Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Enantioselective Catalytic Remote Perfluoroalkylation of α-Branched Enals driven by Light

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A. General Information

The NMR spectra were recorded at 300 MHz, 400 MHz and 500 MHz spectrometers for ^{1}H or at 75 MHz, 101 MHz and 126 MHz for ^{13}C or 376 MHz for ^{19}F, respectively. The chemical shifts (δ) for ^{1}H and ^{13}C signals are given in ppm relative to residual signals of the solvents ($CHCl_3$ at 7.26 ppm in ^{1}H NMR and at 77.16 ppm in ^{13}C NMR spectra). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), hept (heptet), m (multiplet), br (broad).

High-resolution mass spectra (HRMS) were obtained from the ICIQ High-Resolution Mass Spectrometry Unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization or atmospheric pressure chemical ionization. X-ray data were obtained from the ICIQ X-Ray Unit using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector. Optical rotations were measured on a Polarimeter Jasco P-1030 and are reported as follows: [α]D ambient temperature (c in g per 100 mL, solvent). Cyclic voltammetry studies were carried out on a Princeton Applied Research PARSTAT 2273 potentiostat, offering compliance voltage up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 2 A current range. UV-Vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D2 and W light sources. *The authors are indebted to the team of the Research Support Area at ICIQ, particularly to the X-ray, NMR, and High-Resolution Mass Spectrometry Units.*

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased, anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using flash column chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF254, 0.25 mm) were employed, using UV light as the visualizing agent and basic aqueous potassium permanganate ($KMnO_4$) stain solution and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator (in vacuo at 40 ºC, >5 mbar).

Determination of Enantiomeric Purity. UPC^2 analysis on chiral stationary phase was performed on a Waters ACQUITY® instrument using IA-3, ID-3, IE-3, IG-3, and OJ-3 chiral columns. The exact conditions for the analyses are specified in the experimental section of the individual compounds. UPC^2 traces were compared to racemic samples prepared using the optimised conditions with a 1:1 mixture of (*R*)- and (*S*)-catalyst **A** or **C**, both commercially available from Sigma Aldrich.

Materials. The synthesis of commercially unavailable enal substrates and catalysts is described in section B. All other starting materials used in this study are commercial and were purchased in the highest purity available from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, Apollo and CarboSynth, and used as received, without further purification.

Experimental Setup. The reaction setup used in this study consists of an aluminium supported single-LED connected to a power supply to modulate the light intensity. The single LED is provided of a plastic 3D-printed support above which is placed an aluminium fitter for the reaction vials. The latter is provided with inlet and outlet holes through which the refrigerating liquid flows. The setup is connected by rubber tubes to a Huber minichiller set to -12 ºC which cools the aluminium plate and the reaction (the temperature of the reaction mixture was measured to be -10 ºC). The setup is finally inserted in a homemade plastic cover to provide a closed space in which an Argon/Nitrogen atmosphere is created to prevent any water condensation during the

reaction. The irradiance of the single LED is measured before every reaction trough the aid of a photodiode and is generally stable on 100 mW/cm^2.

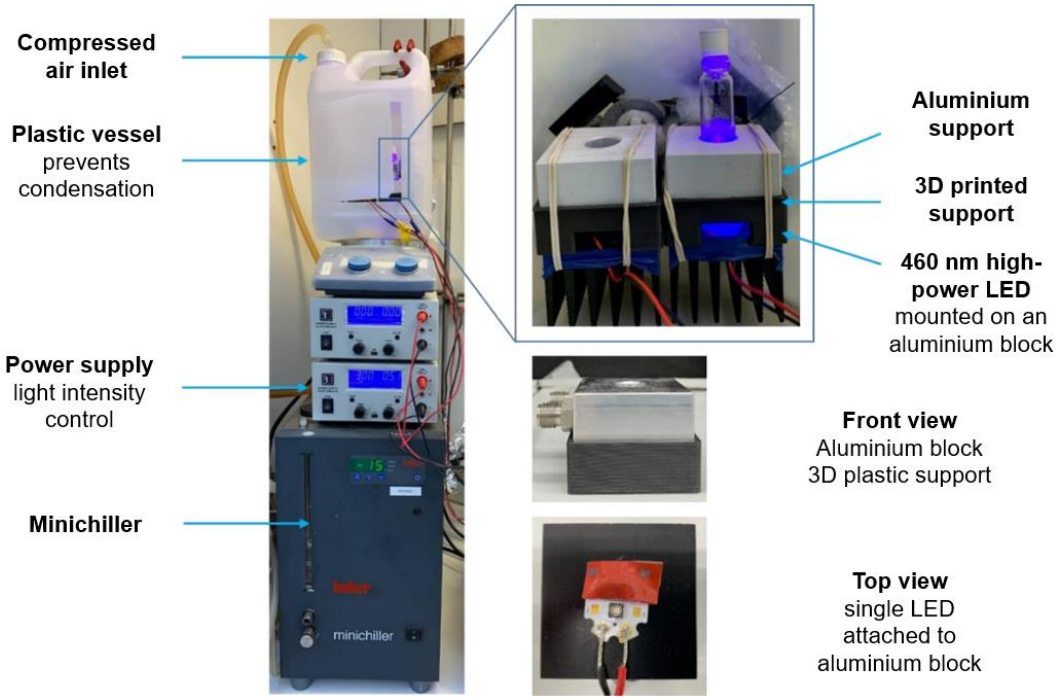


Figure S1: Photoreactor used for the catalytic reactions.

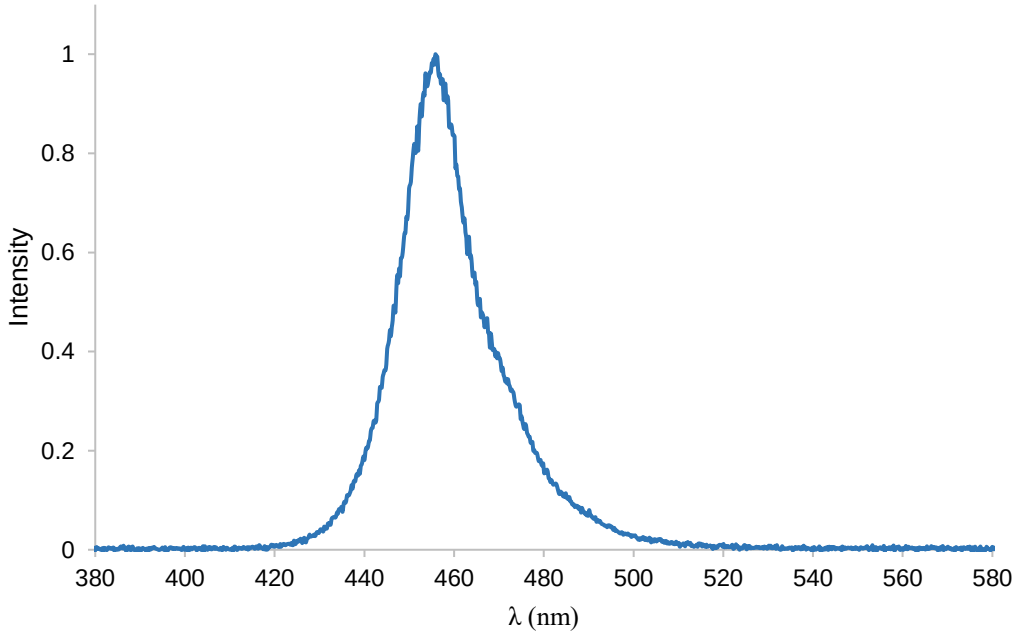


Figure S2: Emission spectrum of the 465 nm LED strip used in this study.

B. Synthesis of Enal Substrates 1

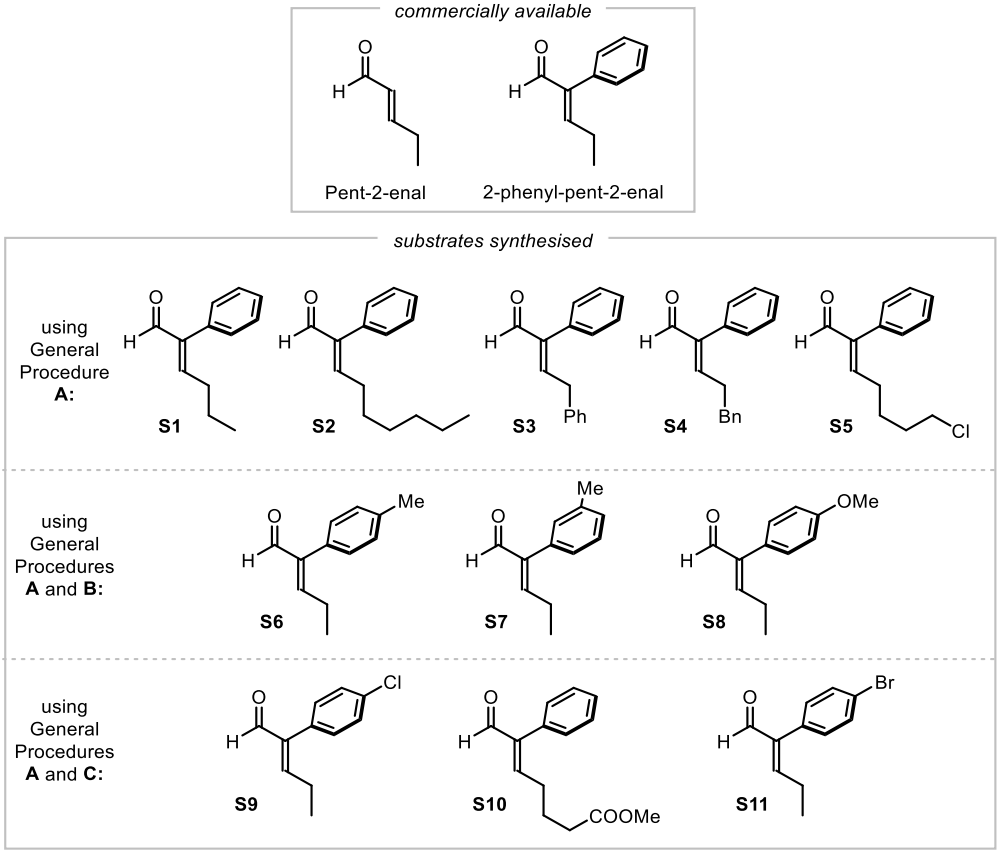
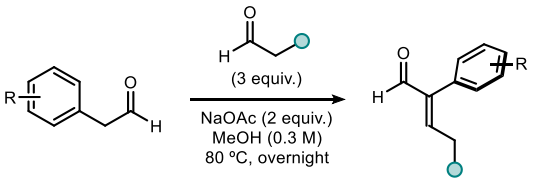


Figure S3: The enal substrates used in this study.

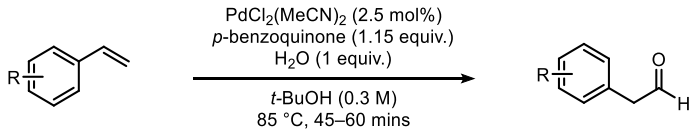
Pent-2-enal and 2-phenyl-pent-2enal are commercially available and were used without prior purification. Enals **S1–5** were prepared by aldol condensation following General Procedure **A** as described below. Substrates **S6–8** were prepared by a two-step sequence, starting from the corresponding styrene, following General Procedure **B**, followed by aldol condensation using General Procedure **A**. Enals **S9–11** were prepared from the corresponding alcohol using general procedure **C** followed by General Procedure **A**.

General Procedure A:



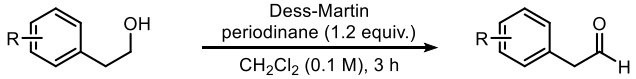
Based on a reported procedure:[3] to a stirred solution of 2-aryl acetaldehyde (1 equiv.) in MeOH (0.3 M) was added the corresponding aldehyde (3 equiv.), NaOAc (2 equiv.), and the resulting mixture heated to reflux overnight. The mixture was concentrated in vacuo and the residue suspended in Et_2O. The organic solution was washed twice with brine (2 × 10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/EtOAc) to afford the enal product.

General Procedure B:



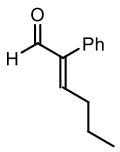
Following a modified known procedure:[1] to a stirred solution of $PdCl_2(MeCN)_2$ (2.5 mol%) and benzoquinone (1.15 equiv.) in *t*-BuOH (0.3 M) was added distilled H_2O (1 equiv.) and the requisite styrene derivative (1 equiv.). The resulting mixture was stirred at 85 °C for 45–60 minutes (until consumption of starting material judged by TLC analysis). The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2. The organic solution was washed once with water, brine, and then dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The aldehyde was further purified by vacuum distillation before use in the next step.

General Procedure C:



Following a modified known procedure:[2] to a solution of the requisite alcohol (1 equiv.) in CH_2Cl_2 (0.1 M) was added Dess-Martin periodinane (1.2 equiv.) at room temperature. After 3 hours, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (20 mL) and $Na_2S_2O_3$ (20 mL), and the mixture was left to stir for a further 30 minutes. The resulting mixture was extracted with CH_2Cl_2 (2 × 25 mL), and the combined organic extracts were washed with brine (15 mL), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo. The crude residue was purified by flash chromatography to give the corresponding aldehyde.

Characterisation Data of substrates S1–11:

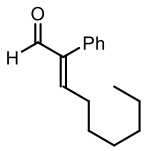


2-phenylnonen-2-enal S1

Synthesized according to General Procedure **A** using 2-phenyl-acetaldehyde (240 mg, 2.0 mmol) and pentanal (433 mg, 6.0 mmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/Et_2O 95:5) to afford **S1** as a colorless oil (185 mg, 53%) with spectroscopic data in accordance with the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.45 – 7.34 (m, 3H), 7.20 – 7.16 (m, 2H), 6.75 (t, *J* = 7.5 Hz, 1H), 2.37 (q, *J* = 7.5 Hz, 2H), 1.56 (q, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 193.8, 156.4, 144.1, 132.7, 129.4, 128.2, 127.9, 31.7, 22.1, 13.8.

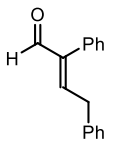


2-phenylnonen-2-enal S2

Synthesized according to General Procedure **A** using 2-phenyl-acetaldehyde (1.00 g, 8.32 mmol) and heptanal (3.35 g, 25.0 mmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 9:1 to 7:3) to afford **S2** as a colourless oil (590 mg, 30%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.43 – 7.33 (m, 3H), 7.18 – 7.13 (m, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 2.36 (q, *J* = 7.5 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.33 – 1.22 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 156.8, 144.0, 132.8, 129.5, 128.3, 128.0, 31.6, 29.9, 29.1, 28.9, 22.6, 14.2.

HRMS (ESI$^+$) $C_{15}H_{20}O$ [M+Na]$^+$: found 239.1400, required 239.1406 (–2.5 ppm).



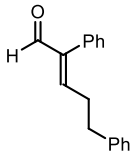
(*E*)-2,4-diphenylbut-2-enal S3

Synthesized according to General Procedure **A** (self-condensation) using 2-phenyl-acetaldehyde (240 mg, 2.0 mmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/Et_2O 95:5 to 85:15) to afford **S3** as a colorless oil (293 mg, 66%) with spectroscopic data in accordance with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.43 – 7.33 (m, 3H), 7.18 – 7.13 (m, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 2.36 (q, *J* = 7.5 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.33 – 1.22 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 156.8, 144.0, 132.8, 129.5, 128.3, 128.0, 31.6, 29.9, 29.1, 28.9, 22.6, 14.2.

(5-phenyl)2-phenylpent-2-enal S4



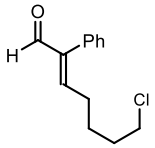
Synthesized according to General Procedure **A** using 2-phenyl-acetaldehyde and hydrocinnamaldehyde. The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 9:1 to 7:3) to afford product in 31% yield as a colorless oil.

^{1}H NMR (500 MHz, CDCl3) δ 9.60 (s, 1H), 7.40 – 7.27 (m, 5H), 7.21 (m, 1H), 7.17 – 7.09 (m, 2H), 7.10 – 7.00 (m, 2H), 2.82 (m, 2H), 2.74 – 2.64 (m, 2H).

^{13}C NMR (126 MHz, CDCl3) δ 193.7, 154.9, 144.6, 140.4, 132.6, 129.5, 128.7, 128.5, 128.4, 128.1, 126.5, 34.9, 31.5.

HRMS (ESI$^+$) $C_{17}H_{16}O$ $[M+H]^+$: found 237.1271, required 237.1274 (–1.3 ppm).

(7-chloro)-2-phenyheptan-2-enal S5



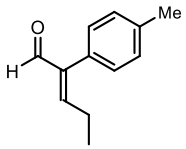
Synthesized according to General Procedure **A** using 2-phenyl-acetaldehyde (1.80 g, 15.0 mmol) and 5-chloropentanal (603 mg, 5.0 mmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford **S5** as a colorless oil (423 mg, 38%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.43 – 7.38 (m, 2H), 7.37 – 7.33 (m, 1H), 7.16 – 7.13 (m, 2H), 6.71 (t, *J* = 7.5 Hz, 1H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.40 (q, *J* = 7.5 Hz, 2H), 1.81 – 1.75 (m, 2H), 1.72 – 1.65 (m, 2H).

^{13}C NMR (126 MHz, CDCl3) δ 191.6, 147.2, 145.2, 130.5, 128.2, 128.7, 128.5, 38.4, 32. 5, 30.6, 29.1, 29.1, 22.9.

HRMS (ESI$^+$) $C_{15}H_{20}O$ $[M+Na]^+$: found 239.1412, required 239.1411 (+0.4 ppm).

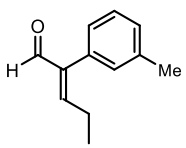
(*E*)-2-(*p*-tolyl)pent-2-enal S6



Synthesized according to General Procedure **A** using 2-(*p*-tolyl)acetaldehyde (189 mg, 1.4 mmol) and propionaldehyde (300 μL, 4.23 mmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 95:5) to afford **S6** as a colorless oil (141 mg, 58%) with spectroscopic data in accordance with the literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.71 (t, J = 7.5 Hz, 1H), 2.49 – 2.33 (m, 5H), 1.14 (t, J = 7.5 Hz 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 157.7, 143.3, 137.7, 129.6, 129.3, 129.0, 23.3, 21.3, 13.3.

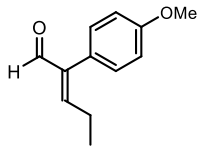


(*E*)-2-(*m*-tolyl)pent-2-enal S7

Synthesized according to General Procedure **A** using 2-(*m*-tolyl)acetaldehyde (751 mg, 5.60 mmol) and propionaldehyde (933 µL, 16.8 mmol). The crude mixture was purified by flash column chromatography (hexane/CH_2Cl_2 95:5) to afford **S7** as a colorless oil (439 mg, 45%) with spectroscopic data in accordance with the literature.[4]

^{1}H NMR (500 MHz, CDCl3) δ 9.63 (s, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.03 – 6.94 (m, 2H), 6.71 (t, J = 7.5 Hz, 1H), 2.47 – 2.33 (m, 5H), 1.13 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 193.9, 157.7, 143.6, 137.8, 132.5, 130.0, 128.7, 128.1, 126.4, 23.2, 21.5, 13.3.

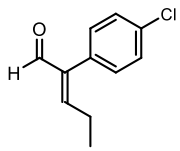


(*E*)-2-(4-methoxyphenyl)pent-2-enal S8

Synthesized according to General Procedure **A** using 2-(4-methoxyphenyl)acetaldehyde (1.50 g, 10.0 mmol) and propionaldehyde (2.2 mL, 16.8 mmol). The crude mixture was purified by flash column chromatography (hexane/EtOAc 90:10) to afford **S8** as a yellow oil (856 mg, 45%) with spectroscopic data in accordance with the literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 3.85 (s, 3H), 2.42 (p, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H).

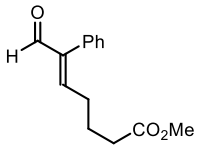
^{13}C NMR (126 MHz, CDCl3) δ 194.2, 159.3, 157.5, 142.9, 130.6, 124.7, 113.7, 55.3, 23.2.



(*E*)-2-(4-chlorophenyl)pent-2-enal S9

Synthesized according to General Procedure **A** using 2-(4-chlorophenyl)acetaldehyde (1.36 g, 8.80 mmol) and propionaldehyde (3.2 mL, 44.0 mmol, 5 equiv.). The crude mixture was purified by flash column chromatography (hexane/EtOAc 90:10) to afford **S9** as a yellow oil (330 mg, 19%), with spectroscopic data in accordance with the literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.40 – 7.35 (m, 2H), 7.12 – 7.07 (m, 2H), 6.72 (t, *J* = 7.6 Hz, 1H), 2.37 (p, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H).

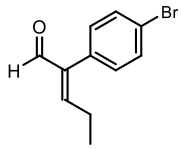


Methyl (*E*)-7-oxo-6-phenylhept-5-enoate S10

Synthesized according to General Procedures **A** using 2-phenyl-acetaldehyde (2.00 g, 15.4 mmol) and methyl-5-oxopentanoate (5.54 g, 46.1 mmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2 to 7:3) to afford **S10** as a colourless oil (1.40 g, 39%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.43 – 7.31 (m, 3H), 7.22 – 7.08 (m, 2H), 6.69 (t, *J* = 7.5 Hz, 1H), 3.63 (s, 3H), 2.35–2.45 (m, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.84 (tt, *J* = 7.5, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.6, 173.4, 154.6, 144.8, 132.5, 129.5, 128.4, 128.2, 51.7, 33.4, 29.2, 24.1.

HRMS (ESI$^+$) $C_{14}H_{16}O_3$ $[M+Na]^+$: found: 255.0990, required 255.0992 (0.8 ppm).



(*E*)-2-(4-chlorophenyl)pent-2-enal S11

Synthesized according to General Procedure **A** using 2-(4-chlorophenyl)acetaldehyde (2.09 g, 10.5 mmol) and propionaldehyde (3.79 mL, 52.5 mmol, 5 equiv.). The crude mixture was purified by flash column chromatography (hexane/EtOAc 90:10) to afford **S11** as a yellow oil (524 mg, 21%) with spectroscopic data in accordance with the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.56 – 7.51 (m, 2H), 7.06 – 7.01 (m, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 2.36 (p, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 158.3, 142.6, 131.6, 131.5, 131.3, 122.4, 23.4, 13.4.

C. Unsuccessful Substrates

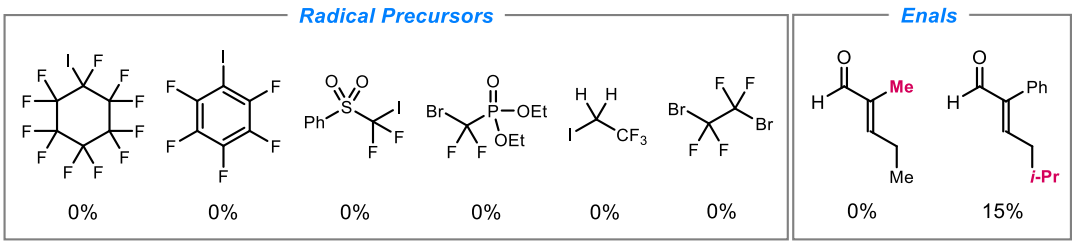


Figure S4: Survey of unsuccessful substrates tested under the optimized conditions: enal **1** (3 equiv.), radical precursor **2** (0.2 mmol, 1 equiv.), *cis*-catalyst **M** (20 mol%), 2,6-lutidine (1-2 equiv.) in Et_2O (0.7 M) at –10 °C for 20 h under blue light irradiation (460 nm, 100 mWcm^{-2}).

D. Catalyst Synthesis

Catalysts **A** and **C** were purchased from Sigma Aldrich and used as received. Catalysts **B**, **D–G** were synthesized from *L*-proline following reported procedures.[6] Catalysts **H–N** were synthesized from *trans*-4-Hydroxy-*L*-proline.[7] *Cis*-catalysts **I–N** were synthesized according to the reported 5-step route described below (Figure S5).[7] Characterization data for optimal *cis*-catalyst **M** is reported below.

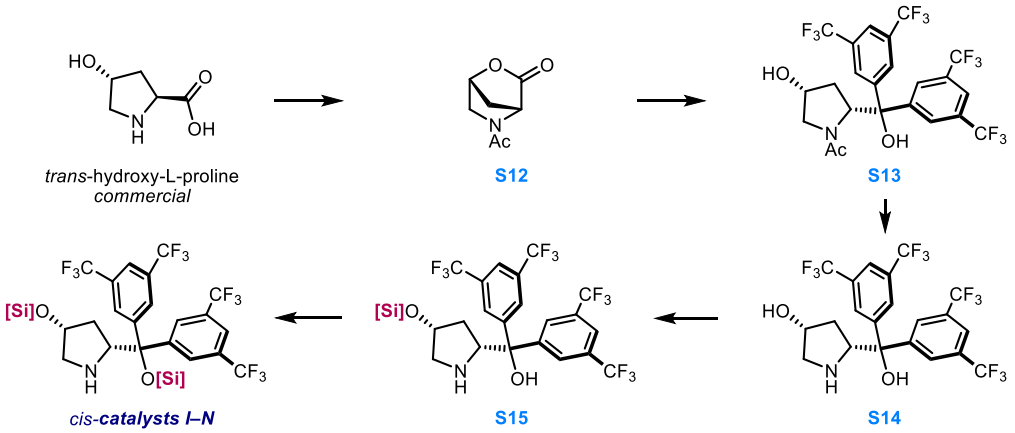
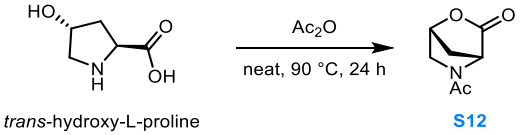


Figure S5: Synthetic route to cis-catalysts **I**–**N**.

(1*R*,4*R*)-5-Acetyl-2-oxa-5-azabicyclo[2.2.1]heptan-3-one (S12)

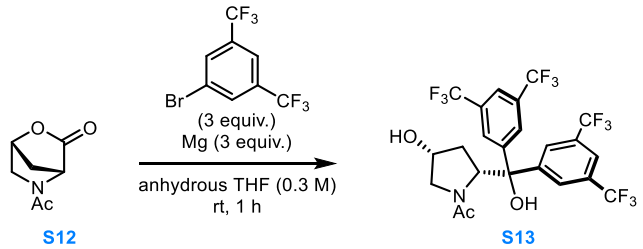


A suspension of *trans*-4-hydroxy-*L*-proline (10.0 g, 76 mmol) in acetic anhydride (50 mL, 534 mmol) was stirred at 90 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. *i*-PrOH (50 mL) was added under

rapid stirring and the resulting mixture was stored in the freezer at –20 °C for 16 h. The resulting white precipitate was filtered off and washed with hexane (3 x 25 mL). Drying under vacuum afforded lactone **S12** as a white solid (7.1 g, 60%), which was used without further purification. Characterization data was in accordance with the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18–5.14 (m, 1H), 5.07 (s, 0.36H), 4.46–4.44 (m, 0.64H), 3.71–3.51 (m, 2H), 2.35–2.24 (m, 1H), 2.17 (s, 1.91H), 2.14–2.09 (m, 0.67H), 2.05 (s, 1.10H), 1.99–1.90 (m, 0.36H).

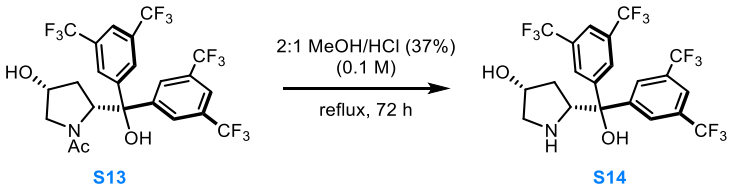
1-((2*R*,4*R*)-2-(Bis(3,5-bis(trifluoromethyl)phenyl)(hydroxy)methyl)-4-hydroxypyrrolidin-1-yl)ethan-1-one (S13)



In an oven-dried two-necked round bottom flask, equipped with a septum and condenser, Mg turnings (3.3 g, 137 mmol) were stirred under vacuum for 30 minutes. Anhydrous THF (60 mL) was added, followed by one crystal of I_2. 1-Bromo-3,5-bis(trifluoromethyl)benzene (25.2 mL, 137 mmol) was added dropwise, maintaining a controlled exothermic reaction while the colour changed gradually from red-brown to grey. After the solution cooled to room temperature, lactone **S12** (7.1 g, 46 mmol) was added in one portion, and the reaction stirred for 1 h. The mixture was cooled to 0 °C and carefully quenched with aqueous HCl (1 N, 100 mL). The mixture was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic layers washed once with brine, dried over anhydrous magnesium sulfate, filtered, and then concentrated *in vacuo* to afford prolinol **S13** as a dark brown oil (13.9 g, 52%) which was used without further purification. Characterization data was in accordance with the literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.89 (s, 1H), 7.82 (s, 2H), 7.70 (s, 1H), 6.69 (brs, 1H), 5.35 (dd, *J* = 9.3, 1.9 Hz, 1H), 4.53 (m, 1H), 4.04 (brs, 1H), 3.87 (dd, *J* = 11.9, 6.6 Hz, 1H), 3.61 (dd, *J* = 11.8, 2.3 Hz, 1H), 2.32 (ddd, *J* = 15.3, 9.3, 6.4 Hz, 1H), 1.80 (s, 3H), 1.75 (d, *J* = 14.8 Hz, 1H).

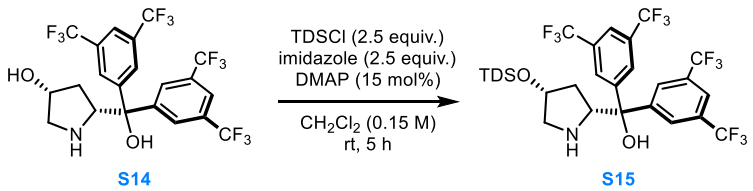
(3*R*,5*R*)-5-(bis(3,5-bis(trifluoromethyl)phenyl)(hydroxy)methyl)-pyrrolidin-3-ol (S14)



A suspension of prolinol **S2** (2.80 g, 4.80 mmol) and conc. HCl (37% in water, ca. 12 M, 15 mL) in MeOH (30 mL) was heated to reflux for 72 h. Excess MeOH removed *in vacuo* and the remaining solution was neutralized by careful addition of saturated aqueous Na_2CO_3. Addition was continued with frequent testing of the solution with pH indicator paper until a pH of ~10 was measured. The mixture was then extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed once with brine, dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to afford a brown foam. The crude product was purified by column chromatography on silica (hexane/EtOAc 1:1) to afford prolinol **S3** (1.90 g, 72%) as a light brown foam with spectroscopic data in accordance with the literature.[7]

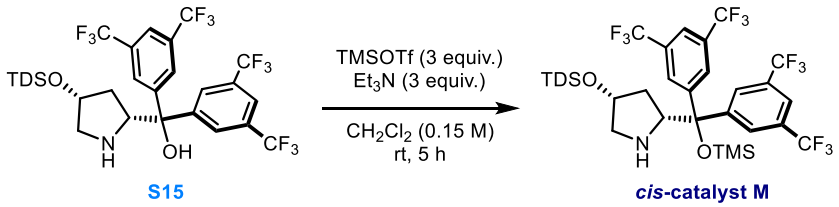
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.98 (s, 2H), 7.77 (s, 2H), 5.13 (brs, 1H), 4.50 (dd, *J* = 9.4, 5.0 Hz, 1H), 4.44 – 4.36 (m, 1H), 3.16 – 3.04 (m, 2H), 2.09 (ddd, *J* = 14.8, 9.4, 5.7 Hz, 1H), 1.83 (brs, 2H), 1.58 (ddt, *J* = 14.5, 5.1, 1.5 Hz, 1H).

Bis(3,5-bis(trifluoromethyl)phenyl)((2*R*,4*R*)-4-(((2,3-dimethylbutan-2-yl)dimethylsilyl)oxy)pyrrolidin-2-yl)methanol (S4)



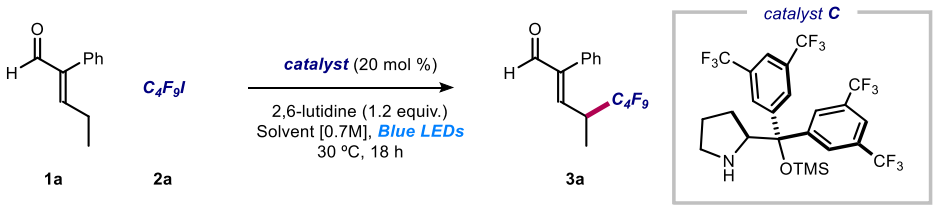
To a rapidly stirred solution of prolinol **S3** (3.30 g, 6.10 mmol), imidazole (1.04 g, 15.2 mmol), and DMAP (112 mg, 0.91 mmol) in CH_2Cl_2 (40 mL) was added TDSCl (2.94 g, 15.24 mmol) dropwise at room temperature. The solution was stirred at room temperature for 5 h, before H_2O (30 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 50 mL), and the combined organic layers were washed once with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* to afford crude prolinol **S15** as a light brown oil which was sufficiently pure to be taken on to the next step.

(2*R*,4*R*)-2-(Bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)-methyl)-4-(((2,3-dimethylbutan-2-yl)dimethylsilyl)oxy)pyrrolidine (*cis*-catalyst M)



To a solution of prolinol **S15** (4.17 g, 6.10 mmol) and triethylamine (2.6 mL, 18.29 mmol) in CH_2Cl_2 (40 mL) was added TMSOTf (3.3 mL, 18.29 mmol) dropwise at 0 °C under strong stirring. The resulting solution was stirred at 23 °C for 5 h. The reaction was quenched with H_2O and extracted with CH_2Cl_2 (3 x 50 mL). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* to afford a brown oil. Purification by silica gel column chromatography (hexane/Et_2O 98:2) to afford catalyst **M** as a pale-yellow oil (3.46 g, 75% over two steps).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.84 (s, 2H), 7.80 (s, 2H), 4.21 (ddd, *J* = 7.0, 4.0, 1.1 Hz, 1H), 3.99 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.90 (dd, *J* = 11.7, 5.9 Hz, 1H), 2.42 (dd, *J* = 11.7, 4.8 Hz, 1H), 1.88 (dt, *J* = 13.8, 7.2 Hz, 1H), 1.49 (p, *J* = 6.9 Hz, 1H), 1.30 (ddd, *J* = 13.1, 9.5, 5.9 Hz, 1H), 0.77 (d, *J* = 6.9 Hz, 6H), 0.71 (d, *J* = 2.9 Hz, 6H), -0.02 (d, *J* = 1.8 Hz, 6H), -0.07 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 146.2, 131.8 (q, $^2J_{CF}$ = 33 Hz), 131.3 (q, $^2J_{CF}$ = 33 Hz), 128.9 (d, $^3J_{CF}$ = 2.5 Hz), 128.1 (d, $^3J_{CF}$ = 2.5 Hz), 123.4 (dd, $^1J_{CF}$ = 272.1, 14.4 Hz), 122.0 (m, overlapped signals), 82.1, 72.2, 64.5, 55.8, 37.9, 34.2, 24.8, 20.3, 20.3, 18.6, 18.5, 2.0, –2.71.
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.83 (s, 6F), -62.89 (s, 6F).
HRMS (ESI$^+$) $C_{32}H_{42}F_{12}NO_2Si_2$ $[M+H]^+$: found 756.2588, required 756.2557 (+4.1 ppm).

E. Optimization of the reaction conditions



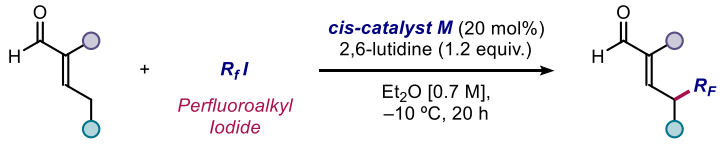
entry	solvent	yield **3a** (%)[a]	e.r. **3a** [b]
1	THF	63	83:17
2	Et_2O	96	83:17
3	toluene	77	84:16
4	DCM	60	83:17
5	DMF	0	/
6[c]	Et_2O	0	/
7[d]	Et_2O	0	/

Table S1: [a] Reaction performed on a 0.2 mmol scale using 3 equiv. of **1a**. Yield of **3a** determined by ^{1}H NMR analysis of the crude mixture using trimethyl orthoformate as internal standard. [b] Enantiomeric ratio of **3a** determined by derivatization to the corresponding 2,4-dinitrophenyl hydrazine prior to injection in UPC[2]. [c] Reaction conducted in the absence of catalyst. [d] Reaction conducted in the absence of light.

F. Experimental Procedures and Characterization of Products

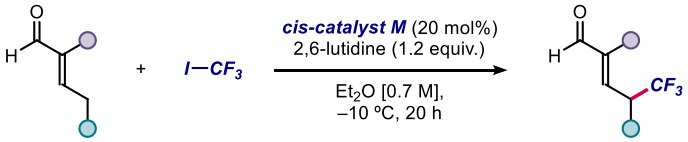
F1. General Procedures for the asymmetric γ-perfluoroalkylation of enals

General Procedure D: γ-perfluoroalkylation using liquid or solid perfluoroalkyl iodides



To an oven-dried 5 mL vial, equipped with a Teflon septum screw cap and a magnetic stirring bar, was added *cis*-catalyst **M** (40 µmol, 20 mol%), degassed Et_2O (300 µL, 0.7 M), enal **1** (600 µmol, 3 equiv.), 2,6-lutidine (240 µmol, 1.2 equiv.), and perfluoroalkyl iodide **2** (200 µmol, 1 equiv.). The vial was purged with argon before being capped and sealed with parafilm and placed in the photoreactor set-up (see section **A**) with the LED irradiance fixed at 150 mW/cm^2. The reaction was stirred at –10 °C for 18 hours, before subjection of the mixture to silica gel column chromatography (silica pre-treated with triethylamine, elution solvent pre-cooled to <10 °C). The enantiomeric excess of the product was determined by conversion of the aldehyde product to the corresponding 2,4-dinitrophenyl hydrazone prior to chiral UPC^2 analysis: the purified γ-perfluoroalkyl enal **3** was dissolved in 1 mL of CH_2Cl_2 and 1 mL of MeOH then 2,4-dinitrophenyl hydrazine hydrochloride (1.5 equiv.) and 3 drops of concentrated HCl were added. The mixture was stirred for 10 minutes, then the solvents evaporated and the crude purified with preparative TLC on silica gel (hexane/EtOAc 9:1). **Notes**: if the substrate enal **1** was not colorless (e.g. pale yellow), it was first diluted with Et_2O, filtered through a pad of activated charcoal and the solvent removed under reduced pressure. If the radical precursor **2** appeared pink/purple in color (indicating the presence of I_2), it was diluted with Et_2O and washed with a saturated solution of $Na_2S_2O_3$ and dried over $MgSO_4$ prior to use.

General Procedure E: γ-Trifluoromethylation of enals (gaseous reagent)

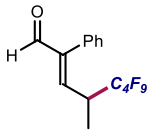


An argon-purged Schlenk tube, equipped with a rubber septum and a magnetic stirring bar, was cooled in a dry-ice/acetone bath to –78 °C. Under a gentle flow of Argon, trifluoromethyl iodide (1 equiv.) was condensed in the tared Schlenk tube using a rubber tube fitted with an 18-gauge needle (see Figure S6 below). Et_2O (300 µL), 2,6-lutidine (1.2 equiv.), enal **1** (3 equiv.), *cis*-catalyst **M** (20 mol%) and DMSO (25 µL) were added sequentially, and the tube sealed with parafilm. The Schlenk tube was removed from the cooling bath and transferred to the pre-cooled photoreactor. The remainder of the procedure follows the instructions described in General Procedure **D**.

Figure S6: Gaseous CF_3I is transferred to the reaction vessel (Schlenk tube). CF_3I was allowed to evaporate at room temperature through tubing fitted with an air-tight needle, which was inserted into the septum of a Schlenk tube cooled at –78 °C under argon using a dry ice/acetone bath.

F2. Characterization of Products 3

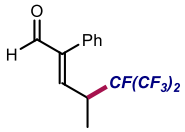
(*S*,*E*)-4-(Perfluorobutyl)-2-phenylpent-2-enal (3a)



Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and perfluorobutyl iodide (69 mg, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3a** (54 mg, 72% yield) as a colourless oil. The enantiomeric ratio of the product was determined by UPC[2] analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm; τ_{minor} = 4.3 min, τ_{major} = 4.5 min), 93:7 e.r.

$[\alpha]_D^{20}$ = -56.1 (c=0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.68 (s, 1H), 7.55 – 7.35 (m, 3H), 7.13 – 7.08 (m, 2H), 6.64 (d, J = 10.4 Hz, 1H), 3.49 – 3.39 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 192.6, 146.4, 145.9, 131.4, 128.7 (2C), 128.7, 36.9, 13.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –81.0 (t, J = 10.3 Hz, 3F), –115.5 – –120.0 (m, 2F), –120.3 – –122.8 (m, 2F), –124.6 – –127.1 (m, 2F).
HRMS (ESI$^+$) $C_{15}H_{11}F_9O$ $[M+Na]^+$: found: 401.0553, required 401.0558 (–1.2 ppm).

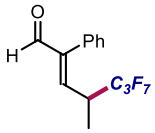
(*S*,*E*)-4-(Perfluoroisopropyl)-2-phenylpent-2-enal (3b)



Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and heptafluoro-2-iodopropane (28.5 µL, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3b** (47 mg, 71% yield) as a colourless oil. The enantiomeric ratio of the product was determined by UPC[2] analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 4.5 min, τ_{major} = 4.7 min), 88:12 e.r. $[\alpha]_D^{20}$ = -17.0 (c=0.5, $CHCl_3$).

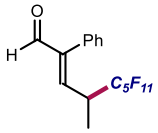
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.68 (s, 1H), 7.52 – 7.37 (m, 3H), 7.13 – 7.06 (m, 2H), 6.68 (d, J = 10.8, 1H), 3.59 – 3.45 (m, 1H), 1.33 (d, J = 8.3 Hz, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 192.7, 146.8, 146.2, 131.2, 128.8, 128.7, 128.3, 35.4, 14.5.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –73.1 (m, 6F), –178.4 (m, 1F).
HRMS (ESI$^+$) $C_{14}H_{11}F_7O$ [M+Na]$^+$: found 351.0581, required 351.0590 (–2.6 ppm).

(*S*,*E*)-4-(Perfluoropropyl)-2-phenylpent-2-enal (3c)



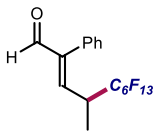
Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and heptafluoro-1-iodopropane (28.5 µL, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3c** (39 mg, 60% yield) as a colourless oil. The enantiomeric ratio of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 375 nm: τ_{minor} = 6.3 min, τ_{major} = 6.6 min), 92:8 e.r. $[\alpha]_D^{20}$ = +11.3 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.68 (s, 1H), 7.52 – 7.34 (m, 3H), 7.14 – 7.07 (m, 2H), 6.63 (d, J = 10.4 Hz, 1H), 3.53 – 3.33 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 192.7, 146.4, 145.9, 131.4, 128.8, 128.7, 128.7, 36.7, 13.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –80.8 (m, 3F), –116.1 – –120.9 (m, 2F), –123.5 – –126.8 (m, 2F).
HRMS (ESI$^+$) $C_{14}H_{11}F_7O$ [M+Na]$^+$: found 351.0592; required: 351.0590 (+0.6 ppm).

(*S*,*E*)-4-(Perfluoropentyl)-2-phenylpent-2-enal (3d)



Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and perfluoropentyl iodide (79 mg, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3d** (63 mg, 74% yield) as a colourless oil. The enantiomeric ratio of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 350 nm: τ_{minor} = 5.8 min, τ_{major} = 6.0 min), 89:11 e.r. $[\alpha]_D^{20}$ = -40.7 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.68 (s, 1H), 7.52 – 7.35 (m, 3H), 7.13 – 7.08 (m, 2H), 6.64 (d, *J* = 10.5 Hz, 1H), 3.52 – 3.40 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 192.6, 146.4, 145.9, 131.4, 128.7, 128.7, 128.7, 37.0, 13.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –80.8 (m, 3F), –115.4 – –119.5 (m, 2F), –119.7 – –121.8 (m, 2F), –122.8 (m, 2F), –125.4 – –127.0 (m, 2F).
HRMS (ESI$^+$) $C_{16}H_{11}F_{11}O$ [M+Na]$^+$: found: 451.0511, required 451.0526 (–3.3 ppm).

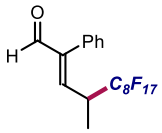
(*S*,*E*)-4-(Perfluorohexyl)-2-phenylpent-2-enal (3e)



Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and perfluorohexyl iodide (89 mg, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3e** (67 mg, 70% yield) as a white solid. The enantiomeric ratio of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 4.0 min, τ_{major} = 4.1 min), 91:9 e.r. $[\alpha]_D^{20}$ = -22.3 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.68 (s, 1H), 7.47 – 7.37 (m, 3H), 7.13 – 7.07 (m, 2H), 6.64 (d, *J* = 10.5 Hz, 1H), 3.47 – 3.38 (m, 1H), 1.30 (d, *J* = 7.0 Hz, 3H).

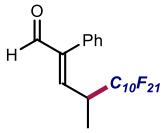
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ_C: 192.6, 146.4, 145.9, 131.4, 128.7, 128.7, 128.7, 37.0, 13.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –80.8 (m, 3F), –115.1 – –119.4 (m, 2F), –119.6 – –121.6 (m, 2F), –122.0 (m, 2F), –122.8 (m, 2F), –126.0 – –126.3 (m, 2F).
HRMS (ESI$^+$) $C_{17}H_{11}F_{13}O$ $[M+H]^+$: found: 479.0685, required 479.0675 (+2.1 ppm).

(*S*,*E*)-4-(Perfluorooctyl)-2-phenylpent-2-enal (3f)



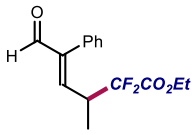
Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and heptadecafluoro-1-iodooctane (53.5 µL, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 85:15) to afford product **3f** (65 mg, 56% yield) as a white solid. The enantiomeric ratio of the product was determined by UPC^2 analysis on a Daicel Chiralpak IB column (eluent: CO_2/EtOH = 97:3; flow rate 2 mL/min, λ = 375 nm. τ_{minor} = 3.3 min, τ_{major} = 3.5 min), 89:11 e.r. $[\alpha]_D^{20}$ = +5.0 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.68 (s, 1H), 7.55 – 7.36 (m, 3H), 7.15 – 7.05 (m, 2H), 6.64 (d, *J* = 10.5 Hz, 1H), 3.51 – 3.38 (m, 1H), 1.30 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 192.6, 146.43 145.9, 131.4, 128.7, 128.7, 128.7, 37.0, 13.0.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –80.8 (t, *J* = 10.3 Hz, 3F), –115.3 – –119.3 (m, 2F), –119.4 – –121.5 (m, 2F), –121.6 – –122.0 (m, 6F), –122.7 (m, 2F), –126.1 (m, 2F).
HRMS (ESI$^+$) $C_{19}H_{11}F_{17}O$ $[M+Na]^+$: found 601.0431, required 601.0427 (–0.7 ppm).

(*S*,*E*)-4-(Perfluorodecyl)-2-phenylpent-2-enal (3g)



Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and perfluorodecyl iodide (129 mg, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3g** (84 mg, 62% yield) as a white solid. The enantiomeric excess of the product was determined by chiral HPLC analysis on a Daicel Chiralpak IC-3 column (eluent: *n*-hexane/*i*-PrOH 80:20; flow rate 1 mL/min, λ = 254 nm: τ_{minor} = 13.3 min, τ_{major} = 17.0 min), 86:14 e.r. $[\alpha]_D^{20}$ = -24.9 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.69 (s, 1H), 7.51 – 7.35 (m, 3H), 7.10 (m, 2H), 6.64 (d, *J* = 10.4 Hz, 1H), 3.52 – 3.40 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ_C: 192.6, 146.4, 145.9, 131.4, 128.7, 128.7, 128.7, 37.0, 13.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –80.8 (t, *J* = 9.5 Hz, 3F), –115.6 – –119.2 (m, 2F), –119.6 – –121.5 (m, 2F), –121.9 (m, 10F), –122.7 (m, 2F), –126.2 (m, 2F).
HRMS (ESI$^+$) $C_{21}H_{11}F_{21}O$ $[M+Na]^+$: found 701.0374, required 701.0367 (+1.0 ppm).

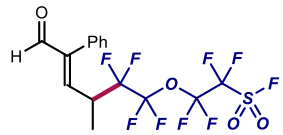
Ethyl (*S*,*E*)-2,2-difluoro-3-methyl-6-oxo-5-phenylhex-4-enoate (3h)



Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and ethyl 2,2-difluoro-2-iodoacetate (50.0 mg, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 3:2) to afford product **3h** (37.9 mg, 67 % yield) as a colourless oil. The enantiomeric excess of the product was determined by chiral UPC^2 analysis on a Daicel Chiralpak IC-3 column (eluent: *n*-hexane/*i*-PrOH 80:20; flow rate 1 mL/min, λ = 254 nm: τ_{minor} = 2.2 min, τ_{major} = 2.1 min), 88:12 e.r. $[\alpha]_D^{20}$ = -81.1 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.69 (s, 1H), 7.49 – 7.33 (m, 3H), 7.18 – 7.12 (m, 2H), 6.65 (d, *J* = 10.6 Hz, 1H), 4.38 – 4.22 (m, 2H), 3.53 – 3.36 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 3H).

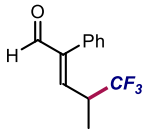
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ_C: 193.0, 163.3, 148.0, 146.3, 131.6, 129.0, 128.6, 117.6, 115.6, 113.6, 63.1, 38.8, 29.7, 13.9, 13.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: -62.75 – -63.13 (m, 1F), -108.83 – -115.21 (m, 1F).
HRMS (ESI^+) $C_{15}H_{16}F_2O_3$ $[M+Na]^+$: found 305.0973, required 305.0960 (+4.3 ppm).

(*S*,*E*)-1,1,2,2-tetrafluoro-2-((1,1,2,2-tetrafluoro-3-methyl-6-oxo-5-phenylhex-4-en-1-yl)oxy)ethane-1-sulfonyl fluoride (3i)



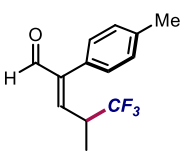
Synthesized according to General Procedure **D** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethane-1-sulfonyl fluoride (85.2 mg, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3h** (36.4 mg, 40 % yield) as a colourless oil. The enantiomeric excess of the product was determined by chiral UPC^2 analysis on a Daicel Chiralpak IE column (eluent: *n*-hexane/*i*-PrOH 80:20; flow rate 2 mL/min, λ = 360 nm: τ_{minor} = 4.2 min, τ_{major} = 4.4 min), 84:16 e.r. $[\alpha]_D^{20}$ = -35.0 (c = 0.5, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.70 (s, 1H), 7.51 – 7.36 (m, 3H), 7.17 – 7.07 (m, 2H), 6.63 (d, *J* = 10.5 Hz, 1H), 3.40 (dtq, *J* = 17.5, 10.5, 6.9 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 4H).
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ_C: 192.6, 146.0, 131.2, 128.8, 128.7, 128.7, 36.4, 36.2, 36.2, 36.0, 29.7, 13.1.
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: -81.99 (m, 2F), -83.00 – -85.33 (m, 2F), -112.20 (m, 2F), -118.52 – -123.09 (m, 2F).
HRMS (ESI^+) $C_{15}H_{11}F_9O_4S$ $[M+Na]^+$: found 481.0126, required 481.0127 (+0.2 ppm).

(*S*,*E*)-4-(Trifluoromethyl)-2-phenylpent-2-enal (3j)



Synthesized according to General Procedure **E** using phenylpent-2-enal **1a** (96 mg, 600 µmol) and trifluoromethyl iodide (39.8 mg, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford **3j** as a colorless oil (31.2 mg, 56% yield). The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 360 nm. τ_{minor} = 5.3 min, τ_{major} = 5.5 min), 87:13 er.
$[\alpha]_D^{20}$ = -12.3 (c = 0.5, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.50 – 7.38 (m, 3H), 7.14 (m, 2H), 6.57 (d, *J* = 10.4 Hz, 1H), 3.43 – 3.24 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 192.7, 146.7, 146.4, 131.4, 129.0, 128.7, 127.8, 38.7, 13.8.
^{19}F NMR (282 MHz, $CDCl_3$) δ_F: –71.6 (m, 3F).
HRMS (ESI^+) $C_{12}H_{11}F_3O$ $[M+Na]^+$: found 251.0654, required 251.0654 (+0.0 ppm).

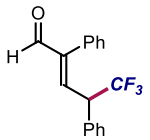
(*S*,*E*)-4-(Trifluoromethyl)-2-(*p*-tolyl)pent-2-enal (3k)



Synthesized according to General Procedure **E** using phenylpent-2-enal **S6** (96 mg, 600 µmol) and trifluoromethyl iodide (39.8 mg, 200 µmol) as reaction partners. The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford **3k** (21 mg, 43% yield) as a colorless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 360 nm: τ_{minor} = 5.4 min, τ_{major} = 5.7 min), 86:14 e.r. $[\alpha]_D^{20}$ = -17.4 (c = 0.5, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.67 (s, 1H), 7.25 – 7.22 (m, 2H), 7.05 – 7.00 (m, 2H), 6.54 (d, *J* = 10.4 Hz, 1H), 3.41 – 3.29 (m, 1H), 2.39 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 3H).

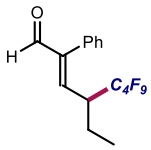
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 192.9, 146.7, 146.2, 146.2, 138.6, 129.4, 128.9, 38.8, 21.4, 13.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -71.5 (d, *J* = 8.1 Hz, 3F).
HRMS (ESI$^+$) $C_{13}H_{13}F_3O$ [M+Na]$^+$: found 265.0815, required 265.0811 (+1.5 ppm).

(*S*,*E*)-4-(Trifluoromethyl)-2-phenylnon-2-enal (3l)



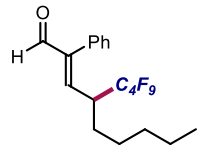
Synthesized according to General Procedure **E** using phenylpent-2-enal **S3** (96 mg, 600 µmol) and trifluoromethyl iodide (39.8 mg, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/Et_2O 98:2) to afford product **3l** (29 mg, 36% yield) as a colorless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 360 nm. τ_{Major} = 5.8 min, τ_{Minor} = 5.6 min.) 85:15 e.r. $[\alpha]_D^{20}$ = +7.6 (c = 0.2, $CHCl_3$)
HRMS (ESI): m/z calculated for $[C_{17}H_{13}O_1F_3Na]^+$ [M]$^+$: 313.0816; found: 313.0811. (+1.6 ppm)
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s,1), 7.40 (m 6H), 7.24 (m, 1H), 7.07 – 6.98 (m, 3H), 4.37 (dq, J = 10.6, 8.7 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 147.1, 144.0, 133.4, 131.4, 129.4, 129.2, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 49.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -68.57 (d, J = 8.7 Hz)

(*S*,*E*)-4-(Perfluorobutyl)-2-phenylhex-2-enal (3m)



Synthesized according to General Procedure **D** using 2-phenylhex-2-enal **S1** (105 mg, 600 µmol) and perfluorobutyl iodide **2a** (34.6 µL, 200 µmol) The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc 8:2) to afford product **3m** (49 mg, 62% yield) as a colourless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 360 nm: τ_{minor}= 6.1 min, τ_{major} = 6.3 min), 91:9 e.r. $[\alpha]_D^{20}$ = -8.0 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.72 (s, 1H), 7.48 – 7.35 (m, 3H), 7.11 (m, 2H), 6.54 (dd, J = 10.8, 2.0 Hz, 1H), 3.37 – 3.20 (m, 1H), 1.94 (m, 1H), 1.65 (m, 1H), 0.86 (t, J = 7.5 Hz, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 192.5, 172.3, 148.2, 144.0, 131.2, 129.1, 128.9, 128.9, 51.9, 41.4, 30.3, 22.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: –81.1 (m, 3F), –114. 5 – –116.5 (m, 2F), –120.2 – –122.0 (m, 2F), –126.0 (m, 2F).
HRMS (ESI$^+$) $C_{16}H_{13}F_9O$ [M+Na]$^+$: found 415.0715, required 415.0706 (+2.2 ppm).

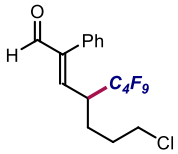
(*S*,*E*)-4-(Perfluorobutyl)-2-phenylnon-2-enal (3n)



Synthesized according to General Procedure **D** using 2-phenylnon-2-enal **S2** (130 mg, 600 µmmol) and perfluorobutyl iodide **2a** (34.6 µL, 200 µmmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3n** (65 mg, 75% yield) as a colorless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 4.4 min, τ_{major} = 4.6 min), 90:10 e.r. $[\alpha]_D^{20}$ = -13.3 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.71 (s, 1H), 7.48 – 7.34 (m, 3H), 7.19 – 7.04 (m, 2H), 6.54 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.43 – 3.30 (m, 1H), 3.46 – 3.32 (m, 1H), 1.91 – 1.80 (m, 1H), 1.62 (m, 1H), 1.38 – 1.01 (m, 6H), 0.84 (t, *J* = 7.3 Hz, 3H).

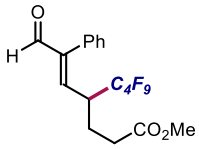
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ_C: 192.9, 147.6, 145.9, 131.7, 129.2, 128.7 (2C), 42.0, 31.5, 27.2, 26.2, 22.5, 14.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: –81.1 (m, 3F), –113. 9 – –116.5 (m, 2F), –119.4 – –123.0 (m, 2F), –126.0 (m, 2F).
HRMS (ESI^+) $C_{19}H_{19}F_9O$ $[M+Na]^+$: found 457.1198, required 457.1184 (+2.9 ppm).

(*S*,*E*)-7-Chloro-4-(perfluorobutyl)-2-phenylhept-2-enal (3o)



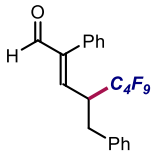
Synthesized according to General Procedure **D** using 7-chloro-2-phenylhept-2-enal **S5** (134 mg, 600 µmol) and perfluorobutyl iodide **2a** (34.6 µL, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3o** (36 mg, 41% yield) as a colorless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 360 nm: τ_{minor} = 4.6 min, τ_{major} = 4.8 min), 88:12 e.r. $[\alpha]_D^{20}$ = -4.1 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.72 (s, 1H), 7.51 – 7.35 (m, 3H), 7.13 – 7.08 (m, 2H), 6.56 (dd, *J* = 10.7, 1.5 Hz, 1H), 3.45 – 3.27 (m, 3H), 2.05 (m, 1H), 1.82 – 1.70 (m, 2H), 1.60 – 1.48 (m, 1H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ_C: 192.5, 147.8, 144.6, 131.4, 129.0, 128.9 (2C), 43.9, 41.5, 29.4, 24.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: –81.0 (m, 3F), –112.9 – –116.6 (m, 2F), –118.9 – –122.7 (m, 2F), –125.0– –127.1 (m, 2F).
HRMS (ESI^+) $C_{17}H_{14}ClF_9O$ $[M+Na]^+$: found 463.0483, required 463.0482 (+0.2 ppm).

