Supporting Information

General Experimental

NMR Spectroscopy

^{1}H NMR spectra were recorded using either a Bruker AV400 spectrometer at 400 MHz, a Bruker AV600 spectrometer at 600 MHz or a Bruker AV800 spectrometer at 800 MHz. ^{13}C NMR spectra were recorded using either a Bruker AV400 spectrometer at 100 MHz a Bruker AV600 spectrometer at 150 MHz or a Bruker AV800 spectrometer at 200 MHz. Residual solvent peaks were used as an internal reference for ^{1}H NMR spectra (chloroform-*d* δ 7.26 ppm, benzene-d_6 δ 7.16 ppm, THF-d_8 δ 1.72, 3.58 ppm, methanol-d_4 δ 3.31 ppm, DMSO-d_6 δ 2.50 ppm) and ^{13}C NMR spectra (chloroform-*d* δ 77.16 ppm, benzene-d_6 δ 128.06 ppm, THF-d_8 δ 67.21, 25.31 ppm, methanol-d_4 δ 49.00 ppm, DMSO-d_6 δ 39.52 ppm).

Proton decoupled ^{31}P data were acquired at 162 MHz on a Bruker AV400 spectrometer or at 243 MHz on a Bruker AV600 spectrometer.

Coupling constants (*J*) are quoted to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used to describe ^{1}H NMR,: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The abbreviation d = doublet was used to describe ^{13}C or ^{31}P multiplicities.

Samples of the catalysts were measured using Wilmad® low pressure/vacuum NMR tubes prepared in the glovebox.

Infrared Spectroscopy

IR spectra were recorded on an Alpha-P Bruker FT-IR Spectrometer.

Mass Spectrometry

HRMS measurements were performed by an Agilent LC-MS time-of-flight mass spectrometer or on Waters Xevo G2-S QTOF (ESI or APPI). High resolution mass are given in *m/z*. Samples of the catalysts were prepared in the glovebox in dry and degassed MeOH.

Chromatography

Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade).

Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualized under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating.

Melting Points

Melting points were measured on a Büchi melting point apparatus, model B-540, and are uncorrected.

Optical Rotations

Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter.

Experimental procedures and reagents

All commercially available chemicals were used as purchased for the synthesis of substrates. All reactions out of the glovebox were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. Diethyl ether, dichloromethane, toluene and THF were purified by an Innovative Technology Solvent Delivery System.

The synthesis of diazaphospholene derivatives was performed in a MB-200-B MOD Glove Box Workstation (O_2 level <0.6 ppm, H_2O level <0.1 ppm) using oven-dried Schlenk flasks. Solvents were distilled and degassed using freeze-pump-that cycles prior to use in the glovebox. Tribromophosphine 99.999% was purchased from Apollo Scientific and used as received in the glovebox. Reduction reactions were set up in the glovebox in oven-dried test tubes sealed with rubber septa and secured with parafilm. Solid reagents were weighed into the reaction vessels using a Mettler-Toledo XS205 DualRange analytical balance. All analytical samples of air-sensitive diazaphospholenes were prepared inside the glovebox prior to analysis.

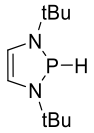
Full Reaction Optimization

Entry	Catalyst (mol %)	Reducing Agent (Eq.)	Solvent (M)	Time (min)	Yield (%)
1	P2 (10)	HBpin (1.1)	THF	10	93
2	P2 (10)	Ph_2SiH_2 (1.1)	THF	10	0
3	P3 (10)	Ph_2SiH_2 (1.1)	THF	10	85
4	P3 (10)	$PhSiH_3$ (1.1)	THF	10	87
5	P3 (10)	Ph_3SiH (1.1)	THF	60	0
6	P3 (10)	$PhMe_2SiH$ (1.1)	THF	60	0
7	P3 (10)	Et_3SiH (1.1)	THF	60	0
8	P3 (10)	$(EtO)_3SiH$ (1.1)	THF	60	0
9	P3 (10)	Me_2ClSiH (1.1)	THF	60	0
10	P3 (10)	Ph_2SiH_2 (0.55)	THF	10	86
11	P3 (10)	$PhSiH_3$ (0.35)	THF	10	92
12	P3 (10)	$PhSiH_3$ (0.35)	MeCN	10	67
13	P3 (10)	$PhSiH_3$ (0.35)	PhMe	10	88
14	P3 (10)	$PhSiH_3$ (0.35)	Et_2O	10	37
15	P3 (10)	$PhSiH_3$ (0.35)	CH_2Cl_2	10	81
16	P3 (5)	$PhSiH_3$ (0.35)	THF	60	93
17	**P3 (2)**	**$PhSiH_3$ (0.35)**	**THF**	**120**	**97**
18	P3 (1)	$PhSiH_3$ (0.35)	THF	6 h	75
19	-	$PhSiH_3$	THF	6 h	0

Experimental Procedures and Characterisation Data

Synthesis and Characterisation of Diazaphospholene Catalysts and Reagents P1-P3

1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole (P1)



$LiAlH_4$ (1.250 ml, 2.4 M in THF, 3.00 mmol) was added dropwise to a suspension of 2-bromo-1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole (2.79 g, 10 mmol)[1] in degassed THF (70 ml) at -78 °C. The reaction was stirred for 30 minutes at this temperature, then warmed to room temperature and stirred for another 30 minutes. The THF was removed *in vacuo*, and the residue was suspended in hexane and filtered through celite. The filtrate was collected and concentrated *in vacuo* to give a dark yellow oil. This oil was then purified by distillation (0.95 mbar, 50 – 53 °C) to give a pale yellow oil. All spectroscopic data matched that previously reported in the literature.[2]

Appearance: Pale yellow oil;

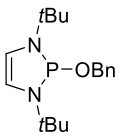
^{1}H NMR (400 MHz, Benzene-d_6): δ 6.16 (d, *J* = 184.5 Hz, 1H), 5.99 (d, *J* = 4.0 Hz, 2H), 1.15 (s, 18H) ppm;

^{31}P NMR (162 MHz Benzene-d_6): δ 57.46 (d, *J* = 184.6 Hz) ppm;

^{1}H NMR (400 MHz, THF-d_8): δ 6.04 (d, *J* = 4.0 Hz, 2H), 5.66 (d, *J* = 183.2 Hz, 1H), 1.20 (s, 18H) ppm;

^{31}P NMR (162 MHz, THF-d_8): δ 56.58 (d, *J* = 183.4 Hz) ppm.

2-(Benzyloxy)-1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole (P2)



Synthesised according to the procedure previously reported by our group.[3]

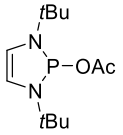
Appearance: White solid;

^{1}H NMR (800 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.26 (d, *J* = 7.1 Hz, 2 H), 7.21 (dd, *J* = 7.1, 7.1 Hz, 1 H), 6.08 (d, *J* = 1.7 Hz, 2 H), 4.22 (d, *J* = 4.7 Hz, 2 H), 1.40 (s, 18 H) ppm;

^{13}C NMR (201 MHz, $CDCl_3$): δ 140.1, 128.2 (x2), 127.1 (x2), 126.9, 112.3 (x2), 63.6 (d, $J_{c\text{-}p}$ = 3.9 Hz), 53.01 (d, $J_{c\text{-}p}$ = 16.3 Hz) (x2), 31.1 (d, $J_{c\text{-}p}$ = 10.1 Hz) (x6).ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 94.2 ppm.

1,3-Di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphol-2-yl acetate (P3)



Inside the glovebox, silver(I) acetate (2.50 g, 15.0 mmol) was added portionwise to a solution of 2-bromo-1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaphosphole[1] (4.19 g, 15.0 mmol) in THF (30 mL) at room temperature. The reaction was stirred for 3 hours, after which the volatiles were removed *in vacuo*. The residue was suspended in toluene and filtered through celite. The filtrate was concentrated *in vacuo* to give a light brown oil (3.14 g, 81 %).

Appearance: Light brown oil;

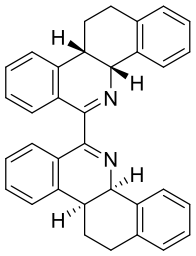
^{1}H NMR (400 MHz, Benzene-d_6) δ 5.98 (d, *J* = 1.7 Hz, 2H), 1.69 (s, 3H), 1.34 (d, *J* = 1.6 Hz, 18H) ppm;

^{13}C NMR (101 MHz, Benzene-d_6) δ 171.88, 113.94 (d, *J* = 9.1 Hz), 53.74 (d, *J* = 12.3 Hz), 30.97 (d, *J* = 10.5 Hz), 22.86 ppm;

^{31}P NMR (162 MHz, Benzene-d_6): δ 104.5 ppm.

Synthesis and Characterization of Precatalyst P5 and its Intermediates

(4b*R*, 4'b*R*,10b*S*,10'b*S*)-4b, 4'b,10b,10'b,11,11',12,12'-Octahydro-6,6'-bibenzo[*c*]phenanthridine P5a



According to the procedure previously reported by our group,[3] (4bR,10bS)-4b,10b,11,12-tetrahydrobenzo[c]phenanthridin-6(5H)-one (499 mg, 2 mmol) was dissolved in dry toluene (20 mL), before freshly distilled phosphoryl trichloride (1.17 mL, 12.5 mmol) was added dropwise *via* syringe to the stirred mixture. The mixture was heated at 90 ^{o}C for 2 hours, after which, it was cooled to room temperature and the solvent was removed *in vacuo*. The resulting residue was cooled to -30 ^{o}C in an acetonitrile/LN_2 bath, and a mixture of 5 % Et_3N in Et_2O was added dropwise to the flask. The mixture was then stirred at room temperature for 10 minutes. It was then filtered over basic alumina, eluting with 5 % Et_3N in Et_2O. The filtrate was concentrated under reduced pressure to give the desired imidoyl chloride, which was used immediately without further purification.

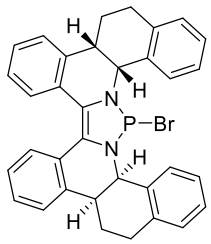
Inside the glovebox, a flame-dried Schlenk flask was charged with $NiBr_2(PPh_3)_2$ (743 mg, 1 mmol), PPh_3 (525 mg, 2 mmol), Zn dust (392 mg, 6 mmol), oil-free NaH (384 mg, 16 mmol) and the crude imidoyl chloride in dry and degassed toluene (13 mL). The flask was removed from the glovebox and heated to 50 ^{o}C and stirred for 16 hours. The reaction was cooled and added dropwise to a flask containing a saturated solution of EDTA in ammonia (25 %) at 0 ^{o}C. The solution was diluted with EtOAc, and the resulting dark grey mixture was stirred under air at room temperature until good separation of the biphasic mixture was achieved (approximately 3 hours). The aqueous layer was separated and extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude material by flash chromatography (gradient 10 %-40 % EtOAc:pentane) afforded the title product

as an off-white solid (241 mg, 52 %). All spectroscopic data matched that previously reported in the literature.[4]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.36 (td, *J* = 7.4, 1.3 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.09 (m, 3H), 4.88 (d, *J* = 6.2 Hz, 1H), 3.15 (ddd, *J* = 12.6, 6.2, 3.1 Hz, 1H), 3.06 – 2.93 (m, 2H), 2.23 (tdd, *J* = 12.8, 10.5, 6.7 Hz, 1H), 1.96 – 1.86 (m, 1H) ppm;

HRMS (APCI): calculated for $[C_{34}H_{28}N_2+H]^+$: 465.2325, found: 465.2330.

2-Bromo-1,3,2-diazaphospholene P5b



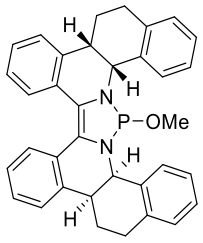
PBr_3 (22.3 µL, 237 µmol) was added dropwise to a solution of **P5a** (110 mg, 237 µmol) and cyclohexene (71.9 µL, 710 µmol) in CH_2Cl_2 (4 mL) at room temperature. The reaction was stirred for 1 hour, then concentrated *in vacuo*. The residue was suspended in hexane (2 mL) and sonicated. The precipitate was removed by filtration and the filtrate collected and concentrated *in vacuo* to give a bright yellow powder (130 mg, 95 %). All spectroscopic data matched that previously reported in the literature.[4]

Appearance: Yellow solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.69 (dd, *J* = 7.4, 2.7 Hz, 2H), 7.39 – 7.27 (m, 8H), 7.24 – 7.11 (m, 4H), 4.94 (dd, *J* = 9.5, 3.0 Hz, 2H), 3.30 – 3.14 (m, 4H), 3.02 (ddd, *J* = 18.0, 11.7, 7.0 Hz, 2H), 2.39 (qd, *J* = 13.2, 6.6 Hz, 2H), 2.08 – 1.94 (m, 2H) ppm;

^{31}P NMR (162 MHz, $CDCl_3$): δ 180.6 ppm.

Precatalyst P5



A flame-dried Schlenk tube inside the glovebox was charged with bromodiazaphospholene **P5b** (110 mg, 0.191 mmol) and solid sodium methanolate (21 mg, 0.382 mmol) followed by THF (0.5 mL). The mixture was stirred for one hour, then evaporated to dryness under high vacuum. The crude compound was suspended in toluene (1 mL) and stirred for several minutes. Finally, the suspension was filtered on a small pad of celite, rinsed with toluene (3x0.5 mL) and evaporated to dryness again to give the title compound as a bright yellow solid (94 mg, 93 %). All spectroscopic data matched that previously reported in the literature.[4]

Appearance: Yellow solid;

Melting Point: 124 – 127 °C;

$[\alpha]_D^{20}$: −12.4 (c = 1.0, CH_2Cl_2);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.25 – 7.00 (m, 14H), 4.64 (dd, *J* = 5.9, 2.3 Hz, 1H), 4.57 – 4.49 (m, 1H), 3.18 – 2.85 (m, 6H), 2.71 (d, *J* = 9.4 Hz, 3H), 2.46 – 2.22 (m, 2H), 1.93 (ddd, *J* = 18.0, 11.8, 3.7 Hz, 2H);

^{31}P NMR (162 MHz, $CDCl_3$): δ 104.6 ppm;

HRMS (APCI): calculated for $[C_{35}H_{31}N_2OP+H]^+$: 527.2247, found: 527.2250.

Synthesis and Characterisation of Substrates 1a-1w and their Intermediates

Substrates **1a-1j**, **1q-1t**, and **1v**-**1w** are commercially available and were used as received.

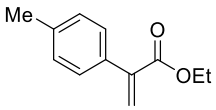
General Procedure for the olefination of ethyl aryl-2-oxoacetates (GP 1)

A solution of KHMDS (0.997 g, 5.00 mmol) in THF (5.0 mL) was added dropwise to a solution of methyltriphenylphosphonium bromide (1.786 g, 5.00 mmol) in THF (10.0 mL) at -78 ^{o}C. After stirring for 15 minutes, the reaction was allowed to warm to room temperature and stirred for a further 1 hour. The solution was then cooled to -78 ^{o}C and a solution of ethyl aryl-2-oxoacetate (5.00 mmol) in THF (5.0 mmol) was added dropwise. The reaction was stirred for 1 hour at -78 ^{o}C, then allowed to warm to room temperature and stirred until analysis by TLC indicated complete consumption of the starting material. The reaction was quenched by the addition of 2 M HCl (10 mL) and the product extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude residue was dissolved in EtOH (15 mL), and $ZnCl_2$ (2.044 g, 15.0 mmol) was added. The resulting suspension was stirred vigorously for 30 minutes, after which, the precipitate was removed by filtration and the filtrate concentrated *in vacuo*. Purification of the crude residue by flash chromatography yielded the desired products.

General Procedure for the hydrolysis of ethyl 2-aryl-acrylates (GP 2)

A mixture of ethyl 2-aryl-acrylate (3.00 mmol) and lithium hydroxide (359 mg, 15.0 mmol) in THF:MeOH:H_2O (1:1:1, 12 mL) was heated to 90 ^{o}C and stirred vigorously until analysis by TLC indicated complete consumption of the starting material. After cooling to room temperature, the reaction mixture was acidified with 2 M HCl (8 mL) and the product extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*, giving the desired product.

Ethyl 2-(*p*-tolyl)acrylate (S1)



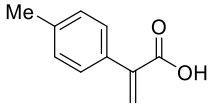
The title compound was synthesized from ethyl 2-(*p*-tolyl)-2-oxoacetate (961 mg, 5.00 mmol) according to **GP 1**, giving **S1** as a colourless oil (748 mg, 79 %). All spectroscopic data matched that previously reported in the literature.[4]

Appearance: Colourless oil;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.29 (d, *J* = 1.3 Hz, 1H), 5.85 (d, *J* = 1.3 Hz, 1H), 4.29 (d, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 141.5, 138.0, 134.0, 128.9, 128.1, 125.6, 61.0, 21.2, 14.3 ppm.

2-(*p*-Tolyl)acrylic acid (1k)



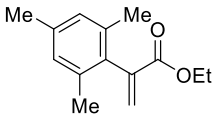
The title compound was synthesized from ethyl 2-(*p*-tolyl)acrylate (571 mg, 3.00 mmol) according to **GP 2**, giving **1k** as a white solid (460 mg, 95 %). All spectroscopic data matched that previously reported in the literature.[4]

Appearance: White solid;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.1 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.51 (s, 1H), 6.01 (s, 1H), 2.38 (s, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 140.5, 138.3, 133.3, 128.9, 128.8, 128.4, 21.3 ppm.

Ethyl 2-mesitylacrylate (S2)



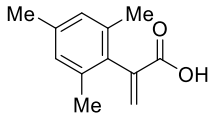
The title compound was synthesized from ethyl 2-mesityl-2-oxoacetate (1.101 g, 5.00 mmol) according to **GP 1**, giving **S2** as a colourless oil (843 mg, 77 %). All spectroscopic data matched that previously reported in the literature.[5]

Appearance: Colourless oil;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.89 (s, 2H), 6.64 (d, *J* = 1.8 Hz, 1H), 5.62 – 5.58 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 2.15 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.72, 140.26, 137.15, 136.10, 134.08, 129.22, 128.16, 61.03, 21.19, 20.35, 14.36 ppm.

2-Mesitylacrylic acid (1l)



The title compound was synthesized from ethyl 2-mesitylacrylate (655 mg, 3.00 mmol) according to **GP 2**, giving **1l** as a white solid (523 mg, 92 %).

Appearance: White solid;

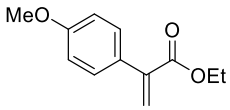
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.90 (s, 2H), 6.76 (s, 1H), 5.75 (s, 1H), 2.29 (s, 3H), 2.16 (s, 6H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.62, 139.33, 137.65, 136.21, 133.17, 131.80, 128.31, 21.20, 20.37 ppm;

IR (ATR): ν_{max} = 2917, 1687, 1620, 1420, 1306, 1221, 962, 851 cm^{-1};

HRMS (ESI): calculated for $[C_{12}H_{14}O_2\text{-}H]^-$: 189.0921, found: 189.0920.

Ethyl 2-(4-methoxyphenyl)acrylate (S3)



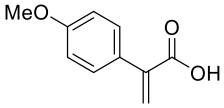
The title compound was synthesized from ethyl 2-(4-methoxyphenyl)-2-oxoacetate (1.041 g, 5.00 mmol) according to **GP 1**, giving **S3** as a colourless oil (624 mg, 61 %). All spectroscopic data matched that previously reported in the literature.[4]

Appearance: Colourless oil;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.25 (s, 1H), 5.83 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.23, 159.70, 141.04, 129.61, 129.35, 125.08, 113.64, 61.19, 55.42, 14.37 ppm.

2-(3,5-Difluorophenyl)acrylic acid (1m)



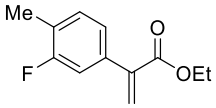
The title compound was synthesized from ethyl 2-(4-methoxyphenyl)acrylate (619 mg, 3.00 mmol) according to **GP 2**, giving **1m** as a white solid (389 mg, 73 %). All spectroscopic data matched that previously reported in the literature.[4]

Appearance: White solid;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.34 (m, 2H), 7.02 – 6.82 (m, 2H), 6.46 (s, 1H), 5.96 (s, 1H), 3.83 (s, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.22, 159.86, 140.03, 129.82, 128.68, 128.13, 113.72, 55.46 ppm.

