

ELECTRONIC SUPPLEMENTARY INFORMATION

An efficient and regioselective synthetic approach towards fluorinated quinolinyolphosphonates

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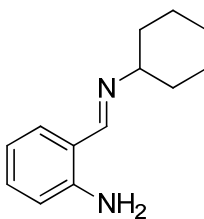
General Remarks

All reagents from commercial suppliers were used without further purification. All solvents were freshly distilled before use from appropriate drying agents. All other reagents were recrystallized. Reactions were performed under atmosphere of dry argon. Analytical TLCs were performed with silica gel 60 F₂₅₄ plates. Column chromatography was carried out using silica gel 60 (230–400 mesh ASTM). Melting points were determined without correction. NMR spectra were obtained on a spectrometer operating at 400 MHz for ¹H (TMS), 376 MHz for ¹⁹F (CFC1₃), 161 MHz for ³¹P (H₃PO₄) and 100 MHz for ¹³C (TMS). All measurements were accomplished in the solution in CDCl₃. Mass spectrometry was established on a MicroTOF-Q fitted with an ESI source.

Procedure for the Preparation of Imine Derivatives 2a-d.

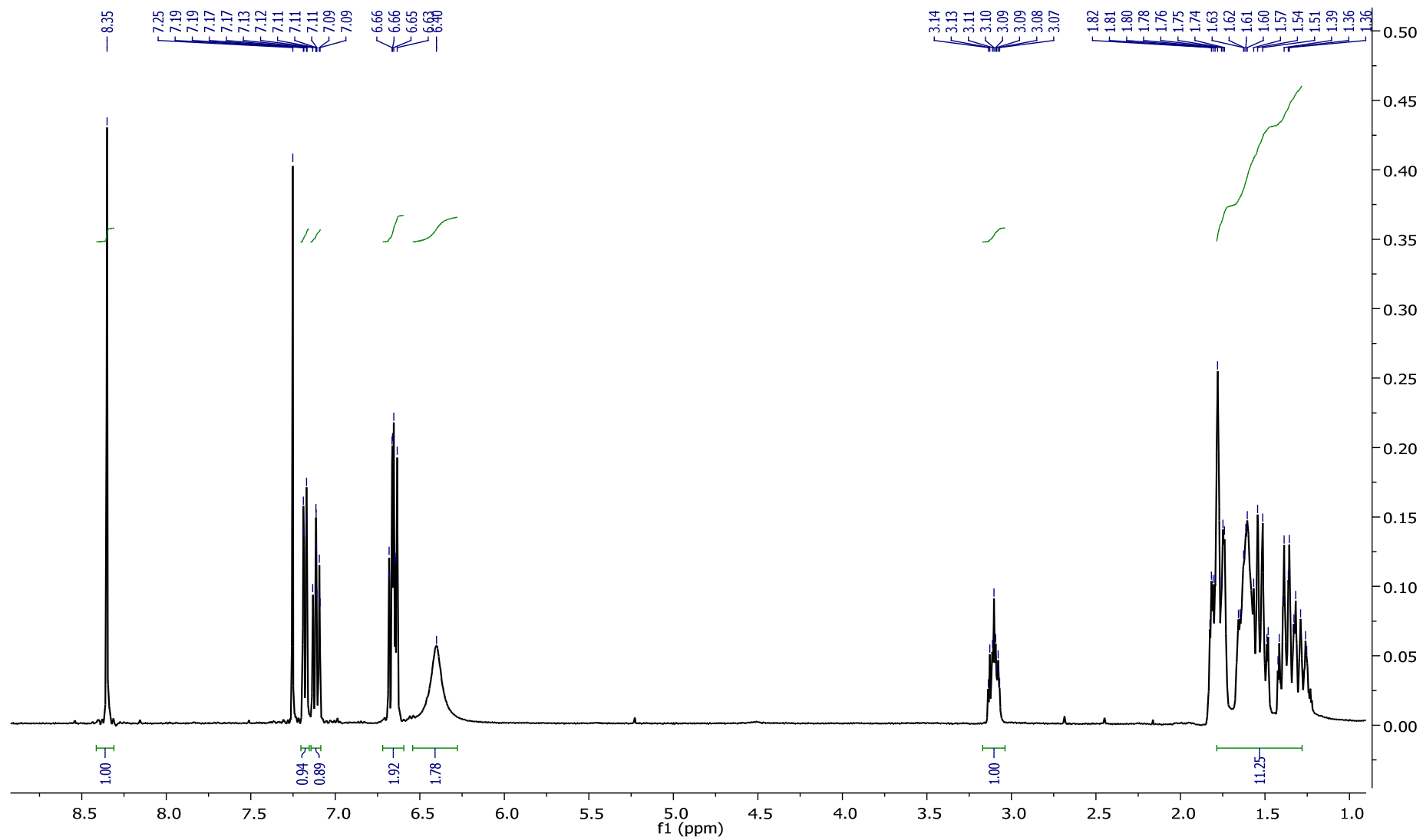
To the mixture of a nitrobenzaldehyde and MgSO_4 in dry DCM a cyclohexylamine was added slowly. Then the suspension was refluxed for 4h, then cooled down to ambient temperature and filtered off the remained MgSO_4 . The filtrate was next concentrated under reduced pressure to give pure imine derivative. Subsequently an imine was dissolved in ethanol and warmed up to 80 °C. To the hot solution solid Na_2S (hydrate) was slowly added. The solution was maintained for additional 20 min, cooled down to 0 °C and kept for 4h. Thus formed precipitate was filtered off and the solution concentrated under reduced pressure. To the crude product H_2O was added and a new drop of precipitate was formed, filtered off, washed with H_2O (3×100 mL) and dried to produce pure (2-(cyclohexylimino)-methyl)aniline derivatives.

1. 2-((cyclohexylimino)methyl)aniline **2a**

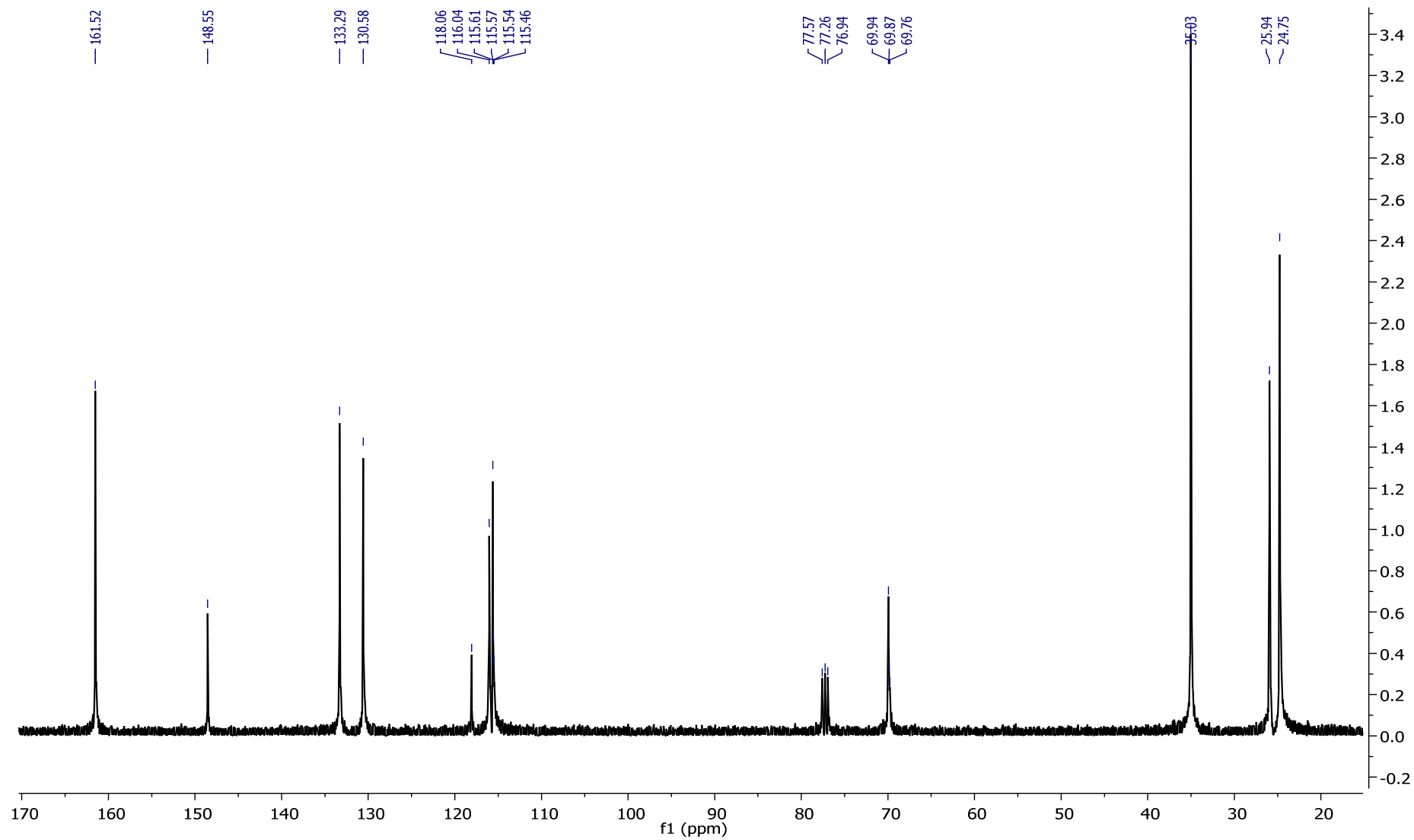


Yellowish solid (90%), Mp = 45–48 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.35–1.82 (m, 10H), 3.10 (m, 1H), 6.40 (br s, 2H), 6.62 (d, $J = 8.3$ Hz, 1H), 6.66 (td, $J = 7.5$ Hz, $J = 1.3$ Hz, 1H), 7.11 (td, $J = 7.2$ Hz, $J = 1.9$ Hz, 1H), 7.18 (dd, $J = 7.7$ Hz, $J = 1.9$ Hz, 1H), 8.35 (s, 1H); ^{13}C NMR (100 MHz) δ 24.7, 25.9, 35.0, 69.0, 115.4, 115.6, 118.0, 130.5, 133.3, 148.5, 161.5; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{19}\text{N}_2$ $[\text{M}+\text{H}]^+$ 203.1543, found 203.1543.

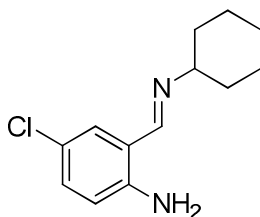
^1H NMR



^{13}C NMR

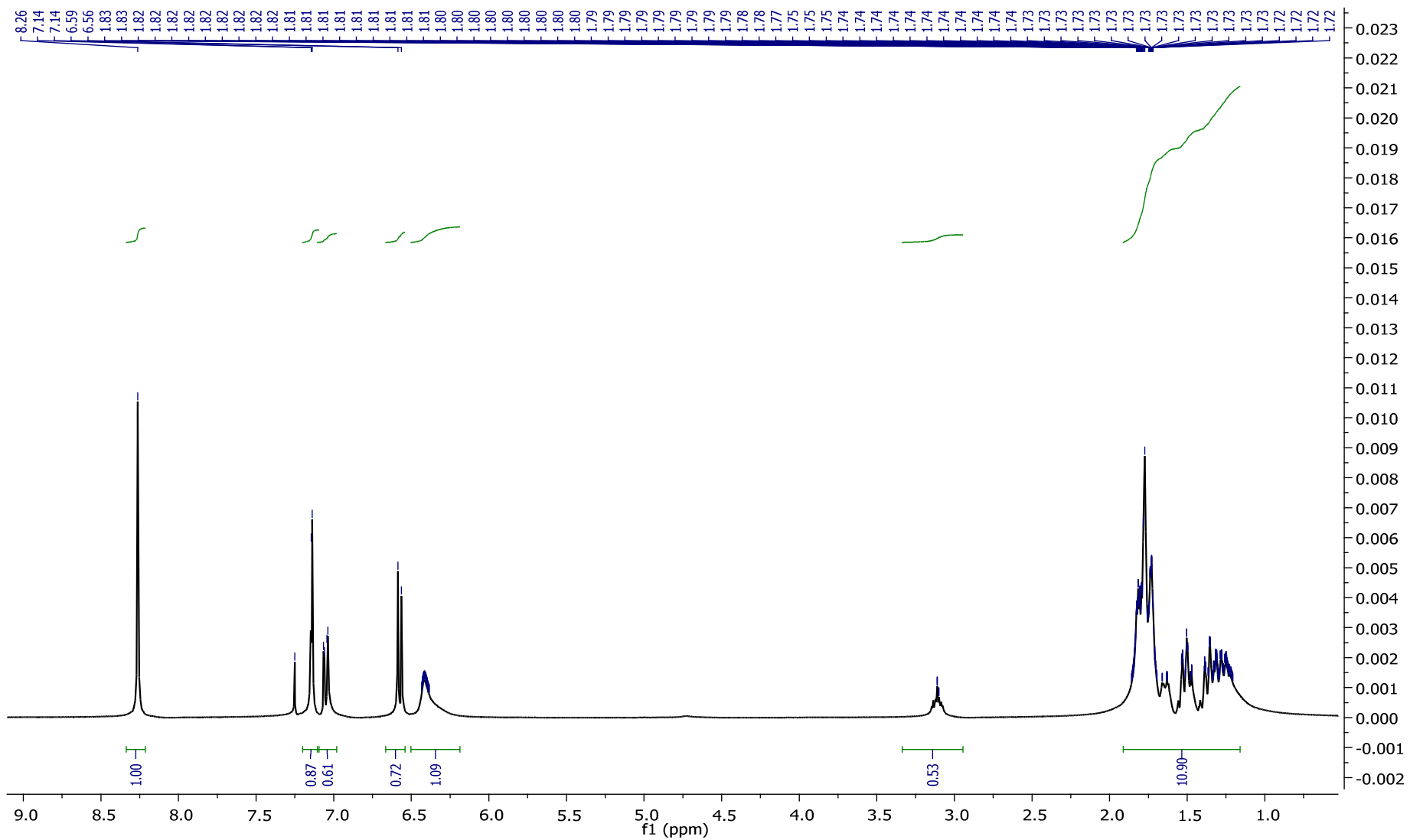


2. 4-chloro-2-((cyclohexylimino)methyl)aniline **2b**

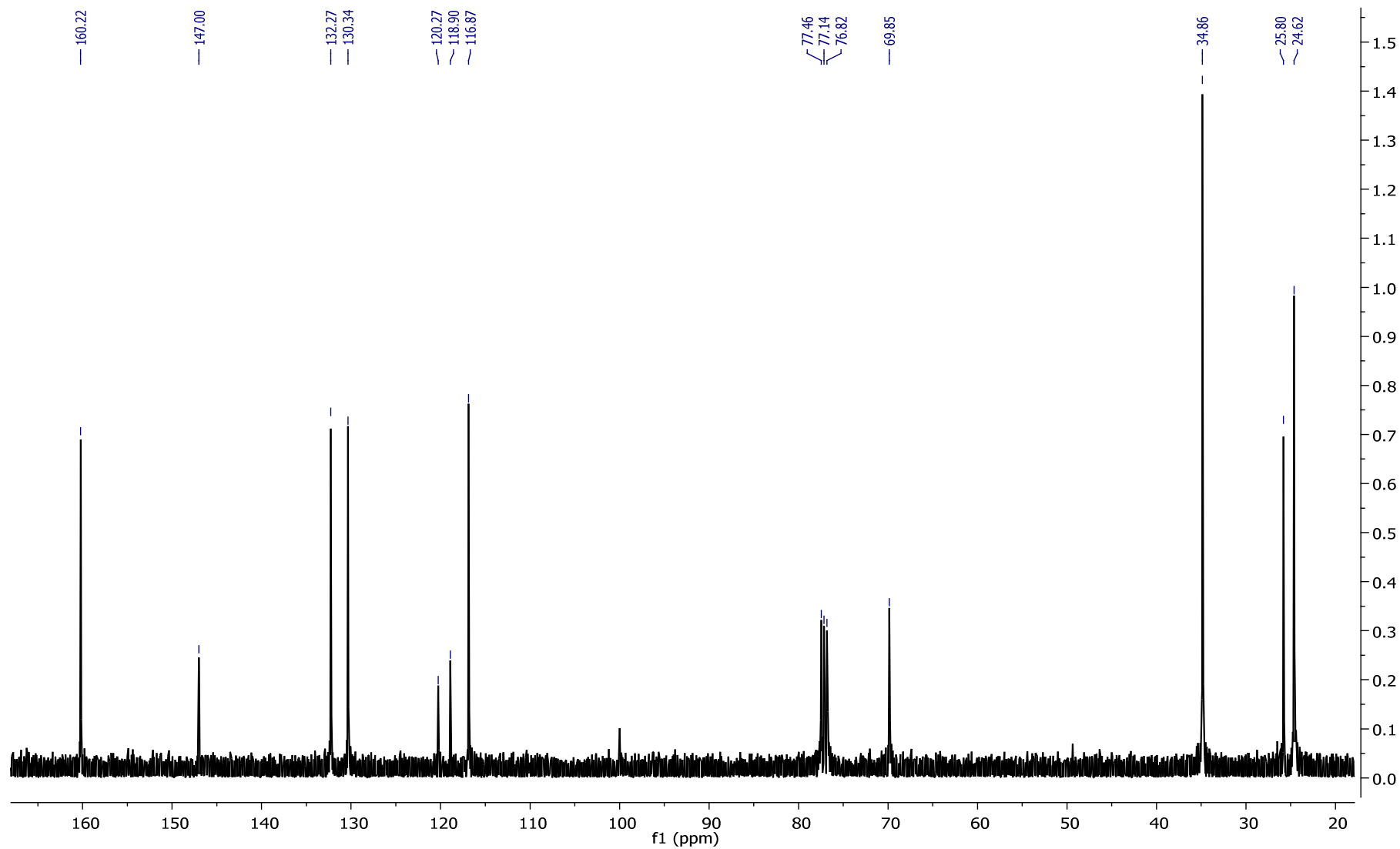


Yellowish solid (85%), Mp = 91–93 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.72–1.81 (m, 10H), 3.11 (m, 1H), 6.40 (br s, 2H), 6.57 (d, $J = 9.5$ Hz, 1H), 7.05 (dd, $J = 9.5$ Hz, $J = 1.9$ Hz, 1H), 7.14 (d, $J = 1.9$ Hz, 1H), 8.26 (s, 1H); ^{13}C NMR (100 MHz) δ 24.6, 25.8, 34.9, 69.8, 116.8, 118.9, 120.3, 130.3, 132.3, 147.0, 160.2; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{18}\text{ClN}_2$ $[\text{M}+\text{H}]^+$ 237.1153, found 237.1146.

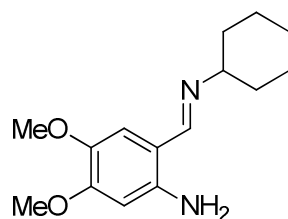
¹H NMR



^{13}C NMR

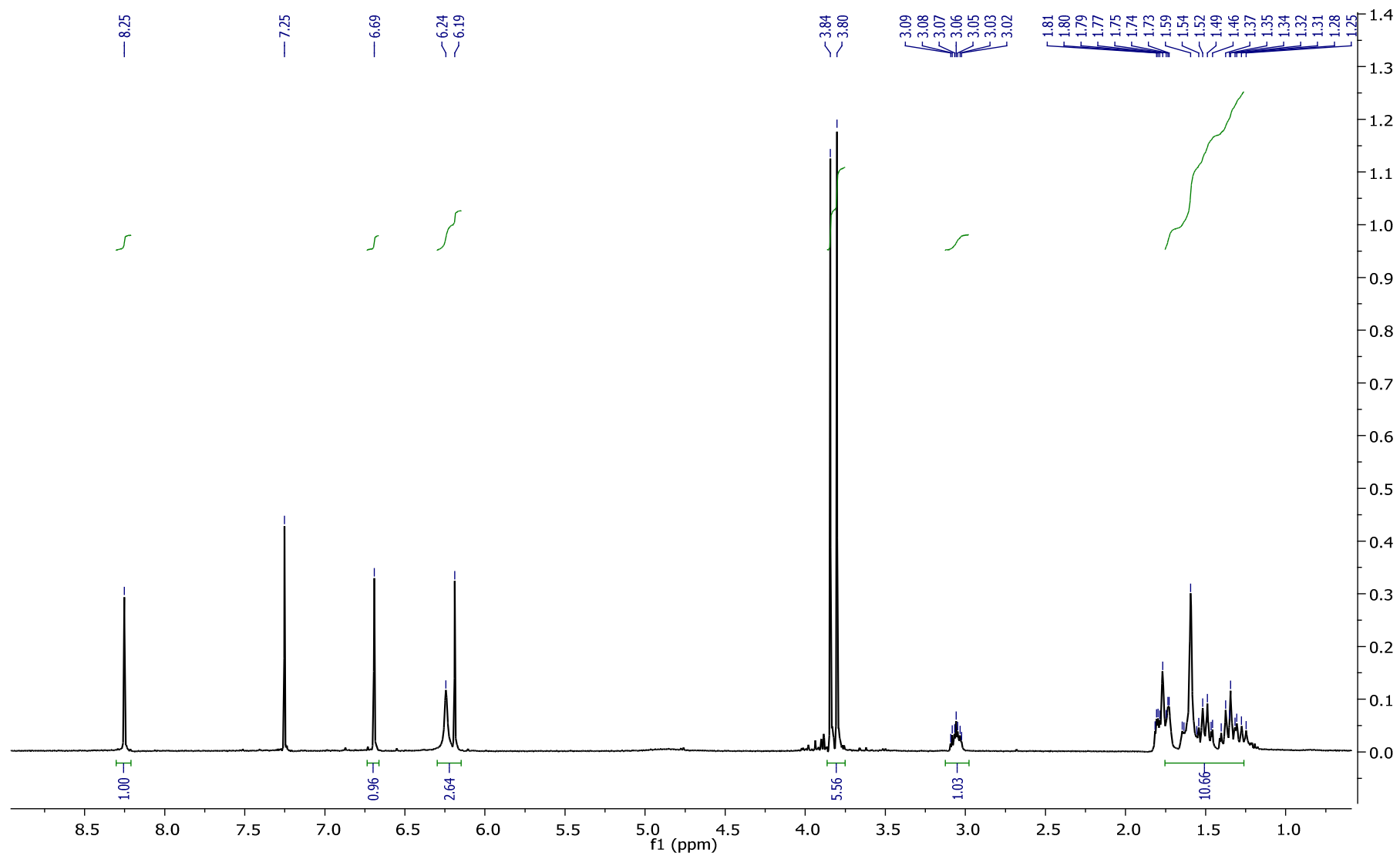


3. 2-((cyclohexylimino)methyl)-4,5-dimethoxyaniline **2c**

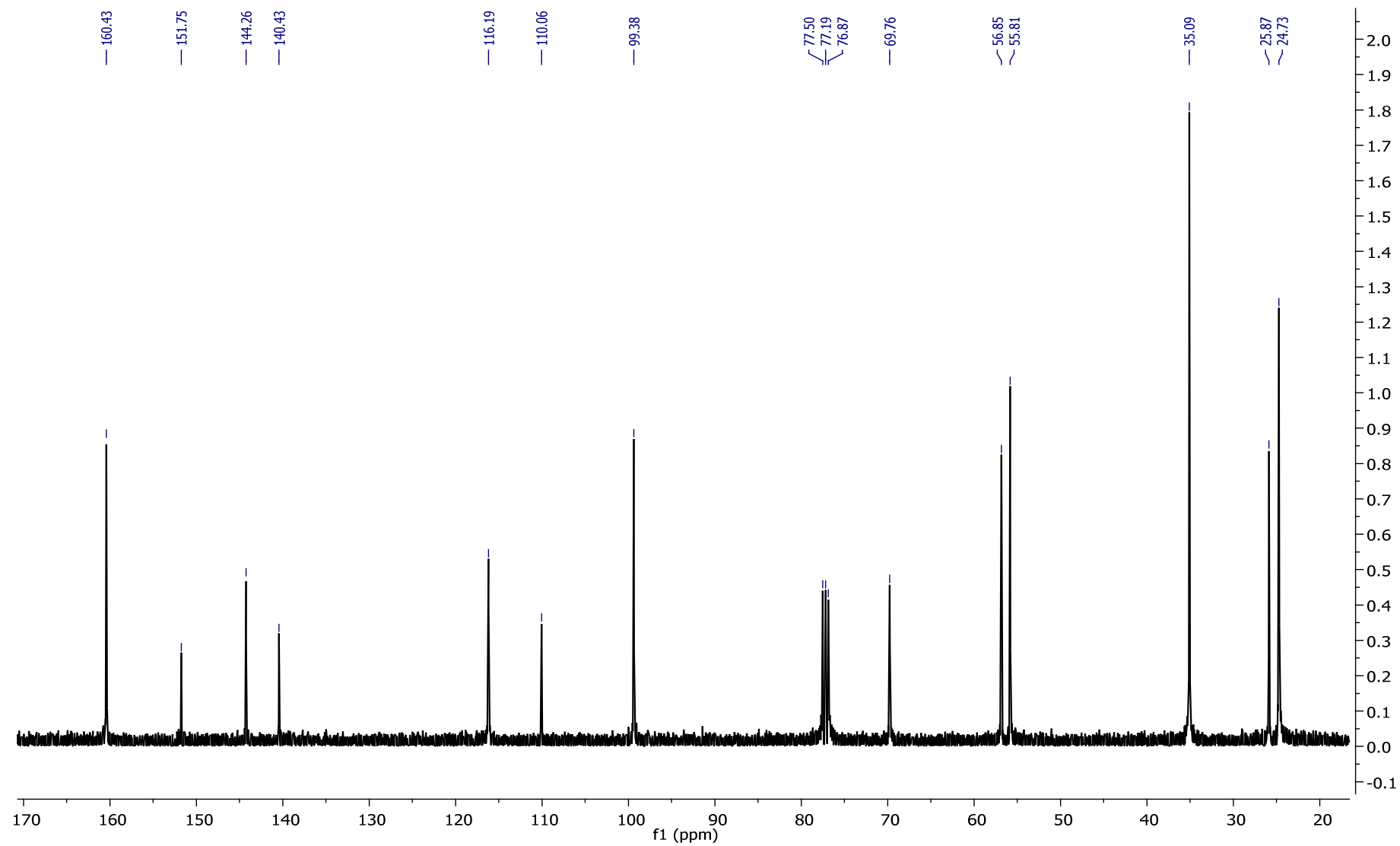


Yellowish solid (85%); Mp = 134–137 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.25–1.81 (m, 10H), 3.06 (m, 1H), 2.80 (s, 2H), 3.84 (s, 3H), 6.19 (s, 1H), 6.24 (br s, 2H), 6.69 (s, 1H), 8.25 (s, 1H); ^{13}C NMR (100 MHz) δ 24.7, 25.8, 35.1, 55.8, 56.8, 69.7, 99.4, 110.1, 116.2, 140.4, 144.3, 151.7, 160.4; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 263.1754, found 263.1751.

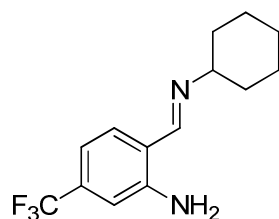
^1H NMR



^{13}C NMR

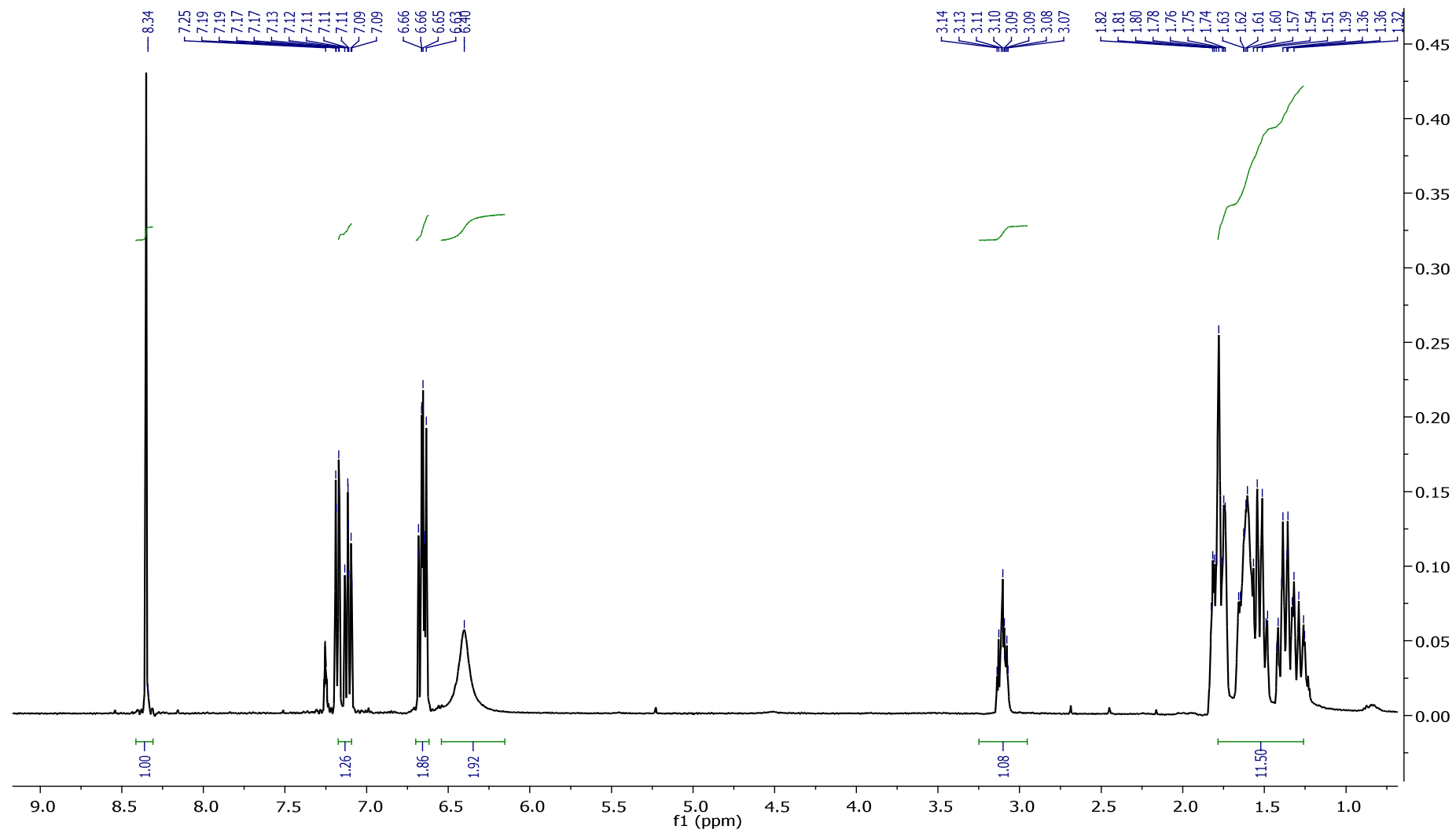


4. 2-((cyclohexylimino)methyl)-5-(trifluoromethyl)aniline **2d**.

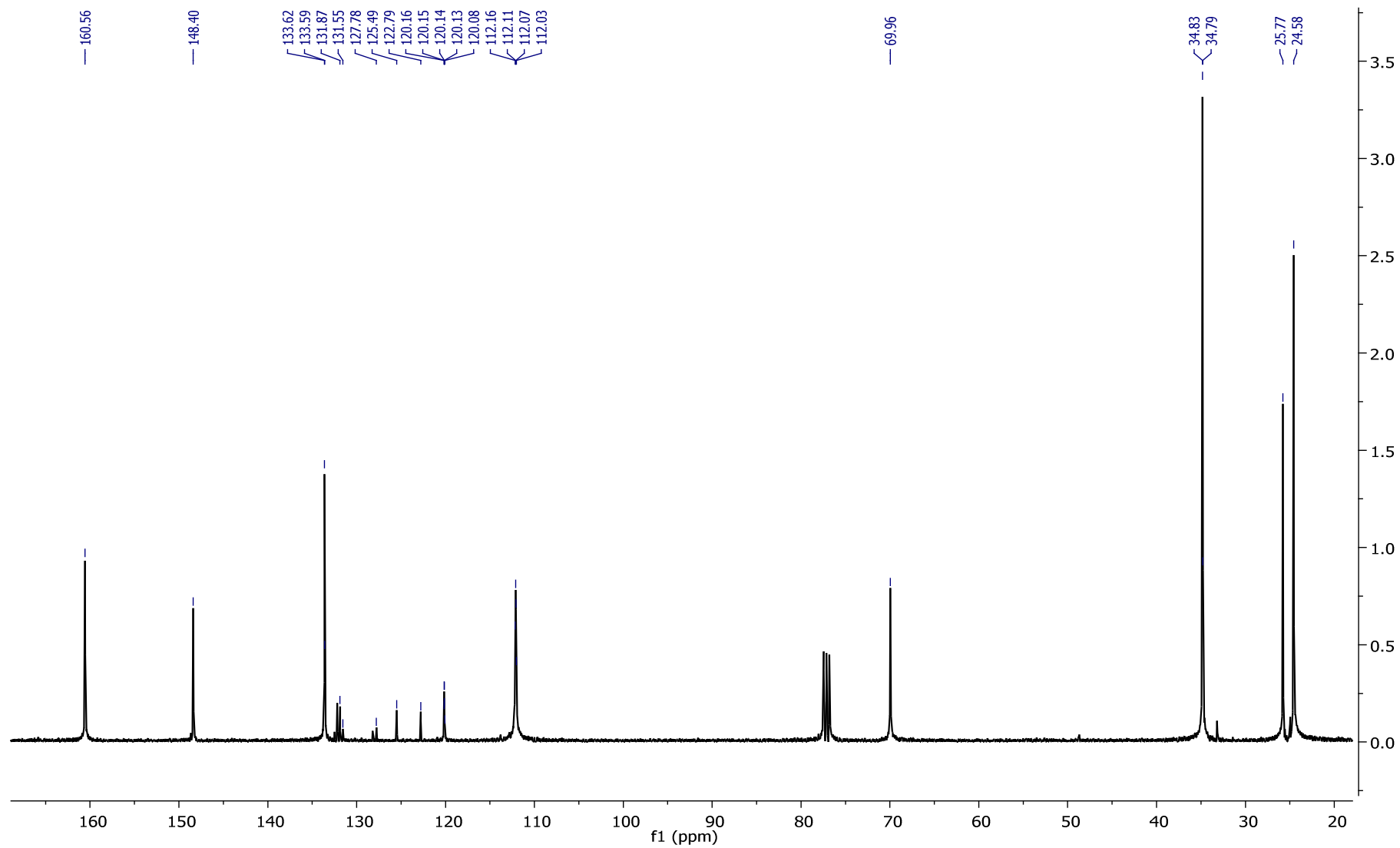


Yellowish crystals (80%); Mp = 60–63 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.53–1.84 (m, 10H), 3.14 (m, 1H), 6.64 (br s, 2H), 6.84 (m, 2H), 7.27 (s, 1H), 8.38 (s, 1H); ^{13}C NMR (100 MHz) δ 24.6, 25.7, 34.8, 69.9, 112.3, 120.1, 123.5 (q, $^1J_{\text{C-F}} = 275.1$ Hz), 131.5 (q, $^2J_{\text{C-F}} = 30.5$ Hz), 133.6, 148.4, 160.5; ^{19}F NMR (376 MHz) δ -63.1; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$ 271.1417, found 271.1412.

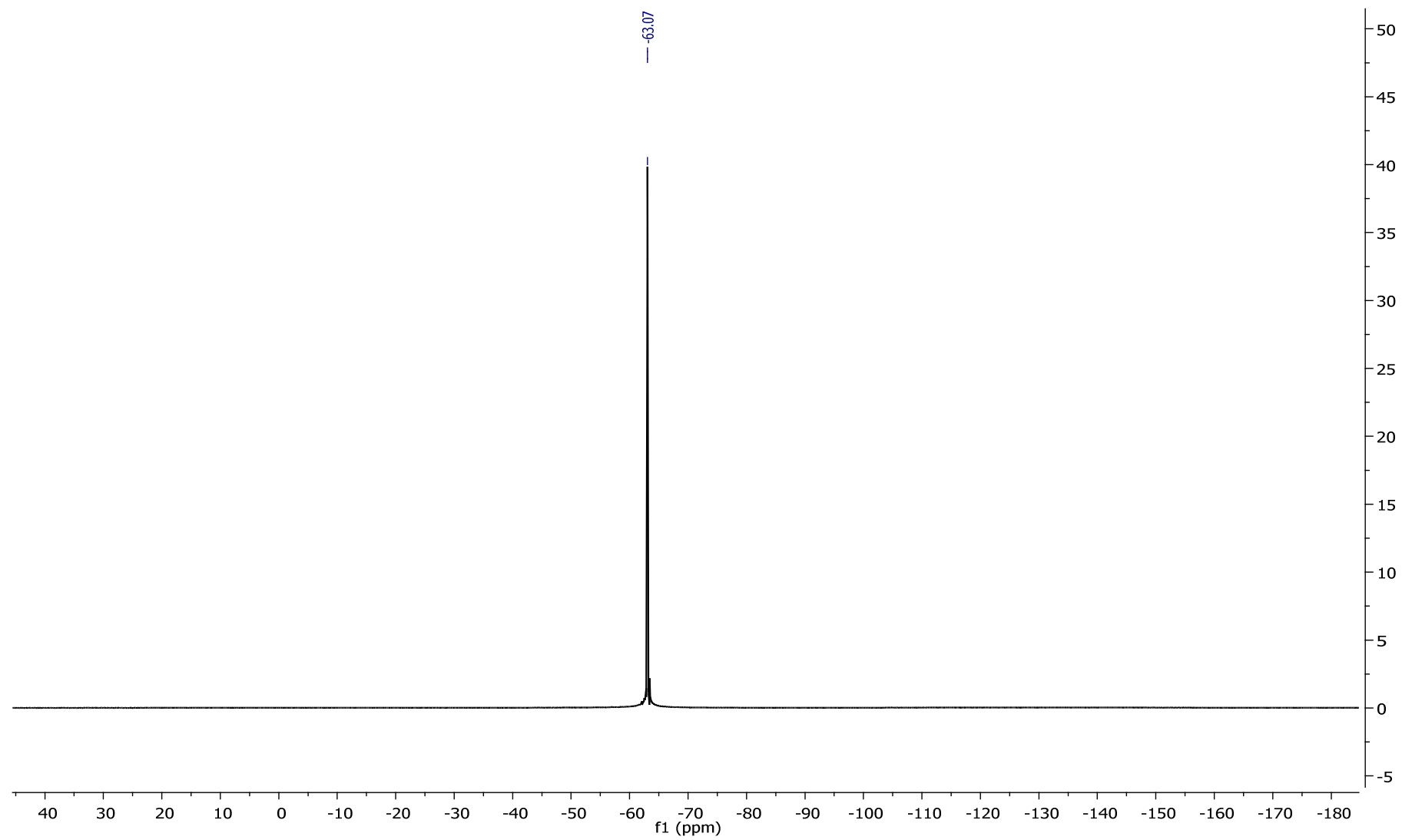
¹H NMR



^{13}C NMR



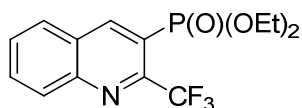
^{19}F NMR



General procedure for the preparation of CF₂-containing quinolinylphosphonates 4a-t

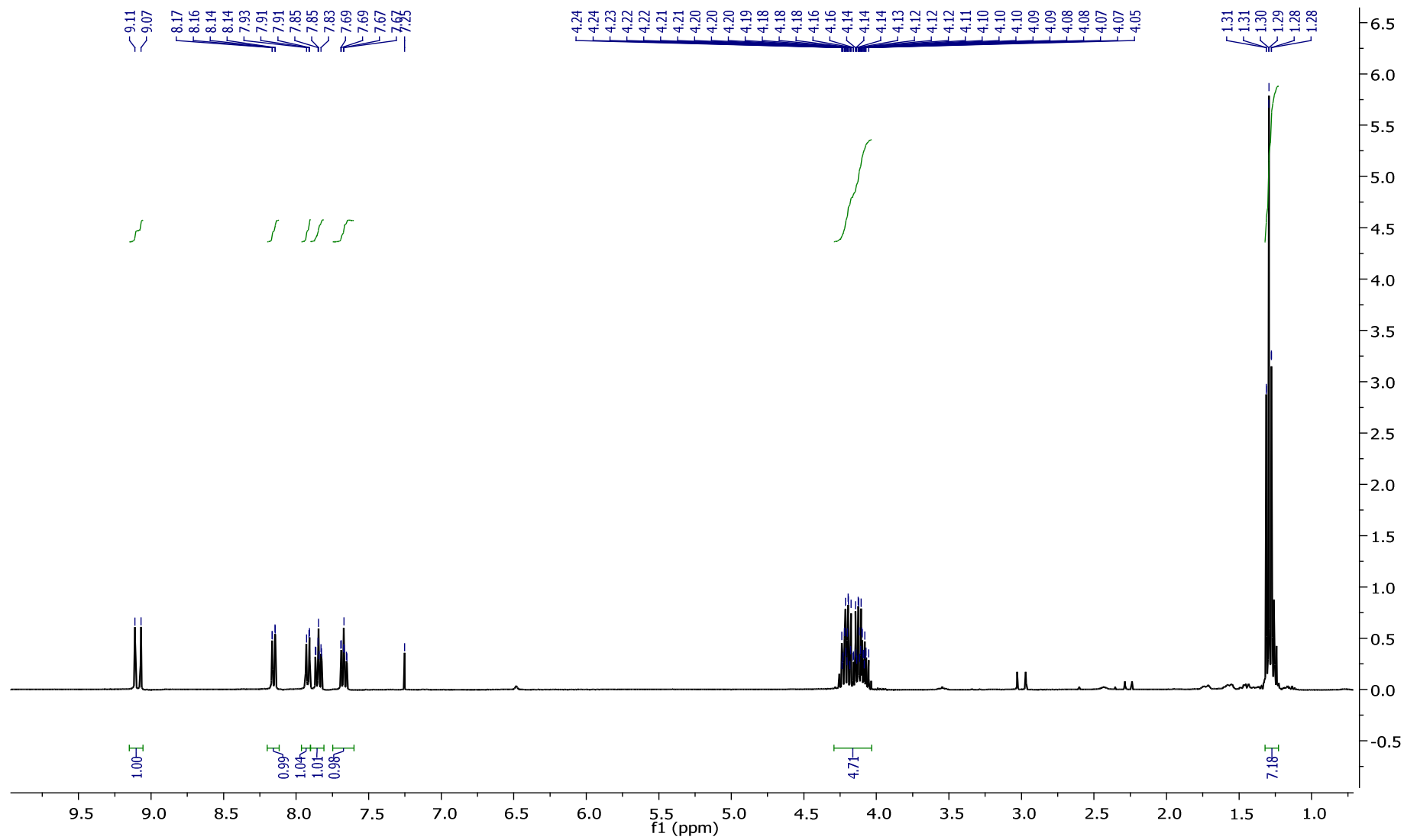
The mixture of 2-((cyclohexylimino)methyl)aniline derivative **2** (5 mmol) and K₂CO₃ (5 mmol) was dissolved in dry toluene (25 ml) at ambient temperature. To the reaction mixture an alkyne **3** (5 mmol) was charged slowly. The solution was warmed up to reflux and stirred for 10–12 hours. The K₂CO₃ was filtered off and the remained solution concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using DCM:EtOAc (5:1 ratio) as eluent.

1. Diethyl (2-(trifluoromethyl)quinolin-3-yl)phosphonate **4a**

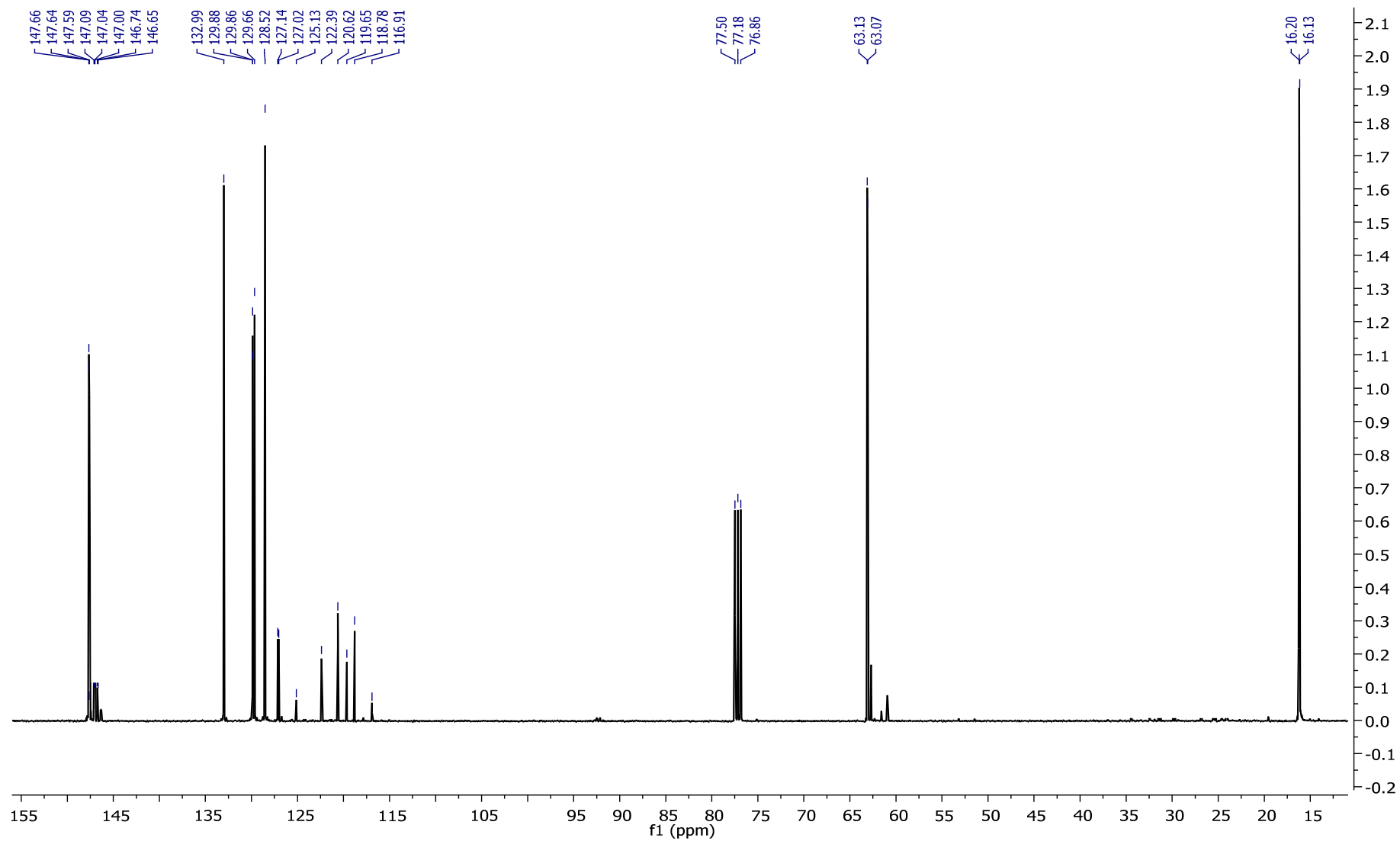


Yellowish oil (97%); ^1H NMR (400 MHz, CDCl_3) δ 1.30 (t, $J = 7.1$ Hz, 6H), 4.15 (m, 4H), 7.67 (td, $J = 8.2$ Hz, $J = 1.1$ Hz, 1H), 7.85 (td, $J = 8.2$ Hz, $J = 1.3$ Hz, 1H), 7.92 (d, $J = 8.2$ Hz, 1H), 8.15 (dd, $J = 8.7$ Hz, $J = 0.7$ Hz, 1H), 9.09 (d, $^3J_{\text{H-P}} = 16.5$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.1 (d, $J = 6.5$ Hz), 63.1 (d, $J = 5.9$ Hz), 119.8 (d, $^1J_{\text{C-P}} = 186.5$ Hz), 121.4 (q, $^1J_{\text{C-F}} = 275.7$ Hz), 127.1 (d, $^3J_{\text{C-P}} = 12.1$ Hz), 128.5, 129.6, 129.8, 132.9, 147.5 (qd, $^2J_{\text{C-F}} = 35.9$ Hz, $^2J_{\text{C-P}} = 8.4$ Hz), 147.6 (d, $^2J_{\text{C-P}} = 6.8$ Hz); ^{19}F NMR (376 MHz) δ -63.8; ^{31}P NMR (161 MHz) δ 13.6; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 334.0814, found 334.0812.