Methyl (*S*,*E*)-7-oxo-6-phenyl-4-(perfluorobutyl)hept-5-enoate (3p)



Synthesized according to General Procedure **D** using methyl (*E*)-7-oxo-6-phenylhept-5-enoate **S10** (139 mg, 600 µmol) and perfluorobutyl iodide **2a** (34.6 µL, 200 µmmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3p** (54 mg, 60% yield) as a colorless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IB column (eluent: CO_2/MeOH = 90:10; flow rate 2 mL/min, λ = 375 nm: τ_{minor} = 4.2 min, τ_{major} = 4.4 min), 93:7 e.r.
$[\alpha]_D^{20}$ = -12.2 (c = 0.1, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.71 (s, 1H), 7.45 – 7.39 (m, 3H), 7.12 – 7.07 (m, 2H), 6.52 (dd, *J* = 10.9, 1.8 Hz, 1H), 3.55 (s, 3H), 3.54 – 3.48 (m, 1H), 2.34 – 2.26 (m, 1H), 2.26 – 2.20 (m, 1H), 2.19 – 2.10 (m, 1H), 1.95 – 1.84 (m, 1H).
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 192.5, 172.3, 148.2, 144.0, 131.2, 129.1, 128.9, 128.9, 51.9, 41.4 (t, $^2J_{CF}$ = 21.5 Hz), 30.3, 22.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -81.0, -114.8 – -115.6 (m), -120.0 – -122.2 (m), -125.9 – -126.1 (m). HRMS (ESI^+) $C_{18}H_{15}F_9O_3$ $[M+Na]^+$: found 473.0771, required 473.0770 (+0.2 ppm)

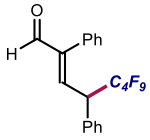
(*S*,*E*)-4-(Perfluorobutyl)-2,5-diphenylpent-2-enal (3q)



Synthesized according to General Procedure **D** using 2,5-diphenylpent-2-enal **S4** (142 mg, 600 µmol) and perfluorobutyl iodide (34.6 µL, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3q** (54 mg, 59% yield) as a colourless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a

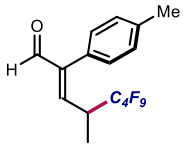
Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor}= 4.7 min, τ_{major}= 4.9 min), 90:10 e.r. $[\alpha]_D^{20}$ = +31.2 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.63 (s, 1H), 7.27 – 7.23 (m, 4H), 7.22 – 7.10 (m, 2H), 7.00 – 6.93 (m, 2H), 6.54 (dd, *J* = 10.9, 2.1 Hz, 1H), 6.35 – 6.29 (m, 2H), 3.60 – 3.46 (m, 1H), 3.30 (dd, *J* = 13.6, 3.2 Hz, 1H), 2.78 (dd, *J* = 13.6, 10.8 Hz, 1H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 192.6, 148.2, 143.9, 135.9, 131.0, 129.7, 128.9, 128.7, 128.4, 128.2, 127.4, 44.6, 33.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -81.0 (m, 3F), -112.5 – -117.6 (m, 2F), -118.6 – -123.2 (m, 2F), -125.7 – -126.3 (m, 2F).
HRMS (ESI$^+$) $C_{21}H_{15}F_9O$ [M+Na]$^+$: found 477.0871, required 477.0871 (+0.0 ppm).

(*S*,*E*)-4-(Perfluorobutyl)-2,4-diphenylbut-2-enal (3r)



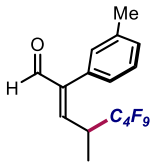
Synthesized according to General Procedure **D** using 2,4-diphenylbut-2-enal **S3** (133 mg, 600 µmol) and nonafluoro-1-iodobutane (34.6 µL, 600 µL). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3r** (55 mg, 62% yield) as a colourless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak OJ column (eluent: CO_2/MeCN = 90:10; flow rate 2 mL/min, λ = 350 nm: τ_{minor} = 2.7 min, τ_{major} = 2.9 min), 89:11 e.r. $[\alpha]_D^{20}$ = +44.5 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.74 (s, 1H), 7.44 – 7.36 (m, 6H), 7.24 – 7.19 (m, 2H), 7.13 – 7.03 (m, 2H), 7.02 – 6.96 (d, 10.5 Hz, 1H), 4.44 (m, 1H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 192.5, 146.3, 143.7, 131.2, 129.3, 129.3, 129.0, 128.9, 128.9, 128.6, 127.8, 47.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: –81.1 (m, 3F), –111.8 – –115.9 (m, 2F), –121.0 (m, 2F), –126.0 (m, 2F). HRMS (ESI$^+$) $C_{20}H_{13}F_9O$ [M+Na]$^+$: found 463.0715, required 463.0727 (–2.6 ppm).

(*S*,*E*)-4-(Perfluorobutyl)-2-(*p*-tolyl)pent-2-enal (3s)



Synthesized according to General Procedure **D** using 2-(*p*-tolyl)pent-2-enal **S6** (105 mg, 600 µmol) and perfluorobutyl iodide **2a** (34.6 µL, 200 µmol. The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3s** (50 mg, 64% yield) as a colourless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 360 nm: τ_{minor} = 4.4 min, τ_{major} = 4.6 min), 90:10 e.r. $[\alpha]_D^{20}$ = +21.0 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.67 (s, 1H), 7.26 – 7.21 (m, 2H), 7.02 – 6.96 (m, 2H), 6.61 (dd, *J* = 10.4, 2.1 Hz, 1H), 3.51 – 3.42 (m, 1H), 2.39 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 192.9, 146.2, 145.9, 138.6, 129.5, 128.6, 128.3, 37.0, 21.4, 13.2
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.0 (m, 3F), -115.2 – -119.9 (m, 2F), -120.3 – -122.9 (m, 2F), 125.0 – -126.9 (m, 2F).HRMS (ESI$^+$) $C_{16}H_{13}F_9O$ [M+Na]$^+$: found 415.0731, required 415.0715 (+3.8 ppm).

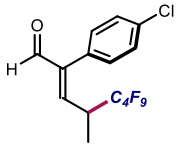
(*S*,*E*)-4-(Perfluorobutyl)-2-(*m*-tolyl)pent-2-enal (3t)



Synthesized according to General Procedure **D** using 2-(*m*-tolyl)pent-2-enal **S7** (600 µmol, 105 mg) and perfluorobutyl iodide **2a** (34.6 µL, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3t** (37 mg, 47% yield) as a colourless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a

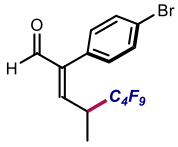
Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 360 nm, τ_{minor} = 4.3 min, τ_{major} = 4.4 min), 90:10 e.r. $[\alpha]_D^{20}$ = -15.9 (c = 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.67 (s, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 6.92 – 6.87 (m, 2H), 6.62 (dd, *J* = 10.4, 2.2 Hz, 1H), 3.52 – 3.38 (m, 1H), 2.38 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 192.9, 146.4, 146.2, 138.6, 131.5, 129.6, 129.5, 128.8, 125.9, 37.0, 21.6, 13.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ_F: -81.0 (m, 3F), -115.5 – -119.7 (m, 2F), -120.2 – -123.1 (m, 2F), -126.1 (m, 2F).
HRMS (ESI$^+$) $C_{16}H_{13}F_9O$ [M+Na]$^+$: found 415.0715, required 415.0720 (–1.2 ppm)

(*S*,*E*)-4-(Perfluorobutyl)-2-(*p*-chlorophenyl)pent-2-enal (3u)



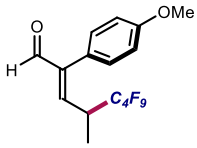
Synthesized according to General Procedure **D** using 2-(*p*-chlorophenyl)pent-2-enal **S9** (117 mg, 600 μmol) and perfluorobutyl iodide **2a** (34.6 μL, 200 μmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford **3u** (50 mg, 61% yield) as a colorless oil. The enantiomeric excess of the product was determined UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 4.6 min, τ_{major} = 4.9 min), 92:8 e.r. $[\alpha]_D^{20}$ = -46.3 (c = 0.5, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 9.66 (s, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.65 (dd, *J* = 10.5, 2.2 Hz, 1H), 3.41 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 192.4, 147.1, 145.0, 135.1, 130.3, 129.8, 129.2, 37.1, 13.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ_F: -80.4 – -81.1 (m, 3F), -115.4 – -119.8 (m, 2F), -119.9 – -123.1 (m, 2F), -125.1 – -127.0 (m, 2F).
HRMS (ESI$^+$) $C_{15}H_{10}ClF_9O$ [M+Na]$^+$: found 435.0169, required 435.0174 (–1.1 ppm).

(*S*,*E*)-4-(Perfluorobutyl)-2-(*p*-bromophenyl)pent-2-enal (3v)



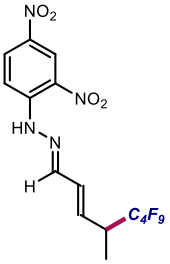
Synthesized according to General Procedure **D** using 2-(*p*-bromophenyl)pent-2-enal **S11** (96 mg, 600 μmol) and perfluorobutyl iodide **2a** (34.6 μL, 200 μmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3v** (31.2 mg, 56% yield) as a colourless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 1 mL/min, λ = 211 nm: τ_{minor} = 6.6 min, τ_{major} = 6.9 min), 89:11 e.r. $[\alpha]_D^{20}$ = -12.7 (c = 0.1, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.66 (s, 1H), 7.64 – 7.52 (m, 2H), 7.02 – 6.94 (m, 2H), 6.65 (dd, *J* = 10.5, 2.1 Hz, 1H), 3.53 – 3.31 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 192.3, 147.0 (d, *J* = 5.1 Hz), 145.0 (d, *J* = 1.8 Hz), 132.2, 130.6, 130.3, 77.4, 37.1 (dd, *J* = 23.7, 21.1 Hz), 13.1 (t, *J* = 4.8 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (m, 3F), -115.7 – -119.6 (m, 2F), -120.4 – -122.7 (m, 2F), -126.2 (m, 2F).
HRMS (ESI$^+$) $C_{15}H_{10}BrF_9O$ [M+Na]$^+$: found 478.9656, required 478.9664 (–1.6 ppm).

(*S*,*E*)-4-(Perfluorobutyl)-2-(*p*-methoxyphenyl)pent-2-enal (3w)



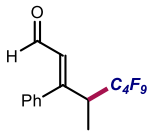
Synthesized according to General Procedure **D** using 2-(*p*-methoxyphenyl)pent-2-enal **S8** (114 mg 600 µmol) and perfluorobutyl iodide **2a** (34.6 µL, 200 µmol). The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 7:3) to afford **3w** as a colorless oil (42 mg, 51% yield). The enantiomeric excess of the product was determined by UPC[2] analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 4.5 min, τ_{major} = 4.8 min), 90:10 e.r. $[\alpha]_D^{20}$ = -40.1 (c = 0.5, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.66 (s, 1H), 7.07 – 7.00 (m, 2H), 7.00 – 6.90 (m, 2H), 6.59 (dd, *J* = 10.5, 2.1 Hz, 1H), 3.84 (s, 3H), 3.56 – 3.44 (m, 1H), 1.30 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 193.2, 160.0, 146.3, 145.6, 130.2, 123.5, 114.4, 54.9, 37.2, 13.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -81.0 (m, 3F), -115.4 – -119.5 (m, 2F), -119.9 – -123.1 (m, 2F), -125.2 – -126.9 (m, 2F).
HRMS (ESI$^-$) $C_{16}H_{13}F_9O_2$ $[M]^-$: found 408.0783, required 408.0777 (+1.5 ppm).

(*S*,*E*)-4-(Perfluorobutyl)-pent-2-enal 2,4-dinitrophenyl hydrazone (S16, from 3x)



Synthesized according to General Procedure **D** using pent-2-enal (600 µmol, 50.5 mg) and perfluorobutyl iodide **2a** (34.6 µL, 200 µmol). At the end of the reaction, an internal standard was added (trimethyl orthoformate) and an 1H NMR experiment was conducted to analyse the reaction outcome. To the crude mixture containing product **3x** was added 1 mL of MeOH, 2,4-dinitrophenyl hydrazine hydrochloride (164.2 mg, 700 µmol) and 3 drops of concentrated HCl. After 10 minutes of stirring the solvents were evaporated and the crude mixture purified by flash column chromatography on silica gel (hexane/EtOAc 9:1) to afford product **S16** (30.2 mg, 50% yield) as an orange solid. The enantiomeric excess of the product was determined by UPC[2] analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 355 nm: τ_{minor} = 4.4 min, τ_{major} = 4.6 min), 50:50 e.r.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.16 (d, *J* = 2.6 Hz, 1H), 8.36 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.97 (d, *J* = 9.6 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 1H), 6.53 (dd, *J* = 15.7, 9.1 Hz, 1H), 6.16 (dd, *J* = 15.9, 8.6 Hz, 1H), 3.34 – 3.18 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 150.3, 147.9, 144.6, 138.5, 136.8, 130.1, 130.0, 123.4, 116.7, 40.5, 30.9, 29.7, 13.0, 12.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -81.01 (tt, *J* = 9.7, 3.1 Hz, 3F), -114.33 – -119.44 (m, 2F), -119.61 – -122.70 (m, 2F), -123.89 – -128.29 (m,2F).
HRMS (ESI$^+$) $C_{15}H_{11}F_9N_4O_4$ $[M+Na]^+$: found 505.0531, required 505.0529 (+0.5 ppm).

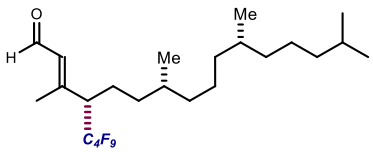
(*S*,*E*)-4-(Perfluorobutyl)-3-phenylpent-2-enal (3y)



Synthesized according to General Procedure **D** using 3-phenylhex-2-enal (48.1 mg, 300 µmol) and perfluorobutyl iodide **2a** (17.3 µL, 100 µmol) The crude mixture was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 8:2) to afford product **3y** (12.4 mg, 31 % yield) as a colourless oil. The enantiomeric excess of the product was determined by UPC[2] analysis on a Daicel Chiralpak IE column (eluent: CO_2/MeOH = 90:10; flow rate 1 mL/min, λ = 360 nm: τ_{minor}= 7.2 min, τ_{major} = 7.4 min), 64:36 e.r. $[\alpha]_D^{20}$ = -8.0 (c = 0.5, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: δ 9.45 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.38 (m, 3H), 7.38 – 7.26 (m, 2H), 6.37 (d, *J* = 7.6 Hz, 1H), 3.48 (m, 1H), 1.51 (d, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ_C: 192.8, 159.1, 136.8, 131.9, 129.6, 128.9, 128.6, 44.5, 44.3, 44.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -81.01 (m, 3F), -108.15 – -117.95 (m, 2F), -120.86 (m, 2F), -125.76 – -126.22 (m, 2F).
HRMS (ESI^+) $C_{15}H_{11}F_9O$ $[M+Na]^+$: found 401.0548, required 401.0558 (+2.7 ppm).

(4*S*,7*R*,11*R*,*E*)-4-(Perfluorobutyl)-3,7,11,15-tetramethylhexadec-2-enal (3z)



Synthesized according to General Procedure **D** using *phytal* (88.4 mg, 300 µmol) and perfluorobutyl iodide **2a** (17.3 µL, 100 µmol). The crude mixture was purified by flash column chromatography on silica gel (pentane/CH_2Cl_2 8:2) to afford product **3z** (66.0 mg, 64% yield as a 1.5:1 mixture of *E* and *Z*) as a colourless oil. The enantiomeric excess of the product was determined by UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 1 mL/min, λ = 360 nm: *Z* isomer: τ_{minor} = 5.8 min, τ_{major} = 5.9 min; *E* isomer: τ_{minor} = 6.4 min, τ_{major} = 6.8 min), *Z* isomer: 50:50 er; *E* isomer: 50:50 e.r.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: δ 10.09 (d, *J* = 7.6 Hz, 1H), 5.99 (d, *J* = 6.2 Hz, 1H), 2.99 – 2.83 (m, 1H), 2.21 (s, 3H), 2.02 – 1.83 (m, 1H), 1.84 – 1.65 (m, 1H), 1.53 (dq, *J* = 13.2, 6.6 Hz, 2H), 1.35 – 1.00 (m, 15H), 1.01 – 0.76 (m, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 190.4, 190.4, 154.1, 154.1, 154.0, 153.9, 132.7, 132.7, 51.9, 51.7, 51.5, 51.3, 39.4, 37.4, 37.3, 37.3, 37.3, 36.6, 36.6, 34.0, 33.9, 33.7, 33.6, 32.8, 32.7, 32.6, 32.6, 32.5, 29.7, 28.0, 24.8, 24.4, 24.3, 22.7, 22.6, 22.5, 22.4, 19.7, 19.7, 19.6, 19.6, 19.3, 19.2, 14.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -80.54 – -80.79 (m, 3F), -110.27 – -115.24 (m, 2F), -119.80 – -122.76 (m, 2F), -124.24 – -126.79 (m, 2F).
HRMS (ESI^+) $C_{24}H_{37}F_9O$ $[M+Na]^+$: found 535.2601, required 535.2593 (+1.6 ppm).

G. Mechanistic Investigations

G1. UV-Vis Spectroscopy

UV-Vis spectroscopic measurements were recorded on a Shimadzu UV-2401PC spectrophotometer and measured using a quartz cuvette with path length of 1 cm. The samples were prepared using a concentration of 0.6 M in Et_2O.

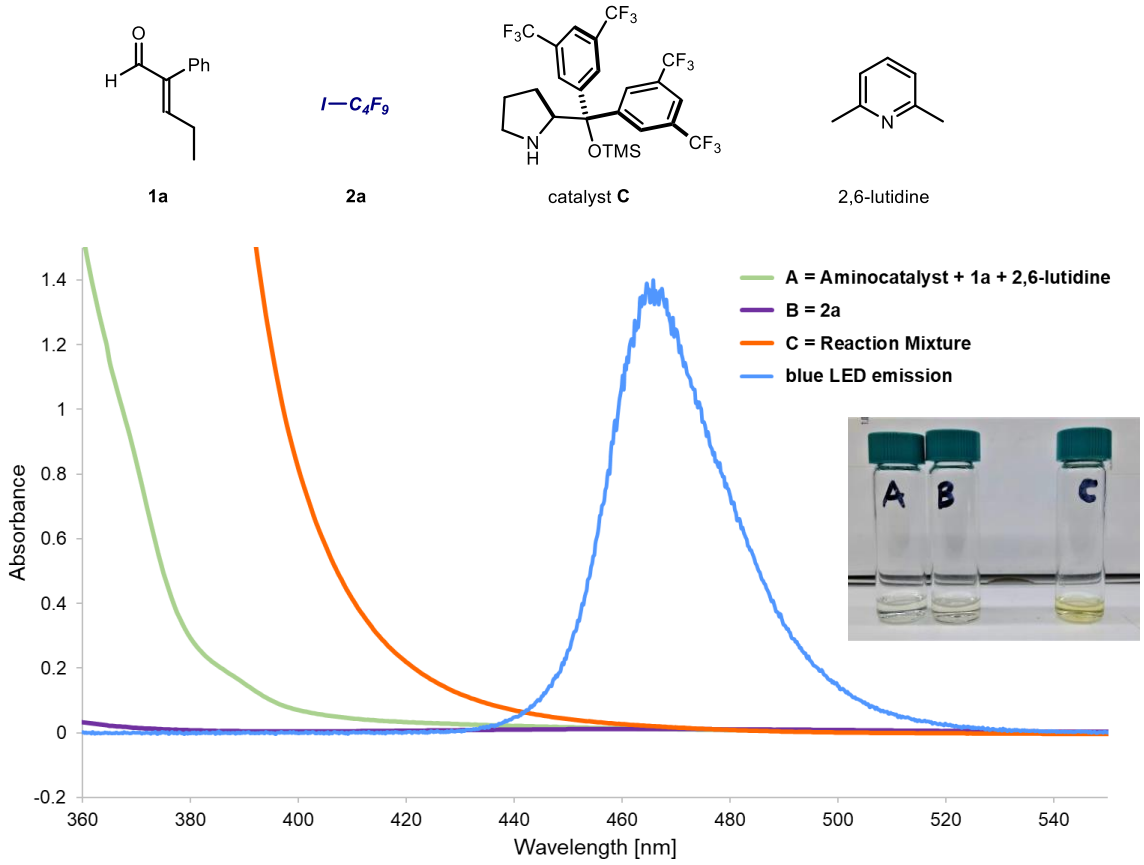


Figure S7: UV-vis absorption profiles for vial A: catalyst **C**, enal **1a** and 2,6-lutidine in Et_2O (all 0.6 M); vial B: perfluoroalkyl iodide **2a** in Et_2O (0.6 M); vial C: mixture of catalyst **C**, enal **1a**, perfluoroalkyl iodide **2a** and 2,6-lutidine in Et_2O (all 0.6 M). Blue line indicates normalized emission spectrum of the single high-power LED (460 nm, 100 mW/cm^2) used in the reaction.

G2. Quantum Yield Measurements

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure[8] outlined in the Handbook of Photochemistry.[9] The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed.

The following solutions were prepared and stored in a dark laboratory (red light):

1. Potassium ferrioxalate solution: 294.8 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 139 µL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).
2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask).
3. Buffer solution: 2.47 g of NaOAc and 0.5 mL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).

The actinometry measurements were carried out as follows:

1. 1 mL of the actinometer solution was added to a vial. The vial was placed in the reactor.
2. The solution was irradiated at 460 nm (irradiance 238 mW/cm^2). This procedure was repeated 4 times, quenching the solutions after different time intervals: 5 sec, 10 sec, 15 sec, and 20 sec. Then a model reaction was set following the general procedure **D** (the reaction was conducted at room temperature), placed in the irradiation set up and it has been irradiated for 30 minutes. This procedure has been performed twice with different irradiation times (45 min and 60 min).
3. After irradiation, the actinometer solutions were removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. These flasks were filled to the 10 mL mark with water (HPLC grade).
4. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

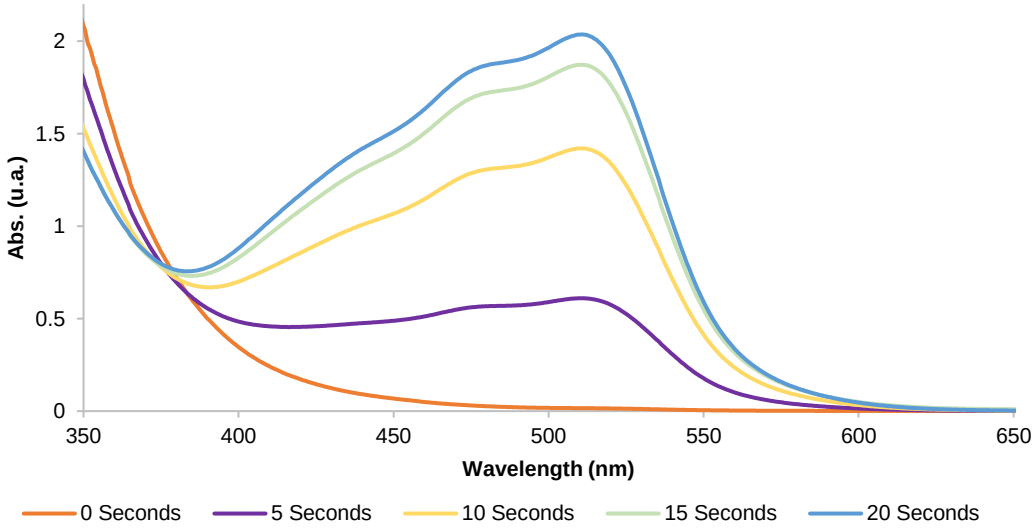


Figure S8: Actinometry measurements: UV-Vis spectra of the actinometer solutions irradiated for different periods of times (up to 20 seconds).

The moles of Fe^{2+} formed for each sample is determined using Beers' Law (Eq. 1):

$$\text{Moles of Fe(II)} = \frac{V_1\, V_3\, \Delta A(510\text{ nm})}{10^3\, V_2\, l\, \epsilon\,(510\text{ nm})} \quad \text{(Eq. 1)}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), $\Delta A(510\text{ nm})$ is the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\varepsilon(510\text{ nm})$ is the extinction coefficient the complex $Fe(phen)_3^{2+}$ at 510 nm (11100 L mol^{-1} cm^1). The moles of Fe^{2+} formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time ($q^0_{n,p}$) using the following Equation 2:

$$\Phi(\lambda) = \frac{dx/dt}{q^0_{n,p}\,[1 - 10^{-A(\lambda)}]} \quad \text{(Eq. 2)}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 458 nm is 1.2, [1-$10^{-A(\lambda)}$] is the ratio of absorbed photons by the solution, and $A(\lambda)$ is the absorbance of the actinometer at the wavelength used to carry out the experiments (460 nm).[10] The absorbance at 460 nm A(460 nm) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in a 10 mm path quartz cuvette, obtaining an absorbance of **0.142**. The photon flux, $q^0_{n,p}$, was determined to be **2.54 x 10^{-7}** einstein/s.

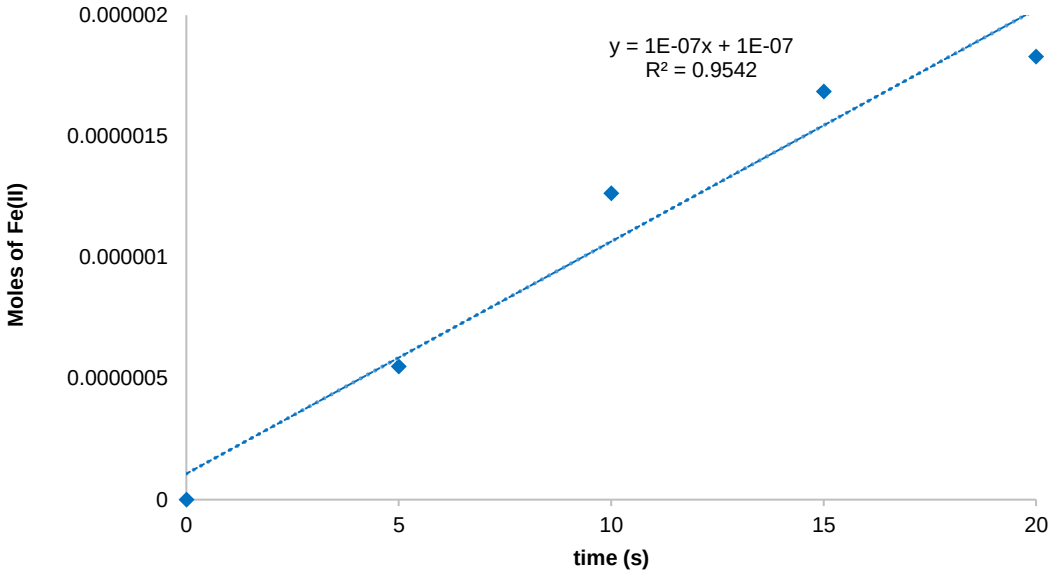


Figure S9: Plot of the moles of Fe(II), generated by irradiation of the actinometer solutions. against time.

The moles of product **3a** formed for the model reaction were determined by GC measurement (FID detector) using 1,3,5-trimethoxybenzene as internal standard. The moles of product per unit of time are related to the number of photons absorbed. The photons absorbed are correlated to the number of incident photons by the use of Equation 1. According to this, if we plot the moles of product (x) versus the moles of incident photons ($q^0_{n,p}\cdot dt$), the slope is equal to:

$$\text{slope} = \Phi[1 - 10^{-A(460\text{ nm})}] \quad \text{(Eq. 3)}$$

Φ is the quantum yield to be determined and A(460 nm) is the absorption of the reaction under study. A(460 nm) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 0.2 was determined for the model reaction mixture.

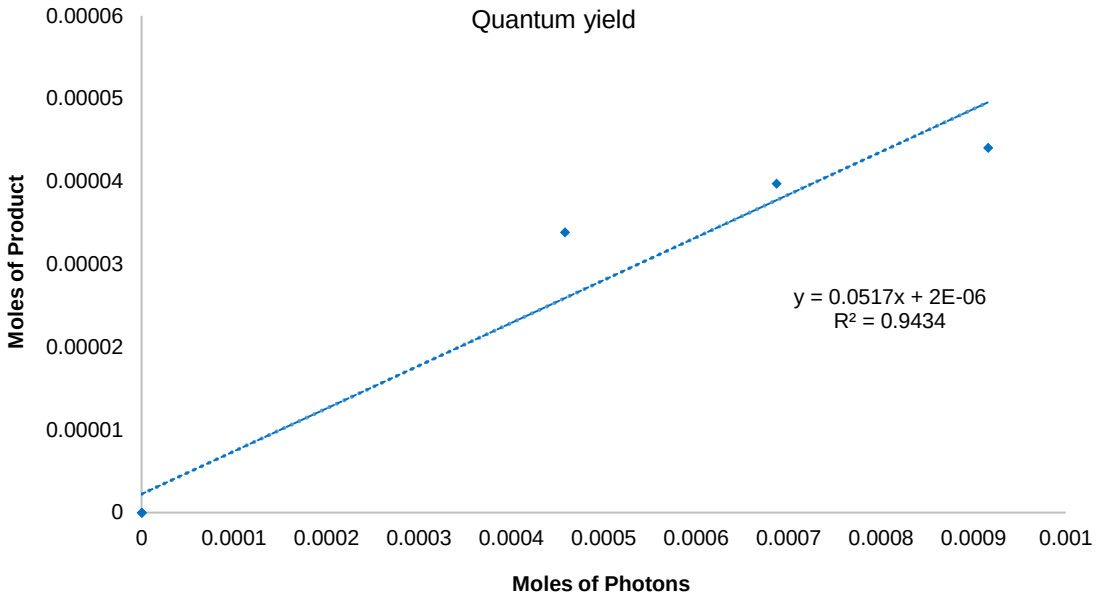
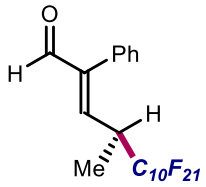


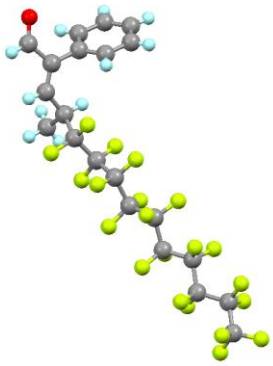
Figure S10: Determination of the quantum yield.

The quantum yield of the reaction between **1a** and **2a** using 460 nm irradiation was measured to be **1.14**. A quantum yield greater than 1 indicates that a chain mechanism is operative, as each mole of photons absorbed leads to greater than 1 mole of product.

H. X-ray Crystallographic Data

Single crystals of compound **3g** were obtained by placing 20 mg of the compound in a 5 mL glass vial, followed by dissolution in hot *n*-hexane/diethyl ether solution (4:1). The solution was allowed to cool to room temperature, before the vial's screw-cap was pierced with a needle and the vial placed on a lab shelf for 4 days. *Data Collection.* Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoKα radiation.Montel mirrors and a Cryostream Plus low temperature device (T = 100K). Full-sphere data collection was used with ω and φ scans.





Empirical formula	$C_{21}H_{11}F_{21}O$
Formula weight	678.05
Temperature	100(2)K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	$P2_1$
Cell lengths dimensions:	***a***= 5.6498(2) Å. ***b***= 9.6522(3) Å. ***c***= 22.2488(6) Å.
Cell angles dimensions	α= 90°; β=92.285(2)°; γ = 90°
Volume:	1212.33 $Å^3$
Z	2
Density (calculated)	1.858 Mg/m^3
Absorption coefficient	2.088 mm^{-1}
F(000)	668
Crystal size	0.100 x 0.100 x 0.100 mm^3
Theta range for data collection	1.987 to 67.986°
Index ranges	-6<=h<=4,-11<=k<=11,-24<=l<=26
Reflections collected	14295
Independent reflections	4183[R(int) = 0.0389]
Completeness to theta	67.894°, 96.9%
Absorption correction	Multi-scan
Max. and min. transmission	0.75 and 0.62
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4183/ 1/ 389
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1162
R indices (all data)	R1 = 0.0476, wR2 = 0.1184
Flack parameter	x =0.00(6)
Largest diff. peak and hole	0.443 and -0.295 e.$Å^{-3}$

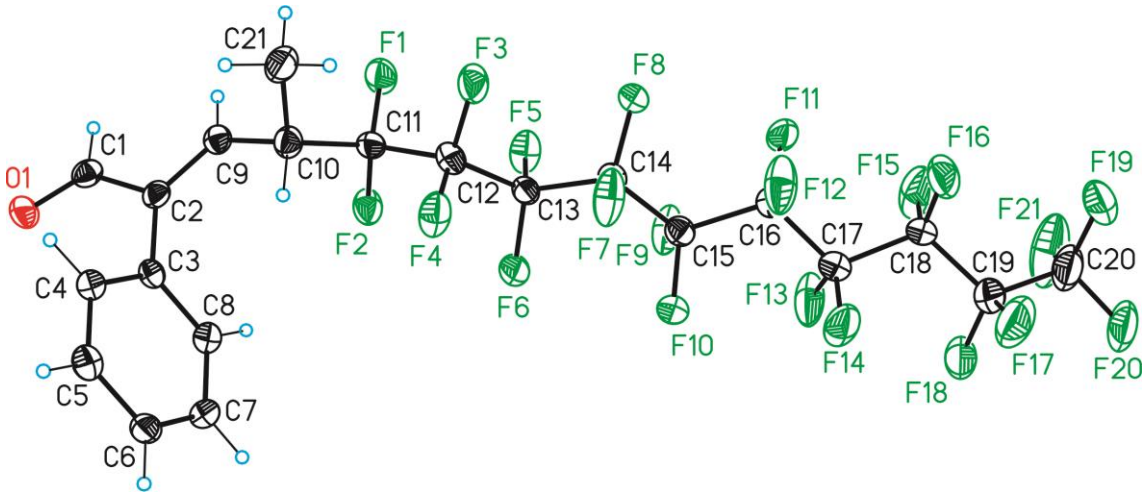


Figure S11: Ortep-plot (50%) for compound (*S*)-**3g**.

I. References

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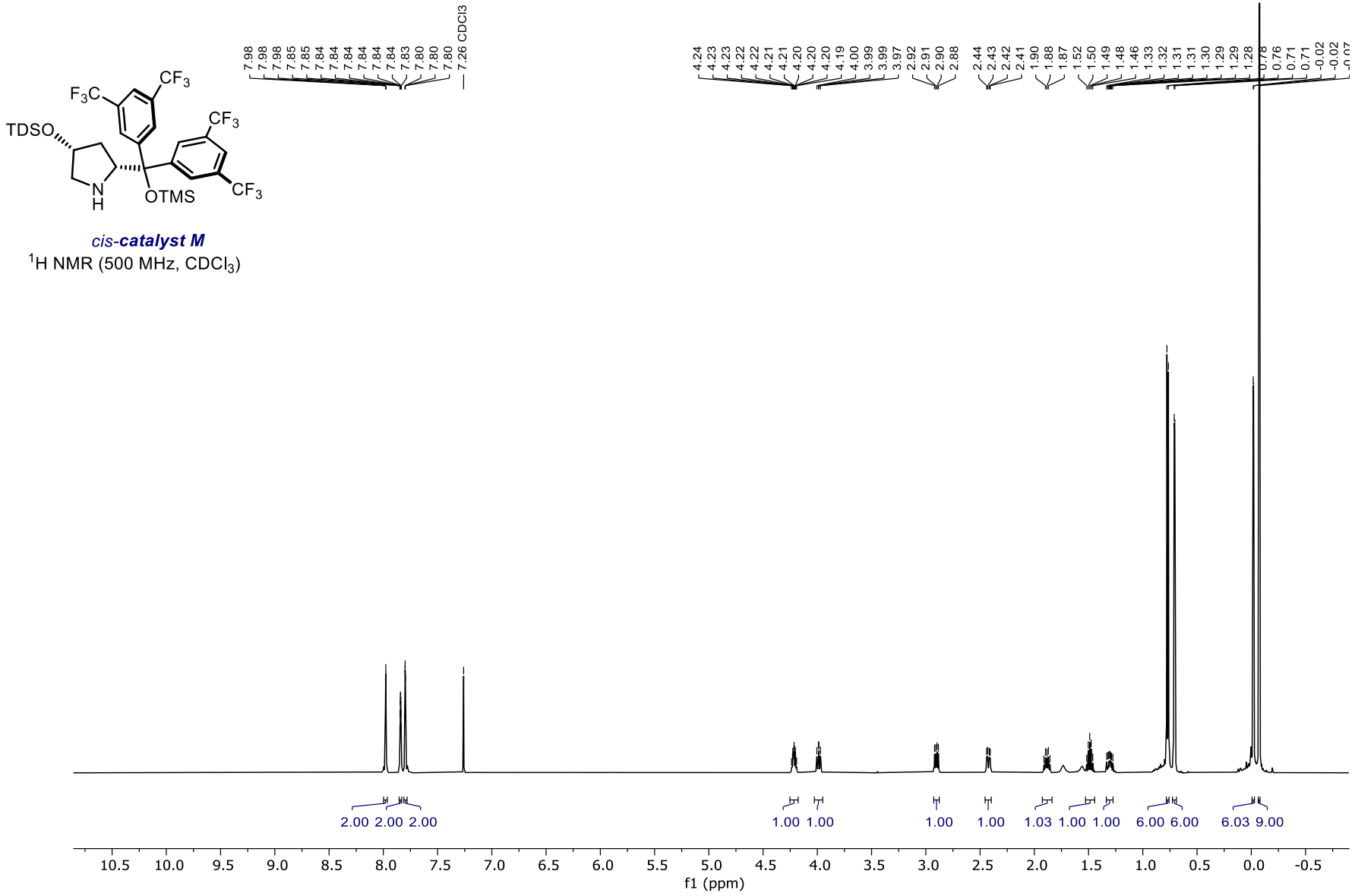
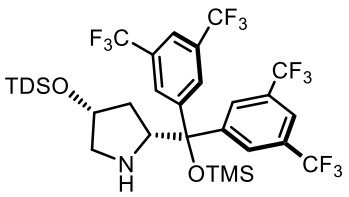
J. NMR Spectra



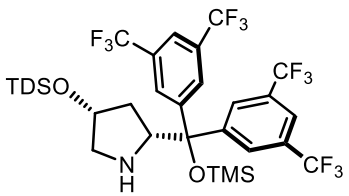
***cis*-catalyst M**

^{1}H NMR (500 MHz, $CDCl_3$)



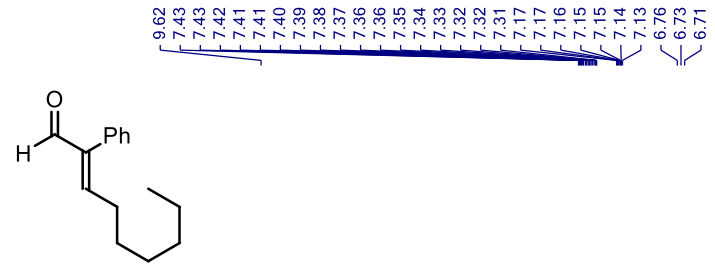
cis-**Catalyst M**

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

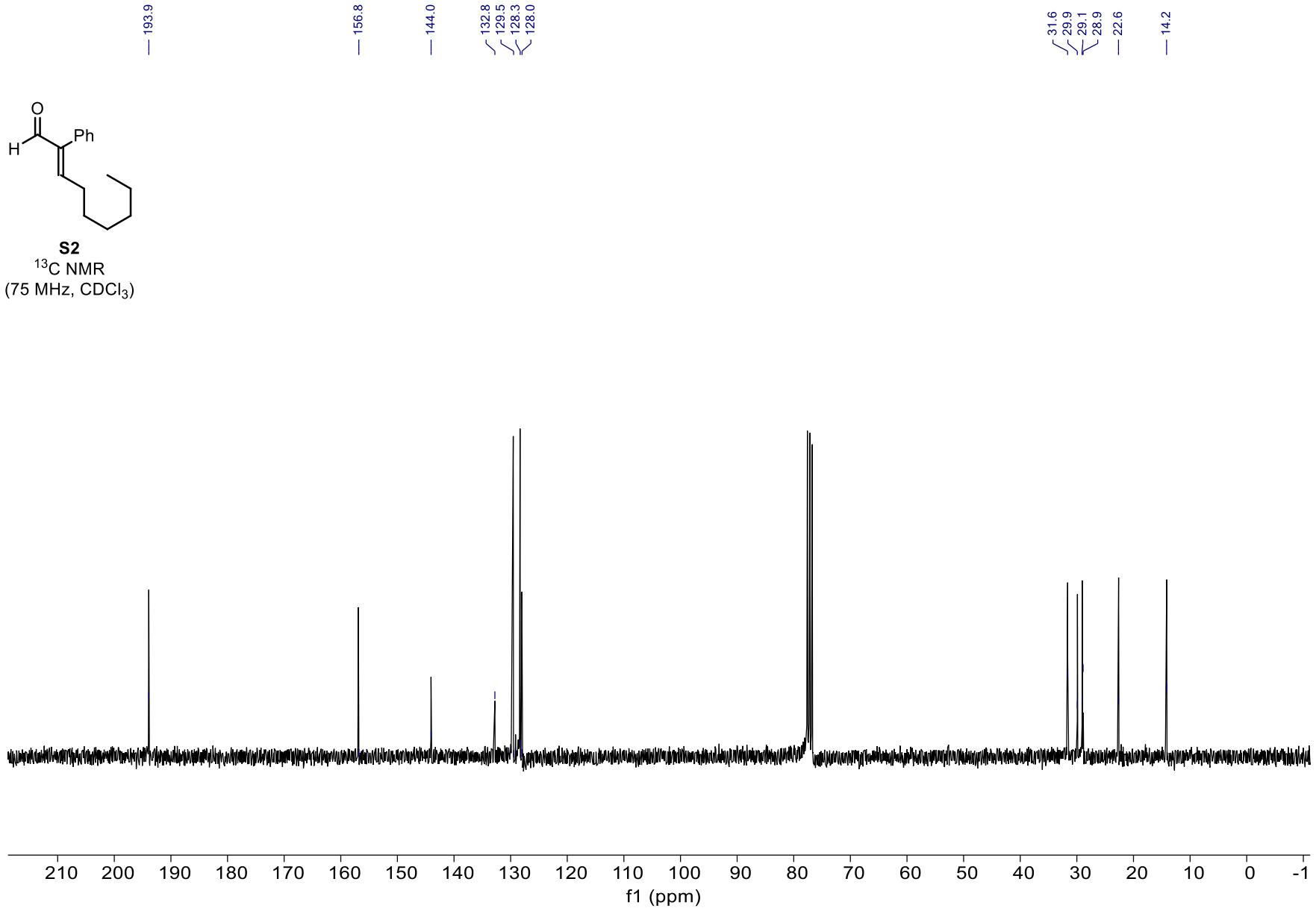


cis-***Catalyst M***

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



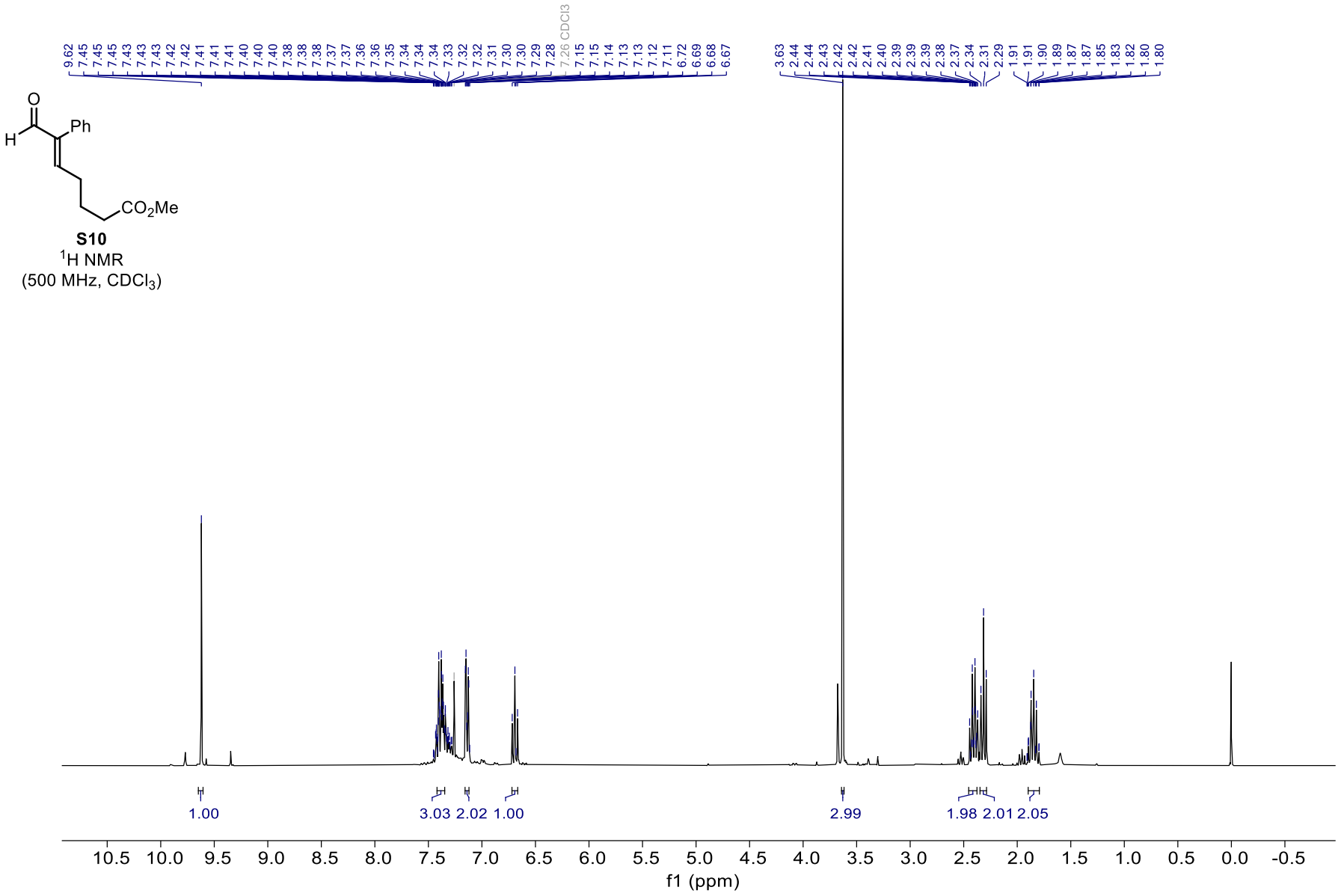
S2
^{1}H NMR
(300 MHz, $CDCl_3$)

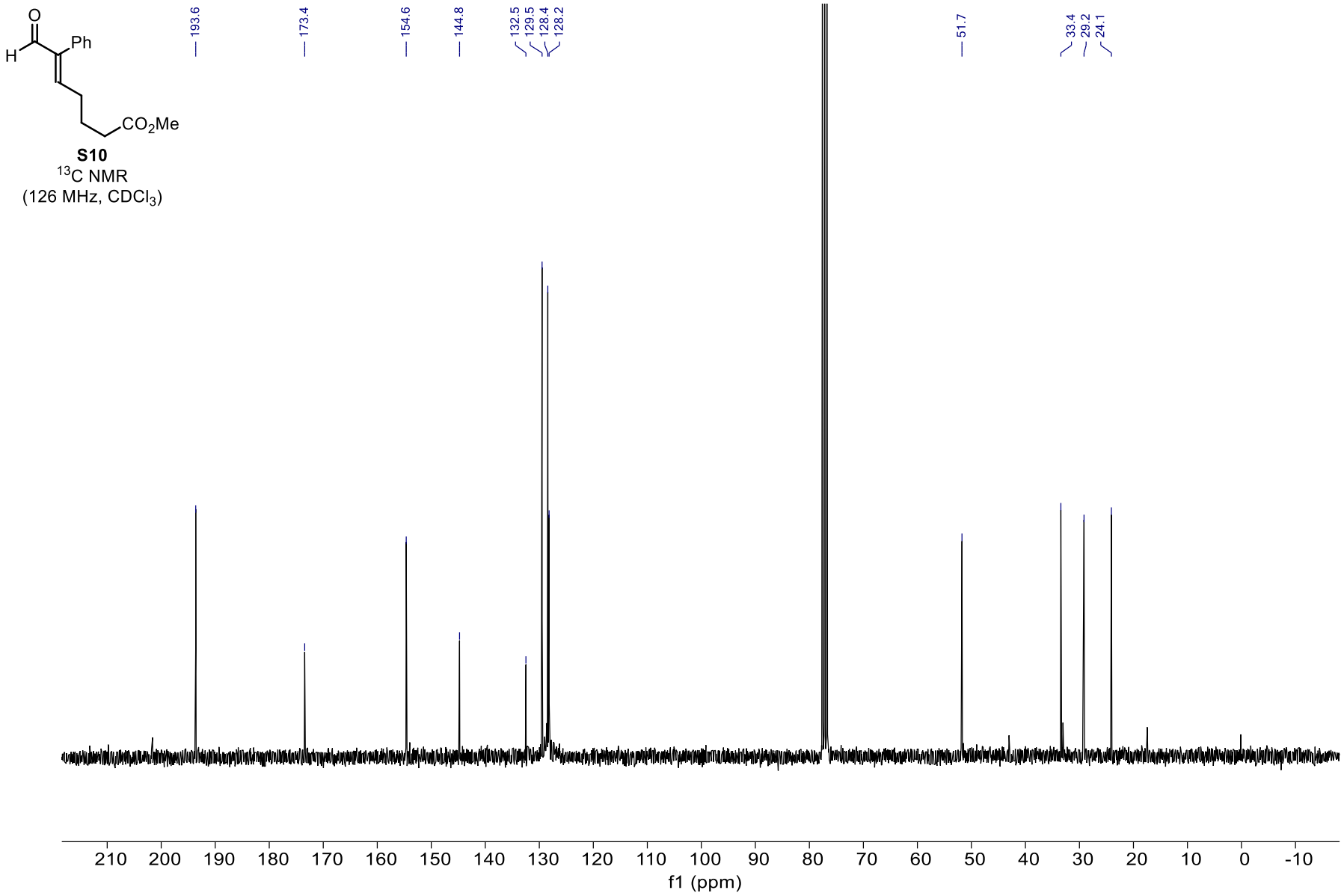


S2

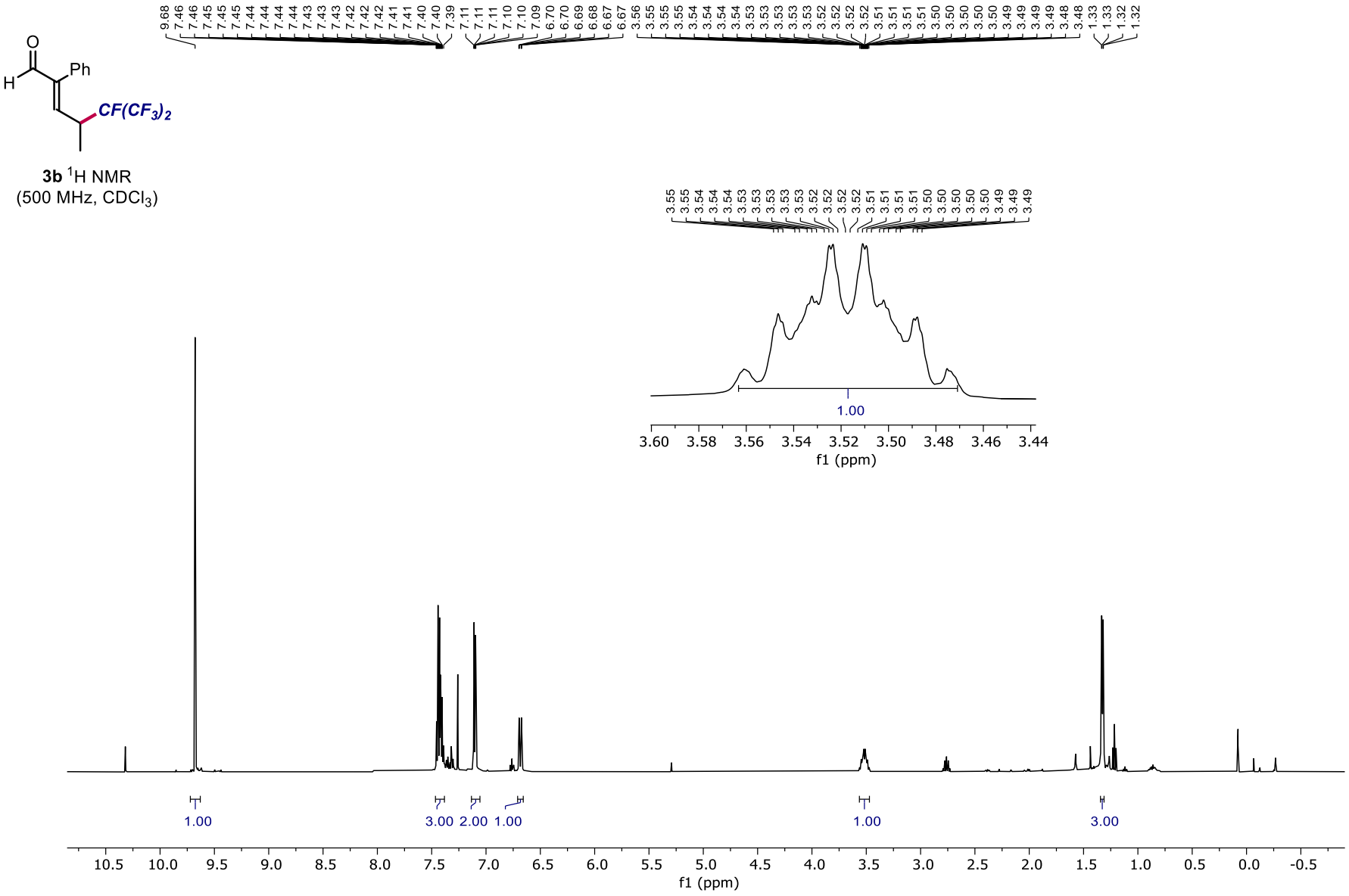
^{13}C NMR

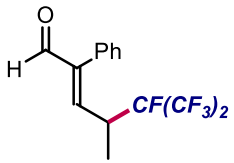
(75 MHz, $CDCl_3$)


O
H
Ph
CO2Me
S10
1H NMR
(500 MHz, CDCl3)
9.62
7.45
7.45
7.45
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.26 CDCl3
7.15
7.15
7.14
7.13
7.13
7.12
7.11
6.72
6.69
6.68
6.67
3.63
2.44
2.44
2.43
2.42
2.42
2.41
2.40
2.39
2.39
2.39
2.38
2.37
2.34
2.31
2.29
1.91
1.91
1.90
1.89
1.87
1.87
1.85
1.83
1.82
1.80
1.80
1.00
3.03
2.02
1.00
2.99
1.98
2.01
2.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

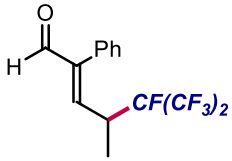


S10
^{13}C NMR
(126 MHz, $CDCl_3$)

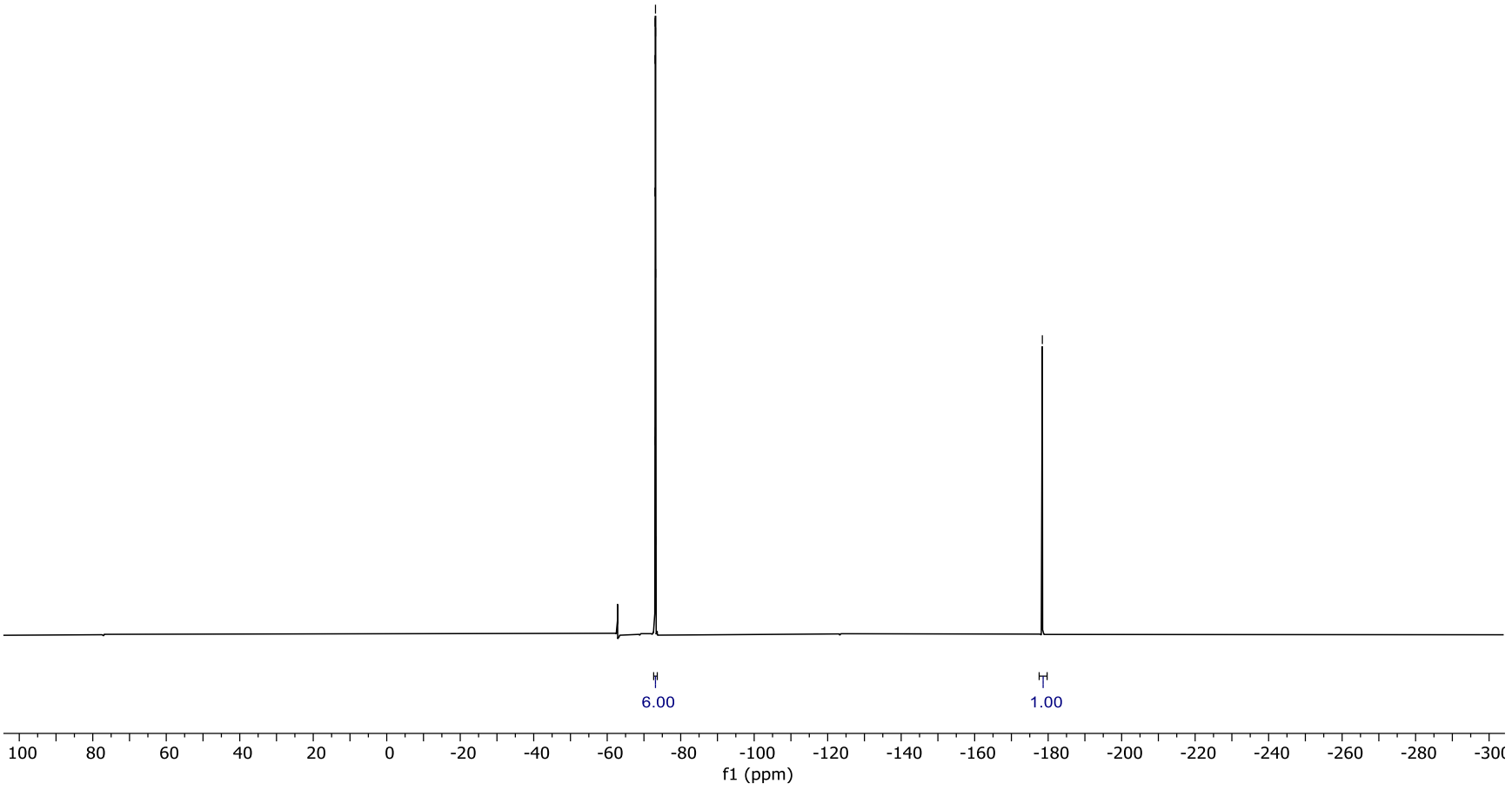

O
H
Ph
CF(CF3)2
3b 1H NMR
(500 MHz, CDCl3)
1.00
3.60 3.58 3.56 3.54 3.52 3.50 3.48 3.46 3.44
f1 (ppm)
1.00
3.00
2.00
1.00
1.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

