2H, *minor*), 7.31 (dd, J_1 = 8.0 Hz, J_2 = 6.8 Hz, 1H, *major*), 7.15 (d, J = 7.6 Hz, 2H, *minor*), 7.10 (d, J = 7.2 Hz, 1H, *major*), 6.86 (d, J = 8.4 Hz, 1H, *major*), 6.78 (d, J = 8.4 Hz, 2H, *minor*), 6.23 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H, *major*), 6.04 (dd, J_1 = 8.0 Hz, J_2 = 2.8 Hz, 1H, *major*), 4.64 (d, J = 11.6 Hz, 1H, *minor*), 4.59 (d, J = 12.0 Hz, 1H, *minor*), 4.36 (d, J = 14.4 Hz, 1H, *minor*), 4.31 (d, J = 14.8 Hz, 1H, *minor*), 4.20-4.10 (m, 2H, *major*), 3.83 (dd, J_1 = 16.0 Hz, J_2

= 10.8 Hz, 1H, *major*), 3.58 (dd, J_1 = 12.4 Hz, J_2 = 12.0 Hz, 1H, *major*), 1.61 (d, *J* = 2.6 Hz, 15H, *minor*), 1.49 (d, *J* = 2.5 Hz, 15H, *major*);

^{31}P {^{1}H} NMR (162 MHz, CD_3OD): (mixture where the half open form is major) δ 30.2 (*minor*), 13.5 (*major*);

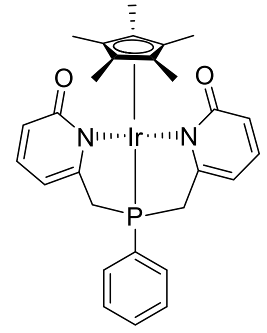
^{1}H NMR (400 MHz, D_2O): (closed form) δ 7.96-7.90 (m, 2H), 7.84-7.77 (m, 3H), 7.68 (t, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 11.5 Hz, 1H), 4.31 (d, *J* = 14.4 Hz, 1H), 4.26 (d, *J* = 14.4 Hz, 1H), 1.56 (d, *J* = 2.6 Hz, 15H);

^{31}P {^{1}H} NMR (162 MHz, D_2O): (closed form) δ 30.2;

^{13}C {^{1}H} NMR (100 MHz, D_2O): δ (closed form) 164.6 (d, J_{P-C} = 2.5 Hz, *quat-C*), 156.4 (d, J_{P-C} = 2.8 Hz, *quat-C*), 140.4 (*C*H), 131.8 (d, J_{P-C} = 3.5 Hz, *C*H), 130.5 (d, J_{P-C} = 9.7 Hz, *C*H), 128.4 (d, J_{P-C} = 12.1 Hz, *C*H), 120.3 (d, J_{P-C} = 66.1 Hz, *quat-C*), 112.7 (d, J_{P-C} = 11.5 Hz, *C*H), 109.5 (*C*H), 94.6 (d, J_{P-C} = 2.7 Hz, *quat-C*), 39.1 (d, J_{P-C} = 38.0 Hz, CH_2), 7.2 (CH_3);

HRMS(ESI-TOF): calc'd for $IrC_{28}H_{32}ClN_2O_2P$ $[M+H]^+$ 687.15136; found 687.1506.

C. 2. Synthesis of the complex Ir-2



The ligand **L2-H** (40 mg, 0.12 mmol, 1.0 equiv.) was dissolved in well degassed water (2 mL) under argon atmosphere at room temperature. After stirring the solution for 5 minutes, KO^{t}Bu (28 mg, 0.25 mmol, 2.1 mmol) was added and the solution was stirred for 30 minutes. After $[Cp*IrCl_2]_2$ (45 mg, 0.06 mmol, 0.5 equiv.) was added to the solution. The reaction mixture was allowed to stir at room temperature for 16h. Disappearance of the peak at -14 ppm in the ^{31}P NMR indicated the completion of the reaction. Then solvent was evaporated using vacuum. The solid was dissolved in degassed DCM and was cannulated to remove KCl. The collected solution was dried under vacuum to afford the desired Ir-complex with 75% yield (60 mg) as yellow solid.

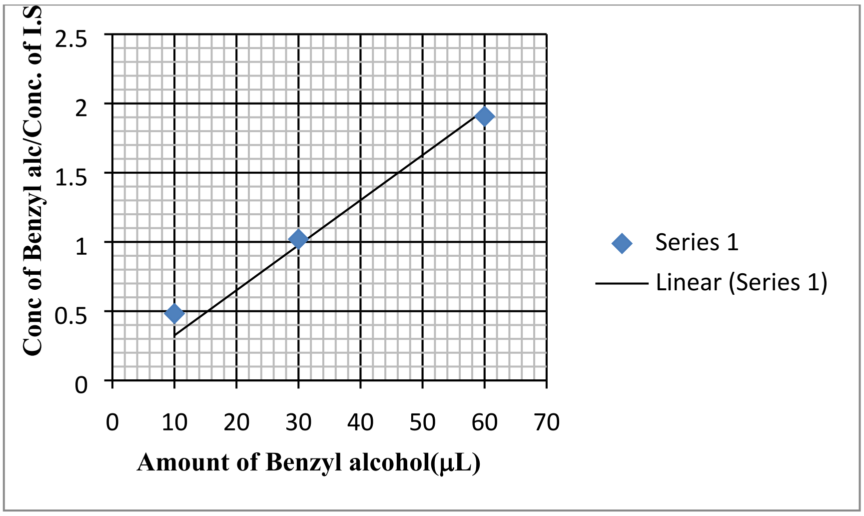
^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.65-7.60 (m, 5H), 6.93-6.88 (m, 2H), 5.99 (t, *J* = 8.5 Hz, 4H), 3.89 (dd, J_1 = 16.7 Hz, J_2 = 11.2 Hz, 2H), 3.61 (dd, J_1 = 16.8 Hz, J_2 = 13.7 Hz, 2H), 1.64 (d, *J* = 2.7 Hz, 15H);

^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): δ 27.0;

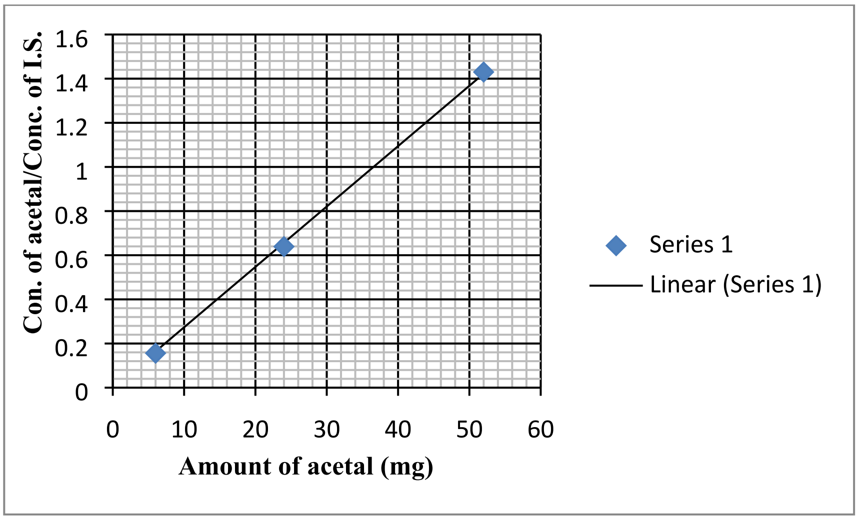
$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 154.11 (d, $J_{P\text{–}C}$ = 2.8 Hz, *quat-C*), 136.3 (*C*H), 132.6 (d, $J_{P\text{–}C}$ = 3.3 Hz, *C*H), 131.3 (d, $J_{P\text{–}C}$ = 9.2 Hz, *C*H), 130.0 (d, $J_{P\text{–}C}$ = 11.2 Hz, *C*H), 115.2 (br, *C*H), 105.4 (*C*H), 102.7 (br, *C*H), 94.8 (d, $J_{P\text{–}C}$ = 3.1 Hz, *quat-C*), 41.9 (d, $J_{P\text{–}C}$ = 37.7 Hz, *C*H_2), 10.3 (*C*H_3);

D. Optimization of reaction conditions

1) Internal Standard Studies

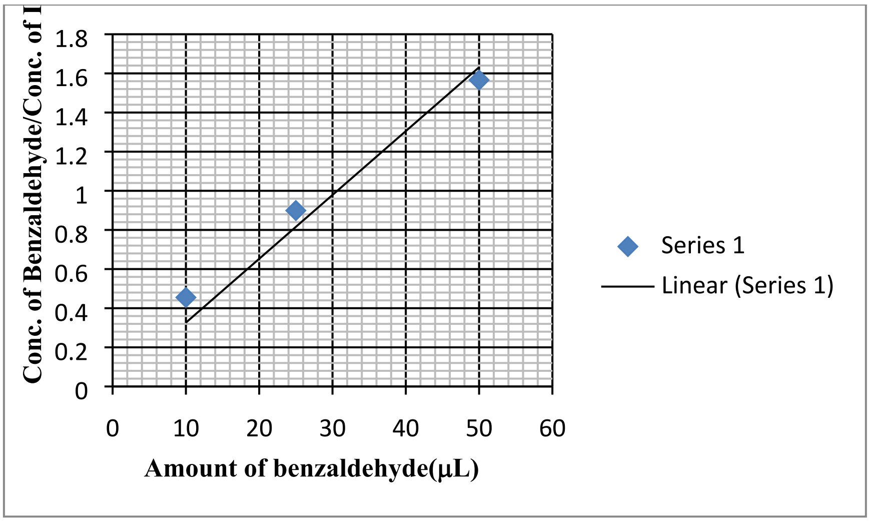


Internal Standard graph for calculation of conversion of benzyl alcohol



Internal Standard graph for calculation of yield of acetal from benzyl alcohol

E. 1.



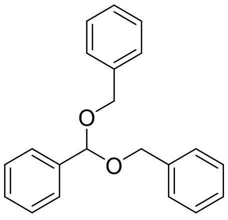
Internal Standard graph for calculation of yield of benzaldehyde

General procedure for the direct synthesis of acetals from primary alcohols

To a stirred solution of ligand **L2-H** (0.01 mmol, 1 mol%) in dry and degassed THF (0.5 mL), $[Cp^*IrCl_2]_2$ (0.005 mmol, 0.5 mol%) was added. After stirring this solution for 5 min, the appropriate alcohol (1.0 mmol) was added. This reaction mixture was stirred in a preheated oil bath at required temperature. The reaction was monitored by GC analysis. After reaction was complete (or further improvement in the product peak was not observed), the reaction was stopped. Then the reaction mixture was cooled to room temperature and solvent was evaporated. The crude reaction mixture was purified by column chromatography using silica gel columns using petroleum ether and ethyl acetate mixture as eluent to get the desired acetals.

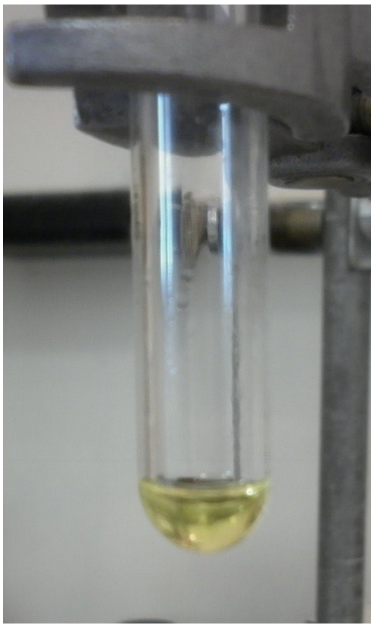
E. 2. Analytical data

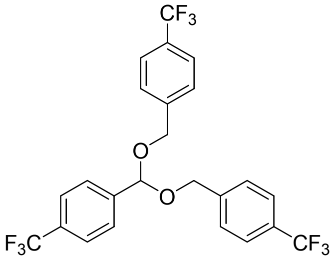
(phenylmethylene)bis(oxy)bis(methylene)dibenzene : Prepared by stirring benzyl alcohol (1.0 mmol) with the precatalyst and ligand in THF at 170 ^{o}C for 16h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 94% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.64-7.62 (m, ArC*H*, 2H), 7.48-7.33 (m, ArC*H*, 13H), 5.82 (s, OC*H*O,1H),



4.67 (s, OC*H*$_2$, 4H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 139.0 (*quat-C*), 138.7 (*quat-C*), 128.9 (Ar*C*H), 128.8 (Ar*C*H), 128.7 (Ar*C*H), 128.2 (Ar*C*H), 128.0 (Ar*C*H), 127.3 (Ar*C*H), 101.2 (O*C*HO), 67.7 (O*C*H$_2$); HRMS (ESI-TOF) : calc'd for $C_{21}H_{20}O_2Na$ [M+Na]$^+$ 327.1361; found 327.1359 (1 ppm).

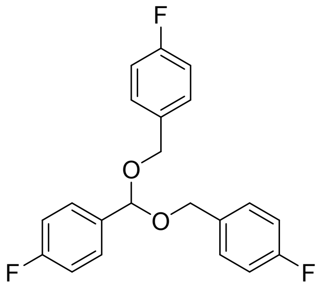
Below a picture of the resulting mixture after reaction.





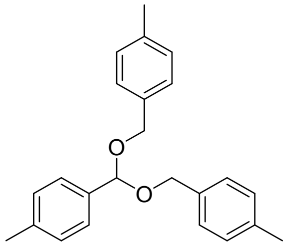
4,4'-((4-(trifluoromethyl)phenyl)methylene)bis(oxy)bis(methylene)bis((trifluoromethyl)benzene) : Prepared by stirring (4-(trifluoromethyl)phenyl)methanol (1.0 mmol) with the precatalyst and ligand in THF at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 68% yield. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.71 (dd (AB type), J_1 = 14.6 Hz, J_2 = 8.6 Hz, ArC*H*, 4H), 7.62 (d, J = 8.0 Hz, ArC*H*, 4H), 7.48 (d, J = 8.0 Hz, ArC*H*, 4H), 5.87 (s, OC*H*O,1H), 4.68 (dd (AB type), J_1 = 15.0 Hz, J_2 = 13.2 Hz, OC*H*$_2$, 4H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 142.5 (d, $^5J_{\mathrm{C-F}}$ = 1.1 Hz, *quat-C*), 142.3 (d, $^5J_{\mathrm{C-F}}$ = 1.2 Hz, *quat-C*), 131.2 (q, $^2J_{\mathrm{C-F}}$ = 33.2 Hz, Ar*C*), 130.2 (q, $^2J_{\mathrm{C-F}}$ = 32.0 Hz, Ar*C*), 128.1 (Ar*C*H), 127.8 (Ar*C*H), 125.8-125.7 (m, *C*F$_3$ and Ar*C*H), 100.7 (O*C*HO), 67.0 (O*C*H$_2$); HRMS (ESI-TOF) : calc'd for $C_{24}H_{17}F_9O_2Na$ [M+Na]$^+$ 531.0977; found 531.0982.

4,4'-((4-fluorophenyl)methylene)bis(oxy)bis(methylene)bis(fluorobe

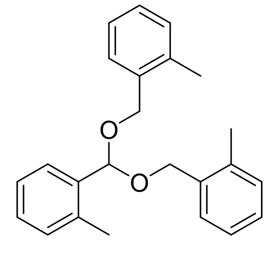


nzene): Prep-ared by stirring (4-fluorophenyl)methanol (1.0 mmol) with the precatalyst and ligand in THF at 170 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 61% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54-7.50 (m, Ar*CH*, 2H), 7.34-7.30 (m, Ar*CH*, 4H), 7.11-7.02 (m, Ar*CH*, 6H), 5.71 (s, O*CH*O,1H), 4.54 (s, O*CH*$_2$, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 163.3 (d, $^1J_{C-F}$ = 244.7 Hz, Ar*C*), 162.7 (d, $^1J_{C-F}$ = 243.4 Hz, Ar*C*), 134.8 (d, $^4J_{C-F}$ = 3.1 Hz, Ar*C*), 134.4 (d, $^4J_{C-F}$ = 3.2 Hz, Ar*C*), 130.0 (d, $^3J_{C-F}$ = 8.1 Hz, Ar*C*H), 129.1 (d, $^3J_{C-F}$ = 8.2 Hz, Ar*C*H), 115.5 (d, $^2J_{C-F}$ = 21.3 Hz, Ar*C*H), 115.5 (d, $^2J_{C-F}$ = 21.5 Hz, Ar*C*H), 100.5 (O*C*HO), 67.0 (O*C*H$_2$); ^{19}F NMR (376 MHz): δ -114.3, -115.6; HRMS (ESI-TOF) : calc'd for $C_{21}H_{17}F_3O_2Na$ [M+Na]$^+$ 381.1078; found 381.1075 (1 ppm).

4,4'-(p-tolylmethylene)bis(oxy)bis(methylene)bis(methylbenzene) : Prepared by stirring *p*-tolylmethanol (1.0 mmol) with the precatalyst and ligand in THF at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 19 : 1) afforded the product as a colourless oil with 60% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.46 (d, *J* = 8.0 Hz, Ar*CH*, 2H), 7.28-7.18 (m, Ar*CH*, 10H), 5.72 (s, O*CH*O,1H), 4.58 (s, O*CH*$_2$, 4H), 2.39 (s, Ar*CH*$_3$, 3H), 2.38 (s, Ar*CH*$_3$, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 138.7 (*quat-C*), 137.7 (*quat-C*), 136.2 (*quat-C*), 135.7 (*quat-C*), 129.4 (Ar*C*H), 129.3 (Ar*C*H), 128.3 (Ar*C*H), 127.2 (Ar*C*H), 101.0 (O*C*HO), 67.5 (O*C*H$_2$), 21.4 (*C*H$_3$), 21.3 (*C*H$_3$); HRMS (ESI-TOF) : calc'd for $C_{24}H_{26}O_2Na$ [M+Na]$^+$ 369.1830; found 369.1828 (1 ppm).

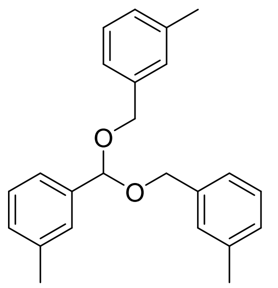


2,2'-(o-tolylmethylene)bis(oxy)bis(methylene)bis(methylbenzene) : Prepared by stirring *o*-tolylmethanol (1.0 mmol) with the precatalyst and ligand in THF at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 19 : 1) afforded the product as a colourless oil with 63% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68-7.66 (m, Ar*CH*, 1H), 7.32-7.14 (m, Ar*CH*, 11H), 5.83 (s, O*CH*O,1H), 4.58 (s, O*CH*$_2$, 4H), 2.36 (s, Ar*CH*$_3$, 3H), 2.30 (s, Ar*CH*$_3$, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 137.1 (*quat-C*), 136.9 (*quat-C*), 136.6 (*quat-C*), 136.6 (*quat-C*), 130.9 (Ar*C*H), 130.4 (Ar*C*H), 129.0 (Ar*C*H), 128.8 (Ar*C*H), 128.1 (Ar*C*H), 127.2 (Ar*C*H), 126.1 (Ar*C*H), 125.8 (Ar*C*H), 100.0 (O*C*HO), 66.4

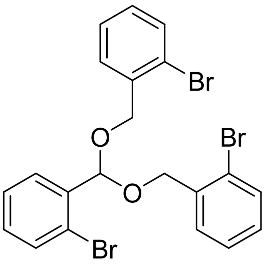


(O*C*H$_2$), 19.0 (*C*H$_3$), 19.0 (*C*H$_3$); HRMS (ESI-TOF) : calc'd for $C_{24}H_{26}O_2Na$ $[M+Na]^+$ 369.1825; found 369.1825.

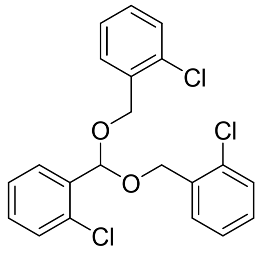
3,3'-(m-tolylmethylene)bis(oxy)bis(methylene)bis(methylbenzene) : Prepared by stirring *m*-tolylmethanol (1.0 mmol) with the precatalyst and ligand in THF at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 19 : 1) afforded the product as a colourless oil with 68% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.36-7.10 (m, ArC*H*, 12H), 5.67 (s, OC*H*O,1H), 4.56 (s, OC*H*$_2$, 4H), 2.38 (s, ArC*H*$_3$, 3H), 2.35 (s, ArC*H*$_3$, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 138.9 (*quat-C*), 138.6 (*quat-C*), 138.5 (*quat-C*), 138.4 (*quat-C*), 129.6 (Ar*C*H), 129.0 (Ar*C*H), 128.6 (Ar*C*H), 128.6 (Ar*C*H), 128.5 (Ar*C*H), 127.8 (Ar*C*H), 125.3 (Ar*C*H), 124.3 (Ar*C*H), 101.3 (O*C*HO), 67.8 (O*C*H$_2$), 21.6 (*C*H$_3$), 21.5 (*C*H$_3$); HRMS (ESI-TOF) : calc'd for $C_{24}H_{26}O_2Na$ $[M+Na]^+$ 369.1830; found 369.1833 (1 ppm).



2,2'-((2-bromophenyl)methylene)bis(oxy)bis(methylene)bis(bromobenzene) : Prepared by stirring (2-bromophenyl)methanol (1.0 mmol) with the precatalyst and ligand in THF at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 61% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.82 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, ArC*H*, 1H), 7.60 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, ArC*H*, 1H), 7.54 (t, J = 7.2 Hz, ArC*H*, 4H), 7.40 (t, J = 7.6 Hz, ArC*H*, 1H), 7.33 (t, J = 7.6 Hz, ArC*H*, 2H), 7.26 (dt, J_1 = 8.0 Hz, J_2 = 1.6 Hz, ArC*H*, 1H), 7.17 (dt, J_1 = 8.0 Hz, J_2 = 1.2 Hz, ArC*H*, 2H), 6.06 (s, OC*H*O,1H), 4.75 (dd (AB type), J_1 = 16.0 Hz, J_2 = 12.4 Hz, OC*H*$_2$, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 137.6 (*quat-C*), 137.2 (*quat-C*), 133.4 (Ar*C*H), 132.8 (Ar*C*H), 130.8 (Ar*C*H), 130.0 (Ar*C*H), 129.5 (Ar*C*H), 129.1 (Ar*C*H), 127.9 (Ar*C*H), 127.8 (Ar*C*H), 123.4 (*quat-C*), 123.2 (*quat-C*), 101.6 (O*C*HO), 68.4 (O*C*H$_2$); HRMS (ESI-TOF) : calc'd for $C_{21}H_{17}Br_3O_2Na$ $[M+Na]^+$ 560.8676; found 560.8673 (1 ppm).

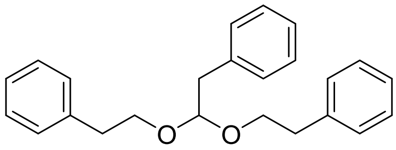


2,2'-((2-chlorophenyl)methylene)bis(oxy)bis(methylene)bis(chlorobenzene) : Prepared by stirring (2-chlorophenyl)methanol (1.0 mmol) with the precatalyst and ligand in THF at 150 °C for 24h under argon atmosphere. Purification by

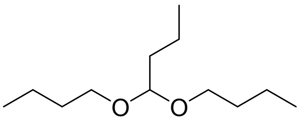


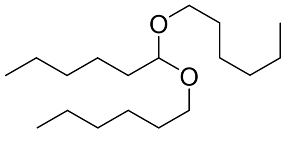
silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 58% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.83 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, Ar*CH*, 1H), 7.53 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, Ar*CH*, 2H), 7.42-7.32 (m, Ar*CH*, 5H), 7.30-7.22 (m, Ar*CH*, 4H), 6.11 (s, OC*H*O,1H), 4.77 (dd (AB type), J_1 = 14.0 Hz, J_2 = 13.6 Hz, OC*H$_2$*, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 136.0 (*quat-C*), 135.8 (*quat-C*), 133.7 (*quat-C*), 133.4 (*quat-C*), 130.5 (Ar*C*H), 130.1 (Ar*C*H), 129.8 (Ar*C*H), 129.6 (Ar*C*H), 129.3 (Ar*C*H), 128.8 (Ar*C*H), 127.3 (Ar*C*H), 127.2 (Ar*C*H), 99.6 (O*C*HO), 66.1 (O*C*H_2); HRMS (ESI-TOF) : calc'd for $C_{21}H_{17}Cl_3O_2Na$ $[M+Na]^+$ 429.0192; found 429.0188 (1 ppm).

(2,2'-(2-phenylethane-1,1-diyl)bis(oxy)bis(ethane-2,1-diyl))dibenzene : Prepared by stirring 2-phenylethanol (1.0 mmol) with the precatalyst and ligand in THF at 170 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 19 : 1) afforded the product as a colourless oil with 69% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.29-7.16 (m, Ar*H*, 15H), 4.64 (t, *J* = 5.6 Hz, OC*H*O, 1H), 3.78-3.72 (m, OC*H$_2$*, 2H), 3.59-3.53 (m, OC*H$_2$*, 2H), 2.88 (d, *J* = 5.6 Hz, CHC*H$_2$*, 2H), 2.80 (t, *J* = 5.6 Hz, OCH_2C*H$_2$*, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 139.7 (*quat-C*), 137.7 (*quat-C*), 130.0 (Ar*C*H), 129.4 (Ar*C*H), 128.6 (Ar*C*H), 128.5 (Ar*C*H), 126.6 (Ar*C*H), 126.5 (Ar*C*H), 104.3 (O*C*HO), 67.4 (O*C*H_2), 40.9 (CH*C*H_2), 36.7 (OCH_2*C*H_2); HRMS (ESI-TOF) for $C_{24}H_{26}O_2Na$ $[M+Na]^+$: calcd : 369.1825. Found : 369.1828.



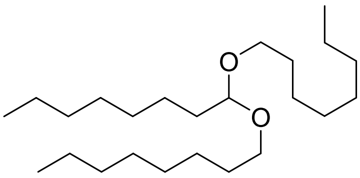
1,1-dibutoxybutane : Prepared by stirring 1-butanol (1.0 mmol) with the precatalyst and ligand in THF at 130 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pentane : diethyl ether = 19 : 1) afforded the product as a colourless oil with 74% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.42 (t, *J* = 5.6 Hz, OC*H*O, 1H), 3.57-3.52 (m, C*H$_2$*, 2H), 3.39-3.35 (m, C*H$_2$*, 2H), 1.55-1.48 (m, C*H$_2$*, 6H), 1.40-1.32 (m, C*H$_2$*, 6H), 0.93-0.89 (two overlapped triplets, J_1 = 7.2 Hz, J_2 = 7.2 Hz, C*H$_3$*, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 103.4 (O*C*HO), 66.7 (O*C*H_2), 36.2 (*C*H_2), 32.5 (*C*H_2), 19.9 (*C*H_2), 18.5 (*C*H_2), 14.2 (*C*H_3), 14.1 (*C*H_3); HRMS (ESI) for $C_{12}H_{26}O_2Na$ $[M+Na]^+$: calcd : 225.1825. Found : 225.1823.