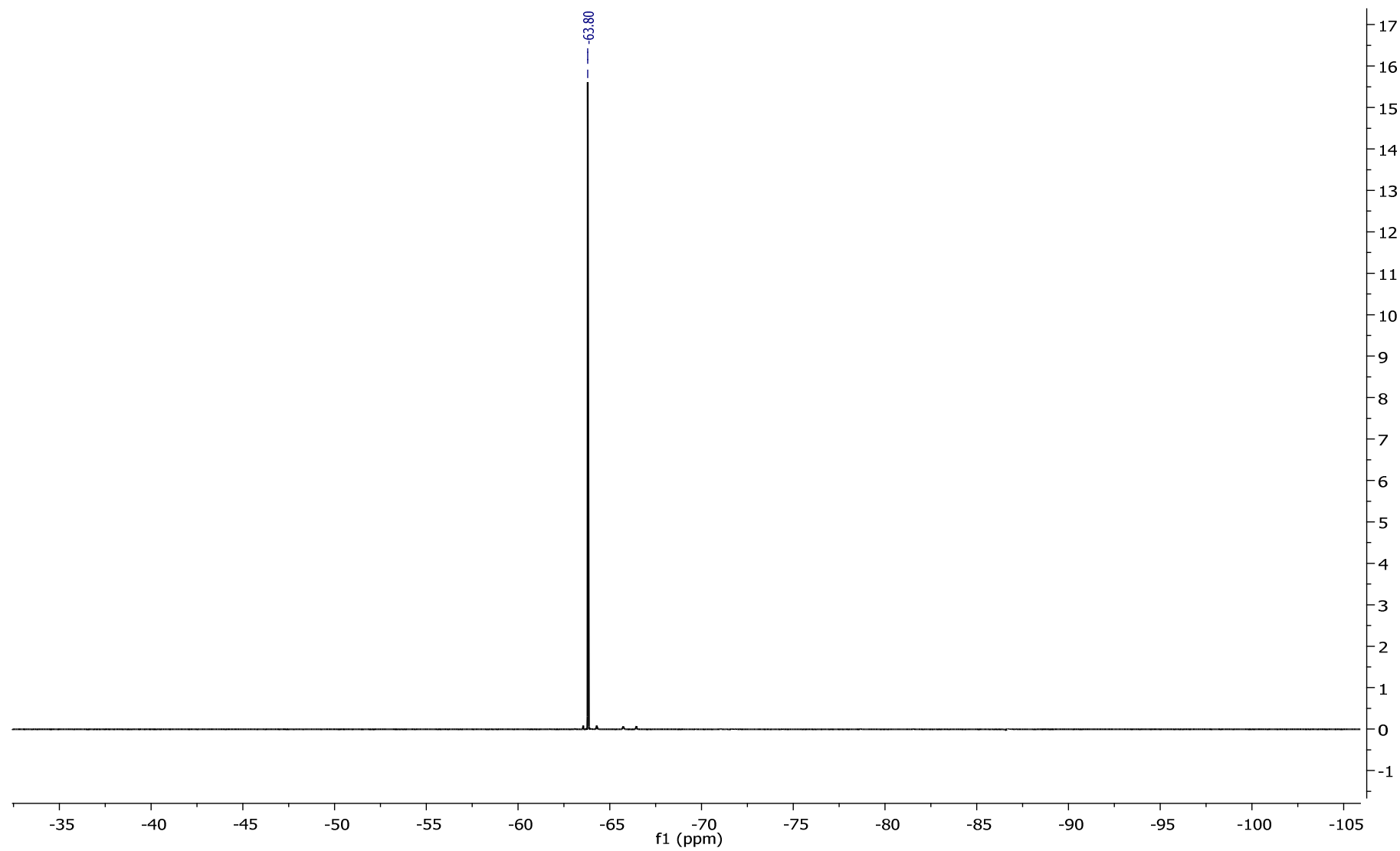
¹H NMR



¹³C NMR

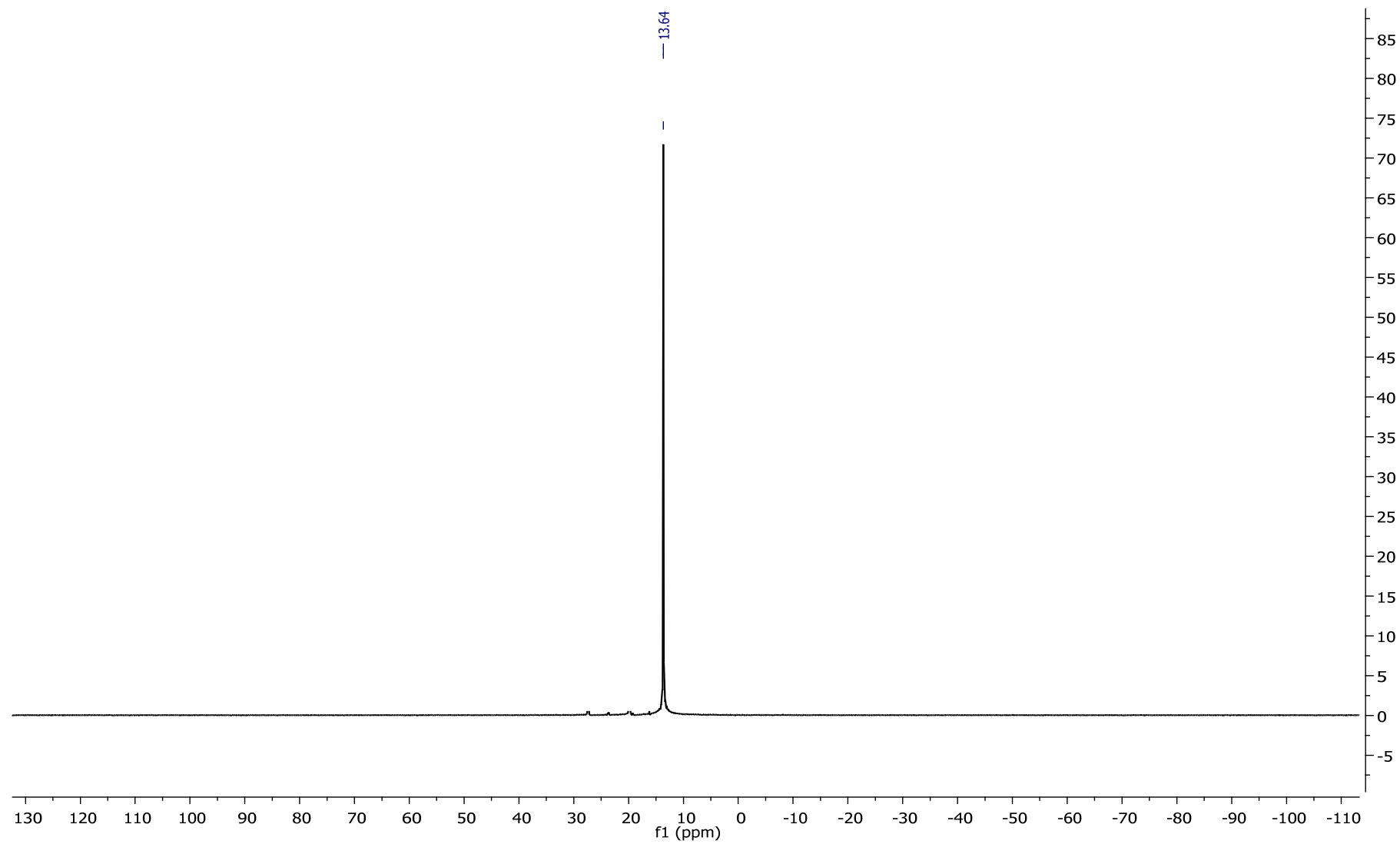


^{19}F NMR

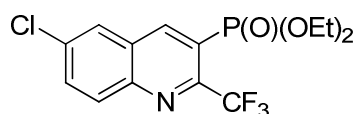


S21

^{31}P NMR

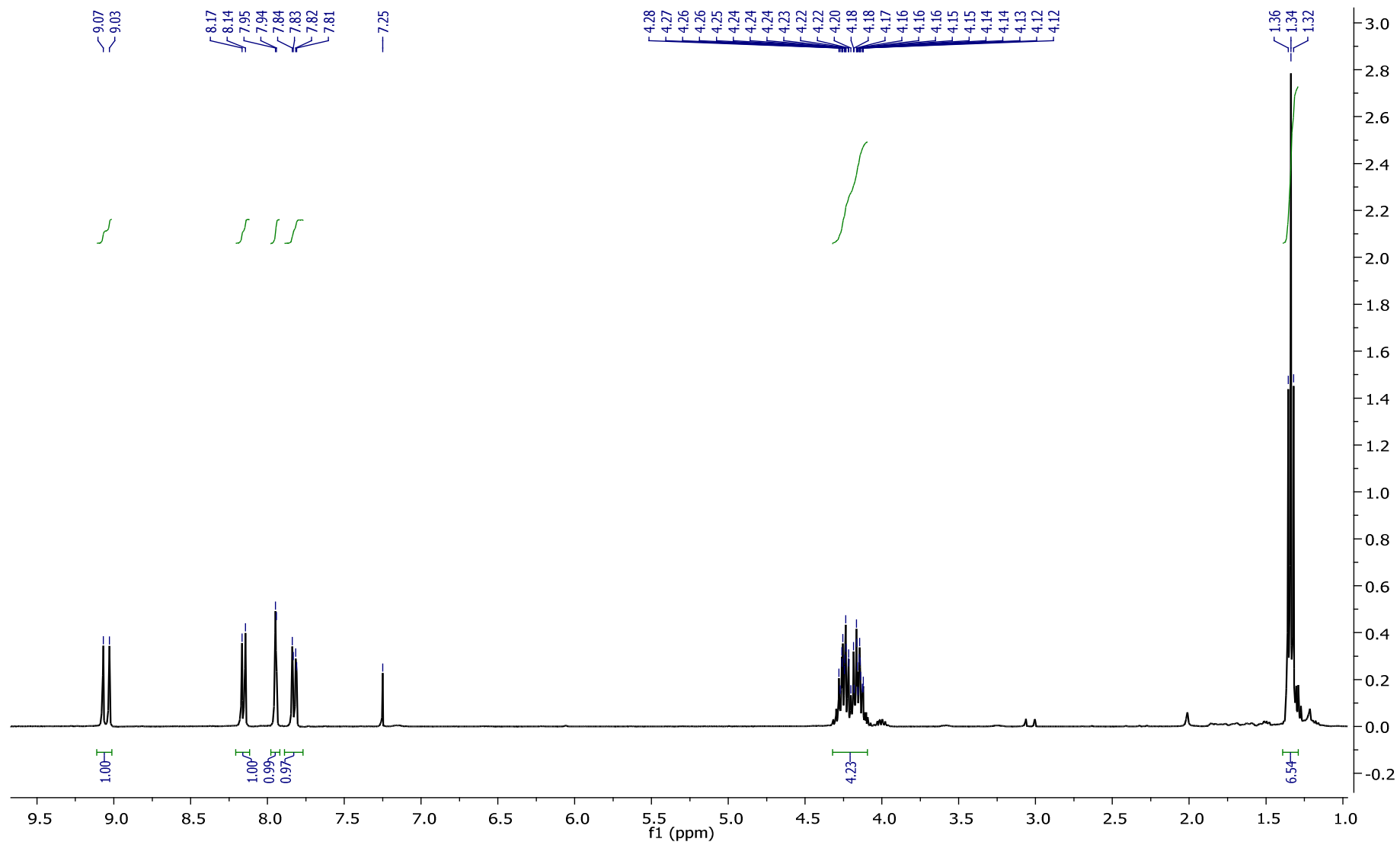


2. Diethyl (6-chloro-2-(trifluoromethyl)quinolin-3-yl)phosphonate **4b**

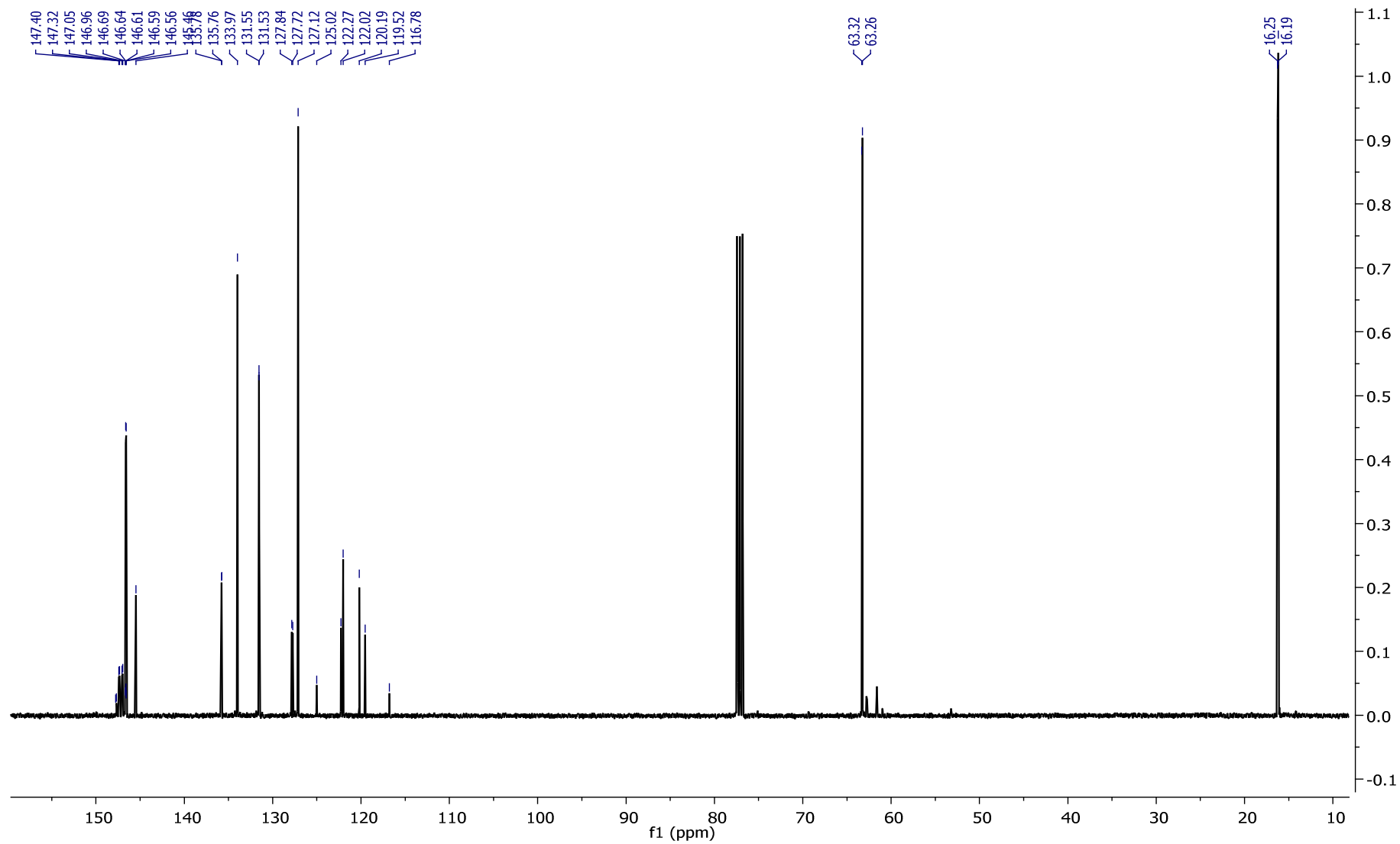


Colourless oil (91%); ^1H NMR (400 MHz, CDCl_3) δ 1.34 (t, $J = 6.7$ Hz, 6H), 4.16 (m, 2H), 4.24 (m, 2H), 7.84 (dd, $J = 8.6$ Hz, $J = 2.4$ Hz, 1H), 7.95 (d, $J = 2.7$ Hz, 1H), 8.15 (d, $J = 8.9$ Hz, 1H), 9.05 (d, $^3J_{\text{H-P}} = 16.1$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.2 (d, $J = 6.5$ Hz), 63.3 (d, $J = 6.2$ Hz), 121.5 (q, $^1J_{\text{C-F}} = 278.6$ Hz), 121.8 (d, $^1J_{\text{C-P}} = 183.7$ Hz), 127.1, 127.8 (d, $^3J_{\text{C-P}} = 11.5$ Hz), 131.5, 133.9, 135.7 (d, $^4J_{\text{C-P}} = 1.8$ Hz), 145.6, 146.6 (d, $^2J_{\text{C-P}} = 6.6$ Hz), 147.2 (qd, $^2J_{\text{C-F}} = 36.2$ Hz, $^2J_{\text{C-P}} = 7.8$ Hz); ^{19}F NMR (376 MHz) δ -63.8; ^{31}P NMR (161 MHz) δ 12.9; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{14}\text{ClF}_3\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 390.0244, found 390.0245.

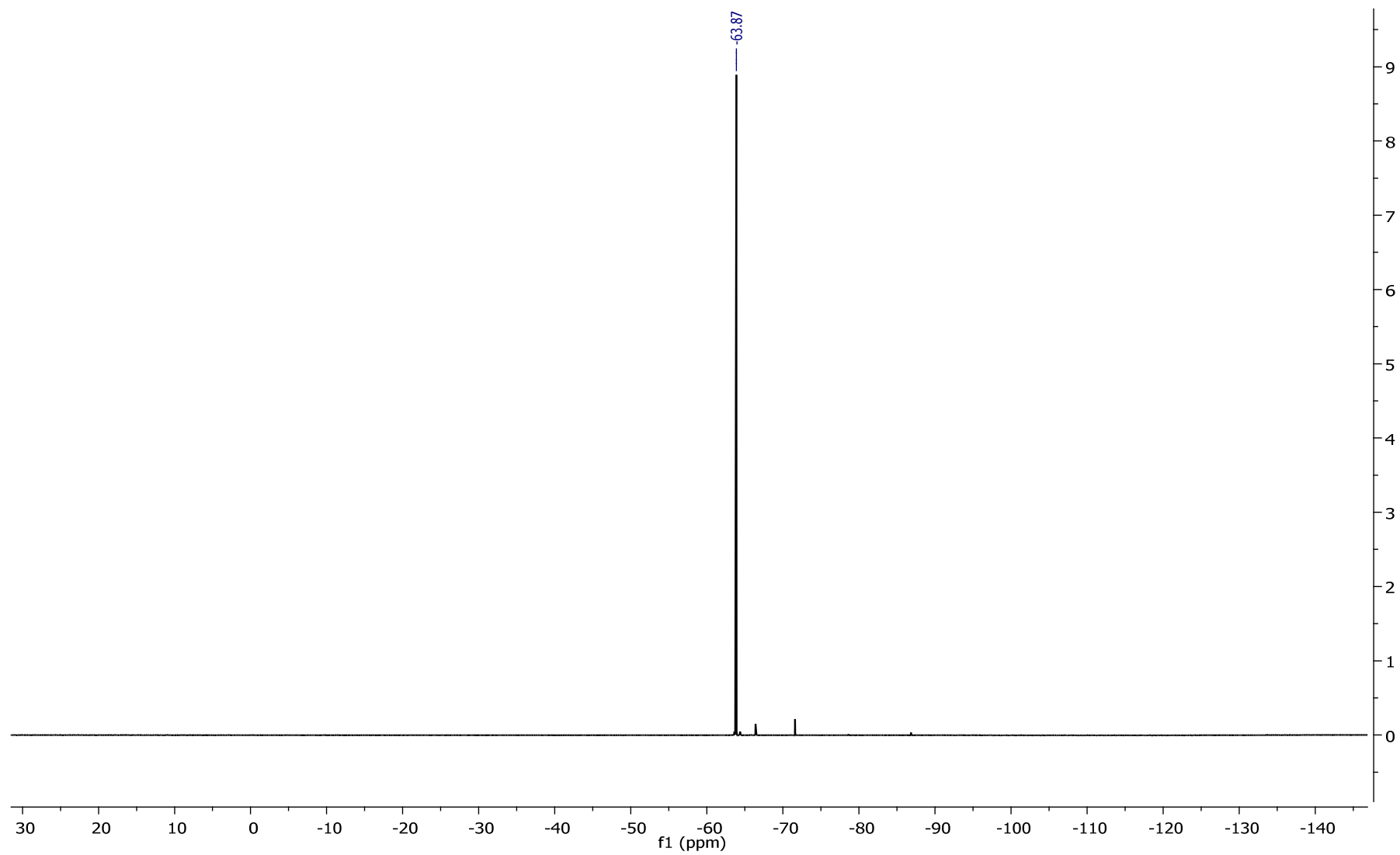
¹H NMR



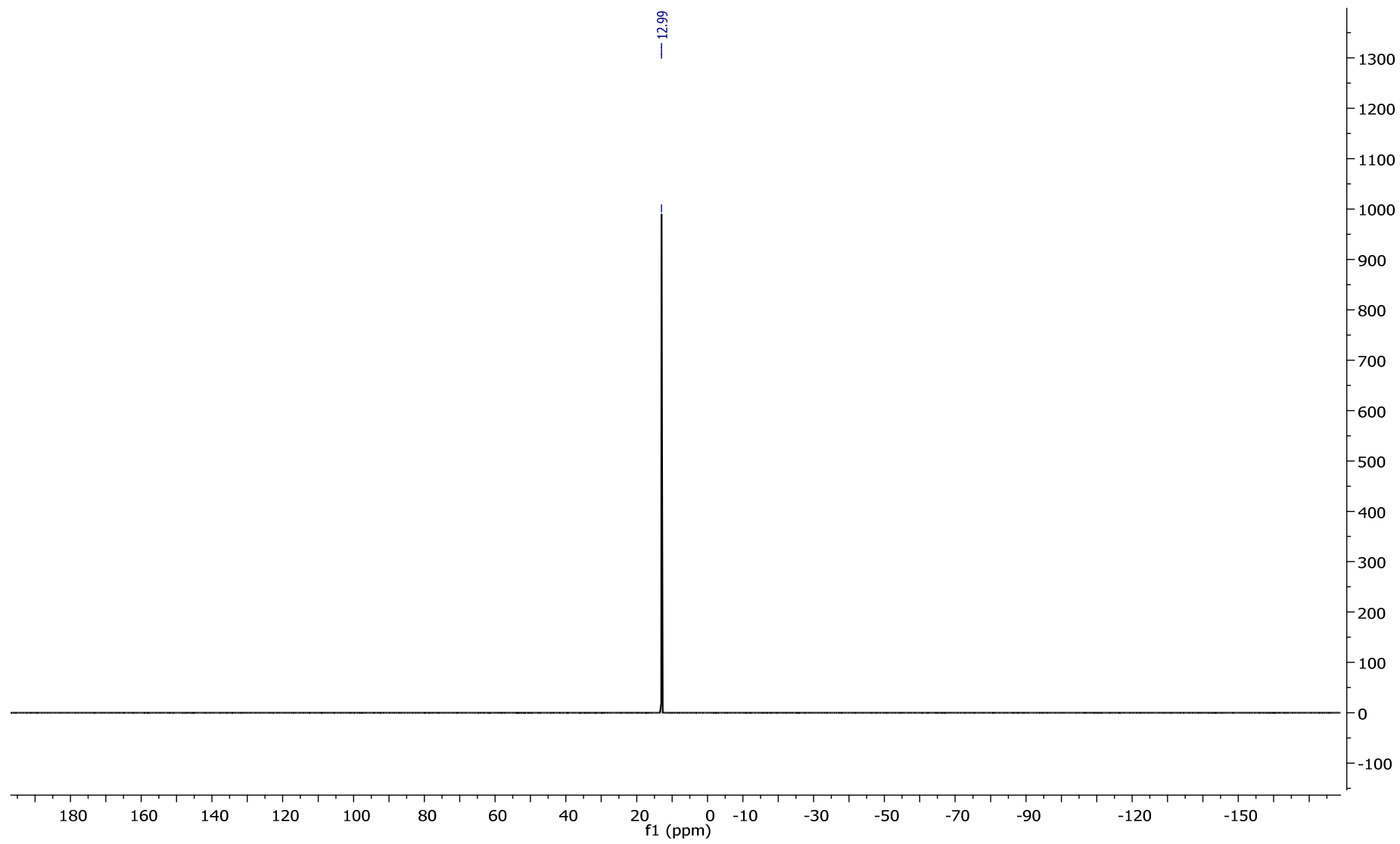
^{13}C NMR



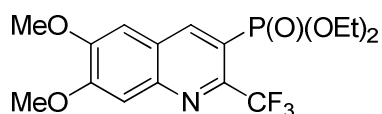
^{19}F NMR



^{31}P NMR

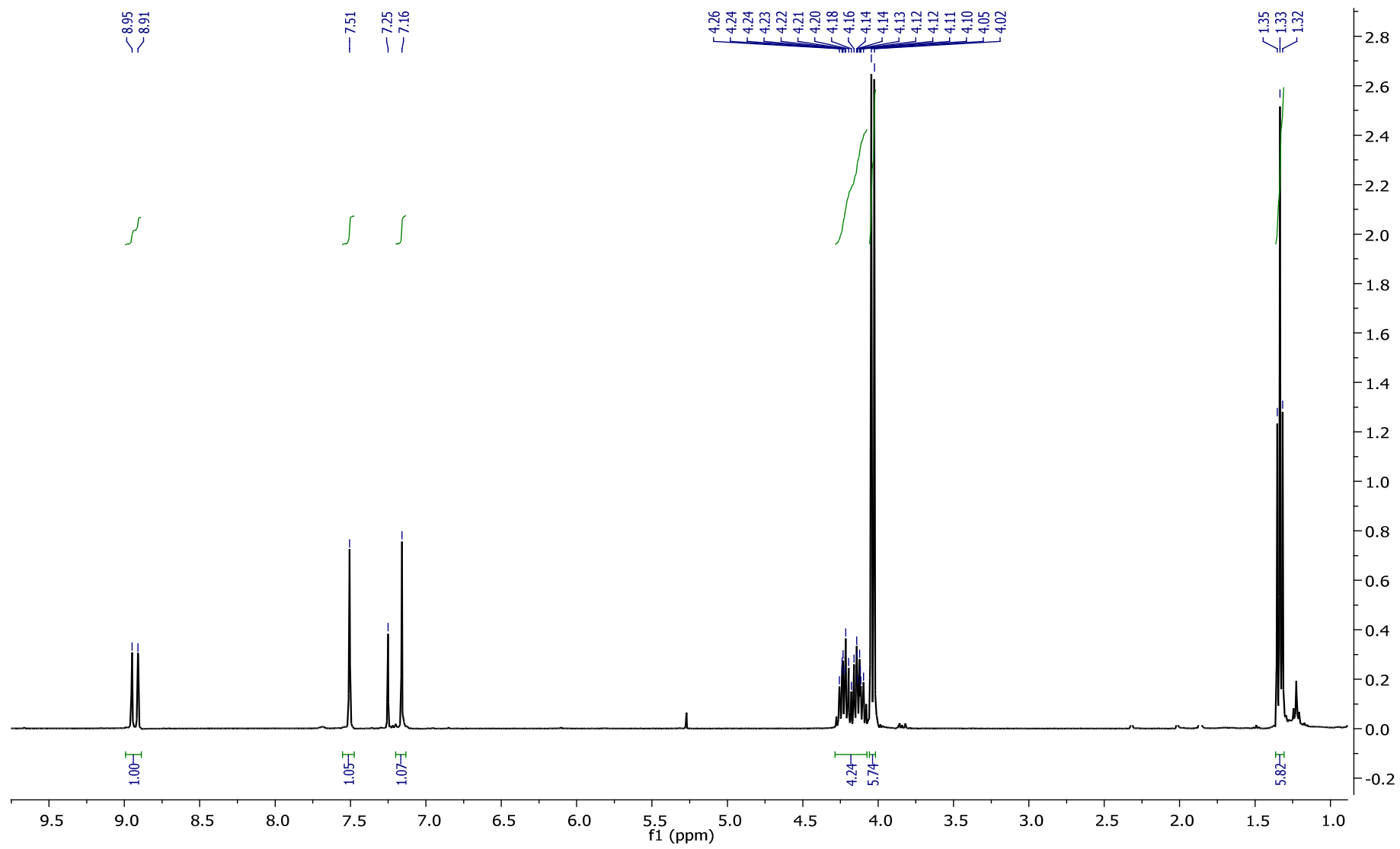


3. Diethyl (6,7-dimethoxy-2-(trifluoromethyl)quinolin-3-yl)phosphonate **4c**

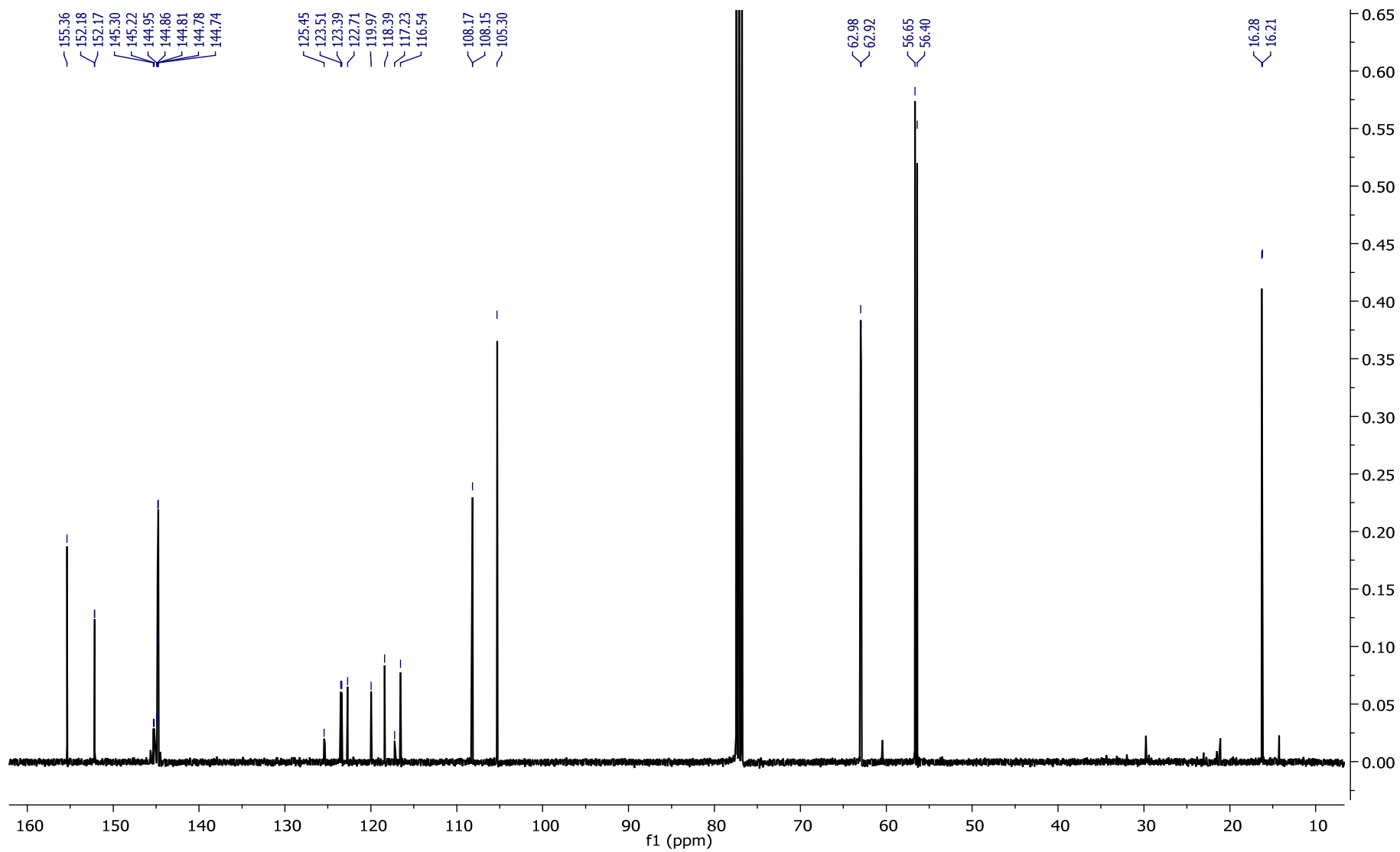


Yellowish crystals (80%); Mp = 186–190 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.33 (t, $J = 7.2$ Hz, 6H), 4.02 (s, 3H), 4.05 (s, 3H), 4.13 (m, 2H), 4.23 (m, 2H), 7.16 (s, 1H), 7.51 (s, 1H), 8.93 (d, $^3J_{\text{H-P}} = 16.2$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.2 (d, $J = 6.4$ Hz), 56.4, 56.6, 62.9 (d, $J = 6.1$ Hz), 105.3, 108.2, 117.4 (d, $^1J_{\text{C-P}} = 186.7$ Hz), 117.4 (q, $^1J_{\text{C-F}} = 275.8$ Hz), 123.5 (d, $^3J_{\text{C-P}} = 11.1$ Hz), 144.8 (d, $^2J_{\text{C-P}} = 7.4$ Hz), 145.1 (qd, $^2J_{\text{C-F}} = 35.4$ Hz, $^2J_{\text{C-P}} = 8.7$ Hz), 152.2, 155.4; ^{19}F NMR (376 MHz) δ -63.3; ^{31}P NMR (161 MHz) δ 14.7 Hz; HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{19}\text{F}_3\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]^+$ 416.0845, found 416.0858.

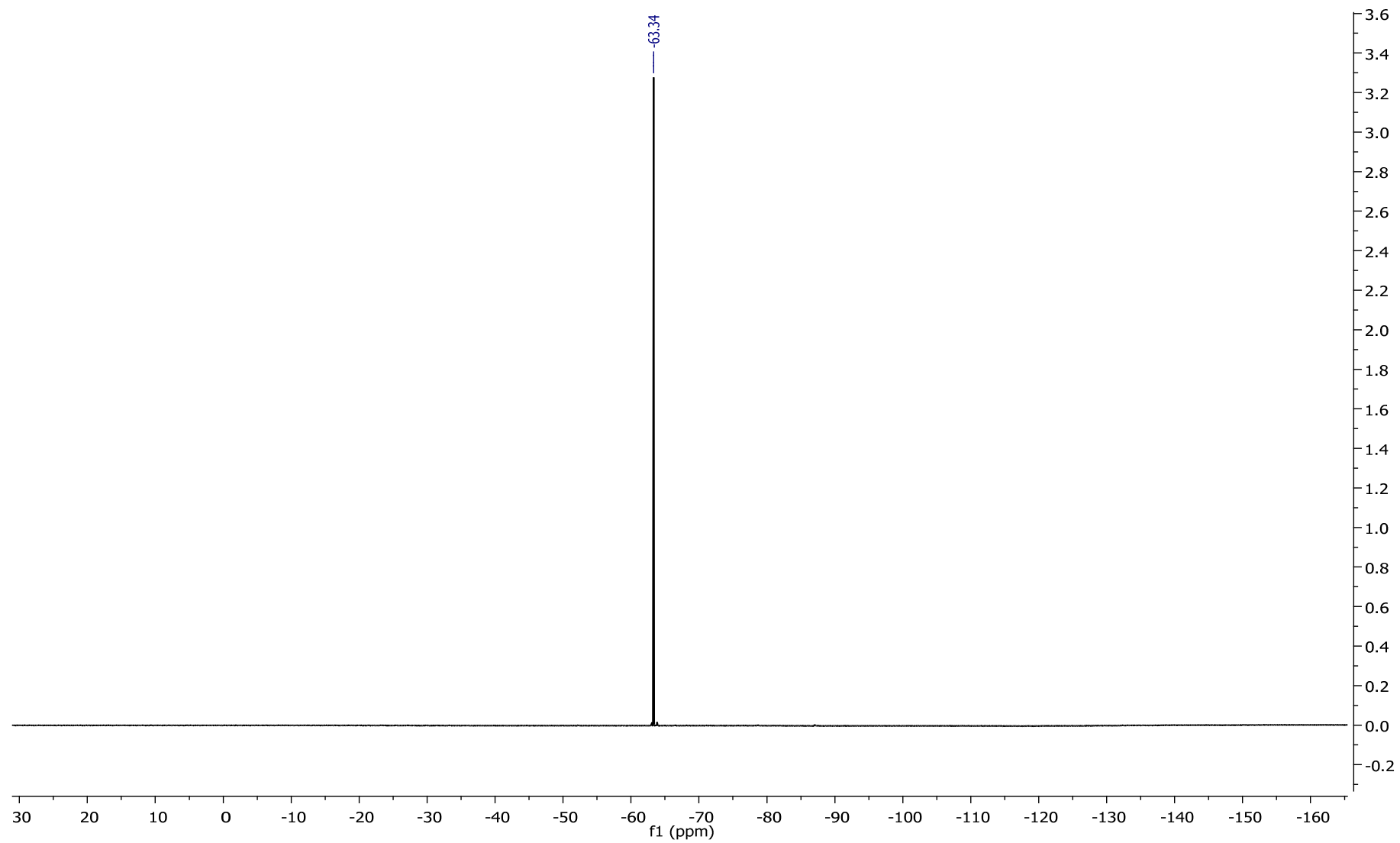
^1H NMR



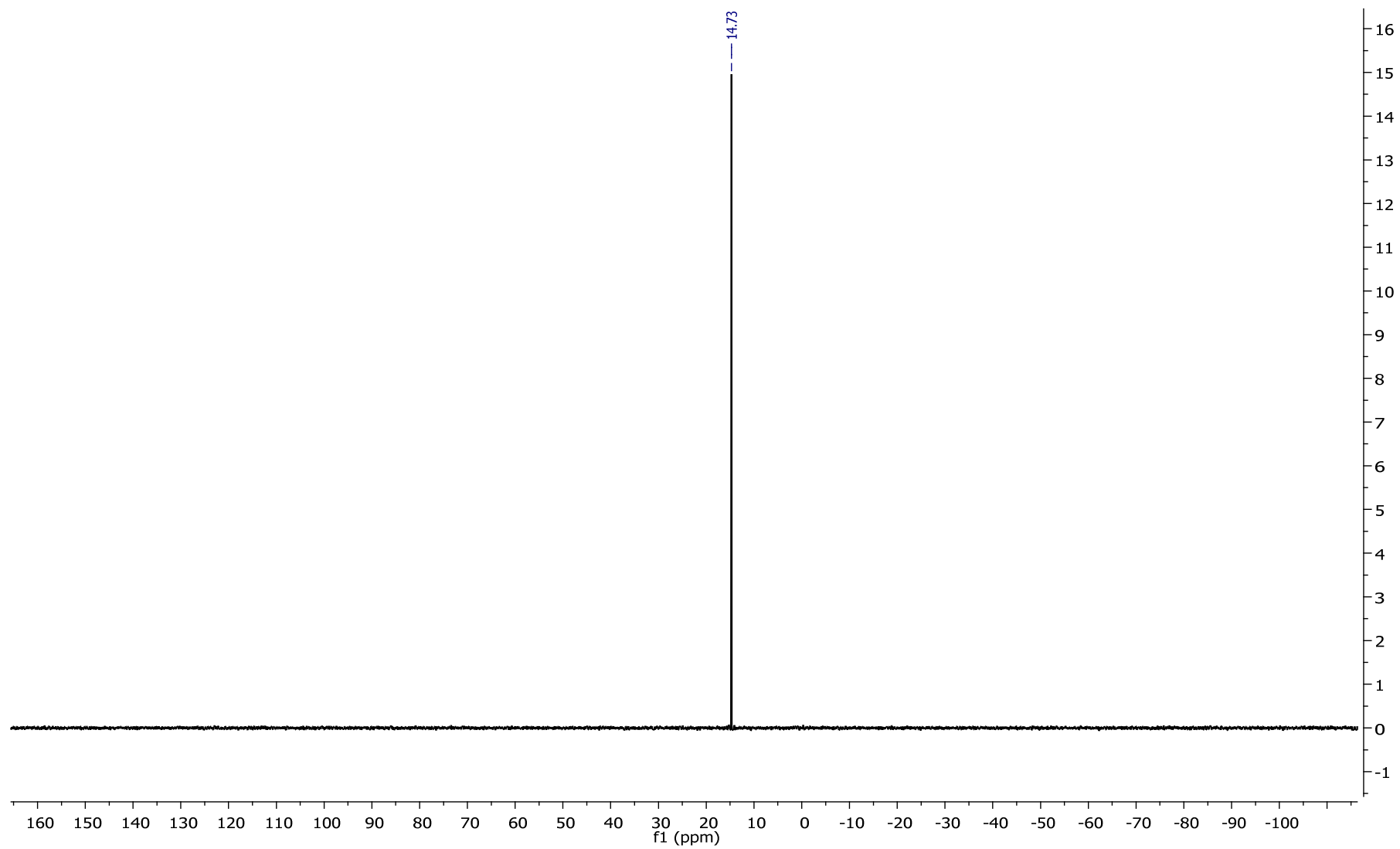
^{13}C NMR



^{19}F NMR



^{31}P NMR



X-Ray crystallography:

A block-shaped single crystal of **3j** with dimensions 0.18 mm x 0.18 mm x 0.45 mm was mounted on a Hampton cryo-loop for indexing and intensity data collection at 100° K on a Bruker APEX II CCD using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program. [G. M. Sheldrick, SADABS, Program for empirical X-ray absorption correction, Bruker-Nonius, **1990**]

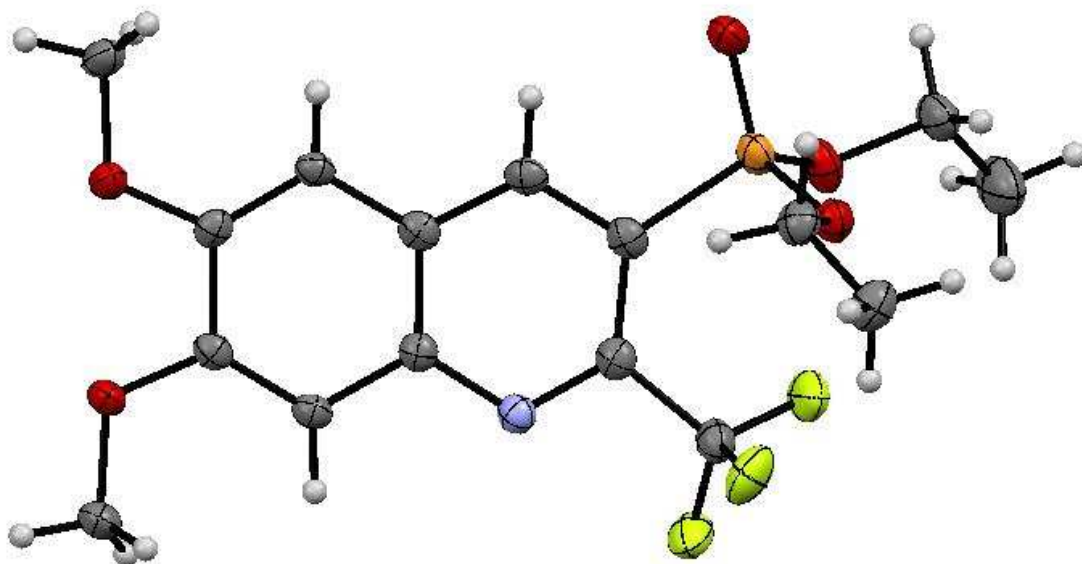
Direct methods were used for structure solution of all structures (SHELXS-97). Structural refinement was obtained from successive Fourier maps (SHELXL-97). [G. M. Sheldrick, *Acta Crystallogr.* **2007**, A64, 112-122.] All heavy atoms (C, N, O, Br, P, F) were refined anisotropically whereas the hydrogen atoms were found through calculated constrained positions. The crystallographic data for are summarized in Table S1.

Table S1. Crystal data for **4c**.

