

*Supporting Information for:*

**Synthesis of chiral fluorinated acyclic quaternary carbon center via  
stereodefined polysubstituted silyl enolates**

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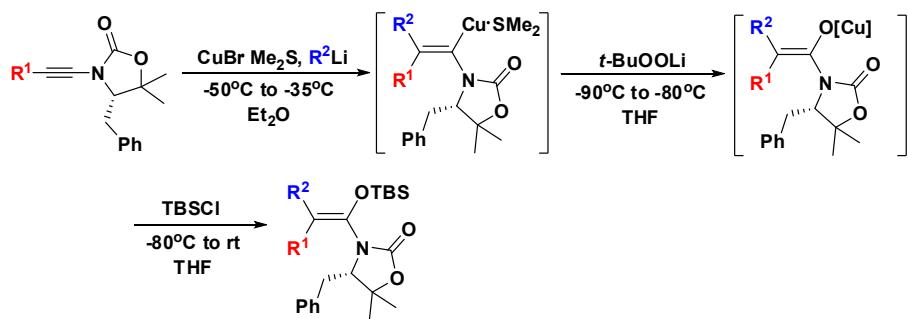
## 1. General information

All reactions were carried out in a flame-dried glassware under positive pressure of argon in dry solvents using standard Schlenk techniques unless otherwise indicated. Progress of the reactions was monitored by analytical TLC using glass plates pre-coated with silica gel with F254 indicator (Merck). Visualization of spots was done using UV light (254 nm), iodine, *p*-anisaldehyde, phosphomolybdic acid (PMA), and Hanessian's (cerium ammonium molybdate) stains. All organometallic compounds, dry solvents and reagents were transferred using plastic single-use graduated syringes and oven-dried stainless steel needles. Purification of crude mixtures was accomplished by preparative flash column chromatography on silica gel 60A (GraceResolv), aluminum oxide 90 neutral (Merck) or Florisil® Adsorbent 100-200 mesh (Fluka) using gradient mixtures of ethyl acetate / *n*hexane (unless otherwise indicated). <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Bruker Avance 200 (200 MHz <sup>1</sup>H, 50 MHz <sup>13</sup>C), Bruker Avance 300 (300 MHz <sup>1</sup>H, 75 MHz <sup>13</sup>C) or Bruker Avance AV 400 (400 MHz <sup>1</sup>H, 100 MHz <sup>13</sup>C) spectrometers. Chemical shifts values ( $\delta$ ) are reported in ppm (calibration of spectra to the residual peak of chloroform:  $\delta = 7.26$  ppm (s) for <sup>1</sup>H NMR;  $\delta = 77.00$  ppm for <sup>13</sup>C NMR). All the proton spectra reported as following:  $\delta$  value (multiplicity, J coupling constant (in Hz), number of nuclei). Multiplicity contractions used: (s) – singlet, (d) – doublet, (dd) – doublet of doublet, (t) – triplet, (q) – quartet, (m) – multiplet, and (br) – broad signal. Optical specific rotations are measured with an UniPol L 1000. High performance liquid chromatography (HPLC) spectra were recorded on AgilentTM 1100 Series equipment with a variable wavelength UV analytical detector. MS and HRMS mass spectrometry was carried out on a APCI instrument by Maxis Impact (Bruker) and on a LCT Premier (Waters).

All solvents were purified and dried immediately prior to use: THF and diethyl ether (HPLC grade, non-stabilized, BioLab) were dried using Innovative Technology PureSolv PS-MD-2 solvent purifier (aluminum oxide columns) and kept under positive pressure of nitrogen (99.9999% purity grade); toluene was distilled from sodium metal under argon; dichloromethane was distilled from calcium hydride under argon. Methyl lithium solution in diethyl ether (1.60 M), *n*-butyllithium solution in hexane (1.60 M), *n*-pentyllithium solution in heptane (2.20M), and *n*-hexyllithium solution in hexane (2.30M) were purchased from Aldrich and used as received. *tert*-Butylhydroperoxide (TBHP) solution in nonane (5.5 M, over 4Å MS) and terminal alkynes, *N*-bromosuccinimide, silver nitrate, (*S*)-4-benzyl-2-oxazolidinone, copper (I) bromide – dimethylsulfide complex, copper(II) sulfate pentahydrate, 1,10-phenanthroline, trimethylchlorosilane (TMSCl), triethylchlorosilane (TESCl), *tert*-butyldimethylsilyl chloride

(TBSCl), were purchased from commercial suppliers. (*S*)-5,5-dimethyl-4-benzyl -2-oxazolidinone (SuperQuat) and (*S*)-5,5-diethyl-4-benzyl -2-oxazolidinone was prepared from commercially available starting materials and reagents according to published procedure<sup>1</sup>. All starting chiral ynamides were prepared on a multi-gram scale according to a modified literature procedure<sup>2</sup>.

## 2. General procedure for the preparation of silyl enol ether derivatives



$\text{CuBr}\bullet\text{Me}_2\text{S}$  complex (1.10 mmol, 1.1 equiv) was placed into a flame-dried three-necked round-bottomed flask equipped with a magnetic stirring bar and connected to an argon line. Dry diethyl ether (10.0 ml) was added through a septum, and the system was cooled to  $-50^\circ\text{C}$  using acetone-liquid nitrogen bath. A solution of alkyllithium (1.30 mmol, 1.3 equiv), was added dropwise, and the reaction mixture was allowed to warm to  $-40^\circ\text{C}$  and stirred for 30 min at this temperature to form a bright yellow opaque solution in case of methylolithium, dark-yellow in case of *n*-butyllithium, orange to dark-brown in case of *n*-pentyl and *n*-hexyllithium. The reaction mixture was cooled to  $-50^\circ\text{C}$  and a solution of the starting alkynyl carbamate (1.00 mmol, 1.0 equiv) in 3 ml of diethyl ether was added dropwise; the reaction mixture was allowed to warm to  $-40^\circ\text{C}$ , and stirred at this temperature for 1 h (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent) to form a solution of vinylcuprate.

In a separate flask connected to an argon line, a solution of 1.54 mmol (1.54 equiv) of *t*-BuOOtLi was prepared as follow. Dry THF (5.0 ml) was added to flame dried three-necked round-bottomed flask *via* a syringe followed by addition of a solution of *tert*-butyl hydroperoxide in nonane (0.28 ml of commercially available 5.5 M solution; 1.54 equiv, 1.54 mmol). The resulting solution was cooled to  $-90^\circ\text{C}$  and a solution of methylolithium (1.60 M in diethyl ether, 1.80 mmol, 1.80 equiv) was added dropwise keeping the indicated temperature. The resulting solution of lithium *tert*butyleroxide was allowed to warm to  $-80^\circ\text{C}$  and stir for 10 min prior to use in the following reaction step. Upon completion of the first step, the reaction mixture was cooled to  $-90^\circ\text{C}$  and the freshly prepared solution of lithium *tert*-butyleroxide in THF (1.54 mmol, 1.54 equiv) was transferred *via* a cannula. The resulting reaction mixture was allowed to warm up slowly to  $-80^\circ\text{C}$  and stirred at the indicated temperature for 2 h (monitored by TLC on

silica gel using 20% ethyl acetate in hexane as eluent) to form a brown opaque solution.

Upon completion of the second step, *tert*-butyldimethylsilyl chloride (TBSCl) (3.2 mmol, 3 equiv) in 5 ml THF was added to the reaction mixture at -80 °C and then warm up to room temperature. The mixture was stirred for about 3 hours (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent). The reaction mixture was filtered through prewashed short pad of silica, and then washed thoroughly with 20% ethyl acetate in hexane. The solvent was evaporated and pure product silyl enol ether was obtained by flash column chromatography (SiO<sub>2</sub>, eluting with 50:1 to 15:1 hexane/ethyl acetate).

### 3. General procedure for the fluorination reaction

1.5 ml solvent was added to a flame-dried tube contained silyl enol ether (0.1 mmol), and then stirred at the indicated temperature. “F” source (1.4 eq ) was added to the reaction mixture, and then slowly warm up to room temperature overnight. After the starting material was consumed completely (monitored by TLC), 2 ml water (2 ml) was added to the reaction mixture to quench the reaction. The aqueous solution was extracted with diethyl ether (3 × 5 mL) and the organic layer was combined, dried (anhydrous Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo. The dr was determined by <sup>19</sup>F NMR of the crude product, and pure product was obtained by column chromatography.

Screening of additives (LiCl, AcOLi, LiF, CsF, Sm(OTf)<sub>3</sub>, Zn(OTf)<sub>2</sub>, Sc(OTf)<sub>3</sub>) experiments give no better results.

### 4. Analytical datas of silyl enol ether derivatives and fluorination products

#### (*S,E*)-4-benzyl-3-(1-(*tert*-butyldimethylsilyloxy)-2-methylhex-1-enyl)-5,5-dimethyloxazolidin-2-one (**1g<sub>a</sub>**)

Purification was performed with hexane/ethyl acetate = 25/1 to provide **1G<sub>a</sub>** in 65% yield as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.08-0.14 (m, 6H), 0.83-0.88 (m, 3H), 0.91 (s, 9H), 1.00 (s, 3H), 1.21-1.29 (m, 4H), 1.34 (s, 3H), 1.41-1.48 (m, 1H), 1.59 (s, 3H), 1.94-2.03 (m, 1H), 2.48 (dd, *J* = 14.0, 10.4 Hz, 1H), 3.00 (dd, *J* = 14.0, 4.0 Hz, 1H), 3.93 (dd, *J* = 10.4, 4.0 Hz, 1H), 7.02-7.25 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.2, -3.9, 14.1, 15.1, 18.0, 22.5, 23.0, 25.7, 27.3, 30.0, 32.0, 33.7, 65.1, 81.5, 118.0, 126.7, 128.6, 128.9, 131.9, 136.8, 154.7; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 22.2; [MH]<sup>+</sup> Calcd. for C<sub>25</sub>H<sub>42</sub>NO<sub>3</sub>Si 432.2928; found: 432.2933

#### (*S,E*)-4-benzyl-3-(1-(*tert*-butyldimethylsilyloxy)-2-methyloct-1-enyl)-5,5-dimethyloxazolidin-2-one (**1g<sub>b</sub>**)

Purification was performed with hexane/ethyl acetate = 25/1 to provide **1G<sub>b</sub>** in 72% yield as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.08 (s, 3H), 0.13 (s, 3H), 0.82 (s, 3H), 0.90-1.02 (m, 12H), 1.05-1.25 (m, 7H), 1.34 (s, 3H), 1.42-1.52 (m, 1H), 1.59 (s, 3H), 1.85-2.05 (m, 2H), 2.45-2.53 (m, 1H), 2.96-3.05 (m, 1H), 3.91-3.95 (m, 1H), 7.05-7.25 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.2, -3.9, 14.1, 15.1, 18.0, 22.4, 22.6, 25.7, 27.3, 27.8, 29.6, 31.8, 32.3, 33.7, 65.0, 81.5, 118.0, 126.7, 128.6, 128.8, 132.0, 136.8, 154.7; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 22.2; [MH]<sup>+</sup> Calcd. for C<sub>27</sub>H<sub>46</sub>NO<sub>3</sub>Si 460.3241; found: 460.3304

*(S,E)*-4-benzyl-3-(1-(tert-butyldimethylsilyloxy)-2-ethyloct-1-enyl)-5,5-dimethyloxazolidin-2-one  
**(1g<sub>c</sub>)**

Purification was performed with hexane/ethyl acetate = 25/1 to provide **1g<sub>c</sub>** in 56% yield as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.09 (s, 3H), 0.15 (s, 3H), 0.80-1.00 (m, 18H), 1.15-1.30 (m, 7H), 1.34 (s, 3H), 1.40-1.52 (m, 1H), 1.85-2.05 (m, 3H), 2.08-2.20 (m, 1H), 2.48 (dd, *J* = 13.2, 10.8 Hz, 1H), 3.01 (dd, *J* = 14.0, 3.2 Hz, 1H), 3.94 (dd, *J* = 10.8, 3.2 Hz, 1H), 6.90-7.30 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.4, -3.8, 12.3, 14.0, 18.0, 21.5, 22.5, 22.7, 25.7, 27.3, 27.8, 29.7, 29.9, 31.8, 33.4, 65.1, 81.5, 124.0, 126.8, 128.7, 128.9, 131.7, 136.9, 154.7; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 21.5; [MH]<sup>+</sup> Calcd. for C<sub>28</sub>H<sub>48</sub>NO<sub>3</sub>Si 474.3403; found: 474.3396

*(S,E)*-4-benzyl-3-(2-butyl-1-(tert-butyldimethylsilyloxy)oct-1-enyl)-5,5-dimethyloxazolidin-2-one  
**(1g<sub>d</sub>)**

Purification was performed with hexane/ethyl acetate = 25/1 to provide **1g<sub>d</sub>** in 58% yield as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.09 (s, 3H), 0.15 (s, 3H), 0.80-0.85 (m, 6H), 0.92 (s, 9H), 0.96 (s, 3H), 1.15-1.30 (m, 11H), 1.34 (s, 3H), 1.40-1.50 (m, 1H), 1.85-2.12 (m, 3H), 2.10-2.20 (m, 1H), 2.47 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.00 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.93 (dd, *J* = 10.8, 4.0 Hz, 1H), 7.07-7.26 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.4, -3.9, 14.0, 14.1, 18.0, 22.4, 22.6, 23.0, 25.7, 27.3, 27.8, 28.2, 29.8, 29.9, 30.0, 31.7, 33.3, 65.1, 81.5, 122.8, 126.8, 128.7, 128.8, 131.9, 136.9, 154.7; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 21.6; [MH]<sup>+</sup> Calcd. for C<sub>30</sub>H<sub>52</sub>NO<sub>3</sub>Si 502.3711; found: 502.3734

*(S,E)*-4-benzyl-3-(1-(tert-butyldimethylsilyloxy)-2-methyl-4-phenylbut-1-enyl)-5,5-dimethyloxazolidin-2-one  
**(1g<sub>e</sub>)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **1g<sub>e</sub>** in 61% yield as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.09 (s, 3H), 0.16 (s, 3H), 0.92 (s, 9H), 0.95 (s, 3H), 1.25 (s, 3H), 1.67 (s, 3H), 2.07-2.13 (m, 1H), 2.20-2.27 (m, 1H), 2.28-2.38 (m, 1H), 2.60-2.70 (m, 1H), 2.75-2.83 (m, 2H), 3.89 (dd, *J* = 10.4, 4.0 Hz, 1H), 7.00-7.24 (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.2, -4.0, 15.2, 18.0, 22.4, 25.7, 27.2, 33.1, 34.1, 35.0, 64.9, 81.7, 116.7, 125.8, 126.6, 128.3, 128.5, 128.5, 128.8, 132.8, 136.7, 142.5, 154.7; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 22.6; [MH]<sup>+</sup> Calcd. for C<sub>29</sub>H<sub>42</sub>NO<sub>3</sub>Si 480.2934; found: 480.2963

*(S,Z)*-4-benzyl-3-(2-butyl-1-(tert-butyldimethylsilyloxy)oct-1-enyl)-5,5-dimethyloxazolidin-2-one  
**(1g<sub>f</sub>)**

Purification was performed with hexane/ethyl acetate = 25/1 to provide **1g<sub>f</sub>** in 48% yield as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.09 (s, 3H), 0.15 (s, 3H), 0.76-0.80 (m, 3H), 0.83-0.88 (m, 3H), 0.92 (s, 9H), 0.97 (s, 3H), 1.15-1.30 (m, 11H), 1.34 (s, 3H), 1.40-1.50 (m, 1H), 1.85-1.95 (m, 2H), 1.95-2.05 (m, 1H), 2.11-2.20 (m, 1H), 2.47 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.00 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.93 (dd, *J* = 10.8, 4.0 Hz, 1H), 7.08-7.26 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.4, -3.9, 14.0, 14.0, 18.0, 22.6, 23.2, 25.7, 27.3, 27.6, 28.5, 29.6, 29.8, 30.1, 31.8, 33.3, 65.2, 81.5, 122.8, 126.8, 128.7, 128.8, 131.9, 136.8, 154.7; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 21.6; [MH]<sup>+</sup> Calcd. for C<sub>30</sub>H<sub>52</sub>NO<sub>3</sub>Si 502.3711; found: 502.3707

*(S,Z)*-4-benzyl-3-(1-(tert-butyldimethylsilyloxy)-2-isopropyloct-1-enyl)-5,5-dimethyloxazolidin-2-

**one (**1g<sub>g</sub>**)**

Purification was performed with hexane/ethyl acetate = 25/1 to provide **1g<sub>g</sub>** in 45% yield as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.09 (s, 3H), 0.15 (s, 3H), 0.78-0.85 (m, 4H), 0.89-0.97 (m, 17H), 1.15-1.25 (m, 7H), 1.30-1.38 (m, 3H), 1.45-1.55 (m, 1H), 1.92 (t, J = 8.0 Hz, 2H), 2.51 (dd, J = 14.0, 10.8 Hz, 1H), 2.88 (m, 1H), 2.99 (dd, J = 14.0, 3.6 Hz, 1H), 3.93 (dd, J = 10.8, 4.0 Hz, 1H), 7.05-7.25 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.6, -3.7, 14.0, 18.0, 20.2, 21.8, 22.7, 25.7, 27.1, 28.0, 30.0, 30.4, 31.6, 65.4, 81.5, 126.8, 127.6, 128.7, 128.8, 132.0, 136.8, 154.9; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 21.1; [MH]<sup>+</sup> Calcd. for C<sub>29</sub>H<sub>50</sub>NO<sub>3</sub>Si 488.3554; found: 488.3544

**(S,E)-4-benzyl-3-(1-(tert-butyldimethylsilyloxy)-2-cyclopropylprop-1-enyl)-5,5-dimethyloxazolidin-2-one (**1g<sub>h</sub>**)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **1g<sub>h</sub>** in 52% yield as white solid . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.09 (s, 3H), 0.13 (s, 3H), 0.33-0.40 (m, 1H), 0.45-0.55 (m, 2H), 0.58-0.65 (m, 1H), 0.89 (s, 9H), 1.06 (s, 3H), 1.27 (s, 3H), 1.35 (s, 3H), 1.53-1.65 (m, 1H), 2.58 (dd, J = 14.0, 4.0 Hz, 1H), 3.03 (dd, J = 10.4, 4.0 Hz, 1H), 3.98 (dd, J = 10.4, 4.0 Hz, 1H), 7.06-7.24 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.1, -4.0, 3.6, 3.7, 10.9, 11.9, 18.0, 22.6, 25.7 27.4, 33.8, 65.2, 81.5, 117.3, 126.6, 128.5, 128.9, 132.8, 136.9, 154.6; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 22.1; [MH]<sup>+</sup> Calcd. for C<sub>24</sub>H<sub>38</sub>NO<sub>3</sub>Si 416.2621; found: 416.2650

**(S,E)-4-benzyl-3-(1-(tert-butyldimethylsilyloxy)-2-phenylprop-1-enyl)-5,5-dimethyloxazolidin-2-one (**1g<sub>i</sub>**)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **1g<sub>i</sub>** in 48% yield as white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.14 (s, 3H), 0.25 (s, 3H), 0.79 (s, 3H), 0.87 (s, 3H), 0.94 (s, 9H), 1.93 (s, 3H), 2.14-2.19 (m, 1H), 2.81-2.86 (m, 1H), 3.82-3.85 (m, 1H), 7.12-7.26 (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.1, -4.0, 18.1, 18.4, 21.3, 25.7, 26.4, 32.9, 65.9, 81.8, 120.2, 126.5, 126.7, 127.8, 128.0, 128.5, 128.7, 133.9, 136.6, 140.7, 155.7; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 22.8; [M]<sup>+</sup> Calcd. for C<sub>27</sub>H<sub>37</sub>NO<sub>3</sub>Si 451.2543; found: 451.2520

**(S,E)-4-benzyl-3-(1-(tert-butyldimethylsilyloxy)-2-phenylbut-1-enyl)-5,5-dimethyloxazolidin-2-one (**1g<sub>j</sub>**)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **1g<sub>j</sub>** in 46% yield as colorless oil.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.14 (s, 3H), 0.27 (s, 3H), 0.72 (s, 3H), 0.83 (s, 3H), 0.86 (t, J = 7.6 Hz, 3H), 0.94 (s, 9H), 2.18 (dd, J = 14.0, 10.8 Hz, 1H), 2.25-2.35 (m, 1H), 2.40-2.50 (m, 1H), 2.91 (dd, J = 14.0, 3.6 Hz, 1H), 3.82 (dd, J = 10.8, 3.6 Hz, 1H), 7.05-7.35 (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -5.2, -4.0, 12.3, 18.0, 21.1, 24.7, 25.6, 26.4, 32.7, 65.8, 81.8, 126.4, 126.5, 126.7, 127.7, 128.6, 128.7, 128.7, 133.3, 136.7, 139.1, 155.4; <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 22.1; [MH]<sup>+</sup> Calcd. for C<sub>28</sub>H<sub>40</sub>NO<sub>3</sub>Si 466.2777; found: 466.2770

**(S,E)-4-benzyl-3-(1-(tert-butyldimethylsilyloxy)-2-phenylhex-1-enyl)-5,5-dimethyloxazolidin-2-one (**1g<sub>k</sub>**)**

Purification was performed with hexane/ethyl acetate = 20/1 to provide **1g<sub>k</sub>** in 57% yield as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.14 (s, 3H), 0.28 (s, 3H), 0.75 (s, 3H), 0.77 (t, J = 6.4 Hz, 3H), 0.83 (s, 3H), 0.95 (s, 9H), 1.19-1.24 (m, 4H), 2.22 (dd, J = 14.0, 10.4 Hz, 1H),

2.28-2.35 (m, 1H), 2.47-2.45 (m, 1H), 2.94 (dd,  $J = 14.0, 4.0$  Hz, 1H), 3.82 (dd,  $J = 10.4, 4.0$  Hz, 1H), 7.15-7.30 (m, 10H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.1, -3.8, 14.0, 18.1, 21.2, 22.8, 25.7, 26.5, 29.9, 31.5, 32.8, 65.8, 81.8, 125.2, 126.5, 127.8, 128.7, 128.7, 128.8, 133.6, 136.8, 139.5, 155.2;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.2;  $[\text{M}]^+$  Calcd. for  $\text{C}_{30}\text{H}_{43}\text{NO}_3\text{Si}$  493.3012; found: 493.3015

*(S,E)-4-benzyl-3-(11,11-diisopropyl-2,2,3,3,6,12-hexamethyl-4,10-dioxa-3,11-disilatridec-5-en-5-yl)-5,5-dimethyloxazolidin-2-one (**1gi**)*

Purification was performed with hexane/ethyl acetate = 30/1 to provide **1gi** in 54% yield as colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.08 (s, 3H), 0.13 (s, 3H), 0.91 (s, 9H), 0.96-1.01 (m, 24 H), 1.33 (s, 3H), 1.52-1.58 (m, 1H), 1.61 (s, 3H), 1.65-1.75 (m, 1H), 1.95-2.15 (m, 2H), 2.49 (dd,  $J = 14.0, 4.0$  Hz, 1H), 3.99 (dd,  $J = 10.4, 4.0$  Hz, 1H), 3.58-3.70 (m, 2H), 3.93 (dd,  $J = 10.4, 4.0$  Hz, 1H), 7.05-7.25 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.2, -4.0, 12.0, 15.1, 18.0, 18.0, 22.4, 25.7, 27.3, 28.9, 31.3, 33.7, 63.7, 65.0, 81.5, 117.5, 126.7, 128.6, 128.8, 132.2, 136.8, 154.7;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.4, 22.3;  $[\text{MH}]^+$  Calcd. for  $\text{C}_{33}\text{H}_{60}\text{NO}_3\text{Si}_2$  590.4055; found: 590.4039

*(S,E)-5-(4-benzyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-5-(tert-butyldimethylsilyloxy)-4-methylpent-4-enyl pivalate (**1gm**)*

Purification was performed with hexane/ethyl acetate = 15/1 to provide **1gm** in 64% yield as colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.08 (s, 3H), 0.13 (s, 3H), 0.91 (s, 9H), 1.01 (s, 3H), 1.13 (s, 9H), 1.34 (s, 3H), 1.61 (s, 3H), 1.62-1.75 (m, 1H), 1.75-1.85 (m, 1H), 1.94-2.04 (m, 1H), 2.05-2.18 (m, 1H), 2.50 (dd,  $J = 14.0, 10.0$  Hz, 1H), 2.99 (dd,  $J = 14.0, 4.4$  Hz, 1H), 3.90-4.07 (m, 3H), 7.05-7.25 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.2, -4.0, 15.1, 18.0, 22.5, 25.7, 27.0, 27.2, 27.3, 29.1, 33.7, 38.7, 64.5, 64.9, 81.6, 116.6, 126.7, 128.6, 128.8, 132.7, 136.6, 154.7, 178.5;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.7;  $[\text{MH}]^+$  Calcd. for  $\text{C}_{29}\text{H}_{48}\text{NO}_5\text{Si}$  518.3302; found: 518.3363

*(S,E)-5-(4-benzyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-5-(tert-butyldimethylsilyloxy)-4-methylpent-4-enyl benzoate (**1gn**)*

Purification was performed with hexane/ethyl acetate = 12/1 to provide **1gn** in 64% yield as colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.08 (s, 3H), 0.14 (s, 3H), 0.91 (s, 9H), 0.97 (s, 3H), 1.21 (s, 3H), 1.64 (s, 3H), 1.77-1.86 (m, 1H), 1.92-2.00 (m, 1H), 2.06-2.15 (m, 1H), 2.15-2.25 (m, 1H), 2.44 (d,  $J = 14.0, 10.0$  Hz, 1H), 2.96 (dd,  $J = 14.0, 4.4$  Hz, 1H), 3.92 (dd,  $J = 10.0, 4.4$  Hz, 1H), 4.20-4.35 (m, 2H), 7.00-7.05 (m, 2H), 7.10-7.15 (m, 1H), 7.17-7.22 (m, 2H), 7.32-7.37 (m, 2H), 7.42-7.50 (m, 1H), 7.95-8.02 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.2, -4.0, 15.0, 18.0, 22.4, 25.7, 27.0, 27.2, 29.1, 33.6, 64.9, 65.0, 81.6, 116.5, 126.7, 128.3, 128.5, 128.7, 129.6, 132.8, 154.7, 166.6;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.7;  $[\text{MH}]^+$  Calcd. for  $\text{C}_{31}\text{H}_{44}\text{NO}_5\text{Si}$  538.2989; found: 538.2986

*(S)-4-benzyl-3-((R)-2-fluoro-2-methylhexanoyl)-5,5-dimethyloxazolidin-2-one (**2ga**)*

Purification was performed with hexane/ethyl acetate = 15/1 to provide **2ga** as colorless oil, yield 90%, dr 93:7.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.83 (t,  $J = 6.8$  Hz, 3H), 1.27-1.31 (m, 10H), 1.62 (d,  $J = 22$  Hz, 3H), 1.79-1.95 (m, 1H), 2.07-2.25 (m, 1H), 2.85 (dd,  $J = 14.4, 9.6$  Hz, 1H), 3.09 (14.4, 4.0 Hz, 1H), 4.42 (dd,  $J = 9.6, 4.0$  Hz, 1H), 7.20-7.35 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$

13.6, 22.1, 22.3(d,  $J_{C-F} = 24.2$  Hz), 22.6, 25.2 (d,  $J_{C-F} = 3.5$  Hz), 28.0, 35.1, 36.6, 36.8, 65.4, 82.6, 97.7 (d,  $J_{C-F} = 184.3$  Hz), 126.9, 128.7, 129.1, 136.6, 151.0, 172.7 (d,  $J_{C-F} = 26.8$  Hz);  $^{19}\text{F}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -148.5(m, 1F, major diastereomer), -148.0 (m, 1F, minor diastereomer); HRMS:  $[\text{MH}]^+$  Calcd. for  $\text{C}_{19}\text{H}_{27}\text{NO}_3\text{F}$  336.1975; found: 336.1976.

**(S)-4-benzyl-3-((R)-2-fluoro-2-methyloctanoyl)-5,5-dimethyloxazolidin-2-one (**2g<sub>b</sub>**)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **2g<sub>b</sub>** as colorless oil, yield 81%, dr 92:8.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.80 (t,  $J = 6.8$  Hz, 3H), 1.25-1.50 (m, 14H), 1.62 (d,  $J = 22$  Hz, 3H), 1.84-1.88 (m, 1H), 2.10-2.22 (m, 1H), 2.85 (dd,  $J = 14.4, 9.6$  Hz, 1H), 3.10 (dd,  $J = 14.4, 4.0$  Hz, 1H), 4.42 (dd,  $J = 9.6, 4.0$  Hz, 1H), 7.16-7.24 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 22.2, 22.3, 22.5, 23.1 (d,  $J_{C-F} = 3.6$  Hz), 28.0, 29.2, 31.6, 35.2, 37.0 (d,  $J_{C-F} = 22.3$  Hz), 65.4, 82.6, 97.8 (d,  $J_{C-F} = 184.3$  Hz), 126.9, 128.7, 129.1, 136.6, 151.0, 172.8 (d,  $J_{C-F} = 26.8$  Hz);  $^{19}\text{F}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -148.4(m, 1F, major diastereomer), -147.9 (m, 1F, minor diastereomer); HRMS:  $[\text{MH}]^+$  Calcd. for  $\text{C}_{21}\text{H}_{31}\text{NO}_3\text{F}$  364.2272; found: 364.2282.

**(S)-4-benzyl-3-((R)-2-ethyl-2-fluorooctanoyl)-5,5-dimethyloxazolidin-2-one (**2g<sub>c</sub>**)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **2g<sub>c</sub>** as colorless oil, yield 76%, dr 90:10.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.80 (t,  $J = 6.8$  Hz, 3H), 0.87 (t,  $J = 6.8$  Hz, 3H), 1.18-1.27 (m, 13H), 1.28-1.32 (m, 1H), 1.78-2.00 (m, 2H), 2.15-2.28 (m, 2H), 2.82 (dd,  $J = 14.4, 9.6$  Hz, 1H), 3.11 (dd,  $J = 14.4, 4.0$  Hz, 1H), 4.48 (dd,  $J = 9.6, 4.0$  Hz, 1H), 7.18-7.26 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.8 (d,  $J_{C-F} = 5.0$  Hz), 14.0, 22.2, 22.5, 23.1 (d,  $J_{C-F} = 3.6$  Hz), 28.1, 28.4 (d,  $J_{C-F} = 23.1$  Hz), 29.3, 31.6, 35.1, 35.2 (d,  $J_{C-F} = 22.4$  Hz), 65.6, 82.4, 101.0 (d,  $J_{C-F} = 185.8$  Hz), 126.9, 128.7, 129.1, 136.7, 151.0, 172.2 (d,  $J_{C-F} = 26.8$  Hz);  $^{19}\text{F}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -156.3 (m, 1F); HRMS:  $[\text{MH}]^+$  Calcd. for  $\text{C}_{22}\text{H}_{33}\text{NO}_3\text{F}$  378.2444; found: 378.2441.

**(S)-4-benzyl-3-((R)-2-butyl-2-fluorooctanoyl)-5,5-dimethyloxazolidin-2-one (**2g<sub>d</sub>**)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **2g<sub>d</sub>** as colorless oil, yield 74%, dr 84:16.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.76-0.86 (m, 6H), 1.05-1.31 (m, 16H), 1.33-1.47 (m, 2H), 1.80-1.95 (m, 2H), 2.11-2.33 (m, 2H), 2.83 (dd,  $J = 14.4, 9.6$  Hz, 1H), 3.11 (dd,  $J = 14.4, 4.0$  Hz, 1H), 4.48 (dd,  $J = 9.6, 4.0$  Hz, 1H), 7.15-7.28 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.9, 14.0, 22.3, 22.5, 22.7, 23.1 (d,  $J_{C-F} = 3.5$  Hz), 25.7 (d,  $J_{C-F} = 3.7$  Hz), 28.1, 29.3, 31.6, 35.1 (d,  $J_{C-F} = 21.8$  Hz), 35.2, 35.5 (d,  $J_{C-F} = 22.4$  Hz), 65.6, 82.4, 100.8 (d,  $J_{C-F} = 185.4$  Hz), 126.9, 128.7, 129.1, 136.7, 151.0, 172.2 (d,  $J_{C-F} = 26.7$  Hz);  $^{19}\text{F}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -153.9 (m, 1F); HRMS:  $[\text{MH}]^+$  Calcd. for  $\text{C}_{24}\text{H}_{37}\text{NO}_3\text{F}$  406.2752; found: 406.2748.

**(S)-4-benzyl-3-((R)-2-fluoro-2-methyl-4-phenylbutanoyl)-5,5-dimethyloxazolidin-2-one (**2g<sub>e</sub>**)**

Purification was performed with hexane/ethyl acetate = 12/1 to provide **2g<sub>e</sub>** as colorless oil, yield 75%, dr 92:8.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.28 (s, 3H), 1.30 (s, 3H), 1.68 (d,  $J = 22.0$  Hz, 3H), 2.15-2.25 (m, 1H), 2.45-2.65 (m, 2H), 2.70-2.75 (m, 1H), 2.81 (dd,  $J = 14.4, 9.6$  Hz, 1H), 3.05 (dd,  $J = 14.4, 4.0$  Hz, 1H), 4.41 (dd,  $J = 9.6, 4.0$  Hz, 1H), 7.10-7.25 (m, 10H);  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  22.1, 22.3 (d,  $J_{C-F} = 24.0$  Hz), 28.0, 29.4 (d,  $J_{C-F} = 4.2$  Hz), 35.1, 38.8 (d,  $J_{C-F} = 22.4$  Hz), 65.4, 82.7, 97.3 (d,  $J_{C-F} = 185.1$  Hz), 126.0, 126.9, 128.4, 128.4, 128.6, 129.1, 136.5, 140.9, 151.0, 172.2 (d,  $J_{C-F} = 26.7$  Hz);  $^{19}\text{F}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -149.0 (m, 1F); HRMS:  $[\text{MH}]^+$  Calcd. for  $\text{C}_{23}\text{H}_{27}\text{NO}_3\text{F}$  384.1975; found: 384.2010.

**(S)-4-benzyl-3-((S)-2-butyl-2-fluorooctanoyl)-5,5-dimethyloxazolidin-2-one (2g<sub>f</sub>)**

Purification was performed with hexane/ethyl acetate = 20/1 to provide **2g<sub>f</sub>** as colorless oil, yield 69%, dr 87:13. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.75-0.87 (m, 6H), 1.06-1.33 (m, 16 H), 1.34-1.46 (m, 2H), 1.80-1.95 (m, 2H), 2.11-2.35 (m, 2H), 2.83 (dd, J = 14.4, 9.6 Hz, 1H), 3.13 (dd, J = 14.4, 4.0 Hz, 1H), 4.48 (dd, J = 9.6, 4.0 Hz, 1H), 7.15-7.25 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.9, 14.0, 22.2, 22.5, 22.7, 23.5 (d, J<sub>C-F</sub> = 3.7 Hz), 25.3 (d, J<sub>C-F</sub> = 3.5 Hz), 28.1, 29.2, 31.6, 35.2, 35.3 (d, J<sub>C-F</sub> = 21.9 Hz), 35.3 (d, J<sub>C-F</sub> = 22.6 Hz), 65.6, 82.4, 100.7 (d, J<sub>C-F</sub> = 185.4 Hz), 126.9, 128.7, 129.1, 136.7, 151.0, 172.2 (d, J<sub>C-F</sub> = 26.7 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -153.9 (m, 1F); HRMS: [MH]<sup>+</sup> Calcd. for C<sub>24</sub>H<sub>37</sub>NO<sub>3</sub>F 406.2757; found: 406.2764.

**(S)-4-benzyl-3-((S)-2-fluoro-2-isopropyloctanoyl)-5,5-dimethyloxazolidin-2-one (2g<sub>g</sub>)**

Purification was performed with hexane/ethyl acetate = 20/1 to provide **2g<sub>g</sub>** as colorless oil, yield 61%, dr 71:29. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.79 (t, J = 6.8 Hz, 3H), 0.83-0.95 (m, 6H), 0.98-1.10 (m, 1H), 1.15-1.29 (m, 12H), 1.32-1.45 (m, 1H), 1.76-1.95 (m, 1H), 2.15-2.45 (m, 1H), 2.52-2.76 (m, 1H), 2.82 (dd, J = 14.4, 9.6 Hz, 1H), 3.13-3.18 (m, 1H), 4.45-4.49 (m, 1H), 7.23-7.25 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.0 (13.9), 15.9 (d, J<sub>C-F</sub> = 4.2 Hz) (15.8), 17.1 (d, J<sub>C-F</sub> = 4.6 Hz), 22.2 (22.3), 22.5 (22.4), 23.5 (d, J<sub>C-F</sub> = 3.5 Hz) (23.9), 28.0 (28.2), 29.3 (29.3), 31.5 (31.9), 31.7 (31.8), 32.7 (d, J<sub>C-F</sub> = 22.7 Hz) (32.8), 35.1, 65.8 (65.6), 82.3 (82.3), 102.9 (d, J<sub>C-F</sub> = 189.3 Hz), 126.8, 128.7, 129.0 (129.0), 136.8 (136.8), 151.0 (151.0), 172.0 (d, J<sub>C-F</sub> = 26.9 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -167.5 (m, 1F, major diastereomer), -167.9 (m, 1F, minor diastereomer); HRMS: [MH]<sup>+</sup> Calcd. for C<sub>23</sub>H<sub>35</sub>NO<sub>3</sub>F 392.2601; found: 392.2696.

**(S)-4-benzyl-3-((R)-2-cyclopropyl-2-fluoropropanoyl)-5,5-dimethyloxazolidin-2-one (2g<sub>h</sub>)**

Purification was performed with hexane/ethyl acetate = 20/1 to provide **2g<sub>h</sub>** as colorless oil, yield 70%, dr 86:14. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.34-0.55 (m, 4H), 1.30 (s, 3H), 1.33 (s, 3H), 1.66 (d, J = 25.6 Hz, 3H), 1.75-1.90 (m, 1H), 2.88 (dd, J = 14.4, 9.6 Hz, 1H), 3.08 (dd, J = 14.4, 4.0 Hz, 1H), 4.46 (dd, J = 9.6, 4.0 Hz, 1H), 7.15-7.24 (m, 5H); <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 0.8 (d, J<sub>C-F</sub> = 3.8 Hz), 1.1 (d, J<sub>C-F</sub> = 6.2 Hz), 16.0 (d, J<sub>C-F</sub> = 22.2 Hz), 21.8 (d, J<sub>C-F</sub> = 24.6 Hz), 22.1, 28.1, 35.1, 65.4, 82.6, 95.4 (d, J<sub>C-F</sub> = 185.0 Hz), 126.9, 128.7, 129.1, 136.6, 151.1, 172.5 (d, J<sub>C-F</sub> = 28.0 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -161.1 (m, 1F, major diastereomer), -159.3 (m, 1F, minor diastereomer); HRMS: [MH]<sup>+</sup> Calcd. for C<sub>18</sub>H<sub>23</sub>NO<sub>3</sub>F 320.1656; found: 320.1655

**(S)-4-benzyl-3-((R)-2-fluoro-2-phenylpropanoyl)-5,5-dimethyloxazolidin-2-one (2g<sub>i</sub>)**

Purification was performed with hexane/ethyl acetate = 12/1 to provide **2g<sub>i</sub>** as colorless oil, yield 83%, dr 97:3. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.17 (s, 3H), 1.29 (s, 3H), 1.80 (d, J = 22.4 Hz, 3H), 2.78 (dd, J = 14.4, 9.6 Hz, 1H), 3.06 (dd, J = 14.4, 4.0 Hz, 1H), 4.50 (dd, J = 9.6, 4.0 Hz, 1H), 7.15-7.35 (m, 10 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 22.1, 26.6 (d, J<sub>C-F</sub> = 25.4 Hz), 28.1, 35.1, 64.6, 82.2, 97.1 (d, J<sub>C-F</sub> = 188.2 Hz), 124.4 (d, J<sub>C-F</sub> = 6.8 Hz), 126.9, 128.2, 128.3 (d, J<sub>C-F</sub> = 1.1 Hz), 128.7, 129.2, 136.4, 138.4 (d, J<sub>C-F</sub> = 21.2 Hz), 149.8, 171.3 (d, J<sub>C-F</sub> = 28.0 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -146.0 (m, 1F, major diastereomer), -142.1 (m, 1F, minor diastereomer); HRMS: [MH]<sup>+</sup> Calcd. for C<sub>21</sub>H<sub>23</sub>NO<sub>3</sub>F 356.1662; found: 356.1650.

**(S)-4-benzyl-3-((R)-2-fluoro-2-phenylbutanoyl)-5,5-dimethyloxazolidin-2-one (2g<sub>j</sub>)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **2g<sub>j</sub>** as colorless oil, yield 85%, dr 96:4. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.88 (t, *J* = 9.6 Hz, 3H), 1.15 (s, 3H), 1.36 (s, 3H), 2.10-2.25 (m, 1H), 2.35-2.52 (m, 1H), 2.78 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.21 (dd, *J* = 14.4, 4.0 Hz, 1H), 4.57 (dd, *J* = 9.6, 4.0 Hz, 1H), 7.25-7.35 (m, 10H); <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 7.5 (d, *J<sub>C-F</sub>* = 3.6 Hz), 22.2, 27.9, 33.3 (d, *J<sub>C-F</sub>* = 19.2 Hz), 34.7, 64.7, 82.1, 99.4 (d, *J<sub>C-F</sub>* = 154.9 Hz), 124.7, 124.8, 126.9, 128.0, 128.7, 129.1, 136.3, 136.9 (d, *J<sub>C-F</sub>* = 17.1 Hz), 150.0, 171.8 (d, *J<sub>C-F</sub>* = 22.8 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -163.8 (m, 1F, major diastereomer), -162.2 (m, 1F, minor diastereomer); HRMS: [MH]<sup>+</sup> Calcd. for C<sub>22</sub>H<sub>25</sub>NO<sub>3</sub>F 370.1813; found: 370.1758.

**(S)-4-benzyl-3-((R)-2-fluoro-2-phenylhexanoyl)-5,5-dimethyloxazolidin-2-one (**2g<sub>k</sub>**)**

Purification was performed with hexane/ethyl acetate = 15/1 to provide **2g<sub>k</sub>** as colorless oil, yield 85%, dr 95:5. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.88 (t, *J* = 9.6 Hz, 3H), 1.18 (s, 3H), 1.28-1.32 (m, 4H), 1.39 (s, 3H), 2.08-2.21 (m, 1H), 2.25-2.50 (m, 1H), 2.81 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.23 (dd, *J* = 14.4, 4.0 Hz, 1H), 4.59 (dd, *J* = 9.6, 4.0 Hz, 1H), 7.24-7.48 (m, 10H); <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 13.8, 22.2, 22.6, 25.1 (d, *J<sub>C-F</sub>* = 2.6 Hz), 27.9, 34.7, 39.9 (d, *J<sub>C-F</sub>* = 18.7 Hz), 64.7, 82.2, 99.2 (d, *J<sub>C-F</sub>* = 154.5 Hz), 124.7, 124.8, 126.9, 128.0 (d, *J<sub>C-F</sub>* = 5.1 Hz), 128.7, 129.1, 136.3, 137.2 (d, *J<sub>C-F</sub>* = 17.1 Hz), 150.0, 171.9 (d, *J<sub>C-F</sub>* = 22.8 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -161.4 (m, 1F, major diastereomer), -159.6 (m, 1F, minor diastereomer); HRMS: [MH]<sup>+</sup> Calcd. for C<sub>24</sub>H<sub>29</sub>NO<sub>3</sub>F 398.2126; found: 398.2135

**(S)-4-benzyl-3-((R)-2-fluoro-2-methyl-5-(triisopropylsilyloxy)pentanoyl)-5,5-dimethyloxazolidin-2-one (**2g<sub>l</sub>**)**

Purification was performed with hexane/ethyl acetate = 18/1 to provide **2g<sub>l</sub>** as colorless oil, yield 52%, dr 90:10. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.95-1.05 (m, 21H), 1.28 (s, 3H), 1.31 (s, 3H), 1.42-1.55 (m, 1H), 1.58-1.70 (m, 4H), 1.90-2.05 (m, 1H), 2.20-2.37 (m, 1H), 2.84 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.10 (dd, *J* = 14.4, 4.0 Hz, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 4.42 (dd, *J* = 9.6, 4.0 Hz, 1H), 7.19-7.24 (m, 5H); <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 11.9, 18.0, 22.2, 22.4 (d, *J<sub>C-F</sub>* = 24.1 Hz), 26.9 (d, *J<sub>C-F</sub>* = 3.3 Hz), 28.0, 33.6 (d, *J<sub>C-F</sub>* = 22.4 Hz), 35.2, 62.9, 65.4, 82.5, 97.7 (d, *J<sub>C-F</sub>* = 184.6 Hz), 126.9, 128.7, 129.1, 136.6, 150.9, 172.7 (d, *J<sub>C-F</sub>* = 26.8 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -148.8 (d, *J* = 5.4 Hz, 1F, major diastereomer), -148.7 (m, 1F, minor diastereomer); <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ 12.5; [MH]<sup>+</sup> Calcd. for C<sub>27</sub>H<sub>45</sub>NO<sub>3</sub>FSi 494.3096; found: 494.3079

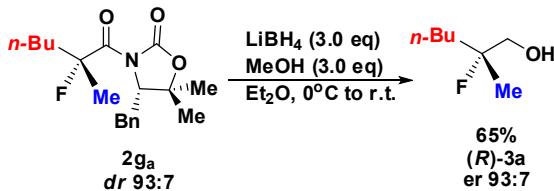
**(R)-5-((S)-4-benzyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-4-fluoro-4-methyl-5-oxopentyl pivalate (**2g<sub>m</sub>**)**

Purification was performed with hexane/ethyl acetate = 10/1 to provide **2g<sub>m</sub>** as colorless oil, yield 82%, dr 94:6. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.12 (s, 9H), 1.13 (s, 3H), 1.29 (s, 3H), 1.45-1.77 (s, 5H), 1.85-2.03 (m, 1H), 2.18-2.35 (m, 1H), 2.86 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.10 (dd, *J* = 14.4, 4.0 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 4.42 (dd, *J* = 9.6, 4.0 Hz, 1H), 7.10-7.29 (m, 5H); <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 22.1, 22.3 (d, *J<sub>C-F</sub>* = 24.0 Hz), 22.7 (d, *J<sub>C-F</sub>* = 3.8 Hz), 27.1, 27.9, 33.6 (d, *J<sub>C-F</sub>* = 22.6 Hz), 35.1, 38.7, 63.7, 65.3, 82.7, 97.3 (d, *J<sub>C-F</sub>* = 185.3 Hz), 126.9, 128.6, 129.1, 136.5, 150.9, 172.2 (d, *J<sub>C-F</sub>* = 26.6 Hz), 178.4; <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -149.4 (m, 1F, major diastereomer), -148.5 (m, 1F, minor diastereomer); [MH]<sup>+</sup> Calcd. for C<sub>23</sub>H<sub>33</sub>FNO<sub>5</sub> 422.2343; found: 422.2352.

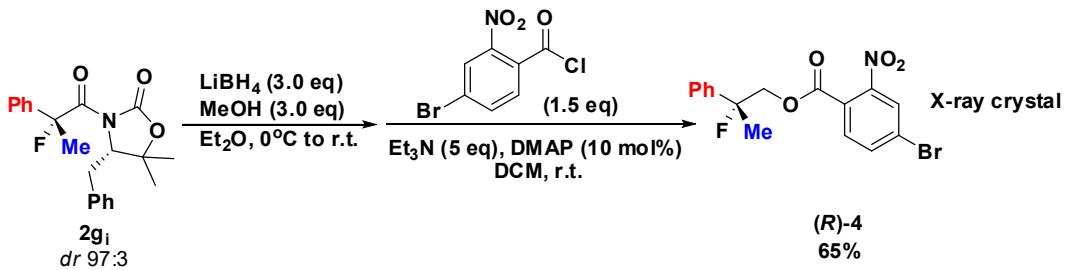
*(R)*-5-((*S*)-4-benzyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-4-fluoro-4-methyl-5-oxopentyl benzoate (**2g<sub>n</sub>**)

Purification was performed with hexane/ethyl acetate = 12/1 to provide **2g<sub>n</sub>** as colorless oil, yield 82%, dr 93:7. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.29 (s, 3H), 1.30 (s, 3H), 1.64-1.73 (m, 4H), 1.80-1.95 (m, 1H), 1.95-2.10 (m, 1H), 2.30-2.45 (m, 1H), 2.84 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.09 (dd, *J* = 14.4, 4.0 Hz, 1H), 4.20-4.30 (m, 1H), 4.42 (dd, *J* = 9.6, 4.0 Hz, 1H), 7.12-7.22 (m, 5H), 7.32-7.40 (m, 2H), 7.46-7.50 (m, 1H), 7.96-7.99 (m, 2H); <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 22.1, 22.3 (d, *J<sub>C-F</sub>* = 23.9 Hz), 22.8 (d, *J<sub>C-F</sub>* = 3.9 Hz), 27.9, 33.7 (d, *J<sub>C-F</sub>* = 22.5), 35.1, 64.4, 65.3, 82.7, 97.3 (d, *J<sub>C-F</sub>* = 185.2 Hz), 126.9, 128.3, 128.6, 129.1, 129.5, 130.2, 132.9, 136.4, 150.9, 166.4, 172.2 (d, *J<sub>C-F</sub>* = 26.6 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -149.5 (m, 1F, major diastereomer), -149.0 (m, 1F, minor diastereomer); [MH]<sup>+</sup> Calcd. for C<sub>25</sub>H<sub>29</sub>FNO<sub>5</sub> 442.2030; found: 422.2048.

## 5. Derivative of fluorinated product **2g<sub>a</sub>** and **2g<sub>j</sub>**



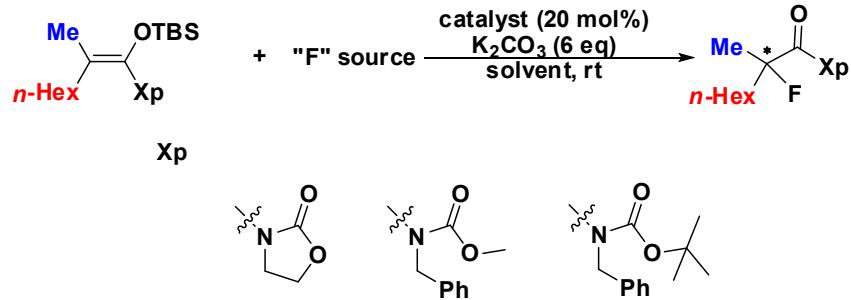
**(R)-3a** was prepared according to the previously published procedure<sup>3</sup>. To a stirred solution of **2h<sub>a</sub>** (0.6 mmol, 1.0 equiv, *d.r.* 93:7) in dry diethyl ether (5 ml) at 0 °C was added abs. methanol (3.0 equiv) followed by solid LiBH4 (1.8 mmol, 3.0 equiv). The resulting mixture was stirred at 0 °C for 1 h then was allowed to warm to room temperature and stirred for additional one hour. After completion of the reaction (monitored by TLC on silica gel using 20% diethyl ether in hexane as eluent), the reaction was quenched by slow addition of water. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3x10 ml). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and the residue was purified by column chromatography (solvent gradient 0-10% diethyl ether in hexane) providing **(R)-3a** in 65% yield (53 mg, 0.39 mmol) as a colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.83-0.87 (m, 3H), 1.12-1.32 (m, 7H), 1.50-1.64 (m, 2H), 1.85-1.98 (m, 1H), 3.42-3.58 (m, 2H); <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 13.9, 20.7 (d, *J<sub>C-F</sub>* = 24.3 Hz), 23.1, 25.5 (d, *J<sub>C-F</sub>* = 6.1 Hz), 35.9 (d, *J<sub>C-F</sub>* = 22.1 Hz), 68.1 (d, *J<sub>C-F</sub>* = 23.9 Hz), 97.7 (d, *J<sub>C-F</sub>* = 165.7 Hz); <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -154.7 (m, 1F).