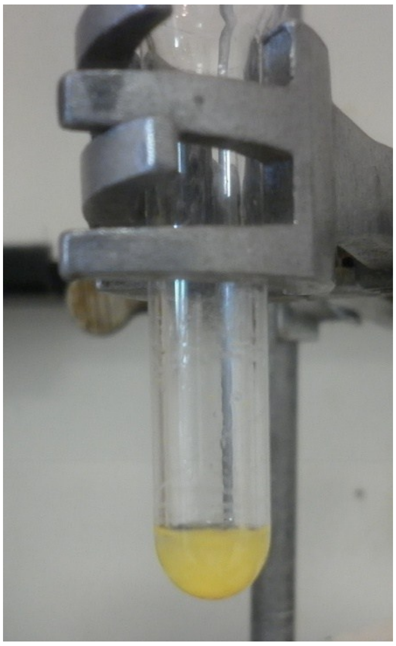


1,1-bis(hexyloxy)hexane : Prepared by stirring 1-hexanol (1.0 mmol) with the precatalyst and ligand in THF at 150 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pentane : diethyl ether = 19 : 1) afforded the product as a colourless oil with 76% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.41 (t, J = 5.6 Hz, OC*H*O, 1H), 3.56-3.51 (m, CH_2, 2H), 3.40-3.35 (m, CH_2, 2H), 1.60-1.50 (m, CH_2, 6H), 1.38-1.24 (br, CH_2, 18H), 0.89 (t, J = 7.0 Hz, CH_3, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 103.7 (O*C*HO), 66.0 (OCH_2), 34.0 (CH_2), 32.2 (CH_2), 32.2 (CH_2), 30.4 (CH_2), 26.4 (CH_2), 24.9 (CH_2), 23.1 (CH_2), 23.1 (CH_2), 14.3 (CH_3), 14.2 (CH_3); HRMS (ESI-TOF) : calc'd for $C_{18}H_{38}O_2Na$ $[M+Na]^+$ 309.2770; found 309.2770.

1,1-bis(octyloxy)octane : Prepared by stirring 1-octanol (1.0 mmol) with the precatalyst and ligand in THF at 170 °C for 24h under argon atmosphere. Purification by silica gel column chromatography (pentane : diethyl ether = 19 : 1) afforded the product as a colourless oil with 71% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.41 (t, J = 5.6 Hz, OC*H*O, 1H), 3.56-3.51 (m, C*H*$_2$, 2H), 3.40-3.34 (m, C*H*$_2$, 2H), 1.58-1.50 (m, C*H*$_2$, 6H), 1.28 (br, C*H*$_2$, 30H), 0.89 (t, J = 6.8 Hz, C*H*$_3$, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 103.7 (O*C*HO), 66.0 (O*C*H$_2$), 34.1 (*C*H$_2$), 32.3 (*C*H$_2$), 32.3 (*C*H$_2$), 30.4 (*C*H$_2$), 29.9 (*C*H$_2$), 29.9 (*C*H$_2$), 29.8 (*C*H$_2$), 29.7 (*C*H$_2$), 26.8 (*C*H$_2$), 25.2 (*C*H$_2$), 23.1 (*C*H$_2$), 14.3 (*C*H$_3$); HRMS (ESI-TOF) : calc'd for $C_{24}H_{50}O_2Na$ $[M+Na]^+$ 393.3703; found 393.3704.

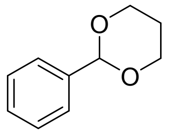


Below a picture of the reaction after completion



F. Procedure for the synthesis of cross acetal from benzyl alcohol and propanediol

To a stirred solution of ligand $P(NOH)_2$ (0.01 mmol, 1 mol%) in dry and degassed THF (0.5 mL), $[Cp^*IrCl_2]_2$ (0.005 mmol, 0.5 mol%) was added. After stirring this solution for 5 min, benzyl alcohol (1.0 mmol) and propanediol (1.5 mmol) were added. This reaction mixture was stirred in a preheated oil bath at 170 °C for 24 hours under argon atmosphere. The reaction was monitored by GC analysis. The reaction was stopped when no further improvement in the product peak was observed. After the reaction mixture was cooled to room temperature and solvent was evaporated. The crude reaction mixture was purified by silica gel column chromatography using petroleum ether and ethyl acetate mixture (9 : 1) as eluent to get the desired acetal as a colourless oil with 30% yield.

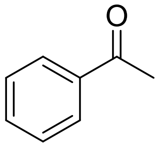


2-phenyl-1,3-dioxane : ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.46-7.43 (m, Ar*H*, 2H), 7.38-7.31 (m, Ar*H*, 3H), 5.48 (s, OC*H*O, 1H), 4.25-4.20 (m, OC*H₂*, 2H), 4.01-3.94 (m, OC*H₂*, 2H), 2.23-2.11 (m, C*H₂*, 1H), 1.44 (doublet of septet, J_1 = 13.6 Hz, J_2 = 1.6 Hz, C*H₂*, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 139.6 (*quat-C*), 129.0 (Ar*C*H), 128.5 (Ar*C*H), 126.4 (Ar*C*H), 101.9 (O*C*HO), 67.8 (O*C*H₂), 26.3 (*C*H₂); HRMS (ESI) for $C_{10}H_{12}O_2Na$ $[M+Na]^+$: calcd : 187.0730. Found : 187.0730.

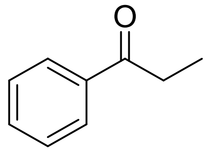
G. 1. General procedure for the dehydrogenation of secondary alcohols

To a stirred solution of ligand $P(NOH)_2$ (0.01 mmol, 1 mol%) in dry and degassed toluene (0.5 mL), $[Cp^*IrCl_2]_2$ (0.005 mmol, 0.5 mol%) was added. After stirring this solution for 5 min, the appropriate secondary alcohol (1.0 mmol) was added. This reaction mixture was stirred in a preheated oil bath at 170 °C. The reaction was monitored by GC analysis. After reaction was complete (or further improvement in the product peak was not observed), the reaction was stopped. Then the reaction mixture was cooled to room temperature and solvent was evaporated. The crude reaction mixture was purified by column chromatography using silica gel columns using petroleum ether and ethyl acetate mixture as eluent to get the desired ketones.

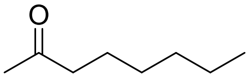
G. 2. Analytical data



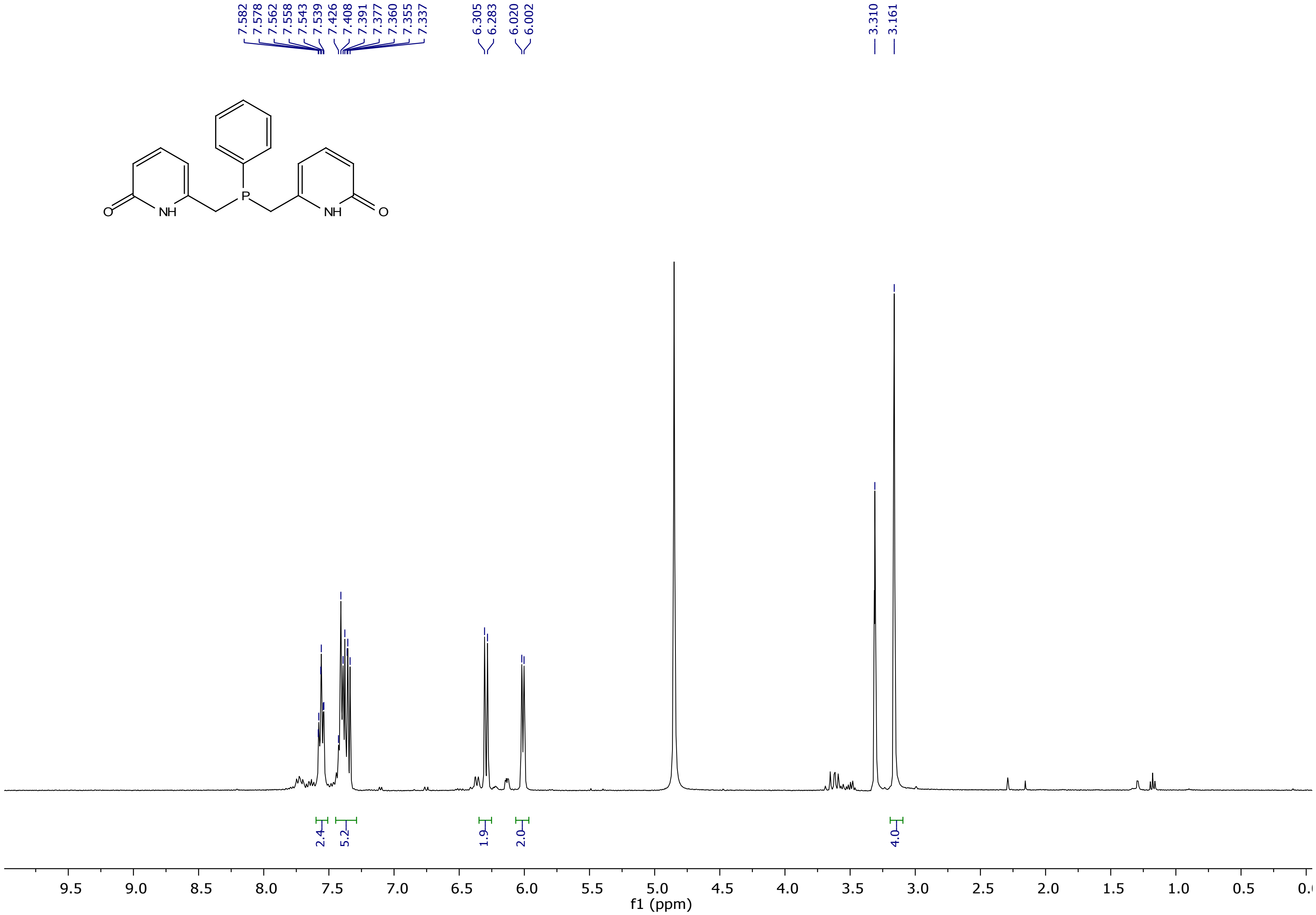
Acetophenone : Obtained by stirring 1-phenylethanol (1.0 mmol) with the precatalyst and ligand in toluene at 170 °C for 16h under argon atmosphere. Purification by silica gel column chromatography (pentane : diethyl ether = 9 : 1) afforded the product as a colourless liquid with 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (m, Ar*H*, 2H), 7.59-7.55 (m, Ar*H*, 1H), 7.49-7.45 (m, Ar*H*, 2H), 2.61 (s, C*H$_3$*, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.2 (*quat-C*), 137.1 (*quat-C*), 133.1 (Ar*C*H), 128.6 (Ar*C*H), 128.3 (Ar*C*H), 26.6 (*C*H$_3$).

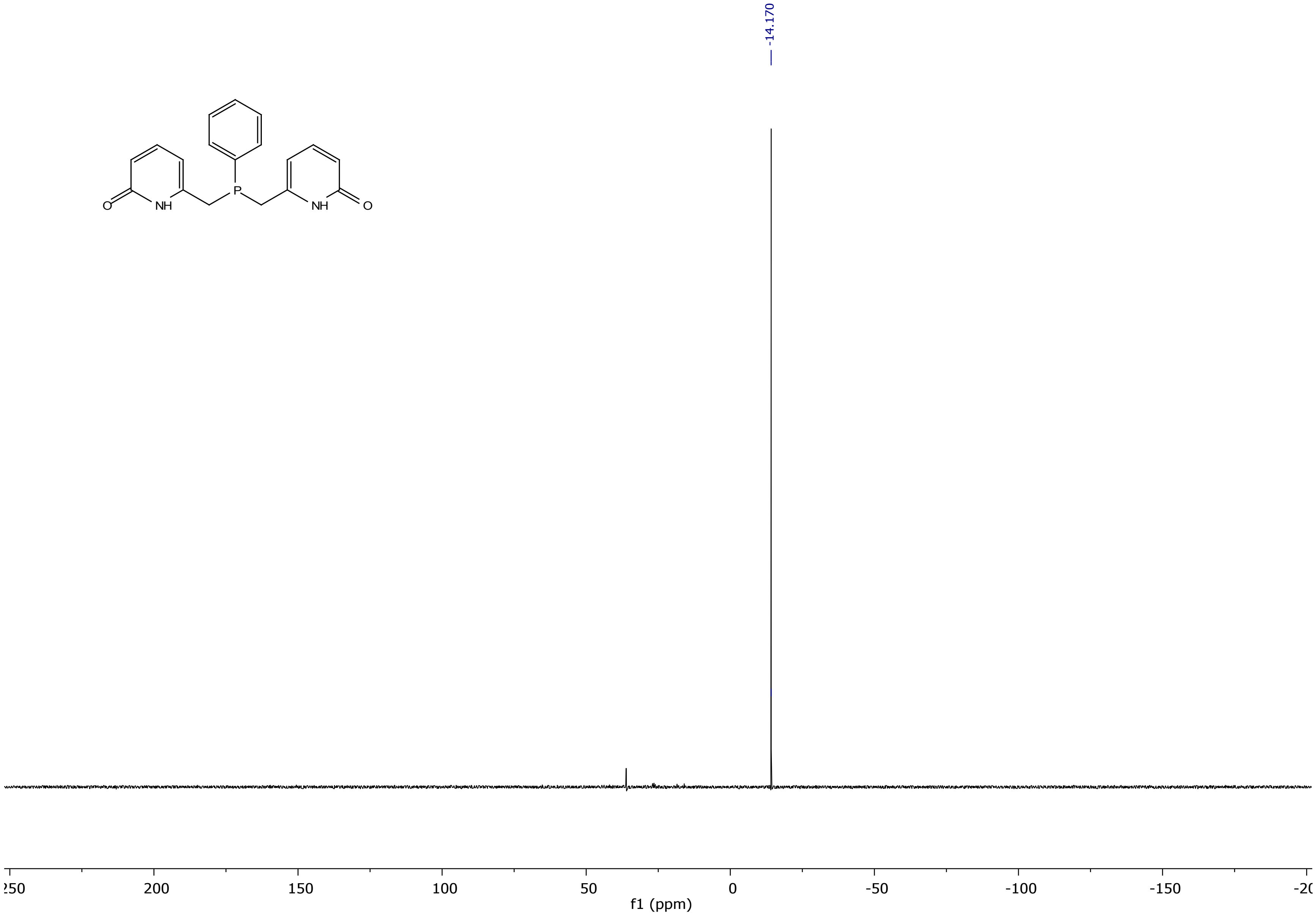


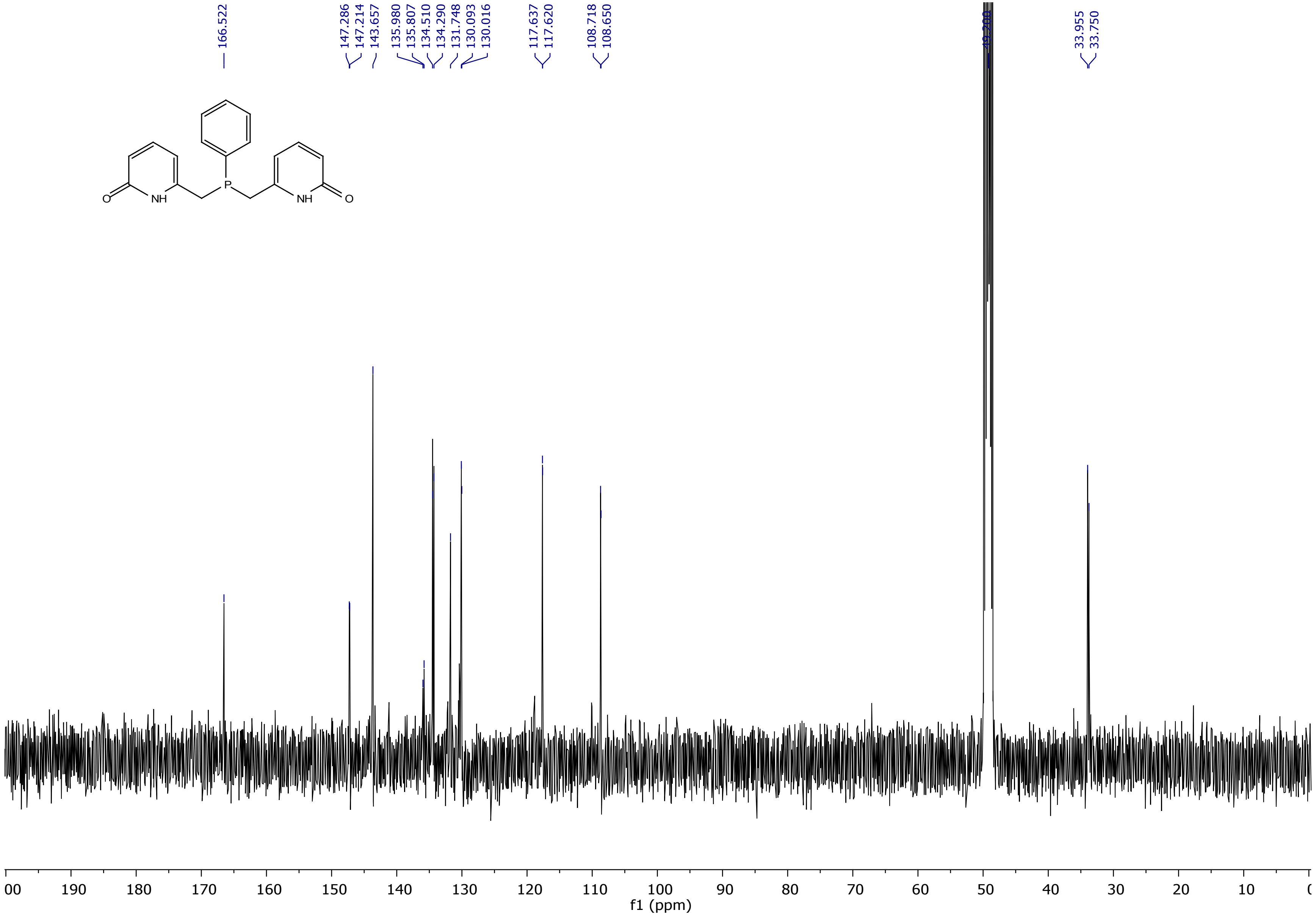
Propiophenone : Obtained by stirring 1-phenylpropan-1-ol (1.0 mmol) with the precatalyst and ligand in toluene at 170 °C for 18h under argon atmosphere. Purification by silica gel column chromatography (pentane : diethyl ether = 9 : 1) afforded the product as a colourless liquid with 60% yield. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.97-7.95 (m, Ar*H*, 2H), 7.59-7.55 (m, Ar*H*, 1H), 7.49-7.45 (m, Ar*H*, 2H), 3.00(q, *J* = 7.2 Hz, C*H$_2$*, 2H), 1.20 (t, *J* = 7.2 Hz, C*H$_3$*, 3H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 200.8 (*quat-C*), 137.5 (*quat-C*), 133.1 (Ar*C*H), 128.9 (Ar*C*H), 128.2 (Ar*C*H), 32.1 (*C*H$_2$), 8.4 (*C*H$_3$).

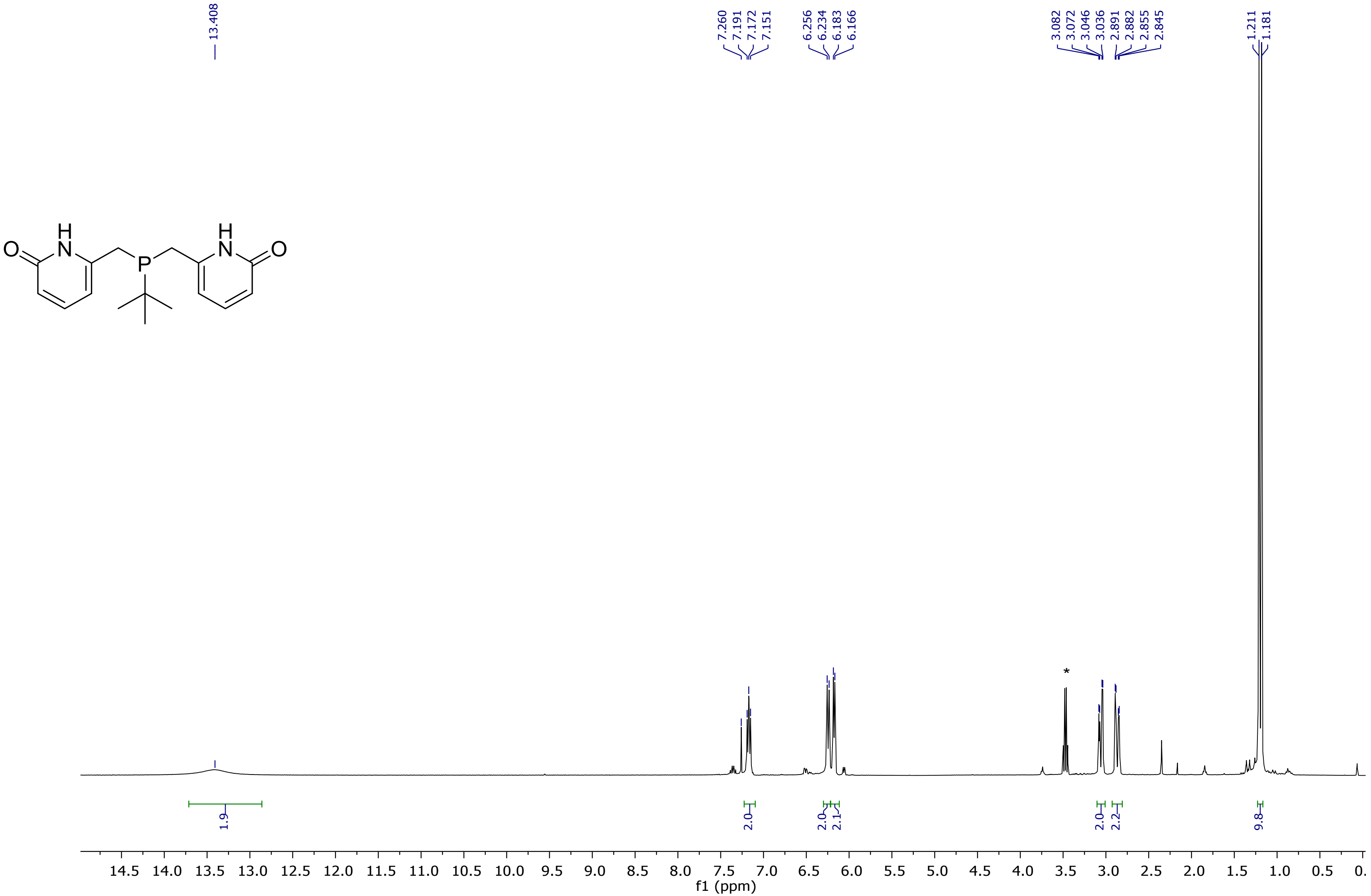


Octan-2-one : Obtained by stirring 2-octanol (1.0 mmol) with the precatalyst and ligand in toluene at 170 °C for 18h under argon atmosphere. Purification by silica gel column chromatography (pet. ether : EtOAc = 19 : 1) afforded the product as a colourless liquid with 75% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.41 (t, *J* = 7.6 Hz, C*H$_2$*, 2H), 2.12 (s, C*H$_3$*, 3H), 1.58-1.52 (m, C*H$_2$*, 2H), 1.30-1.27 (m, 3C*H$_2$*, 6H), 0.87 (t, *J* = 6.8 Hz, C*H$_3$*, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 209.5 (*quat-C*), 44.0 (*C*H$_2$), 31.7 (*C*H$_2$), 30.0 (*C*H$_3$), 29.0 (*C*H$_2$), 24.0 (*C*H$_2$), 22.6 (*C*H$_2$), 14.2 (*C*H$_3$).

