Supplementary Materials for

# Enantioselective Intermolecular Radical C–H Amination

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**This PDF file includes:**

## Table of Contents

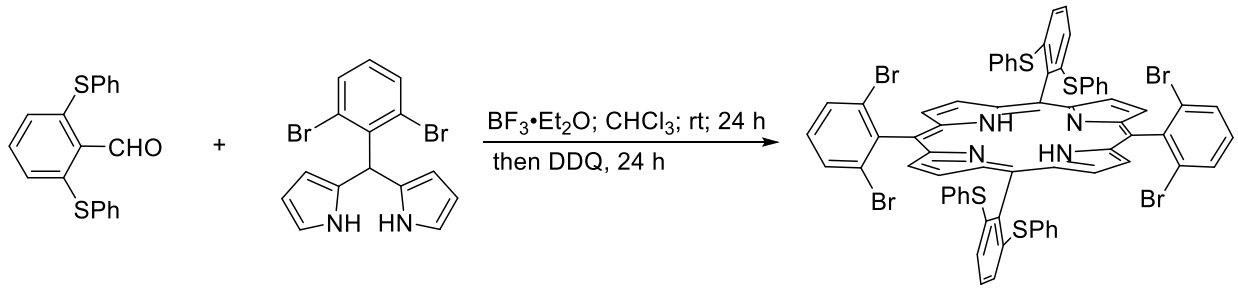
## 1. General Considerations

Proton nuclear magnetic resonance ($^{1}$H NMR) spectra and carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on a Varian 600-MHz or Bruker 500-MHz or Bruker 400- MHz instrument. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = 7.26 ppm, $(CH_3)_2CO$ = 2.05 ppm, $(CH_3)_2SO$ = 2.5 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = 77.00 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS and JEOL Accu TOF Dart at the Mass Spectrometry Facility, Boston College. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel OD-H, OJ-H, AD-H, IA, IB, IC, ID, IE, IF and Whelk columns. The UV-Vis absorption spectra in the range 200–700 nm were measured with an Evolution 300 UV-VIS spectrophotometer using quartz cuvettes with 1.0 dm optical path length.

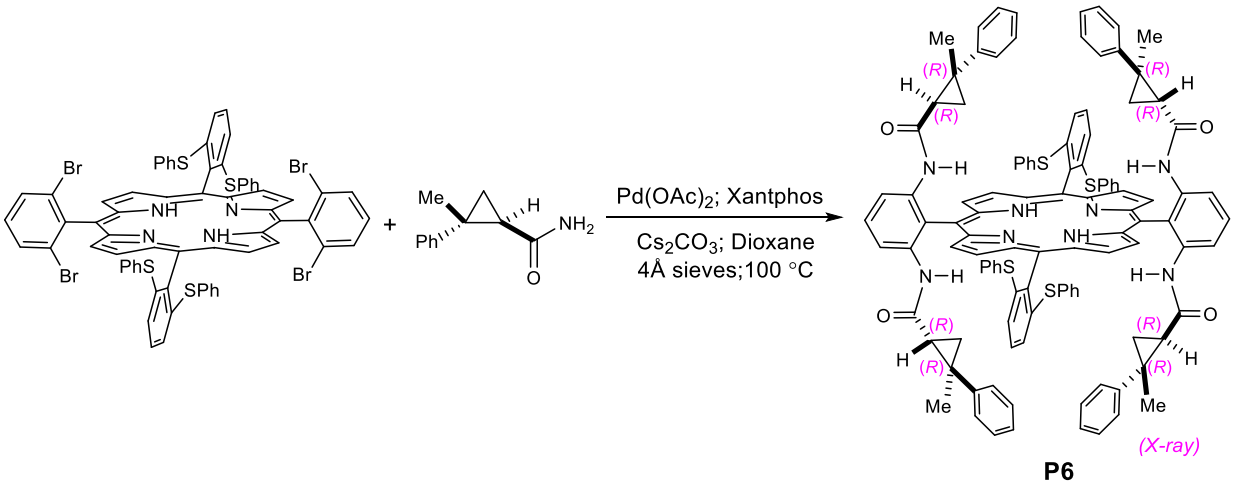
Unless otherwise noted, all catalytic reactions were performed under an atmosphere of $N_2$, in oven-dried glassware following standard vacuum line techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Anhydrous solvents as well as other commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, Strem, Oakwood Products Inc., TCI, or Matrix Scientific and used as received unless otherwise stated. All azides were synthesized according to the reported procedure (*1*, *2*). Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm).

## 2. Synthesis of Catalysts and Substrates

### 2.1. Synthesis of [Co(P6)] (P6 = 2,6-DiPhS-QingPhyrin)

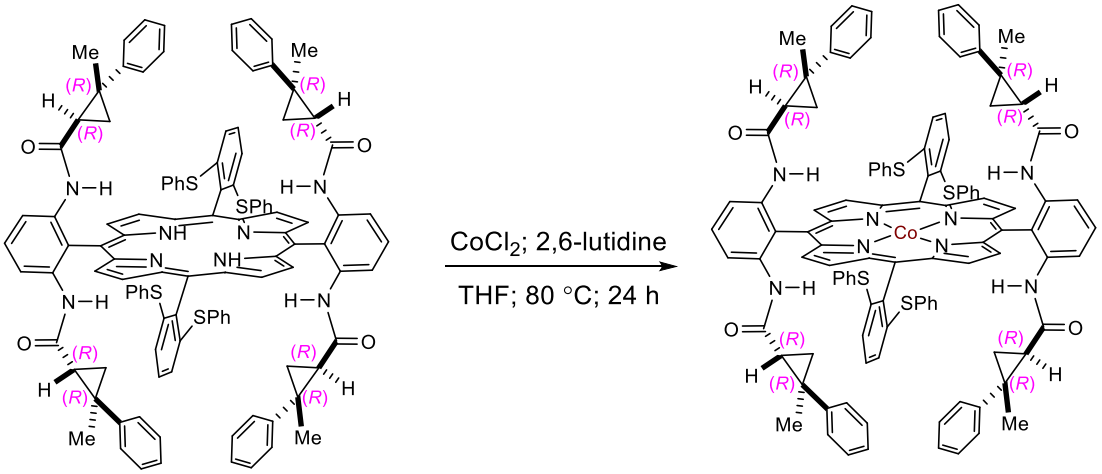



5,15-bis(2,6-bis(phenylthio)phenyl)-10,20-bis(2,6-dibromophenyl)porphyrin was synthesized through modified procedure of our reported method (*3*) : A mixture of 2,6-bis(phenylthio)benzaldehyde (*4*) (828 mg, 2.6 mmol), *meso*-(2,6-dibromophenyl)dipyrromethane (1 g, 2.6 mmol) in chloroform (300 mL) was purged with nitrogen for 5 min. Boron trifluoride diethyl etherate (0.26 mL) was added dropwise via a syringe and the flask was wrapped with aluminum foil to shield it from light. The solution was stirred under a nitrogen atmosphere at room temperature for 24 h, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (700 mg, 3 mmol) was added as powder at one time. After 24 h, 1 mL of triethylamine was added. The reaction solution was then allowed to sit in refrigerator for overnight to precipitate the product. The precipitate was then filtrated out through Büchner funnel. The residue was washed several times with methanol and then hexanes to afford the pure compound **5,15-bis(2,6-bis(phenylthio)phenyl)-10,20-bis(2,6-dibromophenyl)porphyrin** (510 mg, 29% yield). $^{1}$H NMR (600 MHz, DMSO-$d_6$): δ 8.77 (brs, 4H), 8.62 (m, 4H), 8.21 (d, $J$ = 8.3 Hz, 4H), 7.76 (t, $J$ = 8.4 Hz, 2H), 7.67 (t, $J$ = 8.3 Hz, 2H), 7.30 (d, $J$ = 8.3 Hz, 4H), 7.27 – 7.19 (m, 20H), -2.48 (s, 2H). $^{13}$C NMR spectrum could not be obtained due to poor solubility of the compound. UV–vis ($CHCl_3$), $\lambda_{max}$ nm (log ε): 432 (5.42), 524 (4.37), 560 (3.72), 598 (3.95), 654 (3.36). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{68}H_{43}Br_4N_4S_4$: 1358.9104; Found: 1358.9092.



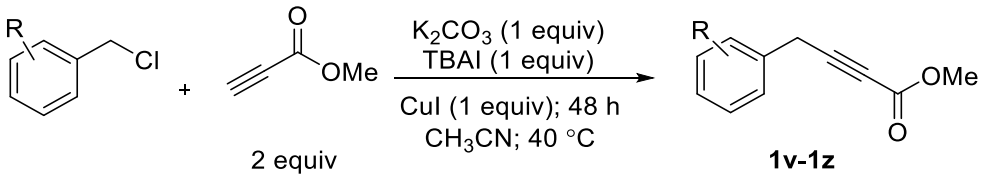

**P6**

**P6** was synthesized according to our previously reported procedure (*3*). The 5,15-bis(2,6-bis(phenylthio)phenyl)-10,20-bis(2,6-dibromophenyl)porphyrin (360 mg, 0.26 mmol), (1*R*,2*R*)-2-methyl-2-phenylcyclopropane-1-carboxamide (*5*) (528 mg, 3 mmol), $Pd(OAc)_2$ (27 mg, 0.12 mmol), Xantphos (138 mg, 0.24 mmol), 4 Å molecular sieves and $Cs_2CO_3$ (1.95 g, 6 mmol) were placed in an oven-dried, re-sealable Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen for three times. The screw cap was replaced with a rubber septum, and dioxane (24 mL) was added via syringe. The tube was purged with nitrogen for 1 min, and then the septum was replaced with the Teflon screw cap. The tube was sealed, and its contents were heated at 100 $^{o}$C for 72 h with stirring. The resulting mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a short pad of silica gel and concentrated in vacuo. The crude product was then purified by flash chromatography (silica gel, EtOAc/hexanes = 1/3, v/v) to give the desired product **P6** (300 mg, 66% yield). $^{1}$H NMR (600 MHz, $CDCl_3$): δ 8.96 – 8.91 (m, 8H), 8.51 (brs, 4H), 7.91 (brs, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.21 – 7.15 (m, 24H), 6.83 (s, 4H), 6.33 (brs, 4H), 6.14 (brs, 8H), 6.01 (brs, 8H), 1.12 (brs, 12H), 0.71 (brs, 4H), 0.54 (brs, 4H), 0.36 (brs, 4H), -2.06 (s, 2H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 168.74, 144.36, 143.09, 138.88, 137.20, 133.54, 133.47, 130.21, 129.88, 129.28, 128.31, 127.31, 125.67, 125.14, 121.72, 118.26, 117.06, 108.19, 30.65, 28.83, 19.30, 18.96. UV–vis ($CHCl_3$), $\lambda_{max}$ nm (log ε): 436 (5.28), 524 (4.29), 5.64 (3.70), 596 (3.9), 650 (3.47). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{112}H_{91}N_8O_4S_4$: 1739.6046; Found: 1739.6077.

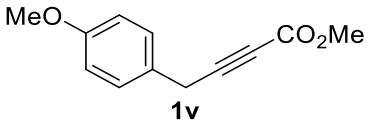



[Co(**P6**)] was synthesized according to our previously reported procedure (*3*). Free base porphyrin **P6** (230 mg, 0.13 mmol) and anhydrous $CoCl_2$ (170 mg, 1.3 mmol) were placed in an oven-dried, re-sealable Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. The screw cap was replaced with a rubber septum, 2,6-lutidine (139 mg, 1.3 mmol) and dry THF (5 mL) were added via syringe. The tube was purged with nitrogen for 1 min, and then the septum was replaced with the Teflon screw cap. The tube was sealed, and its contents were heated at 80 $^{o}$C for 24 h with stirring. The resulting mixture was cooled to room temperature, diluted with ethyl acetate, and transferred to a separatory funnel. The mixture was washed with water 3 times and concentrated in vacuo. The pure compound [Co(**P6**)] was obtained after flash column chromatography (200 mg, 86% yield). UV–vis ($CHCl_3$), $\lambda_{max}$ nm (log ε): 426 (5.18), 532 (4.2), 570 (3.94). HRMS (ESI) ($[M]^+$) Calcd. for $C_{112}H_{89}CoN_8O_4S_4$: 1796.5222, Found: 1796.5177.

## 2.2. Synthesis of Substrates

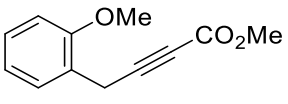



**1v**–**1z** were synthesized according to reported procedure (*6*). An oven-dried round-bottom flask with a stir bar was charged with CuI (5 mmol), $K_2CO_3$ (5 mmol) and tetrabutylammonium iodide (5 mmol). The flask was placed under a nitrogen atmosphere, and then anhydrous acetonitrile (25 mL) was added via syringe. Next, the benzyl chloride (5 mmol) was added via syringe (if the benzyl chloride was a solid, it was added before the flask was placed under nitrogen), followed by methyl propiolate (10 mmol). The reaction mixture was stirred at 40 °C for 48 h, and then the reaction was quenched with saturated aqueous $NH_4Cl$. The reaction mixture was extracted twice with $Et_2O$, and the combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography (hexanes/ethyl acetate, 40:1 to 20:1 gradient) to afford the products **1v**-**1z**.




**1v**

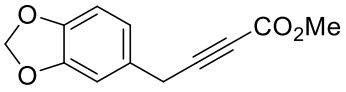
**Methyl 4-(4-methoxyphenyl)but-2-ynoate 1v**. Yellow oil. Yield: 81%. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.68 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 158.76, 154.12, 129.01, 125.95, 114.18, 87.19, 74.27, 55.29, 52.60, 24.14. This compound is known.




**1w**

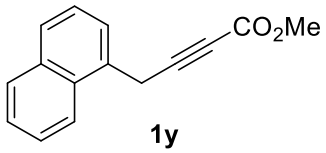
**Methyl 4-(2-methoxyphenyl)but-2-ynoate 1w**. Yellow oil. Yield: 73%. $^1$H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.1 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.70 (s, 2H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 156.64, 154.18,

128.91, 128.47, 122.44, 120.56, 110.11, 87.19, 74.21, 55.28, 52.59, 19.45. This compound is known.




**1x**

**Methyl 4-(benzo[d][1,3]dioxol-5-yl)but-2-ynoate 1x**. Yellow oil. Yield: 80%. $^{1}$H NMR (600 MHz, $CDCl_3$) δ 6.80 (s, 1H), 6.80 – 6.75 (m, 2H), 5.94 (s, 2H), 3.77 (s, 3H), 3.64 (s, 2H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 154.03, 147.94, 146.74, 127.55, 121.02, 108.52, 108.36, 101.24, 86.75, 74.41, 52.62, 24.65. IR (neat, $cm^{-1}$): 2898, 2237, 1708, 1487, 1241, 1034, 750. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{12}H_{11}O_4$: 219.06519, Found: 219.06505.




**1y**

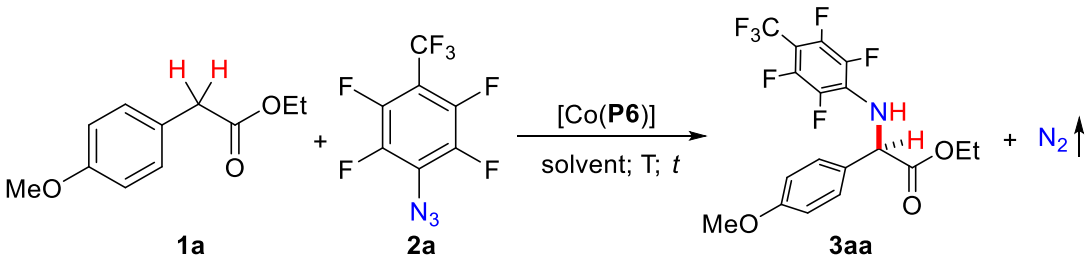
**Methyl 4-(naphthalen-1-yl)but-2-ynoate 1y**. Yellow oil. Yield: 73%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.53 (m, 1H), 7.45 (dd, *J* = 8.3, 7.0 Hz, 1H), 4.13 (s, 2H), 3.77 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 154.08, 133.72, 131.17, 129.81, 128.83, 128.20, 126.53, 126.10, 125.97, 125.53, 122.99, 86.35, 75.27, 52.64, 22.88. This compound is known.


**1z**

**Methyl 4-(thiophen-2-yl)but-2-ynoate 1z.** Yellow oil. Yield: 49%. $^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 5.0 Hz, 1H), 6.96 (m, 1H), 6.93 (m, 1H), 3.89 (s, 2H), 3.76 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 153.79, 135.77, 126.93, 125.86, 124.72, 85.34, 74.04, 52.60, 19.73. IR (neat, $cm^{-1}$): 2953, 2238, 1707, 1433, 1249, 1078, 699. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_9H_9O_2S$: 181.03178, Found: 181.03123.

## 3. Optimization of Reaction Conditions

**Table S1. Optimization of Reaction Conditions using [Co(P6)]**[a]




1a 2a 3aa

| entry | temp ($^{o}$C) | solvent | yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|
| 1 | 40 | benzene | 43 | 97 |
| 2 | 60 | benzene | 80 | 88 |
| 3 | 40 | fluobenzene | 12 | 92 |
| 4 | 40 | hexane | 26 | 95 |
| 5 | 40 | α,α,α-trifluorotoluene | 25 | 96 |
| 6[d] | 40 | α,α,α-trifluorotoluene | 68 | 97 |
| 7[e] | 40 | α,α,α-trifluorotoluene | 95 | 97 |
| 8[e] | 20 | α,α,α-trifluorotoluene | 38 | 97 |

[a] Carried out with **1a** (0.10 mmol) and **2a** (0.15 mmol) in the presence of 4Å MS by [Co(**P6**)] (2 mol %) in solvent (0.5 mL) for 24 h. [b] Isolated yields. [c] Determined by chiral HPLC. [d] [Co(**P6**)] (4 mol %) and 24 h. [e] [Co(**P6**)] (4 mol %) and 48 h.

## 4. DFT-Generated Stereochemical Models for [Co(P6)]-Catalyzed C–H Amination

### 4.1. Computational Details and Simplifications

The calculations were performed using the Gaussian 09 D.01 program. Considering the time cost and computing resource for the large system with [Co(**P6**)], all the structures were optimized at the BP86 (*7, 8*) level of density functional theory with the basis set LANL2DZ (*9, 10*) in the gas phase at room temperature. Frequency calculations were performed to verify the transition states. Intrinsic reaction coordinate (IRC) (*11*) calculations were carried out to make sure that every transition state links relevant intermediates. Due to the large size and conformational complexity of the system under investigation, no efforts have been made to improve the accuracy of single point energies at the B3LYP6 (*10*)/def2-tzvp (*9*, *10*) level of theory along with Grimme's dispersion correction (D3BJ) (*12*)and SMD (*13*) model (in trifluorotoluene).

### 4.2. Transition States of Radical Substitution Step

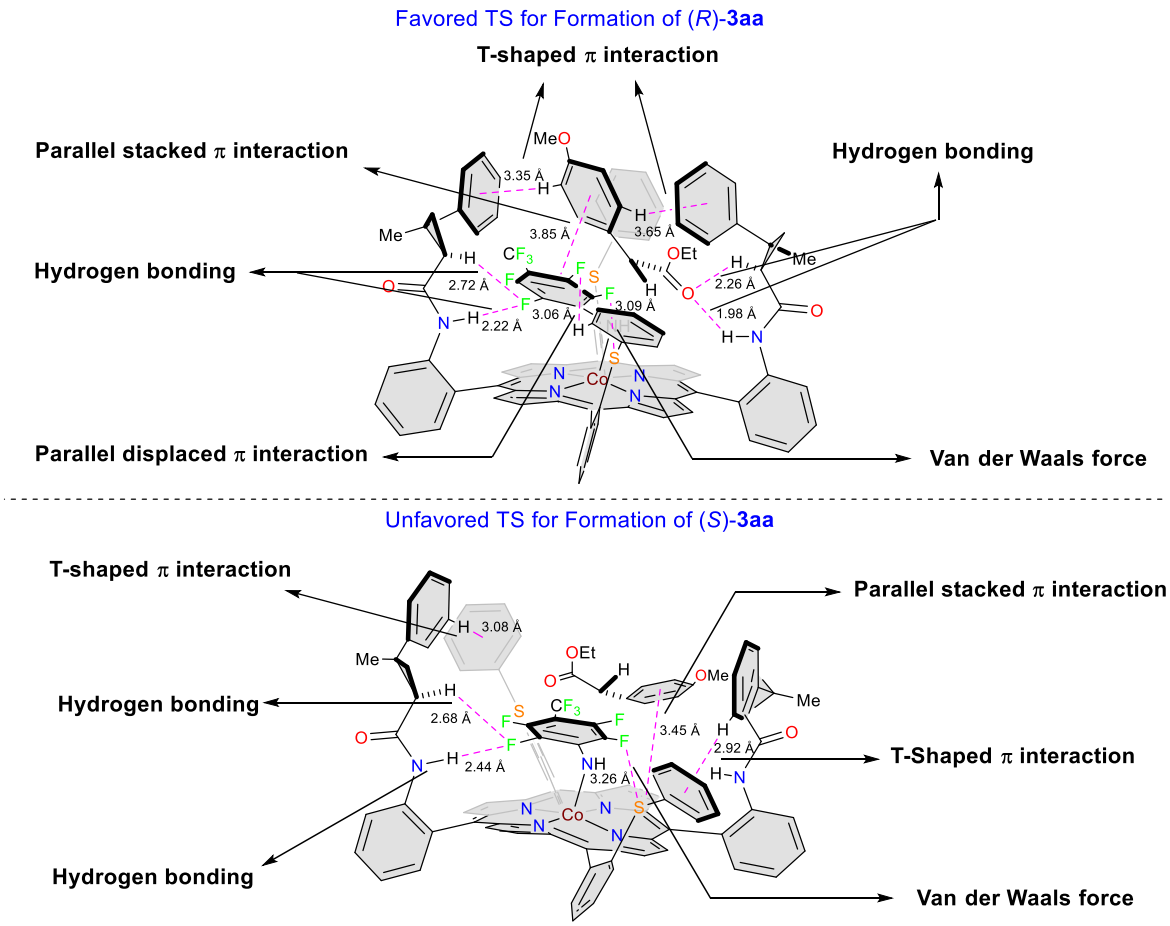



**Figure S1.** DFT-generated stereochemical models for [Co(**P6**)]-catalyzed C–H amination. Substituents at Bottom Side Omitted for Clarity

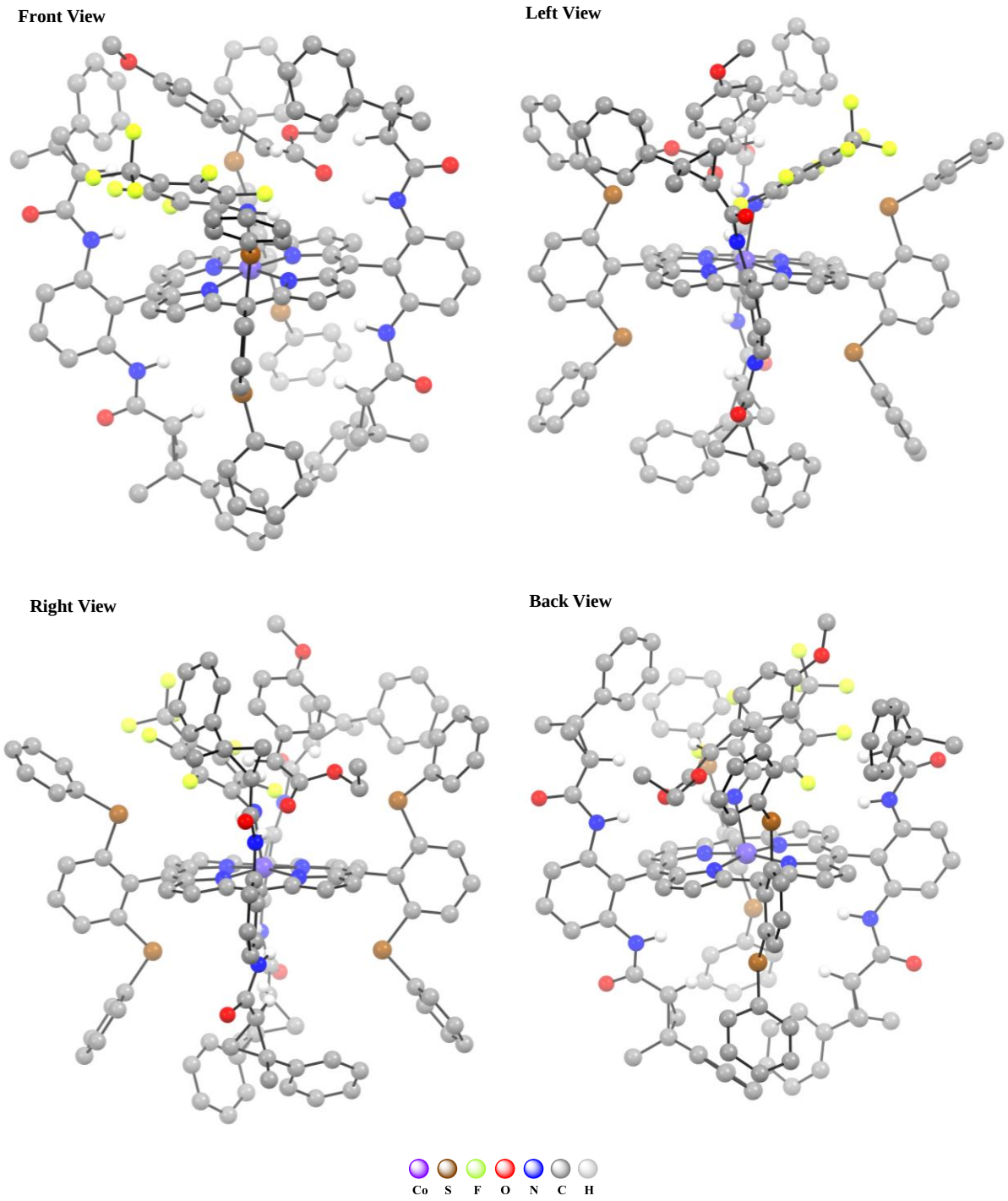



**Figure S2.** Favored transition state structure for formation of (*R*)-**3aa**; ball and stick model; most hydrogen atoms have been omitted for clarity.

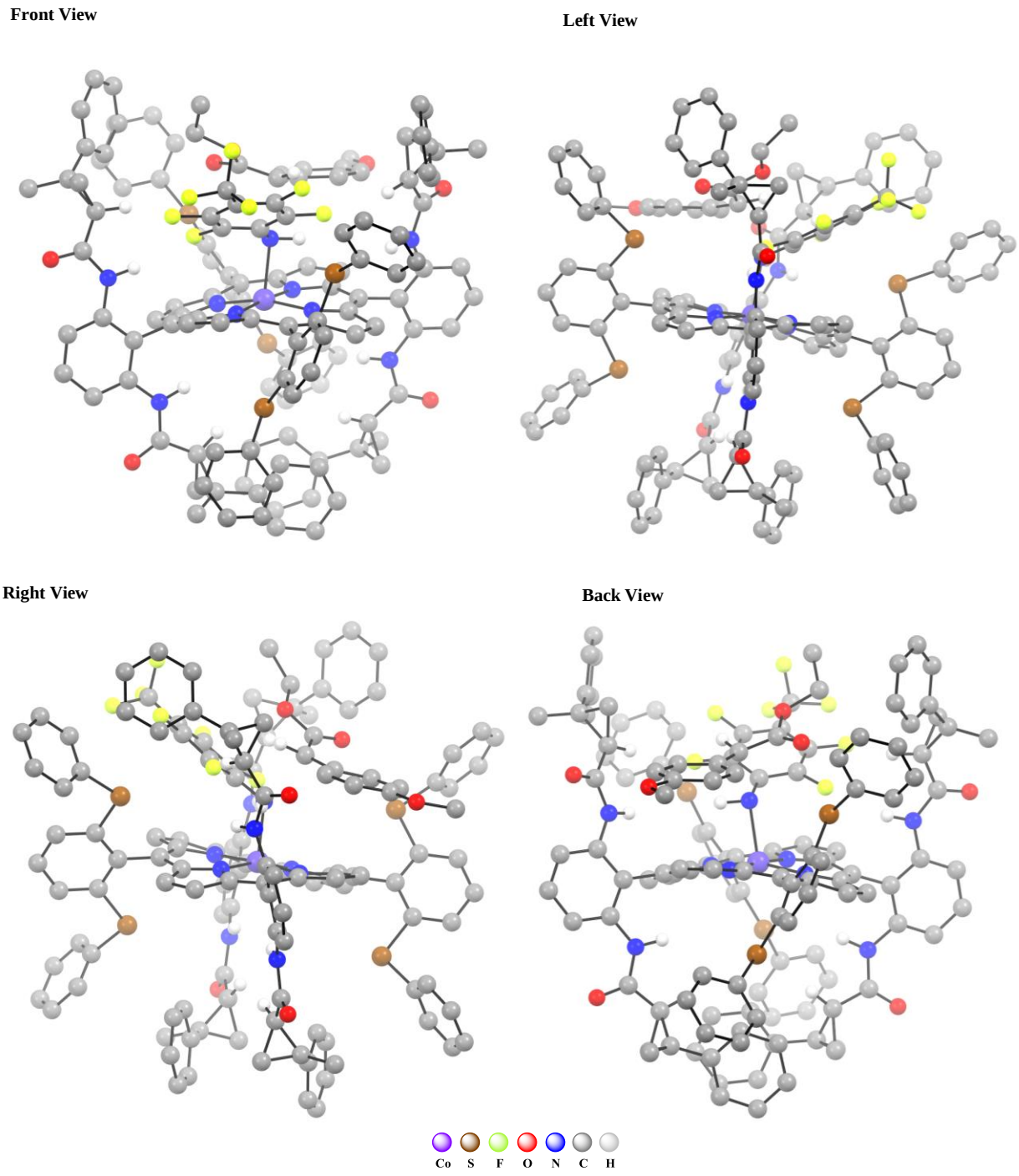



**Figure S3.** Unfavored transition state structure for formation of (*S*)-**3aa**; ball and stick model; most hydrogen atoms have been omitted for clarity.

**XYZ Coordinate**

TS for (*R*)-**3aa**

G = -6916.656735

| | XYZ Coordinate | | |
|---|---|---|---|
| | X | Y | Z |
| H | 3.976490 | 10.686526 | -1.150360 |
| C | 3.452595 | 9.728580 | -1.051731 |
| H | 4.120114 | 8.975292 | -2.990130 |
| H | 2.643873 | 10.186610 | 0.924963 |
| C | 3.532687 | 8.767128 | -2.088676 |
| H | -2.462585 | 8.381398 | -2.408236 |
| C | 2.702126 | 9.448721 | 0.116639 |
| H | -7.920704 | 5.468117 | -3.940280 |
| C | -2.146599 | 7.387165 | -2.071996 |
| H | -0.113768 | 8.016713 | -1.619362 |
| C | 2.861821 | 7.525884 | -1.963311 |
| H | -4.094531 | 6.484705 | -2.416280 |
| C | -7.393807 | 5.356411 | -2.986075 |
| C | 2.029393 | 8.209409 | 0.248964 |
| H | -8.920198 | 6.398950 | -1.827709 |
| C | -0.823055 | 7.184263 | -1.631024 |
| C | -3.066722 | 6.318785 | -2.082186 |
| C | -7.956677 | 5.877269 | -1.795890 |
| C | 2.107861 | 7.256476 | -0.795863 |
| C | -6.147167 | 4.683749 | -2.948805 |
| H | 2.929211 | 6.772489 | -2.754345 |
| H | -5.702723 | 4.281310 | -3.865401 |
| H | 1.453989 | 7.979934 | 1.152289 |
| F | 4.377872 | 4.693775 | -3.973472 |
| F | 4.805698 | 2.748731 | -5.039284 |
| C | -7.276203 | 5.718735 | -0.562638 |
| C | -0.415801 | 5.897862 | -1.205639 |
| C | -2.653956 | 5.035231 | -1.653464 |
| C | -5.470589 | 4.531870 | -1.714244 |
| H | -0.737749 | 3.756086 | -3.623267 |
| C | 4.811375 | 3.355291 | -3.775792 |
| H | -7.709877 | 6.116041 | 0.362171 |
| C | -6.033224 | 5.041725 | -0.517753 |
| S | 1.305305 | 5.592469 | -0.582441 |
| C | -1.313972 | 4.786838 | -1.219645 |
| F | 3.777990 | 0.576868 | -4.039908 |

| | | | |
|---|---|---|---|
| S | -3.856971 | 3.607513 | -1.650560 |
| C | -0.655394 | 2.747471 | -3.220966 |
| H | -0.514916 | 1.391603 | -4.983270 |
| F | 6.191309 | 3.455366 | -3.390243 |
| H | -1.126431 | -1.832494 | -8.568992 |
| C | 3.994315 | 2.635634 | -2.742022 |
| C | -0.544911 | 1.556316 | -3.907124 |
| O | 3.145484 | -1.919783 | -6.820483 |
| H | -7.208174 | 0.127533 | -5.689756 |
| C | -0.996501 | -1.693265 | -7.489602 |
| H | -5.503138 | 4.909207 | 0.431451 |
| H | 1.177504 | -1.916178 | -7.563351 |
| C | 3.509965 | 1.311131 | -2.886388 |
| C | 0.298806 | -1.742079 | -6.941698 |
| C | -2.130908 | -1.493043 | -6.679813 |
| H | -3.135793 | -1.518781 | -7.099678 |
| F | 4.292937 | 4.507153 | -1.216800 |
| C | -0.909172 | 3.389129 | -0.797918 |
| C | 3.738711 | 3.254104 | -1.490602 |
| H | -7.633353 | 2.718209 | -1.203523 |
| C | -0.668078 | 2.426430 | -1.800650 |
| C | -7.350563 | -0.924674 | -5.378611 |
| C | 2.966286 | -2.029173 | -5.563944 |
| C | -8.026706 | 1.776304 | -1.600795 |
| C | 0.472354 | -1.555400 | -5.541928 |
| H | 5.663737 | -1.947225 | -6.071621 |
| H | -6.188692 | 1.288074 | -2.666764 |
| C | -7.209709 | 0.965236 | -2.426410 |
| H | 7.697061 | 4.360349 | 1.490944 |
| H | -8.427476 | -1.160464 | -5.473482 |
| H | -1.446208 | 5.060827 | 1.451477 |
| C | 2.784339 | 0.668792 | -1.868642 |
| C | -9.352216 | 1.382835 | -1.301211 |
| C | -1.962976 | -1.283690 | -5.284714 |
| H | -6.776702 | -1.575428 | -6.057323 |
| H | -9.986178 | 2.017755 | -0.670813 |
| N | 1.747856 | -1.733937 | -4.930750 |
| C | -0.482298 | 0.494300 | -2.911693 |
| C | -0.652210 | -1.254053 | -4.703189 |
| F | 2.431793 | -0.669778 | -2.057509 |
| C | -7.700811 | -0.255899 | -2.952462 |
| C | 4.040670 | -2.536647 | -4.645815 |
| C | 2.987182 | 2.619664 | -0.500129 |

| | | | |
|---|---|---|---|
| C | 5.516128 | -2.401453 | -5.085910 |
| C | -6.907218 | -1.117994 | -3.919214 |
| N | -3.105451 | -1.113106 | -4.437270 |
| C | -9.854260 | 0.164756 | -1.823409 |
| H | 4.329334 | -3.811389 | -7.169811 |
| C | 7.062568 | 4.098447 | 2.346431 |
| C | -1.242315 | 4.005026 | 1.622203 |
| H | 5.212937 | 4.772991 | 1.399216 |
| N | -0.513393 | 1.033788 | -1.604784 |
| C | -9.032258 | -0.645705 | -2.637593 |
| C | -0.939694 | 3.048118 | 0.568002 |
| C | 2.451767 | 1.302890 | -0.638707 |
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| H | -2.930726 | -0.704106 | -3.514144 |
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| O | -4.687322 | -2.262791 | -5.742367 |
| C | 5.665030 | 4.330241 | 2.294032 |
| H | -10.881030 | 5 -0.14834 | 1 -1.597567 |
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| H | 1.762657 | -1.710419 | -3.905902 |
| H | 3.844669 | -2.440024 | -3.571726 |
| H | 8.715506 | 3.360380 | 3.564863 |
| F | 2.813252 | 3.248581 | 0.740274 |
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| C | 4.621965 | -4.523421 | -6.381282 |
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| H | -9.419876 | -1.590761 | -3.039780 |
| C | 4.896511 | -3.796397 | -5.055064 |
| H | -5.022273 | -0.962062 | -2.652428 |
| H | 5.676032 | 1.789883 | 0.444728 |
| C | -1.221674 | 3.316930 | 2.815465 |
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| H | -1.409101 | 3.691952 | 3.820407 |
| C | o -0.30553 | 6 0.05526 | 2 0.128075 |
| H | 1.623766 | 1.273480 | 1.186666 |
| C | 5.720565 | 0.760838 | 0.067573 |

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| H | 3.770922 | 4.198473 | 3.360876 |
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| H | 3.826431 | 1.313165 | 1.761924 |
| H | -6.743851 | -2.810125 | -2.415572 |
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| H | 3.245051 | -5.231818 | -3.367490 |
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| H | 7.263668 | 2.800319 | 5.533218 |
| C | 4.306201 | -5.457131 | -3.203386 |
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| C | 4.823917 | -0.219591 | 0.614359 |
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| H | 5.117733 | 4.970591 | 6.934923 |
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| C | -4.958413 | 1.222580 | 4.173037 |
| H | 9.206686 | -0.976971 | -3.615541 |
| C | -0.880110 | 0.910467 | 3.478787 |
| C | 6.782846 | -0.923478 | -1.332758 |
| C | 4.191331 | 4.487995 | 6.569144 |
| C | 3.204338 | -0.504686 | 2.661072 |
| C | 4.548473 | 3.202826 | 5.807484 |
| O | 2.365148 | 0.041794 | 3.440067 |
| N | -3.602537 | 0.866281 | 4.259234 |
| O | 7.690993 | -1.375141 | -2.287535 |
| H | -8.730216 | -0.357243 | 1.001498 |
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| H | 2.180294 | -2.260785 | 4.272129 |
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| H | 1.346133 | 1.228825 | 4.653656 |
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| C | -2.654995 | 1.301891 | 5.236261 |
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| C | 3.243686 | -2.497329 | 4.101891 |
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| H | 3.533361 | 4.269142 | 7.426209 |
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| H | -7.552525 | 1.123664 | 5.127180 |
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| H | -4.154654 | 1.764597 | 6.740064 |
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| C | 2.149145 | 2.117658 | 6.344540 |

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| C | -0.642617 | -1.507127 | 4.138086 |
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| H | -0.791190 | -1.349987 | 5.205964 |
| H | 3.982687 | -1.033995 | 5.558246 |
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| C | -4.498939 | -6.028630 | 3.379800 |
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TS for (*S*)-**3aa**

G = -6916.653518

| | XYZ Coordinate | | |
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| | X | Y | Z |
| H | -7.758415 | -8.005923 | 2.128014 |
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| H | -8.775079 | -4.330560 | 4.082358 |
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| H | -6.362846 | -4.576396 | -0.169538 |
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| H | -5.629276 | -1.342029 | 8.271755 |
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| H | -4.577352 | -3.656932 | 5.006482 |
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| H | -1.542687 | 2.323790 | 6.131610 |
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| F | -4.332953 | 0.341601 | -3.495036 |
| H | -5.604443 | 2.876766 | -5.187182 |
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| H | -1.233044 | 10.957812 | -1.311497 |
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| C | -3.962083 | 4.376451 | -5.661379 |
| C | -3.343111 | 2.982841 | -5.267087 |
| C | 0.288087 | 7.909340 | -1.840609 |
| H | -0.218958 | -7.408590 | -2.920835 |
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| H | 0.917069 | 7.381583 | -2.565523 |
| C | -2.805466 | 2.366043 | 1.657899 |
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| H | -3.499539 | 1.560259 | 1.921561 |
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| H | -4.221453 | 5.814218 | -7.269777 |
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| C | -3.764320 | 6.677744 | -2.567270 |
| H | 1.315287 | 5.817490 | 5.533873 |
| H | -0.419785 | -5.036563 | 1.517586 |
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| H | -0.183083 | 5.682483 | 3.686574 |
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| H | -2.023211 | 9.751517 | 0.750264 |
| C | -0.180034 | -3.979286 | 1.618661 |
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| H | -1.427218 | -1.502103 | 4.267393 |
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| C | -0.933861 | -2.331334 | -1.735067 |
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| C | -0.985687 | 7.899046 | 0.261438 |
| C | -3.265007 | 3.179155 | 0.500396 |
| H | -1.238380 | 4.656459 | 1.679579 |
| H | -3.018406 | 7.003362 | -1.834446 |
| C | 0.323774 | -3.313299 | 2.718362 |
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| S | 0.271494 | 5.444286 | -0.418889 |
| N | -1.240281 | 1.734377 | -5.415874 |
| O | -2.764687 | 4.239430 | 0.047646 |
| H | 0.587628 | -3.716890 | 3.695741 |
| H | -1.312416 | 1.736021 | -4.391998 |
| N | -0.259625 | -1.087010 | -1.707776 |
| H | -2.377560 | 5.358324 | -3.606198 |
| O | -4.452792 | 2.615370 | -0.004251 |
| H | -2.557241 | 5.751519 | -6.620029 |
| N | 0.092760 | -1.723904 | 0.989190 |
| H | -1.107717 | -1.483407 | -4.970409 |
| H | -7.063031 | 3.348557 | -0.075096 |
| S | 1.135833 | -4.785270 | -2.429105 |
| C | 1.384414 | -6.003724 | -4.981163 |
| H | 0.686762 | -5.228193 | -5.314683 |
| C | 0.476325 | -1.915899 | 2.335408 |
| C | 1.766287 | -6.066627 | -3.618588 |
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| H | -0.362835 | -1.473753 | 7.740798 |
| C | 0.152574 | -1.284935 | 5.635780 |
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| C | 2.687922 | -7.043874 | -3.171642 |
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| H | -4.940772 | 4.443159 | -0.980436 |
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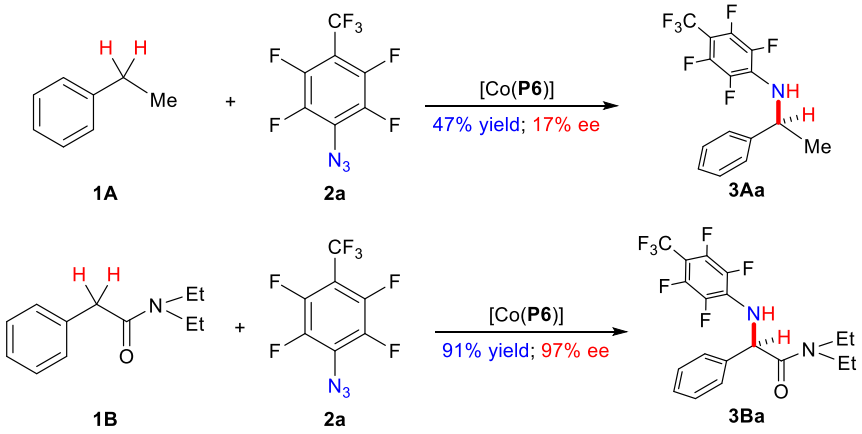
| H | 3.941455 | -8.726077 | -3.754041 |
| N | 1.131461 | 0.861431 | 1.448554 |
| C | 1.147372 | 0.416402 | 2.788577 |
| H | -6.803667 | 1.936619 | -1.146046 |
| C | 1.189316 | 1.312624 | -2.712646 |
| C | 0.819269 | 0.452153 | -5.052300 |
| C | 1.980203 | 5.547793 | 0.315527 |
| H | 2.068307 | 7.725793 | 0.355192 |
| H | -7.162572 | 3.541967 | -1.853343 |
| C | 1.798777 | 2.506061 | -0.927110 |
| C | 1.780907 | -1.701004 | 7.404912 |
| C | 1.599564 | 2.190241 | 1.503080 |
| C | 1.965858 | 2.977786 | 0.389988 |
| C | 2.595867 | 6.794238 | 0.579257 |
| C | 1.967407 | 2.445137 | -3.202442 |
| C | 1.555752 | 1.495464 | 3.678679 |
| H | -4.681489 | 3.045477 | -2.061691 |
| C | 2.332537 | 3.187348 | -2.100962 |
| C | 1.349982 | 0.478488 | -7.837676 |
| C | 1.822550 | 2.590322 | 2.885555 |
| H | 2.009321 | -1.857323 | 8.465411 |
| C | 2.640290 | 4.312555 | 0.615645 |
| C | 2.541472 | -1.525479 | 5.088180 |
| H | 1.626647 | 1.404545 | 4.761459 |
| H | 2.180436 | 2.632795 | -4.254054 |
| C | 2.007855 | -0.159498 | -5.577639 |
| C | 2.830575 | -1.737571 | 6.464179 |
| H | 1.549713 | 0.484972 | -8.915605 |
| H | 3.735063 | -4.871241 | 0.344824 |
| H | 2.916284 | 4.105844 | -2.065840 |
| C | 2.270426 | -0.147571 | -6.974395 |
| H | 2.167350 | 3.578093 | 3.185156 |
| H | 2.609751 | -0.758888 | -3.676212 |
| H | 3.628135 | -3.547021 | -1.768091 |
| N | 2.910357 | -0.770998 | -4.655830 |
| C | 3.894900 | 6.832317 | 1.128778 |
| H | 3.245099 | -1.404670 | 3.132044 |
| N | 3.558795 | -1.591260 | 4.090160 |
| C | 4.629947 | -4.779803 | -0.282069 |

| | | | |
|---|---|---|---|
| C | 4.570418 | -4.026565 | -1.479323 |
| C | 3.973917 | 4.391552 | 1.128791 |
| H | 4.371298 | 7.798185 | 1.333667 |
| H | 3.861391 | -1.932848 | 6.761829 |
| H | 3.181018 | -0.619472 | -7.345149 |
| H | 4.659639 | -4.755699 | -4.779442 |
| C | 4.594192 | 5.636137 | 1.390911 |
| C | 4.171795 | -1.328471 | -4.911185 |
| C | 5.834185 | -5.420097 | 0.096737 |
| C | 4.907584 | -1.946963 | 4.252376 |
| H | 5.879193 | -6.011038 | 1.019665 |
| H | 4.508318 | -1.447944 | -2.722158 |
| O | 4.673629 | -1.419452 | -6.079119 |
| C | 5.708661 | -3.896447 | -2.313817 |
| S | 4.915770 | 2.799323 | 1.342761 |
| C | 5.562528 | -4.121165 | -4.852404 |
| C | 4.910112 | -1.790364 | -3.684203 |
| C | 5.656910 | -3.171892 | -3.648229 |
| H | 5.099922 | -2.065989 | 2.045079 |
| O | 5.430258 | -2.181487 | 5.391063 |
| C | 5.685193 | -2.074562 | 2.972809 |
| H | 5.524982 | -3.556827 | -5.799049 |
| H | 5.615025 | 5.668918 | 1.782525 |
| H | 5.785874 | 0.082978 | 1.032909 |
| C | 6.980540 | -5.292145 | -0.727391 |
| H | 6.444340 | -4.789755 | -4.869450 |
| C | 6.915766 | -4.536478 | -1.920174 |
| H | 6.632220 | 0.993968 | -1.133254 |
| C | 6.793421 | -0.181941 | 0.691030 |
| C | 6.454602 | -1.875397 | -3.783866 |
| C | 6.354793 | 3.339156 | 2.389356 |
| C | 7.272910 | 0.333251 | -0.537415 |
| H | 7.718841 | 3.484760 | 0.698017 |
| C | 7.157845 | -1.539173 | 2.848384 |
| C | 6.901894 | -3.037936 | 2.994427 |
| H | 7.920617 | -5.778598 | -0.439537 |
| H | 5.232574 | 3.214418 | 4.252354 |
| C | 7.611610 | 3.577946 | 1.783557 |
| H | 7.028881 | -3.682411 | 2.119031 |
| H | 6.863241 | -1.644016 | -4.773583 |
| C | 6.204765 | 3.427743 | 3.795224 |
| C | 7.600356 | -1.033682 | 1.485667 |
| H | 7.026112 | -1.514315 | -2.923313 |

| | | | |
|---|---|---|---|
| H | 7.114328 | -3.488331 | 3.970017 |
| H | 7.807631 | -4.431518 | -2.551069 |
| H | 7.538537 | 0.306917 | 3.955673 |
| C | 7.791011 | -0.768143 | 4.016501 |
| H | 7.443090 | -1.161942 | 4.985762 |
| C | 8.573441 | 0.003507 | -0.988215 |
| C | 8.723820 | 3.919496 | 2.591916 |
| C | 8.903103 | -1.363658 | 1.020835 |
| C | 7.318657 | 3.775529 | 4.596799 |
| H | 8.947422 | 0.404969 | -1.937951 |
| C | 9.387610 | -0.851383 | -0.203823 |
| C | 8.578026 | 4.022833 | 3.996322 |
| H | 8.892879 | -0.858777 | 3.968209 |
| H | 9.698619 | 4.097158 | 2.123743 |
| H | 7.204991 | 3.839186 | 5.685092 |
| H | 9.533792 | -2.030347 | 1.623099 |
| H | 10.393930 | -1.118523 | -0.548805 |
| H | 9.440960 | 4.283844 | 4.620000 |

### 4.3. Comparative Study on Intermolecular C–H Amination Reactions of Ethyl Benzene and Arylacetamide



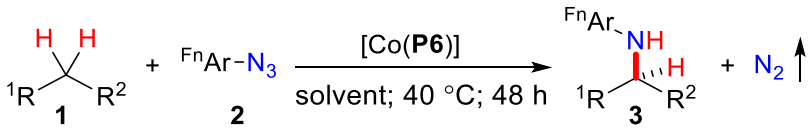

An oven dried Schlenk tube was charged with catalyst ([Co(**P6**)], 4 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and **1A** or **1B** (0.1 mmol), azide **2a** (1.5 equiv) and α,α,α-trifluorotoluene (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 °C for 48 h. Following completion of the reaction, the reaction mixture was concentrated and then directly purified by flash chromatography give the product **3Aa** or **3Ba**.

**3Aa**: Yield: 47%. $[\alpha]_D^{20}$= -8° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.22 (m, 3H), 5.01 (m, 1H), 4.43 (d, *J* = 8.6 Hz, 1H), 1.58 (d, *J* = 6.7 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.78 (dm, *J* = 258.9 Hz), 143.60, 136.66 (dm, *J* = 240.3 Hz), 130.29 (m), 128.88, 127.70, 125.43, 121.51 (q, *J* = 272.8 Hz), 96.52 (m), 54.54 (t, *J* = 4.3 Hz), 24.58. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.01 (t, *J* = 20.8 Hz, 3F), -143.31 (m, 2F), -158.97 (m, 2F). IR (neat, $cm^{-1}$): 3340, 2930, 1656, 1512, 1334, 1237, 1133, 984, 872. HRMS (DART) ($[M]^+$) Calcd. for: $C_{15}H_{10}F_7N$: 337.06960, Found: 337.06953. HPLC analysis: ee = 17%. IA (98% hexane: 2% isopropanol, 0.8 ml/min): $t_{major}$ = 5.57 min, $t_{minor}$ = 5.38 min.

**3Ba**: Yield: 91%. $[\alpha]_D^{20}$= -135° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.31 (m, 1H), 6.07 (br, 1H), 5.61 (d, *J* = 8.6 Hz, 1H), 3.47 (dq, *J* = 13.9, 7.1 Hz, 1H), 3.34 (m, 2H), 3.19 (dq, *J* = 14.4, 7.0 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 168.35, 144.78 (dm, *J* = 256.0 Hz), 137.34, 137.20 (dm,

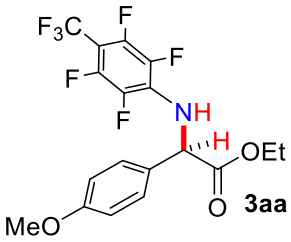
*J* = 239.8 Hz), 129.70 (m), 129.26, 128.81, 127.48, 121.50 (q, *J* = 272.7, 272.3 Hz), 97.04 (m), 58.24 (t, *J* = 3.9 Hz), 41.28, 40.91, 13.47, 12.47. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.07 (t, *J* = 20.9 Hz, 3F), -143.50 (m, 2F), -157.60 (m, 2F). IR (neat, $cm^{-1}$): 3340, 2979, 1652, 1506, 1334, 1133, 979, 883. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{19}H_{18}F_7N_2O$: 423.13033, Found: 423.13019. HPLC analysis: ee = 97%. IA (80% hexane: 20% isopropanol, 0.5 ml/min): $t_{major}$ = 7.60 min, $t_{minor}$ = 8.19 min.

## 5. General Procedure for [Co(P6)] Catalyzed C–H Amination with Fluoroaryl Azides

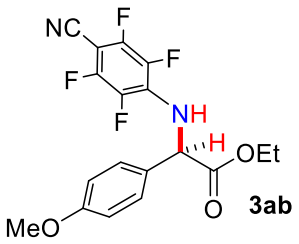



An oven dried Schlenk tube was charged with catalyst ([Co(**P6**)], 4 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and C–H substrate (0.1 mmol), azide (1.2 or 1.5 equiv) and solvent (α,α,α-trifluorotoluene or benzene) (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 °C for 48 h. Following completion of the reaction, the reaction mixture was concentrated and then directly purified by flash chromatography.

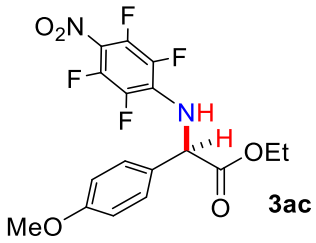
### 5.1. Enantioselective C–H Amination of 1a with Various Fluoroaryl Azides



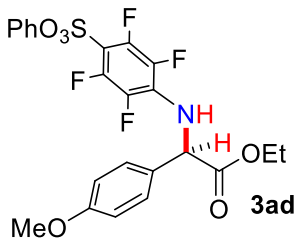

**Ethyl (*R*)-2-(4-methoxyphenyl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) acetate 3aa** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 95%. $[\alpha]_D^{20}$= -90° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 5.42 (m, 2H), 4.25 (m, 2H), 3.80 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 171.03, 160.00, 144.77 (dm, *J* = 249.9 Hz), 136.93 (dm, *J* = 241.6 Hz), 129.25 (t, *J* = 11.1 Hz), 128.65, 128.15, 121.44 (q, *J* = 272.8 Hz), 114.50, 97.39 (m), 62.30, 60.06, 55.25. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.11 (t, *J* = 20.9 Hz, 3F), -143.03 (m, 2F), -158.56 (m, 2F). IR (neat, $cm^{-1}$): 3387, 2915, 2848, 1737, 1657, 1509, 1332, 1235, 1176, 1131, 713. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{18}H_{13}F_7NO_3$: 424.0784, Found: 424.0793. HPLC analysis: ee = 97%. Whelk (99.5% hexane: 0.5% isopropanol, 1 ml/min): $t_{major}$ = 7.48 min, $t_{minor}$ = 9.68 min.



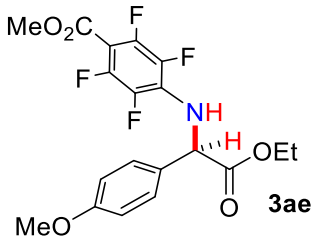

**Ethyl (*R*)-2-((4-cyano-2,3,5,6-tetrafluorophenyl)amino)-2-(4-methoxyphenyl)acetate 3ab** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 53%. $[\alpha]_D^{20}$= -200° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.66 (br, 1H), 5.42 (d, *J* = 7.5 Hz, 1H), 4.20 (m, 2H), 3.79 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.71, 160.08, 147.58 (dm, *J* = 254.7 Hz), 135.99 (dm, *J* = 245.8 Hz), 131.30 (m), 128.30, 128.11, 114.55, 108.53 (t, *J* = 3.6 Hz), 80.82 (t, *J* = 17.7 Hz), 62.49, 59.95, 55.27, 13.93. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -134.81 (m, 2F), -157.67 (m, 2F). IR (neat, $cm^{-1}$): 3383, 2983, 2235, 1737, 1656, 1510, 1178, 837. HRMS (DART) ($[M+NH_4]^+$) Calcd. for: $C_{18}H_{18}F_4N_3O_3$: 400.12788, Found: 400.12793. HPLC analysis: ee = 90%. IC (90% hexane: 10% isopropanol, 0.8 ml/min): $t_{major}$ = 22.20 min, $t_{minor}$ = 23.52 min.




**Ethyl (*R*)-2-(4-methoxyphenyl)-2-((2,3,5,6-tetrafluoro-4-nitrophenyl)amino)acetate 3ac** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 60%. $[\alpha]_D^{20}$= -245° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.65 (d, *J* = 8.4 Hz, 1H), 5.41 (d, *J* = 8.4 Hz, 1H), 4.22 (m, 2H), 3.79 (s, 3H), 1.21 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 173.34, 162.77, 144.86 (dm, *J* = 261.3 Hz), 138.83 (dm, *J* = 243.6 Hz), 132.97 (t, *J* = 10.7 Hz), 130.86, 130.74, 122.72, 117.22, 65.19, 62.63, 57.90, 16.61. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -146.96 (m, 2F), -158.46 (m, 2F). IR (neat, $cm^{-1}$): 3379, 2983, 1737, 1640, 1549, 1334, 1177, 1027, 769. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{17}H_{15}F_4N_2O_5$: 403.09116, Found: 403.09007. HPLC analysis: ee = 96%. IC (90% hexane: 10% isopropanol, 0.8 ml/min): $t_{major}$ = 18.12 min, $t_{minor}$ = 18.83 min.

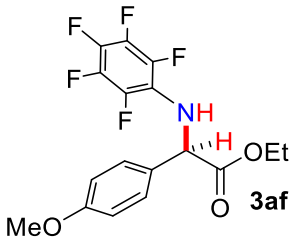



**Ethyl (*R*)-2-(4-methoxyphenyl)-2-((2,3,5,6-tetrafluoro-4-(phenoxysulfonyl)phenyl amino) acetate 3ad** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 60%. $[\alpha]_D^{20}$= -67° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.32 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 5.67 (d, *J* = 7.3 Hz, 1H), 5.42 (d, *J* = 7.3 Hz, 1H), 4.21 (m, 2H), 3.81 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.70, 160.08, 149.10, 145.45 (dm, *J* = 260.8 Hz), 136.93 (dm, *J* = 246.1 Hz), 131.71 (m), 129.92, 128.28, 128.13, 127.59, 121.70, 114.55, 102.01 (m), 62.50, 59.93, 55.29, 13.93. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -136.72 (m, 2F), -157.89 (m, 2F). IR (neat, $cm^{-1}$): 3383, 2936, 1737, 1636, 1501, 1200, 1144, 777. HRMS (DART) ($[M+NH_4]^+$) Calcd. for: $C_{23}H_{23}F_4N_2O_6S$: 531.12075, Found: 531.12103. HPLC analysis: ee = 87%. ODH (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 25.48 min, $t_{minor}$ = 27.93 min.

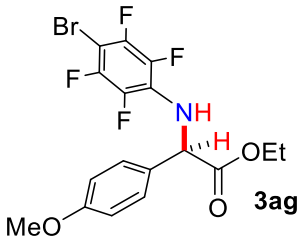



**Methyl (*R*)-4-((2-ethoxy-1-(4-methoxyphenyl)-2-oxoethyl)amino)-2,3,5,6-tetrafluorobenzoate 3ae** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 87%. $[\alpha]_D^{20}$= -212° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.40 (m, 2H), 4.19 (m, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.07, 160.90 (t, *J* = 3.0 Hz), 159.92, 146.17 (dm, *J* = 253.4 Hz), 136.84 (dm, *J* = 238.9 Hz), 129.07 (m), 128.75, 128.14, 114.43, 99.86 (t, *J* = 14.3 Hz), 62.22, 60.13, 55.24, 52.52, 13.94. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -140.24 (m, 2F), -159.03 (m, 2F). IR (neat, $cm^{-1}$): 3385, 2957, 2840, 1731, 1652, 1512, 1232, 1180, 1026. HRMS (DART) ($[M+NH_4]^+$) Calcd. for: $C_{19}H_{21}F_4N_2O_5$: 433.13811, Found: 433.13813. HPLC

analysis: ee = 96%. IC (90% hexane: 10% isopropanol, 0.8 ml/min): $t_{major}$ = 18.16 min, $t_{minor}$ = 19.37 min.

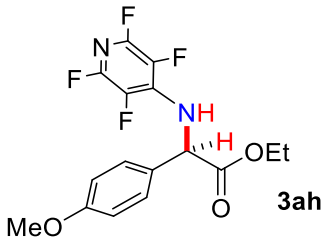



**Ethyl (*R*)-2-(4-methoxyphenyl)-2-((perfluorophenyl)amino)acetate 3af** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 72%. $[\alpha]_D^{20}$= -60° (*c* = 0.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.26 (d, *J* = 9.0 Hz, 1H), 4.88 (br, 1H), 4.19 (m, 2H), 3.78 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.50, 159.81, 138.32 (dm, *J* = 238.8 Hz), 137.95 (dm, *J* = 246.0 Hz), 134.22 (dm, *J* = 244.1 Hz), 128.86, 128.19, 121.56 (m), 114.35, 62.01, 60.88 (t, *J* = 3.6 Hz), 55.22, 13.96. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ. -158.03 (m, 2F), -164.50 (m, 2F), -170.12 (m, 1F). IR (neat, $cm^{-1}$): 3379, 2938, 1736, 1611, 1511, 1247, 1176, 1022, 967, 836. HRMS (ESI-negative) ([M-H]$^-$) Calcd. for: $C_{17}H_{13}F_5NO_3$: 374.0816, Found: 374.0826. HPLC analysis: ee = 95%. Whelk (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 6.59 min, $t_{minor}$ = 7.90 min.



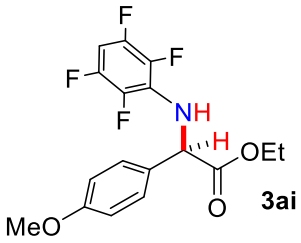

**Ethyl (*R*)-2-((4-bromo-2,3,5,6-tetrafluorophenyl)amino)-2-(4-methoxyphenyl)acetate 3ag** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 64%. $[\alpha]_D^{20}$= -54° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.34 (d, *J* = 8.5 Hz, 1H), 5.13 (d, *J* = 8.5 Hz, 1H), 4.24 (m, 2H), 3.78 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.35, 159.84, 145.08 (dm, *J* = 243.0 Hz), 138.01 (dm, *J* = 241.7 Hz), 131.11, 128.91, 128.18, 125.34 (t, *J* = 12.3 Hz), 114.37,

86.91 (t, $J$ = 23.0 Hz), 62.07, 60.50 (t, $J$ = 3.9 Hz), 55.22, 13.96. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -136.17 (m, 2F), -156.76 (m, 2F). IR (neat, $cm^{-1}$): 3382, 2936, 1735, 1641, 1494, 1248, 1177, 1032, 947, 833, 796, 622, 529. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{17}H_{13}BrF_4NO_3$: 434.0015, Found: 434.0026. HPLC analysis: ee = 95%. ADH (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 7.79 min, $t_{minor}$ = 8.46 min.



**3ah**

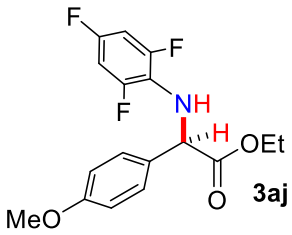
**Ethyl (*R*)-2-(4-methoxyphenyl)-2-((perfluoropyridin-4-yl)amino)acetate 3ah** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 87%. $[\alpha]_D^{20}$= -97° ($c$ = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, $J$ = 9.0 Hz, 2H), 6.89 (d, $J$ = 8.5 Hz, 2H), 5.74 (m, 1H), 5.47 (d, $J$ = 7.5 Hz, 1H), 4.27 (m, 2H), 3.80 (s, 3H), 1.22 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.69, 160.07, 144.05 (td, $J$ = 15.5, 235.4 Hz), 135.76 (m), 131.47 (dm, $J$ = 246.4 Hz), 128.38, 128.13, 114.54, 62.45, 59.61 (t, $J$ = 3.8 Hz), 55.28, 13.93. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -93.85 (m, 2F), -162.63 (m, 2F). IR (neat, $cm^{-1}$): 3386, 2939, 1736, 1646, 1479, 1248, 1151, 1030, 940, 836, 727, 624. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{16}H_{13}F_4N_2O_3$: 357.0862, Found: 357.0873. HPLC analysis: ee = 93%. Whelk (97% hexane: 3% isopropanol, 1 ml/min): $t_{major}$ = 8.47 min, $t_{minor}$ = 9.62 min.



**3ai**

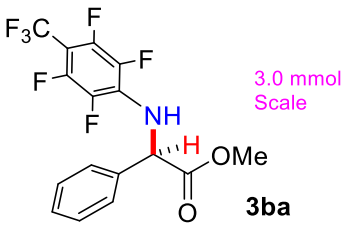
**Ethyl (*R*)-2-(4-methoxyphenyl)-2-((2,3,5,6-tetrafluorophenyl)amino)acetate 3ai** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 34%. $[\alpha]_D^{20}$= -110° ($c$ = 0.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, $J$ = 8.5 Hz, 2H), 6.86 (d, $J$ = 8.0 Hz, 2H), 6.39 (m, 1H), 5.36 (d, $J$ = 9.0 Hz, 1H), 5.08 (d, $J$ = 8.8 Hz, 1H), 4.25 (dq, $J$ =

10.8, 7.1 Hz, 1H), 4.14 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.78 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.54, 159.76, 146.32 (dm, *J* = 243.0 Hz), 137.70 (dm, *J* = 238.6 Hz), 129.19, 128.21, 126.28 (m), 114.32, 94.68 (t, *J* = 23.1 Hz), 61.97, 60.59 (t, *J* = 4.1 Hz), 55.24, 13.98. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -141.45 (m, 2F), -158.70 (m, 2F). IR (neat, $cm^{-1}$): 3384, 2937, 1735, 1651, 1610, 1510, 1459, 1248, 1176, 1031, 920, 797, 711. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{17}H_{14}F_4NO_3$: 356.0910, Found: 356.0918. HPLC analysis: ee = 91%. Whelk (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 7.23 min, $t_{minor}$ = 8.94 min.

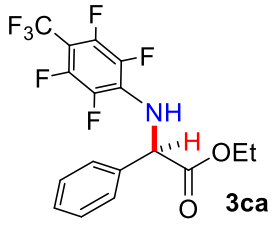



**Ethyl (*R*)-2-(4-methoxyphenyl)-2-((2,4,6-trifluorophenyl)amino)acetate 3aj** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 30%. $[\alpha]_D^{20}$= -76° (*c* = 0.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.55 (t, *J* = 7.8 Hz, 2H), 5.23 (d, *J* = 8.8 Hz, 1H), 4.64 (d, *J* = 9.4 Hz, 1H), 4.17 (m, 2H), 3.77 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 172.01, 159.58, 156.15 – 154.11 (m, 2C), 129.53, 128.24, 120.23 (m), 114.14, 100.18 (m), 61.66, 61.44 (t, *J* = 3.8 Hz), 55.20, 14.00. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -120.48 (t, *J* = 8.6 H, 1F), -124.21 (m, 2F). IR (neat, $cm^{-1}$): 3457, 2962, 1735, 1609, 1508, 1442, 1247, 1175, 1114, 1032, 995, 833, 571. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{17}H_{15}F_3NO_3$: 338.1004, Found: 338.1000. HPLC analysis: ee = 49%. OJH (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 12.51 min, $t_{minor}$ = 18.37 min.

## 5.2. Enantioselective C–H Amination of Various Arylacetate Esters with 2a

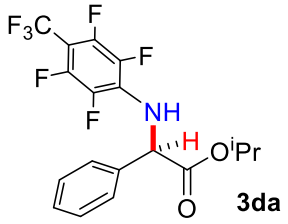



**Methyl (*R*)-2-phenyl-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)acetate 3ba** was obtained through the general procedure on 3 mmol scale using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 75%. $[\alpha]_D^{20}$ = -97° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.36 (m, 5H), 5.49 (m, 2 H), 3.76 (s, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 171.29, 144.86 (dm, *J* = 254.75 Hz), 137.03 (dm, *J* = 239.38 Hz), 136.50, 129.20, 129.07, 126.93, 121.41 (q, *J* = 271.1 Hz), 97.60 (m), 60.54 (t, *J* = 4.1 Hz), 53.21. $^{19}F$ NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.60 (t, *J* = 20.7 Hz, 3F), -143.31 (m, 2F), -158.98 (m, 2F). IR (neat, $cm^{-1}$): 3390, 2959, 1742, 1656, 1508, 1331, 1293, 1236, 1177, 1129, 1069, 967, 875, 698. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{16}H_9F_7NO_2$: 380.0522, Found: 380.0527. HPLC analysis: ee = 96%. ODH (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 5.99 min, $t_{minor}$ = 7.16 min.

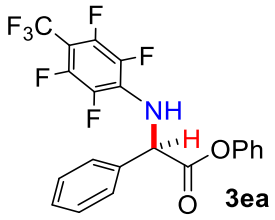



**Ethyl (*R*)-2-phenyl-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)acetate 3ca** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 82%. $[\alpha]_D^{20}$= -84° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.34 (m, 5H), 5.48 (m, 2H), 4.27 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.77, 144.84 (dm, *J* = 257.5 Hz), 136.96 (dm, *J* = 241.3 Hz), 136.65, 129.12, 128.96, 126.88, 121.42 (q, *J* = 269.9 Hz), 62.43, 60.61 (t, *J* = 4 Hz), 13.92. $^{19}F$ NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.58 (t, *J* = 20.7 Hz, 3F), -143.38 (m, 2F), -159.05 (m, 2F). IR (neat, $cm^{-1}$): 3396, 2973, 1736, 1505, 1291, 1134, 954, 696. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{17}H_{11}F_7NO_2$: 394.0678, Found:

394.0687. HPLC analysis: ee = 95%. ODH (97% hexane: 3% isopropanol, 1 ml/min): $t_{major}$ = 8.38 min, $t_{minor}$ = 9.16 min.

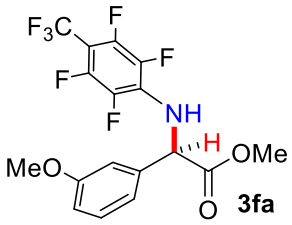



**Isopropyl (*R*)-2-phenyl-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)acetate 3da** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 61%. $[\alpha]_D^{20}$= -199° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 5.52 – 5.40 (m, 2H), 5.06 (p, *J* = 6.2 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.06 (d, *J* = 6.2 Hz, 3H). $^{13}$C NMR (62.5 MHz, $CDCl_3$): δ 170.26, 144.86 (dm, *J* = 253.9 Hz), 136.95 (dm, *J* = 240.7 Hz), 136.76, 129.27 (m), 129.04, 128.85, 126.80, 121.44 (q, *J* = 271.3 Hz), 97.30 (m), 70.34, 60.72, 21.60, 21.15. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): -55.56 (t, *J* = 21.1 Hz, 3F), -143.46 (m, 2F), -159.13 (m, 2F). IR (neat, $cm^{-1}$): 3391, 2990, 1733, 1652, 1506, 1330, 1291, 1139, 1099, 957, 878, 710. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{18}H_{13}F_7NO_2$: 408.0835, Found: 408.0842. HPLC analysis: ee = 97%. Whelk (100% hexane, 1 ml/min): $t_{major}$ = 8.14 min, $t_{minor}$ = 8.74 min.

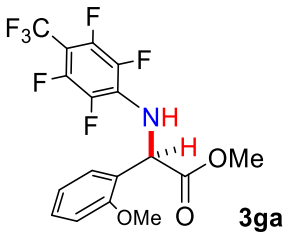



**Phenyl (*R*)-2-phenyl-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)acetate 3ea** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 50%. $[\alpha]_D^{20}$= -92° (*c* = 0.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.40 (m, 5H), 7.37 – 7.33 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.99 – 6.93 (m, 2H), 5.74 (d, *J* = 8.0 Hz, 1H), 5.39 (d, *J* = 8.0 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 169.63, 150.20, 144.83 (dm, *J* = 240.9 Hz), 137.03 (dm, *J* = 240.5 Hz), 135.99, 129.55, 129.44, 129.41, 129.01 (m), 127.11, 126.46, 121.37 (q, *J* = 272.9 Hz), 120.90, 97.89 (m), 60.88. $^{19}$F NMR (376 MHz, $CDCl_3$): δ -55.12 (t, *J* =

20.9 Hz, 3F), -142.60 (m, 2F), -158.48 (m, 2F). IR (neat, $cm^{-1}$): 3394, 2924, 1759, 1656, 1509, 1332, 1236, 1190, 1130, 979, 958, 880, 713, 687. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{21}H_{11}F_7NO_2$: 442.0678, Found: 442.0683. HPLC analysis: ee = 94%. ADH (99% hexane: 1% isopropanol, 0.7 ml/min): $t_{major}$ = 17.11 min, $t_{minor}$ = 10.23 min.

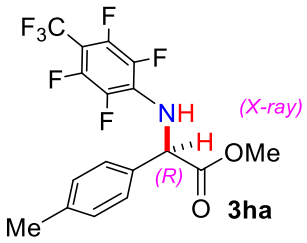



**Methyl (*R*)-2-(3-methoxyphenyl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) acetate 3fa** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 61%. $[\alpha]_D^{20}$= -93° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.89 (m, 2H), 5.45 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 171.18, 160.09, 144.91 (dm, *J* = 250.8 Hz), 137.93, 136.94 (dm, *J* = 223.4 Hz), 130.26, 129.04 (m), 121.39 (q, *J* = 272.6 Hz), 119.09, 114.28, 112.79, 97.62 (m), 60.47 (t, *J* = 4.1 Hz), 55.30, 53.24. $^{19}F$ NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.60 (t, *J* = 20.7 Hz, 3F), -143.29 (m, 2F), -158.94 (m, 2F). IR (neat, $cm^{-1}$): 3390, 2959, 1743, 1657, 1508, 1330, 1235, 1129, 970, 714. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{17}H_{11}F_7NO_3$: 410.0627, Found: 410.0634. HPLC analysis: ee = 93%. ADH (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 6.40 min, $t_{minor}$ = 7.14 min.

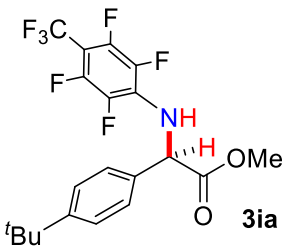



**Methyl (*R*)-2-(2-methoxyphenyl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) acetate 3ga** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 52%. $[\alpha]_D^{20}$= -152° (*c* = 0.6, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.34 (dt, *J* = 2.0, 7.8 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 6.97 (dt, *J* = 0.5, 7.5 Hz, 1H),

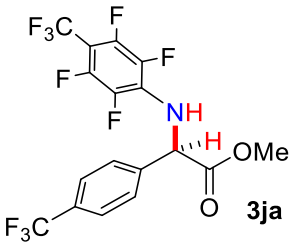
6.93 (d, *J* = 8.0 Hz, 1H), 5.69 (d, *J* = 9.5 Hz, 1H), 5.46 (d, *J* = 9.0 Hz, 1H), 3.87 (s, 3H), 3.73 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.45, 156.99, 144.80 (dm, *J* = 255.4 Hz), 137.18 (dm, *J* = 239.1 Hz), 130.37, 130.02 (m), 129.57, 124.92, 121.48 (q, *J* = 271.4 Hz), 121.12, 111.38, 97.42 (m), 57.73 (t, *J* = 4.5 Hz), 55.62, 52.93. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.55 (t, *J* = 20.9 Hz, 3F), -143.77 (m, 2F), -159.09 (m, 2F). IR (neat, $cm^{-1}$): 3389, 2956, 2844, 1746, 1655, 1509, 1331, 1236, 1128, 967, 874, 754, 713. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{17}H_{11}F_7NO_3$: 410.0627, Found: 410.0622. HPLC analysis: ee = 95%. Whelk (99.5% hexane: 0.5% isopropanol, 1 ml/min): $t_{major}$ = 8.27 min, $t_{minor}$ = 11.14 min.




**Methyl (*R*)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)-2-(p-tolyl)acetate 3ha** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 70%. $[\alpha]_D^{20}$= -88° (*c* = 0.5, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.45 (m, 2H), 3.75 (s, 3H), 2.34 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.46, 144.75 (dm, *J* = 258.8 Hz), 139.06, 136.89 (dm, *J* = 237.8 Hz), 133.51, 129.88, 129.27 (m), 126.82, 121.42 (q, *J* = 269.8 Hz), 97.35 (m), 60.29 (t, *J* = 4.0 Hz), 53.15, 21.13. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.59 (t, *J* = 20.7 Hz, 3F), -143.39 (m, 2F), -158.97 (m, 2F). IR (neat, $cm^{-1}$): 3374, 2957, 2924, 1738, 1656, 1505, 1456, 1291, 1176, 1139, 1010, 968, 874, 711, 619. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{17}H_{11}F_7NO_2$: 394.0678, Found: 394.0692. HPLC analysis: ee = 94%. OJH (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 8.52 min, $t_{minor}$ = 5.25 min.

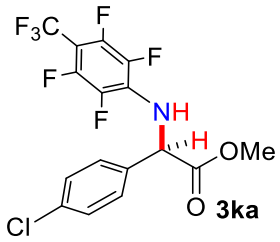



**Methyl (*R*)-2-(4-(tert-butyl)phenyl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) acetate 3ia** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 57%. $[\alpha]_D^{20}$ = -76° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.49 (d, *J* = 8.0 Hz, 1H), 5.37 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 1.32 (s, 9H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 171.46, 152.16, 144.88 (dm, *J* = 256.2 Hz), 136.99 (dm, *J* = 239.3 Hz), 133.36, 129.26 (m), 126.58, 126.19, 121.46 (q, *J* = 271.0 Hz), 97.22 (m), 60.27 (t, *J* = 4.1 Hz), 53.09, 34.64, 31.19. $^{19}F$ NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.55 (t, *J* = 21.1 Hz, 3F), -143.42 (m, 2F), -159.16 (m, 2F). IR (neat, $cm^{-1}$): 3408, 2974, 1738, 1656, 1546, 1505, 1462, 1328, 1133, 1082, 1008, 962, 875, 712, 667. HRMS (ESI-negative) ([M-H]$^-$) Calcd. for: $C_{20}H_{17}F_7NO_2$: 436.1147**,** Found: 436.1165. HPLC analysis: ee = 88%. Whelk (100% hexane, 0.8 ml/min): $t_{major}$ = 10.65 min, $t_{minor}$ = 11.36 min.

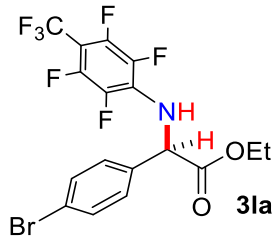



**Methyl (*R*)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)-2-(4-(trifluoromethyl)phenyl)acetate 3ja** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 41%. $[\alpha]_D^{20}$= -65° (*c* = 0.7, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 5.67 – 5.49 (m, 2H), 3.79 (s, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.55, 144.79 (dm, *J* = 255.0 Hz), 140.50, 136.85 (tdd, *J* = 4.9, 15.2, 239.4 Hz), 131.28 (q, *J* = 32.6 Hz), 128.57 (m), 127.34, 126.19 (q, *J* = 3.8 Hz), 123.73 (q, *J* = 270.6 Hz), 121.31 (q, *J* = 273.5 Hz), 98.05 (m), 60.05, 53.56. $^{19}F$ NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.66 (t, *J* = 20.9 Hz, 3F), -63.32 (s, 3F), -142.80 (m, 2F), -159.00 (m, 2F). IR (neat, $cm^{-1}$): 3392, 2963,

1745, 1658, 1509, 1322, 1124, 1067, 968, 876, 713. HRMS (ESI-negative) ([M-H]$^-$) Calcd. for: $C_{17}H_8F_{10}NO_2$: 448.0395, Found: 448.0407. HPLC analysis: ee = 92%. ADH (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 5.94 min, $t_{minor}$ = 5.67 min.

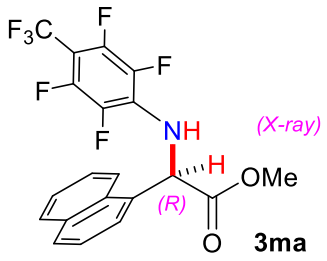



**Methyl (*R*)-2-(4-chlorophenyl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl) amino) acetate 3ka** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 60%. $[\alpha]_D^{20}$= -125° (*c* = 0.8, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 4H), 5.53 (br, 1H), 5.47 (d, *J* = 8.0 Hz, 1H), 3.77 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.89, 144.83 (dm, *J* = 254.6 Hz), 136.90 (dm, *J* = 240.6 Hz), 135.04, 129.41, 128.68 (m), 128.25, 121.32 (q, *J* = 272. 7 Hz), 97.96 (m), 59.79 (t, *J* = 4.1 Hz), 53.41. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.64 (t, *J* = 20.7 Hz, 3F), -143.00 (m, 2F), -158. 92 (m, 2F). IR (neat, cm$^{-1}$): 3390, 2959, 1743, 1656, 1509, 1332, 1131, 968, 876, 770, 712. HRMS (ESI-negative) ([M-H]$^-$) Calcd. for:$C_{16}H_8ClF_7NO_2$: 414.0132, Found: 414.0145. HPLC analysis: ee = 93%. OJH (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 12.07 min, $t_{minor}$ = 7.60 min.

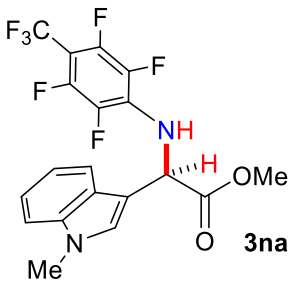



**Ethyl (*R*)-2-(4-bromophenyl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)acetate 3la** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 67%. $[\alpha]_D^{20}$= -178° (*c* = 0.5, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.53 (br, 1H), 5.42 (d, *J* = 8.0 Hz, 1H), 4.22 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 170.30, 144.80 (dm, *J* = 243.9 Hz), 136.77 (dm, *J* = 248.0 Hz), 132.31, 128.80 (m), 128.51, 123.11, 121.33 (q, *J* =

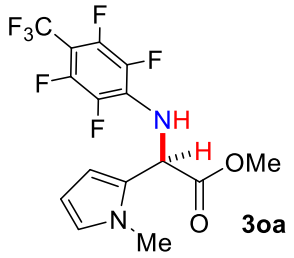
265.1 Hz), 97.82 (m), 62.72, 59.98 (t, $J$ = 4.0 Hz), 13.92. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.62 (t, $J$ = 21.1 Hz, 3F), -143.05 (m, 2F), -158.99 (m, 2F). IR (neat, $cm^{-1}$): 3391, 2990, 1733, 1652, 1506, 1456, 1330, 1291, 1139, 1099, 957, 878, 710, 630. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for:$C_{17}H_{10}BrF_7NO_2$: 471.9783, Found: 471.9796. HPLC analysis: ee = 92%. Whelk (99.5% hexane: 0.5% isopropanol, 1 ml/min): $t_{major}$ = 6.48 min, $t_{minor}$ = 6.99 min.




**Methyl (*R*)-2-(naphthalen-1-yl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) acetate 3ma** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 68%. $[\alpha]_D^{20}$= -68° ($c$ = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, $J$ = 8.5 Hz, 1H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.63 – 7.56 (m, 2H), 7.48 (m, 2H), 6.31 (d, $J$ = 8.0 Hz, 1H), 5.36 (br, 1H), 3.75 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 171.75, 144.82 (dm, $J$ = 255.1 Hz), 136.94 (dm, $J$ = 241.0 Hz), 134.19, 132.20, 130.84, 129.98, 129.28 (m), 129.12, 127.20, 126.30, 125.33, 125.15, 122.82, 121.43 (q, $J$ = 272.5 Hz), 97.46 (m), 57.56, 53.19. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.61 (t, $J$ = 20.7 Hz, 3F), -143.22 (m, 2F), -159.29 (m, 2F). IR (neat, $cm^{-1}$): 3396, 2967, 1748, 1660, 1510, 1331, 1285, 1121, 998, 961, 792, 775, 714. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{20}H_{11}F_7NO_2$: 430.0678, Found: 430.0687. HPLC analysis: ee = 88%. Whelk (99.5% hexane: 0.5% isopropanol, 1 ml/min): $t_{major}$ = 8.91 min, $t_{minor}$ = 10.80 min.

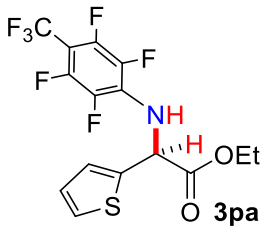



**Methyl (*R*)-2-(1-methyl-1H-indol-2-yl)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)acetate 3na** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 90%. $[\alpha]_D^{20}$= -53° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.15 (s, 1H), 5.80 (d, *J* = 8.0 Hz, 1H), 5.35 (br, 1H), 3.79 (s, 3H), 3.76 (s, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 171.74, 144.76 (dm, *J* = 244.3 Hz), 137.02 (dm, *J* = 240.6 Hz), 137.19, 129.60 (m), 128.28, 125.36, 122.48, 121.45 (q, *J* = 271.0 Hz), 120.25, 118.87, 109.78, 109.43, 97.01 (m), 54.25 (t, *J* = 4.5 Hz), 53.00, 32.95. $^{19}F$ NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.06 (t, *J* = 21.1 Hz, 3F), -143.12 (m, 2F), -158.69 (m, 2F). IR (neat, $cm^{-1}$): 3367, 2954, 1732, 1655, 1508, 1330, 1237, 1125, 943, 876, 742, 713. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{19}H_{12}F_7N_2O_2$: 433.0787, Found: 433.0792. HPLC analysis: ee = 93%. ADH (99% hexane: 1% isopropanol, 1 ml/min): $t_{major}$ = 9.05 min, $t_{minor}$ = 15.23 min.




**Methyl (*R*)-2-(1-methyl-1H-pyrrol-2-yl)-2-((2,3,5,6-tetrafluoro-4 -(trifluoromethyl)phenyl)amino)acetate 3oa** was obtained through the general procedure using 1.5 equiv of azide with α,α,α-trifluorotoluene as solvent. Yield: 75%. $[\alpha]_D^{20}$= -106° (*c* = 0.5, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 6.65 (t, *J* = 2.0 Hz, 1H), 6.08 (m, 2H), 5.59 (d, *J* = 9.0 Hz, 1H), 4.97 (m, 1H), 3.79 (s, 3H), 3.71 (s, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 170.55, 144.87 (dm, *J* = 254.3 Hz), 137.19 (dm, *J* = 240.5 Hz), 129.30 (m), 126.63, 124.30, 121.38 (q, *J* = 271.9 Hz), 108.14, 107.53, 98.04 (m),

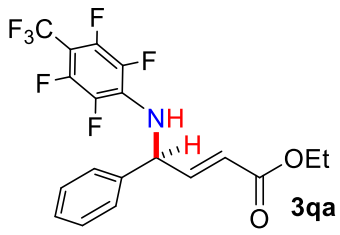
53.72 (t, $J$ = 4.8 Hz), 53.13, 33.92. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.63 (t, $J$ = 20.7 Hz, 3F), -143.12 (m, 2F), -158.84 (m, 2F). IR (neat, $cm^{-1}$): 3389, 2958, 1746, 1655, 1509, 1332, 1232, 1129, 1080, 965, 876, 713. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{15}H_{10}F_7N_2O_2$: 383.0630, Found: 383.0637. HPLC analysis: ee = 98%. ADH (99% hexanes: 1% isopropanol, 1 ml/min): $t_{major}$ = 5.91 min, $t_{minor}$ = 6.54 min.



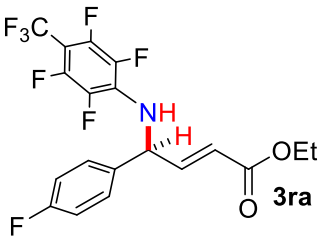
**3pa**

**Methyl (*S*)-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)-2-(thiophen-2-yl)acetate 3pa** was obtained through the general procedure using 1.5 equiv of azide with $PhCF_3$ as solvent. Yield: 88%. $[\alpha]_D^{20}$= -120° ($c$ = 0.2, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.30 (dd, $J$ = 1.0, 5.0 Hz, 1H), 7.10 (d, $J$ = 3.5 Hz, 1H), 6.98 (dd, $J$ = 3.5, 5.0 Hz, 1H), 5.74 (d, $J$ = 8.5 Hz, 1H), 5.38 (d, $J$ = 8.0 Hz, 1H), 4.28 (m, 2H), 1.28 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 169.85, 144.86 (dm, $J$ = 254.1 Hz), 139.18, 137.18 (dm, $J$ = 240.9 Hz), 128.91 (m), 127.24, 126.46, 126.38, 121.38 (q, $J$ = 272.1 Hz), 97.98 (m), 62.78, 56.44 (t, $J$ = 4.6 Hz), 13.97. $^{19}$F NMR (376 MHz, $CFCl_3$, $CDCl_3$): δ -55.16 (t, $J$ = 21.1 Hz, 3F), -142.63 (m, 2F), -157.89 (m, 2F). IR (neat, $cm^{-1}$): 3384, 2984, 1740, 1655, 1508, 1334, 1231, 1132, 978, 713. HRMS (ESI-negative) ($[M-H]^-$) Calcd. for: $C_{15}H_9F_7NO_2S$: 400.0242, Found: 400.0252. HPLC analysis: ee = 91%. ODH (99% hexane: 1% isopropanol, 0.7 ml/min): $t_{major}$ = 8.04 min, $t_{minor}$ = 11.78 min.

### 5.3. Enantioselective C–H Amination of Various Arylcrotonate Esters with 2a

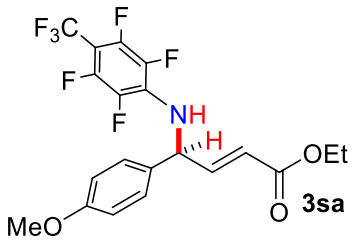



**Ethyl (*S*,*E*)-4-phenyl-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)but-2-enoate 3qa** was obtained through the general procedure using 1.5 equiv of azide with benzene as solvent. Yield: 64%. $[\alpha]_D^{20}$= -55° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.36 (m, 1H), 7.31–7.29 (m, 2H), 7.10 (dd, *J* = 15.6, 5.6 Hz, 1H), 5.99 (dd, *J* = 15.7, 1.5 Hz, 1H), 5.60 (dd, *J* = 8.4, 5.9 Hz, 1H), 4.49 (d, *J* = 8.6 Hz, 1H), 4.20 (qd, *J* = 7.2, 1.3 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 165.64, 146.03, 144.66 (dm, *J* = 264.9 Hz), 138.64, 136.48 (dm, *J* = 241.3 Hz), 129.38 (m), 129.29, 128.78, 126.89, 122.60, 121.30 (q, *J* = 272.9 Hz), 97.65 (m), 60.77, 59.42 (t, *J* = 4.6 Hz), 14.08. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -55.10 (t, *J* = 20.8 Hz, 3F), -142.46 (m, 2F), -158.06 (m, 2F). IR (neat, $cm^{-1}$): 3339, 2986, 1715, 1657, 1512, 1334, 1234, 1134, 974, 713. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{19}H_{15}F_7NO_2$: 422.09855, Found: 422.09960. HPLC analysis: ee = 94%. ODH (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 13.13 min, $t_{minor}$ = 17.29 min.

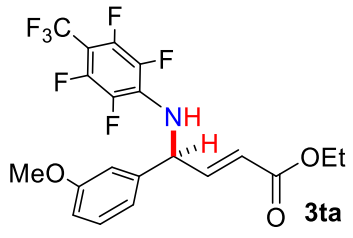



**Ethyl (*S*,*E*)-4-(4-fluorophenyl)-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)but-2-enoate 3ra** was obtained through the general procedure using 1.5 equiv of azide with benzene as solvent. Yield: 53%. $[\alpha]_D^{20}$= -69° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.30 (m, 2H), 7.12 – 7.05 (m, 3H), 5.98 (dd, *J* = 15.8, 1.4 Hz, 1H), 5.60 (m, 1H), 4.45 (d, *J* = 8.7 Hz, 1H), 4.21 (qd, *J* = 7.3, 1.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 165.53, 162.69 (d, *J* = 248.5 Hz), 145.65, 144.81 (dm, *J* = 255.2 Hz), 136.79 (dm, *J* = 241.4 Hz), 134.49

(d, $J$ = 3.4 Hz), 129.20 (m), 128.75, 128.69, 122.90, 121.25 (q, $J$ = 272.6 Hz), 116.35, 116.20, 97.90 (m), 60.85, 58.72 (t, $J$ = 4.6 Hz), 14.07. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.12 (t, $J$ = 20.9 Hz, 3F), -112.42 (m, 1F), -142.28 (m, 2F), -157.92 (m, 2F). IR (neat, $cm^{-1}$): 3339, 2987, 1715, 1657, 1510, 1335, 1232, 1135, 975, 714. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{19}H_{14}F_8NO_2$: 440.08913, Found: 440.08805. HPLC analysis: ee = 97%. ODH (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 12.78 min, $t_{minor}$ = 16.42 min.

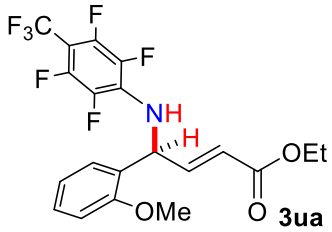



**Ethyl (*S*,*E*)-4-(4-methoxyphenyl)-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) but-2-enoate 3sa** was obtained through the general procedure using 1.5 equiv of azide with benzene as solvent. Yield: 70%. $[\alpha]_D^{20}$= -75° ($c$ = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, $J$ = 8.4 Hz, 2H), 7.10 (dd, $J$ = 15.6, 5.5 Hz, 1H), 6.92 (d, $J$ = 8.4 Hz, 2H), 5.98 (dd, $J$ = 15.6, 1H), 5.56 (m, 1H), 4.43 (br, 1H), 4.21 (q, $J$ = 7.1 Hz, 2H), 3.81 (s, 3H), 1.29 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.82, 159.06, 146.40, 145.10 (dm, $J$ = 252.1 Hz), 136.59 (dm, $J$ = 245.95 Hz), 135.62, 129.59 (m), 126.74, 126.32, 121.40 (q, $J$ = 272.6 Hz), 114.68, 97.90, 60.80, 58.95 (q, $J$ = 4.7 Hz), 55.33, 14.16. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -55.08 (t, $J$ = 20.8 Hz, 3F), -142.58 (m, 2F), -158.12 (m, 2F). IR (neat, $cm^{-1}$): 3341, 1716, 1656, 1511, 1334, 1234, 1177, 1134, 974, 713. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{20}H_{17}F_7NO_3$: 452.10912, Found: 452.11023. HPLC analysis: ee = 95%. ODH (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 16.13 min, $t_{minor}$ = 18.83 min.




**Ethyl (*S*,*E*)-4-(3-methoxyphenyl)-4-((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl) amino) but-2-enoate 3ta** was obtained through the general procedure using 1.5 equiv of azide with

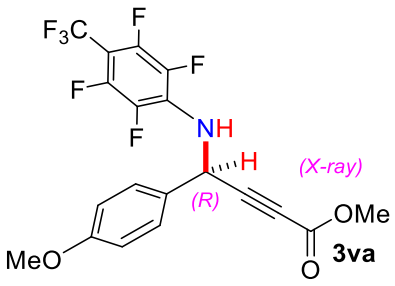
benzene as solvent. Yield: 63%. $[\alpha]_D^{20}$= -83° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 15.6, 5.6 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.83 (s, 1H), 6.00 (d, *J* = 15.8 Hz, 1H), 5.57 (dd, *J* = 5.4, 9.0 Hz, 1H), 4.50 (d, *J* = 9.1 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 165.72, 160.25, 146.03, 144.92 (dm, *J* = 257.9 Hz), 140.27, 136.84 (dm, *J* = 241.5), 130.51, 122.64, 121.39 (q, *J* = 272.5 Hz), 119.01, 113.82, 112.99, 97.67 (m), 60.85, 59.47, 55.24, 14.14. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.12 (t, *J* = 20.8 Hz, 3F), -142.51 (m, 2F), -158.06 (m, 2F). IR (neat, $cm^{-1}$): 3342, 2940, 1715, 1657, 1512, 1334, 1234, 1134, 713. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{20}H_{17}F_7NO_3$: 452.10912, Found: 452.10866. HPLC analysis: ee = 95%. ODH (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 16.19 min, $t_{minor}$ = 20.91 min.



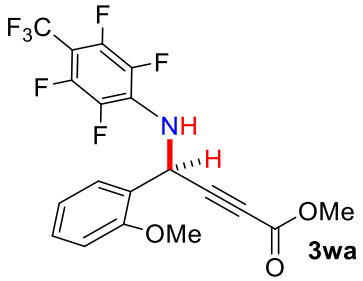
**3ua**

**Ethyl (*S*,*E*)-4-(2-methoxyphenyl)-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) but-2-enoate 3ua** was obtained through the general procedure using 1.5 equiv of azide with benzene as solvent. Yield: 70%. $[\alpha]_D^{20}$= -97° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.33 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.15 (dd, *J* = 15.7, 5.5 Hz, 1H), 7.01 – 6.90 (m, 2H), 5.97 (d, *J* = 16.1 Hz, 1H), 5.71 (dd, *J* = 9.5, 5.4 Hz, 1H), 5.29 (d, *J* = 9.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 166.14, 156.96, 146.38, 144.59 (dm, *J* = 247.0 Hz), 137.08 (dm, *J* = 241.1 Hz), 130.18 (m), 130.08, 128.80, 126.54, 121.85, 121.51 (q, *J* = 272.4 Hz), 121.25, 111.48, 97.10 (m), 60.70, 57.68 (t, *J* = 5.1 Hz), 55.50, 14.21. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.06 (t, *J* = 20.8 Hz, 3F), -143.07 (m, 2F), -158.58 (m, 2F). IR (neat, $cm^{-1}$): 3369, 2982, 1718, 1656, 1512, 1332, 1234, 1132, 876, 713. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{20}H_{17}F_7NO_3$: 452.10912, Found: 452.10854. HPLC analysis: ee = 95%. ODH (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 11.60 min, $t_{minor}$ = 12.89 min.

### 5.4. Enantioselective C–H Amination of Various Aryltetrolate Esters with 2a

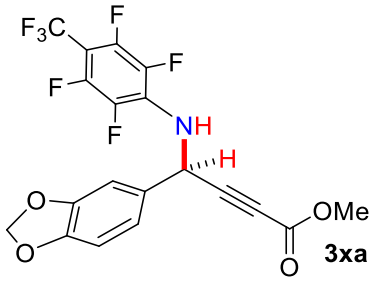



**Methyl (*R*)-4-(4-methoxyphenyl)-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) but-2-ynoate 3va** was obtained through the general procedure using 1.2 equiv of azide with benzene as solvent. Yield: 83%. $[\alpha]_D^{20}$= 35° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 5.79 (d, *J* = 9.2 Hz, 1H), 4.43 (d, *J* = 9.2 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 163.02, 156.01, 147.47 (dm, *J* = 241.2 Hz), 140.04 (dm, *J* = 239.0 Hz), 131.42 (m), 131.16, 130.84, 123.95 (q, *J* = 271.4 Hz), 117.26, 101.53 (m), 87.02, 80.20, 58.08, 55.51, 53.03, 32.34. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.23 (t, *J* = 21.3 Hz, 3F), -142.12 (m, 2F), -156.66 (m, 2F). IR (neat, $cm^{-1}$): 3344, 2957, 2845, 2240, 1721, 1595, 1512, 1336, 1229, 1033, 990, 715. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{19}H_{13}F_7NO_3$: 436.07782, Found: 436.07846. HPLC analysis: ee = 93%. ASH (90% hexanes: 10% isopropanol, 0.8 ml/min): $t_{major}$ = 11.99 min, $t_{minor}$ = 14.42 min.



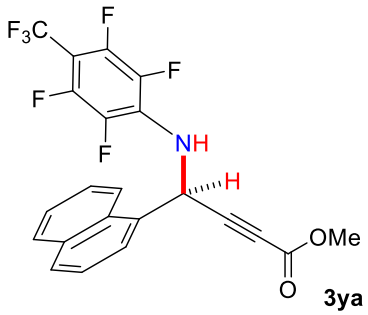

**Methyl (*S*)-4-(2-methoxyphenyl)-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) but-2-ynoate 3wa** was obtained through the general procedure using 1.2 equiv of azide with benzene as solvent. Yield: 89%. $[\alpha]_D^{20}$= 9° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.41

(d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 5.98 (d, *J* = 9.6 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 3.90 (s, 3H), 3.76 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 156.92, 153.58, 144.78 (dm, *J* = 256.5 Hz), 137.42 (dm, *J* = 242.0 Hz), 130.81, 129.16 (m), 128.70, 124.48, 121.37 (q, *J* = 273.4 Hz), 121.08, 111.52, 98.45 (m), 84.89, 76.08, 55.67, 52.78, 47.47. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.18 (t, *J* = 21.0 Hz, 3F), -142.60 (m, 2F), -157.45 (m, 2F). IR (neat, $cm^{-1}$): 2935, 2237, 1729, 1599, 1495, 1337, 1142, 992, 876, 716. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{19}H_{13}F_7NO_3$: 436.07782, Found: 436.07780. HPLC analysis: ee = 90%. OJH (90% hexane: 10% isopropanol, 0.8 ml/min): $t_{major}$ = 18.90 min, $t_{minor}$ = 16.36 min.

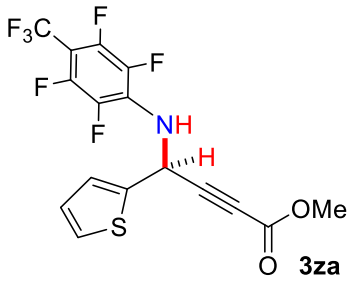


**3xa**

**Methyl (*R*)-4-(benzo[d][1,3]dioxol-5-yl)-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl) amino) but-2-ynoate 3xa** was obtained through the general procedure using 1.2 equiv of azide with benzene as solvent. Yield: 81%. $[\alpha]_D^{20}$= 17° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.1 Hz, 1H), 7.00 (s, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.01 (s, 2H), 5.74 (d, *J* = 9.3 Hz, 1H), 4.45 (d, *J* = 9.3 Hz, 1H), 3.79 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 153.29, 148.56, 148.48, 144.80 (dm, *J* = 261.4 Hz), 137.51 (dm, *J* = 242.3 Hz), 129.90, 128.63 (m), 121.28 (q, *J* = 273.3 Hz), 121.01, 108.71, 107.50, 101.64, 99.08 (m), 84.05, 77.63, 52.99, 50.64. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.25 (t, *J* = 20.9 Hz, 3F), -142.02 (m, 2F), -156.60 (m, 2F). IR (neat, $cm^{-1}$): 2917, 2240, 1724, 1596, 1495, 1335, 1221, 1140, 991, 715. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{19}H_{11}F_7NO_4$: 450.05708, Found: 450.05914. HPLC analysis: ee = 94%. ASH (90% hexane: 10% isopropanol, 0.8 ml/min): $t_{major}$ = 16.53 min, $t_{minor}$ = 13.61 min.




**Methyl (*S*)-4-(naphthalen-1-yl)-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino) but-2-ynoate 3ya** was obtained through the general procedure using 1.2 equiv of azide with benzene as solvent. Yield: 90%. $[\alpha]_D^{20}$= 10° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.01 – 7.86 (m, 3H), 7.67 – 7.50 (m, 3H), 6.58 (d, *J* = 9.4 Hz, 1H), 4.50 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 155.98, 147.53 (dm, *J* = 262.3 Hz), 140.26 (dm, *J* = 258.0 Hz), 136.79, 133.68, 133.32, 132.89, 131.84, 131.47 (m), 130.04, 129.14, 128.65, 127.95, 125.31, 123.96 (q, *J* = 273.3 Hz), 101.82 (m), 86.65, 81.01, 55.65, 51.21. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -55.22 (t, *J* = 20.9 Hz, 3F), -141.89 (m, 2F), -156.81 (m, 2F). IR (neat, $cm^{-1}$): 3344, 2957, 2240, 1719, 1659, 1511, 1335, 1230, 778, 714. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{16}H_9F_7SNO_2$: 456.08290, Found: 456.08188. HPLC analysis: ee = 59%. ASH (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 9.96 min, $t_{minor}$ = 7.30 min.




**Methyl (*S*)-4-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)-4-(thiophen-2-yl)but-2-ynoate 3za** was obtained through the general procedure using 1.2 equiv of azide with benzene as solvent. Yield: 80%. $[\alpha]_D^{20}$= 57° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.28 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.06 (d, *J* = 9.7 Hz, 1H), 4.58 (d, *J* = 9.7 Hz, 2H), 3.80 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.15, 144.85 (dm, *J* = 257.8 Hz), 138.97, 137.60 (dm, *J* = 242.3 Hz), 128.22 (m), 127.23, 127.18, 127.14, 121.24 (q, *J* =

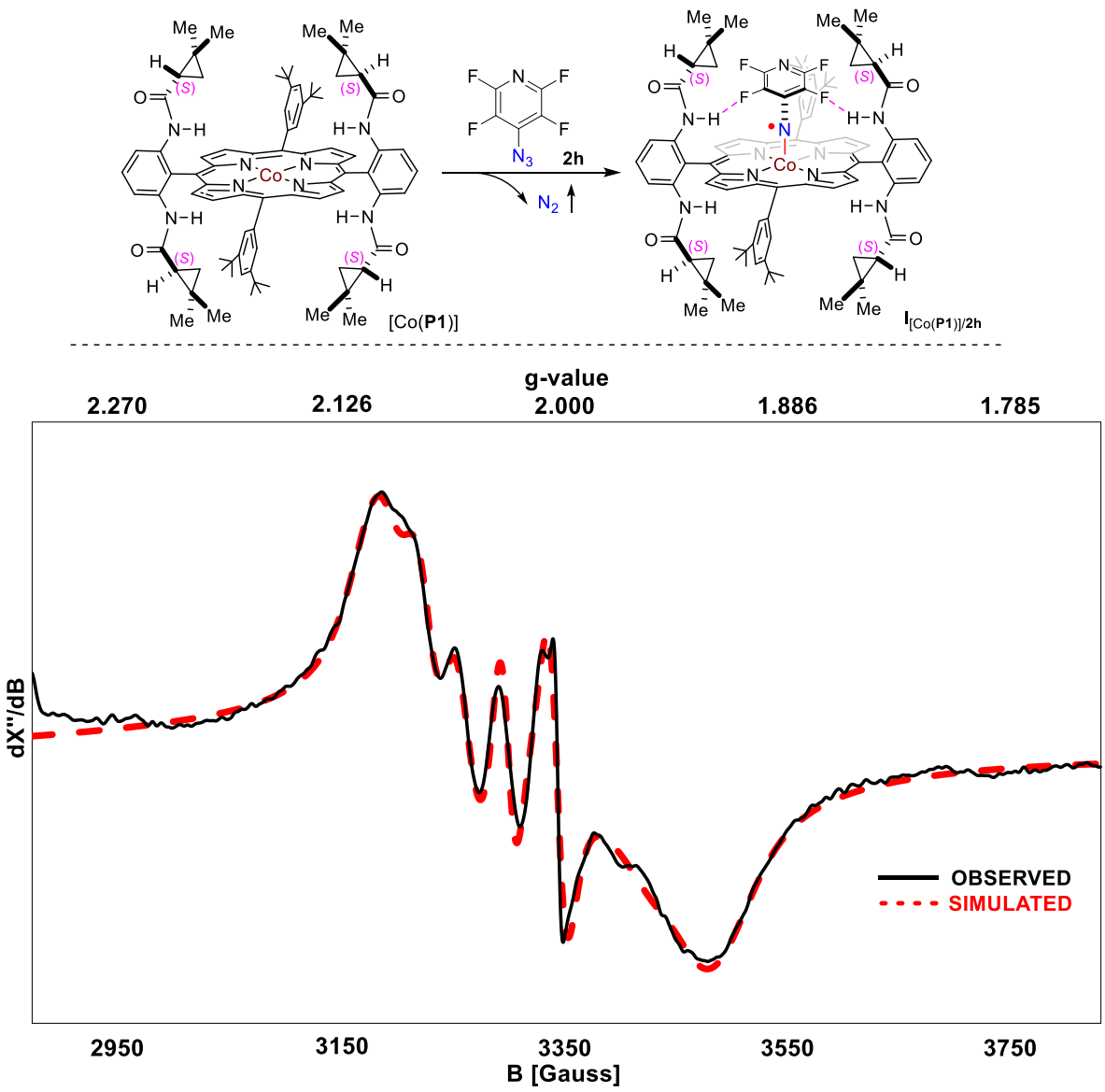
273.3 Hz), 99.66 (m), 83.17, 76.92, 53.05, 46.66. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -55.37 (t, *J* = 21.0 Hz, 3F), -141.82 (m, 2F), -156.20 (m, 2F). IR (neat, $cm^{-1}$): 3337, 2958, 2246, 1720, 1511, 1336, 1231, 971, 714. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{16}H_9F_7SNO_2$: 412.02367, Found: 412.02432. HPLC analysis: ee = 99%. ODH (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 15.90 min, $t_{minor}$ = 18.87 min.

## 6. Characterization of α-Co(III)-Aminyl Radicals by EPR and HRMS

### 6.1. Procedure for EPR Experiment

Catalyst [Co(Por)] (0.001 mmol) was placed into an oven-dried EPR tube. This EPR tube was then capped with a rubber septum and was fasten with Parafilm. The tube was evacuated and backfilled with nitrogen for three times. Then azide **2** (0.05 mmol) in 0.5 mL benzene was added into this tube through gas-tight syringe. The cap of EPR tube was further sealed with vacuum grease. The reaction mixture was shaken well at r.t. for 10 min. Then the sample was ready for EPR experiment.

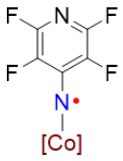
X-band EPR spectra were recorded with a Bruker EMX-Plus spectrometer (Bruker BioSpin). Simulations of the EPR spectra were performed by iteration of the isotropic g-values and line widths using the EPR simulation software SpinFit in Xenon. Experimental X-band EPR isotropic spectra of α-Co(III)-Aminyl Radical **I** in benzene was recorded at r.t. (Freq = 9.42 GHz; mod. amp. = 4 G; microwave power = 20 mW).




Experimental and simulated X-Band EPR spectra for α-Co(III)-aminyl radical $I_{[Co(\mathbf{P1})]/\mathbf{2h}}$ in benzene at r.t.

## EPR simulation details:

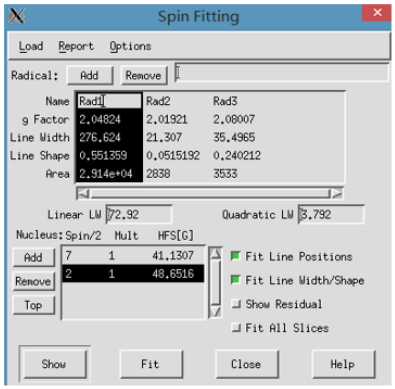
$^{N\alpha}\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{2h}}$: 29140/(29140 + 2838 + 3533) = 82%



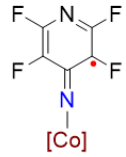
g = 2.04824

$A_{(Co)}$ = 41.1307 x 2.04824 x 1.399611451 = 117.9 MHz

$A_{(N)}$ = 48.6516 x 2.04824 x 1.399611451 = 139.5 MHz



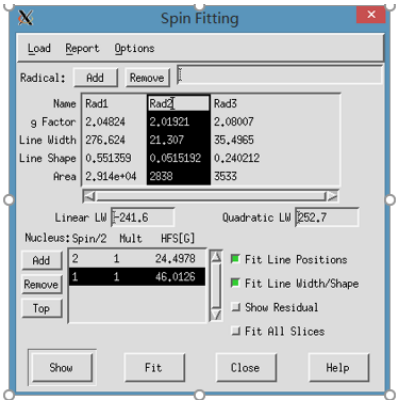

$^{C\gamma}\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{2h}}$: 2838/(29140 + 2838 + 3533) = 8%



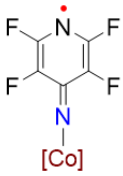
g = 2.01921

$A_{(N)}$ = 24.4978 x 2.01921 x 1.399611451 = 69.2 MHz

$A_{(F)}$ = 46.0126 x 2.01921 x 1.399611451 = 130.0 MHz



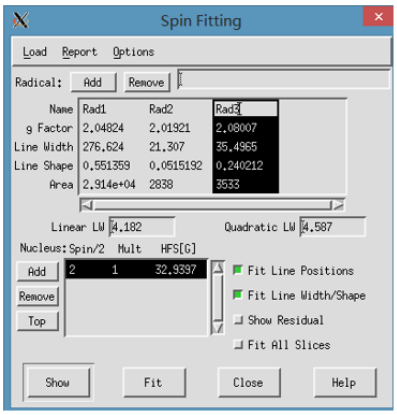

$^{N\varepsilon}\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{2h}}$: 3533/(29140 + 2838 + 3533) = 10%

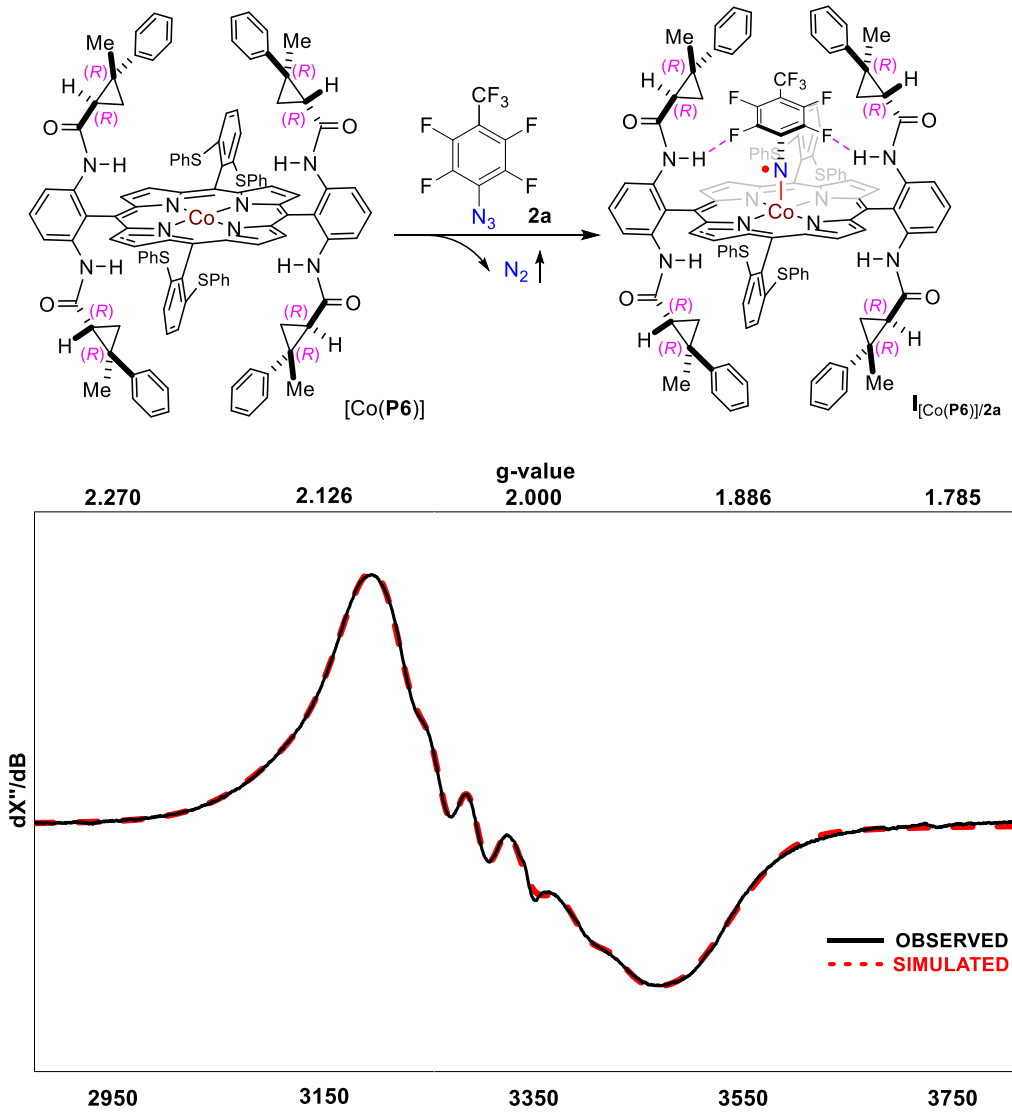


g = 2.08007

$A_{(N)}$ = 32.9397 x 2.08007 x 1.399611451 = 95.9 MHz

$A_{(F)}$ = 0 MHz

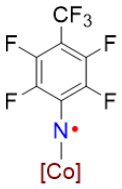





Experimental and simulated X-Band EPR spectra for α-Co(III)-aminyl radical $\mathbf{I}_{[Co(\mathbf{P6})]/\mathbf{2a}}$ in benzene at RT.

