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# Enantioselective radical C–H amination for the synthesis of $\beta$ -amino alcohols

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## Supplementary Information

### Enantioselective radical C-H amination for the synthesis of $\beta$ -amino alcohols

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## I. General Information

All chemicals and reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros, TCI, or ChemImpLex. Solvents were purified in the following manner. Acetonitrile and amine bases were distilled over calcium hydride.  $\text{CH}_2\text{Cl}_2$ , THF,  $\text{Et}_2\text{O}$ , and DMF were degassed with  $\text{N}_2$  and dried by passing through columns containing alumina, copper, or molecular sieves. Flash column chromatography, or preparative thin-layer chromatography, was performed with Silicycle F60 (230-400 mesh) silica gel. Thin layer chromatography (TLC) analyses were performed using EMD 60 F254 TLC plates and visualized by fluorescence quenching or  $\text{KMnO}_4$  stain. All yields are averages of at least two experimental runs.

Nuclear magnetic resonance (NMR) spectra ( $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{13}\text{C}$ ) were recorded using either a Bruker AVIII 400 or AVIII 600 MHz NMR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in parts per million and referenced to residual  $\text{CHCl}_3$  signals in  $\text{CDCl}_3$  ( $^1\text{H}$ :  $\delta$  7.26;  $^{13}\text{C}$ :  $\delta$  77.16), benzene in  $\text{C}_6\text{D}_6$  ( $^1\text{H}$ :  $\delta$  7.16;  $^{13}\text{C}$ :  $\delta$  128.06), or DMSO in  $\text{DMSO-d}_6$  ( $^1\text{H}$ :  $\delta$  2.50);  $^{19}\text{F}$  chemical shifts are reported in ppm relative to  $\text{CFCl}_3$  as the external standard.  $^1\text{H}$  NMR data are reported as follows: chemical shifts ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, ap = apparent), coupling constant (Hz), relative integral. Data for  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR are reported in terms of chemical shift and multiplicity where appropriate. High-resolution Mass Spectrometry (HRMS) data were obtained using Bruker MicroTOF (ESI). Infrared (IR) spectra were recorded using a Thermo Fisher Nicolet iS10 FT-IR and are reported in terms of frequency of absorption ( $\text{cm}^{-1}$ ).

High Pressure Liquid chromatography (HPLC) was performed on an Agilent InfinityLab LC Series 1260 Infinity II Quaternary System using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. Optical rotations were recorded on a Perkin-Elmer Model 241 polarimeter at Mercury 578nm.

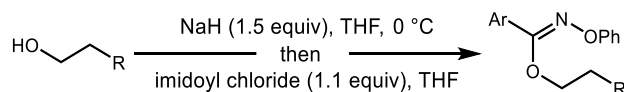
Photochemical reactions were performed by placing reaction vessels approximately 10 cm away from one 90 W blue LED lamp (Kessil A360WE tuna blue) or two 45 W blue LED lamps (Kessil A160WE tuna blue). The temperature of the reaction was maintained at approximately 25 °C with a fan. The reaction set-ups can be seen below. Photochemical reactions with UV light were performed using a Rayonet RPR-100 Photochemical Reactor with 300 nm bulbs.





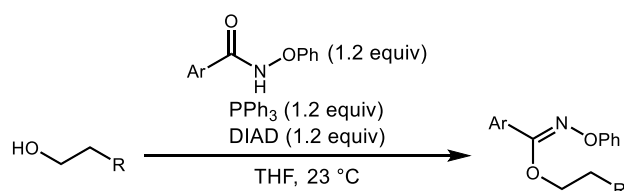
## II. General Procedure

### General Procedure 1 (GP1)<sup>1</sup>



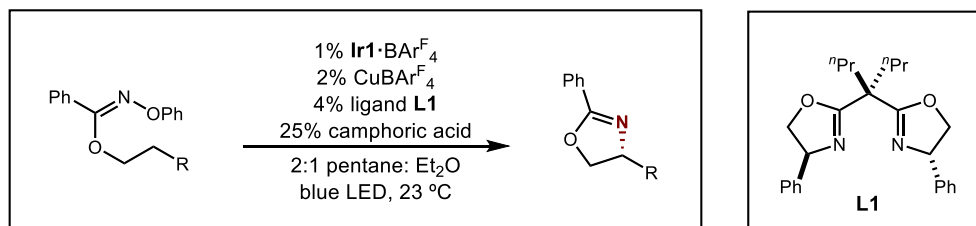
To a flame-dried round bottom flask equipped with a stir bar was added alcohol (2 mmol, 1.0 equiv) and dry THF (20 mL). NaH (60% dispersion in mineral oil, 3.0 mmol, 1.5 equiv) was carefully added to the stirring dispersion. The mixture was allowed to stir for 1 hour at room temperature. Imidoyl chloride (2.2 mmol, 1.1 equiv) was added and the resulting solution was stirred until full consumption of alcohol. Upon completion, silica gel was added to quench the reaction, then the solvent was removed by vacuum. The residue was purified by column chromatography to afford the corresponding oxime in 80-99% yield.

### General Procedure 2 (GP2)



To a flame-dried round bottom flask equipped with a stir bar was added alcohol (2 mmol, 1.0 equiv), PPh<sub>3</sub> (2.4 mmol, 1.2 equiv), and dry THF (20 mL). DIAD (2.4 mmol, 1.2 equiv) was carefully added, followed by portion-wise addition of amide (2.4 mmol, 1.2 equiv). The resulting solution was stirred until full consumption of alcohol. Upon completion, silica gel was added to quench the reaction and the solvent was removed by vacuum. The residue was purified by column chromatography to afford the corresponding oxime imidate in 50-99% yield.

### General Procedure 3 (GP3)



To an oven-dried 2-dram vial equipped with a stir bar was added imidate (0.1 mmol) and (1R,3S)-(+)-camphoric acid (0.025 mmol, 0.25 equiv). After the vial was transferred into a glovebox, 1 mL of a 0.002M [solution of \*\*L1\*\*· \$\text{CuBAR}^{\text{F}}\_4\$](#)  (2 mol%) in  $\text{Et}_2\text{O}$  and 1 mL of a 0.001M [solution of \*\*Ir1\*\*](#) (1 mol%) in  $\text{Et}_2\text{O}$  were added. After diluting with 4 mL of pentane, the vial was then sealed with parafilm and removed from the glovebox. The reaction was irradiated with a 455 nm blue LED for 1 hour. Two fans were employed to cool the reaction setup. Upon completion, the reaction was concentrated and the crude oxazoline was loaded directly onto silica gel and purified by column chromatography. Enantioselectivity was determined by HPLC analysis of the purified oxazoline product.

Catalyst solutions:

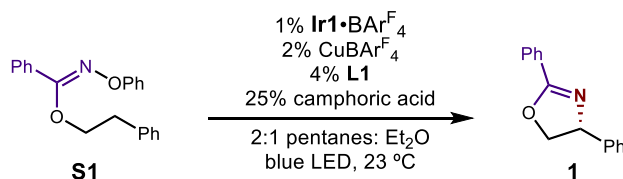
**L1**· $\text{CuBAR}^{\text{F}}_4$ : To an oven-dried 20 mL vial equipped with a stir bar was added **L1** (0.08 mmol, 2.0 eq) and [Cu\(MeCN\) \$\_4\$ BAR \$^{\text{F}}\_4\$](#)  (0.04 mmol, 1 equiv) in a glove box.  $\text{Et}_2\text{O}$  (20 mL) was added and stirred at 23 °C for 1 hour to afford the title solution.

**Ir1**: To an oven-dried 20 mL vial was added [\[Ir{dF\(CF \$\_3\$ \)ppy} \$\_2\$ \(dtbbpy\)\] BAR \$^{\text{F}}\_4\$](#)  (0.02 mmol, 36 mg) in a glove box.  $\text{Et}_2\text{O}$  (20 mL) was then added to afford the title solution.

Notes:

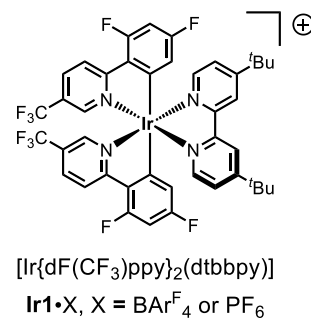
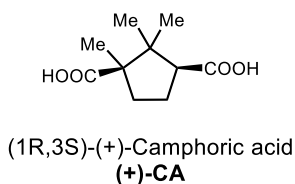
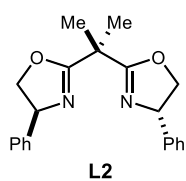
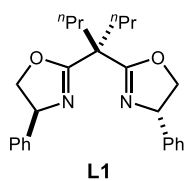
- Both pentane and  $\text{Et}_2\text{O}$  were purified by solvent system and then transferred in glovebox and stored with pre-activated 4Å molecular sieves.
- L1**· $\text{CuBAR}^{\text{F}}_4$  can be generated outside of the glovebox using Schlenk technique and solvent degassed using a freeze-pump-thaw technique.
- If the oxazoline product co-elutes with phenol byproduct, after column chromatography the material was dissolved in 20 mL  $\text{EtOAc}$  and then washed with 1 M NaOH, water, and brine sequentially. The organic phase was then dried over  $\text{Na}_2\text{SO}_4$  and concentrated to afford the pure oxazoline.
- Racemic samples were prepared from a 50:50 mixture of enantiopure catalysts, since smaller, achiral ligands are less efficient for this C-H amination.

**Table 1.** Reaction optimization.



| entry           | CuX                                  | Ligand    | co-catalyst          | solvent                                 | results <sup>a</sup> |
|-----------------|--------------------------------------|-----------|----------------------|-----------------------------------------|----------------------|
| 1               | Cu(OTf) <sub>2</sub>                 | L2        | AcOH                 | benzene : DMAc = 9:1                    | 78%, 34%ee           |
| 2               | Cu(OTf) <sub>2</sub>                 | L2        | AcOH                 | MeCN : DMAc = 10:5                      | 78%, 37%ee           |
| 3               | Cu(OTf) <sub>2</sub>                 | L2        | AcOH                 | MeCN : DMAc = 20:1                      | 34%, 39%ee           |
| 4               | Cu(OTf) <sub>2</sub>                 | L2        | AcOH                 | pentanes : Et <sub>2</sub> O = 2:1      | 42%, 61%ee           |
| 5               | Cu(OTf) <sub>2</sub>                 | L2        | (+)-CA               | pentanes : Et <sub>2</sub> O = 2:1      | 38%, 82%ee           |
| 6               | CuBAR <sup>F</sup> <sub>4</sub>      | L2        | AcOH                 | pentanes : Et <sub>2</sub> O = 2:1      | 68%, 56%ee           |
| 7               | CuBAR <sup>F</sup> <sub>4</sub>      | L2        | (+)-CA               | pentanes : Et <sub>2</sub> O = 2:1      | 90%, 85%ee           |
| 8               | CuBAR <sup>F</sup> <sub>4</sub>      | L1        | AcOH                 | pentanes : Et <sub>2</sub> O = 2:1      | 75%, 83%ee           |
| 9               | <b>CuBAR<sup>F</sup><sub>4</sub></b> | <b>L1</b> | <b>(+)-CA</b>        | <b>pentanes : Et<sub>2</sub>O = 2:1</b> | <b>95%, 94%ee</b>    |
| 10 <sup>b</sup> | CuBAR <sup>F</sup> <sub>4</sub>      | L1        | (+)-CA               | pentanes : Et <sub>2</sub> O = 2:1      | 94%, 92%ee           |
| 11              | Cu(OTf) <sub>2</sub>                 | L1        | (+)-CA               | pentanes : Et <sub>2</sub> O = 2:1      | 87%, 83%ee           |
| 12              | CuBAR <sup>F</sup> <sub>4</sub>      | L1        | none                 | pentanes : Et <sub>2</sub> O = 2:1      | 16%, 85%ee           |
| 13              | CuBAR <sup>F</sup> <sub>4</sub>      | none      | (+)-CA               | pentanes : Et <sub>2</sub> O = 2:1      | 20%, 0%ee            |
| 14 <sup>c</sup> | CuBAR <sup>F</sup> <sub>4</sub>      | L1        | (+)-CA               | pentanes : Et <sub>2</sub> O = 2:1      | 0%                   |
| 15              | CuBAR <sup>F</sup> <sub>4</sub>      | L1        | (-)-CA               | pentanes : Et <sub>2</sub> O = 2:1      | 93%, 93%ee           |
| 16              | CuBAR <sup>F</sup> <sub>4</sub>      | L1        | adamantyl acid       | pentanes : Et <sub>2</sub> O = 2:1      | 84%, 92%ee           |
| 17              | CuBAR <sup>F</sup> <sub>4</sub>      | L1        | phosphoric acid      | pentanes : Et <sub>2</sub> O = 2:1      | 15%, 36%ee           |
| 18              | CuBAR <sup>F</sup> <sub>4</sub>      | L1        | trifluoroacetic acid | pentanes : Et <sub>2</sub> O = 2:1      | 41%, 18%ee           |

<sup>a</sup> Reactions were run with 0.05 mmol of **1a**, <sup>1</sup>H NMR yield based on **S1** using N,N-dimethyl-2,2,2-trifluoroacetamide as the internal standard. <sup>b</sup> Using **Ir1**•PF<sub>6</sub> instead of **Ir1**•BARF<sub>4</sub>. <sup>c</sup> without Ir photoredox catalyst.



#### IV. Synthesis of Catalysts and Ligand

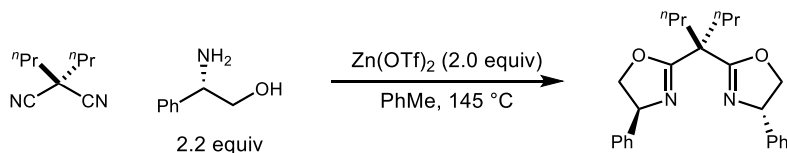
##### Synthesis of $\text{Cu}(\text{MeCN})_4\text{BAR}^{\text{F}_4}$

$\text{Cu}(\text{I})\text{Cl}$  (100 mg, 1.0 mmol, 1 equiv) and  $\text{NaBAR}^{\text{F}_4}$  (985 mg, 1.1 mmol, 1.1 equiv) were dissolved in freshly distilled MeCN (50 mL) and stirred at room temperature for 1 h. The crude mixture was filtered through 0.45  $\mu\text{m}$  nylon membrane Millipore filters. The resulting solution was concentrated under the flow of  $\text{N}_2$  and dried under reduced pressure to give the titled compound as a white solid (1.09 g, quant.).

##### Synthesis of $(\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy}))\text{BAR}^{\text{F}_4}$

In an oven dried 2-dram vial equipped with PTFE septa cap,  $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{Cl}]_2$  (74 mg, 0.05 mmol, 1 equiv) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (34 mg, 0.125 mmol, 2.5 equiv) were added. The vial was then evacuated and refilled three times with  $\text{N}_2$ . Ethylene glycol (3 mL) was then added via syringe. The reaction mixture was then heated to 150  $^\circ\text{C}$  for 16 h. After this time the flask was allowed to return to room temperature. The mixture was diluted in water (10 mL) and hexane (10 mL). The aqueous phase was then separated and then re-extracted with hexane (2 x 10 mL). The aqueous phase was transferred to a flask that was heated at 80  $^\circ\text{C}$  for 1 hour to remove residual hexane. The flask was allowed to return to room temperature, and  $\text{NaBAR}^{\text{F}_4}$  (266 mg, 0.3 mmol, 6 equiv) was added with stirring, and a vibrant yellow precipitate was formed. Ethyl acetate was added to dissolve the solid, and the organic phase was washed with water. Then, the organic layer was dried with  $\text{MgSO}_4$ , filtered, evaporated under reduced pressure. The crude material was loaded onto silica gel and purified ( $\text{CH}_2\text{Cl}_2$  to 10% acetone in  $\text{CH}_2\text{Cl}_2$ ) to yield the  $(\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy}))\text{BAR}^{\text{F}_4}$  as a bright yellow solid.

##### Synthesis of BOX-ligand (*S,S*)-L1



Following reported procedure with slight modification<sup>2,3</sup>: Di-*tert*-Pr malononitrile (2.0 mmol, 1.0 equiv) was dissolved in PhMe (30 mL) and to the solution was added (*S*)-2-phenyl glycinol (5.0 mmol, 2.5 equiv), and  $\text{Zn}(\text{OTf})_2$  (5.0 mmol, 2.5 equiv). The reaction mixture was sealed and heated at 145  $^\circ\text{C}$  for 48 h. The reaction mixture was cooled to ambient temperature and quenched with sat.  $\text{Na}_2\text{CO}_3$  (30 mL). After extraction with  $\text{CH}_2\text{Cl}_2$  (100 mL x 1, 50 mL x 3), the combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , concentrated, and loaded onto silica gel and purified (hexane/ethyl acetate = 9:1) to afford the ligand (*S,S*)-L1.

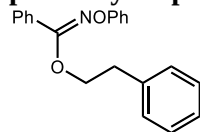
The enantiomer, (*R,R*)-L1, was synthesized by the same protocol utilizing (*R*)-2-phenyl glycinol.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.31 (m, 4H), 7.29 – 7.24 (m, 6H), 5.24 (dd,  $J$  = 10.1, 8.1 Hz, 2H), 4.66 (dd,  $J$  = 10.2, 8.4 Hz, 2H), 4.11 (t,  $J$  = 8.2 Hz, 2H), 2.16 – 2.02 (m, 4H), 1.41 – 1.30 (m, 4H), 0.97 (t,  $J$  = 7.3 Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  169.30 (s), 142.56 (s), 128.82 (s), 127.67 (s), 126.90 (s), 75.16 (s), 69.76 (s), 46.45 (s), 35.26 (s), 17.57 (s), 14.58 (s).

**Absolute stereochemistry:** The (*S,S*)-L1 catalyst affords oxazoline (*R*)-1, which matches the HPLC trace of a sample independently synthesized from (*R*)-2-phenyl glycinol.

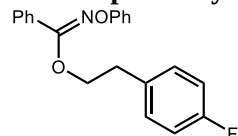
## V. Synthesis of Oxime Imidates

### phenethyl N-phenoxybenzimidate (S1)



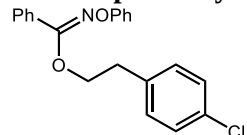
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.78 – 7.70 (m, 2H), 7.43 (dt,  $J$  = 9.1, 1.7 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.12 – 7.05 (m, 6H), 7.04 – 6.99 (m, 2H), 6.93 – 6.88 (m, 1H), 4.45 (t,  $J$  = 6.9 Hz, 2H), 2.81 (t,  $J$  = 6.9 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.11 (s), 156.74 (s), 138.09 (s), 131.67 (s), 130.57 (s), 129.69 (s), 129.41 (s), 128.77 (s), 128.52 (s), 127.82 (s), 126.82 (s), 122.39 (s), 114.89 (s), 73.51 (s), 36.89 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  340.1308, found: 340.1303.

### 4-fluorophenethyl N-phenoxybenzimidate (S2)



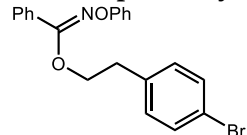
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.73 (dd,  $J$  = 7.9, 1.7 Hz, 2H), 7.43 (dd,  $J$  = 8.7, 1.0 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.12 – 7.04 (m, 3H), 6.97 – 6.89 (m, 1H), 6.82 – 6.67 (m, 4H), 4.34 (t,  $J$  = 6.8 Hz, 2H), 2.67 (t,  $J$  = 6.8 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -116.43 (tt,  $J$  = 8.3, 5.6 Hz).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  162.25 (d,  $J$  = 244.3 Hz), 160.05 (s), 156.66 (s), 133.72 (d,  $J$  = 3.2 Hz), 131.54 (s), 130.85 (d,  $J$  = 7.8 Hz), 130.68 (s), 129.74 (s), 128.56 (s), 127.73 (s), 122.49 (s), 115.48 (d,  $J$  = 21.2 Hz), 114.85 (s), 73.29 (s), 35.92 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  358.1214, found: 358.1199.

### 4-chlorophenethyl N-phenoxybenzimidate (S3)



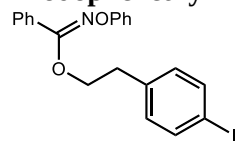
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.75 – 7.70 (m, 2H), 7.46 – 7.39 (m, 2H), 7.25 – 7.18 (m, 2H), 7.12 – 7.00 (m, 5H), 6.94 – 6.89 (m, 1H), 6.70 (d,  $J$  = 8.2 Hz, 2H), 4.31 (t,  $J$  = 6.8 Hz, 2H), 2.68 – 2.55 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.03 (s), 156.60 (s), 136.53 (s), 132.76 (s), 131.49 (s), 130.74 (s), 130.71 (s), 129.74 (s), 128.86 (s), 128.57 (s), 127.71 (s), 122.52 (s), 114.84 (s), 73.05 (s), 36.03 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  374.0918, found: 374.0912.

### 4-bromophenethyl N-phenoxybenzimidate (S4)



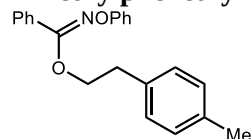
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.73 – 7.69 (m, 2H), 7.42 (dt,  $J$  = 9.0, 1.7 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.12 – 7.05 (m, 3H), 6.95 – 6.89 (m, 1H), 6.63 (d,  $J$  = 8.2 Hz, 2H), 4.31 (t,  $J$  = 6.8 Hz, 2H), 2.59 (t,  $J$  = 6.8 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.02 (s), 156.60 (s), 137.00 (s), 131.48 (s), 131.11 (s), 130.71 (s), 129.75 (s), 128.57 (s), 127.70 (s), 122.52 (s), 120.81 (s), 114.84 (s), 72.97 (s), 36.08 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  418.0413, found: 418.0410.

#### 4-iodophenethyl N-phenoxybenzimidate (S5)



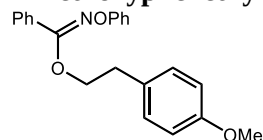
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.74 – 7.68 (m, 2H), 7.46 – 7.36 (m, 4H), 7.25 – 7.18 (m, 2H), 7.13 – 7.06 (m, 3H), 6.95 – 6.89 (m, 1H), 6.51 (d,  $J$  = 8.0 Hz, 2H), 4.30 (t,  $J$  = 6.8 Hz, 2H), 2.58 (t,  $J$  = 6.8 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.01 (s), 156.60 (s), 137.83 (s), 137.64 (s), 131.47 (s), 131.38 (s), 130.71 (s), 129.74 (s), 128.57 (s), 127.71 (s), 122.51 (s), 114.84 (s), 92.12 (s), 72.97 (s), 36.19 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  466.0274, found: 466.0265.

#### 4-methylphenethyl N-phenoxybenzimidate (S6)



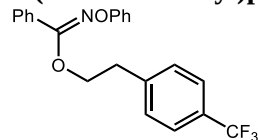
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.79 – 7.75 (m, 2H), 7.47 – 7.41 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 3H), 7.00 – 6.93 (m, 4H), 6.93 – 6.89 (m, 1H), 4.48 (t,  $J$  = 6.9 Hz, 2H), 2.84 (t,  $J$  = 6.9 Hz, 2H), 2.11 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.14 (s), 156.78 (s), 136.12 (s), 135.00 (s), 131.74 (s), 130.55 (s), 129.69 (s), 129.48 (s), 129.34 (s), 128.50 (s), 127.85 (s), 122.36 (s), 114.90 (s), 73.74 (s), 36.53 (s), 21.03 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  354.1465, found: 354.1460.

#### 4-methoxyphenethyl N-phenoxybenzimidate (S7)



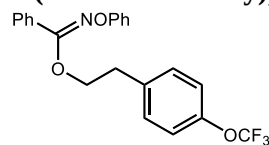
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.82 – 7.76 (m, 2H), 7.47 – 7.42 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 3H), 6.99 – 6.94 (m, 2H), 6.91 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 6.74 (d,  $J$  = 8.7 Hz, 2H), 4.46 (t,  $J$  = 6.9 Hz, 2H), 3.31 (s, 3H), 2.82 (t,  $J$  = 6.9 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.14 (s), 159.09 (s), 156.82 (s), 131.74 (s), 130.57 (s), 130.38 (s), 129.90 (s), 129.70 (s), 128.53 (s), 127.85 (s), 122.37 (s), 114.90 (s), 114.34 (s), 73.84 (s), 54.81 (s), 36.08 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  370.1414, found: 370.1404.

#### 4-(trifluoromethyl)phenethyl N-phenoxybenzimidate (S8)



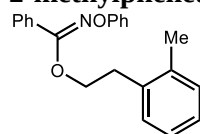
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.68 (dt,  $J$  = 3.9, 2.3 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.28 (d,  $J$  = 8.0 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.09 (qdd,  $J$  = 5.9, 2.7, 1.7 Hz, 3H), 6.92 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 6.81 (d,  $J$  = 8.0 Hz, 2H), 4.31 (t,  $J$  = 6.7 Hz, 2H), 2.63 (t,  $J$  = 6.7 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –62.09 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  159.97 (s), 156.52 (s), 142.26 (s), 131.38 (s), 130.79 (s), 129.77 (s), 129.69 (s), 129.12 (q,  $J$  = 32.2 Hz), 128.58 (s), 127.64 (s), 125.57 (q,  $J$  = 3.7 Hz), 125.10 (q,  $J$  = 275.3 Hz), 122.61 (s), 114.82 (s), 72.70 (s), 36.40 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  408.1182, found: 408.1176.

#### 4-(trifluoromethoxy)phenethyl N-phenoxybenzimidate (S9)



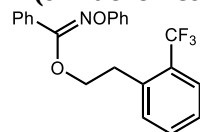
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.71 – 7.67 (m, 2H), 7.44 – 7.40 (m, 2H), 7.24 – 7.19 (m, 2H), 7.11 – 7.05 (m, 3H), 6.92 (tt,  $J$  = 7.4, 1.0 Hz, 1H), 6.86 (d,  $J$  = 7.9 Hz, 2H), 6.77 – 6.72 (m, 2H), 4.31 (t,  $J$  = 6.7 Hz, 2H), 2.62 (t,  $J$  = 6.7 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –57.74 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.01 (s), 156.60 (s), 148.29 (s), 136.98 (s), 131.42 (s), 130.74 (s), 130.70 (s), 129.76 (s), 128.56 (s), 127.69 (s), 122.56 (s), 121.28 (q,  $J$  = 256.5 Hz), 121.26 (s), 114.83 (s), 72.93 (s), 35.94 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  424.1131, found: 402.1298.

#### 2-methylphenethyl N-phenoxybenzimidate (S10)



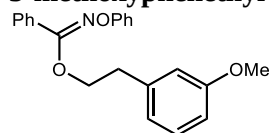
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.77 – 7.72 (m, 2H), 7.46 – 7.41 (m, 2H), 7.23 – 7.17 (m, 2H), 7.12 – 7.05 (m, 3H), 7.06 – 6.99 (m, 3H), 6.99 – 6.95 (m, 1H), 6.91 (t,  $J$  = 7.3 Hz, 1H), 4.51 – 4.34 (m, 2H), 2.88 (t,  $J$  = 7.2 Hz, 2H), 2.04 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.15 (s), 156.89 (s), 136.66 (s), 136.01 (s), 131.62 (s), 130.62 (s), 130.58 (s), 130.07 (s), 129.69 (s), 128.56 (s), 127.86 (s), 127.07 (s), 126.47 (s), 122.40 (s), 114.91 (s), 72.49 (s), 34.04 (s), 19.35 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  354.1465, found: 354.1459.

#### 2-(trifluoromethyl)phenethyl N-phenoxybenzimidate (S11)



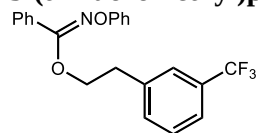
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.76 – 7.72 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 (d,  $J$  = 7.8 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.12 – 7.05 (m, 4H), 6.95 (t,  $J$  = 7.6 Hz, 1H), 6.91 (tt,  $J$  = 7.4, 1.0 Hz, 1H), 6.79 (t,  $J$  = 7.6 Hz, 1H), 4.42 (t,  $J$  = 6.8 Hz, 2H), 3.13 (t,  $J$  = 6.7 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –59.25 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.06 (s), 156.73 (s), 136.57 (s), 132.26 (s), 131.90 (s), 131.33 (s), 130.66 (s), 129.70 (s), 129.14 (q,  $J$  = 29.6 Hz), 128.60 (s), 127.74 (s), 126.91 (s), 126.25 (q,  $J$  = 5.7 Hz), 125.26 (d,  $J$  = 273.9 Hz), 122.47 (s), 114.88 (s), 72.36 (s), 33.50 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  408.1182, found: 408.1161.

#### 3-methoxyphenethyl N-phenoxybenzimidate (S12)



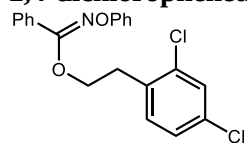
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.81 – 7.75 (m, 2H), 7.46 – 7.40 (m, 2H), 7.23 – 7.17 (m, 2H), 7.12 – 7.03 (m, 4H), 6.91 (dd,  $J$  = 10.8, 3.9 Hz, 1H), 6.77 (d,  $J$  = 1.7 Hz, 1H), 6.70 (dd,  $J$  = 7.9, 2.0 Hz, 2H), 4.48 (t,  $J$  = 6.9 Hz, 2H), 3.30 (s, 3H), 2.83 (t,  $J$  = 6.9 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.46 (s), 160.11 (s), 156.70 (s), 139.64 (s), 131.69 (s), 130.57 (s), 129.78 (s), 129.69 (s), 128.52 (s), 127.84 (s), 122.37 (s), 121.68 (s), 115.20 (s), 114.90 (s), 112.55 (s), 73.54 (s), 54.72 (s), 36.96 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  370.1414, found: 370.1401.

### 3-(trifluoromethyl)phenethyl (Z)-N-phenoxybenzimidate (S13)



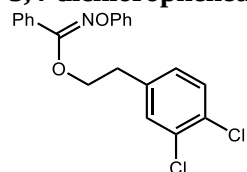
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.71 – 7.67 (m, 2H), 7.41 (dd,  $J$  = 8.7, 1.0 Hz, 2H), 7.32 (s, 1H), 7.24 (d,  $J$  = 7.8 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.11 – 7.06 (m, 3H), 6.96 (d,  $J$  = 7.6 Hz, 1H), 6.93 – 6.90 (m, 1H), 6.86 (t,  $J$  = 7.7 Hz, 1H), 4.27 (t,  $J$  = 6.6 Hz, 2H), 2.59 (t,  $J$  = 6.6 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –62.21 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  159.99 (s), 156.42 (s), 139.28 (s), 132.72 (s), 131.39 (s), 130.97 (q,  $J$  = 31.9 Hz), 130.73 (s), 129.74 (s), 129.14 (s), 128.57 (s), 127.64 (s), 126.17 (q,  $J$  = 3.7 Hz), 124.98 (q,  $J$  = 272.3 Hz), 123.65 (q,  $J$  = 3.8 Hz), 122.55 (s), 114.82 (s), 72.72 (s), 36.34 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  408.1182, found: 408.1179.

### 2,4-dichlorophenethyl N-phenoxybenzimidate (S14)



Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.76 – 7.70 (m, 2H), 7.42 (dt,  $J$  = 9.1, 1.7 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.13 (d,  $J$  = 2.1 Hz, 1H), 7.10 – 7.05 (m, 3H), 6.94 – 6.89 (m, 1H), 6.78 (dd,  $J$  = 8.2, 2.1 Hz, 1H), 6.70 (d,  $J$  = 8.2 Hz, 1H), 4.38 (t,  $J$  = 6.7 Hz, 2H), 2.85 (t,  $J$  = 6.7 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.01 (s), 156.55 (s), 135.17 (s), 134.26 (s), 133.44 (s), 132.45 (s), 131.35 (s), 130.72 (s), 129.73 (s), 129.56 (s), 128.60 (s), 127.70 (s), 127.27 (s), 122.54 (s), 114.87 (s), 71.08 (s), 33.91 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  408.0529, found: 408.0549.

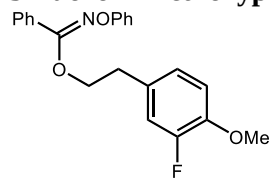
### 3,4-dichlorophenethyl N-phenoxybenzimidate (S15)



Prepared following [GP1](#).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 – 7.68 (m, 2H), 7.43 (dd,  $J$  = 8.8, 1.0 Hz, 2H), 7.26 – 7.18 (m, 2H), 7.13 – 7.07 (m, 3H), 7.01 – 6.89 (m, 3H), 6.49 (dd,  $J$  = 8.2, 2.1 Hz, 1H), 4.20 (t,  $J$  = 6.6 Hz, 2H), 2.45 (t,  $J$  = 6.6 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.96 (s), 156.43 (s), 138.40 (s), 132.74 (s), 131.41 (s), 131.34 (s), 130.99 (s), 130.79 (s), 130.55 (s), 129.77 (s), 128.73 (s), 128.62 (s), 127.64 (s), 122.60 (s), 114.83 (s), 72.55 (s), 35.66 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  408.0529, found: 408.0516.

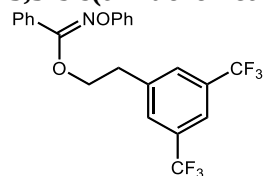


### 3-fluoro-4-methoxyphenethyl N-phenoxybenzimidate (S16)



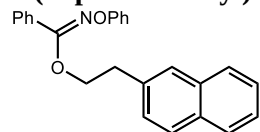
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.81 – 7.74 (m, 2H), 7.45 (dd,  $J$  = 8.7, 1.0 Hz, 2H), 7.26 – 7.18 (m, 2H), 7.12 – 7.06 (m, 3H), 6.91 (tt,  $J$  = 7.4, 1.0 Hz, 1H), 6.78 (dd,  $J$  = 12.0, 2.1 Hz, 1H), 6.67 (d,  $J$  = 8.3 Hz, 1H), 6.45 (t,  $J$  = 8.5 Hz, 1H), 4.35 (t,  $J$  = 6.8 Hz, 2H), 3.28 (s, 3H), 2.67 (t,  $J$  = 6.8 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –134.33 – –134.47 (m).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.08 (s), 156.68 (s), 153.03 (d,  $J$  = 246.4 Hz), 147.05 (d,  $J$  = 10.7 Hz), 131.59 (s), 130.98 (d,  $J$  = 6.0 Hz), 130.66 (s), 129.73 (s), 128.57 (s), 127.77 (s), 124.91 (d,  $J$  = 3.5 Hz), 122.46 (s), 117.17 (d,  $J$  = 18.0 Hz), 114.87 (s), 113.92 (d,  $J$  = 2.1 Hz), 73.29 (s), 55.84 (s), 35.83 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  388.1319, found: 388.1312.

### 3,5-bis(trifluoromethyl)phenethyl N-phenoxybenzimidate (S17)

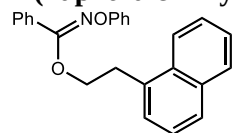


Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.70 – 7.65 (m, 2H), 7.64 (s, 1H), 7.40 (dd,  $J$  = 8.7, 0.9 Hz, 2H), 7.31 (s, 2H), 7.24 – 7.20 (m, 2H), 7.11 – 7.07 (m, 3H), 6.92 (t,  $J$  = 6.9 Hz, 1H), 4.13 (t,  $J$  = 6.4 Hz, 2H), 2.41 (t,  $J$  = 6.4 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –62.53 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  159.85 (s), 155.98 (s), 141.03 (s), 131.82 (q,  $J$  = 33.1 Hz), 131.17 (s), 130.86 (s), 129.78 (s), 129.60 (s), 128.63 (s), 127.45 (s), 123.92 (q,  $J$  = 272.7 Hz), 122.72 (s), 120.74 (dt,  $J$  = 7.7, 3.8 Hz), 114.78 (s), 71.97 (s), 35.93 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  476.1056, found: 476.1059.

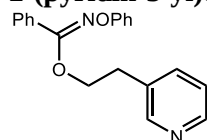
### 2-(naphthalen-2-yl)ethyl N-phenoxybenzimidate (S18)



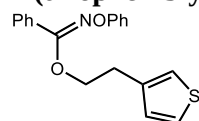
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.77 – 7.72 (m, 2H), 7.63 (d,  $J$  = 7.7 Hz, 1H), 7.59 (d,  $J$  = 7.8 Hz, 1H), 7.57 (d,  $J$  = 8.4 Hz, 1H), 7.45 (dd,  $J$  = 11.9, 11.0 Hz, 3H), 7.30 – 7.23 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 (dd,  $J$  = 8.4, 1.6 Hz, 1H), 7.08 – 7.04 (m, 1H), 7.01 (t,  $J$  = 7.5 Hz, 2H), 6.92 (t,  $J$  = 7.3 Hz, 1H), 4.53 (t,  $J$  = 6.9 Hz, 2H), 2.97 (t,  $J$  = 6.9 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.12 (s), 156.78 (s), 135.56 (s), 134.18 (s), 132.95 (s), 131.62 (s), 130.58 (s), 129.71 (s), 128.50 (s), 128.48 (s), 128.16 (s), 128.00 (s), 127.94 (s), 127.80 (s), 127.69 (s), 126.29 (s), 125.78 (s), 122.42 (s), 114.91 (s), 73.46 (s), 37.02 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  390.1465, found: 390.1450.

**2-(naphthalen-1-yl)ethyl N-phenoxybenzimidate (S19)**

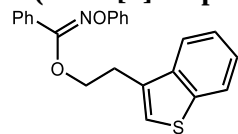
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.83 – 7.79 (m, 1H), 7.77 – 7.72 (m, 2H), 7.66 – 7.62 (m, 1H), 7.55 (p,  $J$  = 3.2 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.28 – 7.17 (m, 6H), 7.11 – 7.03 (m, 3H), 6.91 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 4.59 (t,  $J$  = 7.3 Hz, 2H), 3.34 (t,  $J$  = 7.3 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.12 (s), 156.71 (s), 134.47 (s), 133.81 (s), 132.62 (s), 131.59 (s), 130.56 (s), 129.68 (s), 129.18 (s), 128.54 (s), 127.84 (s), 127.80 (s), 127.68 (s), 126.38 (s), 125.85 (s), 125.80 (s), 123.87 (s), 122.40 (s), 114.95 (s), 72.65 (s), 33.85 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  390.1465, found: 390.1465.

**2-(pyridin-3-yl)ethyl N-phenoxybenzimidate (S20)**

Prepared following [GP1](#).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (d,  $J$  = 1.8 Hz, 1H), 8.51 (dd,  $J$  = 4.8, 1.6 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.63 (ddd,  $J$  = 7.8, 2.2, 1.7 Hz, 1H), 7.49 – 7.39 (m, 1H), 7.39 – 7.29 (m, 4H), 7.29 – 7.26 (m, 3H), 7.24 – 7.21 (m, 1H), 7.04 (ddd,  $J$  = 7.2, 4.3, 1.3 Hz, 1H), 4.66 (t,  $J$  = 6.7 Hz, 2H), 3.14 (t,  $J$  = 6.7 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  159.35, 156.51, 150.61, 148.39, 136.73, 133.38, 130.78, 130.64, 129.48, 128.59, 127.49, 123.54, 122.33, 114.54, 77.37, 77.16, 76.95, 72.66, 34.04. HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  319.1447, found: 319.1561.

**2-(thiophen-3-yl)ethyl N-phenoxybenzimidate (S21)**

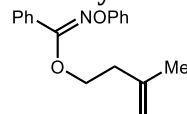
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.76 (dd,  $J$  = 7.5, 2.0 Hz, 2H), 7.43 (d,  $J$  = 8.5 Hz, 2H), 7.20 (dd,  $J$  = 13.6, 4.8 Hz, 2H), 7.14 – 7.06 (m, 3H), 6.88 (ddd,  $J$  = 9.8, 7.8, 5.1 Hz, 2H), 6.75 – 6.66 (m, 2H), 4.38 (t,  $J$  = 6.7 Hz, 2H), 2.77 (t,  $J$  = 6.7 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.09 (s), 156.75 (s), 138.21 (s), 131.63 (s), 130.61 (s), 129.71 (s), 128.55 (s), 128.54 (s), 127.79 (s), 125.73 (s), 122.42 (s), 122.15 (s), 114.86 (s), 72.90 (s), 31.25 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  346.0872, found: 346.0863.

**2-(benzo[b]thiophen-3-yl)ethyl N-phenoxybenzimidate (S22)**

Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.76 (d,  $J$  = 6.7 Hz, 2H), 7.57 (d,  $J$  = 8.0 Hz, 1H), 7.44 (dd,  $J$  = 11.1, 8.4 Hz, 3H), 7.20 (t,  $J$  = 8.0 Hz, 2H), 7.13 (t,  $J$  = 7.4 Hz, 1H), 7.11 – 7.03 (m, 4H), 6.92 (t,  $J$  = 7.3 Hz, 1H), 6.81 (s, 1H), 4.48 (t,  $J$  = 6.9 Hz, 2H), 2.98 (t,  $J$  = 6.8 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.08 (s), 156.70 (s), 140.87 (s), 139.33 (s), 132.27 (s), 131.49 (s), 130.64 (s), 129.72 (s), 128.58

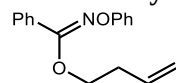
(s), 127.78 (s), 124.59 (s), 124.27 (s), 123.54 (s), 123.13 (s), 122.47 (s), 121.86 (s), 114.90 (s), 71.73 (s), 29.48 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+Na]^+$  396.1029, found: 396.1020.

**3-methylbut-3-en-1-yl N-phenoxybenzimidate (S23)**



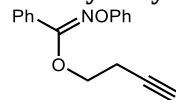
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.98 – 7.91 (m, 2H), 7.45 (dd,  $J$  = 8.7, 1.0 Hz, 2H), 7.21 (td,  $J$  = 7.4, 2.5 Hz, 2H), 7.14 – 7.10 (m, 3H), 6.95 – 6.88 (m, 1H), 4.79 (d,  $J$  = 9.1 Hz, 2H), 4.41 (td,  $J$  = 6.7, 1.4 Hz, 2H), 2.28 (t,  $J$  = 6.7 Hz, 2H), 1.56 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.11 (s), 156.62 (s), 141.73 (s), 131.90 (s), 130.63 (s), 129.70 (s), 128.56 (s), 127.77 (s), 122.38 (s), 114.86 (s), 112.90 (s), 71.34 (s), 38.44 (s), 22.44 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+Na]^+$  304.1308, found: 304.1305.

**but-3-en-1-yl N-phenoxybenzimidate (S24)**



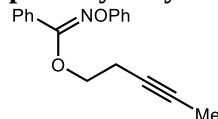
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.95 – 7.90 (m, 2H), 7.46 – 7.42 (m, 2H), 7.24 – 7.18 (m, 2H), 7.14 – 7.09 (m, 3H), 6.95 – 6.88 (m, 1H), 5.68 (ddt,  $J$  = 17.0, 10.2, 6.8 Hz, 1H), 5.06 – 4.93 (m, 2H), 4.26 (t,  $J$  = 6.6 Hz, 2H), 2.26 (qt,  $J$  = 6.6, 1.3 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.10 (s), 156.62 (s), 134.41 (s), 131.82 (s), 130.62 (s), 129.71 (d,  $J$  = 8.5 Hz), 128.56 (s), 127.77 (s), 122.38 (s), 117.45 (s), 114.87 (s), 72.30 (s), 34.91 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+Na]^+$  290.1151, found: 290.1154.

**but-3-yn-1-yl N-phenoxybenzimidate (S25)**



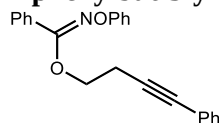
Prepared following [GP1](#).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.01 – 7.93 (m, 2H), 7.41 – 7.35 (m, 2H), 7.23 – 7.17 (m, 2H), 7.15 – 7.10 (m, 3H), 6.91 (tt,  $J$  = 7.6, 1.1 Hz, 1H), 4.24 (t,  $J$  = 6.6 Hz, 2H), 2.24 (td,  $J$  = 6.6, 2.7 Hz, 2H), 1.71 (t,  $J$  = 2.7 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  159.92 (s), 156.20 (s), 131.52 (s), 130.73 (s), 129.67 (s), 128.54 (s), 122.47 (s), 114.88 (s), 80.51 (s), 70.88 (s), 70.57 (s), 20.60 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+Na]^+$  288.0995, found: 288.0999.

**pent-3-yn-1-yl N-phenoxybenzimidate (S26)**



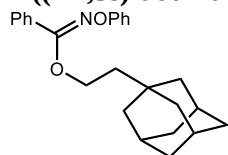
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.03 – 7.97 (m, 2H), 7.42 – 7.37 (m, 2H), 7.22 – 7.17 (m, 2H), 7.14 – 7.10 (m, 3H), 6.93 – 6.87 (m, 1H), 4.34 (t,  $J$  = 6.7 Hz, 2H), 2.43 – 2.33 (m, 2H), 1.47 (t,  $J$  = 2.5 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.01 (s), 156.54 (s), 131.69 (s), 130.65 (s), 129.65 (s), 128.52 (s), 122.41 (s), 114.91 (s), 77.76 (s), 75.59 (s), 71.72 (s), 21.07 (s), 3.28 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+Na]^+$  302.1151, found: 302.1147.

#### 4-phenylbut-3-yn-1-yl N-phenoxybenzimidate (S27)



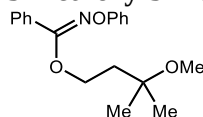
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.07 – 8.03 (m, 2H), 7.45 – 7.40 (m, 4H), 7.23 – 7.18 (m, 2H), 7.13 – 7.09 (m, 3H), 7.01 – 6.95 (m, 3H), 6.92 (ddd,  $J = 7.4, 2.0, 1.0$  Hz, 1H), 4.35 (t,  $J = 6.4$  Hz, 2H), 2.52 (t,  $J = 6.4$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  159.99 (s), 156.50 (s), 132.01 (s), 131.60 (s), 130.73 (s), 129.68 (s), 128.59 (s), 128.57 (s), 128.13 (s), 124.16 (s), 122.48 (s), 114.94 (s), 86.74 (s), 82.91 (s), 71.16 (s), 21.65 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  364.1308, found: 364.1302.

#### 2-((1R,3S)-adamantan-1-yl)ethyl N-phenoxybenzimidate (S28)



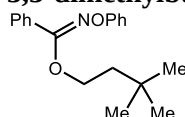
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.96 (dt,  $J = 5.1, 3.8$  Hz, 2H), 7.55 – 7.46 (m, 2H), 7.24 – 7.18 (m, 2H), 7.15 – 7.12 (m, 3H), 6.91 (tt,  $J = 7.4, 1.0$  Hz, 1H), 4.45 (t,  $J = 7.4$  Hz, 2H), 1.83 (s, 3H), 1.65 – 1.48 (m, 9H), 1.42 (d,  $J = 2.4$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.25 (s), 157.06 (s), 132.01 (s), 130.59 (s), 129.72 (s), 128.63 (s), 127.82 (s), 122.34 (s), 114.89 (s), 69.60 (s), 44.28 (s), 42.68 (d,  $J = 21.9$  Hz), 37.23 (s), 31.89 (s), 29.00 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  398.2091, found: 398.2090.

#### 3-methoxy-3-methylbutyl N-phenoxybenzimidate (S29)

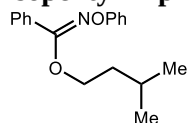


Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.94 – 7.90 (m, 2H), 7.48 (dt,  $J = 9.1, 1.7$  Hz, 2H), 7.23 – 7.18 (m, 2H), 7.14 – 7.10 (m, 3H), 6.90 (tt,  $J = 7.4, 1.0$  Hz, 1H), 4.60 – 4.48 (m, 2H), 2.91 (s, 3H), 1.96 – 1.86 (m, 2H), 0.98 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.22 (s), 156.99 (s), 131.91 (s), 130.57 (s), 129.69 (s), 128.61 (s), 127.84 (s), 122.32 (s), 114.89 (s), 73.20 (s), 69.85 (s), 48.96 (s), 40.46 (s), 25.18 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  336.1570, found: 336.1572.

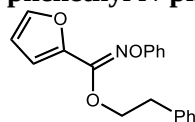
#### 3,3-dimethylbutyl N-phenoxybenzimidate (S30)



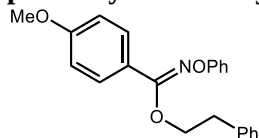
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.98 – 7.90 (m, 2H), 7.52 – 7.44 (m, 2H), 7.24 – 7.19 (m, 2H), 7.15 – 7.11 (m, 3H), 6.91 (tt,  $J = 7.4, 1.0$  Hz, 1H), 4.52 – 4.28 (m, 2H), 1.70 – 1.52 (m, 2H), 0.81 (s, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.20 (s), 156.90 (s), 132.00 (s), 130.59 (s), 129.71 (s), 128.61 (s), 127.78 (s), 122.34 (s), 114.85 (s), 70.76 (s), 43.43 (s), 29.69 (s), 29.58 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  320.1621, found: 320.1623.

**isopentyl N-phenoxybenzimidate (S31)**

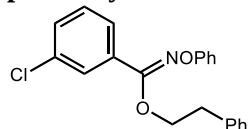
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.97 – 7.90 (m, 2H), 7.50 – 7.44 (m, 2H), 7.25 – 7.18 (m, 2H), 7.15 – 7.10 (m, 3H), 6.91 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 4.31 (t,  $J$  = 6.7 Hz, 2H), 1.76 – 1.64 (m, 1H), 1.50 (q,  $J$  = 6.8 Hz, 2H), 0.79 (d,  $J$  = 6.7 Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.19 (s), 156.96 (s), 131.96 (s), 130.59 (s), 129.70 (s), 128.59 (d,  $J$  = 7.8 Hz), 127.73 (s), 122.34 (s), 114.87 (s), 71.67 (s), 39.14 (s), 25.04 (s), 22.57 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  306.1465, found: 306.1465.

**phenethyl N-phenoxyfuran-2-carbimidate (S32)**

Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.49 – 7.43 (m, 2H), 7.19 – 7.16 (m, 3H), 7.15 (s, 1H), 7.12 – 7.08 (m, 2H), 7.07 – 7.01 (m, 3H), 6.96 (dd,  $J$  = 1.7, 0.8 Hz, 1H), 6.90 – 6.85 (m, 1H), 4.39 (t,  $J$  = 6.9 Hz, 2H), 2.80 (t,  $J$  = 6.9 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.00 (s), 150.44 (s), 145.62 (s), 144.58 (s), 137.99 (s), 129.67 (s), 129.40 (s), 128.73 (s), 126.83 (s), 114.86 (s), 113.51 (s), 111.44 (s), 73.64 (s), 36.77 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  330.1101, found: 330.1099.

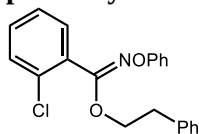
**phenethyl 4-methoxy-N-phenoxybenzimidate (S33)**

Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.75 – 7.70 (m, 2H), 7.46 (dt,  $J$  = 9.1, 1.7 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.14 – 7.10 (m, 2H), 7.06 (dd,  $J$  = 7.2, 5.2 Hz, 3H), 6.91 (tdd,  $J$  = 7.1, 3.3, 2.3 Hz, 1H), 6.73 – 6.67 (m, 2H), 4.50 (t,  $J$  = 6.9 Hz, 2H), 3.21 (s, 3H), 2.85 (t,  $J$  = 6.9 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  162.03 (s), 160.24 (s), 156.98 (s), 138.23 (s), 129.69 (s), 129.47 (s), 129.43 (s), 128.77 (s), 126.80 (s), 123.90 (s), 122.23 (s), 114.89 (s), 114.06 (s), 73.46 (s), 54.81 (s), 36.92 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  370.1414, found: 370.1412.

**phenethyl 3-chloro-N-phenoxybenzimidate (S34)**

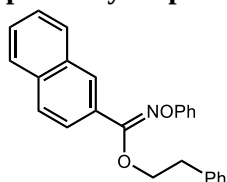
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.87 (t,  $J$  = 1.8 Hz, 1H), 7.60 (ddd,  $J$  = 7.9, 1.6, 1.1 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.31 – 7.27 (m, 2H), 7.22 (tt,  $J$  = 8.1, 1.6 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.12 – 7.08 (m, 2H), 7.01 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 6.84 (t,  $J$  = 7.9 Hz, 1H), 4.53 (t,  $J$  = 6.8 Hz, 2H), 2.84 (t,  $J$  = 6.8 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  159.84 (s), 155.13 (s), 137.91 (s), 134.71 (s), 133.64 (s), 130.59 (s), 129.74 (s), 129.34 (s), 128.84 (s), 127.98 (s), 127.74 (s), 126.98 (s), 125.67 (s), 122.63 (s), 114.84 (s), 73.79 (s), 36.75 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  374.0918, found: 374.0913.

### phenethyl 2-chloro-N-phenoxybenzimidate (S35)



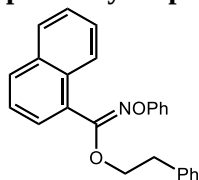
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.53 (d,  $J = 8.5$  Hz, 2H), 7.19 – 7.12 (m, 2H), 7.09 – 7.04 (m, 2H), 7.04 – 6.97 (m, 4H), 6.96 (dd,  $J = 7.1$ , 2.1 Hz, 1H), 6.86 (t,  $J = 7.3$  Hz, 1H), 6.75 – 6.66 (m, 2H), 3.97 (t,  $J = 6.9$  Hz, 2H), 2.76 (t,  $J = 6.9$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.47 (s), 156.33 (s), 137.75 (s), 134.23 (s), 132.24 (s), 131.37 (s), 129.99 (s), 129.89 (s), 129.64 (s), 129.51 (s), 128.75 (s), 126.90 (s), 126.84 (s), 122.12 (s), 114.87 (s), 71.46 (s), 36.70 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  352.1099, found: 352.1089.

### phenethyl N-phenoxy-2-naphthimidate (S36)



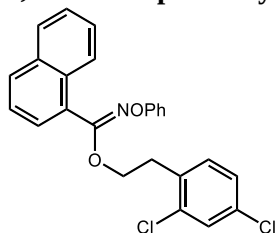
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.09 (s, 1H), 8.02 (dd,  $J = 8.6$ , 1.6 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.49 (dd,  $J = 8.6$ , 0.8 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.14 – 7.02 (m, 5H), 6.94 (t,  $J = 7.3$  Hz, 1H), 4.53 (t,  $J = 6.7$  Hz, 2H), 2.87 (t,  $J = 6.7$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.14 (s), 156.90 (s), 138.30 (s), 134.81 (s), 133.45 (s), 129.75 (s), 129.51 (s), 129.11 (s), 129.04 (s), 128.82 (s), 128.17 (s), 128.14 (s), 127.98 (s), 127.33 (s), 126.88 (s), 126.61 (s), 124.64 (s), 122.50 (s), 114.98 (s), 73.58 (s), 36.90 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  390.1465, found: 390.1453.

### phenethyl N-phenoxy-1-naphthimidate (S37)



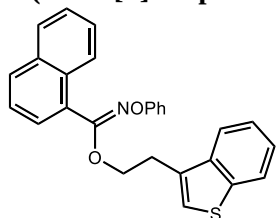
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.07 (dq,  $J = 6.9$ , 3.4 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.55 – 7.51 (m, 2H), 7.27 (dd,  $J = 7.0$ , 1.2 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.09 – 6.99 (m, 5H), 6.98 – 6.94 (m, 2H), 6.88 (tt,  $J = 7.4$ , 1.0 Hz, 1H), 3.75 (t,  $J = 6.6$  Hz, 2H), 2.66 (t,  $J = 6.6$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  161.00 – 160.08 (m), 158.26 – 157.13 (m), 137.85 (s), 133.72 (s), 132.12 – 131.95 (m), 130.81 (s), 129.70 (s), 129.55 (s), 129.17 (s), 128.68 (s), 128.67 (s), 127.75 – 127.72 (m), 127.70 (s), 126.84 (s), 126.65 (s), 125.42 (s), 125.23 (s), 121.98 (s), 114.85 (s), 71.16 (s), 36.82 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  390.1465, found: 390.1466.

### 2,4-dichlorophenethyl N-phenoxy-1-naphthimide (S38)



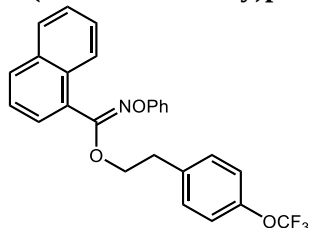
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 – 7.95 (m, 2H), 7.94 – 7.86 (m, 1H), 7.58 – 7.53 (m, 2H), 7.52 – 7.47 (m, 2H), 7.31 (ddd,  $J$  = 8.9, 5.5, 1.9 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.22 (d,  $J$  = 8.2 Hz, 1H), 7.12 (dd,  $J$  = 8.2, 2.1 Hz, 1H), 7.01 (tt,  $J$  = 7.2, 1.2 Hz, 1H), 4.05 (t,  $J$  = 6.7 Hz, 2H), 3.14 – 2.97 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  159.71 (s), 157.99 (s), 134.95 (s), 133.51 (s), 133.50 (s), 133.47 (s), 132.80 (s), 131.61 (s), 131.22 (s), 129.39 (s), 129.38 (s), 129.05 (s), 128.72 (s), 127.74 (s), 127.24 (s), 126.75 (s), 126.46 (s), 125.25 (s), 124.77 (s), 122.03 (s), 114.68 (s), 68.95 (s), 34.04 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  458.0685, found: 458.0688.

### 2-(benzo[b]thiophen-3-yl)ethyl N-phenoxy-1-naphthimide (S39)



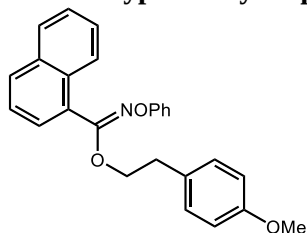
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.08 – 8.02 (m, 1H), 7.64 – 7.59 (m, 2H), 7.52 (ddd,  $J$  = 5.2, 2.7, 1.1 Hz, 3H), 7.25 (dd,  $J$  = 7.0, 1.2 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.16 (dd,  $J$  = 2.9, 1.2 Hz, 3H), 7.15 – 7.14 (m, 1H), 7.07 – 6.98 (m, 3H), 6.92 – 6.85 (m, 1H), 3.78 (t,  $J$  = 6.7 Hz, 2H), 2.82 (dt,  $J$  = 6.8, 3.3 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.68 (s), 157.88 (s), 140.75 (s), 139.21 (s), 133.69 (s), 132.05 (s), 131.95 (s), 130.83 (s), 129.73 (s), 129.19 (s), 128.69 (s), 127.73 (s), 127.47 (s), 126.71 (s), 125.27 (s), 125.23 (s), 124.45 (s), 124.13 (s), 123.91 (s), 123.00 (s), 122.06 (s), 121.81 (s), 114.86 (s), 69.47 (s), 29.47 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  446.1185, found: 446.1183.

### 4-(trifluoromethoxy)phenethyl N-phenoxy-1-naphthimide (S40)



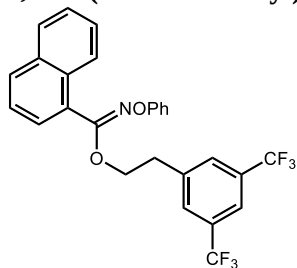
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.02 – 7.98 (m, 1H), 7.59 – 7.50 (m, 4H), 7.28 (dd,  $J$  = 7.0, 1.2 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.09 (dd,  $J$  = 8.2, 7.1 Hz, 1H), 6.88 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 6.82 (d,  $J$  = 7.9 Hz, 2H), 6.73 – 6.66 (m, 2H), 3.63 (t,  $J$  = 6.4 Hz, 2H), 2.47 (t,  $J$  = 6.4 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.62 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.58 (s), 157.85 (s), 148.30 (d,  $J$  = 1.6 Hz), 136.74 (s), 133.74 (s), 131.99 (s), 130.99 (s), 130.87 (s), 129.75 (s), 129.11 (s), 128.76 (s), 127.73 (s), 127.49 (s), 126.76 (s), 125.24 (s), 125.22 (s), 122.14 (s), 121.26 (q,  $J$  = 256.5 Hz), 121.14 (s), 114.77 (s), 70.68 (s), 35.85 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  474.1287, found: 474.1291.

#### 4-methoxyphenethyl N-phenoxy-1-naphthimide (S41)



Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.11 – 8.06 (m, 1H), 7.64 – 7.60 (m, 2H), 7.56 – 7.51 (m, 2H), 7.32 (dd,  $J$  = 7.0, 1.2 Hz, 1H), 7.21 – 7.17 (m, 4H), 7.08 (dd,  $J$  = 8.3, 7.0 Hz, 1H), 6.92 – 6.84 (m, 3H), 6.71 – 6.64 (m, 2H), 3.77 (t,  $J$  = 6.7 Hz, 2H), 3.28 (s, 3H), 2.67 (t,  $J$  = 6.6 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.75 (s), 159.09 (s), 158.11 (s), 133.73 (s), 132.12 (s), 130.81 (s), 130.52 (s), 129.70 (s), 129.18 (s), 128.67 (s), 127.80 (s), 127.69 (s), 126.66 (s), 125.45 (s), 125.25 (s), 121.97 (s), 114.86 (s), 114.25 (s), 71.51 (s), 54.78 (s), 36.01 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  398.1751, found: 398.1736.

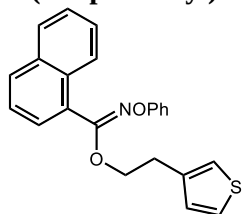
#### 3,5-bis(trifluoromethyl)phenethyl N-phenoxy-1-naphthimide (S42)



Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.93 – 7.89 (m, 1H), 7.64 (s, 1H), 7.60 (dd,  $J$  = 8.8, 1.0 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.33 (s, 2H), 7.24 (dd,  $J$  = 7.0, 1.2 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.09 (dd,  $J$  = 8.2, 7.0 Hz, 1H), 6.90 – 6.86 (m, 1H), 3.44 (t,  $J$  = 6.0 Hz, 2H), 2.23 (t,  $J$  = 6.0 Hz, 2H).  $^{19}\text{F}$  NMR (377 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -62.46 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.48 (s), 157.16 (s), 140.91 (s), 133.76 (s), 131.90 (s), 131.75 (q,  $J$  = 33.0 Hz), 131.07 (s), 129.79 (s), 129.78 (s), 129.72 (s), 129.00 (s), 128.82 (s), 127.81 (s), 127.30 (s), 126.84 (s), 125.24 (s), 125.00 (s), 123.94 (q,  $J$  = 272.8 Hz), 122.28 (s), 120.78 (dt,  $J$  = 7.7, 3.8 Hz), 114.75 (s), 69.66 (s), 35.71 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  526.1212, found: 526.1218.

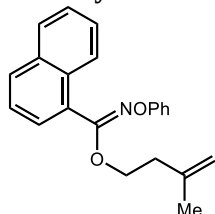


### 2-(thiophen-3-yl)ethyl N-phenoxy-1-naphthimide (S43)



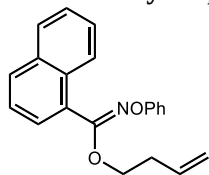
Prepared following [GP2](#).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.12 – 8.03 (m, 1H), 7.63 – 7.57 (m, 2H), 7.57 – 7.50 (m, 2H), 7.32 (dd,  $J$  = 7.0, 1.2 Hz, 1H), 7.24 – 7.13 (m, 4H), 7.09 (dd,  $J$  = 8.3, 7.0 Hz, 1H), 6.91 – 6.84 (m, 1H), 6.83 (dd,  $J$  = 4.9, 2.9 Hz, 1H), 6.74 (dd,  $J$  = 4.9, 1.3 Hz, 1H), 6.68 (ddt,  $J$  = 2.9, 1.4, 0.8 Hz, 1H), 3.68 (t,  $J$  = 6.4 Hz, 2H), 2.61 (t,  $J$  = 6.4 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.43 (d,  $J$  = 50.8 Hz), 157.75 (d,  $J$  = 45.5 Hz), 137.83 (d,  $J$  = 33.4 Hz), 133.65 (d,  $J$  = 16.8 Hz), 132.02 (d,  $J$  = 13.0 Hz), 130.73 (d,  $J$  = 21.8 Hz), 129.72 (s), 129.14 (s), 128.93 (s), 128.69 (s), 127.74 (s), 127.69 (s), 126.69 (s), 125.56 (s), 125.36 (s), 125.27 (s), 122.33 (s), 122.03 (s), 114.84 (s), 70.57 (s), 31.07 (d,  $J$  = 7.1 Hz). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  396.1029, found: 396.1022.

### 3-methylbut-3-en-1-yl N-phenoxy-1-naphthimide (S44)

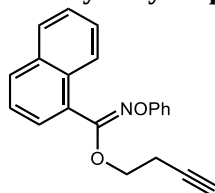


Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.22 – 8.17 (m, 1H), 7.61 – 7.58 (m, 2H), 7.55 (dd,  $J$  = 13.7, 5.3 Hz, 2H), 7.51 (dd,  $J$  = 7.0, 1.2 Hz, 1H), 7.24 – 7.15 (m, 5H), 7.12 (dd,  $J$  = 8.2, 7.0 Hz, 1H), 4.74 – 4.61 (m, 2H), 3.70 (t,  $J$  = 6.7 Hz, 2H), 2.14 (t,  $J$  = 6.6 Hz, 2H), 1.45 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.72 (s), 157.97 (s), 141.52 (s), 133.79 (s), 132.18 (s), 130.85 (s), 129.68 (s), 129.11 (s), 128.72 (s), 127.94 (s), 127.70 (s), 126.72 (s), 125.50 (s), 125.26 (s), 121.96 (s), 114.82 (s), 112.99 (s), 69.28 (s), 38.17 (s), 22.64 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  354.1465, found: 354.1468.

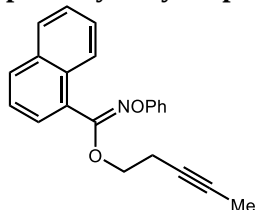
### but-3-en-1-yl N-phenoxy-1-naphthimide (S45)



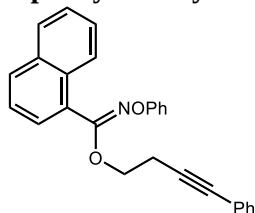
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.18 (d,  $J$  = 8.4 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.55 (dd,  $J$  = 13.3, 4.9 Hz, 2H), 7.49 (dd,  $J$  = 7.0, 1.1 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.14 – 7.09 (m, 1H), 6.90 – 6.84 (m, 1H), 5.63 – 5.54 (m, 1H), 4.93 – 4.90 (m, 1H), 4.89 (t,  $J$  = 1.2 Hz, 1H), 3.59 (t,  $J$  = 6.6 Hz, 2H), 2.17 – 2.09 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.71 (s), 157.93 (s), 133.85 (s), 133.81 (s), 132.16 (s), 130.84 (s), 129.68 (s), 129.11 (s), 128.71 (s), 127.97 (s), 127.70 (s), 126.72 (s), 125.53 (s), 125.26 (s), 121.99 (s), 117.55 (s), 114.85 (s), 69.85 (s), 34.54 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  340.1308, found: 340.1304.

**but-3-yn-1-yl N-phenoxy-1-naphthimide (S46)**

Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.18 (dd,  $J = 8.2, 0.9$  Hz, 1H), 7.60 – 7.51 (m, 4H), 7.48 (dd,  $J = 7.0, 1.2$  Hz, 1H), 7.25 – 7.17 (m, 4H), 7.10 (dd,  $J = 8.3, 7.0$  Hz, 1H), 6.86 (tt,  $J = 7.4, 1.1$  Hz, 1H), 3.60 (t,  $J = 6.7$  Hz, 2H), 2.15 (td,  $J = 6.7, 2.7$  Hz, 2H), 1.62 (t,  $J = 2.7$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.60 (s), 157.31 (s), 133.81 (s), 132.08 (s), 130.98 (s), 129.67 (s), 129.24 (s), 128.71 (s), 127.77 (s), 127.56 (s), 126.72 (s), 125.49 (s), 125.23 (s), 122.07 (s), 114.85 (s), 79.77 (s), 70.68 (s), 68.23 (s), 20.27 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  316.1332, found: 316.1324.

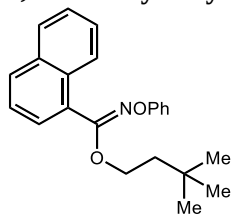
**pent-3-yn-1-yl N-phenoxy-1-naphthimide (S47)**

Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.20 (d,  $J = 8.3$  Hz, 1H), 7.59 – 7.48 (m, 5H), 7.24 – 7.14 (m, 5H), 7.10 (dd,  $J = 8.2, 7.1$  Hz, 1H), 3.72 (t,  $J = 6.9$  Hz, 2H), 2.37 – 2.21 (m, 2H), 1.38 (t,  $J = 2.5$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.66 (s), 157.58 (s), 133.81 (s), 132.12 (s), 130.94 (s), 129.66 (s), 129.21 (s), 128.72 (s), 127.72 (s), 126.70 (s), 125.50 (s), 125.24 (s), 122.01 (s), 114.87 (s), 77.85 (s), 74.73 (s), 69.01 (s), 20.78 (s), 3.25 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  352.1308, found: 352.1308.

**4-phenylbut-3-yn-1-yl N-phenoxy-1-naphthimide (S48)**

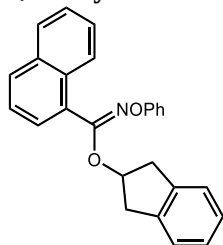
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.25 (d,  $J = 8.4$  Hz, 1H), 7.61 – 7.50 (m, 5H), 7.39 – 7.34 (m, 2H), 7.23 – 7.17 (m, 2H), 7.17 (s, 1H), 7.15 (t,  $J = 2.1$  Hz, 1H), 7.10 (dd,  $J = 8.2, 7.0$  Hz, 1H), 6.98 – 6.91 (m, 3H), 6.86 (tt,  $J = 7.4, 1.0$  Hz, 1H), 3.73 (t,  $J = 6.7$  Hz, 2H), 2.45 (t,  $J = 6.7$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.64 (s), 157.57 (s), 133.83 (s), 132.09 (s), 132.05 (s), 131.01 (s), 129.68 (s), 129.34 (s), 128.73 (s), 128.53 (s), 128.11 (d,  $J = 1.8$  Hz), 127.80 (s), 127.62 (s), 126.72 (s), 125.50 (s), 125.29 (s), 124.06 (s), 122.07 (s), 114.89 (s), 85.89 (s), 82.99 (s), 68.50 (s), 21.40 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  414.1465, found: 414.1456.

### 3,3-dimethylbutyl N-phenoxy-1-naphthimide (S49)



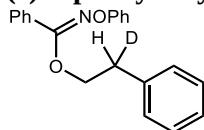
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.21 (d,  $J$  = 8.4 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.59 – 7.50 (m, 3H), 7.28 – 7.21 (m, 1H), 7.19 (ddd,  $J$  = 6.6, 3.6, 1.7 Hz, 3H), 7.16 – 7.10 (m, 1H), 6.91 – 6.84 (m, 1H), 3.75 (td,  $J$  = 7.2, 1.8 Hz, 2H), 1.52 – 1.43 (m, 2H), 0.66 (s, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.78 (s), 158.20 (s), 133.77 (s), 132.24 (s), 130.82 (s), 129.69 (s), 129.04 (s), 128.73 (s), 127.98 (s), 127.68 (s), 126.74 (s), 125.50 (s), 125.27 (s), 121.91 (s), 114.80 (s), 68.19 (s), 43.30 (s), 29.51 (s), 21.14 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  348.1958, found: 348.1951.

### 2,3-dihydro-1H-inden-2-yl N-phenoxy-1-naphthimide (S50)

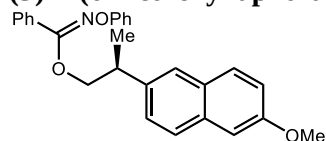


Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.33 (d,  $J$  = 8.4 Hz, 1H), 7.57 (t,  $J$  = 7.0 Hz, 3H), 7.49 (ddd,  $J$  = 4.3, 3.2, 1.7 Hz, 2H), 7.30 – 7.18 (m, 2H), 7.15 – 7.11 (m, 3H), 7.03 – 6.99 (m, 2H), 6.93 – 6.89 (m, 2H), 6.85 (tt,  $J$  = 7.4, 1.0 Hz, 1H), 4.90 – 4.75 (m, 1H), 3.16 (dd,  $J$  = 16.5, 3.8 Hz, 2H), 2.69 (dd,  $J$  = 16.6, 6.7 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.53 (s), 157.09 (s), 140.30 (s), 133.94 (s), 132.21 (s), 130.94 (s), 129.64 (s), 129.20 (s), 128.76 (s), 128.52 (s), 127.63 (s), 127.06 (s), 126.66 (s), 125.70 (s), 125.26 (s), 124.85 (s), 122.04 (s), 114.82 (s), 81.64 (s), 40.43 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  402.1465, found: 402.1463.

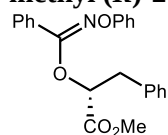
### (±)-2-phenylethyl-2-d-N-phenoxybenzimidate (S51)



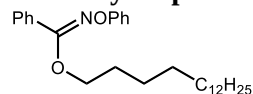
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.77 – 7.73 (m, 2H), 7.46 – 7.41 (m, 2H), 7.22 – 7.18 (m, 3H), 7.13 – 7.00 (m, 7H), 6.91 (tt,  $J$  = 7.4, 1.0 Hz, 1H), 4.44 (d,  $J$  = 6.8 Hz, 2H), 2.86 – 2.68 (m, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  160.12 (s), 156.74 (s), 138.05 (s), 131.67 (s), 130.56 (s), 129.69 (s), 129.40 (s), 128.77 (s), 128.52 (s), 128.35 (s), 127.82 (s), 126.83 (s), 122.39 (s), 114.89 (s), 36.86 – 36.14 (m). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  341.1376 found: 341.1762.

**(S)-2-(6-methoxynaphthalen-2-yl)propyl N-phenoxybenzimidate (S52)**

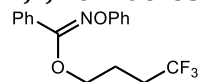
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.70 (m, 2H), 7.57 (d,  $J$  = 8.4 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.24 – 7.18 (m, 4H), 7.07 – 6.98 (m, 3H), 6.96 (d,  $J$  = 2.5 Hz, 1H), 6.91 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 4.51 (dd,  $J$  = 6.9, 2.2 Hz, 2H), 3.41 (s, 3H), 3.25 (dd,  $J$  = 13.9, 6.9 Hz, 1H), 1.32 (d,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  160.16 (s), 158.11 (s), 156.85 (s), 138.54 (s), 134.29 (s), 131.61 (s), 130.52 (s), 129.72 (s), 129.71 (s), 129.65 (s), 128.48 (s), 127.82 (s), 127.45 (s), 126.62 (s), 126.58 (s), 122.39 (s), 119.35 (s), 114.91 (s), 105.94 (s), 78.13 (s), 54.82 (s), 40.84 (s), 18.10 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  434.1727, found: 434.1726.

**methyl (R)-2-((phenoxyimino)(phenyl)methoxy)-3-phenylpropanoate (S53)**

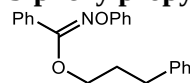
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 – 7.67 (m, 2H), 7.48 – 7.37 (m, 2H), 7.36 – 7.27 (m, 8H), 7.26 – 7.12 (m, 2H), 7.10 – 6.93 (m, 1H), 5.73 (dd,  $J$  = 8.2, 4.6 Hz, 1H), 3.64 (s, 3H), 3.31 (ddd,  $J$  = 22.5, 14.2, 6.4 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  170.54 (s), 159.04 (s), 154.35 (s), 136.00 (s), 130.94 (s), 130.67 (s), 129.67 (s), 129.40 (s), 128.70 (s), 128.31 (s), 127.67 (s), 127.30 (s), 122.39 (s), 114.47 (s), 81.09 (s), 52.30 (s), 39.62 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  398.1368, found: 398.1394.

**hexadecyl N-phenoxybenzimidate (S54)**

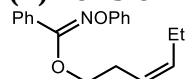
Prepared following [GP2](#).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.81 (m, 1H), 7.50 – 7.38 (m, 2H), 7.36 – 7.27 (m, 2H), 7.05 – 6.97 (m, 1H), 4.41 (t,  $J$  = 6.7 Hz, 1H), 1.80 (dt,  $J$  = 14.6, 6.7 Hz, 1H), 1.51 – 1.39 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.56 (s), 157.18 (s), 131.17 (s), 130.60 (s), 129.40 (s), 128.54 (s), 127.60 (s), 122.08 (s), 114.58 (s), 73.27 (s), 32.08 (s), 30.36 (s), 29.86 (3C, s), 29.83 (s), 29.81 (s), 29.80 (s), 29.72 (s), 29.68 (s), 29.52 (s), 29.44 (s), 25.89 (s), 22.85 (s), 14.27 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  438.3367, found: 438.3343.

**4,4,4-trifluorobutyl N-phenoxybenzimidate (S55)**

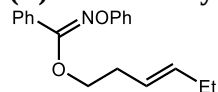
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.82 – 7.77 (m, 2H), 7.44 – 7.40 (m, 2H), 7.26 – 7.18 (m, 2H), 7.14 – 7.08 (m, 3H), 6.92 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 3.89 (t,  $J$  = 6.2 Hz, 2H), 1.90 – 1.74 (m, 2H), 1.55 (ddd,  $J$  = 13.9, 10.1, 6.1 Hz, 2H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –66.21 (t,  $J$  = 11.0 Hz).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  159.94 (s), 156.46 (s), 131.29 (s), 130.81 (s), 129.76 (s), 128.71 (s), 127.65 (q,  $J$  = 276.1 Hz), 127.54 (s), 122.61 (s), 114.80 (s), 70.97 (s), 30.42 (q,  $J$  = 29.0 Hz), 23.15 (q,  $J$  = 3.0 Hz). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  346.1025, found: 346.1013.

**3-phenylpropyl N-phenoxybenzimidate (S56)**

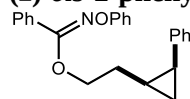
Prepared following [GP2](#).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89z – 7.79 (m, 2H), 7.50 – 7.39 (m, 3H), 7.35 – 7.27 (m, 6H) 7.23 – 7.18 (m, 3H), 7.02 (tt,  $J$  = 7.3, 1.2 Hz, 1H), 4.44 (t,  $J$  = 6.4 Hz, 2H), 2.90 – 2.77 (m, 2H), 2.25 – 2.05 (m, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  159.50, 157.05, 141.39, 131.02, 130.67, 129.42, 128.65, 128.62, 128.58, 127.58, 126.18, 122.15, 114.57, 77.37, 77.16, 76.95, 72.22, 32.14, 32.01. HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  354.1470, found: 354.1585.

**(Z)-hex-3-en-1-yl-N-phenoxybenzimidate (S57)**

Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (ddd,  $J$  = 4.5, 2.5, 1.5 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.22 – 7.19 (m, 2H), 7.14 – 7.10 (m, 3H), 6.91 (tt,  $J$  = 7.4, 1.1 Hz, 1H), 5.48 – 5.41 (m, 1H), 5.39 – 5.25 (m, 1H), 4.29 (t,  $J$  = 6.8 Hz, 2H), 2.44 – 2.28 (m, 2H), 1.99 – 1.85 (m, 2H), 0.84 (t,  $J$  = 7.5 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  160.14, 156.72, 134.64, 131.88, 130.60, 129.68, 128.56, 127.82, 124.34, 122.36, 114.88, 72.64, 28.61, 20.96, 14.34. HRMS (ESI-TOF) calcd For  $[\text{M}+\text{H}]^+$  202.1232, found: 202.1220.

**(E)-hex-3-en-1-yl-N-phenoxybenzimidate (S58)**

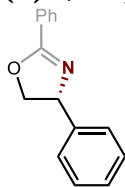
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (ddd,  $J$  = 4.4, 2.4, 1.5 Hz, 2H), 7.51 – 7.40 (m, 2H), 7.24 – 7.18 (m, 2H), 7.14 – 7.10 (m, 3H), 6.94 – 6.87 (m, 1H), 5.45 (dt,  $J$  = 15.2, 6.3, 1.2 Hz, 1H), 5.32 (dt,  $J$  = 15.1, 6.8, 1.5 Hz, 1H), 4.31 (t,  $J$  = 6.7 Hz, 3H), 2.30 (qd,  $J$  = 6.7, 1.1 Hz, 2H), 1.94 – 1.83 (m, 1H), 0.88 (t,  $J$  = 7.5 Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  160.15 (s), 156.77 (s), 135.34 (s), 131.93 (s), 130.58 (s), 129.68 (s), 128.53 (s), 127.83 (s), 124.71 (s), 122.34 (s), 114.89 (s), 72.91 (s), 33.93 (s), 26.01 (s), 13.81 (s). HRMS (ESI-TOF) calcd for  $[\text{M}+\text{H}]^+$  202.1232, found: 202.1236.

**(±)-cis-2-phenylcyclopropyl)ethyl-N-phenoxybenzimidate (S59)**

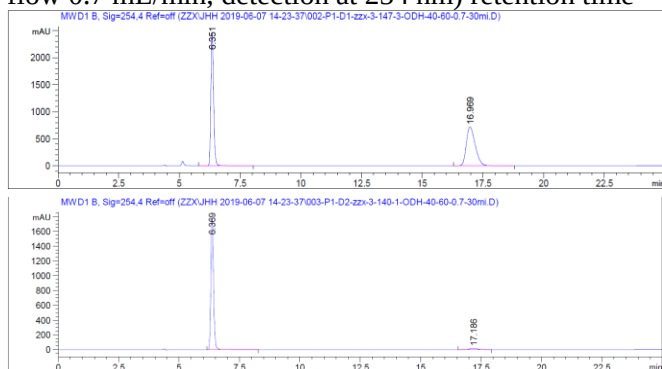
Prepared following [GP1](#).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 – 7.75 (m, 2H), 7.50 – 7.45 (m, 3H), 7.45 – 7.37 (m, 2H), 7.37 – 7.31 (m, 3H), 7.28 – 7.16 (m, 4H), 7.04 (t,  $J$  = 7.2 Hz, 1H), 4.35 (tdd,  $J$  = 13.2, 8.3, 5.0 Hz, 2H), 2.34 – 2.13 (m, 1H), 1.66 (dt,  $J$  = 13.2, 6.7 Hz, 1H), 1.50 – 1.41 (m, 1H), 1.34 (dd,  $J$  = 14.6, 6.4 Hz, 1H), 1.07 (td,  $J$  = 8.5, 5.2 Hz, 1H), 0.83 – 0.75 (m, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  159.51 (s), 157.17 (s), 138.91 (s), 130.57 (s), 129.38 (s), 129.11 (s), 128.51 (s), 128.17 (s), 127.62 (s), 126.03 (s), 122.08 (s), 114.58 (s), 72.80 (s), 29.50 (s), 20.89 (s), 15.54 (s), 9.48 (s). HRMS (ESI-TOF) calcd for  $[\text{M}+\text{Na}]^+$  380.1626, found: 380.1632.

## VI. Enantioselective, Radical C-H Amination of Alcohols

### (*R*)-2,4-diphenyl-4,5-dihydrooxazole (1)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **1** as colorless oil (17.8 mg, 80% yield, 94% e.e.).  $[\alpha]^{20}_D = +30.2$  ( $c = 0.63$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 – 8.03 (m, 2H), 7.54 – 7.49 (m, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 5.40 (dd,  $J = 10.1, 8.2$  Hz, 1H), 4.80 (dd,  $J = 10.1, 8.4$  Hz, 1H), 4.29 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.89 (s), 142.53 (s), 131.68 (s), 128.90 (s), 128.62 (s), 128.52 (s), 127.76 (s), 127.72 (s), 126.90 (s), 75.03 (s), 70.28 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  224.1070, found: 224.1065. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.4 min (major) and 17.2 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.351         | VV R | 0.1180      | 1.89679e4    | 2458.34595   | 50.9531 |
| 2      | 16.969        | BB   | 0.3937      | 1.82583e4    | 720.31042    | 49.0469 |

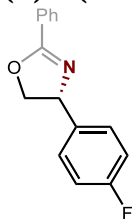
Totals : 3.72261e4 3178.65637

Signal 1: MWD1 B, Sig=254,4 Ref=off

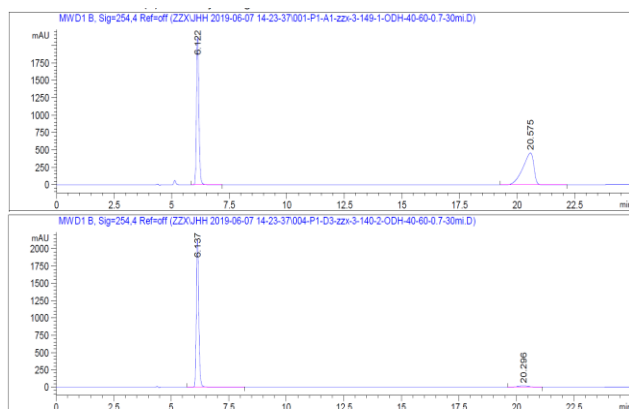
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.369         | BV R | 0.1171      | 1.35848e4    | 1773.37244   | 97.1401 |
| 2      | 17.186        | BB   | 0.3759      | 399.94699    | 16.55442     | 2.8599  |

Totals : 1.39848e4 1789.92686

### (*R*)-4-(4-fluorophenyl)-2-phenyl-4,5-dihydrooxazole (2)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **2** as white solid (23.7 mg, 98% yield, 93% e.e.);  $[\alpha]^{20}_D = +31.0$  ( $c = 0.98$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 – 8.01 (m, 2H), 7.52 (ddd,  $J = 8.6, 2.4, 1.2$  Hz, 1H), 7.48 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 7.09 – 7.00 (m, 2H), 5.38 (dd,  $J = 10.0, 8.2$  Hz, 1H), 4.79 (dd,  $J = 10.1, 8.4$  Hz, 1H), 4.23 (t,  $J = 8.3$  Hz, 1H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.95 – -115.14 (m).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.00 (s), 163.25 (s), 161.62 (s), 138.33 (d,  $J = 3.2$  Hz), 131.78 (s), 128.58 (d,  $J = 9.2$  Hz), 128.51 (d,  $J = 8.3$  Hz), 127.57 (s), 115.72 (d,  $J = 21.5$  Hz), 74.99 (s), 69.60 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  242.0976, found: 242.0978. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.1 min (major) and 20.3 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.122         | BB   | 0.1106      | 1.53942e4    | 2122.58203   | 50.1572 |
| 2      | 20.575        | BB   | 0.5020      | 1.52976e4    | 457.64206    | 49.8428 |

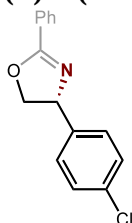
Totals : 3.06918e4 2580.22409

Signal 1: MWD1 B, Sig=254,4 Ref=off

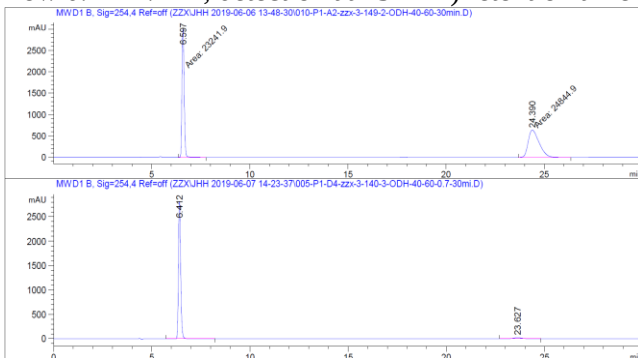
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.137         | VV R | 0.1133      | 1.55941e4    | 2131.94092   | 96.4175 |
| 2      | 20.296        | BB   | 0.4499      | 579.40979    | 20.00721     | 3.5825  |

Totals : 1.61735e4 2151.94813

### (R)-4-(4-chlorophenyl)-2-phenyl-4,5-dihydrooxazole (3)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **3** as white solid (22.3 mg, 87% yield, 94% e.e.).  $[\alpha]^{20}_D = +26.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 – 8.00 (m, 2H), 7.55 – 7.49 (m, 1H), 7.48 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.22 (m, 2H), 5.37 (dd,  $J = 10.1, 8.2$  Hz, 1H), 4.79 (dd,  $J = 10.1, 8.4$  Hz, 1H), 4.22 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.18 (s), 141.06 (s), 133.54 (s), 131.82 (s), 129.02 (s), 128.62 (s), 128.56 (s), 128.25 (s), 127.49 (s), 74.84 (s), 69.60 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  258.0680, found: 258.0675. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 23.6 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.597         | MM   | 0.1288      | 2.32419e4    | 3007.40649   | 48.3332 |
| 2      | 24.390        | MM   | 0.6471      | 2.48449e4    | 639.87775    | 51.6668 |

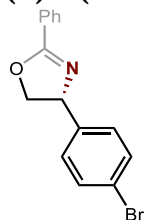
Totals : 4.80868e4 3647.28424

Signal 1: MWD1 B, Sig=254,4 Ref=off

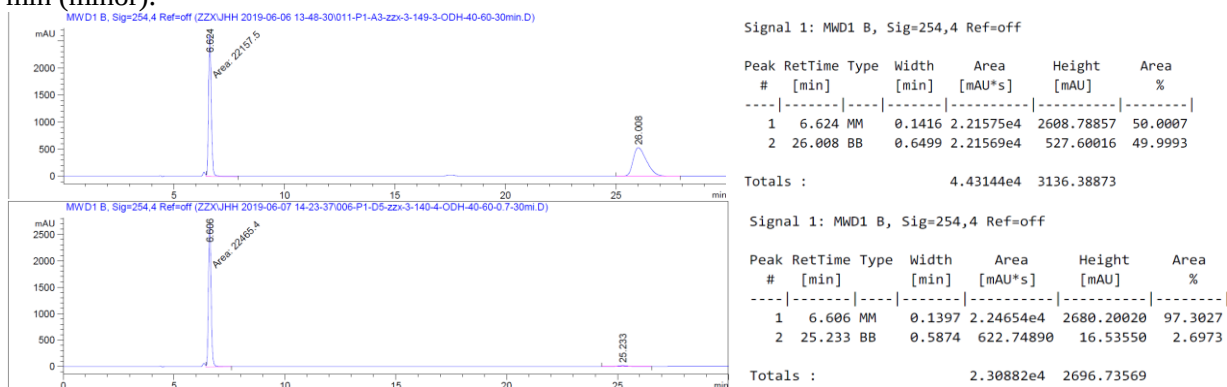
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.412         | VV R | 0.1238      | 2.26457e4    | 2817.16431   | 96.9008 |
| 2      | 23.627        | BB   | 0.5405      | 724.27490    | 20.78698     | 3.0992  |

Totals : 2.33700e4 2837.95129

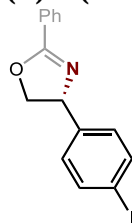
**(R)-4-(4-bromophenyl)-2-phenyl-4,5-dihydrooxazole (4)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **4** as white solid (26.9 mg, 89% yield, 95% e.e.).  $[\alpha]^{20} = +21.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (dd,  $J = 8.3, 1.3$  Hz, 2H), 7.54 – 7.50 (m, 1H), 7.50 – 7.47 (m, 2H), 7.46 – 7.41 (m, 2H), 7.21 – 7.17 (m, 2H), 5.35 (dd,  $J = 10.1, 8.2$  Hz, 1H), 4.79 (dd,  $J = 10.1, 8.4$  Hz, 1H), 4.22 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.22 (s), 141.59 (s), 131.98 (s), 131.83 (s), 128.62 (s), 128.61 (s), 128.56 (s), 127.48 (s), 121.65 (s), 74.78 (s), 69.65 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  302.0175, found: 302.0170. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 23.6 min (minor).

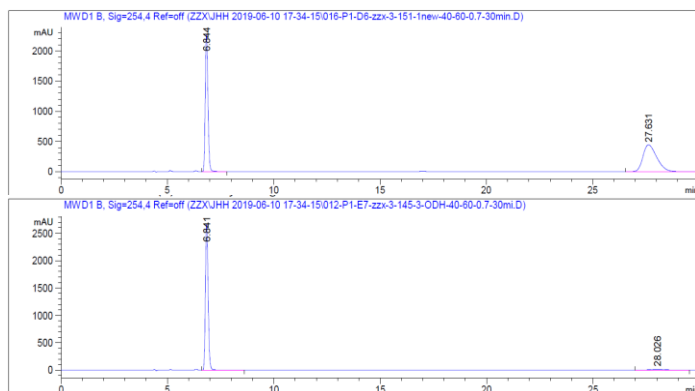


**(R)-4-(4-iodophenyl)-2-phenyl-4,5-dihydrooxazole (5)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **5** as off white solid (27.6 mg, 79% yield, 93% e.e.).  $[\alpha]^{20} = +16.2$  ( $c = 1.2$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 8.00 (m, 2H), 7.68 (d,  $J = 8.3$  Hz, 2H), 7.55 – 7.48 (m, 1H), 7.44 (t,  $J = 7.7$  Hz, 2H), 7.06 (d,  $J = 8.3$  Hz, 2H), 5.34 (dd,  $J = 10.0, 8.3$  Hz, 1H), 4.79 (dd,  $J = 10.1, 8.5$  Hz, 1H), 4.21 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.22 (s), 142.26 (s), 137.94 (s), 131.83 (s), 128.86 (s), 128.62 (s), 128.56 (s), 127.47 (s), 93.19 (s), 74.75 (s), 69.72 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  350.0036, found: 350.0022. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.8 min (major) and 28.0 min (minor).





Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.844         | VB   | 0.1321      | 1.95473e4    | 2277.75317   | 49.5497 |
| 2      | 27.631        | BBA  | 0.6923      | 1.99026e4    | 444.57852    | 50.4503 |

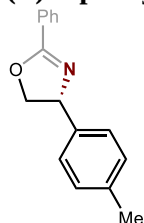
Totals : 3.94499e4 2722.33170

Signal 1: MWD1 B, Sig=254,4 Ref=off

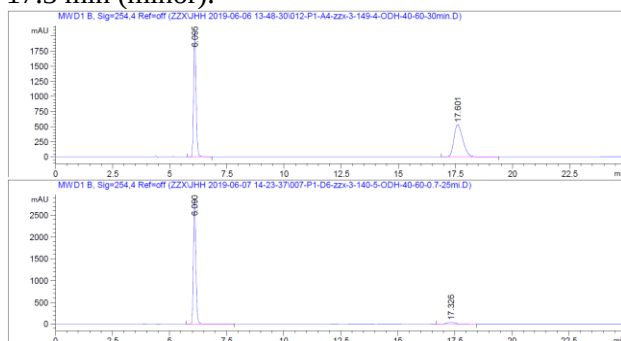
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.841         | BB   | 0.1339      | 2.33520e4    | 2674.28198   | 96.4062 |
| 2      | 28.026        | BB   | 0.6746      | 870.51117    | 19.89026     | 3.5938  |

Totals : 2.42225e4 2694.17225

### (R)-2-phenyl-4-(p-tolyl)-4,5-dihydrooxazole (6)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **6** as colorless oil (21.2 mg, 89% yield, 91% e.e.).  $[\alpha]^{20} = +31.3$  ( $c = 0.9$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 7.6$  Hz, 2H), 7.51 (t,  $J = 7.4$  Hz, 1H), 7.44 (t,  $J = 7.5$  Hz, 2H), 7.21 (d,  $J = 8.1$  Hz, 2H), 7.17 (d,  $J = 7.9$  Hz, 2H), 5.37 (t,  $J = 8.9$  Hz, 1H), 4.78 (dd,  $J = 9.9, 8.4$  Hz, 1H), 4.27 (t,  $J = 8.2$  Hz, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.70 (s), 139.54 (s), 137.40 (s), 131.61 (s), 129.54 (s), 128.60 (s), 128.49 (s), 127.77 (s), 126.79 (s), 75.07 (s), 70.02 (s), 21.23 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  238.1226, found: 238.1228. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.1 min (major) and 17.3 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.095         | BV R | 0.1126      | 1.53308e4    | 2065.51587   | 51.5671 |
| 2      | 17.601        | BB   | 0.4193      | 1.43990e4    | 532.74329    | 48.4329 |

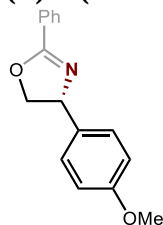
Totals : 2.97298e4 2598.25916

Signal 1: MWD1 B, Sig=254,4 Ref=off

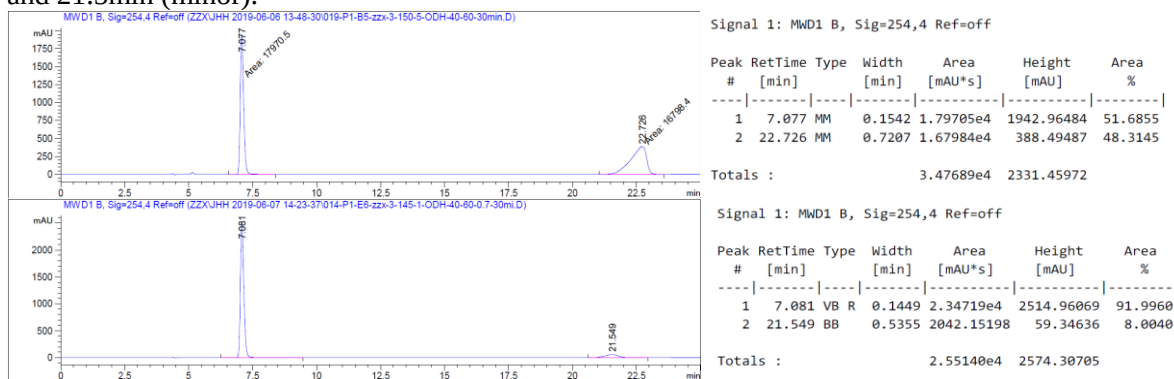
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.090         | VV R | 0.1196      | 2.17744e4    | 2833.34668   | 95.3901 |
| 2      | 17.326        | BB   | 0.3999      | 1052.29211   | 40.93980     | 4.6099  |

Totals : 2.28267e4 2874.28648

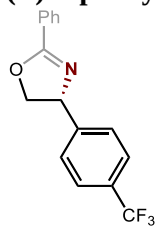
**(R)-4-(4-methoxyphenyl)-2-phenyl-4,5-dihydrooxazole (7)**



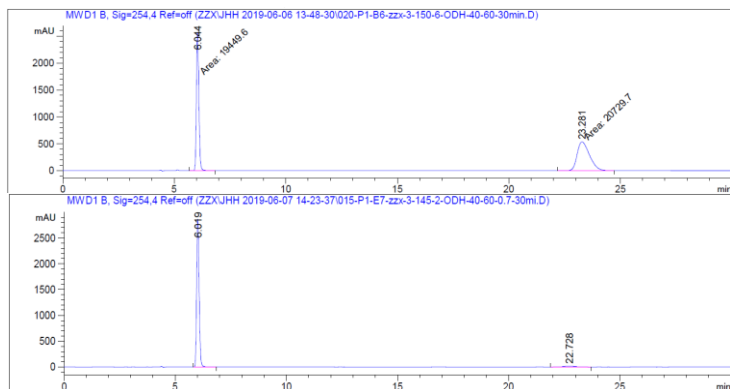
The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **7** as colorless oil (21.3 mg, 80% yield, 84% e.e.).  $[\alpha]^{20}_D = +42.1$  ( $c = 1.1$ ,  $\text{CHCl}_3$ ).  $R_f = 0.35$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 – 8.01 (m, 2H), 7.51 (t,  $J = 7.4$  Hz, 1H), 7.44 (t,  $J = 7.6$  Hz, 2H), 7.25 – 7.21 (m, 2H), 6.93 – 6.86 (m, 2H), 5.35 (dd,  $J = 9.9, 8.2$  Hz, 1H), 4.77 (dd,  $J = 10.0, 8.4$  Hz, 1H), 4.26 (t,  $J = 8.2$  Hz, 1H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.63 (s), 159.26 (s), 134.64 (s), 131.65 (s), 128.57 (d,  $J = 10.4$  Hz), 128.49 (s), 128.03 (s), 127.71 (s), 114.28 (s), 75.10 (s), 69.68 (s), 55.43 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  254.1176, found: 254.1180. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.1 min (major) and 21.5min (minor).



**(R)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (8)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **8** as white solid (20.4 mg, 70% yield, 95% e.e.).  $[\alpha]^{20}_D = +11.6$  ( $c = 0.7$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 – 8.02 (m, 2H), 7.62 (d,  $J = 8.1$  Hz, 2H), 7.56 – 7.50 (m, 1H), 7.49 – 7.41 (m, 4H), 5.46 (dd,  $J = 10.0, 8.4$  Hz, 1H), 4.84 (dd,  $J = 10.2, 8.5$  Hz, 1H), 4.25 (t,  $J = 8.3$  Hz, 1H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.50 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.50 (s), 146.53 (s), 131.94 (s), 130.07 (q,  $J = 32.4$  Hz), 128.66 (s), 128.61 (s), 127.41 (s), 127.25 (s), 125.88 (q,  $J = 3.7$  Hz), 124.26 (q,  $J = 272.0$  Hz), 74.67 (s), 69.81 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  292.0944, found: 292.0942. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.1 min (major) and 22.7 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.044         | MM   | 0.1260      | 1.94496e4    | 2572.87939   | 48.4070 |
| 2      | 23.281        | MM   | 0.6417      | 2.07297e4    | 538.41278    | 51.5930 |

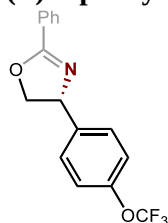
Totals : 4.01793e4 3111.29218

Signal 1: MWD1 B, Sig=254,4 Ref=off

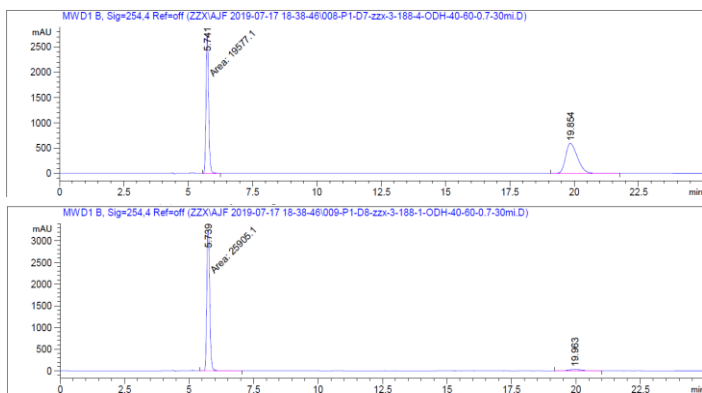
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.019         | BB   | 0.1187      | 2.17356e4    | 2858.75146   | 97.4265 |
| 2      | 22.728        | BB   | 0.5400      | 574.13104    | 16.25970     | 2.5735  |

Totals : 2.23098e4 2875.01117

## (R)-2-phenyl-4-(4-(trifluoromethoxy)phenyl)-4,5-dihydrooxazole (9)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **9** as white solid (29.0 mg, 94% yield, 92% e.e.).  $[\alpha]^{20}_D = +23.0$  (c = 1.1, CHCl<sub>3</sub>).  $R_f = 0.5$  (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (dd,  $J = 8.3, 1.2$  Hz, 2H), 7.52 (ddd,  $J = 6.9, 2.5, 1.2$  Hz, 1H), 7.48 – 7.42 (m, 2H), 7.34 (dd,  $J = 9.0, 2.3$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 5.41 (dd,  $J = 10.0, 8.2$  Hz, 1H), 4.81 (dd,  $J = 10.1, 8.5$  Hz, 1H), 4.25 (t,  $J = 8.3$  Hz, 1H). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -57.90 (s). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  165.25 (s), 148.81 (d,  $J = 1.7$  Hz), 141.29 (s), 131.87 (s), 128.64 (s), 128.58 (s), 128.34 (s), 127.47 (s), 121.46 (s), 120.61 (q,  $J = 257.1$  Hz), 74.84 (s), 69.57 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+H]^+$  308.0893, found: 308.0889. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.7 min (major) and 20.0 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

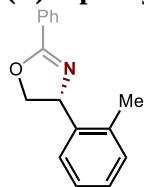
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.741         | MM   | 0.1183      | 1.95771e4    | 2758.96924   | 51.0646 |
| 2      | 19.854        | BB   | 0.4925      | 1.87607e4    | 590.70105    | 48.9354 |

Totals : 3.83378e4 3349.67029

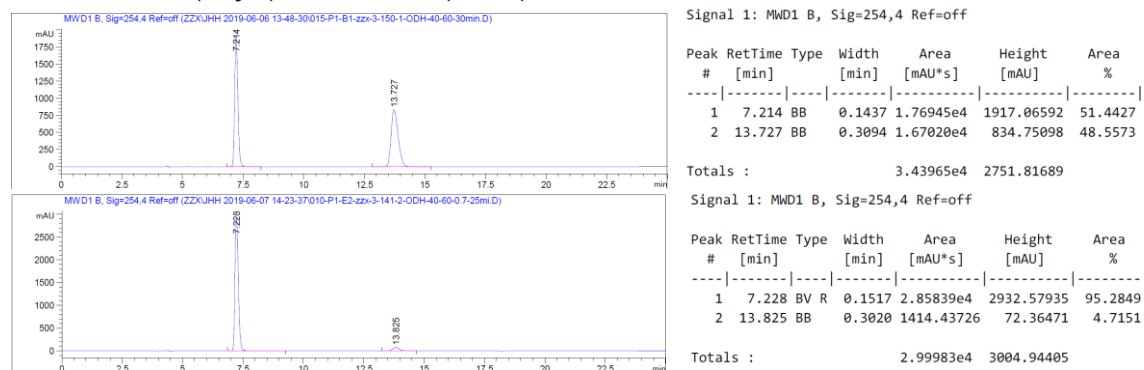
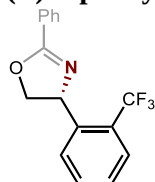
Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.739         | MM   | 0.1332      | 2.59051e4    | 3241.69141   | 96.1449 |
| 2      | 19.963        | BB   | 0.4727      | 1038.70300   | 34.16099     | 3.8551  |

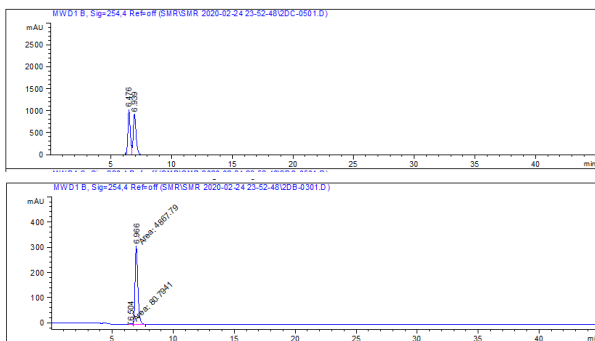
Totals : 2.69438e4 3275.85239

**(R)-2-phenyl-4-(o-tolyl)-4,5-dihydrooxazole (10)**

The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **10** as light-yellow oil (22.6 mg, 95% yield, 91% e.e.).  $[\alpha]_D^{20} = -40.2$  ( $c = 0.8$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 – 8.05 (m, 2H), 7.52 (dd,  $J = 10.6, 4.2$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 7.36 – 7.30 (m, 1H), 7.24 – 7.16 (m, 3H), 5.61 (dd,  $J = 9.8, 8.8$  Hz, 1H), 4.85 (dd,  $J = 10.2, 8.1$  Hz, 1H), 4.15 (t,  $J = 8.3$  Hz, 1H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.96 (s), 140.96 (s), 134.73 (s), 131.64 (s), 130.39 (s), 128.57 (s), 128.53 (s), 127.80 (s), 127.45 (s), 126.63 (s), 126.25 (s), 74.33 (s), 67.11 (s), 19.66 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  238.1226, found: 238.1230. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.2 min (major) and 13.8min (minor).

**(R)-2-phenyl-4-(2-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (11)**

The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **11** as colorless oil (22.6 mg, 81% yield, 97% e.e.).  $[\alpha]_D^{20} = -72.5$  ( $c = 0.8$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (dd,  $J = 5.1, 3.3$  Hz, 1H), 7.68 (d,  $J = 7.8$  Hz, 1H), 7.58 – 7.52 (m, 1H), 7.51 (d,  $J = 7.7$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 1H), 7.39 (t,  $J = 7.6$  Hz, 1H), 5.83 (t,  $J = 9.2$  Hz, 1H), 4.83 (t,  $J = 9.2$  Hz, 1H), 4.11 (t,  $J = 8.4$  Hz, 1H).  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -58.96 (s).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  166.00 (s), 141.23 (s), 132.70 (s), 131.91 (s), 128.65 (s), 128.62 (s), 128.07 (s), 127.60 (s), 127.47 (s), 127.42 (s), 125.82 (q,  $J = 5.7$  Hz), 124.52 (q,  $J = 272.9$  Hz), 75.32 (d,  $J = 1.6$  Hz), 66.13 (d,  $J = 1.7$  Hz). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  292.0944, found: 292.0943. HPLC (CHIRALCEL IC, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 97.5/2.5, flow 0.5 mL/min, detection at 254 nm) retention time = 7.0 min (major) and 6.5min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

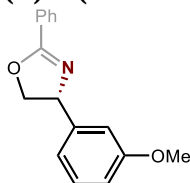
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.476         | BV   | 0.2095      | 1.43813e4    | 1039.05750   | 48.8334 |
| 2      | 6.939         | VB   | 0.2395      | 1.50684e4    | 937.62451    | 51.1666 |

Signal 1: MWD1 B, Sig=254,4 Ref=off

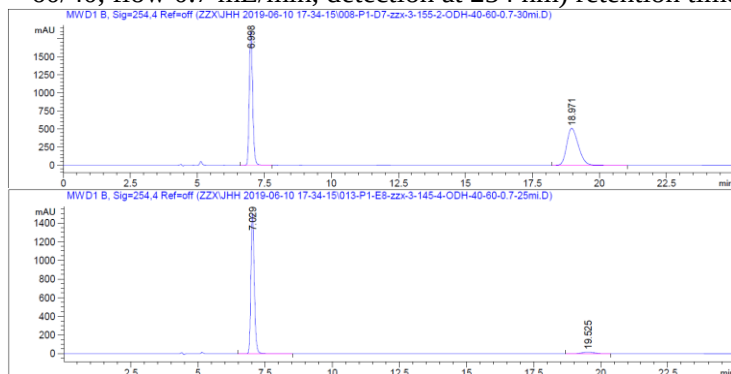
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.504         | MM   | 0.2520      | 80.79411     | 5.34289      | 1.6327  |
| 2      | 6.966         | MM   | 0.2610      | 4867.78613   | 310.80933    | 98.3673 |

Totals : 4948.58024 316.15222

## (R)-4-(3-methoxyphenyl)-2-phenyl-4,5-dihydrooxazole (12)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **12** as light-yellow oil (20.1 mg, 79% yield, 93% e.e.).  $[\alpha]^{20}_D = +13.9$  (c = 0.8, CHCl<sub>3</sub>).  $R_f = 0.4$  (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (dd,  $J = 5.2, 3.3$  Hz, 2H), 7.56 – 7.52 (m, 1H), 7.49 – 7.44 (m, 2H), 7.32 – 7.27 (m, 1H), 6.93 (d,  $J = 7.6$  Hz, 1H), 6.91 – 6.88 (m, 1H), 6.86 (ddd,  $J = 8.2, 2.6, 0.8$  Hz, 1H), 5.40 (dd,  $J = 10.1, 8.2$  Hz, 1H), 4.82 (dd,  $J = 10.1, 8.4$  Hz, 1H), 4.30 (t,  $J = 8.3$  Hz, 1H), 3.82 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  164.95 (s), 160.11 (s), 144.15 (s), 131.68 (s), 129.94 (s), 128.62 (s), 128.50 (s), 127.69 (s), 119.18 (s), 113.14 (s), 112.53 (s), 74.91 (s), 70.17 (s), 55.38 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+H]^+$  254.1176, found: 254.1178. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.0 min (major) and 19.5min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.998         | BB   | 0.1351      | 1.63067e4    | 1844.36023   | 51.7283 |
| 2      | 18.971        | BB   | 0.4640      | 1.52171e4    | 510.09470    | 48.2717 |

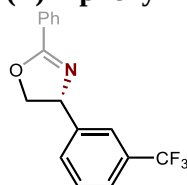
Totals : 3.15238e4 2354.45493

Signal 1: MWD1 B, Sig=254,4 Ref=off

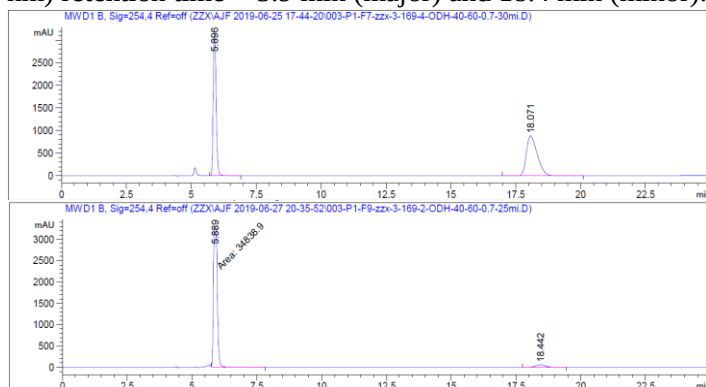
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.029         | BB   | 0.1363      | 1.34429e4    | 1504.06396   | 96.2603 |
| 2      | 19.525        | BB   | 0.4760      | 522.26007    | 17.21135     | 3.7397  |

Totals : 1.39651e4 1521.27532

**(R)-2-phenyl-4-(3-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (13)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **13** as colorless oil (24.8 mg, 85% yield, 91% e.e.).  $[\alpha]^{20} = +10.8$  (c = 0.6, CHCl<sub>3</sub>); R<sub>f</sub> = 0.5 (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.09 – 8.01 (m, 2H), 7.62 – 7.42 (m, 7H), 5.46 (dd, J = 10.1, 8.4 Hz, 1H), 4.85 (dd, J = 10.2, 8.5 Hz, 1H), 4.25 (t, J = 8.4 Hz, 1H). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -62.58 (s). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 165.54 (s), 143.54 (s), 131.94 (s), 131.25 (q, J = 32.3 Hz), 130.32 (s), 129.42 (s), 128.69 (s), 128.61 (s), 127.40 (s), 124.67 (q, J = 3.8 Hz), 124.20 (q, J = 272.3 Hz), 123.78 (q, J = 3.7 Hz), 74.74 (s), 69.86 (s). HRMS (ESI-TOF) *m/z* calcd for [M+H]<sup>+</sup> 292.0944, found: 292.0939. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.9 min (major) and 18.4 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.896         | VB   | 0.1242      | 2.47665e4    | 3134.37671   | 49.0380 |
| 2      | 18.071        | BB   | 0.4495      | 2.57382e4    | 884.45087    | 50.9620 |

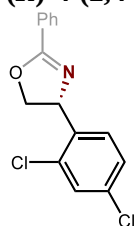
Totals : 5.05046e4 4018.82758

Signal 1: MWD1 B, Sig=254,4 Ref=off

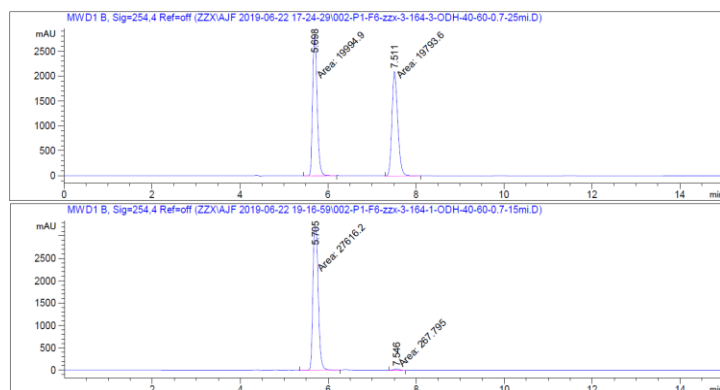
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.889         | MM   | 0.1759      | 3.48389e4    | 3301.81152   | 95.6240 |
| 2      | 18.442        | BB   | 0.4306      | 1594.32922   | 57.65599     | 4.3760  |

Totals : 3.64333e4 3359.46751

**(R)-4-(2,4-dichlorophenyl)-2-phenyl-4,5-dihydrooxazole (14)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **14** as colorless oil (25.7 mg, 88% yield, 98% e.e.).  $[\alpha]^{20} = -142.2$  (c = 0.9, CHCl<sub>3</sub>). R<sub>f</sub> = 0.5 (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.06 (dd, J = 8.2, 1.1 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.37 (m, 2H), 7.28 – 7.22 (m, 1H), 5.68 (dt, J = 12.0, 6.1 Hz, 1H), 4.98 – 4.90 (m, 1H), 4.14 – 4.05 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 165.88 (s), 139.47 (s), 133.88 (s), 132.99 (s), 131.93 (s), 129.18 (s), 128.92 (s), 128.61 (s), 128.60 (s), 127.54 (s), 127.48 (s), 74.09 (s), 66.91 (s). HRMS (ESI-TOF) *m/z* calcd for [M+H]<sup>+</sup> 292.0290, found: 292.0288. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.7 min (major) and 7.5 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.698         | MM   | 0.1182      | 1.99949e4    | 2819.32544   | 50.2529 |
| 2      | 7.511         | MM   | 0.1567      | 1.97936e4    | 2105.10864   | 49.7471 |

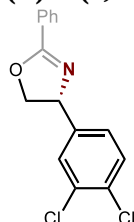
Totals : 3.97885e4 4924.43408

Signal 1: MWD1 B, Sig=254,4 Ref=off

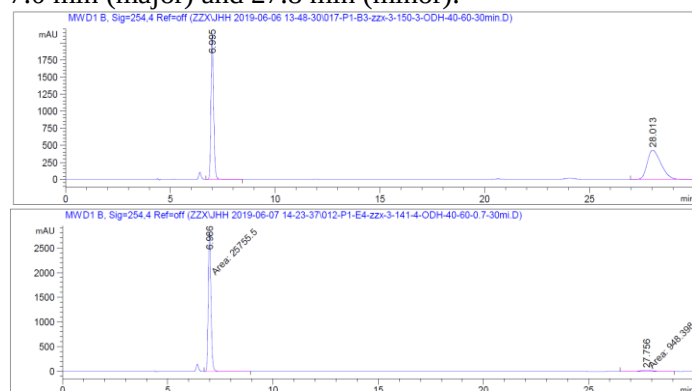
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.705         | MM   | 0.1445      | 2.76162e4    | 3184.60791   | 99.0396 |
| 2      | 7.546         | MM   | 0.1515      | 267.79507    | 29.46397     | 0.9604  |

Totals : 2.78840e4 3214.07188

### (R)-4-(3,4-dichlorophenyl)-2-phenyl-4,5-dihydrooxazole (15)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **15** as colorless oil (25.4 mg, 87% yield, 93% e.e.).  $[\alpha]^{20} = +10.3$  ( $c = 1.2$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 – 8.00 (m, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.43 (m, 2H), 7.43 (s, 1H), 7.42 – 7.40 (m, 1H), 7.15 (dd,  $J = 8.3, 2.1$  Hz, 1H), 5.35 (dd,  $J = 10.1, 8.2$  Hz, 1H), 4.80 (dd,  $J = 10.2, 8.5$  Hz, 1H), 4.21 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.57 (s), 142.80 (s), 132.99 (s), 131.98 (s), 131.77 (s), 130.84 (s), 128.90 (s), 128.67 (s), 128.61 (s), 127.28 (s), 126.24 (s), 74.59 (s), 69.17 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  292.0290, found: 292.0293. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.0 min (major) and 27.8 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.995         | VV R | 0.1373      | 1.85921e4    | 2099.09326   | 48.8745 |
| 2      | 28.013        | BBA  | 0.7032      | 1.94484e4    | 428.77771    | 51.1255 |

Totals : 3.80406e4 2527.87097

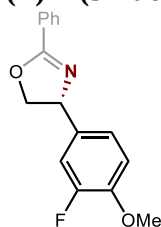
Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.986         | MM   | 0.1524      | 2.57555e4    | 2817.45313   | 96.4485 |
| 2      | 27.756        | MM   | 0.7535      | 948.39771    | 20.97867     | 3.5515  |

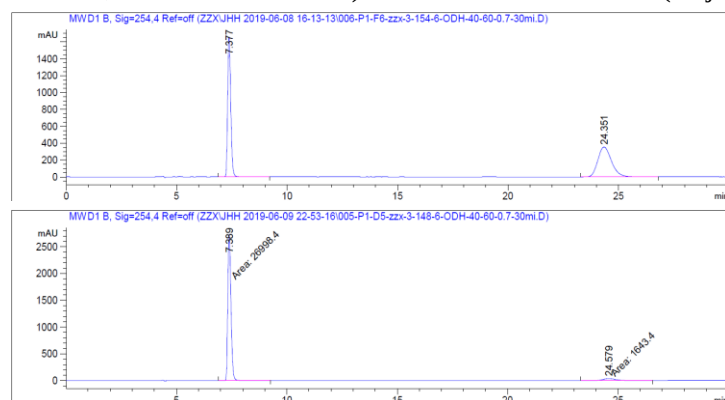
Totals : 2.67039e4 2838.43180



**(R)-4-(3-fluoro-4-methoxyphenyl)-2-phenyl-4,5-dihydrooxazole (16)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **16** as white solid (24.5 mg, 90% yield, 89% e.e.).  $[\alpha]^{20} = +32.2$  (c = 1.0, CHCl<sub>3</sub>).  $R_f = 0.35$  (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 – 8.00 (m, 2H), 7.55 – 7.49 (m, 1H), 7.47 – 7.41 (m, 2H), 7.09 – 7.00 (m, 2H), 6.93 (dd,  $J = 10.5, 6.3$  Hz, 1H), 5.32 (dt,  $J = 17.6, 8.8$  Hz, 1H), 4.76 (dd,  $J = 10.1, 8.4$  Hz, 1H), 4.22 (t,  $J = 8.2$  Hz, 1H), 3.87 (s, 3H). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -134.42 (dd,  $J = 11.6, 8.7$  Hz). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  165.00 (s), 152.69 (d,  $J = 246.4$  Hz), 147.22 (d,  $J = 10.8$  Hz), 135.67 (d,  $J = 5.6$  Hz), 131.77 (s), 128.60 (s), 128.53 (s), 127.53 (s), 122.58 (d,  $J = 3.6$  Hz), 114.65 (d,  $J = 18.8$  Hz), 113.71 (d,  $J = 1.9$  Hz), 74.86 (s), 69.37 (d,  $J = 1.0$  Hz), 56.49 (s). HRMS (ESI-TOF)  $m/z$  calcd for [M+H]<sup>+</sup> 272.1081, found: 272.1086. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.4 min (major) and 24.6 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.377         | VV R | 0.1485      | 1.60161e4    | 1661.53918   | 51.1962 |
| 2      | 24.351        | BB   | 0.6661      | 1.52676e4    | 354.72174    | 48.8038 |

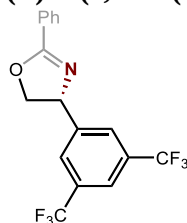
Totals : 3.12837e4 2016.26093

Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.389         | MM   | 0.1653      | 2.69984e4    | 2721.34863   | 94.2622 |
| 2      | 24.579        | MM   | 0.7591      | 1643.39893   | 36.07991     | 5.7378  |

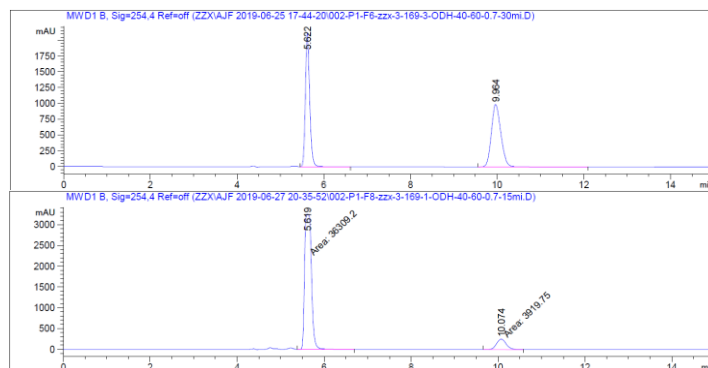
Totals : 2.86418e4 2757.42854

**(R)-4-(3,5-bis(trifluoromethyl)phenyl)-2-phenyl-4,5-dihydrooxazole (17)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **17** as colorless oil (28.4 mg, 79% yield, 80% e.e.).  $[\alpha]^{20} = -3.3$  (c = 0.9, CHCl<sub>3</sub>).  $R_f = 0.35$  (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 – 8.03 (m, 2H), 7.83 (s, 1H), 7.79 (s, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.44 (m, 2H), 5.54 (dd,  $J = 10.2, 8.6$  Hz, 1H), 4.90 (dd,  $J = 10.3, 8.6$  Hz, 1H), 4.25 (t,  $J = 8.6$  Hz, 1H). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -62.83 (s). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  166.17 (s), 145.13 (s), 132.25 (q,  $J = 33.3$  Hz), 132.20 (s), 128.77 (s), 128.69 (s), 127.23 (d,  $J = 2.6$  Hz), 127.08 (s), 126.35 – 120.29 (m), 121.86 (q,  $J = 3.8$  Hz), 121.83 (q,  $J = 3.8$  Hz), 74.39 (s), 69.48 (s). HRMS (ESI-TOF)  $m/z$  calcd for [M+H]<sup>+</sup> 360.0818, found: 360.0816. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.6 min (major) and 10.1 min (minor).





Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.622         | BB   | 0.1105      | 1.49890e4    | 2120.51099   | 49.8577 |
| 2      | 9.964         | BB   | 0.2380      | 1.50746e4    | 988.01202    | 50.1423 |

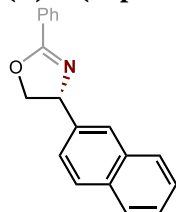
Totals : 3.00636e4 3108.52301

Signal 1: MWD1 B, Sig=254,4 Ref=off

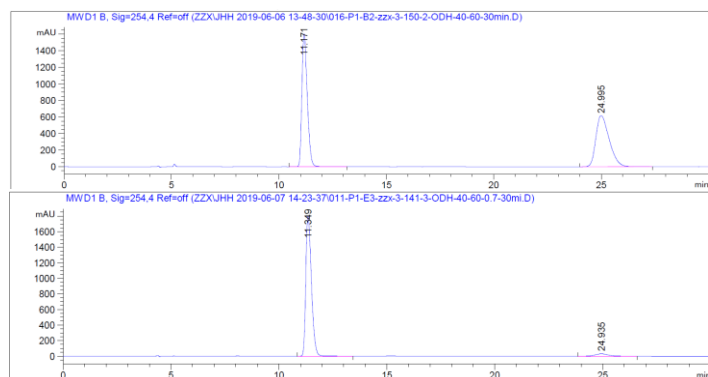
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.619         | MM   | 0.1858      | 3.63092e4    | 3256.20972   | 90.2564 |
| 2      | 10.074        | MM   | 0.2609      | 3919.75415   | 250.41586    | 9.7436  |

Totals : 4.02289e4 3506.62558

### (R)-4-(naphthalen-2-yl)-2-phenyl-4,5-dihydrooxazole (18)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **18** as yellow oil (25.2 mg in 92% yield, 93% e.e.).  $[\alpha]^{20}_D = +36.3$  (c = 0.9, CHCl<sub>3</sub>).  $R_f = 0.5$  (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (dd,  $J = 8.3, 1.2$  Hz, 2H), 7.88 – 7.78 (m, 4H), 7.56 – 7.51 (m, 1H), 7.50 – 7.45 (m, 4H), 7.41 (dd,  $J = 8.5, 1.7$  Hz, 1H), 5.58 (dd,  $J = 10.0, 8.3$  Hz, 1H), 4.87 (dd,  $J = 10.1, 8.4$  Hz, 1H), 4.36 (t,  $J = 8.3$  Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  165.05 (s), 139.79 (s), 133.56 (s), 133.08 (s), 131.74 (s), 128.88 (s), 128.68 (s), 128.56 (s), 128.06 (s), 127.82 (s), 127.72 (s), 126.35 (s), 126.02 (s), 125.70 (s), 124.77 (s), 74.90 (s), 70.40 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+H]^+$  274.1226, found: 274.1224. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 11.3 min (major) and 24.9 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.171        | BB   | 0.2690      | 2.78874e4    | 1602.53662   | 51.2126 |
| 2      | 24.995        | BB   | 0.6637      | 2.65668e4    | 617.83759    | 48.7874 |

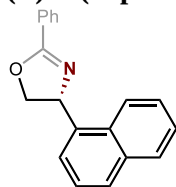
Totals : 5.44542e4 2220.37421

Signal 1: MWD1 B, Sig=254,4 Ref=off

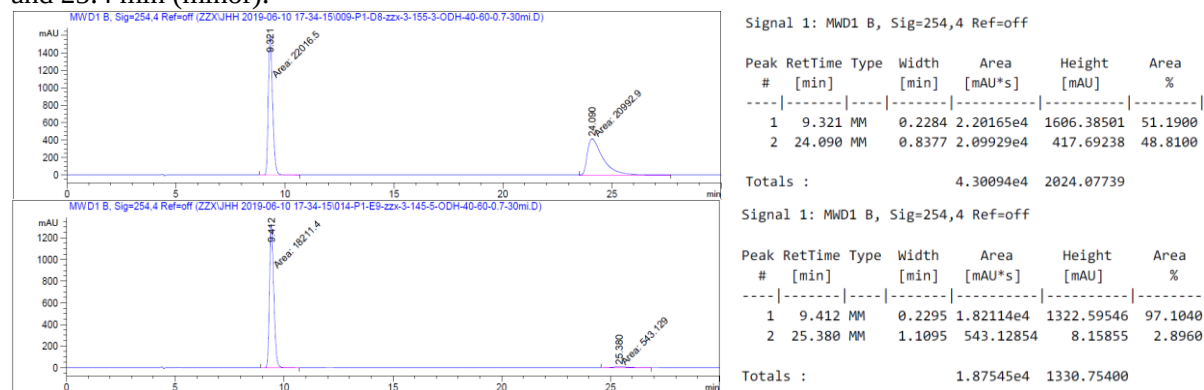
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.349        | BB   | 0.2782      | 3.24965e4    | 1804.06079   | 96.4417 |
| 2      | 24.935        | BB   | 0.6400      | 1198.98596   | 28.90377     | 3.5583  |

Totals : 3.36954e4 1832.96456

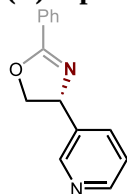
**(R)-4-(naphthalen-1-yl)-2-phenyl-4,5-dihydrooxazole (19)**



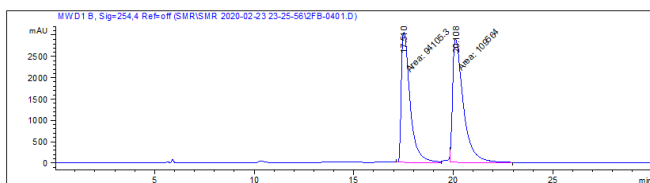
The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **19** as yellow oil (27.1 mg, 99% yield, 94% e.e.).  $[\alpha]^{20} = -251.5$  ( $c = 0.9$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (dd,  $J = 8.2, 1.1$  Hz, 2H), 7.92 (d,  $J = 7.9$  Hz, 1H), 7.87 (d,  $J = 8.2$  Hz, 1H), 7.81 (d,  $J = 8.2$  Hz, 1H), 7.61 (d,  $J = 7.1$  Hz, 1H), 7.59 – 7.51 (m, 3H), 7.48 (dt,  $J = 7.8, 6.8$  Hz, 3H), 6.14 (dd,  $J = 10.1, 8.5$  Hz, 1H), 5.07 (dd,  $J = 10.4, 8.2$  Hz, 1H), 4.23 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.12 (s), 138.75 (s), 134.02 (s), 131.73 (s), 130.77 (s), 129.21 (s), 128.64 (s), 128.58 (s), 128.01 (s), 127.84 (s), 126.44 (s), 125.91 (s), 125.76 (s), 123.61 (s), 122.91 (s), 74.65 (s), 66.83 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  274.1226, found: 274.1229. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 9.4 min (major) and 25.4 min (minor).



**(R)-2-phenyl-4-(pyridin-3-yl)-4,5-dihydrooxazole (20)**



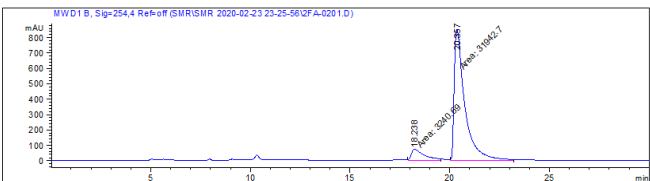
The reaction was conducted on a 0.05 mmol scale according to the [GP3](#) and yielding 65% by  $^1\text{H}$ NMR using 1,2-dichloroethane as an internal standard. The crude mixture was purified by column chromatography affording oxazoline **20** as an off-white solid (12 mg, 82% e.e.).  $R_f = 0.4$  (dichloromethane : isopropanol = 9:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 – 8.54 (m, 1H), 8.10 – 8.00 (m, 1H), 7.65 (d,  $J = 7.9$  Hz, 1H), 7.53 (t,  $J = 7.4$  Hz, 1H), 7.45 (t,  $J = 7.7$  Hz, 1H), 7.31 (dd,  $J = 7.7, 4.8$  Hz, 1H), 5.44 (dd,  $J = 10.0, 8.2$  Hz, 1H), 4.85 (dd,  $J = 10.1, 8.6$  Hz, 1H), 4.27 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.51 (s), 149.00 (s), 148.40 (s), 134.48 (s), 131.86 (s), 128.54 (s), 128.49 (s), 127.36 (s), 127.15 (s), 123.83 (s), 74.50 (s), 67.77 (s). HRMS (ESI) calcd. For  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  255.1016, found: 255.1028. HPLC (CHIRALCEL IC, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 18.2 min (minor) and 20.4 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 17.510        | MM   | 0.5141      | 9.41053e4    | 3050.61011   | 46.2050 |
| 2      | 20.108        | MM   | 0.6338      | 1.09564e5    | 2880.98706   | 53.7950 |

Totals : 2.03669e5 5931.59717

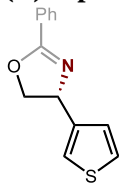


Signal 1: MWD1 B, Sig=254,4 Ref=off

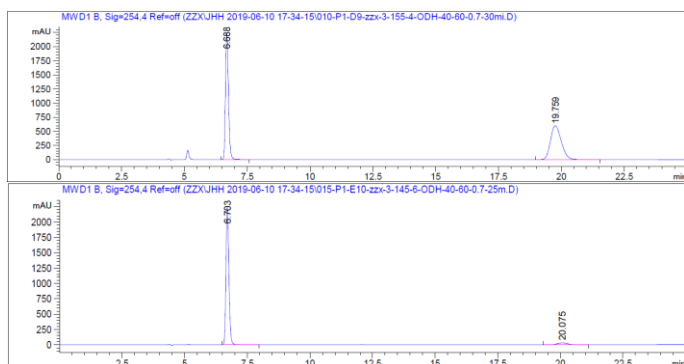
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 18.238        | MM   | 0.7627      | 3240.68994   | 70.81785     | 9.2109  |
| 2      | 20.357        | MM   | 0.6244      | 3.19427e4    | 852.58484    | 90.7891 |

Totals : 3.51834e4 923.40269

## (R)-2-phenyl-4-(thiophen-3-yl)-4,5-dihydrooxazole (21)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **21** as yellow solid (19.1 mg, 83% yield, 90% e.e.).  $[\alpha]^{20}_D = +56.0$  (c = 0.7, CHCl<sub>3</sub>).  $R_f$  = 0.5 (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 – 7.99 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 (t,  $J$  = 7.6 Hz, 2H), 7.33 (dd,  $J$  = 5.0, 3.0 Hz, 1H), 7.23 (d,  $J$  = 2.4 Hz, 1H), 7.04 (dd,  $J$  = 5.0, 1.1 Hz, 1H), 5.47 (dd,  $J$  = 9.7, 8.2 Hz, 1H), 4.74 (dd,  $J$  = 9.9, 8.3 Hz, 1H), 4.32 (t,  $J$  = 8.1 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  164.71 (s), 143.32 (s), 131.68 (s), 128.58 (s), 128.50 (s), 127.68 (s), 126.74 (s), 126.14 (s), 121.59 (s), 74.15 (s), 66.12 (s). HRMS (ESI-TOF)  $m/z$  calcd for [M+H]<sup>+</sup> 230.0634, found: 230.0640. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.7 min (major) and 20.1 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.688         | BB   | 0.1276      | 1.83624e4    | 2239.88159   | 50.8676 |
| 2      | 19.759        | BB   | 0.4611      | 1.77360e4    | 599.51001    | 49.1324 |

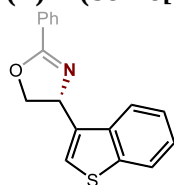
Totals : 3.60985e4 2839.39160

Signal 1: MWD1 B, Sig=254,4 Ref=off

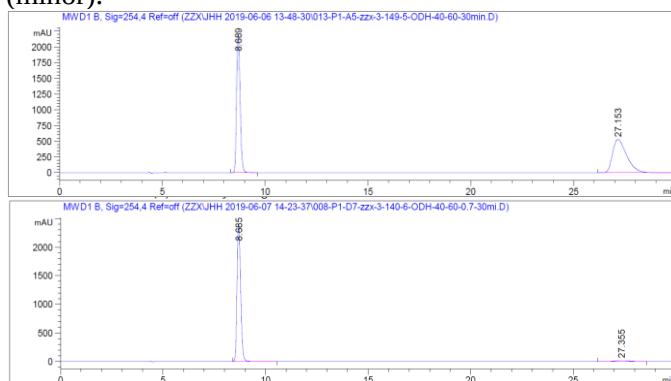
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.703         | BB   | 0.1255      | 1.83654e4    | 2244.23218   | 95.0644 |
| 2      | 20.075        | BB   | 0.4526      | 953.49457    | 32.66257     | 4.9356  |

Totals : 1.93189e4 2276.89474

**(R)-4-(benzo[b]thiophen-3-yl)-2-phenyl-4,5-dihydrooxazole (22)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **22** as yellow oil (25.8 mg in 92% yield, 95% e.e.).  $[\alpha]^{20}_D = -95.4$  ( $c = 0.9$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1). Prepared following general procedure 3.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (dt,  $J = 8.4, 1.6$  Hz, 2H), 7.91 – 7.86 (m, 1H), 7.72 – 7.68 (m, 1H), 7.55 – 7.51 (m, 1H), 7.49 – 7.44 (m, 2H), 7.42 – 7.35 (m, 3H), 5.75 (ddd,  $J = 10.1, 8.1, 0.8$  Hz, 1H), 4.89 (dd,  $J = 10.2, 8.3$  Hz, 1H), 4.40 (t,  $J = 8.2$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.18 (s), 141.35 (s), 137.35 (s), 137.03 (s), 131.80 (s), 128.65 (s), 128.56 (s), 127.61 (s), 124.59 (s), 124.33 (s), 123.30 (s), 123.17 (s), 121.58 (s), 73.09 (s), 65.48 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  280.0791, found: 280.0787. HPLC (CHIRALCEL OD-H, 0.46\*25 cm,  $5\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 8.7 min (major) and 27.4 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.689         | BB   | 0.1835      | 2.62553e4    | 2195.23096   | 50.8943 |
| 2      | 27.153        | BB   | 0.7318      | 2.53326e4    | 529.86591    | 49.1057 |

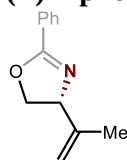
Totals : 5.15879e4 2725.09686

Signal 1: MWD1 B, Sig=254,4 Ref=off

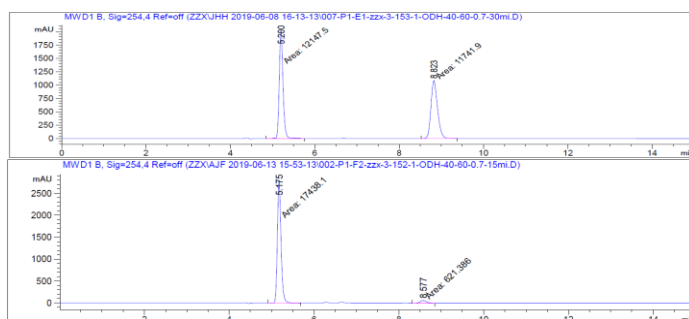
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.685         | BB   | 0.1864      | 2.88912e4    | 2400.40479   | 97.3497 |
| 2      | 27.355        | BB   | 0.7099      | 786.53906    | 16.68736     | 2.6503  |

Totals : 2.96777e4 2417.09214

**(R)-2-phenyl-4-(prop-1-en-2-yl)-4,5-dihydrooxazole (23)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **23** as yellow oil (15.4 mg, 82% yield, 94% e.e.).  $[\alpha]^{20}_D = +56.8$  ( $c = 0.4$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.96 (m, 2H), 7.52 – 7.46 (m, 1H), 7.44 – 7.39 (m, 2H), 5.06 – 4.99 (m, 1H), 4.94 – 4.87 (m, 1H), 4.82 (dd,  $J = 9.9, 8.0$  Hz, 1H), 4.53 (dd,  $J = 10.1, 8.3$  Hz, 1H), 4.18 (t,  $J = 8.1$  Hz, 1H), 1.76 – 1.72 (m, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.49 (s), 144.59 (s), 131.57 (s), 128.52 (s), 128.48 (s), 127.77 (s), 112.56 (s), 71.89 (s), 71.65 (s), 18.53 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  188.1070, found: 188.1068. Note: The titled compound has a low boiling point. HPLC (CHIRALCEL OD-H, 0.46\*25 cm,  $5\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.1 min (major) and 8.6 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.200         | MM   | 0.1002      | 1.21475e4    | 2020.13623   | 50.8490 |
| 2      | 8.823         | MM   | 0.1810      | 1.17419e4    | 1081.21387   | 49.1510 |

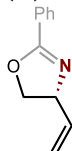
Totals : 2.38894e4 3101.35010

Signal 1: MWD1 B, Sig=254,4 Ref=off

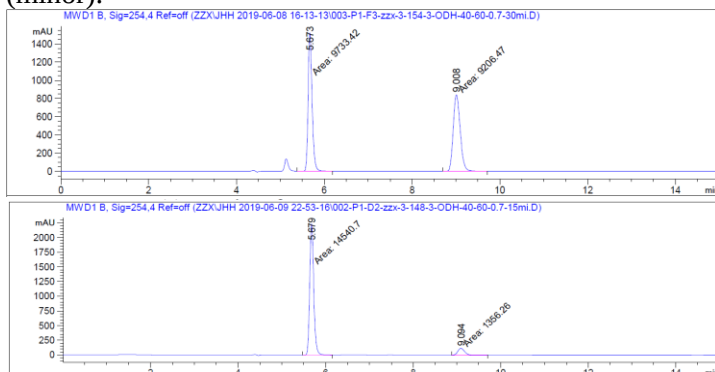
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.175         | MM   | 0.1037      | 1.74381e4    | 2802.04370   | 96.5592 |
| 2      | 8.577         | MM   | 0.1758      | 621.38580    | 58.92362     | 3.4408  |

Totals : 1.80595e4 2860.96732

## (R)-2-phenyl-4-vinyl-4,5-dihydrooxazole (24)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **24** as yellow oil (13.9 mg, 80% yield, 83% e.e.).  $[\alpha]^{20} = +49.7$  ( $c = 0.4$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.95 (m, 2H), 7.51 – 7.46 (m, 1H), 7.44 – 7.37 (m, 2H), 5.91 (ddd,  $J = 17.2, 10.2, 7.2$  Hz, 1H), 5.33 (dt,  $J = 17.1, 1.2$  Hz, 1H), 5.24 – 5.18 (m, 1H), 4.81 (dt,  $J = 8.2, 7.3$  Hz, 1H), 4.57 (dd,  $J = 9.8, 8.3$  Hz, 1H), 4.14 (t,  $J = 8.2$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.57 (s), 138.10 (s), 131.60 (s), 128.50 (s), 128.46 (s), 127.71 (s), 116.91 (s), 72.48 (s), 69.00 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  174.0913, found: 174.0937. HPLC (CHIRALCEL OD-H, 0.46\*25 cm,  $5\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.6 min (major) and 9.1 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.673         | MM   | 0.1068      | 9733.41797   | 1519.37622   | 51.3911 |
| 2      | 9.008         | MM   | 0.1823      | 9206.46973   | 841.79034    | 48.6089 |

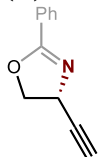
Totals : 1.89399e4 2361.16656

Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.679         | MM   | 0.1083      | 1.45407e4    | 2236.84790   | 91.4684 |
| 2      | 9.094         | MM   | 0.1915      | 1356.25635   | 118.02303    | 8.5316  |

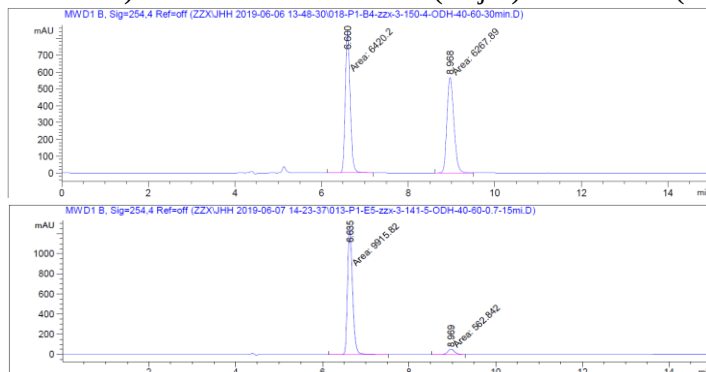
Totals : 1.58969e4 2354.87093

## (R)-4-ethynyl-2-phenyl-4,5-dihydrooxazole (25)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **25** as yellow solid (16.9 mg, 99% yield, 89% e.e.).  $[\alpha]^{20} = +5.5$  ( $c = 0.6$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (ddd,  $J = 8.5, 7.2, 1.3$  Hz, 2H), 7.52 – 7.47 (m, 1H), 7.44 – 7.37 (m, 2H), 5.00 (ddd,  $J = 10.4, 8.4, 2.3$  Hz, 1H), 4.63 (dd,  $J = 10.1, 8.1$  Hz, 1H), 4.40 (t,  $J = 8.3$  Hz, 1H), 2.45 (d,  $J = 2.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.91 (s), 131.96 (s), 128.66 (s), 128.49 (s), 127.16 (s), 82.73 (s), 73.04 (s), 72.74 (s), 57.21 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  172.0757, found: 172.0775.

HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 9.0 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.600         | MM   | 0.1279      | 6420.19531   | 836.29132    | 50.6002 |
| 2      | 8.968         | MM   | 0.1833      | 6267.88770   | 569.80121    | 49.3998 |

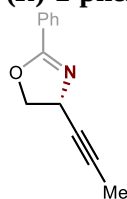
Totals : 1.26881e4 1406.09253

Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.635         | MM   | 0.1301      | 9915.81543   | 1270.17615   | 94.6287 |
| 2      | 8.969         | MM   | 0.1815      | 562.84192    | 51.67743     | 5.3713  |

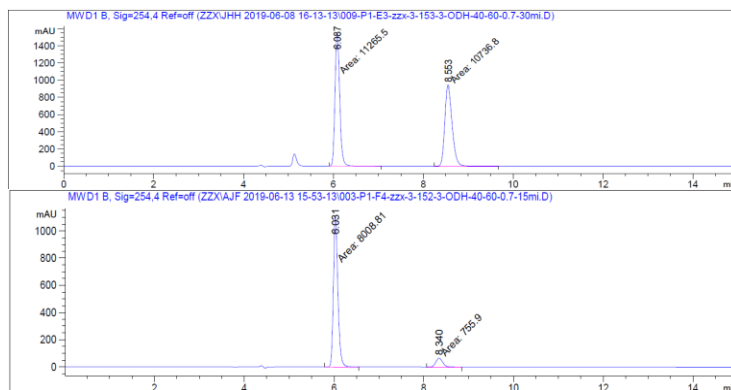
Totals : 1.04787e4 1321.85358

### (R)-2-phenyl-4-(prop-1-yn-1-yl)-4,5-dihydrooxazole (26)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **26** as colorless oil (17.9 mg, 96% yield, 83% e.e.).  $[\alpha]^{20}_D = +24.3$  (c = 0.1, CHCl<sub>3</sub>).  $R_f$  = 0.5 (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 – 7.95 (m, 2H), 7.48 (t,  $J$  = 7.4 Hz, 1H), 7.40 (t,  $J$  = 7.7 Hz, 2H), 5.00 – 4.93 (m, 1H), 4.59 (dd,  $J$  = 9.9, 8.0 Hz, 1H), 4.31 (t,  $J$  = 8.3 Hz, 1H), 1.85 (d,  $J$  = 2.3 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  165.34 (s), 131.79 (s), 128.61 (s), 128.43 (s), 127.38 (s), 80.86 (s), 78.00 (s), 73.40 (s), 57.55 (s), 3.84 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+H]^+$  186.0913, found: 186.0915.

Note: this compound is unstable under room temperature when exposed with air. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.0 min (major) and 8.3 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.087         | MM   | 0.1211      | 1.12655e4    | 1551.07471   | 51.2016 |
| 2      | 8.553         | MM   | 0.1889      | 1.07368e4    | 947.31860    | 48.7984 |

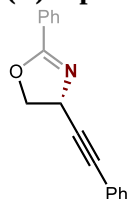
Totals : 2.20023e4 2498.39331

Signal 1: MWD1 B, Sig=254,4 Ref=off

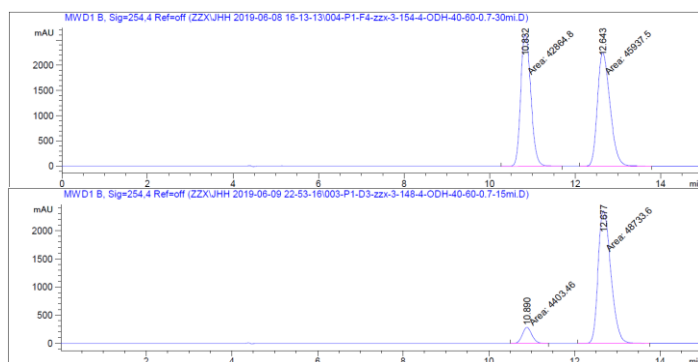
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.031         | MM   | 0.1199      | 8008.81104   | 1113.62805   | 91.3756 |
| 2      | 8.340         | MM   | 0.1896      | 755.90027    | 66.45437     | 8.6244  |

Totals : 8764.71130 1180.08242

**(R)-2-phenyl-4-(phenylethynyl)-4,5-dihydrooxazole (27)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **27** as yellow oil (22.1 mg, 89% yield, 83% e.e.).  $[\alpha]^{20} = +45.8$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).  $R_f = 0.5$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (ddd,  $J = 8.5, 6.9, 5.0$  Hz, 2H), 7.54 – 7.48 (m, 1H), 7.48 – 7.40 (m, 4H), 7.34 – 7.27 (m, 3H), 5.29 – 5.19 (m, 1H), 4.70 (dt,  $J = 18.0, 9.0$  Hz, 1H), 4.48 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.70 (s), 131.96 (s), 131.91 (s), 128.68 (s), 128.55 (s), 128.51 (s), 128.37 (s), 127.39 (s), 122.79 (s), 87.91 (s), 84.56 (s), 73.33 (s), 58.08 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  248.1070, found: 248.1081. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 10.8 min (minor) and 12.7 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.832        | MM   | 0.2740      | 4.28648e4    | 2607.40527   | 48.2699 |
| 2      | 12.643        | MM   | 0.3402      | 4.59375e4    | 2250.67676   | 51.7301 |

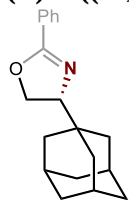
Totals : 8.88024e4 4858.08203

Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.890        | MM   | 0.2577      | 4403.45850   | 284.80005    | 8.2870  |
| 2      | 12.677        | MM   | 0.3454      | 4.87336e4    | 2351.63208   | 91.7130 |

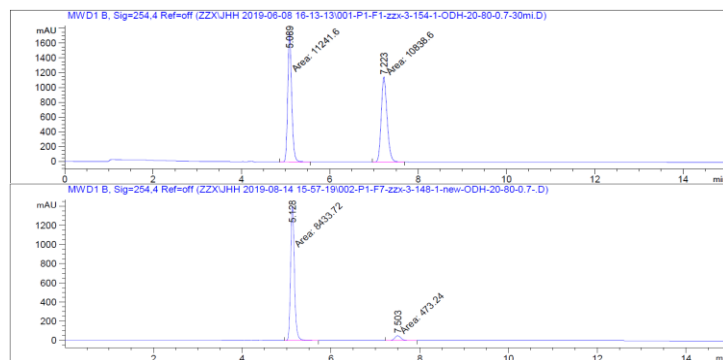
Totals : 5.31370e4 2636.43213

**(R)-4-((3r,5r,7r)-adamantan-1-yl)-2-phenyl-4,5-dihydrooxazole (28)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **28** as white solid (10.2 mg, 36% yield, 89% e.e.).  $[\alpha]^{20} = +78.1$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).  $R_f = 0.65$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.93 (m, 2H), 7.50 – 7.43 (m, 1H), 7.40 (ddt,  $J = 8.4, 6.8, 1.4$  Hz, 2H), 4.37 – 4.22 (m, 2H), 3.88 (dd,  $J = 9.9, 7.8$  Hz, 1H), 1.99 (d,  $J = 2.7$  Hz, 3H), 1.78 – 1.61 (m, 9H), 1.51 – 1.42 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.20 (s), 131.20 (s), 128.38 (s), 128.37 (s), 128.17 (s), 76.42 (s), 67.41 (s), 38.66 (s), 37.32 (s), 35.97 (s), 28.38 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  282.1852, found: 282.1852. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.1 min (major) and 7.5 min (minor).





Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.089         | MM   | 0.1065      | 1.12416e4    | 1759.91113   | 50.9127 |
| 2      | 7.223         | MM   | 0.1568      | 1.08386e4    | 1152.22266   | 49.0873 |

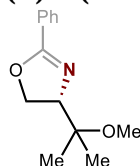
Totals : 2.20802e4 2912.13379

Signal 1: MWD1 B, Sig=254,4 Ref=off

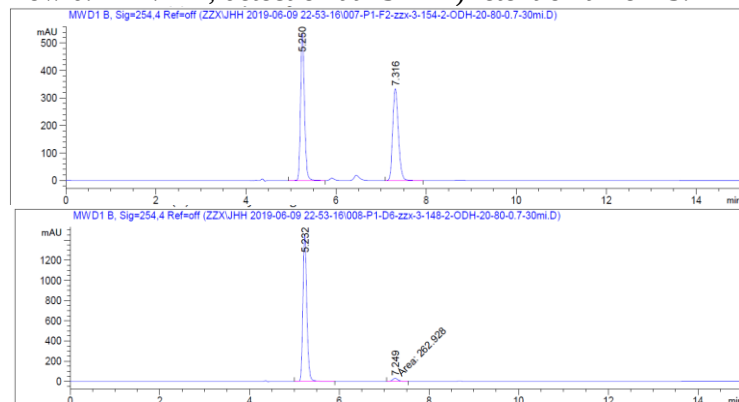
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.128         | MM   | 0.1001      | 8433.71777   | 1403.91760   | 94.6869 |
| 2      | 7.503         | MM   | 0.1593      | 473.23987    | 49.52729     | 5.3131  |

Totals : 8906.95764 1453.44489

### (R)-4-(2-methoxypropan-2-yl)-2-phenyl-4,5-dihydrooxazole (29)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **29** as colorless oil (10.3 mg, 47% yield, 94% e.e.).  $[\alpha]_D^{20} = +56.1$  ( $c = 0.3$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.93 (m, 2H), 7.50 – 7.45 (m, 1H), 7.42 – 7.36 (m, 2H), 4.44 (dd,  $J = 8.6, 7.7$  Hz, 1H), 4.38 (dd,  $J = 9.9, 8.6$  Hz, 1H), 4.31 (dd,  $J = 9.9, 7.6$  Hz, 1H), 3.26 (s, 3H), 1.34 (s, 3H), 1.10 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.55 (s), 131.40 (s), 128.46 (s), 128.39 (s), 128.04 (s), 76.68 (s), 74.55 (s), 68.98 (s), 49.76 (s), 22.98 (s), 19.50 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  220.1332, found: 220.1348. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.2 min (major) and 7.2 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.250         | BV   | 0.0913      | 3167.54565   | 533.44989    | 52.3726 |
| 2      | 7.316         | BB   | 0.1326      | 2880.54688   | 334.17133    | 47.6274 |

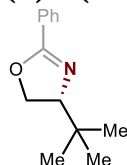
Totals : 6048.09253 867.62122

Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.232         | BB   | 0.0910      | 8633.24609   | 1460.73108   | 97.0445 |
| 2      | 7.249         | MM   | 0.1439      | 262.92847    | 30.44355     | 2.9555  |

Totals : 8896.17456 1491.17463

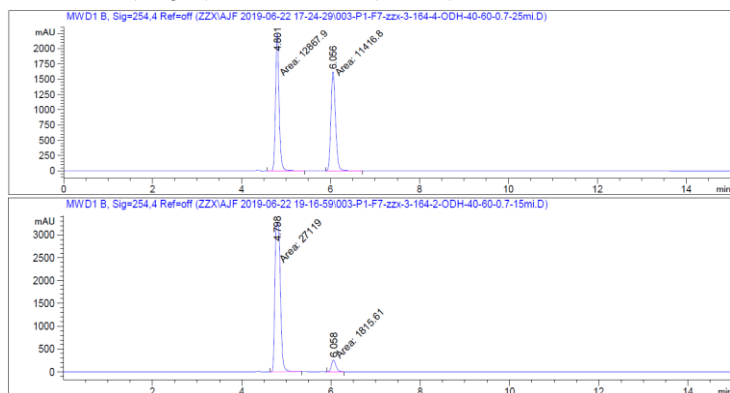
### (R)-4-(tert-butyl)-2-phenyl-4,5-dihydrooxazole (30)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **30** as colorless oil (10.2 mg, 86% yield, 89% e.e.).  $[\alpha]_D^{20} = +79.1$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).  $R_f = 0.65$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.92 (m, 2H), 7.49 – 7.44 (m, 1H), 7.43 – 7.37 (m, 2H), 4.34 (dd,  $J = 10.1, 8.6$  Hz, 1H), 4.26 – 4.21 (m, 1H), 4.05 (dd,  $J = 10.1, 7.7$  Hz, 1H), 0.96 (s, 9H).  $^{13}\text{C}$  NMR (151



MHz, CDCl<sub>3</sub>)  $\delta$  163.38 (s), 131.24 (s), 128.40 (s), 128.37 (s), 128.16 (s), 76.35 (s), 68.86 (s), 34.19 (s), 26.02 (s). HRMS (ESI-TOF)  $m/z$  calcd for [M+H]<sup>+</sup> 204.1383, found: 204.1383. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 4.8 min (major) and 6.1 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 4.801         | MM   | 0.0953      | 1.28679e4    | 2249.95654   | 52.9876 |
| 2      | 6.056         | MM   | 0.1172      | 1.14168e4    | 1624.17896   | 47.0124 |

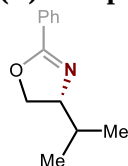
Totals : 2.42847e4 3874.13550

Signal 1: MWD1 B, Sig=254,4 Ref=off

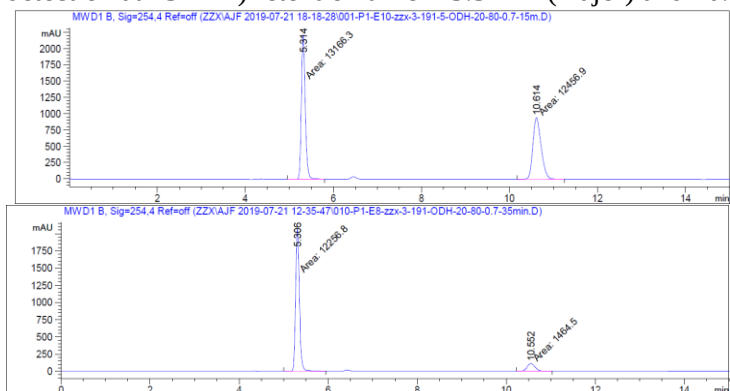
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 4.798         | MM   | 0.1386      | 2.71190e4    | 3261.54224   | 93.7251 |
| 2      | 6.058         | MM   | 0.1181      | 1815.61145   | 256.21985    | 6.2749  |

Totals : 2.89346e4 3517.76208

### (R)-4-isopropyl-2-phenyl-4,5-dihydrooxazole (31)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **31** as colorless oil (9.5 mg, 50% yield, 79% e.e.). [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +16.0 (c = 0.03, CHCl<sub>3</sub>). R<sub>f</sub> = 0.65 (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 – 7.93 (m, 2H), 7.48 – 7.44 (m, 1H), 7.42 – 7.37 (m, 2H), 4.43 – 4.38 (m, 1H), 4.17 – 4.08 (m, 2H), 1.87 (dq,  $J$  = 13.4, 6.7 Hz, 1H), 1.03 (d,  $J$  = 6.8 Hz, 3H), 0.93 (d,  $J$  = 6.8 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  163.50 (s), 131.30 (s), 128.41 (s), 128.39 (s), 128.12 (s), 72.76 (s), 70.22 (s), 32.98 (s), 19.10 (s), 18.21 (s). HRMS (ESI-TOF)  $m/z$  calcd for [M+H]<sup>+</sup> 190.1226, found: 190.1231. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.3 min (major) and 10.6 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.314         | MM   | 0.0988      | 1.31663e4    | 2221.48120   | 51.3842 |
| 2      | 10.614        | MM   | 0.2188      | 1.24569e4    | 948.83929    | 48.6158 |

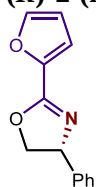
Totals : 2.56232e4 3170.32050

Signal 1: MWD1 B, Sig=254,4 Ref=off

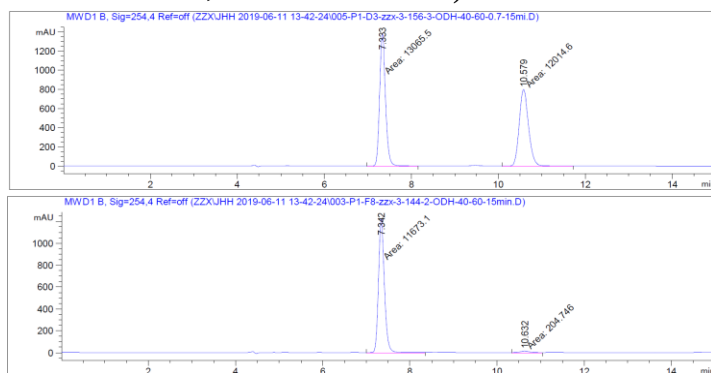
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.306         | MM   | 0.0989      | 1.22568e4    | 2066.40210   | 89.3269 |
| 2      | 10.552        | MM   | 0.2160      | 1464.49622   | 113.00378    | 10.6731 |

Totals : 1.37213e4 2179.40588

**(R)-2-(furan-2-yl)-4-phenyl-4,5-dihydrooxazole (32)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **32** as brown oil (11.9 mg, 56% yield, 97% e.e.).  $[\alpha]^{20} = -6.7$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).  $R_f = 0.50$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.55 (m, 1H), 7.38 – 7.33 (m, 2H), 7.32 – 7.26 (m, 3H), 7.07 – 7.03 (m, 1H), 6.52 (dd,  $J = 3.5, 1.8$  Hz, 1H), 5.39 (dd,  $J = 9.9, 8.4$  Hz, 1H), 4.78 (dd,  $J = 10.0, 8.4$  Hz, 1H), 4.27 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  157.12 (s), 145.54 (s), 142.94 (s), 141.96 (s), 128.88 (s), 127.82 (s), 126.87 (s), 115.00 (s), 111.77 (s), 74.92 (s), 70.16 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  214.0863, found: 214.0875. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.3 min (major) and 10.6 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.333         | MM   | 0.1574      | 1.30655e4    | 1383.31128   | 52.0950 |
| 2      | 10.579        | MM   | 0.2501      | 1.20146e4    | 800.61670    | 47.9050 |

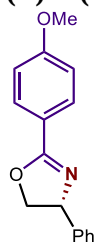
Totals : 2.50800e4 2183.92798

Signal 1: MWD1 B, Sig=254,4 Ref=off

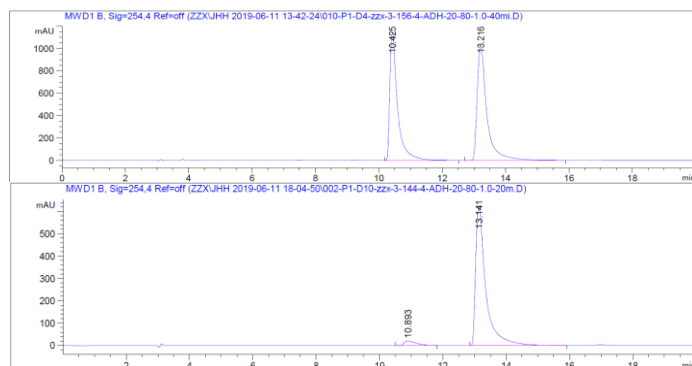
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.342         | MM   | 0.1589      | 1.16731e4    | 1224.39197   | 98.2762 |
| 2      | 10.632        | MM   | 0.2518      | 204.74553    | 13.55276     | 1.7238  |

Totals : 1.18779e4 1237.94473

**(R)-2-(4-methoxyphenyl)-4-phenyl-4,5-dihydrooxazole (33)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **33** as white solid (20.0 mg, 75% yield, 94% e.e.).  $[\alpha]^{20} = +14.7$  ( $c = 0.8$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.97 (m, 2H), 7.35 (dd,  $J = 10.2, 4.7$  Hz, 2H), 7.33 – 7.26 (m, 3H), 6.96 – 6.92 (m, 2H), 5.36 (dd,  $J = 9.9, 8.1$  Hz, 1H), 4.77 (dd,  $J = 10.0, 8.3$  Hz, 1H), 4.25 (t,  $J = 8.2$  Hz, 1H), 3.86 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.66 (s), 162.39 (s), 142.77 (s), 130.34 (s), 128.85 (s), 127.68 (s), 126.89 (s), 120.19 (s), 113.87 (s), 74.93 (s), 70.22 (s), 55.50 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  254.1176, found: 254.1178. HPLC (CHIRALCEL AD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 10.9 min (minor) and 13.1 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.425        | BB   | 0.2499      | 1.93801e4    | 1142.58655   | 47.2194 |
| 2      | 13.216        | BB   | 0.3171      | 2.16626e4    | 1022.95123   | 52.7806 |

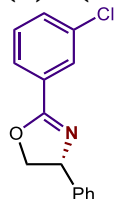
Totals : 4.10427e4 2165.53778

Signal 1: MWD1 B, Sig=254,4 Ref=off

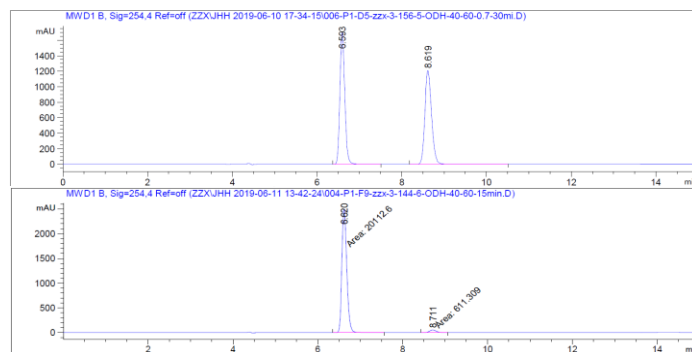
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.893        | BB   | 0.3693      | 506.15628    | 20.13421     | 3.5385  |
| 2      | 13.141        | BB   | 0.3271      | 1.37981e4    | 621.20441    | 96.4615 |

Totals : 1.43042e4 641.33862

### (R)-2-(3-chlorophenyl)-4-phenyl-4,5-dihydrooxazole (34)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **34** as colorless oil (25.4 mg, 99% yield, 93% e.e.).  $[\alpha]^{20}_D = +29.4$  (c = 0.6,  $\text{CHCl}_3$ ).  $R_f = 0.50$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 7.99 (m, 1H), 7.93 (d,  $J = 7.8$  Hz, 1H), 7.54 – 7.43 (m, 1H), 7.41 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 5.40 (dd,  $J = 9.9, 8.5$  Hz, 1H), 4.81 (dd,  $J = 10.1, 8.5$  Hz, 1H), 4.30 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  163.78 (s), 142.12 (s), 134.64 (s), 131.75 (s), 129.85 (s), 129.41 (s), 128.97 (s), 128.76 (s), 127.91 (s), 126.86 (s), 126.72 (s), 75.21 (s), 70.26 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  258.0680, found: 258.0687. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 8.7 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.593         | BB   | 0.1220      | 1.33737e4    | 1696.18701   | 50.2308 |
| 2      | 8.619         | BB   | 0.1700      | 1.32508e4    | 1207.79590   | 49.7692 |

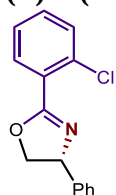
Totals : 2.66244e4 2903.98291

Signal 1: MWD1 B, Sig=254,4 Ref=off

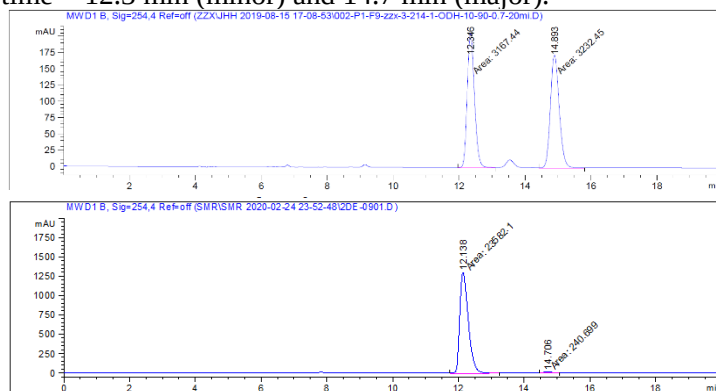
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.620         | MM   | 0.1342      | 2.01126e4    | 2497.48071   | 97.0502 |
| 2      | 8.711         | MM   | 0.1880      | 611.30884    | 54.18674     | 2.9498  |

Totals : 2.07240e4 2551.66746

**(R)-2-(2-chlorophenyl)-4-phenyl-4,5-dihydrooxazole (35)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **35** as white solid (12.6 mg, 49% yield, 98% e.e.).  $[\alpha]^{20}_D = -356.7$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).  $R_f = 0.50$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (dd,  $J = 7.7, 1.6$  Hz, 1H), 7.39 (dd,  $J = 8.0, 1.1$  Hz, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.16 (s, 1H), 5.36 (dd,  $J = 10.2, 8.3$  Hz, 1H), 4.73 (dd,  $J = 10.2, 8.4$  Hz, 1H), 4.20 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  163.74 (s), 142.23 (s), 133.76 (s), 131.91 (s), 131.67 (s), 130.90 (s), 128.93 (s), 127.82 (s), 127.55 (s), 126.87 (s), 126.73 (s), 75.07 (s), 70.55 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  258.0680, found: 258.0676. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 90/10, flow 0.7 mL/min, detection at 254 nm) retention time = 12.3 min (minor) and 14.7 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.346        | MM   | 0.2546      | 3167.43579   | 207.31366    | 49.4921 |
| 2      | 14.893        | MM   | 0.3105      | 3232.44727   | 173.53537    | 50.5079 |

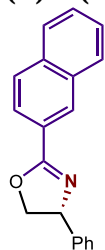
Totals : 6399.88306 380.84903

Signal 1: MWD1 B, Sig=254,4 Ref=off

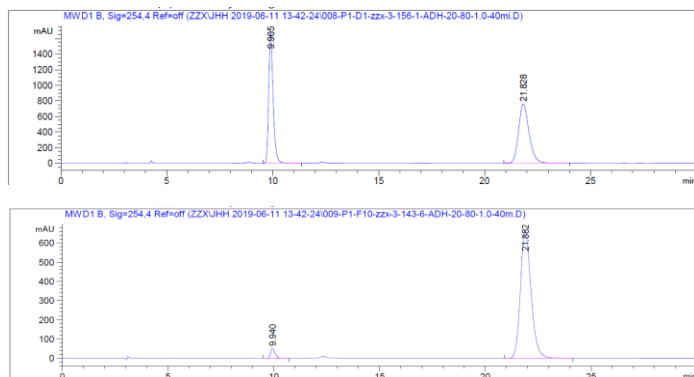
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.138        | MM   | 0.3008      | 2.35821e4    | 1306.82288   | 98.9896 |
| 2      | 14.706        | MM   | 0.3072      | 240.69940    | 13.05796     | 1.0104  |

Totals : 2.38228e4 1319.88084

**(R)-2-(naphthalen-2-yl)-4-phenyl-4,5-dihydrooxazole (36)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **36** as white solid (17.5 mg, 64% yield, 94% e.e.).  $[\alpha]^{20}_D = -13.2$  ( $c = 0.7$ ,  $\text{CHCl}_3$ ).  $R_f = 0.55$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (d,  $J = 0.7$  Hz, 1H), 8.14 (dd,  $J = 8.6, 1.7$  Hz, 1H), 7.97 – 7.85 (m, 3H), 7.60 – 7.50 (m, 2H), 7.41 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 5.45 (dd,  $J = 10.1, 8.2$  Hz, 1H), 4.87 (dd,  $J = 10.1, 8.3$  Hz, 1H), 4.35 (t,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.02 (s), 142.51 (s), 134.99 (s), 132.85 (s), 129.21 (s), 129.08 (s), 128.94 (s), 128.29 (s), 127.93 (s), 127.81 (s), 127.75 (s), 126.94 (s), 126.71 (s), 125.14 (s), 124.99 (s), 75.11 (s), 70.40 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  274.1226, found: 274.1225. HPLC (CHIRALCEL AD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 9.9 min (minor) and 21.8 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

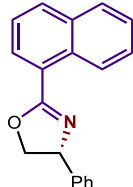
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.905         | BB   | 0.2218      | 2.43878e4    | 1675.89124   | 48.3213 |
| 2      | 21.828        | BB   | 0.5265      | 2.60822e4    | 759.78473    | 51.6787 |

Totals : 5.04700e4 2435.67596  
Signal 1: MWD1 B, Sig=254,4 Ref=off

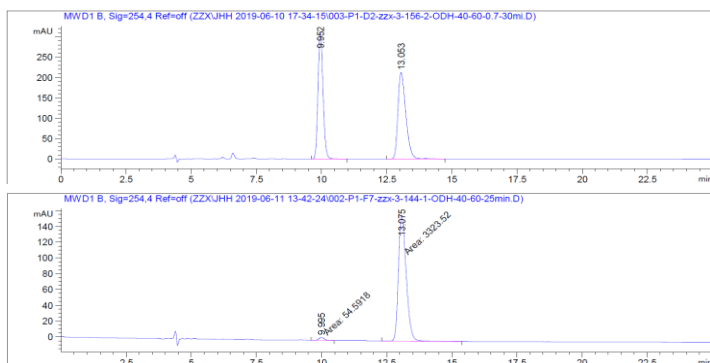
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.940         | BB   | 0.2256      | 747.70868    | 50.82682     | 3.1299  |
| 2      | 21.882        | BB   | 0.5345      | 2.31416e4    | 664.21503    | 96.8701 |

Totals : 2.38893e4 715.04185

### (R)-2-(naphthalen-1-yl)-4-phenyl-4,5-dihydrooxazole (37)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **37** as white solid (21.8 mg, 80% yield, 97% e.e.).  $[\alpha]^{20} = -55.8$  (c = 1.0, CHCl<sub>3</sub>).  $R_f = 0.45$  (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  9.27 (d,  $J = 8.7$  Hz, 1H), 8.21 (dd,  $J = 7.2, 1.2$  Hz, 1H), 8.00 (d,  $J = 8.2$  Hz, 1H), 7.90 (d,  $J = 8.1$  Hz, 1H), 7.61 (ddd,  $J = 8.5, 6.8, 1.4$  Hz, 1H), 7.57 – 7.51 (m, 2H), 7.44 – 7.38 (m, 4H), 7.35 – 7.30 (m, 1H), 5.58 (dd,  $J = 10.1, 8.3$  Hz, 1H), 4.84 (dd,  $J = 10.2, 8.3$  Hz, 1H), 4.31 (t,  $J = 8.2$  Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  164.81 (s), 142.70 (s), 133.92 (s), 132.31 (s), 131.44 (s), 129.48 (s), 128.93 (s), 128.60 (s), 127.75 (s), 127.60 (s), 126.90 (s), 126.73 (s), 126.27 (s), 124.79 (s), 124.42 (s), 73.96 (s), 71.10 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+H]^+$  274.1226, found: 274.1226. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 10.0 min (minor) and 13.1 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.952         | BB   | 0.2088      | 4167.60840   | 310.14563    | 48.5057 |
| 2      | 13.053        | BV R | 0.3209      | 4424.39746   | 212.50104    | 51.4943 |

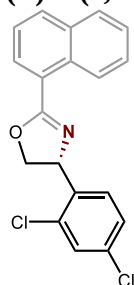
Totals : 8592.00586 522.64667

Signal 1: MWD1 B, Sig=254,4 Ref=off

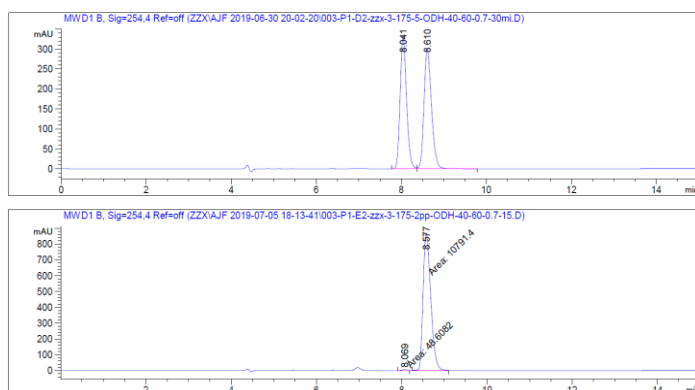
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.995         | MM   | 0.2359      | 54.59175     | 3.85711      | 1.6160  |
| 2      | 13.075        | MM   | 0.3473      | 3323.52148   | 159.50552    | 98.3840 |

Totals : 3378.11324 163.36264

**(R)-4-(2,4-dichlorophenyl)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (38)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **38** as colorless oil (22.5 mg, 64% yield, 99% e.e.).  $[\alpha]^{20}_D = -230$  ( $c = 0.8$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.31 (d,  $J = 8.6$  Hz, 1H), 8.21 (d,  $J = 7.2$  Hz, 1H), 8.02 (d,  $J = 8.1$  Hz, 1H), 7.92 (dd,  $J = 8.1, 0.5$  Hz, 1H), 7.67 – 7.62 (m, 1H), 7.59 – 7.49 (m, 3H), 7.45 (d,  $J = 2.1$  Hz, 1H), 7.27 (dd,  $J = 8.8, 2.4$  Hz, 1H), 5.86 (dd,  $J = 10.3, 8.5$  Hz, 1H), 5.04 – 4.90 (m, 1H), 4.13 (t,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.80 (s), 139.48 (s), 133.95 (s), 133.93 (s), 133.06 (s), 132.64 (s), 131.39 (s), 129.68 (s), 129.24 (s), 129.01 (s), 128.75 (s), 127.74 (s), 127.62 (s), 126.58 (s), 126.36 (s), 124.82 (s), 124.03 (s), 72.90 (s), 67.93 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  342.0447, found: 342.0438. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5  $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 8.0 min (minor) and 8.6 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.041         | BV   | 0.1634      | 3530.28687   | 333.65497    | 48.7898 |
| 2      | 8.610         | VV R | 0.1893      | 3705.42456   | 301.57465    | 51.2102 |

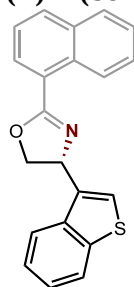
Totals : 7235.71143 635.22961

Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.069         | MM   | 0.1598      | 48.60820     | 5.06933      | 0.4484  |
| 2      | 8.577         | MM   | 0.2062      | 1.07914e4    | 872.11871    | 99.5516 |

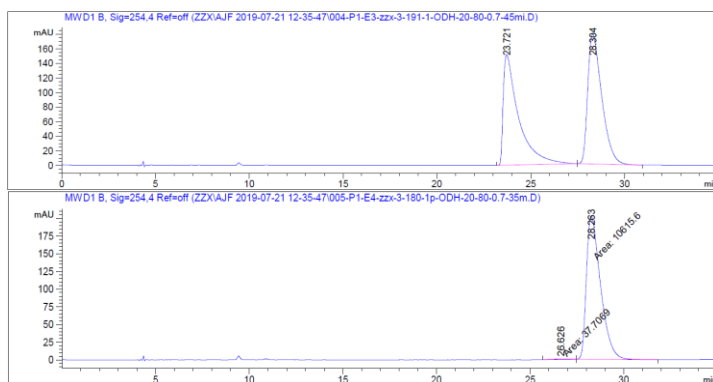
Totals : 1.08400e4 877.18804

**(R)-4-(benzo[b]thiophen-3-yl)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (39)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **39** as light yellow solid (28.0 mg, 85% yield, 99% e.e.).  $[\alpha]^{20}_D = -67.6$  ( $c = 1.1$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.31 (d,  $J = 8.6$  Hz, 1H), 8.23 (dd,  $J = 7.2, 1.1$  Hz, 1H), 8.02 (d,  $J = 8.2$  Hz, 1H), 7.91 (dd,  $J = 7.4, 1.0$  Hz, 2H), 7.84 – 7.74 (m, 1H), 7.63 (ddd,  $J = 8.5, 6.8, 1.3$  Hz, 1H), 7.59 – 7.52 (m, 2H), 7.49 (s, 1H), 7.45 – 7.34 (m, 2H), 5.99 – 5.85 (m, 1H), 4.93 (dd,  $J = 10.2, 8.1$  Hz, 1H), 4.42 (t,  $J = 8.1$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.05 (s), 141.38 (s), 137.45 (s), 137.19 (s), 133.94 (s), 132.47 (s), 131.42 (s), 129.58 (s), 128.67 (s), 127.70 (s), 126.66 (s), 126.33 (s), 124.82 (s),

124.63 (s), 124.38 (s), 124.30 (s), 123.34 (s), 123.15 (s), 121.67 (s), 72.02 (s), 66.41 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+H]^+$  330.0947, found: 330.0942. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 26.6 min (minor) and 28.3 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 23.721        | BB   | 0.8023      | 8609.29688   | 151.20450    | 48.2469 |
| 2      | 28.304        | BB   | 0.7872      | 9234.95703   | 178.02280    | 51.7531 |

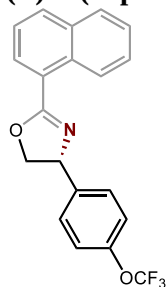
Totals : 1.78443e4 329.22729

Signal 1: MWD1 B, Sig=254,4 Ref=off

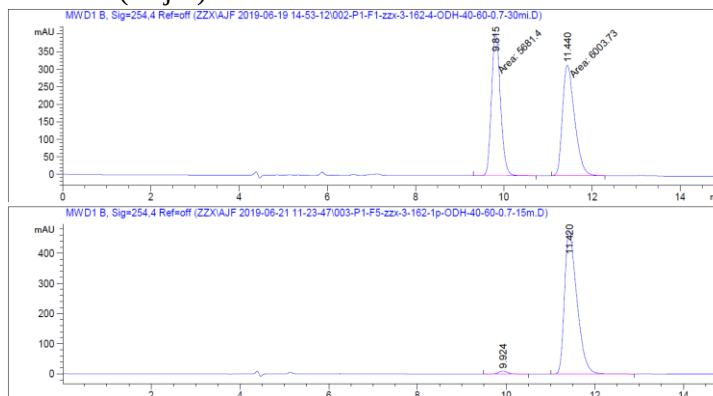
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 26.626        | MM   | 1.0768      | 37.70694     | 5.83615e-1   | 0.3539  |
| 2      | 28.263        | MM   | 0.8739      | 1.06156e4    | 202.45235    | 99.6461 |

Totals : 1.06533e4 203.03596

### (R)-2-(naphthalen-1-yl)-4-(4-(trifluoromethoxy)phenyl)-4,5-dihydrooxazole (40)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **40** as light yellow solid (27.6 mg, 77% yield, 97% e.e.).  $[\alpha]^{20}_D = -66.2$  (c = 0.15, CHCl<sub>3</sub>).  $R_f$  = 0.45 (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  9.29 – 9.18 (m, 1H), 8.20 (dd,  $J$  = 7.2, 1.2 Hz, 1H), 8.00 (t,  $J$  = 9.8 Hz, 1H), 7.91 (t,  $J$  = 9.9 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.56 – 7.50 (m, 2H), 7.46 – 7.36 (m, 2H), 7.24 (d,  $J$  = 8.0 Hz, 2H), 5.58 (dd,  $J$  = 10.1, 8.3 Hz, 1H), 4.83 (dt,  $J$  = 17.9, 9.0 Hz, 1H), 4.27 (t,  $J$  = 8.3 Hz, 1H). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -57.86 (s). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  165.16 (s), 148.80 (d,  $J$  = 1.7 Hz), 141.42 (s), 133.95 (s), 132.54 (s), 131.41 (s), 129.61 (s), 128.69 (s), 128.33 (s), 127.71 (s), 126.61 (s), 126.34 (s), 124.80 (s), 124.11 (s), 121.49 (s), 120.64 (q,  $J$  = 257.0 Hz), 73.72 (s), 70.41 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[M+H]^+$  358.1049, found: 358.1048. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 9.9 min (minor) and 11.4 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.815         | MM   | 0.2341      | 5681.39502   | 404.54816    | 48.6207 |
| 2      | 11.440        | MM   | 0.3176      | 6003.73193   | 315.05478    | 51.3793 |

Totals : 1.16851e4 719.60294

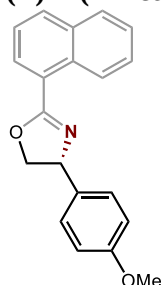
Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.924         | BB   | 0.2192      | 143.23206    | 10.11821     | 1.5371  |
| 2      | 11.420        | BB   | 0.2941      | 9175.25391   | 473.48376    | 98.4629 |

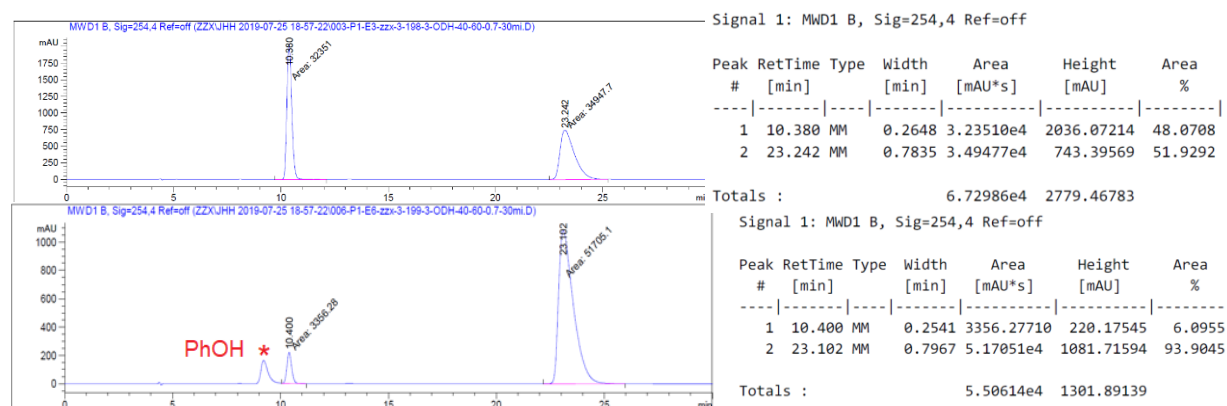
Totals : 9318.48596 483.60197



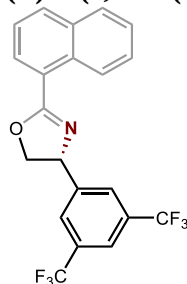
**(R)-4-(4-methoxyphenyl)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (41)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded product **41** as off white solid (24.8 mg, 82% yield, 88% e.e.).  $[\alpha]^{20} = -70.0$  ( $c = 0.8$ ,  $\text{CHCl}_3$ ).  $R_f = 0.35$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.25 (d,  $J = 8.6$  Hz, 1H), 8.19 (dd,  $J = 7.2, 1.1$  Hz, 1H), 7.99 (d,  $J = 8.2$  Hz, 1H), 7.89 (d,  $J = 7.8$  Hz, 1H), 7.60 (ddd,  $J = 8.5, 6.8, 1.3$  Hz, 1H), 7.56 – 7.48 (m, 2H), 7.36 – 7.29 (m, 2H), 6.99 – 6.85 (m, 2H), 5.52 (dd,  $J = 10.0, 8.3$  Hz, 1H), 4.80 (dd,  $J = 10.1, 8.3$  Hz, 1H), 4.28 (t,  $J = 8.2$  Hz, 1H), 3.82 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.53 (s), 159.26 (s), 135.03 – 134.92 (m), 133.92 (s), 132.26 (s), 131.44 (s), 129.43 (s), 128.59 (s), 128.04 (s), 127.57 (s), 126.75 (s), 126.26 (s), 124.80 (s), 124.50 (s), 114.31 (s), 74.06 (s), 70.58 (s), 55.46 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  304.1332, found: 304.1327. HPLC (CHIRALCEL OD-H, 0.46\*25 cm,  $5\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 10.4 min (minor) and 23.1 min (major).



**(R)-4-(3,5-bis(trifluoromethyl)phenyl)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (42)**

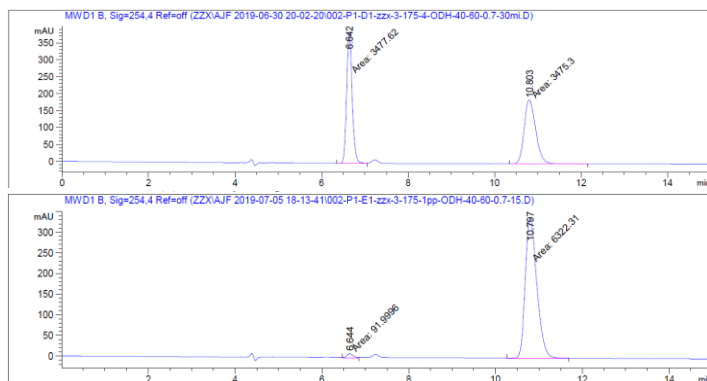


The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded product **42** as colorless oil (26.6 mg, 65% yield, 97% e.e.).  $[\alpha]^{20} = -145.5$  ( $c = 0.6$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.23 (d,  $J = 8.6$  Hz, 1H), 8.22 (dd,  $J = 7.2, 1.0$  Hz, 1H), 8.04 (d,  $J = 8.2$  Hz, 1H), 7.92 (d,  $J = 8.1$  Hz, 1H), 7.87 (d,  $J = 9.9$  Hz, 3H), 7.64 (ddd,  $J = 8.5, 6.8, 1.3$  Hz, 1H), 7.59 – 7.52 (m,



2H), 5.71 (dd,  $J = 10.0, 8.8$  Hz, 1H), 4.92 (dd,  $J = 10.3, 8.5$  Hz, 1H), 4.28 (t,  $J = 8.5$  Hz, 1H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.78 – -62.83 (m).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  166.06 (s), 145.22 (s), 133.97 (s), 132.89 (s), 132.29 (q,  $J = 33.4$  Hz), 131.37 (s), 129.84 (s), 128.80 (s), 127.84 (s), 127.25 (d,  $J = 2.7$  Hz), 126.46 (s), 126.41 (s), 124.82 (s), 123.67 (s), 123.40 (q,  $J = 272.7$  Hz), 121.87 (q,  $J = 3.8$  Hz), 121.84 (q,  $J = 3.8$  Hz), 73.25 (s), 70.32 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  410.0974, found 410.0971.

HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (minor) and 10.8 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.642         | MM   | 0.1500      | 3477.62207   | 386.41479    | 50.0167 |
| 2      | 10.803        | MM   | 0.3075      | 3475.30029   | 188.33817    | 49.9833 |

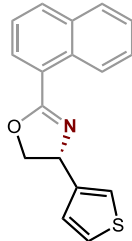
Totals : 6952.92236 574.75296

Signal 1: MWD1 B, Sig=254,4 Ref=off

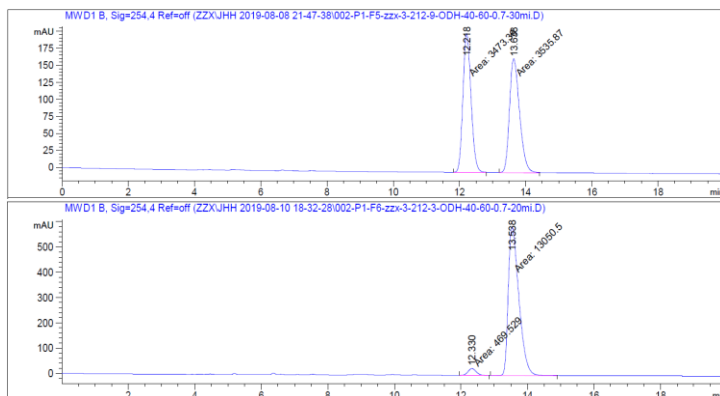
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.644         | MM   | 0.1564      | 91.99960     | 9.80515      | 1.4343  |
| 2      | 10.797        | MM   | 0.3102      | 6322.30713   | 339.68515    | 98.5657 |

Totals : 6414.30672 349.49030

### (R)-2-(naphthalen-1-yl)-4-(thiophen-3-yl)-4,5-dihydrooxazole (43)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **43** as white solid (24.8 mg, 83% yield, 93% e.e.).  $[\alpha]_D^{20} = -38.9$  (c = 0.9,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.23 (d,  $J = 8.7$  Hz, 1H), 8.19 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.99 (d,  $J = 8.2$  Hz, 1H), 7.90 (d,  $J = 8.1$  Hz, 1H), 7.61 (ddd,  $J = 8.5, 6.8, 1.4$  Hz, 1H), 7.57 – 7.47 (m, 2H), 7.36 (dd,  $J = 5.0, 3.0$  Hz, 1H), 7.34 – 7.28 (m, 1H), 7.13 (dd,  $J = 5.0, 1.2$  Hz, 1H), 5.70 – 5.60 (m, 1H), 4.78 (dd,  $J = 10.0, 8.2$  Hz, 1H), 4.35 (t,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.65 (s), 143.48 (s), 133.89 (s), 132.34 (s), 131.38 (s), 129.47 (s), 128.61 (s), 127.60 (s), 126.75 (s), 126.64 (s), 126.28 (s), 126.21 (s), 124.78 (s), 124.36 (s), 121.52 (s), 73.14 (s), 66.94 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  280.0791, found: 280.0783. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 12.3 min (minor) and 13.5 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.218        | MM   | 0.2840      | 3473.35986   | 203.80884    | 49.5541 |
| 2      | 13.638        | MM   | 0.3529      | 3535.87378   | 167.00679    | 50.4459 |

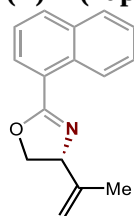
Totals : 7009.23364 370.81563

Signal 1: MWD1 B, Sig=254,4 Ref=off

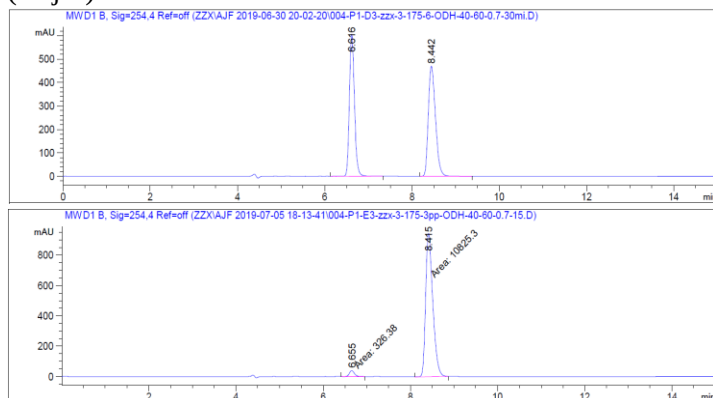
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.330        | MM   | 0.2911      | 469.52914    | 26.88027     | 3.4728  |
| 2      | 13.538        | MM   | 0.3701      | 13050.5      | 587.77069    | 96.5272 |

Totals : 1.35200e4 614.65096

**(R)-2-(naphthalen-1-yl)-4-(prop-1-en-2-yl)-4,5-dihydrooxazole (44)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **44** as yellow oil (19.2 mg, 82% yield, 94% e.e.).  $[\alpha]^{20} = +32.2$  ( $c = 0.7$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.18 (d,  $J = 8.6$  Hz, 1H), 8.13 (d,  $J = 7.2$  Hz, 1H), 7.97 (d,  $J = 8.1$  Hz, 1H), 7.88 (d,  $J = 8.0$  Hz, 1H), 7.68 – 7.58 (m, 1H), 7.52 (dt,  $J = 18.9, 7.6$  Hz, 2H), 5.12 (s, 1H), 5.03 – 4.92 (m, 2H), 4.57 (dd,  $J = 10.0, 8.4$  Hz, 1H), 4.22 (dd,  $J = 11.7, 4.4$  Hz, 1H), 1.84 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.37 (s), 144.71 (s), 133.87 (s), 132.14 (s), 131.36 (s), 129.27 (s), 128.56 (s), 127.50 (s), 126.63 (s), 126.23 (s), 124.77 (s), 124.56 (s), 112.45 (s), 72.69 (s), 70.67 (s), 18.77 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  238.1226, found: 238.1223. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (minor) and 8.4 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.616         | VB R | 0.1205      | 4810.01270   | 606.55359    | 47.7583 |
| 2      | 8.442         | BB   | 0.1727      | 5261.56592   | 469.80887    | 52.2417 |

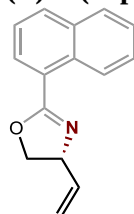
Totals : 1.00716e4 1076.36246

Signal 1: MWD1 B, Sig=254,4 Ref=off

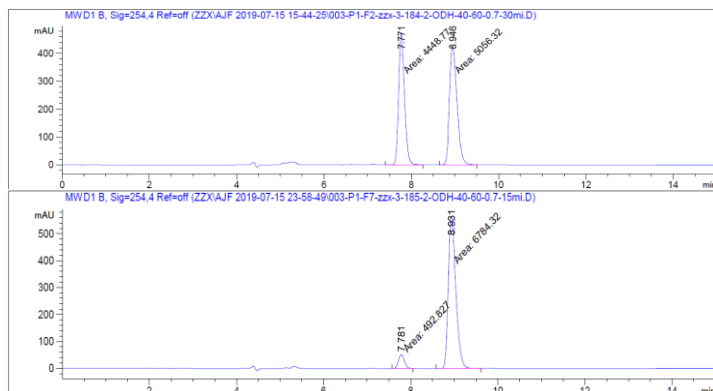
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.655         | MM   | 0.1356      | 326.37958    | 40.10880     | 2.9267  |
| 2      | 8.415         | MM   | 0.1913      | 1.08253e4    | 943.26440    | 97.0733 |

Totals : 1.11516e4 983.37320

**(R)-2-(naphthalen-1-yl)-4-vinyl-4,5-dihydrooxazole (45)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **45** as off white solid (21.6 mg, 91% yield, 87% e.e.).  $[\alpha]^{20} = +68.0$  ( $c = 0.7$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.22 – 9.13 (m, 1H), 8.12 (dd,  $J = 7.3, 1.2$  Hz, 1H), 7.97 (d,  $J = 8.2$  Hz, 1H), 7.91 – 7.83 (m, 1H), 7.61 (ddd,  $J = 8.5, 6.8, 1.4$  Hz, 1H), 7.57 – 7.44 (m, 2H), 6.03 (ddd,  $J = 17.1, 10.2, 6.9$  Hz, 1H), 5.41 (dt,  $J = 17.1, 1.3$  Hz, 1H), 5.26 (dt,  $J = 10.2, 1.1$  Hz, 1H), 5.00 (ddd,  $J = 9.6, 8.1, 7.0$  Hz, 1H), 4.60 (dd,  $J = 9.8, 8.3$  Hz, 1H), 4.18 (t,  $J = 8.2$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.45 (s), 138.24 (d,  $J = 5.8$  Hz), 133.86 (s), 132.21 (s), 131.32 (s), 129.34 (s), 128.55 (s), 127.51 (s), 126.62 (s), 126.23 (s), 124.74 (s), 124.46 (s), 116.75 (s), 71.52 (s), 69.67 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  224.1070, found: 224.1081. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.8 min (minor) and 8.9 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.771         | MM   | 0.1563      | 4448.77246   | 474.42752    | 46.8841 |
| 2      | 8.946         | MM   | 0.1986      | 5056.31592   | 424.25052    | 53.1959 |

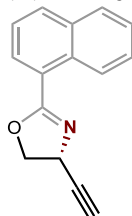
Totals : 9505.08838 898.67804

Signal 1: MWD1 B, Sig=254,4 Ref=off

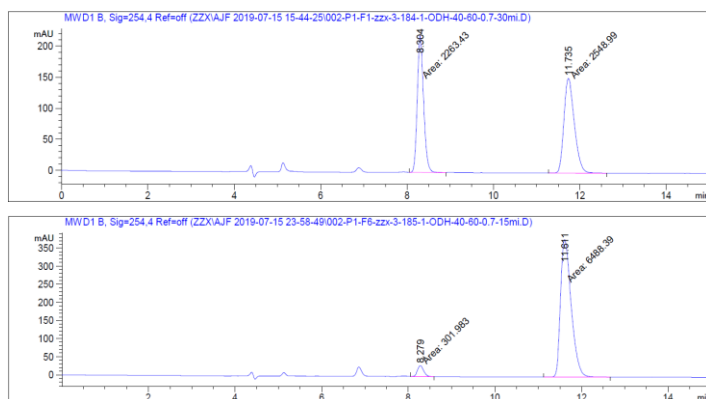
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.781         | MM   | 0.1564      | 492.82687    | 52.50379     | 6.7723  |
| 2      | 8.931         | MM   | 0.2002      | 6784.31934   | 564.70782    | 93.2277 |

Totals : 7277.14621 617.21161

### (R)-4-ethynyl-2-(naphthalen-1-yl)-4,5-dihydrooxazole (46)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **46** as yellow oil (19.2 mg, 87% yield, 91% e.e.).  $[\alpha]^{20} = -28.3$  ( $c = 0.7$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.20 – 9.10 (m, 1H), 8.12 (dd,  $J = 7.3, 1.3$  Hz, 1H), 7.98 (d,  $J = 8.2$  Hz, 1H), 7.91 – 7.84 (m, 1H), 7.62 (ddd,  $J = 8.5, 6.8, 1.4$  Hz, 1H), 7.58 – 7.44 (m, 2H), 5.17 (ddd,  $J = 10.3, 8.3, 2.3$  Hz, 1H), 4.66 (dd,  $J = 10.1, 8.1$  Hz, 1H), 4.44 (t,  $J = 8.2$  Hz, 1H), 2.49 (d,  $J = 2.3$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.79 (s), 133.83 (s), 132.61 (s), 131.25 (s), 129.61 (s), 128.57 (s), 127.65 (s), 126.58 (s), 126.32 (s), 124.67 (s), 123.84 (s), 82.92 (s), 72.81 (s), 72.01 (s), 57.95 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  222.0913, found: 222.0924. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 8.2 min (minor) and 11.6 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.304         | MM   | 0.1711      | 2263.43457   | 220.48286    | 47.0332 |
| 2      | 11.735        | MM   | 0.2785      | 2548.98706   | 152.51952    | 52.9668 |

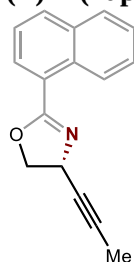
Totals : 4812.42163 373.00238

Signal 1: MWD1 B, Sig=254,4 Ref=off

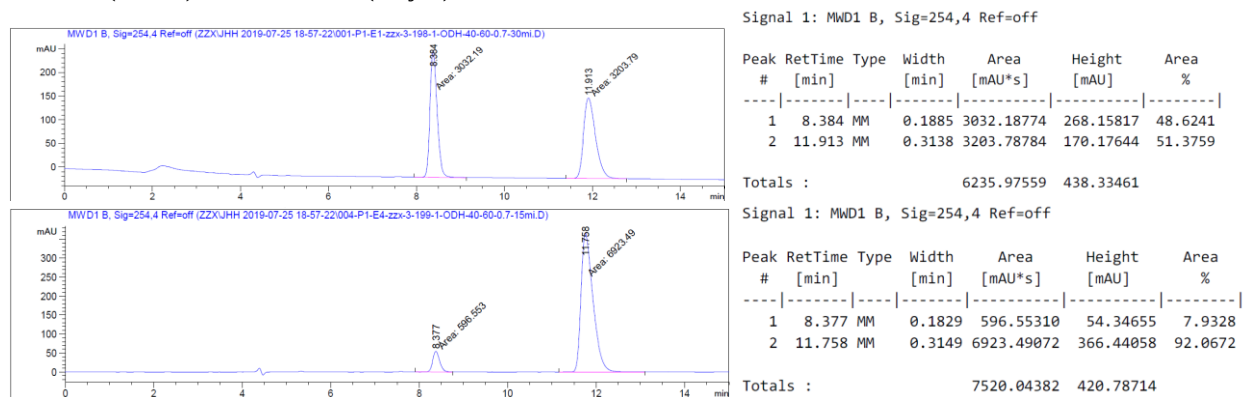
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.279         | MM   | 0.1673      | 301.98322    | 30.08605     | 4.4472  |
| 2      | 11.611        | MM   | 0.2849      | 6488.39258   | 379.63321    | 95.5528 |

Totals : 6790.37579 409.71926

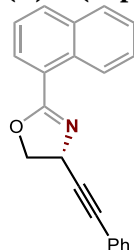
**(R)-2-(naphthalen-1-yl)-4-(prop-1-yn-1-yl)-4,5-dihydrooxazole (47)**



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **47** as yellow oil (21.6 mg, 92% yield, 84% e.e.).  $[\alpha]^{20}_D = -48.4$  ( $c = 0.7$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.14 (dd,  $J = 8.8, 0.7$  Hz, 1H), 8.12 (dd,  $J = 7.3, 1.3$  Hz, 1H), 7.96 (d,  $J = 8.2$  Hz, 1H), 7.91 – 7.80 (m, 1H), 7.60 (ddd,  $J = 8.5, 6.8, 1.4$  Hz, 1H), 7.56 – 7.43 (m, 2H), 5.14 (ddd,  $J = 10.0, 8.5, 2.3$  Hz, 1H), 4.62 (dd,  $J = 10.0, 8.0$  Hz, 1H), 4.36 (dd,  $J = 8.5, 8.0$  Hz, 1H), 1.88 (d,  $J = 2.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.23 (s), 133.82 (s), 132.43 (s), 131.28 (s), 129.53 (s), 128.52 (s), 127.56 (s), 126.69 (s), 126.26 (s), 124.68 (s), 124.11 (s), 80.91 (s), 78.20 (s), 72.43 (s), 58.31 (s), 3.88 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  236.1070, found: 236.1077. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 8.4 min (minor) and 11.8 min (major).

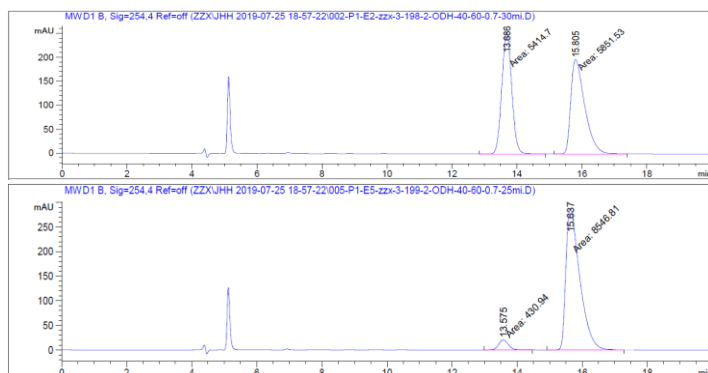


**(R)-2-(naphthalen-1-yl)-4-(phenylethynyl)-4,5-dihydrooxazole (48)**

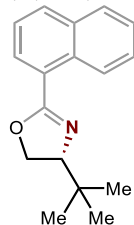


The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **48** as yellow oil (28.5 mg, 96% yield, 90% e.e.).  $[\alpha]^{20}_D = -204.7$  ( $c = 0.15$ ,  $\text{CHCl}_3$ ).  $R_f = 0.45$  (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.18 (d,  $J = 8.7$  Hz, 1H), 8.15 (dd,  $J = 7.3, 1.2$  Hz, 1H), 7.99 (d,  $J = 8.2$  Hz, 1H), 7.88 (dd,  $J = 8.2, 0.6$  Hz, 1H), 7.62 (ddd,  $J = 8.5, 6.8, 1.4$  Hz, 1H), 7.57 – 7.46 (m, 4H), 7.35 – 7.28 (m, 3H), 5.42 (dd,  $J = 10.0, 8.4$  Hz, 1H), 4.74 (dd,  $J = 10.1, 8.0$  Hz, 1H), 4.53 (t,  $J = 8.2$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.60 (s), 133.87 (s), 132.54 (s), 131.96 (s), 131.31 (s), 129.59 (s), 128.58 (s), 128.55 (s), 128.39 (s), 127.65 (s), 126.66 (s), 126.33 (s), 124.72 (s), 124.10 (s), 122.85 (s), 88.12 (s), 84.61 (s), 72.32 (s), 58.82 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  298.1226, found: 298.1226. HPLC

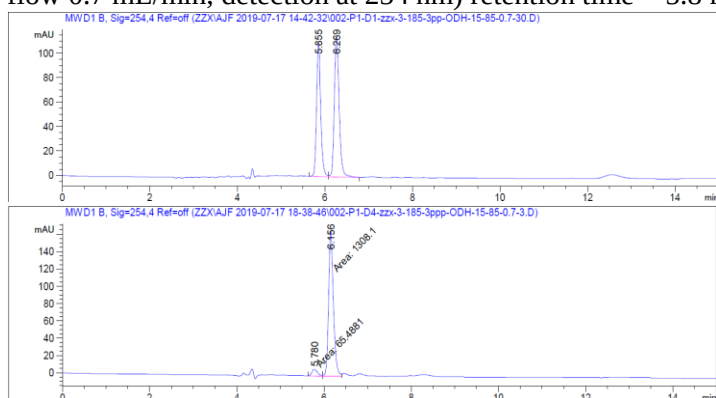
(CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 13.6 min (minor) and 15.6 min (major).



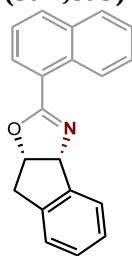
### (R)-4-(tert-butyl)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (49)



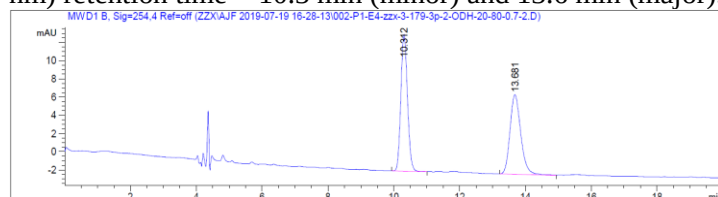
The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **49** as colorless oil (7.6 mg, 30% yield, 91% e.e.).  $[\alpha]_D^{20} = +74.6$  (c = 0.13, CHCl<sub>3</sub>).  $R_f = 0.55$  (hexane : EtOAc = 5:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  9.14 (d,  $J = 8.6$  Hz, 1H), 8.07 (d,  $J = 7.2$  Hz, 1H), 7.95 (d,  $J = 8.2$  Hz, 1H), 7.87 (d,  $J = 8.1$  Hz, 1H), 7.60 (ddd,  $J = 8.5, 6.8, 1.3$  Hz, 1H), 7.55 – 7.45 (m, 2H), 4.40 (dd,  $J = 9.8, 8.5$  Hz, 1H), 4.28 (t,  $J = 8.1$  Hz, 1H), 4.22 (dd,  $J = 9.9, 7.9$  Hz, 1H), 1.05 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  163.35 (s), 133.90 (s), 131.88 (s), 131.44 (s), 129.07 (s), 128.56 (s), 127.42 (s), 126.62 (s), 126.18 (s), 124.94 (s), 124.82 (s), 67.97 (s), 34.28 (s), 29.85 (s), 26.20 (s). HRMS (ESI-TOF)  $m/z$  calcd for [M+H]<sup>+</sup> 254.1539, found: 254.1540. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu$ m, hexane / isopropanol = 85/15, flow 0.7 mL/min, detection at 254 nm) retention time = 5.8 min (minor) and 6.2 min (major).



**(3aR,8aS)-2-(naphthalen-1-yl)-3a,8a-dihydro-8H-indeno[1,2-d]oxazole (50)**



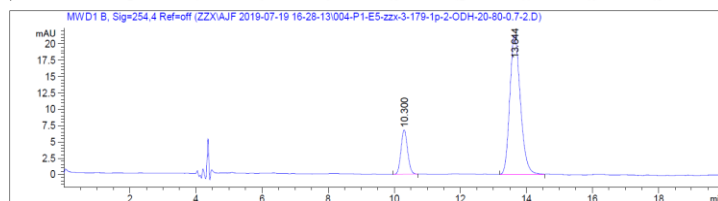
The reaction was conducted on a 0.1 mmol scale according to the [GP3](#). The yield of oxazoline **50** (12% yield, >20:1 d.r., 67% e.e.) was determined by  $^1\text{H}$  NMR using N,N-dimethyl-2,2,2-trifluoroacetamide as internal standard.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.03 (d,  $J$  = 8.5 Hz, 1H), 8.07 – 8.01 (m, 1H), 7.92 (d,  $J$  = 8.2 Hz, 1H), 7.84 (dd,  $J$  = 8.1, 1.4 Hz, 1H), 7.64 (s, 1H), 7.60 – 7.53 (m, 1H), 7.52 – 7.42 (m, 2H), 7.32 – 7.28 (m, 3H), 5.90 (d,  $J$  = 7.9 Hz, 1H), 5.53 (ddd,  $J$  = 8.1, 6.7, 1.7 Hz, 1H), 3.57 (dd,  $J$  = 17.9, 6.7 Hz, 1H), 3.45 (d,  $J$  = 17.9 Hz, 1H). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  286.1226, found: 286.1220. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 10.3 min (minor) and 13.6 min (major).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.312        | BB   | 0.2169      | 209.70259    | 15.02232     | 51.4567 |
| 2      | 13.681        | BB   | 0.3484      | 197.82924    | 8.72775      | 48.5433 |

Totals : 407.53183 23.75007



Signal 1: MWD1 B, Sig=254,4 Ref=off

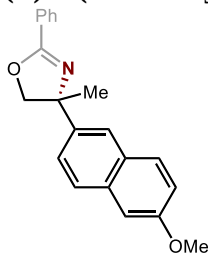
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.300        | BB   | 0.2162      | 94.49783     | 6.79737      | 16.6023 |
| 2      | 13.644        | BB   | 0.3459      | 474.68814    | 21.30805     | 83.3977 |

Totals : 569.18597 28.10542

**(R)-2,4-diphenyl-4,5-dihydrooxazole (51)**

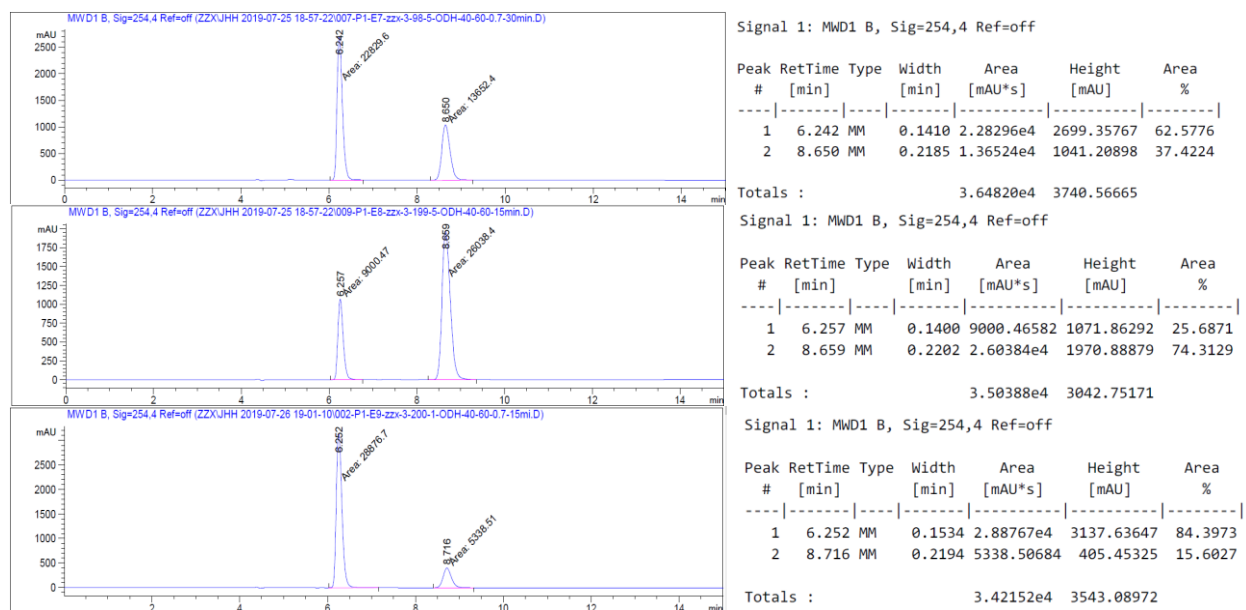
See Mechanistic section ([VIII](#)) for characterization of deuterated product **51**

**(R)-4-(6-methoxynaphthalen-2-yl)-4-methyl-2-phenyl-4,5-dihydrooxazole (52)**

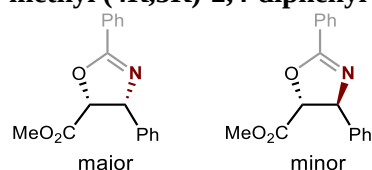


The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **52** as white solid.  $R_f$  = 0.55 (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 – 8.06 (m, 2H), 7.85 (d,  $J$  = 1.9 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.58 – 7.41 (m, 4H), 7.14 (dt,  $J$  = 5.5, 2.5 Hz, 2H), 4.57 – 4.46 (m, 2H), 3.92 (s, 3H), 1.82 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.27 (s), 157.82 (s), 141.93 (s), 133.69 (s), 131.69 (s), 129.76 (s), 128.86 (s), 128.70 (s), 128.55 (s), 127.94 (s), 127.39 (s), 124.59 (s), 123.74 (s), 119.09 (s), 105.69 (s), 80.50 (s), 73.18 (s), 55.44 (s), 29.24 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  318.1489, found: 318.1485. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm)

- 1) For racemic 6.2 min (major) and 8.7 min (minor), 25% e.e..
- 2) For (S,S) 6.2 min (minor) and 8.7 min (major), 49% e.e.,  $[\alpha]^{20} = +36.7$  ( $c = 0.40$ ,  $\text{CHCl}_3$ );
- 3) For (R,R) 6.2 min (major) and 8.7 min (minor), 69% e.e.,  $[\alpha]^{20} = -38.8$  ( $c = 0.49$ ,  $\text{CHCl}_3$ ).



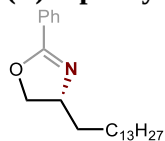
### methyl (4R,5R)-2,4-diphenyl-4,5-dihydrooxazole-5-carboxylate (**53**)



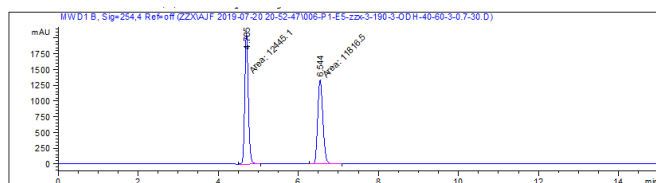
The reaction was conducted on a 0.05 mmol scale according to the [GP3](#) and afforded oxazoline **53** as a mixture of diastereomers by  $^1\text{H}$  NMR analysis using 1,2-dichloroethane as an internal standard (R-catalyst 8:1 cis:trans, 90%; S-catalyst 2:1 cis:trans, 87%).  $R_f = 0.33$  (hexane : EtOAc = 4:1). Major diastereomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (dd,  $J = 8.4, 1.3$  Hz, 2H), 7.63 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.29 (m, 4H), 7.25 – 7.18 (m, 1H), 5.75 (d,  $J = 10.8$  Hz, 1H), 5.39 (d,  $J = 10.8$  Hz, 1H), 3.21 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.82 (s), 164.16 (s), 137.11 (s), 132.09 (s), 129.03 (s), 128.90 (s), 128.63 (s), 128.28 (s), 127.94 (s), 126.64 (s), 81.29 (s), 74.83 (s), 51.74 (s). Minor diastereomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (dd,  $J = 8.4, 1.3$  Hz, 2H), 7.63 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.29 (m, 4H), 7.25 – 7.18 (m, 1H), 5.46 (d,  $J = 6.5$  Hz, 1H), 4.93 (d,  $J = 6.5$  Hz, 1H), 3.88 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.67 (s), 164.95 (s), 141.29 (s), 132.11 (s), 129.54 (s), 128.53 (s), 128.33 (s), 128.21 (s), 127.76 (s), 126.97 (s), 83.32 (s), 73.72 (s), 52.91 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  282.1130, found: 282.1205.



### (R)-2-phenyl-4-tetradecyl-4,5-dihydrooxazole (54)



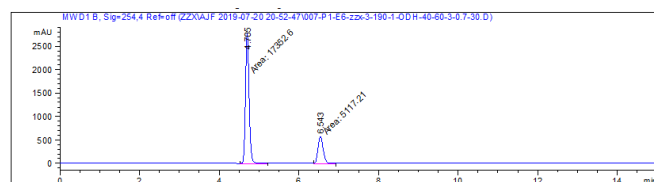
The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **54** as colorless oil (66% yield, 55% e.e.).  $R_f$  = 0.61 (hexane : EtOAc = 4:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 – 7.86 (m, 1H), 7.59 – 7.33 (m, 2H), 4.48 (dd,  $J$  = 9.4, 8.1 Hz, 1H), 4.37 – 4.18 (m, 1H), 4.03 (t,  $J$  = 8.0 Hz, 1H), 1.86 – 1.63 (m, 1H), 1.53 – 1.21 (m, 13H), 0.88 (t,  $J$  = 6.9 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.56 (s), 157.18 (s), 131.17 (s), 130.60 (s), 129.40 (s), 128.54 (s), 127.60 (s), 122.08 (s), 114.58 (s), 73.27 (s), 32.08 (s), 30.36 (s), 29.86 (s), 29.84 – 29.84 (s), 29.83 (s), 29.83 (s), 29.81 (s), 29.80 (s), 29.72 (s), 29.68 (s), 29.52 (s), 29.44 (s), 25.89 (s), 22.85 (s), 14.27 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  344.2948, found: 344.3071. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 4.7 min (major) and 6.5 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 4.705         | MM   | 0.0997      | 1.24451e4    | 2079.80151   | 51.2954 |
| 2      | 6.544         | MM   | 0.1469      | 1.18165e4    | 1340.88123   | 48.7046 |

Totals : 2.42616e4 3420.68274

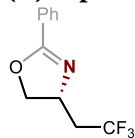


Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 4.705         | MM   | 0.1038      | 1.73526e4    | 2787.43628   | 77.2263 |
| 2      | 6.543         | MM   | 0.1478      | 5117.21045   | 576.86414    | 22.7737 |

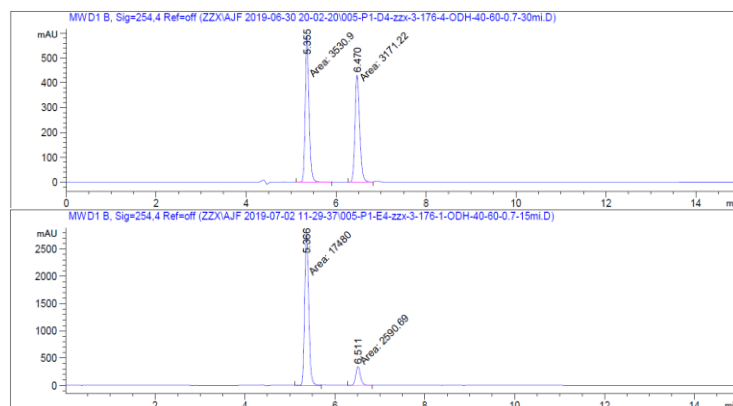
Totals : 2.24698e4 3364.30042

### (R)-2-phenyl-4-(2,2,2-trifluoroethyl)-4,5-dihydrooxazole (55)



The reaction was conducted on a 0.1 mmol scale according to the [GP3](#) and afforded oxazoline **55** as colorless oil (10.1 mg, 44% yield, 74% e.e.).  $[\alpha]^{20}_D$  = +11.2 ( $c$  = 0.5,  $\text{CHCl}_3$ ).  $R_f$  = 0.65 (hexane : EtOAc = 5:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 – 7.91 (m, 2H), 7.50 (ddd,  $J$  = 8.7, 2.6, 1.3 Hz, 1H), 7.45 – 7.39 (m, 2H), 4.64 – 4.53 (m, 2H), 4.20 (t,  $J$  = 7.7 Hz, 1H), 2.79 (dq,  $J$  = 14.9, 11.4, 3.6 Hz, 1H), 2.36 – 2.17 (m, 1H).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.31 (t,  $J$  = 10.9 Hz).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  165.11 (s), 131.91 (s), 128.58 (s), 128.51 (s), 127.26 (s), 126.08 (q,  $J$  = 277.1 Hz), 72.56 (s), 61.32 (q,  $J$  = 2.9 Hz), 39.88 (q,  $J$  = 27.2 Hz). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  230.0787, found: 230.0790. Note: the titled compound has a low boiling point. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.4 min (major) and 6.5 min (minor).





Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.355         | MM   | 0.1002      | 3530.90308   | 587.08289    | 52.6834 |
| 2      | 6.470         | MM   | 0.1224      | 3171.21582   | 431.72452    | 47.3166 |

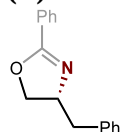
Totals : 6702.11890 1018.80740

Signal 1: MWD1 B, Sig=254,4 Ref=off

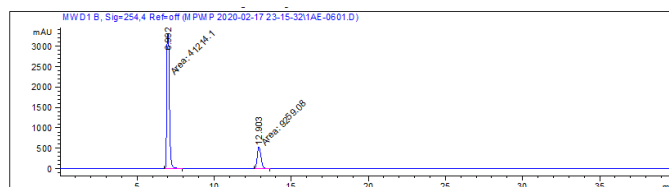
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.366         | MM   | 0.1055      | 1.74800e4    | 2762.57593   | 87.0922 |
| 2      | 6.511         | MM   | 0.1244      | 2590.68945   | 347.00601    | 12.9078 |

Totals : 2.00707e4 3109.58194

### (R)-4-benzyl-2-phenyl-4,5-dihydrooxazole (56)



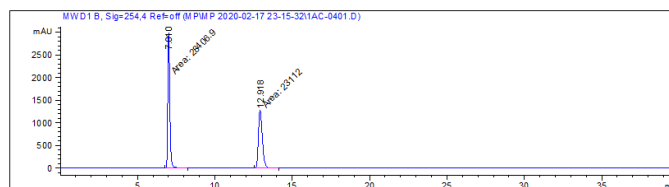
The reaction was conducted on a 0.05 mmol scale according to the [GP3](#) and afforded oxazoline **56** which matched literature precedent<sup>4</sup> (59% yield, 63% e.e.). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.01 – 7.87 (m, 2H), 7.53 – 7.47 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.19 (m, 1H), 4.67 – 4.51 (m, 1H), 4.43 – 4.25 (m, 1H), 4.15 (dd, *J* = 8.3, 7.5 Hz, 1H), 3.25 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.74 (dd, *J* = 13.8, 8.9 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 163.13 (s), 137.17 (s), 130.48 (s), 128.42 (s), 127.71 (s), 127.47 (s), 127.41 (s), 126.96 (s), 125.66 (s), 71.03 (s), 67.06 (s), 41.01 (s). Matches previously reported characterization.



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.010         | MM   | 0.1588      | 2.84069e4    | 2981.59204   | 55.1388 |
| 2      | 12.918        | MM   | 0.3015      | 2.31120e4    | 1277.54309   | 44.8612 |

Totals : 5.15188e4 4259.13513



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.992         | MM   | 0.2081      | 4.12141e4    | 3300.15332   | 81.6555 |
| 2      | 12.903        | MM   | 0.2900      | 9259.07715   | 532.07904    | 18.3445 |

Totals : 5.04732e4 3832.23236

### (R,Z)-4-(but-1-en-1-yl)-2-phenyl-4,5-dihydrooxazole (57, major)

See Mechanistic section ([VIII](#)) for characterization of radical clock **57**

### (R,E)-4-(but-1-en-1-yl)-2-phenyl-4,5-dihydrooxazole (58, major)

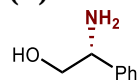
See Mechanistic section ([VIII](#)) for characterization of radical clock **58**

### (R,E)-5-phenylpent-2-en-1-yl benzimidate (59)

See Mechanistic section ([VIII](#)) for characterization of radical clock **59**

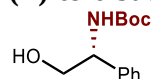
## VII. Post-Functionalization of Oxazolines

### (R)-2-amino-2-phenylethan-1-ol (**60**)

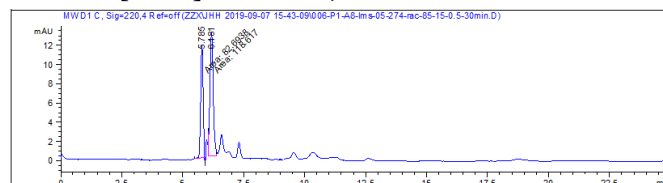


To a vial containing oxazoline **1** (22.3 mg, 0.1 mmol) was added 4 M aq. HCl (0.5 mL), according to the literature<sup>5</sup>. The suspension was heated to 100 °C for 16 hrs. The reaction was allowed to cool to room temperature and quenched with 4M aq. NaOH (0.5 mL). The aqueous solution was extracted with Et<sub>2</sub>O (5 x 10 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo* to afford the amino alcohol **60** as a white solid (10.6 mg, 77%).  $[\alpha]^{20} = -32.0$  (c = 0.125, CHCl<sub>3</sub>) <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 4.05 (dd, *J* = 8.2, 4.4 Hz, 1H), 3.75 (dd, *J* = 10.7, 4.4 Hz, 1H), 3.56 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.06 (s, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  142.95 (s), 128.88 (s), 127.75 (s), 126.65 (s), 68.24 (s), 57.54 (s). HRMS (ESI-TOF) calcd. for [M+H]<sup>+</sup> 138.0919, found: 138.0935.

### (R)-tert-butyl-(2-hydroxy-1-phenylethyl)carbamate (**60Boc**)



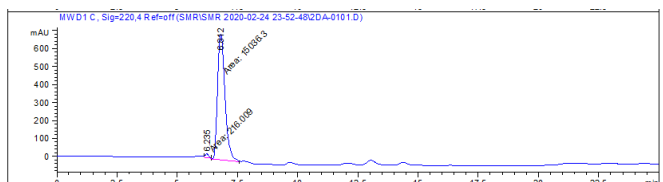
Amino alcohol **60** (9 mg, 0.065 mmol, 1 equiv) and trimethylamine (10.8  $\mu$ L, 0.078 mmol, 1.2 equiv) were dissolved in dry THF (2 mL) and cooled to 0°C. Di-tert-butyl dicarbonate (14.2 mg, 0.065 mmol, 1 equiv) was added to the solution and the mixture was allowed to stir at room temperature overnight. The reaction was concentrated, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and washed with 1M HCl extracting with CH<sub>2</sub>Cl<sub>2</sub>. The solution was dried and concentrated to dryness to afford the pure product **60Boc** (9.4 mg, 61%, 98% e.s.) and was utilized to determine e.s.% of **60**. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.33 (m, 2H), 7.29 (m, 3H), 5.20 (s, 1H), 4.79 (s, 1H), 3.85 (s, 2H), 2.28 (s, 1H), 1.44 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  156.72 – 155.83 (m), 128.99 (s), 127.95 (s), 126.72 (s), 80.16 (s), 67.18 (s), 57.07 (s), 29.85 (s), 28.49 (s). HRMS (ESI-TOF) calcd. for [M+H]<sup>+</sup> 238.1438, found: 238.1461.



