

**Domino [4+1]-Annulation of  $\alpha,\beta$ -Unsaturated  $\delta$ -Amino Esters with Rh(II)-Carbenoids -  
A New Approach towards Multi-Functionalized *N*-Aryl Pyrrolidines**

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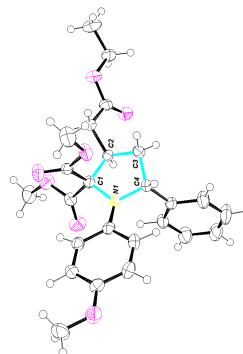
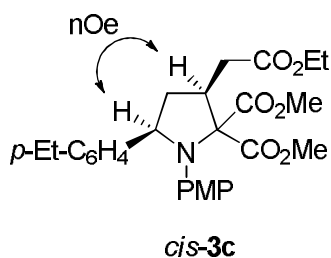
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## The structural and configurational assignment of pyrrolidines **3** and indolinone **6**.

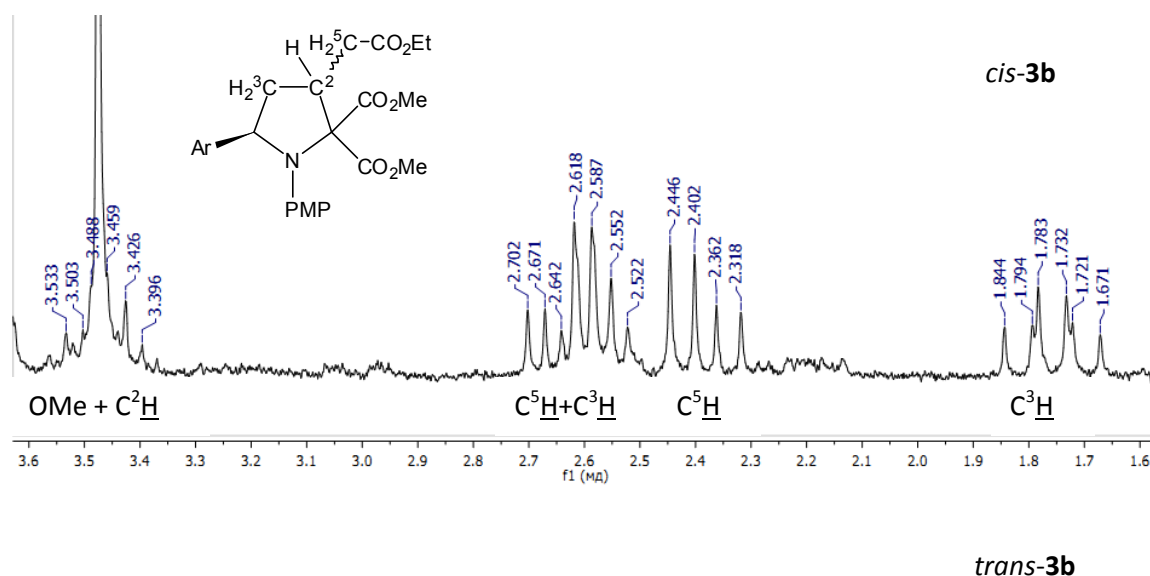
The relative configuration of the *cis*-isomer **3c** was established based on nOe experiments (Figure 2), the structure and configuration of the *trans*-pyrrolidine **3b** was confirmed by X-ray crystal structure analysis (Figure 3). The assignment of configuration of the other pyrrolidines **3** was made by comparison with and analogy of the related spectroscopic data of *cis*- or *trans*-stereoisomers of pyrrolidine **3b**.