To a stirred solution of **2g<sub>j</sub>** (0.4 mmol, 1.0 equiv, *d.r.* 97:3) in dry diethyl ether (5 ml) at 0 °C was added abs. methanol (3.0 equiv) followed by solid LiBH4 (1.2 mmol, 3.0 equiv). The resulting mixture was stirred at 0 °C for 1 h then was allowed to warm to room temperature and

stirred for additional one hour. After completion of the reaction (monitored by TLC on silica gel using 20% diethyl ether in hexane as eluent), the reaction was quenched by slow addition of water. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3x10 ml). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to get the crude product without further purification. Add the crude product to a dry flask containing solution of Et<sub>3</sub>N (5 eq), DMAP (0.1 eq) in DCM (5 ml), followed by adding 4-bromo-2-nitrobenzoyl chloride (1.5 eq). After completion of the reaction (monitored by TLC on silica gel using 20% diethyl ether in hexane as eluent), the reaction was quenched by slow addition of water. The organic phase was separated and the aqueous phase was extracted with DCM (3x10 ml). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and the residue was purified by column chromatography (solvent gradient 0-30% diethyl ether in hexane) providing (*R*)-4 in 65% yield as white solid. The product was recrystallized in pentane/ethyl acetate and afforded colorless needles. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.73 (d, *J* = 22.4 Hz, 3H), 4.42-4.65 (m, 2H), 7.30-7.42 (m, 5H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.99 (d, *J* = 2.0 Hz, 1H); <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>): δ 23.5 (d, *J*<sub>C-F</sub> = 24.5 Hz), 71.0 (d, *J*<sub>C-F</sub> = 24.9 Hz), 95.2 (d, *J*<sub>C-F</sub> = 175.9 Hz), 124.4 (d, *J*<sub>C-F</sub> = 9.1 Hz), 125.4, 126.0, 127.0, 128.2 (d, *J*<sub>C-F</sub> = 1.0 Hz), 128.5 (d, *J*<sub>C-F</sub> = 1.3 Hz), 131.3, 135.8, 140.5 (d, *J*<sub>C-F</sub> = 21.4 Hz), 148.8, 163.9; <sup>19</sup>F NMR (100 MHz, CDCl<sub>3</sub>): δ -153.5 (m, 1F);

## 6. Screening for asymmetric catalytic formation of fluorinated acyclic quaternary carbon center



Entry	Xp	F <sup>+</sup>	catalyst	Solvent	T(°C)	Yield(%)	Ee(%)
1	A	selectfluor	quinine	toluene	rt	48	0
2	A	NFSI	quinine	toluene	rt	58	15
3	A	NFSI	quinine	CH <sub>3</sub> CN	rt	50	25
4	A	NFSI	-	CH <sub>3</sub> CN	rt	trace	-
5	A	NFSI	(DHQ) <sub>2</sub> PHAL	CH <sub>3</sub> CN	-40°C to rt	80	37
6	A	NFSI	(DHQ) <sub>2</sub> AQN	CH <sub>3</sub> CN	-40°C to rt	65	25
7	B	NFSI	(DHQ) <sub>2</sub> PHAL	CH <sub>3</sub> CN	-40°C to rt	75	60
8	B	NFSI	(DHQ) <sub>2</sub> AQN	CH <sub>3</sub> CN	-40°C to rt	77	46
9	B	NFSI	(DHQ) <sub>2</sub> Pyr	CH <sub>3</sub> CN	-40°C to rt	74	31
10	B	NFSI	(DHQD) <sub>2</sub> PHAL	CH <sub>3</sub> CN	-40°C to rt	75	23
11	B	NFSI	(DHQ) <sub>2</sub> PHAL	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CN	-40°C to rt	trace	-
12	B	NFSI	(DHQ) <sub>2</sub> PHAL	hexane	-40°C to rt	trace	-
13	C	NFSI	(DHQ) <sub>2</sub> PHAL	hexane	-40°C to rt	80	58

**General procedure<sup>4</sup>:** catalyst (20 mol%) and “F” source (1.2 equiv) in solvent (1.0 ml) were stirred under nitrogen atmosphere at room temperature for 30 min. K<sub>2</sub>CO<sub>3</sub> (6.0 equiv) was then

added to the solution, and the reaction mixture was stirred for 30 min at -40 °C. A solution of silyl enol ether (0.1 mmol) in solvent (1.0 ml) was added to the catalyst solution. The reaction was stirred at the temperature for 1 to 4 days while monitoring by TLC. The reaction was stopped by addition of aqueous solution of 1N HCl. The reaction mixture was then diluted with AcOEt, washed with saturated aqueous sodium bicarbonate solution, brine, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hexane/AcOE = 20/1. The ee of the product was determined by chiral HPLC.

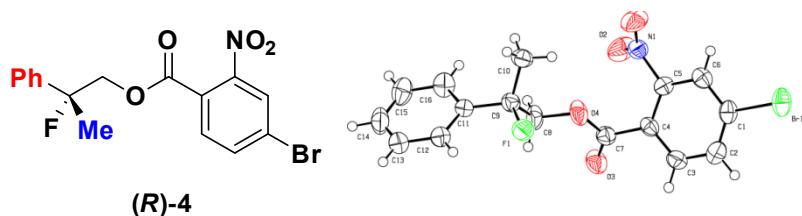
methyl benzyl(2-fluoro-2-methyloctanoyl)carbamate (**2g<sub>0</sub>**)

colorless oil (82%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86 (t,  $J = 7.2$  Hz, 3H), 0.92-1.05 (m, 1H), 1.10-1.35 (m, 7H), 1.60 (d,  $J = 20.8$  Hz, 3H), 1.68-1.82 (m, 1H), 1.92-2.08 (m, 1H), 3.78 (s, 3H), 4.79 (s, 2H), 7.20-7.40 (m, 5H);  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 22.4, 22.8 (d,  $J_{\text{C}-\text{F}} = 3.5$  Hz), 24.1 (d,  $J_{\text{C}-\text{F}} = 23.0$  Hz), 29.1, 31.5, 40.1 (d,  $J_{\text{C}-\text{F}} = 22.5$  Hz), 50.0, 53.9, 99.2 (d,  $J_{\text{C}-\text{F}} = 190.4$  Hz), 127.6, 128.2, 128.4, 136.8, 155.9, 177.5 (d,  $J_{\text{C}-\text{F}} = 24.8$  Hz);  $^{19}\text{F}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -155.5 (m, 1F); HPLC: (AD-H, Hexane/  $i\text{PrOH}=99/1$ , 1.0 ml/ min, 254 nm) tR (minor-isomer)=5.68 min, tR(major-isomer)=5.91 min (59% ee)

## 7. References

1. A. T. Herrmann, L. L. Smith, A. Zakarian, *J. Am. Chem. Soc.*, 2012, **134**, 6976.
  2. (a)Y. Minko, M. Pasco, L. Lercher, M. Botoshansky, I. Marek, *Nature*, 2012, **490**, 522; (b) M. O. Frederick, J. A. Mulder, M. R. Tracey, R. P. Hsung, J. Huang, K. C. Kurtz, L. Shen, C. J. Douglas, *J. Am. Chem. Soc.* 2003, **125**, 2368.
  3. M. Körner, M. Hiersemann, *Org. Lett.* 2007, **9**, 4979.
  4. T. Ishimaru, N. Shibata, T. Horikawa, N. Yasuda, S. Nakamura, T. Toru, M. Shiro, *Angew. Chem. Int. Ed.*, 2008, **47**, 4157.

## 8. X-ray crystallographic analysis data



Crystallographic data for the title structure (**R**)-4 have been deposited with the Cambridge Crystallographic Data Centre, accession number CCDC 1574441.

Table 1. Crystal data and structure refinement for Marek135.

Identification code Marek135 (Jian Qiang Huang)  
Empirical formula C16 H13 Br F N O4

Formula weight	382.18
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P 21 21 2
Unit cell dimensions	a = 29.8490(2) Å alpha = 90 deg. b = 7.0020(2) Å beta = 90 deg. c = 7.6880(8) Å gamma = 90 deg.
Volume	1606.81(17) Å <sup>3</sup>
Z, Calculated density	4, 1.580 Mg/m <sup>3</sup>
Absorption coefficient	2.587 mm <sup>-1</sup>
F(000)	768
Crystal size	0.33 x 0.24 x 0.18 mm
Theta range for data collection	1.36 to 24.38 deg.
Limiting indices	0<=h<=34, 0<=k<=8, 0<=l<=8
Reflections collected / unique	1551 / 1551 [R(int) = 0.0720]
Completeness to theta = 24.38	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6531 and 0.4623
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1551 / 0 / 129
Goodness-of-fit on F <sup>2</sup>	1.122
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.1317
R indices (all data)	R1 = 0.0580, wR2 = 0.1449
Absolute structure parameter	0.00
Largest diff. peak and hole	1.249 and -0.792 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for shelxl.  
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	4461(1)	2238(1)	7151(1)	60(1)
F(1)	6147(1)	8037(7)	396(5)	54(1)
O(1)	6230(2)	3545(12)	5714(8)	78(2)
O(2)	6311(2)	1486(10)	3692(9)	70(2)
O(3)	5721(2)	2222(9)	-430(6)	58(1)
O(4)	6045(2)	4340(8)	1346(6)	54(1)
N(1)	6083(2)	2554(10)	4562(7)	45(2)

C(1)	4861(2)	2396(10)	5260(9)	41(2)
C(2)	4696(2)	2360(10)	3580(10)	48(2)
C(3)	4993(2)	2476(10)	2184(8)	45(2)
C(4)	5450(2)	2627(9)	2468(8)	37(1)
C(5)	5598(2)	2598(10)	4193(8)	36(1)
C(6)	5314(2)	2511(10)	5588(8)	41(2)
C(7)	5754(2)	2975(11)	965(9)	41(2)
C(8)	6367(2)	4861(12)	40(8)	49(2)
C(9)	6529(2)	6845(10)	480(9)	39(2)
C(10)	6709(2)	7068(11)	2329(8)	46(2)
C(11)	6861(2)	7486(11)	-898(8)	40(2)
C(12)	6765(3)	9000(11)	-2011(9)	51(2)
C(13)	7060(3)	9500(14)	-3308(10)	59(2)
C(14)	7450(3)	8502(15)	-3524(11)	63(2)
C(15)	7559(3)	7073(13)	-2411(11)	60(2)
C(16)	7270(3)	6534(11)	-1109(11)	51(2)

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Table 3. Bond lengths [Å] and angles [deg] for shelxl.

Br(1)-C(1)	1.884(6)
F(1)-C(9)	1.415(8)
O(1)-N(1)	1.208(8)
O(2)-N(1)	1.213(8)
O(3)-C(7)	1.199(9)
O(4)-C(7)	1.324(8)
O(4)-C(8)	1.439(8)
N(1)-C(5)	1.474(8)
C(1)-C(6)	1.377(9)
C(1)-C(2)	1.383(10)
C(2)-C(3)	1.394(10)
C(2)-H(2)	0.9300
C(3)-C(4)	1.387(10)
C(3)-H(3)	0.9300
C(4)-C(5)	1.398(9)
C(4)-C(7)	1.488(9)
C(5)-C(6)	1.369(9)
C(6)-H(6)	0.9300
C(8)-C(9)	1.509(11)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(11)	1.518(9)

C(9)-C(10)	1.528(9)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(12)	1.392(10)
C(11)-C(16)	1.402(10)
C(12)-C(13)	1.375(11)
C(12)-H(12)	0.9300
C(13)-C(14)	1.369(13)
C(13)-H(13)	0.9300
C(14)-C(15)	1.355(13)
C(14)-H(14)	0.9300
C(15)-C(16)	1.373(11)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(7)-O(4)-C(8)	117.9(5)
O(1)-N(1)-O(2)	123.6(6)
O(1)-N(1)-C(5)	119.1(6)
O(2)-N(1)-C(5)	117.3(6)
C(6)-C(1)-C(2)	121.5(6)
C(6)-C(1)-Br(1)	118.9(5)
C(2)-C(1)-Br(1)	119.6(5)
C(1)-C(2)-C(3)	119.4(6)
C(1)-C(2)-H(2)	120.3
C(3)-C(2)-H(2)	120.3
C(4)-C(3)-C(2)	120.7(6)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	117.3(6)
C(3)-C(4)-C(7)	119.3(6)
C(5)-C(4)-C(7)	123.2(6)
C(6)-C(5)-C(4)	123.3(6)
C(6)-C(5)-N(1)	117.1(5)
C(4)-C(5)-N(1)	119.5(5)
C(5)-C(6)-C(1)	117.8(6)
C(5)-C(6)-H(6)	121.1
C(1)-C(6)-H(6)	121.1
O(3)-C(7)-O(4)	124.7(7)
O(3)-C(7)-C(4)	124.9(6)
O(4)-C(7)-C(4)	110.2(6)
O(4)-C(8)-C(9)	106.9(6)
O(4)-C(8)-H(8A)	110.3
C(9)-C(8)-H(8A)	110.3

O(4)-C(8)-H(8B)	110.3
C(9)-C(8)-H(8B)	110.3
H(8A)-C(8)-H(8B)	108.6
F(1)-C(9)-C(8)	106.0(6)
F(1)-C(9)-C(11)	108.7(6)
C(8)-C(9)-C(11)	108.9(6)
F(1)-C(9)-C(10)	105.5(5)
C(8)-C(9)-C(10)	114.5(6)
C(11)-C(9)-C(10)	112.9(6)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	118.0(6)
C(12)-C(11)-C(9)	121.3(6)
C(16)-C(11)-C(9)	120.6(6)
C(13)-C(12)-C(11)	120.5(8)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	120.2(8)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	120.3(7)
C(15)-C(14)-H(14)	119.9
C(13)-C(14)-H(14)	119.9
C(14)-C(15)-C(16)	120.8(8)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6
C(15)-C(16)-C(11)	120.1(8)
C(15)-C(16)-H(16)	120.0
C(11)-C(16)-H(16)	120.0

---

Table 4. Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for shelxl.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$$

---

U11	U22	U33	U23	U13	U12
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---

Br(1)	54(1)	64(1)	63(1)	0(1)	26(1)	2(1)
F(1)	40(2)	70(3)	50(2)	6(2)	2(2)	11(2)
O(1)	59(3)	125(6)	49(3)	-32(4)	-7(3)	-19(4)
O(2)	43(3)	92(5)	74(4)	-22(4)	2(3)	17(3)
O(3)	73(3)	63(4)	37(3)	-8(3)	6(2)	-19(3)
O(4)	70(3)	63(3)	28(2)	-11(3)	15(2)	-26(3)
N(1)	41(3)	63(4)	32(3)	-5(3)	2(2)	0(3)
C(1)	40(3)	37(4)	46(3)	-3(4)	13(3)	4(3)
C(2)	39(3)	42(4)	63(4)	3(4)	3(3)	-1(3)
C(3)	49(4)	47(4)	39(3)	8(4)	-6(3)	0(3)
C(4)	48(3)	30(3)	31(3)	2(3)	0(3)	-2(3)
C(5)	34(3)	37(3)	38(3)	-6(3)	-1(2)	2(3)
C(6)	52(4)	36(4)	35(3)	-4(3)	2(3)	0(3)
C(7)	46(4)	42(4)	35(4)	-1(3)	-3(3)	-7(3)
C(8)	55(5)	56(4)	36(4)	-7(4)	15(3)	-19(4)
C(9)	37(3)	43(4)	36(3)	3(3)	2(3)	4(3)
C(10)	47(4)	54(4)	36(3)	1(4)	-6(3)	2(3)
C(11)	37(3)	50(4)	33(3)	4(3)	-4(2)	-6(3)
C(12)	45(4)	56(4)	50(4)	12(4)	-5(3)	-8(3)
C(13)	54(5)	73(5)	51(4)	16(4)	-4(4)	-16(4)
C(14)	65(5)	75(6)	49(4)	-4(5)	15(4)	-32(5)
C(15)	51(4)	60(5)	68(5)	-11(5)	20(4)	-4(4)
C(16)	52(4)	43(4)	60(5)	0(4)	8(4)	5(3)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for shelxl.

	x	y	z	U(eq)
H(2)	4389	2260	3383	57
H(3)	4883	2452	1052	54
H(6)	5423	2530	6721	49
H(8A)	6230	4846	-1104	59
H(8B)	6616	3970	44	59
H(10A)	6788	8379	2529	68
H(10B)	6970	6279	2471	68
H(10C)	6484	6685	3147	68
H(12)	6499	9678	-1877	61

H(13)	6994	10520	-4040	71
H(14)	7641	8805	-4437	76
H(15)	7832	6451	-2531	72
H(16)	7347	5537	-367	62

---

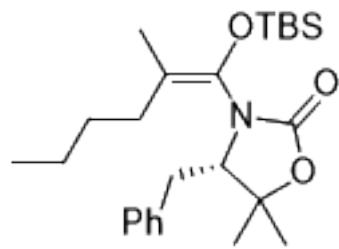
## 9. NMR spectra and HPLC spectra of fluorination products

hjq400

~7.226  
~7.100

3.949  
3.938  
3.923  
3.912

1.594  
1.556  
1.340  
1.281  
1.268  
1.265  
1.257  
0.996  
0.912  
0.876  
0.859  
0.843  
0.133  
0.080



5.27

1.00

0.97

1.02

1.51

2.91

1.16

2.95

4.03

3.23

9.70

3.85

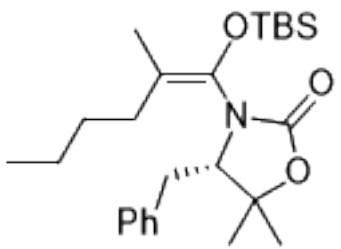
6.25

f1 (ppm)

hjq400

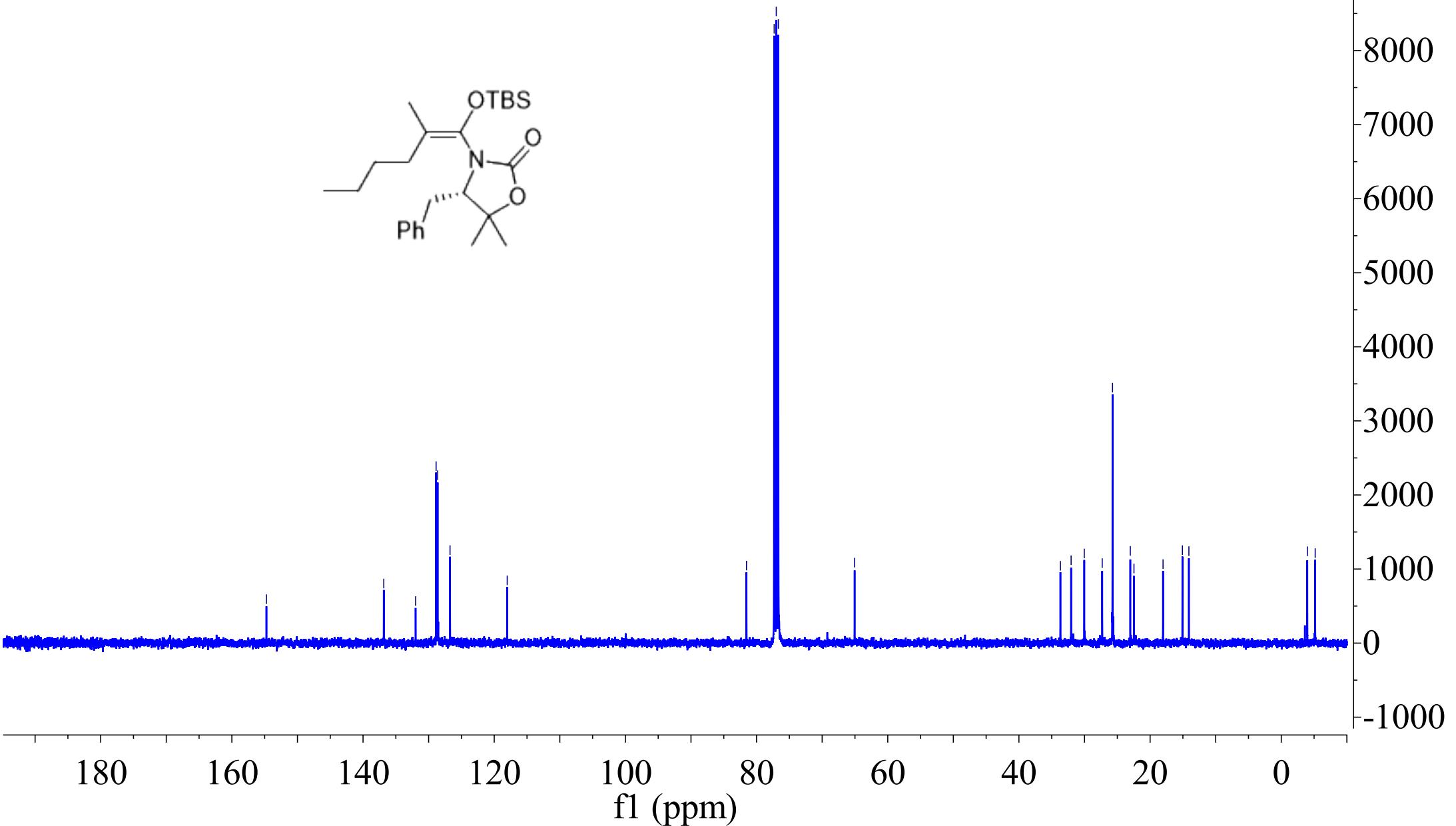
-154.726

136.837  
131.986  
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118.020

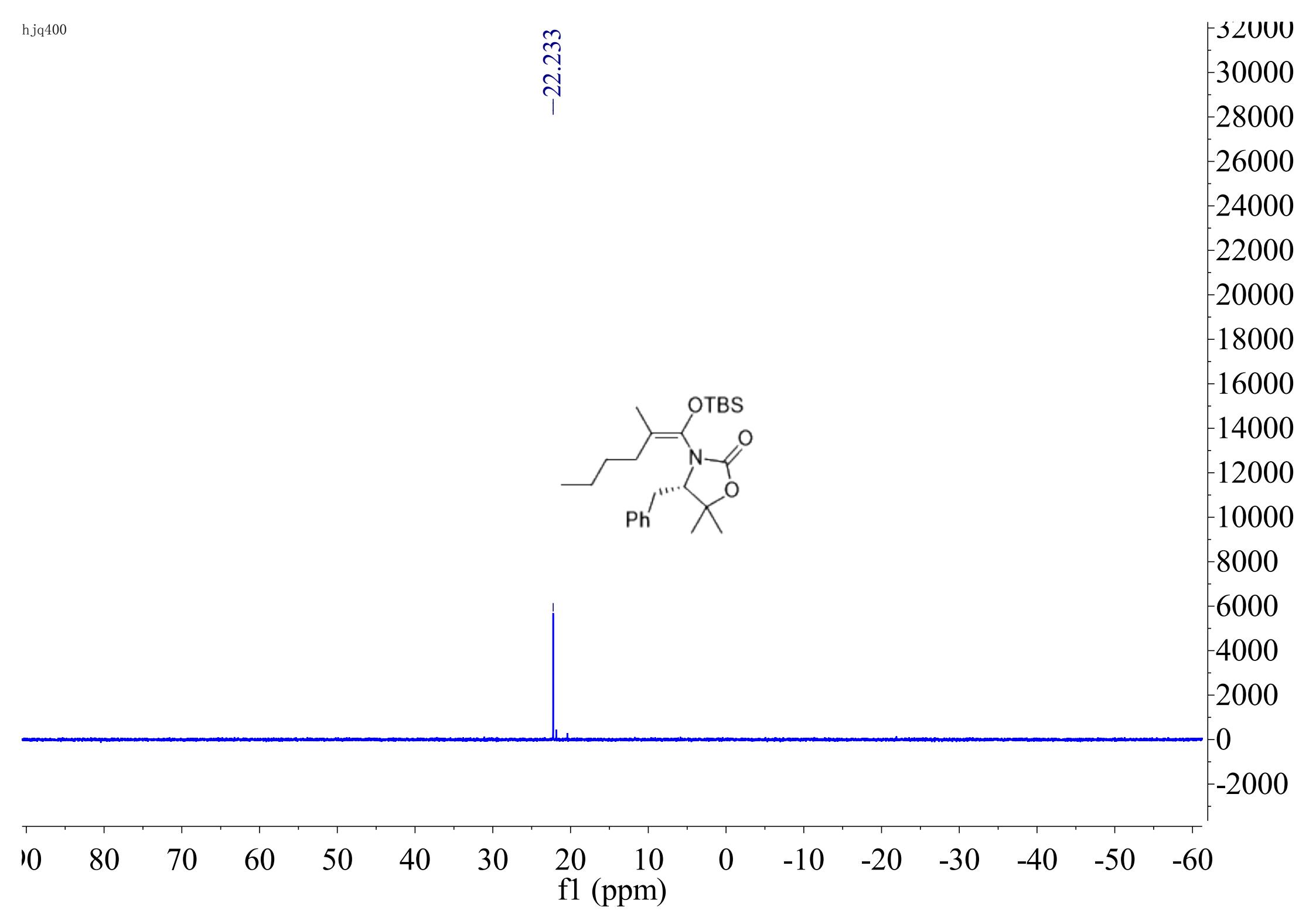
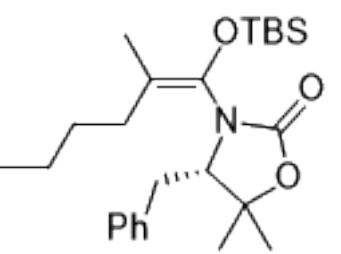


81.536  
77.317  
77.000  
76.682  
-65.053

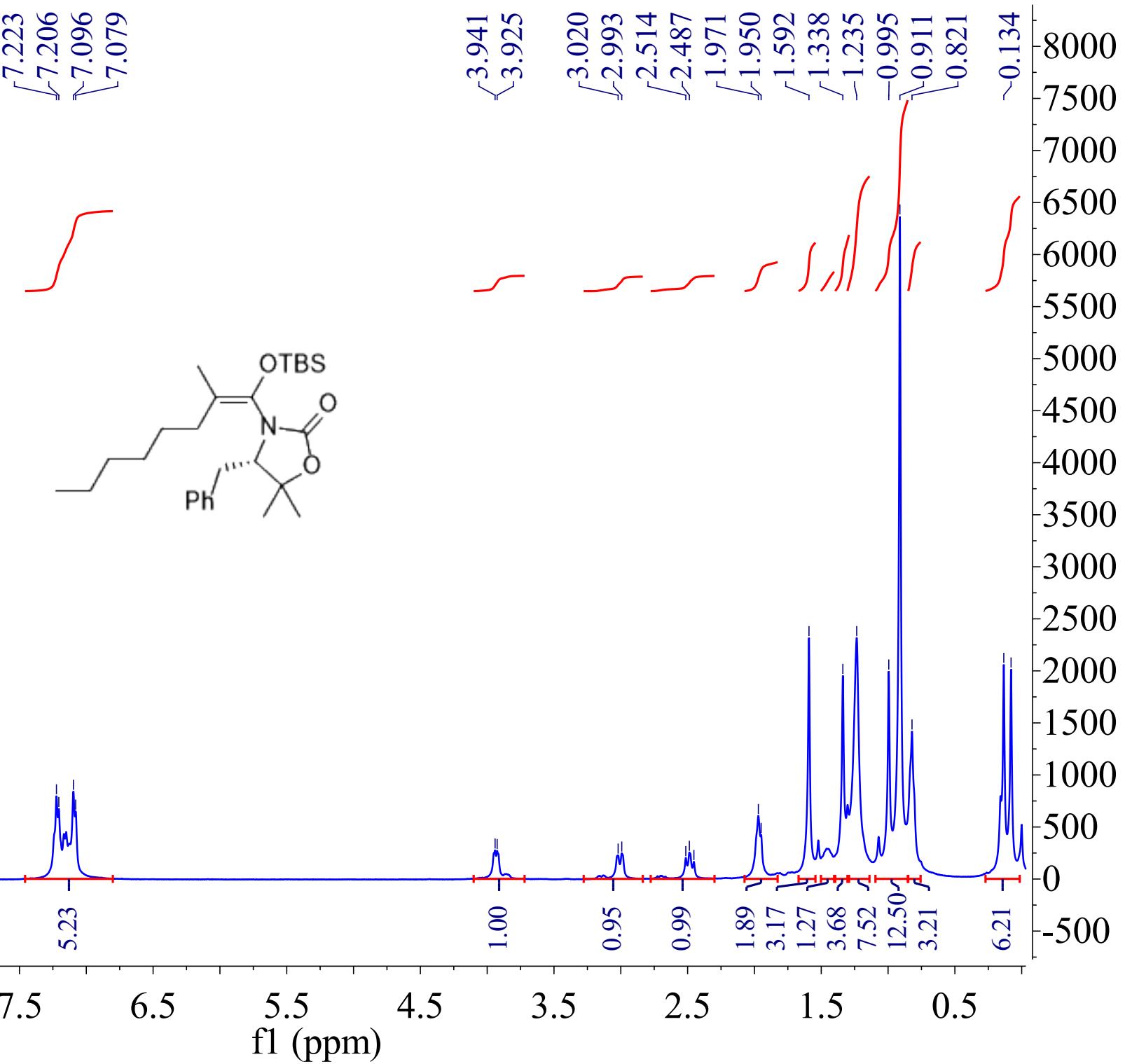
33.675  
32.045  
30.037  
27.302  
25.730  
23.021  
22.461  
~18.028  
15.074  
14.086  
-3.971  
-5.171



-22.233

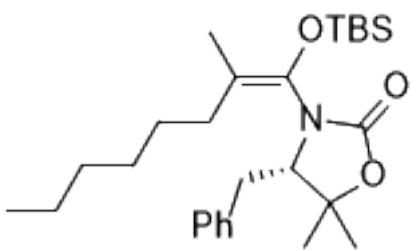


hjq400



hjq400

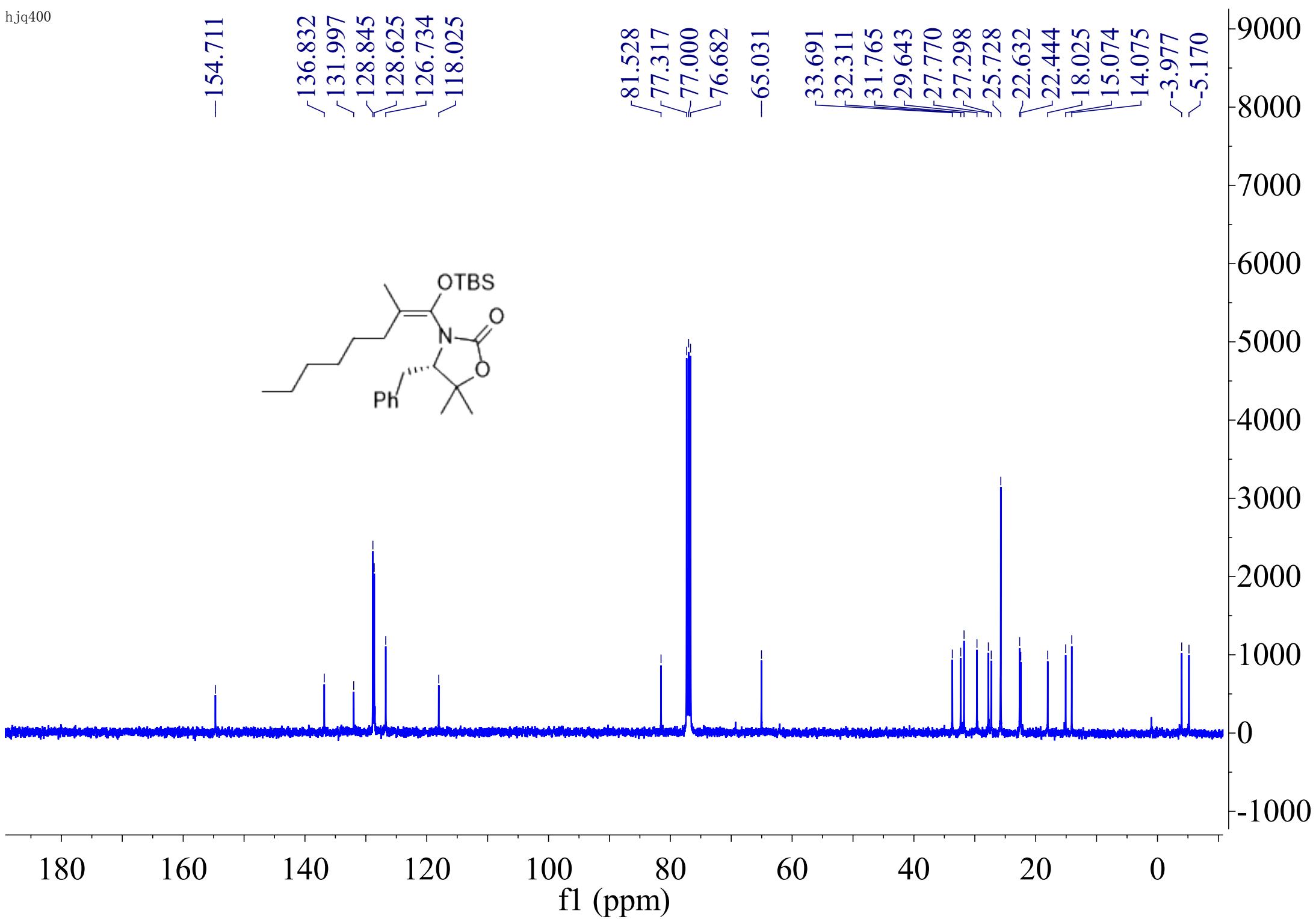
-154.711



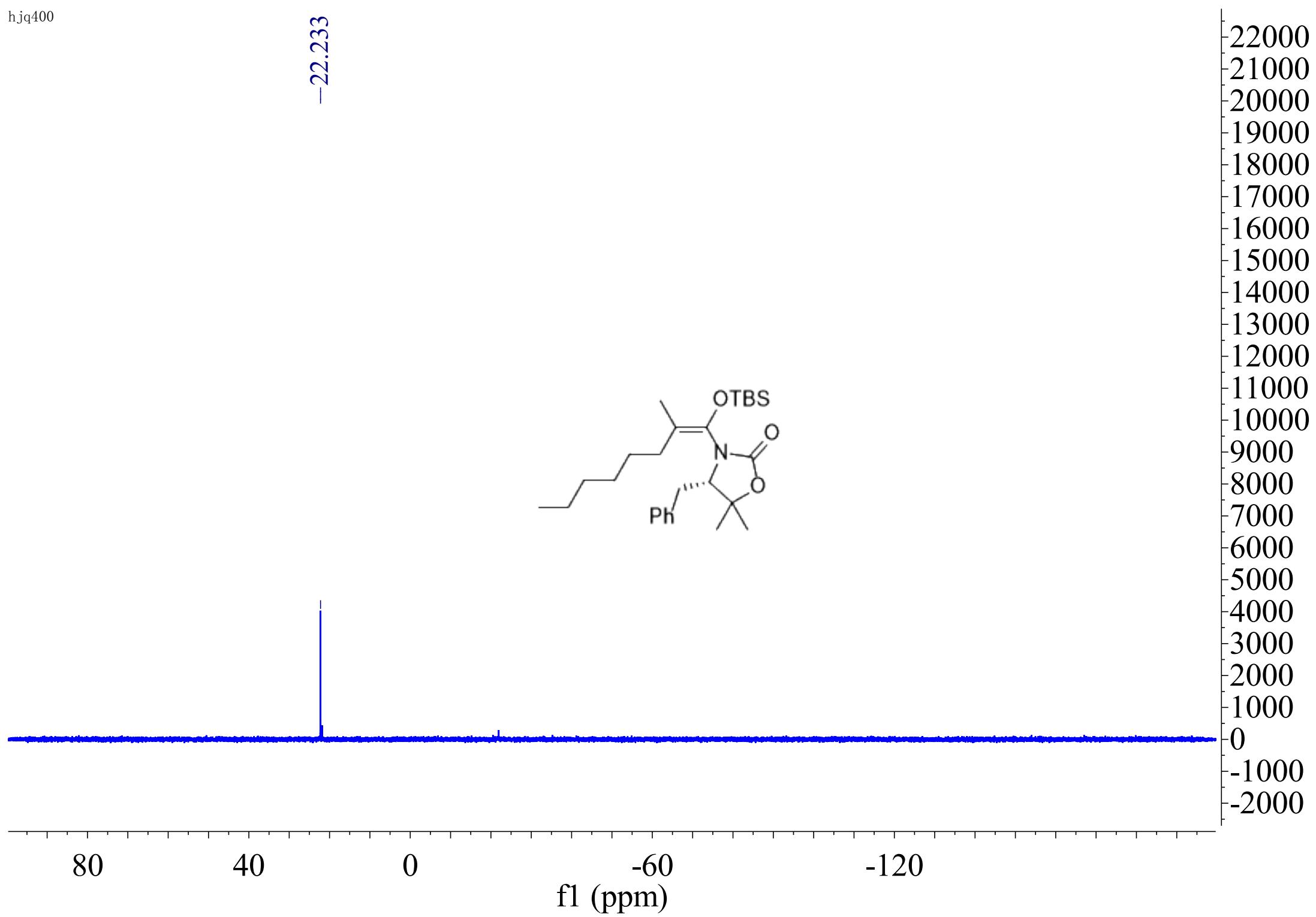
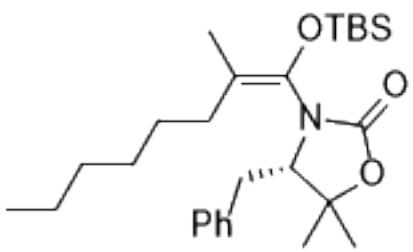
136.832  
131.997  
128.845  
128.625  
126.734  
118.025

81.528  
77.317  
77.000  
76.682  
-65.031

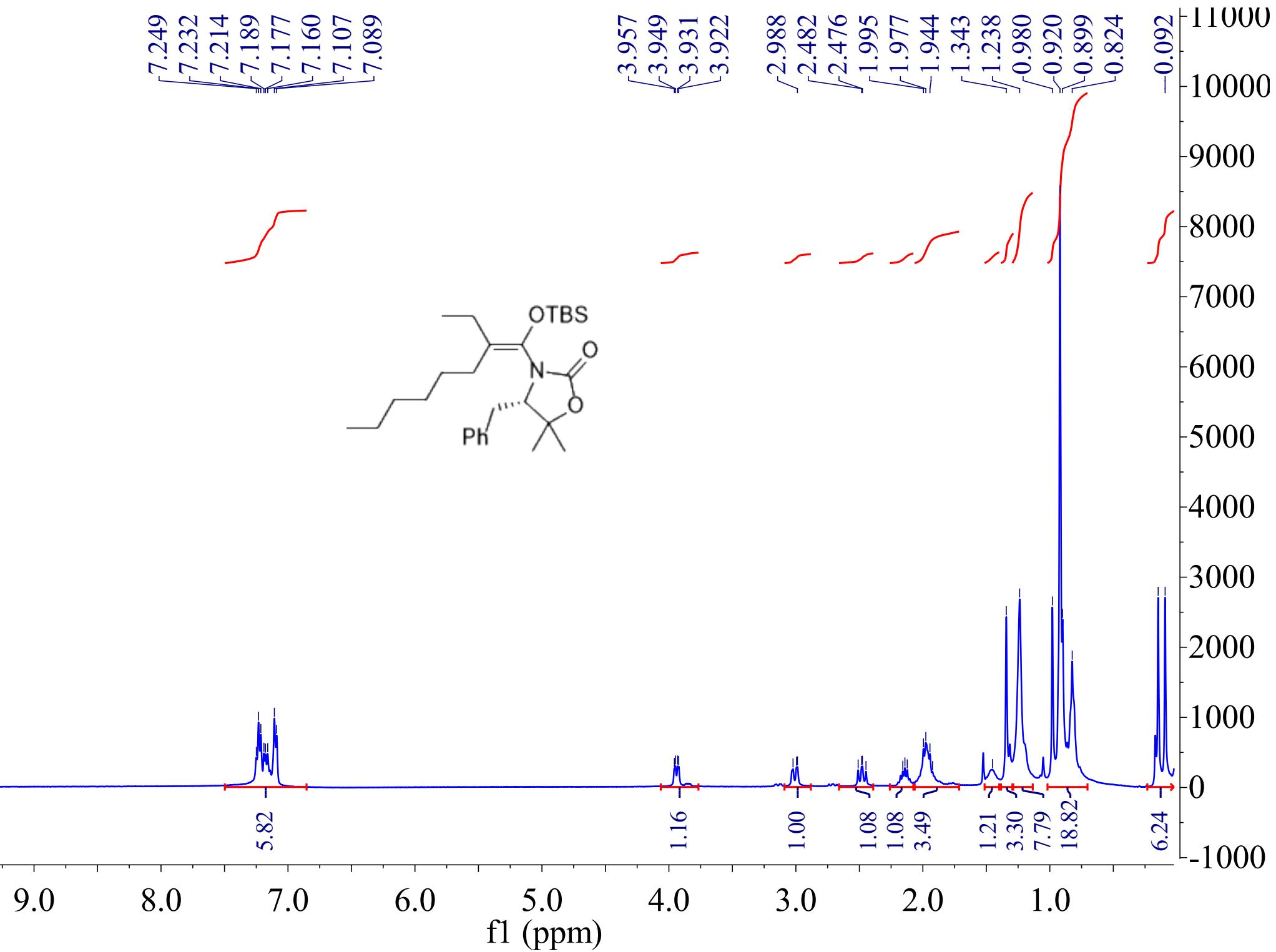
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31.765  
29.643  
27.770  
27.298  
25.728  
22.632  
22.444  
18.025  
15.074  
14.075  
-3.977  
-5.170



-22.233



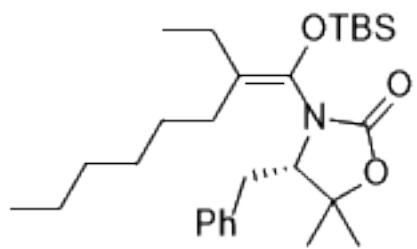
hjq400



hjq400

-154.683

136.878  
131.702  
128.855  
128.702  
126.783  
123.952

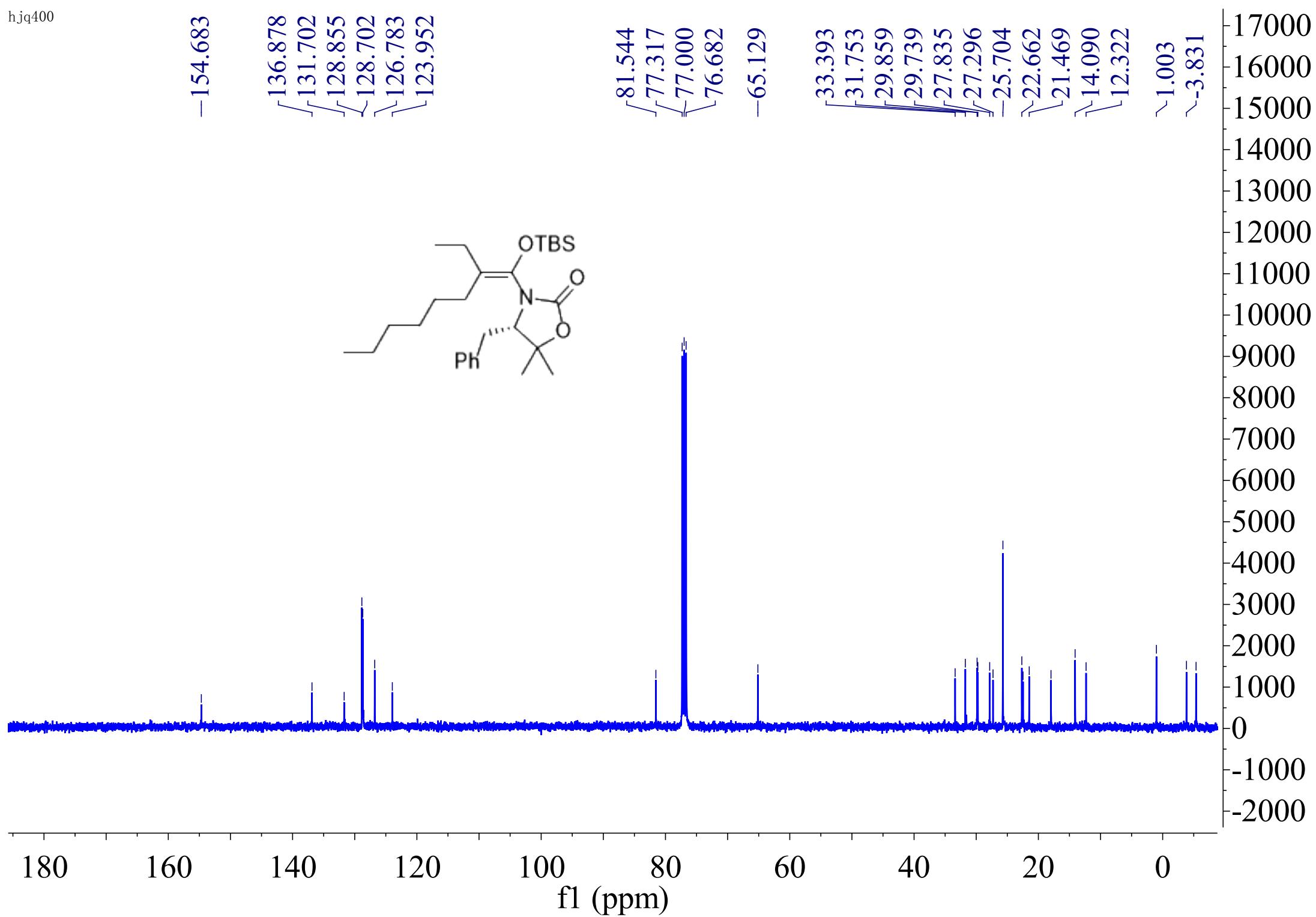


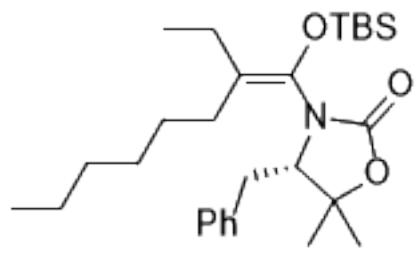
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76.682

-65.129

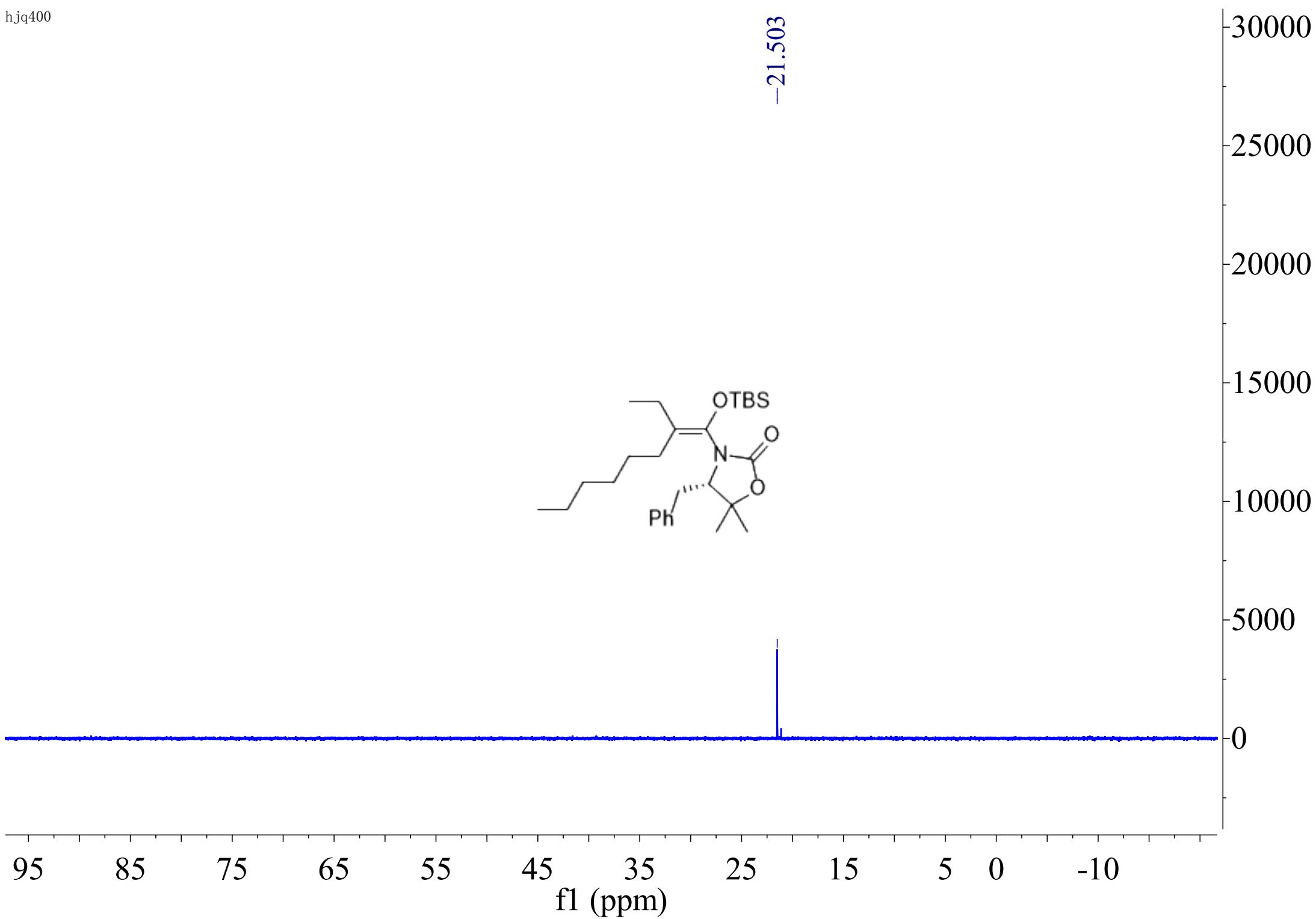
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29.739  
27.835  
27.296  
-25.704  
22.662  
21.469  
14.090  
12.322