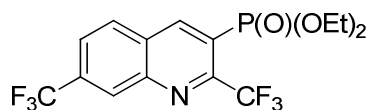
Empirical formula	C ₁₆ H ₁₉ F ₃ NO ₅ P
Formula weight, g/mol	393.29
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , Å	7.4669(6)
<i>b</i> , Å	9.0018(6)
<i>c</i> , Å	12.9910(11)
α , °	93.708(5)
β , °	95.044(6)
γ , °	93.142(5)
Volume, Å ³	866.39(12)
<i>Z</i>	2
<i>D</i> _{calc} , g/cm ³	1.508
Absorption coefficient	0.218
F(000)	408
Crystal size, mm	0.05 x 0.20 x 0.40
Theta range for data collection, °	2.74 – 24.30
Reflections collected	39542

Independent reflections	3497
R(int)	0.094
Observed ($I > 2\sigma(I)$)	2478
Goodness-of-fit on F2	1.024
$R_1[I > 2\sigma(I)]^{[a]}$	0.0426
wR_2 (all data) ^[b]	0.1118

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

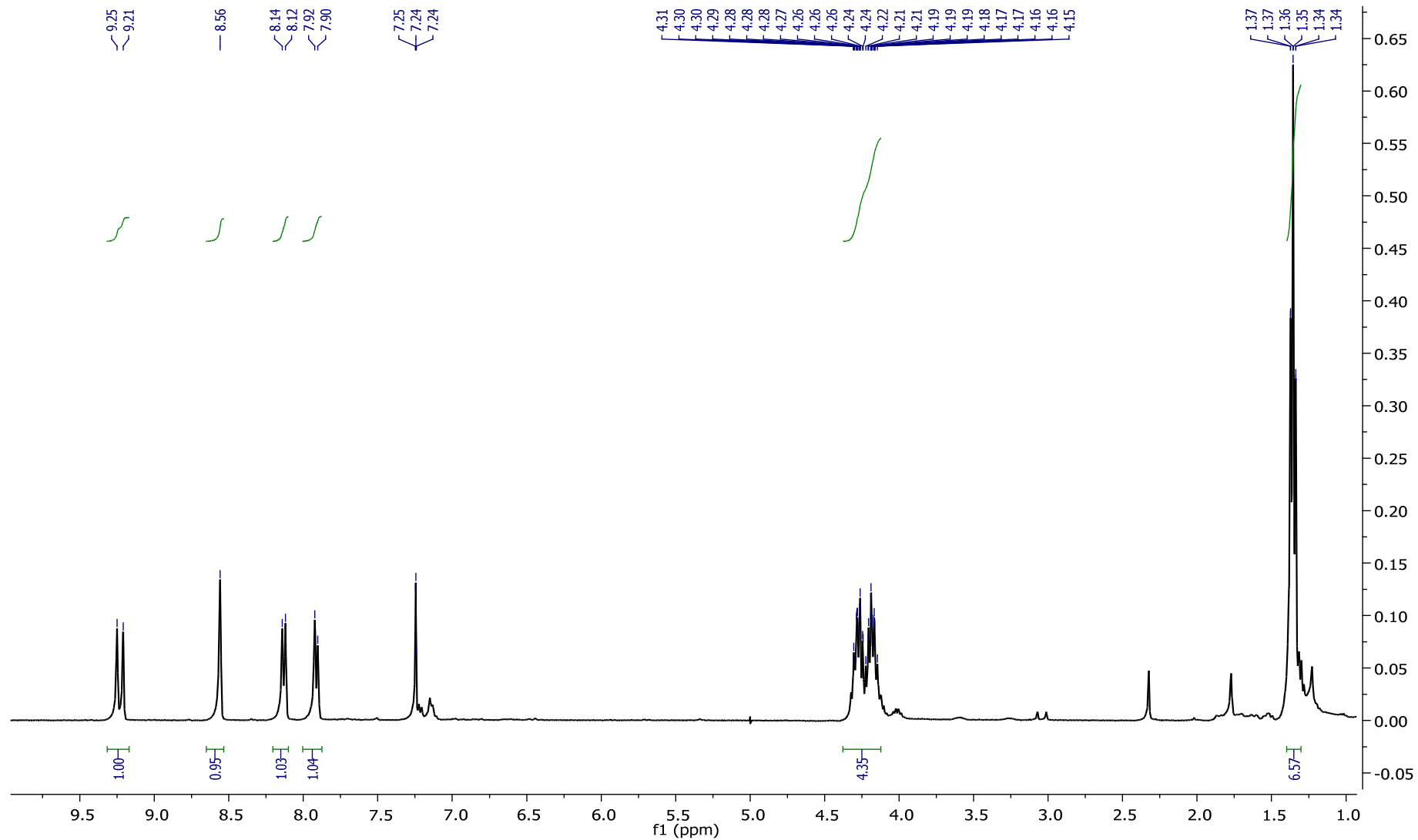


4. Diethyl (2,7-bis(trifluoromethyl)quinolin-3-yl)phosphonate **4d**

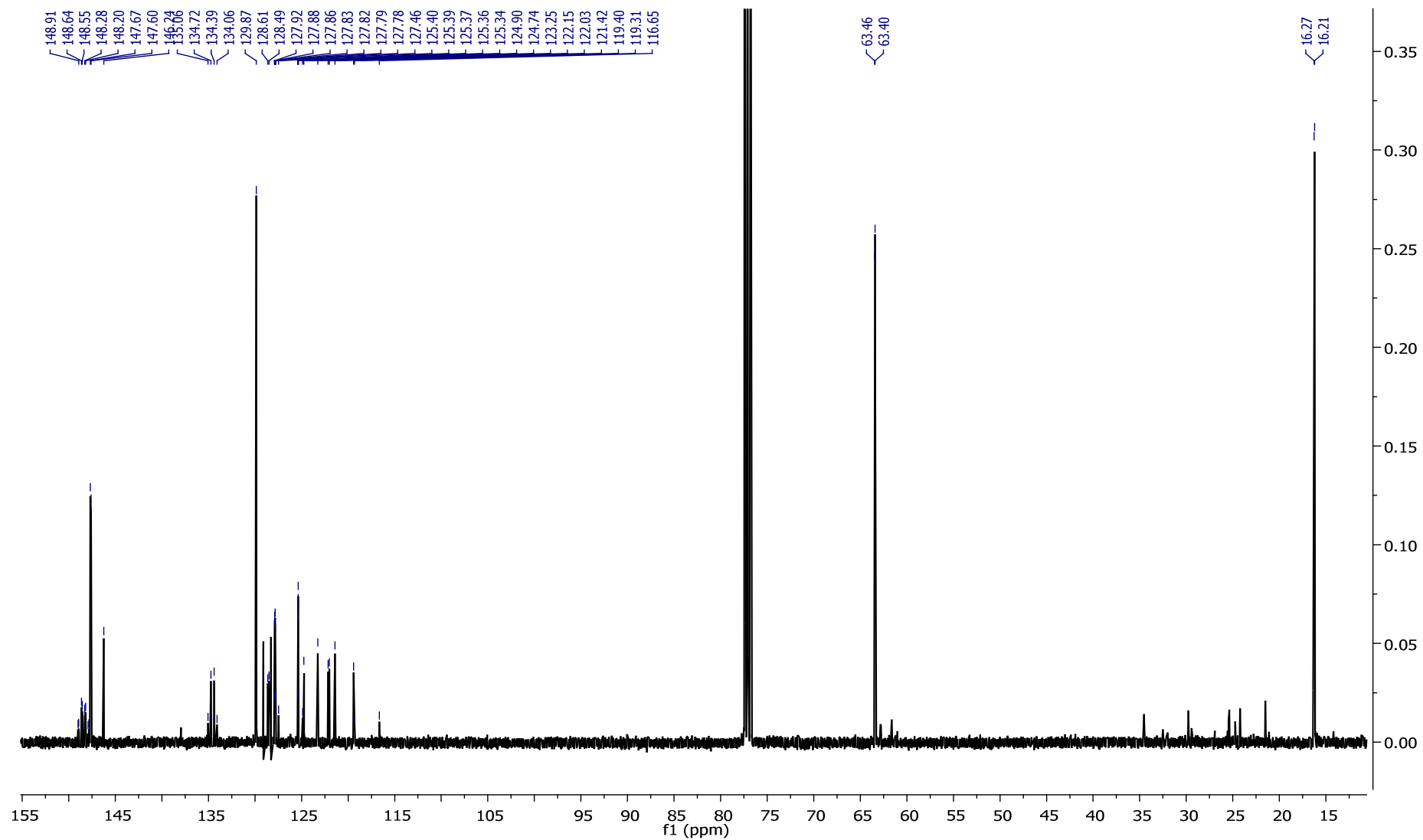


Yellowish oil (99%); ^1H NMR (400 MHz, CDCl_3) δ 1.36 (t, $J = 6.9$ Hz, 6H), 4.18 (m, 2H), 4.28 (m, 2H), 7.91 (d, $J = 8.6$ Hz, 1H), 8.13 (d, $J = 8.6$ Hz, 1H), 8.56 (s, 1H), 9.24 (d, $^3J_{\text{H-P}} = 16.5$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.2 (d, $J = 6.4$ Hz), 63.4 (d, $J = 6.1$ Hz), 120.8 (q, $^1J_{\text{C-F}} = 276.5$ Hz), 122.2 (d, $^1J_{\text{C-P}} = 185.5$ Hz), 123.2 (q, $^1J_{\text{C-F}} = 270.8$ Hz), 125.8 (qd, $^4J_{\text{C-F}} = 3.2$ Hz, $^4J_{\text{C-P}} = 1.2$ Hz), 127.8 (qd, $^4J_{\text{C-F}} = 4.2$ Hz, $^4J_{\text{C-P}} = 1.3$ Hz), 128.5 (dq, $^3J_{\text{C-P}} = 11.9$ Hz, $^5J_{\text{C-F}} = 1.1$ Hz), 129.8, 134.5 (q, $^2J_{\text{C-F}} = 33.6$ Hz), 146.2, 147.7 (d, $^2J_{\text{C-P}} = 6.8$ Hz), 148.6 (qd, $^2J_{\text{C-F}} = 35.8$ Hz, $^2J_{\text{C-P}} = 8.9$ Hz); ^{19}F NMR (376 MHz) δ -63.0 (s, $-\text{CF}_3$), -64.0 (s, $-\text{CF}_3$); ^{31}P NMR (161 MHz) δ 12.5; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{F}_6\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 424.0508, found 424.0508.

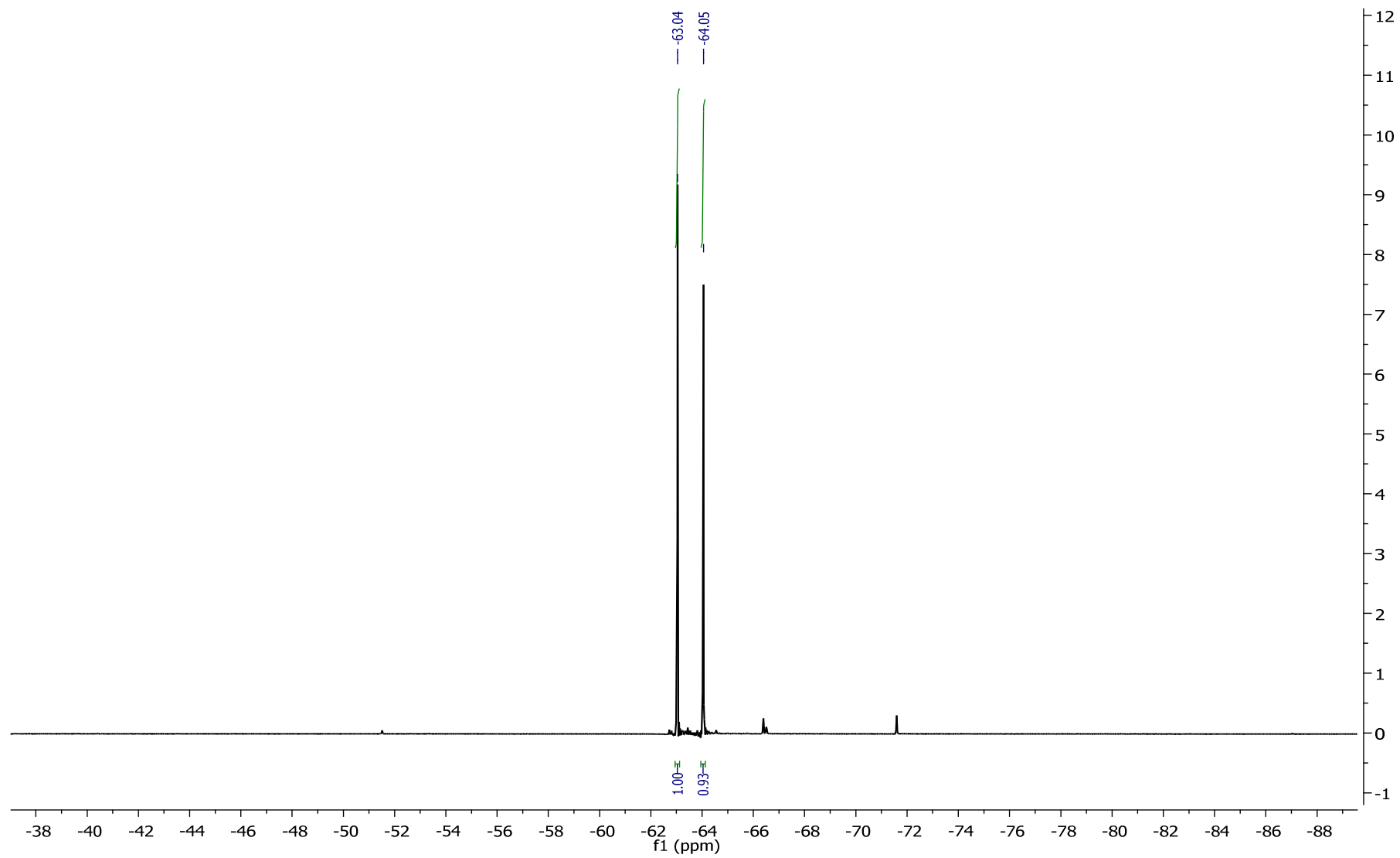
¹H NMR



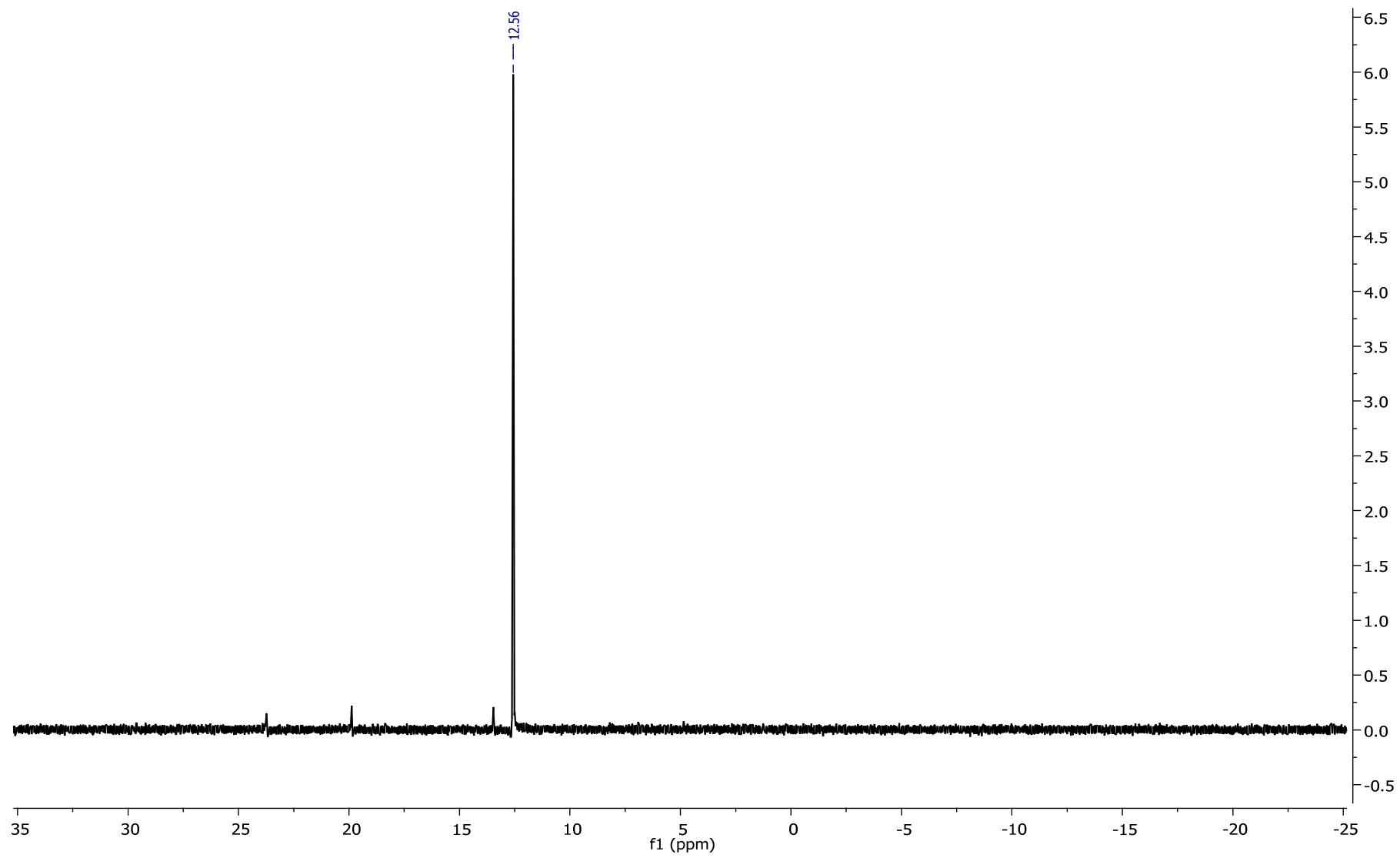
^{13}C NMR



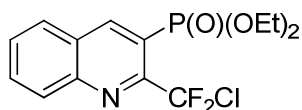
^{19}F NMR



^{31}P NMR

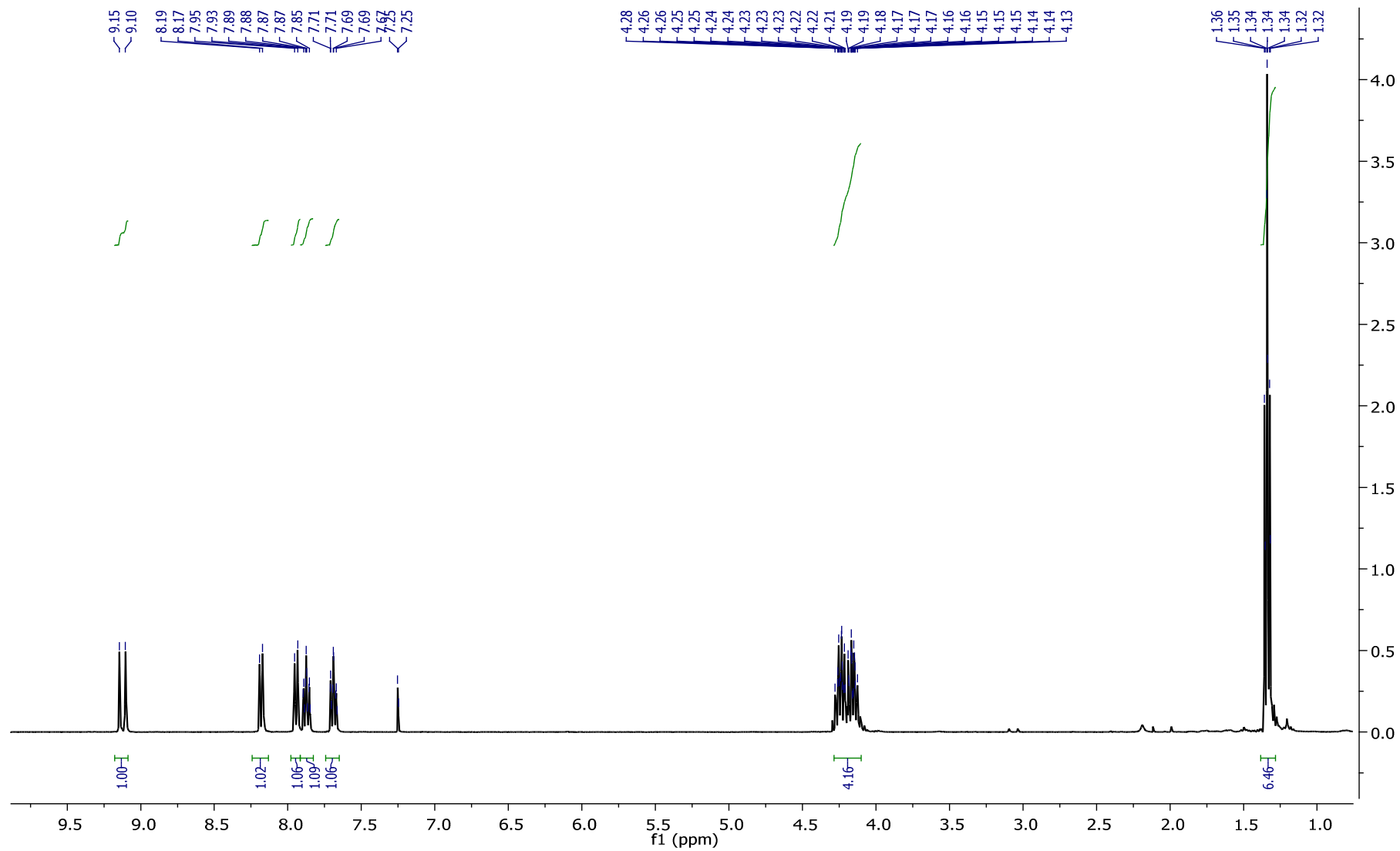


5. Diethyl (2-(chlorodifluoromethyl)quinolin-3-yl)phosphonate **4e**

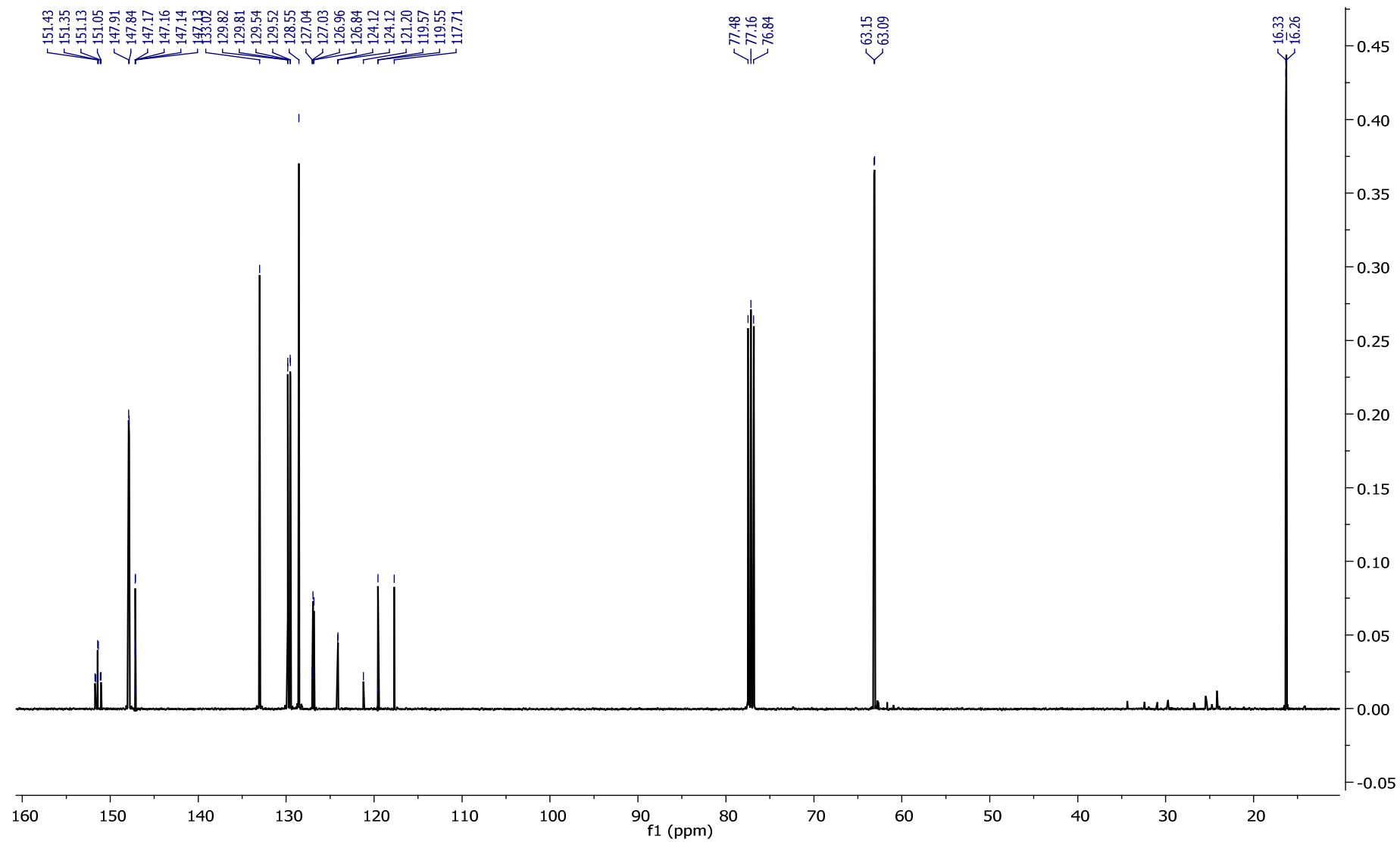


Yellowish oil (90%); ^1H NMR (400 MHz, CDCl_3) δ 1.34 (t, $J = 7.0$ Hz, 6H), 4.15 (m, 2H), 4.22 (m, 2H), 7.69 (td, $J = 8.1$ Hz, $J = 1.1$ Hz, 1H), 7.87 (tt, $J = 6.9$ Hz, $J = 1.4$ Hz, 1H), 7.94 (d, $J = 8.1$ Hz, 1H), 8.18 (d, $J = 8.6$ Hz, 1H), 9.13 (d, $^3J_{\text{H-P}} = 16.4$ Hz, 1H); ^{13}C NMR (161 MHz) δ 16.3 (d, $J = 6.7$ Hz), 63.1 (d, $J = 6.2$ Hz), 118.5 (d, $^1J_{\text{C-P}} = 186.7$ Hz), 124.1 (t, $^1J_{\text{C-F}} = 294.2$ Hz), 126.8 (d, $^3J_{\text{C-P}} = 11.7$ Hz), 128.5, 129.5 (d, $^5J_{\text{C-P}} = 1.2$ Hz), 129.8 (d, $^4J_{\text{C-P}} = 1.5$ Hz), 133.0, 147.2 (dt, $^4J_{\text{C-P}} = 1.4$ Hz, $^4J_{\text{C-F}} = 0.9$ Hz), 147.8 (d, $^2J_{\text{C-P}} = 7.2$ Hz), 151.3 (td, $^2J_{\text{C-F}} = 29.7$ Hz, $^2J_{\text{C-P}} = 8.7$ Hz); ^{19}F NMR (376 MHz) δ -51.9; ^{31}P NMR (161 MHz) δ 13.9; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{15}\text{ClF}_2\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 372.0338, found 372.0323.

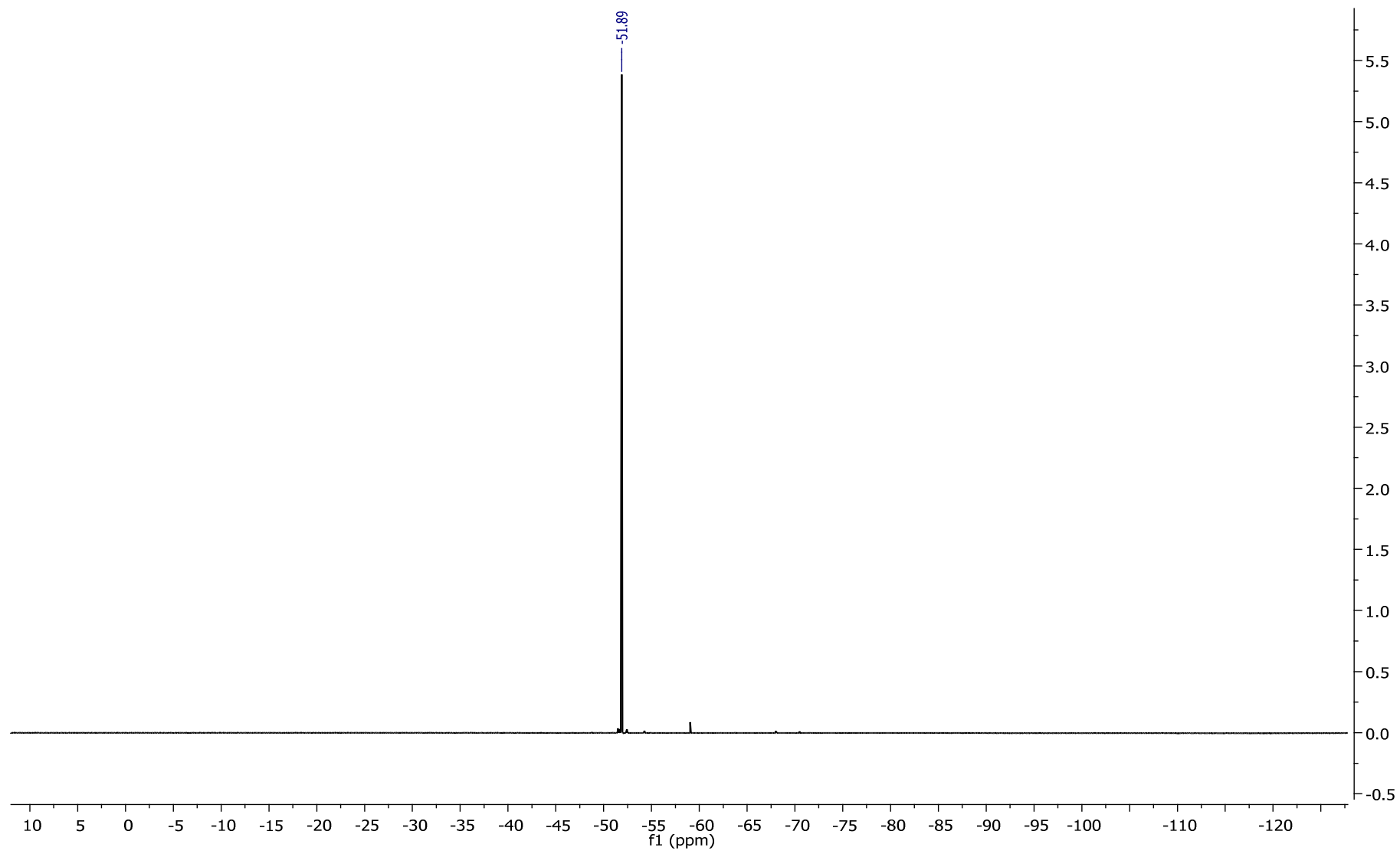
¹H NMR



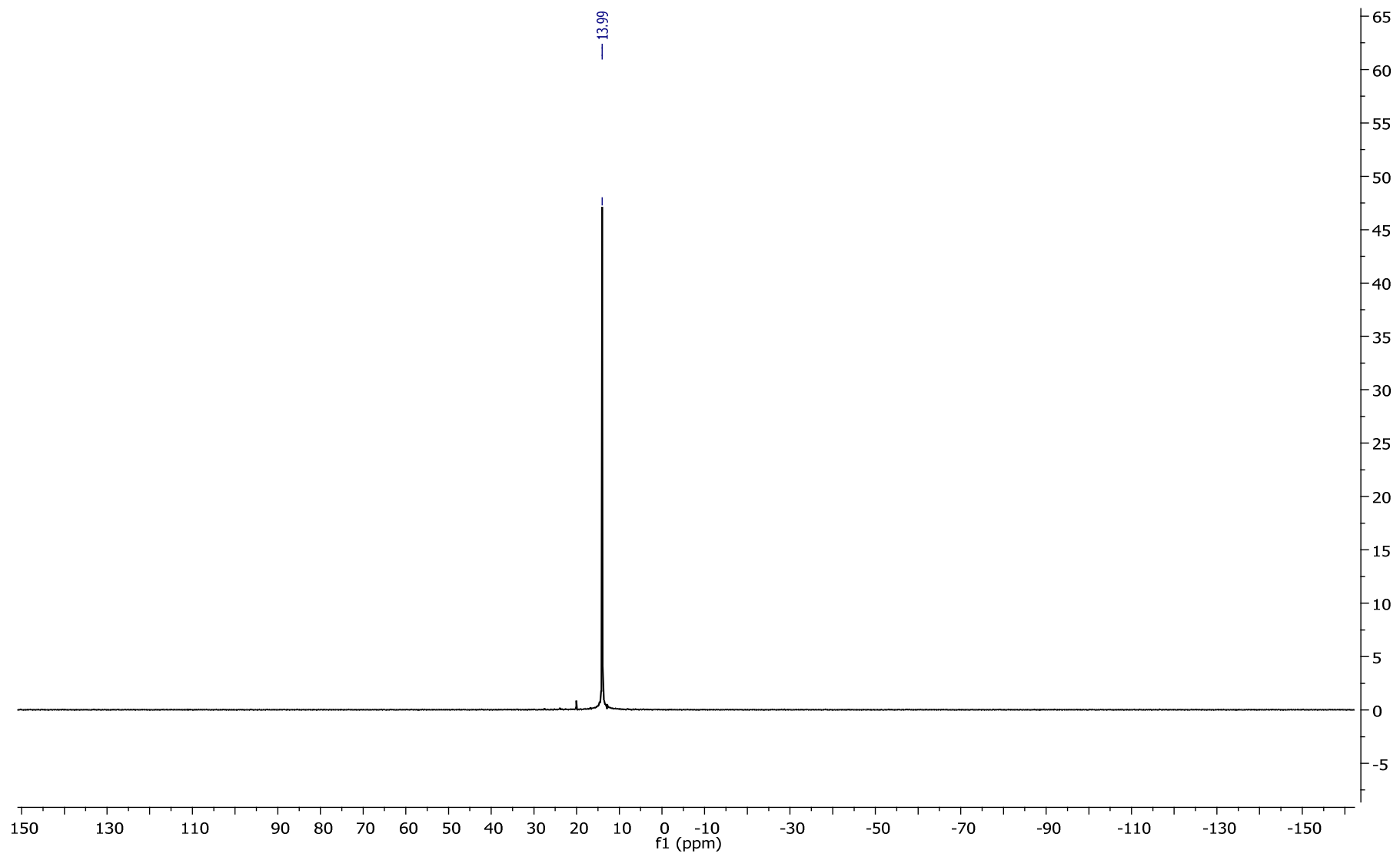
¹³C NMR



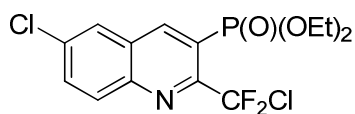
^{19}F NMR



^{31}P NMR

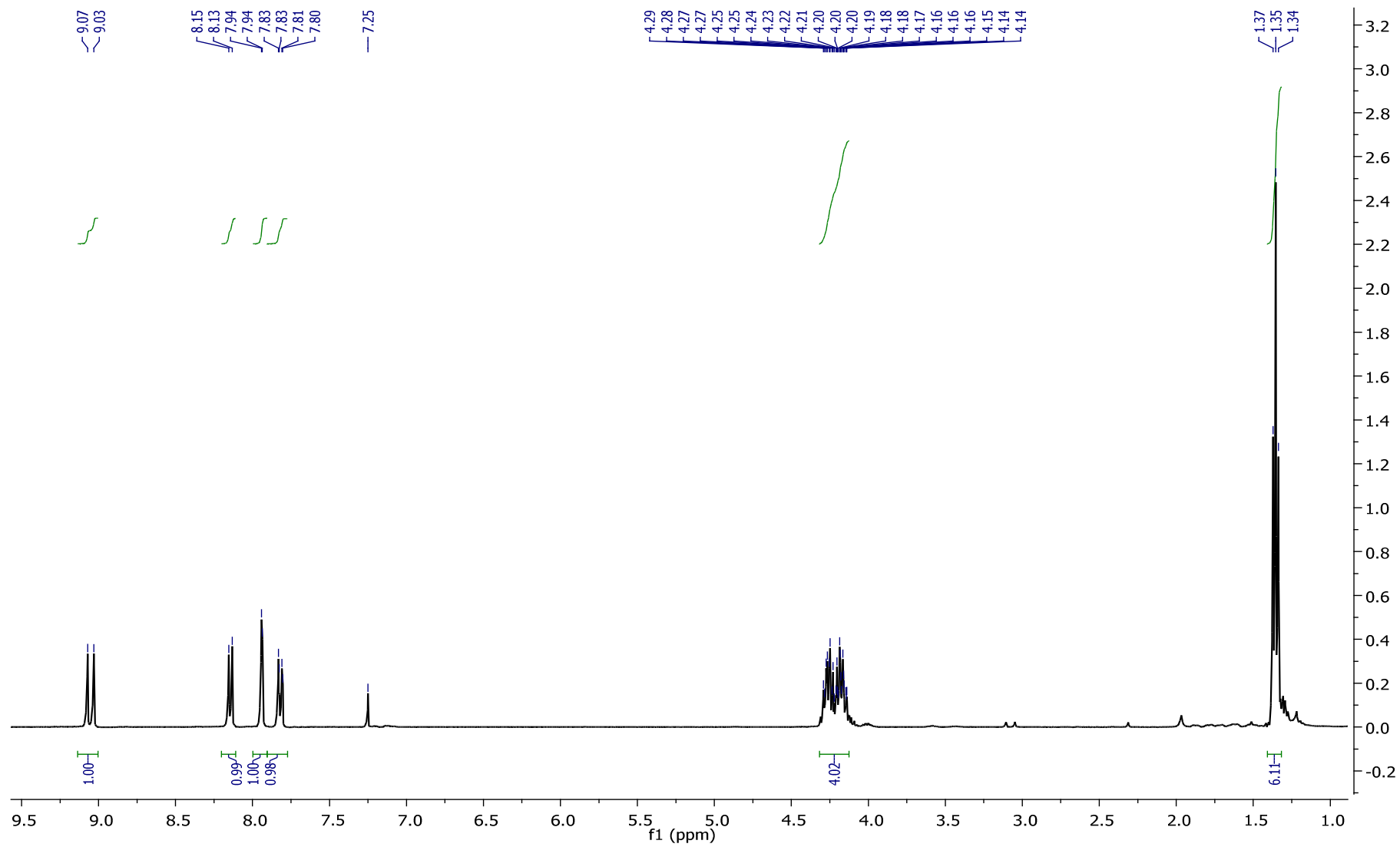


6. Diethyl (6-chloro-2-(chlorodifluoromethyl)quinolin-3-yl)phosphonate **4f**

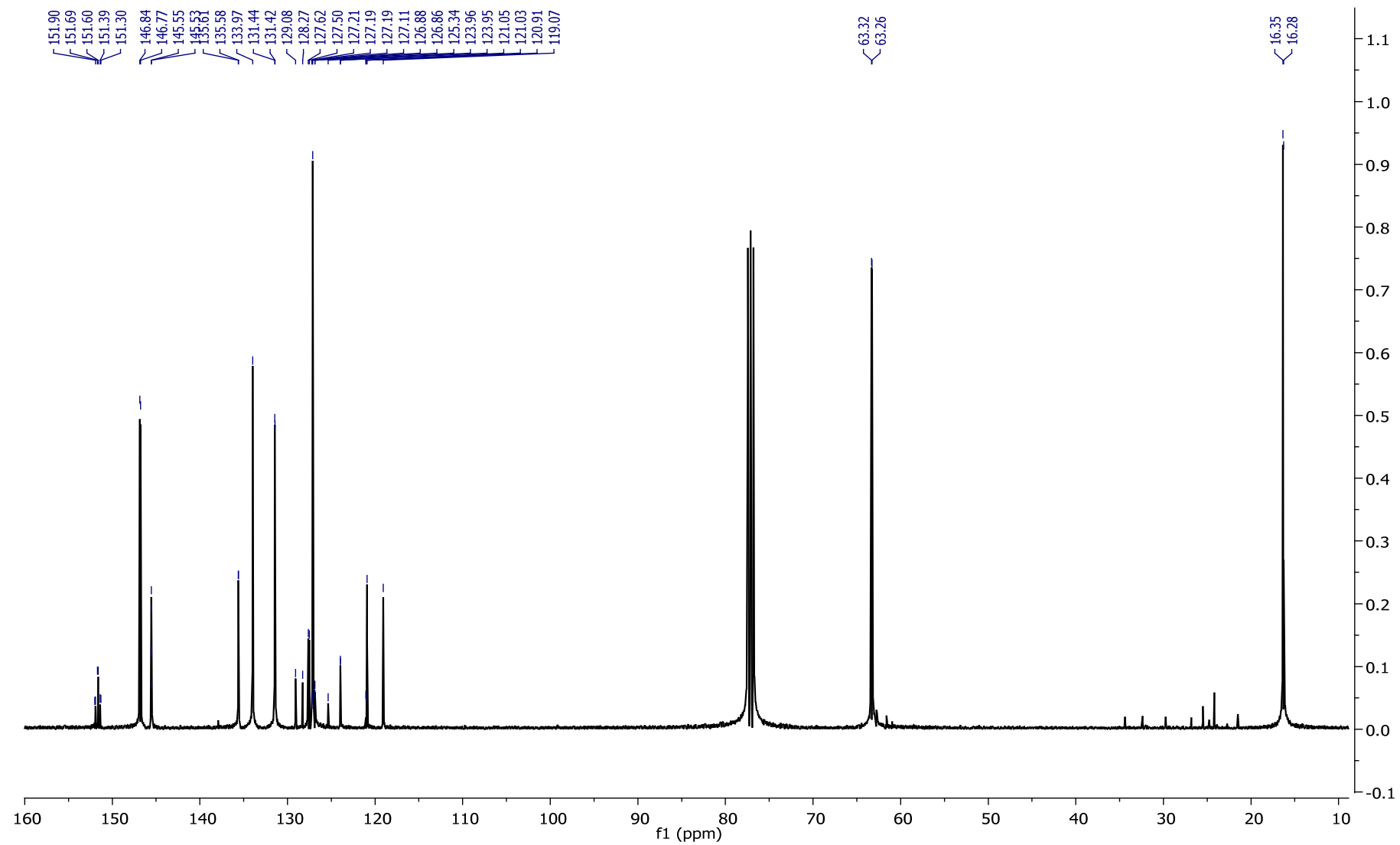


Colourless crystals (81%); Mp = 74–77 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.35 (t, $J = 6.9$ Hz, 6H), 4.16 (m, 2H), 4.22 (m, 2H), 7.82 (dd, $J = 9.1$ Hz, $J = 2.2$ Hz, 1H), 7.94 (d, $J = 2.1$ Hz, 1H), 8.14 (d, $J = 8.8$ Hz, 1H), 9.05 (d, $^3J_{\text{H-P}} = 16.3$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.5$ Hz), 63.3 (d, $J = 6.3$ Hz), 119.8 (d, $^1J_{\text{C-P}} = 186.7$ Hz), 123.9 (td, $^1J_{\text{C-F}} = 293.0$ Hz, $^3J_{\text{C-P}} = 2.1$ Hz), 127.1, 127.5 (d, $^3J_{\text{C-P}} = 12.5$ Hz), 131.5 (d, $^4J_{\text{C-P}} = 1.9$ Hz), 133.9, 135.6 (d, $^5J_{\text{C-P}} = 1.5$ Hz), 145.5 (dt, $^4J_{\text{C-P}} = 1.3$ Hz, $^4J_{\text{C-F}} = 0.9$ Hz), 146.7 (d, $^2J_{\text{C-P}} = 7.1$ Hz), 151.7 (td, $^2J_{\text{C-F}} = 30.1$ Hz, $^2J_{\text{C-P}} = 8.6$ Hz); ^{19}F NMR (376 MHz) δ -52.1; ^{31}P NMR (161 MHz) δ 13.3; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{F}_2\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 405.9949, found 405.9955.