Signal 2: MWD1 C, Sig=220,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.785         | MM   | 0.1183      | 82.69376     | 11.64687     | 41.0777 |
| 2      | 6.181         | MM   | 0.1542      | 118.61689    | 12.82117     | 58.9223 |

Totals : 201.31065 24.46805

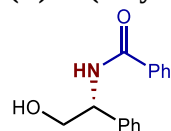


Signal 2: MWD1 C, Sig=220,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.235         | MM   | 0.1695      | 216.00876    | 21.24040     | 1.4162  |
| 2      | 6.812         | MM   | 0.3580      | 1.50363e4    | 700.09528    | 98.5838 |

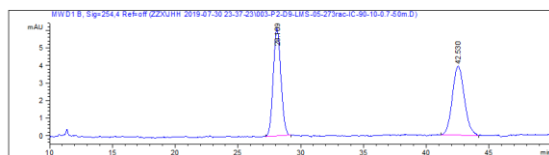
Totals : 1.52523e4 721.33568

### (R)-N-(2-hydroxy-1-phenylethyl)benzamide (**61**)



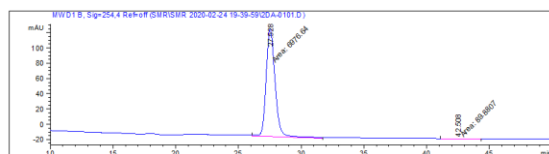
The hydrolysis of oxazoline **1** was prepared from a modified literature procedure<sup>6</sup>. Oxazoline **1** (48.2 mg, 0.1 mmol) 2M HCl (0.2 mL) was dissolved in THF (2 mL) and stirred at room temperature for 12 hrs. The reaction was quenched with 6M NaOH (0.8 mL) and extracted with EtOAc. The solvent was concentrated and loaded onto a silica gel column (hexanes to 50% EtOAc-Hexanes) to afford the pure product **61** as a

white solid (44 mg, 91%, 99% e.s. from 99% e.e. **1**).  $[\alpha]^{20} = 9.2$  ( $c = 0.12$ ,  $\text{CHCl}_3$ )  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.79 (m, 2H), 7.56 – 7.48 (m, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 7.42 – 7.37 (m, 4zH), 7.35 – 7.30 (m, 1H), 6.80 (s, 1H), 5.29 (ddd,  $J = 11.1, 5.5, 3.9$  Hz, 1H), 4.03 (qd,  $J = 11.3, 4.7$  Hz, 2H), 2.51 (s, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  167.97 (s), 139.07 (s), 134.25 (s), 131.95 (s), 129.19 (s), 128.81 (s), 128.20 (s), 127.22 (s), 126.87 (s), 66.94 (s), 56.45 (s). HRMS (ESI-TOF) calcd.  $[\text{M}+\text{Na}]^+$  264.1000, found: 264.1010. HPLC (CHIRALCEL IC, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 90/10, flow 0.7 mL/min, detection at 254 nm)



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 28.109        | BB   | 0.6207      | 260.33878    | 6.11465      | 49.7011 |
| 2      | 42.530        | BB   | 0.7903      | 263.47009    | 3.92946      | 50.2989 |

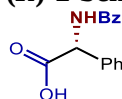


Signal 1: MWD1 B, Sig=254,4 Ref=off

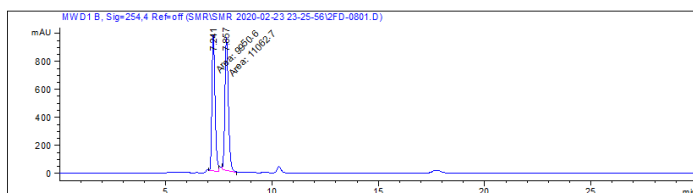
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 27.528        | MM   | 0.8269      | 6976.64160   | 140.62228    | 98.7281 |
| 2      | 42.508        | MM   | 2.7158      | 89.88070     | 5.51595e-1   | 1.2719  |

Totals : 7066.52230 141.17388

## (R)-2-benzamido-2-phenylacetic acid (**62**)



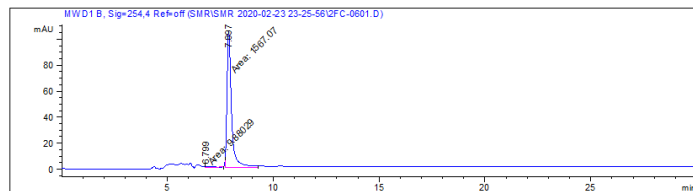
The oxidation of benzamide **61** was afforded from a literature procedure<sup>7</sup>. Amido alcohol **61** (48.2 mg, 0.2 mmol),  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  (16.6 mg, 0.08 mmol, 0.04 equiv), and  $\text{NaIO}_4$  (85.6 mg, 0.8 mmol, 4 equiv) was dissolved in acetonitrile (0.6 mL) and water (0.4 mL) and stirred at room temperature for 2.5 hrs. The reaction was diluted with water and extracted with EtOAc. The solvent was concentrated and analyzed by  $^1\text{H}$ NMR with 1,2-dichloroethane as an internal standard resulting in 47% of product **62**. The crude mixture was triturated with cold diethylether to afford the pure product **62** as an off-white solid (12 mg, 30%, 99% e.s. from 99% e.e. **1**).  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.67 (s, 1H), 7.86 (d,  $J = 7.5$  Hz, 2H), 7.54 (t,  $J = 7.3$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.42 (d,  $J = 7.5$  Hz, 2H), 7.29 (t,  $J = 7.5$  Hz, 2H), 7.22 (t,  $J = 7.2$  Hz, 1H), 5.20 (s, 1H). HRMS (ESI) calcd. For  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  278.0818, found: 278.0181. HPLC (CHIRALCEL IC, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm)



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 7.241         | MM   | 0.1695      | 9950.60254   | 978.71228    | 47.3538 |
| 2      | 7.857         | MM   | 0.1930      | 1.10627e4    | 955.49493    | 52.6462 |

Totals : 2.10133e4 1934.20721

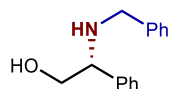


Signal 1: MWD1 B, Sig=254,4 Ref=off

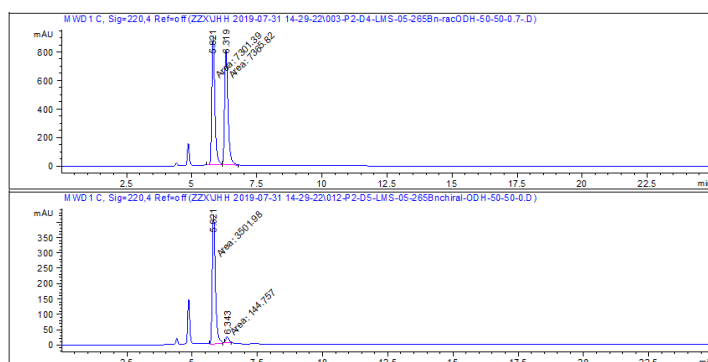
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 6.799         | MM   | 0.3157      | 9.88029      | 5.21579e-1   | 0.6265  |
| 2      | 7.897         | MM   | 0.2496      | 1567.07422   | 104.62268    | 99.3735 |

Totals : 1576.95451 105.14426

### (R)-2-(benzylamino)-2-phenylethan-1-ol (63)



The reduction of oxazoline **1** was performed with the following literature procedure<sup>8</sup>. Oxazoline **1** (22.3 mg, 0.1 mmol) was dissolved in dry THF (0.5 mL) under nitrogen and cooled to 0°C. DIBAL (0.3 mL, 3 equiv, 1.0 M in hexanes) was added dropwise and the mixture gradually warmed to room temperature. The solution was cooled to 0°C and slowly quenched with 1 M HCl. The organic layer was separated and the aqueous layer was basified with 5 M NaOH until pH 14. The solution was extracted with Et<sub>2</sub>O, washed with water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo* to afford the pure product **63** as a white solid (17.9 mg, 79%, 98% e.s. from 94% e.e. **1**).  $[\alpha]^{20}_D = -33.2$  (c = 0.25, CHCl<sub>3</sub>) <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.28 (m, 7H), 7.28 – 7.23 (m, 1H), 3.83 (dd, *J* = 8.6, 4.5 Hz, 1H), 3.77 (d, *J* = 13.0 Hz, 1H), 3.72 (dd, *J* = 10.8, 4.5 Hz, 1H), 3.61 (d, *J* = 13.0 Hz, 1H), 3.57 (dd, *J* = 10.7, 8.7 Hz, 1H), 2.19 (s, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 140.60 (s), 140.16 (s), 128.87 (s), 128.60 (s), 128.37 (s), 127.86 (s), 127.42 (s), 127.25 (s), 66.90 (s), 63.89 (s), 51.31 (s). HRMS (ESI) calcd. for [M+Na]<sup>+</sup> 250.1208, found: 250.1223. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5μm, hexane / isopropanol = 50/50, flow 0.7 mL/min, detection at 220 nm)



Signal 2: MWD1 C, Sig=220,4 Ref=off

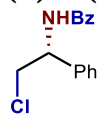
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.821         | MM   | 0.1343      | 7301.39307   | 906.38324    | 49.7804 |
| 2      | 6.319         | MM   | 0.1538      | 7365.81592   | 798.10791    | 50.2196 |

Totals : 1.46672e4 1704.49115

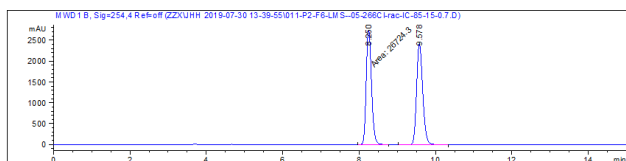
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.821         | MM   | 0.1384      | 3501.97559   | 421.75717    | 96.0305 |
| 2      | 6.343         | MM   | 0.1397      | 144.75726    | 17.26921     | 3.9695  |

Totals : 3646.73285 439.02638

### (R)-N-(2-chloro-1-phenylethyl)benzamide (64)



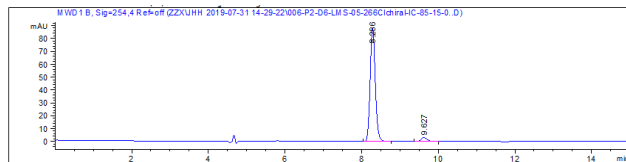
The nucleophilic ring opening of oxazoline **1** was conducted following a modified literature procedure<sup>6</sup>. To a solution of oxazoline **1** (22.3 mg, 0.1 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub>, was added Me<sub>3</sub>SiCl (50.8 μL, 0.4 mmol, 4 equiv, portion-wise, 2 equiv added after 16 hrs). The mixture stirred at room temperature until the reaction reached completion. The reaction was concentrated and analyzed by crude <sup>1</sup>H NMR using 1,2-dichloroethane as an internal standard, which provide a yield of 88% of compound **64**. The mixture was then loaded onto a silica gel column (hexanes – 20% ethyl acetate/hexanes) to afford the desired chloride **60** as an off-white solid (17.2 mg, 69%, 98% e.s. from 94% e.e. **1**).  $[\alpha]^{20}_D = 9.1$  (c = 0.175, CHCl<sub>3</sub>) <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.37 (m, 4H), 7.37 – 7.30 (m, 1H), 6.74 (s, 1H), 5.58 (dt, *J* = 7.8, 5.1 Hz, 1H), 4.04 – 3.97 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.09 (s), 138.56 (s), 134.16 (s), 132.03 (s), 129.02 (s), 128.86 (s), 128.36 (s), 127.20 (s), 126.86 (s), 53.98 (s), 47.90 (s). HRMS (ESI-TOF) calcd. for [M+Na]<sup>+</sup> 282.0662, found: 282.0669. HPLC (CHIRALCEL IC, 0.46\*25 cm, 5μm, hexane / isopropanol = 85/15, flow 0.7 mL/min, detection at 254 nm)



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.250         | MM   | 0.1616      | 2.67243e4    | 2756.47534   | 49.7977 |
| 2      | 9.578         | VB R | 0.1718      | 2.69414e4    | 2419.10278   | 50.2023 |

Totals : 5.36657e4 5175.57813

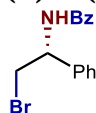


Signal 1: MWD1 B, Sig=254,4 Ref=off

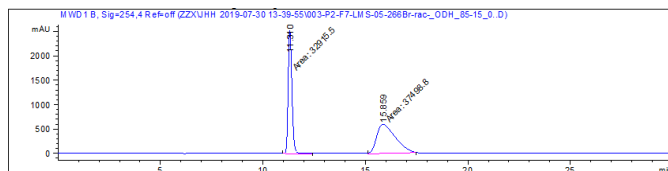
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 8.286         | BB   | 0.1442      | 819.99628    | 88.39642     | 96.0448 |
| 2      | 9.627         | BB   | 0.1695      | 33.76827     | 3.04137      | 3.9552  |

Totals : 853.76455 91.43780

### (R)-N-(2-bromo-1-phenylethyl)benzamide (65)



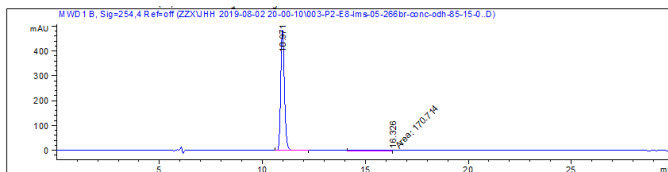
The nucleophilic ring opening of oxazoline **1** was conducted following a modified literature procedure<sup>6</sup>. To a solution of oxazoline **1** (22.3 mg, 0.1 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub>, was added Me<sub>3</sub>SiBr (52.8 μL, 0.4 mmol, 2 equiv portion wise, 2 equiv added after 16 hrs). The mixture stirred at room temperature until the reaction reached completion. The reaction was concentrated and analyzed by crude <sup>1</sup>H NMR using 1,2-dichloroethane as an internal standard, which provide a yield of 89% of compound **65**. The mixture was then loaded onto a silica gel column (hexanes – 20% ethyl acetate/hexanes) to afford the desired bromide **61** as an off-white solid (17.1 mg, 66%, 99% e.s., from 94% e.e. **1**). [α]<sub>D</sub><sup>20</sup> = -66.7 (c = 0.03, CHCl<sub>3</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 – 7.78 (m, 2H), 7.58 – 7.51 (m, 1H), 7.51 – 7.43 (m, 2H), 7.43 – 7.38 (m, 4H), 7.38 – 7.29 (m, 1H), 6.68 (s, 1H), 5.56 (dt, J = 7.7, 5.2 Hz, 1H), 4.05 – 3.75 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 166.98 (s), 138.95 (s), 134.14 (s), 132.05 (s), 129.03 (s), 128.88 (s), 128.38 (s), 127.20 (s), 126.72 (s), 53.53 (s), 37.13 (s). HRMS (ESI-TOF) calcd. for [M+Na]<sup>+</sup> 326.0156, found: 326.0163. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5μm, hexane / isopropanol = 85/15, flow 0.7 mL/min, detection at 254 nm).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 11.310        | MM   | 0.2174      | 3.29155e4    | 2523.24634   | 46.7455 |
| 2      | 15.859        | MM   | 1.0506      | 3.74988e4    | 594.85748    | 53.2545 |

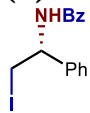
Totals : 7.04143e4 3118.10382



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 10.971        | BB   | 0.1954      | 6128.93408   | 485.19229    | 97.2901 |
| 2      | 16.326        | MM   | 1.5020      | 170.71431    | 1.89436      | 2.7099  |

Totals : 6299.64839 487.08665

### (R)-N-(2-iodo-1-phenylethyl)benzamide (66)

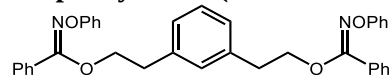


The nucleophilic ring opening of oxazoline **1** was conducted following a modified literature procedure<sup>6</sup>. To a 2-dram vial equipped with PTFE septa cap and magnetic stir bar, was added hexamethyldisilane (0.2 mmol) and I<sub>2</sub> (0.2 mmol) under N<sub>2</sub>. The reaction was refluxed for 2 hours. After cooling to room temperature, this *in situ* generated Me<sub>3</sub>SiI was added to a solution of oxazoline **1** (22.3 mg, 0.1 mmol) in

CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), stirred for 12 hours, and analyzed by crude <sup>1</sup>H NMR using 1,2-dichloroethane as an internal standard, which provide a yield of 66% of compound. The reaction was concentrated, and loaded directly onto alumina to afford the target iodide **66** with reverted oxazoline **1**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 – 7.79 (m, 2H), 7.57 – 7.50 (m, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.30 (m, 5H), 6.59 (s, 1H), 5.33 – 5.25 (m, 1H), 3.69 (ddd, *J* = 20.9, 10.3, 5.7 Hz, 2H).

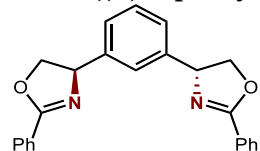
Note: Aluminium oxide, acidic (Brockmann I, 50 – 200 m, LOT: A0303504, CAS: 1344-28-1) was used to isolate the desired product, which is prone to reverting to starting material, oxazoline **1**, by cyclization on itself.

### 1,3-phenylenebis(ethane-2,1-diyl)-bis(N-phenoxybenzimidate) (67)

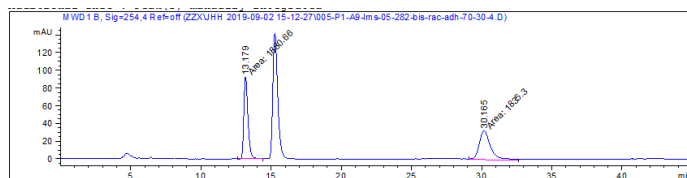


Prepared following [GP1](#) using 2.2 equivalents of imidoyl chloride. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.77 – 7.72 (m, 4H), 7.44 – 7.41 (m, 4H), 7.22 – 7.18 (m, 4H), 7.10 – 7.02 (m, 7H), 6.91 (ddd, *J* = 7.4, 5.4, 1.3 Hz, 5H), 4.45 (t, *J* = 6.9 Hz, 4H), 2.80 (t, *J* = 6.9 Hz, 4H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 160.08 (s), 156.70 (s), 138.33 (s), 131.64 (s), 130.61 (s), 130.36 (s), 129.71 (s), 128.95 (s), 128.53 (s), 127.79 (s), 127.64 (s), 122.42 (s), 114.89 (s), 73.52 (s), 36.79 (s). HRMS (ESI) calcd for [M+Na]<sup>+</sup> 579.2260, found: 579.2257.

### 1,3-bis((R)-2-phenyl-4,5-dihydrooxazol-4-yl)benzene (68)



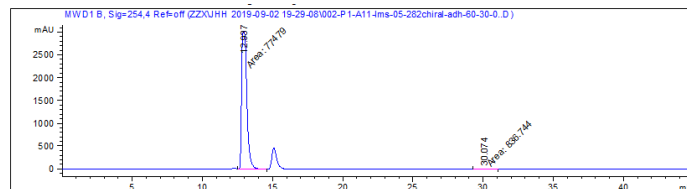
The reaction was conducted on a 0.1 mmol scale according to the [GP3](#). Bis-oxazoline **68** was isolated as a white solid following column chromatography on silica gel (24.3 mg, 66% yield, 98% e.e., 15:1 d.r. determined by <sup>1</sup>H NMR of crude reaction mixture). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 – 7.98 (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.39 (m, 4H), 7.39 – 7.32 (m, 1H), 7.28 – 7.22 (m, 3H), 5.40 (dd, *J* = 10.1, 8.2 Hz, 2H), 4.79 (dd, *J* = 10.1, 8.4 Hz, 2H), 4.27 (t, *J* = 8.3 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.98 (s), 143.03 (s), 131.67 (s), 129.48 (s), 128.63 (s), 128.56 (d, *J* = 11.9 Hz), 127.68 (s), 126.09 (s), 125.42 (s), 74.93 (s), 70.17 (s). HRMS (ESI-TOF) *m/z* calcd for [M+H]<sup>+</sup> 369.1603, found: 369.1610. HPLC (CHIRALCEL AD-H, 0.46\*25 cm, 5μm, hexane / isopropanol = 70/30, flow 0.7 mL/min, detection at 254 nm) retention time = 13.2 min (major) and 30.2 min (minor).



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 13.179        | MM   | 0.3387      | 1880.65784   | 92.54084     | 50.6102 |
| 2      | 30.165        | MM   | 0.9401      | 1835.30457   | 32.53606     | 49.3898 |

Totals : 3715.96240 125.07690



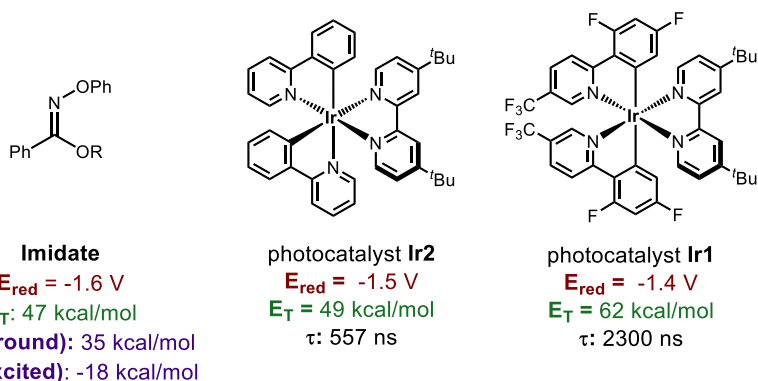
Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 12.937        | MM   | 0.4276      | 7.74790e4    | 3020.24414   | 98.9316 |
| 2      | 30.074        | MM   | 0.9919      | 836.74445    | 14.05898     | 1.0684  |

Totals : 7.83158e4 3034.30312

## VIII. Mechanistic Experiments

### a. Energy Transfer



The CV and DFT experimental data used to compare the ‘energy transfer’ vs ‘electron transfer’ mechanisms can be found in the following sources:

#### imide:

$E_{\text{red}}$ : see reference<sup>1</sup>

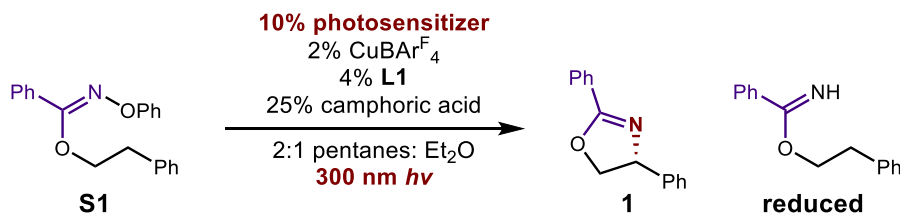
$E_{\text{T}}$ : see calculations below (section IX)

#### photocatalysts:

$E_{\text{red}}$  and  $\tau$ : see reference<sup>9</sup>

$E_{\text{T}}$ : see reference<sup>10</sup>

**Table 2.** Triplet energy sensitizer experiments.

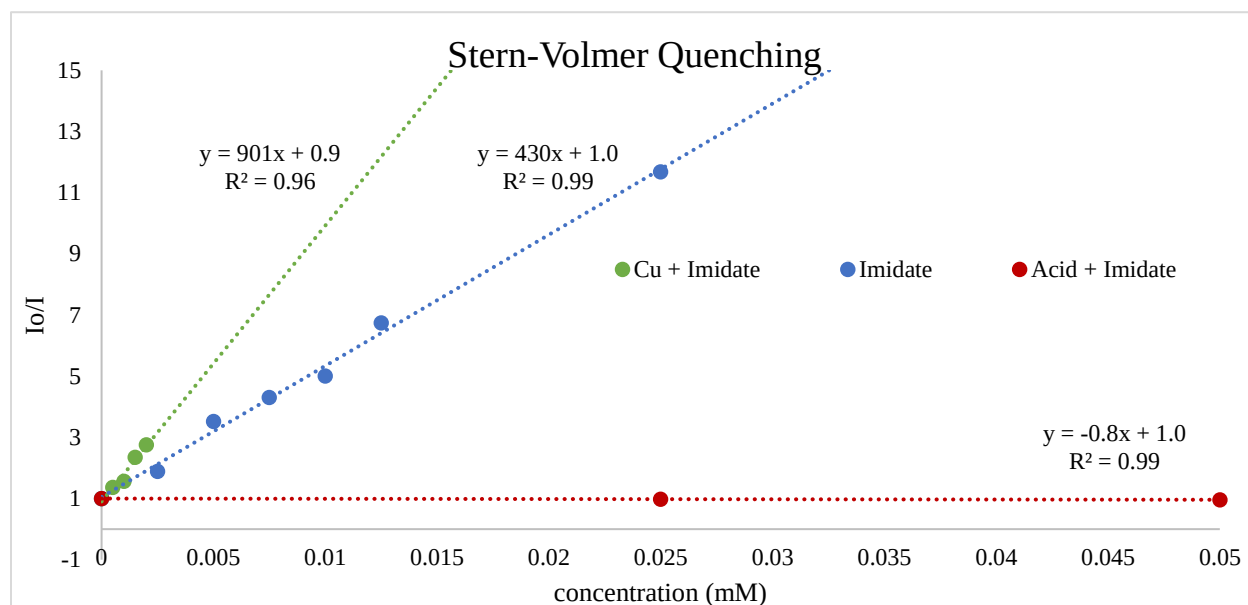


| entry | photosensitizer | $E_{\text{T}}$ (kcal/mol) | <b>1</b> | <b>reduced</b> | <b>S1</b> |
|-------|-----------------|---------------------------|----------|----------------|-----------|
| 1     | none            | -                         | 24%      | 37%            | 23%       |
| 2     | naphthalene     | 61.0                      | 37%      | 33%            | 12%       |
| 3     | xanthone        | 74.1                      | 45%      | 27%            | 17%       |

To probe the role of the Ir photocatalyst as a triplet sensitizer (versus single electron reductant), additional triplet energy sensitizer experiments were conducted. According to the proposed mechanism, the N-centered radical should also be accessible via direct UV irradiation of the oxime imide. To test this, oxime imide **S1** was irradiated with 300 nm light, both in the presence and absence of known UV-absorbing photosensitizers. Oxazoline **1** was formed in all cases, along with the reduction side-product, which is consistent with the proposed triplet energy transfer mechanism to access N-centered radicals via N-O homolysis. Most notably, reactivity with only direct irradiation is inconsistent with an SET based activation.

## b. Stern-Volmer Quenching Studies

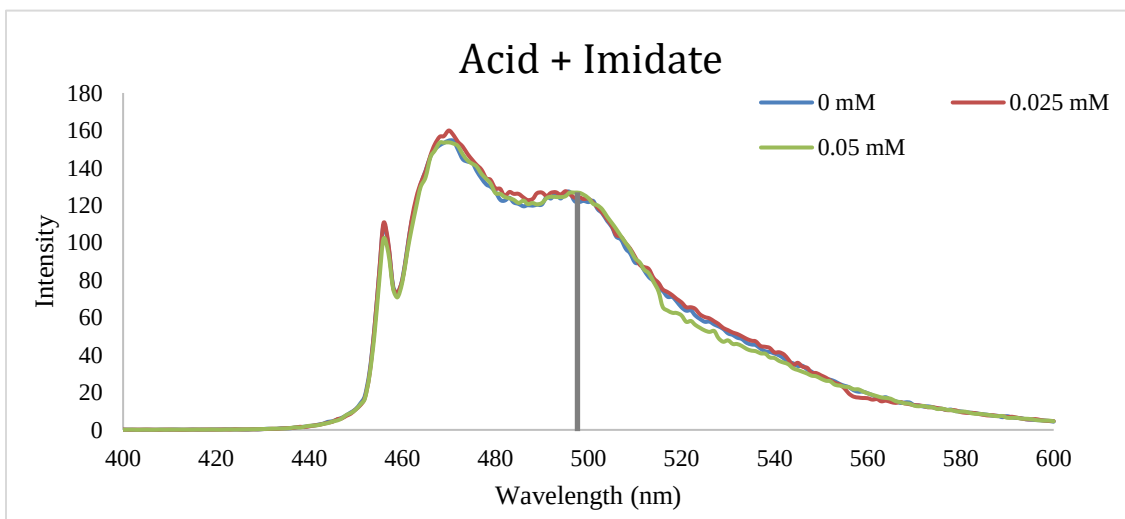
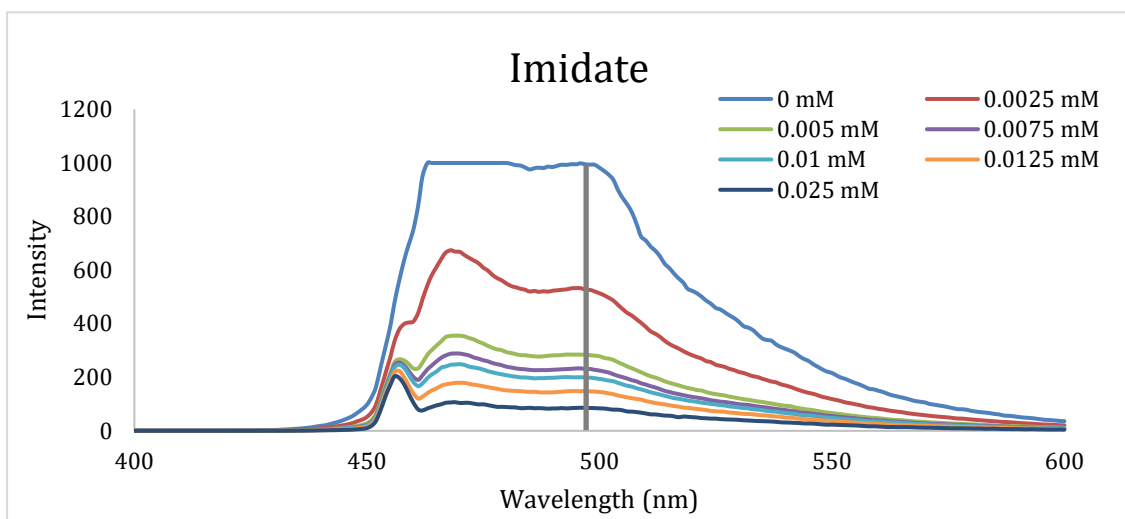
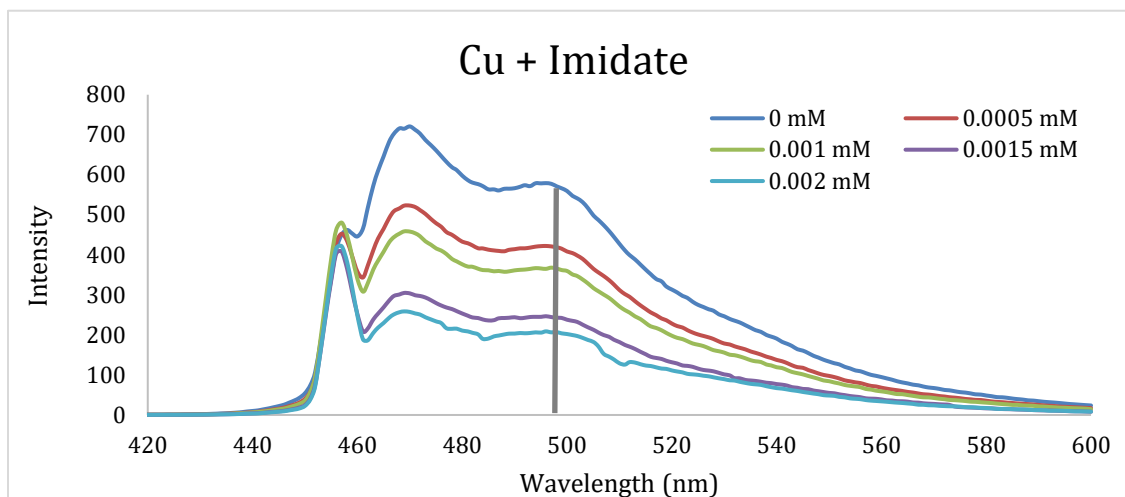
A Stern-Volmer quenching study was conducted to probe the rate of excited state photocatalyst decay in the presence of each reactant or reactant combination. Fluorescence quenching experiments were performed on Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer. A stock solution was prepared of **Ir1**· $\text{BAr}^{\text{F}_4}$  in dry, degassed  $\text{Et}_2\text{O}$  in a glovebox. In a typical experiment, a 0.005 mM solution of **Ir1**· $\text{BAr}^{\text{F}_4}$  was added to varying amount of quencher in 1.0 cm quartz cuvette under  $\text{N}_2$ . The solution was diluted with  $\text{Et}_2\text{O}$  to a 3 mL total volume and the emission spectrum was collected. All solutions were excited at  $\lambda = 455$  nm and emission intensity at  $\lambda = 498$  nm was analyzed. Three separate quenching studies were performed, using imidate **S1**, with or without camphoric acid and  $\text{CuBAr}^{\text{F}_4}$ . For the combination studies, to account for background imidate quenching, imidate **S1** was held constant (0.0005 mM for Cu; 0.025 mM for camphoric acid) and increasing concentrations of the other component was varied.



**Fig. 1.** Excited state photocatalyst quenching is observed for imidate **S1** alone (blue line). Yet, no quenching is observed for camphoric acid and imidate (red line) – suggesting against proton-coupled electron transfer. Significantly increased quenching is observed for Cu and imidate (green line), as indicated by a nearly doubled slope – suggesting Cu is coordinated to imidate during radical initiation.

| Cu + Imidate |     |         | Imidate    |     |         | Acid + Imidate |     |         |
|--------------|-----|---------|------------|-----|---------|----------------|-----|---------|
| conc. (mM)   | I   | $I_0/I$ | conc. (mM) | I   | $I_0/I$ | conc. (mM)     | I   | $I_0/I$ |
| 0            | 571 | 1       | 0          | 994 | 1       | 0              | 122 | 1       |
| 0.0005       | 419 | 1.36    | 0.0025     | 526 | 1.89    | 0.025          | 124 | 0.98    |
| 0.0010       | 366 | 1.56    | 0.0050     | 283 | 3.51    | 0.050          | 127 | 0.96    |
| 0.0015       | 243 | 2.35    | 0.0075     | 231 | 4.30    |                |     |         |
| 0.0020       | 207 | 2.76    | 0.0100     | 198 | 5.02    |                |     |         |
|              |     |         | 0.0125     | 147 | 6.76    |                |     |         |
|              |     |         | 0.0250     | 85  | 11.69   |                |     |         |





### c. Kinetic Isotope Effects (KIE)

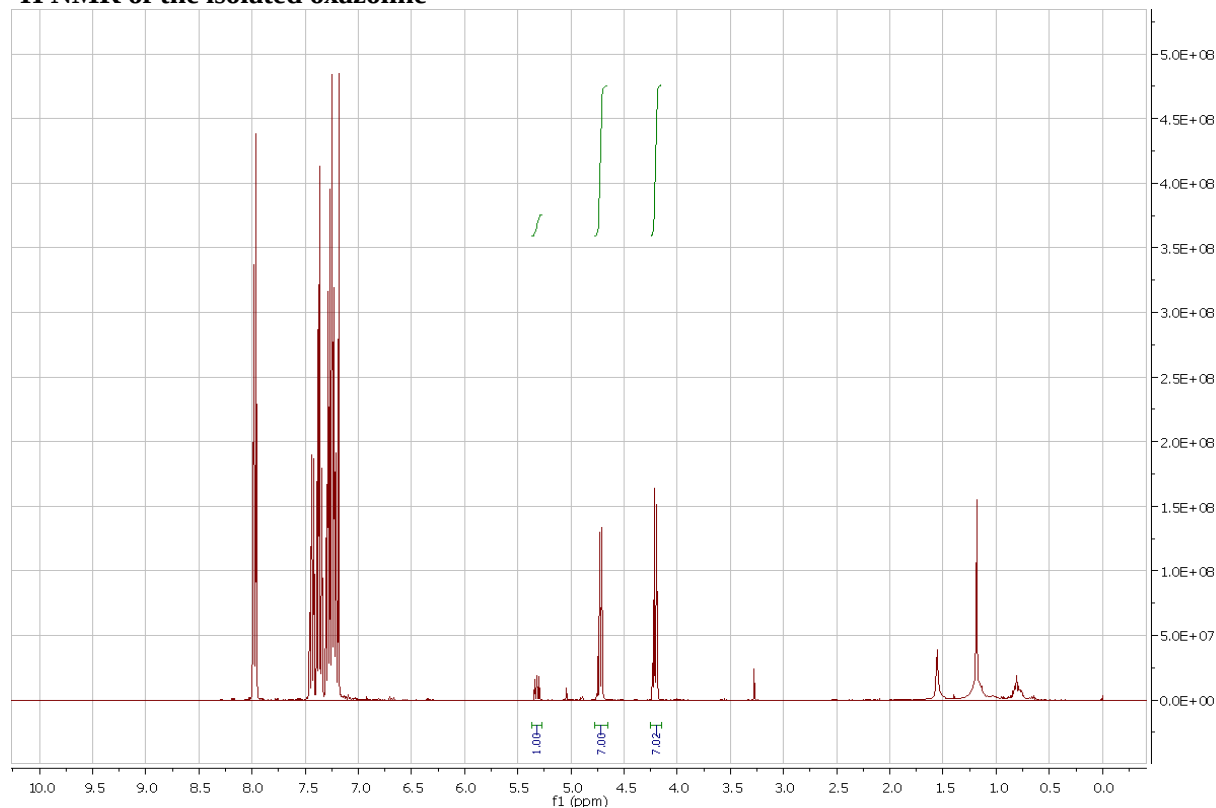
To determine if the hydrogen atom transfer (HAT) step is involved in the product determining step, an intramolecular KIE study was performed. Upon subjecting  $\beta$ -d1 phenylethanol imidate **S51** to **GP3**, the deuterium incorporation was analyzed by  $^1\text{H}$  NMR of the isolated oxazoline. Imidate

Imidate **S51** (15.9 mg, 0.05 mmol) was subjected to **GP3**. The product was isolated following chromatography on silica gel eluting with 10% EtOAc-Hexanes to give a white solid (9 mg, 81%).  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.77 – 7.73 (m, 2H), 7.46 – 7.41 (m, 1H), 7.22 – 7.18 (m, 1H), 7.13 – 7.00 (m, 5H), 6.91 (tt,  $J$  = 7.4, 1.0 Hz, 1H), 4.44 (d,  $J$  = 6.8 Hz, 1H), 2.86 – 2.68 (m, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.90 (s), 142.55 (s), 142.50 (s), 131.68 (s), 128.91 (s), 128.63 (s), 128.52 (s), 127.78 (s), 127.74 (s), 126.90 (s), 75.04 (s), 74.95 (s), 70.30 (s), 70.08 – 69.67 (m), 29.85 (s). HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  260.1263, found: 206.1236.

To calculate KIE, the ratio of *protio*- to *deuterio*-oxazoline formed was determined. The observed 7:1 methylene:methine ratio corresponds to 6/7 (or 86%) D-incorporation. An 86:14 D:H ratio in the product indicates a KIE of 6.1.



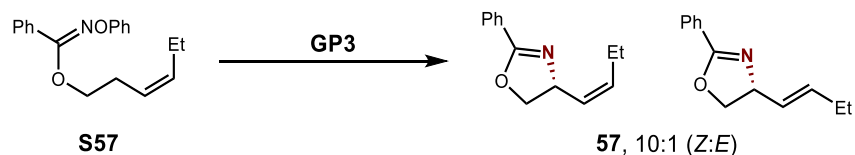
#### $^1\text{H}$ NMR of the isolated oxazoline



#### d. Radical Clock Experiments

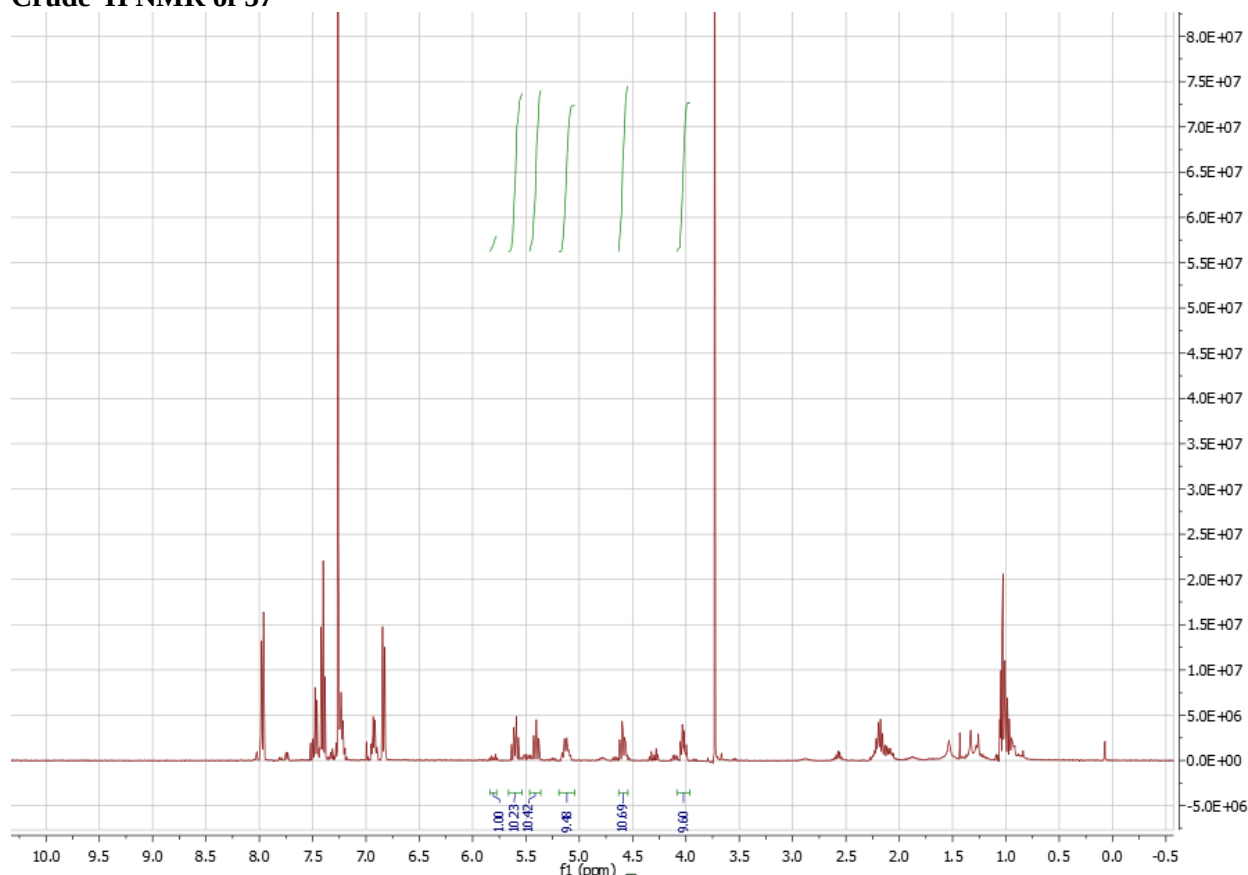
To probe radical character, a series of radical clocks was investigated.

##### Z-alkene radical clock (57)

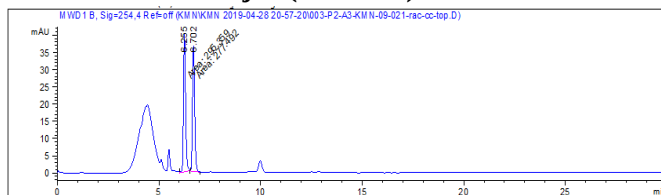


Imidate [S57](#) (14.8 mg, 0.05 mmol) was subjected to [GP3](#). Upon crude  $^1\text{H}$  NMR analysis, a mixture of oxazolines were observed with the major isomer as the *Z*-alkene and the minor as *E* in a 10:1 ratio. The product was isolated following chromatography on silica eluting with 10% EtOAc-Hexanes to give an off-white solid (8.7 mg, 87%, 80% e.e.).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J$  = 7.6 Hz, 2H), 7.48 (t,  $J$  = 7.4 Hz, 1H), 7.40 (t,  $J$  = 7.7 Hz, 2H), 5.66 – 5.56 (m, 1H), 5.40 (dd,  $J$  = 10.6, 9.1 Hz, 1H), 5.11 (dd,  $J$  = 18.1, 9.2 Hz, 1H), 4.65 – 4.55 (m, 1H), 4.02 (t,  $J$  = 8.4 Hz, 1H), 2.28 – 2.11 (m, 2H), 1.04 (t,  $J$  = 7.5 Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  164.54, 134.85, 131.50, 129.44, 128.48, 128.44, 127.88, 77.37, 77.16, 76.95, 73.29, 63.63, 21.31, 14.45. HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  202.1232, found: 202.1220. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 6.1 min (major) and 6.6 min (minor).

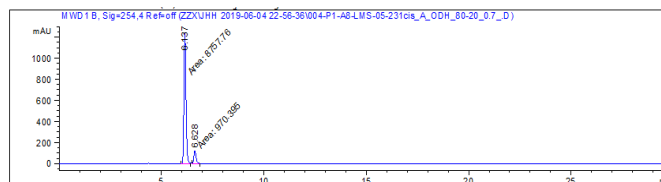
##### Crude $^1\text{H}$ NMR of 57



## HPLC trace for major (Z-alkene) 57



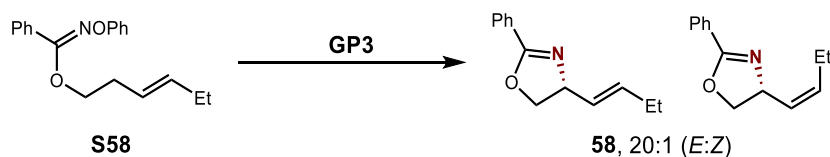
| Peak #   | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|----------|---------------|------|-------------|--------------|--------------|---------|
| 1        | 6.255         | MM   | 0.1220      | 295.35904    | 40.34907     | 51.5594 |
| 2        | 6.702         | MM   | 0.1263      | 277.49243    | 36.62023     | 48.4406 |
| Totals : |               |      |             | 572.85147    | 76.96930     |         |



Signal 1: MWD1 B, Sig=254,4 Ref=off

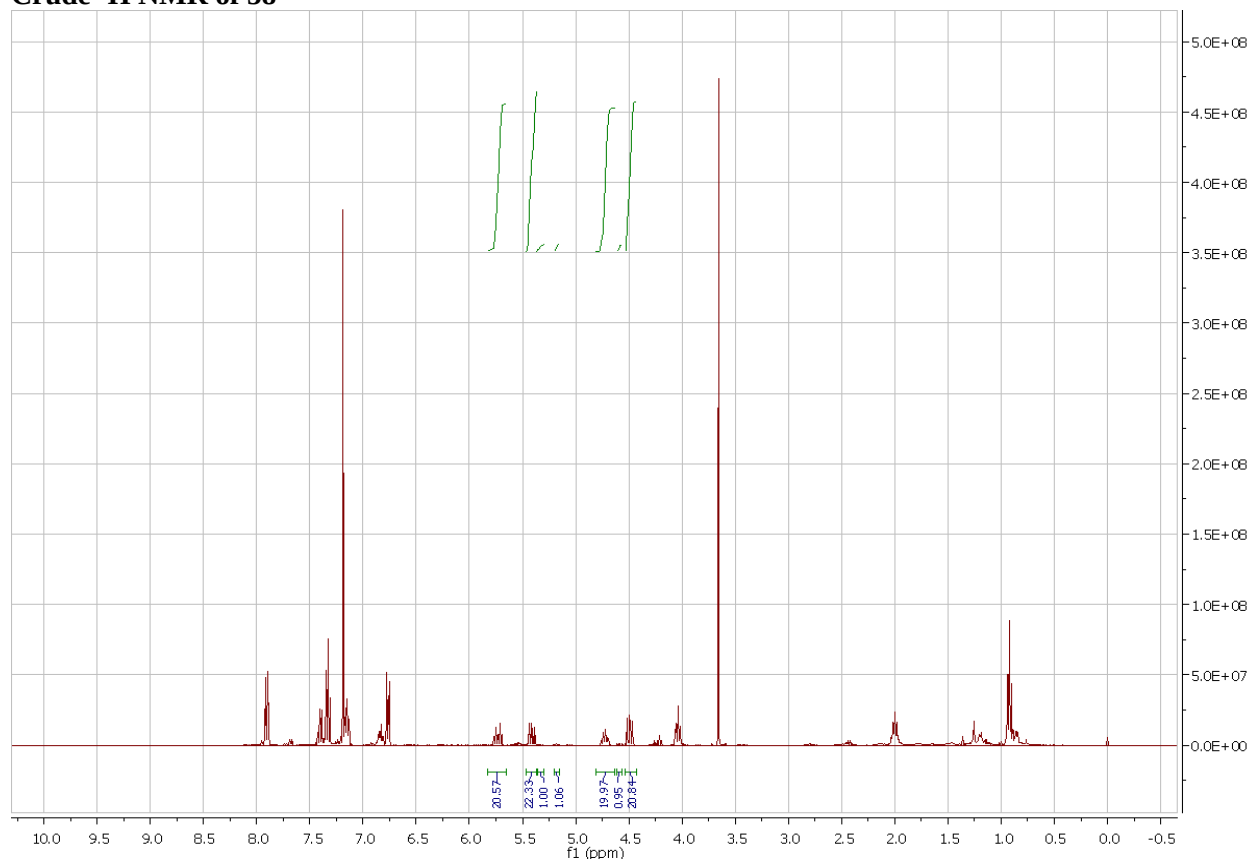
| Peak #   | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|----------|---------------|------|-------------|--------------|--------------|---------|
| 1        | 6.137         | MM   | 0.1172      | 8757.75781   | 1245.30676   | 90.0249 |
| 2        | 6.628         | MM   | 0.1315      | 970.39520    | 122.96706    | 9.9751  |
| Totals : |               |      |             | 9728.15302   | 1368.27382   |         |

## E-alkene radical clock (58)

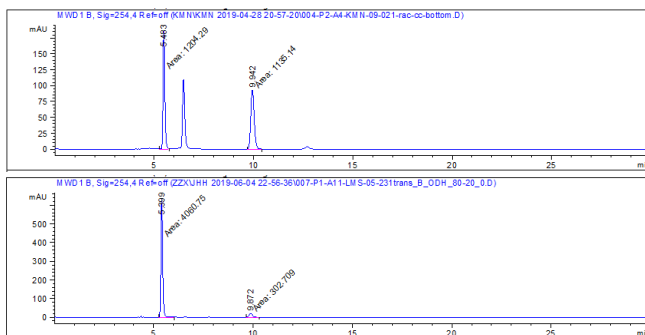


Imidate **S58** (14.8 mg, 0.05 mmol) was subjected to **GP3**. Upon crude  $^1\text{H}$  NMR analysis, the major oxazoline retained the *E*-alkene geometry, while the minor *Z*-alkene was observed in a 20:1 ratio. The product was isolated following chromatography on silica eluting with 10% EtOAc-Hexanes to give an off-white solid (8.6 mg, 85%, 86% e.e.).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 8.4, 1.3$  Hz, 2H), 7.54 – 7.45 (m, 1H), 7.45 – 7.36 (m, 2H), 5.81 (ddd,  $J = 12.5, 6.2, 5.6$  Hz, 1H), 5.48 (ddt,  $J = 15.3, 7.8, 1.6$  Hz, 1H), 4.77 (dd,  $J = 17.5, 8.4$  Hz, 1H), 4.55 (dd,  $J = 9.7, 8.3$  Hz, 1H), 4.08 (t,  $J = 8.3$  Hz, 1H), 2.16 – 2.03 (m, 2H), 1.02 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  164.20, 135.48, 131.50, 128.84, 128.49, 128.44, 72.94, 68.78, 29.86, 25.47, 13.40. HRMS (ESI-TOF)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  202.1232, found: 202.1236. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5 $\mu\text{m}$ , hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.4 min (major) and 9.9 min (minor).

## Crude <sup>1</sup>H NMR of 58



## HPLC trace for major (*E*-alkene) 58



Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.483         | MM   | 0.1069      | 1204.28564   | 187.76015    | 51.4779 |
| 2      | 9.942         | MM   | 0.2015      | 1135.13708   | 93.89842     | 48.5221 |

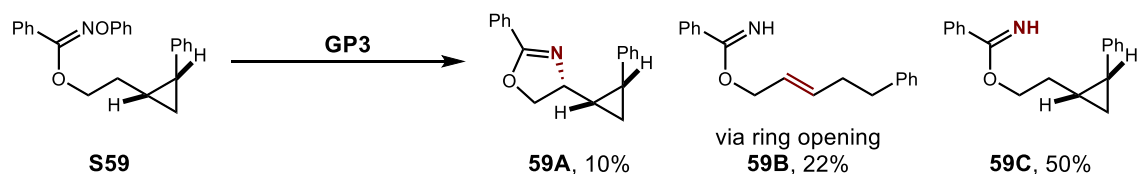
Totals : 2339.42273 281.65857

Signal 1: MWD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 5.399         | MM   | 0.1057      | 4060.75171   | 640.26129    | 93.0626 |
| 2      | 9.872         | MM   | 0.2321      | 302.70880    | 21.73696     | 6.9374  |

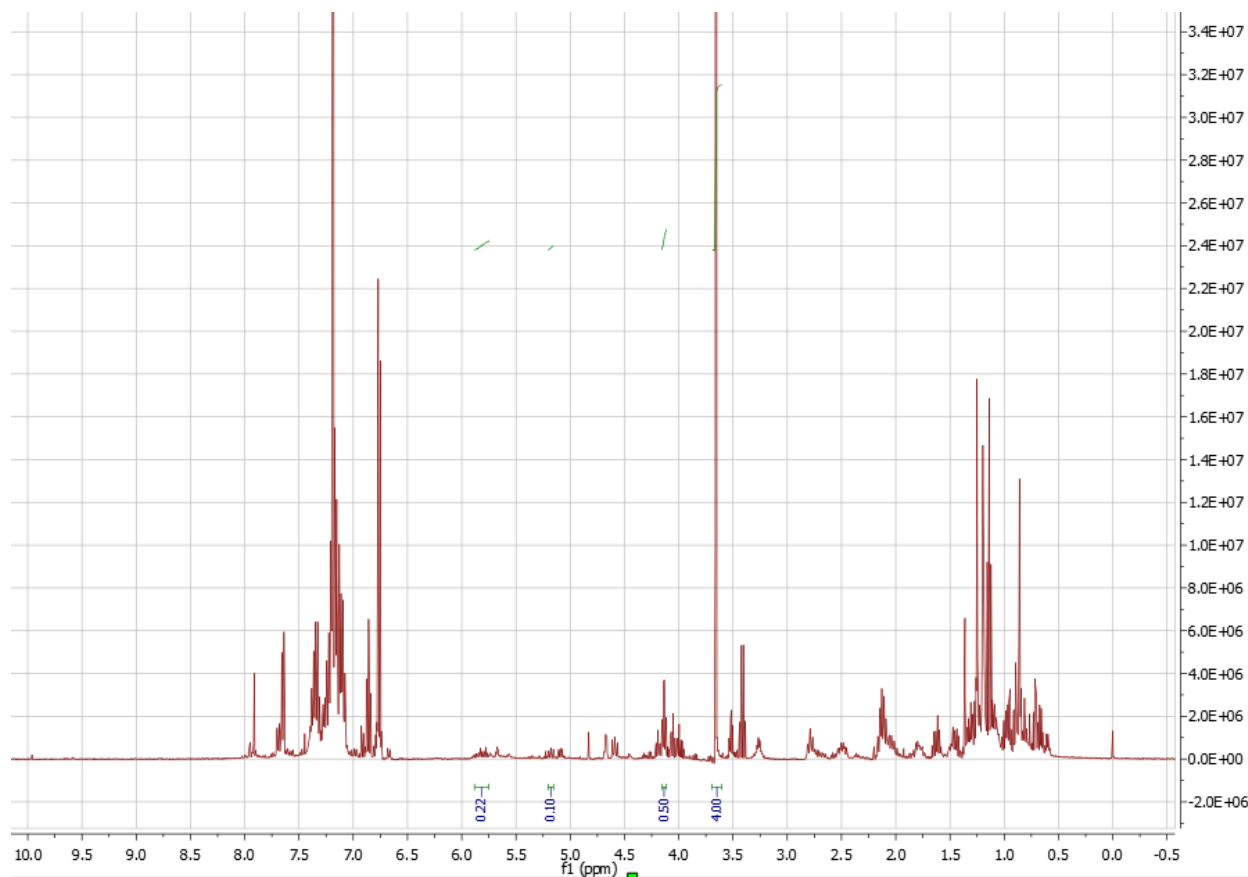
Totals : 4363.46051 661.99825

### Cis-cyclopropyl radical isomerization (59)

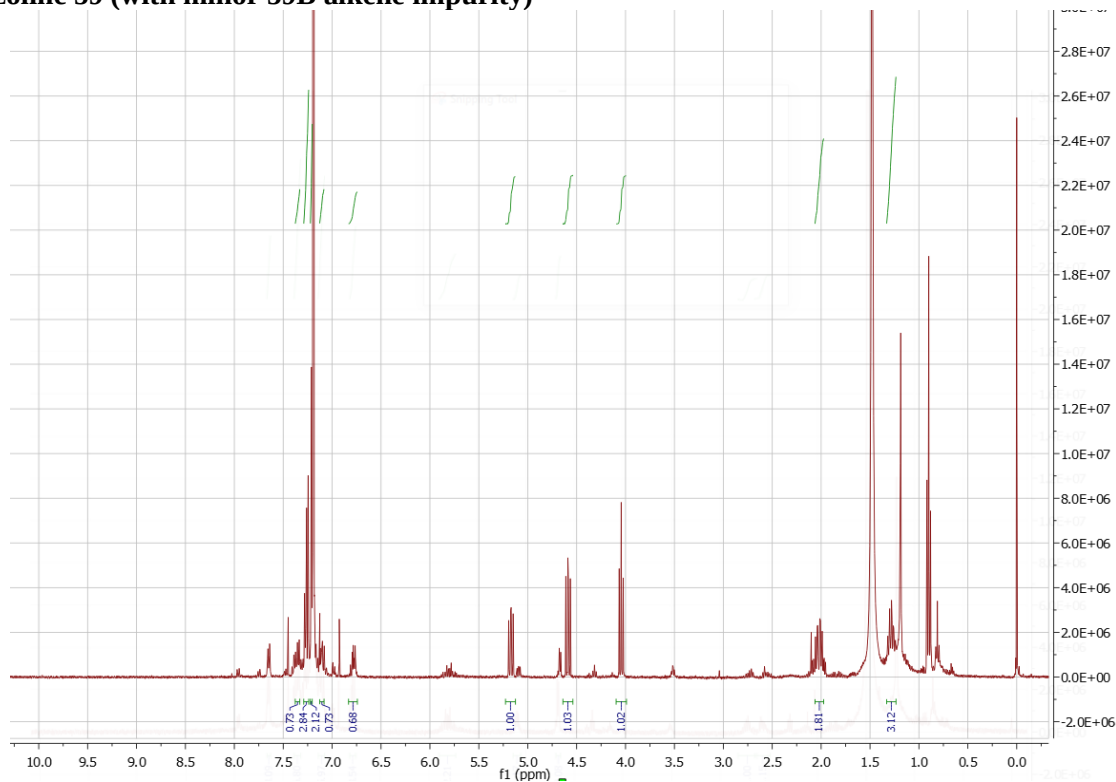


Imidate **S59** was subjected to **GP3** (17.8 mg, 0.05 mmol). Upon crude  $^1\text{H}$  NMR analysis, the oxazoline was observed in 10% by  $^1\text{H}$  NMR analysis. In addition, the ring-opened alkene was observed as a side product, which supports a radical intermediate. The large remainder of the mass balance (50%) is the reduced imidate, which may suggest the  $\beta$  methylene is too sterically encumbered for amination. The mixture was purified by preparatory TLC. No  $^{13}\text{C}$  NMR data is included due to very limited quantity of product obtained.

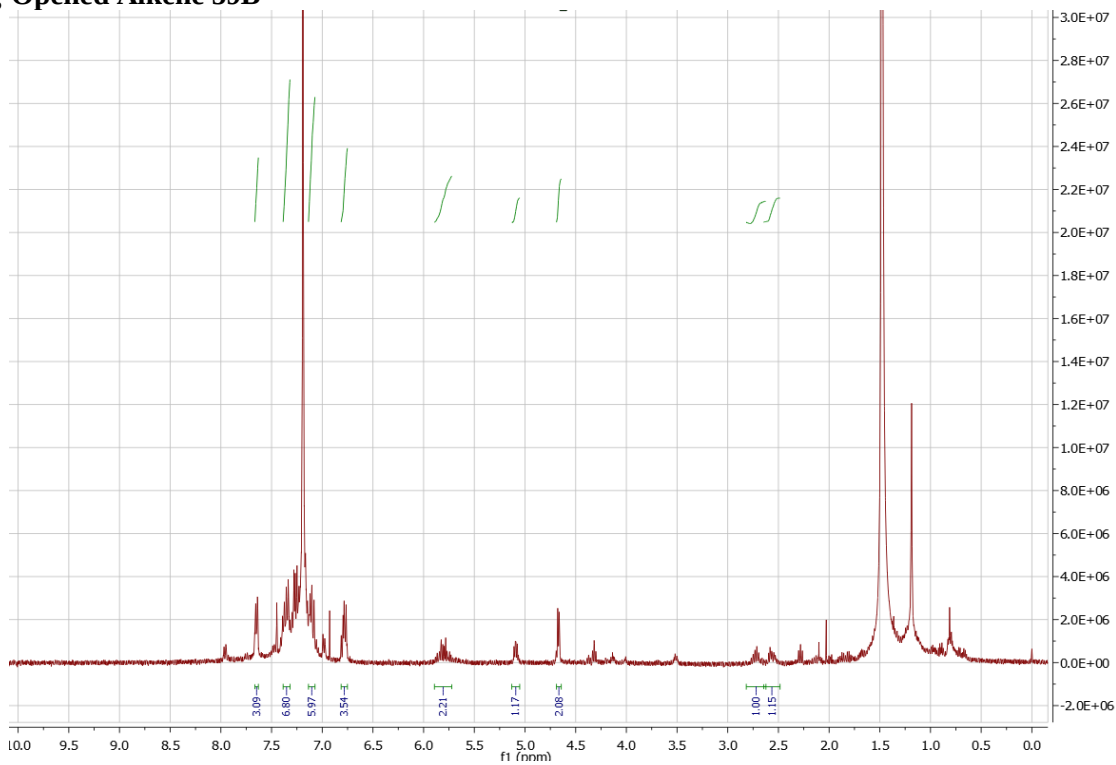
### Crude $^1\text{H}$ NMR of 59



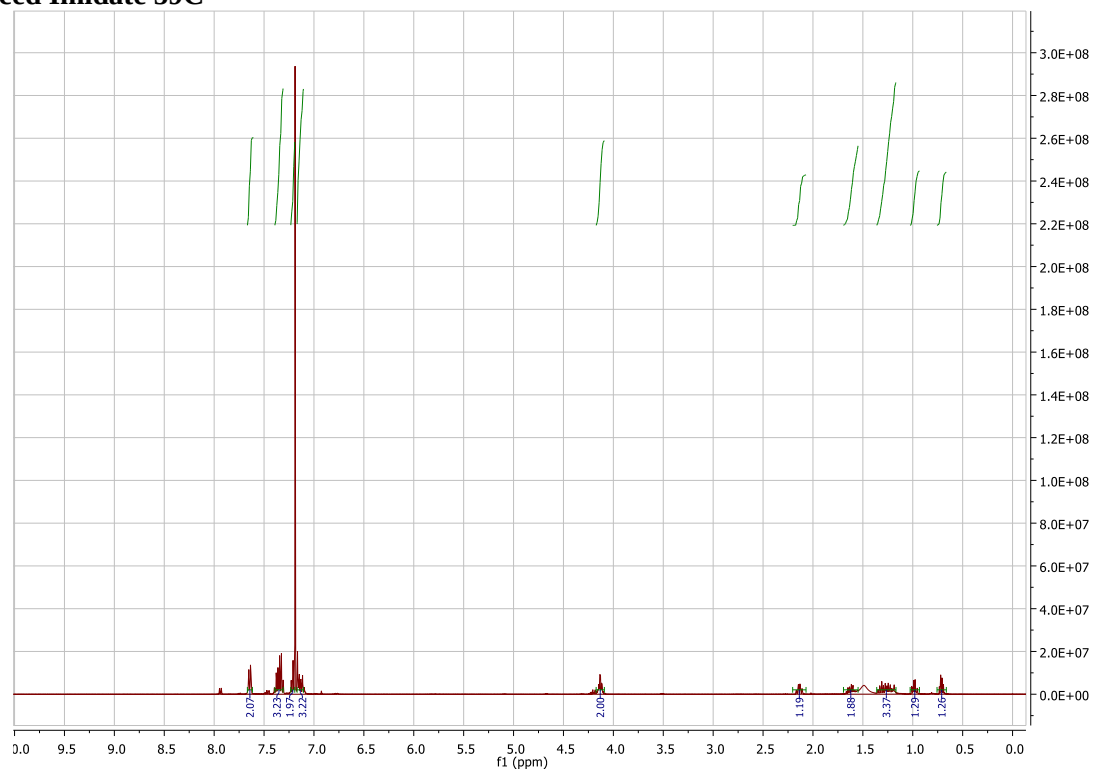
### Oxazoline 59 (with minor 59B alkene impurity)



### Ring-Opened Alkene 59B



## Reduced Imidate 59C



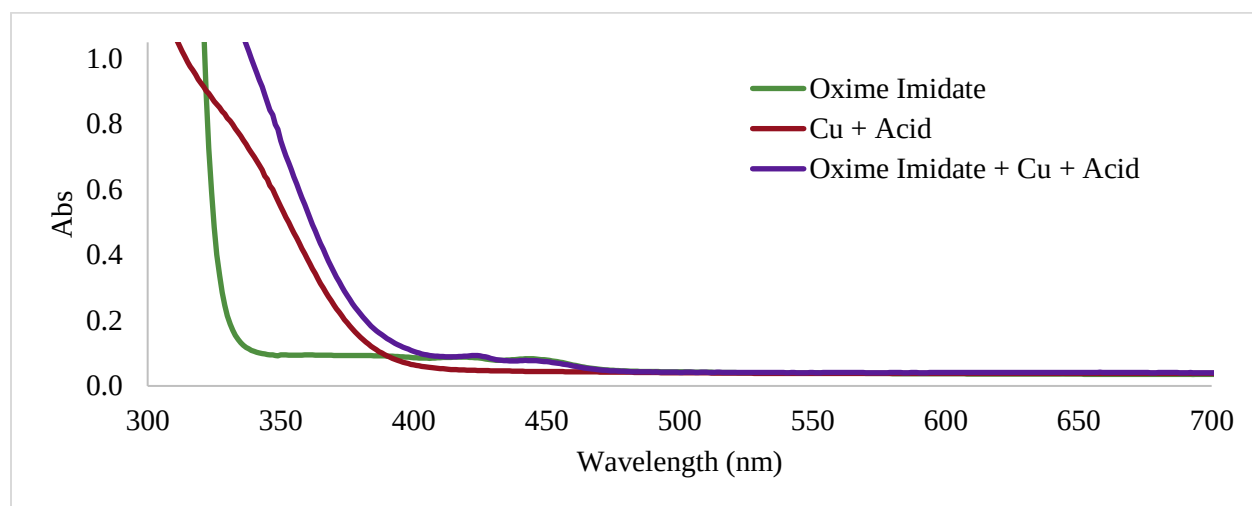


### e. UV-vis Absorption Studies

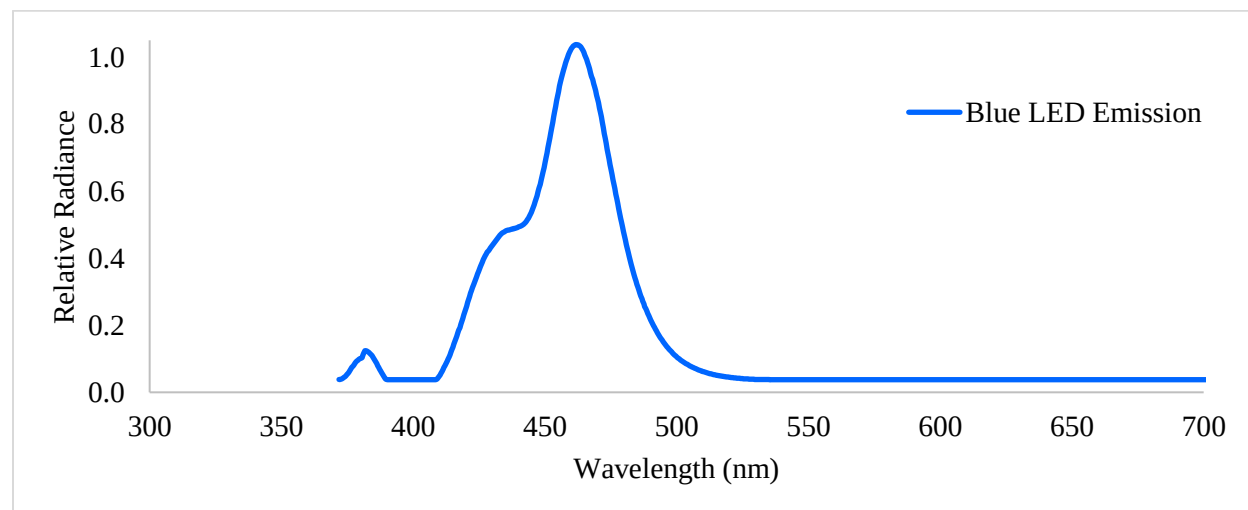
UV-vis absorption studies were conducted to probe the role of the copper, ligand, and (+)-camphoric acid on the activation of the oxime imidates under photolytic conditions.

Absorption experiments were performed on Agilent Technologies Cary 5000 UV-Vis-NIR Spectrophotometer.

All experiments were prepared according to [GP3](#), with the following modifications: 1.0 cm quartz cuvette sealed under N<sub>2</sub> instead of 2-dram vial, and scaled down to 3 mL of total volume. Three separate absorption studies were carried out: imidate [S1](#), imidate S1 with L•CuBArF<sub>4</sub> and (+)-camphoric acid, and L1•CuBArF<sub>4</sub> with (+)-camphoric acid. All solutions were scanned from 800 to 200 nm.



**Fig. 2.** Minimal absorption of all three experiments at  $\lambda > 400$  nm is observed. Imidate **S1** alone (green line) displays a negligible peak at  $\lambda_{417}$  with a  $\epsilon$  of  $5 \text{ M}^{-1}\cdot\text{cm}^{-1}$ . L•CuBArF<sub>4</sub> and (+)-camphoric acid (red line) shows no spectra features  $> 400$  nm, but when combined with Imidate **S1** (purple line), shows a similarly negligible peak at  $\lambda_{423}$  with a  $\epsilon$  of  $6 \text{ M}^{-1}\cdot\text{cm}^{-1}$ .



**Fig. 3.** Emission spectrum of Kessil A160WE tuna blue LED used as irradiation source (data provided by manufacturer). The onset of the major emission peak is  $> 400$  nm.

## IX. Computational Studies

### Computational Details

All calculations were performed using density functional theory as implemented within the Gaussian 16 (revision A.03) suite of programs<sup>11</sup>. Geometry optimizations and vibrational frequency calculations were performed using the  $\omega$ B97X-D functional<sup>12</sup> with the 6-311++G(d,p) basis set<sup>13</sup> to calculate triplet energies, and the M06-2X functional<sup>14</sup> with D3 empirical dispersion correction<sup>15</sup> and the 6-311++G(d,p) basis set to calculate homolytic bond dissociation energies (BDEs). All stationary points were confirmed to have no imaginary frequencies. Total spin squared for all doublets and triplets were confirmed to be within 2% of 0.75 and 2.00, respectively. Reported Gibbs free energies and enthalpies include thermal corrections computed at 298.15 K and 1 atm, and are reported in kcal/mol using the conversion of 1 hartree = 627.509 kcal/mol.

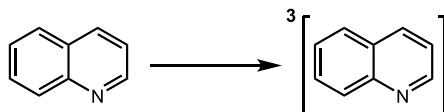
### Calculation of Triplet Energies

The gas phase triplet energies were calculated as follows:

$$E_T = \Delta G^\circ(\text{triplet}) - \Delta G^\circ(\text{singlet})$$

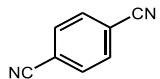
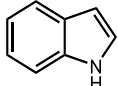
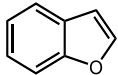
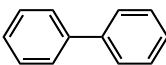
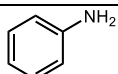
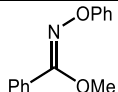
To ensure that the results of our triplet energy ( $E_T$ ) calculations are appropriate, benchmark calculations with a variety of functionals and basis sets were carried out and compared against experimentally measured and reported values for quinoline. As shown in **Table 3**, the combination of the  $\omega$ B97X-D functional with the 6-311++G(d,p) basis set shows agreement between calculated and experimental results. This combination was then applied to a variety of substrates with known triplet energies, as shown in **Table 4**. Finally, this approach was applied to provide the triplet energy for a representative oxime imidate, also in **Table 4**.

**Table 3.** Benchmarking of functional and basis set combinations for the determination of quinoline's triplet energy



| Functional                       | Basis Set            | $E_T$ (calc.)             |
|----------------------------------|----------------------|---------------------------|
| M06-2X                           | 6-311++G(d,p)        | 65.5                      |
| B3LYP                            | AUG-cc-PVTZ          | 59.7                      |
| B3LYP                            | cc-PVTZ              | 59.9                      |
| B3LYP                            | 6-311G(d,p)          | 59.8                      |
| B3LYP                            | 6-311+G (d,p)        | 59.5                      |
| B3LYP                            | 6-311++G(d,p)        | 59.4                      |
| <b><math>\omega</math>B97X-D</b> | <b>6-311++G(d,p)</b> | <b>61.7</b>               |
| N/A                              | N/A                  | 62.4 (exp.) <sup>10</sup> |

**Table 4.** Comparison of calculated and experimental triplet energies for a range of substrate classes with the  $\omega$ B97X-D functional and 6-311++G(d,p) basis set

| Substrate                                                                         | E <sub>T</sub> (calc.) | E <sub>T</sub> (exp.) <sup>10</sup> |
|-----------------------------------------------------------------------------------|------------------------|-------------------------------------|
|  | 66.9                   | 70.3                                |
|  | 70.1                   | 71.3                                |
|  | 69.9                   | 70.8                                |
|  | 70.8                   | 72.0                                |
|  | 69.0                   | 65.5                                |
|  | 76.2                   | 76.8                                |
|  | 47.2                   | N/A                                 |

### Calculation of Homolytic Bond Dissociation Energies

The gas phase BDEs were calculated as follows:

$$\text{N-O BDE} = \Sigma \Delta H^\circ(\text{products}) - \Sigma \Delta H^\circ(\text{starting materials})$$

To ensure that the results of our BDE calculations are appropriate, benchmark calculations with a variety of functionals and basis sets were carried out and compared against experimentally measured and reported BDEs for N,O-dimethylhydroxylamine. As shown in **Table 5**, the combination of the M06-2X-D3 functional with the 6-311++G(d,p) basis set shows agreement between calculated and experimental results. This combination was then applied to a variety of additional hydroxylamine with known BDEs, as shown in **Table 6**.

**Table 5.** Benchmarking of functional and basis set combinations for the determination of N,O-dimethylhydroxylamine's N-O BDE



| Functional       | Basis Set            | N-O BDE                   |
|------------------|----------------------|---------------------------|
| B3LYP            | 6-311G(d,p)          | 47.6                      |
| B3LYP            | 6-311+G(d,p)         | 45.0                      |
| B3LYP            | 6-311++G(d,p)        | 45.0                      |
| B3LYP-D3         | 6-311++G(d,p)        | 46.9                      |
| B3P86            | 6-311+G(d,p)         | 49.6                      |
| $\omega$ B97X-D  | 6-311+G(d,p)         | 50.1                      |
| M05-2X           | 6-311++G(d,p)        | 52.4                      |
| M06-2X           | 6-311+G(d,p)         | 54.1                      |
| M06-2X           | 6-311++G(d,p)        | 54.1                      |
| <b>M06-2X-D3</b> | <b>6-311++G(d,p)</b> | <b>54.2</b>               |
| N/A              | N/A                  | 57.5 (exp.) <sup>16</sup> |

**Table 6.** Comparison of calculated and experimental N-O BDEs for hydroxylamines with the M06-2X-D3 functional and 6-311++G(d,p) basis set

| Substrate | N-O BDE (calc.) | N-O BDE (exp.) <sup>16</sup> |
|-----------|-----------------|------------------------------|
|           | 64.2            | 63.0                         |
|           | 63.2            | 64.9                         |
|           | 60.3            | 54.6                         |

This combination was then used to calculate the N-O BDE for a representative oxime imide from both its singlet and triplet states. As shown in **Table 7**, the N-O BDE from the triplet state is not only weaker than from the singlet state, but are also negative, which suggests spontaneous homolytic cleavage from the triplet state.

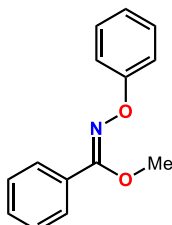
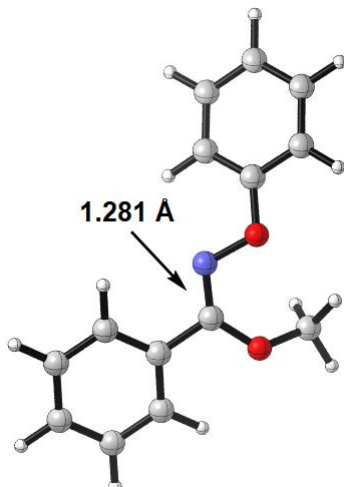
**Table 7.** Representative imide oxime N-O BDEs from the singlet and triplet state with the M06-2X-D3 functional and 6-311++G(d,p) basis set

| Homolytic Cleavage | N-O BDE      |              |
|--------------------|--------------|--------------|
|                    | From Singlet | From Triplet |
|                    | 35.3         | -17.5        |

## Optimized Cartesian Coordinates

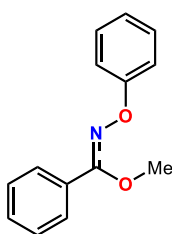
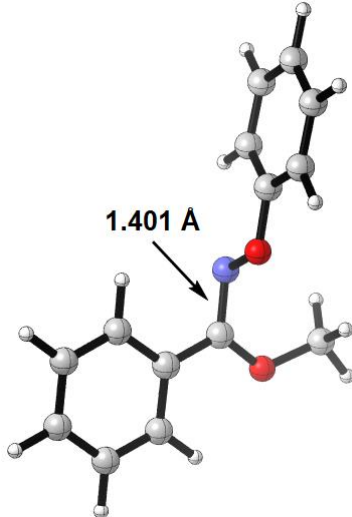
Geometry optimizations and frequency calculations for the determination of triplet energies were carried out using the  $\omega$ B97X-D functional with the 6-311++G(d,p) basis set. Visualization carried out with CYLview<sup>17</sup>. EE = Electronic Energy

### E<sub>T</sub>: Methyl (Z)-N-phenoxybenzimidate (singlet state)

|                                                                                   |             |                                                                                    |             |
|-----------------------------------------------------------------------------------|-------------|------------------------------------------------------------------------------------|-------------|
|  |             |  |             |
| <b>Total EE (hartree)</b>                                                         |             | -746.379313                                                                        |             |
| <b>EE + Zero-Point Energy Correction (hartree)</b>                                |             | -746.137816                                                                        |             |
| <b>EE + Thermal Enthalpy Correction (hartree)</b>                                 |             | -746.122322                                                                        |             |
| <b>EE + Thermal Free Energy Correction (hartree)</b>                              |             | -746.181884                                                                        |             |
| <b>Imaginary Frequencies (cm<sup>-1</sup>)</b>                                    |             | None                                                                               |             |
| <b>Cartesian Coordinates</b>                                                      |             |                                                                                    |             |
| C                                                                                 | -3.43649100 | 0.67240300                                                                         | 0.27511800  |
| C                                                                                 | -2.27885600 | -0.01328600                                                                        | -0.09103800 |
| C                                                                                 | -2.35623600 | -1.37055300                                                                        | -0.41265100 |
| C                                                                                 | -3.57295600 | -2.03198800                                                                        | -0.34914200 |
| C                                                                                 | -4.72523600 | -1.34654100                                                                        | 0.02473900  |
| C                                                                                 | -4.65412800 | 0.00573300                                                                         | 0.33391800  |
| H                                                                                 | -3.37788200 | 1.72734400                                                                         | 0.51058500  |
| H                                                                                 | -1.45778100 | -1.89405200                                                                        | -0.71449100 |
| H                                                                                 | -3.62512800 | -3.08517400                                                                        | -0.60074500 |
| H                                                                                 | -5.54894300 | 0.54617300                                                                         | 0.62103100  |
| H                                                                                 | -5.67619100 | -1.86552400                                                                        | 0.06895500  |
| C                                                                                 | -0.97866900 | 0.69893500                                                                         | -0.13375200 |
| N                                                                                 | 0.08573700  | -0.01283600                                                                        | -0.16250900 |
| O                                                                                 | -1.09120700 | 2.03255600                                                                         | -0.16754100 |
| C                                                                                 | -0.13926300 | 2.86895900                                                                         | 0.49780200  |
| H                                                                                 | -0.68213700 | 3.78234700                                                                         | 0.73905200  |
| H                                                                                 | 0.21686800  | 2.39594900                                                                         | 1.41479300  |
| H                                                                                 | 0.70615200  | 3.08934200                                                                         | -0.15085300 |
| O                                                                                 | 1.23108700  | 0.74545600                                                                         | -0.36339200 |
| C                                                                                 | 2.39200600  | 0.04961000                                                                         | -0.14335700 |
| C                                                                                 | 3.55444800  | 0.70345900                                                                         | -0.54266900 |
| C                                                                                 | 2.44562700  | -1.20280400                                                                        | 0.45523400  |

|   |            |             |             |
|---|------------|-------------|-------------|
| C | 4.78311000 | 0.09434400  | -0.33834900 |
| H | 3.47903400 | 1.67690100  | -1.01283500 |
| C | 3.68779000 | -1.80002800 | 0.64691100  |
| H | 1.53228100 | -1.69391500 | 0.75886000  |
| C | 4.85775900 | -1.16189600 | 0.25662300  |
| H | 5.68789200 | 0.60367900  | -0.65069200 |
| H | 3.73416300 | -2.77849800 | 1.11219000  |
| H | 5.81904200 | -1.63689000 | 0.41285500  |

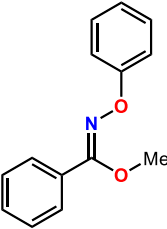
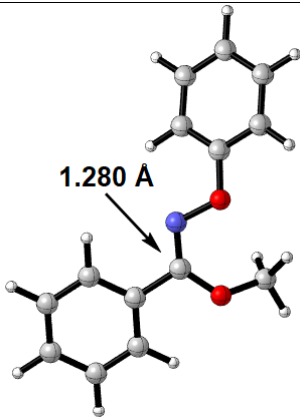
**E<sub>T</sub>: Methyl (Z)-N-phenoxybenzimidate (triplet state)**

|                                                                                   |             |                                                                                     |             |
|-----------------------------------------------------------------------------------|-------------|-------------------------------------------------------------------------------------|-------------|
|  |             |  |             |
| Total EE (hartree)                                                                |             | -746.298501                                                                         |             |
| EE + Zero-Point Energy Correction (hartree)                                       |             | -746.060362                                                                         |             |
| EE + Thermal Enthalpy Correction (hartree)                                        |             | -746.044330                                                                         |             |
| EE + Thermal Free Energy Correction (hartree)                                     |             | -746.106604                                                                         |             |
| Imaginary Frequencies (cm <sup>-1</sup> )                                         |             | None                                                                                |             |
| <S <sup>2</sup> >                                                                 |             | 2.0008                                                                              |             |
| Cartesian Coordinates                                                             |             |                                                                                     |             |
| C                                                                                 | -3.50008600 | 0.47710400                                                                          | -0.19967100 |
| C                                                                                 | -2.19402000 | 0.03115000                                                                          | 0.10886100  |
| C                                                                                 | -1.98652600 | -1.35441300                                                                         | 0.30548100  |
| C                                                                                 | -3.03878600 | -2.24342700                                                                         | 0.19347900  |
| C                                                                                 | -4.32226800 | -1.79205700                                                                         | -0.11532100 |
| C                                                                                 | -4.53979300 | -0.42830300                                                                         | -0.30904000 |
| H                                                                                 | -3.67404900 | 1.53485600                                                                          | -0.35069200 |
| H                                                                                 | -0.99433100 | -1.71730300                                                                         | 0.54758100  |
| H                                                                                 | -2.86066300 | -3.30198700                                                                         | 0.34812300  |
| H                                                                                 | -5.53496700 | -0.06938600                                                                         | -0.54842400 |
| H                                                                                 | -5.14261300 | -2.49486400                                                                         | -0.20301900 |
| C                                                                                 | -1.11811000 | 0.94764000                                                                          | 0.21527300  |
| N                                                                                 | 0.15761600  | 0.55321800                                                                          | 0.64005400  |
| O                                                                                 | -1.37536400 | 2.27029400                                                                          | 0.10174800  |
| C                                                                                 | -0.27230300 | 3.14768200                                                                          | -0.08423900 |
| H                                                                                 | -0.69981900 | 4.14506100                                                                          | -0.16747000 |
| H                                                                                 | 0.41104700  | 3.11027100                                                                          | 0.76833000  |
| H                                                                                 | 0.27245400  | 2.90025200                                                                          | -0.99951300 |

|   |            |             |             |
|---|------------|-------------|-------------|
| O | 0.91216800 | 0.28831800  | -0.46558700 |
| C | 2.21467900 | -0.10309900 | -0.20027600 |
| C | 2.74333600 | -0.19090700 | 1.07970500  |
| C | 2.96986600 | -0.40494000 | -1.32601000 |
| C | 4.06708900 | -0.59291900 | 1.22048200  |
| H | 2.13099400 | 0.04703900  | 1.93776500  |
| C | 4.28901200 | -0.80319300 | -1.16457200 |
| H | 2.51585000 | -0.32714000 | -2.30651900 |
| C | 4.84252300 | -0.89854600 | 0.10836400  |
| H | 4.49265800 | -0.66683600 | 2.21477100  |
| H | 4.88523300 | -1.04138900 | -2.03782000 |
| H | 5.87278200 | -1.21062500 | 0.23212200  |

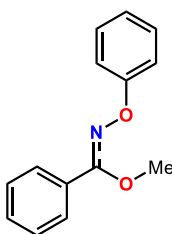
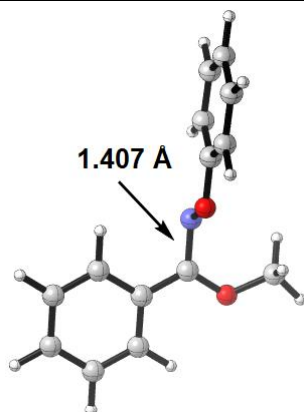
Geometry optimizations and frequency calculations for the determination of BDEs were carried out using the M06-2X functional with D3 empirical dispersion correction, and the 6-311++G(d,p) basis set.

**BDE: Methyl (Z)-N-phenoxybenzimidate (singlet state)**

|                                                                                    |             |                                                                                     |             |
|------------------------------------------------------------------------------------|-------------|-------------------------------------------------------------------------------------|-------------|
|  |             |  |             |
| Total EE (hartree)                                                                 |             | -746.334486                                                                         |             |
| EE + Zero-Point Energy Correction (hartree)                                        |             | -746.092706                                                                         |             |
| EE + Thermal Enthalpy Correction (hartree)                                         |             | -746.077263                                                                         |             |
| EE + Thermal Free Energy Correction (hartree)                                      |             | -746.136665                                                                         |             |
| Imaginary Frequencies (cm <sup>-1</sup> )                                          |             | None                                                                                |             |
| Cartesian Coordinates                                                              |             |                                                                                     |             |
| C                                                                                  | 3.44443500  | 0.69035500                                                                          | -0.21913900 |
| C                                                                                  | 2.28249800  | -0.01684100                                                                         | 0.08887200  |
| C                                                                                  | 2.35643300  | -1.38634600                                                                         | 0.35872200  |
| C                                                                                  | 3.57855500  | -2.03954400                                                                         | 0.30050000  |
| C                                                                                  | 4.73747100  | -1.33334900                                                                         | -0.01594100 |
| C                                                                                  | 4.66782100  | 0.03071700                                                                          | -0.27257100 |
| H                                                                                  | 3.38369600  | 1.75325300                                                                          | -0.41268100 |
| H                                                                                  | 1.45209500  | -1.92249000                                                                         | 0.61672000  |
| H                                                                                  | 3.63062600  | -3.10105600                                                                         | 0.51080000  |
| H                                                                                  | 5.56672200  | 0.58527900                                                                          | -0.51372500 |
| H                                                                                  | 5.69133200  | -1.84584600                                                                         | -0.05615500 |
| C                                                                                  | 0.97786600  | 0.68816700                                                                          | 0.12785400  |
| N                                                                                  | -0.08633400 | -0.02143600                                                                         | 0.14710700  |
| O                                                                                  | 1.07736000  | 2.02500500                                                                          | 0.17030100  |
| C                                                                                  | 0.13518000  | 2.84148700                                                                          | -0.53664300 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 0.68541100  | 3.73833500  | -0.81602800 |
| H | -0.22147300 | 2.32800700  | -1.43025600 |
| H | -0.70877500 | 3.09438000  | 0.10038300  |
| O | -1.22565300 | 0.74560200  | 0.34444600  |
| C | -2.39288000 | 0.05172700  | 0.13977300  |
| C | -3.54988100 | 0.71690200  | 0.53891600  |
| C | -2.45424900 | -1.20827800 | -0.44347500 |
| C | -4.78321000 | 0.11100100  | 0.34949200  |
| H | -3.46246100 | 1.69475900  | 0.99667700  |
| C | -3.70174900 | -1.80163200 | -0.62055800 |
| H | -1.54519300 | -1.70635200 | -0.74692700 |
| C | -4.86693900 | -1.15289400 | -0.23057600 |
| H | -5.68322000 | 0.62775300  | 0.66093400  |
| H | -3.75561300 | -2.78462600 | -1.07363800 |
| H | -5.83056000 | -1.62502600 | -0.37518800 |

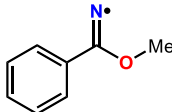
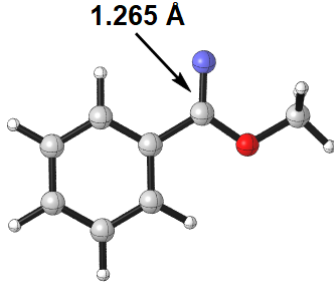
**BDE: Methyl (Z)-N-phenoxybenzimidate (triplet state)**

|                                                                                    |             |                                                                                     |             |
|------------------------------------------------------------------------------------|-------------|-------------------------------------------------------------------------------------|-------------|
|  |             |  |             |
| Total EE (hartree)                                                                 |             | -746.248106                                                                         |             |
| EE + Zero-Point Energy Correction (hartree)                                        |             | -746.009465                                                                         |             |
| EE + Thermal Enthalpy Correction (hartree)                                         |             | -745.99348                                                                          |             |
| EE + Thermal Free Energy Correction (hartree)                                      |             | -746.055371                                                                         |             |
| Imaginary Frequencies (cm <sup>-1</sup> )                                          |             | None                                                                                |             |
| <S <sup>2</sup> >                                                                  |             | 2.0003                                                                              |             |
| Cartesian Coordinates                                                              |             |                                                                                     |             |
| C                                                                                  | 3.50632200  | 0.48346500                                                                          | 0.16938200  |
| C                                                                                  | 2.19643100  | 0.02840600                                                                          | -0.10584800 |
| C                                                                                  | 1.98140700  | -1.36084500                                                                         | -0.26102700 |
| C                                                                                  | 3.03519600  | -2.24836700                                                                         | -0.14087200 |
| C                                                                                  | 4.32460500  | -1.78987100                                                                         | 0.13492800  |
| C                                                                                  | 4.54727200  | -0.42071100                                                                         | 0.28710600  |
| H                                                                                  | 3.67964000  | 1.54526600                                                                          | 0.28656400  |
| H                                                                                  | 0.98368000  | -1.72520000                                                                         | -0.47556900 |
| H                                                                                  | 2.85391500  | -3.30993600                                                                         | -0.26264700 |
| H                                                                                  | 5.54610300  | -0.05733300                                                                         | 0.49970500  |
| H                                                                                  | 5.14481000  | -2.49071200                                                                         | 0.22903200  |
| C                                                                                  | 1.11901100  | 0.94483300                                                                          | -0.21655700 |
| N                                                                                  | -0.15931700 | 0.53884300                                                                          | -0.64313100 |
| O                                                                                  | 1.37771600  | 2.26914400                                                                          | -0.16054600 |



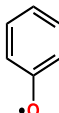
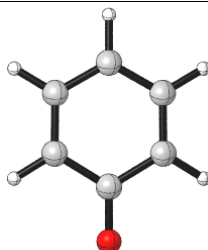
|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 0.27469400  | 3.13118600  | 0.09968300  |
| H | 0.68664300  | 4.13639200  | 0.14214500  |
| H | -0.46717900 | 3.06817800  | -0.69920800 |
| H | -0.19223900 | 2.87580500  | 1.05382400  |
| O | -0.91749500 | 0.30997200  | 0.45983300  |
| C | -2.21902000 | -0.09312300 | 0.19626200  |
| C | -2.98654700 | -0.34912800 | 1.32579700  |
| C | -2.73058400 | -0.23324500 | -1.08682000 |
| C | -4.30413100 | -0.75540400 | 1.16537600  |
| H | -2.53998400 | -0.22949900 | 2.30509000  |
| C | -4.05358200 | -0.64245600 | -1.22573500 |
| H | -2.10710000 | -0.02979000 | -1.94530500 |
| C | -4.84224000 | -0.90324000 | -0.11032700 |
| H | -4.91050500 | -0.95816900 | 2.03972300  |
| H | -4.46729600 | -0.75767700 | -2.22035200 |
| H | -5.87003800 | -1.22116700 | -0.23346000 |

#### BDE: Methyl benzimidate radical

|                                                                                    |             |                                                                                     |             |
|------------------------------------------------------------------------------------|-------------|-------------------------------------------------------------------------------------|-------------|
|  |             |  |             |
| Total EE (hartree)                                                                 |             | -439.502551                                                                         |             |
| EE + Zero-Point Energy Correction (hartree)                                        |             | -439.358785                                                                         |             |
| EE + Thermal Enthalpy Correction (hartree)                                         |             | -439.349017                                                                         |             |
| EE + Thermal Free Energy Correction (hartree)                                      |             | -439.394283                                                                         |             |
| Imaginary Frequencies (cm <sup>-1</sup> )                                          |             | None                                                                                |             |
| <S <sup>2</sup> >                                                                  |             | 0.7501                                                                              |             |
| Cartesian Coordinates                                                              |             |                                                                                     |             |
| C                                                                                  | -0.70224300 | 1.15104000                                                                          | -0.00004000 |
| C                                                                                  | -0.21610100 | -0.15492700                                                                         | -0.00001700 |
| C                                                                                  | -1.10332500 | -1.23309700                                                                         | 0.00002700  |
| C                                                                                  | -2.47105000 | -1.00177800                                                                         | 0.00004000  |
| C                                                                                  | -2.95928000 | 0.30314700                                                                          | 0.00001000  |
| C                                                                                  | -2.07501200 | 1.37581300                                                                          | -0.00002300 |
| H                                                                                  | -0.00614800 | 1.97953400                                                                          | -0.00006600 |
| H                                                                                  | -0.71412500 | -2.24442300                                                                         | 0.00004800  |
| H                                                                                  | -3.15835800 | -1.83905000                                                                         | 0.00007100  |
| H                                                                                  | -2.45248700 | 2.39127300                                                                          | -0.00003900 |
| H                                                                                  | -4.02804800 | 0.48147400                                                                          | 0.00002100  |
| C                                                                                  | 1.25022300  | -0.40941600                                                                         | -0.00002300 |
| N                                                                                  | 1.75079900  | -1.57066200                                                                         | -0.00007900 |
| O                                                                                  | 2.00130300  | 0.71096300                                                                          | 0.00004300  |
| C                                                                                  | 3.41169000  | 0.49754900                                                                          | 0.00003800  |
| H                                                                                  | 3.86267800  | 1.48623900                                                                          | 0.00019500  |

|   |            |             |             |
|---|------------|-------------|-------------|
| H | 3.71052900 | -0.05919100 | 0.89041100  |
| H | 3.71053900 | -0.05890900 | -0.89051000 |

# **BDE: Phenoxy radical**

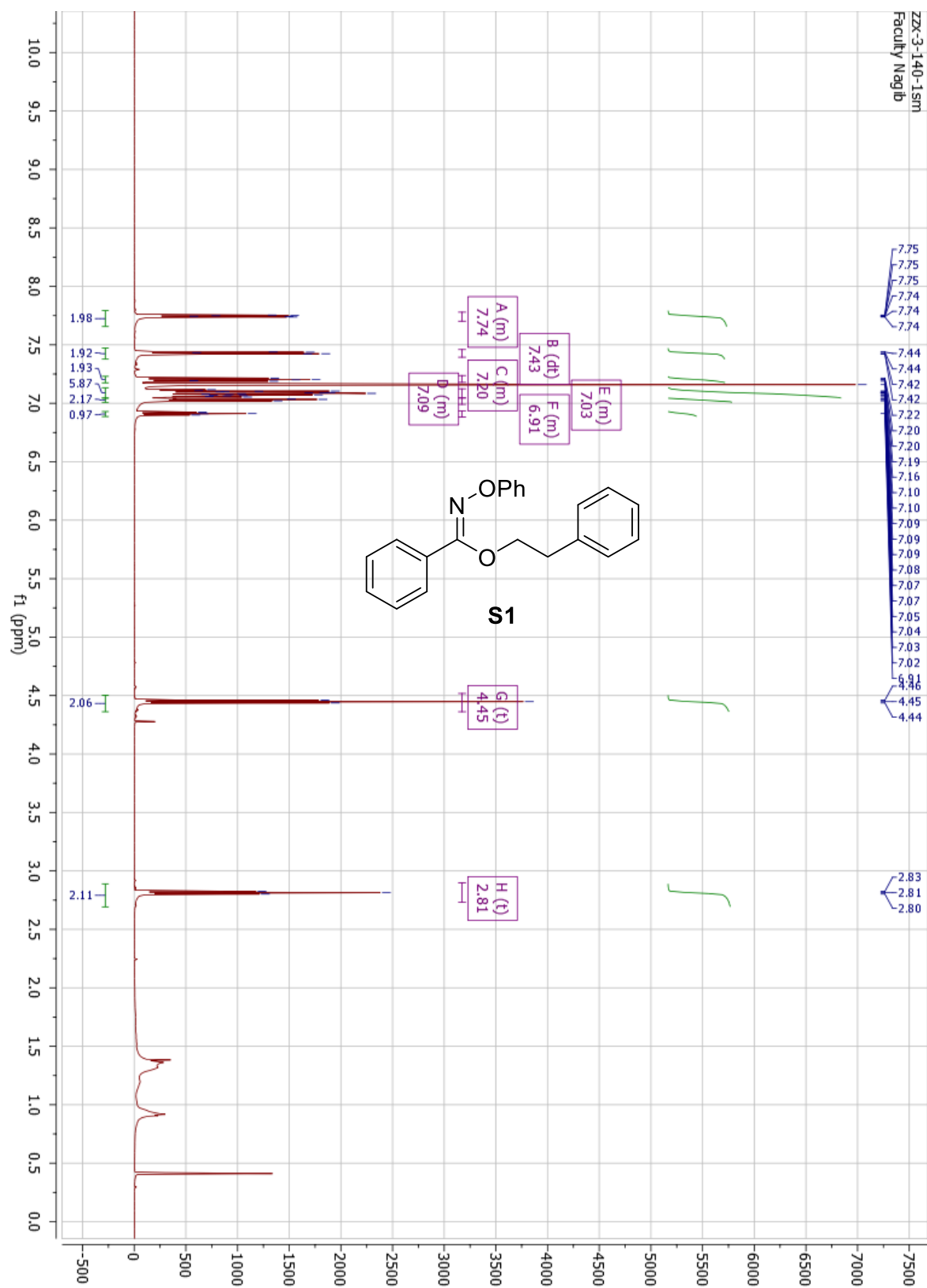
|                                                                                   |                                                                                     |             |             |
|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------|-------------|
|  |  |             |             |
| <b>Total EE (hartree)</b>                                                         |                                                                                     | -306.772895 |             |
| <b>EE + Zero-Point Energy Correction (hartree)</b>                                |                                                                                     | -306.681151 |             |
| <b>EE + Thermal Enthalpy Correction (hartree)</b>                                 |                                                                                     | -306.674896 |             |
| <b>EE + Thermal Free Energy Correction (hartree)</b>                              |                                                                                     | -306.71072  |             |
| <b>Imaginary Frequencies (cm<sup>-1</sup>)</b>                                    |                                                                                     | None        |             |
| <b>&lt;S<sup>2</sup>&gt;</b>                                                      |                                                                                     | 0.7511      |             |
| <b>Cartesian Coordinates</b>                                                      |                                                                                     |             |             |
| O                                                                                 | 2.28954700                                                                          | 0.00000000  | 0.00000100  |
| C                                                                                 | 1.04591300                                                                          | 0.00000000  | 0.00000000  |
| C                                                                                 | 0.28894200                                                                          | 1.23815300  | 0.00000000  |
| C                                                                                 | 0.28894200                                                                          | -1.23815300 | 0.00000000  |
| C                                                                                 | -1.08192400                                                                         | 1.22342800  | 0.00000000  |
| H                                                                                 | 0.85926200                                                                          | 2.15973900  | -0.00000100 |
| C                                                                                 | -1.08192400                                                                         | -1.22342800 | 0.00000000  |
| H                                                                                 | 0.85926200                                                                          | -2.15973900 | -0.00000100 |
| C                                                                                 | -1.77584800                                                                         | 0.00000000  | 0.00000000  |
| H                                                                                 | -1.63995800                                                                         | 2.15250200  | 0.00000000  |
| H                                                                                 | -1.63995800                                                                         | -2.15250200 | 0.00000000  |
| H                                                                                 | -2.85959600                                                                         | 0.00000000  | 0.00000000  |

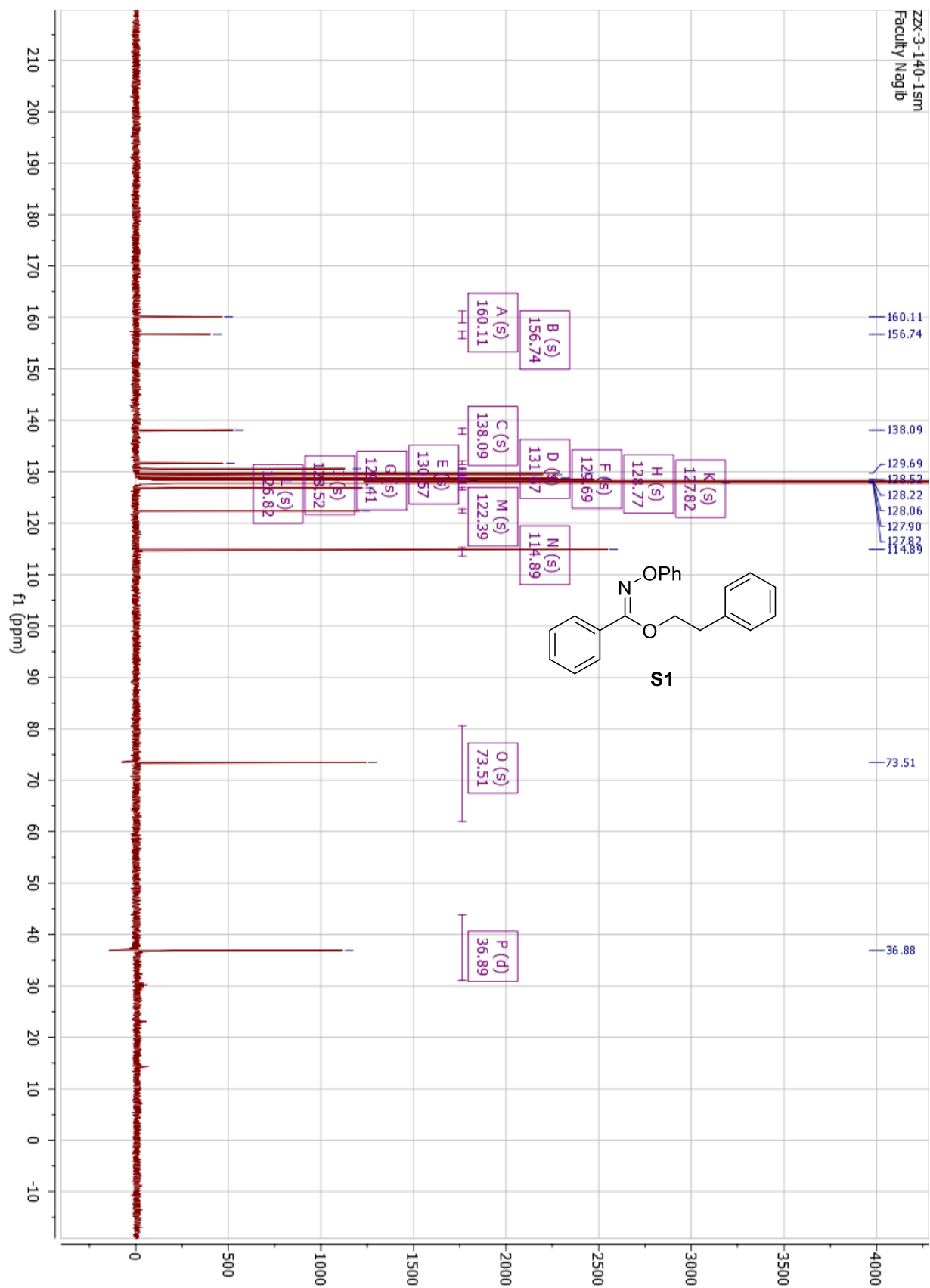
## X. References

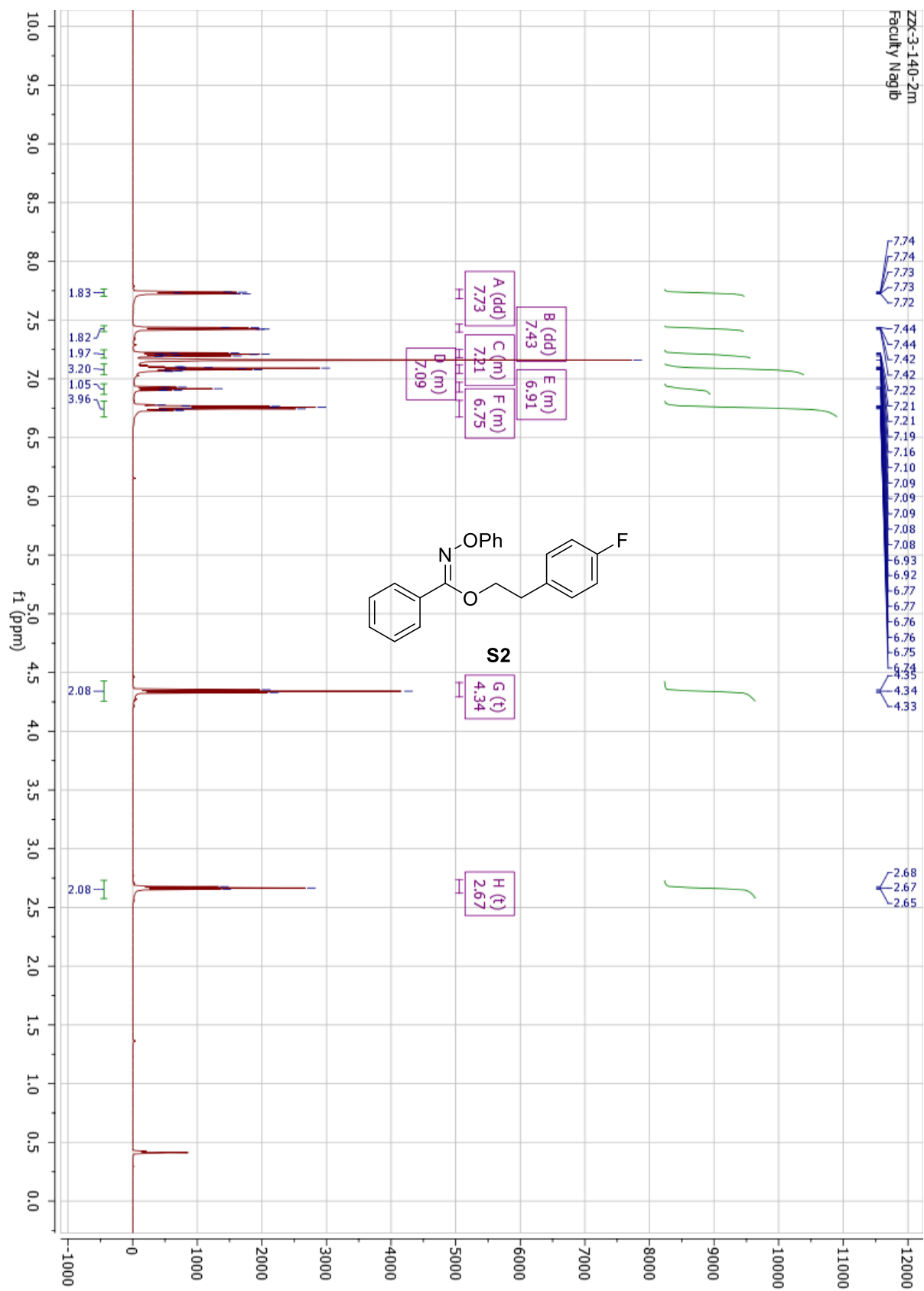
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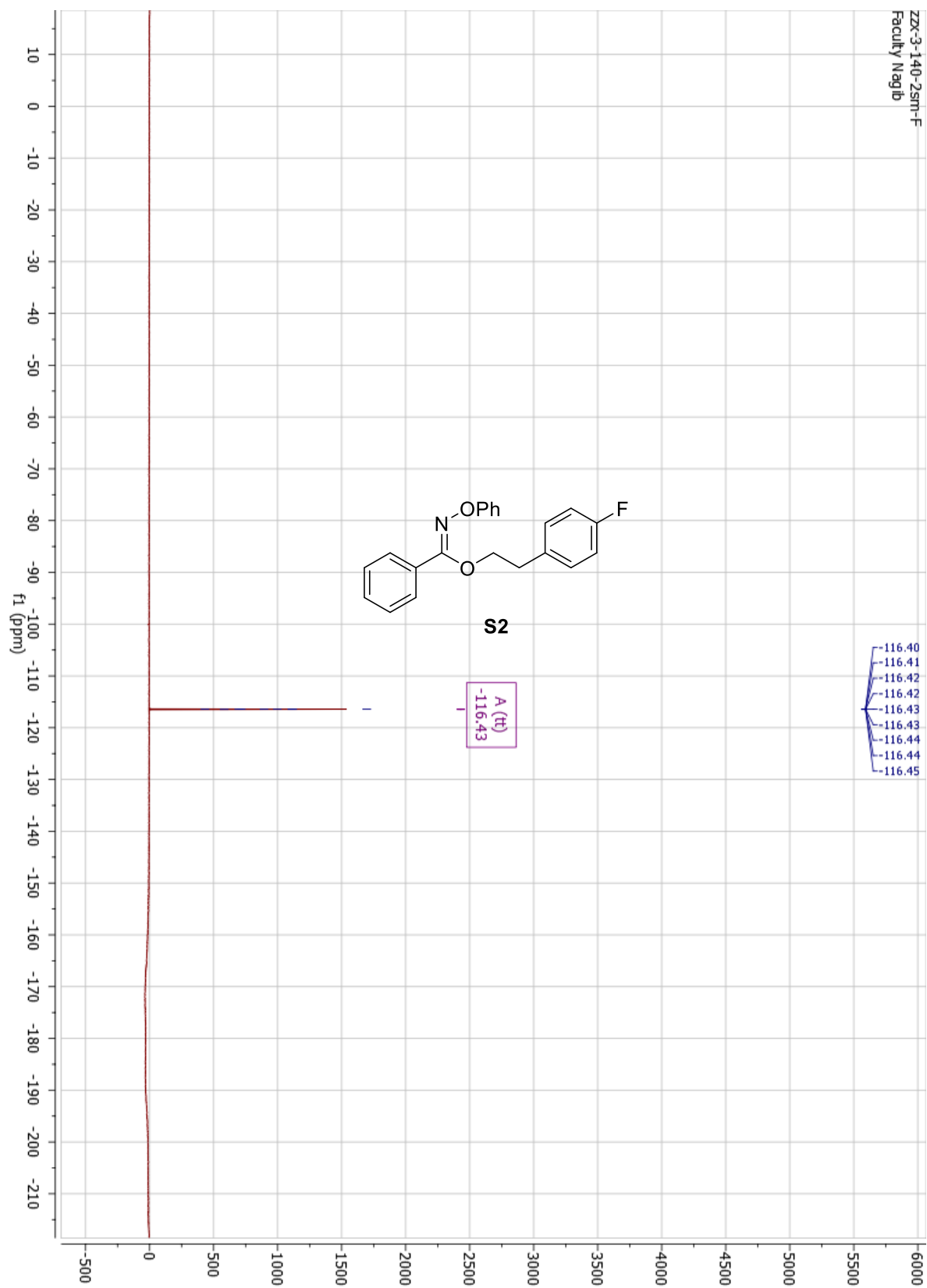
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# XI. NMR Spectra