## EPR Simulation Details:

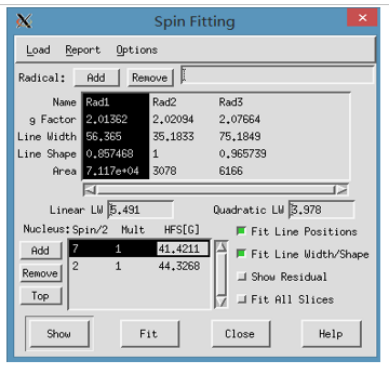
$^{N\alpha}\mathbf{I}_{[Co(\mathbf{P6})]/\mathbf{2a}}$: 71170/(71170 + 3078 + 6166) = 88%



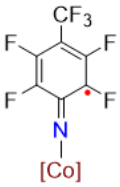

g = 2.01362

A(Co) = 41.4211 x 2.01362 x 1.399611451 = 116.7 MHz

A(N) = 44.3268 x 2.01362 x 1.399611451 = 124.9 MHz



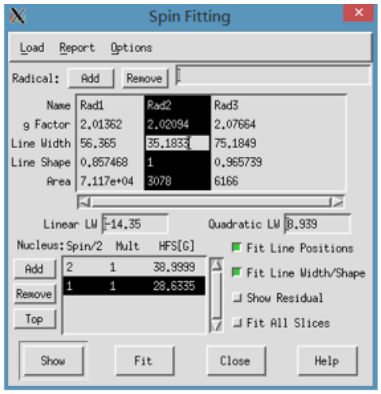

$^{C\gamma}\mathbf{I}_{[Co(\mathbf{P6})]/\mathbf{2a}}$: 3078/(71170 + 3078 + 6166) = 4%



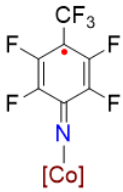

g = 2.02094

A(N) = 38.9999 x 2.02094 x 1.399611451 = 110.3 MHz

A(F) = 28.6335 x 2.02094 x 1.399611451 = 81.0 MHz



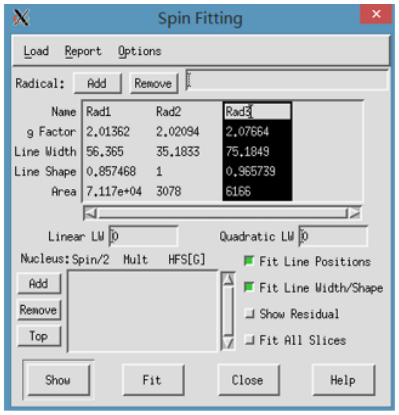

$^{C\varepsilon}\mathbf{I}_{[Co(\mathbf{P6})]}$ : 6166/(71170 + 3078 + 6166) = 8%




g = 2.07664

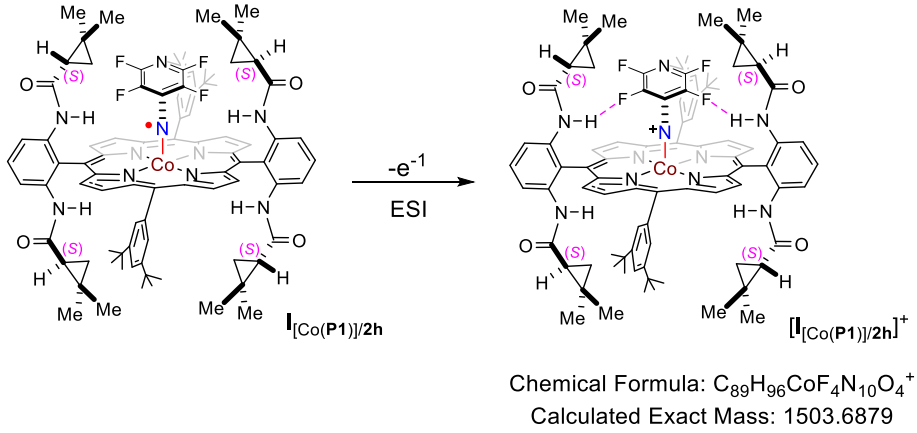
A(N) = 0 MHz

A(F) = 0 MHz



## 6.2. Procedure for HRMS Experiment

$\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{2h}}$ was further detected by high resolution mass spectrometry (HRMS) with ESI ionization. Through gas-tight syringe, the same EPR solution was transferred to a sealed HRMS sample vial, which was pre-evacuated and backfilled with nitrogen. The high-resolution mass spectra (LC-HRMS) (ESI) in the absence of any additives that commonly act as electron carriers for ionization allowed for the detection of the molecular ion signals corresponding to the α-Co(III)-aminyl radical $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{2h}}$ ($[M]^+$ m/z = 1503.6881 (observed)), by the loss of one electron (Figure S4).



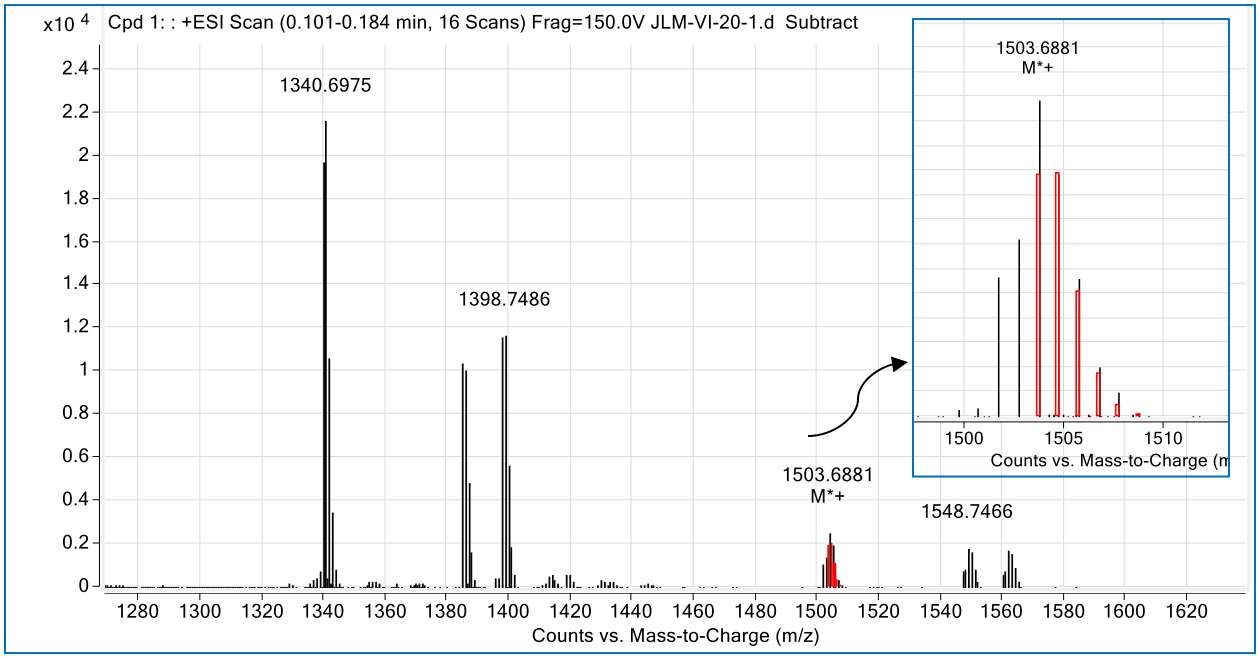
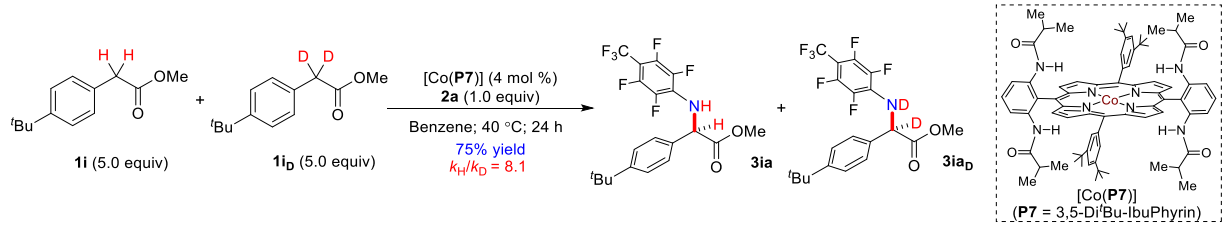



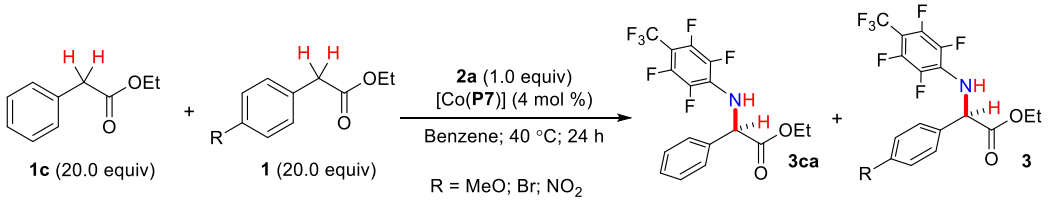

**Figure S4.** HR-ESI-MS spectrum of reaction mixture of azide **2h** and [Co(**P1**)] (the inset red one is the simulated mass spectrum of $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{2h}}$).

## 7. Kinetic Isotope Effect (KIE) Experiment

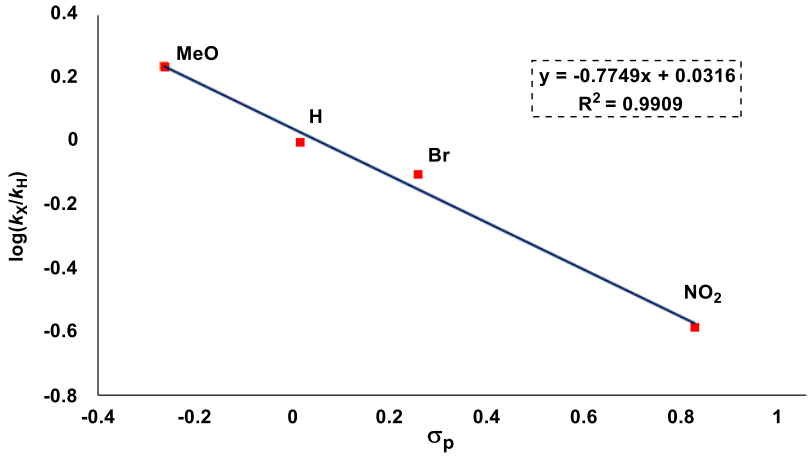



An oven dried Schlenk tube was charged with [Co(**P7**)] (4 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated and back filled with nitrogen for three times. The Teflon screw cap was replaced with a rubber septum and methyl 2-(4-(*tert*-butyl)phenyl)acetate (**1i**, 1 mmol, 5.0 equiv), deuterated methyl 2-(4-(*tert*-butyl)phenyl)acetate (**1i$_D$**, 1 mmol, 5.0 equiv), 4-trifluoromethyl-2,3,5,6-tetrafluorophenyl azide (**2a**, 0.2 mmol, 1 equiv) and benzene (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 $^o$C for 24 h. After completion of the reaction, the reaction mixture was purified by flash column chromatography on silica gel to afford **3ia** together with **3ia$_D$** in 75% overall yield. KIE ($k_H/k_D$) was calculated as 8.1 based on $^1$H-NMR analysis.

## 8. Evaluation of Electronic Effect of C–H Substrates via Hammett Study

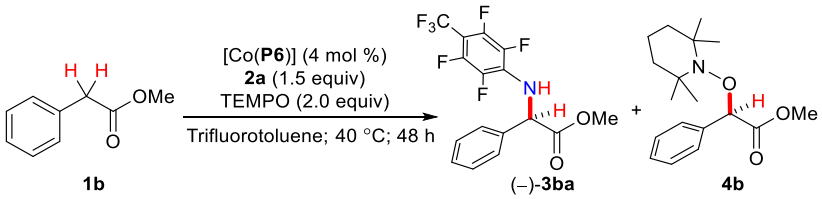



An oven dried Schlenk tube was charged with [Co(**P7**)] (4 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated for 30 s and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and ethyl phenylacetate **1c** (1 mmol, 20 equiv), *para*-substituted methyl phenylacetate **1** (1mmol, 20 equiv), 4-trifluoromethyl-2,3,5,6-tetrafluorophenyl azide (**2a**, 0.05 mmol, 1 equiv) and benzene (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 $^{o}$C for 24 h. Following completion of the reaction, the distribution of the aminated products was determined by $^{19}$F NMR: (1) $k_H/k_{Br}$ = 100/79; (2) $k_{MeO}/k_{NO_2}$ = 100/15; (3) $k_H/k_{NO_2}$ = 100/26. Based on the eqs (1) – (3), the plot of linear free-energy correlation of log($k_X/k_H$) versus $\sigma_p$ was obtained as shown below.



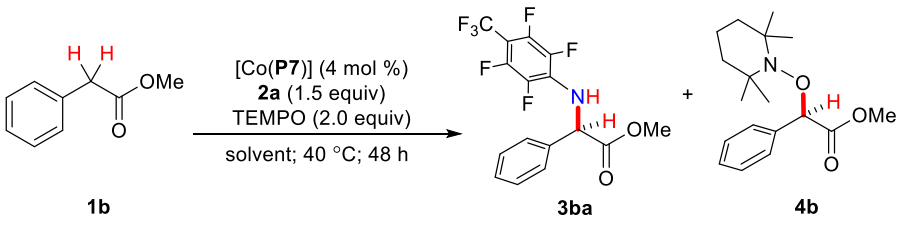

Correlation of log($k_X/k_H$) versus $\sigma_p$ plot for amination of *para*-substituted phenylacetates with azide **2a**.

## 9. Trapping of Alkyl Radical Intermediate



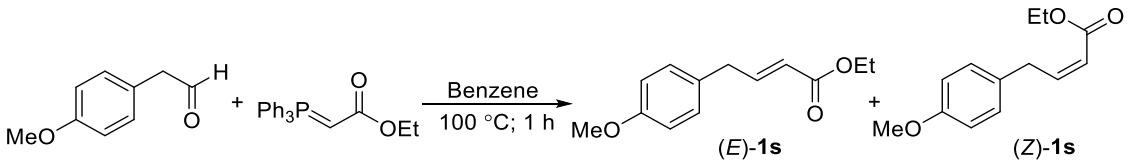

An oven-dried Schlenk tube was charged with [Co(**P6**)] (4 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and methyl phenylacetate (**1b**, 0.1 mmol, 1 equiv), 4-trifluoromethyl-2,3,5,6-tetrafluorophenyl azide (**2a**, 0.15 mmol, 1.5 equiv), TEMPO (2 equiv) and α,α,α-trifluorotoluene (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 °C for 48 h. Following completion of the reaction, the mixture was purified by column chromatography to give amide **3ba** (34% yield, 95% ee) and TEMPO trapped product **4b** (40% yield, 0% ee). **4b**: $^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.33 (m, 2H), 7.29 (m, 1H), 5.21 (s, 1H), 3.65 (s, 3H), 1.51 – 1.25 (m, 6H), 1.23 (s, 3H), 1.13 (s, 3H), 1.07 (s, 3H), 0.71 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 172.45, 138.14, 128.31, 127.93, 126.87, 88.57, 59.89, 51.82, 40.21, 40.08, 33.53, 32.84, 20.13, 17.07. IR (neat, $cm^{-1}$): 2930, 1752, 1738, 1160, 724, 696. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{28}NO_3$: 306.2064 found: 306.2067.

**Table S2. Investigation of Solvent Viscosity Effect using [Co(P7)]**

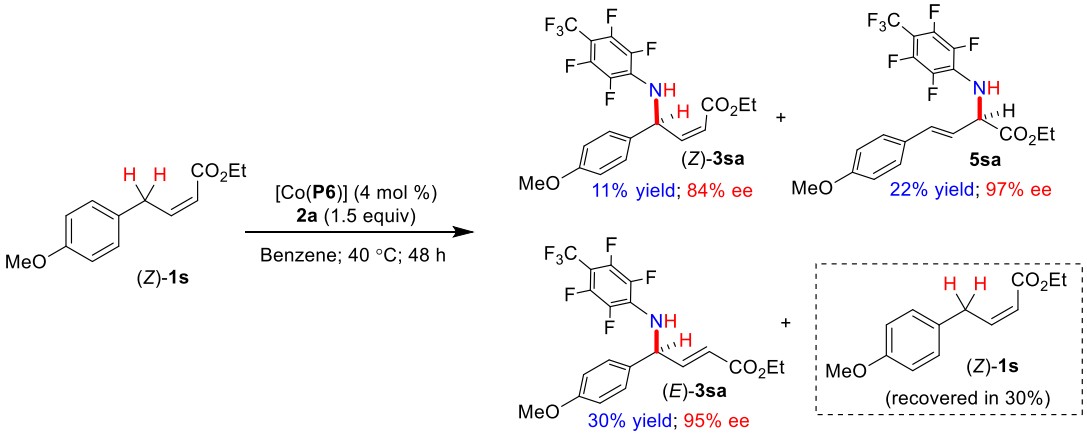



| Solvent | Viscosity | Yield of **3ba** | Yield of **4b** |
|---|---|---|---|
| Hexane | 0.31 (20 °C) | 19% | 48% |
| Benzene | 0.65 (20 °C) | 20% | 60% |
| Trifluorotoluene | -- | 19% | 42% |
| Chlorobenzene | 0.80 (20 °C) | 15% | 42% |
| 1,2-Dichlorobenzene | 1.32 (25 °C) | 21% | 46% |
| 1,4-Dioxane | 1.44 (15 °C) | 0% | 7% |

## 10. Probing Allylic Radical via Olefin Isomerization



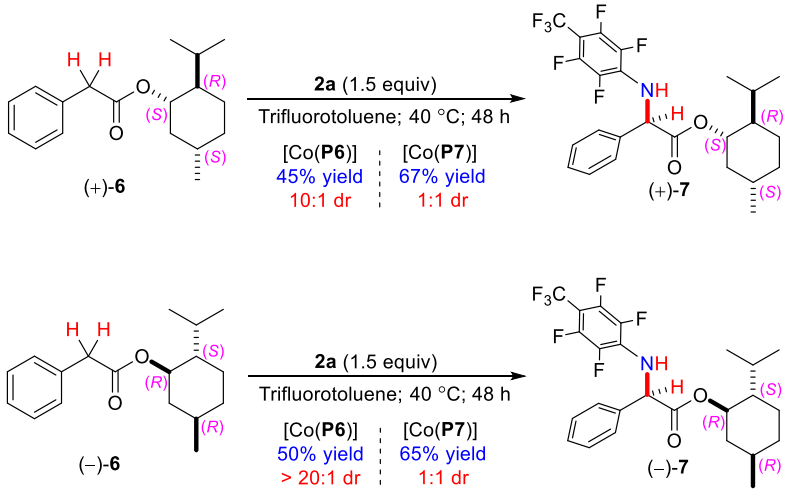

(*Z*)-**1s** was synthesized through Wittig reaction. To a solution of the 2-(4-methoxyphenyl)acetaldehyde (1.2 g, 8.0 mmol) in dry benzene (5 mL) was added $Ph_3P{=}CHCO_2Et$ (2.79 g, 8.0 mmol) and stirred at reflux for 1 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue purified by column chromatography eluted with hexane/EtOAc (40/1 v/v) to afford **1s** as a mixture of geometrical isomers. The mixture was partially separated by silica gel column chromatography to give (*E*)-**1s** (1.50 g, 85%) and pure (*Z*)-**1s** (150 mg, 9%). (*Z*)-**1s**: $^1$H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.32 (dt, J = 11.3, 7.6 Hz, 1H), 5.83 (dt, *J* = 11.4, 1.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.96 (dd, *J* = 7.7, 1.8 Hz, 2H), 3.79 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 166.34, 158.11, 148.31, 131.44, 129.49, 119.52, 113.97, 59.90, 55.19, 34.18, 14.23. IR (neat, $cm^{-1}$): 2932, 1714, 1510, 1245, 1160, 823, 756. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{13}H_{17}O_3$: 221.11722 found: 221.11652.




An oven dried Schlenk tube was charged with [Co(**P6**)] (4 mol %) and 4 Å molecular sieves. The Schlenk tube was then evacuated and back filled with nitrogen for three times. The Teflon screw cap was replaced with a rubber septum and (*Z*)-**1s** (0.10 mmol, 1 equiv), 4-trifluoromethyl-2,3,5,6-tetrafluorophenyl azide (**2a**, 0.15 mmol, 1.5 equiv) and benzene (0.5 mL) were added. The Schlenk tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon

screw cap. The mixture was then stirred at 40 °C. After 48 h, the reaction mixture was concentrated and the yields of all products are calculated based on crude $^1$H NMR with 1,1,2,2-tetrachloroethane as internal standard ((*Z*)-**3sa**: 11% yield; **5sa**: 22% yield; (*E*)-**3sa**: 30% yield; (*Z*)-**1s**: 30% recovered). Crude mixture was purified by PTLC. For product (*Z*)-**3sa**: $[\alpha]_D^{20}$= -25° (*c* = 0.3, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.65 (m, 1H), 6.31 (dd, *J* = 11.5, 9.0 Hz, 1H), 5.92 (dd, *J* = 11.4, 1.1 Hz, 1H), 4.64 (d, *J* = 8.4 Hz, 1H), 4.22 (m, 2H), 3.81 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). $^{19}$F NMR (470 MHz, $CDCl_3$) δ -55.04 (t, *J* = 20.8 Hz, 3F), -142.91 (m, 2F), -158.65 (m, 2F). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.44, 159.54, 147.04, 144.86 (dm, *J* = 245.3 Hz), 136.85 (dm, *J* = 243.4 Hz), 132.27, 129.95, 127.81, 121.49 (q, *J* = 270.0 Hz), 120.97, 114.50, 60.64, 55.29 (2C), 14.12. IR (neat, cm$^{-1}$): 3352, 2917, 1716, 1655, 1510, 1333, 1234, 1176, 972, 714. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{20}H_{17}F_7NO_3$: 452.10912, Found: 452.10941. HPLC analysis: ee = 84%. IA (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 8.24 min, $t_{minor}$ = 7.81 min. For product **5sa**: $[\alpha]_D^{20}$= -50° (*c* = 0.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 7.7 Hz, 2H), 6.69 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 6.6 Hz, 1H), 5.12 (m, 2H), 4.30 (m, 2H), 3.82 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). $^{19}$F NMR (470 MHz, $CDCl_3$) δ -55.04 (t, *J* = 20.8 Hz, 3F), -142.91 (m, 2F), -158.65 (m, 2F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.76, 159.95, 144.81 (dm, *J* = 266.2 Hz), 136.77 (dm, *J* = 243.8 Hz), 134.00, 128.04, 121.43 (q, *J* = 272.6 Hz), 121.37, 114.09, 94.04 (m), 62.37, 58.82, 55.32, 14.09. IR (neat, cm$^{-1}$): 3391, 2938, 1737, 1511, 1334, 1133, 993, 713. HRMS (ESI) ($[M-H]^-$) Calcd. for: $C_{20}H_{15}F_7NO_3$: 450.0946, Found: 450.0951. HPLC analysis: ee = 97%. IA (95% hexane: 5% isopropanol, 0.8 ml/min): $t_{major}$ = 7.46 min, $t_{minor}$ = 8.22 min.

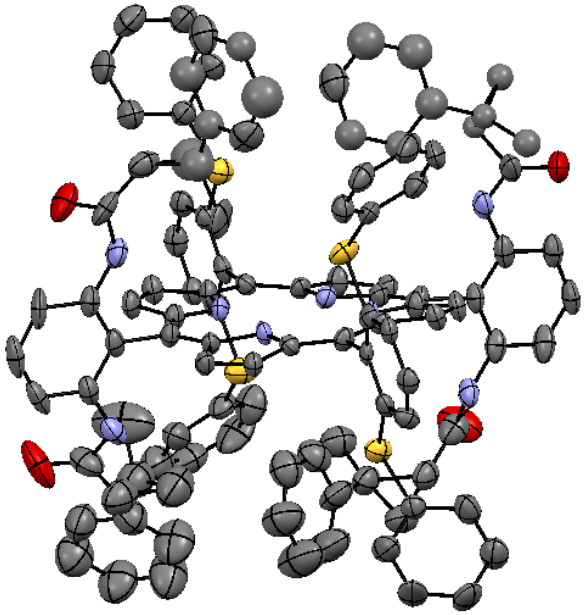
## 11. Evaluation of Diastereoselectivity with Chiral C–H Substrates




First, the reactions were performed with (+)-**6** (*14*) using [Co(**P6**)] or [Co(**P7**)] as catalyst respectively following the general procedure using 1.5 equiv of azide **2a** with α,α,α-trifluorotoluene as solvent. After 48 hours, the dr of products were determined by crude $^{19}$F NMR. The results indicated that when [Co(**P6**)] is used as catalyst, (+)-**7** could be obtained in 45% yield with the dr of 10/1. When [Co(**P7**)] was used as catalyst, (+)-**7** could be obtained in 67% yield with the dr of 1/1. Similar results were achieved when using (−)-**6** as starting material using [Co(**P6**)] or [Co(**P7**)] as catalyst respectively. When [Co(**P6**)] was used as catalyst, (−)-**7** could be obtained in 50% yield with the dr of >20/1. When [Co(**P7**)] was used as catalyst, (−)-**7** could be obtained in 65% yield with the dr of 1/1. (−)-**7**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 5.58 (d, *J* = 7.5 Hz, 1H), 5.42 (d, *J* = 7.8 Hz, 1H), 4.65 (td, *J* = 11.0, 4.4 Hz, 1H), 2.03 (d, *J* = 11.0 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.53 – 1.41 (m, 1H), 1.29 – 1.19 (m, 2H), 1.05 (q, *J* = 11.9 Hz, 1H), 0.97 – 0.76 (m, 6H), 0.55 (d, *J* = 7.0 Hz, 3H), 0.33 (d, *J* = 6.9 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.43, 144.73 (dm, *J* = 257.6 Hz), 136.95, 136.91 (dm, *J* = 242.0 Hz), 129.21 (m), 128.91, 128.88, 126.96, 121.42 (q, *J* = 272.8 Hz), 97.29 (m), 60.76, 47.09, 40.67, 34.03, 31.40, 25.29, 22.88, 21.92, 20.41, 15.45. $^{19}$F NMR (376 MHz, $CDCl_3$): δ -55.08 (t, *J* = 20.9 Hz), -143.01 (m, 3F), -158.67 (m, 2F). IR (neat, $cm^{-1}$): 2954, 2927, 2869, 1497, 1333, 1256, 1137, 986, 695. HRMS (DART) ($[M+H]^+$) Calcd. for: $C_{25}H_{27}F_7NO_2$: 506.19245, Found: 506.18992.

## 12. X-ray Crystallographic Information

### 12.1. Single-crystal X-ray Structure of P6

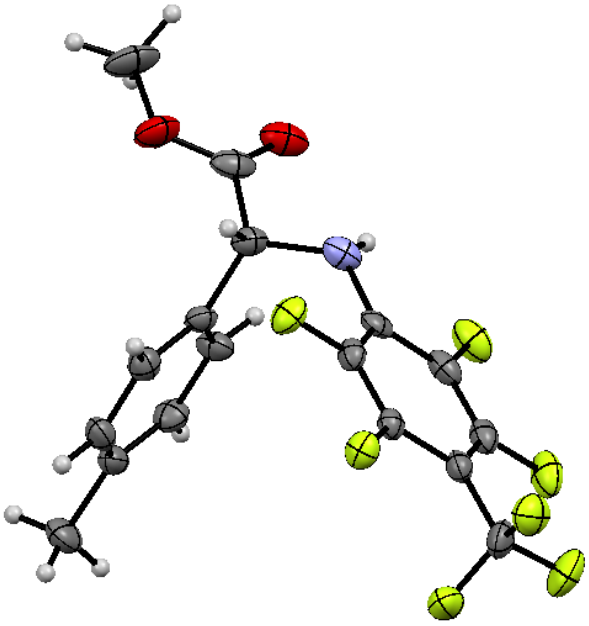


Single-crystal X-ray structure of **P6** with thermal ellipsoids drawn at 50% probability

**P6:** The majority of non-hydrogen atoms were refined anisotropically. Several side arms of porphyrin molecules are disordered over two positions with 1:1 ratio of disordered parts (fixed). Some of disordered atoms have been refined isotropically. Disordered parts have been refined using distance and angular restraints (DFIX, DANG) and constraints (AFIX 66) to keep the geometry chemically feasible. All disordered solvent molecules of toluene, and 1,4-dioxane have been refined using geometry restraints and constraints. There are two symmetrically independent porphyrin molecules in the crystal structure.

| **Crystal Data and Structure Refinement for P6.** | |
|---|---|
| Identification code | **P6** |
| Empirical formula | C256H222N16O11S8 |
| Formula weight | 3954.98 |
| Temperature/K | 100(2) |
| Crystal system | triclinic |
| Space group | P1 |
| a/Å | 13.1087(5) |
| b/Å | 15.9083(5) |
| c/Å | 26.9265(10) |
| α/° | 90.115(2) |
| β/° | 101.243(2) |
| γ/° | 102.434(2) |
| Volume/Å3 | 5372.6(3) |
| Z | 1 |
| ρcalcmg/mm3 | 1.222 |
| m/mm‑1 | 1.285 |
| F(000) | 2086.0 |
| Crystal size/mm3 | 0.11 × 0.1 × 0.08 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection | 6.7 to 131.96° |
| Index ranges | -15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -31 ≤ l ≤ 31 |
| Reflections collected | 66612 |
| Independent reflections | 32728 [Rint = 0.0795, Rsigma = 0.1105] |
| Data/restraints/parameters | 32728/285/2534 |
| Goodness-of-fit on F2 | 1.020 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0958, wR2 = 0.2392 |
| Final R indexes [all data] | R1 = 0.1442, wR2 = 0.2766 |
| Largest diff. peak/hole / e Å-3 | 0.62/-0.46 |
| Flack parameter | 0.09(2) |

## 12.2. Single-crystal X-ray Structure of 3ha



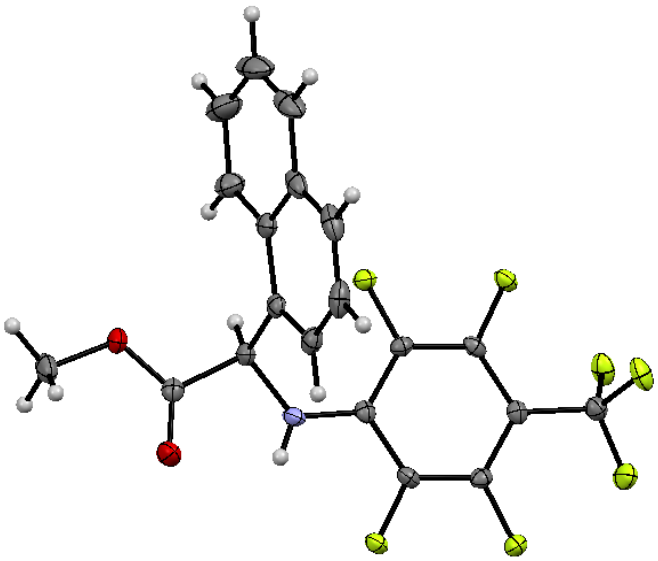
.

Single-crystal X-ray structure of **3ha** with thermal ellipsoids drawn at 50% probability

**3ha**: All non-hydrogen atoms were refined anisotropically. Hydrogen atom of –NH groups has been found from Fourier difference map and were freely refined. Remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2[1.5]Ueq(-CH[-$CH_3$]). Disorderd -$CF_3$ group has been refined with SADI restraints.

| **Crystal Data and Structure Refinement for 3ha** | |
|---|---|
| Identification code | **3ha** |
| Empirical formula | C17 H12 F7 N O2 |
| Formula weight | 395.28 |
| Temperature | 100(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Triclinic, P1 |
| Unit cell dimensions | a = 9.1989(3) A alpha = 92.451(2) deg. |
| | b = 9.2630(3) A beta = 103.071(2) deg. |
| | c = 9.9868(3) A gamma = 94.018(2) deg. |
| Volume | 825.38(5) A^3 |
| Z, Calculated density | 2, 1.590 Mg/m^3 |
| Absorption coefficient | 1.406 mm^-1 |
| F(000) | 400 |
| Crystal size | 0.12 x 0.06 x 0.03 mm |
| Theta range for data collection | 4.55 to 68.70 deg. |
| Limiting indices | -11<=h<=11, -11<=k<=11, -12<=l<=11 |
| Reflections collected / unique | 10750 / 5264 [R(int) = 0.0374] |
| Completeness to theta = 66.60 | 97.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9590 and 0.8494 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 5264 / 31 / 536 |
| Goodness-of-fit on F^2 | 1.057 |
| Final R indices [I>2sigma(I)] | R1 = 0.0403, wR2 = 0.0837 |
| R indices (all data) | R1 = 0.0506, wR2 = 0.0888 |
| Absolute structure parameter | 0.08(11) |
| Largest diff. peak and hole | 0.345 and -0.203 e.A^-3 |

### 12.3. Single-crystal X-ray Structure of 3ma

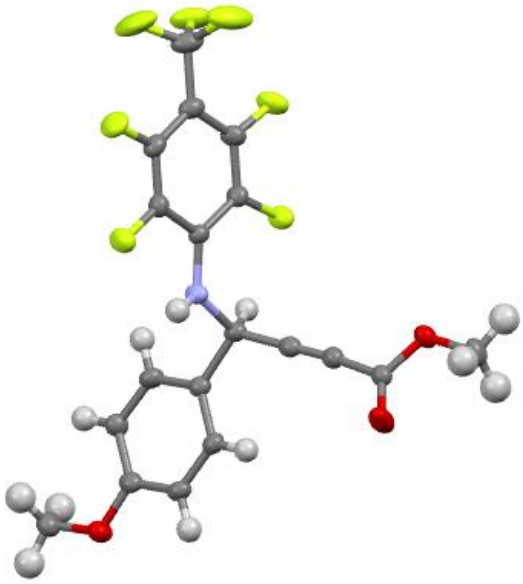


Single-crystal X-ray structure of **3ma** with thermal ellipsoids drawn at 50% probability.

**3ma:** All non-hydrogen atoms were refined anisotropically. The hydrogen atom of –NH group has been found from difference Fourier map and was freely refined. Remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH) and Uiso(H) = 1.5Ueq(-$CH_3$).

| **Crystal Data and Structure Refinement for 3ma** | |
|---|---|
| Identification code | **3ma** |
| Empirical formula | C20H12F7NO2 |
| Formula weight | 431.31 |
| Temperature/K | 100(2) |
| Crystal system | orthorhombic |
| Space group | P212121 |
| a/Å | 7.9791(2) |
| b/Å | 8.3129(2) |
| c/Å | 26.4307(6) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å3 | 1753.13(7) |
| Z | 4 |
| ρcalcmg/mm3 | 1.634 |
| m/mm‑1 | 1.386 |
| F(000) | 872.0 |
| Crystal size/mm3 | 0.12 × 0.03 × 0.02 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection | 6.688 to 137.756° |
| Index ranges | -9 ≤ h ≤ 9, -9 ≤ k ≤ 10, -29 ≤ l ≤ 31 |
| Reflections collected | 23084 |
| Independent reflections | 3224 [Rint = 0.0406, Rsigma = 0.0218] |
| Data/restraints/parameters | 3224/0/276 |
| Goodness-of-fit on F2 | 1.064 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0256, wR2 = 0.0596 |
| Final R indexes [all data] | R1 = 0.0294, wR2 = 0.0613 |
| Largest diff. peak/hole / e Å-3 | 0.20/-0.20 |

### 12.4. Single-crystal X-ray Structure of 3va



Single-crystal X-ray structure of **3va** with thermal ellipsoids drawn at 50% probability

| **Crystal Data and Structure Refinement for 3va** | |
|---|---|
| Identification code | **3va** |
| Empirical formula | C19 H12 F7 N O3 |
| Formula weight | 435.30 |
| Temperature | 173(2) K |
| Wavelength | 1.54178 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1$ |
| Unit cell dimensions | a = 5.5696(4) Å |
| | b = 9.1428(7) Å |
| | c = 17.2564(13) Å |
| Volume | 878.62(11) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.645 $Mg/m^3$ |
| Absorption coefficient | 1.431 $mm^{-1}$ |
| F(000) | 440 |
| Crystal size | 0.580 x 0.140 x 0.100 $mm^3$ |
| Theta range for data collection | 5.127 to 66.601°. |
| Index ranges | -6<=h<=6, -10<=k<=10, -20<=l<=20 |
| Reflections collected | 16507 |
| Independent reflections | 3075 [R(int) = 0.0309] |
| Completeness to theta = 66.601° | 99.3 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7528 and 0.5842 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3075 / 2 / 276 |
| Goodness-of-fit on $F^2$ | 1.053 |
| Final R indices [I>2sigma(I)] | R1 = 0.0289, wR2 = 0.0765 |
| R indices (all data) | R1 = 0.0291, wR2 = 0.0769 |
| Absolute structure parameter | -0.02(4) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.226 and -0.231 $e.Å^{-3}$ |

## 13. Reference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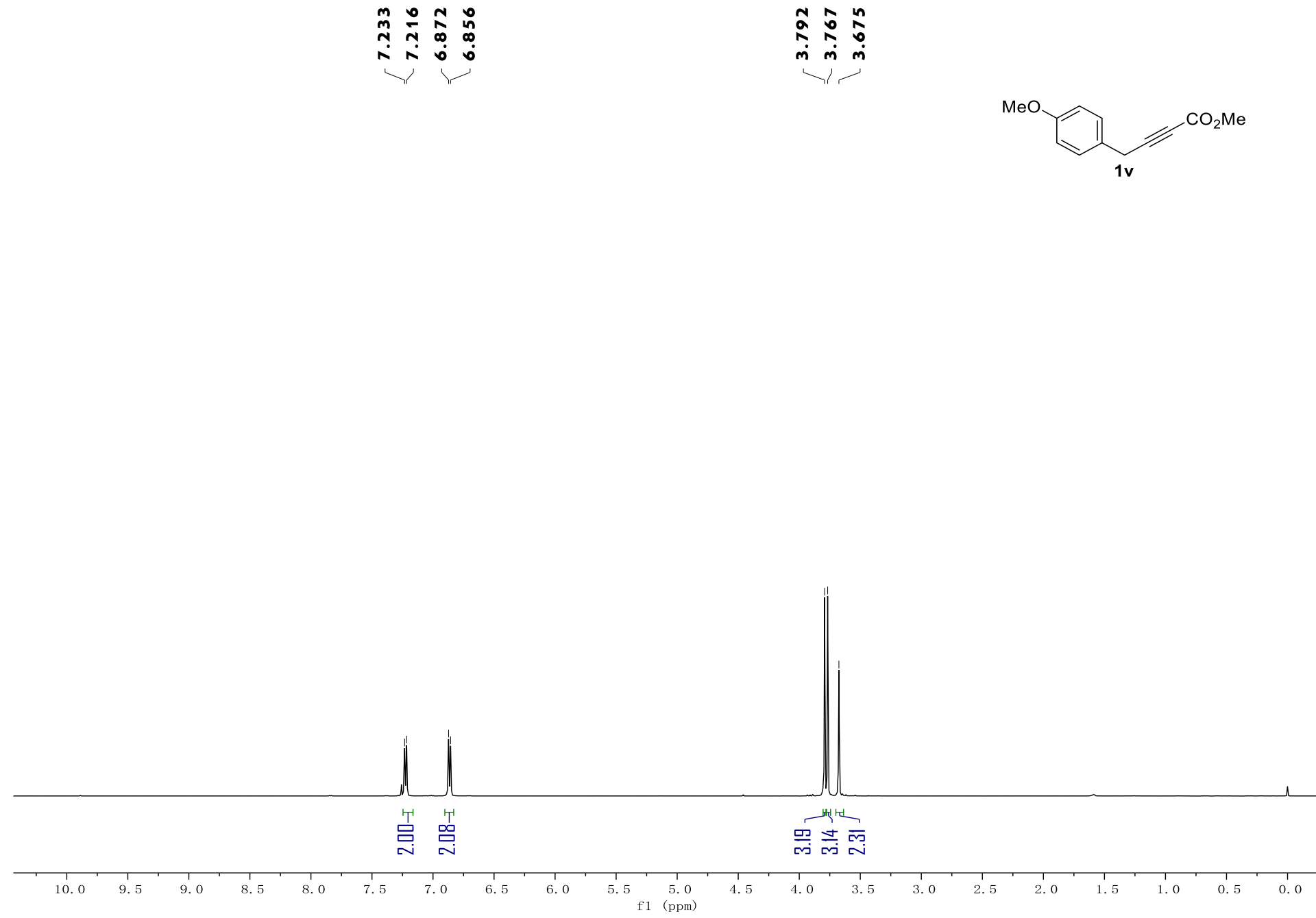
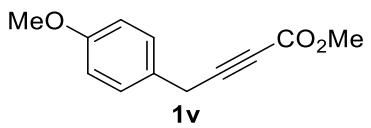
**Copies of NMR/HPLC Spectra**

# $^1$H NMR

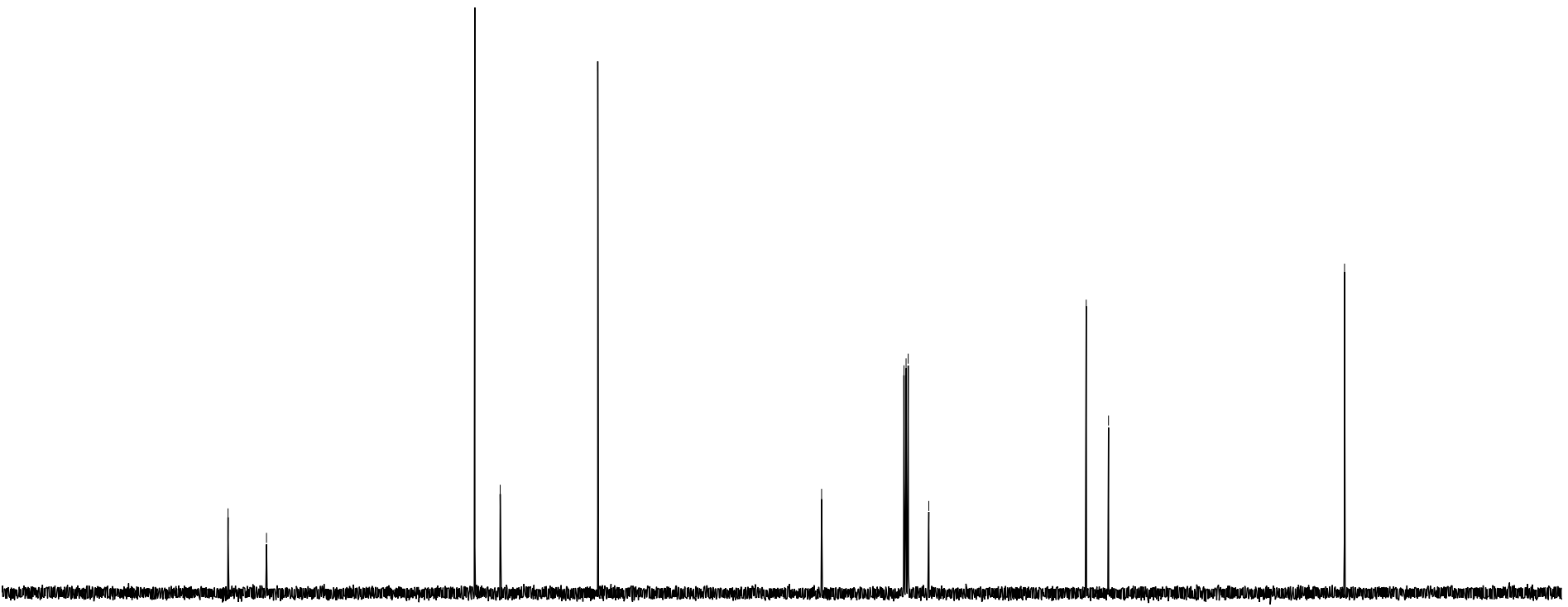

7.233
7.216
6.872
6.856
3.792
3.767
3.675
MeO
CO2Me
1v
2.00
2.08
3.19
3.14
2.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

# $^{13}$C NMR

158.760
154.123
129.010
125.945
114.182
87.195
77.265
77.011
76.756
74.272
55.291
52.601
24.145



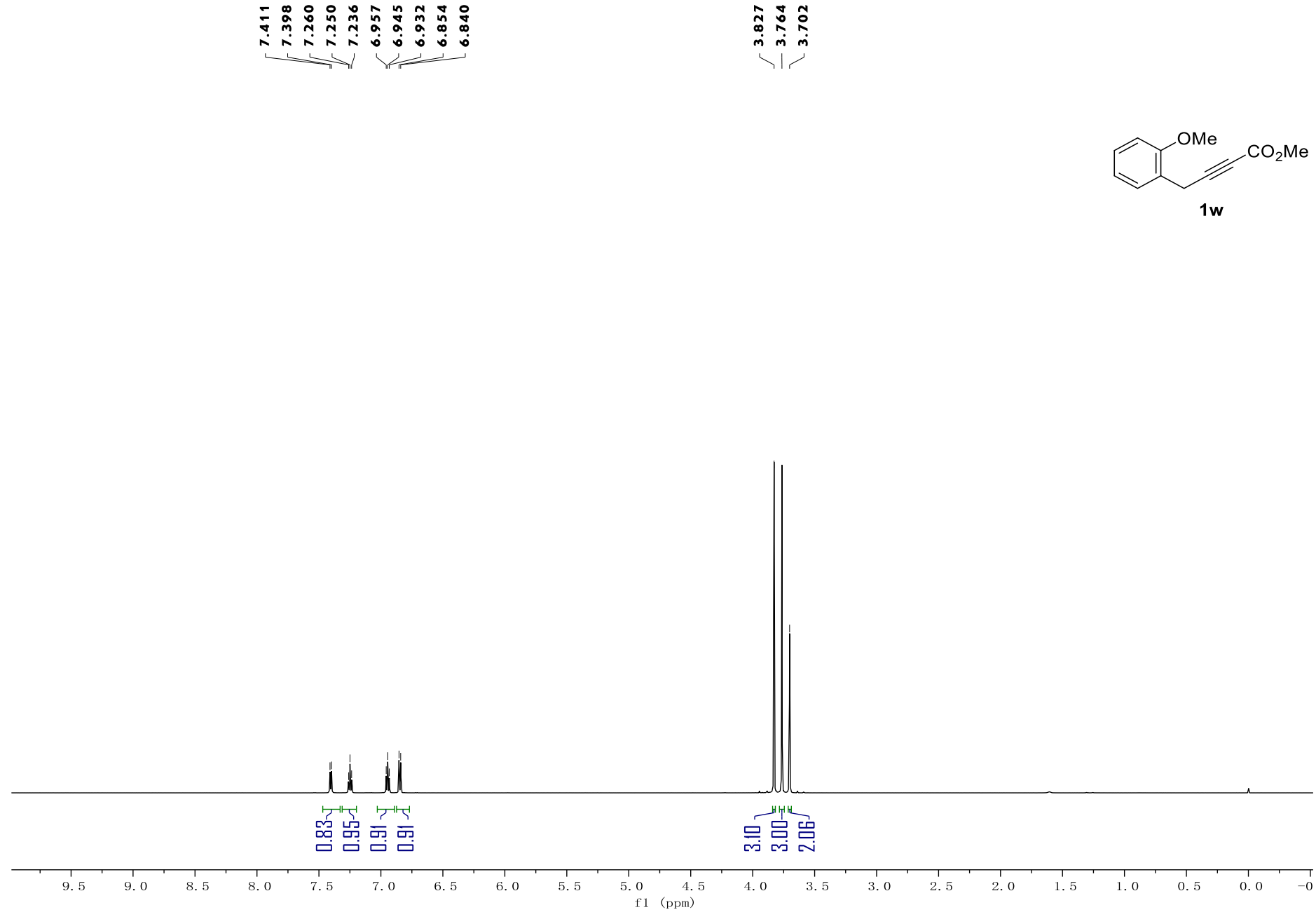

1v



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

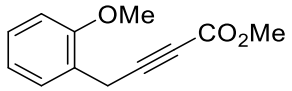
f1 (ppm)

# $^1$H NMR

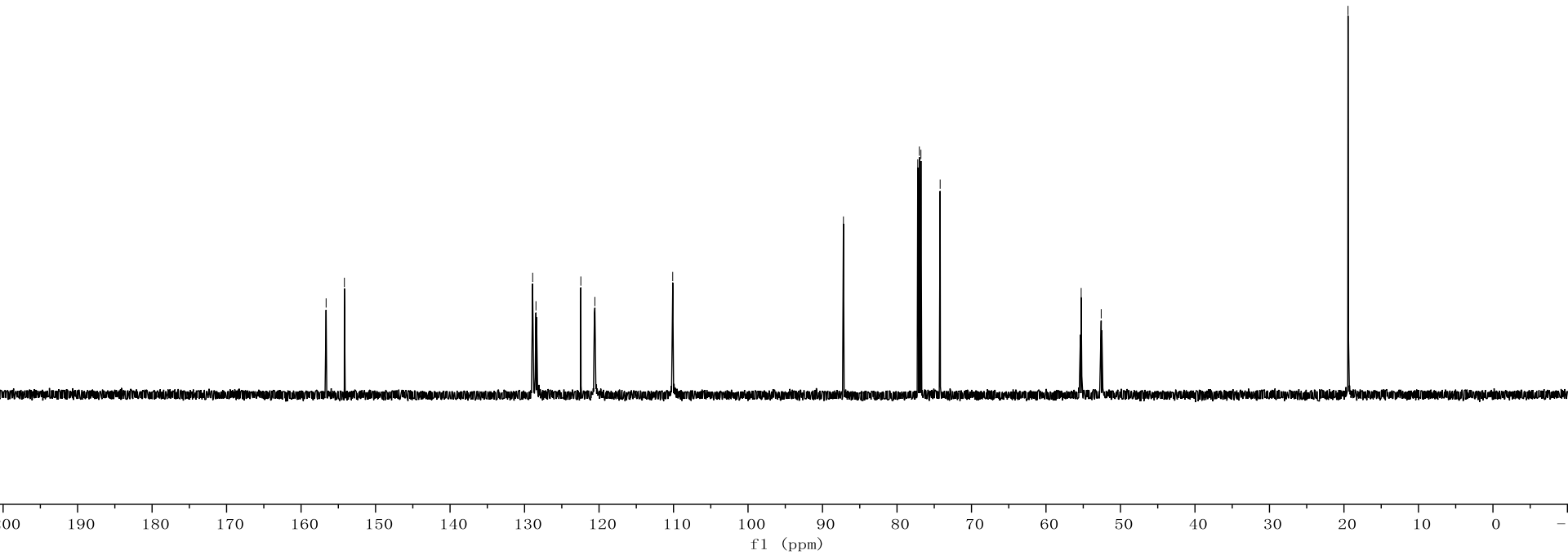

7.411
7.398
7.260
7.250
7.236
6.957
6.945
6.932
6.854
6.840
3.827
3.764
3.702
OMe
CO2Me
1w
0.83
0.95
0.91
0.91
3.10
3.00
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

# $^{13}$C NMR

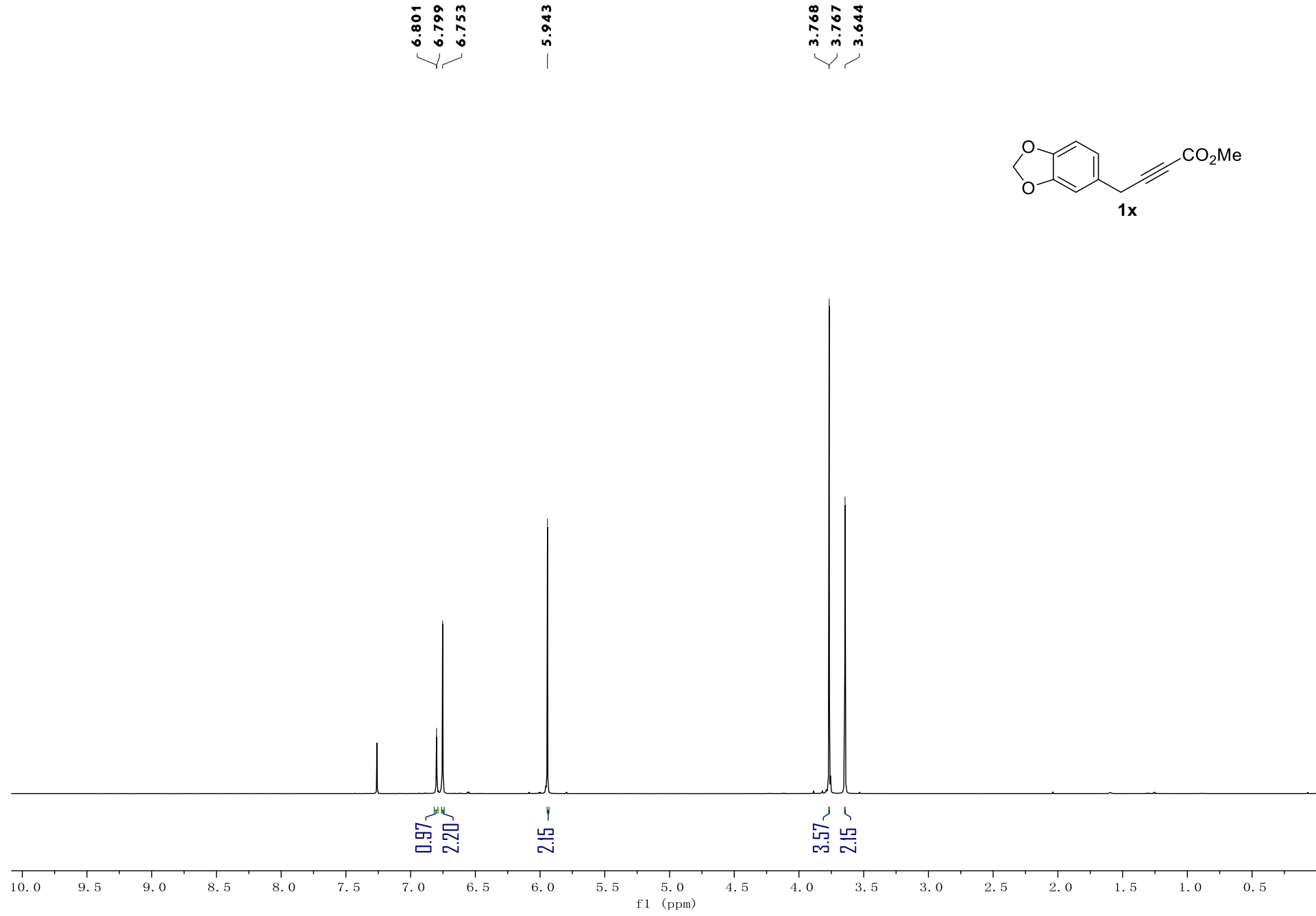
156.640
154.183
128.910
128.466
122.441
120.560
110.108
87.192
77.213
77.001
76.789
74.207
55.277
52.587
19.454




**1w**

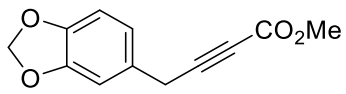


# $^{1}$H NMR

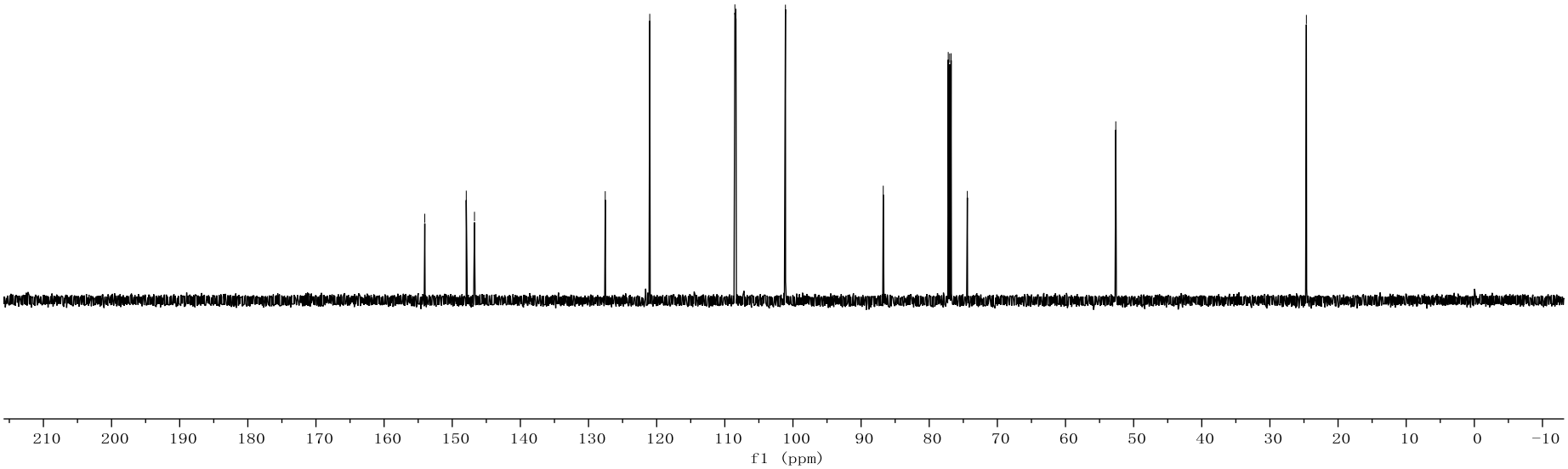

6.801
6.799
6.753
5.943
3.768
3.767
3.644
O
O
O
CO2Me
1x
0.97
2.20
2.15
3.57
2.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

# $^{13}$C NMR

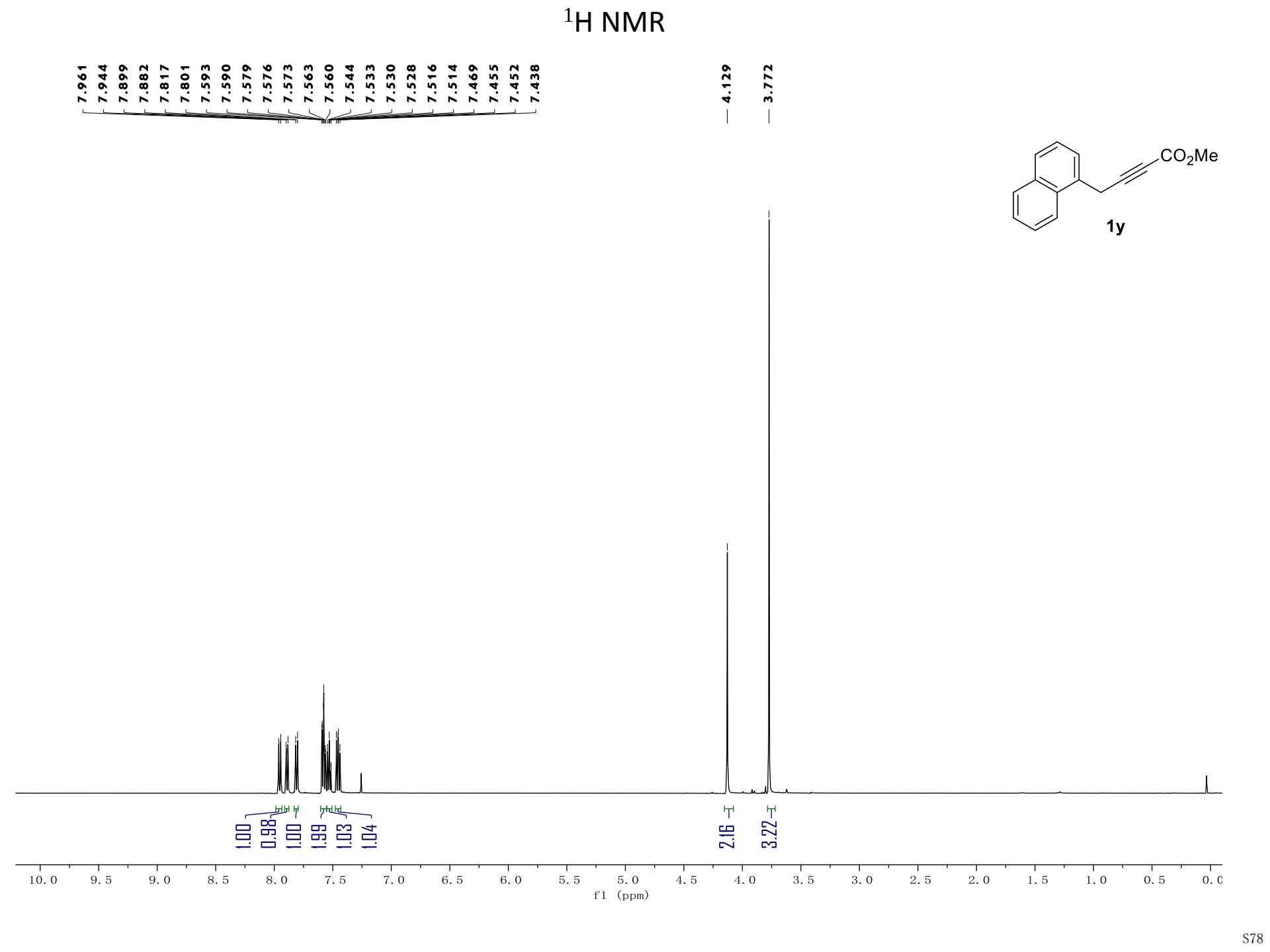
154.030
147.944
146.737
127.546
121.016
108.521
108.364
101.101
86.748
77.212
77.001
76.788
74.408
52.619
24.647



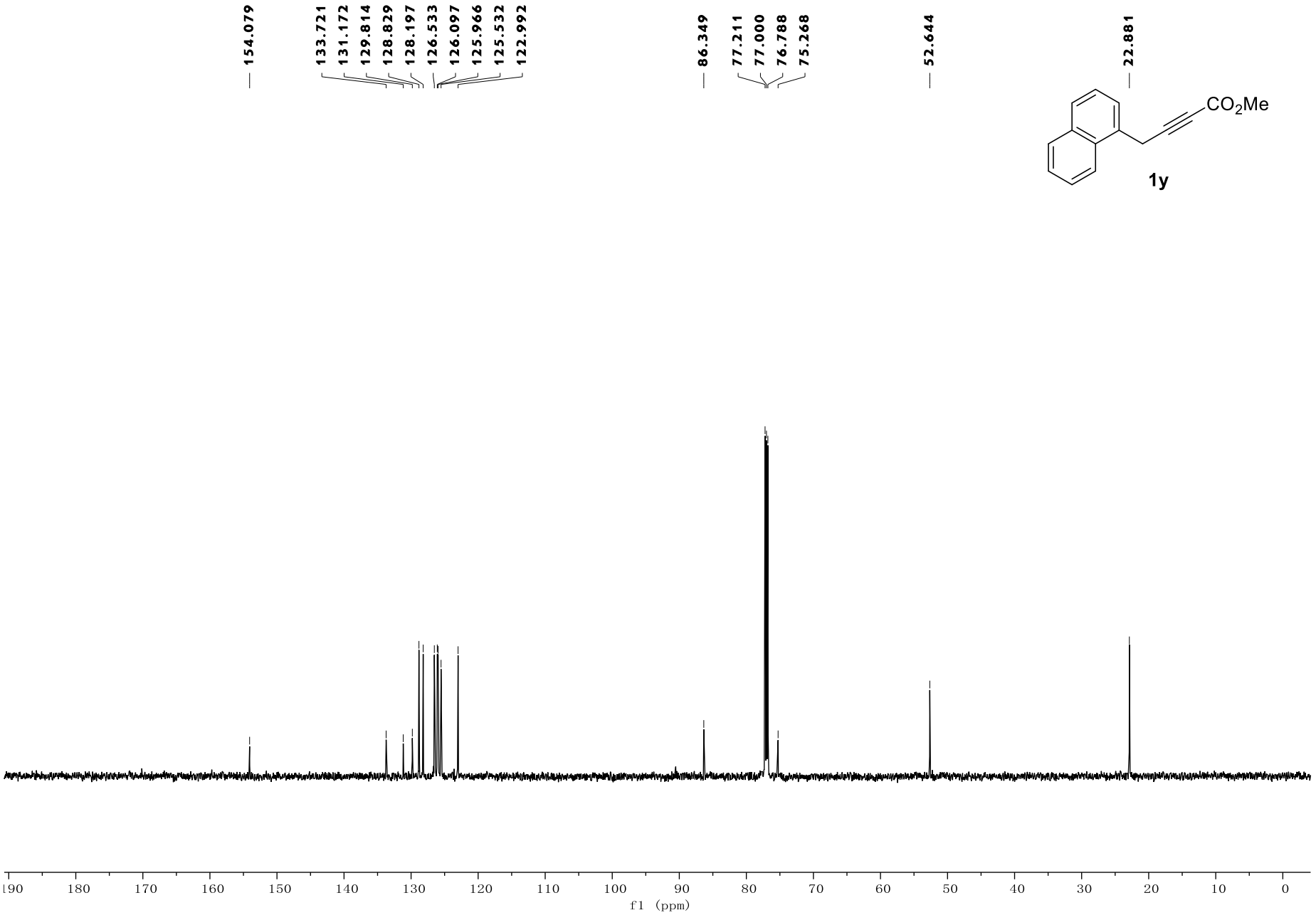

**1x**



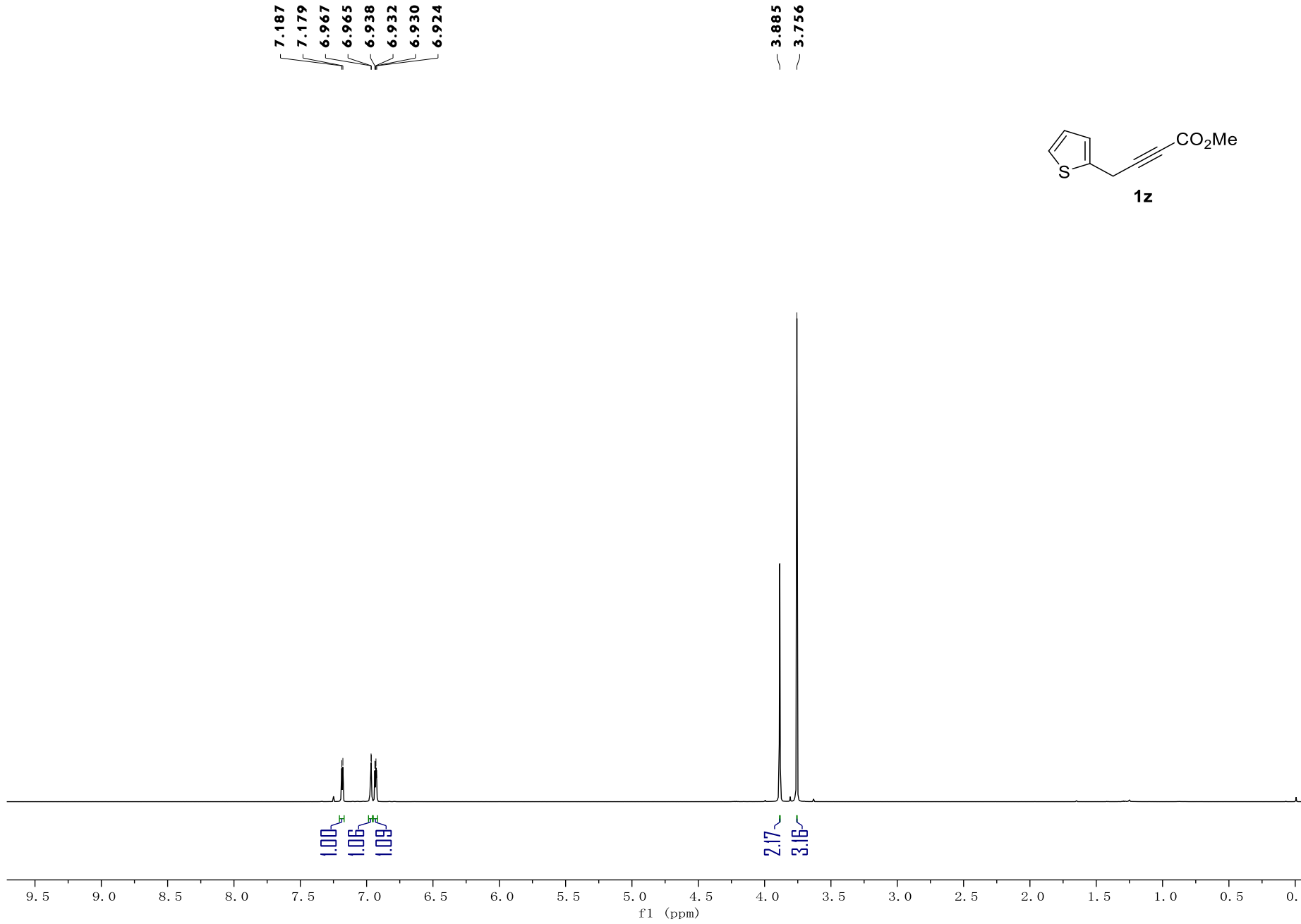
# $^1$H NMR


7.961
7.944
7.899
7.882
7.817
7.801
7.593
7.590
7.579
7.576
7.573
7.563
7.560
7.544
7.533
7.530
7.528
7.516
7.514
7.469
7.455
7.452
7.438
4.129
3.772
CO2Me
1y
1.00
0.98
1.00
1.99
1.03
1.04
2.16
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

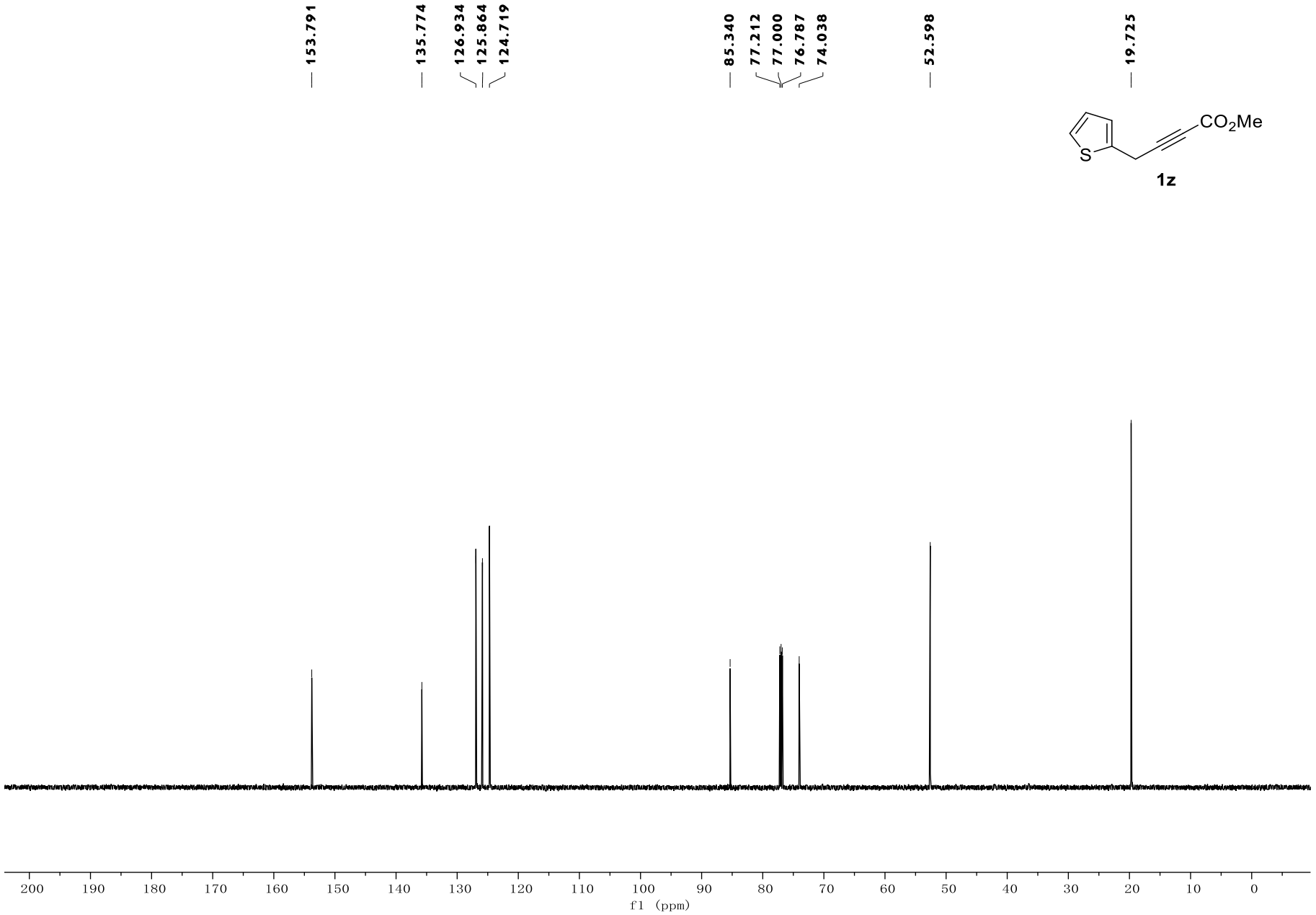
# $^{13}$C NMR


154.079
133.721
131.172
129.814
128.829
128.197
126.533
126.097
125.966
125.532
122.992
86.349
77.211
77.000
76.788
75.268
52.644
22.881
CO2Me
1y
f1 (ppm)

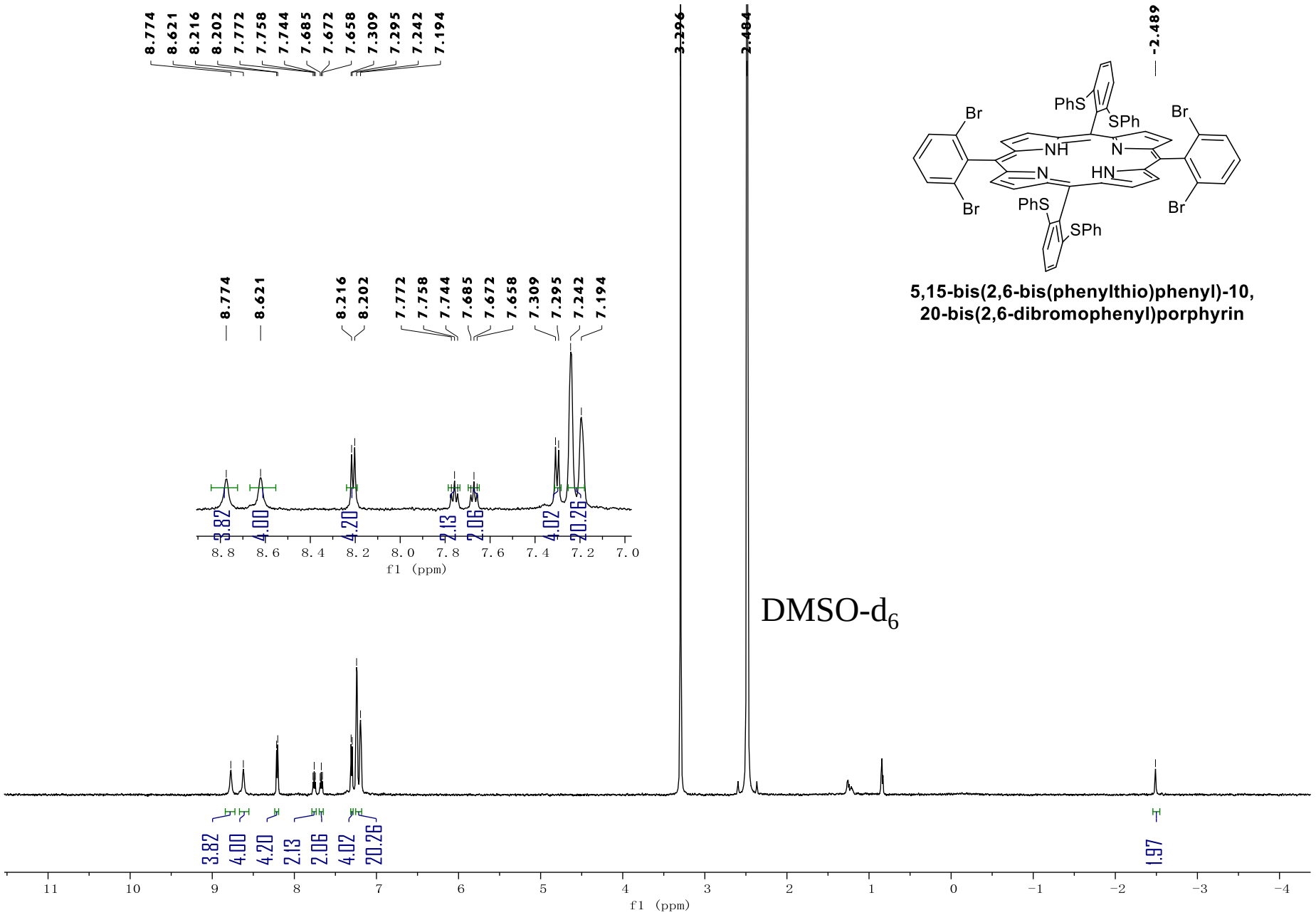
# $^{1}$H NMR


7.187
7.179
6.967
6.965
6.938
6.932
6.930
6.924
3.885
3.756
CO2Me
S
1z
1.00
1.06
1.09
2.17
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

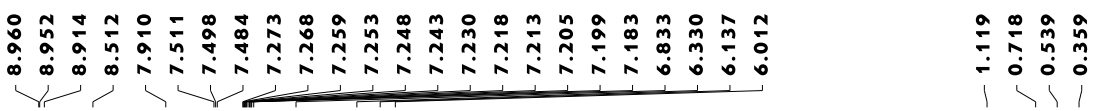
# $^{13}$C NMR

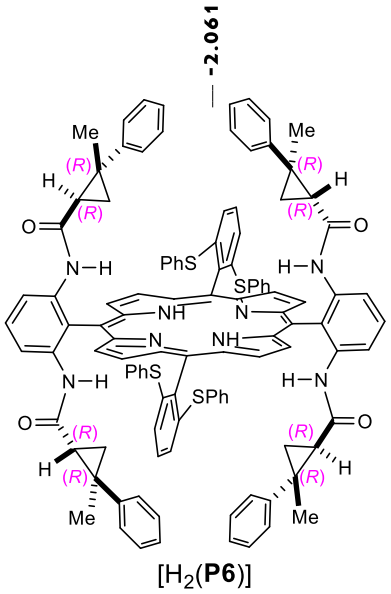

153.791
135.774
126.934
125.864
124.719
85.340
77.212
77.000
76.787
74.038
52.598
19.725
CO2Me
S
1z
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

# $^1$H NMR


8.774
8.621
8.216
8.202
7.772
7.758
7.744
7.685
7.672
7.658
7.309
7.295
7.242
7.194
3.396
2.484
-2.489
3.82
4.00
4.20
2.13
2.06
4.02
20.26
1.97
f1 (ppm)
DMSO-d6
Br
PhS
SPh
NH
N
HN
5,15-bis(2,6-bis(phenylthio)phenyl)-10,
20-bis(2,6-dibromophenyl)porphyrin

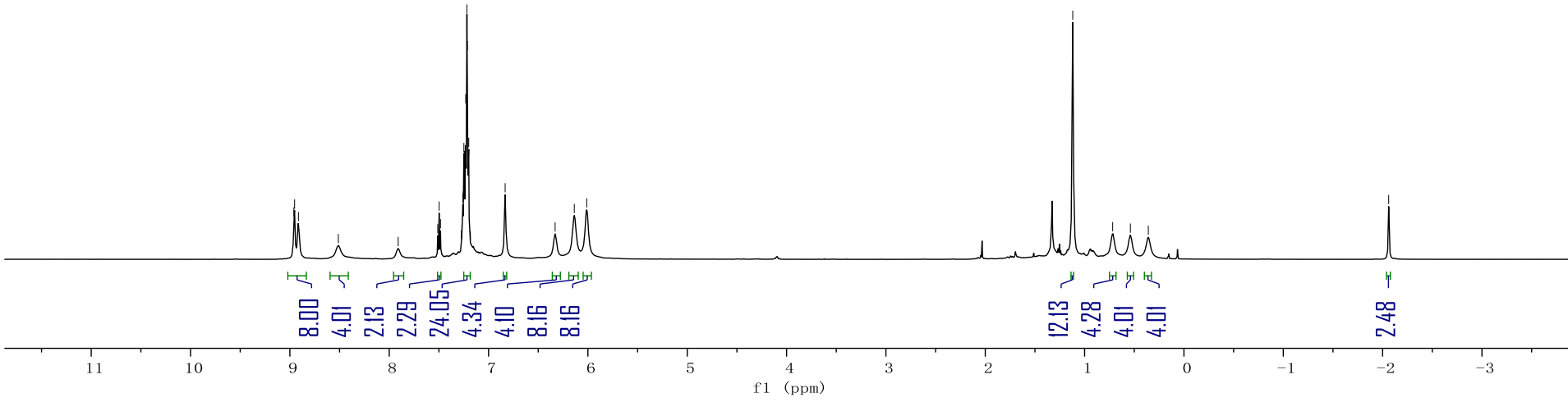
# $^1$H NMR



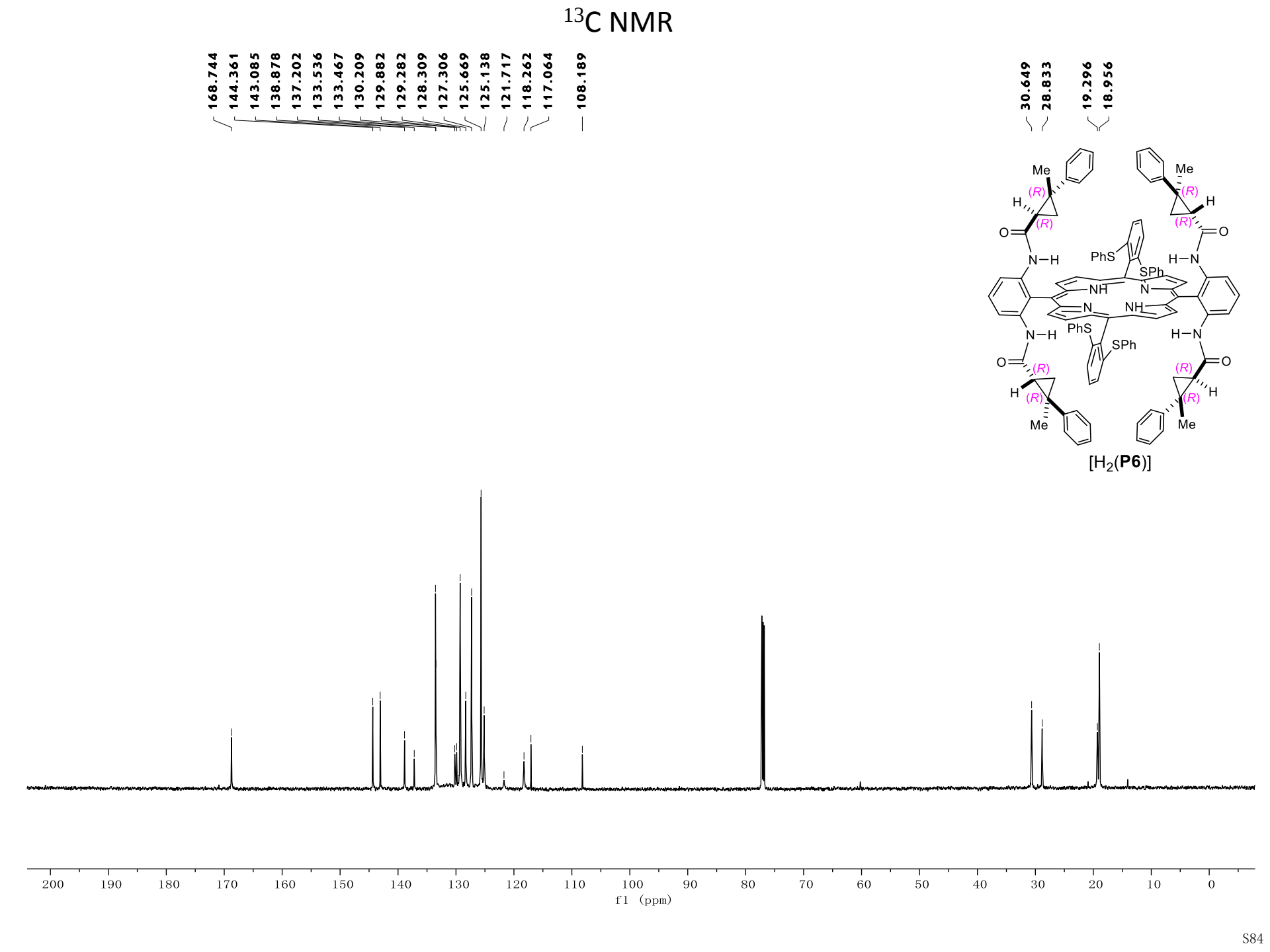




[$H_2$(**P6**)]

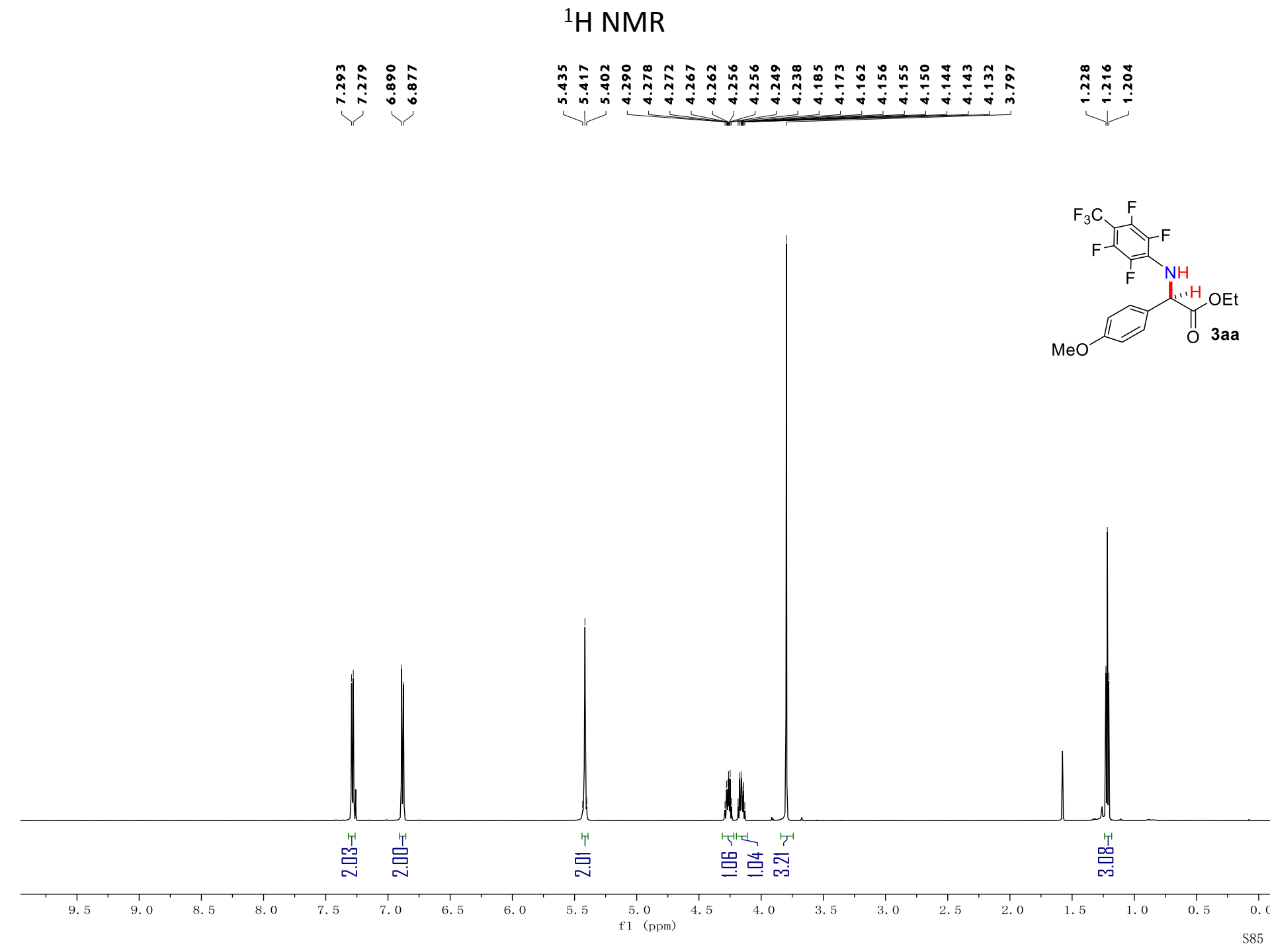
low solubility in $CDCl_3$



# $^{13}$C NMR

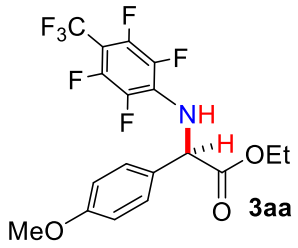

168.744
144.361
143.085
138.878
137.202
133.536
133.467
130.209
129.882
129.282
128.309
127.306
125.669
125.138
121.717
118.262
117.064
108.189
30.649
28.833
19.296
18.956
[H2(P6)]
f1 (ppm)

# $^1$H NMR


7.293
7.279
6.890
6.877
5.435
5.417
5.402
4.290
4.278
4.272
4.267
4.262
4.256
4.256
4.249
4.238
4.185
4.173
4.162
4.156
4.155
4.150
4.144
4.143
4.132
3.797
1.228
1.216
1.204
F3C
F
F
F
F
NH
H
OEt
O
MeO
3aa
2.03
2.00
2.01
1.06
1.04
3.21
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

# $^{13}$C NMR

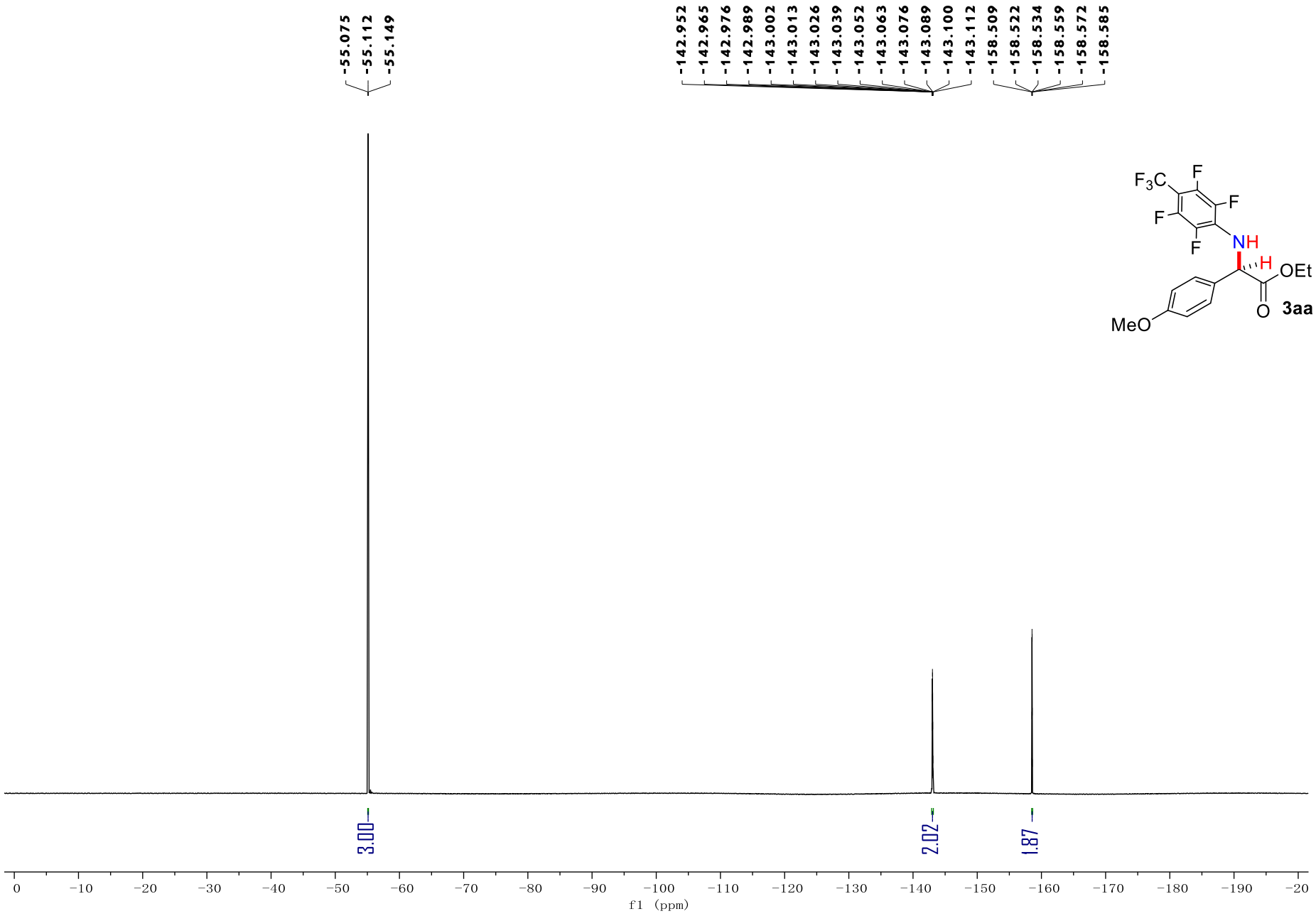
171.030
159.998
145.686
145.613
143.944
143.914
137.780
137.675
136.178
136.072
129.320
129.251
129.173
128.647
128.153
124.154
122.340
120.532
118.728
114.497
97.789
97.520
97.379
97.203
97.059
62.303
60.088
60.060
60.033
55.268
55.247
13.941




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

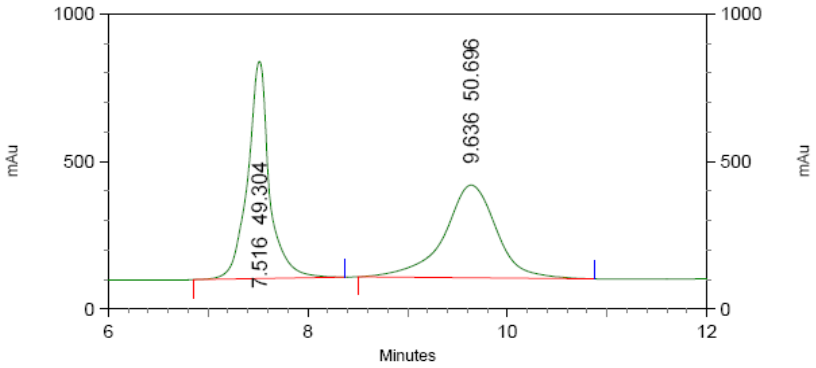
f1 (ppm)

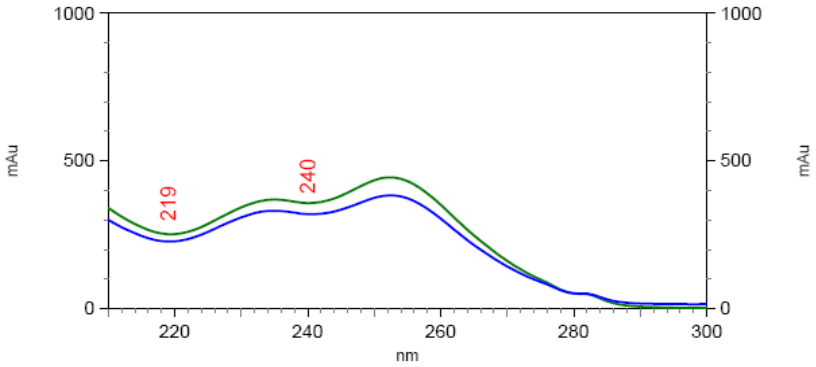
# $^{19}$F NMR

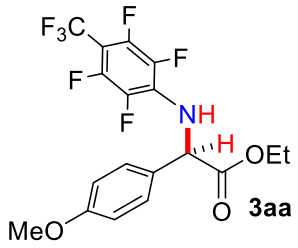

-55.075
-55.112
-55.149
-142.952
-142.965
-142.976
-142.989
-143.002
-143.013
-143.026
-143.039
-143.052
-143.063
-143.076
-143.089
-143.100
-143.112
-158.509
-158.522
-158.534
-158.559
-158.572
-158.585
F3C
F
F
F
F
NH
H
OEt
O
MeO
3aa
3.00
2.02
1.87
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−20
f1 (ppm)

# HPLC

JLM-II-198-2pure-WHELK-0.5@-1mL
C:\EZStart\Projects\Default\Method\yang-ODH 20%0.7ml premix.met
C:\EZStart\Projects\Default\Data\JLM-II-198-2pure-WHELK0.5@1ml



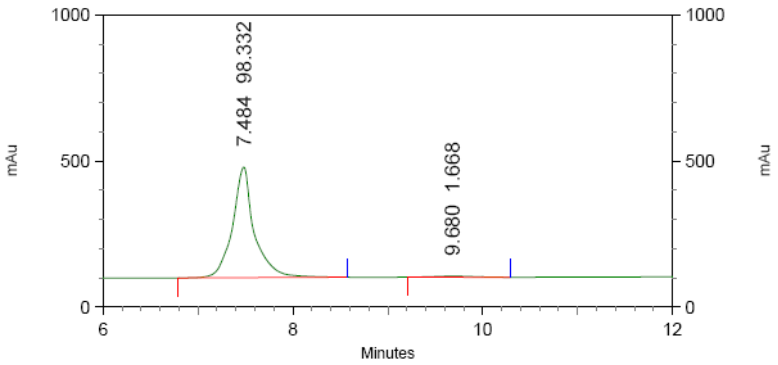



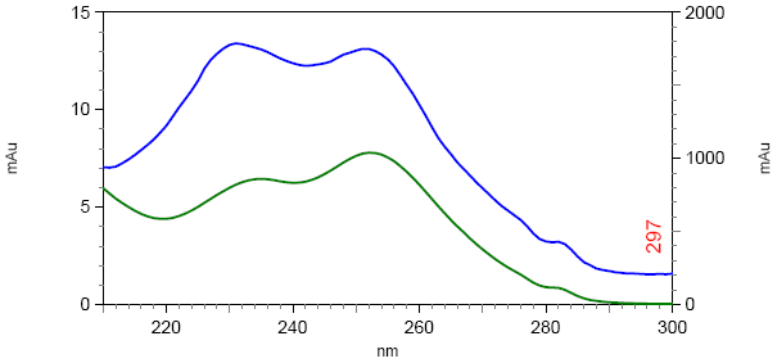

10: 259 nm, 4 nm
Results

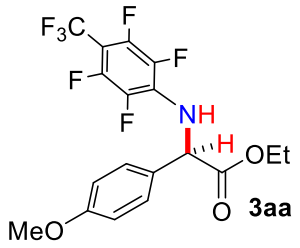
| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 7.516 | 49.304 |
| 2 | | 9.636 | 50.696 |
| Totals | | | 100.000 |

# HPLC

JLM-V-122-3a1-WHELK-0.5@-1mL
C:\EZStart\Projects\Default\Method\yang-ODH 20%0.7ml premix.met
C:\EZStart\Projects\Default\Data\JLM-V-122-3a1-WHELK0.5@1ml



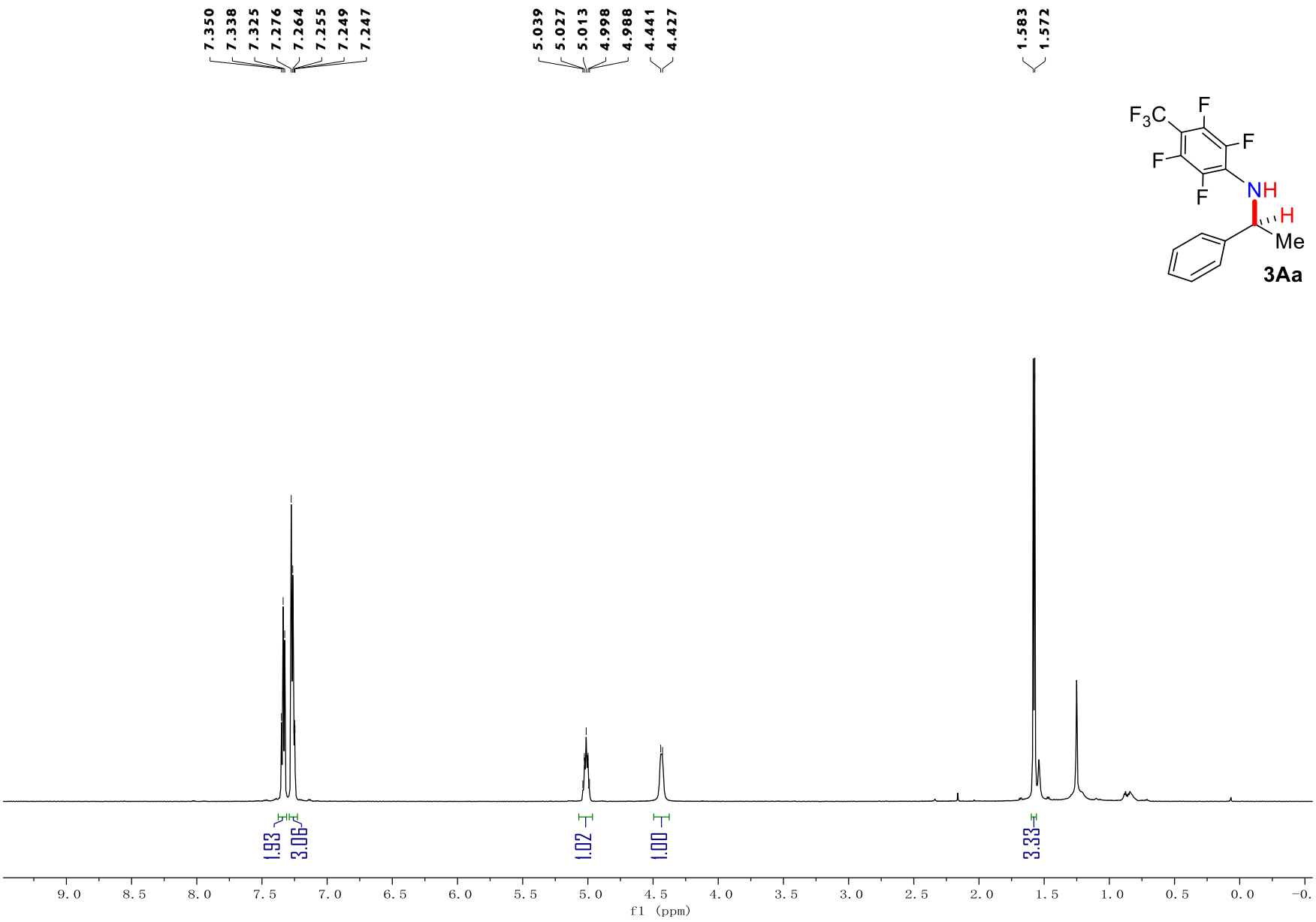



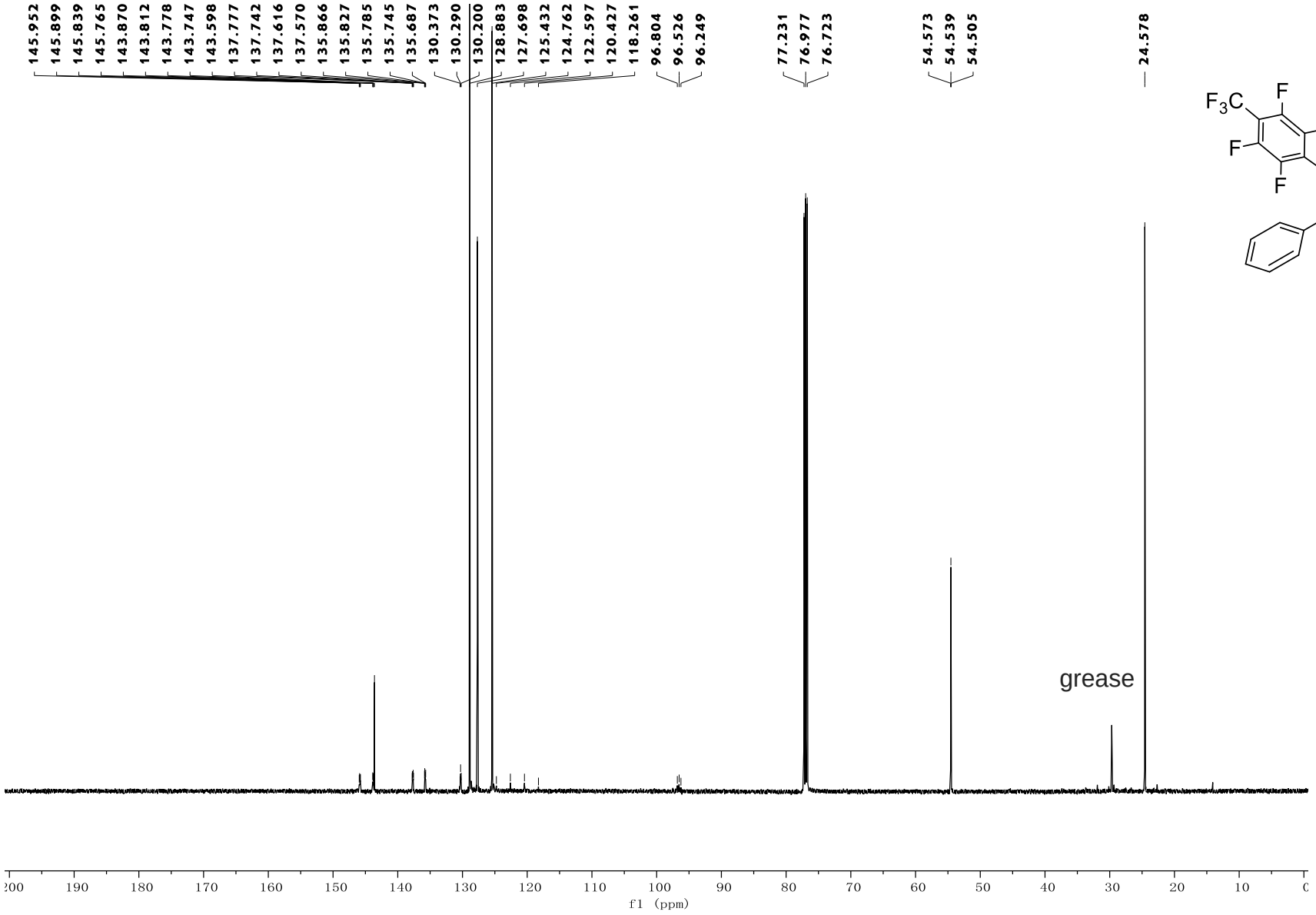

15: 270 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 7.484 | 98.332 |
| 2 | | 9.680 | 1.668 |
| Totals | | | 100.000 |

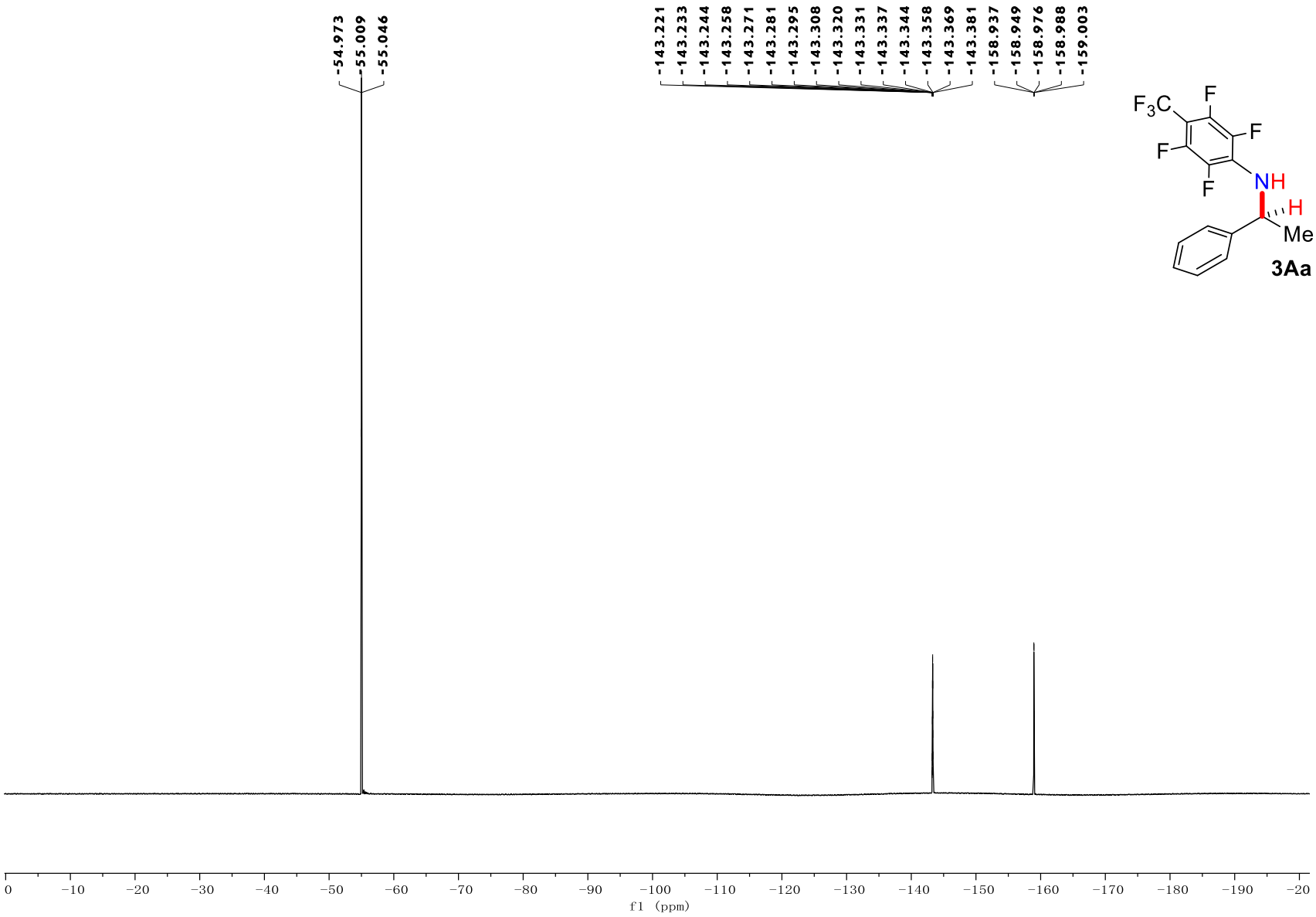
# $^{1}$H NMR


7.350
7.338
7.325
7.276
7.264
7.255
7.249
7.247
5.039
5.027
5.013
4.998
4.988
4.441
4.427
1.583
1.572
F3C
F
F
F
F
NH
H
Me
3Aa
1.93
3.06
1.02
1.00
3.33
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.
f1 (ppm)

# $^{13}$C NMR

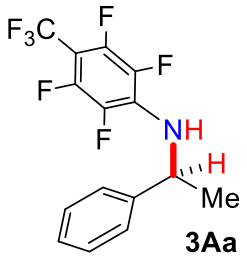

145.952
145.899
145.839
145.765
143.870
143.812
143.778
143.747
143.598
137.777
137.742
137.616
137.570
135.866
135.827
135.785
135.745
135.687
130.373
130.290
130.200
128.883
127.698
125.432
124.762
122.597
120.427
118.261
96.804
96.526
96.249
77.231
76.977
76.723
54.573
54.539
54.505
24.578
grease
f1 (ppm)
F3C
F
F
F
F
NH
H
Me
3Aa

# $^{19}$F NMR

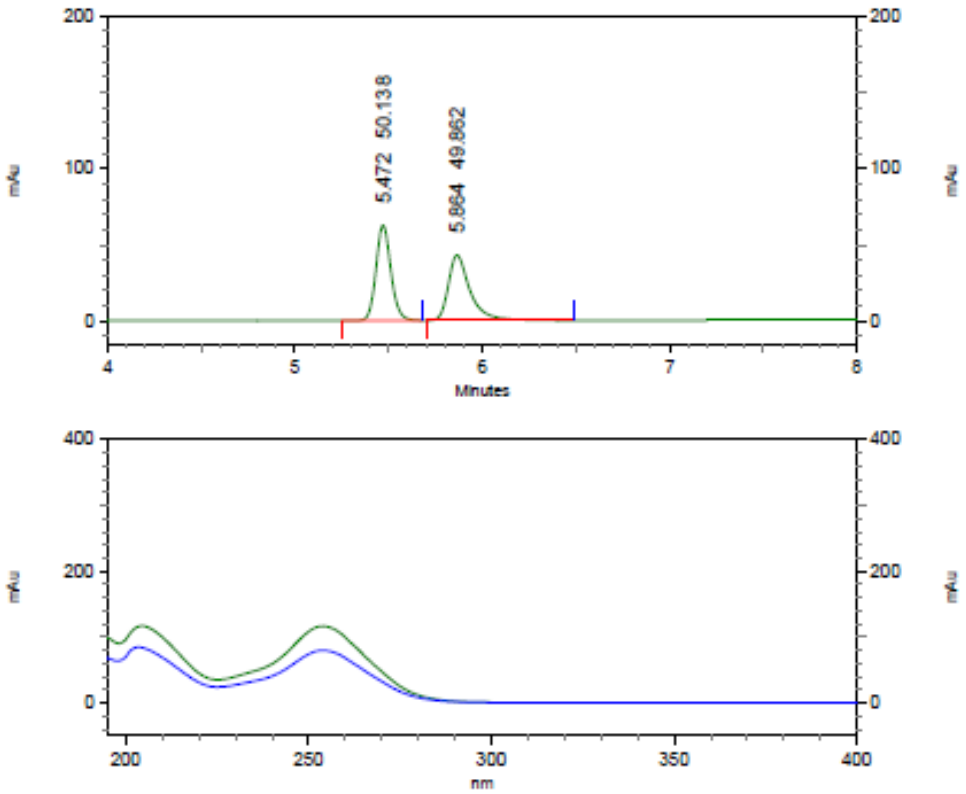

-54.973
-55.009
-55.046
-143.221
-143.233
-143.244
-143.258
-143.271
-143.281
-143.295
-143.308
-143.320
-143.331
-143.337
-143.344
-143.358
-143.369
-143.381
-158.937
-158.949
-158.976
-158.988
-159.003
F3C
F
F
F
F
NH
H
Me
3Aa
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−20
f1 (ppm)

# HPLC

C:\EZStart\Projects\Default\Data\P0X-1937-2%-IA-0.8ml-PURE-1
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard0311.met




**3Aa**

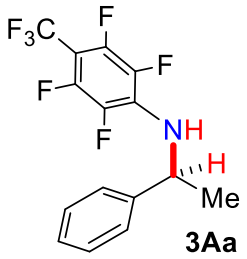



4: 267 nm, 4
nm Results

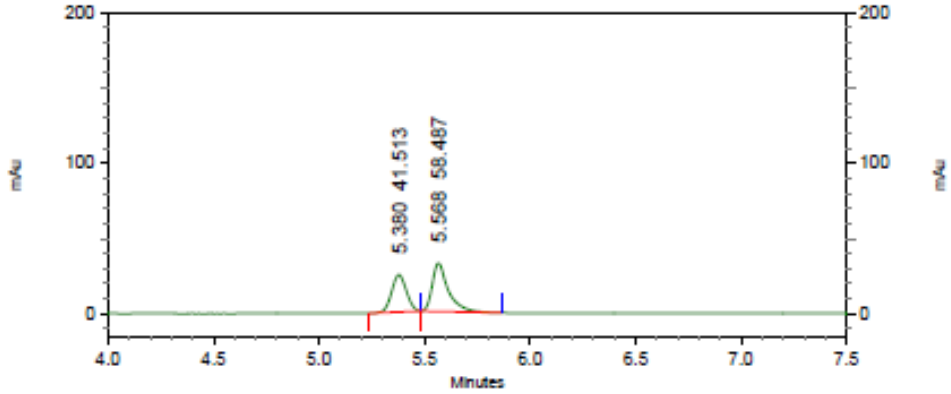
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.472 | 50.138 |
| 2 | 5.864 | 49.862 |
| Totals | | 100.000 |