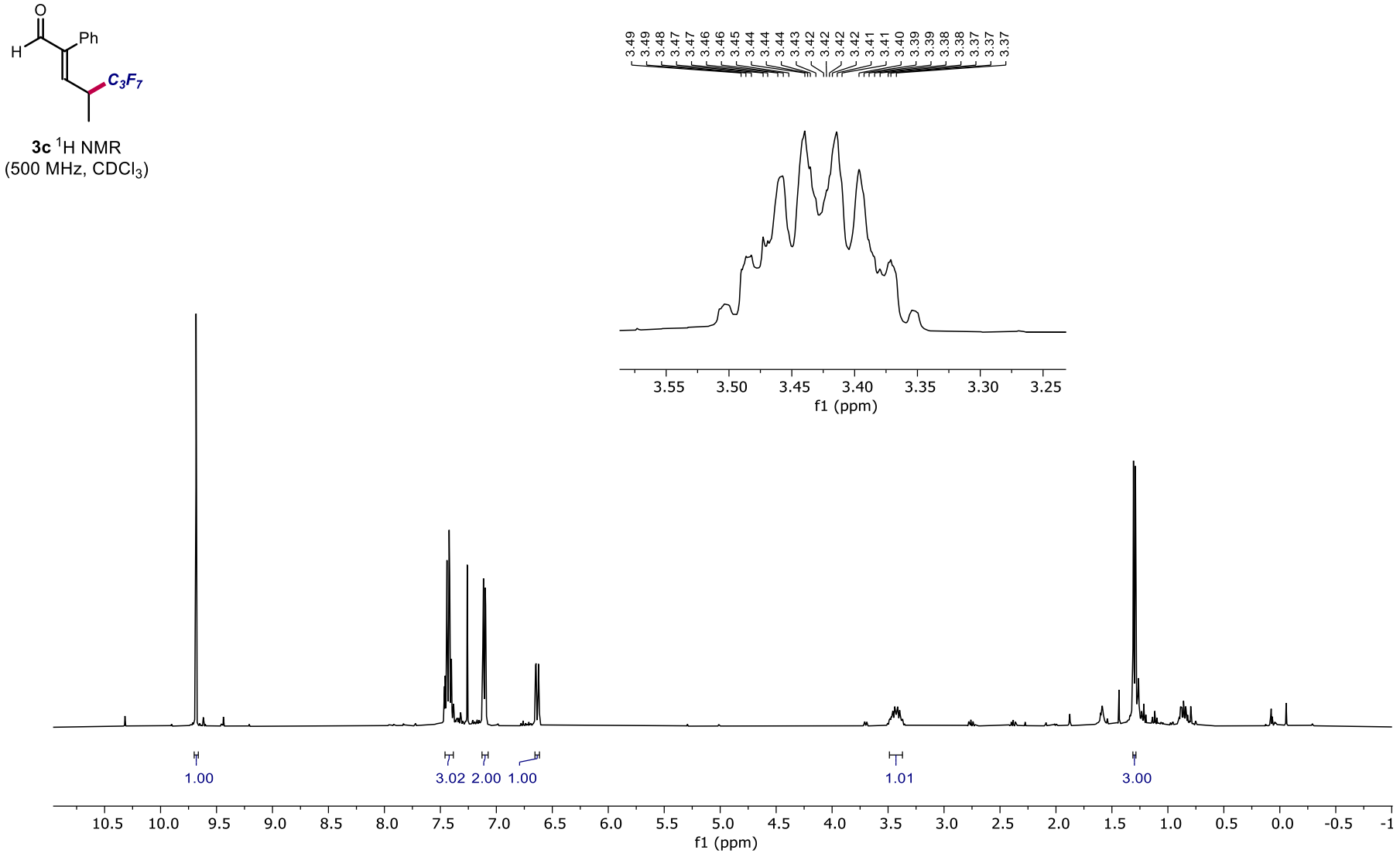


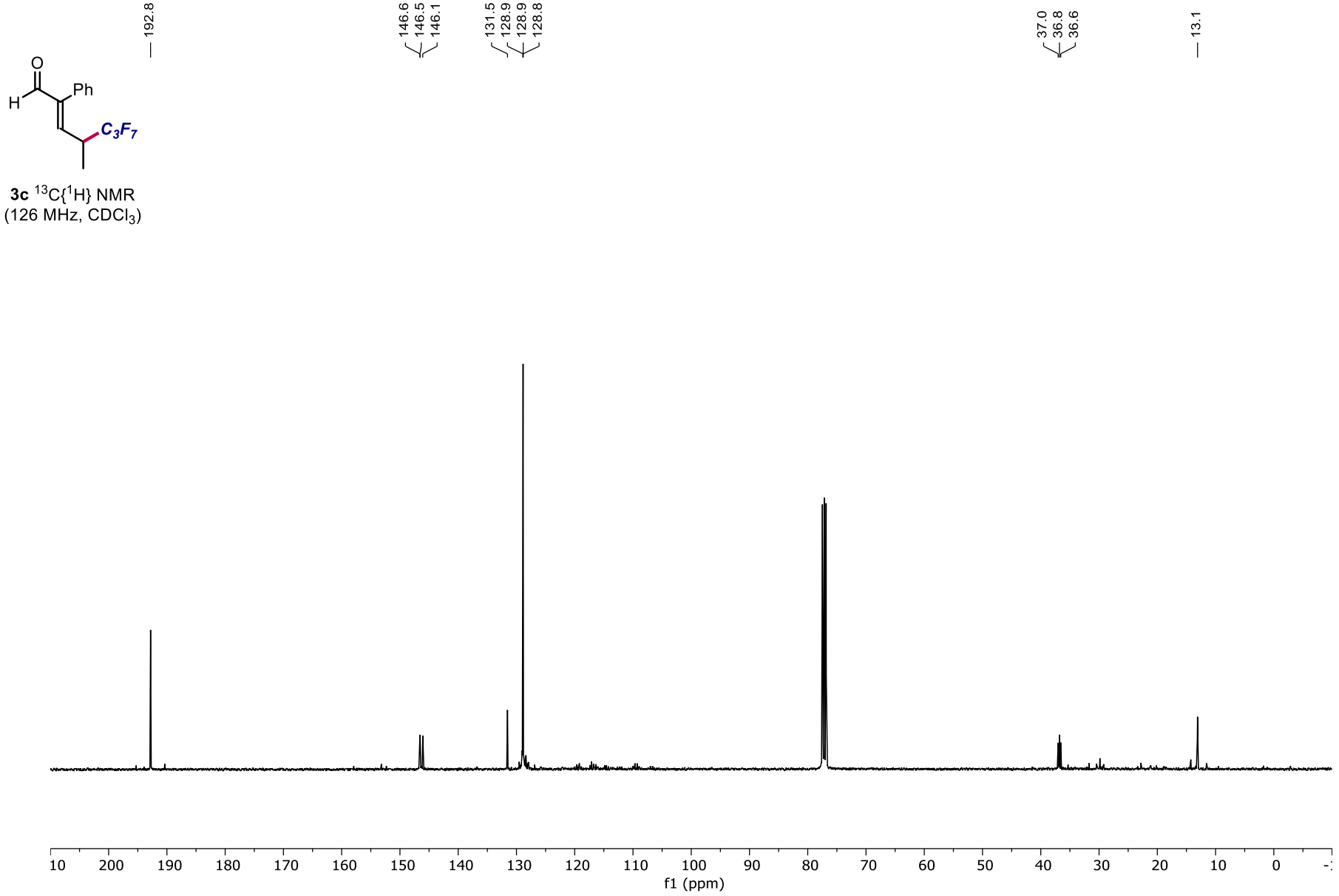
3b $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



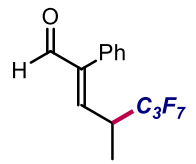
3b $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)



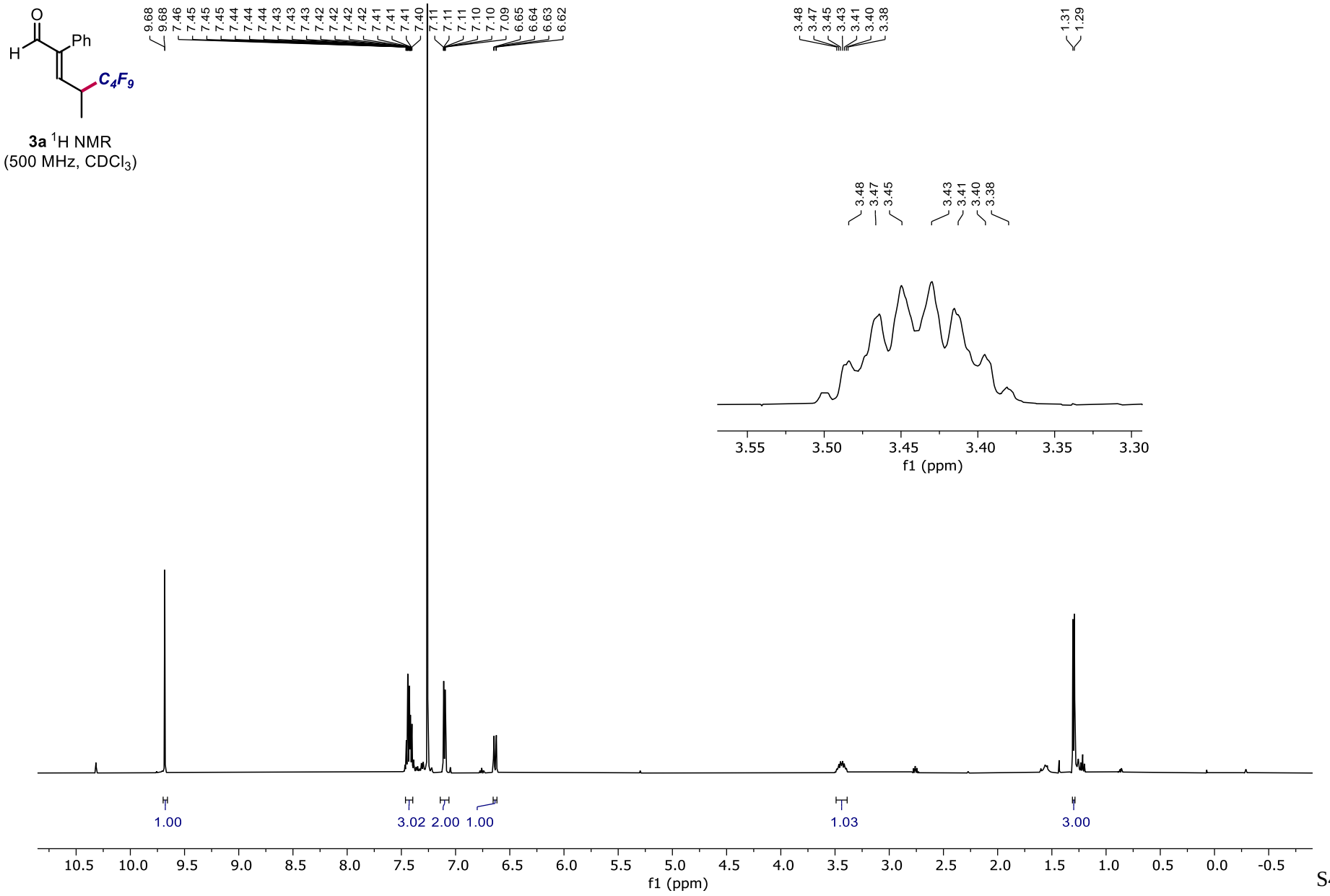

O
H
Ph
C_3F_7
3c ^{1}H NMR
(500 MHz, $CDCl_3$)
f1 (ppm)
1.00
3.02
2.00
1.00
1.01
3.00

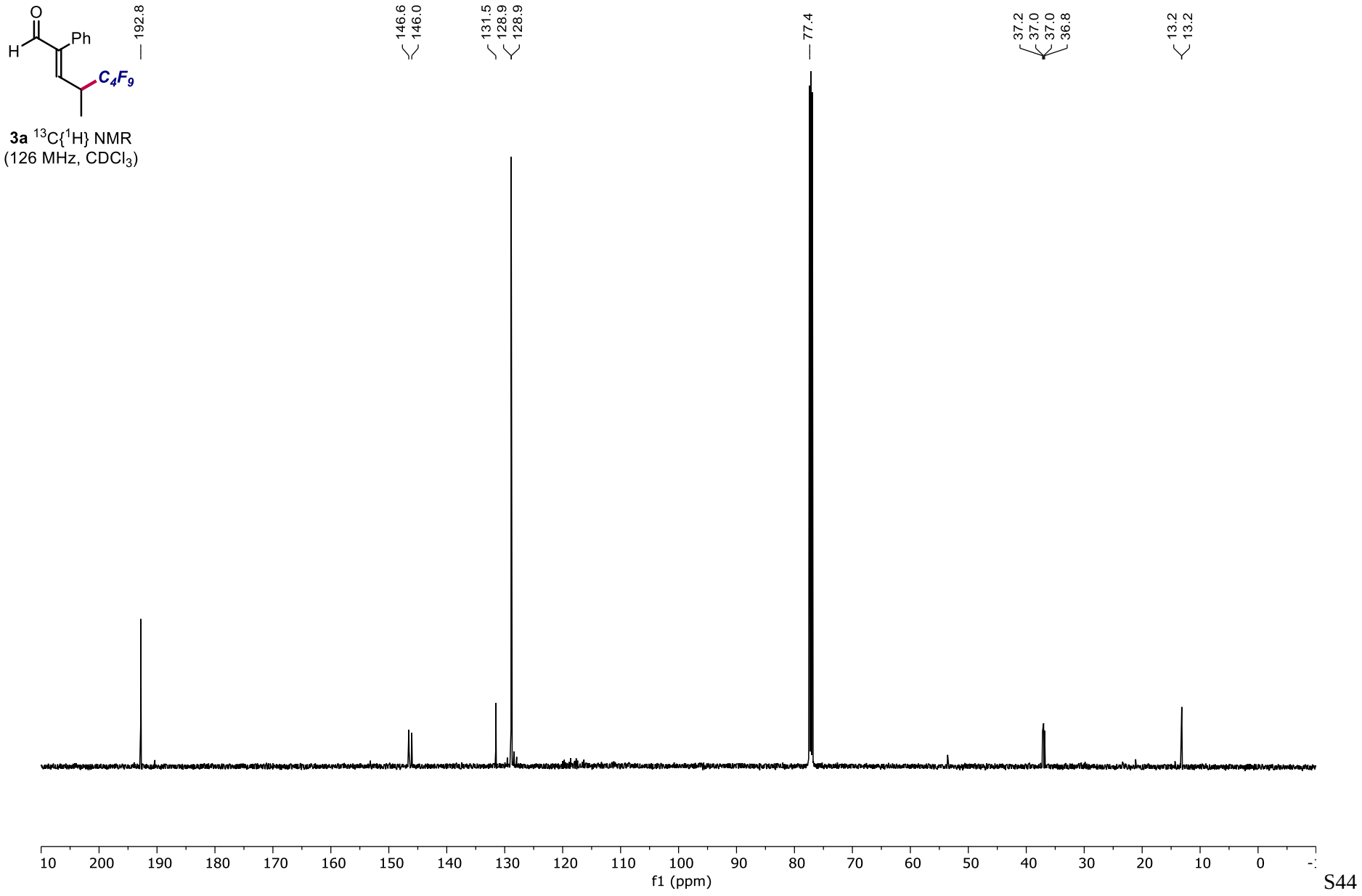


3c $^{13}C\{^1H\}$ NMR
(126 MHz, $CDCl_3$)

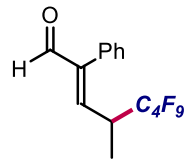


3c $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)

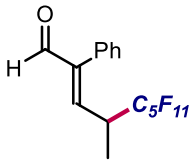

O
H
Ph
C_4F_9
3a ^{1}H NMR
(500 MHz, $CDCl_3$)
9.68 9.68 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.11 7.11 7.11 7.10 7.10 7.09 6.65 6.64 6.63 6.62
3.48 3.47 3.45 3.43 3.41 3.40 3.38
1.31 1.29
3.55 3.50 3.45 3.40 3.35 3.30
f1 (ppm)
1.00 3.02 2.00 1.00 1.03 3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



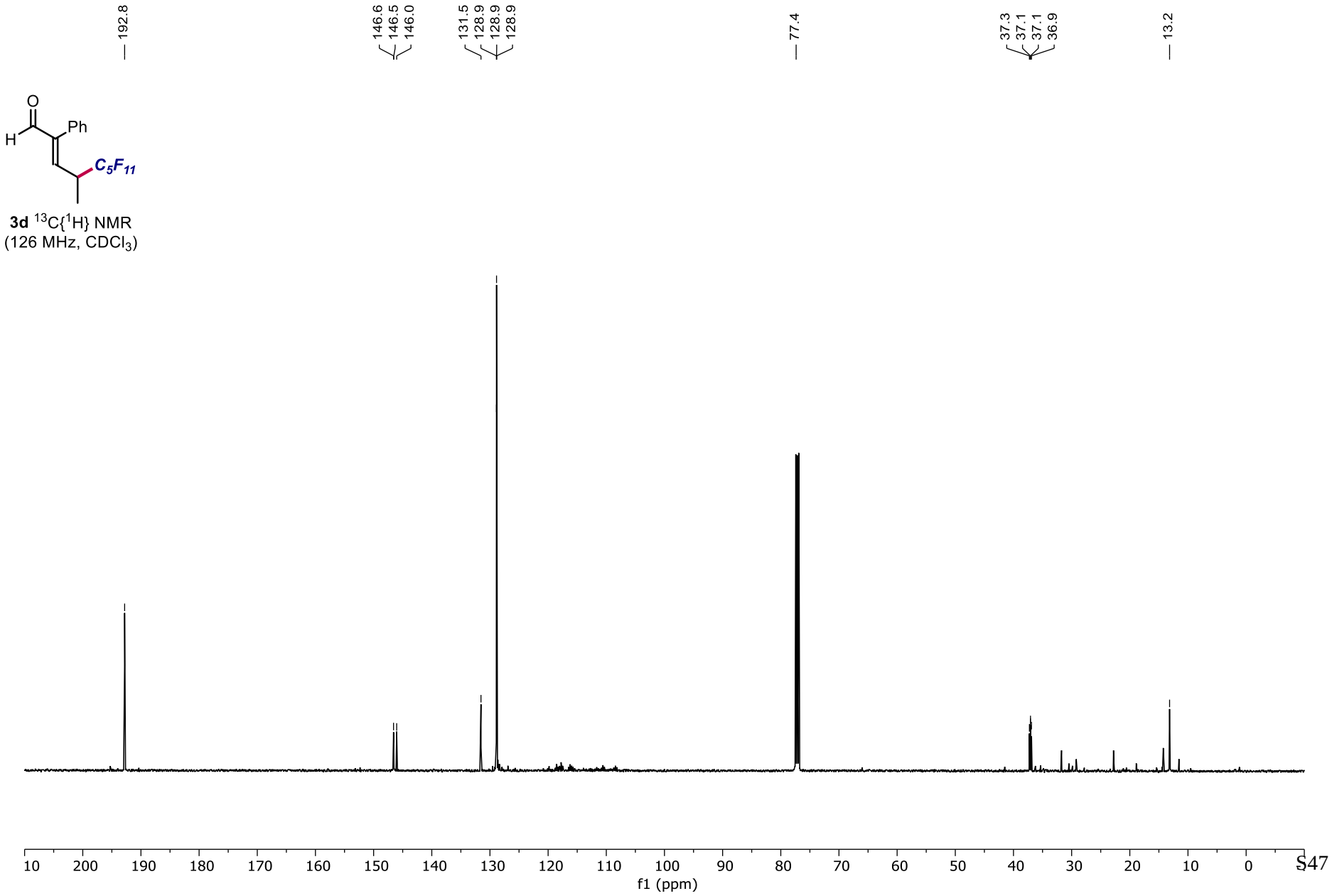
3a $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



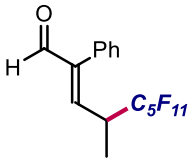
3a $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)



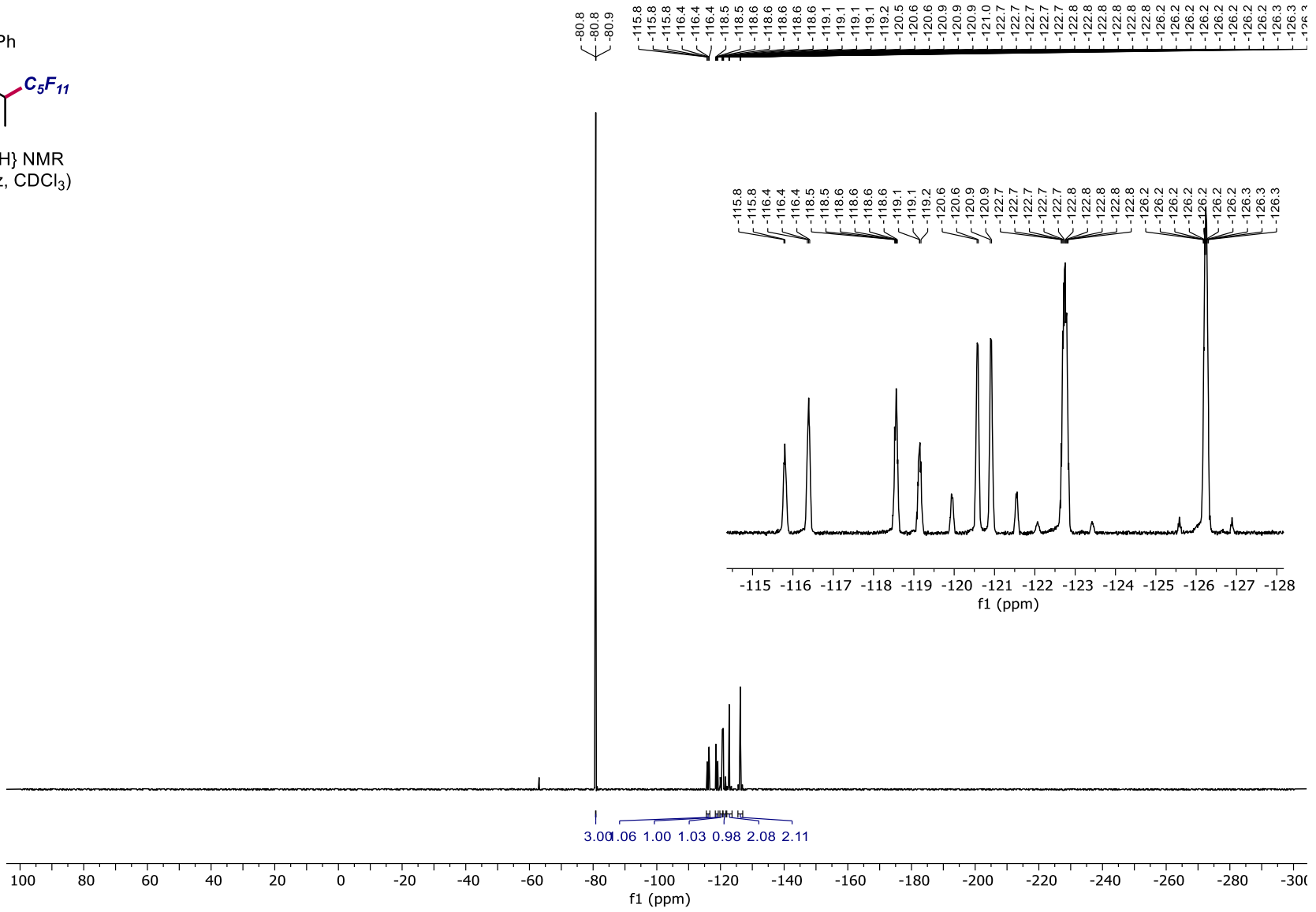
3d ^{1}H NMR
(500 MHz, $CDCl_3$)

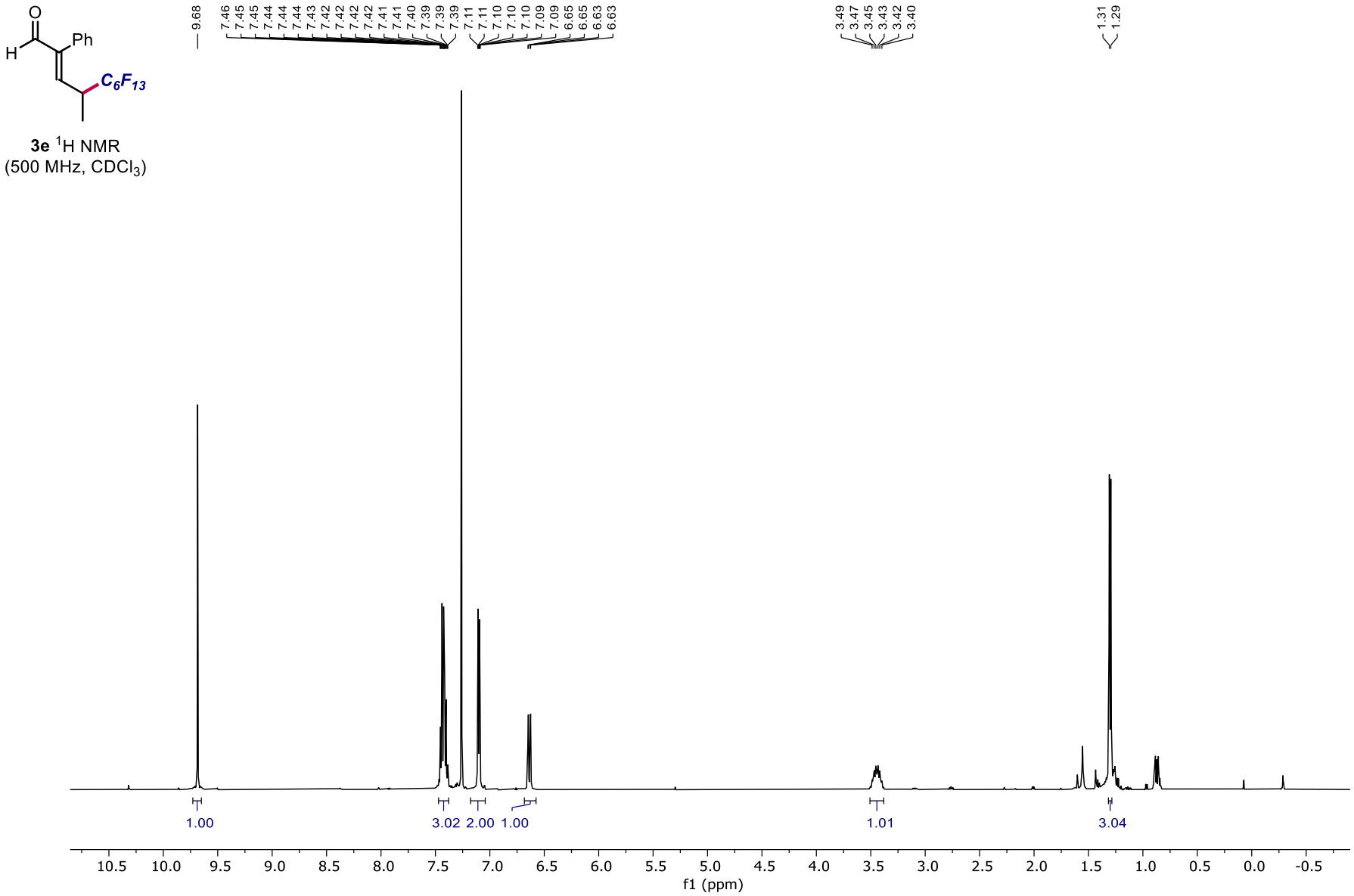


3d $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

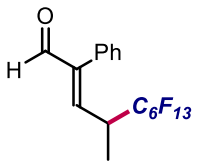


3d $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)

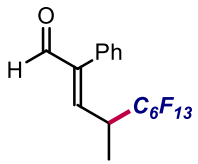




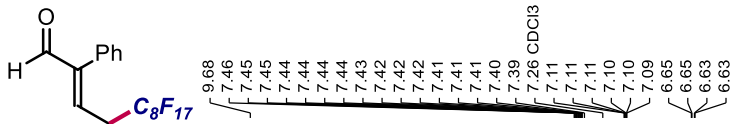
3e ^{1}H NMR
(500 MHz, $CDCl_3$)



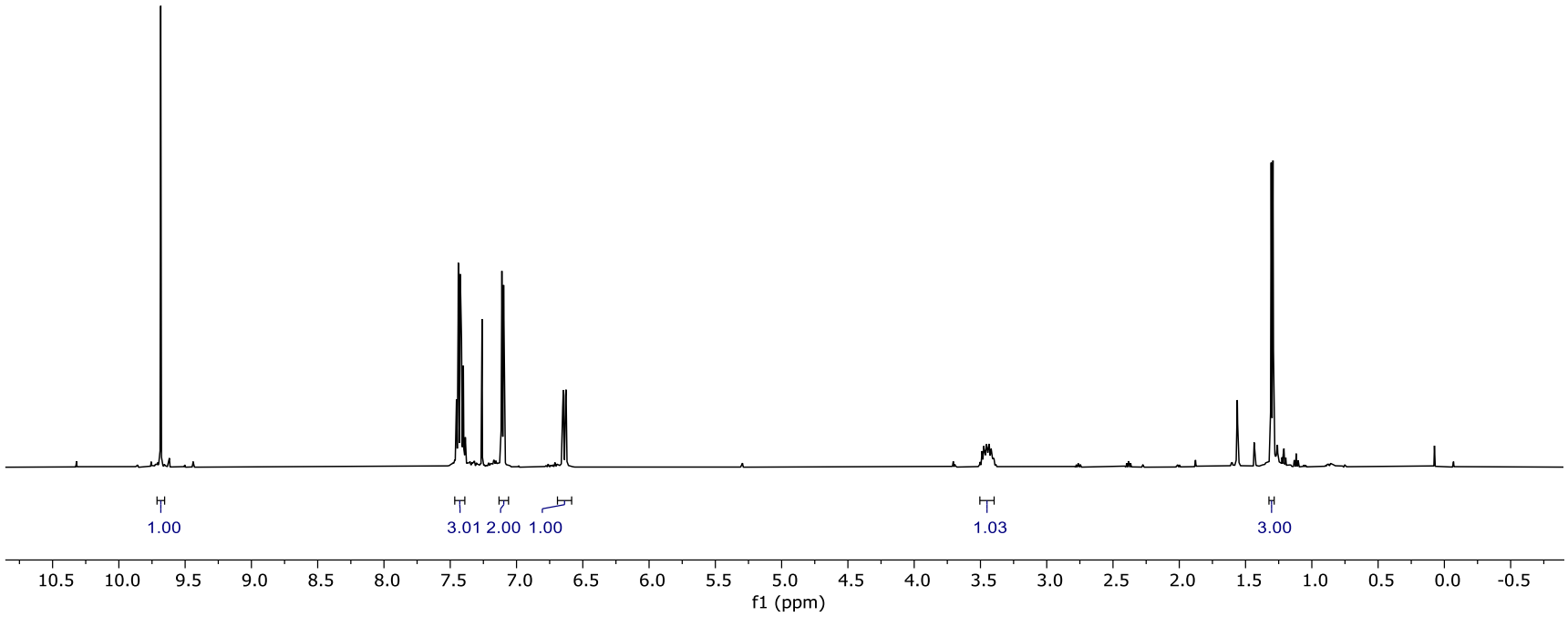
3e $^{13}C\{^1H\}$ NMR
(126 MHz, $CDCl_3$)

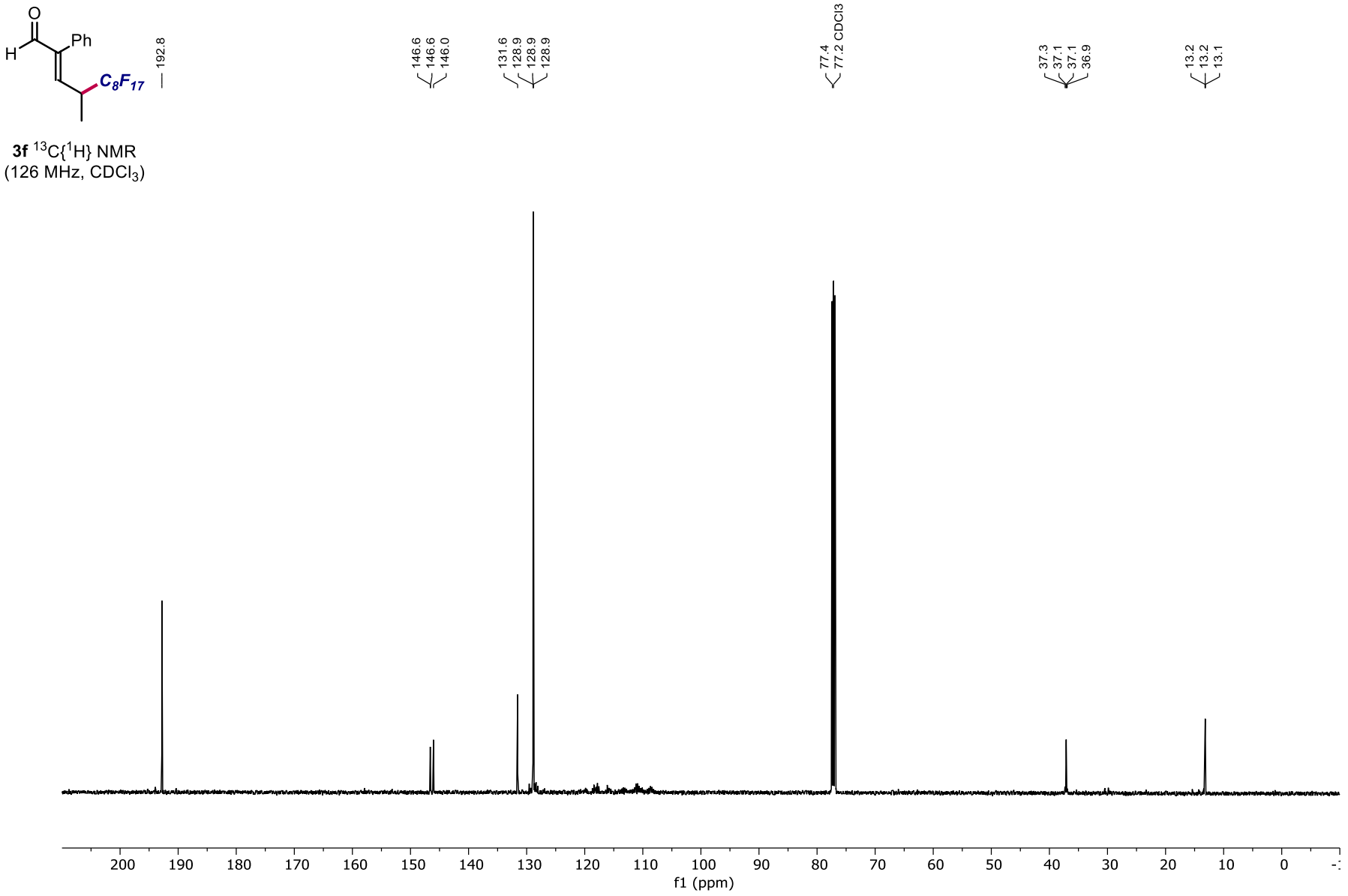


3e $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)

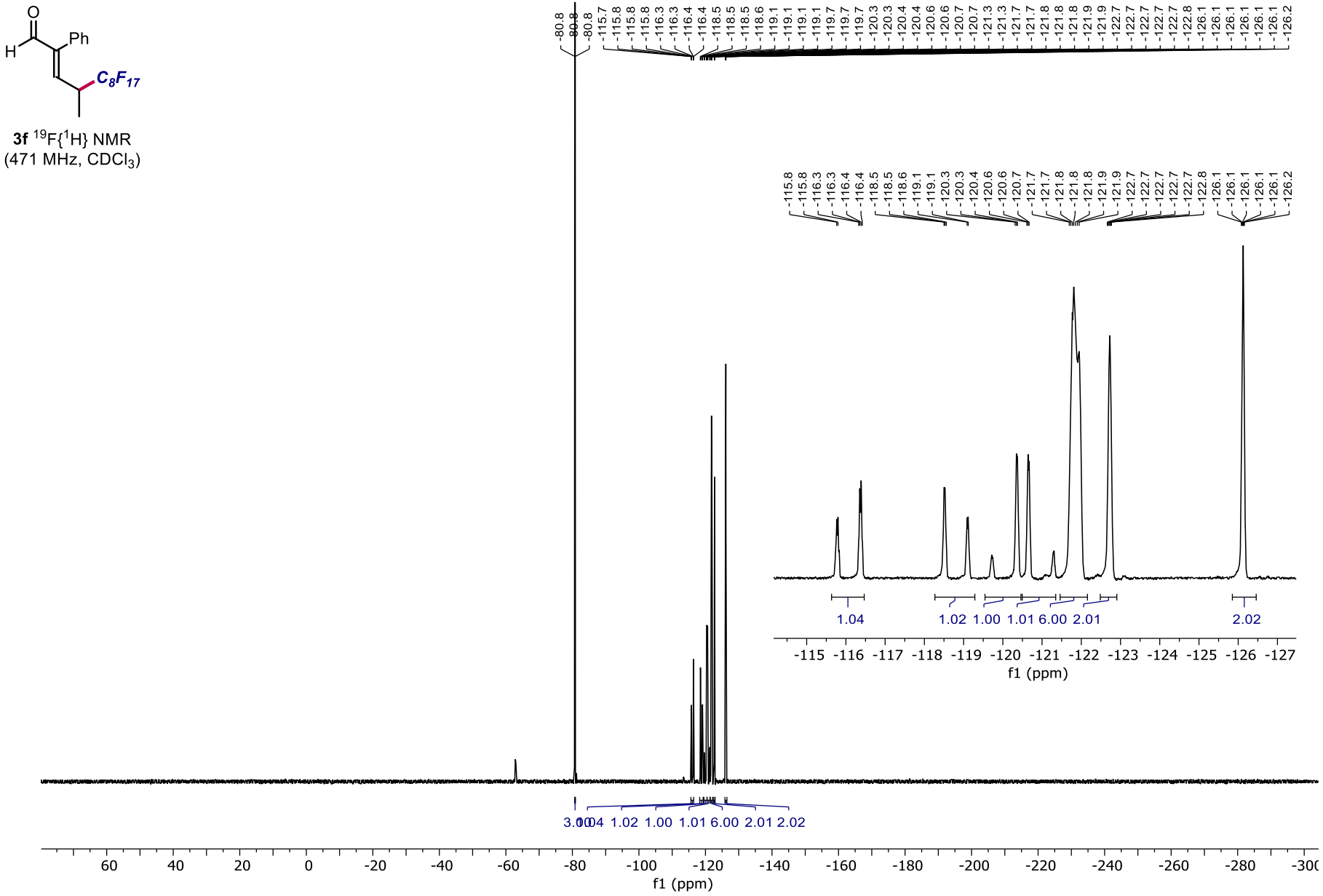


3f ^{1}H NMR
(500 MHz, $CDCl_3$)

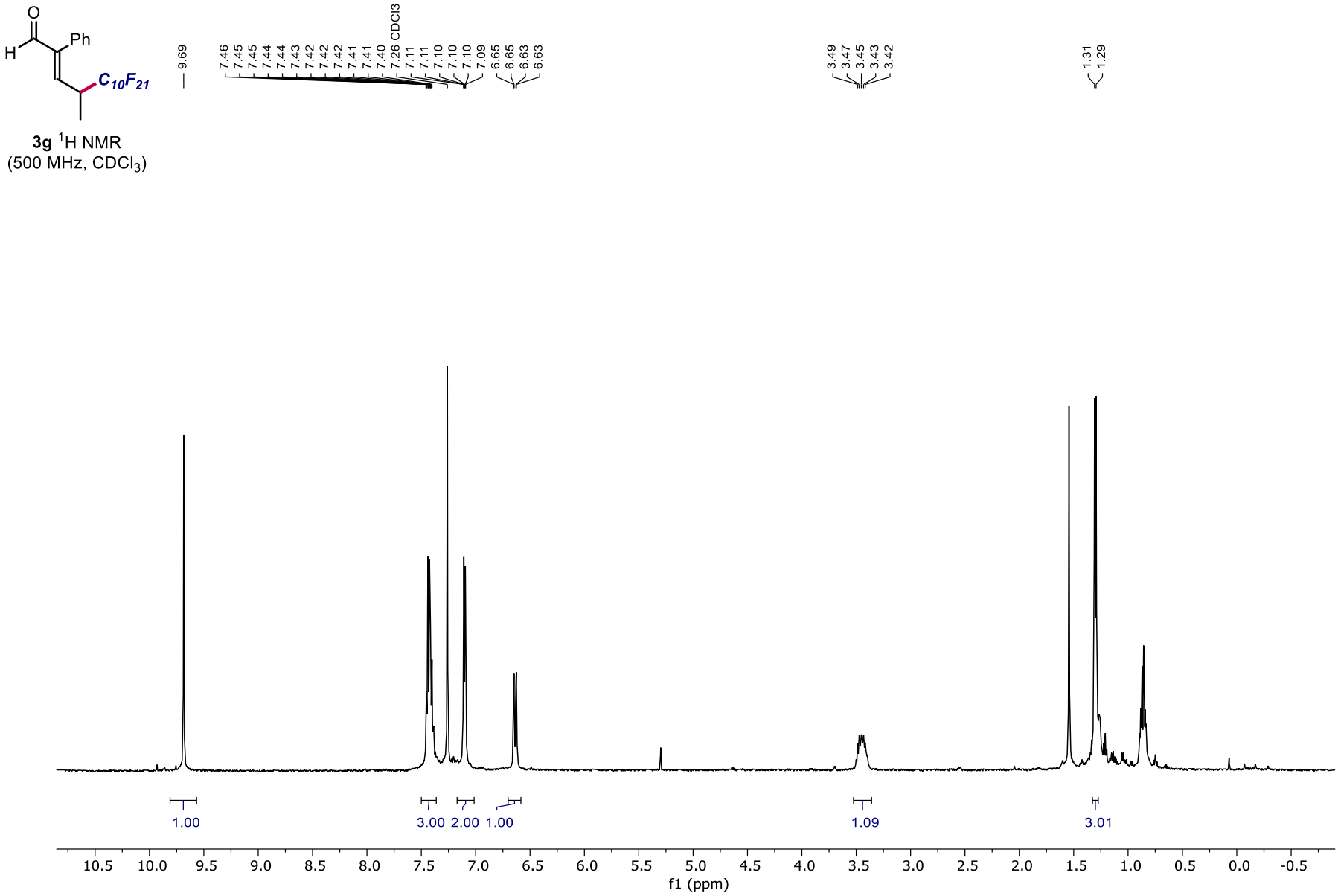




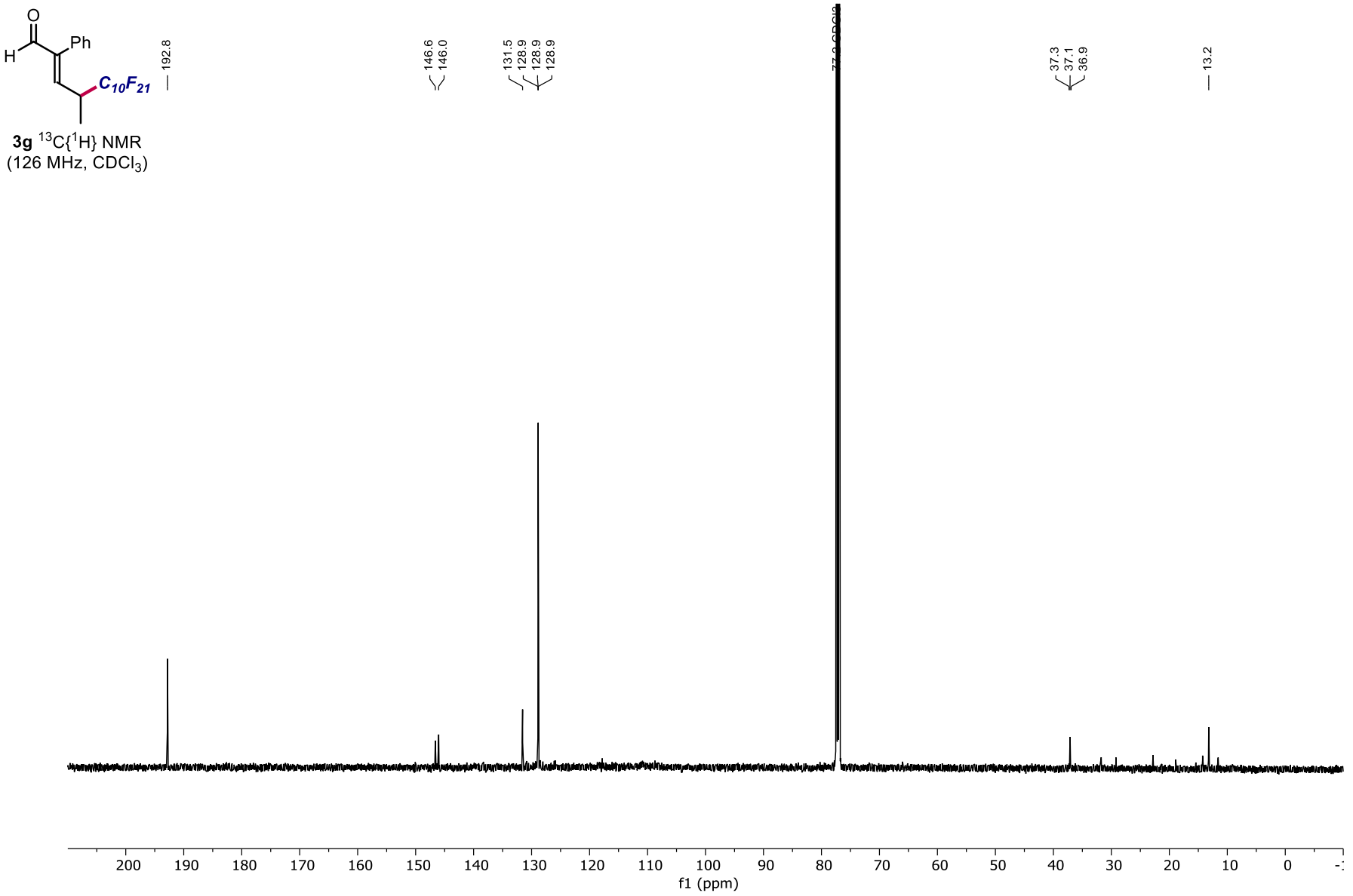
3f $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



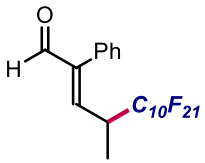
3f $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)



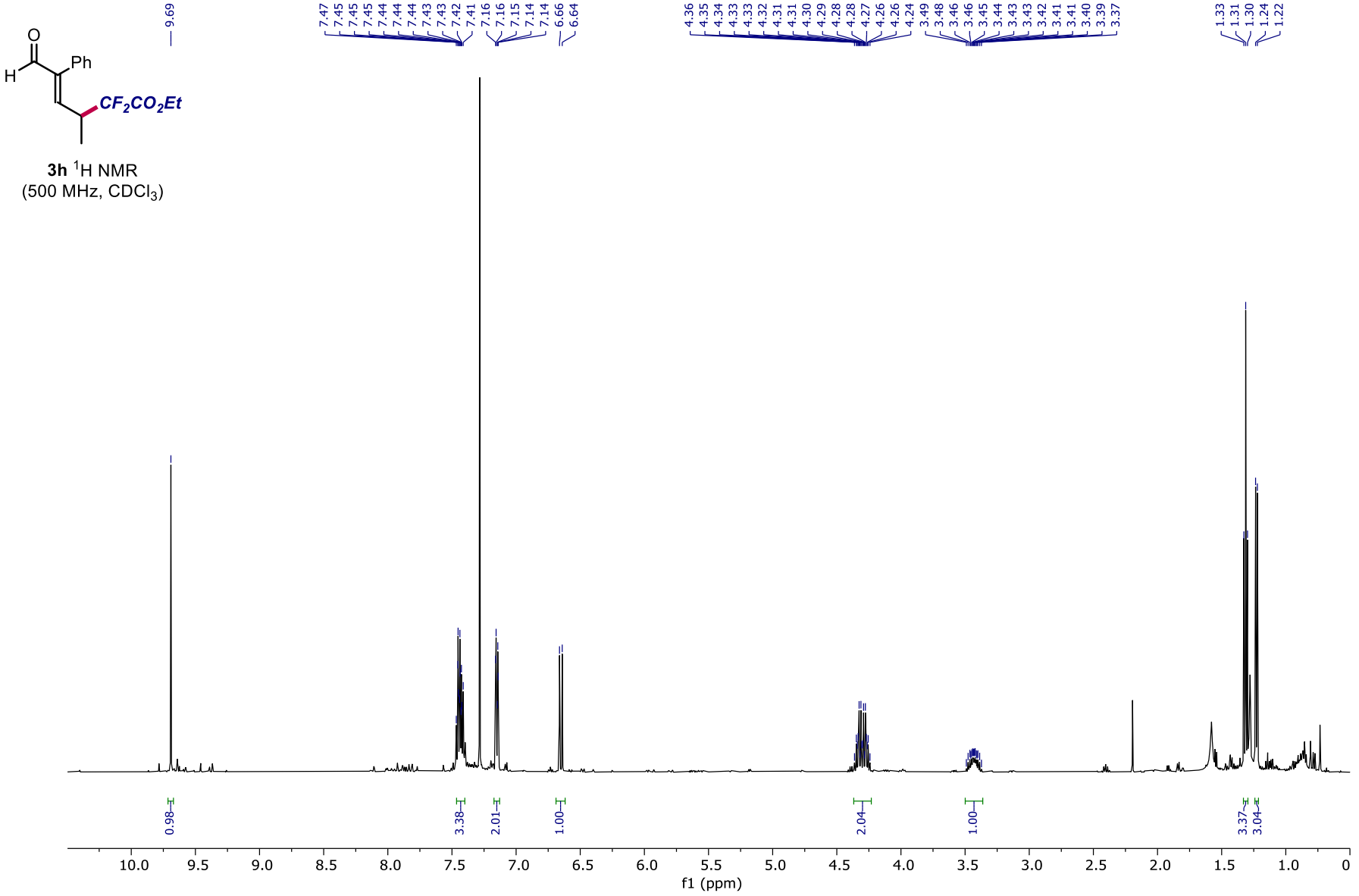
3g ^{1}H NMR
(500 MHz, $CDCl_3$)

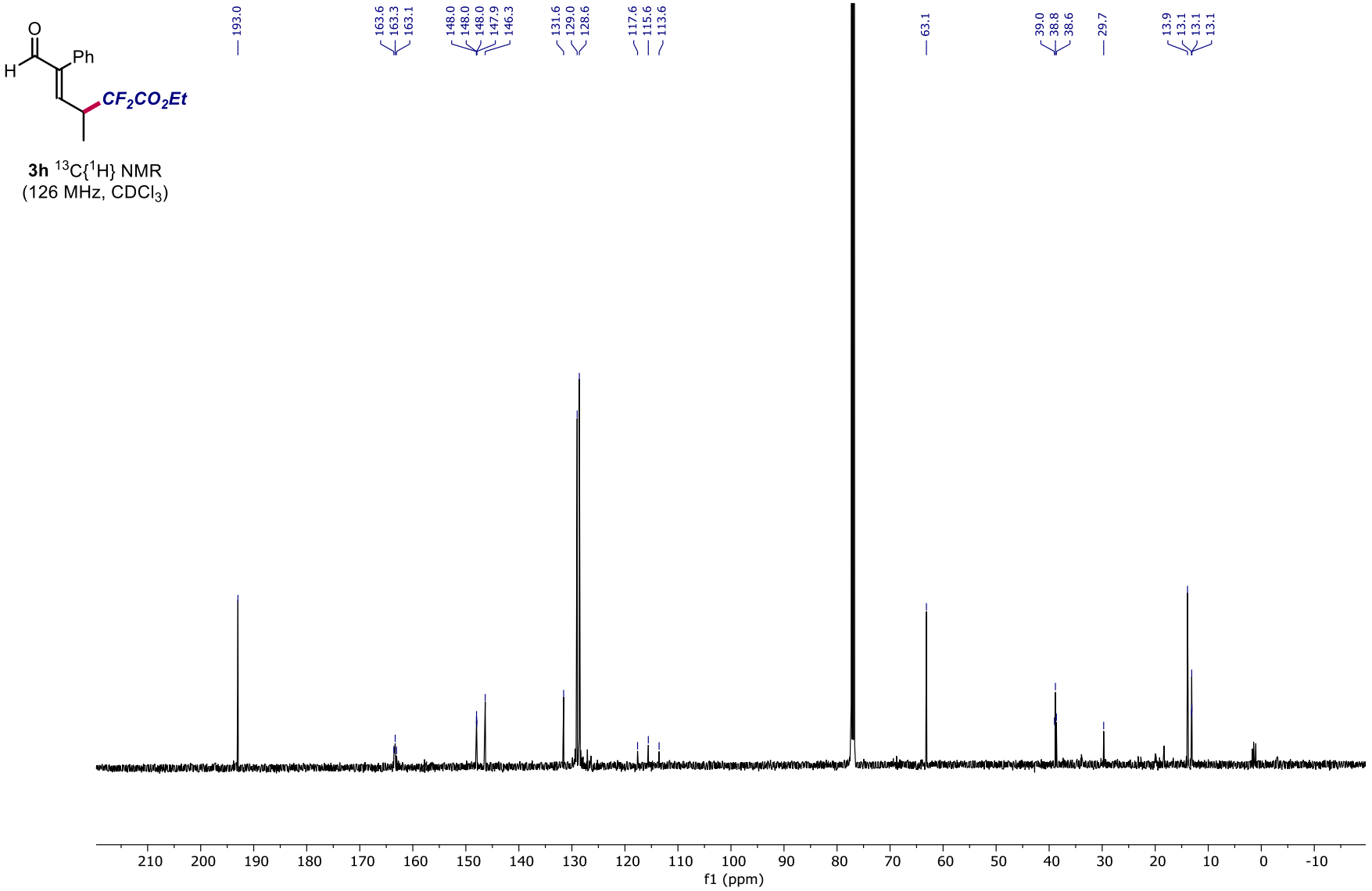


3g $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

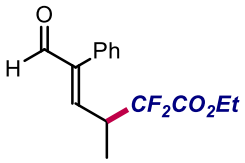


3g $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)

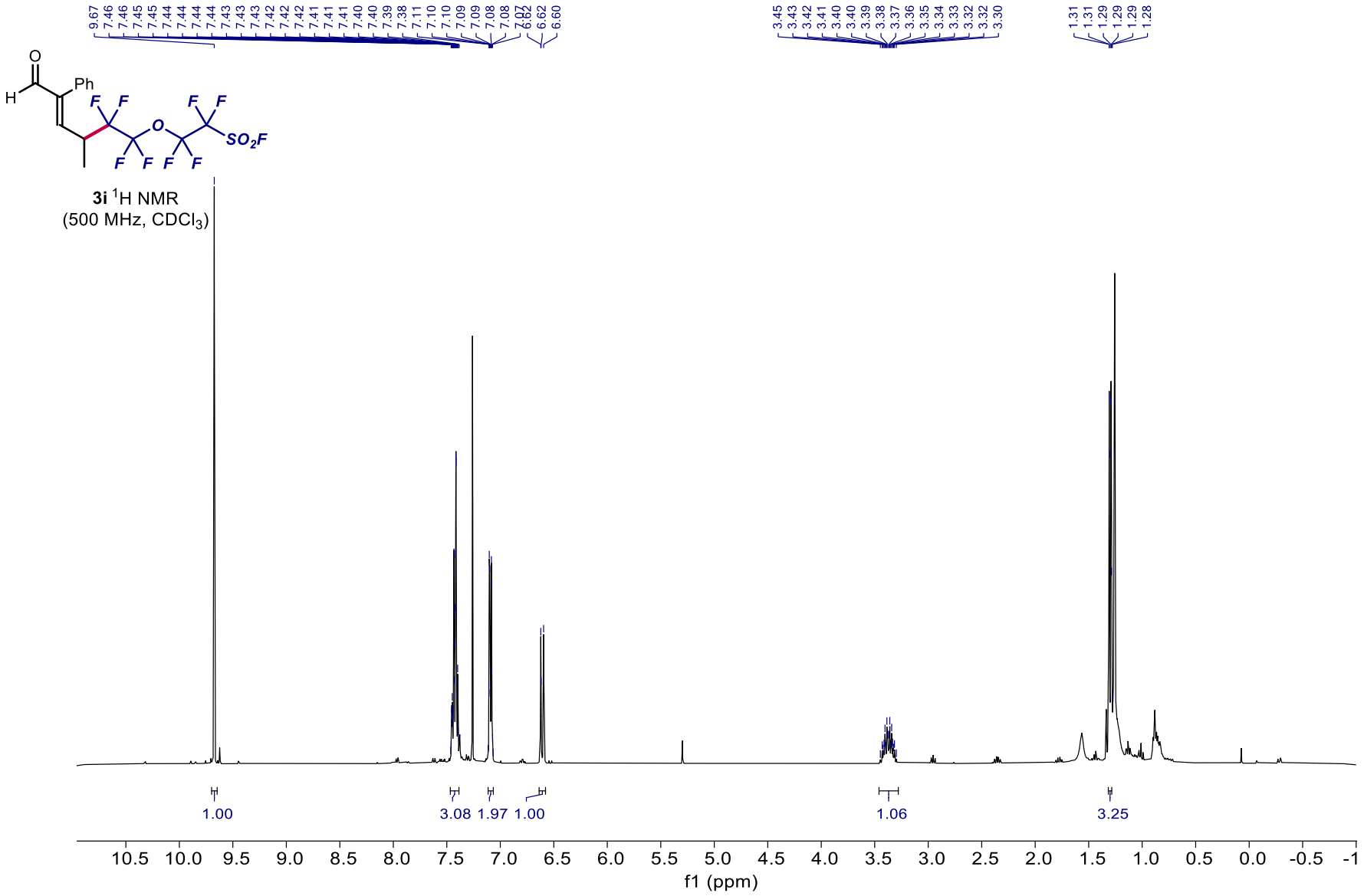

O
H
Ph
CF2CO2Et
3h 1H NMR
(500 MHz, CDCl3)
9.69
7.47
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.41
7.16
7.16
7.15
7.14
7.14
6.66
6.64
4.36
4.35
4.34
4.33
4.33
4.32
4.31
4.31
4.30
4.29
4.28
4.28
4.27
4.26
4.26
4.24
3.49
3.48
3.46
3.46
3.45
3.44
3.43
3.43
3.42
3.41
3.41
3.40
3.39
3.37
1.33
1.31
1.30
1.24
1.22
0.98
3.38
2.01
1.00
2.04
1.00
3.37
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
f1 (ppm)