Ethyl 2-(3-Fluoro-4-methylphenyl)acrylate (S4)



The title compound was synthesized from ethyl 2-(3-fluoro-4-methylphenyl)-2-oxoacetate (1.051 g, 5.00 mmol) according to **GP 1**, giving **S4** as a colourless oil (705 mg, 68 %).

Appearance: Colourless oil;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.06 (m, 3H), 6.33 (d, *J* = 1.1 Hz, 1H), 5.88 (d, *J* = 1.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.28 (d, *J* = 1.8 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H);

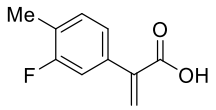
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.61, 160.97 (d, *J* = 244.2 Hz), 140.56 (d, *J* = 2.1 Hz), 136.21 (d, *J* = 8.1 Hz), 131.13 (d, *J* = 5.5 Hz), 126.73, 124.92 (d, *J* = 17.2 Hz), 123.78 (d, *J* = 3.4 Hz), 115.10 (d, *J* = 23.5 Hz), 61.35, 14.50 (d, *J* = 3.5 Hz), 14.35;

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.88

IR (ATR): ν_{max} = 2983, 1718, 1509, 1232, 1201, 1161, 1125, 1079 cm^{-1};

HRMS (ESI): calculated for $[C_{12}H_{13}FO_2+Na]^+$: 231.0792, found: 231.0797.

2-(3-Fluoro-4-methylphenyl)acrylic acid (1n)



The title compound was synthesized from ethyl 2-(3-fluoro-4-methylphenyl)acrylate (625 mg, 3.00 mmol) according to **GP 2**, giving **1n** as a white solid (311 mg, 58 %).

Appearance: White solid;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.70 (bs, 1H), 7.23 – 7.08 (m, 3H), 6.54 (d, *J* = 1.1 Hz, 1H), 6.03 (d, *J* = 1.0 Hz, 1H), 2.29 (d, *J* = 1.9 Hz, 3H);

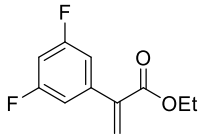
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.76, 160.98 (d, *J* = 244.4 Hz), 139.52, 135.46 (d, *J* = 8.0 Hz), 131.24 (d, *J* = 5.5 Hz), 129.77, 125.28 (d, *J* = 17.2 Hz), 123.96 (d, *J* = 3.4 Hz), 115.30 (d, *J* = 23.6 Hz), 14.52 (d, *J* = 3.6 Hz);

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.60.

IR (ATR): ν_{max} = 2930, 1681, 1610, 1418, 1254, 872, 736, 651 cm^{-1};

HRMS (ESI): calculated for $[C_{10}H_9FO_2\text{-}H]^-$: 179.0514, found: 179.0507.

Ethyl 2-(3,5-difluorophenyl)acrylate (S5)



The title compound was synthesized from ethyl 2-(3,5-difluorophenyl)-2-oxoacetate (1.071 g, 5.00 mmol) according to **GP 1**, giving **S5** as a colourless oil (751 mg, 71 %). All spectroscopic data matched that previously reported in the literature.[4]

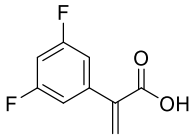
Appearance: Colourless oil;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.98 (d, *J* = 6.7 Hz, 2H), 6.78 (t, *J* = 8.9 Hz, 1H), 6.43 (s, 1H), 5.94 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.84, 163.96 (d, *J* = 13.0 Hz), 161.50 (d, *J* = 12.8 Hz), 139.84, 128.36, 111.59 (dd, *J* = 19.1, 7.3 Hz), 103.66 (t, *J* = 25.4 Hz), 61.59, 14.31 ppm;

^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.31.

2-(3,5-Difluorophenyl)acrylic acid (1o)



The title compound was synthesized from ethyl 2-(3,5-difluorophenyl)acrylate (637 mg, 3.00 mmol) according to **GP 2**, giving **1o** as a white solid (328 mg, 59 %). All spectroscopic data matched that previously reported in the literature.[4]

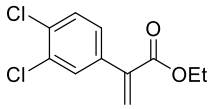
Appearance: White solid;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.00 (d, *J* = 7.0 Hz, 2H), 6.81 (t, *J* = 8.8 Hz, 1H), 6.63 (s, 1H), 6.10 (s, 1H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.68, 164.00 (d, *J* = 12.9 Hz), 161.53 (d, *J* = 12.9 Hz), 139.00 (t, *J* = 9.9 Hz), 138.66 (t, *J* = 2.5 Hz), 131.38, 111.78 (d, *J* = 18.9, 7.1 Hz), 103.99 (t, *J* = 25.3 Hz) ppm;

^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.94.

Ethyl 2-(3,4-dichlorophenyl)acrylate (S6)



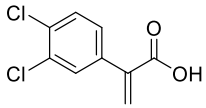
A mixture of ethyl 2-(3,4-dichlorophenyl)acetate (3.50 g, 15.0 mmol), paraformaldehyde (1.26 g, 42.0 mmol), tetrabutylammonium iodide (220 mg, 0.60 mmol) and potassium carbonate (6.20 g, 45.0 mmol) in toluene (20.0 mL) was heated to 60 °C and stirred for 16 hours. After cooling to room temperature, the reaction mixture was diluted with water (10 mL) and the product extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude residue was purified by flash chromatography to give the desired product **S6** as a colourless oil (2.04 g, 55 %). All spectroscopic data matched that previously reported in the literature.[4]

Appearance: Colourless oil;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 2.1 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.27 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.42 (d, *J* = 0.9 Hz, 1H), 5.92 (d, *J* = 0.9 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.00, 139.56, 136.79, 132.46, 132.34, 130.44, 130.15, 128.06, 127.88, 61.57, 14.33 ppm.

2-(3,4-Dichlorophenyl)acrylic acid (1p)



The title compound was synthesized from ethyl 2-(3,4-dichlorophenyl)acrylate (735 mg, 3.00 mmol) according to **GP 2**, giving **1p** as a white solid (518 mg, 80 %).

Appearance: White solid;

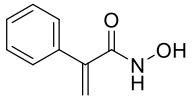
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.61 (s, 1H), 6.07 (s, 1H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.79, 138.51, 135.99, 132.84, 132.49, 131.02, 130.56, 130.27, 127.98 ppm;

IR (ATR): ν_{max} = 2994, 1690, 1613, 1475, 1434, 1229, 903, 822 cm^{-1};

HRMS (ESI): calculated for $[C_9H_6Cl_2O_2\text{-}H]^-$: 214.9672, found: 214.9673.

***N*-Hydroxy-2-phenylacrylamide (1u)**



Oxalyl chloride (263 µL, 3.00 mmol) was added dropwise to a solution of 2-phenylacrylic acid (296 mg, 2.00 mmol) and DMF (2 drops) in CH_2Cl_2 (10.0 mL) at 0 °C. The reaction was allowed to warm to room temperature and stirred for a further 3 hours, after which, the volatile components were

removed *in vacuo*. The crude acid chloride was diluted with EtOAc (10.0 mL) and added dropwise to a mixture of sodium carbonate (254 mg, 2.40 mmol) and hydroxylamine hydrochloride (168 mg, 2.42 mmol) in EtOAc (10.0 mL) and water (10.0 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 12 hours. The two phases were separated and the product was further extracted from the aqueous phase with EtOAc (2 x 10 mL). The combined organic phases were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo* to give the title compound **1u** as an off-white solid (256 mg, 78 %).

Appearance: Off-white solid;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 2H), 7.38 (h, *J* = 3.9, 3.5 Hz, 5H), 6.25 – 6.15 (m, 1H), 5.70 (d, *J* = 0.9 Hz, 1H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.58, 140.94, 135.63, 129.17, 129.04, 128.25, 123.76 ppm;

IR (ATR): ν_{max} = 3281, 3098, 1641, 1594, 1416, 945, 775, 702 cm^{-1};

HRMS (ESI): calculated for $[C_9H_9NO_2+H]^+$: 164.0706, found: 164.0703.

Synthesis and Characterisation of Products 2a-2w

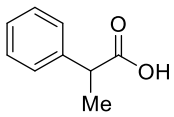
General Producedure for the Reduction of β-Substituted Acrylic Acids (GP 3)

Inside the glovebox, an oven-dried reaction tube was charged with $PhSiH_3$ (8.63 µL, 70.0 µmol, 0.35 eq.), catalyst **P3** (1.03 mg, 4.00 µmol 2 mol %) and THF (200 µL). The substrate (0.2 mmol) was added and the vial was sealed with a rubber septum, secured with parafilm and removed from the glovebox. After 2 hours, the reaction was quenched with 2 M HCl (500 µL), and the product extracted with EtOAc (3 x 1 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography to give the desired compound.

General Producedure for the Reduction of α,β-Disubstituted Acrylic Acids (GP 4)

Inside the glovebox, an oven-dried reaction tube was charged with $PhSiH_3$ (17.3 µL, 140 µmol, 0.70 eq.), catalyst **P3** (1.03 mg, 4.00 µmol 2 mol %) and THF (200 µL). The substrate (0.2 mmol) was added and the vial was sealed with a rubber septum, secured with parafilm and removed from the glovebox. After 6 hours, the reaction was quenched with 2 M HCl (500 µL), and the product extracted with EtOAc (3 x 1 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by flash chromatography to give the desired compound.

2-Phenylpropanoic acid (**2a**)



Using **GP 3**, the title compound was obtained from 2-phenylacrylic acid (29.6 mg, 0.2 mmol) as a white solid (29.0 mg, 97 %). All spectroscopic data was in accordance with that previously reported in the literature.[6]

Appearance: White solid;

Melting Point: 101.2 – 103.7 °C;

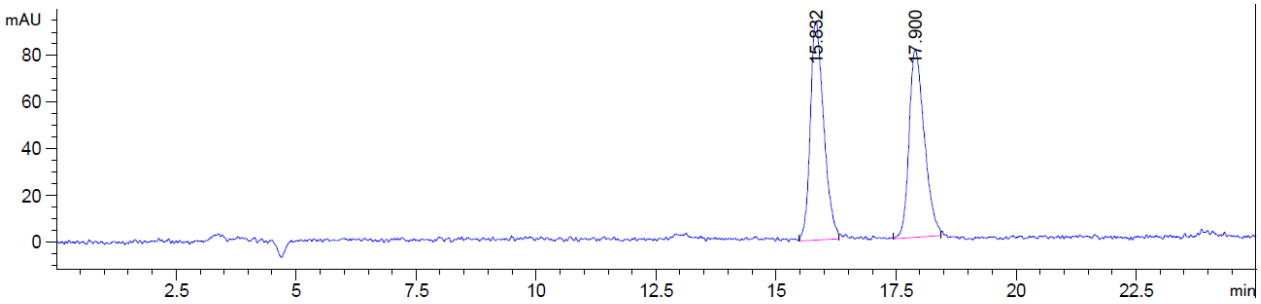
^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.44 (bs, 1H), 7.40 – 7.23 (m, 5H), 3.74 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.51, 139.75, 128.70, 127.61, 127.41, 45.31, 18.12 ppm.

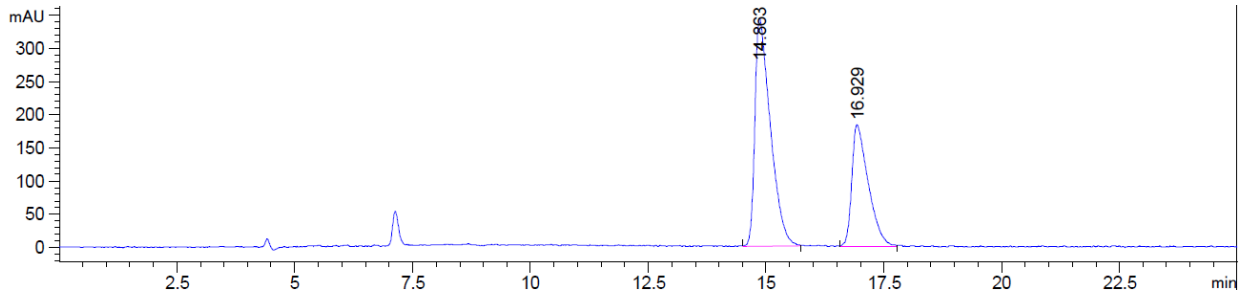
An enantioenriched sample of **2a** was prepared from 2-phenylacrylic acid (14.8 mg, 0.1 mmol) using a modified version of **GP 3** with pre-catalyst **P4** (5.27 mg, 10.0 µmol, 10 mol %) and pinacol borane (16.0 µL, 0.11 mmol) in THF (100 µL) giving the desired compound as a white solid (12.6 mg, 84 %).

$[\alpha]_D^{20}$: +17.1 (c = 1.0, $CHCl_3$);

Chiral HPLC (Chiralpak IB, 98.9:1.0:0.1 hexane:*i*-PrOH:TFA, 1.0 mL/min, 226 nm): t_R (major) 14.9 min, t_R (minor) 16.9 min, 64:36 er.

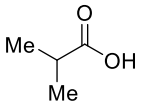


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.832	BV	0.2671	1824.28418	93.73420	50.7657
2	17.900	BV	0.3240	1769.25305	79.99163	49.2343



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.863	VV	0.3144	7847.31396	343.65192	63.8225
2	16.929	VV	0.3337	4448.20605	182.92577	36.1775

Isobutyric acid (**2b**)



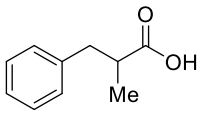
Using **GP 3**, the title compound was obtained from methacrylic acid (17.2 mg, 0.2 mmol) as a colourless film (17.2 mg, 98 %). All spectroscopic data was in accordance with that previously reported in the literature.[7]

Appearance: Colourless film;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.59 (hept, *J* = 7.0 Hz, 1H), 1.20 (d, *J* = 7.0 Hz, 6H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.23, 33.93, 18.90 ppm.

2-Methyl-3-phenylpropanoic acid (**2c**)



Using **GP 3**, the title compound was obtained from 2-benzylacrylic acid (32.4 mg, 0.2 mmol) as a white solid (30.0 mg, 91 %). All spectroscopic data was in accordance with that previously reported in the literature.[8]

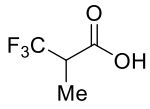
Appearance: White solid;

Melting Point: 37.6 – 38.6 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.40 (bs, 1H), 7.35 – 7.15 (m, 5H), 3.09 (dd, *J* = 13.3, 6.4 Hz, 1H), 2.83 – 2.72 (m, 1H), 2.68 (dd, *J* = 13.4, 8.0 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.31, 139.15, 129.14, 128.57, 126.57, 41.33, 39.43, 16.64 ppm.

3,3,3-Trifluoro-2-methylpropanoic acid (**2d**)



Using **GP 3**, the title compound was obtained from 2-(trifluoromethyl)acrylic acid (28.0 mg, 0.2 mmol) as a colourless film (23.7 mg, 83 %). All spectroscopic data was in accordance with that previously reported in the literature.[9]

Appearance: Colourless film;

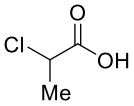
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 3.27 (hep, *J* = 7.7 Hz, 1H), 1.47 (d, *J* = 7.3 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.92, 124.69 (q, *J* = 279.2 Hz), 44.56 (q, *J* = 29.2 Hz), 11.13 (q, *J* = 2.8 Hz) ppm;

^{19}F NMR (376 MHz, Chloroform-*d*) δ -70.06 ppm.

Using **GP 4**, the title compound was obtained from (*E*)-2-methyl-3-phenylacrylic acid (32.4 mg, 0.2 mmol) as a white solid (28.1 mg, 86 %).

2-Chloropropanoic acid (**2e**)



Using **GP 3**, the title compound was obtained from 2-chloroacrylic acid (21.3 mg, 0.2 mmol) as a white solid (19.7 mg, 91 %). All spectroscopic data was in accordance with that previously reported in the literature.[10]

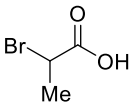
Appearance: White solid;

Melting Point: 81.6 – 83.8 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (bs, 1H), 4.46 (q, *J* = 7.0 Hz, 1H), 1.74 (d, *J* = 7.0 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.67, 52.26, 21.56 ppm.

2-Bromopropanoic acid (**2f**)



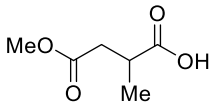
Using **GP 3**, the title compound was obtained from 2-bromoacrylic acid (30.2 mg, 0.2 mmol) as a colourless film (26.9 mg, 88 %). All spectroscopic data was in accordance with that previously reported in the literature.[10]

Appearance: Colourless film;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.41 (q, *J* = 6.9 Hz, 1H), 1.85 (d, *J* = 7.0 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.50, 39.50, 21.62 ppm.

4-Methoxy-2-methyl-4-oxobutanoic acid (**2g**)



Using **GP 3**, the title compound was obtained from 4-methoxy-2-methylene-4-oxobutanoic acid (28.8 mg, 0.2 mmol) as a colourless film (28.7 mg, 98 %). All spectroscopic data was in accordance with that previously reported in the literature.[11]

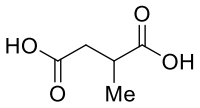
Appearance: Colourless film;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.69 (s, 3H), 3.00 – 2.93 (m, 1H), 2.75 (dd, *J* = 16.7, 8.0 Hz, 1H), 2.43 (dd, *J* = 16.7, 6.0 Hz, 1H), 1.26 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.30, 172.22, 51.86, 37.07, 35.64, 16.84 ppm.

This procedure was repeated on a 10.0 mmol scale, giving the title compound as a colourless liquid (1.45 g, 99 %).

2-Methylsuccinic acid (**2h**)



Using **GP 3**, the title compound was obtained from 2-methylenesuccinic acid (26.0 mg, 0.2 mmol) as a white solid (20.3 mg, 77 %). All spectroscopic data was in accordance with that previously reported in the literature.[12]

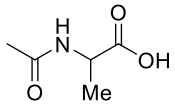
Appearance: White solid;

Melting Point: 108.3 – 113.1 °C;

^{1}H NMR (400 MHz, Methanol-d_4) δ 2.83 (dq, *J* = 14.0, 7.4 Hz, 1H), 2.66 (dd, *J* = 16.7, 8.3 Hz, 1H), 2.39 (dd, *J* = 16.7, 5.8 Hz, 1H), 1.21 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Methanol-d_4) δ 179.21, 175.60, 38.40, 36.98, 17.44 ppm.

Acetylalanine (**2i**)



Using **GP 3**, the title compound was obtained from 2-acetamidoacrylic acid (25.8 mg, 0.2 mmol) as a white solid (23.6 mg, 90 %). All spectroscopic data was in accordance with that previously reported in the literature.[13]

Appearance: White solid;

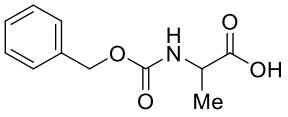
Melting Point: 124.9 – 127.0 °C;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.45 (bs, 1H), 8.14 (d, *J* = 7.3 Hz, 1H), 4.16 (p, *J* = 7.3 Hz, 1H), 1.82 (s, 3H), 1.24 (d, *J* = 7.4 Hz, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.29, 168.97, 47.41, 22.32, 17.20 ppm.

This reaction was repeated on a 10.0 mmol scale, giving the title compound as a white solid (1.27 g, 97 %).

((Benzyloxy)carbonyl)alanine (**2j**)



Using **GP 3**, the title compound was obtained from 2-(((benzyloxy)carbonyl)amino)acrylic acid (44.2 mg, 0.2 mmol) as a white solid (38.0 mg, 85 %). All spectroscopic data was in accordance with that previously reported in the literature.[14]

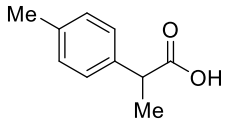
Appearance: White solid;

Melting Point: 84.3 – 84.9 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.28 (m, 5H), 5.27 (d, *J* = 6.3 Hz, 1H), 5.20 – 5.06 (m, 2H), 4.47 – 4.38 (m, 1H), 1.47 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.17, 155.96, 136.21, 128.71, 128.42, 128.29, 67.31, 49.56, 18.50 ppm.