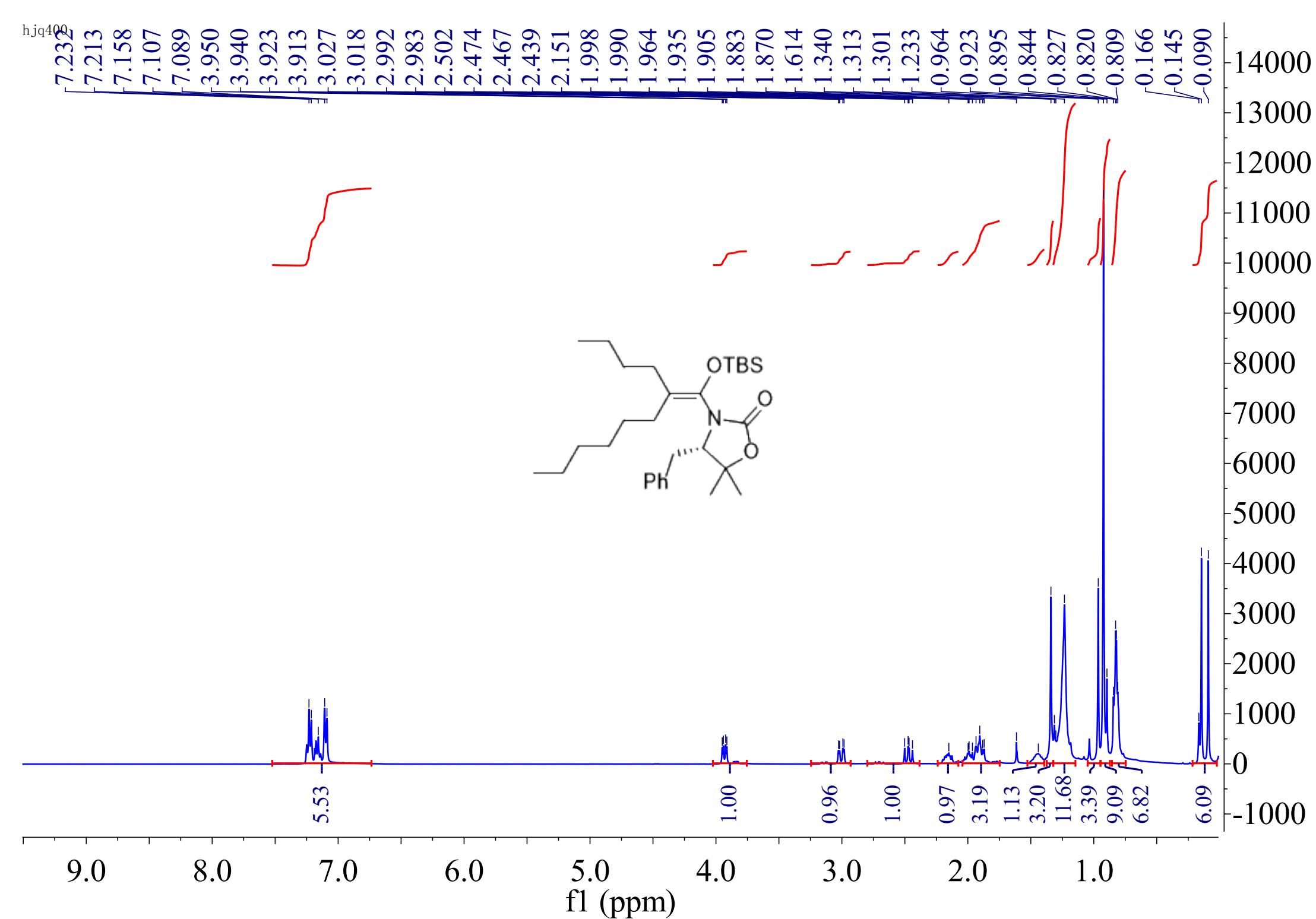
~1.003  
~-3.831





-21.503





hjq400

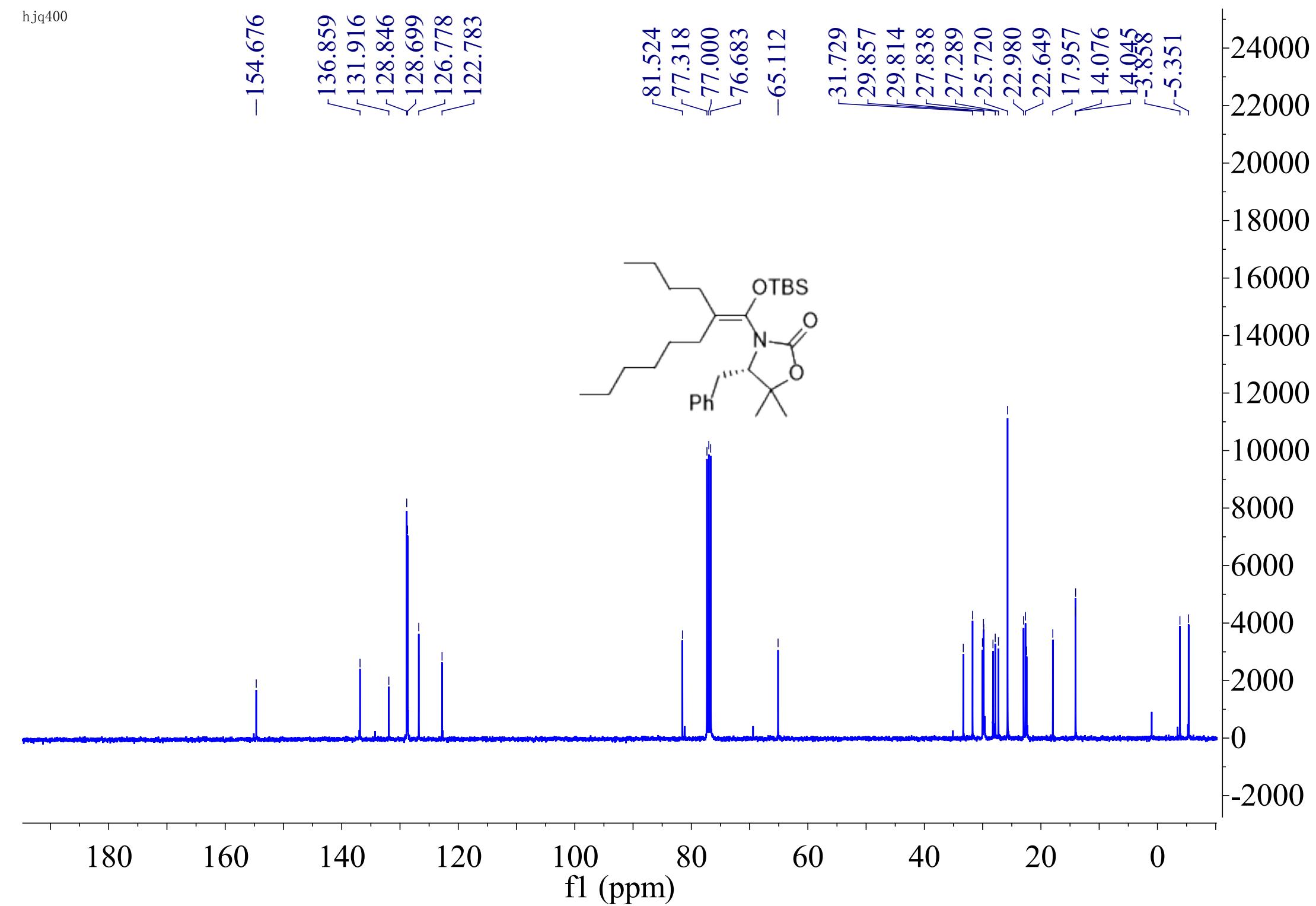
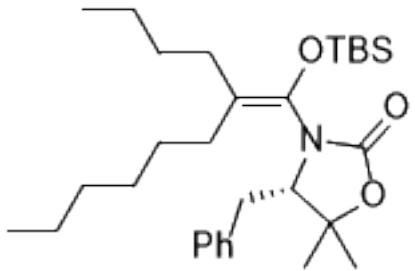
-154.676

136.859  
131.916  
128.846  
128.699  
126.778  
122.783

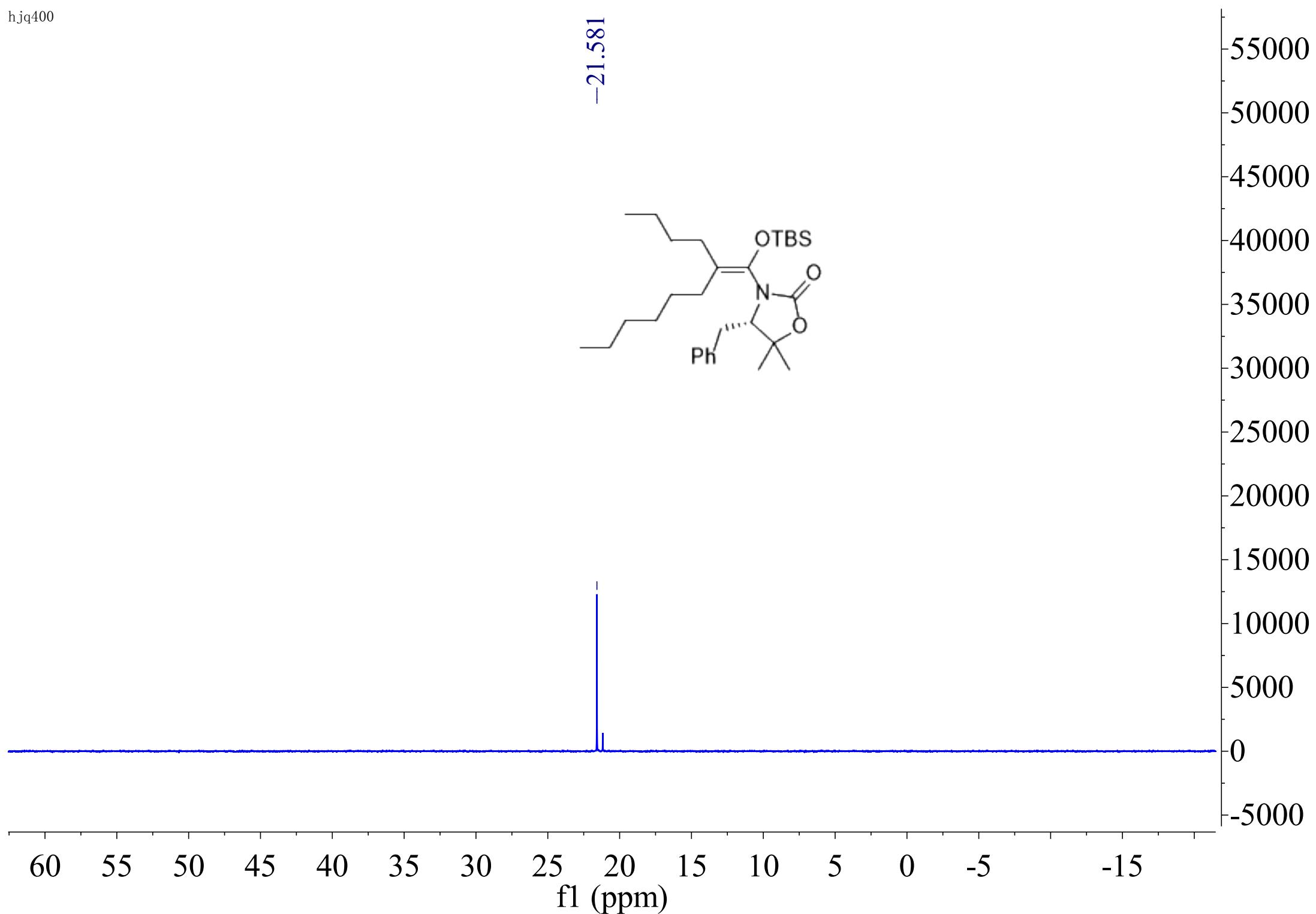
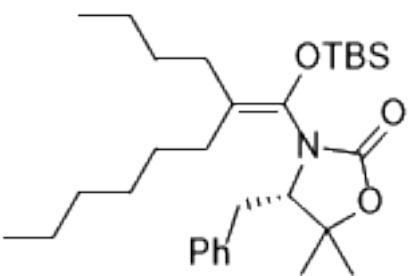
$$\begin{array}{r} 81.524 \\ \{ 77.318 \\ \{ 77.000 \\ \{ 76.683 \\ -65.112 \end{array}$$

The diagram illustrates a sequence of numerical values, each enclosed in a bracket representing its range:

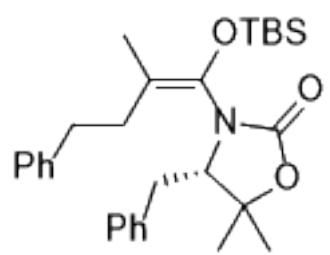
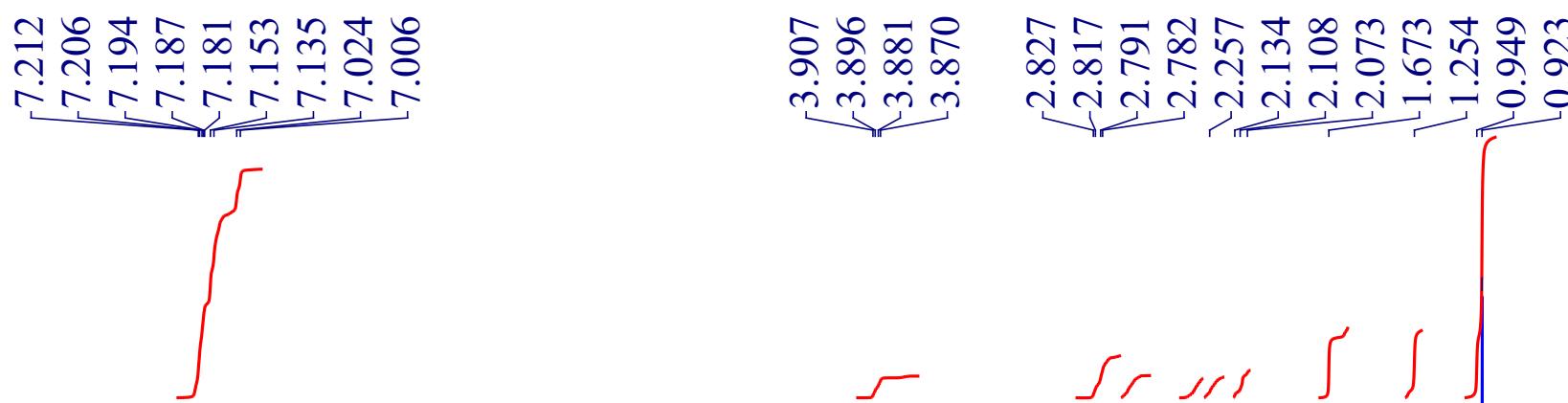
- 31.729
- 29.857
- 29.814
- 27.838
- 27.289
- 25.720
- 22.980
- 22.649
- 17.957
- 14.076
- 14.045
- 3.858
- 5.351



-21.581

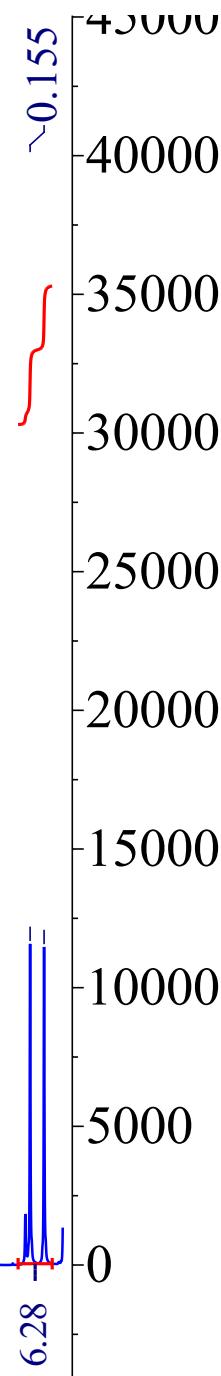


hjq400

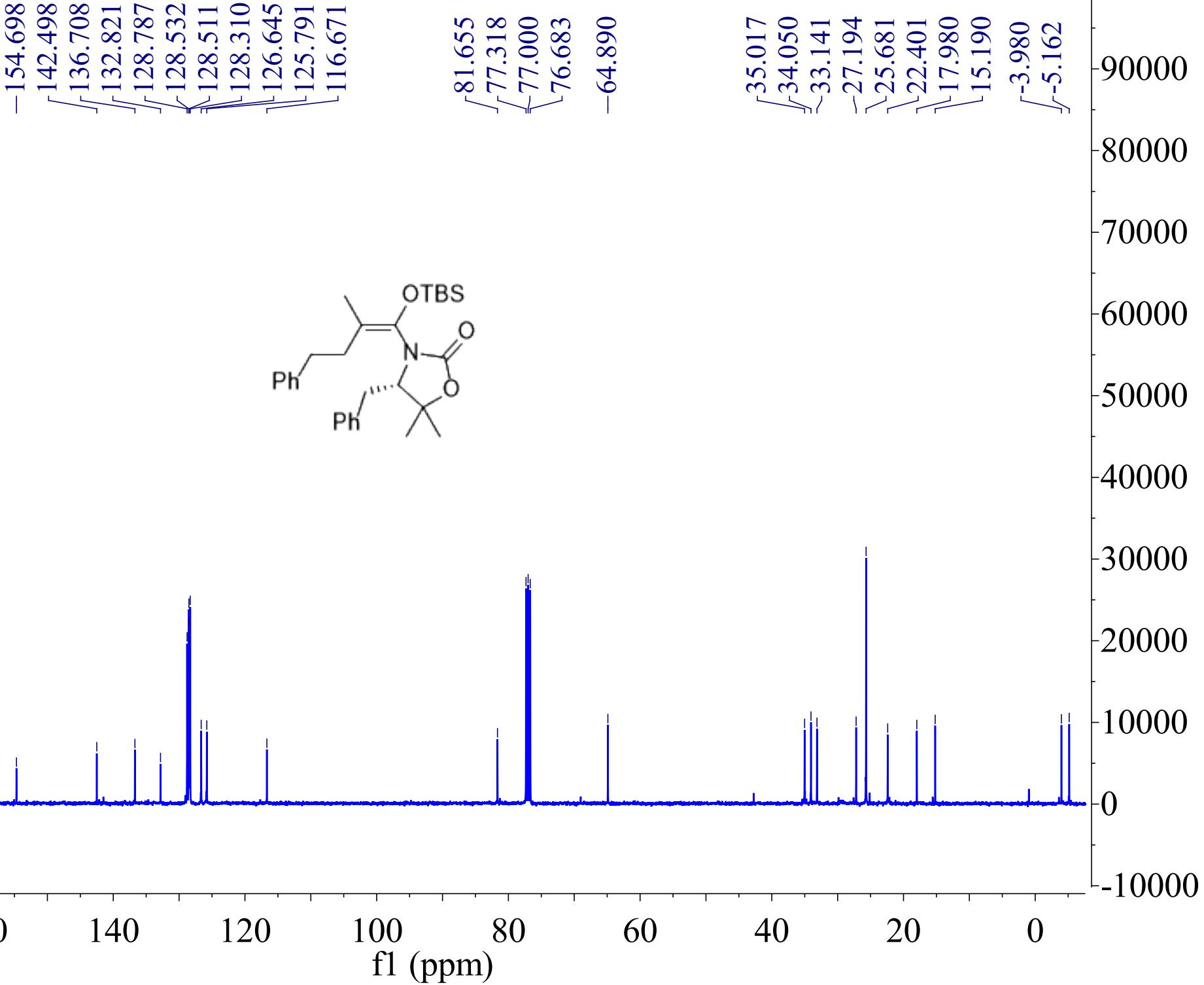


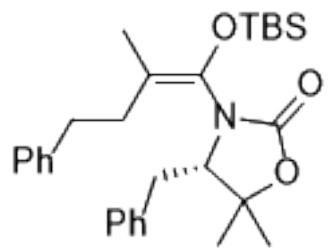
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f1 (ppm)



hjq400



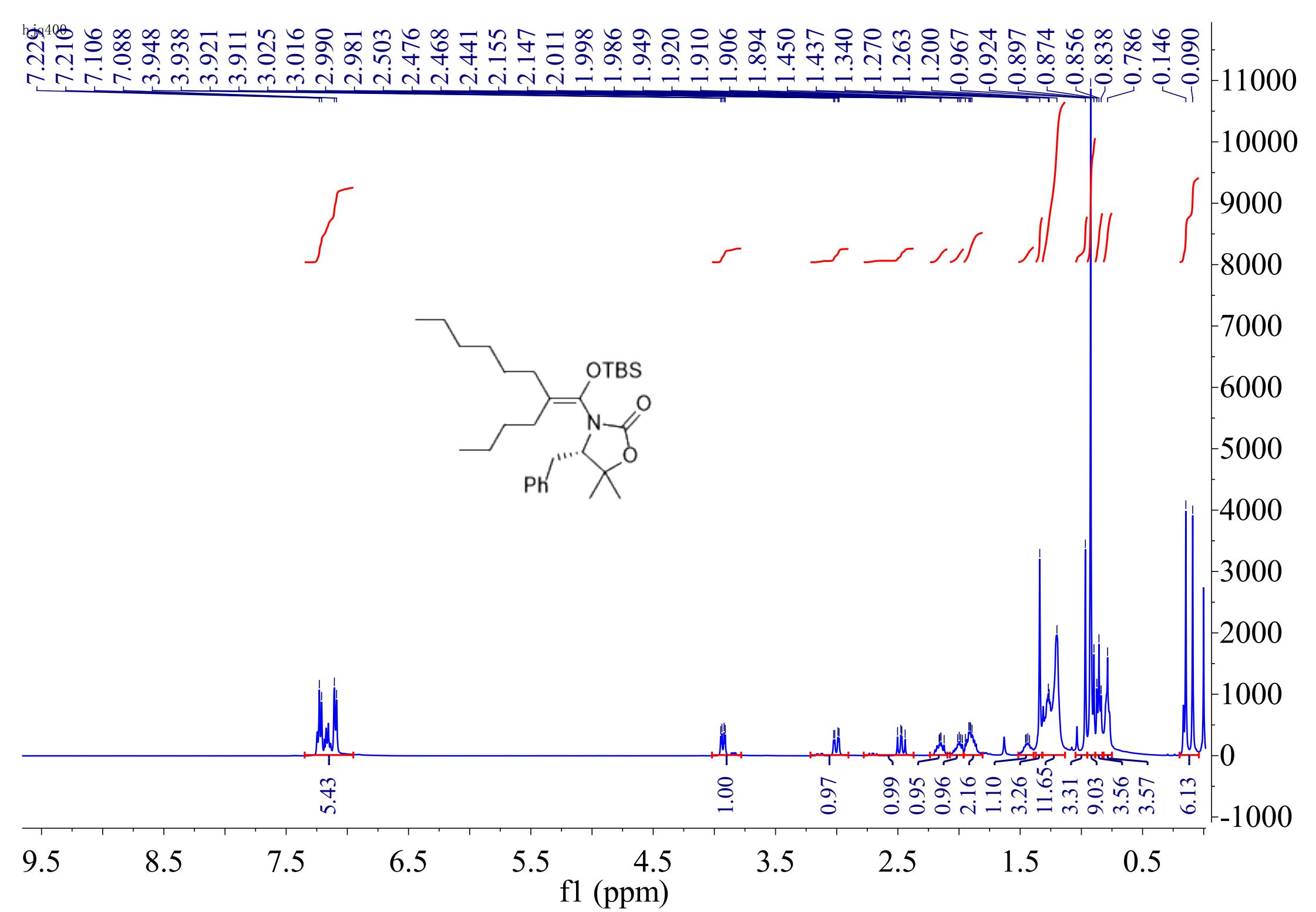


-22.643

85 75 65 55 45 35 25 15 5 0 -10

f1 (ppm)

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100000  
90000  
80000  
70000  
60000  
50000  
40000  
30000  
20000  
10000  
0  
-10000

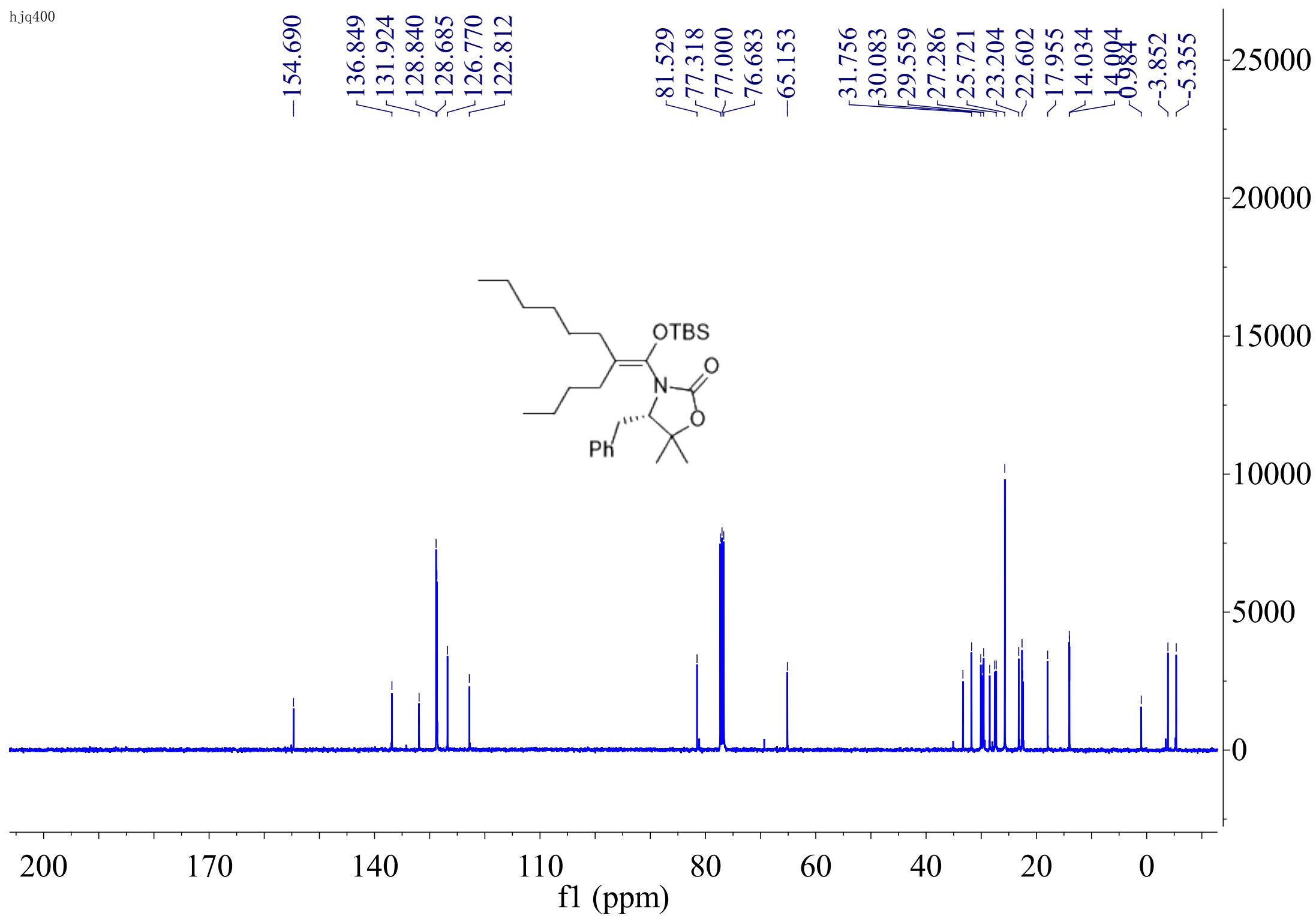
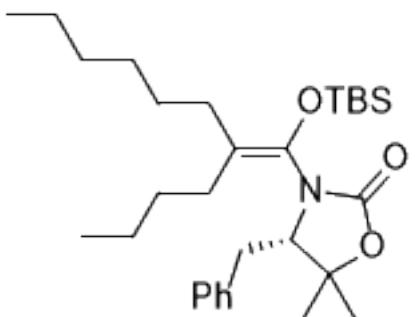


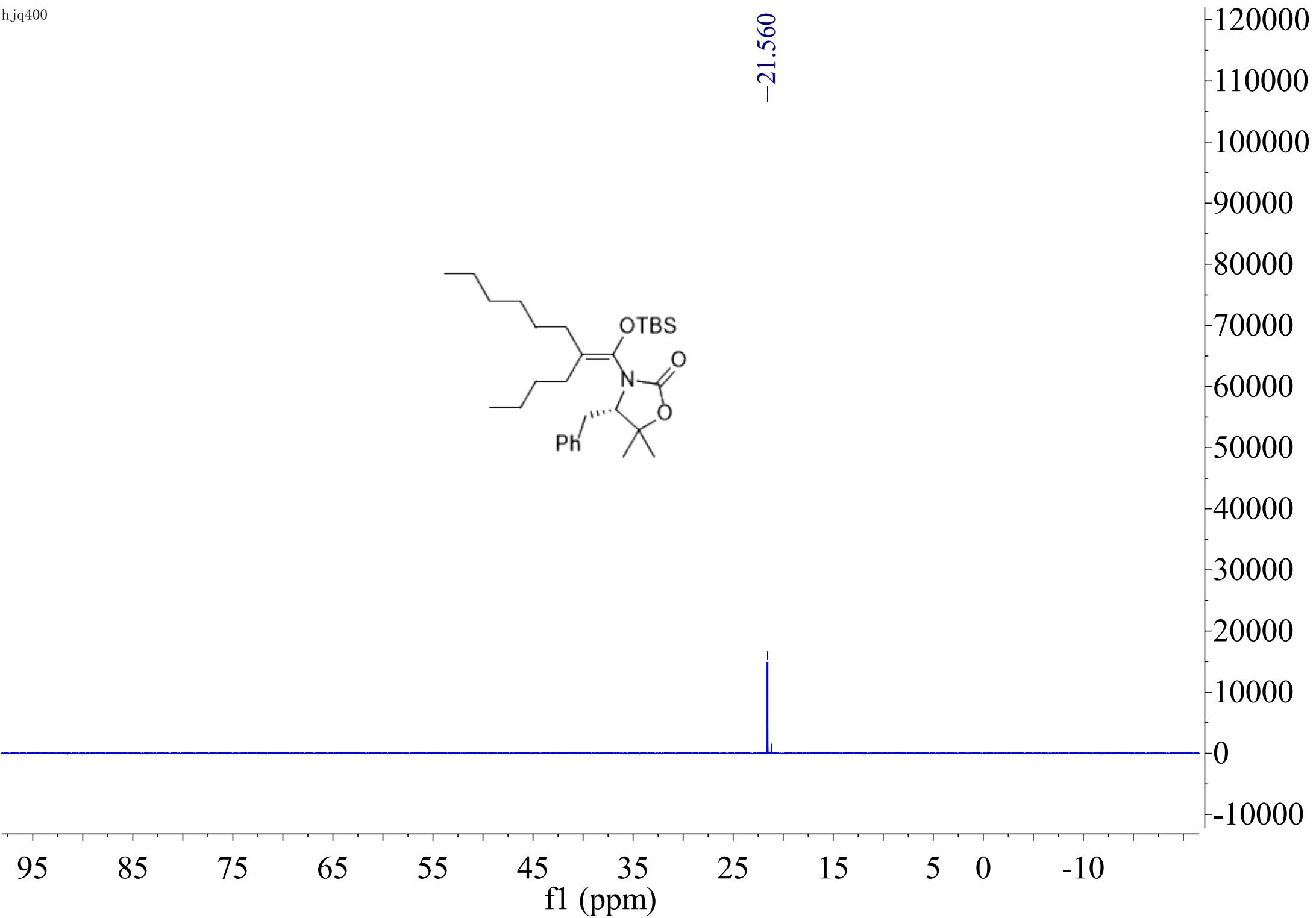
-154.690

136.849  
131.924  
128.840  
128.685  
126.770  
122.812

81.529  
77.318  
77.000  
76.683  
-65.153

31.756  
30.083  
29.559  
27.286  
25.721  
23.204  
22.602  
~17.955  
~14.034  
~14.904  
~0.984  
~-3.852  
~-5.355





hjq400

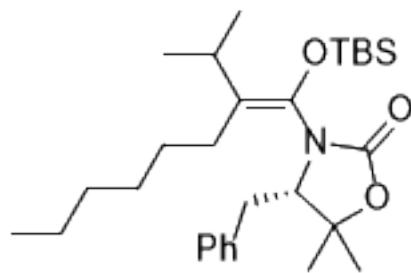
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7.155  
7.108  
7.090

3.951  
3.941  
3.923  
3.914

2.974  
2.878  
2.536  
2.509  
2.501

1.344  
1.234  
0.987  
0.969  
0.948  
0.922  
0.912

~0.148  
23000  
22000  
21000  
20000  
19000  
18000  
17000  
16000  
15000  
14000  
13000  
12000  
11000  
10000  
9000  
8000  
7000  
6000  
5000  
4000  
3000  
2000  
1000  
0  
-1000  
-2000



8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5  
f1 (ppm)

5.61

1.00

1.01

1.19

0.97

2.00

1.24

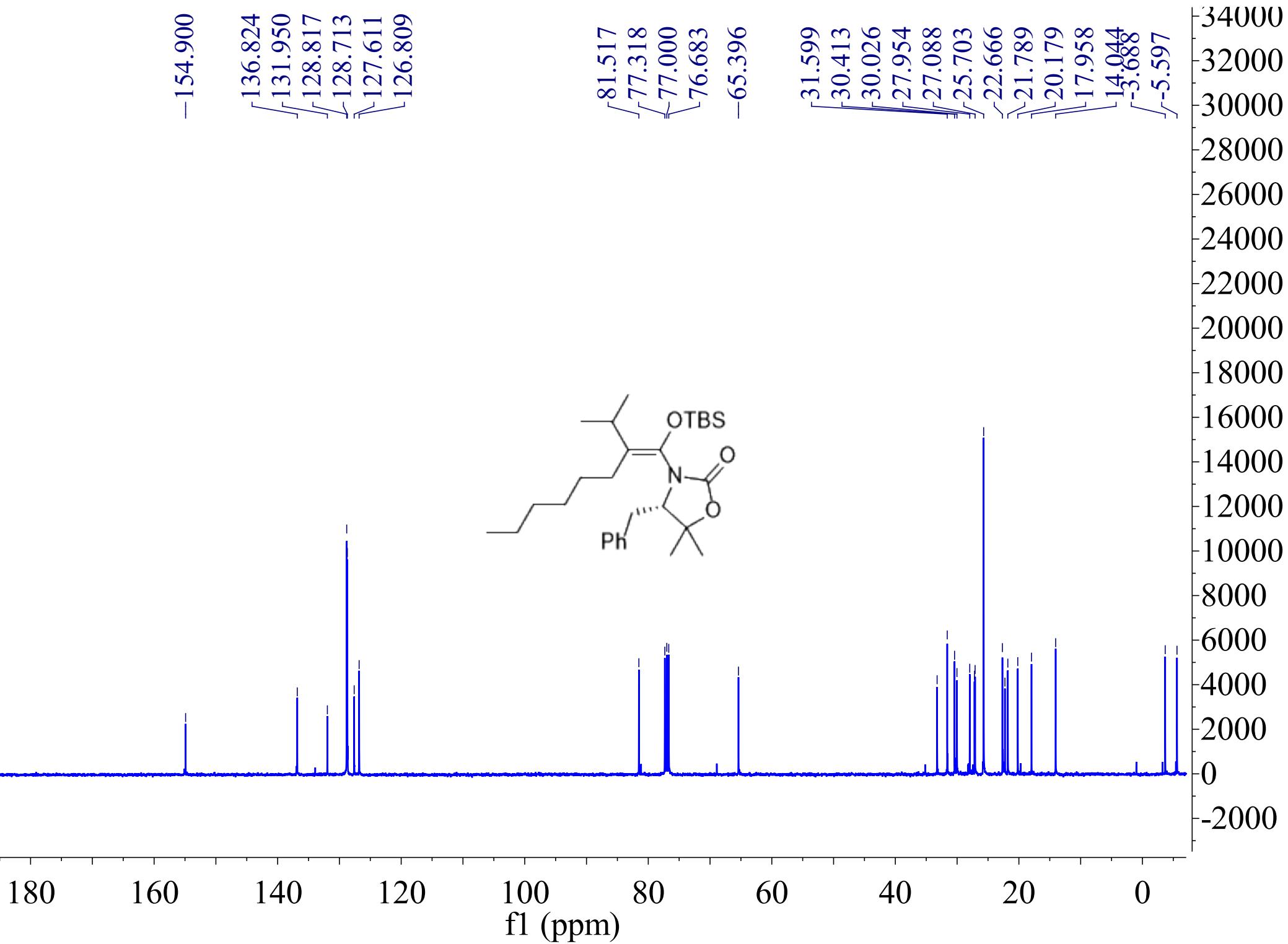
3.17

7.52

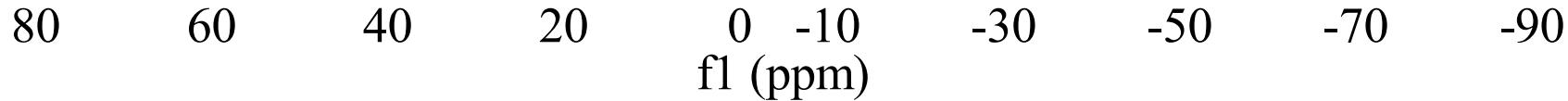
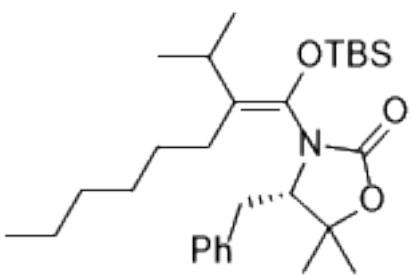
17.67

4.63

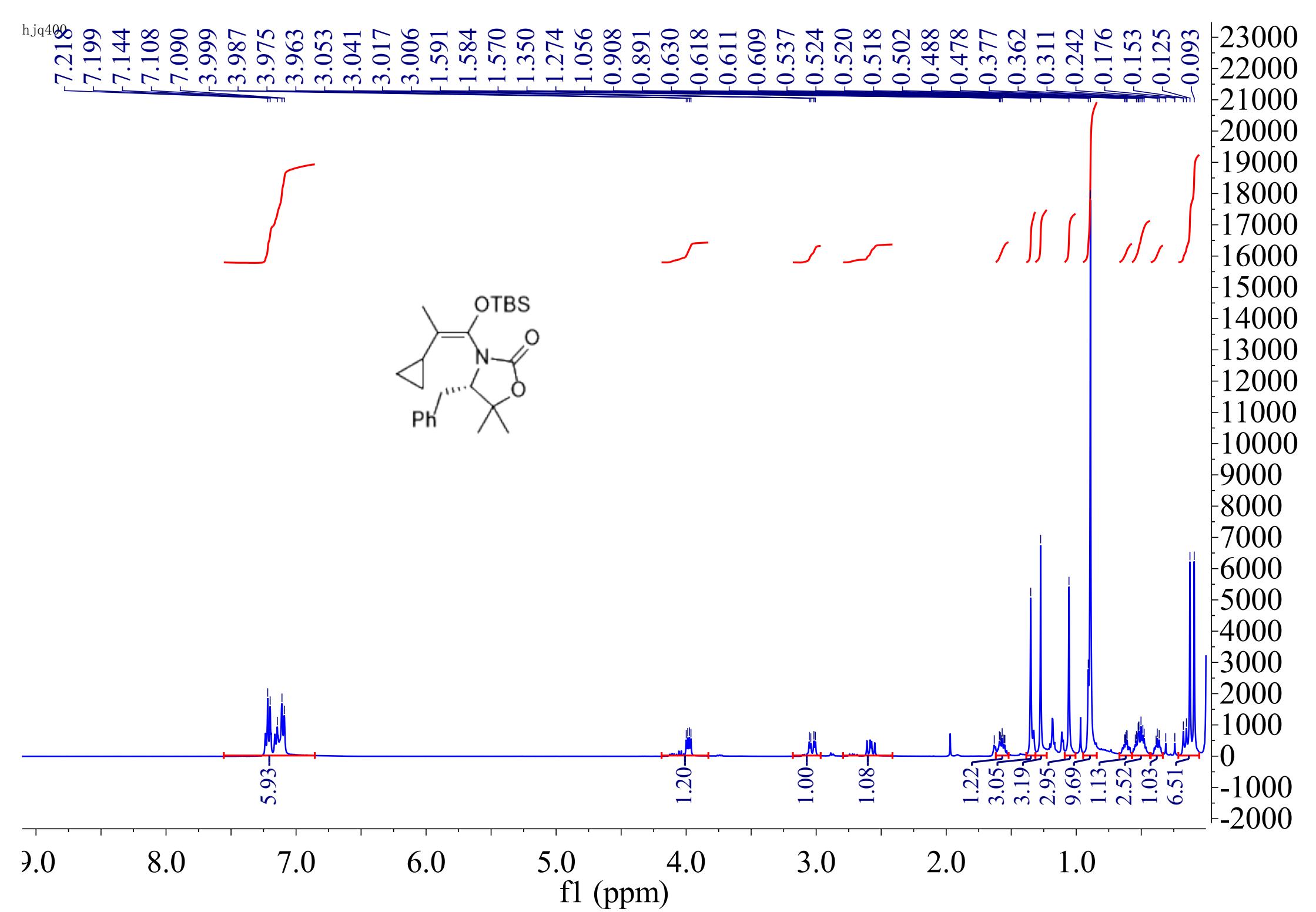
6.26



-21.142



180000  
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160000  
150000  
140000  
130000  
120000  
110000  
100000  
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70000  
60000  
50000  
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30000  
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0  
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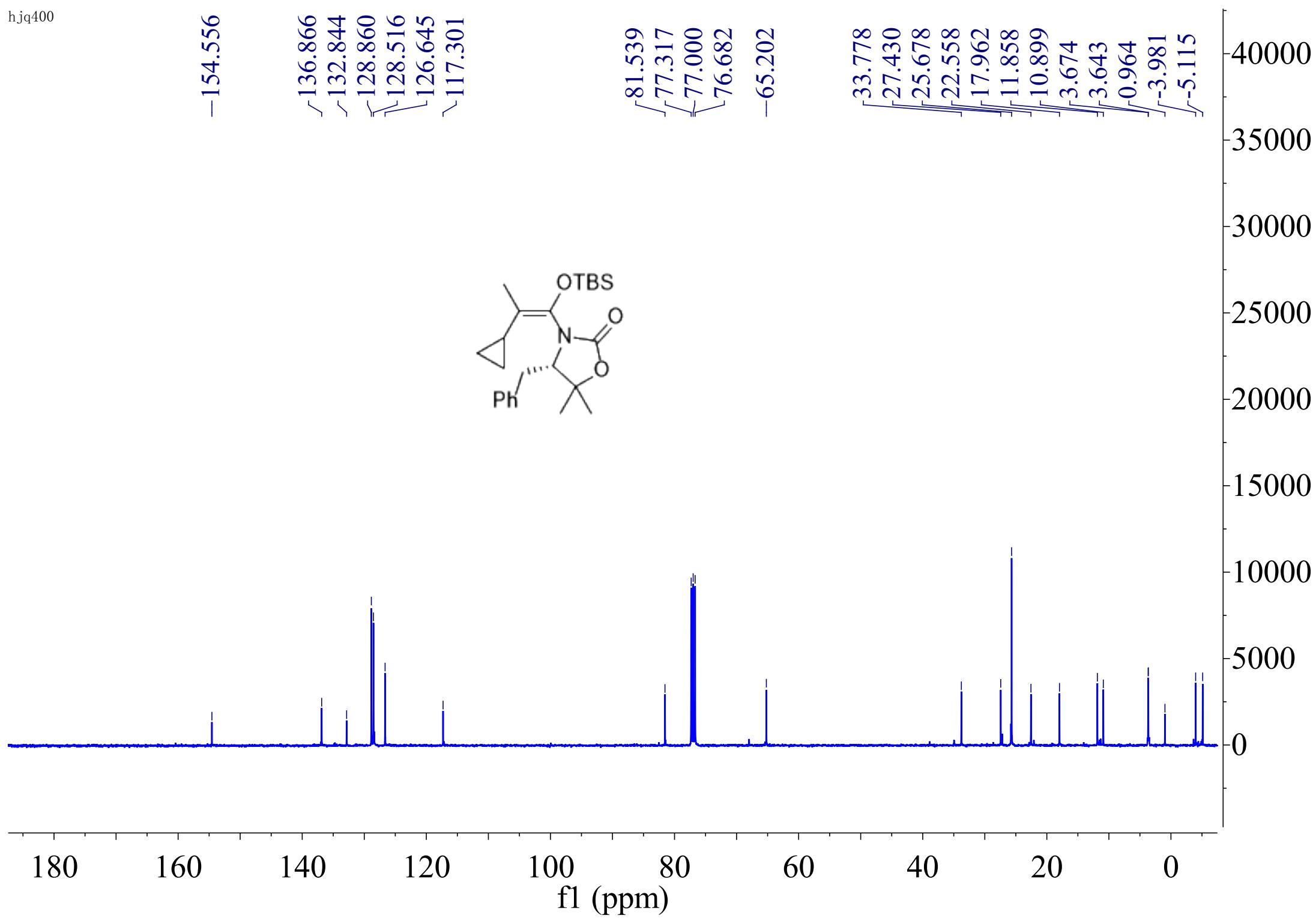
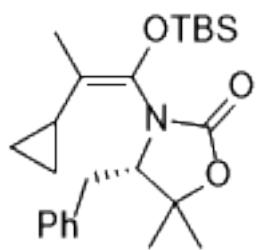
hjq400

-154.556

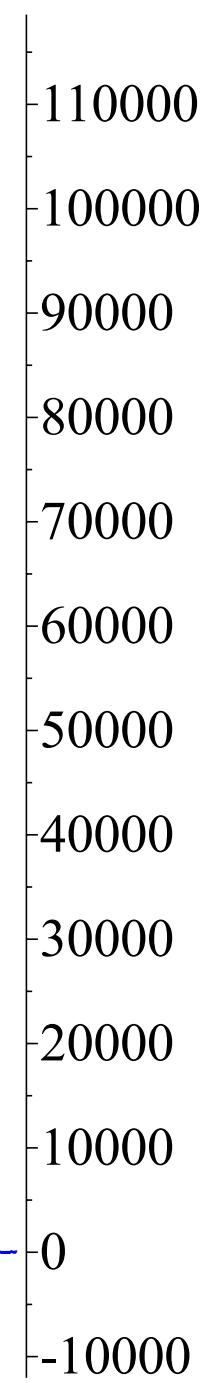
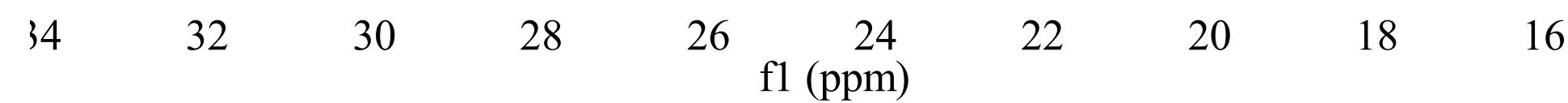
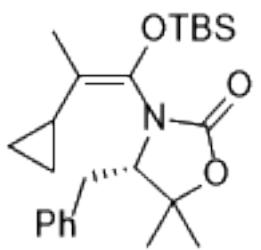
✓ 136.866 ✓ 132.844 ✓ 128.860 ✓ 128.516 ✓ 126.645 ✓ 117.301

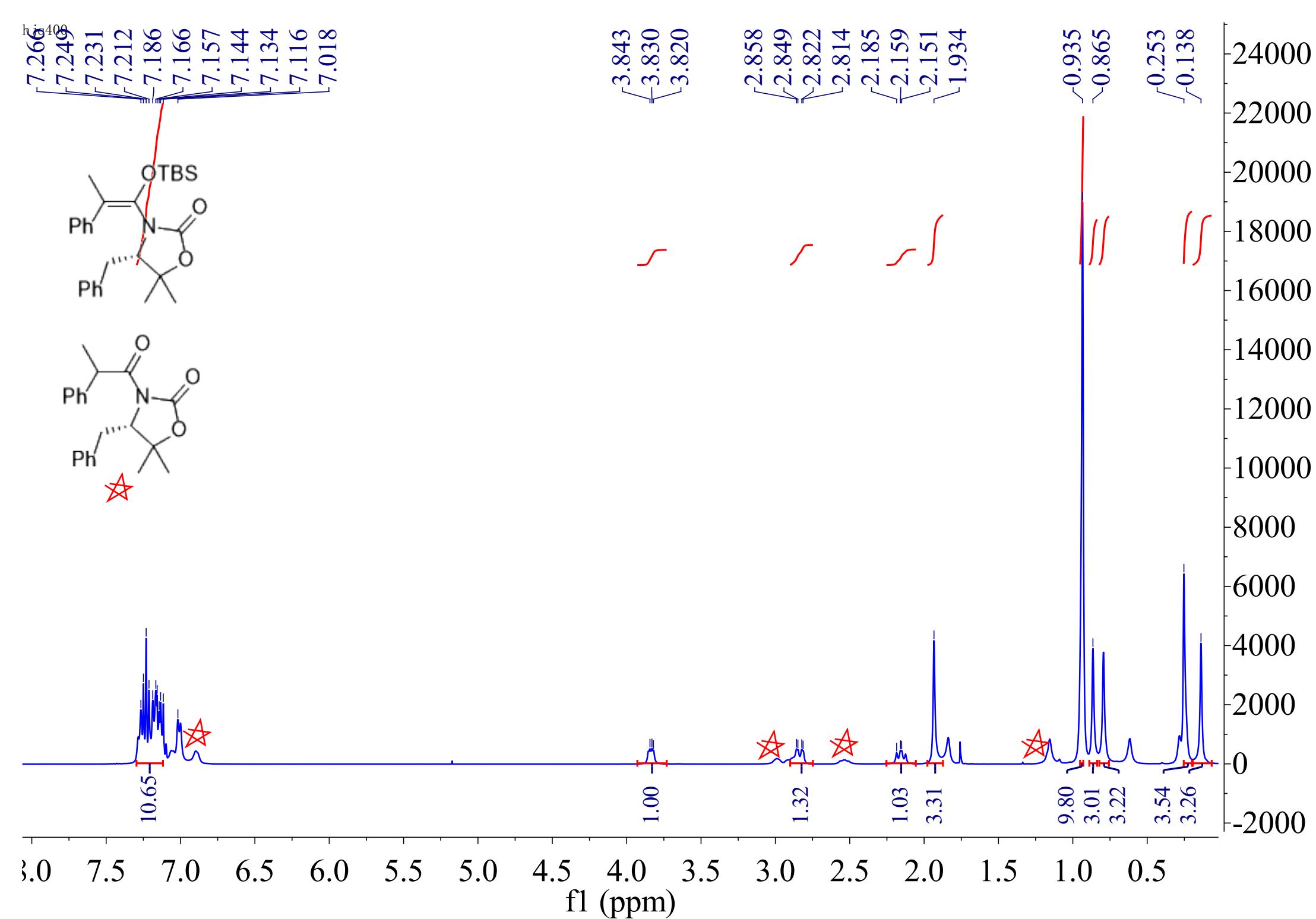
$$\begin{array}{r} 81.539 \\ \{ 77.317 \\ \{ 77.000 \\ \{ 76.682 \\ -65.202 \end{array}$$

k	Silhouette Coefficient
2	0.77
3	0.96
4	0.92
5	0.88
6	0.85
7	0.82
8	0.79
9	0.76
10	0.73
11	0.70
12	0.67
13	0.64
14	0.61
15	-0.51