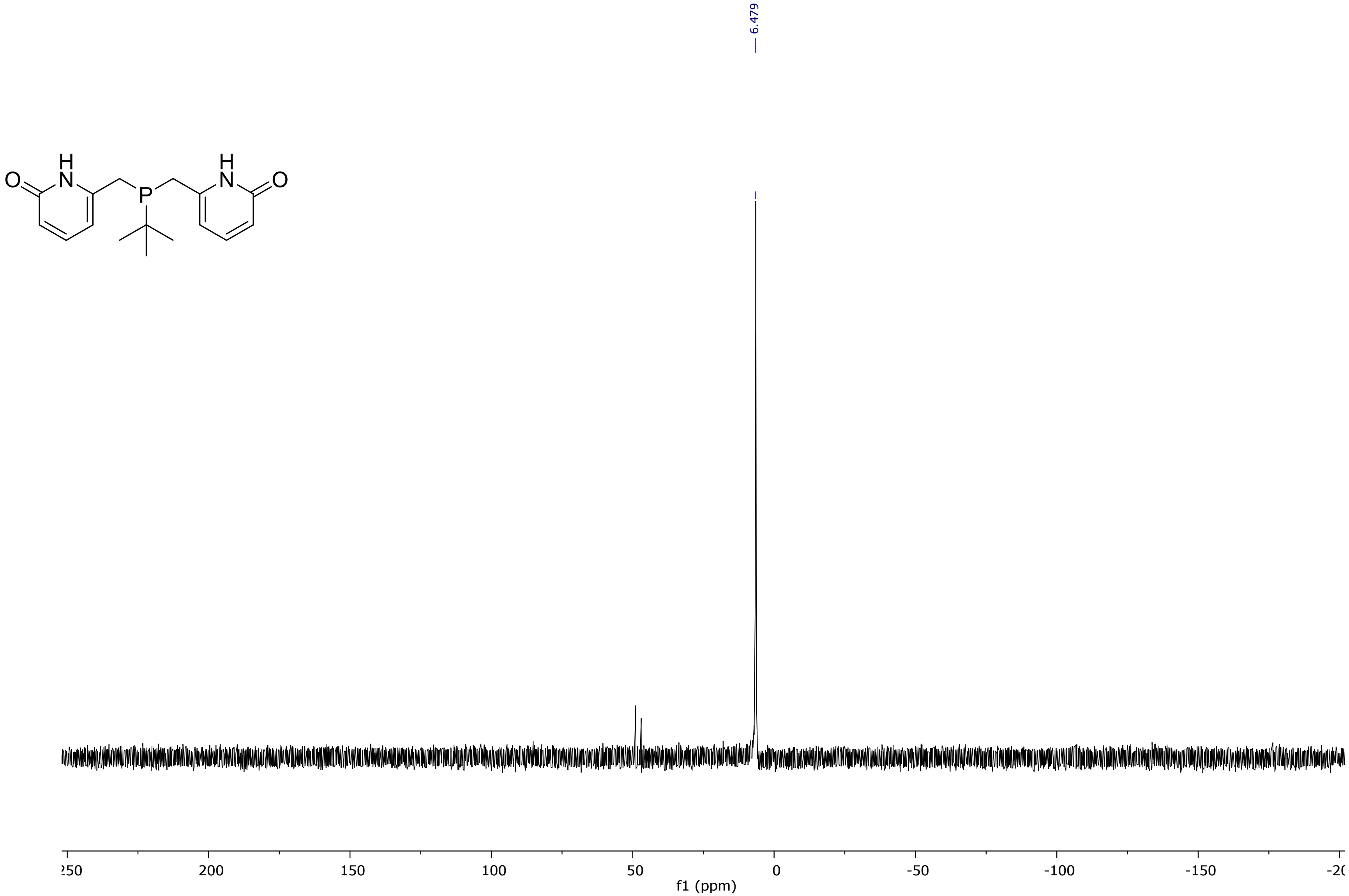

7.582
7.578
7.562
7.558
7.543
7.539
7.426
7.408
7.391
7.377
7.360
7.355
7.337
6.305
6.283
6.020
6.002
3.310
3.161
O
NH
P
NH
O
2.4
5.2
1.9
2.0
4.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

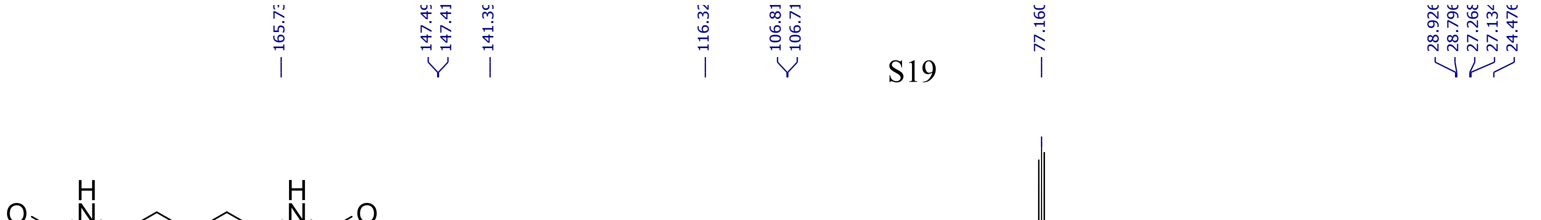

-14.170
O
NH
P
NH
O
250
200
150
100
50
0
-50
-100
-150
-20
f1 (ppm)

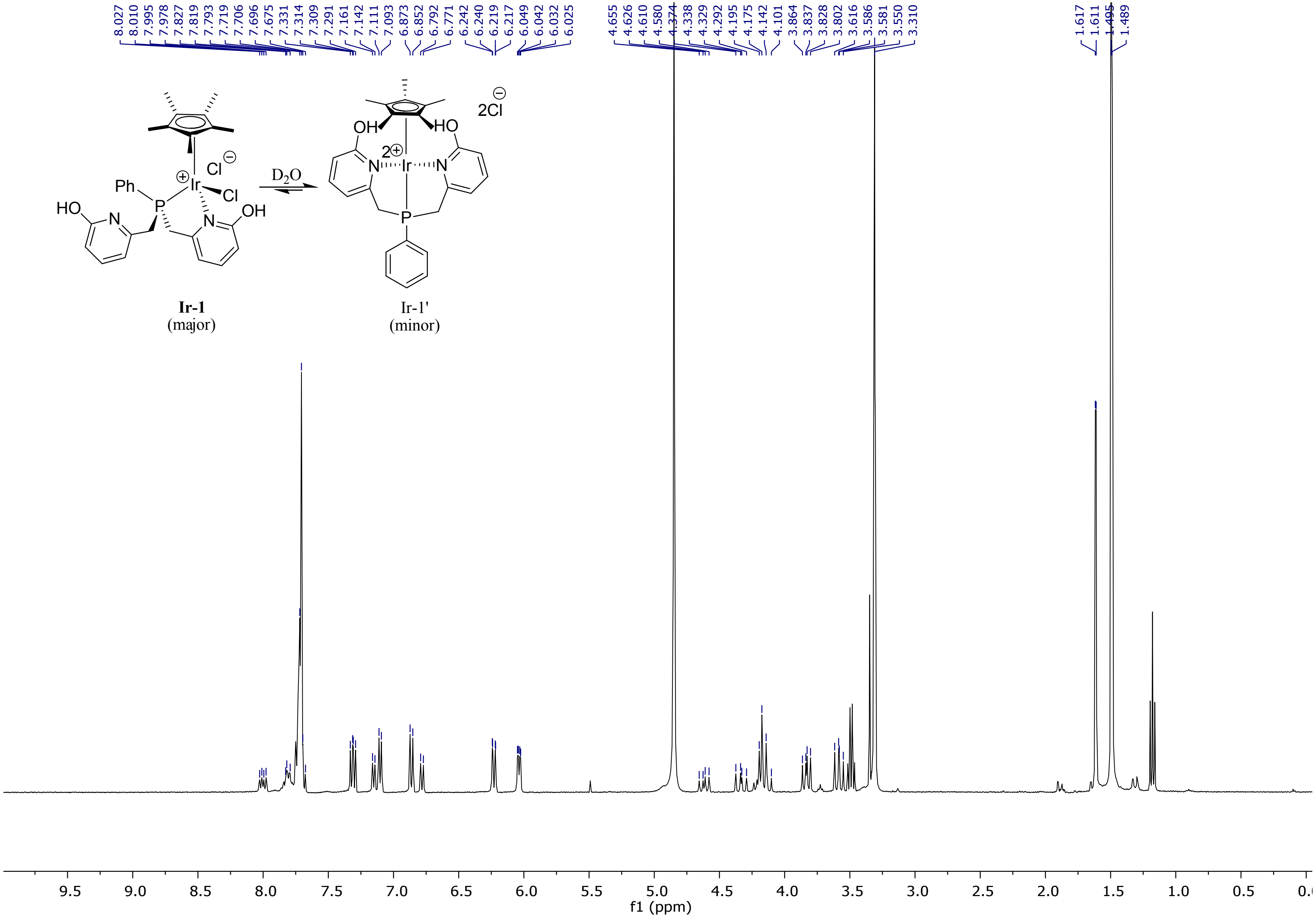

166.522
147.286
147.214
143.657
135.980
135.807
134.510
134.290
131.748
130.093
130.016
117.637
117.620
108.718
108.650
49.200
33.955
33.750
O
NH
P
NH
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

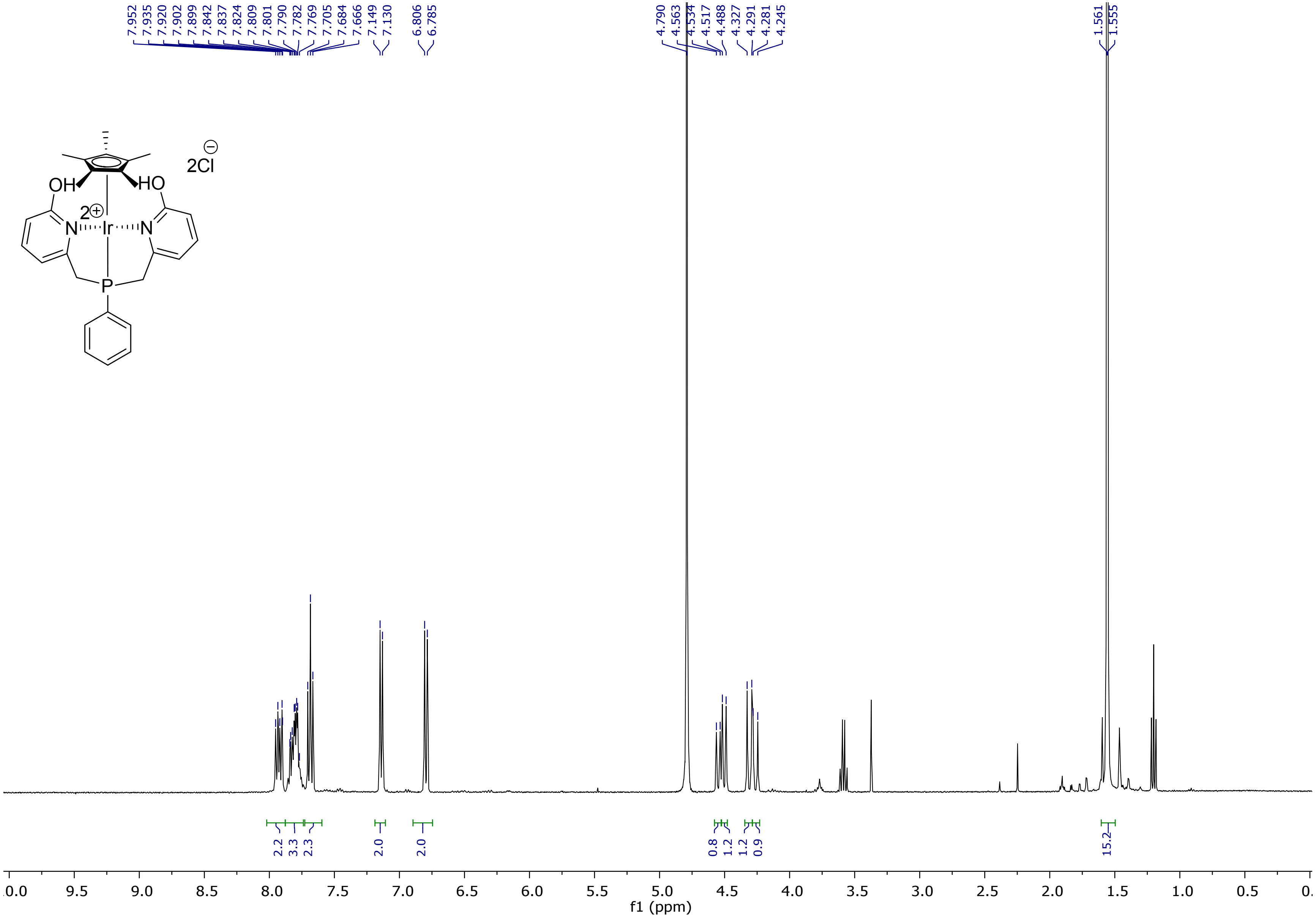


* - peak from Diethylether

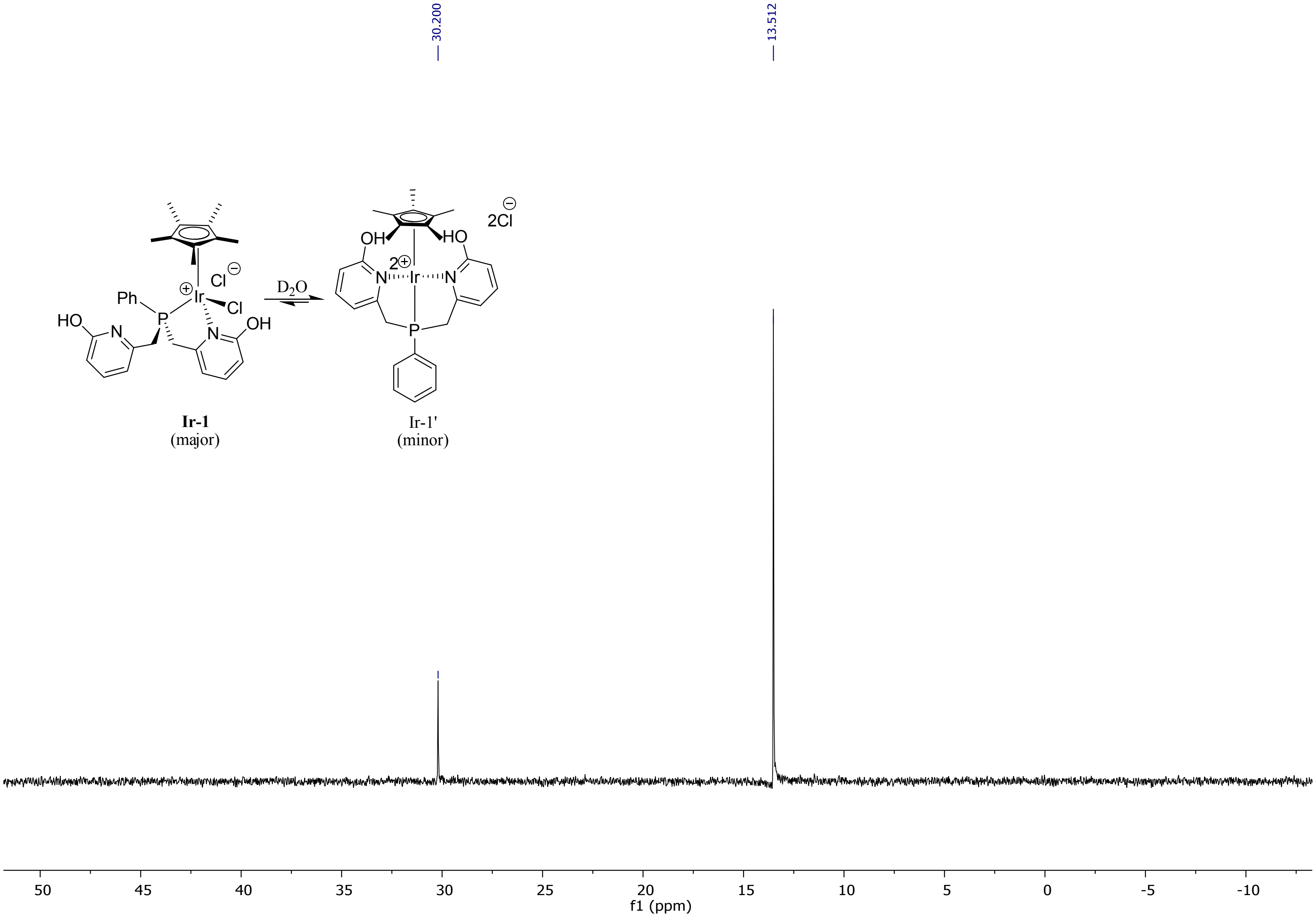

6.479
O
H
N
P
250
200
150
100
50
0
-50
-100
-150
-20
f1 (ppm)

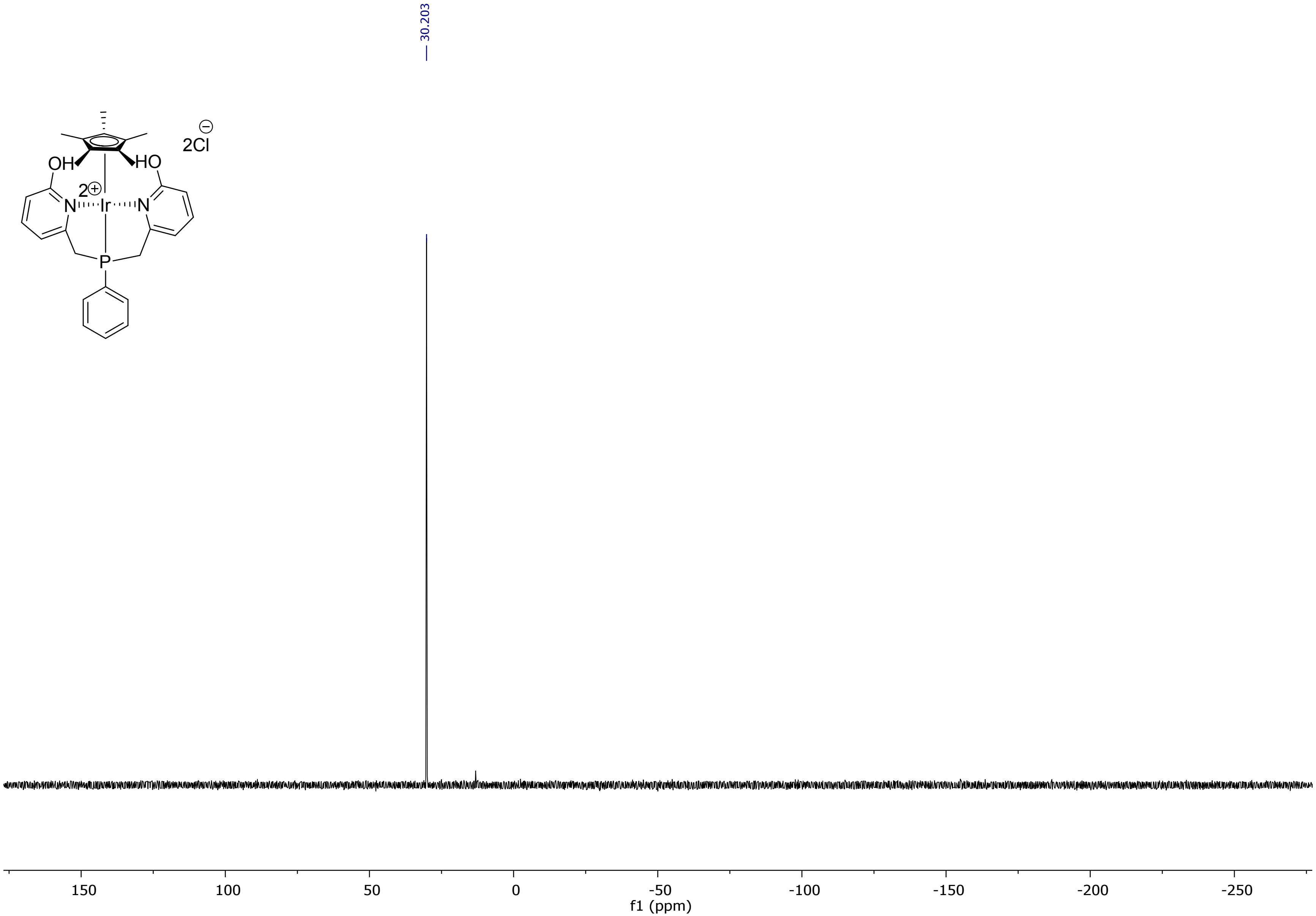

165.73
147.49
147.41
141.39
116.32
106.81
106.71
77.160
28.926
28.796
27.266
27.134
24.476
O
H
N
H
N
O

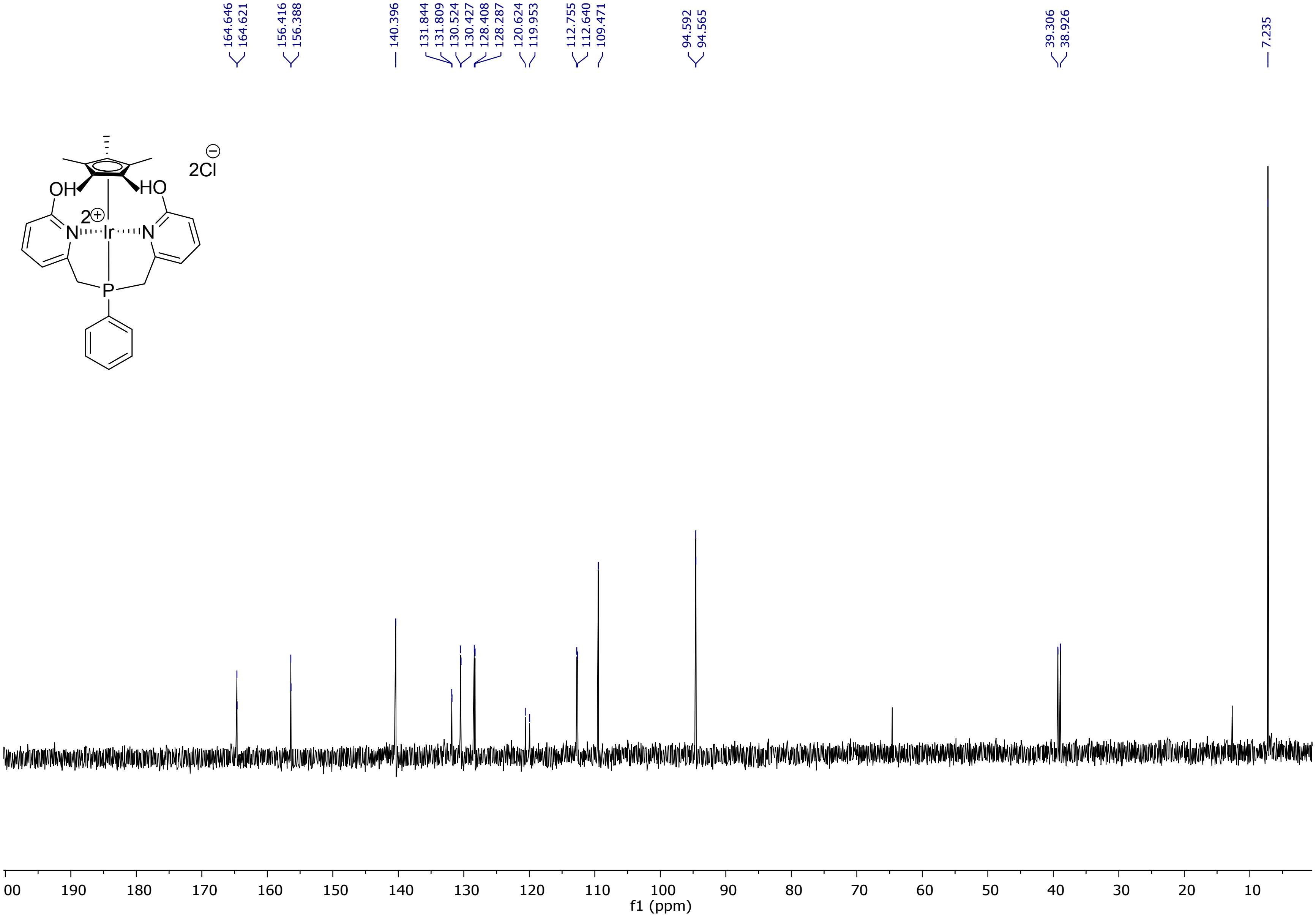

8.027
8.010
7.995
7.978
7.827
7.819
7.793
7.719
7.706
7.696
7.675
7.331
7.314
7.309
7.291
7.161
7.142
7.111
7.093
6.873
6.852
6.792
6.771
6.242
6.240
6.219
6.217
6.049
6.042
6.032
6.025
4.655
4.626
4.610
4.580
4.374
4.338
4.329
4.292
4.195
4.175
4.142
4.101
3.864
3.837
3.828
3.802
3.616
3.586
3.581
3.550
3.310
1.617
1.611
1.495
1.489
Ph
P
Ir
Cl
Cl
HO
N
N
OH
D2O
OH
HO
N
Ir
N
P
2⊕
2Cl⊖
Ir-1
(major)
Ir-1'
(minor)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