2-(*p*-Tolyl)propanoic acid (**2k**)



Using **GP 3**, the title compound was obtained from 2-(*p*-tolyl)acrylic acid (32.4 mg, 0.2 mmol) as a white solid (28.9 mg, 88 %). All spectroscopic data was in accordance with that previously reported in the literature.[15]

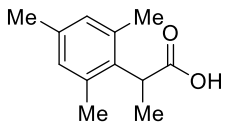
Appearance: White solid;

Melting Point: 32.7 – 34.1 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 2.33 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.86, 137.22, 136.94, 129.50, 127.59, 45.05, 21.20, 18.25 ppm.

2-Mesitylpropanoic acid (**2l**)



Using **GP 3**, the title compound was obtained from 2-mesitylacrylic acid (38.0 mg, 0.2 mmol) as a white solid (33.5 mg, 87 %). All spectroscopic data was in accordance with that previously reported in the literature.[15]

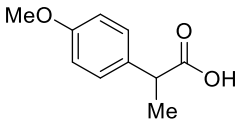
Appearance: White solid;

Melting Point: 101.3 – 104.1 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 6H), 2.26 (s, 3H), 1.44 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.44, 136.52, 136.07, 134.77, 129.93, 40.14, 20.92, 20.41, 15.38 ppm.

2-(4-Methoxyphenyl)propanoic acid (**2m**)



Using **GP 3**, the title compound was obtained from 2-(4-methoxyphenyl)acrylic acid (35.6 mg, 0.2 mmol) as a white solid (32.9 mg, 91 %). All spectroscopic data was in accordance with that previously reported in the literature.[15]

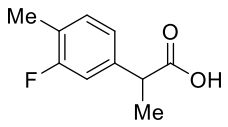
Appearance: White solid;

Melting Point: 50.3 – 52.0 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.97 (bs, 1H), 7.28 – 7.21 (m, 2H), 6.89 – 6.84 (m, 2H), 3.79 (s, 3H), 3.69 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.05, 158.99, 132.00, 128.76, 114.19, 55.41, 44.62, 18.30.

2-(3-fluoro-4-methylphenyl)propanoic acid (**2n**)



Using **GP 3**, the title compound was obtained from 2-(3-fluoro-4-methylphenyl)acrylic acid (36.0 mg, 0.2 mmol) as a colourless film (30.6 mg, 84 %).

Appearance: Colourless film;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (bs, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.02 – 6.95 (m, 2H), 3.69 (q, *J* = 7.2 Hz, 1H), 2.24 (d, *J* = 1.9 Hz, 3H), 1.49 (d, *J* = 7.2 Hz, 3H);

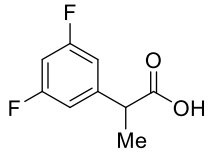
^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.94, 161.41 (d, *J* = 245.1 Hz), 139.38 (d, *J* = 7.5 Hz), 131.68 (d, *J* = 5.5 Hz), 124.05 (d, *J* = 17.1 Hz), 123.15 (d, *J* = 3.3 Hz), 114.35 (d, *J* = 23.0 Hz), 44.85, 18.18, 14.38 (d, *J* = 3.5 Hz);

^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.97 ppm;

IR (ATR): ν_{max} = 2981, 2934, 1704, 1510, 1420, 1244, 1122, 923, 872 cm^{-1};

HRMS (ESI): calculated for $[C_{10}H_{11}FO_2\text{-}H]^-$: 181.0670, found: 181.0672.

2-(3,5-Difluorophenyl)propanoic acid (**2o**)



Using **GP 3**, the title compound was obtained from 2-(3,5-difluorophenyl)acrylic acid (36.8 mg, 0.2 mmol) as a white solid (31.5 mg, 85 %).

Appearance: White solid;

Melting Point: 63.9 – 64.6 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.32 (bs, 1H), 6.86 (qd, *J* = 6.7, 2.3 Hz, 2H), 6.72 (tt, *J* = 8.9, 2.3 Hz, 1H), 3.72 (q, *J* = 7.2 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.60, 163.18 (dd, *J* = 248.8, 12.9 Hz), 143.30 (t, *J* = 9.2 Hz), 110.91 (dd, *J* = 25.7, 11.8 Hz), 103.13 (t, *J* = 25.3 Hz), 45.15, 18.03;

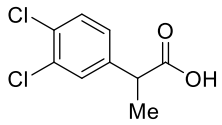
^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.46 ppm;

IR (ATR): ν_{max} = 2987, 1706, 1622, 1595, 1234, 1118, 981, 858 cm^{-1};

HRMS (ESI): calculated for $[C_9H_8F_2O_2\text{-}H]^-$: 185.0420, found: 185.0420.

This procedure was repeated on a 5.00 mmol scale, giving the title compound as a white solid (833 mg, 89 %).

2-(3,4-Dichlorophenyl)propanoic acid (**2p**)



Using **GP 3**, the title compound was obtained from 2-(3,4-dichlorophenyl)acrylic acid (43.4 mg, 0.2 mmol) as a white solid (43.2 mg, 99 %).

Appearance: White solid;

Melting Point: 46.6 – 48.9 °C;

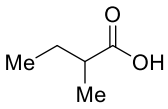
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 2H), 7.16 (dd, *J* = 8.3, 2.1 Hz, 1H), 3.70 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.48, 139.83, 132.85, 131.76, 130.73, 129.85, 127.25, 44.64, 18.12;

IR (ATR): ν_{max} = 2984, 1708, 1473, 1399, 1227, 1134, 1032, 886 cm^{-1};

HRMS (ESI): calculated for $[C_9H_8Cl_2O_2\text{-}H]^-$: 216.9829, found: 216.9827.

2-Methylbutanoic acid (**2q**)



Using **GP 4**, the title compound was obtained from (*E*)-2-methylbut-2-enoic acid (20.0 mg, 0.2 mmol) as a colourless film (16.4 mg, 80 %). All spectroscopic data was in accordance with that previously reported in the literature.[16]

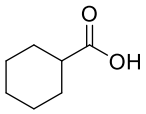
Appearance: Colourless film;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.40 (h, *J* = 6.9 Hz, 1H), 1.71 (dp, *J* = 14.6, 7.4 Hz, 1H), 1.50 (dp, *J* = 14.1, 7.2 Hz, 1H), 1.18 (d, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.96, 41.25, 26.84, 16.64, 11.83 ppm.

This procedure was repeated on a 10.0 mmol scale, giving the title compound as a colourless liquid (980 mg, 96 %).

Cyclohexanecarboxylic acid (**2r**)



Using **GP 4**, the title compound was obtained from cyclohex-1-enecarboxylic acid (25.2 mg, 0.2 mmol) as a white solid (23.4 mg, 91 %). All spectroscopic data was in accordance with that previously reported in the literature.[17]

Appearance: White solid;

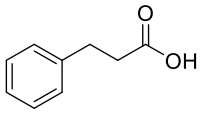
Melting Point: 30.4 – 31.7 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.33 (tt, *J* = 11.2, 3.6 Hz, 1H), 1.94 (dq, *J* = 13.1, 3.6 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.70 – 1.60 (m, 1H), 1.53 – 1.39 (m, 2H), 1.37 – 1.19 (m, 3H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.25, 43.00, 28.93, 25.83, 25.48 ppm.

This procedure was repeated on a 10.0 mmol scale, giving the title compound as a white solid (1.21 g, 94 %).

3-Phenylpropanoic acid (**2s**)



Using **GP 3**, the title compound was obtained from (*E*)-cinnamic acid (29.6 mg, 0.2 mmol) as a white solid (29.7 mg, 99 %). All spectroscopic data was in accordance with that previously reported in the literature.[18]

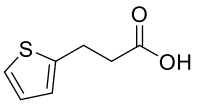
Appearance: White solid;

Melting Point: 46.0 – 48.7 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.15 (bs, 1H), 7.36 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.70 (dd, *J* = 8.4, 7.1 Hz, 2H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.36, 140.27, 128.70, 128.40, 126.52, 35.75, 30.71.

3-(Thiophen-2-yl)propanoic acid (**2t**)



Using **GP 3**, the title compound was obtained from (*E*)-3-(thiophen-2-yl)acrylic acid (30.8 mg, 0.2 mmol) as an off-white solid (24.6 mg, 79 %). All spectroscopic data was in accordance with that previously reported in the literature.[19]

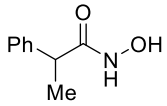
Appearance: Off-white solid;

Melting Point: 48.0 – 49.7 °C;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.99 (bs, 1H), 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.85 (dt, *J* = 3.4, 1.0 Hz, 1H), 3.18 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H) ppm;

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.72, 142.64, 126.91, 124.77, 123.67, 35.90, 24.82.

***N*-Hydroxy-2-phenylpropanamide** (**2u**)



Using a modified **GP 3** with 1-methylimidazole (0.319 µL, 4.00 µmol, 2 mol %) as a co-catalyst, the title compound was obtained from *N*-hydroxy-2-phenylacrylamide (32.6 mg, 0.2 mmol) as a pale brown solid (25.5 mg, 77 %). All spectroscopic data was in accordance with that previously reported in the literature.[20]

Appearance: Pale brown solid;

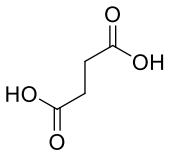
Melting Point: 116.9 – 119.0 °C;

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 1H), 8.77 (d, *J* = 1.5 Hz, 1H), 7.34 – 7.17 (m, 5H), 3.42 (q, *J* = 7.0 Hz, 1H), 1.33 (d, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.20, 141.83, 128.16, 127.24, 126.57, 42.11, 18.19 ppm.

This procedure was repeated on a 5.00 mmol scale, giving the title compound as a pale brown solid (701 mg, 85 %).

Succinic acid (**2v**)



Using **GP 3**, the title compound was obtained from fumaric acid (23.2 mg, 0.2 mmol) as a white solid (19.2 mg, 81 %). All spectroscopic data was in accordance with that previously reported in the literature.[21]

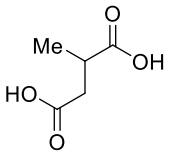
Appearance: White solid;

Melting Point: 185.1 – 187.9 °C;

^{1}H NMR (400 MHz, Deuterium Oxide) δ 2.65 (s, 4H) ppm;

^{13}C NMR (101 MHz, Deuterium Oxide) δ 176.85, 28.54 ppm.

2-Methylsuccinic acid (**2w**)



Using **GP 3**, the title compound was obtained from mesaconic acid (26.0 mg, 0.2 mmol) as a white solid (22.8 mg, 86 %). All spectroscopic data was in accordance with that previously reported in the literature.[22]

Appearance: White solid;

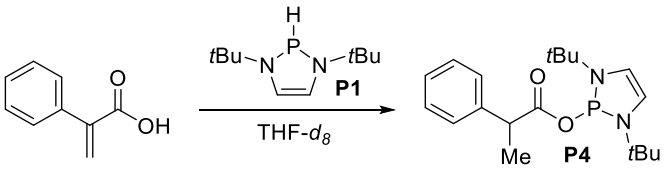
Melting Point: 115.9 – 117.3 °C;

^{1}H NMR (400 MHz, Deuterium Oxide) δ 2.92 – 2.84 (m, 1H), 2.68 (dd, *J* = 17.0, 9.0 Hz, 1H), 2.56 (dd, *J* = 17.1, 5.3 Hz, 1H), 1.20 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Deuterium Oxide) δ 179.97, 176.57, 36.83, 35.66, 16.05 ppm.

NMR Experiments

Stoichiometric Experiment Between P1 and 2-Phenylacrylic Acid



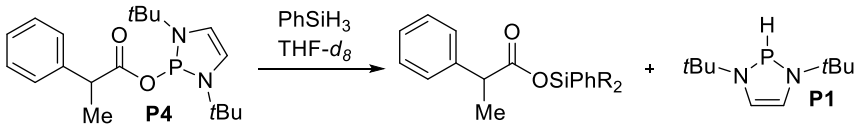
Inside the glovebox, an oven-dried NMR tube was charged with 2-phenylacrylic acid (14.82 mg, 0.1 mmol) and THF-d_8 (500 µL). The sample was capped and sealed with parafilm, then removed from the glovebox, and the ^{1}H NMR spectrum recorded. The tube was returned to the glovebox and frozen in the cold-well using liquid nitrogen. A solution of **P1** (20.03 mg, 0.1 mmol) in THF-d_8 (500 µL) was added to the tube, which was then capped and sealed as before, and removed from the glovebox. The ^{1}H and ^{31}P NMR spectra were immediately recorded using the shim values from the initial spectrum. The NMR data thus obtained indicated clean formation of **P4**.

^{1}H NMR (400 MHz, THF-d_8) δ 7.21 (m, 4H), 7.13 (dq, *J* = 8.7, 4.1 Hz, 1H), 6.18 (d, *J* = 1.8 Hz, 2H), 3.38 (q, *J* = 7.1 Hz, 1H), 1.39 – 1.21 (m, 21H);

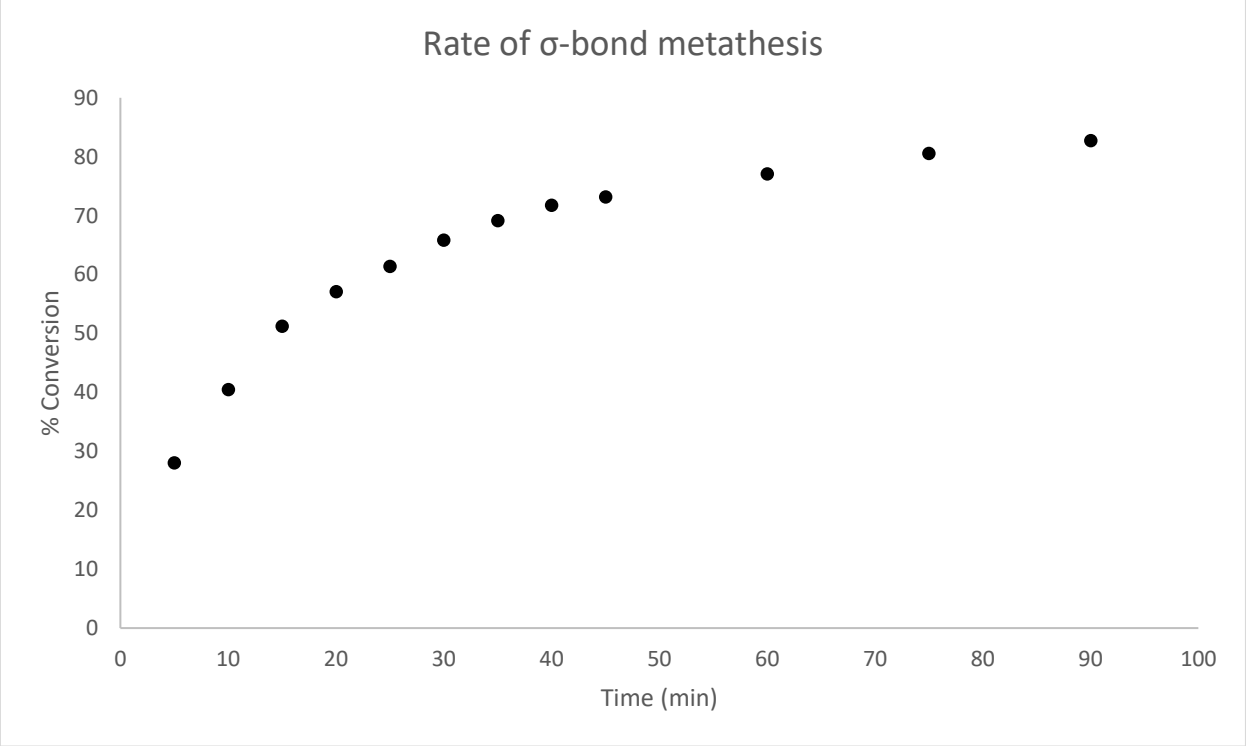
^{13}C NMR (101 MHz, THF-d_8) δ 175.02, 142.75, 128.80, 128.25, 127.04, 114.31 (d, *J* = 9.0 Hz), 54.04 (d, *J* = 12.1 Hz), 47.79, 30.90, 30.80, 18.85;

^{31}P NMR (162 MHz, THF-d_8): δ 105.73 ppm.

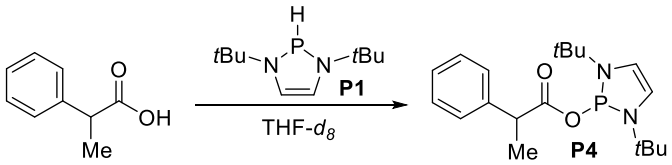
Stoichiometric Experiment Between P4 and $PhSiH_3$



To the solution of **P4** prepared above was added $PhSiH_3$ (4.32 µL, 0.035 mmol). ^{1}H and ^{31}P NMR spectra were recorded at 5 minute intervals as the reaction progressed for the first 45 minutes, and at 15 minute intervals thereafter.

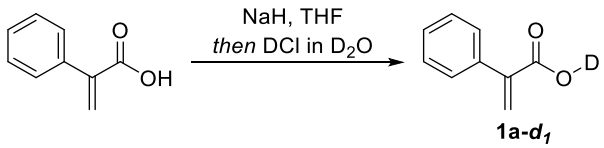


Stoichiometric Experiment Between P1 and 2-Phenylpropionic acid



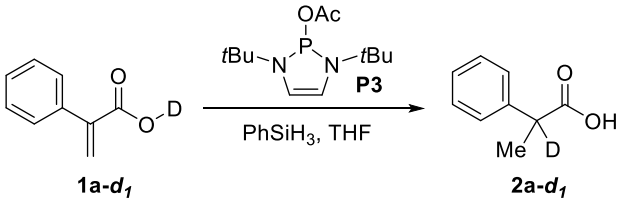
Inside the glovebox, an oven-dried NMR tube was charged with 2-phenylpropionic acid (15.02 mg, 0.1 mmol) and THF-d_8 (500 µL). The sample was capped and sealed with parafilm, then removed from the glovebox, and the ^{1}H NMR spectrum recorded. The tube was returned to the glovebox and frozen in the cold-well using liquid nitrogen. A solution of **P1** (20.03 mg, 0.1 mmol) in THF-d_8 (500 µL) was added to the tube, which was then capped and sealed as before, and removed from the glovebox. The ^{1}H and ^{31}P NMR spectra after 5 hours indicated less than 50 % conversion of the starting materials to **P4**.

*Synthesis of 2-Phenylacrylic acid-d_1 (*1a-d_1*)*



To a solution of 2-phenylacrylic acid (148 mg, 1.00 mmol) in THF (3.0 mL) was added NaH (36.0 mg, 2.00 mmol) portionwise. After bubbling had ceased, the mixture was stirred for a further 30 minutes at room temperature, after which it was quenched by the addition of deuterium chloride in D_2O (20 % by weight, 500 µL). Minimizing exposure to the atmosphere, the reaction was immediately concentrated *in vacuo*. The product was extracted from the crude residue with toluene, and passed through celite to remove any insoluble solids. The eluent was concentrated *in vacuo* and the product thus obtained was further dried by azeotropic distillation with toluene to give a white solid (117 mg, 78 %, 70 % deuterium incorporation by NMR).

*Synthesis of 2-Phenylpropionic acid-d_1 (*2a-d_1*)*



Using **GP 3**, the title compound was obtained from 2-phenylacrylic acid-d_1 (29.8 mg, 0.2 mmol) as a white solid (29.7 mg, 98 %, 80 % deuterium incorporation by NMR).

The deuterium incorporation value is higher for the product than the starting material. This is likely a consequence of exchange of the labile proton/deuterium at the carboxylic acid in the starting material, resulting in an observed value lower than it should be.