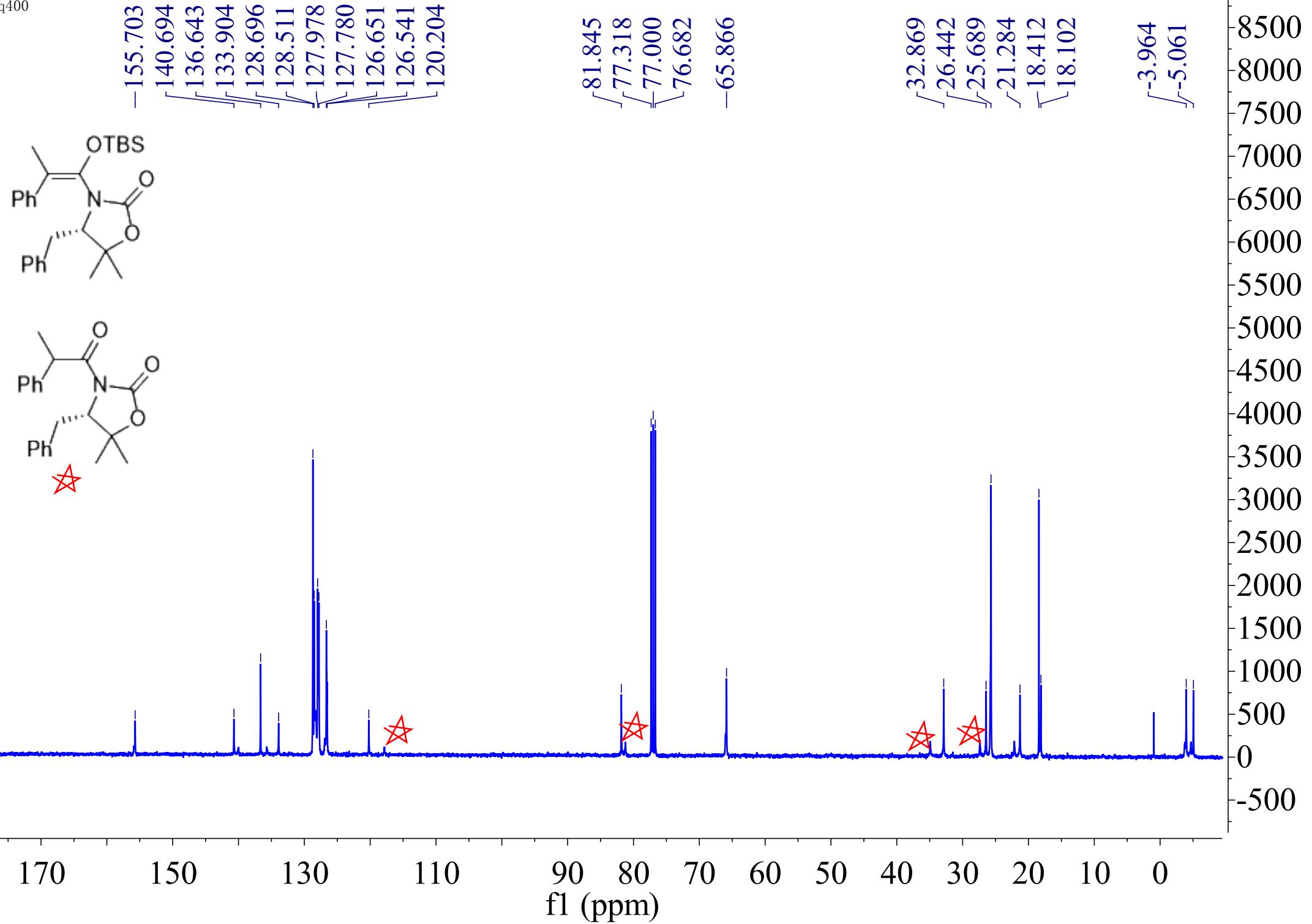


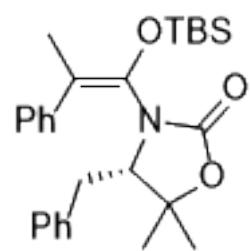
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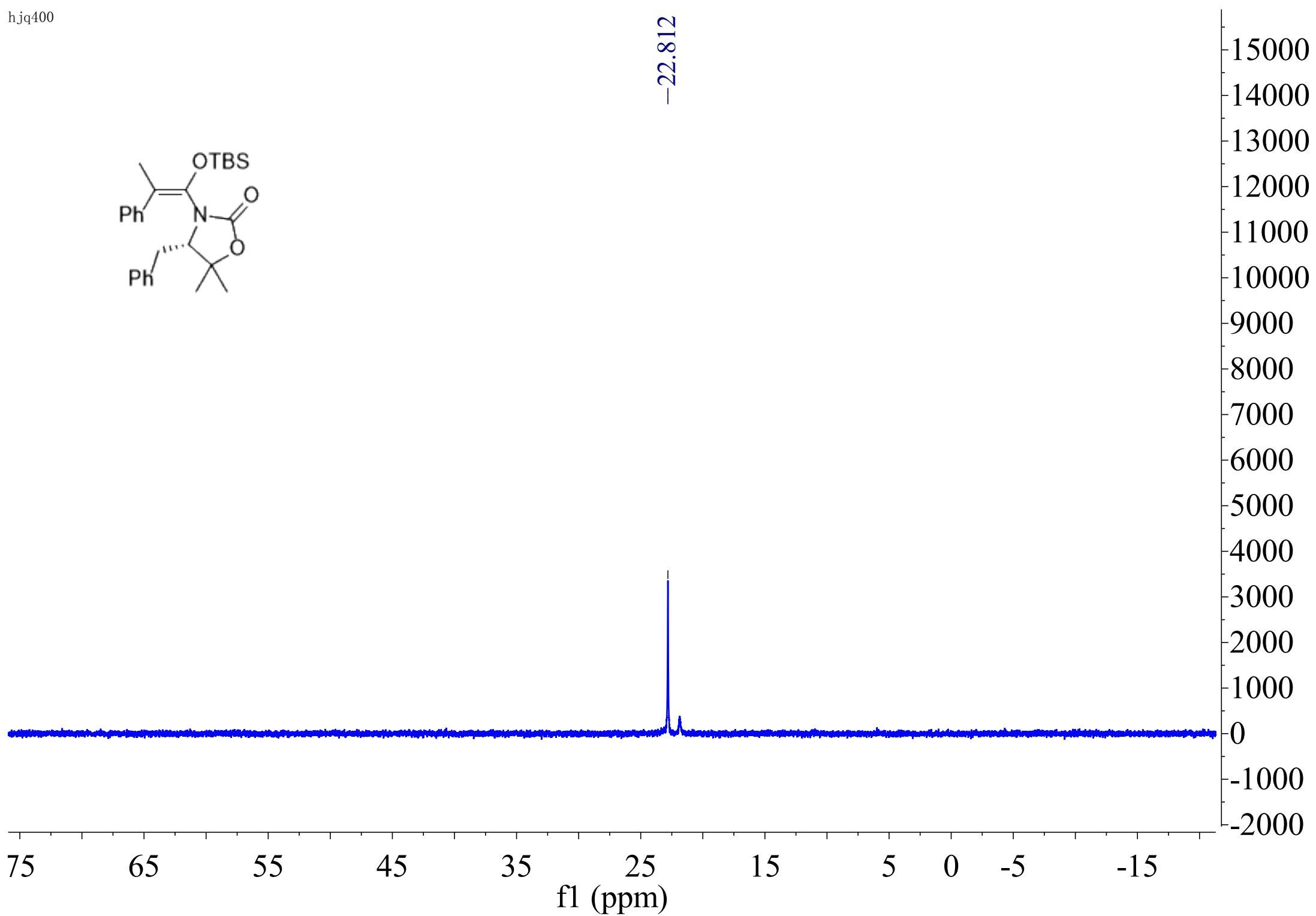


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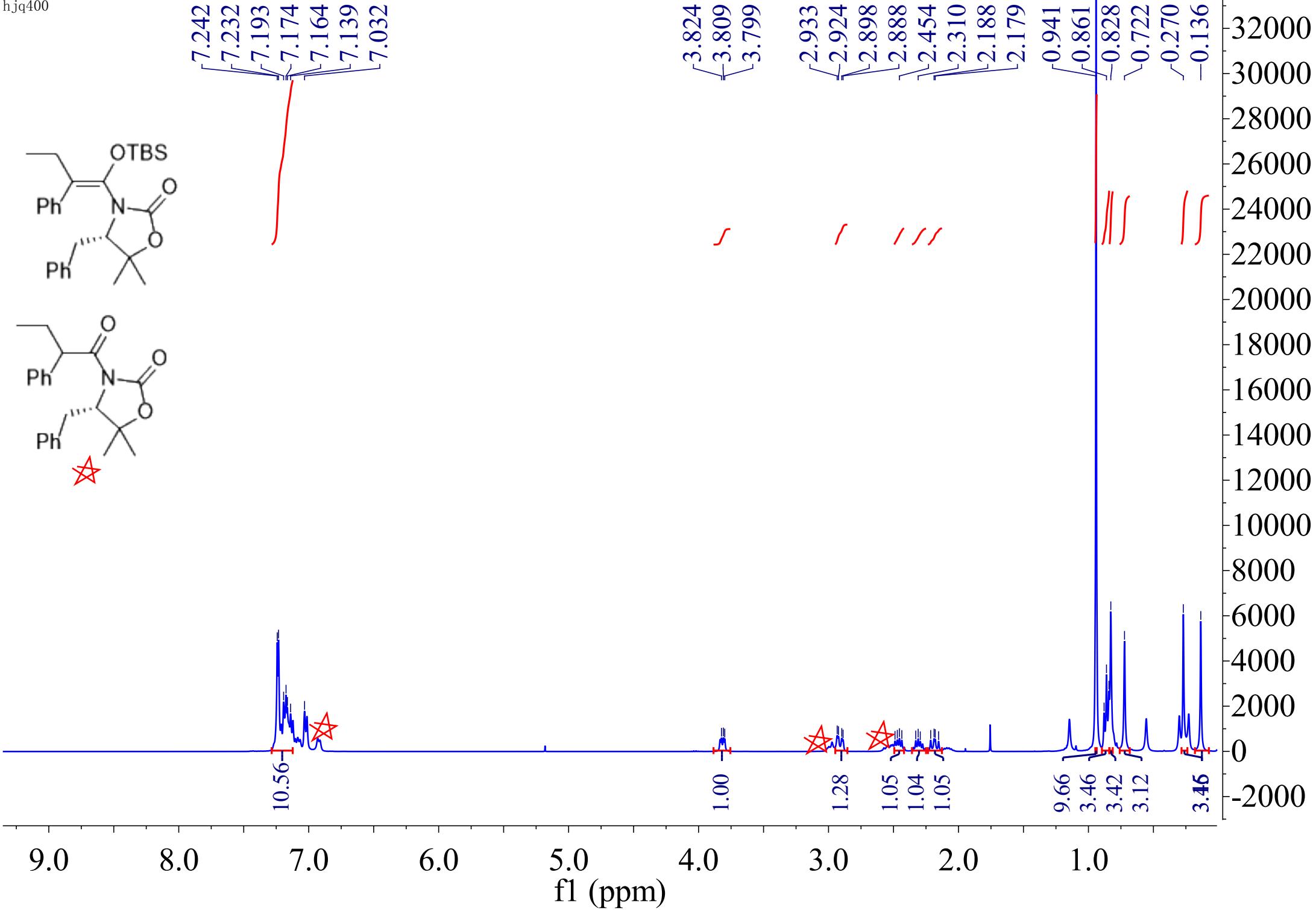




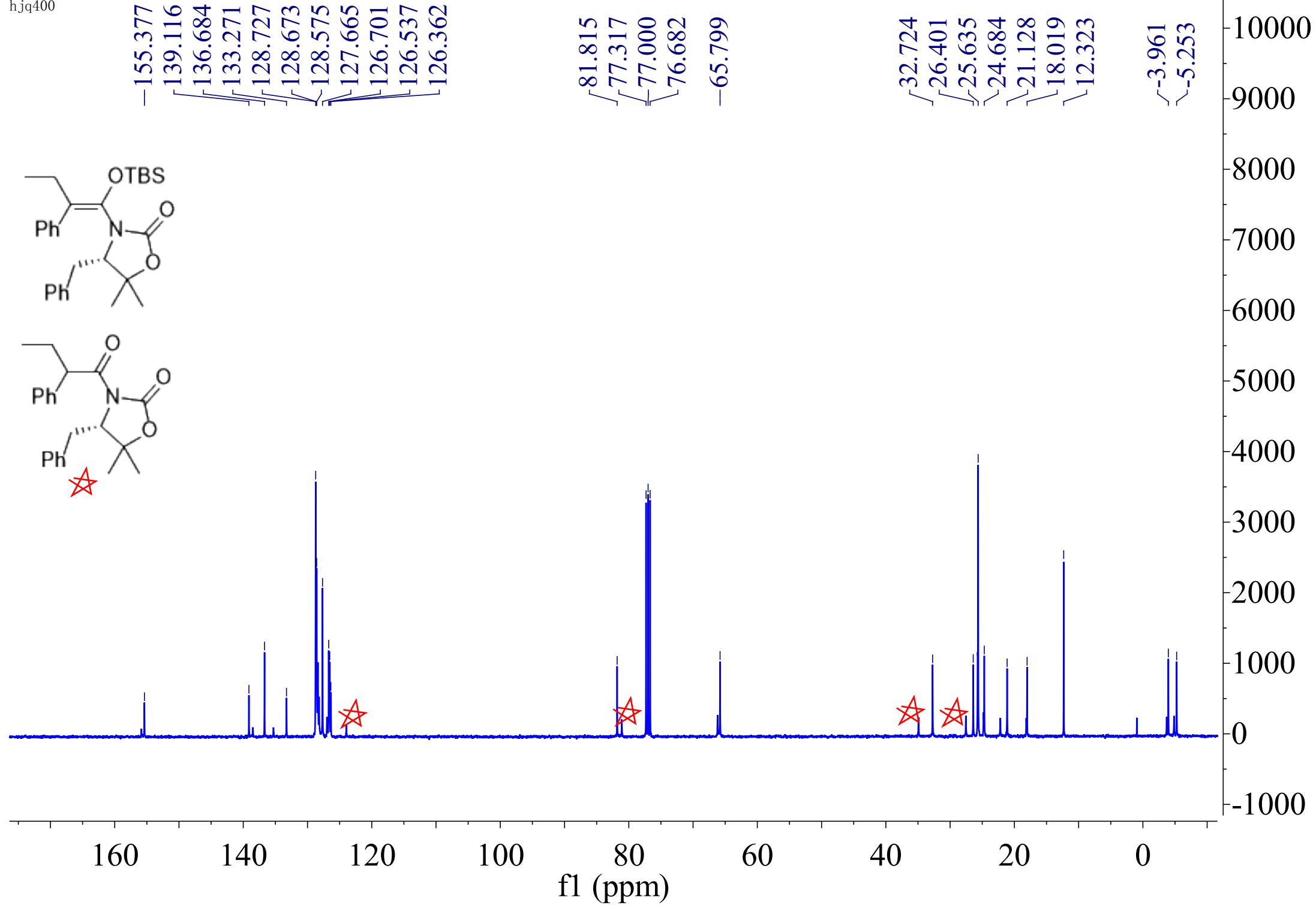
-22.812



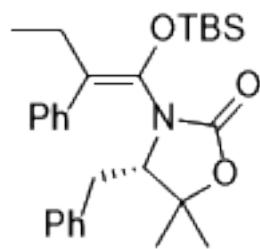
hjq400



hjq400

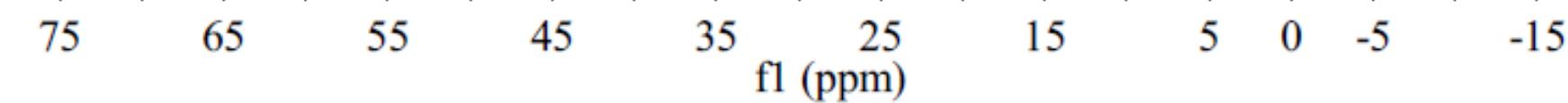


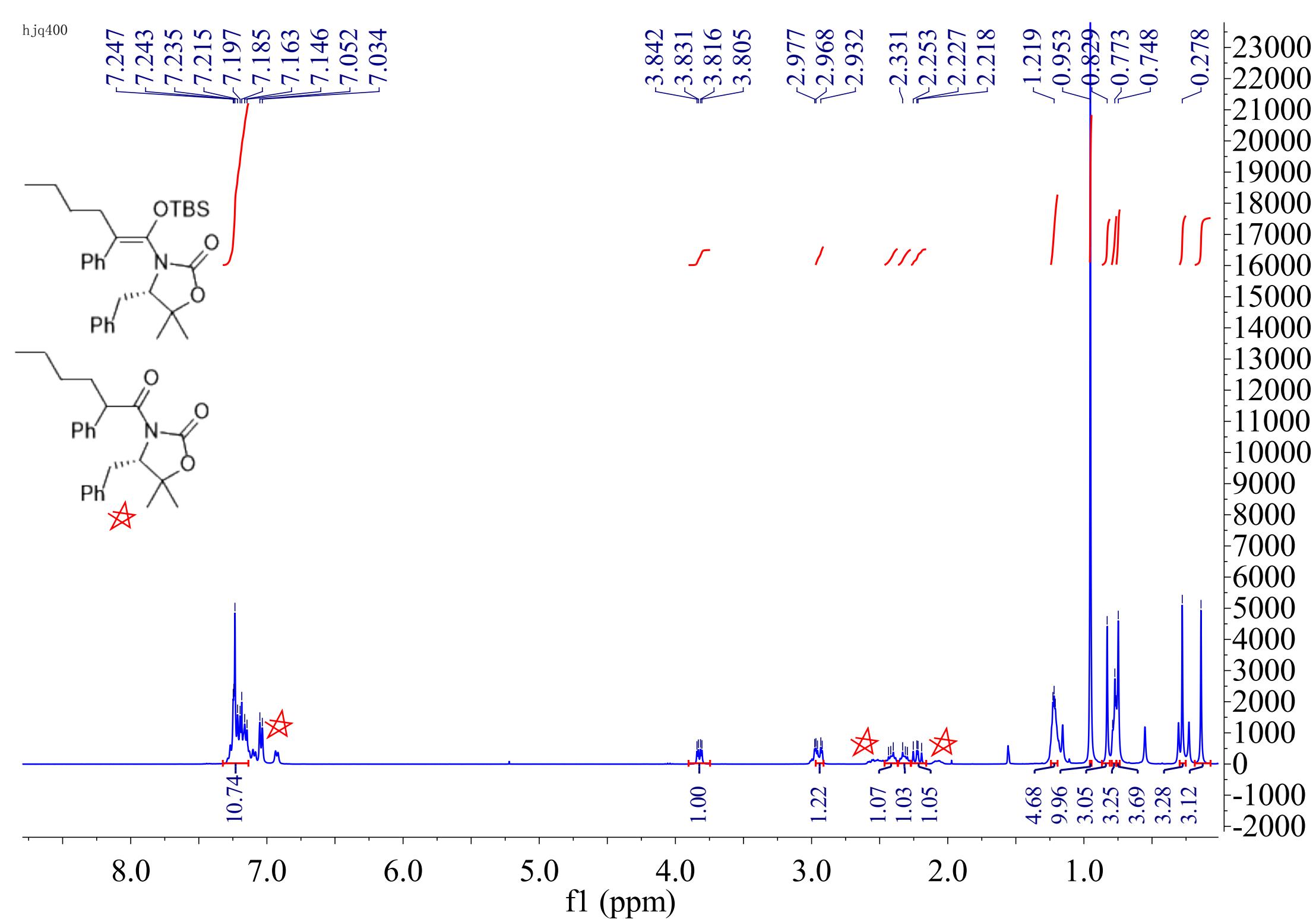
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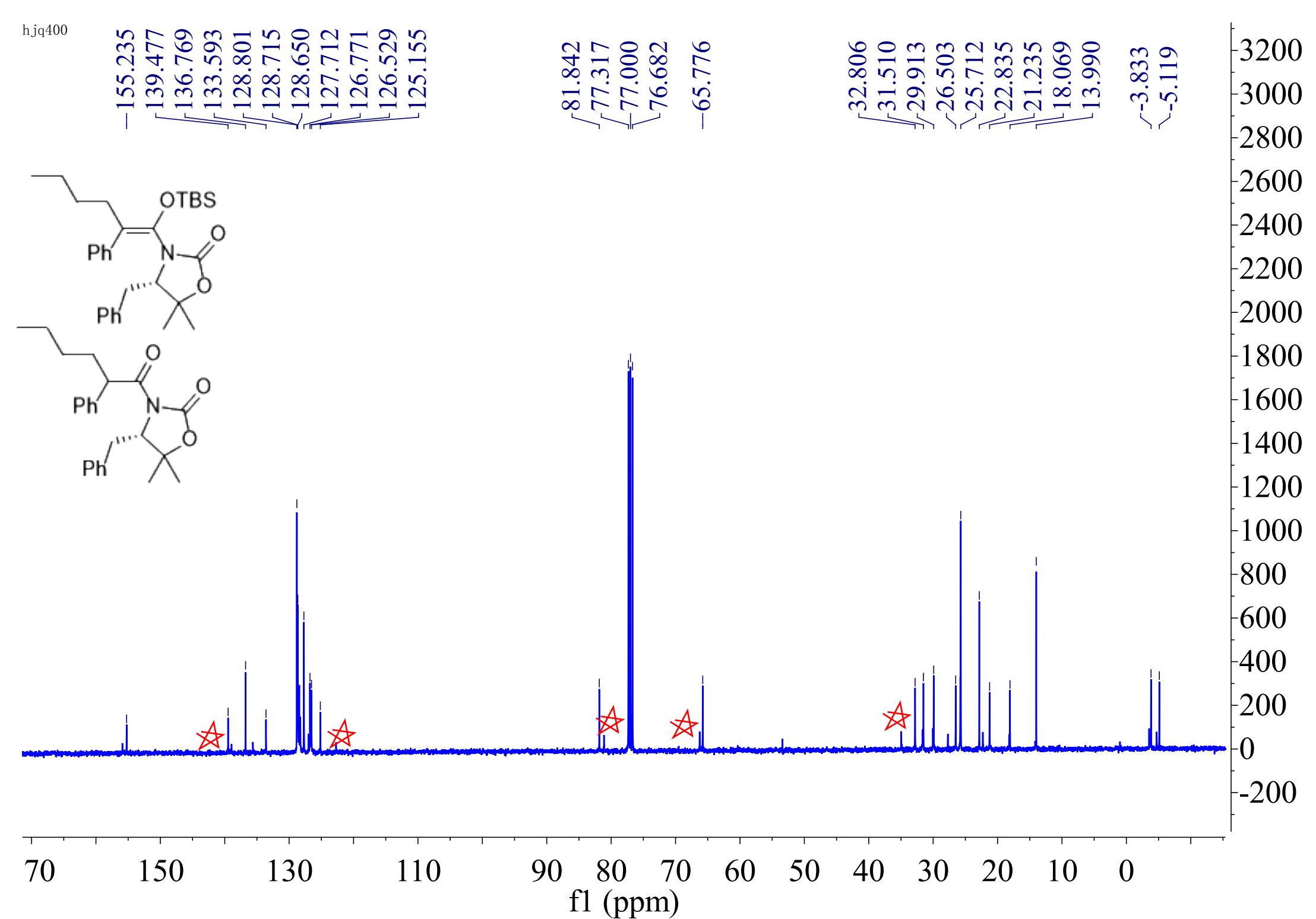


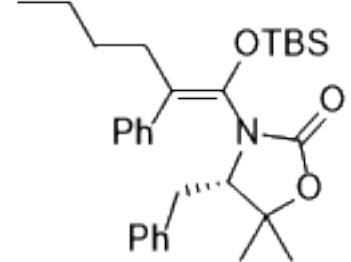
-22.103

20000  
19000  
18000  
17000  
16000  
15000  
14000  
13000  
12000  
11000  
10000  
9000  
8000  
7000  
6000  
5000  
4000  
3000  
2000  
1000  
0  
-1000  
-2000

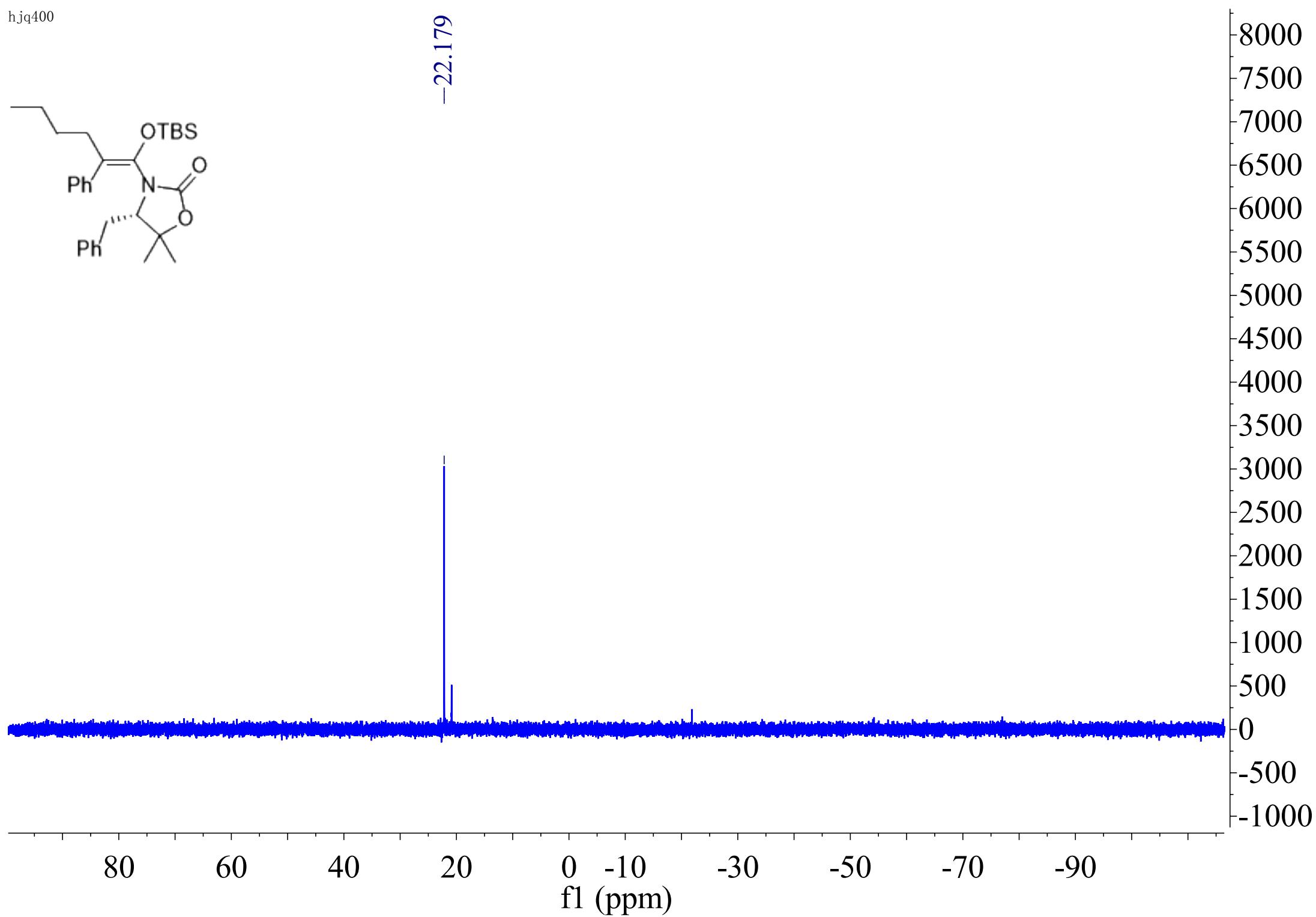


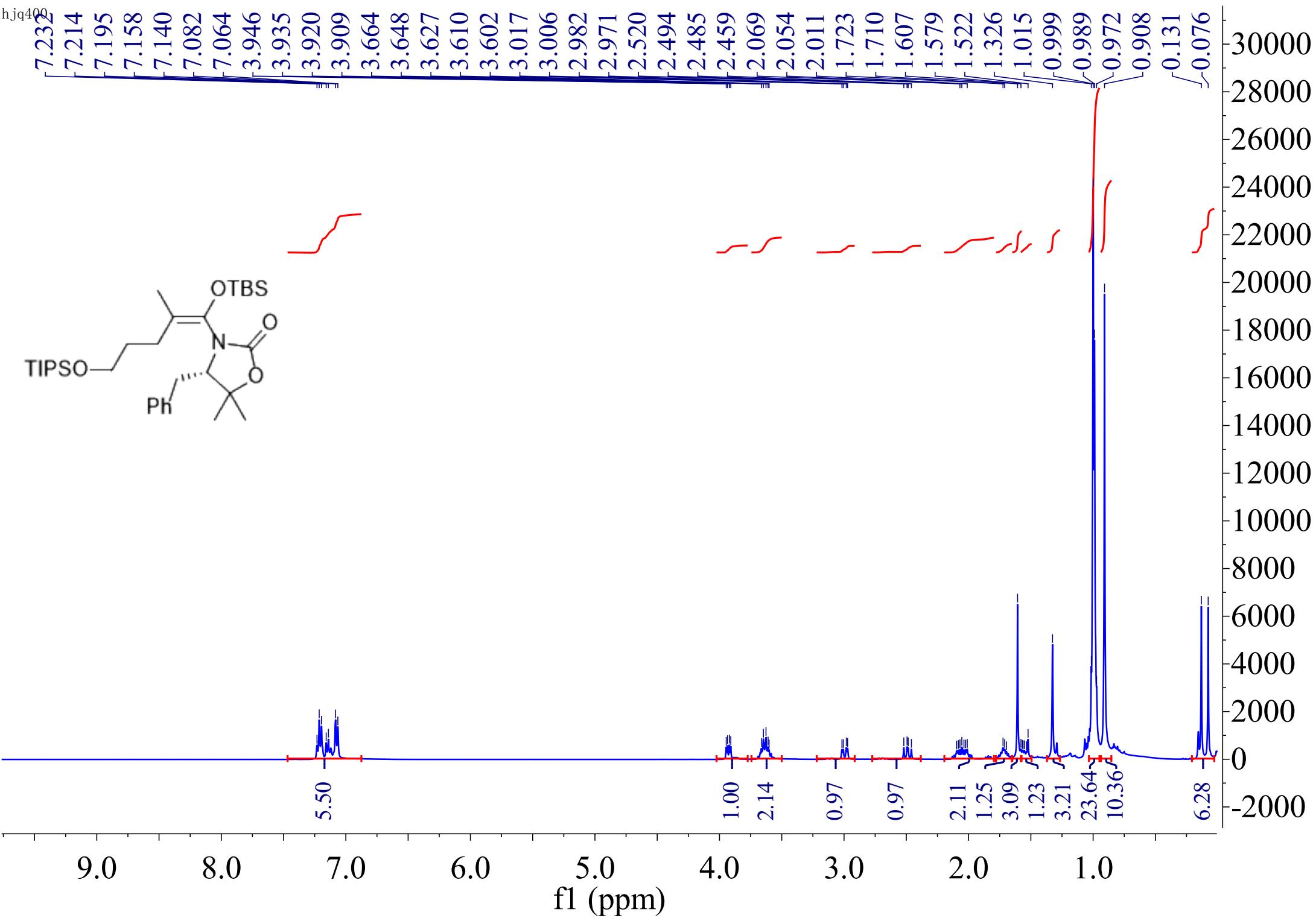




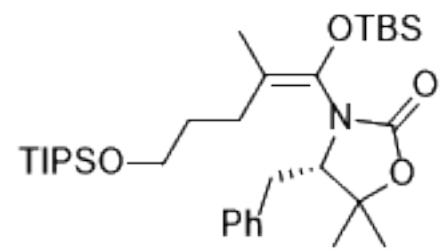


-22.179





hjq400



-154.675

136.756  
132.208  
128.796  
128.580  
126.698  
117.522

f1 (ppm)

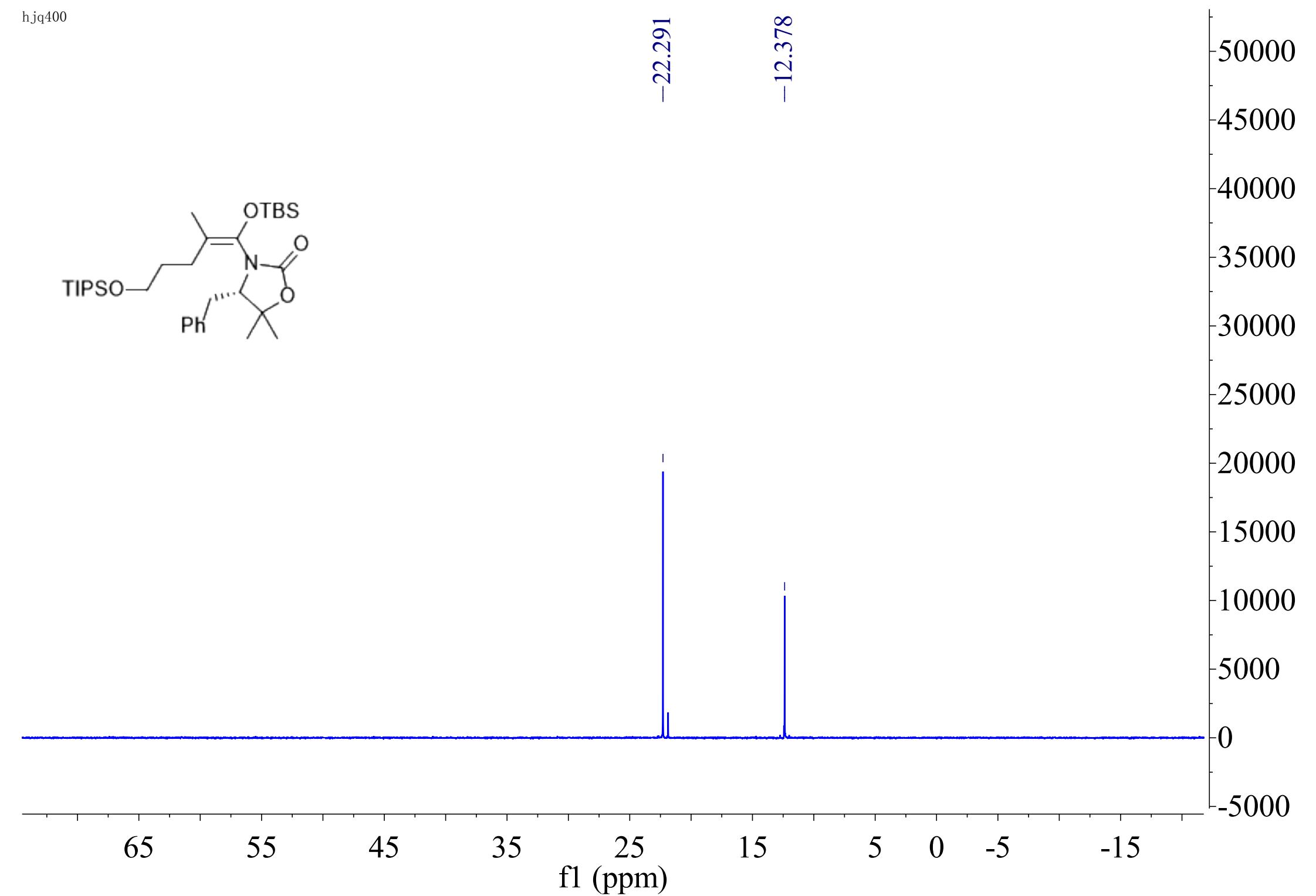
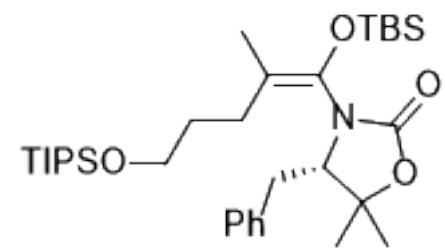
81.471  
77.318  
77.000  
76.682  
64.983  
63.714

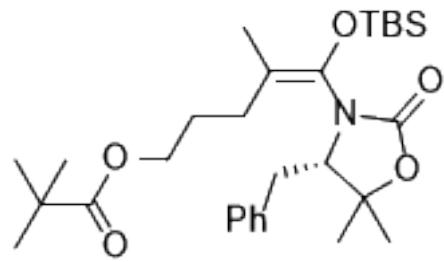
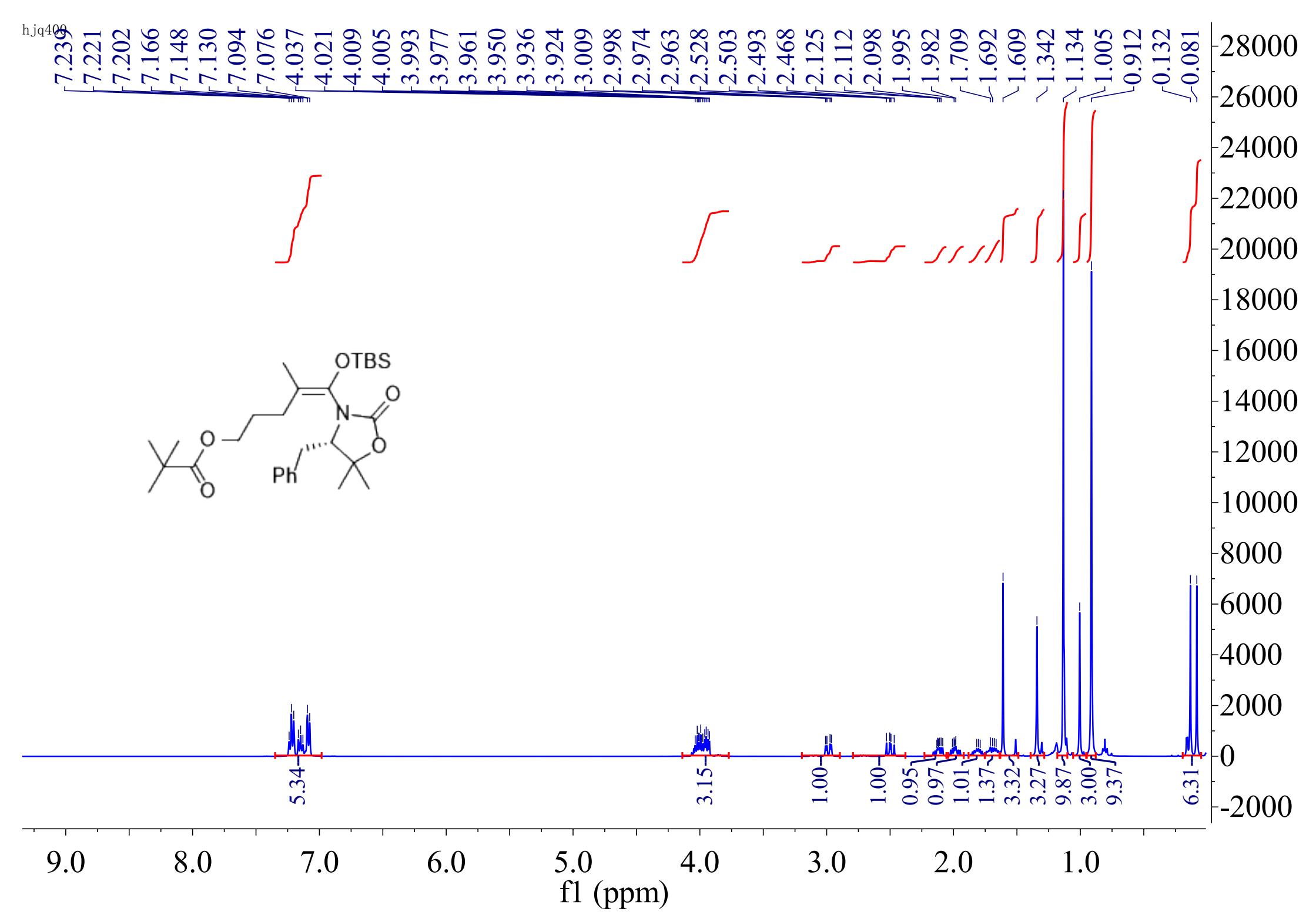
33.699  
31.289  
28.935  
27.268  
25.696  
22.448  
18.020  
17.994  
15.143  
11.973

-5.209

40000  
35000  
30000  
25000  
20000  
15000  
10000  
5000  
0

180 160 140 120 100 80 60 40 20 0





hjq400

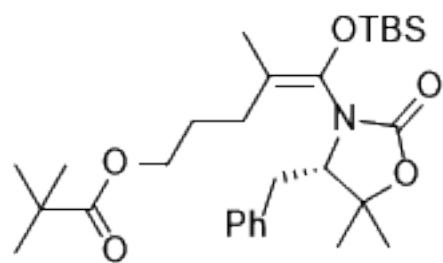
-178.518

-154.702

136.593  
132.720  
128.783  
128.595  
126.742  
116.632

81.551  
77.318  
77.000  
76.683  
64.907  
64.544

38.675  
33.693  
29.103  
27.302  
27.191  
26.974  
25.667  
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17.975  
15.149  
-4.006  
-5.221

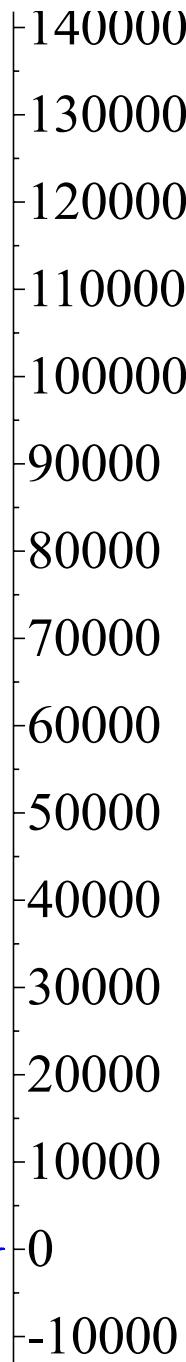


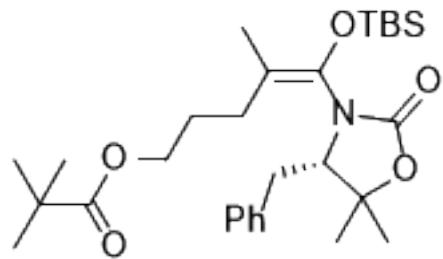
170

140

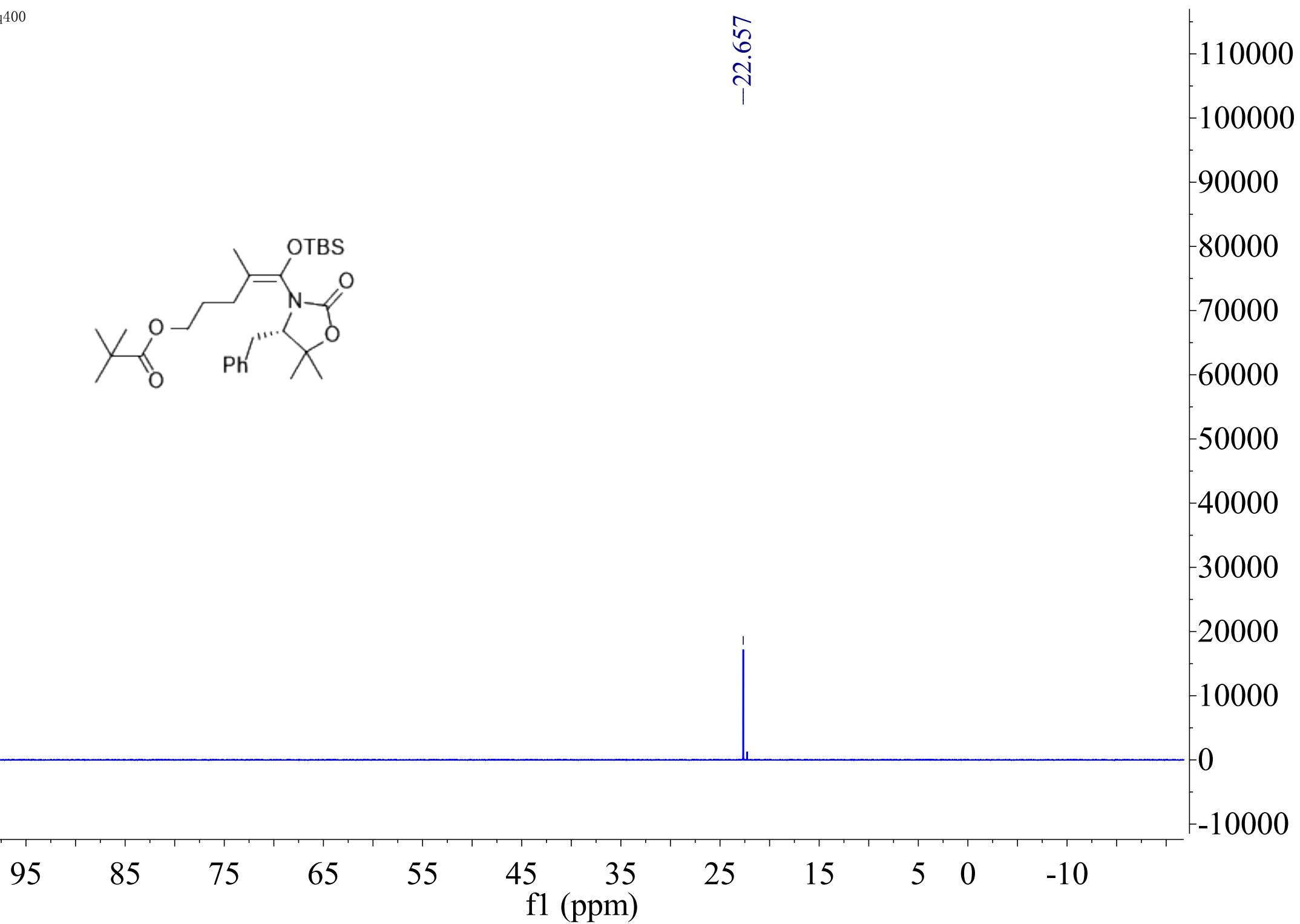
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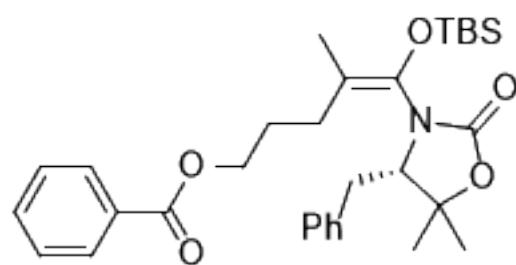
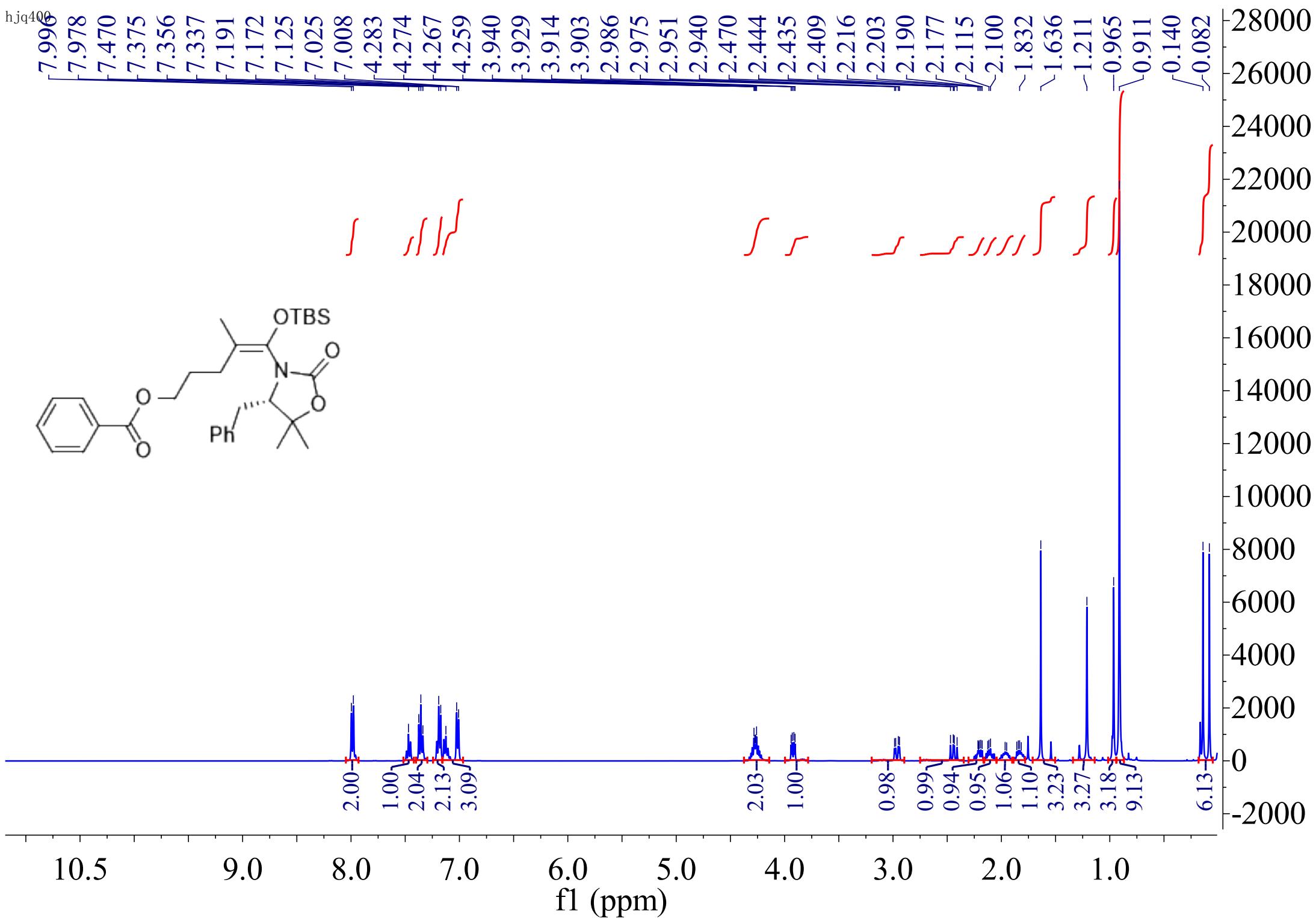
f1 (ppm)



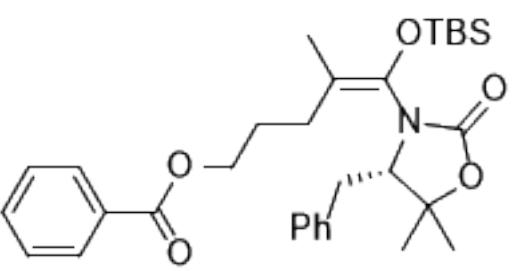


-22.657





hjq400



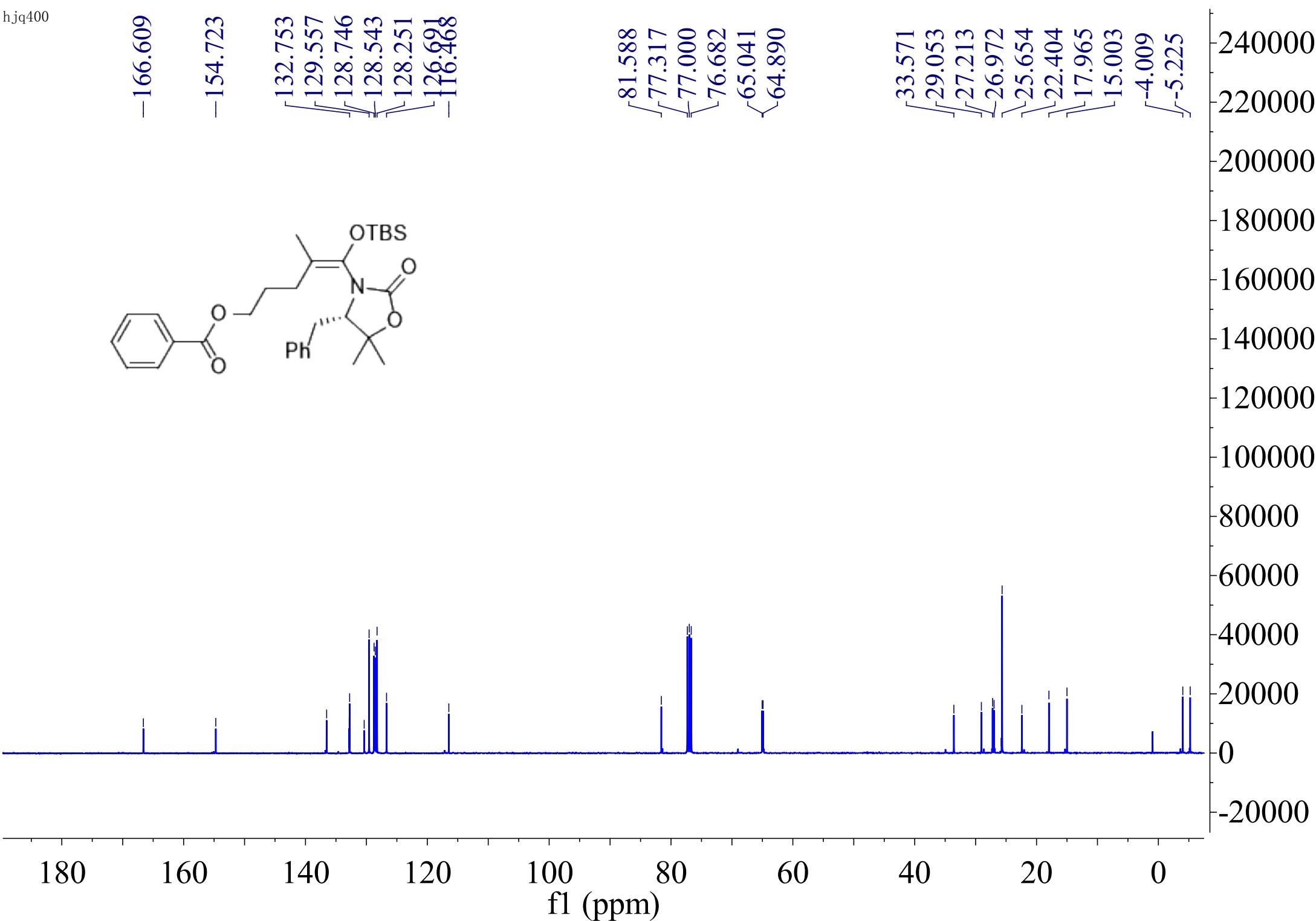
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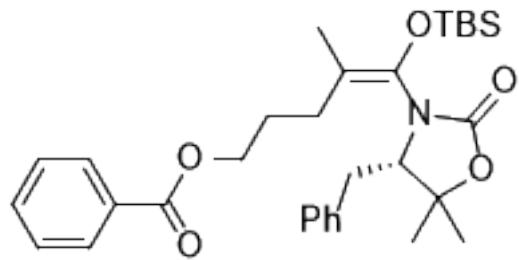
-154.723