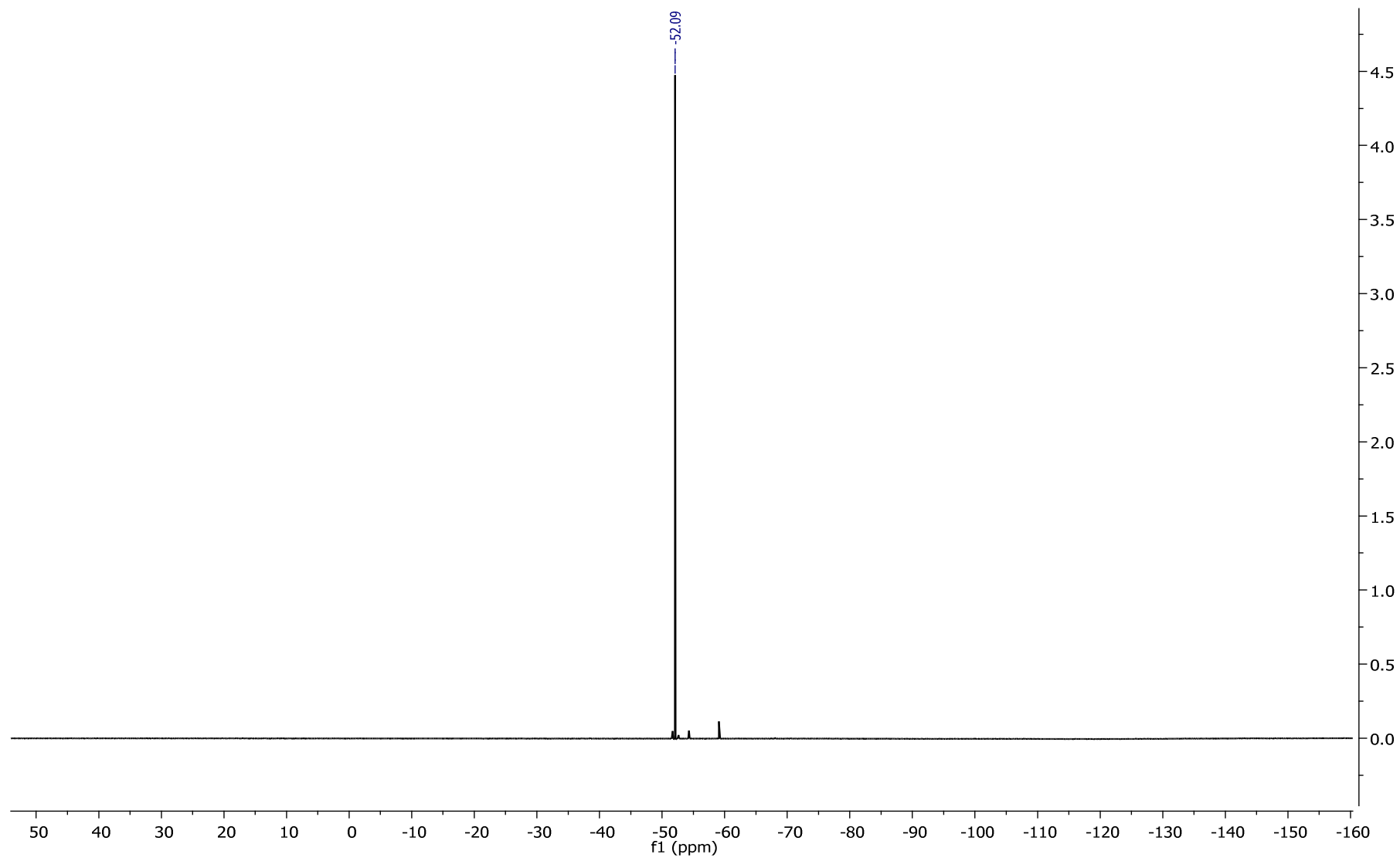
¹H NMR



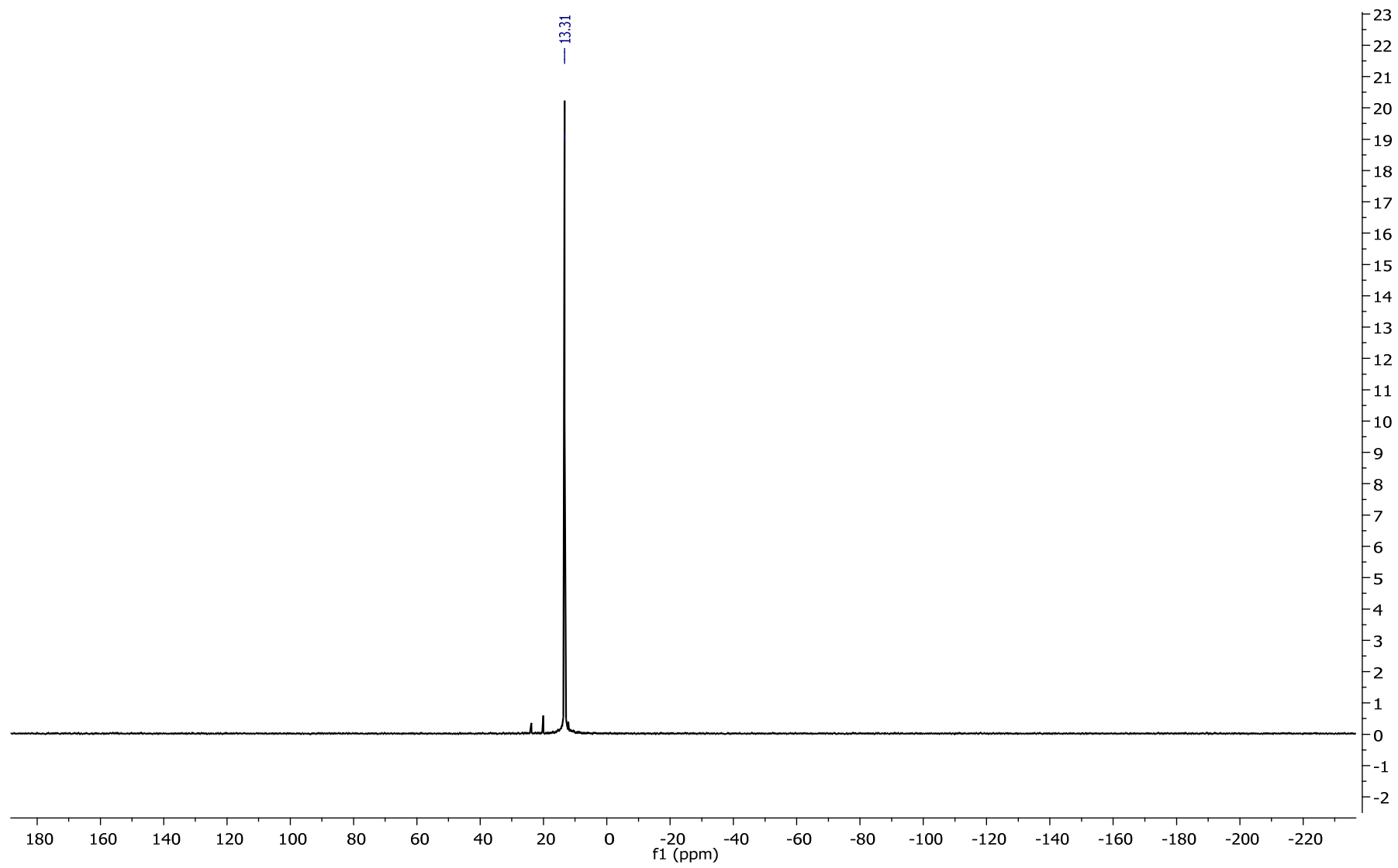
^{13}C NMR



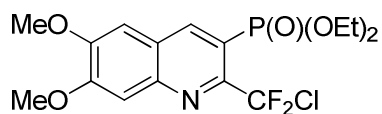
^{19}F NMR



^{31}P NMR

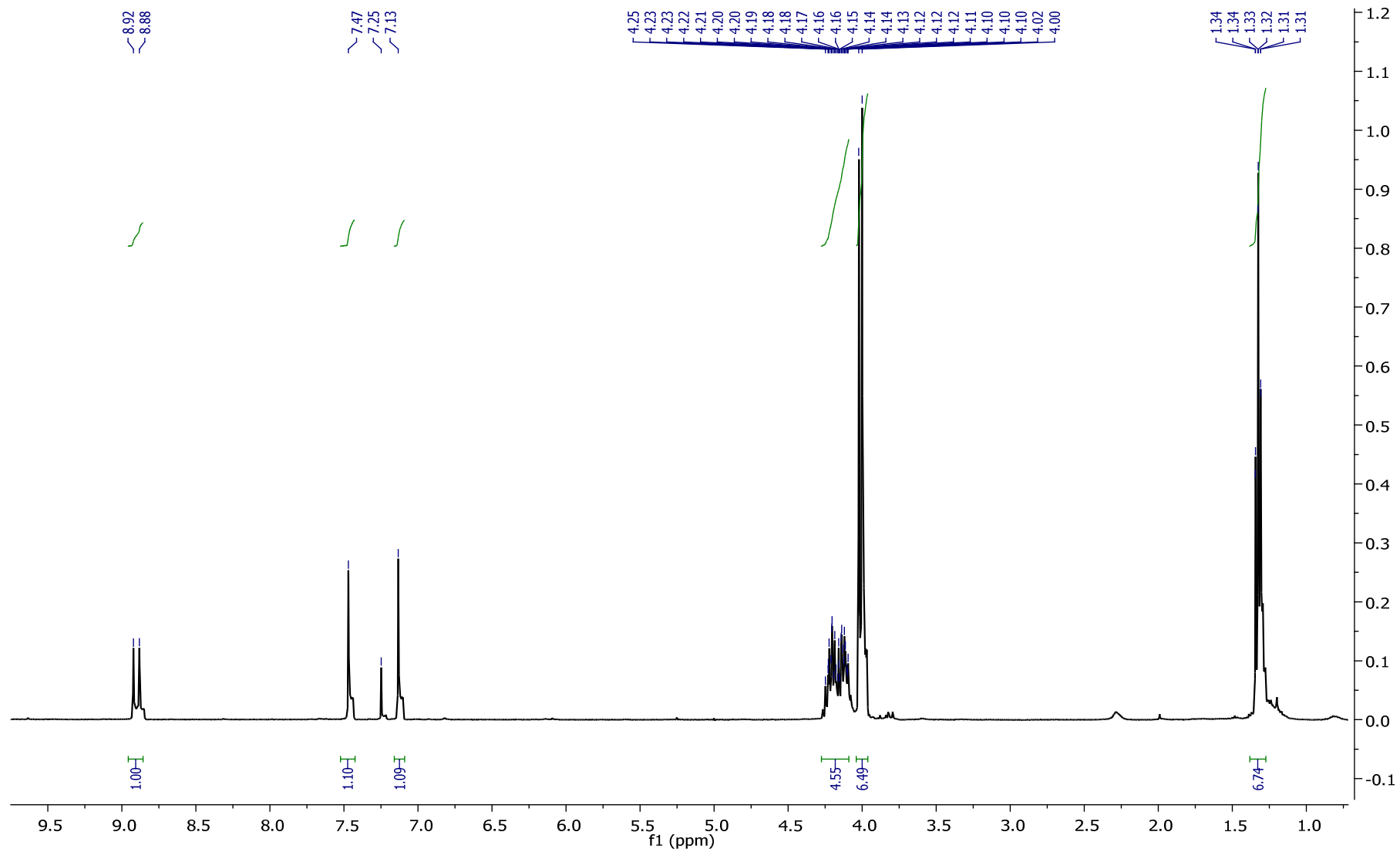


7. Diethyl (2-(chlorodifluoromethyl)-6,7-dimethoxyquinolin-3-yl)phosphonate **4g**

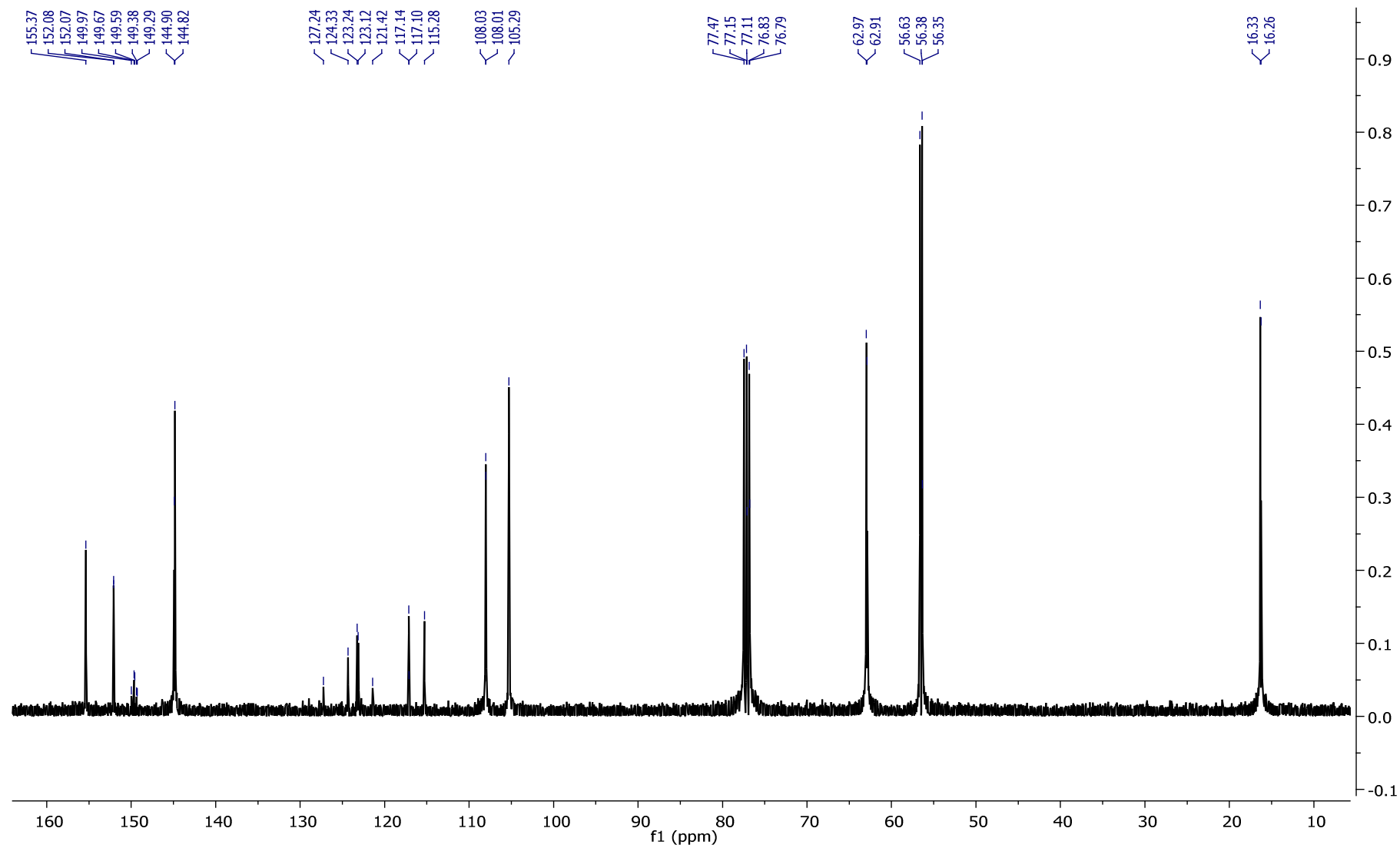


Colourless crystals (71%); Mp = 160–165 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.32 (t, $J = 7.0$ Hz, 6H), 4.00 (s, 3H), 4.02 (s, 3H), 4.12 (m, 2H), 4.21 (m, 2H), 7.13 (s, 1H), 7.47 (s, 1H), 8.89 (d, $^3J_{\text{H-P}} = 15.2$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.2 (d, $J = 6.8$ Hz), 56.3, 56.6, 62.9 (d, $J = 6.1$ Hz), 105.3, 108.0, 116.5 (d, $^1J_{\text{C-P}} = 187.4$ Hz), 123.2 (d, $^3J_{\text{C-P}} = 11.8$ Hz), 124.3 (td, $^1J_{\text{C-F}} = 293.5$ Hz, $^3J_{\text{C-P}} = 3.6$ Hz), 144.9 (d, $^2J_{\text{C-P}} = 7.2$ Hz), 149.6 (td, $^2J_{\text{C-F}} = 29.5$ Hz, $^2J_{\text{C-P}} = 7.3$ Hz), 152.1, 155.3; ^{19}F NMR (376 MHz) δ -51.3; ^{31}P NMR (161 MHz) δ 14.9; HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{19}\text{ClF}_2\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]^+$ 432.0550, found 432.0558.

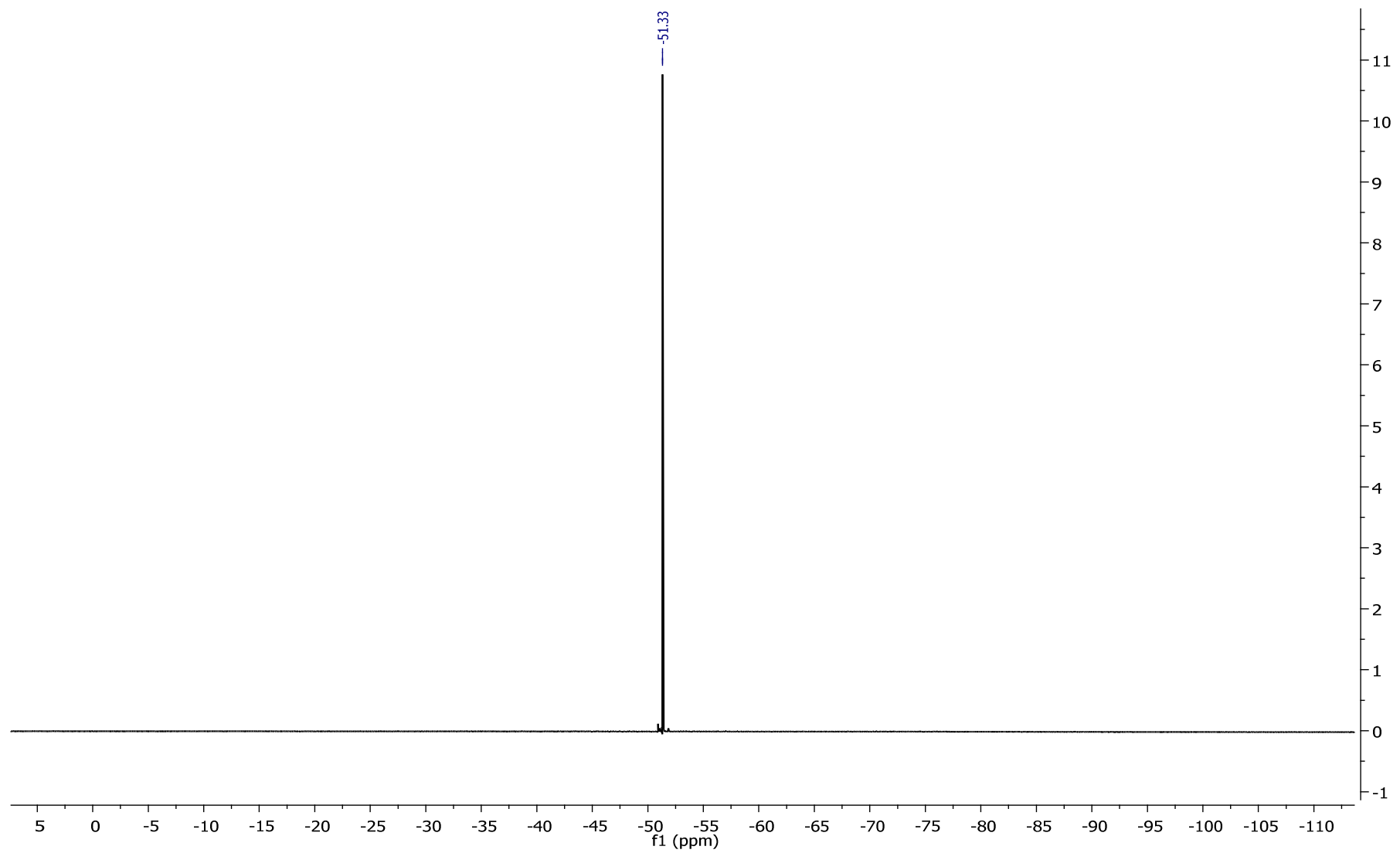
^1H NMR



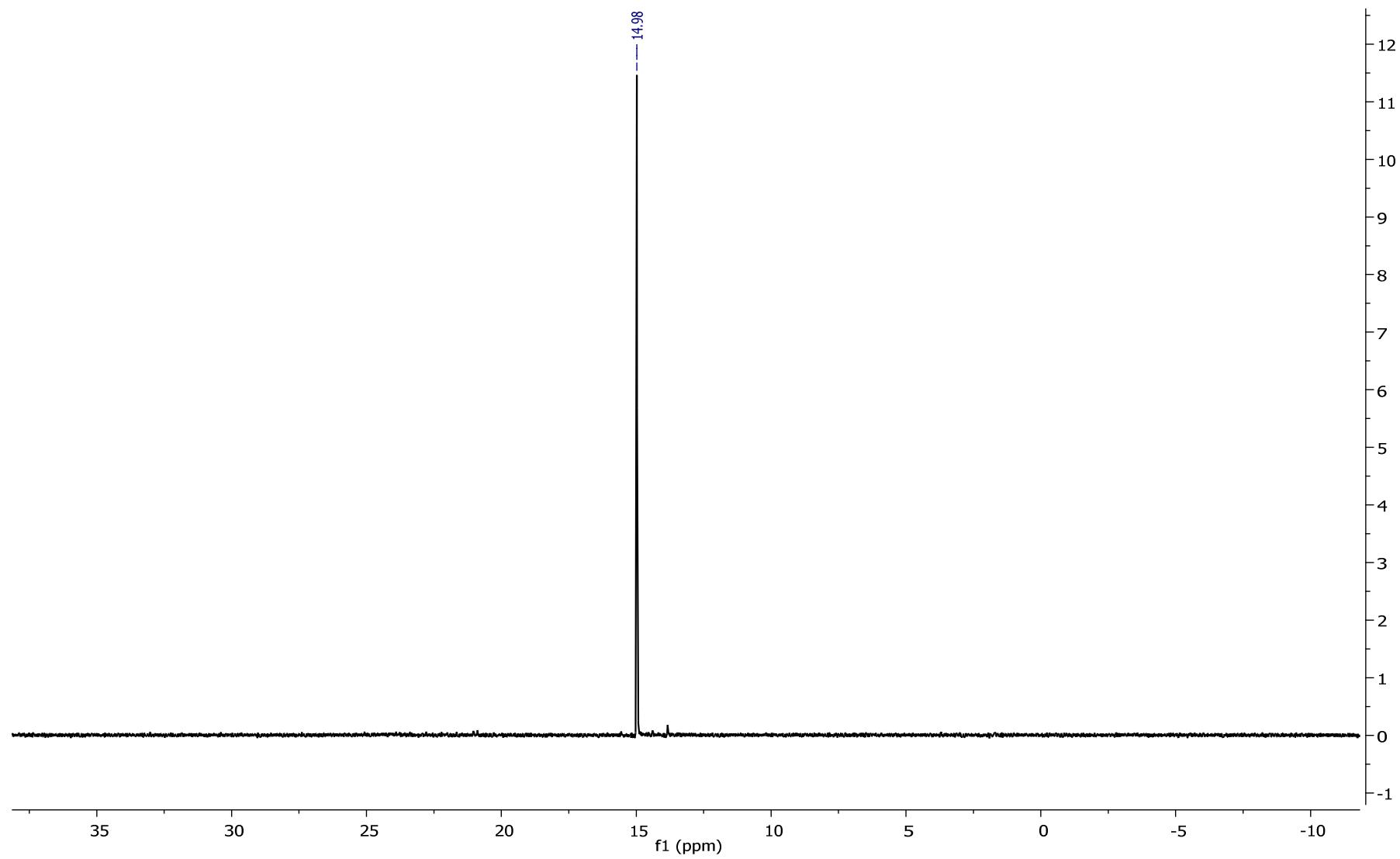
^{13}C NMR



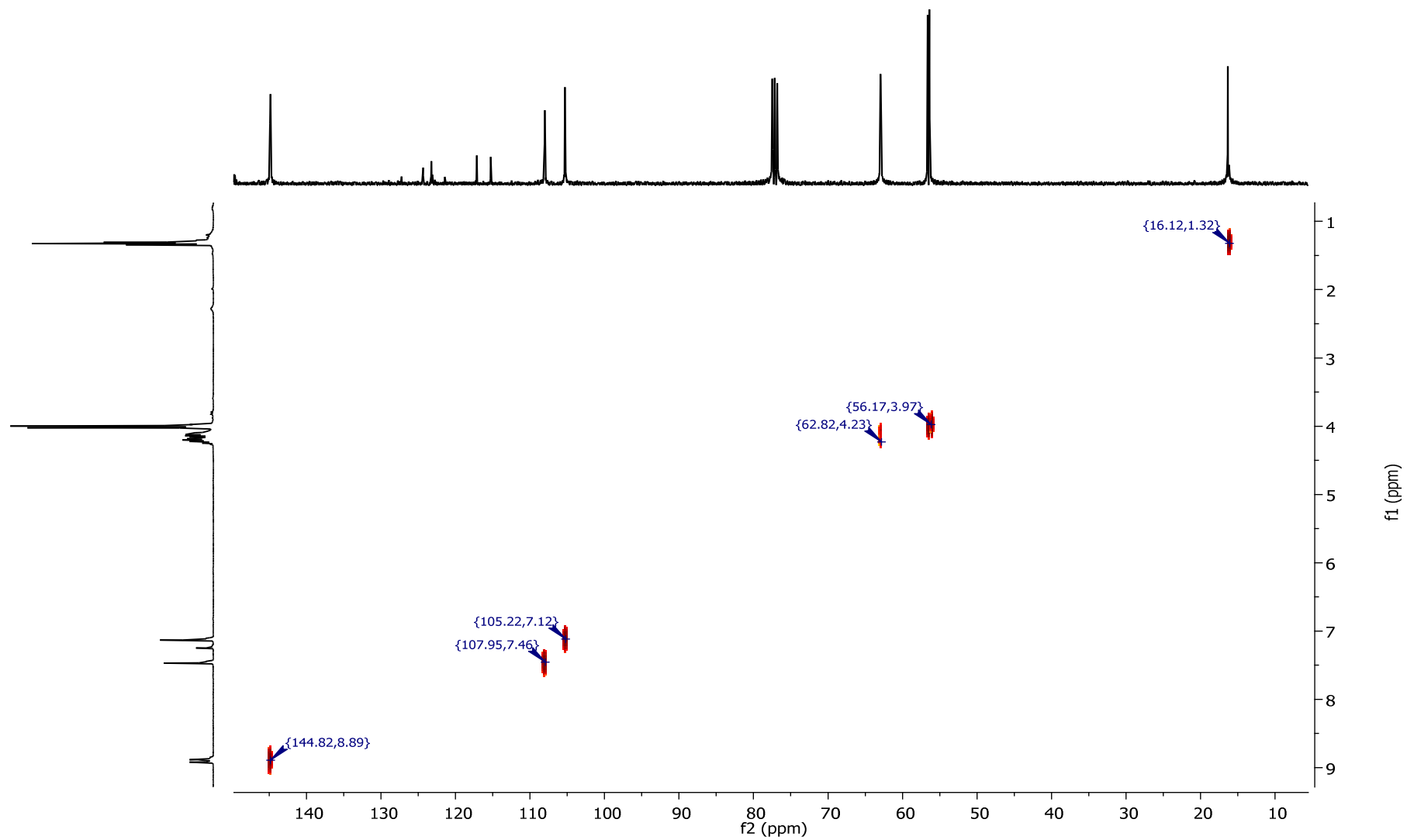
^{19}F NMR



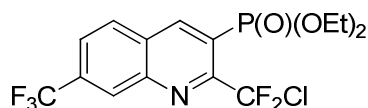
^{31}P NMR



^{13}C - ^1H NMR – HETCOR

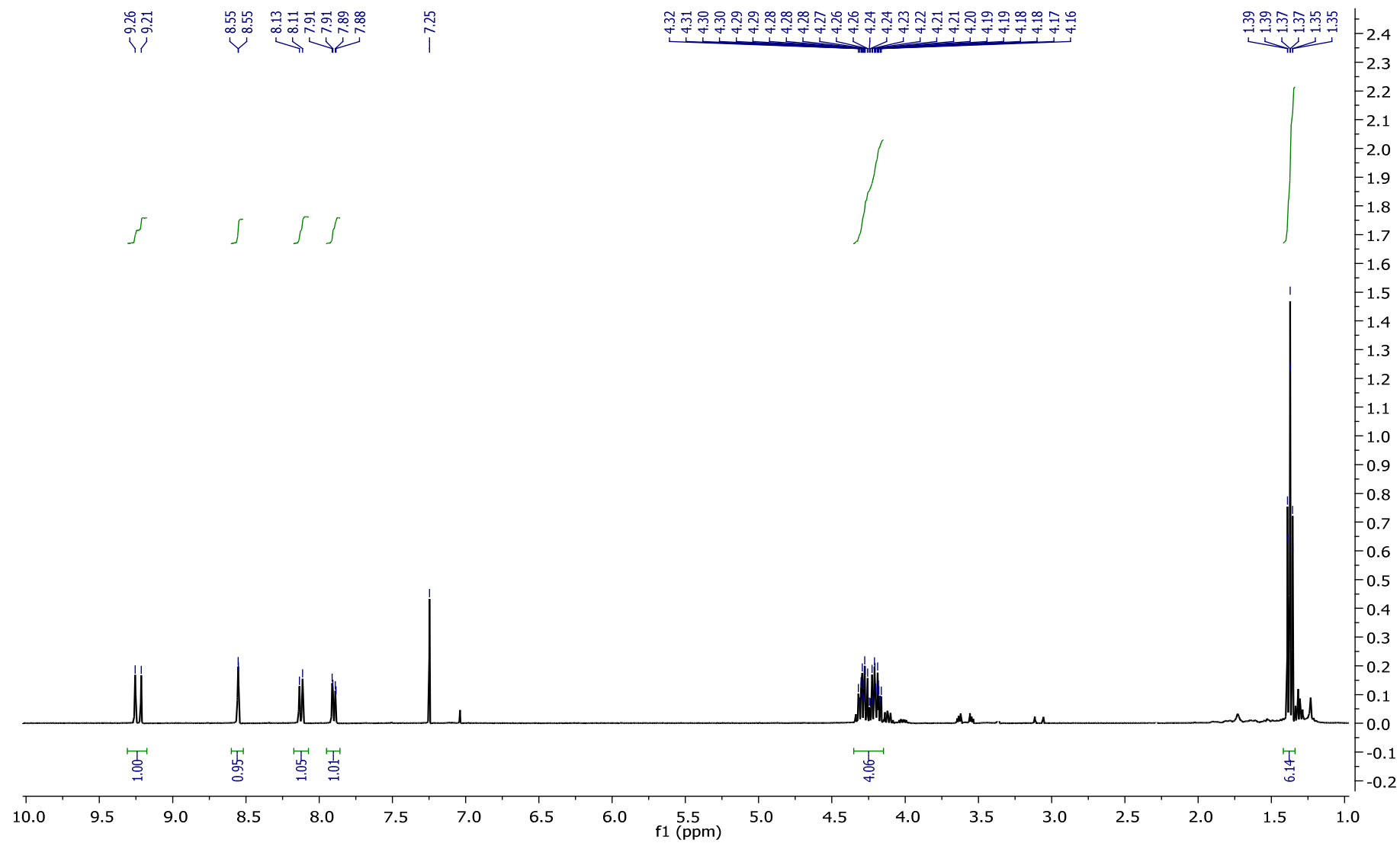


8. Diethyl (2-(chlorodifluoromethyl)-7-(trifluoromethyl)quinolin-3-yl)phosphonate **4h**

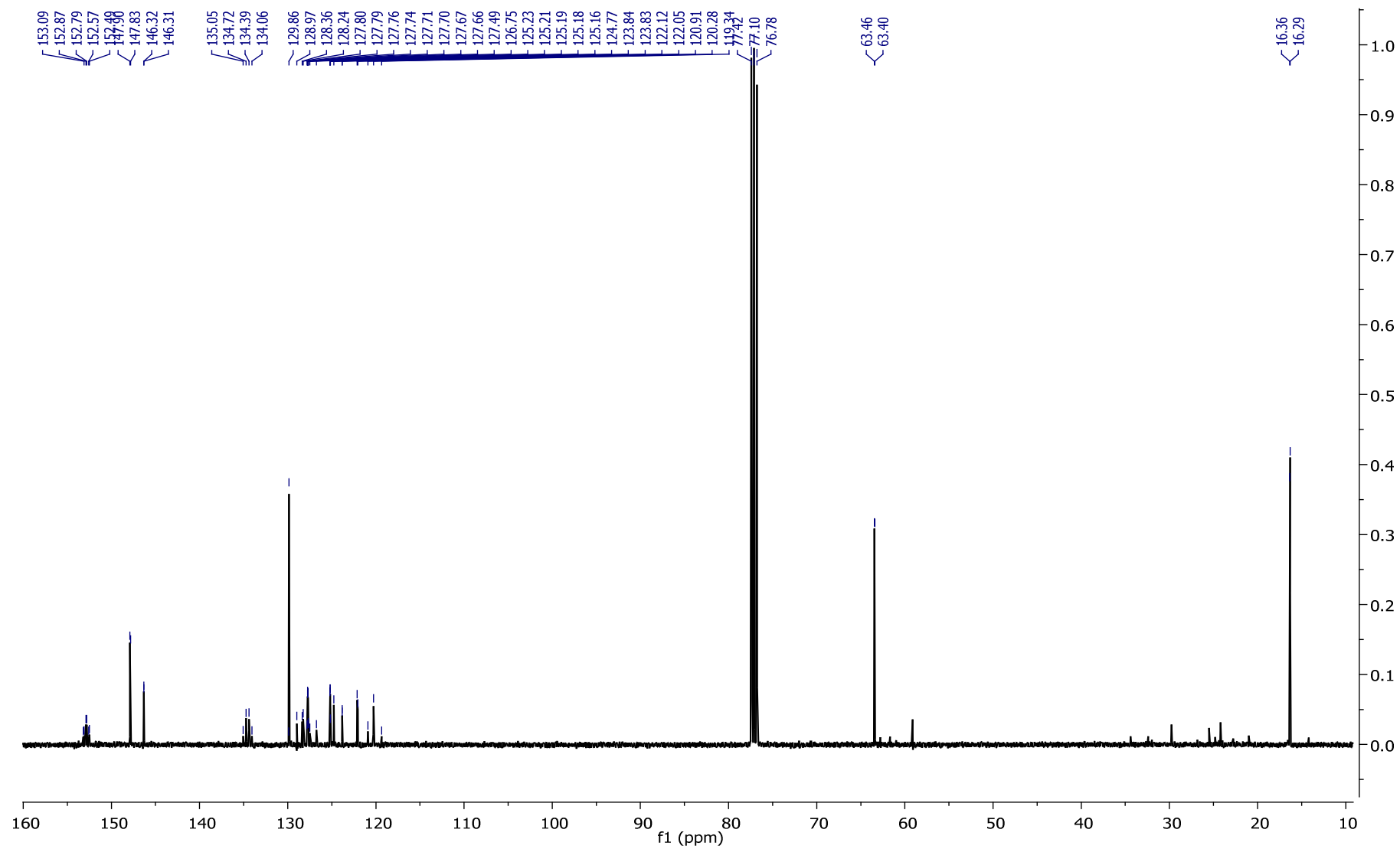


Colourless oil (94%); ^1H NMR (400 MHz, CDCl_3) δ 1.37 (t, $J = 7.1$ Hz, 6H), 4.18 (m, 2H), 4.28 (m, 2H), 7.90 (dd, $J = 8.5$ Hz, $J = 1.6$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 1H), 8.55 (q, $^4J_{\text{H-F}} = 0.9$ Hz, 1H), 9.24 (d, $^3J_{\text{H-P}} = 16.3$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.5$ Hz), 63.4 (d, $J = 6.2$ Hz), 121.2 (d, $^1J_{\text{C-P}} = 184.4$ Hz), 123.4 (q, $^1J_{\text{C-F}} = 274.3$ Hz), 123.8 (td, $^1J_{\text{C-F}} = 293.2$ Hz, $^3J_{\text{C-P}} = 1.1$ Hz), 125.2 (qd, $^4J_{\text{C-F}} = 3.2$ Hz, $^4J_{\text{C-P}} = 1.2$ Hz), 127.7 (qd, $^4J_{\text{C-F}} = 4.3$ Hz, $^4J_{\text{C-P}} = 1.4$ Hz), 128.3 (d, $^3J_{\text{C-P}} = 11.6$ Hz), 129.8, 134.5 (q, $^2J_{\text{C-F}} = 33.4$ Hz), 146.3, 147.8 (d, $^2J_{\text{C-P}} = 6.9$ Hz), 152.8 (td, $^2J_{\text{C-F}} = 30.6$ Hz, $^2J_{\text{C-P}} = 8.2$ Hz); ^{19}F NMR (376 MHz) δ -52.4 (s, - CF_2Cl), -63.0 (s, - CF_3); ^{31}P NMR (161 MHz) δ 12.9; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{ClF}_5\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 440.0212, found 440.0217.

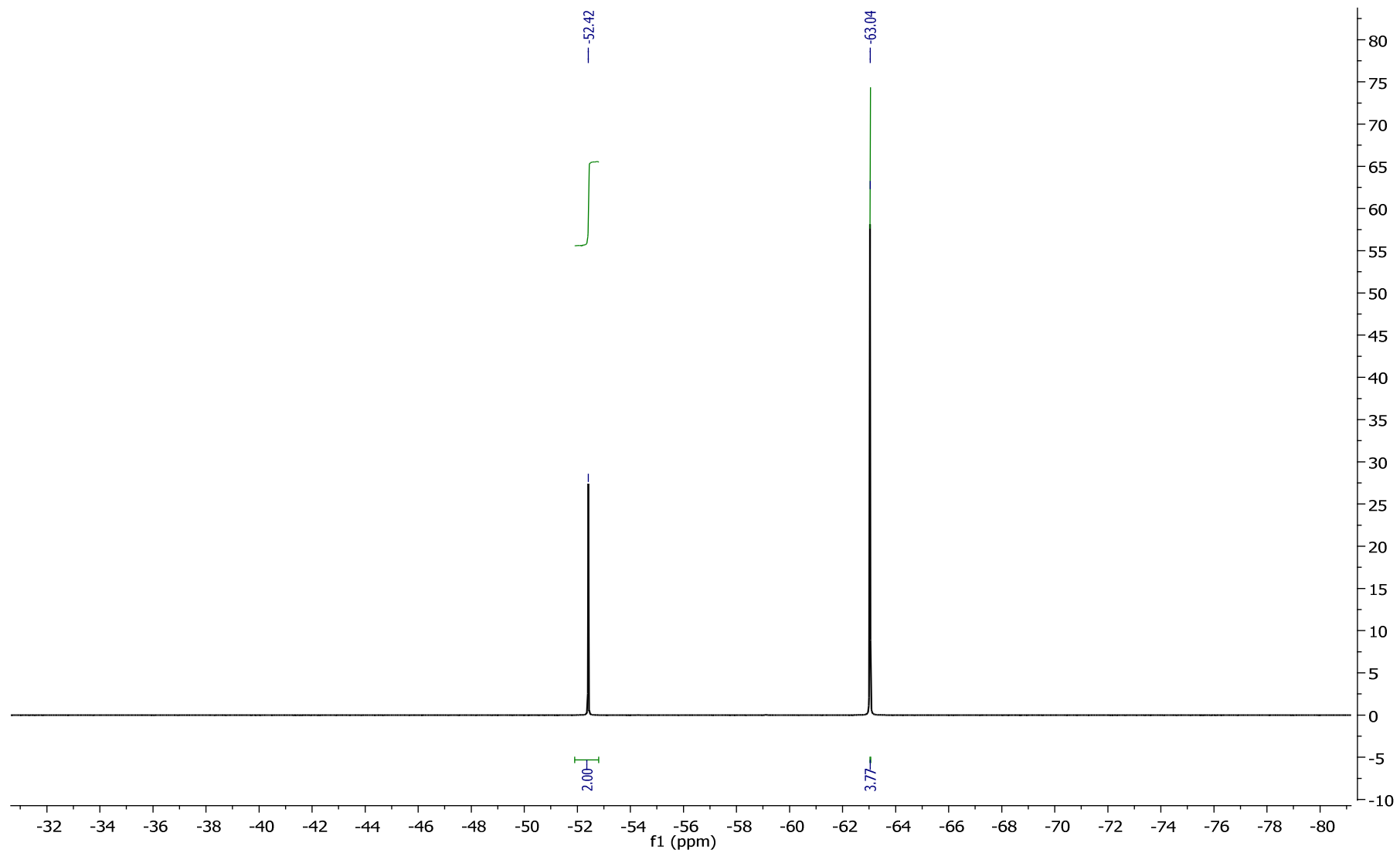
¹H NMR



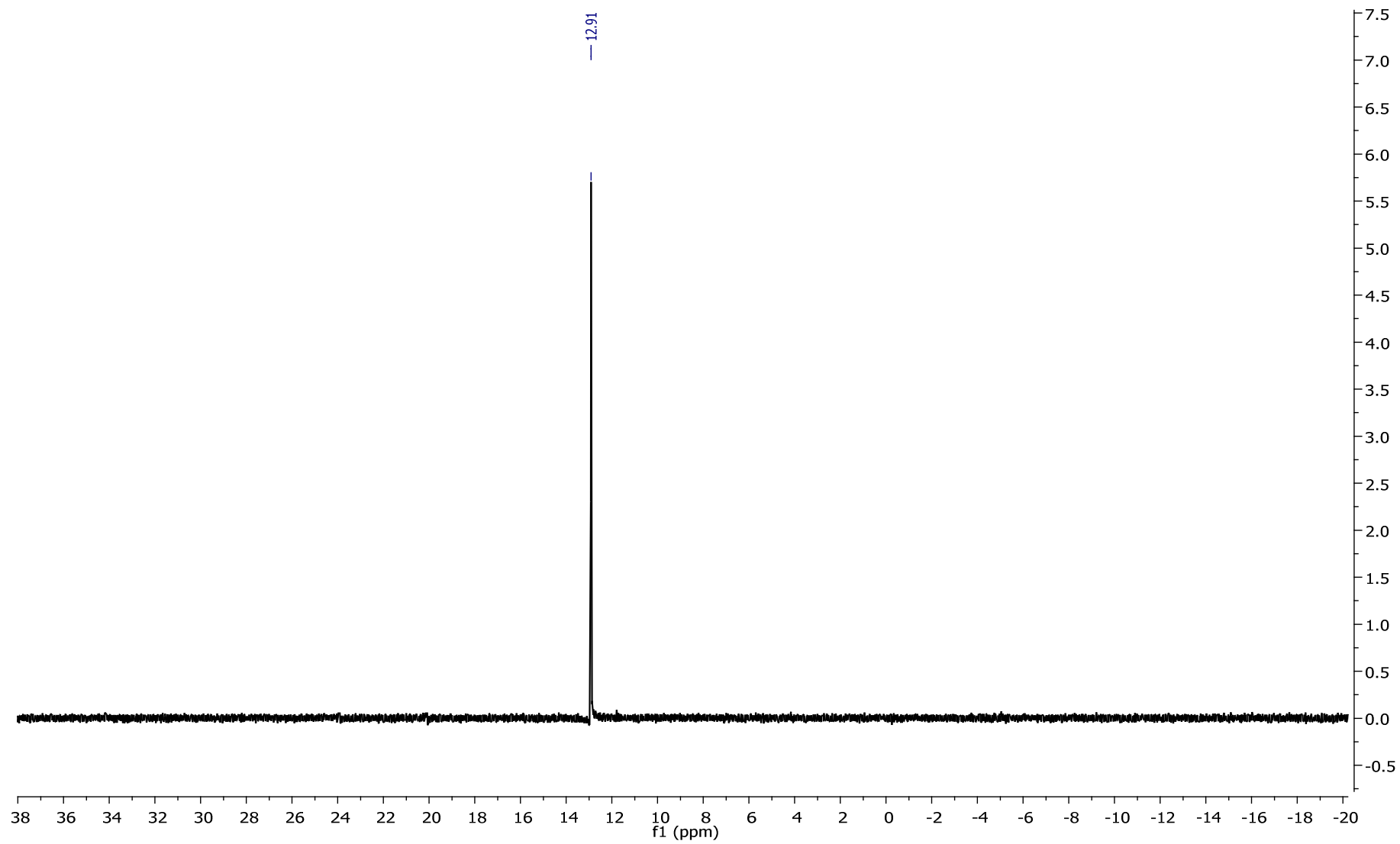
¹³C NMR



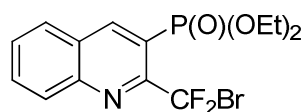
^{19}F NMR



^{31}P NMR

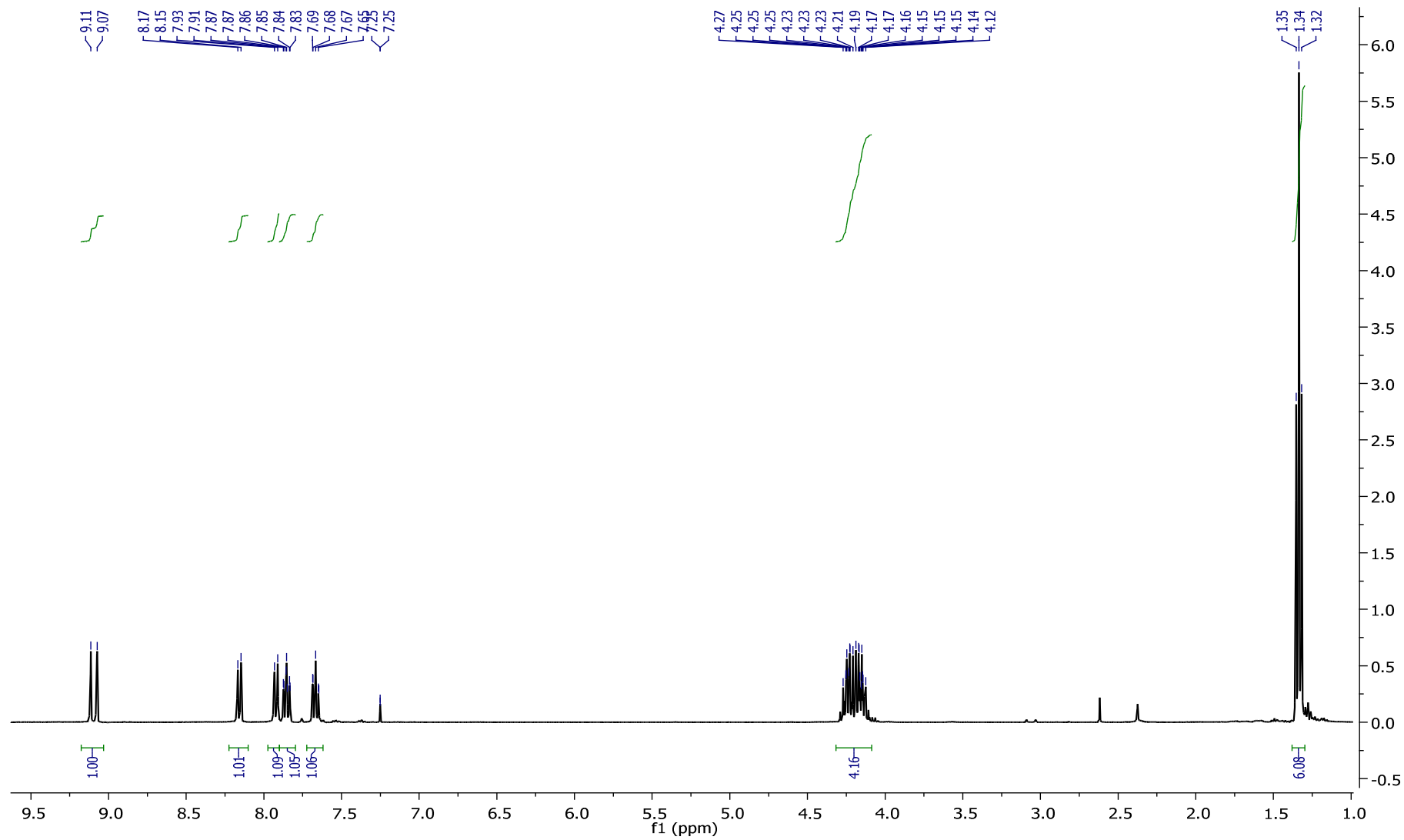


9. Diethyl (2-(bromodifluoromethyl)quinolin-3-yl)phosphonate **4i**

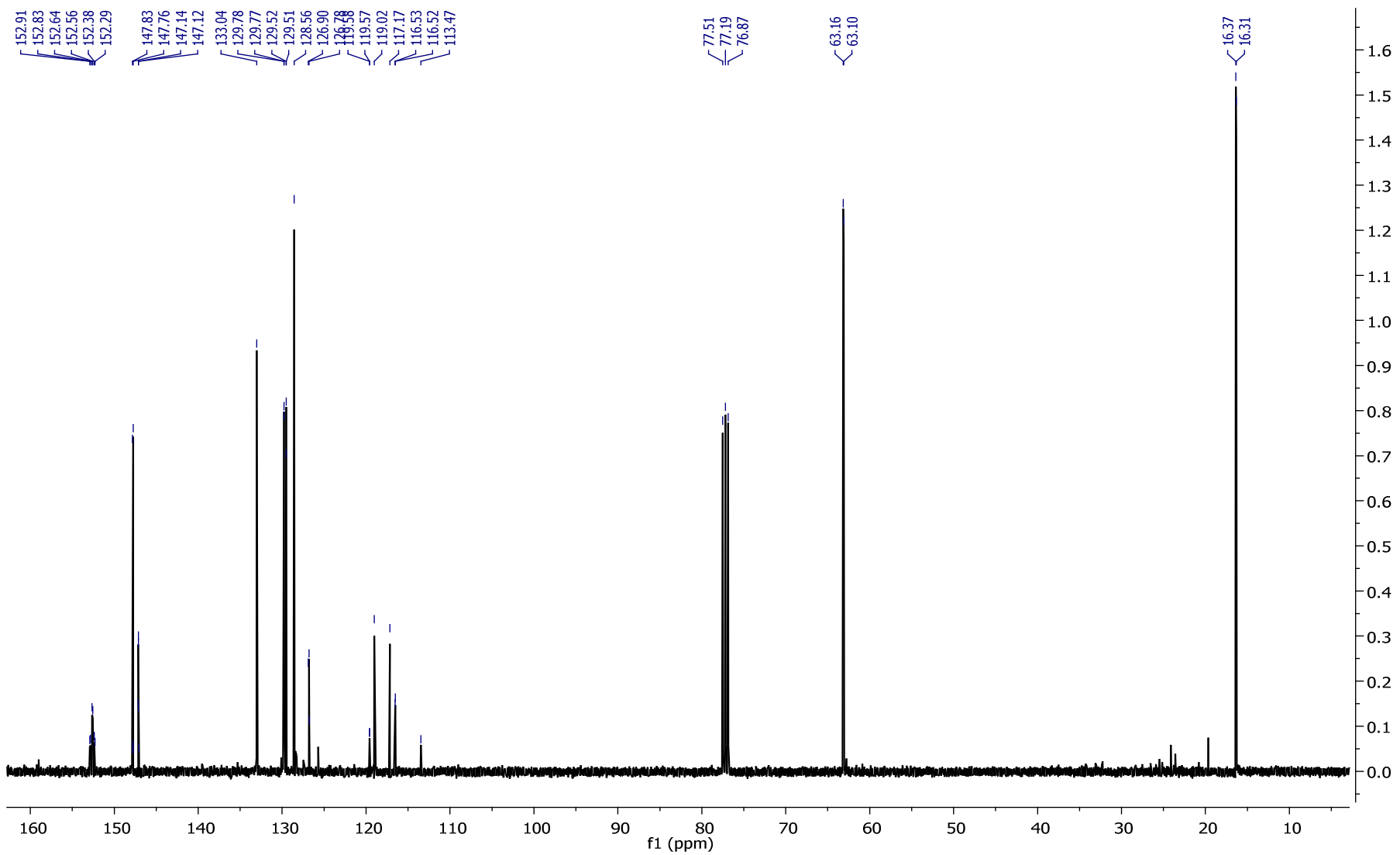


Brownish oil (88%); ^1H NMR (400 MHz, CDCl_3) δ 1.34 (t, $J = 7.2$ Hz, 6H), 4.15 (m, 2H), 4.23 (m, 2H), 7.67 (td, $J = 7.9$ Hz, $J = 0.9$ Hz, 1H), 7.85 (td, $J = 6.9$ Hz, $J = 1.4$ Hz, 1H), 7.92 (d, $J = 8.1$ Hz, 1H), 8.16 (d, $J = 8.3$ Hz, 1H), 9.09 (d, $^3J_{\text{H-P}} = 16.4$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.2$ Hz), 63.1 (d, $J = 6.2$ Hz), 116.5 (td, $^1J_{\text{C-F}} = 306.9$ Hz, $^3J_{\text{C-P}} = 1.4$ Hz), 118.5 (d, $^1J_{\text{C-P}} = 186.2$ Hz), 126.8 (d, $^3J_{\text{C-P}} = 11.5$ Hz), 128.5, 129.5 (d, $^5J_{\text{C-P}} = 1.0$ Hz), 129.8 (d, $^4J_{\text{C-P}} = 1.5$ Hz), 133.0, 147.2 (dt, $^4J_{\text{C-P}} = 1.4$ Hz, $^4J_{\text{C-F}} = 0.9$ Hz), 147.8 (d, $^2J_{\text{C-P}} = 6.7$ Hz), 152.5 (td, $^2J_{\text{C-F}} = 26.8$ Hz, $^2J_{\text{C-P}} = 8.3$ Hz); ^{19}F NMR (376 MHz) δ -47.5; ^{31}P NMR (161 MHz) δ 14.0 (t, $^4J_{\text{P-F}} = 0.9$ Hz); HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{16}\text{BrF}_2\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 394.0014, found 394.0017.