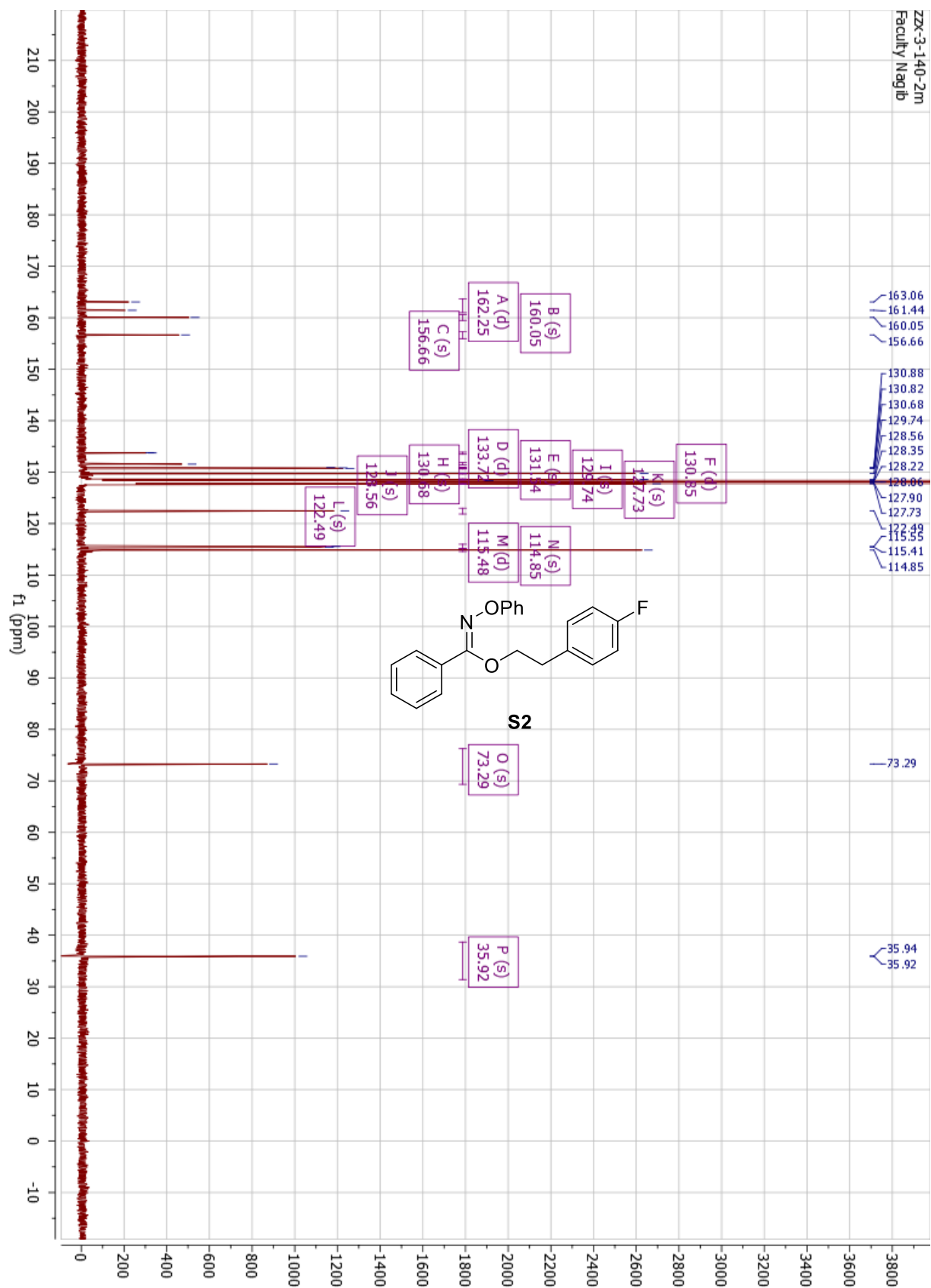


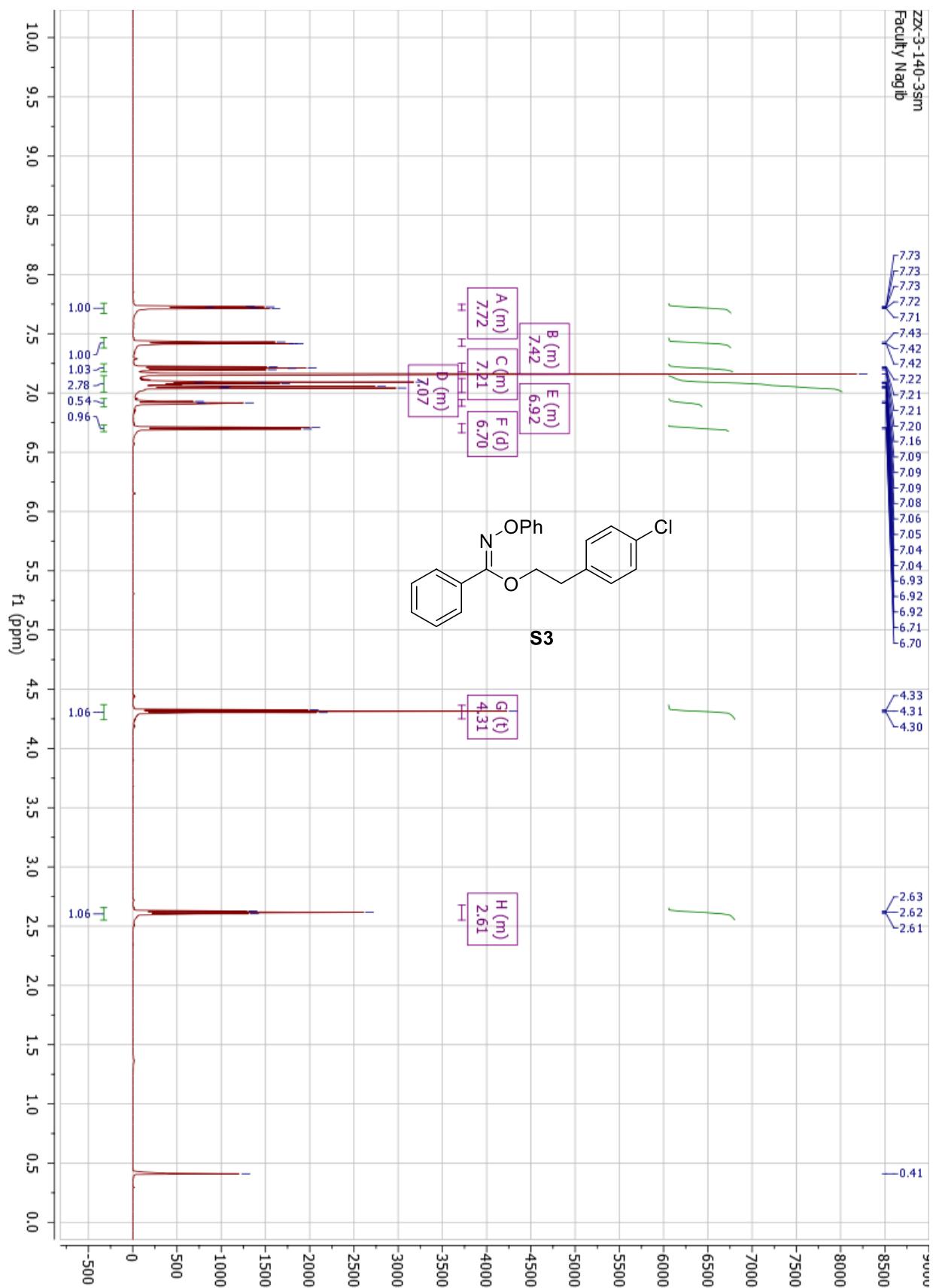


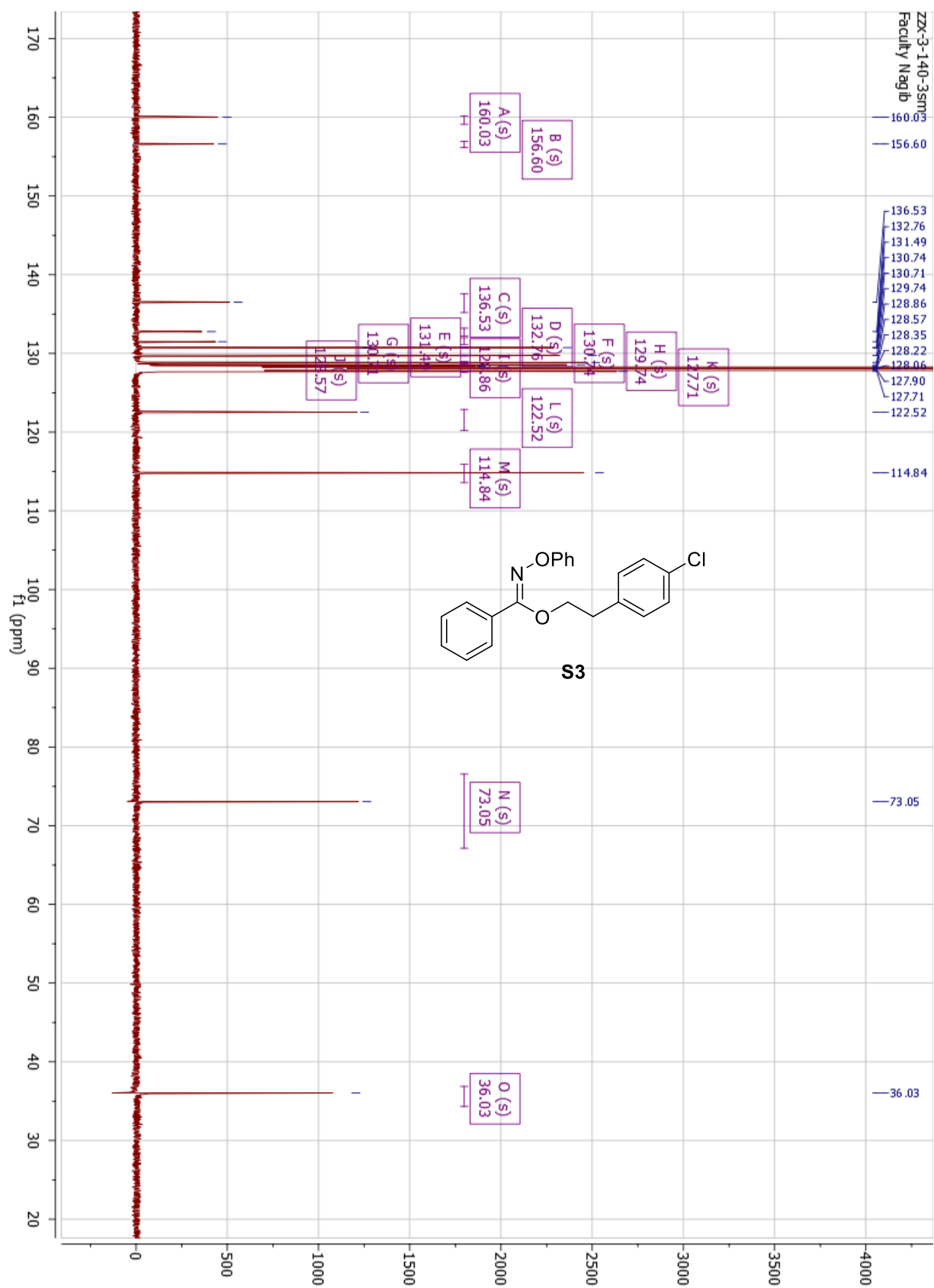


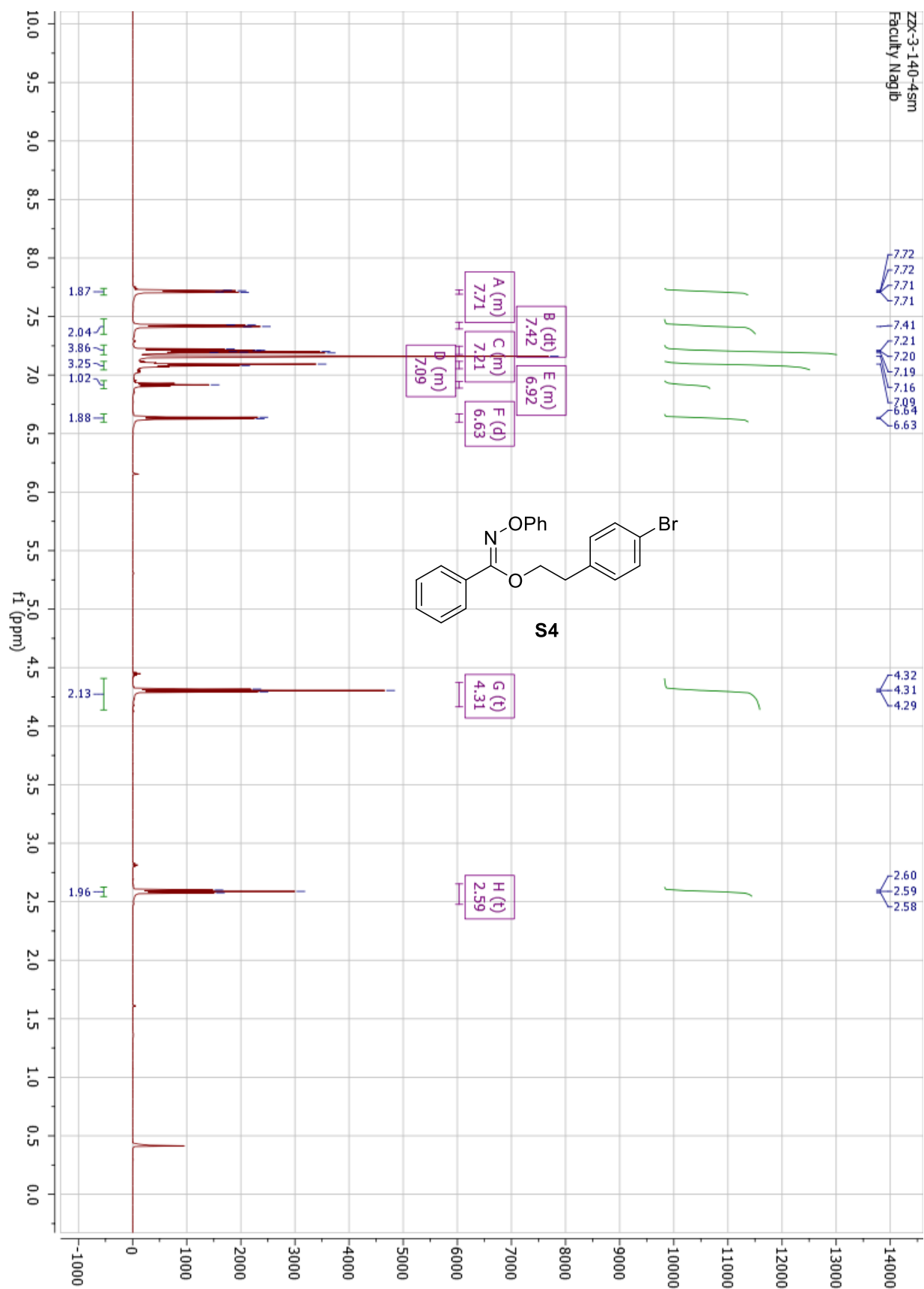


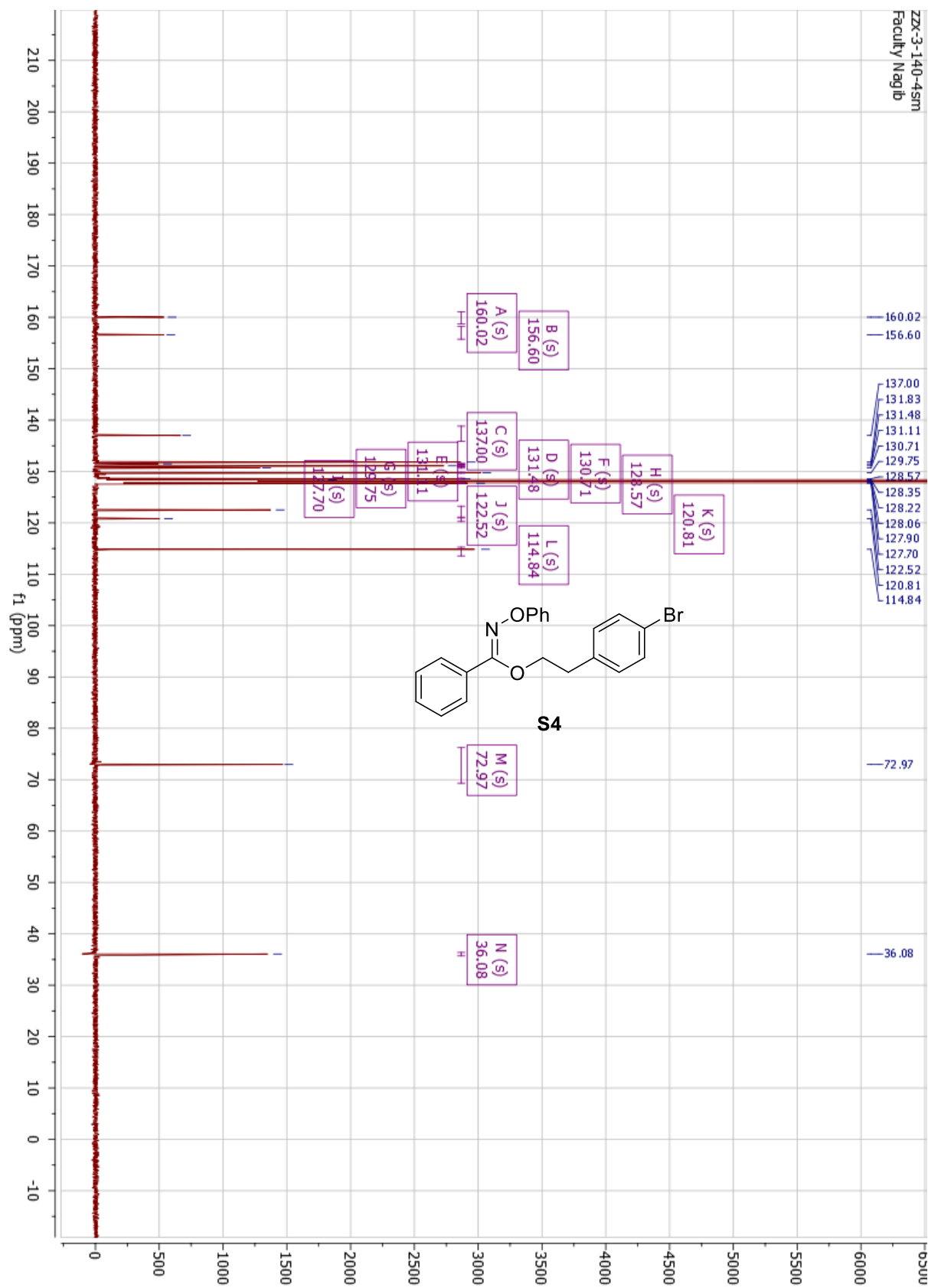


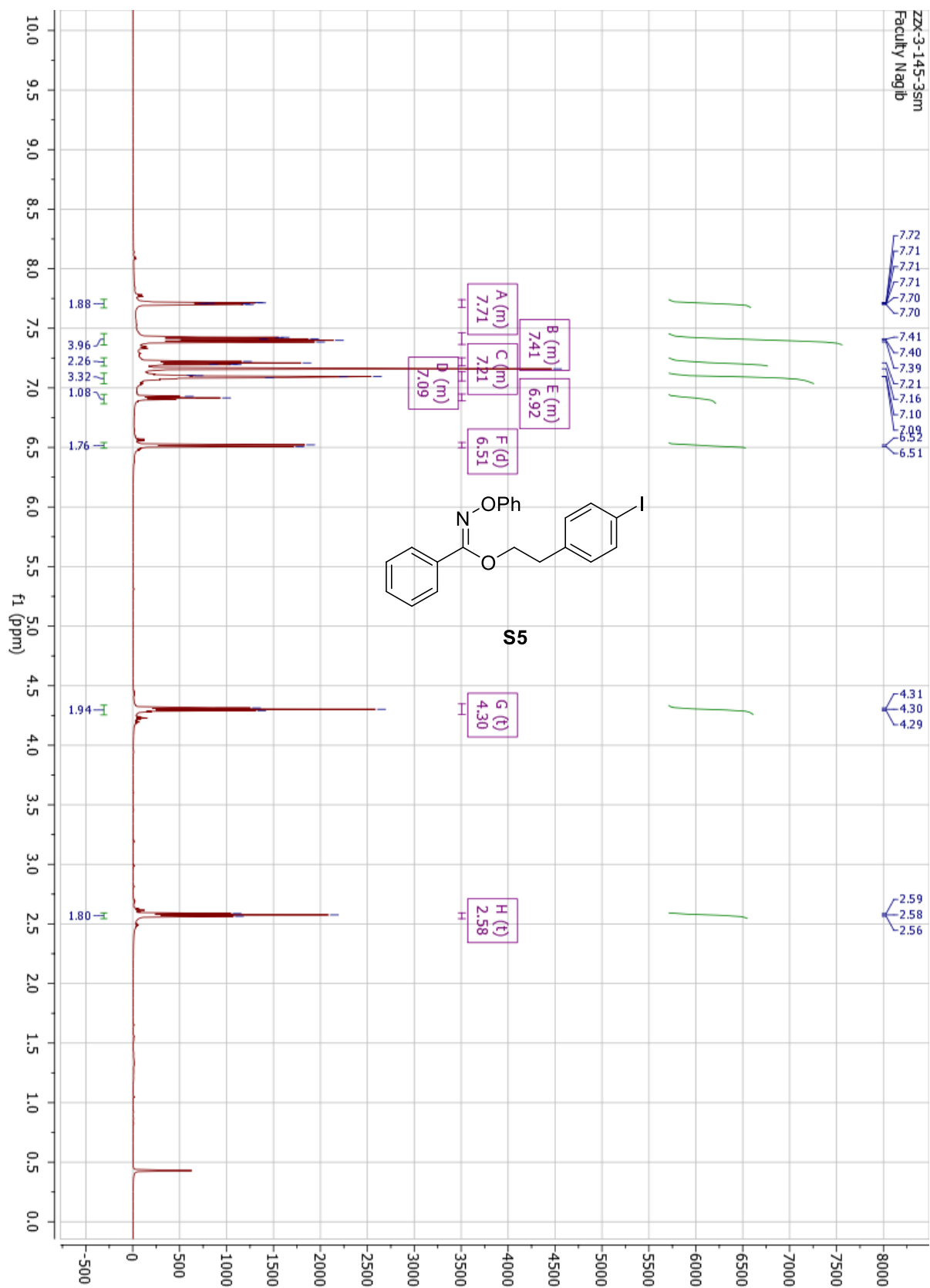


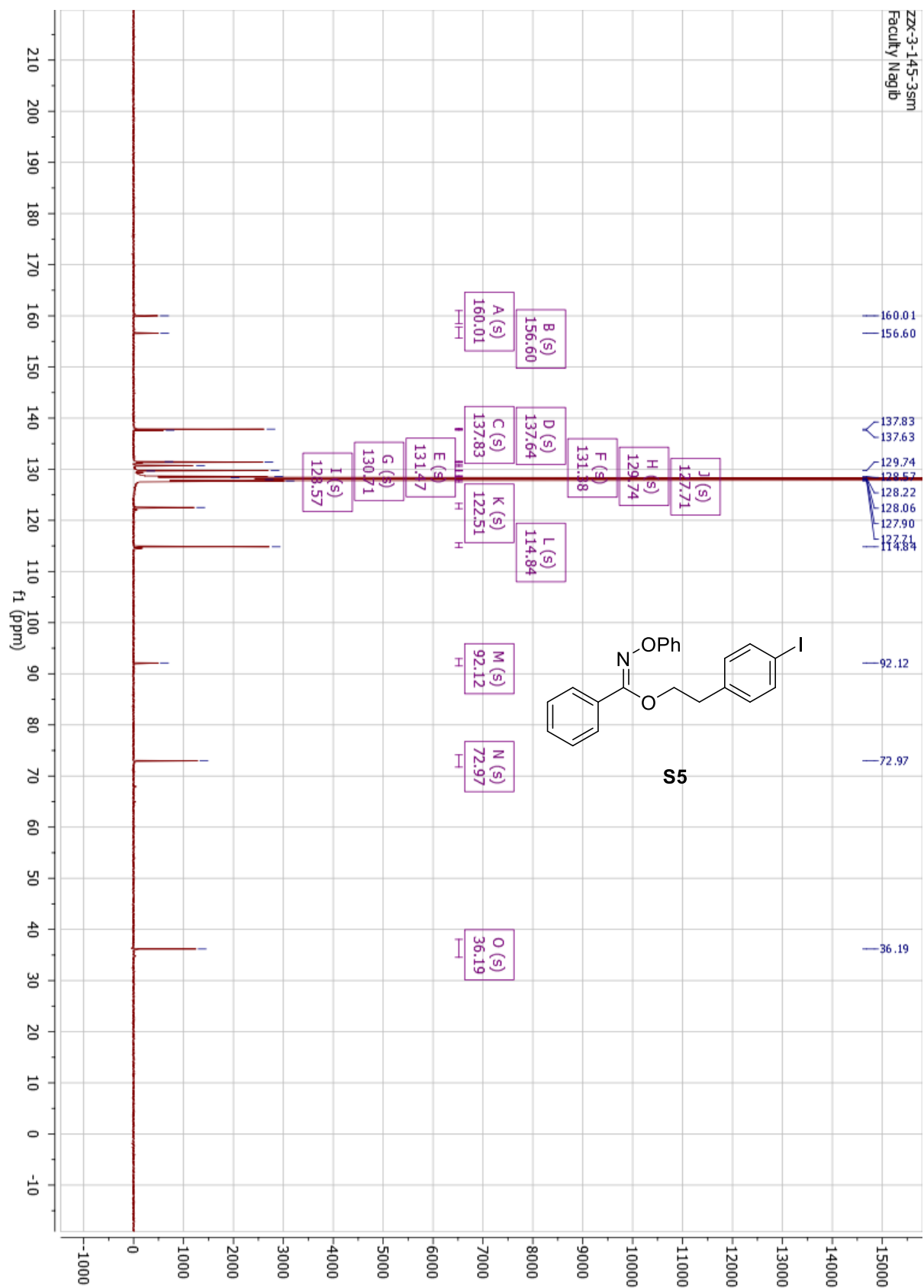


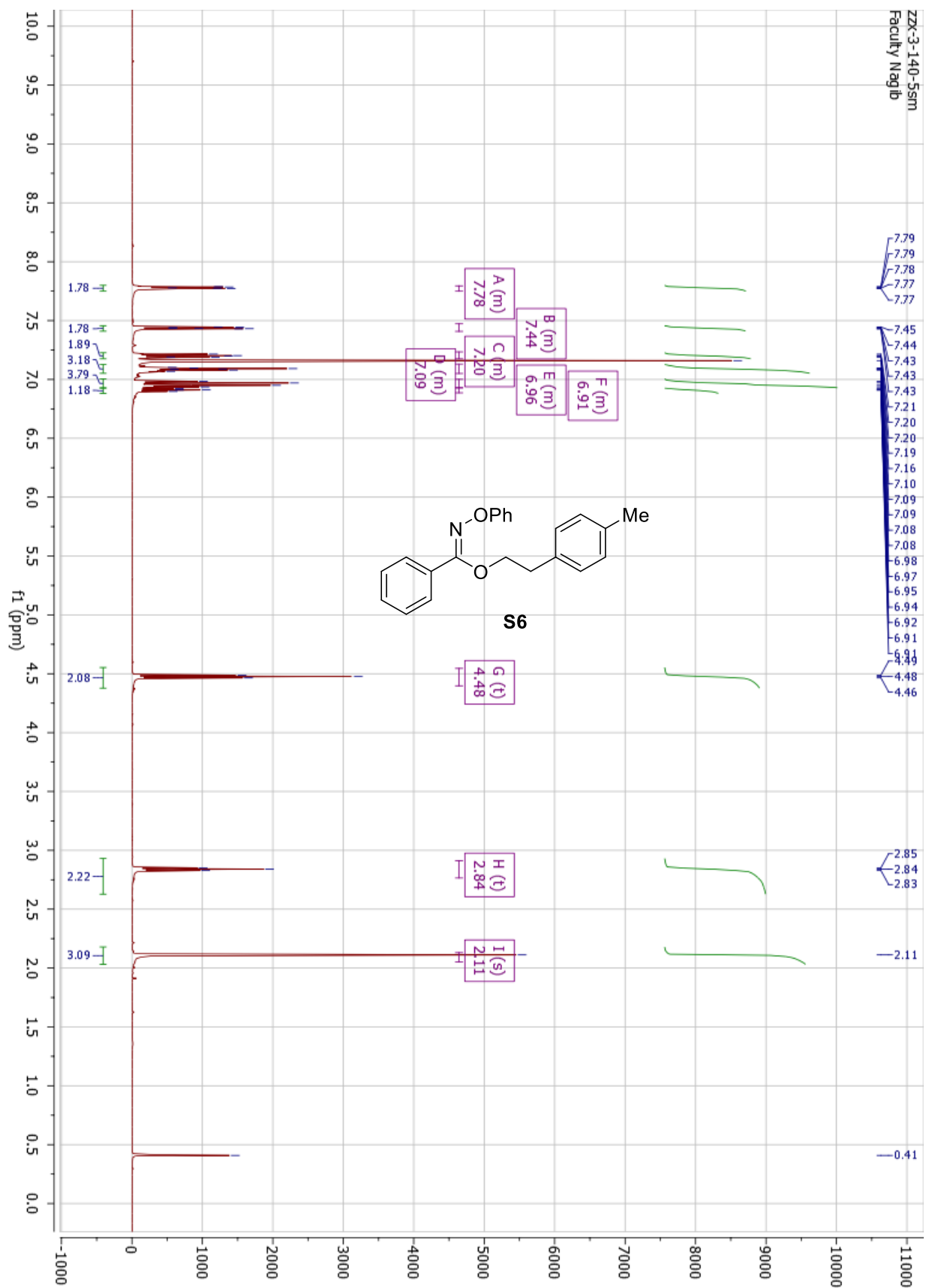




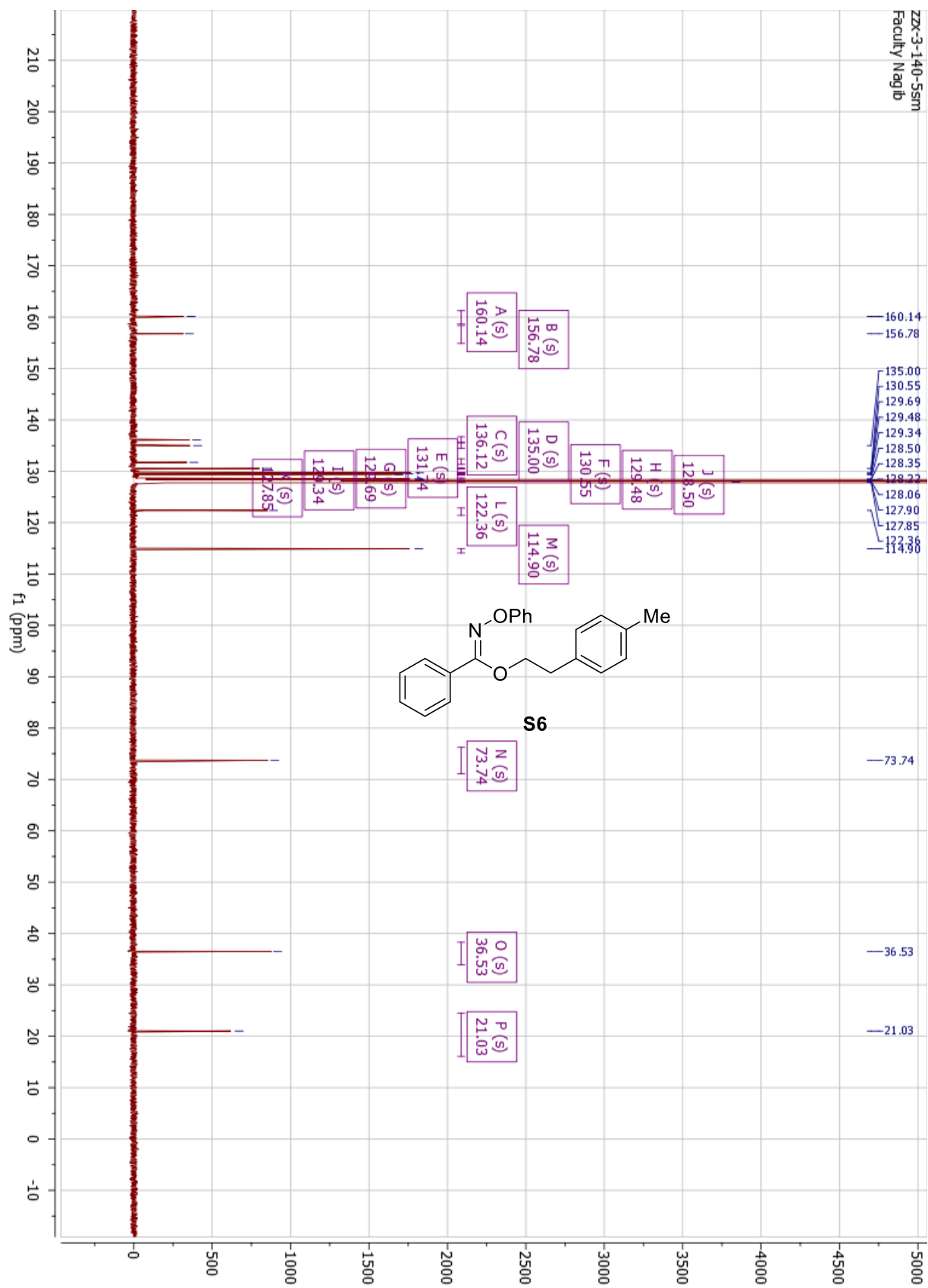


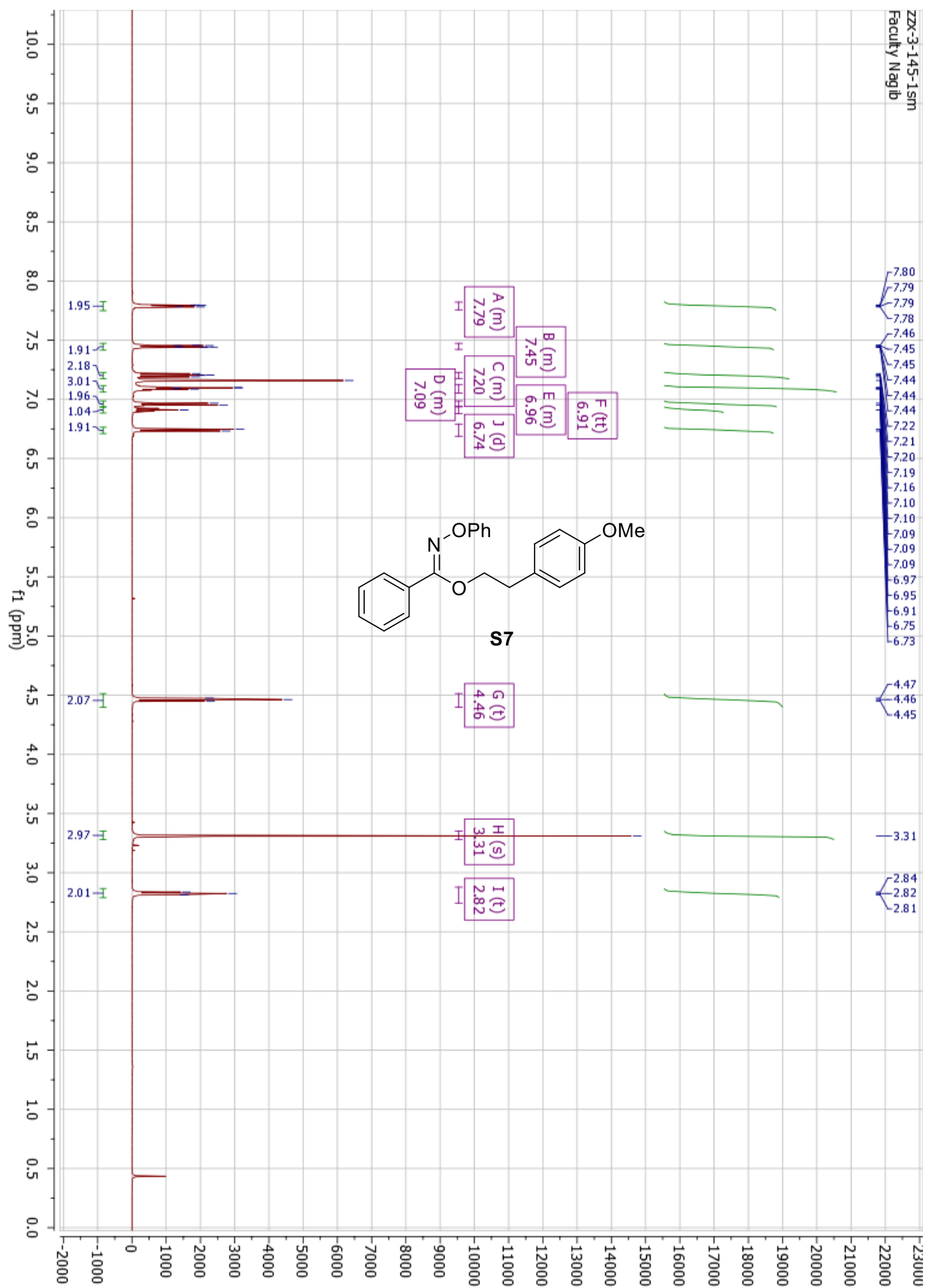


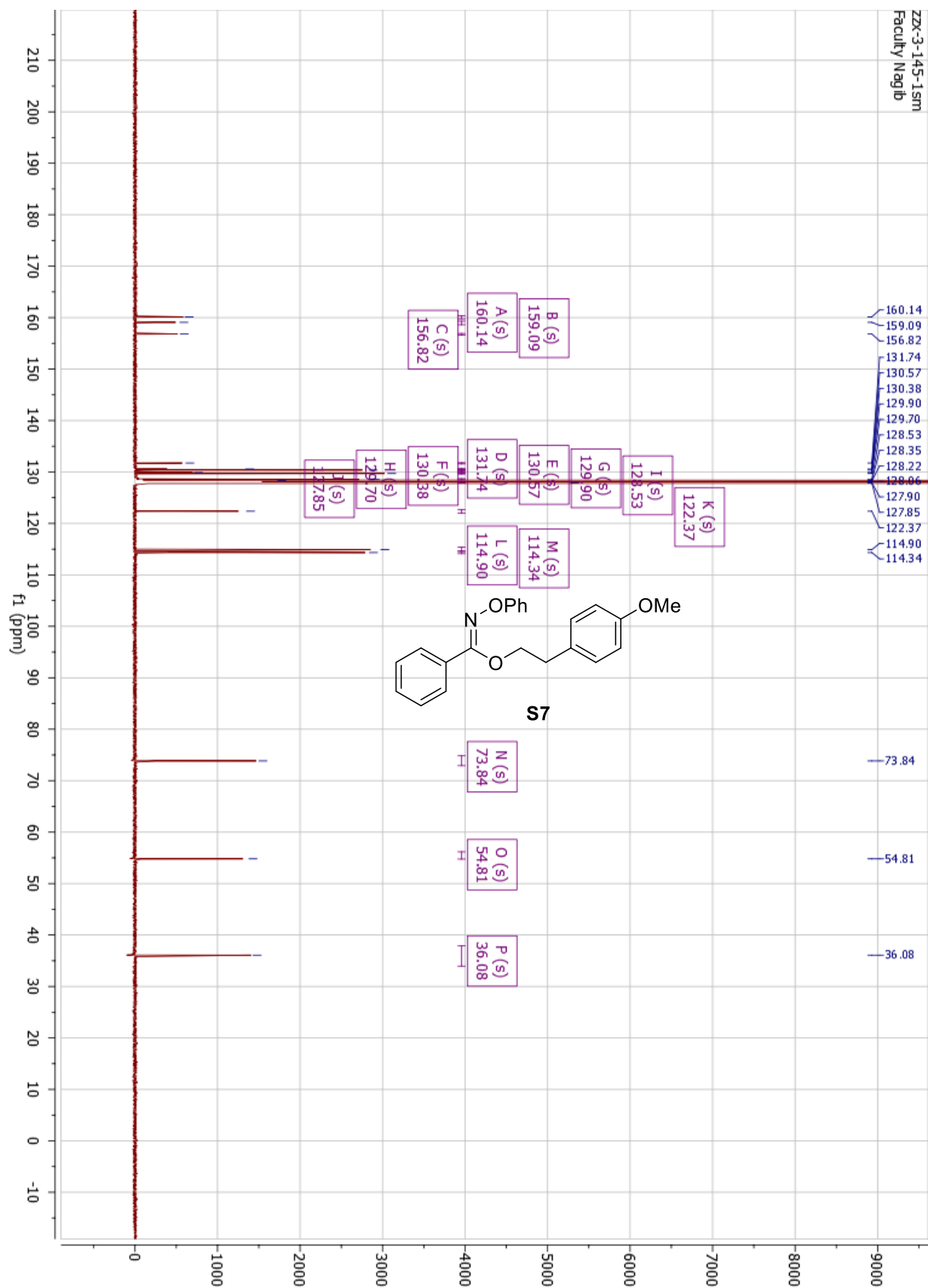


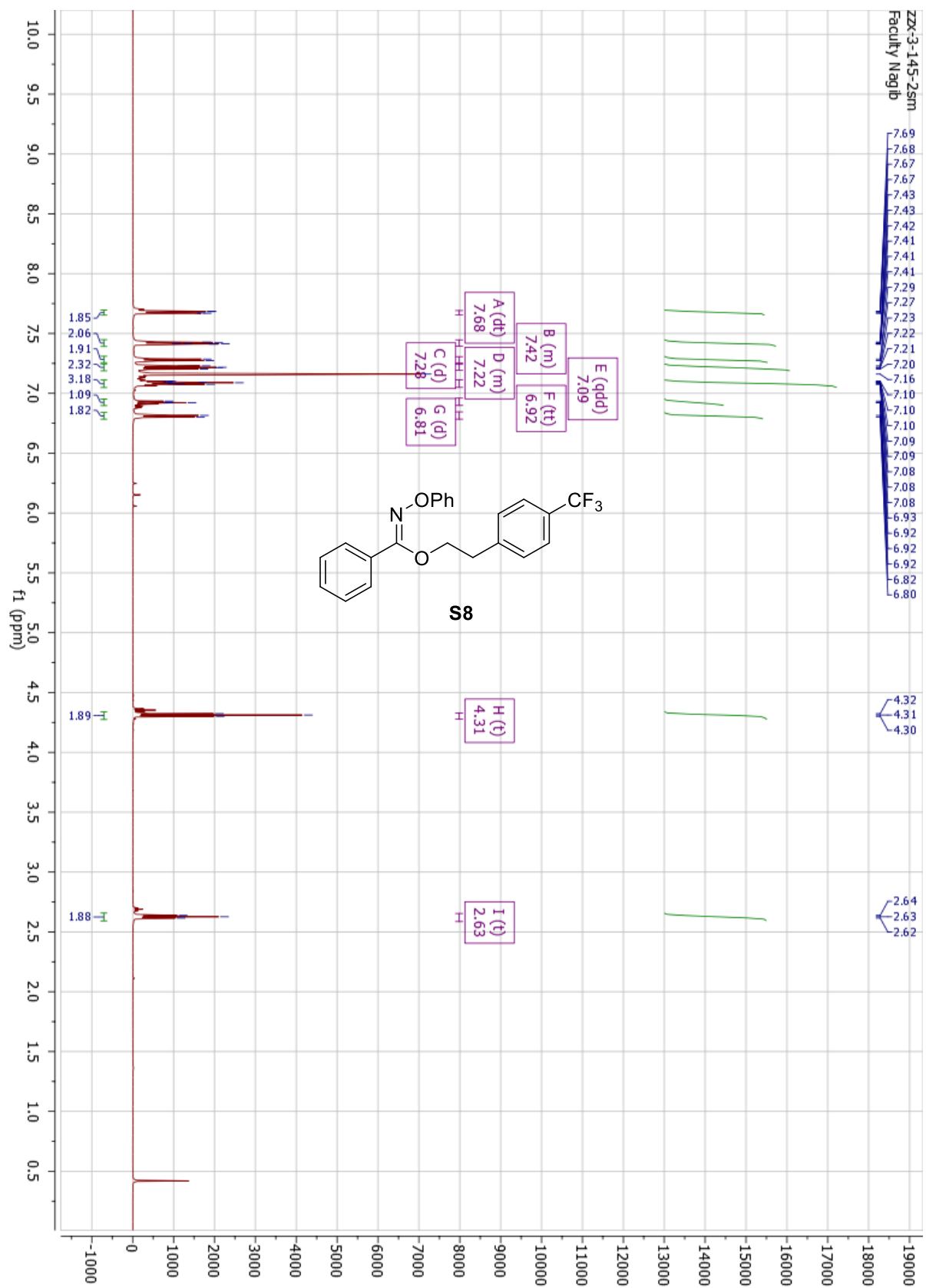


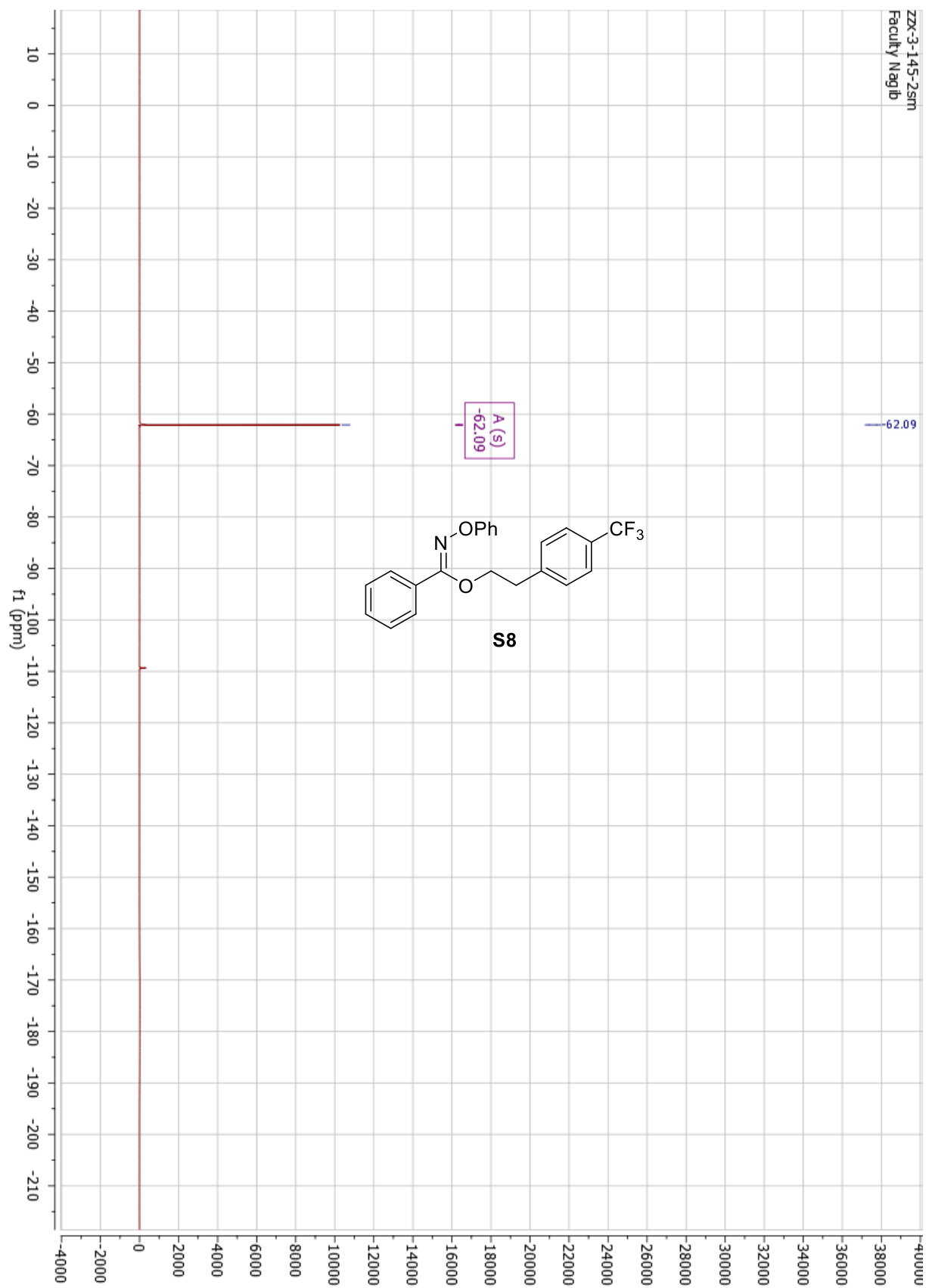


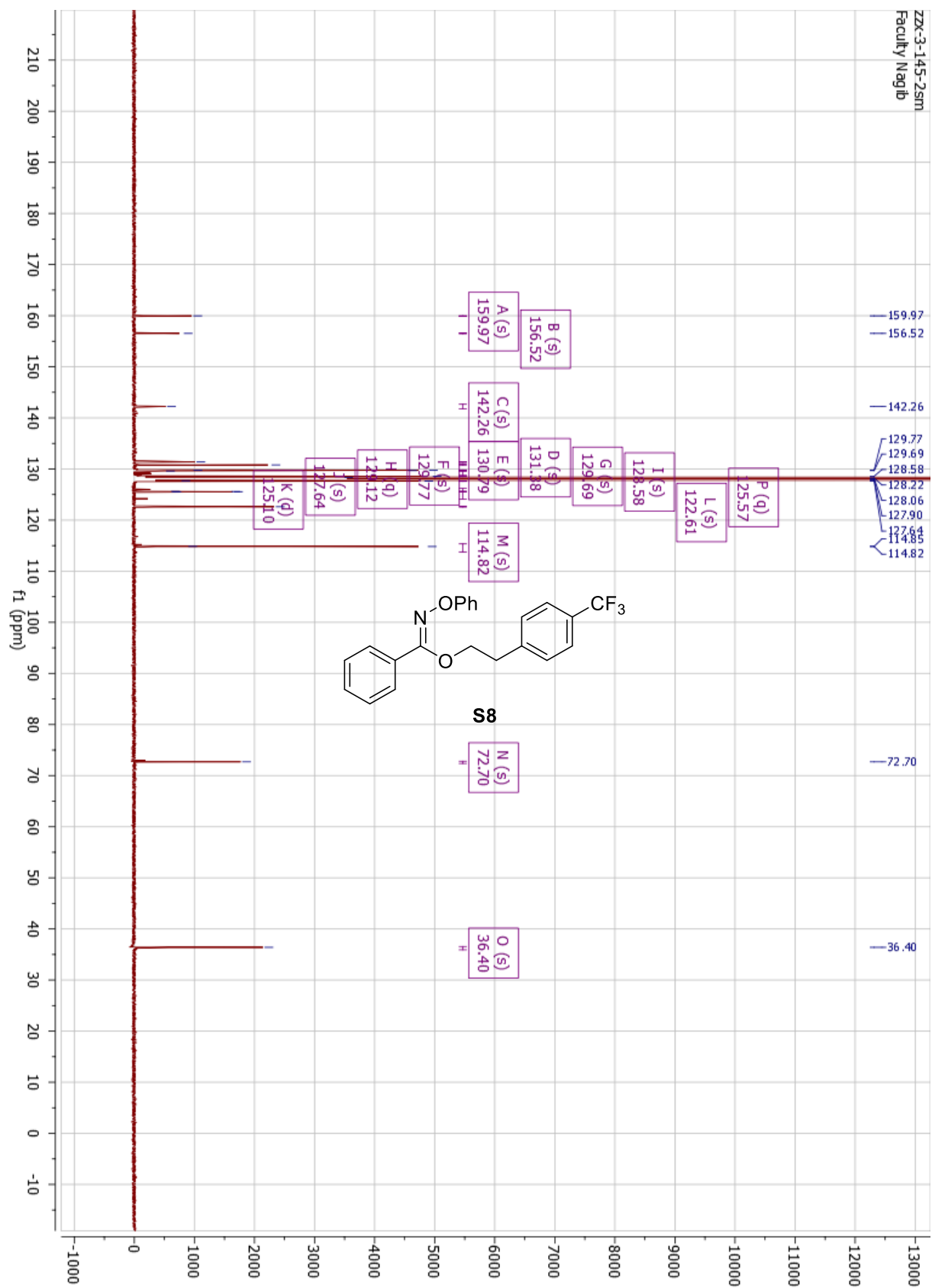


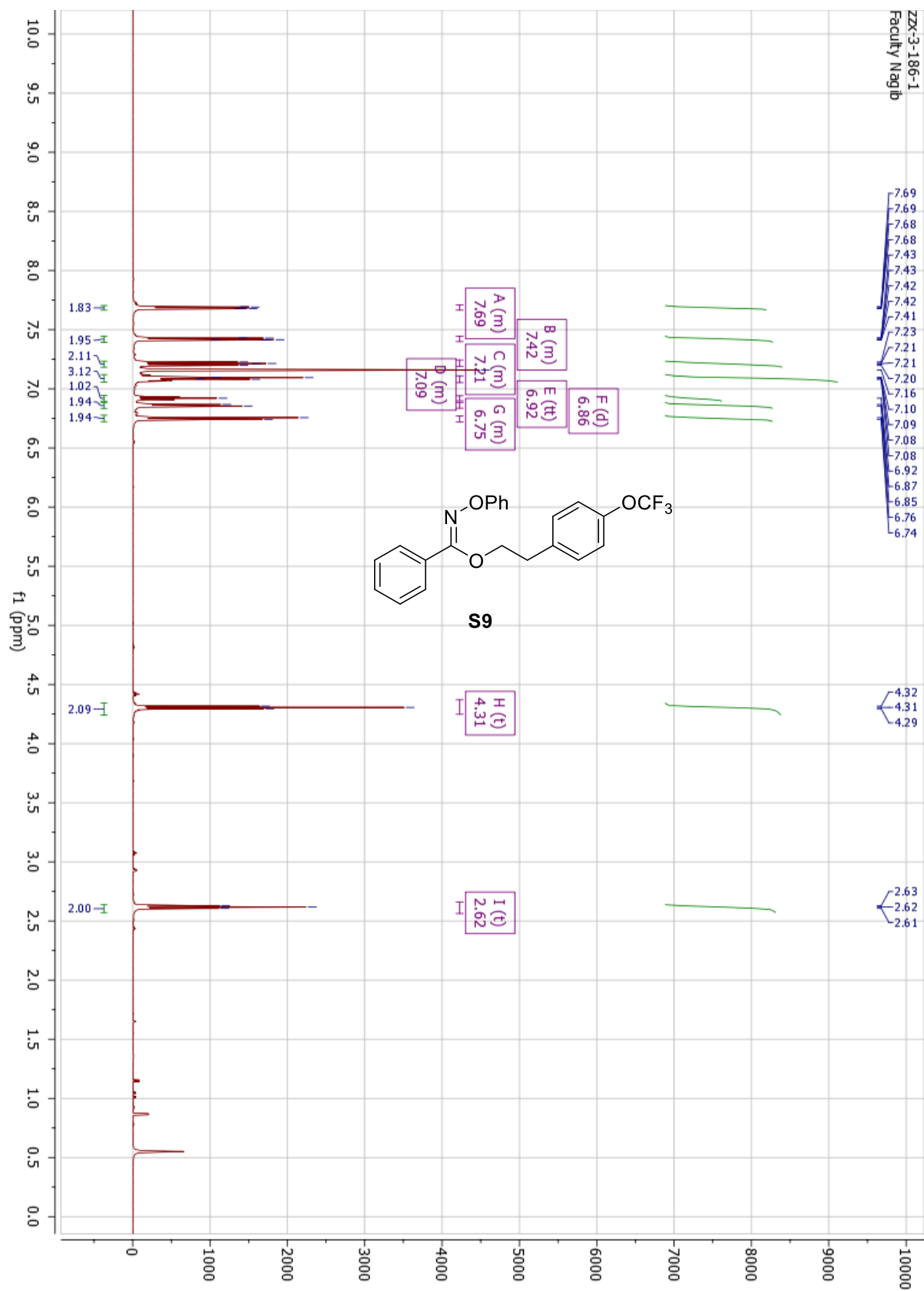


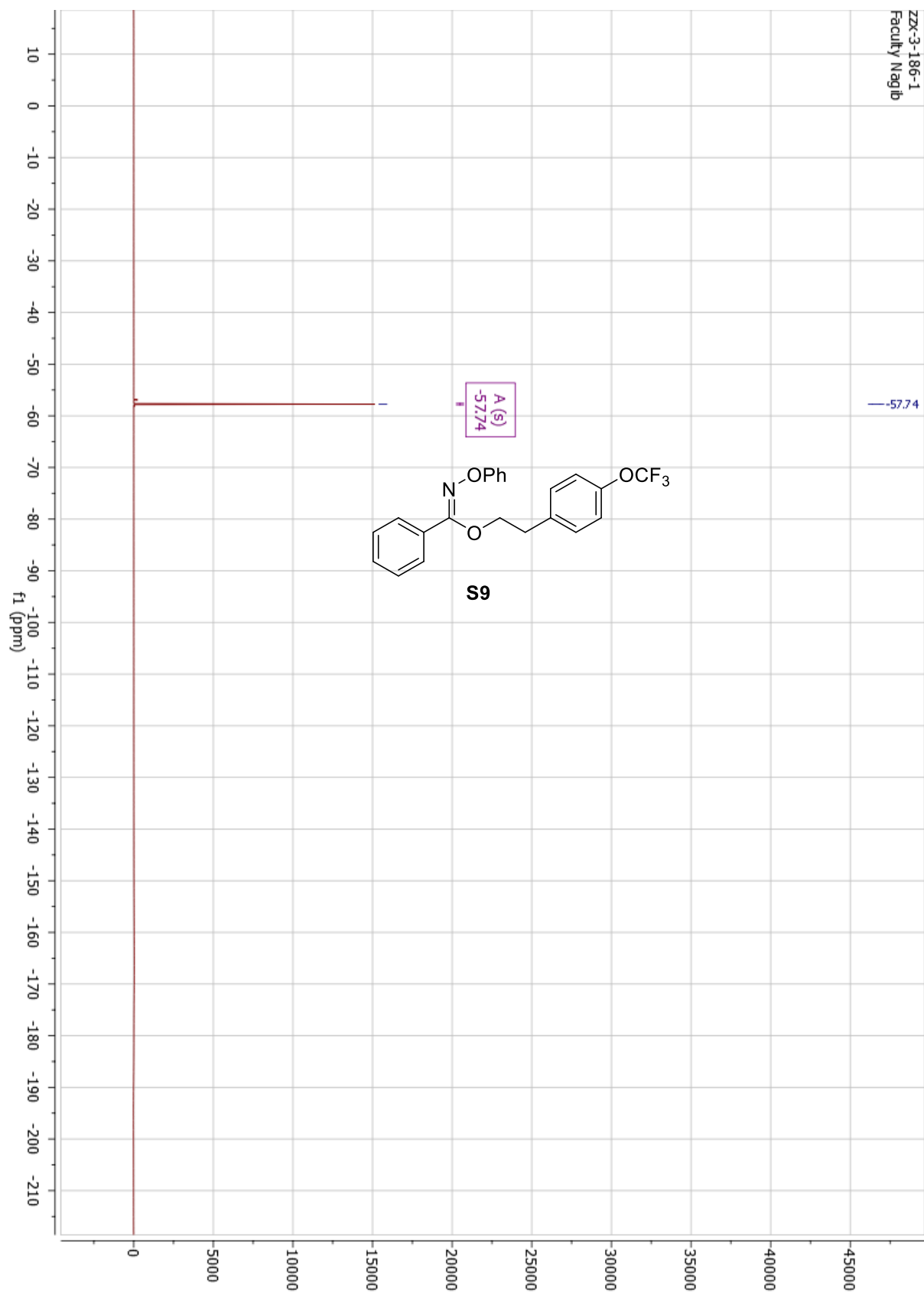




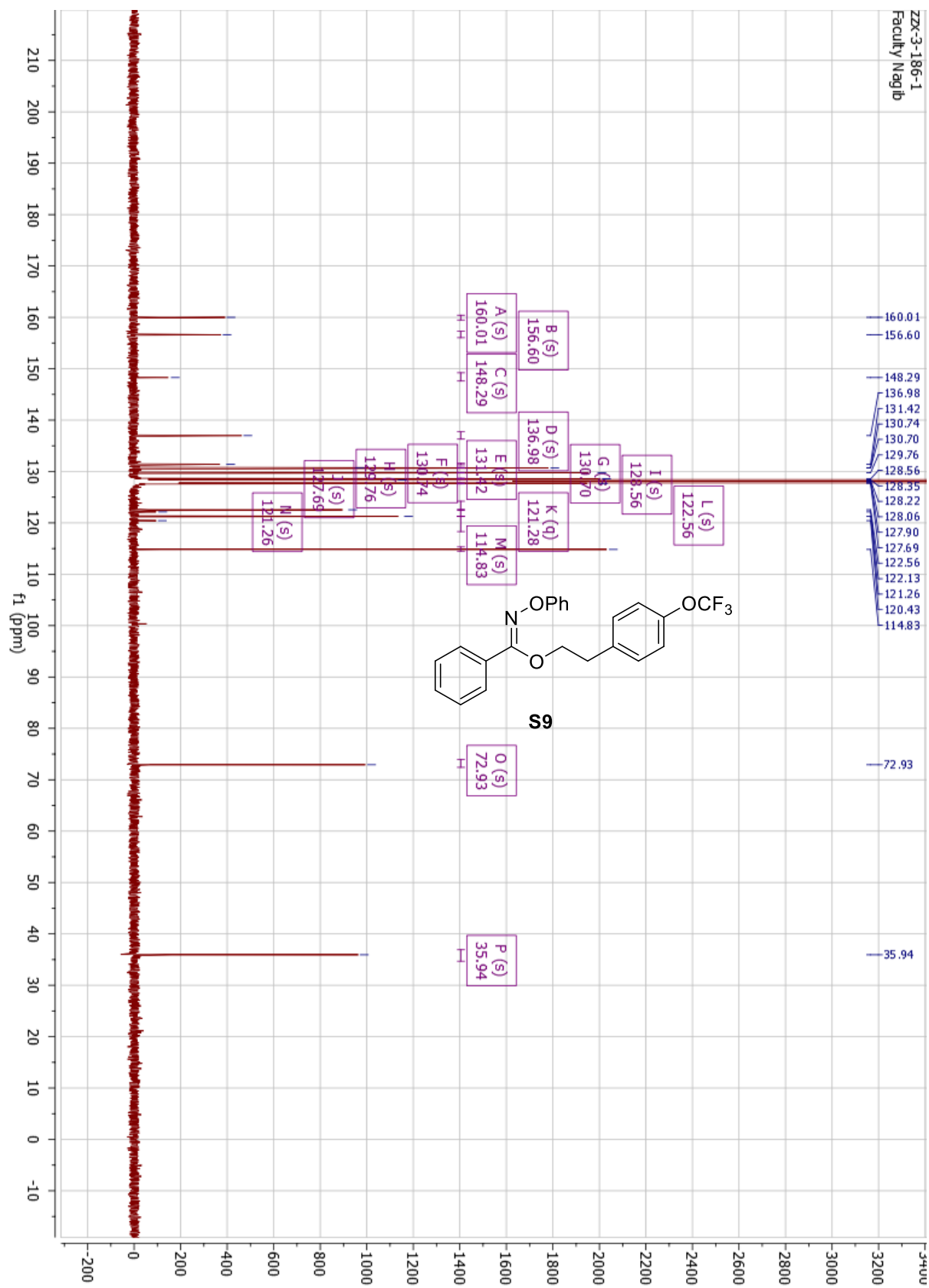


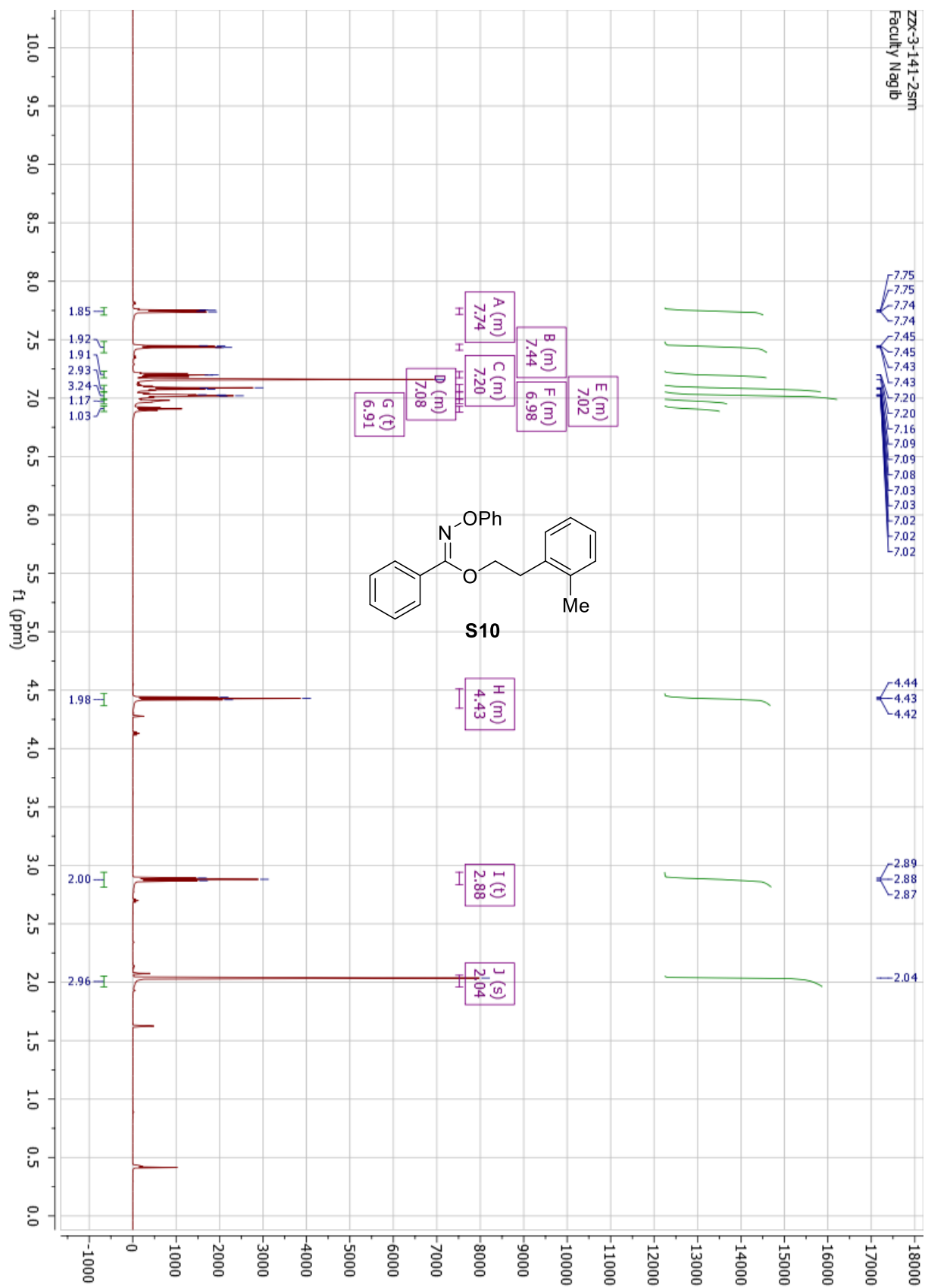


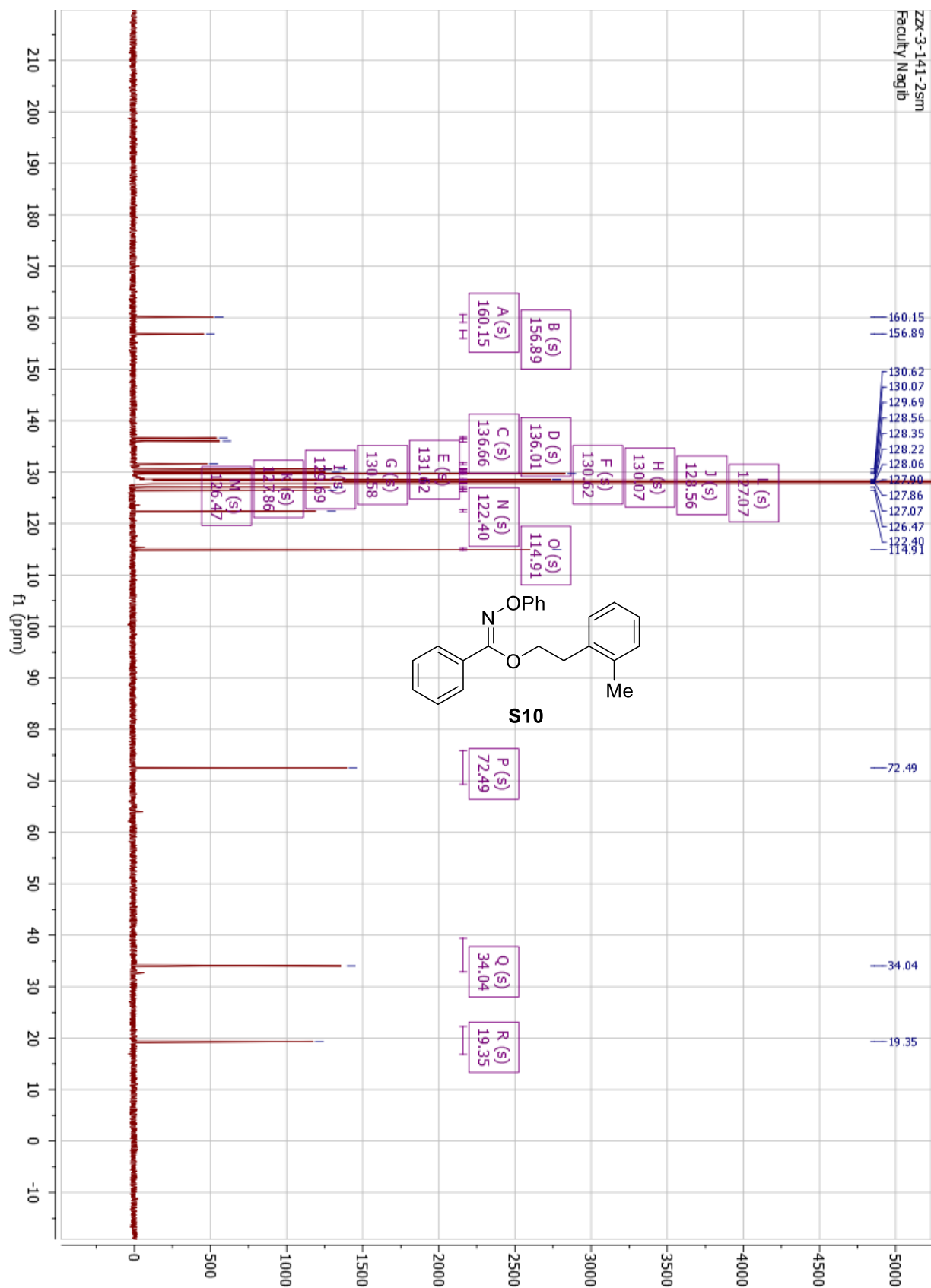


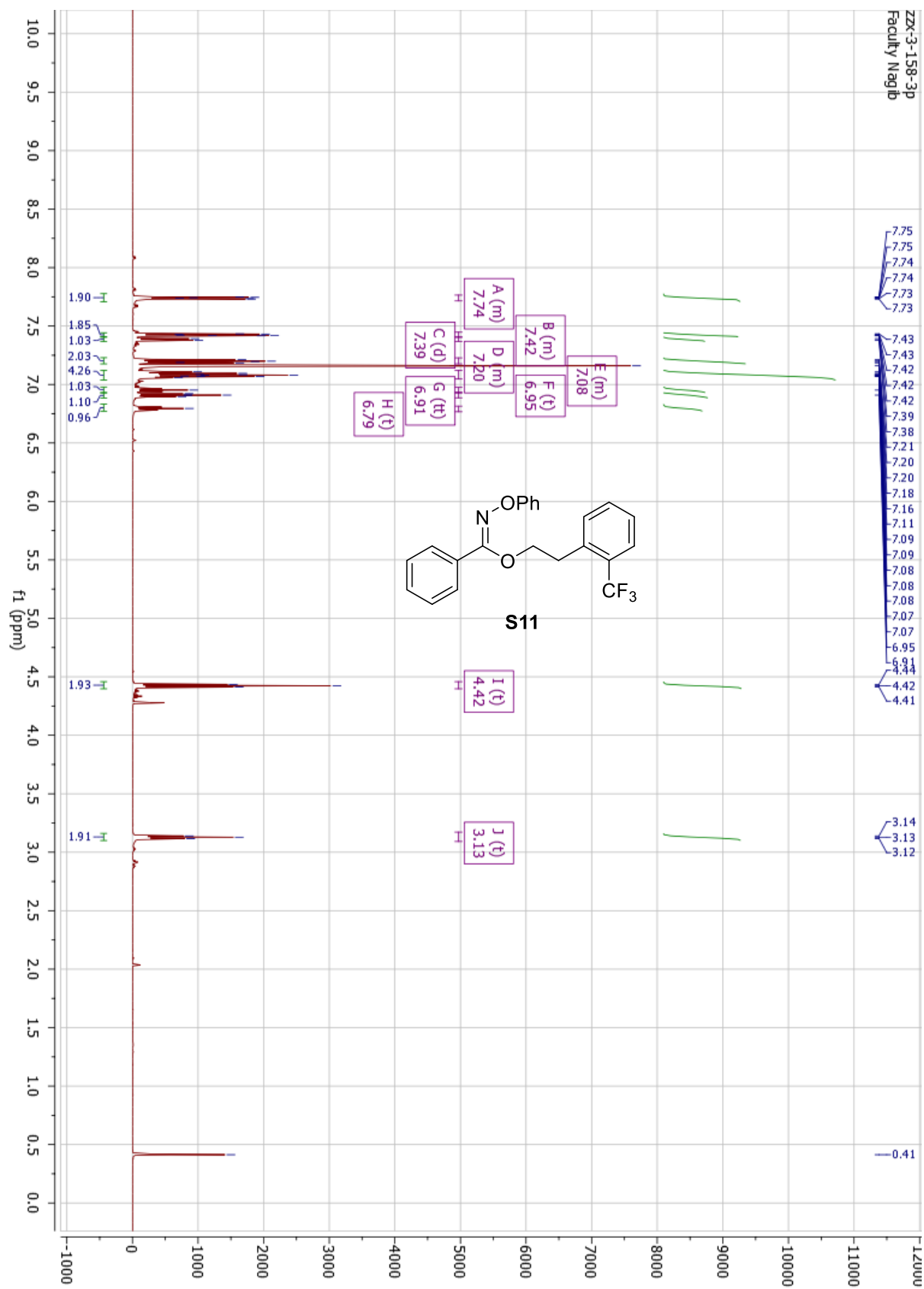


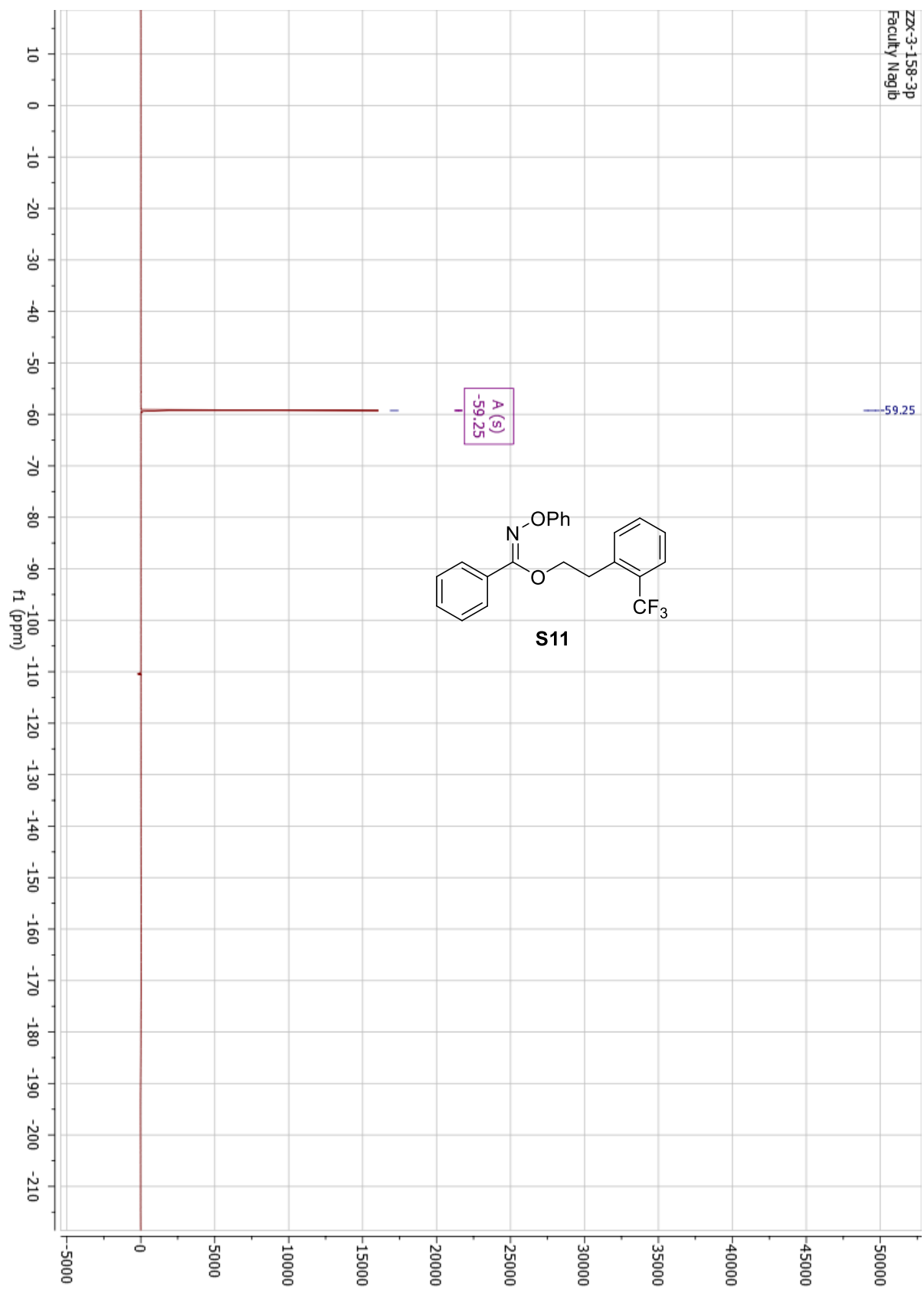


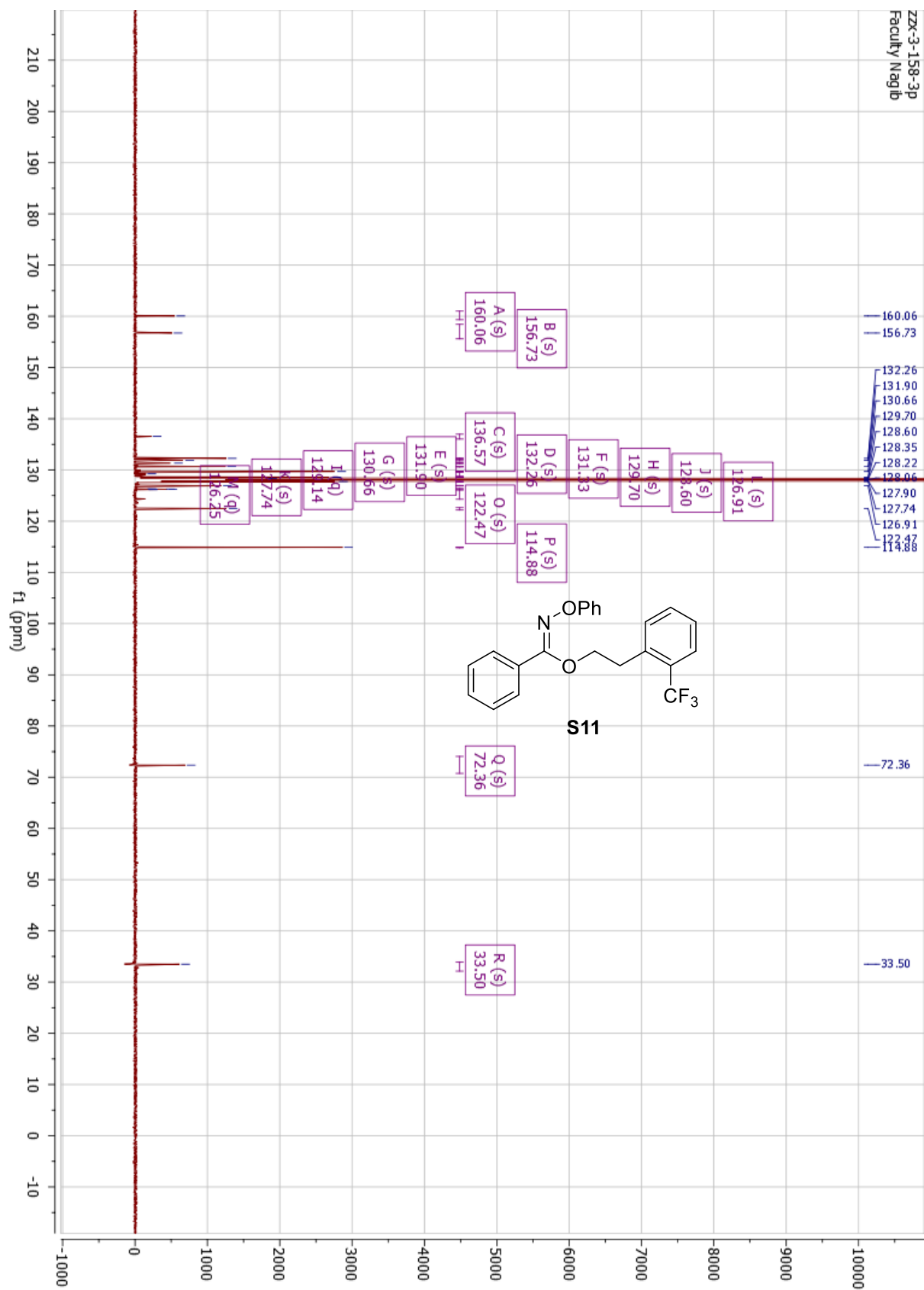


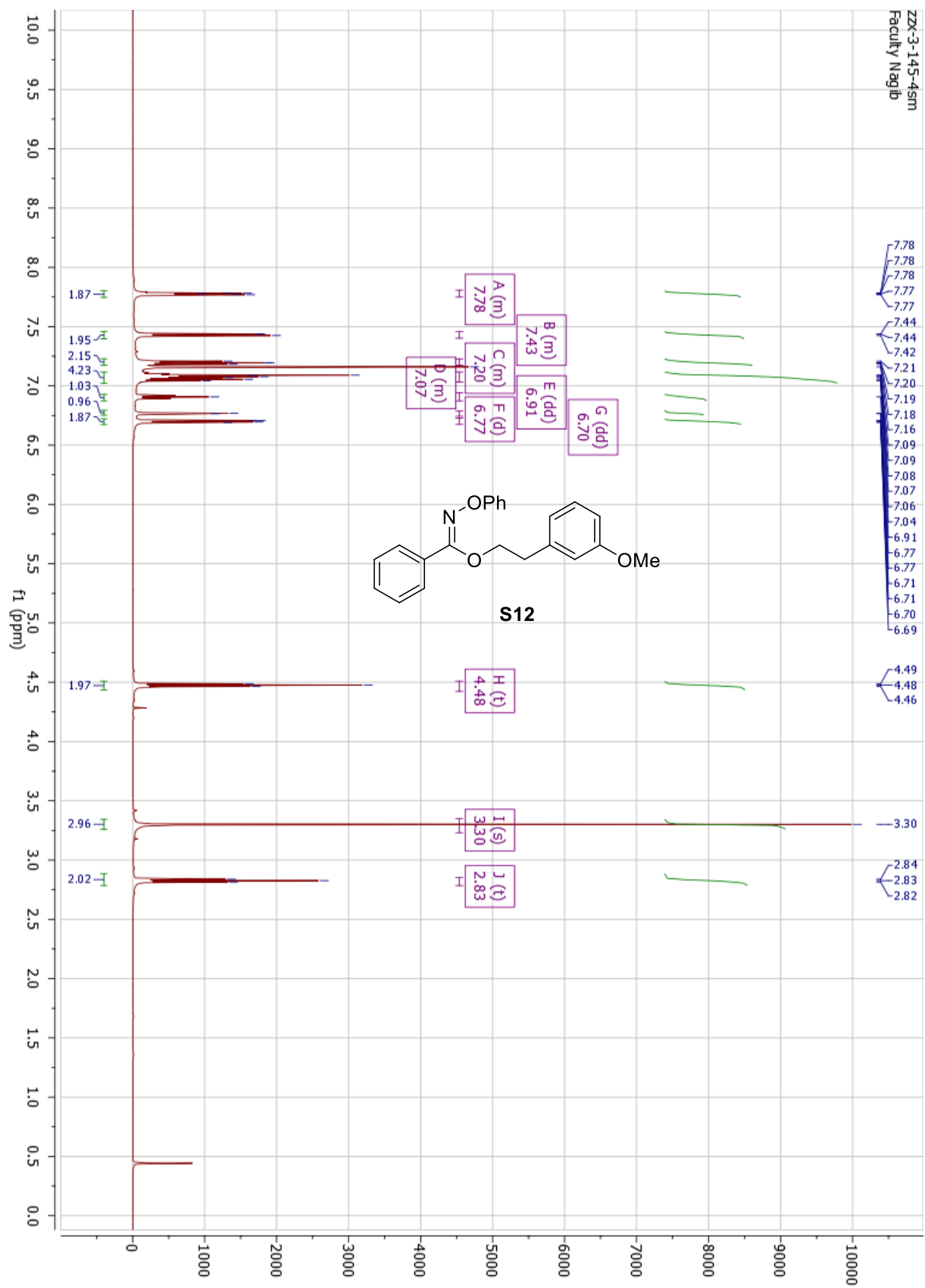








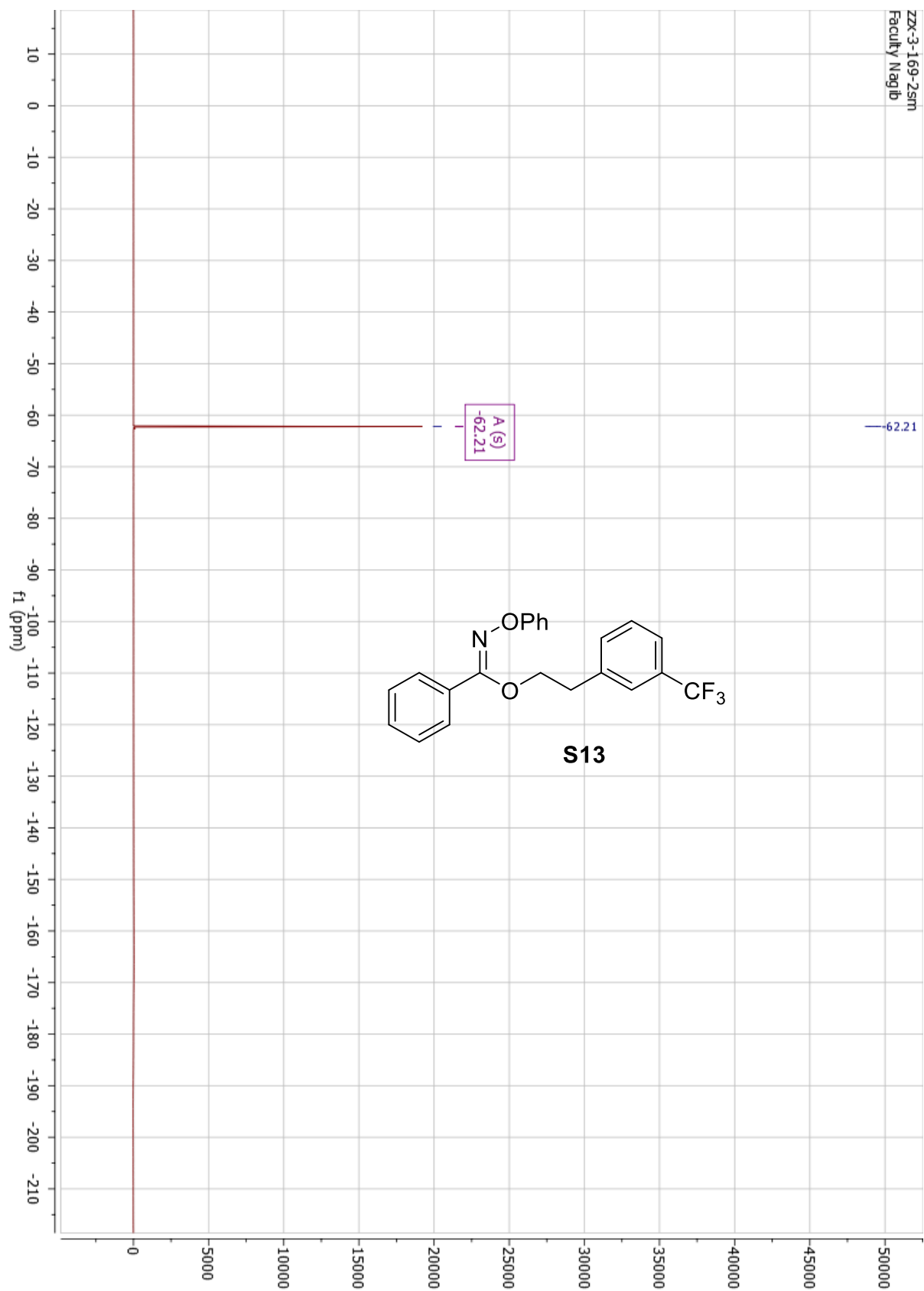


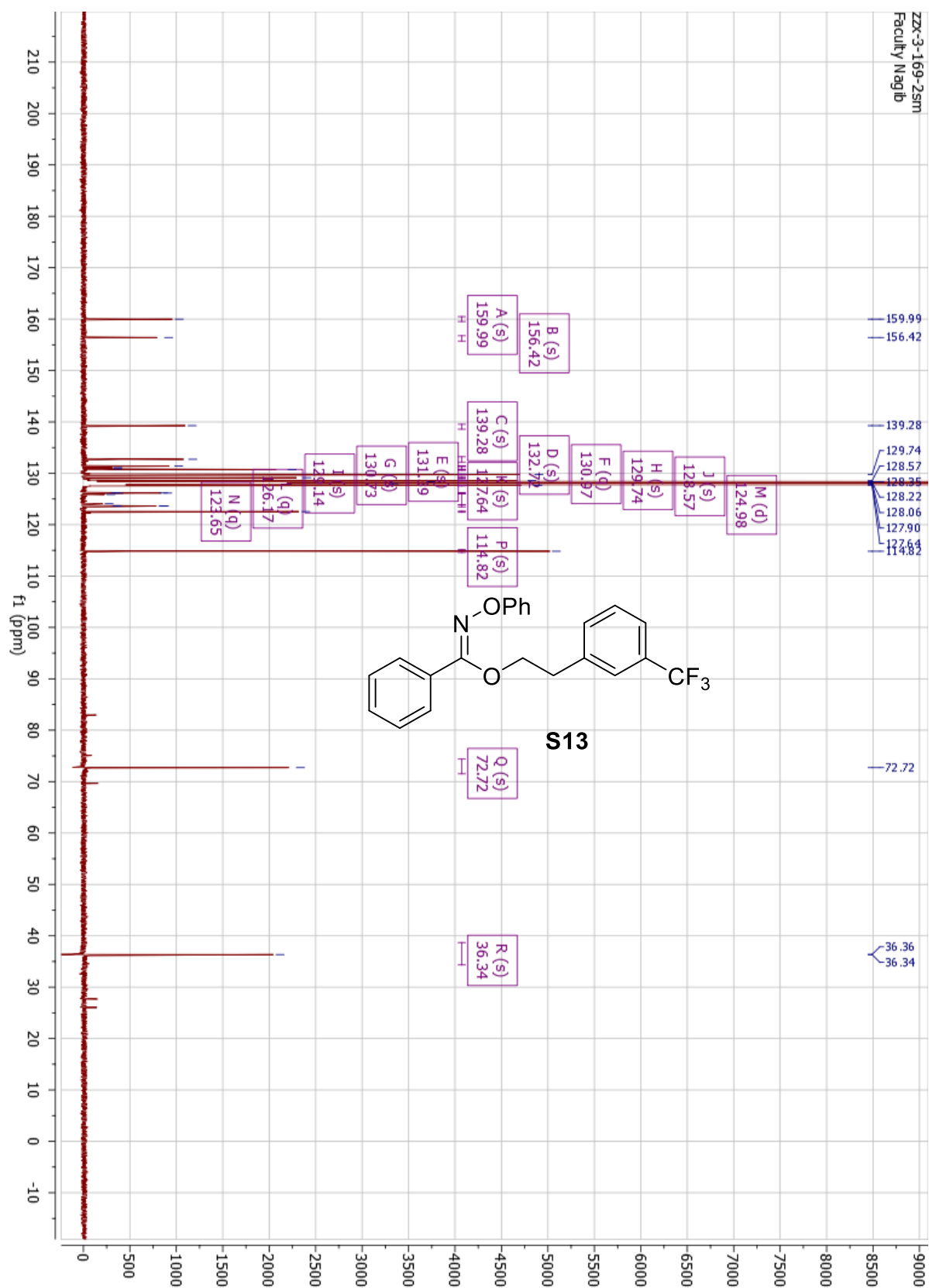


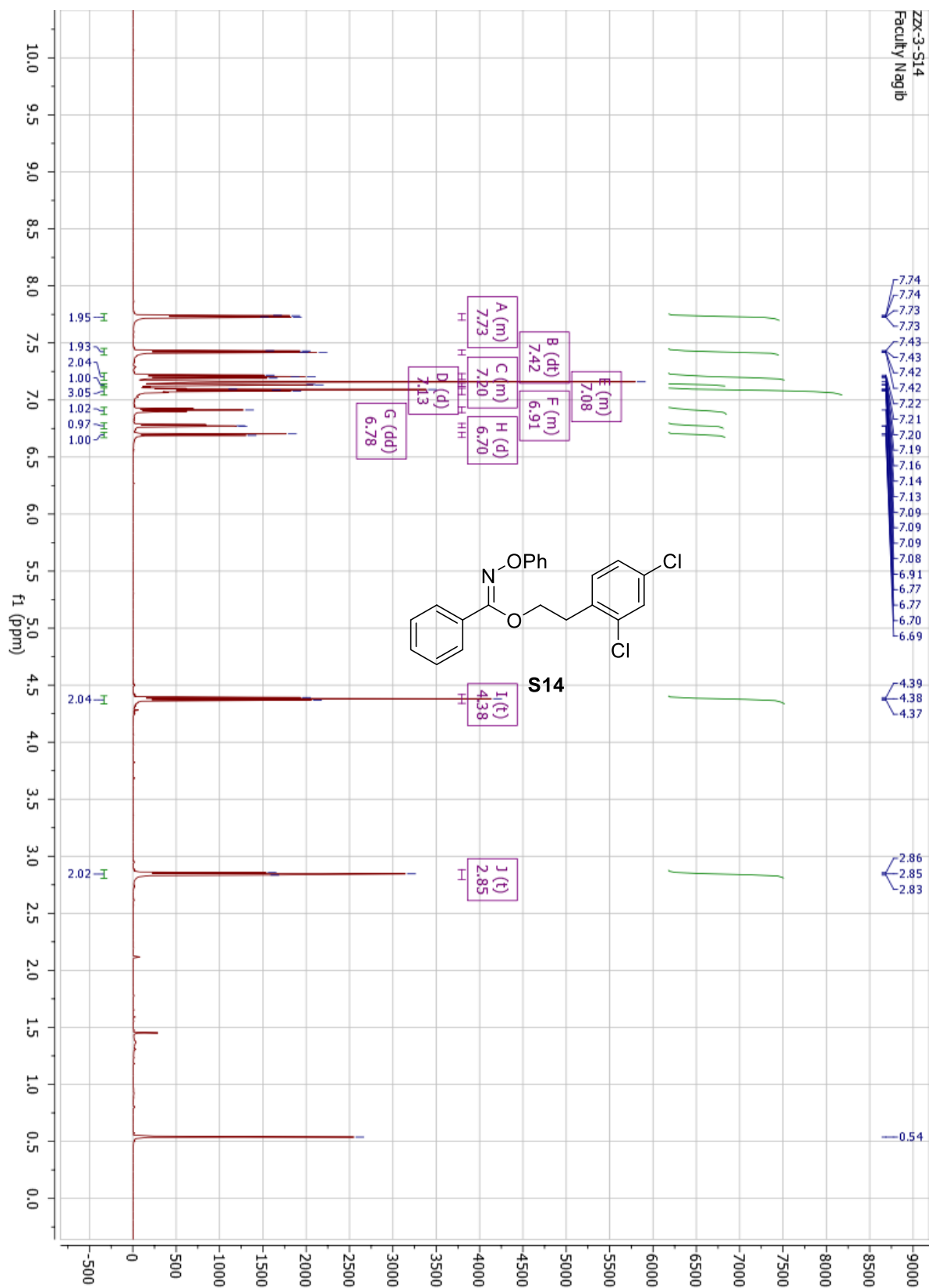


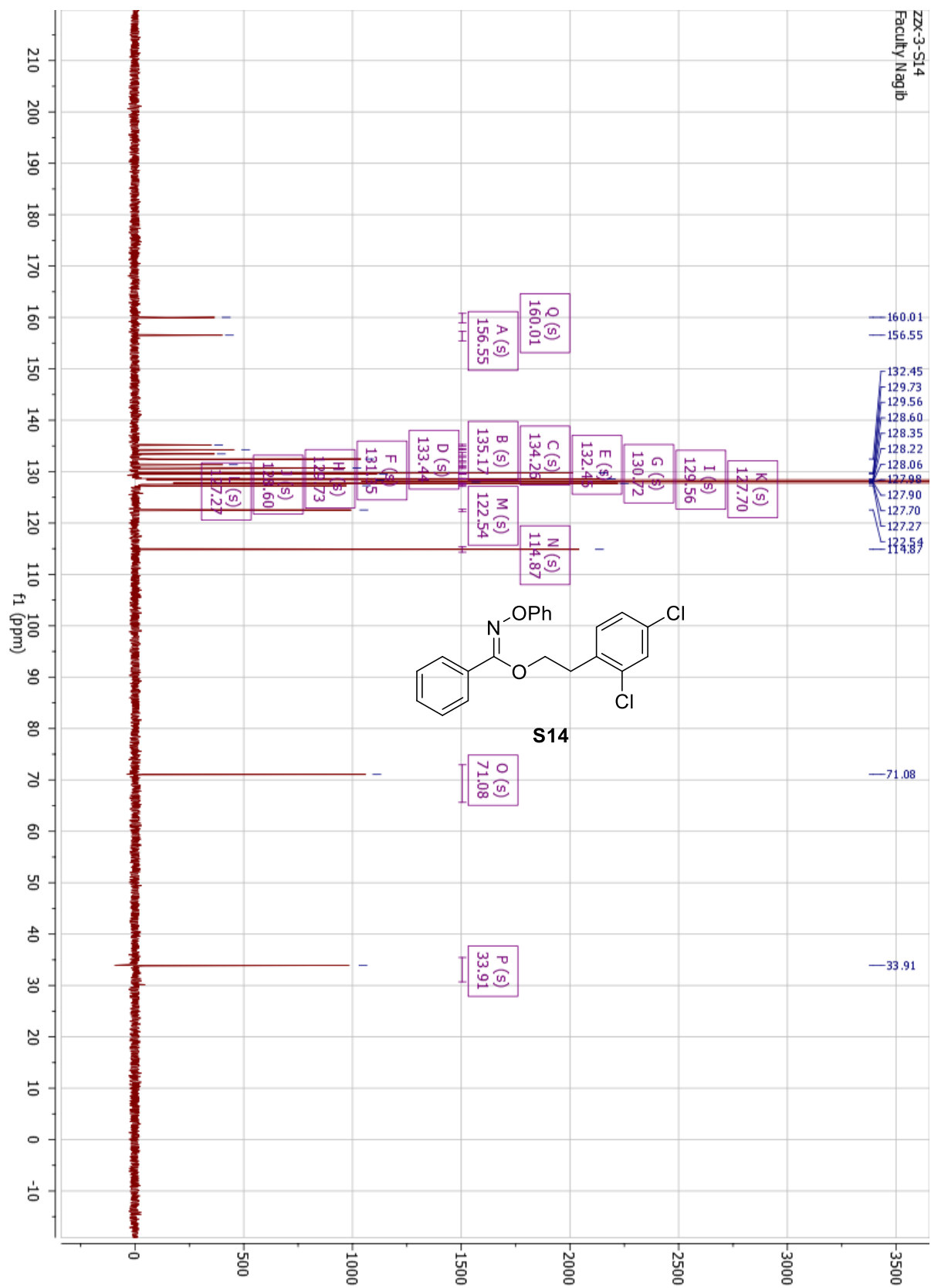


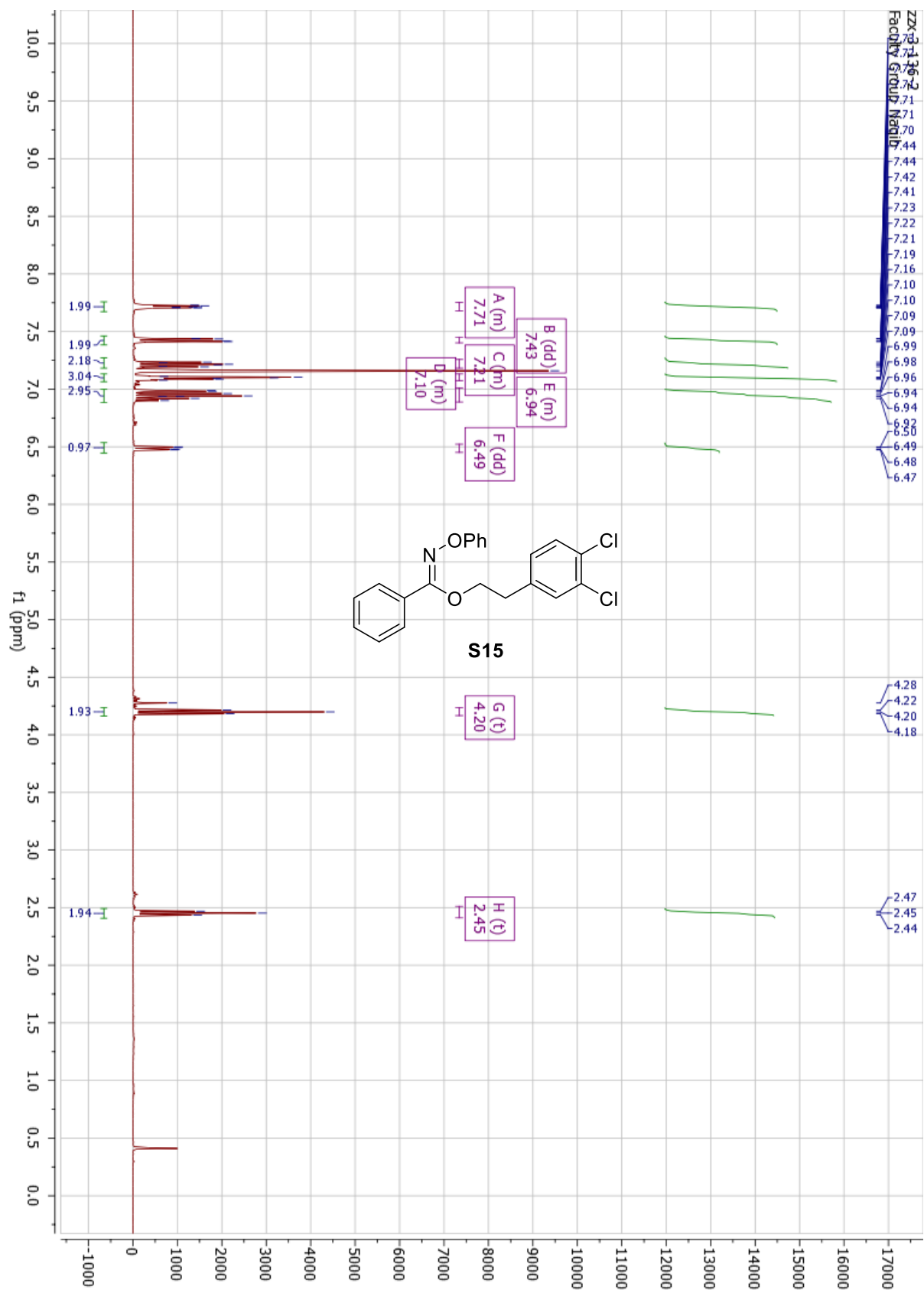




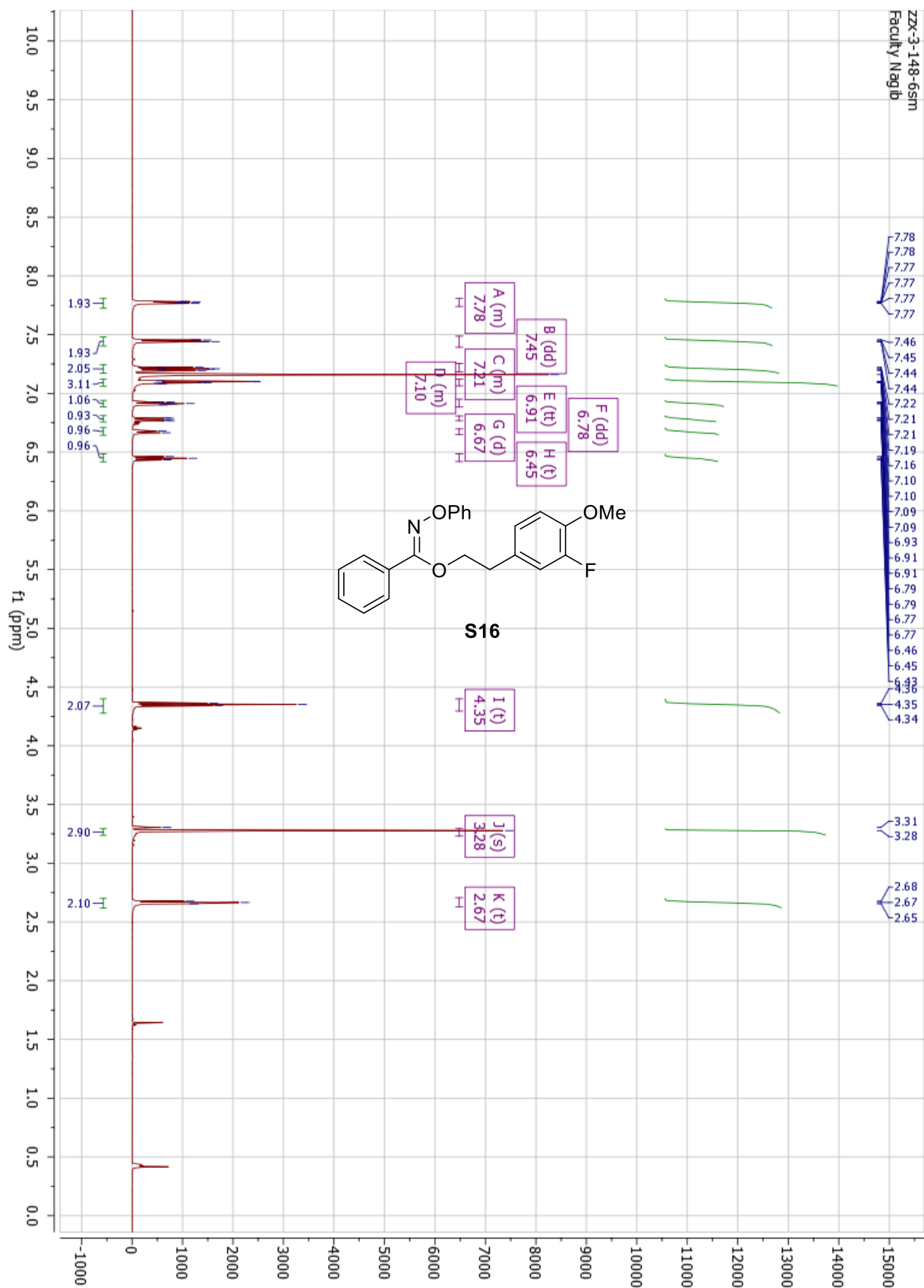




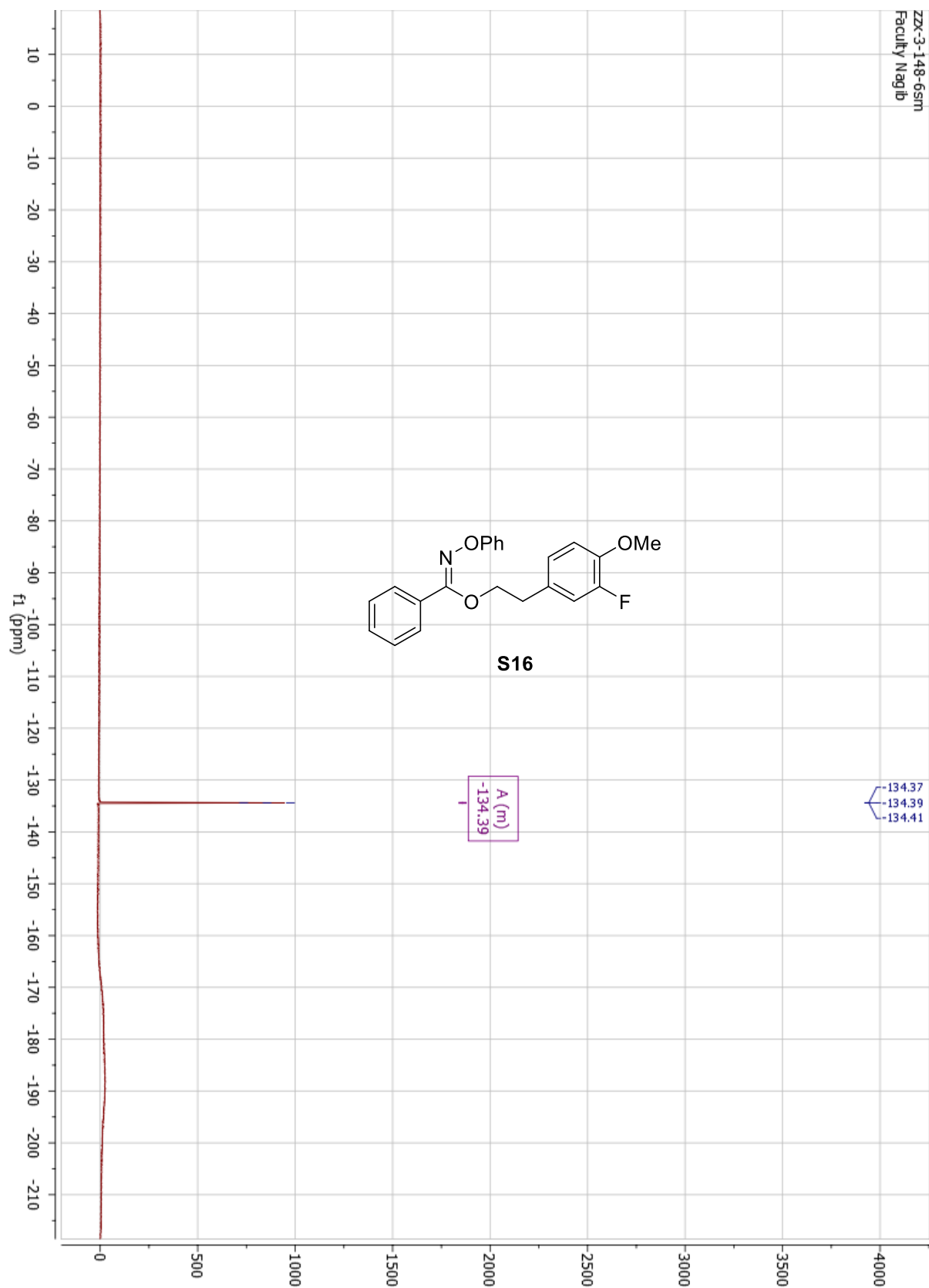


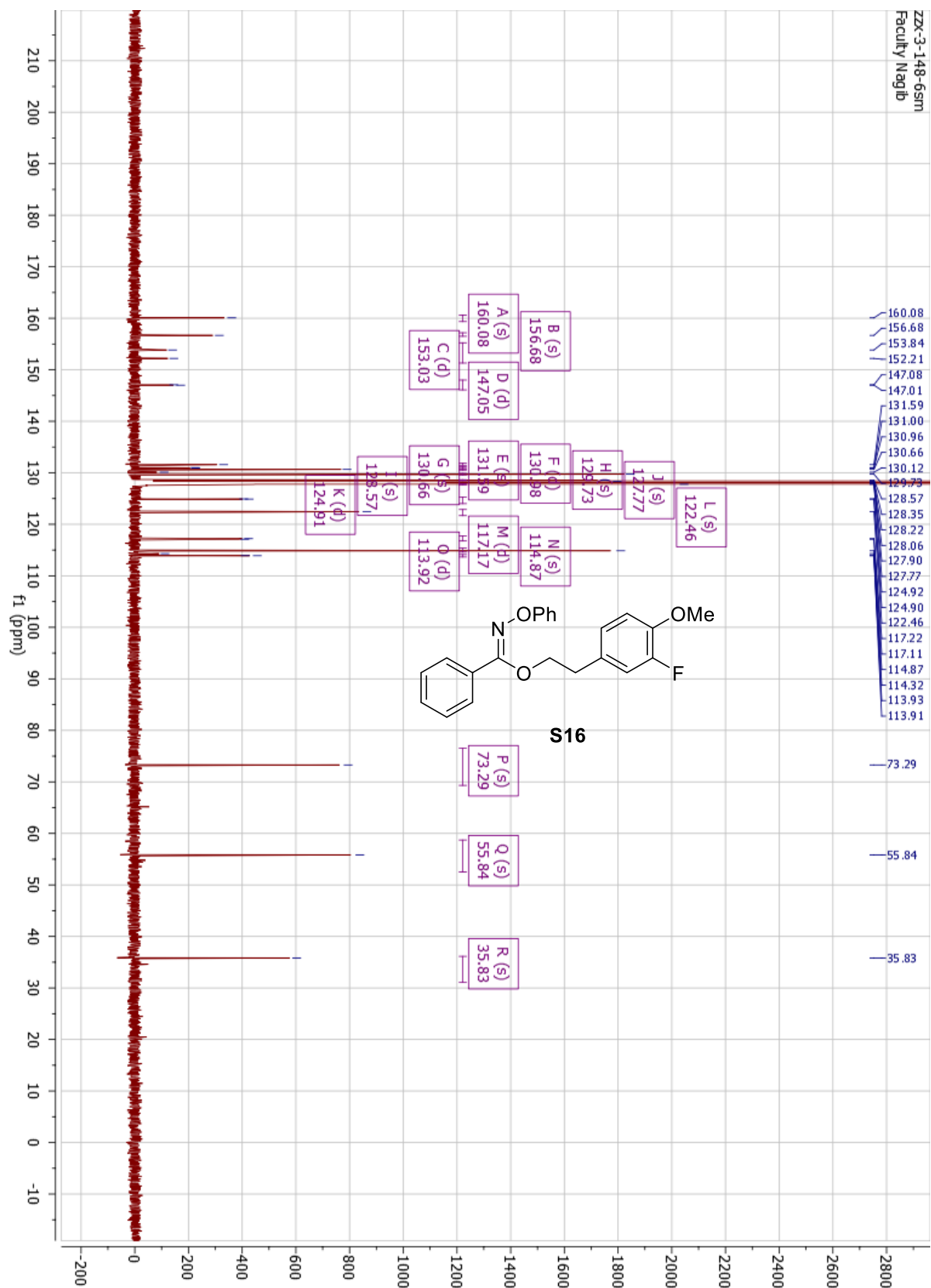








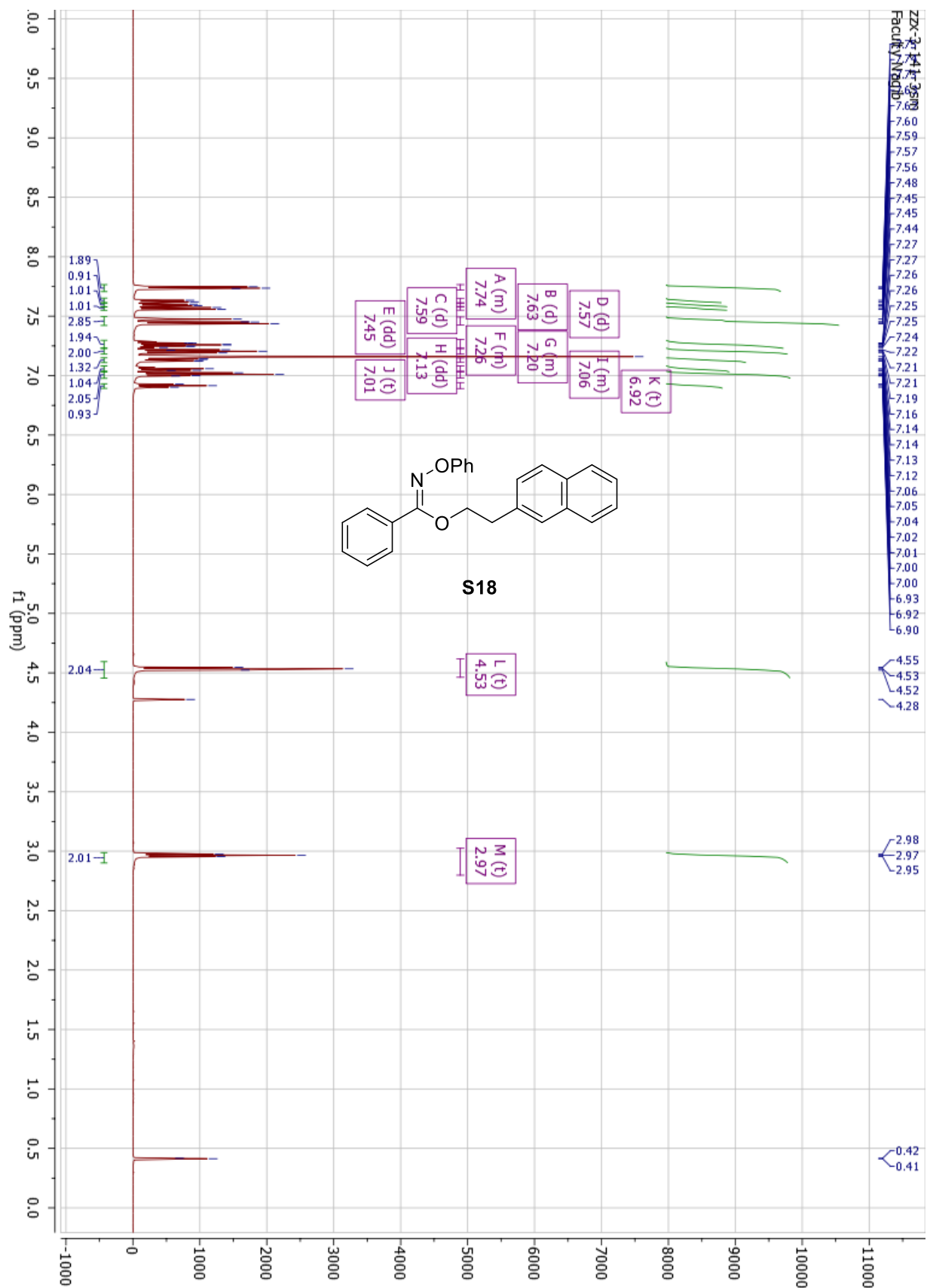


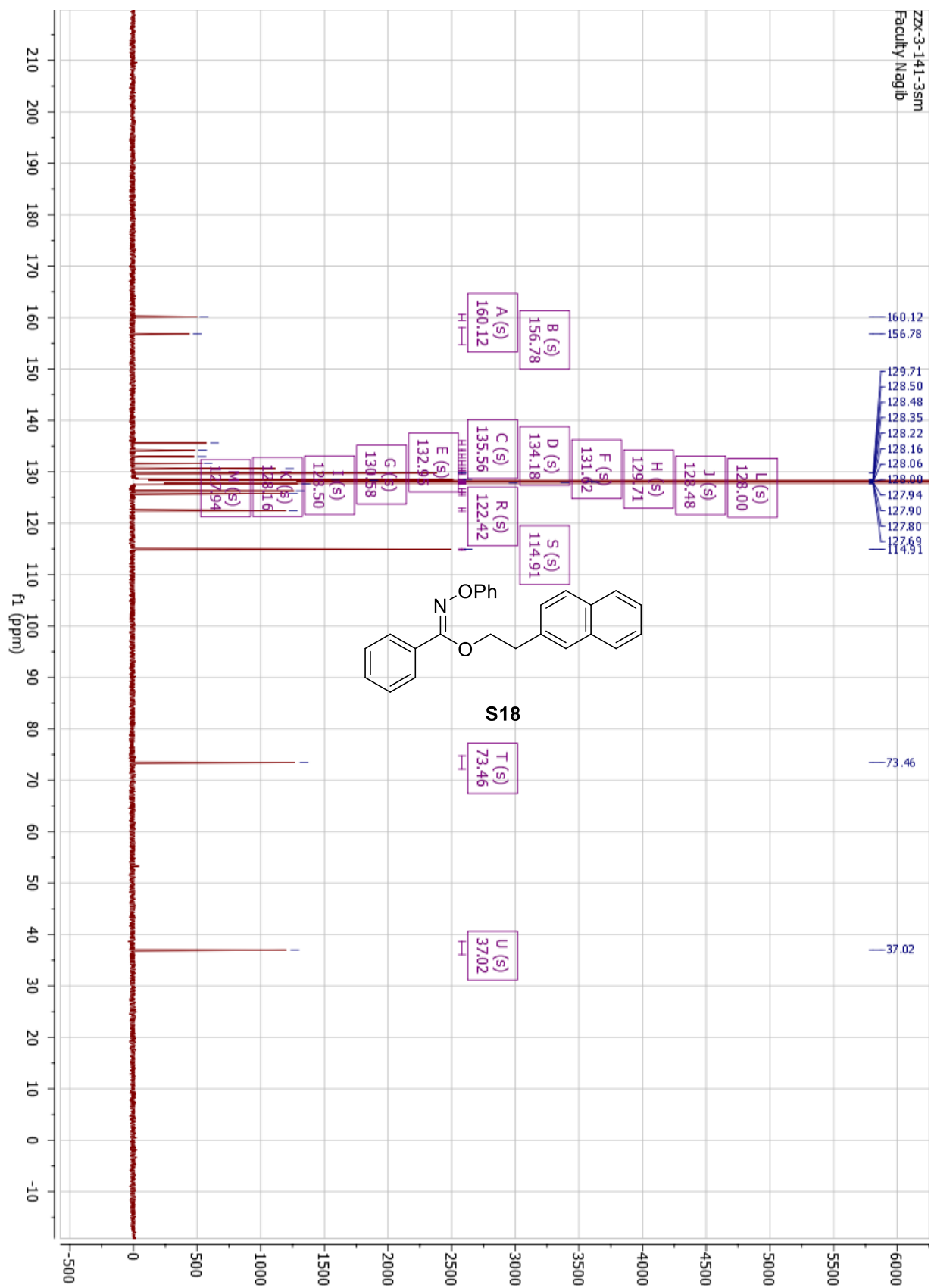


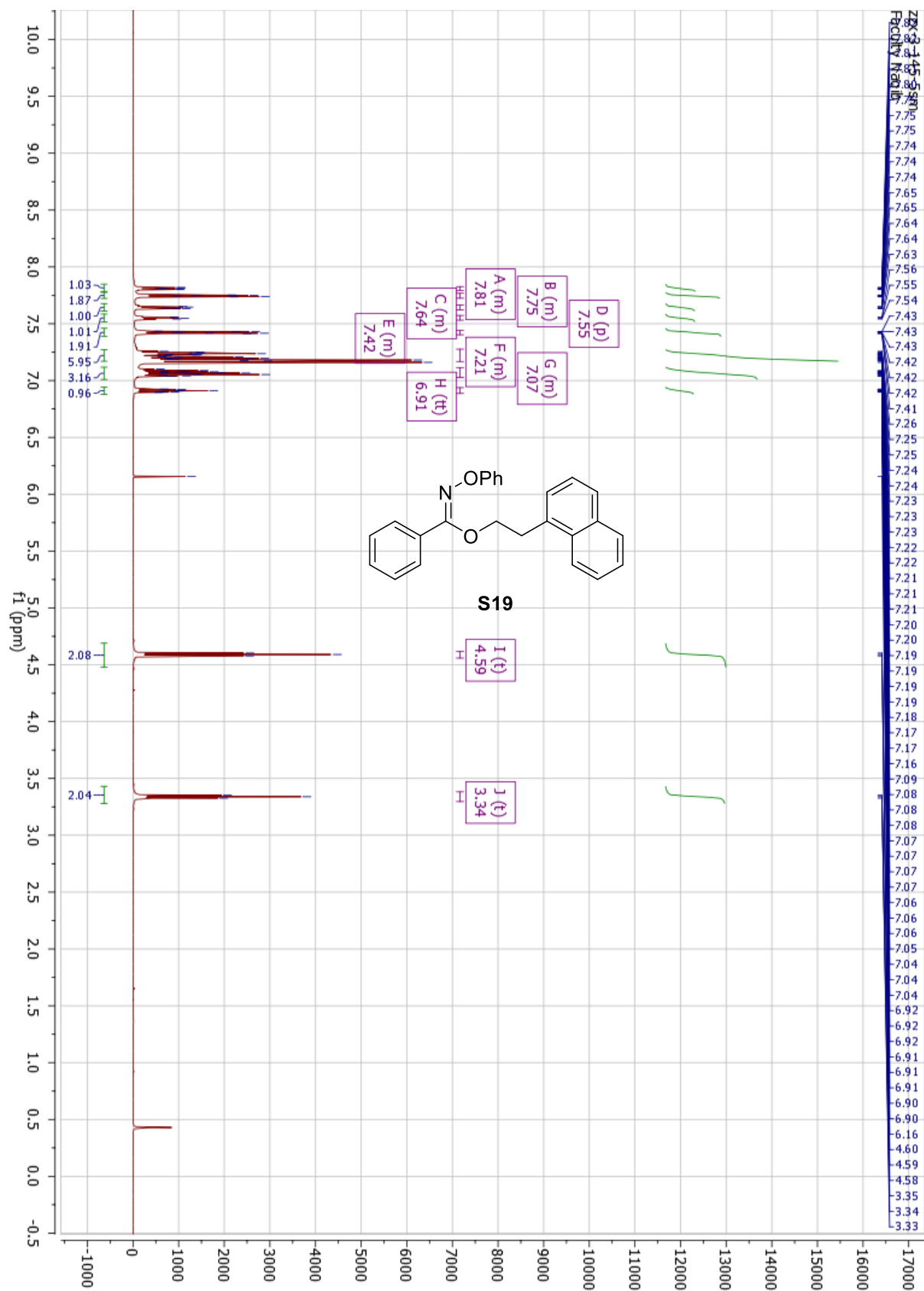