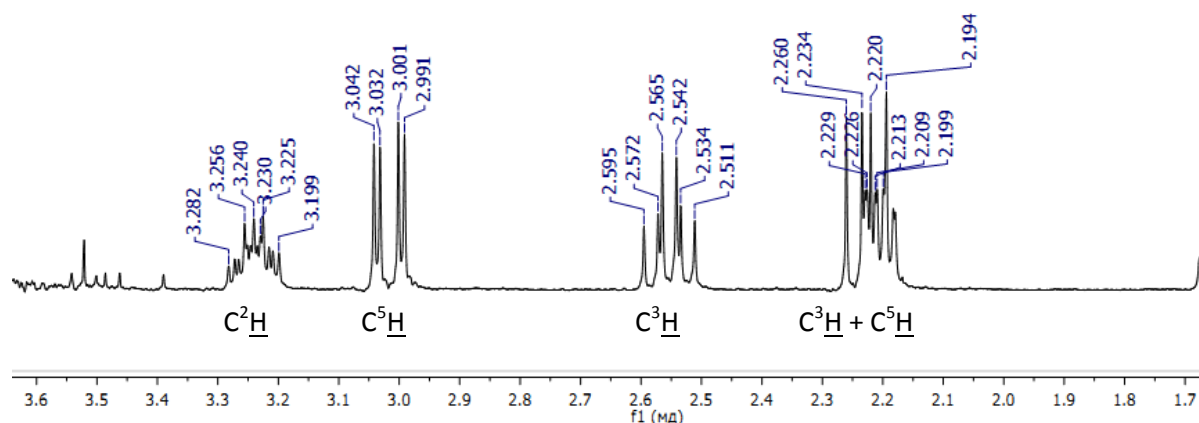


**Figure 2.** Configuration of the minor isomer *cis*-**3c** as revealed by NOESY experiments.

**Figure 3.** ORTEP-generated structure of the major isomer of pyrrolidine *trans*-**3b**.

In the case of *cis*-isomers the signals (doublet of triplets) of one of C<sup>3</sup>-protons are generally located in the area of 1.65-1.85 ppm, while in the spectra of *trans*-isomers the appropriate signals of the protons at C<sup>3</sup> are found at lower field (2.51-2.60 ppm;  $\Delta\delta \sim 0.8$  ppm) (Figure 5). A common feature is also the notable high field shift of the C<sup>2</sup>-protons on going from *cis*- to *trans*-isomers ( $\Delta\delta \sim 0.2$  ppm). In addition, the signals of  $\alpha$ -protons to N-atom of pyrrolidine ring (at  $\sim 5.0$  ppm) in the spectra of *trans*-isomers usually appear as a doublet ( $J \sim 9.0$  Hz), while in the case of *cis*-isomers they are recorded as a doublet of doublets ( $J \sim 10.0, 5.7$  Hz).

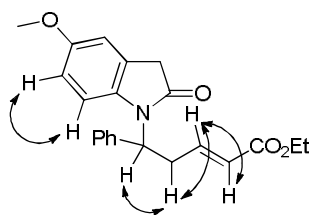




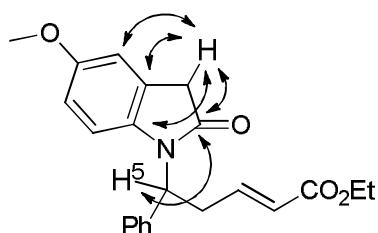
**Figure 5.** Representative splitting of alkyl proton signals in the  $^1\text{H}$  NMR spectra for *cis* - (top) and *trans*- (bottom) stereoisomers by the example of pyrrolidines **3b**.

In the  $^{13}\text{C}$  NMR spectra of *trans*-stereoisomers the signals of tertiary carbon atoms of pyrrolidine ring are usually observed in the area of 76 ppm, whereas in the case of *cis*-isomers they appear at 78 ppm ( $\Delta\delta \sim 2$  ppm). However, by and large the  $^{13}\text{C}$  NMR spectra were found to be less suitable for configurational assignments of pyrrolidines **3**.

In the  $^1\text{H}$  NMR spectra of compound **3i**, the same characteristic signals were observed as with pyrrolidines **3a-h** (Figure 5), among them: the signal of  $\alpha$ -proton to N-atom of heterocycle at  $\sim 5.0$  ppm and a set of signals in the area of 1.5-3.6 ppm related to the protons at  $\text{C}^3$  [2.50 ppm (*trans*) and 1.90 ppm (*cis*);  $\Delta\delta \sim 0.6$ ] as well as to protons at  $\text{C}^2$  [3.57 ppm (*trans*) and 3.08 ppm (*cis*),  $\Delta\delta \sim 0.6$ ]. The essential difference in the chemical shifts of both stereoisomers was also observed for the tertiary C-atom of pyrrolidine ring in the  $^{13}\text{C}$  NMR spectra [76.1 ppm for *trans*- and 86.1 ppm in the case of *cis*-isomer ( $\Delta\delta = 10$  ppm)].