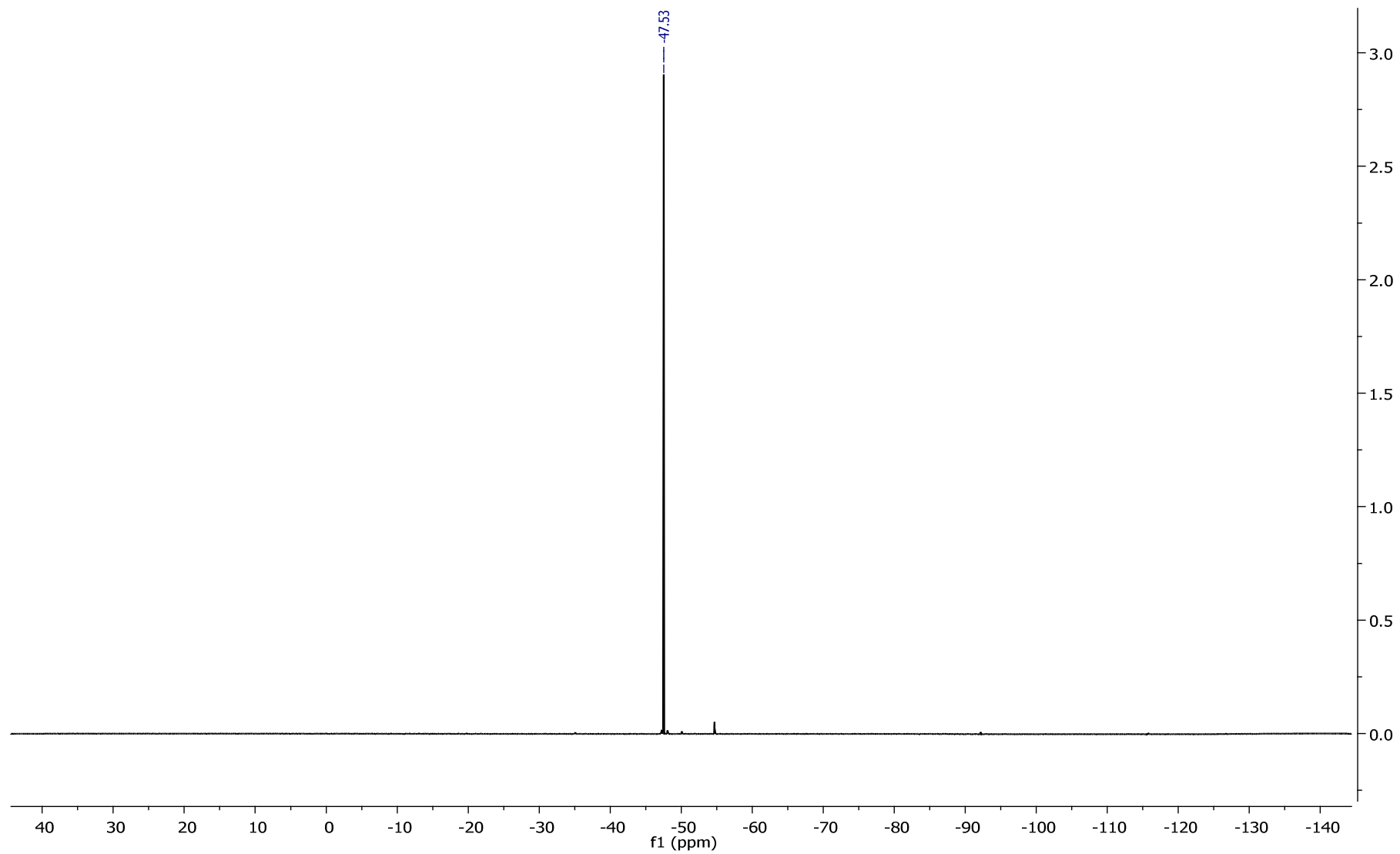
¹H NMR



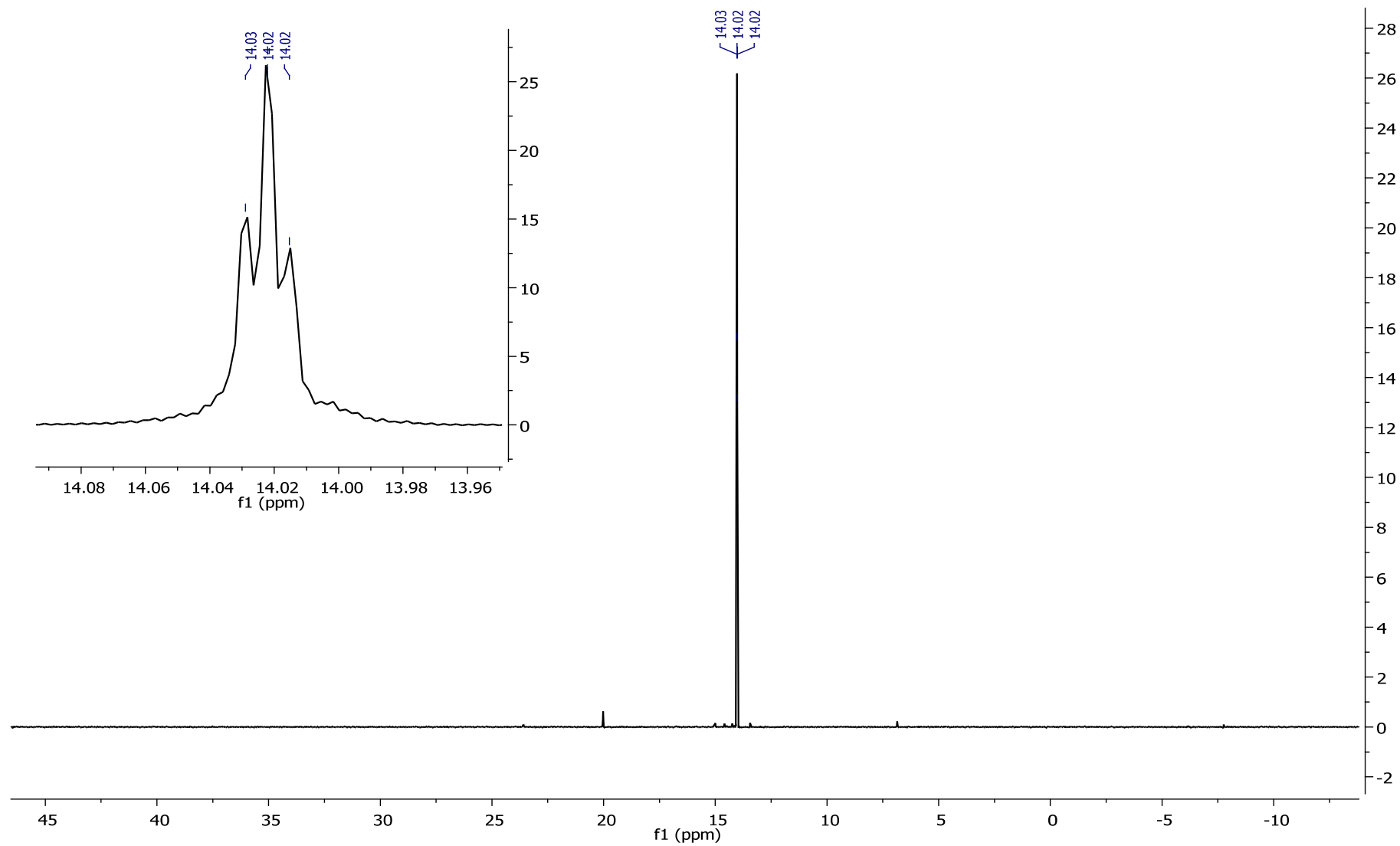
^{13}C NMR



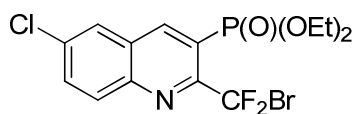
^{19}F NMR



^{31}P NMR

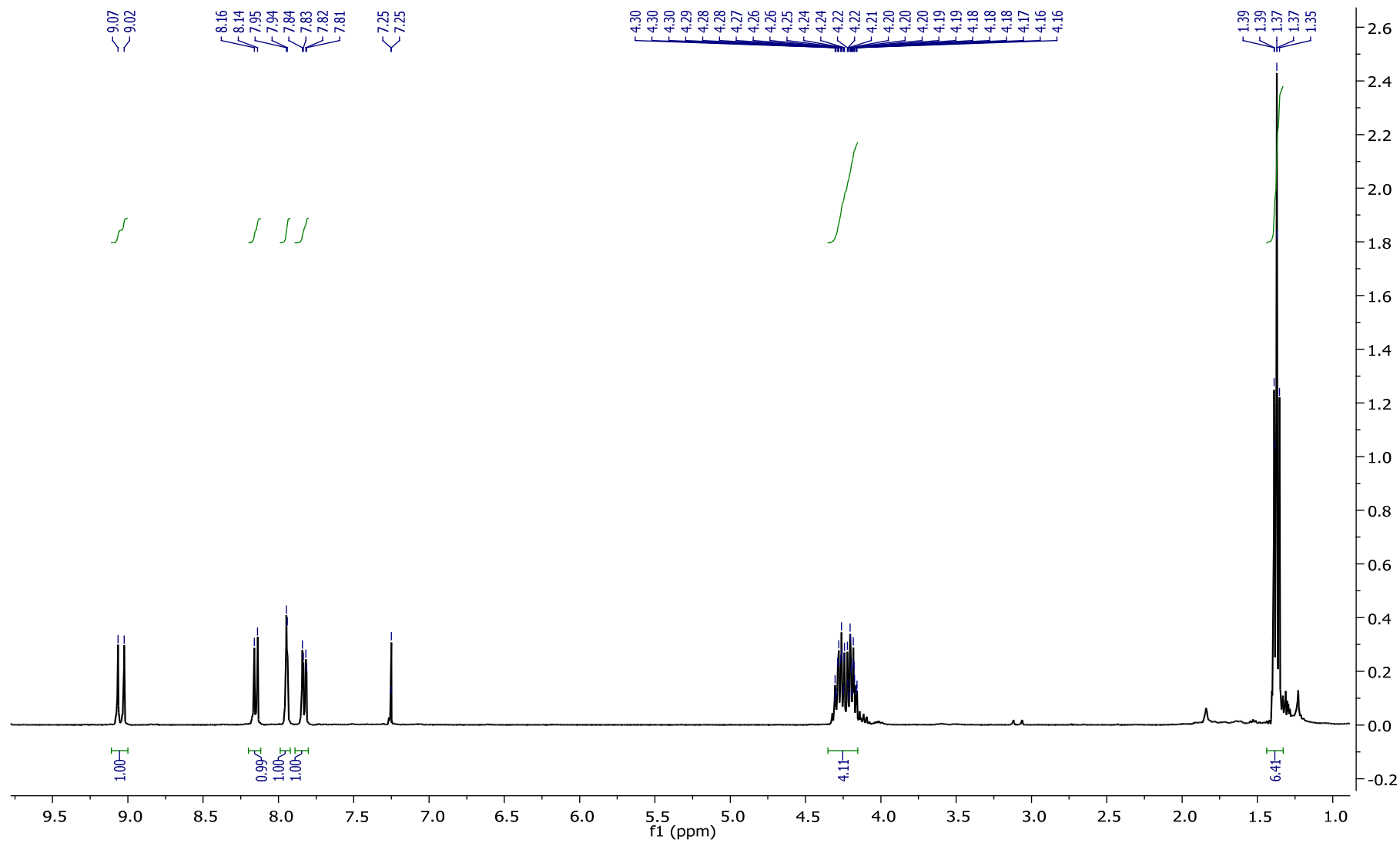


10. Diethyl (2-(bromodifluoromethyl)-6-chloroquinolin-3-yl)phosphonate **4j**

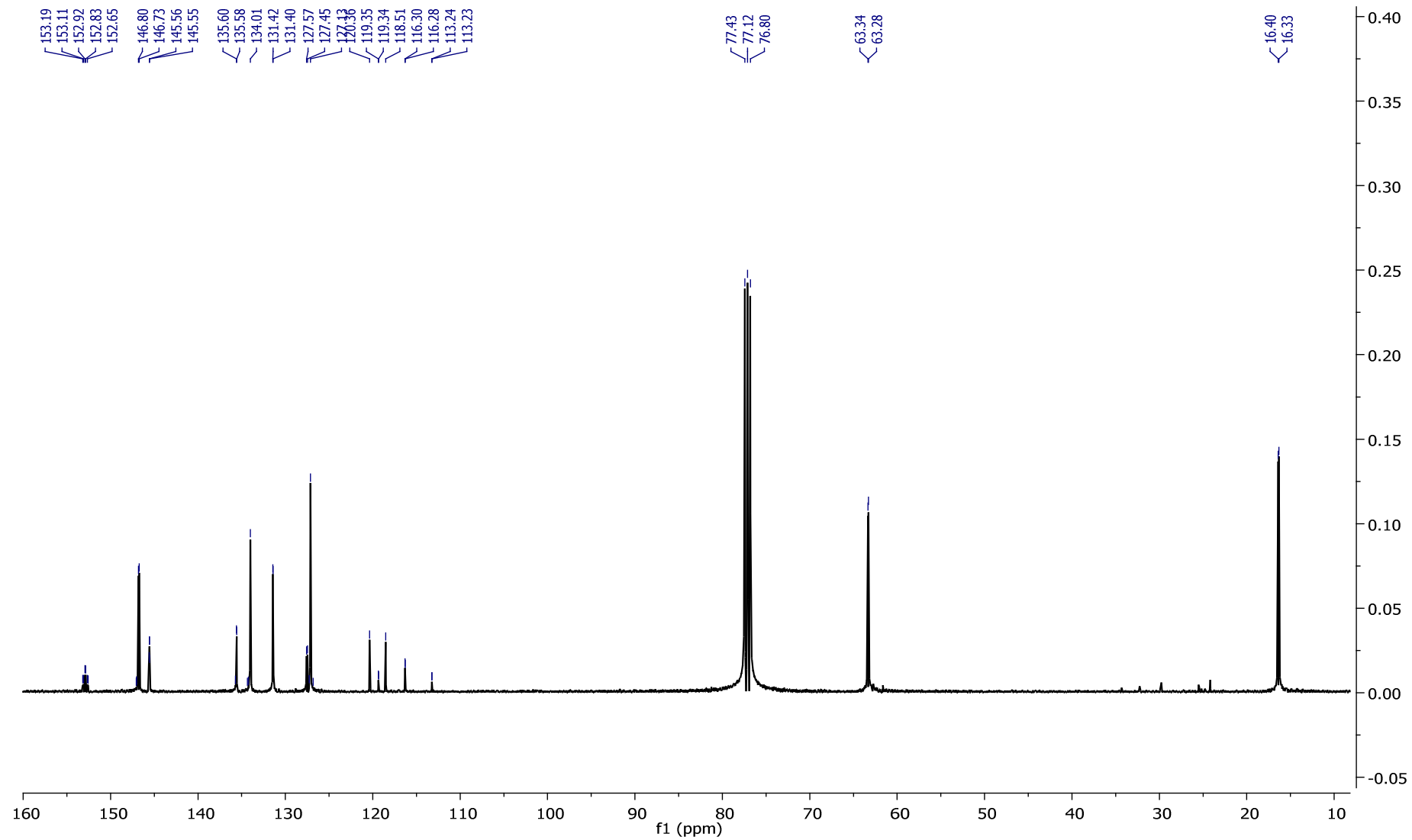


Orange crystals (80%); Mp = 118–121 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.37 (t, $J = 7.0$ Hz, 6H), 4.17 (m, 2H), 4.26 (m, 2H), 7.82 (dd, $J = 8.9$ Hz, $J = 2.2$ Hz, 1H), 7.94 (d, $J = 2.2$ Hz, 1H), 8.15 (d, $J = 9.0$ Hz, 1H), 9.04 (d, $^3J_{\text{H-P}} = 16.3$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.4 (d, $J = 6.6$ Hz), 63.3 (d, $J = 6.2$ Hz), 116.3 (td, $^1J_{\text{C-F}} = 308.9$ Hz, $^3J_{\text{C-P}} = 0.9$ Hz), 119.8 (d, $^1J_{\text{C-P}} = 185.6$ Hz), 127.1, 127.5 (d, $^3J_{\text{C-P}} = 11.9$ Hz), 131.4 (d, $^4J_{\text{C-P}} = 1.9$ Hz), 134.0, 135.6 (d, $^5J_{\text{C-P}} = 1.7$ Hz), 145.5, 146.8 (d, $^2J_{\text{C-P}} = 7.3$ Hz), 152.9 (td, $^2J_{\text{C-F}} = 27.4$ Hz, $^2J_{\text{C-P}} = 8.7$ Hz); ^{19}F NMR (376 MHz) δ -47.8; ^{31}P NMR (161 MHz) δ 13.3; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{14}\text{BrClF}_2\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 449.9443, found 449.9442.

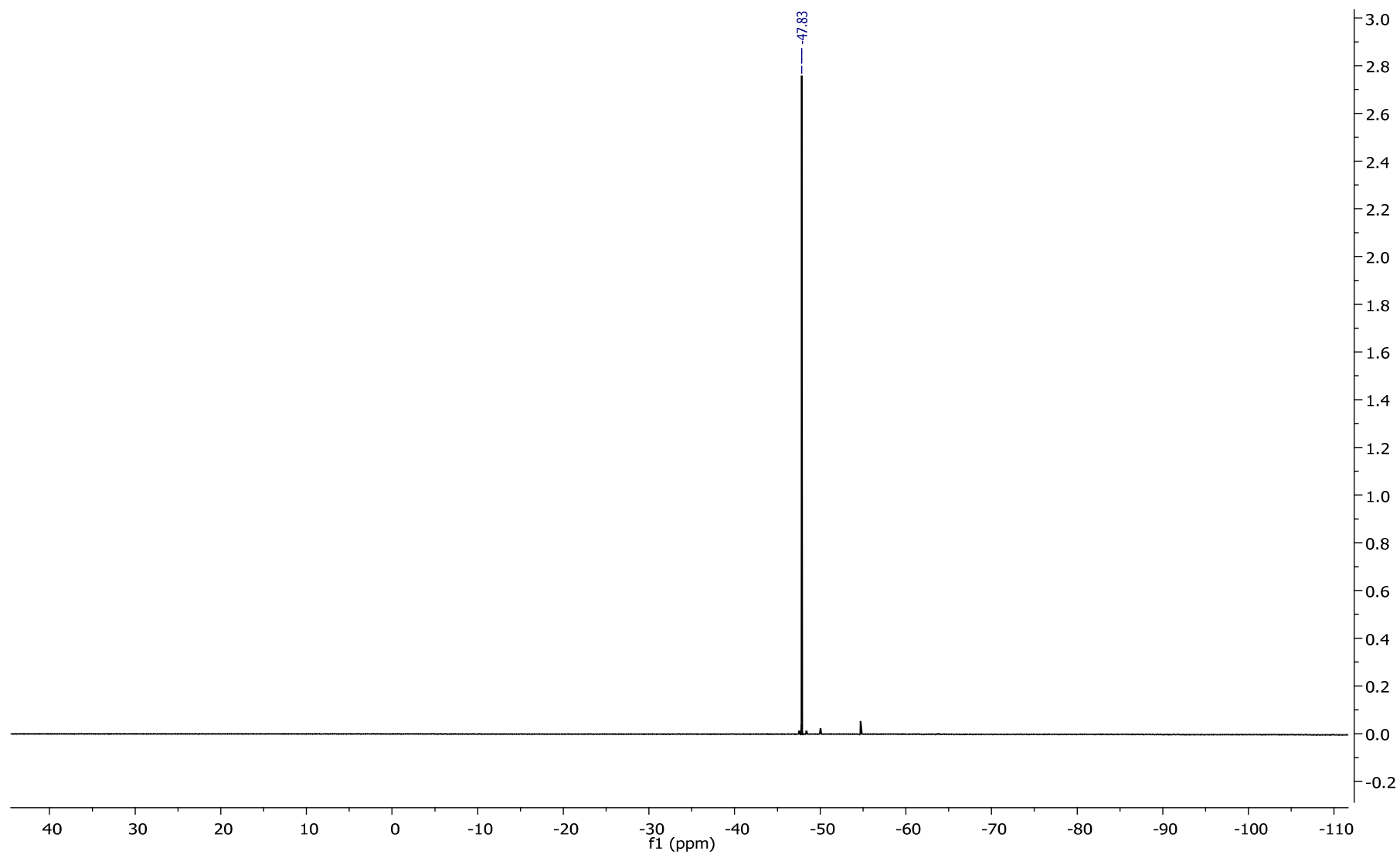
¹H NMR



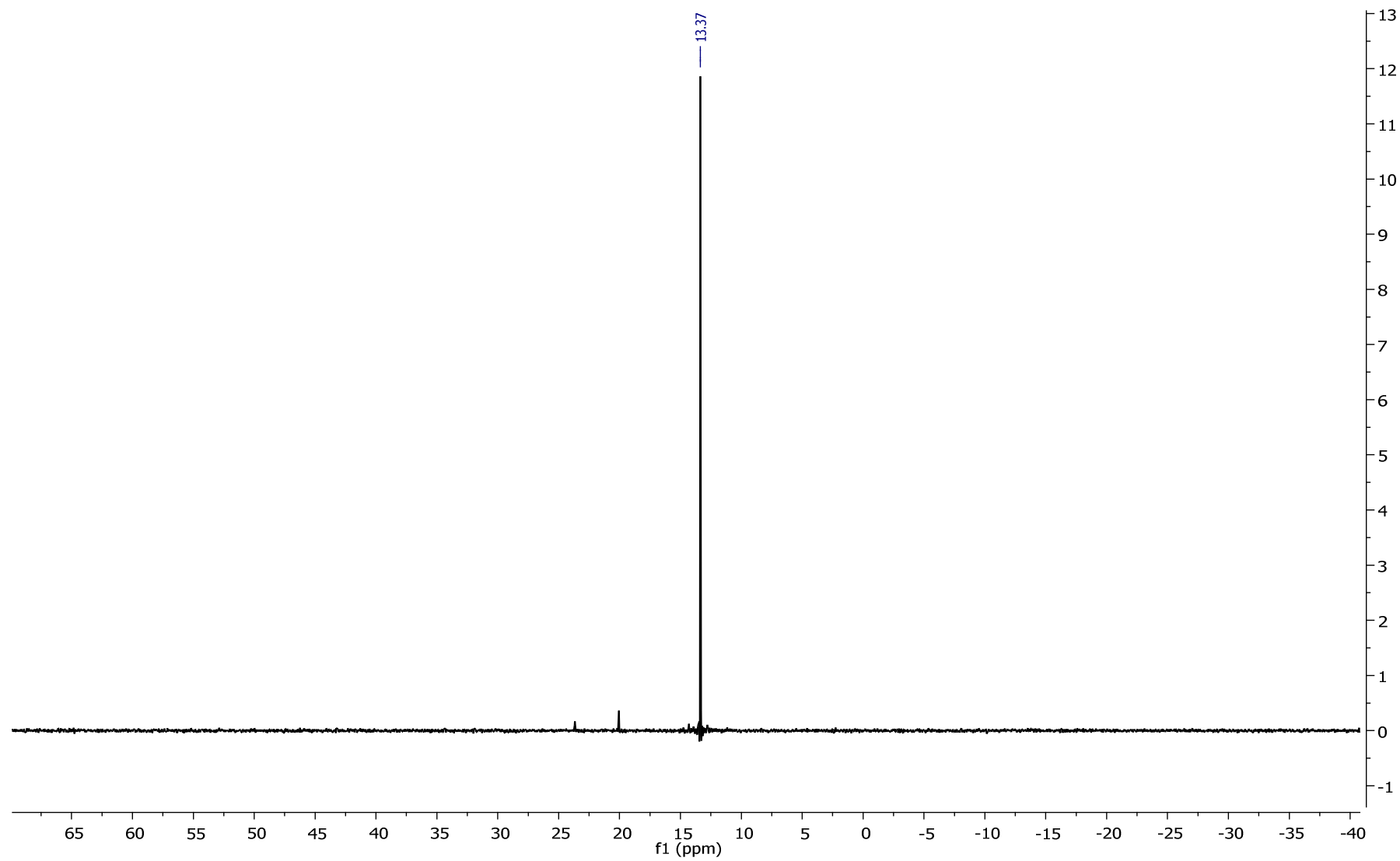
^{13}C NMR



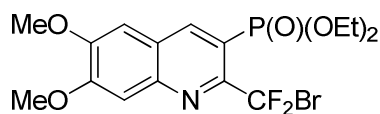
^{19}F NMR



^{31}P NMR

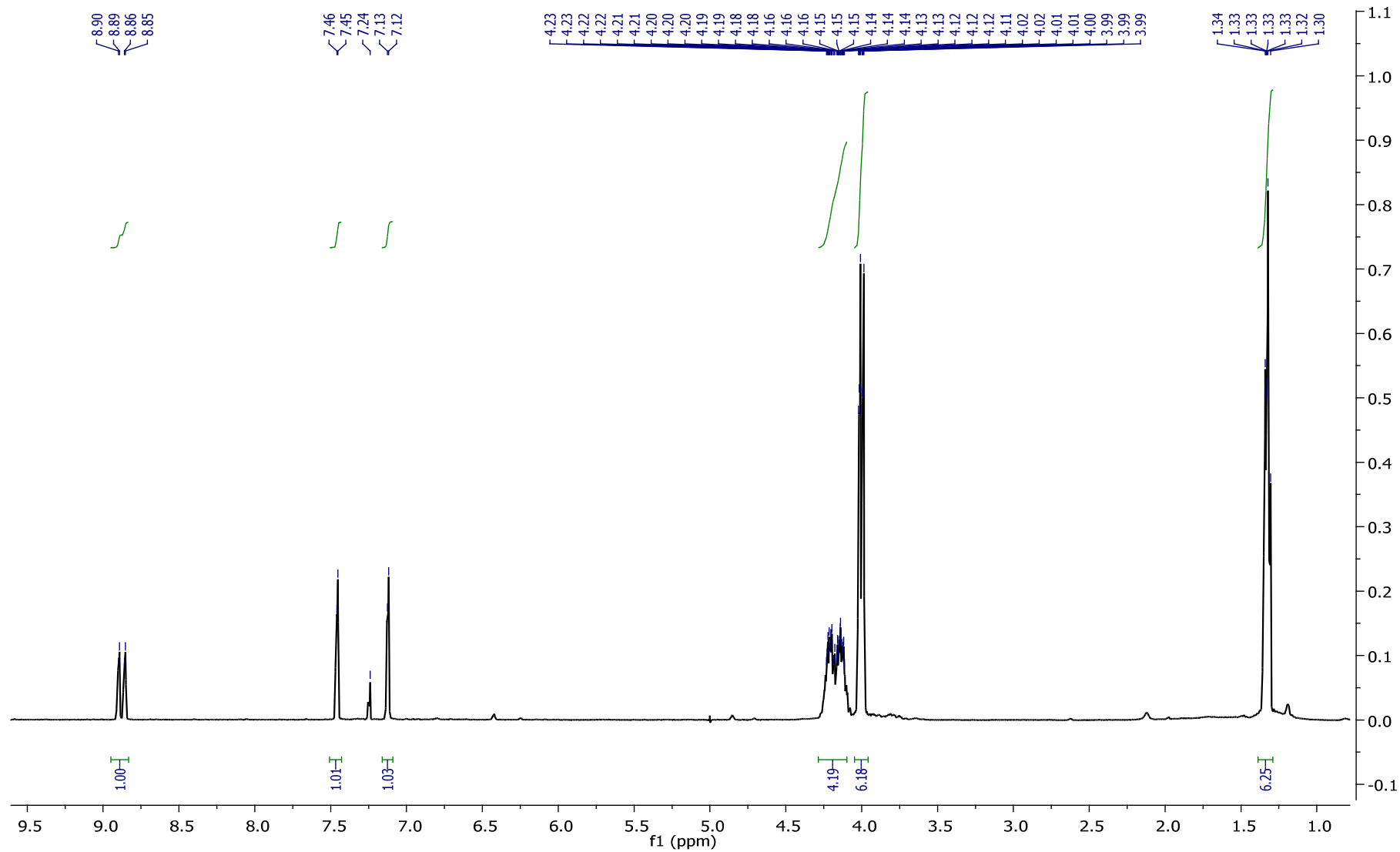


11. Diethyl (2-(bromodifluoromethyl)-6,7-dimethoxyquinolin-3-yl)phosphonate **4k**

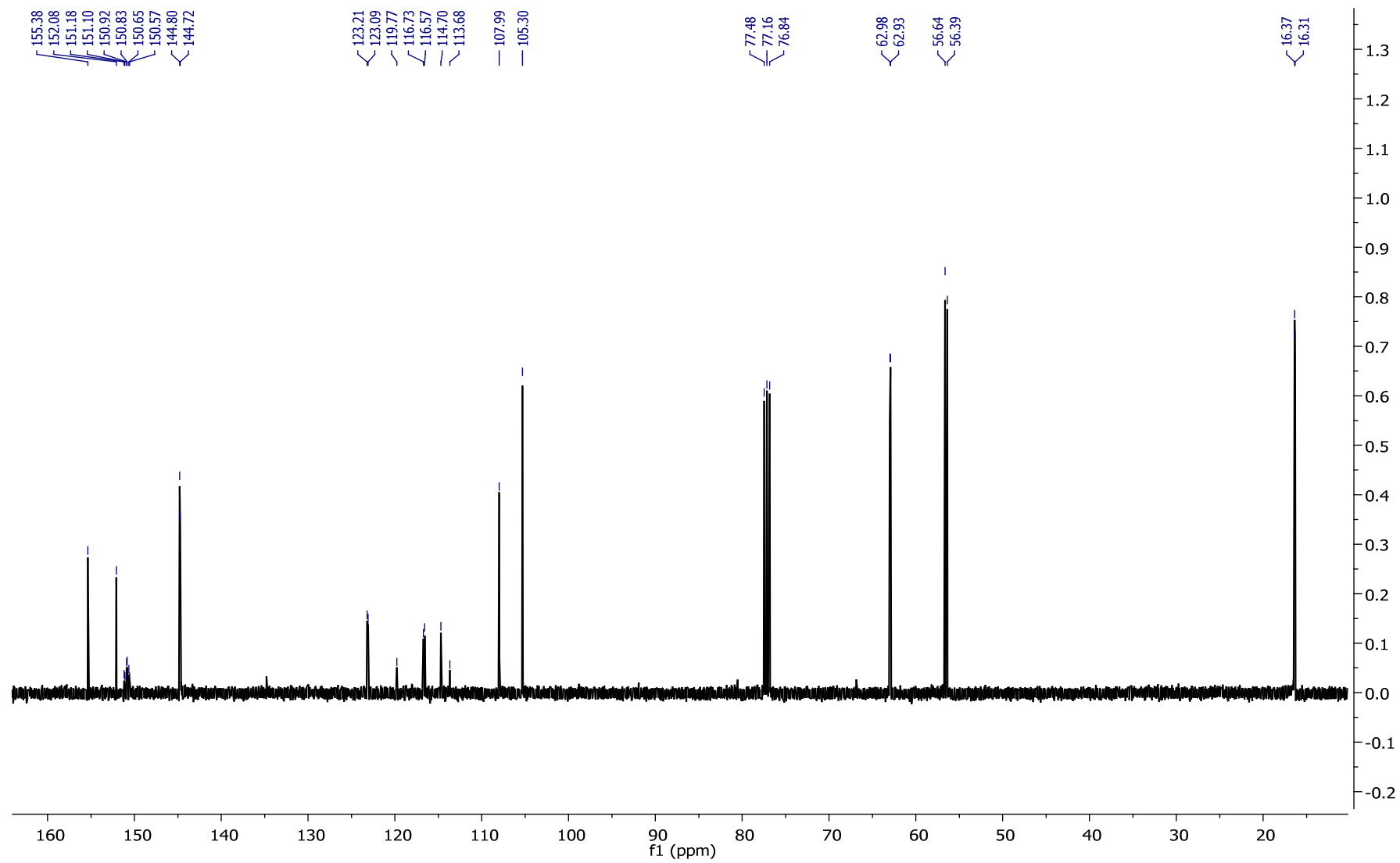


Yellow crystals (71%); Mp = 155–160 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.32 (t, $J = 7.1$ Hz, 6H), 3.99 (s, 3H), 4.01 (s, 3H), 4.12 (m, 2H), 4.22 (m, 2H), 7.12 (s, 1H), 7.45 (s, 1H), 8.87 (d, $^3J_{\text{H-P}} = 16.0$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.6$ Hz), 56.4, 56.6, 62.9 (d, $J = 6.0$ Hz), 105.3, 107.9, 115.9 (d, $^1J_{\text{C-P}} = 187.7$ Hz), 116.9 (t, $^1J_{\text{C-F}} = 306.3$ Hz), 123.1 (d, $^3J_{\text{C-P}} = 10.7$ Hz), 144.8 (d, $^2J_{\text{C-P}} = 7.8$ Hz), 150.9 (td, $^2J_{\text{C-F}} = 26.5$ Hz, $^2J_{\text{C-P}} = 8.6$ Hz), 152.1, 155.4; ^{19}F NMR (376 MHz) δ -46.8; ^{31}P NMR (161 MHz) δ 15.0; HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{20}\text{BrF}_2\text{NO}_5\text{P}$ $[\text{M}+\text{H}]^+$ 454.0225, found 454.0221.

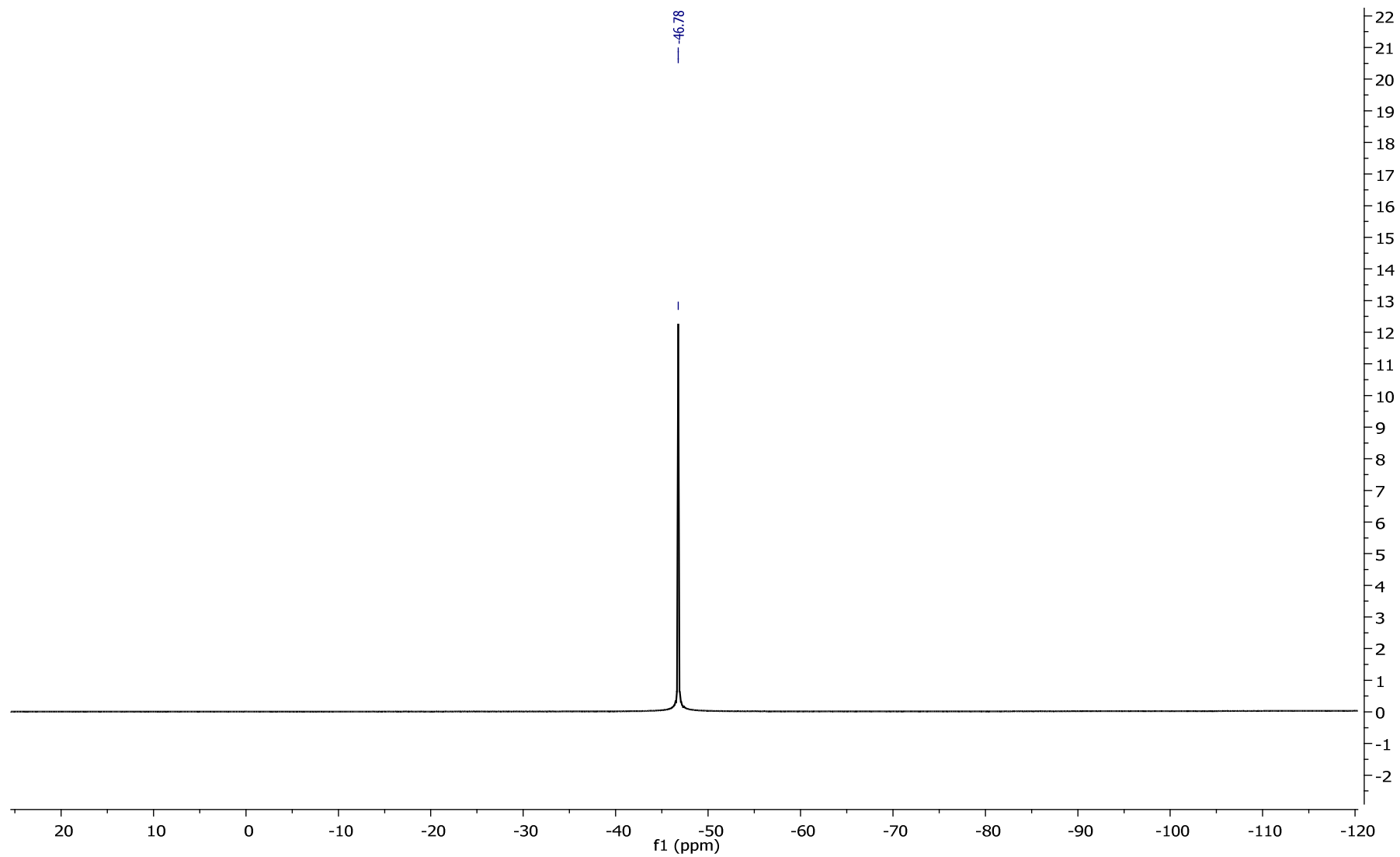
^1H NMR



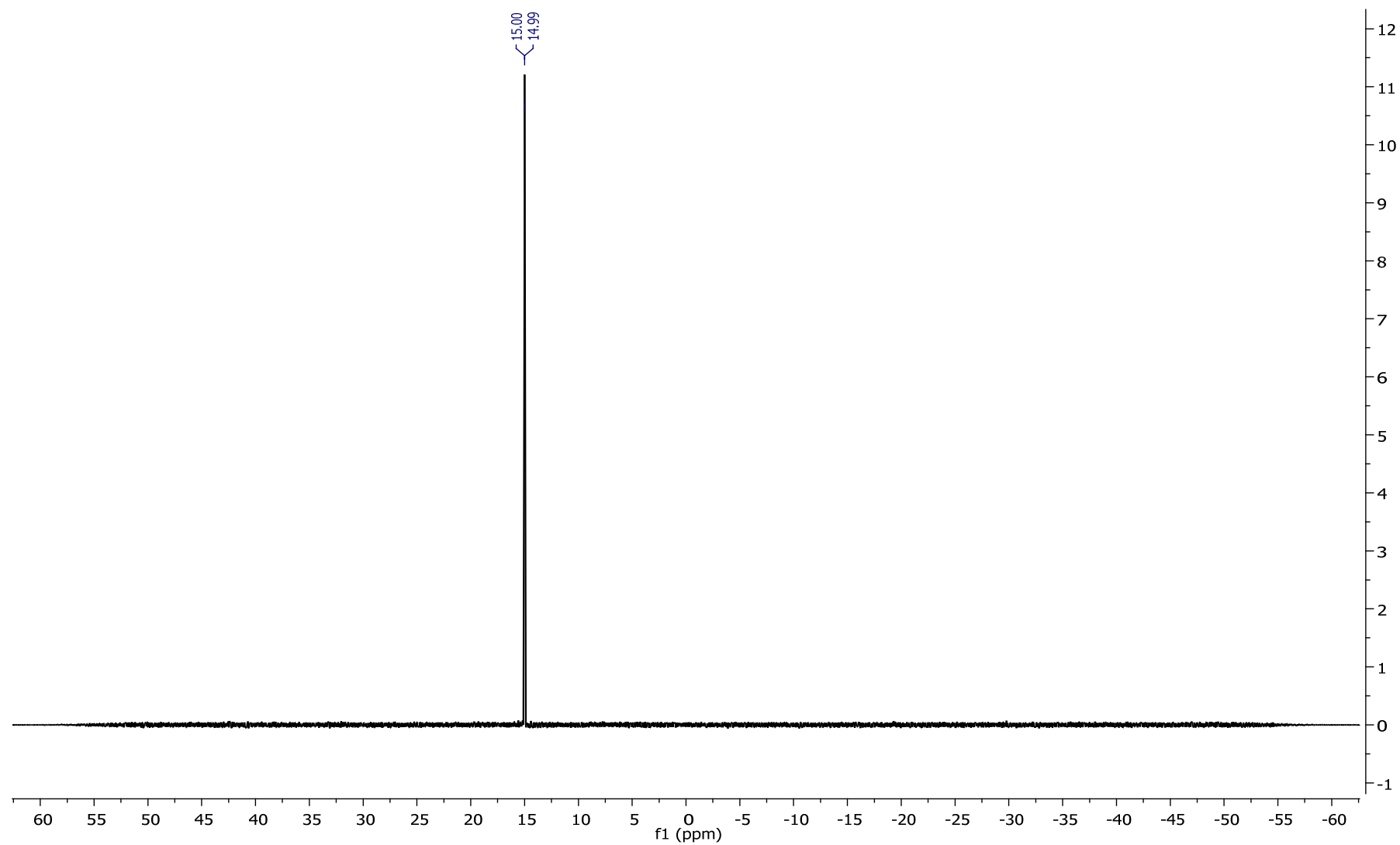
^{13}C NMR



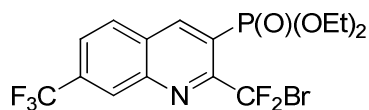
^{19}F NMR



^{31}P NMR

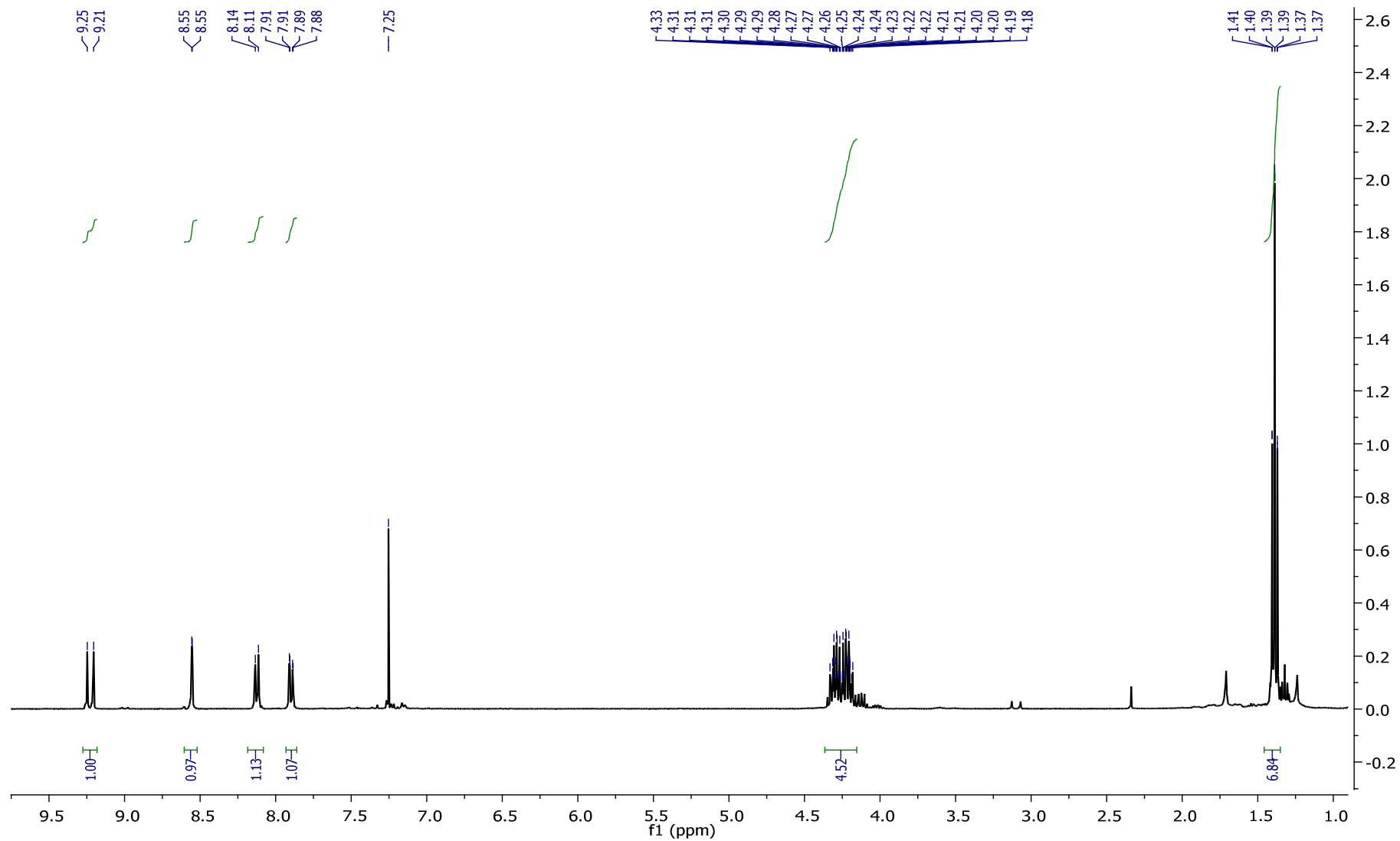


12. Diethyl (2-(bromodifluoromethyl)-7-(trifluoromethyl)quinolin-3-yl)phosphonate **41**

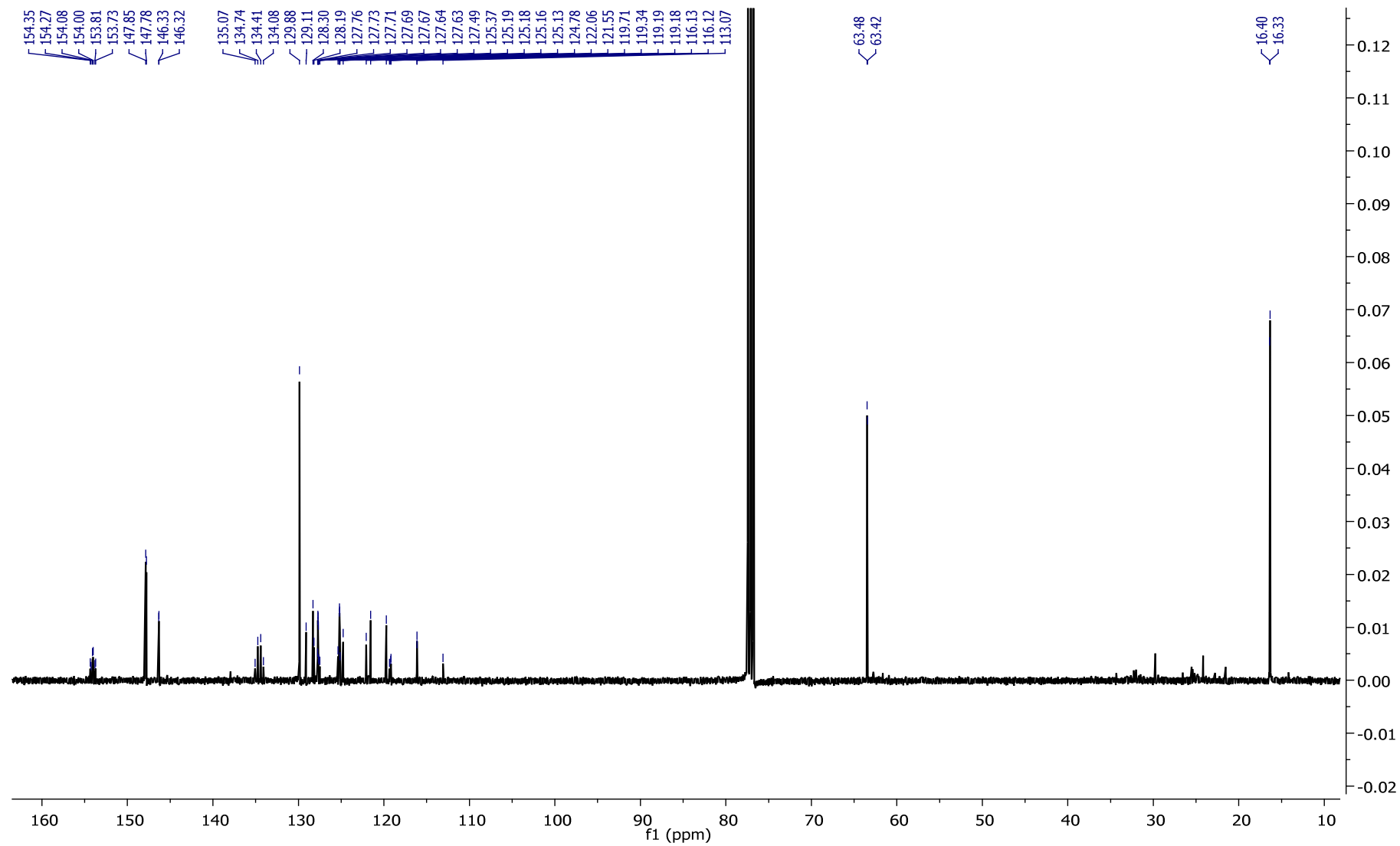


Brownish oil (93%); ^1H NMR (400 MHz, CDCl_3) δ 1.39 (t, $J = 7.0$ Hz, 6H), 4.20 (m, 2H), 4.30 (m, 2H), 7.90 (dd, $J = 8.3$ Hz, $J = 1.9$ Hz, 1H), 8.13 (d, $J = 8.6$ Hz, 1H), 8.55 (q, $^4J_{\text{H-F}} = 0.7$ Hz, 1H), 9.23 (d, $^3J_{\text{H-P}} = 16.3$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.2$ Hz), 63.4 (d, $J = 5.9$ Hz), 116.1 (t, $^1J_{\text{C-F}} = 305.9$ Hz), 120.8 (d, $^1J_{\text{C-P}} = 183.6$ Hz), 123.6 (q, $^1J_{\text{C-F}} = 275.7$ Hz), 125.1 (qd, $^4J_{\text{C-F}} = 2.8$ Hz, $^4J_{\text{C-P}} = 1.3$ Hz), 127.7 (qd, $^4J_{\text{C-F}} = 4.3$ Hz, $^4J_{\text{C-P}} = 1.3$ Hz), 128.2 (d, $^3J_{\text{C-P}} = 10.7$ Hz), 129.8, 134.6 (q, $^2J_{\text{C-F}} = 32.9$ Hz), 146.3, 147.8 (d, $^2J_{\text{C-P}} = 6.5$ Hz), 154.0 (td, $^2J_{\text{C-F}} = 27.6$ Hz, $^2J_{\text{C-P}} = 8.7$ Hz); ^{19}F NMR (376 MHz) δ -48.3 (s, $-\text{CF}_2\text{Br}$), -63.0 (s, $-\text{CF}_3$); ^{31}P NMR (161 MHz) δ 12.9; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{BrF}_5\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 483.9713, found 483.9712.