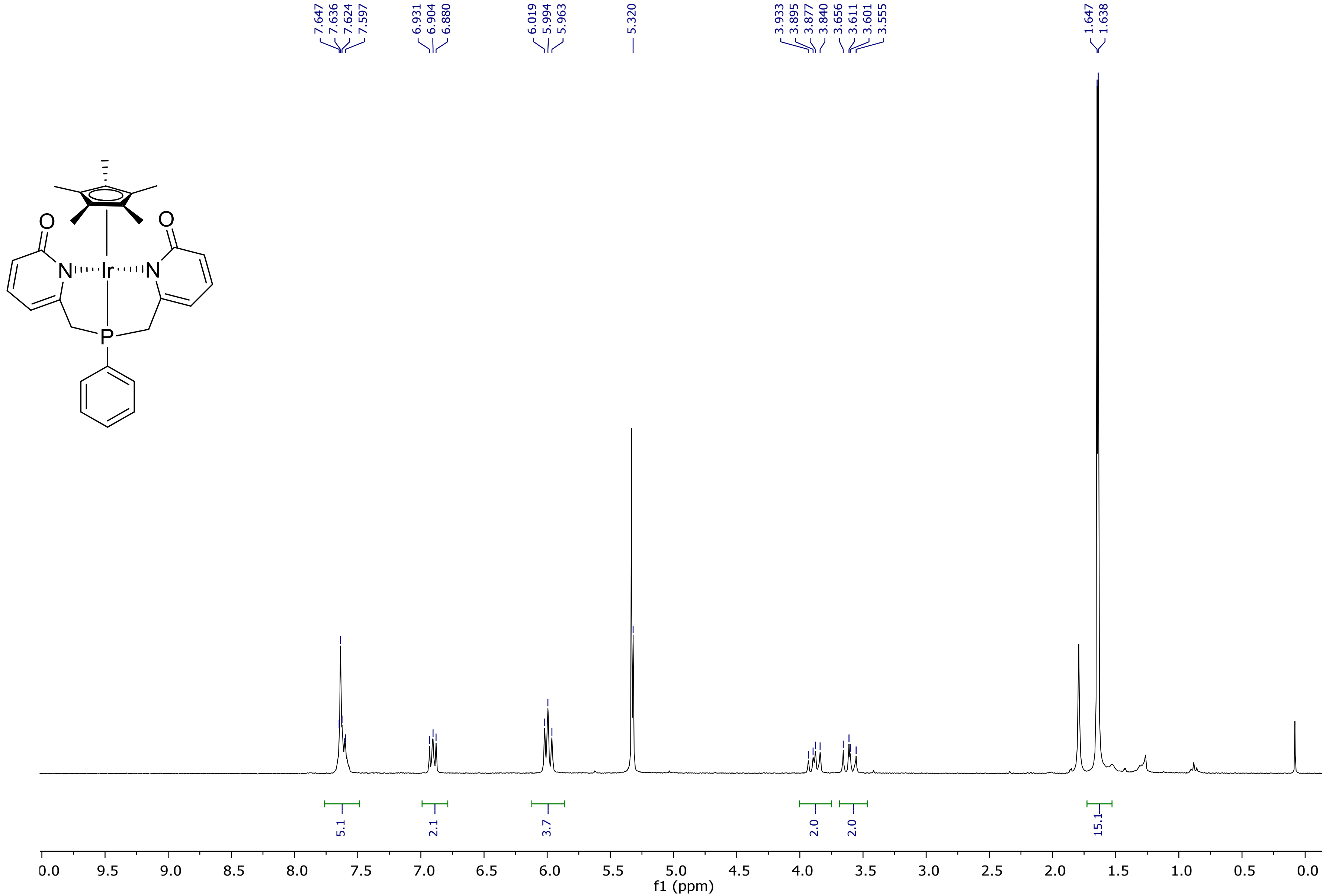


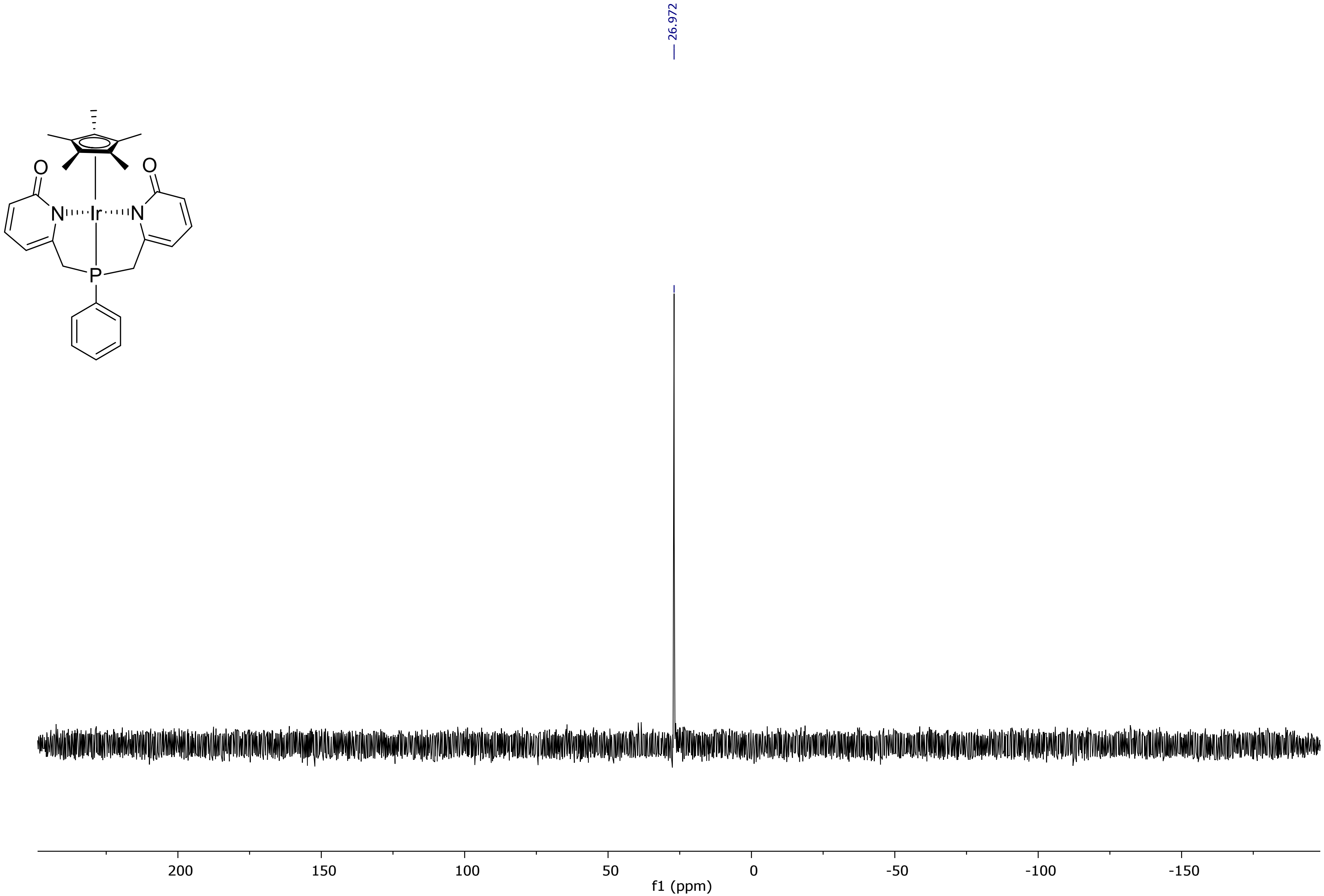
7.952
7.935
7.920
7.902
7.899
7.842
7.837
7.824
7.809
7.801
7.790
7.782
7.769
7.705
7.684
7.666
7.149
7.130
6.806
6.785
4.790
4.563
4.534
4.517
4.488
4.327
4.291
4.281
4.245
1.561
1.555
2Cl
OH
HO
2⊕
N
Ir
N
P
2.2
3.3
2.3
2.0
2.0
0.8
1.2
1.2
0.9
15.2
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

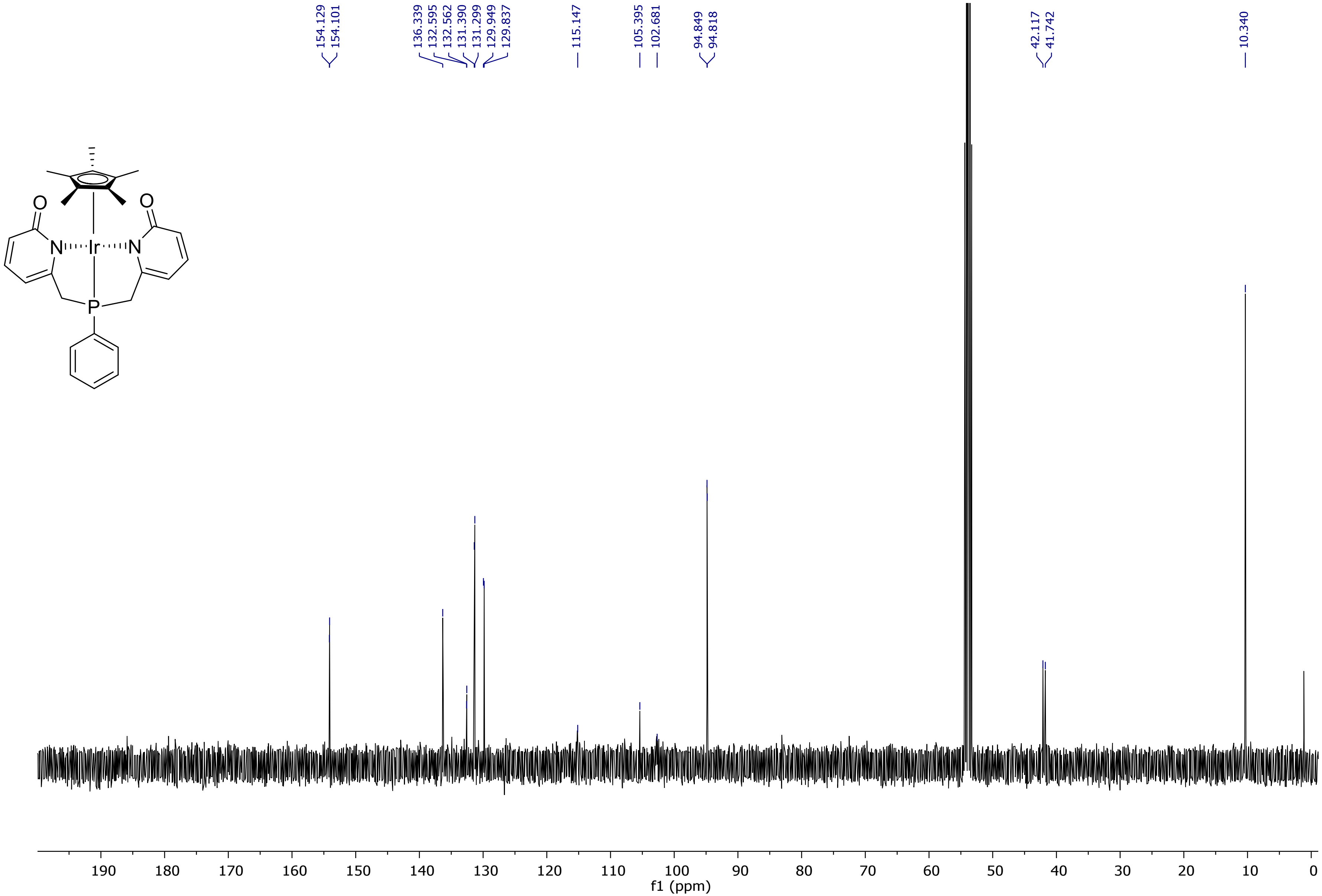

30.200
13.512
Ph
HO
N
P
Ir
Cl
OH
D$_2$O
2Cl
OH
HO
N
Ir
N
P
Ir-1
(major)
Ir-1'
(minor)
50
45
40
35
30
25
20
15
10
5
0
-5
-10
f1 (ppm)

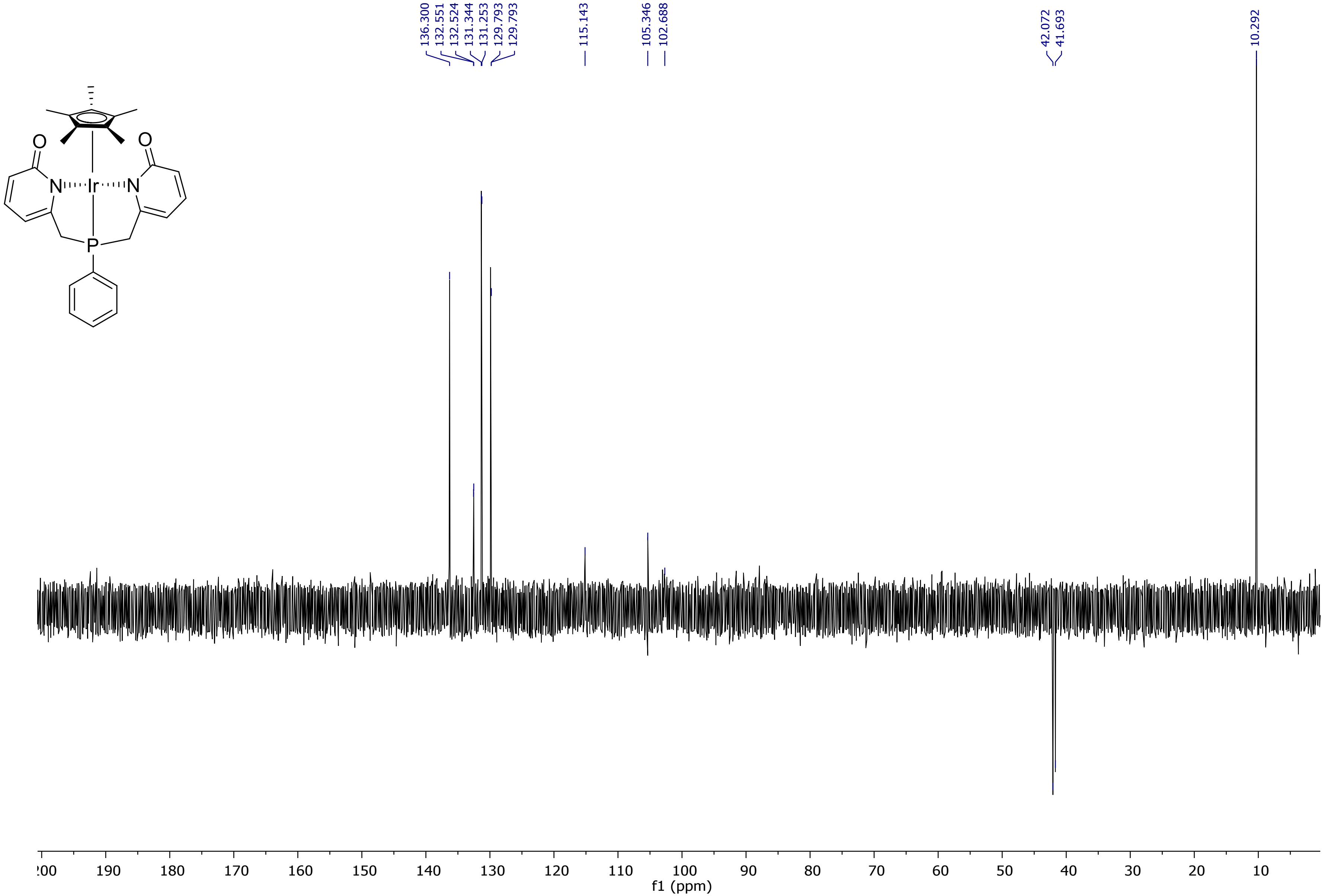

30.203
OH
HO
2Cl⊖
2⊕
N
Ir
N
P
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)

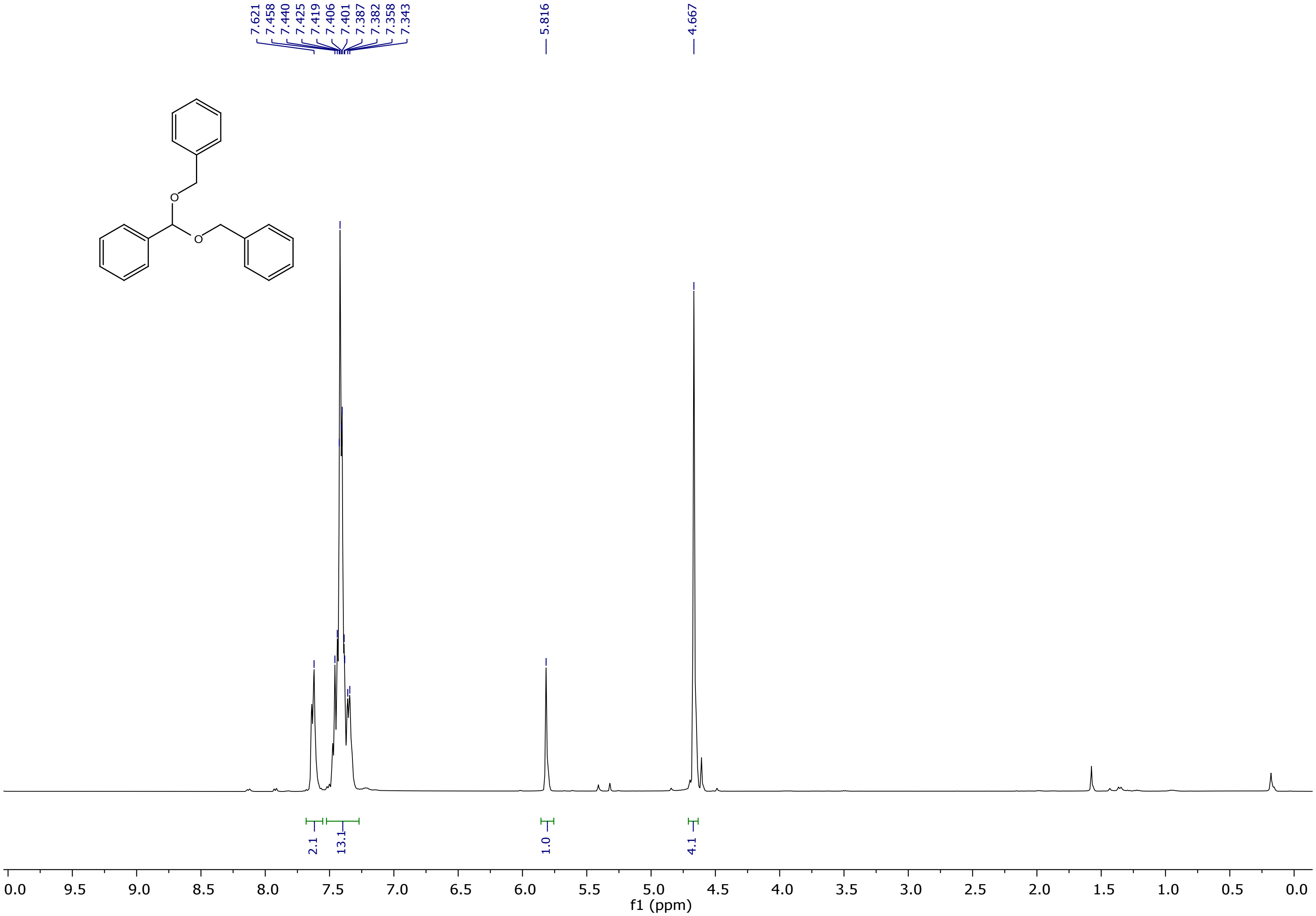

164.646
164.621
156.416
156.388
140.396
131.844
131.809
130.524
130.427
128.408
128.287
120.624
119.953
112.755
112.640
109.471
94.592
94.565
39.306
38.926
7.235
OH
HO
2⊕
N
Ir
N
P
2Cl⊖
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

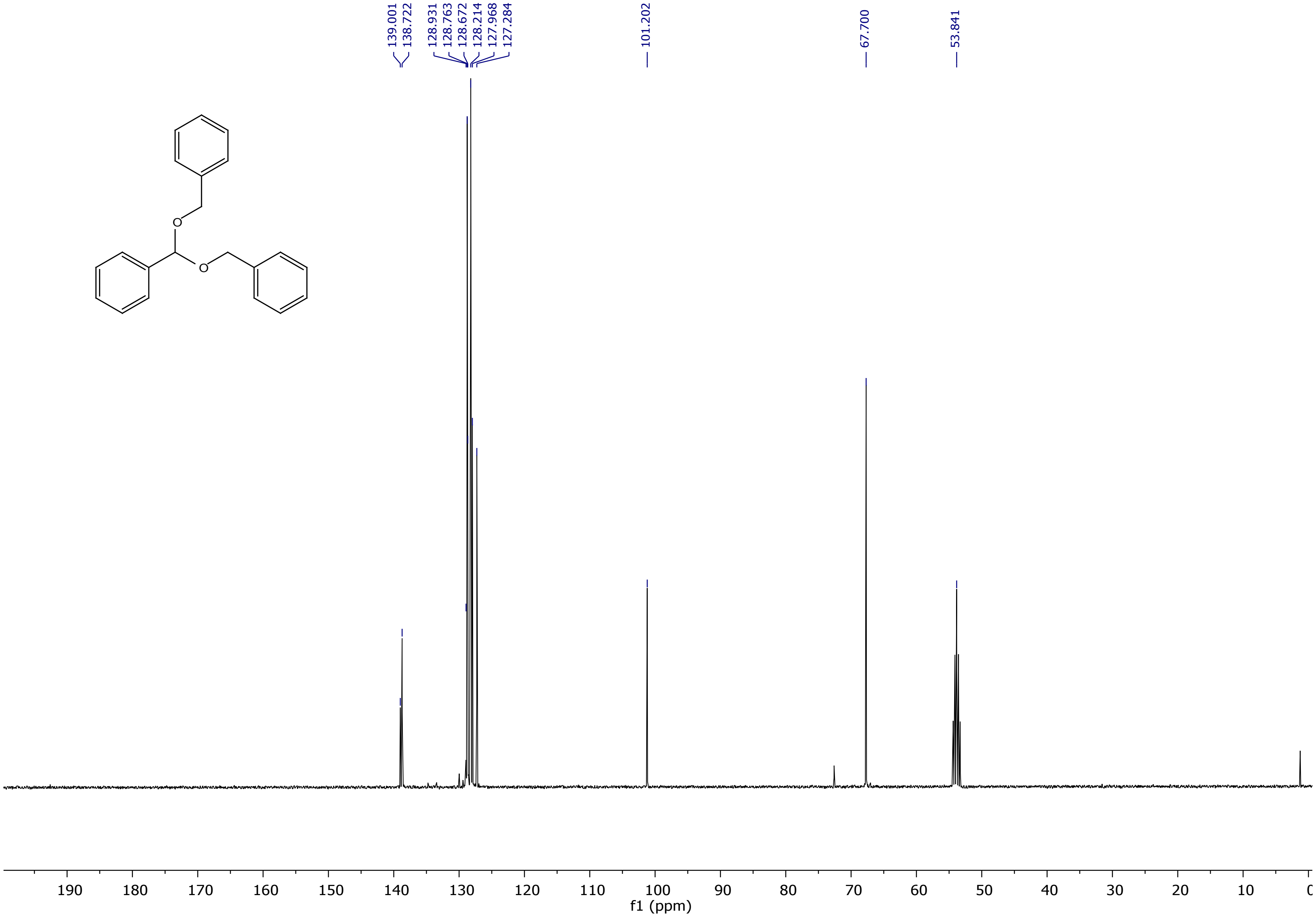

7.647
7.636
7.624
7.597
6.931
6.904
6.880
6.019
5.994
5.963
5.320
3.933
3.895
3.877
3.840
3.656
3.611
3.601
3.555
1.647
1.638
5.1
2.1
3.7
2.0
2.0
15.1
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
O
N
Ir
N
P

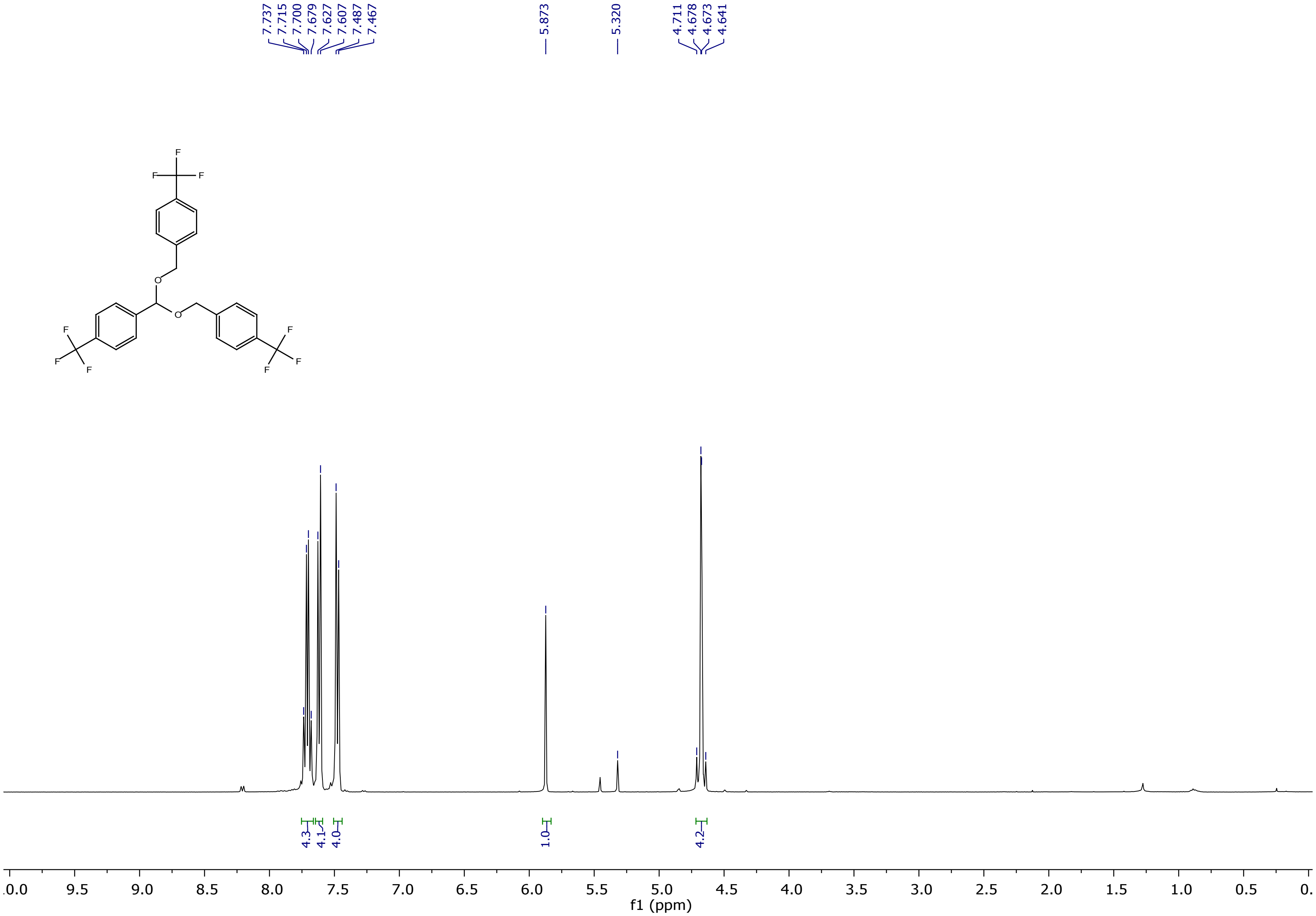

26.972
O
O
N
Ir
N
P
200
150
100
50
0
-50
-100
-150
f1 (ppm)

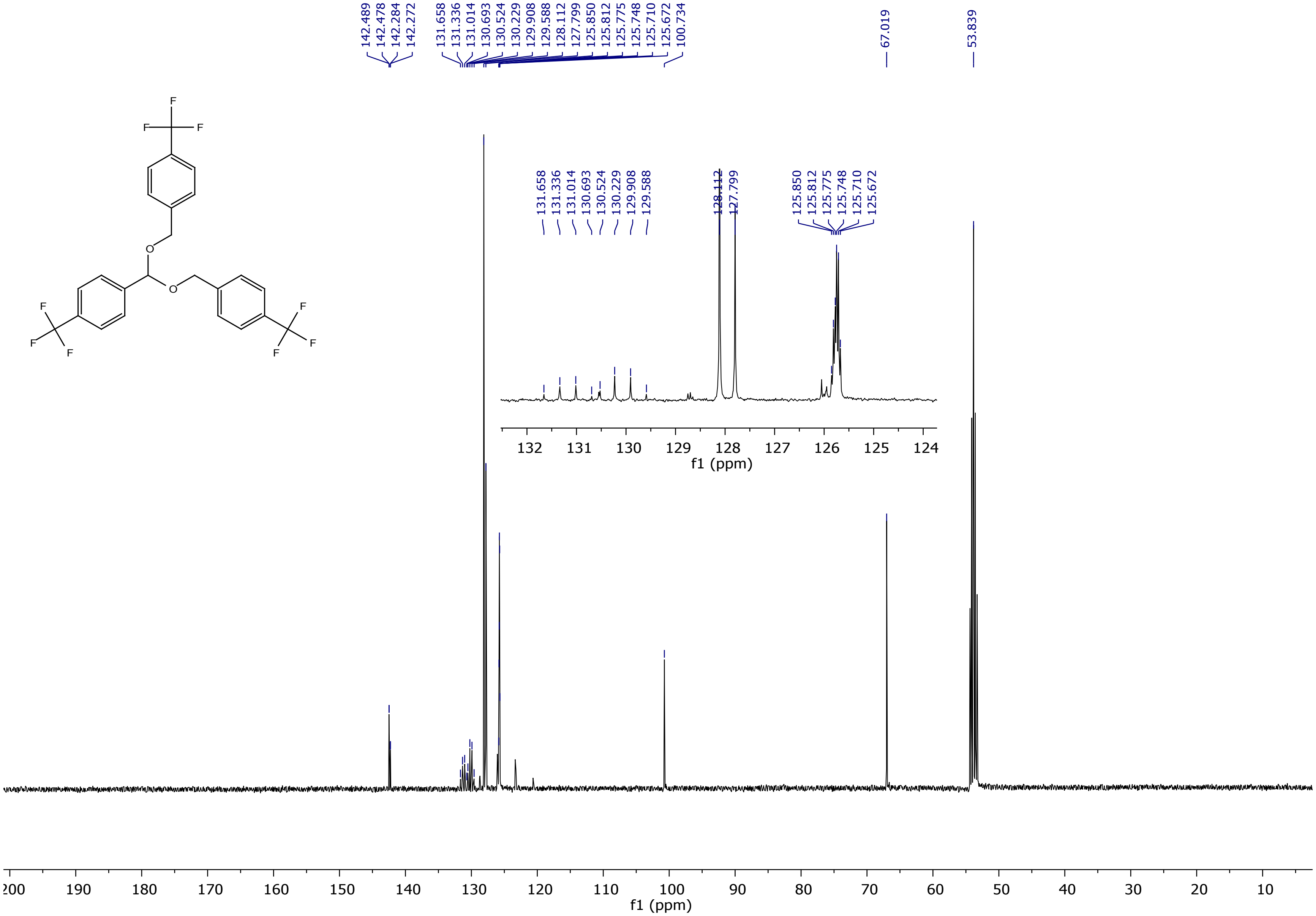

154.129
154.101
136.339
132.595
132.562
131.390
131.299
129.949
129.837
115.147
105.395
102.681
94.849
94.818
42.117
41.742
10.340
O
O
N
Ir
N
P
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