132.753  
129.557  
128.746  
128.543  
128.251  
126.991  
126.968

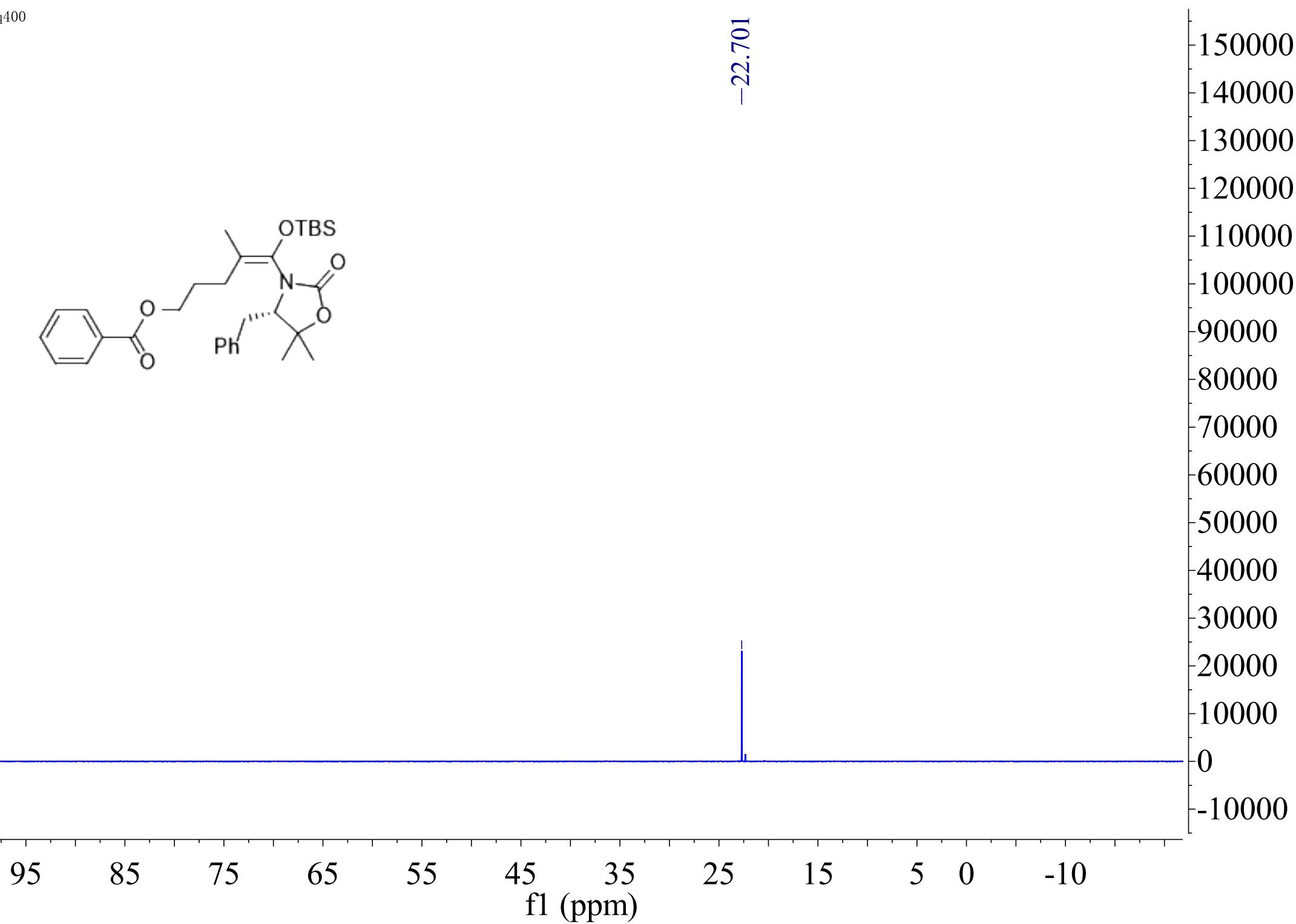
81.588  
77.317  
77.000  
76.682  
65.041  
64.890

33.571  
29.053  
27.213  
26.972  
25.654  
22.404  
17.965  
15.003  
-4.009  
-5.225

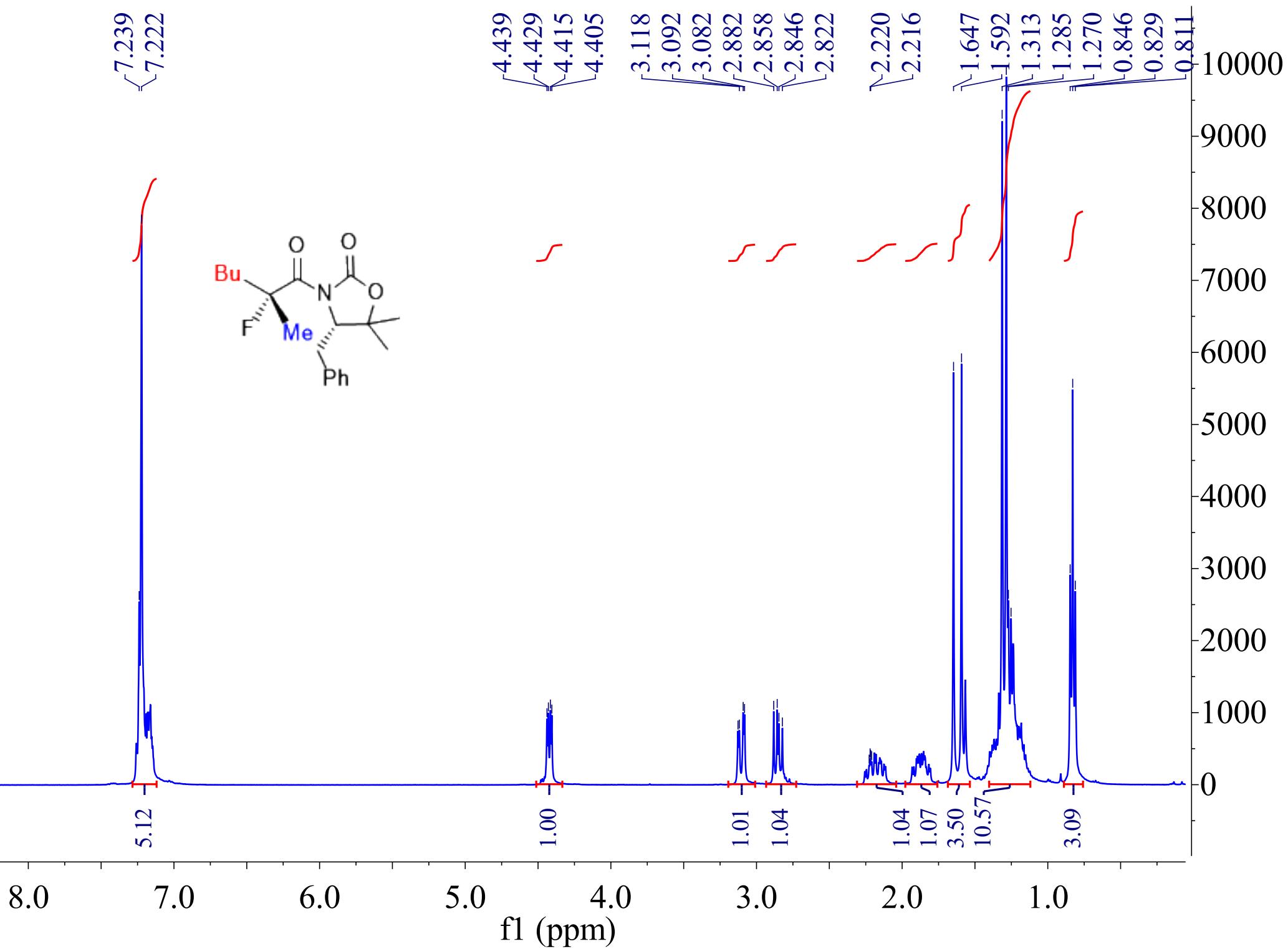




-22.701



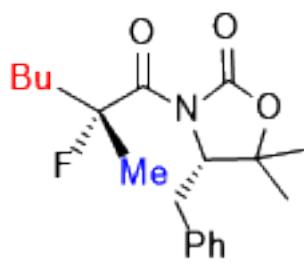
hjq400



hjq400

172.873  
172.605

-150.960



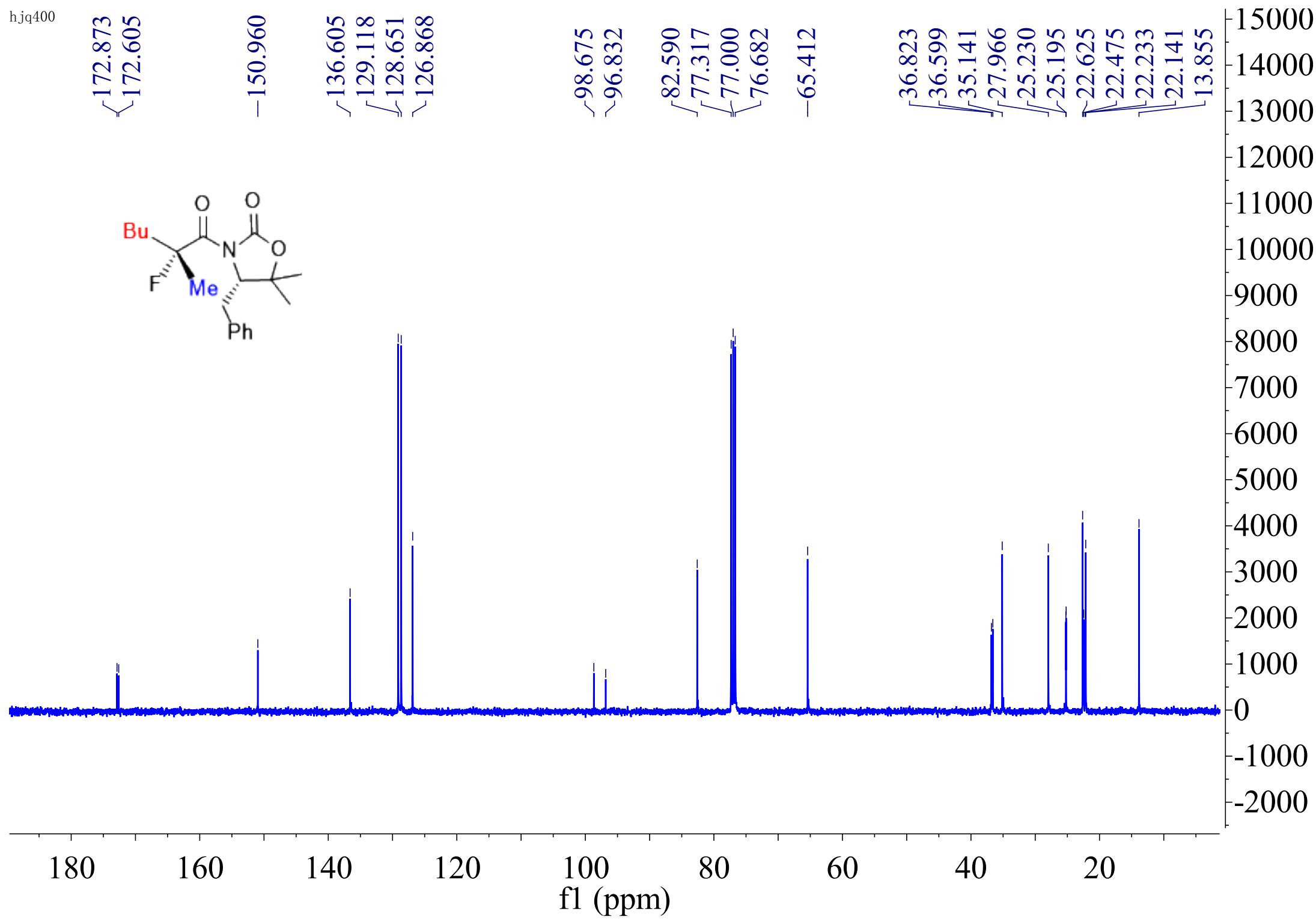
136.605  
129.118  
128.651  
126.868

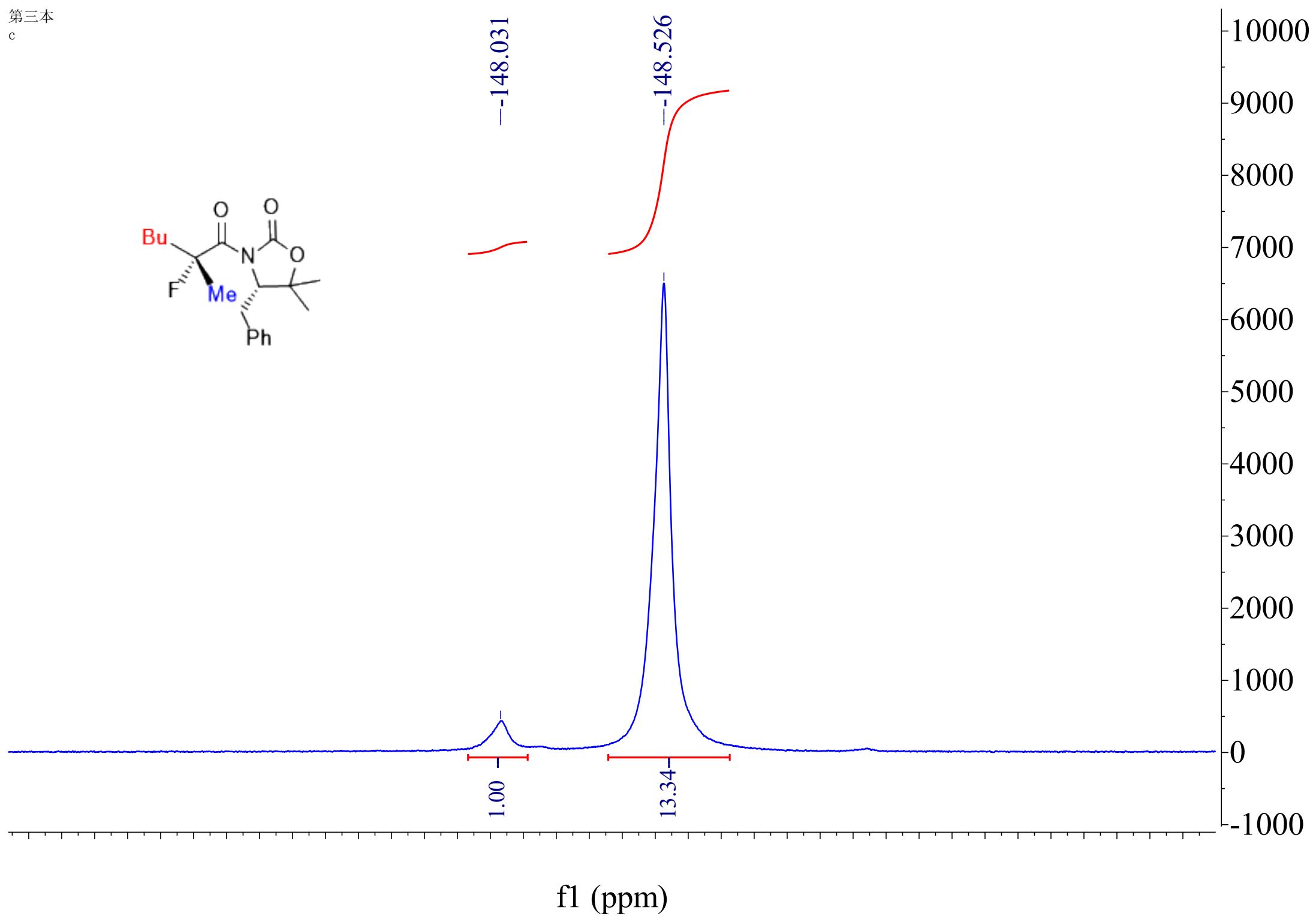
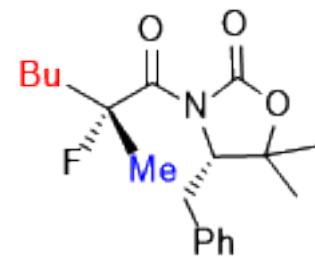
98.675  
96.832

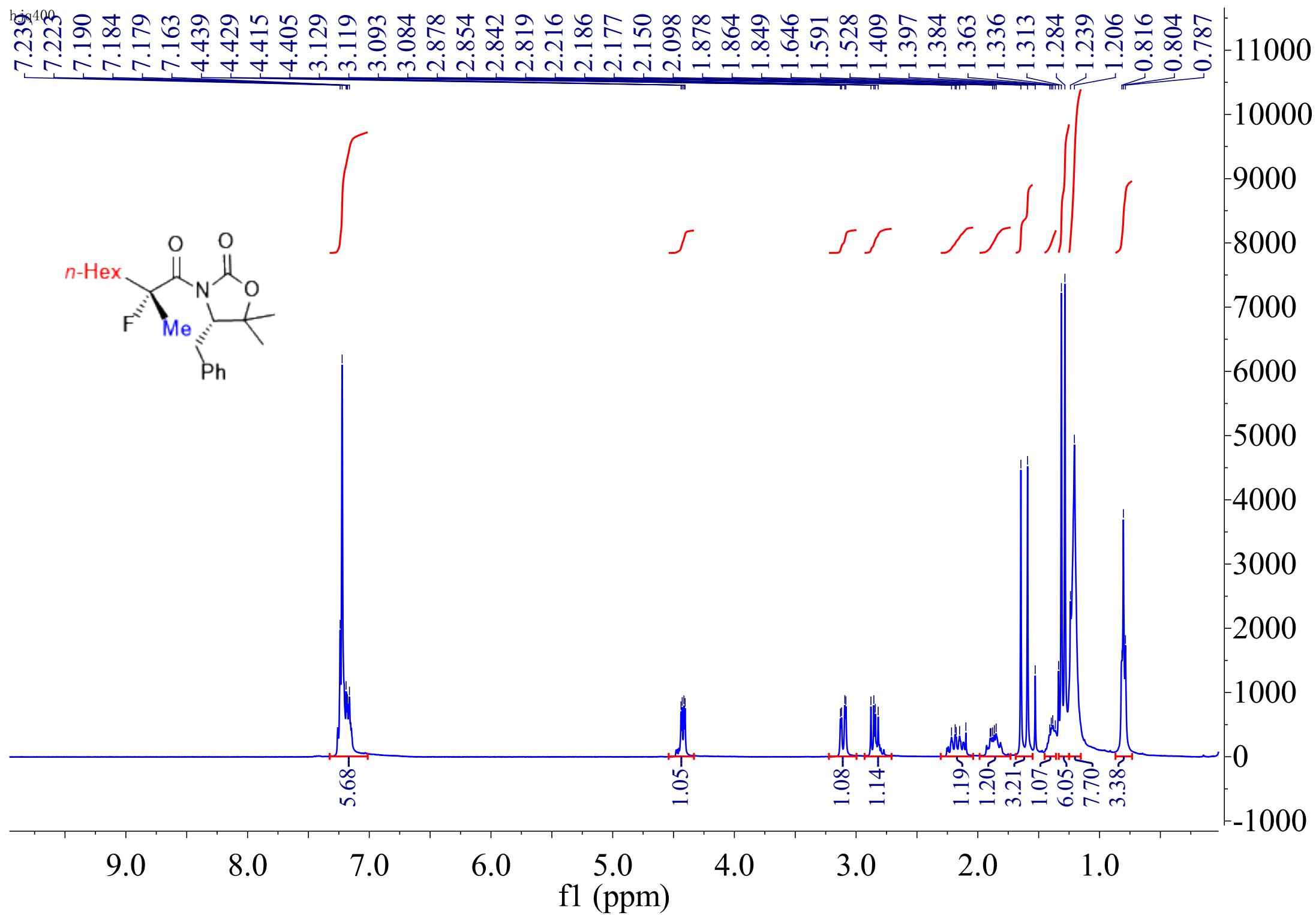
82.590  
77.317  
77.000  
76.682

-65.412

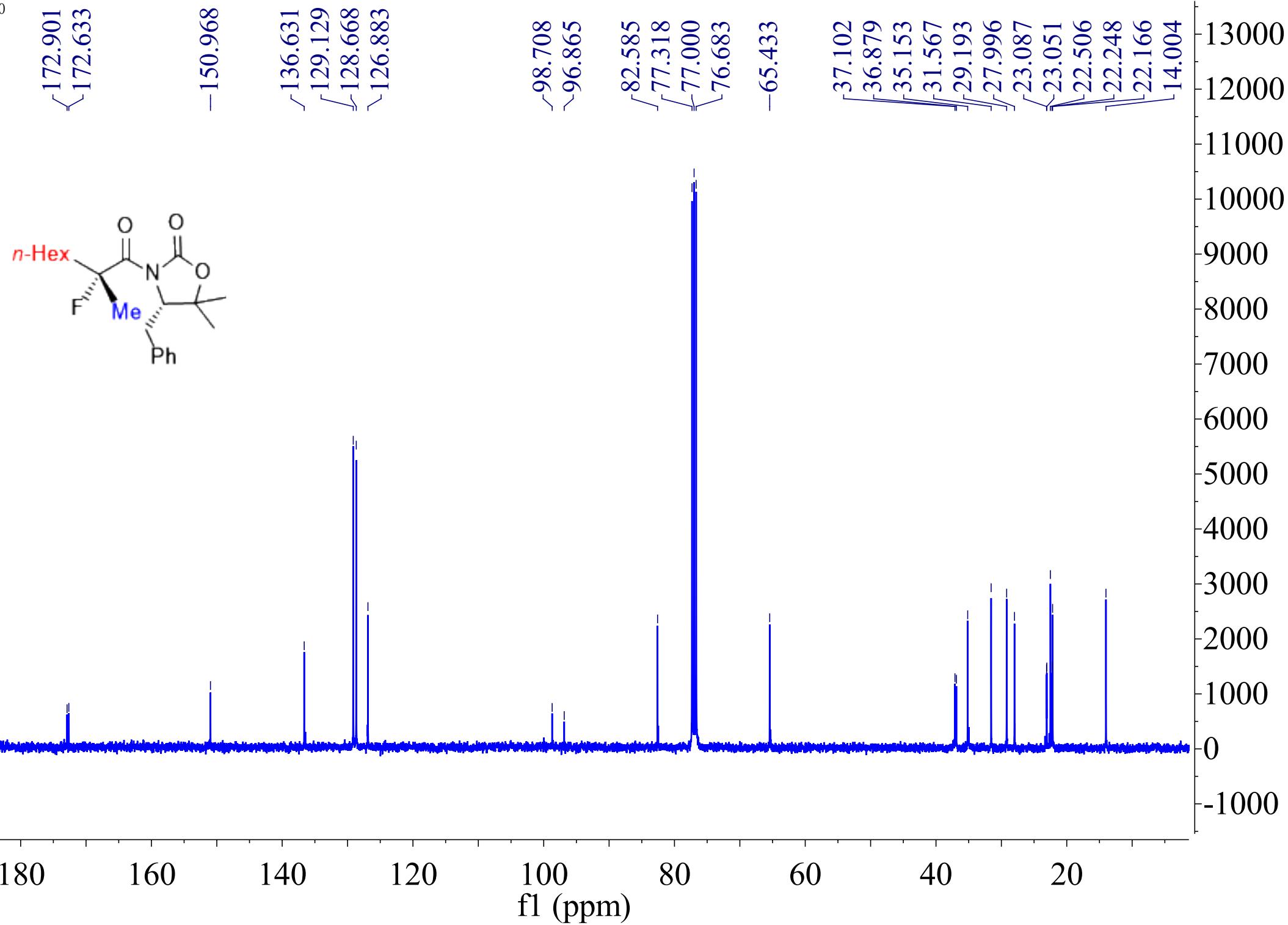
36.823  
36.599  
35.141  
27.966  
25.230  
25.195  
22.625  
22.475  
22.233  
22.141  
13.855

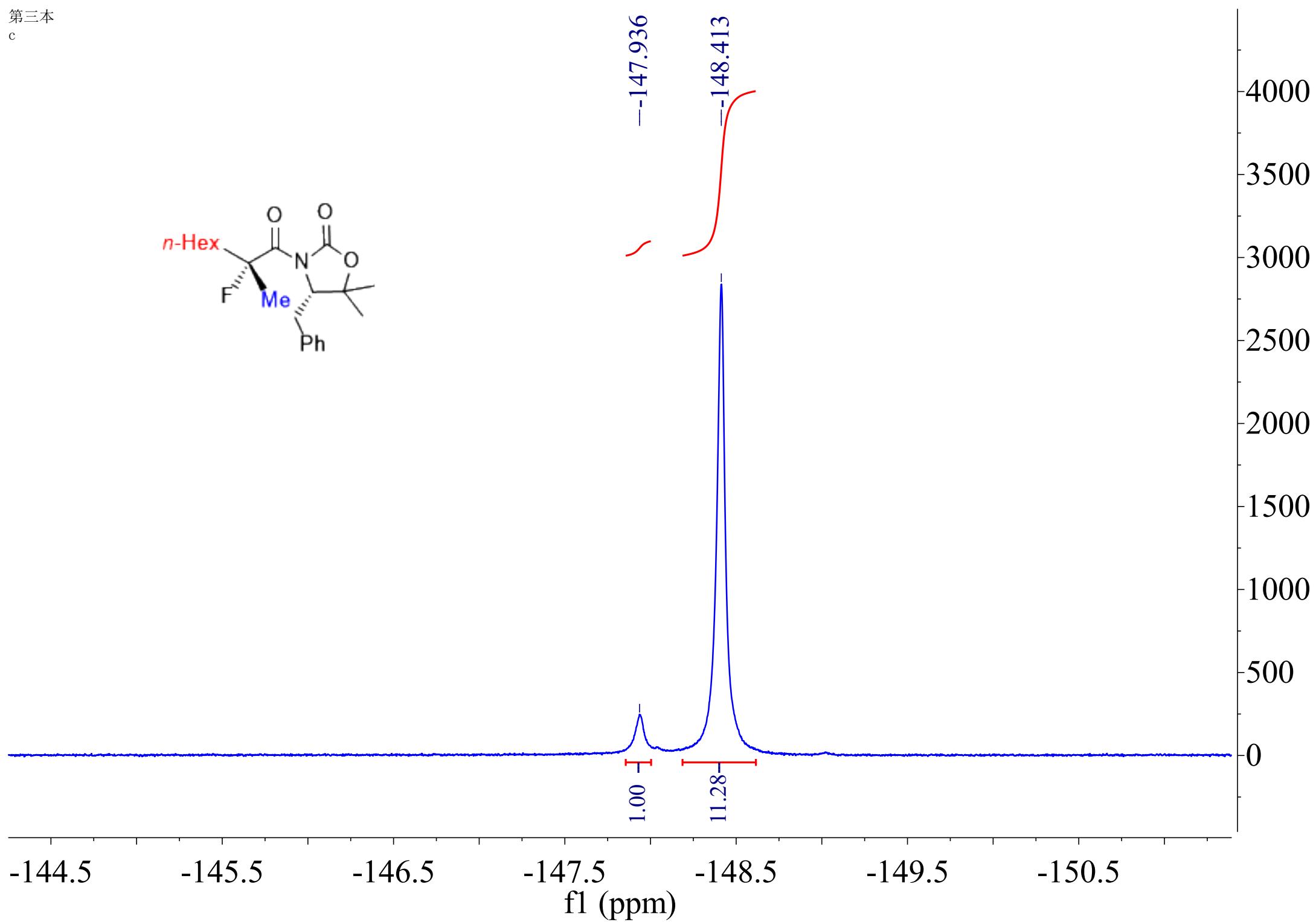
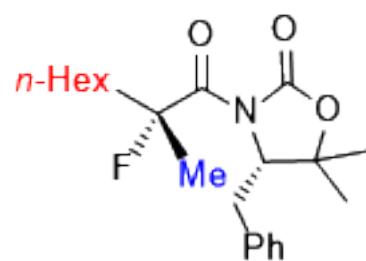




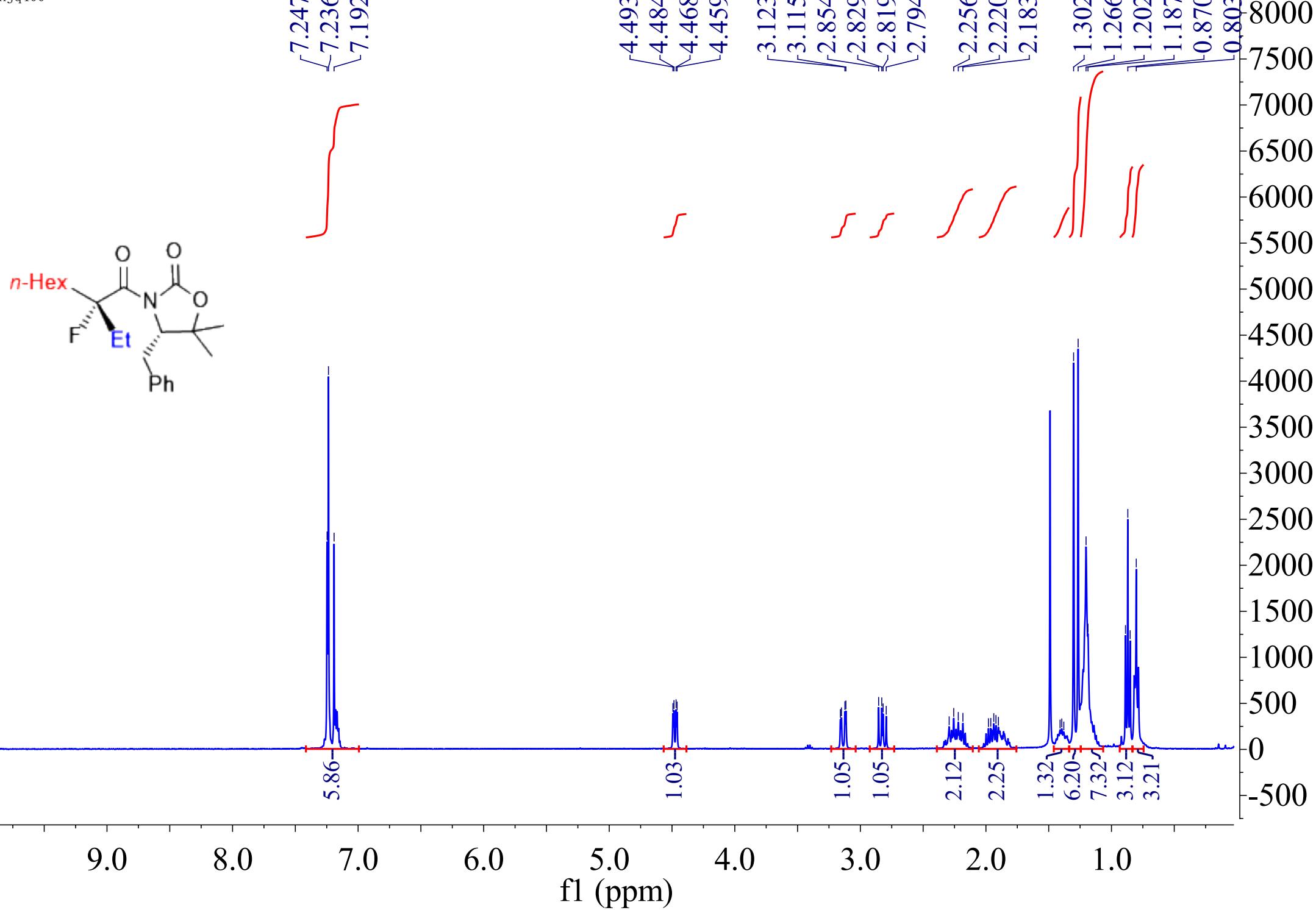


hjq400

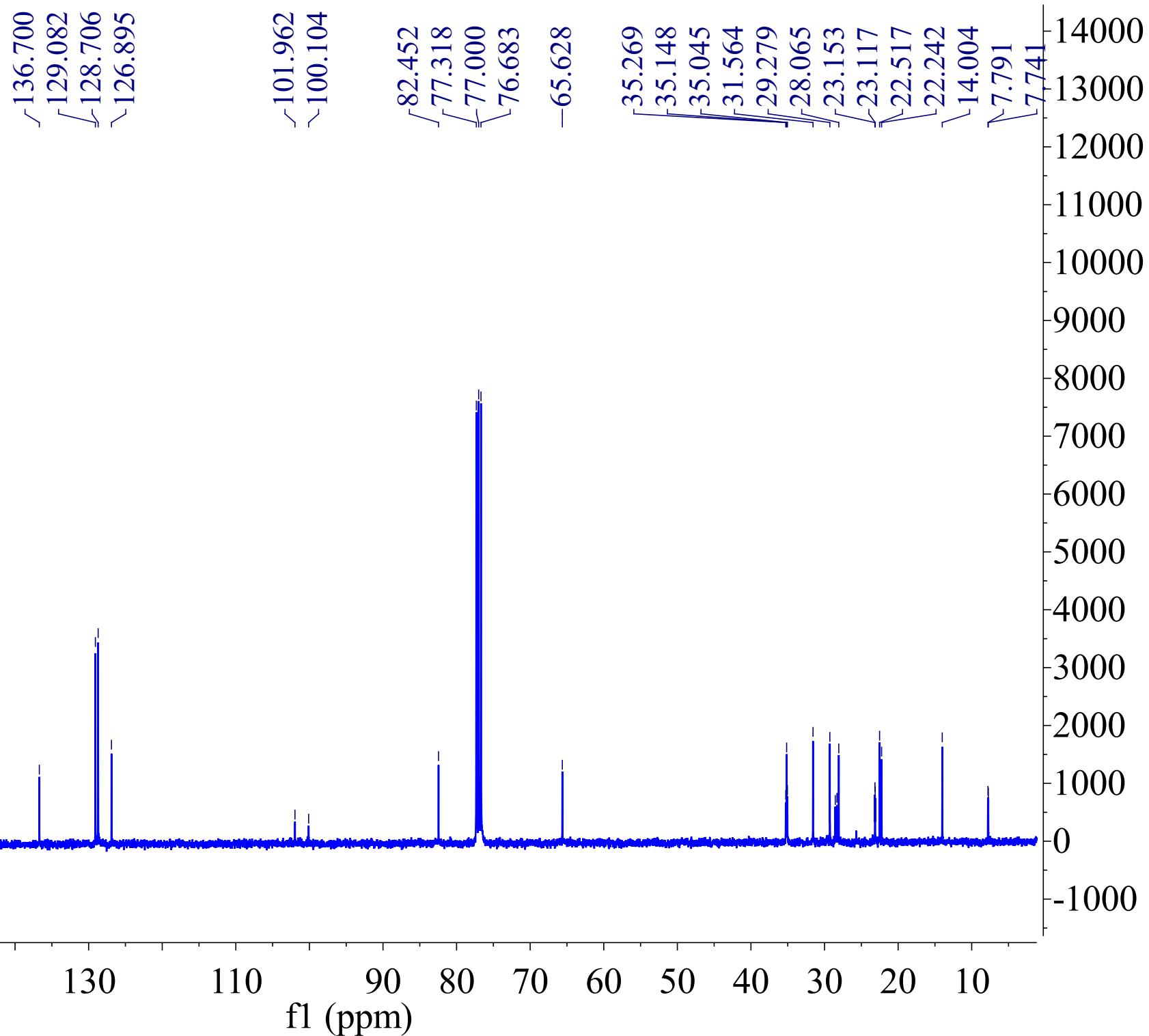
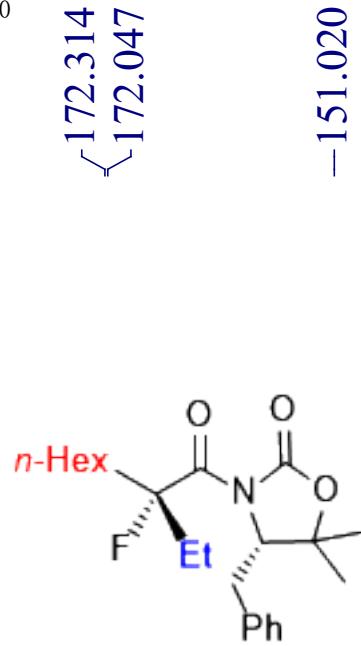


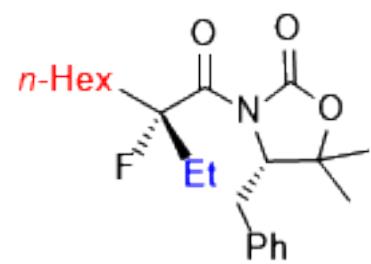


hjq400

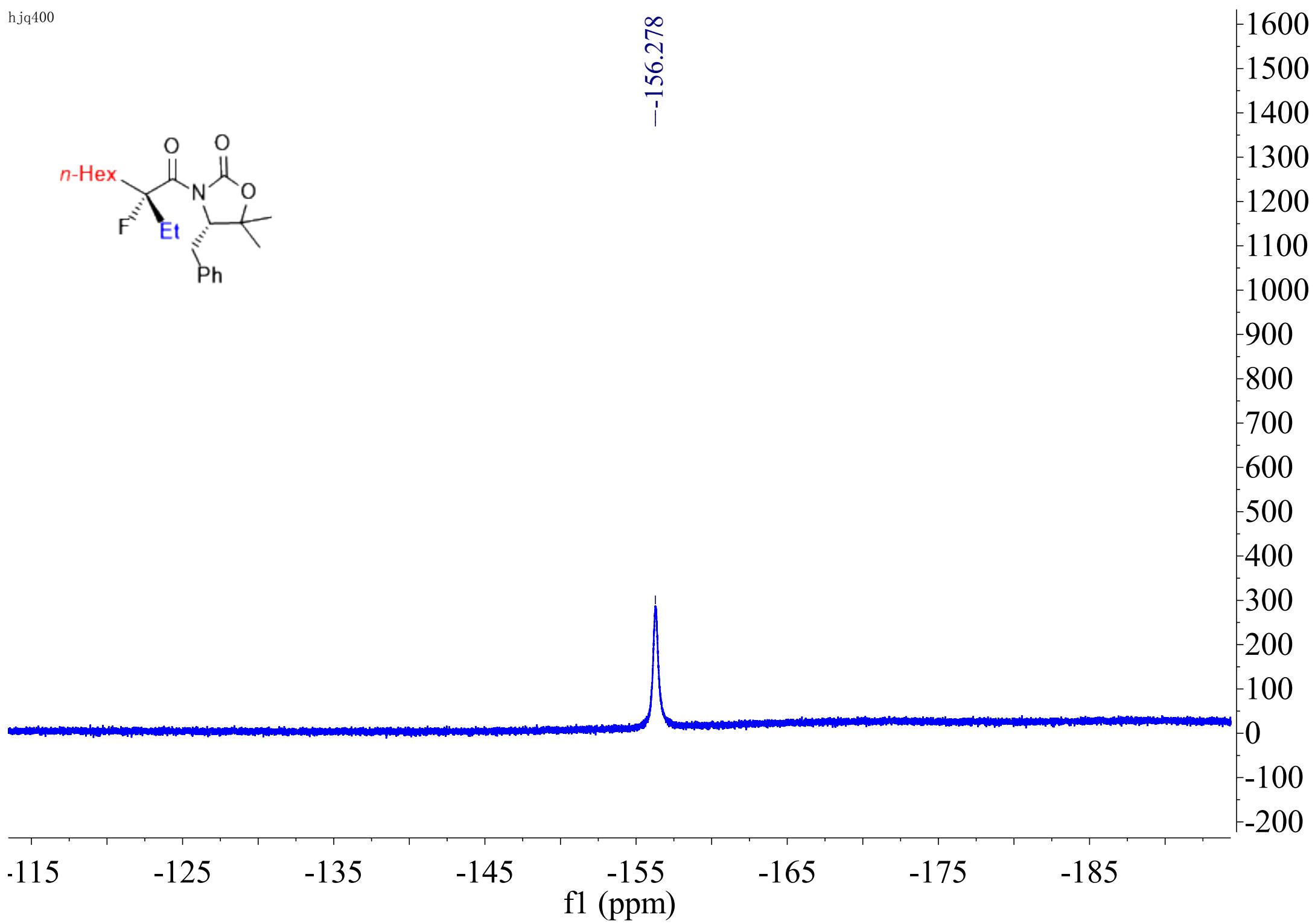


hjq400





-156.278





Operator : SYSTEM

Location : 20

Injection Date : 12/28/2016 8:46:52 AM

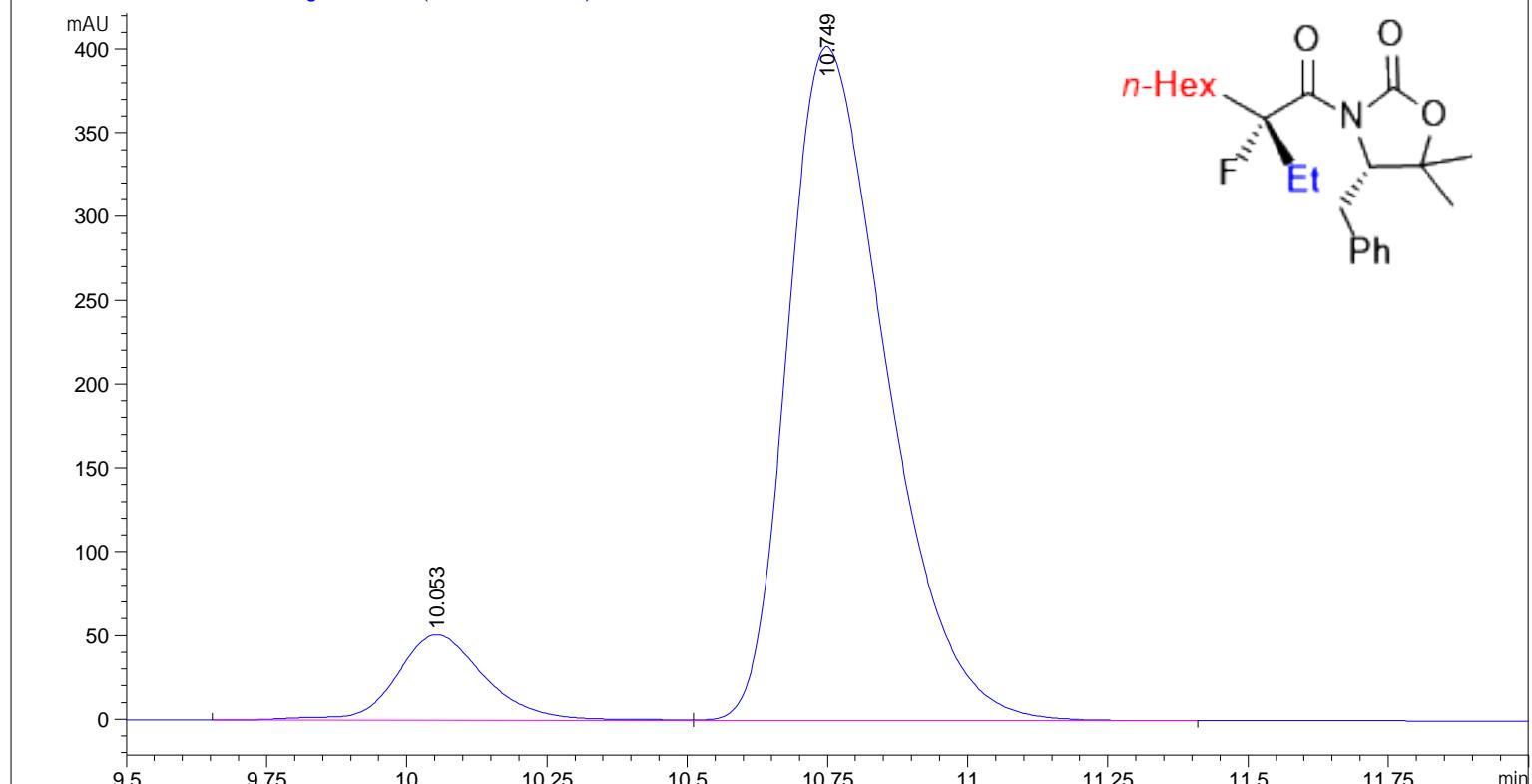
Acq. Method : DEF\_LC.M

Analysis Method : C:\Chem32\1\Methods\DEF\_LC.M

Last changed : 8/31/2017 9:52:09 AM by SYSTEM  
(modified after loading)Sample Info : ad-h  
96  
0.5 ml.min

Additional Info : Peak(s) manually integrated

VWD1 A, Wavelength=250 nm (JQH\303806-2.D)



## Area Percent Report

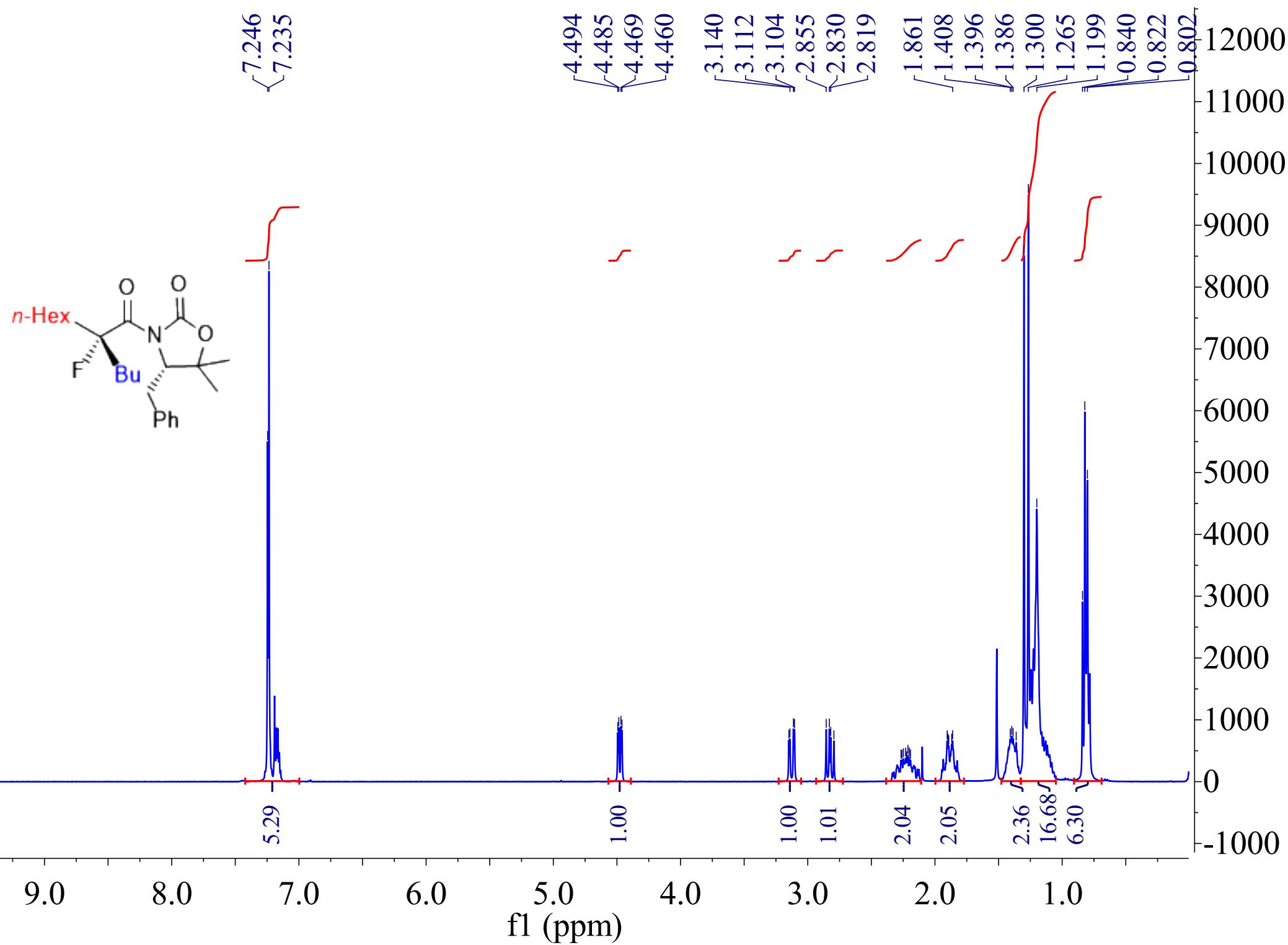
Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.053	BV	0.1660	559.56885	51.00288	10.2229
2	10.749	VB	0.1885	4914.08545	402.26038	89.7771

Totals : 5473.65430 453.26326

hjq400



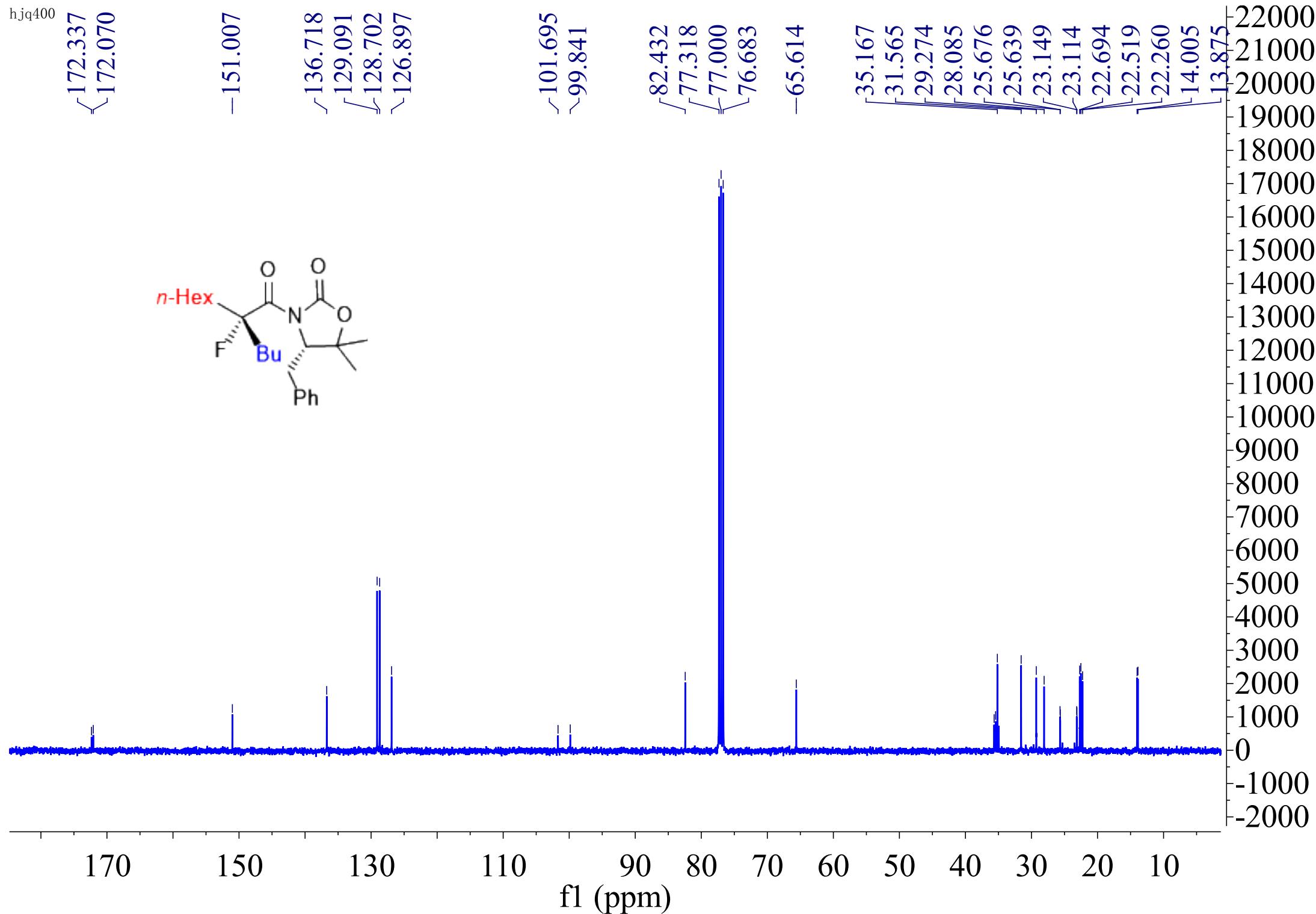
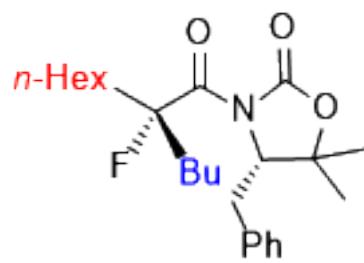
hjq400