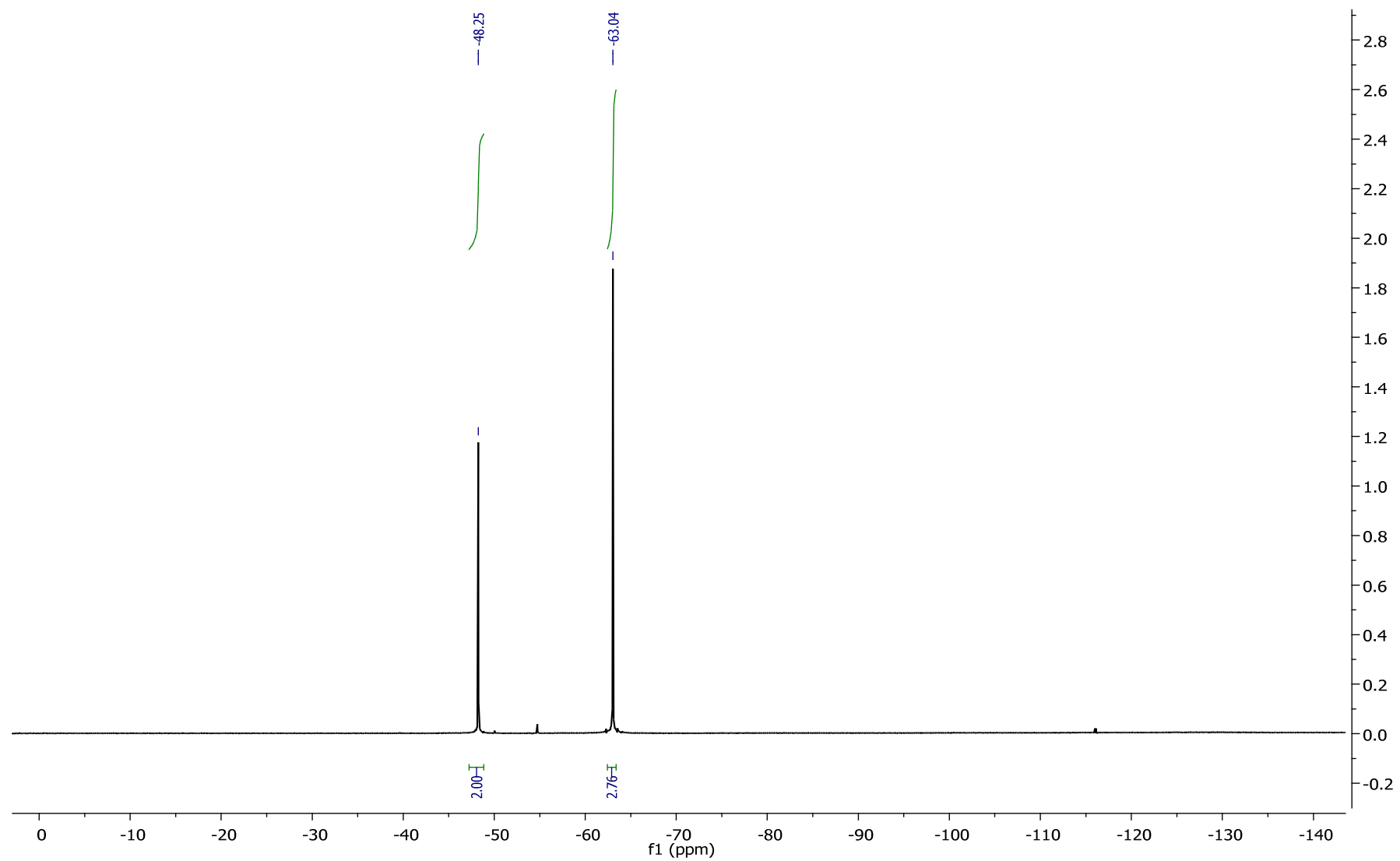
¹H NMR



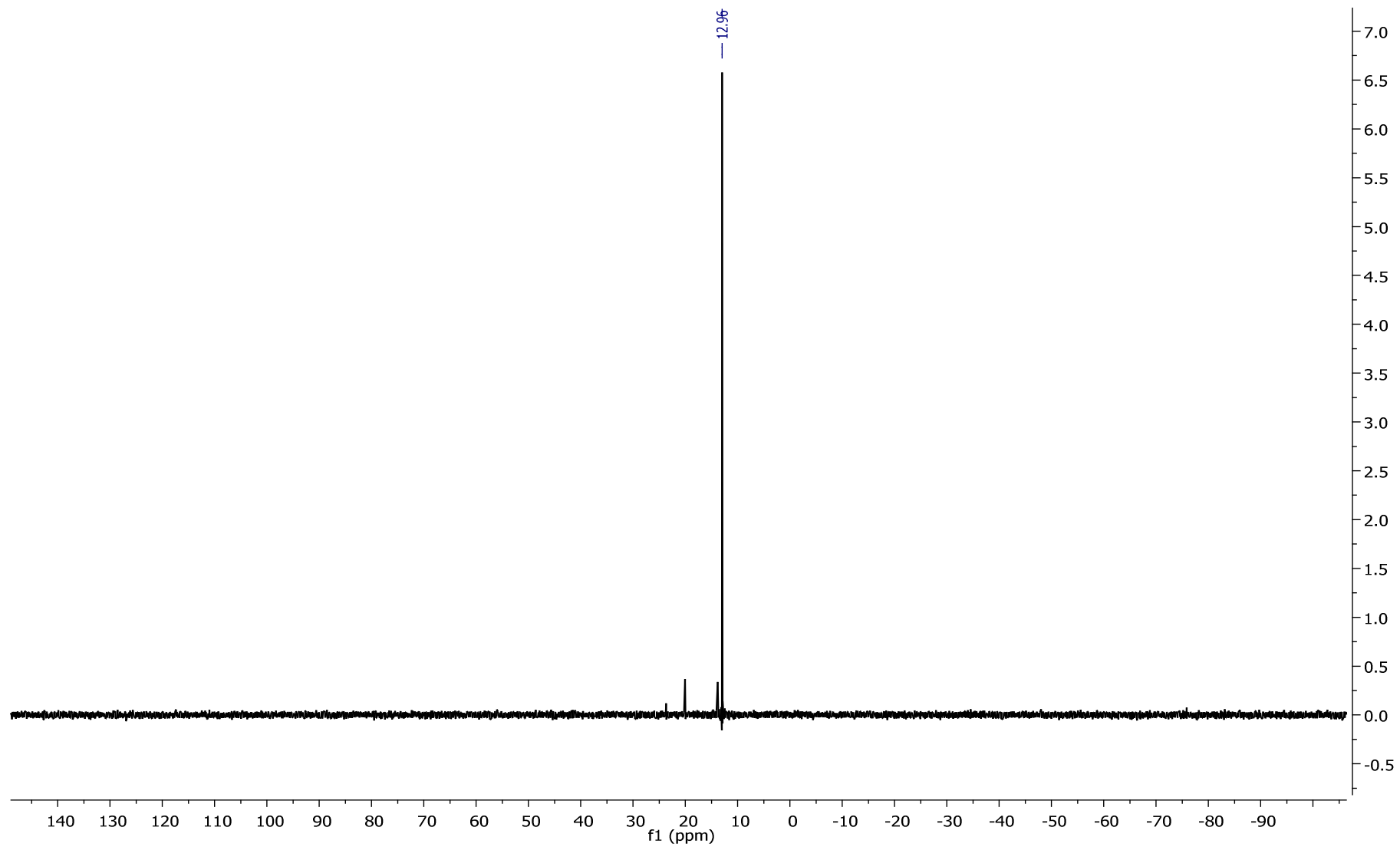
^{13}C NMR



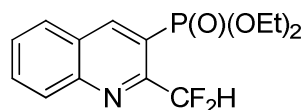
^{19}F NMR



^{31}P NMR

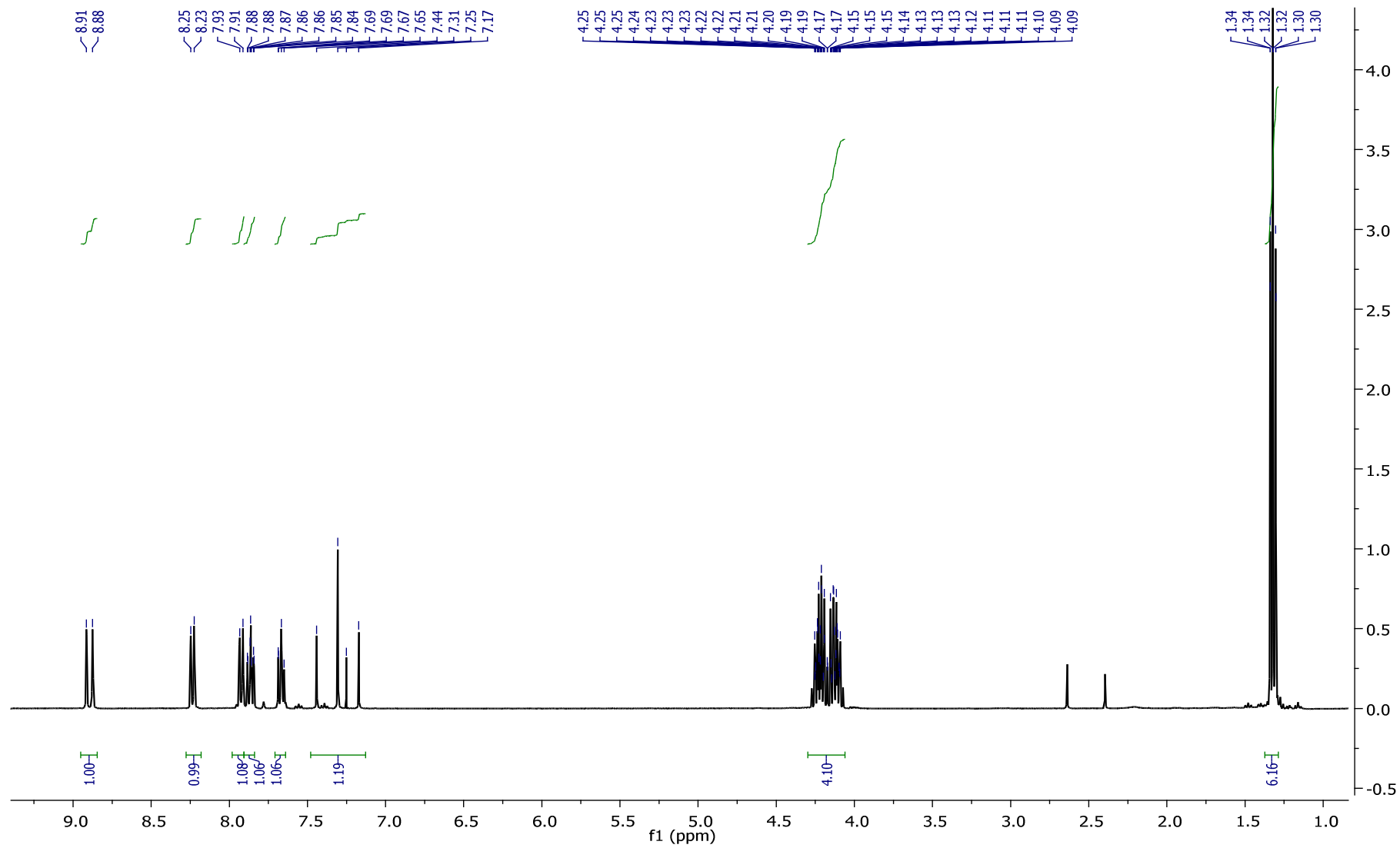


13. Diethyl (2-(difluoromethyl)quinolin-3-yl)phosphonate **4m**

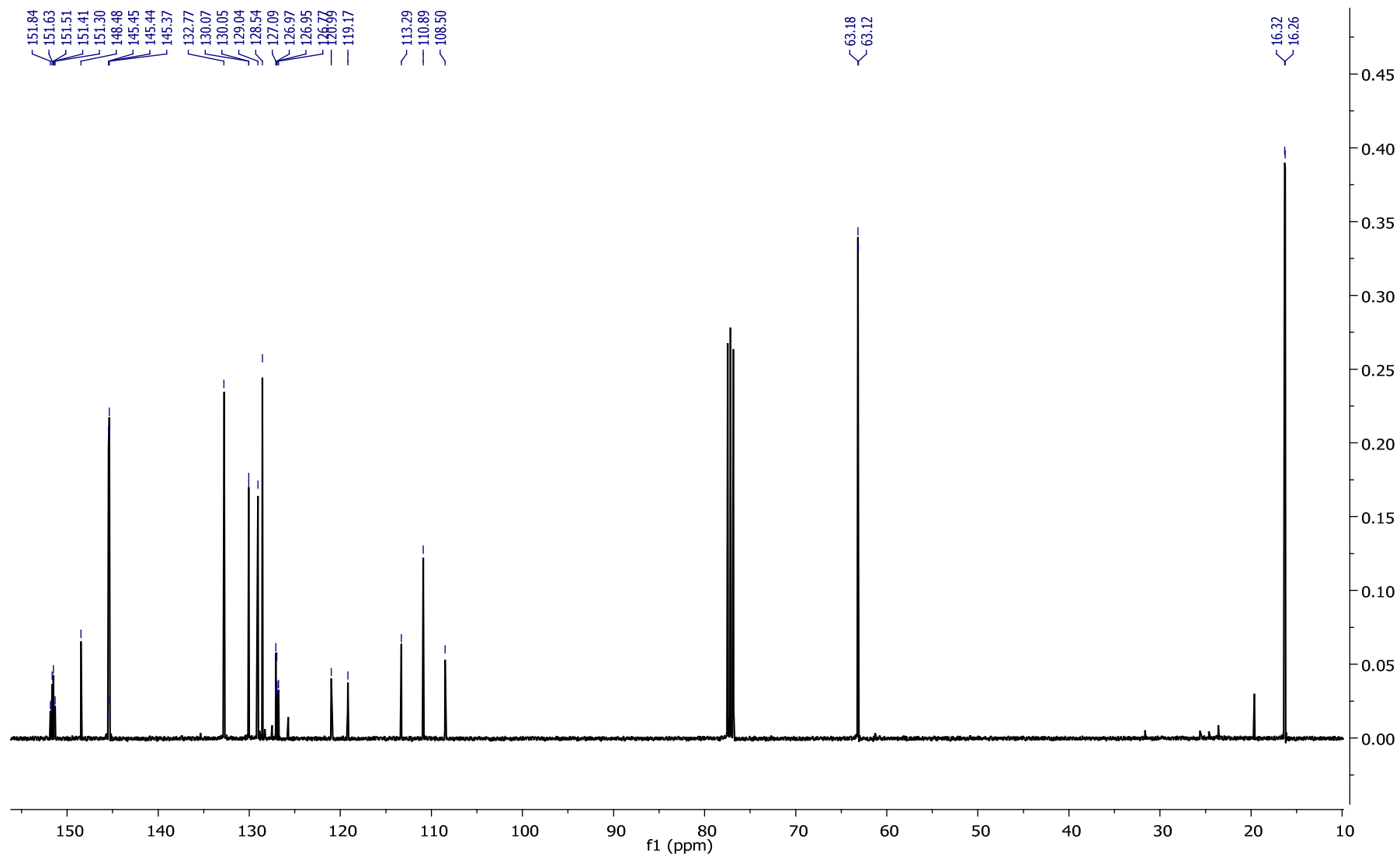


Colourless oil (60%); ^1H NMR (400 MHz, CDCl_3) δ 1.32 (t, $J = 7.1$ Hz, 6H), 4.12 (m, 2H), 4.22 (m, 2H), 7.31 (t, $^2J_{\text{H-F}} = 53.7$ Hz, 1H), 7.67 (td, $J = 7.5$ Hz, $J = 0.7$ Hz, 1H), 7.86 (td, $J = 8.3$ Hz, $J = 1.2$ Hz, 1H), 7.92 (d, $J = 7.5$ Hz, 1H), 8.24 (d, $J = 8.3$ Hz, 1H), 8.90 (d, $^3J_{\text{H-P}} = 15.4$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.4$ Hz), 63.2 (d, $J = 5.8$ Hz), 110.9 (t, $^1J_{\text{C-F}} = 242.1$ Hz), 120.1 (dt, $^1J_{\text{C-P}} = 184.1$ Hz, $^3J_{\text{C-F}} = 2.8$ Hz), 127.0 (dt, $^3J_{\text{C-P}} = 11.9$ Hz, $^5J_{\text{C-F}} = 1.4$ Hz), 128.5, 129.0, 130.1 (d, $^4J_{\text{C-P}} = 1.2$ Hz), 132.7, 145.4 (d, $^2J_{\text{C-P}} = 7.5$ Hz), 148.5, 151.4 (td, $^2J_{\text{C-F}} = 21.7$ Hz, $^2J_{\text{C-P}} = 11.3$ Hz); ^{19}F NMR (376 MHz) δ -115.7 (d, $^2J_{\text{F-H}} = 53.9$ Hz); ^{31}P NMR (161 MHz) δ 15.0 (t, $^4J_{\text{P-F}} = 1.2$ Hz); HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{17}\text{F}_2\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 316.0909, found 316.0912.

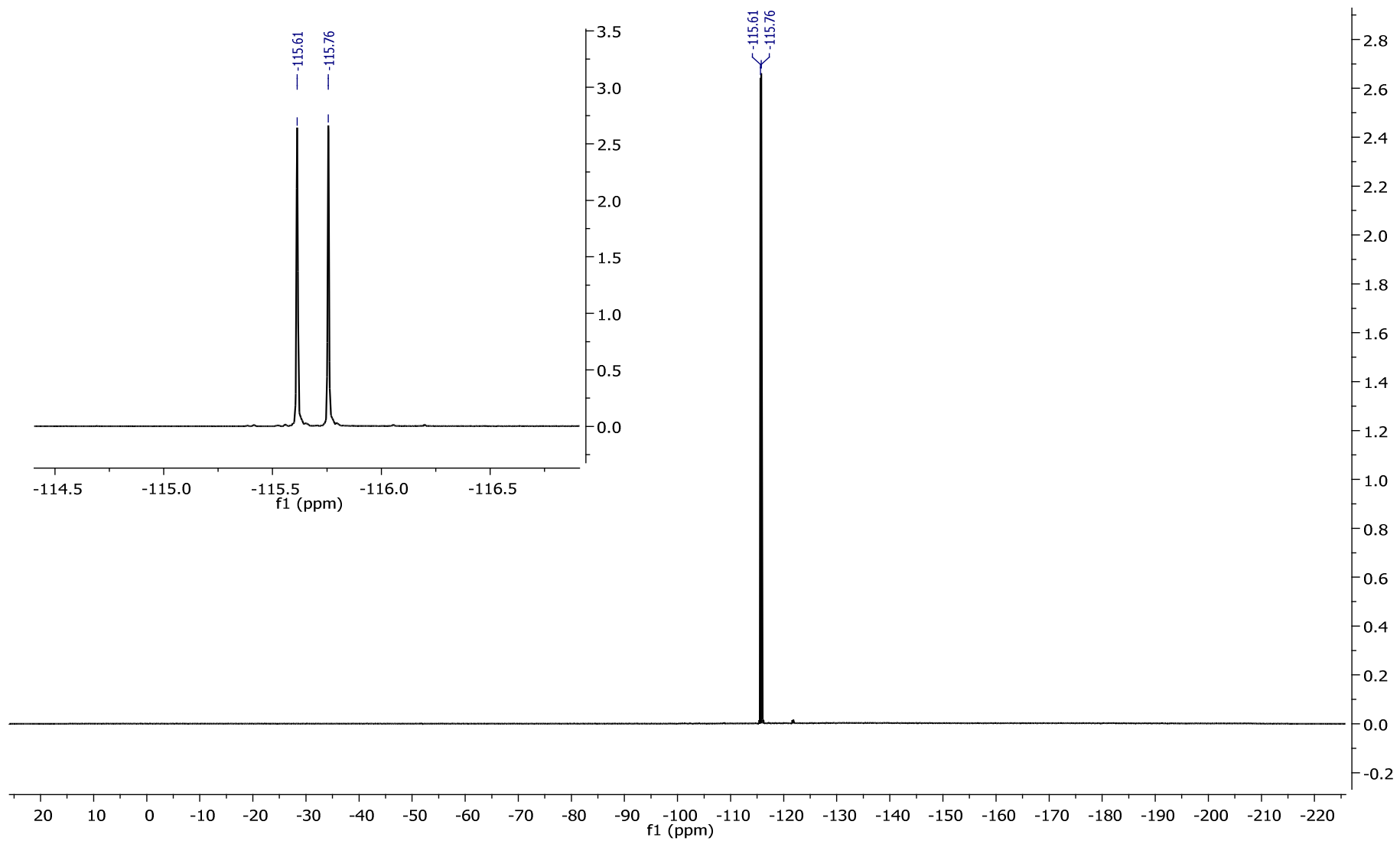
¹H NMR



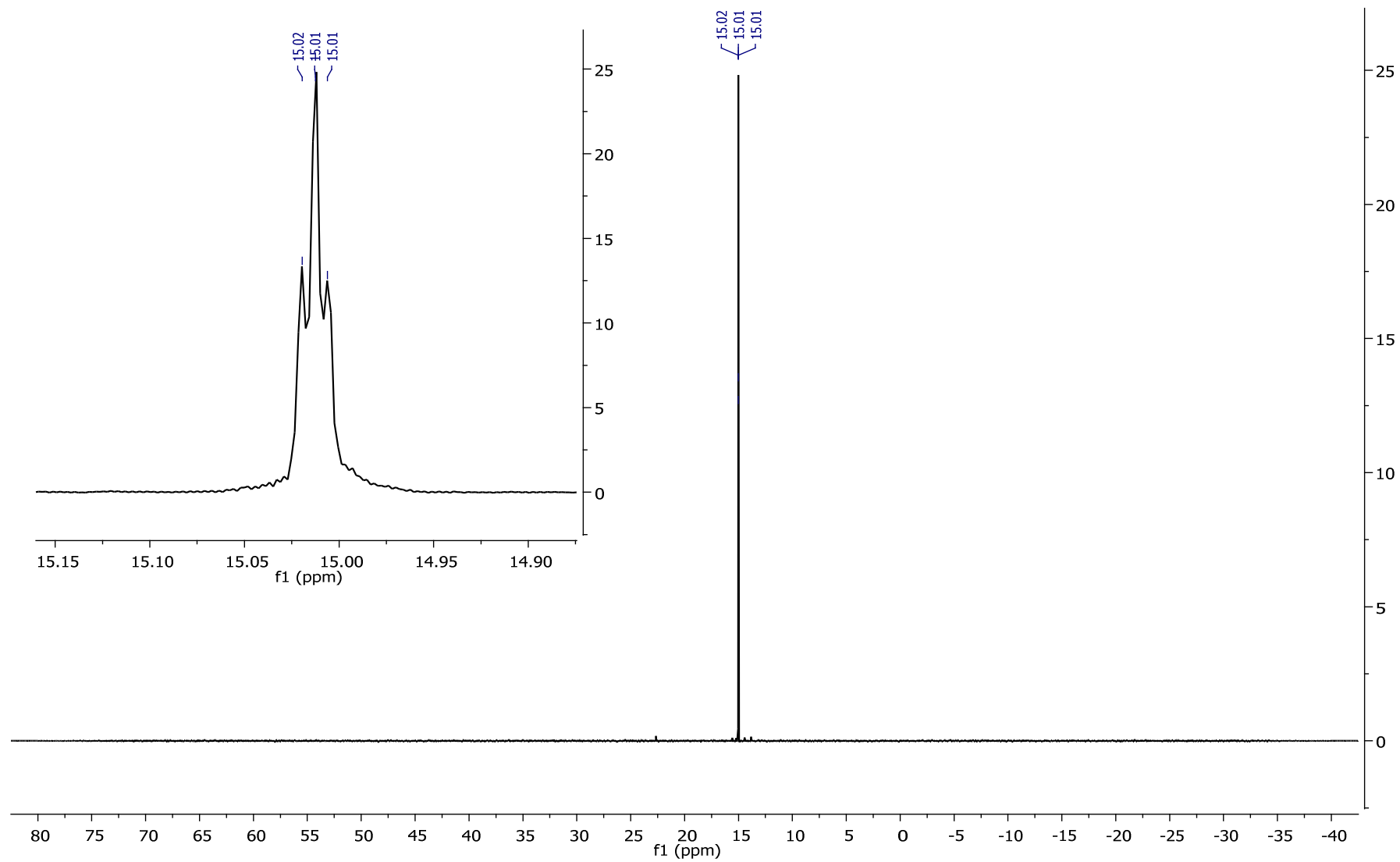
^{13}C NMR



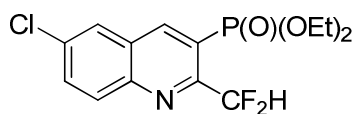
^{19}F NMR



^{31}P NMR

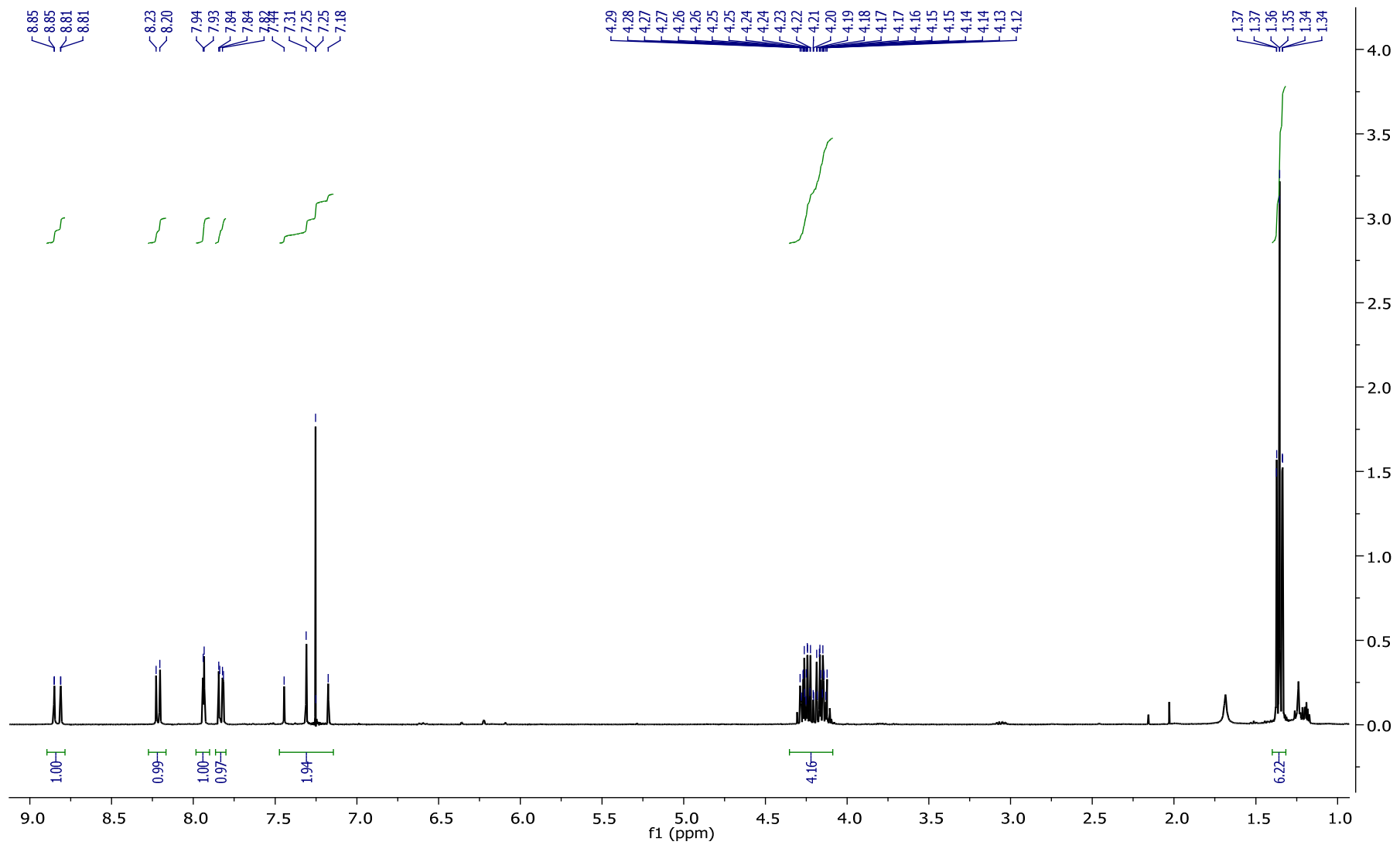


14. Diethyl (6-chloro-2-(difluoromethyl)quinolin-3-yl)phosphonate **4n**

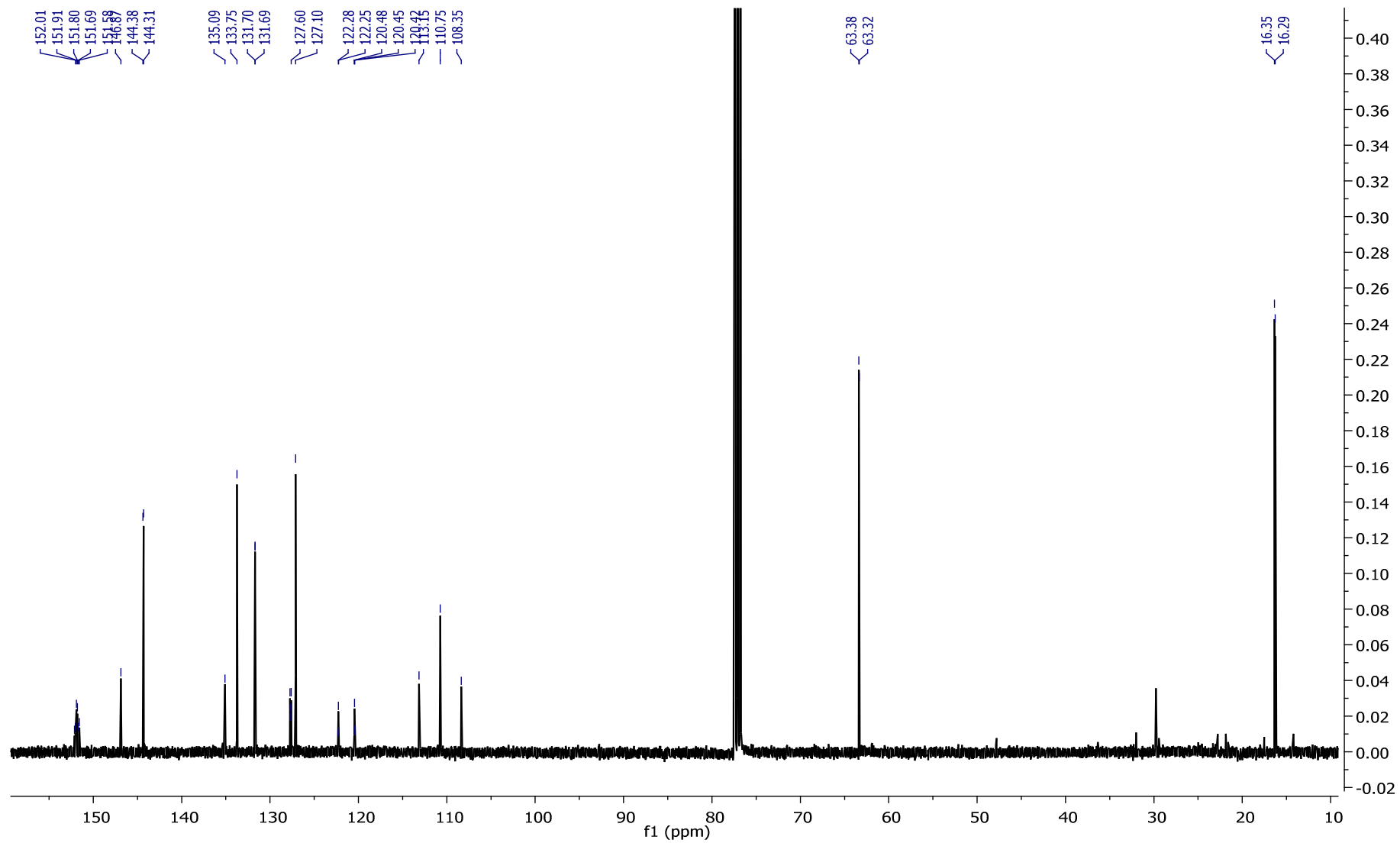


Colourless oil (54%); ^1H NMR (400 MHz, CDCl_3) δ 1.35 (t, $J = 7.2$ Hz, 6H), 4.14 (m, 2H), 4.25 (m, 2H), 7.31 (t, $^2J_{\text{H-F}} = 53.8$ Hz, 1H), 7.82 (dd, $J = 8.9$ Hz, $J = 2.4$ Hz, 1H), 7.93 (d, $J = 2.4$ Hz, 1H), 8.23 (d, $J = 9.3$ Hz, 1H), 8.82 (d, $^3J_{\text{H-P}} = 15.8$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.2$ Hz), 63.3 (d, $J = 5.6$ Hz), 110.7 (t, $^1J_{\text{C-F}} = 242.5$ Hz), 121.3 (dt, $^1J_{\text{C-P}} = 183.7$ Hz, $^3J_{\text{C-F}} = 3.3$ Hz), 127.1, 127.6 (dt, $^3J_{\text{C-P}} = 12.5$ Hz, $^5J_{\text{C-F}} = 1.5$ Hz), 131.7 (d, $^4J_{\text{C-P}} = 1.4$ Hz), 133.7, 135.1 (d, $^5J_{\text{C-P}} = 1.8$ Hz), 144.3 (d, $^2J_{\text{C-P}} = 7.1$ Hz), 146.9, 151.8 (td, $^2J_{\text{C-F}} = 21.8$ Hz, $^2J_{\text{C-P}} = 10.8$ Hz); ^{19}F NMR (376 MHz) δ -115.8 (d, $^2J_{\text{F-H}} = 53.4$ Hz); ^{31}P NMR (161 MHz) δ 14.3; HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{15}\text{ClF}_2\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 372.0338, found 372.0344.

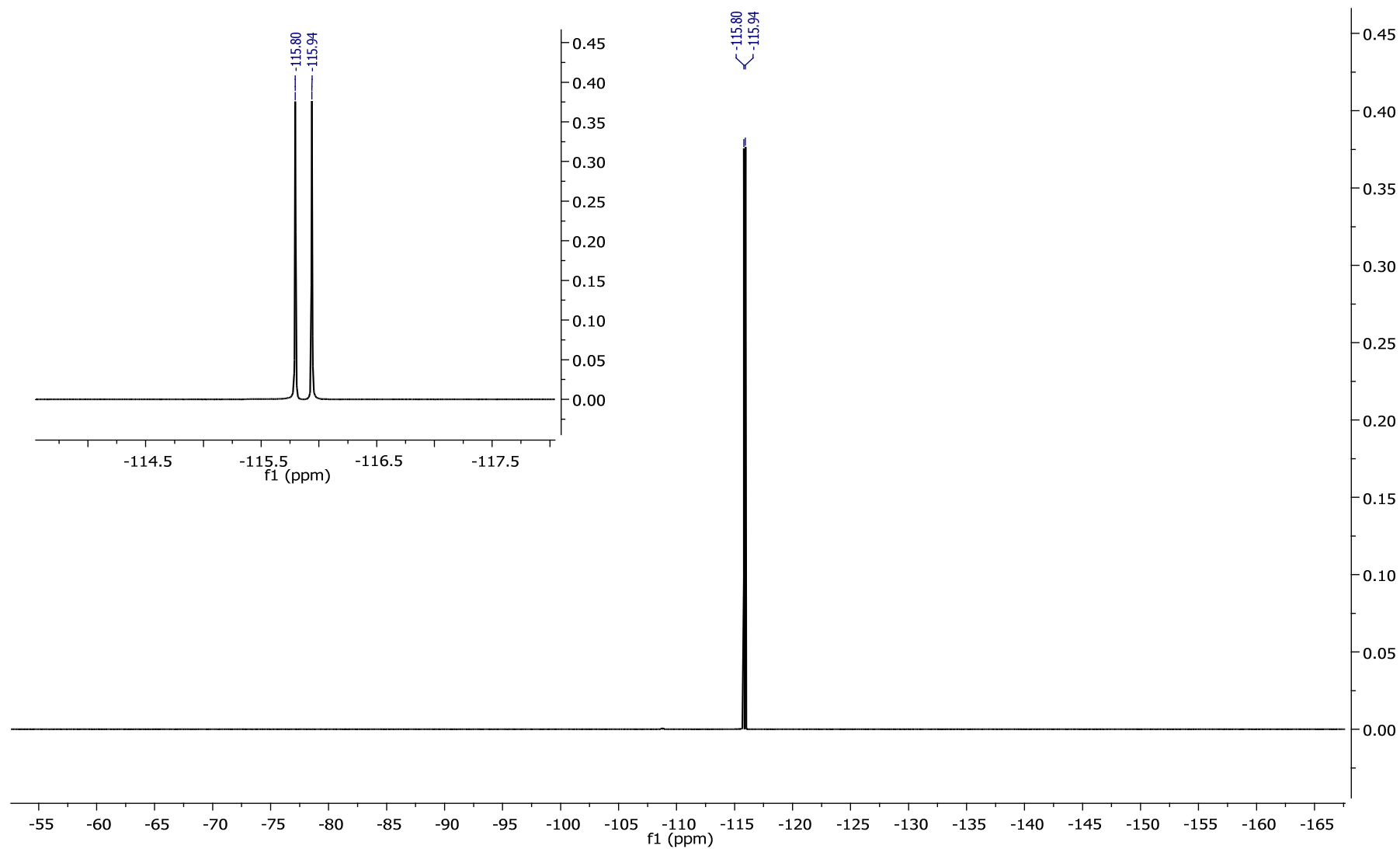
¹H NMR



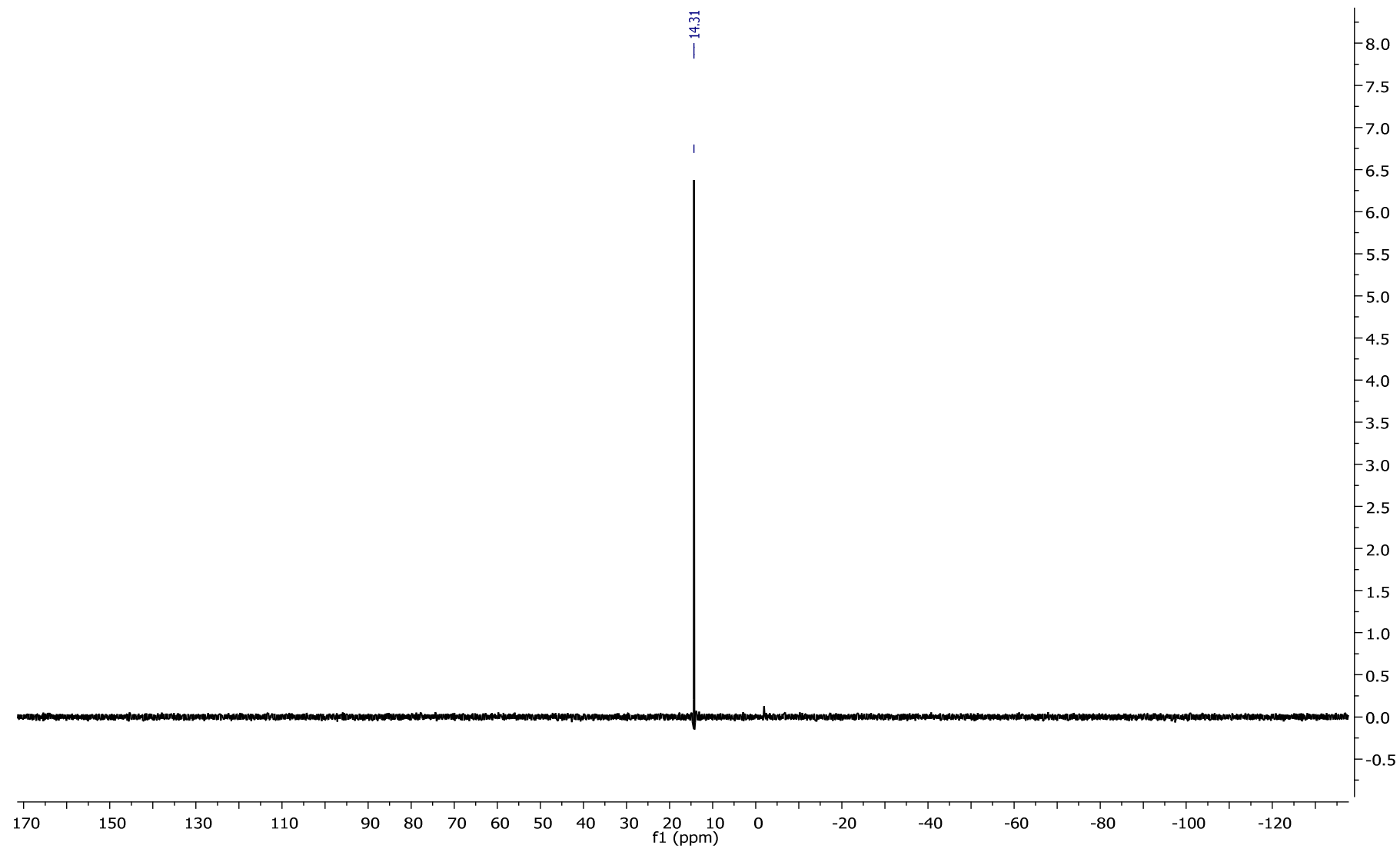
^{13}C NMR



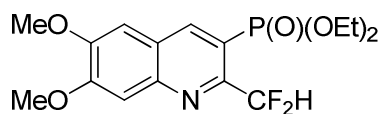
^{19}F NMR



^{31}P NMR

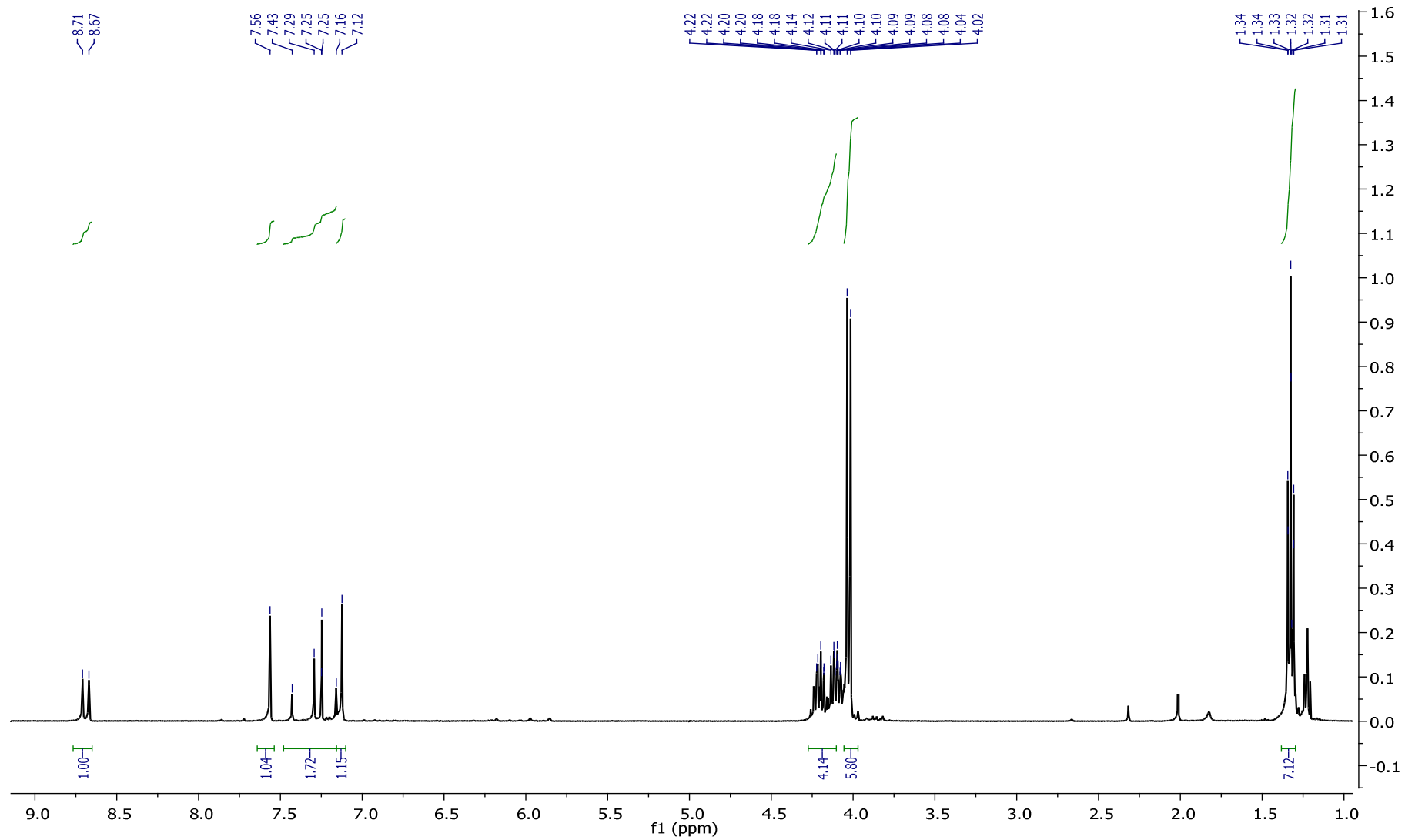


15. Diethyl (2-(difluoromethyl)-6,7-dimethoxyquinolin-3-yl)phosphonate **4o**

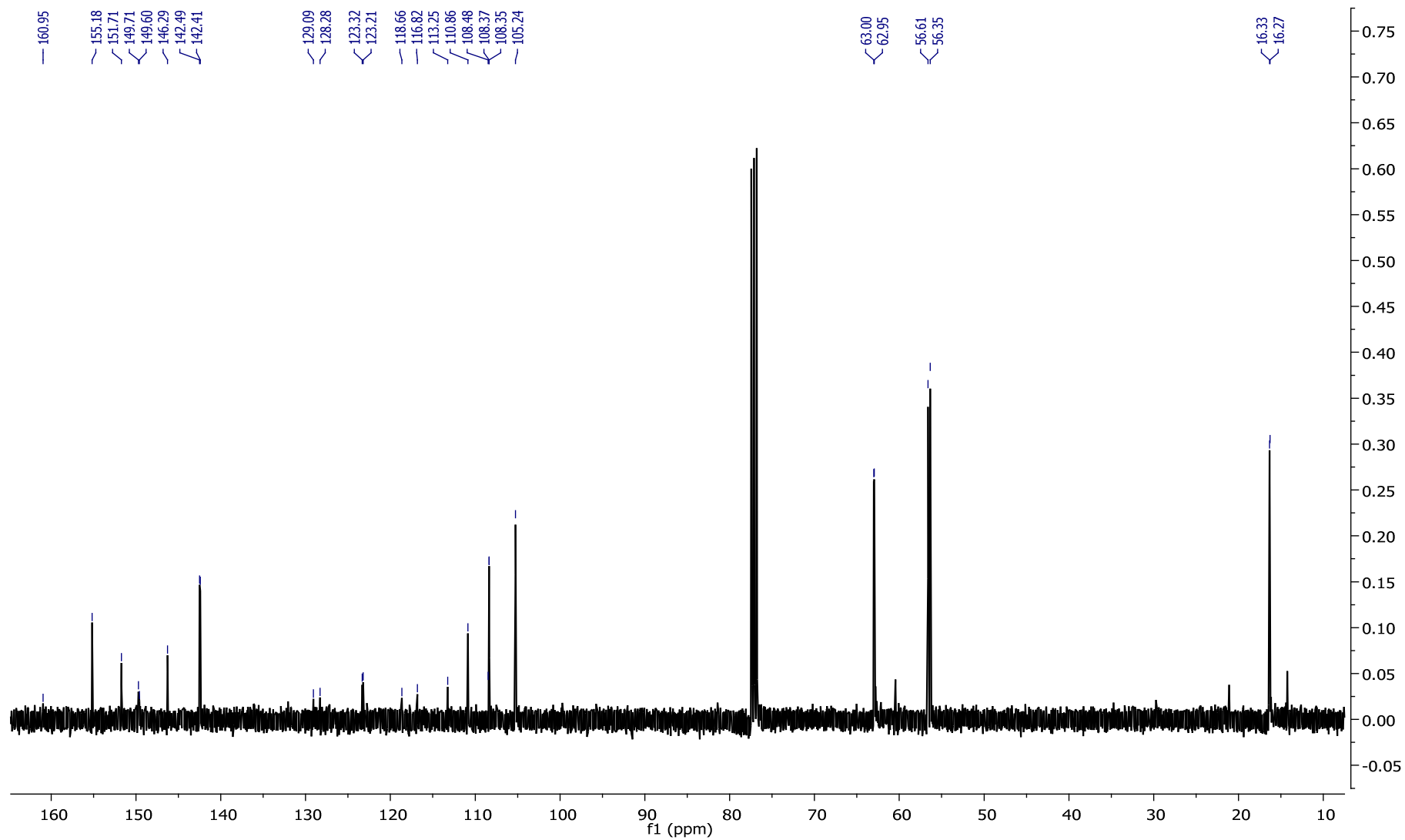


Yellowish crystals (42%); Mp = 169–173 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.33 (t, $J = 7.1$ Hz, 6H), 4.02 (s, 3H), 4.04 (s, 3H), 4.09 (m, 2H), 4.18 (m, 2H), 7.12 (s, 1H), 7.29 (t, $^2J_{\text{H-F}} = 54.0$ Hz, 1H), 7.56 (s, 1H), 8.69 (d, $^3J_{\text{H-P}} = 14.9$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.4$ Hz), 56.4, 56.6, 62.9 (d, $J = 5.3$ Hz), 105.4, 108.3, 110.8 (t, $^1J_{\text{C-F}} = 239.6$ Hz), 117.9 (dt, $^1J_{\text{C-P}} = 184.9$ Hz, $^3J_{\text{C-F}} = 3.4$ Hz), 123.3 (dt, $^3J_{\text{C-P}} = 11.7$ Hz, $^5J_{\text{C-F}} = 0.8$ Hz), 142.4 (d, $^2J_{\text{C-P}} = 6.6$ Hz), 146.9, 149.7 (td, $^2J_{\text{C-F}} = 20.6$ Hz, $^2J_{\text{C-P}} = 11.2$ Hz), 151.7, 155.2; ^{19}F NMR (376 MHz) δ -115.2 (d, $^2J_{\text{F-H}} = 50.5$ Hz); ^{31}P NMR (161 MHz) δ 14.3 (t, $^4J_{\text{P-F}} = 1.3$ Hz); HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{20}\text{F}_2\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]^+$ 398.0939, found 398.0949.