**Figure 6.** Structure of **6** as revealed from  $^1\text{H}$ - $^1\text{H}$ -COSY



**Figure 7.** Structure of **6** as revealed from HMBC

The structure of compound **6** was assigned using a set of spectroscopic methods including in particular two-dimensional NMR-techniques such as  $^1\text{H}$ - $^1\text{H}$ -COSY and HMBC. Thus, correlation between proton  $\text{H}^5$  (5.69 ppm) and  $\text{C}^2$  (175.1 ppm), and correlation of  $\text{CH}_2$  group protons of indole ring (3.55 ppm) with carbon atoms of  $\text{C}=\text{O}$  group (175.1 ppm) and aromatic carbons of indole ring (at 112.1, 126.1, 136.6 ppm) in the HMBC-spectrum (Figures 6 and 7) enabled us to conclude that isolated compound had the structure of indoline-2-one **6**.

## The components of experimental section.

### I. Rhodium tetraacetate-catalyzed reaction of diazomalonate **2a** with aminoester **1a**. Preparation of pyrrolidines **3a**, **5a** and insertion product **4a**.

**Experiment 1.** Dimethyl diazomalonate **2a** (74 mg, 0.46 mmol, 1.1 eq) was added in one portion to a solution of amino ester **1a** (126 mg, 0.43 mmol, 1 eq) and 2 mg of Rh<sub>2</sub>(OAc)<sub>4</sub> in 2 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred overnight, then the solvent was removed *in vacuo*, the residue was separated by flash chromatography (25 g SiO<sub>2</sub>, mixture of Et<sub>2</sub>O and petroleum ether as eluents in gradient regime from 1:5 to 1:1) to afford 9 mg (7%) of starting amine **1a**, 91 mg (50%) of pyrrolidine **3a** as a mixture of *trans*- and *cis*-isomers in the 2.4:1 ratio, and 10 mg (5.5%) of insertion product **4a**. The mixture of isomers **3a** was subjected to preparative TLC to afford 30 mg of *trans*-**3a**, 18 mg of *cis*-**3a** and 36 mg of mixture of isomers.

**Experiment 2.** Dimethyl diazomalonate **2a** (230 mg, 1.46 mmol, 2 eq) was added dropwise during 30 min to a solution of amino ester **1a** (215 mg, 0.73 mmol, 1 eq) and 4 mg of Rh<sub>2</sub>(OAc)<sub>4</sub> in 4 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred overnight, then the solvent was removed *in vacuo* and residue was separated by flash chromatography (40 g SiO<sub>2</sub>, mixture of Et<sub>2</sub>O and petroleum ether as eluents in gradient regime from 1:5 to 2:1) to furnish 80 mg (26%) of pyrrolidine **3a** as a mixture of *trans*- and *cis*-isomers in the 1.5:1 ratio, and 140 mg (35%) of pyrrolidine *trans*-**5a**. The ensuing separation of the mixture of isomers **3a** using preparative TLC gave rise to 25 mg of *trans*-**3a**, 8 mg of *cis*-**3a** and 43 mg of mixture of isomers.

**Experiment 3.** Dimethyl diazomalonate **2a** (477 mg, 3.0 mmol, 4 eq) was added in one portion to a solution of amino ester **1a** (223 mg, 0.76 mmol, 1 eq) and 6 mg of Rh<sub>2</sub>(OAc)<sub>4</sub> in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred overnight then the solvent was removed *in vacuo* and residue was separated by flash chromatography (40 g SiO<sub>2</sub>, mixture of Et<sub>2</sub>O and petroleum ether as eluents in gradient regime from 1:5 to 2:1) to give 200 mg (47%) of pyrrolidine **5a** as a mixture of *trans*- and *cis*- isomers in the 9:1 ratio.