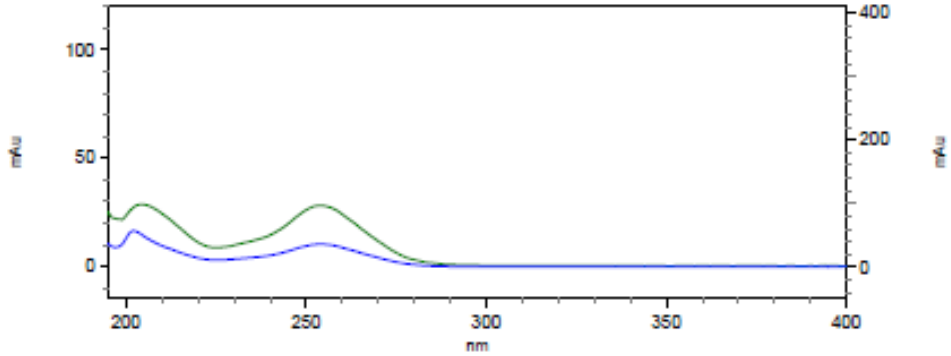
# HPLC

C:\EZStart\Projects\Default\Data\P0X-1938-2%-IA-0.8ml
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard0311.met




3Aa

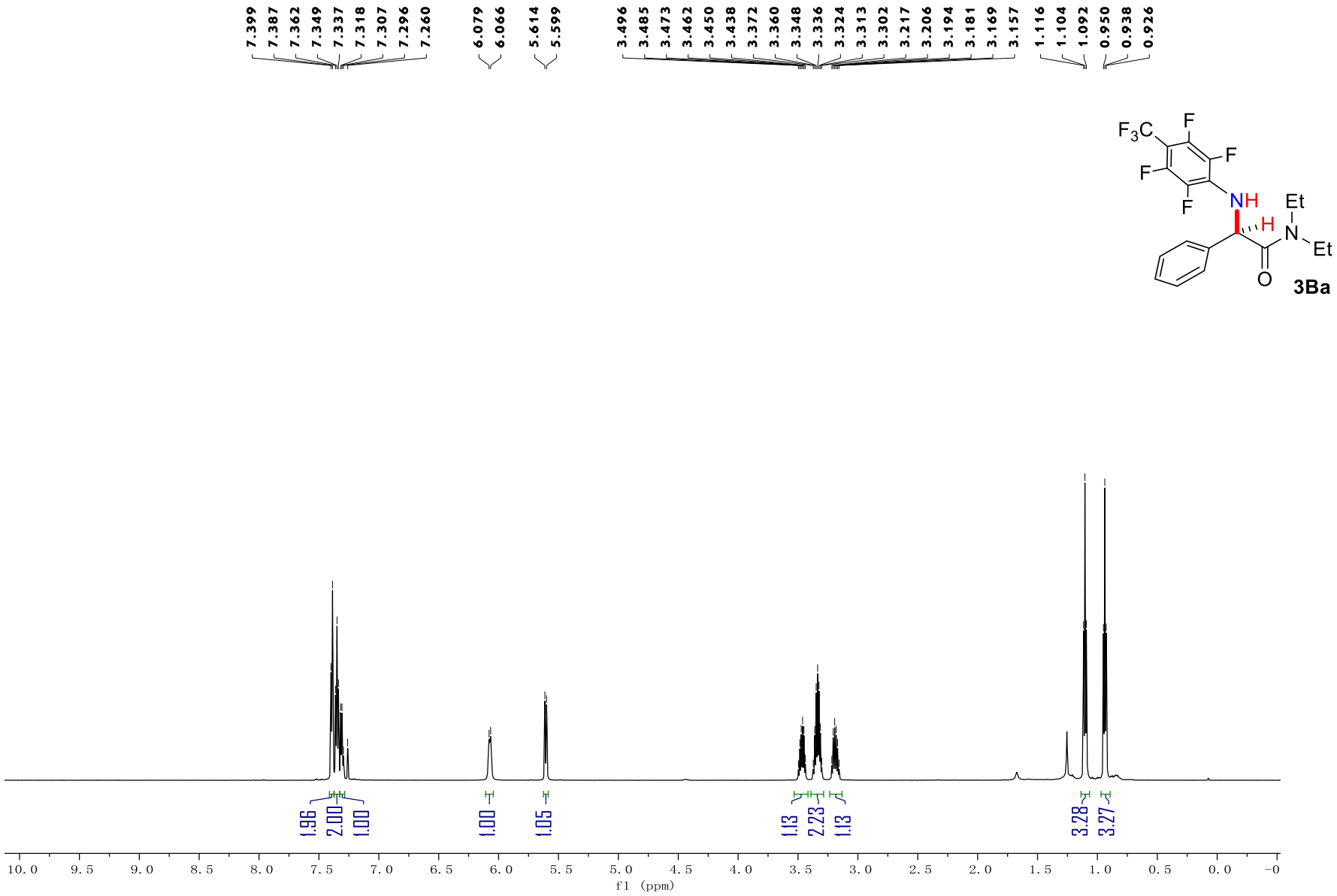


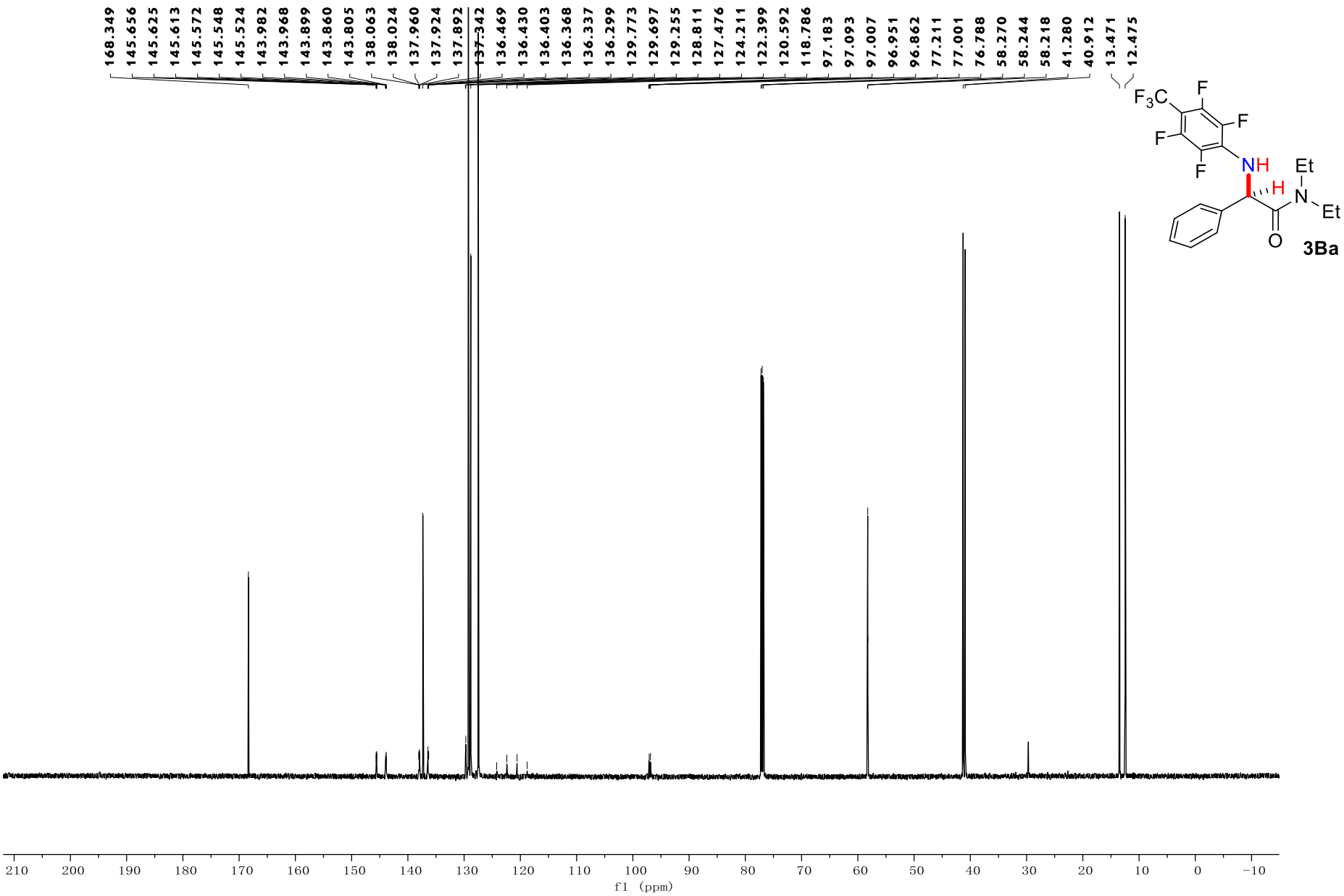

4: 250 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.380 | 41.513 |
| 2 | 5.568 | 58.487 |
| Totals | | 100.000 |

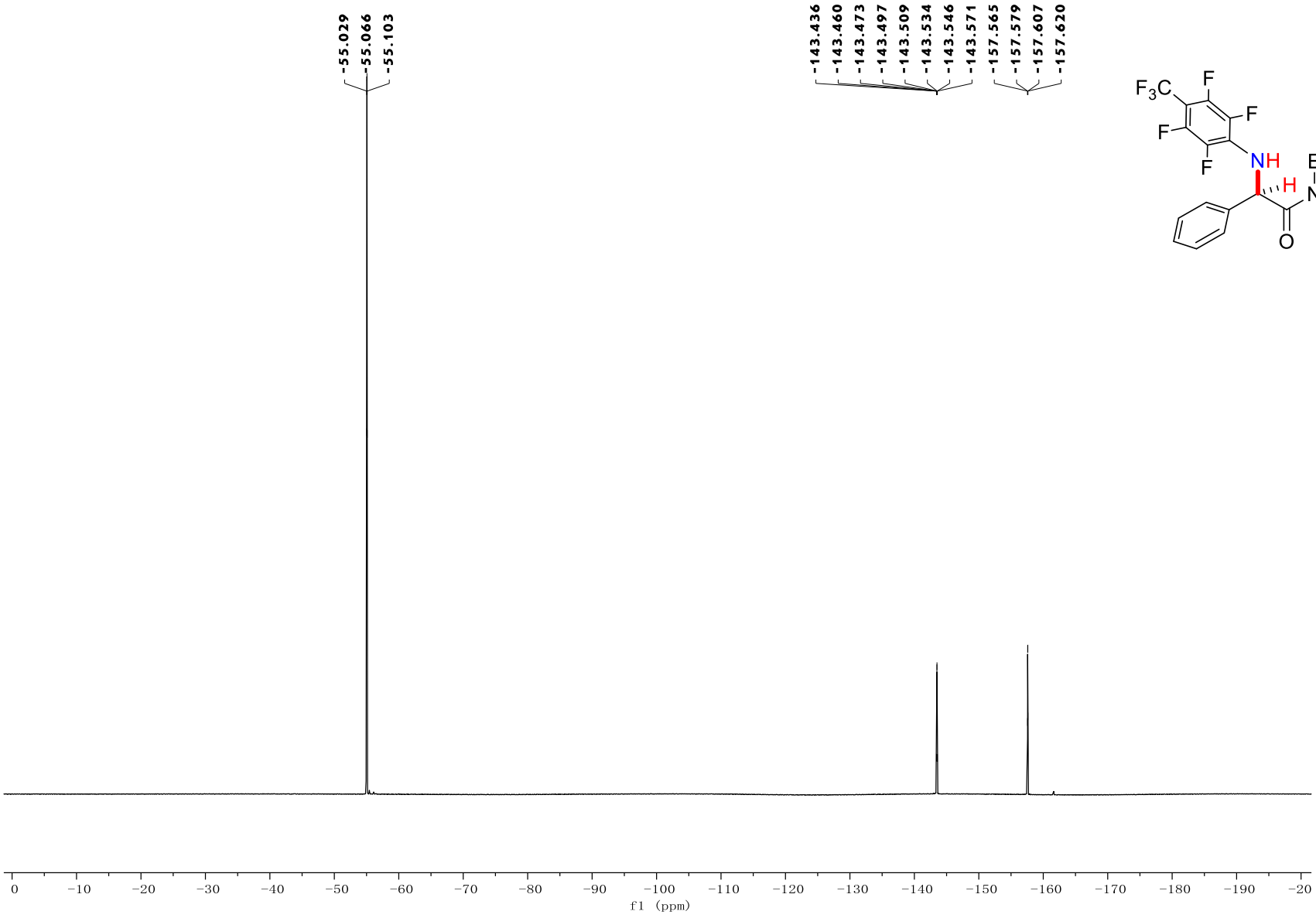
# $^{1}$H NMR


7.399
7.387
7.362
7.349
7.337
7.318
7.307
7.296
7.260
6.079
6.066
5.614
5.599
3.496
3.485
3.473
3.462
3.450
3.438
3.372
3.360
3.348
3.336
3.324
3.313
3.302
3.217
3.206
3.194
3.181
3.169
3.157
1.116
1.104
1.092
0.950
0.938
0.926
F3C
F
F
F
F
NH
H
Et
N
Et
O
3Ba
1.96
2.00
1.00
1.00
1.05
1.13
2.23
1.13
3.28
3.27
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
f1 (ppm)

# $^{13}C$ NMR


168.349
145.656
145.625
145.613
145.572
145.548
145.524
143.982
143.968
143.899
143.860
143.805
138.063
138.024
137.960
137.924
137.892
137.342
136.469
136.430
136.403
136.368
136.337
136.299
129.773
129.697
129.255
128.811
127.476
124.211
122.399
120.592
118.786
97.183
97.093
97.007
96.951
96.862
77.211
77.001
76.788
58.270
58.244
58.218
41.280
40.912
13.471
12.475
F3C
F
F
F
F
NH
H
Et
N
Et
O
3Ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

# $^{19}$F NMR

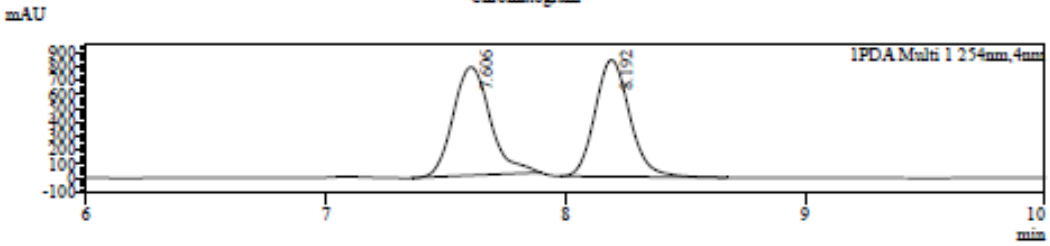

-55.029
-55.066
-55.103
-143.436
-143.460
-143.473
-143.497
-143.509
-143.534
-143.546
-143.571
-157.565
-157.579
-157.607
-157.620
F3C
F
F
F
F
NH
H
Et
N
Et
O
3Ba
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−20
f1 (ppm)

# HPLC

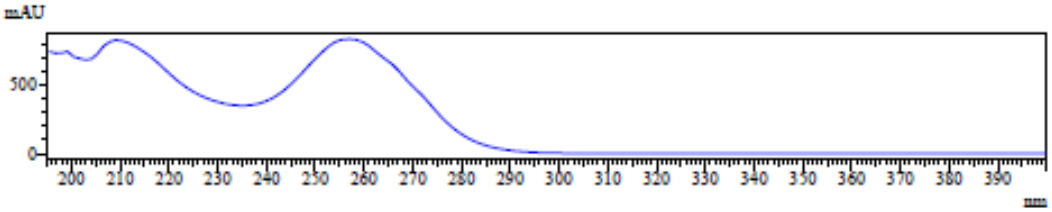
Sample Information

Sample Name : P0X-1948-IA-20%-0.5mL
Sample ID : P0X-1948-IA-20%-0.5mL
Data File : P0X-1948-IA-20%-0.5mL002.lcd
Method File : P0X-20%.0.5.mL-50min.lcm

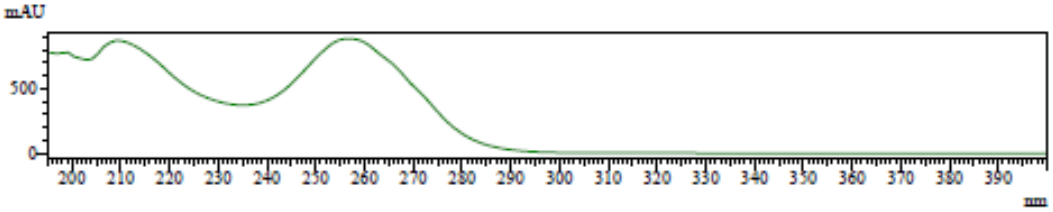
Chromatogram

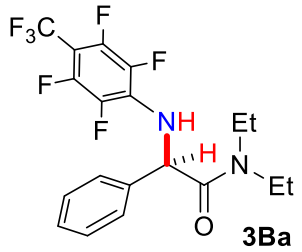



UV Spectrum
Retention time = 7.606




UV Spectrum
Retention time = 8.192



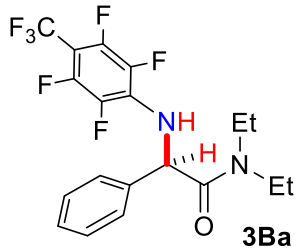




Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 7.606 | 8402484 | 49.855 |
| 2 | 8.192 | 8451195 | 50.145 |
| Total | | 16853680 | 100.000 |

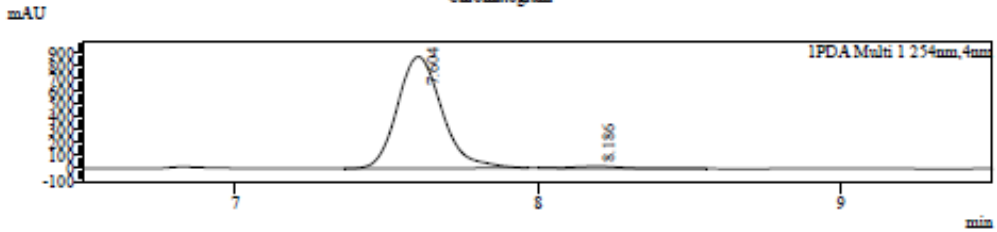
# HPLC



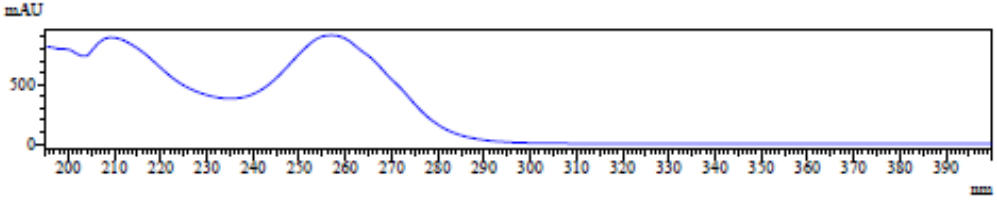

Sample Information

| | |
|---|---|
| Sample Name | : P0X-1949-IA-20%-0.5mL |
| Sample ID | : P0X-1949-IA-20%-0.5mL |
| Data File | : P0X-1949-IA-20%-0.5mL.lcd |
| Method File | : P0X-20%.0.5.mL-50min.lcm |

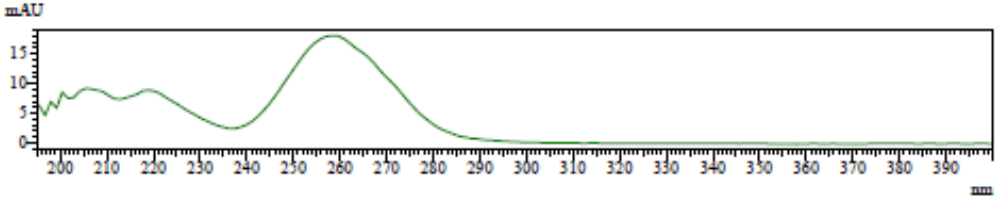
Chromatogram




UV Spectrum
Retention time = 7.604




UV Spectrum
Retention time = 8.186

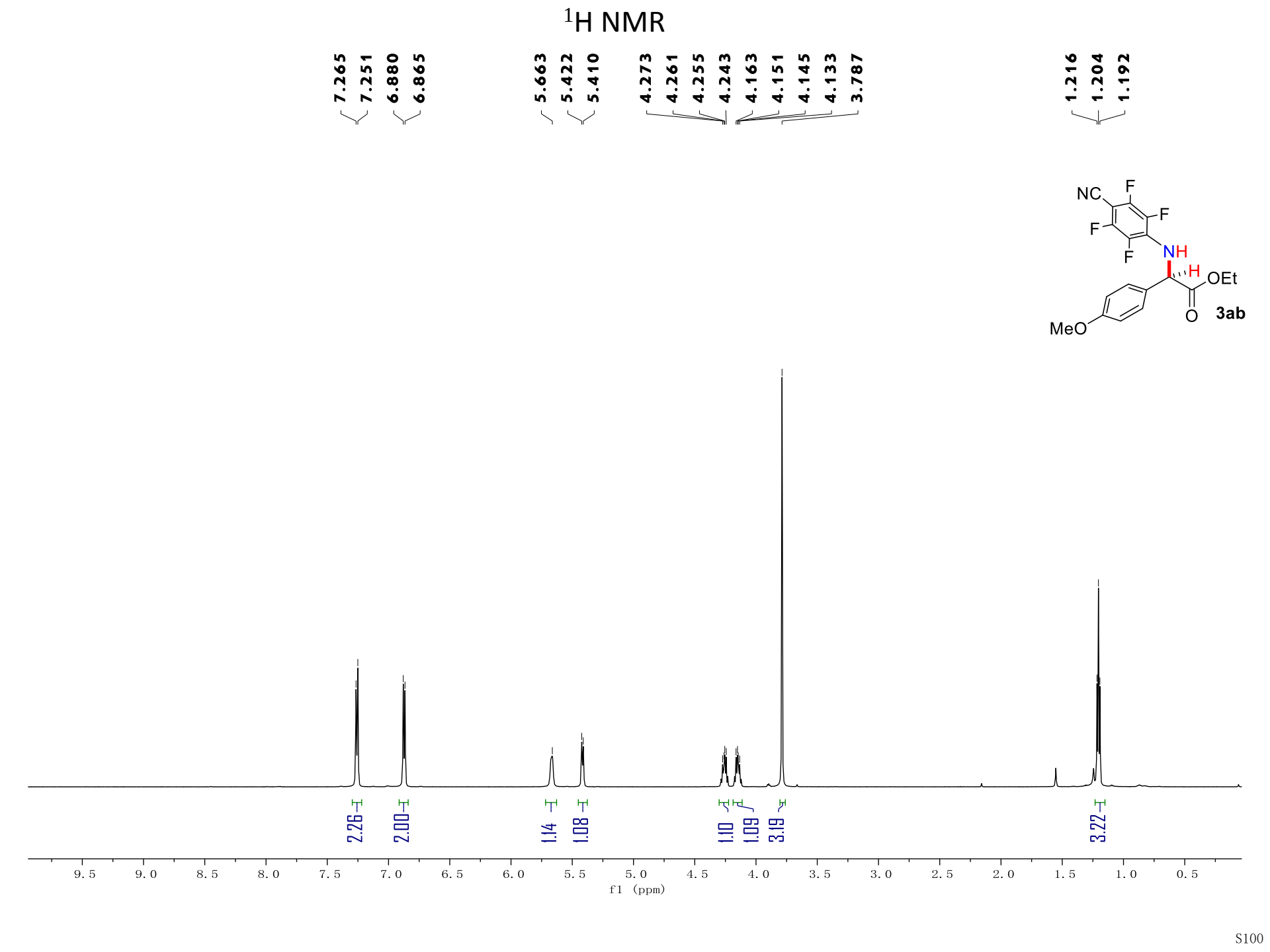



Peak Table

PDA Ch1 254nm

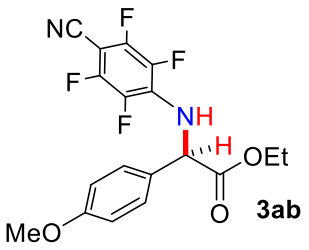
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 7.604 | 8942684 | 98.504 |
| 2 | 8.186 | 135809 | 1.496 |
| Total | | 9078493 | 100.000 |

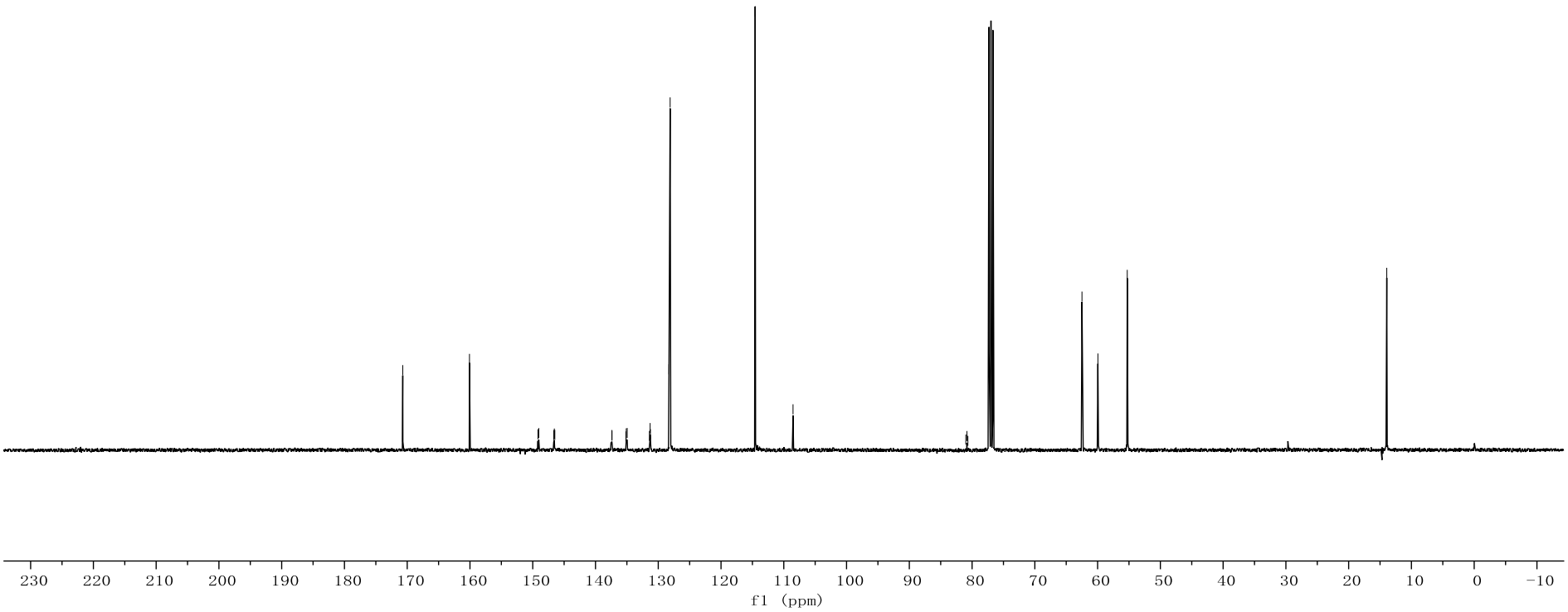
# $^{1}$H NMR


7.265
7.251
6.880
6.865
5.663
5.422
5.410
4.273
4.261
4.255
4.243
4.163
4.151
4.145
4.133
3.787
1.216
1.204
1.192
NC
F
F
F
F
NH
H
OEt
O
MeO
3ab
2.26
2.00
1.14
1.08
1.10
1.09
3.19
3.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

# $^{13}$C NMR

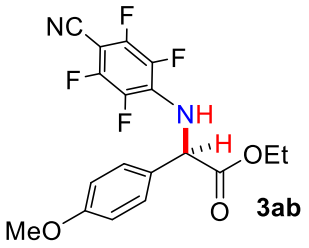
170.707 160.080 149.174 149.036 146.652 146.559 146.479 137.386 137.372 135.160 135.099 134.952 131.407 131.295 131.256 128.297 128.108 114.555 108.563 108.527 108.492 80.997 80.821 80.665 62.489 59.953 55.275 13.927



# $^{19}$F NMR

-134.758
-134.775
-134.786
-134.811
-134.823
-134.840
-157.653
-157.682




2.07
2.00

−10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −20

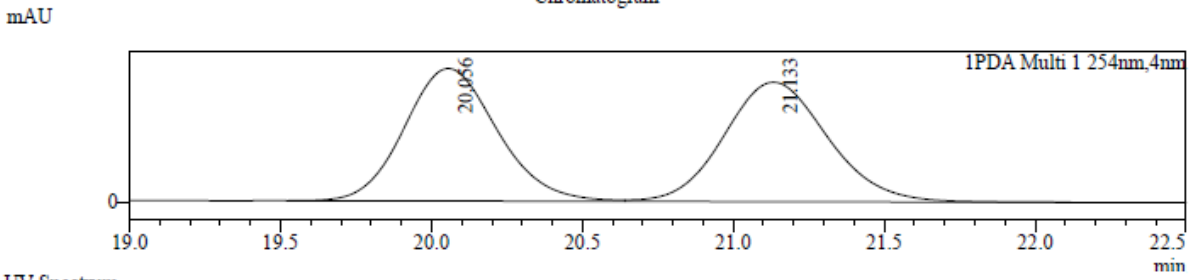
f1 (ppm)

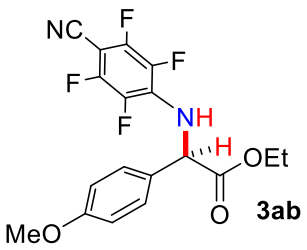
# HPLC

Sample Information

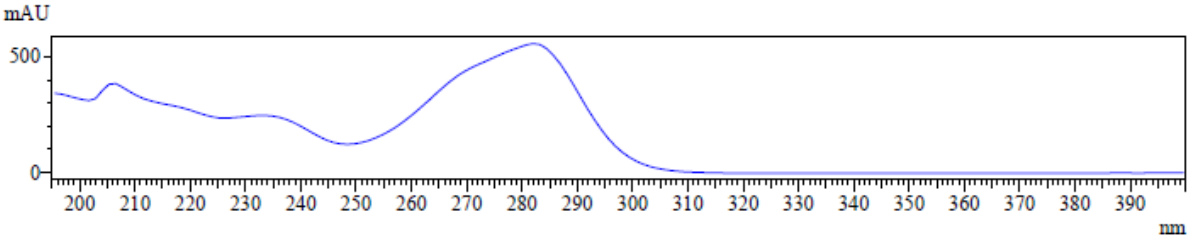
| | |
|---|---|
| Sample Name | : P0X-0809-IC10%-0.8Ml |
| Sample ID | : P0X-0809-IC10%-0.8Ml |
| Data File | : P0X-0809-IC10%-0.8Ml.lcd |
| Method File | : P0X-10%-0.8ml.lcm |

Chromatogram

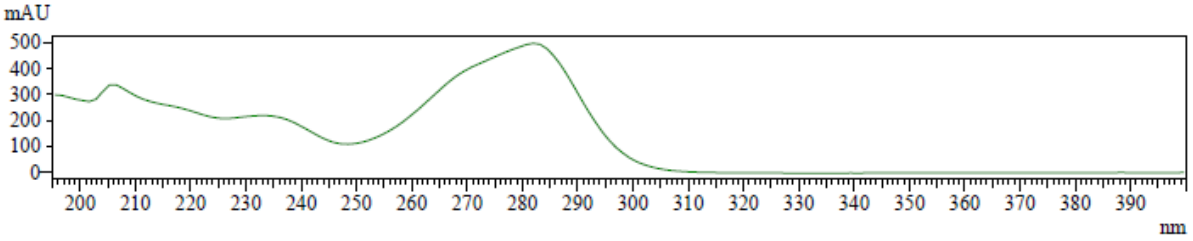



UV Spectrum
Retention time = 20.056




UV Spectrum
Retention time = 21.133




Peak Table

PDA Ch1 254nm

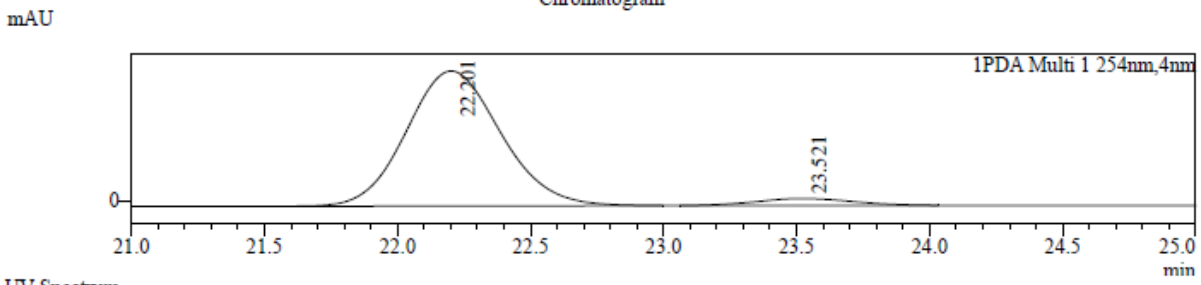
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 20.056 | 3388030 | 49.763 |
| 2 | 21.133 | 3420340 | 50.237 |
| Total | | 6808370 | 100.000 |

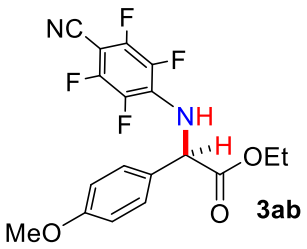
# HPLC

Sample Information

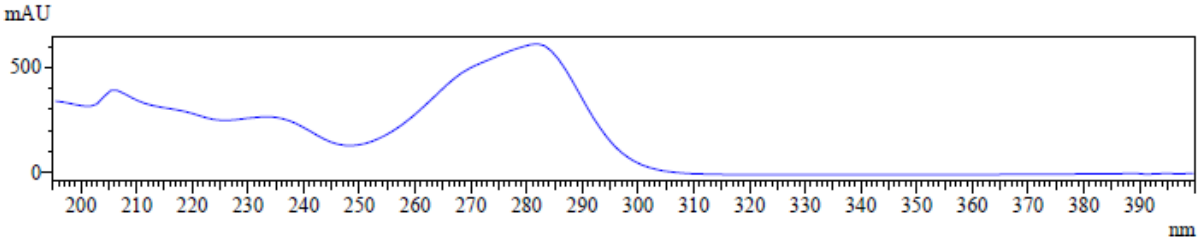
| | |
|---|---|
| Sample Name | : P0X-0810-IC10%-0.8Ml |
| Sample ID | : P0X-0810-IC10%-0.8Ml |
| Data File | : P0X-0810-IC10%-0.8Ml.lcd |
| Method File | : P0X-10%-0.8ml.lcm |

Chromatogram

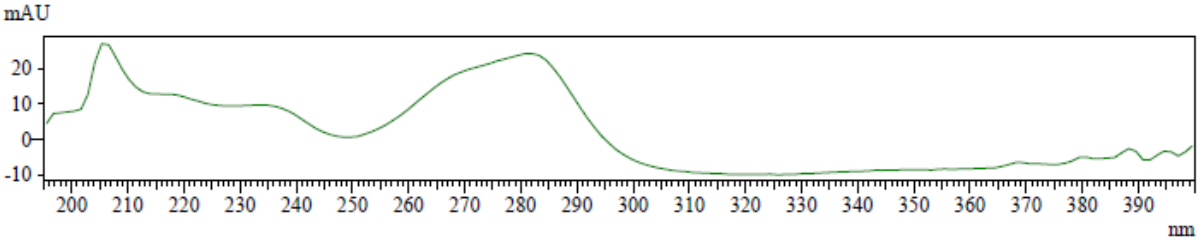



UV Spectrum
Retention time = 22.201




UV Spectrum
Retention time = 23.521

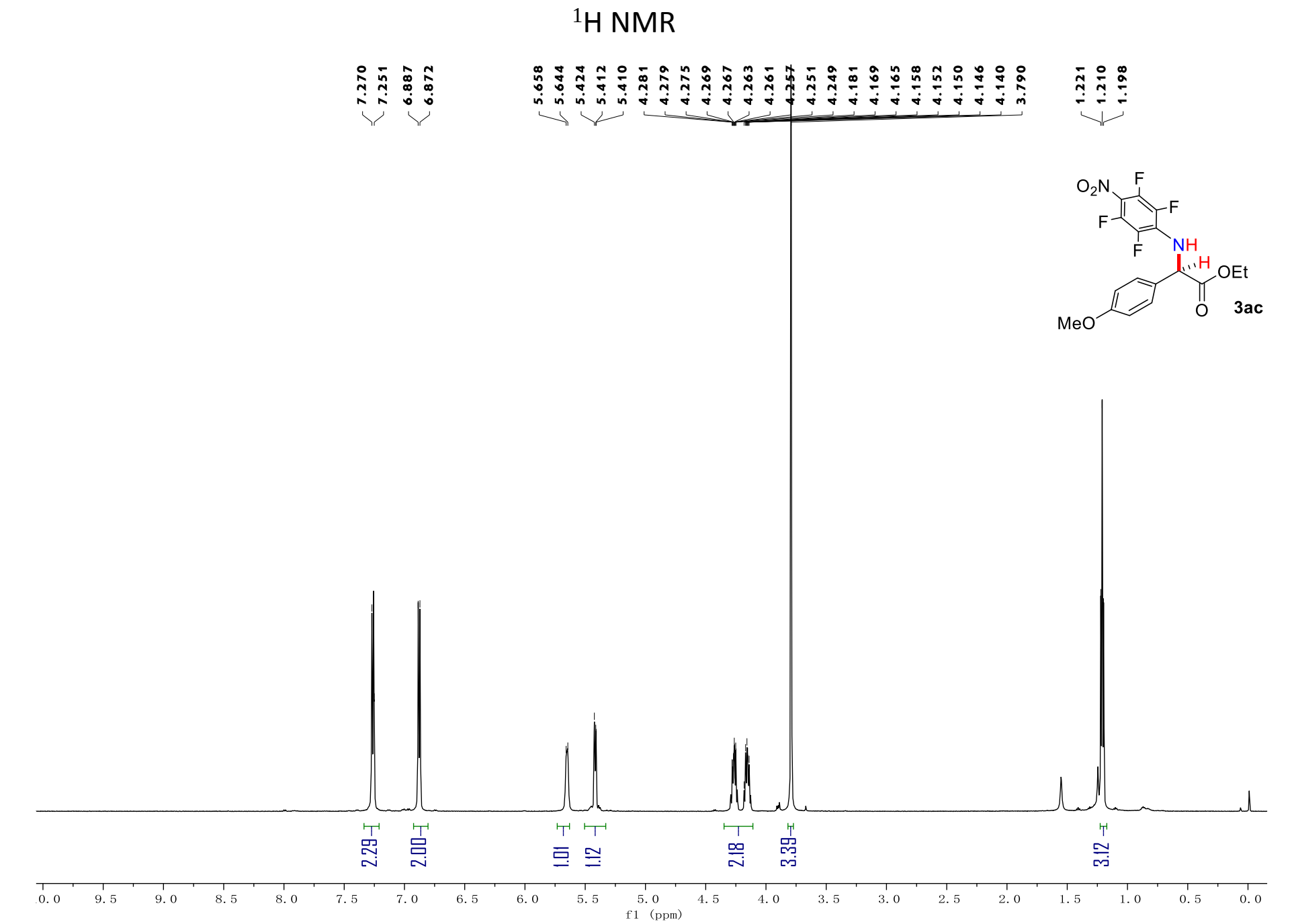



Peak Table

PDA Ch1 254nm

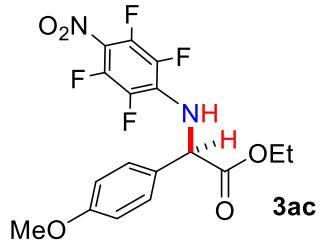
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 22.201 | 4481981 | 95.079 |
| 2 | 23.521 | 231967 | 4.921 |
| Total | | 4713948 | 100.000 |

# $^{1}$H NMR

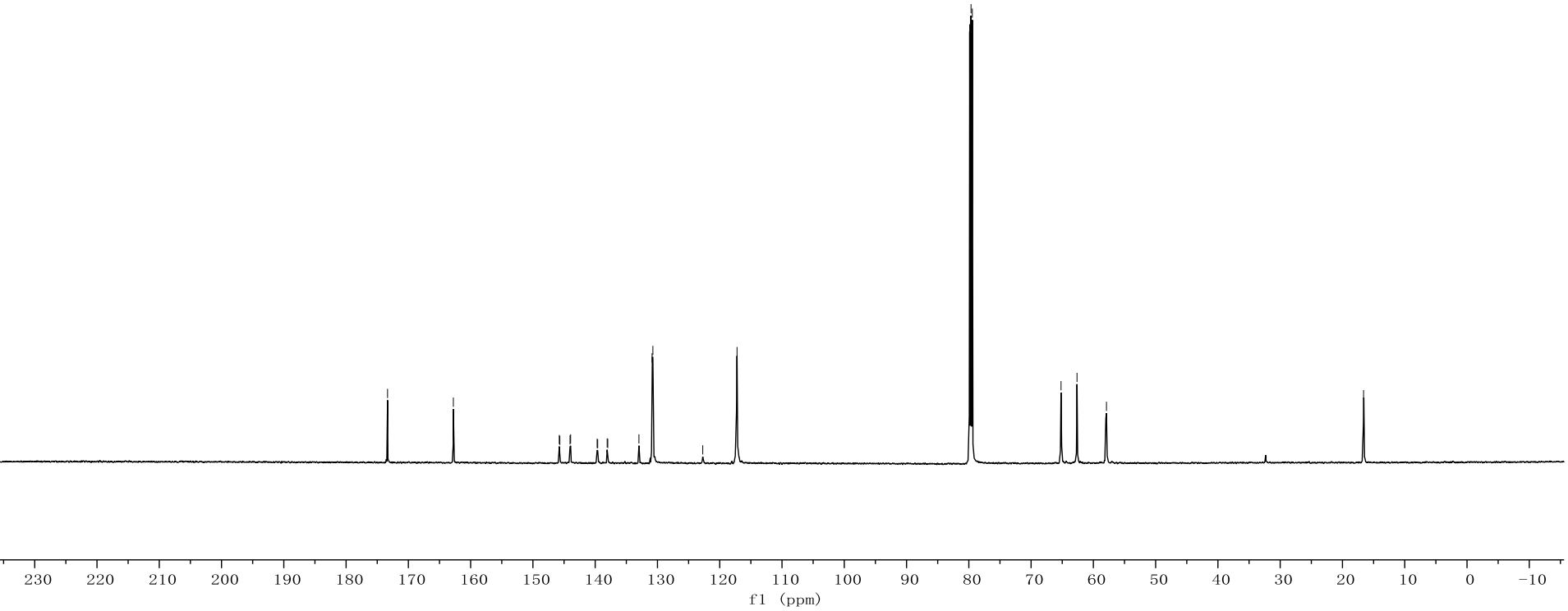

7.270
7.251
6.887
6.872
5.658
5.644
5.424
5.412
5.410
4.281
4.279
4.275
4.269
4.267
4.263
4.261
4.257
4.251
4.249
4.181
4.169
4.165
4.158
4.152
4.150
4.146
4.140
3.790
1.221
1.210
1.198
O2N
F
F
F
F
NH
H
OEt
O
MeO
3ac
2.29
2.00
1.01
1.12
2.18
3.39
3.12
f1 (ppm)

# $^{13}$C NMR

173.340
162.775
145.771
145.674
144.039
143.941
139.687
139.596
138.075
137.977
132.973
130.864
130.735
122.724
117.221
79.862
79.649
79.438
65.194
62.627
57.896
16.610

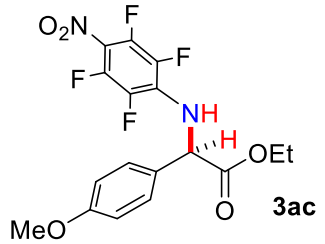


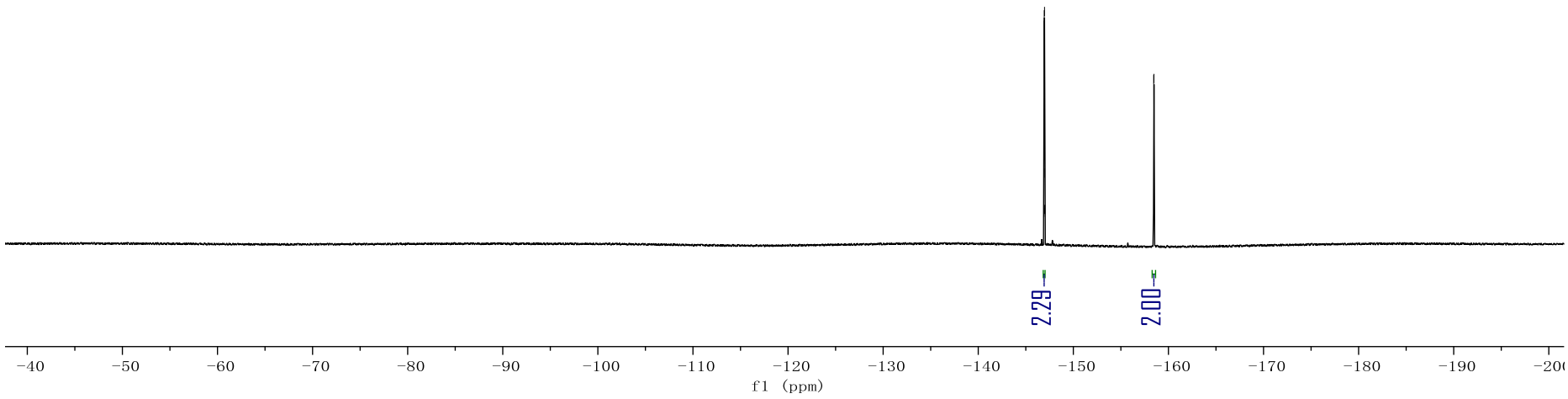

3ac



# $^{19}$F NMR

-146.914
-146.929
-146.941
-146.970
-146.981
-146.997
-158.449
-158.480



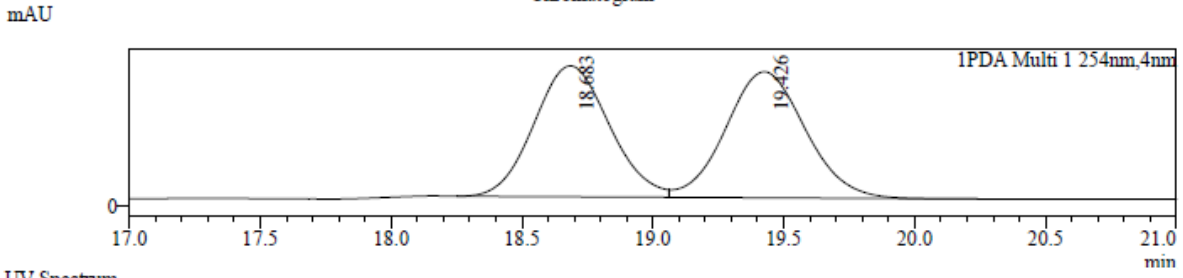



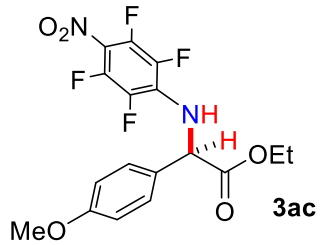
# HPLC

Sample Information

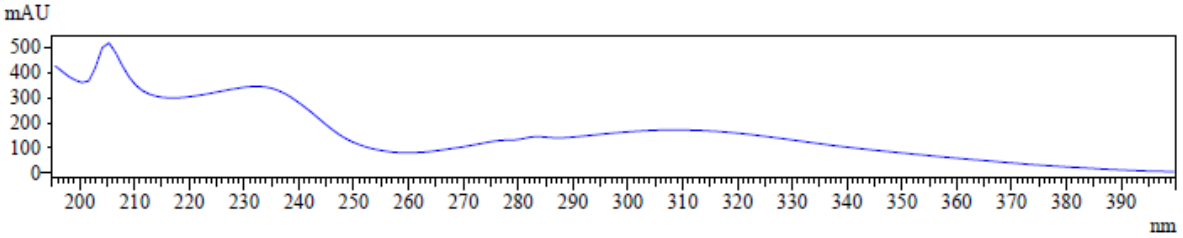
Sample Name : P0X-0721-IC-10%-0.8mL
Sample ID : P0X-0721-IC-10%-0.8mL
Data File : P0X-0721-IC-10%-0.8mL.lcd
Method File : P0X-10%-0.8ml.lcm

Chromatogram

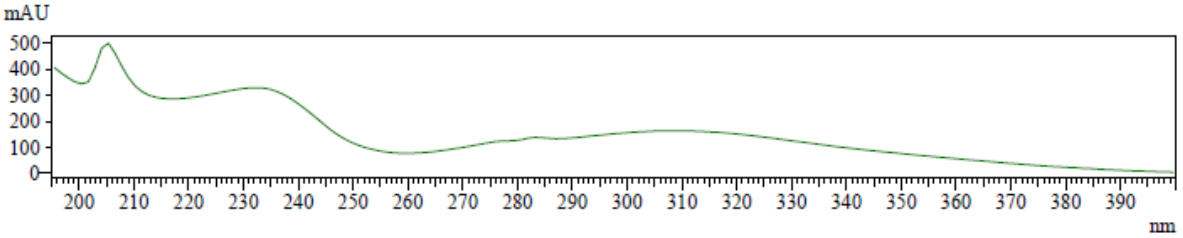



UV Spectrum
Retention time = 18.683




UV Spectrum
Retention time = 19.426




Peak Table

PDA Ch1 254nm

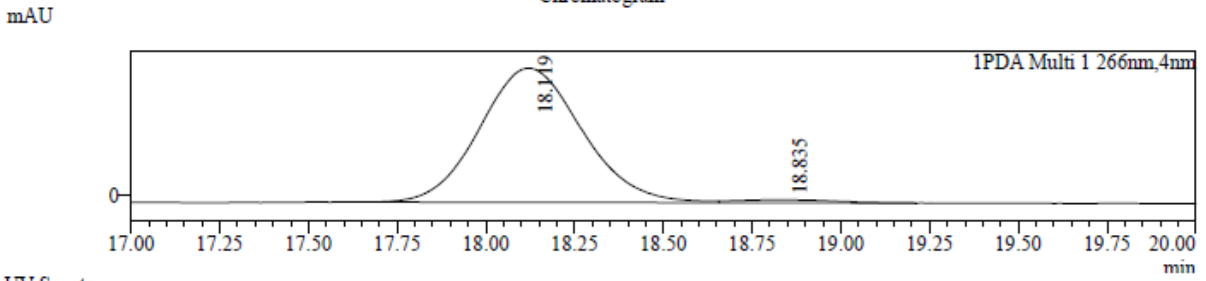
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 18.683 | 1787988 | 49.507 |
| 2 | 19.426 | 1823624 | 50.493 |
| Total | | 3611613 | 100.000 |

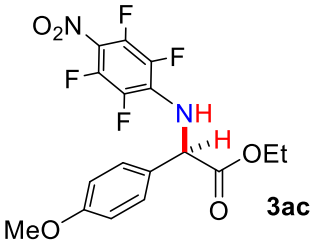
# HPLC

Sample Information

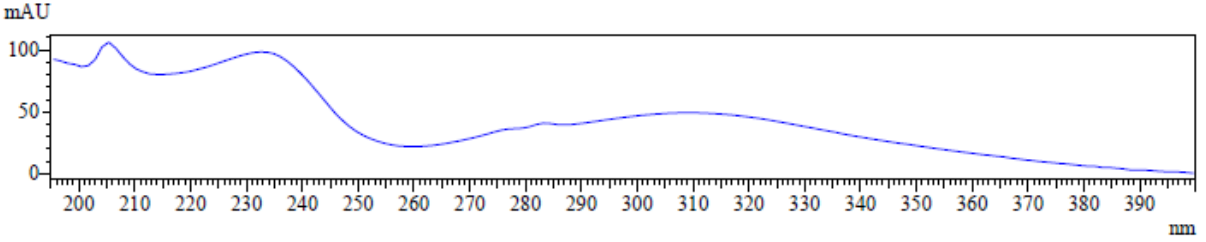
| | |
|---|---|
| Sample Name | : P0X-0722-IC-10%-0.8mL |
| Sample ID | : P0X-0722-IC-10%-0.8mL |
| Data File | : P0X-0722-IC-10%-0.8mL.lcd |
| Method File | : P0X-10%-0.8ml.lcm |

Chromatogram

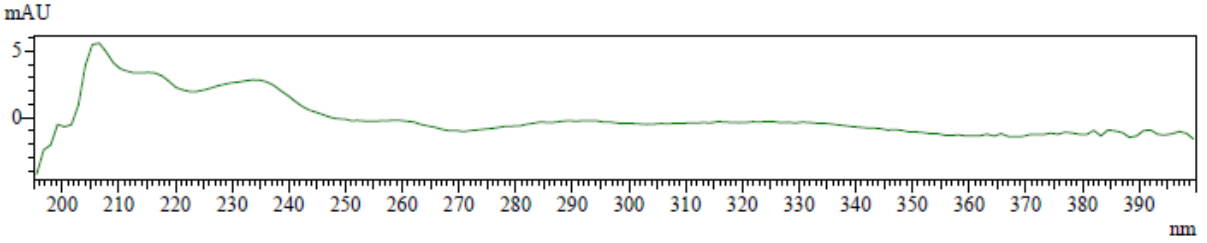



UV Spectrum
Retention time = 18.119




UV Spectrum
Retention time = 18.835



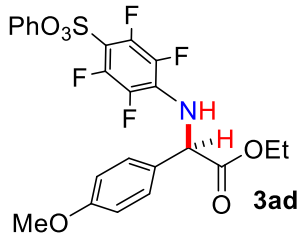

Peak Table

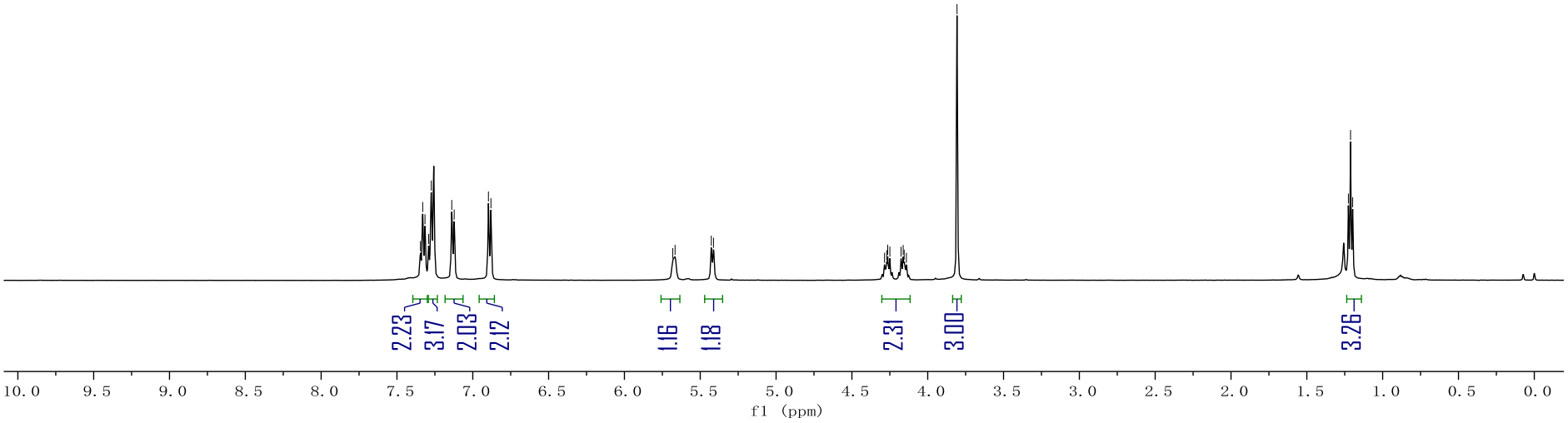
PDA Ch1 266nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 18.119 | 520416 | 97.840 |
| 2 | 18.835 | 11489 | 2.160 |
| Total | | 531905 | 100.000 |

# $^1$H NMR

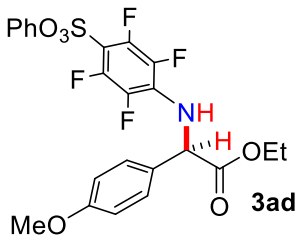
7.345 7.330 7.315 7.291 7.274 7.139 7.123 6.897 6.880 5.681 5.666 5.427 5.412 4.285 4.270 4.264 4.250 4.176 4.162 4.155 4.141 3.807 1.226 1.212 1.198

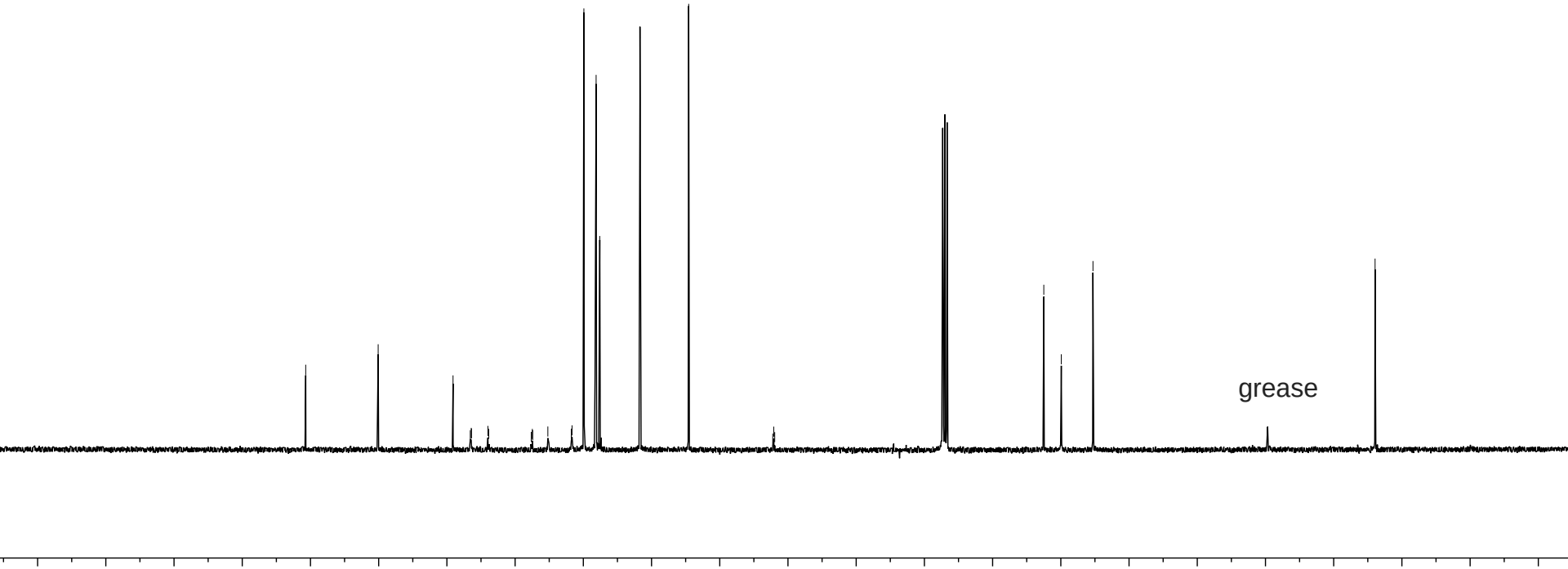


# $^{13}$C NMR

170.697 160.075 149.099 146.573 146.440 146.390 143.991 143.865 137.635 137.478 137.421 135.199 131.764 131.653 129.920 128.126 127.588 121.702 114.553 102.230 102.083 101.939 62.495 59.934 55.289 13.933

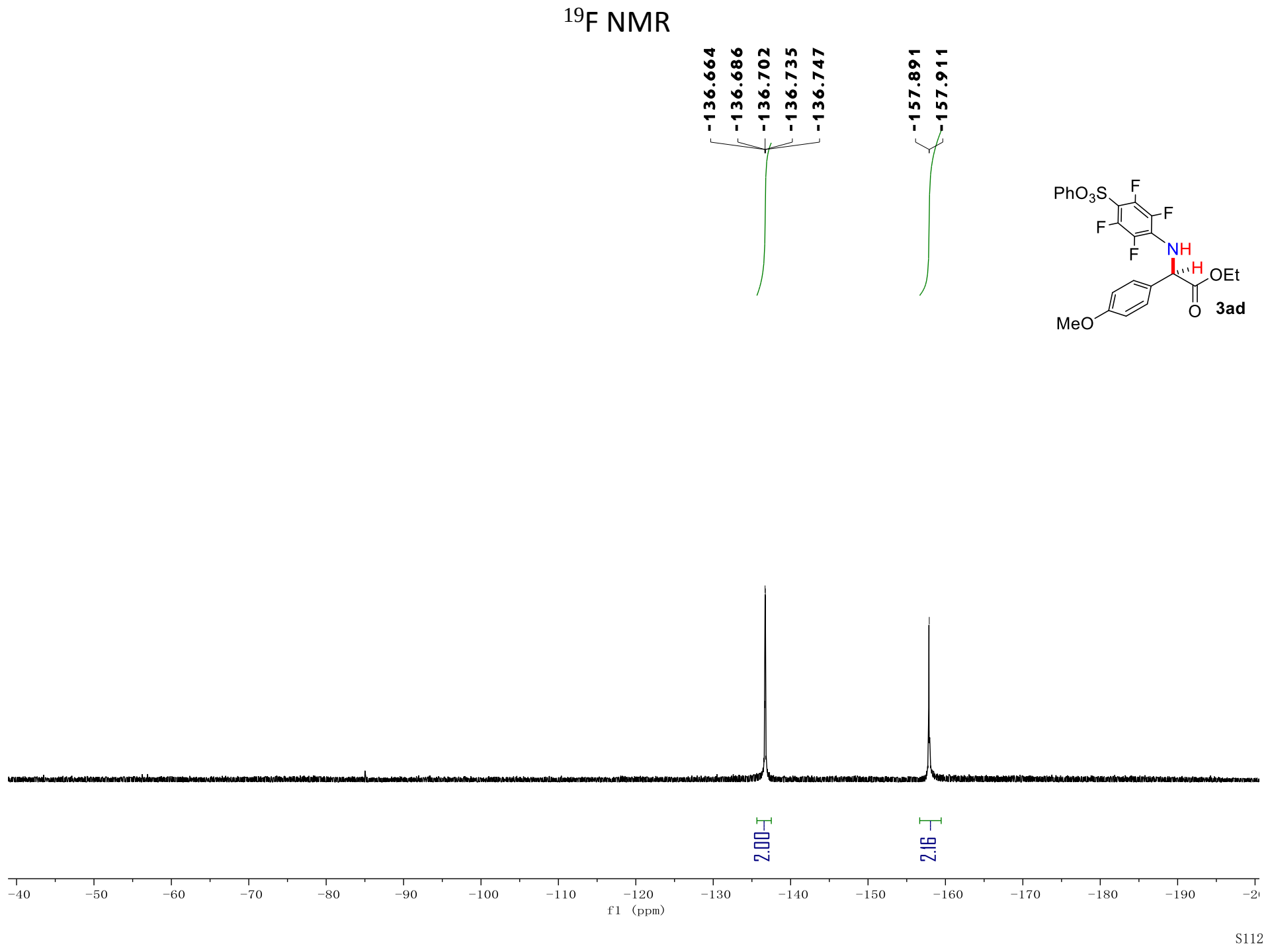



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

# $^{19}$F NMR

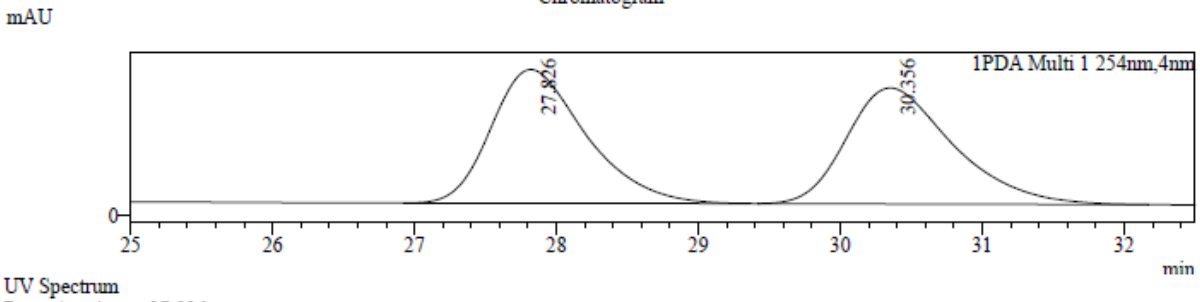

-136.664
-136.686
-136.702
-136.735
-136.747
-157.891
-157.911
PhO3S
F
F
F
F
NH
H
OEt
O
MeO
3ad
2.00
2.16
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

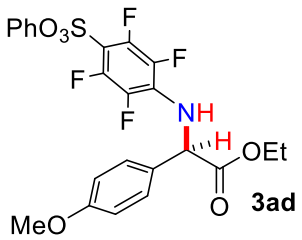
# HPLC

Sample Information

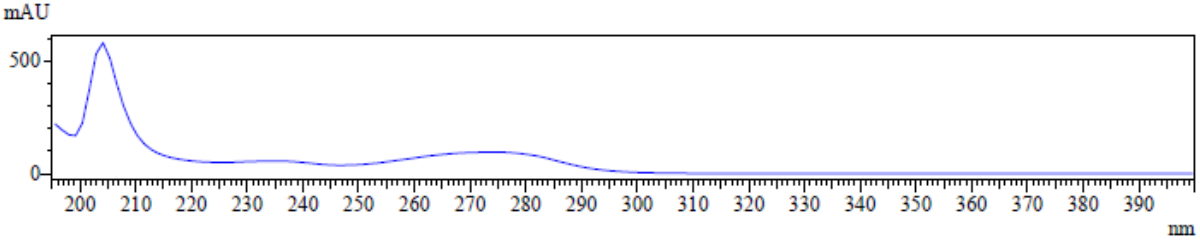
| | |
|---|---|
| Sample Name | : P0X781-ODH-5%-0.8Ml |
| Sample ID | : P0X781-ODH-5%-0.8Ml |
| Data File | : P0X781-ODH-5%-0.8Ml.lcd |
| Method File | : P0X-5.0%-0.8ml.lcm |

Chromatogram

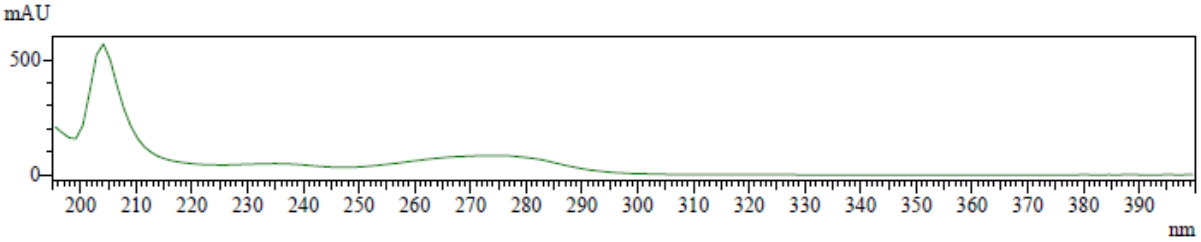



UV Spectrum
Retention time = 27.826




UV Spectrum
Retention time = 30.356




Peak Table

PDA Ch1 254nm

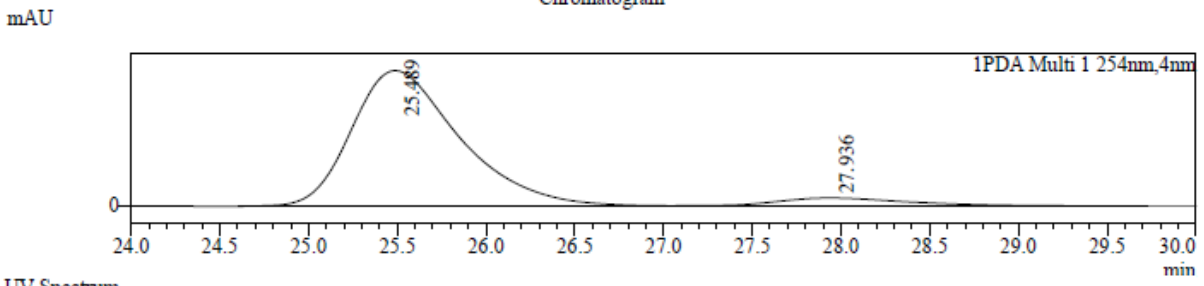
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 27.826 | 2142424 | 50.621 |
| 2 | 30.356 | 2089898 | 49.379 |
| Total | | 4232322 | 100.000 |

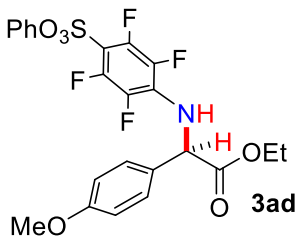
# HPLC

Sample Information

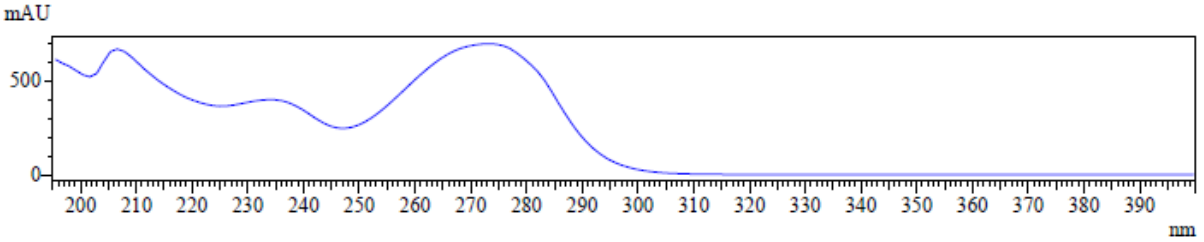
Sample Name : P0X788---ODH-5%-0.8Ml
Sample ID : P0X788---ODH-5%-0.8Ml
Data File : P0X788---ODH-5%-0.8Ml.lcd
Method File : P0X-5.0%-0.8ml.lcm

Chromatogram

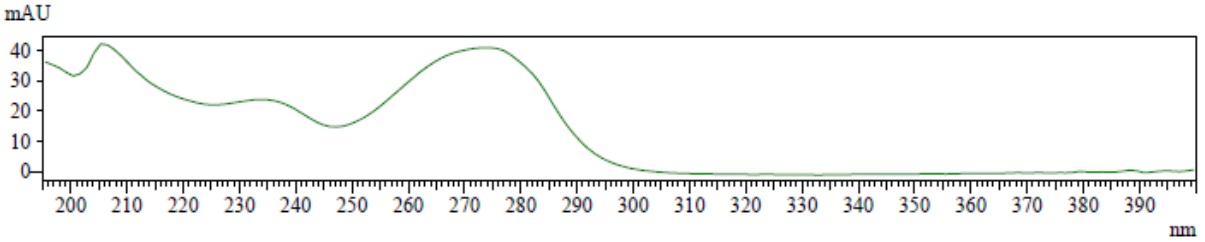



UV Spectrum
Retention time = 25.489




UV Spectrum
Retention time = 27.936

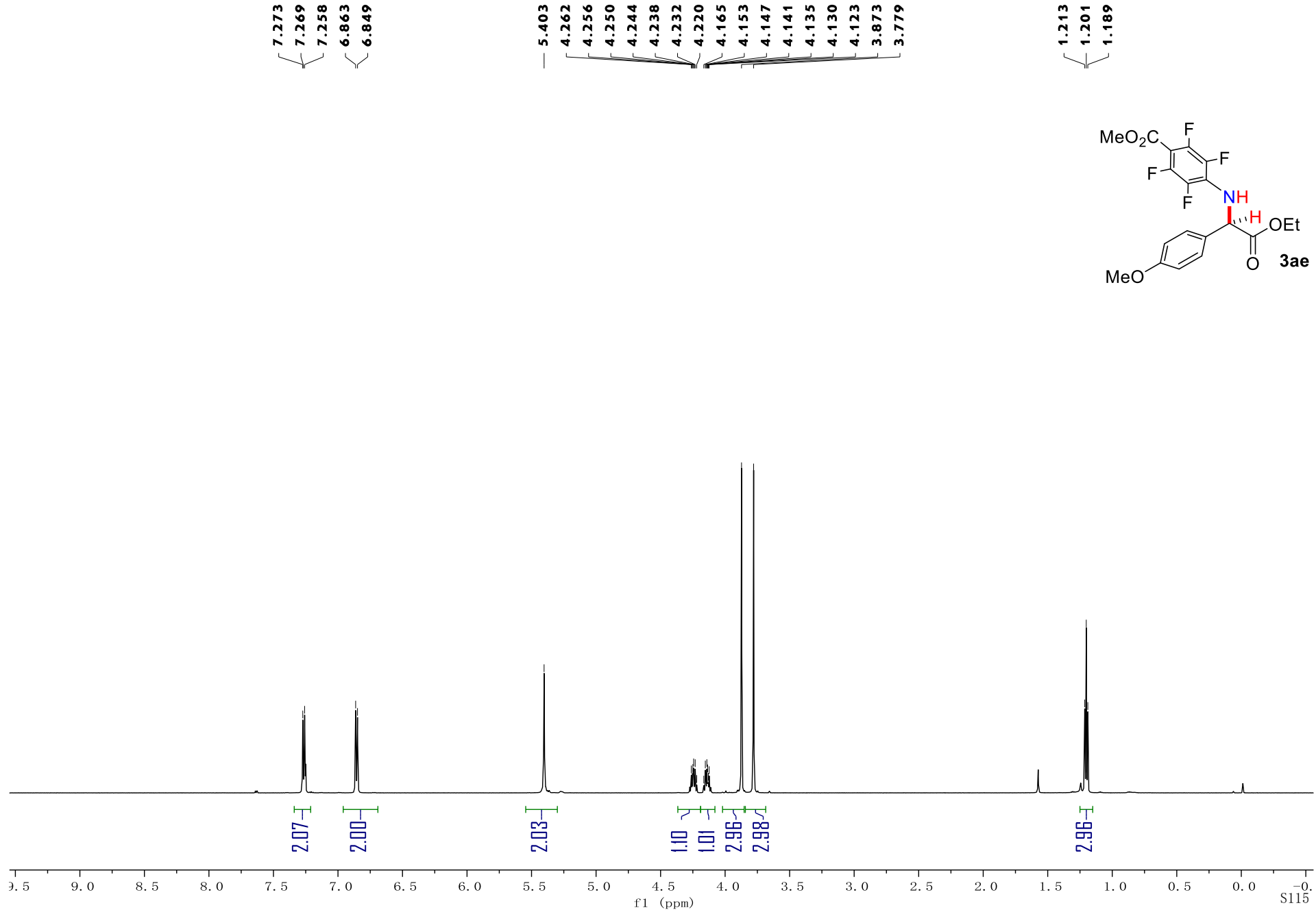



Peak Table

PDA Ch1 254nm

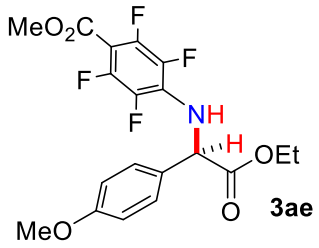
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 25.489 | 14766510 | 93.292 |
| 2 | 27.936 | 1061720 | 6.708 |
| Total | | 15828230 | 100.000 |

# $^1$H NMR


7.273
7.269
7.258
6.863
6.849
5.403
4.262
4.256
4.250
4.244
4.238
4.232
4.220
4.165
4.153
4.147
4.141
4.135
4.130
4.123
3.873
3.779
1.213
1.201
1.189
MeO2C
F
F
F
F
NH
H
OEt
O
MeO
3ae
2.07
2.00
2.03
1.10
1.01
2.96
2.98
2.96
f1 (ppm)
S115

# $^{13}$C NMR

171.066
160.921
160.897
160.873
159.921
147.339
147.312
147.285
147.252
147.233
147.205
147.151
145.310
145.276
145.254
145.226
145.206
145.174
145.146
145.120
137.977
137.942
137.898
137.845
137.809
137.768
136.066
136.024
135.990
135.938
135.902
135.887
135.857
129.163
129.132
129.102
129.071
129.041
128.979
128.817
128.753
128.142
114.435
99.971
99.857
99.744
62.216
60.133
55.240
52.517
13.941




3ae

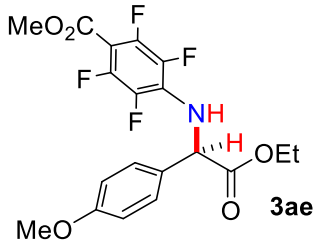


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

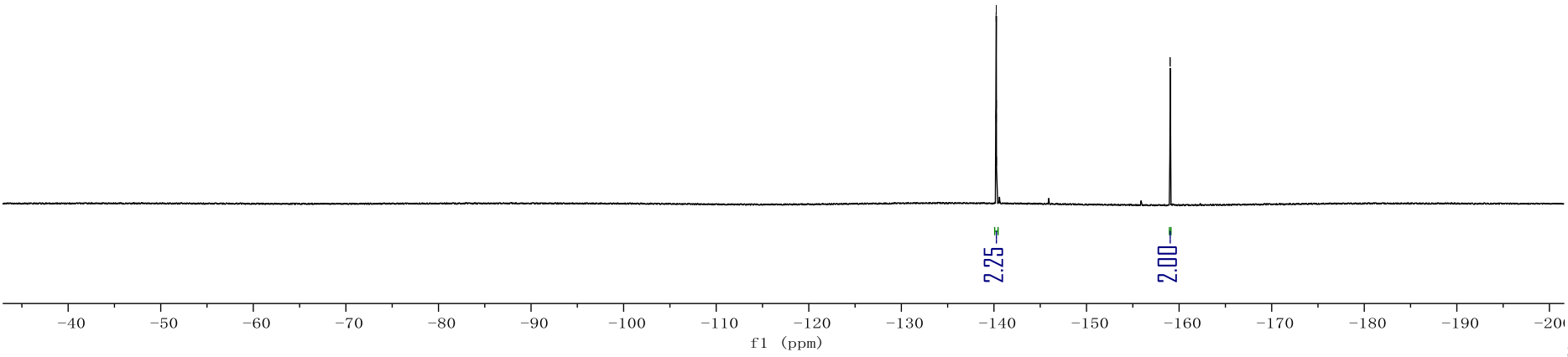
f1 (ppm)

# $^{19}$F NMR

-140.207
-140.217
-140.222
-140.231
-140.254
-140.263
-140.268
-140.279
-159.004
-159.012
-159.019
-159.042
-159.050
-159.057




3ae

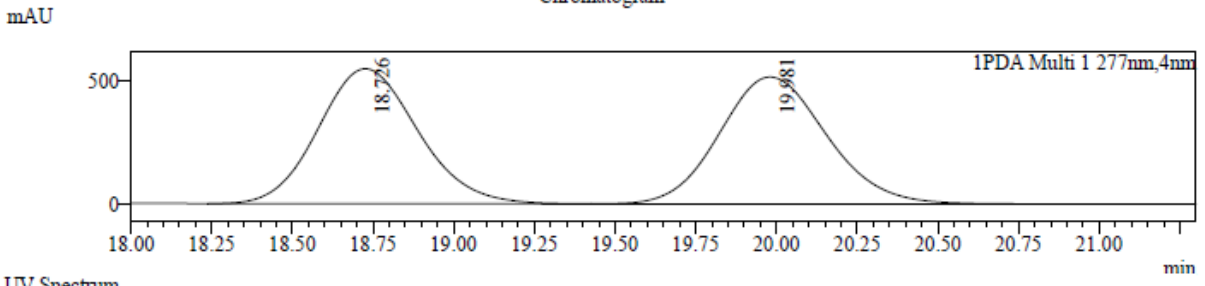


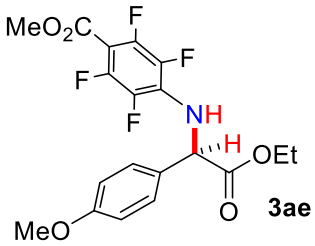
# HPLC

Sample Information

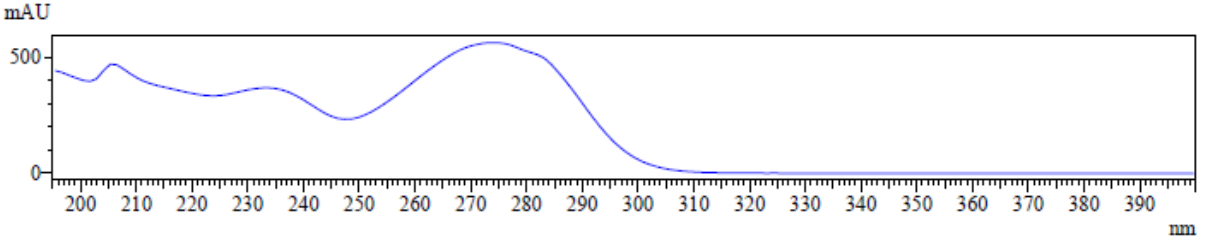
Sample Name : P0X-0711-IC-10%-0.8mL
Sample ID : P0X-0711-IC-10%-0.8mL
Data File : P0X-0711-IC-10%-0.8mL.lcd
Method File : YW-10%-0.8ml.lcm

Chromatogram

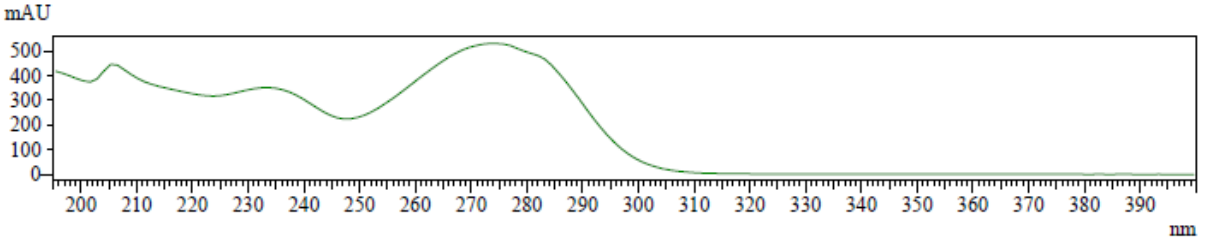



UV Spectrum
Retention time = 18.726




UV Spectrum
Retention time = 19.981




Peak Table

PDA Ch1 277nm

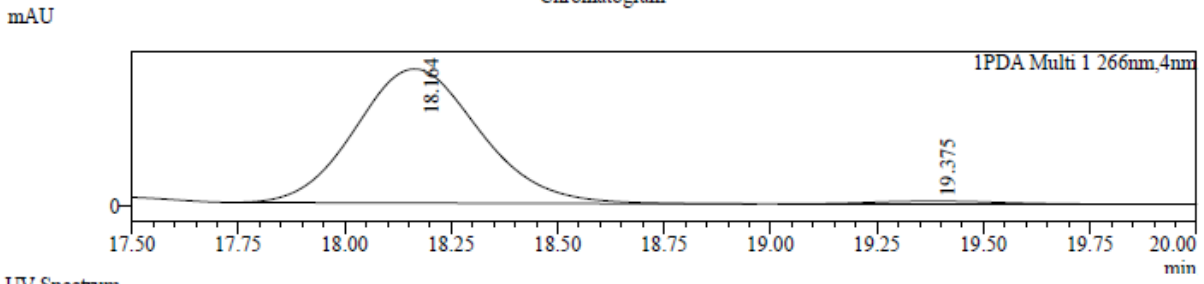
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 18.726 | 11750787 | 49.665 |
| 2 | 19.981 | 11909174 | 50.335 |
| Total | | 23659961 | 100.000 |

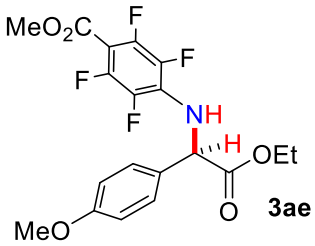
# HPLC

Sample Information

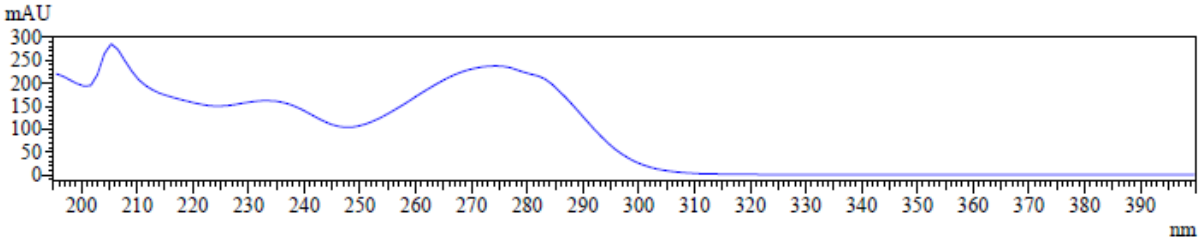
Sample Name : P0X-0712IC-10%-0.8mL
Sample ID : P0X-0712IC-10%-0.8mL
Data File : P0X-0712IC-10%-0.8mL.lcd
Method File : P0X-10%-0.8ml.lcm

Chromatogram

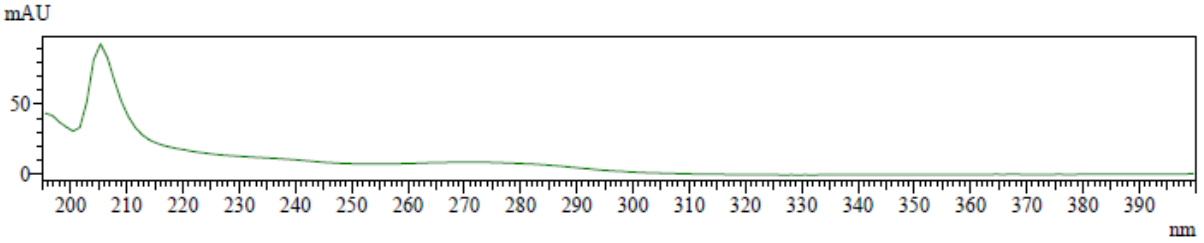



UV Spectrum
Retention time = 18.164




UV Spectrum
Retention time = 19.375

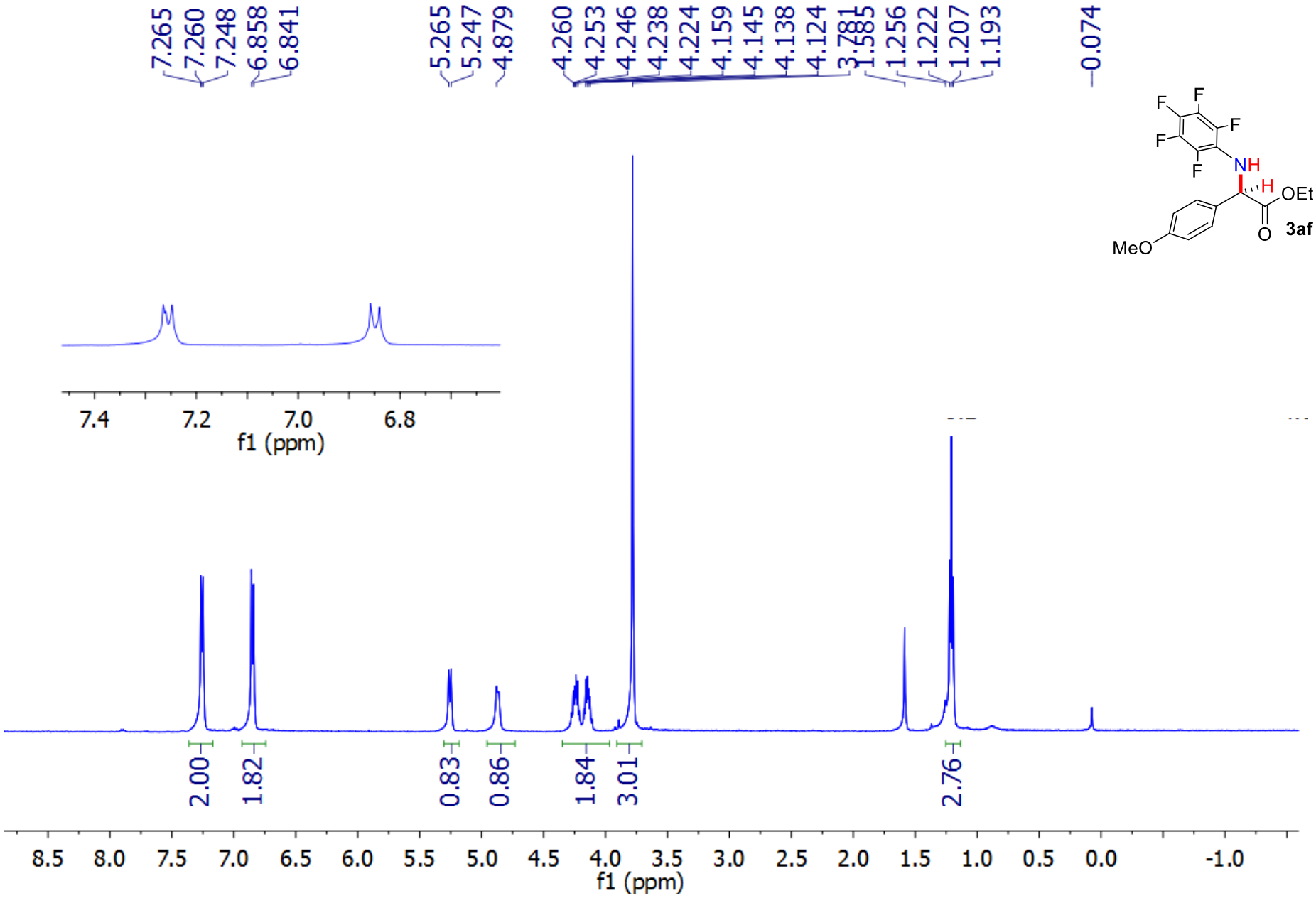



Peak Table

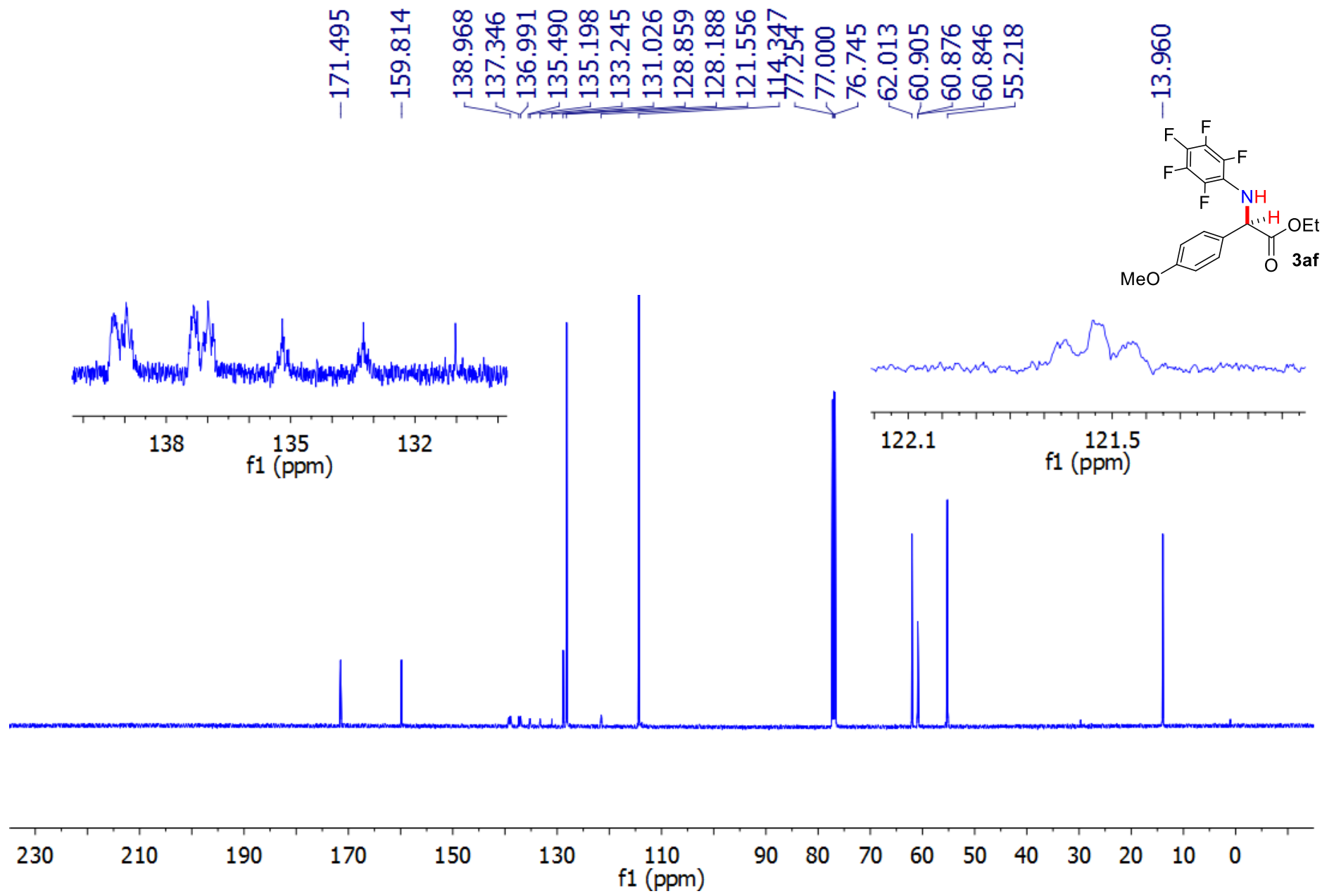
PDA Ch1 266nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 18.164 | 4159076 | 97.883 |
| 2 | 19.375 | 89963 | 2.117 |
| Total | | 4249040 | 100.000 |

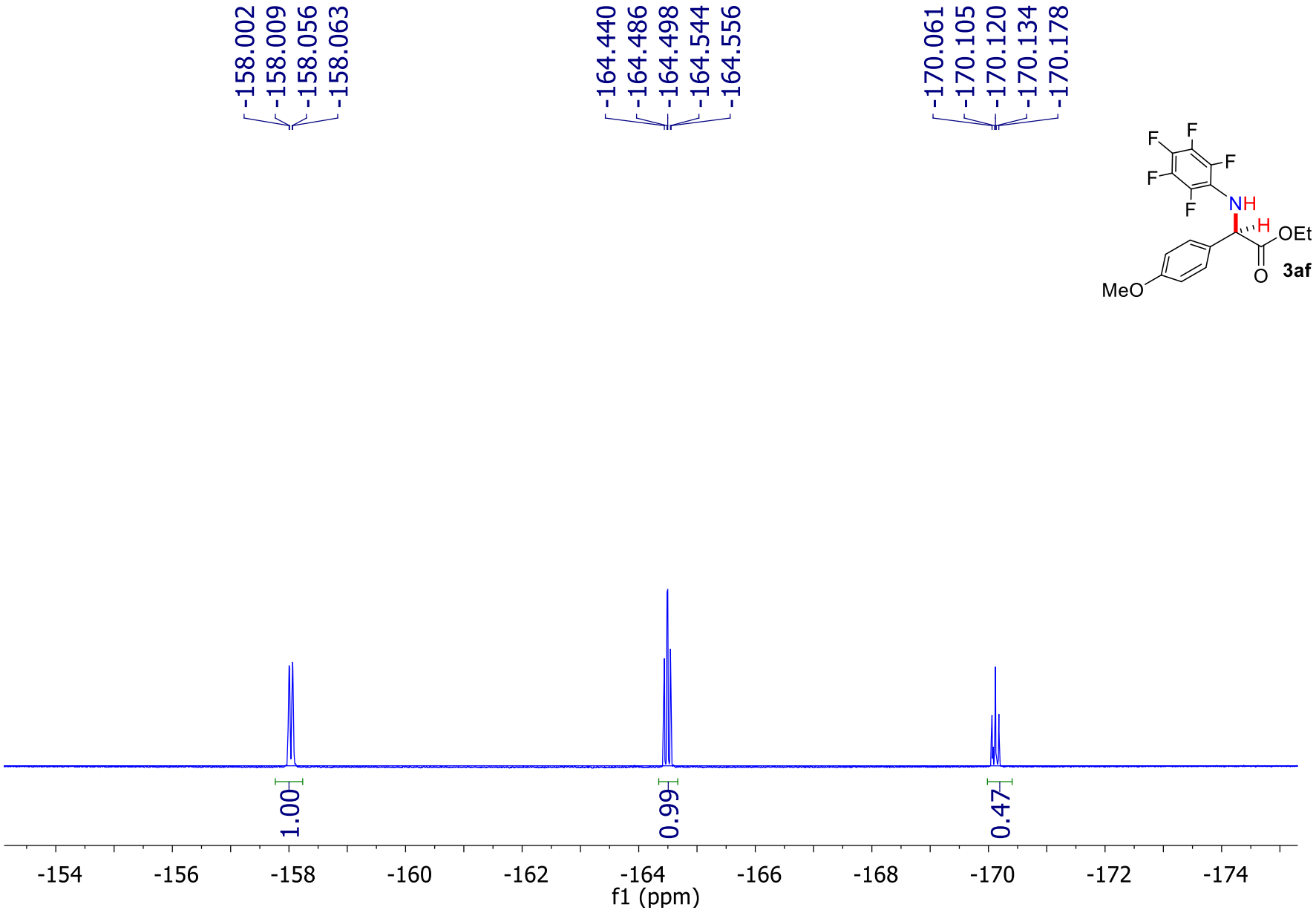
# $^{1}$H NMR


7.265
7.260
7.248
6.858
6.841
5.265
5.247
4.879
4.260
4.253
4.246
4.238
4.224
4.159
4.145
4.138
4.124
3.781
1.585
1.256
1.222
1.207
1.193
0.074
F
F
F
F
F
NH
H
OEt
O
3af
MeO
7.4
7.2
7.0
6.8
f1 (ppm)
2.00
1.82
0.83
0.86
1.84
3.01
2.76
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
-1.0
f1 (ppm)

# $^{13}$C NMR

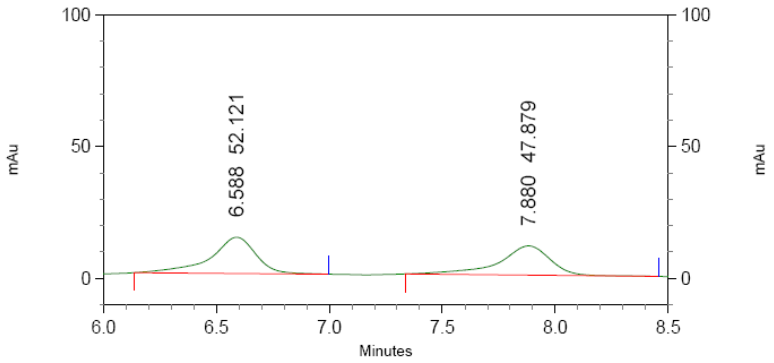

171.495
159.814
138.968
137.346
136.991
135.490
135.198
133.245
131.026
128.859
128.188
121.556
114.347
77.254
77.000
76.745
62.013
60.905
60.876
60.846
55.218
13.960
F
F
F
F
F
NH
H
OEt
O
MeO
3af
138
135
132
f1 (ppm)
122.1
121.5
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

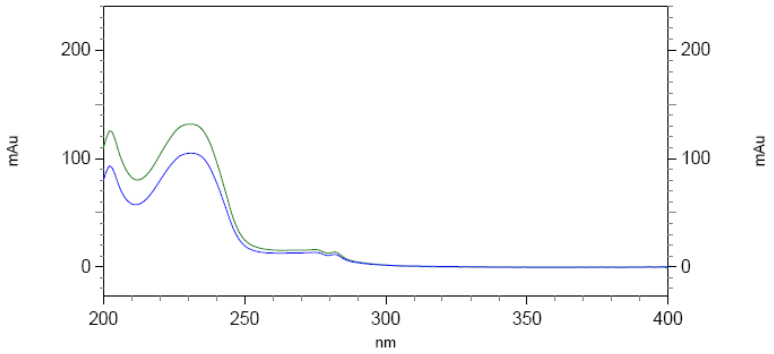
# $^{19}$F NMR

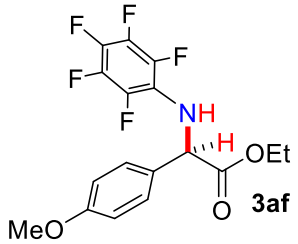

-158.002
-158.009
-158.056
-158.063
-164.440
-164.486
-164.498
-164.544
-164.556
-170.061
-170.105
-170.120
-170.134
-170.178
F
F
F
F
F
NH
H
OEt
O
MeO
3af
1.00
0.99
0.47
-154
-156
-158
-160
-162
-164
-166
-168
-170
-172
-174
f1 (ppm)

# HPLC

JLM-V-213-1-whelk-1@1ml
C:\EZStart\Projects\Default\Method\SMJ.met
C:\EZStart\Projects\Default\Data\JLM-V-213-1-whelk-1@1ml



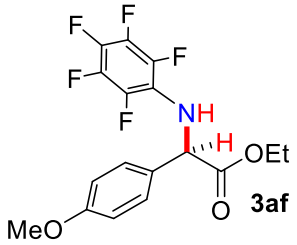

5: 247 nm, 4 nm
Results

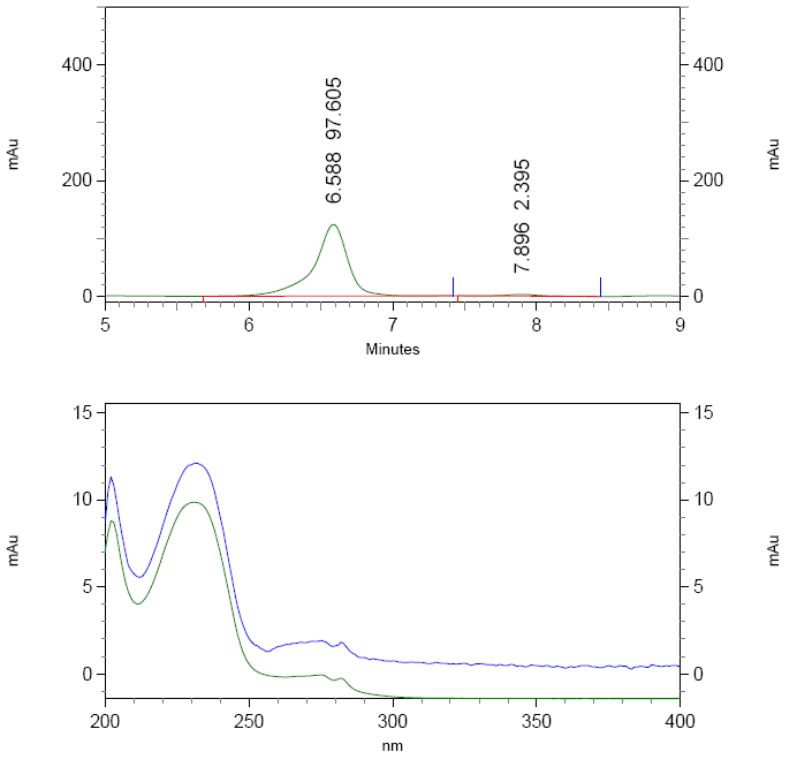
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 6.588 | 52.121 | 1 |
| | 7.880 | 47.879 | 2 |

| Totals | | |
|---|---|---|
| | 100.000 | |

# HPLC

JLM-V-213-2-whelk-1@1ml
C:\EZStart\Projects\Default\Method\SMJ.met
C:\EZStart\Projects\Default\Data\JLM-V-213-2-whelk-1@1ml

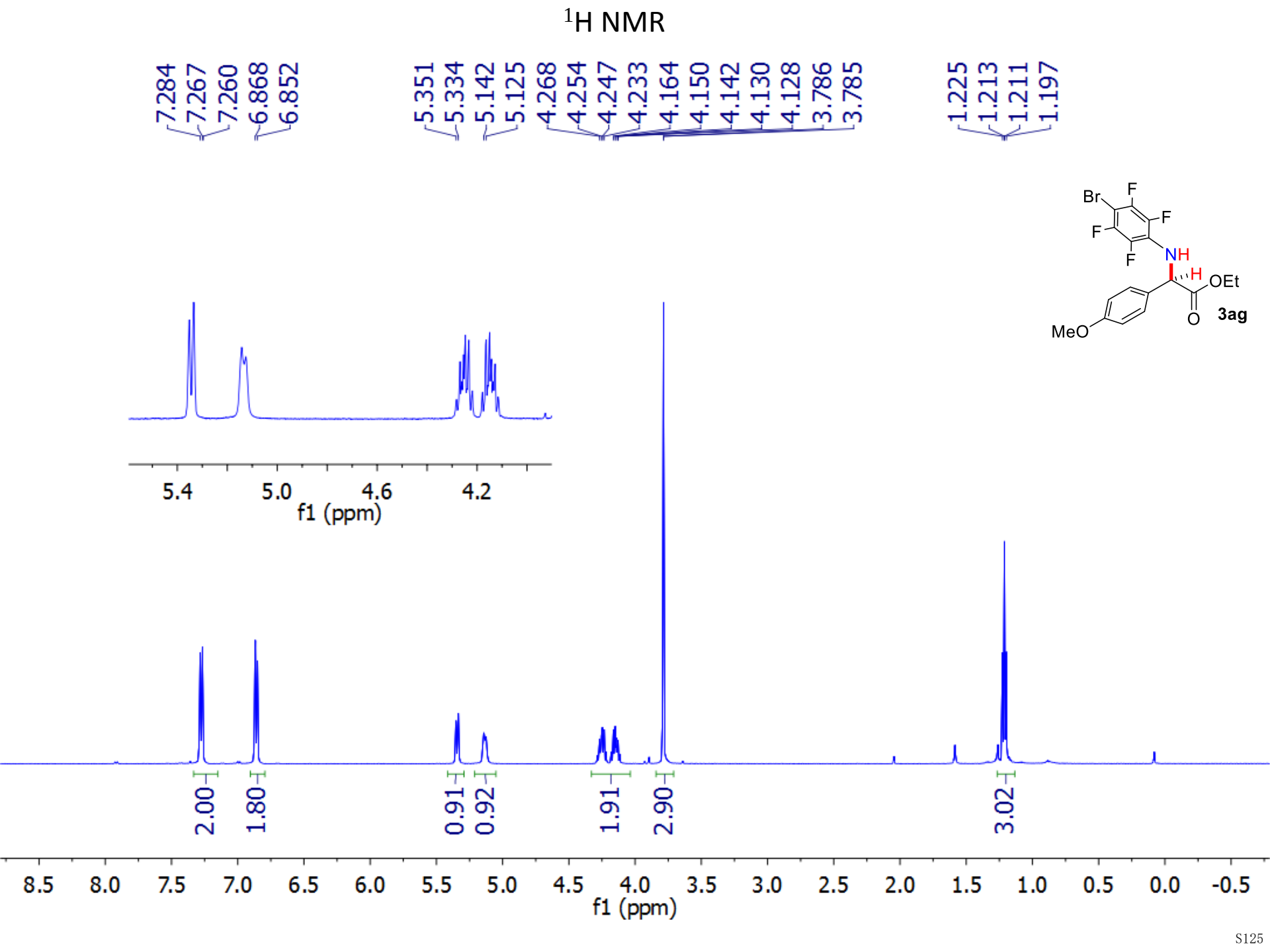


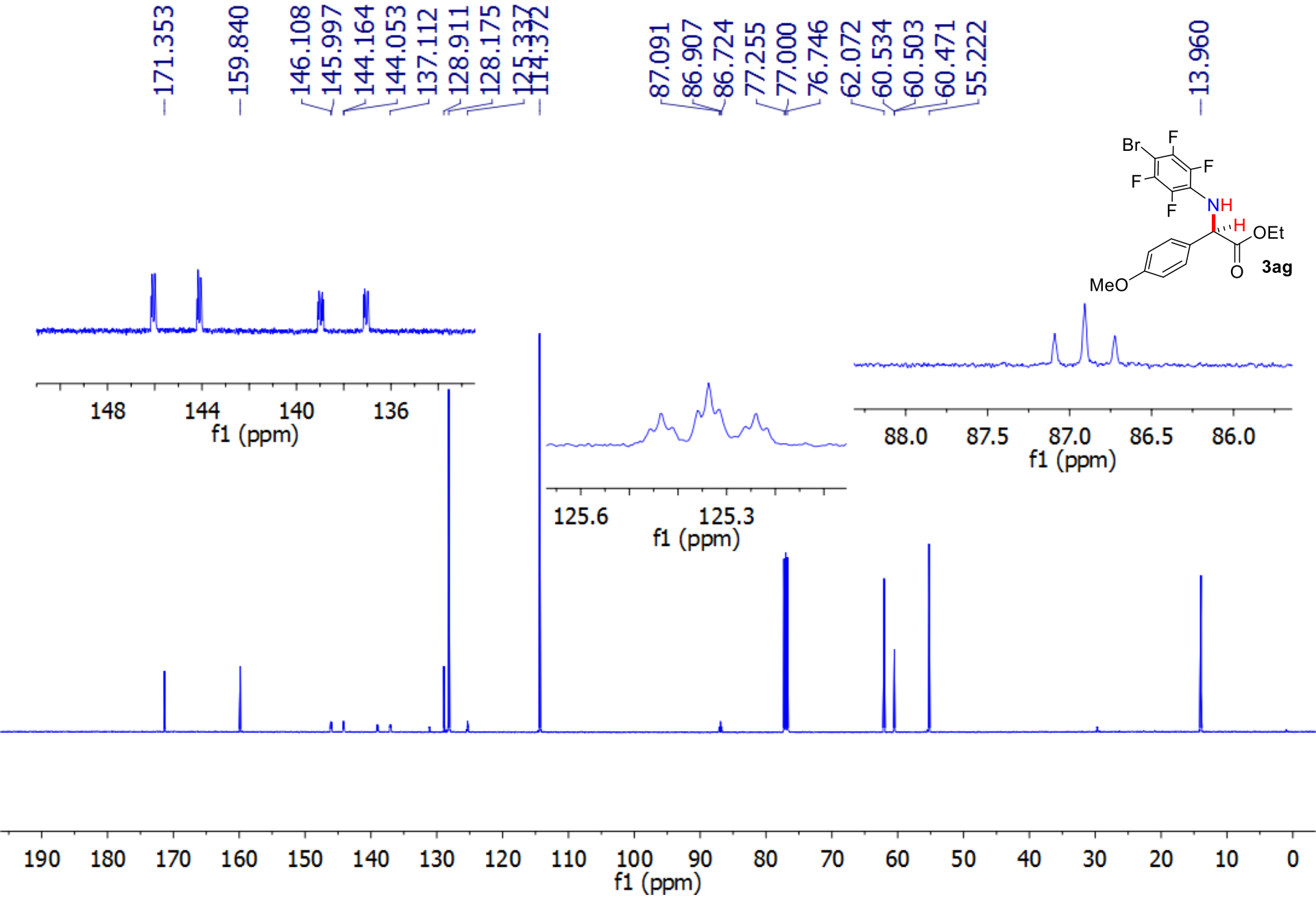

1: 236 nm, 4 nm
Results

| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 6.588 | 97.605 | 1 |
| | 7.896 | 2.395 | 2 |
| Totals | | 100.000 | |

# $^{1}$H NMR

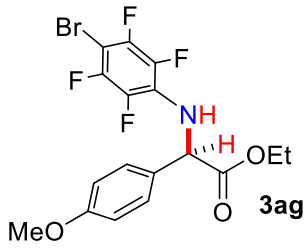

7.284
7.267
7.260
6.868
6.852
5.351
5.334
5.142
5.125
4.268
4.254
4.247
4.233
4.164
4.150
4.142
4.130
4.128
3.786
3.785
1.225
1.213
1.211
1.197
Br
F
F
F
F
NH
H
OEt
O
MeO
3ag
5.4
5.0
4.6
4.2
f1 (ppm)
2.00
1.80
0.91
0.92
1.91
2.90
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

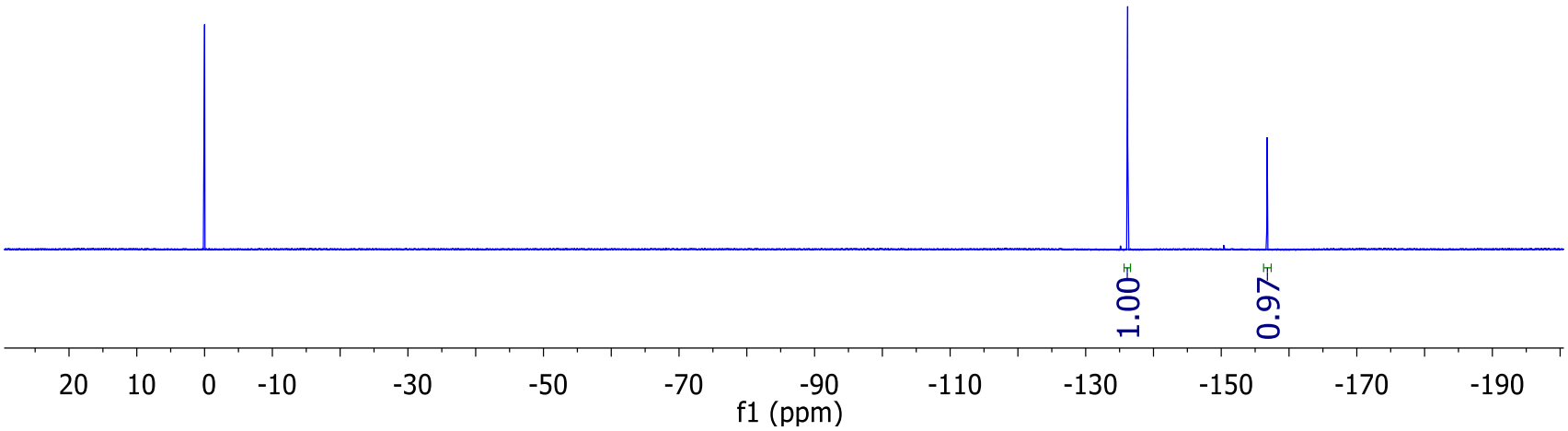
# $^{13}$C NMR


171.353
159.840
146.108
145.997
144.164
144.053
137.112
128.911
128.175
125.337
114.372
87.091
86.907
86.724
77.255
77.000
76.746
62.072
60.534
60.503
60.471
55.222
13.960
Br
F
F
F
F
NH
H
OEt
O
MeO
3ag
148
144
140
136
f1 (ppm)
125.6
125.3
f1 (ppm)
88.0
87.5
87.0
86.5
86.0
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

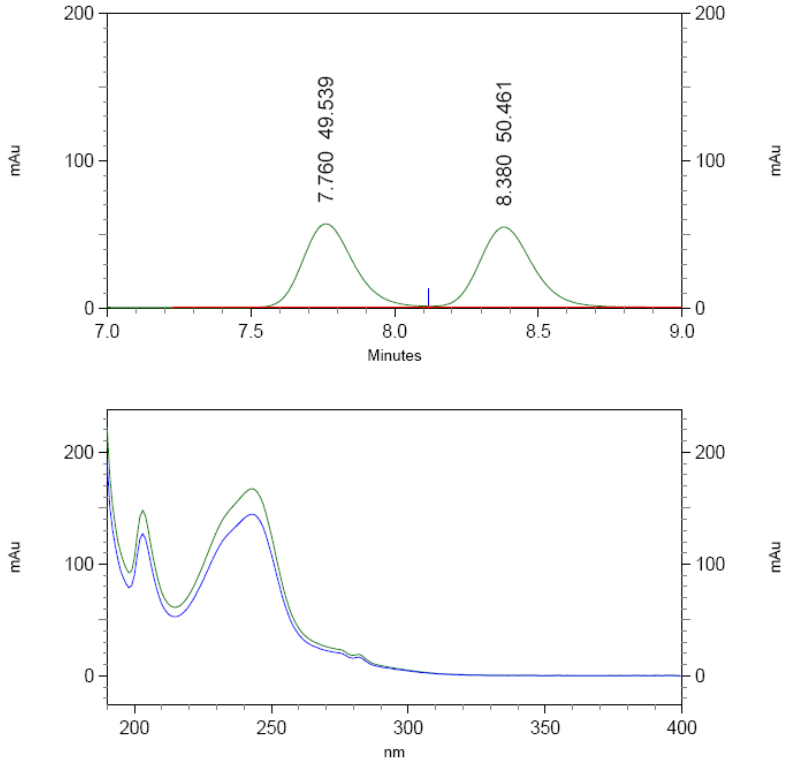
-136.117
-136.129
-136.138
-136.146
-136.188
-136.196
-136.206
-136.218
-156.731
-156.736
-156.780
-156.785

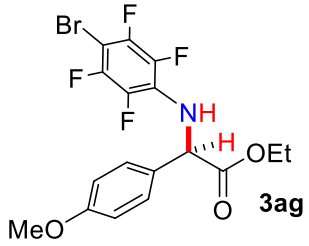


# HPLC

JLM-V-206-1-ADH-1%1ML
C:\EZStart\Projects\Default\Method\shifatest_2,5-dimehoxy.met
C:\EZStart\Projects\Default\Data\JLM-V-206-1-ADH1%1ML