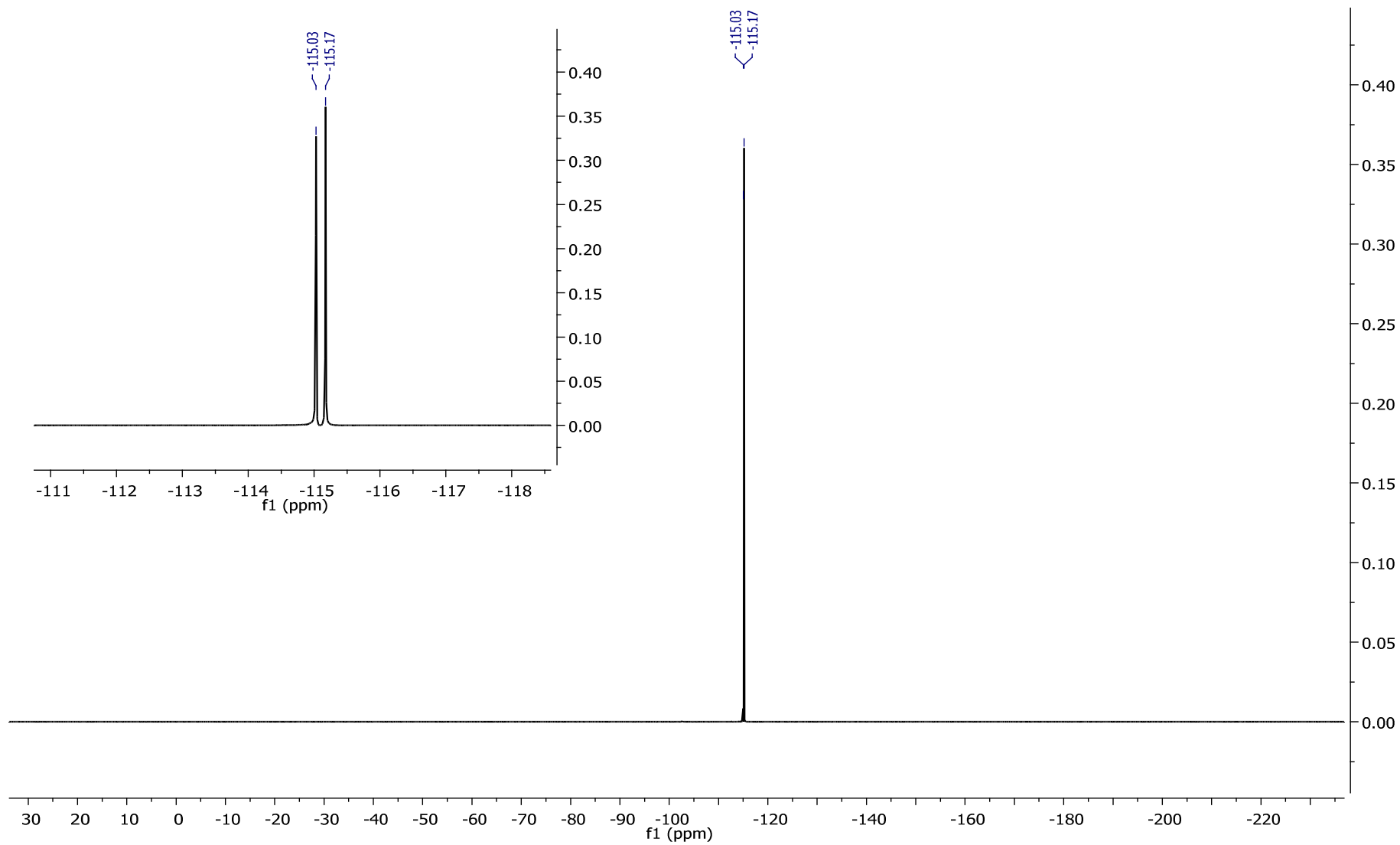
¹H NMR



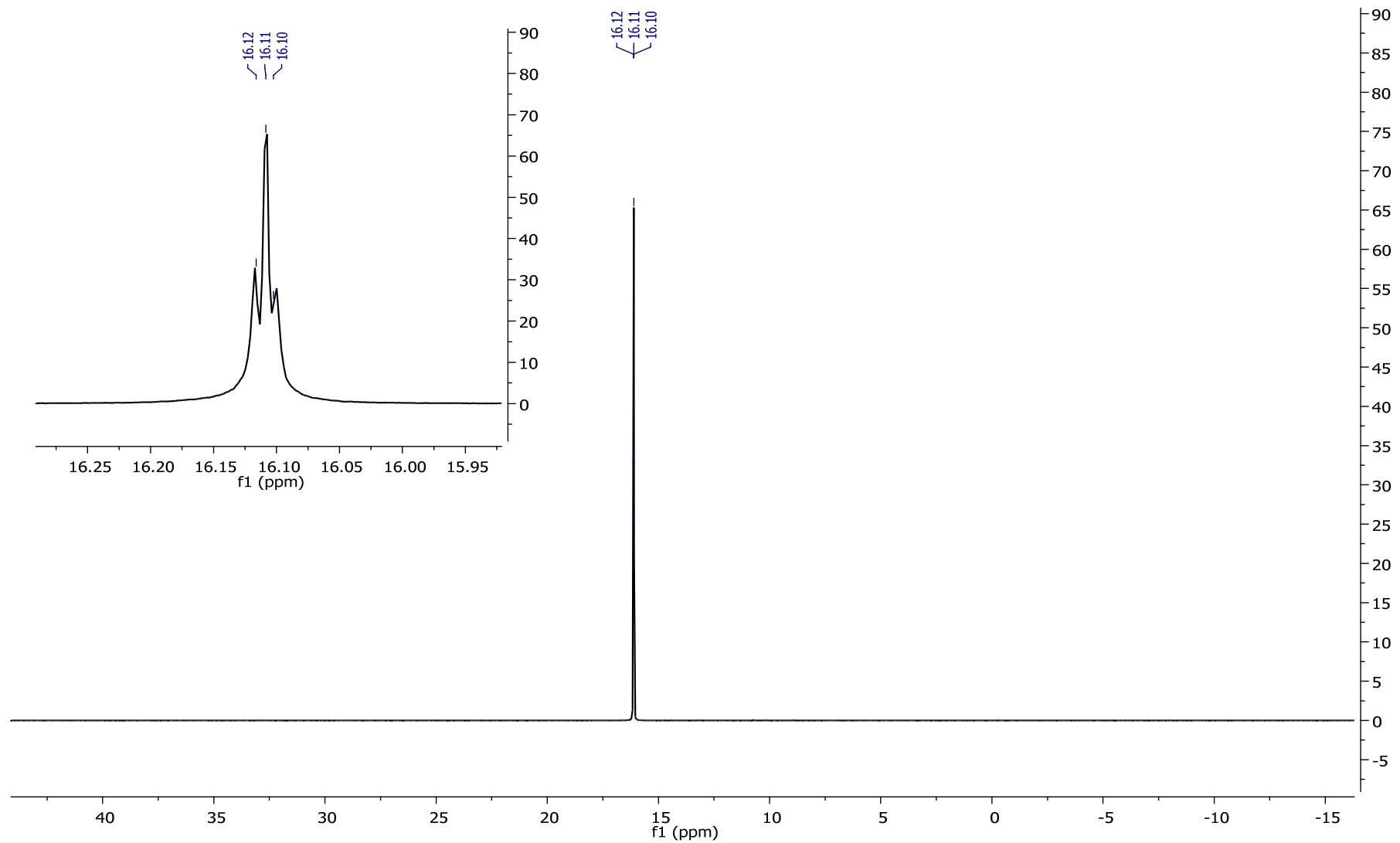
^{13}C NMR



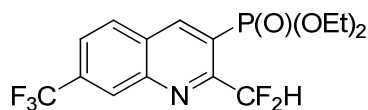
^{19}F NMR



^{31}P NMR

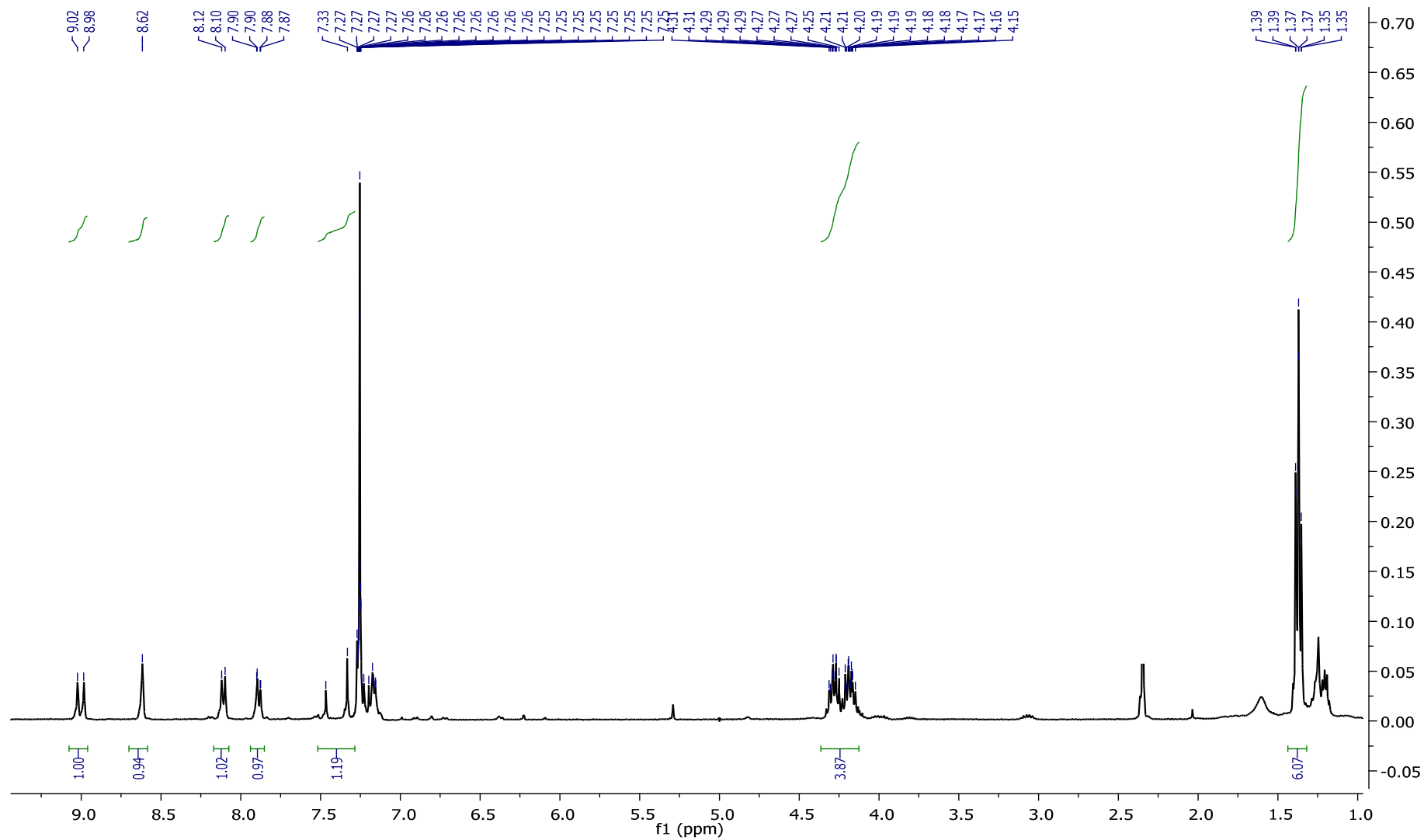


16. Diethyl (2-(difluoromethyl)-7-(trifluoromethyl)quinolin-3-yl)phosphonate **4p**

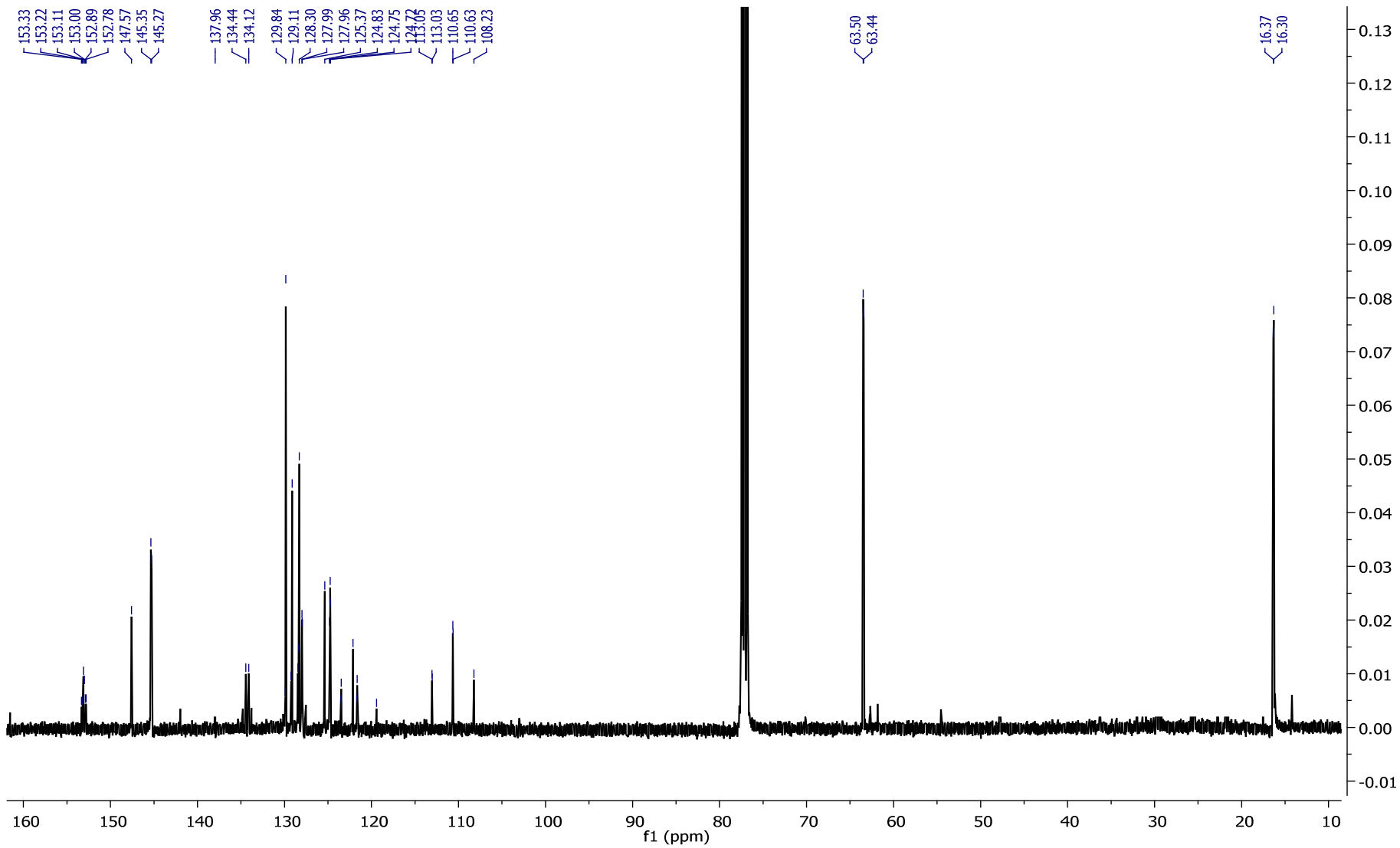


Brownish oil (69%); ^1H NMR (400 MHz, CDCl_3) δ 1.37 (t, $J = 7.0$ Hz, 6H), 4.17 (m, 2H), 4.27 (m, 2H), 7.33 (t, $^2J_{\text{H-F}} = 53.3$ Hz, 1H), 7.89 (dd, $J = 8.5$ Hz, $J = 1.7$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 8.62 (s, 1H), 9.00 (d, $^3J_{\text{H-P}} = 15.7$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.4 (d, $J = 6.3$ Hz), 63.5 (d, $J = 5.8$ Hz), 110.6 (td, $^1J_{\text{C-F}} = 242.0$ Hz, $^3J_{\text{C-P}} = 2.0$ Hz), 122.6 (dt, $^1J_{\text{C-P}} = 183.1$ Hz, $^3J_{\text{C-F}} = 3.1$ Hz), 123.4 (q, $^1J_{\text{C-F}} = 271.9$ Hz), 124.7 (qd, $^4J_{\text{C-F}} = 2.1$ Hz, $^4J_{\text{C-P}} = 1.0$ Hz), 127.9 (qd, $^4J_{\text{C-F}} = 3.8$ Hz, $^4J_{\text{C-P}} = 0.9$ Hz), 128.5 (d, $^3J_{\text{C-P}} = 12.5$ Hz), 129.9, 134.3 (q, $^2J_{\text{C-F}} = 32.6$ Hz), 147.8 (d, $^2J_{\text{C-P}} = 7.9$ Hz), 147.6, 153.1 (td, $^2J_{\text{C-F}} = 23.2$ Hz, $^2J_{\text{C-P}} = 11.6$ Hz); ^{19}F NMR (376 MHz) δ -63.0 (s, $-\text{CF}_3$), -116.0 (d, $^2J_{\text{F-H}} = 52.6$ Hz, $-\text{CF}_2\text{H}$); ^{31}P NMR (161 MHz) δ 13.8; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{16}\text{F}_5\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 384.0782, found 384.0784.

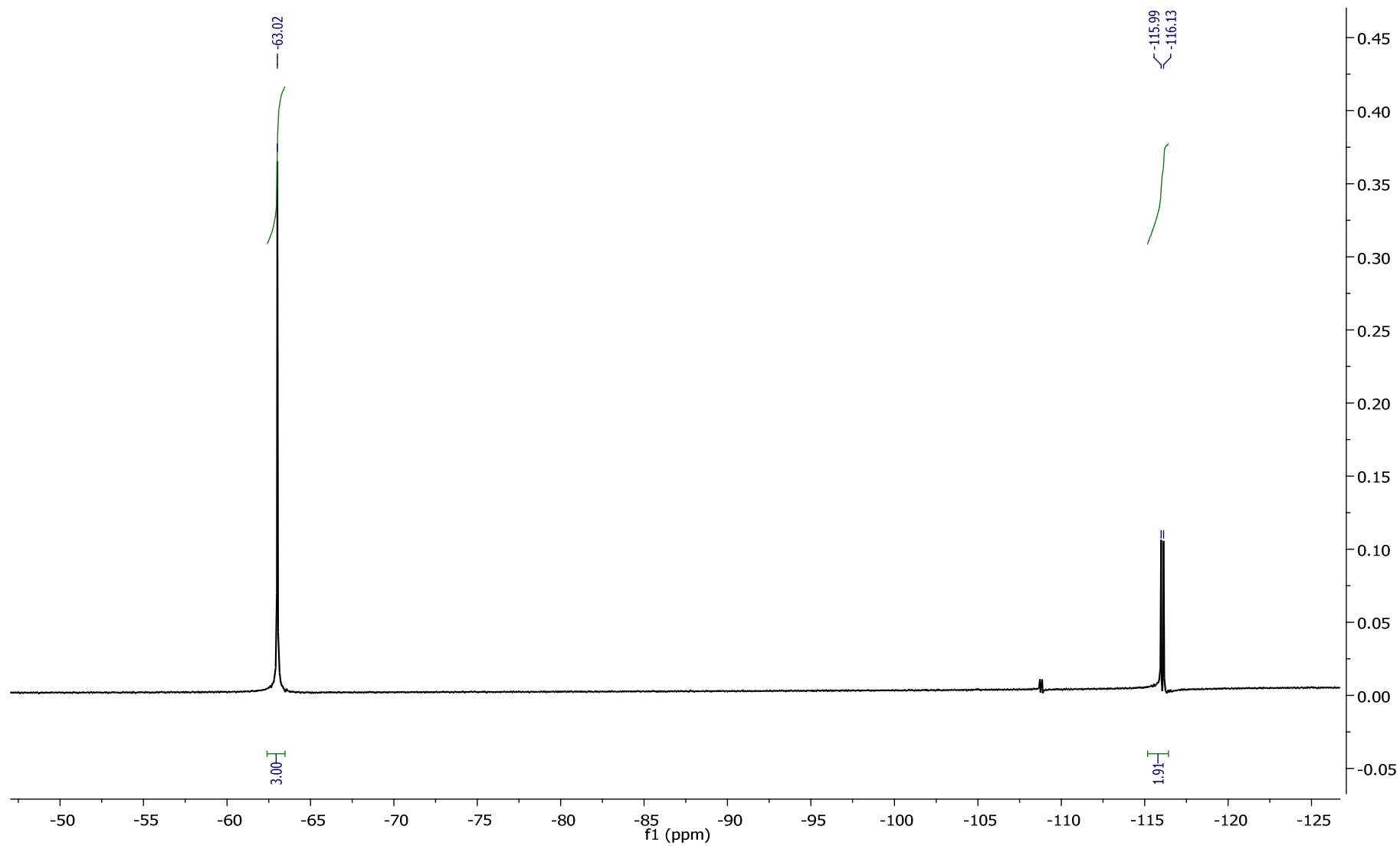
¹H NMR



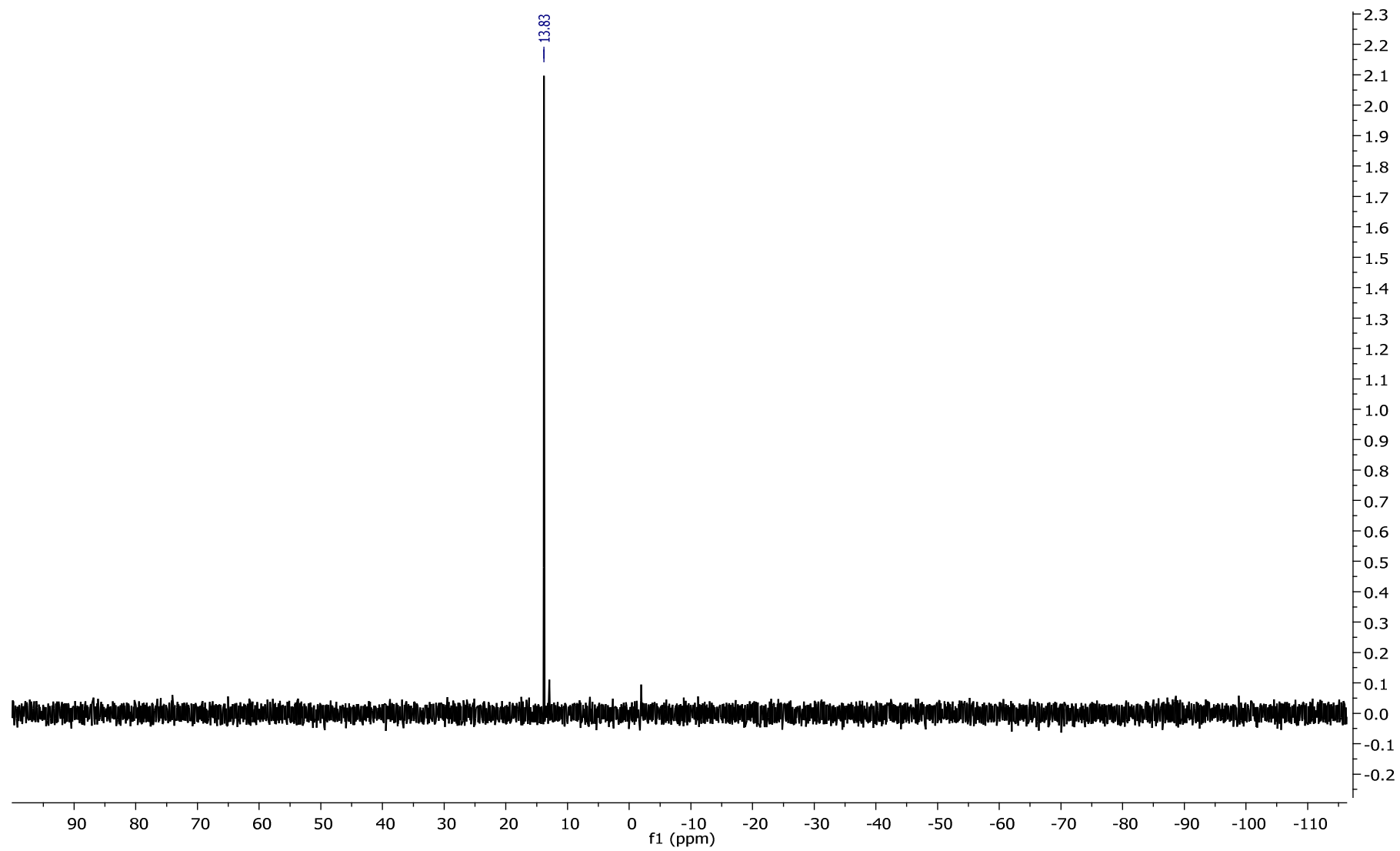
^{13}C NMR



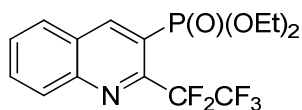
^{19}F NMR



^{31}P NMR

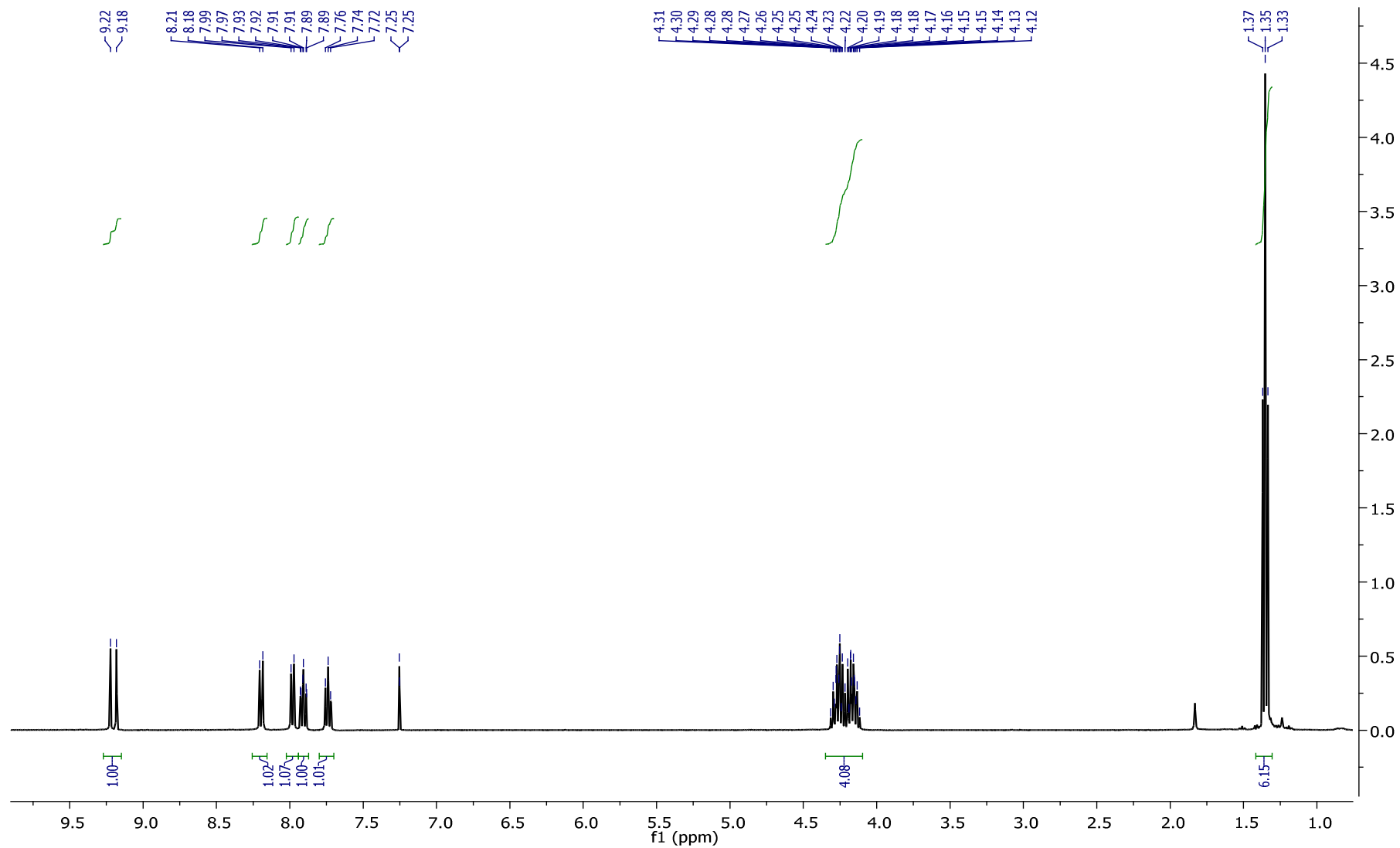


17. Diethyl (2-(perfluoroethyl)quinolin-3-yl)phosphonate **4q**

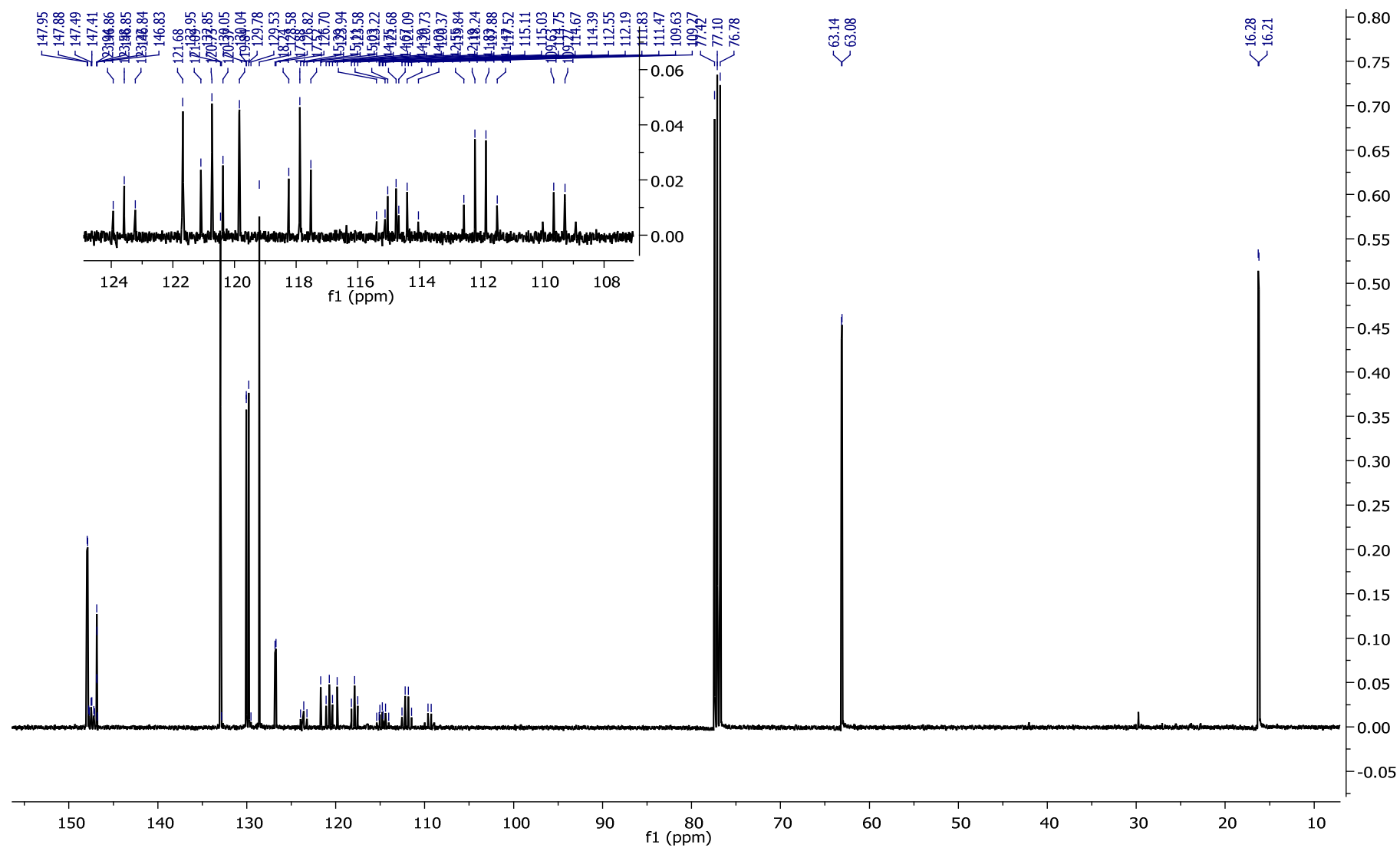


Yellowish oil (65%); ^1H NMR (400 MHz, CDCl_3) δ 1.35 (t, $J = 7.0$ Hz, 6H), 4.15 (m, 2H), 4.25 (m, 2H), 7.74 (t, $J = 7.5$ Hz, 1H), 7.91 (td, $J = 7.2$ Hz, $J = 1.3$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 9.20 (d, $^3J_{\text{H-P}} = 16.5$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.2 (d, $J = 6.5$ Hz), 63.1 (d, $J = 6.2$ Hz), 112.0 (tq, $^1J_{\text{C-F}} = 258.8$ Hz, $^2J_{\text{C-F}} = 34.1$ Hz), 119.0 (qt, $^1J_{\text{C-F}} = 289.5$ Hz, $^2J_{\text{C-F}} = 35.6$ Hz), 120.7 (d, $^1J_{\text{C-P}} = 186.1$ Hz), 126.7 (d, $^3J_{\text{C-P}} = 11.4$ Hz), 128.6, 129.8, 130.0 (d, $^4J_{\text{C-P}} = 1.1$ Hz), 132.9, 146.8 (dt, $^4J_{\text{C-P}} = 1.4$ Hz, $^4J_{\text{C-F}} = 0.9$ Hz), 147.5 (td, $^2J_{\text{C-F}} = 28.9$ Hz, $^2J_{\text{C-P}} = 7.9$ Hz), 147.9 (d, $^2J_{\text{C-P}} = 7.2$ Hz); ^{19}F NMR (376 MHz) δ -79.9 (s, $-\text{CF}_2\text{CF}_3$), -108.1 (s, $-\text{CF}_2\text{CF}_3$); ^{31}P NMR (161 MHz) δ 14.1; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{16}\text{F}_5\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$ 384.0782, found 384.0784.