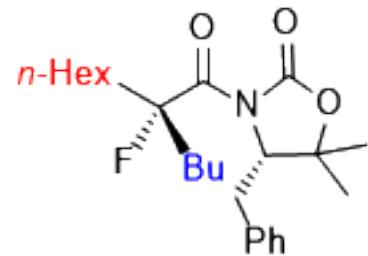
<172.337  
<172.070

-151.007

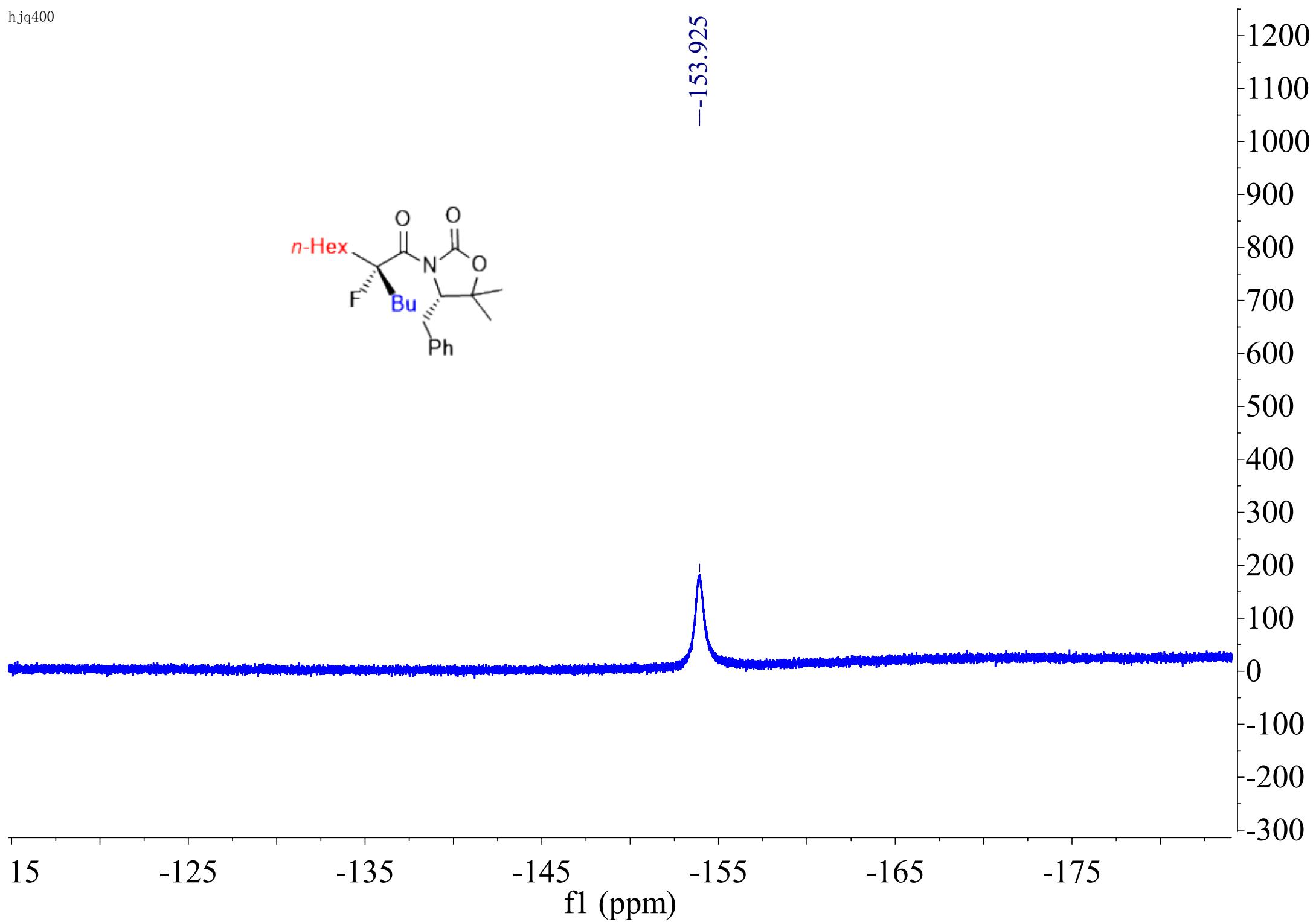
/136.718  
/129.091  
/128.702  
\126.897\101.695  
\99.841/82.432  
/77.318  
/77.000  
\76.683

-65.614

/35.167  
/31.565  
/29.274  
/28.085  
/25.676  
\25.639  
/23.149  
\23.114  
/22.694  
/22.519  
/22.260  
/14.005  
/13.875

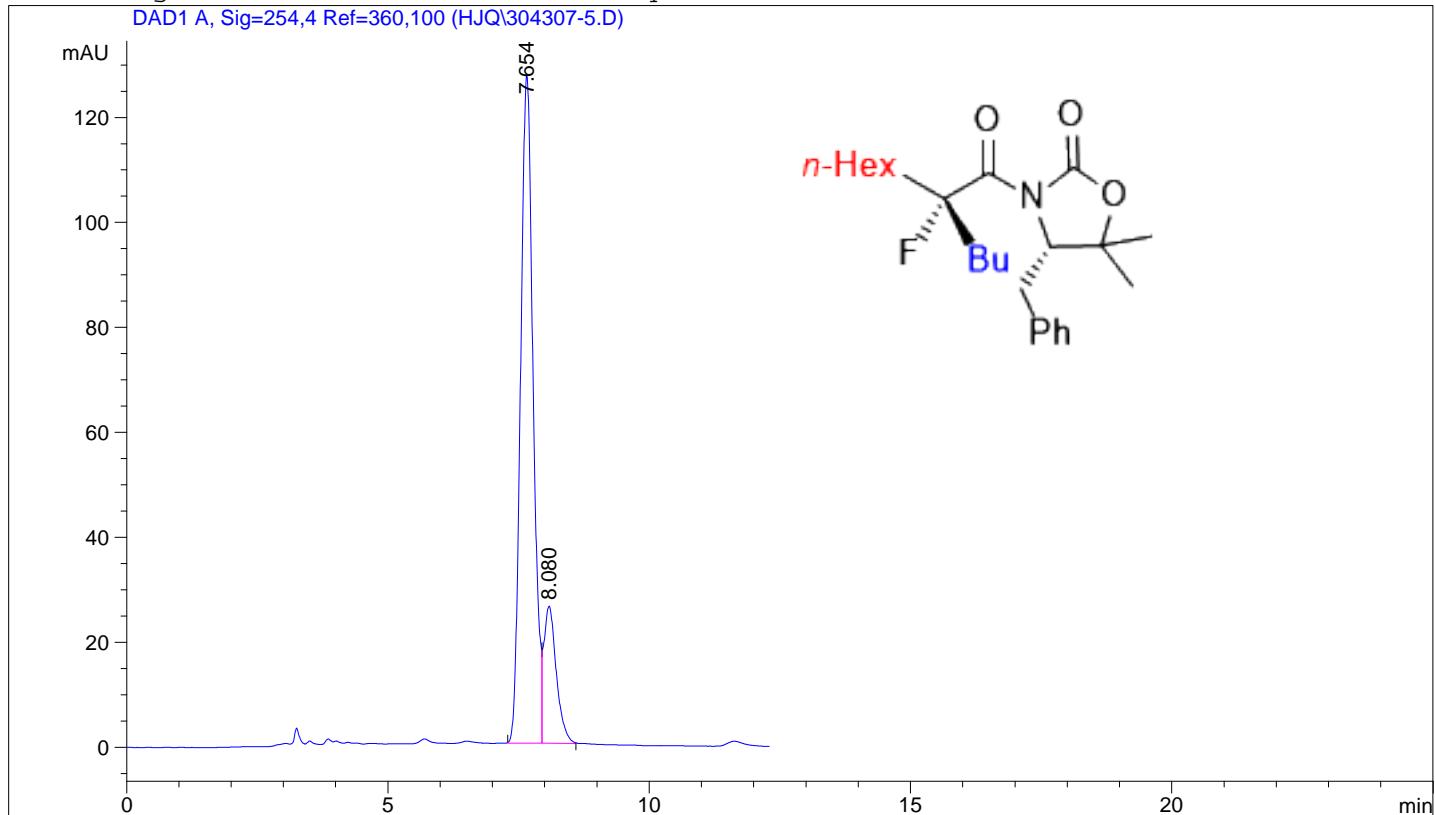


-153.925



OD  
99% Hexane  
1 ml/min  
D406821 large scale

```
=====
Injection Date : 9/14/2016 9:31:48 PM
Sample Name : 304307-5
Acq. Operator : jianqianghuang
Location : Vial 1
Inj Volume : 5 µl
Acq. Method : C:\HPCHEM\1\METHODS\ZACK.M
Last changed : 9/14/2016 9:32:01 PM by jianqianghuang
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ZACK.M
Last changed : 9/26/2016 2:02:36 PM by Kumar
```



```
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/µl] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.654	BV	0.2581	2142.07593	127.44568	83.1714
2	8.080	VB	0.2432	433.41922	26.16926	16.8286

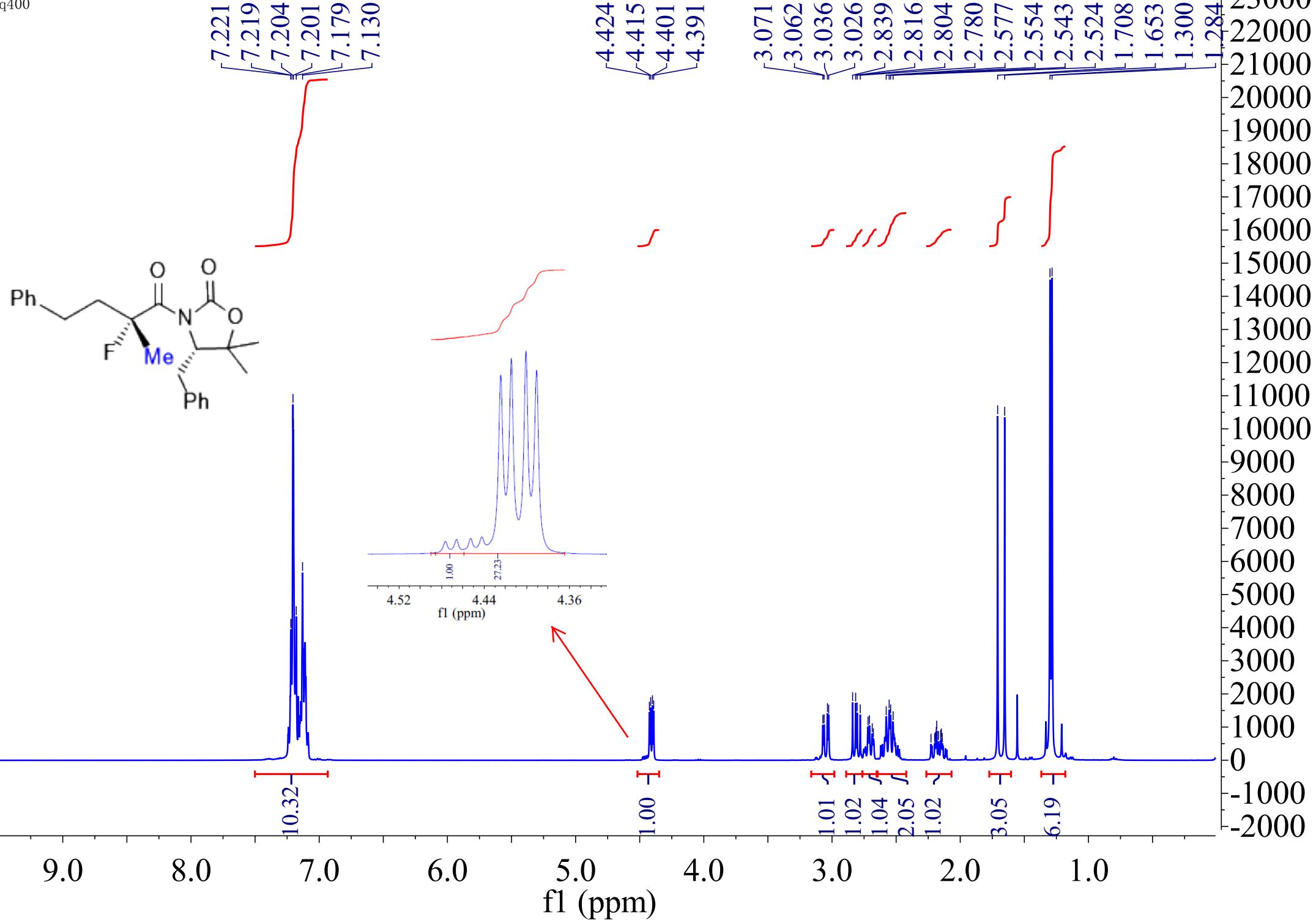
Totals : 2575.49515 153.61494

Results obtained with enhanced integrator!

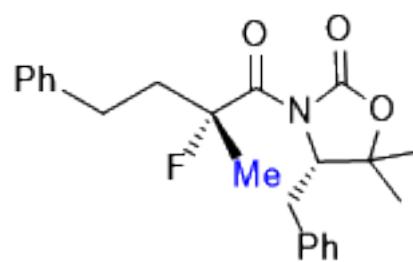
=====

\*\*\* End of Report \*\*\*

hjq400



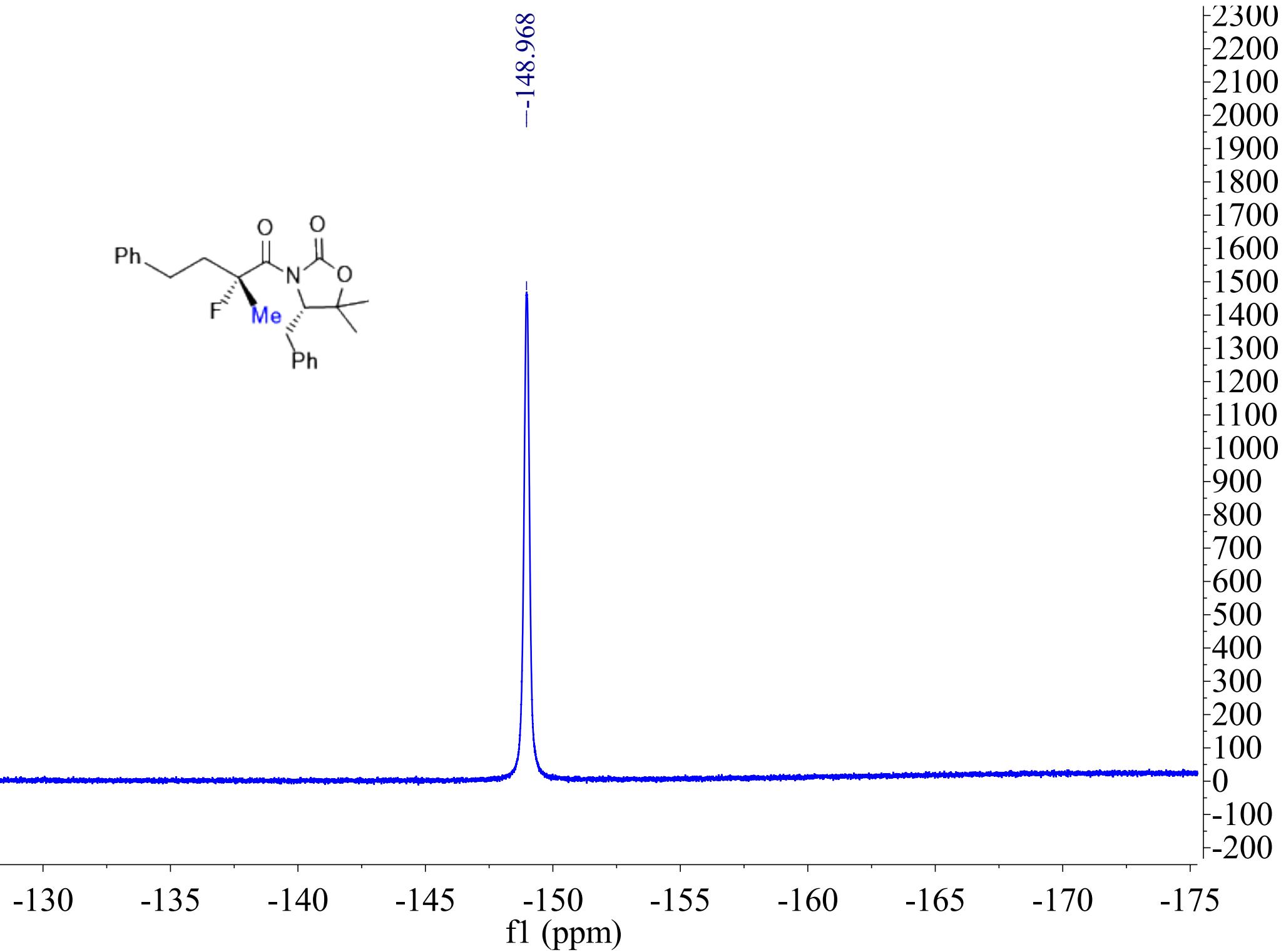
hjq400

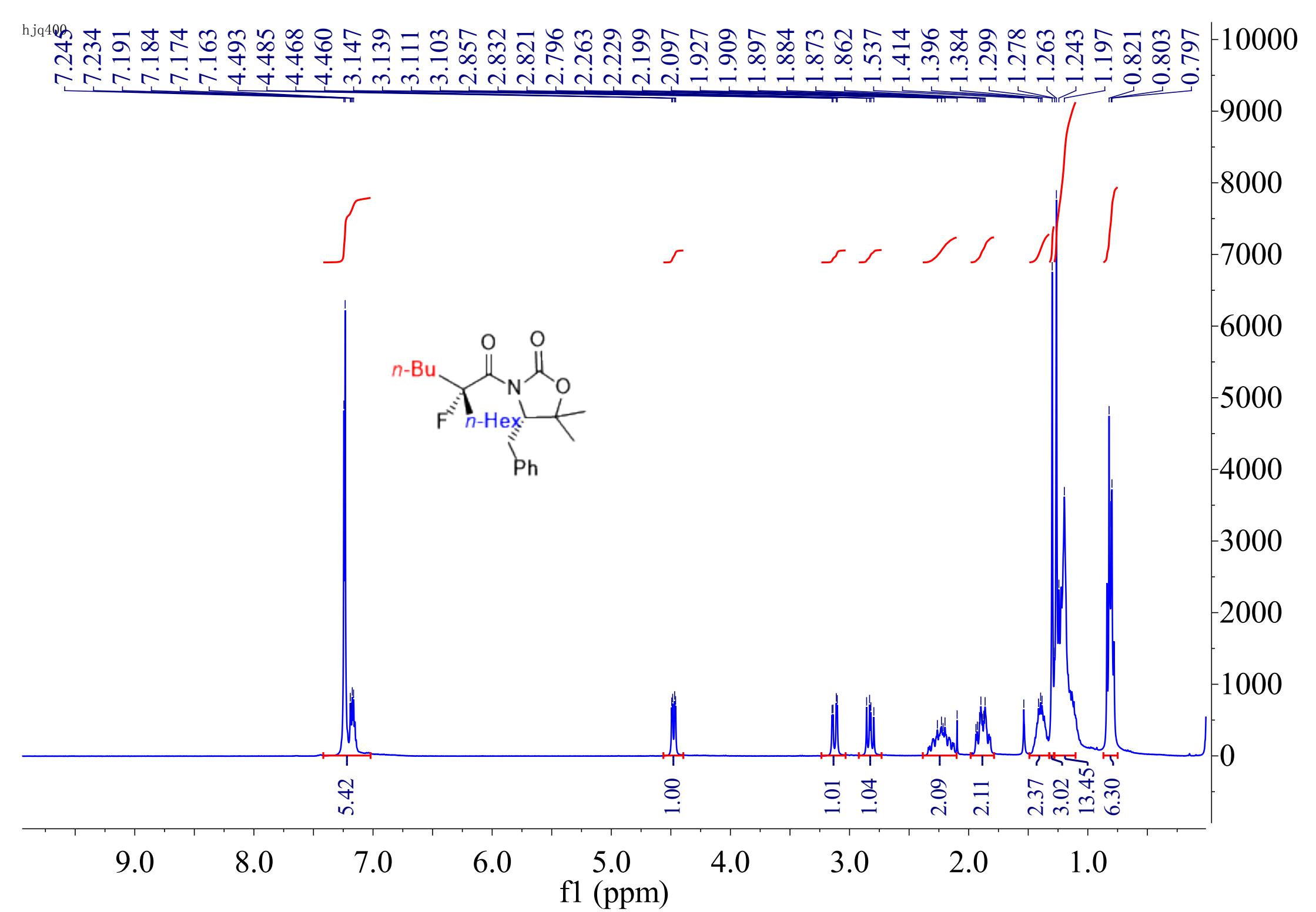
<172.352  
<172.085-150.950  
140.928  
136.521  
129.075  
128.640  
128.395  
128.378  
126.865  
126.013>98.194  
>96.343  
82.696  
77.317  
77.000  
76.682  
-65.36438.932  
38.708  
35.064  
29.417  
29.375  
>27.968  
>22.458  
>22.218  
22.109

170 150 130 110 90 80 70 60 50 40 30 20 10

f1 (ppm)

40000  
35000  
30000  
25000  
20000  
15000  
10000  
5000  
0

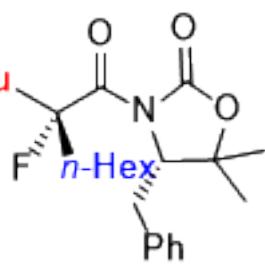




hjq400

172.313

172.047



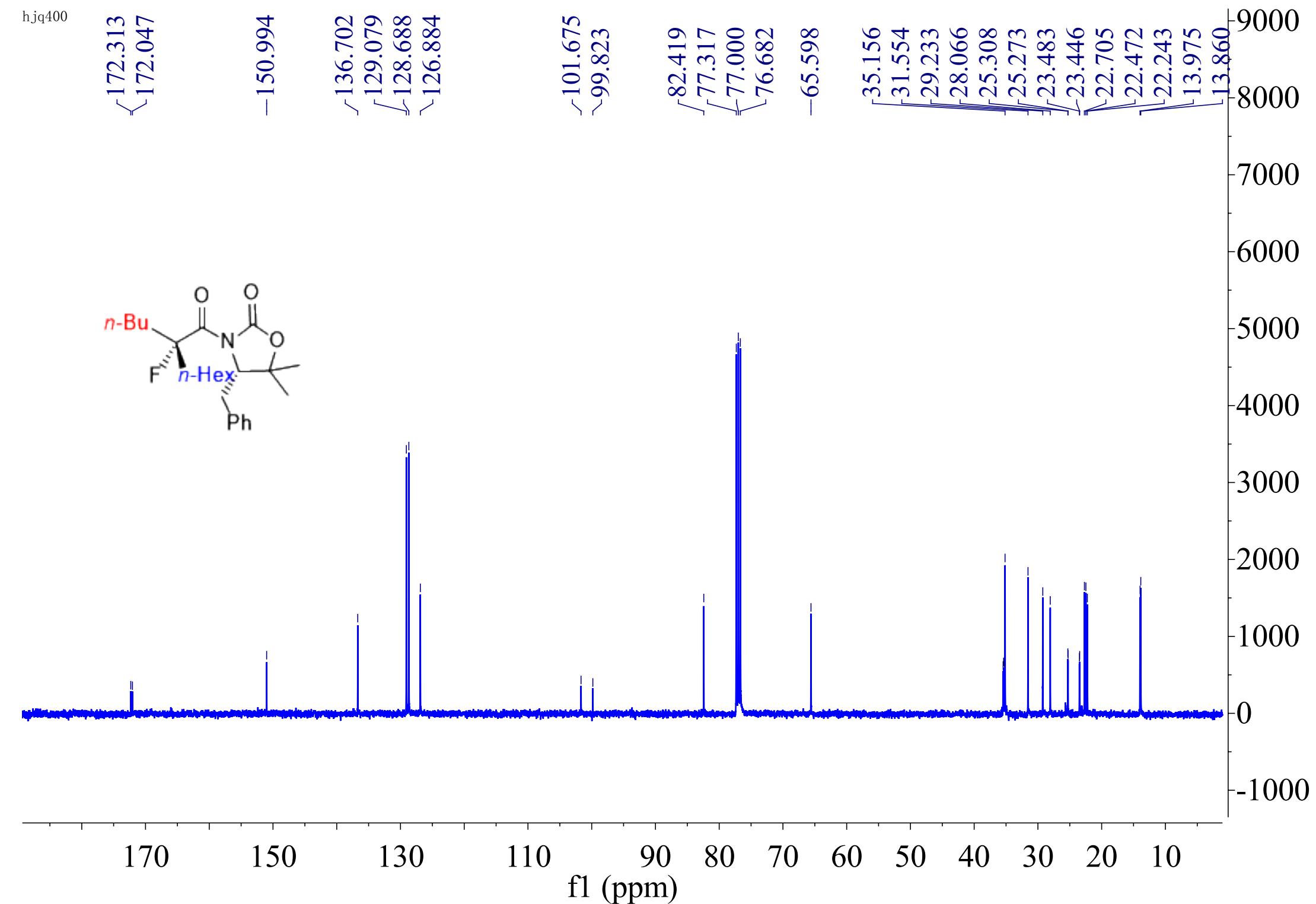
136.702  
129.079  
128.688  
126.884

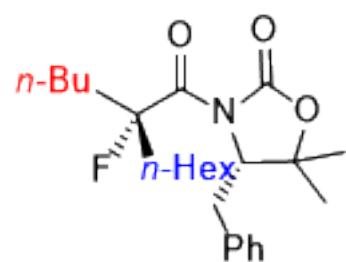
101.675  
99.823

82.419  
77.317  
77.000  
76.682

-65.598

35.156  
31.554  
29.233  
28.066  
25.308  
25.273  
23.483  
23.446  
22.705  
22.472  
22.243  
13.975  
13.860





-153.901

-100

-120

-140

f1 (ppm)

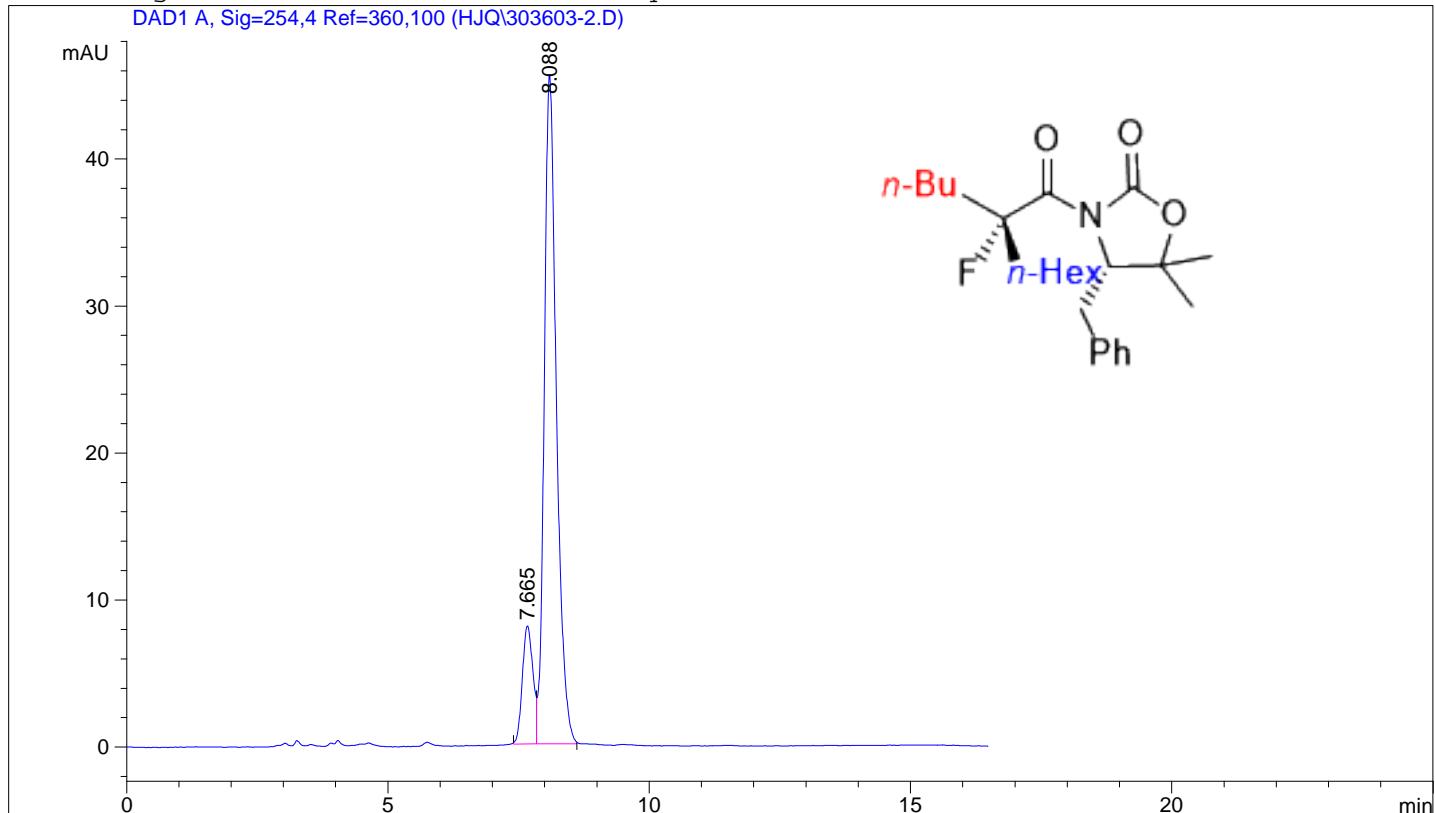
-180

-200

2400  
2200  
2000  
1800  
1600  
1400  
1200  
1000  
800  
600  
400  
200  
0  
-200

OD  
99% Hexane  
1 ml/min  
D406821 large scale

```
=====
Injection Date : 9/14/2016 9:47:08 PM
Sample Name : 303603-2
Acq. Operator : jianqianghuang
Location : Vial 2
Inj Volume : 5 µl
Acq. Method : C:\HPCHEM\1\METHODS\ZACK.M
Last changed : 9/14/2016 9:32:01 PM by jianqianghuang
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ZACK.M
Last changed : 9/26/2016 2:02:36 PM by Kumar
```



```
=====
Area Percent Report
=====
```

```
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/µl] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.665	BV	0.2179	114.22311	8.03265	13.4324
2	8.088	VB	0.2446	736.13391	45.54849	86.5676

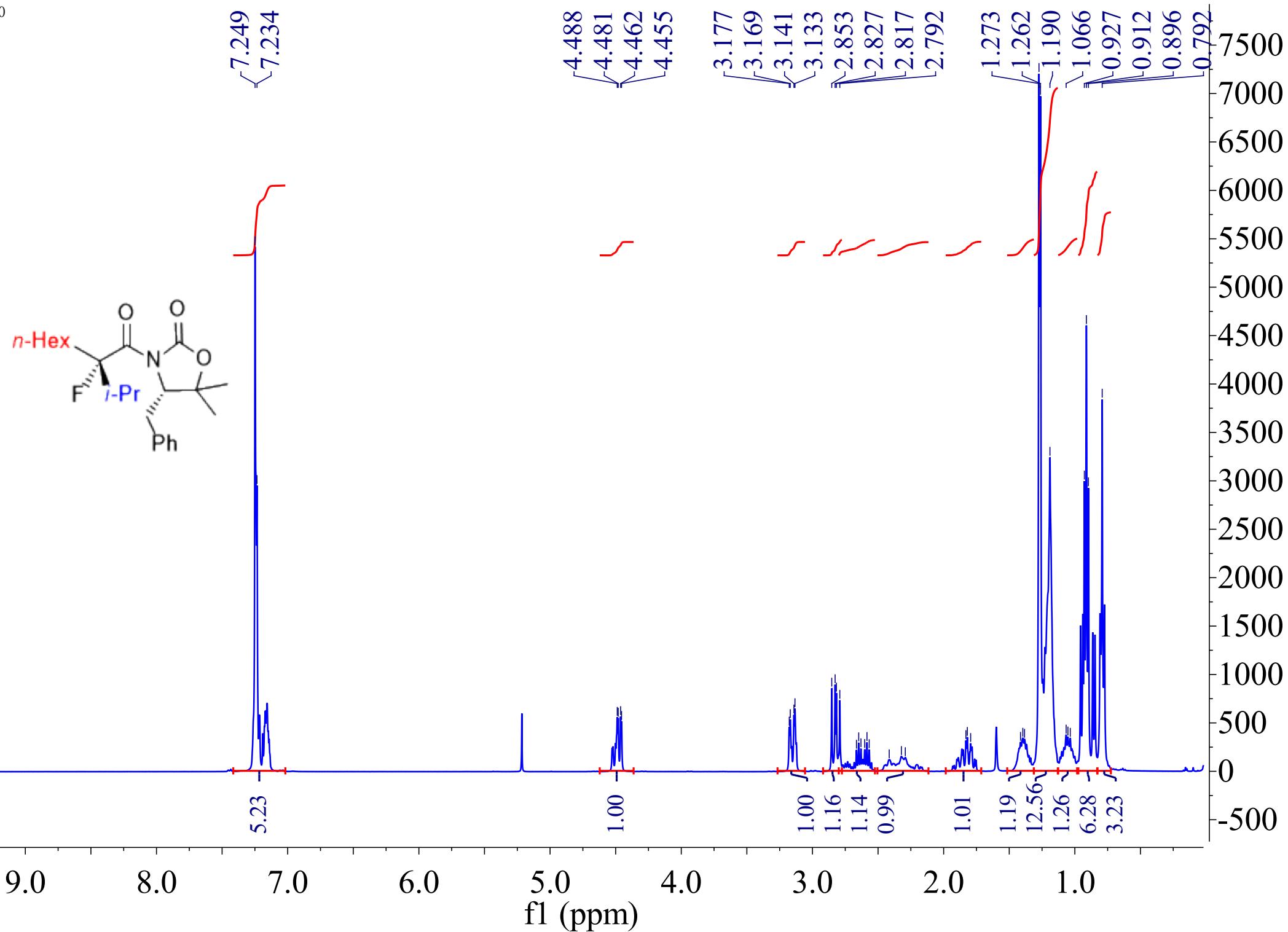
Totals : 850.35702 53.58115

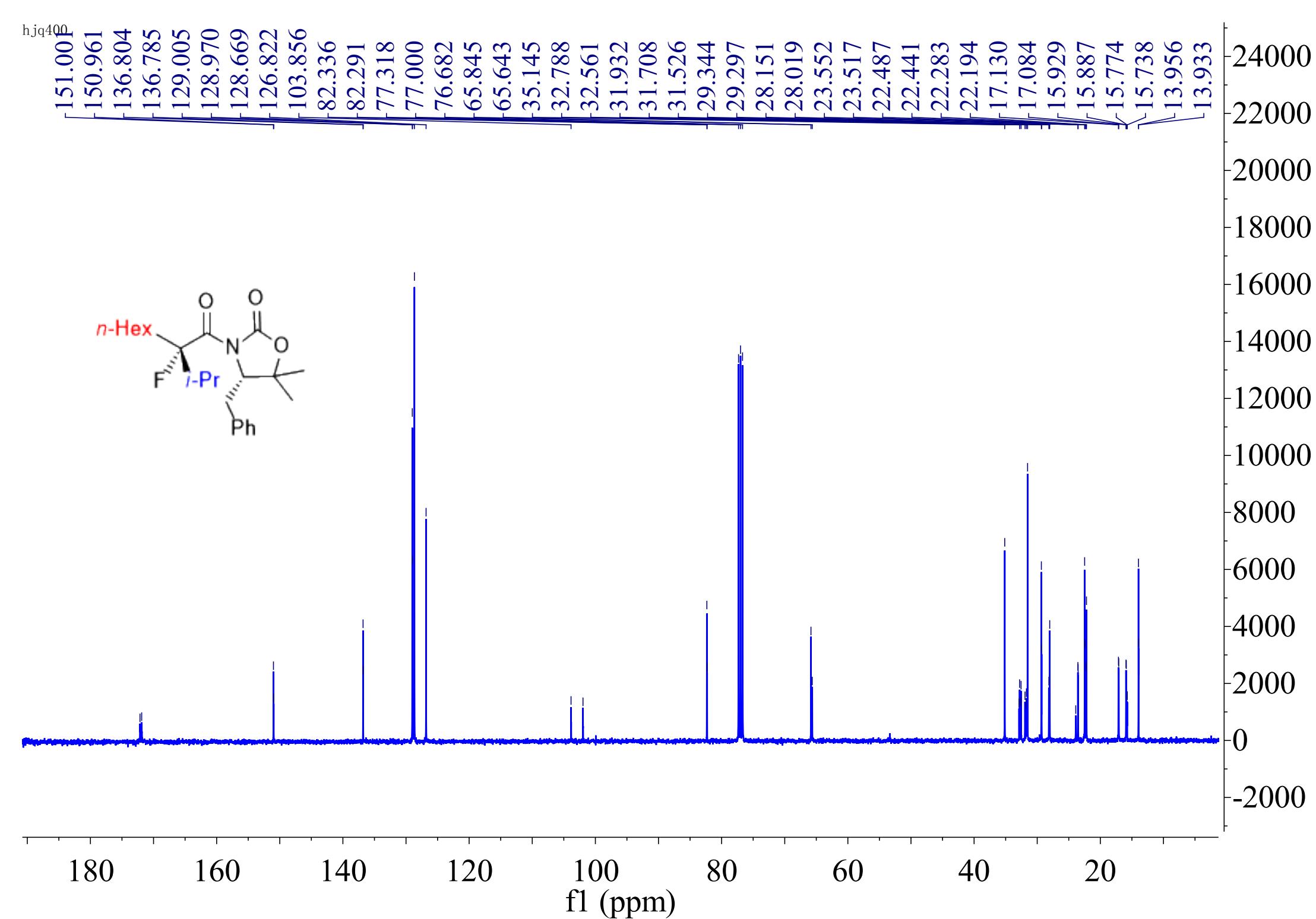
Results obtained with enhanced integrator!

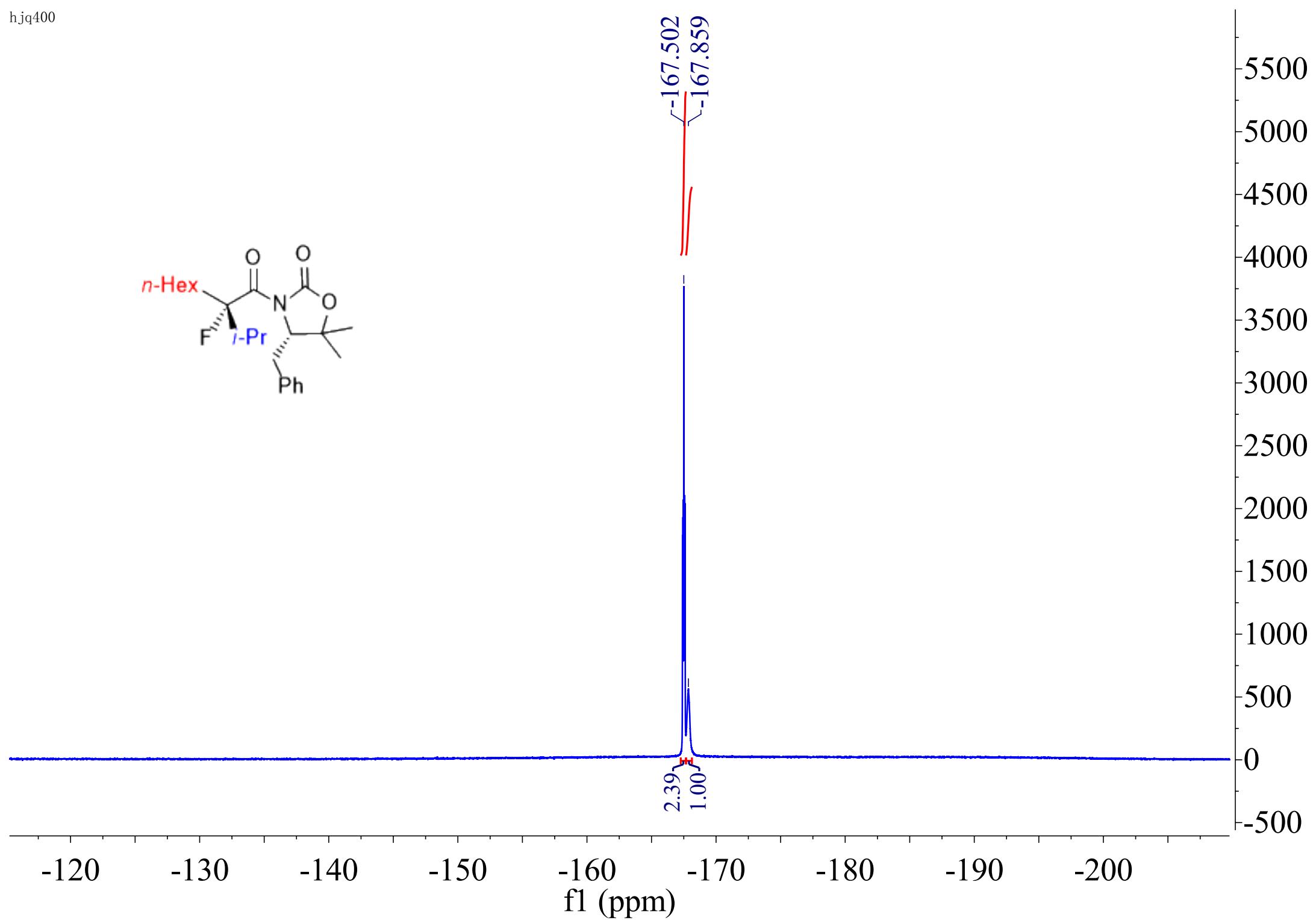
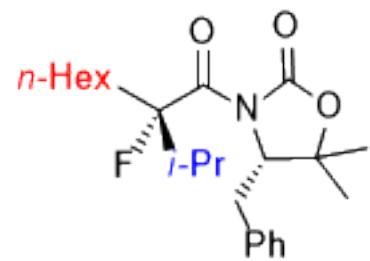
=====

\*\*\* End of Report \*\*\*

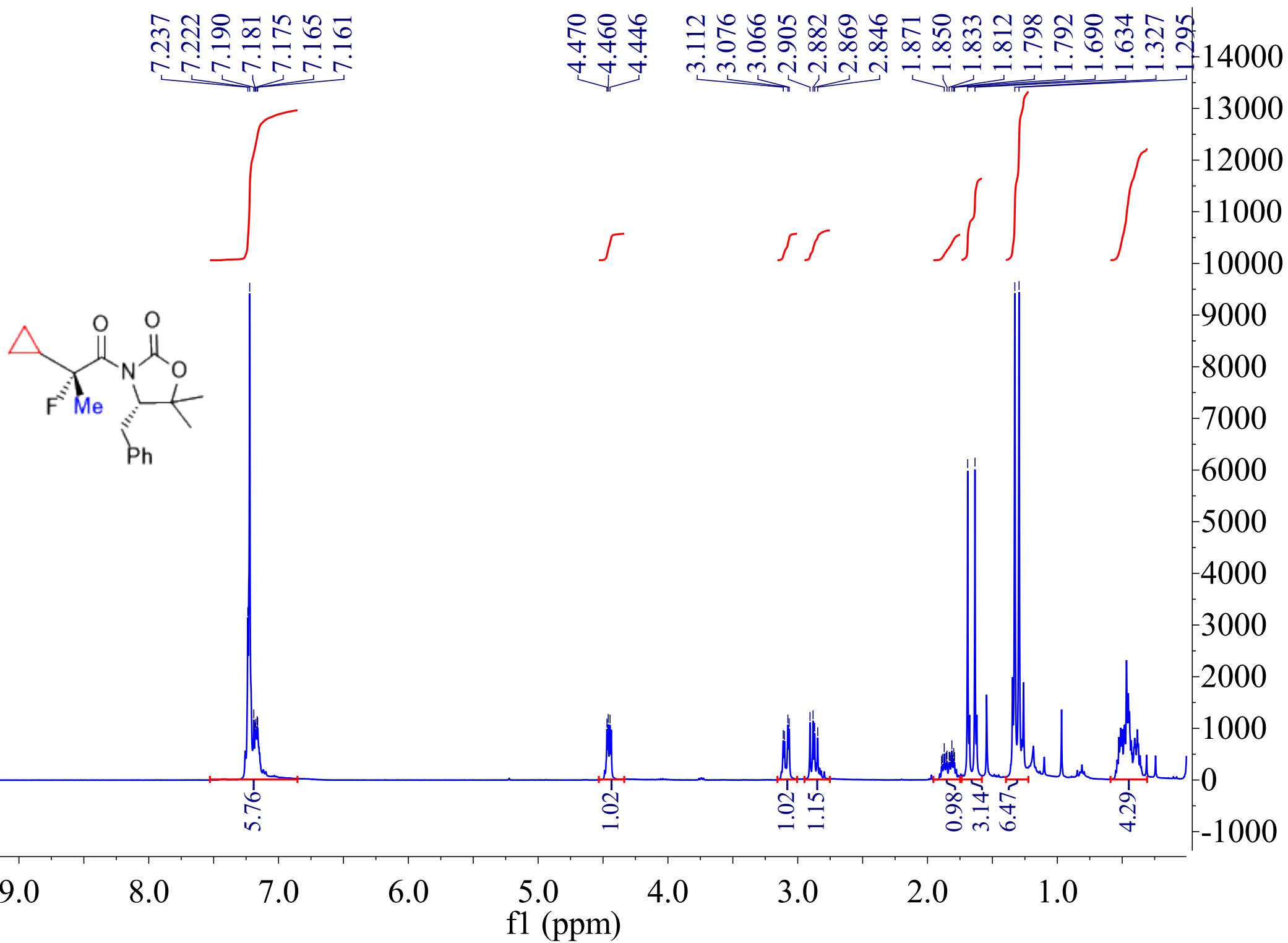
hjq400



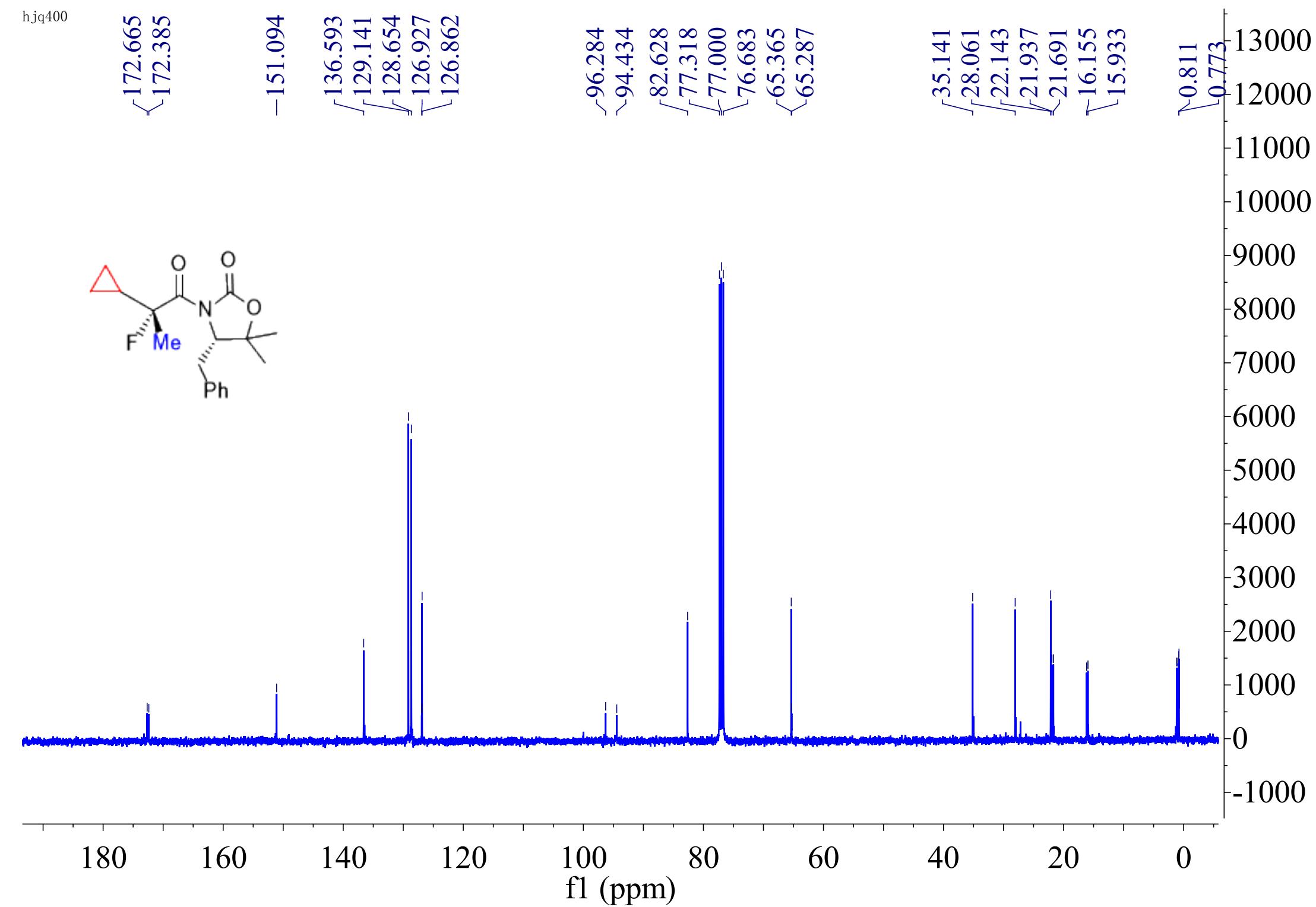
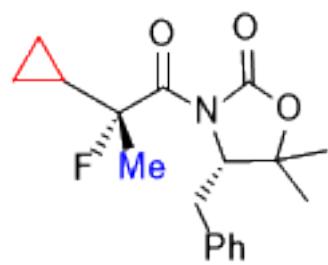