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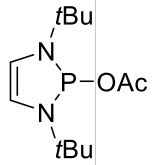
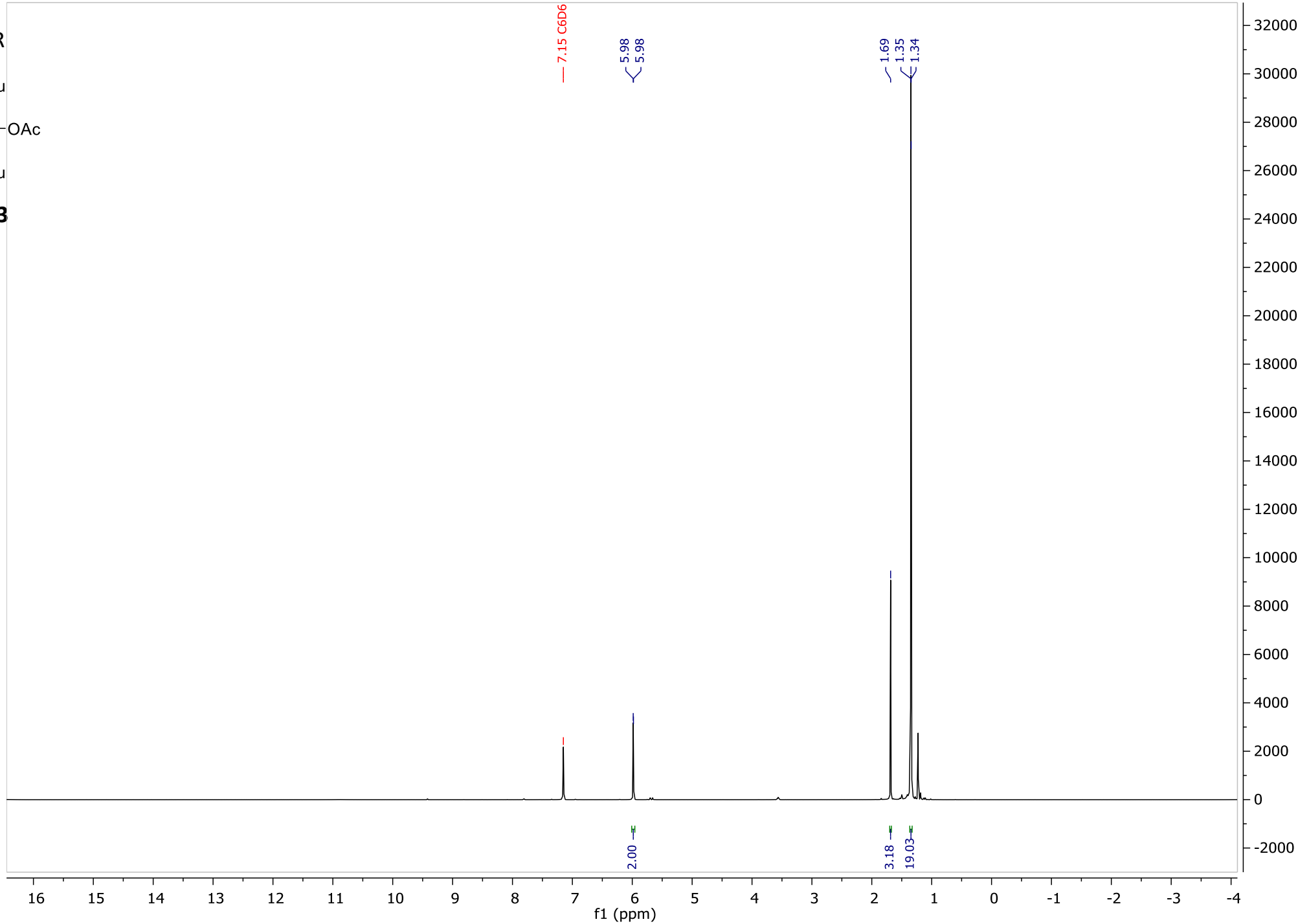
^{1}H, ^{13}C, ^{31}P and ^{19}F NMR Spectra

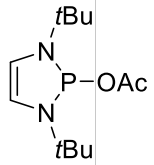
^{1}H NMR


tBu
N
P–OAc
N
tBu

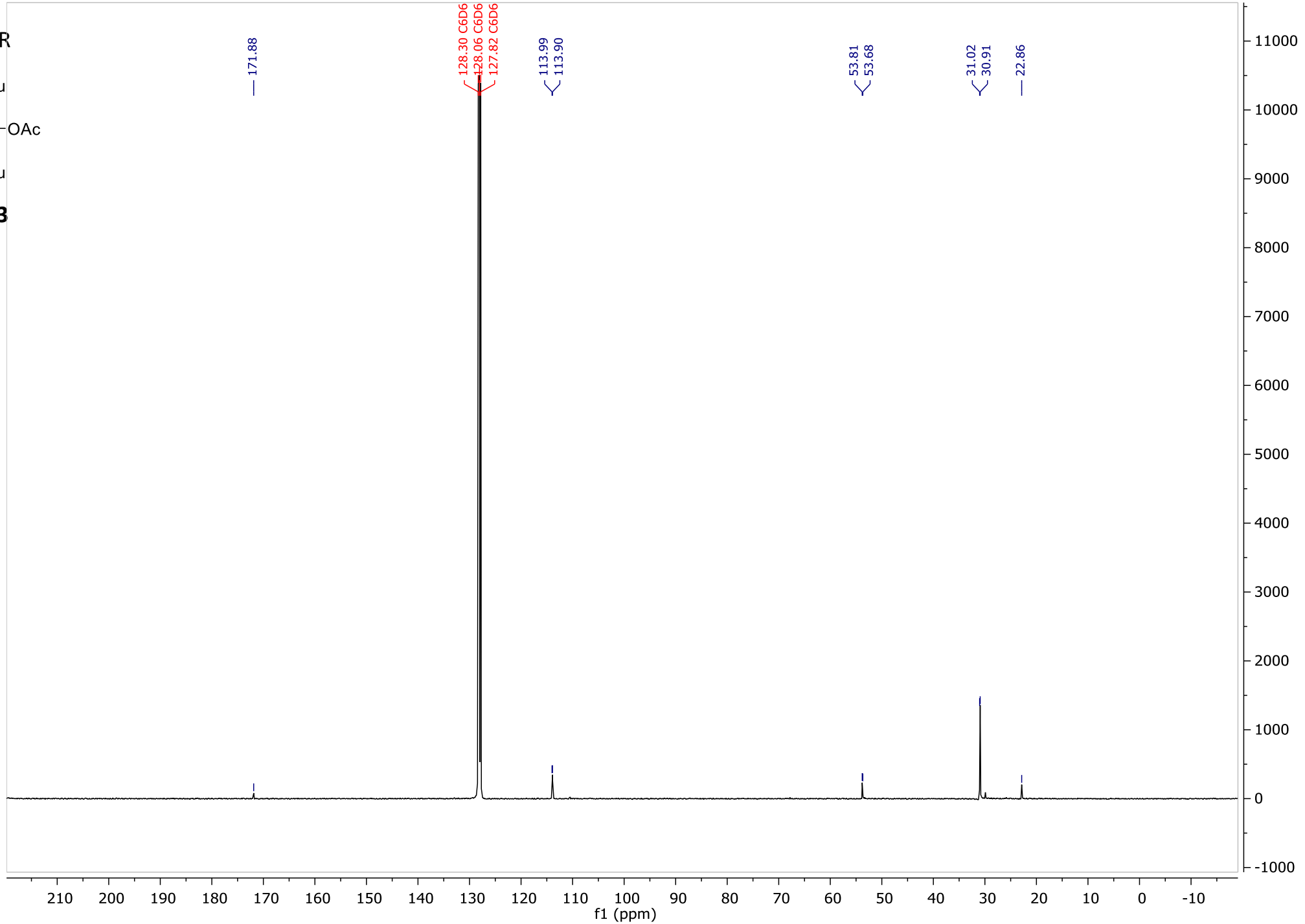
P3


7.15 C6D6
5.98
5.98
1.69
1.35
1.34
2.00
3.18
19.03
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

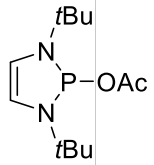
^{13}C NMR


tBu
N
P–OAc
N
tBu

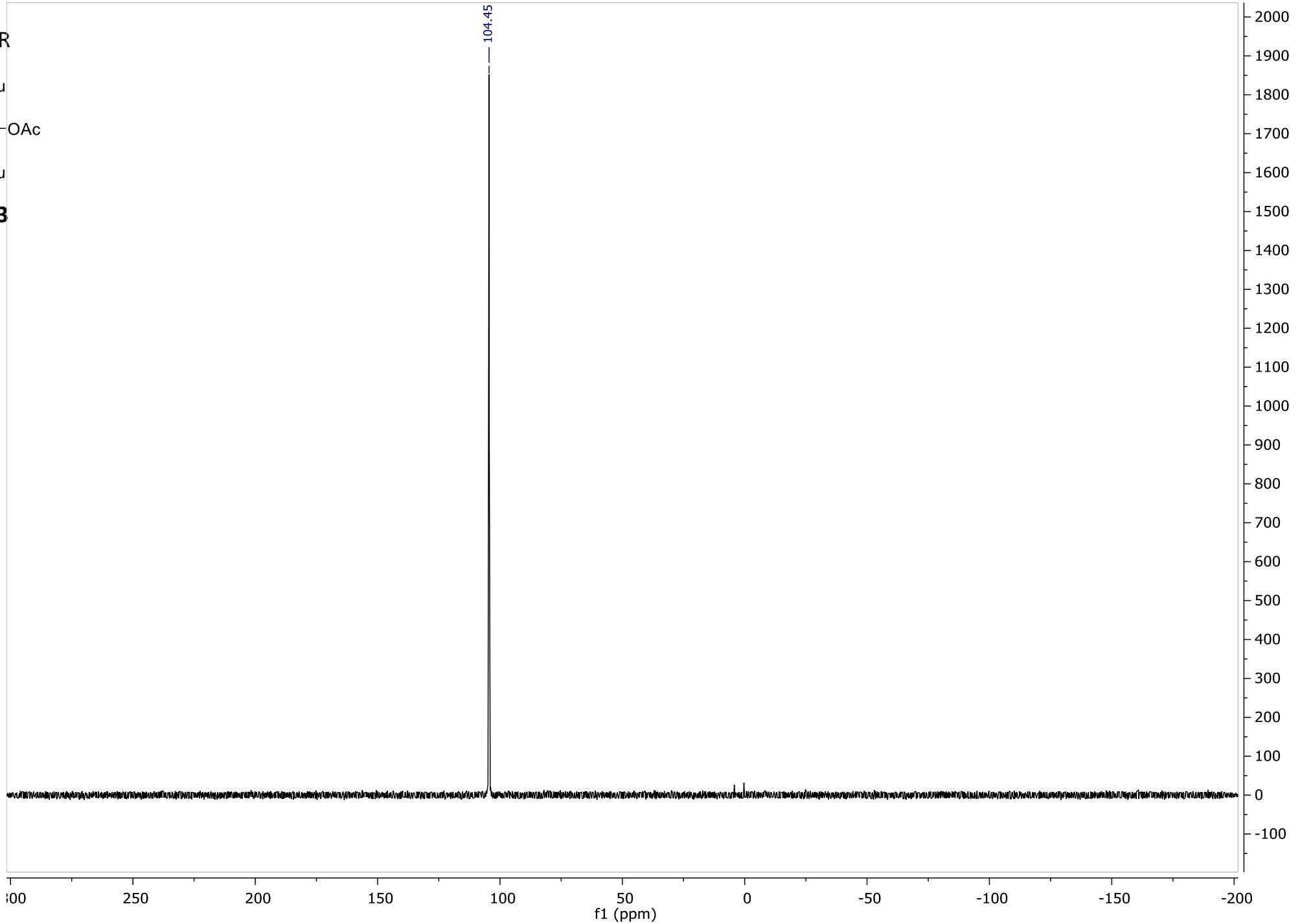
P3


171.88
128.30 C6D6
128.06 C6D6
127.82 C6D6
113.99
113.90
53.81
53.68
31.02
30.91
22.86
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

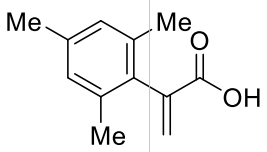
^{31}P NMR


tBu
N
P–OAc
N
tBu

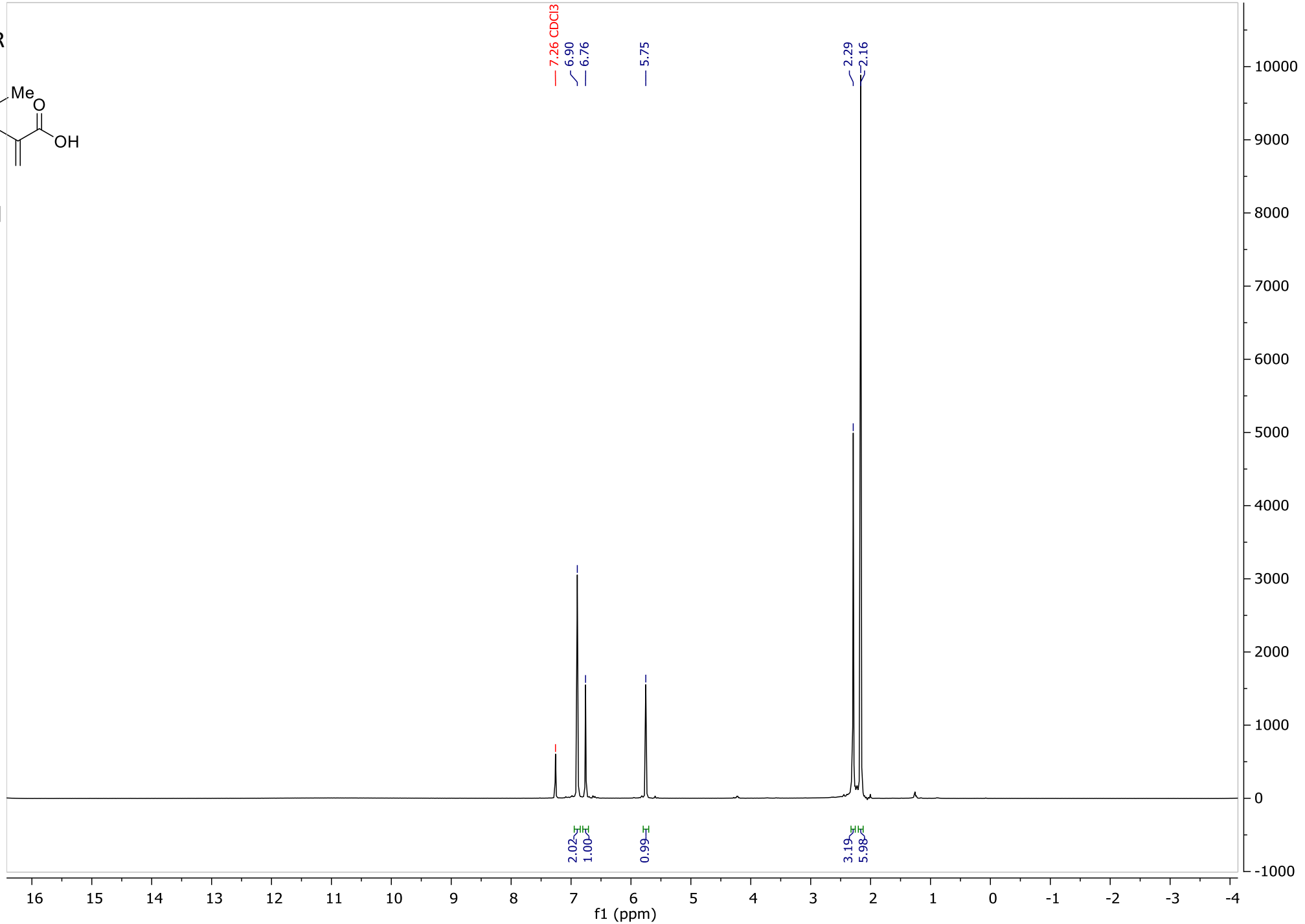
P3


104.45
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
250
200
150
100
50
0
-50
-100
-150
-200
f1 (ppm)

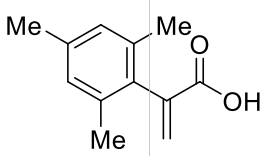
^{1}H NMR


Me
Me
O
OH
Me

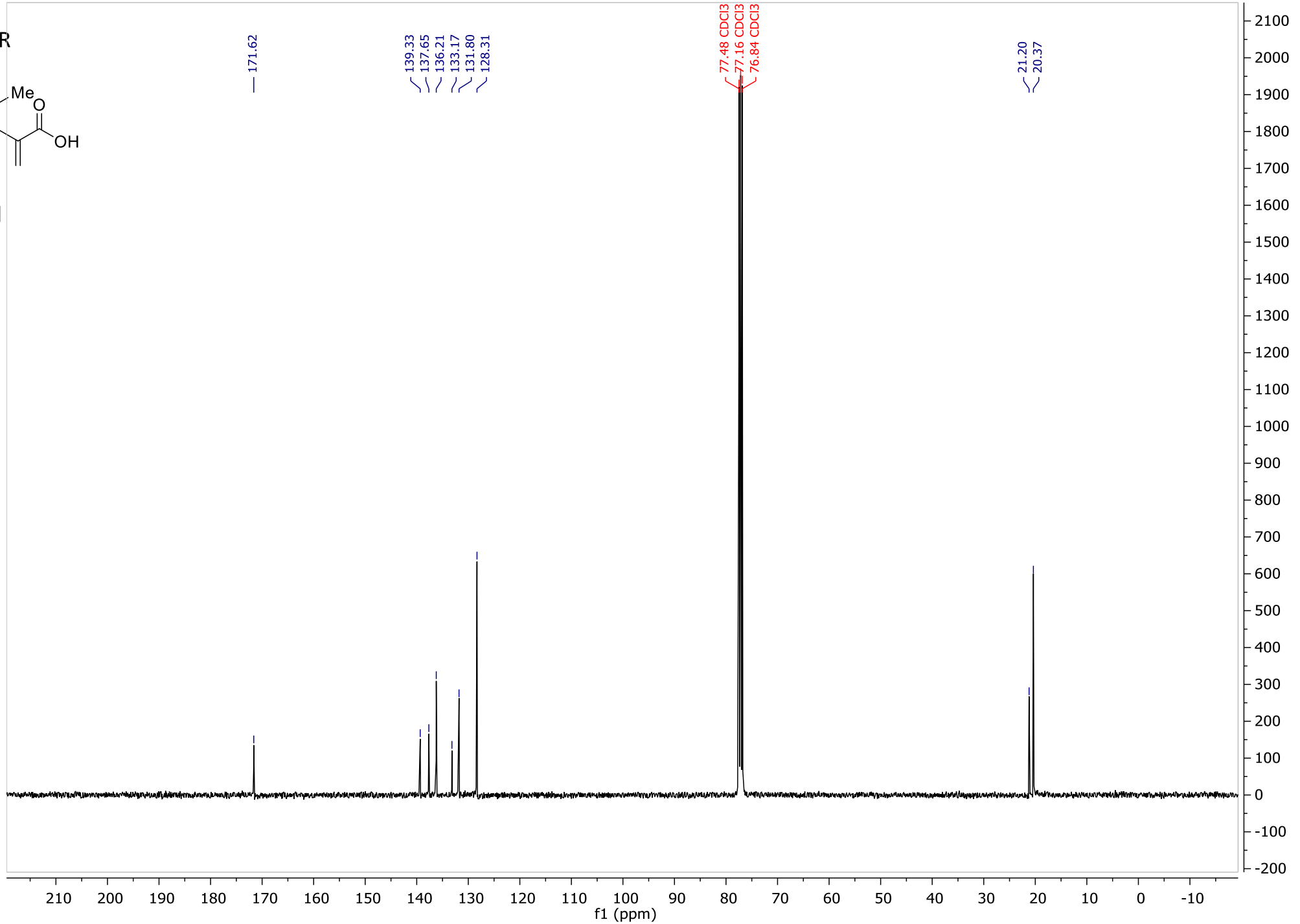
1l


7.26 CDCl3
6.90
6.76
5.75
2.29
2.16
2.02
1.00
0.99
3.19
5.98
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

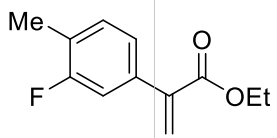
^{13}C NMR


Me
Me
O
OH
Me

1l


171.62
139.33
137.65
136.21
133.17
131.80
128.31
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.20
20.37
f1 (ppm)