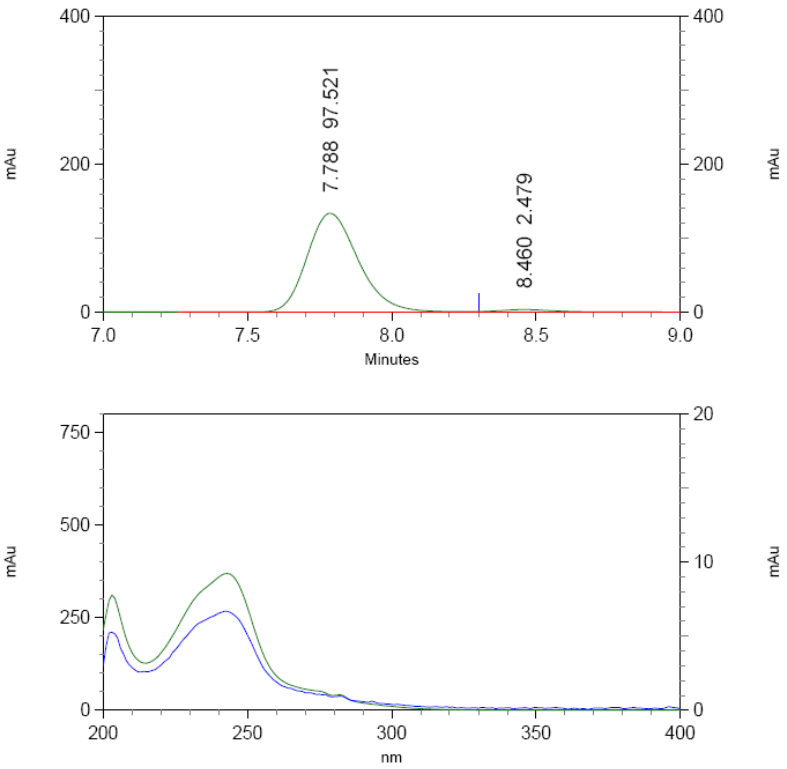



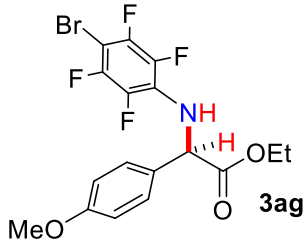

7: 251 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 7.760 | 49.539 |
| 2 | | 8.380 | 50.461 |
| Totals | | | 100.000 |

# HPLC

JLM-V-206-2-ADH-1%1ML
C:\EZStart\Projects\Default\Method\shifatest_2,5-dimehoxy.met
C:\EZStart\Projects\Default\Data\JLM-V-206-2-ADH1%1ML

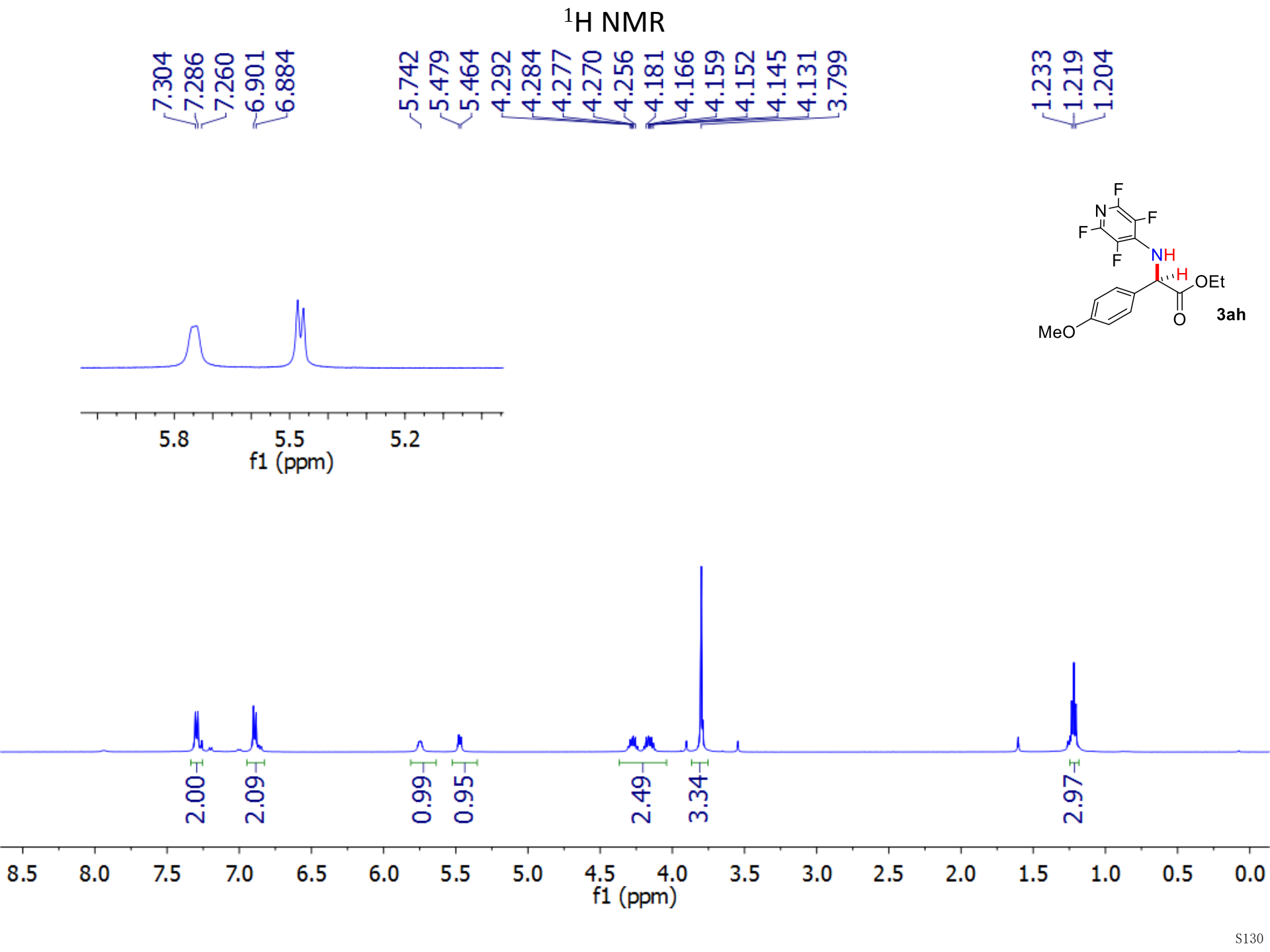


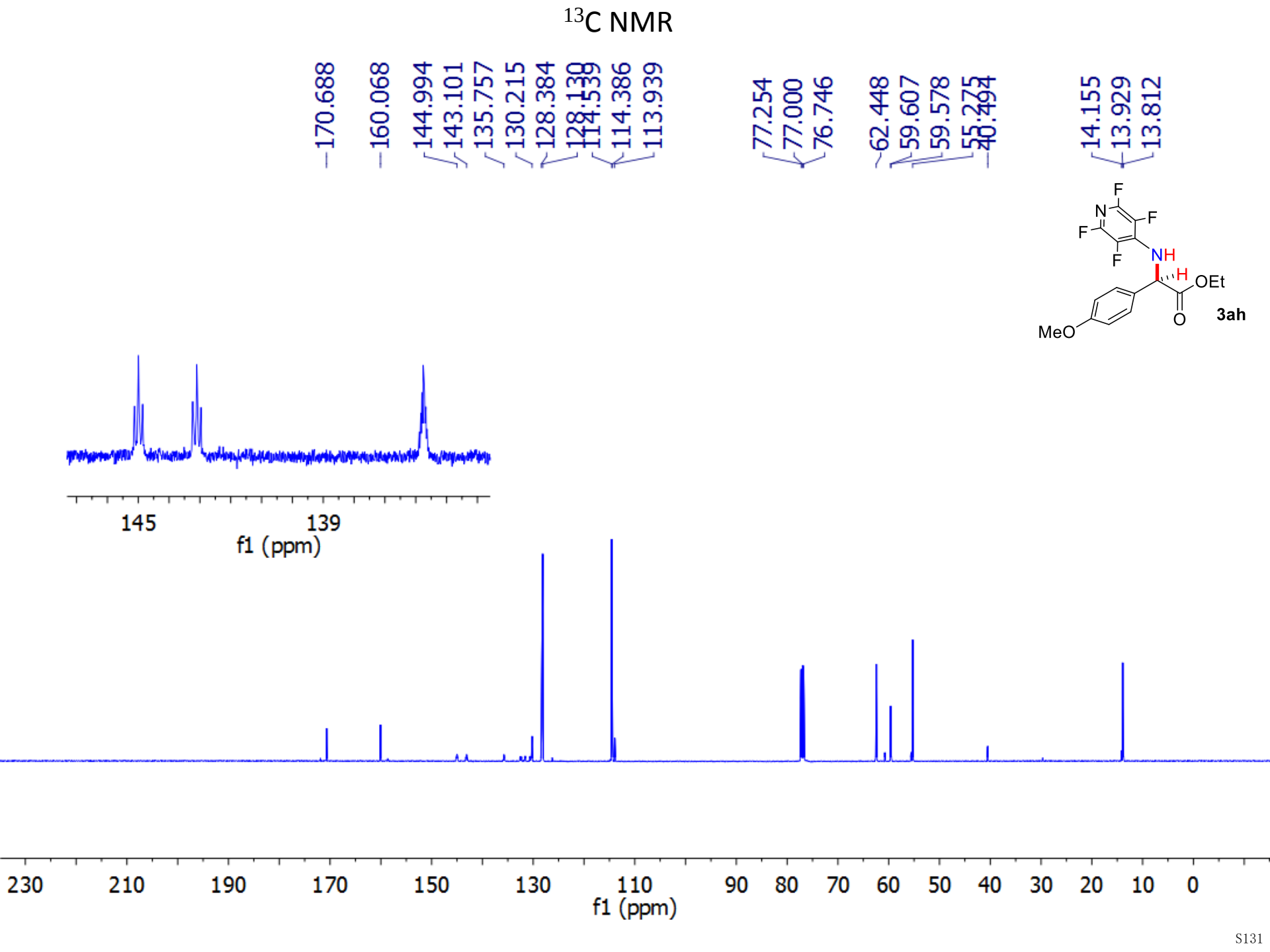

7: 238 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 7.788 | 97.521 |
| 2 | | 8.460 | 2.479 |
| Totals | | | 100.000 |

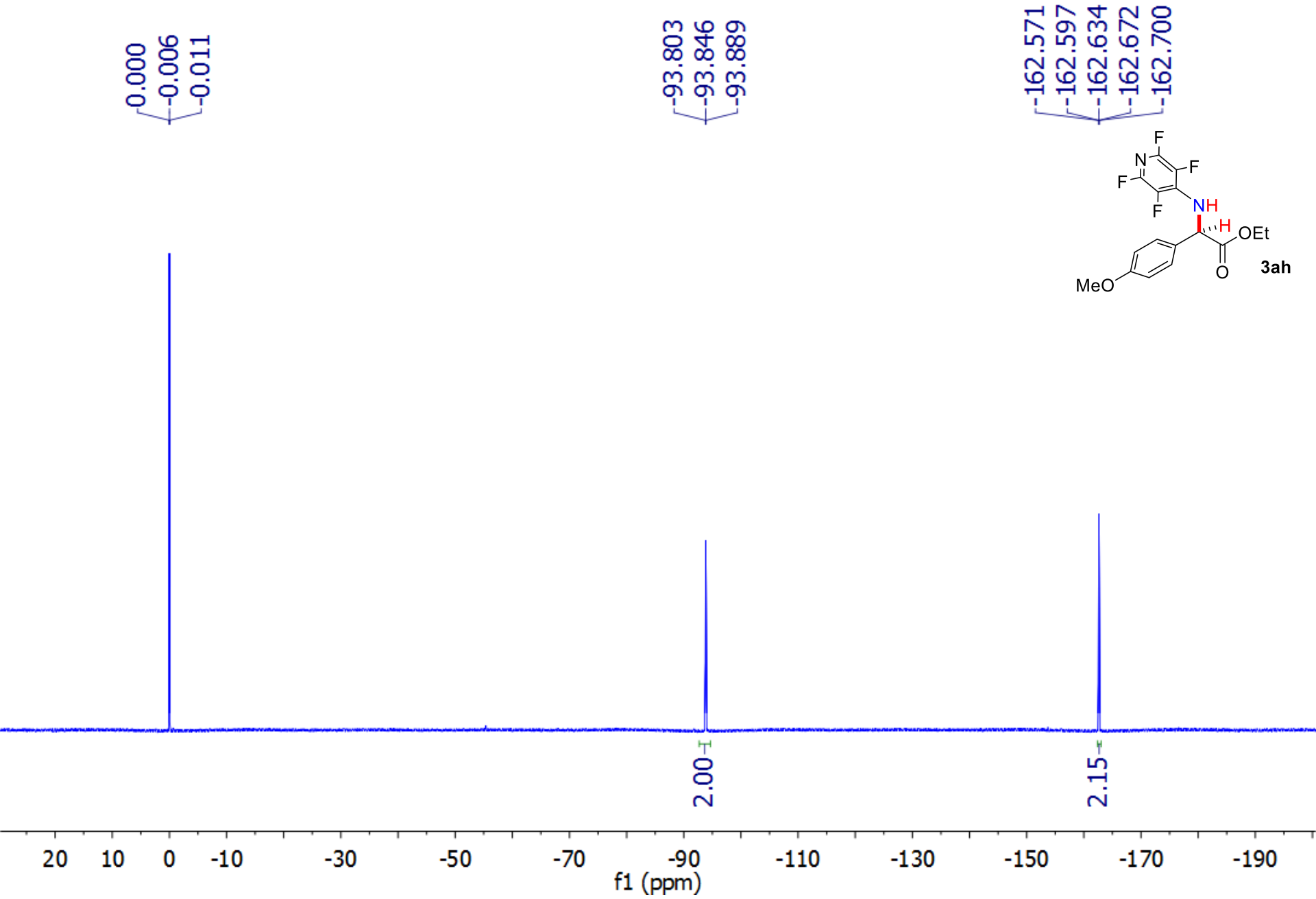
# $^{1}$H NMR


7.304
7.286
7.260
6.901
6.884
5.742
5.479
5.464
4.292
4.284
4.277
4.270
4.256
4.181
4.166
4.159
4.152
4.145
4.131
3.799
1.233
1.219
1.204
F
N
F
F
F
NH
H
OEt
O
MeO
3ah
5.8
5.5
5.2
f1 (ppm)
2.00
2.09
0.99
0.95
2.49
3.34
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

# $^{13}$C NMR

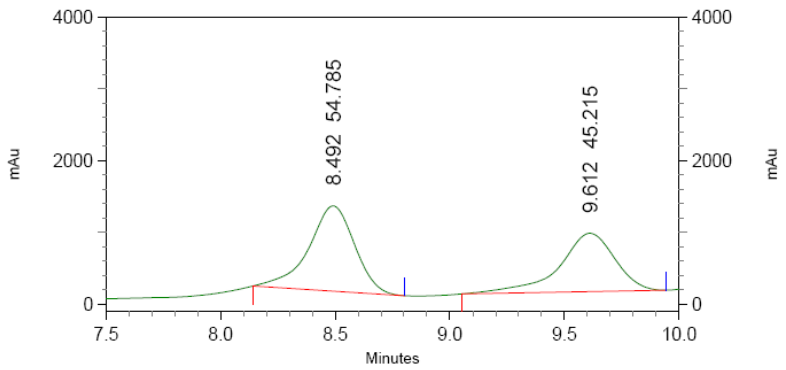

170.688
160.068
144.994
143.101
135.757
130.215
128.384
128.130
114.539
114.386
113.939
77.254
77.000
76.746
62.448
59.607
59.578
55.275
40.494
14.155
13.929
13.812
F
N
F
F
F
NH
H
OEt
O
MeO
3ah
145
139
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

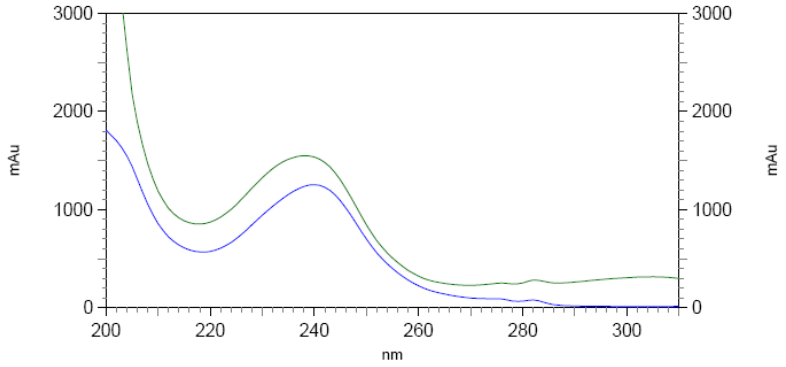
# $^{19}$F NMR

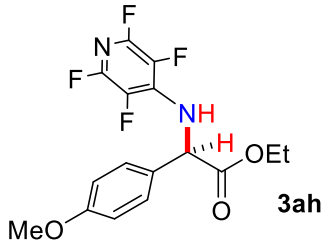

0.000
-0.006
-0.011
-93.803
-93.846
-93.889
-162.571
-162.597
-162.634
-162.672
-162.700
F
N
F
F
F
NH
H
OEt
O
MeO
3ah
2.00
2.15
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-V-174-2-WHELK-3%1ML
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
E:\JLM-V-174-2-WHELK3%1ML




**3ah**

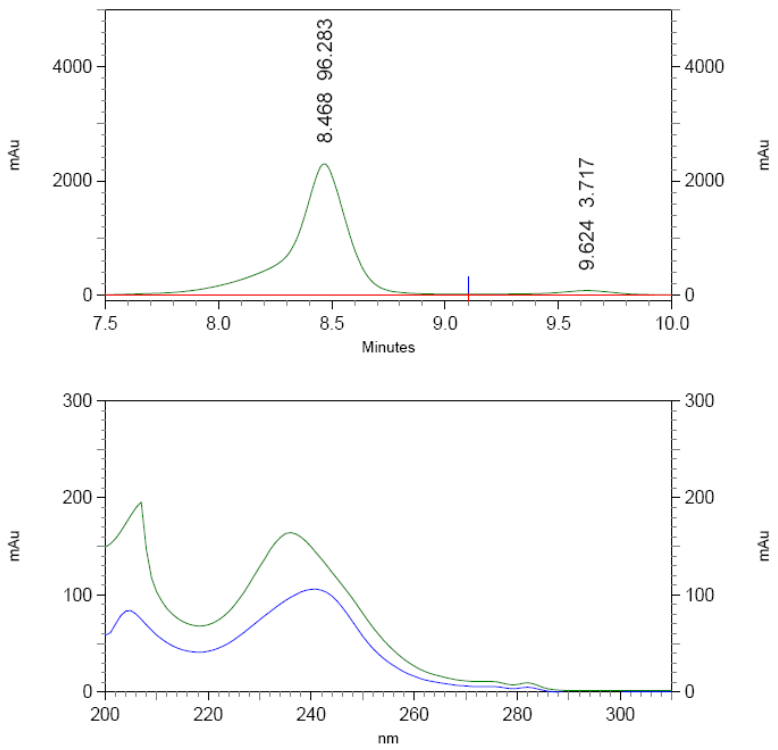
4: 231 nm, 4 nm
Results

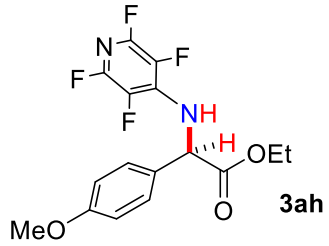
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 8.492 | 54.785 | 1 |
| | 9.612 | 45.215 | 2 |

| Totals | | |
|---|---|---|
| | 100.000 | |

# HPLC

JLM-V-174-1-WHELK-3%1ML
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
E:\JLM-V-174-1-WHELK3%1ML



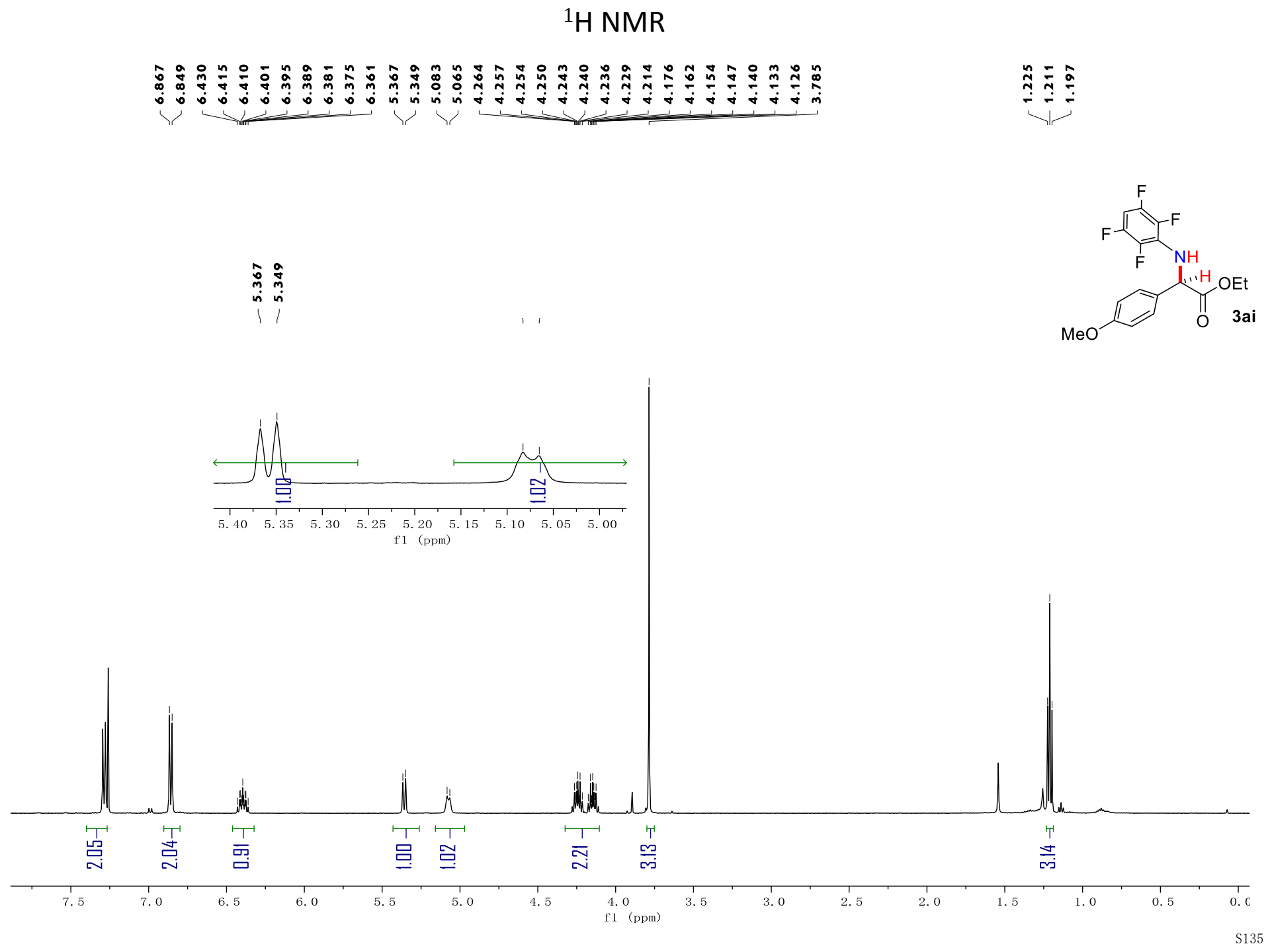

3ah

4: 231 nm, 4 nm
Results

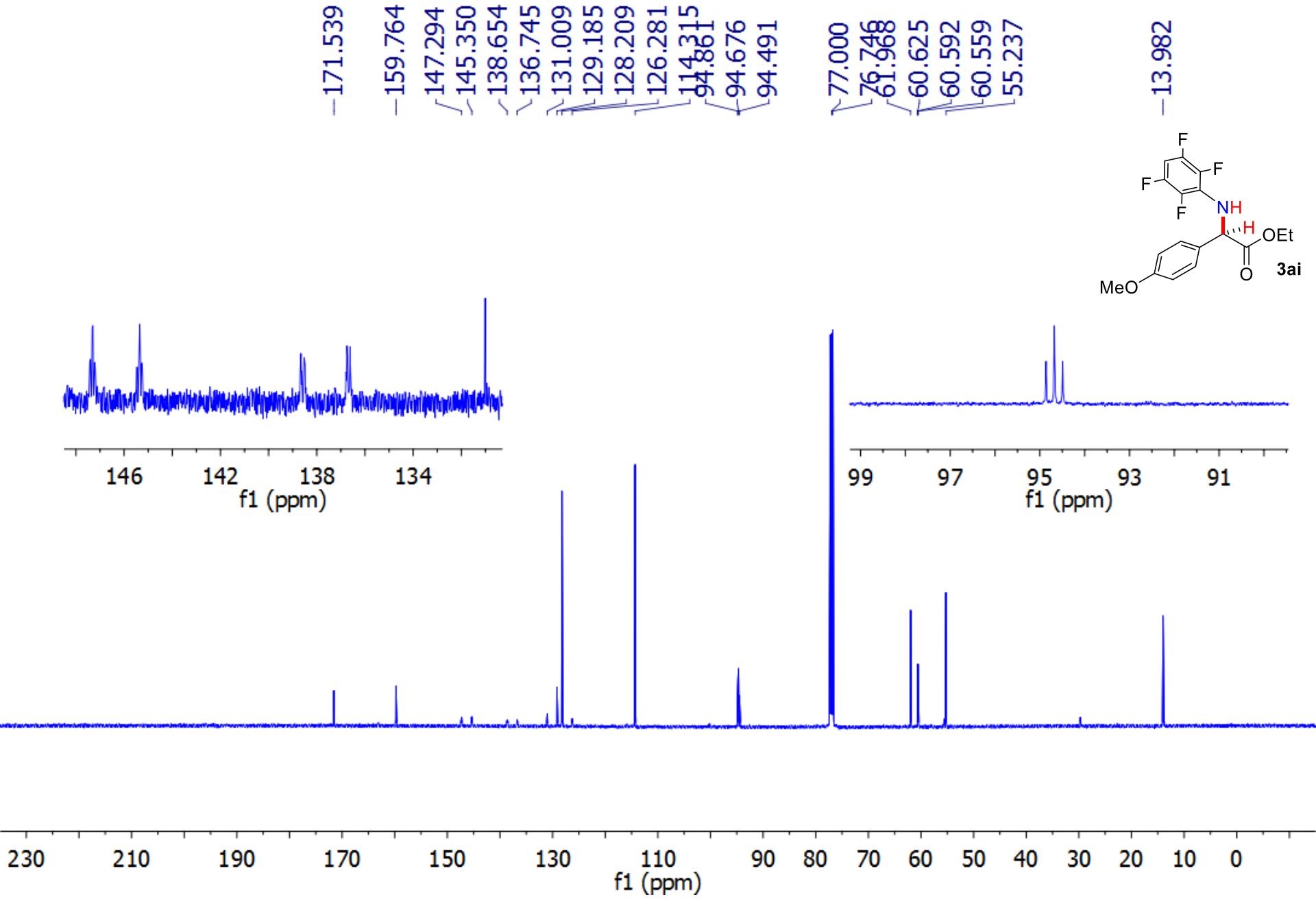
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 8.468 | 96.283 | 1 |
| | 9.624 | 3.717 | 2 |

| Totals | | |
|---|---|---|
| | 100.000 | |

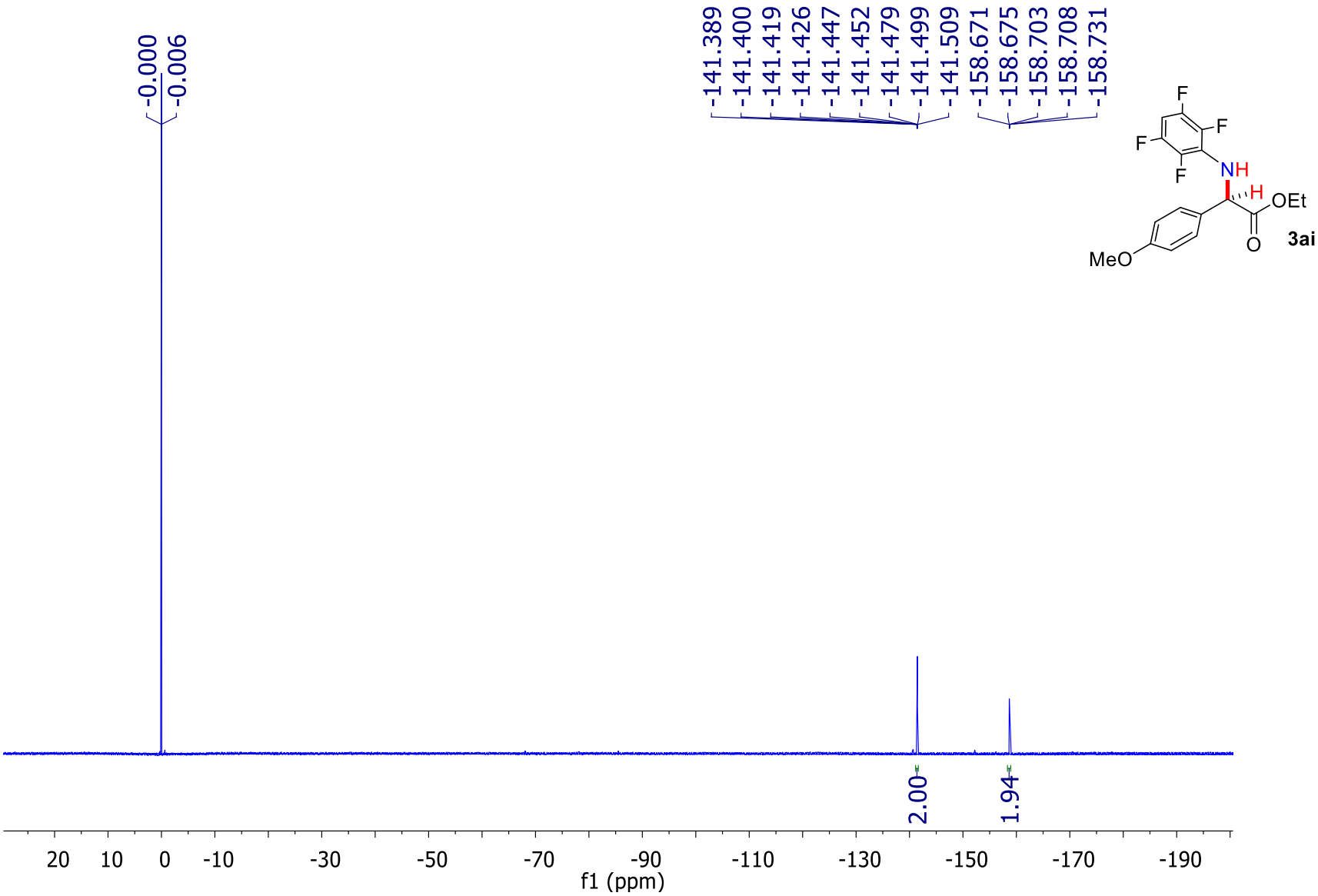
# $^1$H NMR


6.867
6.849
6.430
6.415
6.410
6.401
6.395
6.389
6.381
6.375
6.361
5.367
5.349
5.083
5.065
4.264
4.257
4.254
4.250
4.243
4.240
4.236
4.229
4.214
4.176
4.162
4.154
4.147
4.140
4.133
4.126
3.785
1.225
1.211
1.197
F
F
F
F
NH
H
OEt
O
MeO
3ai
1.00
1.02
5.40 5.35 5.30 5.25 5.20 5.15 5.10 5.05 5.00
f1 (ppm)
2.05
2.04
0.91
1.00
1.02
2.21
3.13
3.14
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

# $^{13}$C NMR

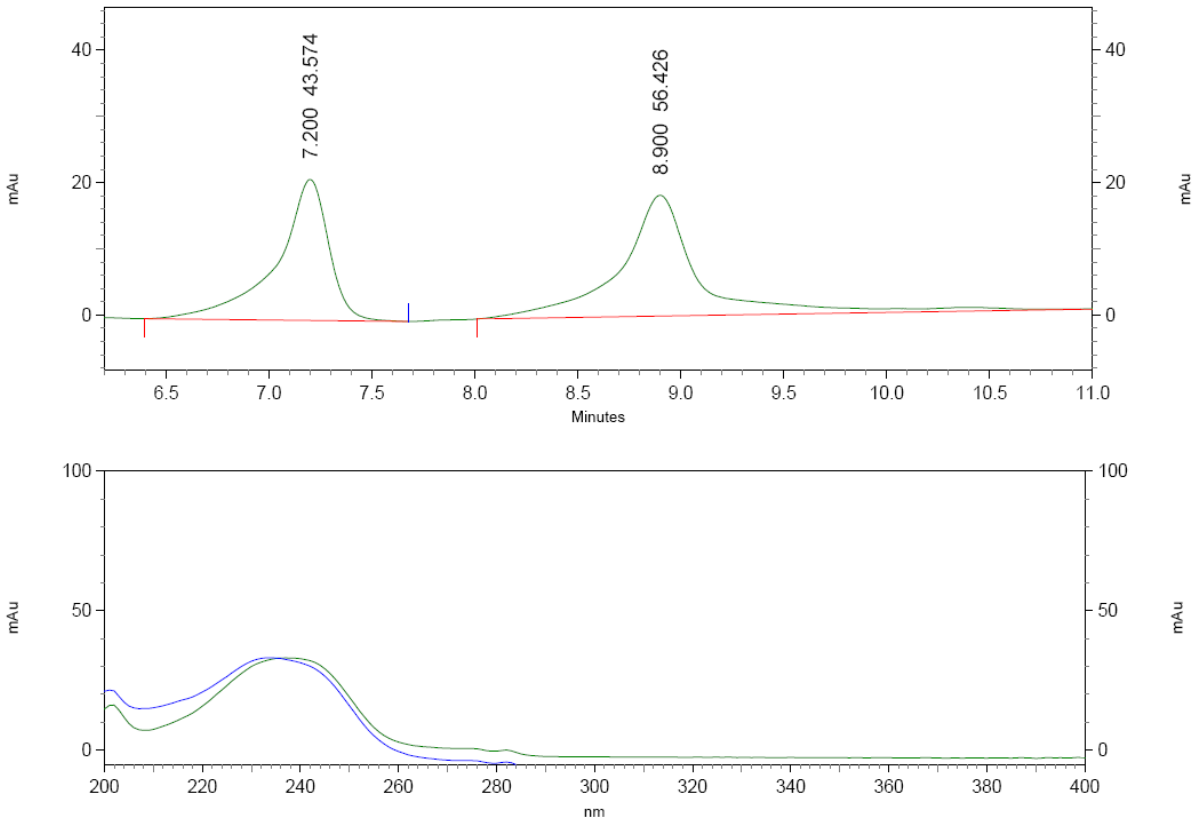

171.539
159.764
147.294
145.350
138.654
136.745
131.009
129.185
128.209
126.281
114.315
94.861
94.676
94.491
77.000
76.746
61.968
60.625
60.592
60.559
55.237
13.982
F
F
F
F
NH
H
OEt
O
MeO
3ai
146
142
138
134
f1 (ppm)
99
97
95
93
91
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

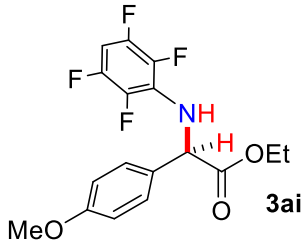
# $^{19}$F NMR


-0.000
-0.006
-141.389
-141.400
-141.419
-141.426
-141.447
-141.452
-141.479
-141.499
-141.509
-158.671
-158.675
-158.703
-158.708
-158.731
F
F
F
F
NH
H
OEt
O
MeO
3ai
2.00
1.94
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-V-227-1-whelk-1@1ml
C:\EZStart\Projects\Default\Data\JLM-V-227-1-whelk-1@1ml
C:\EZStart\Projects\Default\Method\CQL-AD-H10%1.0ml60min.met
AD-H column 20%IPA @ 0.8ml/min



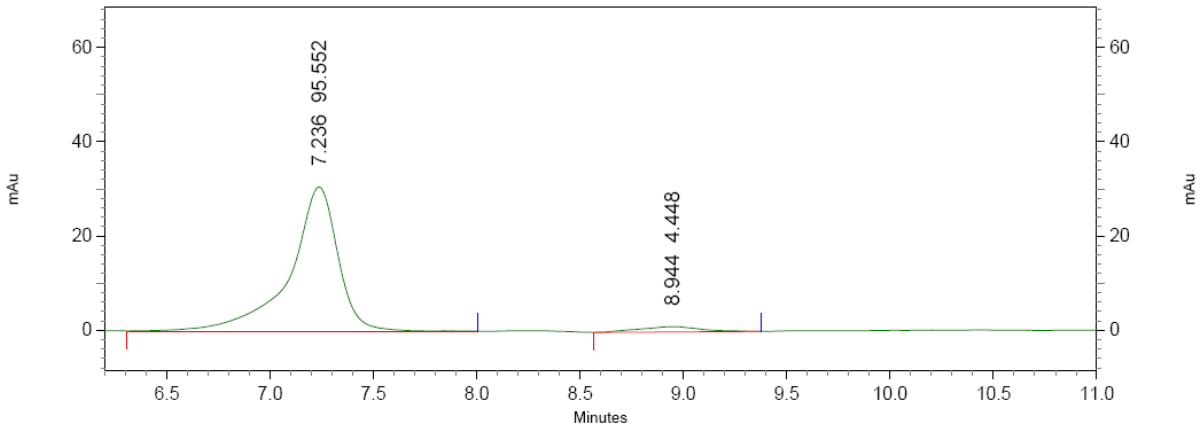

2: 235 nm, 4 nm Results

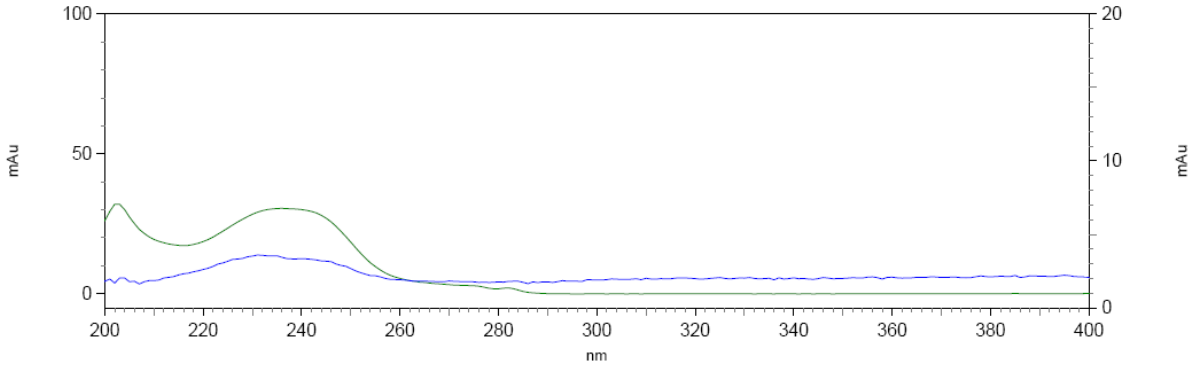
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.200 | 43.574 |
| 2 | 8.900 | 56.426 |

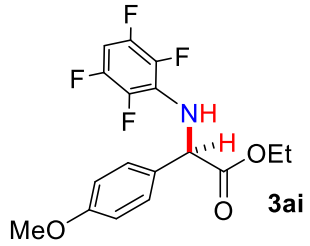
| Totals | |
|---|---|
| | 100.000 |

# HPLC

JLM-V-227-2-whelk-1@1ml
C:\EZStart\Projects\Default\Data\JLM-V-227-2-whelk-1@1ml
C:\EZStart\Projects\Default\Method\CQL-AD-H10%1.0ml60min.met
AD-H column 20%IPA @ 0.8ml/min



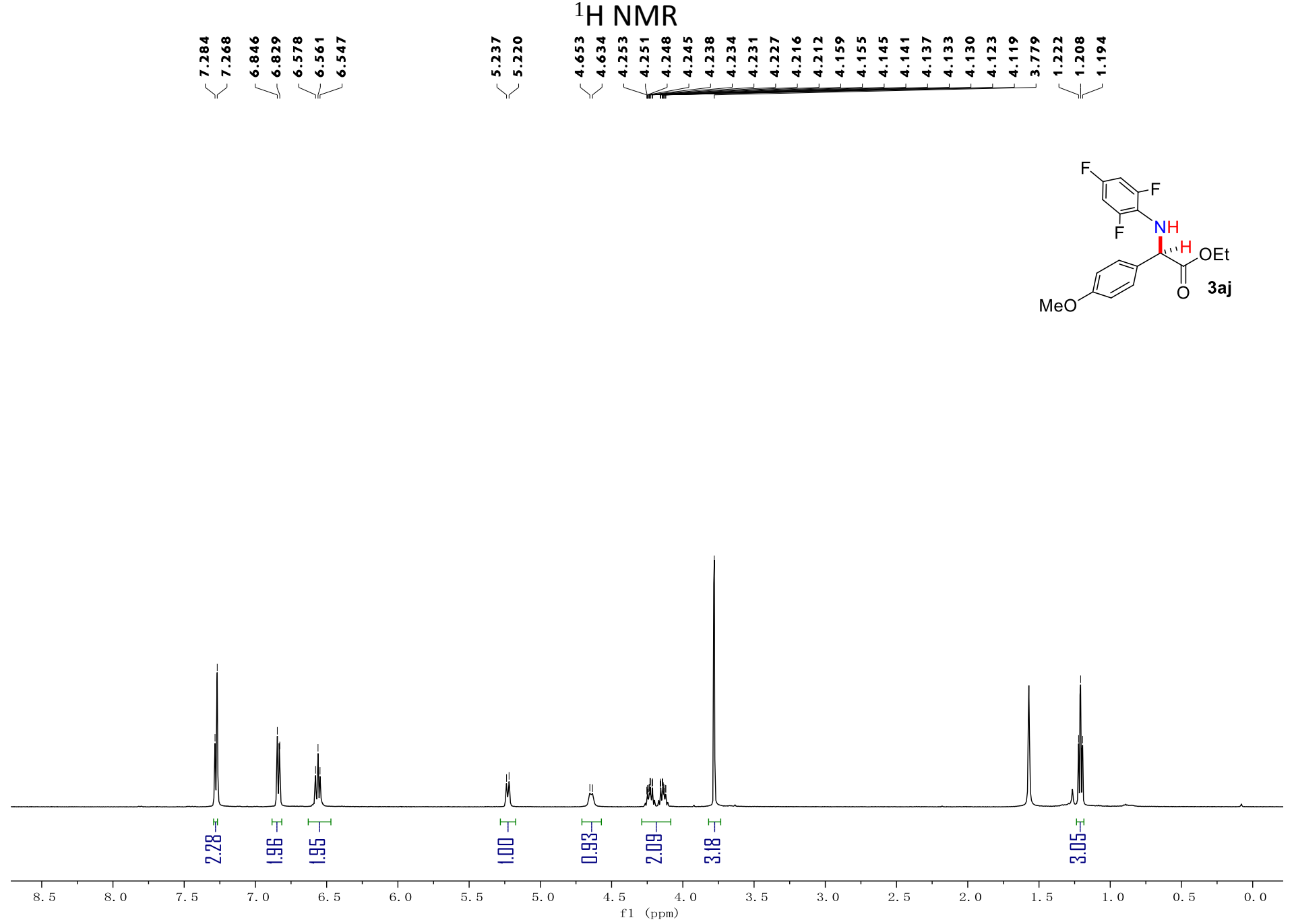



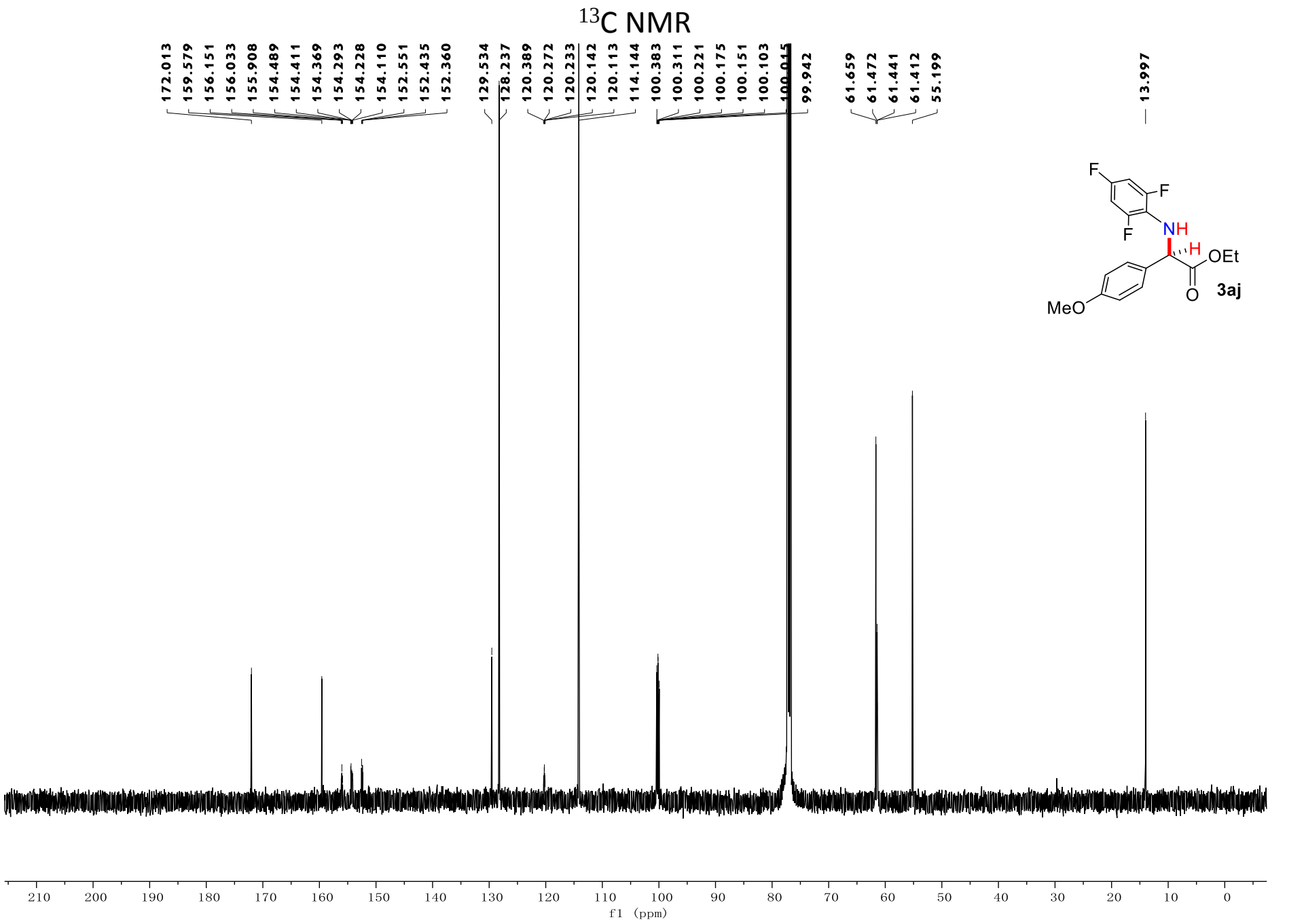

2: 235 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.236 | 95.552 |
| 2 | 8.944 | 4.448 |
| Totals | | 100.000 |

# $^1$H NMR

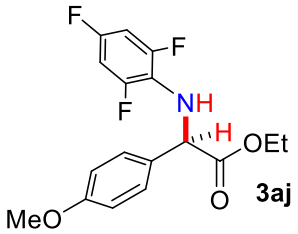

7.284
7.268
6.846
6.829
6.578
6.561
6.547
5.237
5.220
4.653
4.634
4.253
4.251
4.248
4.245
4.238
4.234
4.231
4.227
4.216
4.212
4.159
4.155
4.145
4.141
4.137
4.133
4.130
4.123
4.119
3.779
1.222
1.208
1.194
F
F
F
NH
H
OEt
O
MeO
3aj
2.28
1.96
1.95
1.00
0.93
2.09
3.18
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

# $^{13}$C NMR

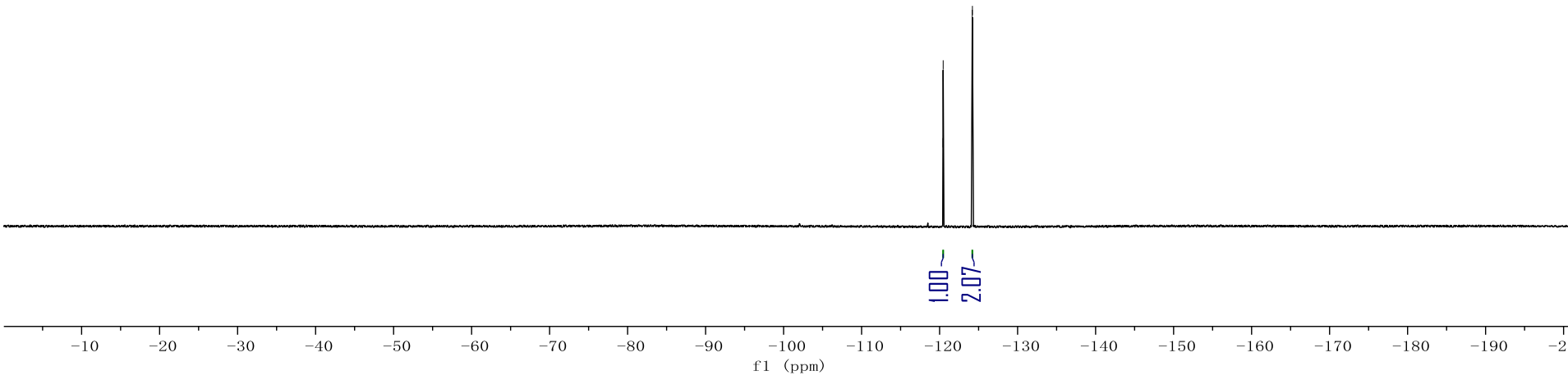

172.013
159.579
156.151
156.033
155.908
154.489
154.411
154.369
154.293
154.228
154.110
152.551
152.435
152.360
129.534
128.237
120.389
120.272
120.233
120.142
120.113
114.144
100.383
100.311
100.221
100.175
100.151
100.103
100.045
99.942
61.659
61.472
61.441
61.412
55.199
13.997
F
F
F
NH
H
OEt
O
MeO
3aj
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

-120.440
-120.459
-120.477
-124.188
-124.206

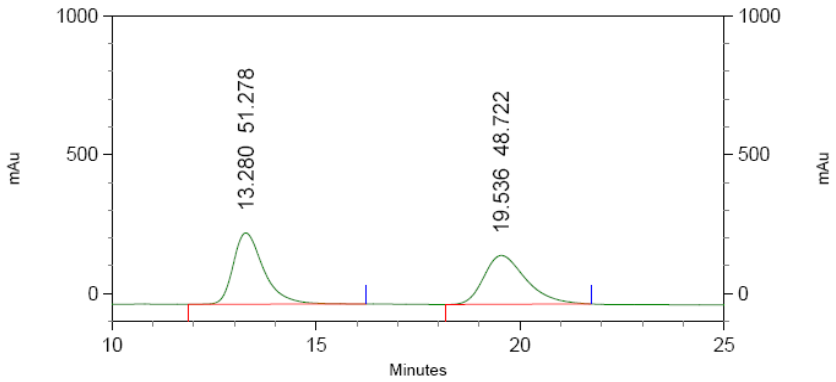


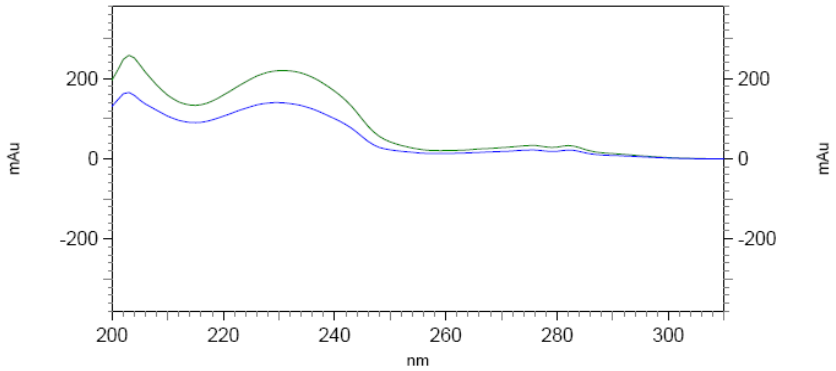

**3aj**

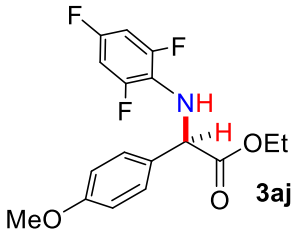


# HPLC

JLM-V-205-1-OJH-1%1ML
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
E:\JLM-V-205-1-OJH-1%1ML



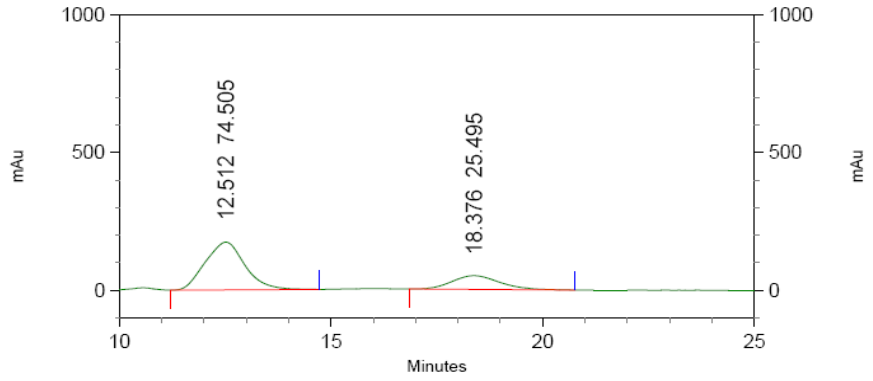

4: 232 nm, 4 nm
Results

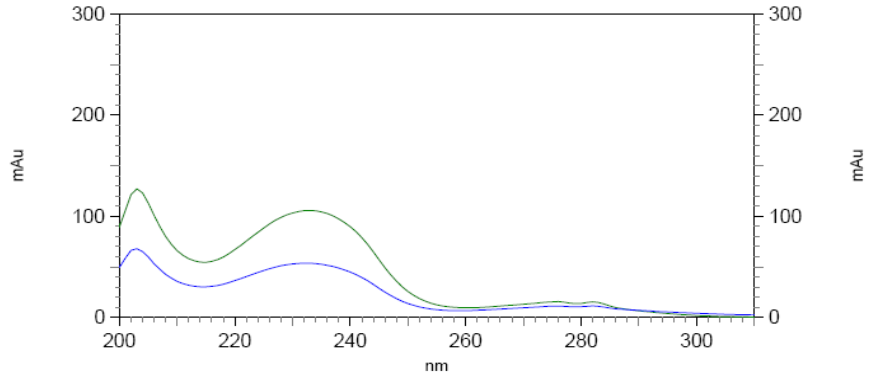
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 13.280 | 51.278 | 1 |
| | 19.536 | 48.722 | 2 |

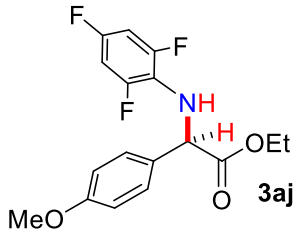
| Totals | | |
|---|---|---|
| | 100.000 | |

# HPLC

JLM-V-205-2-OJH-1%1ML
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
E:\JLM-V-205-2-OJH-1%1ML



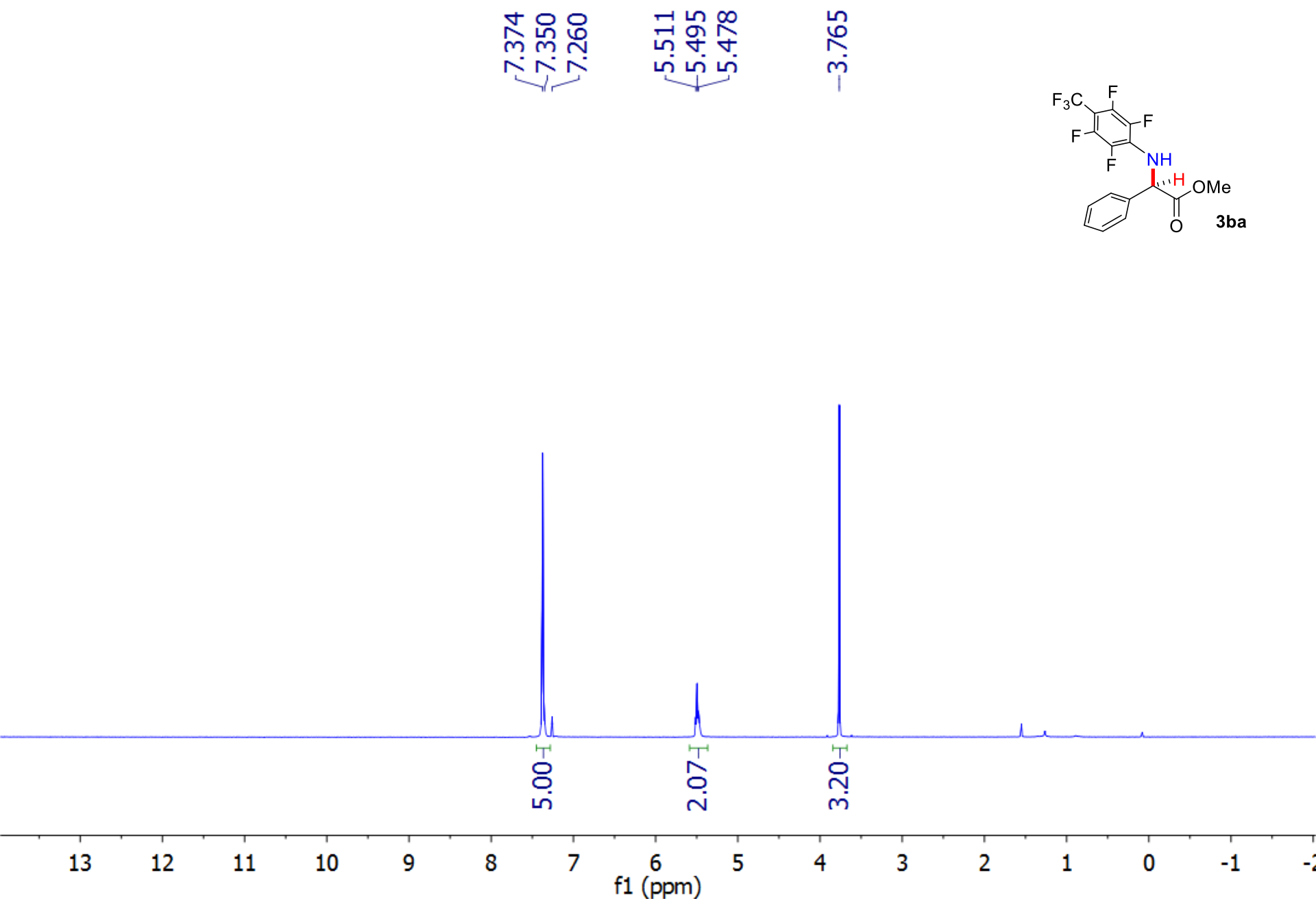




4: 232 nm, 4 nm
Results

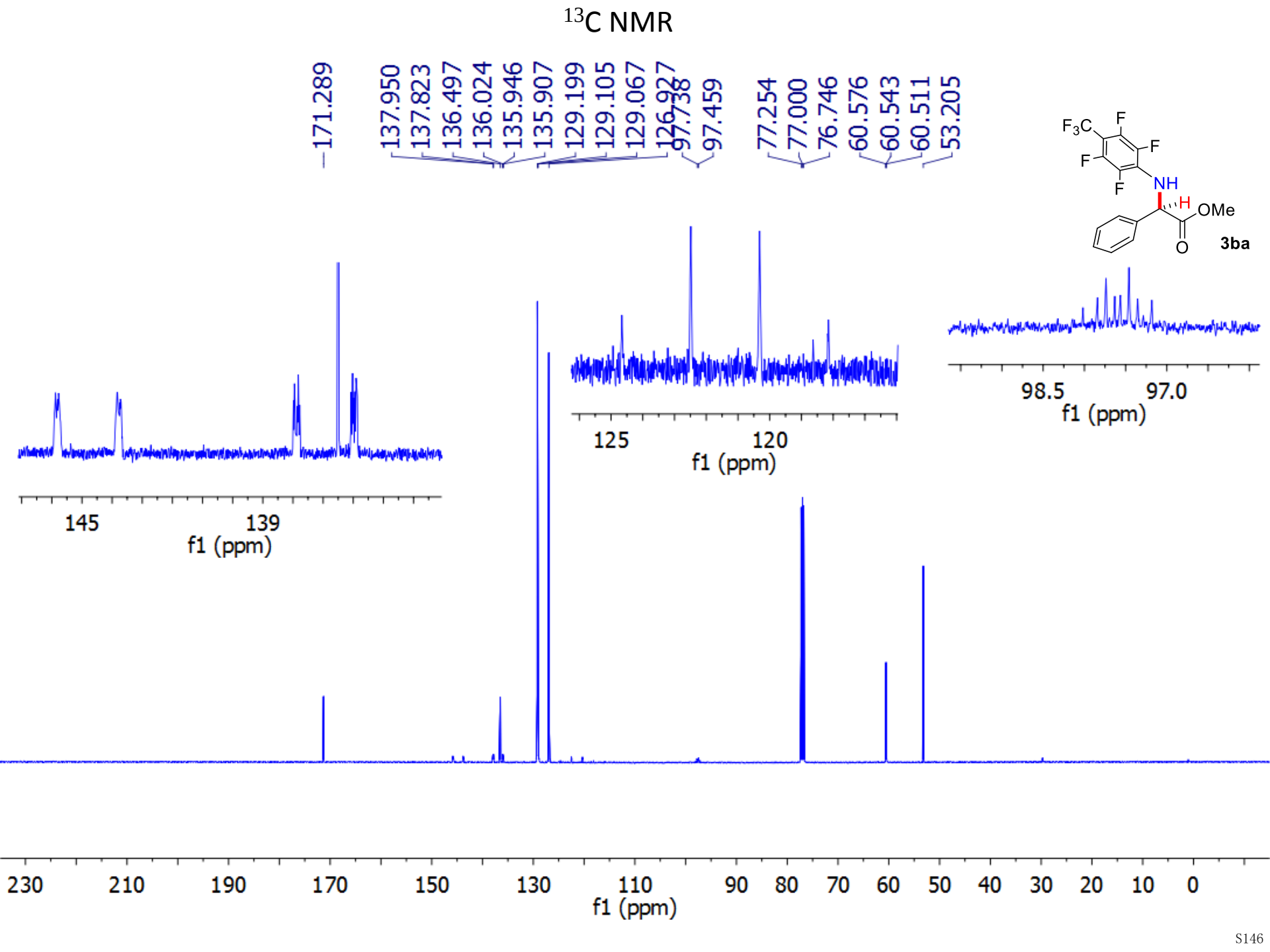
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 12.512 | 74.505 | 1 |
| | 18.376 | 25.495 | 2 |

| Totals | | |
|---|---|---|
| | 100.000 | |

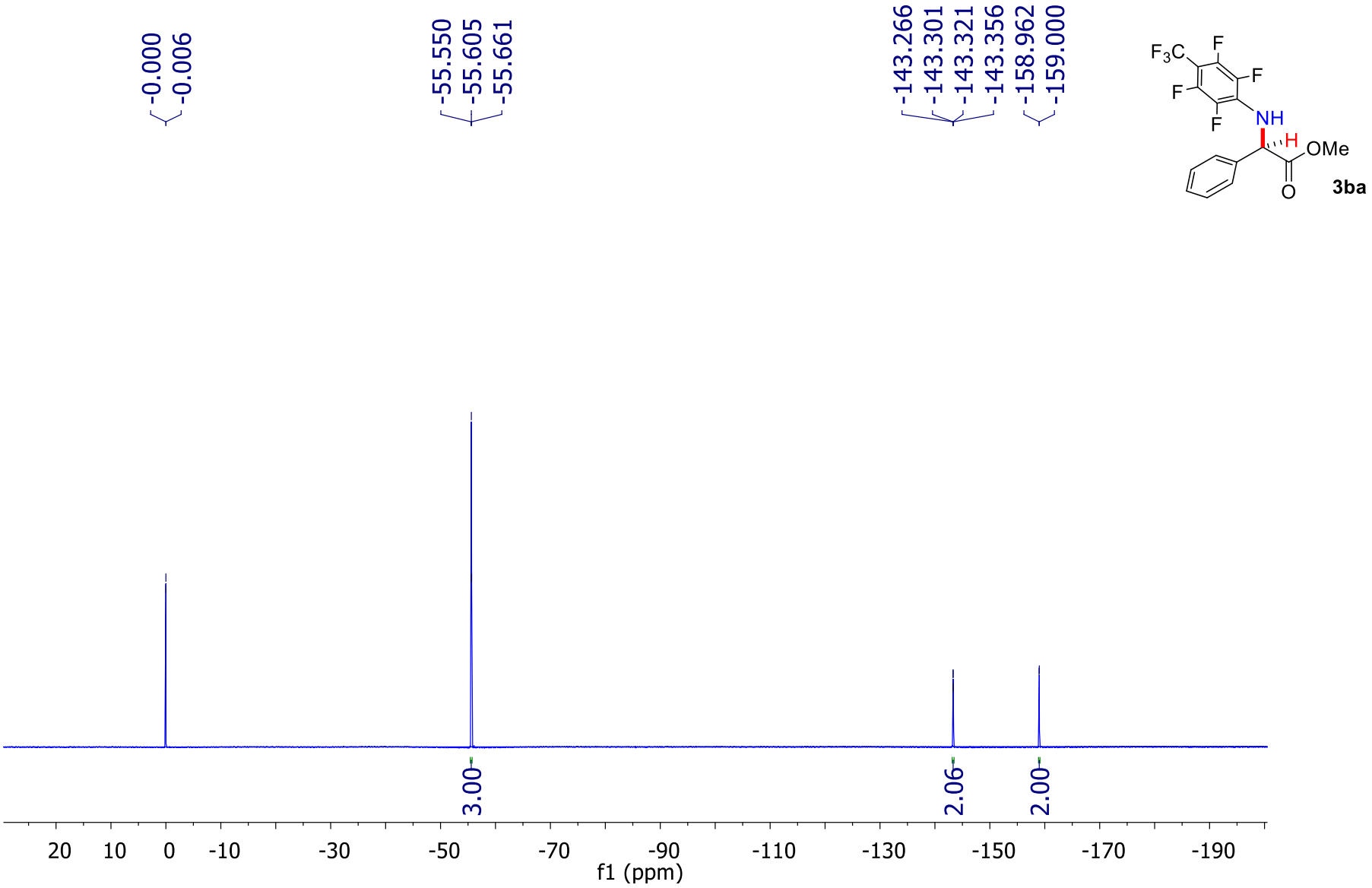
# $^{1}$H NMR


7.374
7.350
7.260
5.511
5.495
5.478
3.765
F3C
F
F
F
F
NH
H
OMe
O
3ba
5.00
2.07
3.20
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

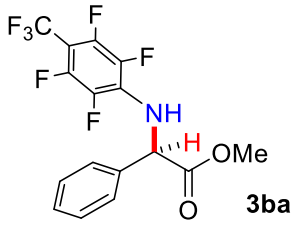
# $^{13}$C NMR


171.289
137.950
137.823
136.497
136.024
135.946
135.907
129.199
129.105
129.067
126.927
97.738
97.459
77.254
77.000
76.746
60.576
60.543
60.511
53.205
F3C
F
F
F
F
NH
H
OMe
O
3ba
145
139
f1 (ppm)
125
120
f1 (ppm)
98.5
97.0
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

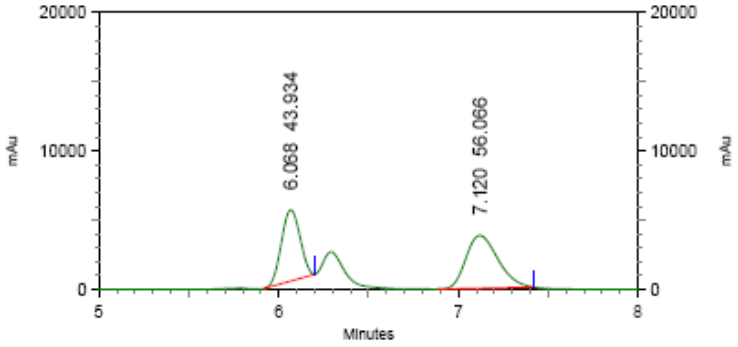

-0.000
-0.006
-55.550
-55.605
-55.661
-143.266
-143.301
-143.321
-143.356
-158.962
-159.000
F3C
F
F
F
NH
H
OMe
O
3ba
3.00
2.06
2.00
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

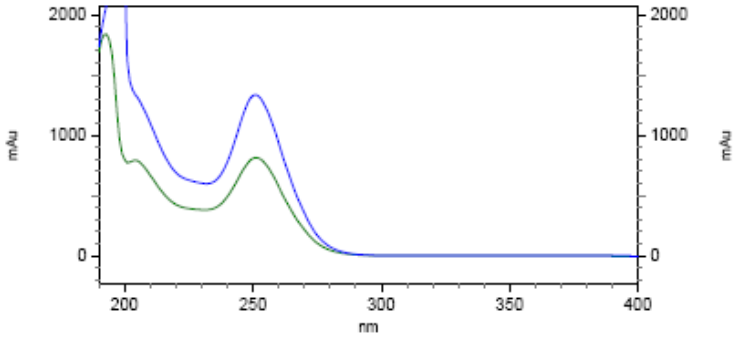
# HPLC



**3ba**

JLM-II-198-1b-ODH1%1ML
C:\EZStart\Projects\Default\Method\JLM-ODH-0.2%-0.7ml.met
C:\EZStart\Projects\Default\Data\JLM-II-198-1b-ODH1%1ML



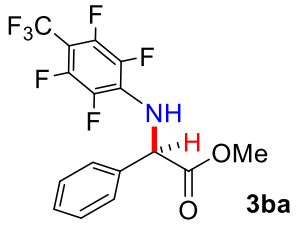




3: 254 nm, 4 nm
Results

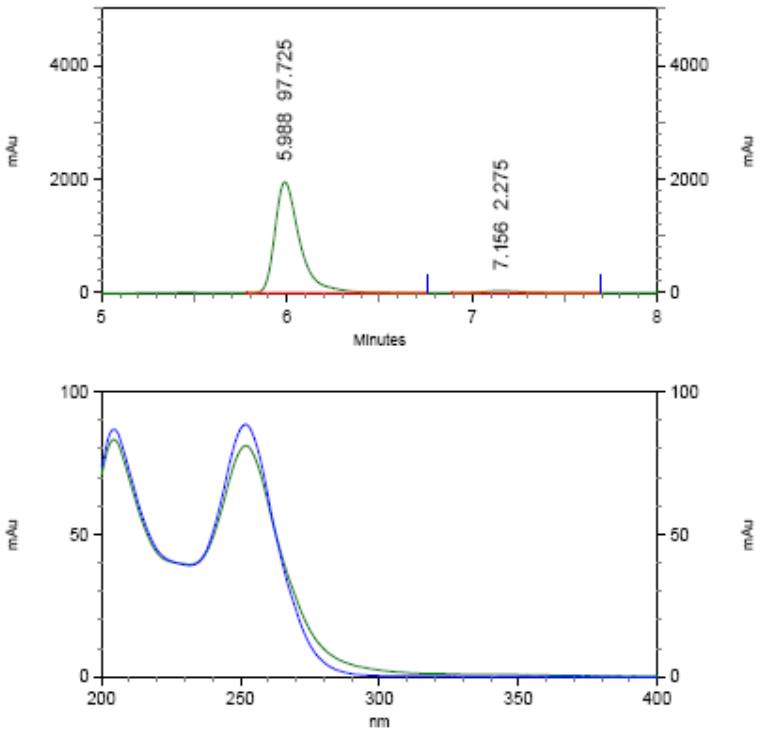
| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 6.068 | 43.934 |
| 2 | | 7.120 | 56.066 |
| Totals | | | 100.000 |

# HPLC

JLM-V-167-1b-ODH1%1ML
C:\EZStart\Projects\Default\Method\JLM-ODH-0.2%-0.7ml.met
C:\EZStart\Projects\Default\Data\JLM-V-167-1b-ODH1%1ML



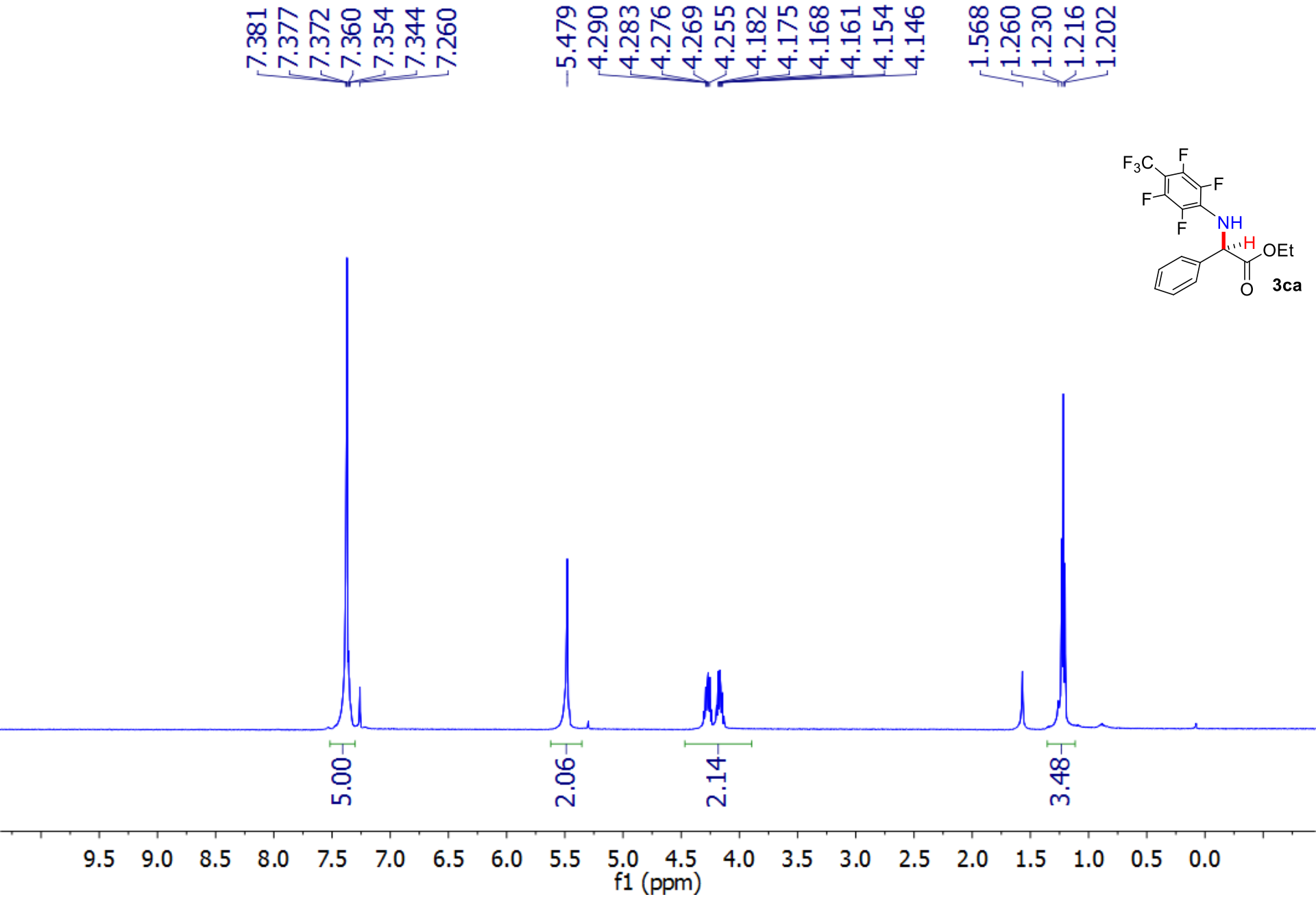

**3ba**



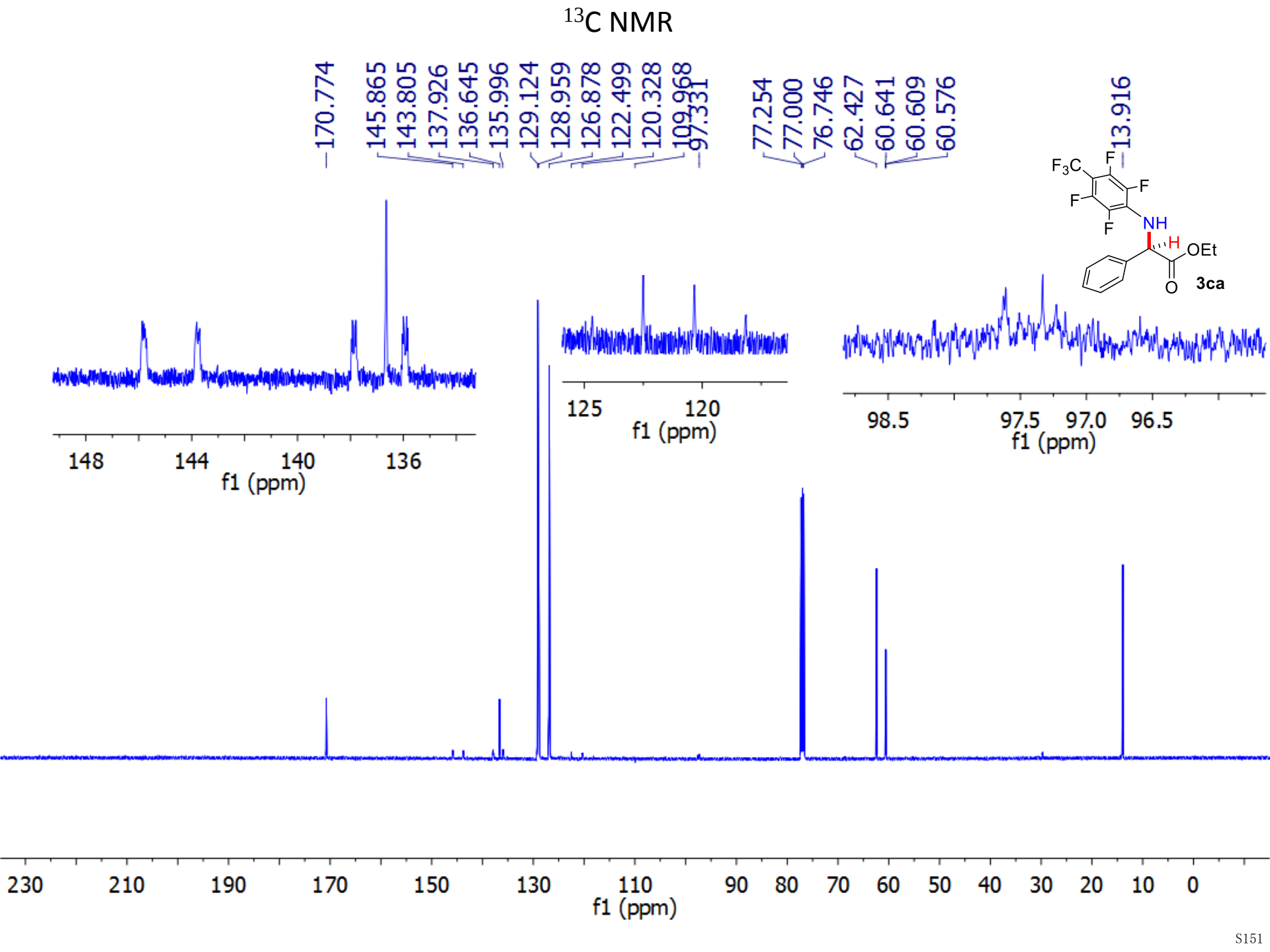

3: 275 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 1.800 | 0.000 |
| 2 | | 5.988 | 97.725 |
| 3 | | 7.156 | 2.275 |
| Totals | | | 100.000 |

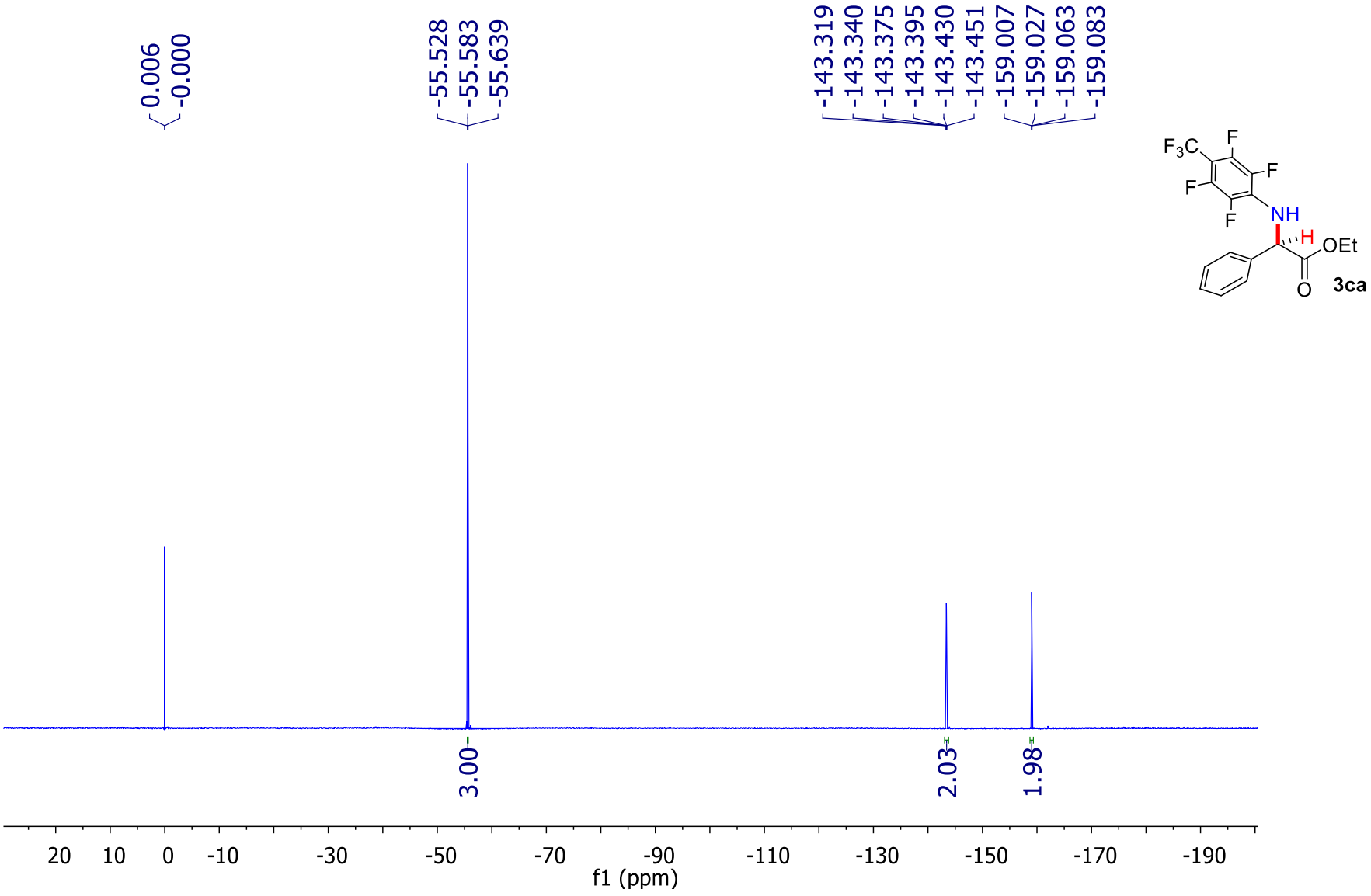
# $^1$H NMR


7.381
7.377
7.372
7.360
7.354
7.344
7.260
5.479
4.290
4.283
4.276
4.269
4.255
4.182
4.175
4.168
4.161
4.154
4.146
1.568
1.260
1.230
1.216
1.202
F3C
F
F
F
F
NH
H
OEt
O
3ca
5.00
2.06
2.14
3.48
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

# $^{13}$C NMR

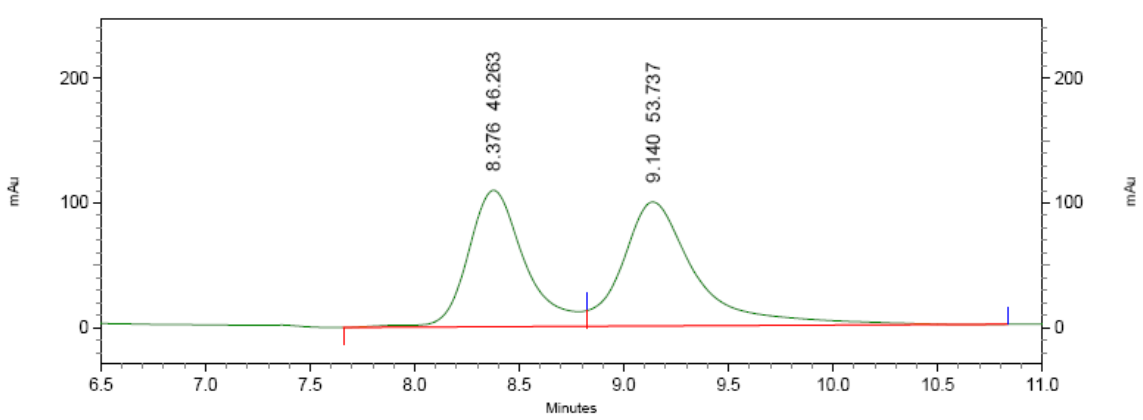

170.774
145.865
143.805
137.926
136.645
135.996
129.124
128.959
126.878
122.499
120.328
109.968
97.331
77.254
77.000
76.746
62.427
60.641
60.609
60.576
13.916
F3C
F
F
F
F
NH
H
OEt
O
3ca
148
144
140
136
f1 (ppm)
125
120
f1 (ppm)
98.5
97.5
97.0
96.5
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

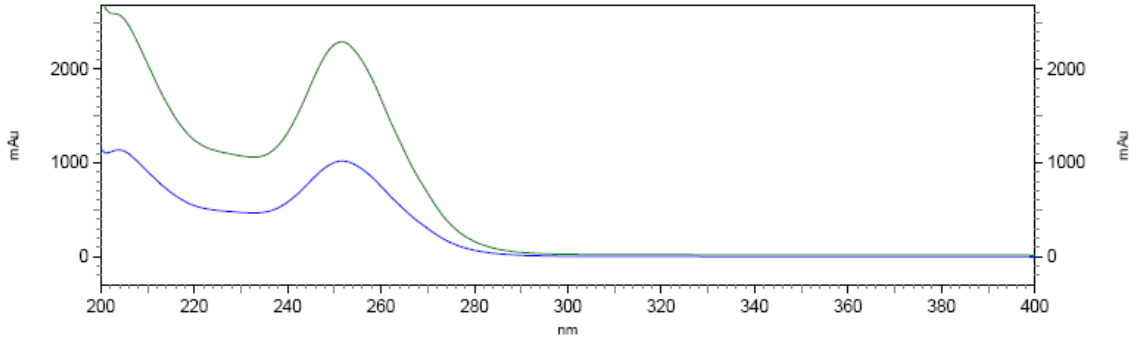
# $^{19}$F NMR

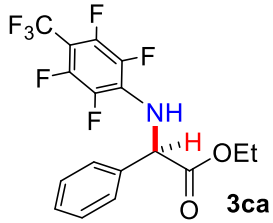

0.006
-0.000
-55.528
-55.583
-55.639
-143.319
-143.340
-143.375
-143.395
-143.430
-143.451
-159.007
-159.027
-159.063
-159.083
F3C
F
F
F
F
NH
H
OEt
O
3ca
3.00
2.03
1.98
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-V-193-1-ODH-3%0.5ML
C:\EZStart\Projects\Default\Data\JLM-V-193-1-ODH-3%0.5ml
C:\EZStart\Projects\Default\Method\CQL-AD-H10%1.0ml60min.met
AD-H column 20%IPA @ 0.8ml/min



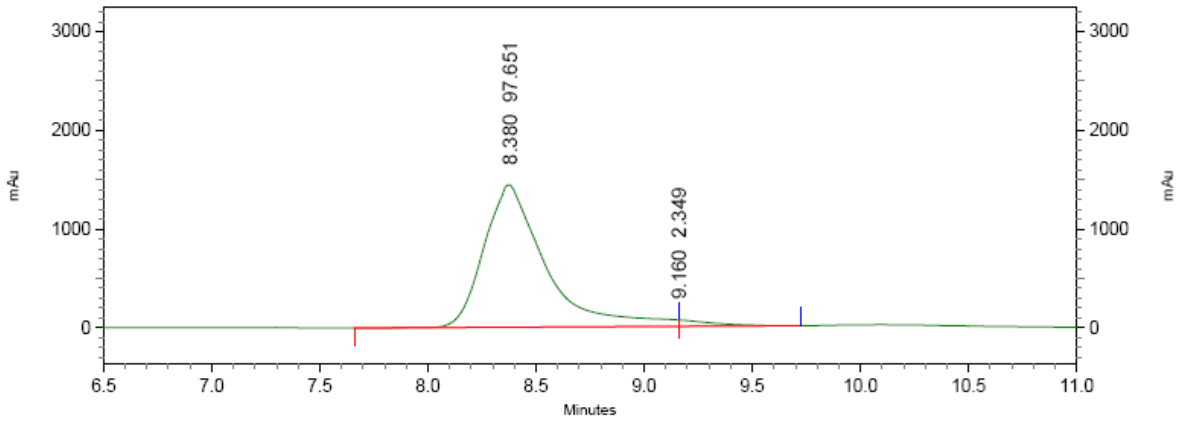



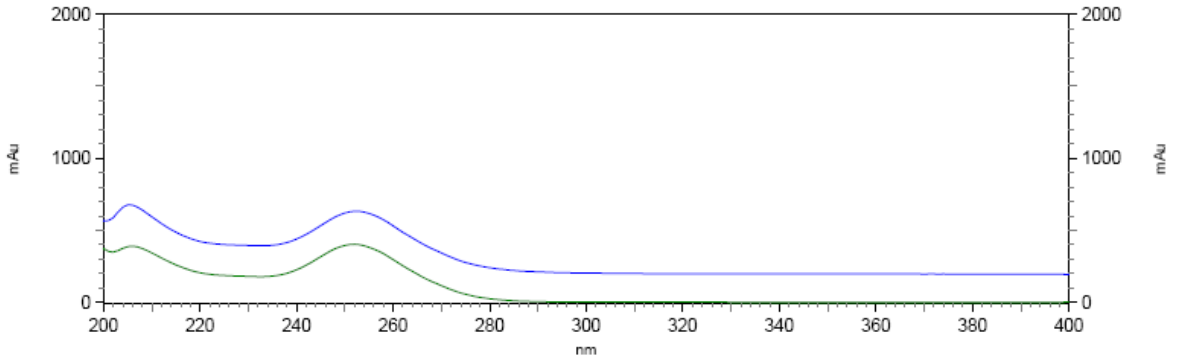

3: 273 nm, 4 nm Results

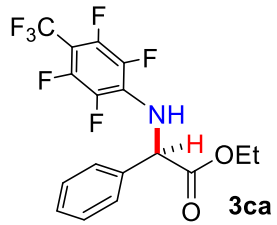
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 8.376 | 46.263 |
| 2 | 9.140 | 53.737 |
| Totals | | 100.000 |

# HPLC

JLM-V-193-2-ODH-3%0.5ML
C:\EZStart\Projects\Default\Data\JLM-V-193-2-ODH-3%0.5ml
C:\EZStart\Projects\Default\Method\CQL-AD-H10%1.0ml60min.met
AD-H column 20%IPA @ 0.8ml/min



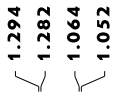

3: 255 nm, 4 nm Results

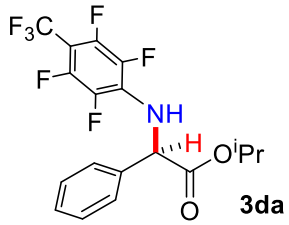
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 8.380 | 97.651 |
| 2 | 9.160 | 2.349 |
| Totals | | 100.000 |

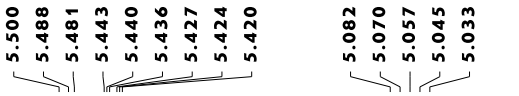
# $^1$H NMR

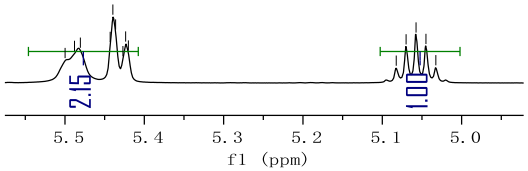

7.370
7.368
7.361

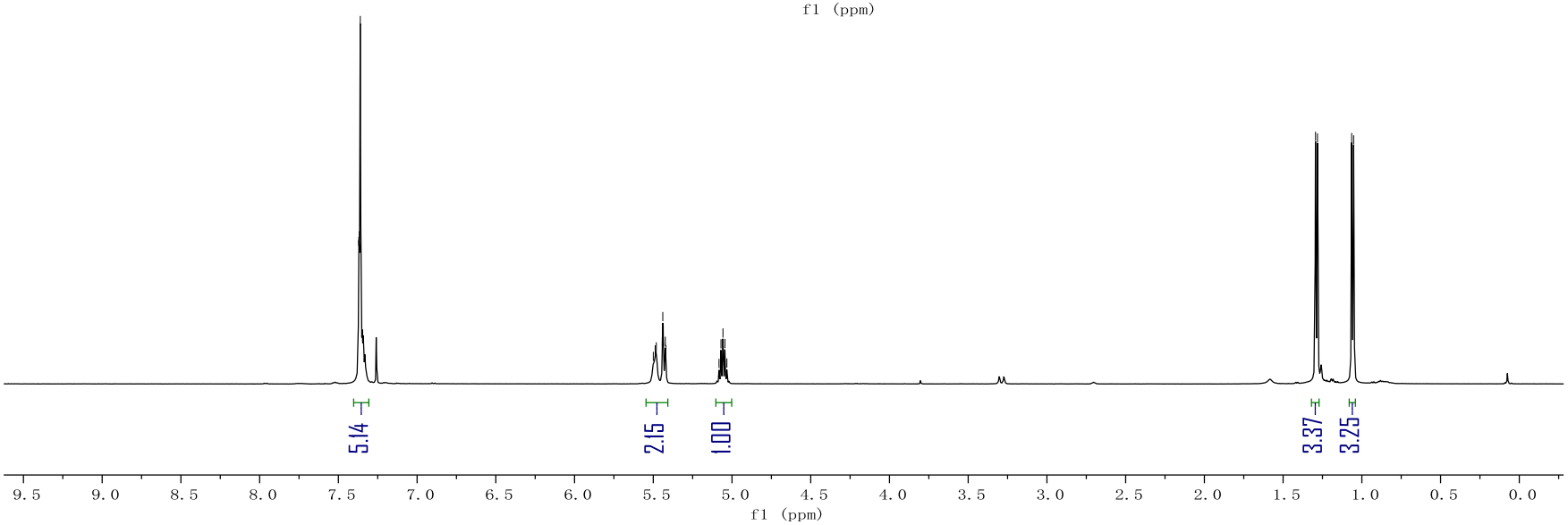

5.500
5.488
5.481
5.443
5.440
5.436
5.427
5.424
5.420
5.082
5.070
5.057
5.045
5.033


1.294
1.282
1.064
1.052

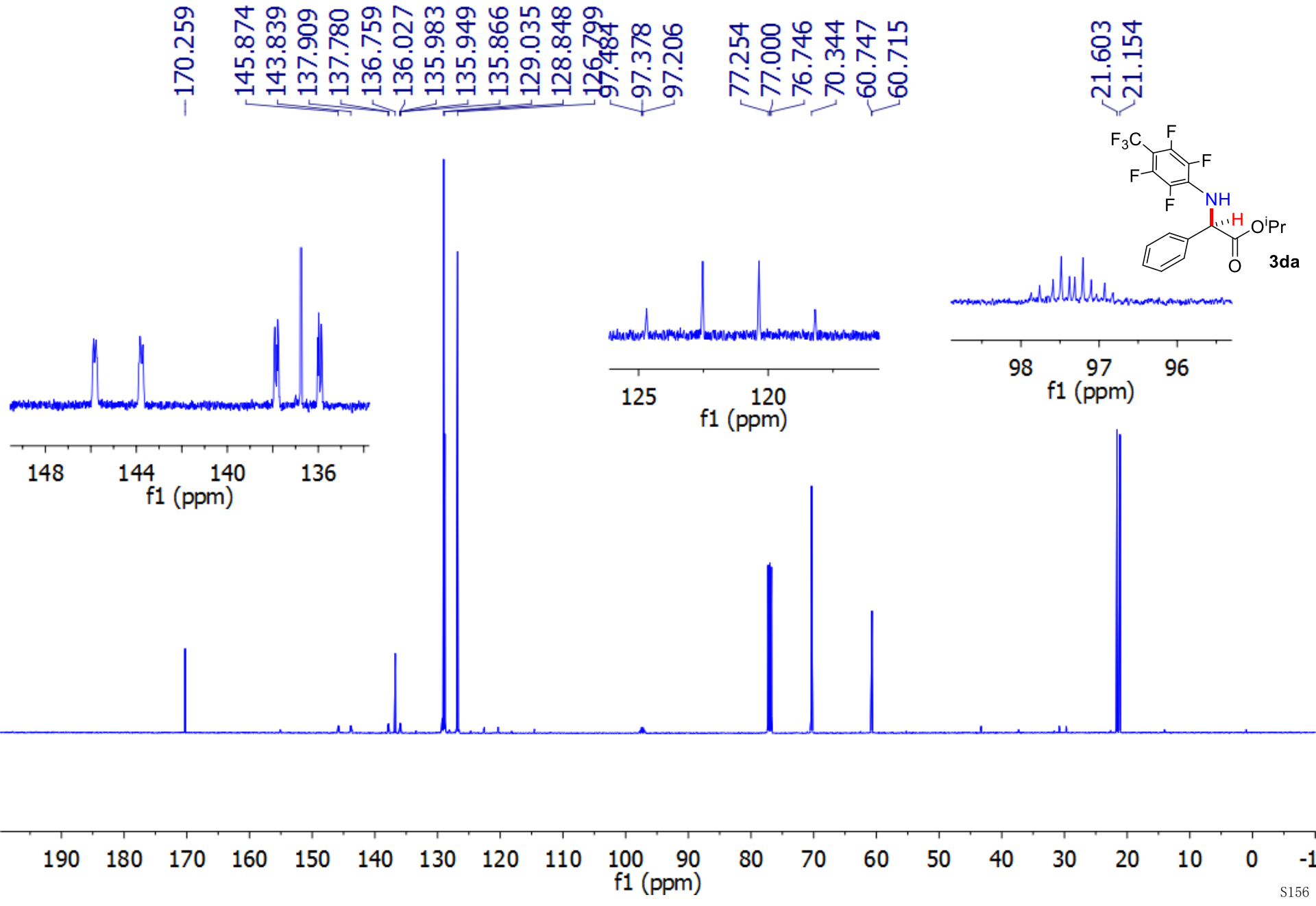

F3C
F
F
F
NH
H
OiPr
O
3da


5.500
5.488
5.481
5.443
5.440
5.436
5.427
5.424
5.420
5.082
5.070
5.057
5.045
5.033

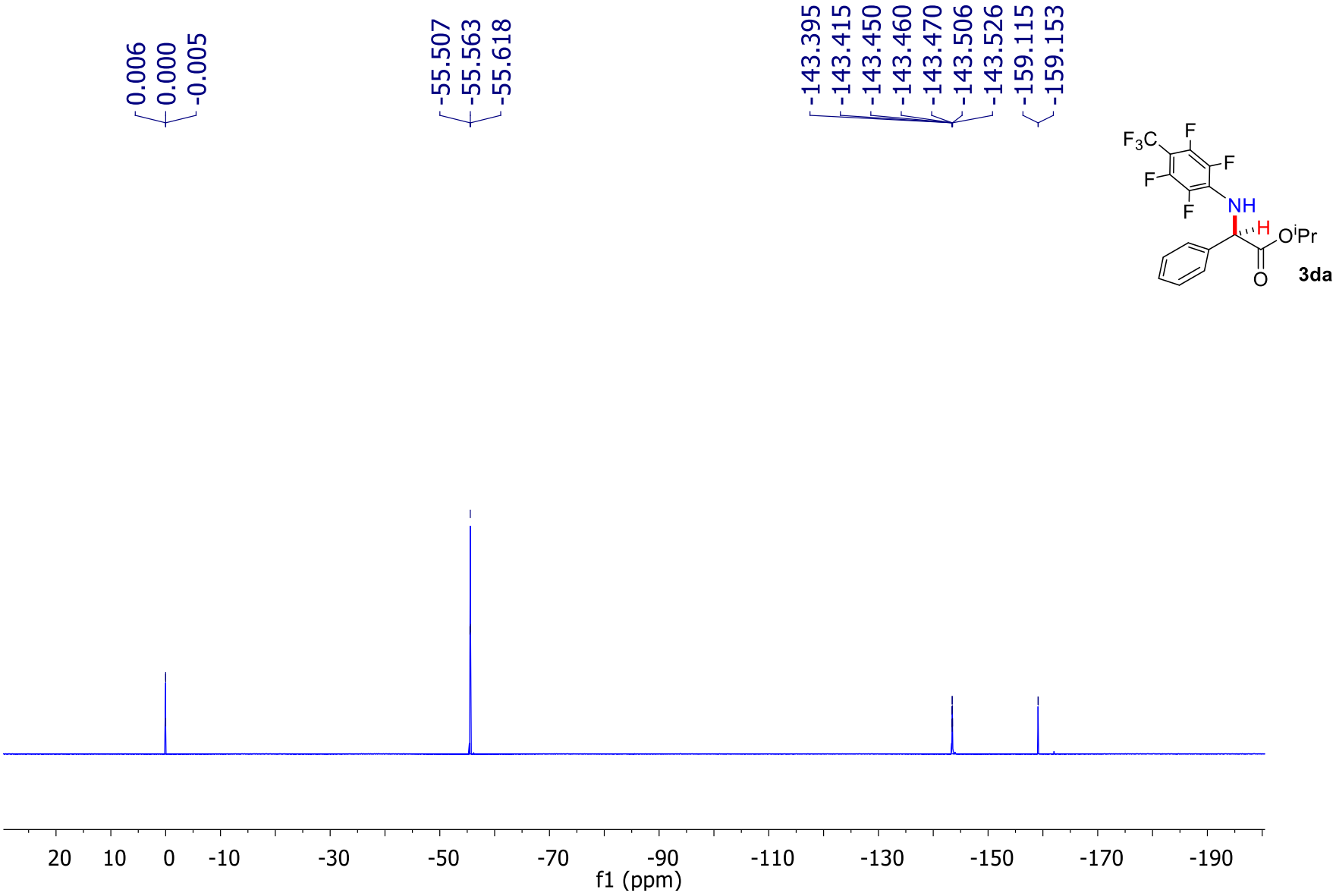

2.15
1.00
5.5
5.4
5.3
5.2
5.1
5.0
f1 (ppm)


5.14
2.15
1.00
3.37
3.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

# $^{13}$C NMR

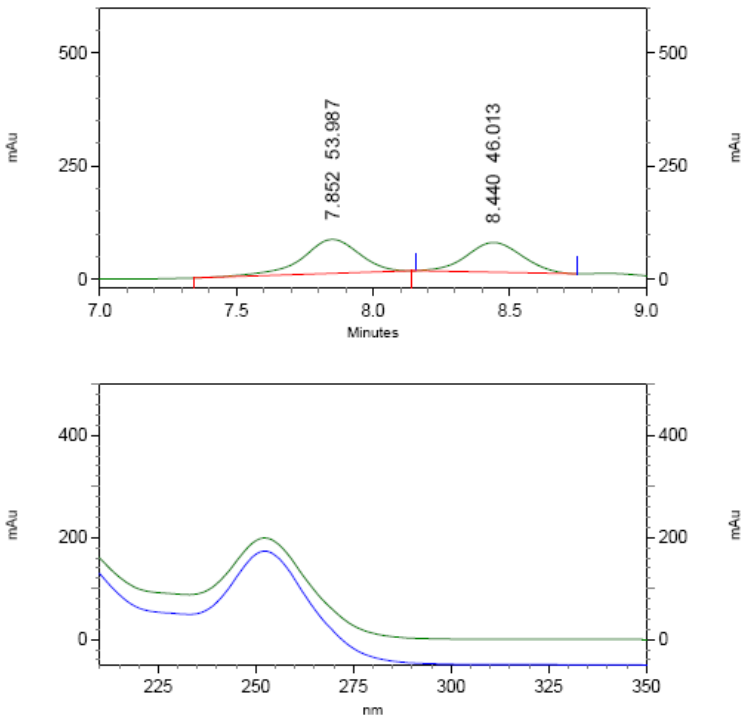

170.259
145.874
143.839
137.909
137.780
136.759
136.027
135.983
135.949
135.866
129.035
128.848
126.799
97.484
97.378
97.206
77.254
77.000
76.746
70.344
60.747
60.715
21.603
21.154
F3C
F
F
F
F
NH
H
OiPr
O
3da
148
144
140
136
f1 (ppm)
125
120
f1 (ppm)
98
97
96
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

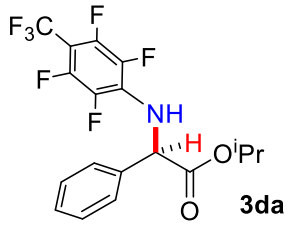
# $^{19}$F NMR


0.006
0.000
-0.005
-55.507
-55.563
-55.618
-143.395
-143.415
-143.450
-143.460
-143.470
-143.506
-143.526
-159.115
-159.153
F3C
F
F
F
F
NH
H
OiPr
O
3da
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-V-168-1A-whelk-0%1ML
C:\EZStart\Projects\Default\Method\JLM-ODH-0%-0.7ml.met
C:\EZStart\Projects\Default\Data\JLM-V-168-1A-whelk-0%1ML



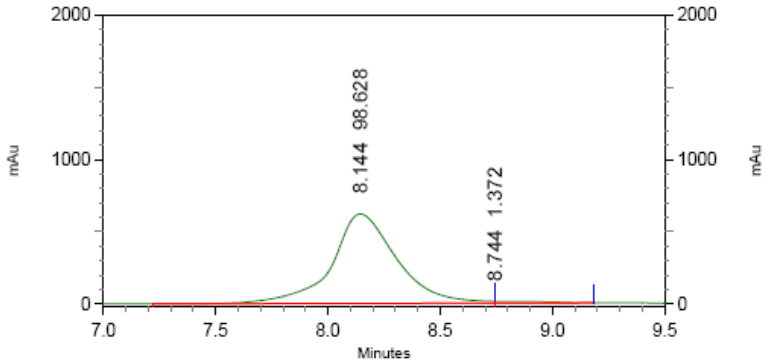

3da

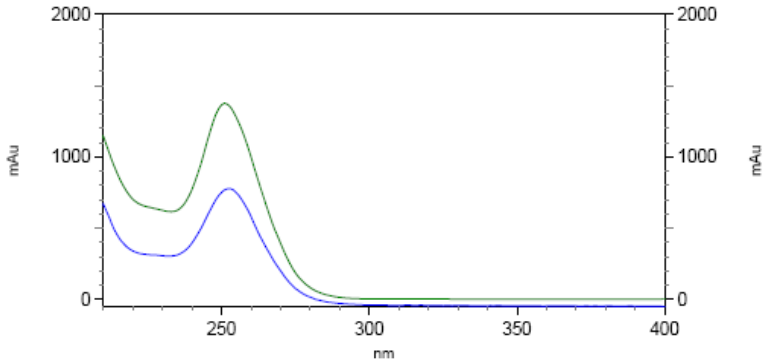
3: 259 nm, 4 nm
Results

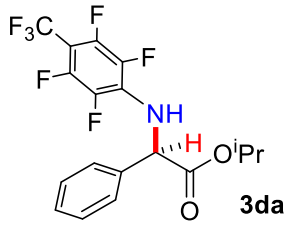
| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 7.852 | 53.987 |
| 2 | | 8.440 | 46.013 |
| Totals | | | 100.000 |

# HPLC

JLM-V-173-whelk-0%1ML
C:\EZStart\Projects\Default\Method\JLM-ODH-0%-0.7ml.met
C:\EZStart\Projects\Default\Data\JLM-V-173-whelk-0%1ML



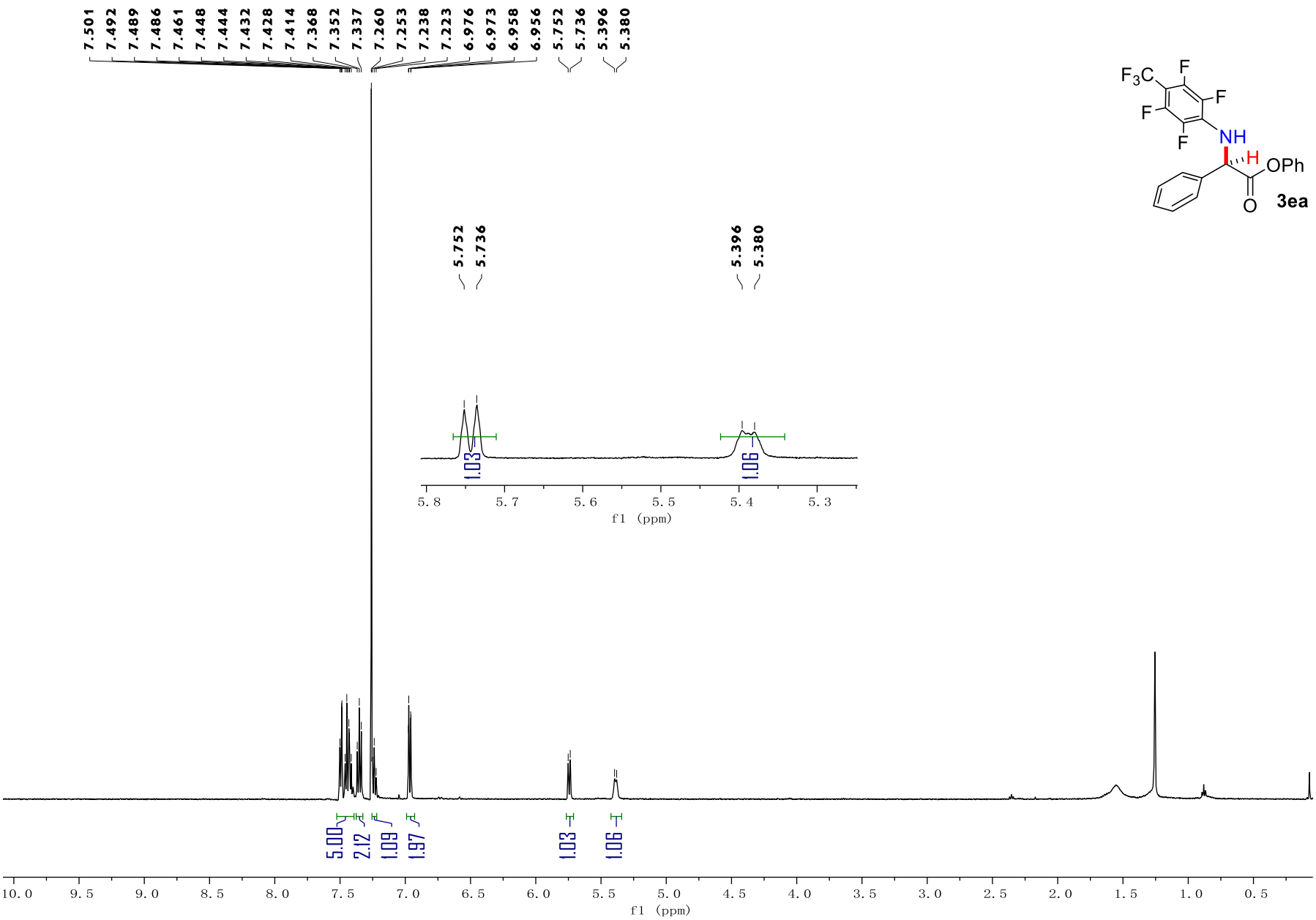




**3da**

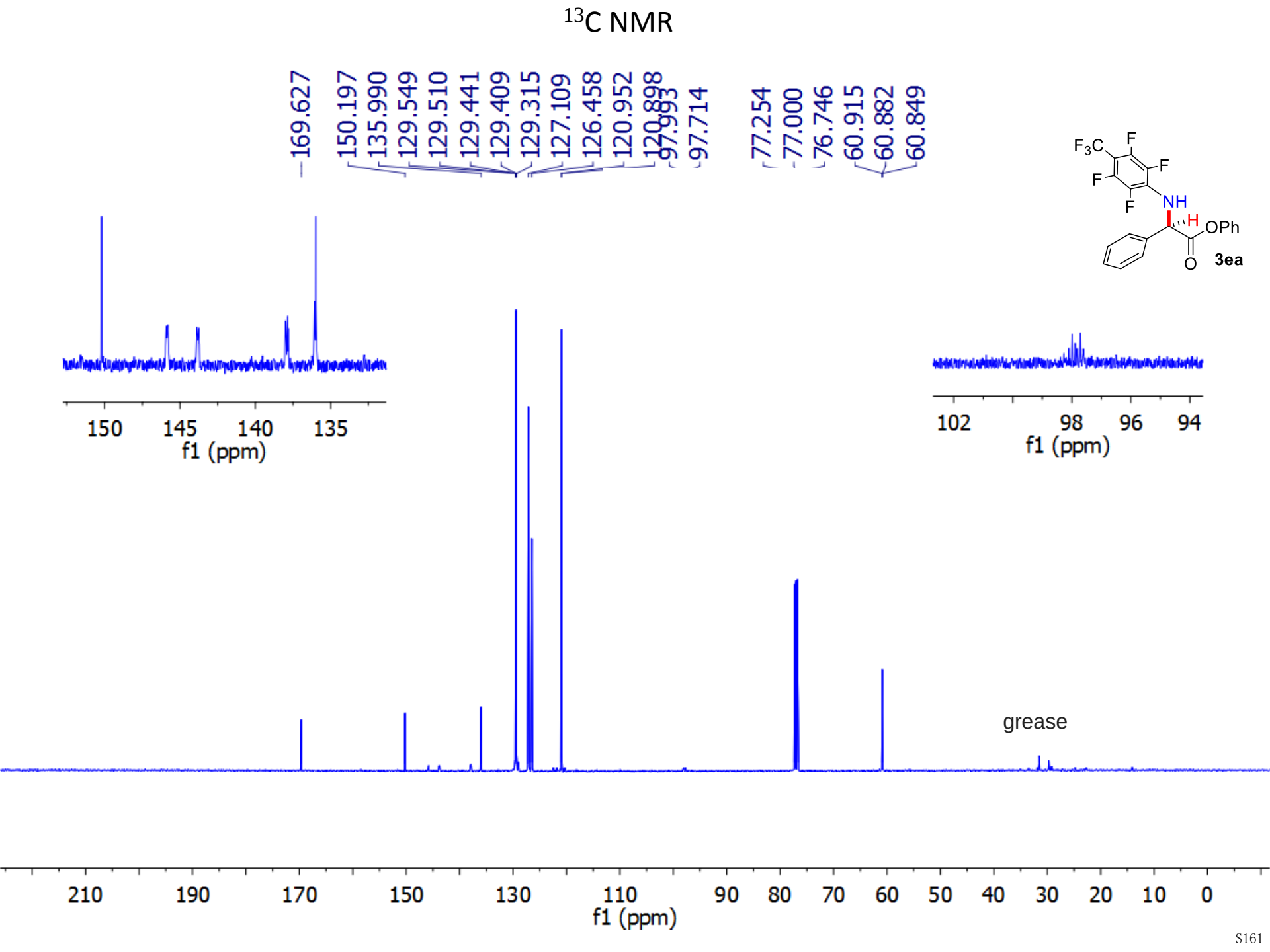
3: 258 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 8.144 | 98.628 |
| 2 | | 8.744 | 1.372 |
| Totals | | | 100.000 |