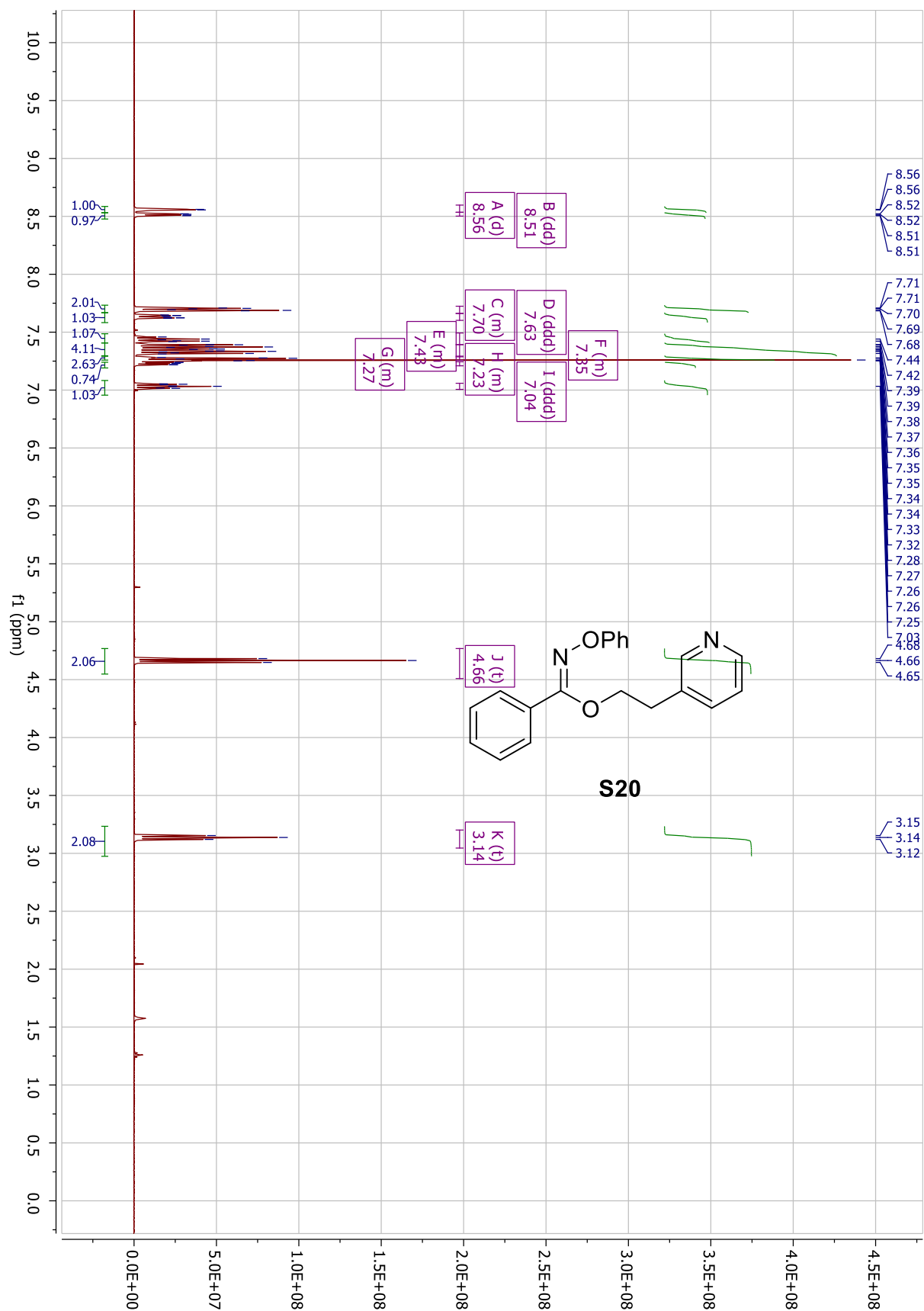


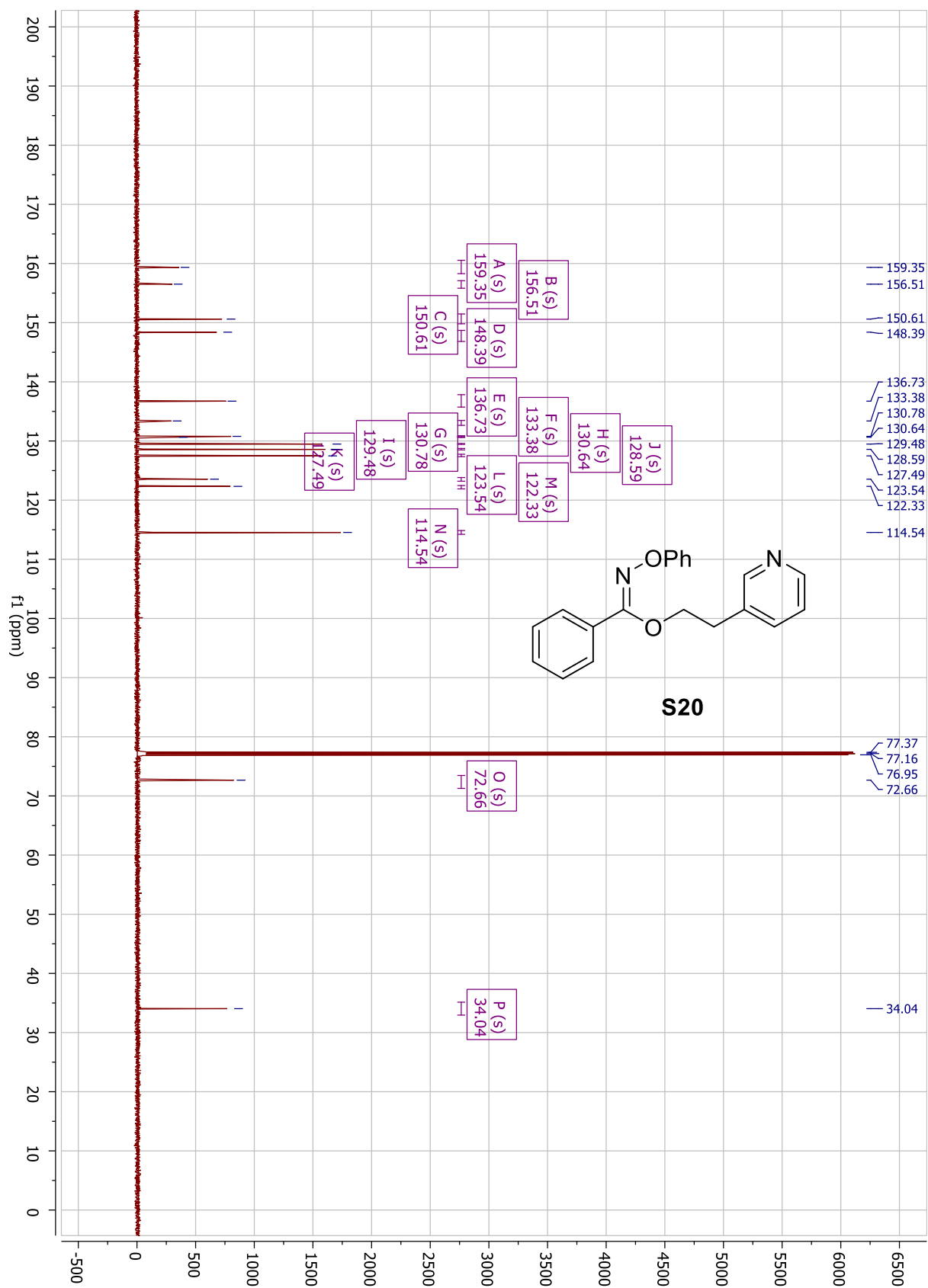


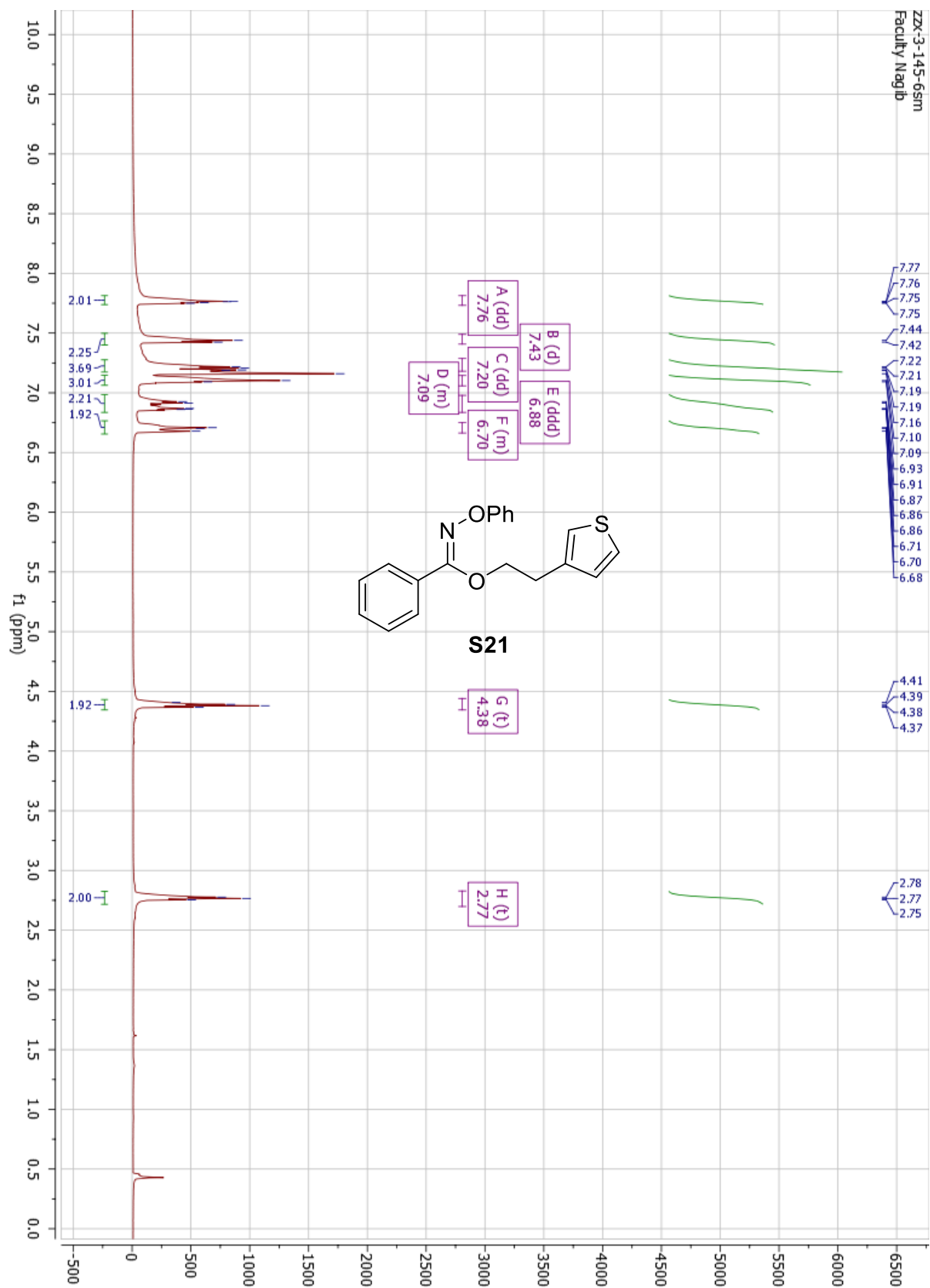


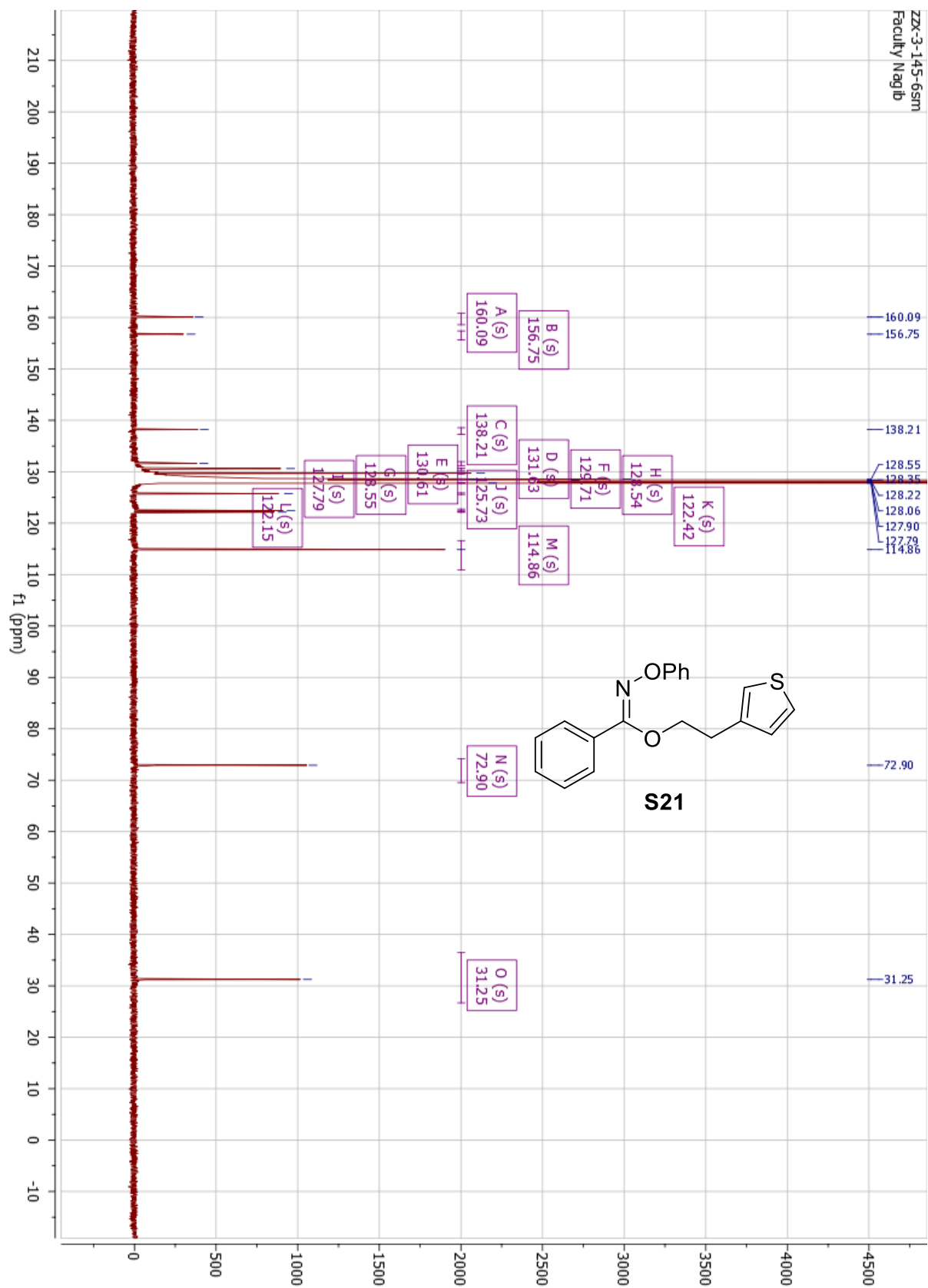


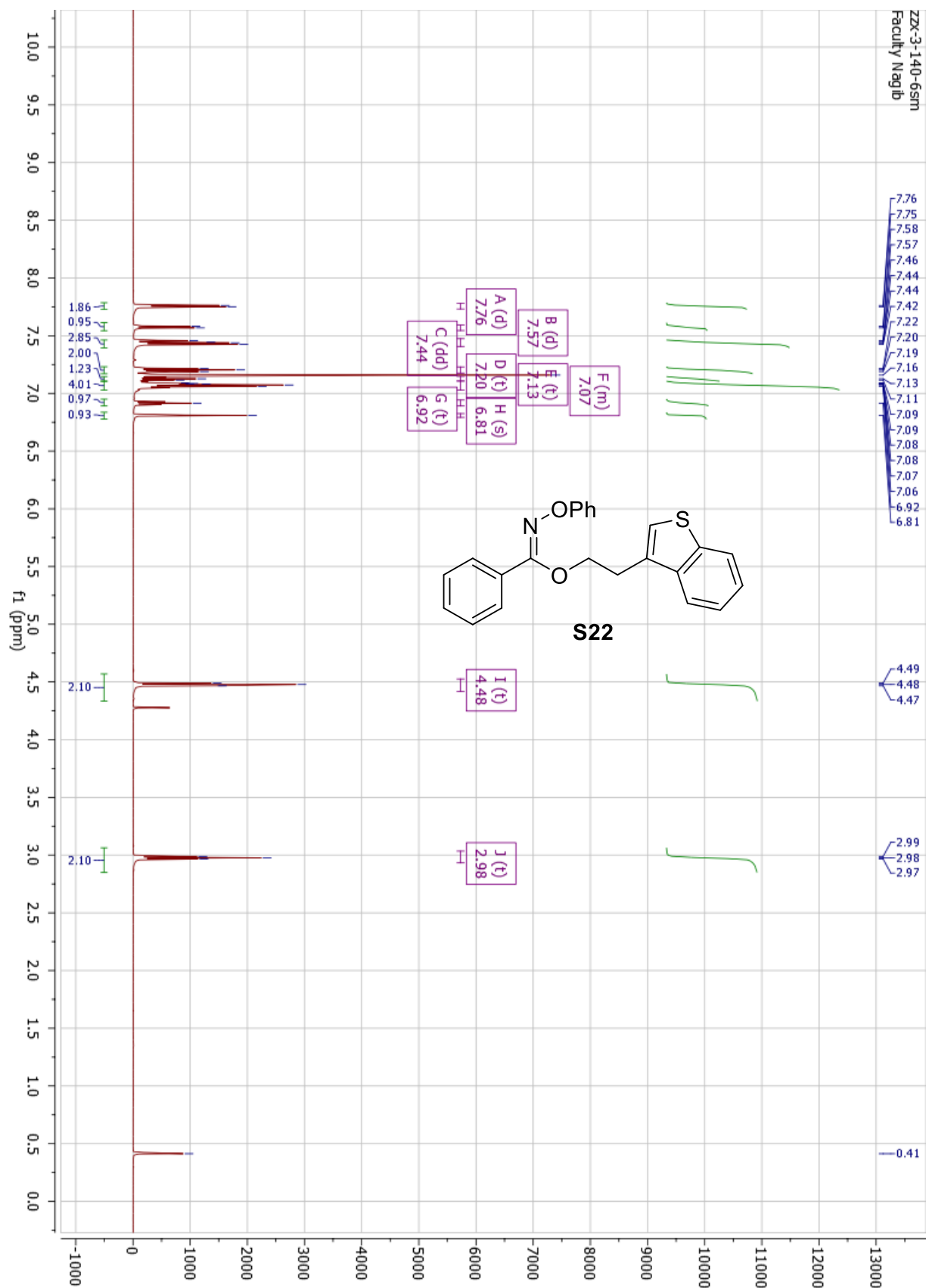


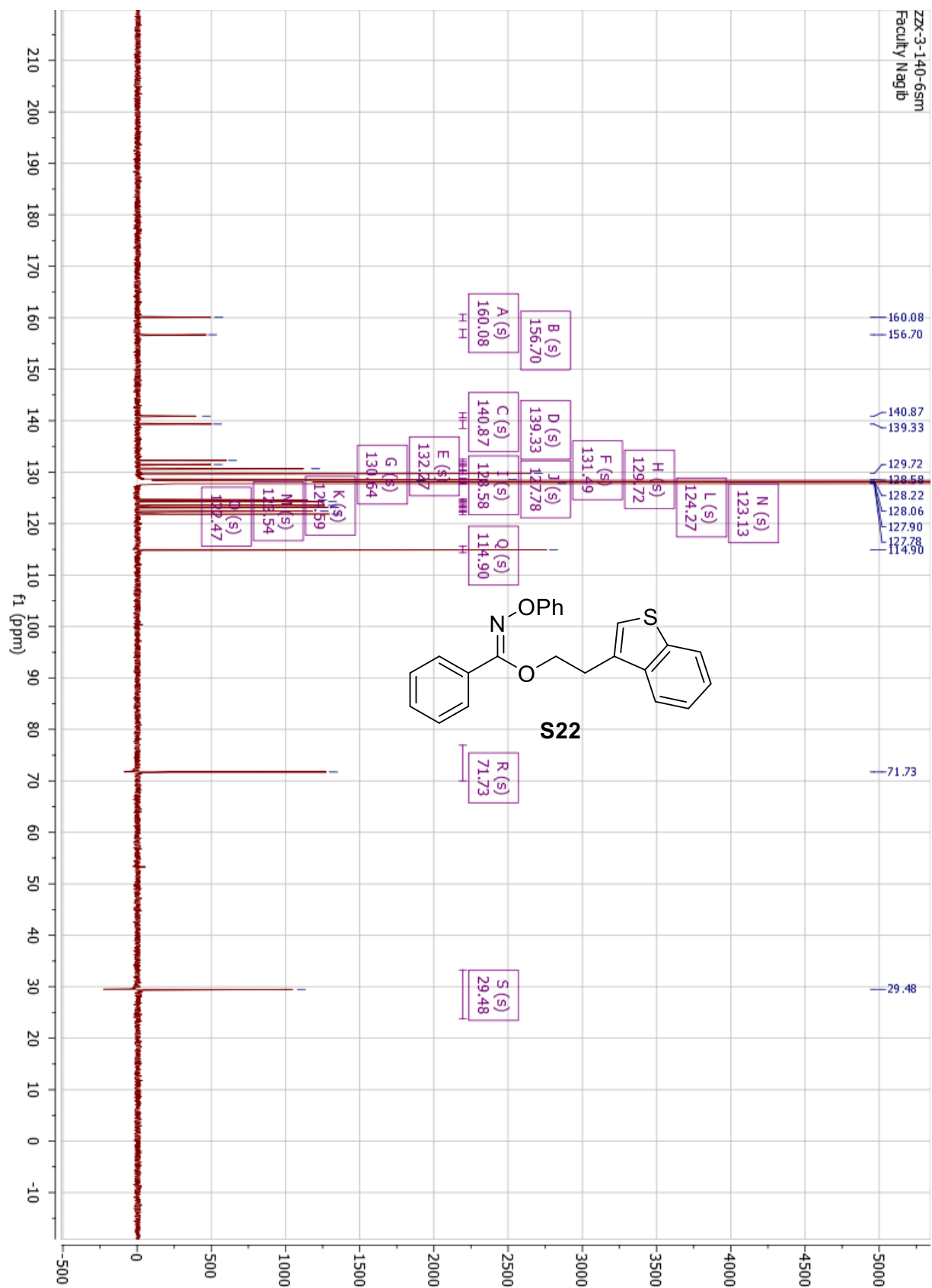


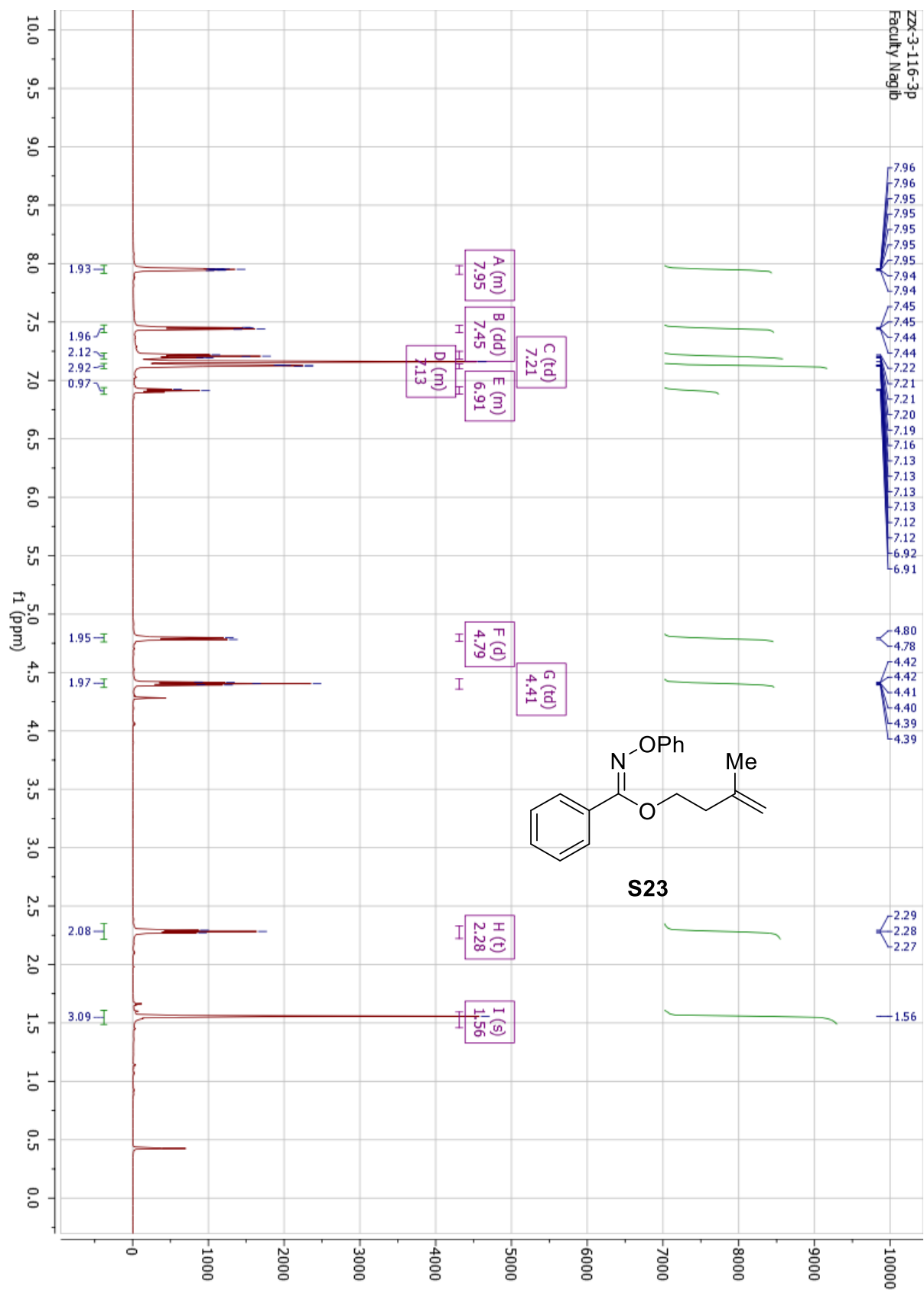






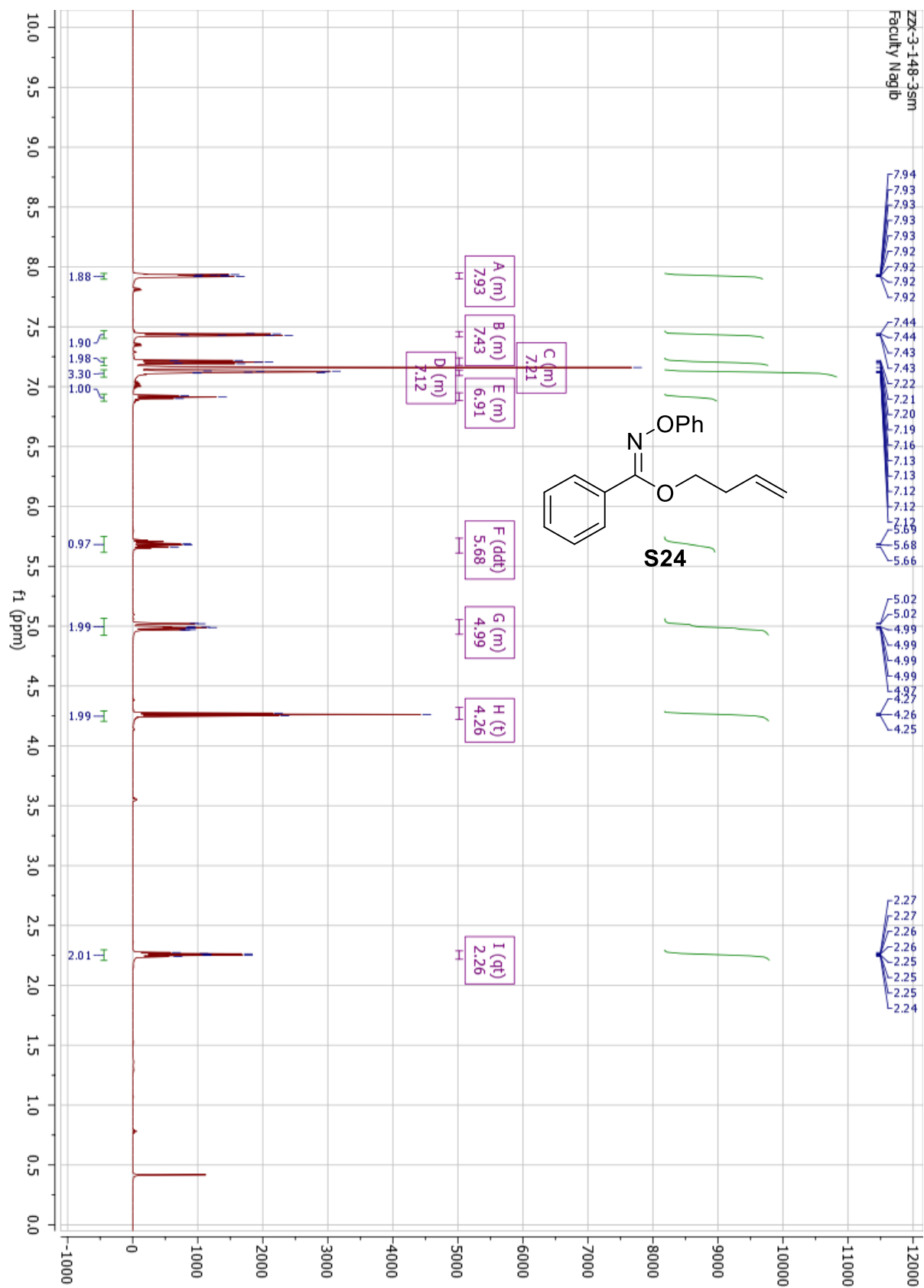


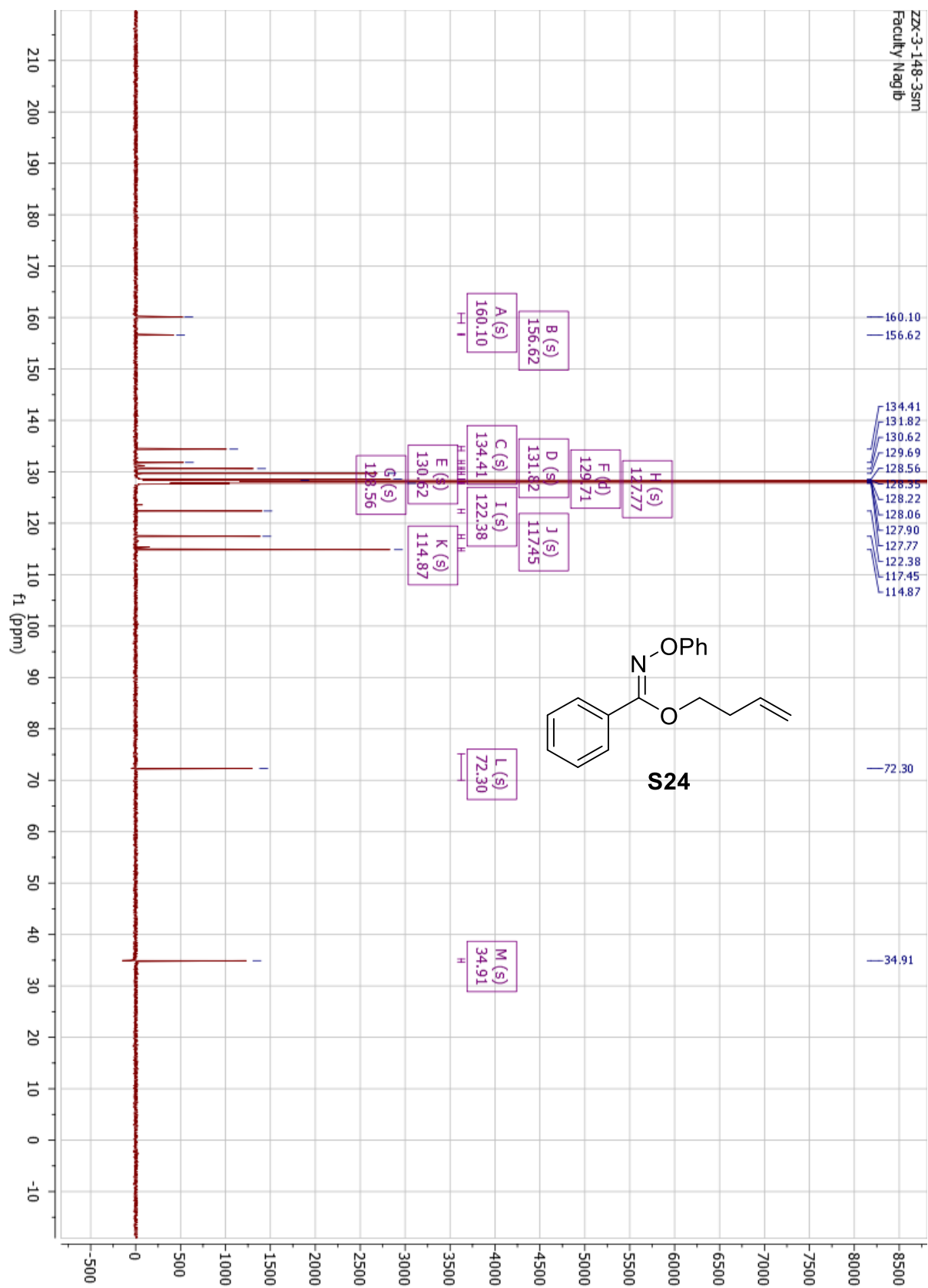


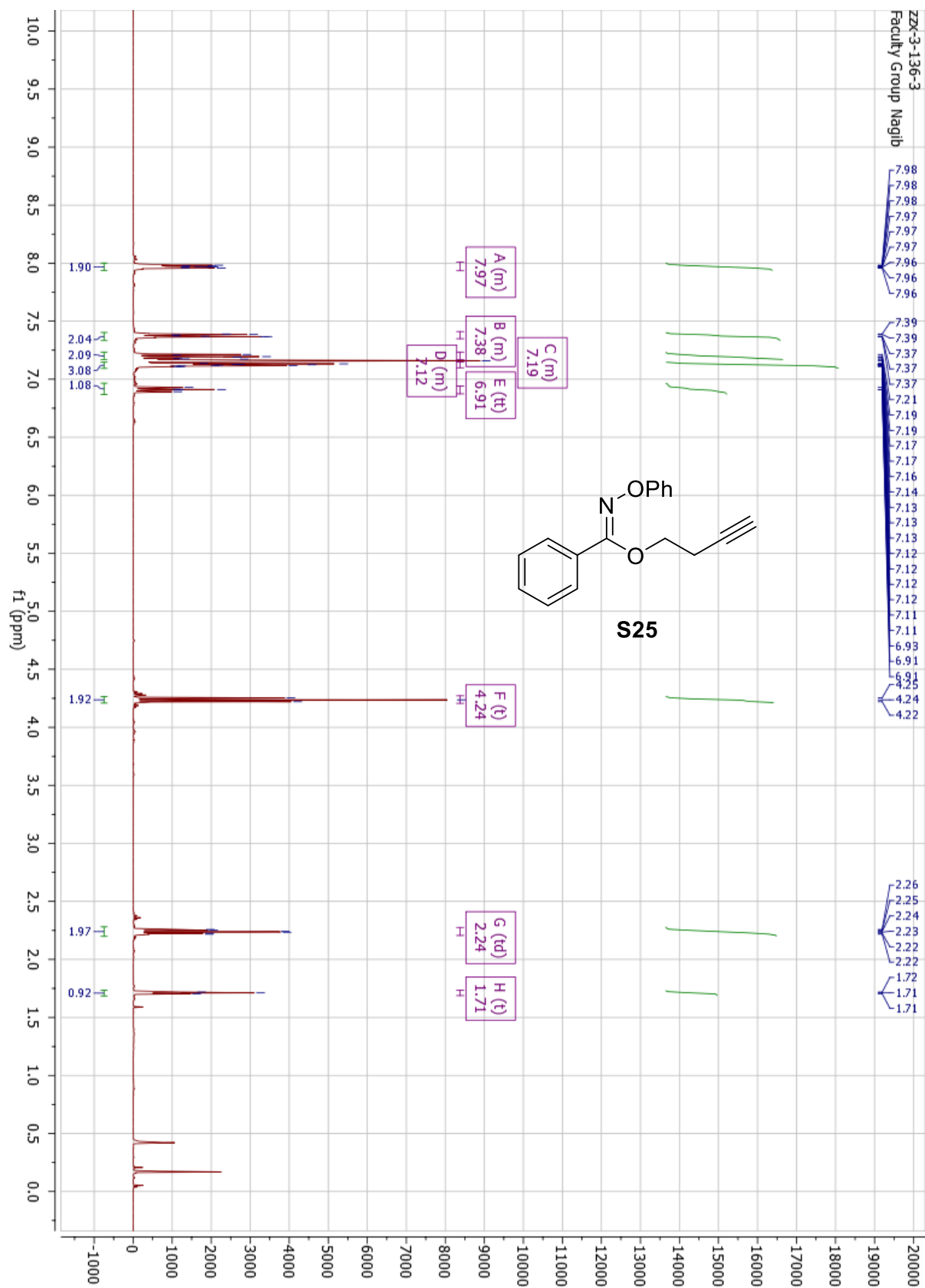


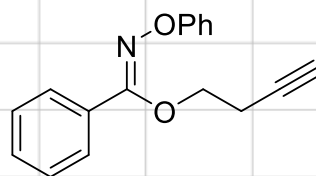




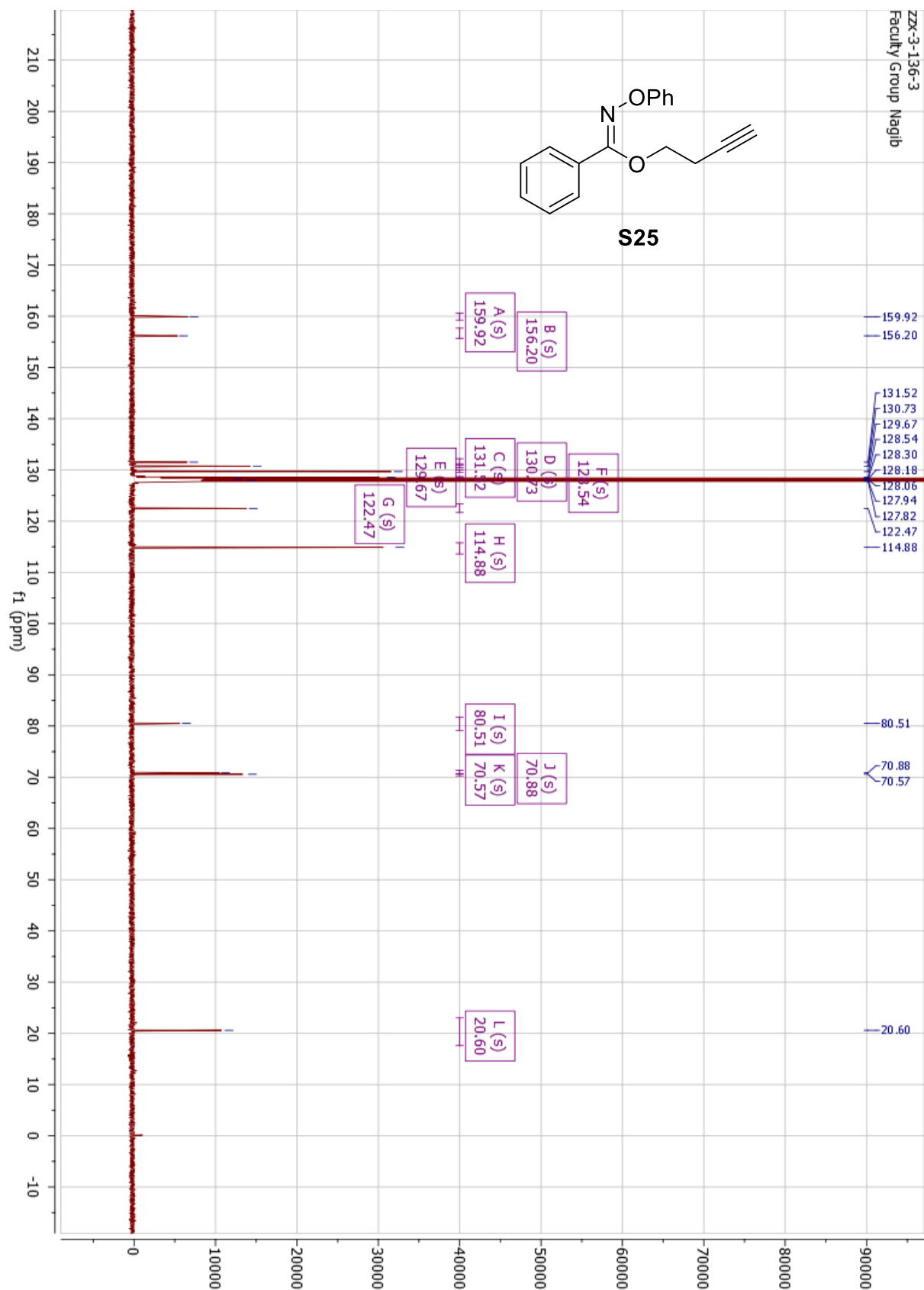


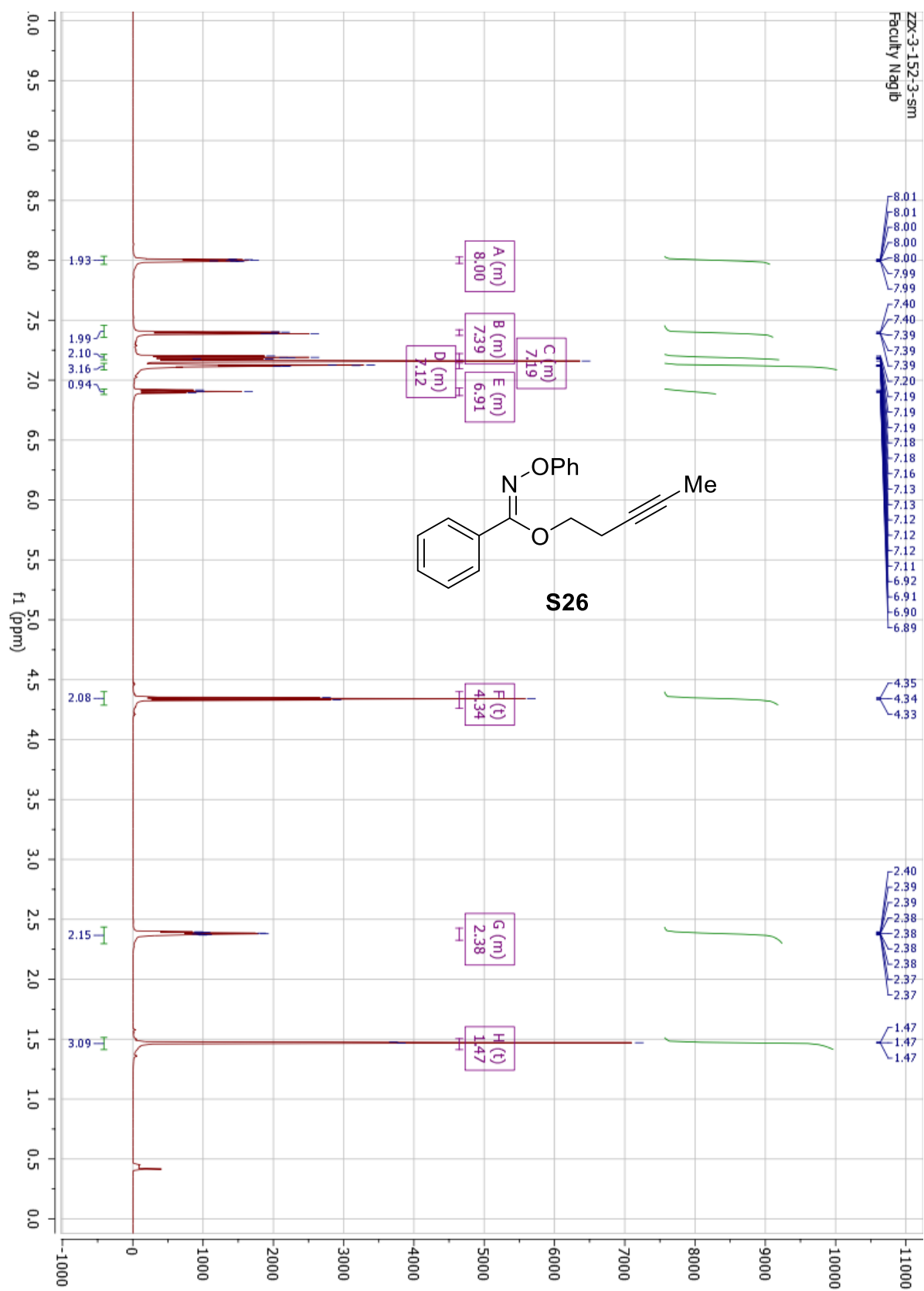


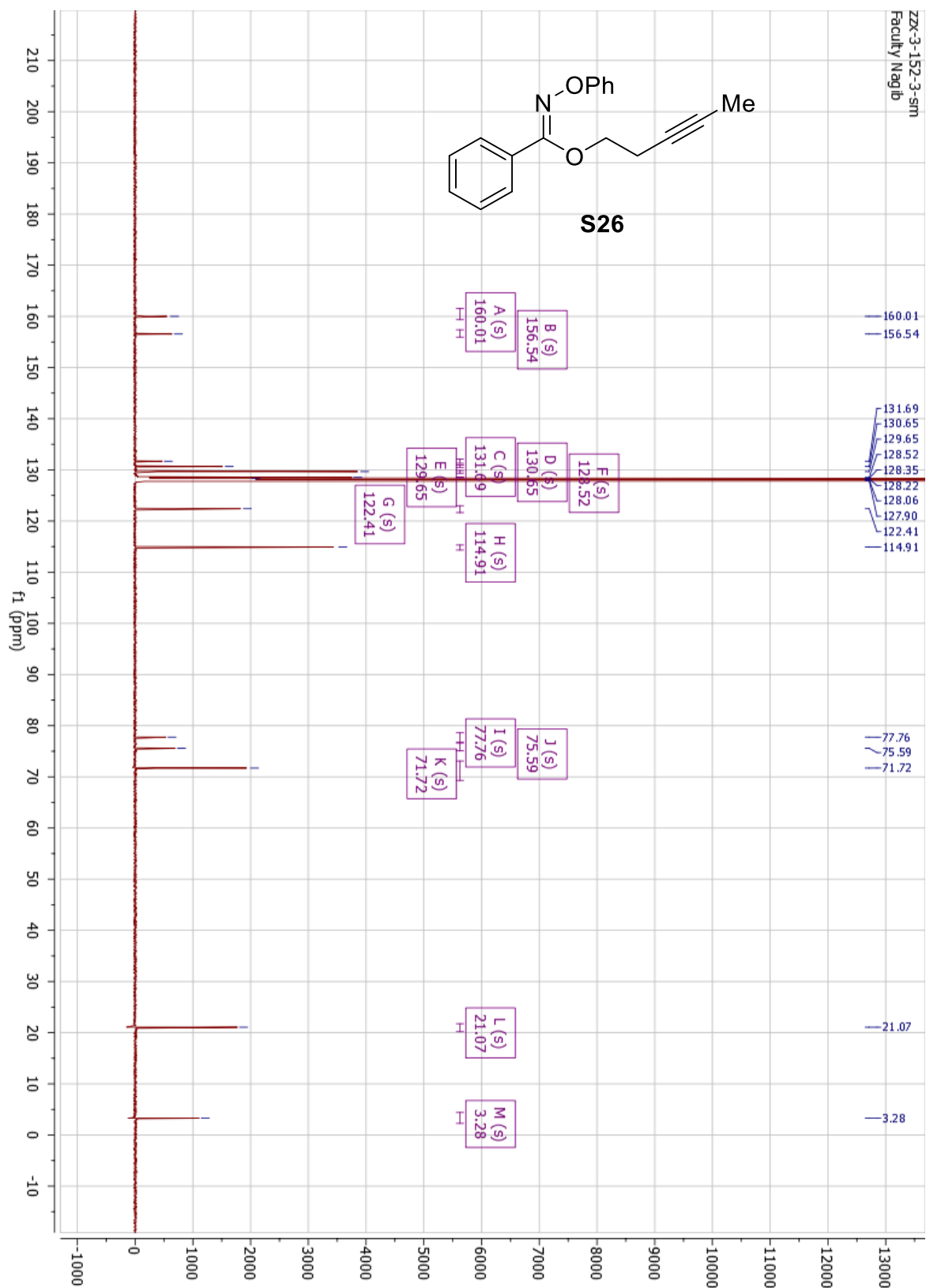


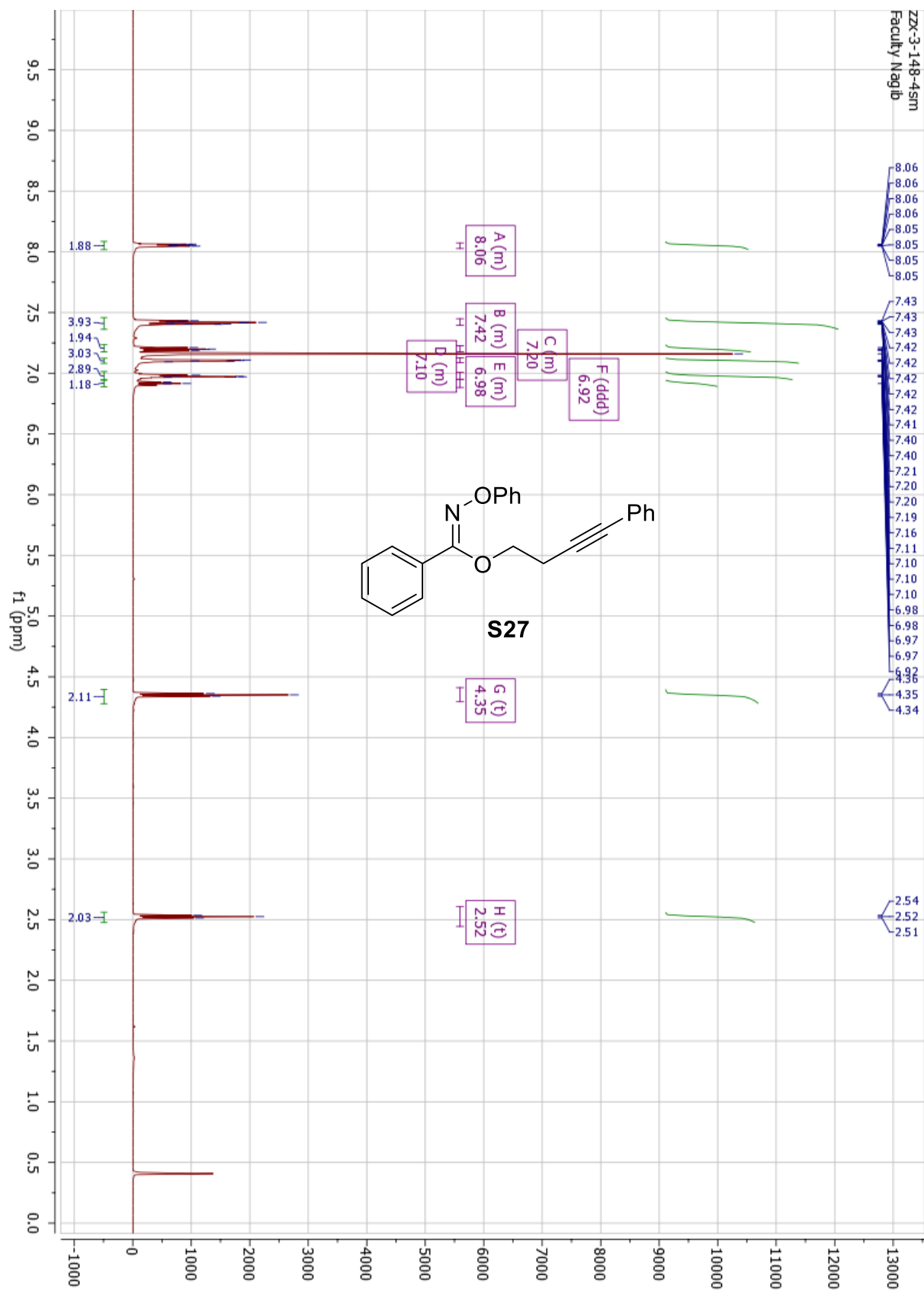


**S25**

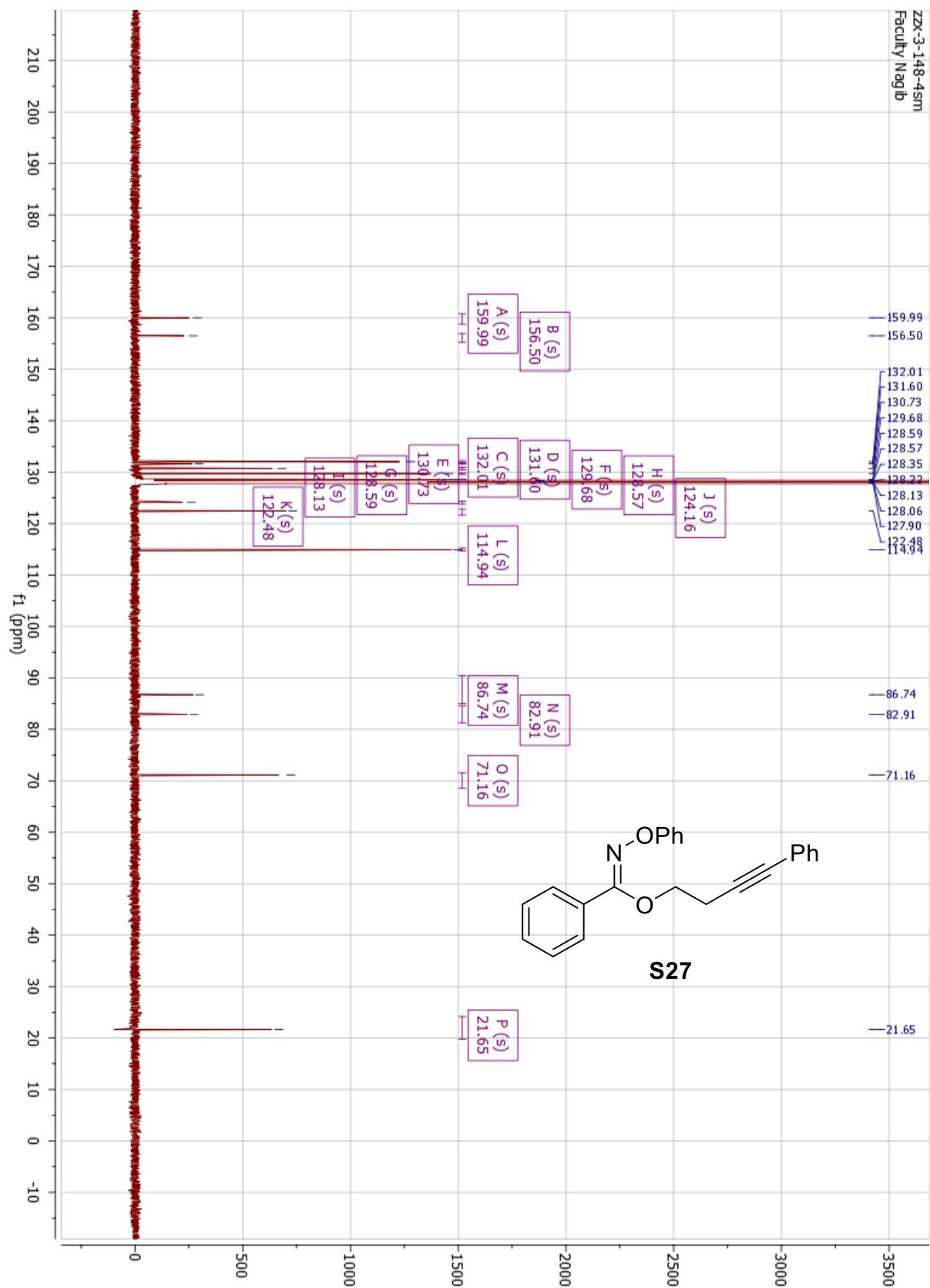


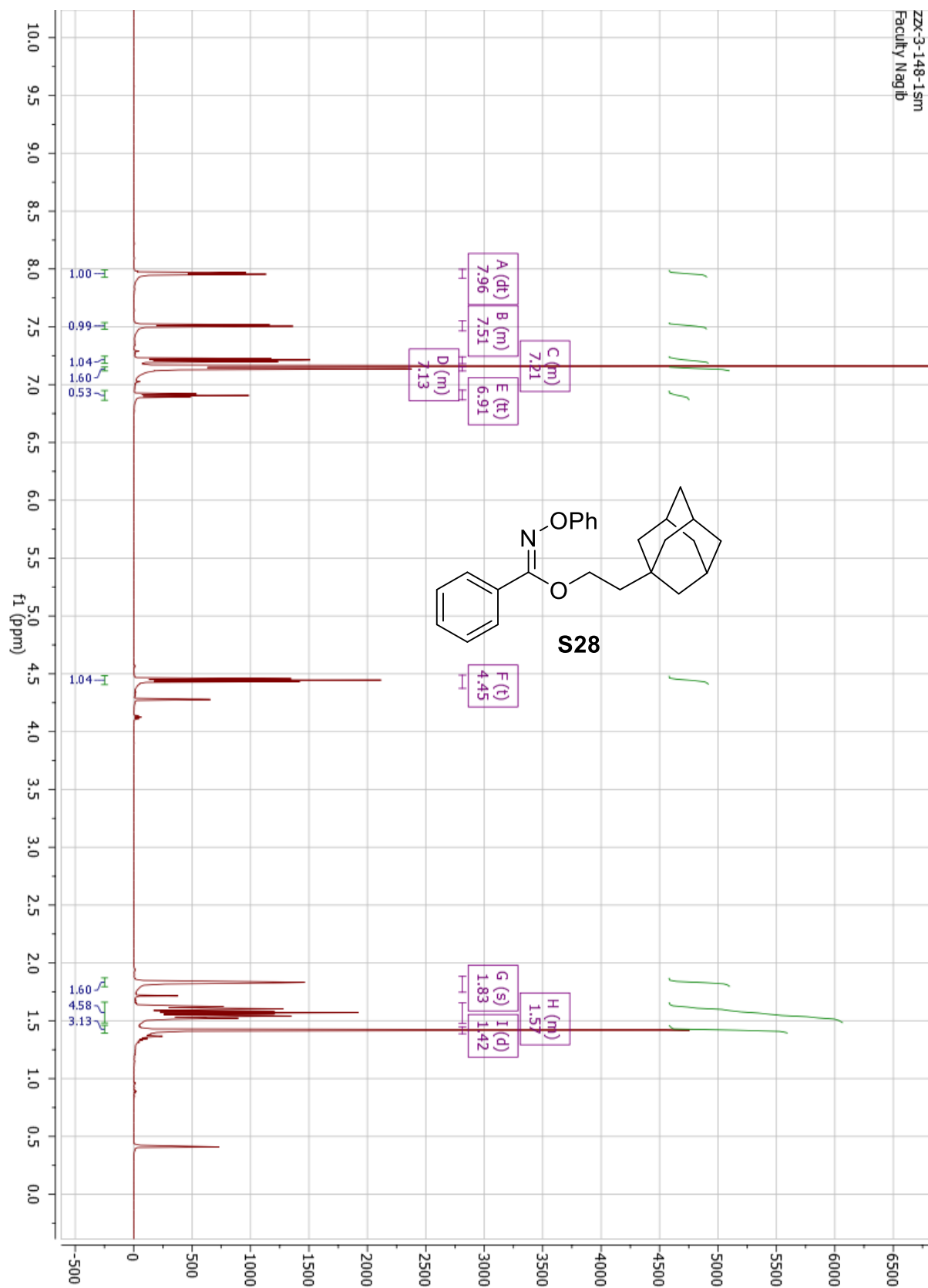


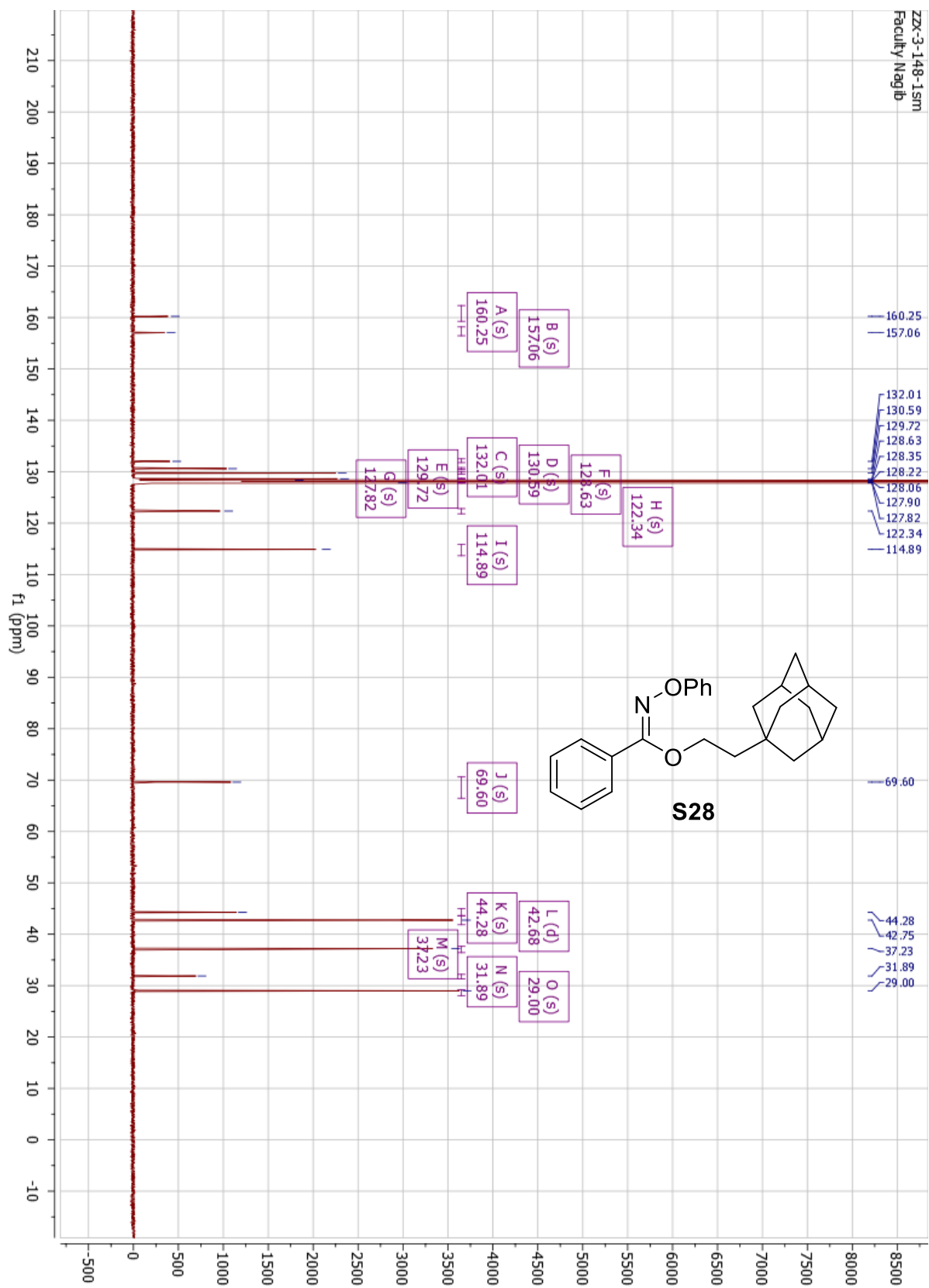


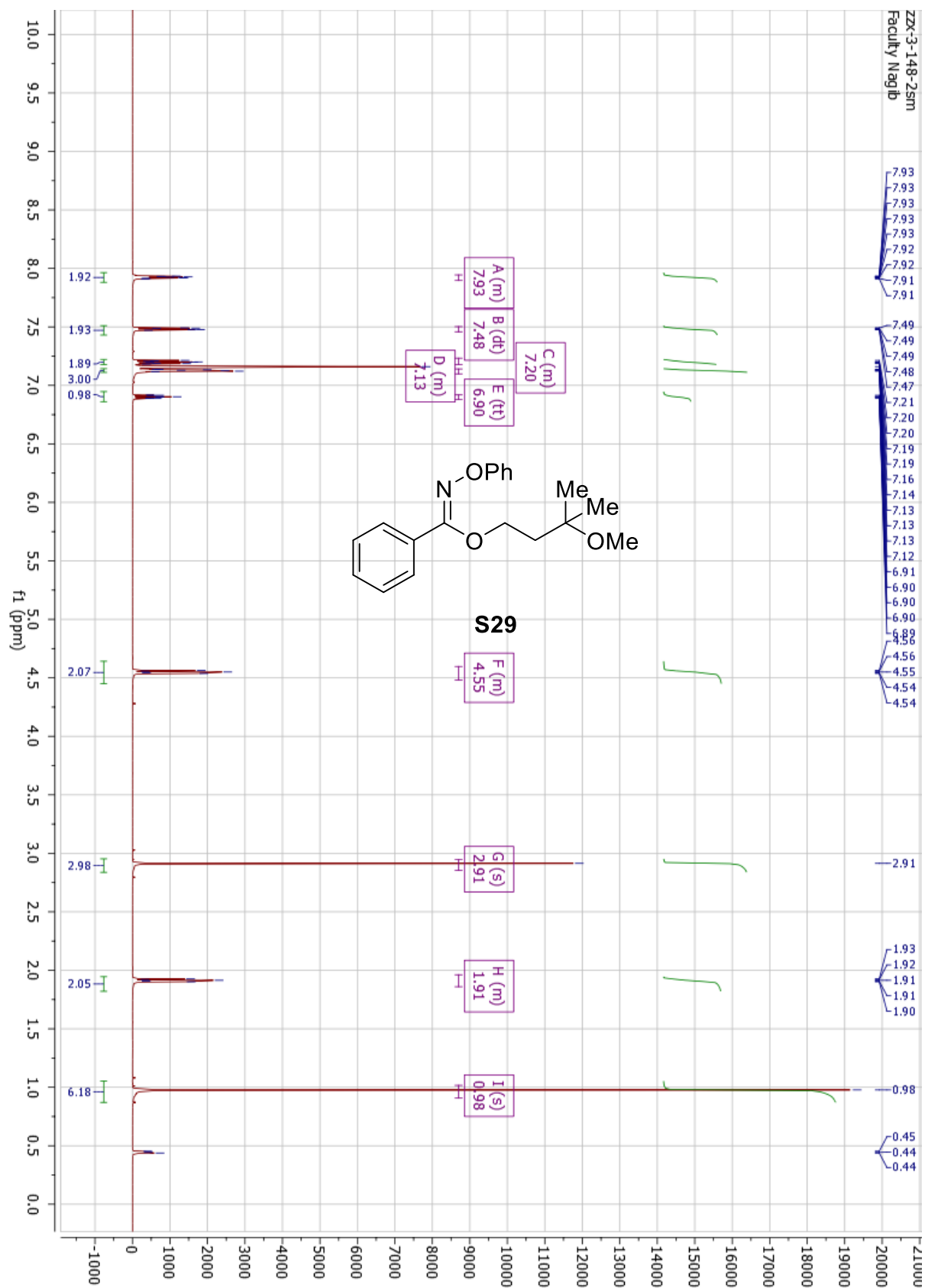


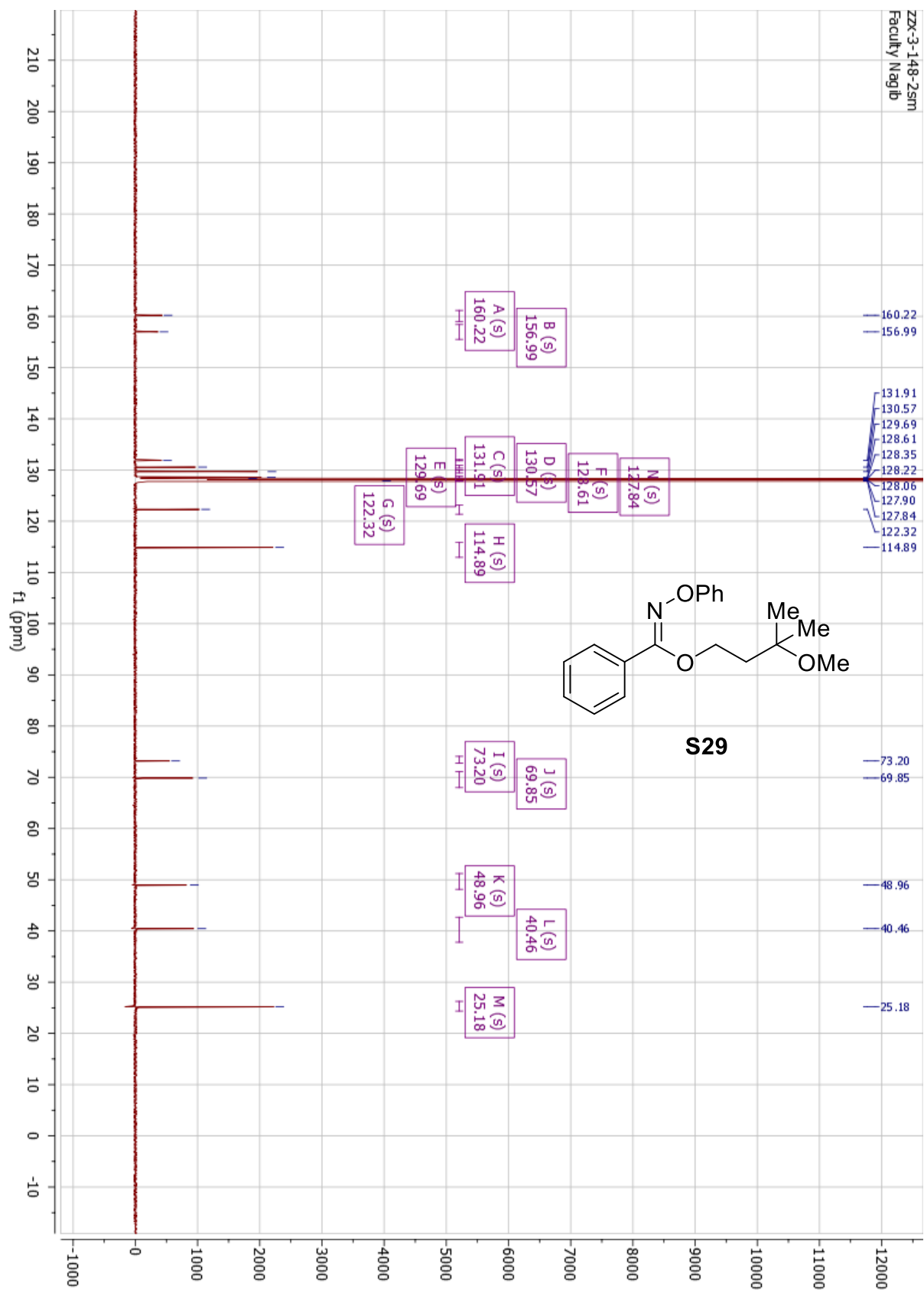


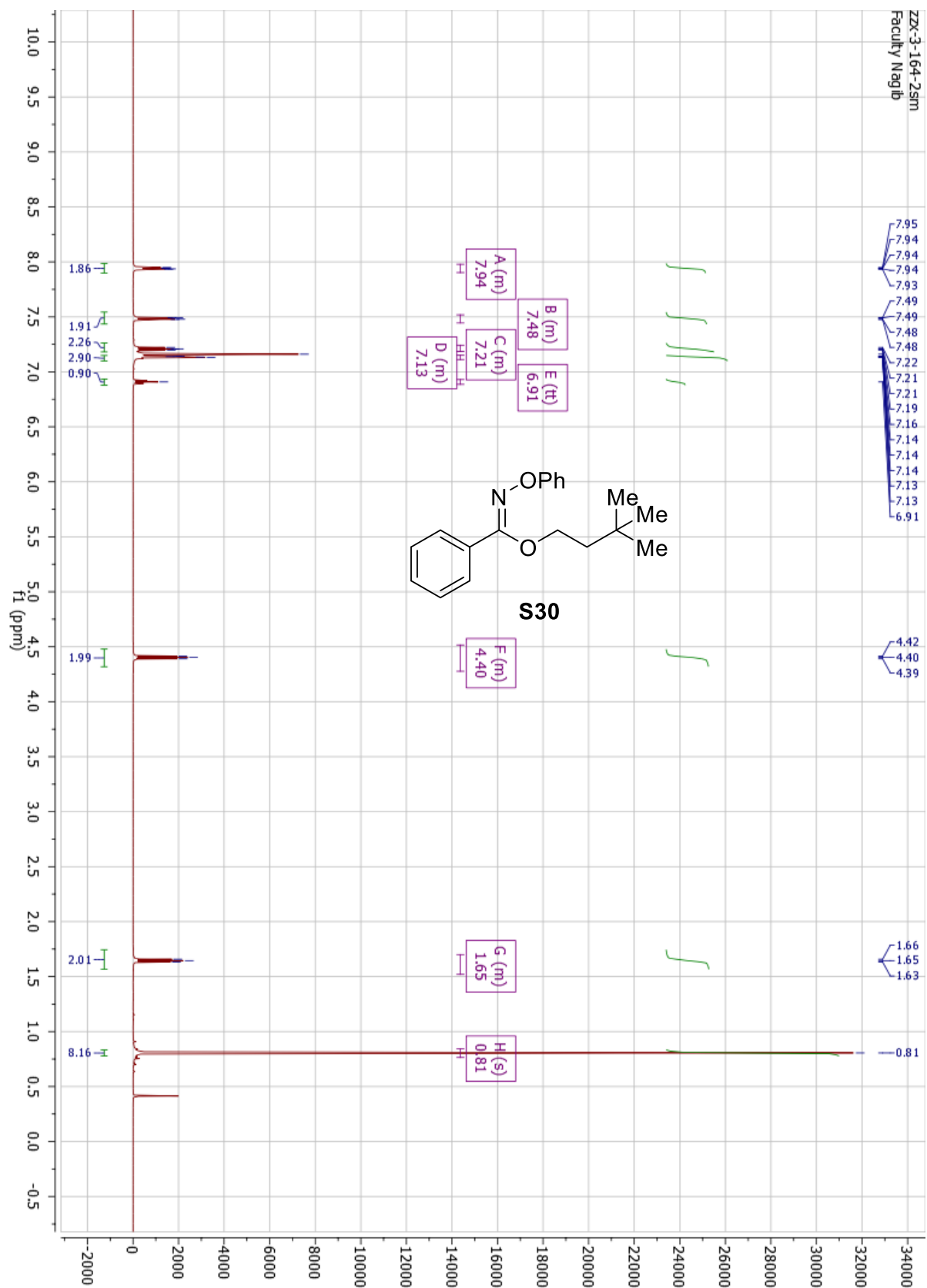


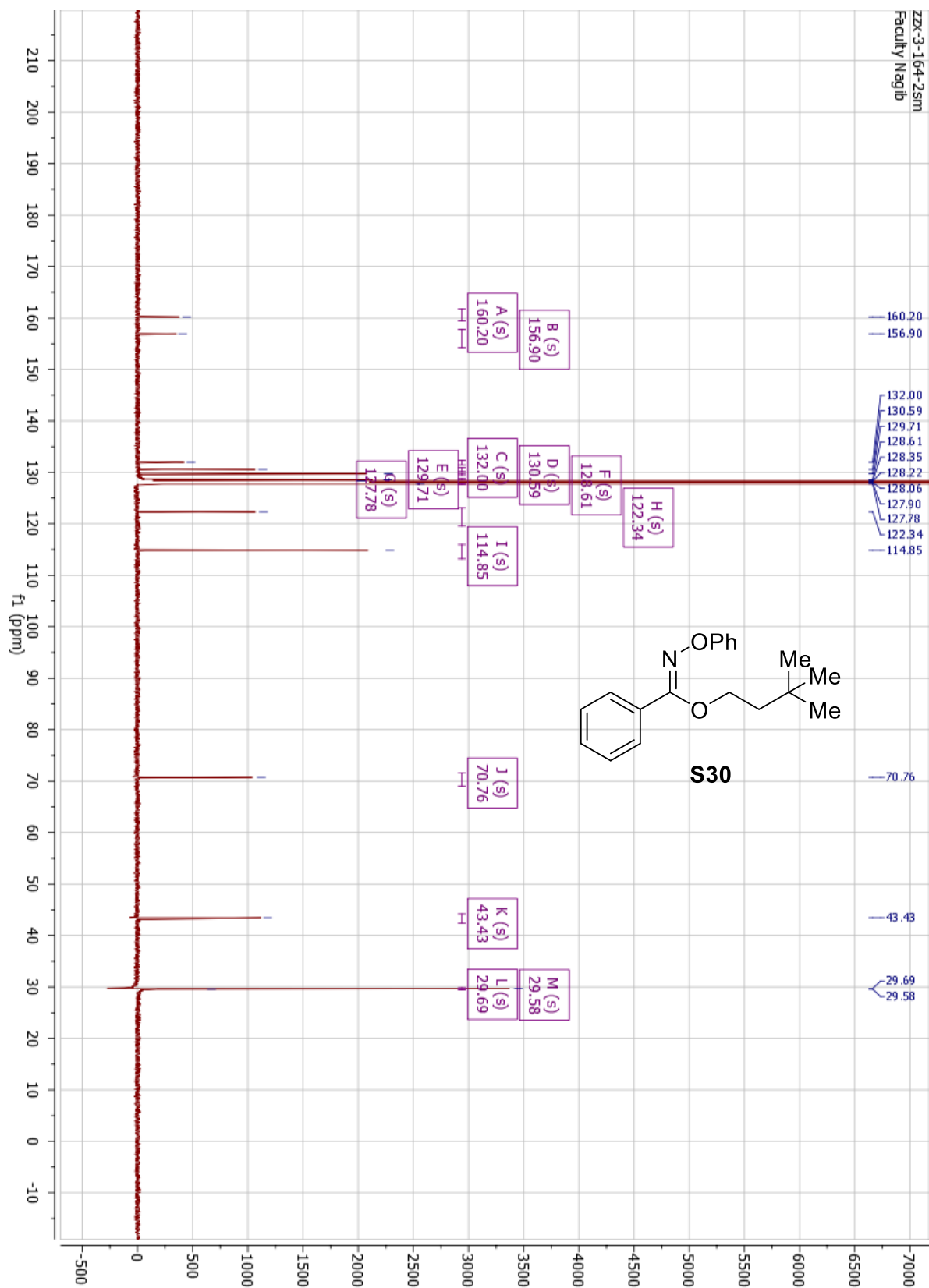


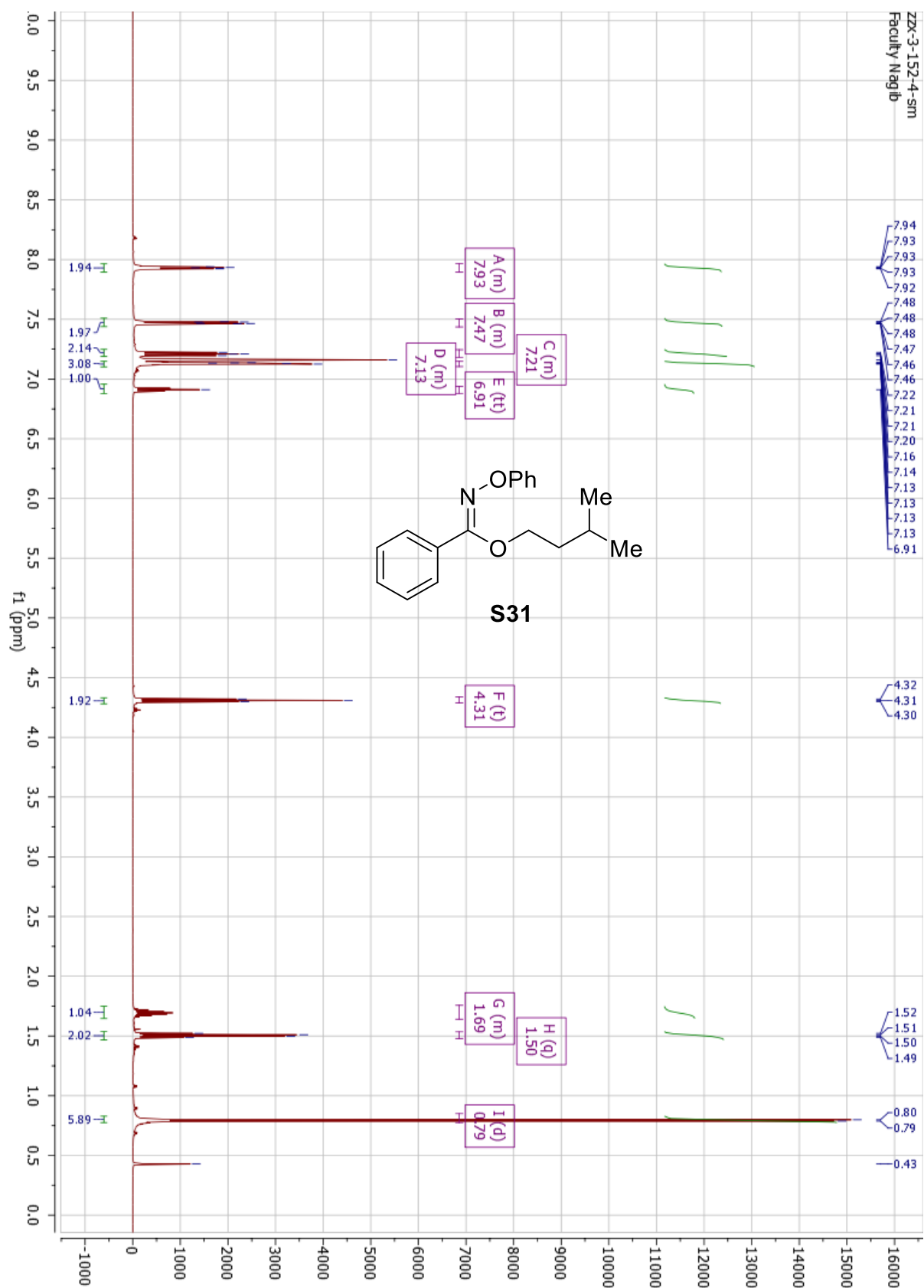






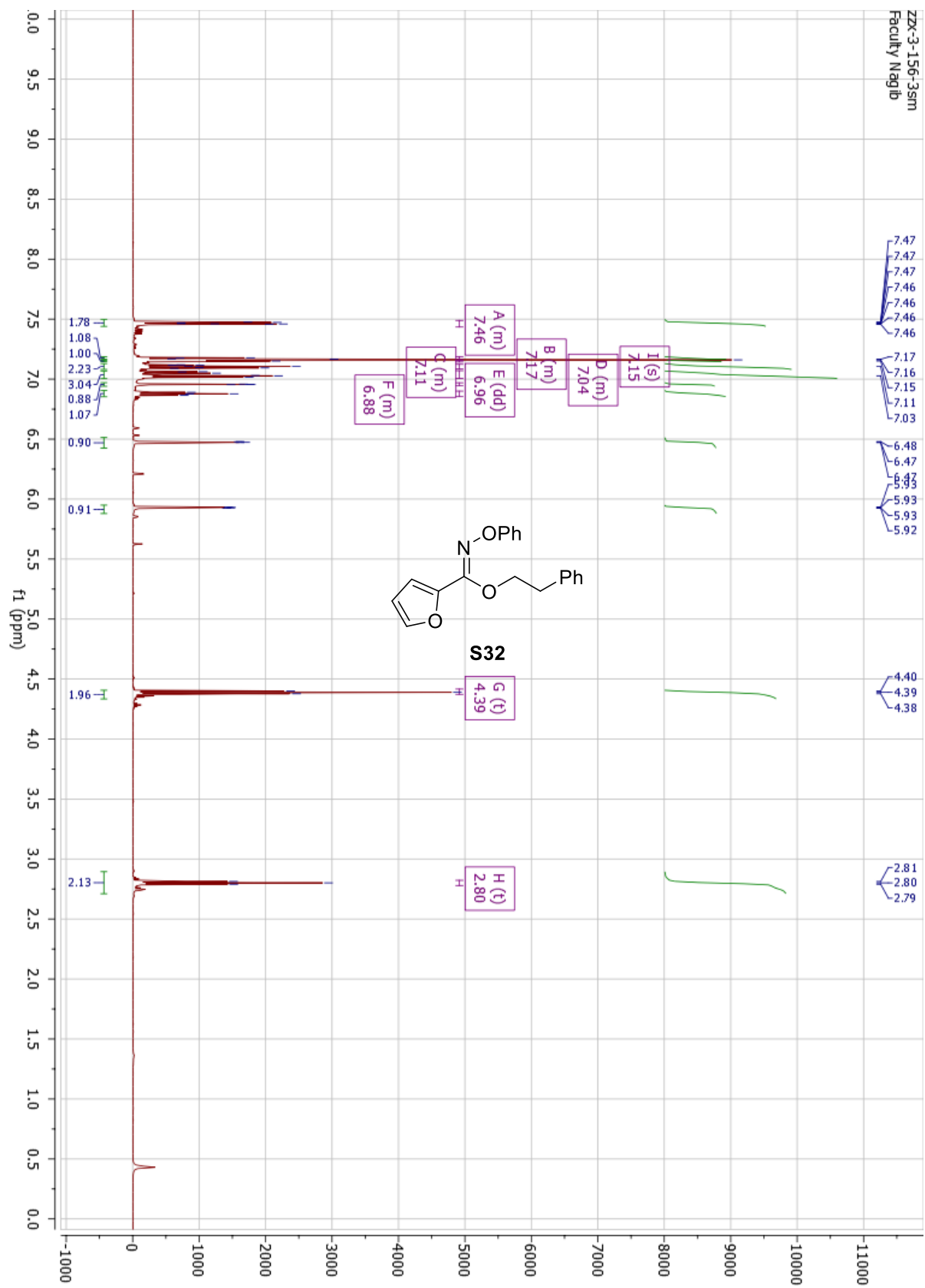


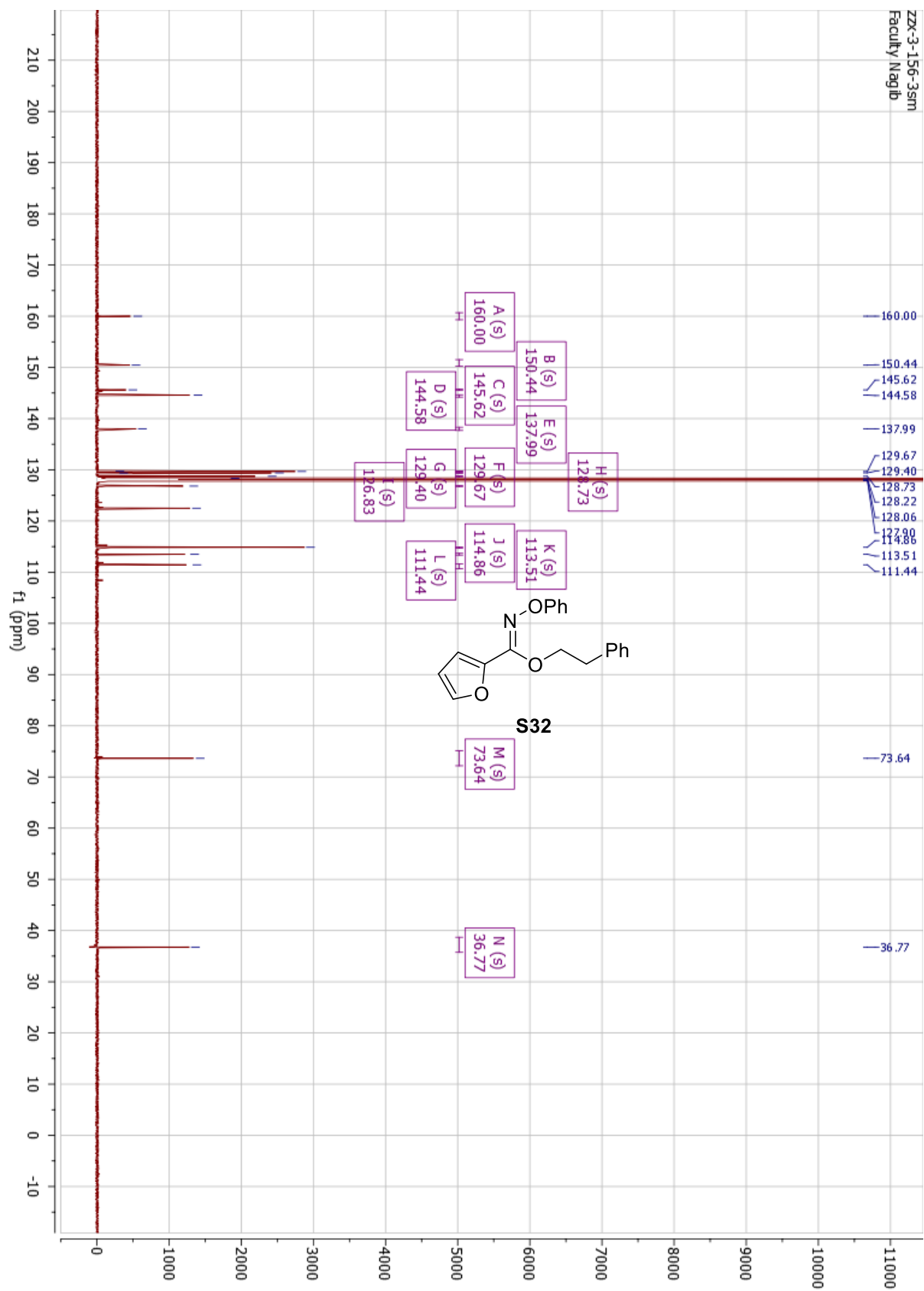


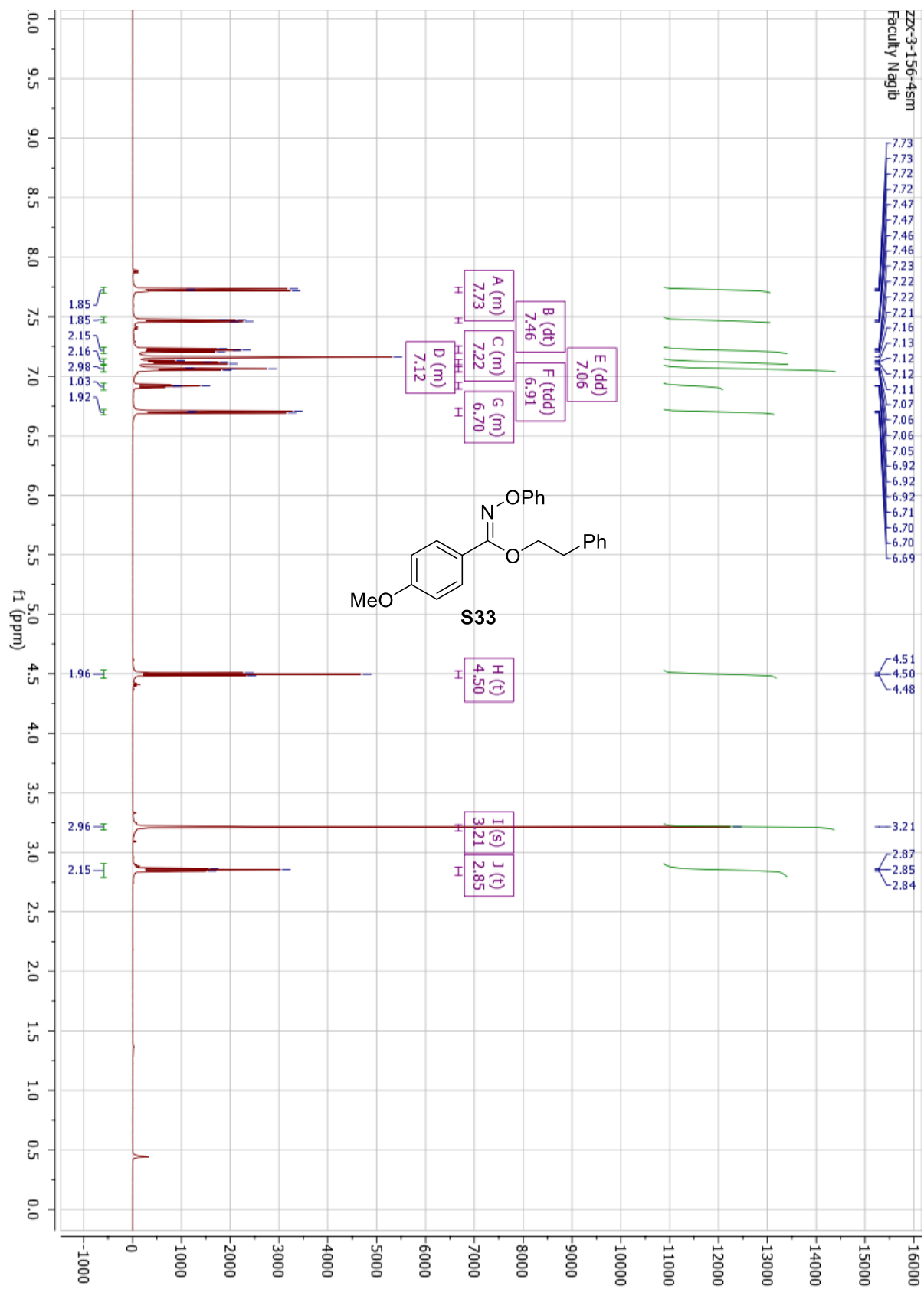


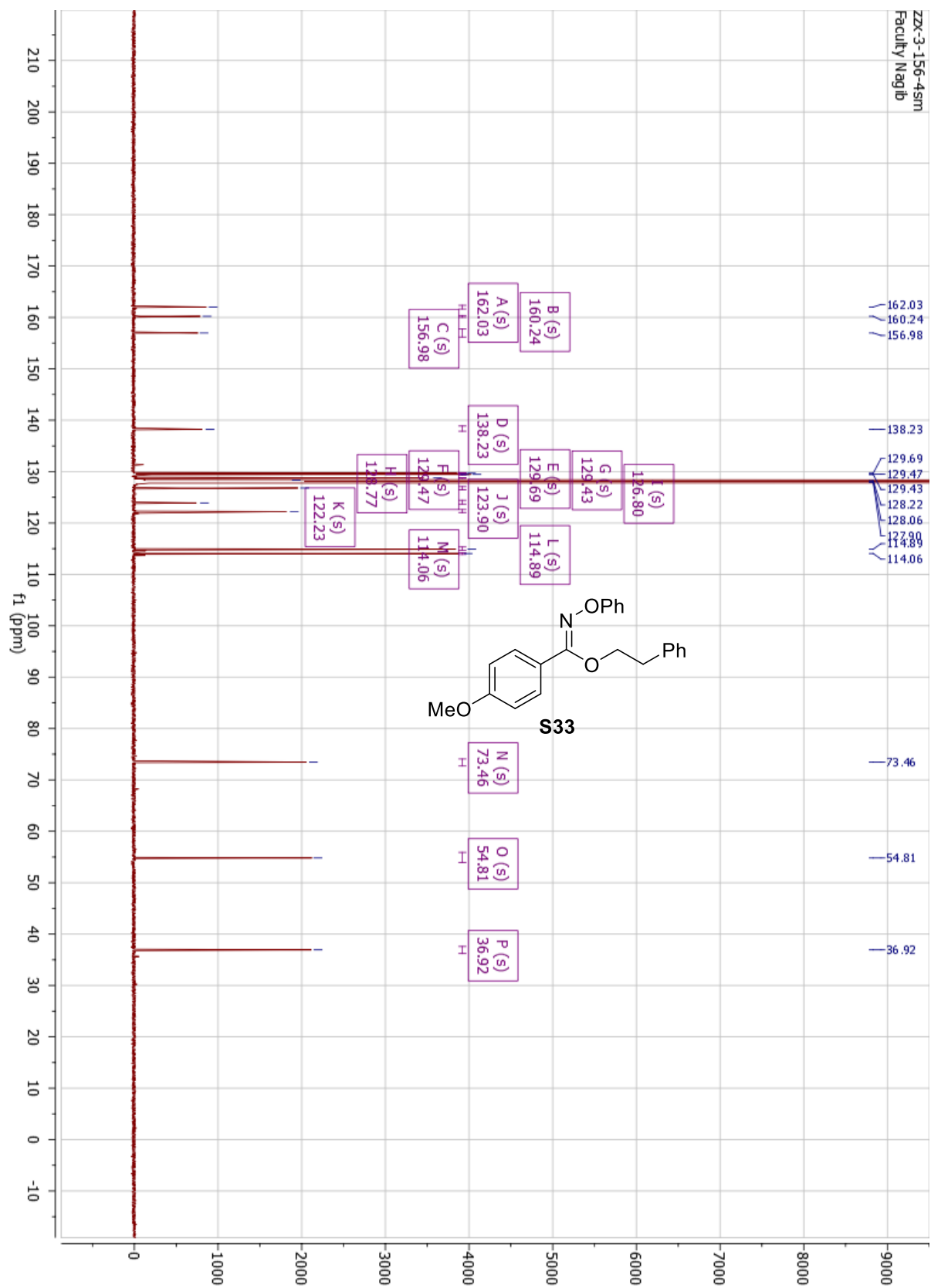


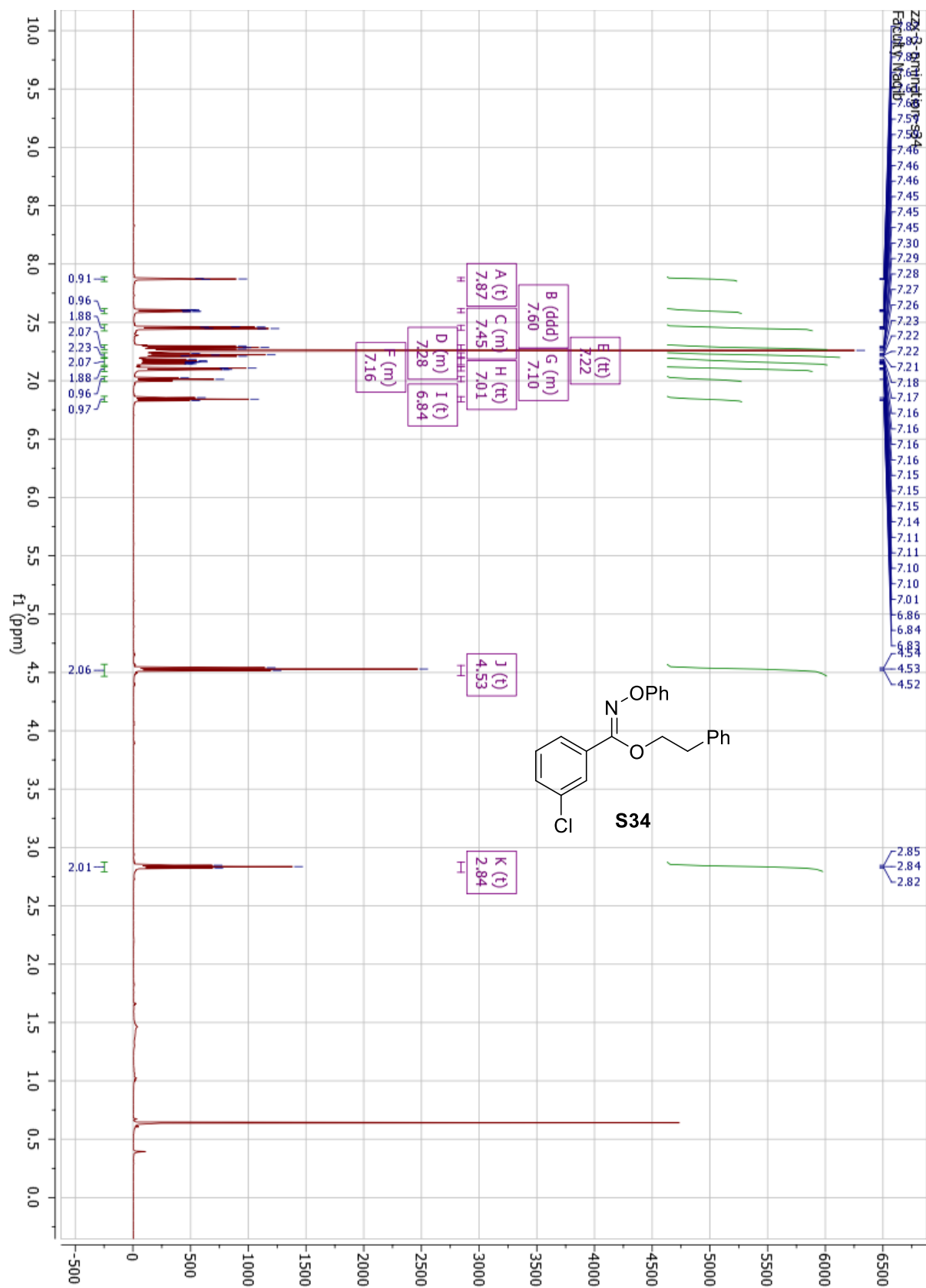




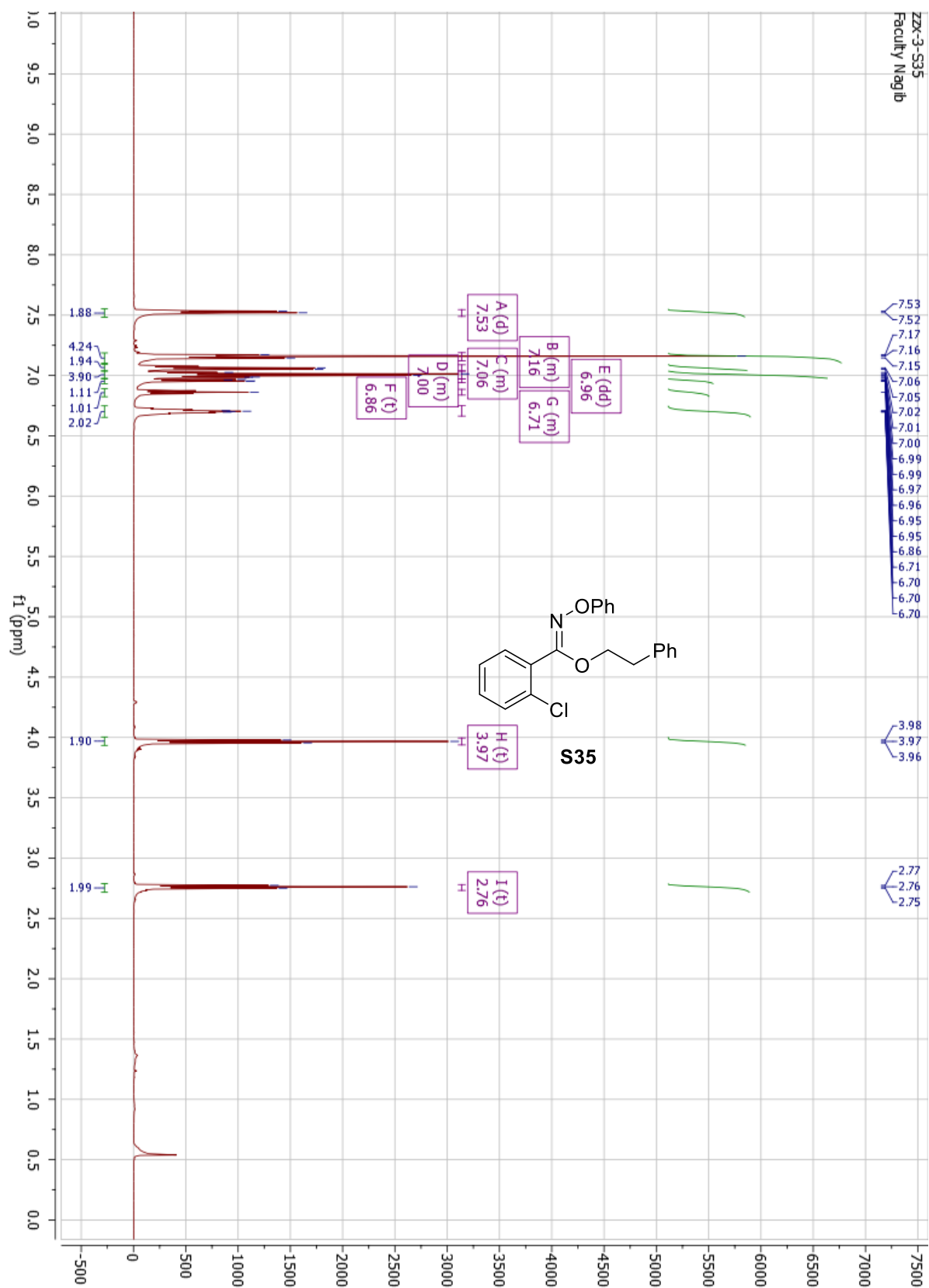




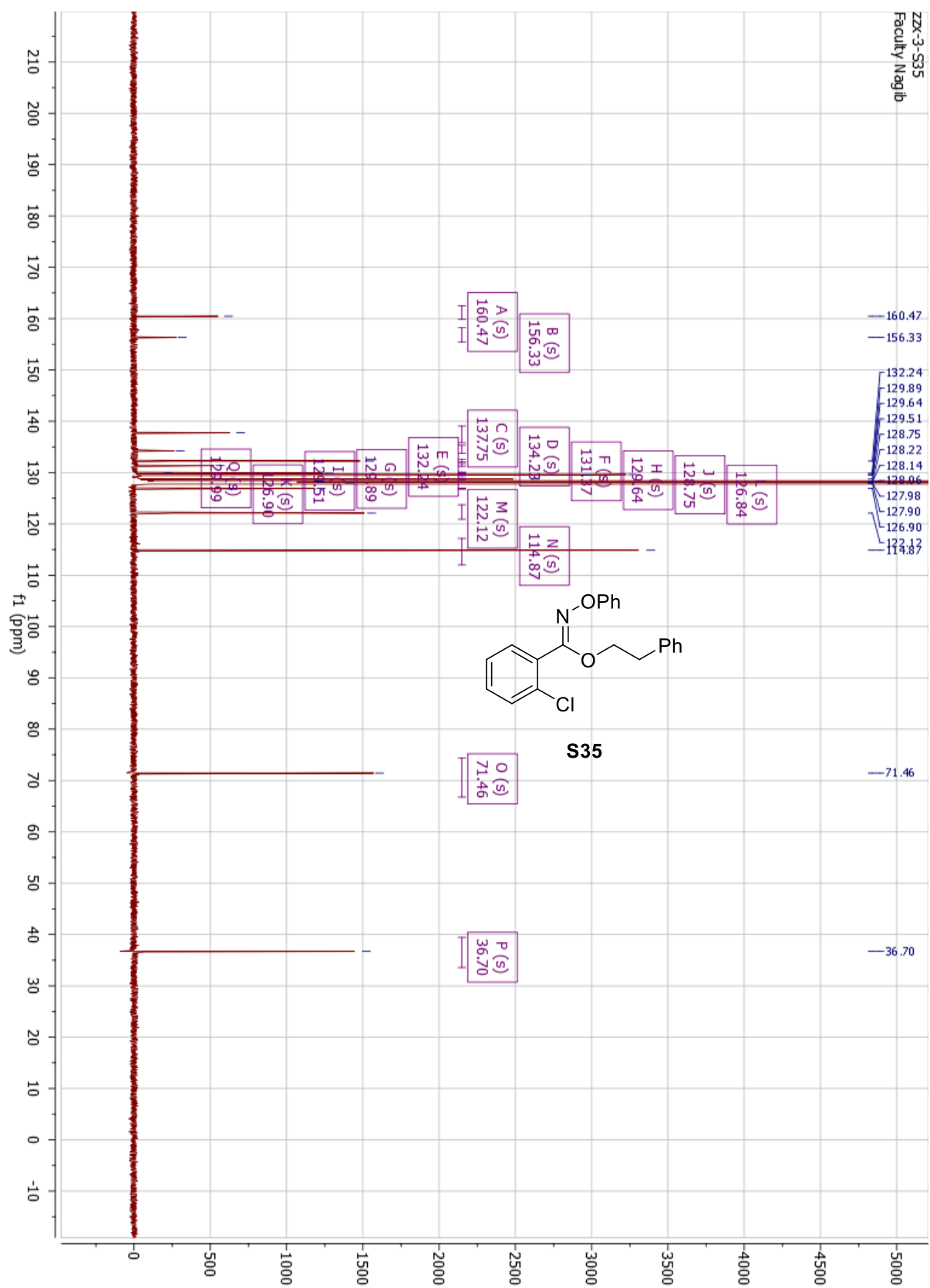


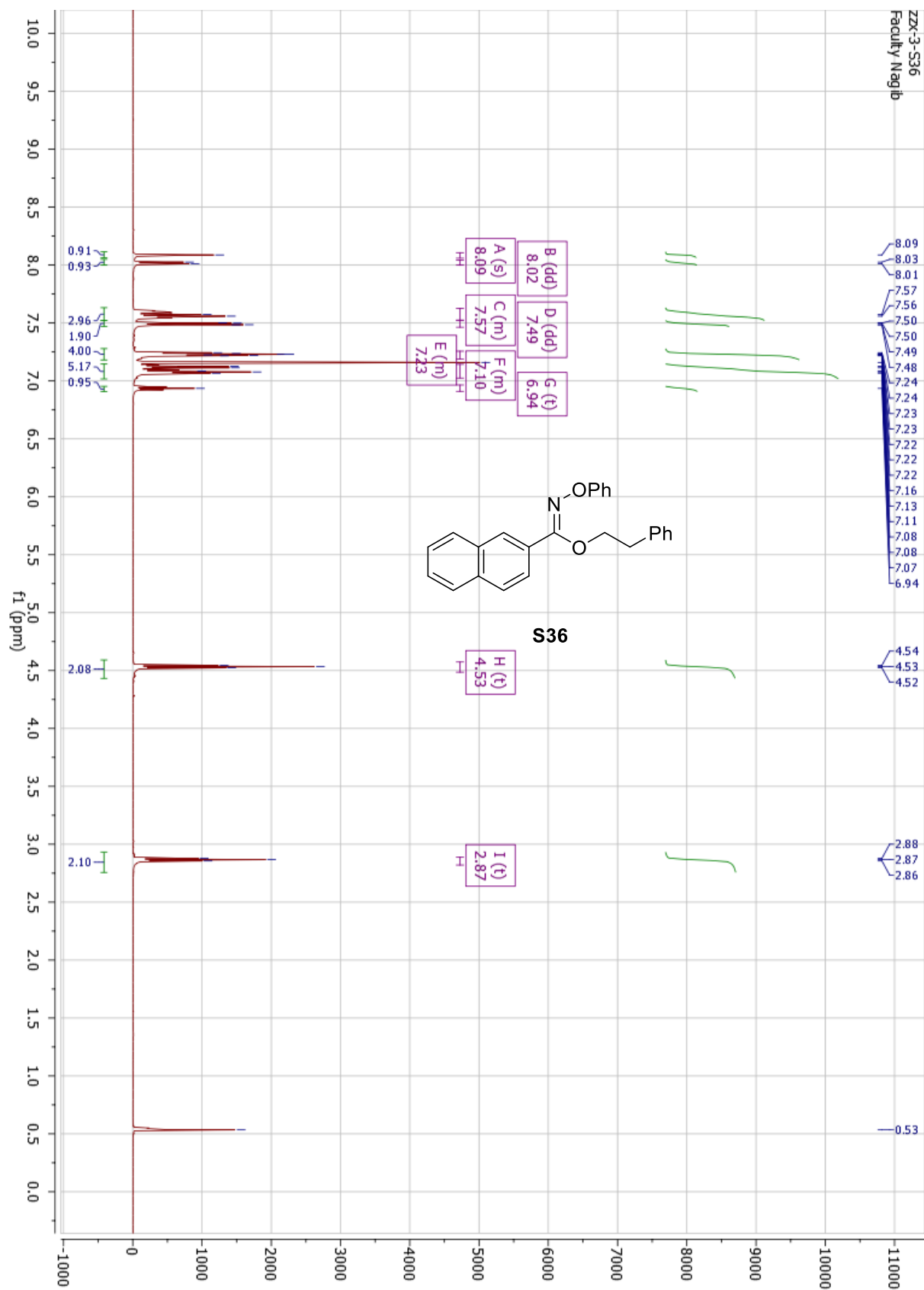




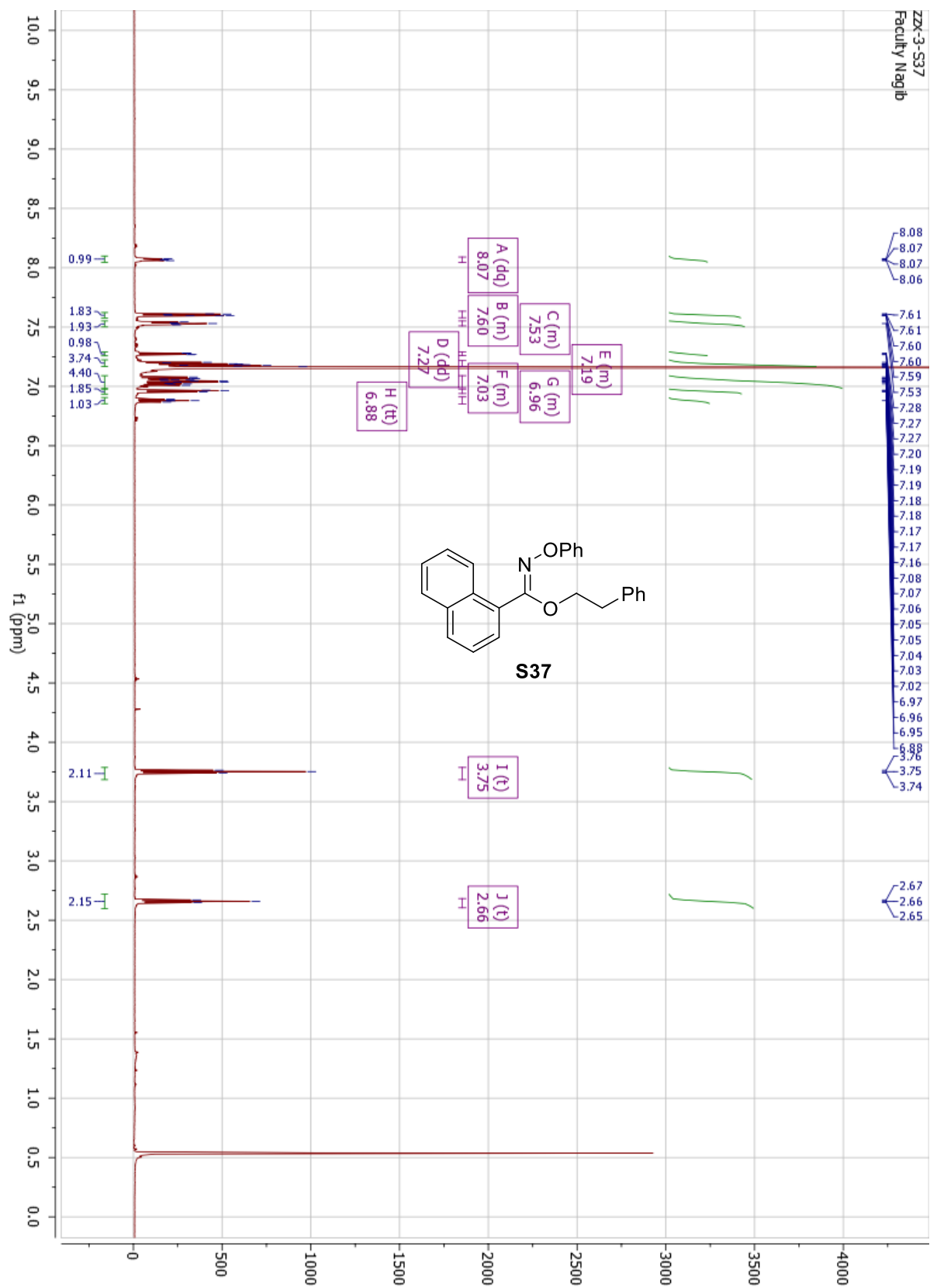


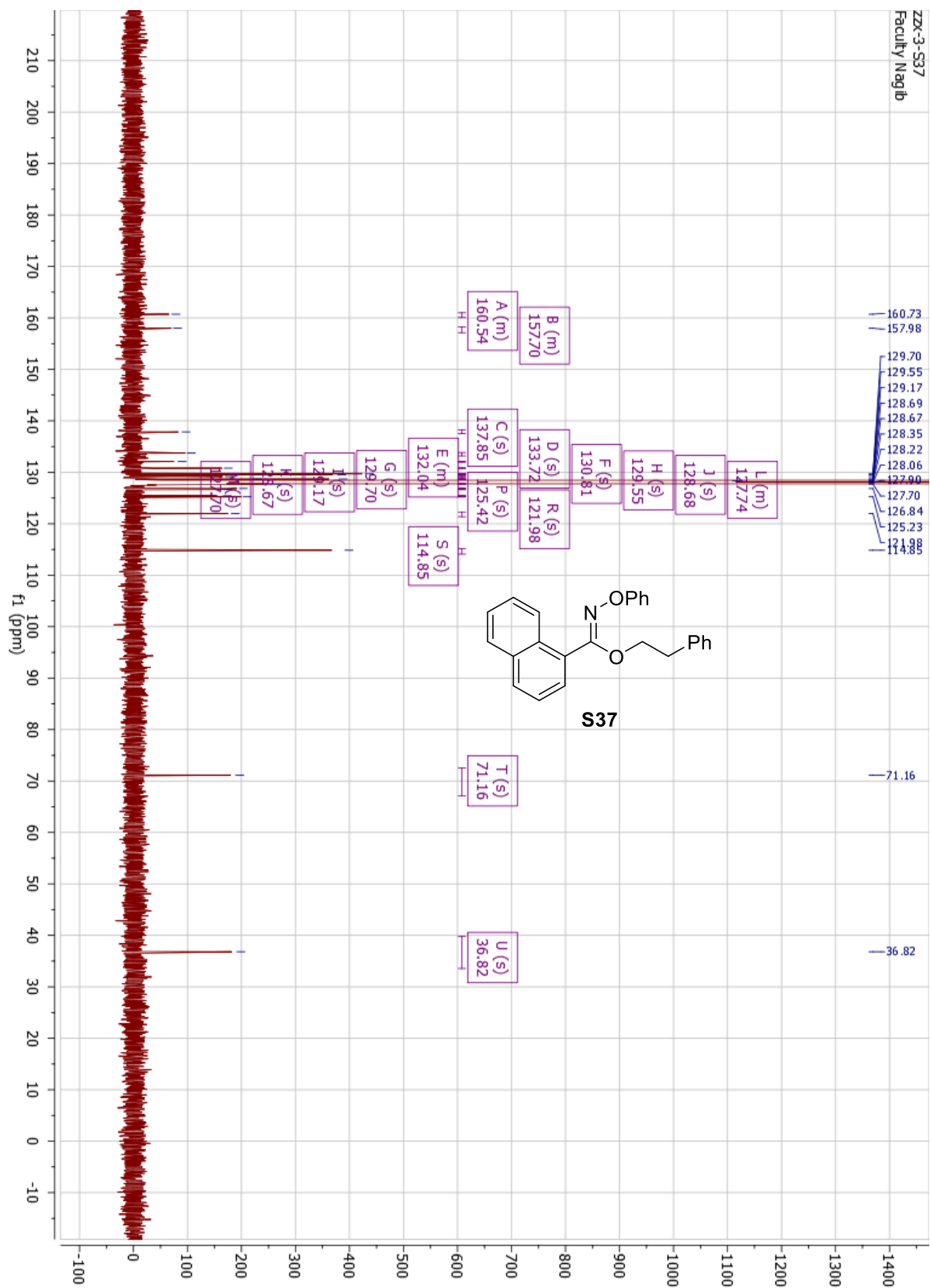