^{1}H NMR


Me
F
O
OEt

S4

7.26 CDCl3
7.17
7.16
7.14
7.13
7.12
7.12
7.11
7.11
7.10
7.09
7.09
6.34
6.33
5.88
5.88
4.32
4.30
4.28
4.26
2.28
2.28
1.35
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2.92
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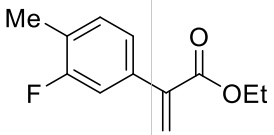
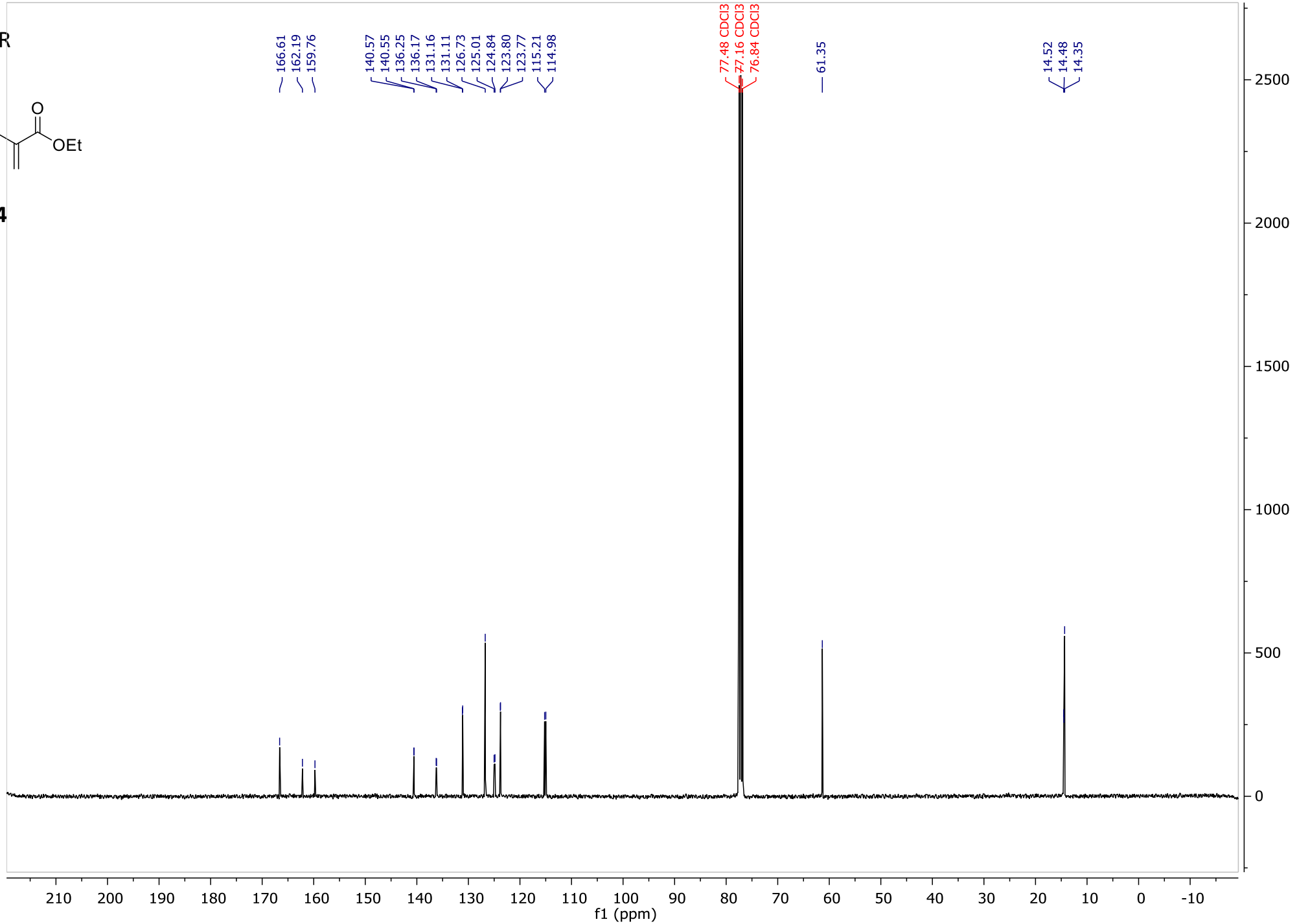
1.97
3.02
2.99
f1 (ppm)

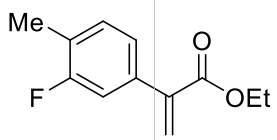
^{13}C NMR


Me
F
O
OEt

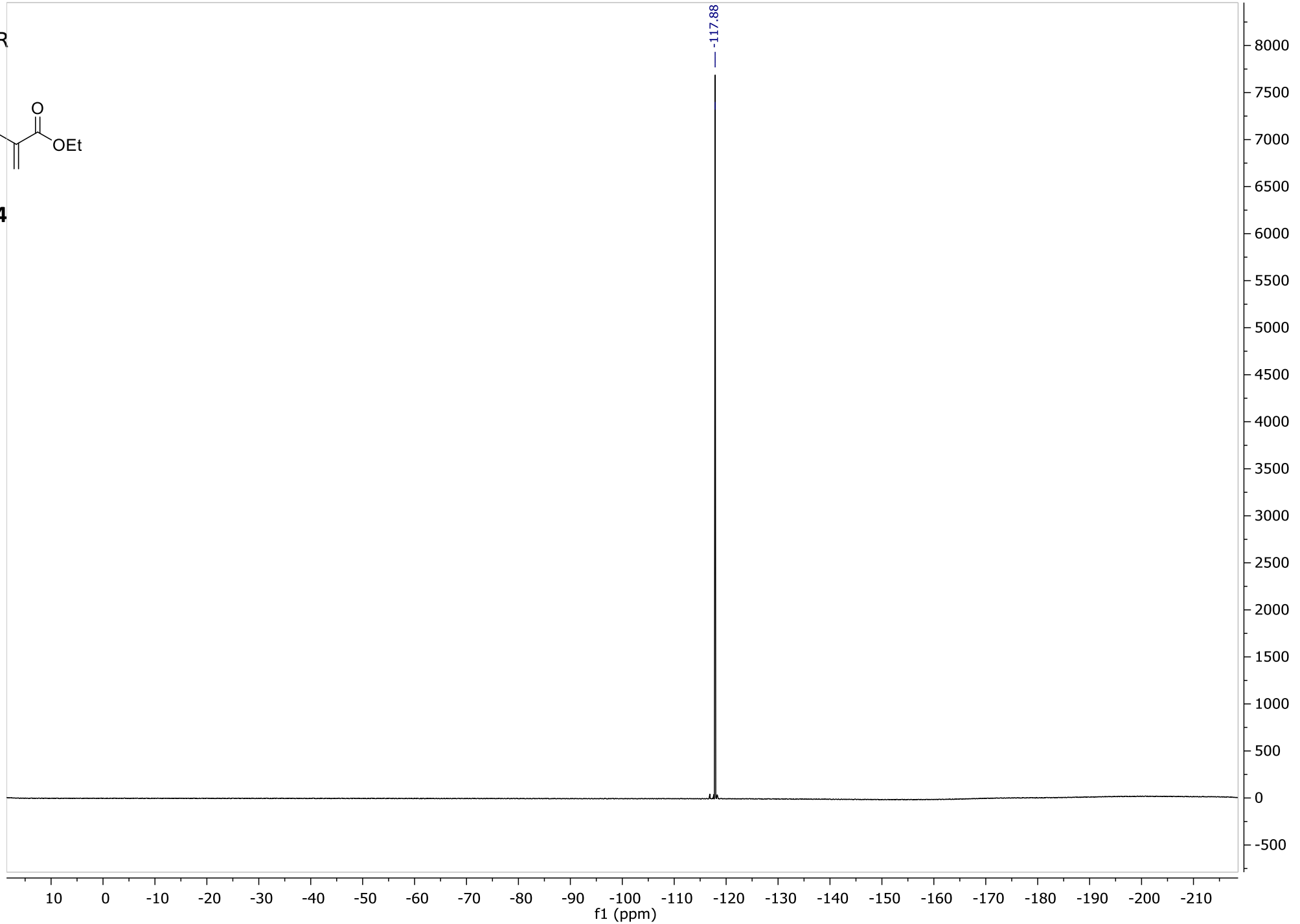
S4


166.61
162.19
159.76
140.57
140.55
136.25
136.17
131.16
131.11
126.73
125.01
124.84
123.80
123.77
115.21
114.98
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.35
14.52
14.48
14.35
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR


Me
F
O
OEt

S4


-117.88
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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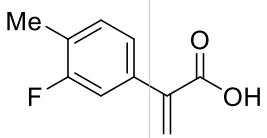
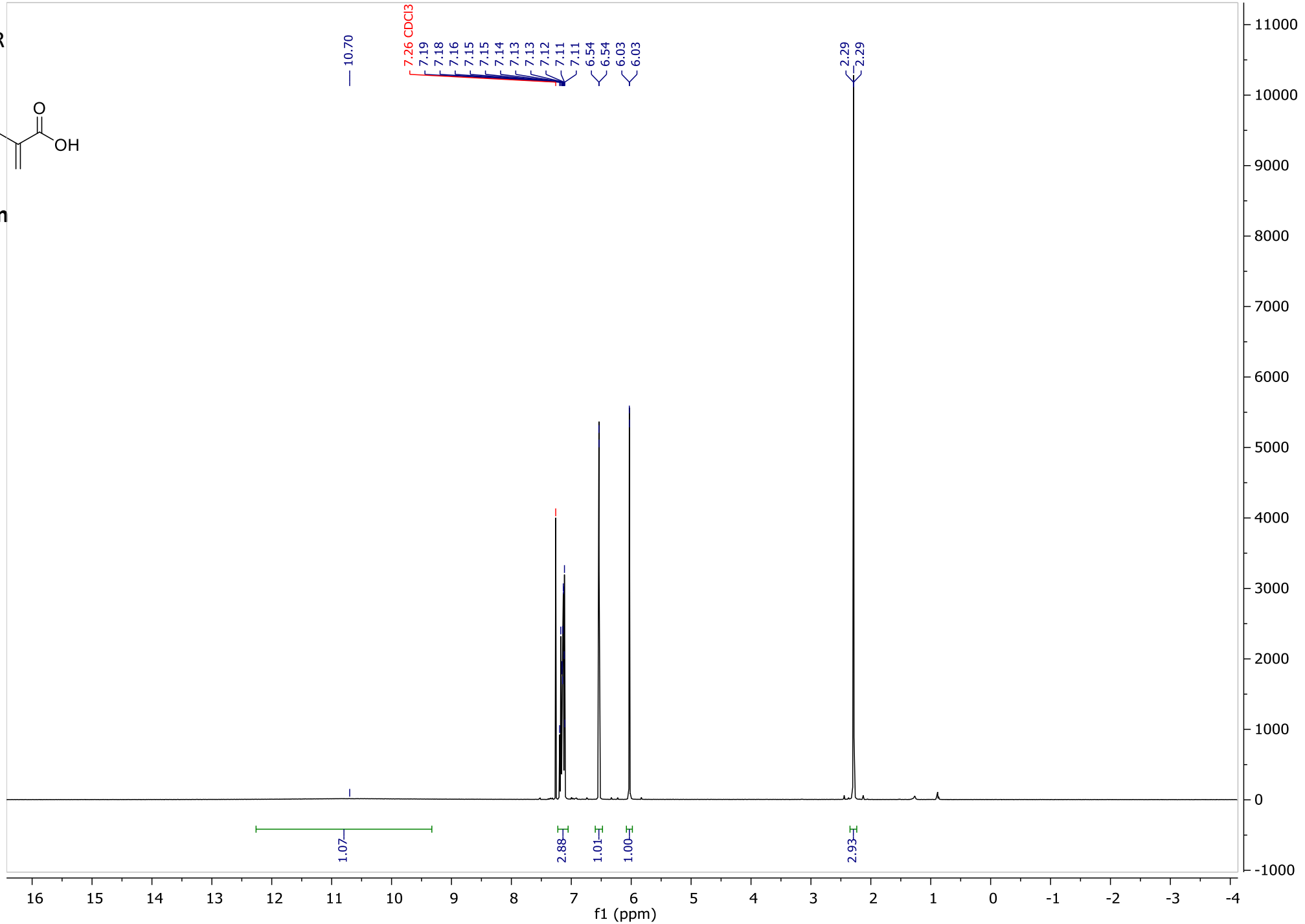
-180
-190
-200
-210
f1 (ppm)

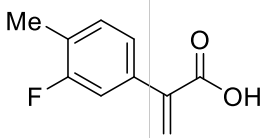
^{1}H NMR


Me
F
O
OH

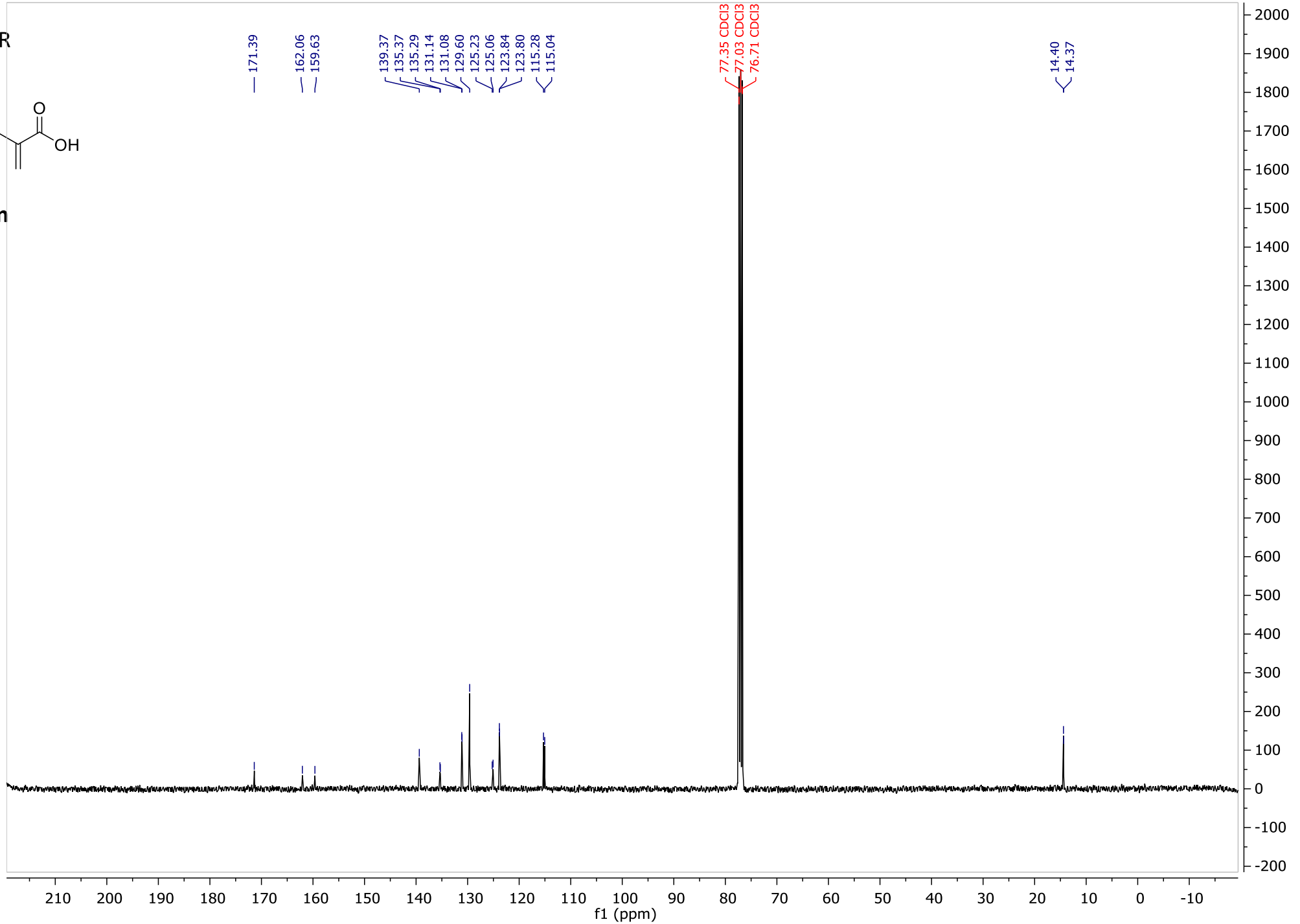
1n


10.70
7.26 CDCl3
7.19
7.18
7.16
7.15
7.15
7.14
7.13
7.13
7.12
7.11
7.11
6.54
6.54
6.03
6.03
2.29
2.29
1.07
2.88
1.01
1.00
2.93
f1 (ppm)

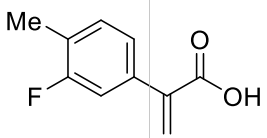
^{13}C NMR


Me
F
O
OH

1n


171.39
162.06
159.63
139.37
135.37
135.29
131.14
131.08
129.60
125.23
125.06
123.84
123.80
115.28
115.04
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
14.40
14.37
f1 (ppm)

^{19}F NMR



1n

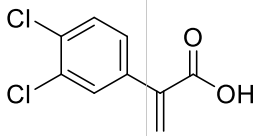
-117.60

7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

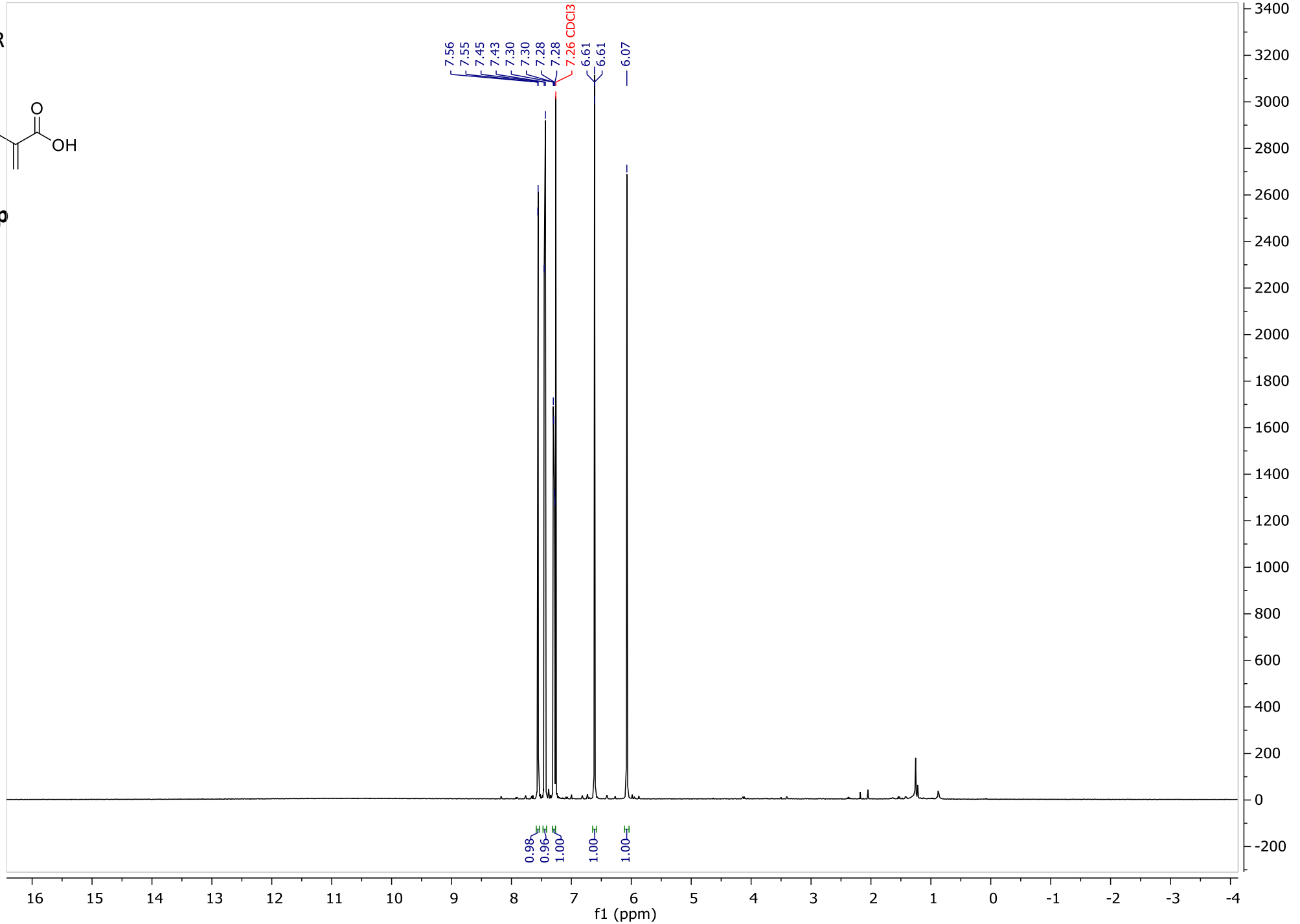
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)