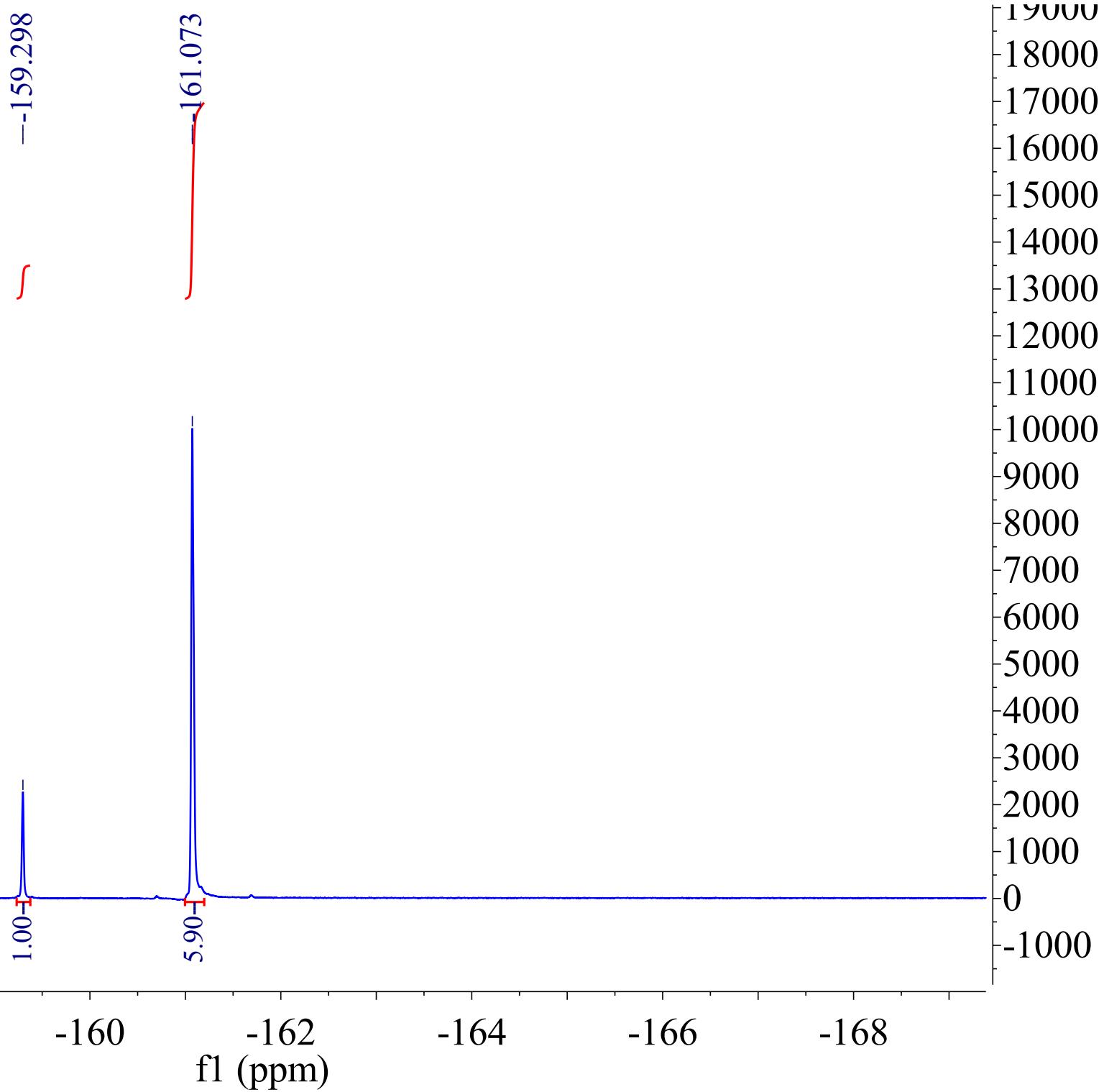
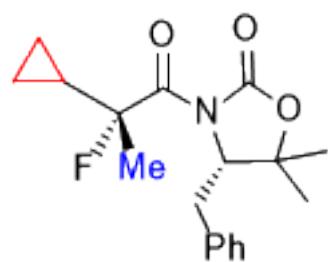


hjq400

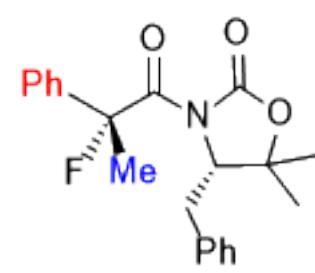


hjq400





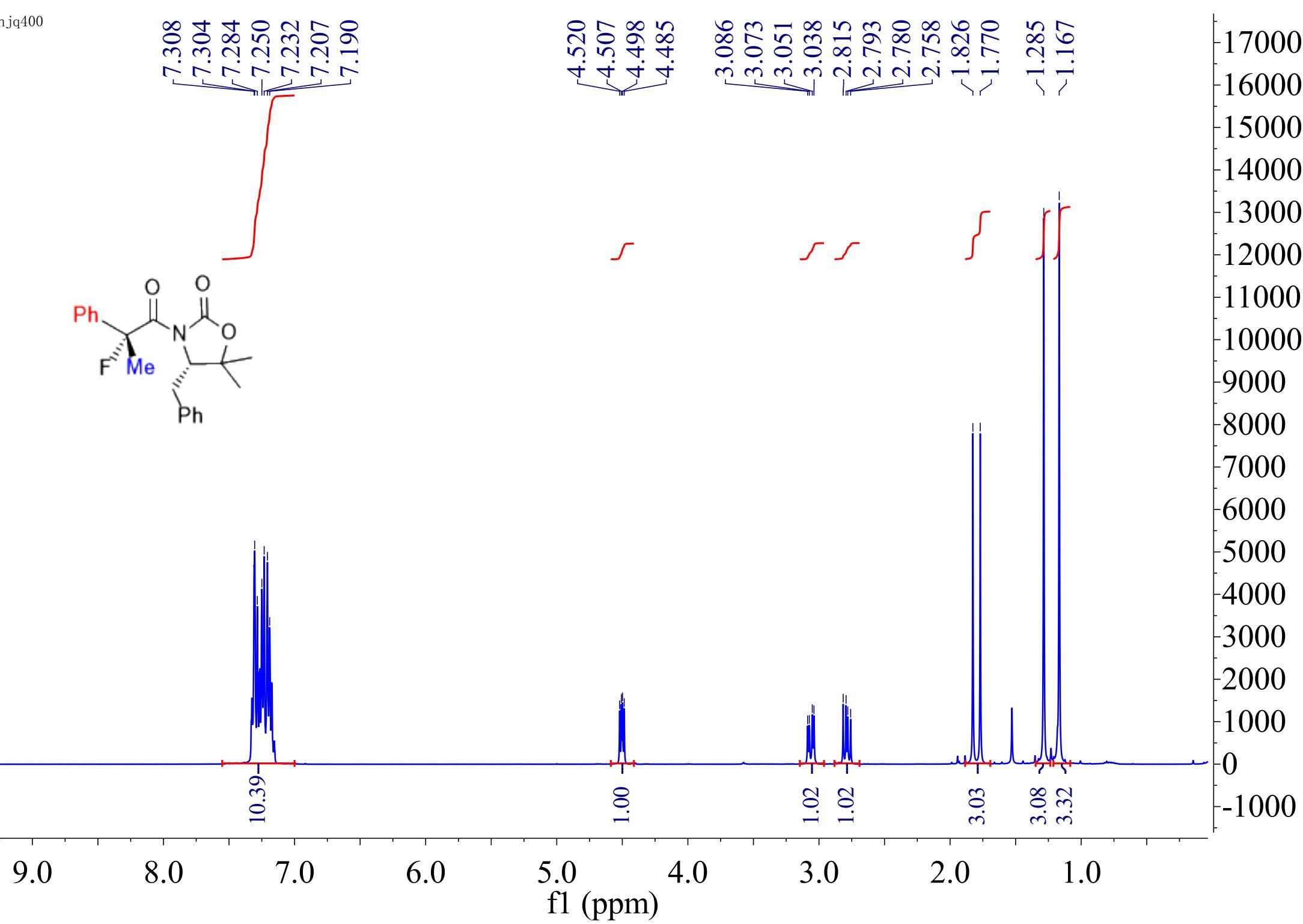
hjq400



7.308  
7.304  
7.284  
7.250  
7.232  
7.207  
7.190

4.520  
4.507  
4.498  
4.485

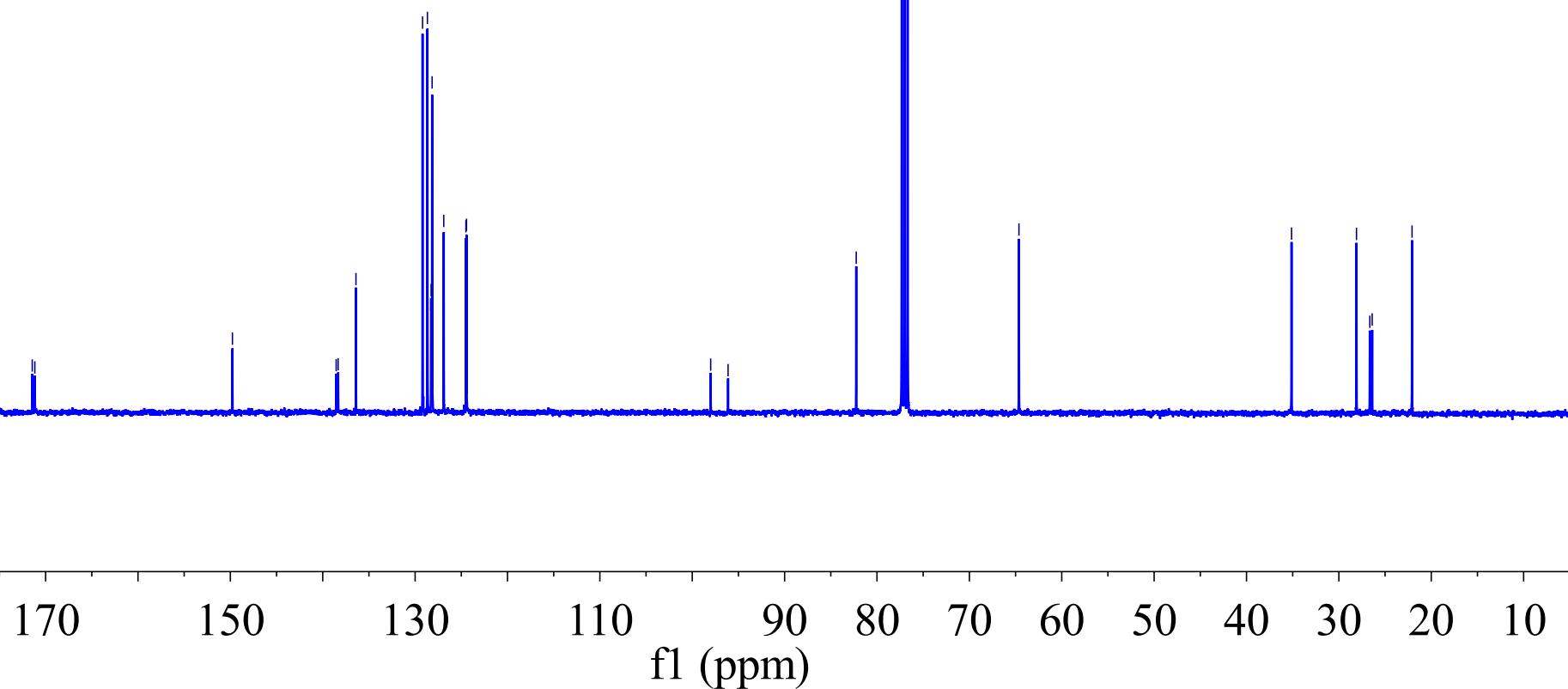
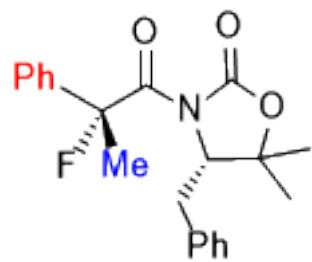
3.086  
3.073  
3.051  
3.038  
2.815  
2.793  
2.780  
2.758  
1.826  
1.770  
-1.285  
-1.167

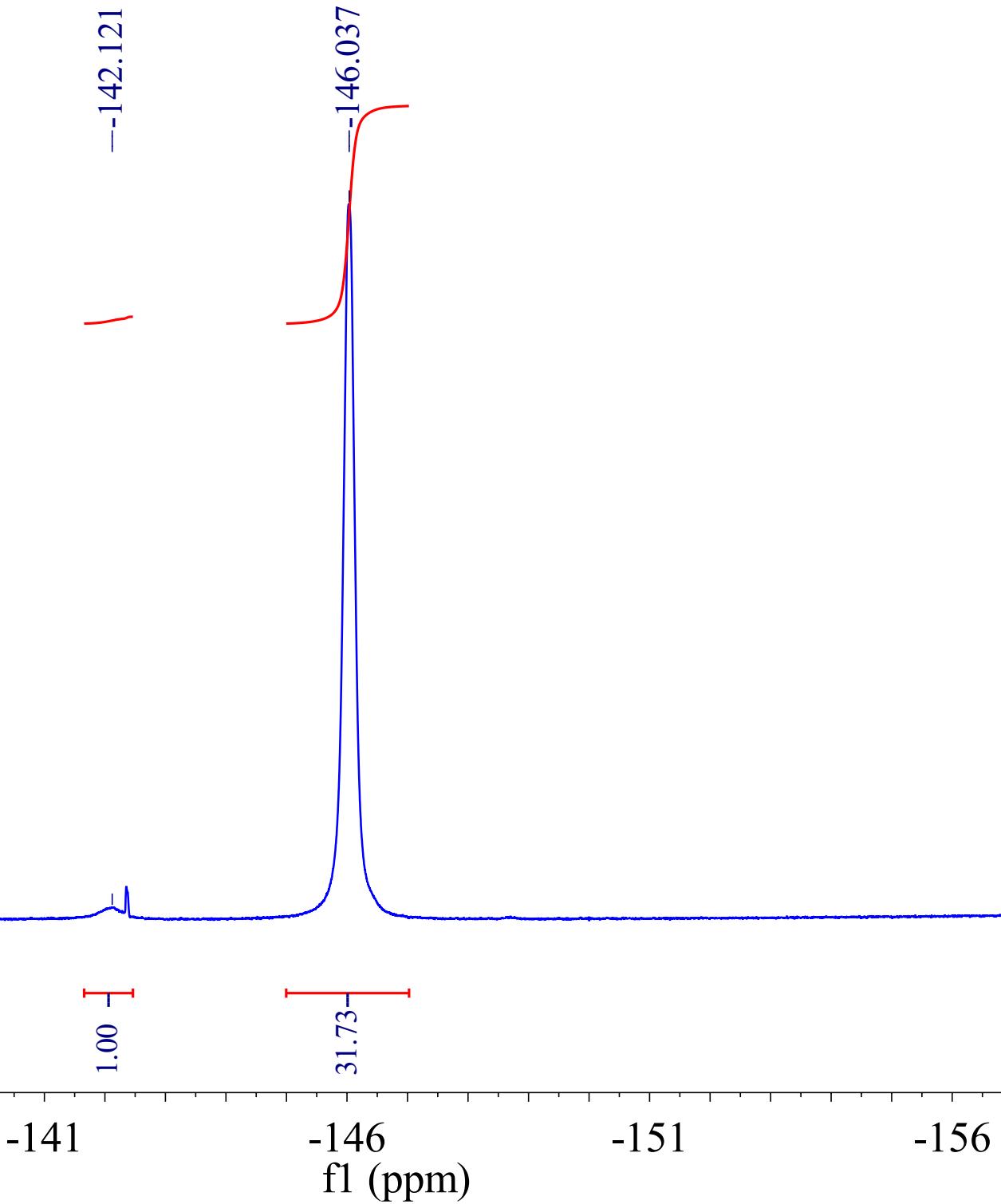
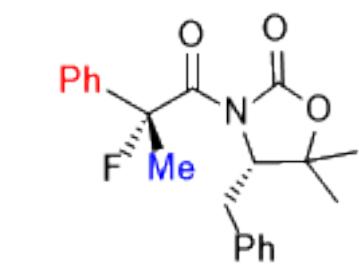


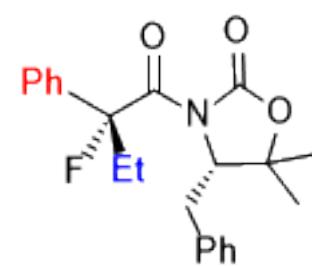
hjq400

<171.447  
<171.167-149.775  
138.546  
138.334  
-136.403  
129.194  
128.669  
128.264  
128.160  
126.899  
124.502  
124.434  
98.003  
96.12182.247  
77.317  
77.000  
76.682

-64.633

35.122  
28.094  
26.649  
26.395  
22.080





7.318  
7.314  
7.309  
7.290  
7.270

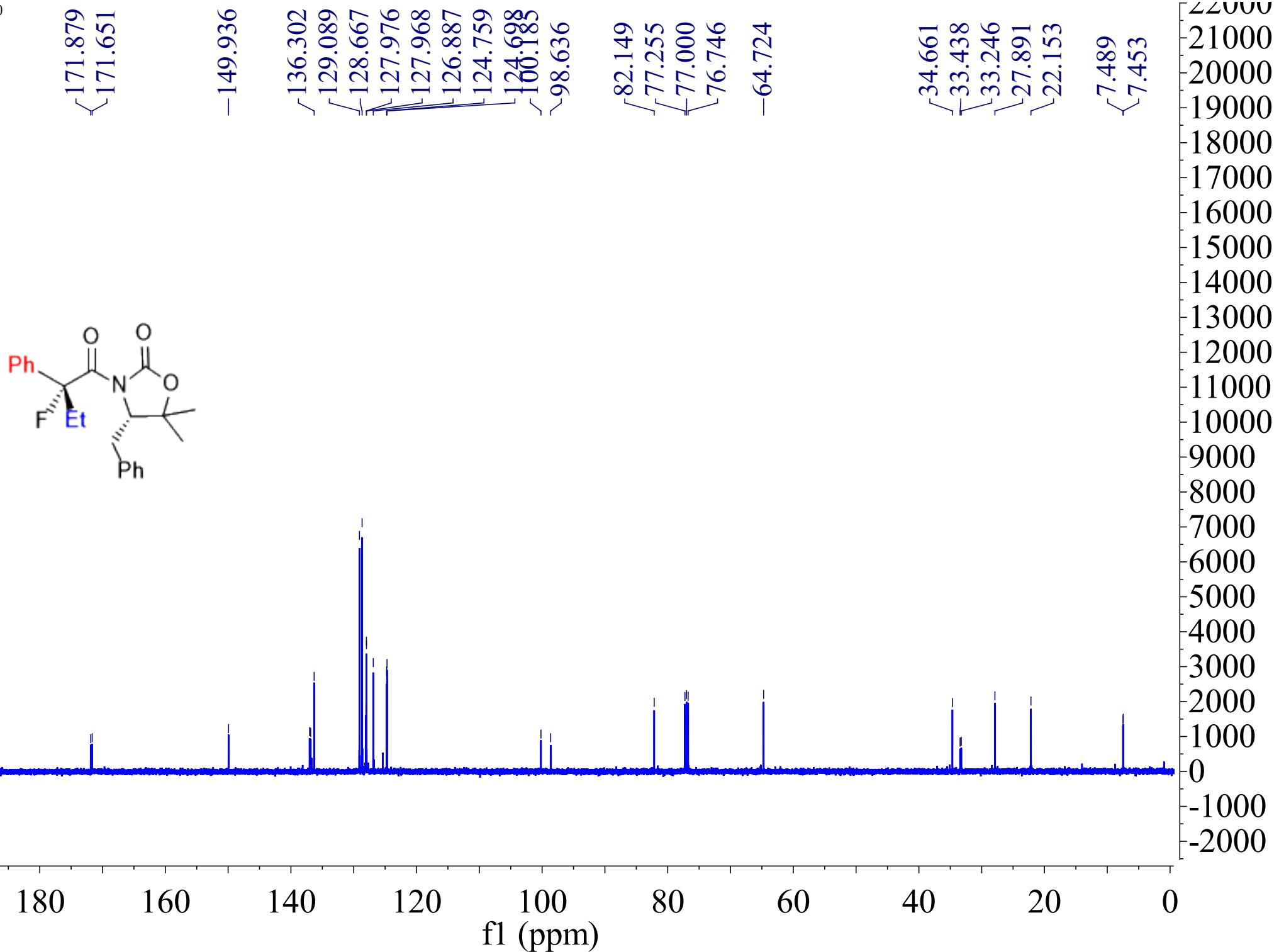
4.589  
4.574  
4.558  
4.543

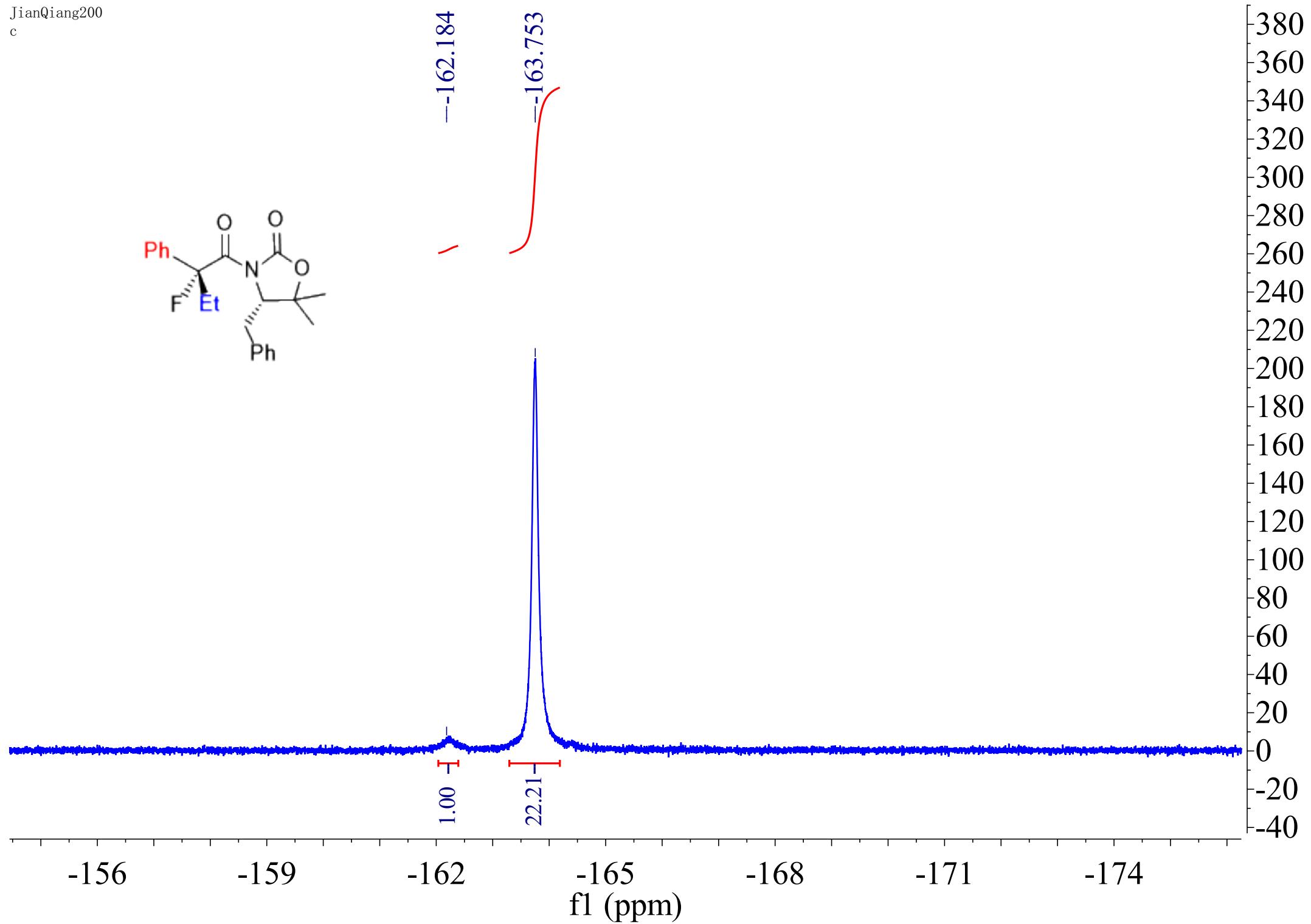
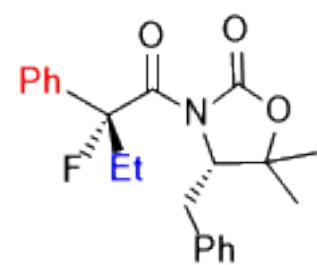
3.244  
3.228  
3.197  
3.181  
2.822  
2.791  
2.775  
2.744  
2.117  
2.992  
1.152  
0.900  
0.876  
0.851

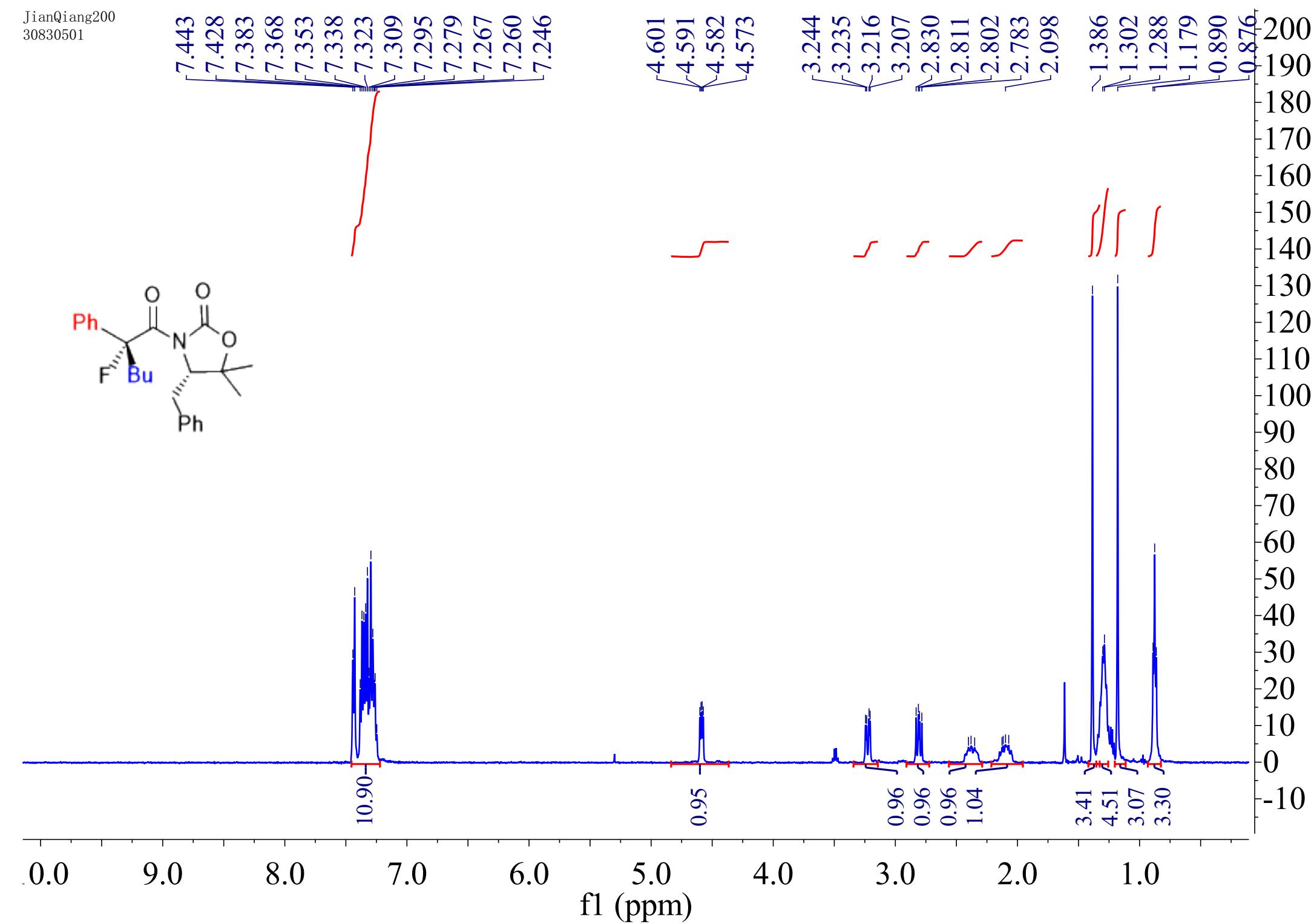
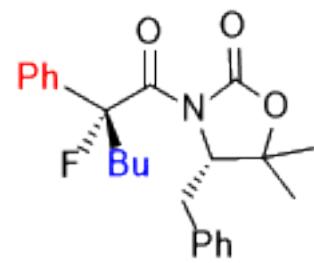
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0

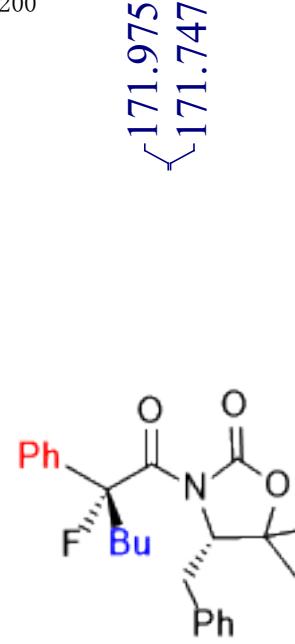
f1 (ppm)

1500  
1400  
1300  
1200  
1100  
1000  
900  
800  
700  
600  
500  
400  
300  
200  
100  
0  
-100









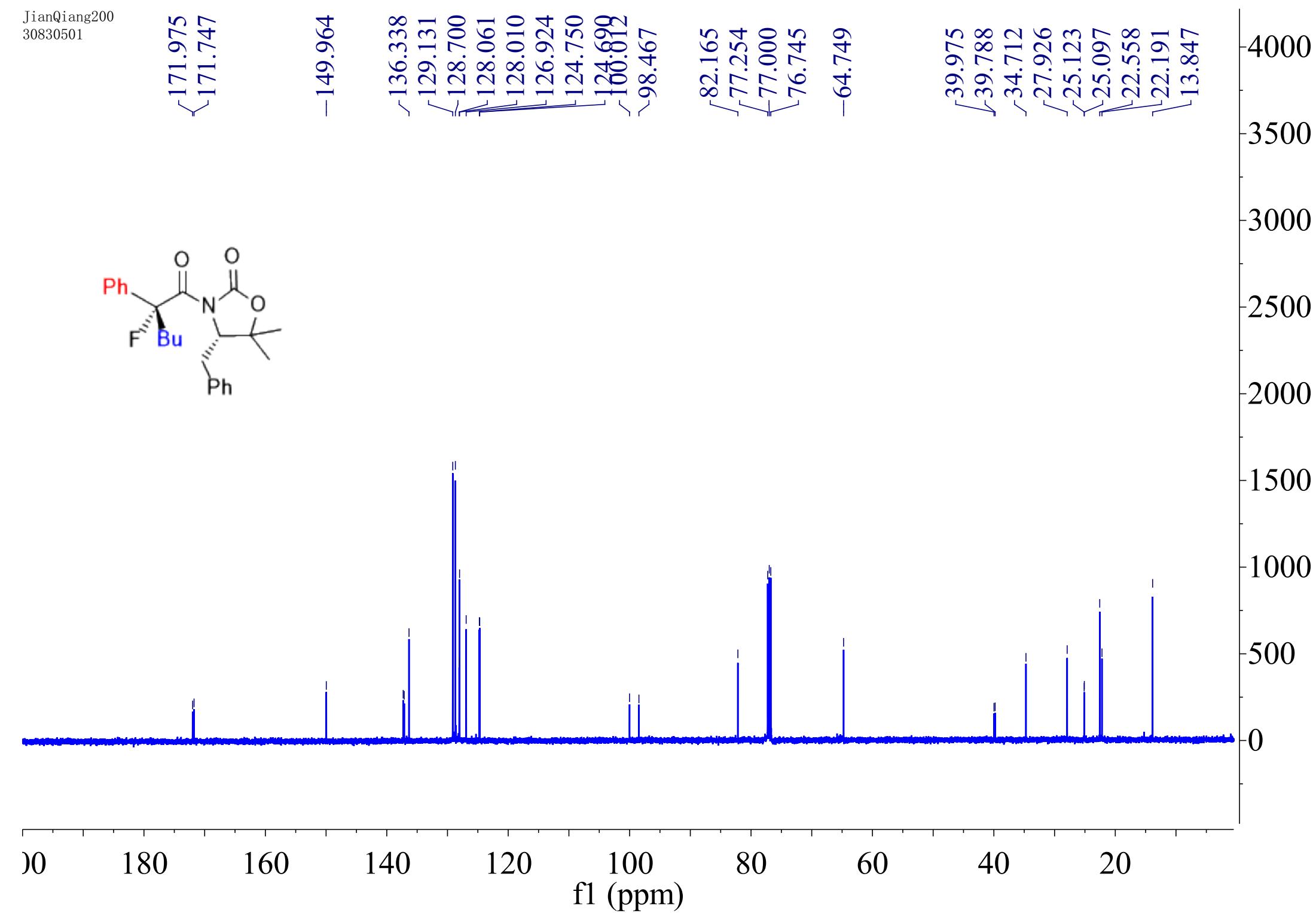
-149.964

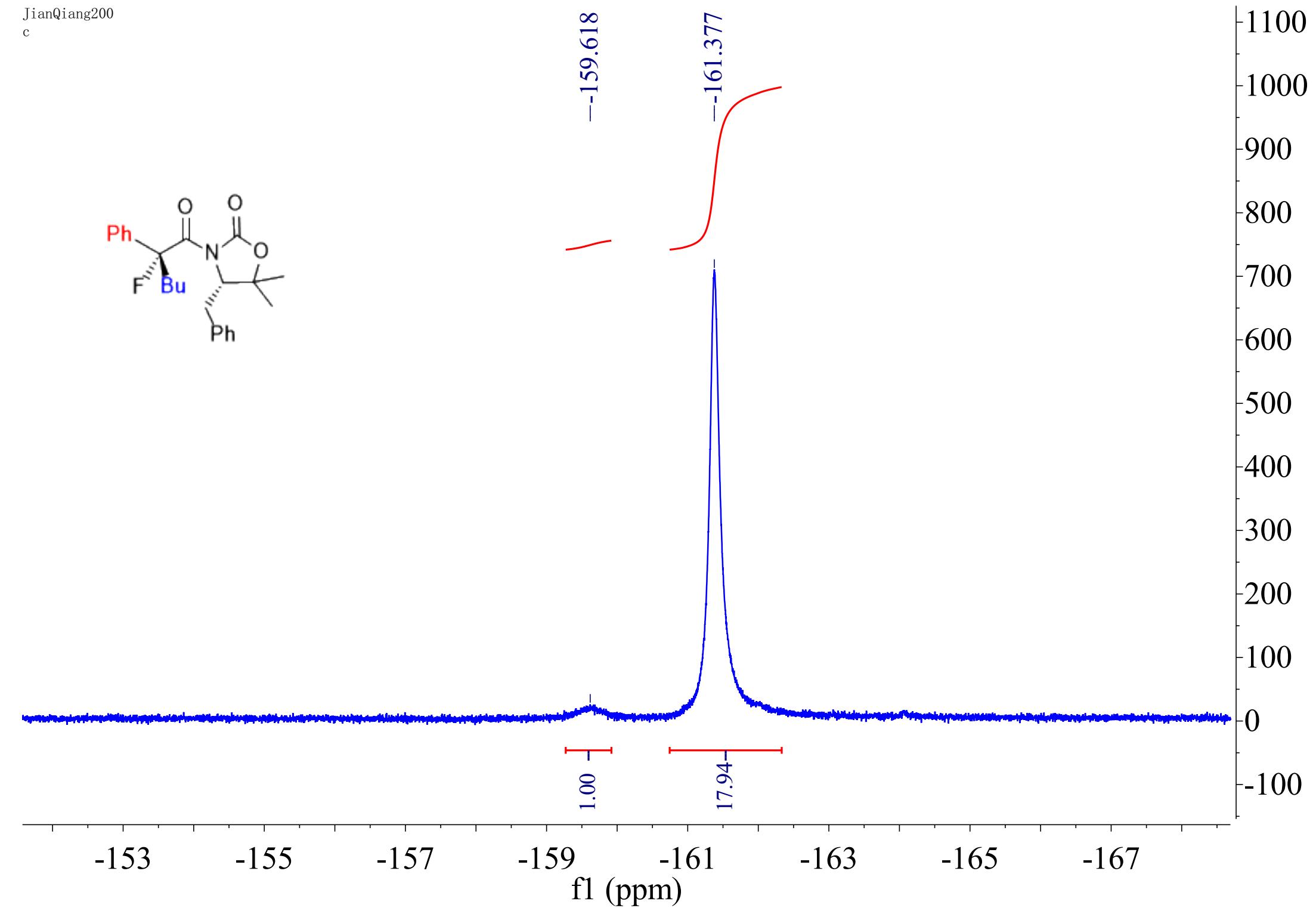
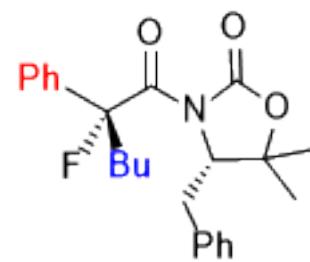
136.338  
129.131  
128.700  
128.061  
128.010  
126.924  
124.750  
124.692  
98.467

82.165  
77.254  
77.000  
76.745

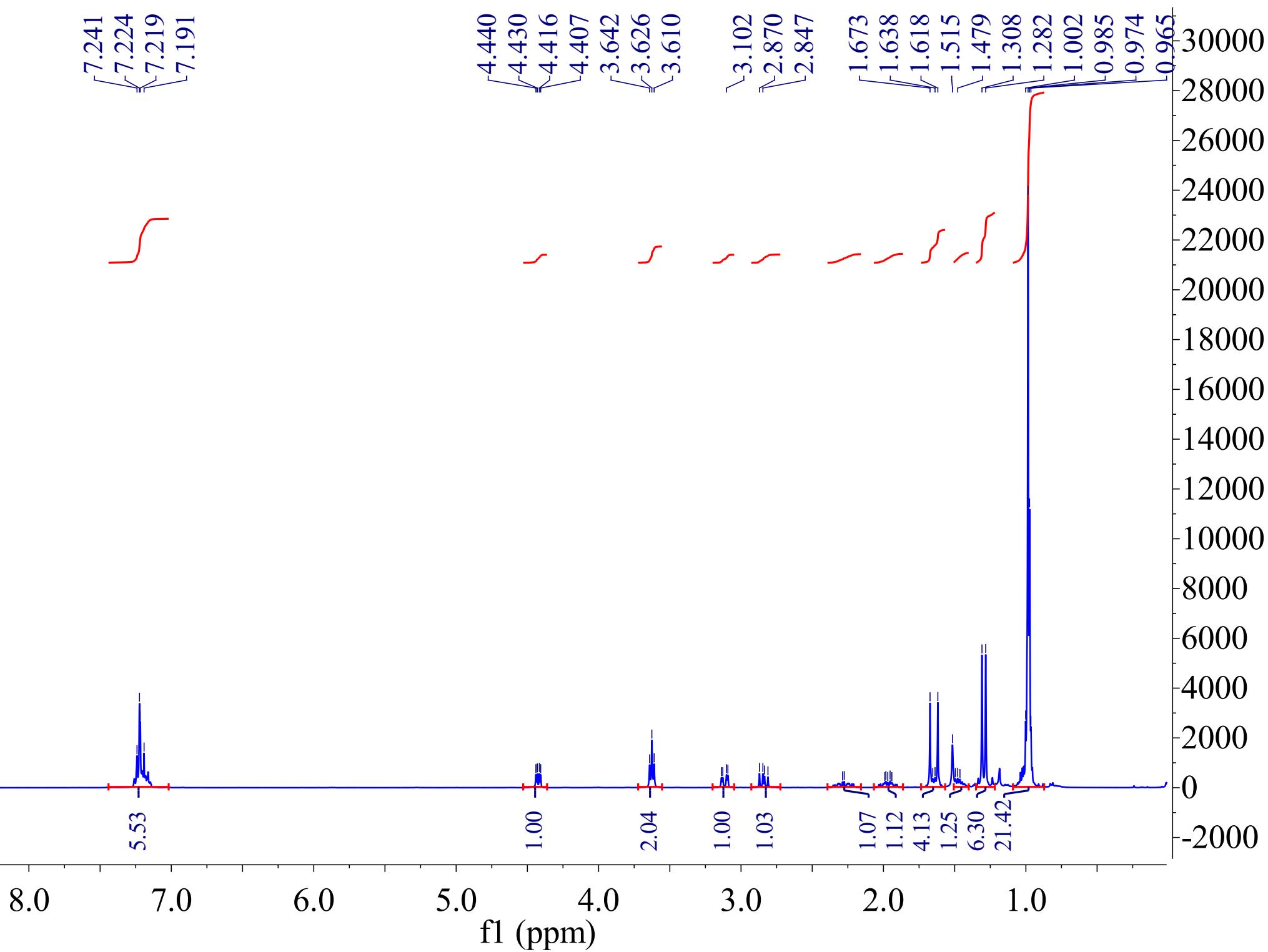
-64.749

39.975  
39.788  
34.712  
27.926  
25.123  
25.097  
22.558  
22.191  
13.847





hjq400



172.826  
172.558

-150.892

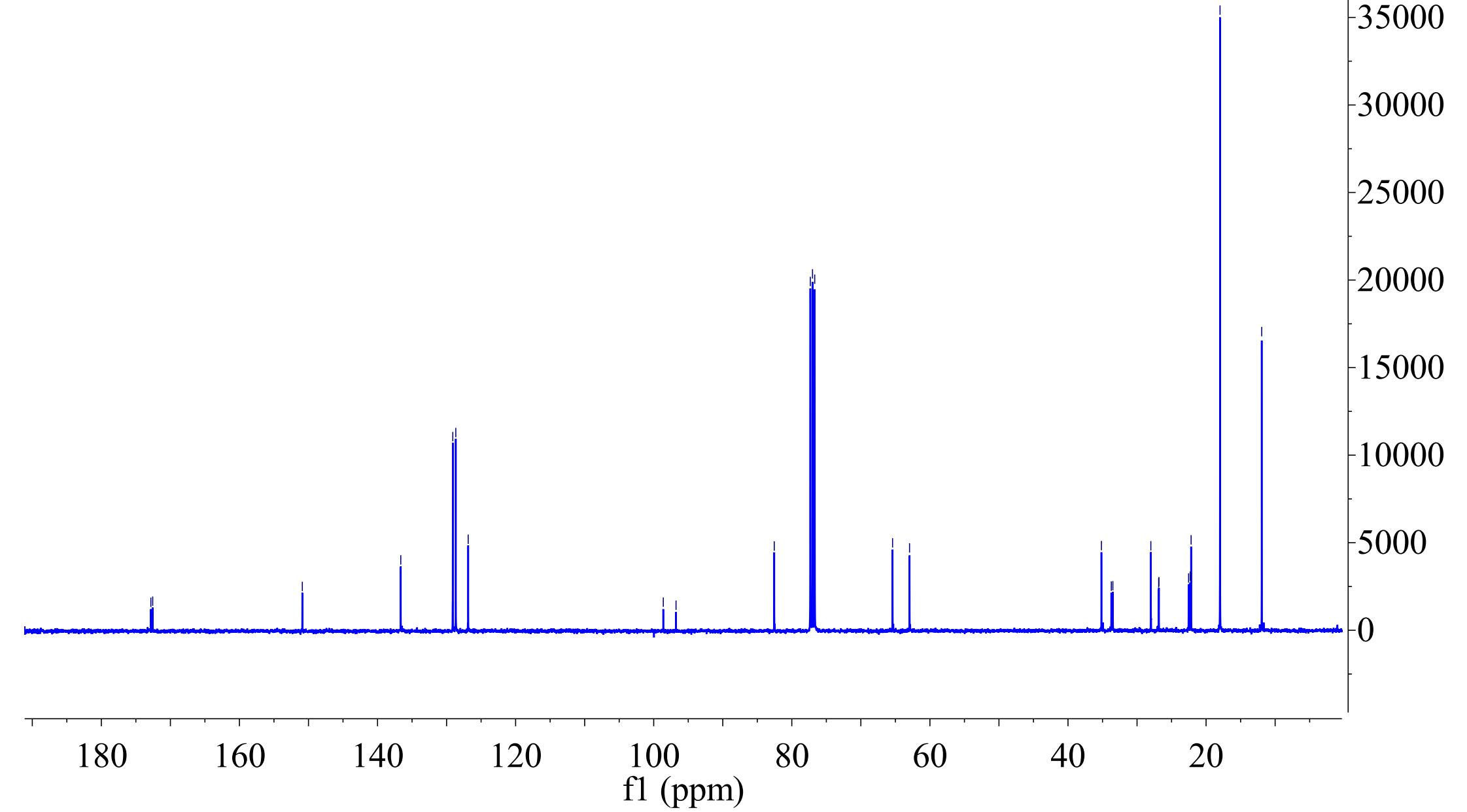
136.633  
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128.665  
126.869

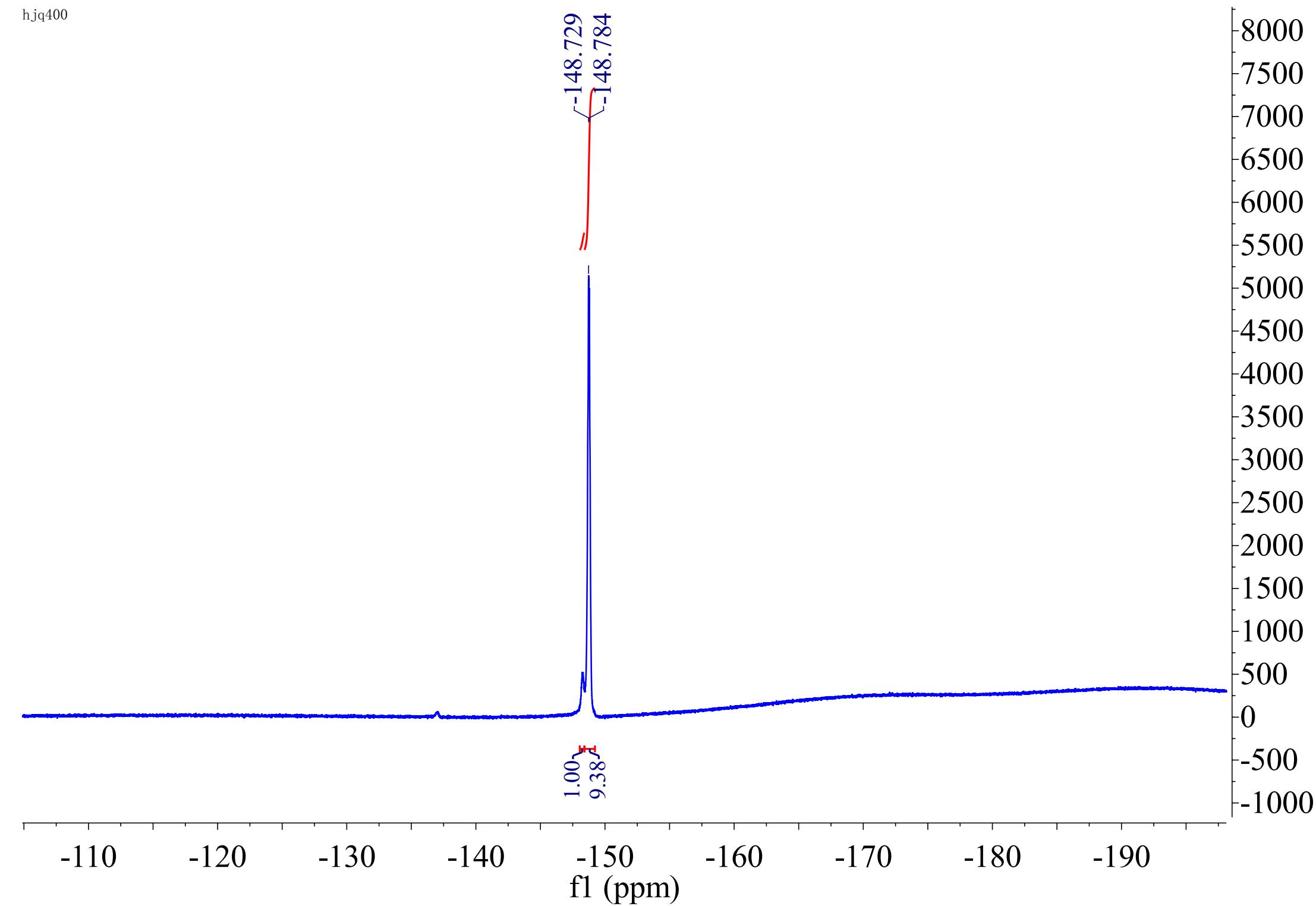
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96.768

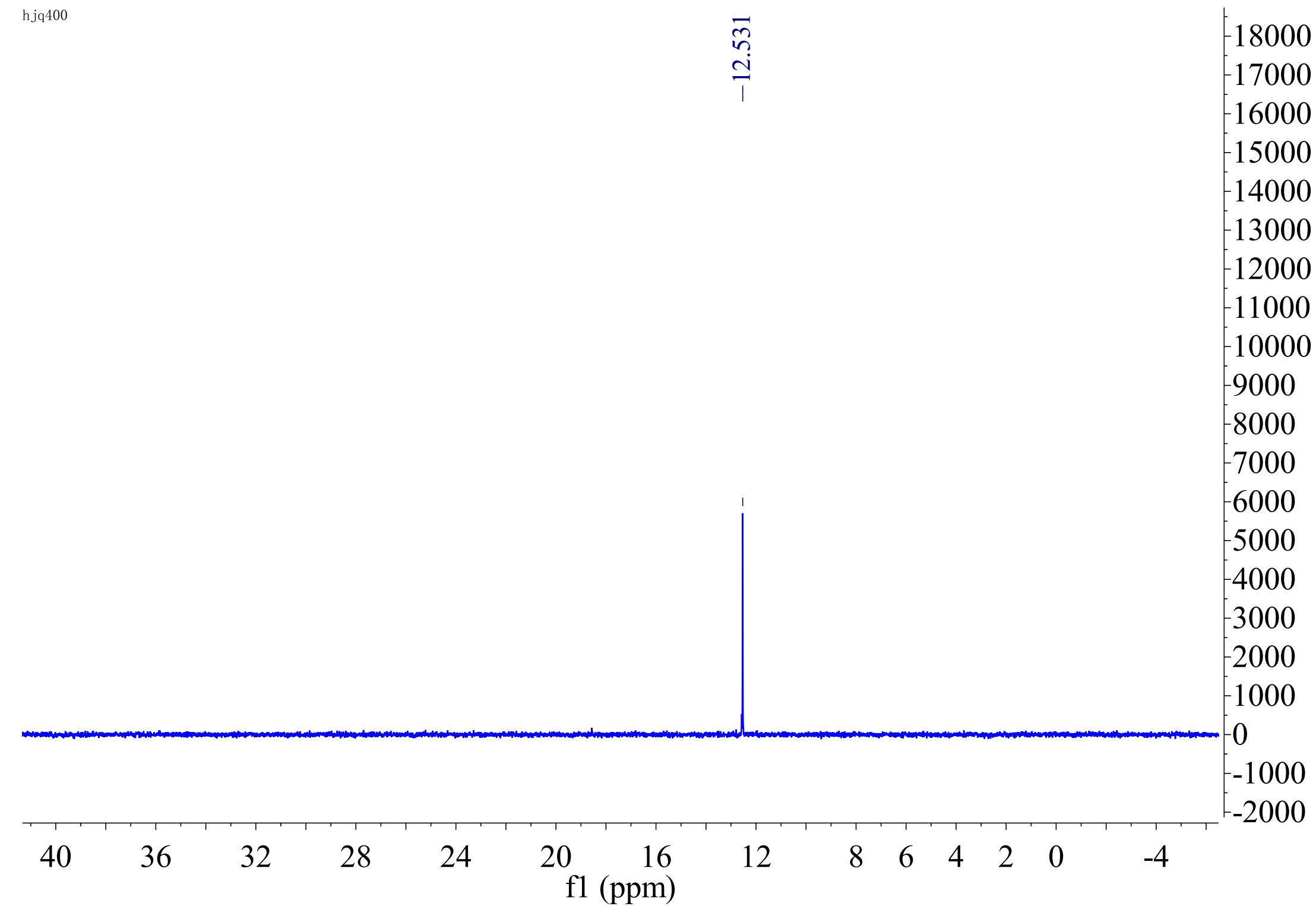
82.542  
77.317  
77.000  
76.683

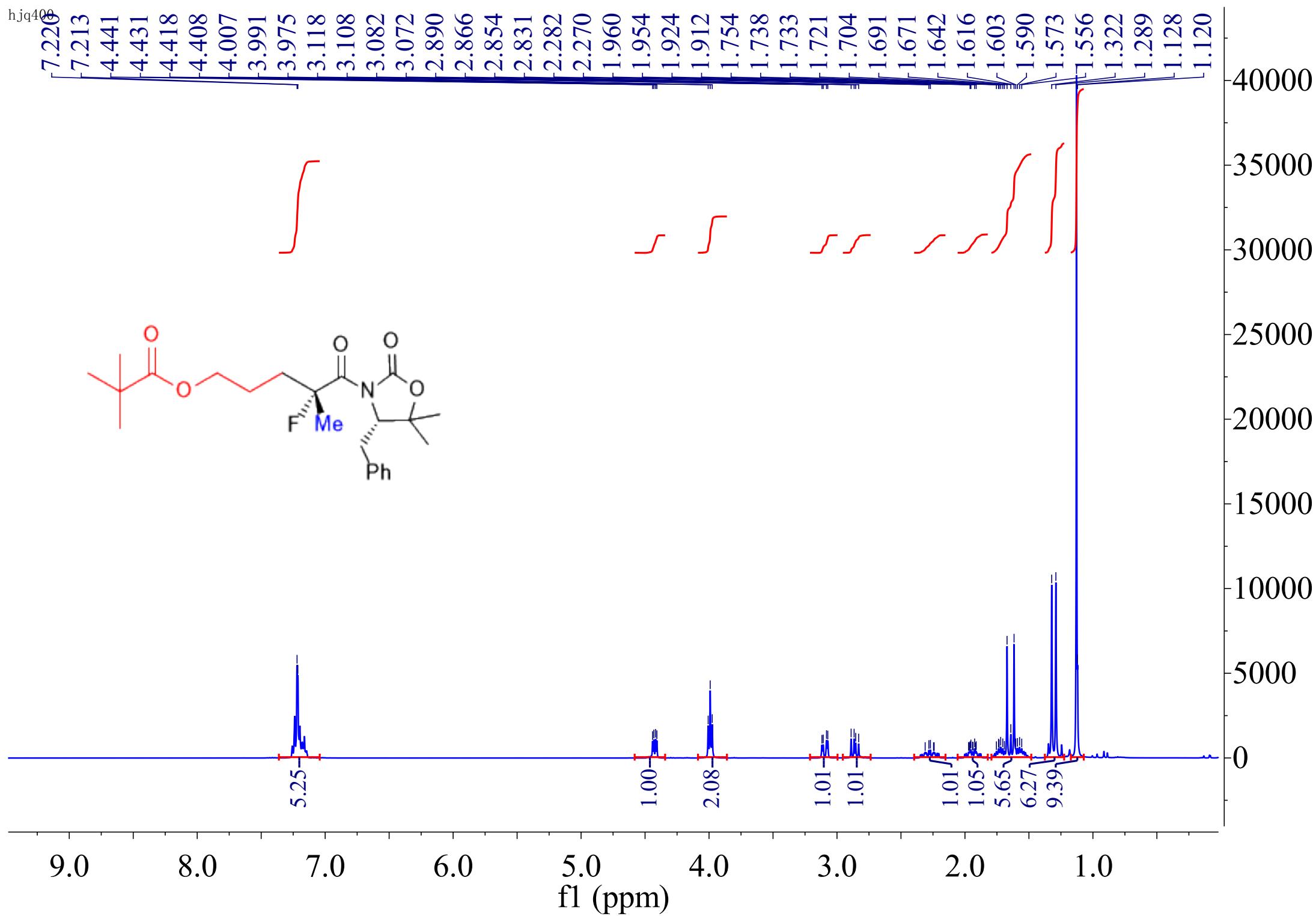
65.406  
62.947

35.158  
33.726  
33.502  
28.001  
26.868  
26.835  
22.532  
22.291  
22.170  
17.981  
11.944