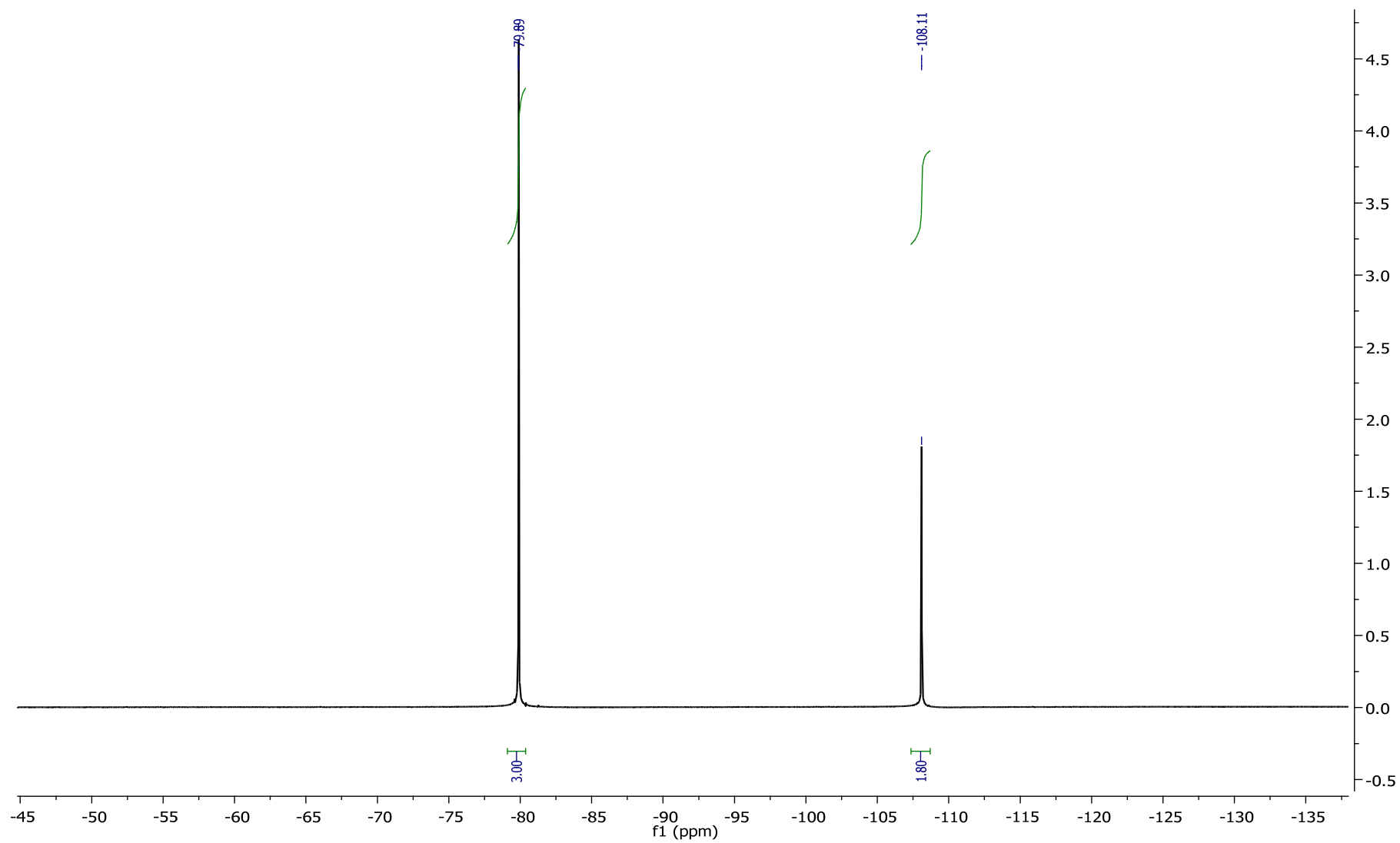
¹H NMR



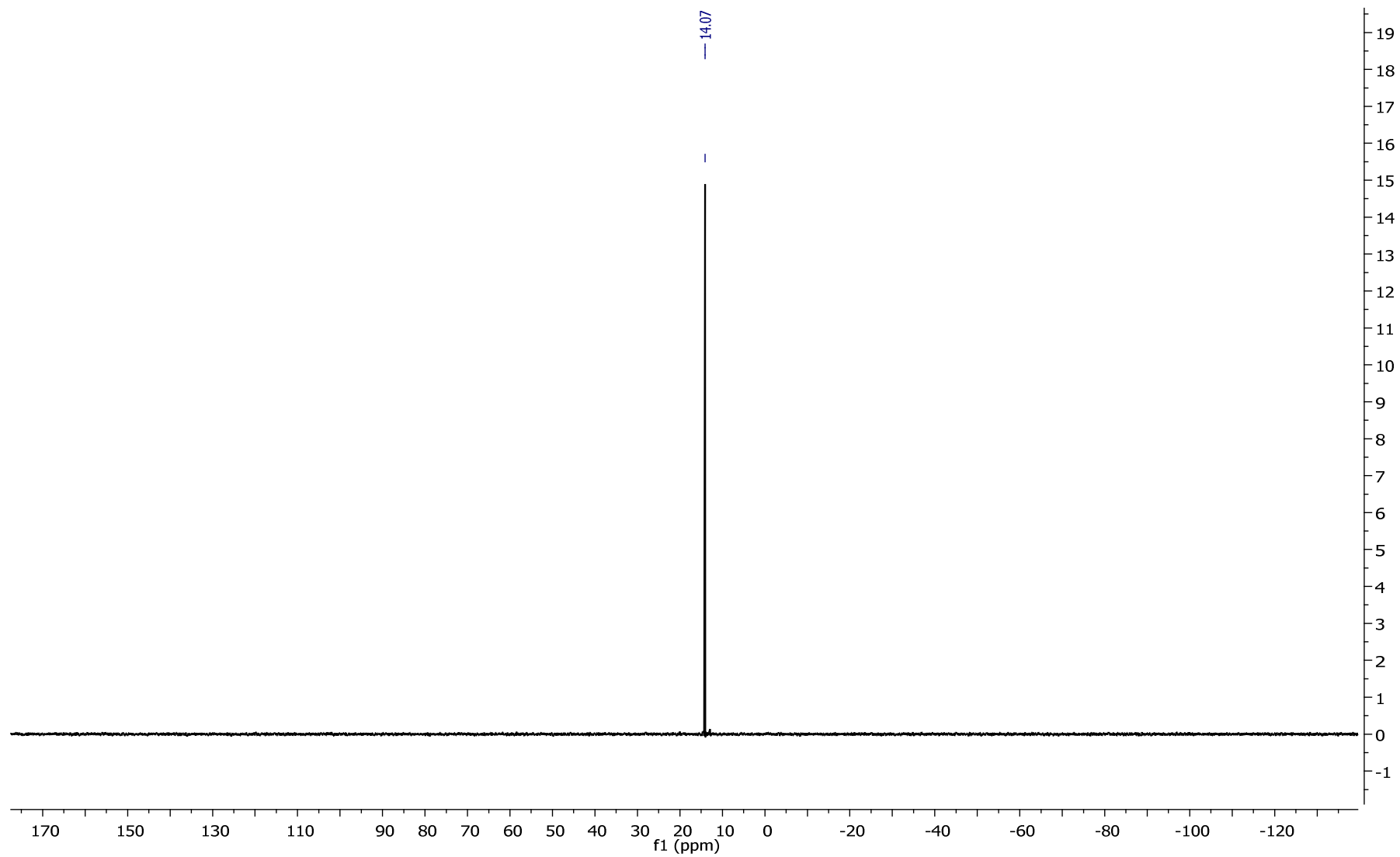
¹³C NMR



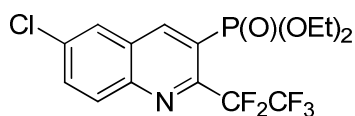
^{19}F NMR



^{31}P NMR

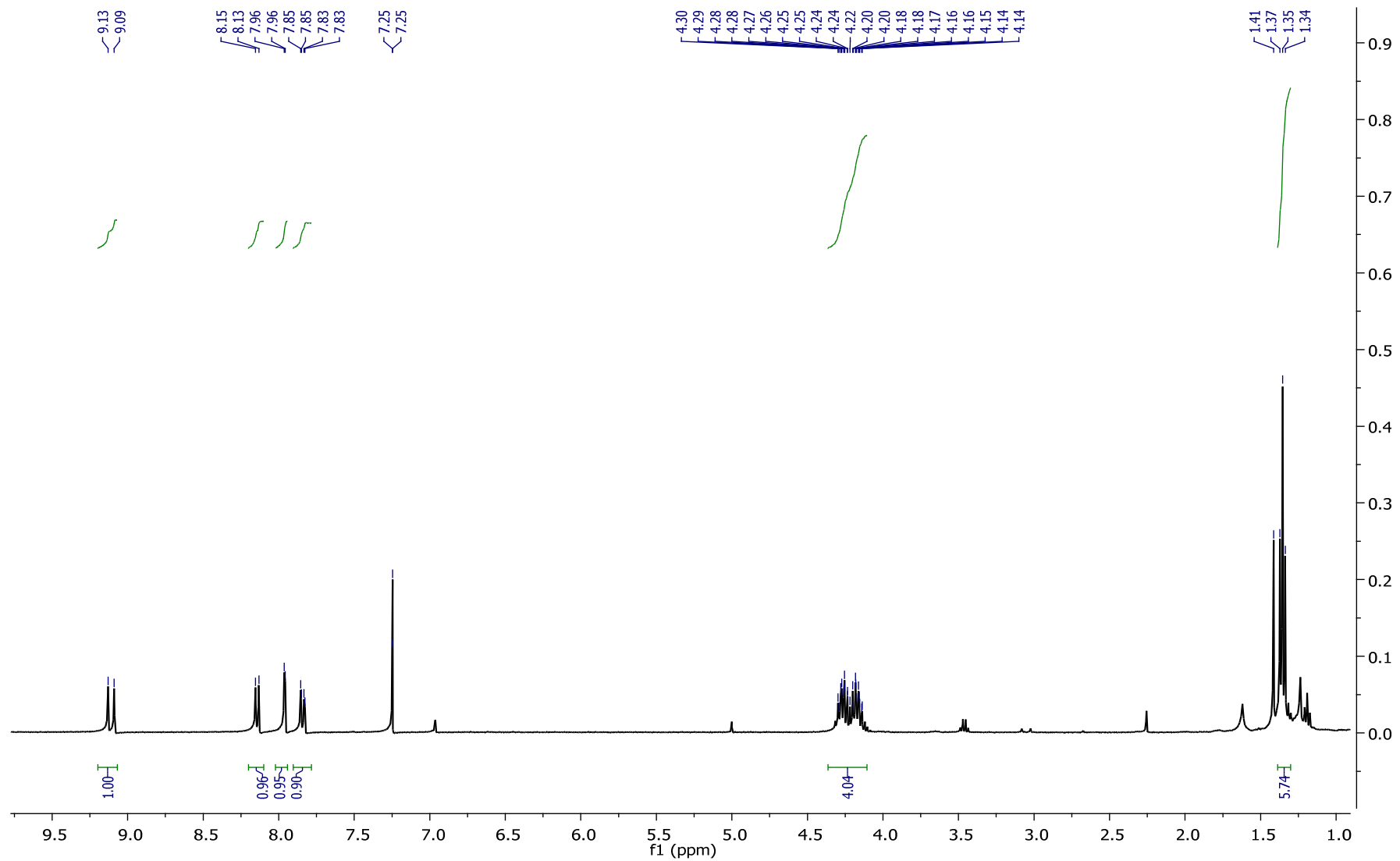


18. Diethyl (6-chloro-2-(perfluoroethyl)quinolin-3-yl)phosphonate **4r**

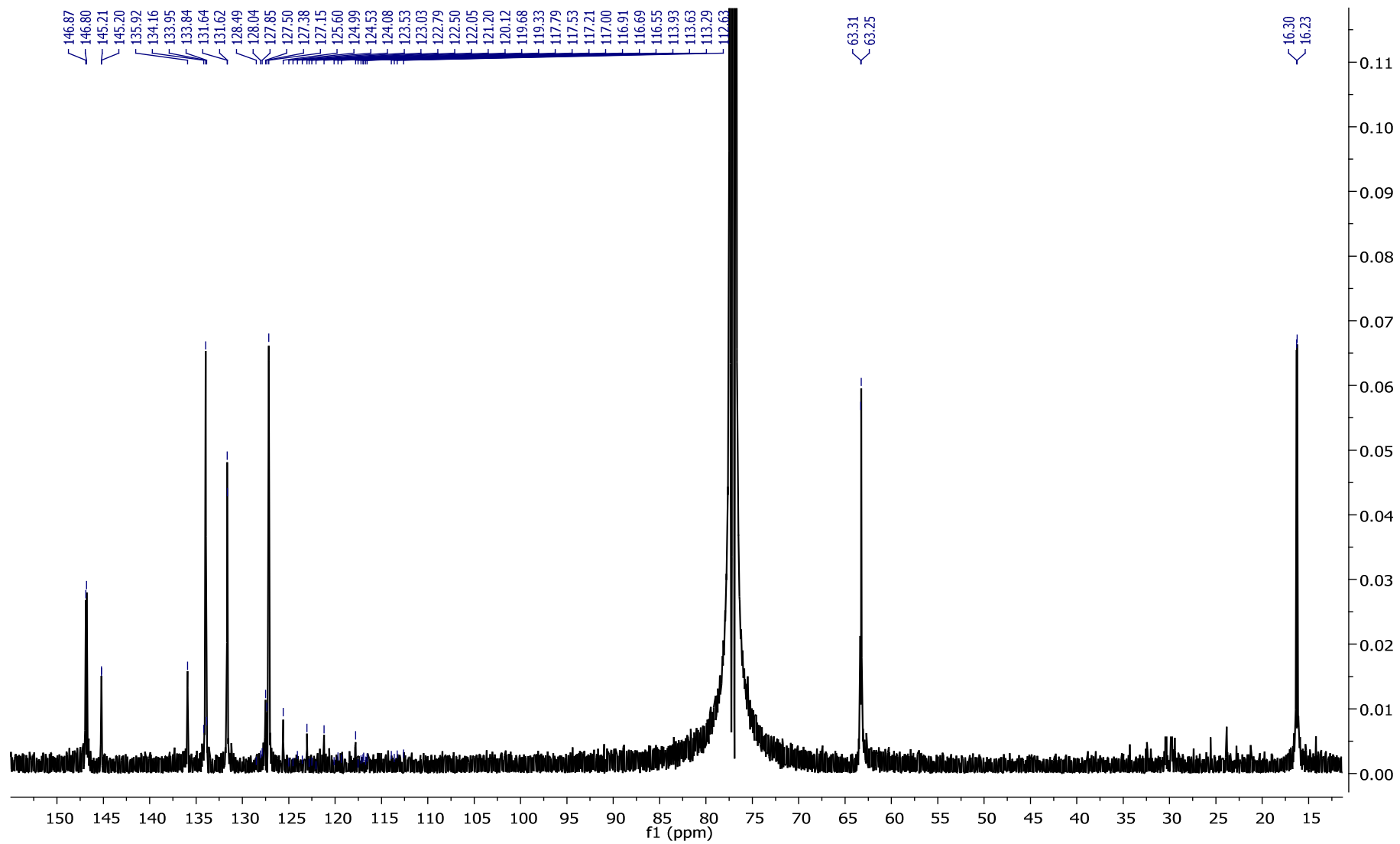


Yellowish oil (53%); ^1H NMR (400 MHz, CDCl_3) δ 1.35 (t, $J = 7.0$ Hz, 6H), 4.15 (m, 2H), 4.26 (m, 2H), 7.83 (dd, $J = 8.9$ Hz, $J = 2.3$ Hz, 1H), 7.96 (d, $J = 2.2$ Hz, 1H), 8.14 (d, $J = 8.9$ Hz, 1H), 9.11 (d, $^3J_{\text{H-P}} = 16.5$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.2$ Hz), 63.2 (d, $J = 6.3$ Hz), 114.5 (tq, $^1J_{\text{C-F}} = 260.1$ Hz, $^2J_{\text{C-F}} = 34.5$ Hz), 122.3 (qt, $^1J_{\text{C-F}} = 287.0$ Hz, $^2J_{\text{C-F}} = 36.5$ Hz), 122.5 (d, $^1J_{\text{C-P}} = 184.8$ Hz), 127.1, 127.4 (d, $^3J_{\text{C-P}} = 11.8$ Hz), 131.6, 133.9, 135.9, 145.2 (dt, $^4J_{\text{C-P}} = 1.7$ Hz, $^4J_{\text{C-F}} = 0.8$ Hz), 146.6 (td, $^2J_{\text{C-F}} = 28.0$ Hz, $^2J_{\text{C-P}} = 7.2$ Hz), 146.8 (d, $^2J_{\text{C-P}} = 7.8$ Hz); ^{19}F NMR (376 MHz) δ -79.9 (s, $-\text{CF}_2\text{CF}_3$), -108.1 (s, $-\text{CF}_2\text{CF}_3$); ^{31}P NMR (161 MHz) δ 13.4; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{ClF}_5\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 440.0212, found 440.0216.

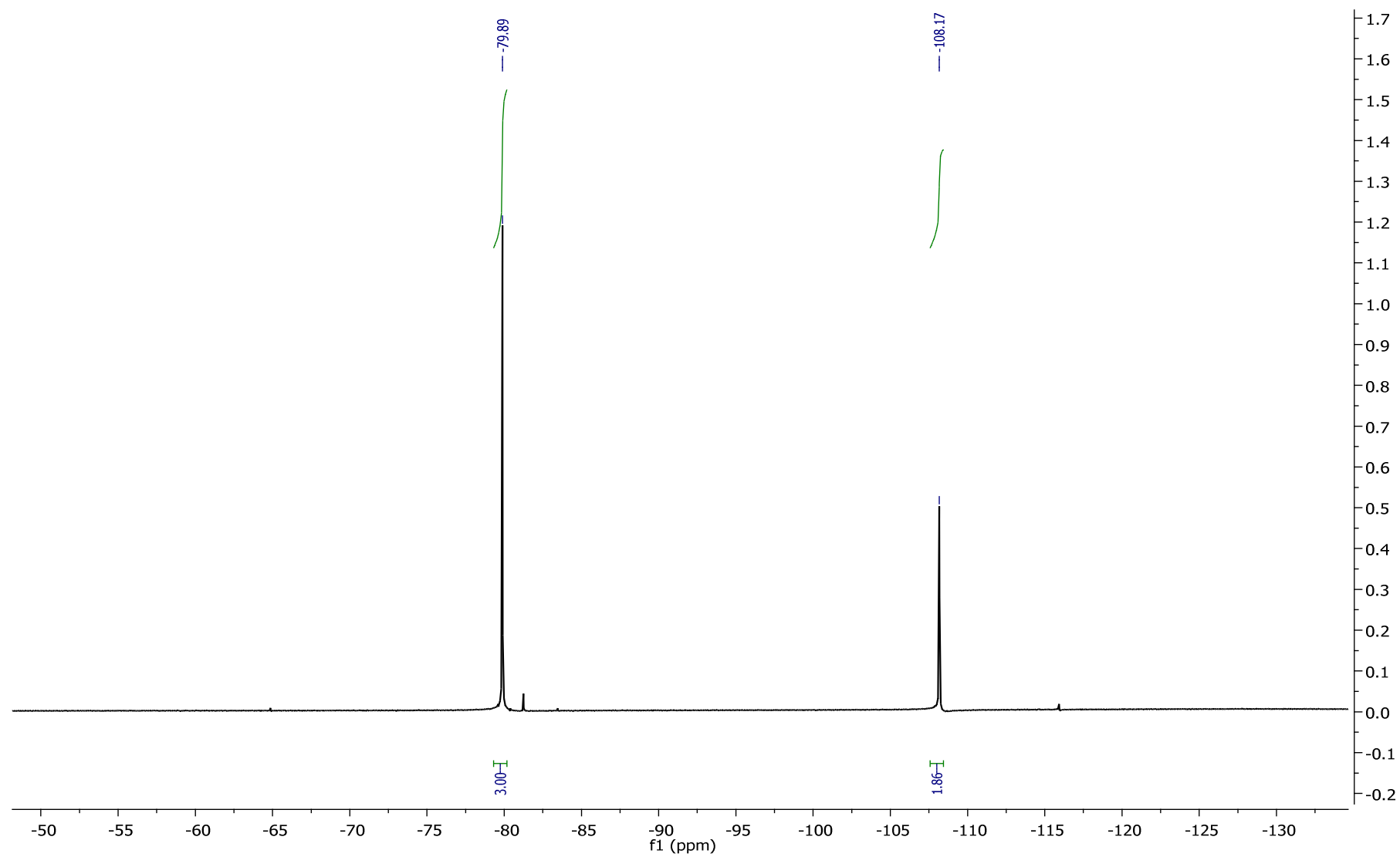
¹H NMR



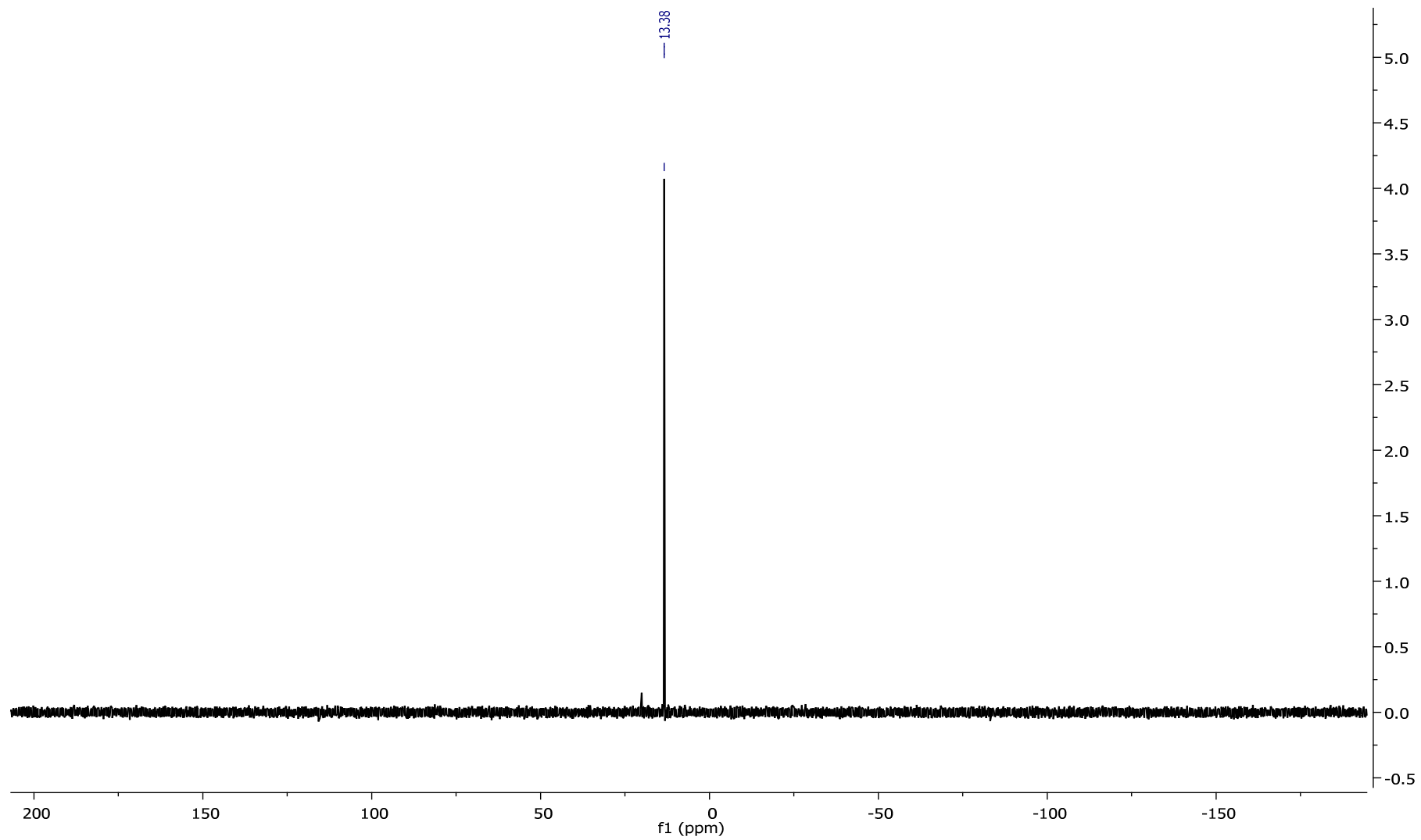
^{13}C NMR



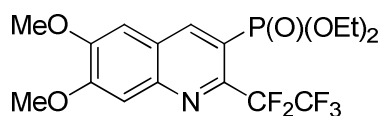
^{19}F NMR



^{31}P NMR

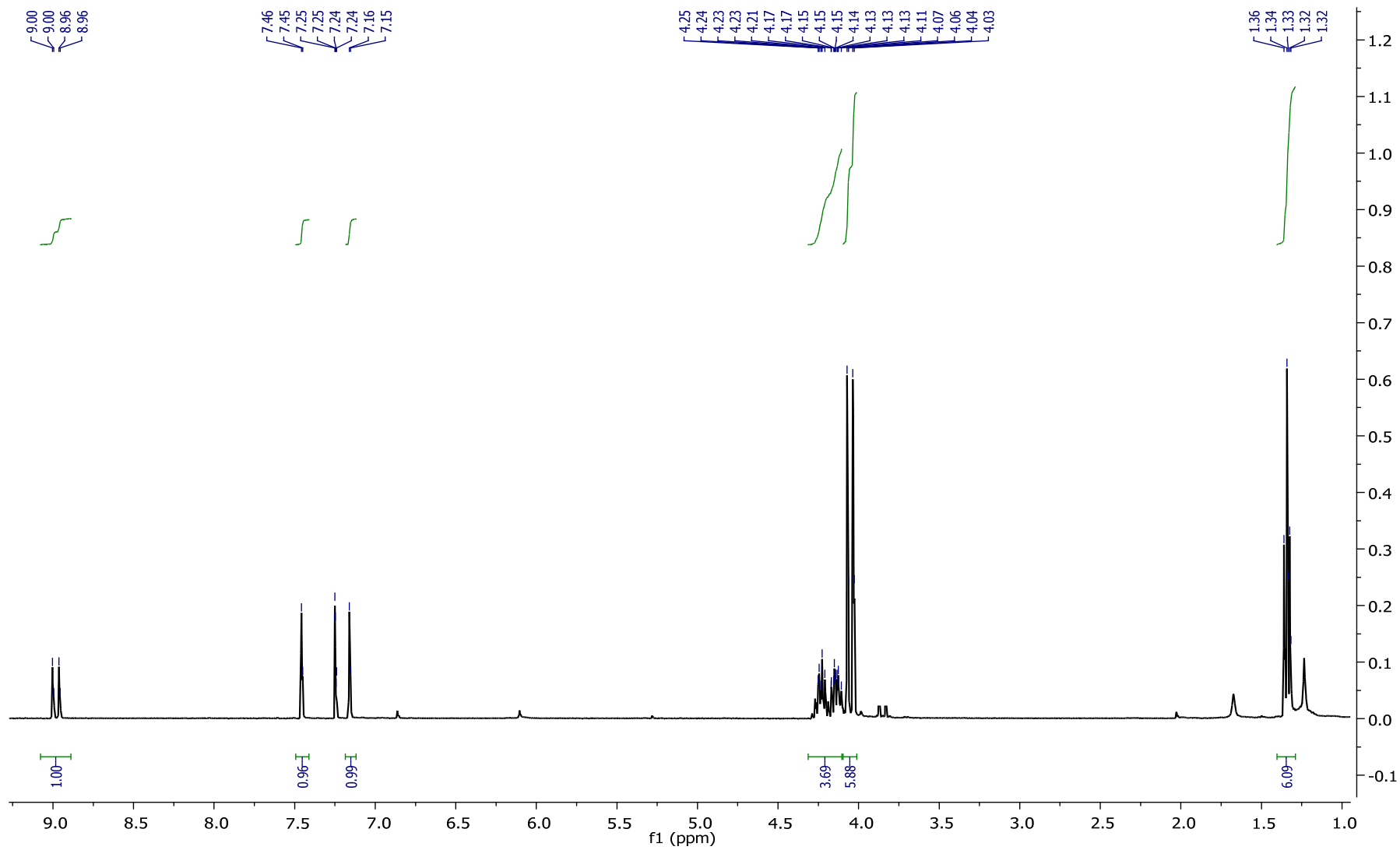


19. Diethyl (6,7-dimethoxy-2-(perfluoroethyl)quinolin-3-yl)phosphonate **4s**

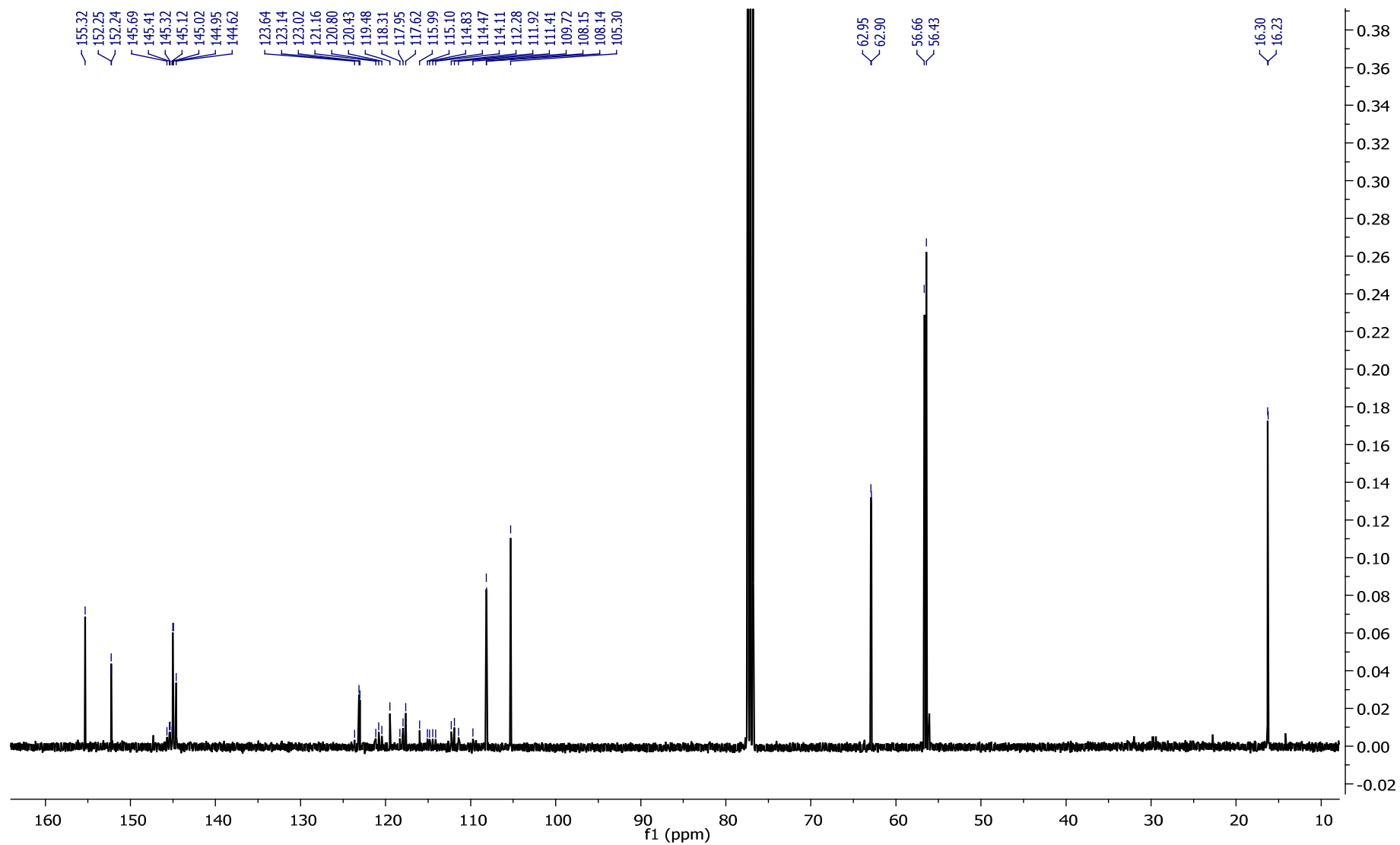


Colourless crystals (40%); Mp = 151–154 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.34 (t, $J = 7.0$ Hz, 6H), 4.04 (s, 3H), 4.07 (s, 3H), 4.13 (m, 2H), 4.24 (m, 2H), 7.16 (s, 1H), 7.46 (s, 1H), 8.97 (d, $^3J_{\text{H-P}} = 16.2$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.4$ Hz), 56.4, 56.7, 62.9 (d, $J = 5.9$ Hz), 105.3, 108.1, 111.9 (tq, $^1J_{\text{C-F}} = 256.7$ Hz, $^2J_{\text{C-F}} = 36.7$ Hz), 118.4 (d, $^1J_{\text{C-P}} = 187.6$ Hz), 119.3 (qt, $^1J_{\text{C-F}} = 288.2$ Hz, $^2J_{\text{C-F}} = 37.9$ Hz), 123.2 (d, $^3J_{\text{C-P}} = 11.7$ Hz), 144.6, 145.0 (d, $^2J_{\text{C-P}} = 6.8$ Hz), 145.3 (td, $^2J_{\text{C-F}} = 27.9$ Hz, $^2J_{\text{C-P}} = 9.5$ Hz), 152.2, 155.3; ^{19}F NMR (376 MHz) δ -80.1 (s, $-\text{CF}_2\text{CF}_3$), -108.1 (s, $-\text{CF}_2\text{CF}_3$); ^{31}P NMR (161 MHz) δ 15.1 (t, $^4J_{\text{F-P}} = 1.5$ Hz); HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{19}\text{F}_5\text{NNaO}_5\text{P}$ $[\text{M}+\text{Na}]^+$ 466.0813, found 466.0814.

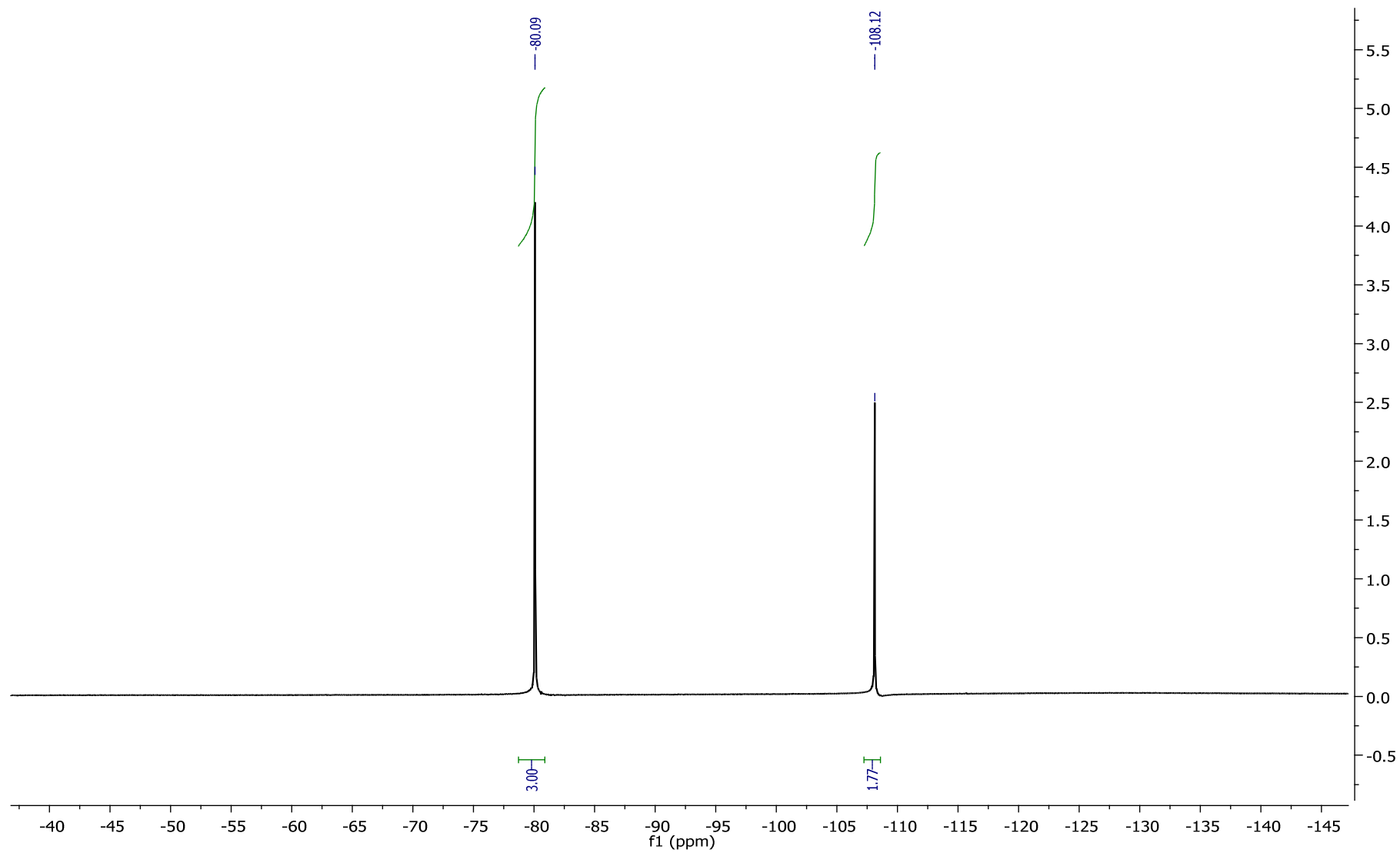
¹H NMR



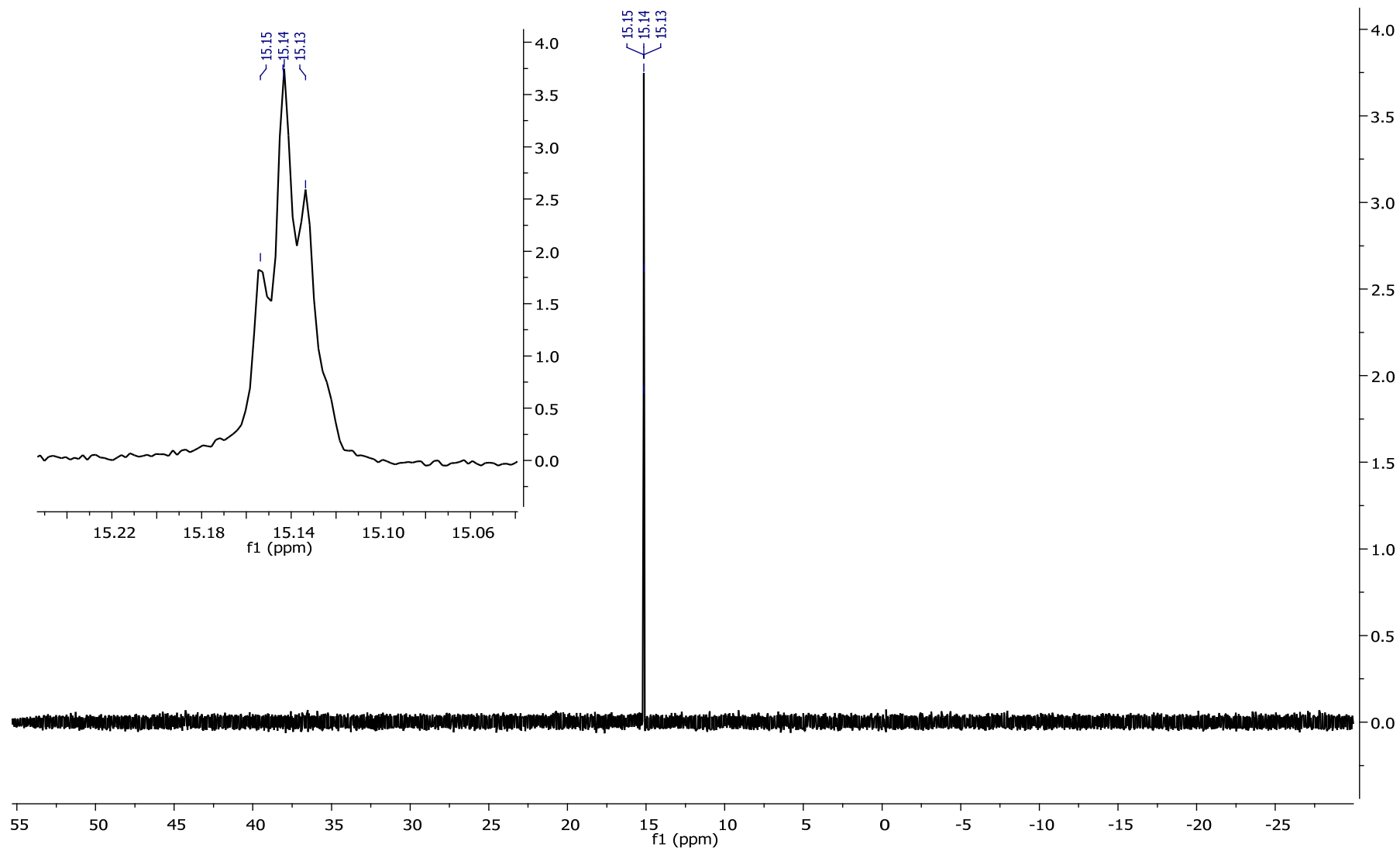
^{13}C NMR



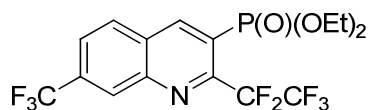
^{19}F NMR



^{31}P NMR

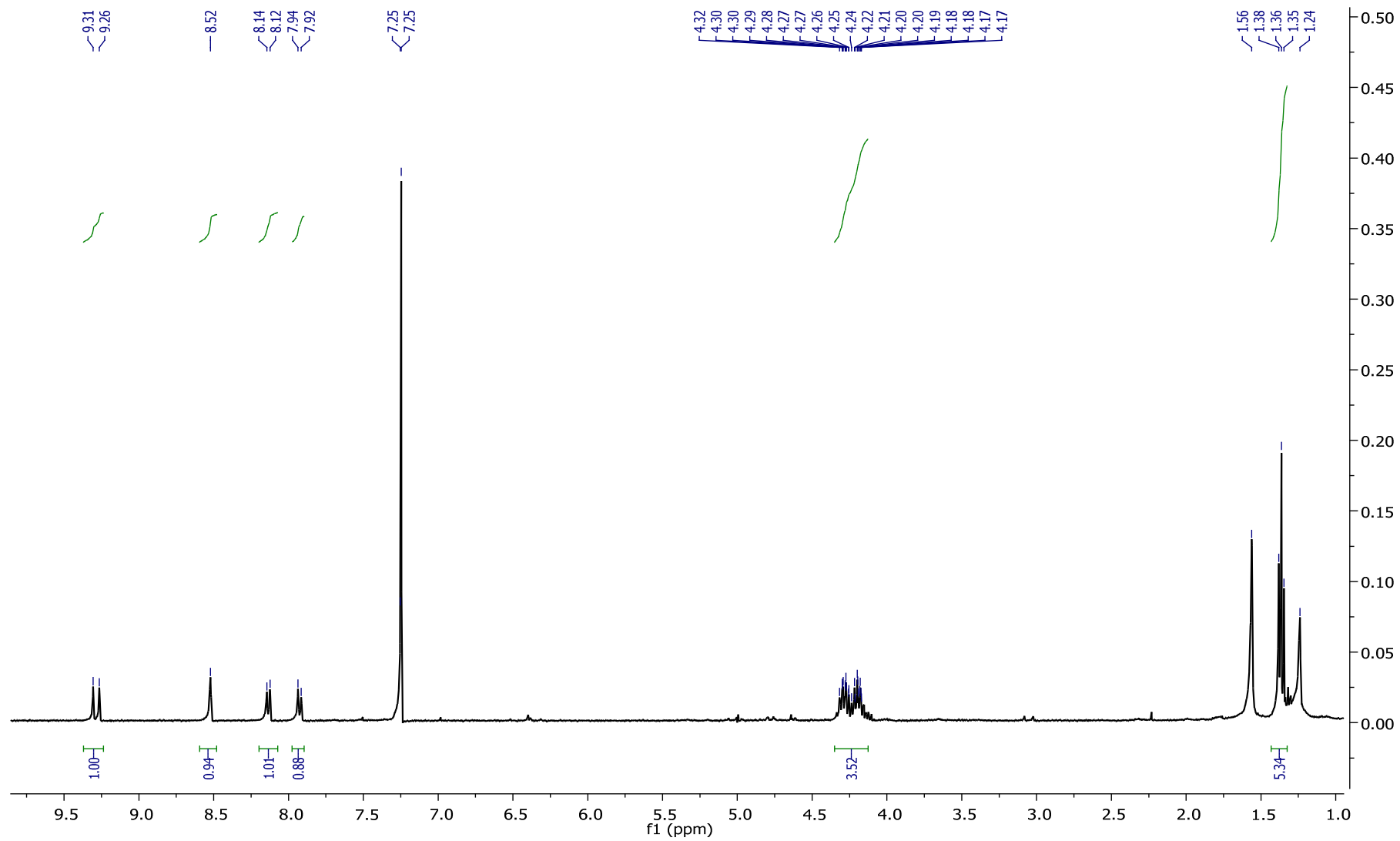


20. Diethyl (2-(perfluoroethyl)-7-(trifluoromethyl)quinolin-3-yl)phosphonate **4t**

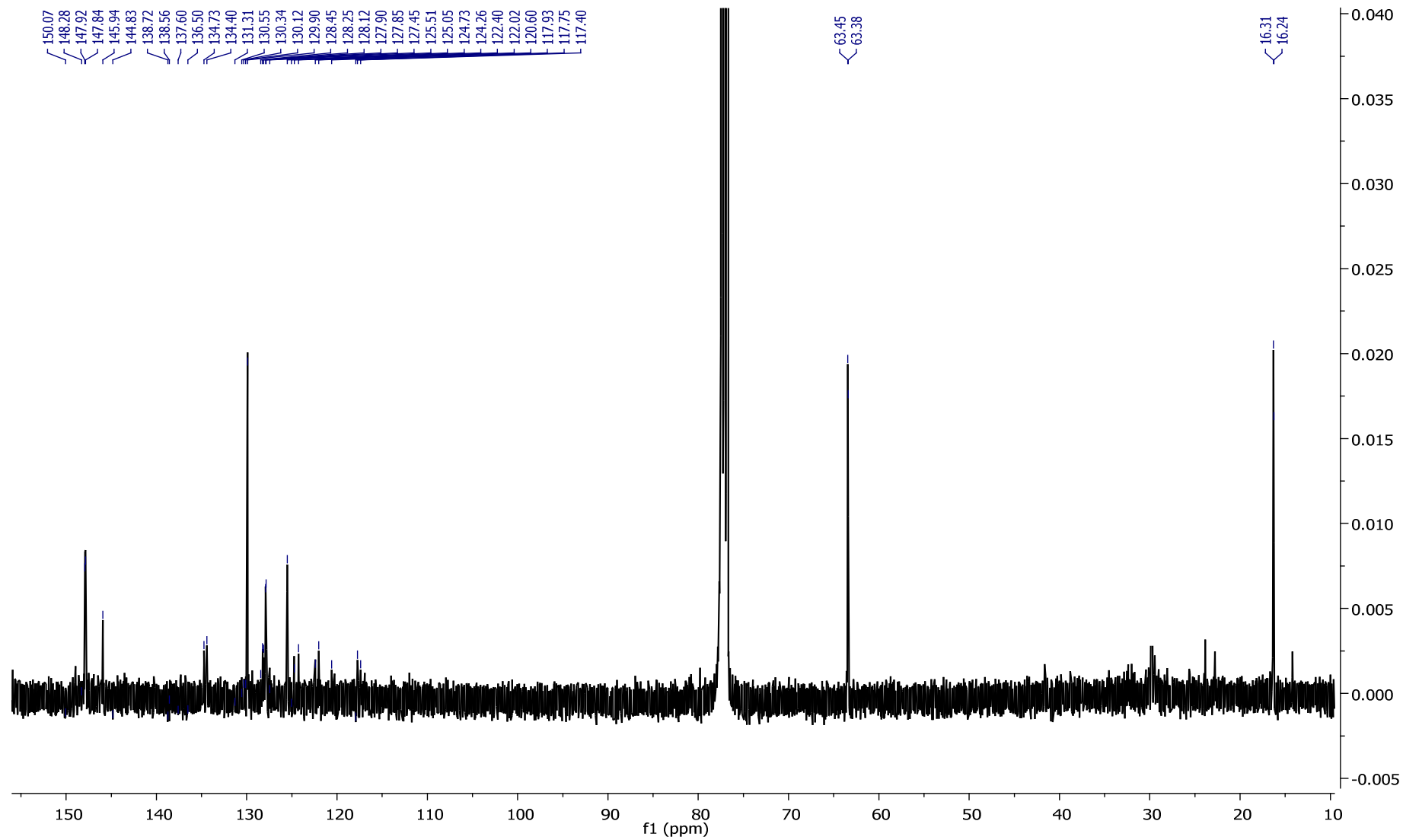


Yellowish oil (67%); ^1H NMR (400 MHz, CDCl_3) δ 1.36 (t, $J = 6.8$ Hz, 6H), 4.18 (m, 2H), 4.28 (m, 2H), 7.92 (d, $J = 9.5$ Hz, 1H), 8.13 (d, $J = 7.9$ Hz, 1H), 8.52 (s, 1H), 9.28 (d, $^3J_{\text{H-P}} = 16.3$ Hz, 1H); ^{13}C NMR (100 MHz) δ 16.3 (d, $J = 6.8$ Hz), 63.4 (d, $J = 6.4$ Hz), 112.9 (tq, $^1J_{\text{C-F}} = 266.4$ Hz, $^2J_{\text{C-F}} = 35.2$ Hz), 122.6 (d, $^1J_{\text{C-P}} = 187.1$ Hz), 122.7 (qt, $^1J_{\text{C-F}} = 288.9$ Hz, $^2J_{\text{C-F}} = 35.6$ Hz), 123.0 (q, $^1J_{\text{C-F}} = 276.0$ Hz), 125.5 (qd, $^4J_{\text{C-F}} = 2.0$ Hz, $^4J_{\text{C-P}} = 0.8$ Hz), 127.8 (qd, $^4J_{\text{C-F}} = 5.0$ Hz, $^4J_{\text{C-P}} = 1.3$ Hz), 128.3 (d, $^3J_{\text{C-P}} = 12.9$ Hz), 134.7 (q, $^2J_{\text{C-F}} = 33.8$ Hz), 145.9, 147.8 (d, $^2J_{\text{C-P}} = 8.6$ Hz), 147.9 (td, $^2J_{\text{C-F}} = 24.0$ Hz, $^2J_{\text{C-P}} = 10.0$ Hz); ^{19}F NMR (376 MHz) δ -62.9 (s, $-\text{CF}_3$), -79.8 (s, $-\text{CF}_2\text{CF}_3$), -108.3 (s, $-\text{CF}_2\text{CF}_3$); ^{31}P NMR (161 MHz) δ 12.9; HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{14}\text{F}_8\text{NNaO}_3\text{P}$ $[\text{M}+\text{Na}]^+$ 474.0574, found 474.0569.

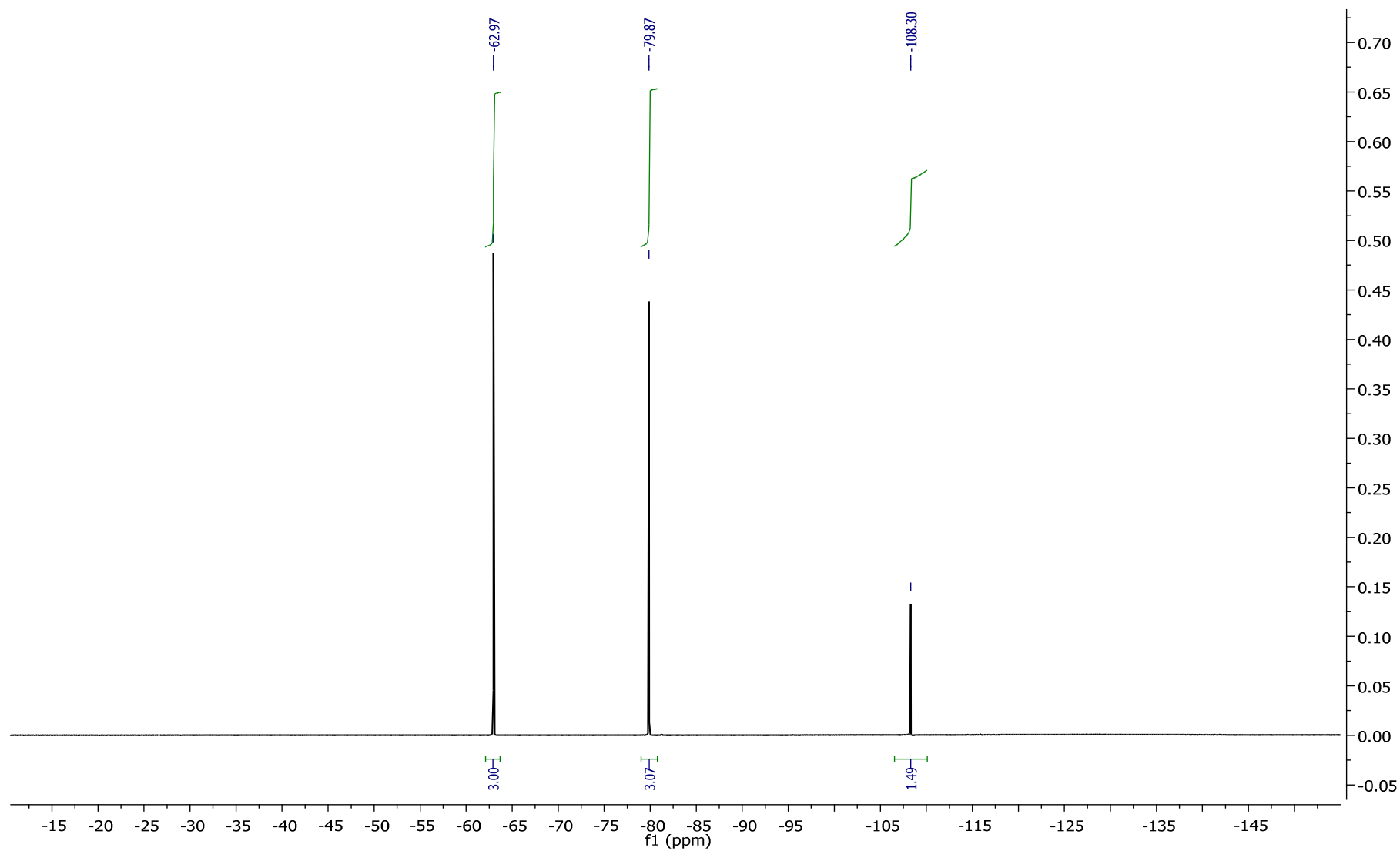
¹H NMR



^{13}C NMR



^{19}F NMR



^{31}P NMR