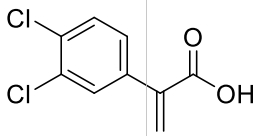
^{1}H NMR


Cl
Cl
O
OH

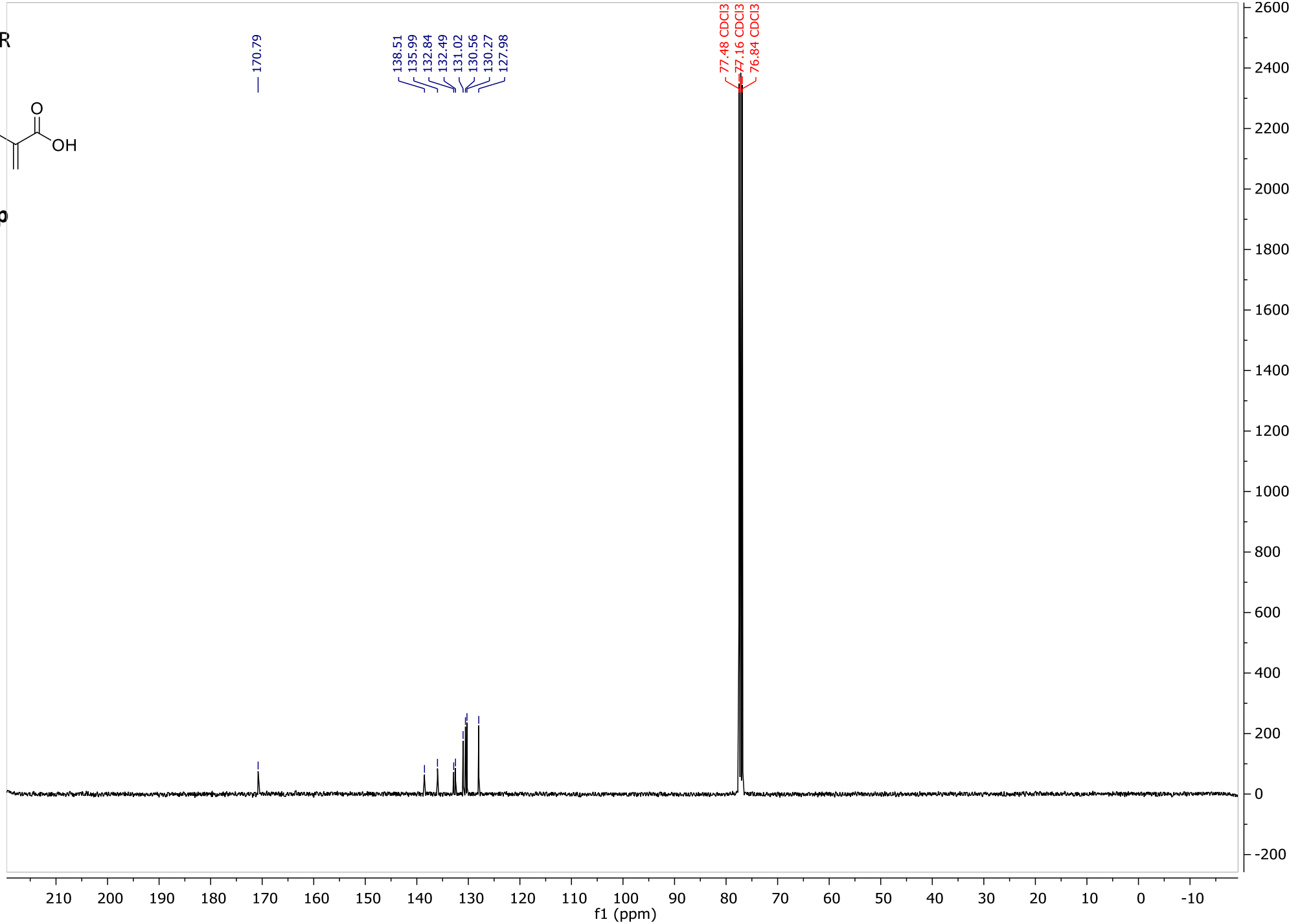
1p


7.56
7.55
7.45
7.43
7.30
7.30
7.28
7.28
7.26 CDCl3
6.61
6.61
6.07
0.98
0.96
1.00
1.00
1.00
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

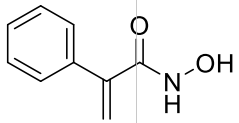
^{13}C NMR


Cl
Cl
O
OH

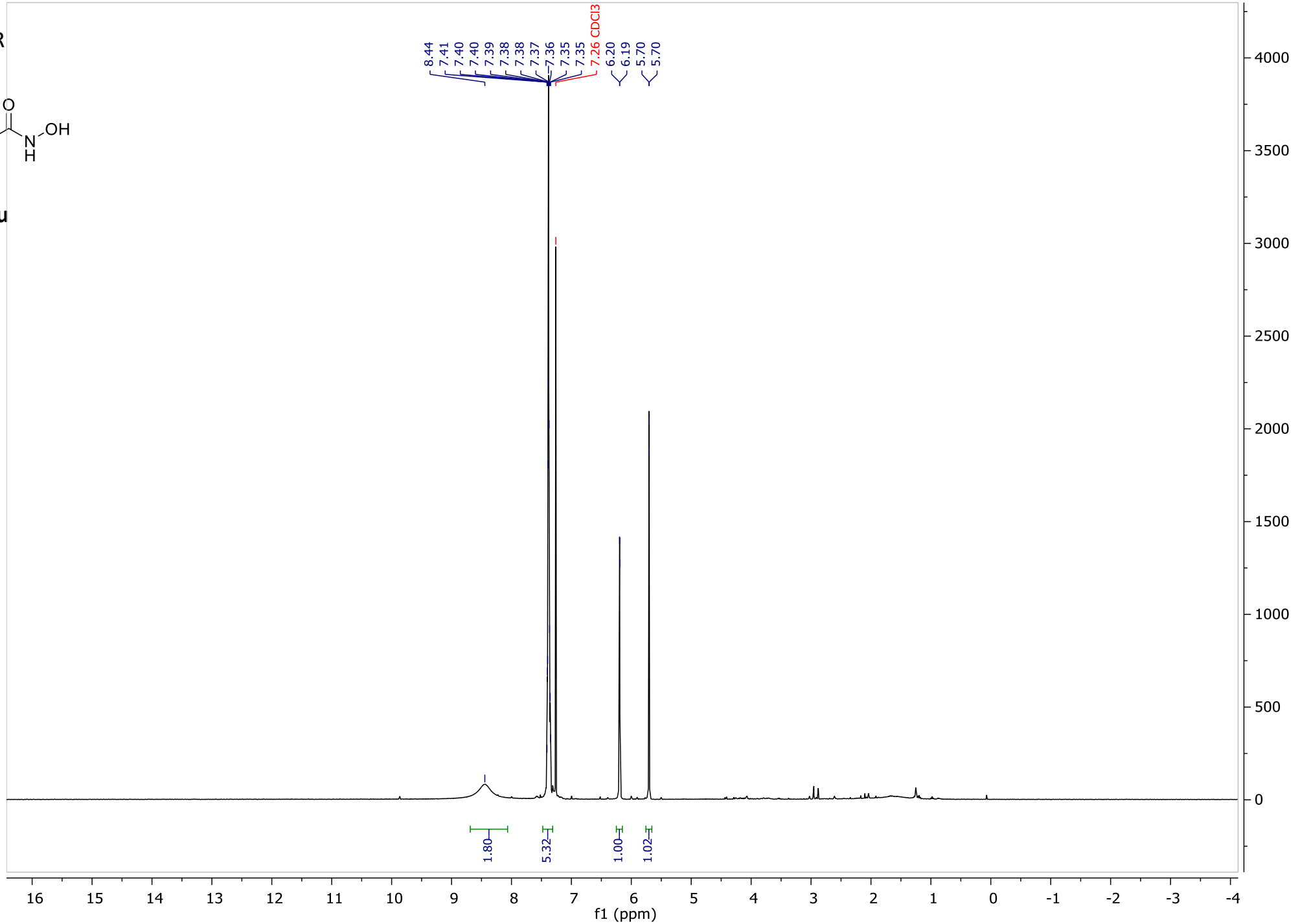
1p


170.79
138.51
135.99
132.84
132.49
131.02
130.56
130.27
127.98
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

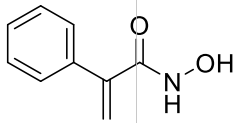
^{1}H NMR


O
N
OH
H

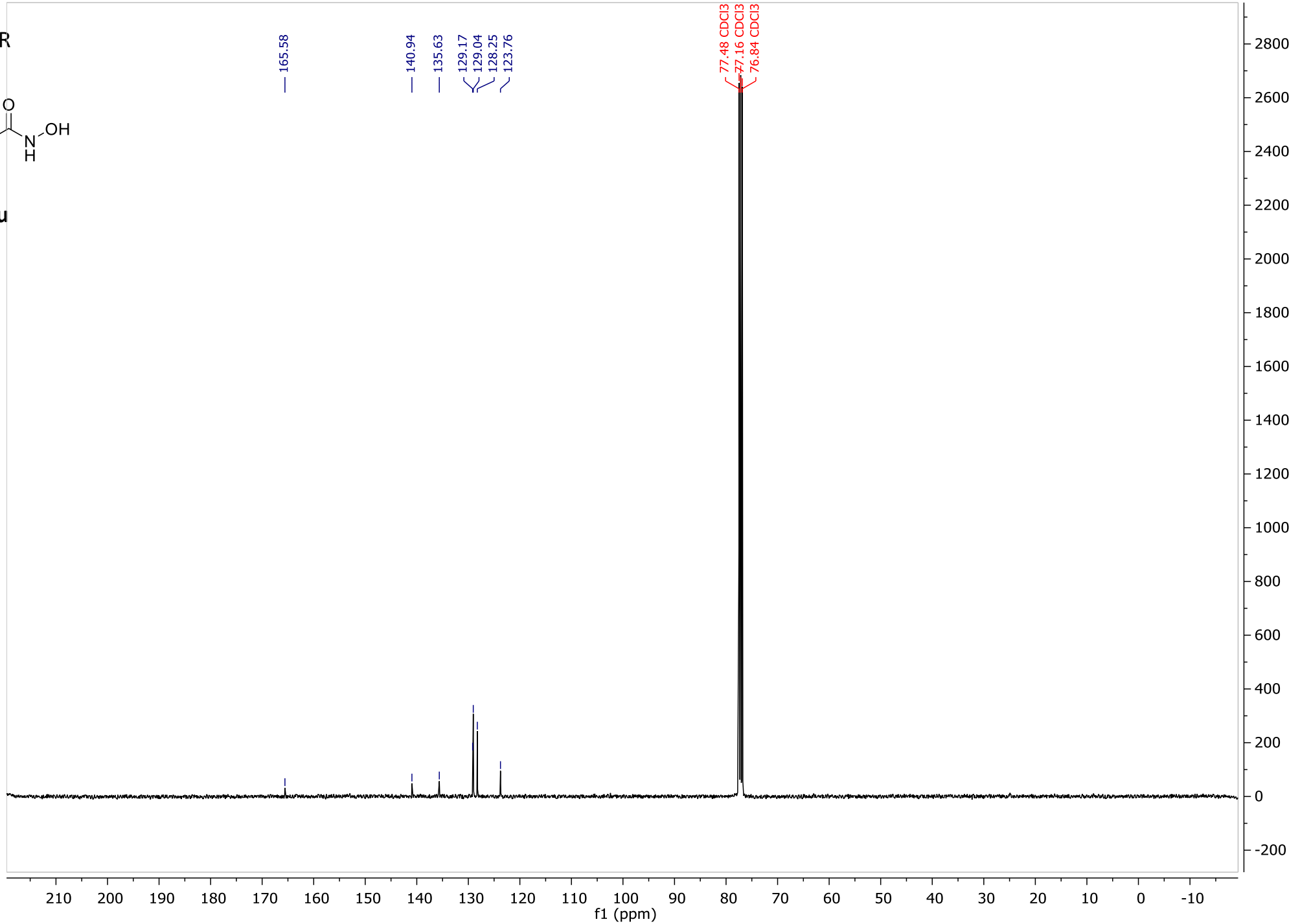
1u


8.44
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.26 CDCl3
6.20
6.19
5.70
5.70
1.80
5.32
1.00
1.02
4000
3500
3000
2500
2000
1500
1000
500
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

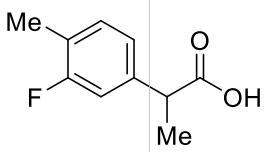
^{13}C NMR


O
N
H
OH

1u


165.58
140.94
135.63
129.17
129.04
128.25
123.76
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

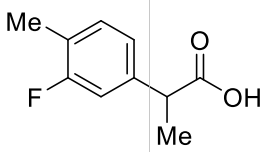
^{1}H NMR


Me
F
O
OH
Me

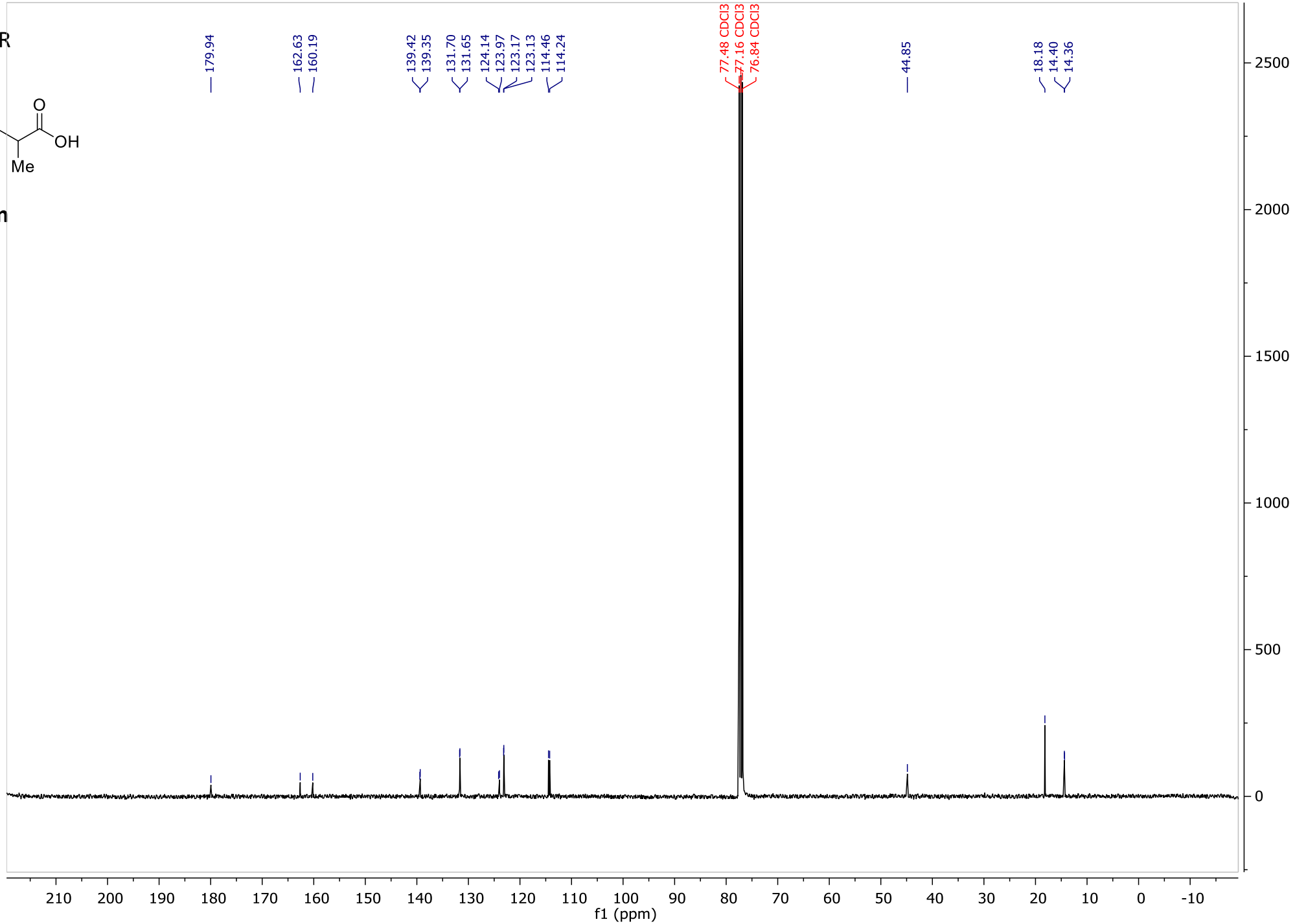
2n

8.69
7.26 CDCl3
7.15
7.13
7.11
7.00
6.99
6.99
6.97
3.72
3.70
3.68
3.67
2.25
2.24
1.50
1.48
1.03
0.99
1.93
1.00
2.96
2.97
f1 (ppm)