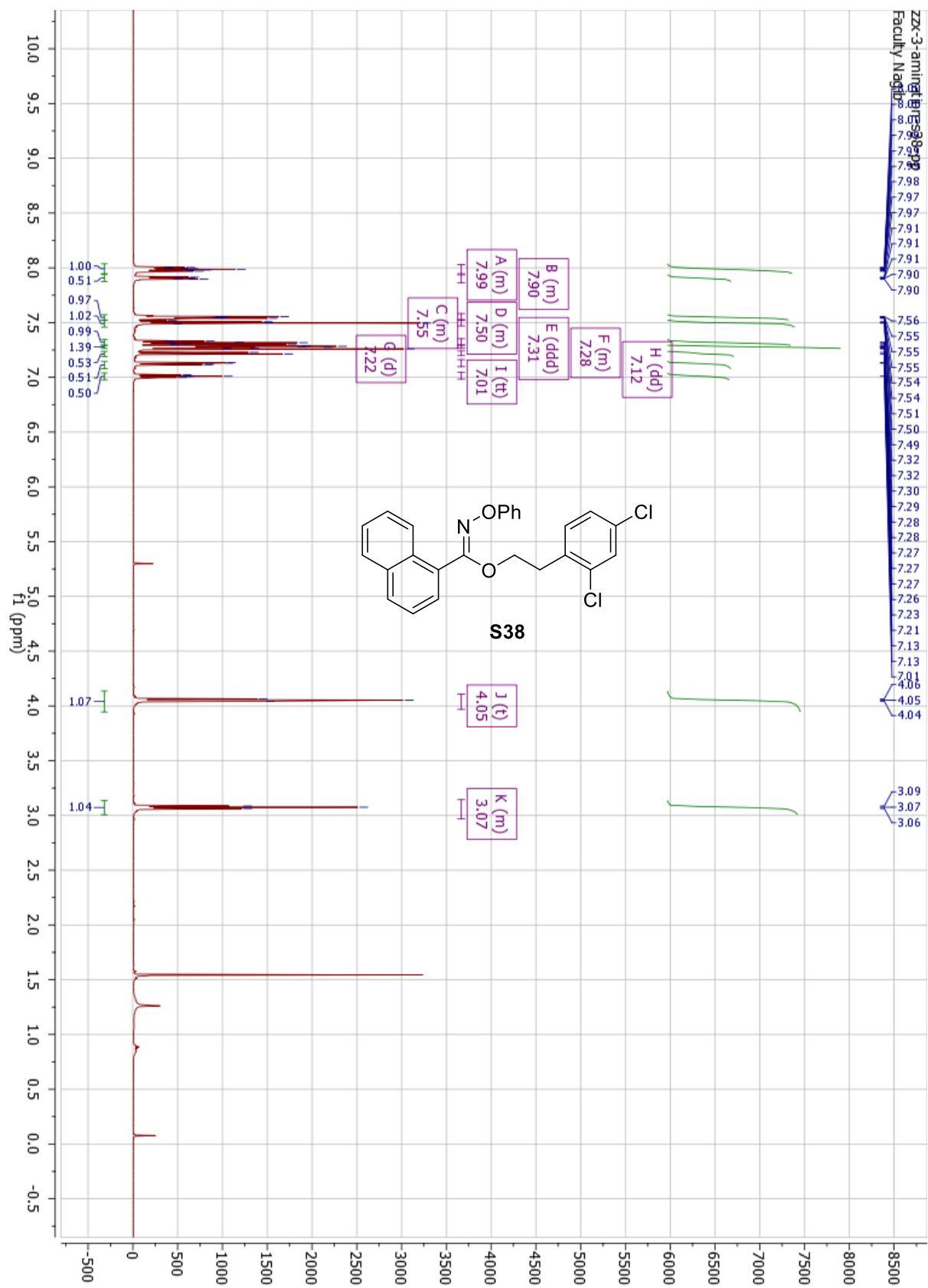


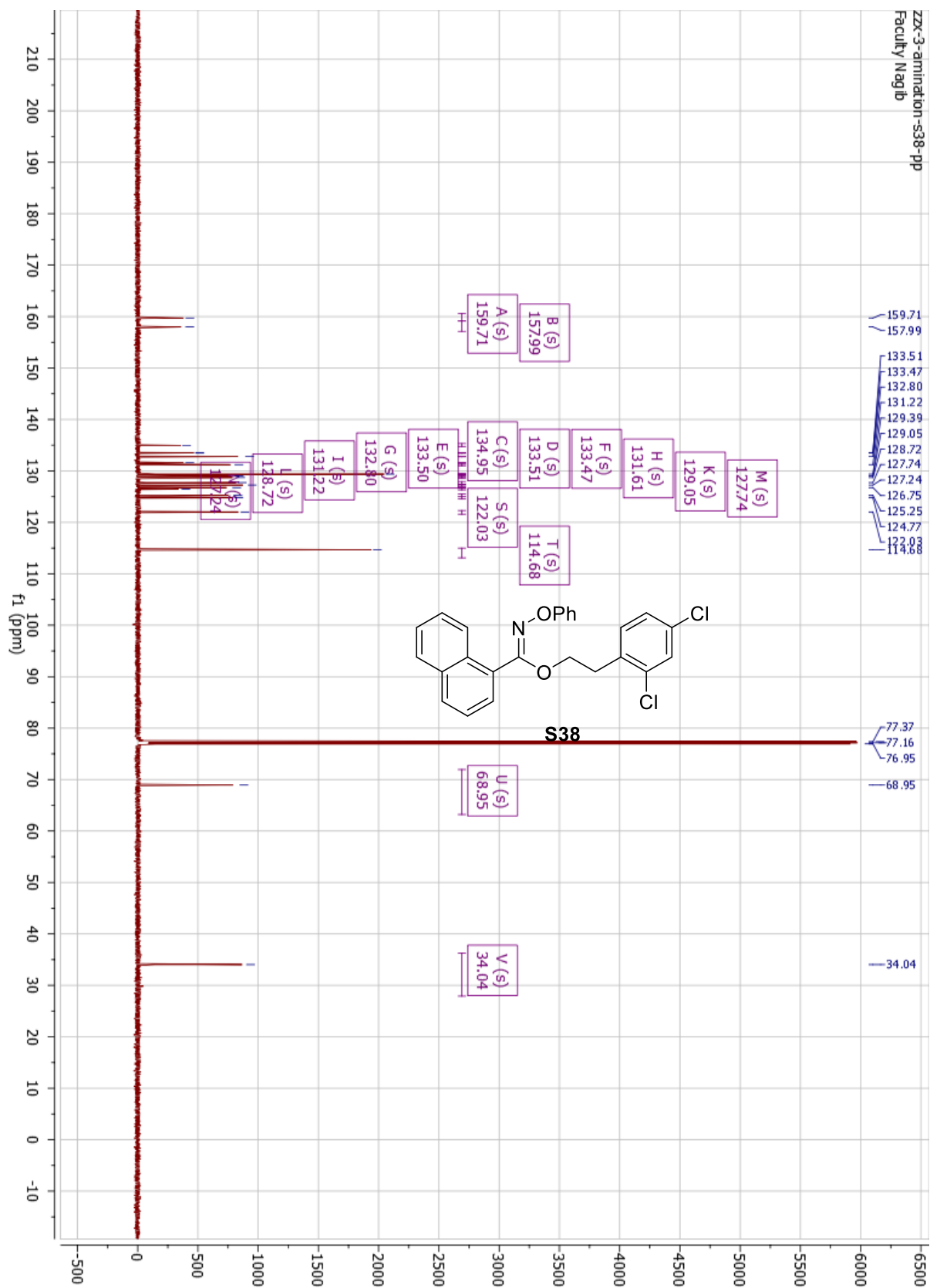


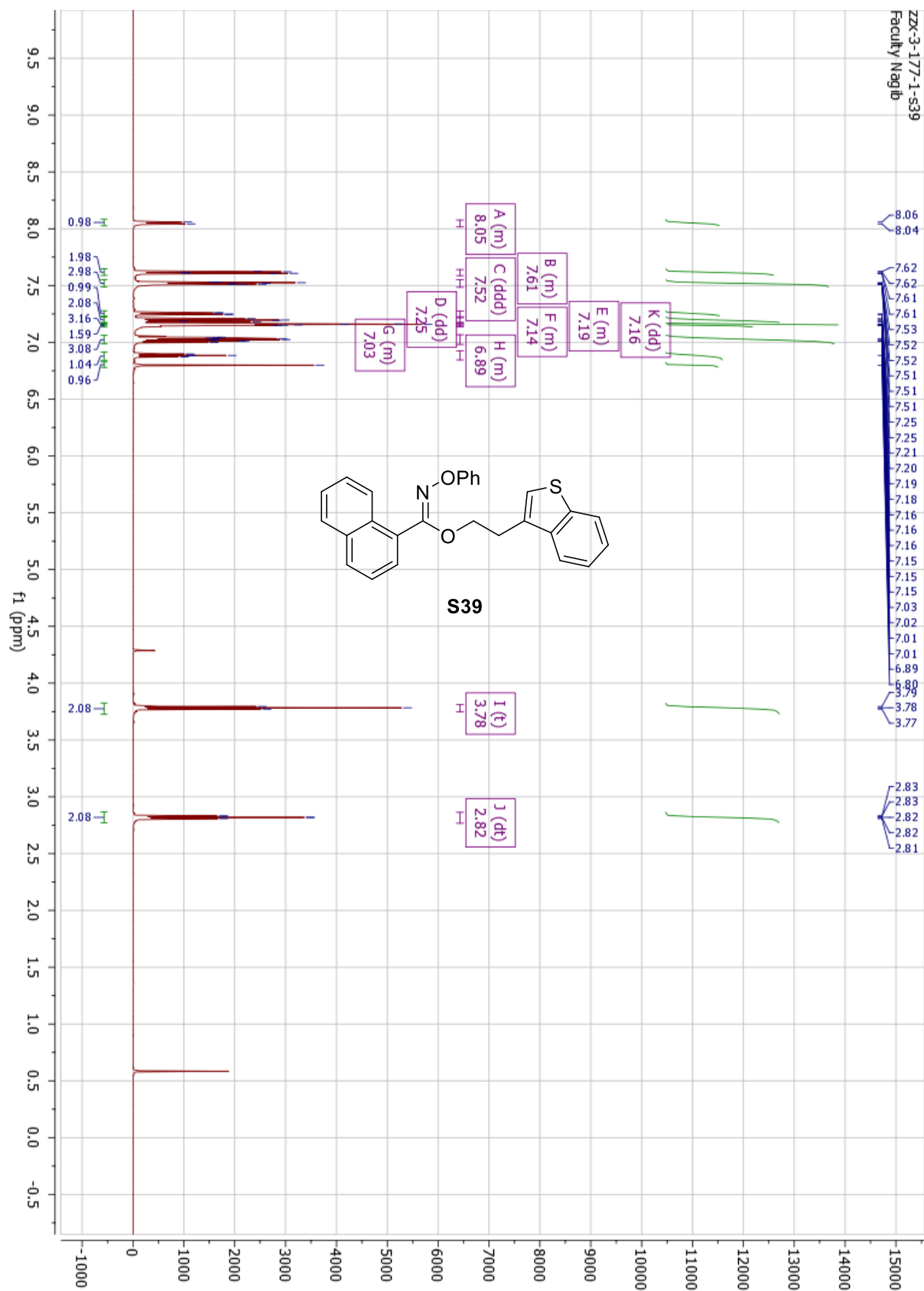




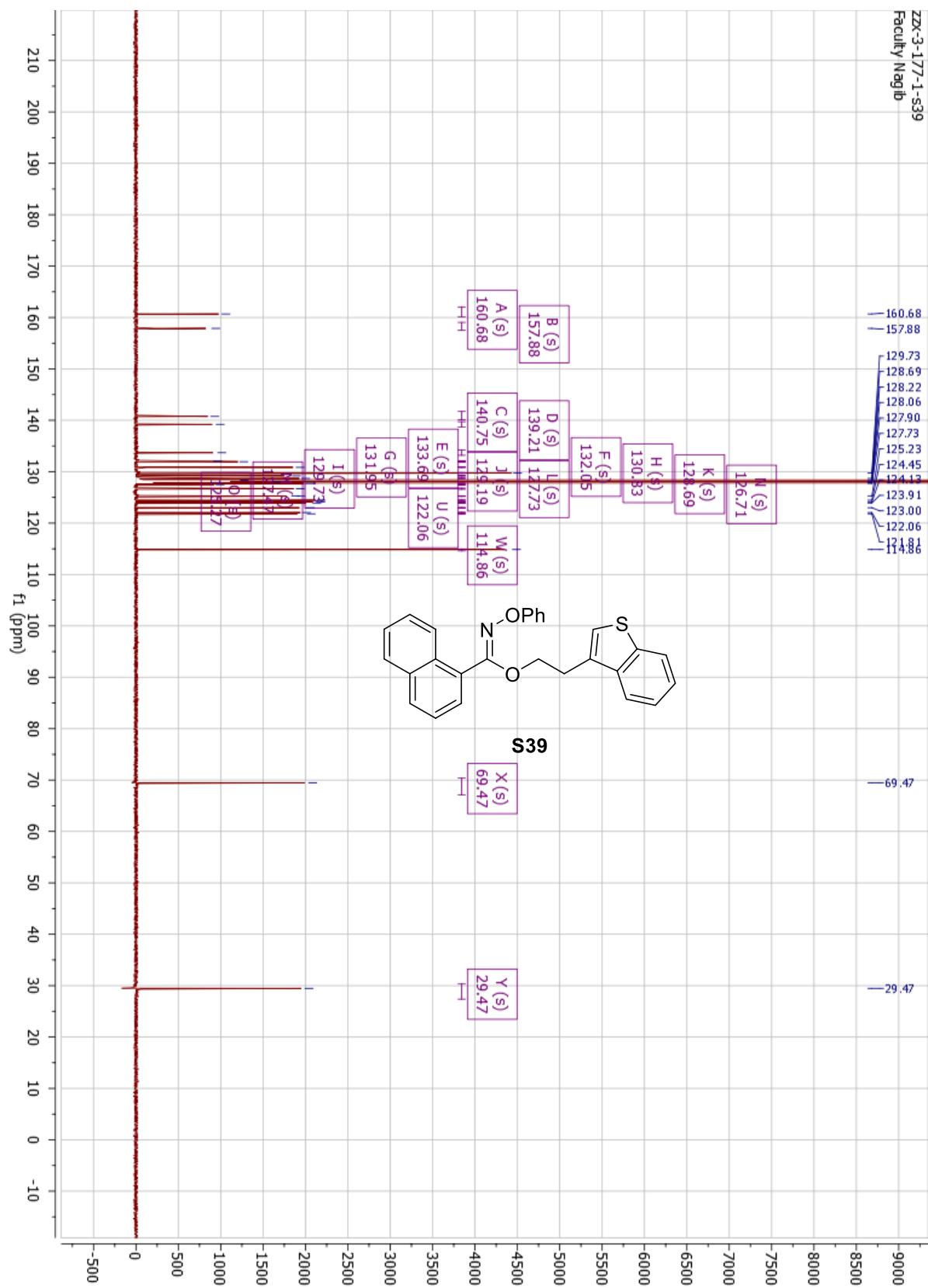


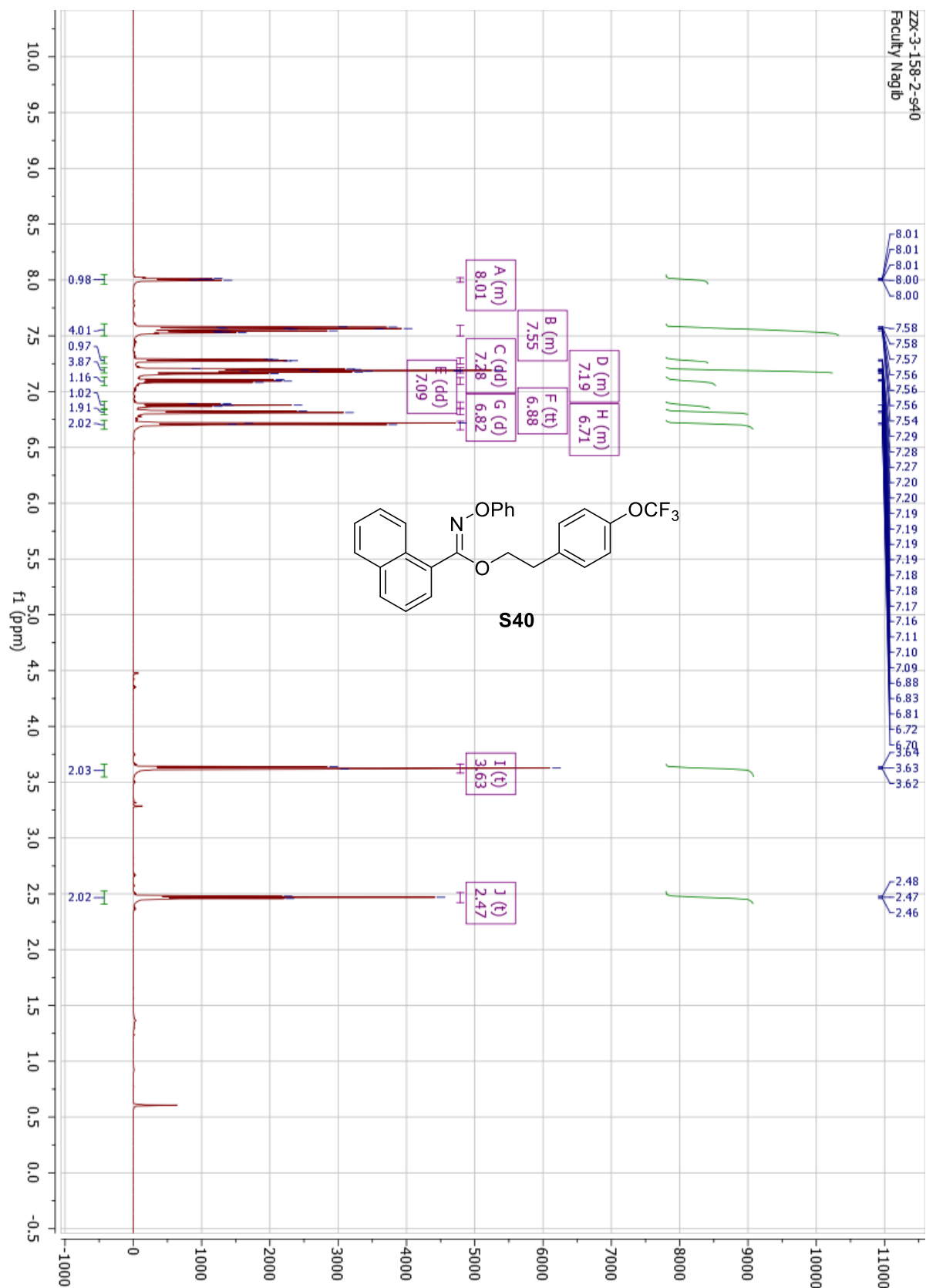


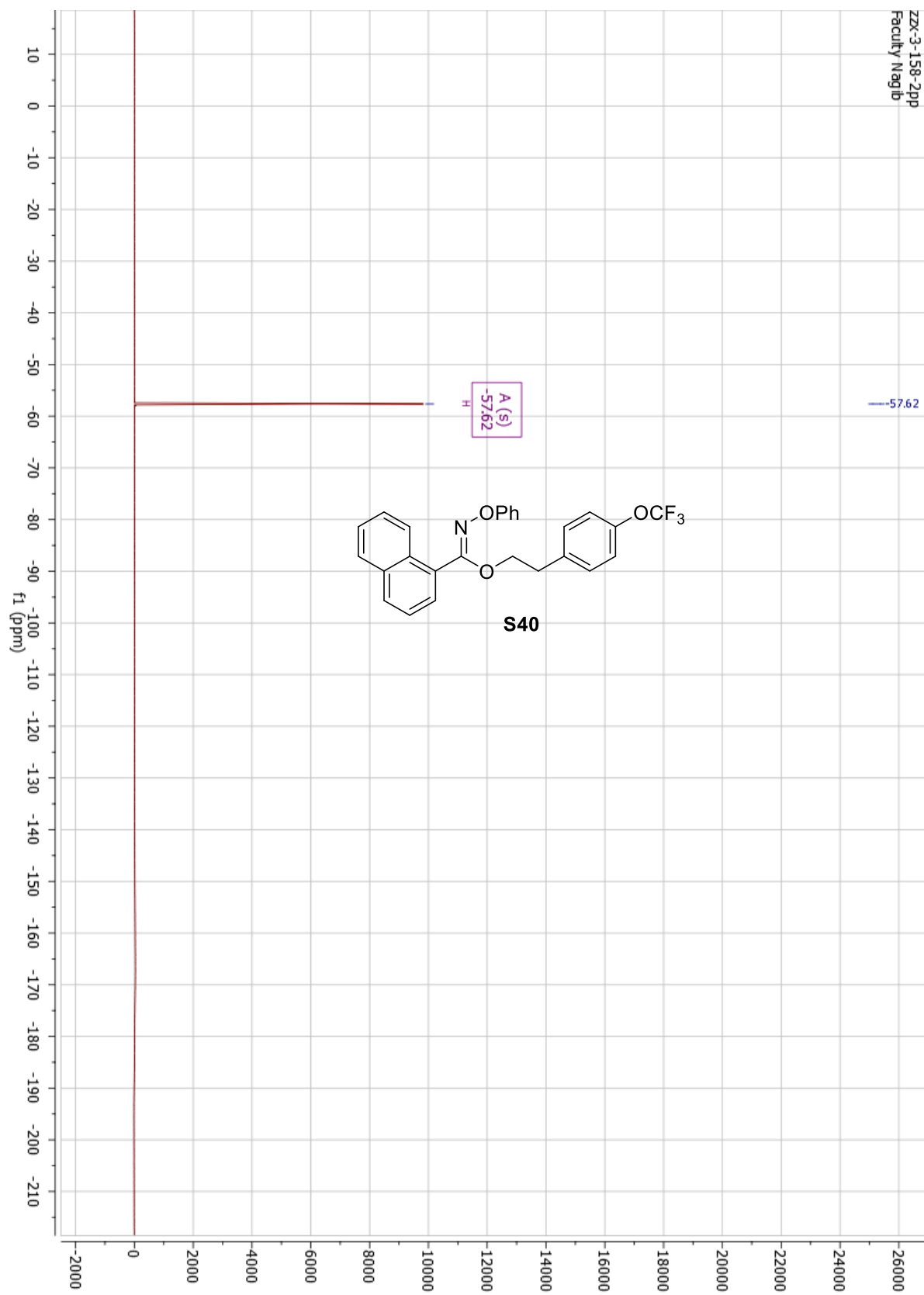




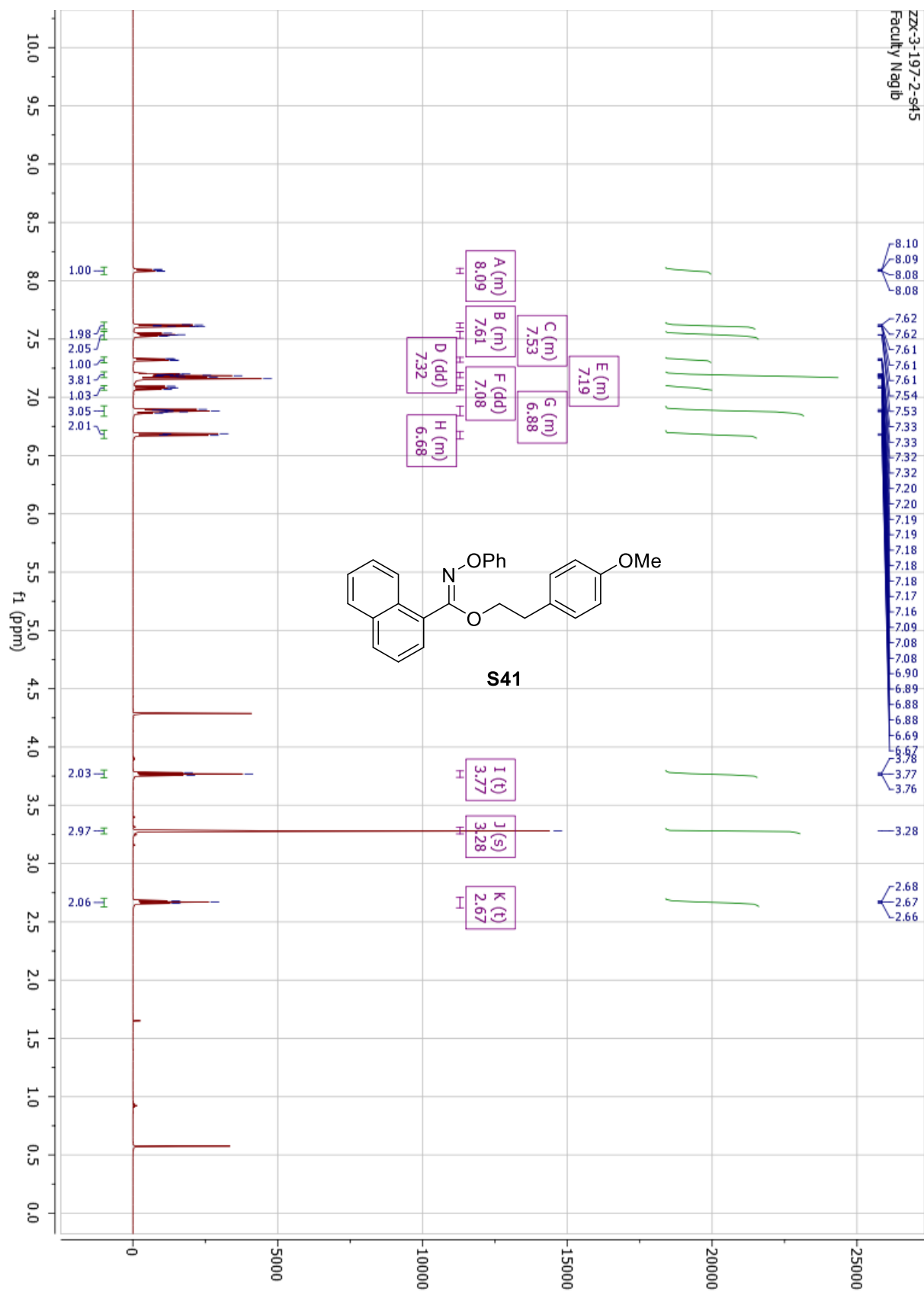


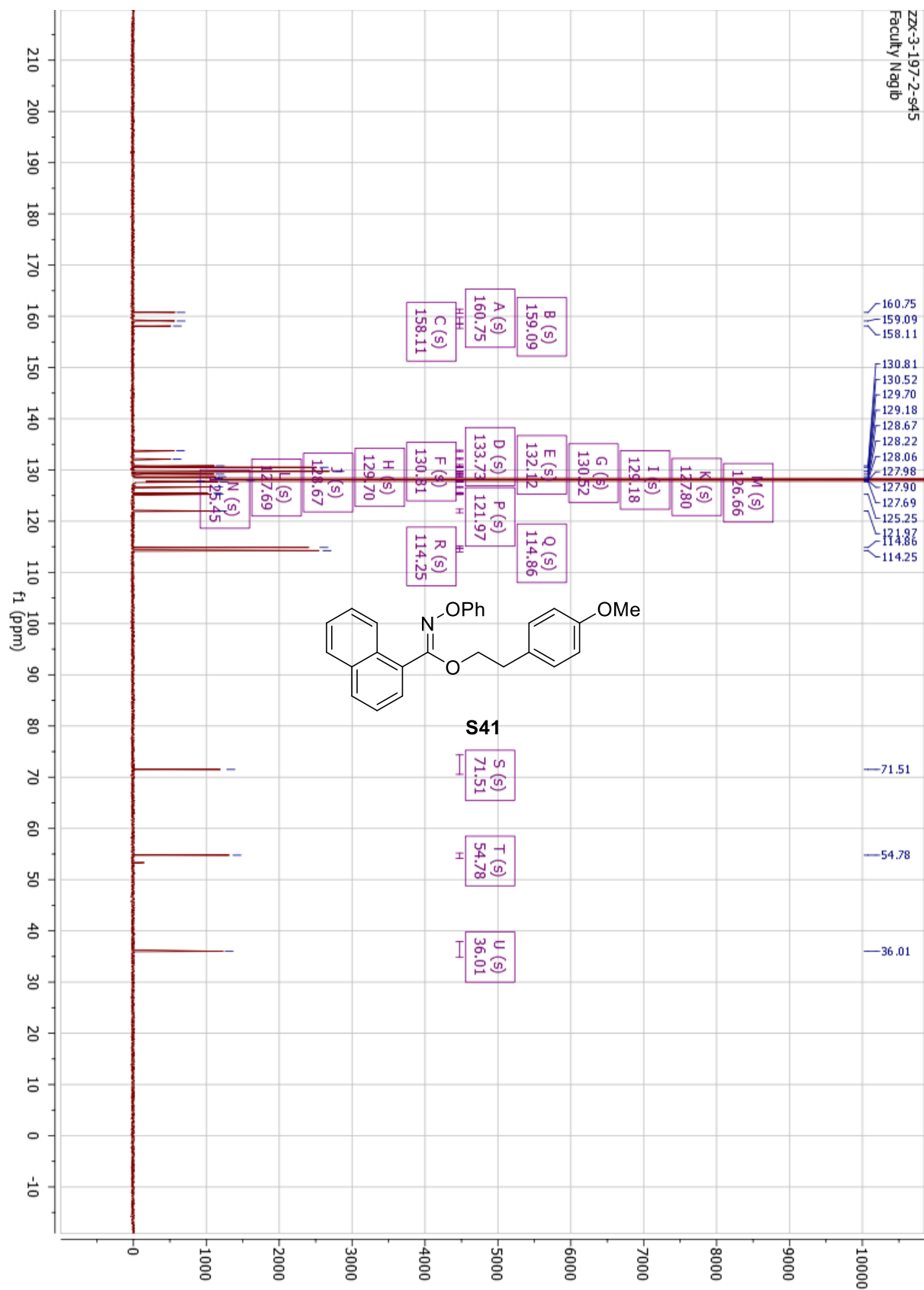


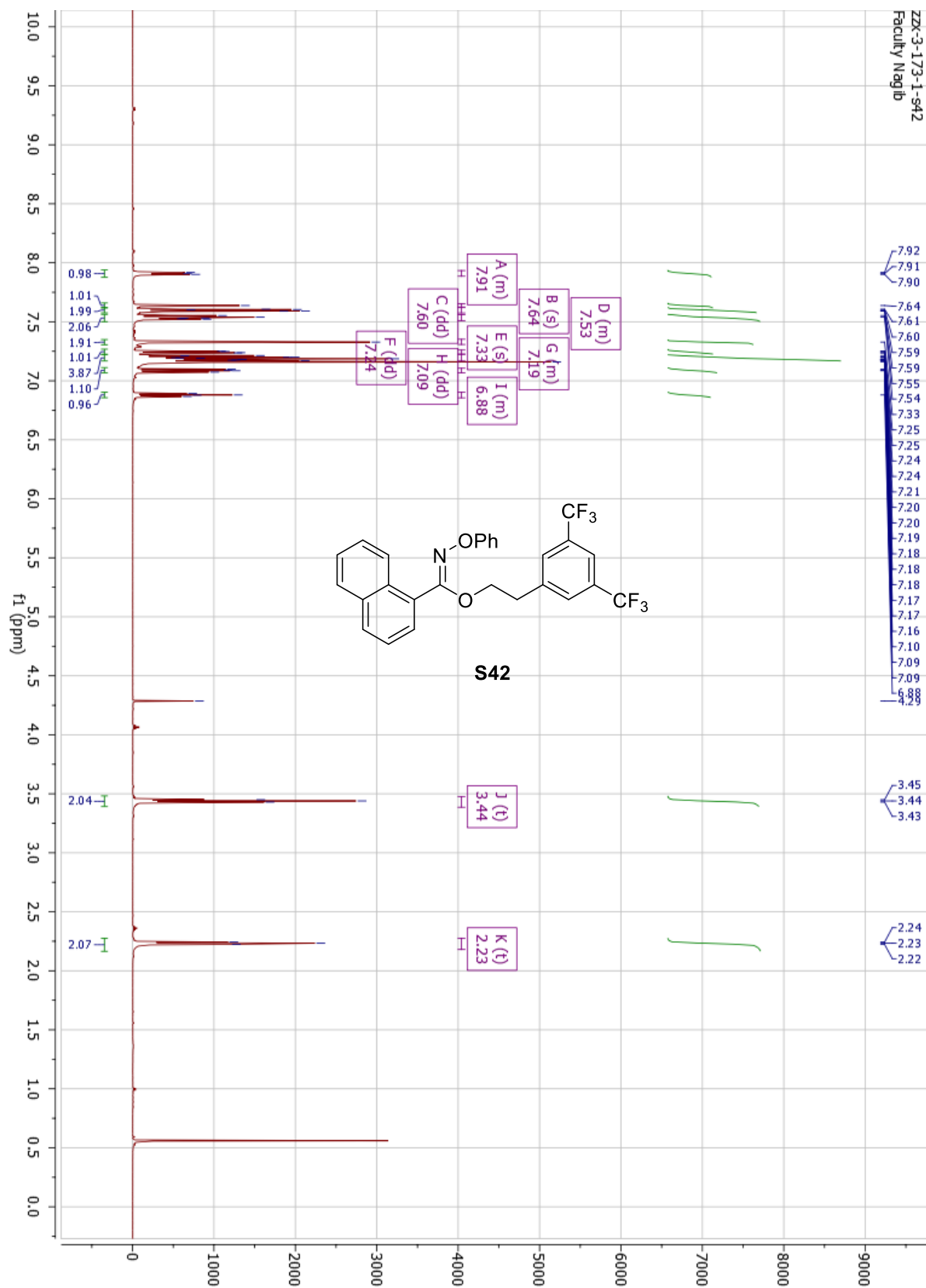


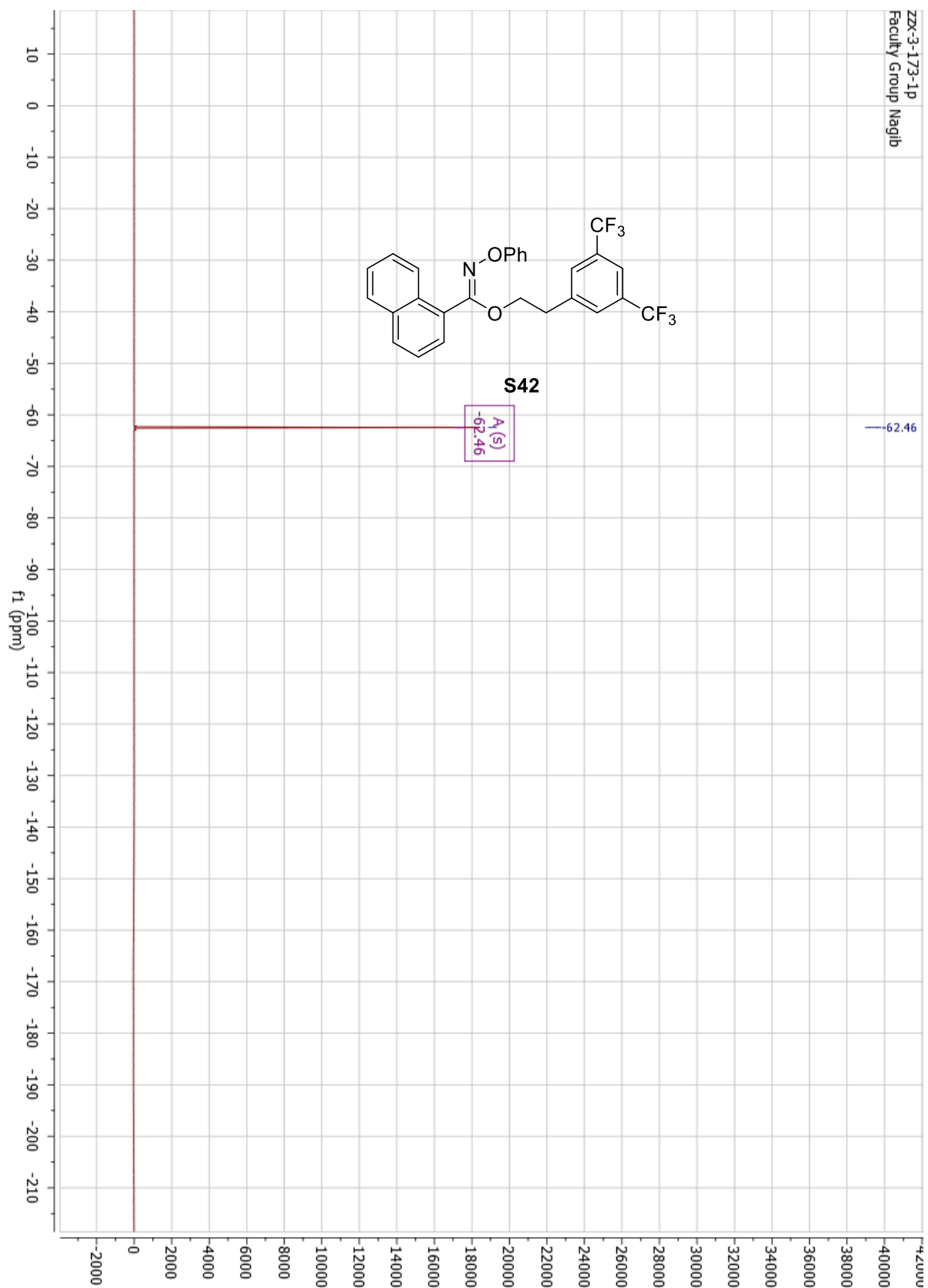




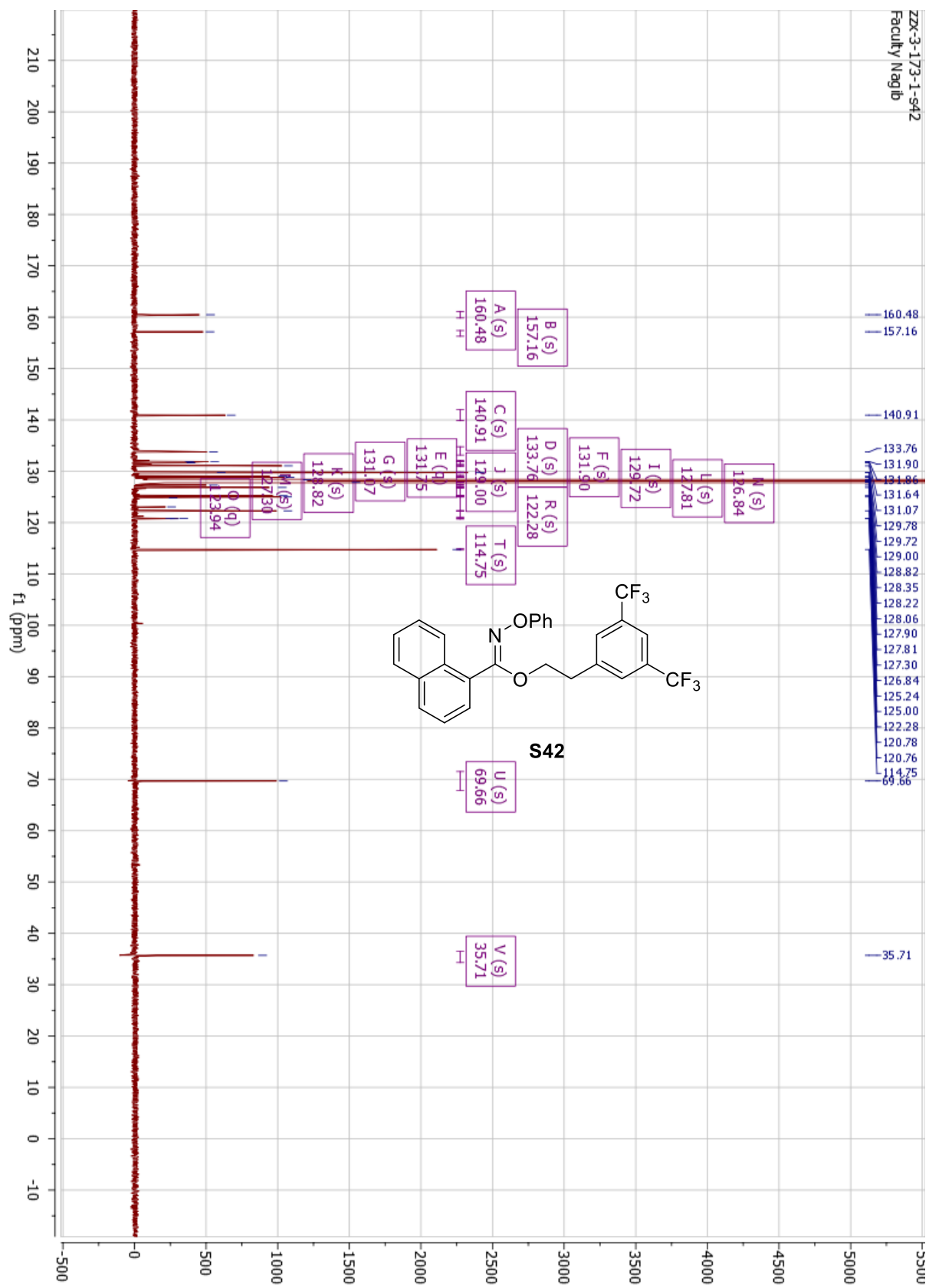


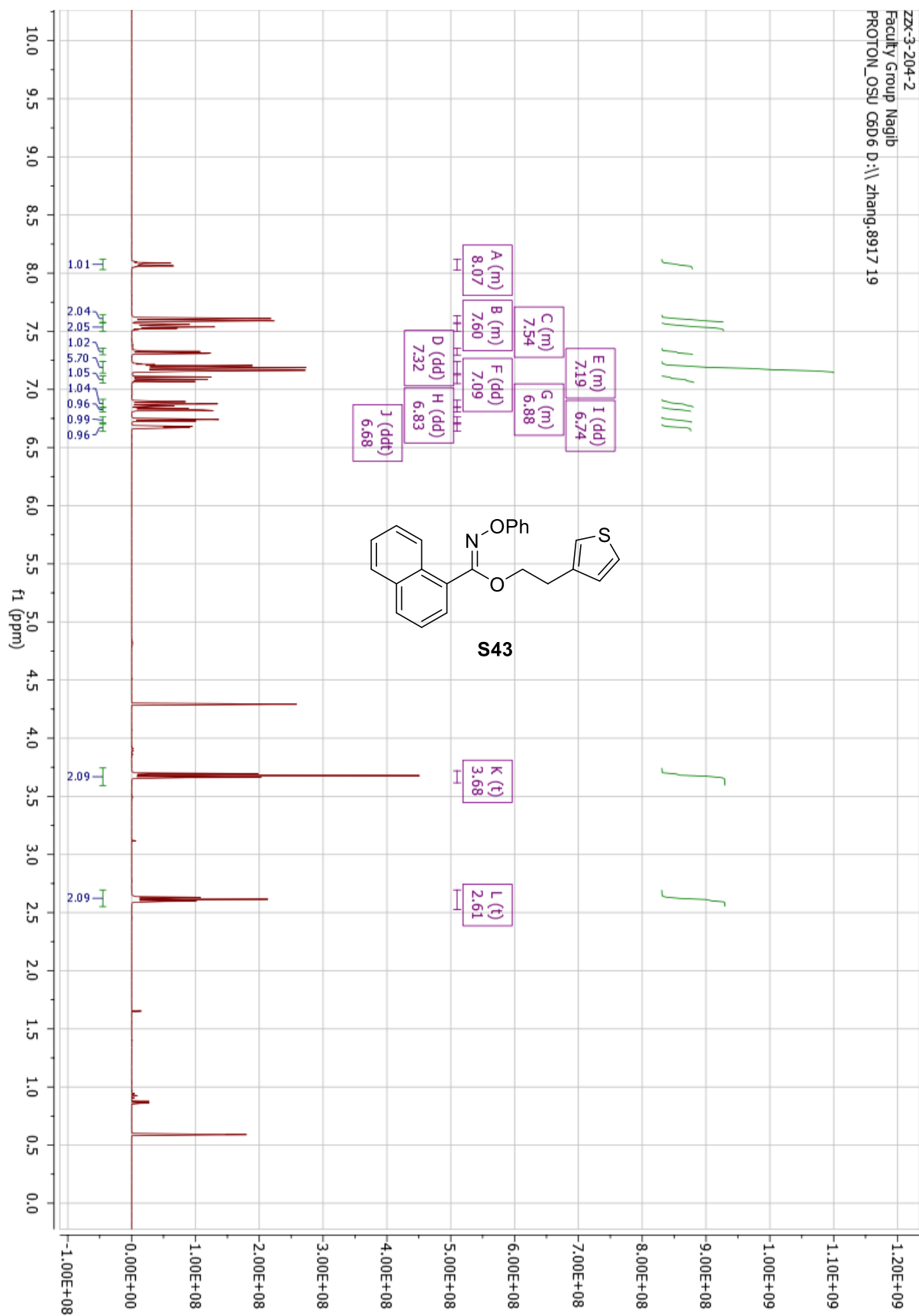


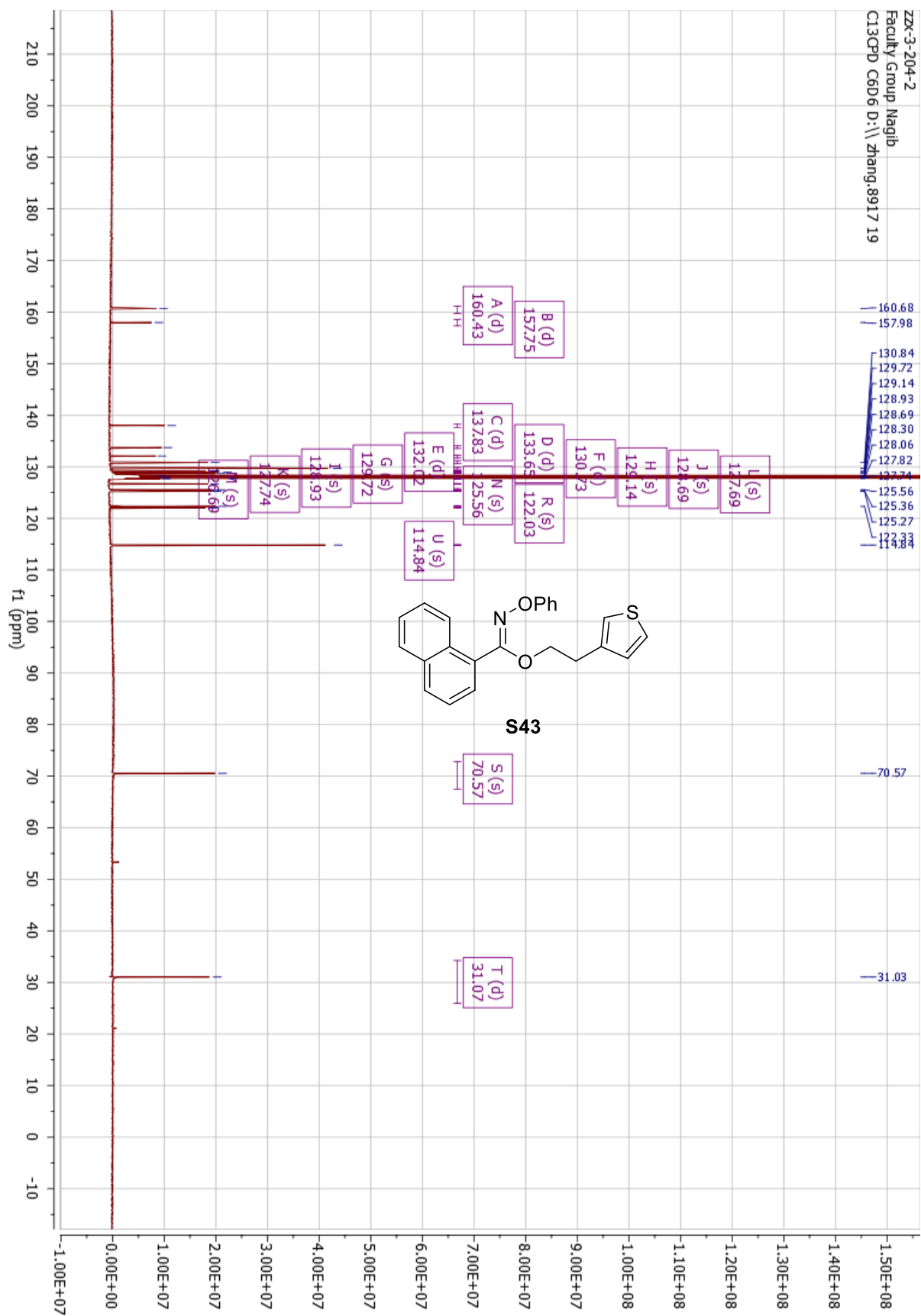


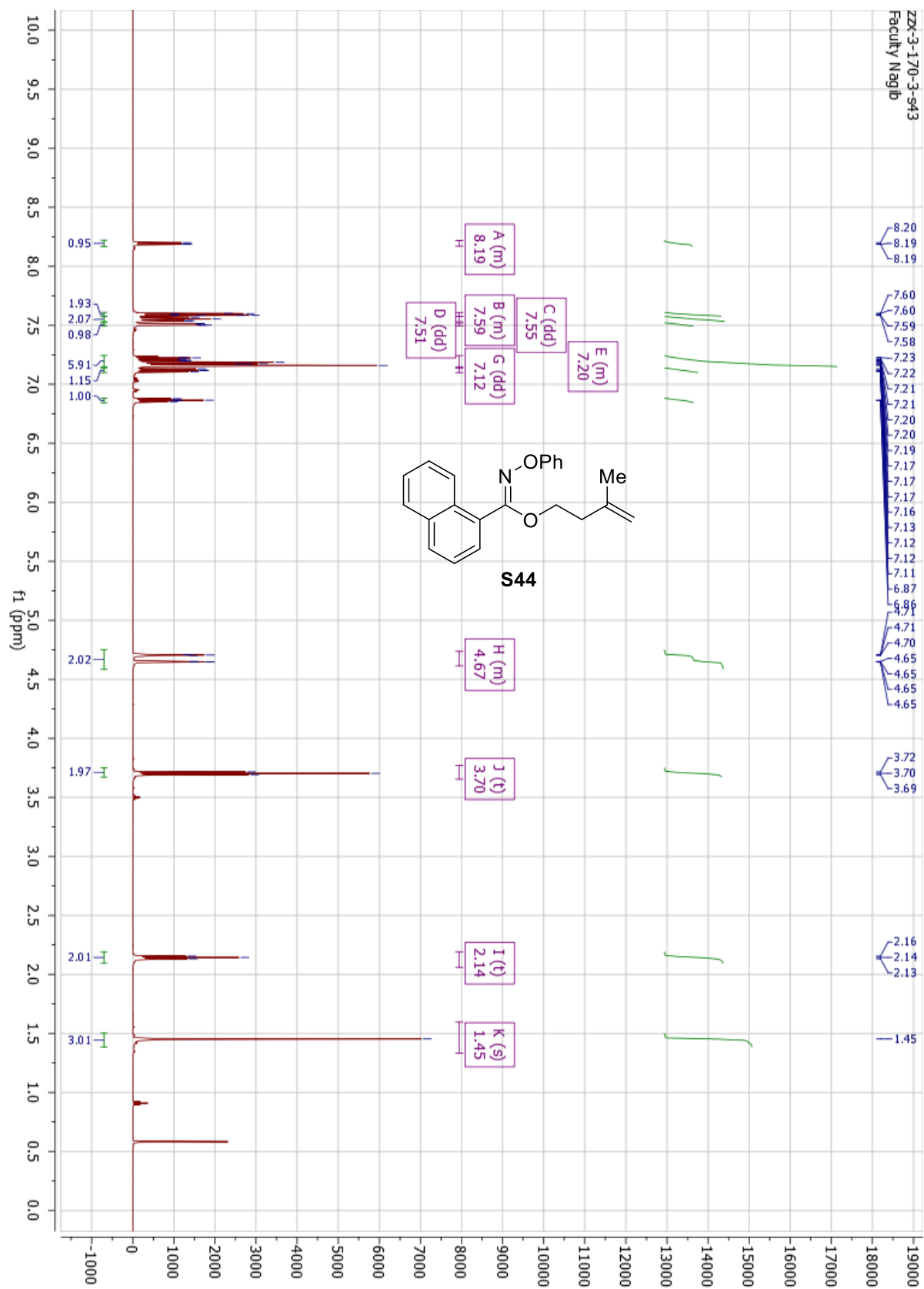


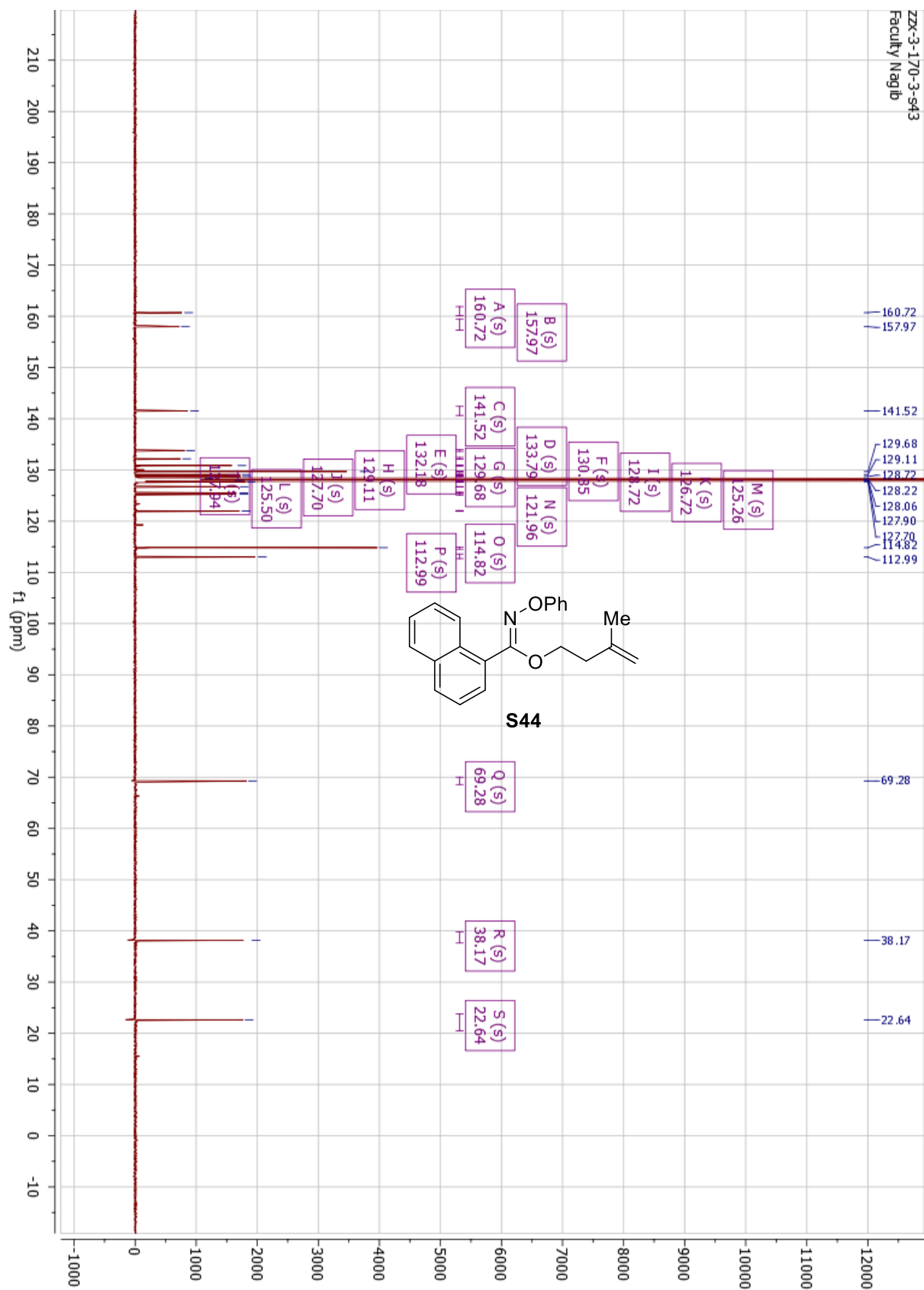


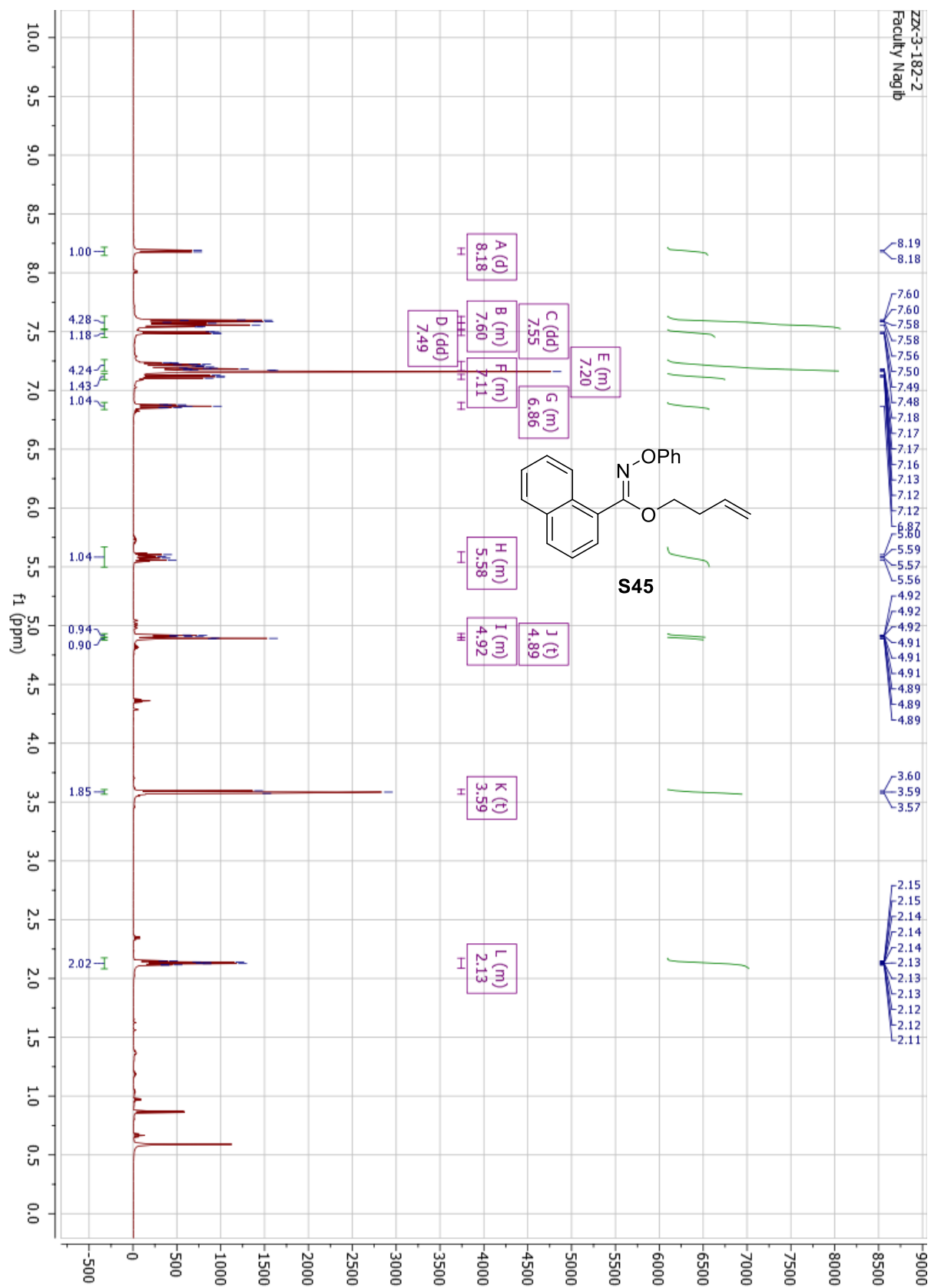


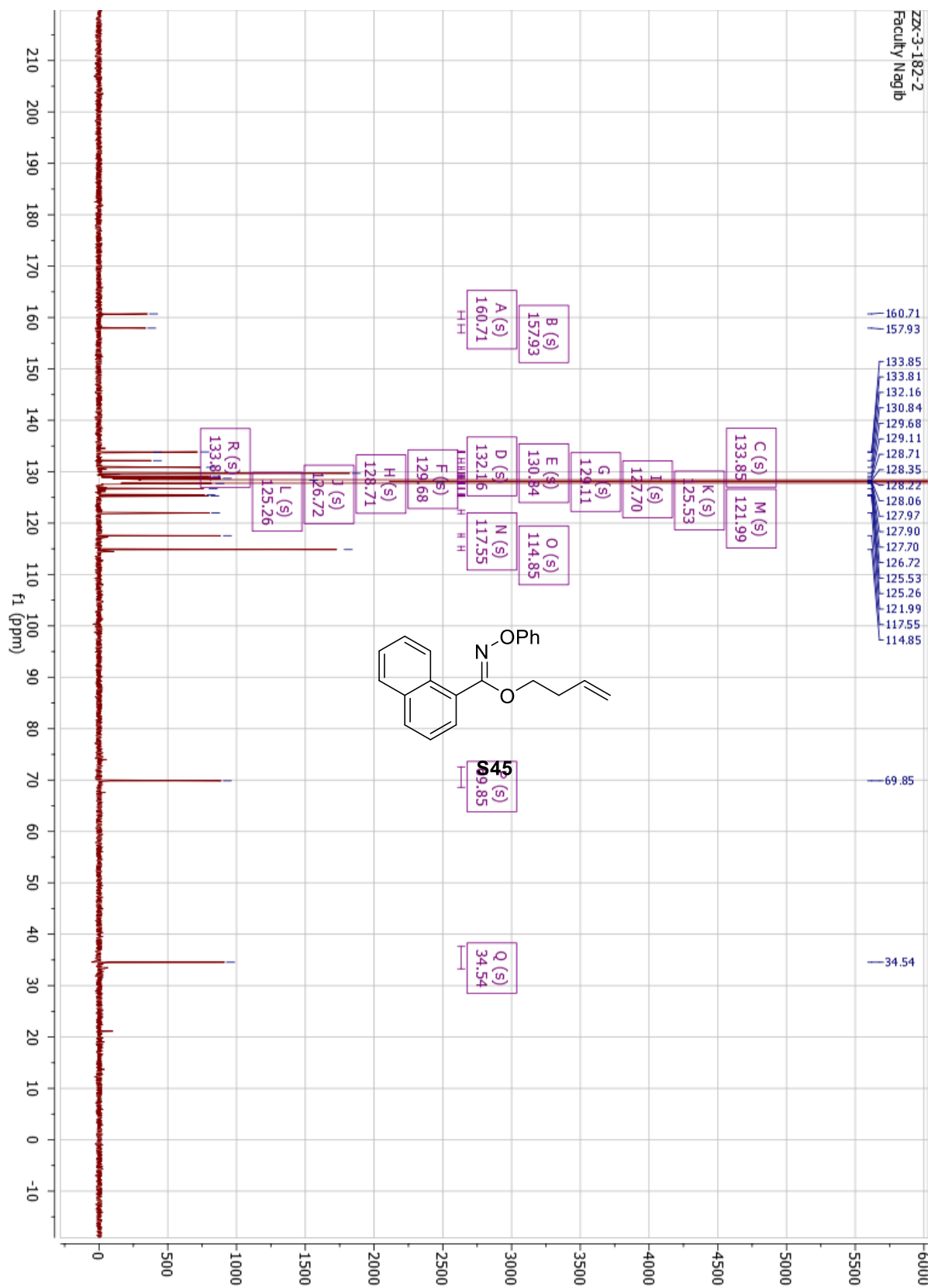


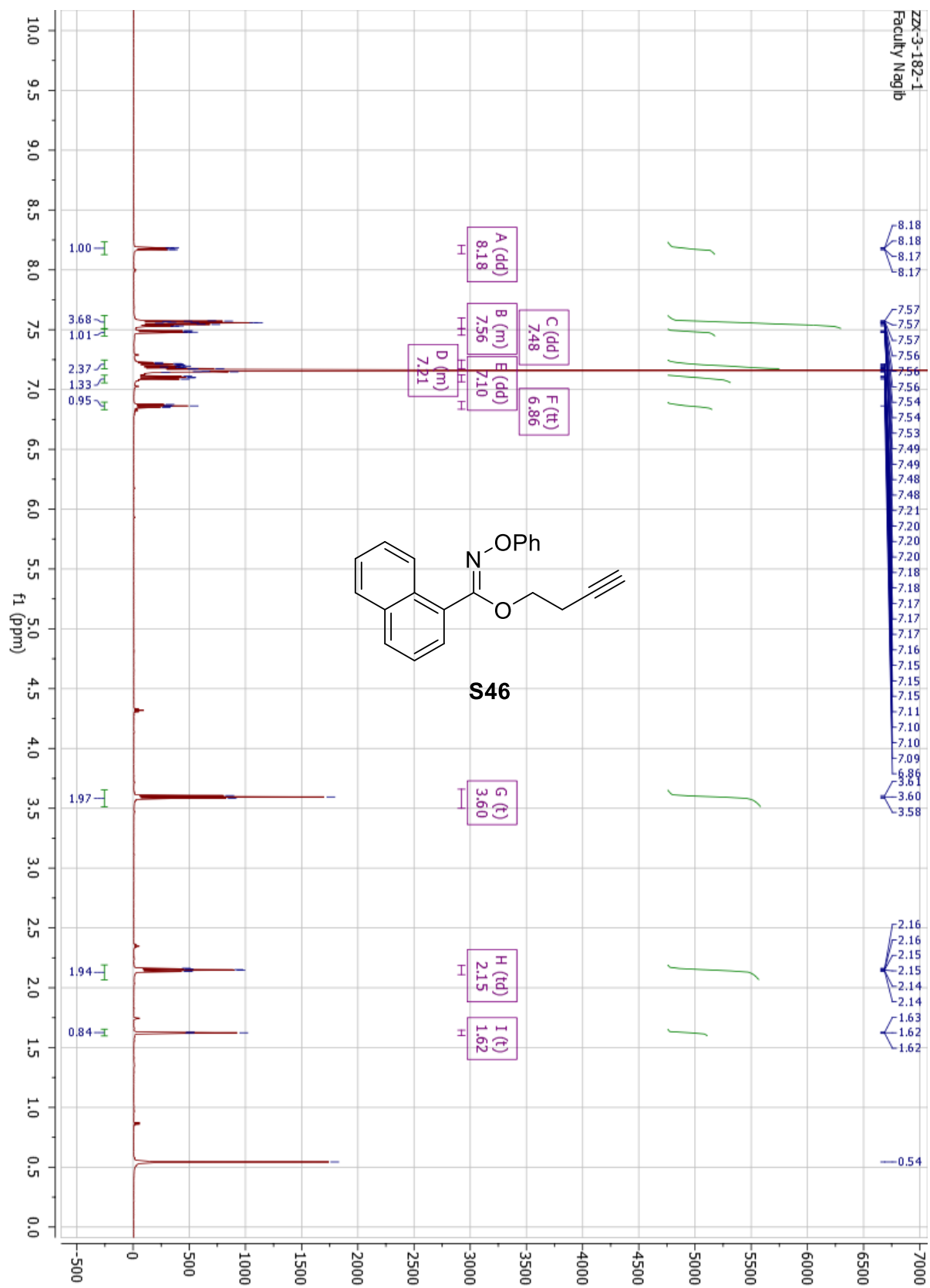




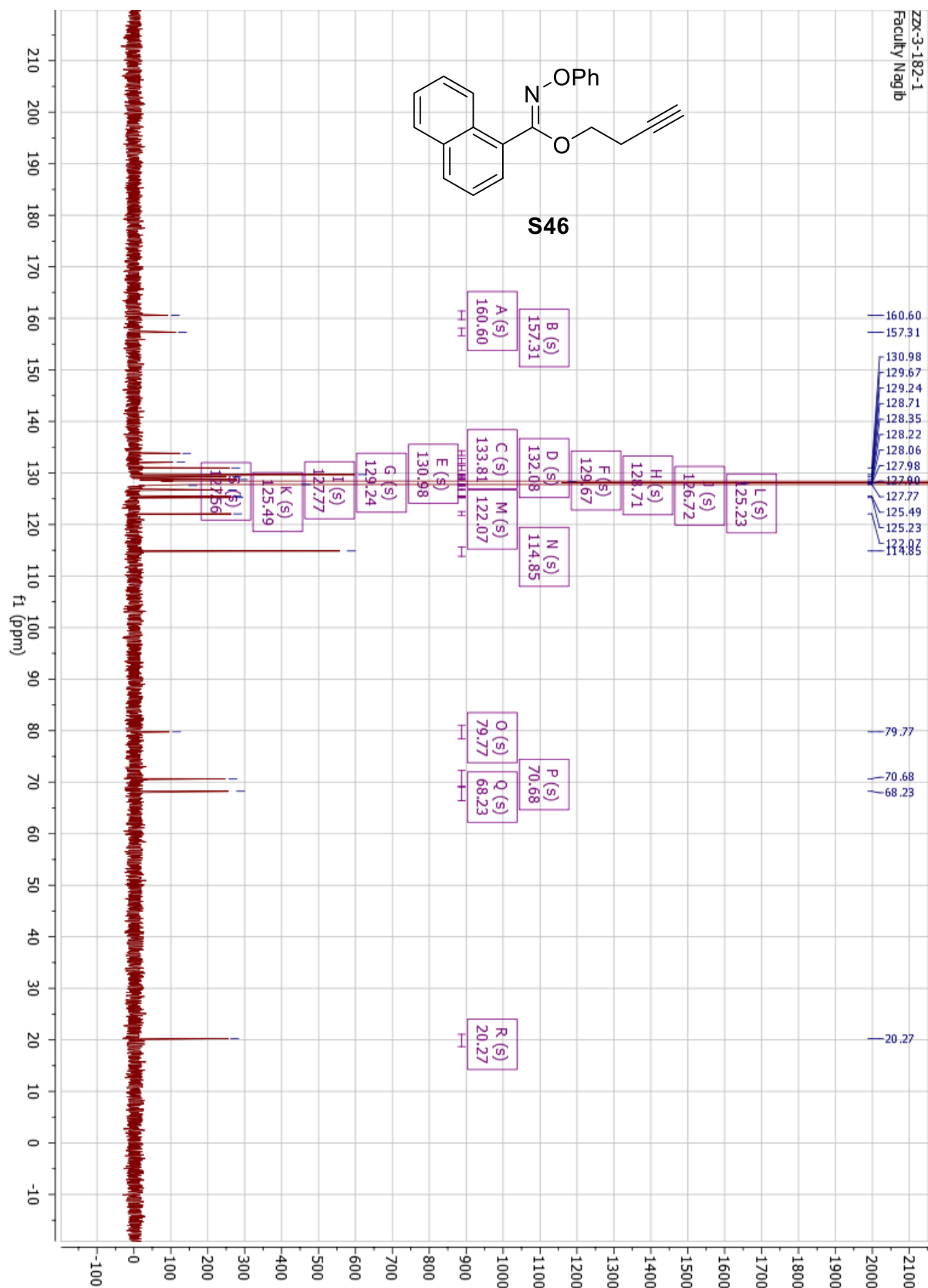




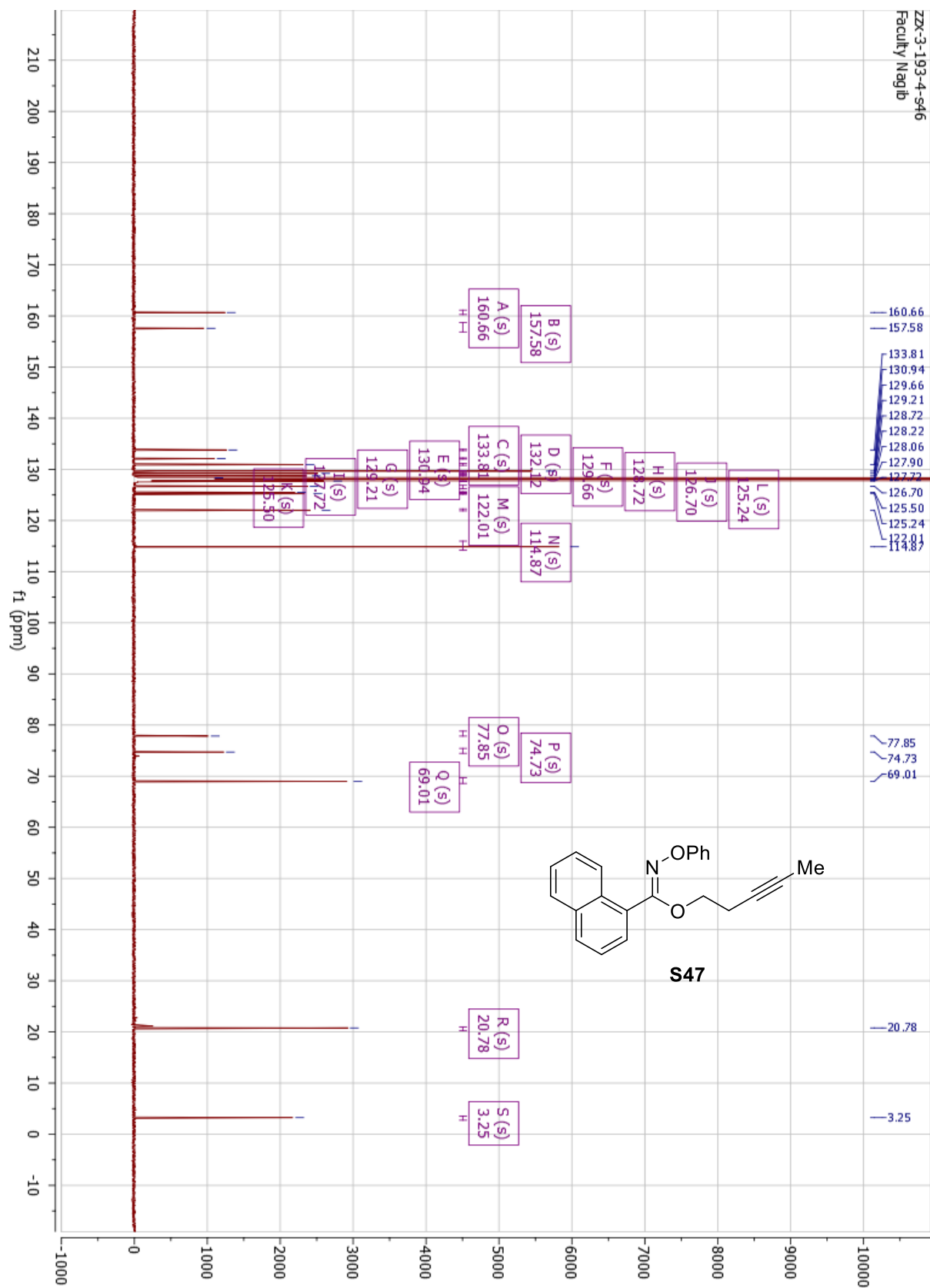


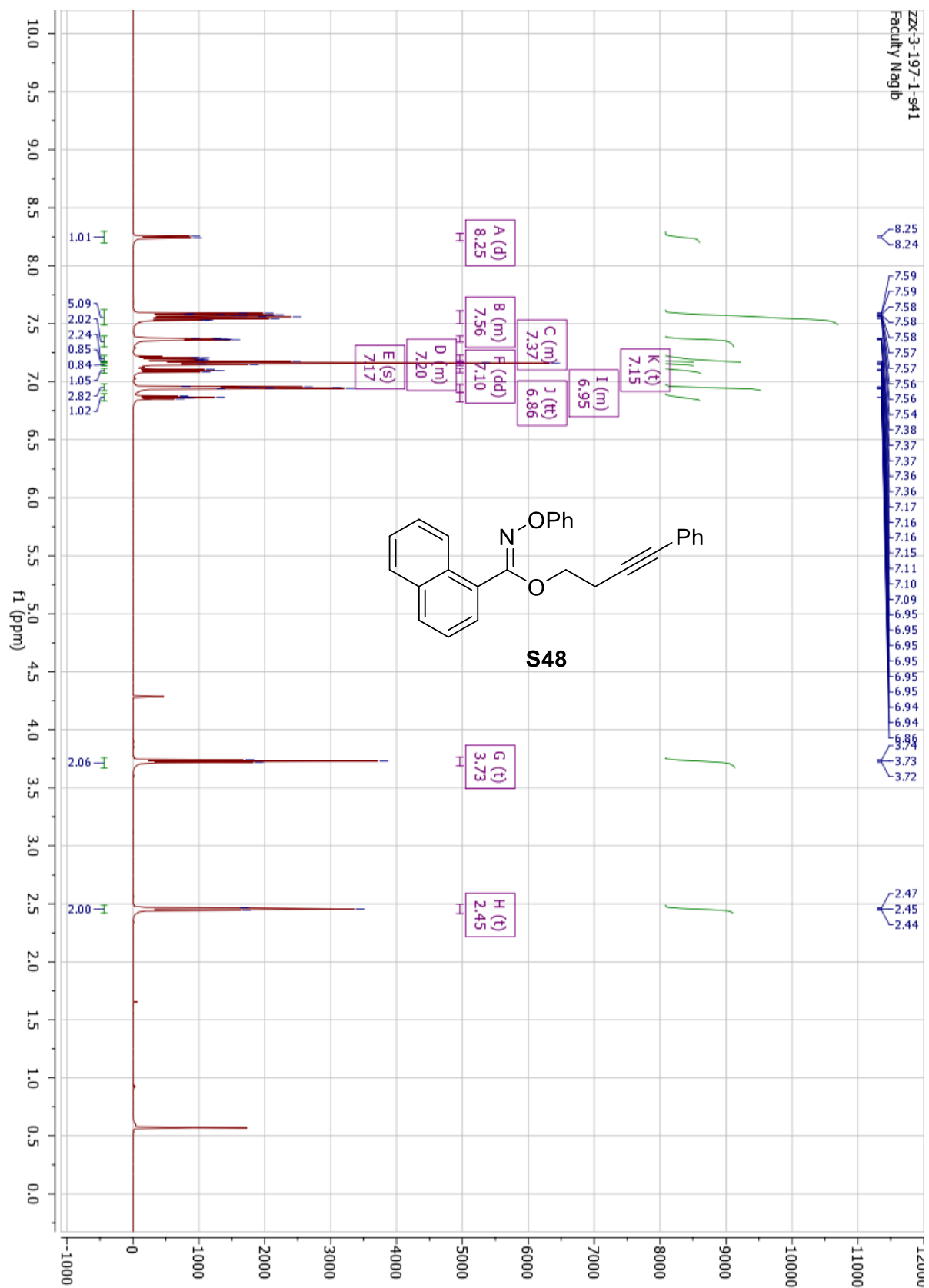


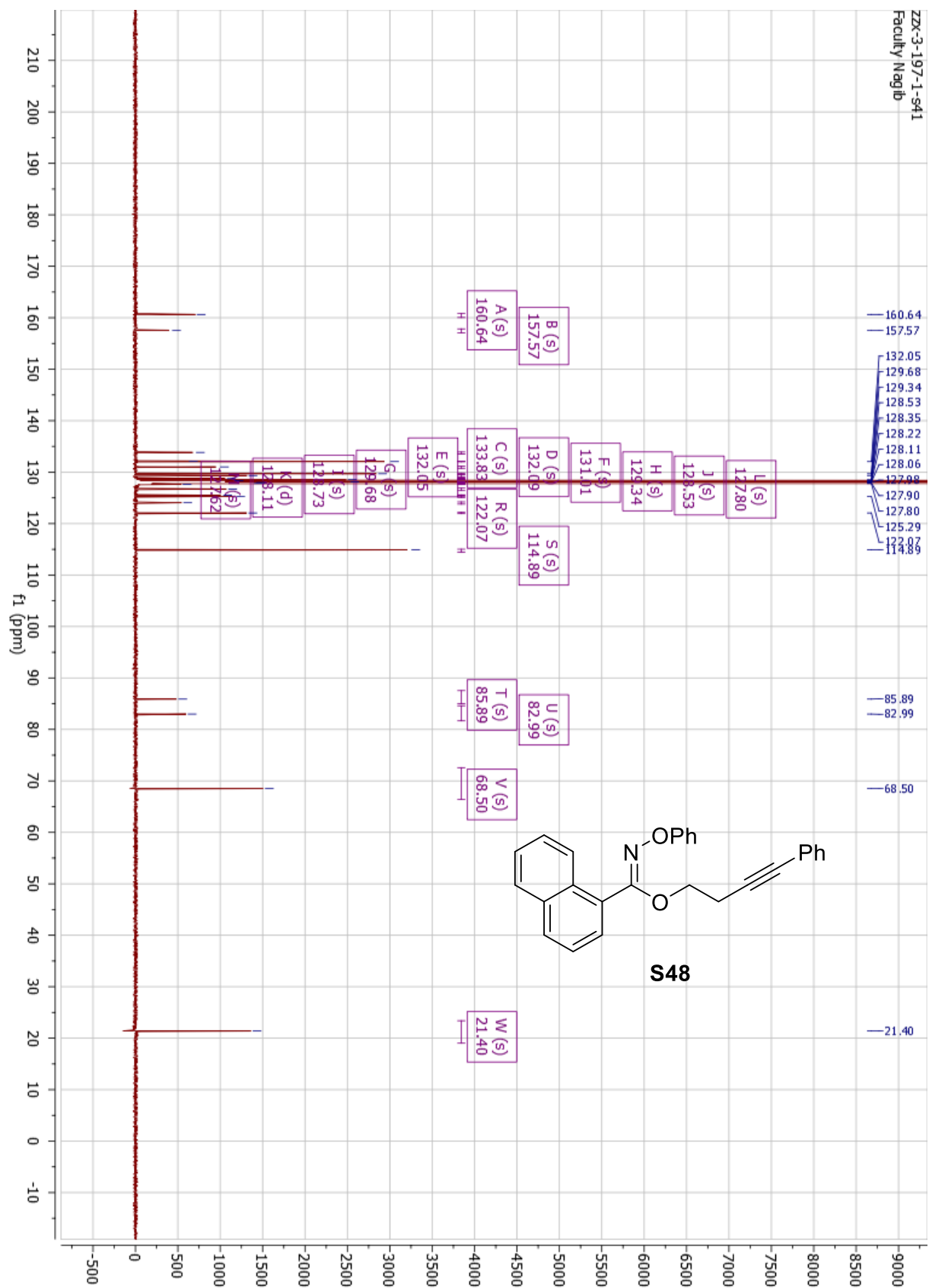


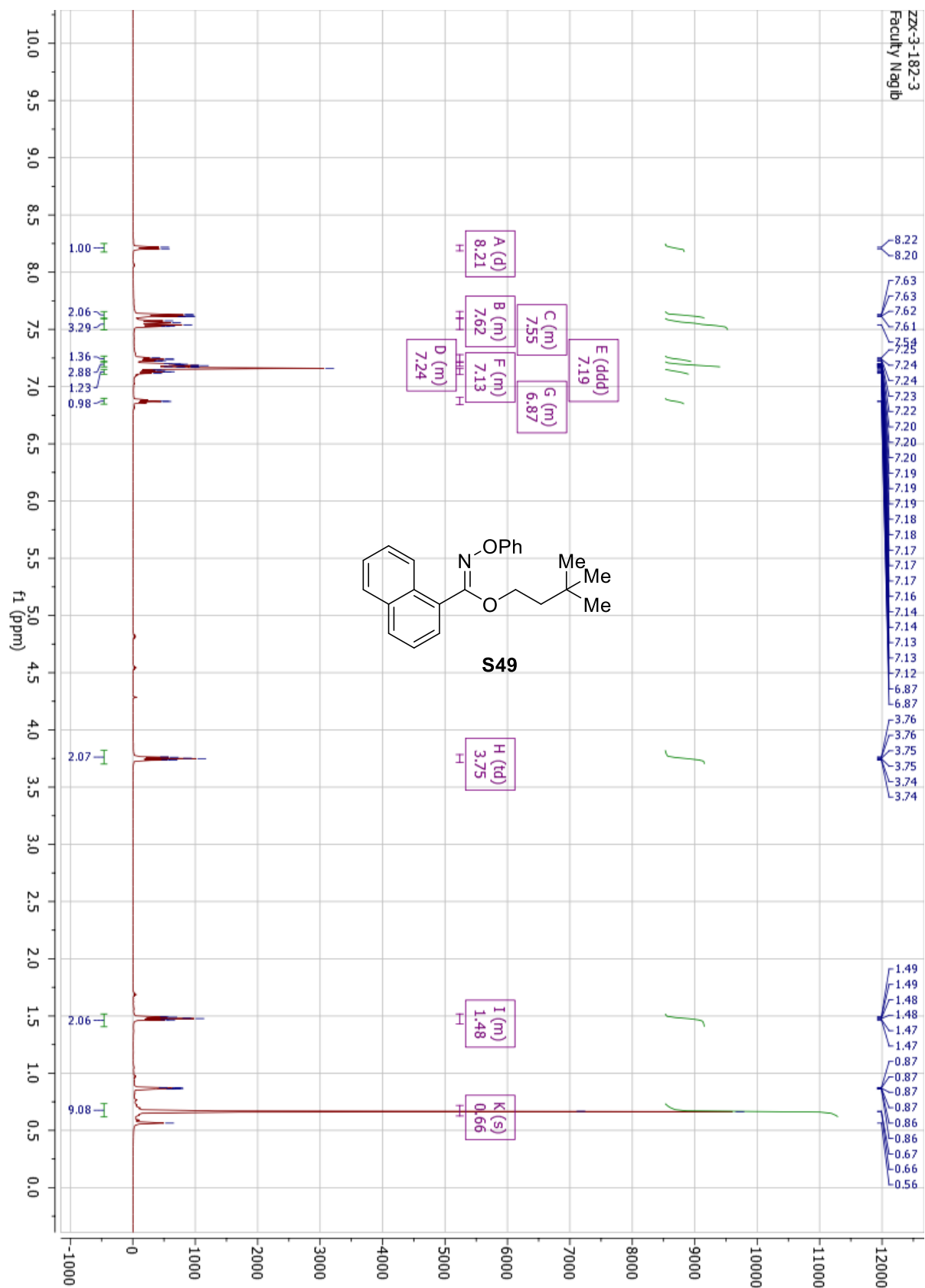


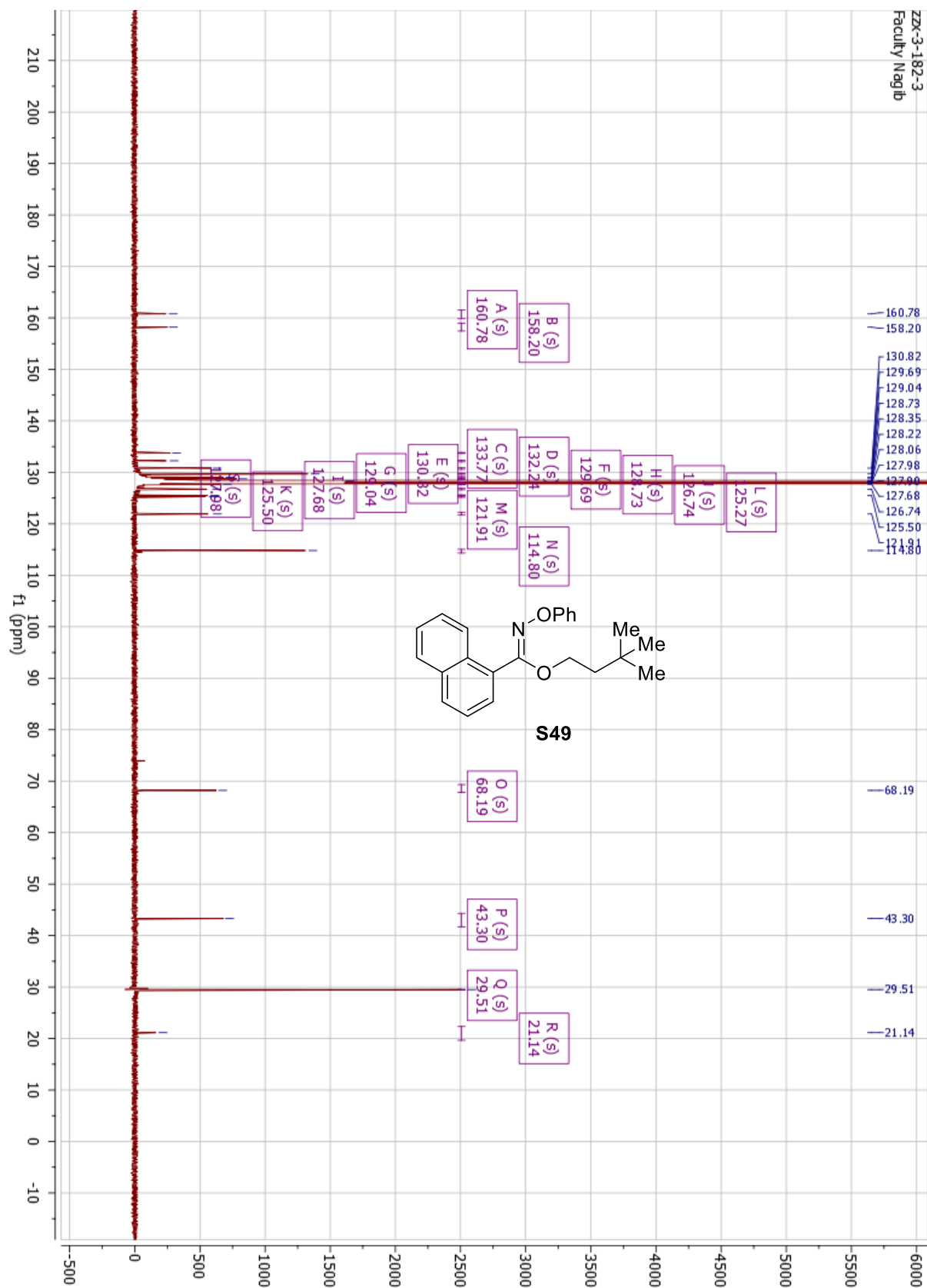


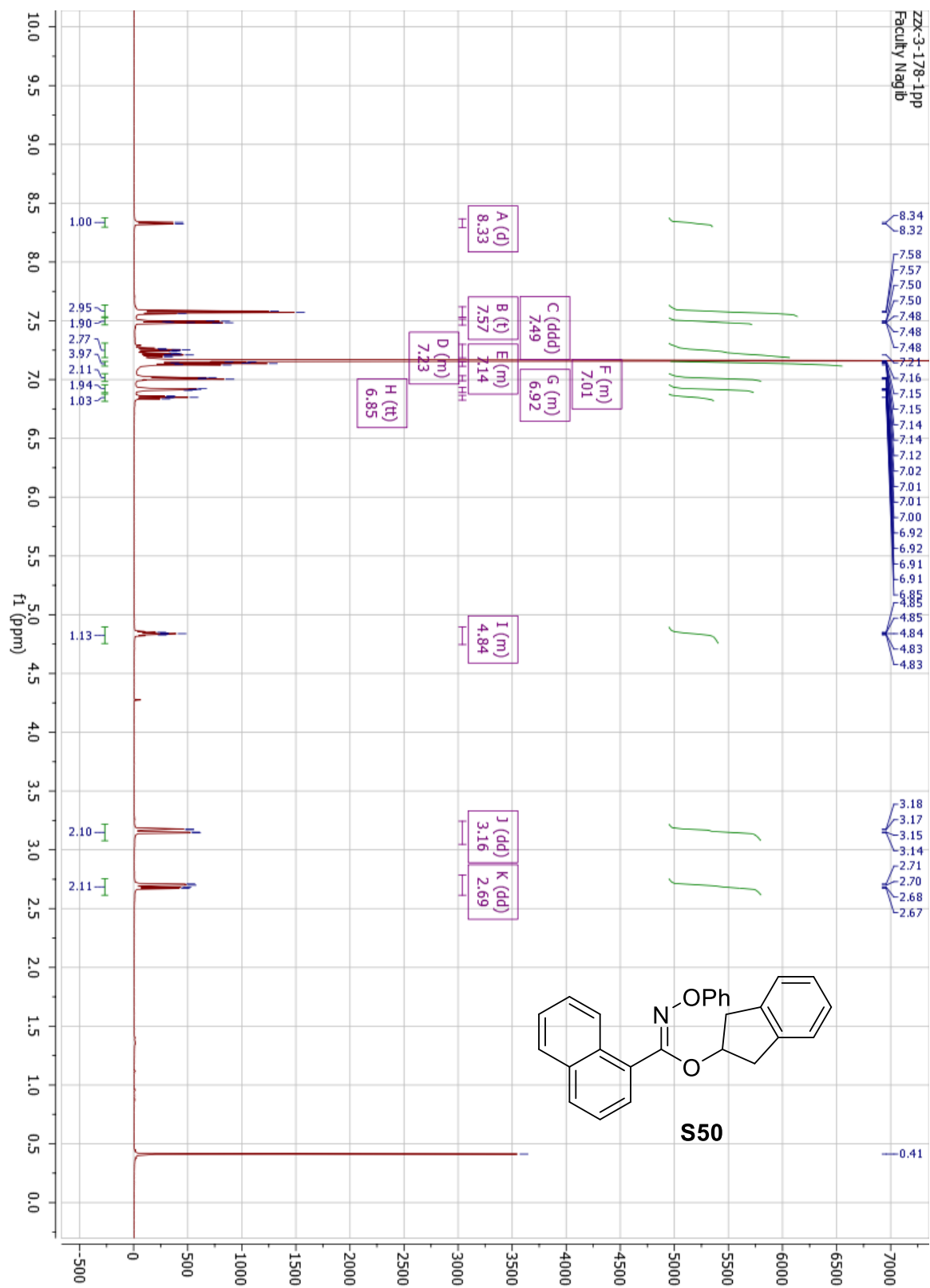




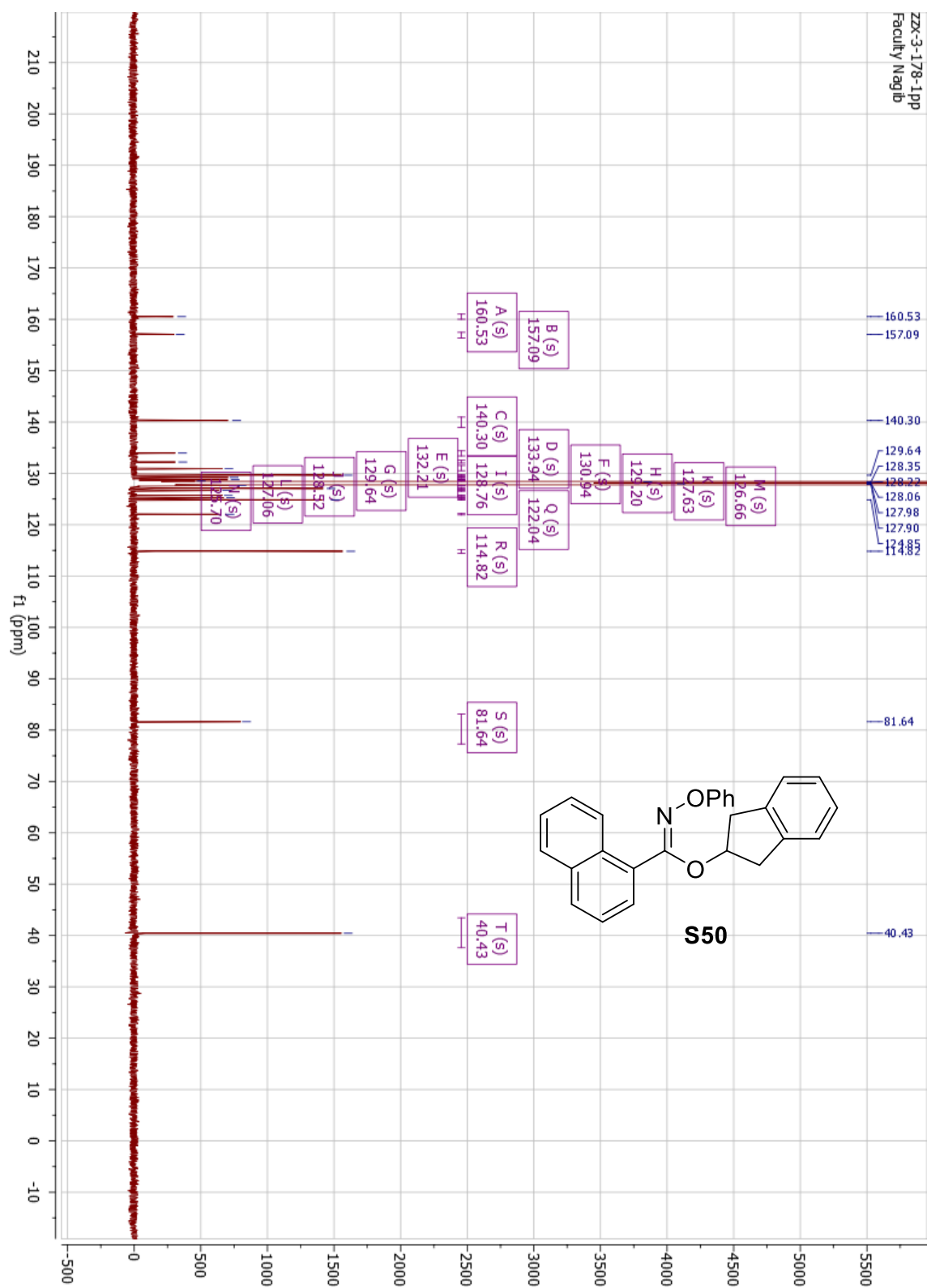




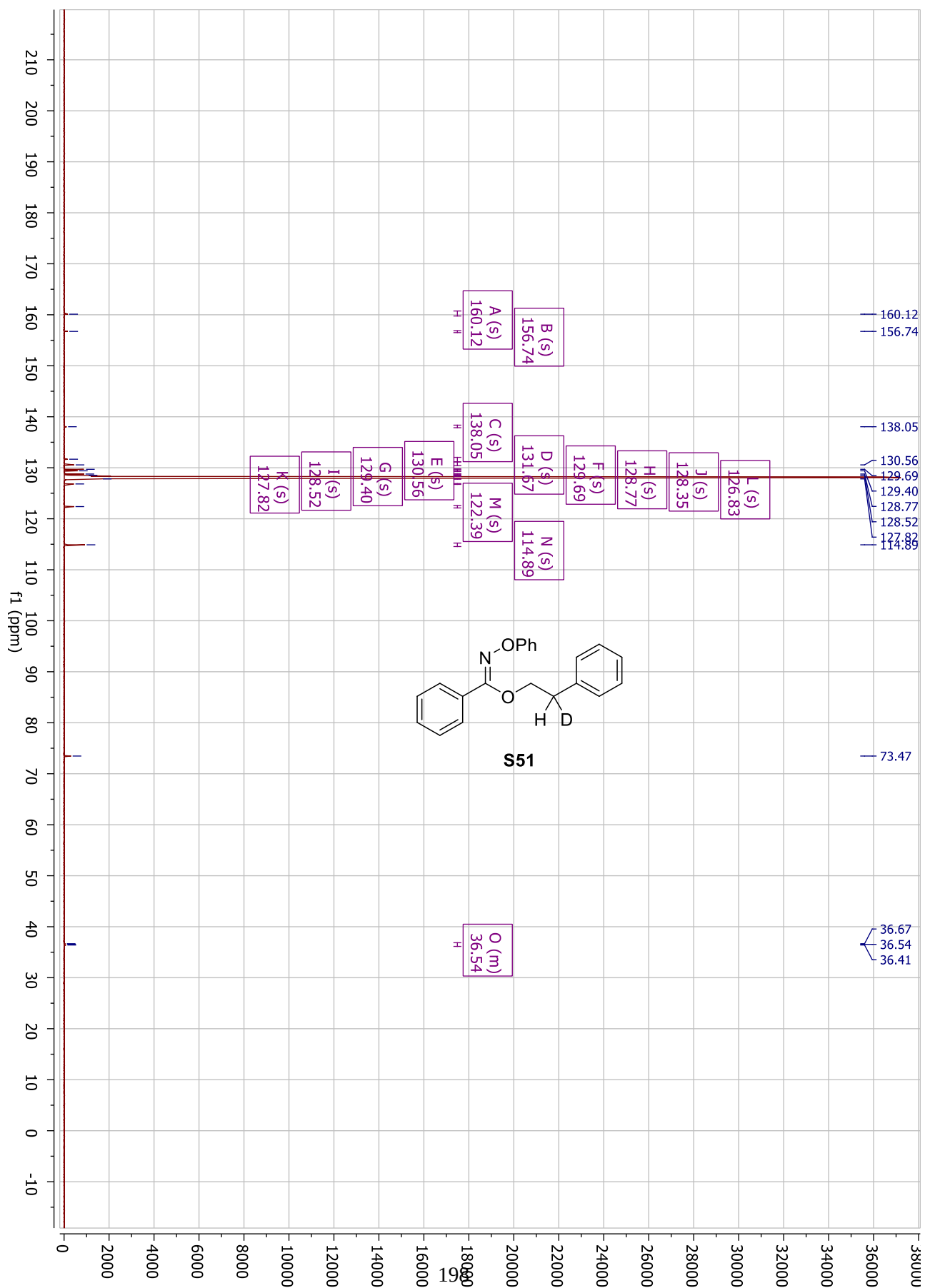


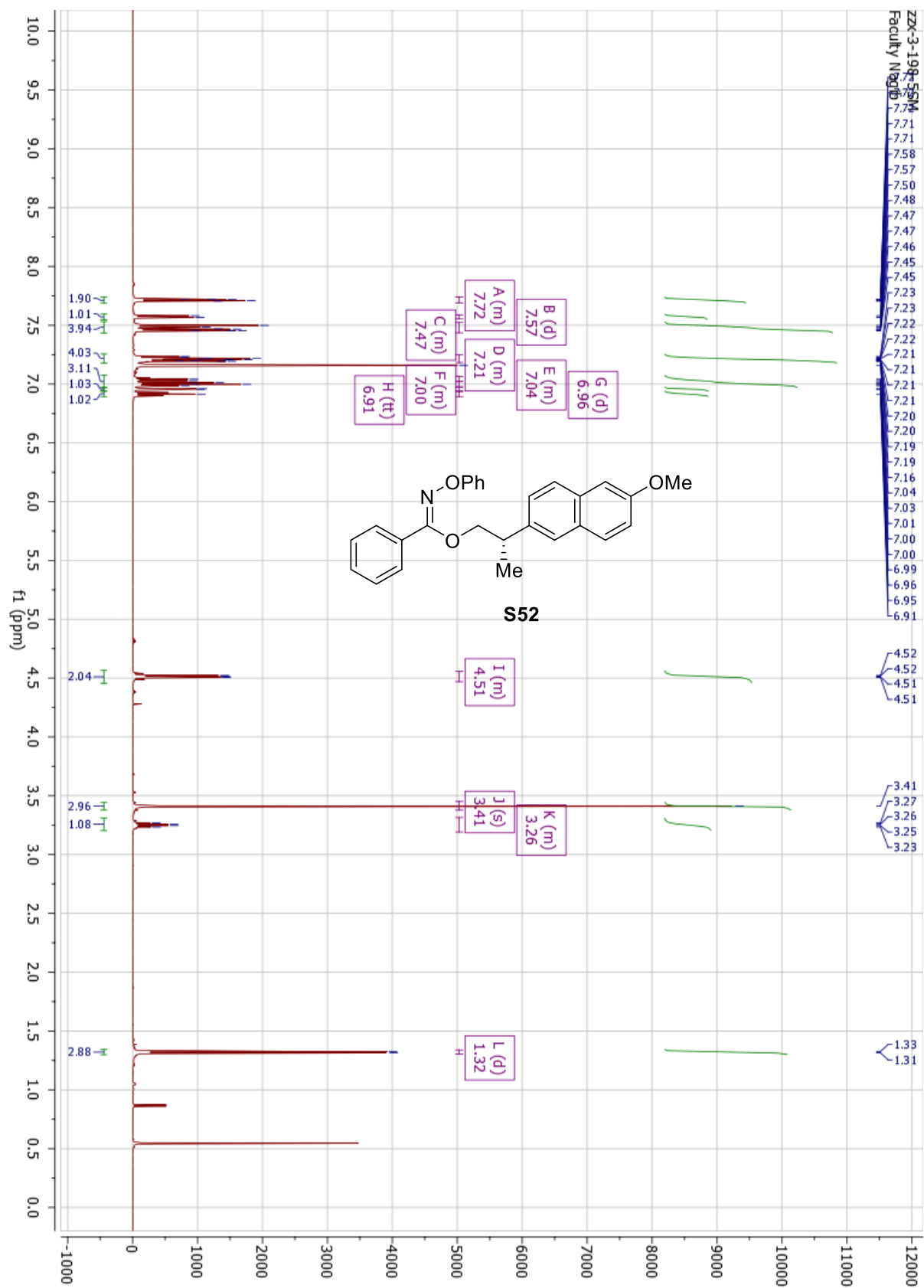


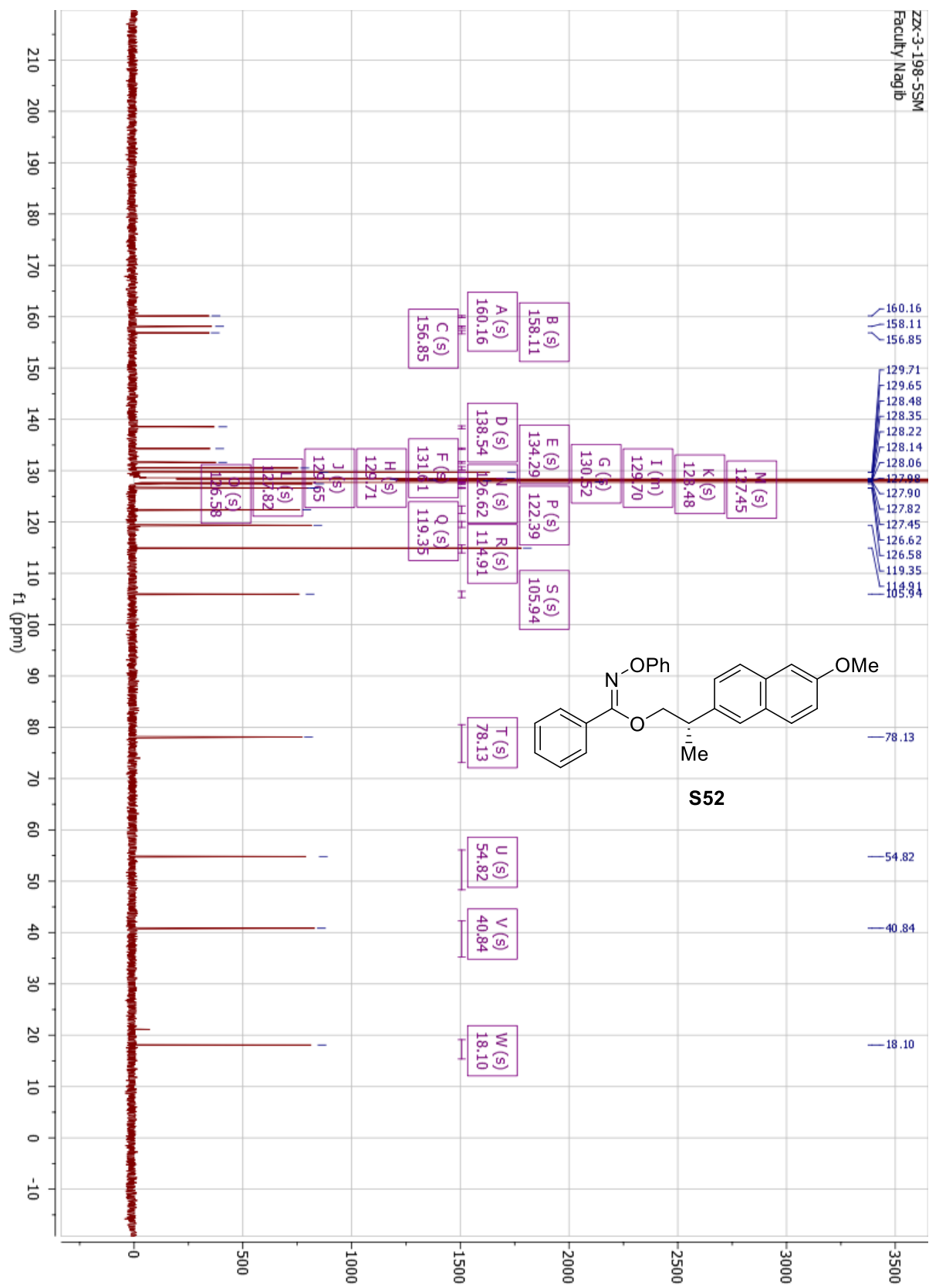


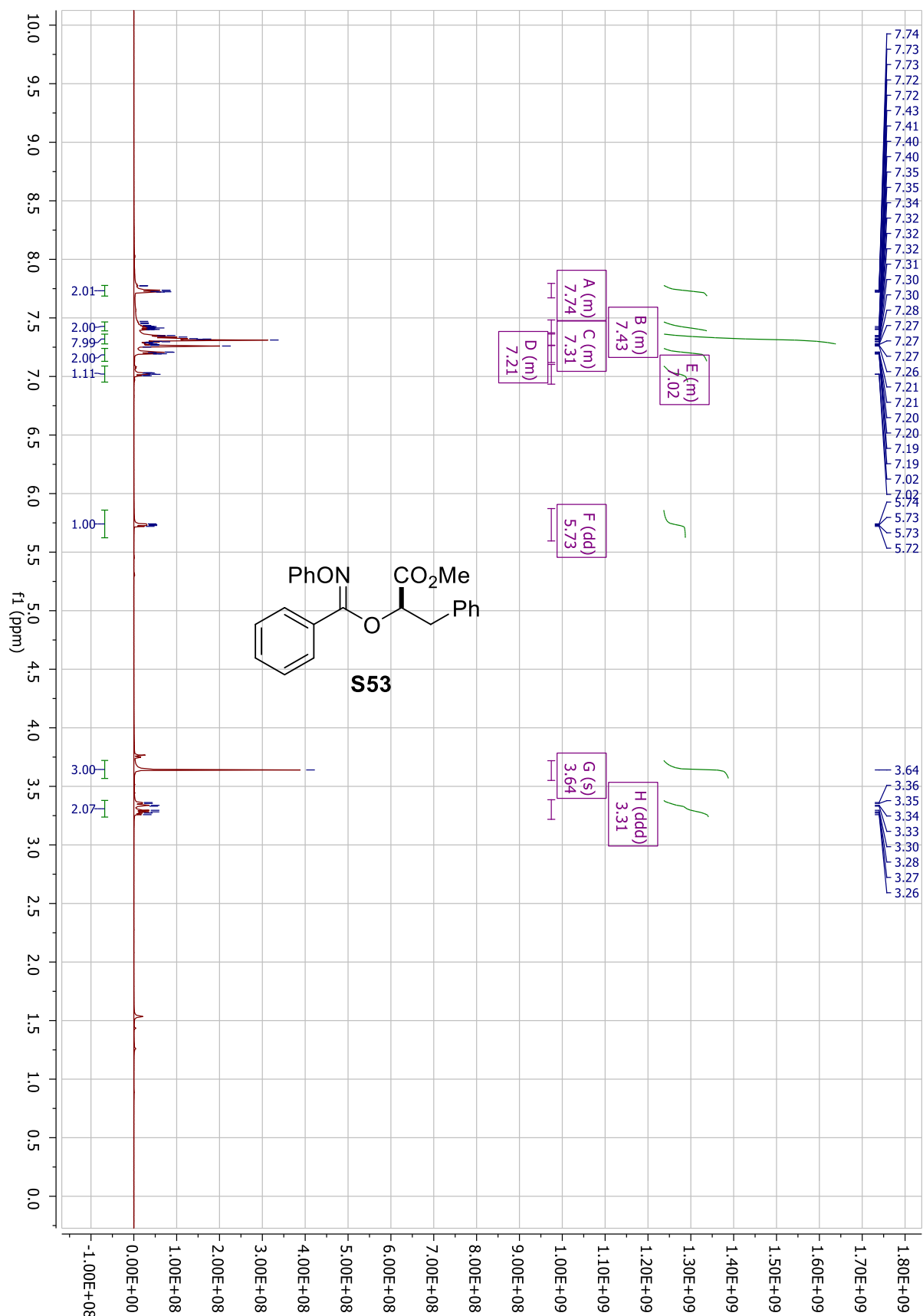


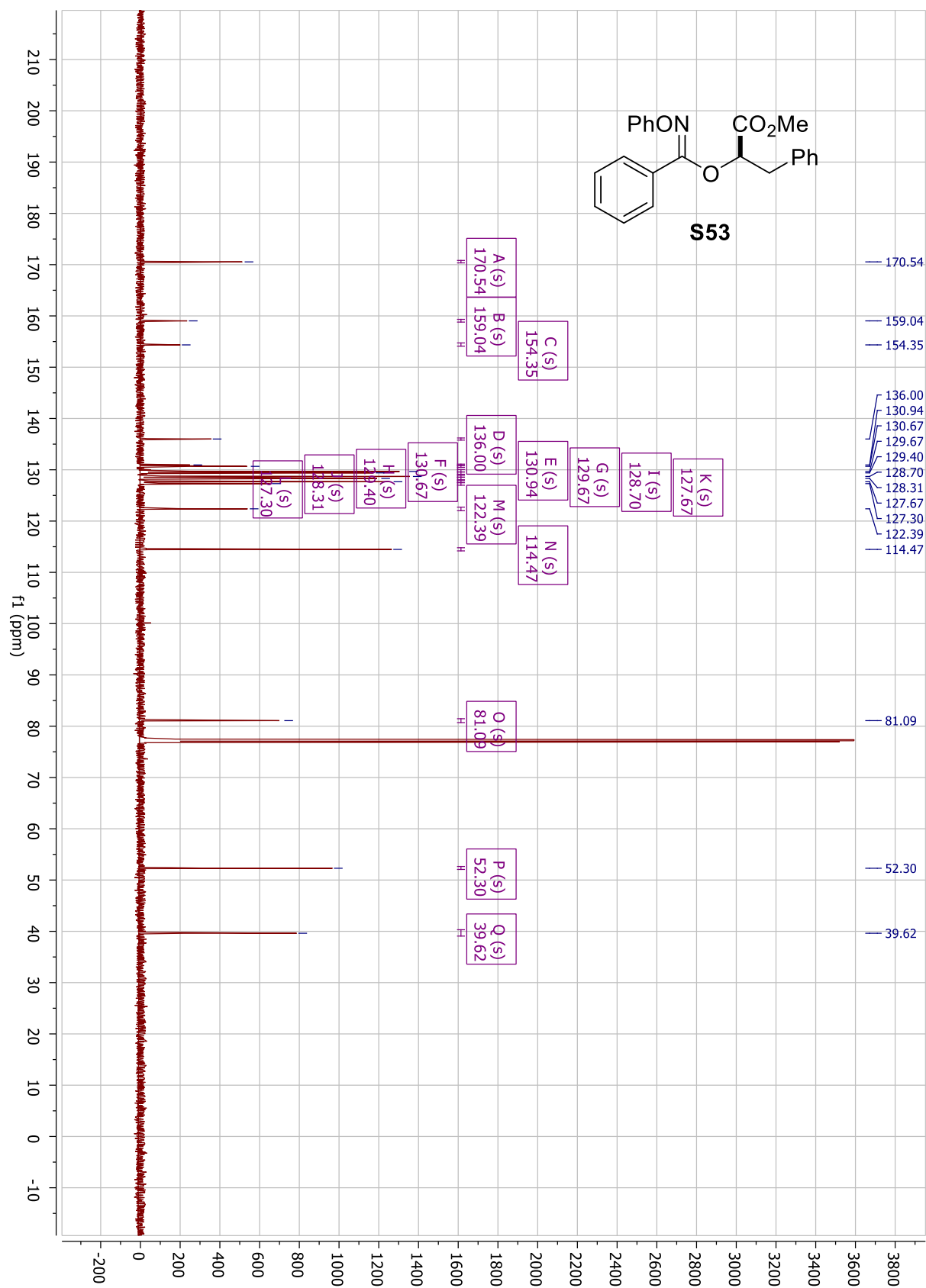


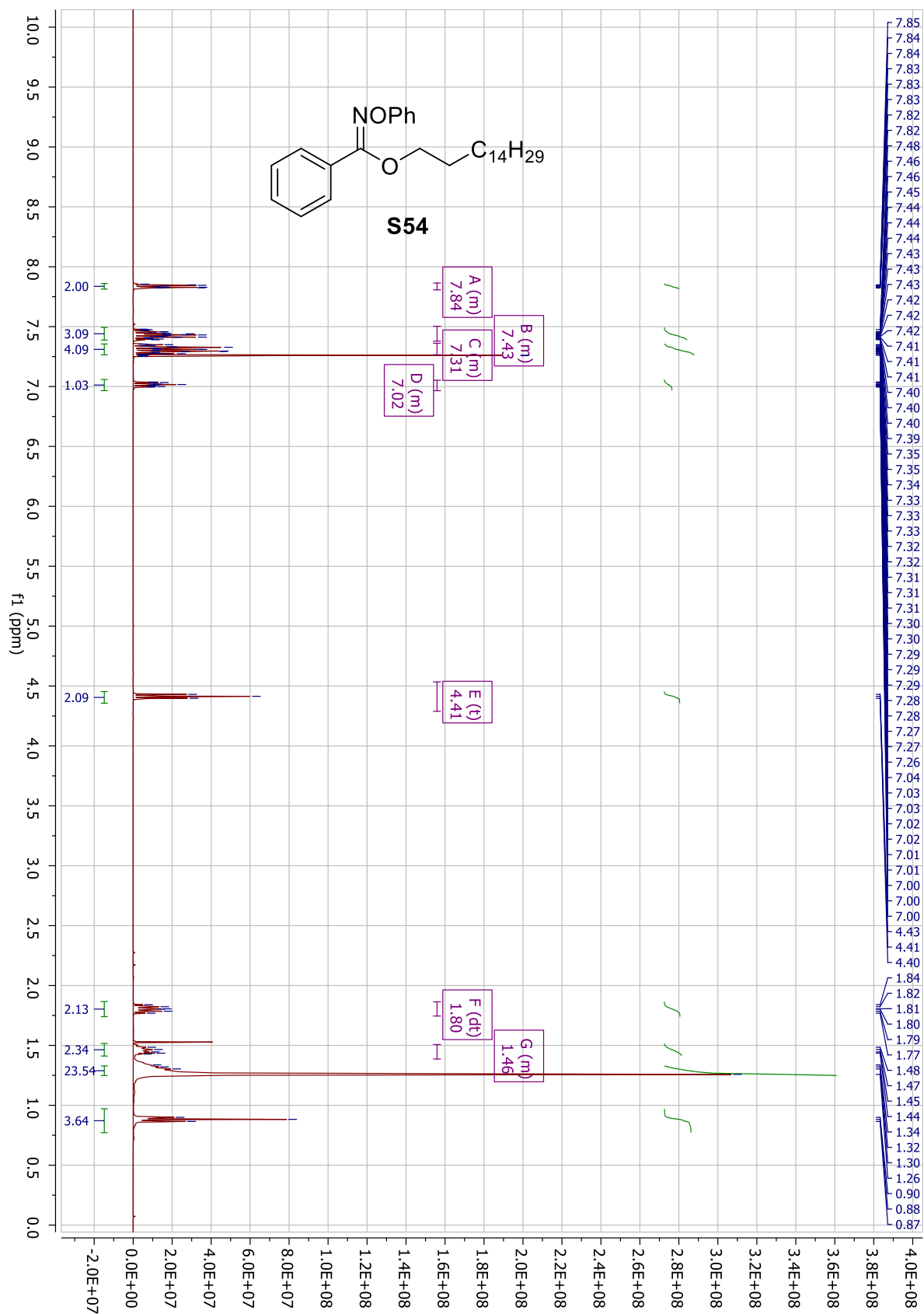




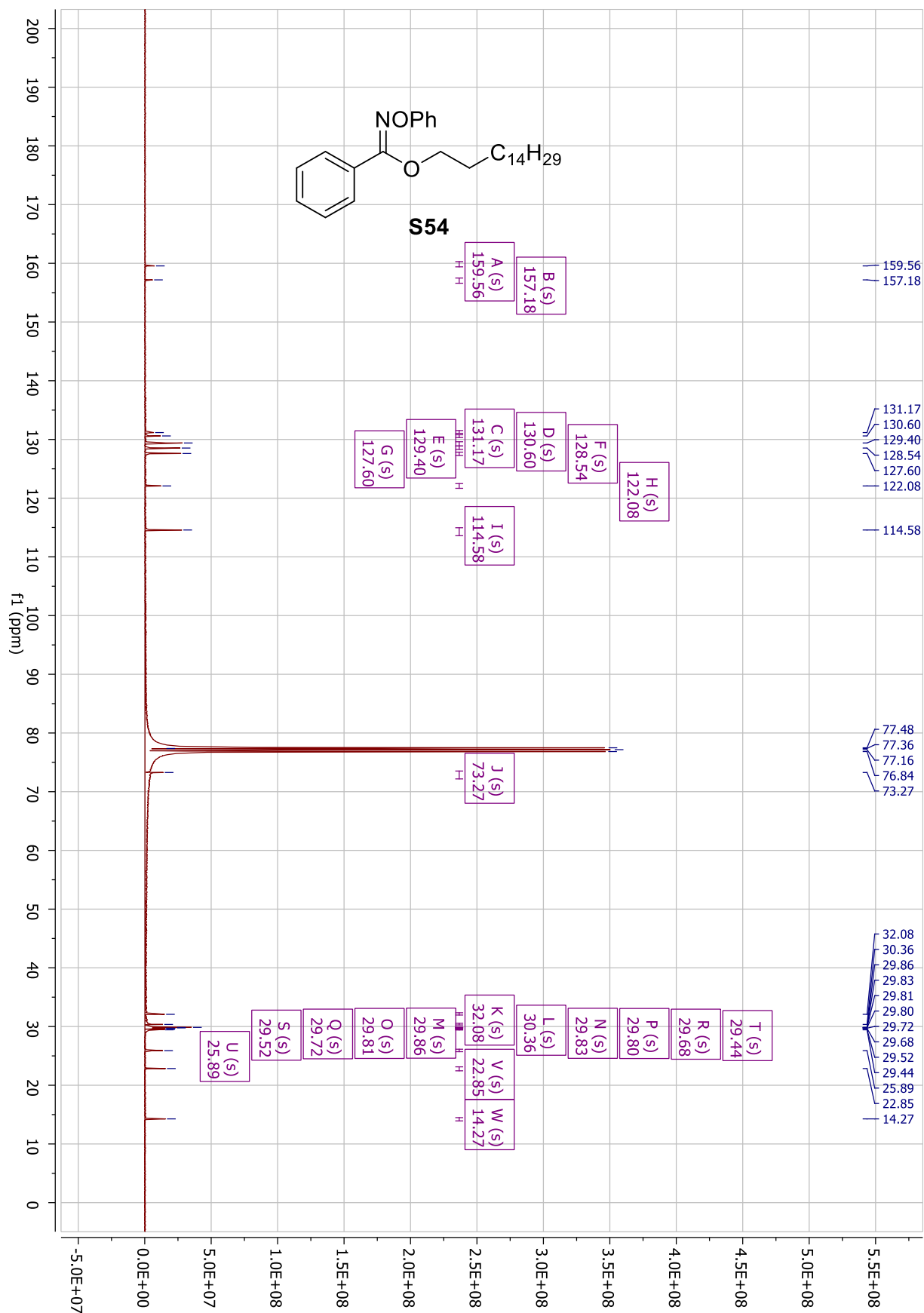


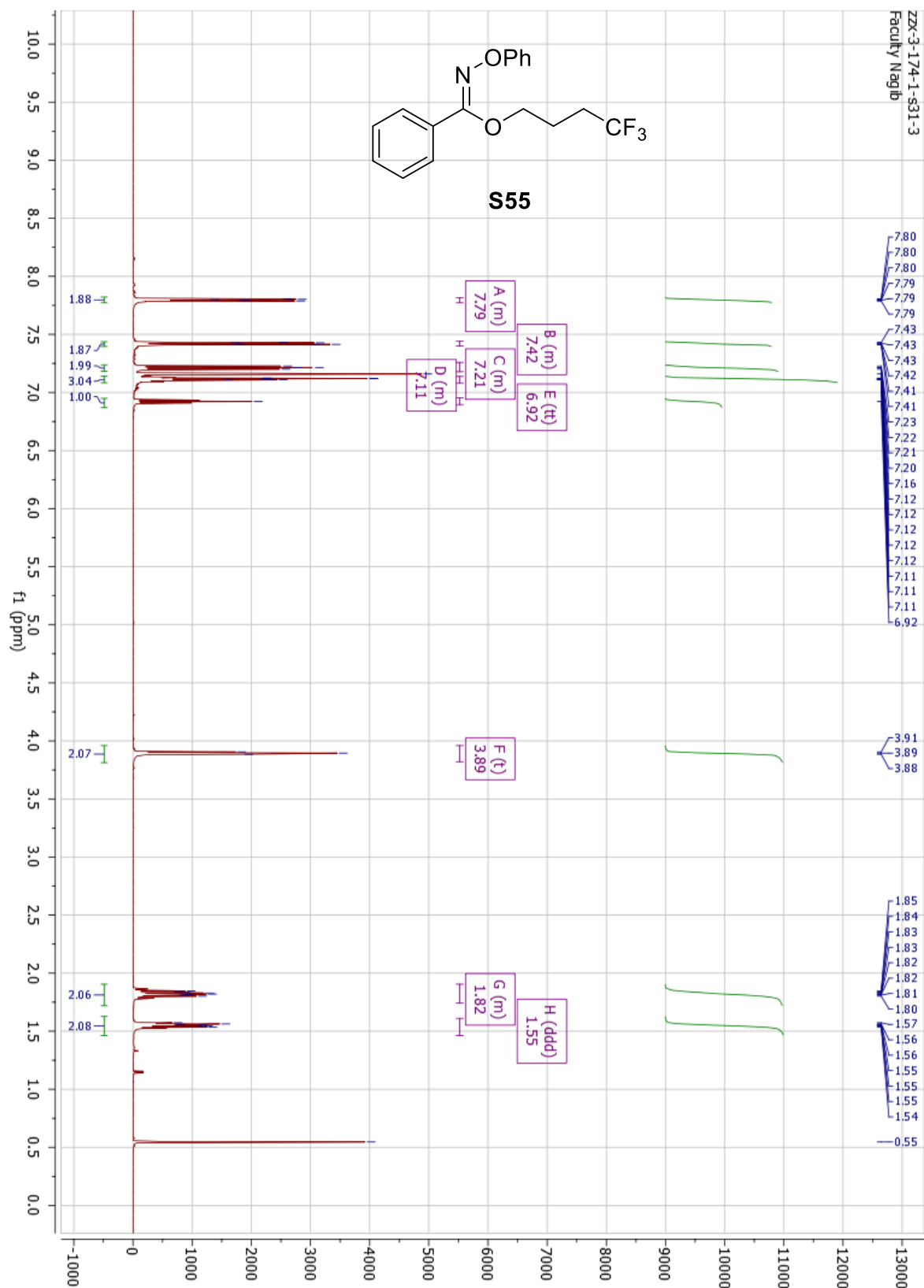