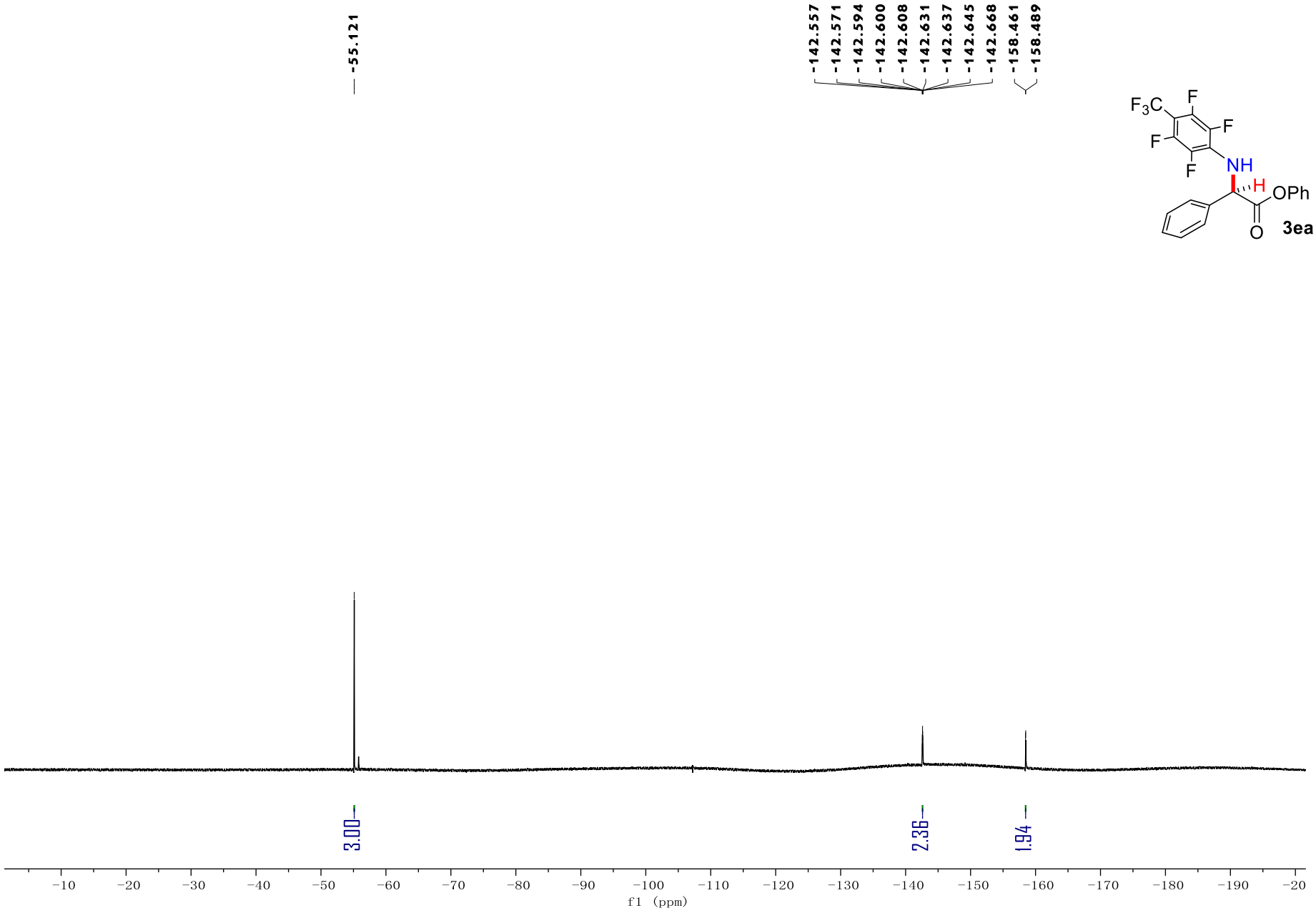
# $^{1}$H NMR


7.501
7.492
7.489
7.486
7.461
7.448
7.444
7.432
7.428
7.414
7.368
7.352
7.337
7.260
7.253
7.238
7.223
6.976
6.973
6.958
6.956
5.752
5.736
5.396
5.380
1.03
1.06
f1 (ppm)
5.00
2.12
1.09
1.97
1.03
1.06
f1 (ppm)
F3C
F
F
F
F
NH
H
OPh
O
3ea

# $^{13}$C NMR

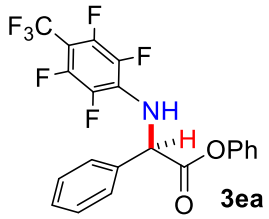

169.627
150.197
135.990
129.549
129.510
129.441
129.409
129.315
127.109
126.458
120.952
120.898
97.993
97.714
77.254
77.000
76.746
60.915
60.882
60.849
F3C
F
F
F
F
NH
H
OPh
O
3ea
150
145
140
135
f1 (ppm)
102
98
96
94
f1 (ppm)
grease
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

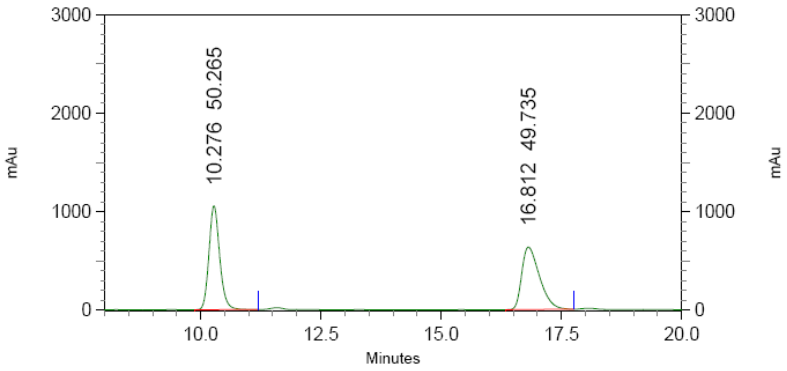
# $^{19}$F NMR

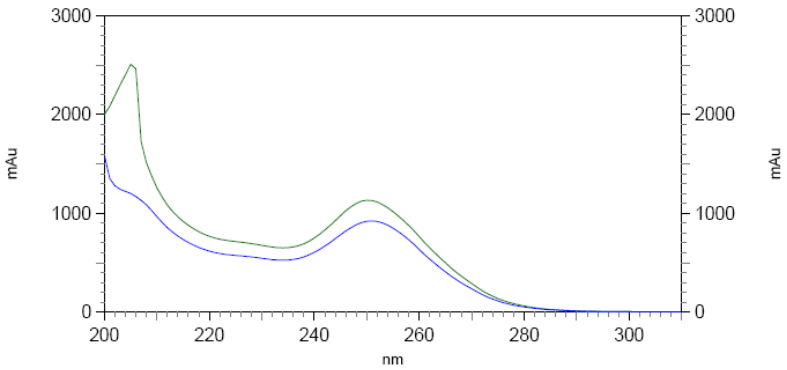

-55.121
-142.557
-142.571
-142.594
-142.600
-142.608
-142.631
-142.637
-142.645
-142.668
-158.461
-158.489
F3C
F
F
F
NH
H
OPh
O
3ea
3.00
2.36
1.94
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

# HPLC

JLM-II-243-1-ADH-1%0.7ML
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
C:\EZStart\Projects\Default\Data\JLM-II-243-1-ADH-1%0.7ML



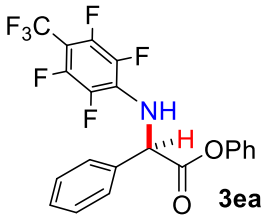

4: 241 nm, 4 nm
Results

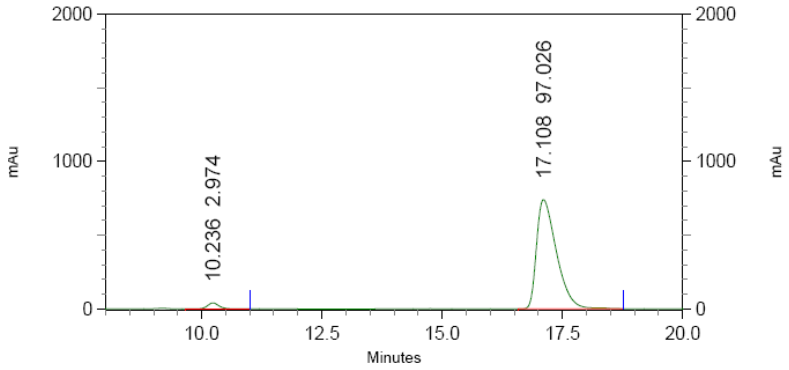
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 10.276 | 50.265 | 1 |
| | 16.812 | 49.735 | 2 |

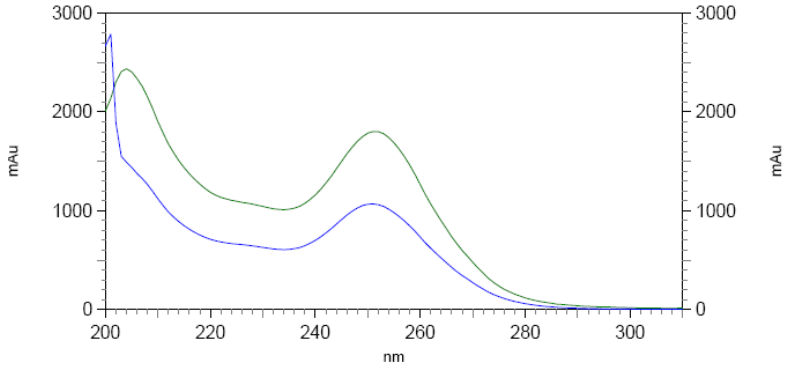
| Totals | | |
|---|---|---|
| | 100.000 | |

# HPLC

JLM-V-199-1A-ADH-1%0.7ML
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
C:\EZStart\Projects\Default\Data\JLM-V-199-1A-ADH-1%0.7ML



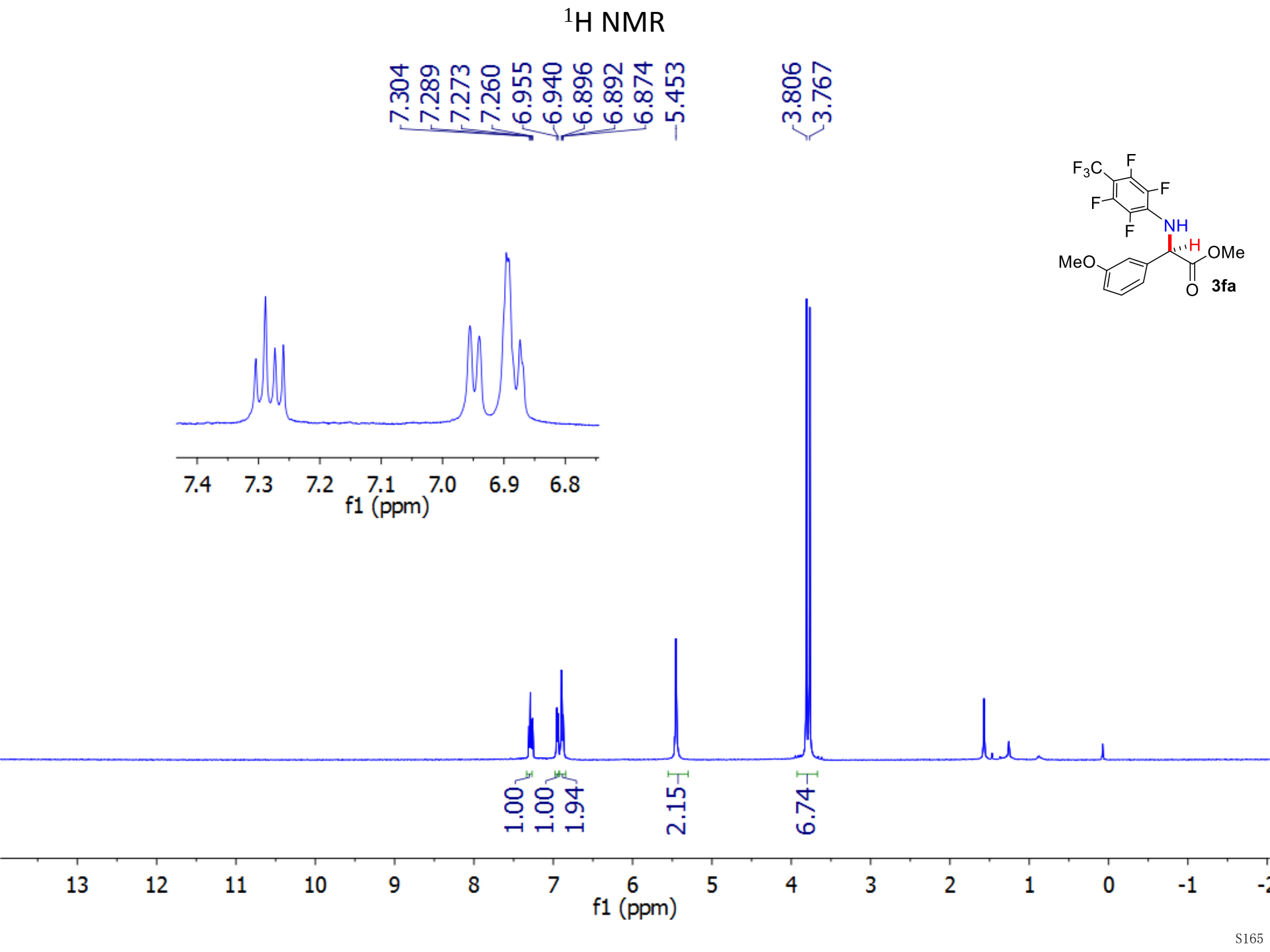




4: 241 nm, 4 nm
Results

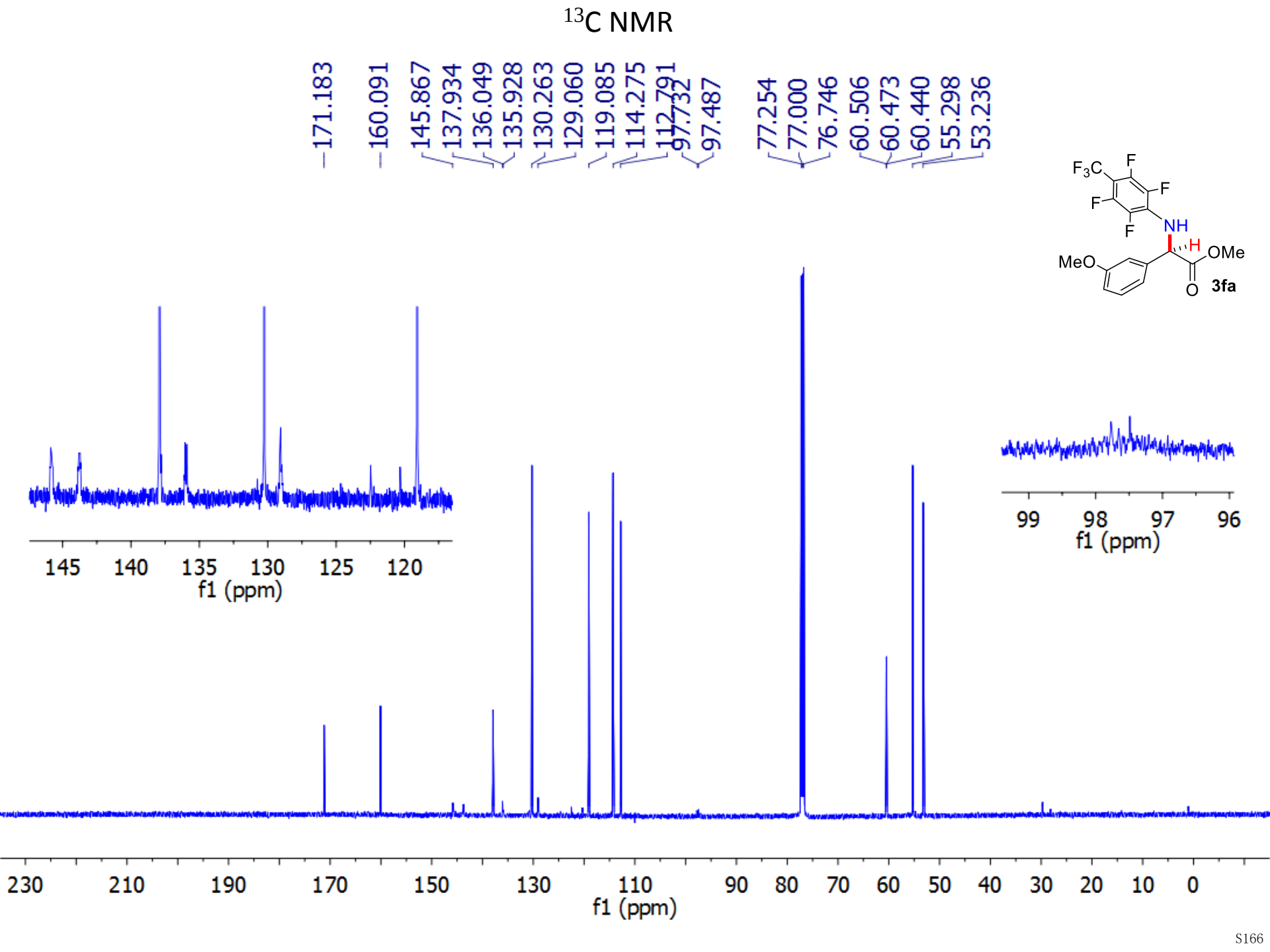
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 10.236 | 2.974 | 1 |
| | 17.108 | 97.026 | 2 |

| Totals | | |
|---|---|---|
| | 100.000 | |

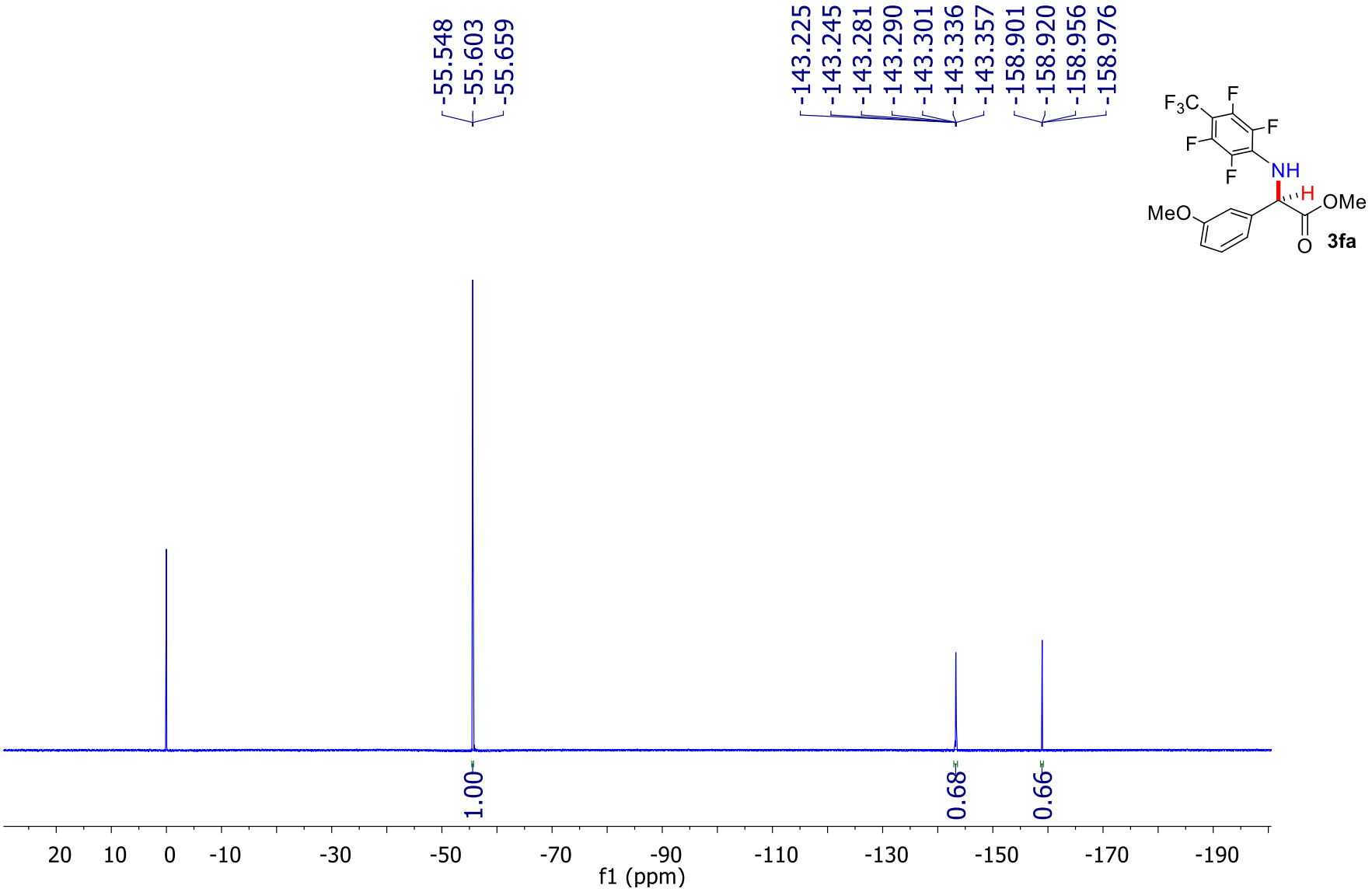
# $^{1}$H NMR


7.304
7.289
7.273
7.260
6.955
6.940
6.896
6.892
6.874
5.453
3.806
3.767
F3C
F
F
F
F
NH
H
OMe
MeO
O
3fa
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
1.00
1.00
1.94
2.15
6.74
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

# $^{13}$C NMR

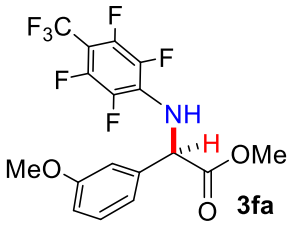

171.183
160.091
145.867
137.934
136.049
135.928
130.263
129.060
119.085
114.275
112.791
97.732
97.487
77.254
77.000
76.746
60.506
60.473
60.440
55.298
53.236
F3C
F
F
F
F
NH
H
OMe
MeO
O
3fa
145 140 135 130 125 120
f1 (ppm)
99 98 97 96
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

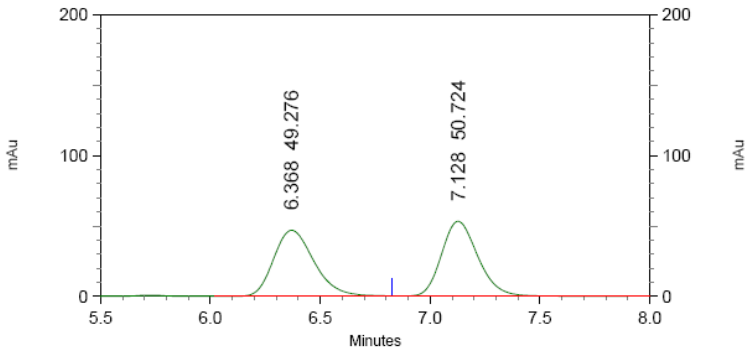
# $^{19}$F NMR

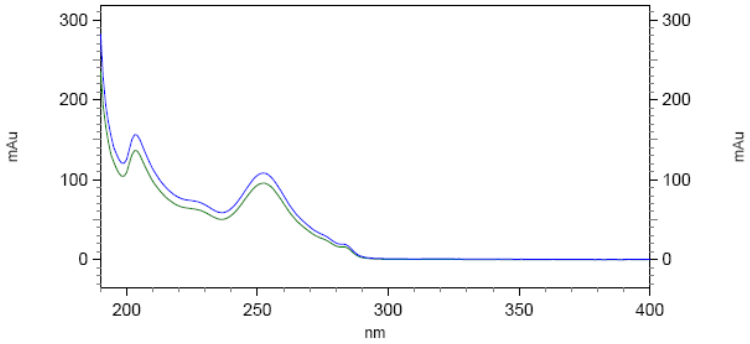

-55.548
-55.603
-55.659
-143.225
-143.245
-143.281
-143.290
-143.301
-143.336
-143.357
-158.901
-158.920
-158.956
-158.976
F3C
F
F
F
F
NH
H
OMe
MeO
O
3fa
1.00
0.68
0.66
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-V-209-1-ADH-1%1ML
C:\EZStart\Projects\Default\Method\shifatest_2,5-dimehoxy.met
C:\EZStart\Projects\Default\Data\JLM-V-209-1-ADH1%1ML



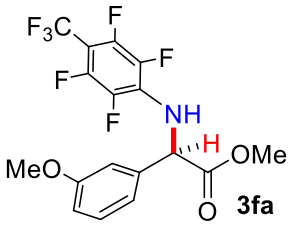



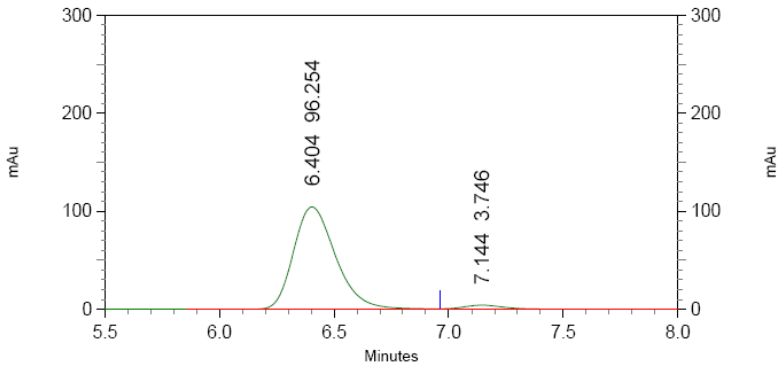

7: 251 nm, 4 nm
Results

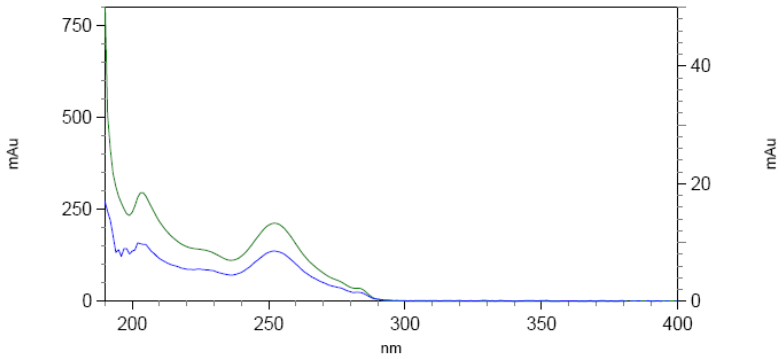
| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 6.368 | 49.276 |
| 2 | | 7.128 | 50.724 |
| Totals | | | 100.000 |

# HPLC

JLM-V-209-2-ADH-1%1ML
C:\EZStart\Projects\Default\Method\shifatest_2,5-dimehoxy.met
C:\EZStart\Projects\Default\Data\JLM-V-209-2-ADH1%1ML



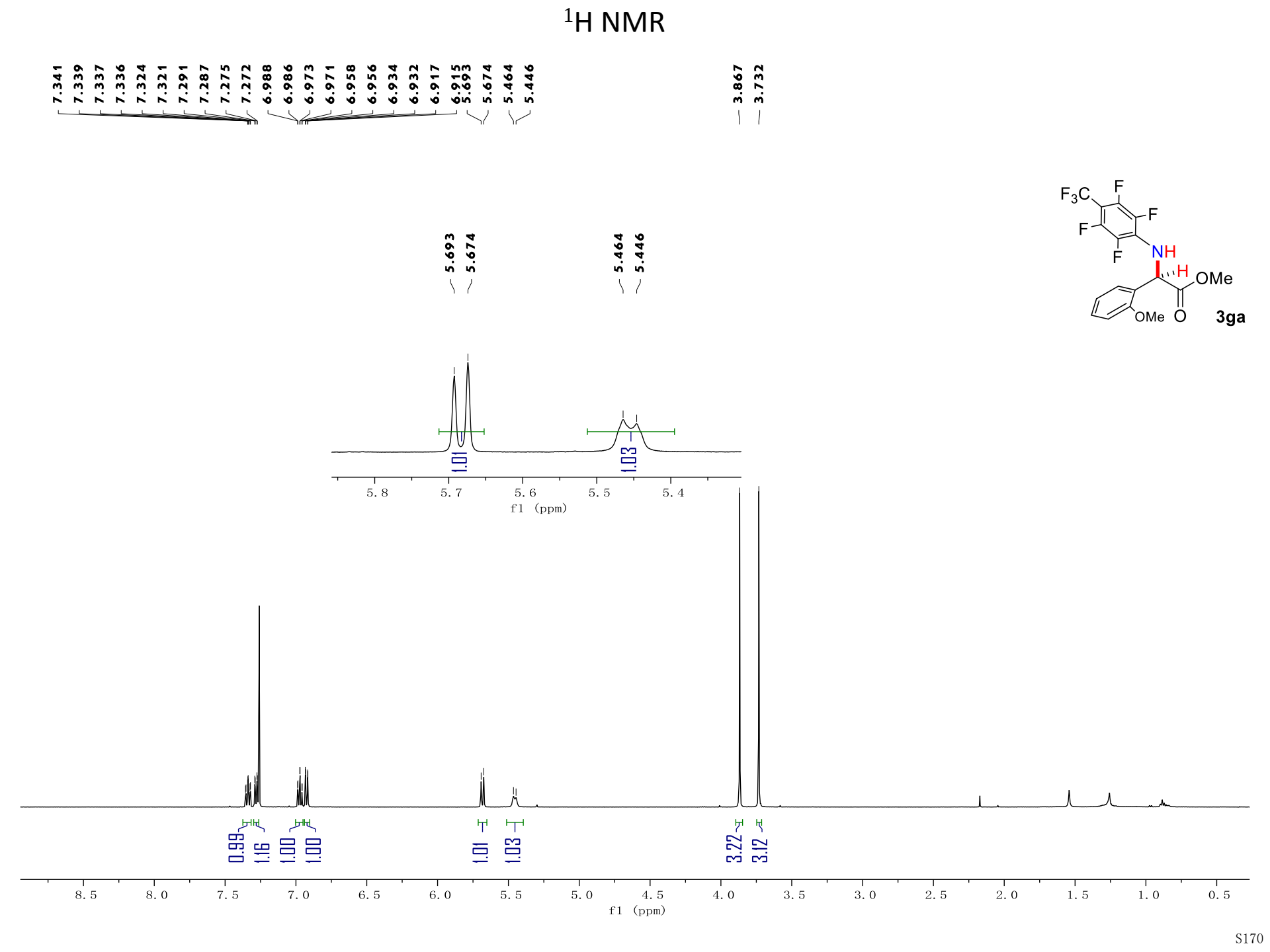



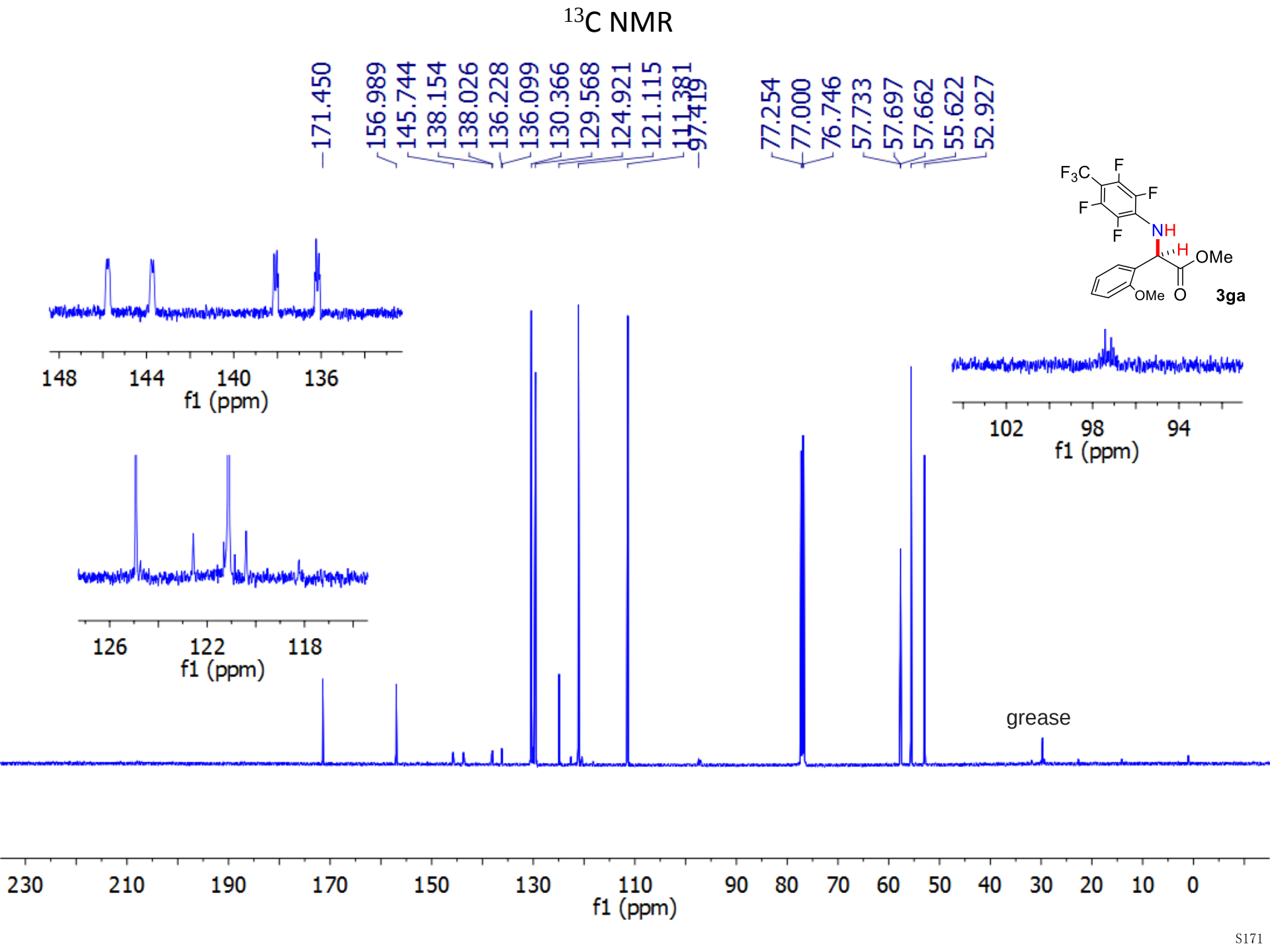

7: 251 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 6.404 | 96.254 |
| 2 | | 7.144 | 3.746 |
| Totals | | | 100.000 |

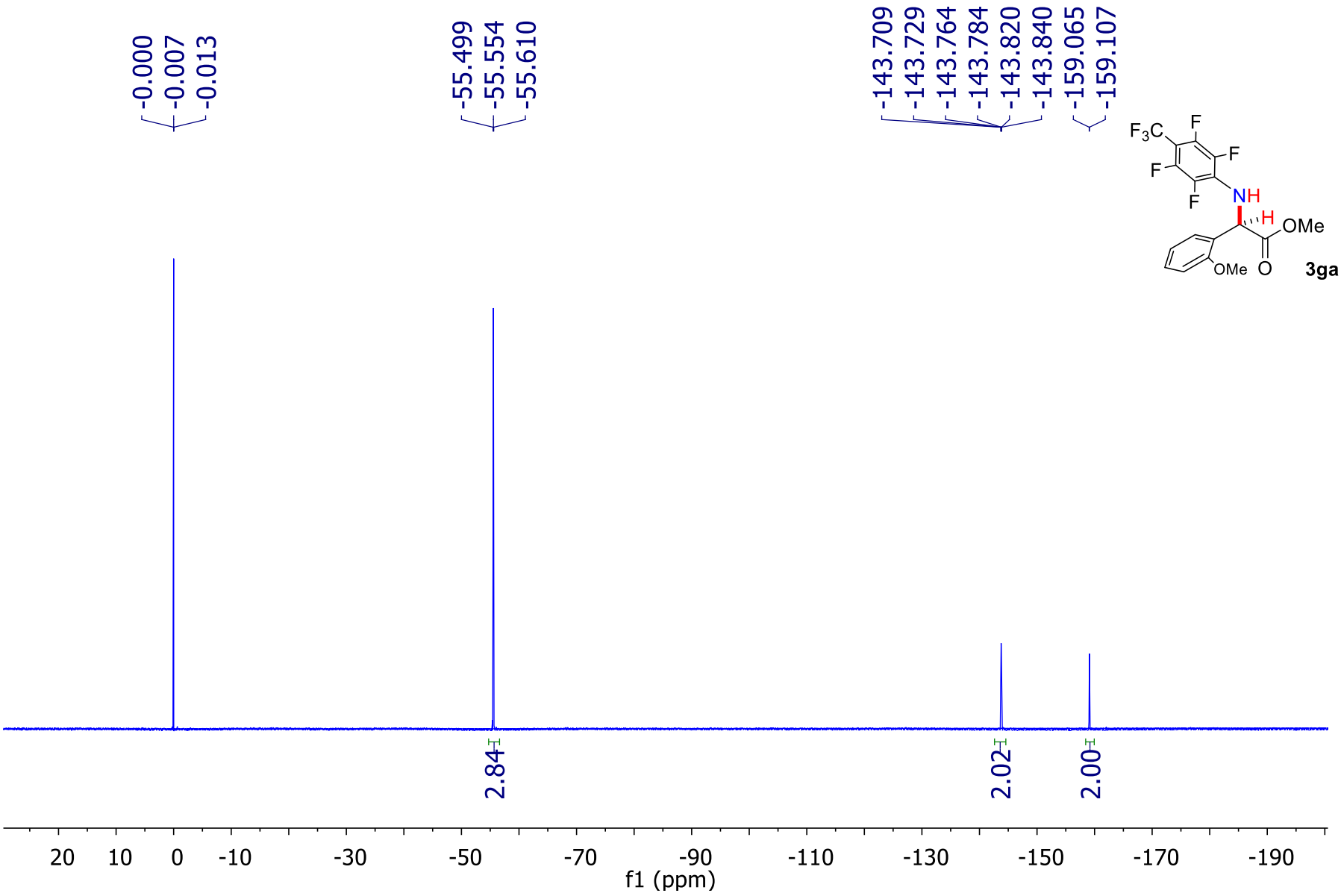
# $^1$H NMR


7.341
7.339
7.337
7.336
7.324
7.321
7.291
7.287
7.275
7.272
6.988
6.986
6.973
6.971
6.958
6.956
6.934
6.932
6.917
6.915
5.693
5.674
5.464
5.446
3.867
3.732
F3C
F
F
F
F
NH
H
OMe
OMe
O
3ga
1.01
1.03
5.8
5.7
5.6
5.5
5.4
f1 (ppm)
0.99
1.16
1.00
1.00
1.01
1.03
3.22
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

# $^{13}$C NMR

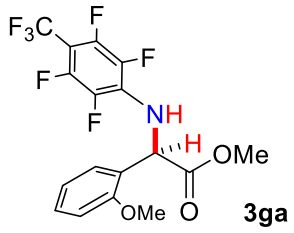

171.450
156.989
145.744
138.154
138.026
136.228
136.099
130.366
129.568
124.921
121.115
111.381
97.419
77.254
77.000
76.746
57.733
57.697
57.662
55.622
52.927
F3C
F
F
F
F
NH
H
OMe
OMe
O
3ga
148
144
140
136
f1 (ppm)
126
122
118
f1 (ppm)
102
98
94
f1 (ppm)
grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

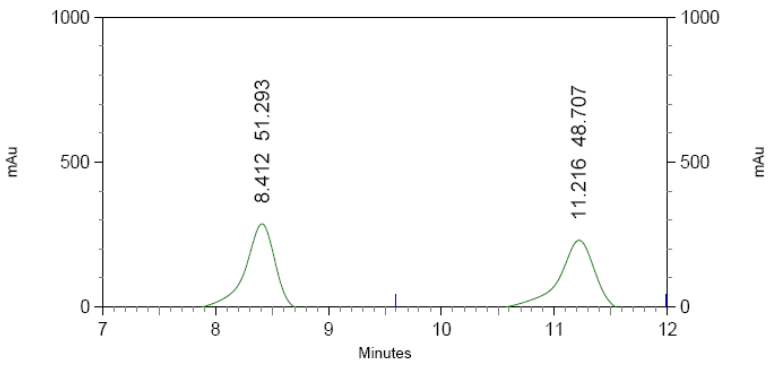

-0.000
-0.007
-0.013
-55.499
-55.554
-55.610
-143.709
-143.729
-143.764
-143.784
-143.820
-143.840
-159.065
-159.107
F3C
F
F
F
F
NH
H
OMe
OMe
O
3ga
2.84
2.02
2.00
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

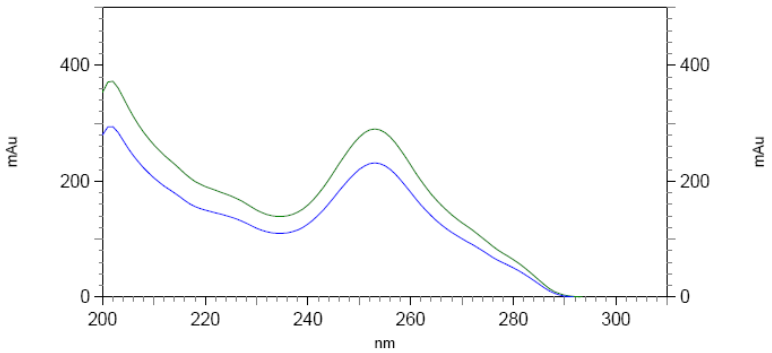
# HPLC

JLM-II-207-1-Whelk-0.5@-1mL
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
E:\JLM-II-207-1-Whelk-0.5 @1ml




**3ga**



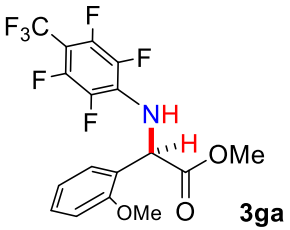

4: 254 nm, 4 nm
Results

| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 8.412 | 51.293 | 1 |
| | 11.216 | 48.707 | 2 |

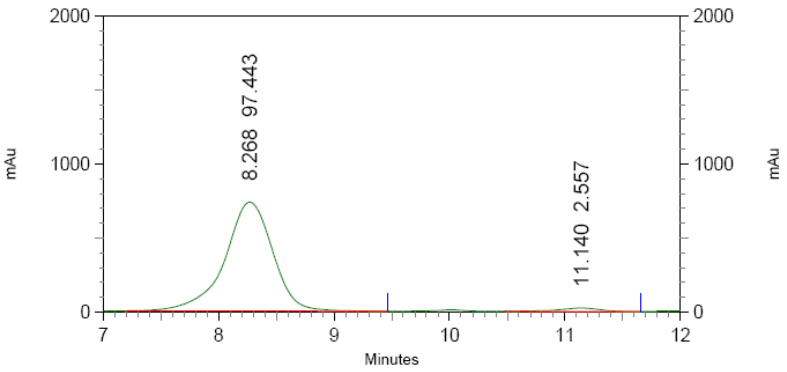
| Totals | | |
|---|---|---|
| | 100.000 | |

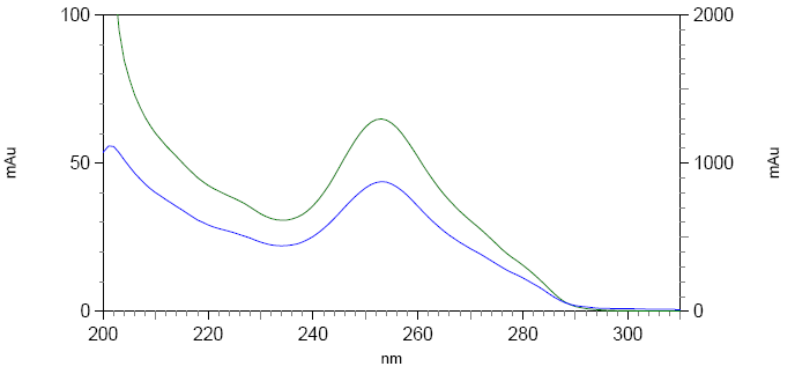
# HPLC

JLM-V-198-1-WHELK-0.5@-1mL
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
E:\JLM-V-198-1-WHELK0.5@1ml




**3ga**

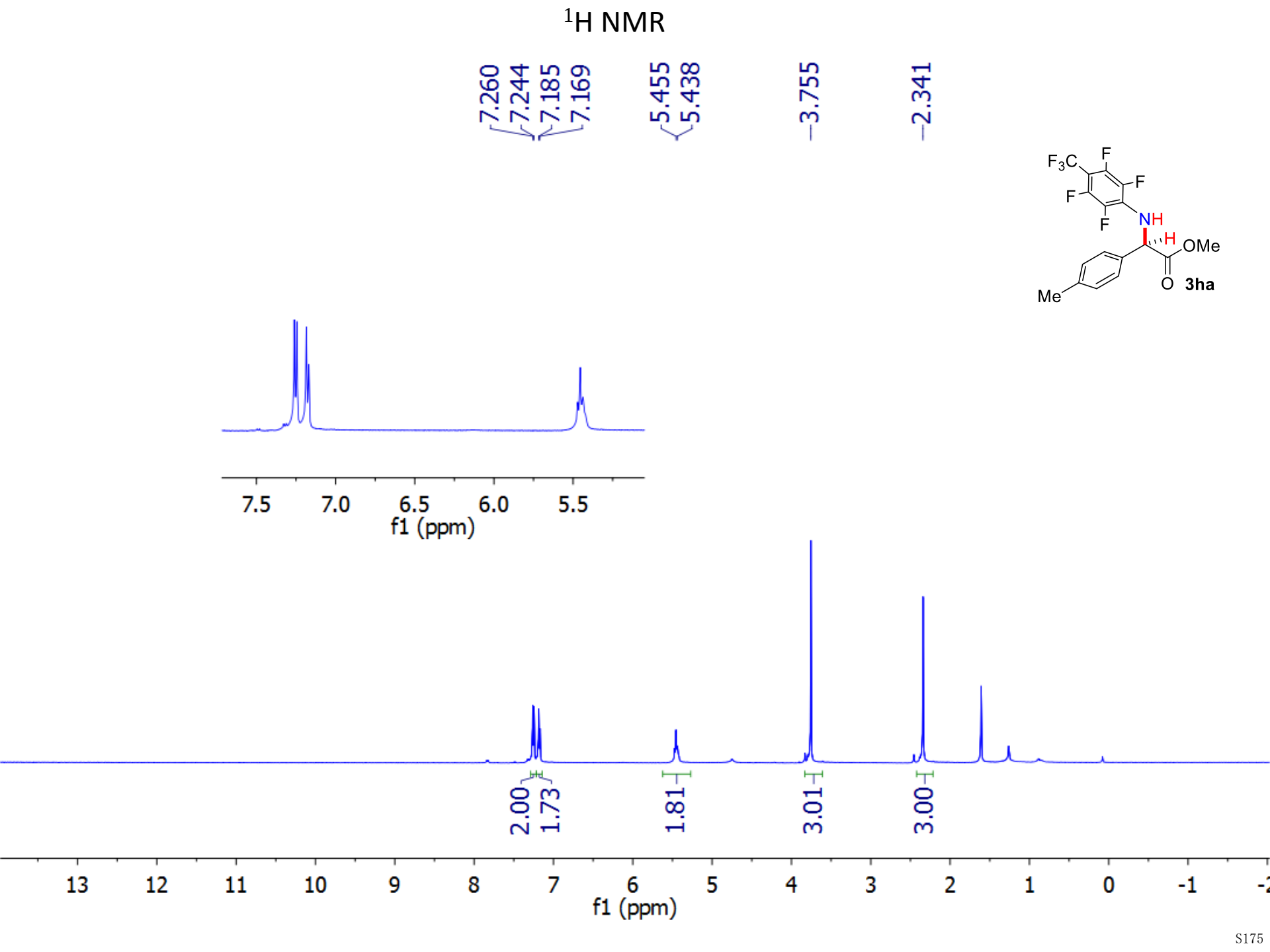



4: 284 nm, 4 nm
Results

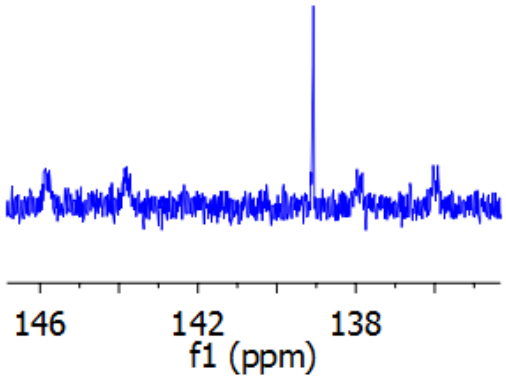
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 8.268 | 97.443 | 1 |
| | 11.140 | 2.557 | 2 |
| Totals | | 100.000 | |

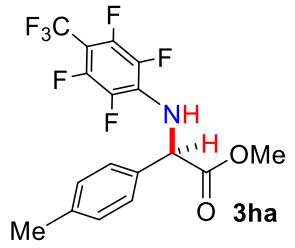
# $^{1}$H NMR


7.260
7.244
7.185
7.169
5.455
5.438
3.755
2.341
F3C
F
F
F
F
NH
H
OMe
O
Me
3ha
7.5
7.0
6.5
6.0
5.5
f1 (ppm)
2.00
1.73
1.81
3.01
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

# $^{13}$C NMR

171.463
145.882
143.715
139.059
137.823
135.940
133.513
129.885
129.646
129.272
126.821
97.452
77.254
77.000
76.746
60.324
60.292
60.259
53.146
21.132

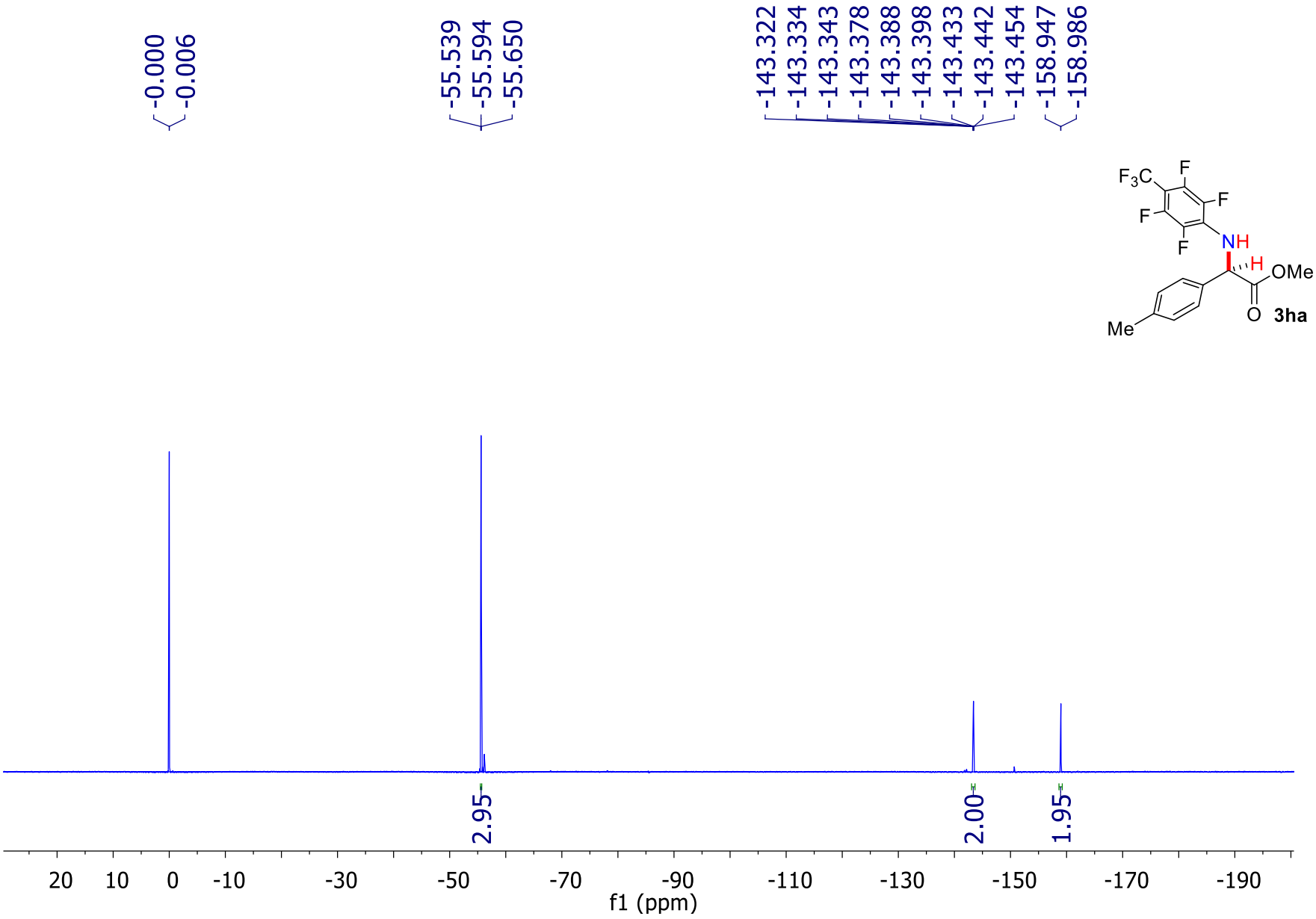



grease

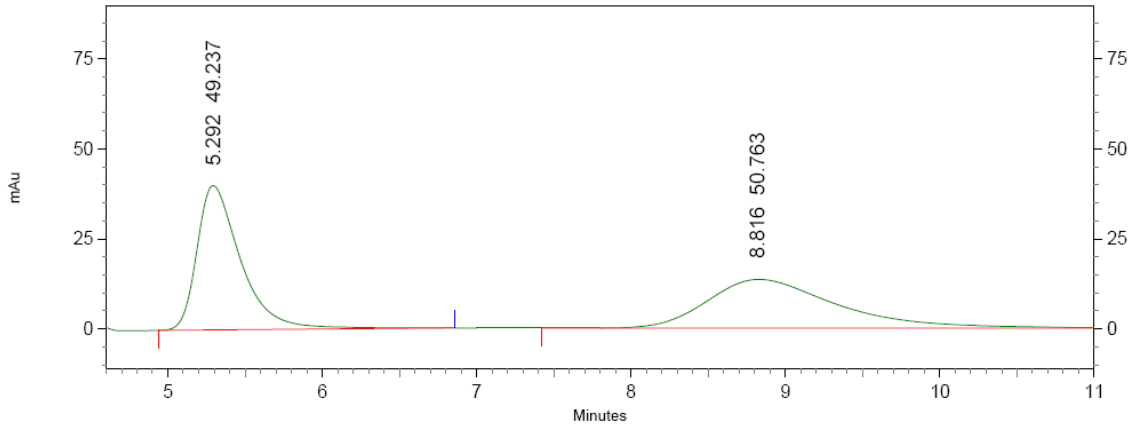
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

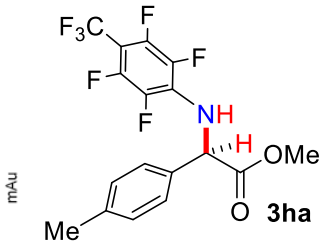
# $^{19}$F NMR

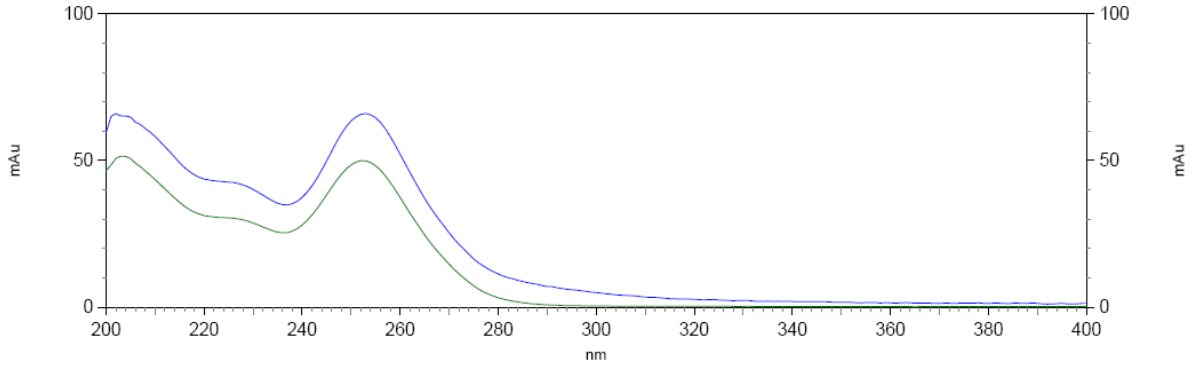

-0.000
-0.006
-55.539
-55.594
-55.650
-143.322
-143.334
-143.343
-143.378
-143.388
-143.398
-143.433
-143.442
-143.454
-158.947
-158.986
F3C
F
F
F
F
NH
H
OMe
O
Me
3ha
2.95
2.00
1.95
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-V-222-1a-OJH-1%1ML
C:\EZStart\Projects\Default\Data\JLM-V-222-1a-OJH-1%1ML
C:\EZStart\Projects\Default\Method\CQL-AD-H10%1.0ml60min.met
AD-H column 20%IPA @ 0.8ml/min



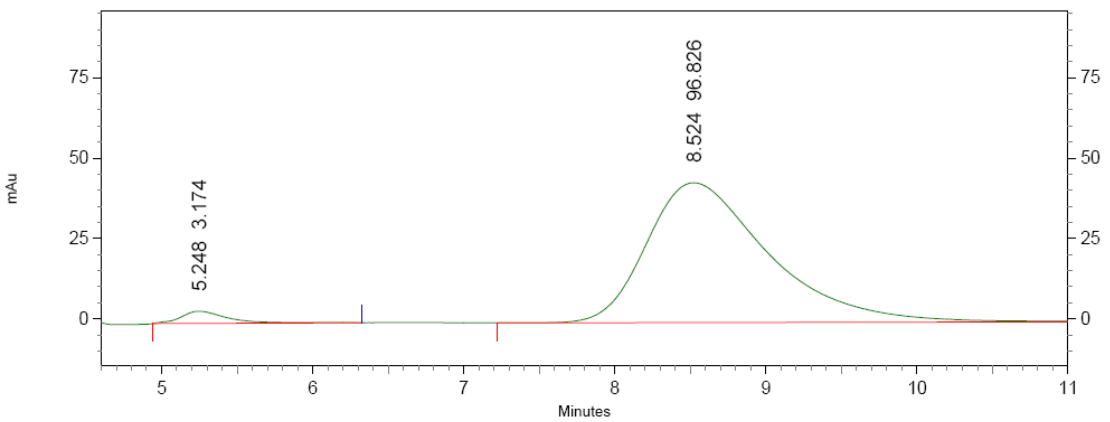

4: 259 nm, 4 nm Results

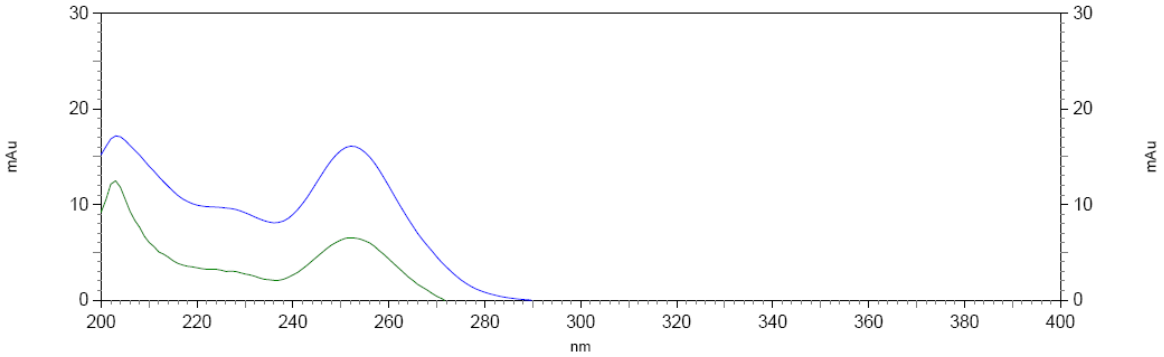
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.292 | 49.237 |
| 2 | 8.816 | 50.763 |

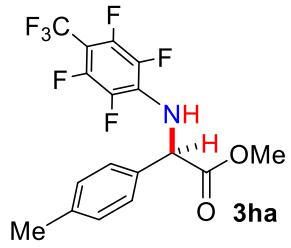
| Totals | |
|---|---|
| | 100.000 |

# HPLC

JLM-V-222-2-OJH-1%1ML
C:\EZStart\Projects\Default\Data\JLM-V-222-2-OJH-1%1ML
C:\EZStart\Projects\Default\Method\CQL-AD-H10%1.0ml60min.met
AD-H column 20%IPA @ 0.8ml/min



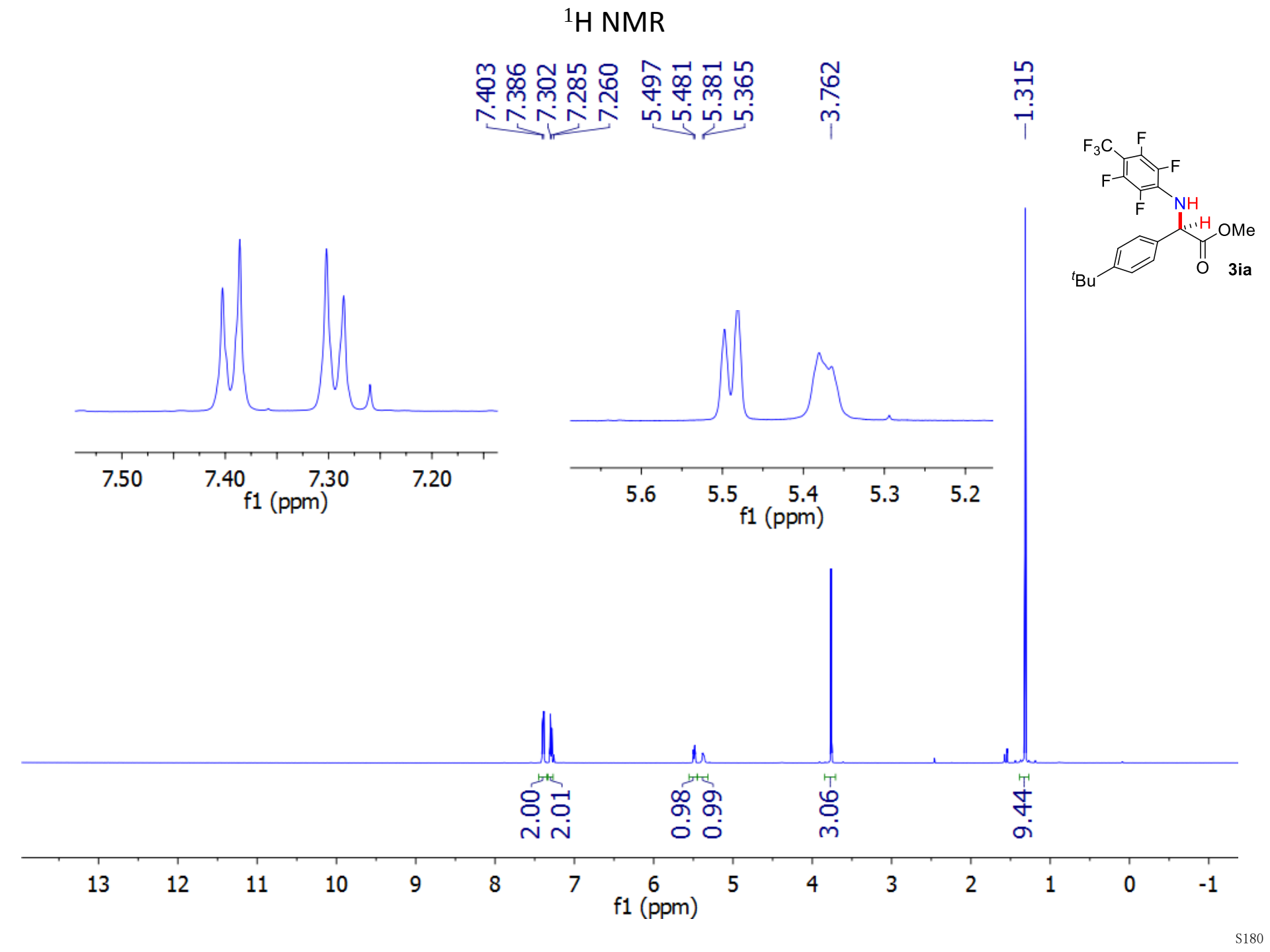



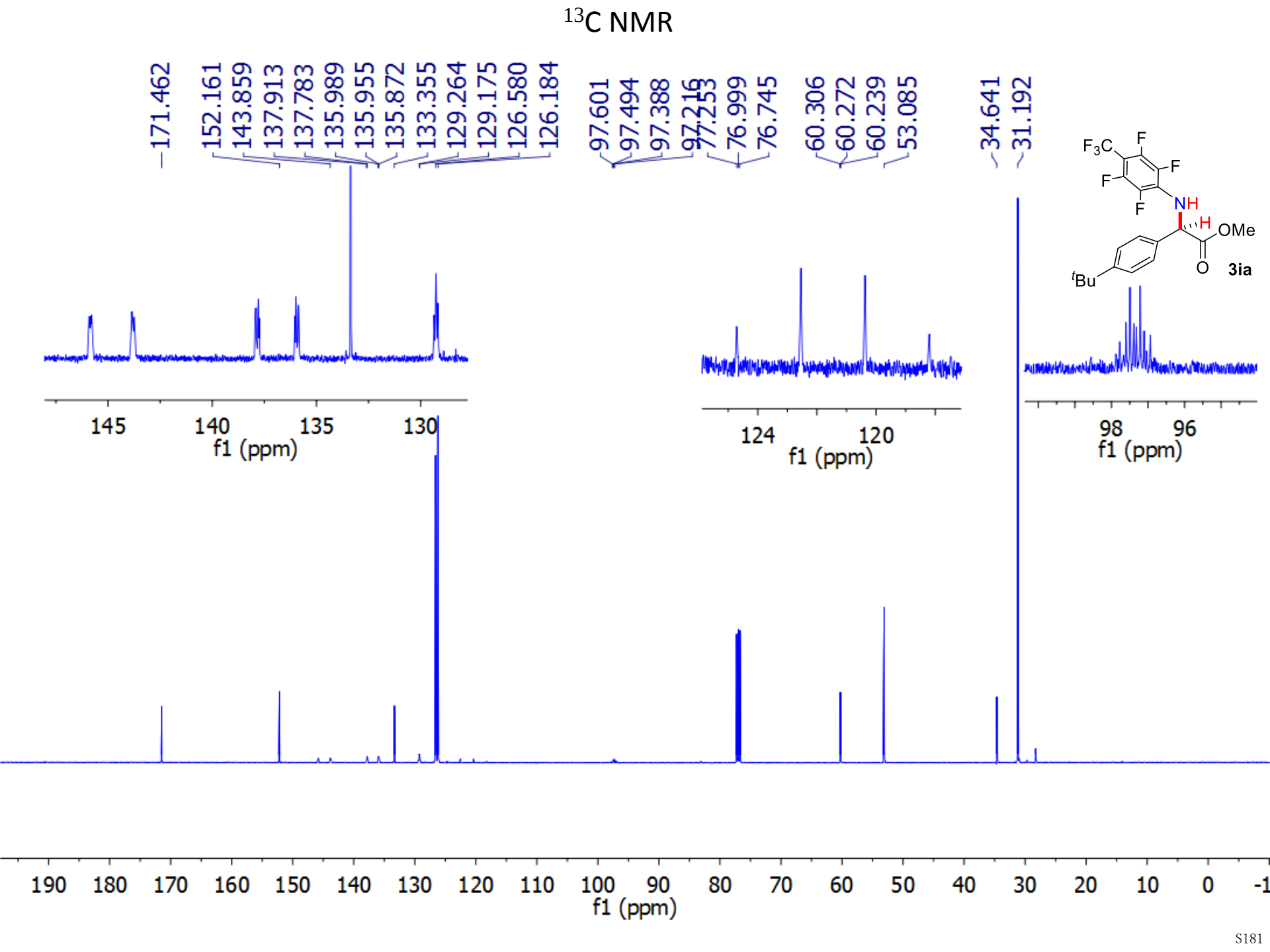

4: 259 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.248 | 3.174 |
| 2 | 8.524 | 96.826 |
| Totals | | 100.000 |

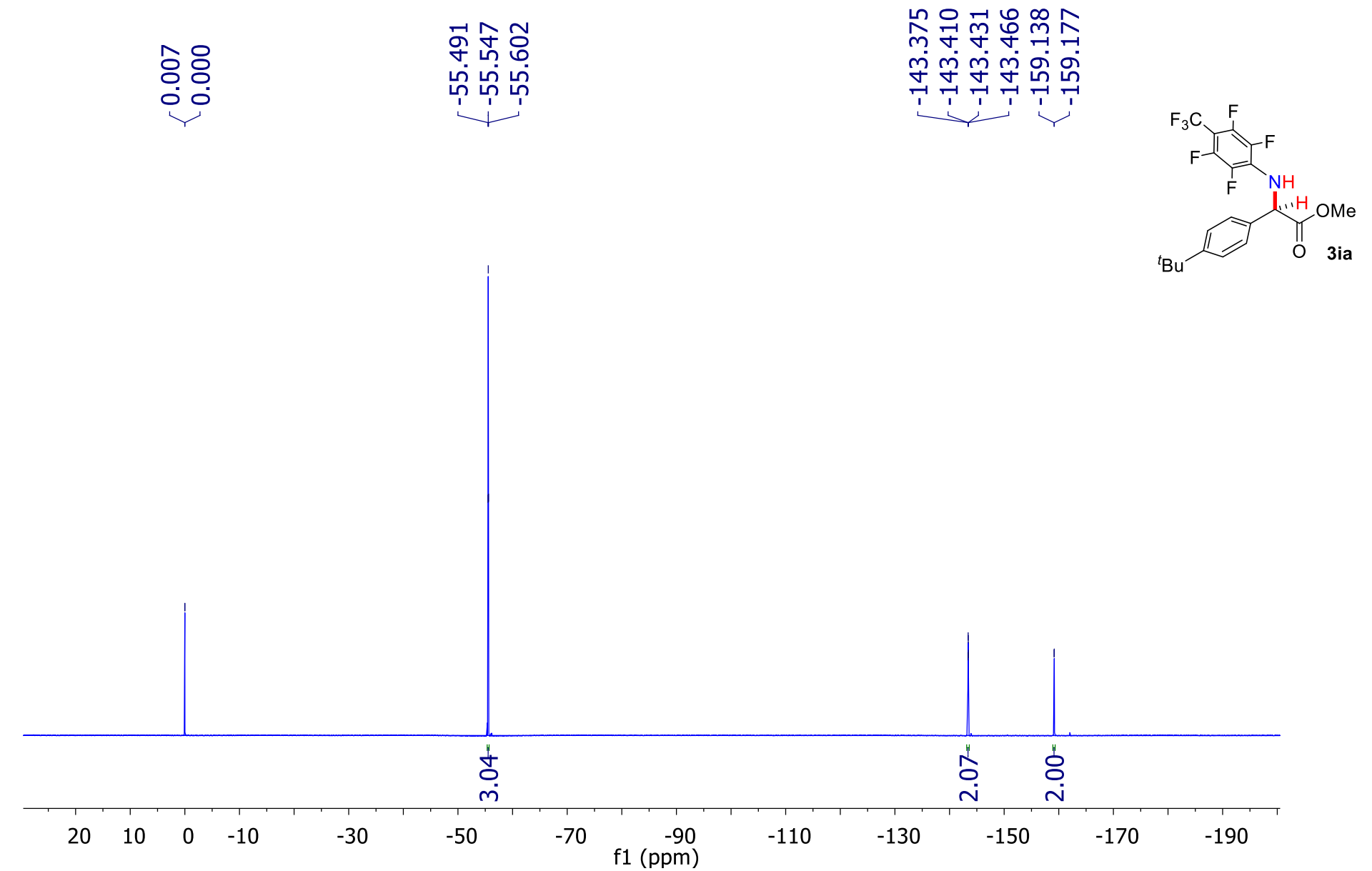
# $^1$H NMR


7.403
7.386
7.302
7.285
7.260
5.497
5.481
5.381
5.365
3.762
1.315
F3C
F
F
F
F
NH
H
OMe
O
tBu
3ia
7.50
7.40
7.30
7.20
f1 (ppm)
5.6
5.5
5.4
5.3
5.2
f1 (ppm)
2.00
2.01
0.98
0.99
3.06
9.44
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

# $^{13}$C NMR

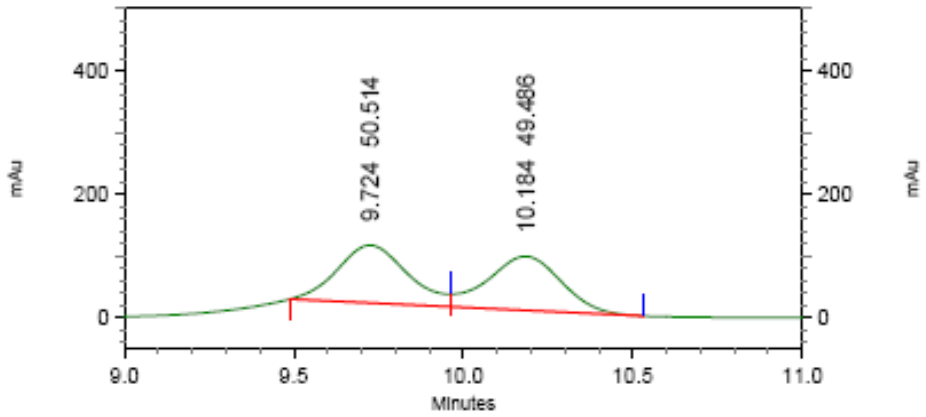

171.462
152.161
143.859
137.913
137.783
135.989
135.955
135.872
133.355
129.264
129.175
126.580
126.184
97.601
97.494
97.388
77.253
76.999
76.745
60.306
60.272
60.239
53.085
34.641
31.192
F3C
F
F
F
F
NH
H
OMe
O
tBu
3ia
145
140
135
130
f1 (ppm)
124
120
f1 (ppm)
98
96
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

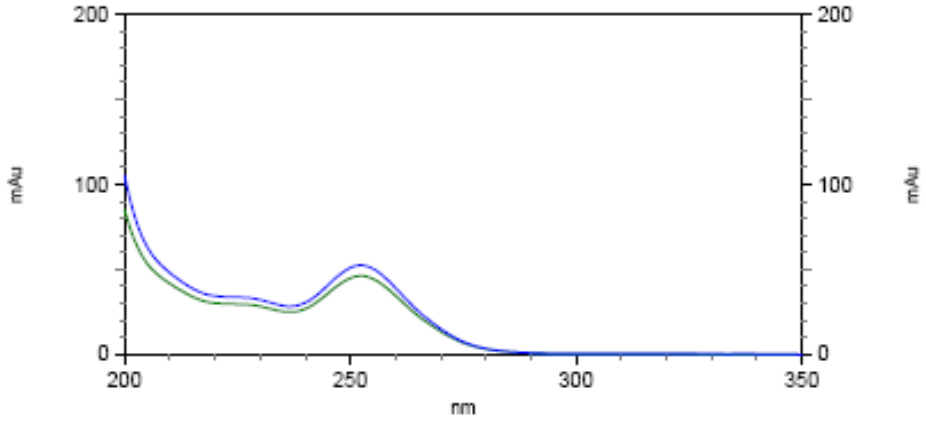
# $^{19}$F NMR

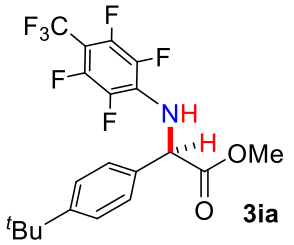

0.007
0.000
-55.491
-55.547
-55.602
-143.375
-143.410
-143.431
-143.466
-159.138
-159.177
F3C
F
F
F
F
NH
H
OMe
O
tBu
3ia
3.04
2.07
2.00
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-V-194-1C-whelk-0%0.8ML
C:\EZStart\Projects\Default\Method\LK-20%-0.8-90min.met
C:\EZStart\Projects\Default\Data\JLM-V-194-1C-whelk-0%0.8ML



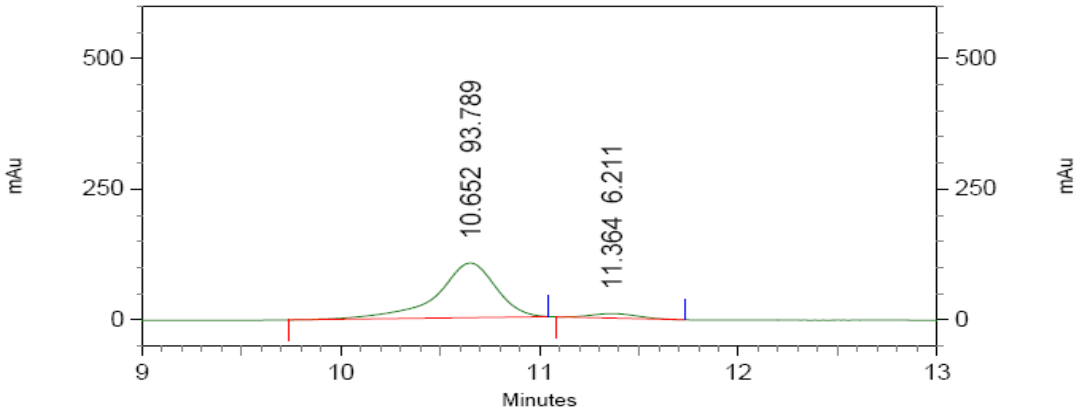



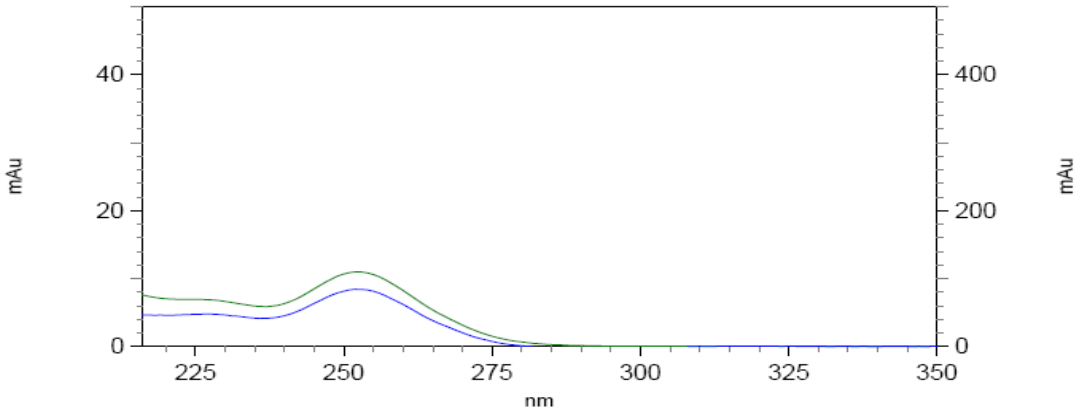

2: 252 nm, 4 nm
Results

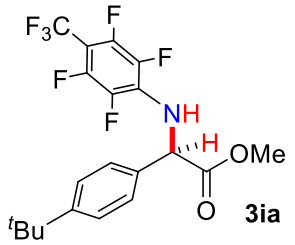
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 9.724 | 50.514 | 1 |
| | 10.184 | 49.486 | 2 |
| Totals | | 100.000 | |

# HPLC

JLM-V-194-2-whelk-0%0.8ML
C:\EZStart\Projects\Default\Method\LK-20%-0.8-90min.met
C:\EZStart\Projects\Default\Data\JLM-V-194-2-whelk-0%0.8ML



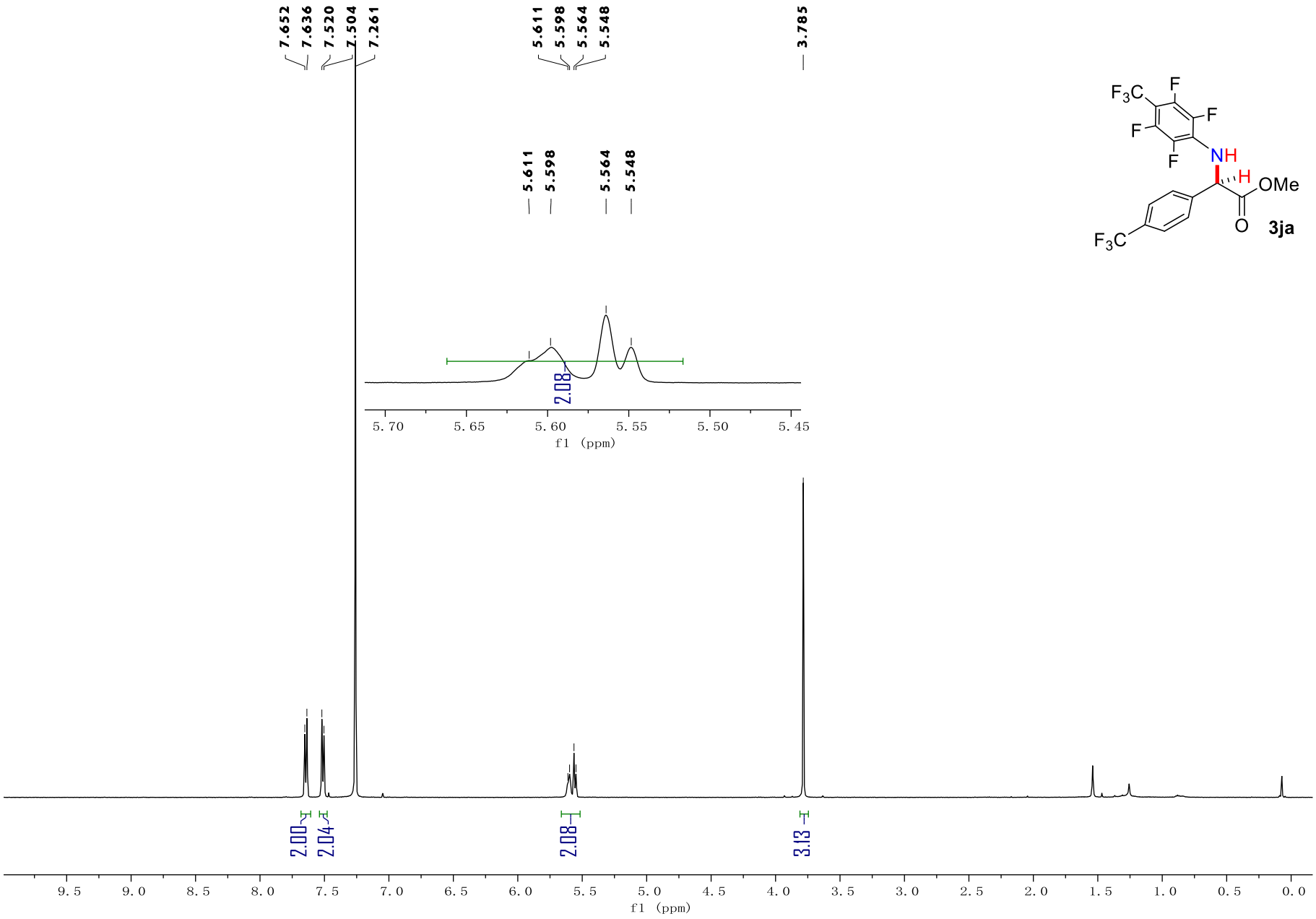




2: 253 nm, 4 nm
Results

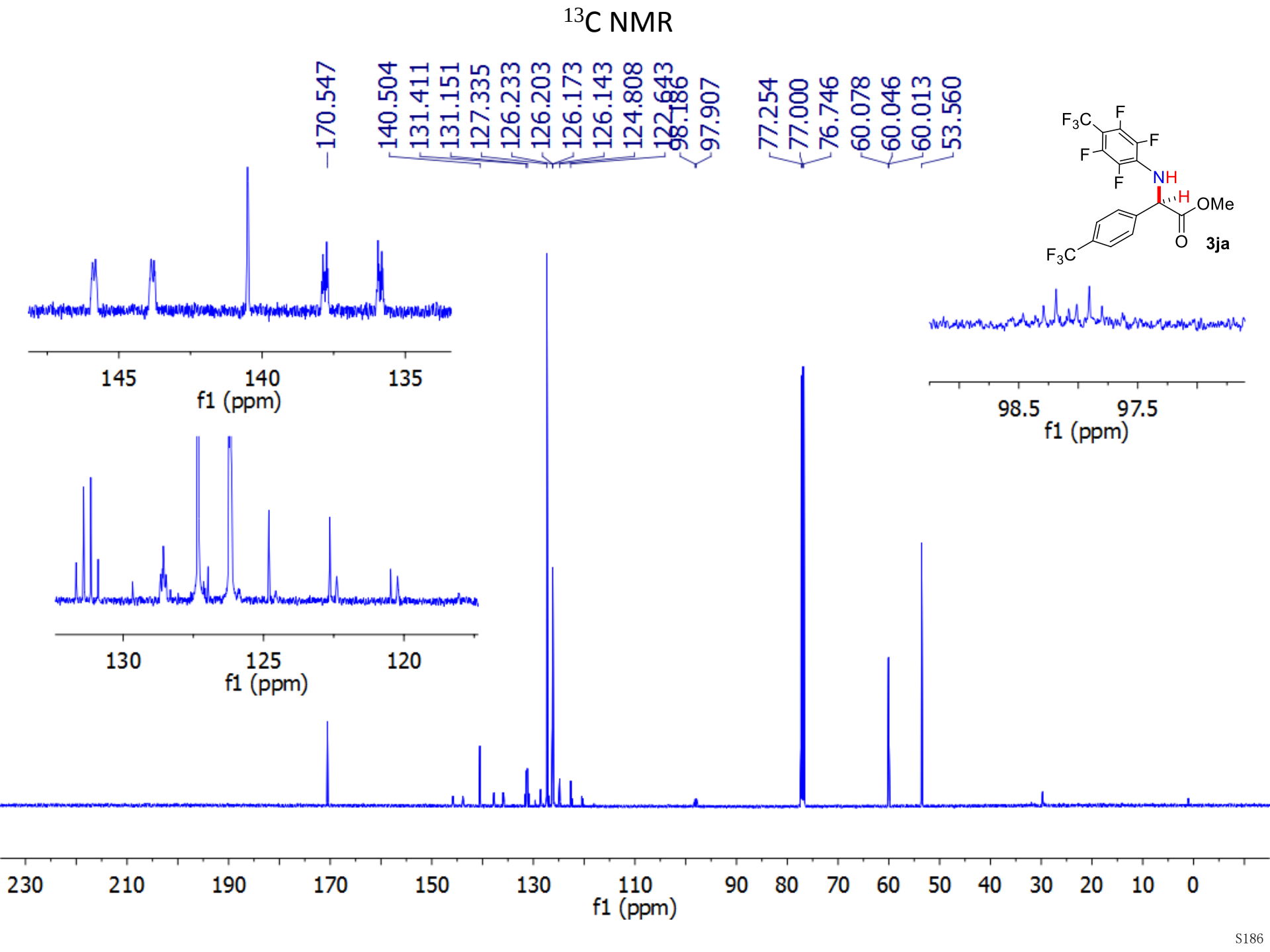
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 10.652 | 93.789 | 1 |
| | 11.364 | 6.211 | 2 |

| Totals | | |
|---|---|---|
| | 100.000 | |

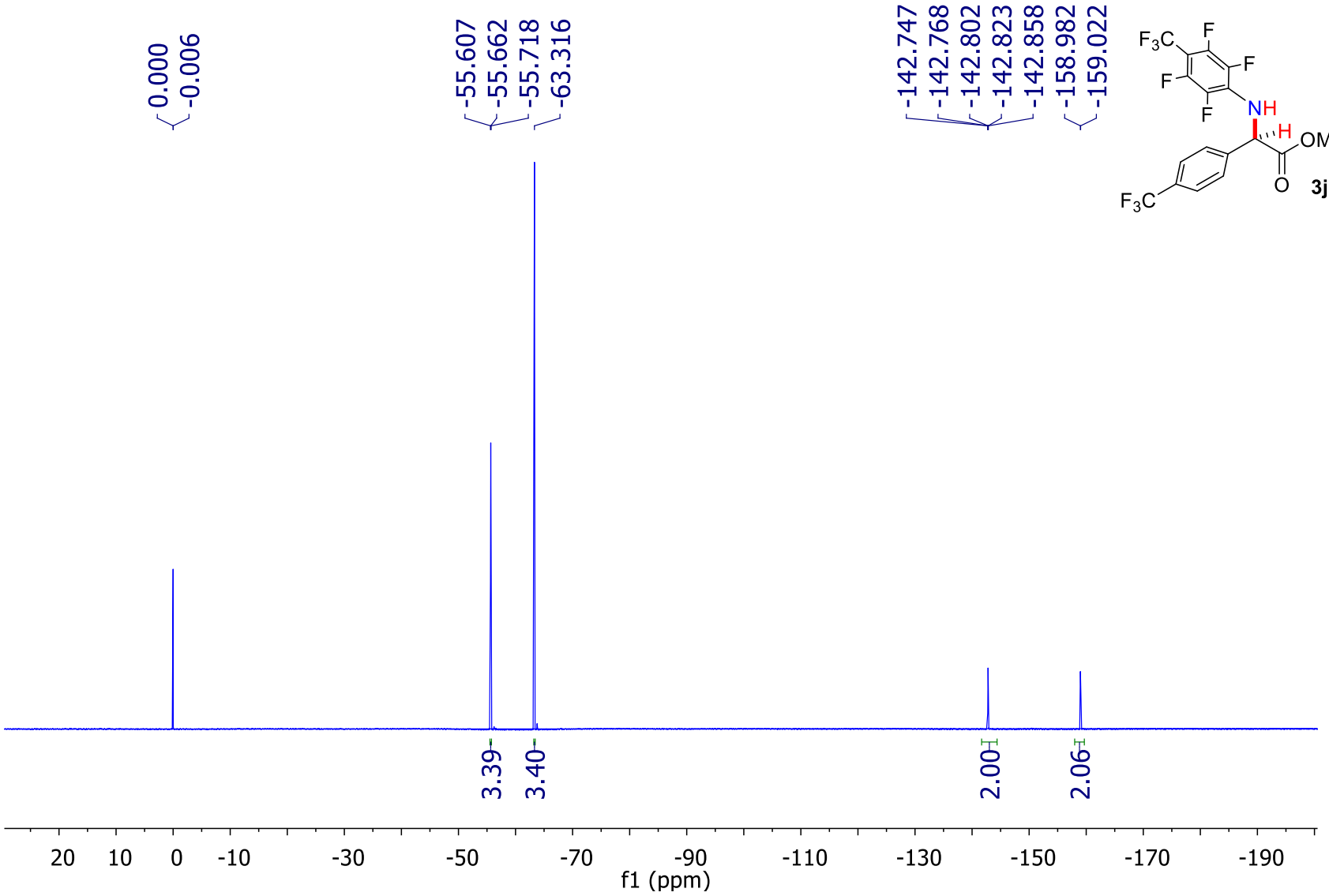
# $^{1}$H NMR


7.652
7.636
7.520
7.504
7.261
5.611
5.598
5.564
5.548
3.785
2.08
5.70
5.65
5.60
5.55
5.50
5.45
f1 (ppm)
2.00
2.04
2.08
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
F3C
F
F
F
NH
H
OMe
O
F3C
3ja

# $^{13}$C NMR

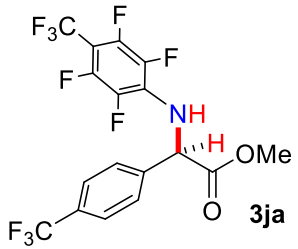

170.547
140.504
131.411
131.151
127.335
126.233
126.203
126.173
126.143
124.808
122.643
98.186
97.907
77.254
77.000
76.746
60.078
60.046
60.013
53.560
F3C
F
F
F
NH
H
OMe
O
F3C
3ja
145
140
135
f1 (ppm)
130
125
120
f1 (ppm)
98.5
97.5
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

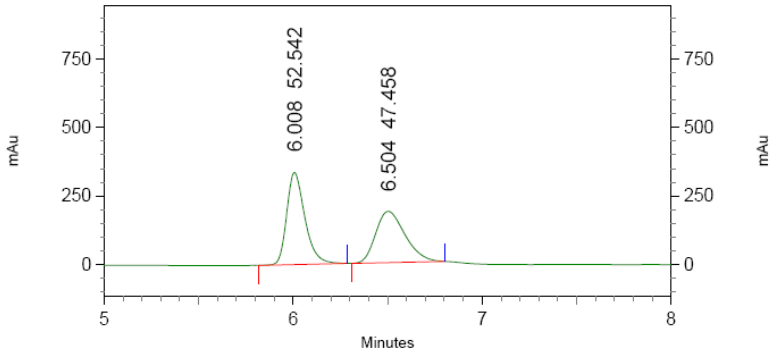

0.000
-0.006
-55.607
-55.662
-55.718
-63.316
-142.747
-142.768
-142.802
-142.823
-142.858
-158.982
-159.022
3.39
3.40
2.00
2.06
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)
F3C
F
F
F
NH
H
OMe
O
F3C
3ja

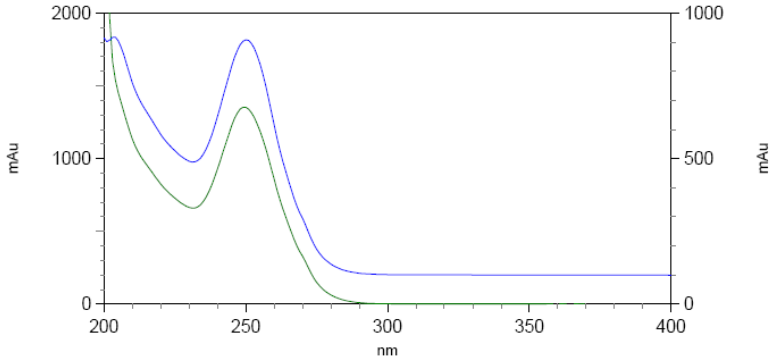
# HPLC

JLM-V-195-1-ADH-1%1ML
C:\EZStart\Projects\Default\Method\JTL-3%-ADH1ml.met
C:\EZStart\Projects\Default\Data\JLM-V-195-1-ADH1%1ML




**3ja**



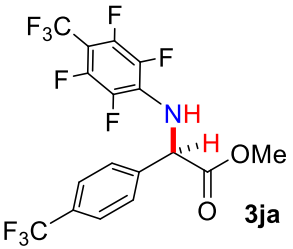

3: 220 nm, 4 nm
Results

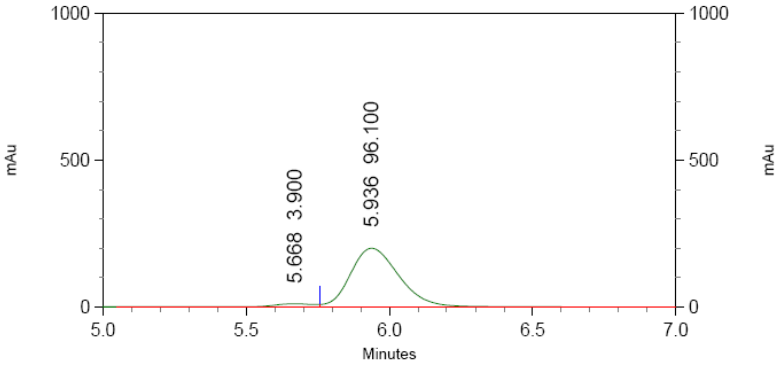
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 6.008 | 52.542 | 1 |
| | 6.504 | 47.458 | 2 |

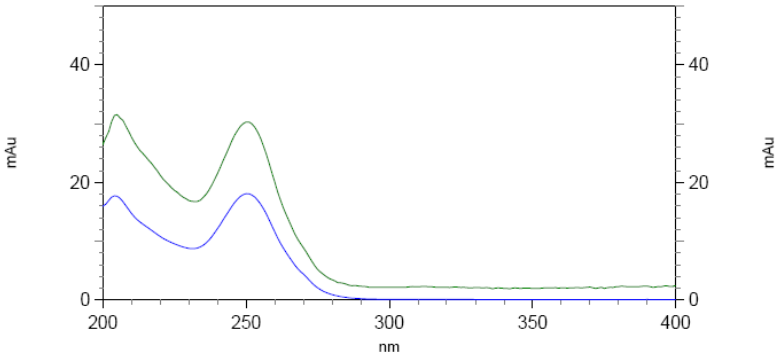
| Totals | | |
|---|---|---|
| | 100.000 | |

# HPLC

JLM-V-204-1A-ADH-1%1ML
C:\EZStart\Projects\Default\Method\shifatest_2,5-dimehoxy.met
C:\EZStart\Projects\Default\Data\JLM-V-204-1A-ADH1%1ML



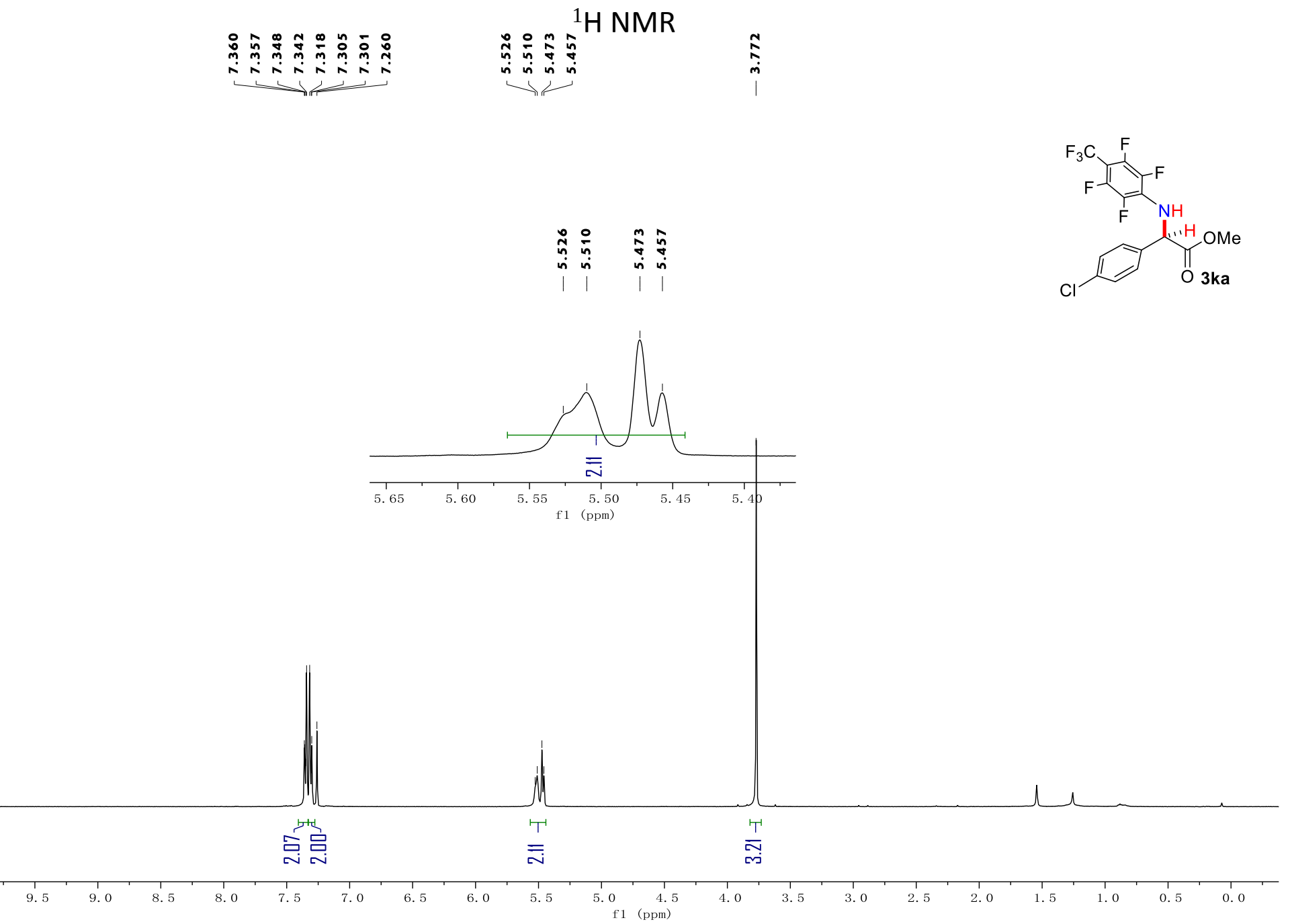



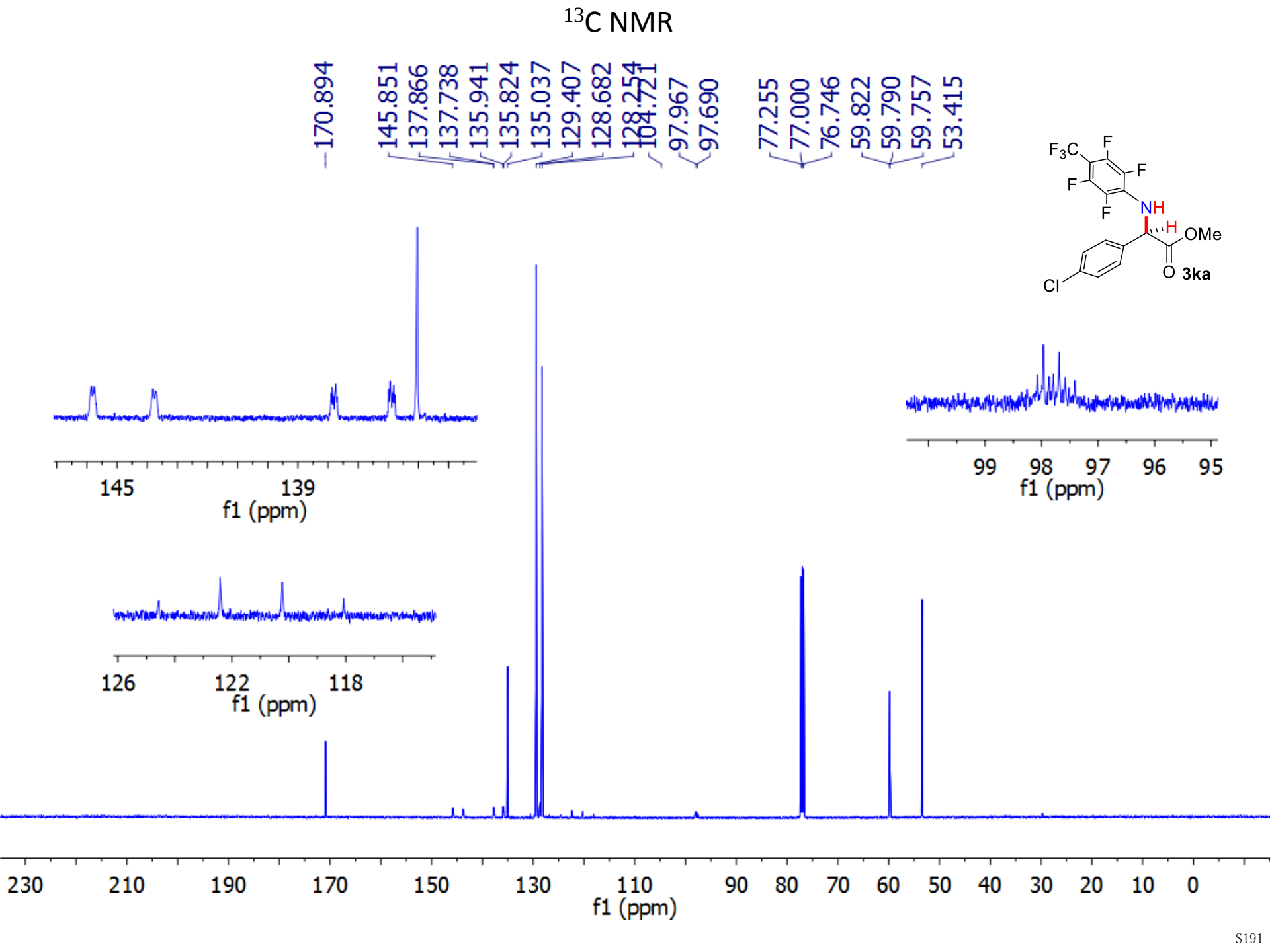

7: 251 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 5.668 | 3.900 |
| 2 | | 5.936 | 96.100 |
| Totals | | | 100.000 |

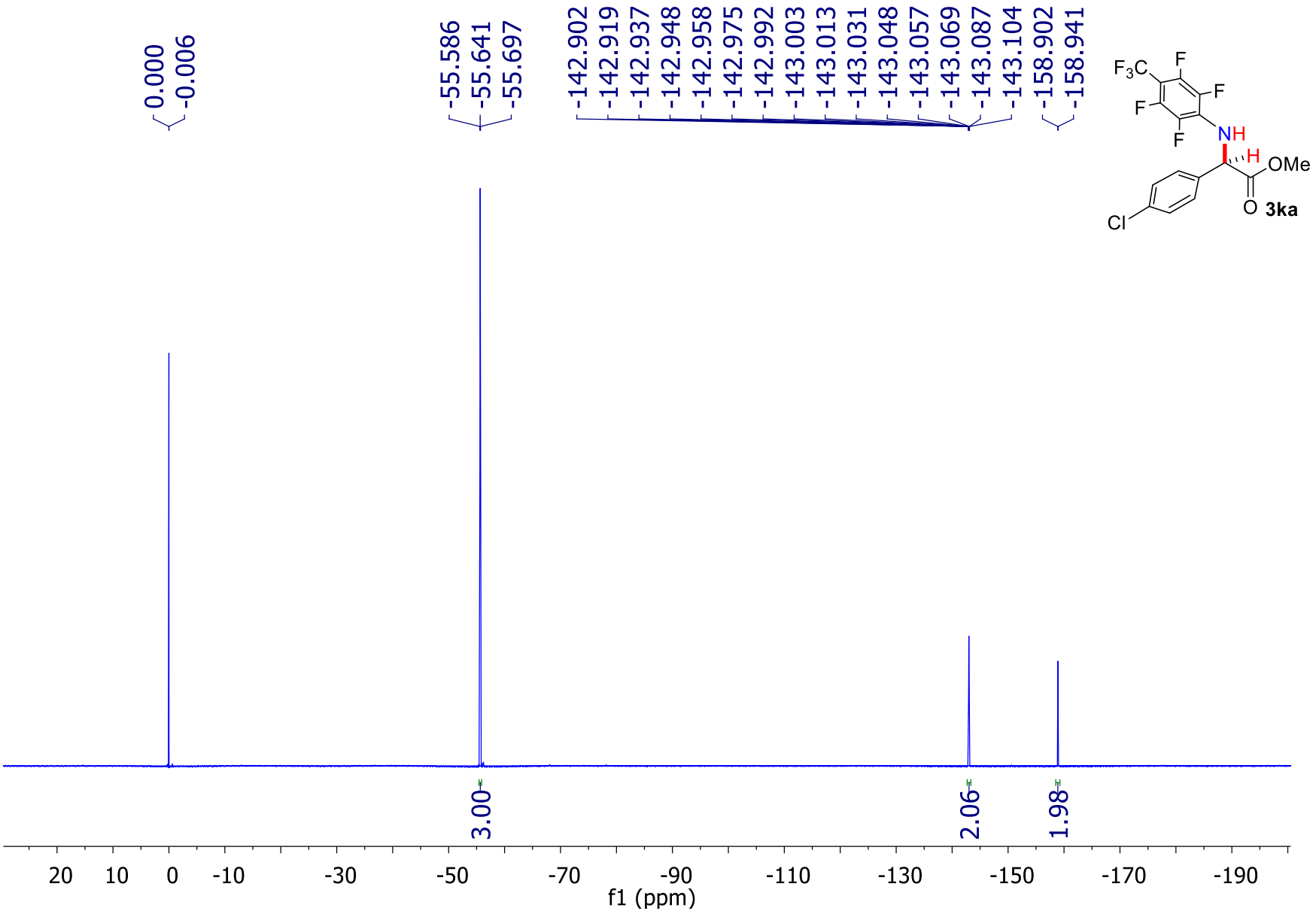
# $^1$H NMR


7.360
7.357
7.348
7.342
7.318
7.305
7.301
7.260
5.526
5.510
5.473
5.457
3.772
F3C
F
F
F
F
NH
H
OMe
O
Cl
3ka
2.11
5.65
5.60
5.55
5.50
5.45
5.40
f1 (ppm)
2.07
2.00
2.11
3.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

# $^{13}$C NMR

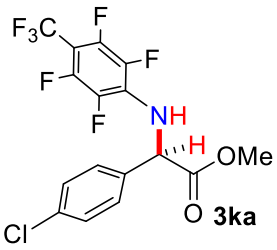

170.894
145.851
137.866
137.738
135.941
135.824
135.037
129.407
128.682
128.254
104.721
97.967
97.690
77.255
77.000
76.746
59.822
59.790
59.757
53.415
F3C
F
F
F
F
NH
H
OMe
O
Cl
3ka
145
139
f1 (ppm)
126
122
118
f1 (ppm)
99
98
97
96
95
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

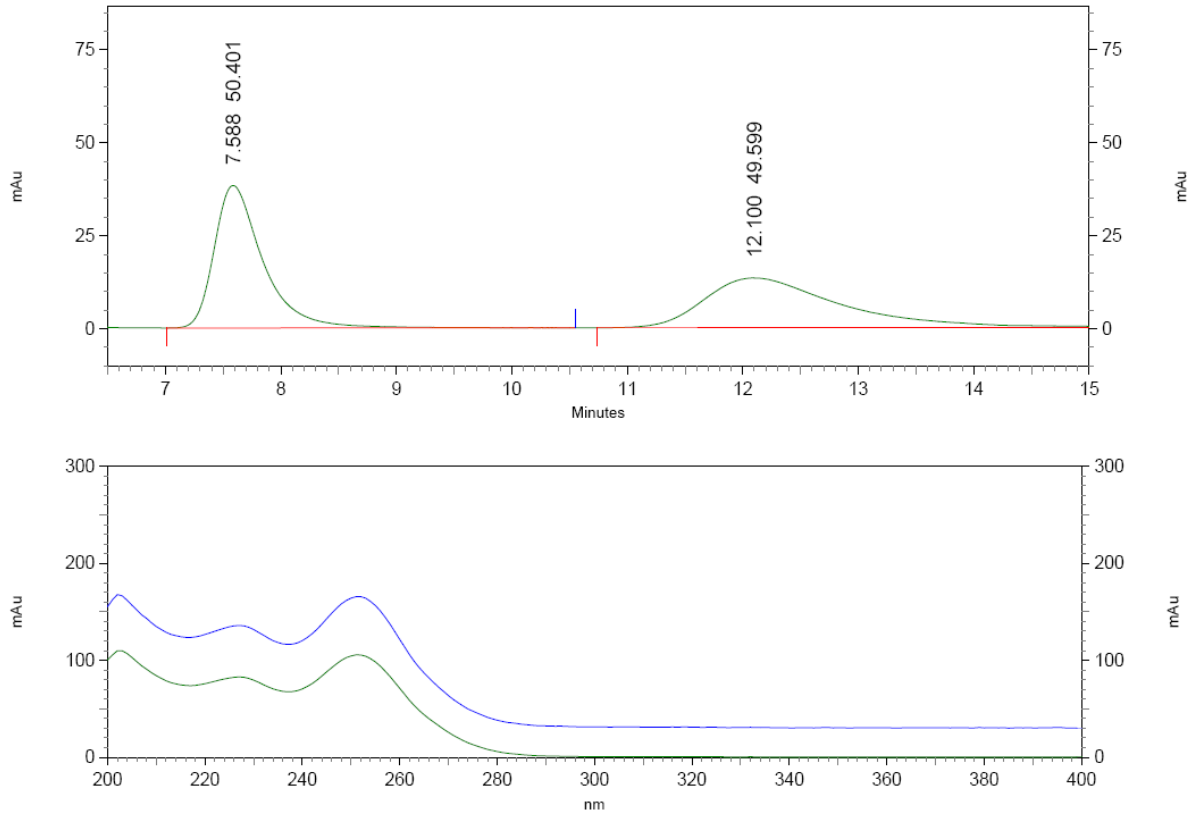
# $^{19}$F NMR


0.000
-0.006
-55.586
-55.641
-55.697
-142.902
-142.919
-142.937
-142.948
-142.958
-142.975
-142.992
-143.003
-143.013
-143.031
-143.048
-143.057
-143.069
-143.087
-143.104
-158.902
-158.941
F3C
F
F
F
F
NH
H
OMe
O
3ka
Cl
3.00
2.06
1.98
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-V-223-1-OJH-1%1ML
C:\EZStart\Projects\Default\Data\JLM-V-223-1-OJH-1%1ML
C:\EZStart\Projects\Default\Method\CQL-AD-H10%1.0ml60min.met
AD-H column 20%IPA @ 0.8ml/min



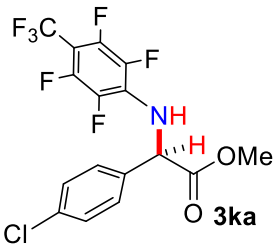



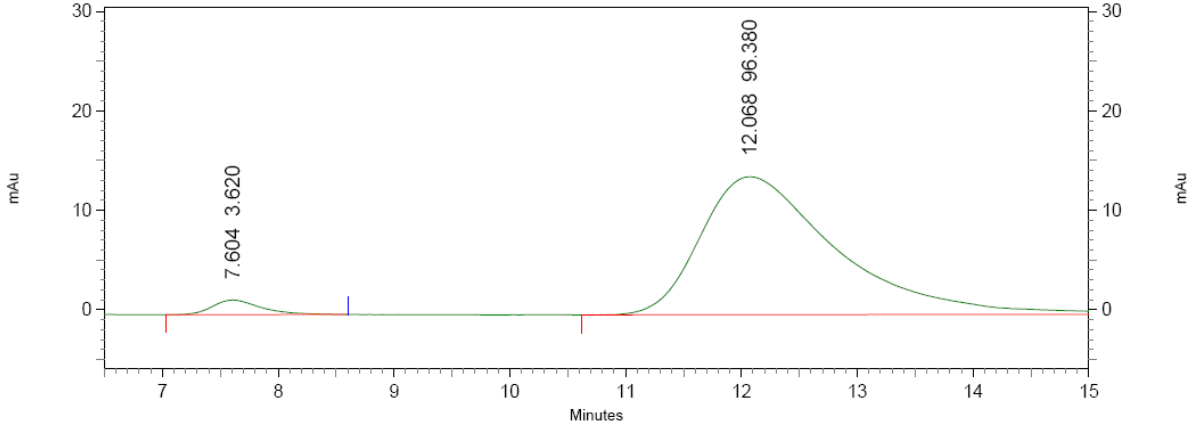

4: 259 nm, 4 nm Results

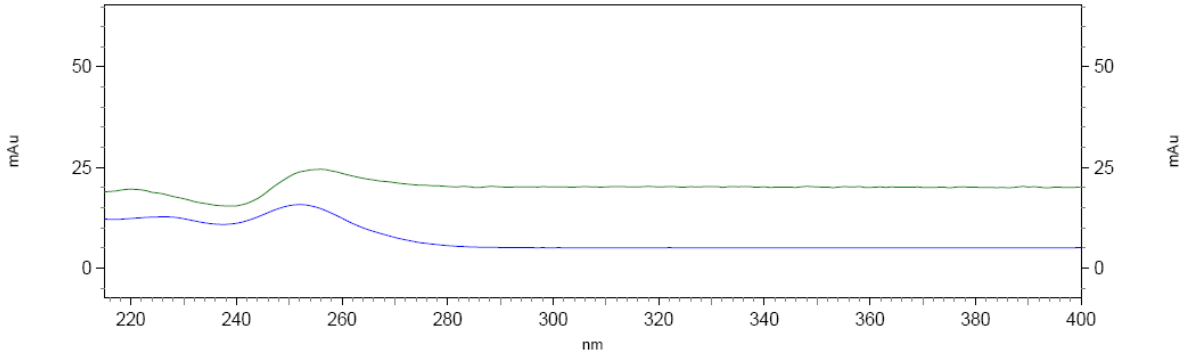
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.588 | 50.401 |
| 2 | 12.100 | 49.599 |
| Totals | | 100.000 |

# HPLC

JLM-V-223-2-OJH-1%1ML
C:\EZStart\Projects\Default\Data\JLM-V-223-2-OJH-1%1ML
C:\EZStart\Projects\Default\Method\CQL-AD-H10%1.0ml60min.met
AD-H column 20%IPA @ 0.8ml/min