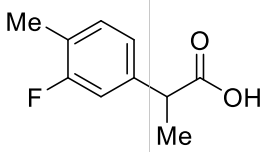
^{13}C NMR


Me
F
O
OH
Me

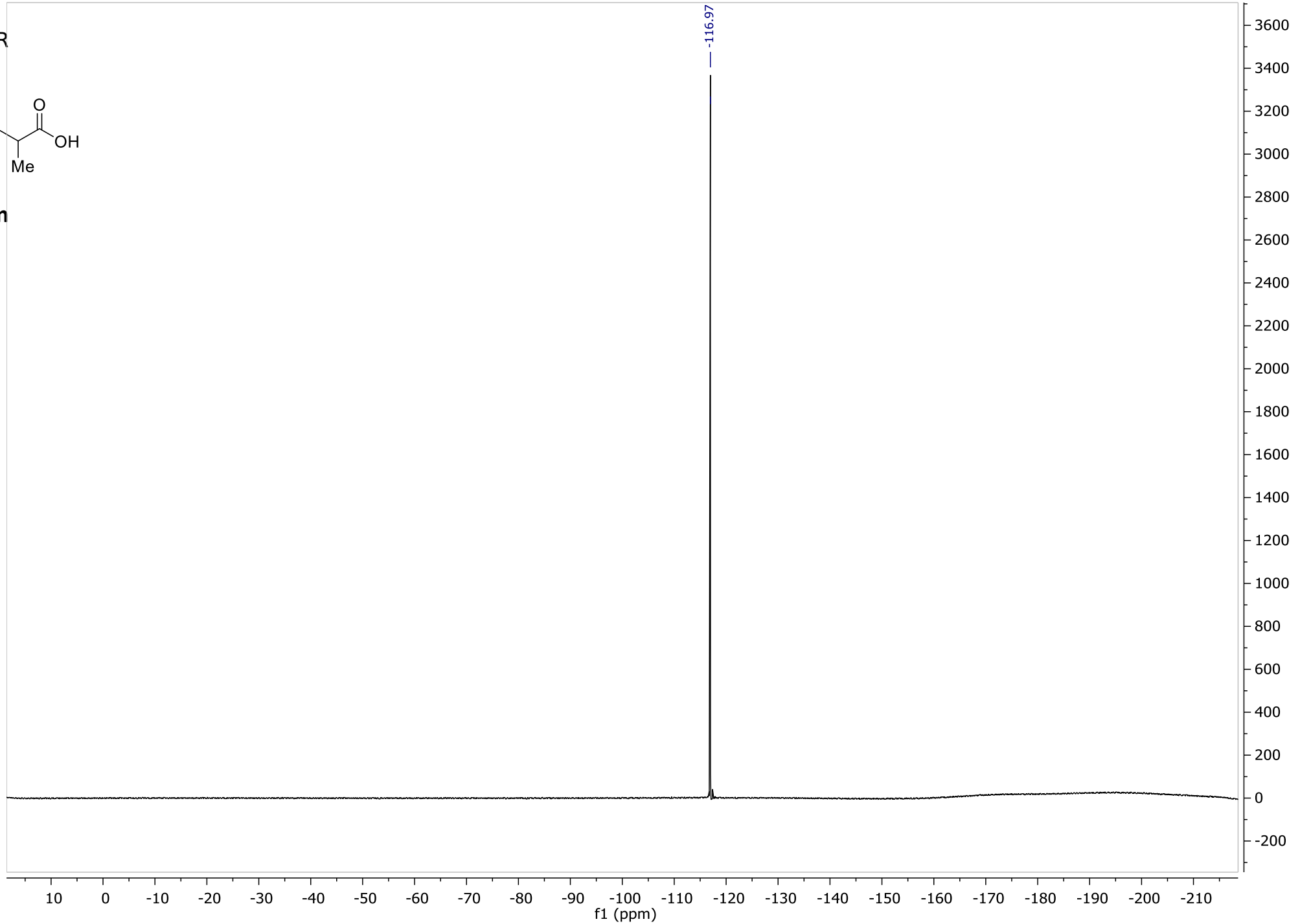
2n


179.94
162.63
160.19
139.42
139.35
131.70
131.65
124.14
123.97
123.17
123.13
114.46
114.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.85
18.18
14.40
14.36
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

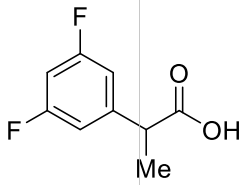
^{19}F NMR


Me
F
O
OH
Me

2n


-116.97
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

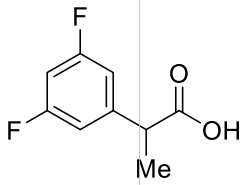
^{1}H NMR


F
O
F
OH
Me

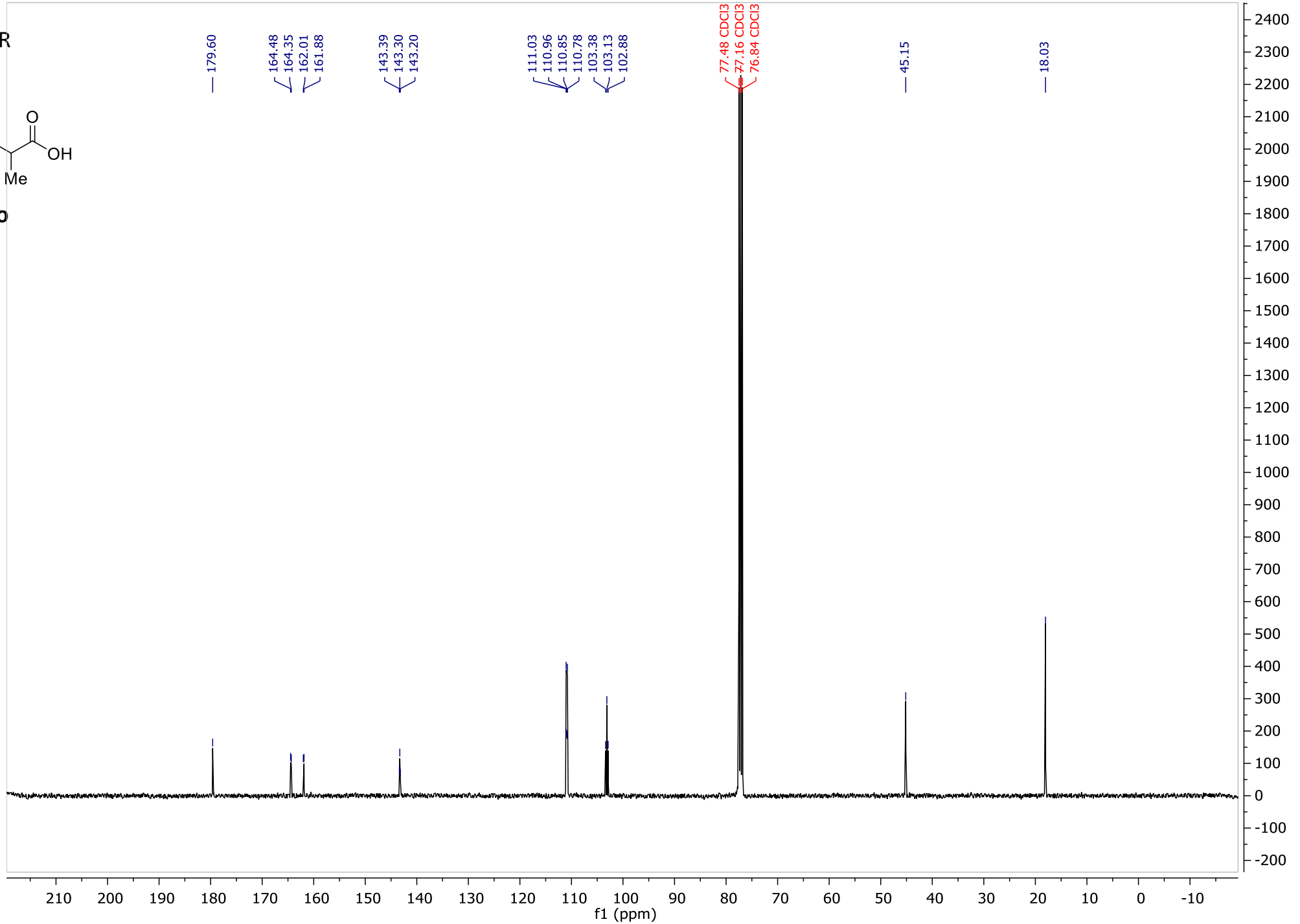
2o

10.32
7.26
6.89
6.88
6.87
6.87
6.85
6.85
6.84
6.83
6.75
6.75
6.74
6.73
6.72
6.72
6.71
6.70
6.70
3.75
3.73
3.71
3.69
1.52
1.50
1.08
1.96
0.95
1.00
3.13
f1 (ppm)

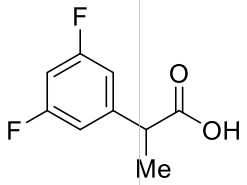
^{13}C NMR


F
O
F
OH
Me

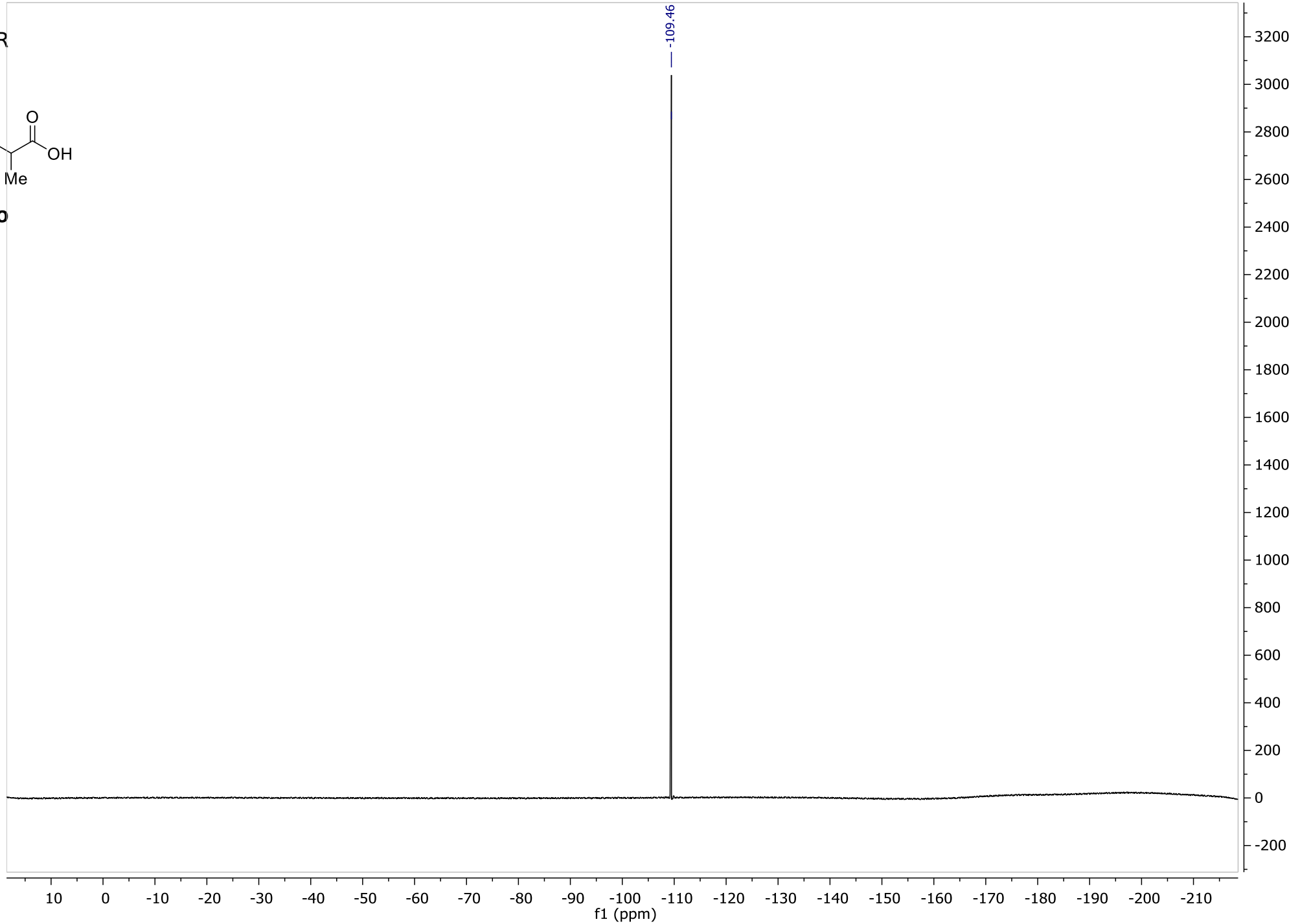
2o


179.60
164.48
164.35
162.01
161.88
143.39
143.30
143.20
111.03
110.96
110.85
110.78
103.38
103.13
102.88
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.15
18.03
f1 (ppm)

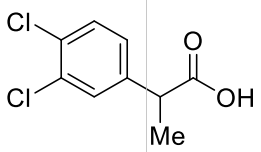
^{19}F NMR


F
O
F
OH
Me

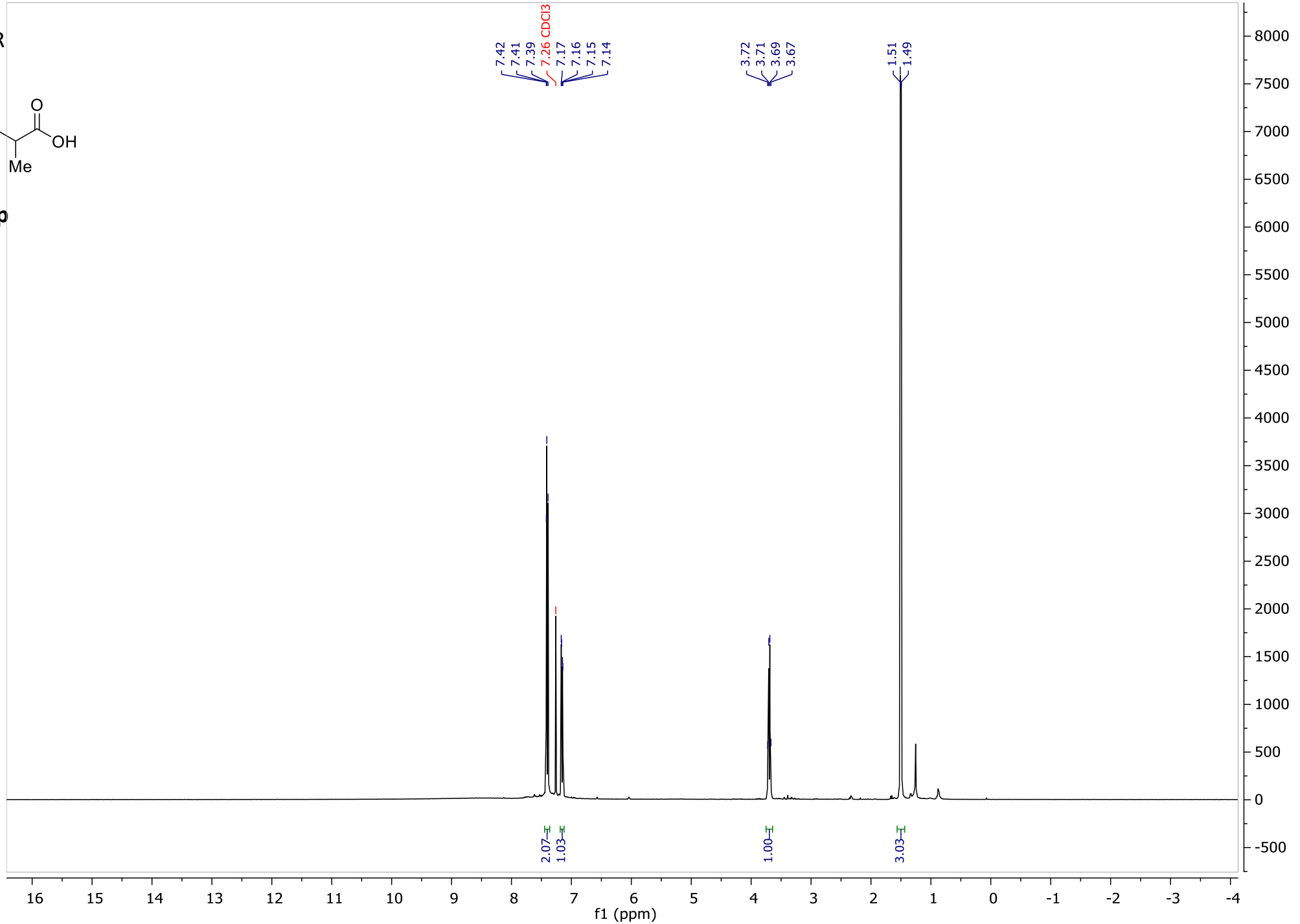
2o


-109.46
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

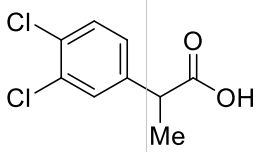
^{1}H NMR


Cl
Cl
O
OH
Me

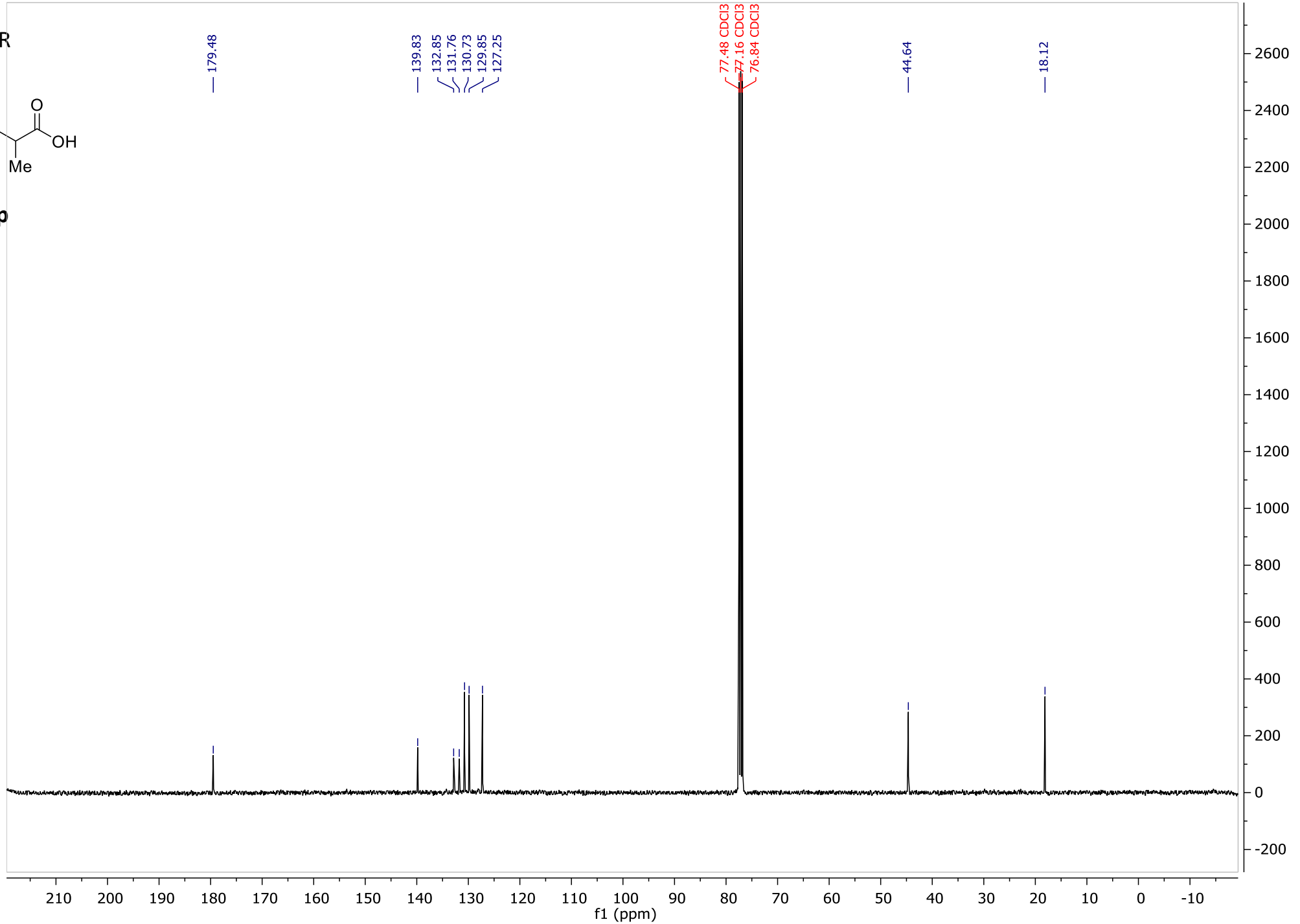
2p


7.42
7.41
7.39
7.26 CDCl3
7.17
7.16
7.15
7.14
3.72
3.71
3.69
3.67
1.51
1.49
2.07
1.03
1.00
3.03
f1 (ppm)