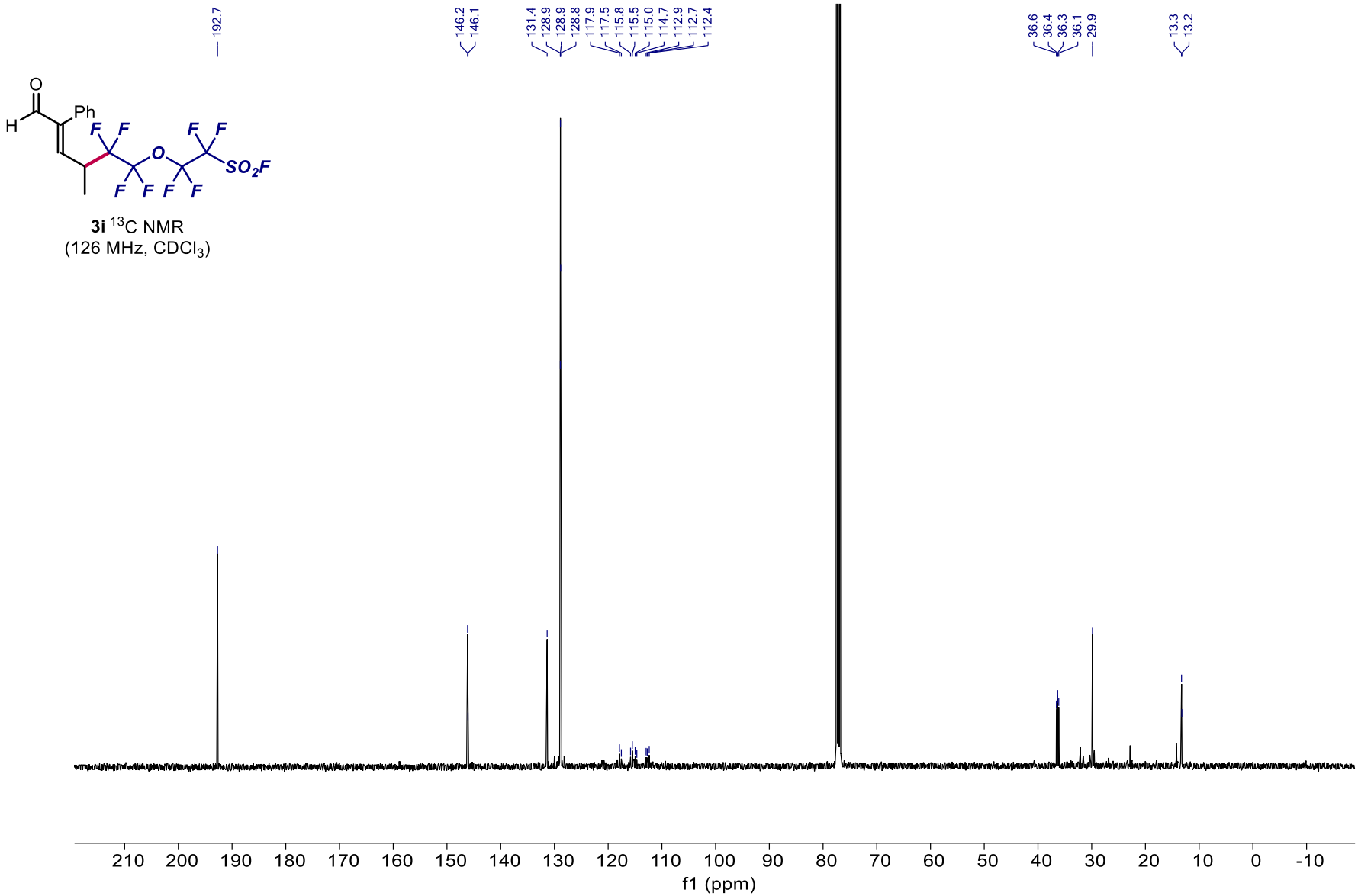


3h $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

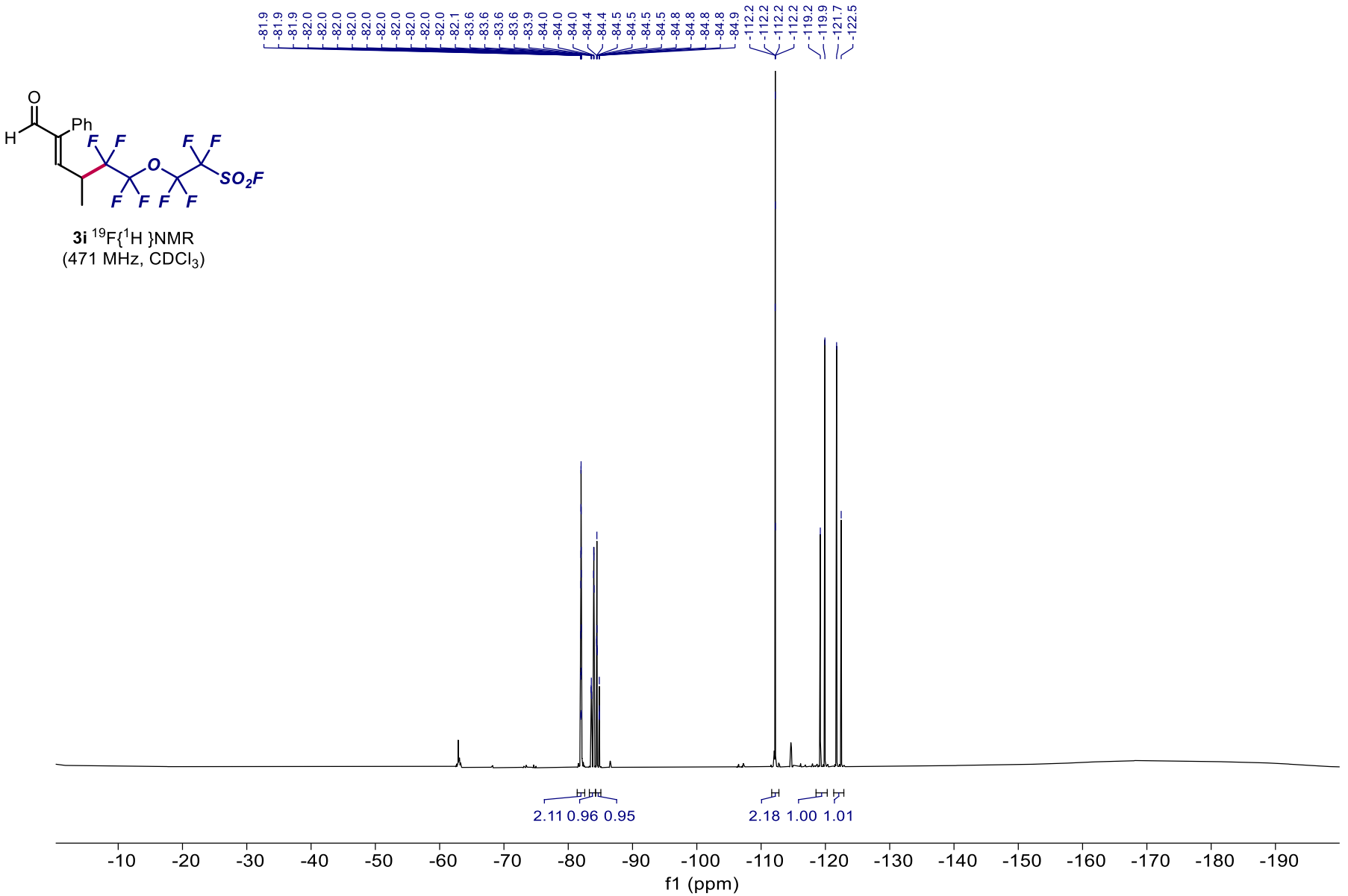


3h $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)

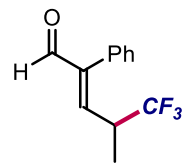

9.67 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.38 7.11 7.10 7.10 7.09 7.09 7.08 7.08 7.07 6.62 6.62 6.60
3.45 3.43 3.42 3.41 3.40 3.40 3.39 3.38 3.37 3.36 3.35 3.34 3.33 3.32 3.32 3.30
1.31 1.31 1.29 1.29 1.29 1.28
O
H
Ph
F F
F F
O
F F F F
SO2F
3i 1H NMR
(500 MHz, CDCl3)
1.00
3.08 1.97 1.00
1.06
3.25
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



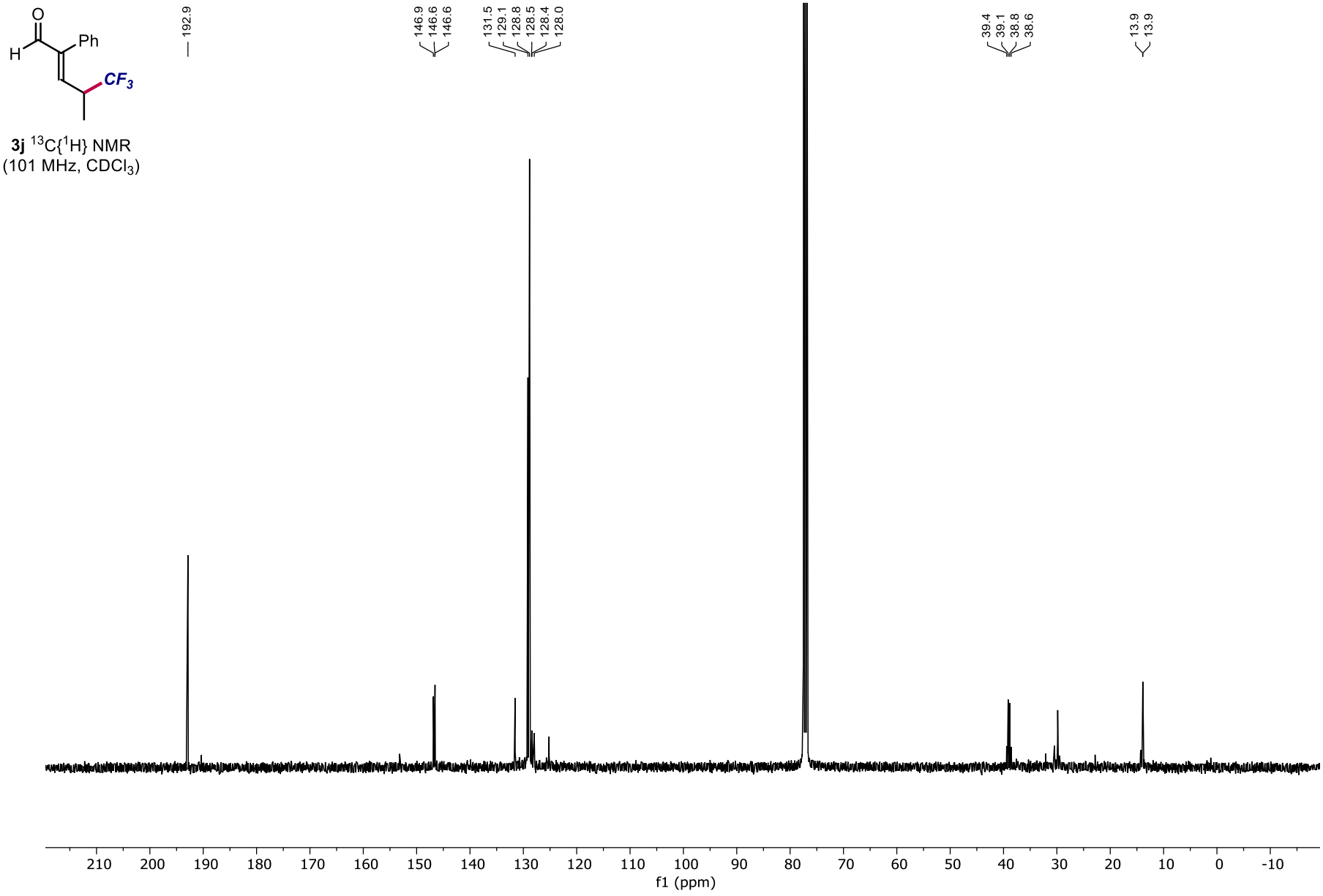
3i ^{13}C NMR
(126 MHz, $CDCl_3$)



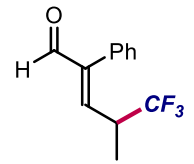
3i $^{19}F\{^{1}H\}$NMR
(471 MHz, $CDCl_3$)



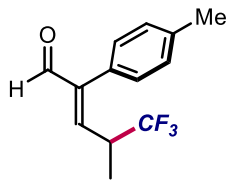
3j ^{1}H NMR
(400 MHz, $CDCl_3$)



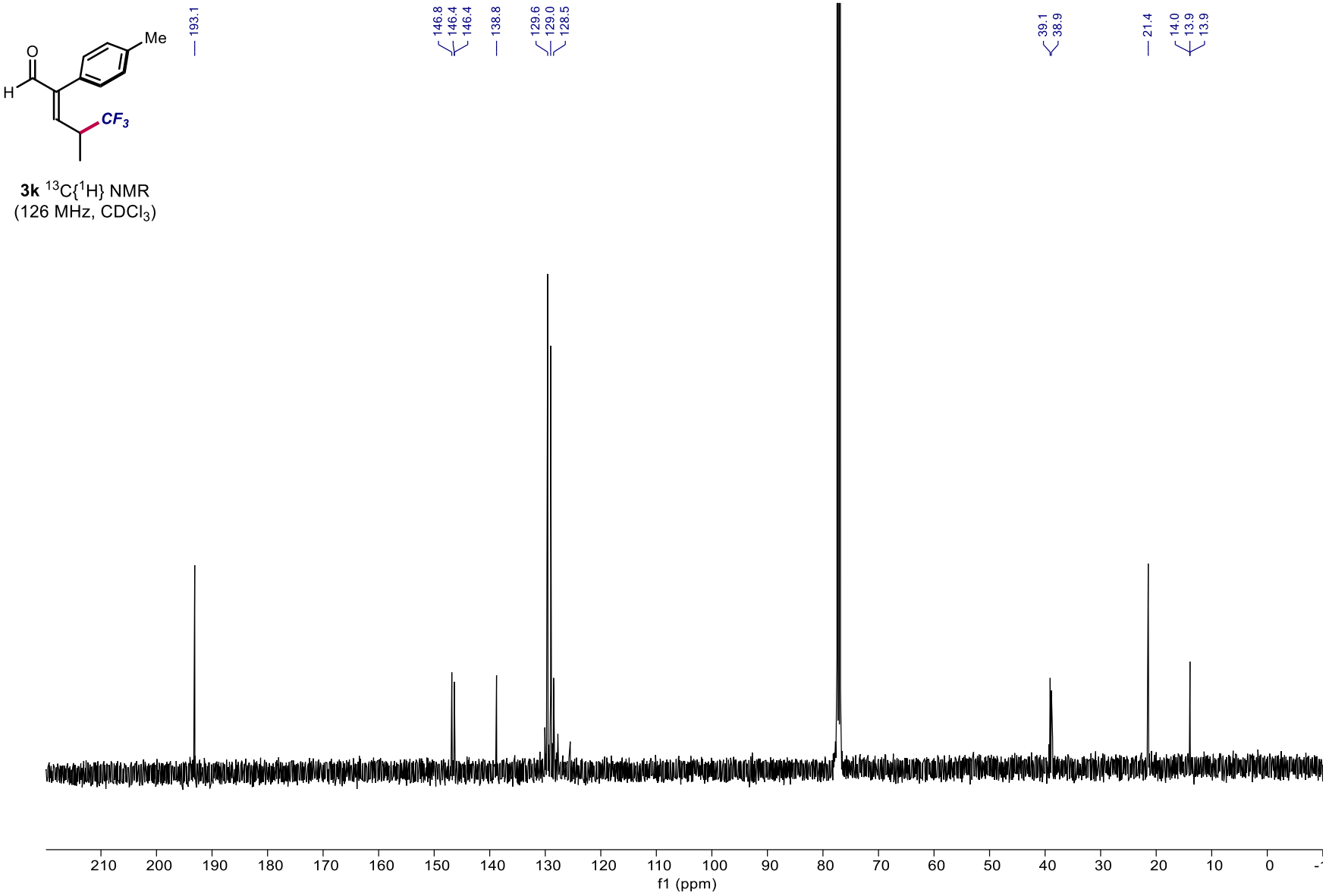
3j $^{13}C\{^{1}H\}$ NMR
(101 MHz, $CDCl_3$)



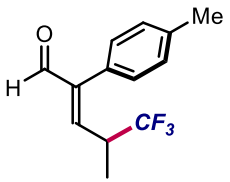
3j $^{19}F\{^{1}H\}$ NMR
(376 MHz, $CDCl_3$)



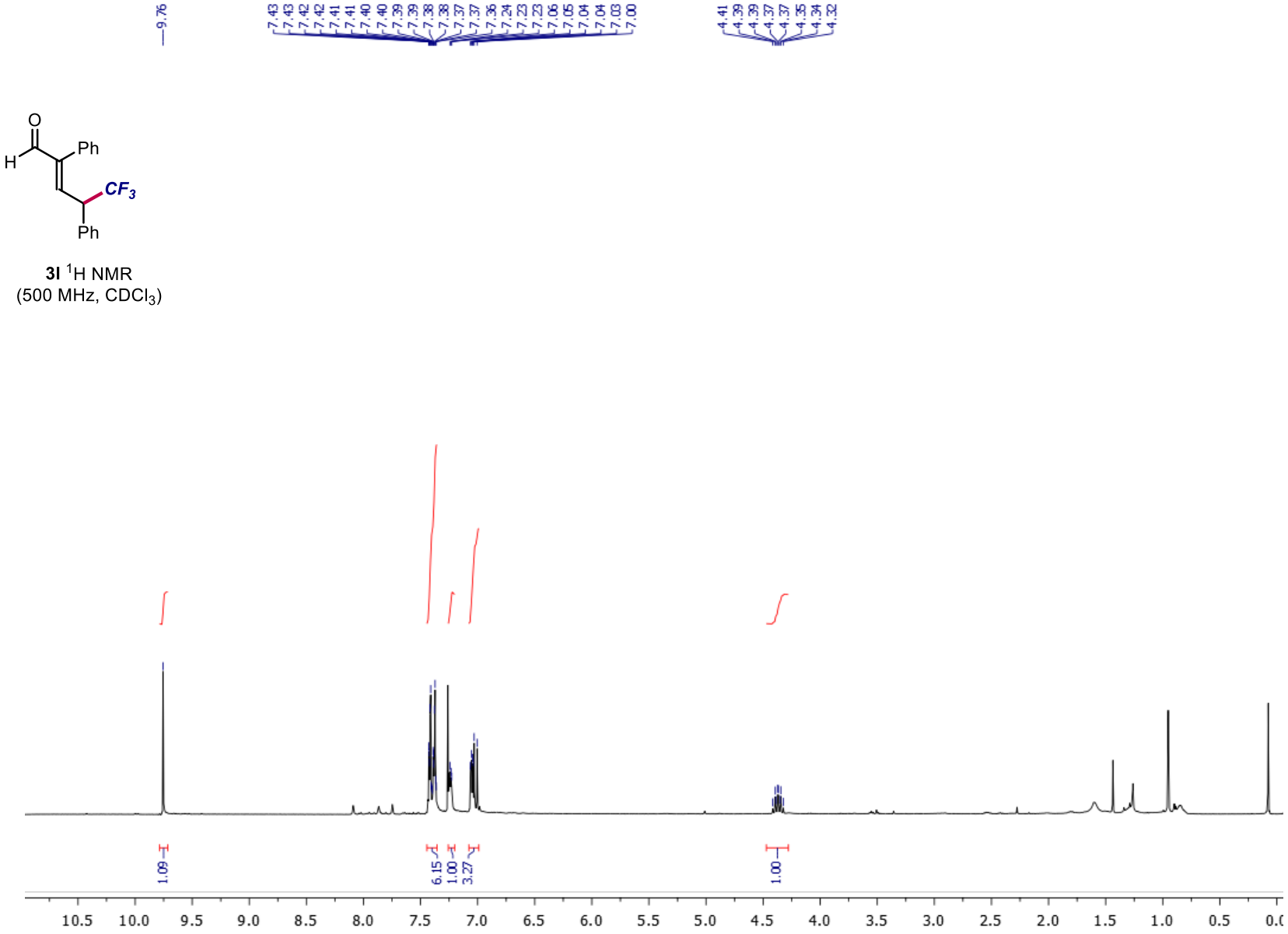
3k ^{1}H NMR
(500 MHz, $CDCl_3$)



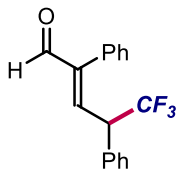
3k $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



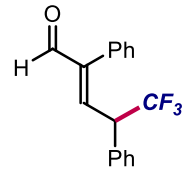
3k $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)



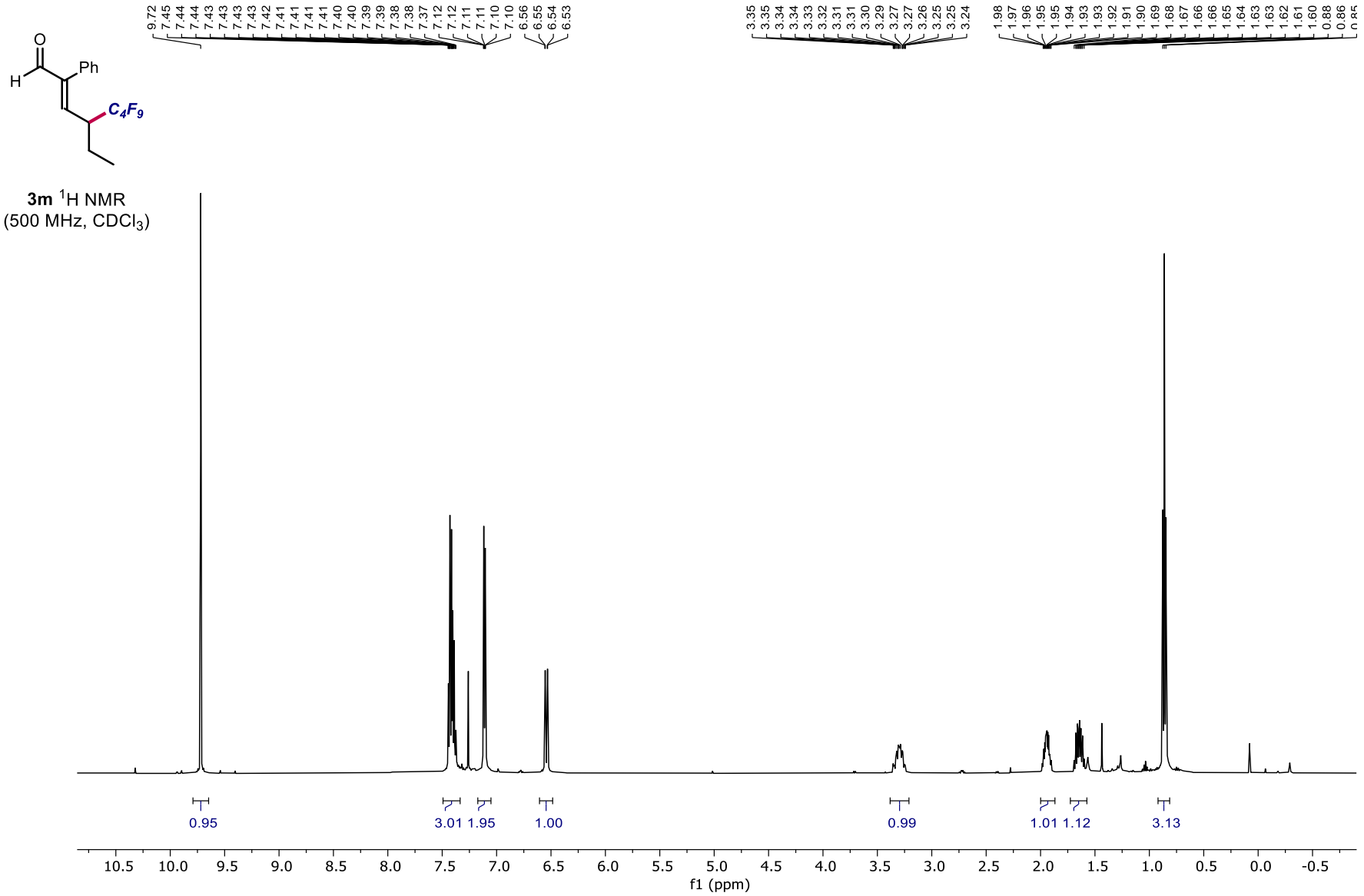
3l ^{1}H NMR
(500 MHz, $CDCl_3$)



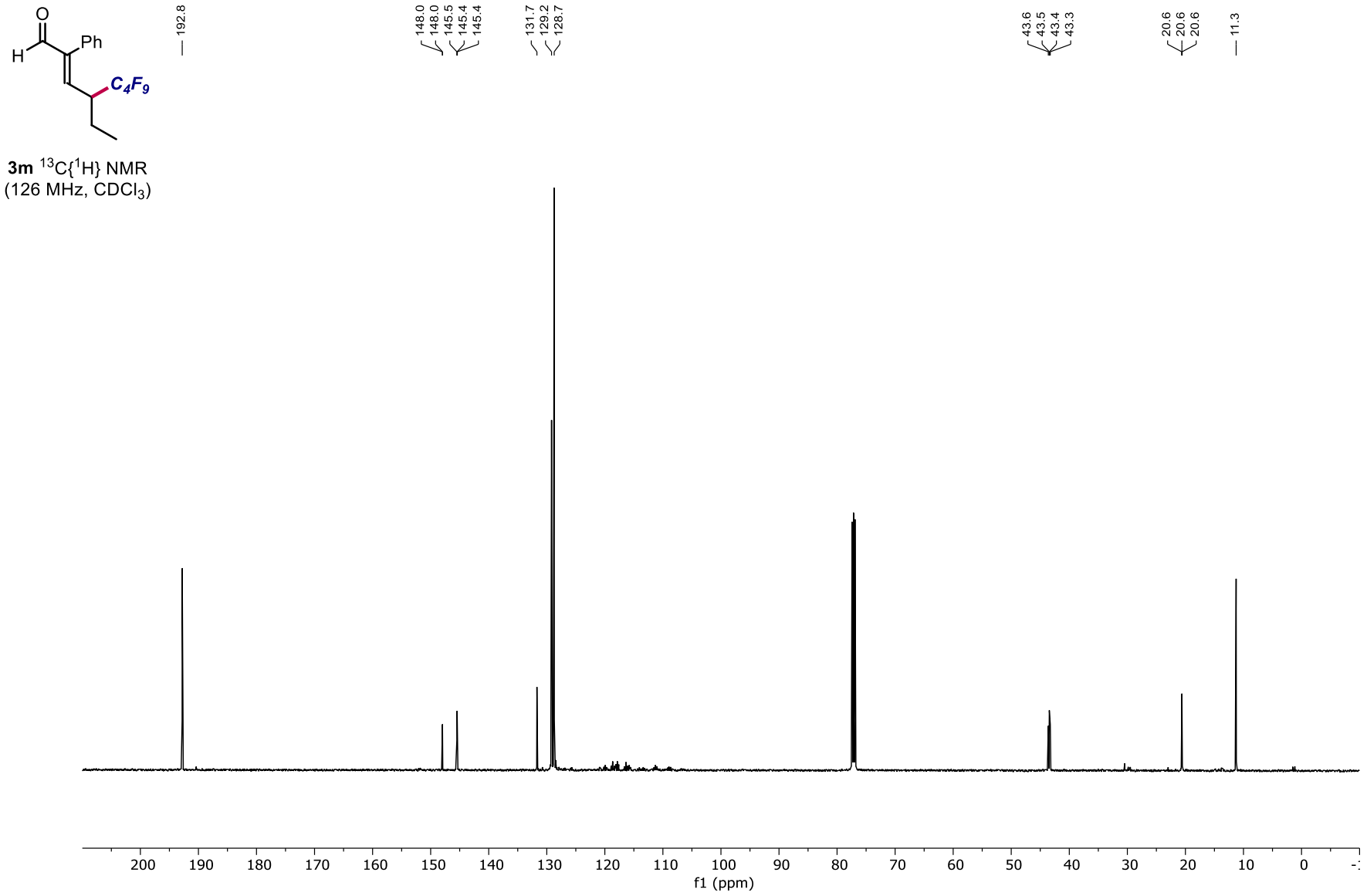
3l $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



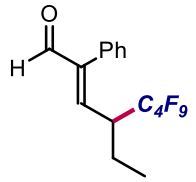
3l $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)



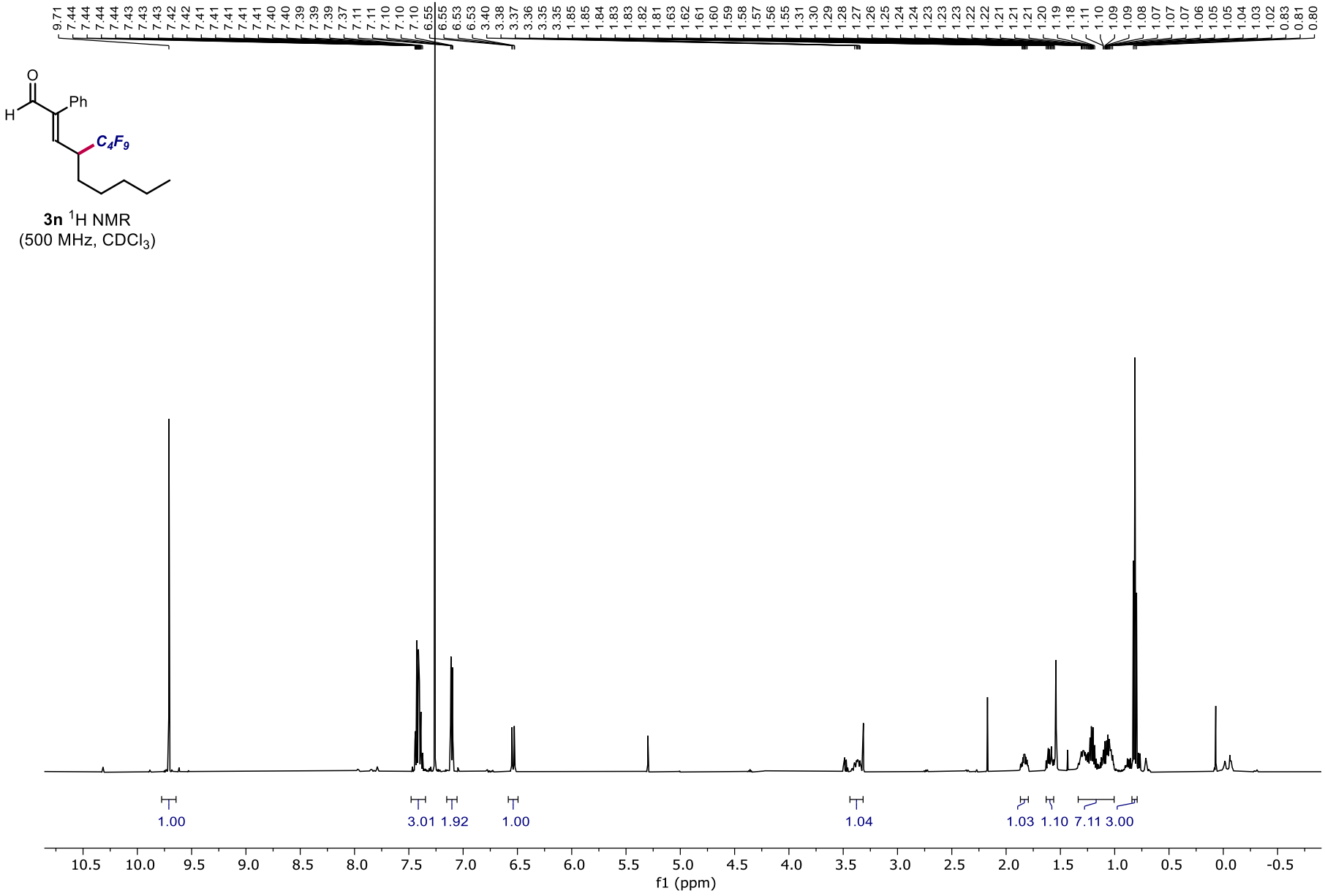
3m ^{1}H NMR
(500 MHz, $CDCl_3$)



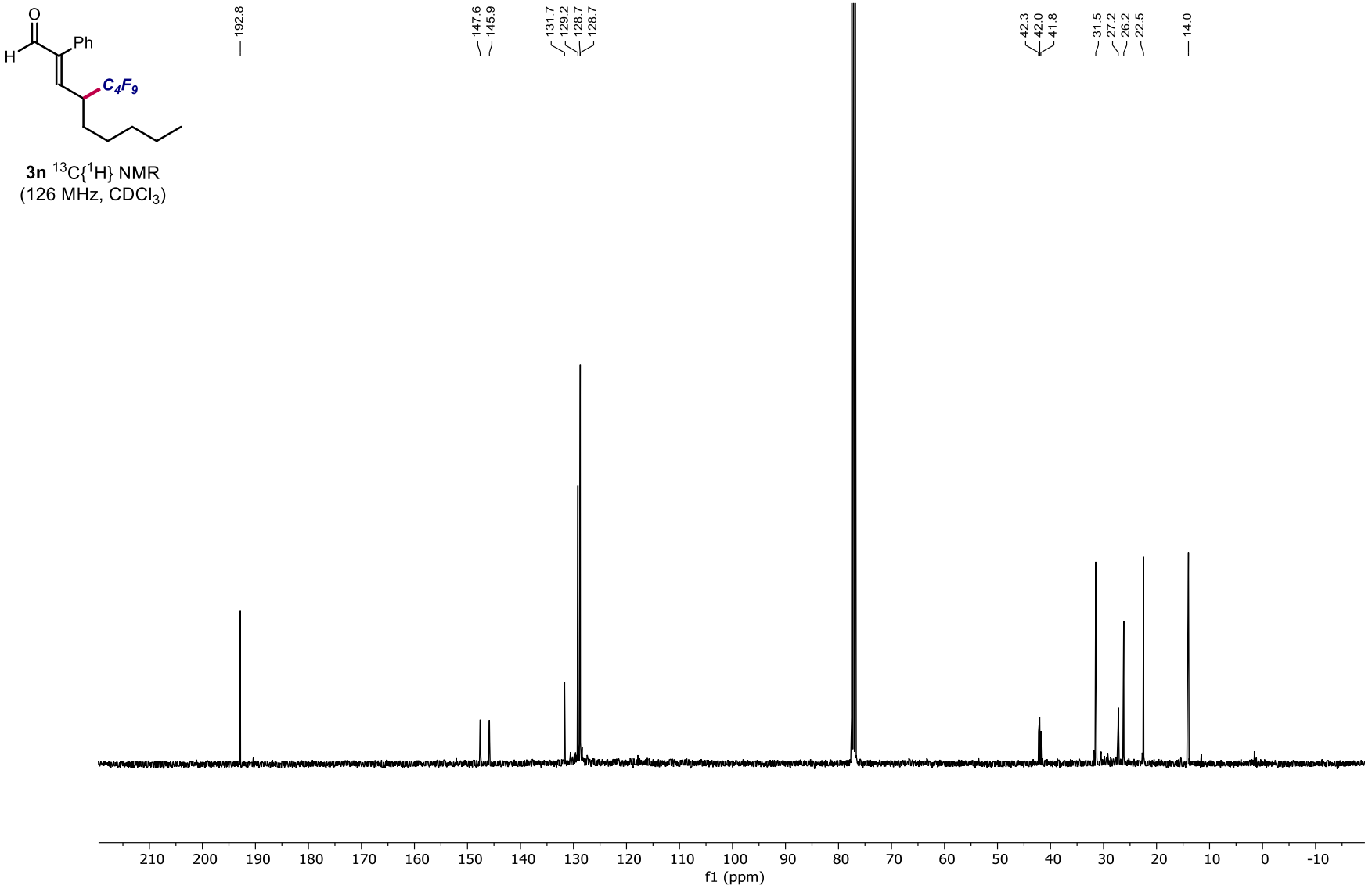
3m $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



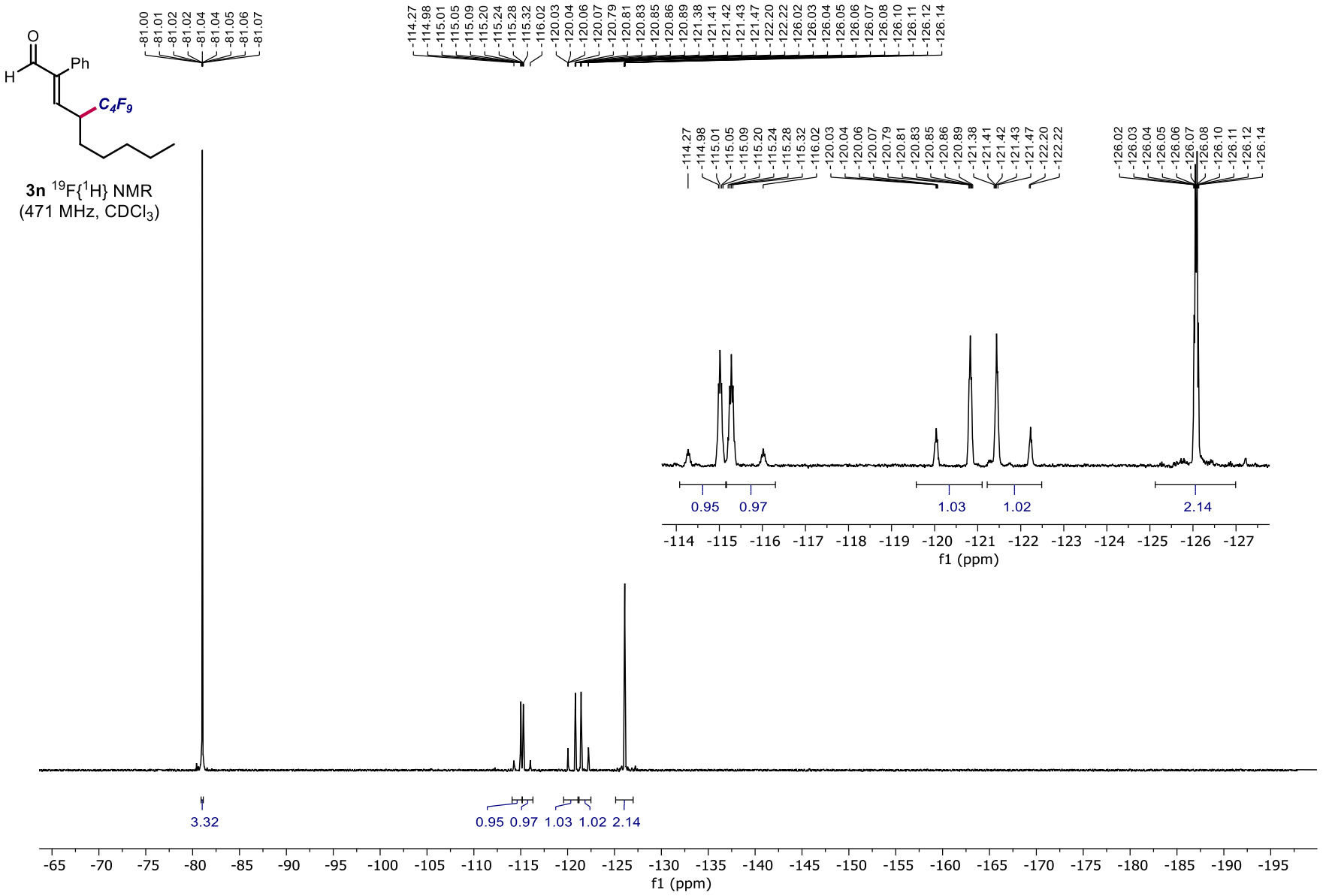
3m $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)

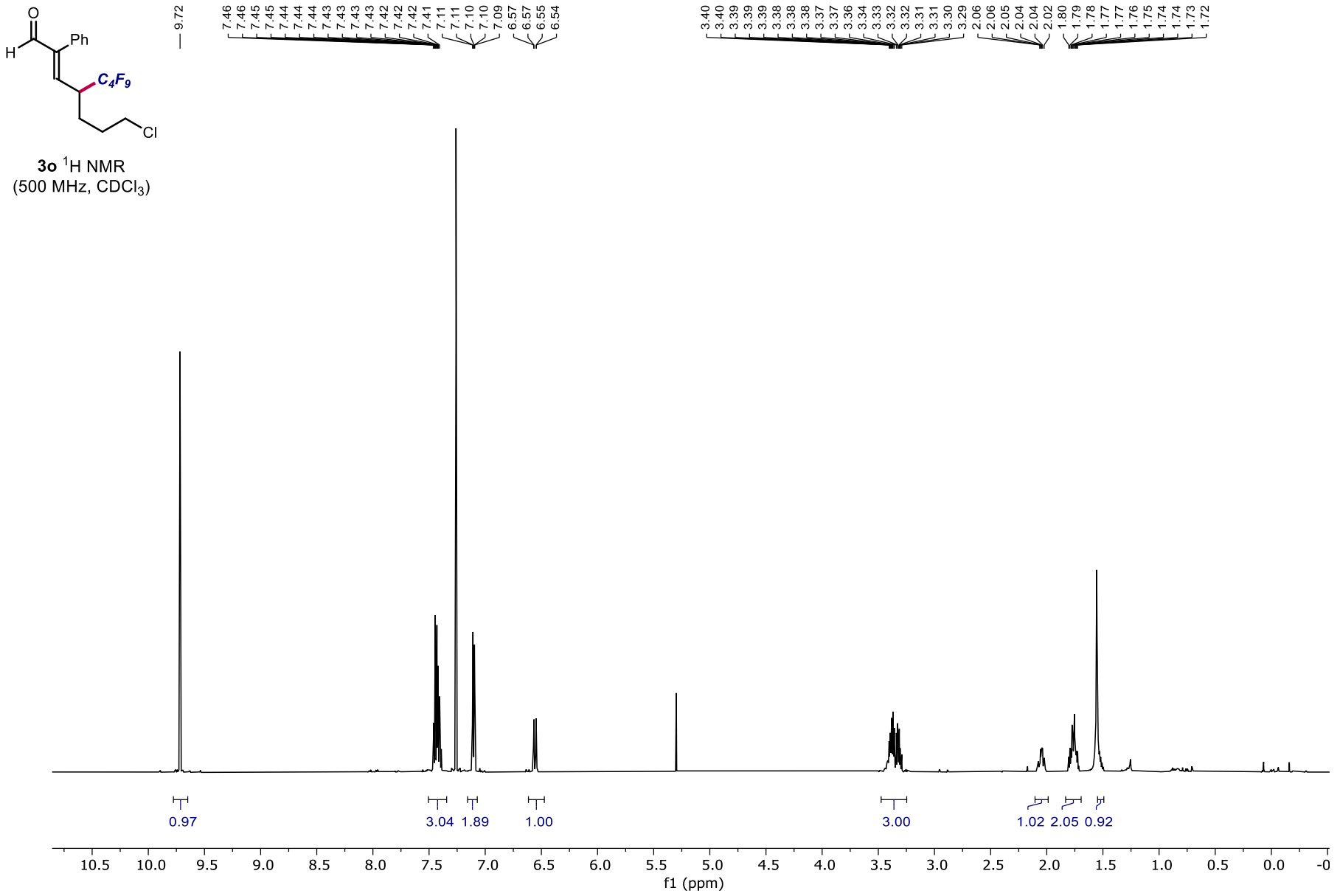


3n ^{1}H NMR
(500 MHz, $CDCl_3$)

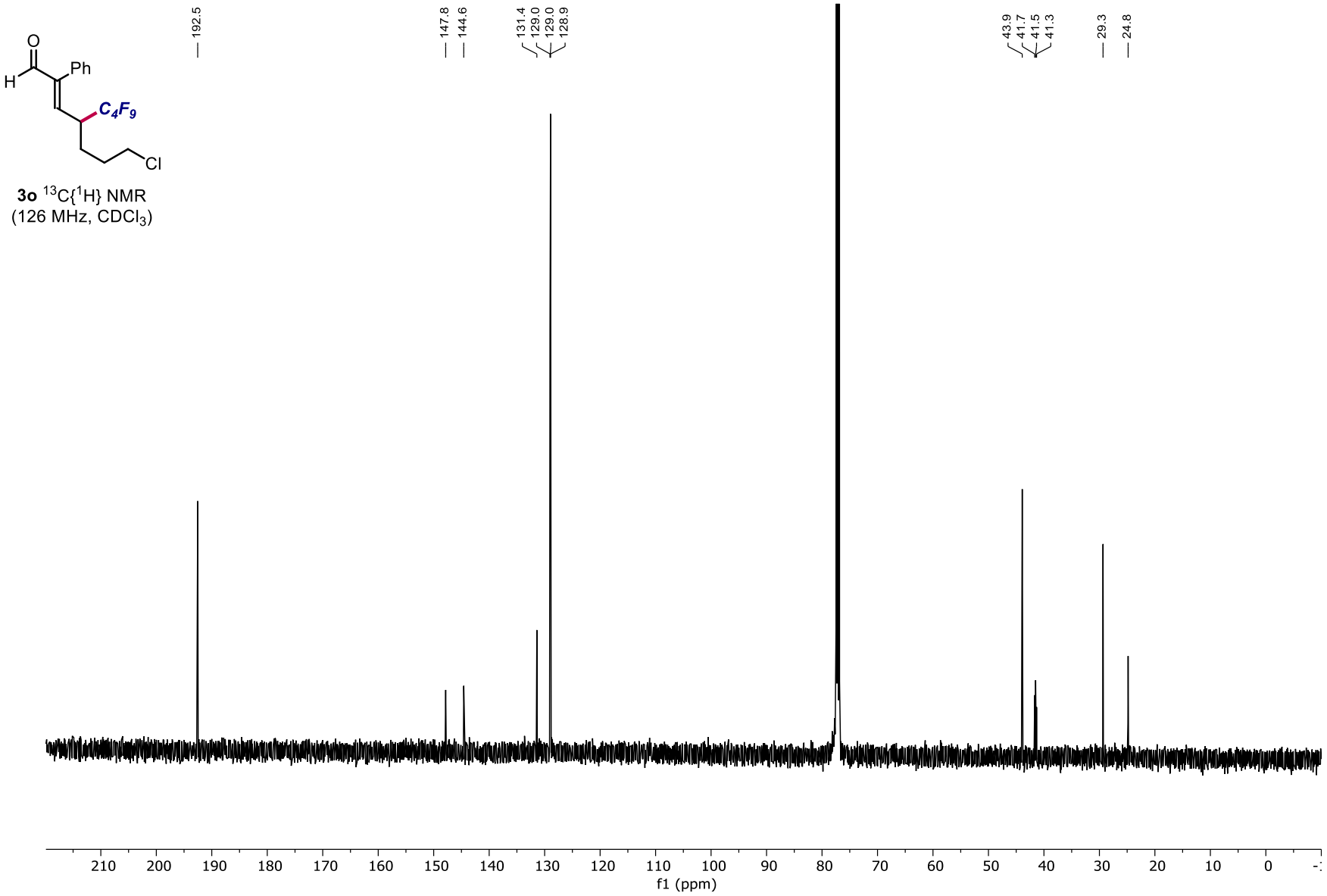


3n $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

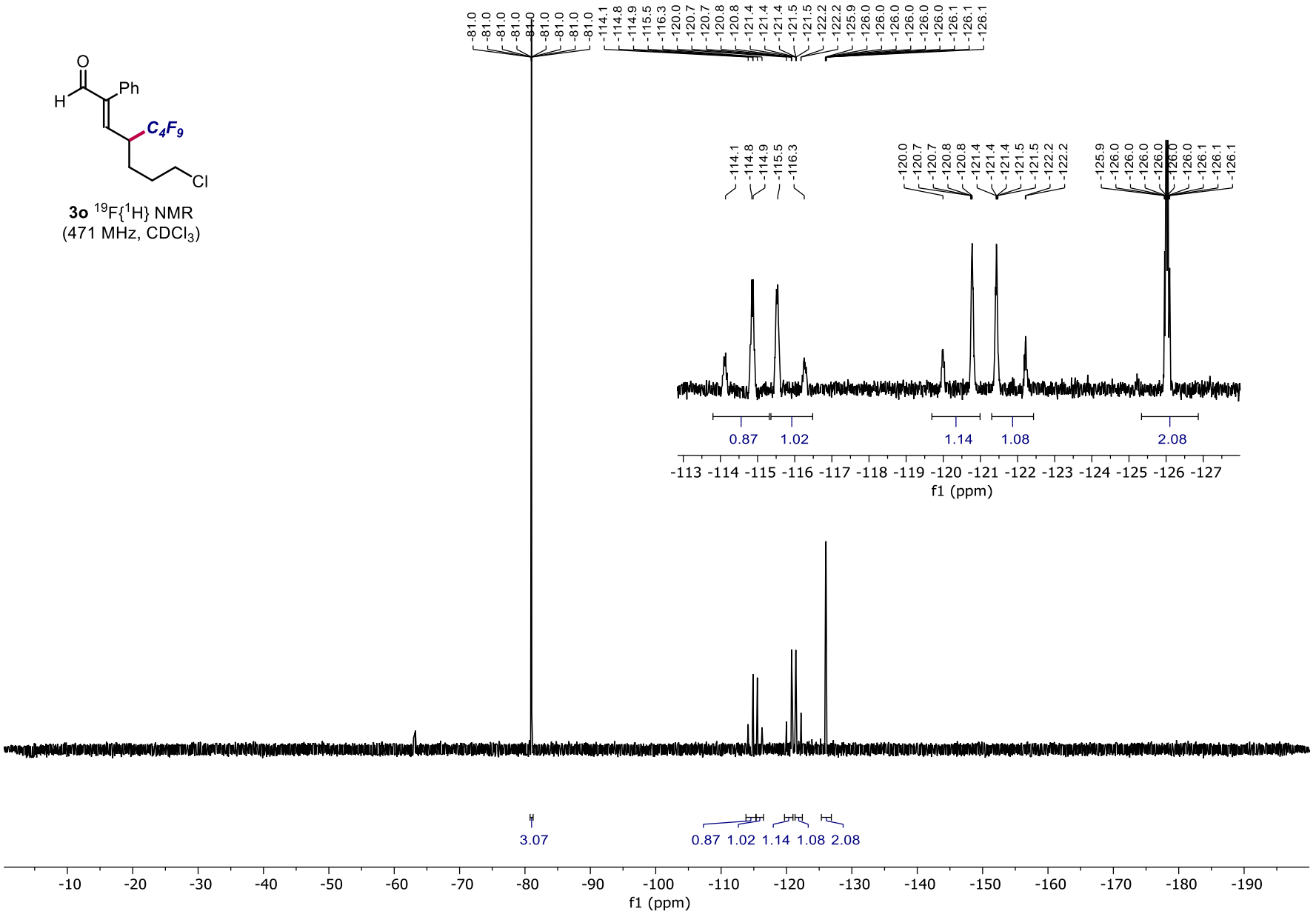

O
H
Ph
C_4F_9
3n $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)
-81.00
-81.01
-81.02
-81.02
-81.04
-81.04
-81.05
-81.06
-81.07
-114.27
-114.98
-115.01
-115.05
-115.09
-115.20
-115.24
-115.28
-115.32
-116.02
-120.03
-120.04
-120.06
-120.07
-120.79
-120.81
-120.83
-120.85
-120.86
-120.89
-121.38
-121.41
-121.42
-121.43
-121.47
-122.20
-122.22
-126.02
-126.03
-126.04
-126.05
-126.06
-126.07
-126.08
-126.10
-126.11
-126.12
-126.14
0.95
0.97
1.03
1.02
2.14
f1 (ppm)
3.32
0.95 0.97 1.03 1.02 2.14
f1 (ppm)

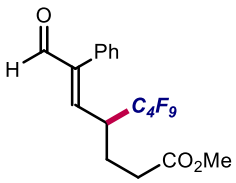


3o ^{1}H NMR
(500 MHz, $CDCl_3$)

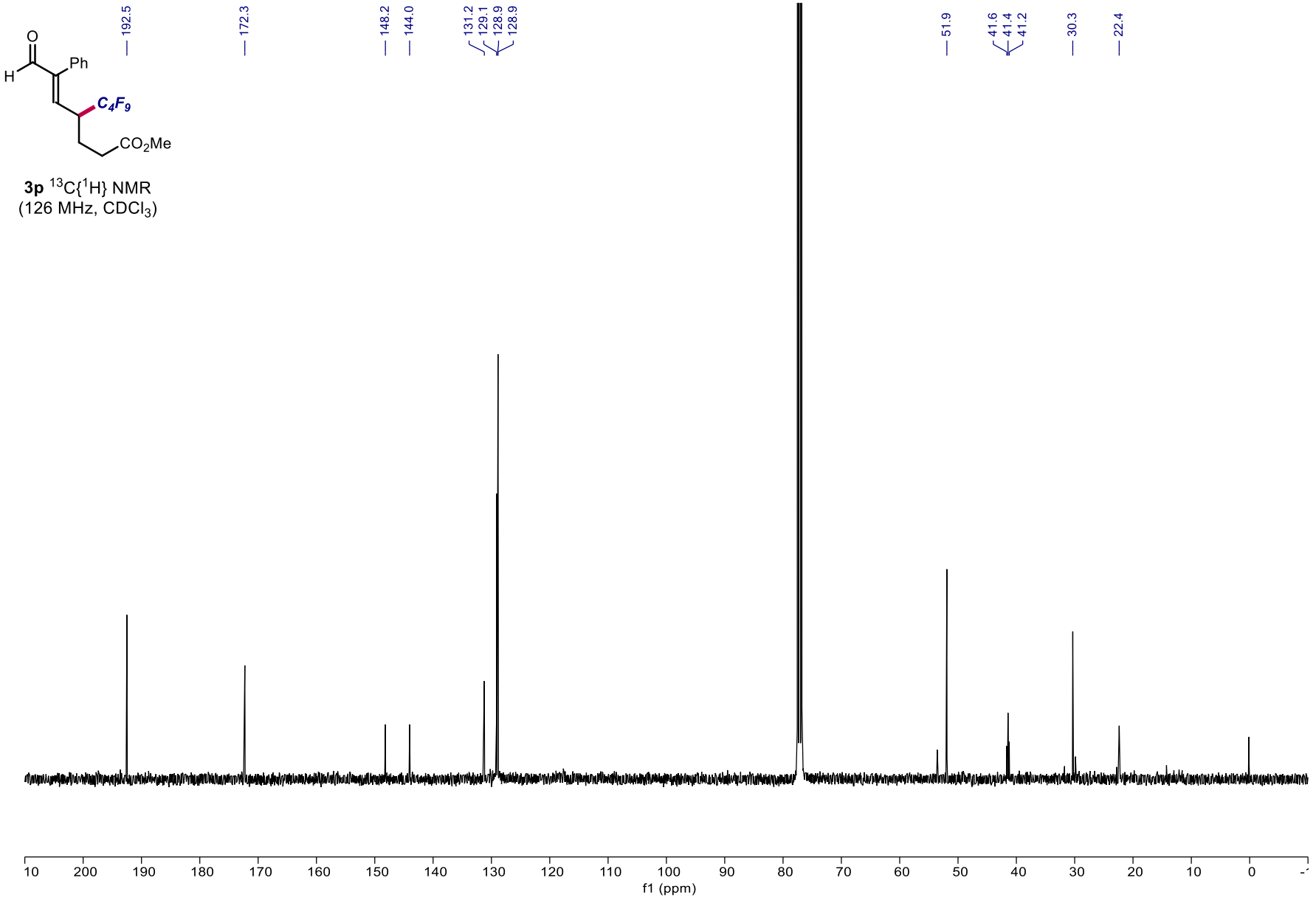


3o $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

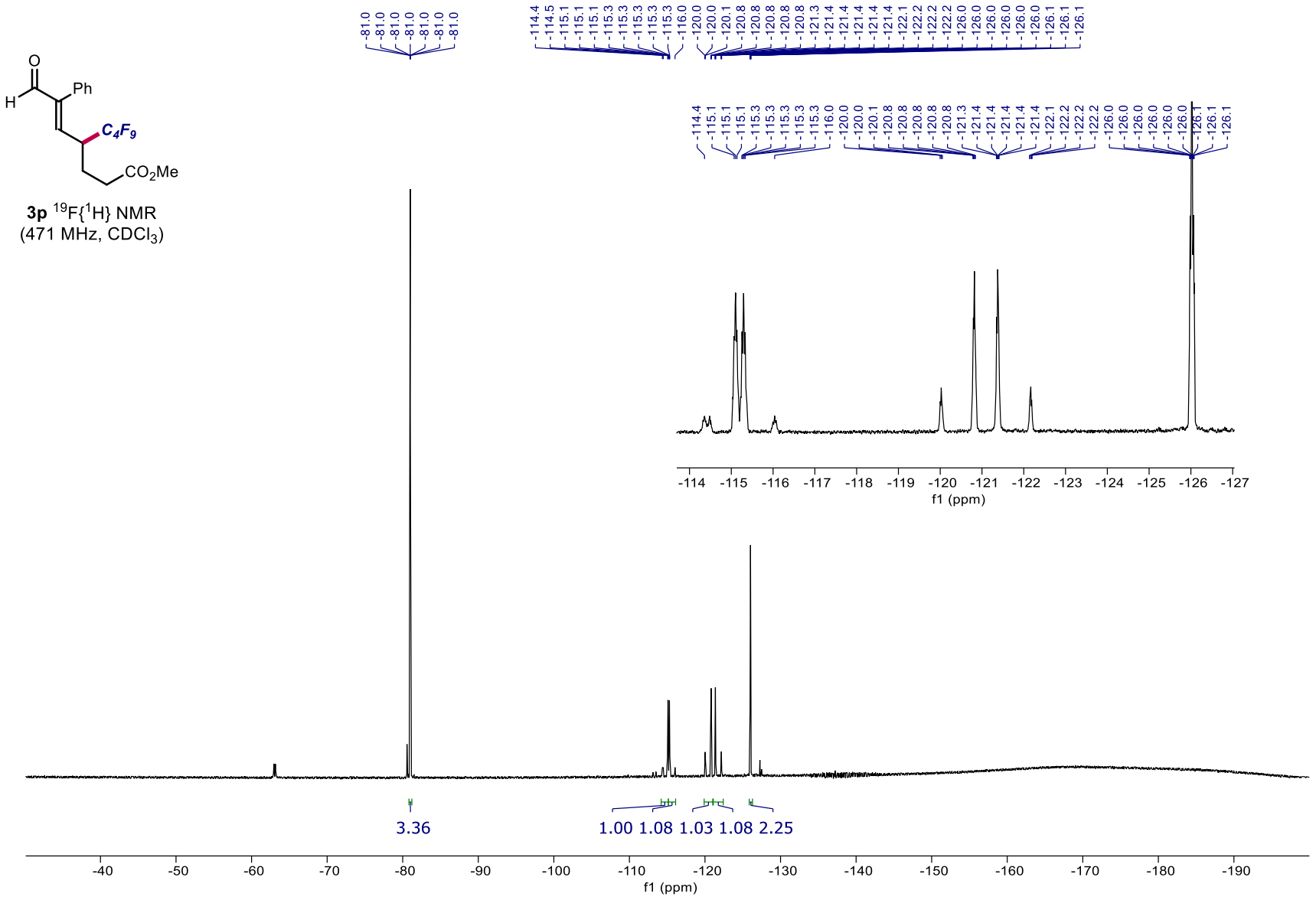

O
H
Ph
C_4F_9
Cl
3o $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)
-81.0 -81.0 -81.0 -81.0 -81.0 -81.0 -81.0 -81.0
-114.1 -114.8 -114.9 -115.5 -116.3
-120.0 -120.7 -120.7 -120.8 -120.8
-121.4 -121.4 -121.4 -121.5 -121.5
-122.2 -122.2 -125.9
-126.0 -126.0 -126.0 -126.0 -126.0 -126.0 -126.1 -126.1
0.87 1.02 1.14 1.08 2.08
f1 (ppm)
3.07
0.87 1.02 1.14 1.08 2.08
f1 (ppm)