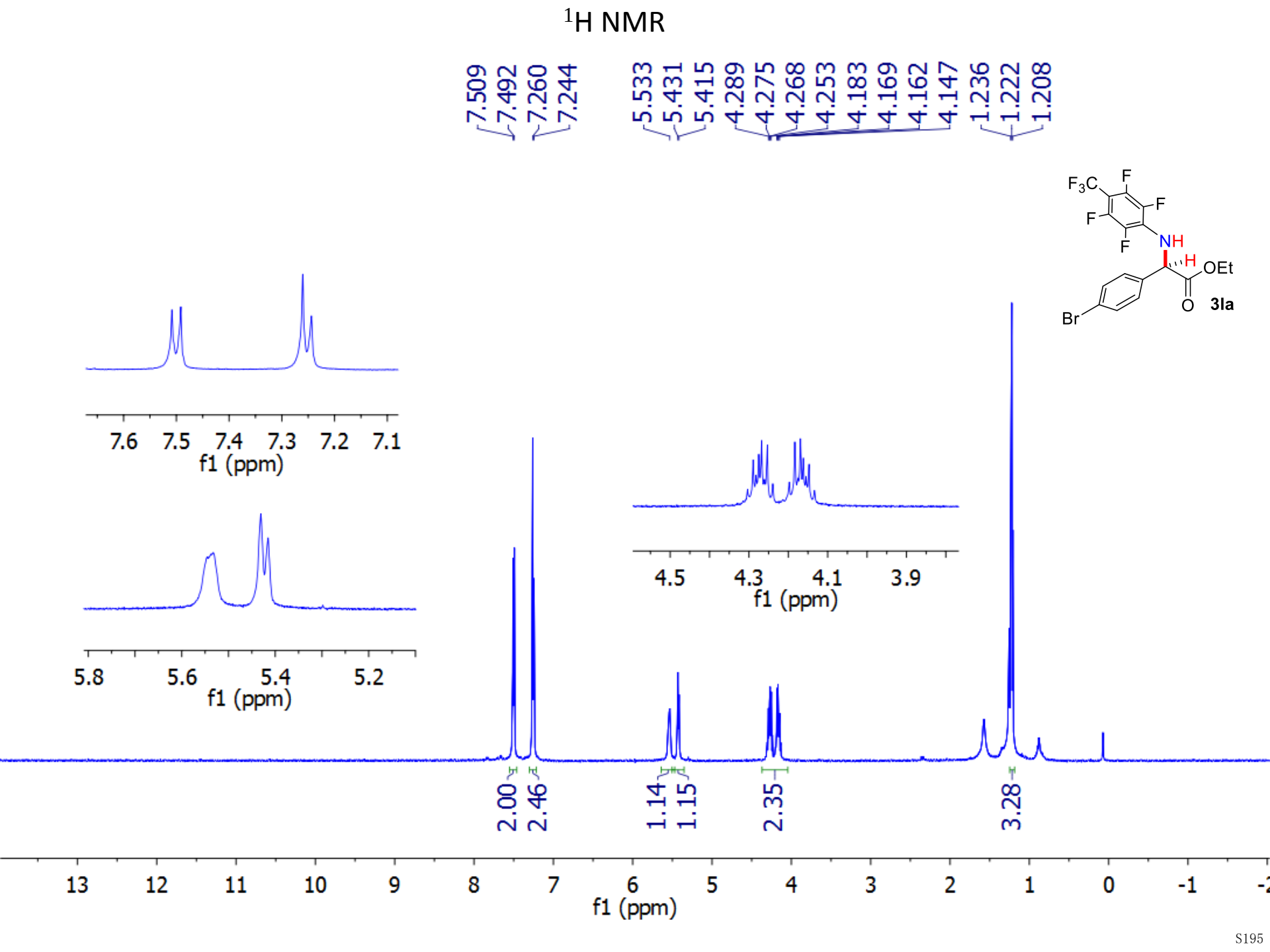




4: 259 nm, 4 nm Results

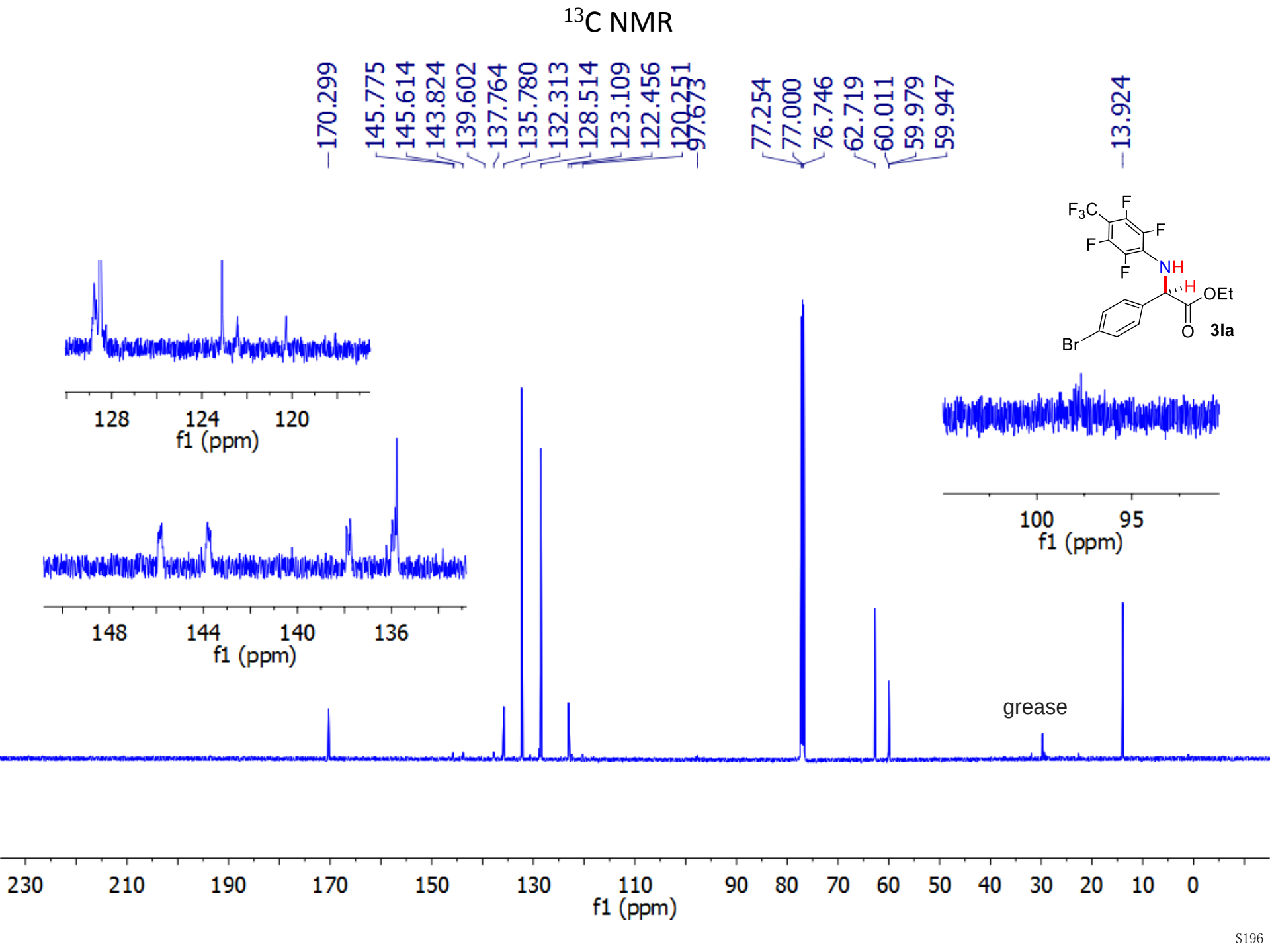
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.604 | 3.620 |
| 2 | 12.068 | 96.380 |

| Totals | |
|---|---|
| | 100.000 |

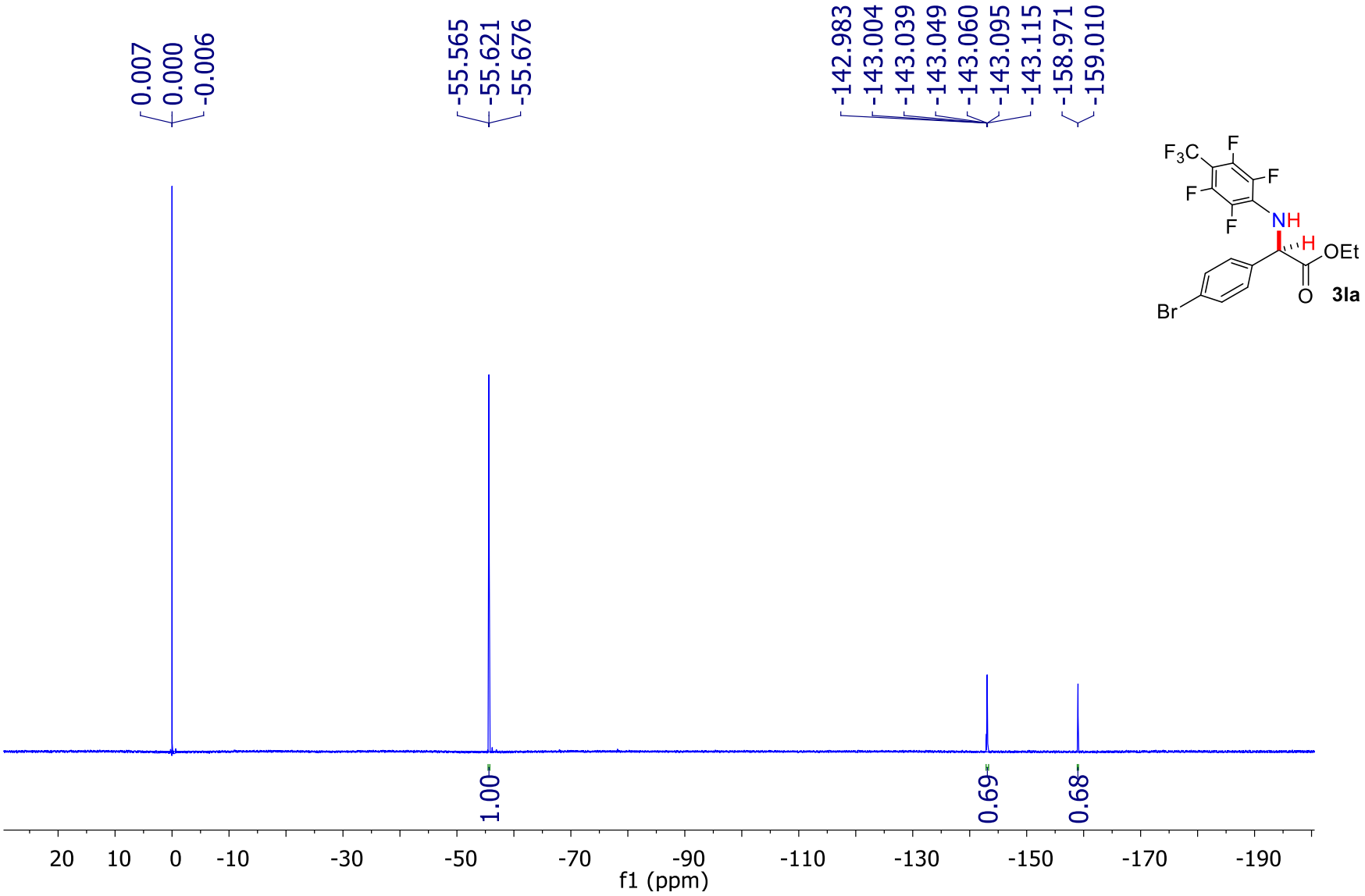
# $^{1}$H NMR


7.509
7.492
7.260
7.244
5.533
5.431
5.415
4.289
4.275
4.268
4.253
4.183
4.169
4.162
4.147
1.236
1.222
1.208
F3C
F
F
F
F
NH
H
OEt
O
Br
3Ia
7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
5.8 5.6 5.4 5.2
f1 (ppm)
4.5 4.3 4.1 3.9
f1 (ppm)
2.00
2.46
1.14
1.15
2.35
3.28
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

# $^{13}$C NMR

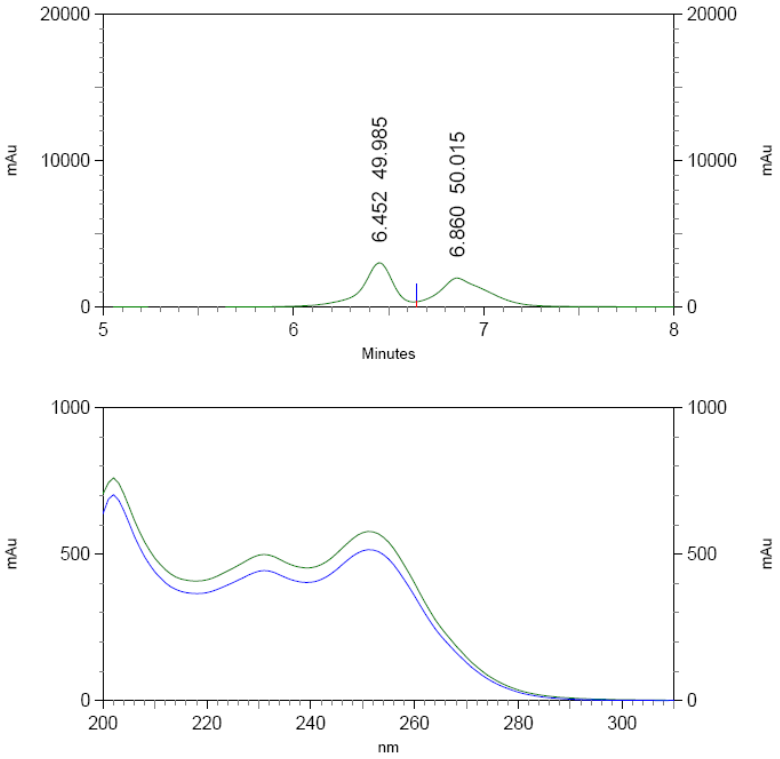

170.299
145.775
145.614
143.824
139.602
137.764
135.780
132.313
128.514
123.109
122.456
120.251
97.673
77.254
77.000
76.746
62.719
60.011
59.979
59.947
13.924
F3C
F
F
F
F
NH
H
OEt
O
Br
3la
128
124
120
f1 (ppm)
148
144
140
136
f1 (ppm)
100
95
f1 (ppm)
grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

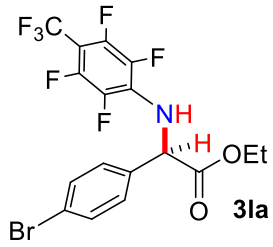
# $^{19}$F NMR


0.007
0.000
-0.006
-55.565
-55.621
-55.676
-142.983
-143.004
-143.039
-143.049
-143.060
-143.095
-143.115
-158.971
-159.010
F3C
F
F
F
F
NH
H
OEt
O
Br
3la
1.00
0.69
0.68
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-III-1-1-Whelk-0.5@-1mL
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
E:\JLM-III-1-1-Whelk-0.5 @1ml



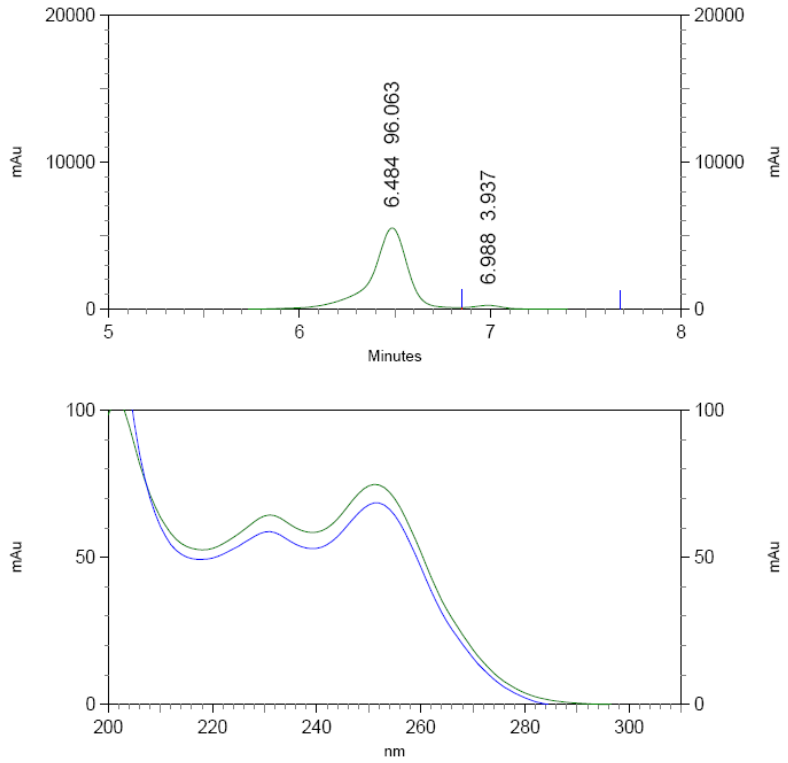



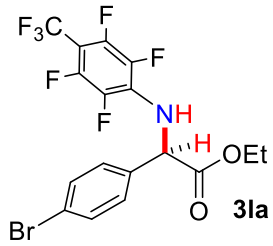

4: 254 nm, 4 nm
Results

| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 6.452 | 49.985 | 1 |
| | 6.860 | 50.015 | 2 |
| Totals | | 100.000 | |

# HPLC

JLM-V-137-1-WHELK-0.5@-1mL
C:\EZStart\Projects\Default\Method\XC-5%-ADH1ml.met
E:\JLM-V-137-1-WHELK0.5@1ml

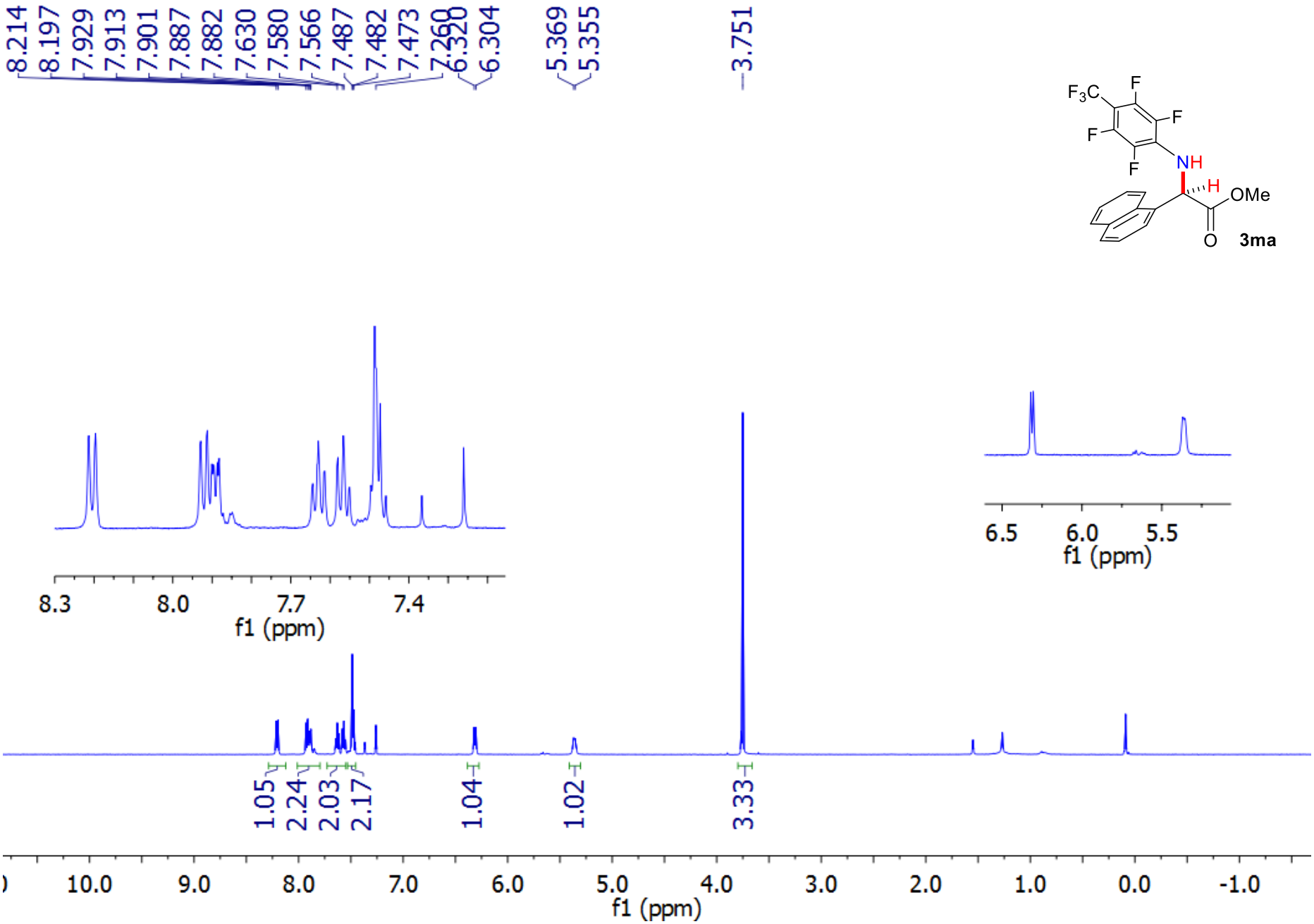


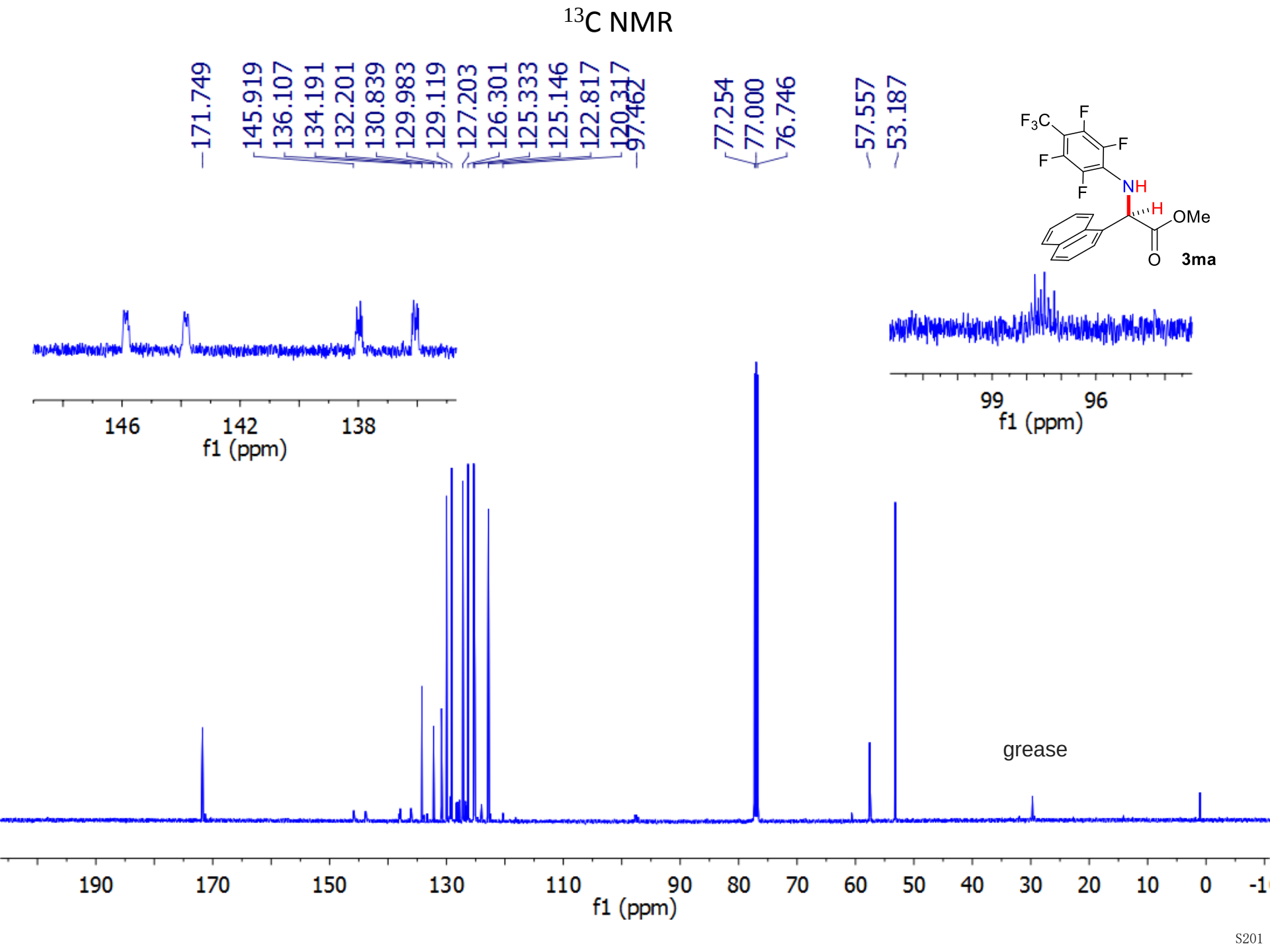

4: 254 nm, 4 nm
Results

| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 6.484 | 96.063 | 1 |
| | 6.988 | 3.937 | 2 |
| Totals | | 100.000 | |

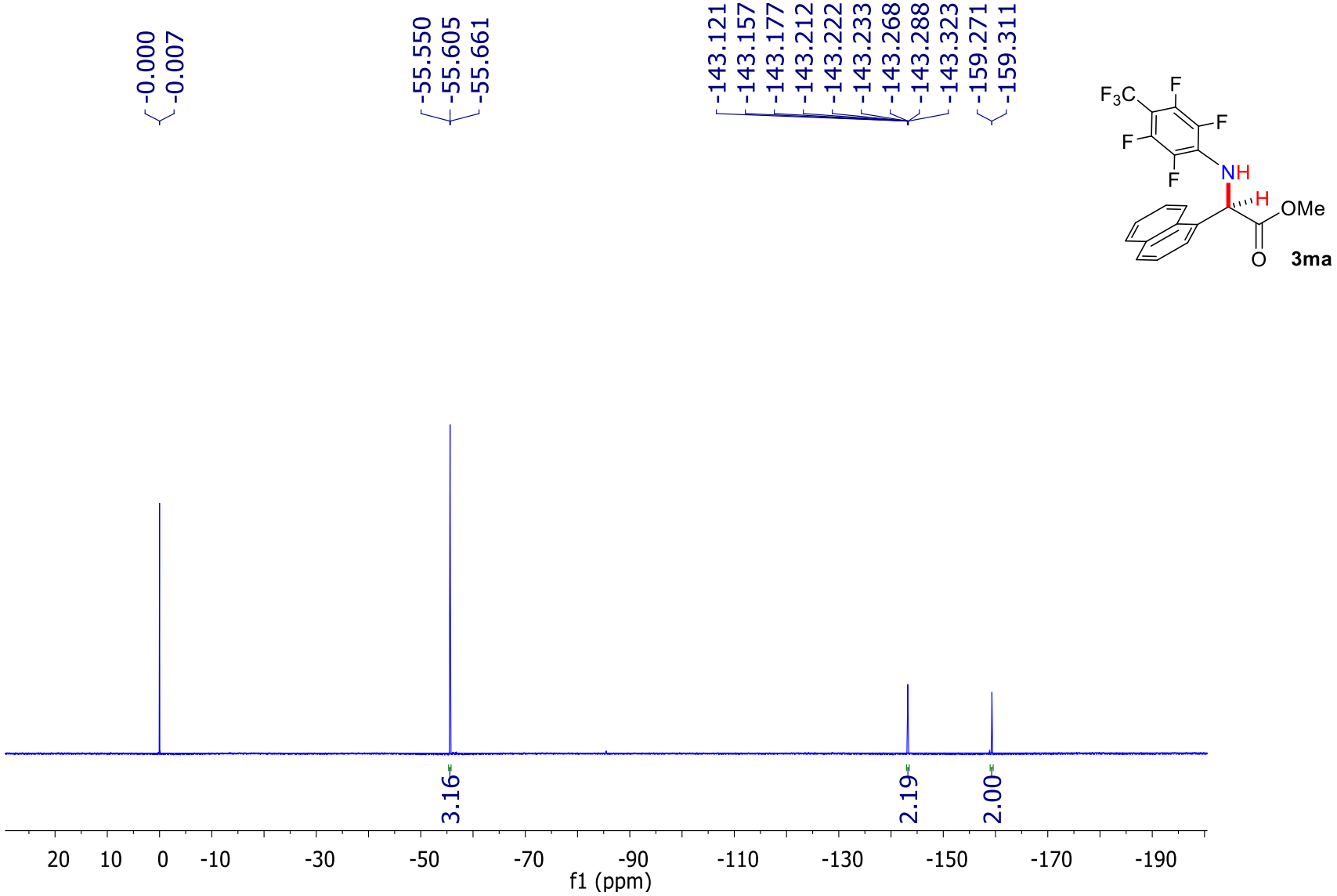
# $^1$H NMR


8.214
8.197
7.929
7.913
7.901
7.887
7.882
7.630
7.580
7.566
7.487
7.482
7.473
7.260
6.320
6.304
5.369
5.355
3.751
F3C
F
F
F
F
NH
H
OMe
O
3ma
8.3
8.0
7.7
7.4
f1 (ppm)
6.5
6.0
5.5
f1 (ppm)
1.05
2.24
2.03
2.17
1.04
1.02
3.33
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

# $^{13}$C NMR

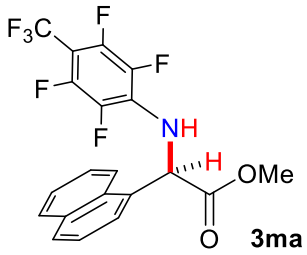

171.749
145.919
136.107
134.191
132.201
130.839
129.983
129.119
127.203
126.301
125.333
125.146
122.817
120.317
97.462
77.254
77.000
76.746
57.557
53.187
F3C
F
F
F
F
NH
H
OMe
O
3ma
146
142
138
f1 (ppm)
99
96
f1 (ppm)
grease
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

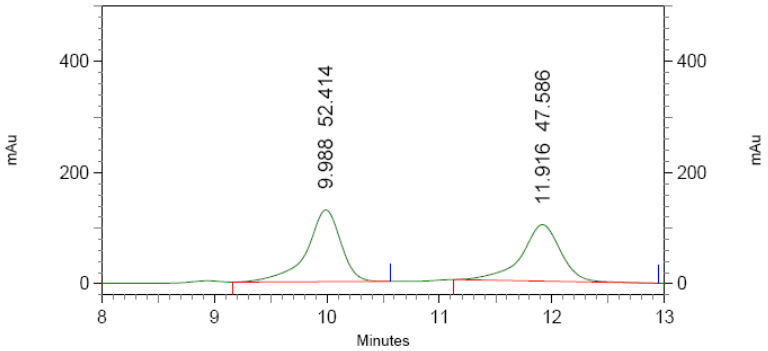
# $^{19}$F NMR

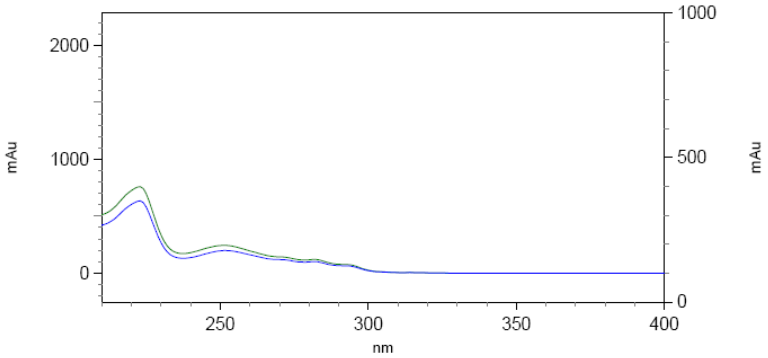

-0.000
-0.007
-55.550
-55.605
-55.661
-143.121
-143.157
-143.177
-143.212
-143.222
-143.233
-143.268
-143.288
-143.323
-159.271
-159.311
F3C
F
F
F
F
NH
H
OMe
O
3ma
3.16
2.19
2.00
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

# HPLC

JLM-II-218-1-WHELK-0.5@1ML
C:\EZStart\Projects\Default\Method\JLM-ODH-0%-0.7ml.met
C:\Documents and Settings\zhang\Desktop\Jin-Lim\HPLC-data\JLM-II-218-1-WHELK-0.5@1ML.dat



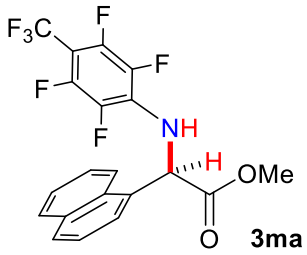



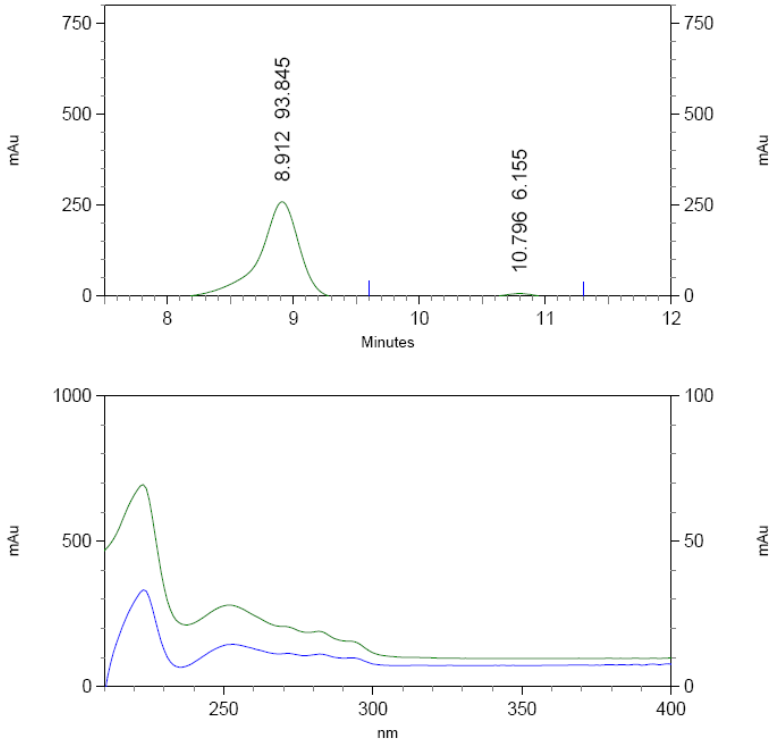

3: 249 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 9.988 | 52.414 |
| 2 | | 11.916 | 47.586 |
| Totals | | | 100.000 |

# HPLC

JLM-V-167-2-WHELK-0.5@-1mL
C:\EZStart\Projects\Default\Method\Joey-ODH-20%-0.8mL.met
C:\EZStart\Projects\Default\Data\JLM-V-167-2-WHELK0.5@1ml

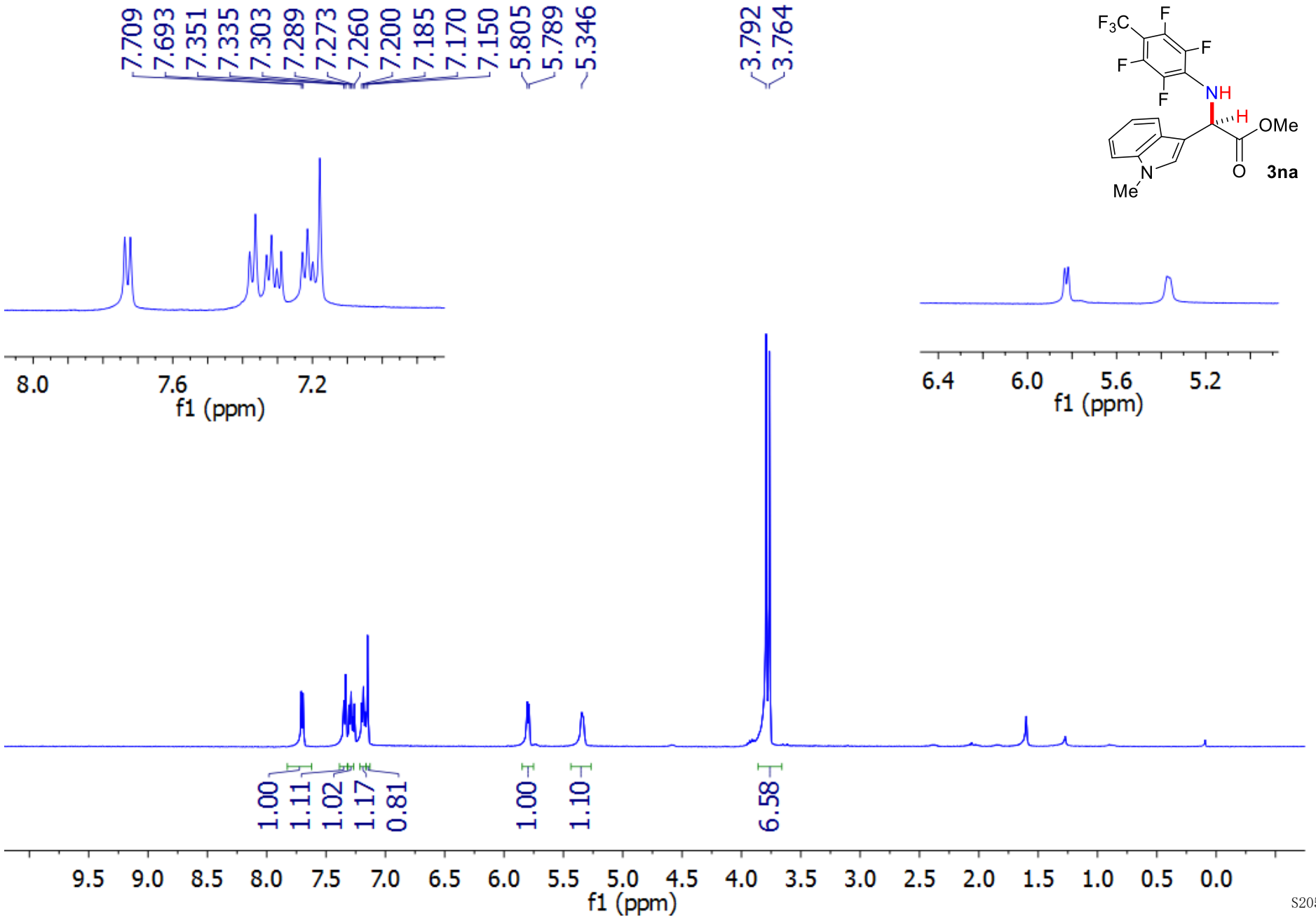


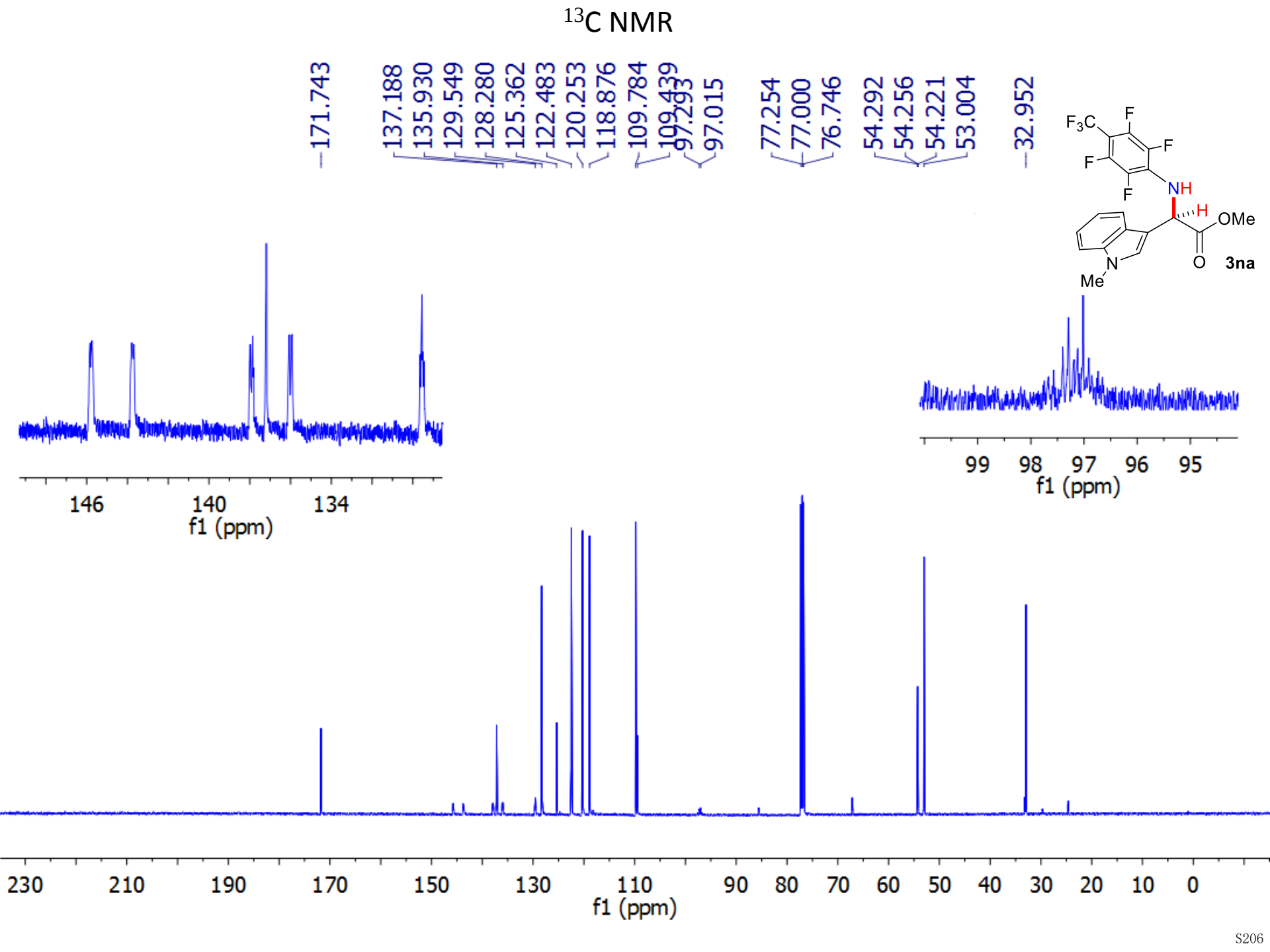

2: 216 nm, 4 nm
Results

| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 8.912 | 93.845 |
| 2 | | 10.796 | 6.155 |
| Totals | | | 100.000 |

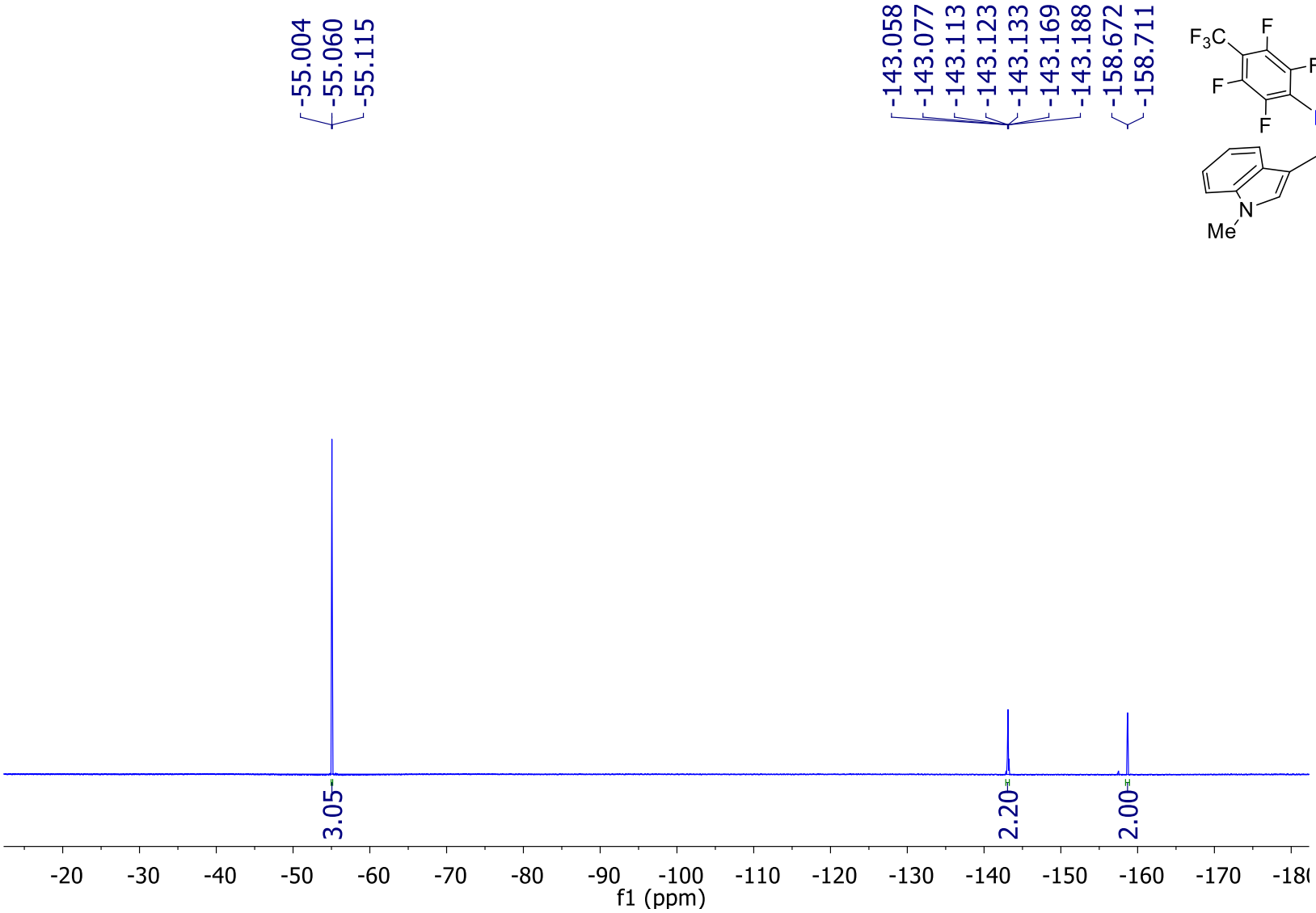
# $^{1}$H NMR


7.709
7.693
7.351
7.335
7.303
7.289
7.273
7.260
7.200
7.185
7.170
7.150
5.805
5.789
5.346
3.792
3.764
F3C
F
F
F
F
NH
H
OMe
O
N
Me
3na
8.0
7.6
7.2
f1 (ppm)
6.4
6.0
5.6
5.2
f1 (ppm)
1.00
1.11
1.02
1.17
0.81
1.00
1.10
6.58
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

# $^{13}$C NMR

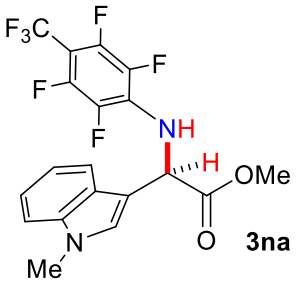

171.743
137.188
135.930
129.549
128.280
125.362
122.483
120.253
118.876
109.784
109.439
97.293
97.015
77.254
77.000
76.746
54.292
54.256
54.221
53.004
32.952
F3C
F
F
F
F
NH
H
OMe
O
N
Me
3na
146
140
134
f1 (ppm)
99
98
97
96
95
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

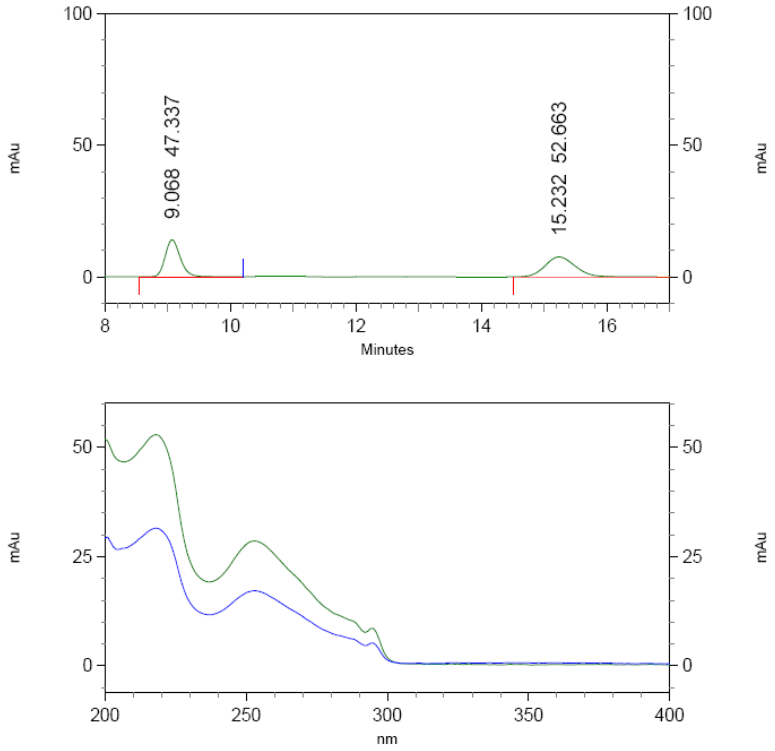

-55.004
-55.060
-55.115
-143.058
-143.077
-143.113
-143.123
-143.133
-143.169
-143.188
-158.672
-158.711
F3C
F
F
F
F
NH
H
OMe
O
N
Me
3na
3.05
2.20
2.00
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

# HPLC

JLM-V-264-1-ADH-1%1ML
E:\SMJ 0% 1mL ADH.met
C:\EZStart\Projects\Default\Data\JLM-V-264-1-ADH1%1ML




**3na**



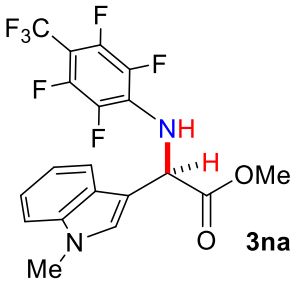

1: 260 nm, 4 nm
Results

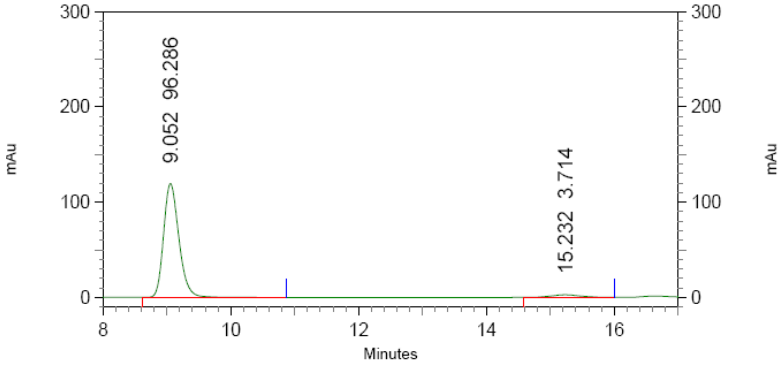
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 9.068 | 47.337 | 1 |
| | 15.232 | 52.663 | 2 |

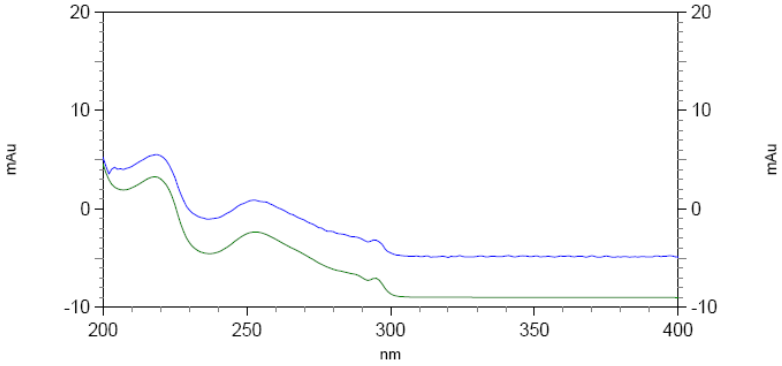
| Totals | | |
|---|---|---|
| | 100.000 | |

# HPLC

JLM-V-264-2-ADH-1%1ML
E:\SMJ 0% 1mL ADH.met
C:\EZStart\Projects\Default\Data\JLM-V-264-2-ADH1%1ML



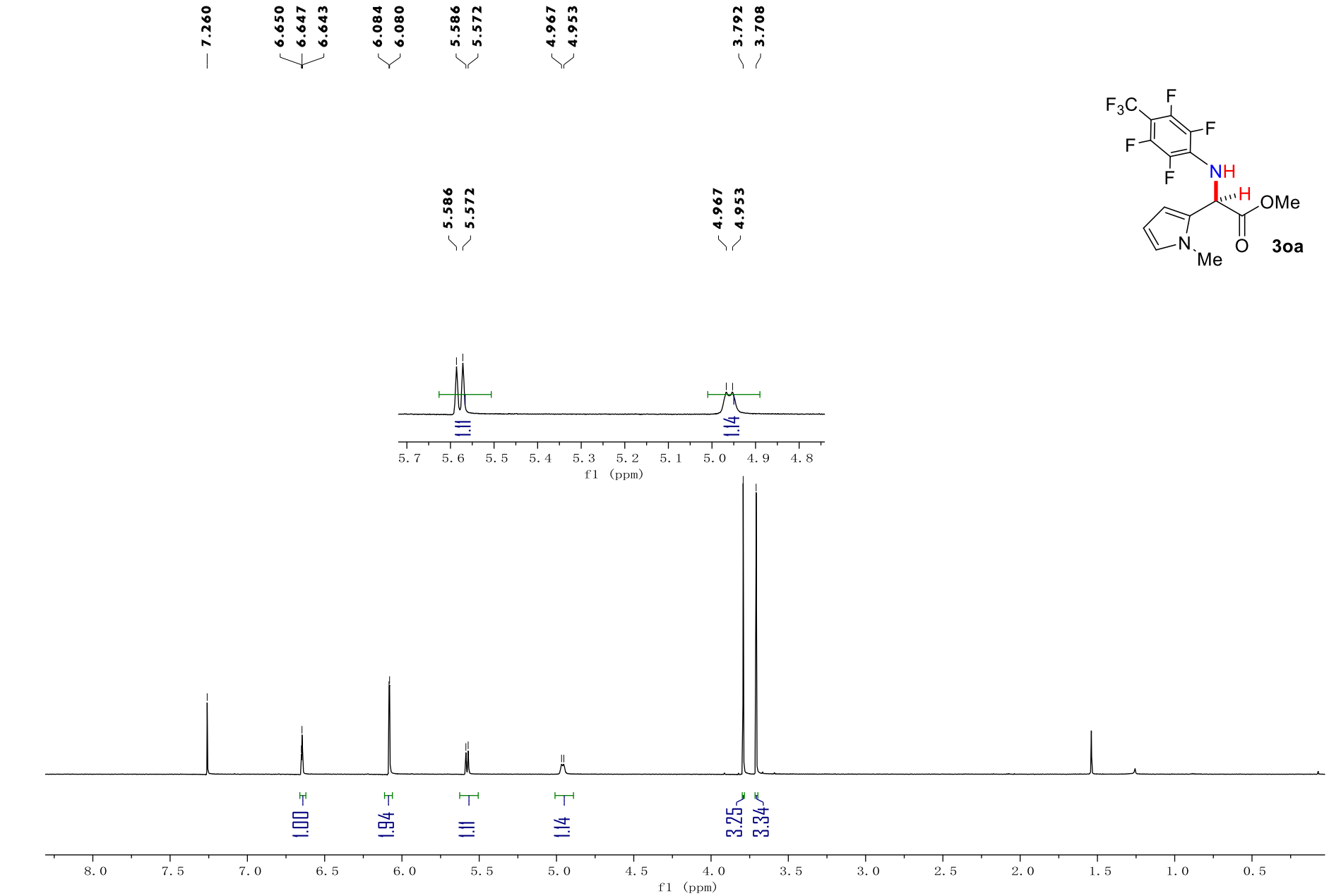




1: 260 nm, 4 nm
Results

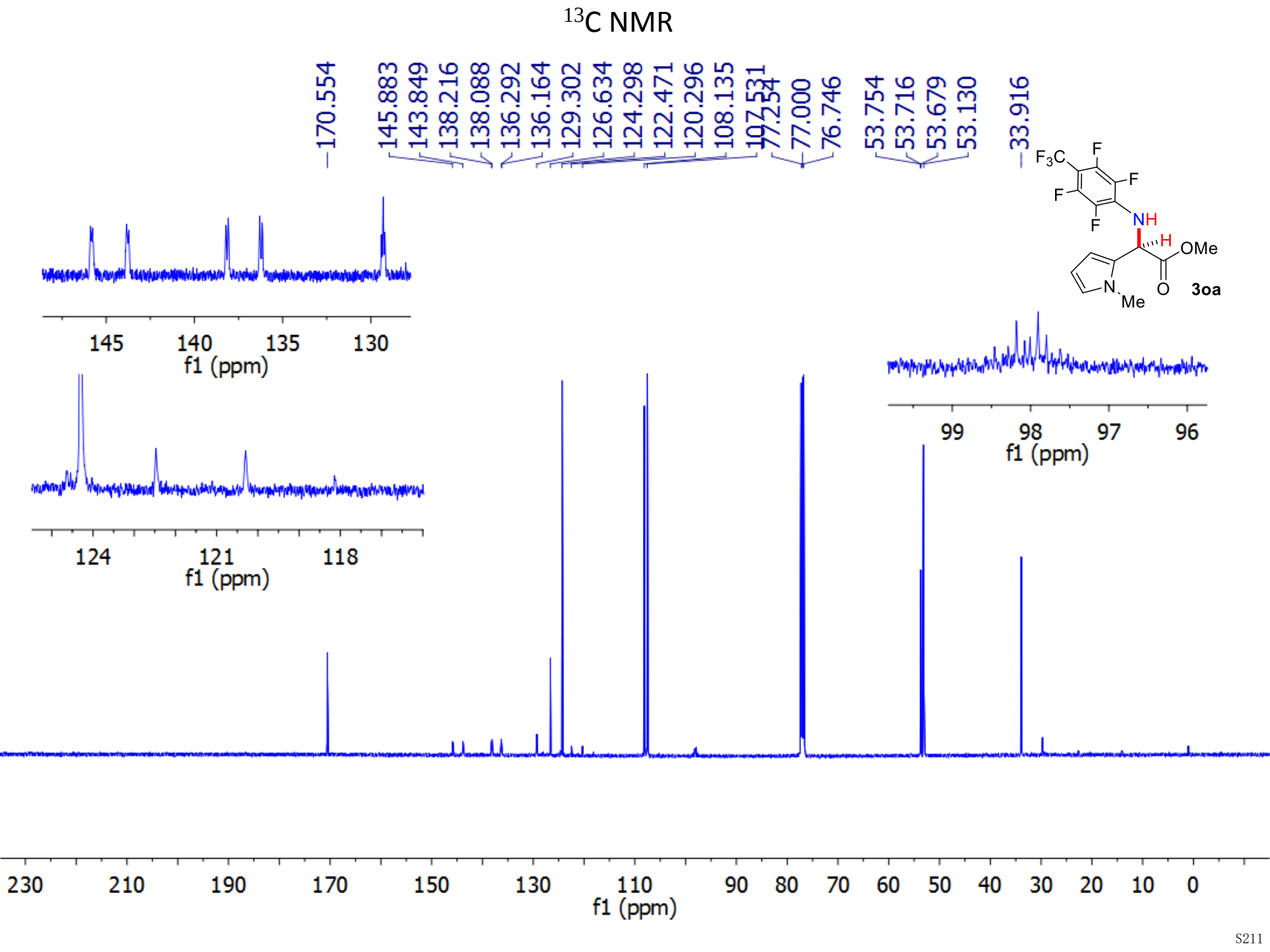
| Name | Retention Time | Area Percent | Pk # |
|---|---|---|---|
| | 9.052 | 96.286 | 1 |
| | 15.232 | 3.714 | 2 |

| Totals | | |
|---|---|---|
| | 100.000 | |

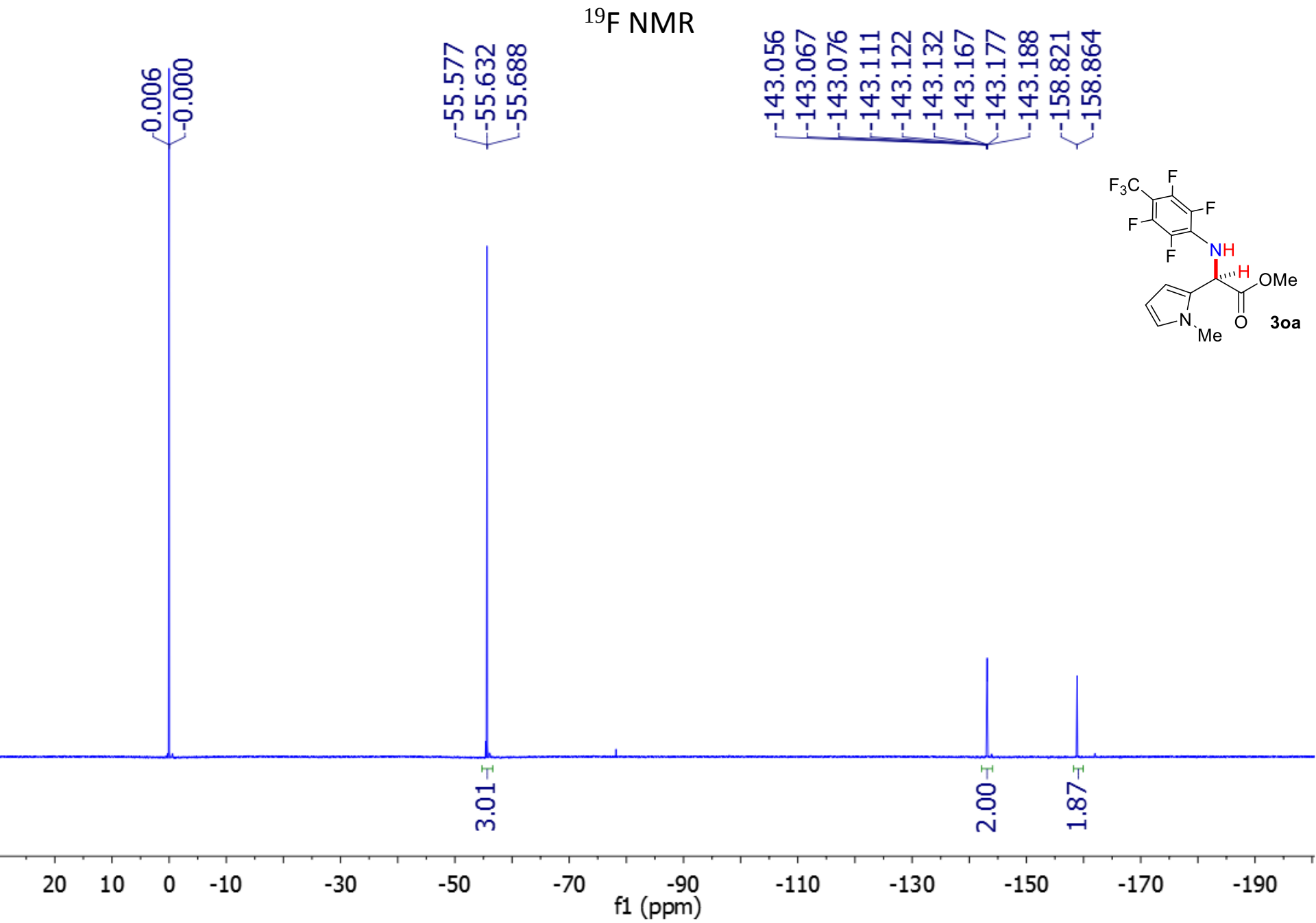
# $^{1}$H NMR


7.260
6.650
6.647
6.643
6.084
6.080
5.586
5.572
4.967
4.953
3.792
3.708
F3C
F
F
F
F
NH
H
OMe
O
N
Me
3oa
1.11
1.14
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8
f1 (ppm)
1.00
1.94
1.11
1.14
3.25
3.34
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

# $^{13}$C NMR

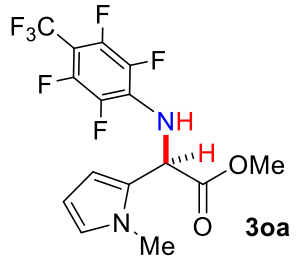

170.554
145.883
143.849
138.216
138.088
136.292
136.164
129.302
126.634
124.298
122.471
120.296
108.135
77.254
77.000
76.746
53.754
53.716
53.679
53.130
33.916
F3C
F
F
F
F
NH
H
OMe
O
N
Me
3oa
145
140
135
130
f1 (ppm)
124
121
118
f1 (ppm)
99
98
97
96
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

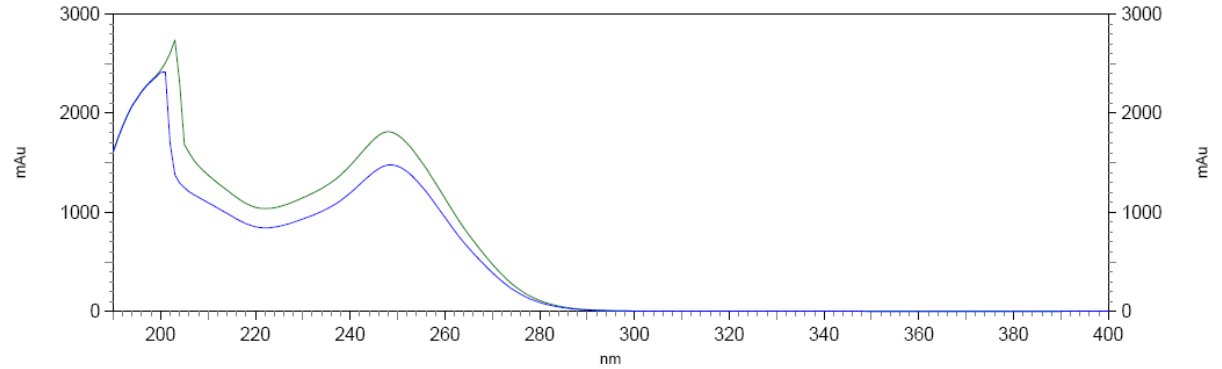

0.006
-0.000
-55.577
-55.632
-55.688
-143.056
-143.067
-143.076
-143.111
-143.122
-143.132
-143.167
-143.177
-143.188
-158.821
-158.864
F3C
F
F
F
F
NH
H
OMe
O
N
Me
3oa
3.01
2.00
1.87
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

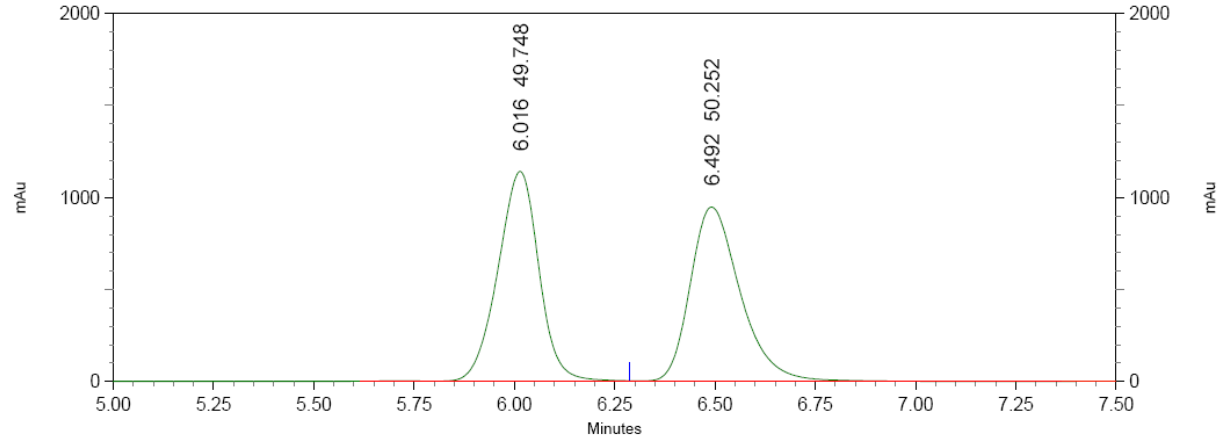
# HPLC

JLM-V-294-1-ADH-1%1ML
C:\EZStart\Projects\Default\Data\JLM-V-294-1-ADH1%1ML
C:\EZStart\Projects\Default\Method\YC-1%-OJH1ml.met
AD-H column 20%IPA @ 0.8ml/min




**3oa**



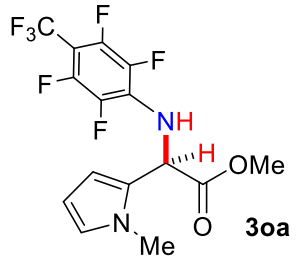



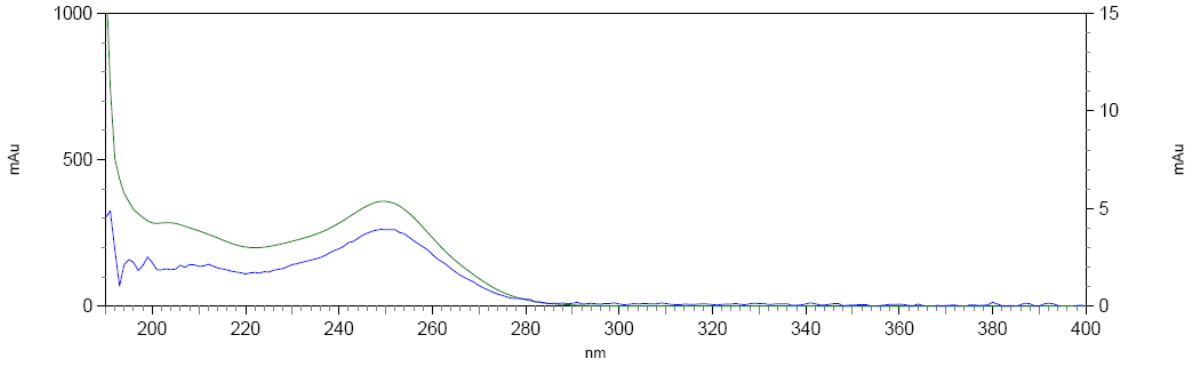

1: 260 nm, 4 nm Results

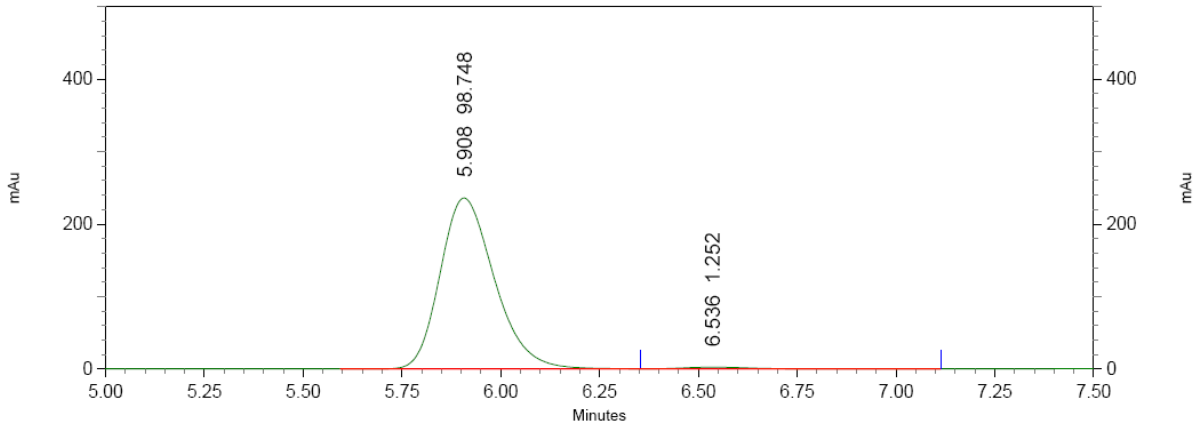
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.016 | 49.748 |
| 2 | 6.492 | 50.252 |
| Totals | | 100.000 |

# HPLC

JLM-V-294-2a-ADH-1%1ML
C:\EZStart\Projects\Default\Data\JLM-V-294-2a-ADH1%1ML
C:\EZStart\Projects\Default\Method\YC-1%-OJH1ml.met
AD-H column 20%IPA @ 0.8ml/min



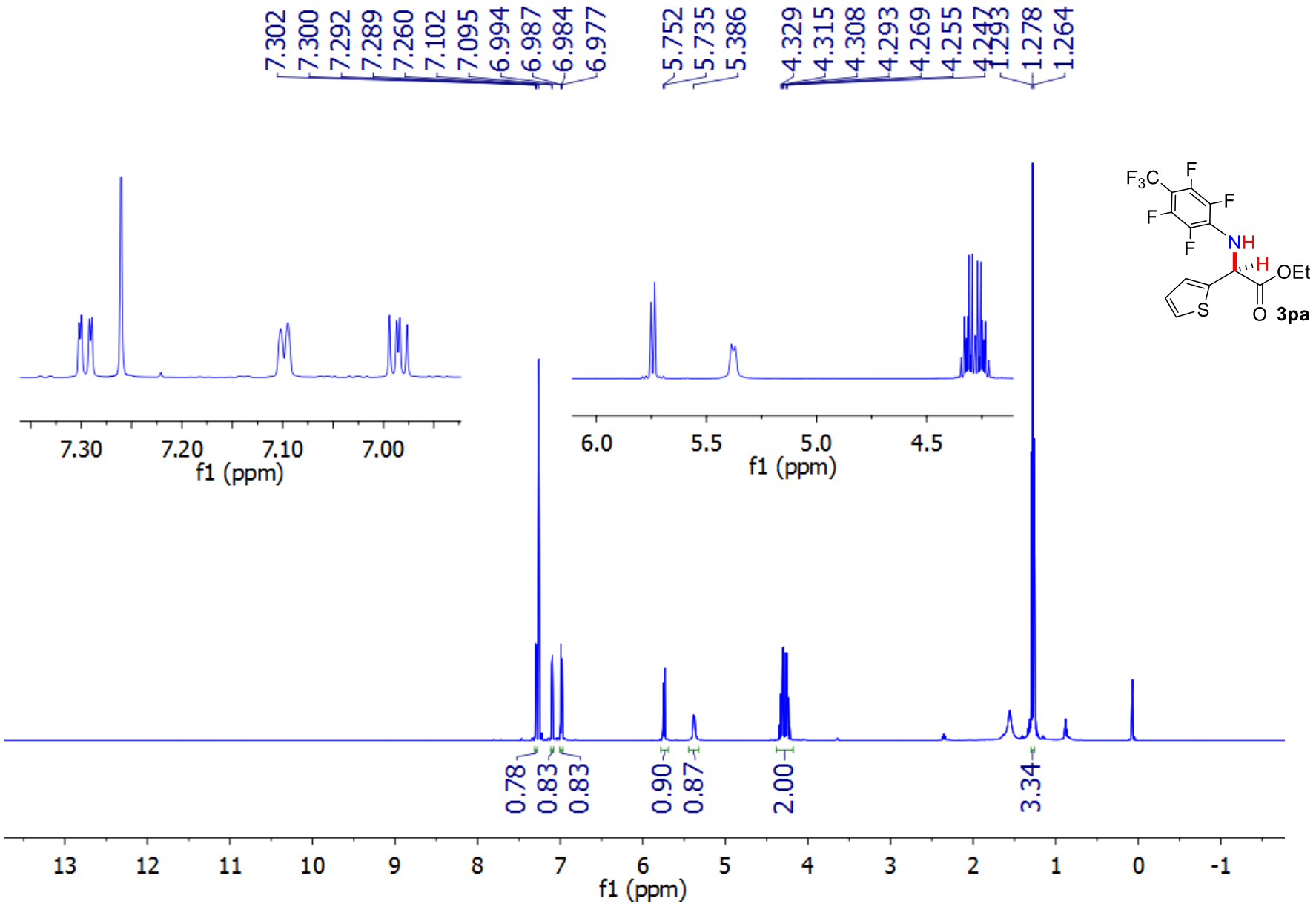



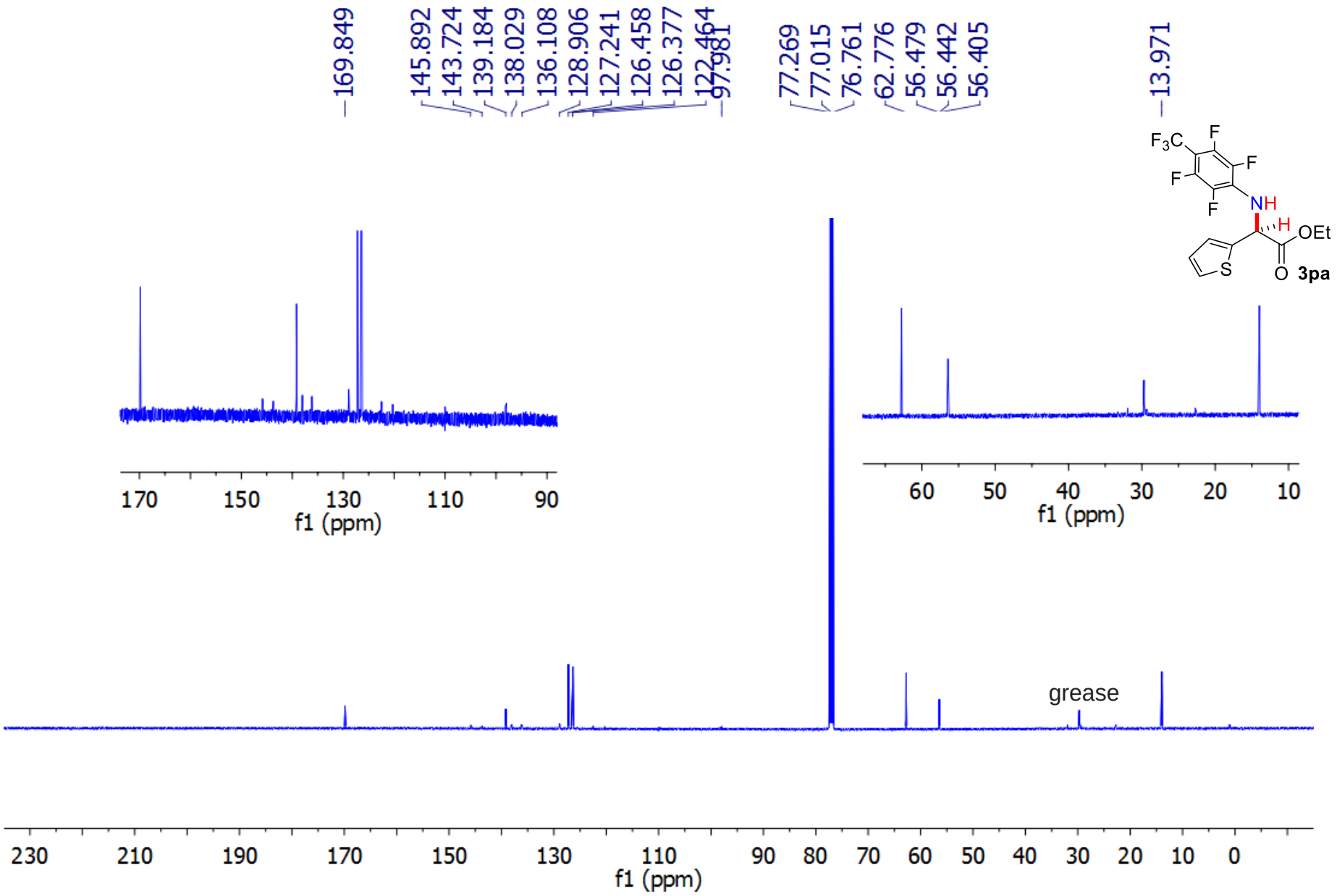

1: 260 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.908 | 98.748 |
| 2 | 6.536 | 1.252 |
| Totals | | 100.000 |

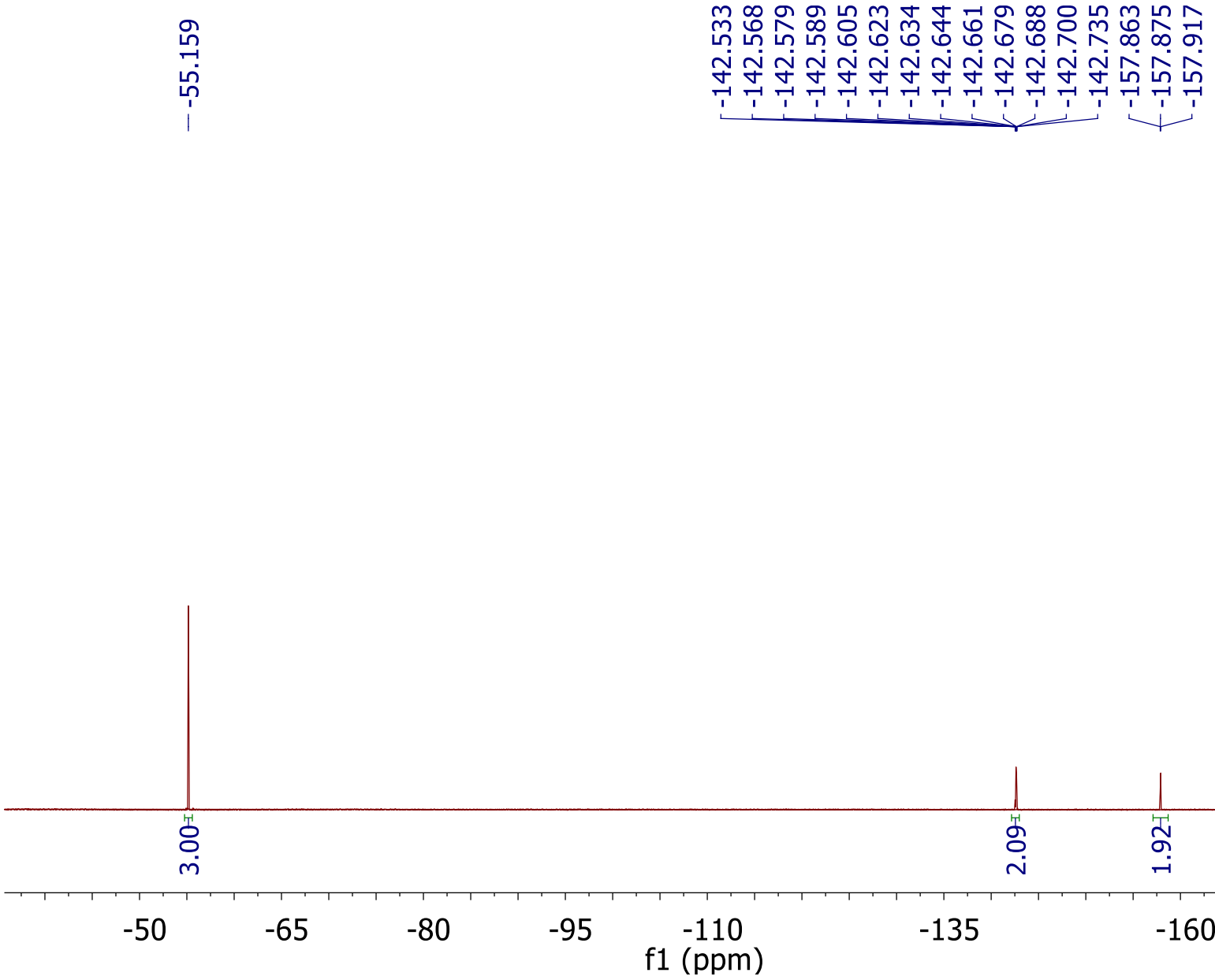
# $^{1}$H NMR

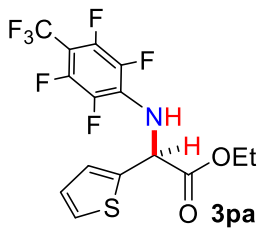

7.302
7.300
7.292
7.289
7.260
7.102
7.095
6.994
6.987
6.984
6.977
5.752
5.735
5.386
4.329
4.315
4.308
4.293
4.269
4.255
4.247
4.243
1.278
1.264
7.30
7.20
7.10
7.00
f1 (ppm)
6.0
5.5
5.0
4.5
f1 (ppm)
F3C
F
F
F
F
NH
H
OEt
S
O
3pa
0.78
0.83
0.83
0.90
0.87
2.00
3.34
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

$^{13}$C NMR


169.849
145.892
143.724
139.184
138.029
136.108
128.906
127.241
126.458
126.377
122.464
97.981
77.269
77.015
76.761
62.776
56.479
56.442
56.405
13.971
F3C
F
F
F
F
NH
H
OEt
S
O
3pa
170
150
130
110
90
f1 (ppm)
60
50
40
30
20
10
f1 (ppm)
grease
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

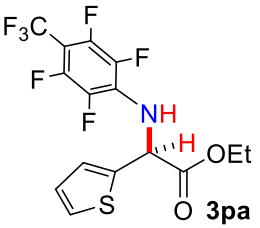
# $^{19}$F NMR

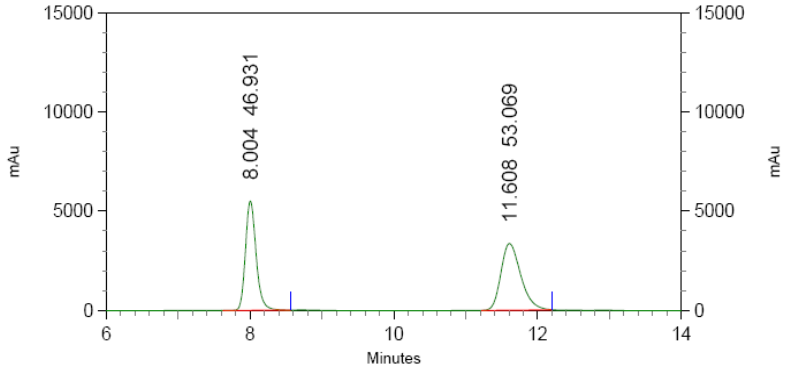

-55.159
-142.533
-142.568
-142.579
-142.589
-142.605
-142.623
-142.634
-142.644
-142.661
-142.679
-142.688
-142.700
-142.735
-157.863
-157.875
-157.917
3.00
2.09
1.92
-50
-65
-80
-95
-110
-135
-160
f1 (ppm)

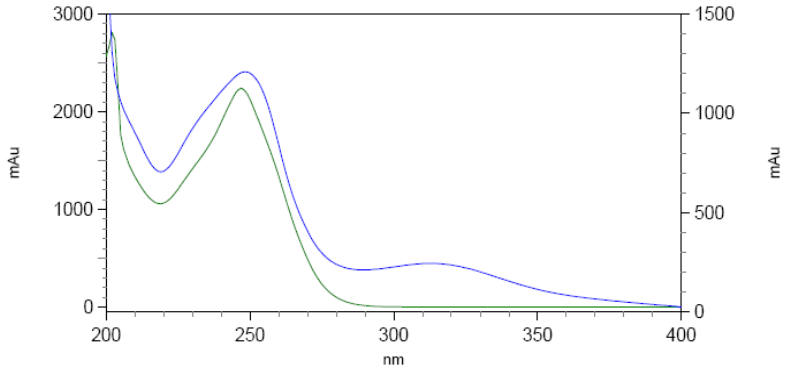

F3C
F
F
F
F
NH
H
OEt
S
O
3pa

# HPLC

JLM-V-144-1a-ODH1%0.7ML
C:\EZStart\Projects\Default\Method\JLM-ODH-0.2%-0.7ml.met
C:\EZStart\Projects\Default\Data\JLM-V-144-1a-ODH1%0.7ML



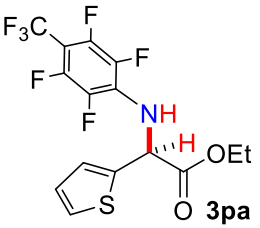

3: 254 nm, 4 nm
Results

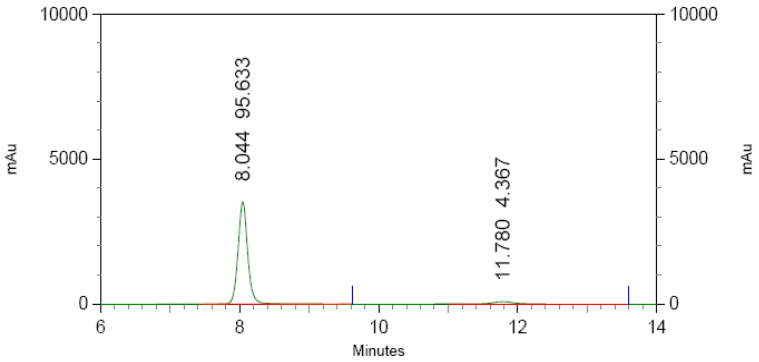
| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 8.004 | 46.931 |
| 2 | | 11.608 | 53.069 |

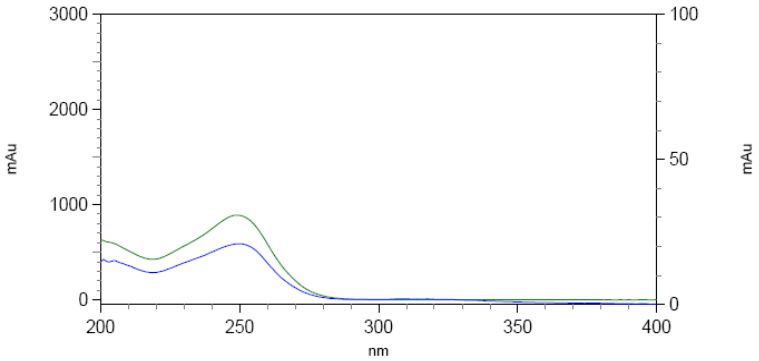
| Totals | 100.000 |
|---|---|

# HPLC

JLM-V-144-2a-ODH1%0.7ML
C:\EZStart\Projects\Default\Method\JLM-ODH-0.2%-0.7ml.met
C:\EZStart\Projects\Default\Data\JLM-V-144-2a-ODH1%0.7ML



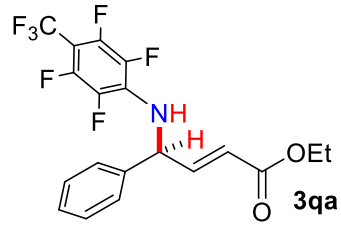



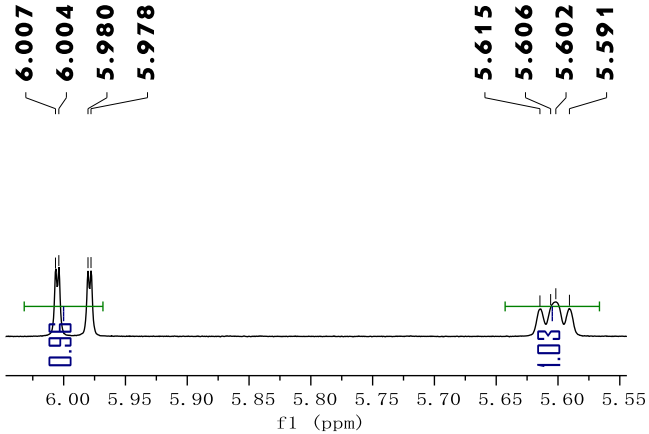

4: 247 nm, 4 nm
Results

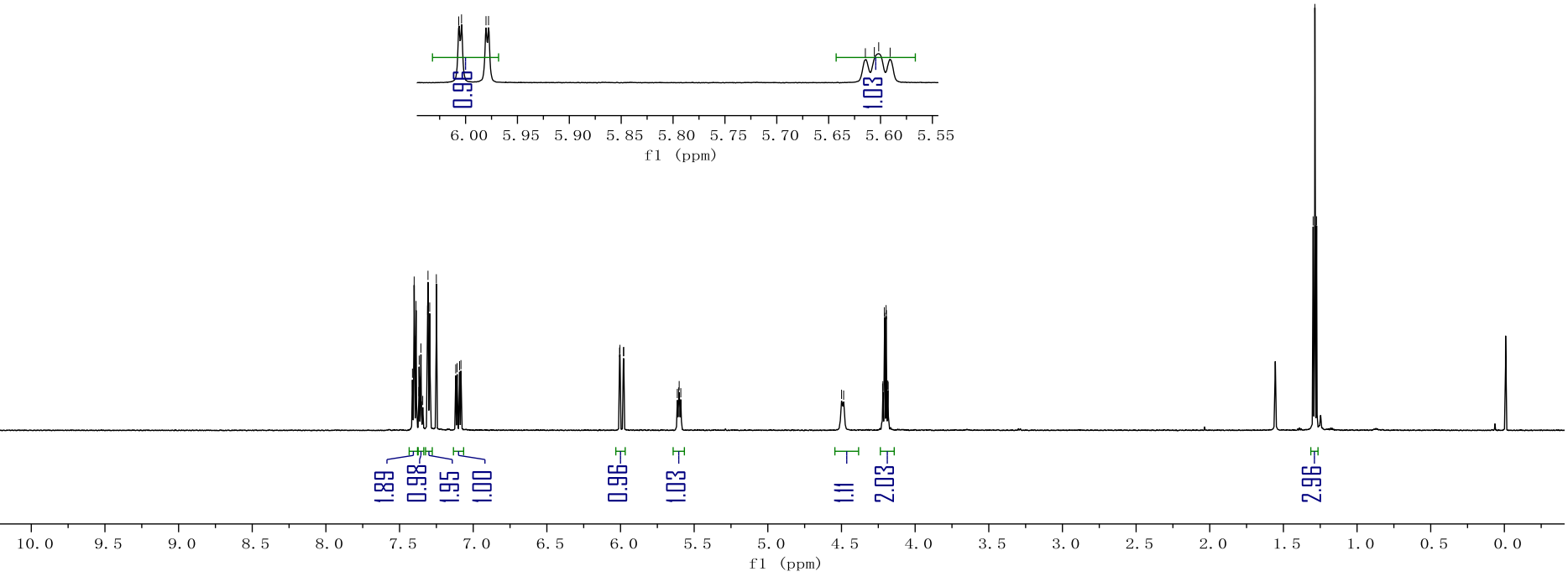
| Pk # | Name | Retention Time | Area Percent |
|---|---|---|---|
| 1 | | 8.044 | 95.633 |
| 2 | | 11.780 | 4.367 |
| Totals | | | 100.000 |

# $^1$H NMR


7.401
7.398
7.388
7.367
7.355
7.355
7.310
7.307
7.298
7.295
7.250
7.119
7.109
7.093
7.083
6.007
6.004
5.980
5.978
5.615
5.606
5.602
5.591
4.500
4.485
4.221
4.219
4.209
4.207
4.197
4.195
4.185
4.183
1.298
1.286
1.274

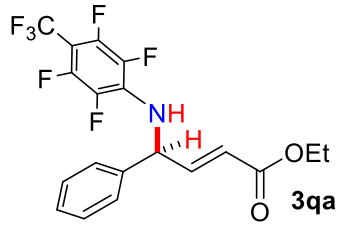

F3C
F
F
F
F
NH
H
OEt
O
3qa


6.007
6.004
5.980
5.978
5.615
5.606
5.602
5.591
0.96
1.03
6.00 5.95 5.90 5.85 5.80 5.75 5.70 5.65 5.60 5.55
f1 (ppm)

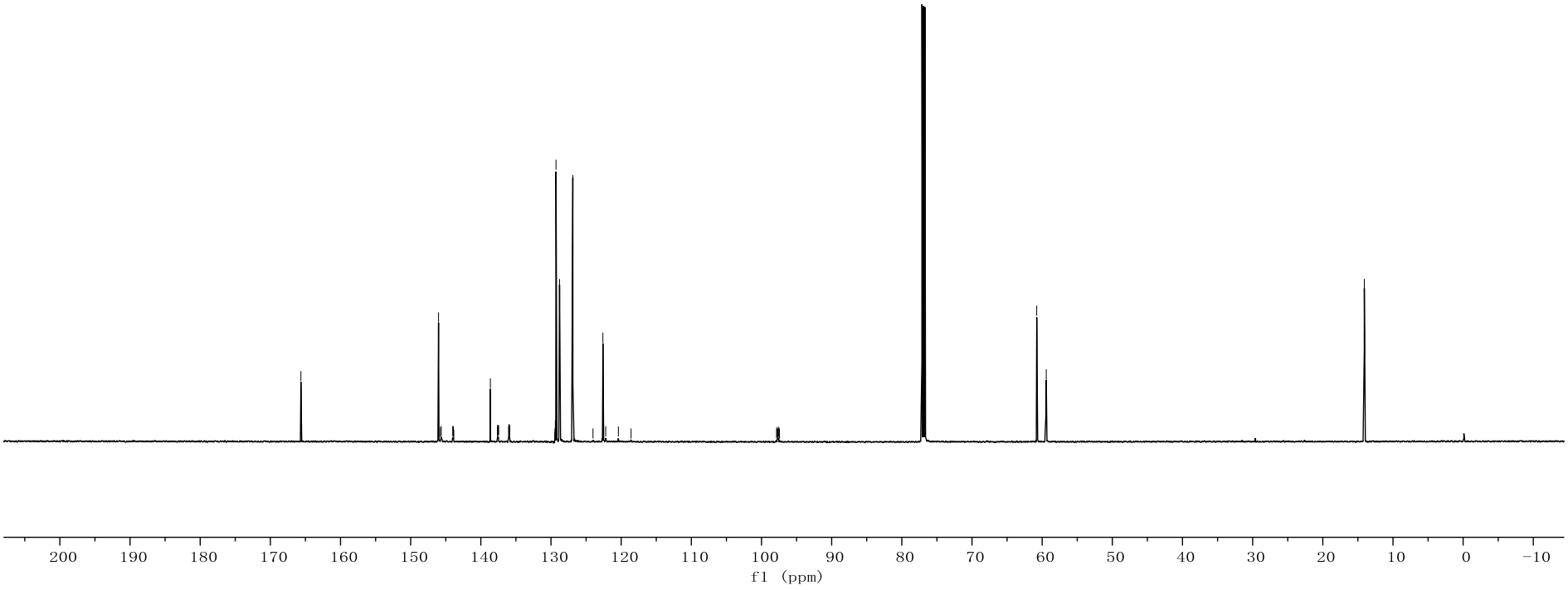

1.89
0.98
1.95
1.00
0.96
1.03
1.11
2.03
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

# $^{13}$C NMR

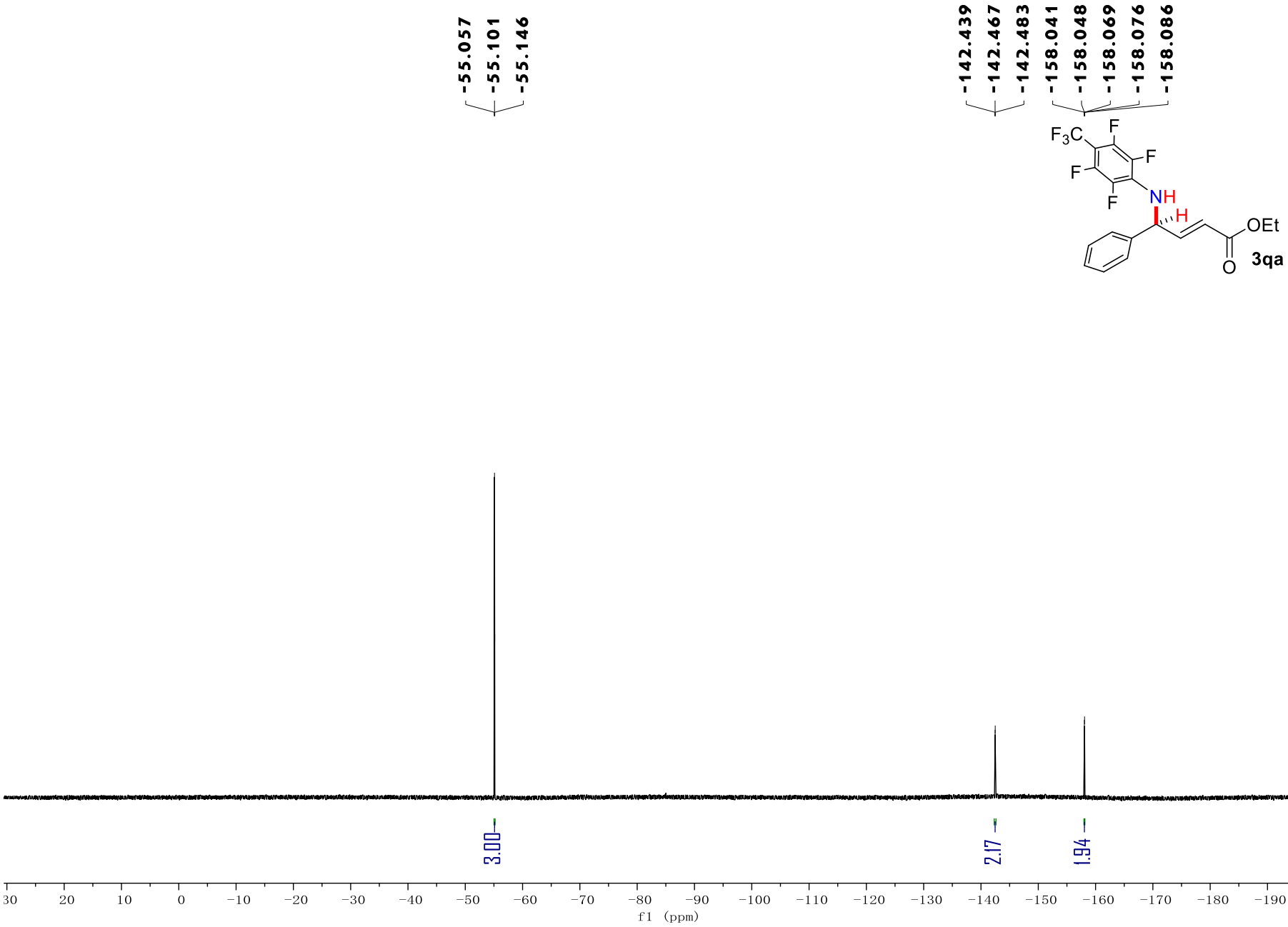
165.644 146.029 145.755 145.649 144.001 143.952 143.936 143.851 138.639 137.639 137.605 137.501 137.467 136.041 136.007 135.977 135.938 135.905 135.872 129.447 129.384 129.361 129.288 128.782 126.889 124.017 122.604 122.207 120.397 118.586 97.856 97.768 97.679 97.623 97.535 97.444 60.775 59.447 59.416 59.386 14.083




**3qa**



# $^{19}$F NMR

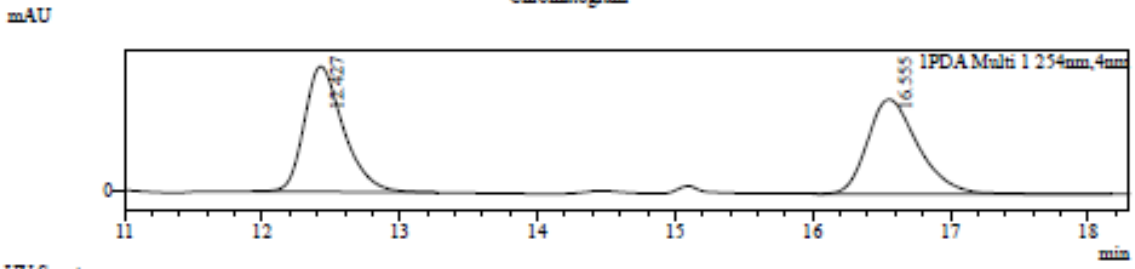

-55.057
-55.101
-55.146
-142.439
-142.467
-142.483
-158.041
-158.048
-158.069
-158.076
-158.086
F3C
F
F
F
F
NH
H
OEt
O
3qa
3.00
2.17
1.94
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −2
f1 (ppm)

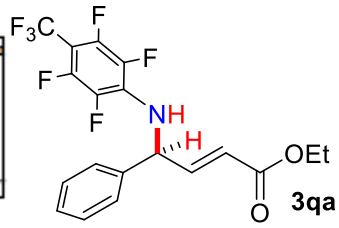
# HPLC

Sample Information

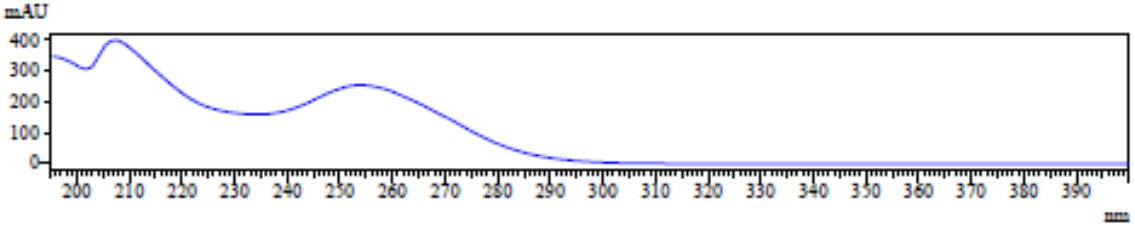
| | |
|---|---|
| Sample Name | : P0X403-ODH-5%0.8mL |
| Sample ID | : P0X403-ODH-5%0.8mL |
| Data File | : P0X403-ODH-5%0.8mL.lcd |
| Method File | : XXW-5%.0.8.mL.lcm |

Chromatogram

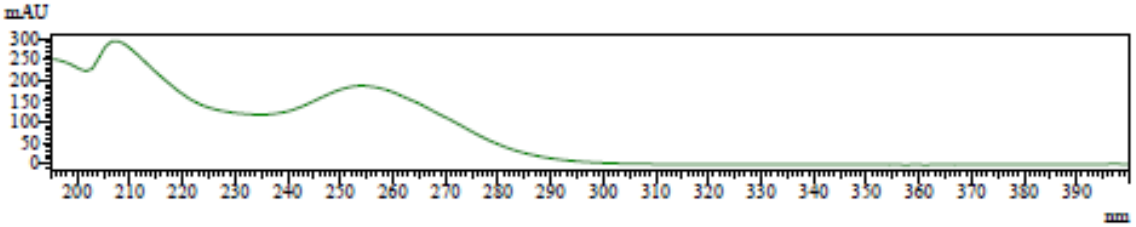



UV Spectrum
Retention time = 12.427




UV Spectrum
Retention time = 16.555




Peak Table

PDA Ch1 254nm

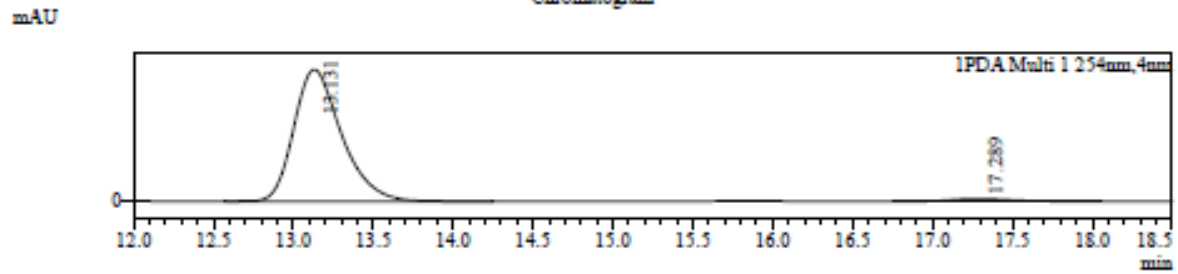
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 12.427 | 4973148 | 50.583 |
| 2 | 16.555 | 4858545 | 49.417 |
| Total | | 9831693 | 100.000 |

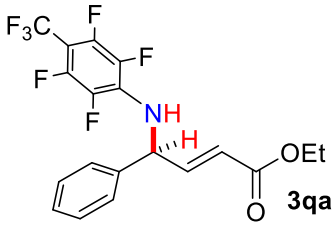
# HPLC

Sample Information

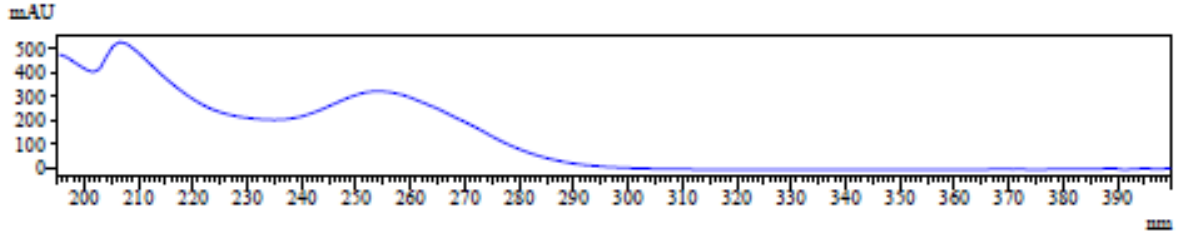
| | |
|---|---|
| Sample Name | : P0X413-ODH-5%0.8mL |
| Sample ID | : P0X413-ODH-5%0.8mL |
| Data File | : P0X413-ODH-5%0.8mL.lcd |
| Method File | : P0X-5%.0.8.mL-15Min.lcm |

Chromatogram

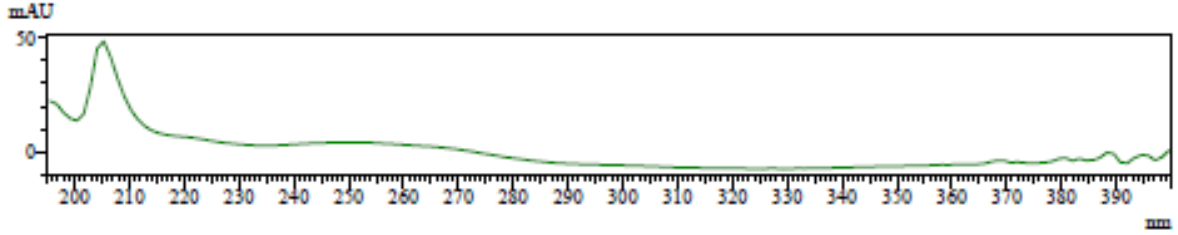



UV Spectrum
Retention time = 13.131




UV Spectrum
Retention time = 17.289




Peak Table

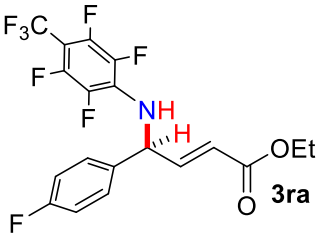
PDA Ch1 254nm

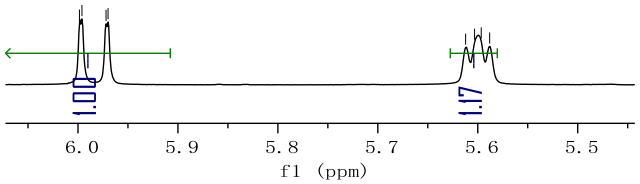
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 13.131 | 6677753 | 97.205 |
| 2 | 17.289 | 191990 | 2.795 |
| Total | | 6869744 | 100.000 |

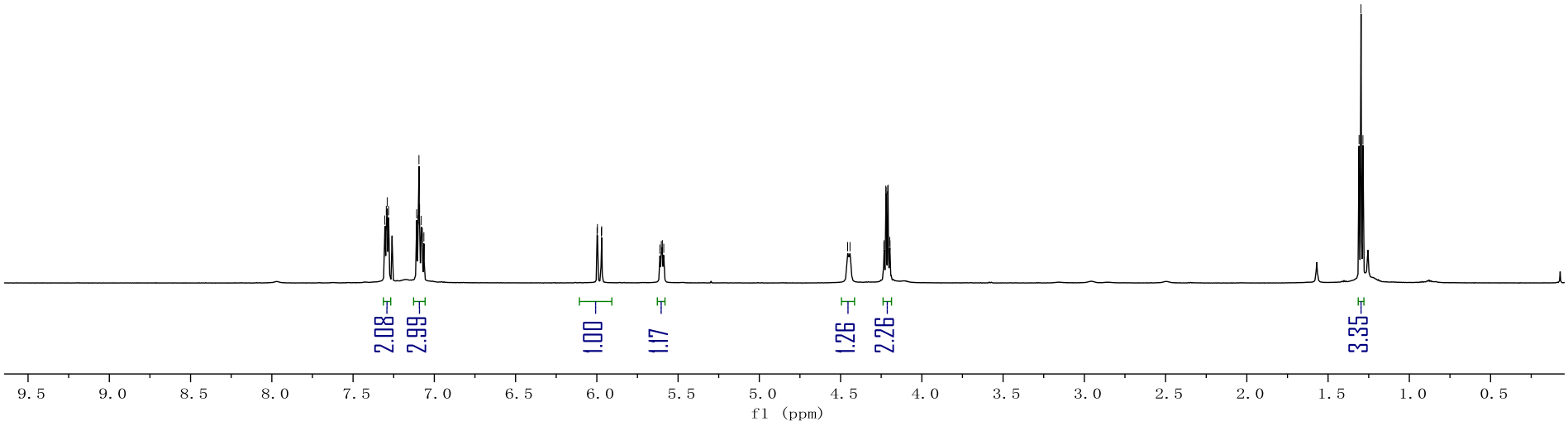
# $^1$H NMR

7.304 7.296 7.290 7.281 7.109 7.100 7.095 7.090 7.080 7.074 7.064 5.999 5.996 5.972 5.970 5.612 5.603 5.597 5.588 4.457 4.442 4.234 4.231 4.228 4.221 4.219 4.210 4.208 4.197 4.196 1.309 1.298 1.286

5.999 5.996 5.972 5.970 5.612 5.603 5.597 5.588

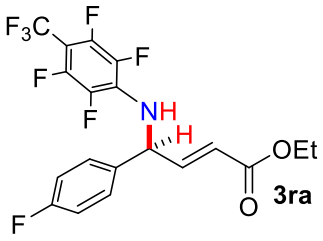


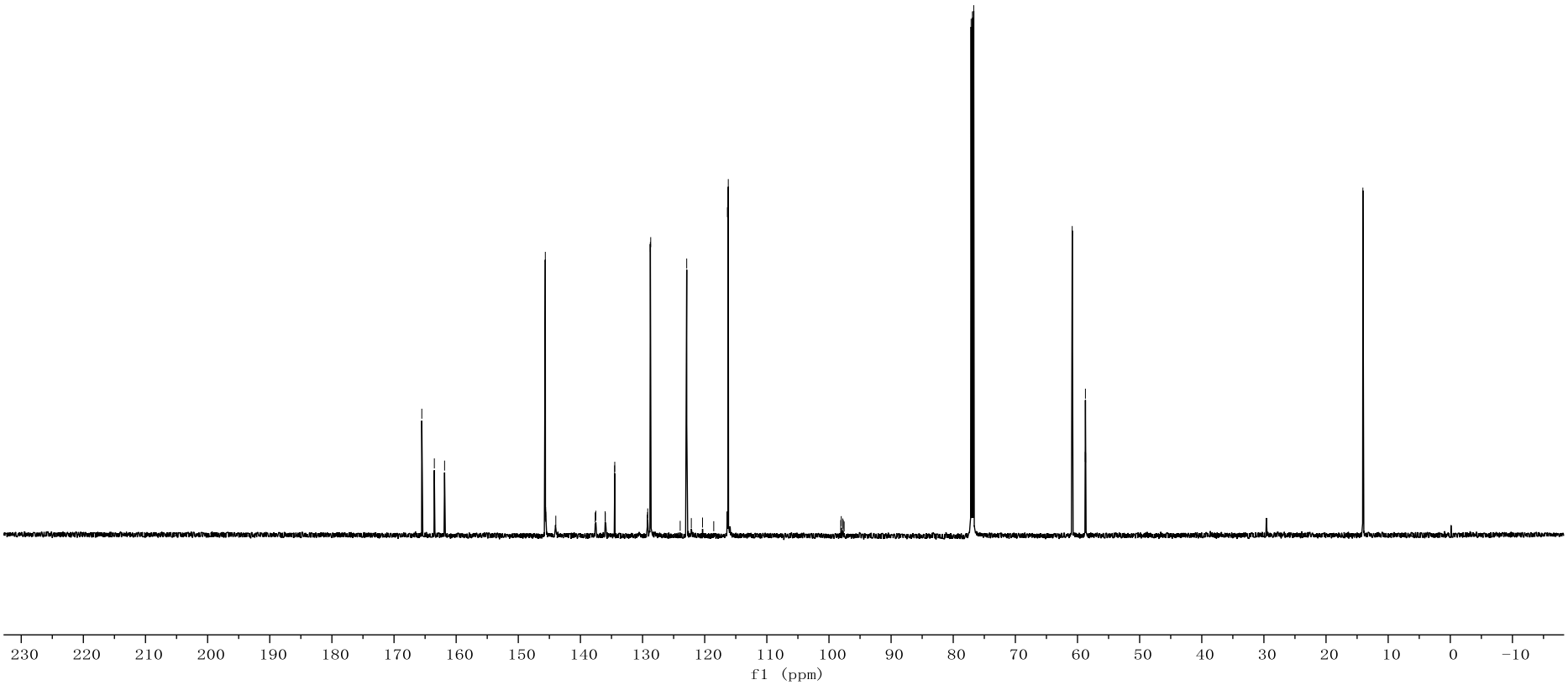



# $^{13}$C NMR

165.529 163.513 161.865 145.709 145.653 145.608 145.585 143.964 137.624 137.516 136.025 135.996 134.500 134.477 129.242 129.192 129.168 128.747 128.690 123.946 122.895 122.156 120.351 118.544 116.348 116.203 98.109 98.021 97.789 97.700 97.557 77.125 76.912 76.701 60.849 58.754 58.724 58.693 14.071