### II. Rh(II)-Catalyzed decomposition of diazomalonates **2a** and **2b** in the presence of aminoesters **1b-h**. Preparation of pyrrolidines **3b-h**.

**Pyrrolidine 3b.** a) Catalytic decomposition of diazomalonate **2a** (178 mg, 1.13 mmol, 2 eq) at r.t. for 15 h in the presence of amino ester **1b** (174 mg, 0.56 mmol, 1 eq) in 3 ml of DCM with 3 mg (0.6 mol-%) of Rh<sub>2</sub>(OAc)<sub>4</sub> gave rise to pyrrolidine **3b** in the yield of 169 mg (69%) as a mixture of *trans*- and *cis*- isomers in the 3:1 ratio. After preparative TLC 40 mg of *trans*-**3b**, 4 mg of *cis*-**3b** and 100 mg of mixture of isomers were isolated.

b) Catalytic decomposition of diazomalonate **2a** (79 mg, 0.5 mmol, 2 eq) at r.t. for 1.5 h in the presence of amino ester **1b** (81 mg, 0.25 mmol, 1 eq) in 5 ml of DCM with 4.5 mg (2 mol-%) of Rh<sub>2</sub>(OAc)<sub>4</sub> furnished pyrrolidine **3b** in the yield of 74 mg (65%) as a mixture of *trans*- and *cis*-isomers in the ratio 1.8:1. The succeeding preparative TLC provided 10 mg of *trans*-**3b**, 3 mg of *cis*-**3b** and 51 mg of mixture of isomers.

c) Catalytic decomposition of diazomalonate **2a** (63 mg, 0.4 mmol, 2 eq) at r.t. for 2 h in the presence of amino ester **1b** (65 mg, 0.2 mmol, 1 eq) in 5 ml of DCM with 6 mg (2 mol-%) of Rh<sub>2</sub>(Oct)<sub>4</sub> gave rise to pyrrolidine **3b** in the yield of 62 mg (68%) as a mixture of *trans*- and *cis*-isomers in the 1.7:1 ratio. The subsequent preparative TLC of this mixture afforded 7 mg of *trans*-**3b**, 2 mg of *cis*-**3b** and 43 mg of mixture of isomers.

**Pyrrolidine 3b'.** Catalytic decomposition of diazomalonate **2b** (88 mg, 0.47 mmol, 2 eq) at r.t. for 16 h in the presence of amino ester **1b** (77 mg, 0.24 mmol, 1 eq) in 3 ml of DCM with 2 mg



(1 mol-%) of  $\text{Rh}_2(\text{OAc})_4$  furnished pyrrolidine **3b'** in the yield of 81 mg (70%) as a mixture of *trans*- and *cis*- isomers in the ratio 1.2:1. The ensuing preparative TLC afforded 25 mg of *trans*-**3b**, 19 mg of *cis*-**3b** and 32 mg of inseparated mixture of isomers.

**Pyrrolidine 3c** (*Experiment with  $\text{Rh}_2(\text{OAc})_4$* ). Catalytic decomposition of diazomalonate **2a** (79 mg, 0.5 mmol, 2.5 eq) at r.t. for 5 h in the presence of amino ester **1c** (71 mg, 0.2 mmol, 1 eq) in 5 ml of DCM with 4.5 mg (2 mol-%) of  $\text{Rh}_2(\text{OAc})_4$  gave rise to pyrrolidine **3c** in the yield of 70 mg (72%) as a mixture of *trans*- and *cis*- isomers in the ratio 1.5:1. After preparative TLC of this mixture, 22 mg of *trans*-**3c**, 12 mg of *cis*-**3c** and 30 mg of mixture of isomers were obtained.