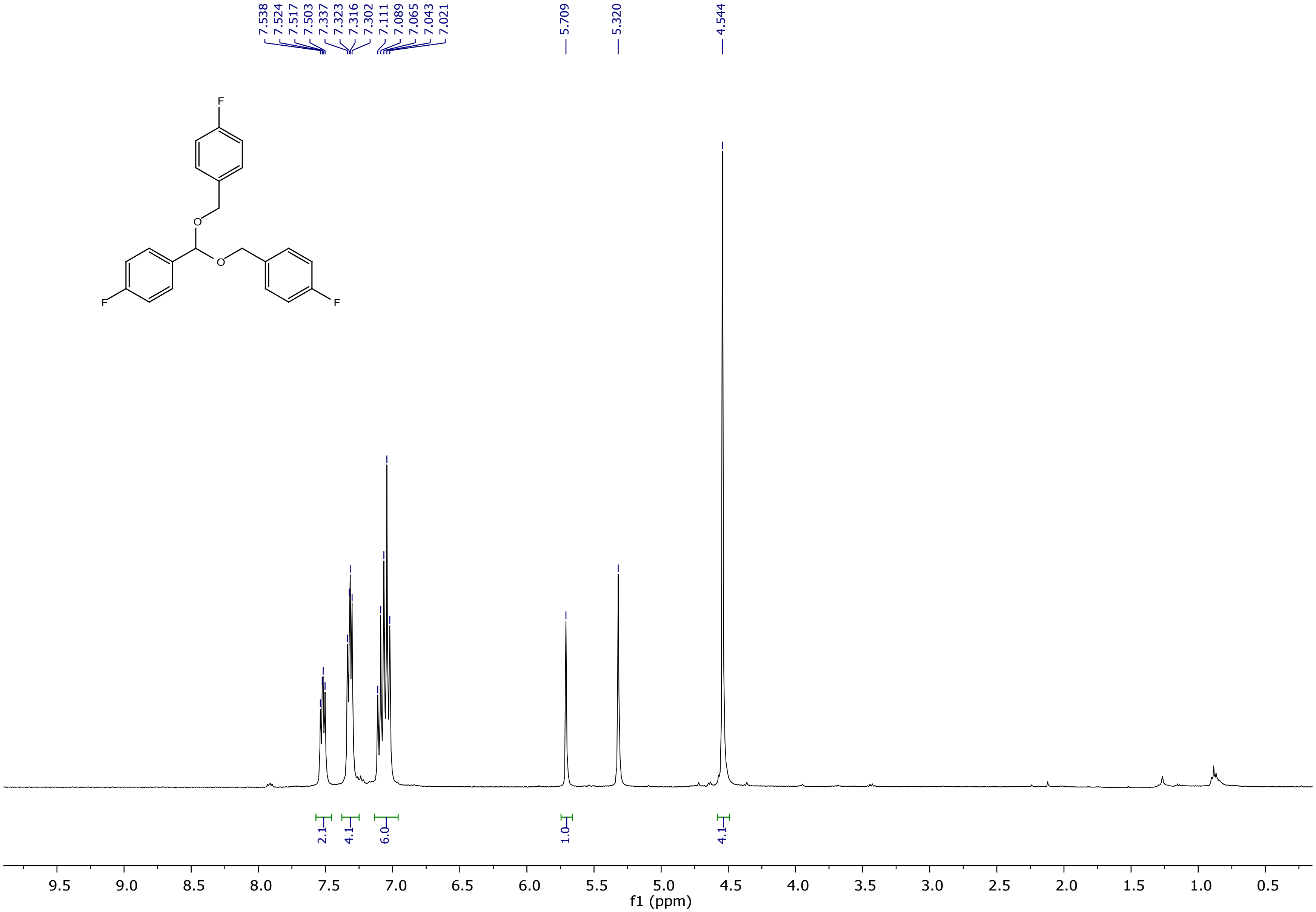

136.300
132.551
132.524
131.344
131.253
129.793
129.793
115.143
105.346
102.688
42.072
41.693
10.292
O
O
N
Ir
N
P
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

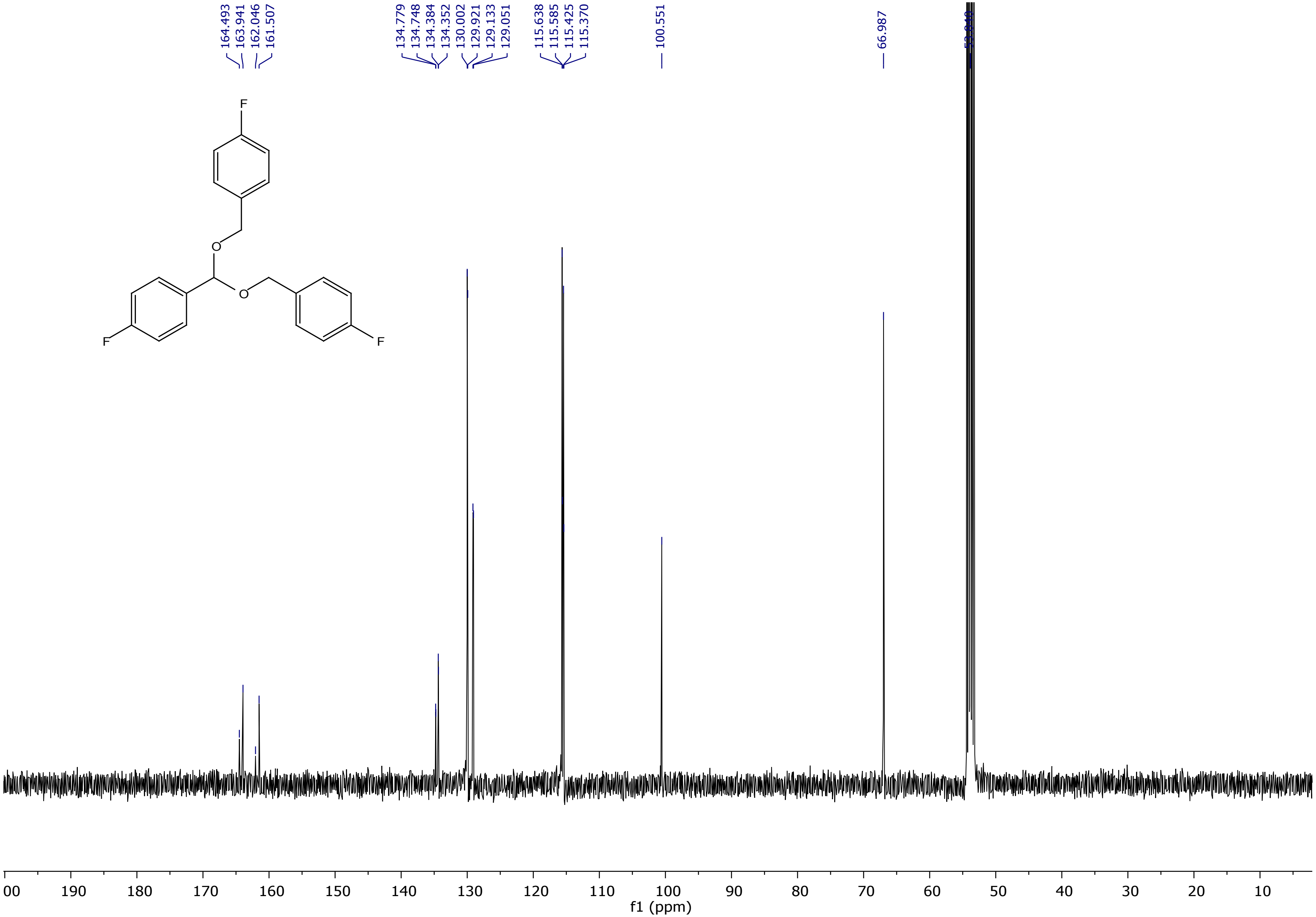

7.621
7.458
7.440
7.425
7.419
7.406
7.401
7.387
7.382
7.358
7.343
5.816
4.667
O
O
2.1
13.1
1.0
4.1
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


139.001
138.722
128.931
128.763
128.672
128.214
127.968
127.284
101.202
67.700
53.841
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

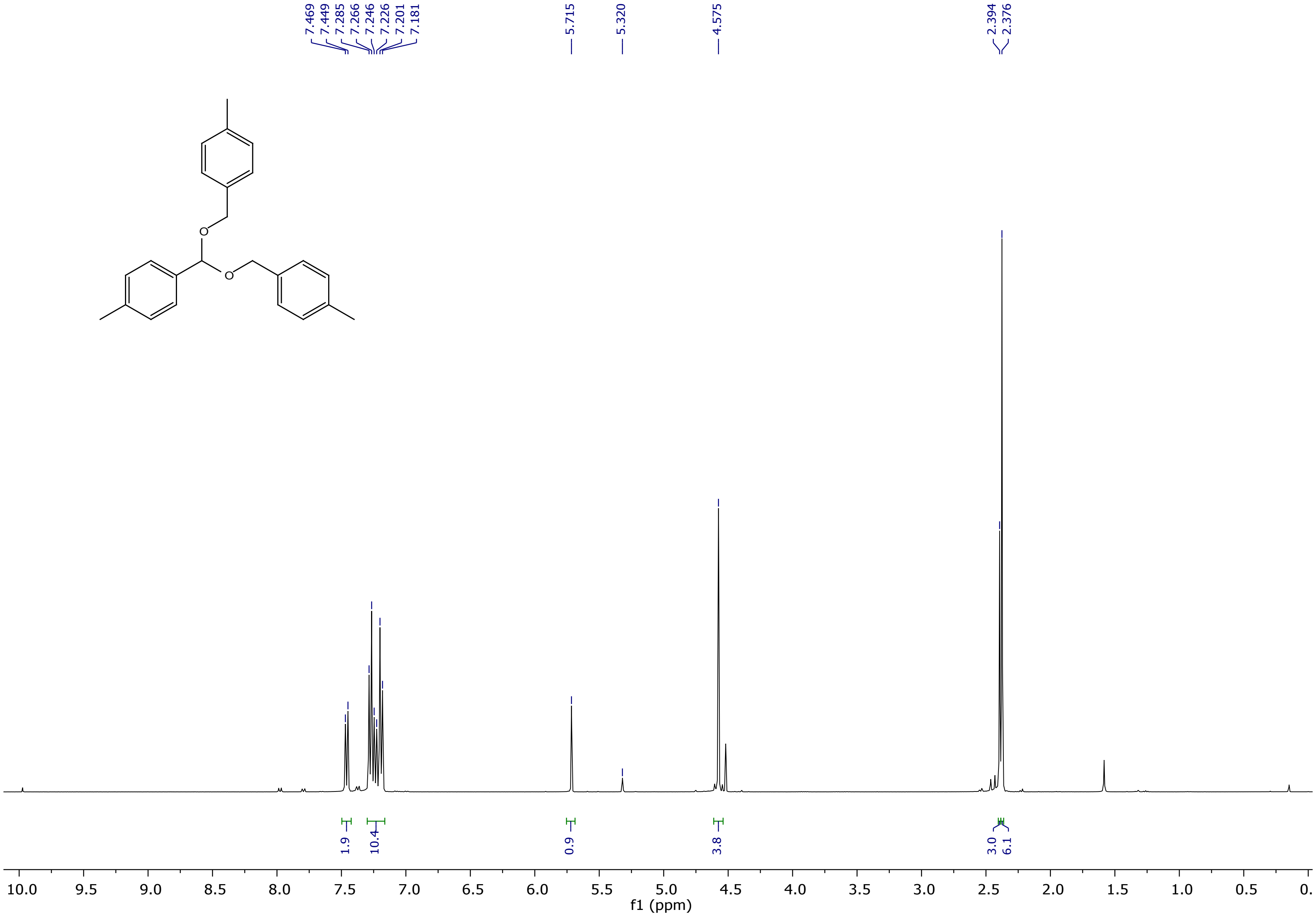

7.737
7.715
7.700
7.679
7.627
7.607
7.487
7.467
5.873
5.320
4.711
4.678
4.673
4.641
F
F
F
O
O
F
F
F
F
F
F
4.3
4.1
4.0
1.0
4.2
.0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

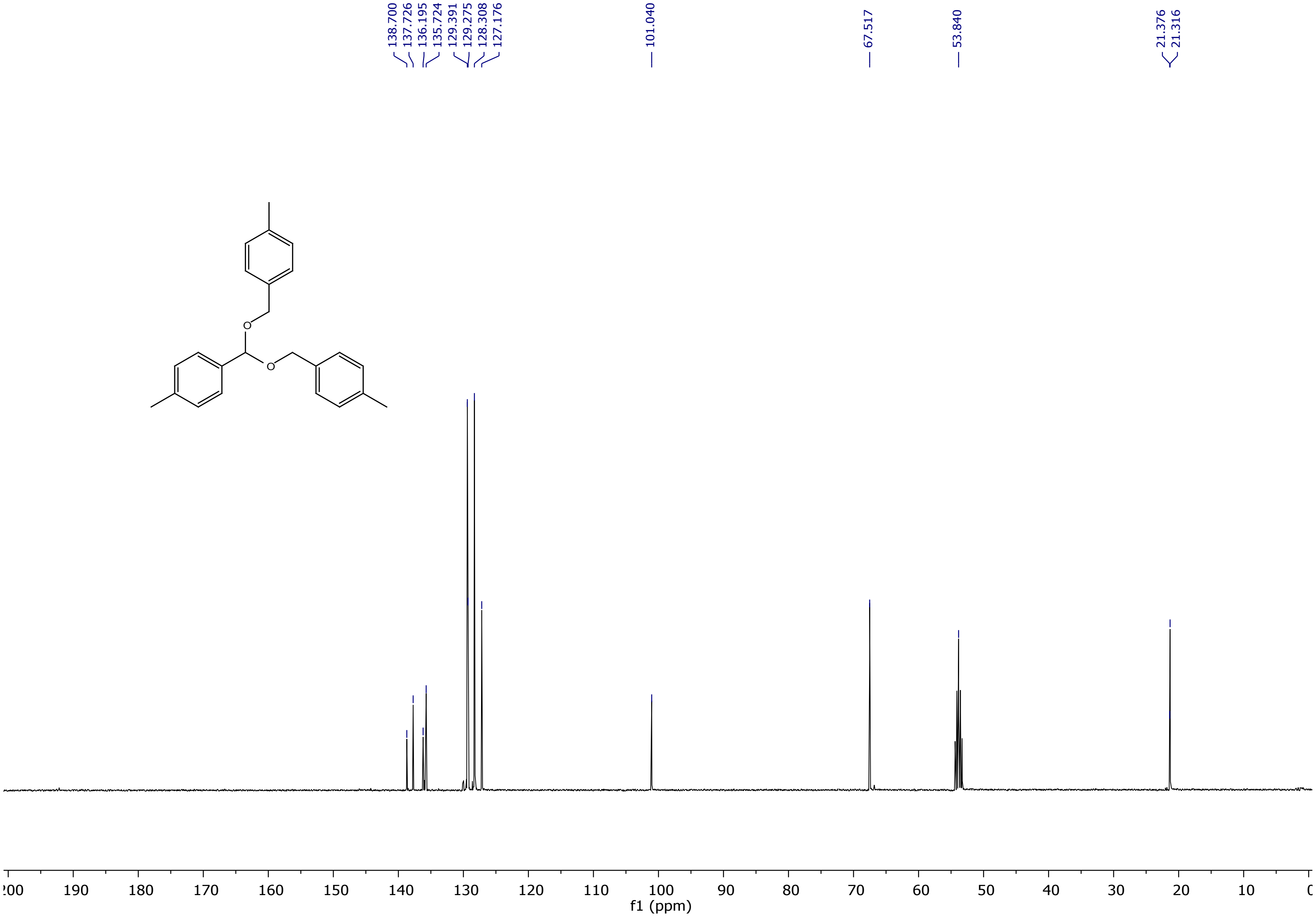

142.489
142.478
142.284
142.272
131.658
131.336
131.014
130.693
130.524
130.229
129.908
129.588
128.112
127.799
125.850
125.812
125.775
125.748
125.710
125.672
100.734
67.019
53.839
F
F
F
O
O
F
F
F
F
F
F
131.658
131.336
131.014
130.693
130.524
130.229
129.908
129.588
128.112
127.799
125.850
125.812
125.775
125.748
125.710
125.672
132
131
130
129
128
127
126
125
124
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

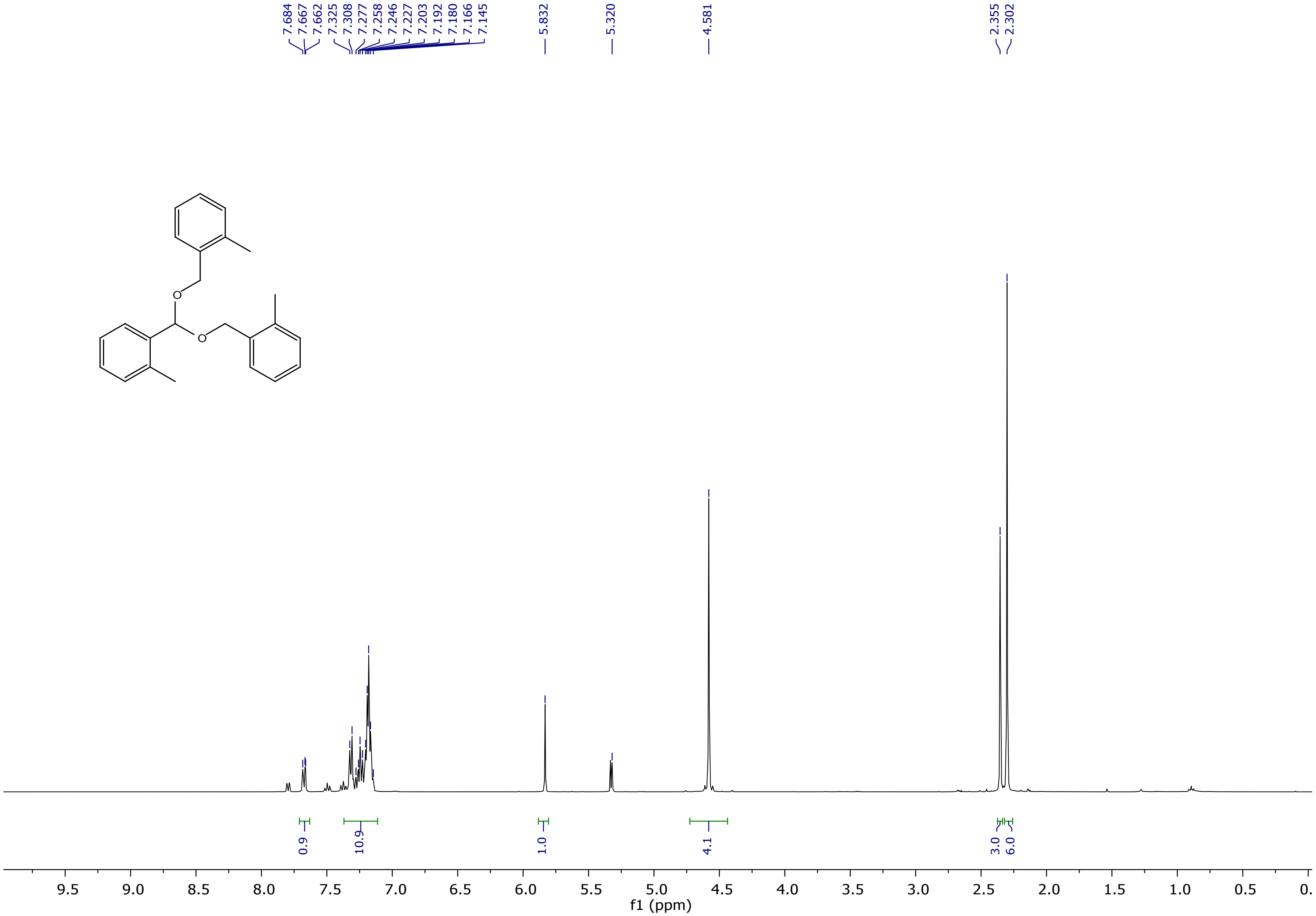

7.538
7.524
7.517
7.503
7.337
7.323
7.316
7.302
7.111
7.089
7.065
7.043
7.021
5.709
5.320
4.544
F
O
O
F
F
2.1
4.1
6.0
1.0
4.1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

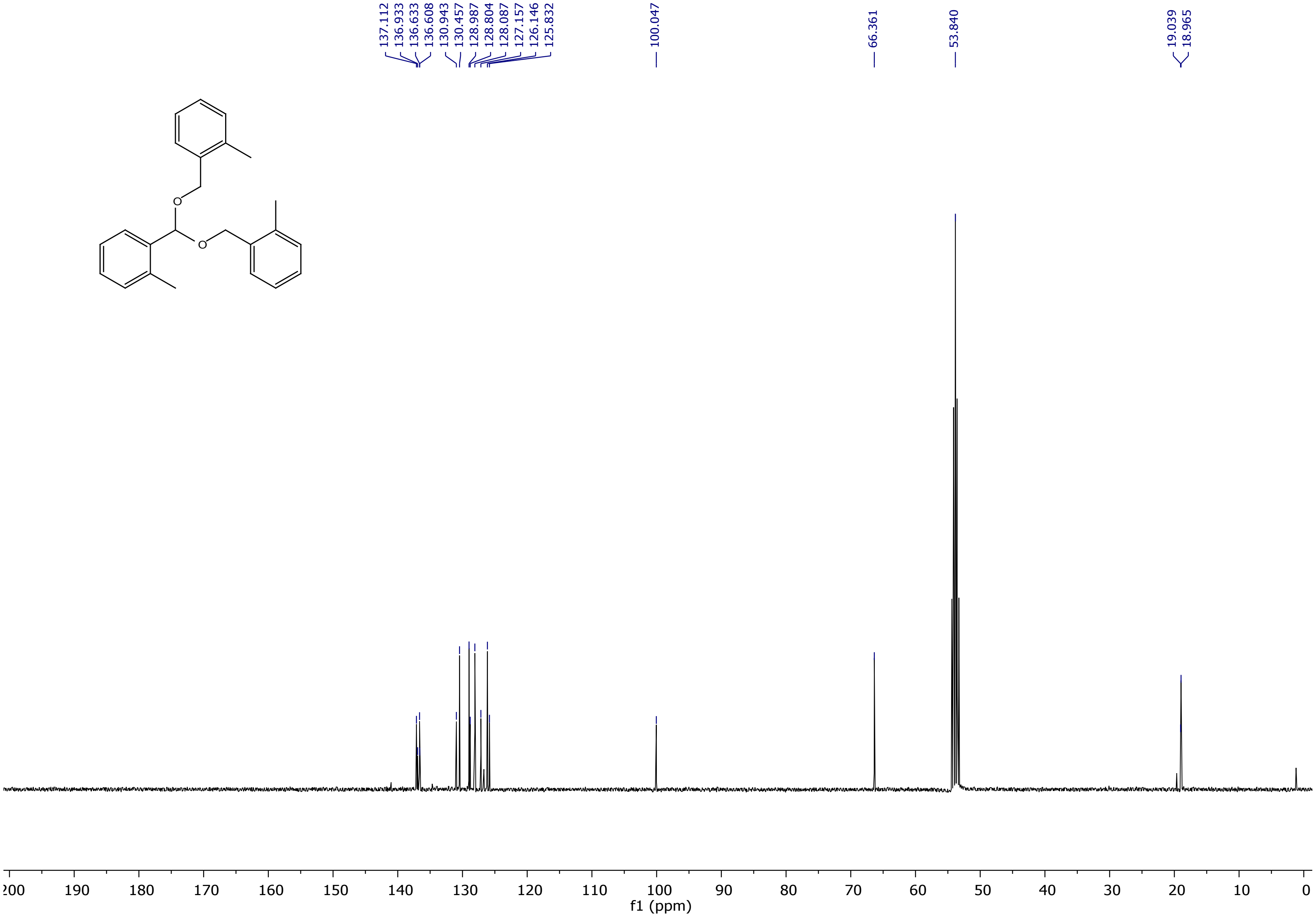

164.493
163.941
162.046
161.507
134.779
134.748
134.384
134.352
130.002
129.921
129.133
129.051
115.638
115.585
115.425
115.370
100.551
66.987
53.840
F
O
O
F
F
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