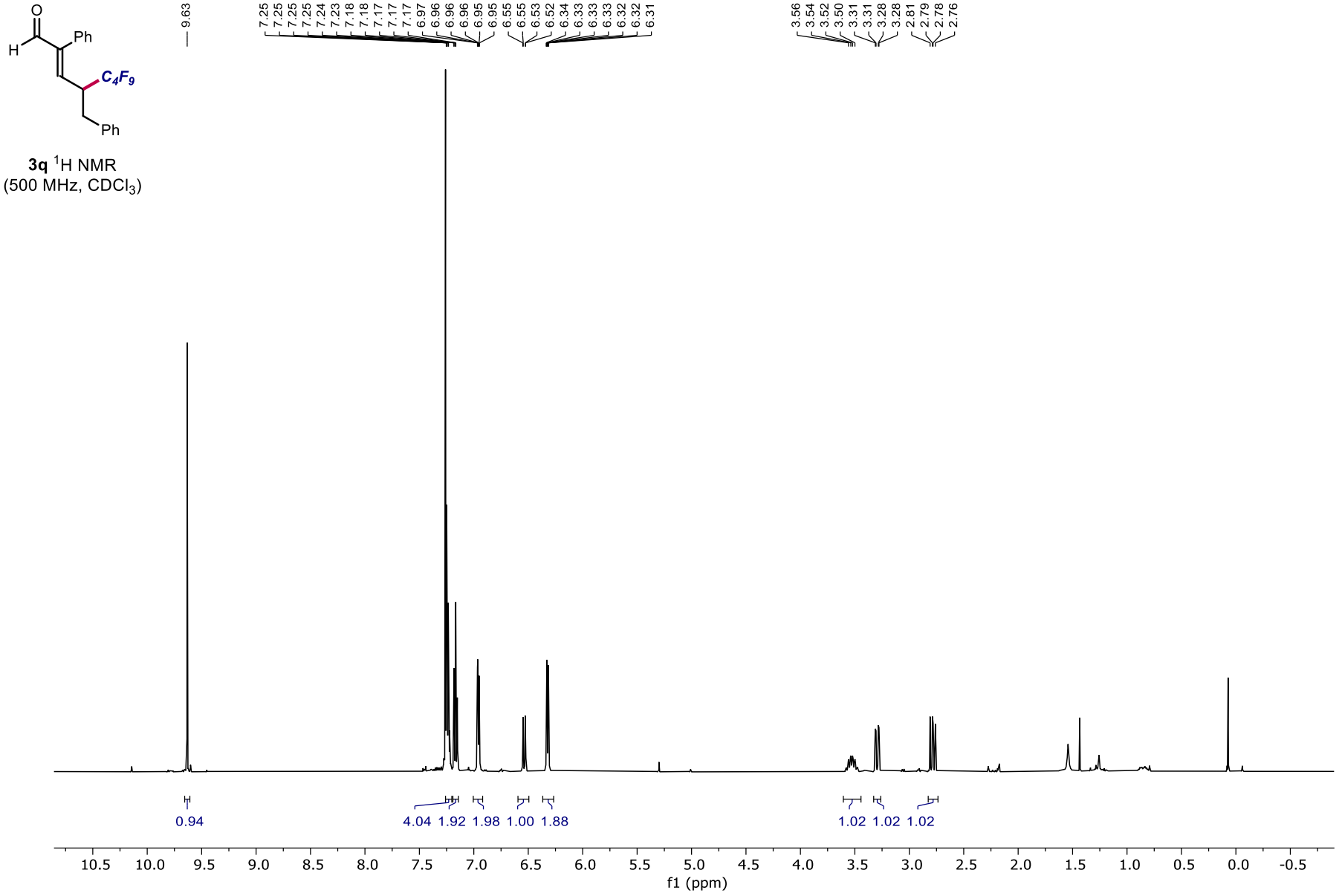


3p ^{1}H NMR
(500 MHz, $CDCl_3$)

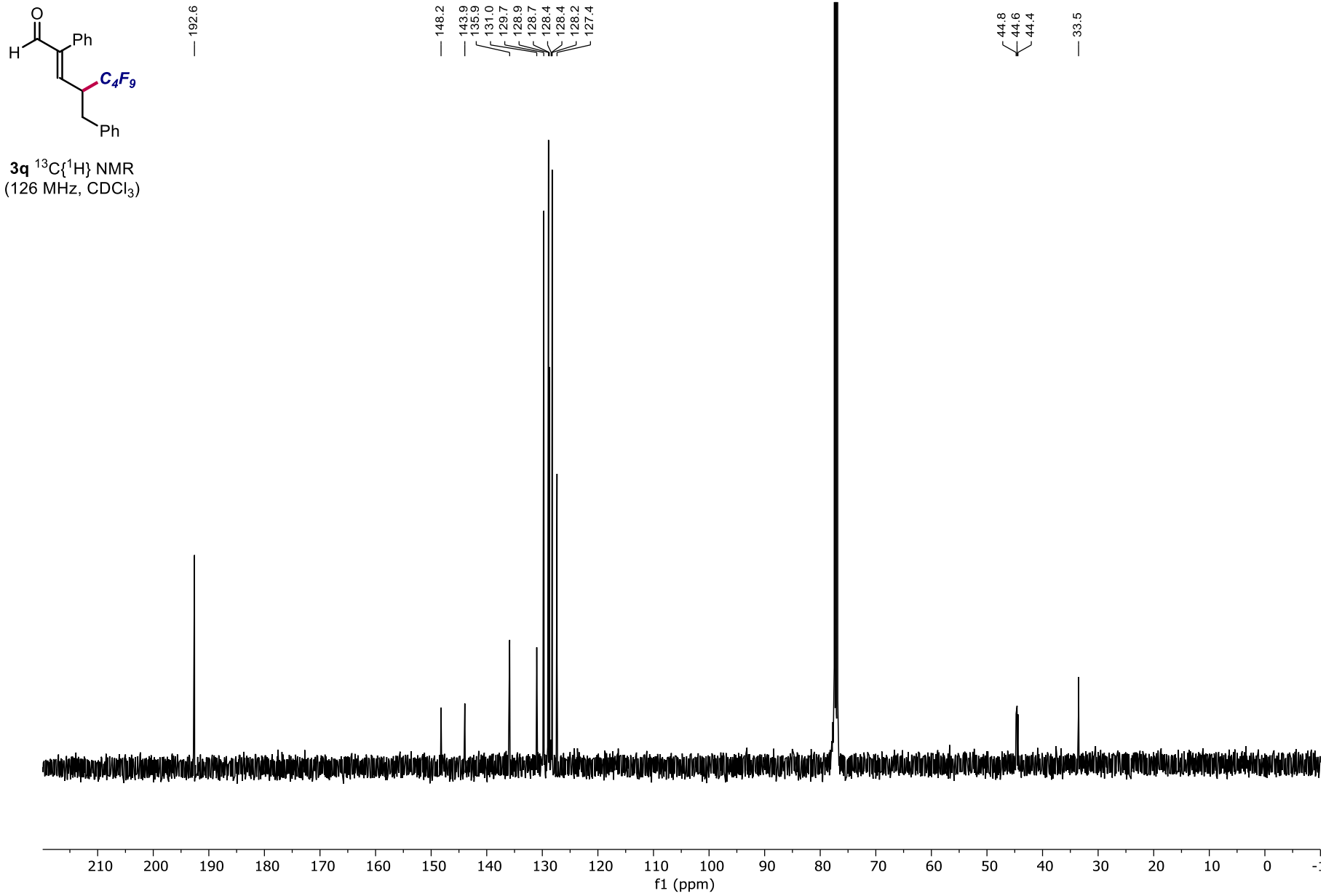


3p $^{13}C\{^1H\}$ NMR
(126 MHz, $CDCl_3$)

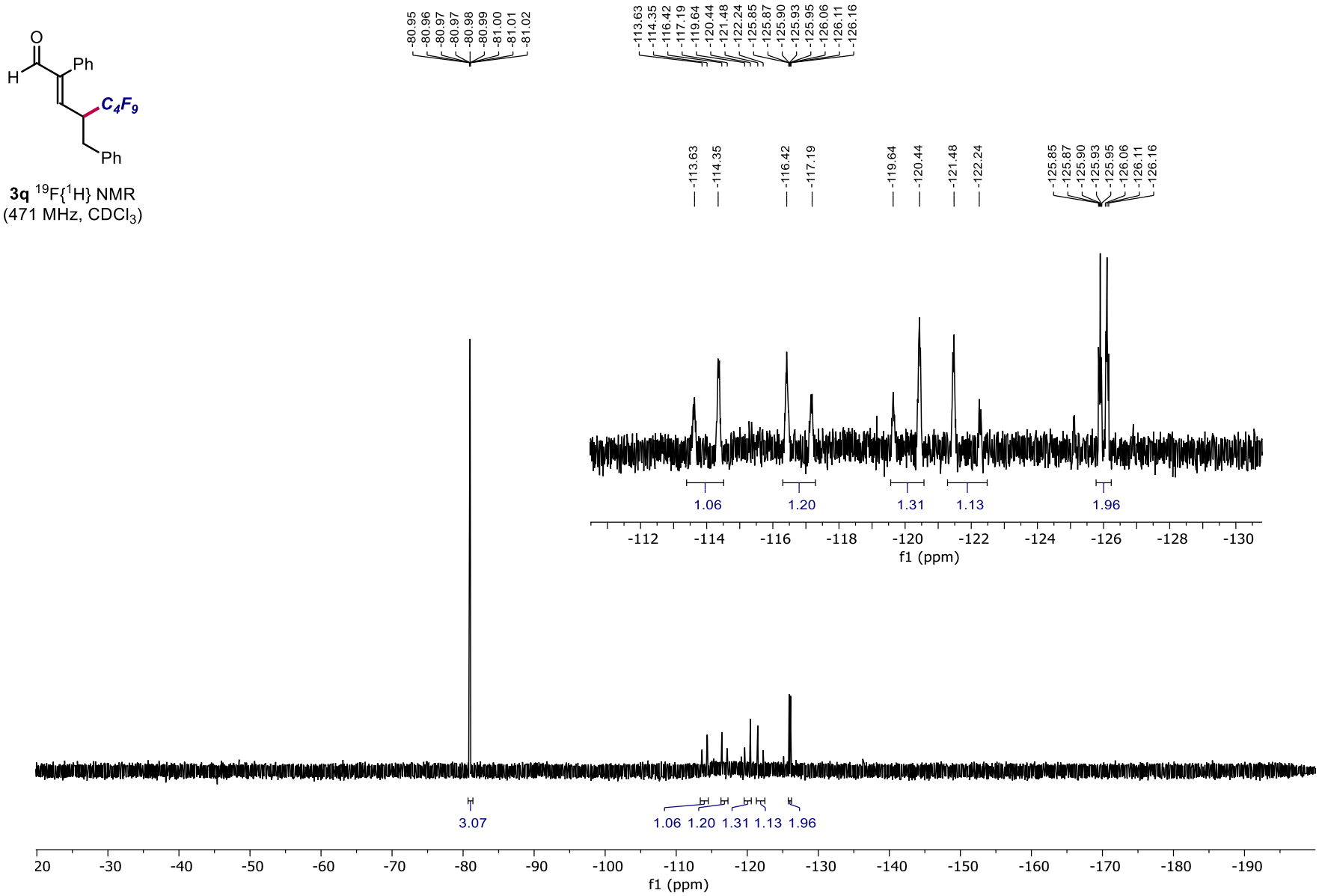

O
H
Ph
C_4F_9
CO_2Me
3p $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)
-81.0 -81.0 -81.0 -81.0 -81.0 -81.0 -81.0
-114.4 -114.5 -115.1 -115.1 -115.1 -115.3 -115.3 -115.3 -115.3 -115.3 -116.0 -120.0 -120.0 -120.1 -120.8 -120.8 -120.8 -120.8 -120.8 -121.3 -121.4 -121.4 -121.4 -121.4 -121.4 -122.1 -122.2 -122.2 -122.2 -126.0 -126.0 -126.0 -126.0 -126.0 -126.0 -126.1 -126.1 -126.1
-114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127
f1 (ppm)
3.36
1.00 1.08 1.03 1.08 2.25
-40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)



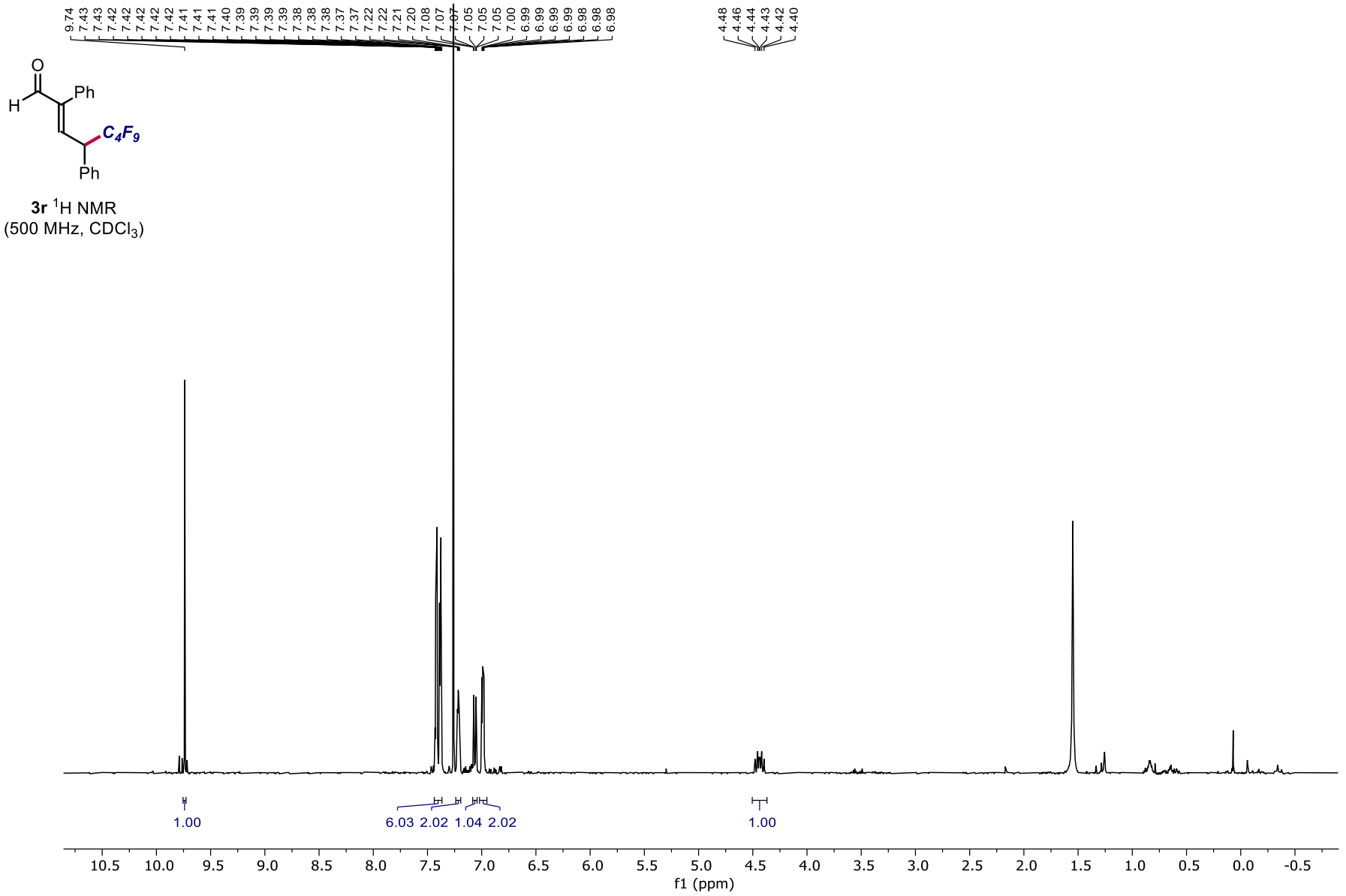
3q ^{1}H NMR
(500 MHz, $CDCl_3$)



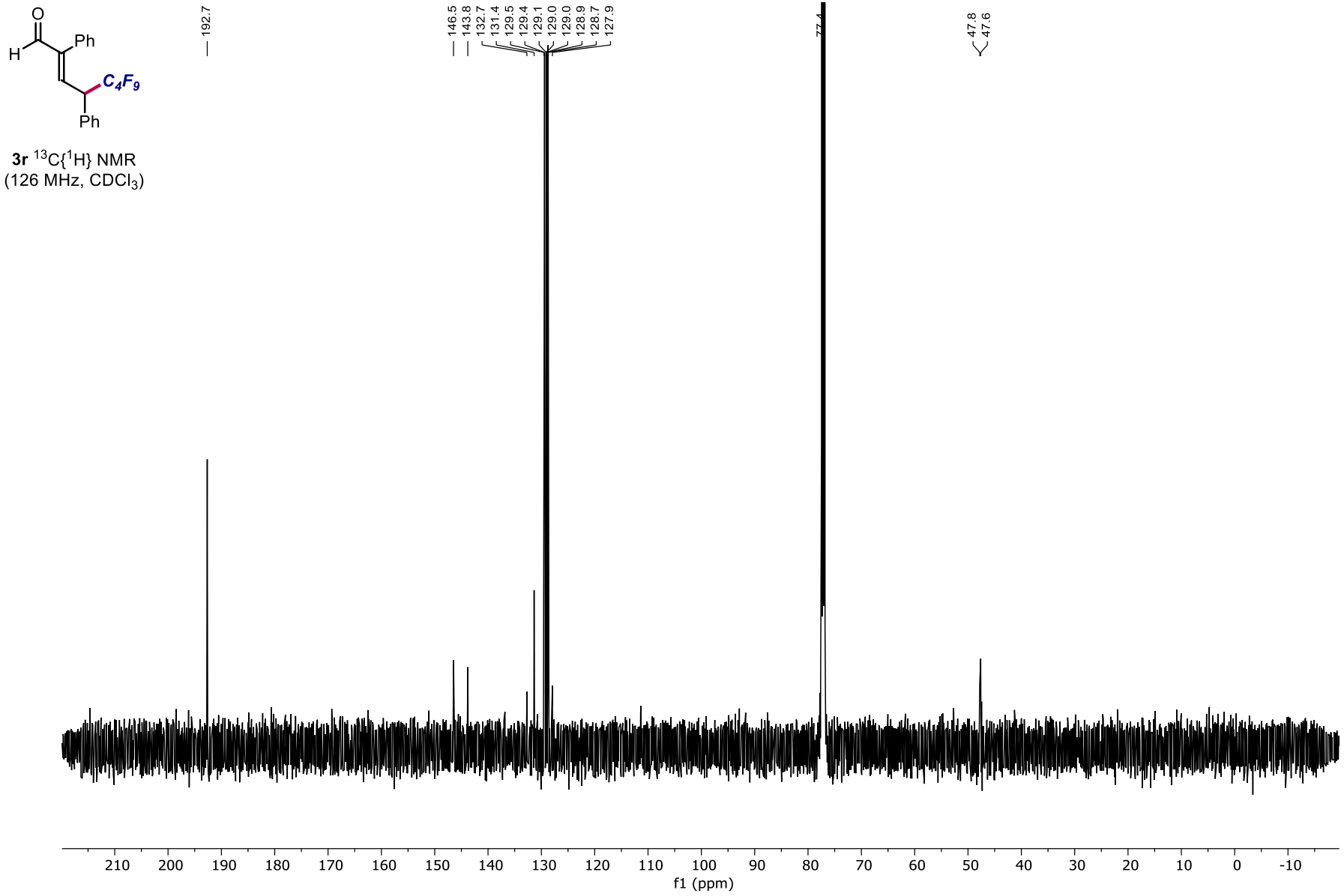
3q $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



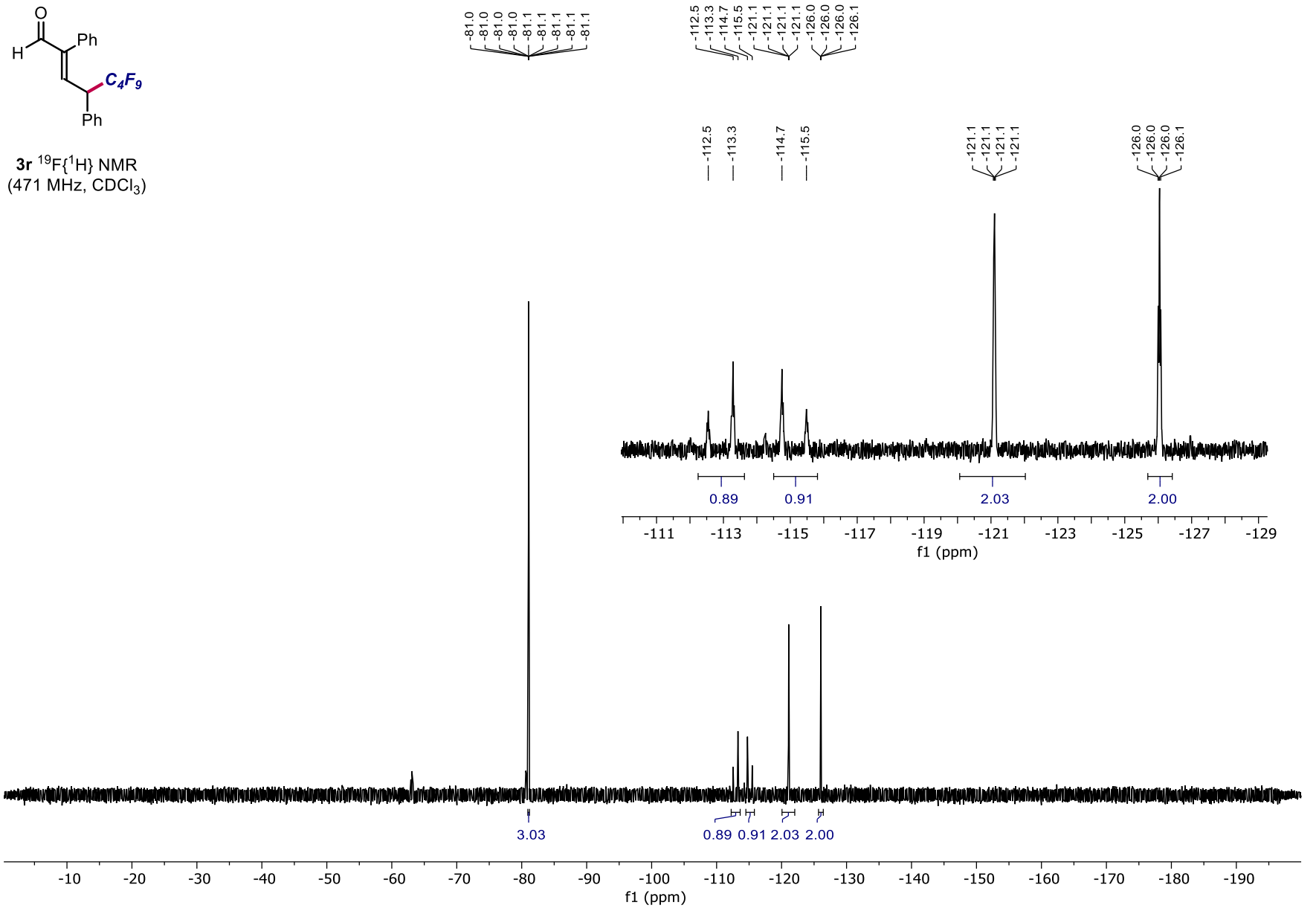
3q $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)



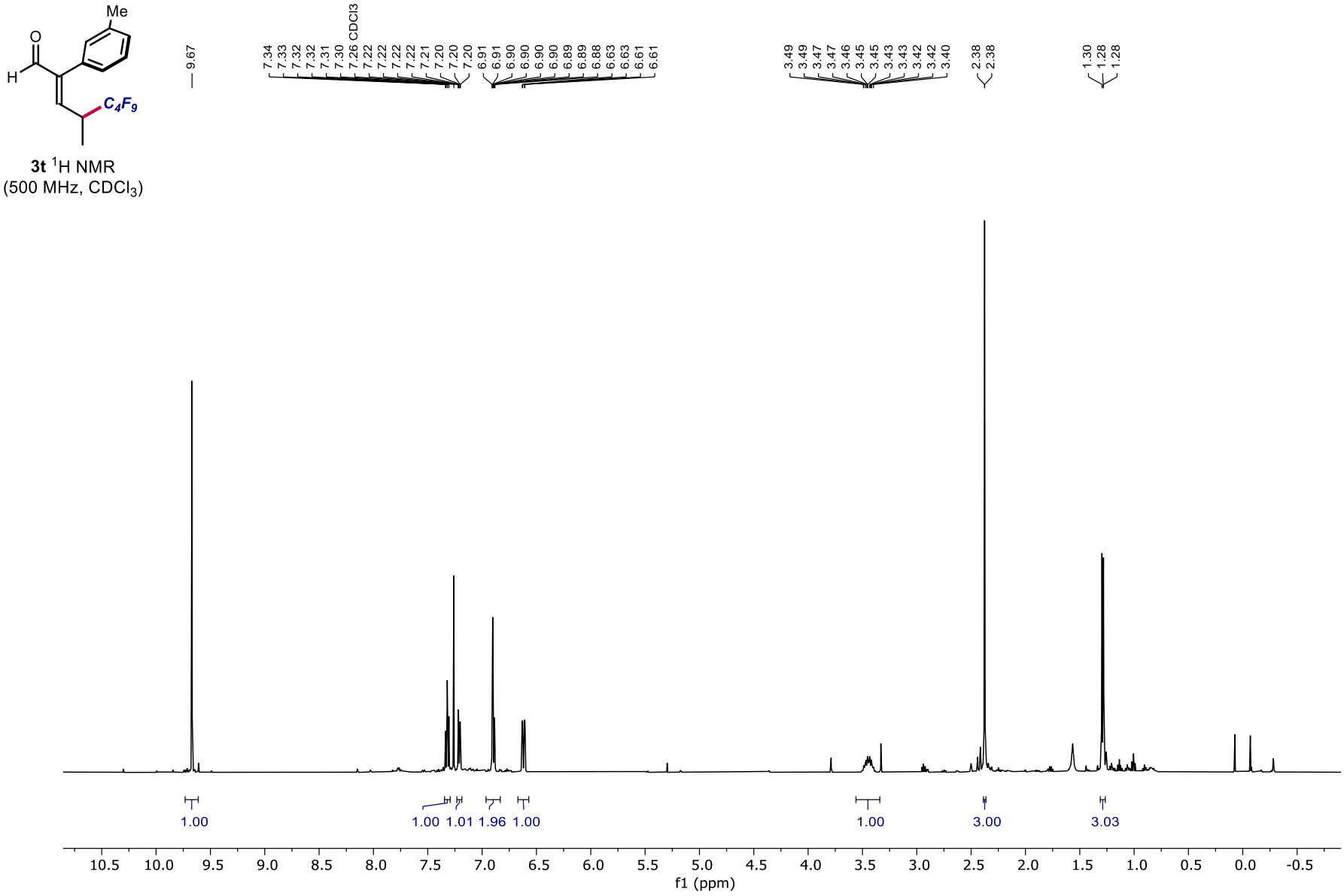
3r ^{1}H NMR
(500 MHz, $CDCl_3$)



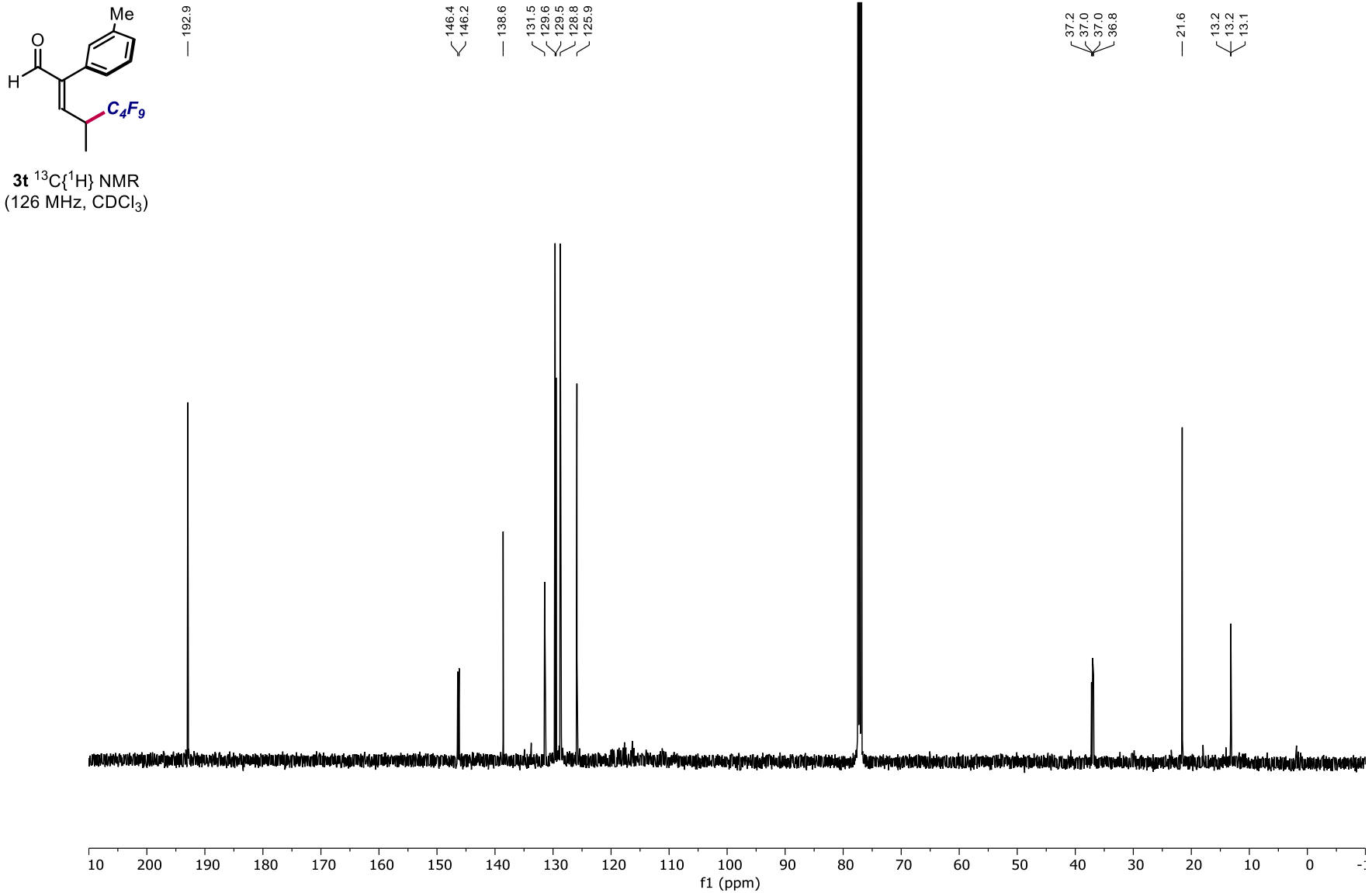
3r $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



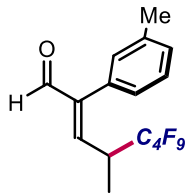
3r $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)



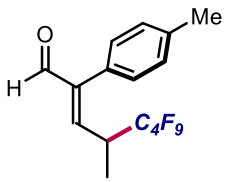
3t ^{1}H NMR
(500 MHz, $CDCl_3$)



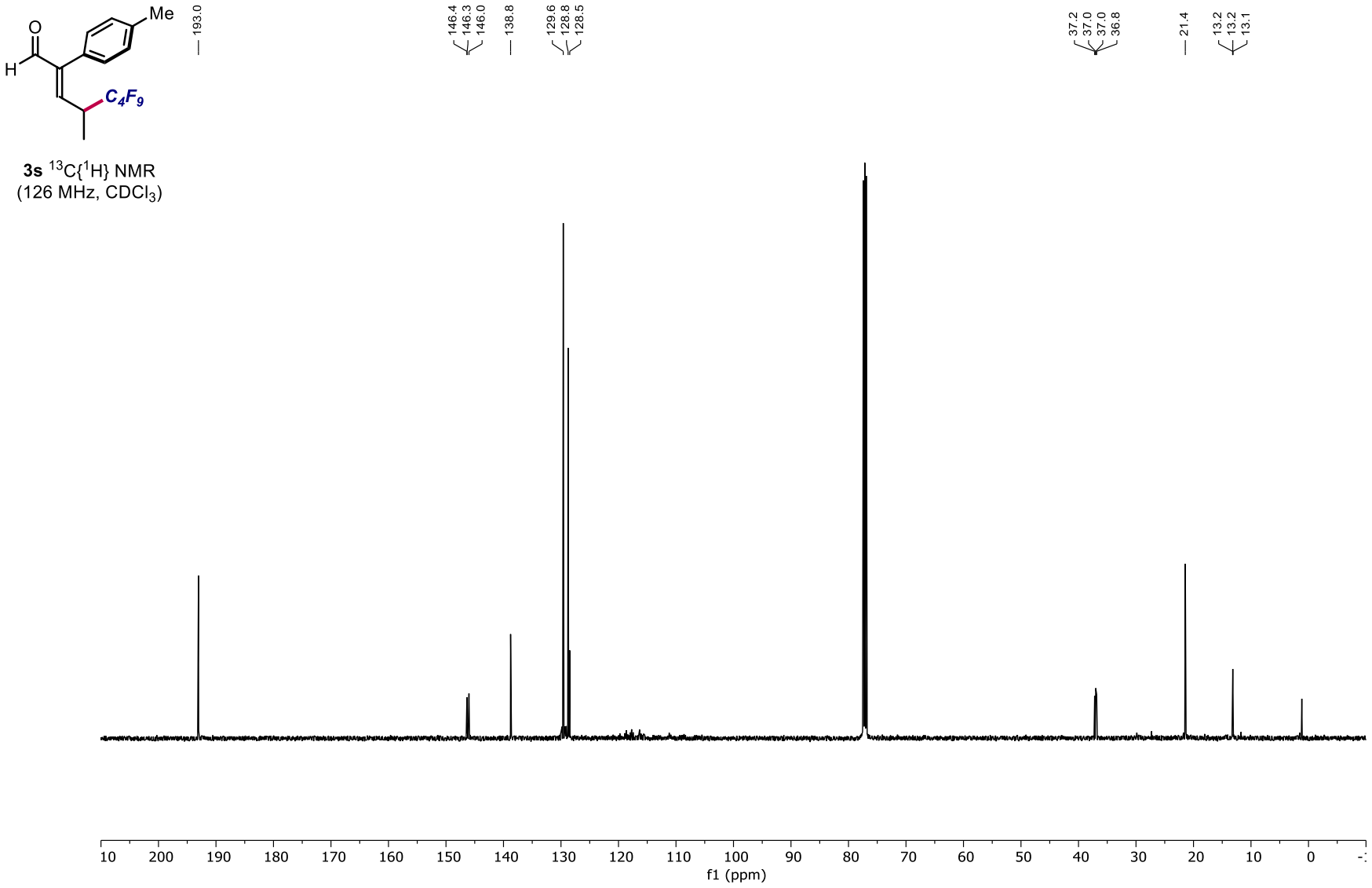
3t $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



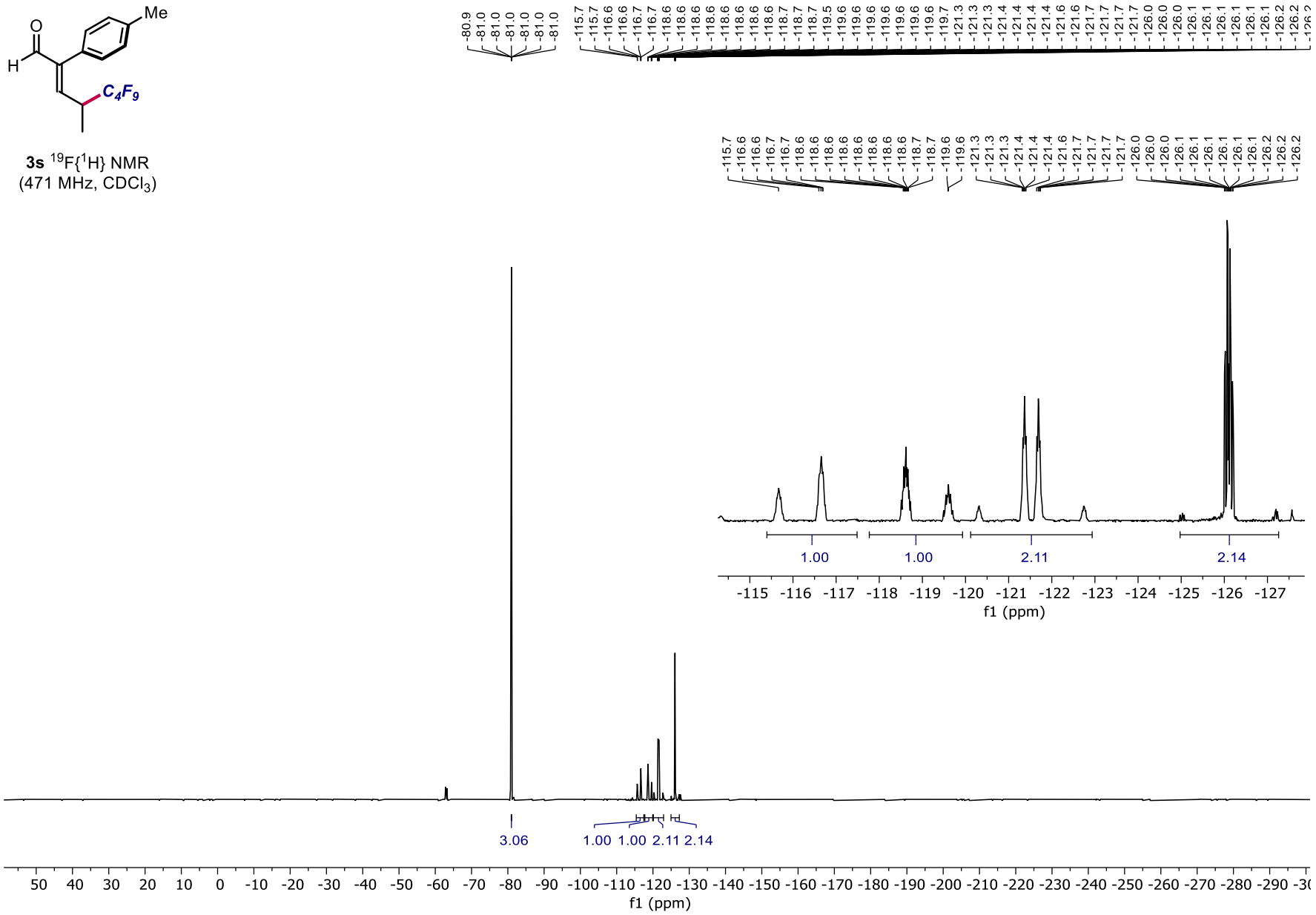
3t $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)

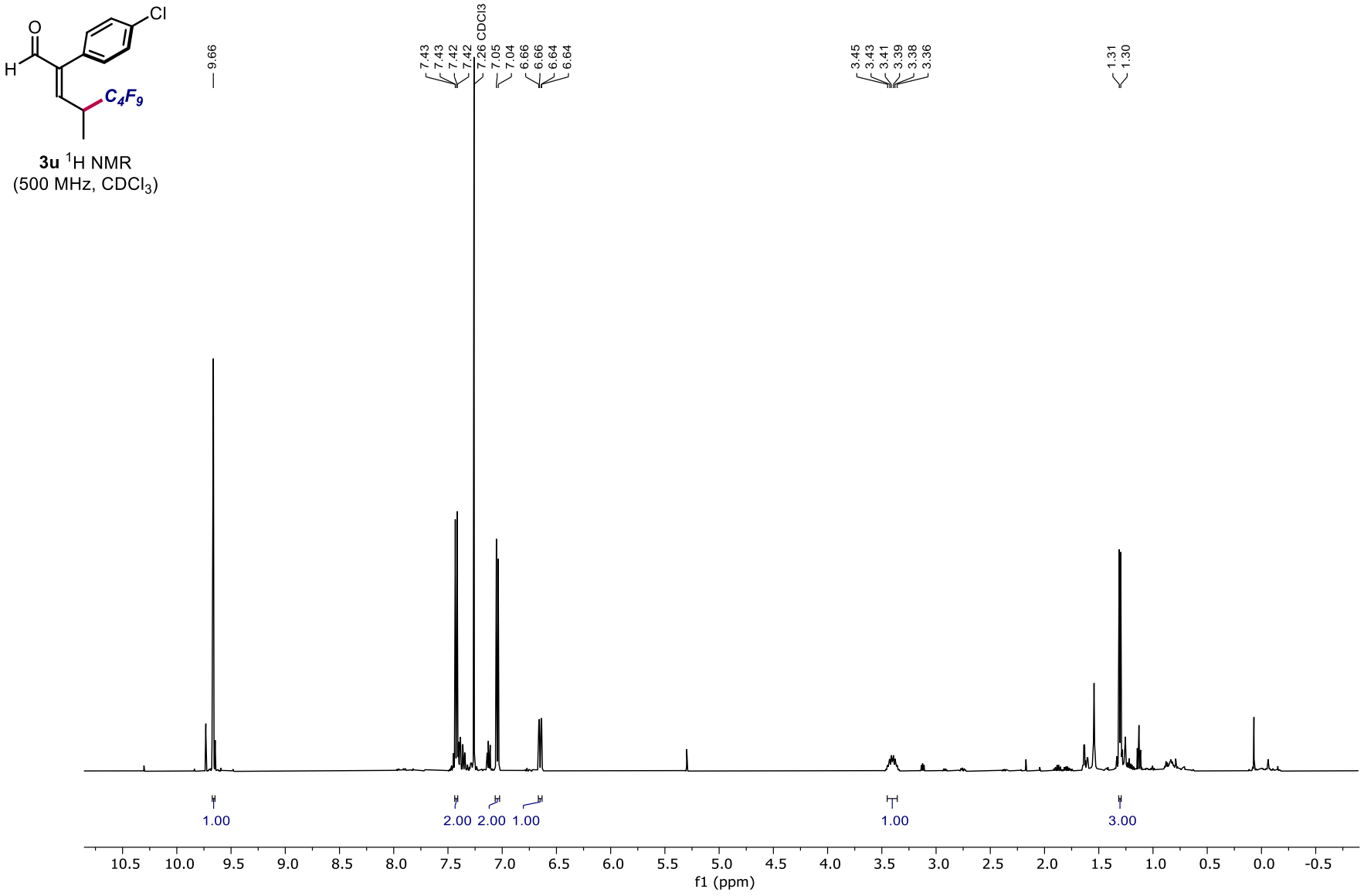


3s ^{1}H NMR
(500 MHz, $CDCl_3$)

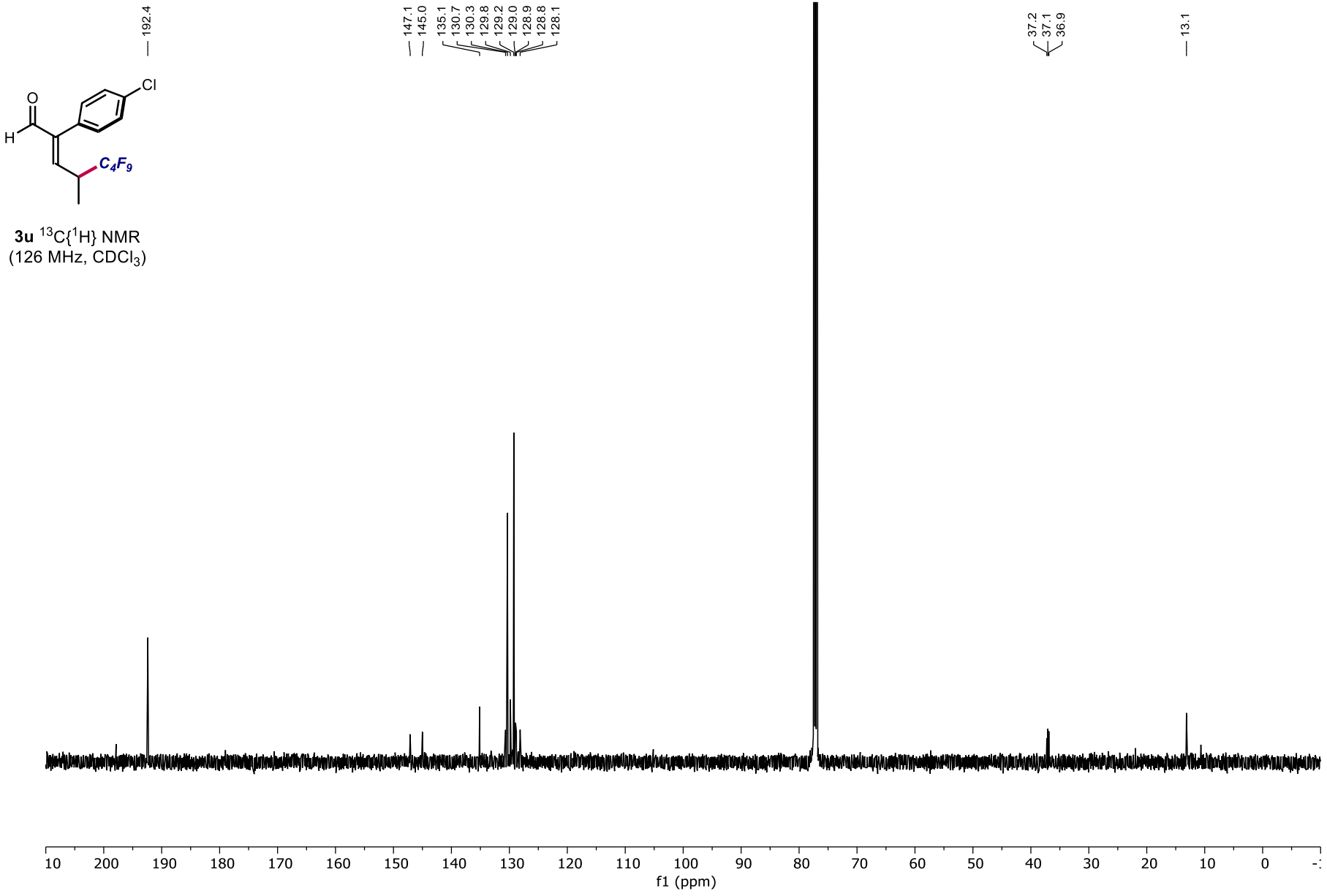


3s $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

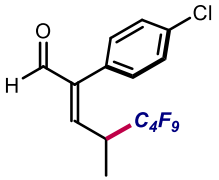

Me
O
H
C_4F_9
3s $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)
1.00
1.00
2.11
2.14
f1 (ppm)
3.06
1.00 1.00 2.11 2.14
f1 (ppm)



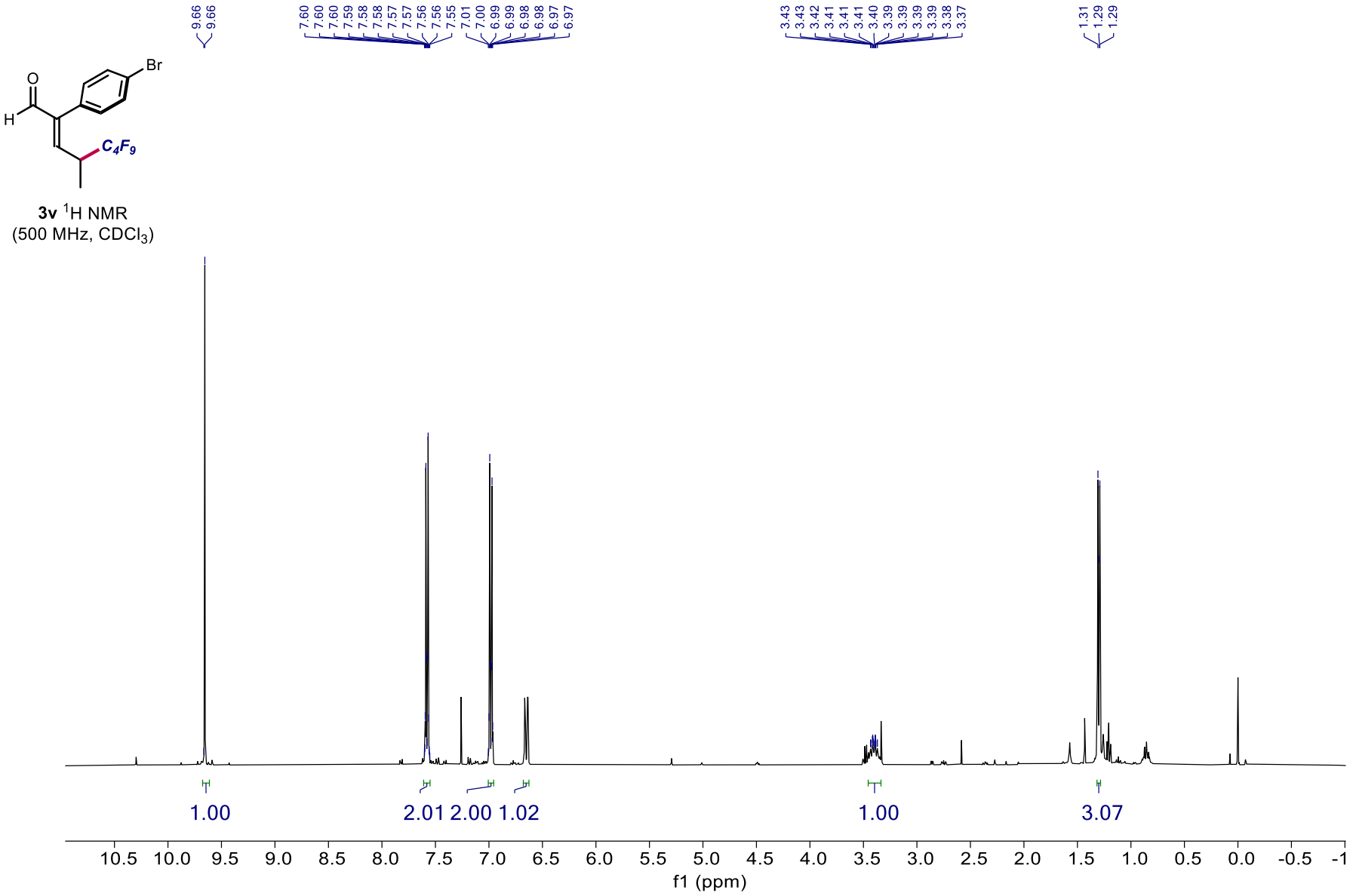
3u ^{1}H NMR
(500 MHz, $CDCl_3$)



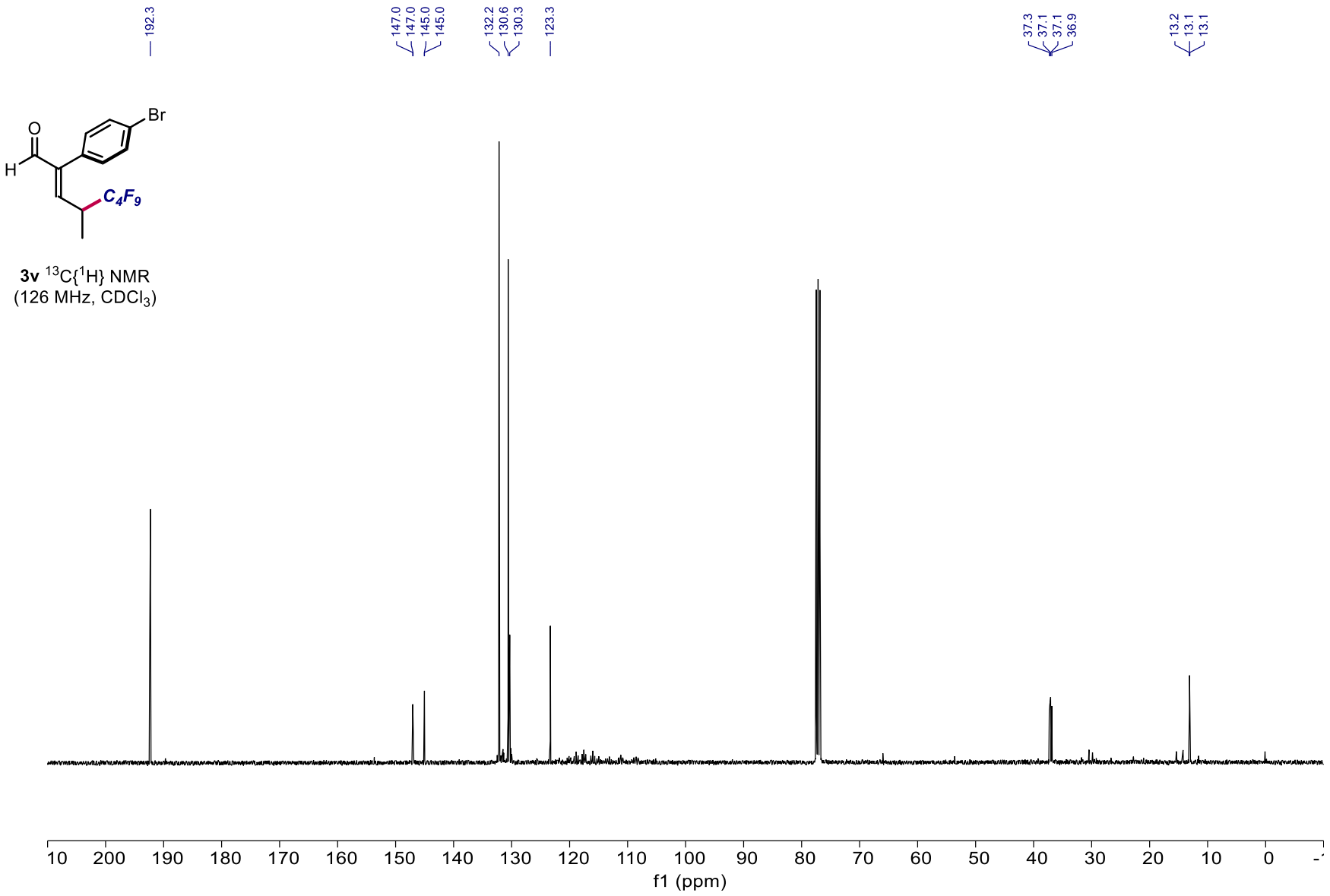
3u $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



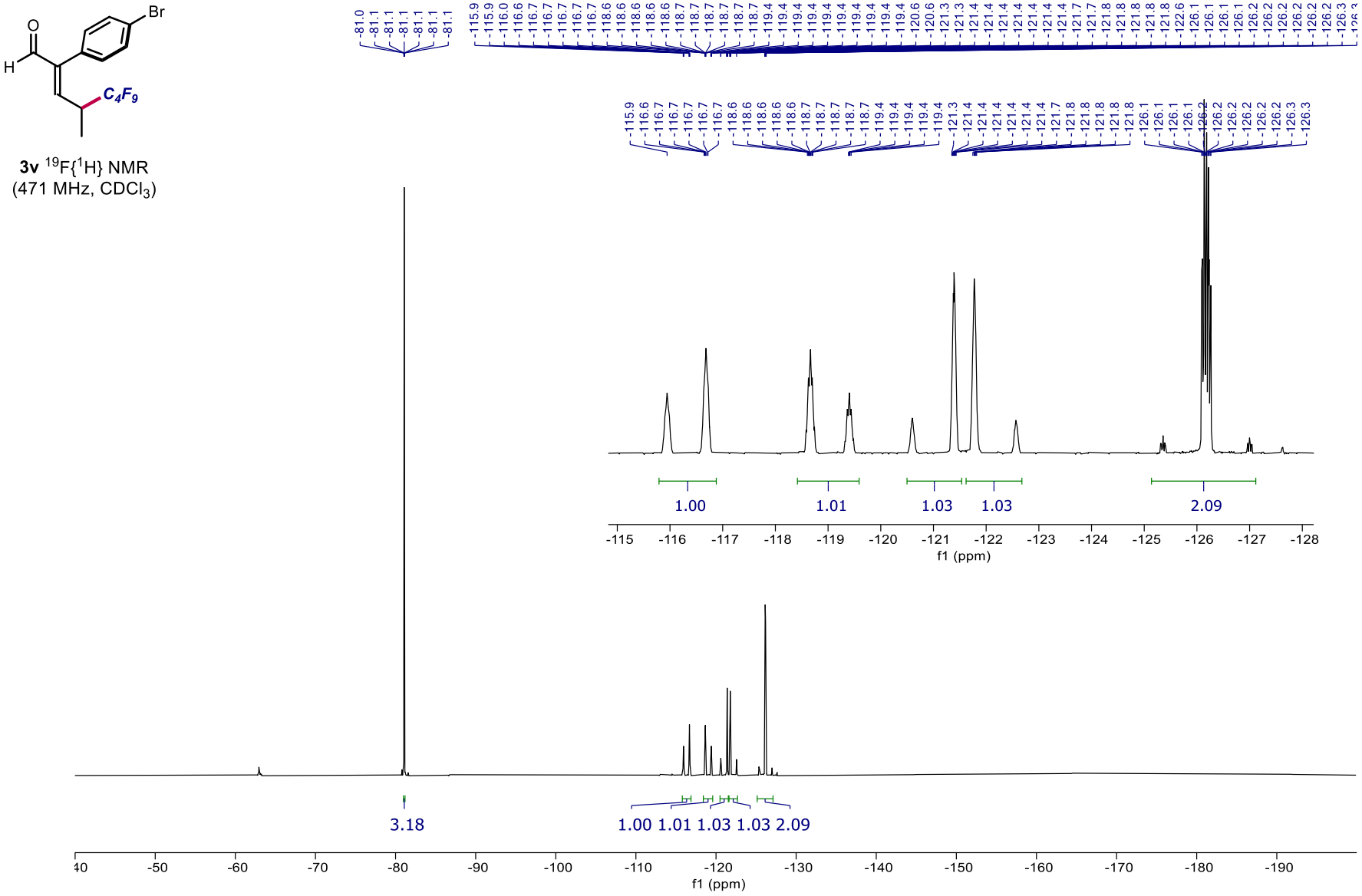
3u $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)