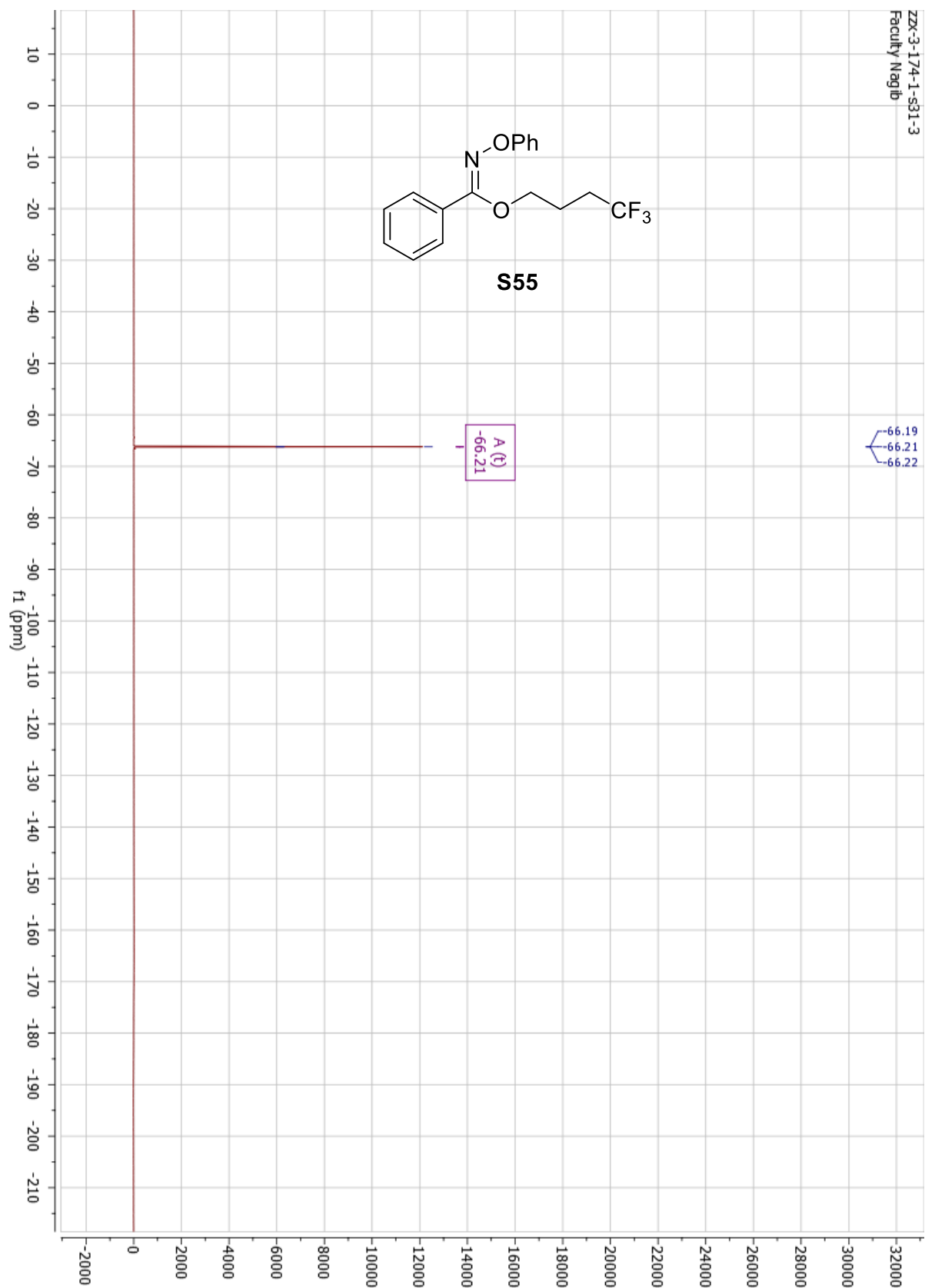


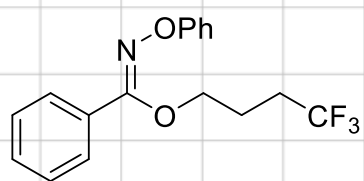




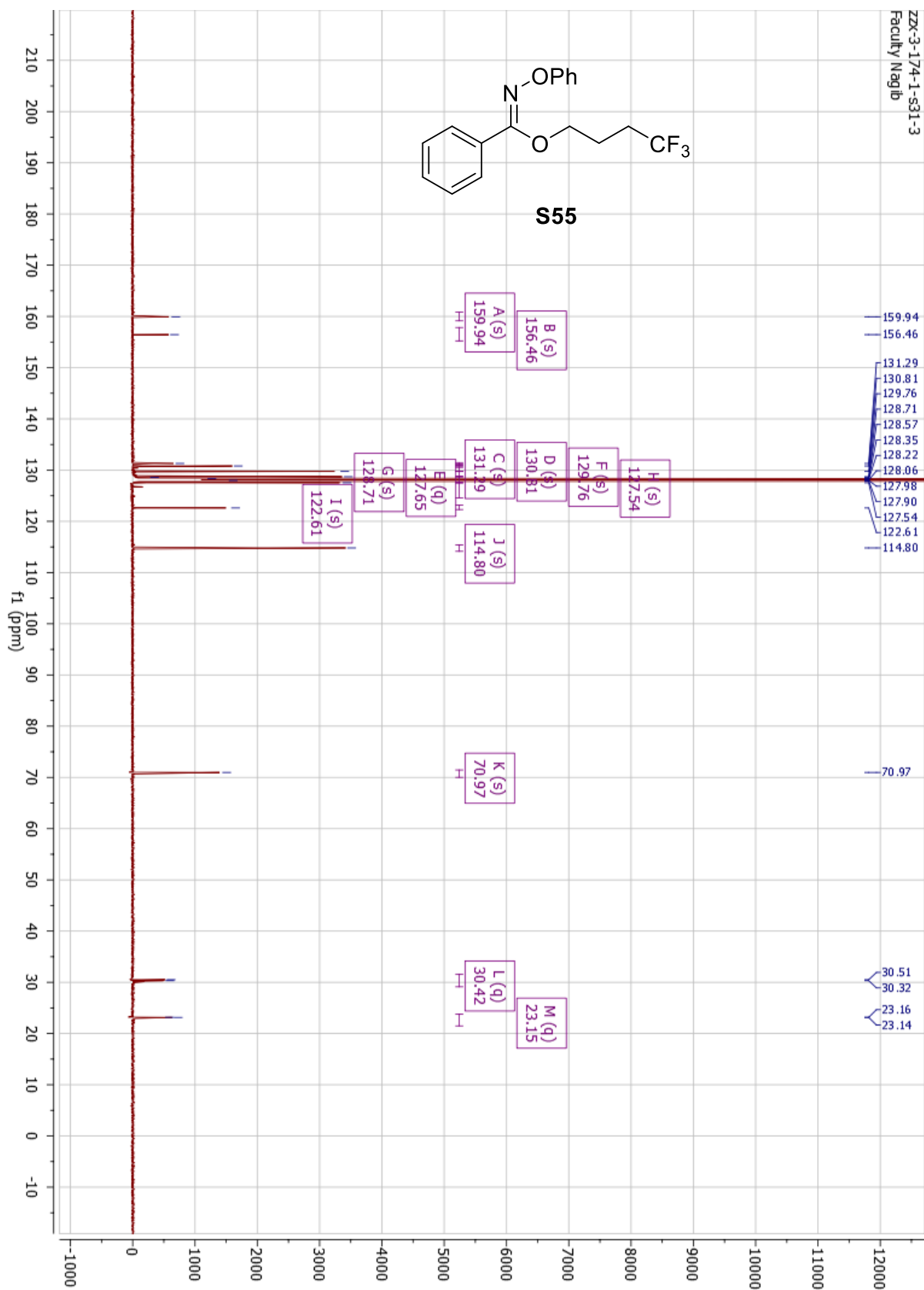


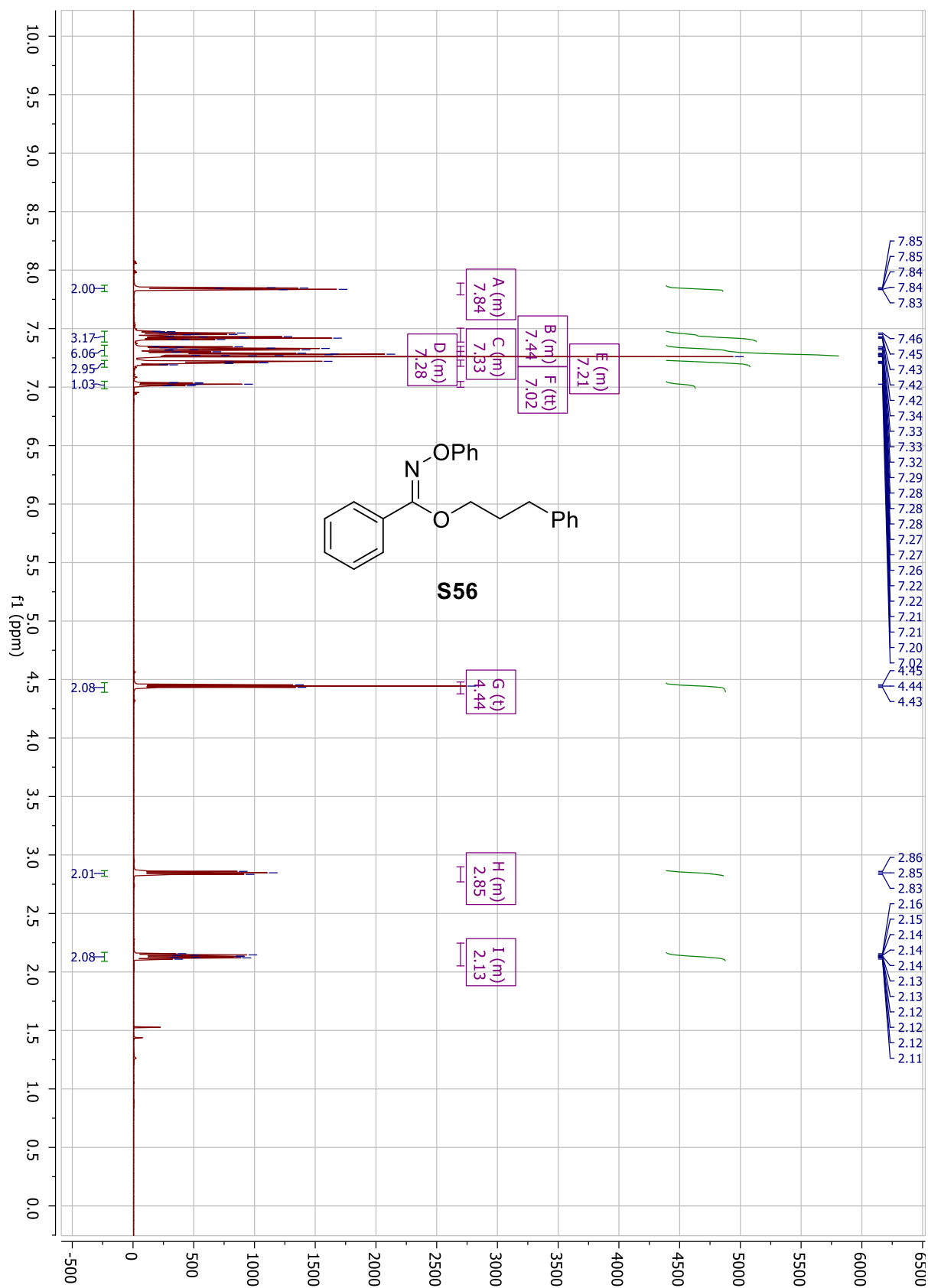


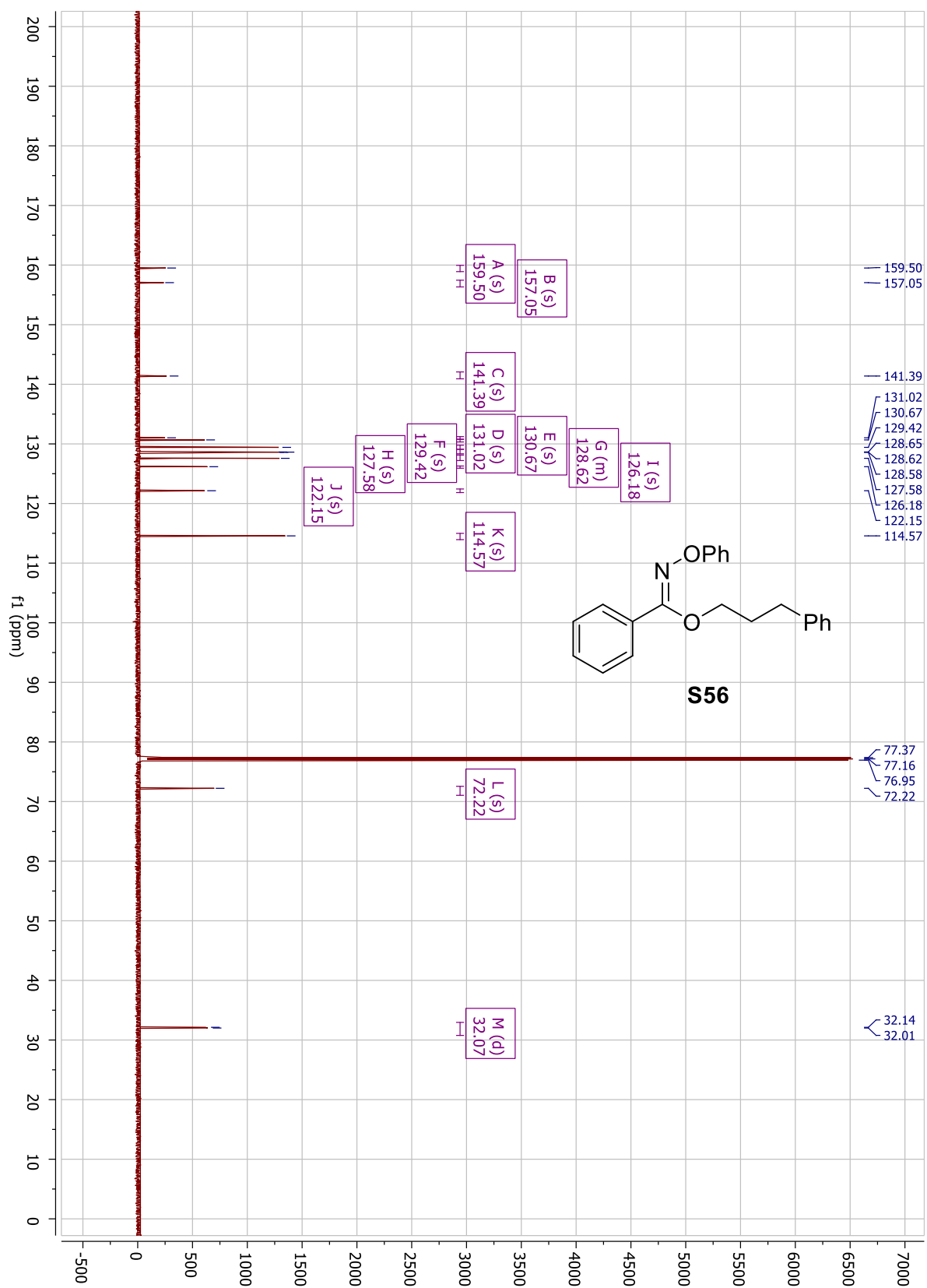


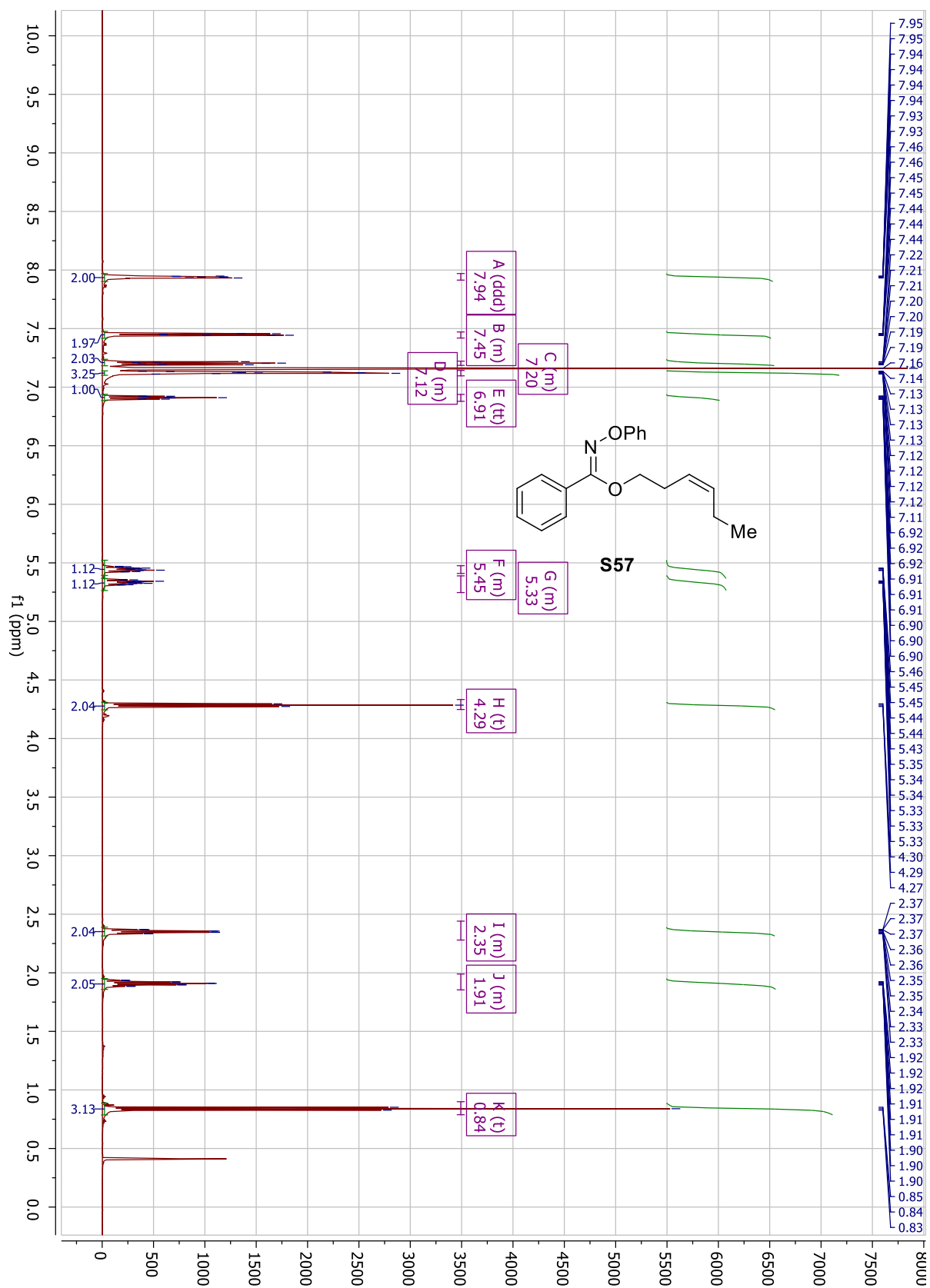


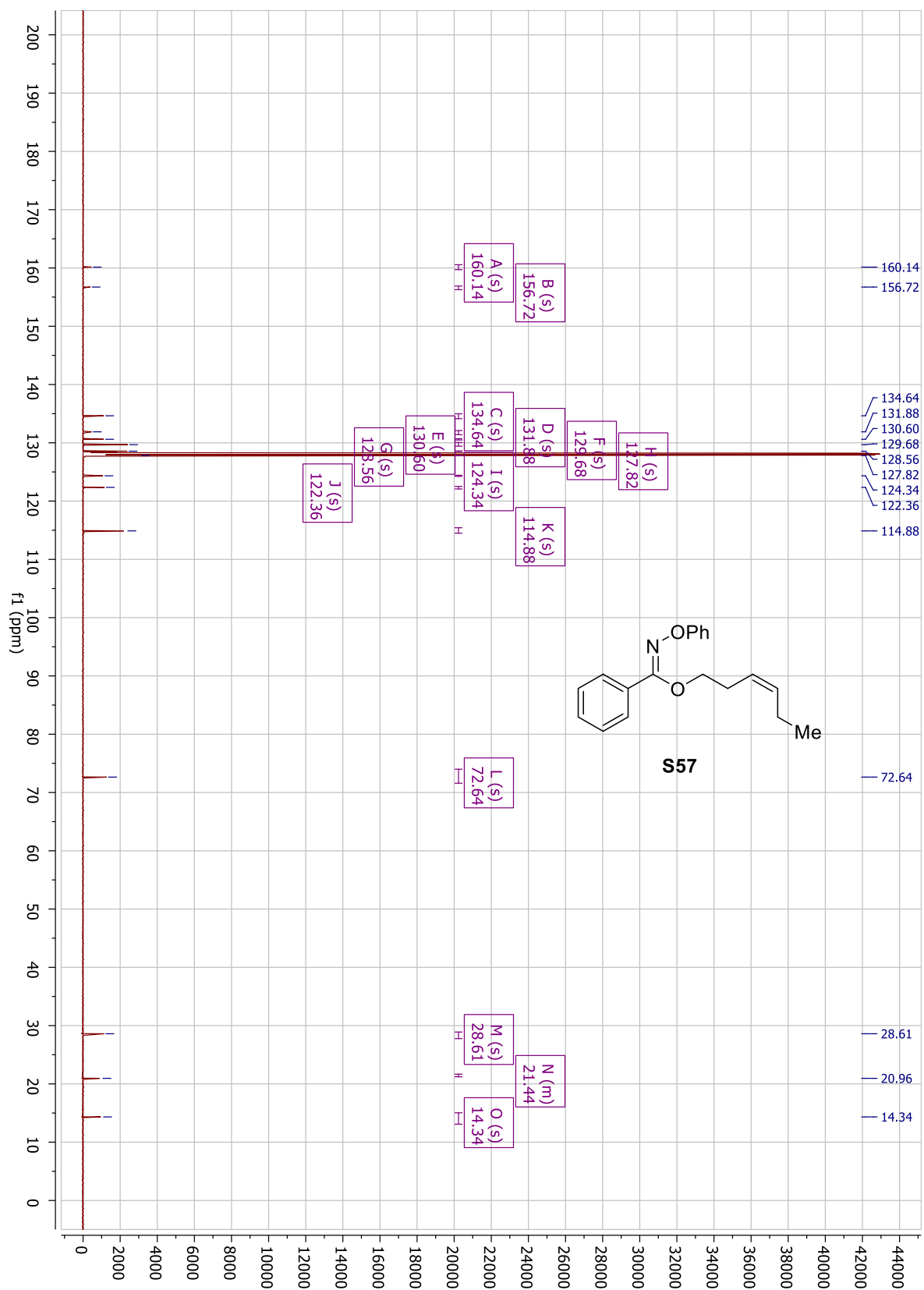
**S55**



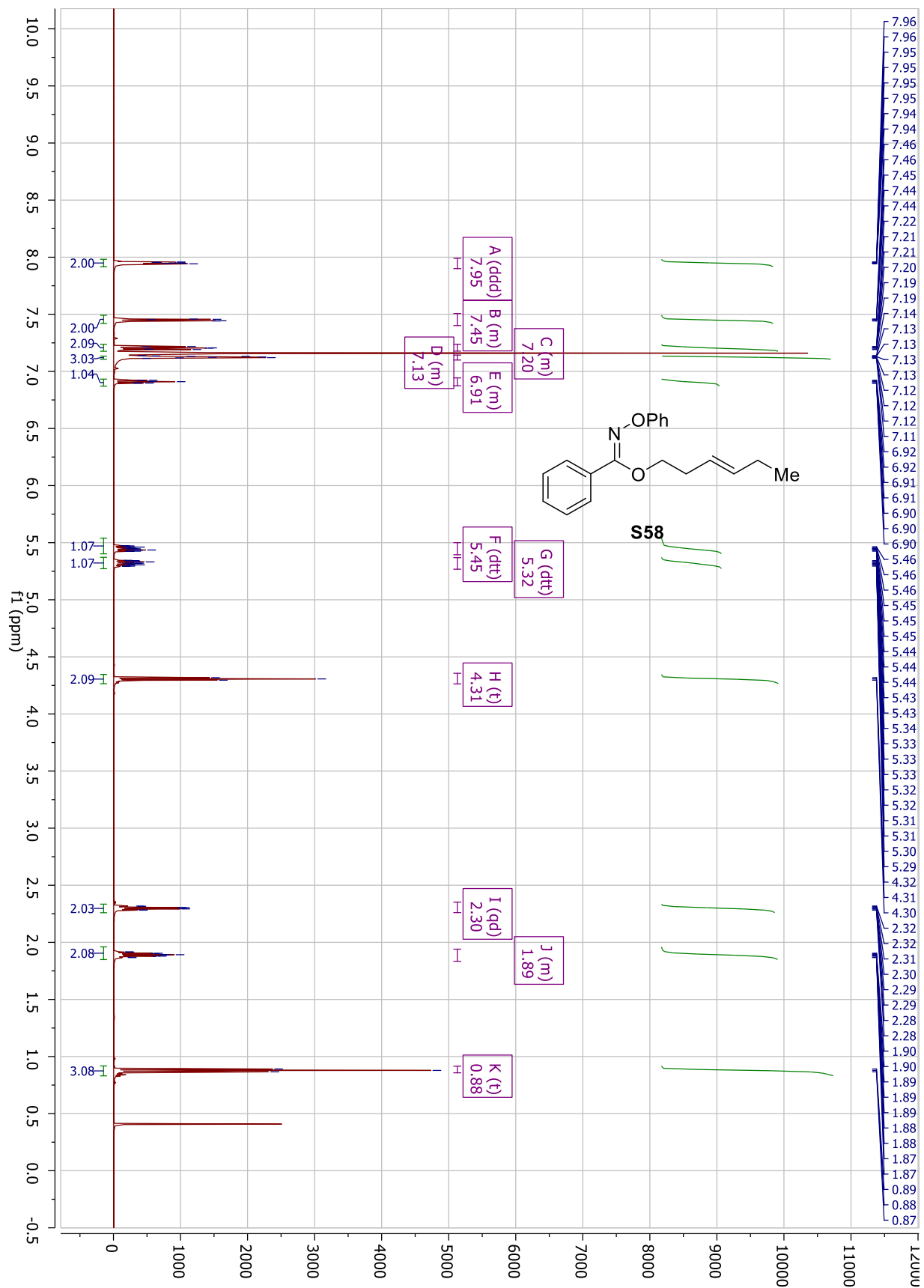


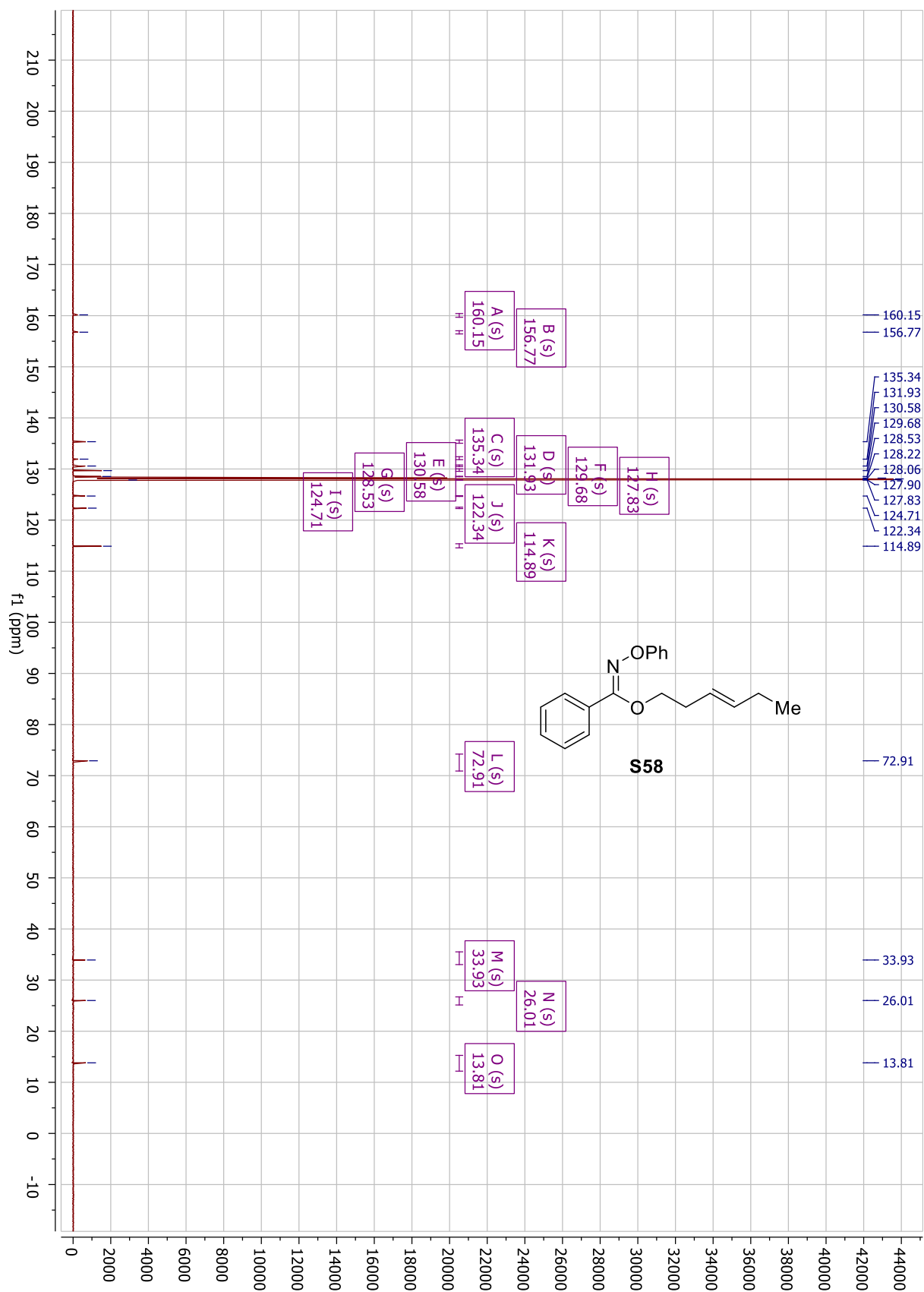


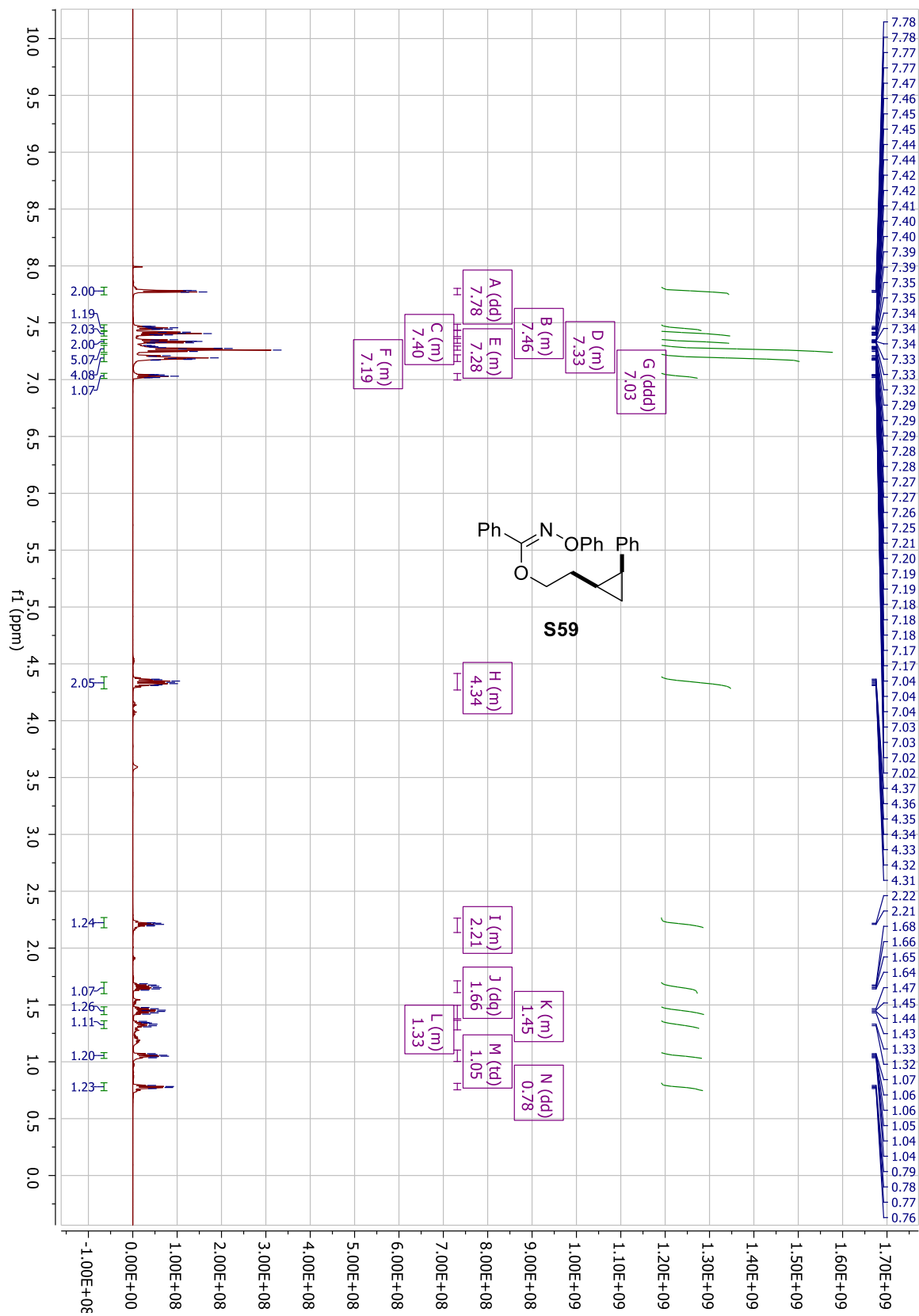


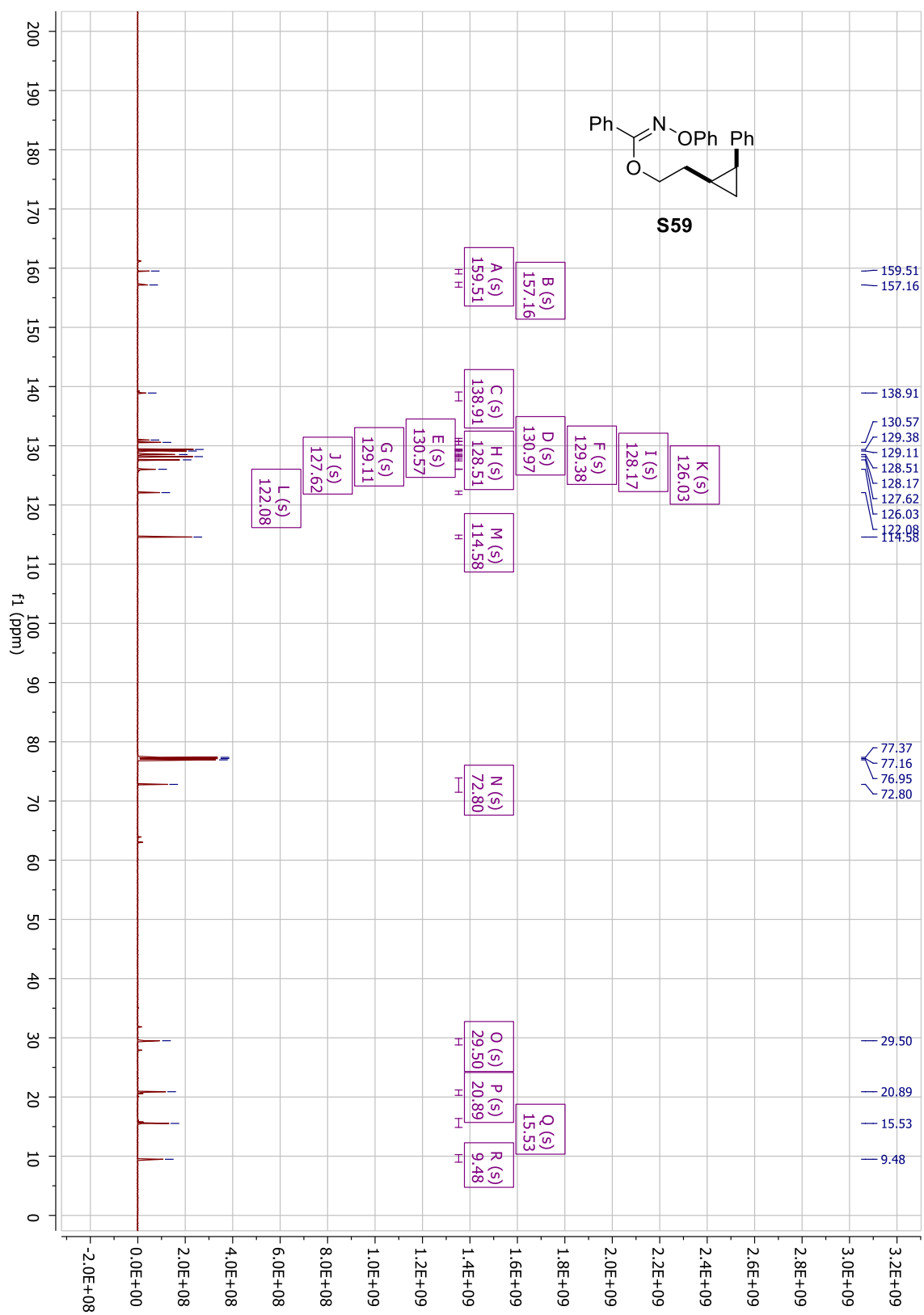


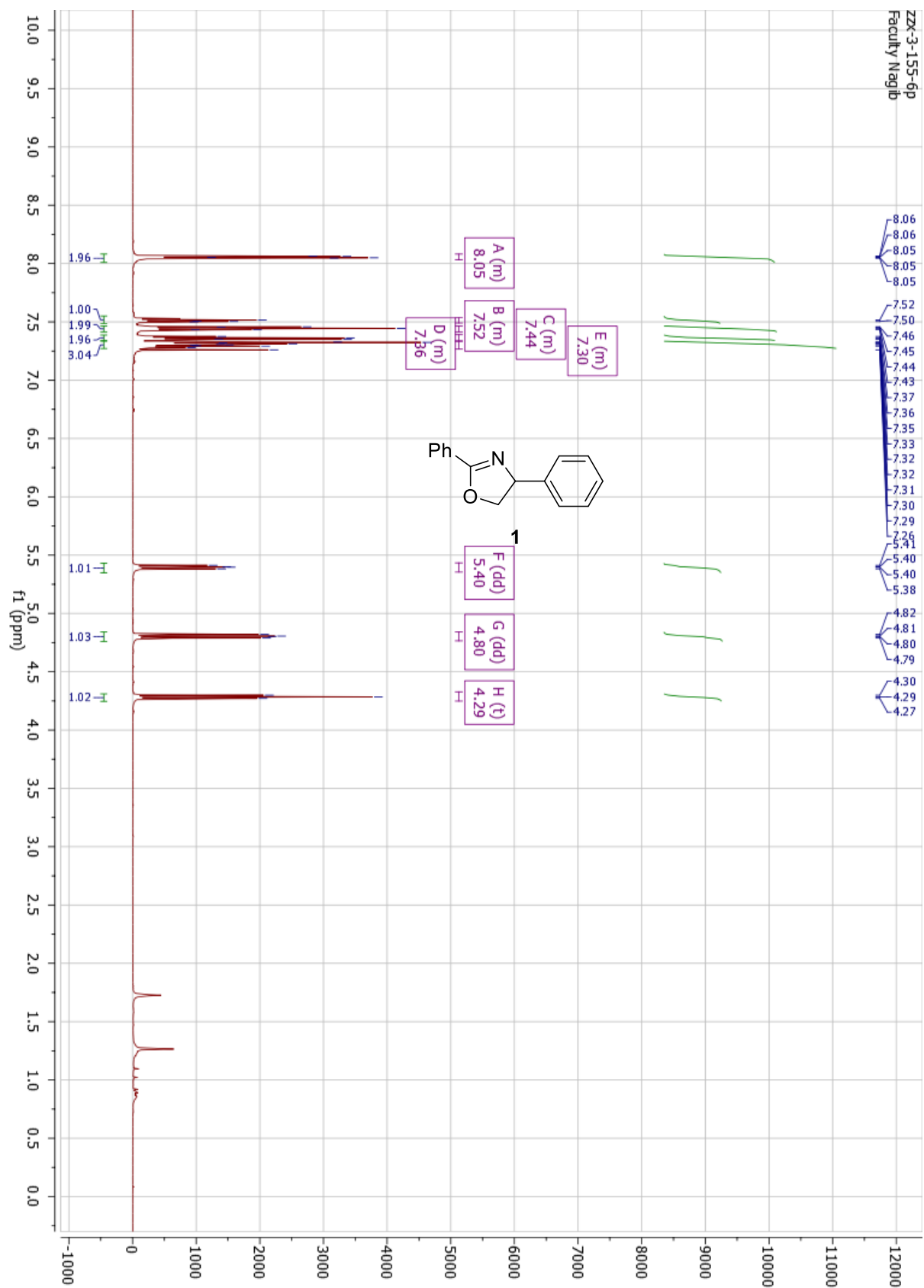


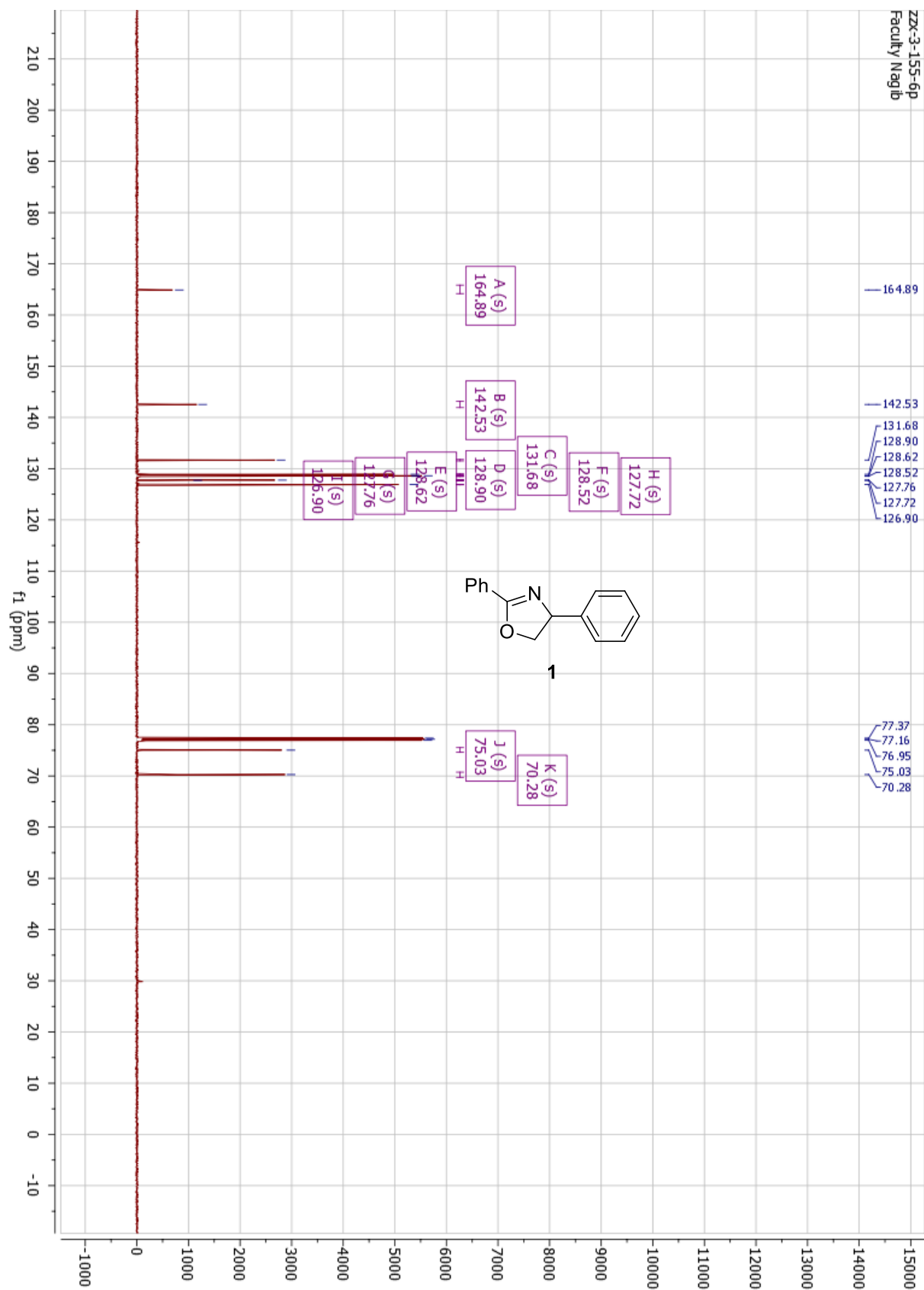


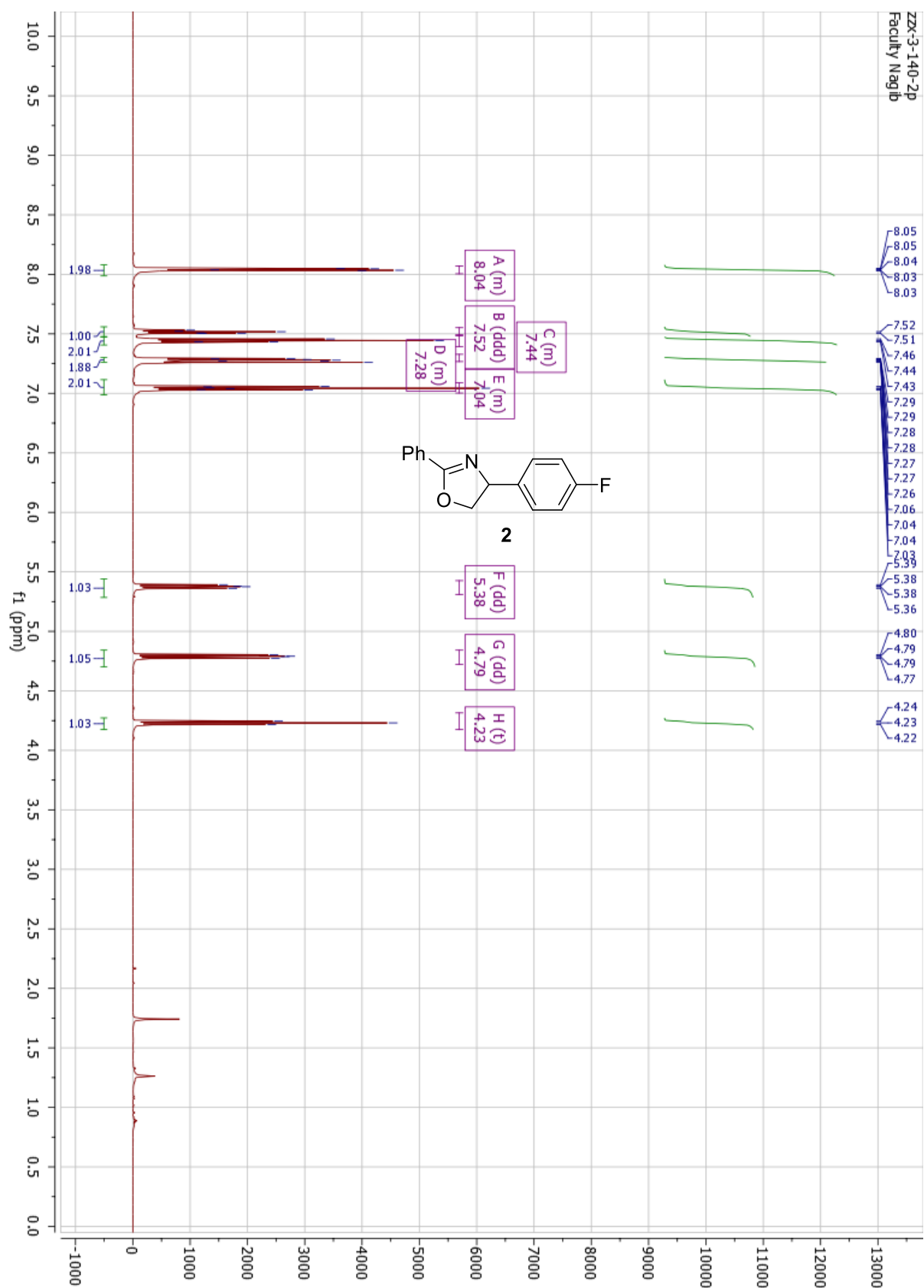


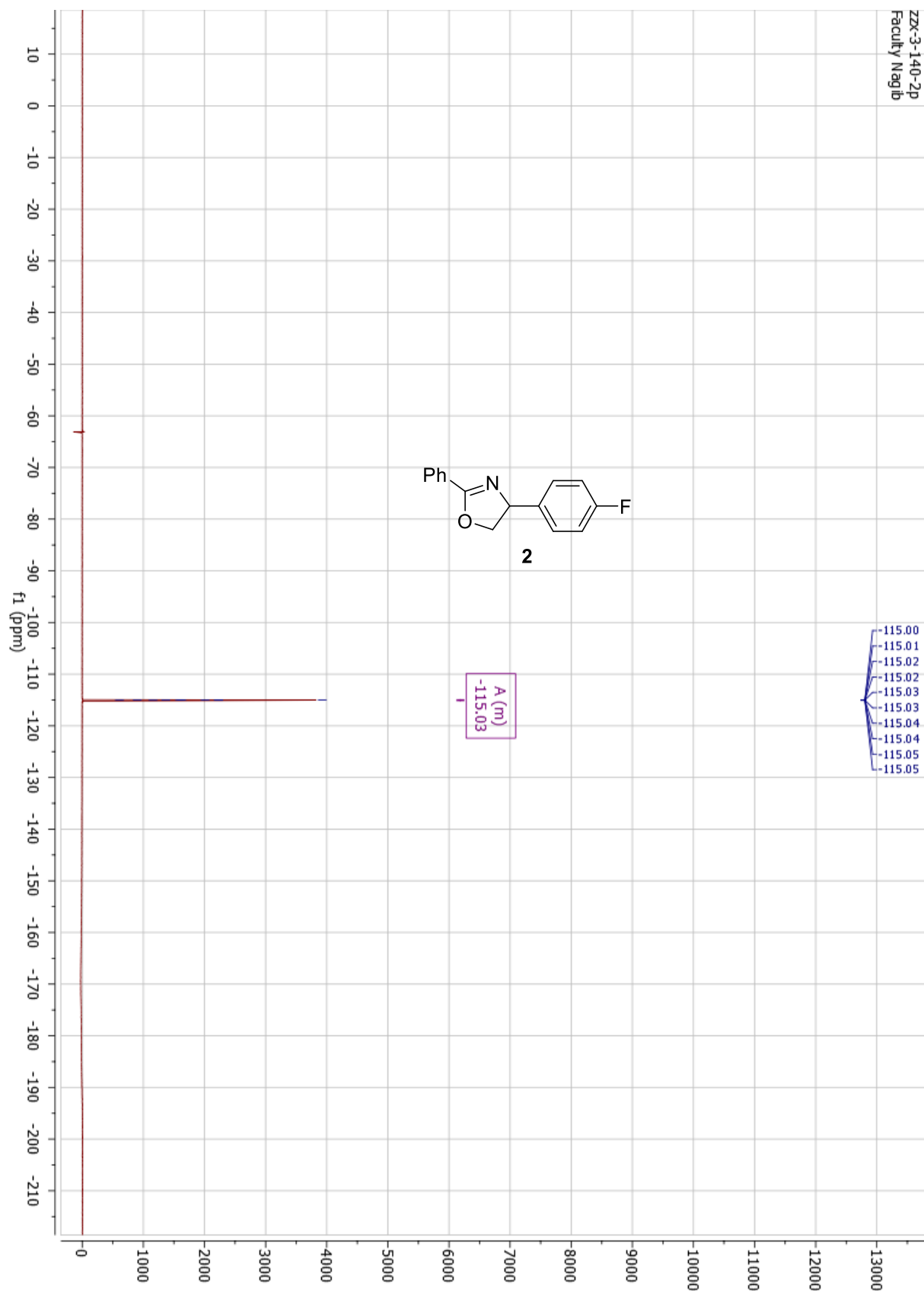




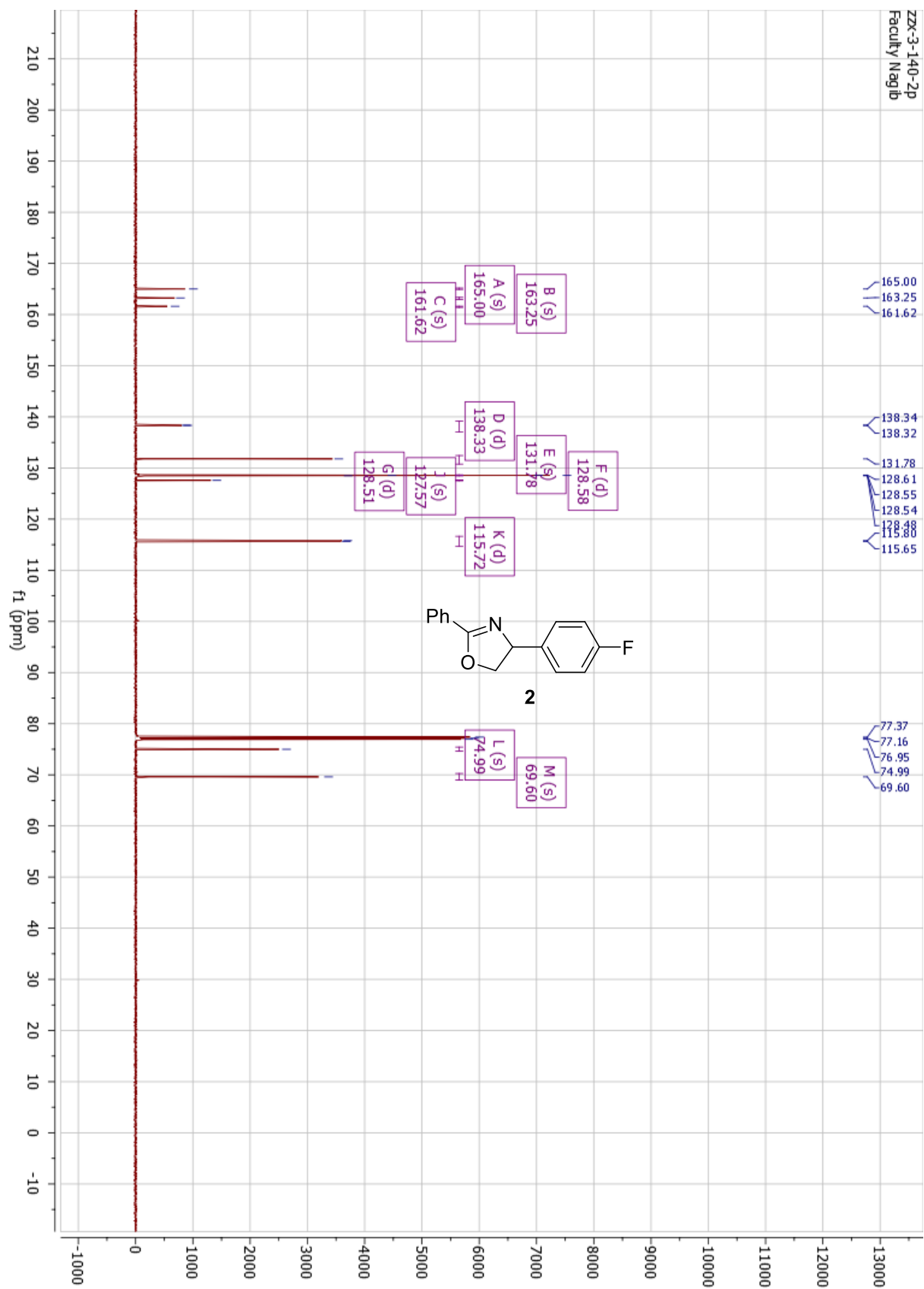


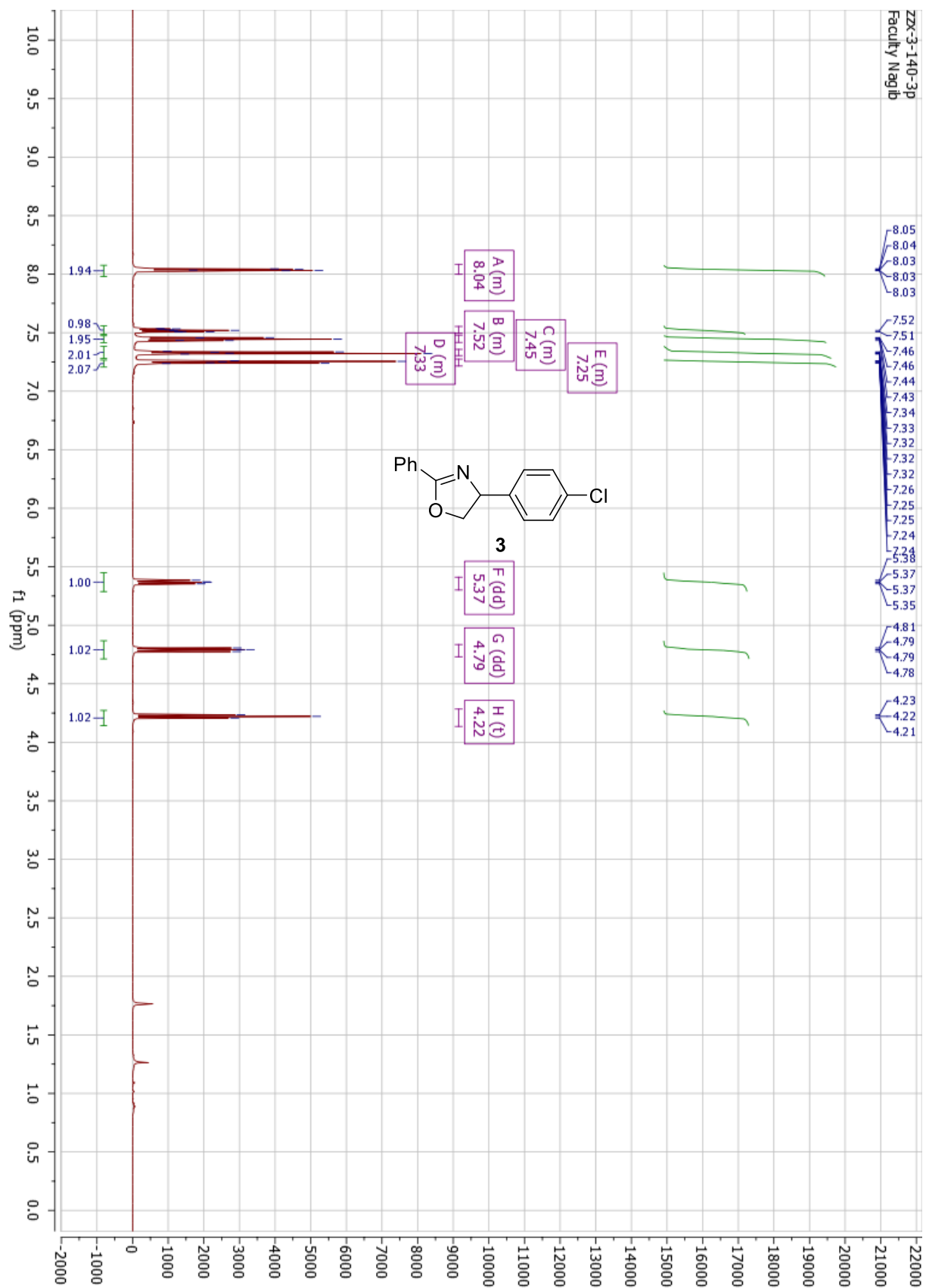


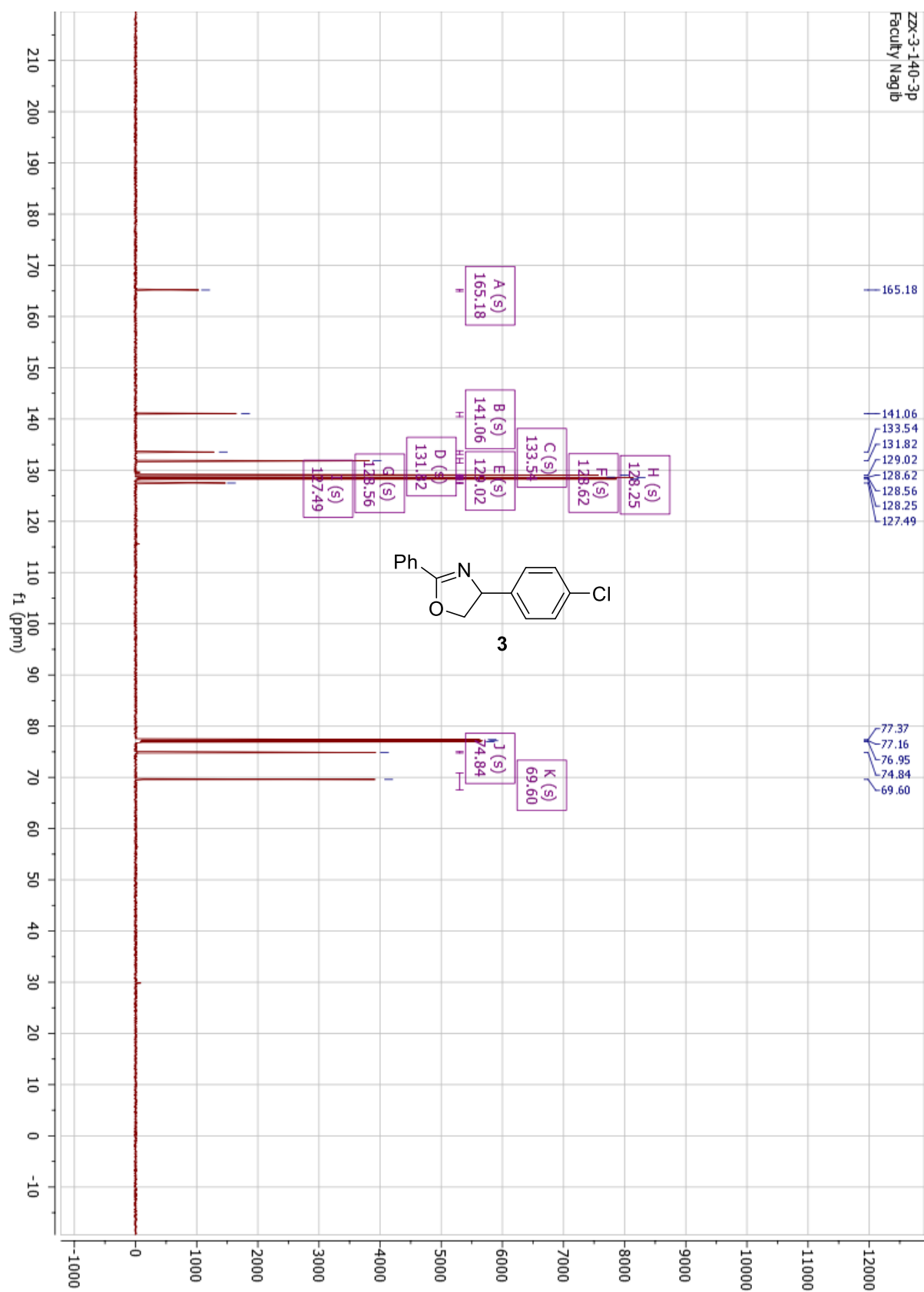


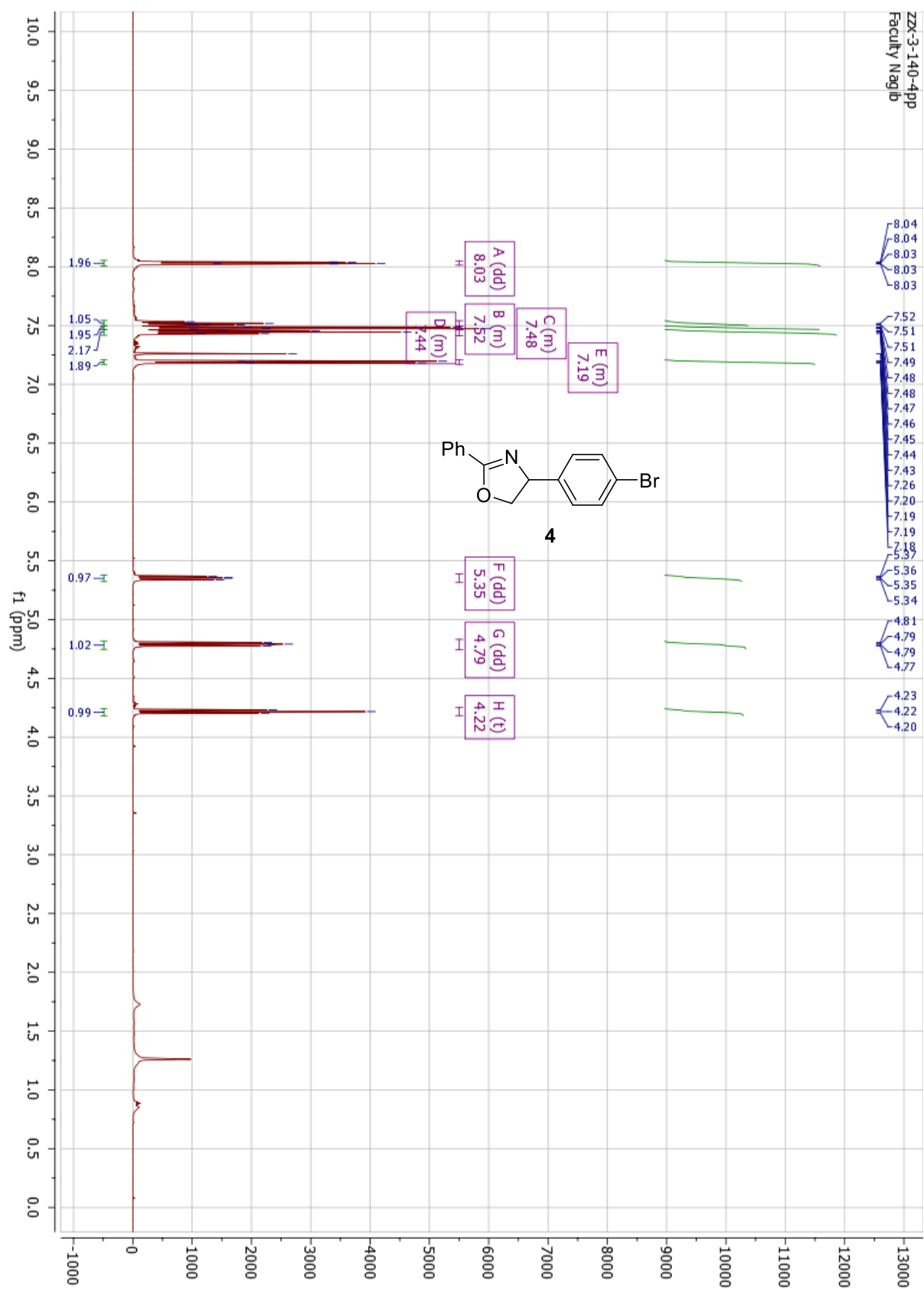


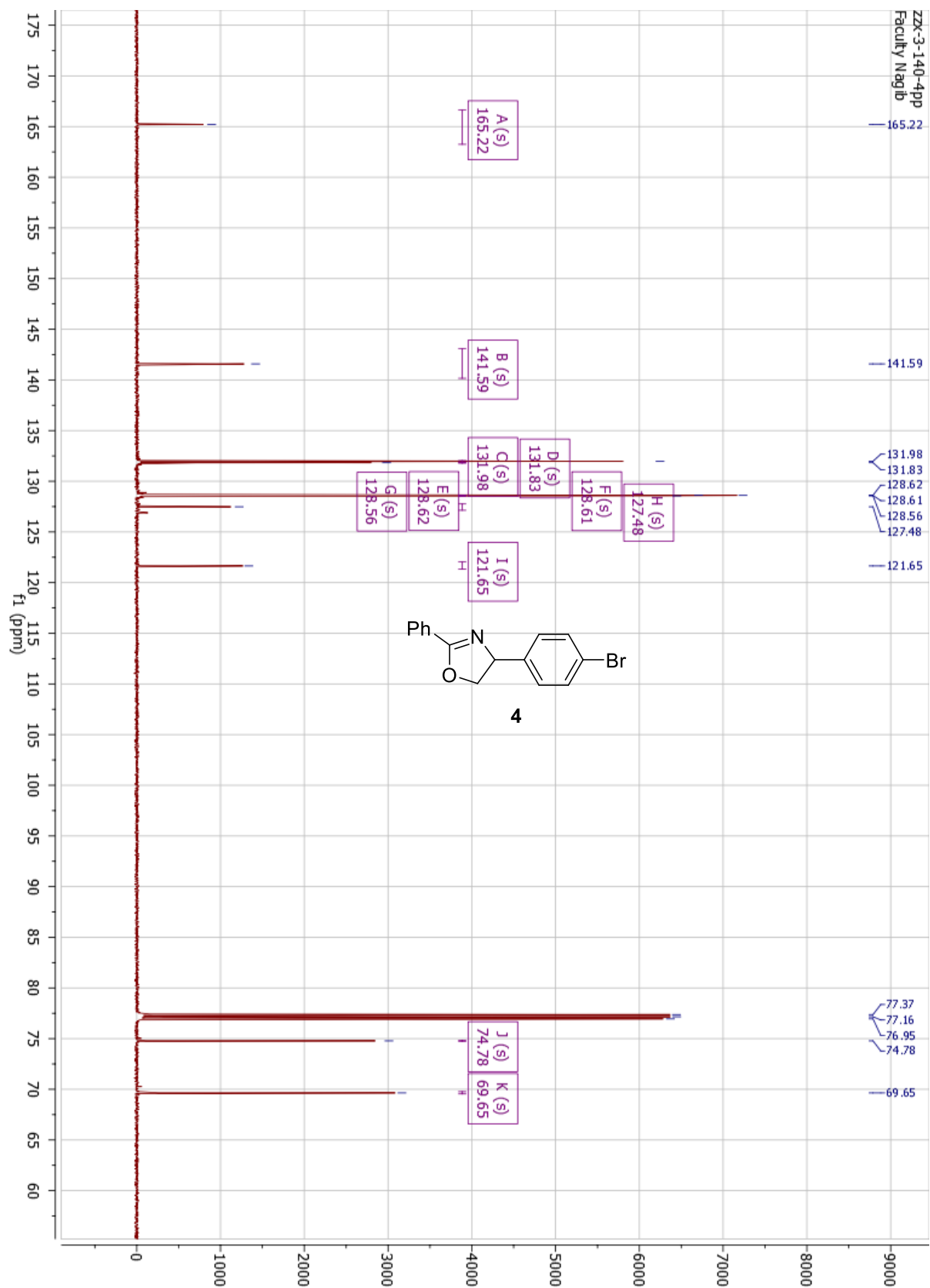


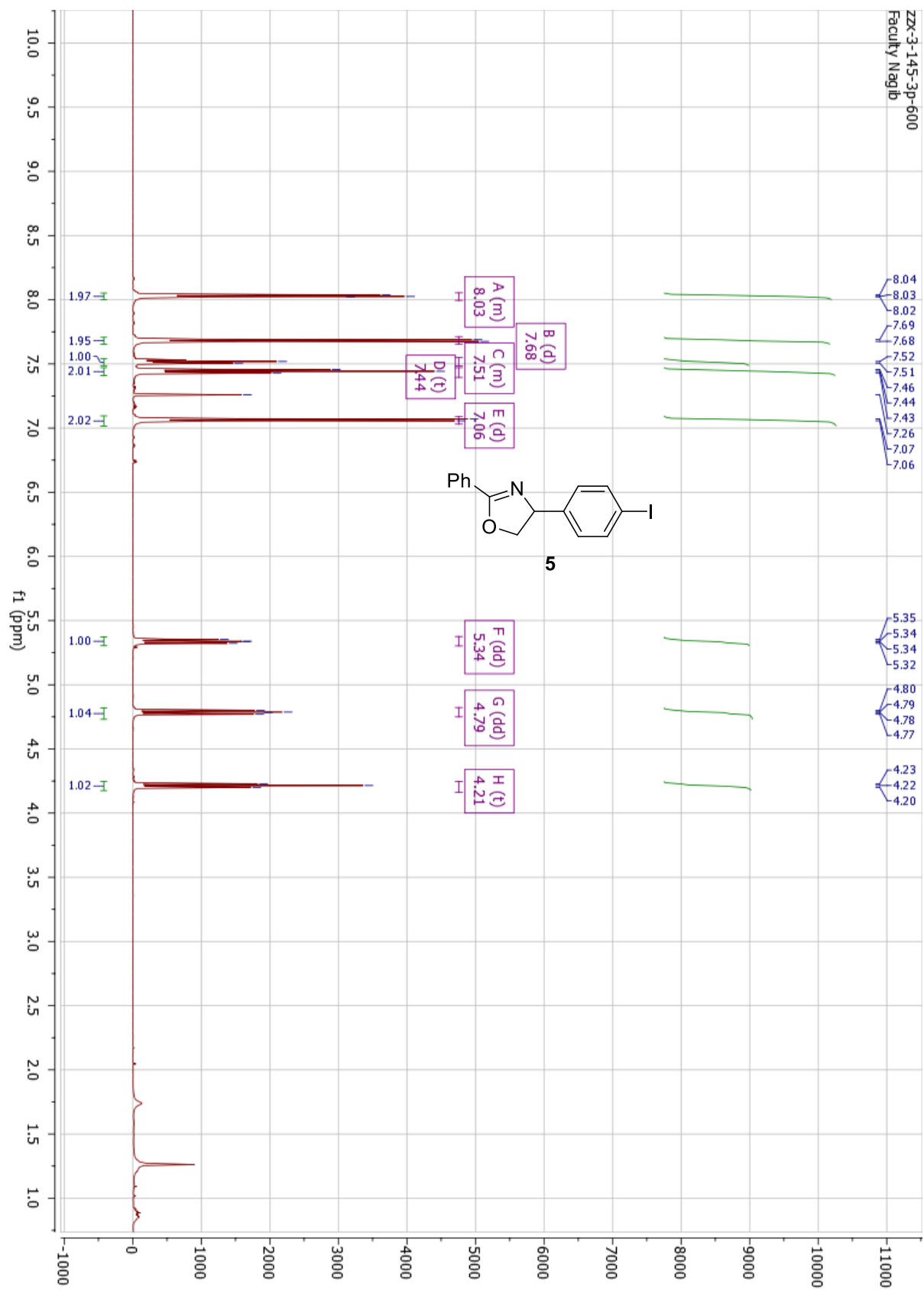


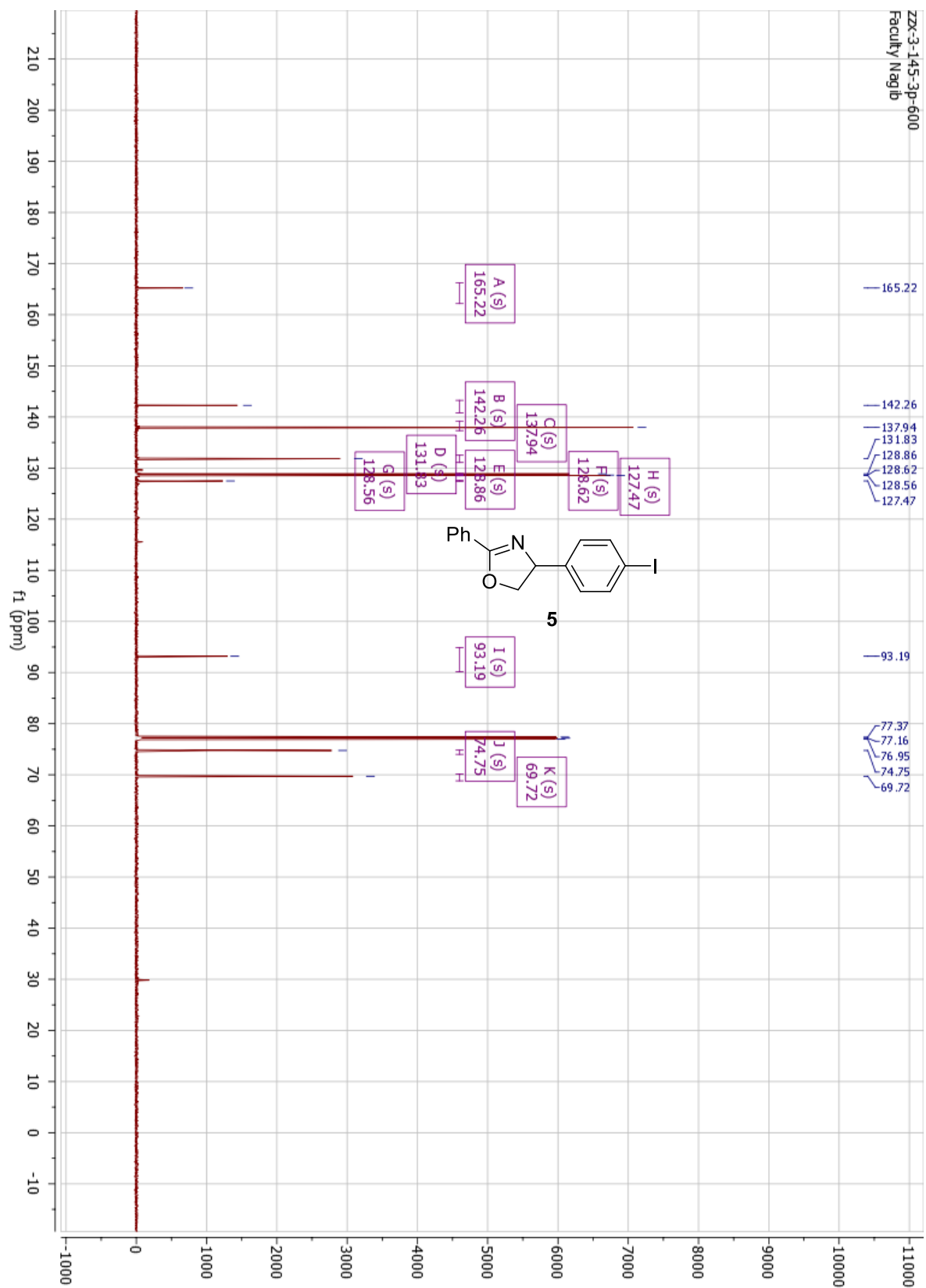


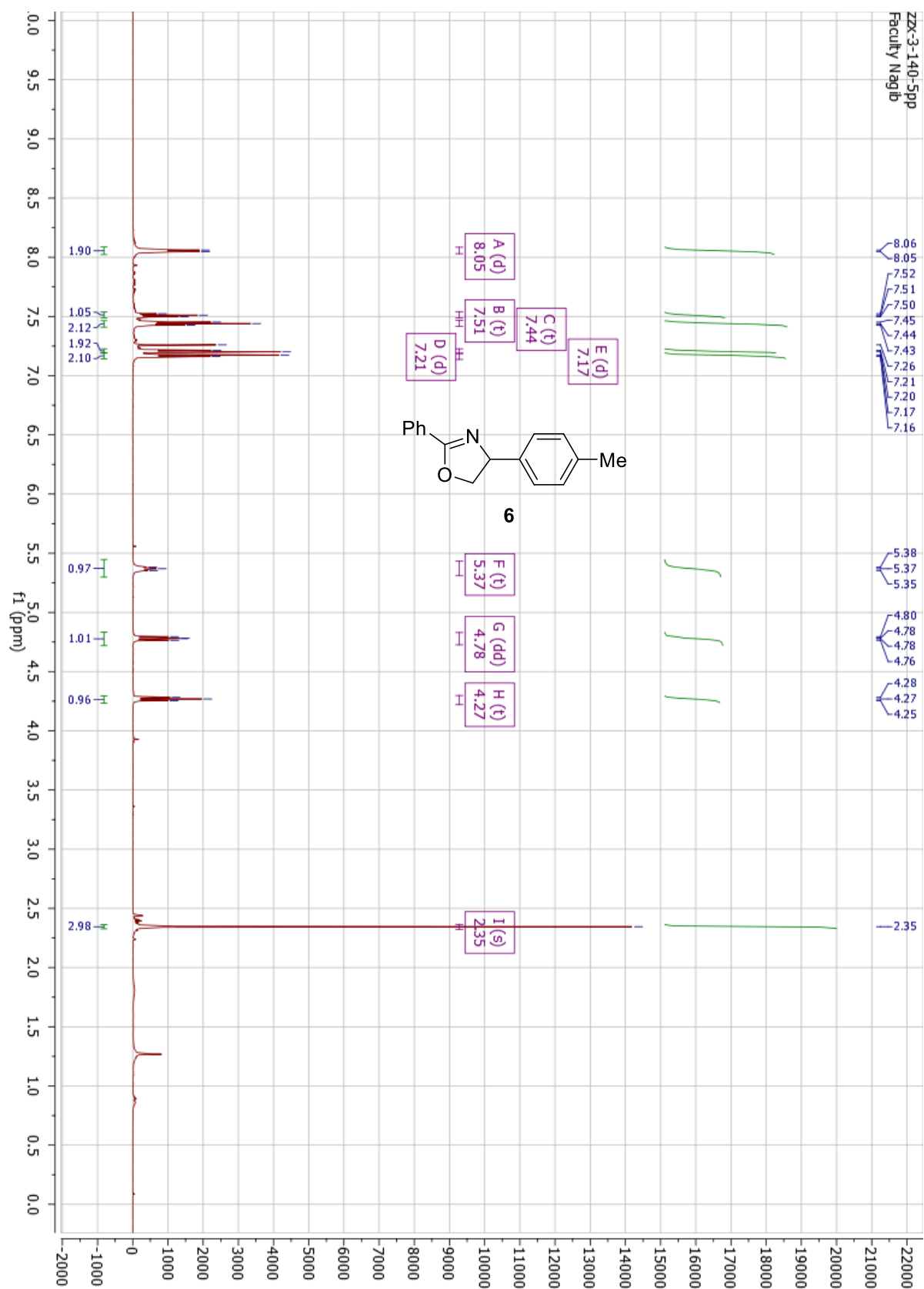




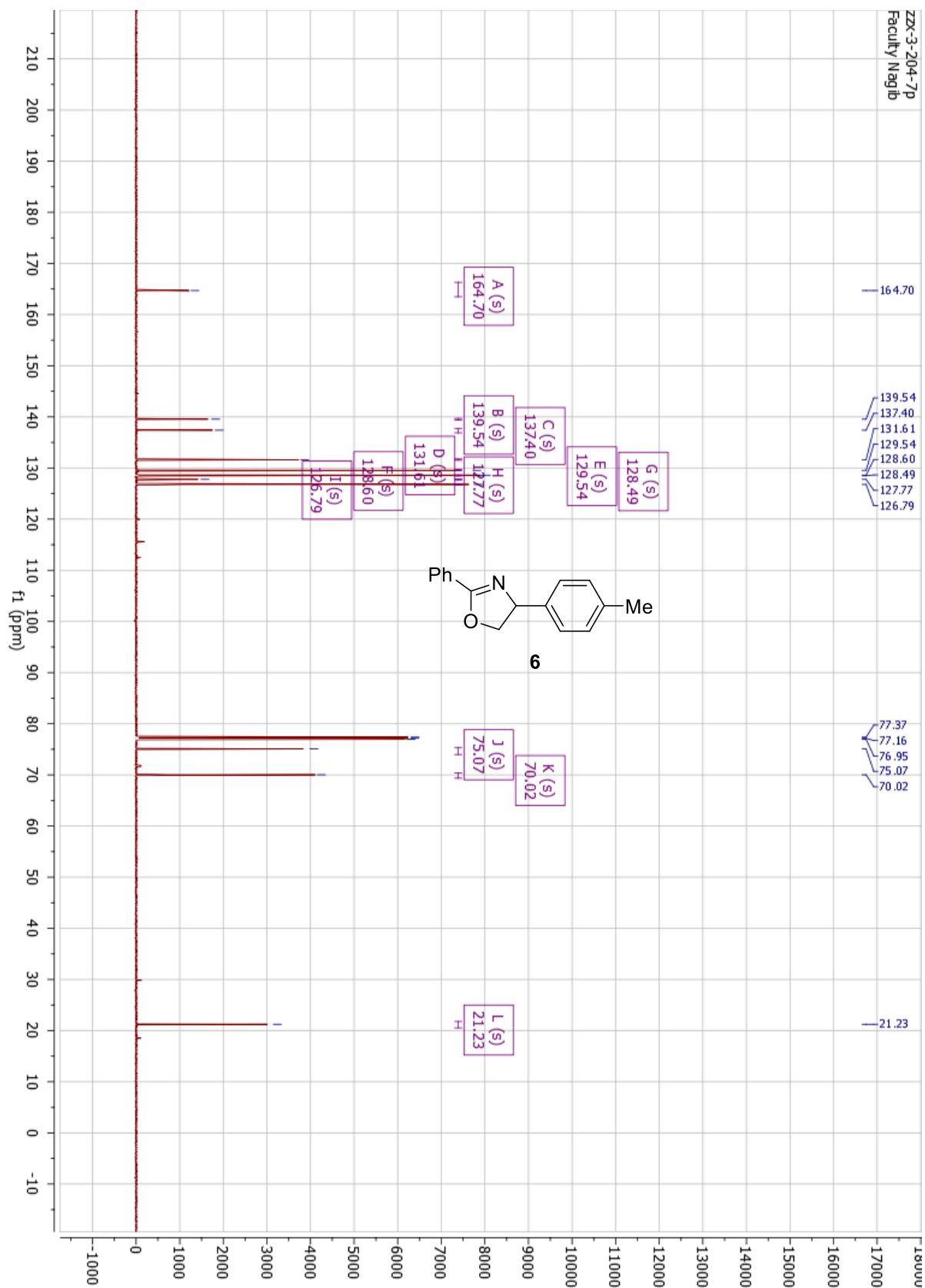


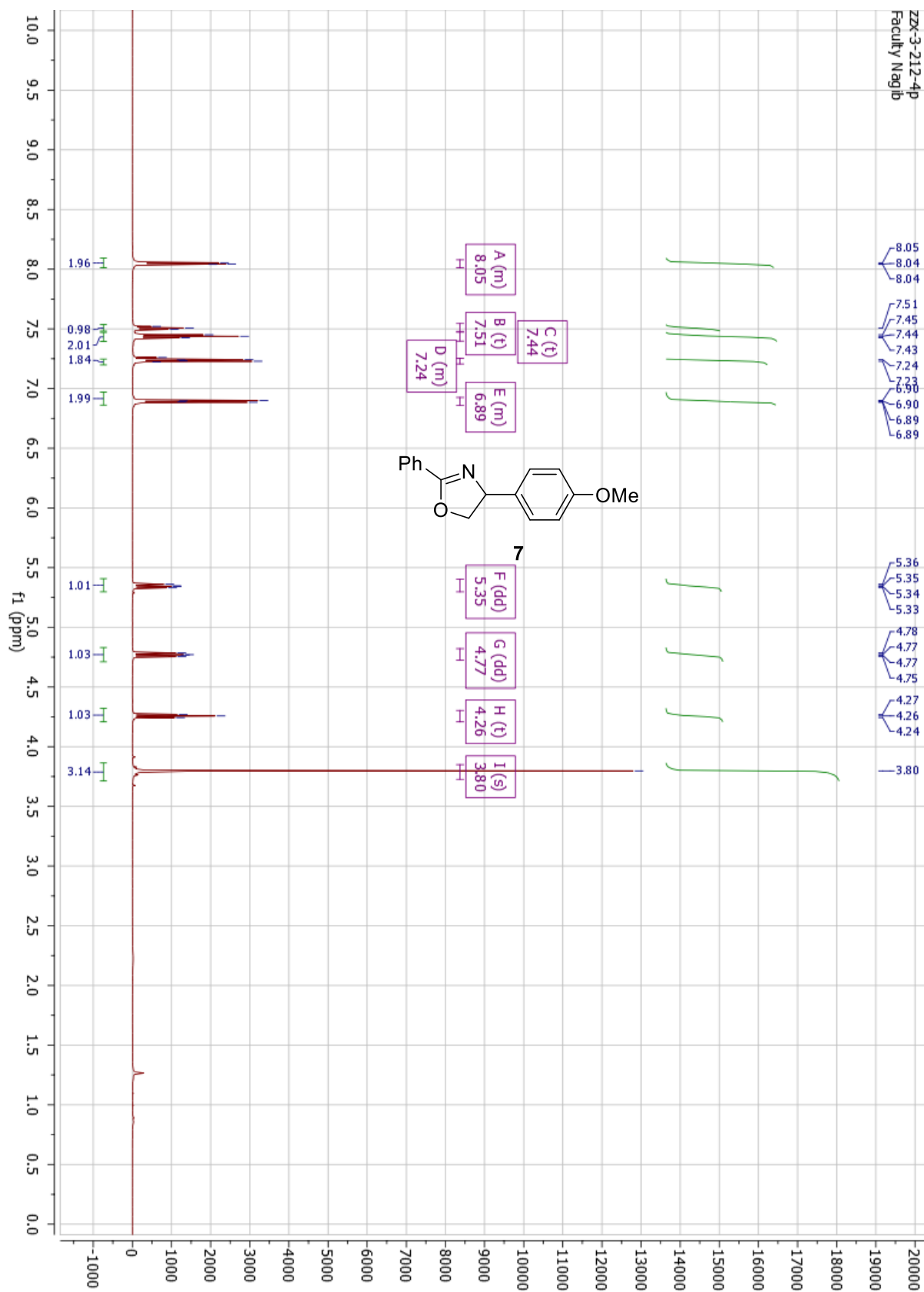


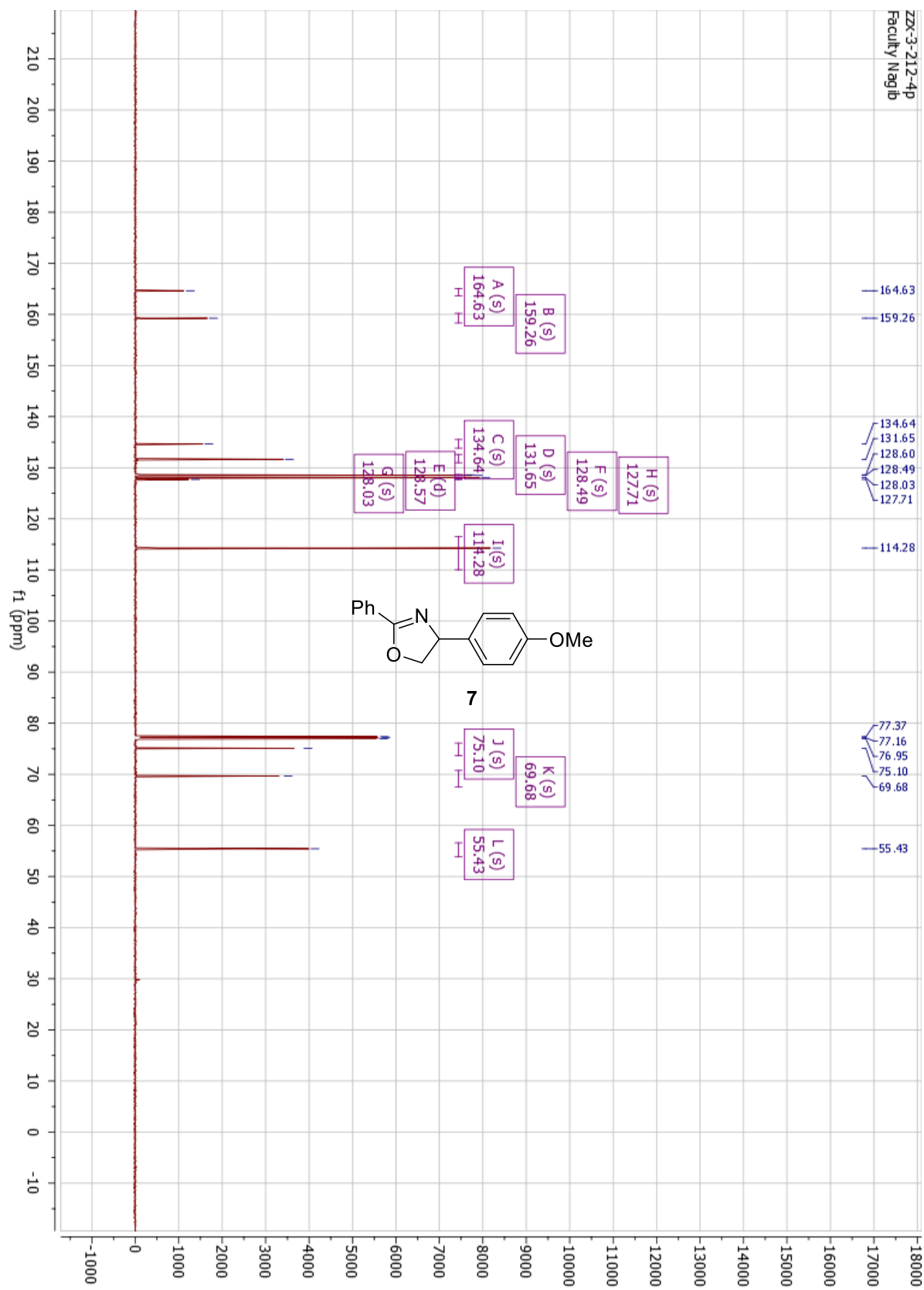


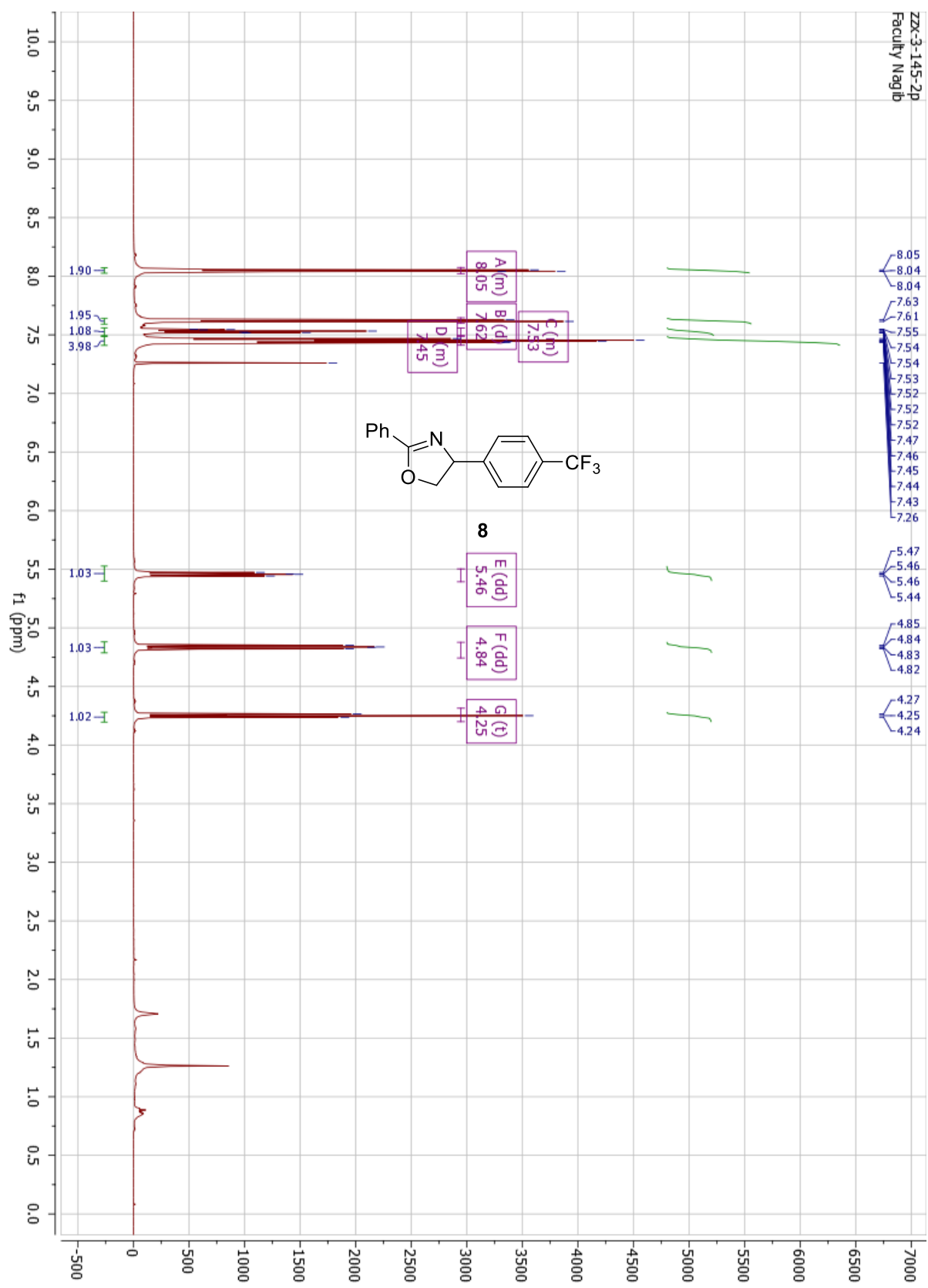


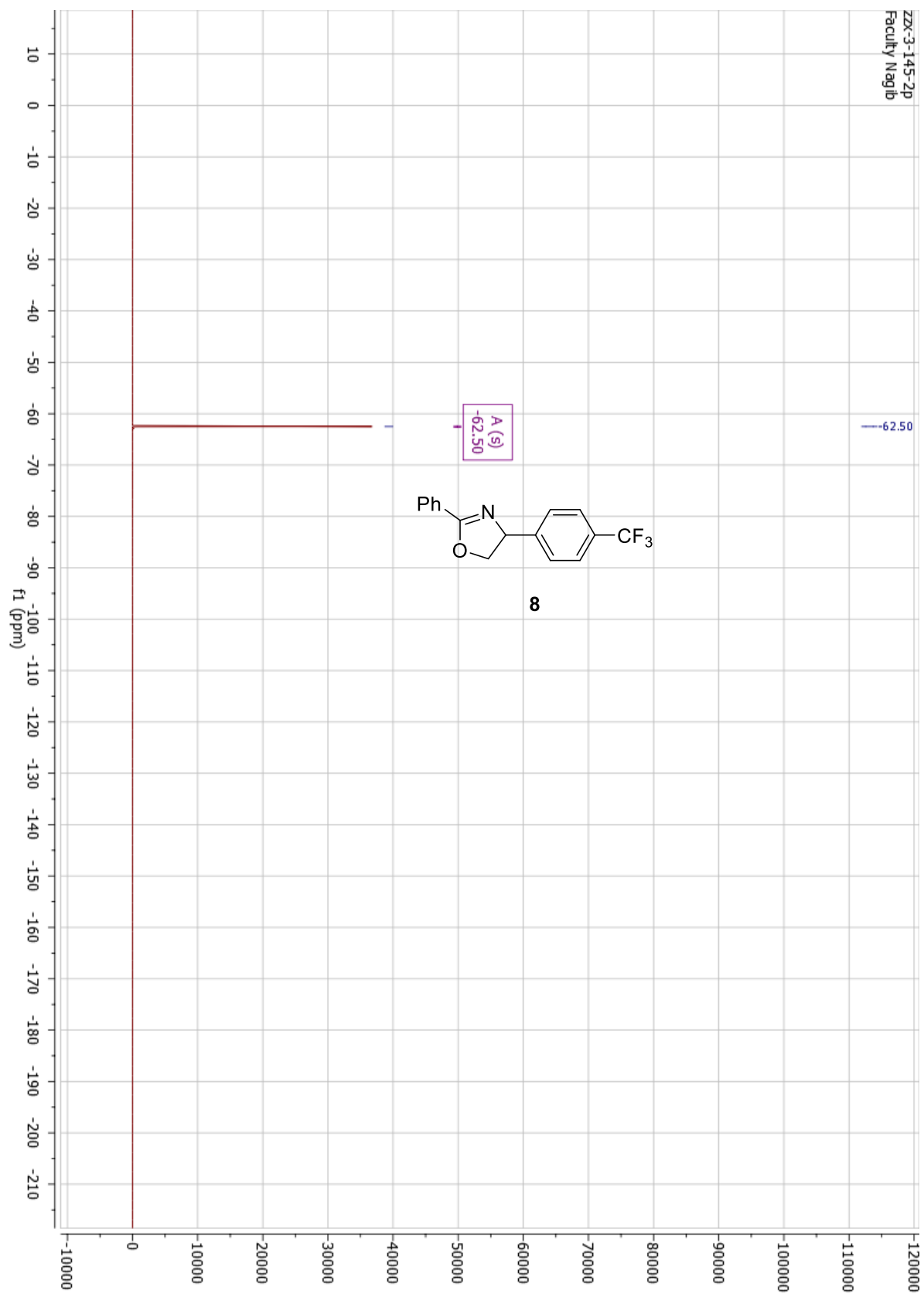


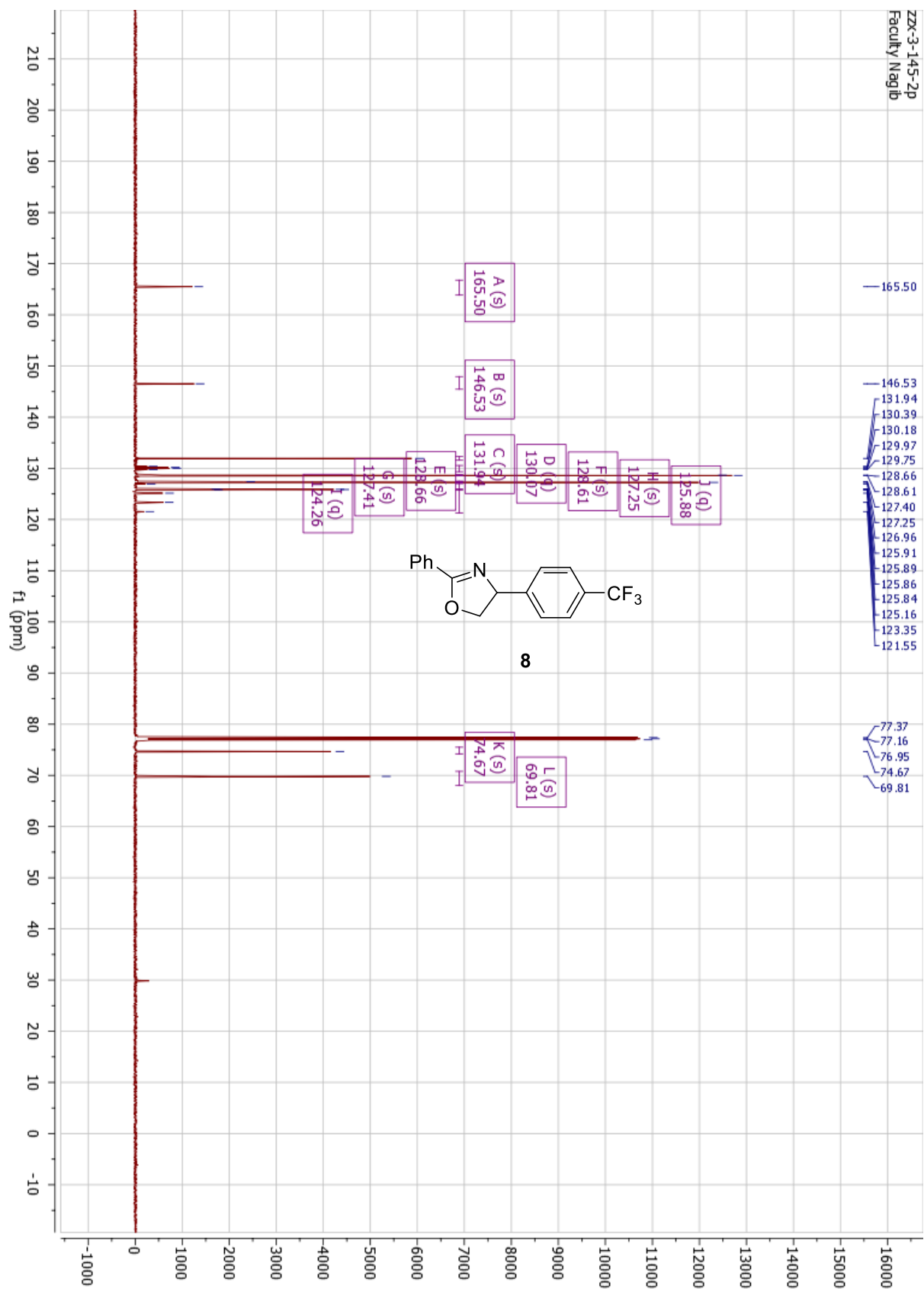


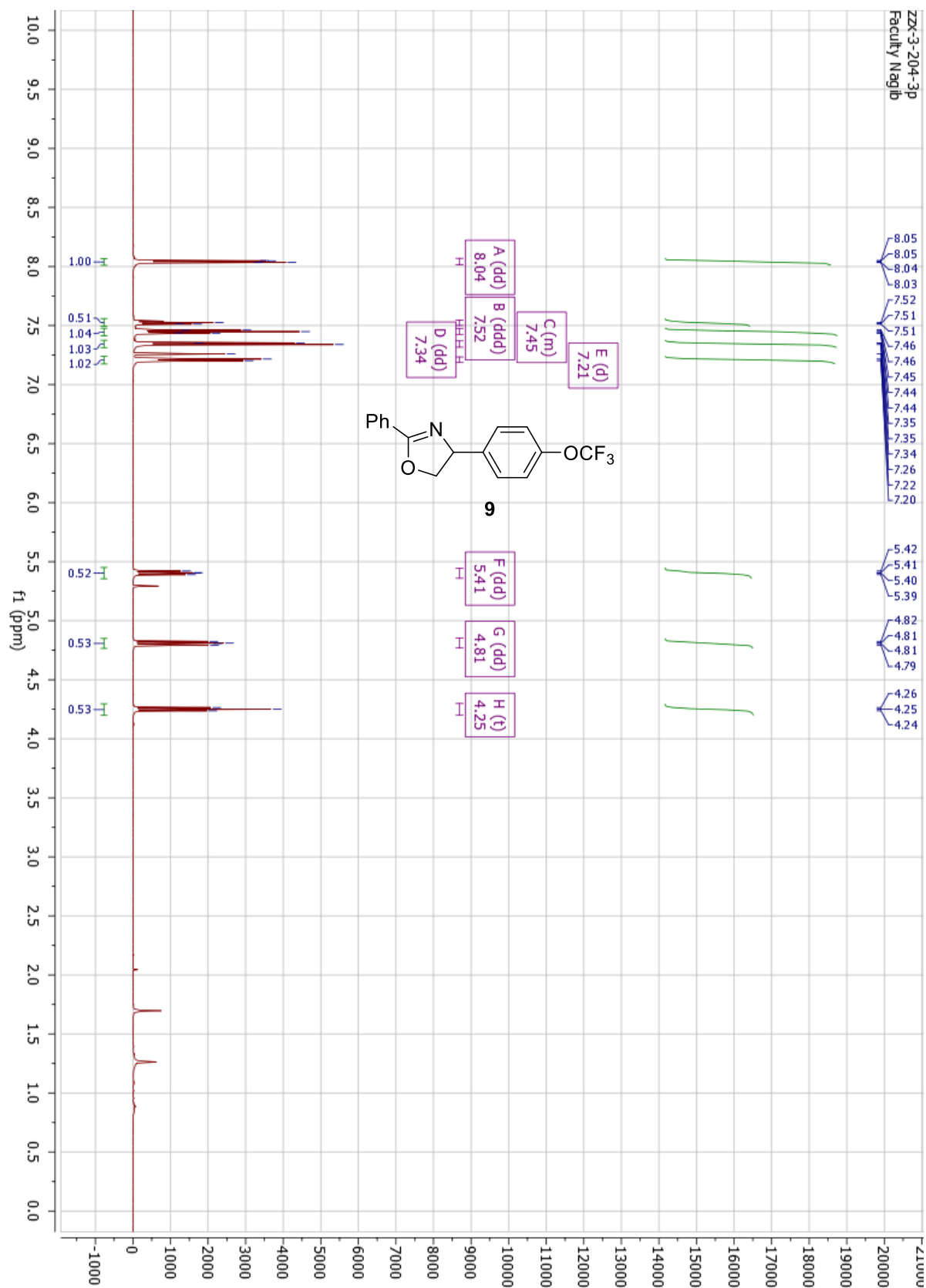


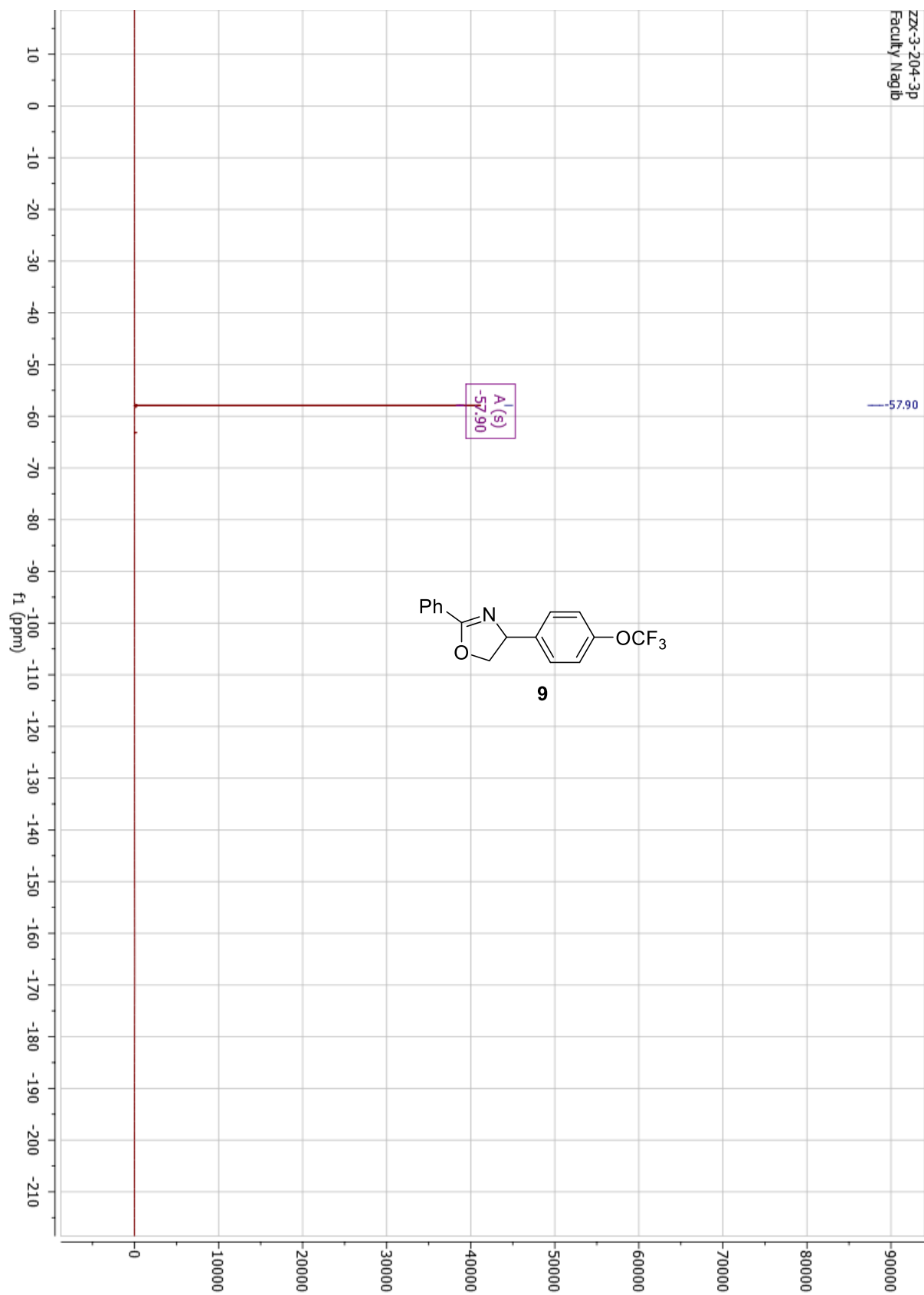






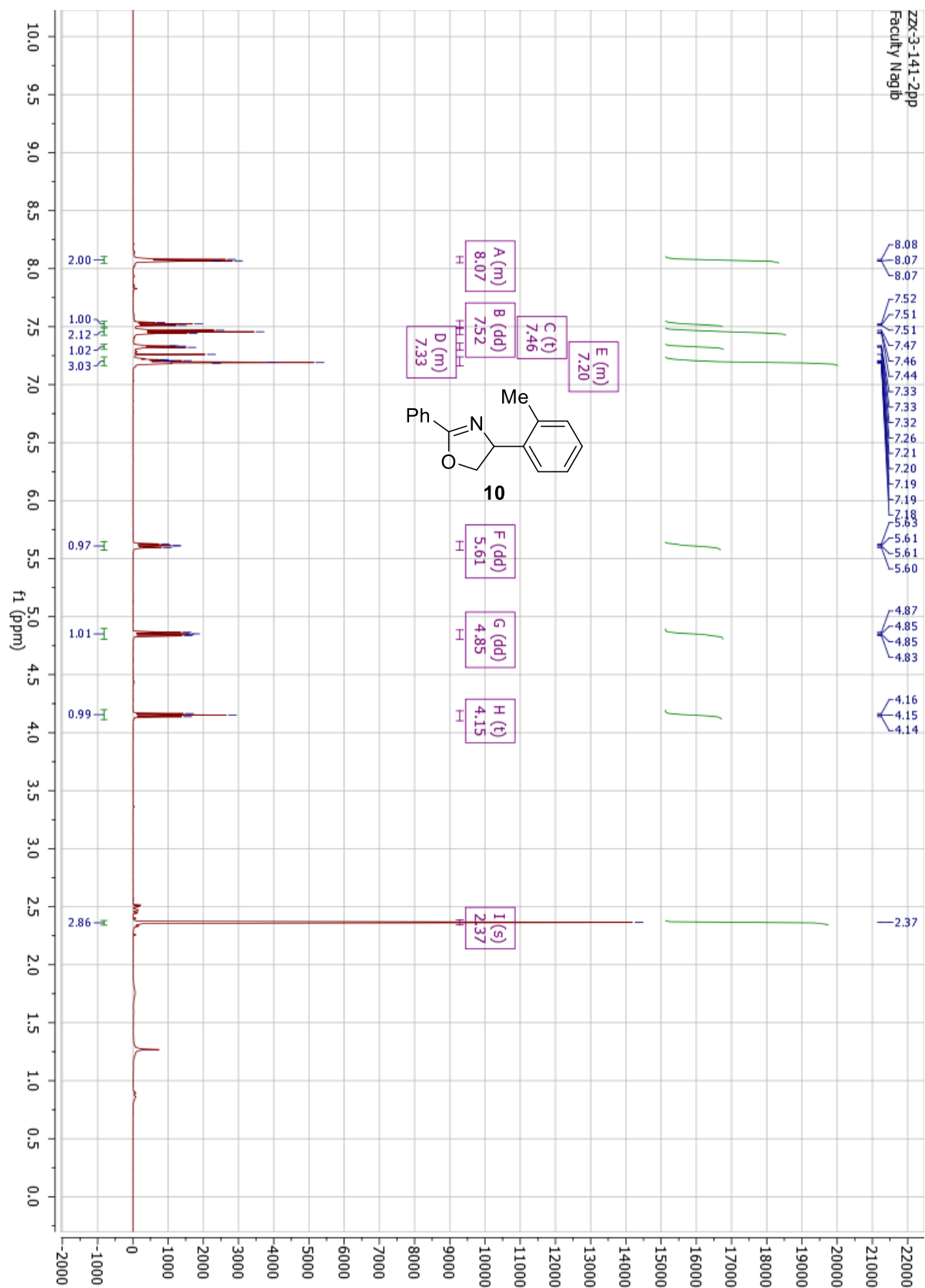


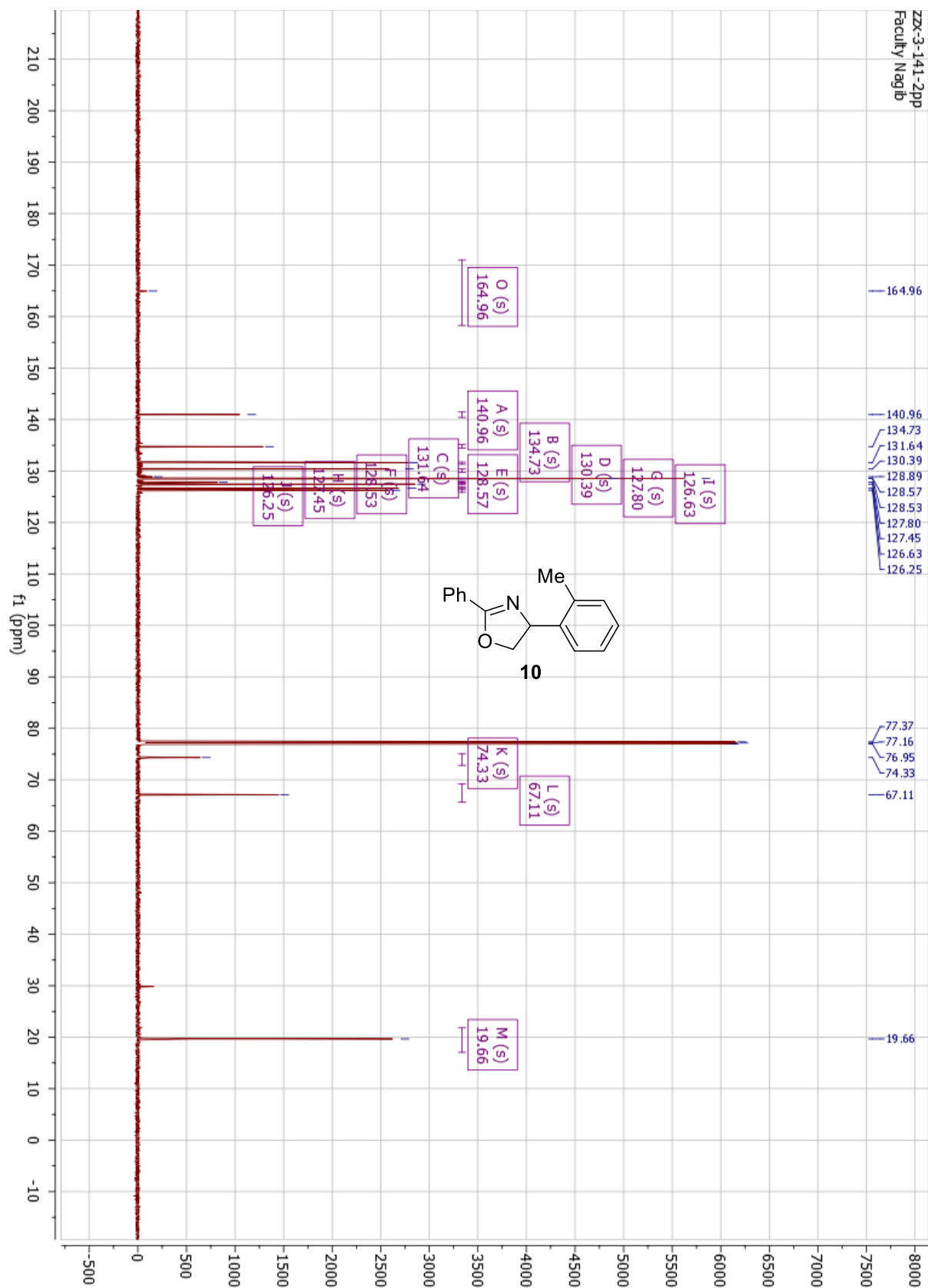


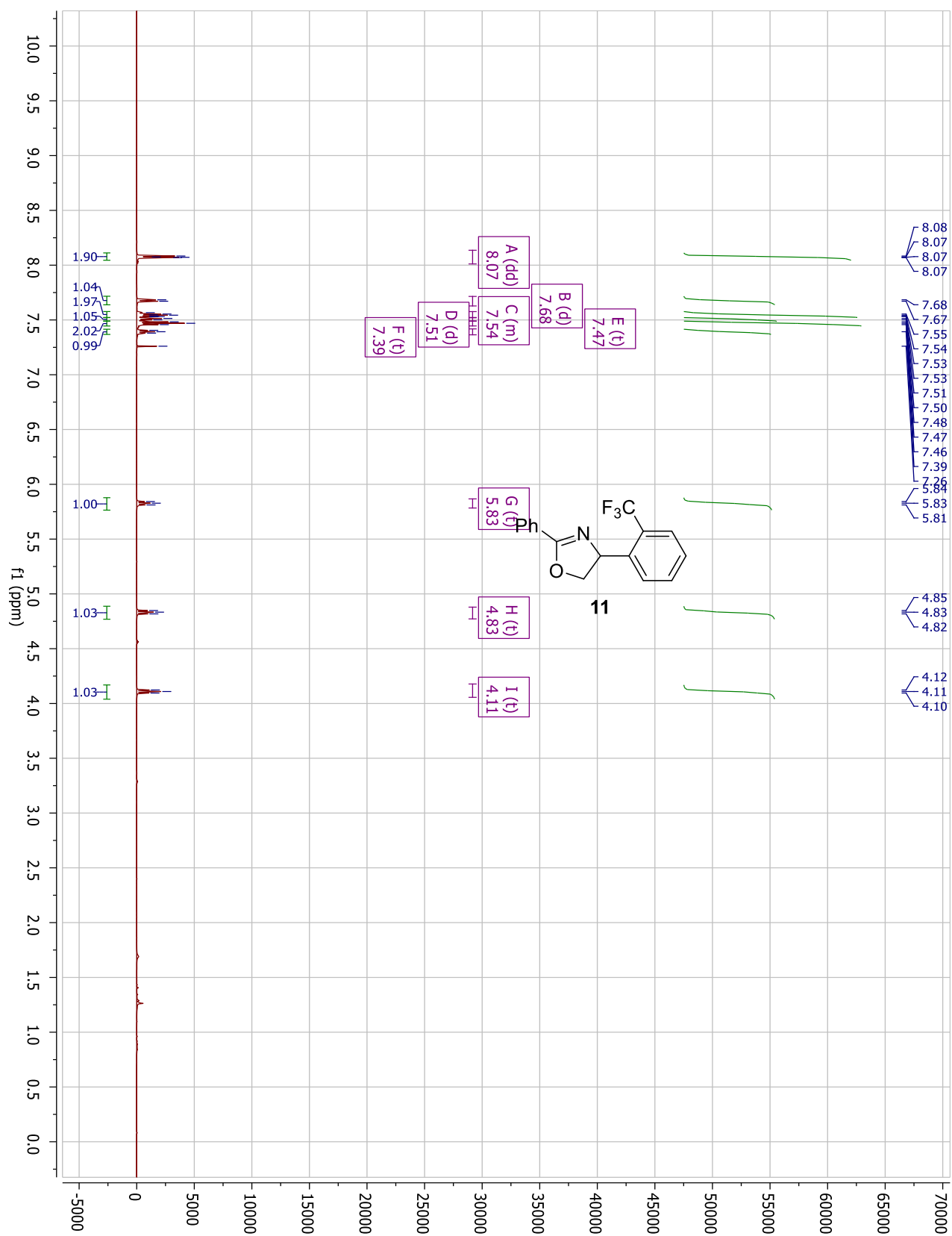