**Pyrrolidine 3c** (*Experiment with  $\text{Rh}_2(\text{Oct})_4$* ). Catalytic decomposition of diazomalonate **2a** (63 mg, 0.4 mmol, 2.5 eq) at r.t. for 2 h in the presence of aminoester **1c** (71 mg, 0.2 mmol, 1 eq) in 5 ml of DCM with 6 mg (2 mol-%) of  $\text{Rh}_2(\text{Oct})_4$  provided pyrrolidine **3c** in the yield of 79 mg (82%) as a mixture of *trans*- and *cis*- isomers in the 1.7:1 ratio. The subsequent preparative TLC afforded 26 mg of *trans*-**3c**, 14 mg of *cis*-**3c** and 32 mg of mixture of isomers.

**Pyrrolidine 3d**. Catalytic decomposition of diazomalonate **2a** (55 mg, 0.35 mmol, 2 eq) at r.t. for 2 h in the presence of amino ester **1d** (65 mg, 0.17 mmol, 1 eq) in 5 ml of DCM with 6 mg (2 mol-%) of  $\text{Rh}_2(\text{Oct})_4$  gave rise to pyrrolidine **3d** in the yield of 68 mg (79%) as a mixture of *trans*- and *cis*- isomers in the 1.8:1 ratio. After preparative TLC, 27 mg of *trans*-**3d**, 17 mg of *cis*-**3d** and 24 mg of mixture of isomers were isolated.

**Pyrrolidine 3e**. Catalytic decomposition of diazomalonate **2a** (95 mg, 0.6 mmol, 2 eq) at r.t. for 18 h in the presence of amino ester **1e** (114 mg, 0.3 mmol, 1 eq) in 5 ml of DCM with 9 mg (2 mol-%) of  $\text{Rh}_2(\text{Oct})_4$  produced pyrrolidine **3e** in the yield of 95 mg (79%) as a mixture of *trans*- and *cis*- isomers in the ratio 2.1:1. The succeeding preparative TLC afforded 30 mg of *trans*-**3e**, 4 mg of *cis*-**3e** and 56 mg of mixture of isomers.

**Pyrrolidine 3f**. Catalytic decomposition of diazomalonate **2a** (95 mg, 0.6 mmol, 2 eq) at r.t. for 17 h in the presence of amino ester **1f** (102 mg, 0.3 mmol, 1 eq) in 5 ml of DCM with 9 mg (2 mol-%) of  $\text{Rh}_2(\text{Oct})_4$  provided pyrrolidine **3f** in the yield of 108 mg (76%) as a mixture of *trans*- and *cis*-isomers in the ratio 2.4:1. After preparative TLC, 26 mg of *trans*-**3f**, 3 mg of *cis*-**3f** and 71 mg of mixture of isomers were obtained.

**Pyrrolidine 3g**. Catalytic decomposition of **2a** (95 mg, 0.6 mmol, 2 eq) at r.t. for 4 h in the presence of amino ester **1g** (108 mg, 0.3 mmol, 1 eq) in 5 ml of DCM with 9 mg (2 mol-%) of  $\text{Rh}_2(\text{Oct})_4$  furnished pyrrolidine **3g** in the yield of 110 mg (75%) as a mixture of *trans*- and *cis*-isomers in the 1.8:1 ratio. The succeeding preparative TLC afforded 20 mg of *trans*-**3g**, 6 mg of *cis*-**3g** and 79 mg of inseparated mixture of isomers.

**Pyrrolidine 3h**. Catalytic decomposition of diazomalonate **2a** (95 mg, 0.6 mmol, 2 eq) at r.t. for 23 h in presence of amino ester **1h** (105 mg, 0.3 mmol, 1 eq) in 5 ml of DCM with 9 mg (2 mol-%) of  $\text{Rh}_2(\text{Oct})_4$  gave rise to pyrrolidine **3h** in yield of 60 mg (42%) as a mixture of *trans*- and *cis*-isomers in a 2.4:1 ratio. After preparative TLC, 16 mg of *trans*-**3h**, 7 mg of *cis*-**3h** and 32 mg of mixture of isomers were isolated.

### III. Cu(II)-Catalyzed decomposition of diazomalonate **2a** in the presence of amino ester **1b**. Preparation of pyrrolidines **3b**.