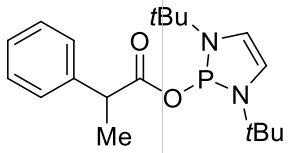
^{13}C NMR


Cl
Cl
O
OH
Me

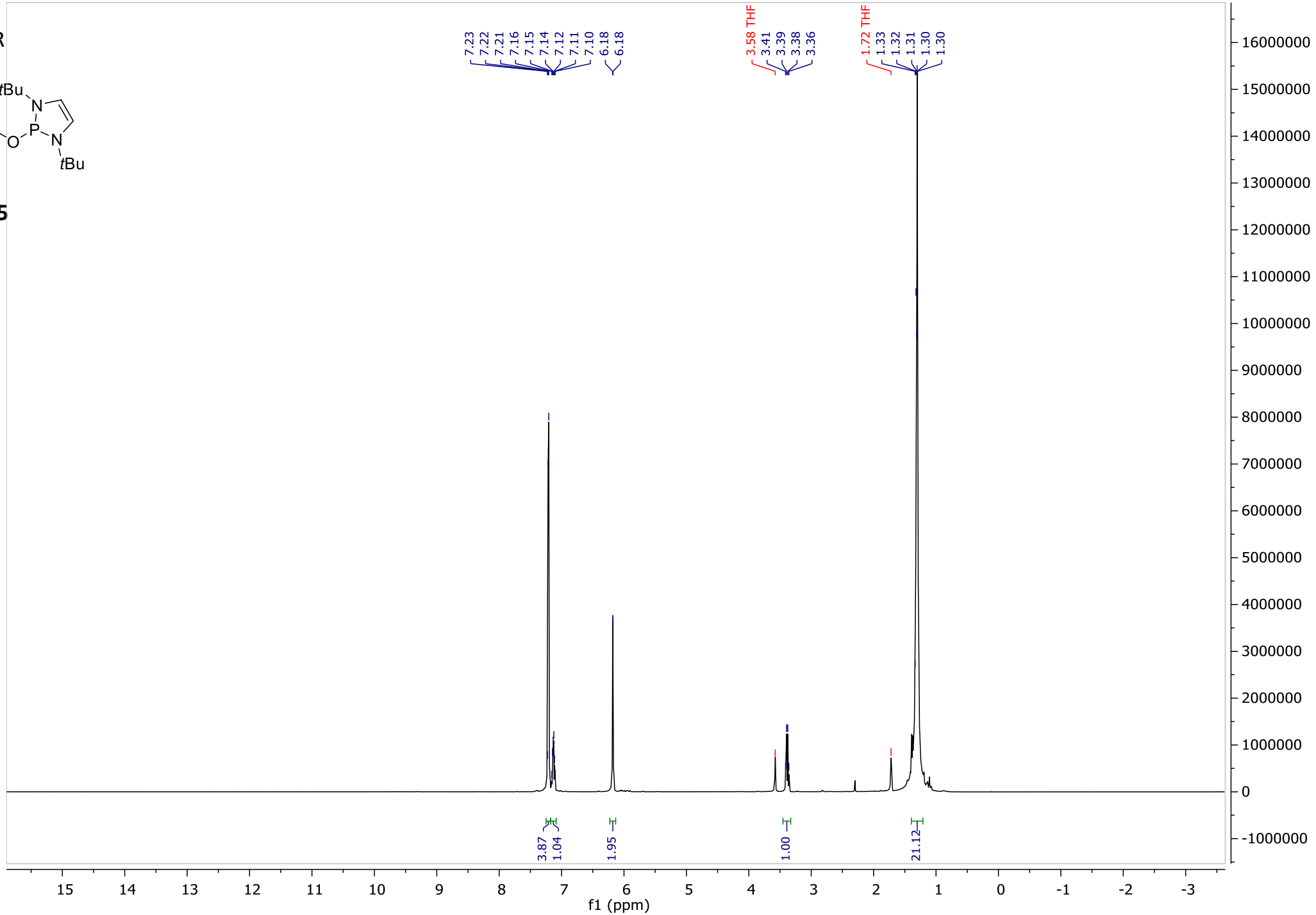
2p


179.48
139.83
132.85
131.76
130.73
129.85
127.25
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.64
18.12
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

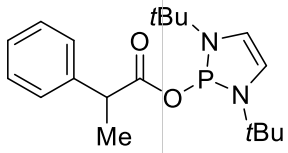
^{1}H NMR


tBu
N
O
P
O
N
tBu
Me

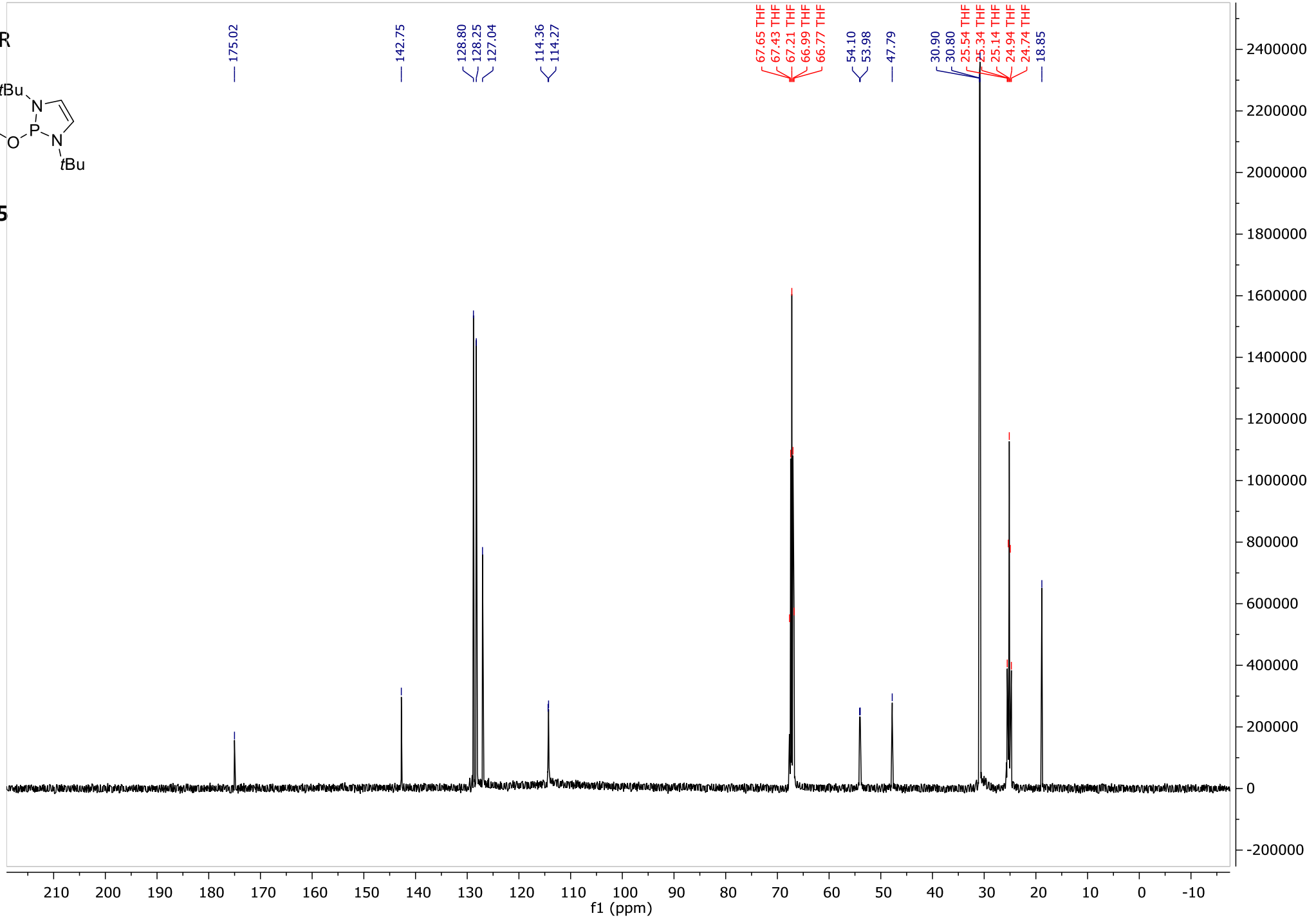
P5


7.23
7.22
7.21
7.16
7.15
7.14
7.12
7.11
7.10
6.18
6.18
3.58 THF
3.41
3.39
3.38
3.36
1.72 THF
1.33
1.32
1.31
1.30
1.30
3.87
1.04
1.95
1.00
21.12
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

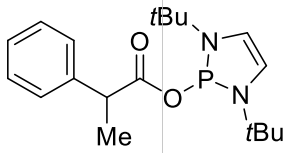
^{13}C NMR


tBu
O
N
P
O
N
tBu
Me

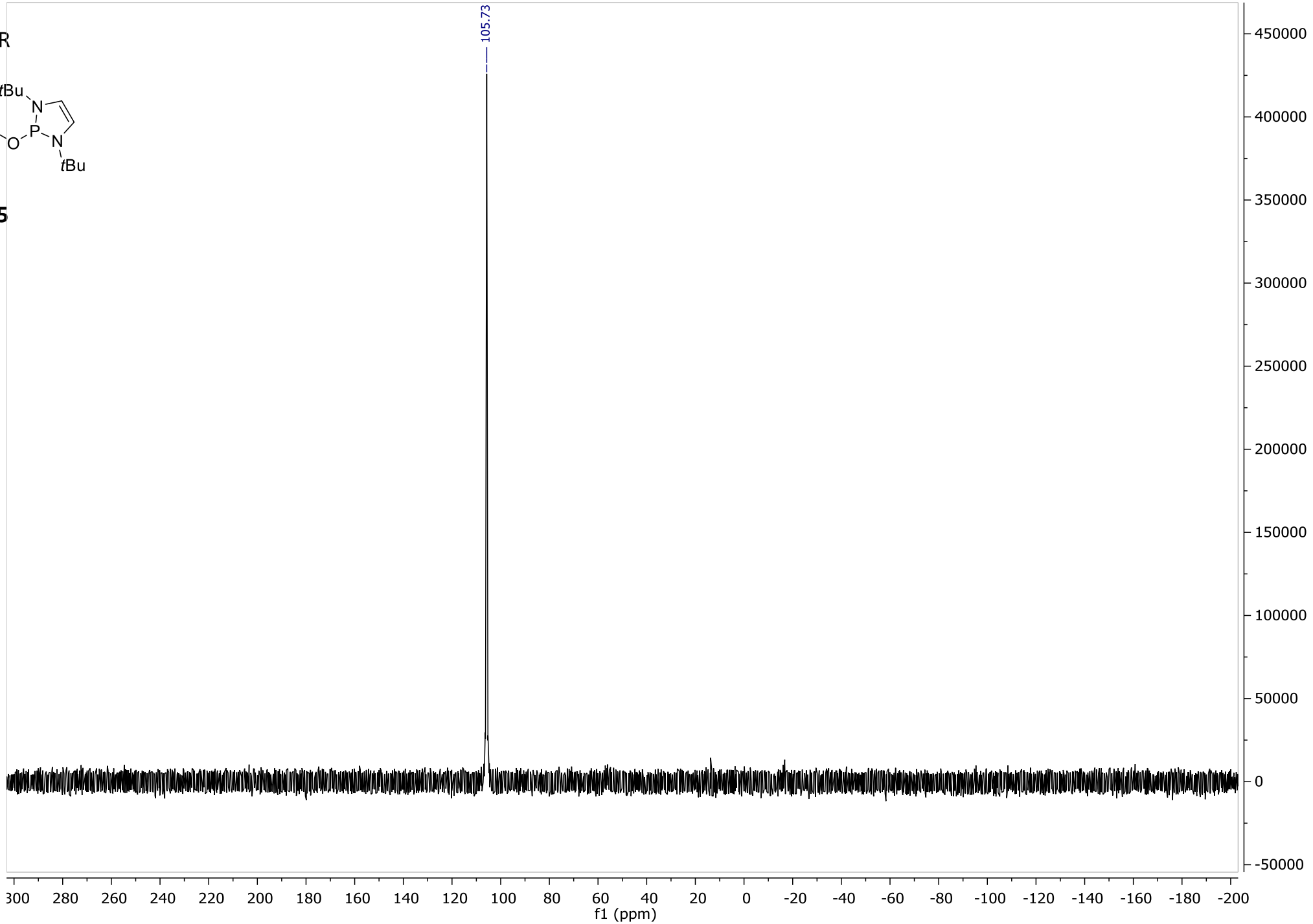
P5


175.02
142.75
128.80
128.25
127.04
114.36
114.27
67.65 THF
67.43 THF
67.21 THF
66.99 THF
66.77 THF
54.10
53.98
47.79
30.90
30.80
25.54 THF
25.34 THF
25.14 THF
24.94 THF
24.74 THF
18.85
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

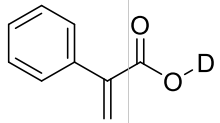
^{31}P NMR

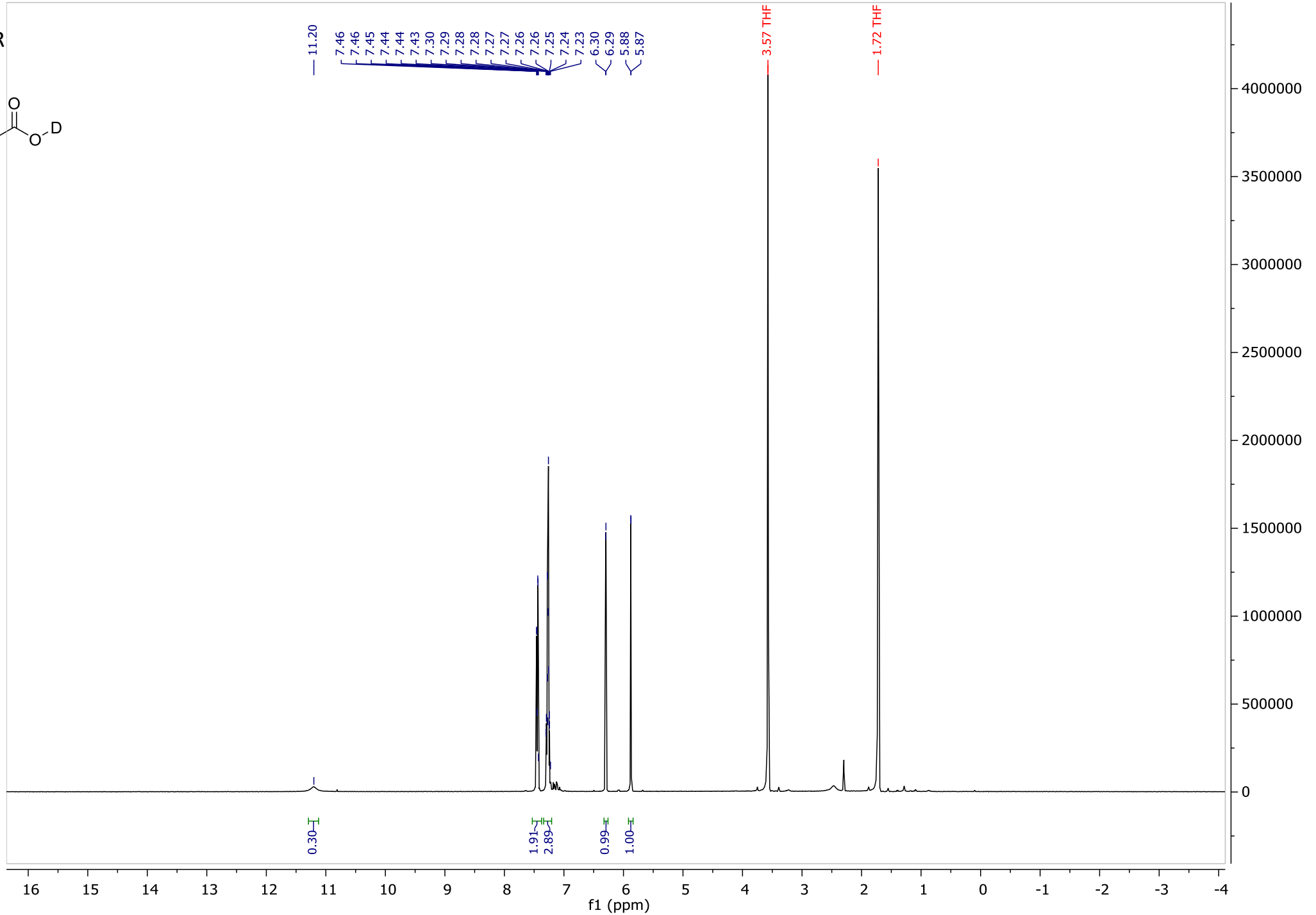

tBu
N
O
P
O
N
Me
tBu

P5

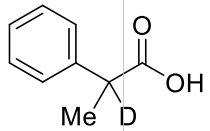

105.73
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

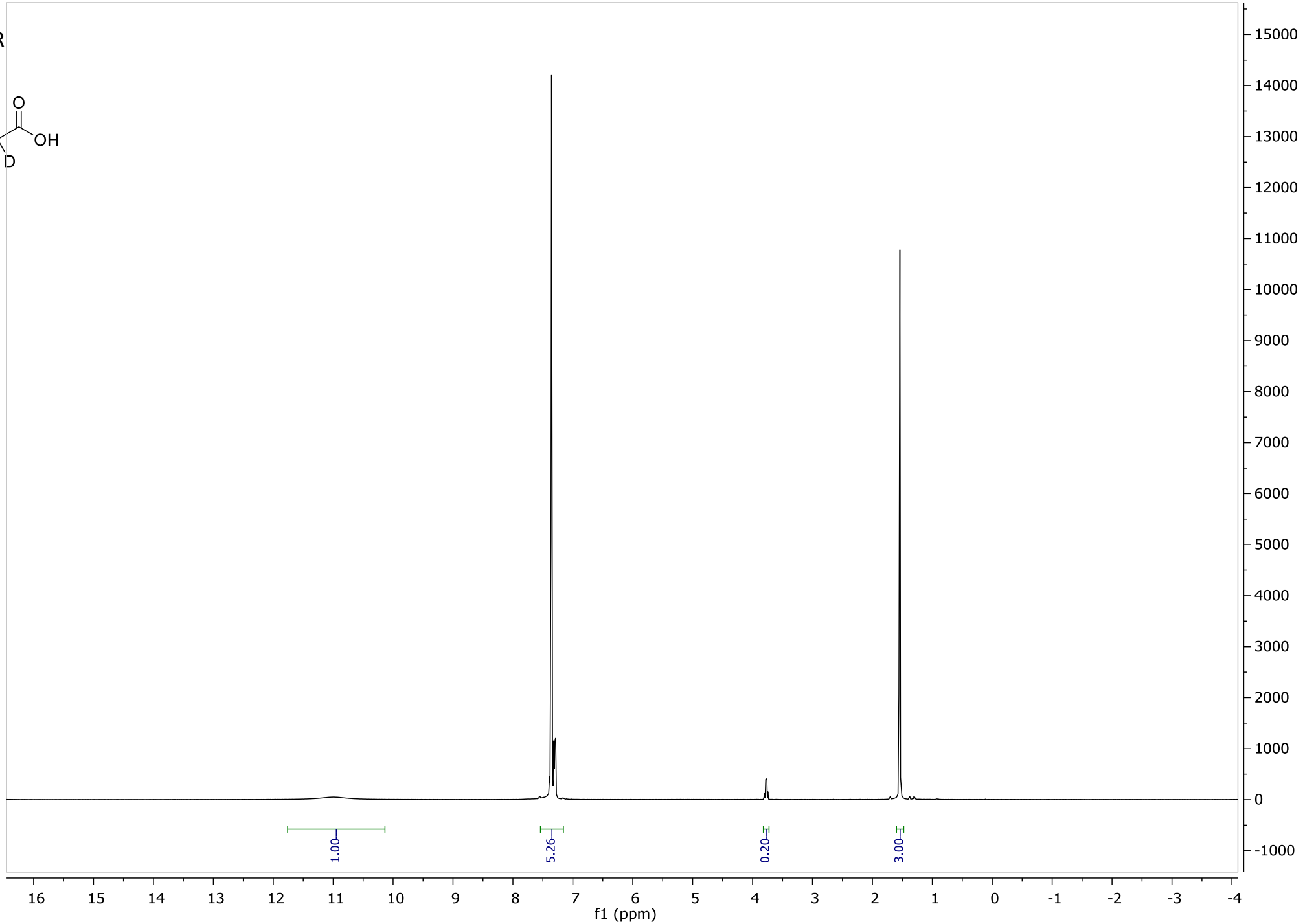
^{1}H NMR


O
O
D


11.20
7.46
7.46
7.45
7.44
7.44
7.43
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.23
6.30
6.29
5.88
5.87
3.57 THF
1.72 THF
0.30
1.91
2.89
0.99
1.00
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

^{1}H NMR


O
OH
Me
D


15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
5.26
0.20
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)