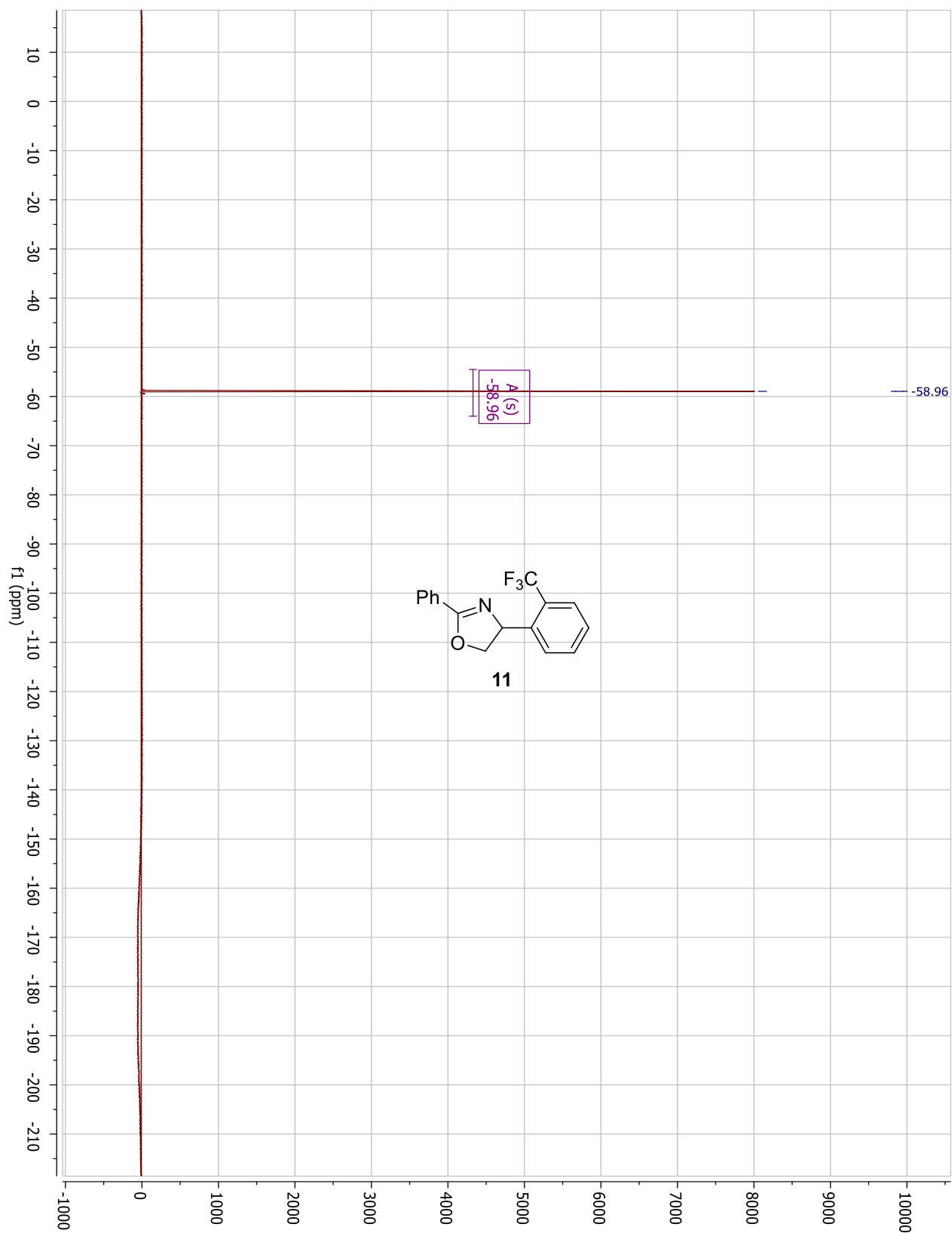


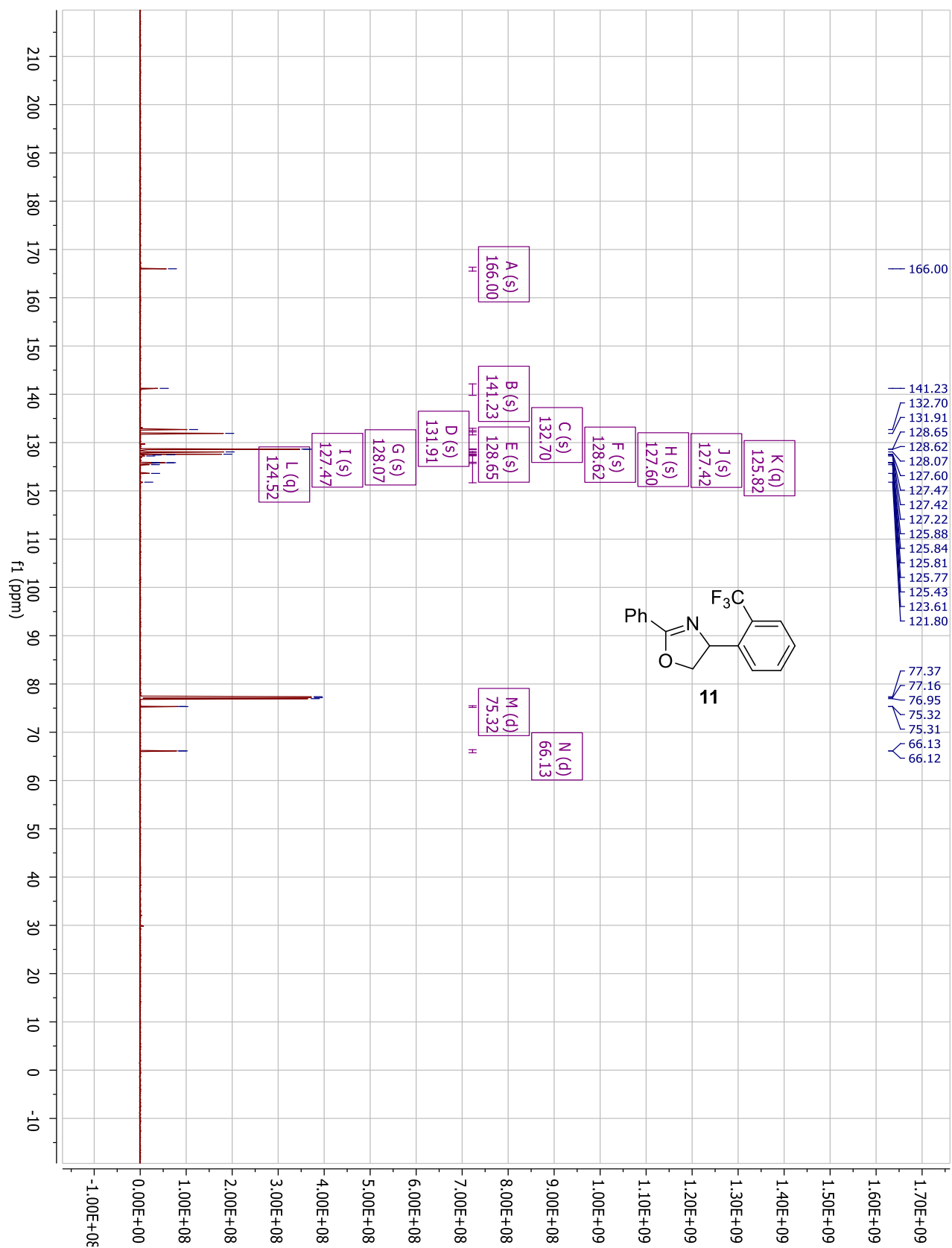


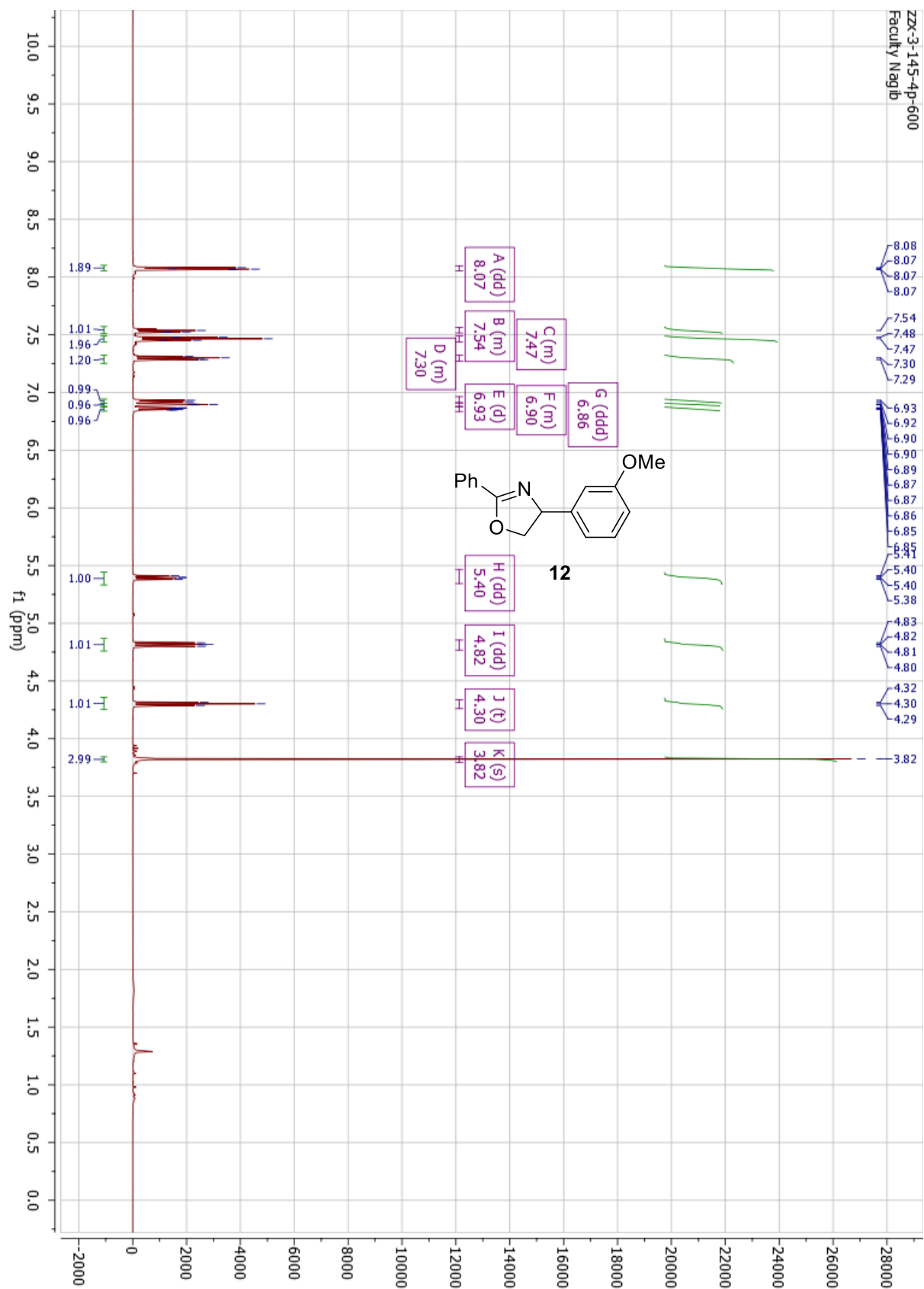


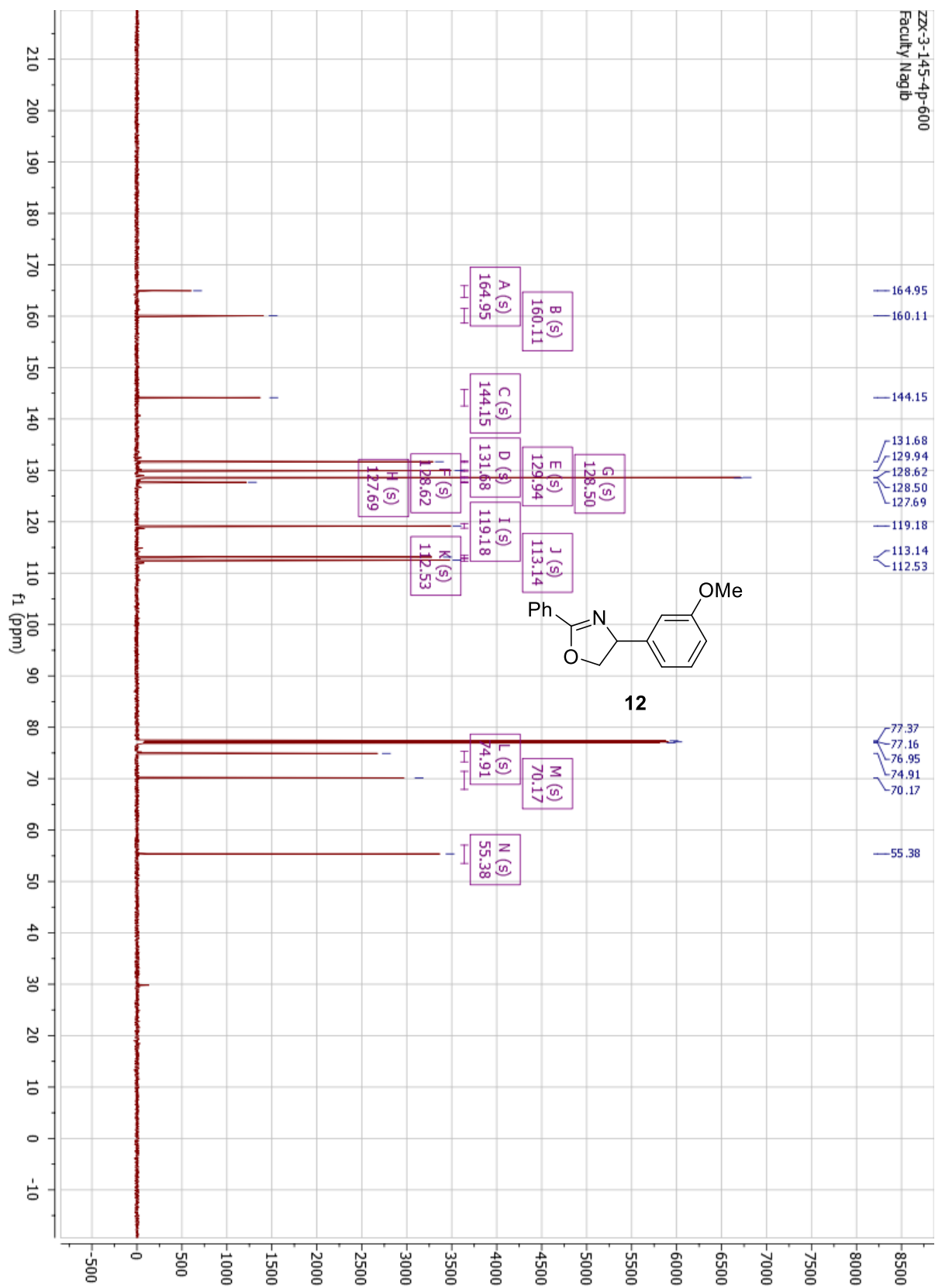




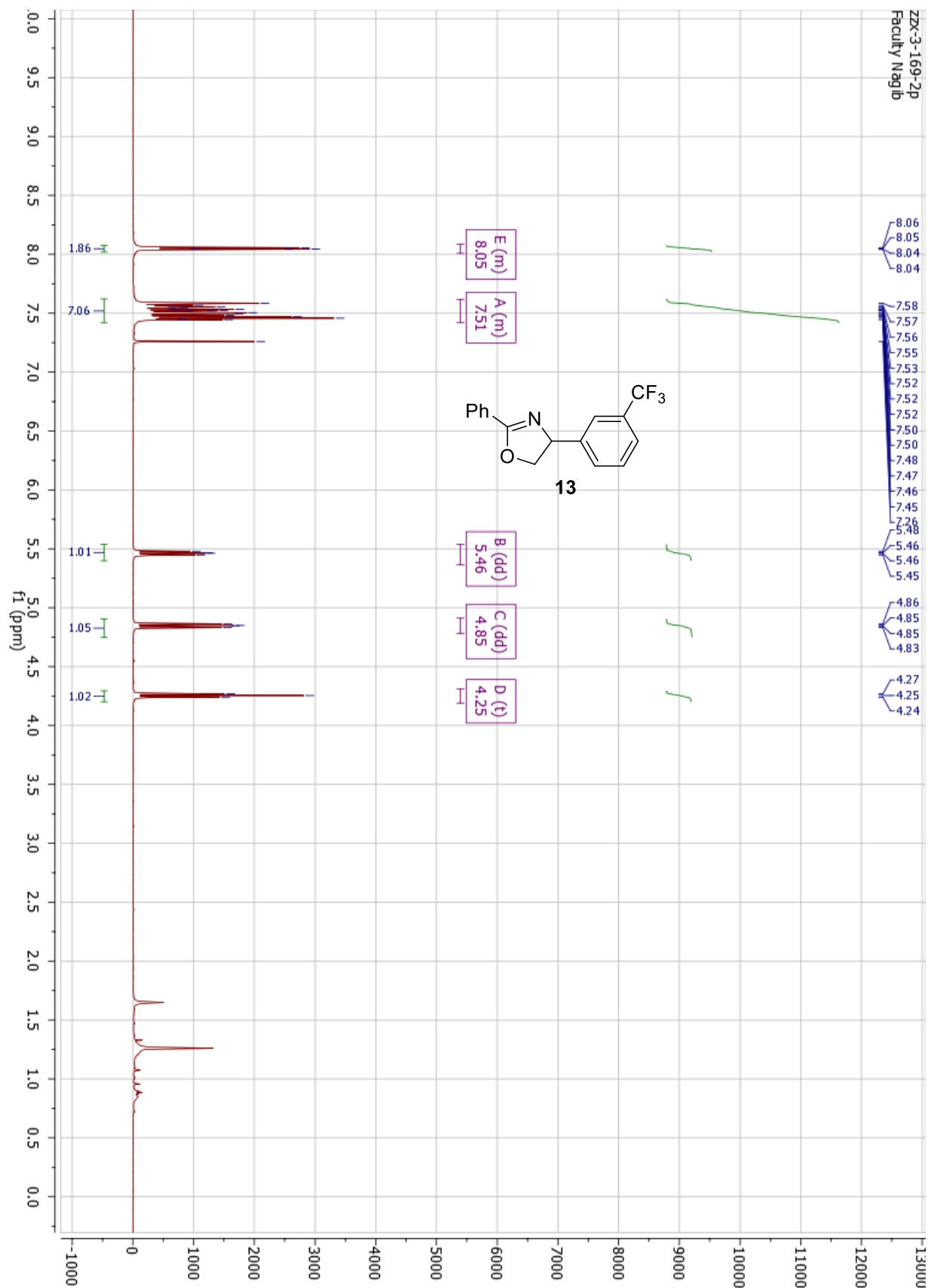


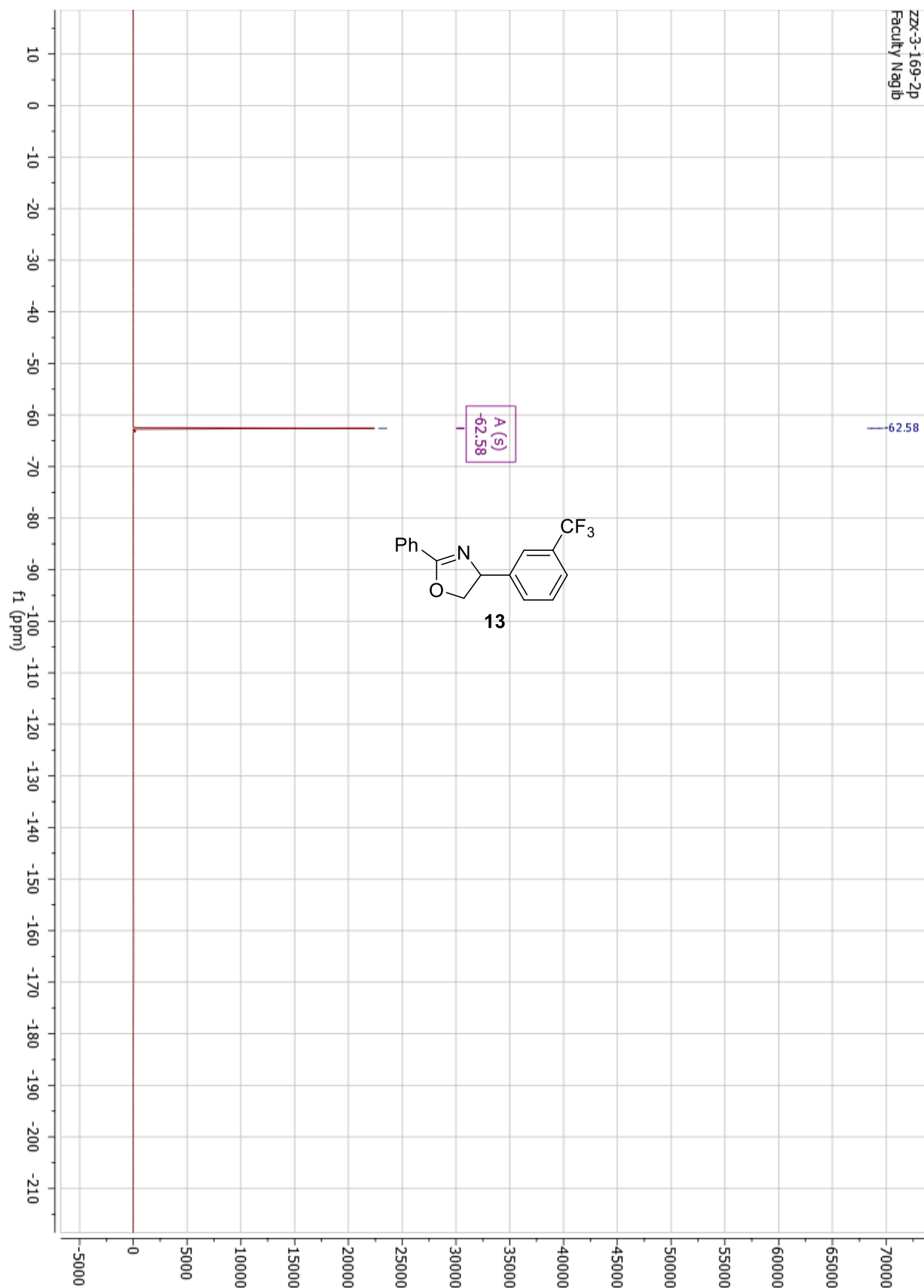


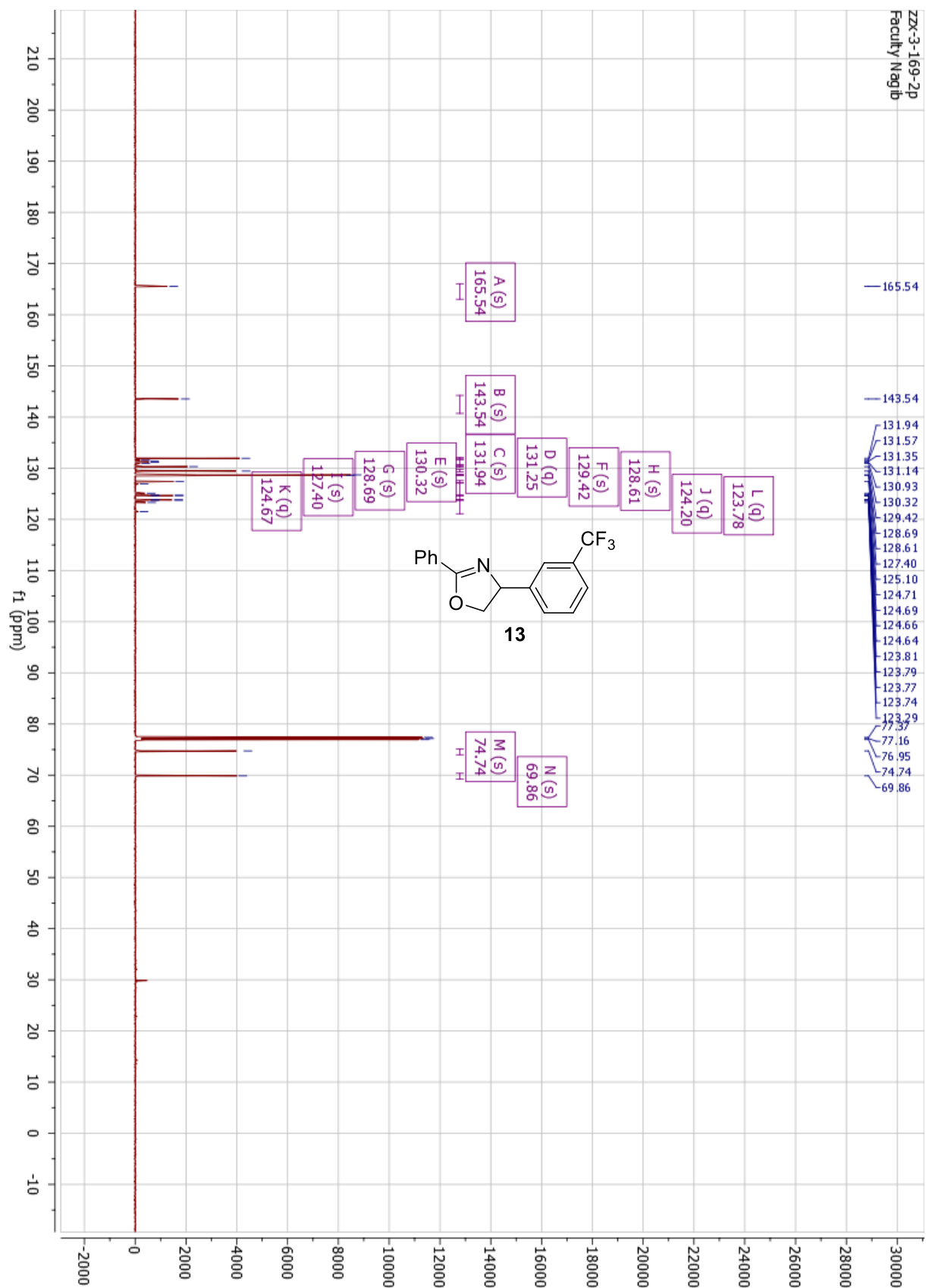


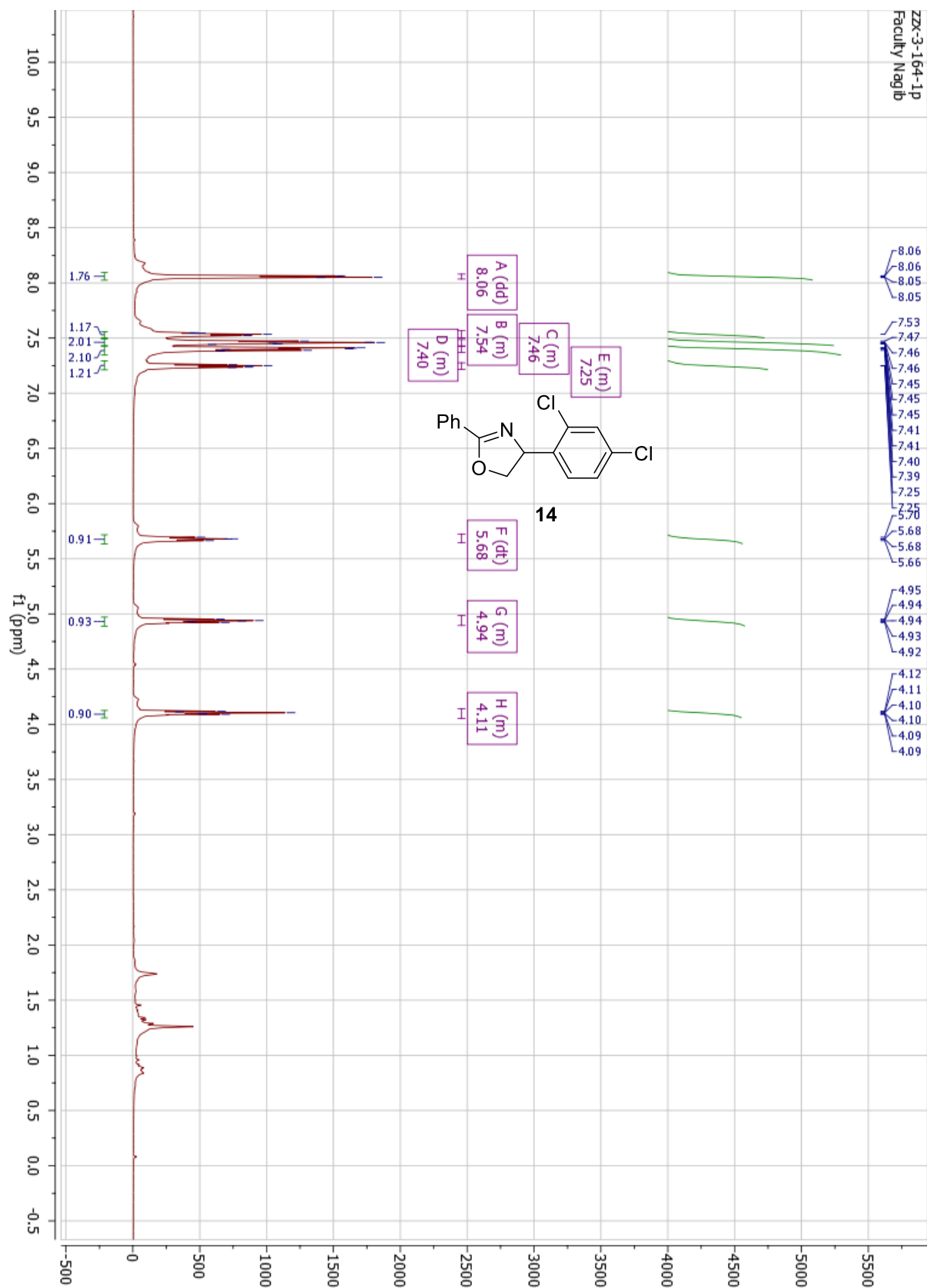


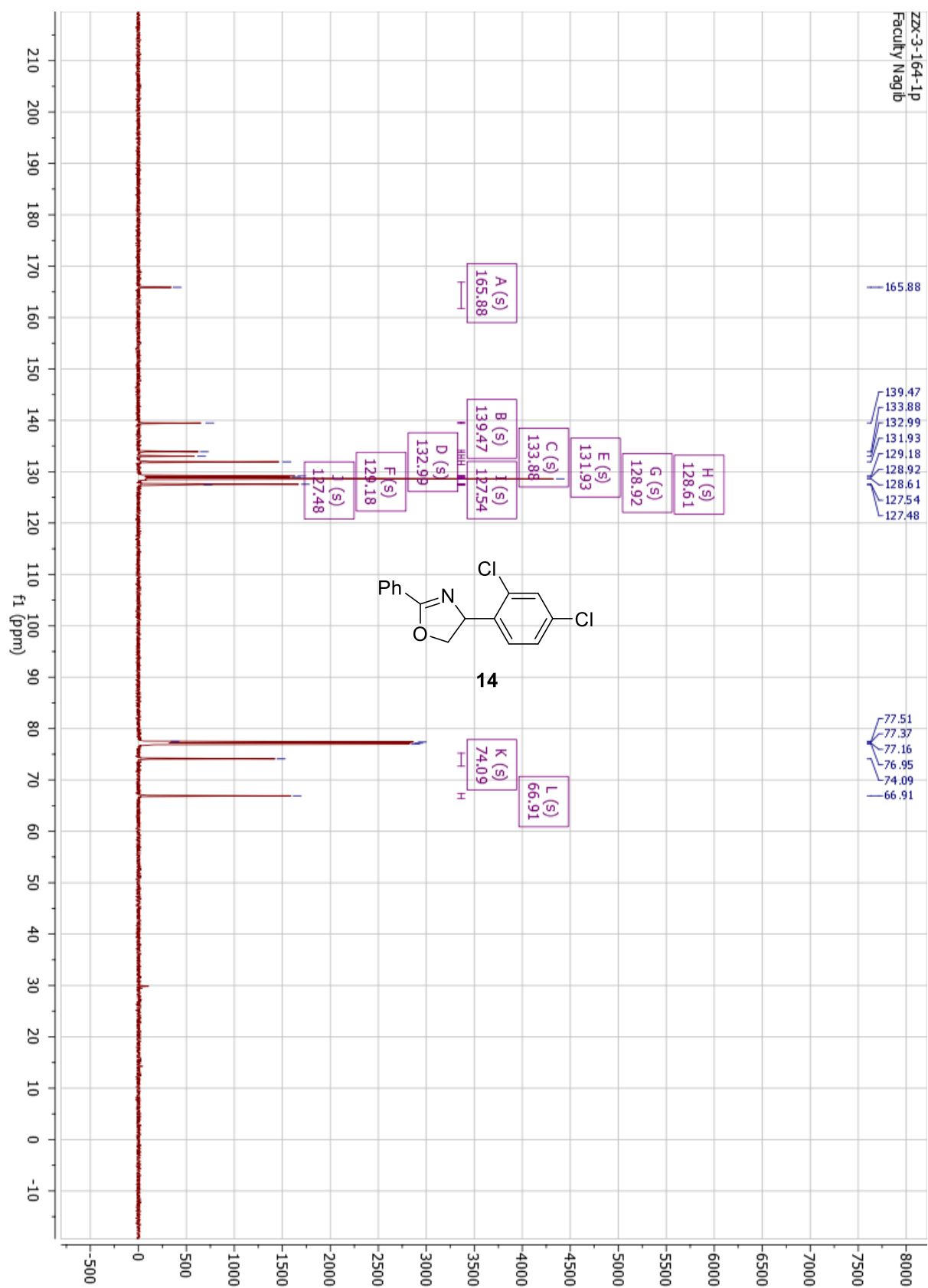


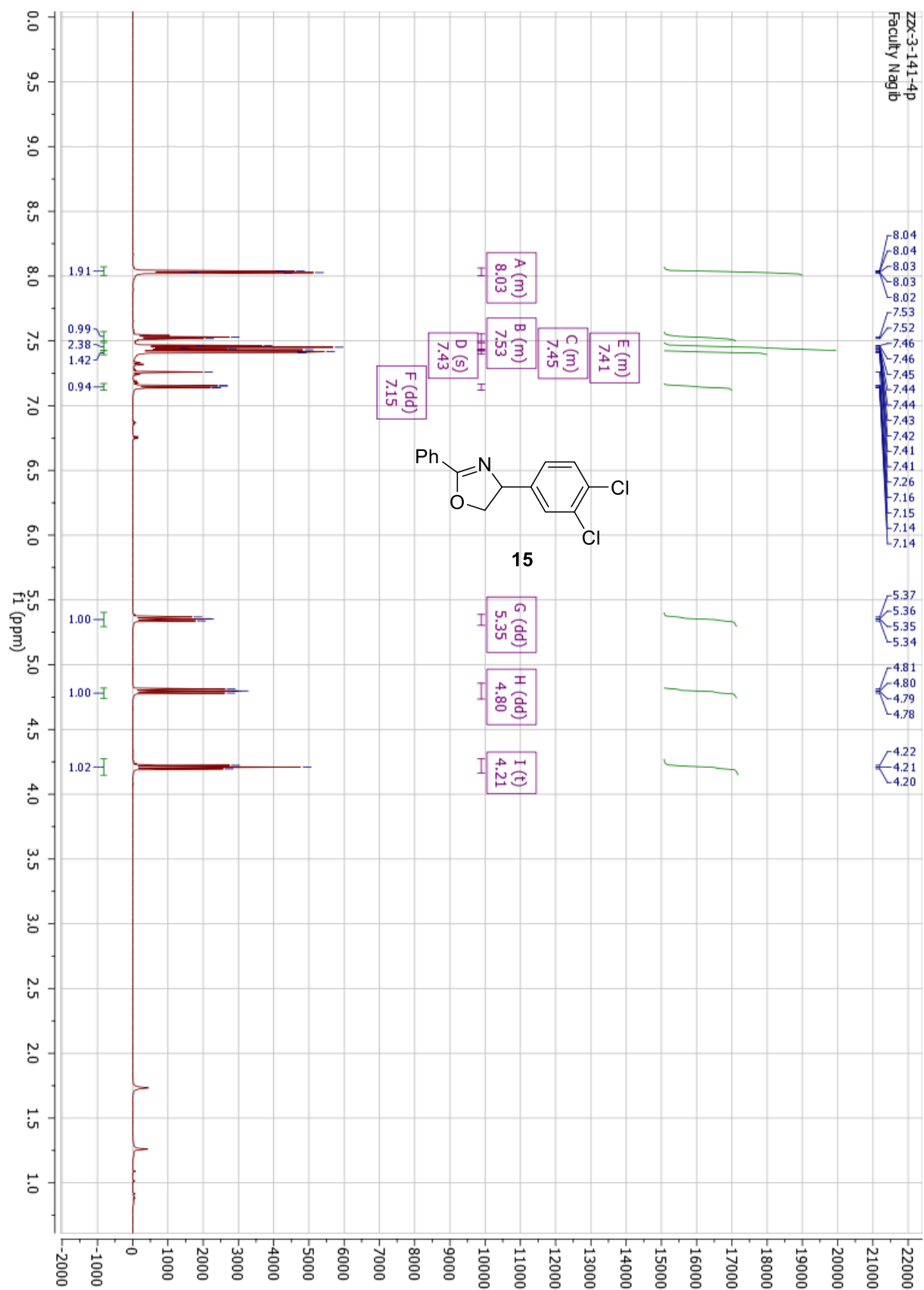


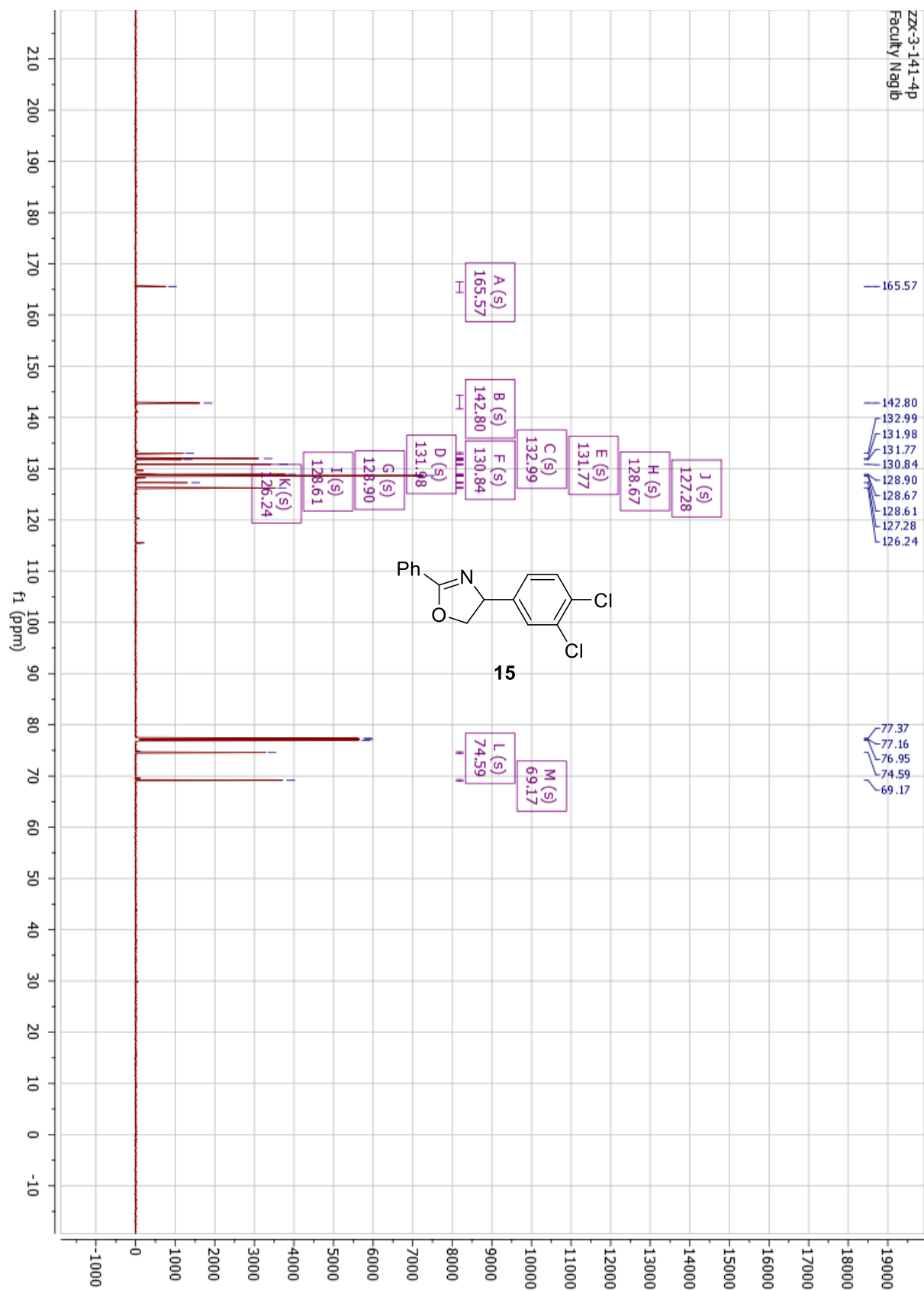


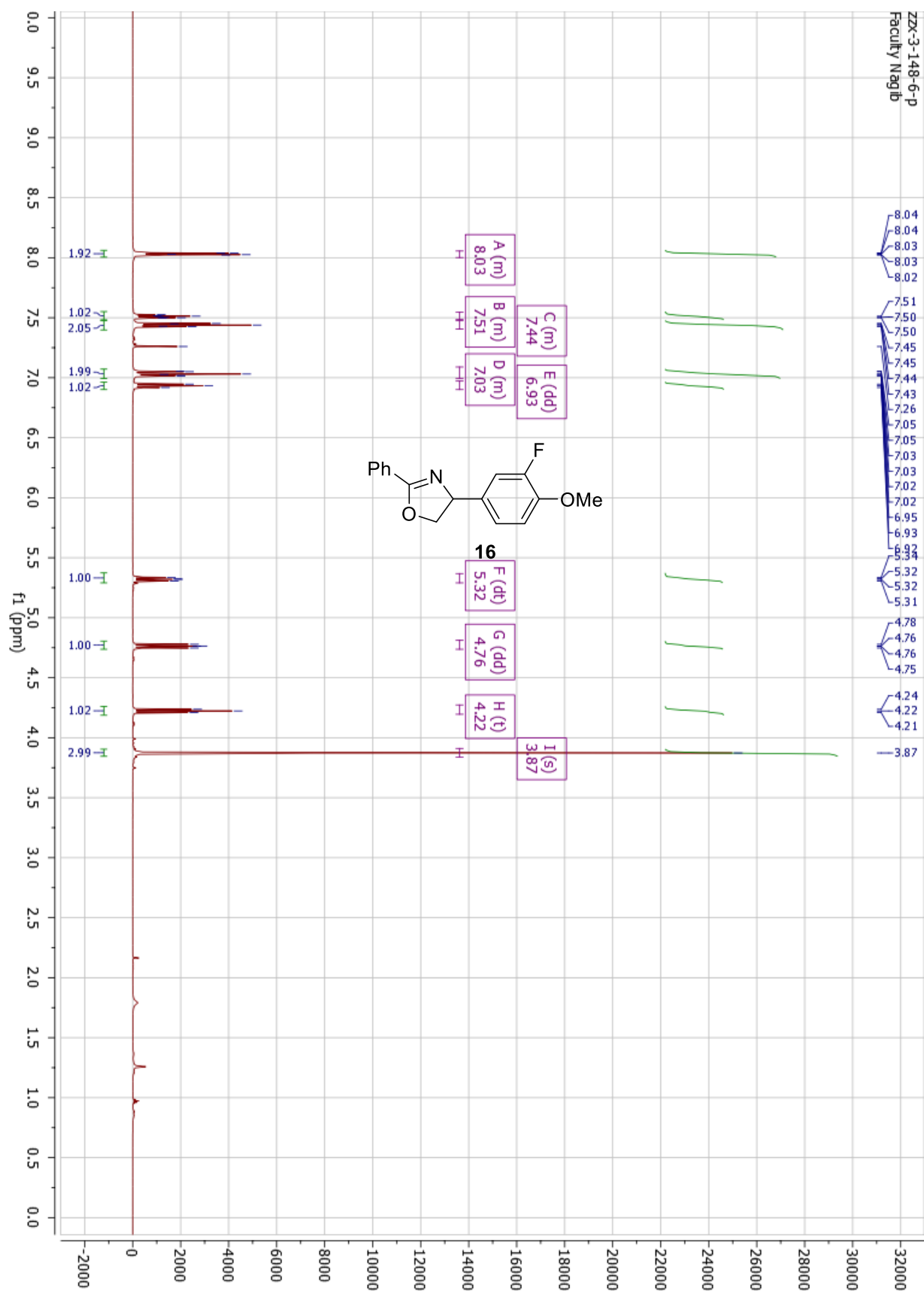




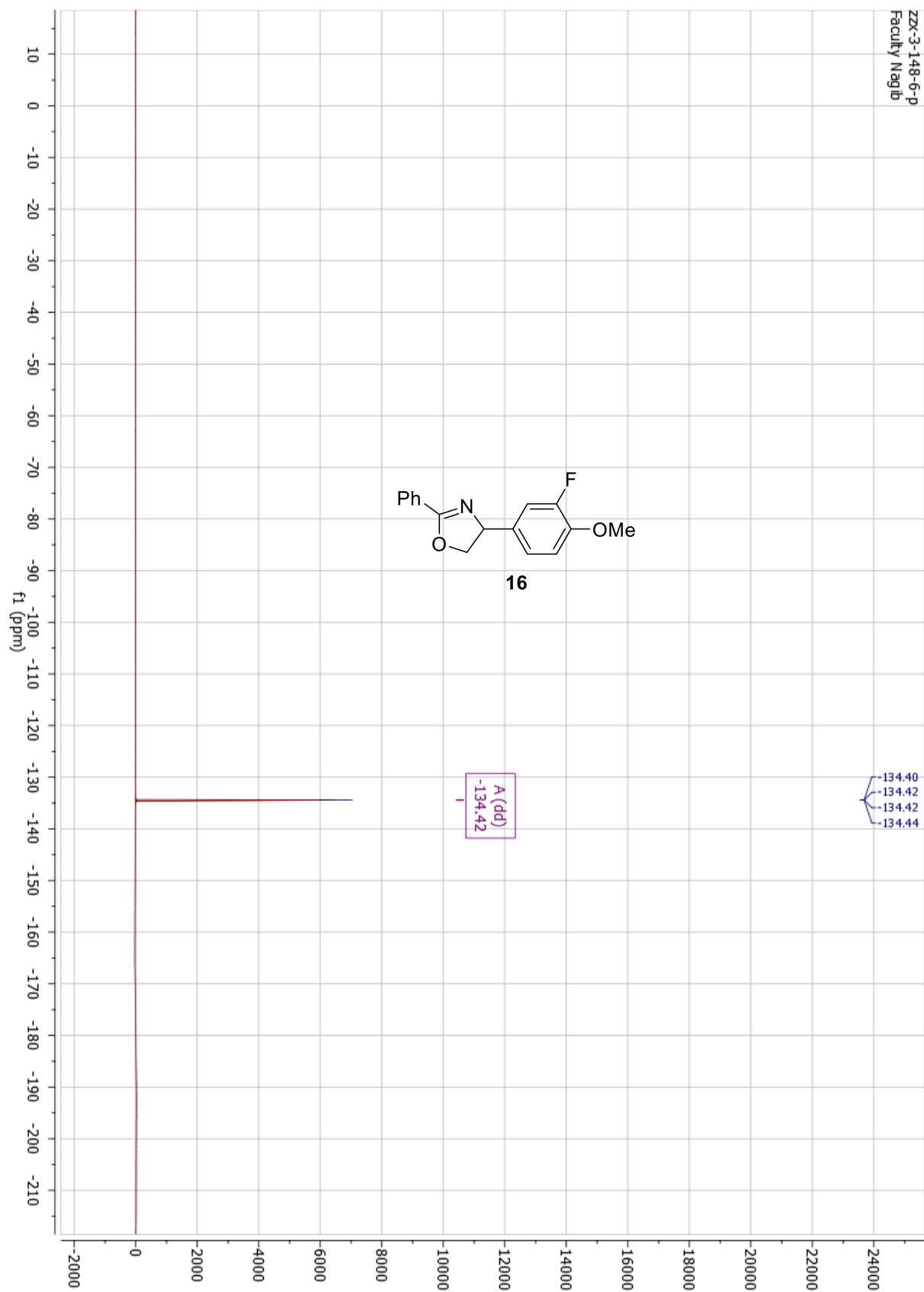


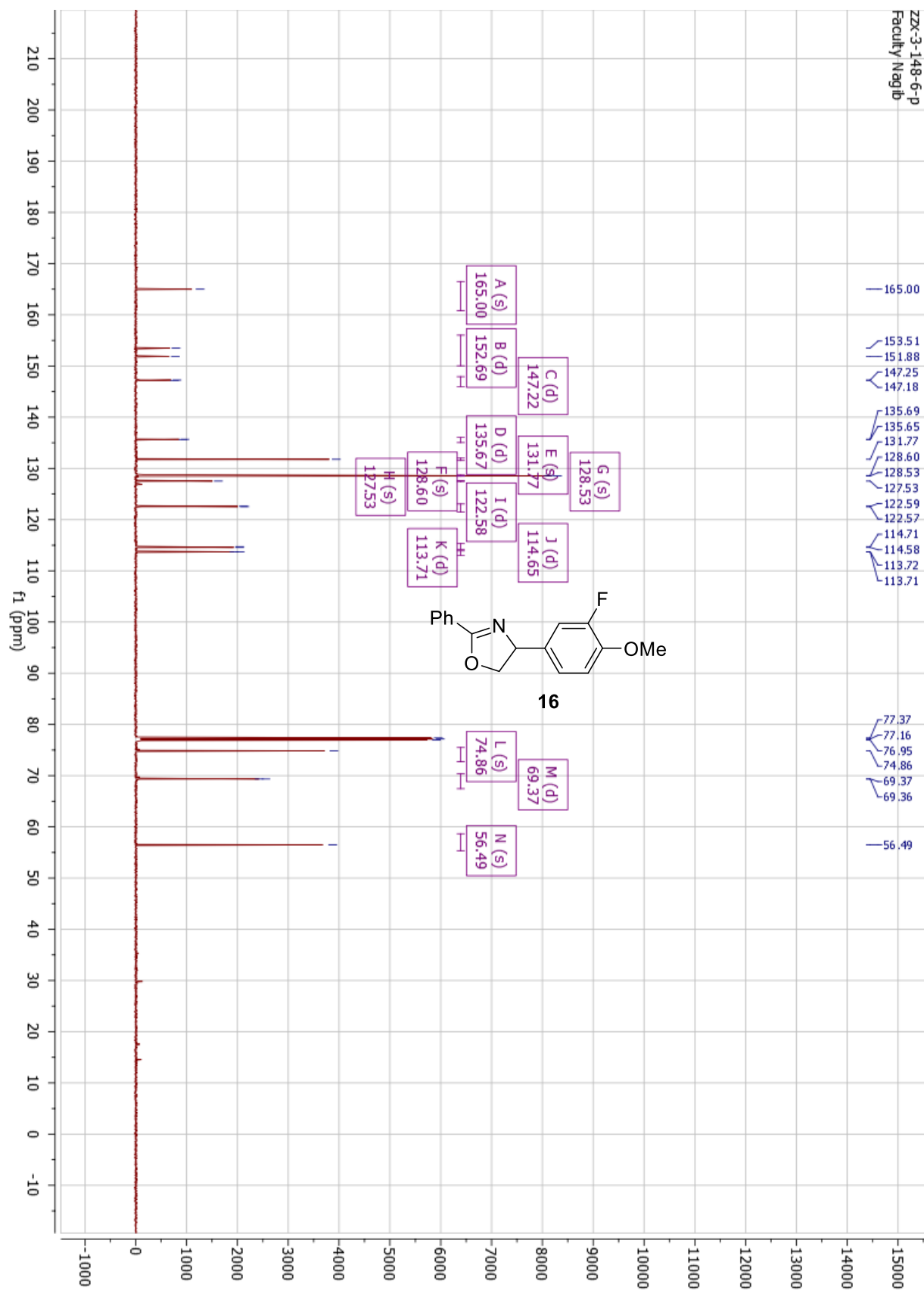


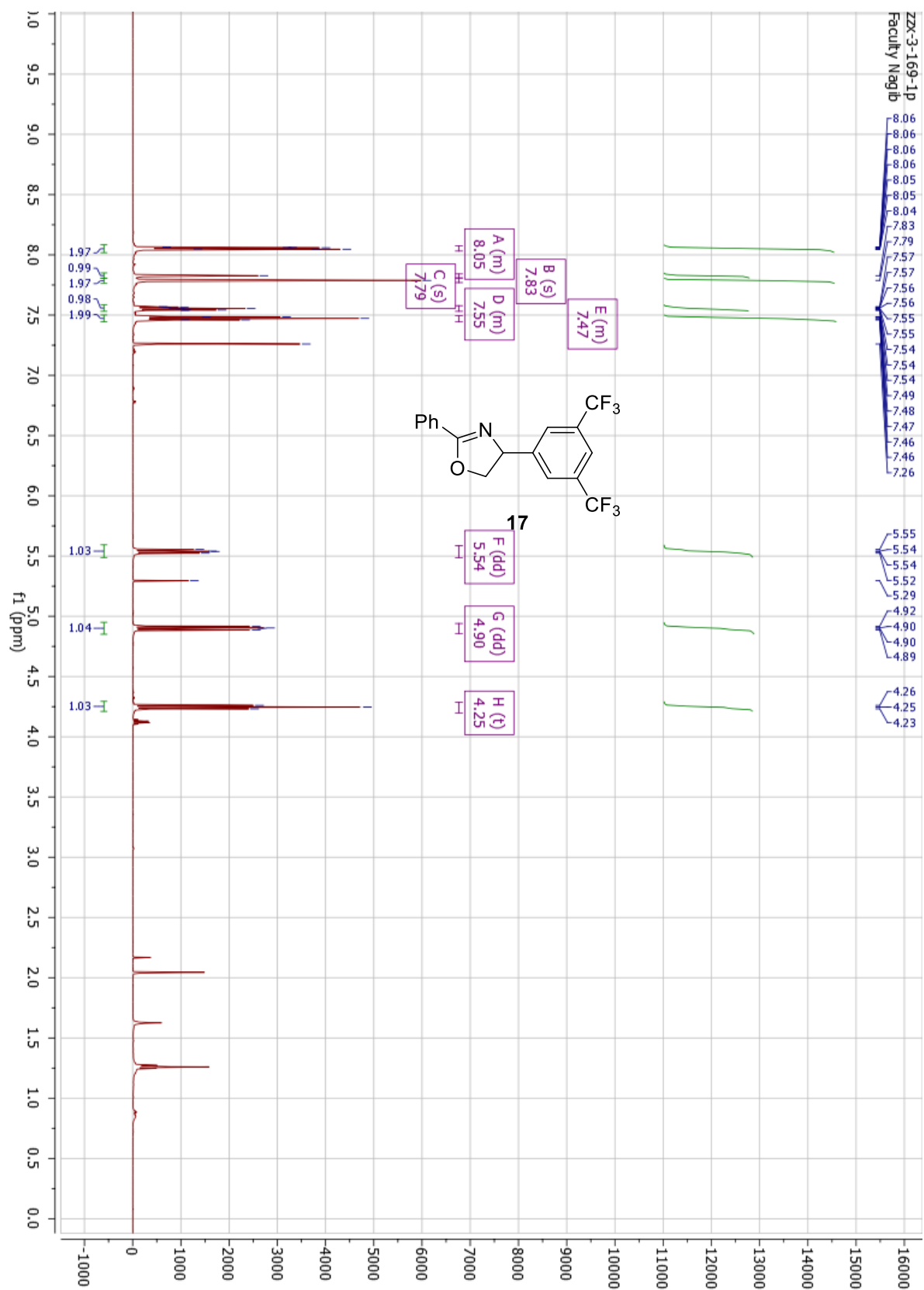


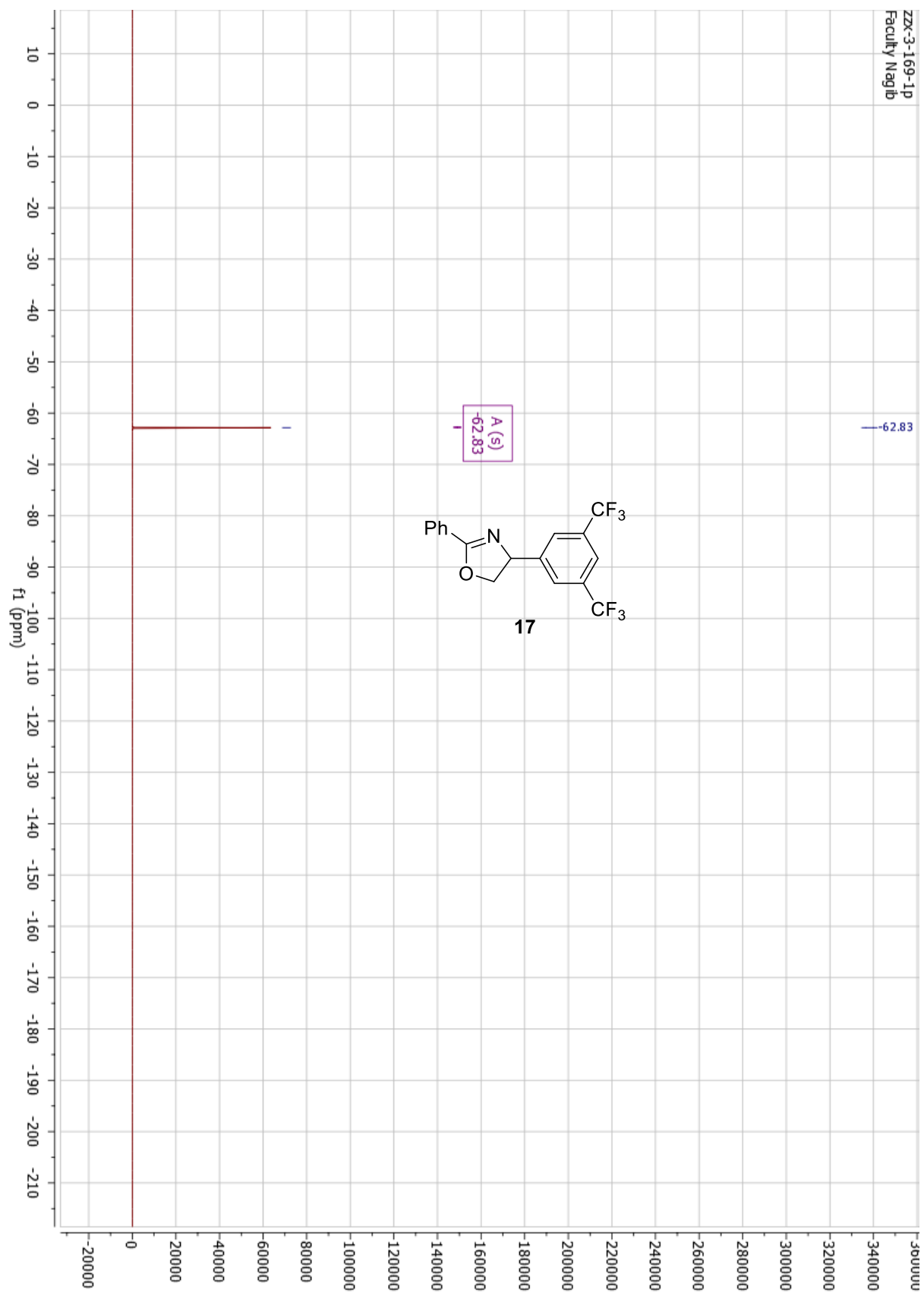


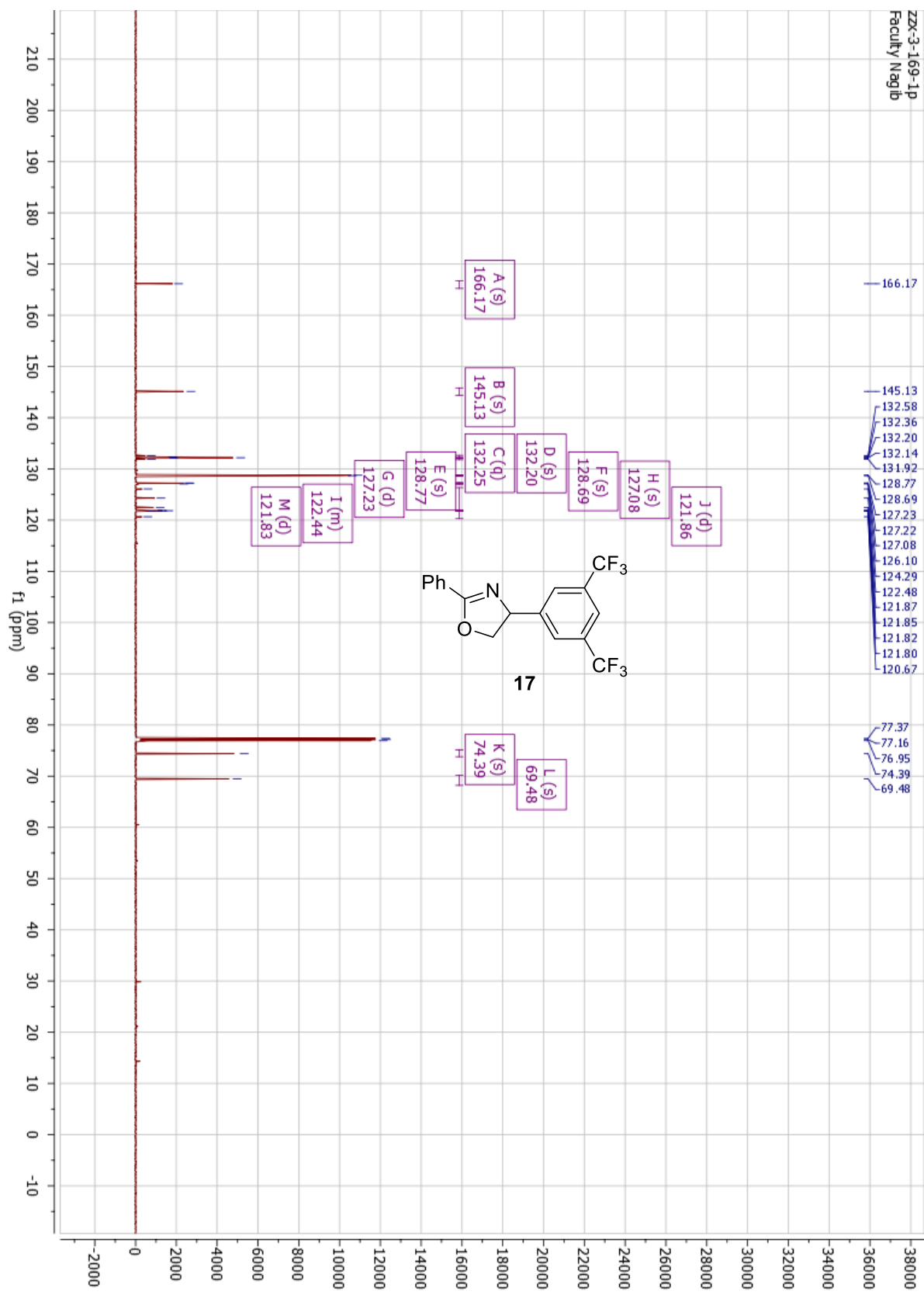


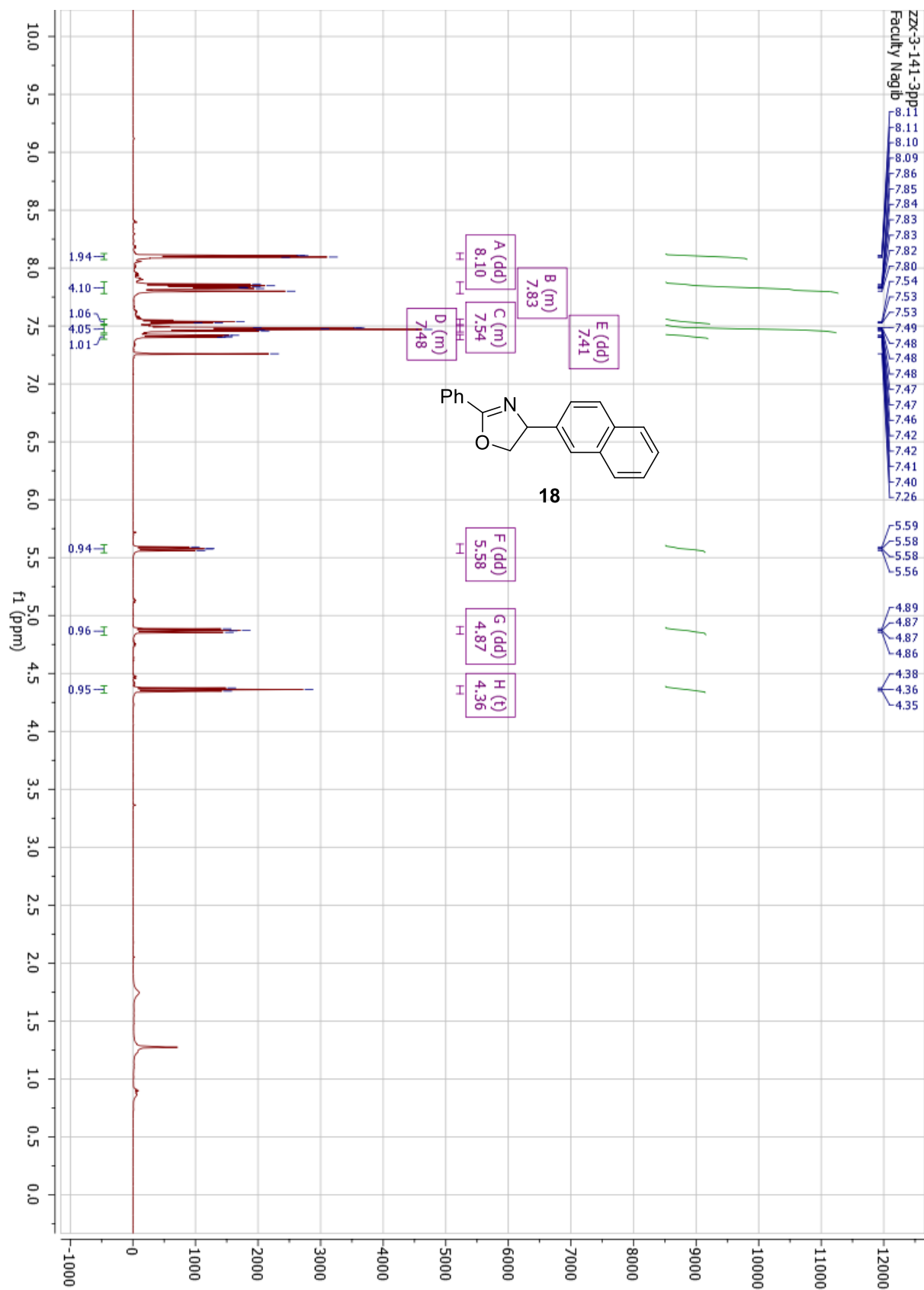


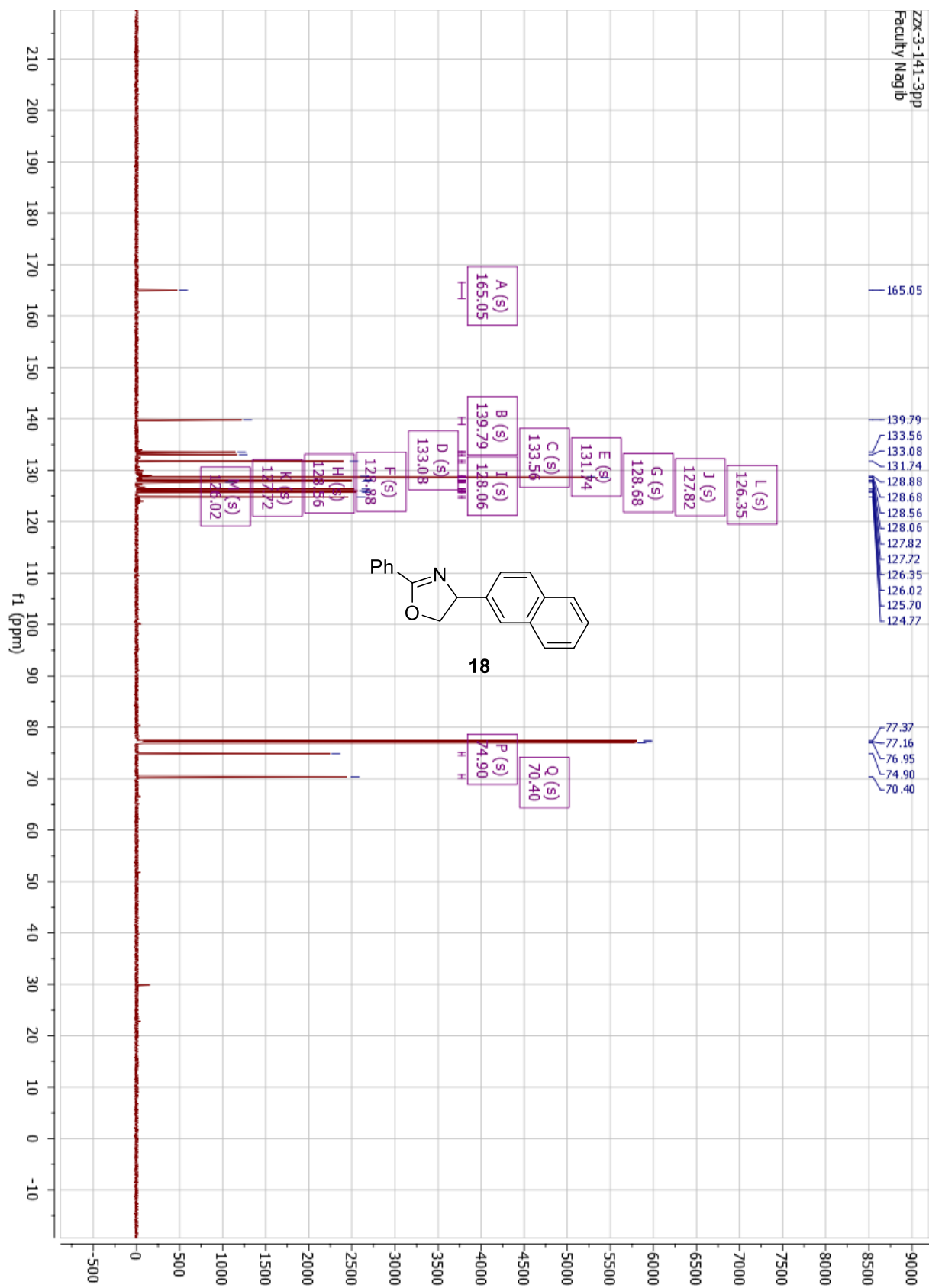


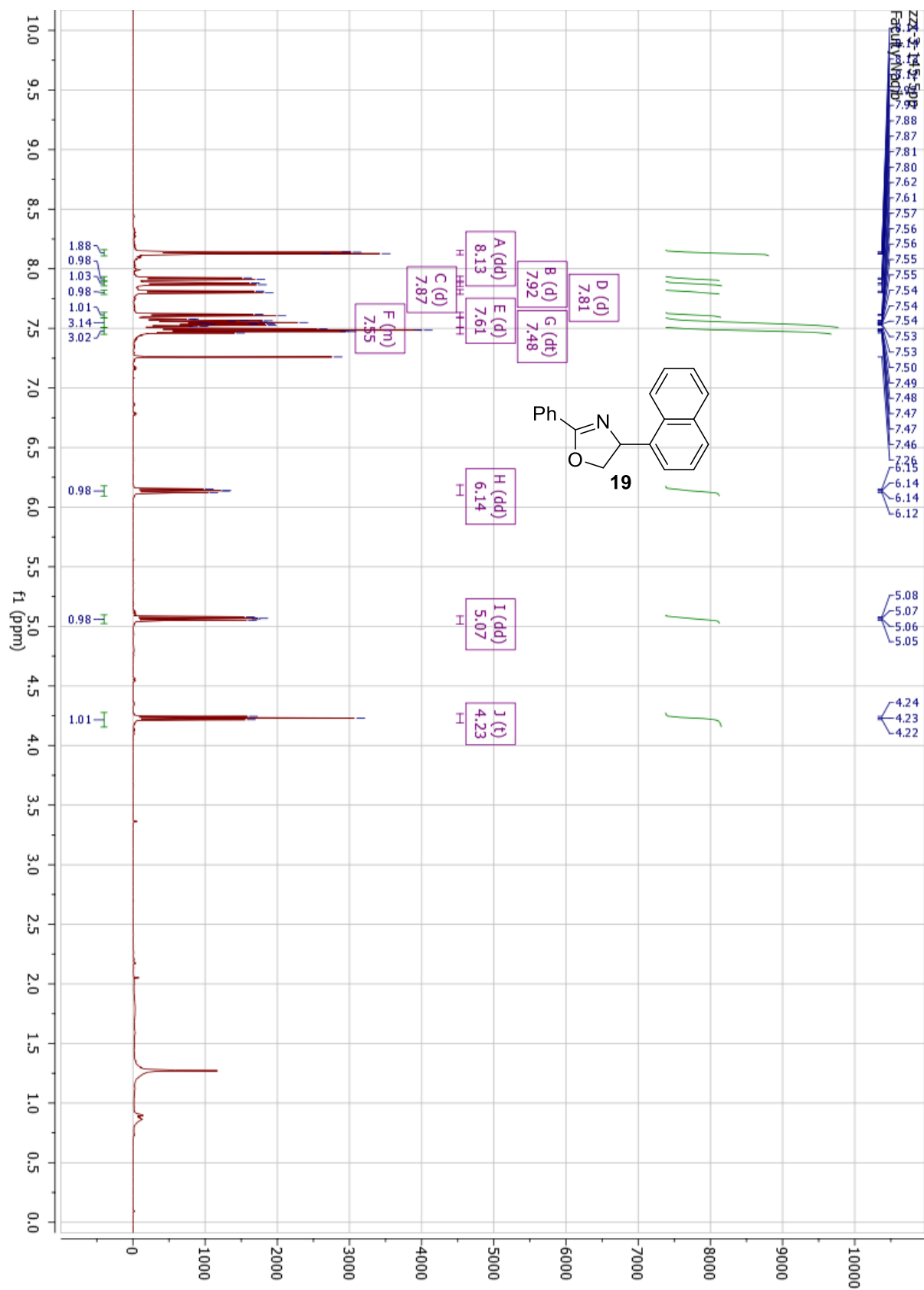




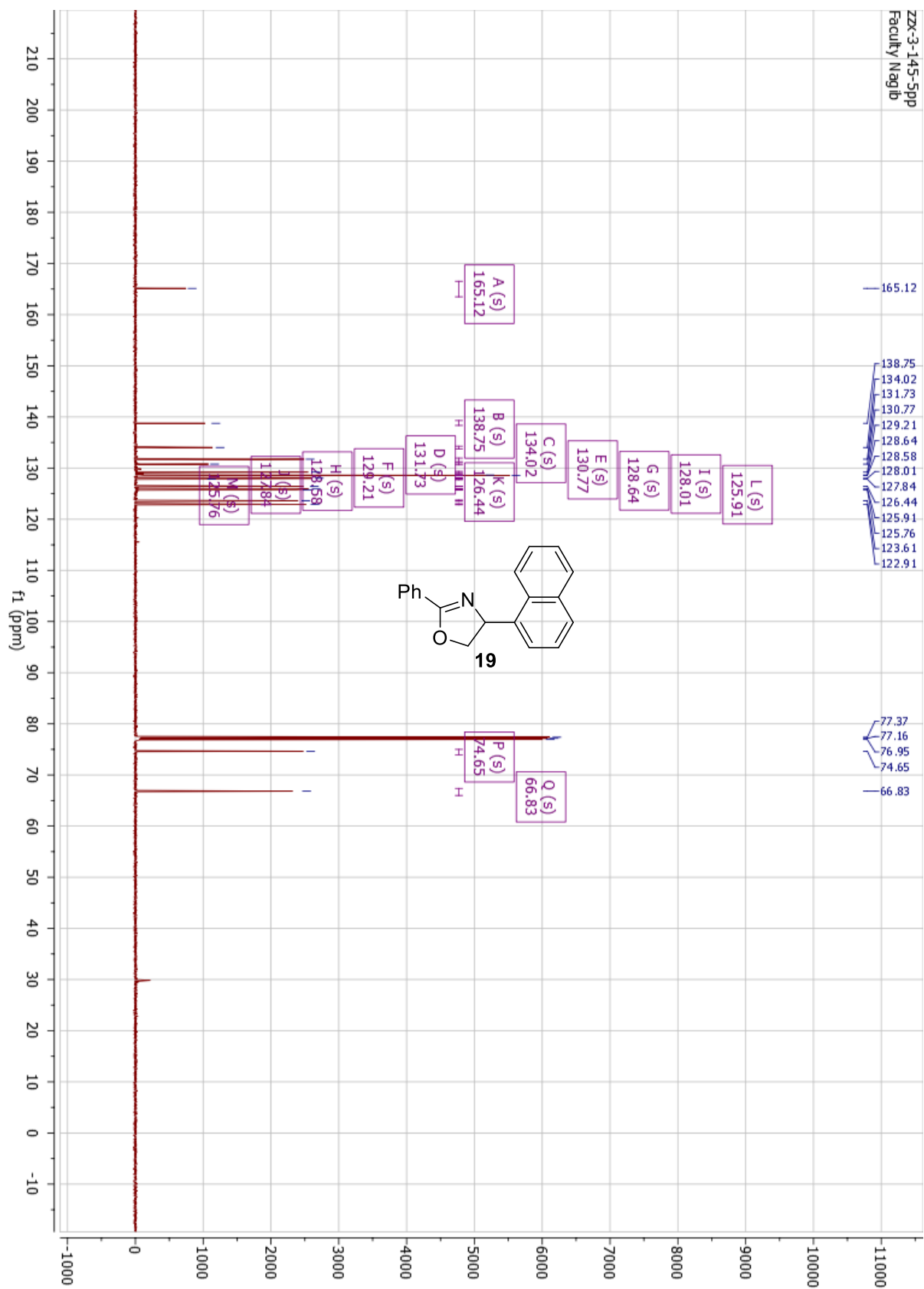


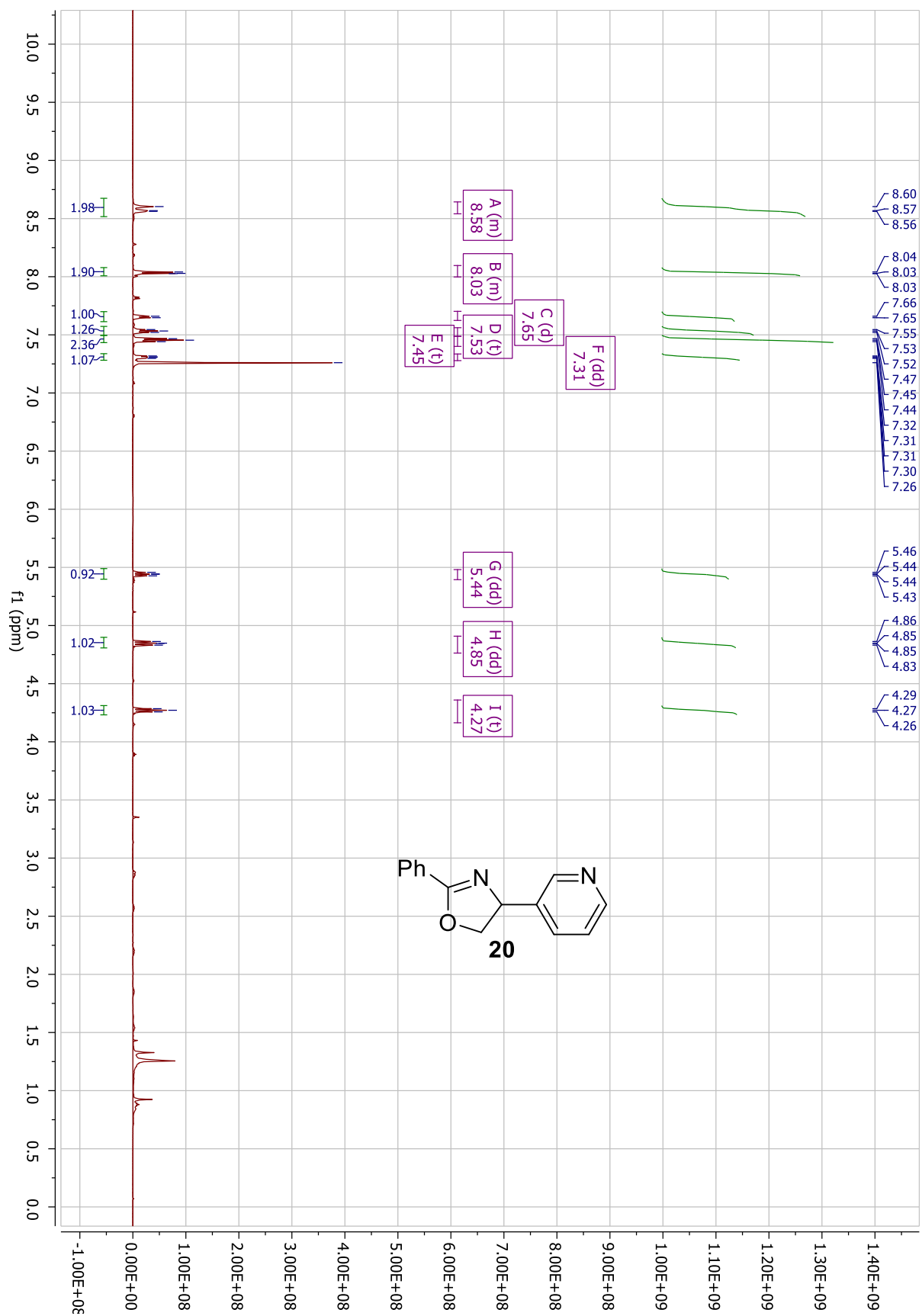


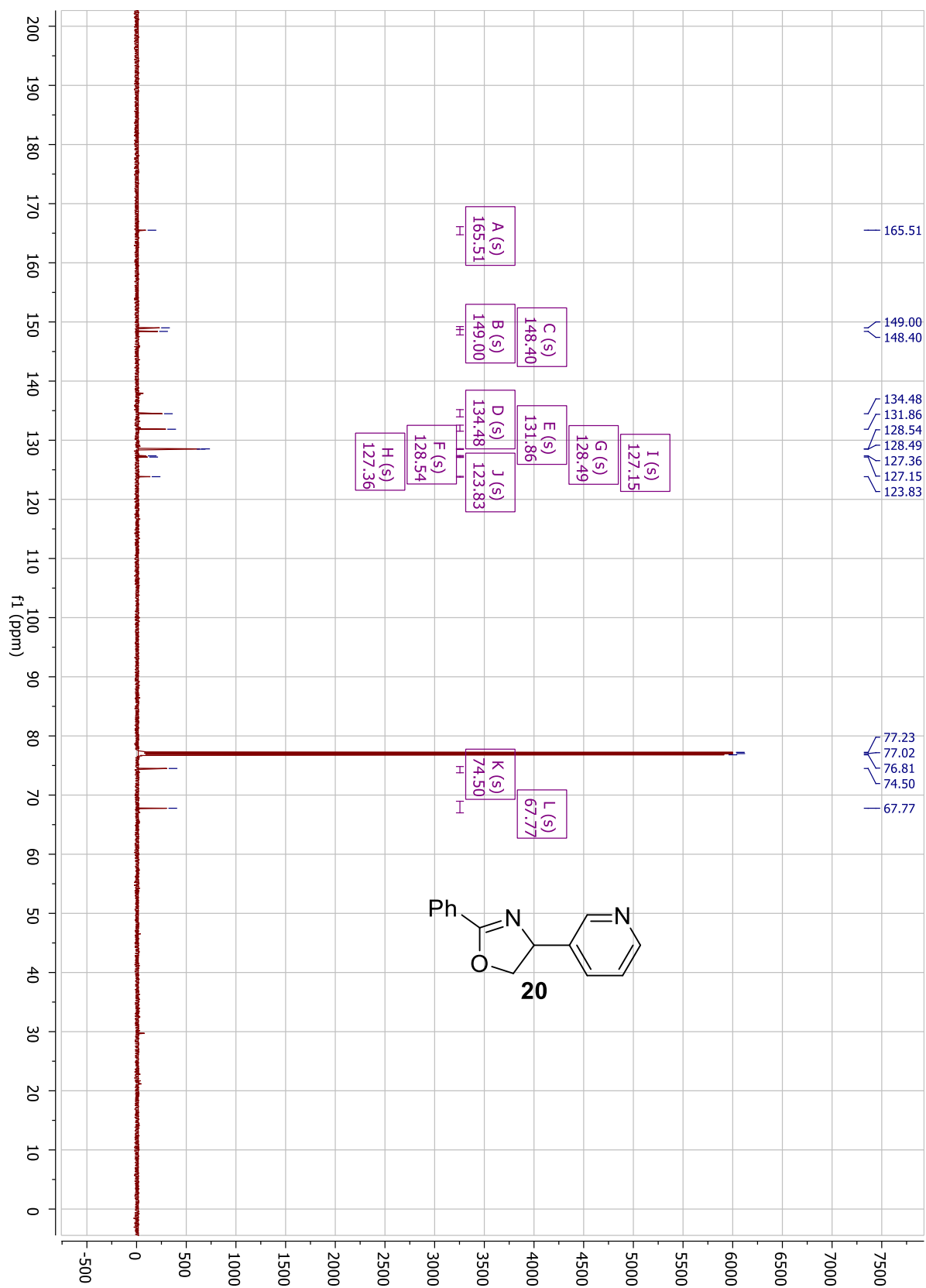


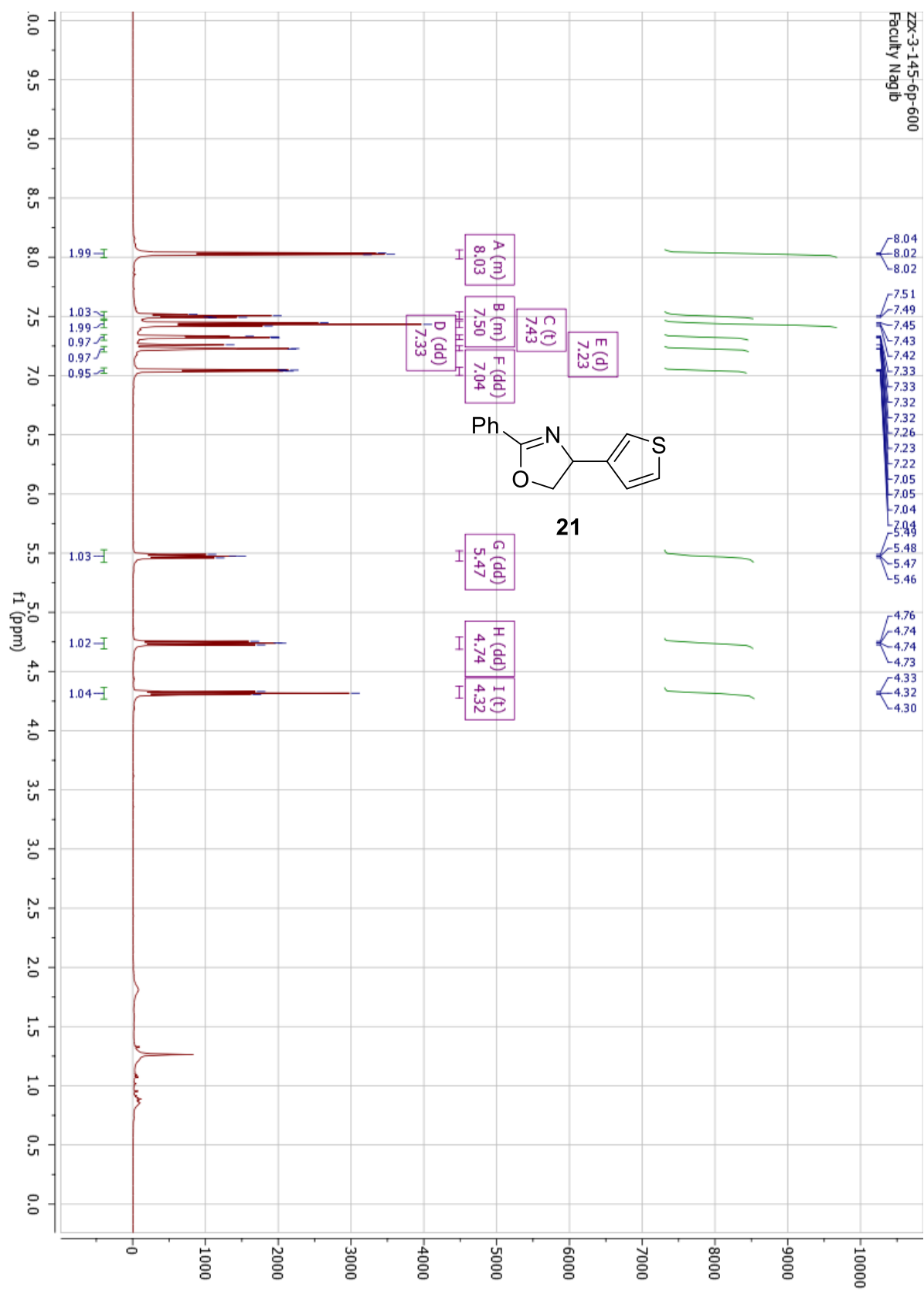


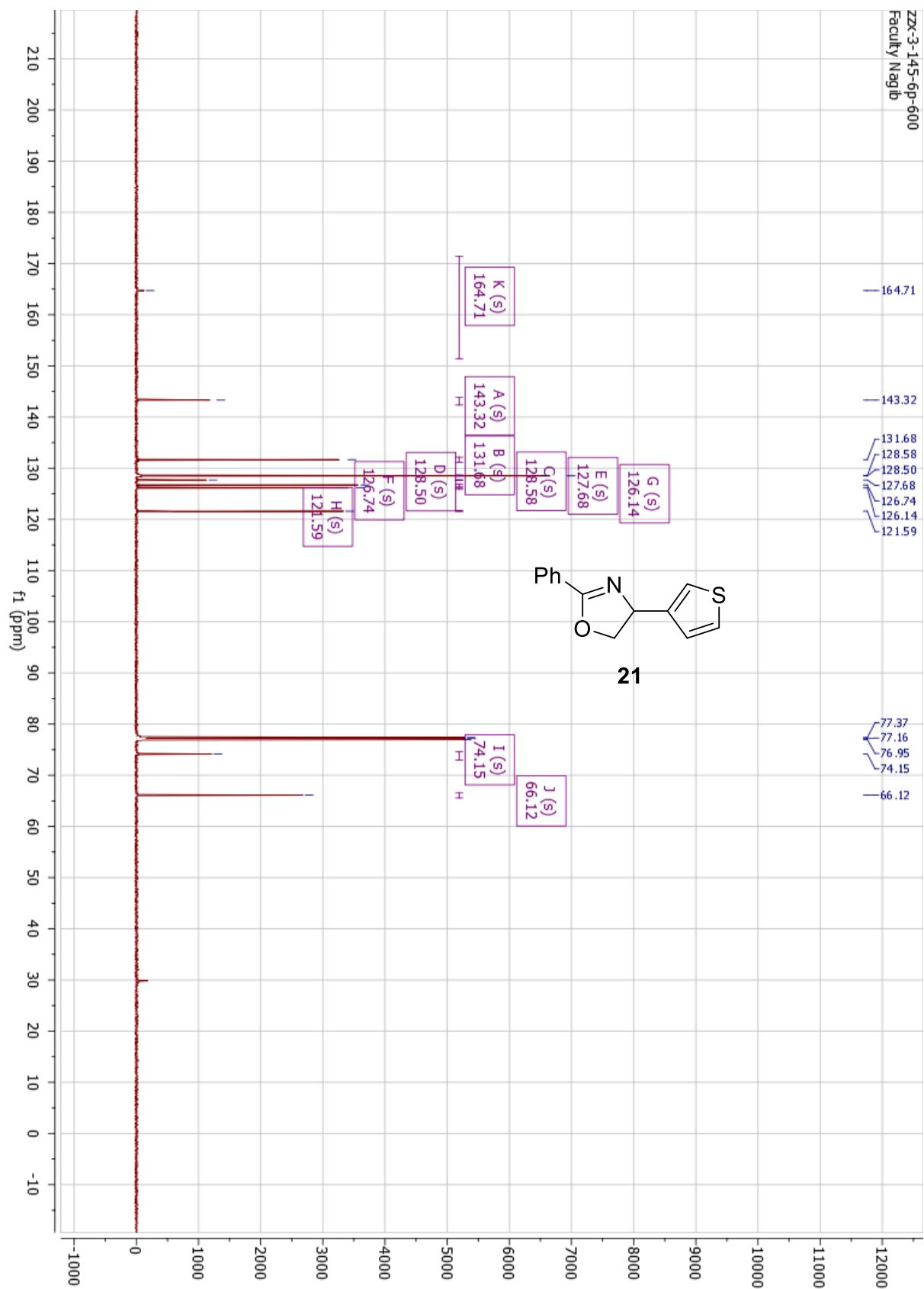


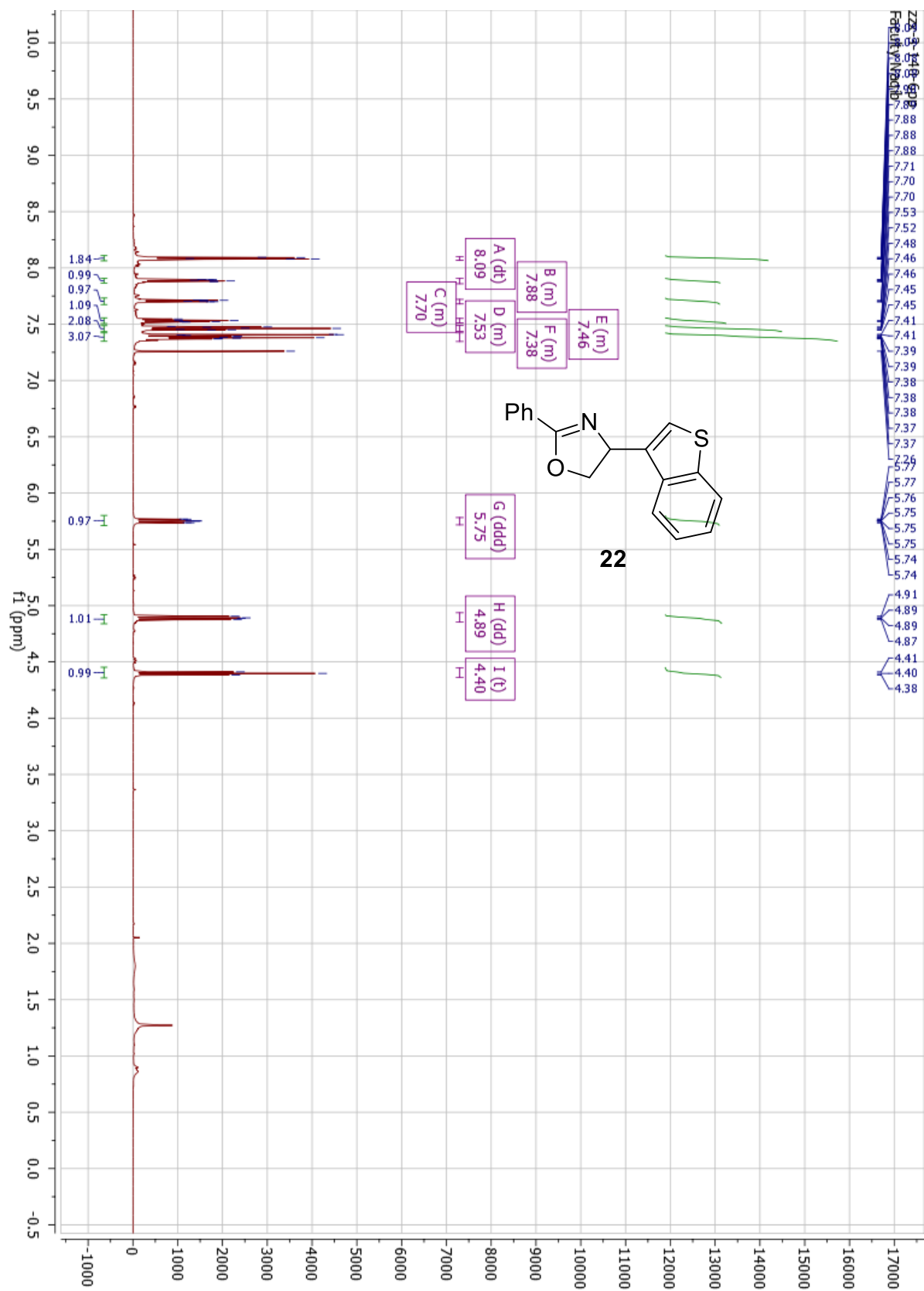


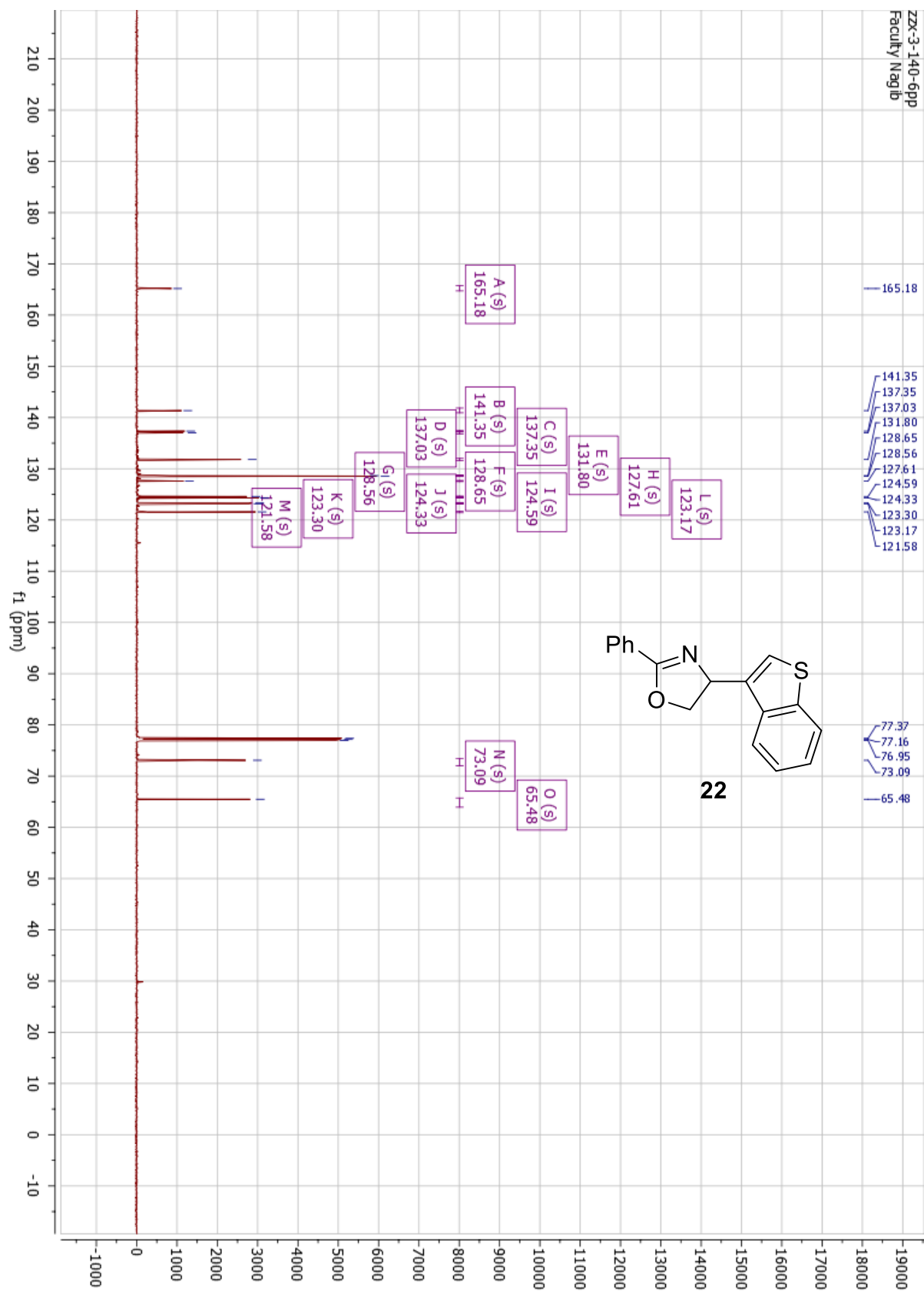


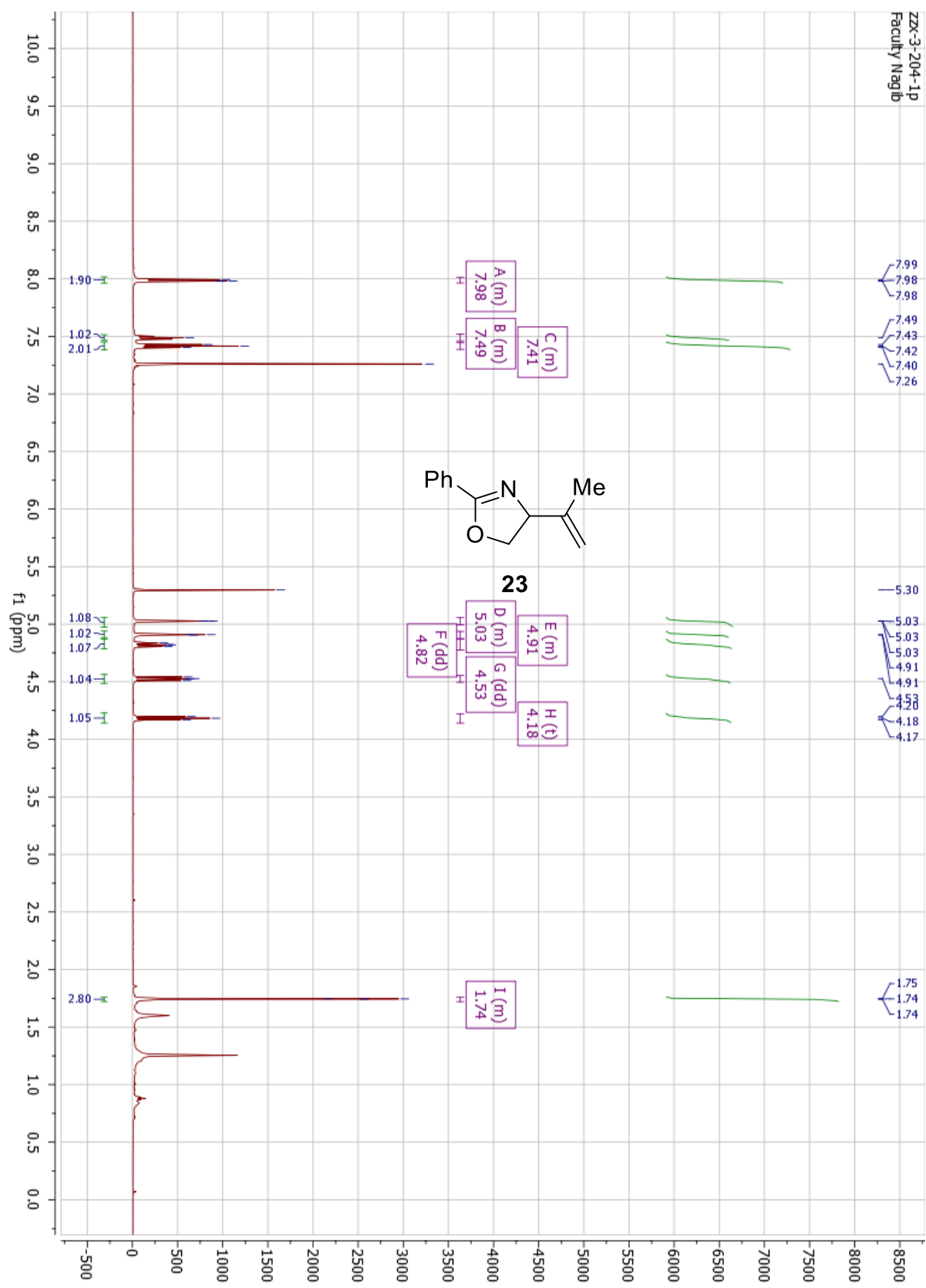




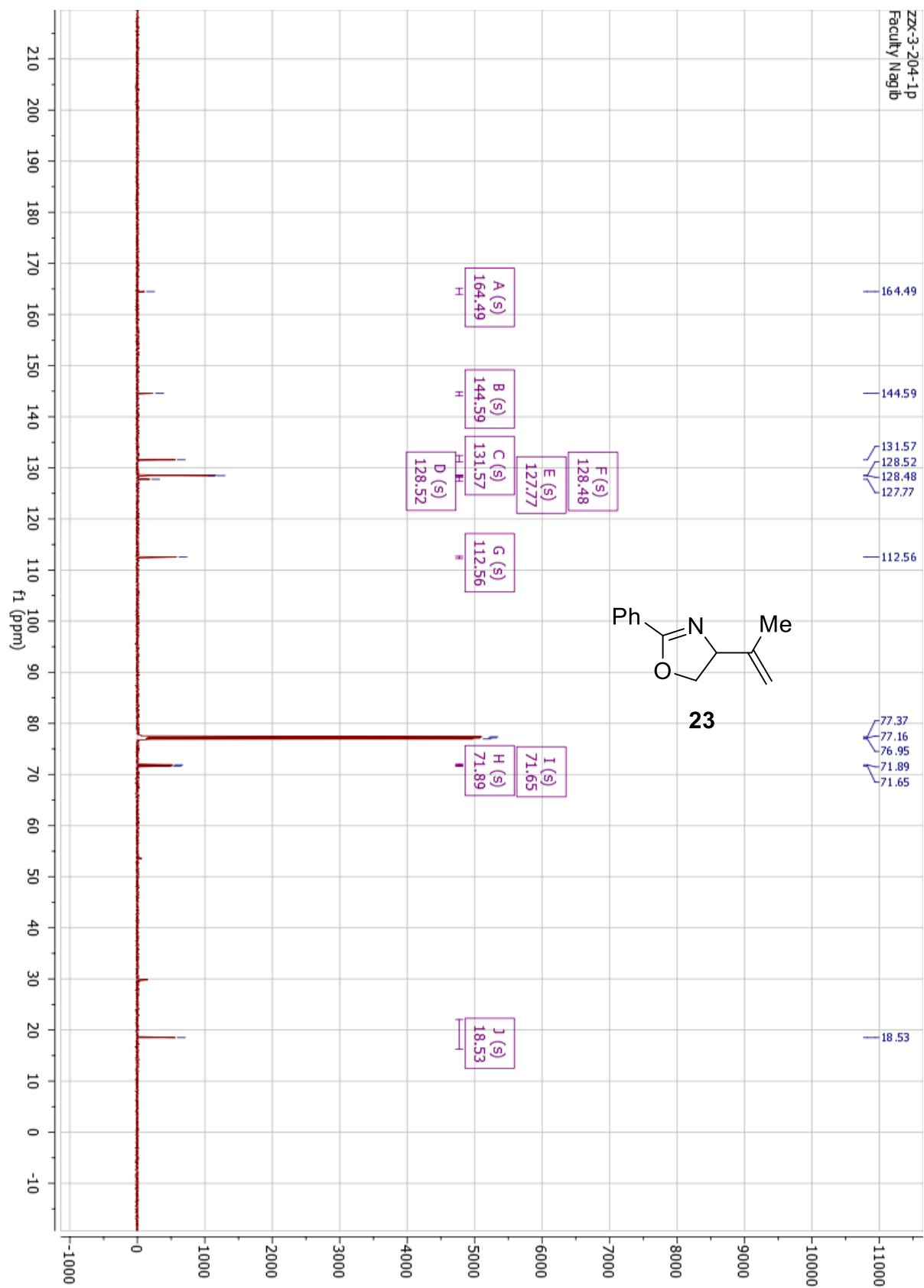


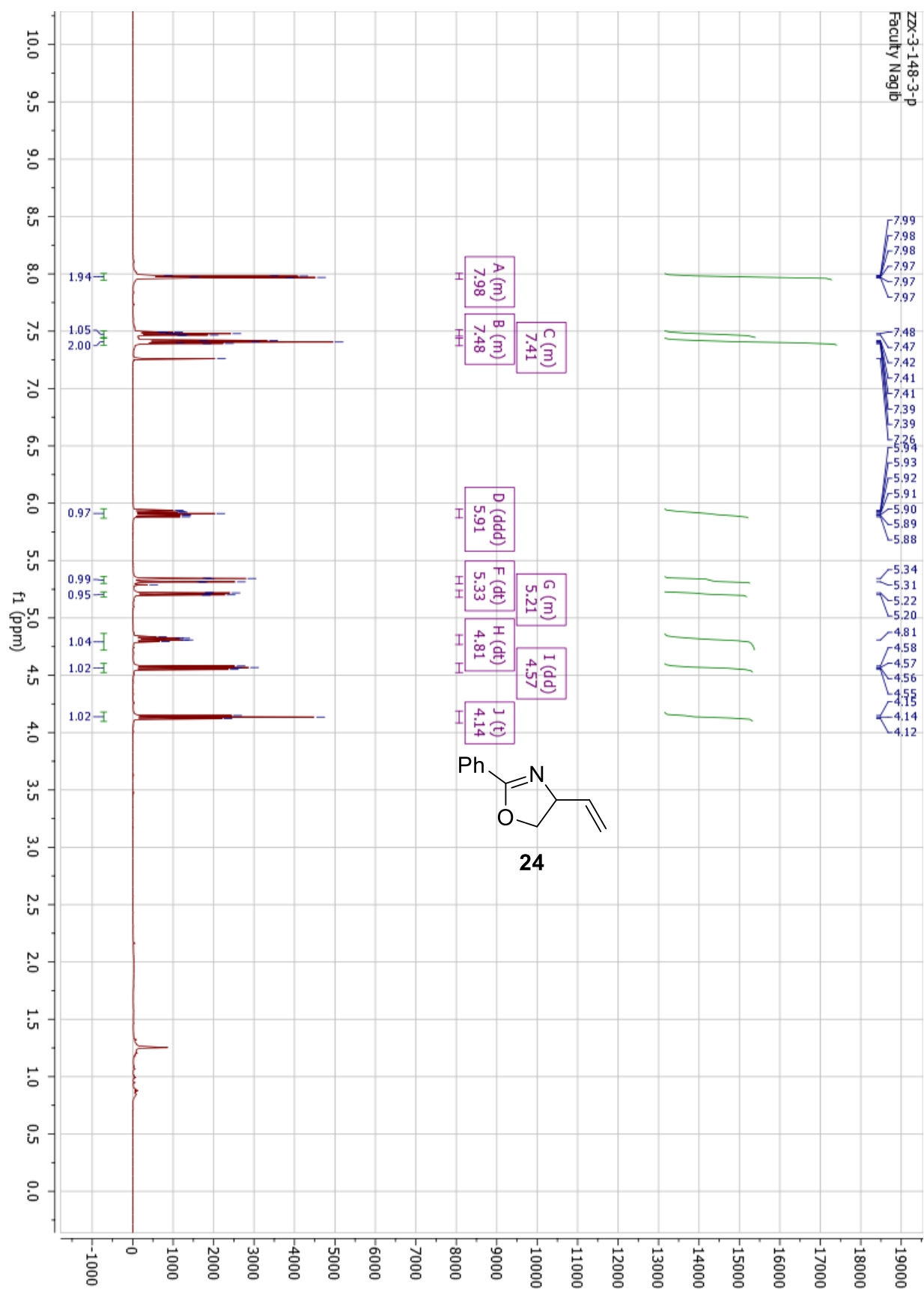


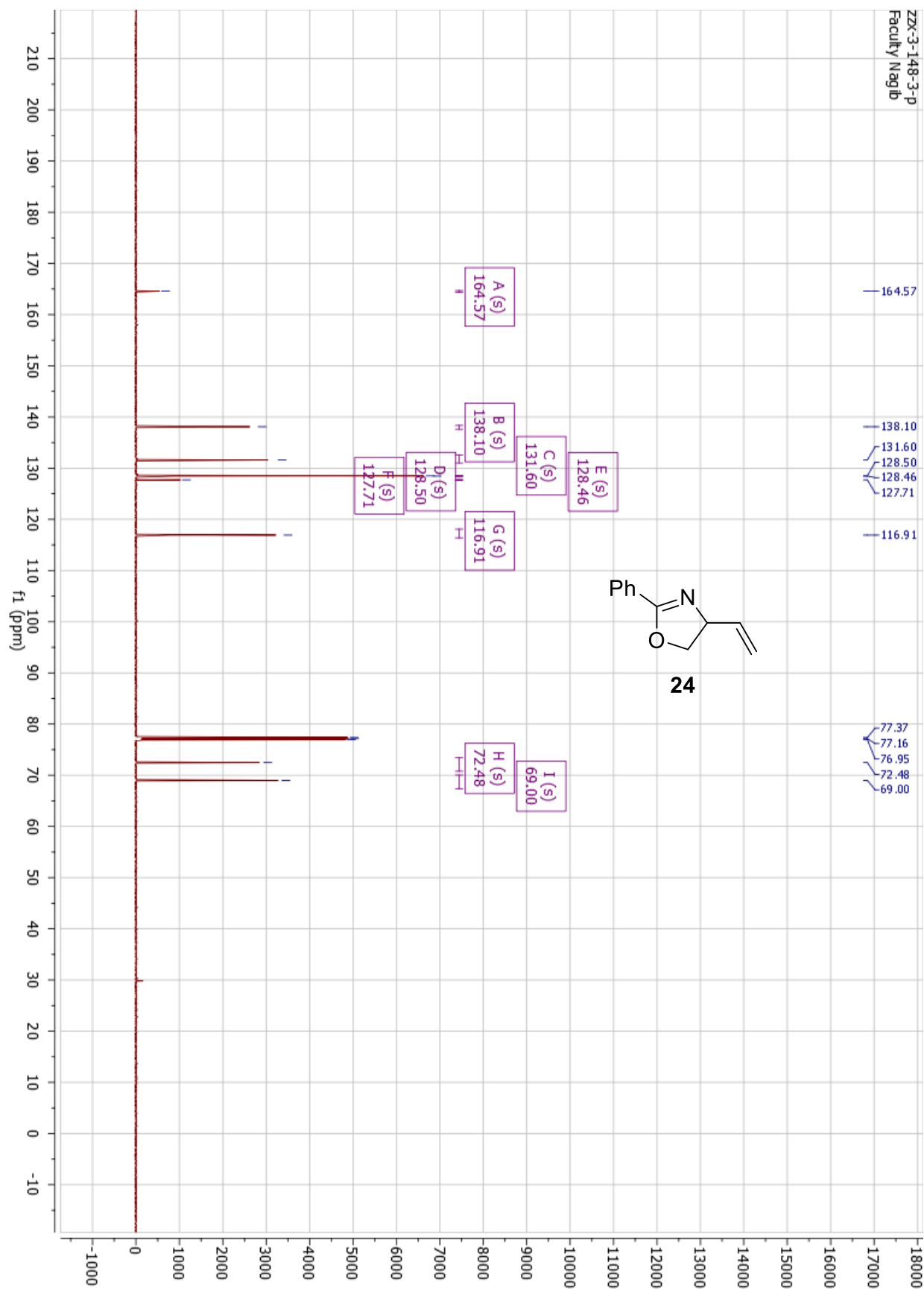


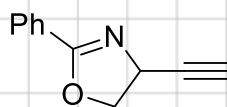












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