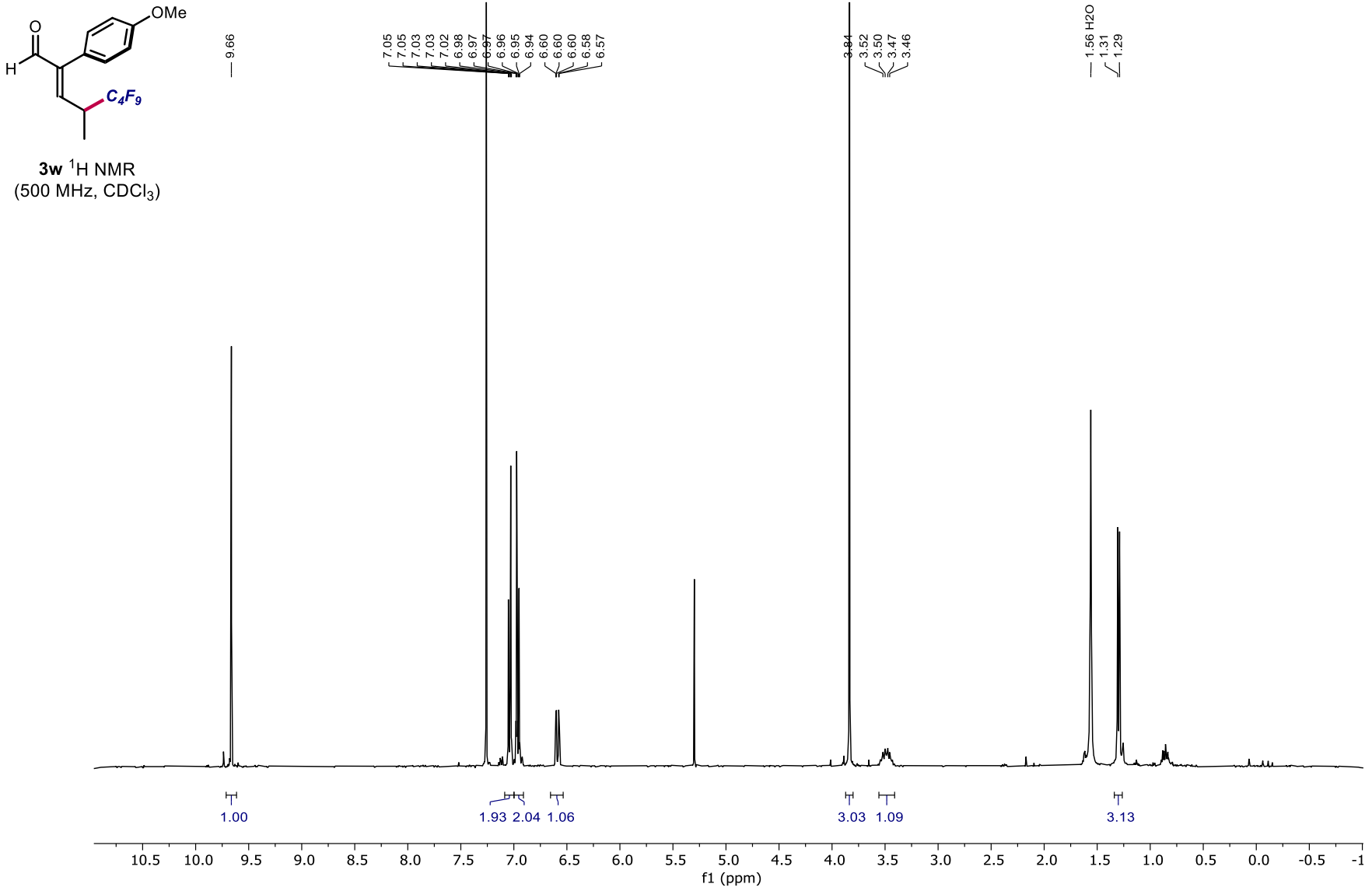


3v ^{1}H NMR
(500 MHz, $CDCl_3$)

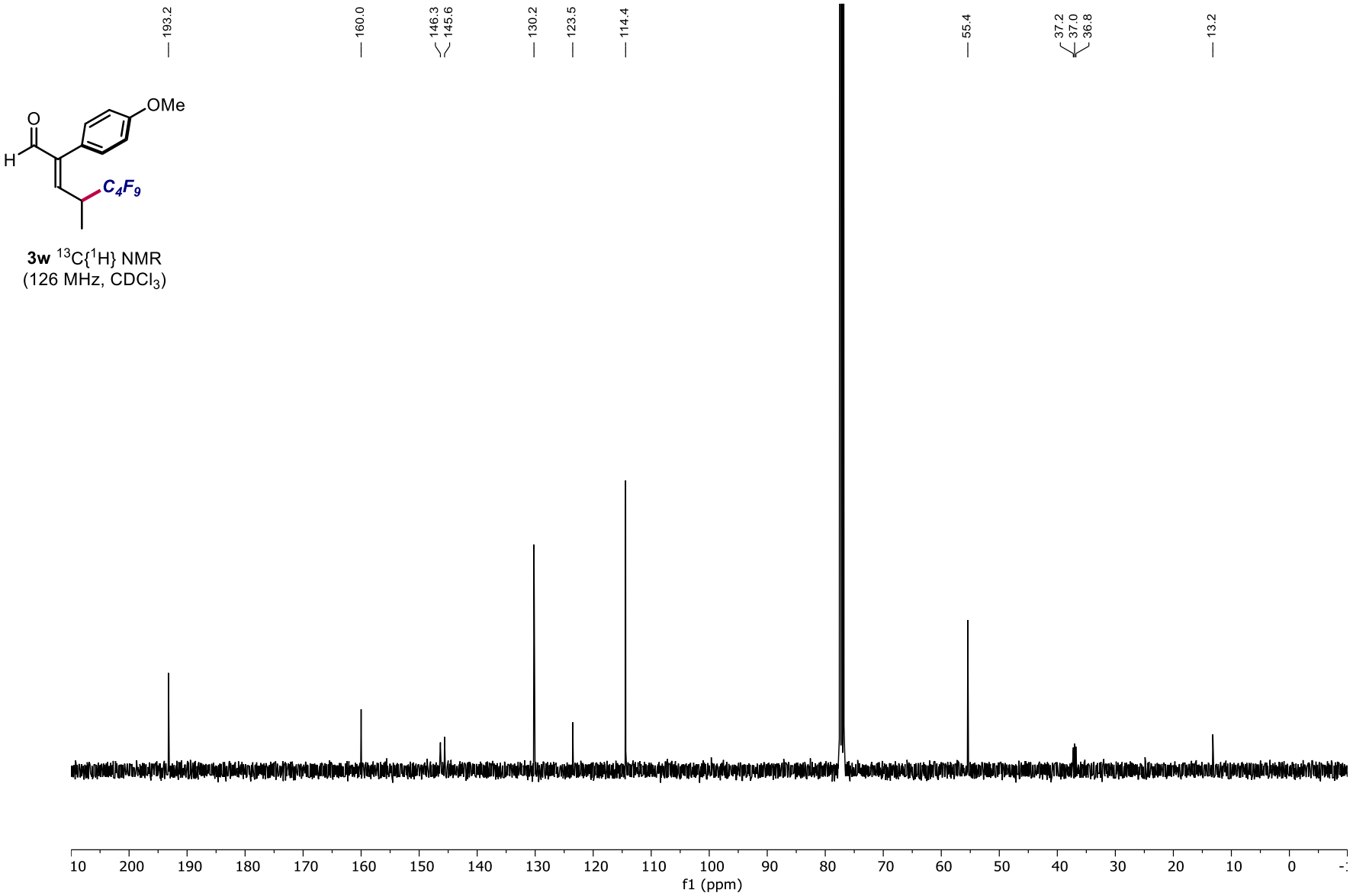


3v $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

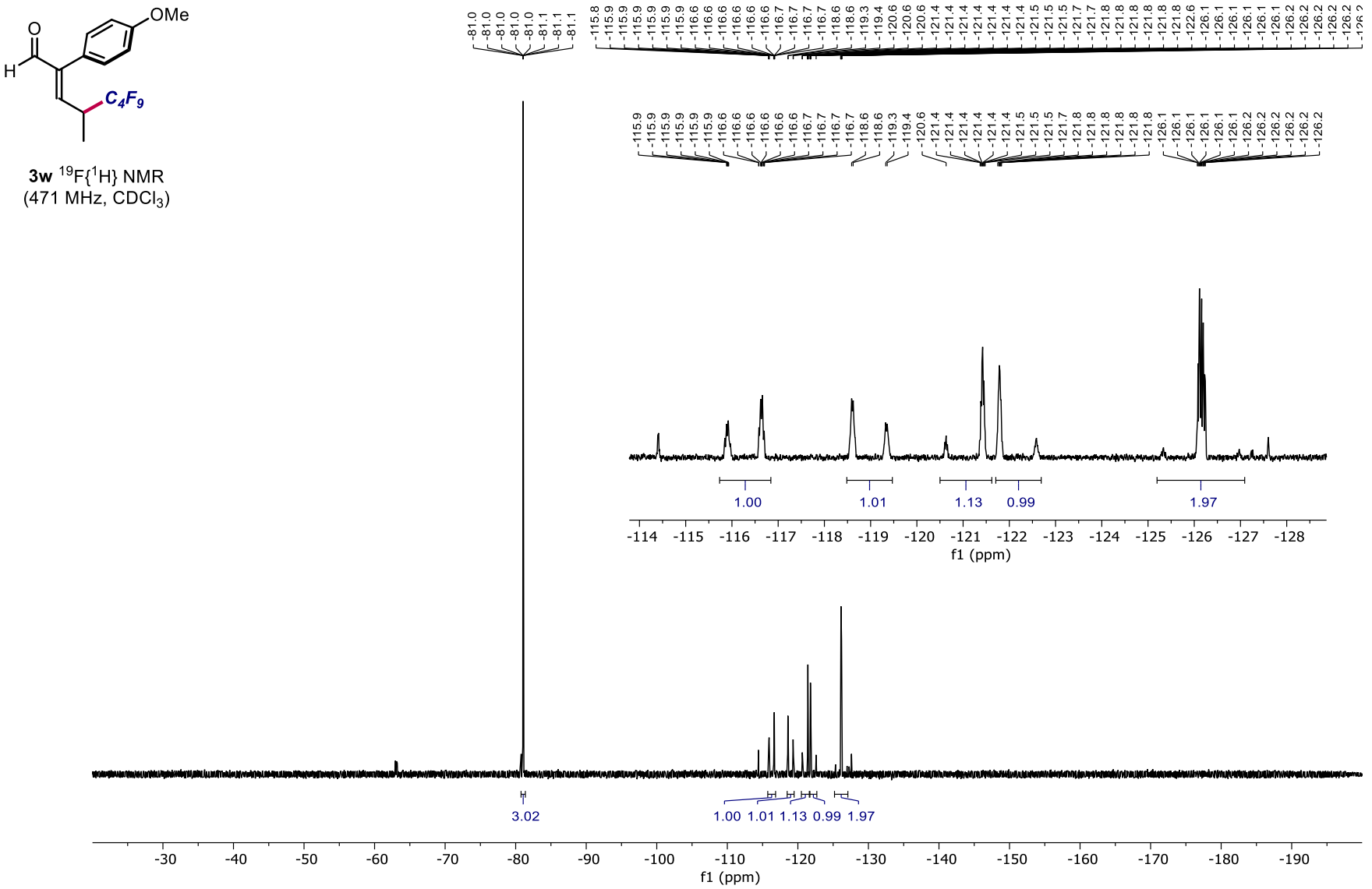

O
H
Br
C_4F_9
3v $^{19}F\{^1H\}$ NMR
(471 MHz, $CDCl_3$)
1.00
1.01
1.03
1.03
2.09
f1 (ppm)
3.18
1.00 1.01 1.03 1.03 2.09
f1 (ppm)



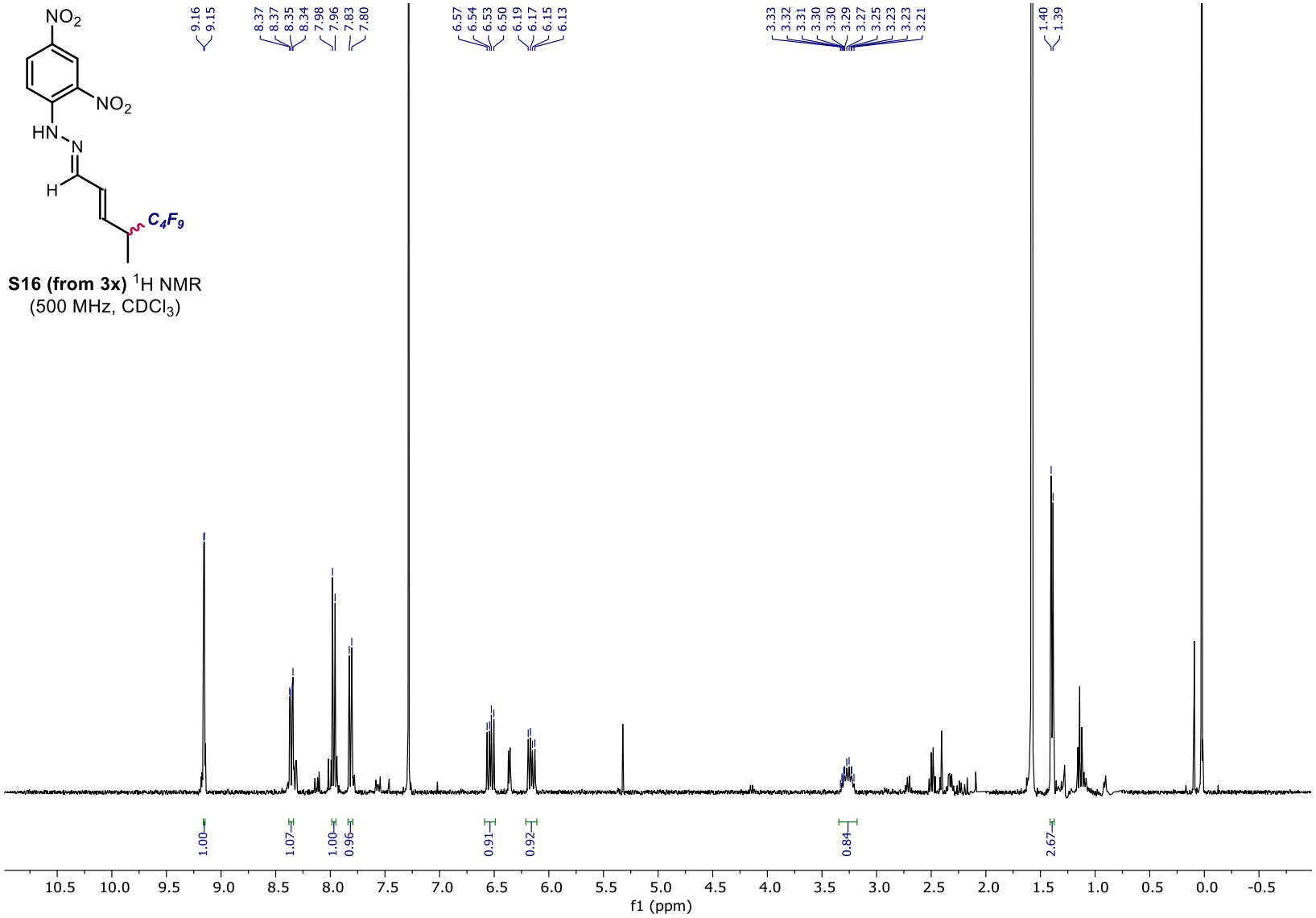
3w ^{1}H NMR
(500 MHz, $CDCl_3$)



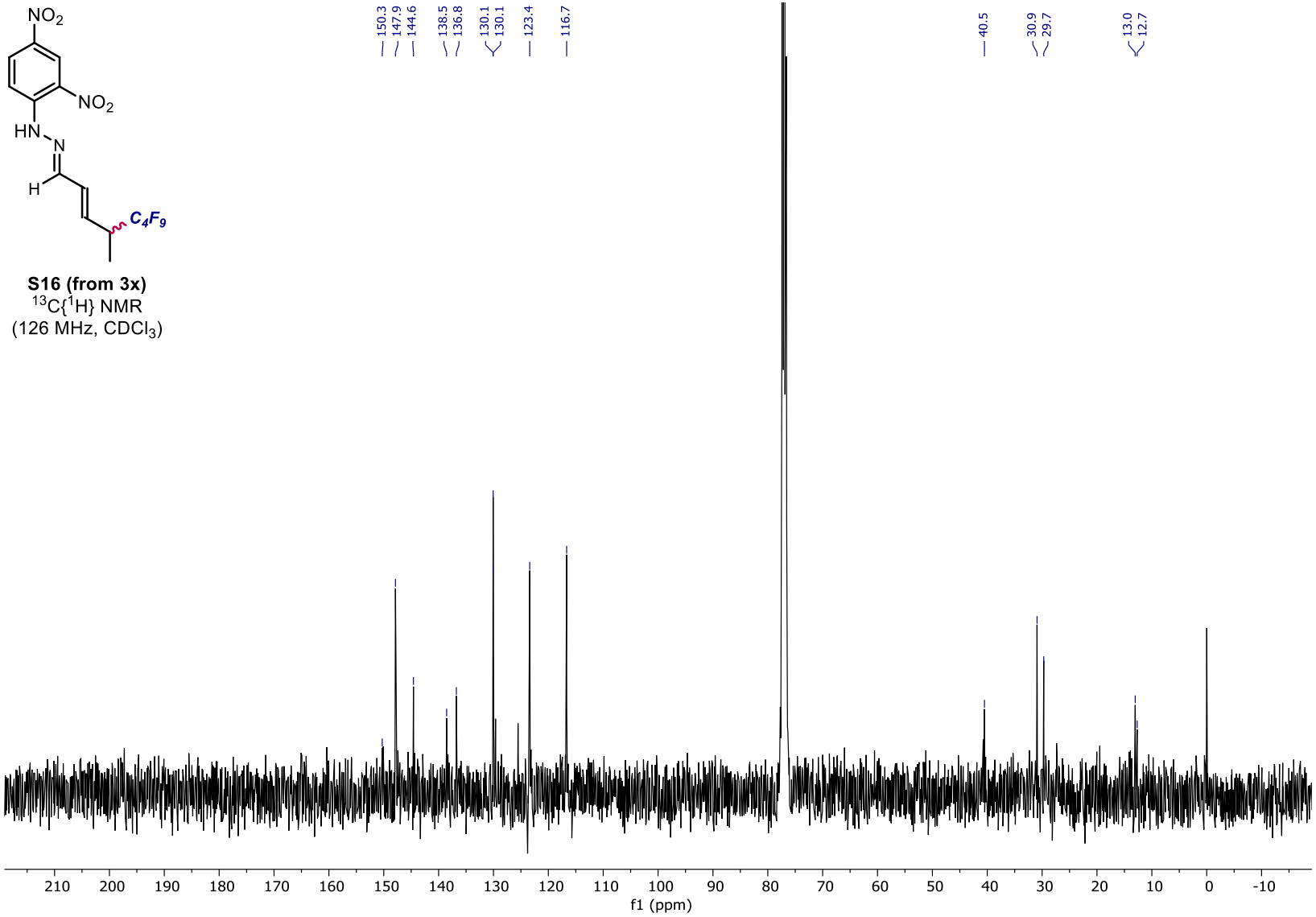
3w $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



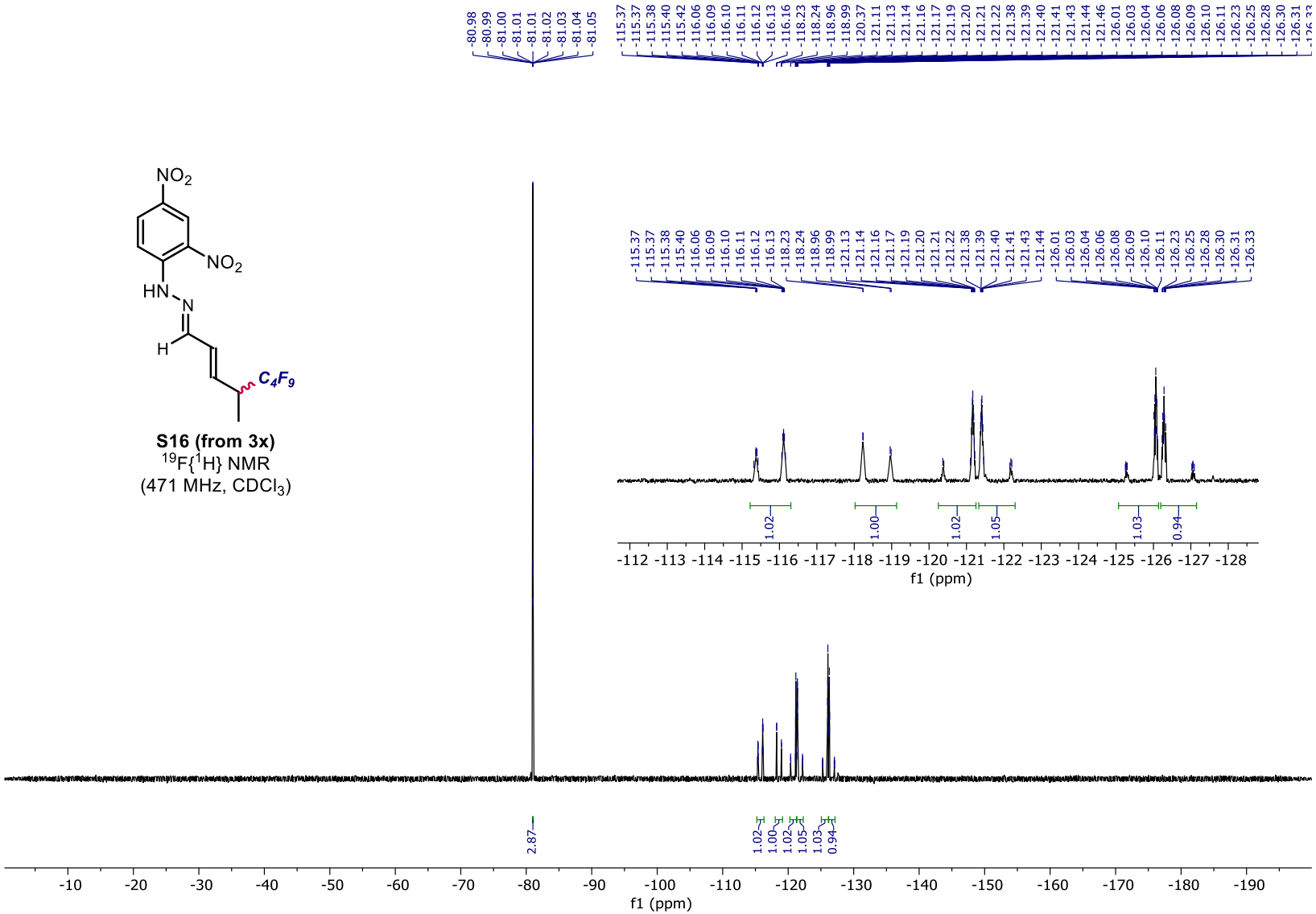
3w $^{19}F\{^{1}H\}$ NMR
(471 MHz, $CDCl_3$)

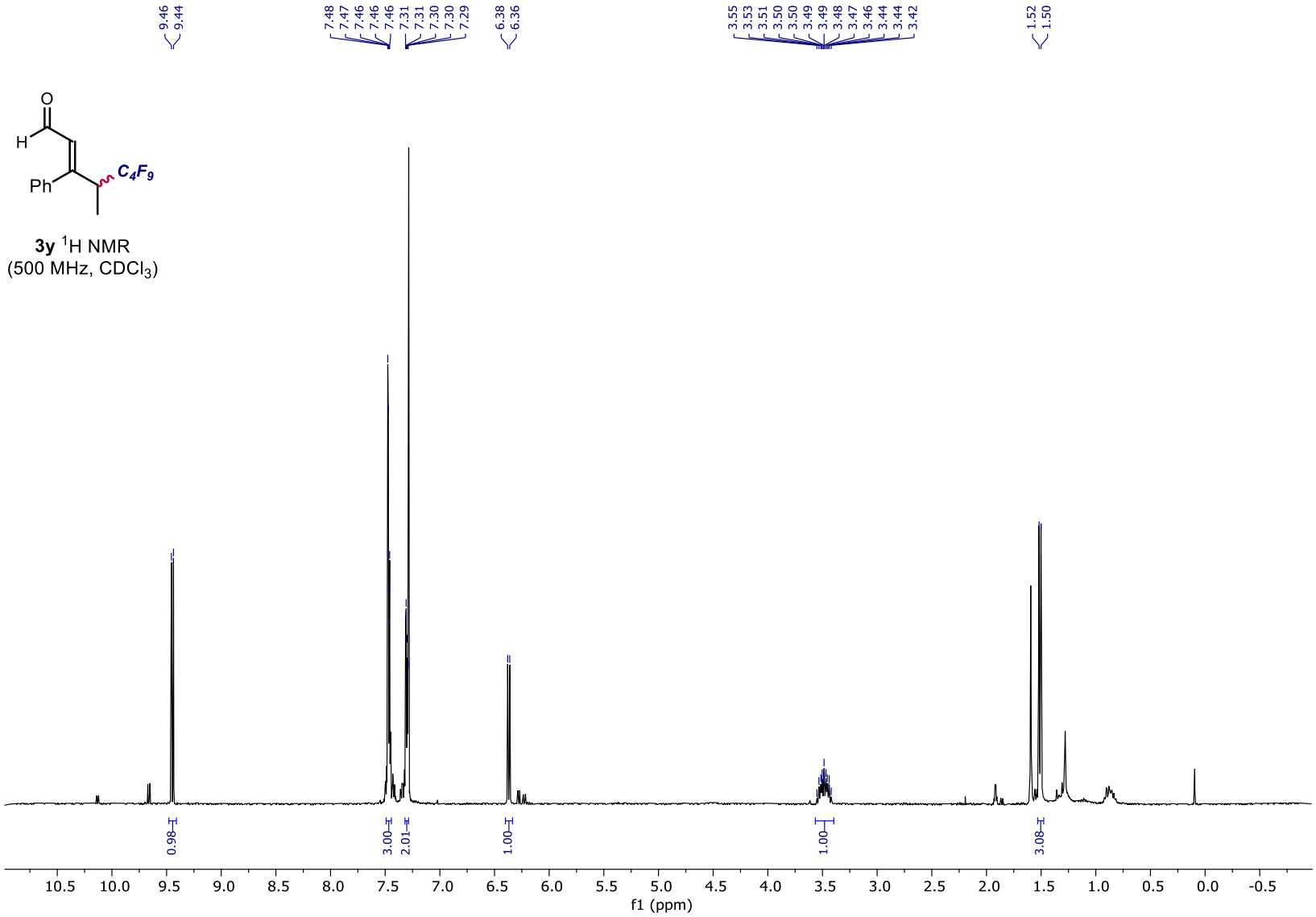


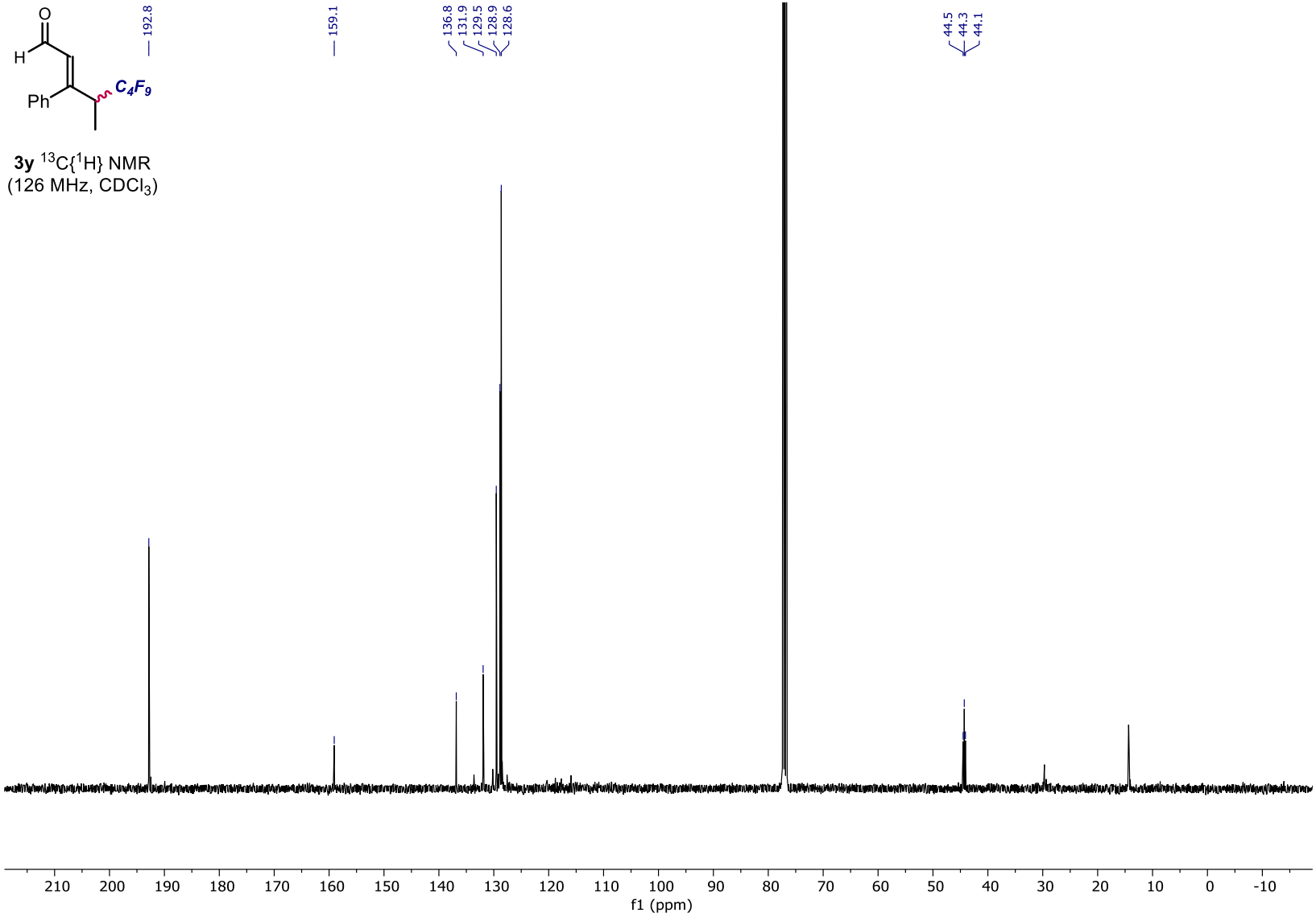
S16 (from 3x) ^{1}H NMR
(500 MHz, $CDCl_3$)



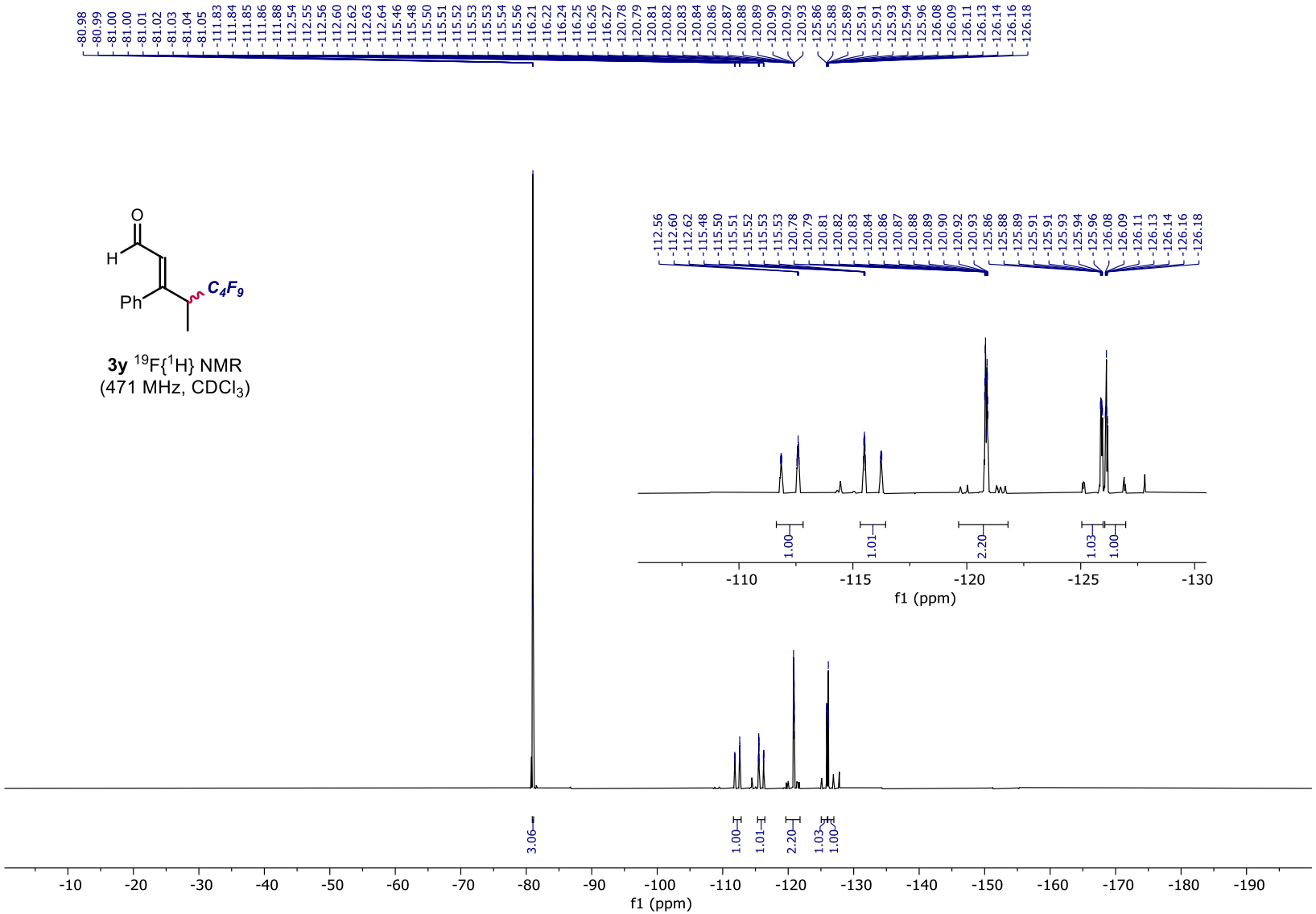
S16 (from 3x)
$^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

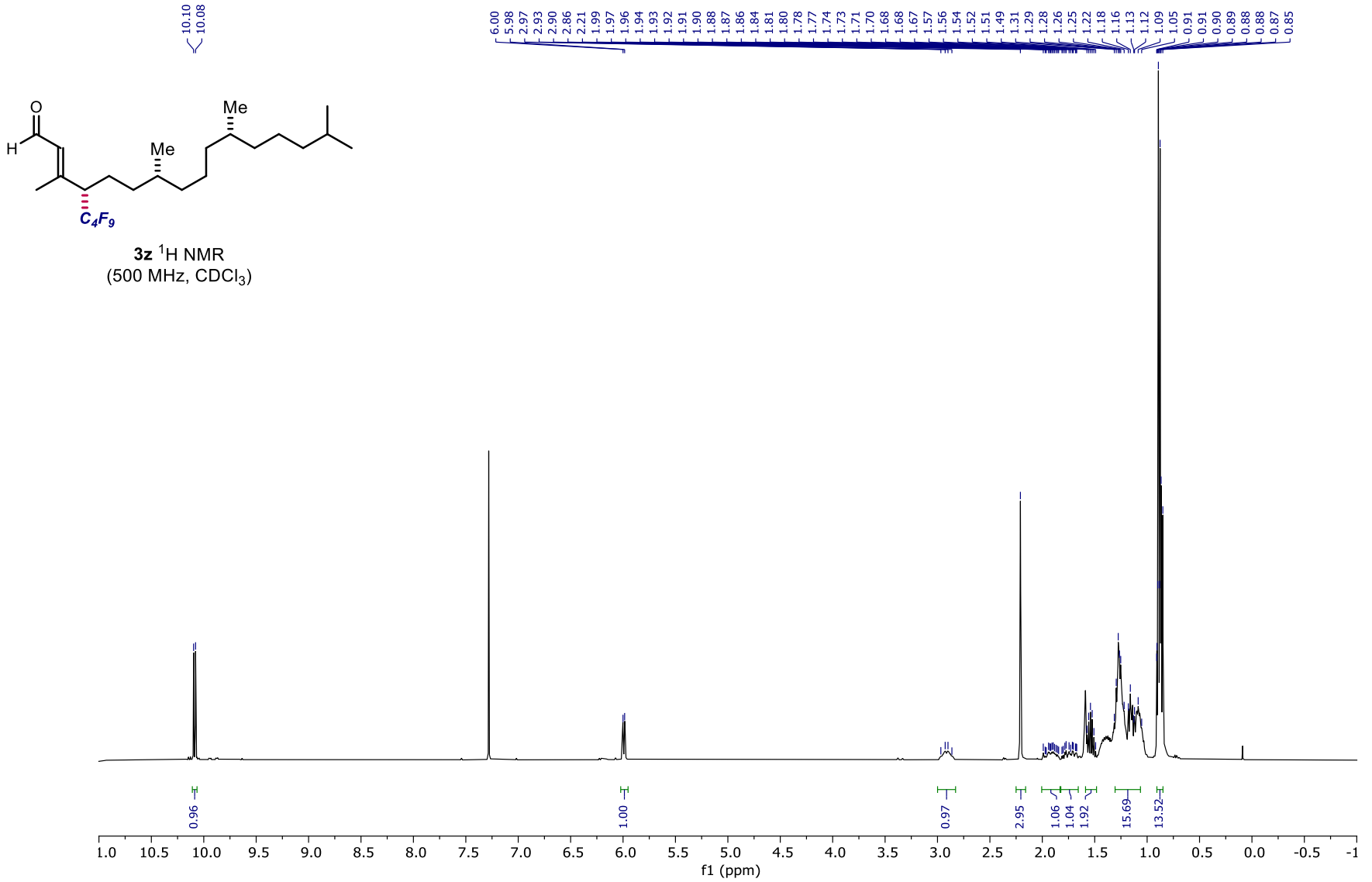

NO2
NO2
HN
N
H
C4F9
S16 (from 3x)
19F{1H} NMR
(471 MHz, CDCl3)
f1 (ppm)
f1 (ppm)


9.46
9.44
7.48
7.47
7.46
7.46
7.46
7.31
7.31
7.30
7.30
7.29
6.38
6.36
3.55
3.53
3.51
3.50
3.50
3.49
3.49
3.48
3.47
3.46
3.44
3.44
3.42
1.52
1.50
O
H
Ph
C4F9
3y 1H NMR
(500 MHz, CDCl3)
0.98
3.00
2.01
1.00
1.00
3.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

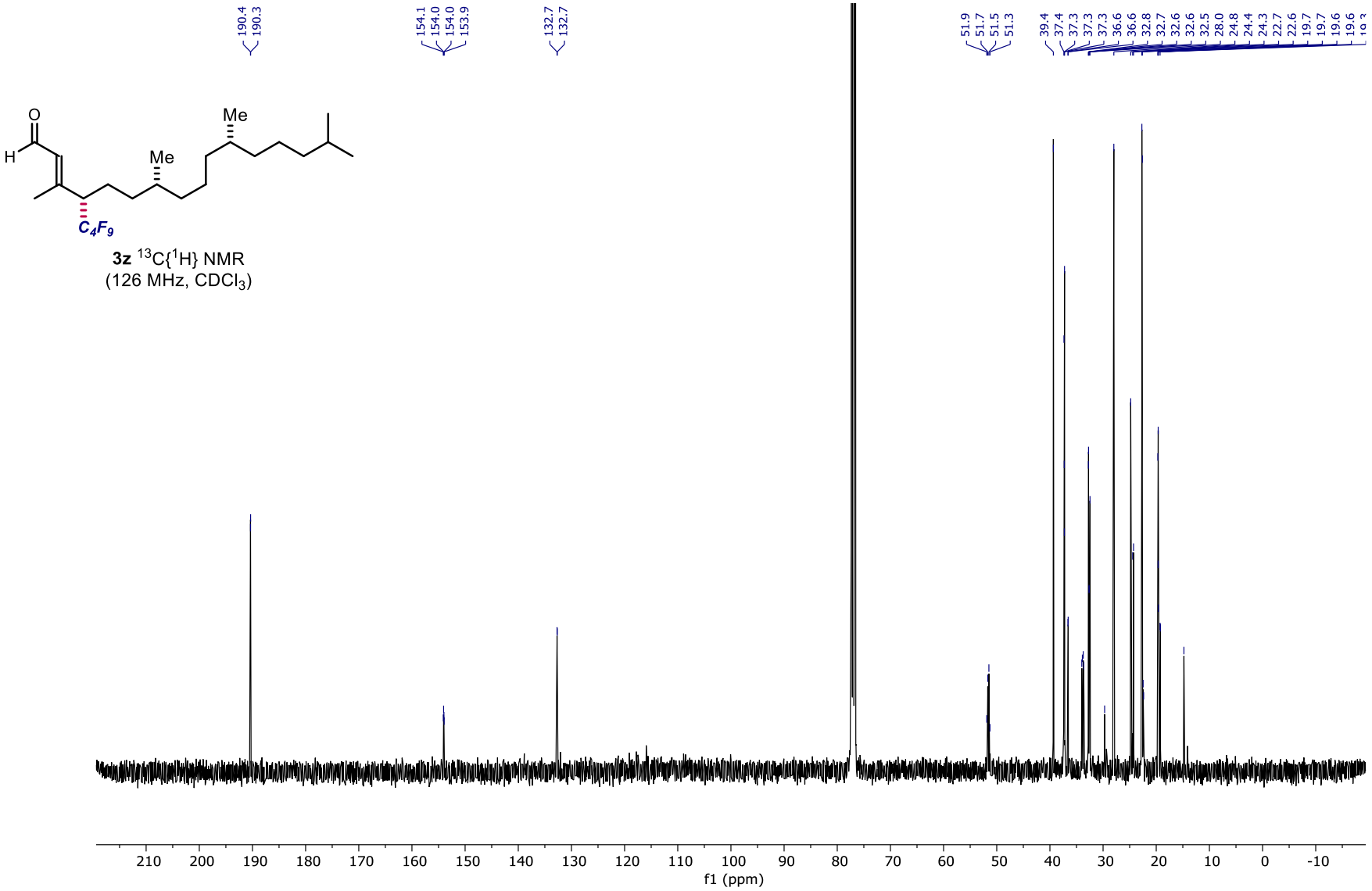


3y $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

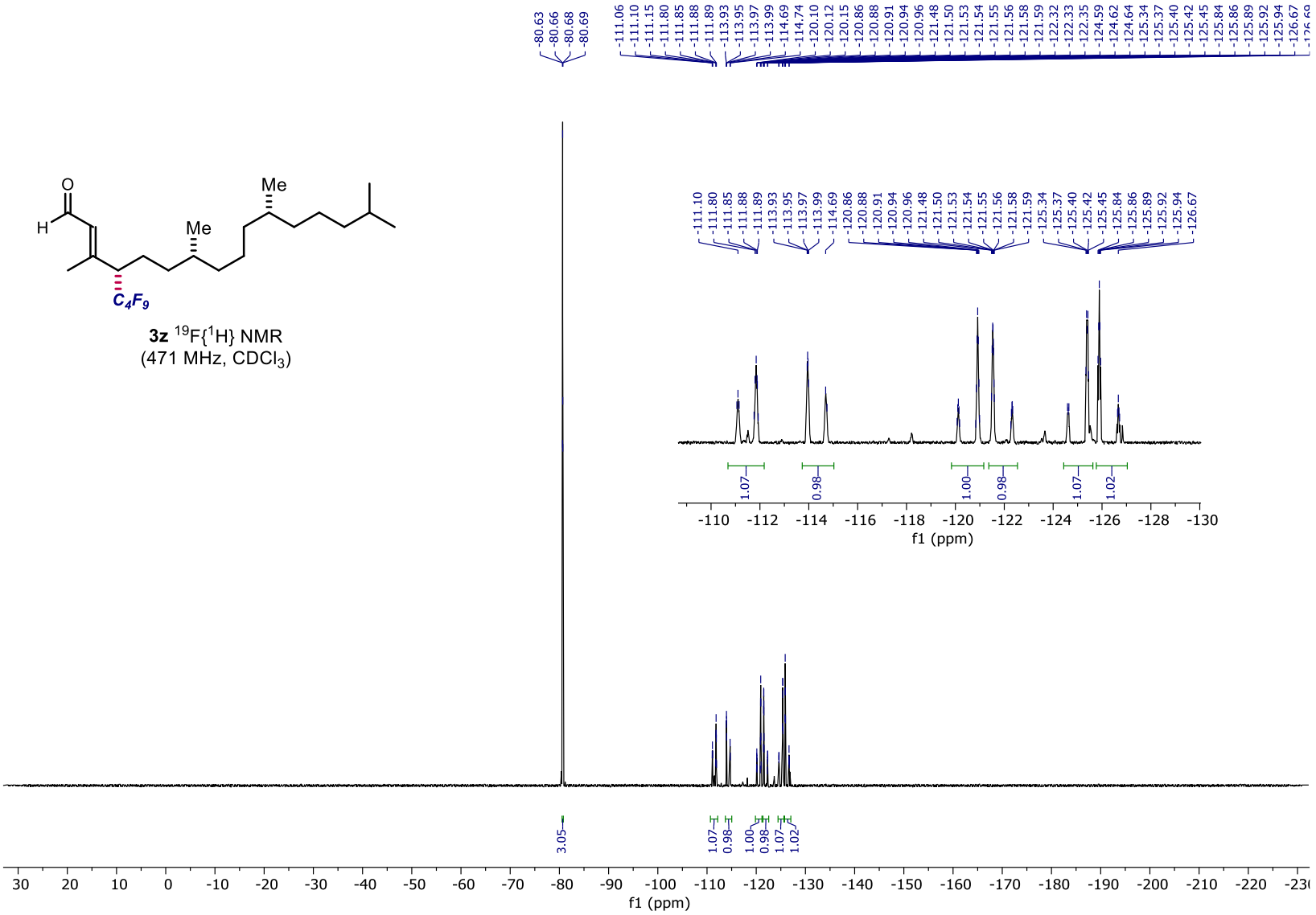

-80.98
-80.99
-81.00
-81.00
-81.01
-81.02
-81.03
-81.04
-81.05
-111.83
-111.84
-111.85
-111.86
-111.88
-112.54
-112.55
-112.56
-112.60
-112.62
-112.63
-112.64
-115.46
-115.48
-115.50
-115.51
-115.52
-115.53
-115.53
-115.54
-115.56
-116.21
-116.22
-116.24
-116.25
-116.26
-116.27
-120.78
-120.79
-120.81
-120.82
-120.83
-120.84
-120.86
-120.87
-120.88
-120.89
-120.90
-120.92
-120.93
-125.86
-125.88
-125.89
-125.91
-125.91
-125.93
-125.94
-125.96
-126.08
-126.09
-126.11
-126.13
-126.14
-126.16
-126.18
O
H
Ph
C4F9
3y 19F{1H} NMR
(471 MHz, CDCl3)
-112.56
-112.60
-112.62
-115.48
-115.50
-115.51
-115.52
-115.53
-115.53
-120.78
-120.79
-120.81
-120.82
-120.83
-120.84
-120.86
-120.87
-120.88
-120.89
-120.90
-120.92
-120.93
-125.86
-125.88
-125.89
-125.91
-125.91
-125.93
-125.94
-125.96
-126.08
-126.09
-126.11
-126.13
-126.14
-126.16
-126.18
1.00
1.01
2.20
1.03
1.00
-110
-115
-120
-125
-130
f1 (ppm)
3.06
1.00
1.01
2.20
1.03
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)



3z ^{1}H NMR
(500 MHz, $CDCl_3$)

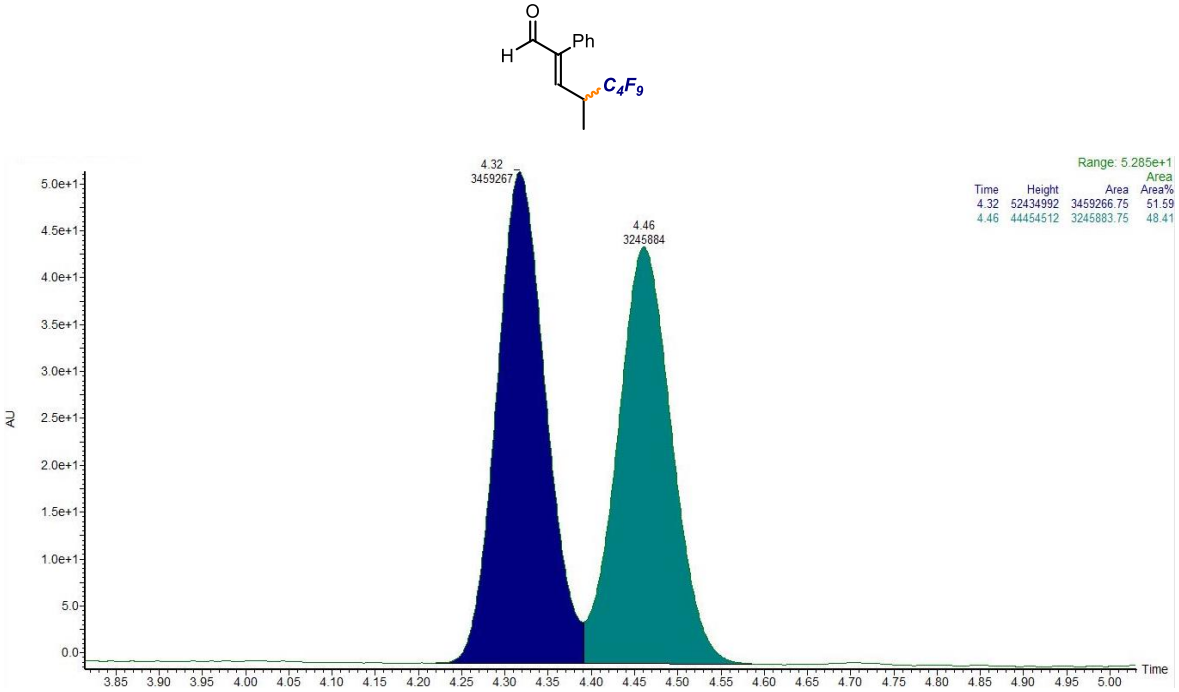


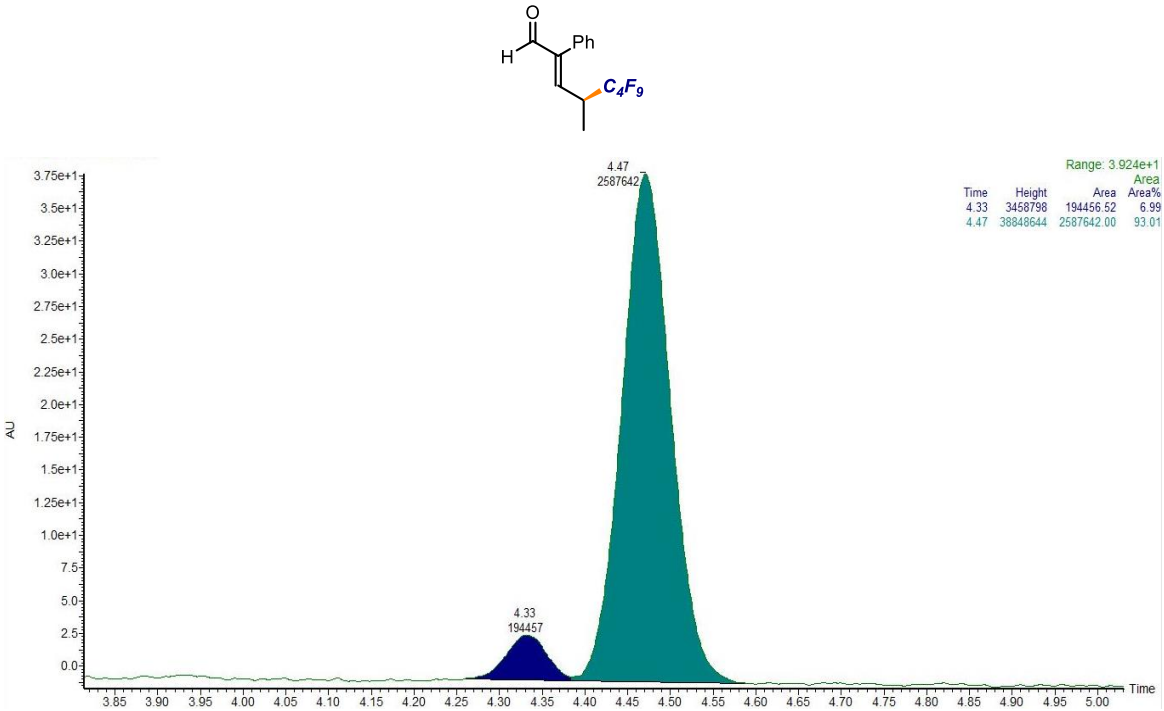
3z $^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)


O
H
Me
Me
C4F9
3z 19F{1H} NMR
(471 MHz, CDCl3)
f1 (ppm)

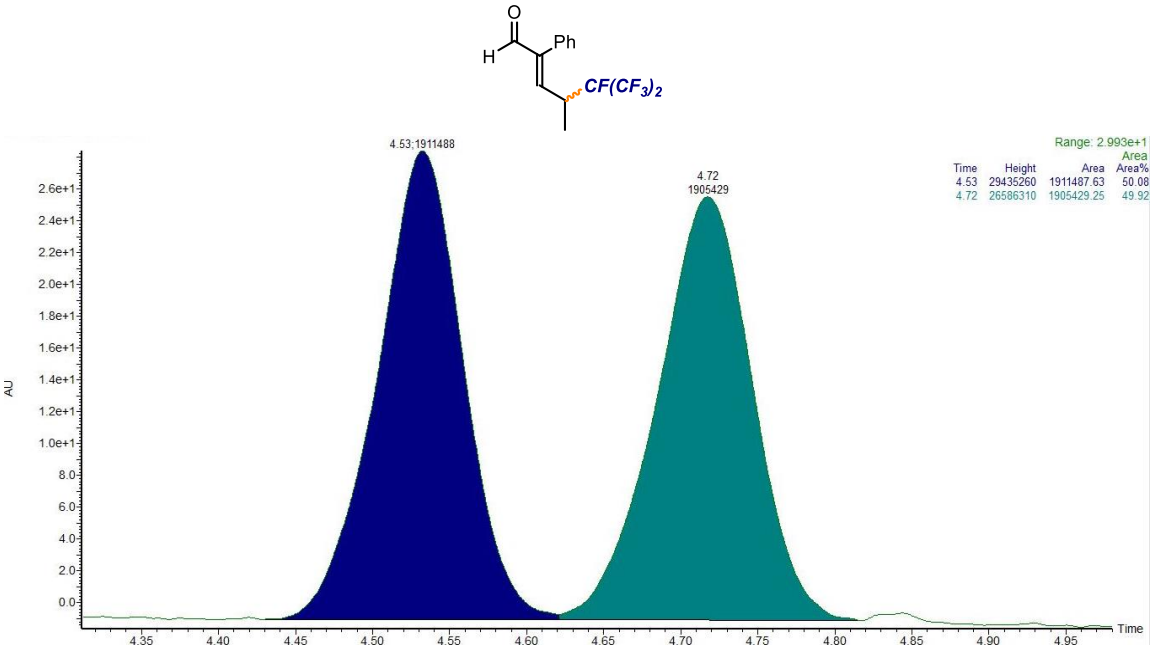
K. UPC^2 Traces

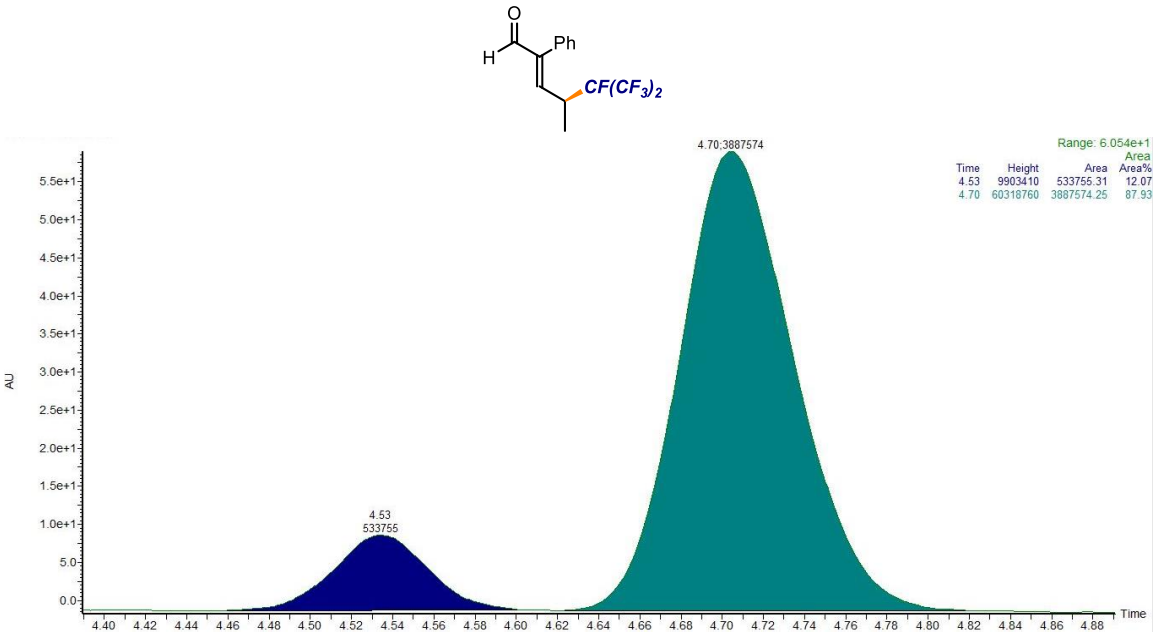
3a - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm; τ_{minor} = 4.3 min, τ_{major} = 4.5 min), 93:7 e.r.