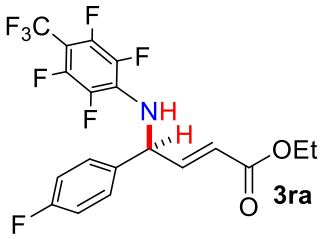
# $^{19}$F NMR

-55.080
-55.117
-55.154

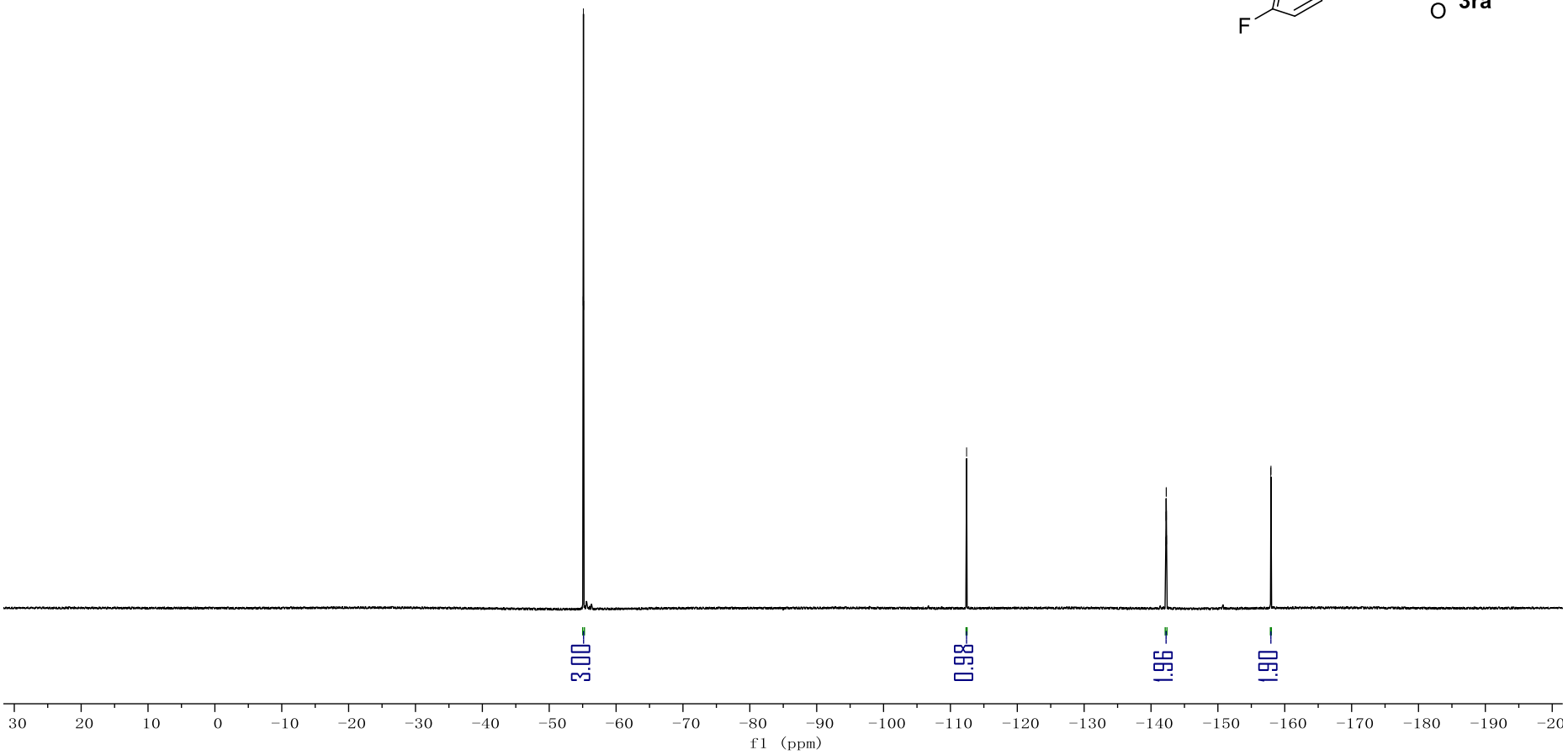
-112.406
-112.413
-112.421
-112.427
-112.430
-112.436

-142.232
-142.246
-142.270
-142.276
-142.283
-142.306
-142.320

-157.900
-157.908
-157.914
-157.931
-157.937
-157.945
-157.952




**3ra**

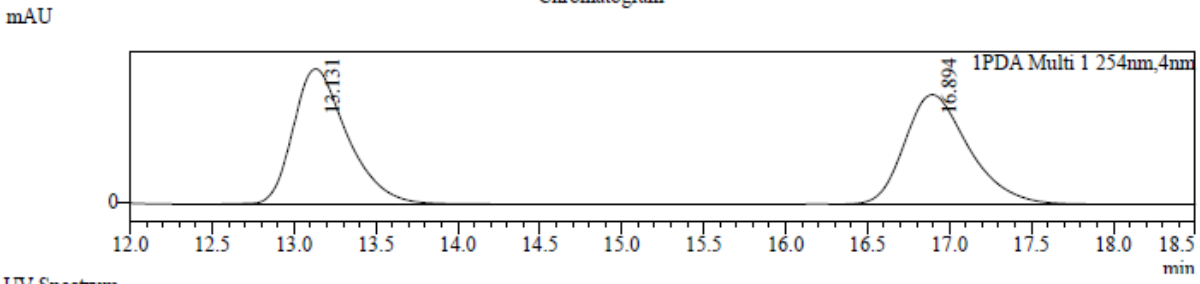


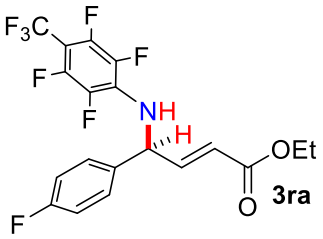
# HPLC

Sample Information

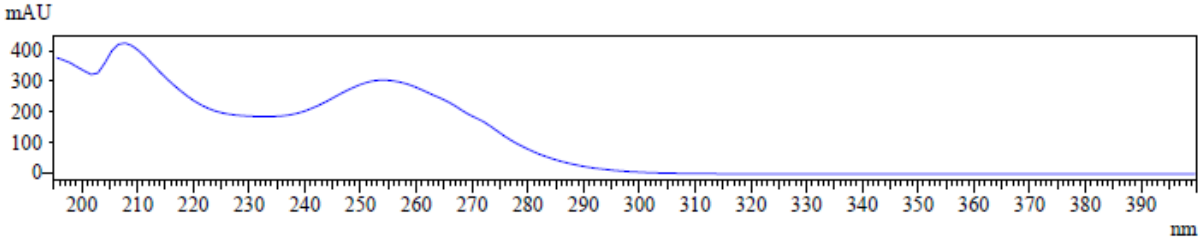
Sample Name : P0X-0575-ODH-5%0.8mL
Sample ID : P0X-0575-ODH-5%0.8mL
Data File : P0X-0575-ODH-5%0.8mL.lcd
Method File : XXW-5%.0.8.mL.lcm

Chromatogram

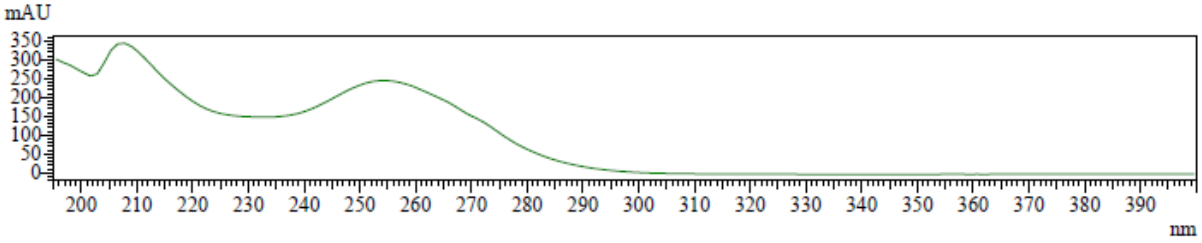



UV Spectrum
Retention time = 13.131




UV Spectrum
Retention time = 16.894




Peak Table

PDA Ch1 254nm

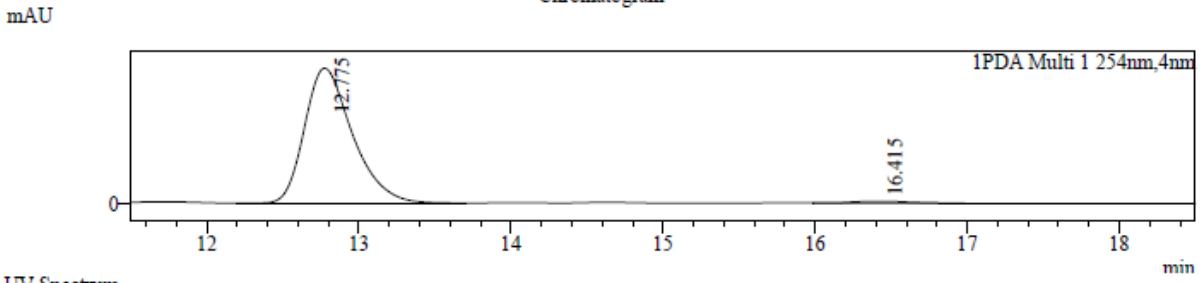
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 13.131 | 7006663 | 51.058 |
| 2 | 16.894 | 6716174 | 48.942 |
| Total | | 13722837 | 100.000 |

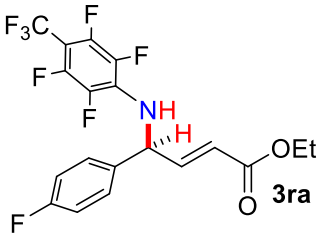
# HPLC

Sample Information

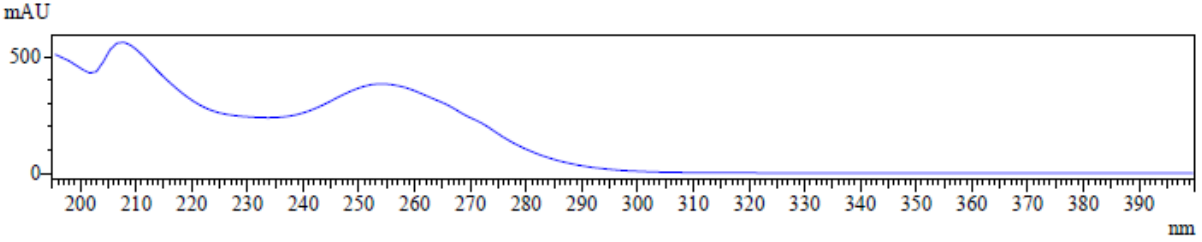
Sample Name : P0X-0576-ODH-5%0.8mL
Sample ID : P0X-0576-ODH-5%0.8mL
Data File : P0X-0576-ODH-5%0.8mL.lcd
Method File : XXW-5%.0.8.mL.lcm

Chromatogram

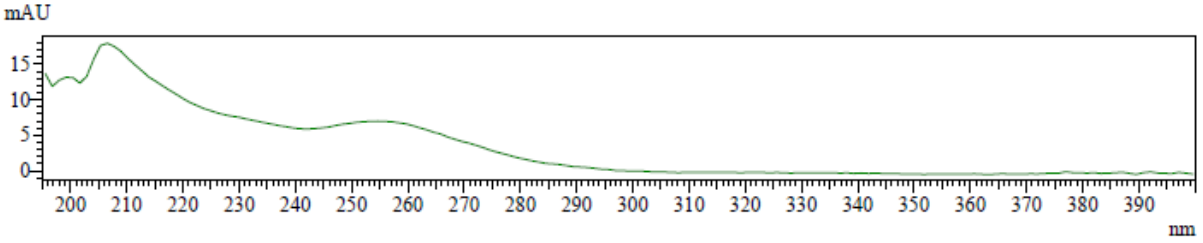



UV Spectrum
Retention time = 12.775




UV Spectrum
Retention time = 16.415



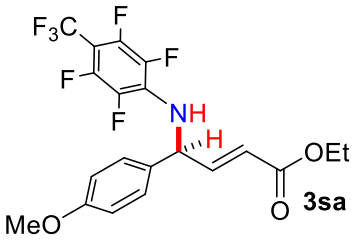

Peak Table

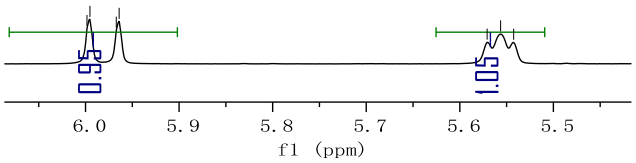
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 12.775 | 8307811 | 98.288 |
| 2 | 16.415 | 144733 | 1.712 |
| Total | | 8452543 | 100.000 |

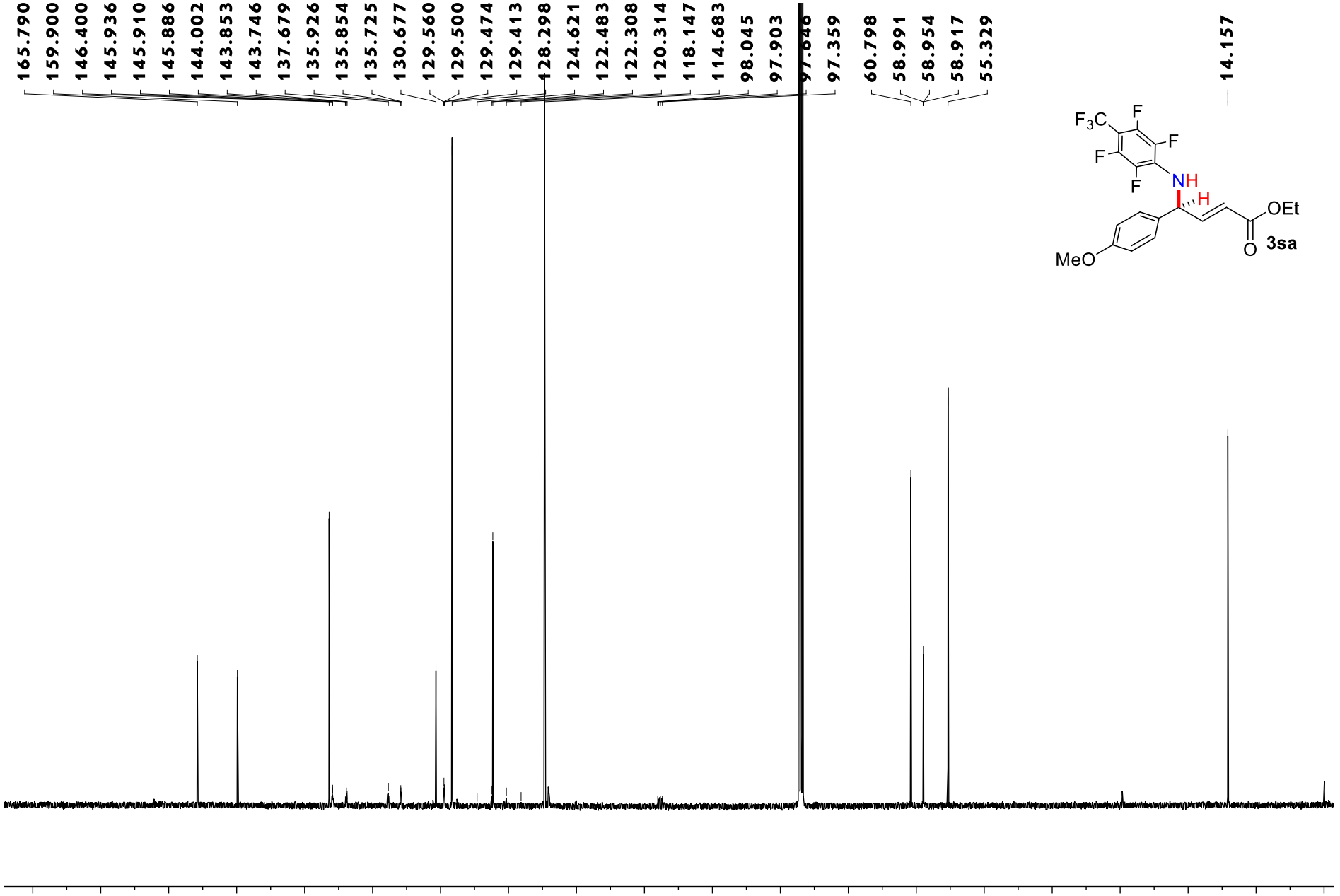
# $^1$H NMR

7.259 7.232 7.216 7.118 7.107 7.087 7.076 6.925 6.909 5.998 5.995 5.967 5.964 5.571 5.556 5.542 4.446 4.439 4.430 4.421 4.229 4.215 4.201 4.186 3.813 1.307 1.294 1.279

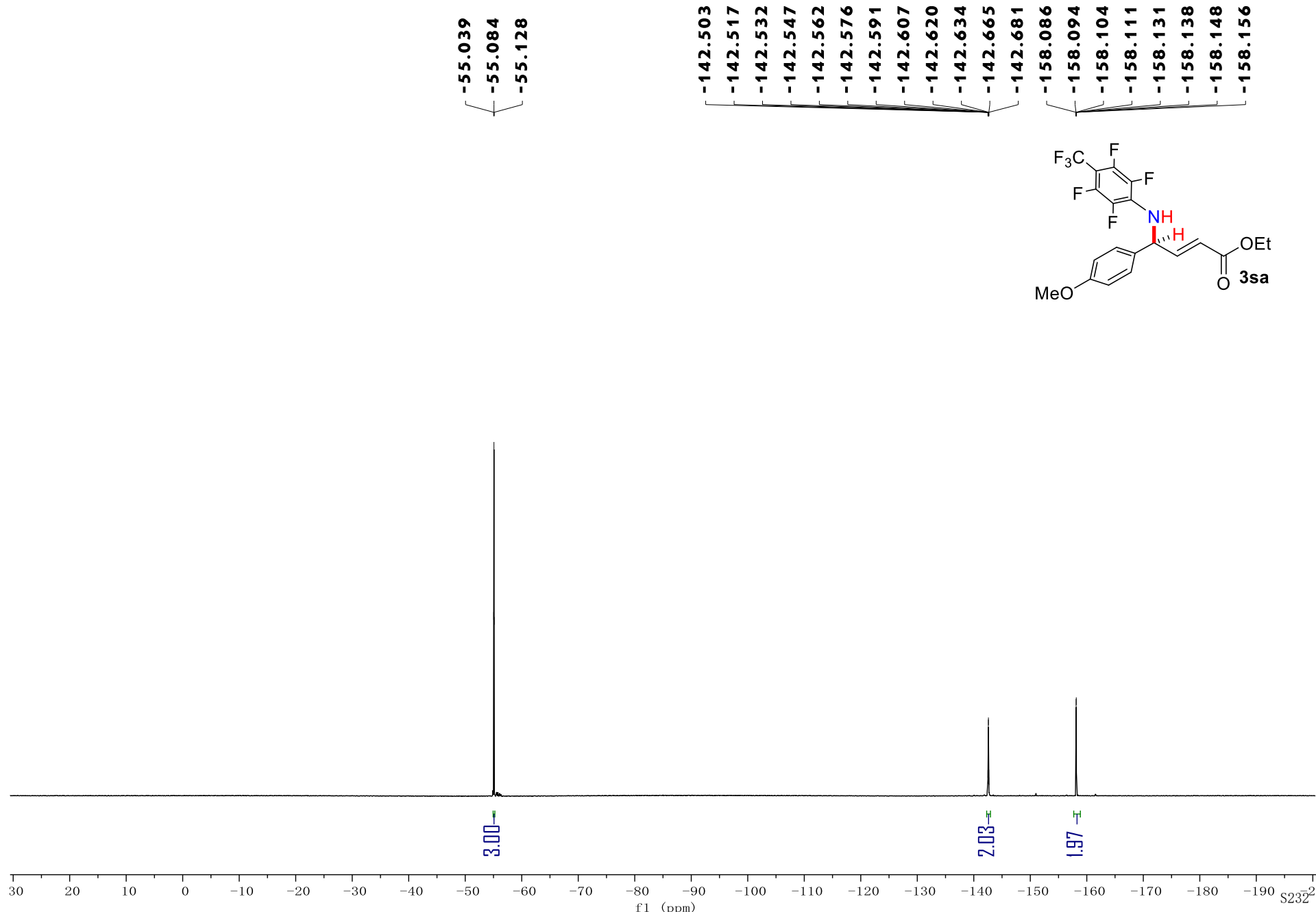


# $^{13}$C NMR


165.790
159.900
146.400
145.936
145.910
145.886
144.002
143.853
143.746
137.679
135.926
135.854
135.725
130.677
129.560
129.500
129.474
129.413
128.298
124.621
122.483
122.308
120.314
118.147
114.683
98.045
97.903
97.848
97.359
60.798
58.991
58.954
58.917
55.329
14.157
F3C
F
F
F
F
NH
H
OEt
O
MeO
3sa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

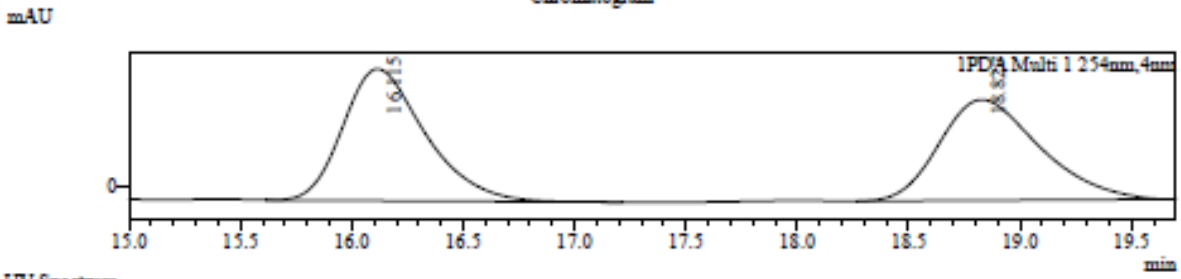

-55.039
-55.084
-55.128
-142.503
-142.517
-142.532
-142.547
-142.562
-142.576
-142.591
-142.607
-142.620
-142.634
-142.665
-142.681
-158.086
-158.094
-158.104
-158.111
-158.131
-158.138
-158.148
-158.156
F3C
F
F
F
F
NH
H
OEt
O
MeO
3sa
3.00
2.03
1.97
f1 (ppm)

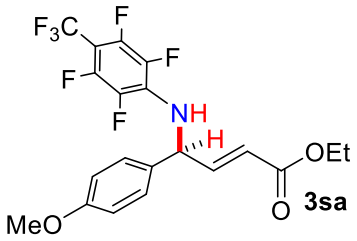
# HPLC

Sample Information

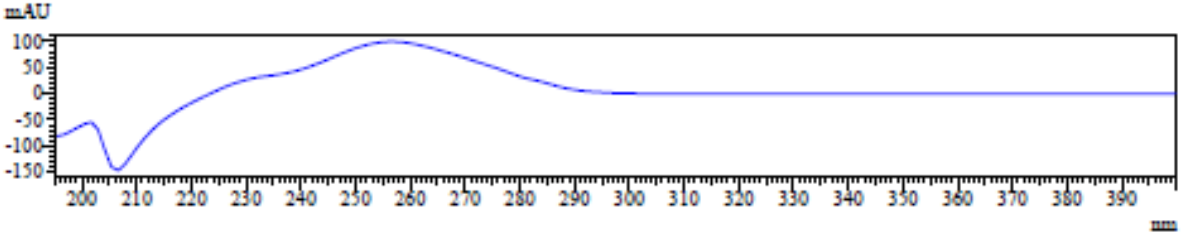
| | |
|---|---|
| Sample Name | : P0X-0548-3-ODH-5%0.8mL |
| Sample ID | : P0X-0548-3-ODH-5%0.8mL |
| Data File | : P0X-0548-3-ODH-5%0.8mL.lcd |
| Method File | : XXW-5%.0.8.mL.lcm |

Chromatogram

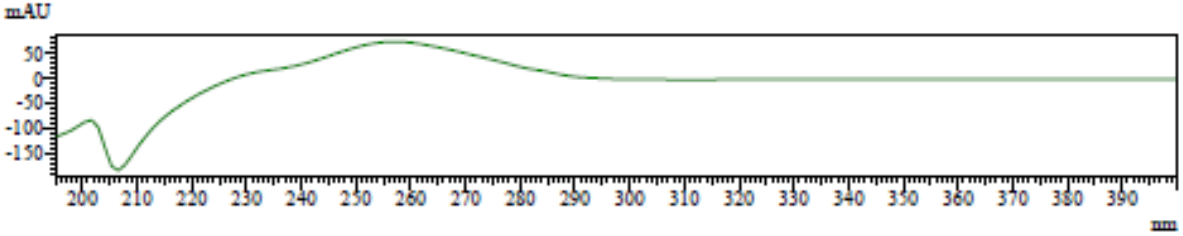



UV Spectrum
Retention time = 16.115




UV Spectrum
Retention time = 18.827




Peak Table

PDA Ch1 254nm

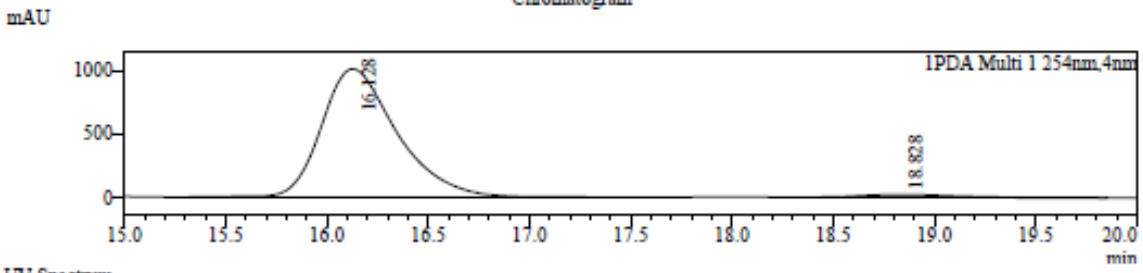
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 16.115 | 2740801 | 51.715 |
| 2 | 18.827 | 2559026 | 48.285 |
| Total | | 5299827 | 100.000 |

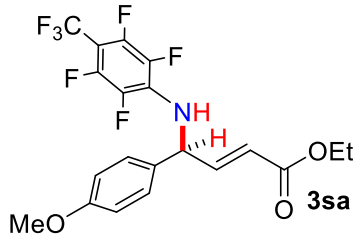
# HPLC

Sample Information

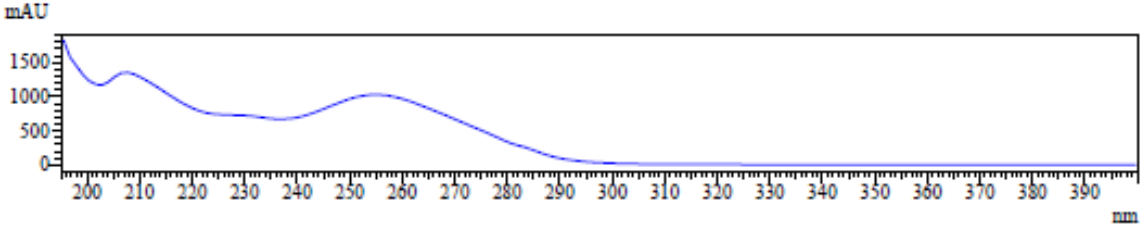
| | |
|---|---|
| Sample Name | : P0X-0582-ODH-5%0.8mL |
| Sample ID | : P0X-0582-ODH-5%0.8mL |
| Data File | : P0X-0582-ODH-5%0.8mL.lcd |
| Method File | : P0X-5.0%-0.8ml.lcm |

Chromatogram

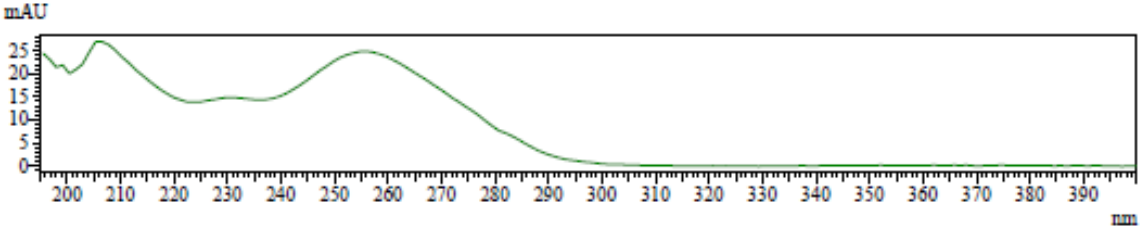



UV Spectrum
Retention time = 16.128




UV Spectrum
Retention time = 18.828

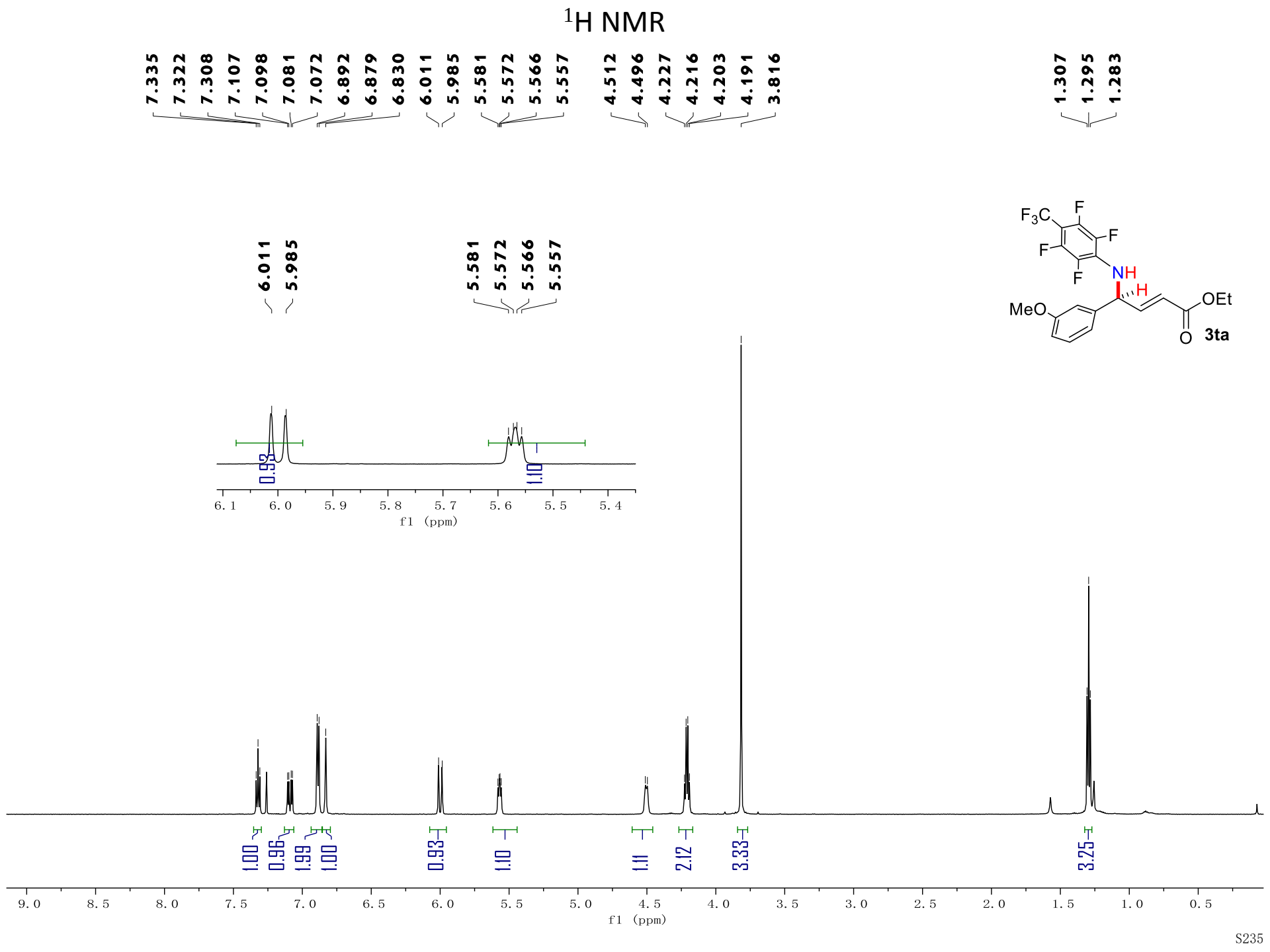



Peak Table

PDA Ch1 254nm

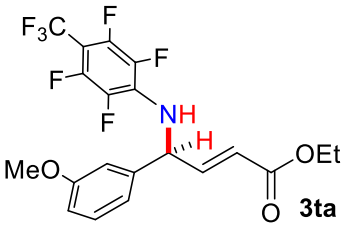
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 16.128 | 26349173 | 97.394 |
| 2 | 18.828 | 704902 | 2.606 |
| Total | | 27054075 | 100.000 |

# $^1$H NMR


7.335
7.322
7.308
7.107
7.098
7.081
7.072
6.892
6.879
6.830
6.011
5.985
5.581
5.572
5.566
5.557
4.512
4.496
4.227
4.216
4.203
4.191
3.816
1.307
1.295
1.283
F3C
F
F
F
F
NH
H
MeO
OEt
O
3ta
0.93
1.10
f1 (ppm)
1.00
0.96
1.99
1.00
0.93
1.10
1.11
2.12
3.33
3.25
f1 (ppm)

# $^{13}C$ NMR

165.721 160.248 146.029 145.780 144.070 140.270 137.698 137.591 136.095 135.991 130.509 129.456 124.103 122.743 122.642 122.289 120.481 119.007 118.664 113.819 112.991 97.847 97.707 97.616 97.528 77.210 76.998 76.786 60.852 59.473 55.239 14.143

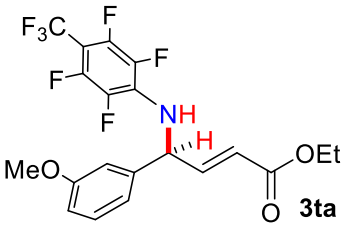


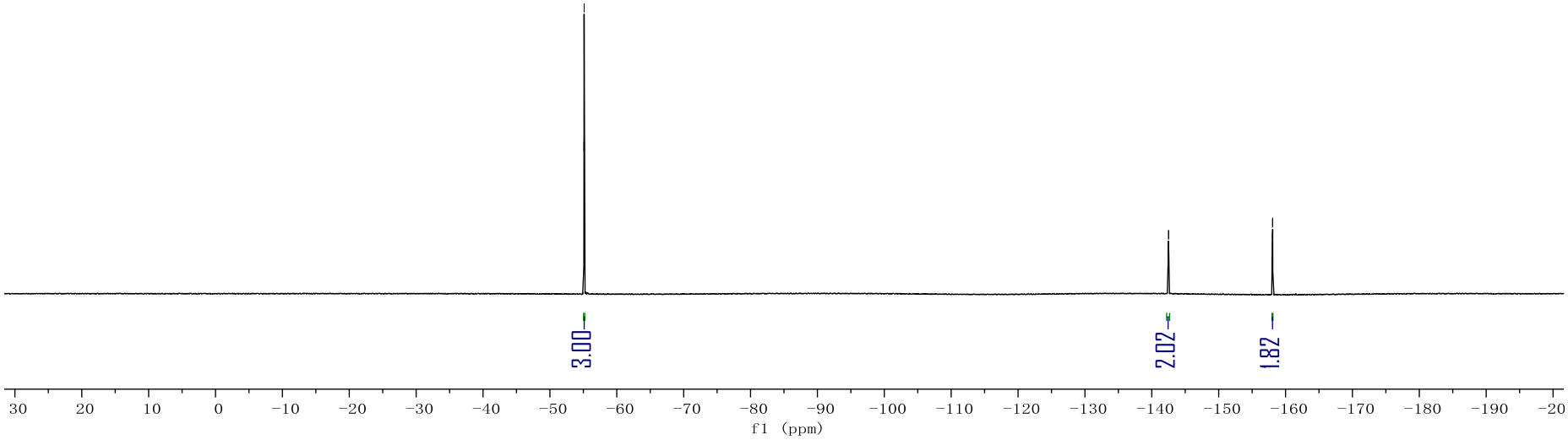

**3ta**

# $^{19}$F NMR

-55.080
-55.117
-55.154

-142.464
-142.471
-142.477
-142.501
-142.508
-142.514
-142.538
-142.544
-142.552
-158.031
-158.038
-158.045
-158.051
-158.068
-158.074
-158.082
-158.089



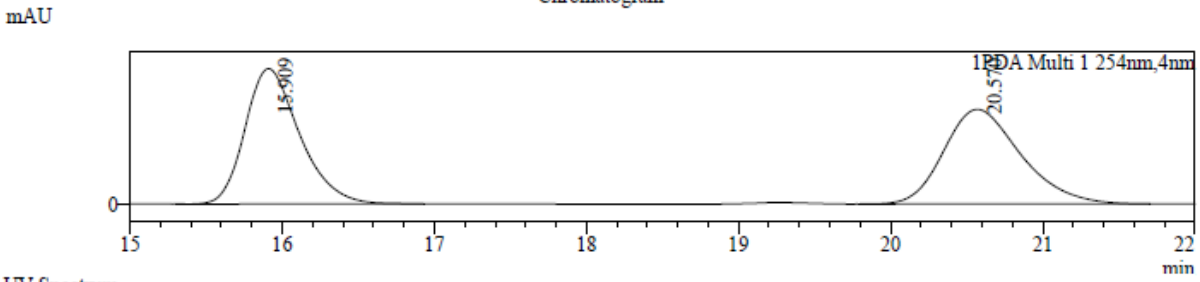



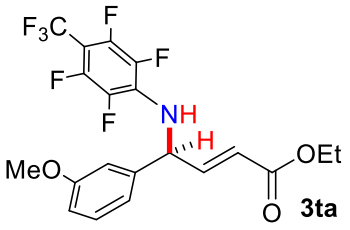
# HPLC

Sample Information

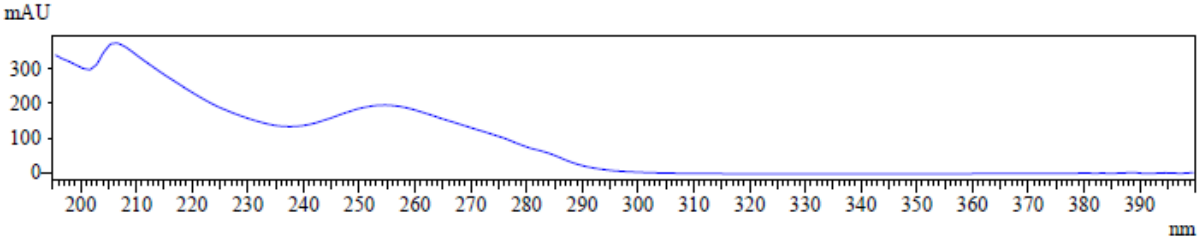
| | |
|---|---|
| Sample Name | : P0X-0731ODH-5%-0.8mL |
| Sample ID | : P0X-0731ODH-5%-0.8mL |
| Data File | : P0X-0731ODH-5%-0.8mL.lcd |
| Method File | : P0X-5.0%-0.8ml.lcm |

Chromatogram

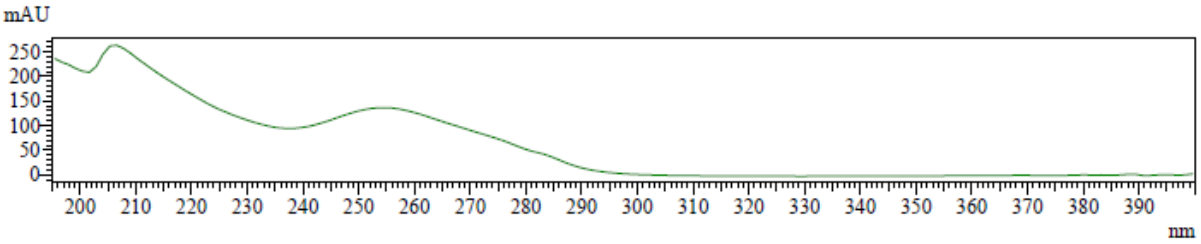



UV Spectrum
Retention time = 15.909




UV Spectrum
Retention time = 20.570




Peak Table

PDA Ch1 254nm

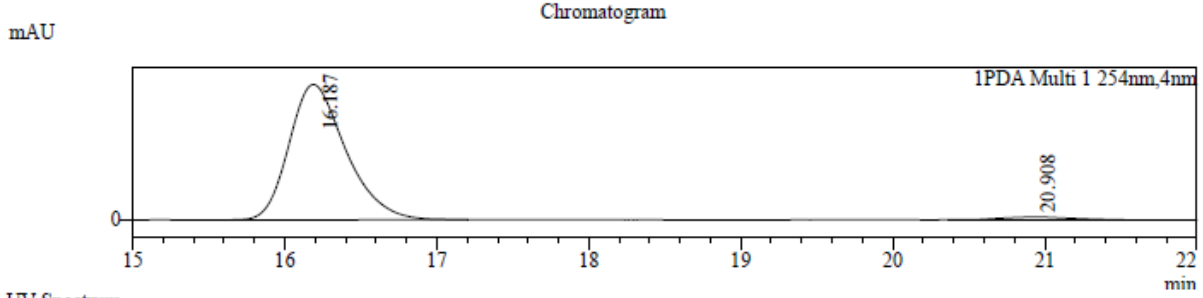
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 15.909 | 4776937 | 50.343 |
| 2 | 20.570 | 4711898 | 49.657 |
| Total | | 9488835 | 100.000 |

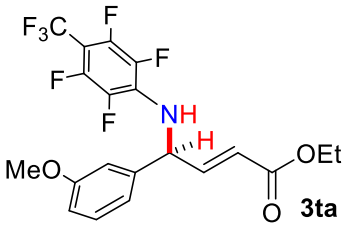
# HPLC

Sample Information

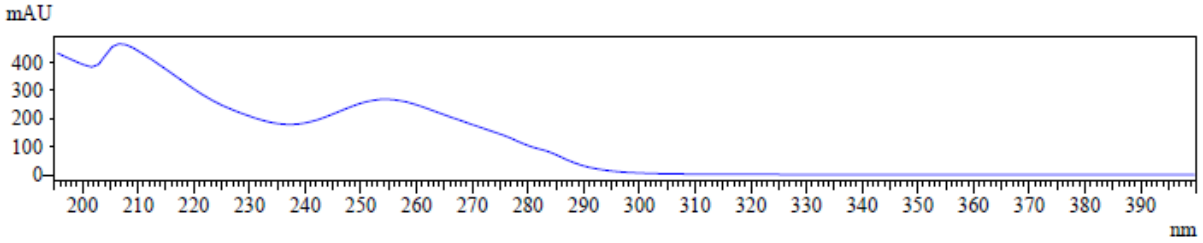
Sample Name : P0X-0732-ODH-5%-0.8mL
Sample ID : P0X-0732-ODH-5%-0.8mL
Data File : P0X-0732-ODH-5%-0.8mL.lcd
Method File : P0X-5.0%-0.8ml.lcm

Chromatogram

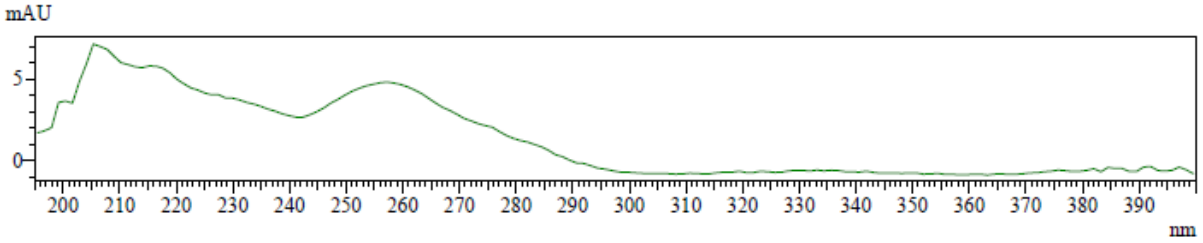



UV Spectrum
Retention time = 16.187




UV Spectrum
Retention time = 20.908

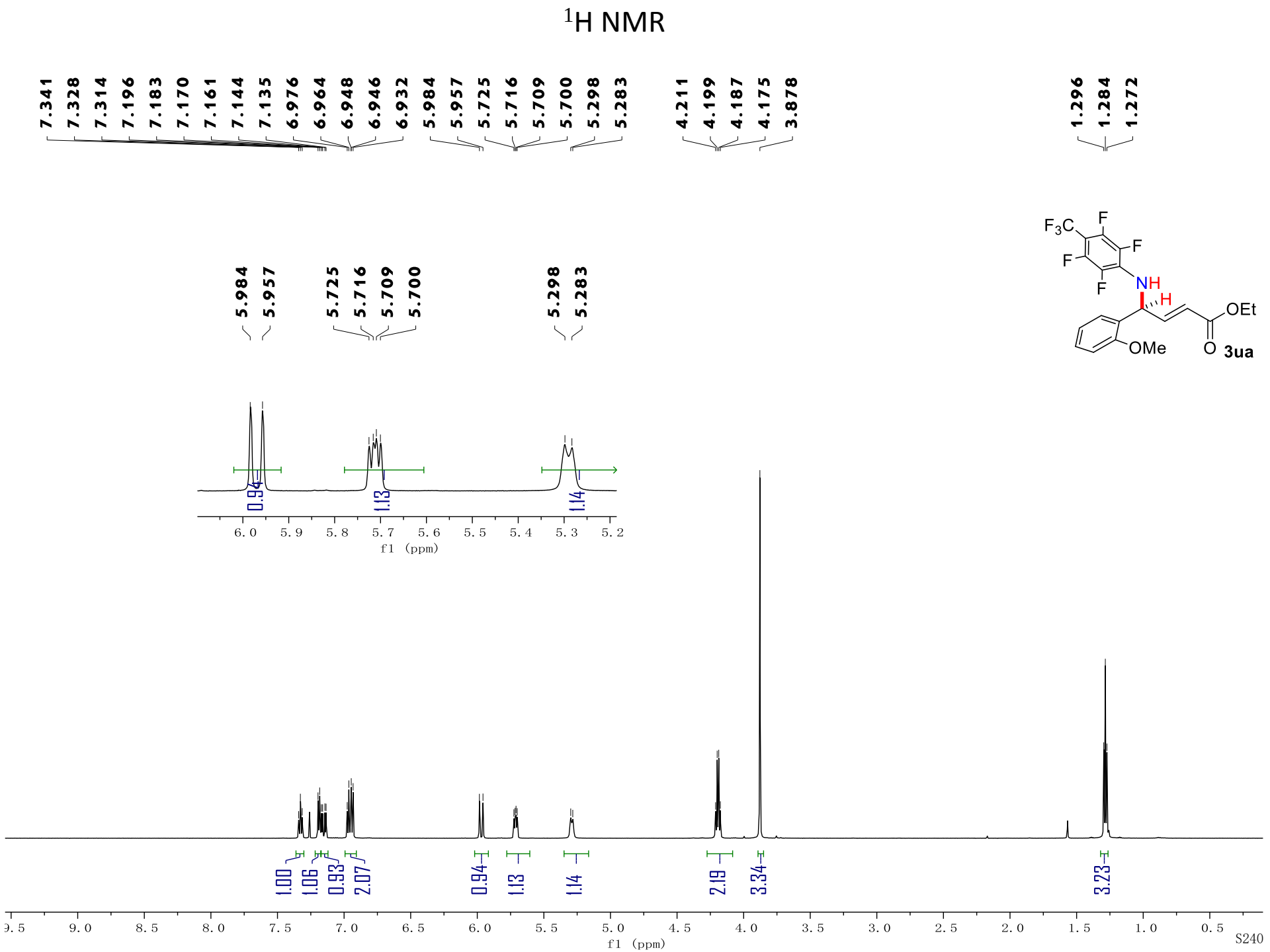



Peak Table

PDA Ch1 254nm

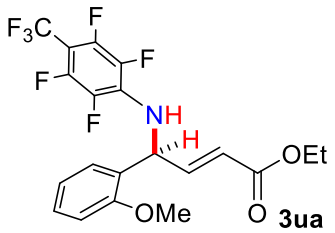
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 16.187 | 6937205 | 97.368 |
| 2 | 20.908 | 187500 | 2.632 |
| Total | | 7124705 | 100.000 |

# $^{1}$H NMR

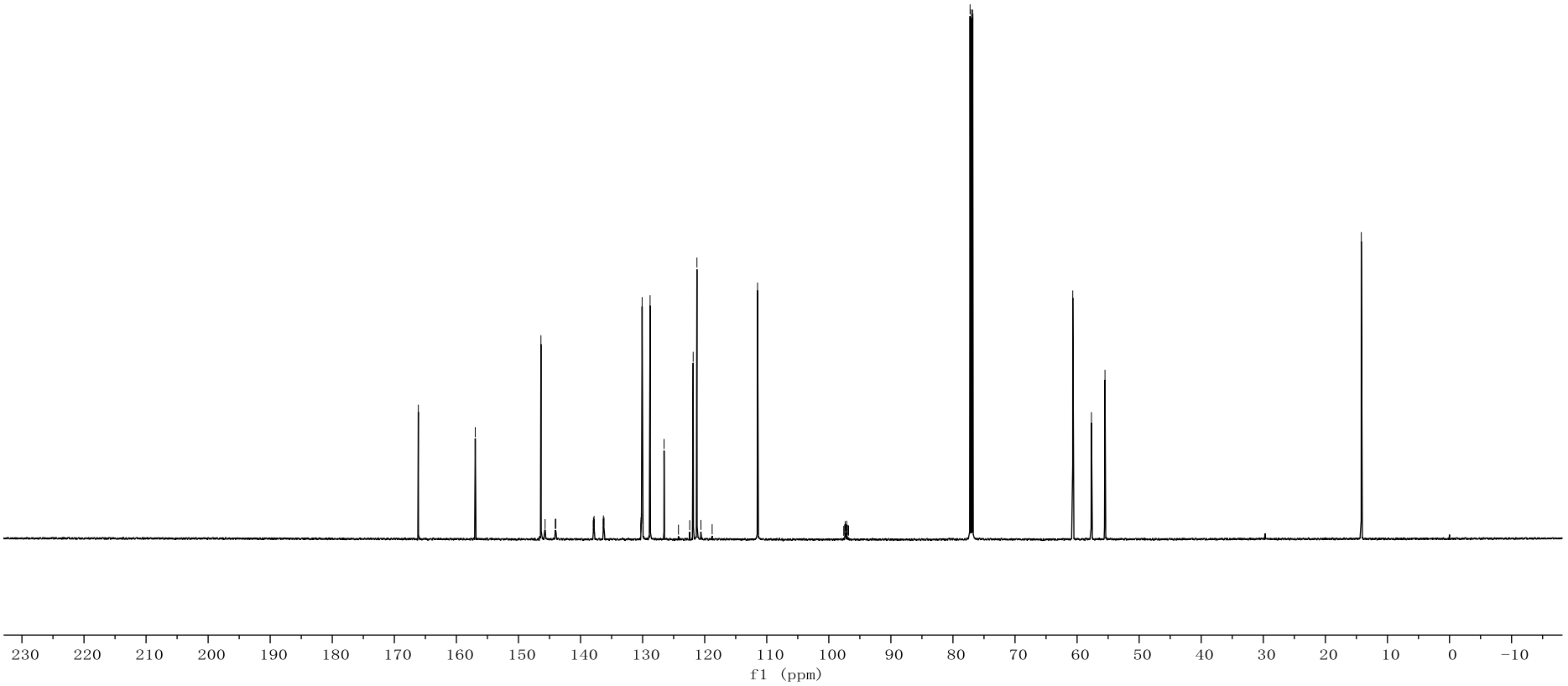

7.341
7.328
7.314
7.196
7.183
7.170
7.161
7.144
7.135
6.976
6.964
6.948
6.946
6.932
5.984
5.957
5.725
5.716
5.709
5.700
5.298
5.283
4.211
4.199
4.187
4.175
3.878
1.296
1.284
1.272
F3C
F
F
F
F
NH
H
OEt
O
OMe
3ua
0.94
1.13
1.14
f1 (ppm)
1.00
1.06
0.93
2.07
0.94
1.13
1.14
2.19
3.34
3.23
f1 (ppm)

# $^{13}$C NMR

166.138 156.963 146.383 145.710 144.074 143.979 137.954 137.922 137.886 137.849 137.816 137.782 136.357 136.321 136.292 136.254 136.224 130.283 130.257 130.233 130.209 130.187 130.164 130.077 128.796 126.542 122.414 121.855 121.249 120.608 118.798 111.484 97.453 97.364 97.221 97.131 77.243 77.031 76.818 60.697 57.719 57.685 57.651 55.505 14.208



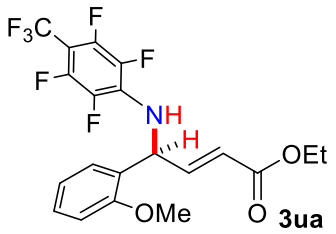

3ua



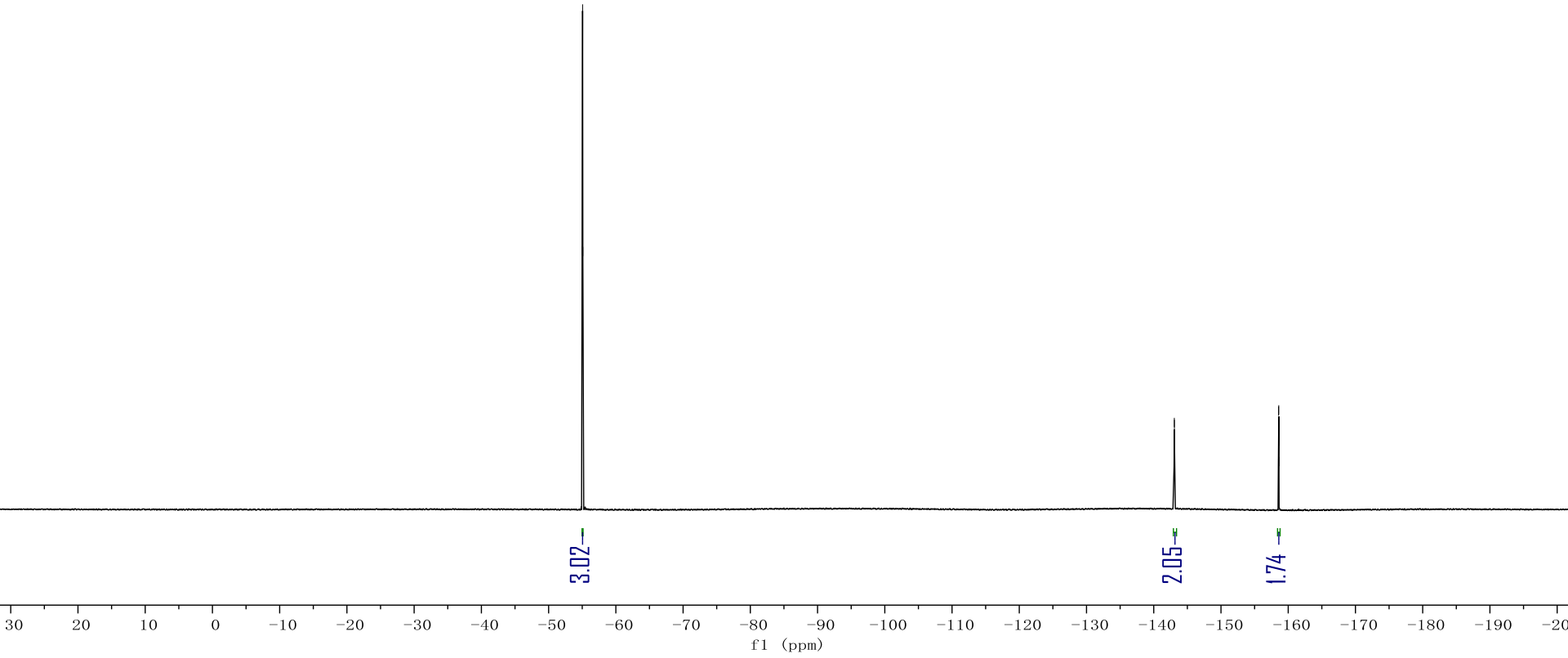
# $^{19}$F NMR

-55.018
-55.055
-55.092

-143.025
-143.037
-143.061
-143.073
-143.097
-143.109
-158.551
-158.560
-158.567
-158.589
-158.595
-158.602
-158.610




**3ua**

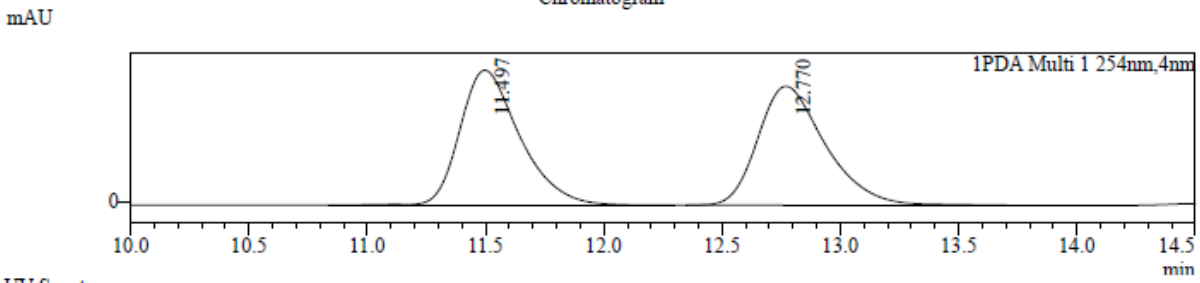


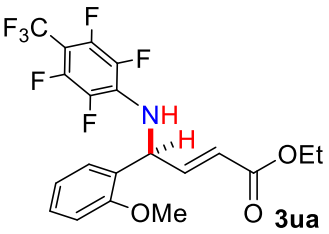
# HPLC

Sample Information

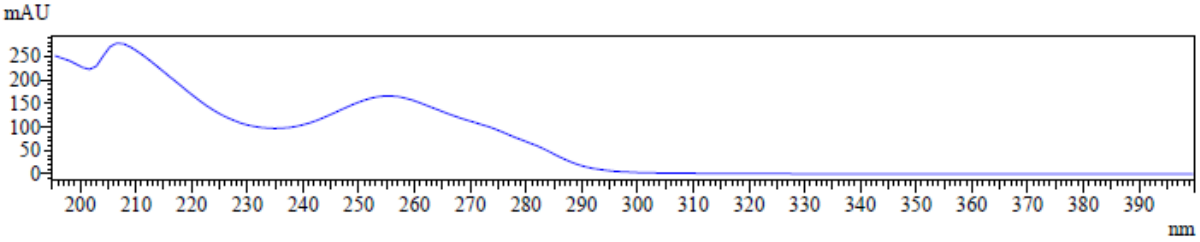
| | |
|---|---|
| Sample Name | : P0X-0676-ODH-5%-0.8mL |
| Sample ID | : P0X-0676-ODH-5%-0.8mL |
| Data File | : P0X-0676-ODH-5%-0.8mL.lcd |
| Method File | : P0X-5.0%-0.8ml.lcm |

Chromatogram

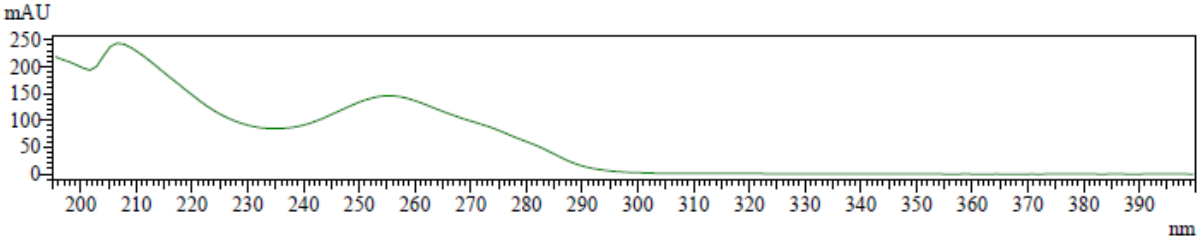



UV Spectrum
Retention time = 11.497




UV Spectrum
Retention time = 12.770




Peak Table

PDA Ch1 254nm

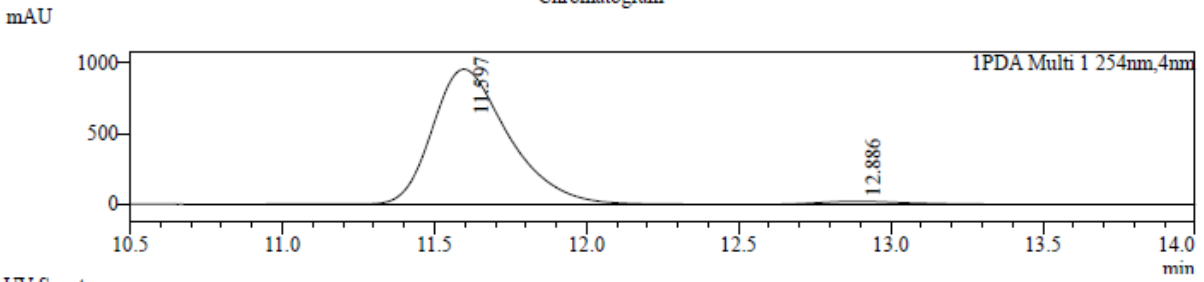
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 11.497 | 2956116 | 50.097 |
| 2 | 12.770 | 2944648 | 49.903 |
| Total | | 5900764 | 100.000 |

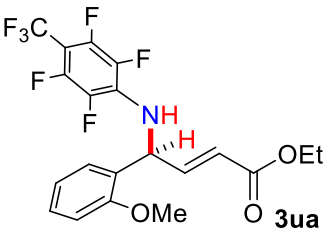
# HPLC

Sample Information

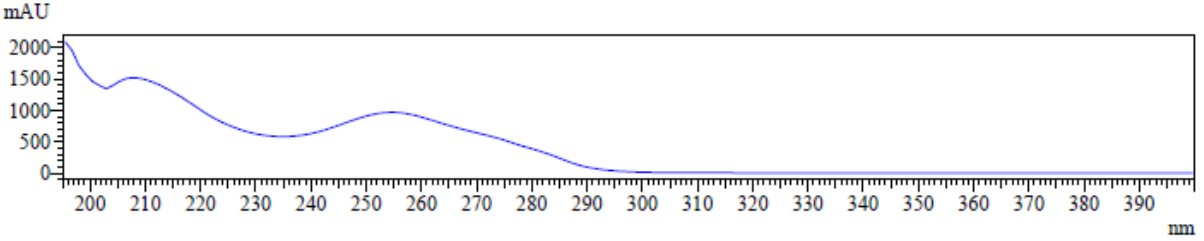
Sample Name : P0X-0677ODH-5%-0.8mL
Sample ID : P0X-0677ODH-5%-0.8mL
Data File : P0X-0677-ODH-5%-0.8mL.lcd
Method File : P0X-5.0%-0.8ml.lcm

Chromatogram

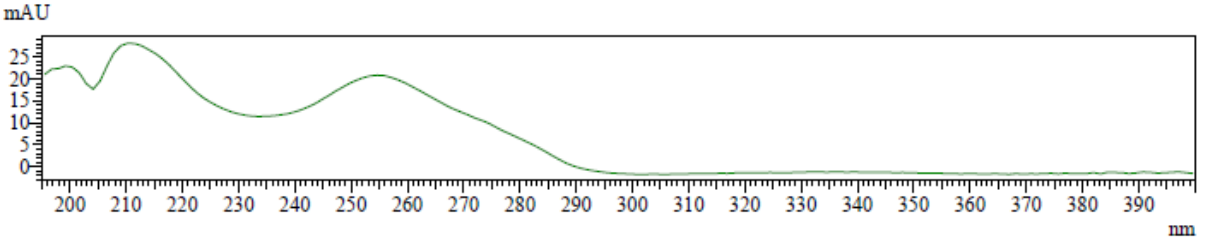



UV Spectrum
Retention time = 11.597




UV Spectrum
Retention time = 12.886

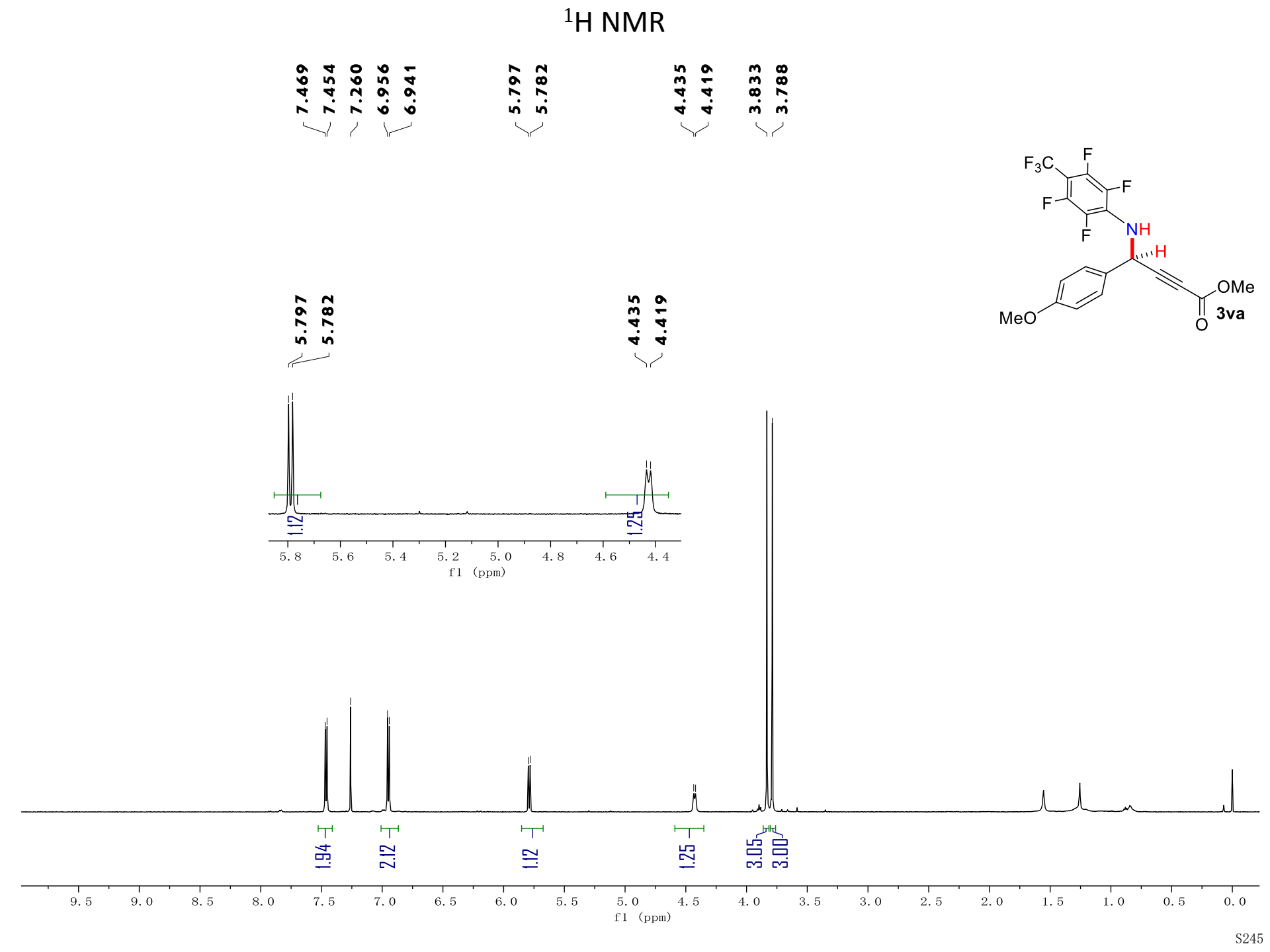



Peak Table

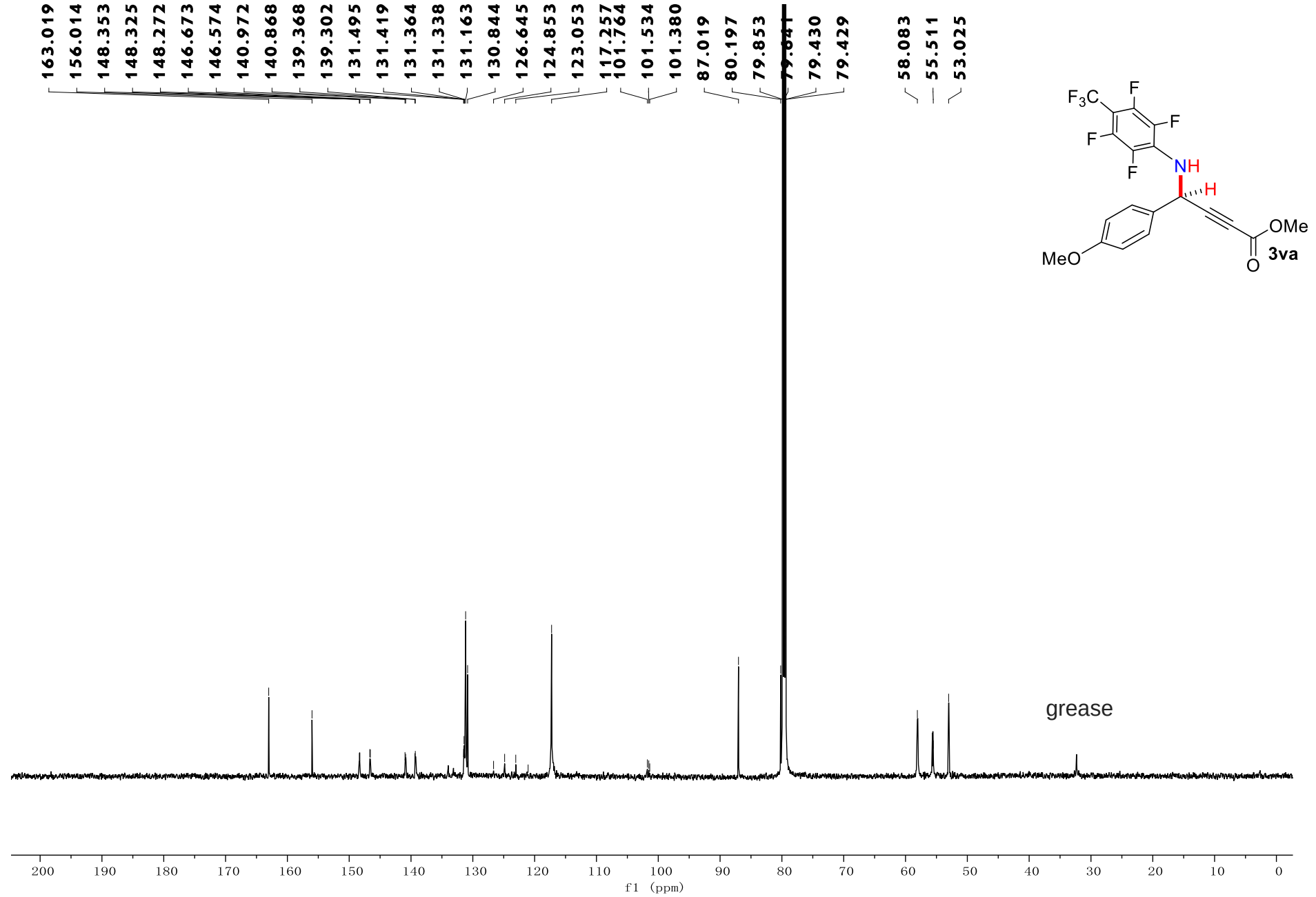
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 11.597 | 16688022 | 97.412 |
| 2 | 12.886 | 443332 | 2.588 |
| Total | | 17131354 | 100.000 |

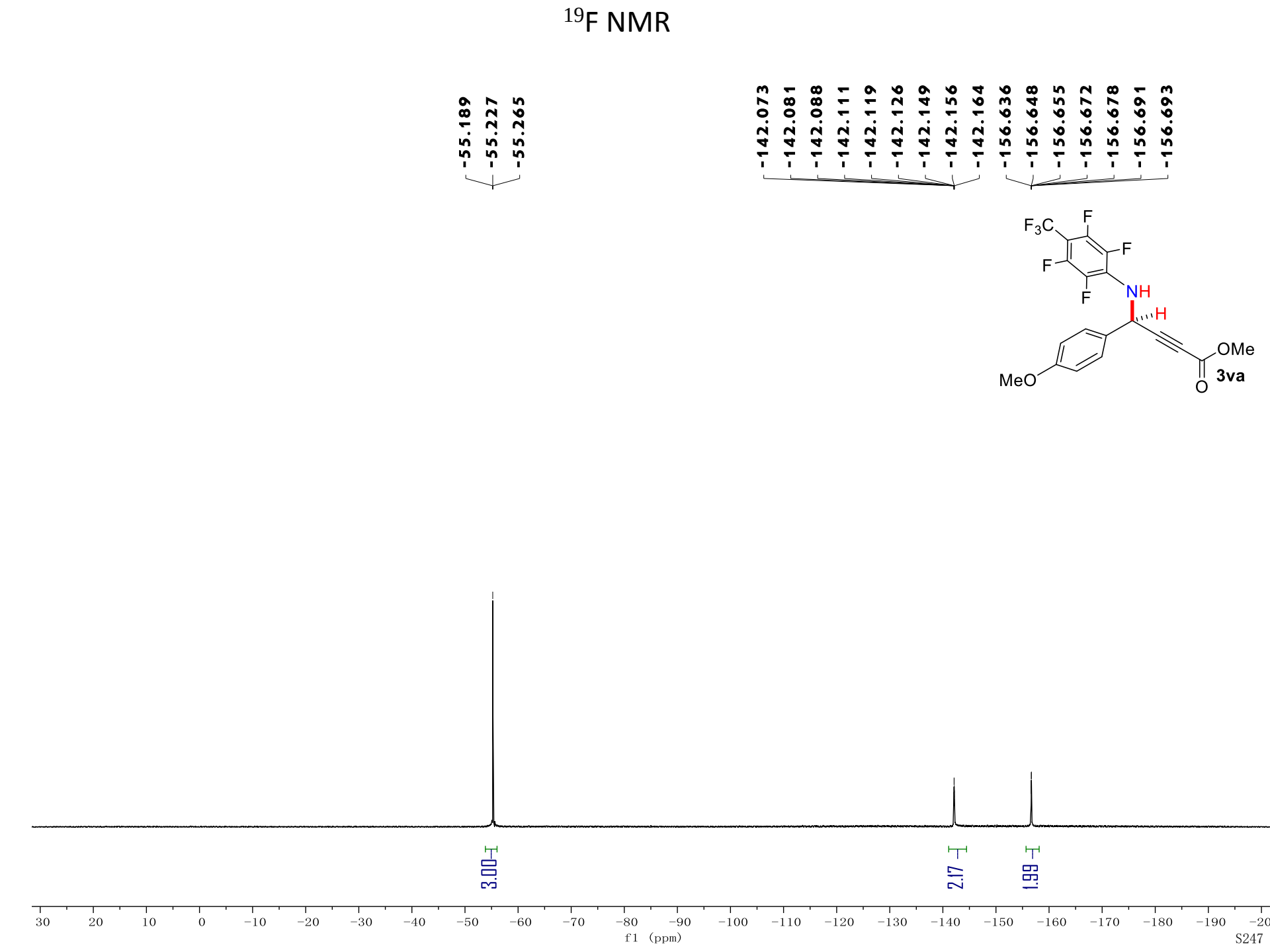
# $^{1}$H NMR


7.469
7.454
7.260
6.956
6.941
5.797
5.782
4.435
4.419
3.833
3.788
F3C
F
F
F
F
NH
H
OMe
MeO
O
3va
1.12
1.25
f1 (ppm)
1.94
2.12
1.12
1.25
3.05
3.00
f1 (ppm)

# $^{13}$C NMR


163.019
156.014
148.353
148.325
148.272
146.673
146.574
140.972
140.868
139.368
139.302
131.495
131.419
131.364
131.338
131.163
130.844
126.645
124.853
123.053
117.257
101.764
101.534
101.380
87.019
80.197
79.853
79.841
79.430
79.429
58.083
55.511
53.025
F3C
F
F
F
NH
H
OMe
MeO
O
3va
grease
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

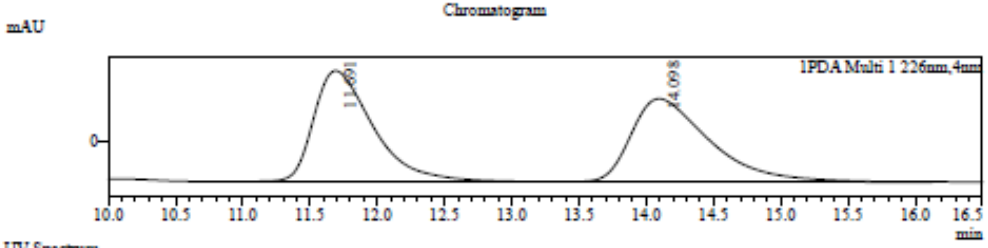

-55.189
-55.227
-55.265
-142.073
-142.081
-142.088
-142.111
-142.119
-142.126
-142.149
-142.156
-142.164
-156.636
-156.648
-156.655
-156.672
-156.678
-156.691
-156.693
F3C
F
F
F
NH
H
MeO
OMe
O
3va
3.00
2.17
1.99
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −20
f1 (ppm)

# HPLC

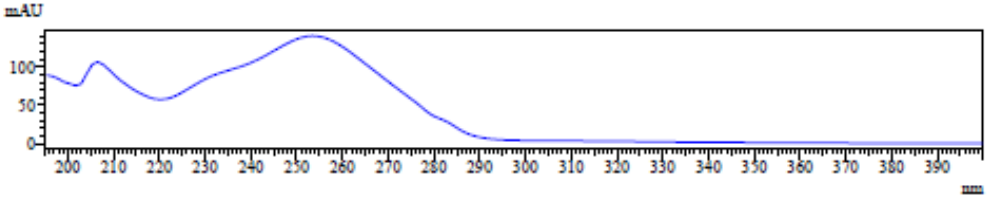
Sample Information

| | |
|---|---|
| Sample Name | : P0X-0587-ASH-10%0.8mL |
| Sample ID | : P0X-0587-ASH-10%0.8mL |
| Data File | : P0X-0587-ASH-10%0.8mL.lcd |
| Method File | : YW-10%-0.8ml.lcm |

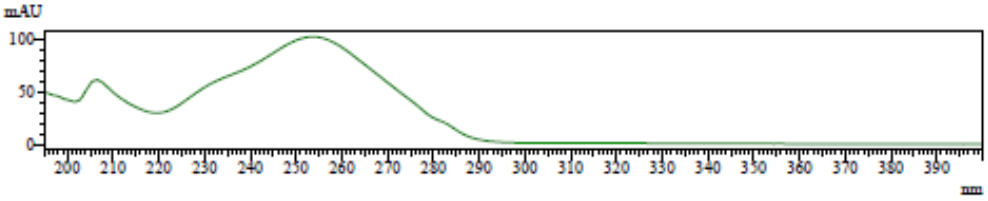
Chromatogram




UV Spectrum
Retention time = 11.691



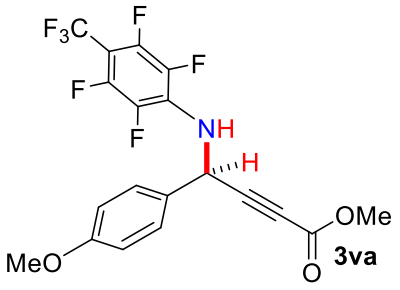

UV Spectrum
Retention time = 14.098




Peak Table

PDA Ch1 226nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 11.691 | 3451401 | 50.530 |
| 2 | 14.098 | 3379031 | 49.470 |
| Total | | 6830432 | 100.000 |

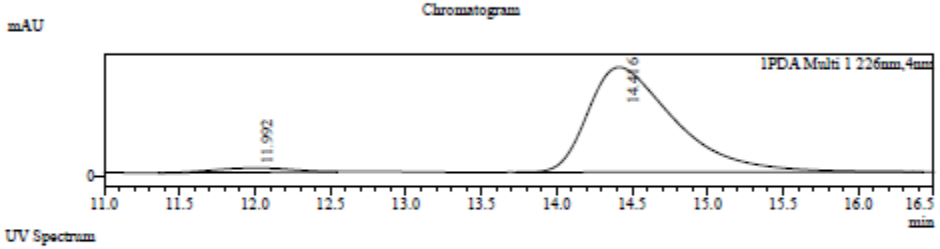


# HPLC

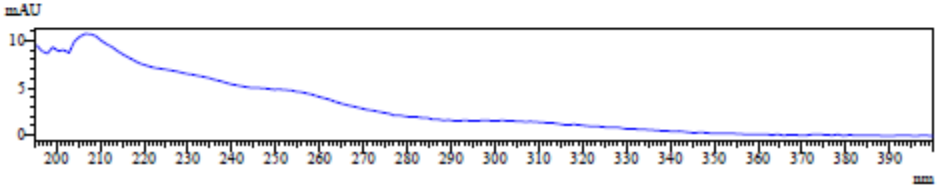
Sample Information

| | |
|---|---|
| Sample Name | : P0X-0588-ASH-10%0.8mL |
| Sample ID | : P0X-0588-ASH-10%0.8mL |
| Data File | : P0X-0588-ASH-10%0.8mL.lcd |
| Method File | : YW-10%-0.8ml.lcm |

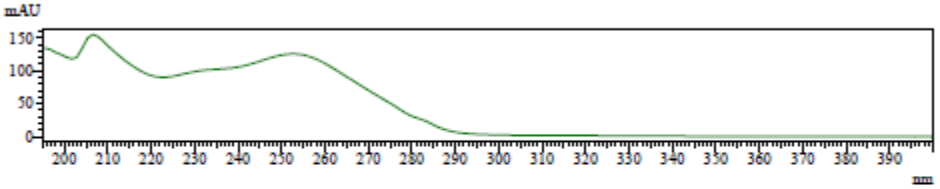
Chromatogram




UV Spectrum
Retention time = 11.992



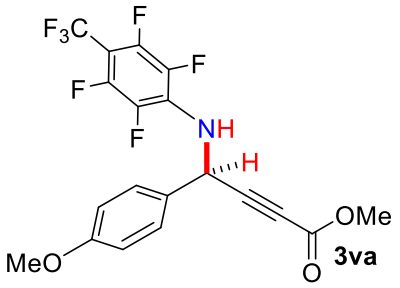

UV Spectrum
Retention time = 14.416



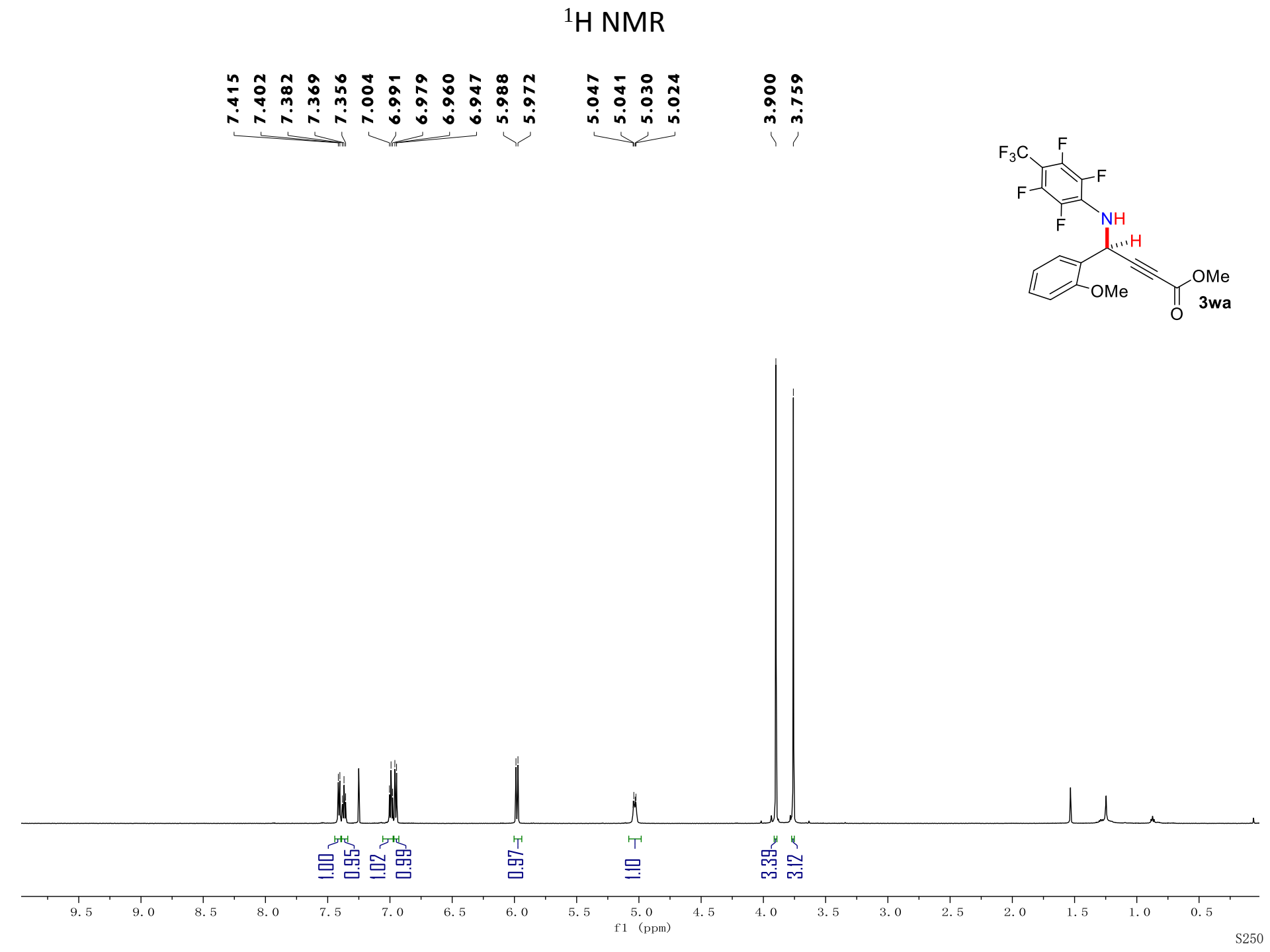

Peak Table

PDA Ch1 226nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 11.992 | 131952 | 3.505 |
| 2 | 14.416 | 3632225 | 96.495 |
| Total | | 3764177 | 100.000 |

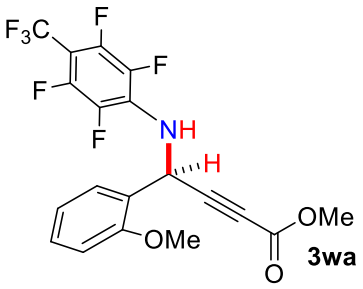


# $^{1}$H NMR


7.415
7.402
7.382
7.369
7.356
7.004
6.991
6.979
6.960
6.947
5.988
5.972
5.047
5.041
5.030
5.024
3.900
3.759
F3C
F
F
F
F
NH
H
OMe
OMe
O
3wa
1.00
0.95
1.02
0.99
0.97
1.10
3.39
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

# $^{13}$C NMR

156.920
153.579
145.631
143.931
138.272
138.164
136.666
136.561
130.813
129.281
129.254
129.181
129.105
129.081
128.701
124.482
124.086
122.278
121.081
120.465
111.519
98.566
98.566
98.335
98.117
84.891
77.212
77.000
76.789
76.080
55.671
52.781
47.466

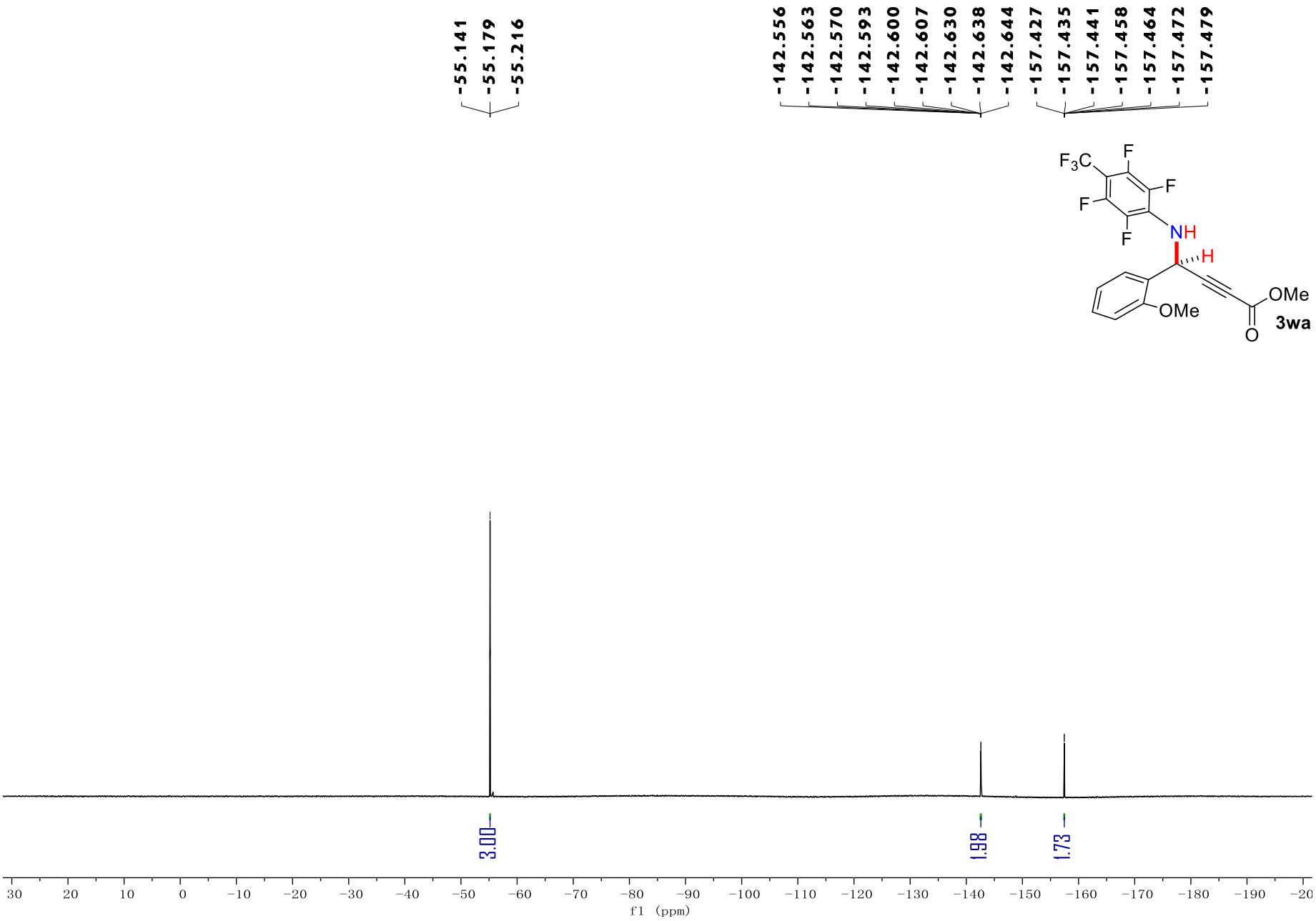



**3wa**

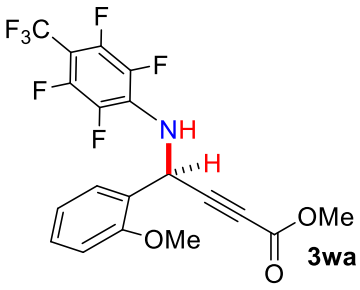
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

# $^{19}$F NMR


-55.141
-55.179
-55.216
-142.556
-142.563
-142.570
-142.593
-142.600
-142.607
-142.630
-142.638
-142.644
-157.427
-157.435
-157.441
-157.458
-157.464
-157.472
-157.479
F3C
F
F
F
NH
H
OMe
OMe
O
3wa
3.00
1.98
1.73
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −20
f1 (ppm)

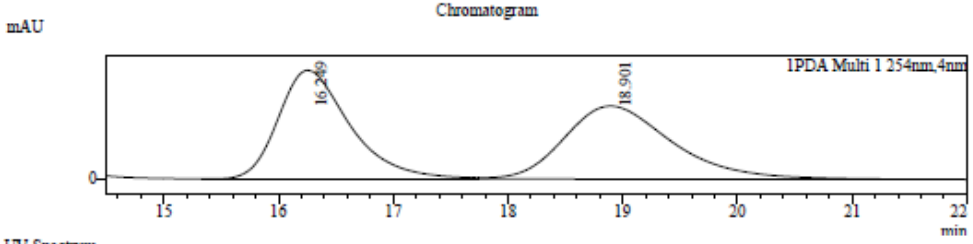
# HPLC



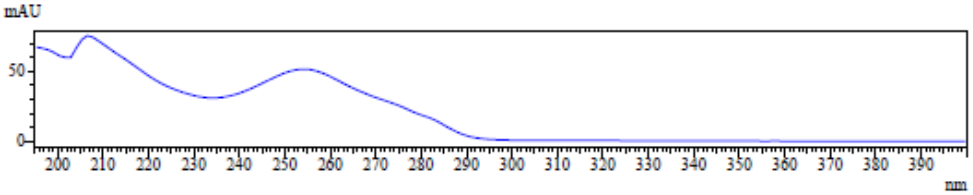

Sample Information

| | |
|---|---|
| Sample Name | : P0X-0602-OJH10%-0.8mL |
| Sample ID | : P0X-0602-OJH10%-0.8mL |
| Data File | : P0X-0602-OJH10%-0.8mL.lcd |
| Method File | : YW-10%-0.8ml.lcm |

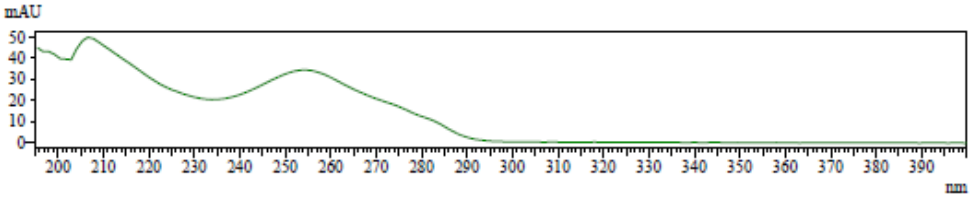
Chromatogram




UV Spectrum
Retention time = 16.249




UV Spectrum
Retention time = 18.901




Peak Table

PDA Ch1 254nm

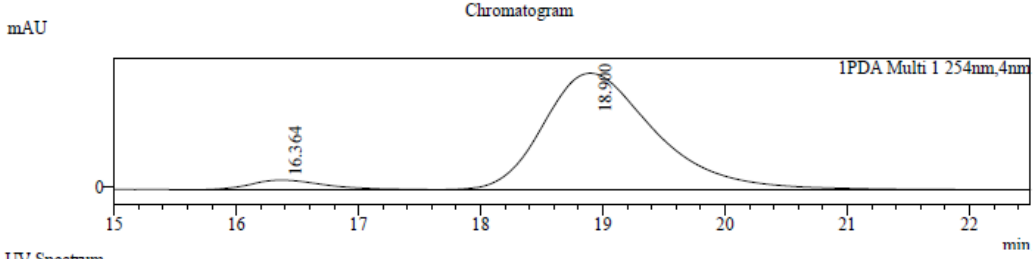
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 16.249 | 2206862 | 49.676 |
| 2 | 18.901 | 2235673 | 50.324 |
| Total | | 4442536 | 100.000 |

# HPLC

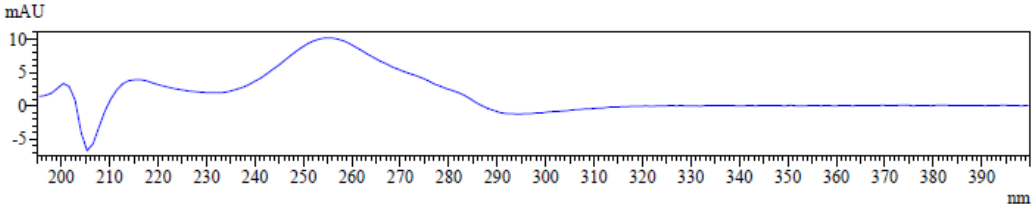
Sample Information

| | |
|---|---|
| Sample Name | : P0X-0603-OJH-10%-0.8mL |
| Sample ID | : P0X-0603-OJH-10%-0.8mL |
| Data File | : P0X-0603-OJH-10%-0.8mL.lcd |
| Method File | : YW-10%-0.8ml.lcm |

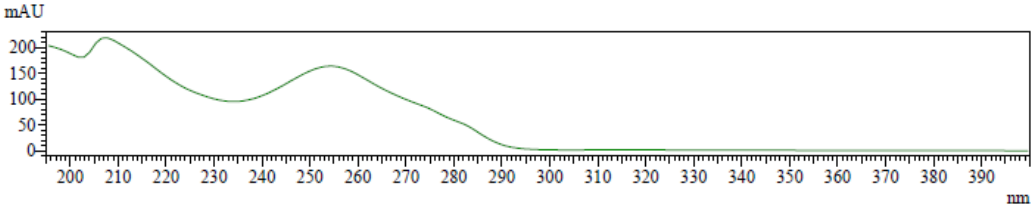
Chromatogram




UV Spectrum
Retention time = 16.364



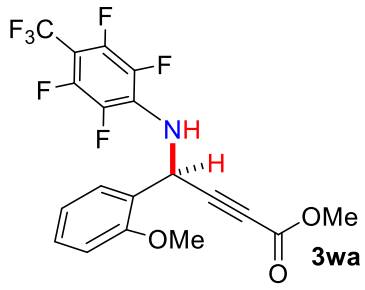

UV Spectrum
Retention time = 18.900



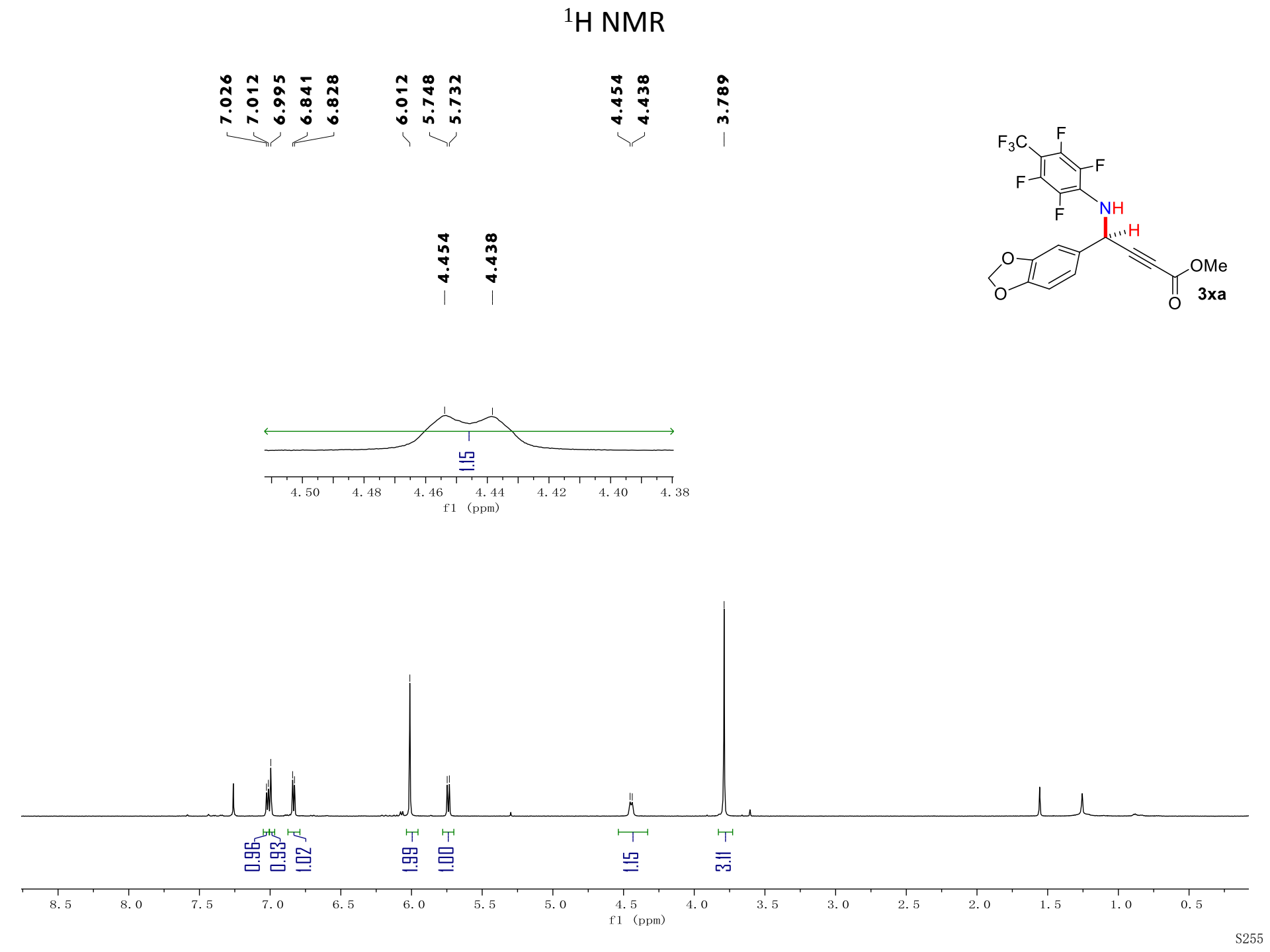

Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 16.364 | 582768 | 5.218 |
| 2 | 18.900 | 10586414 | 94.782 |
| Total | | 11169182 | 100.000 |

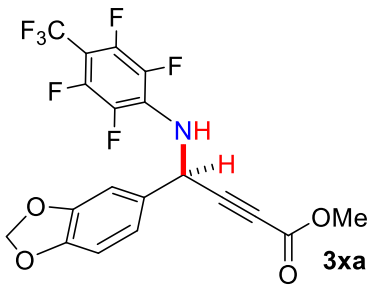


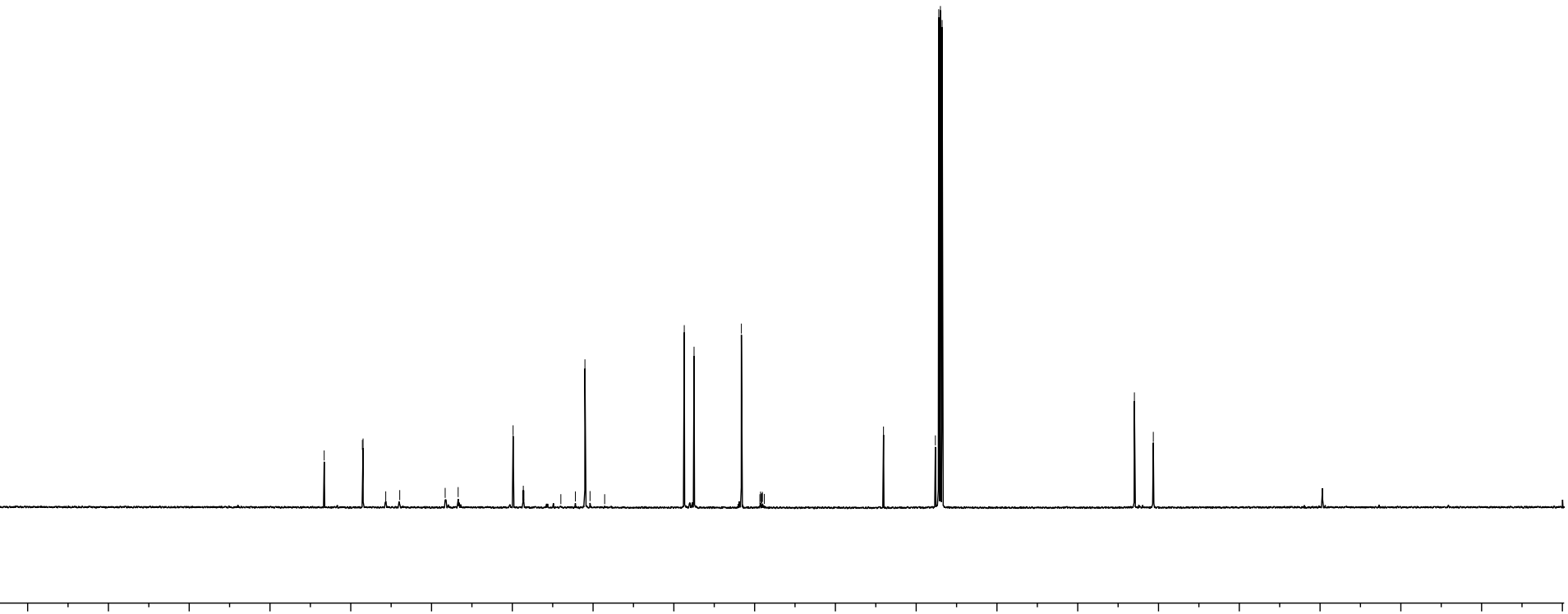
# $^1$H NMR


7.026
7.012
6.995
6.841
6.828
6.012
5.748
5.732
4.454
4.438
3.789
4.454
4.438
F3C
F
F
F
F
NH
H
O
O
OMe
O
3xa
1.15
4.50
4.48
4.46
4.44
4.42
4.40
4.38
f1 (ppm)
0.96
0.93
1.02
1.99
1.00
1.15
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

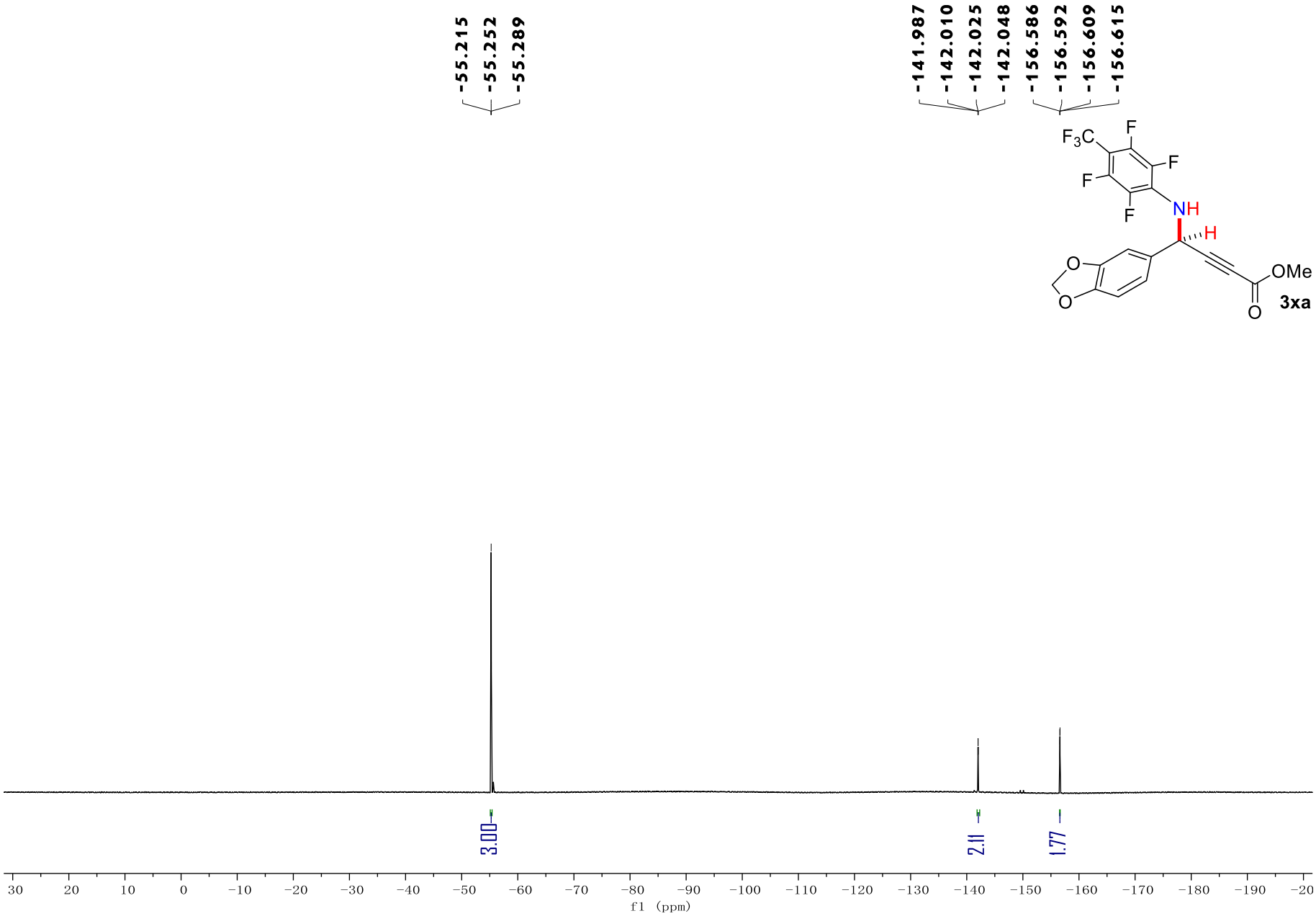
# $^{13}$C NMR

153.289
148.563
148.476
145.670
143.937
138.311
136.705
129.902
128.715
128.660
128.638
128.615
128.562
123.990
122.190
121.009
120.378
118.567
108.711
108.708
107.500
101.641
99.353
99.264
99.176
99.118
99.033
98.800
84.046
77.625
77.211
77.000
76.788
52.987
50.644



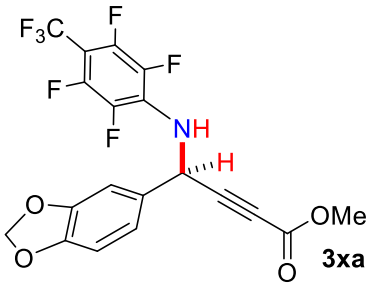
# $^{19}$F NMR


-55.215
-55.252
-55.289
-141.987
-142.010
-142.025
-142.048
-156.586
-156.592
-156.609
-156.615
F3C
F
F
F
F
NH
H
O
O
OMe
O
3xa
3.00
2.11
1.77
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −20
f1 (ppm)

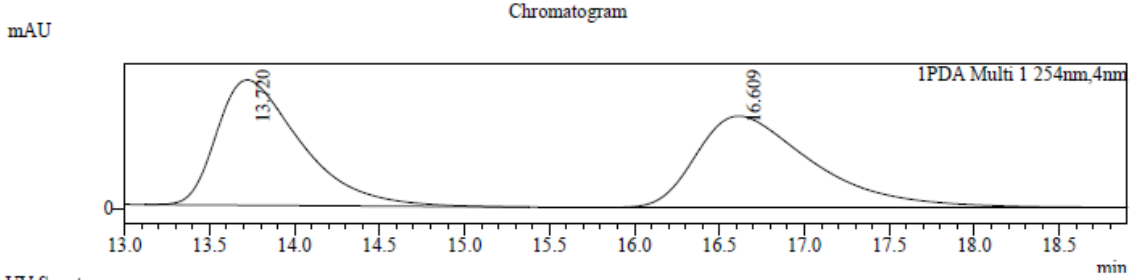
# HPLC

Sample Information

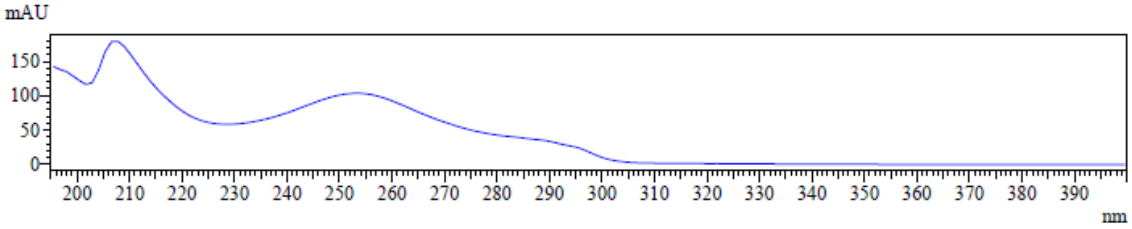
| | |
|---|---|
| Sample Name | : P0X-0627-ASH-10%-0.8mL |
| Sample ID | : P0X-0627-ASH-10%-0.8mL |
| Data File | : P0X-0627-ASH-10%-0.8mL.lcd |
| Method File | : P0X-10%-0.8ml.lcm |



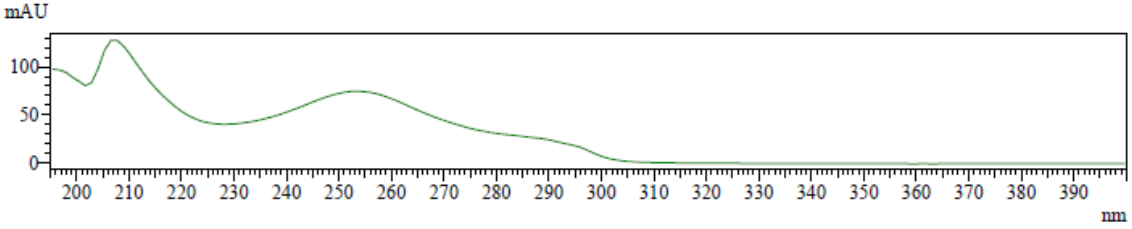

Chromatogram




UV Spectrum
Retention time = 13.720




UV Spectrum
Retention time = 16.609




Peak Table

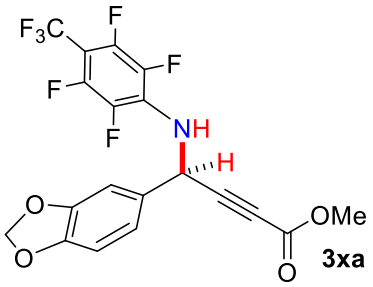
PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 13.720 | 3433019 | 49.735 |
| 2 | 16.609 | 3469604 | 50.265 |
| Total | | 6902624 | 100.000 |

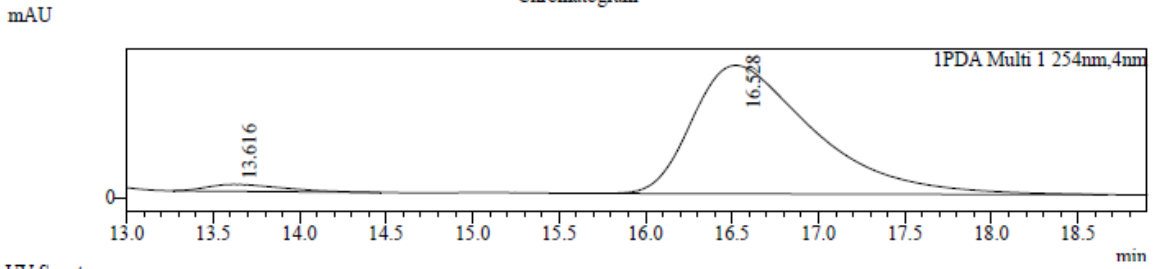
# HPLC

Sample Information

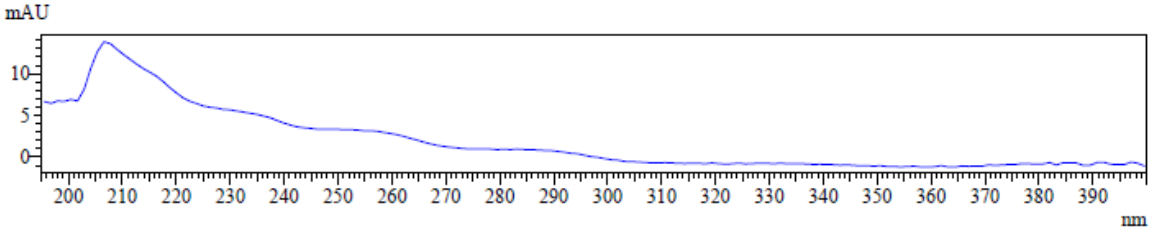
Sample Name : P0X-0628X-ASH-10%-0.8mL
Sample ID : P0X-0628X-ASH-10%-0.8mL
Data File : P0X-0628X-ASH-10%-0.8mL.lcd
Method File : P0X-10%-0.8ml.lcm