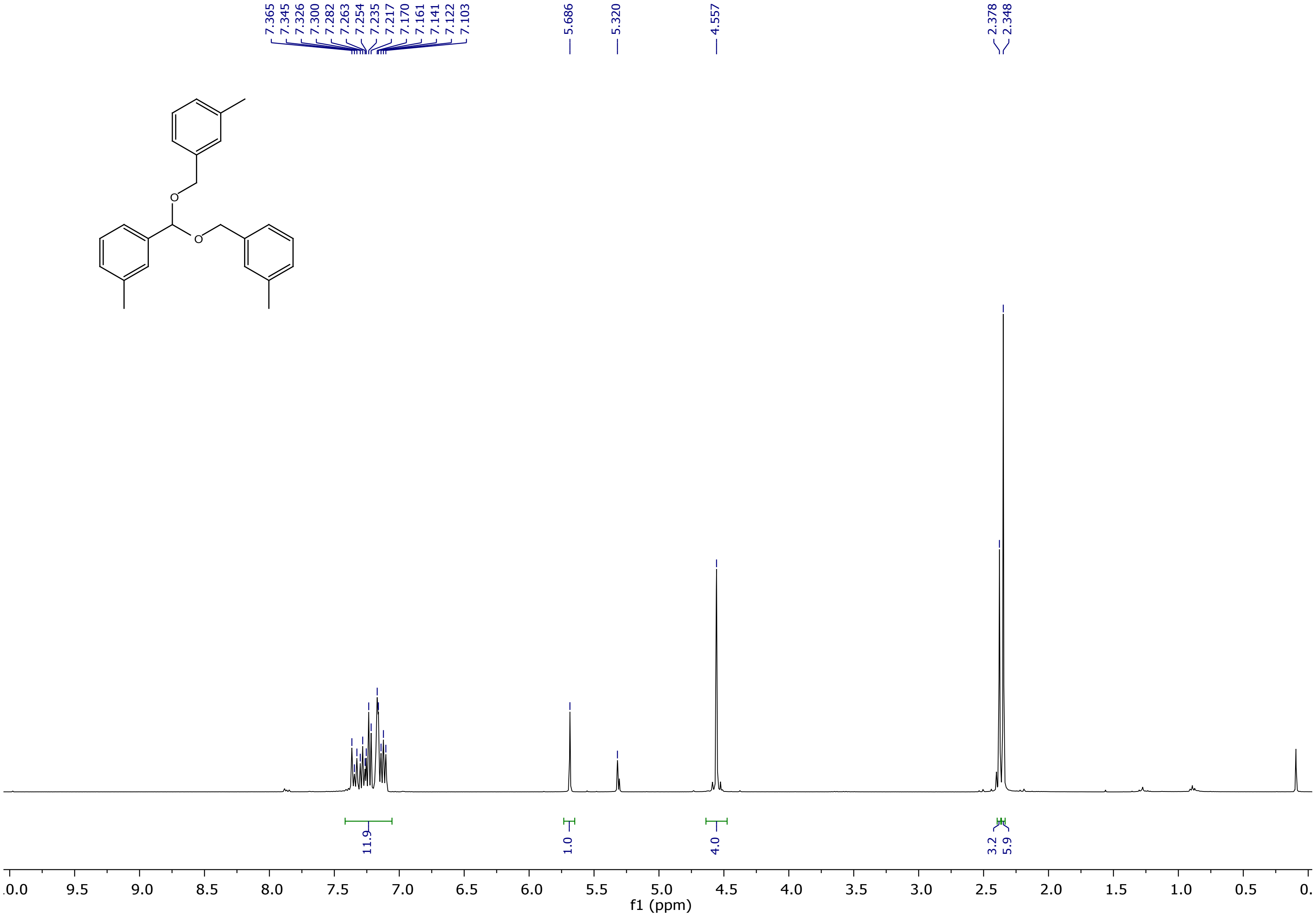

-114.271
-115.630
F
O
O
F
F
-85
-90
-95
-100
-105
-110
-115
-120
-125
f1 (ppm)

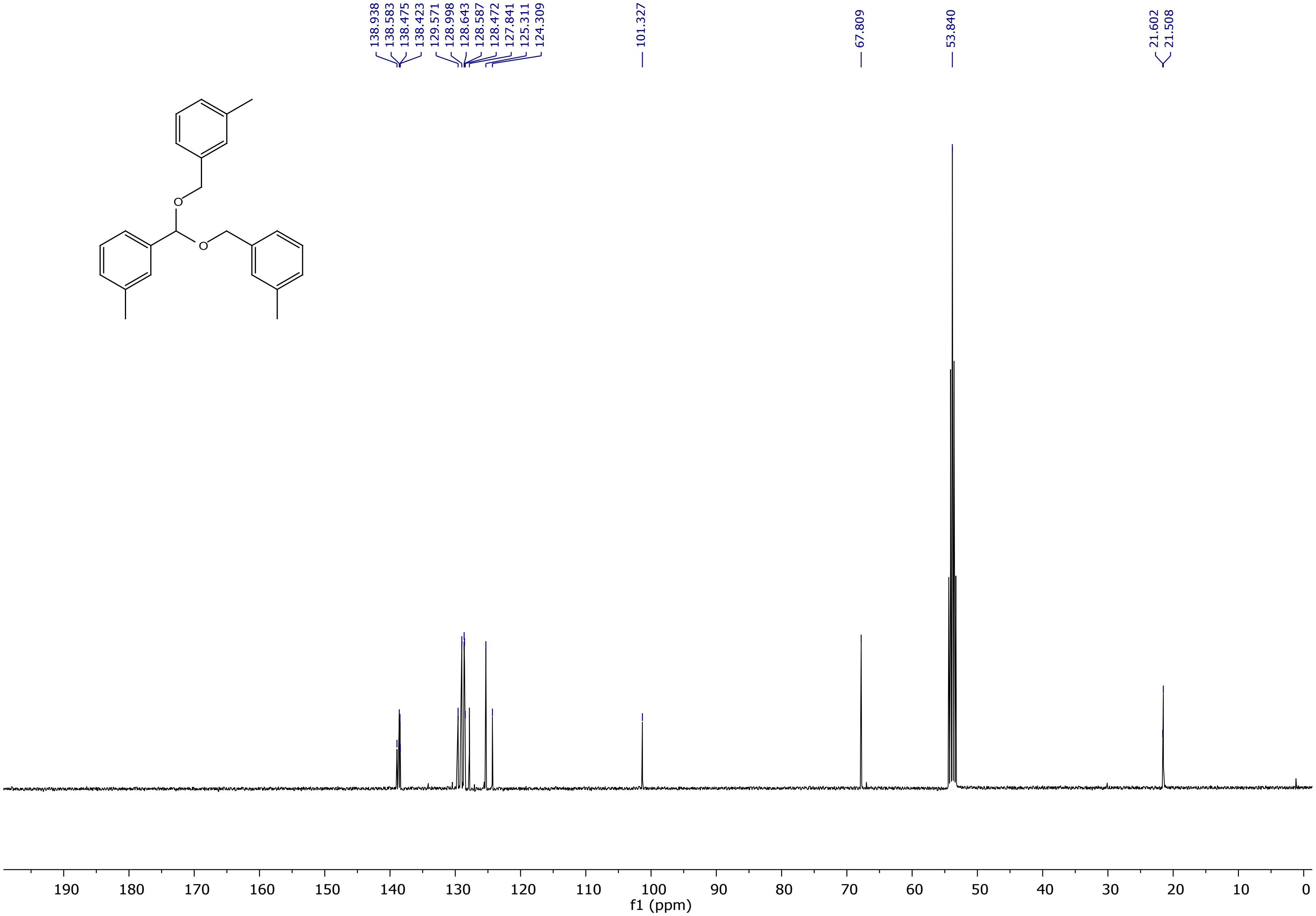

7.469
7.449
7.285
7.266
7.246
7.226
7.201
7.181
5.715
5.320
4.575
2.394
2.376
O
O
1.9
10.4
0.9
3.8
3.0
6.1
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

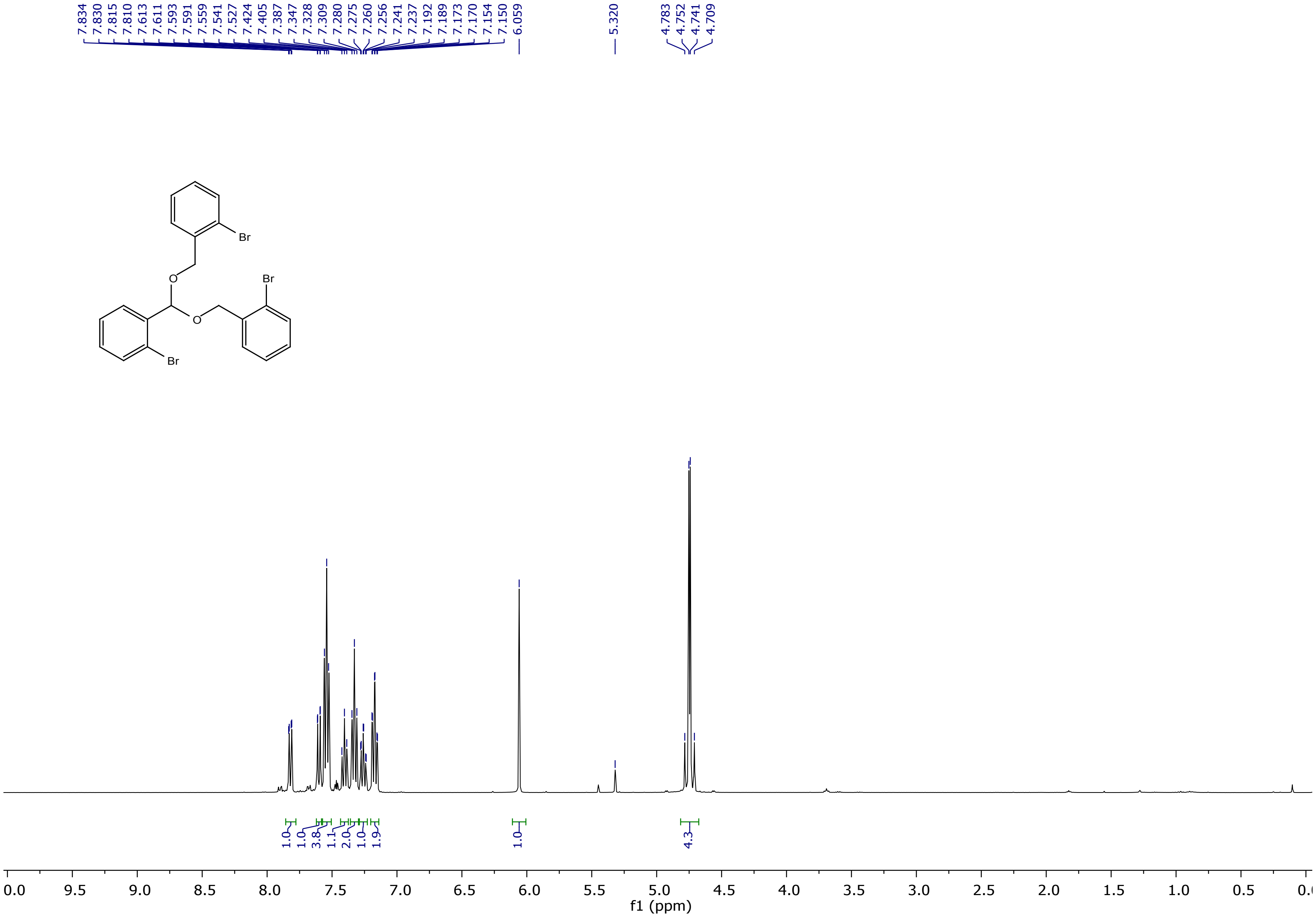

138.700
137.726
136.195
135.724
129.391
129.275
128.308
127.176
101.040
67.517
53.840
21.376
21.316
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

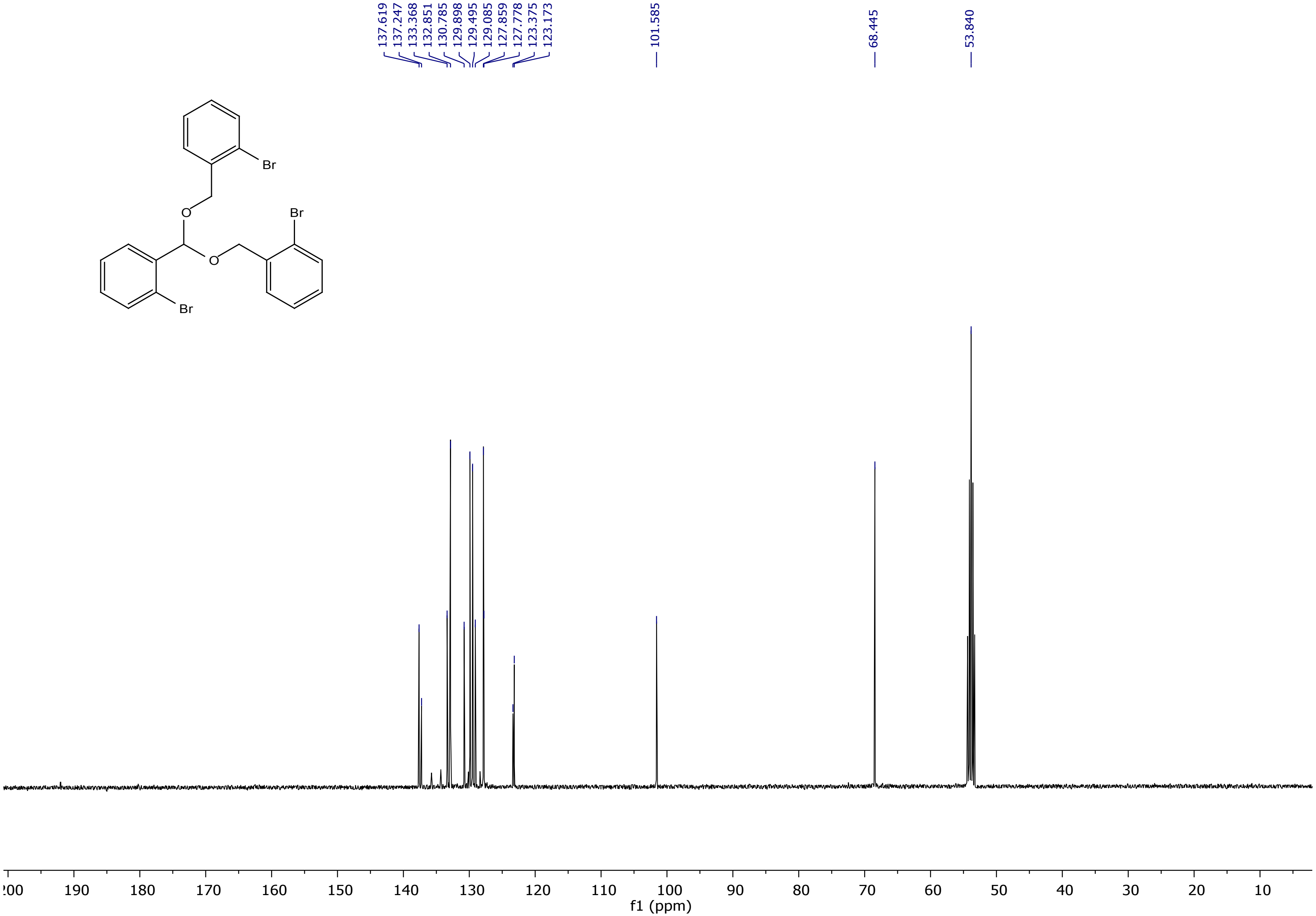

7.684
7.667
7.662
7.325
7.308
7.277
7.258
7.246
7.227
7.203
7.192
7.180
7.166
7.145
5.832
5.320
4.581
2.355
2.302
0.9
10.9
1.0
4.1
3.0
6.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)
O
O

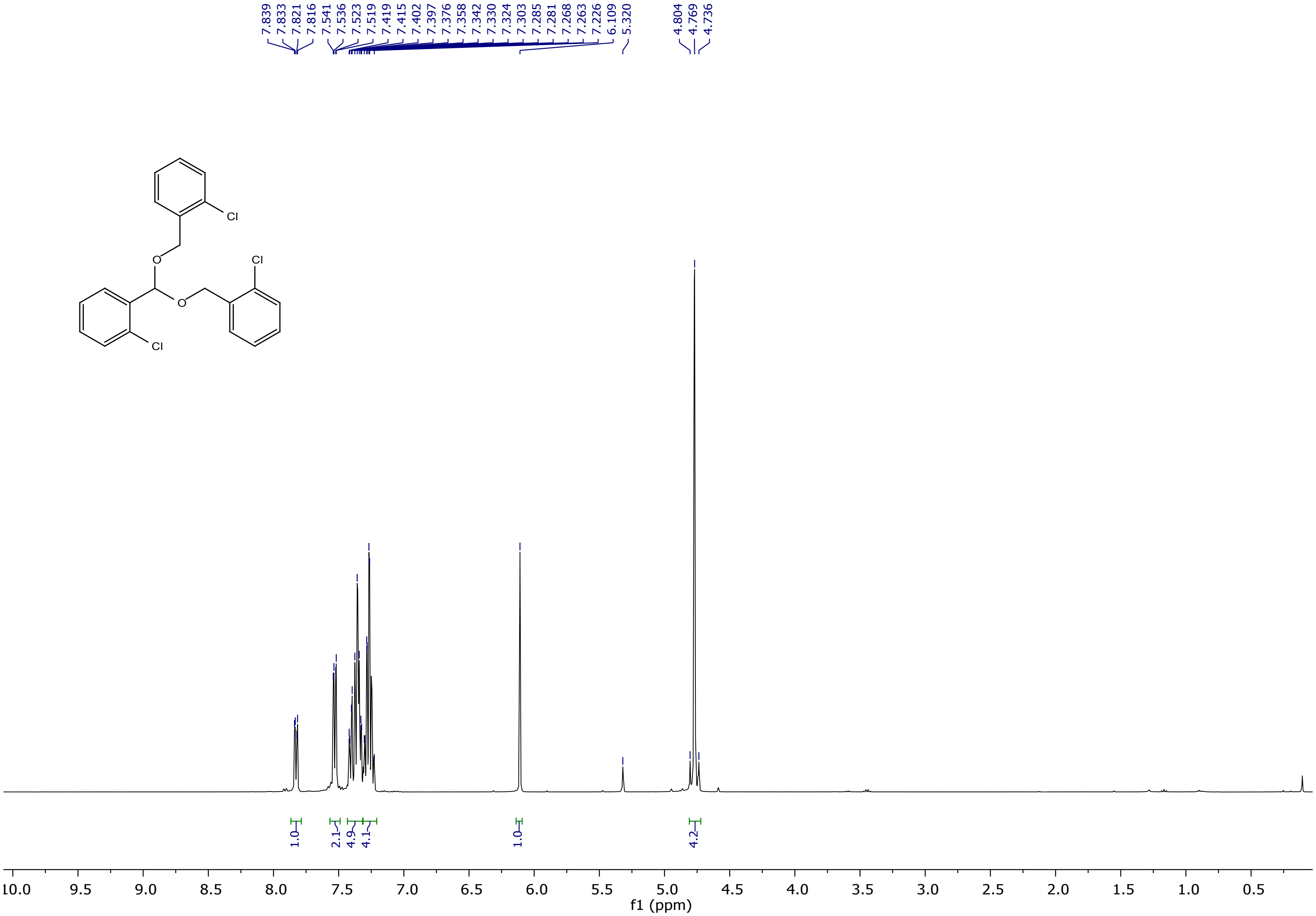

137.112
136.933
136.633
136.608
130.943
130.457
128.987
128.804
128.087
127.157
126.146
125.832
100.047
66.361
53.840
19.039
18.965
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

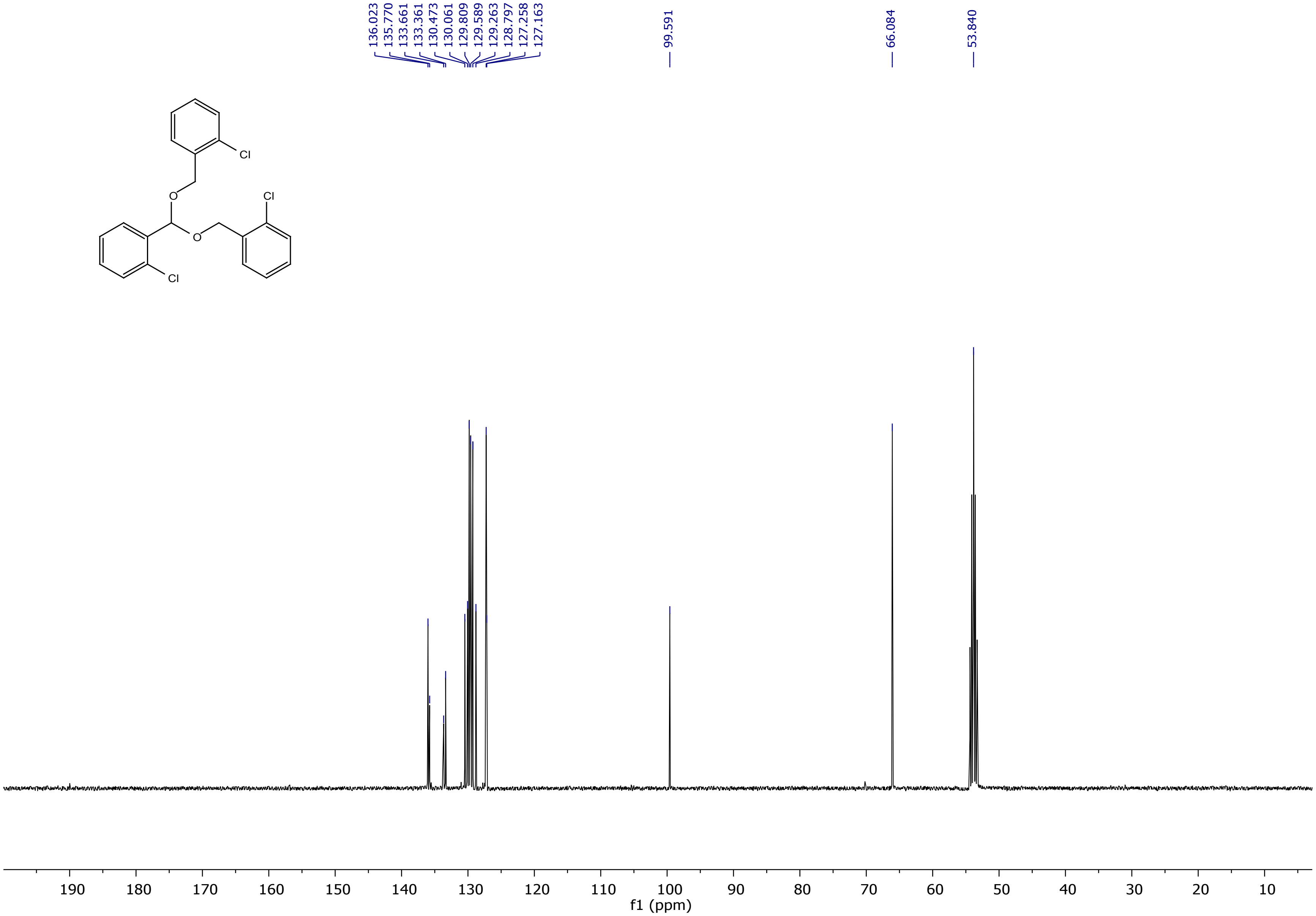

7.365
7.345
7.326
7.300
7.282
7.263
7.254
7.235
7.217
7.170
7.161
7.141
7.122
7.103
5.686
5.320
4.557
2.378
2.348
O
O
11.9
1.0
4.0
3.2
5.9
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

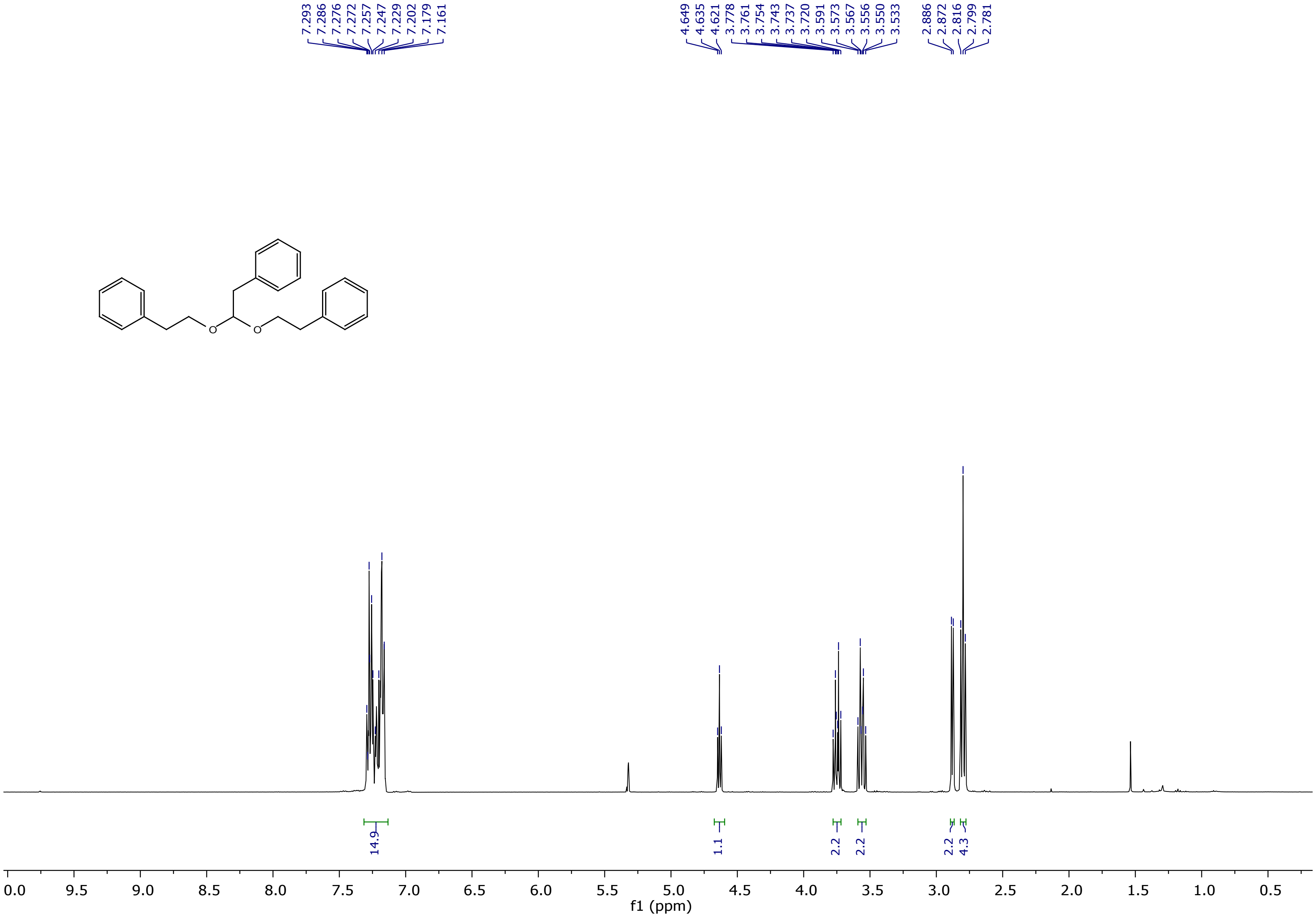

138.938
138.583
138.475
138.423
129.571
128.998
128.643
128.587
128.472
127.841
125.311
124.309
101.327
67.809
53.840
21.602
21.508
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