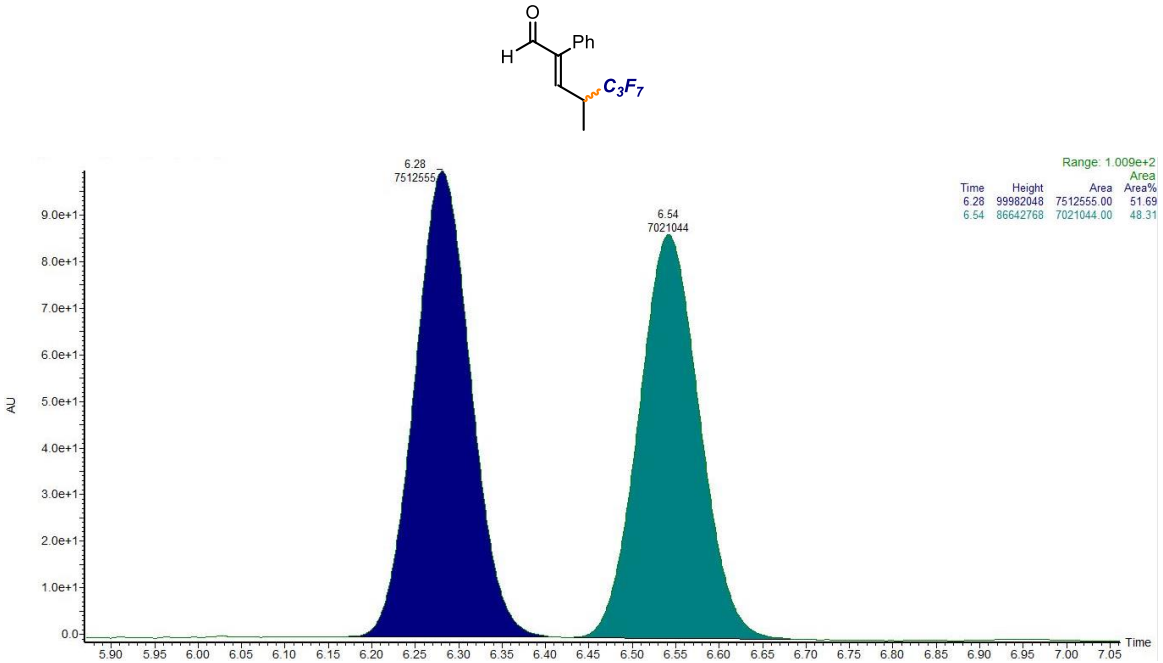


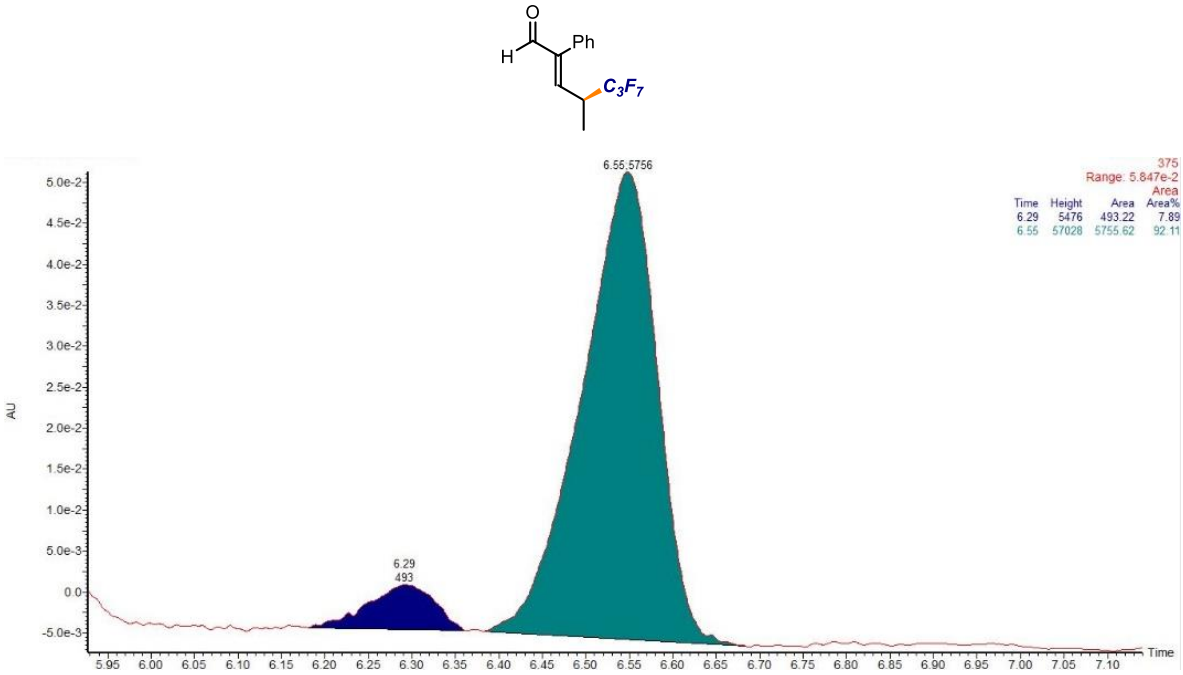
3b - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 4.5 min, τ_{major} = 4.7 min), 88:12 er.



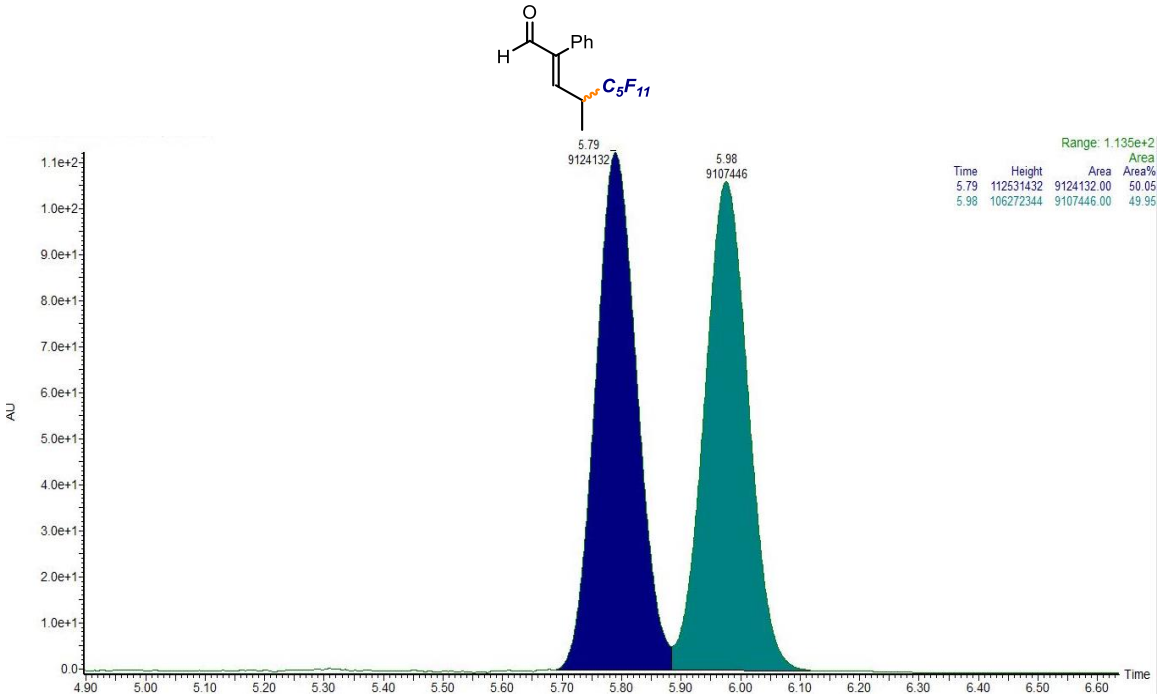


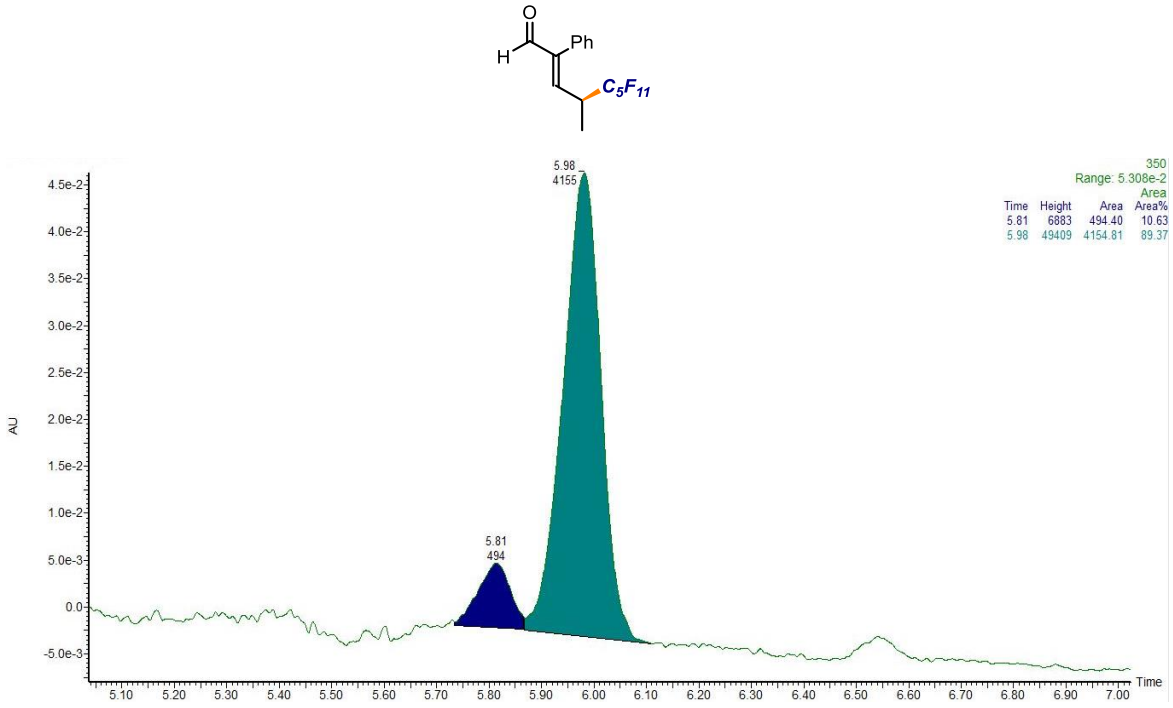
3c - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 375 nm: τ_{minor} = 6.3 min, τ_{major} = 6.6 min), 89:11 er.



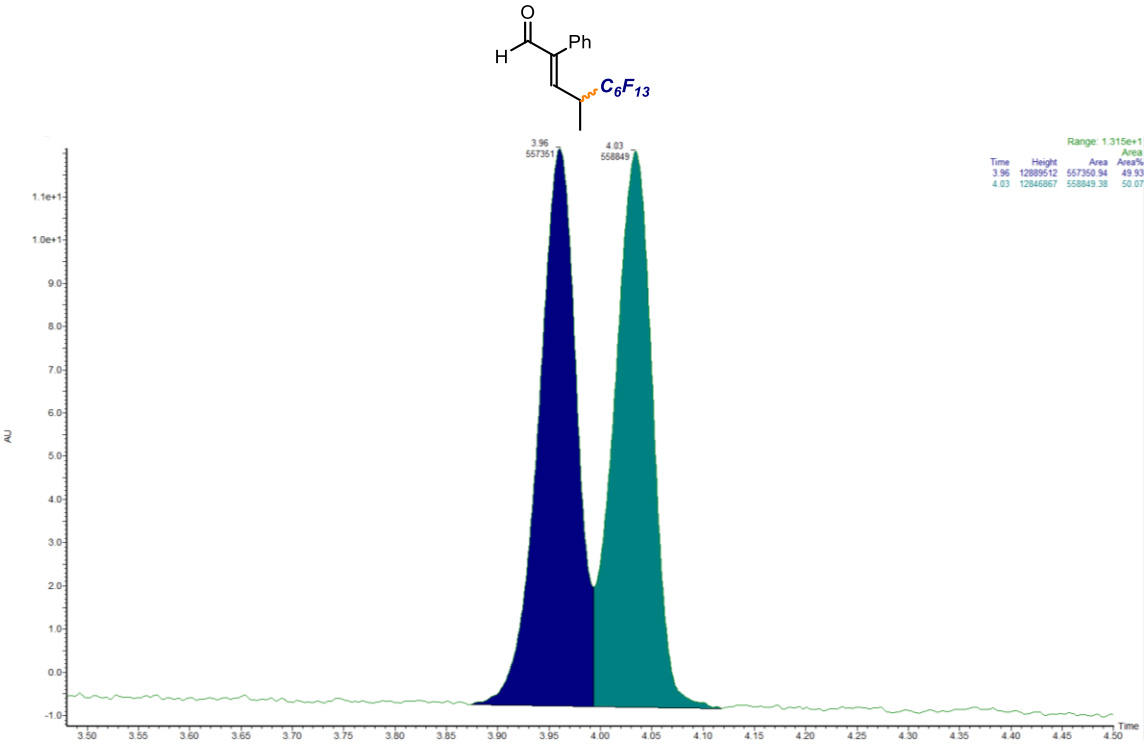


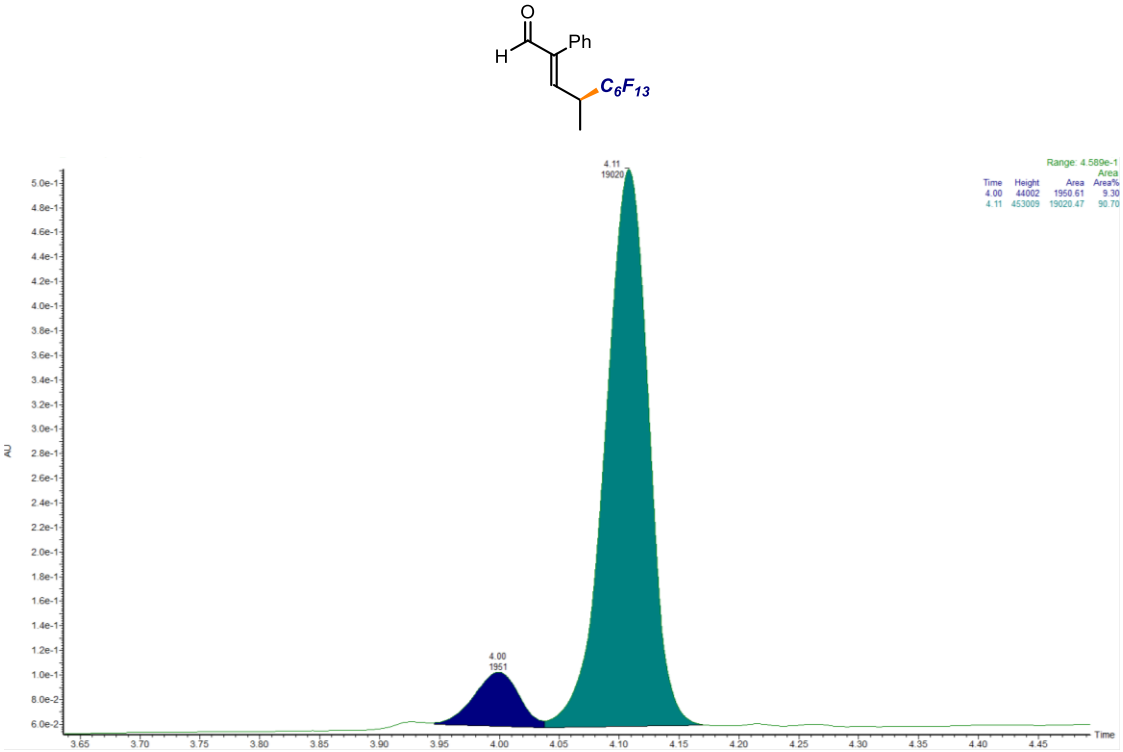
3d - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 350 nm: τ_{minor} = 5.8 min, τ_{major} = 6.0 min), 92:8 er.



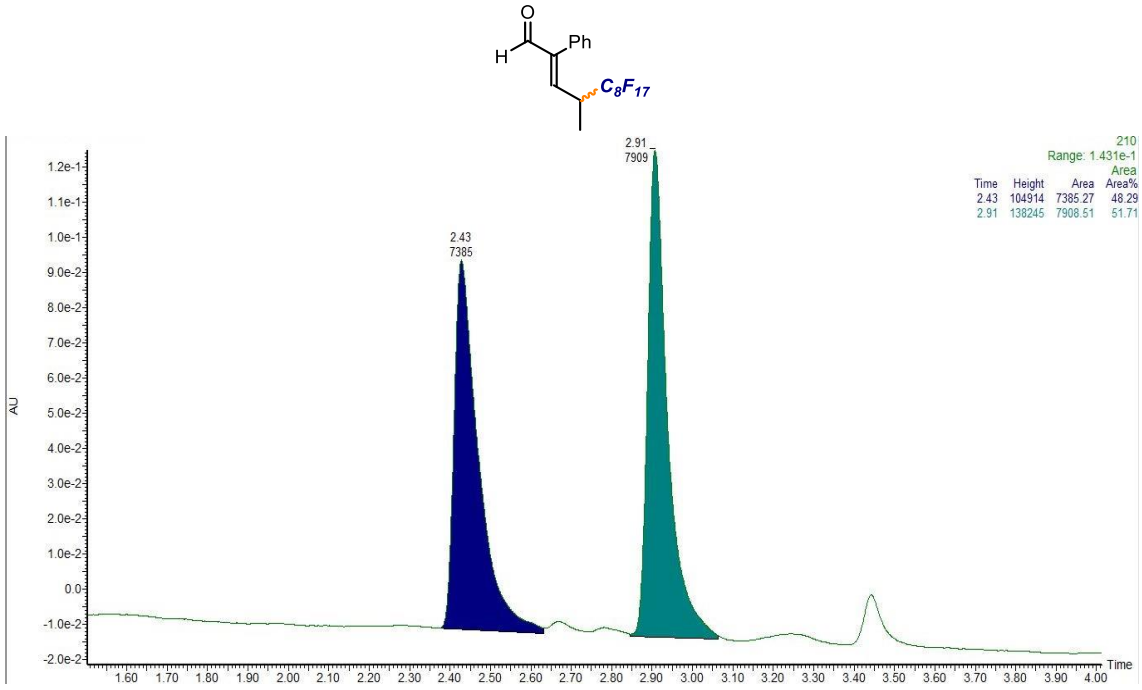


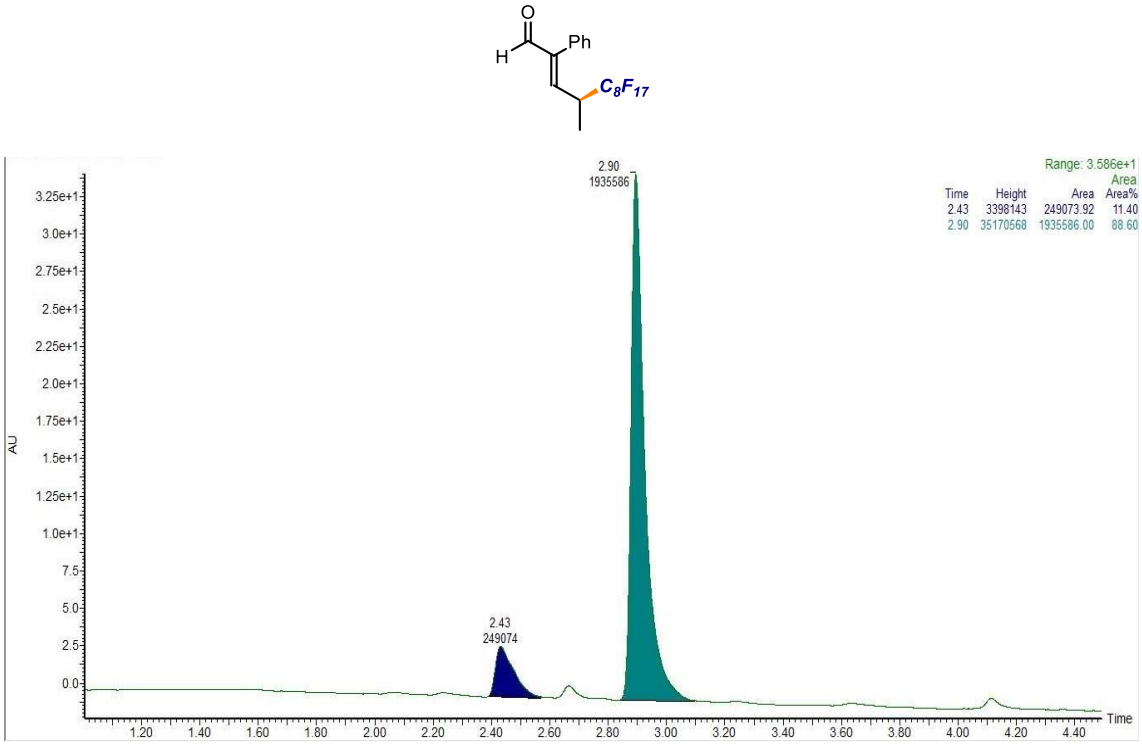
3e - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 4.0 min, τ_{major} = 4.1 min), 91:9 er.



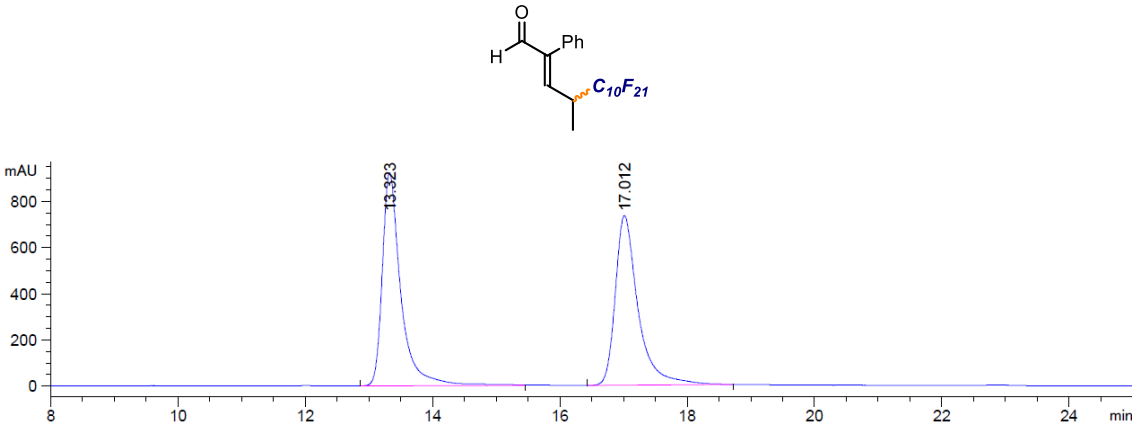


3f - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 4.0 min, τ_{major} = 4.1 min), 89:11 er.

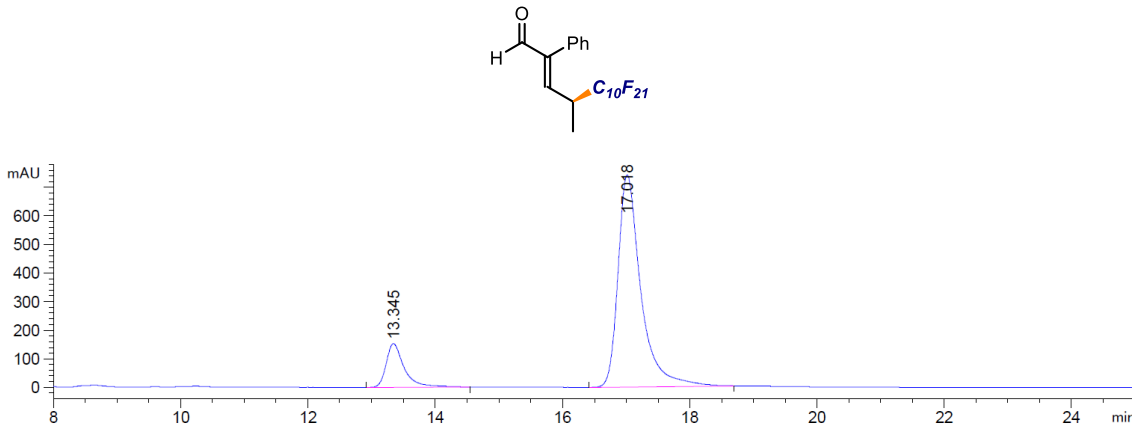




3g - Chiral HPLC analysis on a Daicel Chiralpak IC-3 column (eluent: *n*-hexane/*i*-PrOH 80:20; flow rate 1 mL/min, λ = 254 nm: τ_{minor} = 13.3 min, τ_{major} = 17.0 min), 86:14 er.

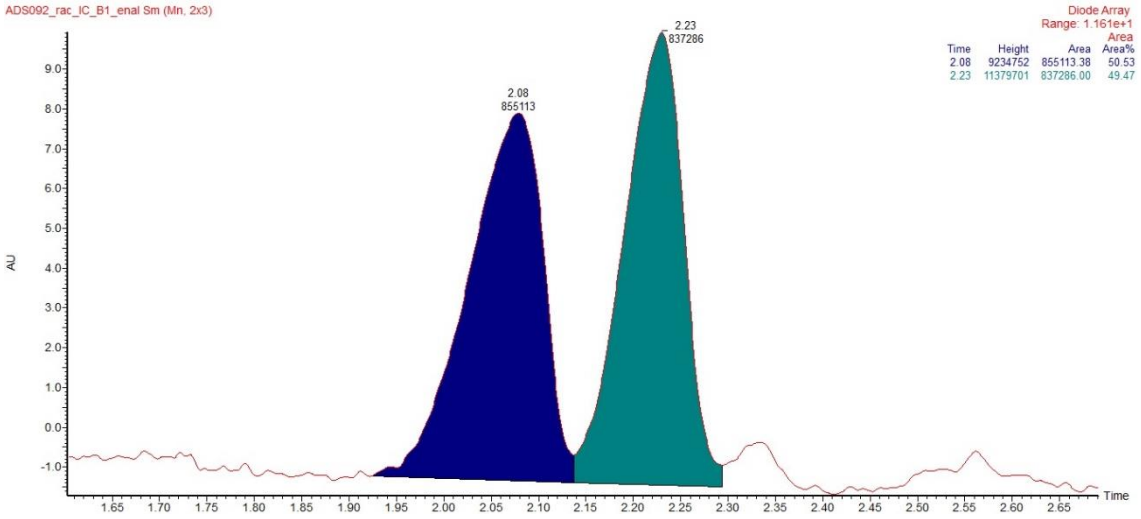


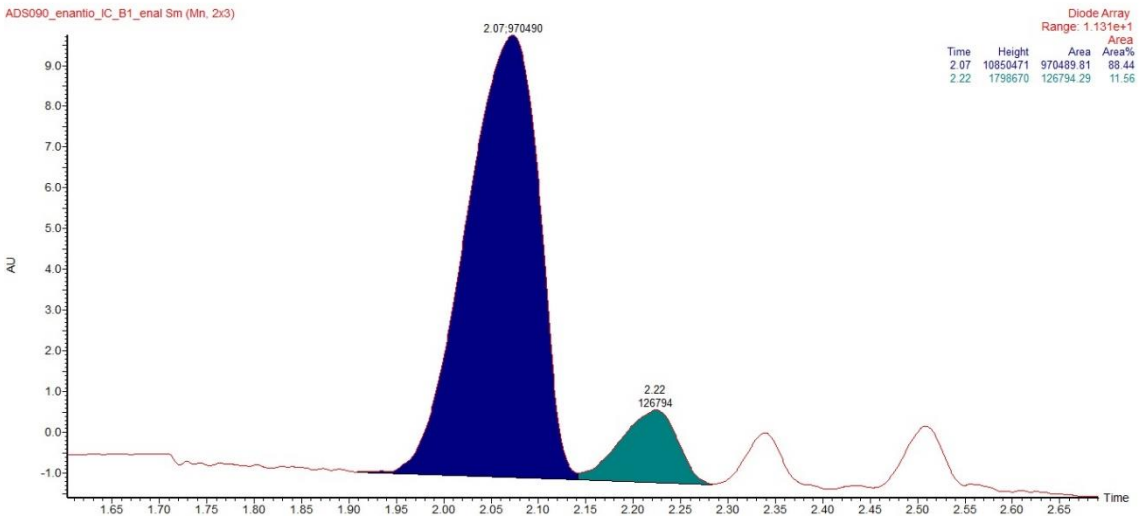
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.323	BV	0.2998	1.87222e4	922.55328	50.5785
2	17.012	BV	0.3657	1.82939e4	734.15399	49.4215



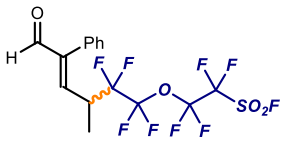
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.345	BB	0.2878	3003.66333	153.13341	13.9692
2	17.018	BB	0.3717	1.84983e4	742.44879	86.0308

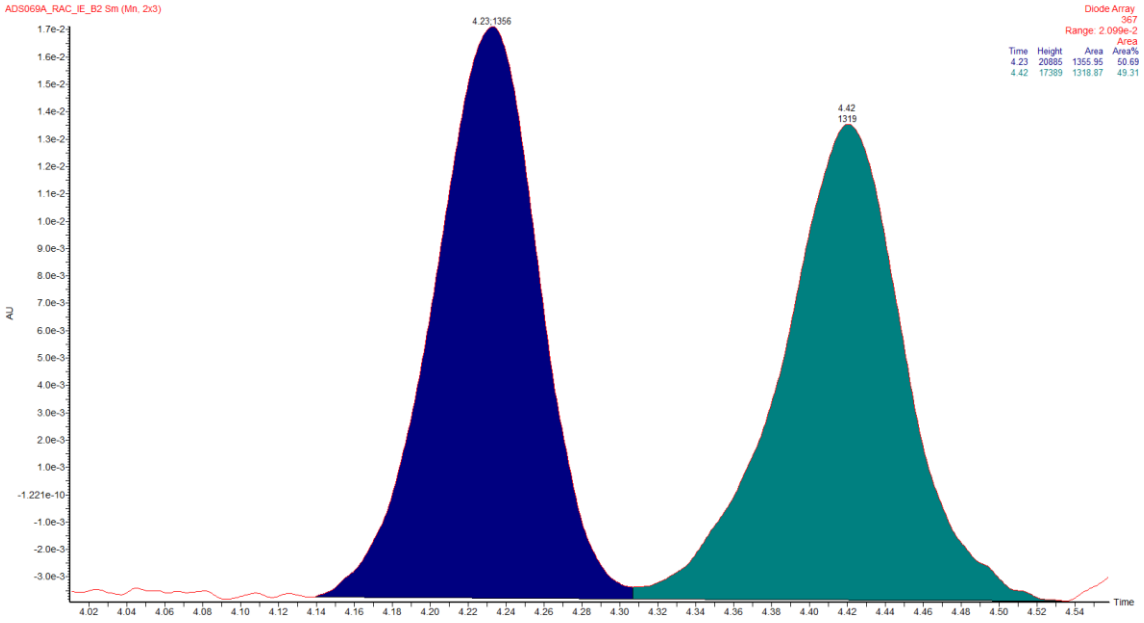
3h - UPC^2 analysis on a Daicel Chiralpak IC-3 column (eluent: *n*-hexane/*i*-PrOH 80:20; flow rate 1 mL/min, λ = 254 nm: τ_{minor} = 2.2 min, τ_{major} = 2.1 min), 88:12 er.

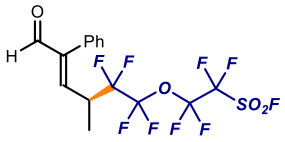


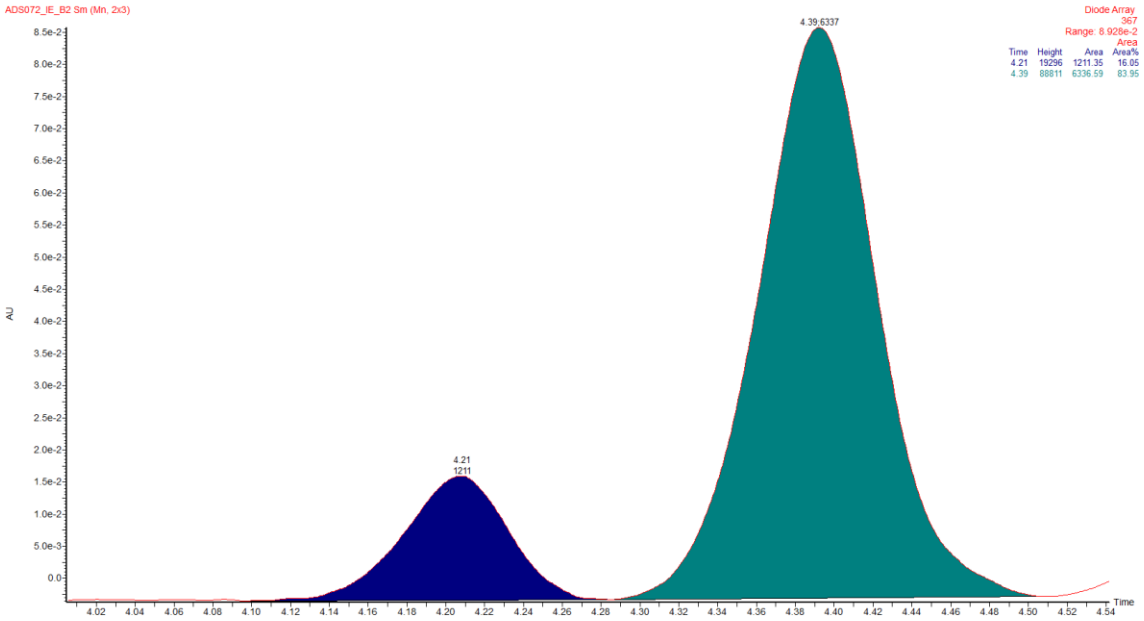


3i - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: *n*-hexane/*i*-PrOH 80:20; flow rate 2 mL/min, λ = 360 nm: τ_{minor} = 4.2 min, τ_{major} = 4.4 min), 84:16 er.

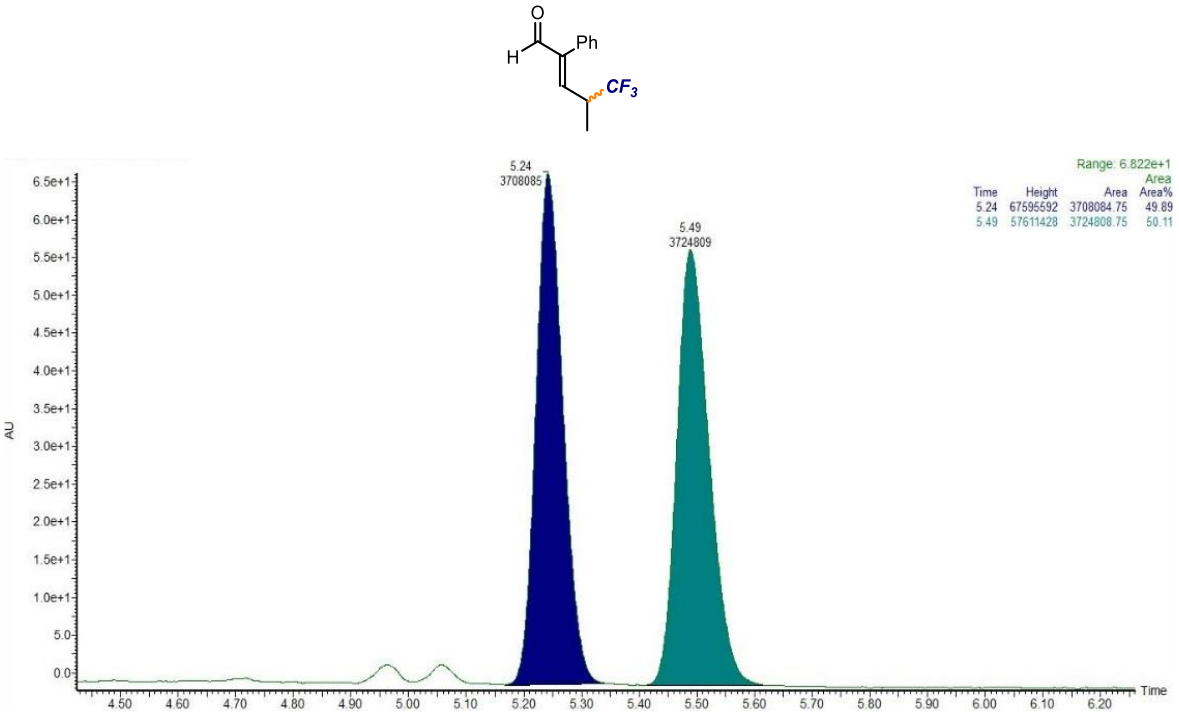


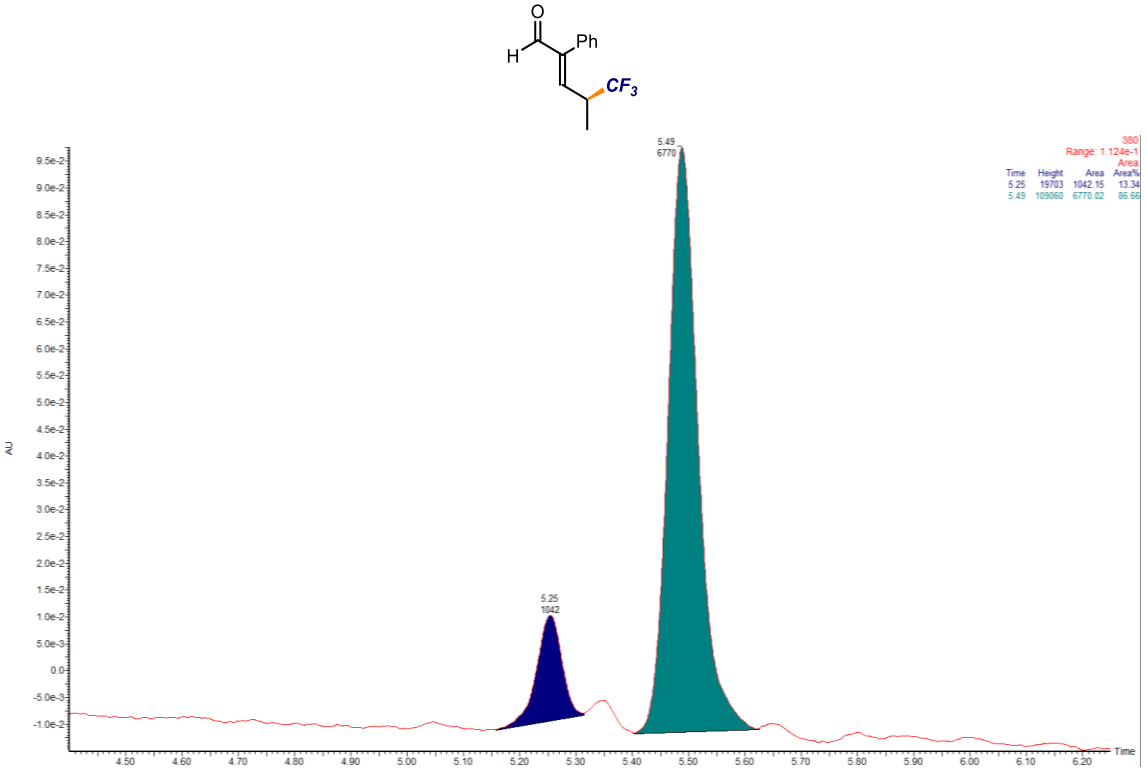




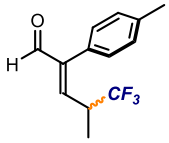


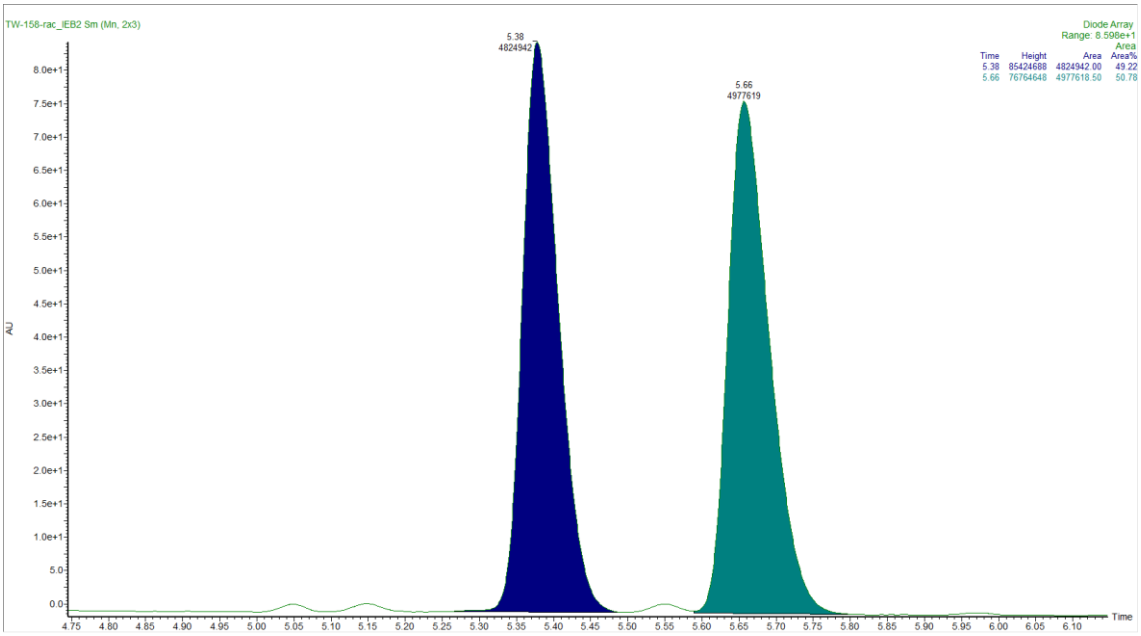
3j - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 5.3 min, τ_{major} = 5.5 min), 87:13 er.

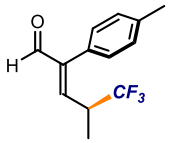


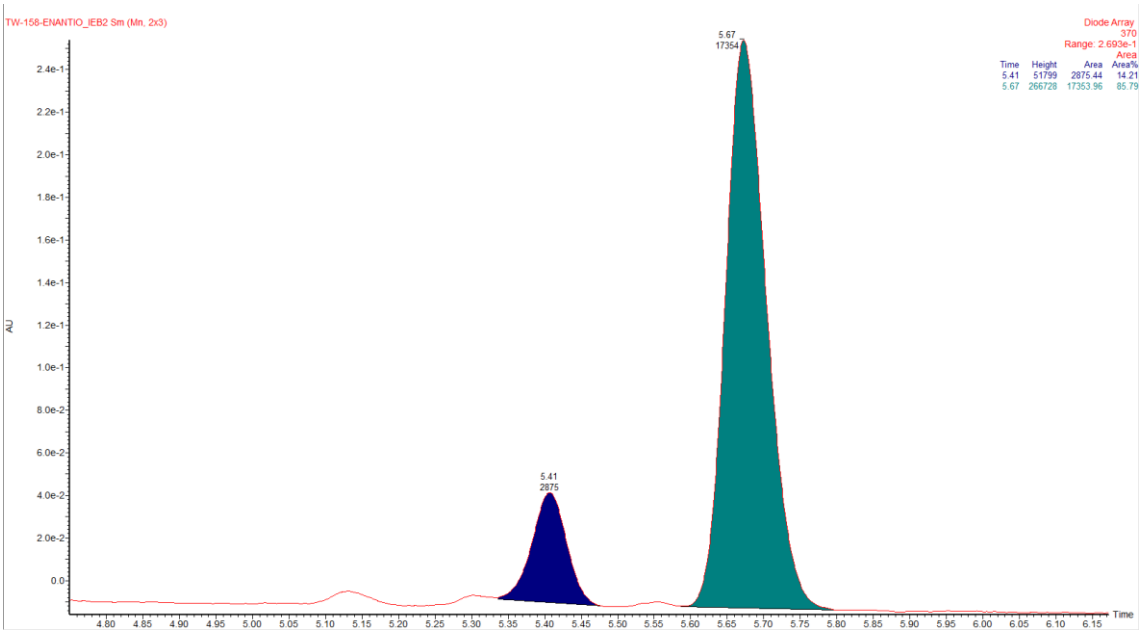


3k - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 5.3 min, τ_{major} = 5.5 min), 87:13 er.

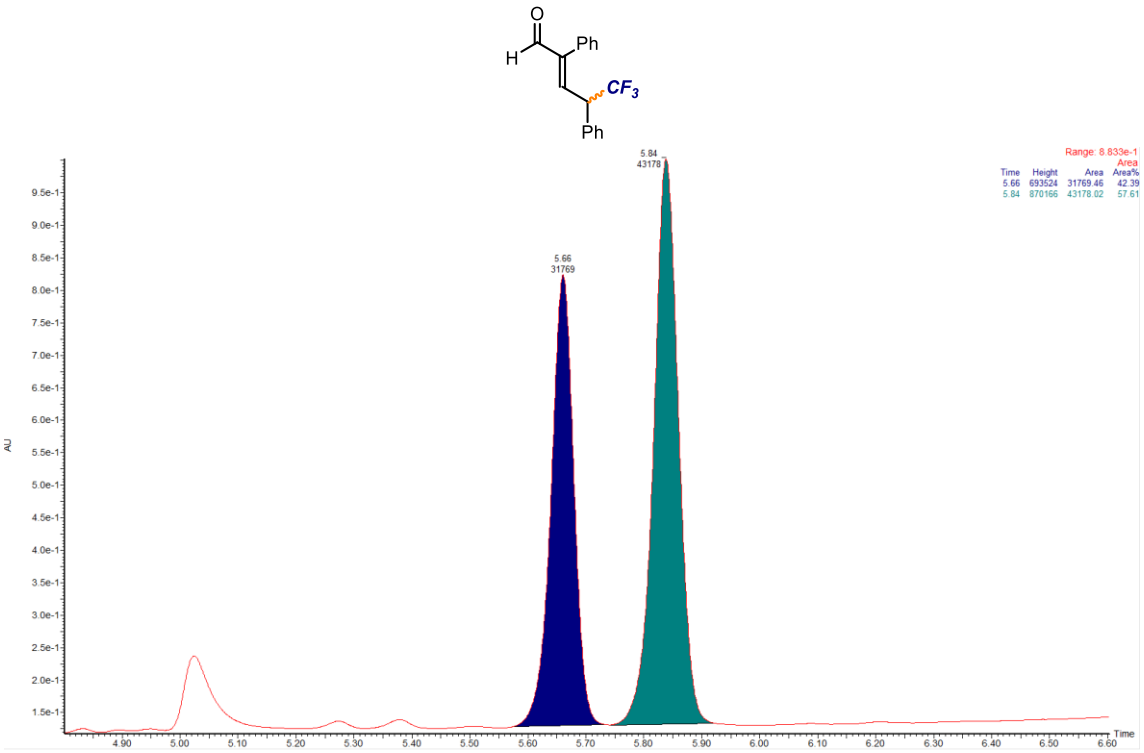


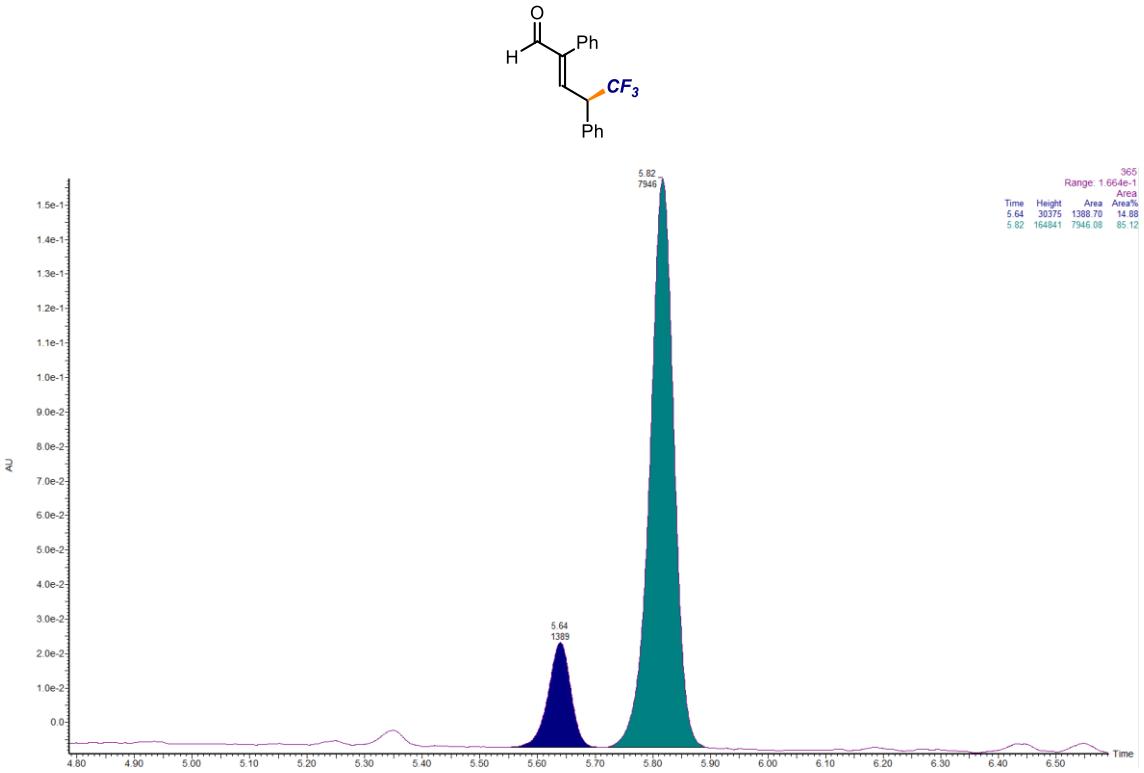




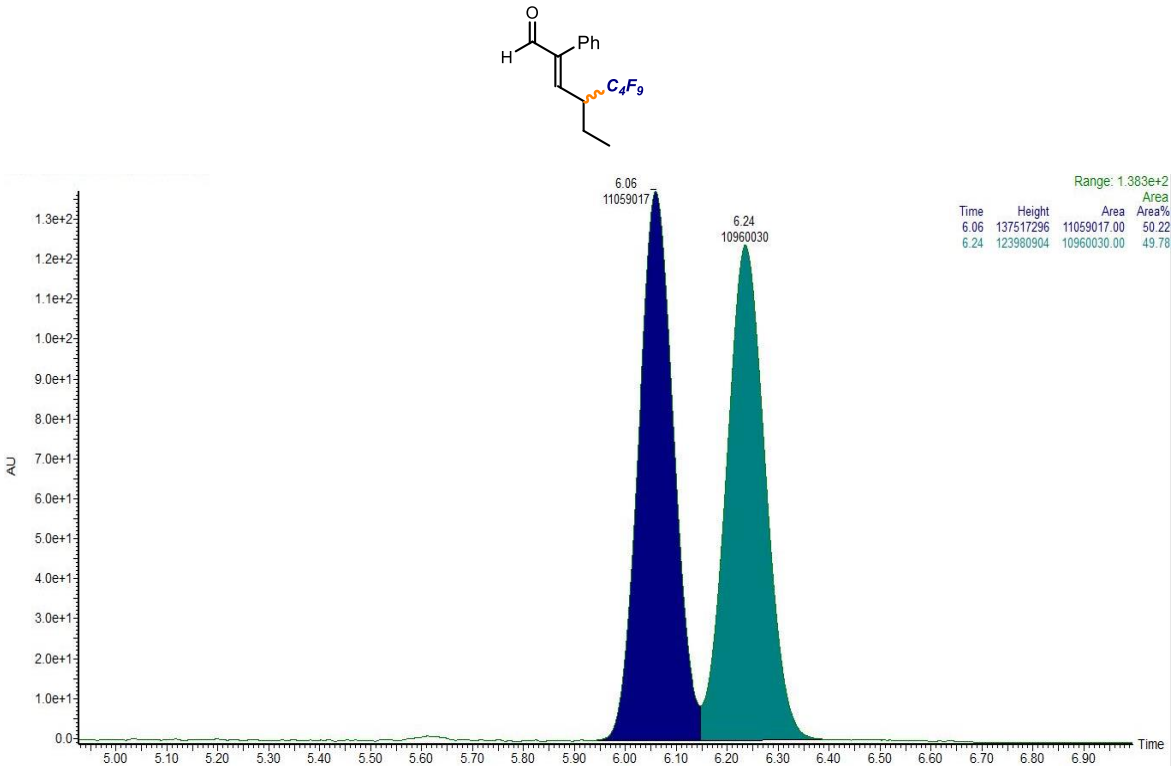


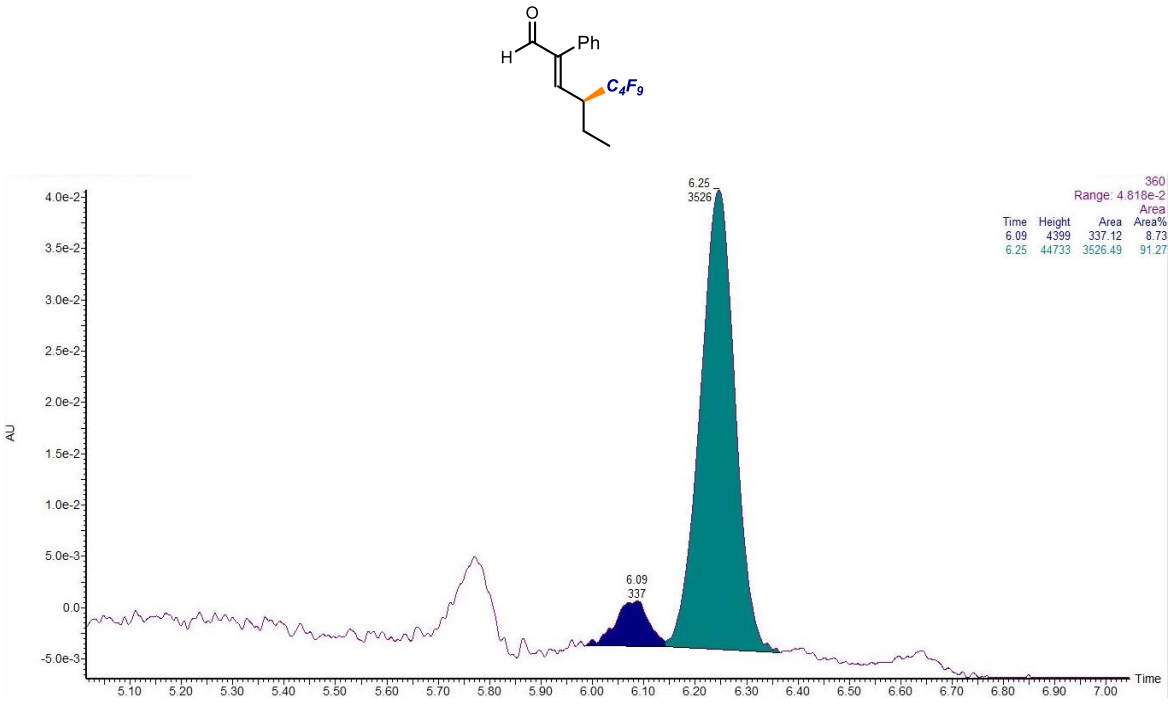
3l - UPC^2 analysis on a Daicel Chiralpak IB column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm: τ_{minor} = 5.66 min, τ_{major} = 5.84 min), 87:13 er.



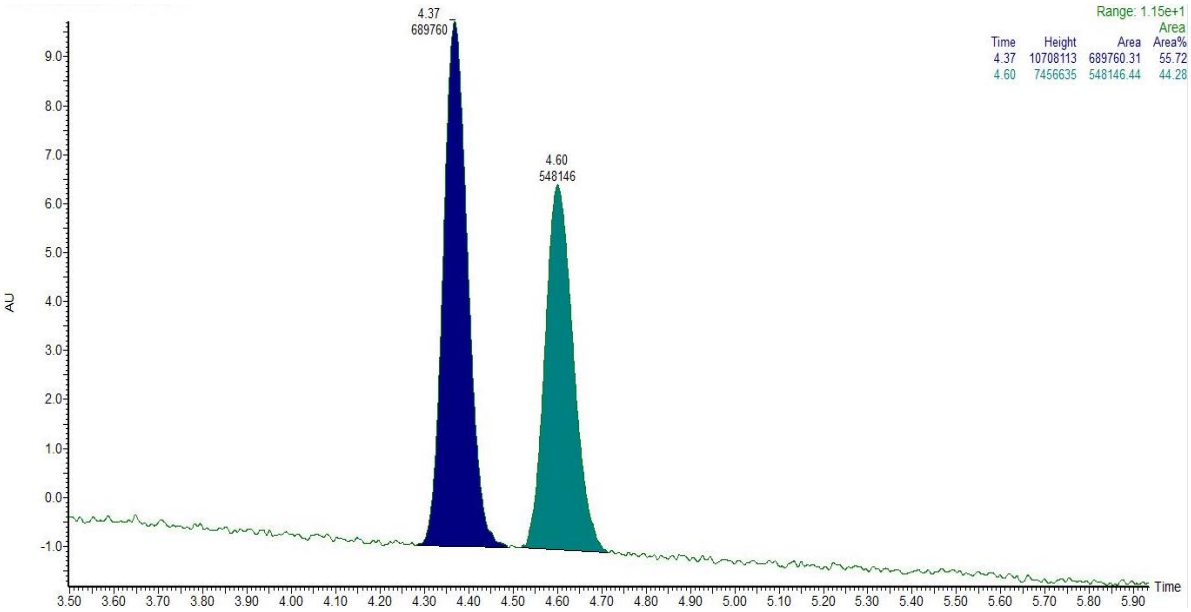


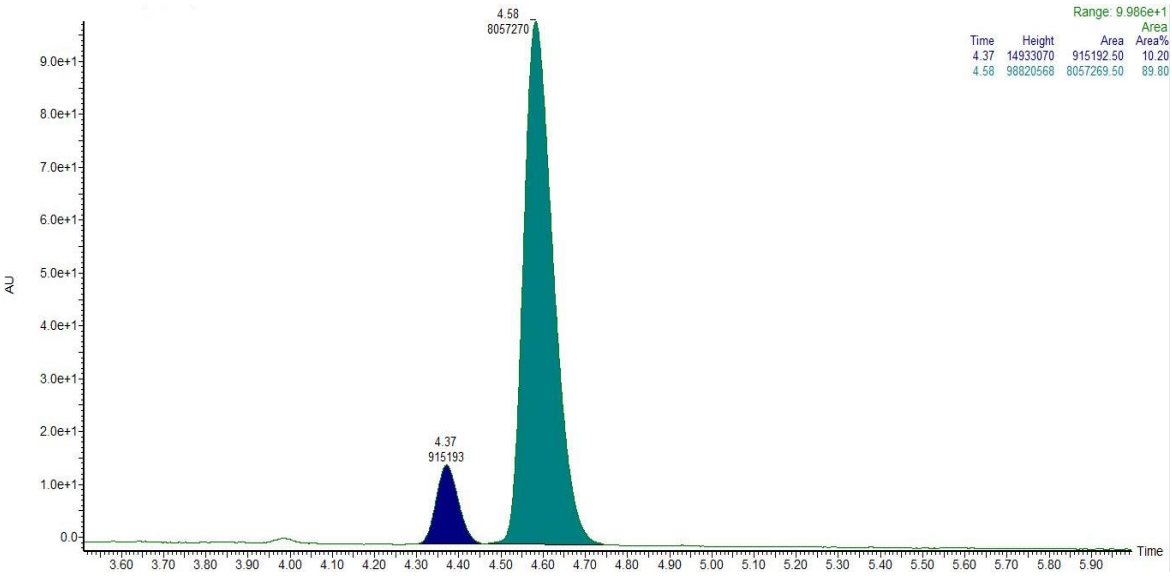
3m - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm, τ_{minor} = 6.1 min, τ_{major} = 6.3 min), 91:9 er.