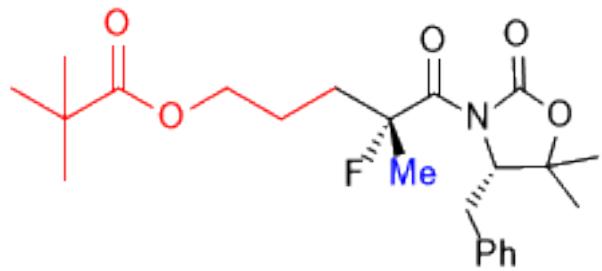


hjq400

✓178.413  
✓172.369  
✓172.103

-150.887

✓136.455  
✓129.091  
✓128.643  
✓126.890



✓98.181  
✓96.328

✓82.703  
✓77.318  
✓77.000  
✓76.683

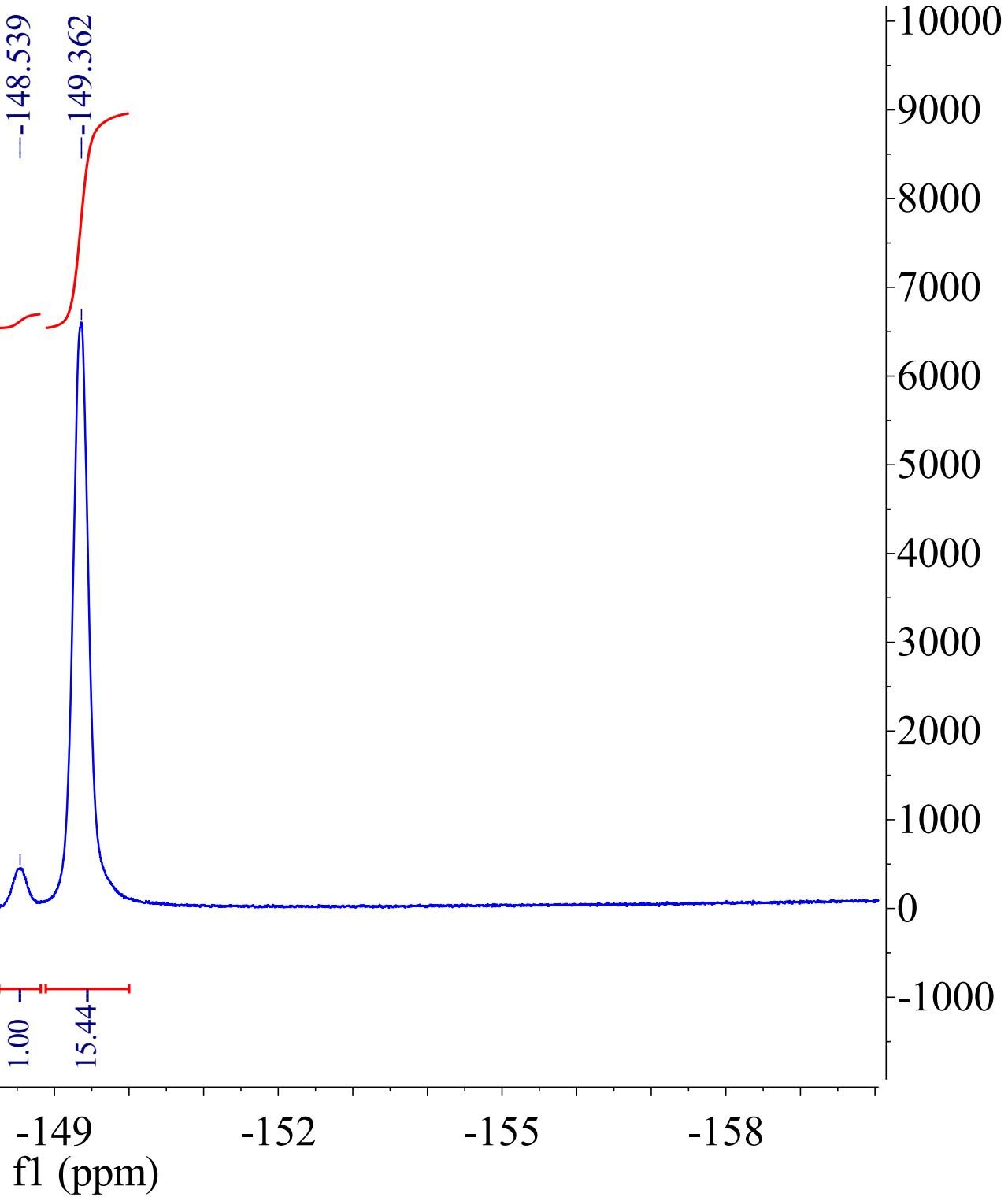
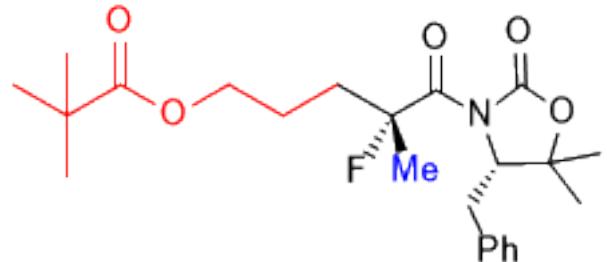
✓65.331  
✓63.694

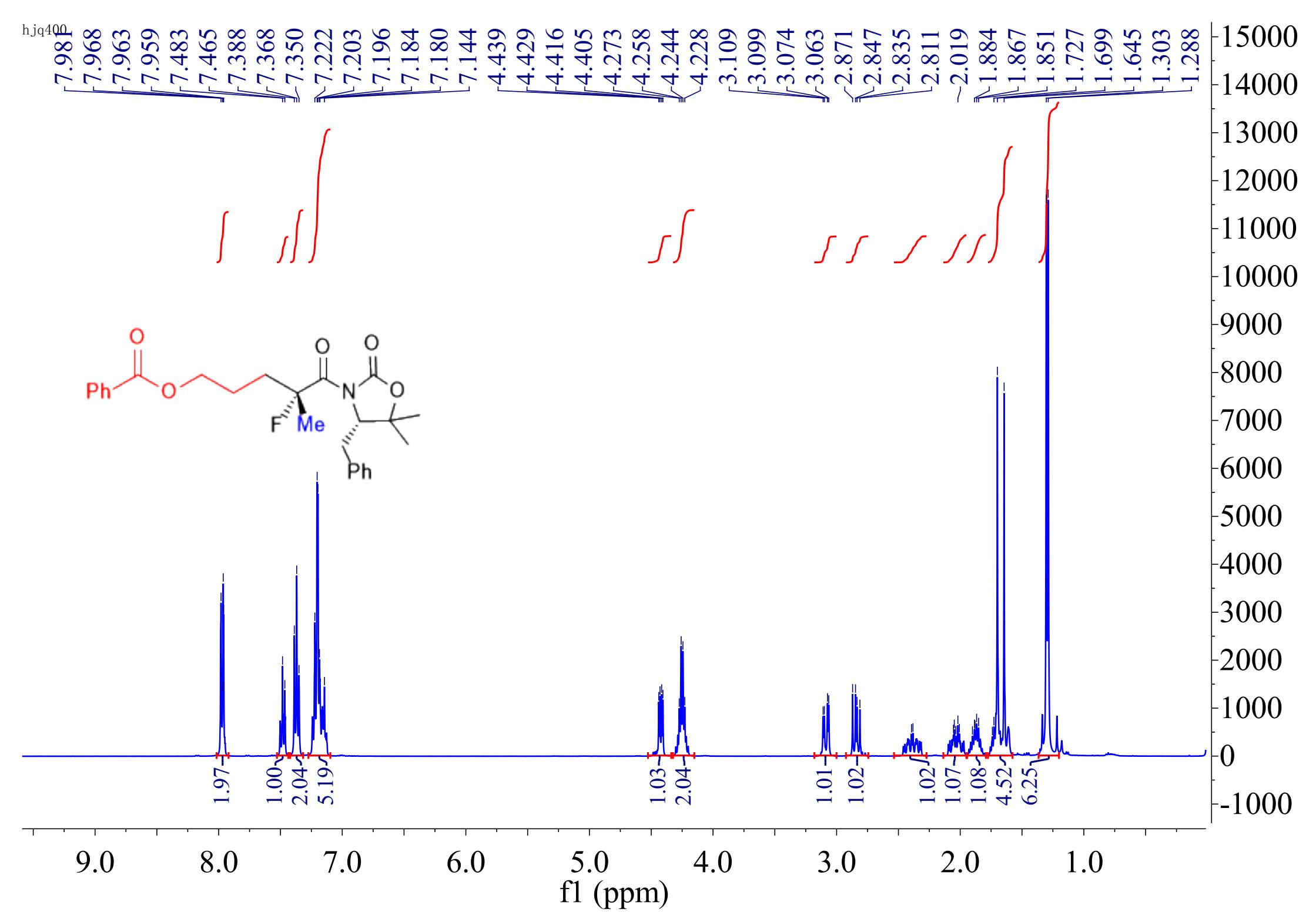
✓38.688  
✓35.103  
✓33.707  
✓33.481  
✓27.936  
✓27.129  
✓22.709  
✓22.671  
✓22.400  
✓22.160  
✓22.104

180 160 140 120 100 80 60 40 20

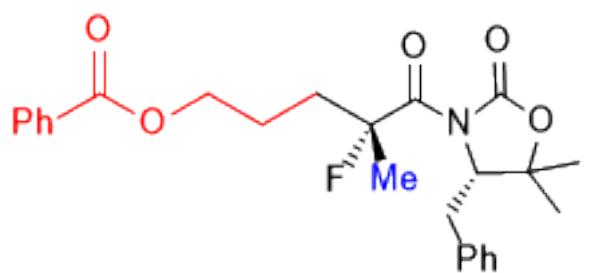
f1 (ppm)

22000  
21000  
20000  
19000  
18000  
17000  
16000  
15000  
14000  
13000  
12000  
11000  
10000  
9000  
8000  
7000  
6000  
5000  
4000  
3000  
2000  
1000  
0  
-1000  
-2000





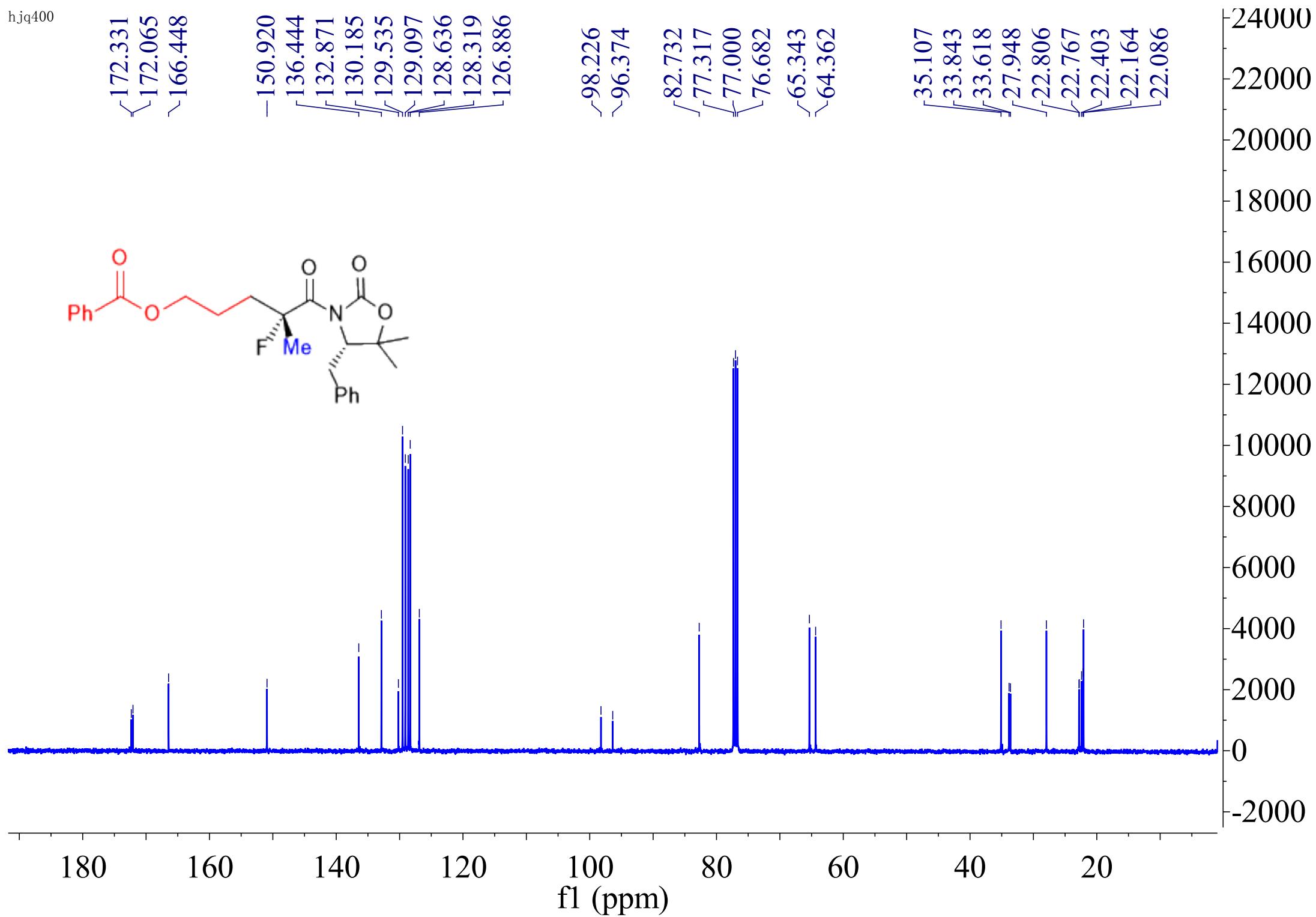
hjq400

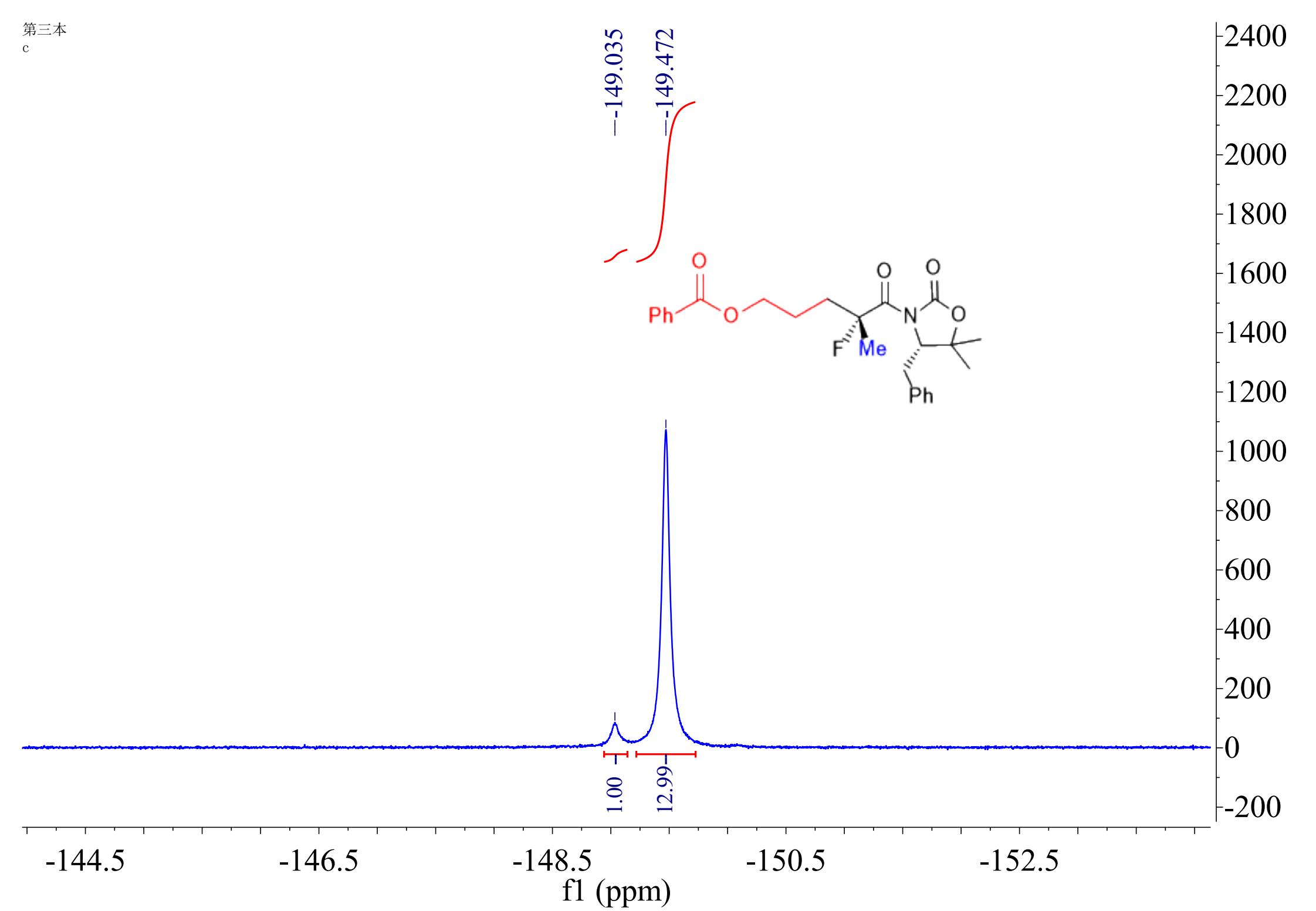


<172.331  
 172.065  
 \166.448  
 -150.920  
 136.444  
 132.871  
 130.185  
 129.535  
 129.097  
 128.636  
 128.319  
 126.886

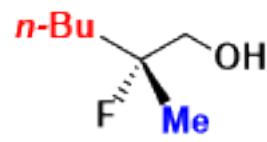
98.226  
 \96.374  
 82.732  
 77.317  
 77.000  
 76.682  
 65.343  
 \64.362

35.107  
 33.843  
 33.618  
 27.948  
 22.806  
 22.767  
 22.403  
 22.164  
 22.086

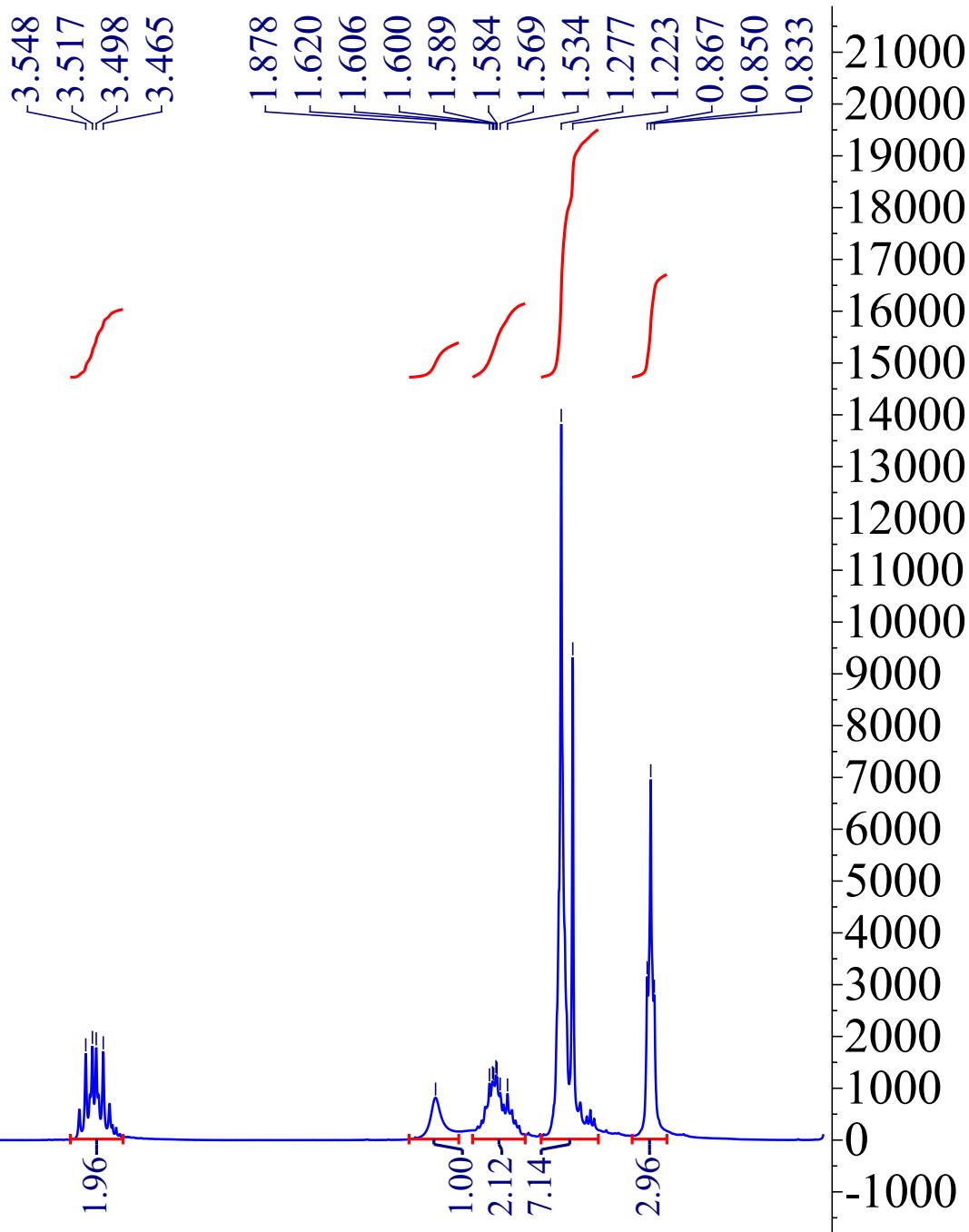


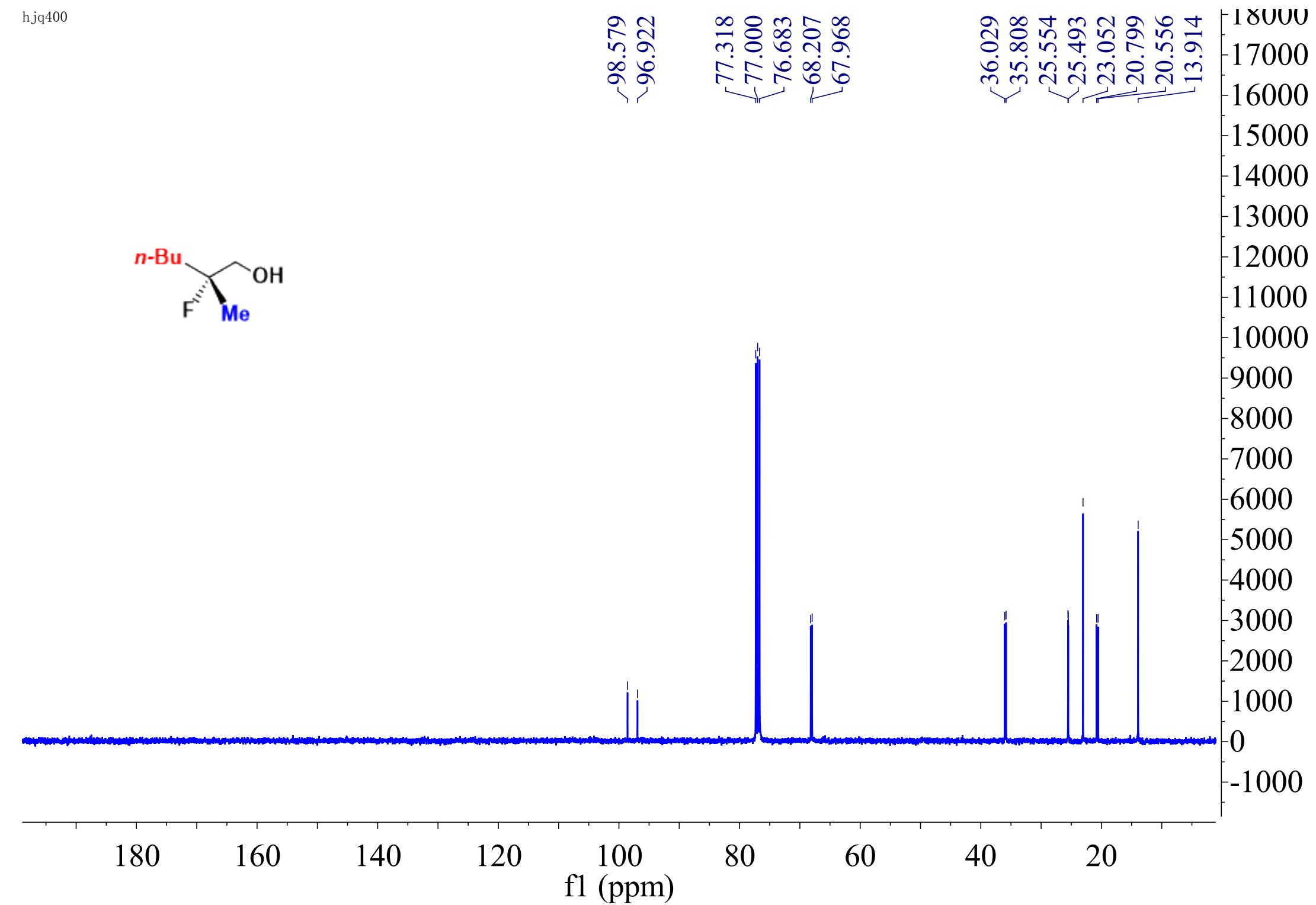
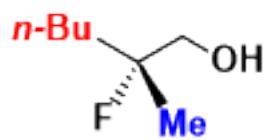


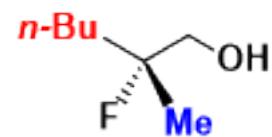
hjq400



f1 (ppm)

3.548  
3.517  
3.498  
3.4651.878  
1.620  
1.606  
1.600  
1.589  
1.584  
1.569  
1.534  
1.277  
1.22321000  
20000  
19000  
18000  
17000  
16000  
15000  
14000  
13000  
12000  
11000  
10000  
9000  
8000  
7000  
6000  
5000  
4000  
3000  
2000  
1000  
0  
-1000



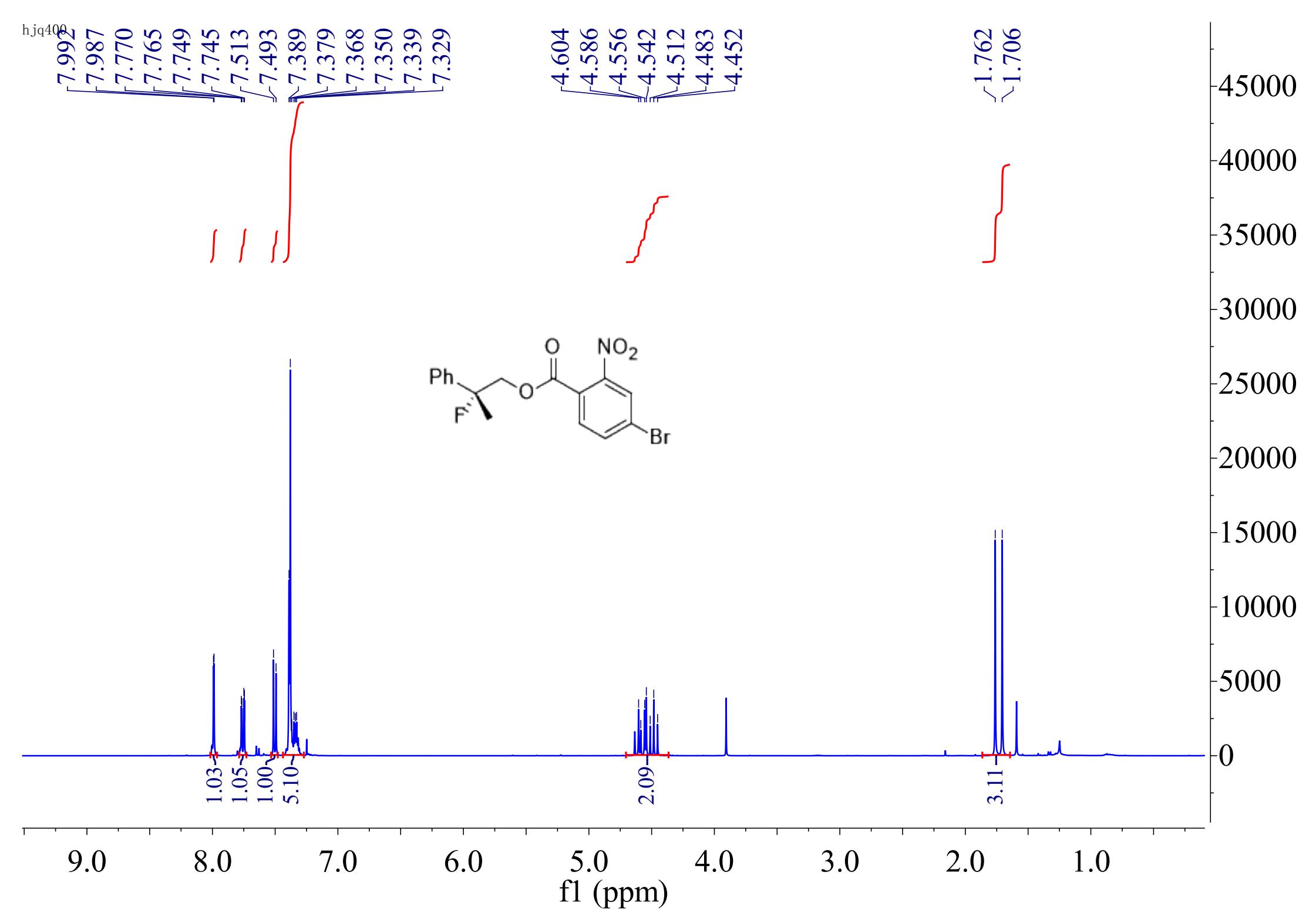


-154.708

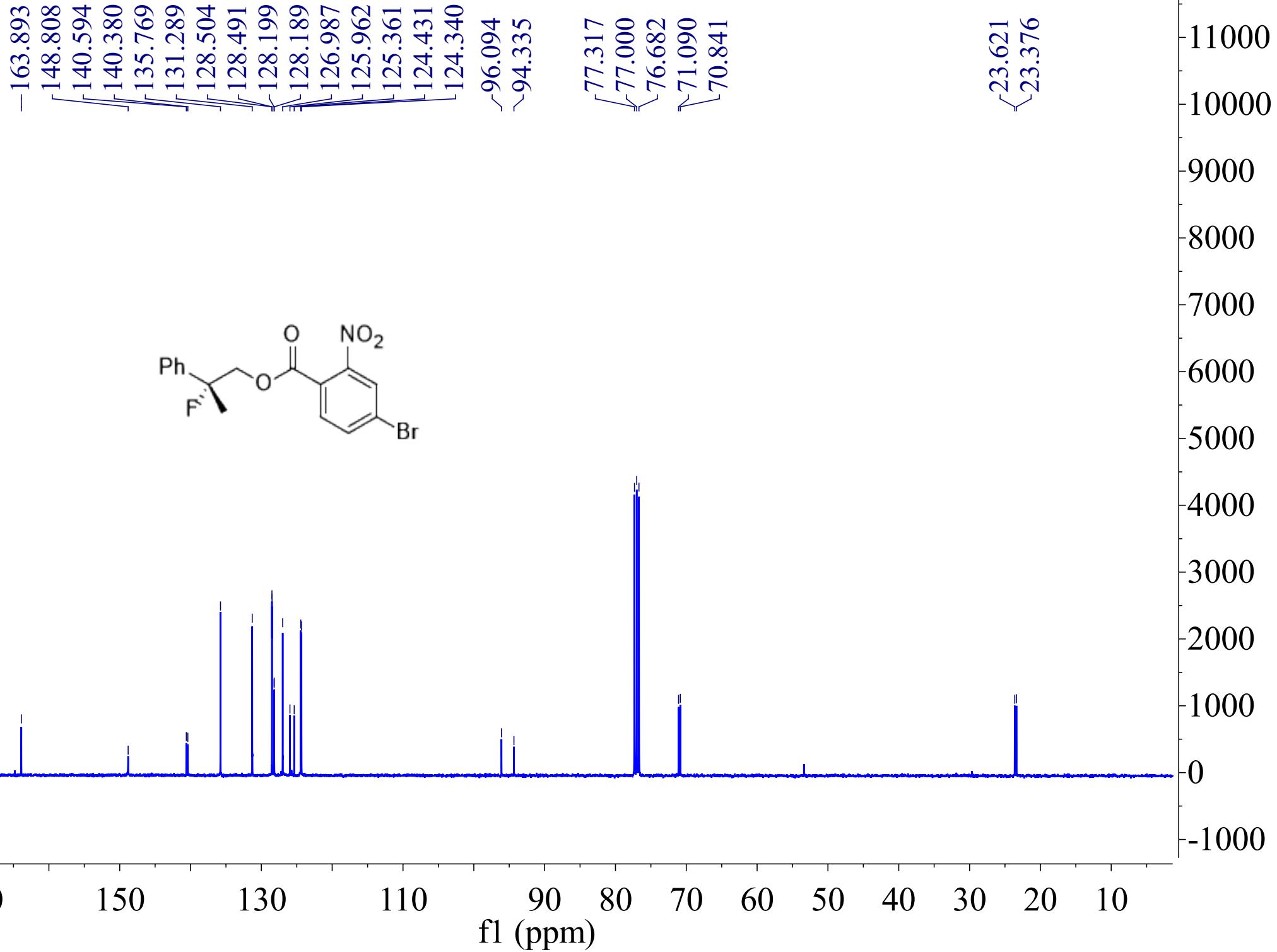
-40 -60 -80 -100 -120 -140 -160 -180 -200

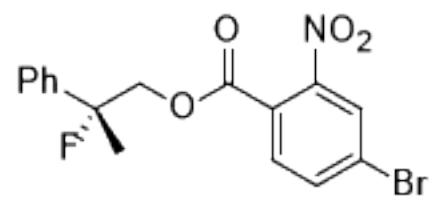
f1 (ppm)

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

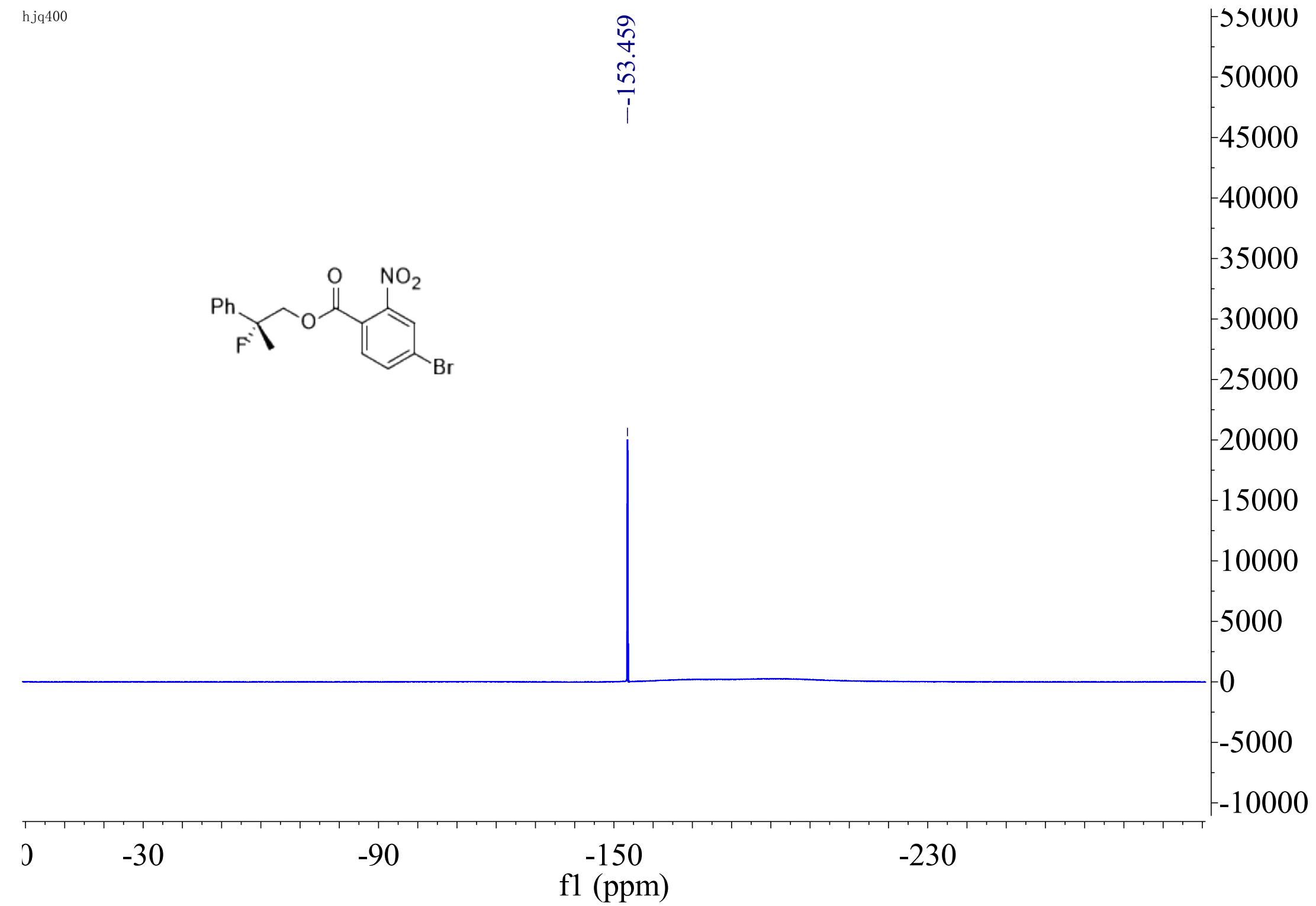


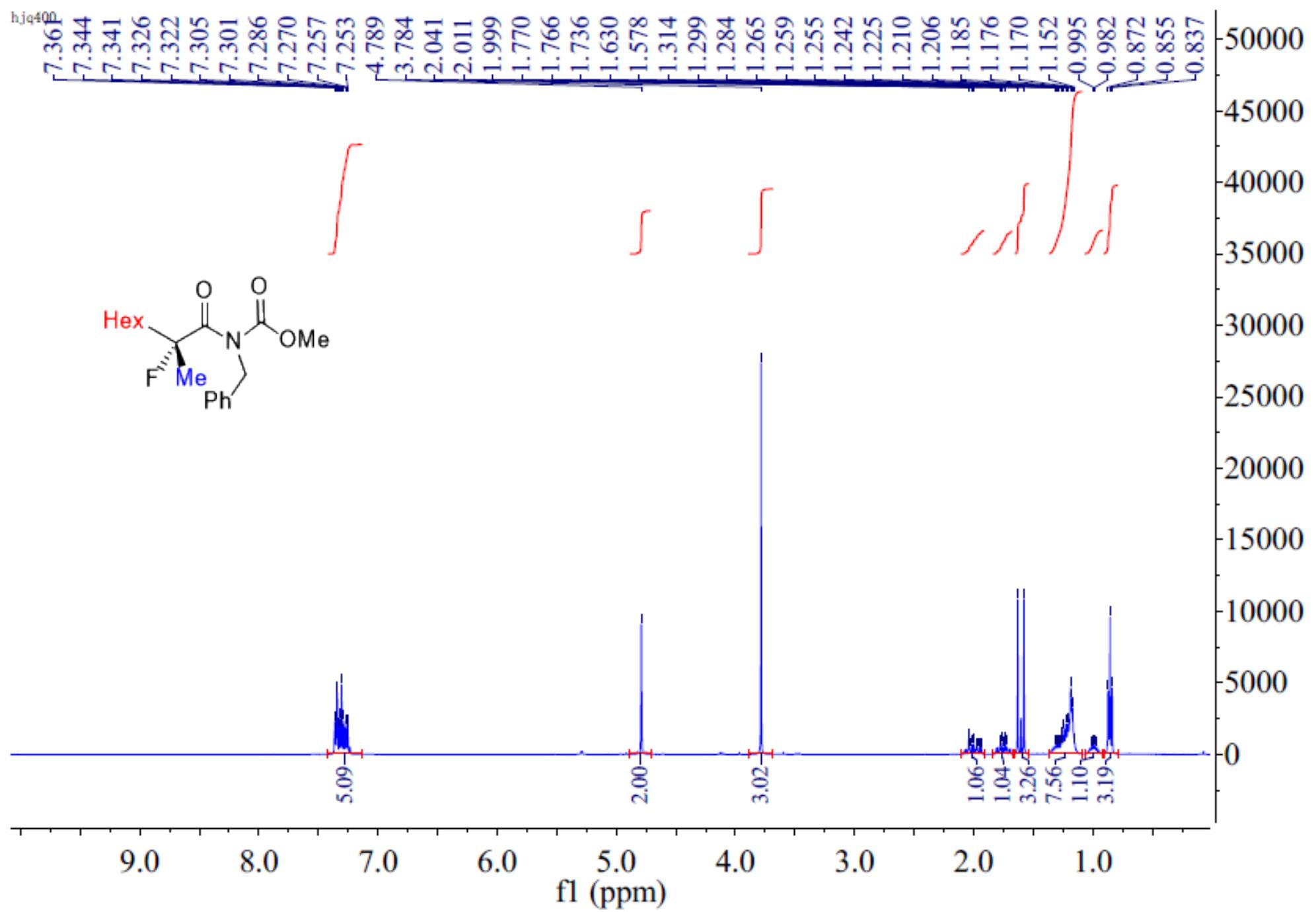
hjq400



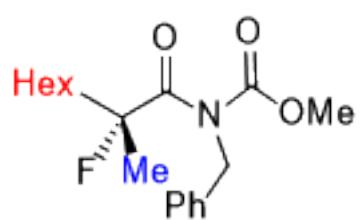


-153.459





hjq400



177.618  
177.370

-155.854

136.838  
128.414  
128.224  
127.619

100.142  
98.238

77.317  
77.000  
76.683

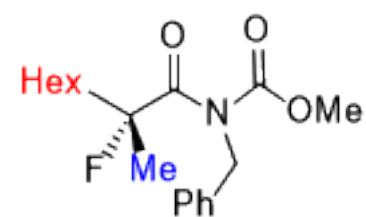
-53.903  
-50.019

39.964  
31.476  
29.143  
24.215  
23.985  
22.840  
22.805  
22.444  
14.003

180 160 140 120 100 80 60 40 20 0

f1 (ppm)

9000  
8000  
7000  
6000  
5000  
4000  
3000  
2000  
1000  
0  
-1000



-155.474

-95

-115

-140

-165

-190

f1 (ppm)

11000  
10000  
9000  
8000  
7000  
6000  
5000  
4000  
3000  
2000  
1000  
0  
-1000



Operator : SYSTEM

Location : 11

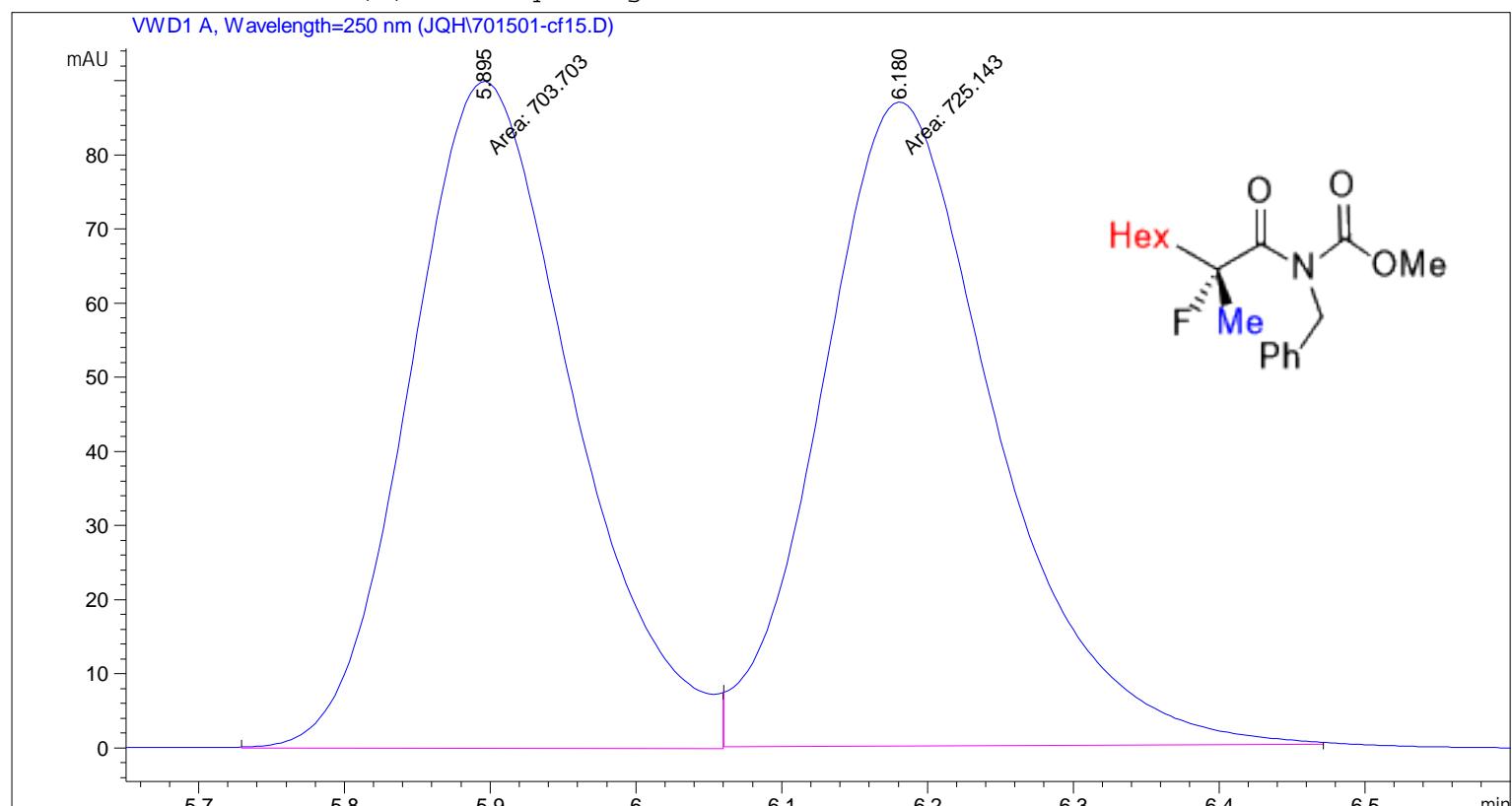
Injection Date : 2/26/2017 11:29:00 AM

Acq. Method : DEF\_LC.M

Analysis Method : C:\Chem32\1\Methods\DEF\_LC.M

Last changed : 9/6/2017 1:28:58 PM by SYSTEM  
(modified after loading)Sample Info : ad-h q1046 add  
99/1  
1

Additional Info : Peak(s) manually integrated

=====  
Area Percent Report  
=====

Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.895	MM	0.1303	703.70343	89.99191	49.2498
2	6.180	MM	0.1390	725.14276	86.97044	50.7502

Totals : 1428.84619 176.96235



Operator : SYSTEM

Location : 13

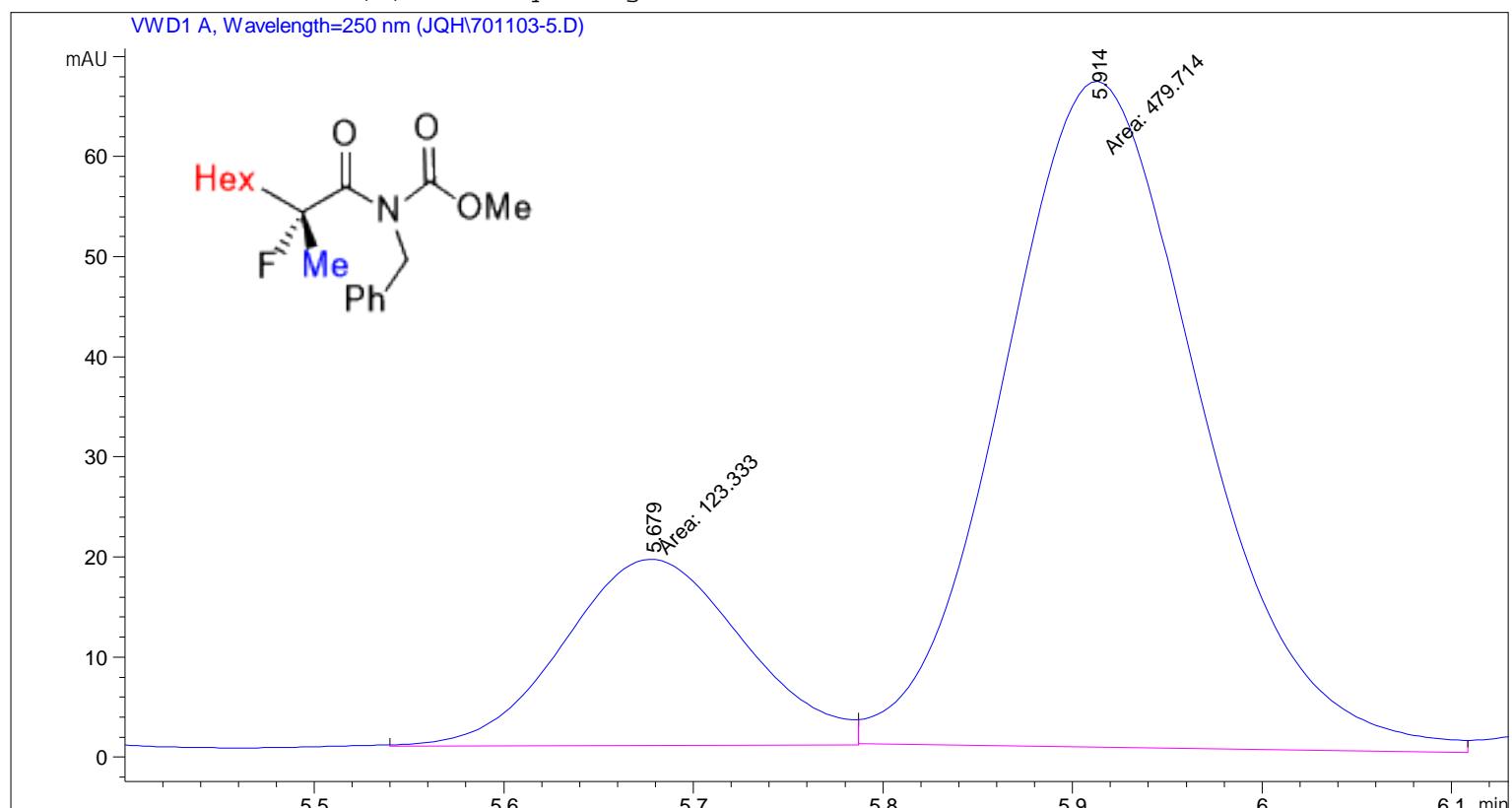
Injection Date : 1/8/2017 11:09:20 AM

Acq. Method : DEF\_LC.M

Analysis Method : C:\Chem32\1\Methods\DEF\_LC.M

Last changed : 9/6/2017 1:25:10 PM by SYSTEM  
(modified after loading)Sample Info : ad-h  
99  
1.0

Additional Info : Peak(s) manually integrated



## Area Percent Report

Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.679	MM	0.1104	123.33300	18.62747	20.4516
2	5.914	MM	0.1202	479.71408	66.49714	79.5484

Totals : 603.04708 85.12461