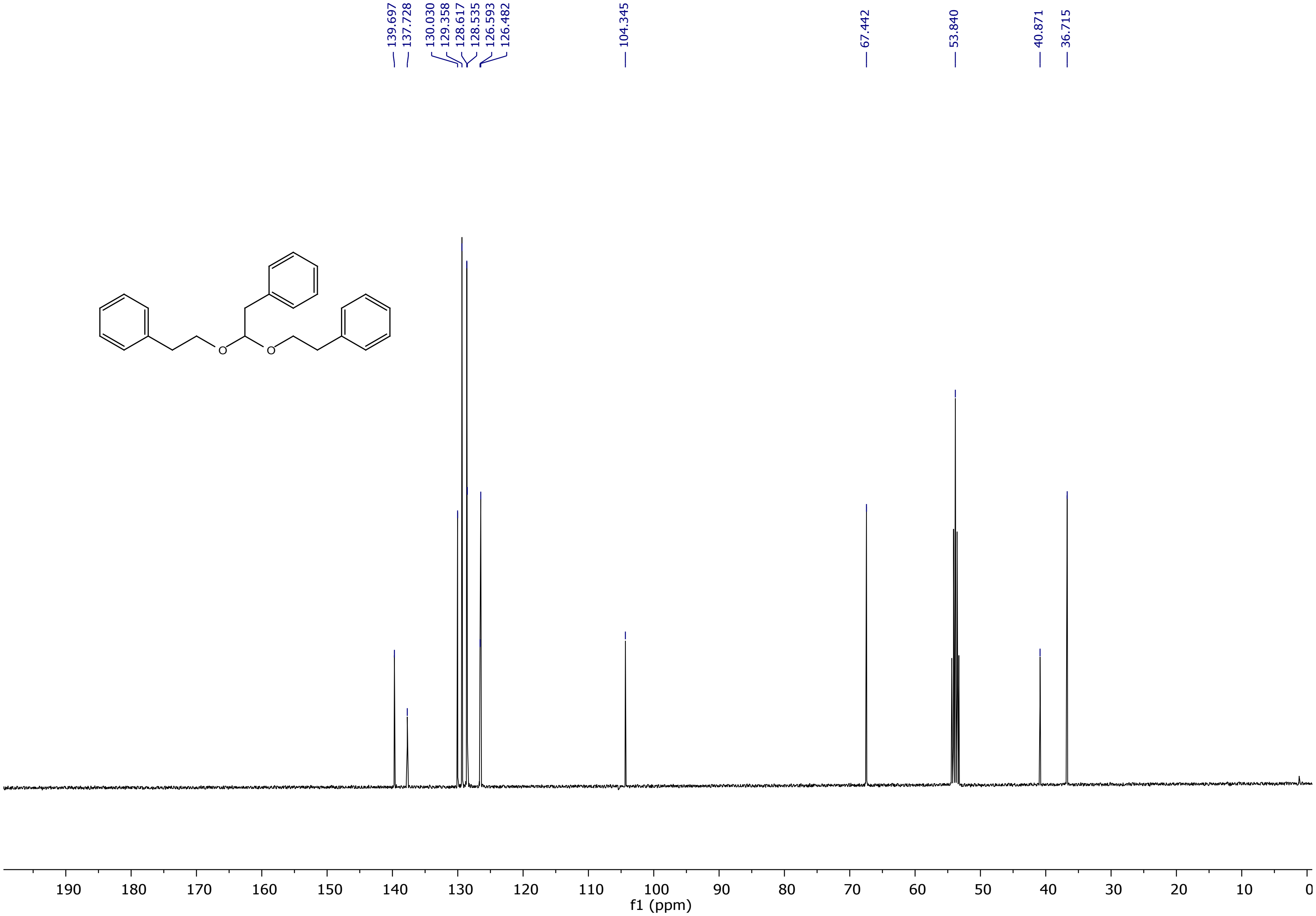

7.834
7.830
7.815
7.810
7.613
7.611
7.593
7.591
7.559
7.541
7.527
7.424
7.405
7.387
7.347
7.328
7.309
7.280
7.275
7.260
7.256
7.241
7.237
7.192
7.189
7.173
7.170
7.154
7.150
6.059
5.320
4.783
4.752
4.741
4.709
Br
O
Br
O
Br
1.0
1.0
3.8
1.1
2.0
1.0
1.9
1.0
4.3
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

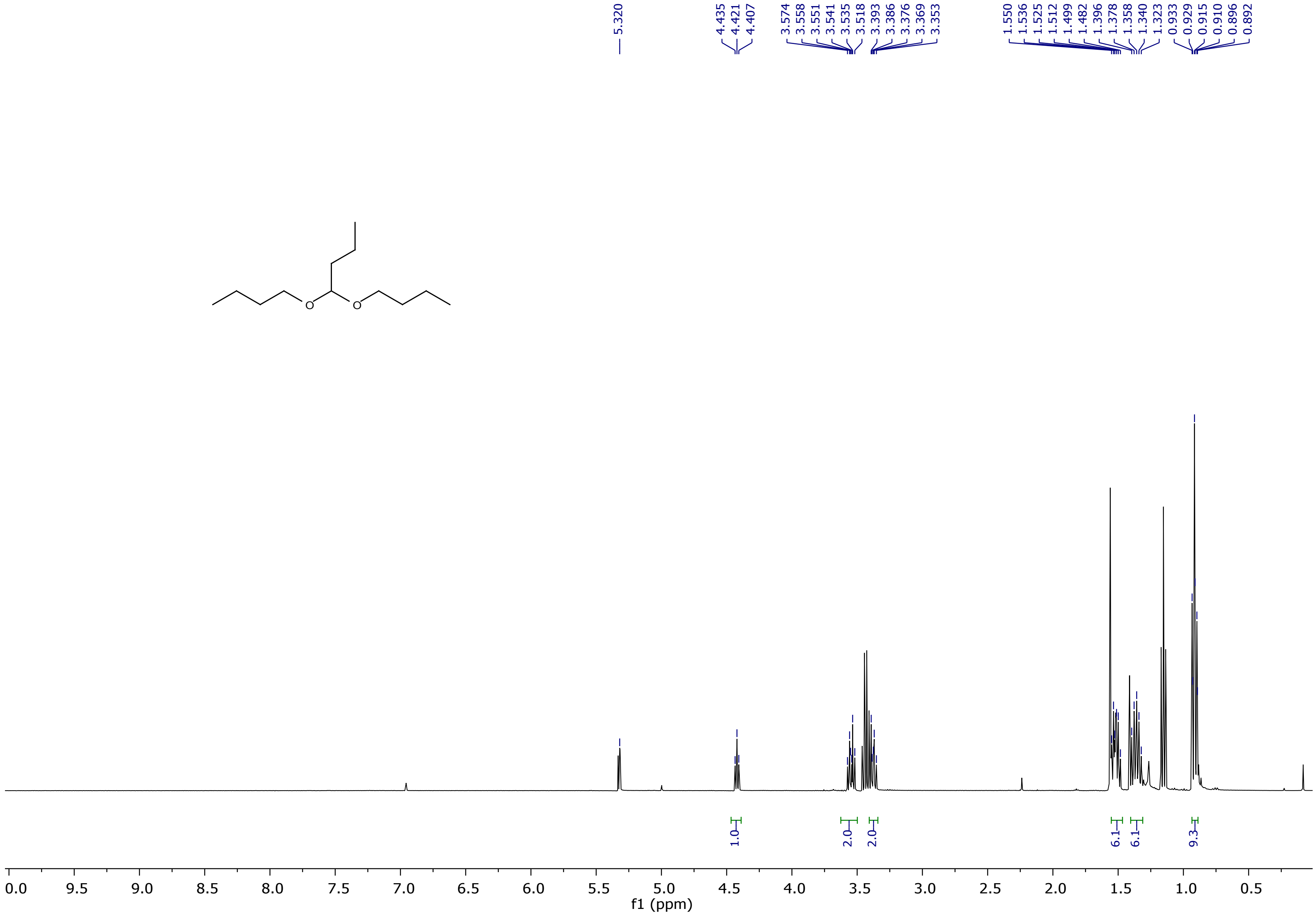

137.619
137.247
133.368
132.851
130.785
129.898
129.495
129.085
127.859
127.778
123.375
123.173
101.585
68.445
53.840
Br
O
Br
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.839
7.833
7.821
7.816
7.541
7.536
7.523
7.519
7.419
7.415
7.402
7.397
7.376
7.358
7.342
7.330
7.324
7.303
7.285
7.281
7.268
7.263
7.226
6.109
5.320
4.804
4.769
4.736
Cl
O
O
Cl
Cl
1.0
2.1
4.9
4.1
1.0
4.2
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

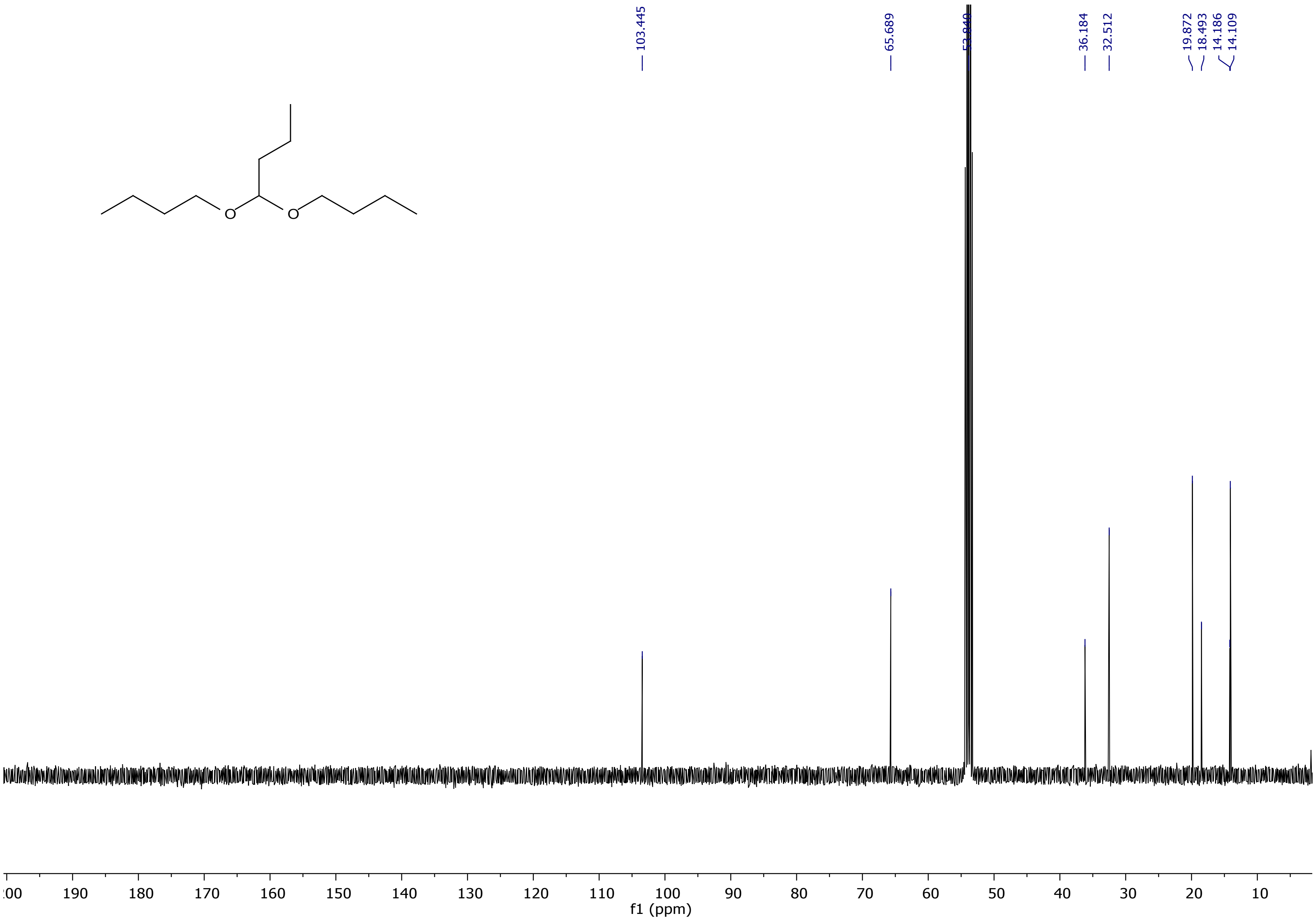

136.023
135.770
133.661
133.361
130.473
130.061
129.809
129.589
129.263
128.797
127.258
127.163
99.591
66.084
53.840
Cl
O
Cl
O
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

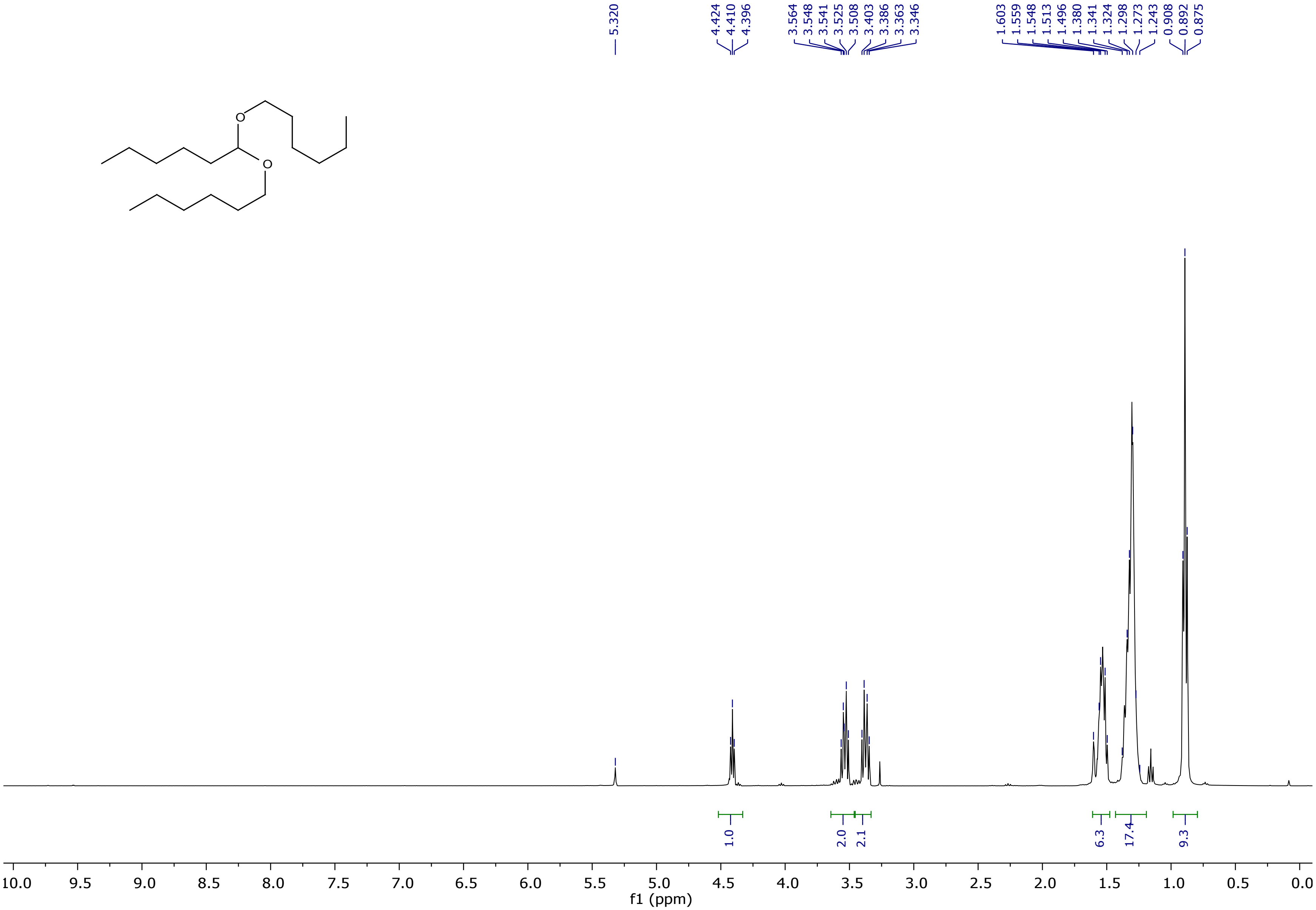

7.293
7.286
7.276
7.272
7.257
7.247
7.229
7.202
7.179
7.161
4.649
4.635
4.621
3.778
3.761
3.754
3.743
3.737
3.720
3.591
3.573
3.567
3.556
3.550
3.533
2.886
2.872
2.816
2.799
2.781
O
O
14.9
1.1
2.2
2.2
2.2
4.3
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

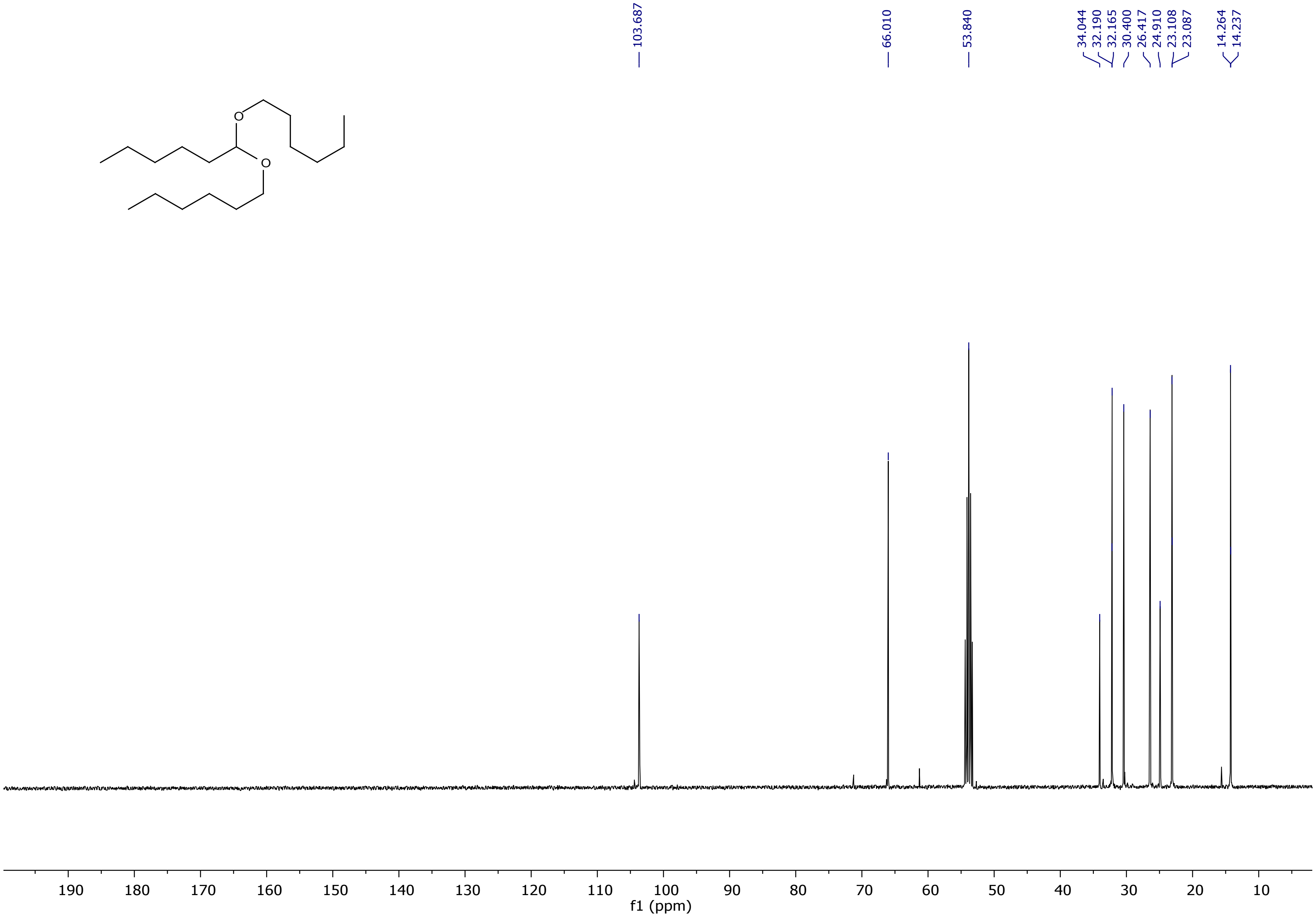

139.697
137.728
130.030
129.358
128.617
128.535
126.593
126.482
104.345
67.442
53.840
40.871
36.715
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

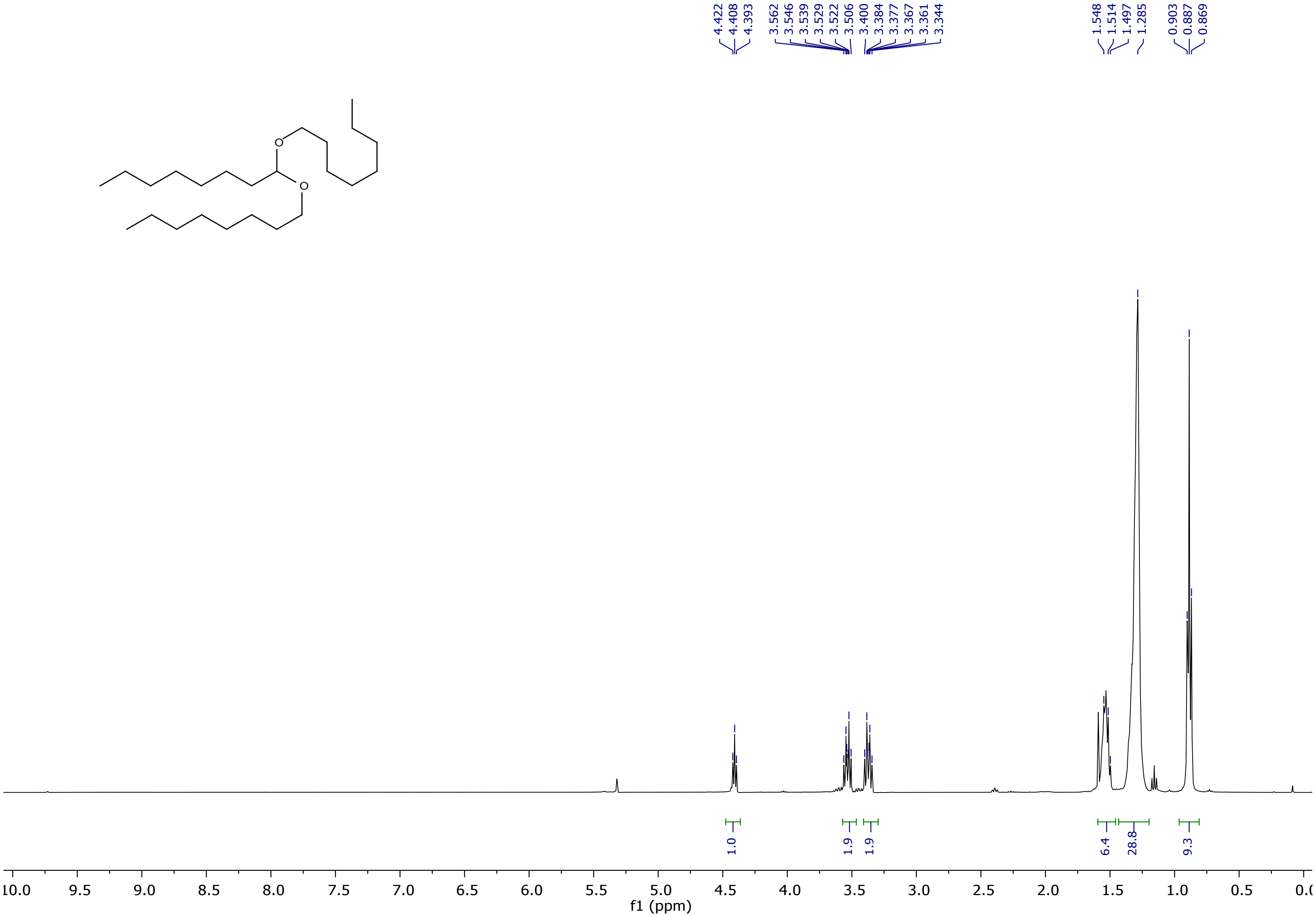


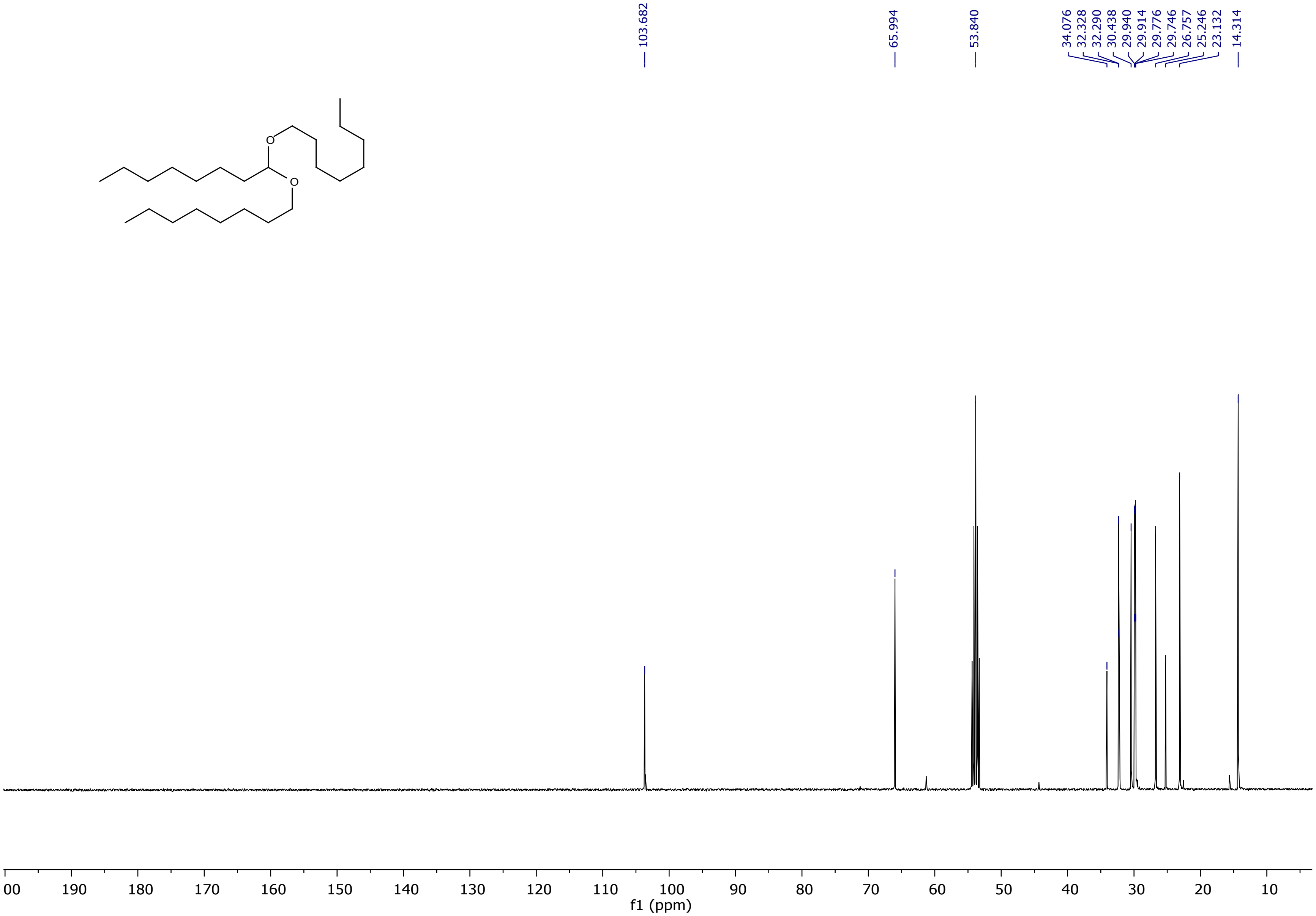
5.320
4.435
4.421
4.407
3.574
3.558
3.551
3.541
3.535
3.518
3.393
3.386
3.376
3.369
3.353
1.550
1.536
1.525
1.512
1.499
1.482
1.396
1.378
1.358
1.340
1.323
0.933
0.929
0.915
0.910
0.896
0.892
O
O
1.0
2.0
2.0
6.1
6.1
9.3
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