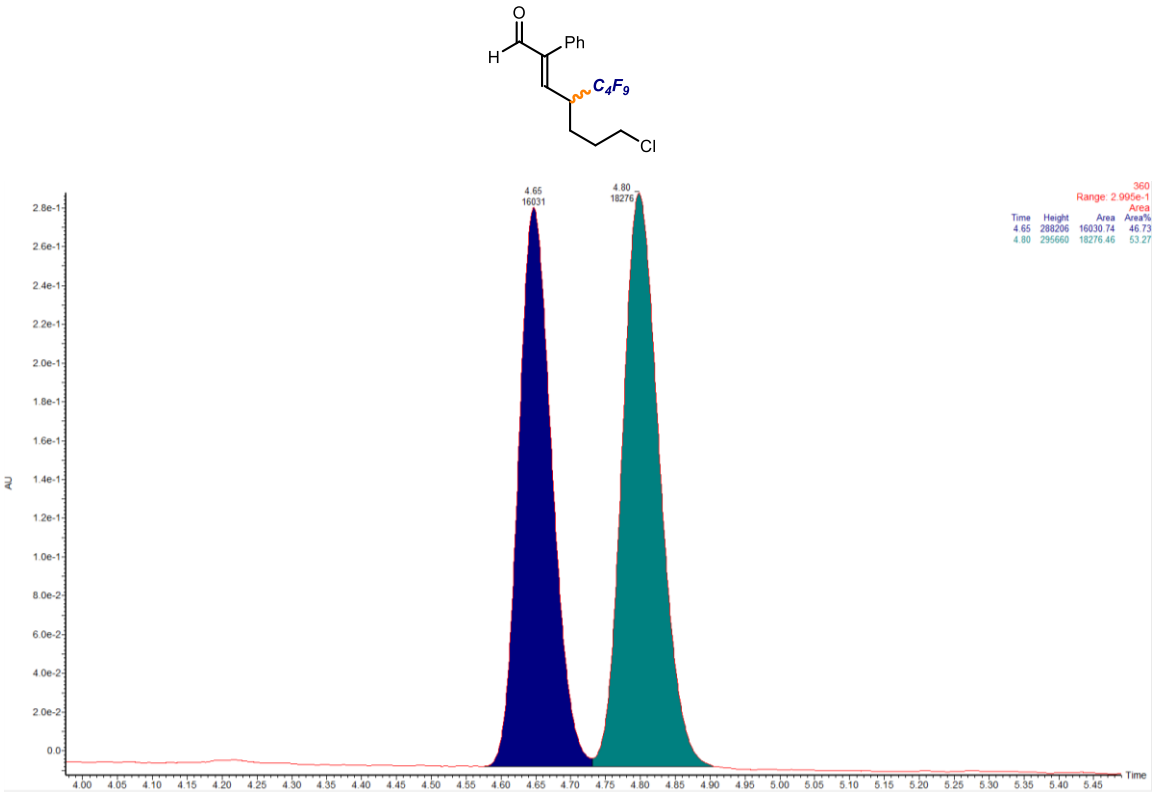


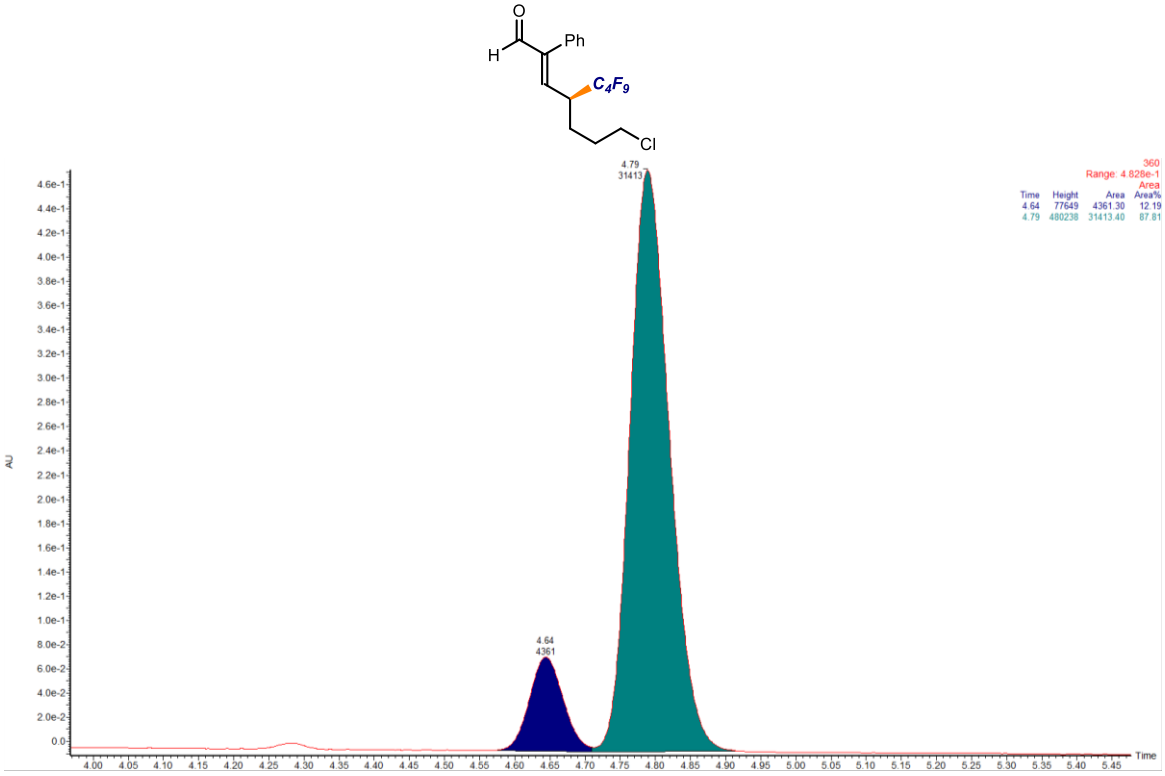
3n - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm, τ_{minor} = 4.4 min, τ_{major} = 4.6 min), 90:10 er.



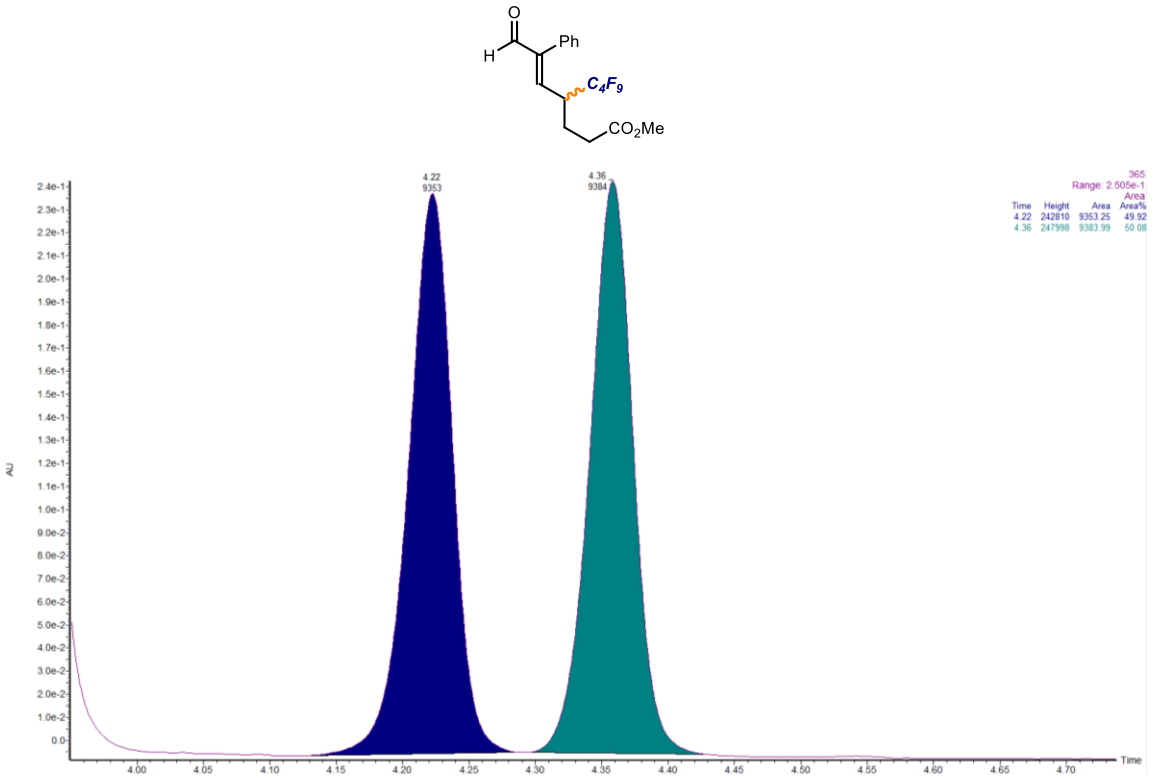


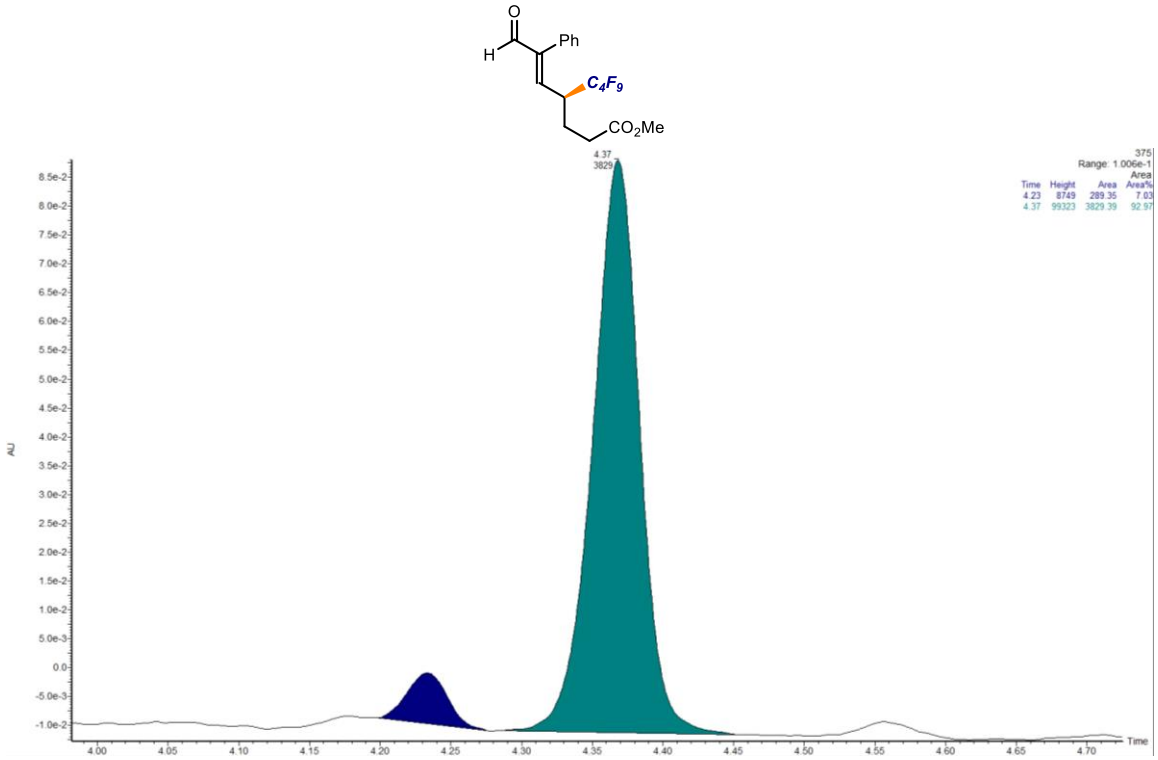
3o - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 360 nm, τ_{minor} = 4.6 min, τ_{major} = 4.8 min), 88:12 er.



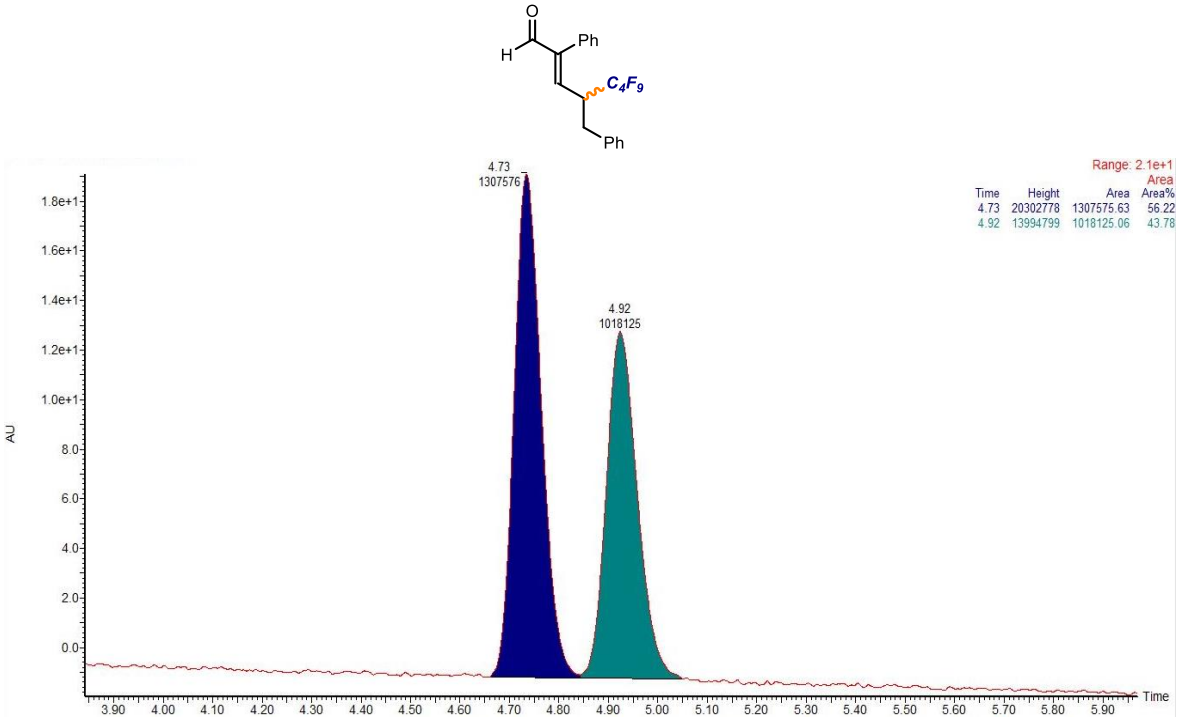


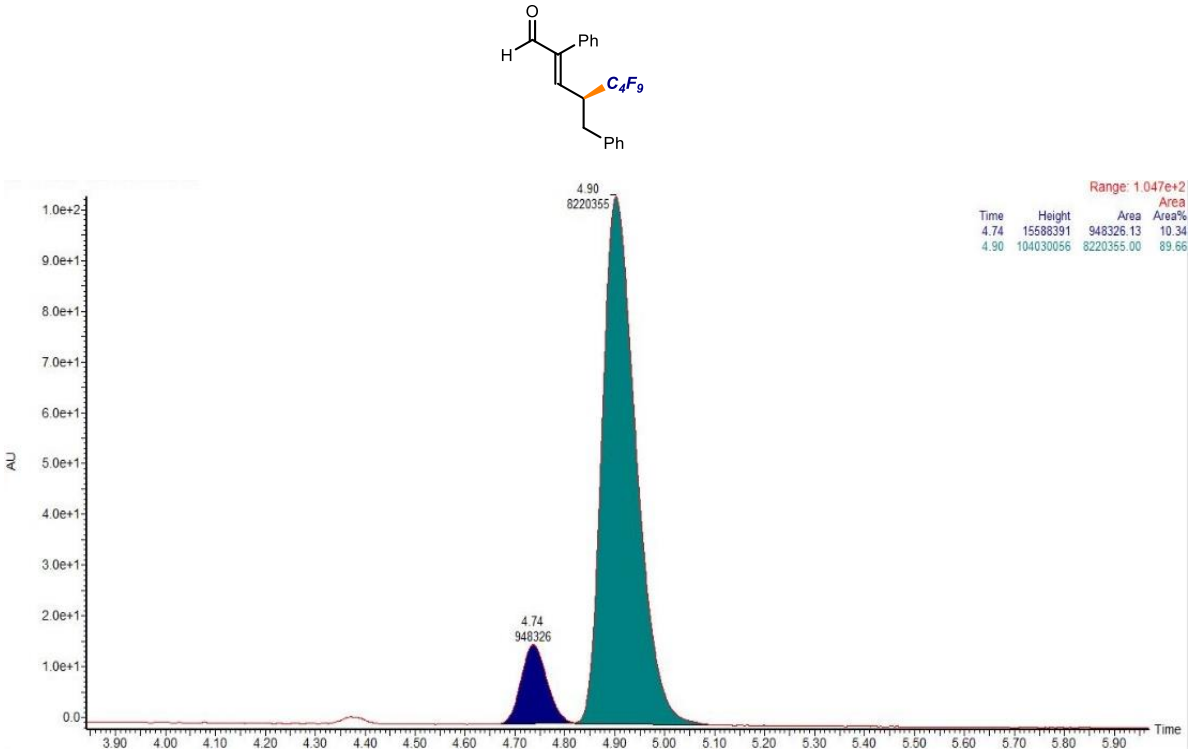
3p - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm, τ_{minor} = 4.2 min, τ_{major} = 4.4 min), 93:7 er.



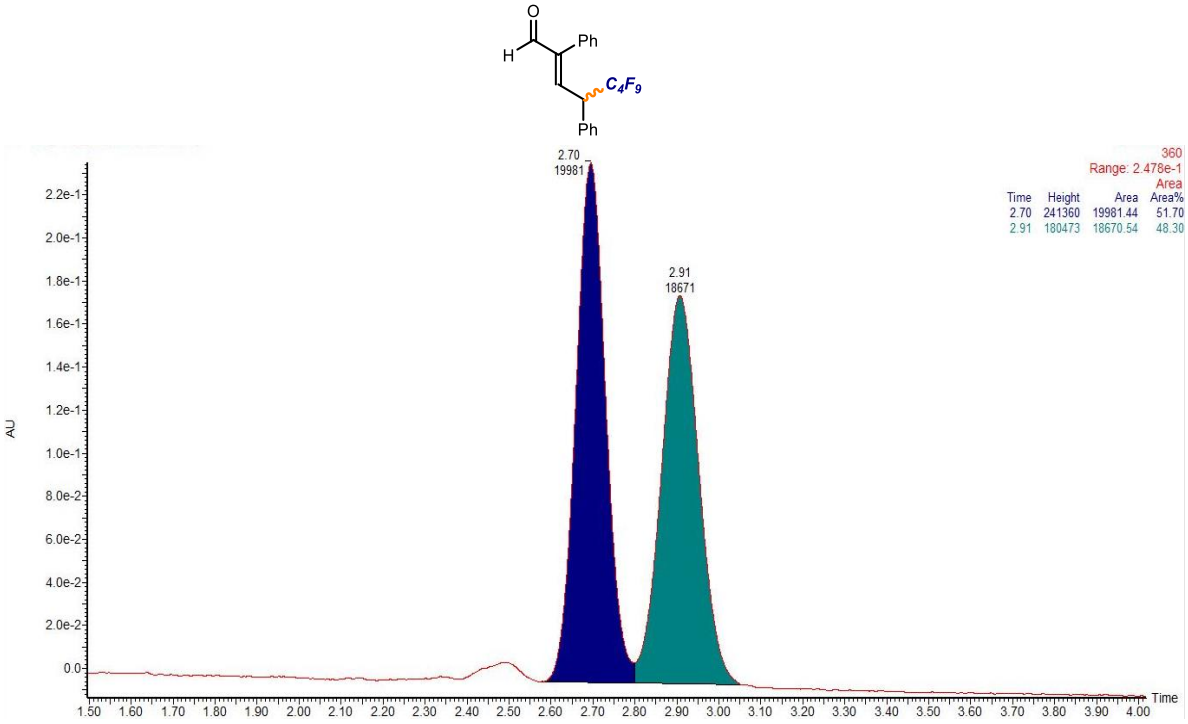


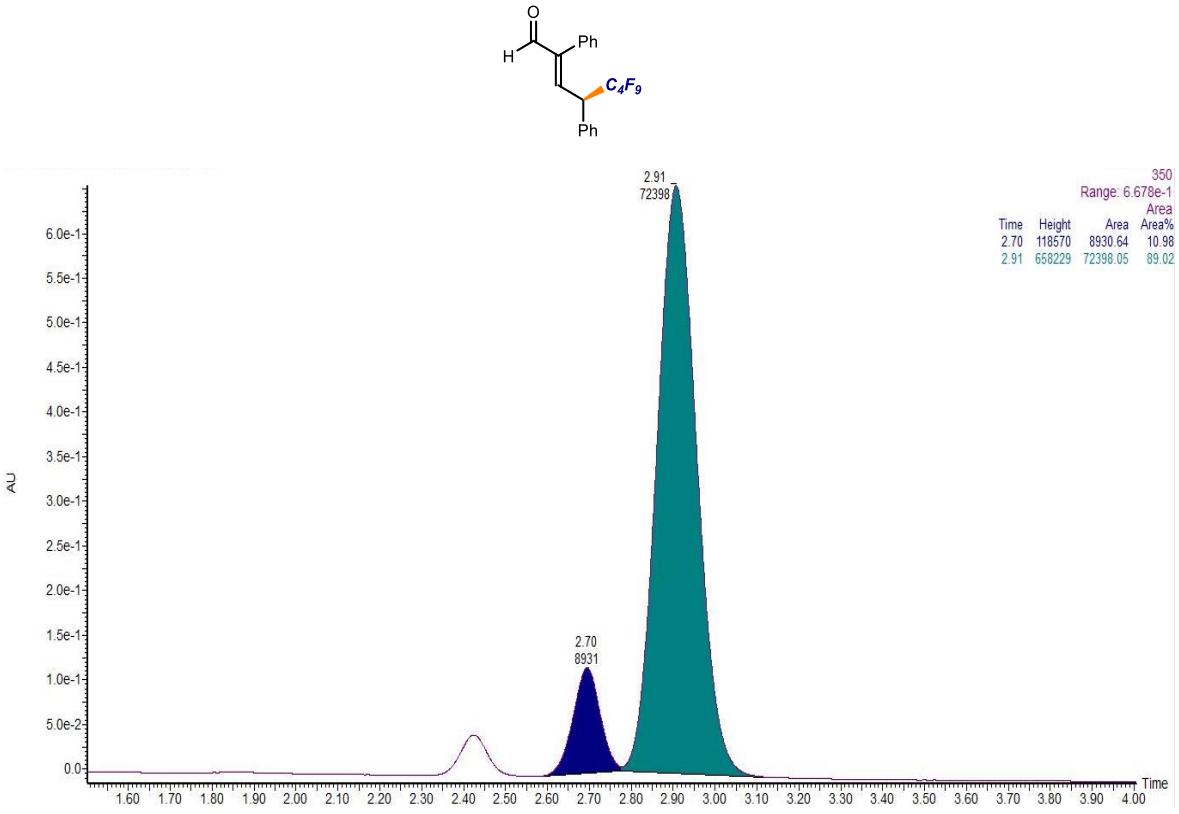
3q - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm, τ_{minor} = 4.7 min, τ_{major} = 4.9 min), 90:10 er.



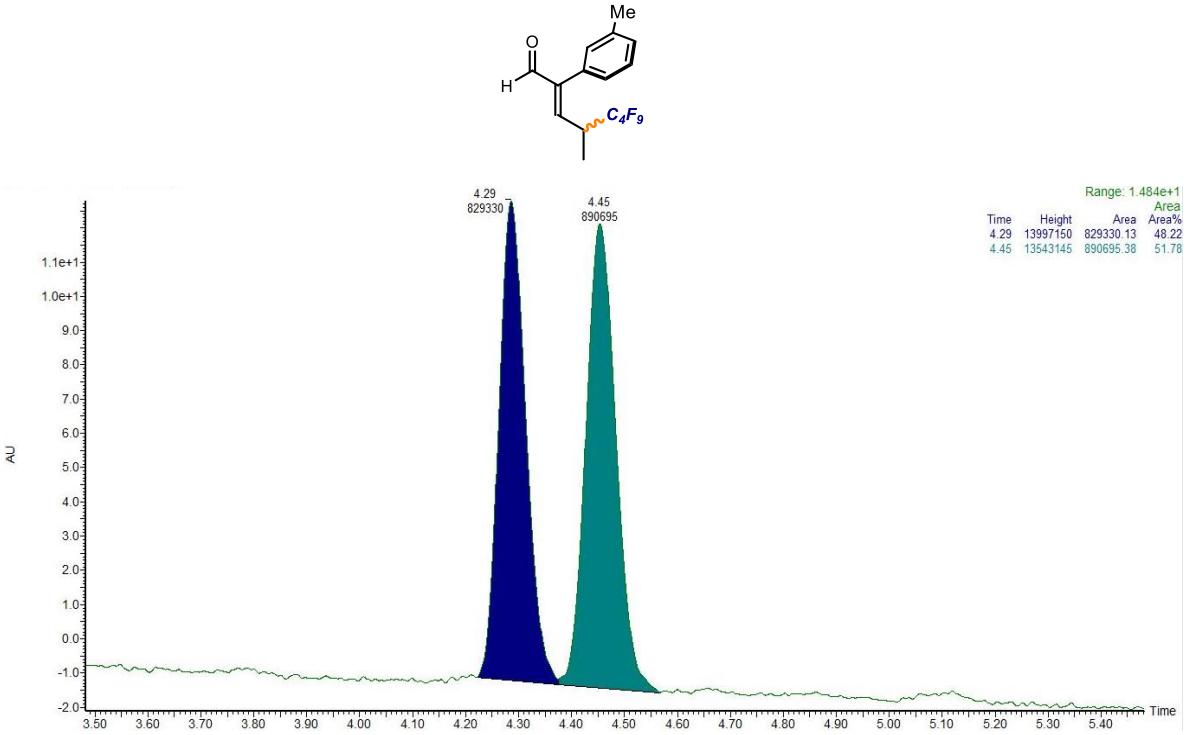


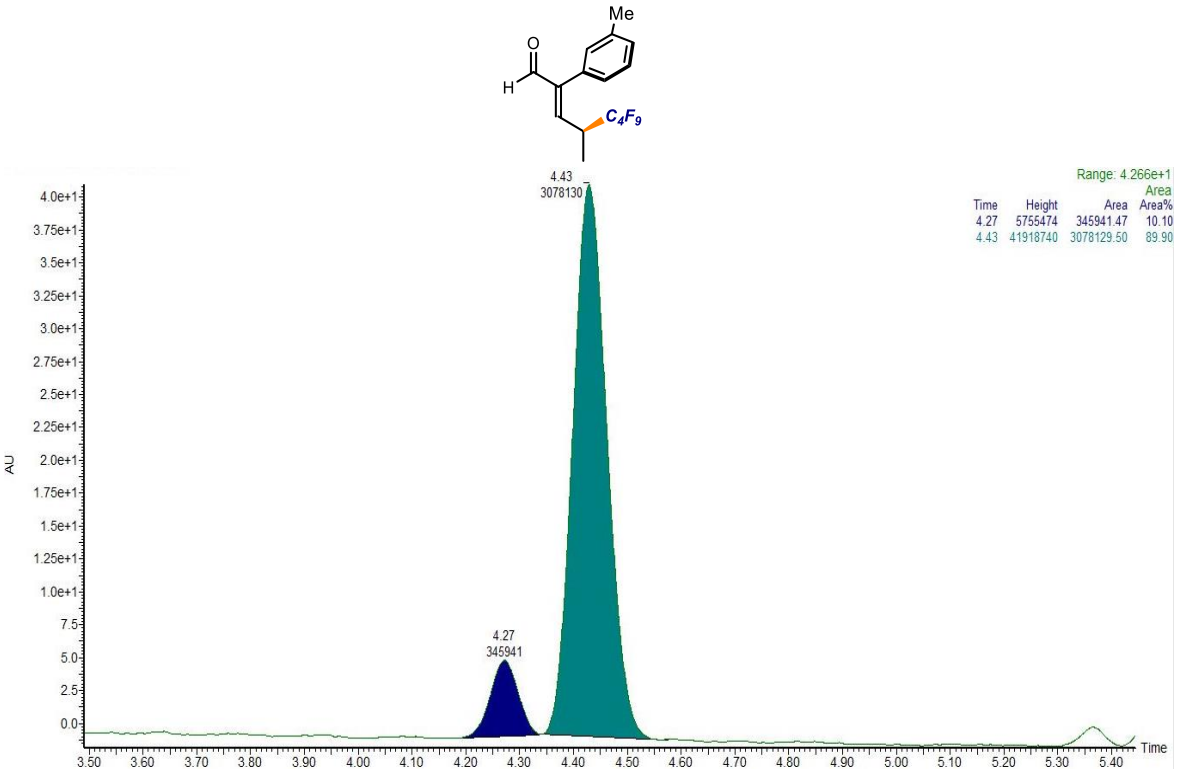
3r - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 350 nm, τ_{minor} = 2.7 min, τ_{major} = 2.9 min), 89:11 er.



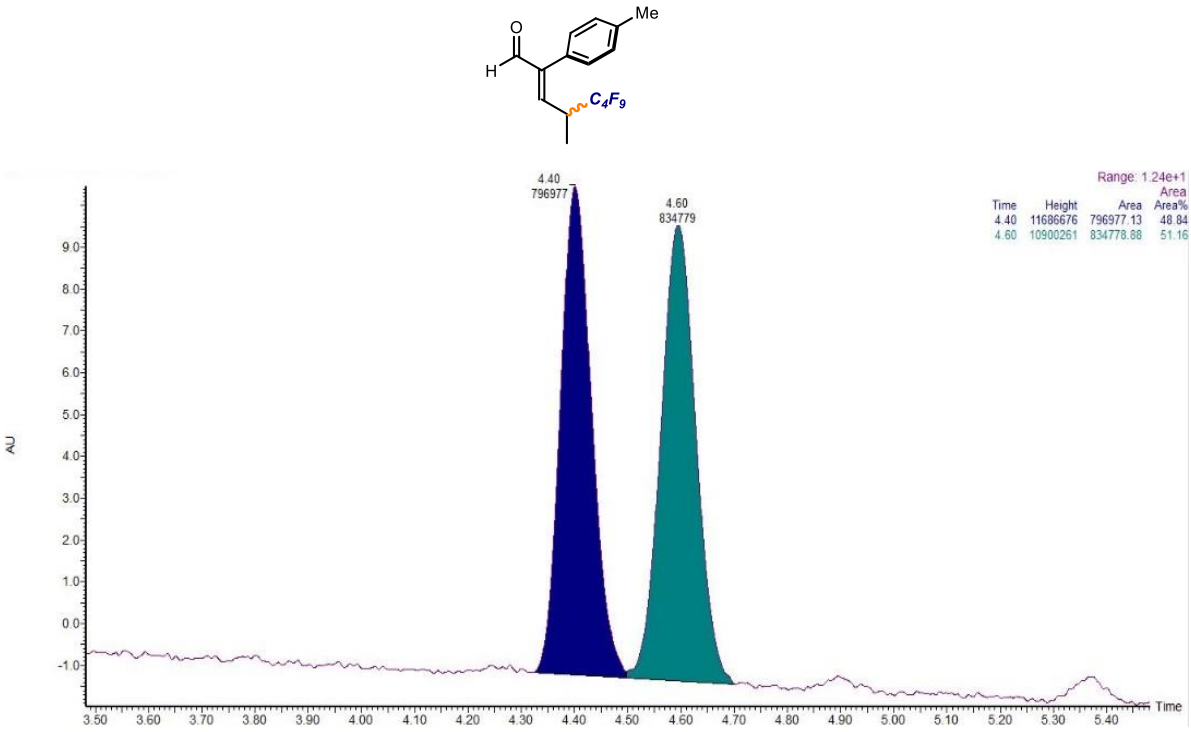


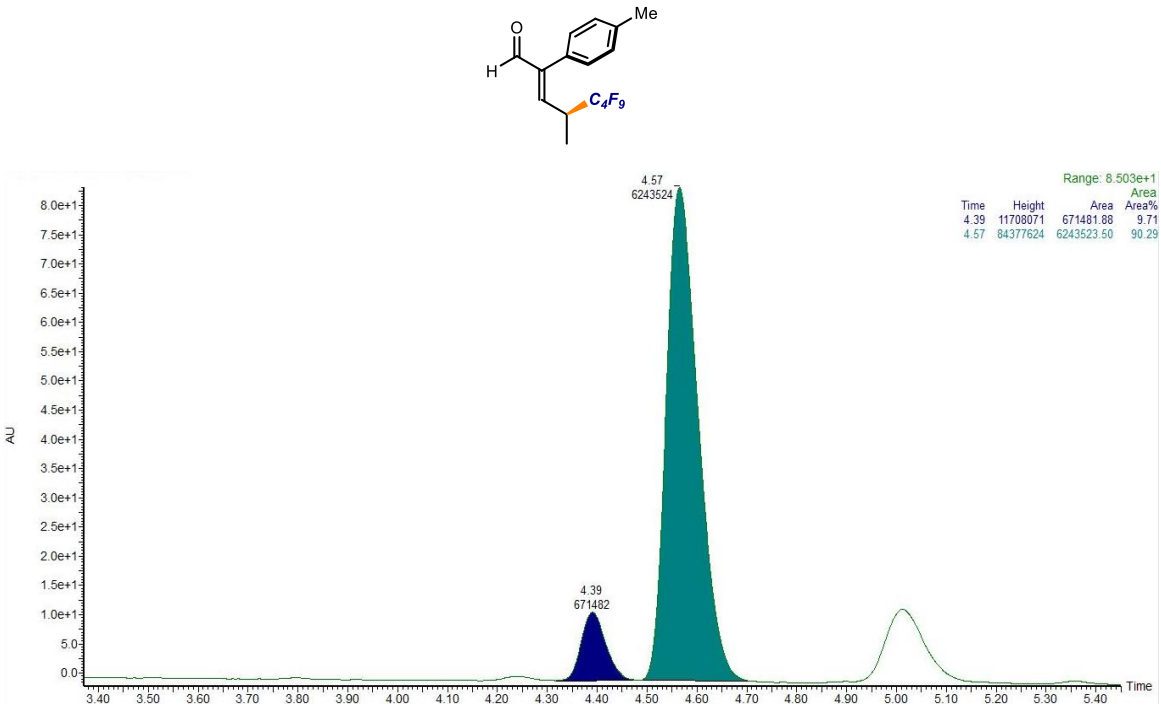
3t - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 360 nm, τ_{minor} = 4.3 min, τ_{major} = 4.4 min), 90:10 er.



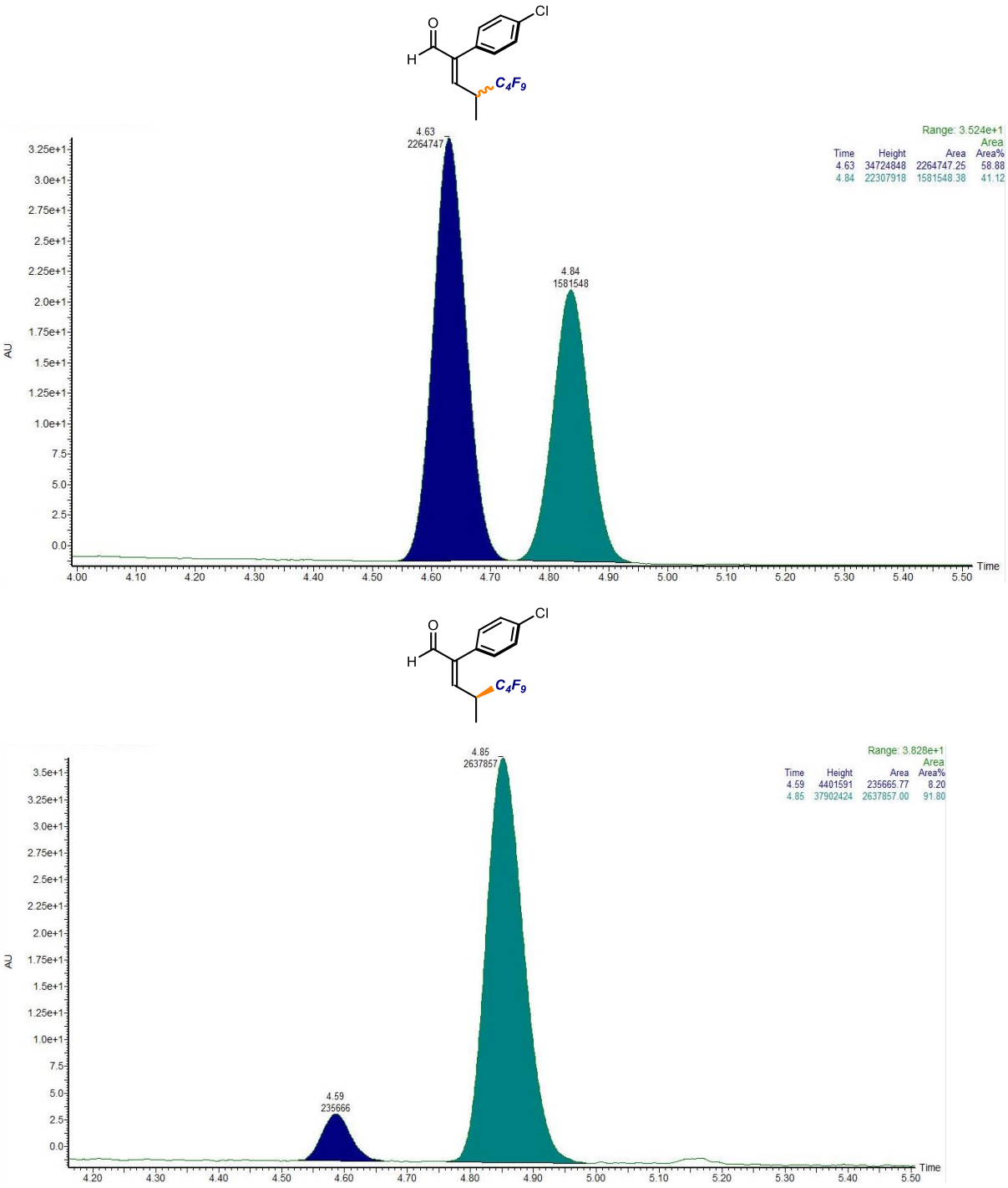


3s - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm, τ_{minor} = 4.4 min, τ_{major} = 4.6 min), 90:10 er.

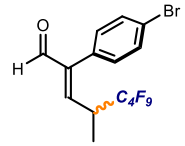


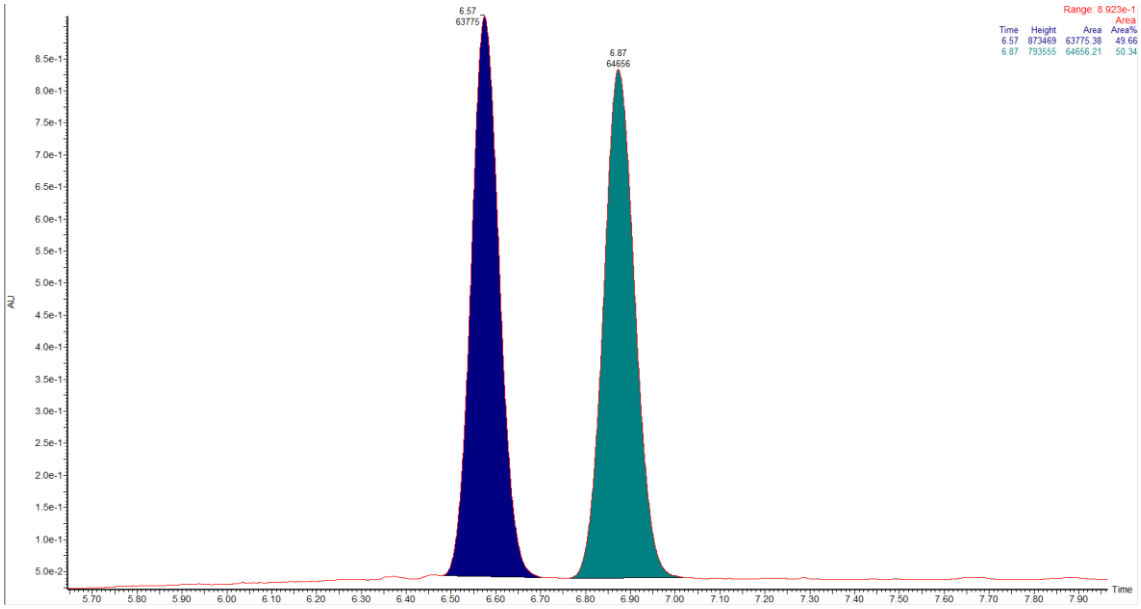


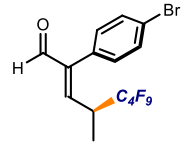
3u - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm, τ_{minor} = 4.6 min, τ_{major} = 4.9 min), 92:8 er.

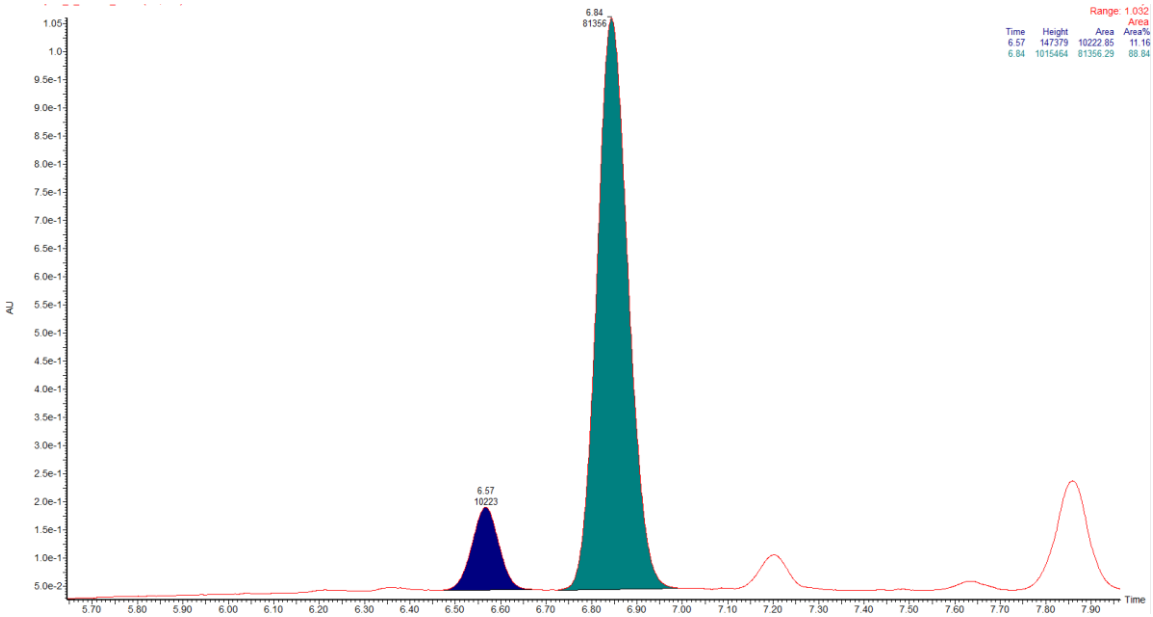


3v - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm, τ_{minor} = 6.6 min, τ_{major} = 7.0 min), 89:11 er.

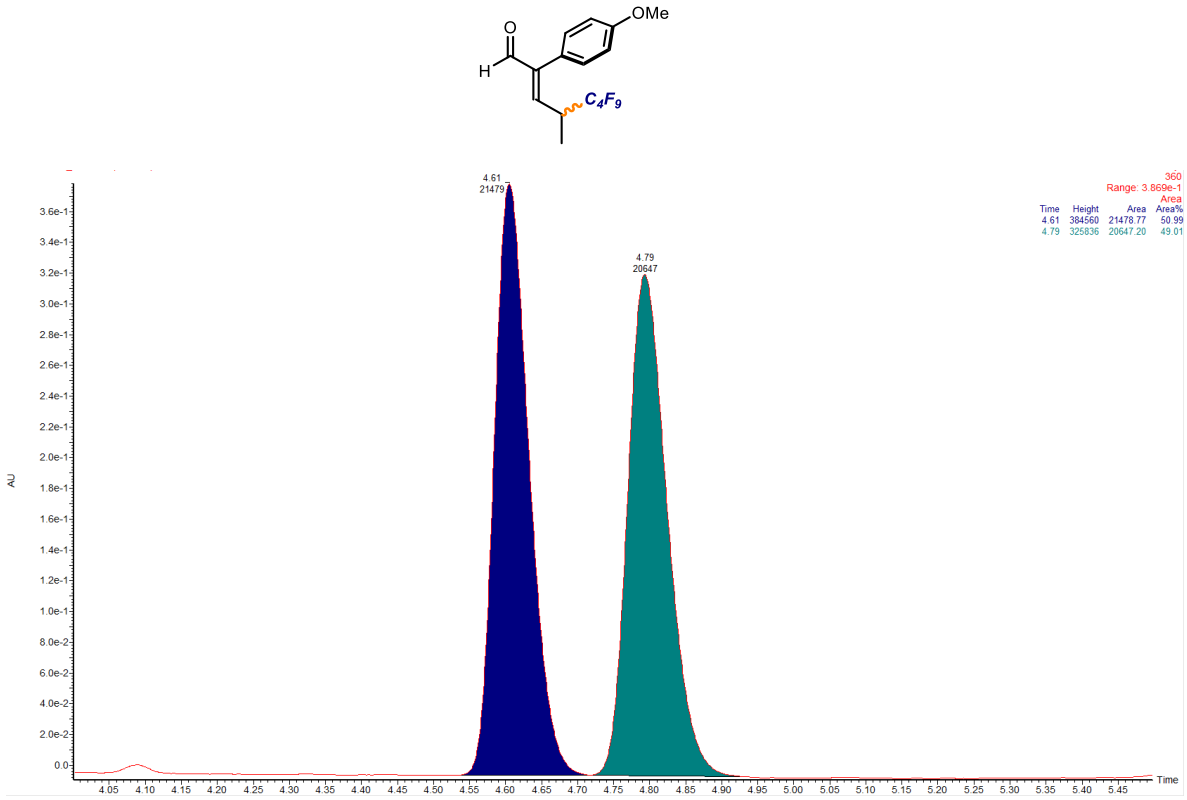


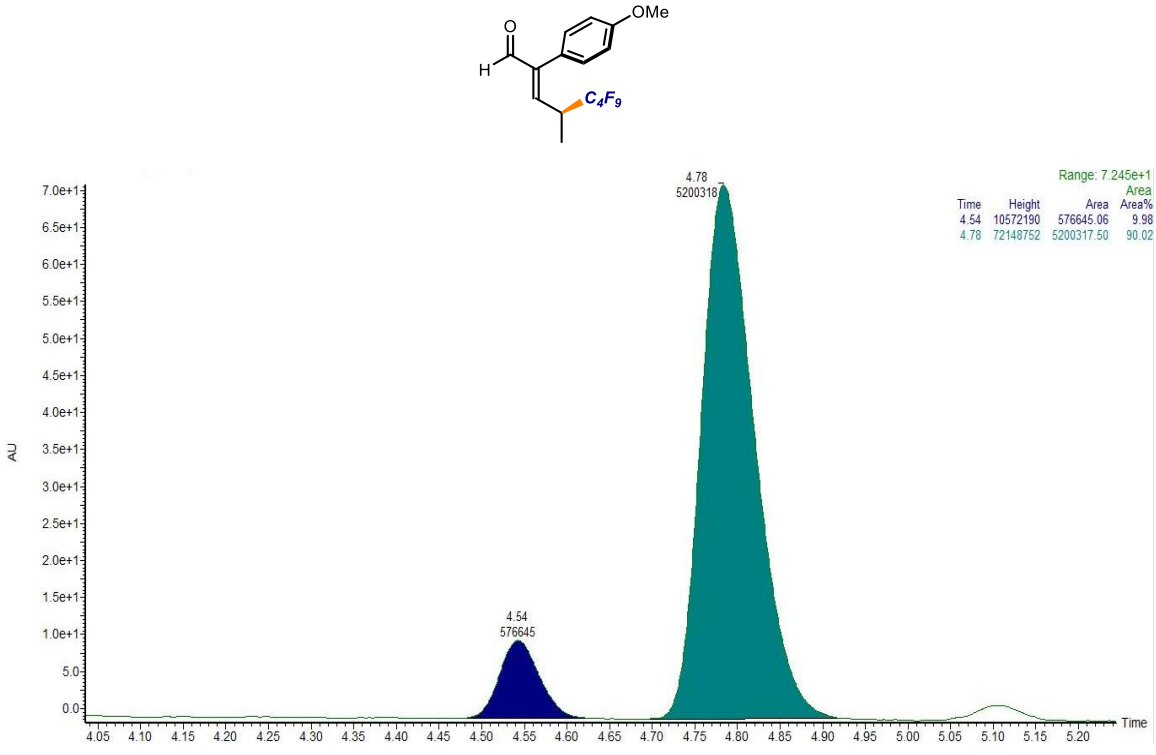




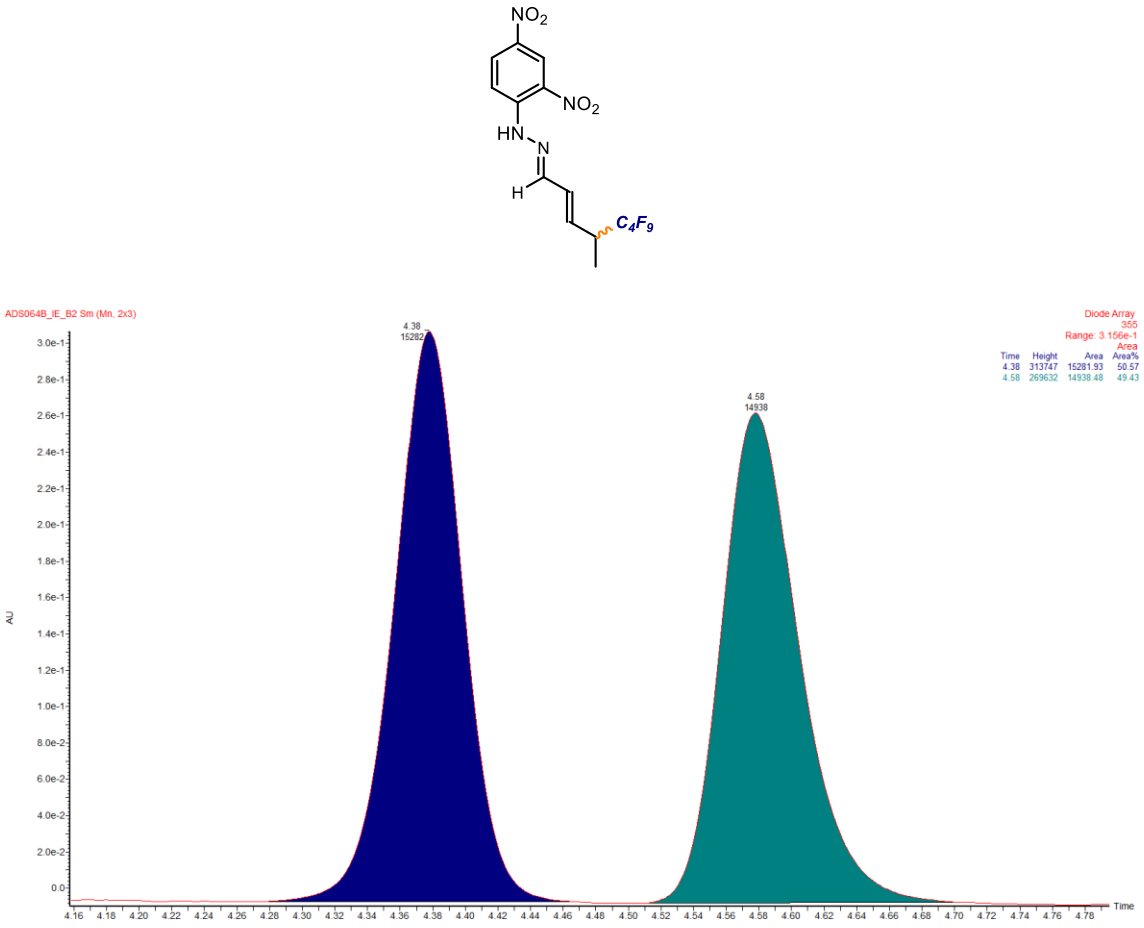


3w - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/*i*-PrOH = 90:10; flow rate 2 mL/min, λ = 211 nm, τ_{minor} = 4.5 min, τ_{major} = 4.8 min), 90:10 er.

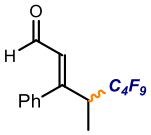


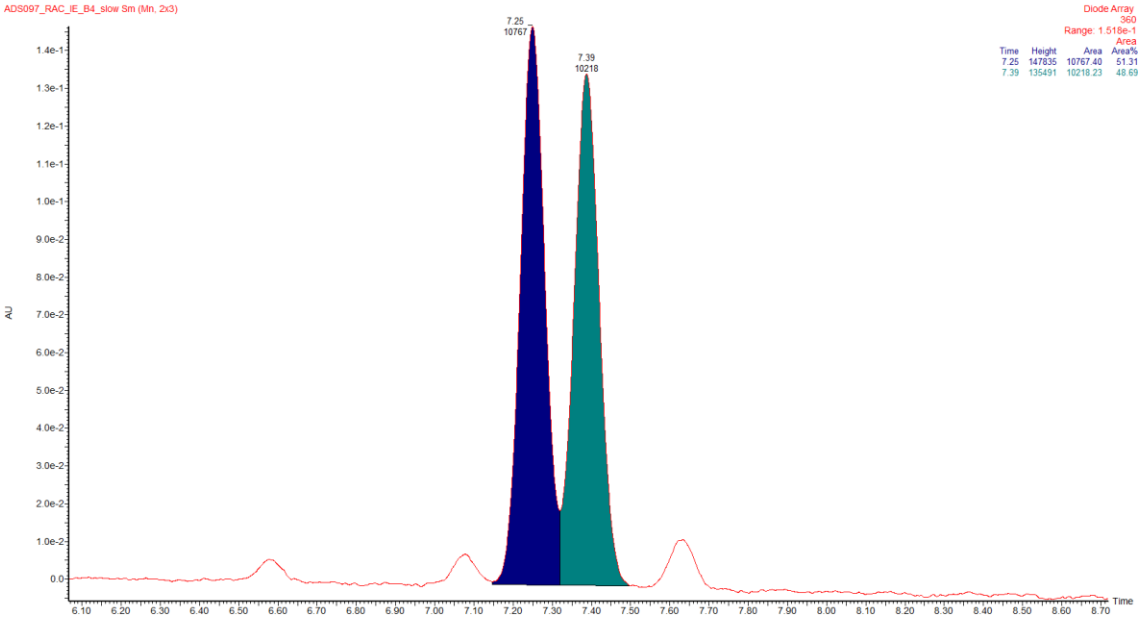


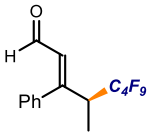
S16 (3x) - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 2 mL/min, λ = 355 nm: τ_{minor} = 4.4 min, τ_{major} = 4.6 min), 50:50 er.

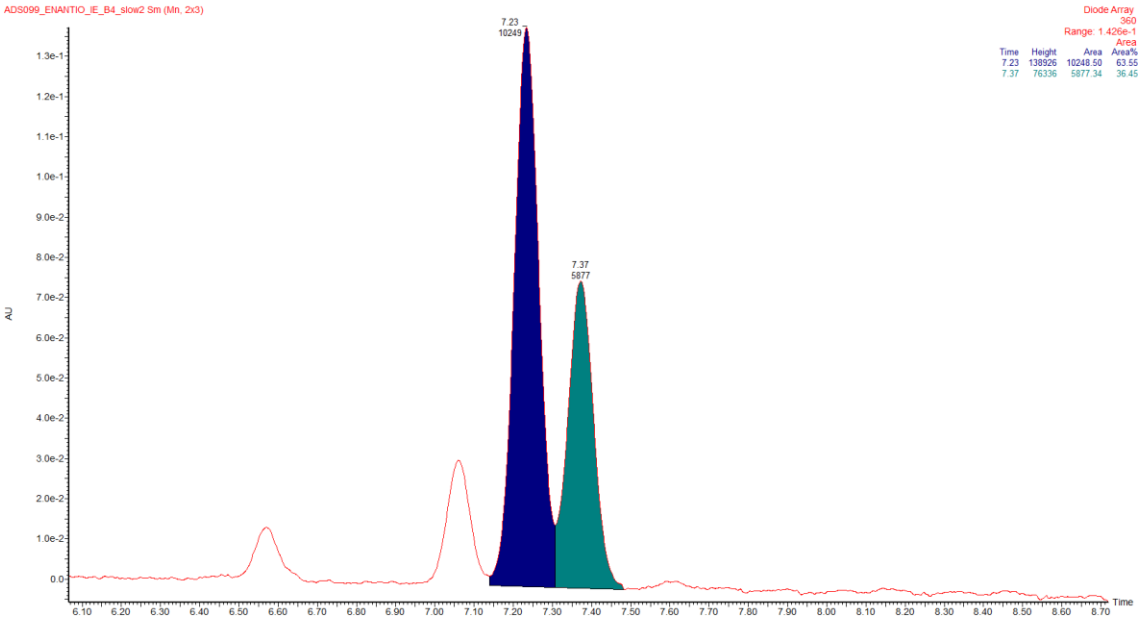


3y - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/MeOH = 90:10; flow rate 1 mL/min, λ = 360 nm: τ_{minor}= 7.2 min, τ_{major} = 7.4 min), 64:36 er.









3z - UPC^2 analysis on a Daicel Chiralpak IE column (eluent: CO_2/IPA = 90:10; flow rate 1 mL/min, λ = 360 nm: *Z* isomer: τ_{minor} = 5.8 min, τ_{major} = 5.9 min; *E* isomer: τ_{minor} = 6.4 min, τ_{major} = 6.8 min), *Z* isomer: 50:50 er; *E* isomer: 50:50 er.