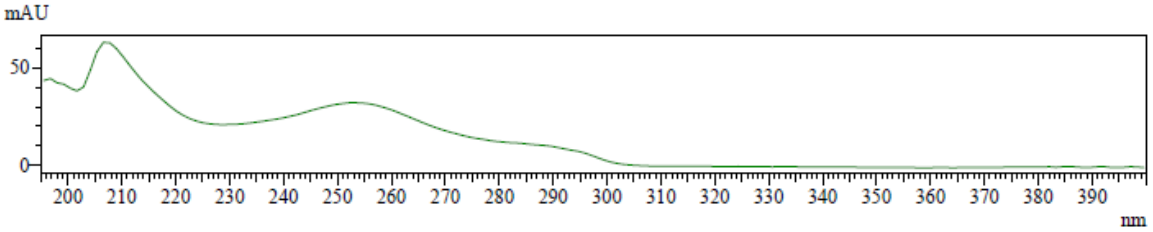

Chromatogram




UV Spectrum
Retention time = 13.616




UV Spectrum
Retention time = 16.528

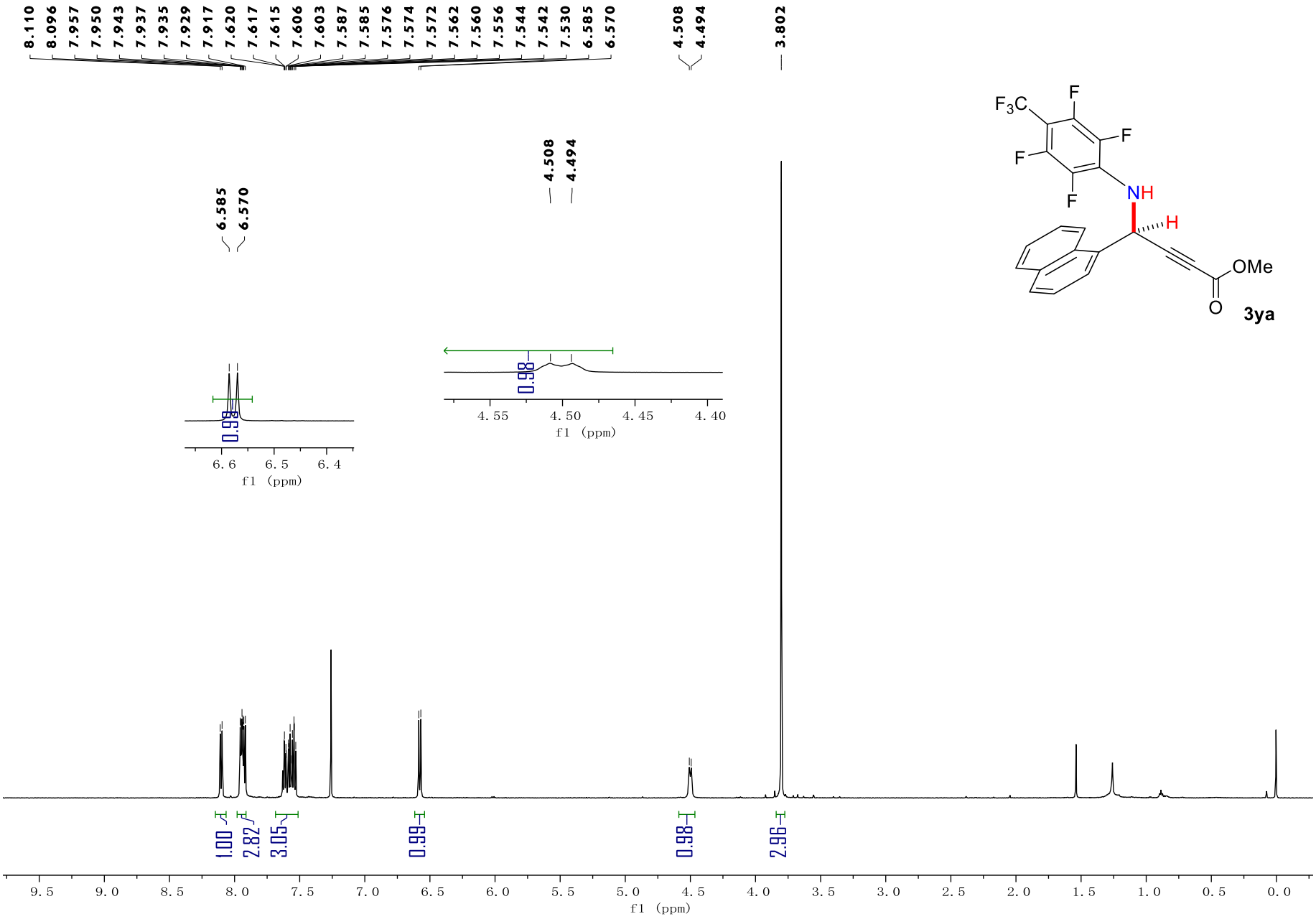



Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 13.616 | 49819 | 3.221 |
| 2 | 16.528 | 1496756 | 96.779 |
| Total | | 1546574 | 100.000 |

# $^1$H NMR

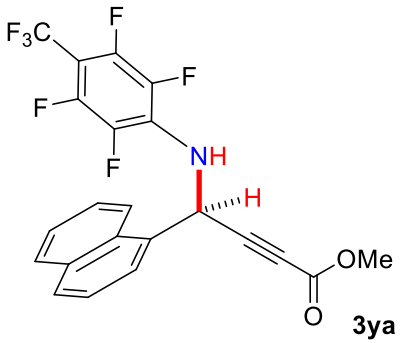

8.110
8.096
7.957
7.950
7.943
7.937
7.935
7.929
7.917
7.620
7.617
7.615
7.606
7.603
7.587
7.585
7.576
7.574
7.572
7.562
7.560
7.556
7.544
7.542
7.530
6.585
6.570
4.508
4.494
3.802
F3C
F
F
F
F
NH
H
OMe
O
3ya
6.585
6.570
0.98
6.6
6.5
6.4
f1 (ppm)
4.508
4.494
0.98
4.55
4.50
4.45
4.40
f1 (ppm)
1.00
2.82
3.05
0.99
0.98
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

# $^{13}$C NMR

155.983 148.404 146.665 141.116 139.405 136.790 133.681 133.318 132.893 131.838 131.549 131.474 131.397 130.044 129.139 128.645 127.953 125.307 124.864 123.051 102.000 101.768 101.679

86.652 81.007

55.654 51.215



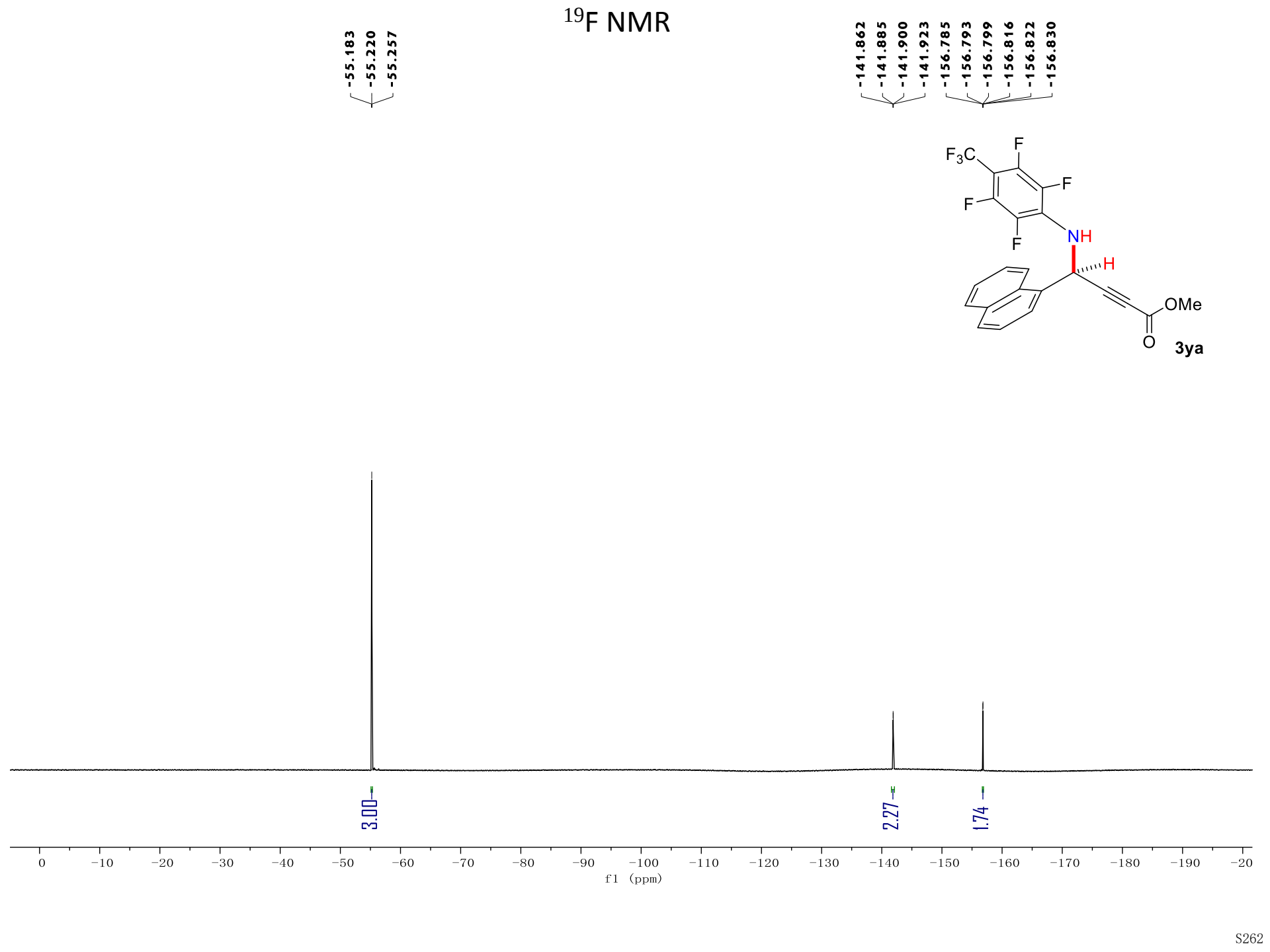

**3ya**

grease

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

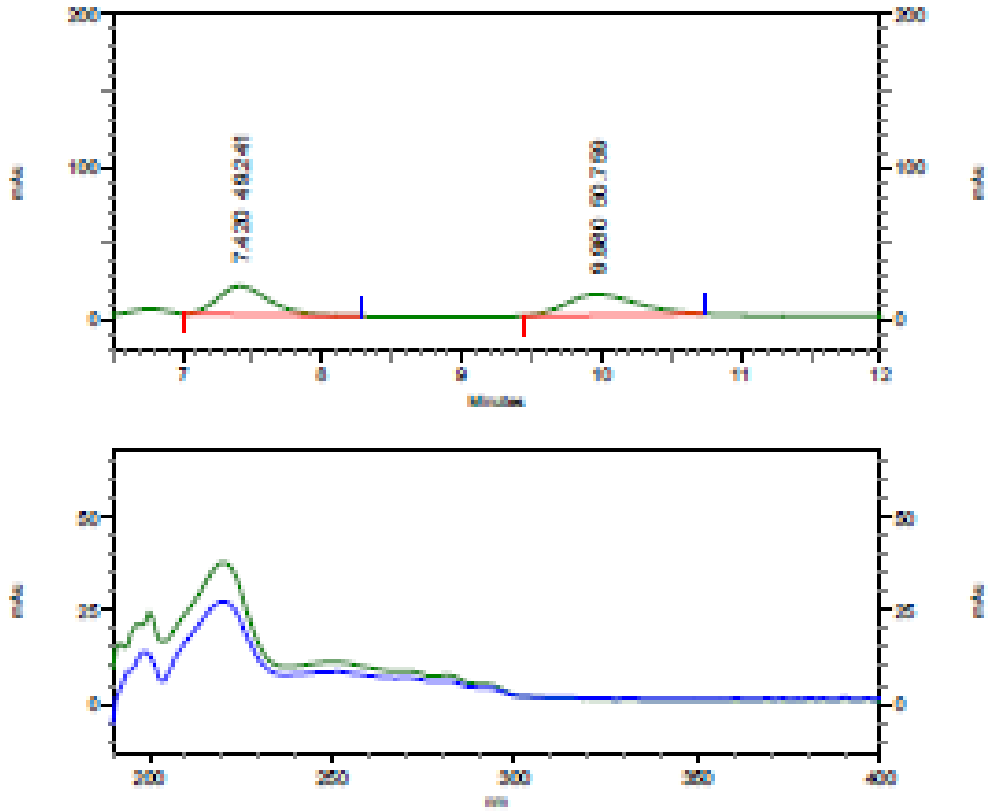
f1 (ppm)

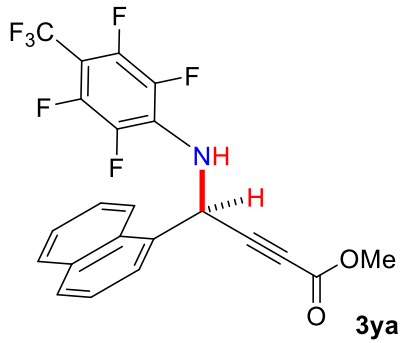
# $^{19}$F NMR


-55.183
-55.220
-55.257
-141.862
-141.885
-141.900
-141.923
-156.785
-156.793
-156.799
-156.816
-156.822
-156.830
F3C
F
F
F
F
NH
H
OMe
O
3ya
3.00
2.27
1.74
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−20
f1 (ppm)

# HPLC

C:\EZStart\Projects\Default\Data\POX0891ASH-5%-0.8mL
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



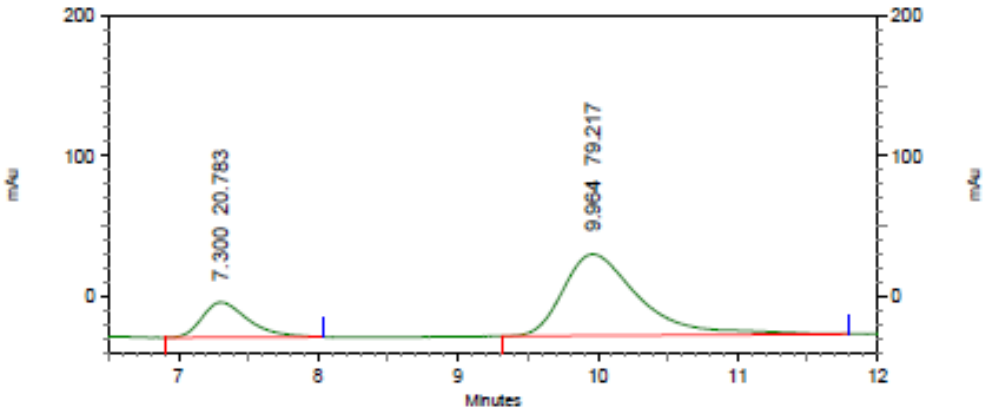



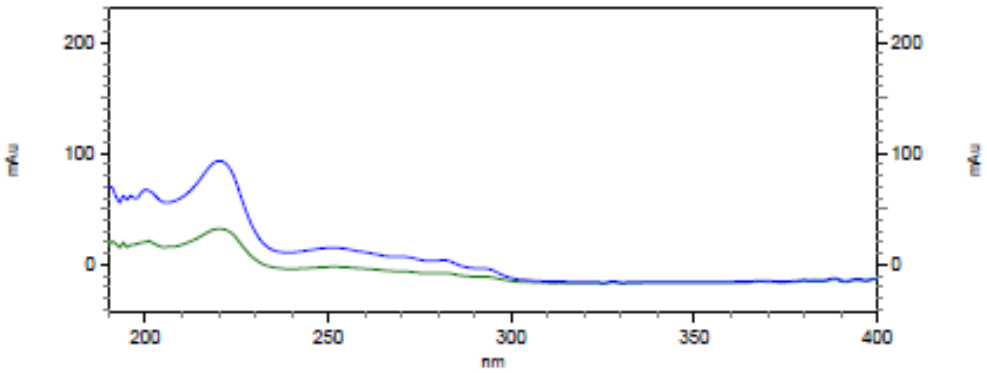

4: 250 nm, 4
nm Results

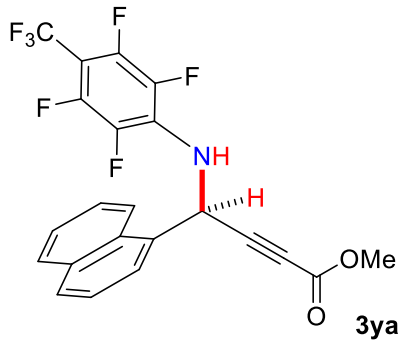
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.420 | 49.241 |
| 2 | 9.980 | 50.759 |
| Totals | | 100.000 |

# HPLC

C:\EZStart\Projects\Default\Data\P0X0608ASH-5%-0.8mL
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



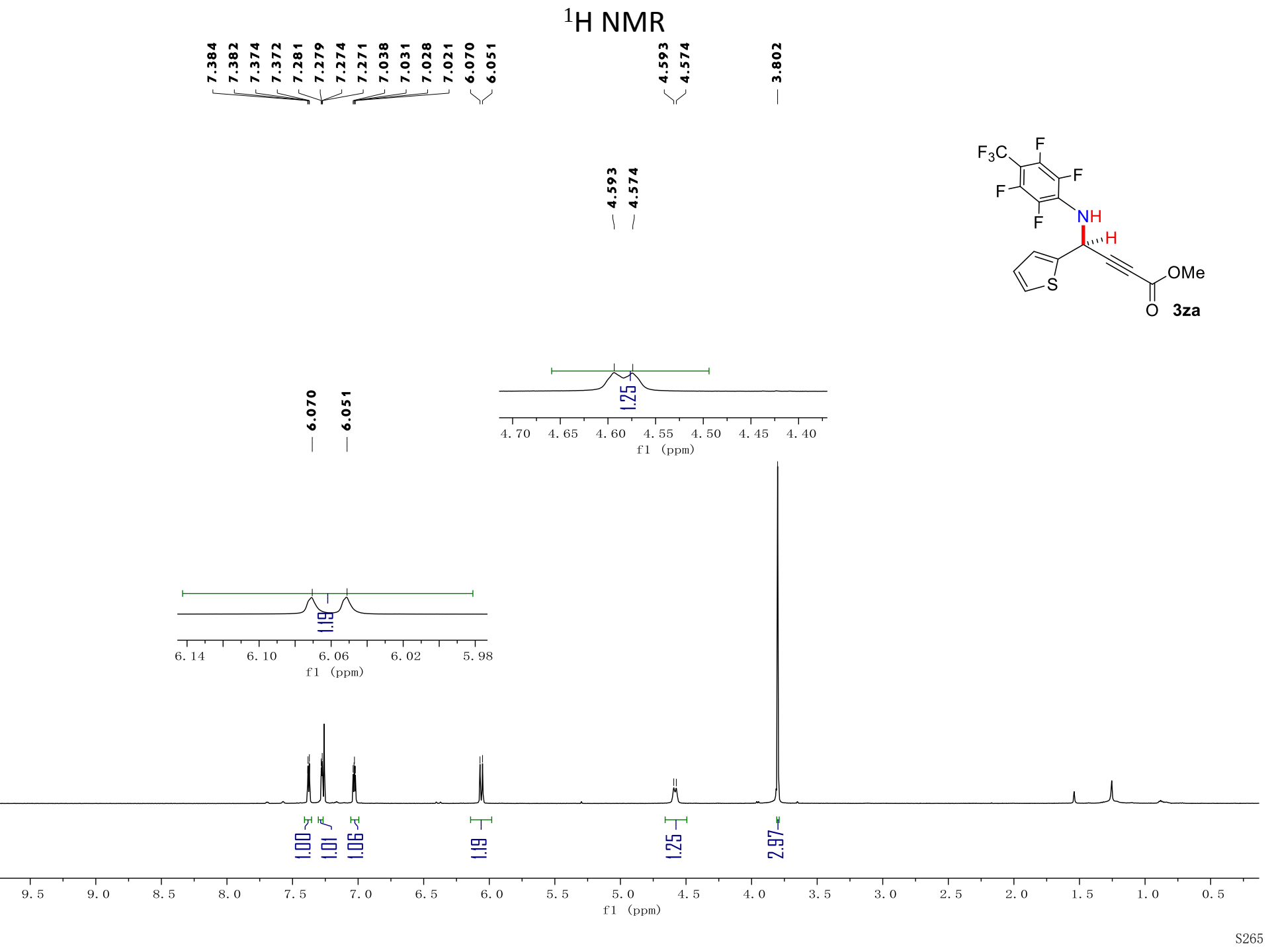




**3ya**

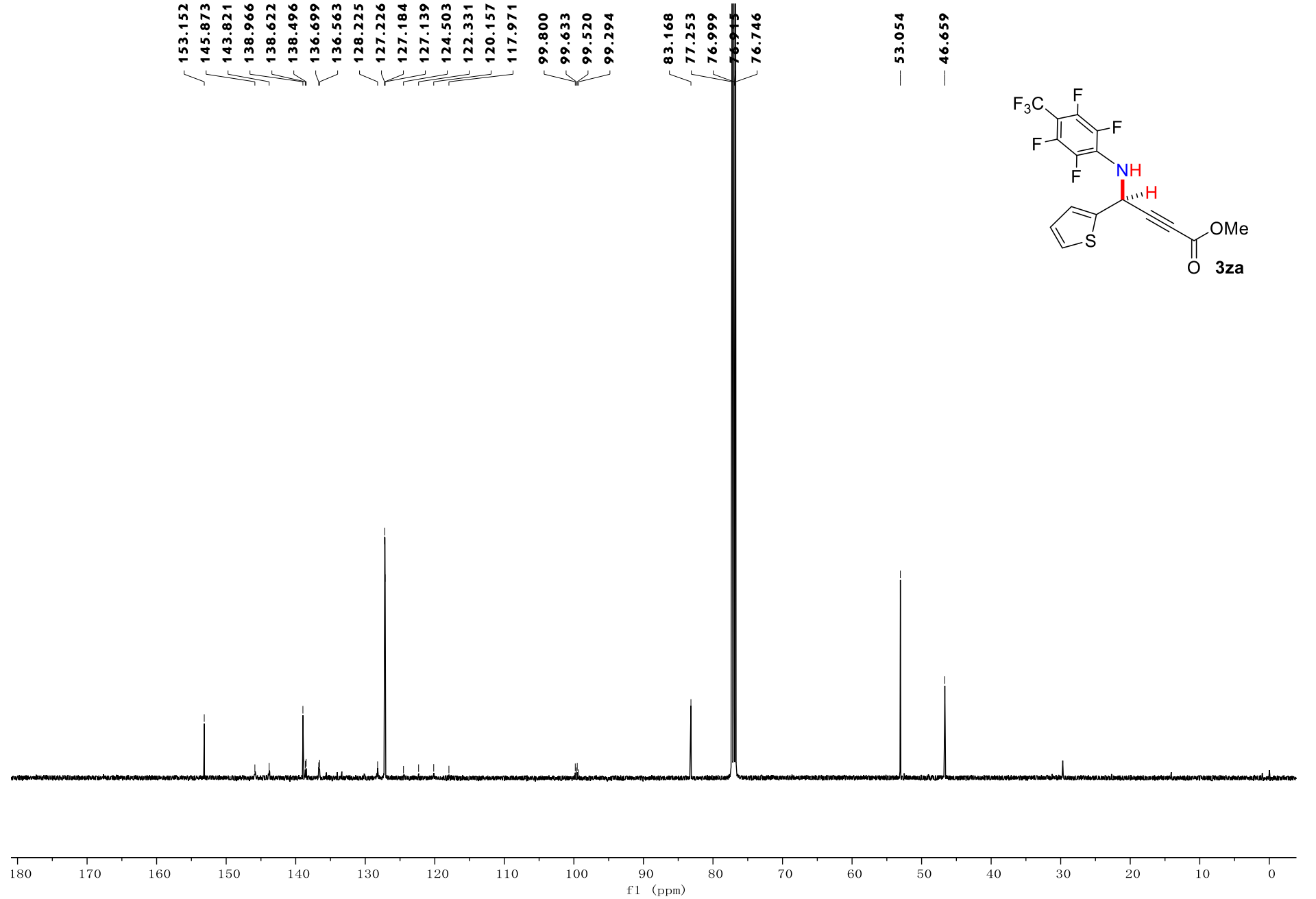
4: 250 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.300 | 20.783 |
| 2 | 9.964 | 79.217 |
| Totals | | 100.000 |

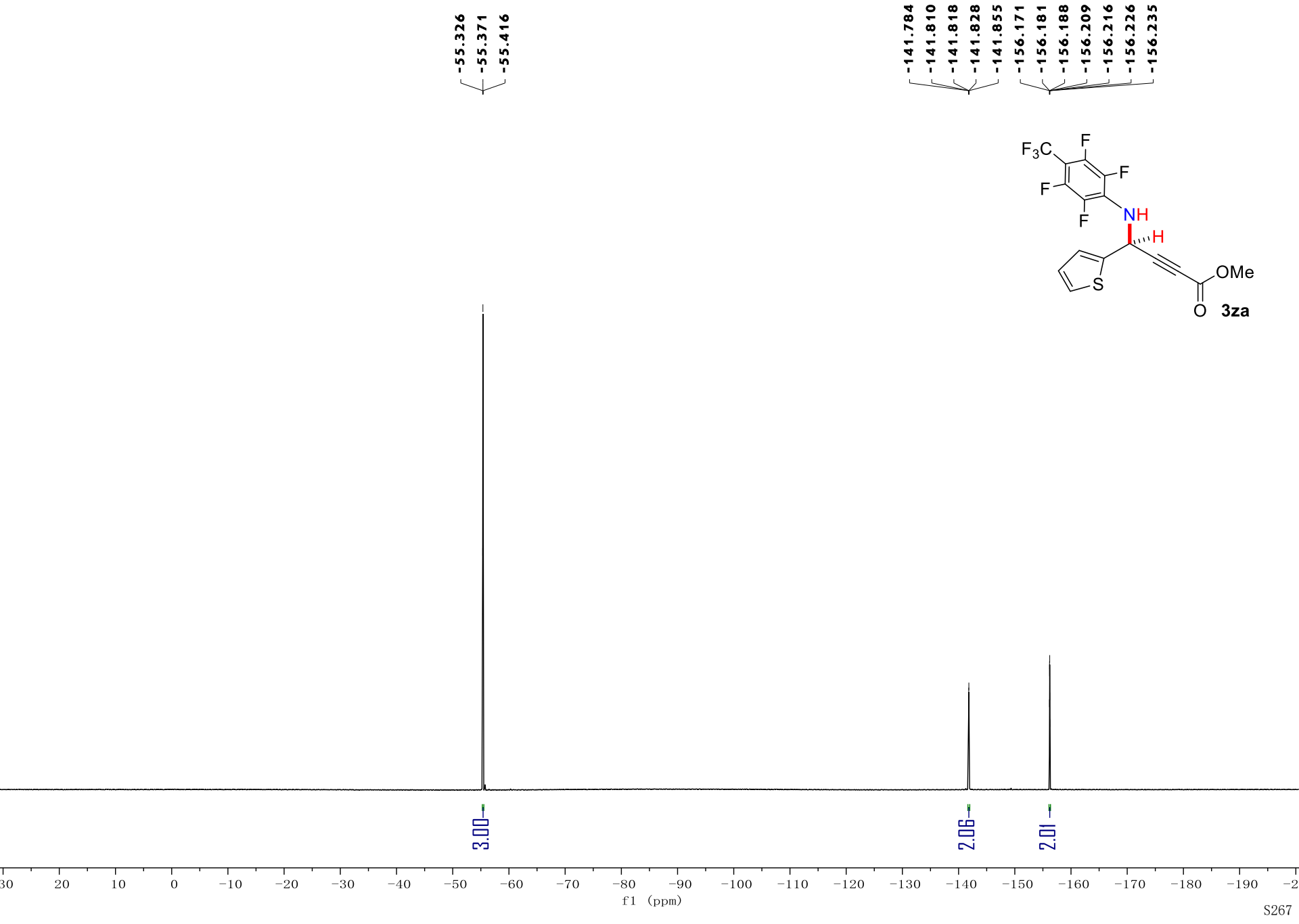
# $^1$H NMR


7.384
7.382
7.374
7.372
7.281
7.279
7.274
7.271
7.038
7.031
7.028
7.021
6.070
6.051
4.593
4.574
3.802
F3C
F
F
F
F
NH
H
S
OMe
O
3za
1.25
4.70 4.65 4.60 4.55 4.50 4.45 4.40
f1 (ppm)
1.19
6.14 6.10 6.06 6.02 5.98
f1 (ppm)
1.00
1.01
1.06
1.19
1.25
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

# $^{13}$C NMR


153.152
145.873
143.821
138.966
138.622
138.496
136.699
136.563
128.225
127.226
127.184
127.139
124.503
122.331
120.157
117.971
99.800
99.633
99.520
99.294
83.168
77.253
76.999
76.915
76.746
53.054
46.659
F3C
F
F
F
F
NH
H
S
OMe
O
3za
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

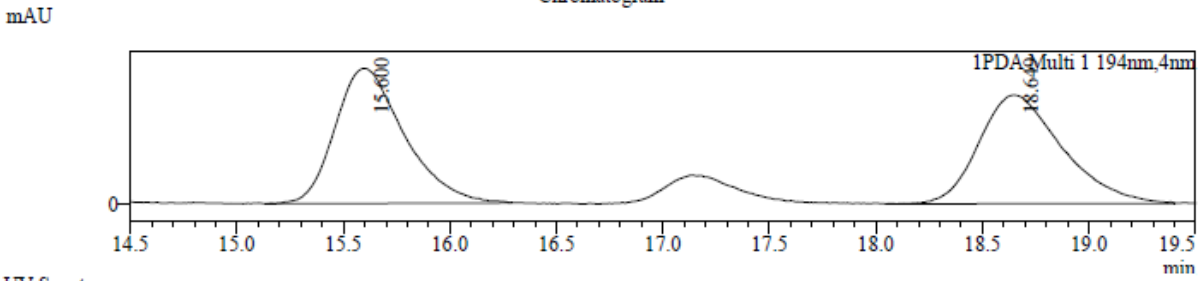

-55.326
-55.371
-55.416
-141.784
-141.810
-141.818
-141.828
-141.855
-156.171
-156.181
-156.188
-156.209
-156.216
-156.226
-156.235
F3C
F
F
F
F
NH
H
S
OMe
O
3za
3.00
2.06
2.01
f1 (ppm)

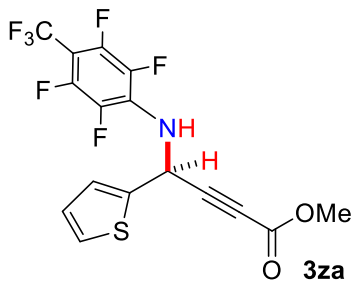
# HPLC

Sample Information

| | |
|---|---|
| Sample Name | : P0X0768-ODH-5%-0.8 |
| Sample ID | : P0X0768-ODH-5%-0.8 |
| Data File | : P0X0768-ODH-5%-0.8.lcd |
| Method File | : P0X-5.0%-0.8ml.lcm |

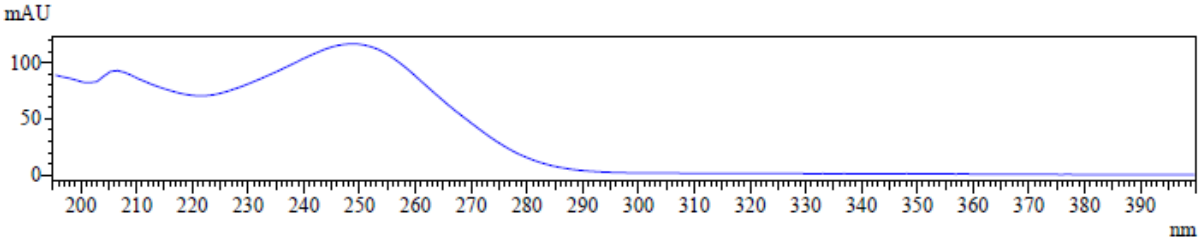
Chromatogram



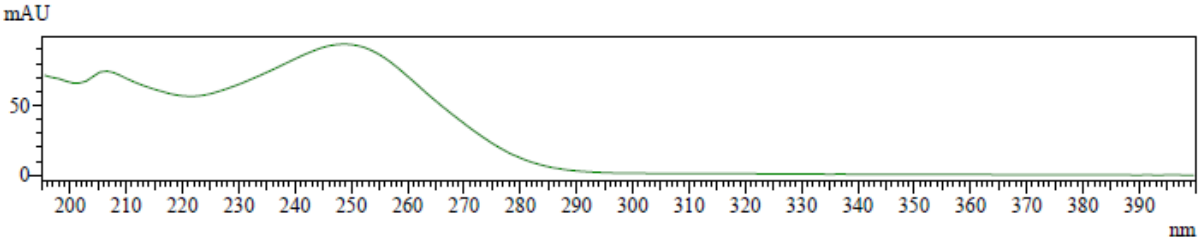




**3za**

UV Spectrum
Retention time = 15.600




UV Spectrum
Retention time = 18.649




Peak Table

PDA Ch1 194nm

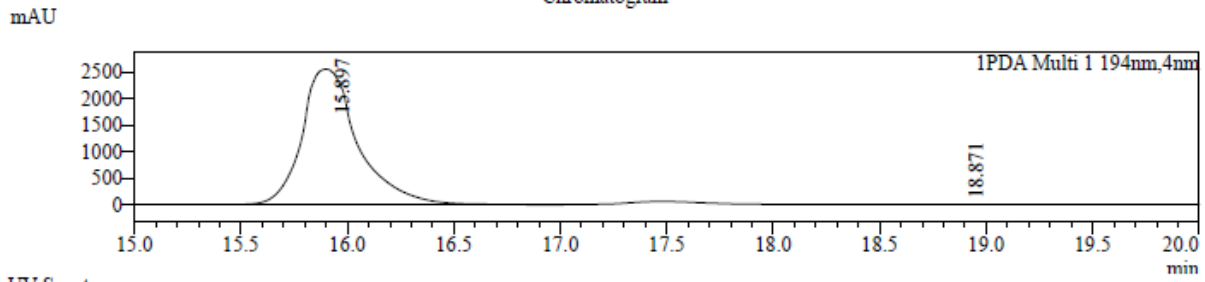
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 15.600 | 2006994 | 50.817 |
| 2 | 18.649 | 1942426 | 49.183 |
| Total | | 3949419 | 100.000 |

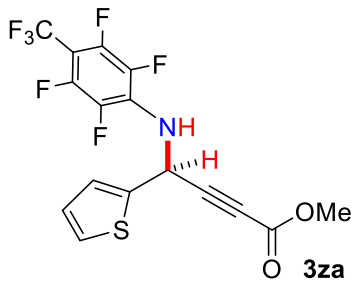
# HPLC

Sample Information

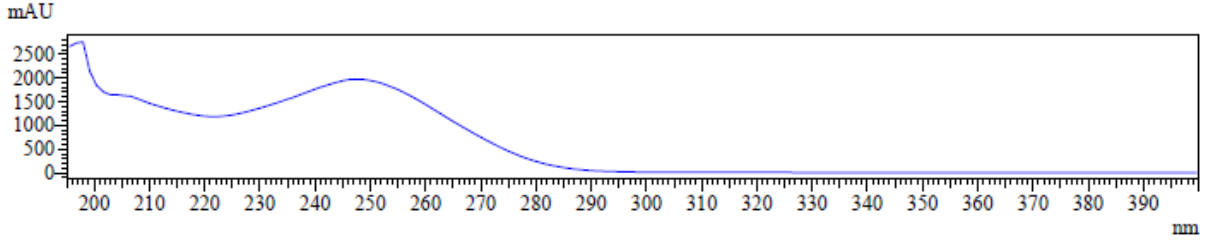
Sample Name : P0X-0769-ODH-5%-0.8
Sample ID : P0X-0769-ODH-5%-0.8
Data File : P0X-0769-ODH-5%-0.8.lcd
Method File : P0X-5.0%-0.8ml.lcm

Chromatogram

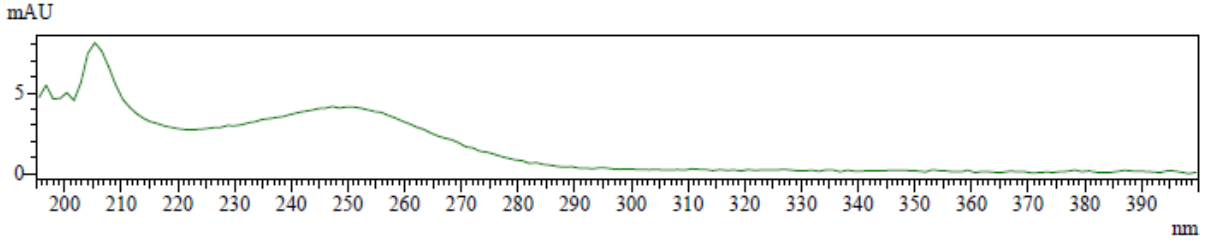



UV Spectrum
Retention time = 15.897




UV Spectrum
Retention time = 18.871

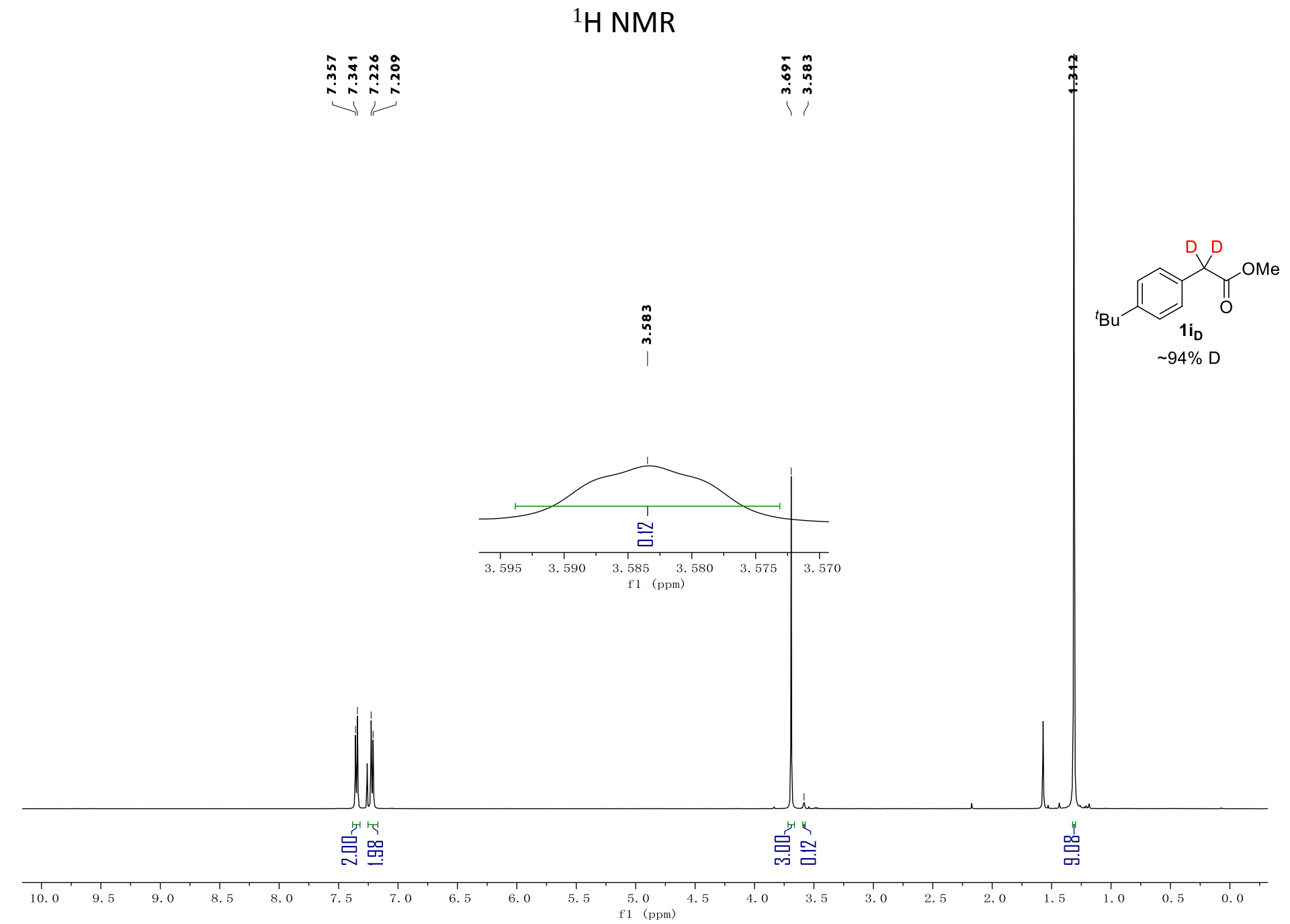



Peak Table

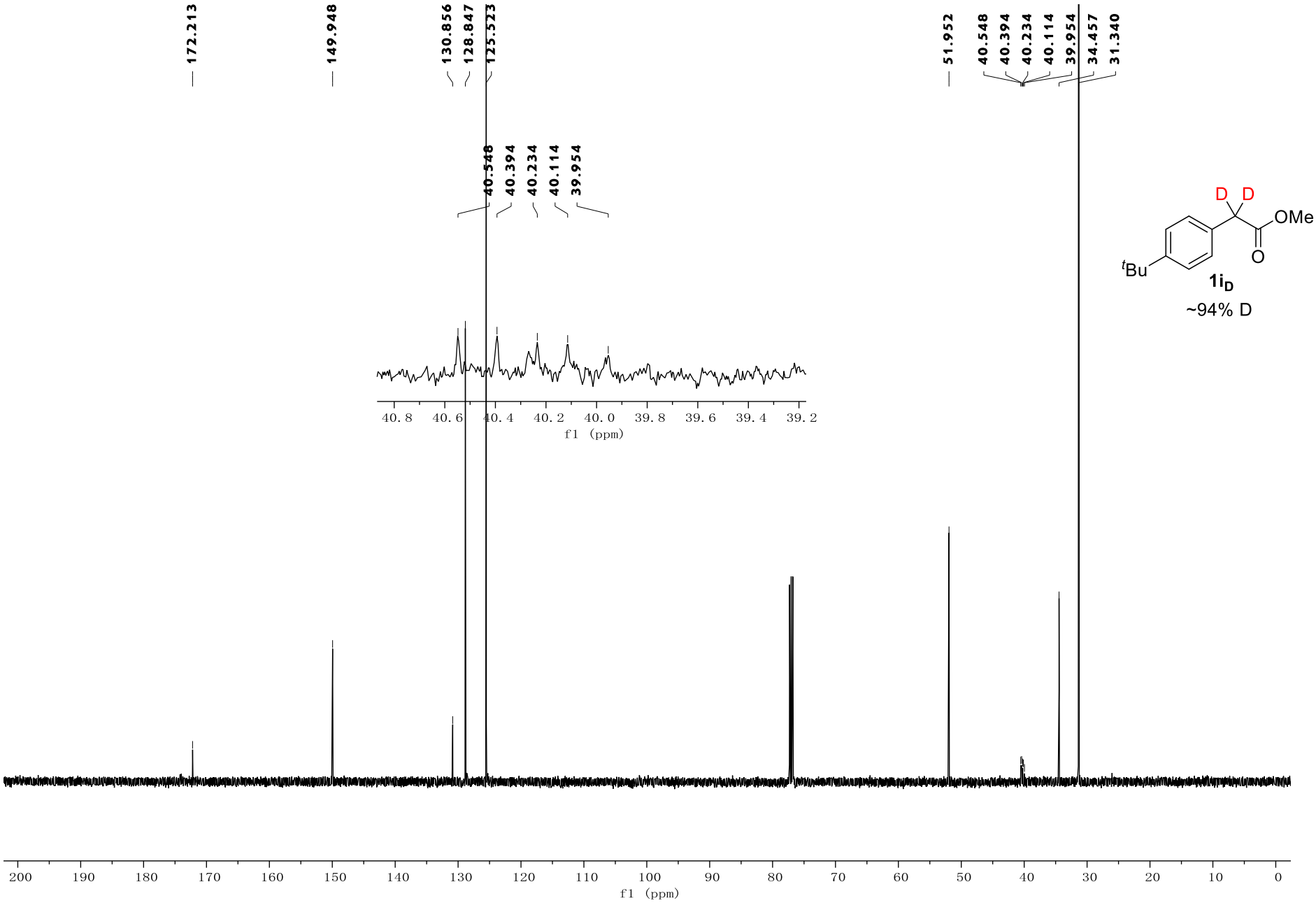
PDA Ch1 194nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 15.897 | 46609958 | 99.862 |
| 2 | 18.871 | 64216 | 0.138 |
| Total | | 46674174 | 100.000 |

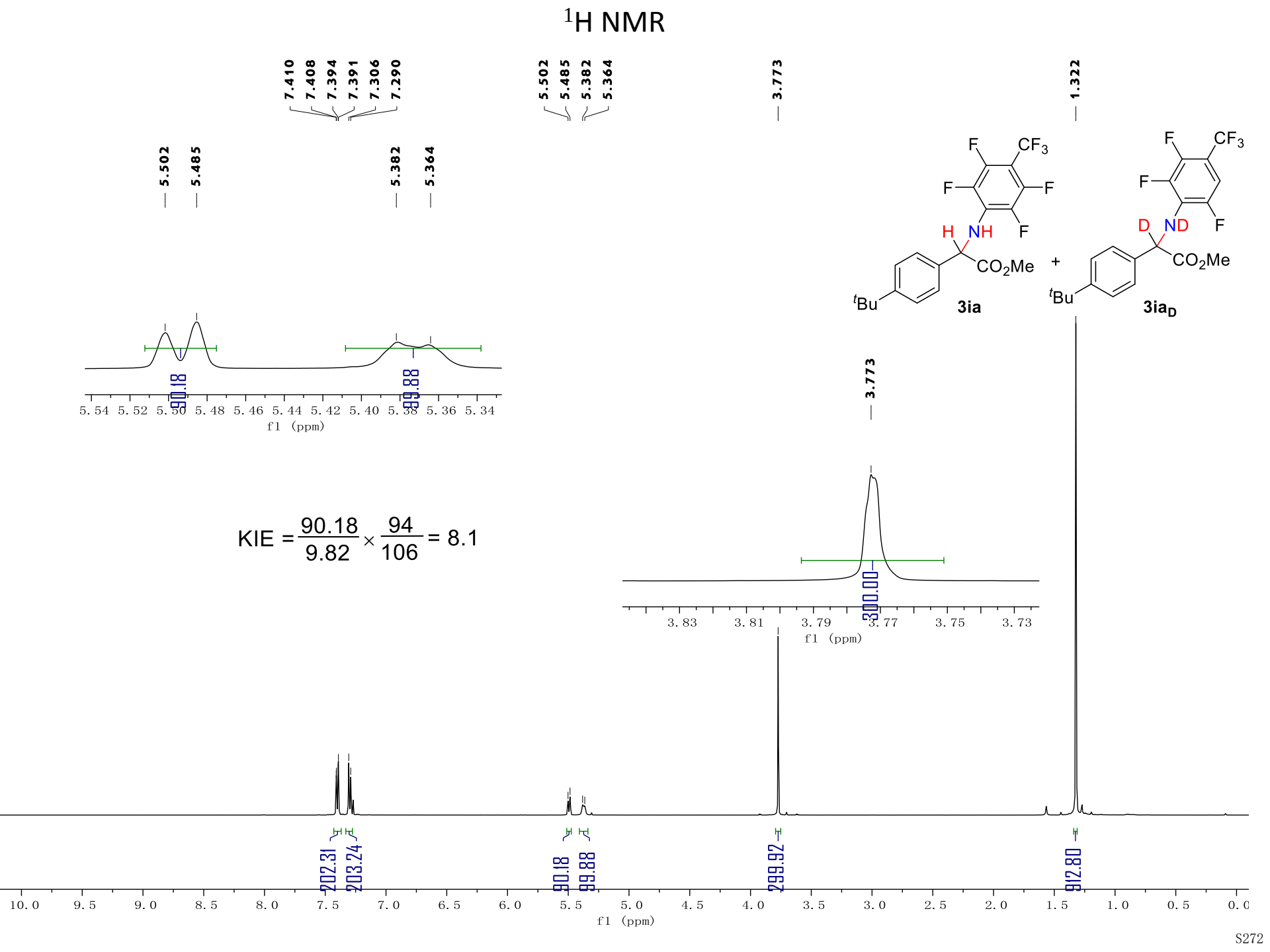
# $^1$H NMR


7.357
7.341
7.226
7.209
3.691
3.583
1.312
3.583
0.12
3.595
3.590
3.585
3.580
3.575
3.570
f1 (ppm)
D D
OMe
O
tBu
1i_D
~94% D
2.00
1.98
3.00
0.12
9.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

# $^{13}$C NMR

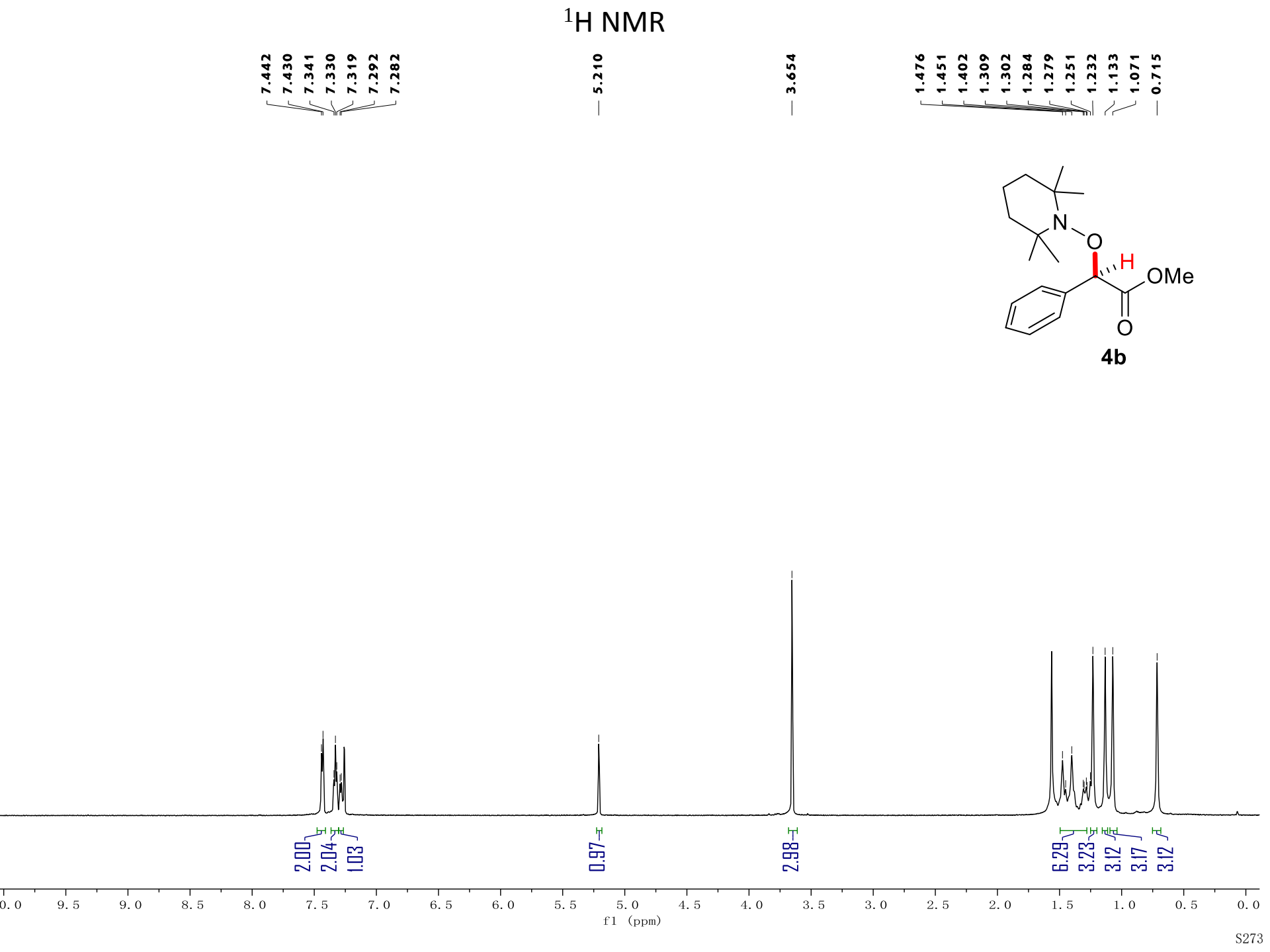

172.213
149.948
130.856
128.847
125.523
51.952
40.548
40.394
40.234
40.114
39.954
34.457
31.340
40.548
40.394
40.234
40.114
39.954
40.8 40.6 40.4 40.2 40.0 39.8 39.6 39.4 39.2
f1 (ppm)
D D
OMe
O
tBu
1i_D
~94% D
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

# $^1$H NMR

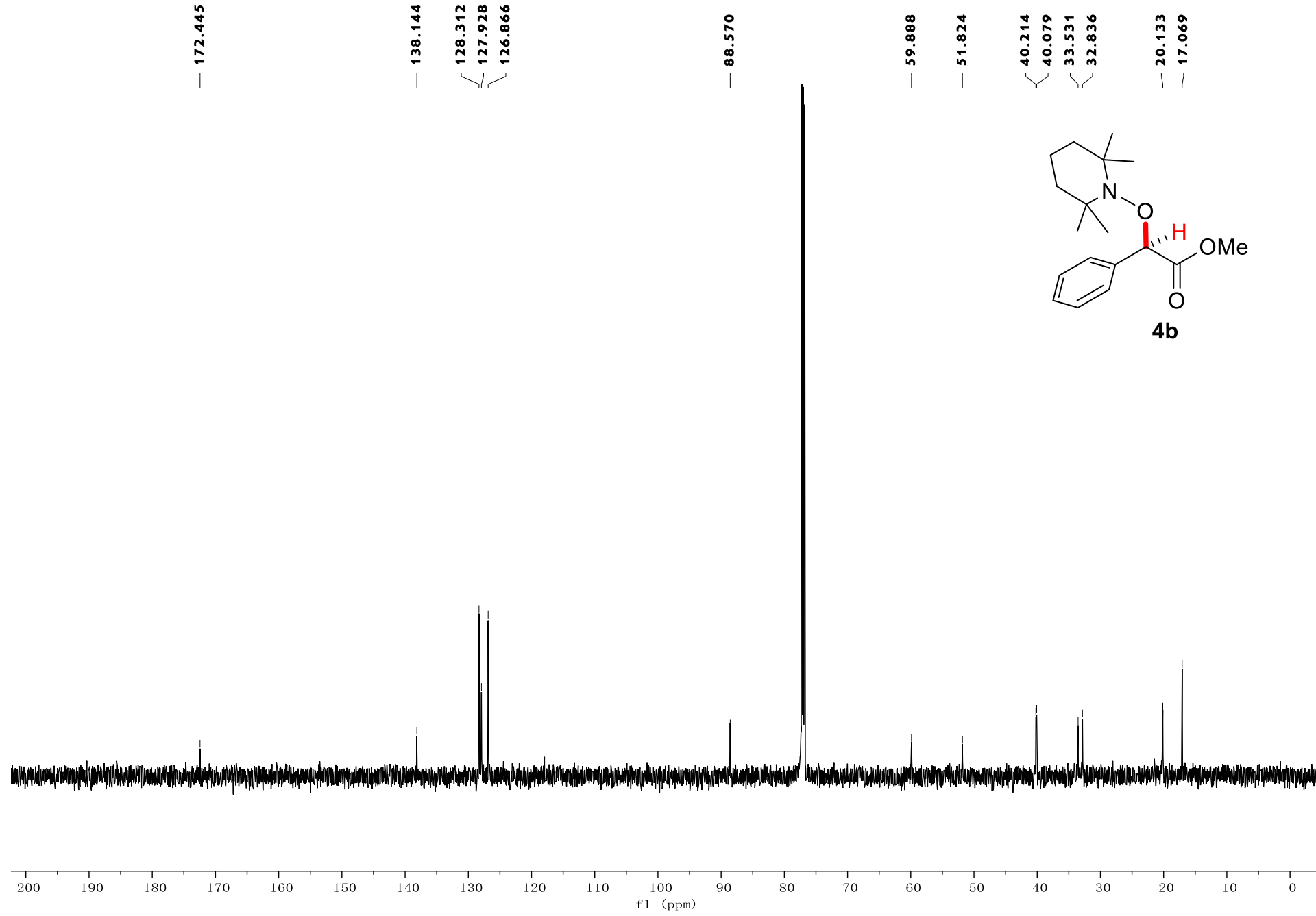



$$\text{KIE} = \frac{90.18}{9.82} \times \frac{94}{106} = 8.1$$

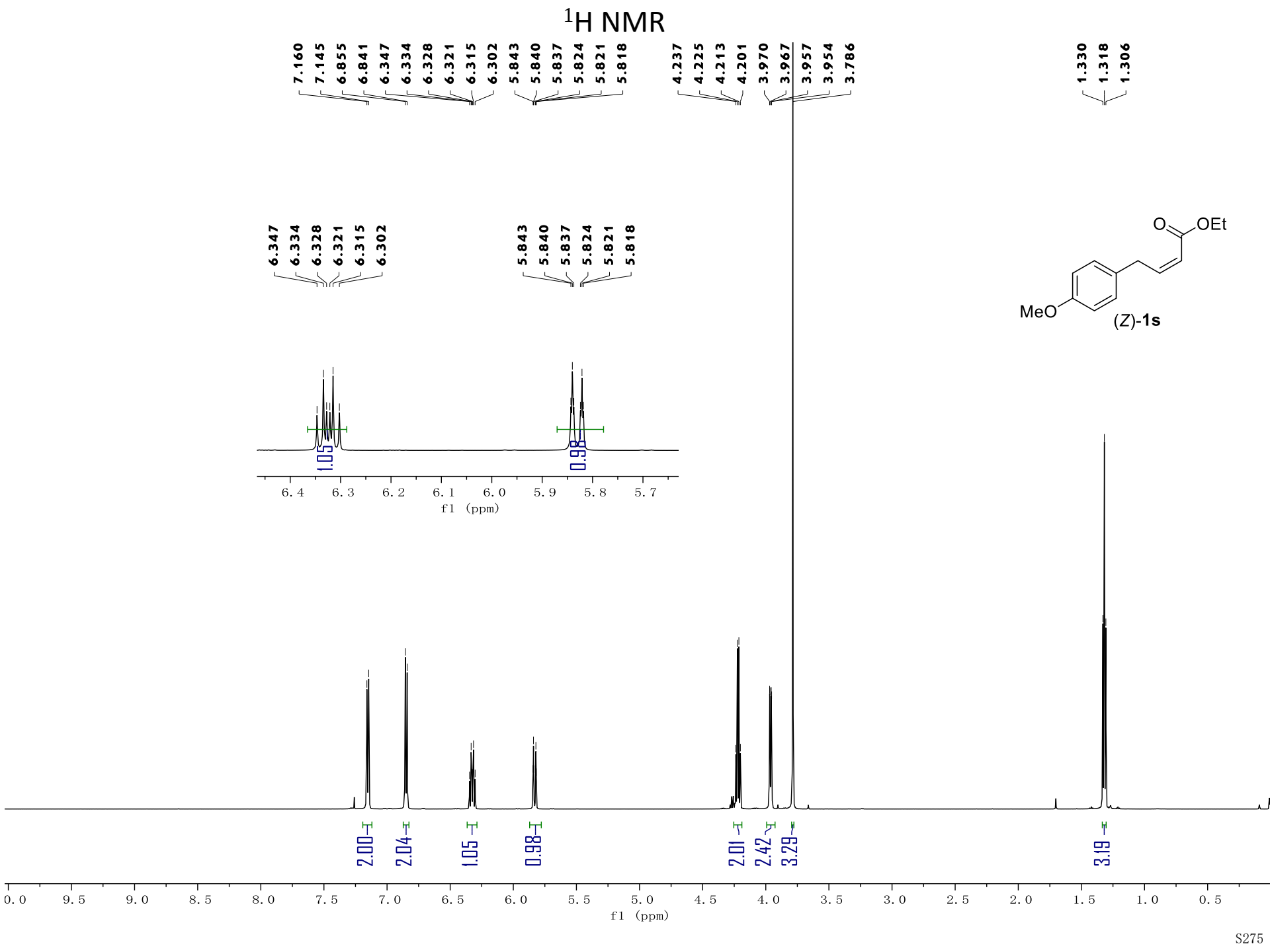
# $^{1}$H NMR


7.442
7.430
7.341
7.330
7.319
7.292
7.282
5.210
3.654
1.476
1.451
1.402
1.309
1.302
1.284
1.279
1.251
1.232
1.133
1.071
0.715
N
O
H
OMe
O
4b
2.00
2.04
1.03
0.97
2.98
6.29
3.23
3.12
3.17
3.12
f1 (ppm)

# $^{13}$C NMR

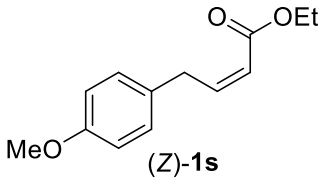

172.445
138.144
128.312
127.928
126.866
88.570
59.888
51.824
40.214
40.079
33.531
32.836
20.133
17.069
N
O
H
OMe
O
4b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{1}$H NMR

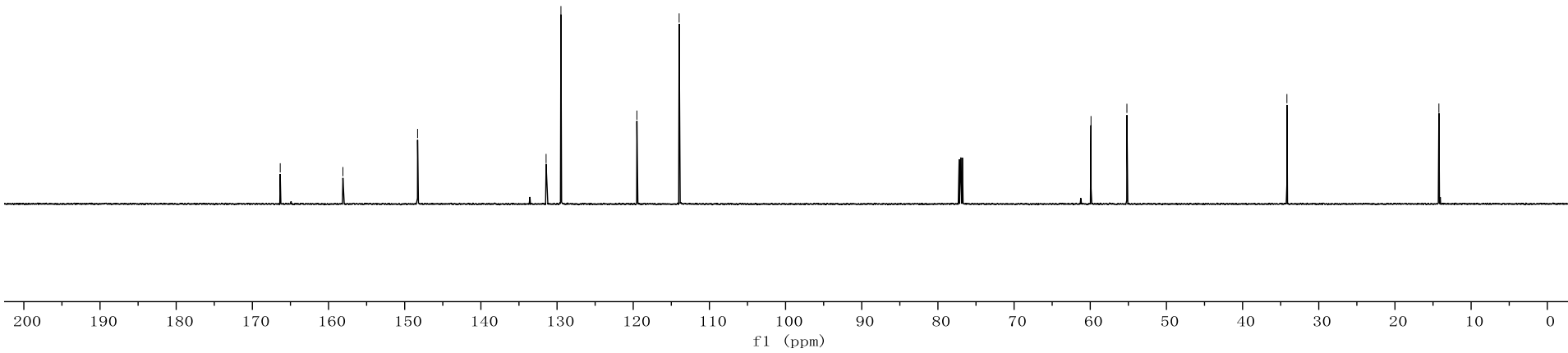

7.160
7.145
6.855
6.841
6.347
6.334
6.328
6.321
6.315
6.302
5.843
5.840
5.837
5.824
5.821
5.818
4.237
4.225
4.213
4.201
3.970
3.967
3.957
3.954
3.786
1.330
1.318
1.306
1.05
0.98
f1 (ppm)
O
OEt
MeO
(Z)-1s
2.00
2.04
1.05
0.98
2.01
2.42
3.29
3.19
f1 (ppm)

# $^{13}$C NMR

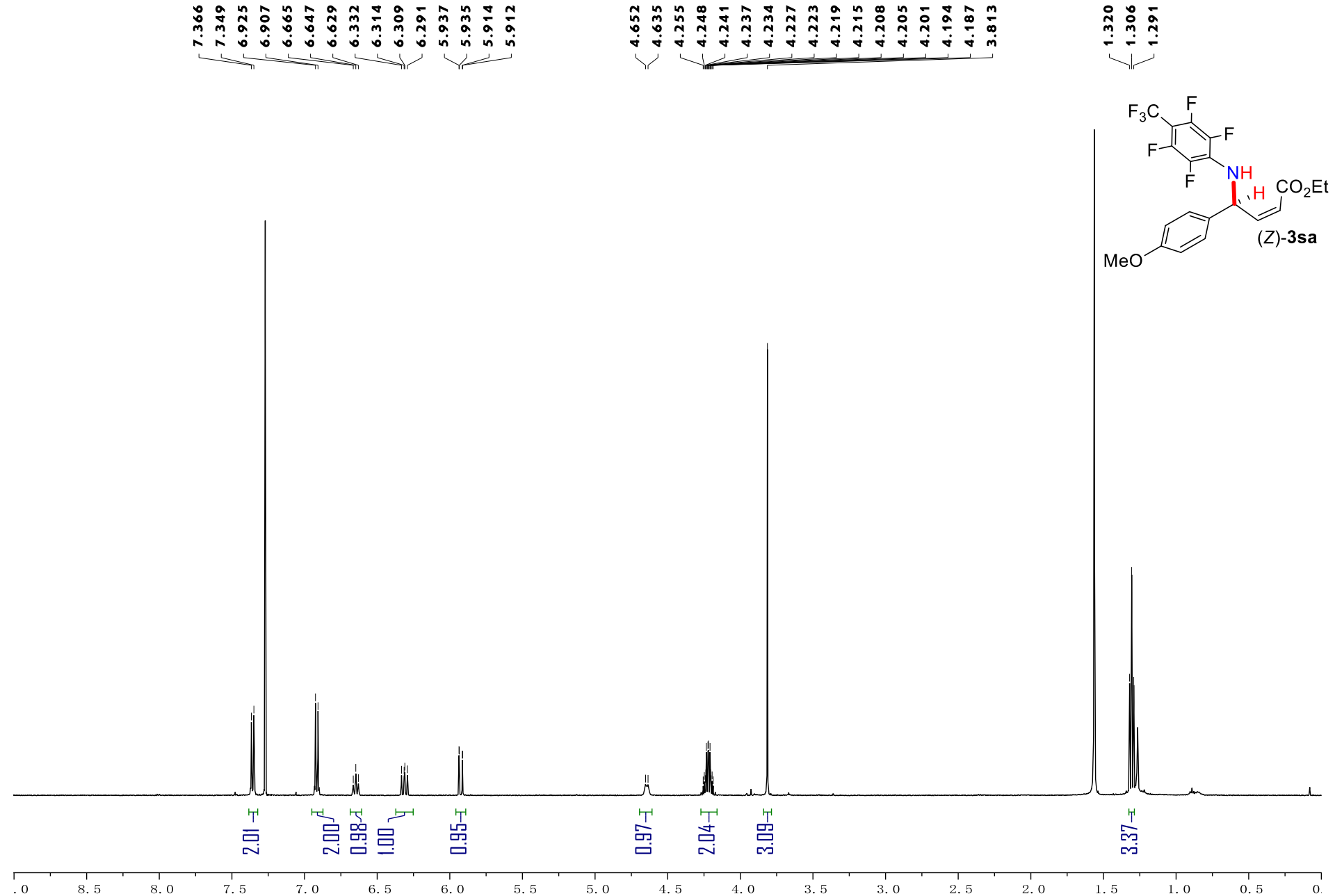
166.345
158.113
148.309
131.437
129.490
129.480
119.517
113.972
59.902
55.187
34.184
14.231



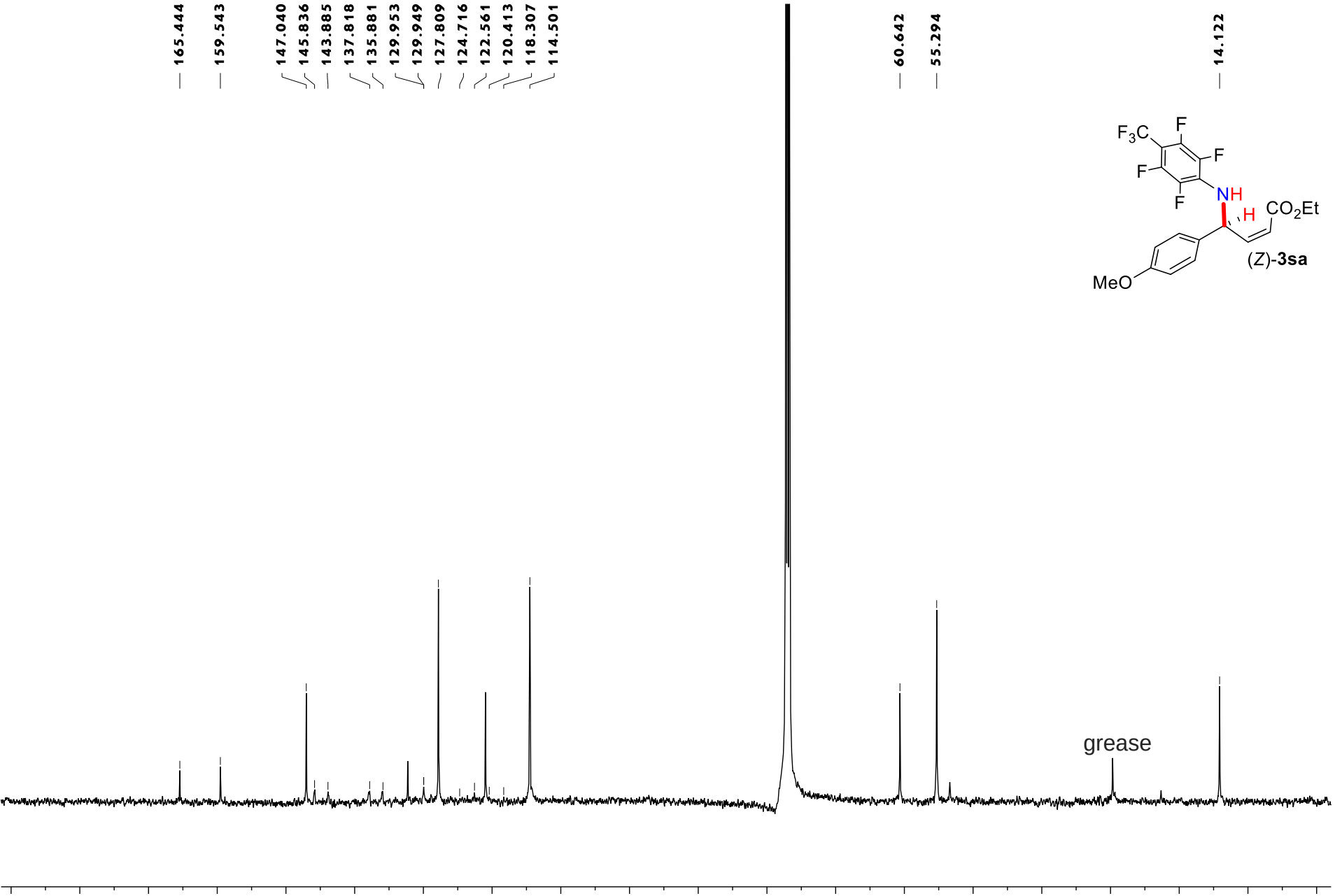

(*Z*)-**1s**



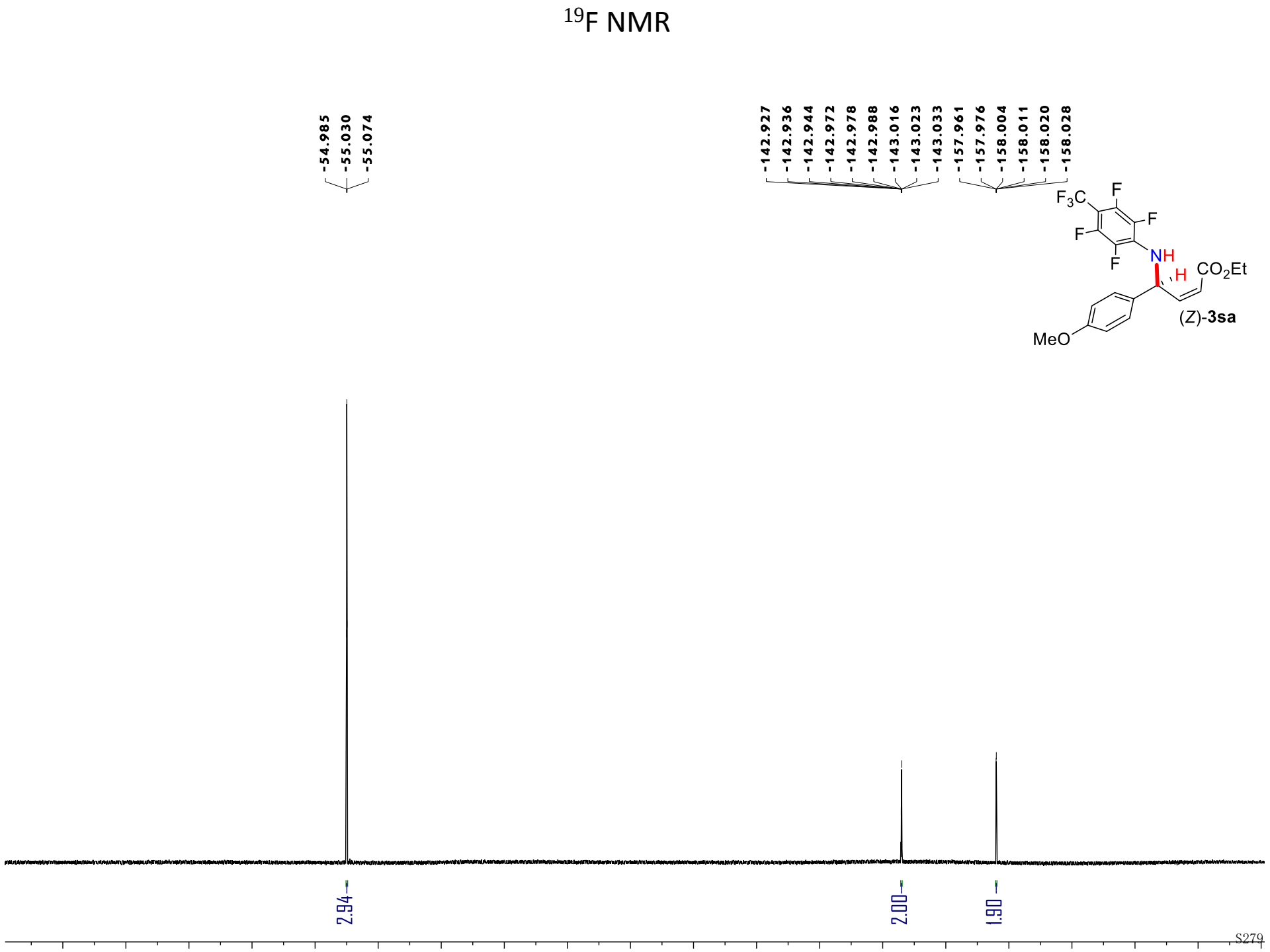
# $^{1}$H NMR


7.366
7.349
6.925
6.907
6.665
6.647
6.629
6.332
6.314
6.309
6.291
5.937
5.935
5.914
5.912
4.652
4.635
4.255
4.248
4.241
4.237
4.234
4.227
4.223
4.219
4.215
4.208
4.205
4.201
4.194
4.187
3.813
1.320
1.306
1.291
F3C
F
F
F
F
NH
H
CO2Et
MeO
(Z)-3sa
2.01
2.00
0.98
1.00
0.95
0.97
2.04
3.09
3.37
f1 (ppm)

# $^{13}$C NMR


165.444
159.543
147.040
145.836
143.885
137.818
135.881
129.953
129.949
127.809
124.716
122.561
120.413
118.307
114.501
60.642
55.294
14.122
F3C
F
F
F
F
NH
H
CO2Et
MeO
(Z)-3sa
grease
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# $^{19}$F NMR

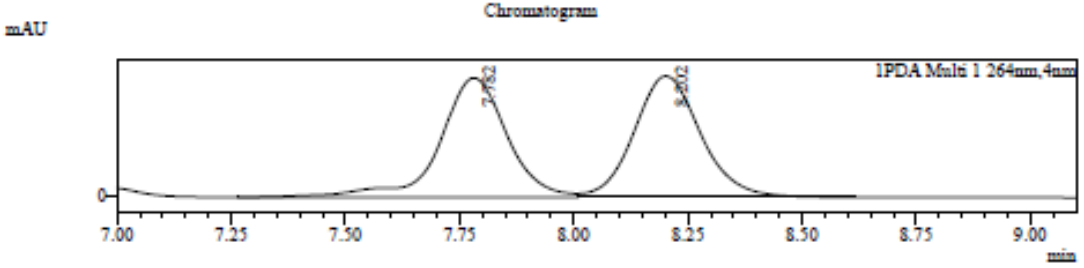

-54.985
-55.030
-55.074
-142.927
-142.936
-142.944
-142.972
-142.978
-142.988
-143.016
-143.023
-143.033
-157.961
-157.976
-158.004
-158.011
-158.020
-158.028
F3C
F
F
F
F
NH
H
CO2Et
MeO
(Z)-3sa
2.94
2.00
1.90

# HPLC

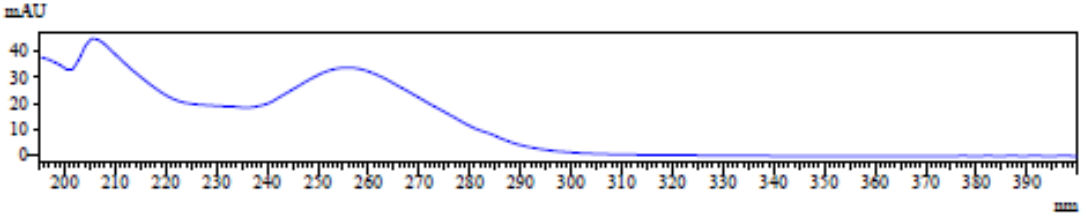
Sample Information

| | |
|---|---|
| Sample Name | : P0X-0548-2-IA5%-0.8mL.lcd |
| Sample ID | : P0X-0548-2-IA5%-0.8mL.lcd |
| Data File | : P0X-0548-2-IA5%-0.8mL.lcd |
| Method File | : P0X-5%.0.8.mL-30min.lcm |

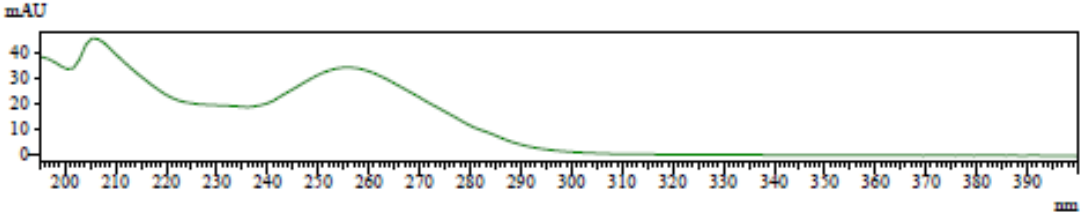
Chromatogram

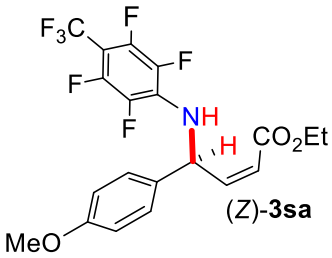



UV Spectrum
Retention time = 7.782




UV Spectrum
Retention time = 8.202




Peak Table

PDA Ch1 264nm

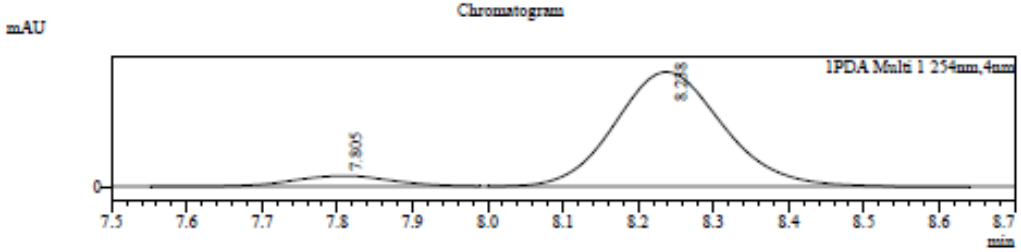
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 7.782 | 297484 | 49.962 |
| 2 | 8.202 | 297940 | 50.038 |
| Total | | 595424 | 100.000 |

# HPLC

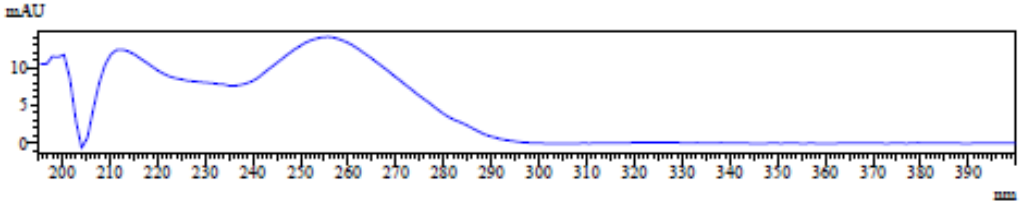
Sample Information

| | |
|---|---|
| Sample Name | : P0X-1252-2-IA-5%-0.8mL.lcd |
| Sample ID | : P0X-1252-2-IA-5%-0.8mL.lcd |
| Data File | : P0X-1252-2-IA-5%-0.8mL.lcd |
| Method File | : P0X-5%.0.8.mL-30min.lcm |

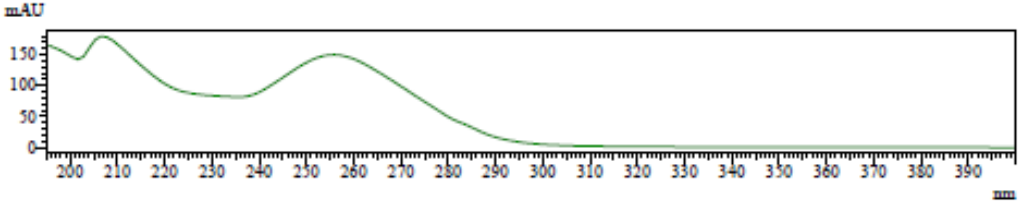
Chromatogram




UV Spectrum
Retention time = 7.805



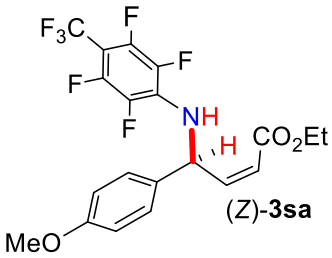

UV Spectrum
Retention time = 8.238



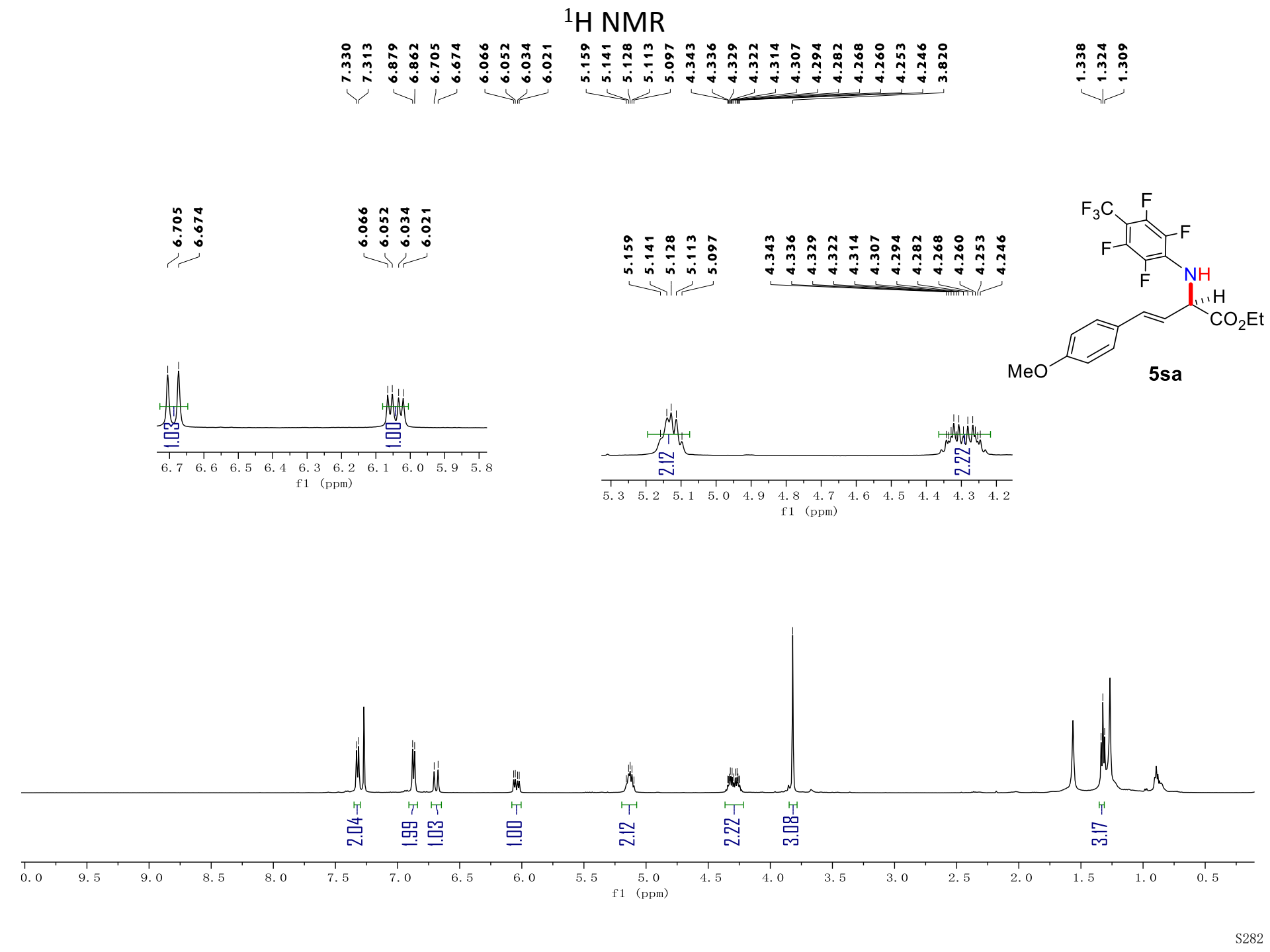

Peak Table

PDA Ch1 254nm

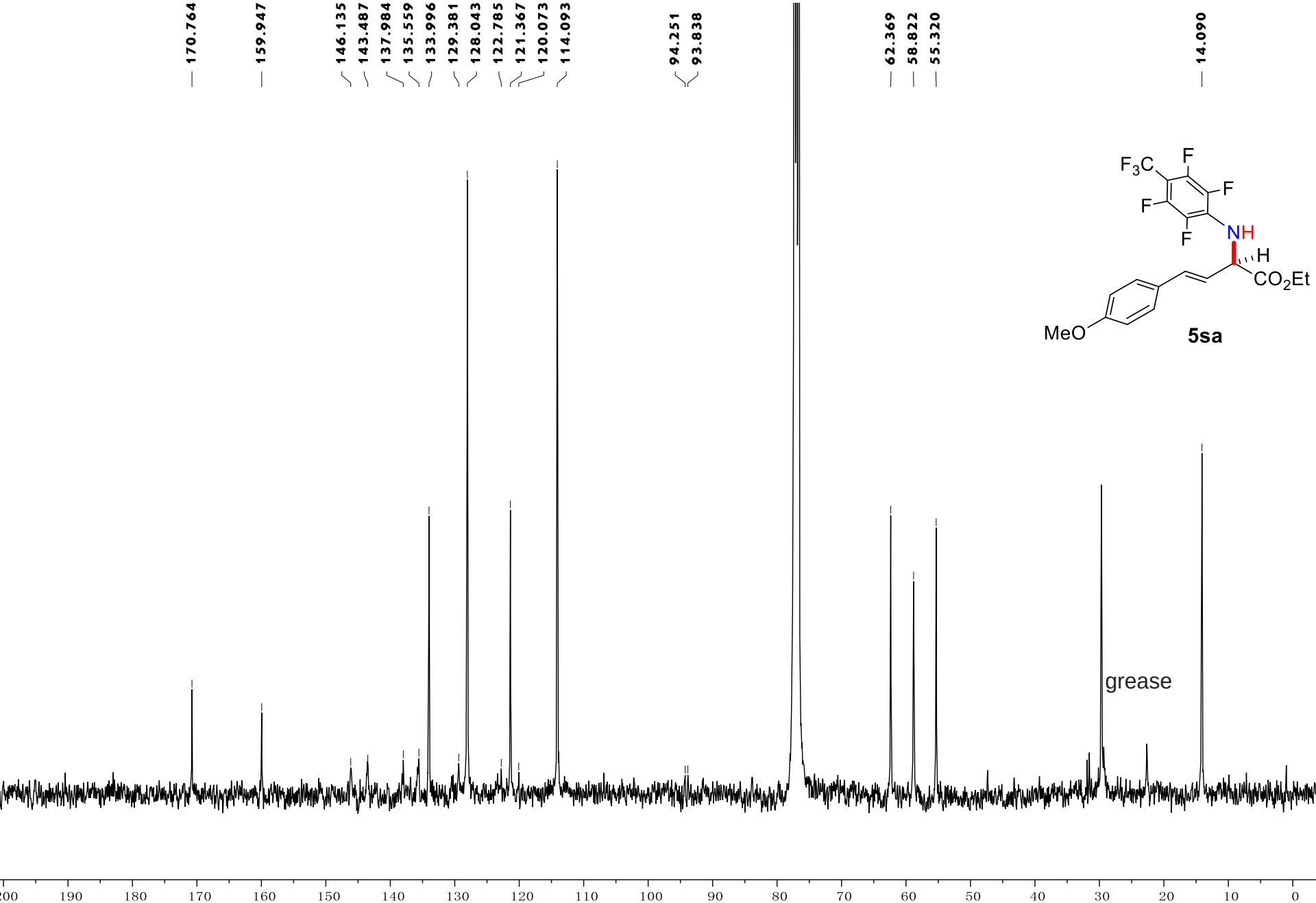
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 7.805 | 122218 | 7.666 |
| 2 | 8.238 | 1471999 | 92.334 |
| Total | | 1594217 | 100.000 |



# $^1$H NMR


7.330
7.313
6.879
6.862
6.705
6.674
6.066
6.052
6.034
6.021
5.159
5.141
5.128
5.113
5.097
4.343
4.336
4.329
4.322
4.314
4.307
4.294
4.282
4.268
4.260
4.253
4.246
3.820
1.338
1.324
1.309
1.03
1.00
f1 (ppm)
2.12
2.22
f1 (ppm)
F3C
F
F
F
F
NH
H
CO2Et
MeO
5sa
2.04
1.99
1.03
1.00
2.12
2.22
3.08
3.17
f1 (ppm)

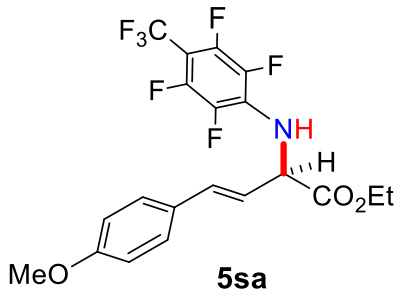
# $^{13}$C NMR


170.764
159.947
146.135
143.487
137.984
135.559
133.996
129.381
128.043
122.785
121.367
120.073
114.093
94.251
93.838
62.369
58.822
55.320
14.090
F3C
F
F
F
F
NH
H
CO2Et
MeO
5sa
grease
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

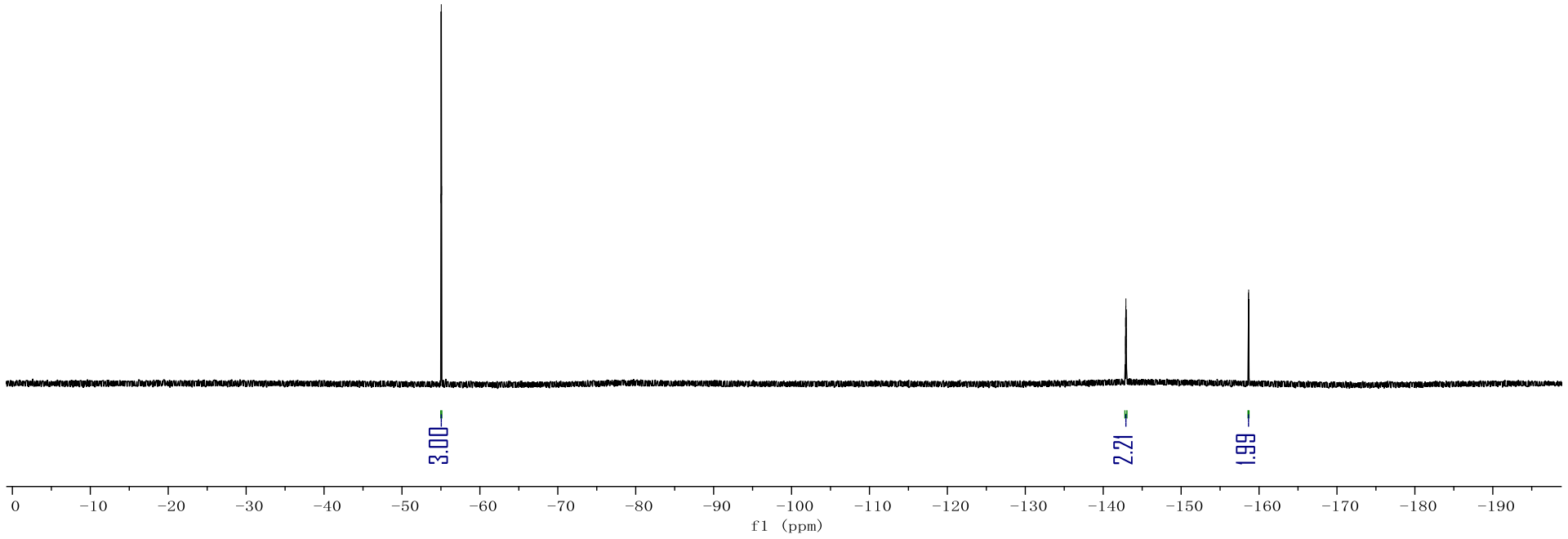
# $^{19}$F NMR

-55.000
-55.044
-55.088

-142.853
-142.861
-142.870
-142.898
-142.906
-142.914
-142.942
-142.950
-142.958
-158.633
-158.668




**5sa**

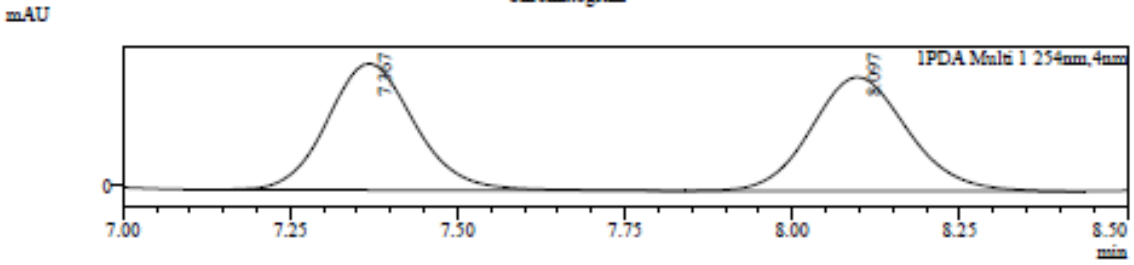


# HPLC

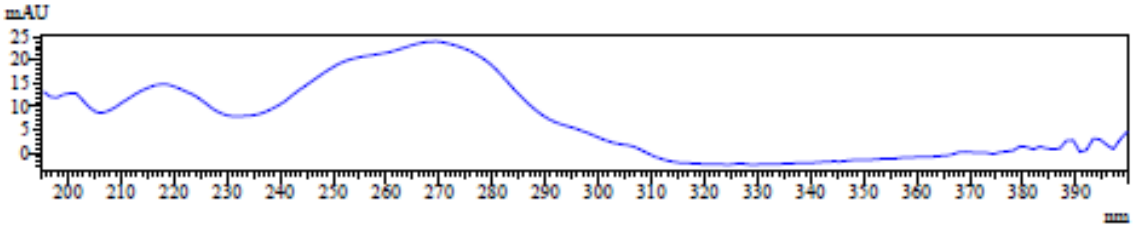
Sample Information

Sample Name : P0X-548-4-IA5%0.8mL.lcd
Sample ID : P0X-548-4-IA5%0.8mL.lcd
Data File : P0X-548-4-IA5%0.8mL.lcd
Method File : P0X-5%.0.8.mL-30min.lcm

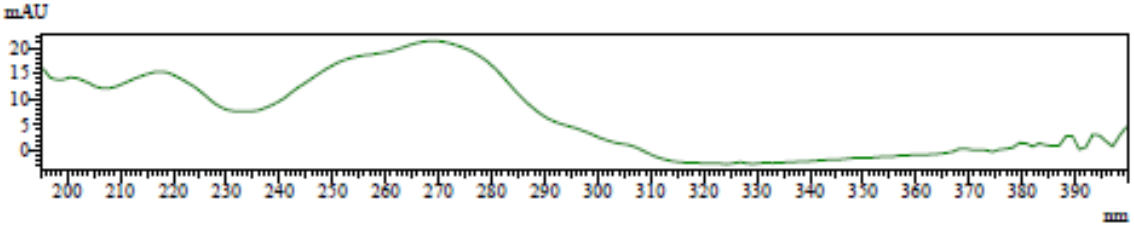
Chromatogram

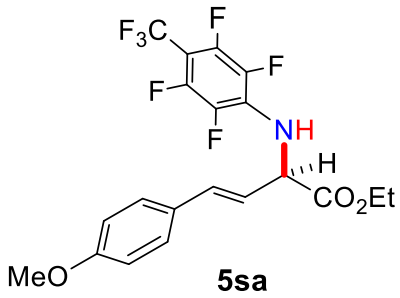



UV Spectrum
Retention time = 7.367




UV Spectrum
Retention time = 8.097




**5sa**

Peak Table

PDA Ch1 254nm

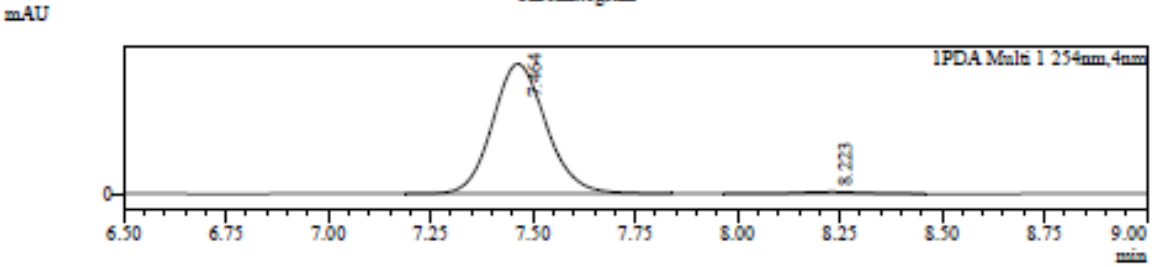
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 7.367 | 191108 | 50.186 |
| 2 | 8.097 | 189691 | 49.814 |
| Total | | 380799 | 100.000 |

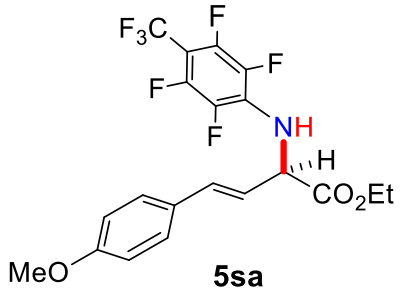
# HPLC

Sample Information

| | |
|---|---|
| Sample Name | : P0X-1252-4-IA-5%-0.8mL.lcd |
| Sample ID | : P0X-1252-4-IA-5%-0.8mL.lcd |
| Data File | : P0X-1252-4-IA-5%-0.8mL.lcd |
| Method File | : P0X-5%.0.8.mL-30min.lcm |

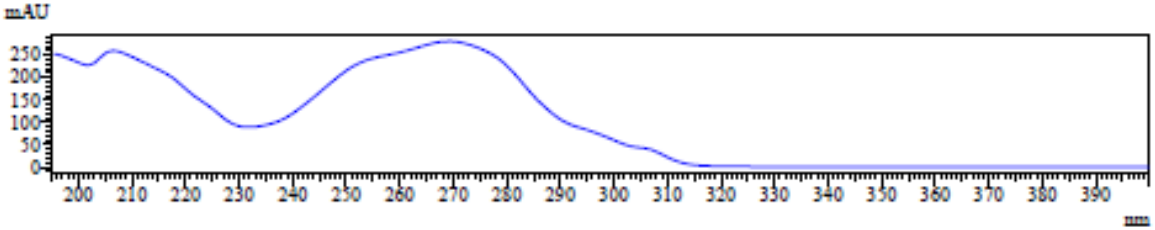
Chromatogram



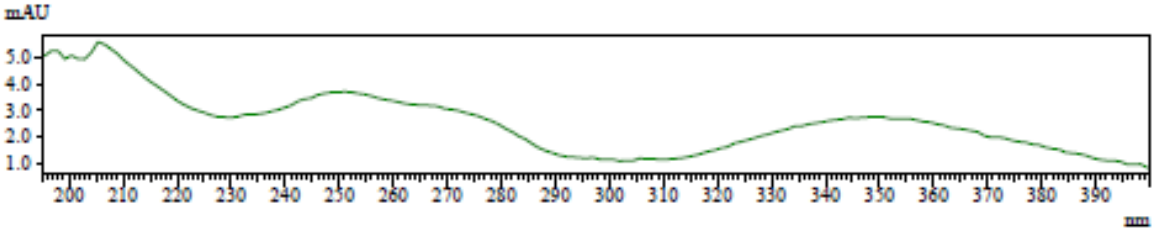




**5sa**

UV Spectrum
Retention time = 7.464




UV Spectrum
Retention time = 8.223



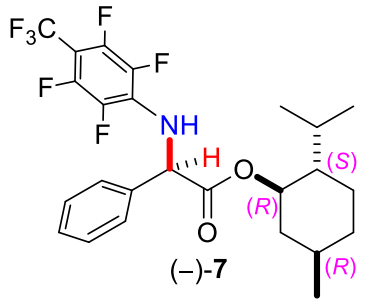

Peak Table

PDA Ch1 254nm

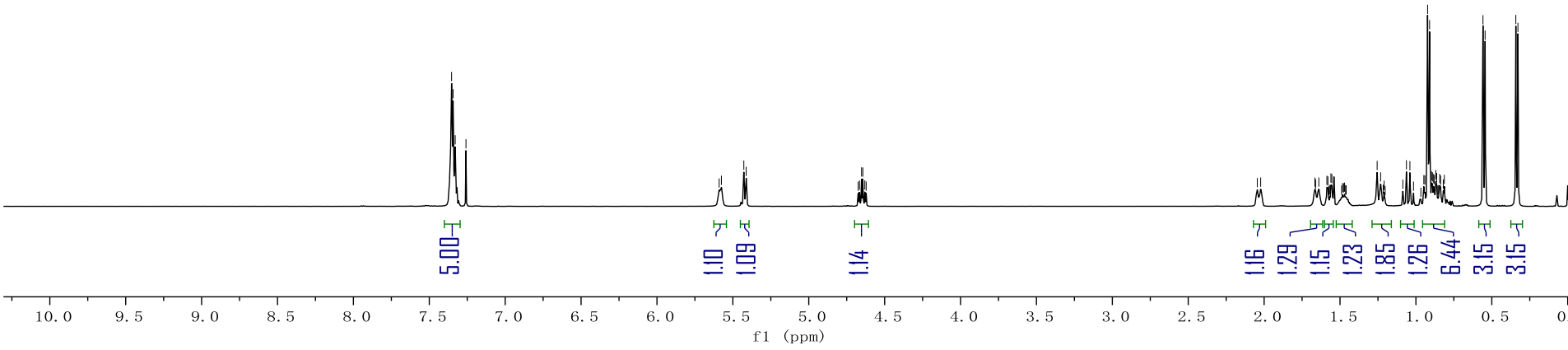
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 7.464 | 2170314 | 98.575 |
| 2 | 8.223 | 31383 | 1.425 |
| Total | | 2201697 | 100.000 |

# $^1$H NMR

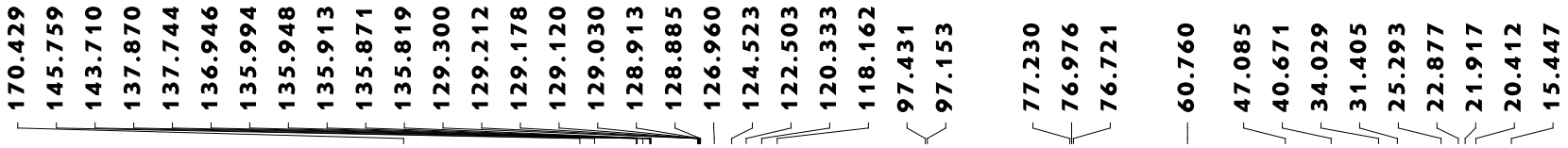
7.353 7.348 7.343 7.338 7.334 7.329 7.258 5.590 5.575 5.428 5.412 4.652 4.644 2.045 2.023 1.665 1.661 1.640 1.587 1.580 1.560 1.554 1.256 1.232 1.086 1.062 1.040 0.948 0.941 0.923 0.910 0.897 0.891 0.884 0.878 0.869 0.863 0.844 0.837 0.820 0.813 0.558 0.544 0.342 0.328

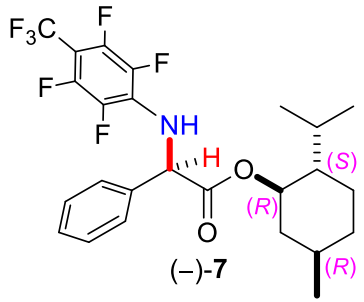



(–)-**7**



# $^{13}$C NMR

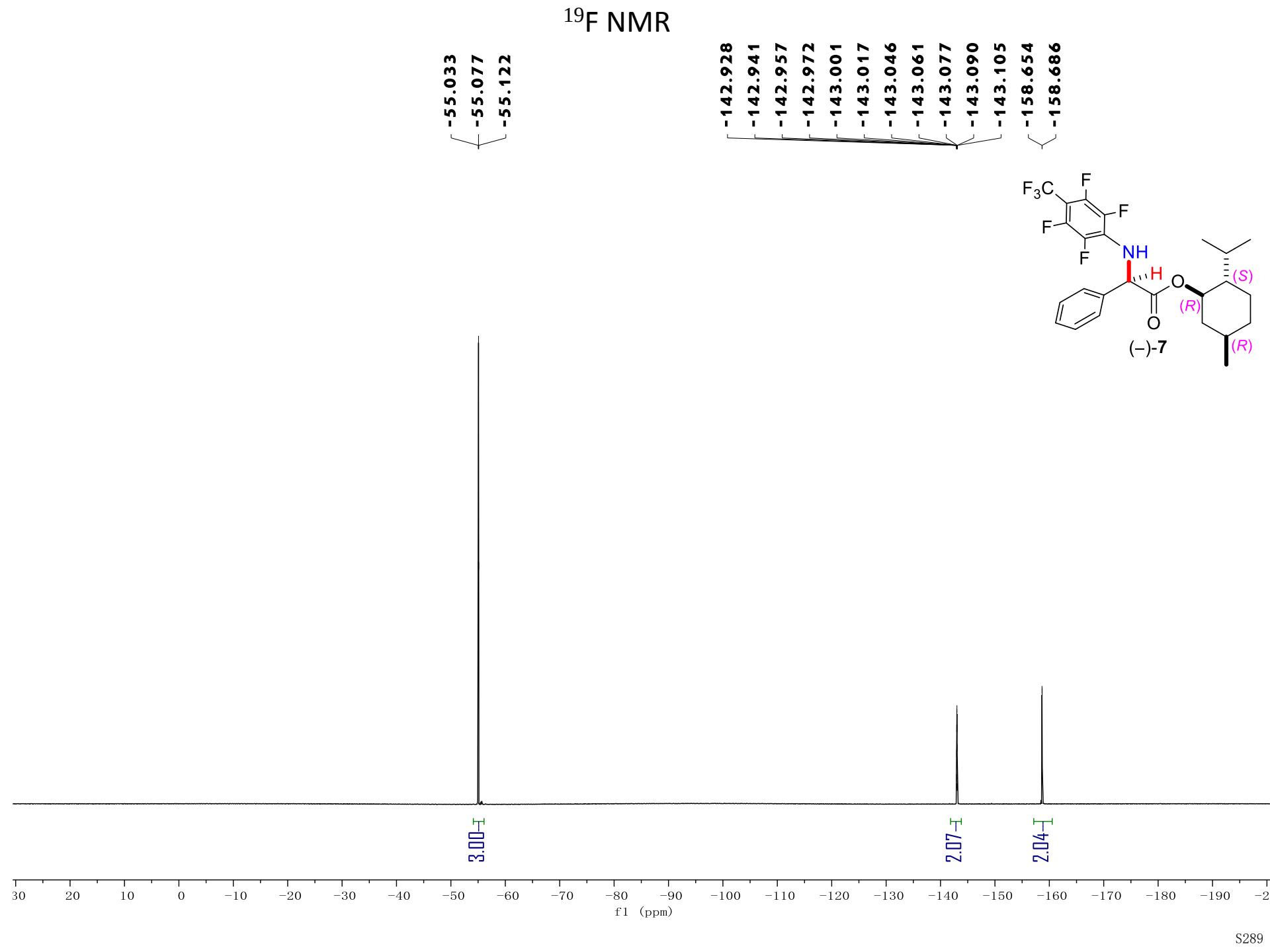

170.429
145.759
143.710
137.870
137.744
136.946
135.994
135.948
135.913
135.871
135.819
129.300
129.212
129.178
129.120
129.030
128.913
128.885
126.960
124.523
122.503
120.333
118.162
97.431
97.153
77.230
76.976
76.721
60.760
47.085
40.671
34.029
31.405
25.293
22.877
21.917
20.412
15.447


F3C
F
F
F
F
NH
H
O
O
(S)
(R)
(R)

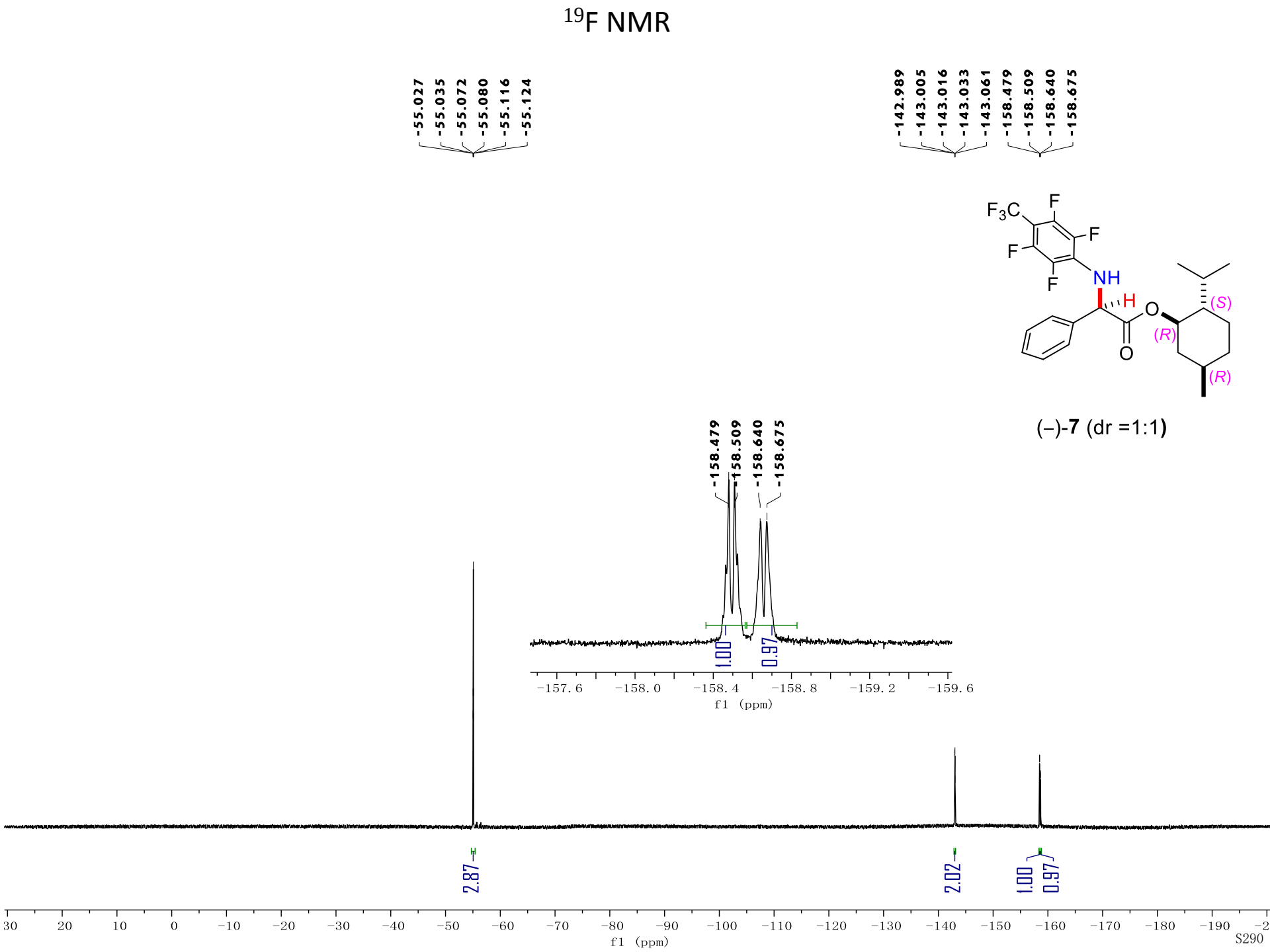
(–)-**7**


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

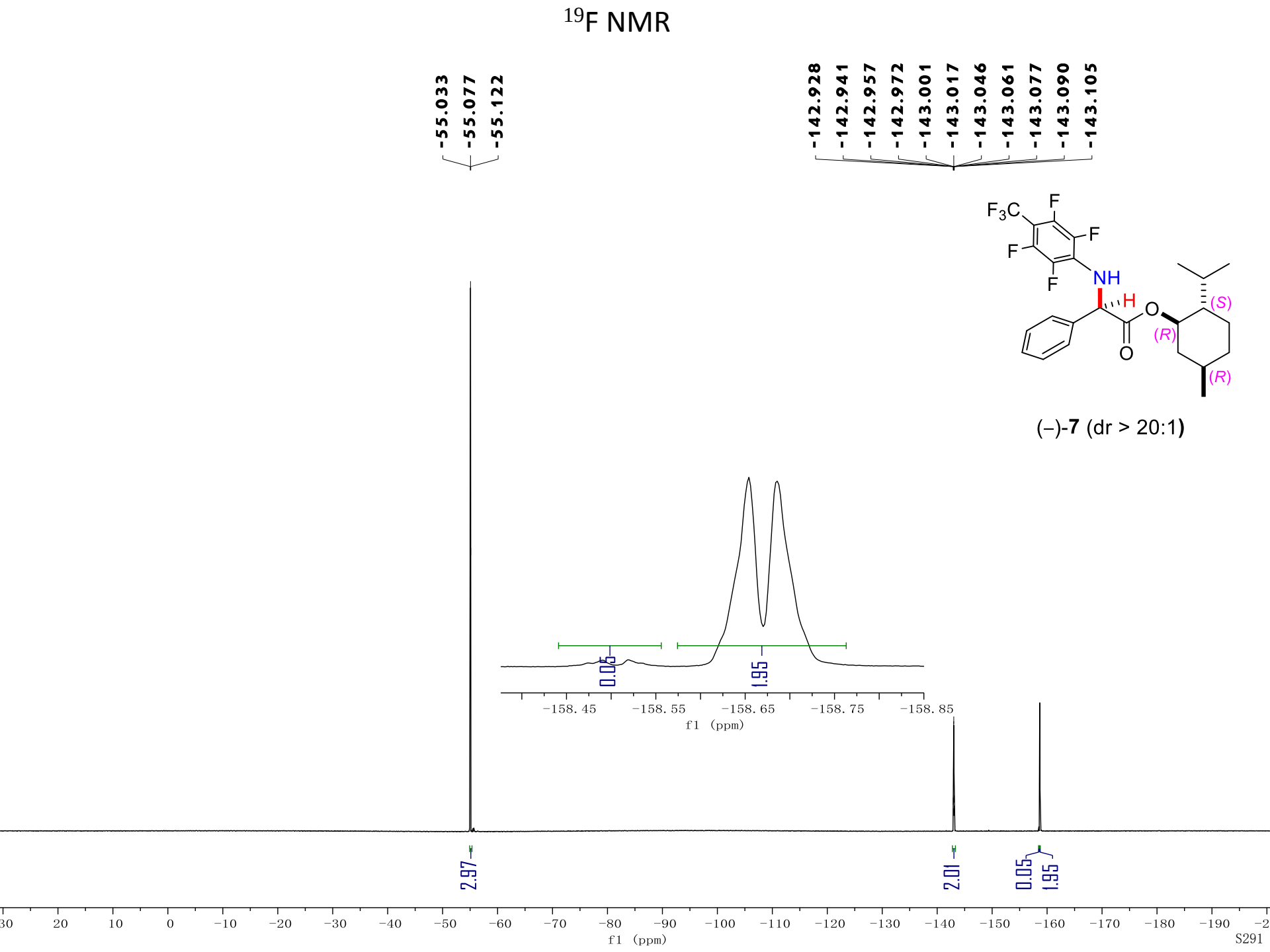
# $^{19}$F NMR


-55.033
-55.077
-55.122
-142.928
-142.941
-142.957
-142.972
-143.001
-143.017
-143.046
-143.061
-143.077
-143.090
-143.105
-158.654
-158.686
F3C
F
F
F
F
NH
H
O
O
(S)
(R)
(R)
(–)-7
3.00
2.07
2.04
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −2
f1 (ppm)

# $^{19}$F NMR


-55.027
-55.035
-55.072
-55.080
-55.116
-55.124
-142.989
-143.005
-143.016
-143.033
-143.061
-158.479
-158.509
-158.640
-158.675
F3C
F
F
F
F
NH
H
O
O
(S)
(R)
(R)
(–)-7 (dr =1:1)
-158.479
-158.509
-158.640
-158.675
1.00
0.97
−157.6
−158.0
−158.4
−158.8
−159.2
−159.6
f1 (ppm)
2.87
2.02
1.00
0.97
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

# $^{19}$F NMR




(–)-**7** (dr > 20:1)