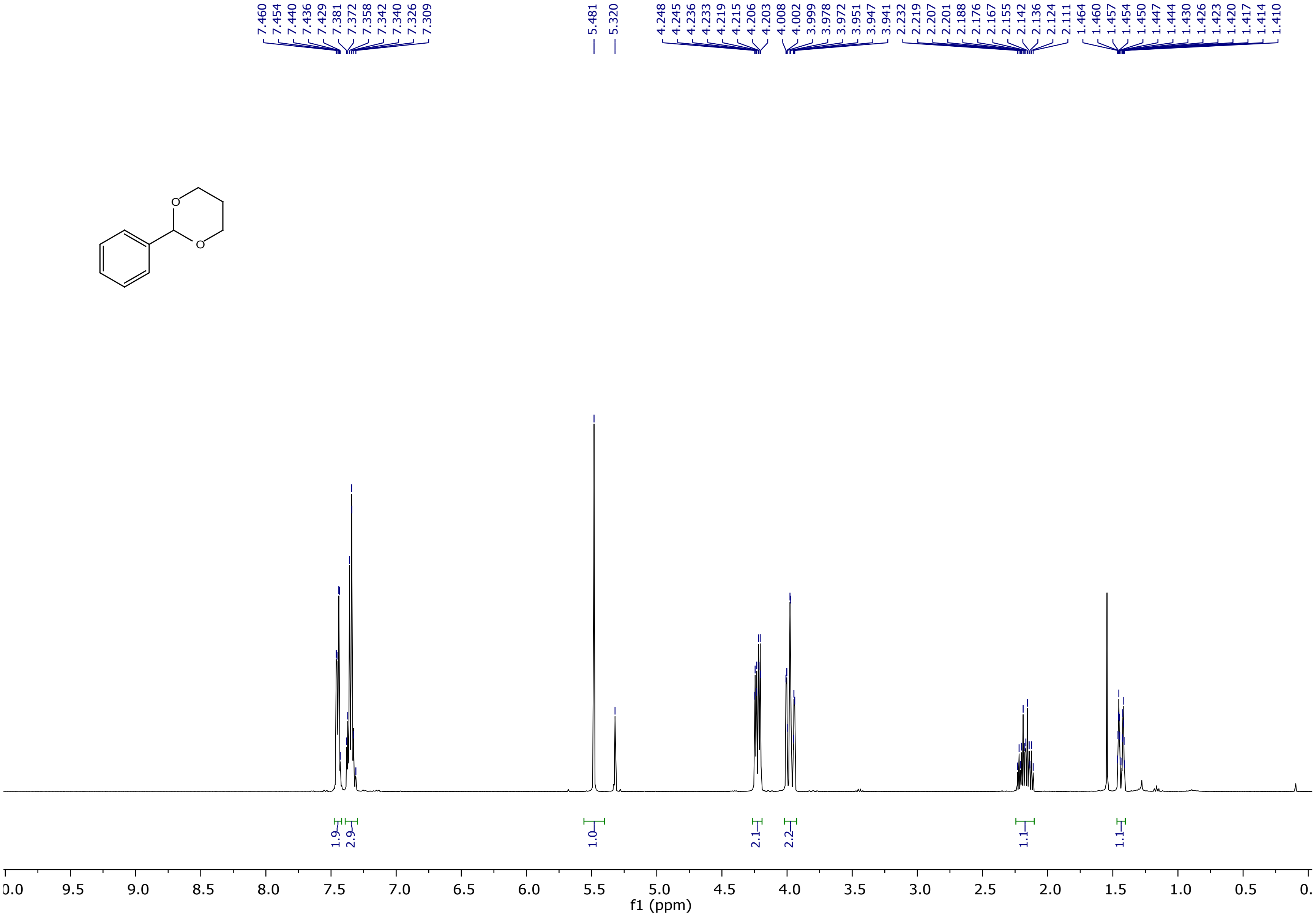

103.445
65.689
53.840
36.184
32.512
19.872
18.493
14.186
14.109
O
O
:00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

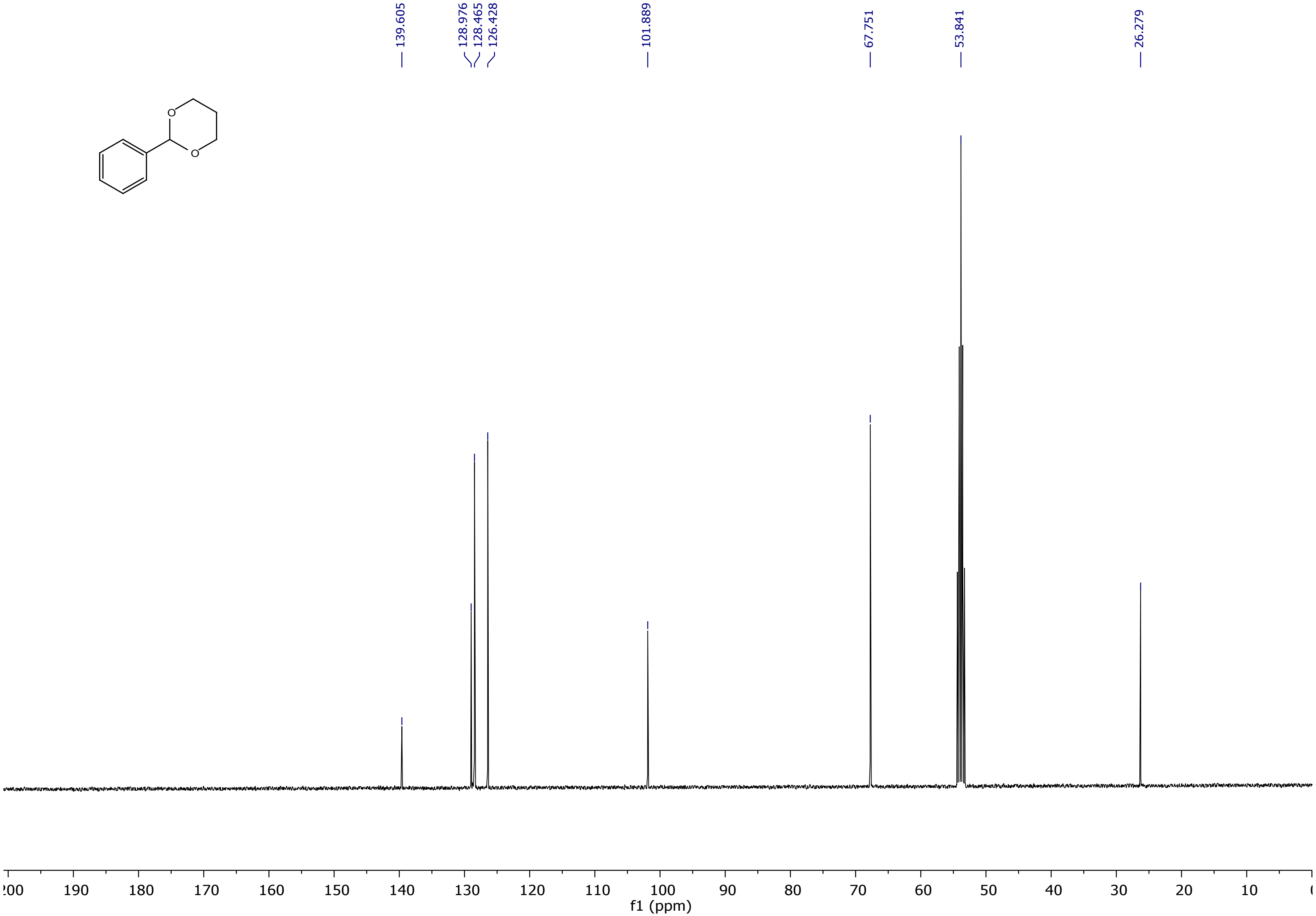

5.320
4.424
4.410
4.396
3.564
3.548
3.541
3.525
3.508
3.403
3.386
3.363
3.346
1.603
1.559
1.548
1.513
1.496
1.380
1.341
1.324
1.298
1.273
1.243
0.908
0.892
0.875
O
O
1.0
2.0
2.1
6.3
17.4
9.3
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

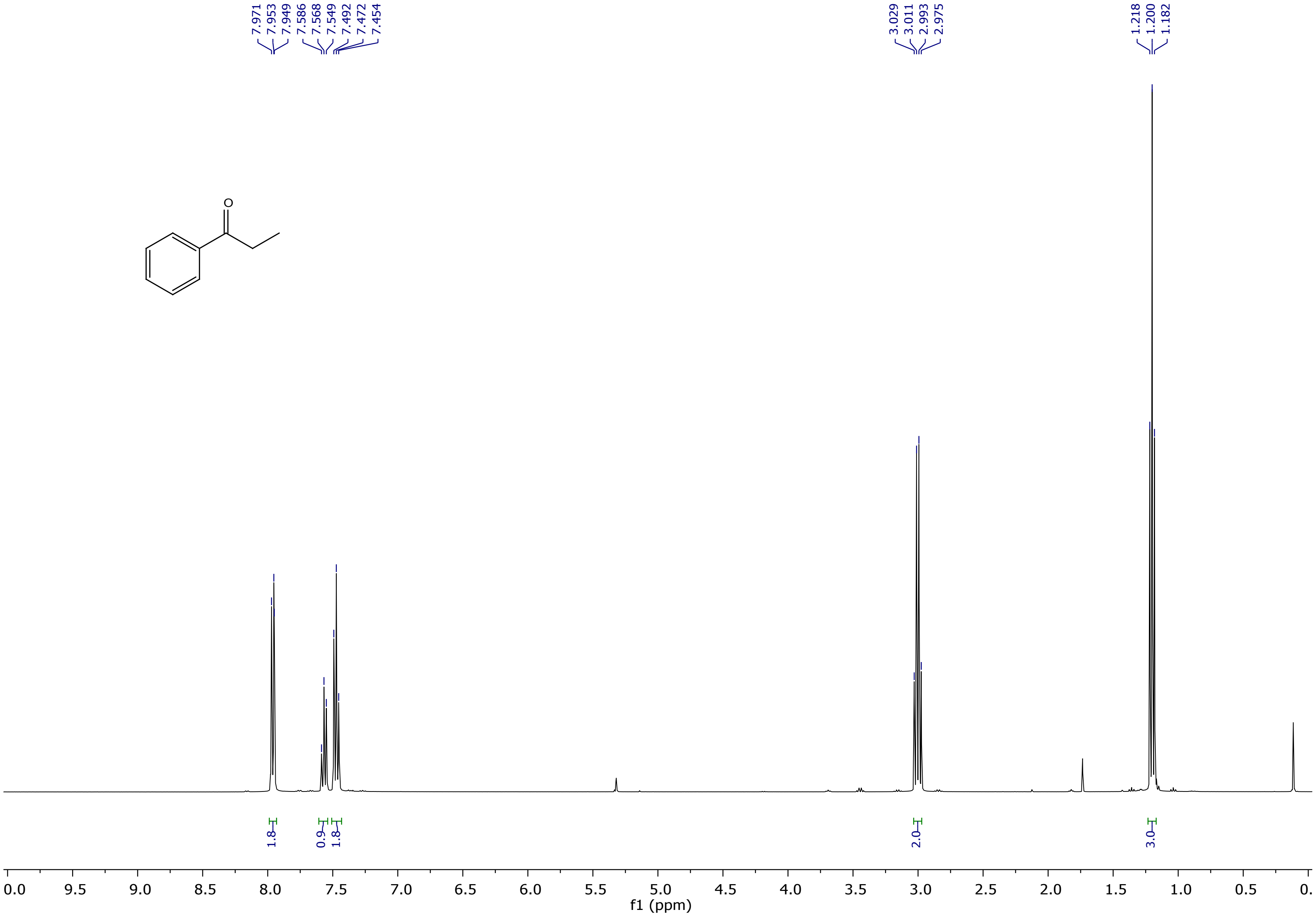

103.687
66.010
53.840
34.044
32.190
32.165
30.400
26.417
24.910
23.108
23.087
14.264
14.237
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

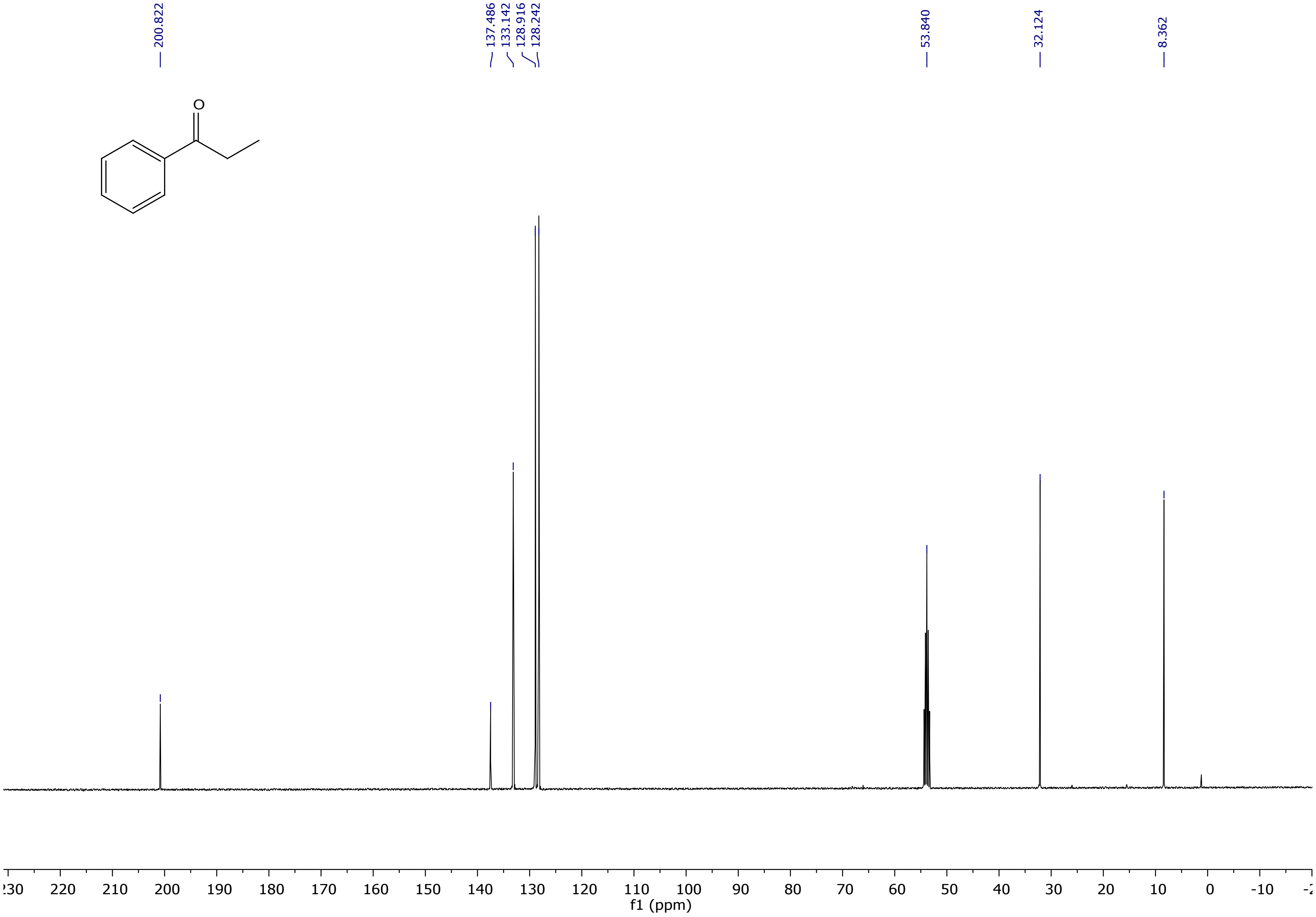

4.422
4.408
4.393
3.562
3.546
3.539
3.529
3.522
3.506
3.400
3.384
3.377
3.367
3.361
3.344
1.548
1.514
1.497
1.285
0.903
0.887
0.869
O
O
1.0
1.9
1.9
6.4
28.8
9.3
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

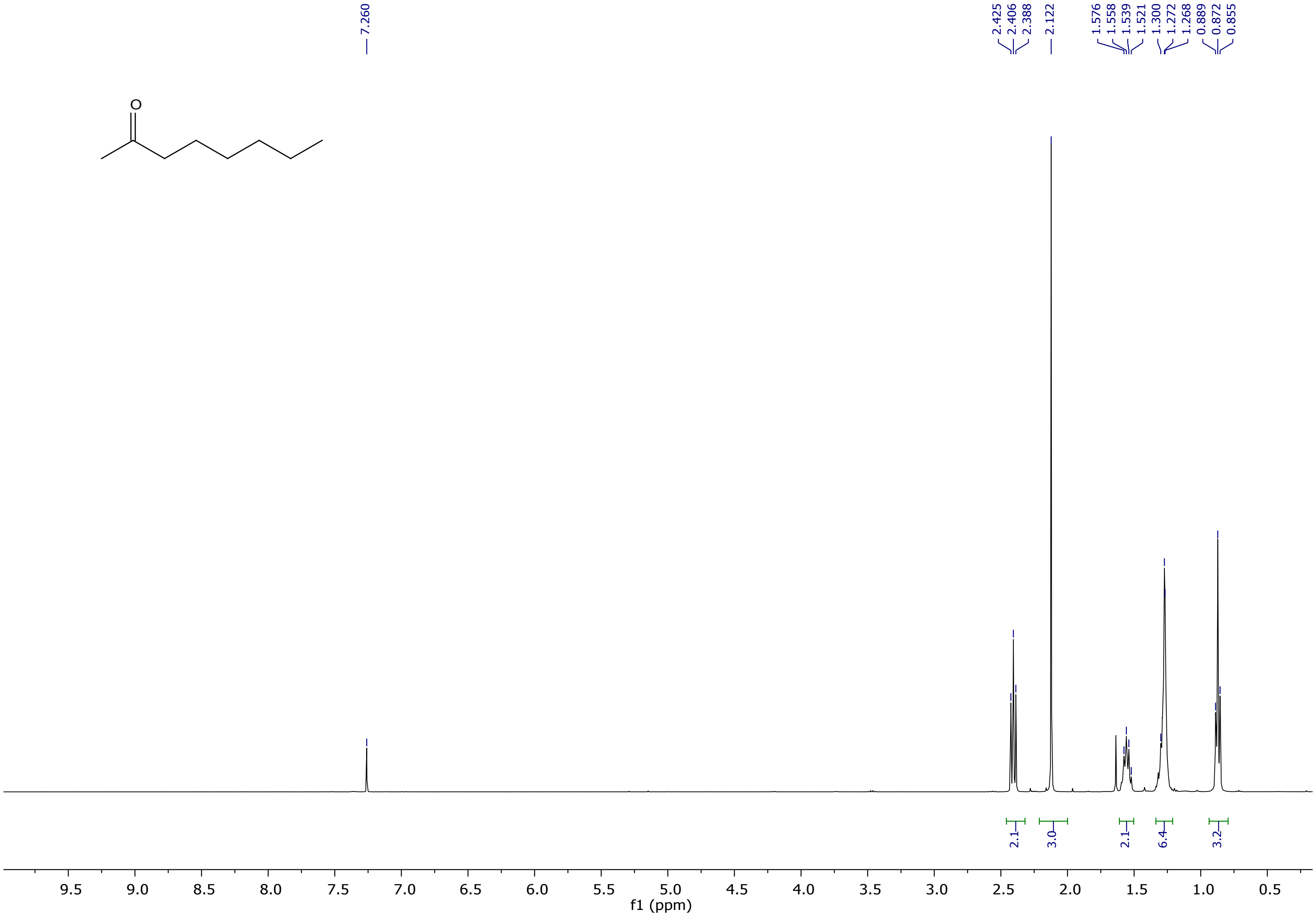

103.682
65.994
53.840
34.076
32.328
32.290
30.438
29.940
29.914
29.776
29.746
26.757
25.246
23.132
14.314
O
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

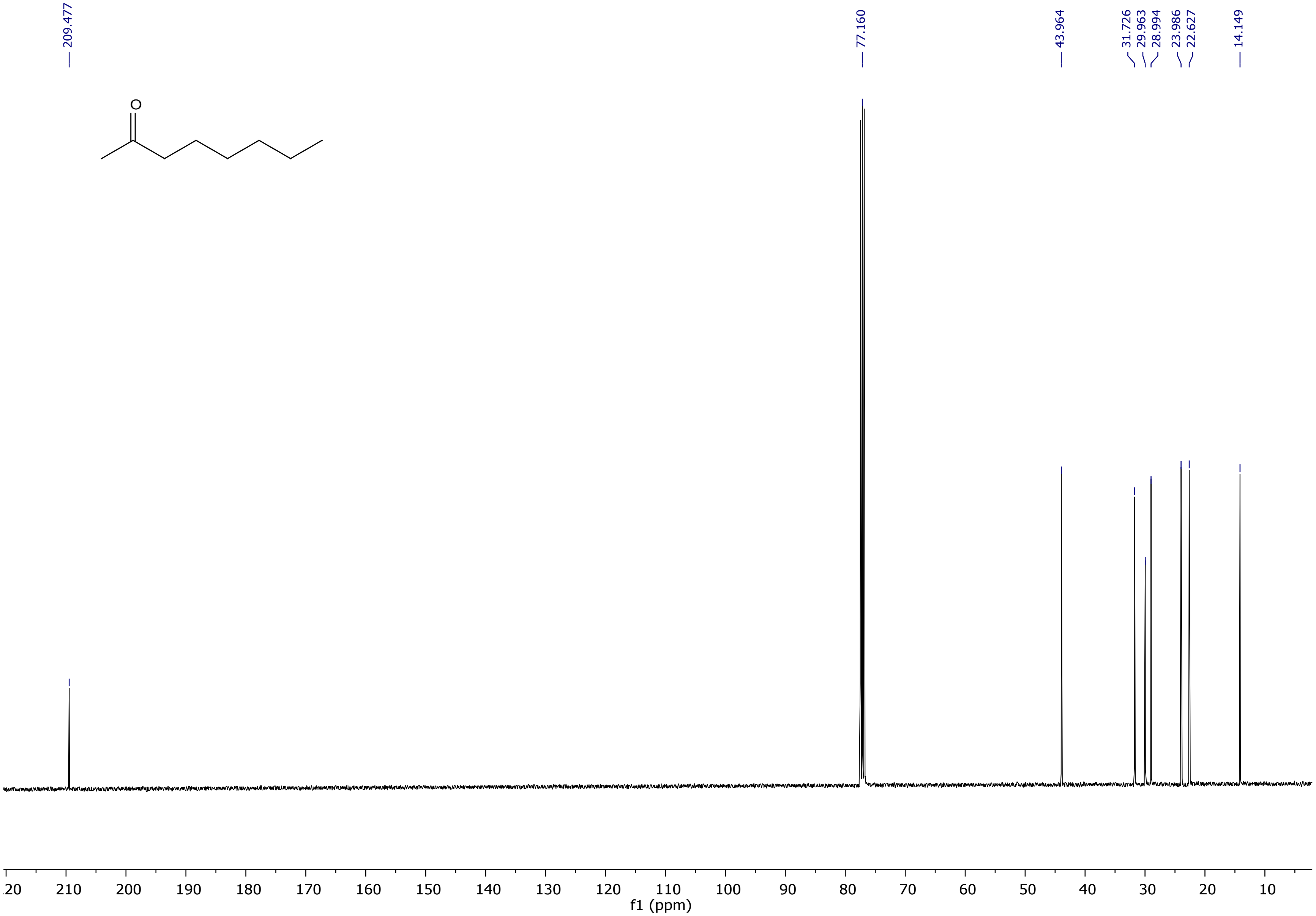

7.460
7.454
7.440
7.436
7.429
7.381
7.372
7.358
7.342
7.340
7.326
7.309
5.481
5.320
4.248
4.245
4.236
4.233
4.219
4.215
4.206
4.203
4.008
4.002
3.999
3.978
3.972
3.951
3.947
3.941
2.232
2.219
2.207
2.201
2.188
2.176
2.167
2.155
2.142
2.136
2.124
2.111
1.464
1.460
1.457
1.454
1.450
1.447
1.444
1.430
1.426
1.423
1.420
1.417
1.414
1.410
O
O
1.9
2.9
1.0
2.1
2.2
1.1
1.1
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


139.605
128.976
128.465
126.428
101.889
67.751
53.841
26.279
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.971
7.953
7.949
7.586
7.568
7.549
7.492
7.472
7.454
3.029
3.011
2.993
2.975
1.218
1.200
1.182
O
1.8
0.9
1.8
2.0
3.0
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


200.822
137.486
133.142
128.916
128.242
53.840
32.124
8.362
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.260
2.425
2.406
2.388
2.122
1.576
1.558
1.539
1.521
1.300
1.272
1.268
0.889
0.872
0.855
O
2.1
3.0
2.1
6.4
3.2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


209.477
77.160
43.964
31.726
29.963
28.994
23.986
22.627
14.149
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)