Diazomalonate **2a** (0.4-0.75 mmol) in 1 ml of benzene was added in one portion to solution of amino ester **1b** (0.2-0.25 mmol) in benzene (2-4 ml) with 5-10 mol % of Cu(II)-catalyst. Reaction mixture was refluxed until disappearance of starting amino ester (3–7.5 h, monitoring by TLC). Then, the solvent was removed *in vacuo* and residue was purified by flash

chromatography (silica gel, eluent hexane / Et<sub>2</sub>O, 10:1 → 1:1) to afford pyrrolidine **3b** as a mixture of *trans*- and *cis*- isomers which was separated using preparative TLC.

**Experiment with Cu(OAc)<sub>2</sub>.** Catalytic decomposition of diazomalonate **2a** (63 mg, 0.4 mmol, 2 eq) at 80 °C for 7.5 h in the presence of aminoester **1b** (65 mg, 0.2 mmol, 1 eq) with 7 mg of Cu(OAc)<sub>2</sub> (10 mol%) in 5 ml of benzene provided pyrrolidine **3b** in the yield of 19 mg (21%) as a mixture of *trans*- and *cis*- isomers in the 1:1 ratio.

**Experiment with Cu(hfacac)<sub>2</sub>.** Catalytic decomposition of diazomalonate **2a** (57 mg, 0.36 mmol, 2.4 eq) at 80 °C for 3 h in the presence of amino ester **1b** (49 mg, 0.2 mmol, 1 eq) with 7 mg of Cu(hfAcAc)<sub>2</sub> (5 mol%) in 3 ml of benzene gave rise to pyrrolidine **3b** in the yield of 35 mg (51%) as a mixture of *trans*- and *cis*- isomers in the ratio 1:1.

**Experiment with Cu(OTf)<sub>2</sub>.** Catalytic decomposition of diazomalonate **2a** (79 mg, 0.75 mmol, 3 eq) at 80 °C for 3 h in the presence of amino ester **1b** (81 mg, 0.25 mmol, 1 eq) with 18 mg of Cu(OTf)<sub>2</sub> (6.5 mol%) in 5 ml of benzene furnished pyrrolidine **3b** in the yield of 56 mg (49%) as a mixture of *trans*- and *cis*- isomers in the 1.9:1 ratio.

#### IV. Attempts to carry out catalytic decomposition of diazomalonate **2a** using Cu(II), Fe(III) and Ru(II)-complexes in presence of amino ester **1b**.

**Experiment with Cu(OAc)<sub>2</sub>.** Diazomalonate **2a** (32 mg, 0.2 mmol, 2 eq) in 1 ml of DCM was added in one portion to a solution of amino ester **1b** (32.5 mg, 0.1 mmol, 1 eq) in 4 ml of DCM with 2 mg of Cu(OAc)<sub>2</sub> (5 mol%) and reaction mixture was stirred at r.t. for 2 h but according to TLC no reaction took place.

**Experiment with Cu(AcAc)<sub>2</sub>.** Diazomalonate **2a** (57 mg, 0.36 mmol, 2.4 eq) in 1 ml of benzene was added in one portion to a solution of amino ester **1b** (49 mg, 0.2 mmol, 1 eq) in 2 ml of benzene with 5 mg of Cu(AcAc)<sub>2</sub> (5 mol%) and reaction mixture was refluxed for 3 h but no significant changes in it were observed.

**Experiment with Fe(acac)<sub>3</sub>.** Diazomalonate **2a** (94.8 mg, 0.3 mmol, 2 eq) in 1 ml of trifluorotoluene was added in one portion to a solution of amino ester **1b** (97.5 mg, 0.3 mmol, 1 eq) in 2 ml of trifluorotoluene with 11 mg of Fe(AcAc)<sub>3</sub> (5 mol%) and reaction mixture was refluxed for 5 h but according to TLC no notable changes were observed.

**Experiment with [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>.** Diazomalonate **2a** (32 mg, 0.2 mmol, 2 eq) in 1 ml of DCM was added in one portion to a solution of amino ester **1b** (65 mg, 0.2 mmol, 1 eq) in 2 ml of DCM with 3 mg of [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (2 mol%) and reaction mixture was stirred for 8 h but according to TLC no reaction took place.

#### V. Rh(II)-Catalyzed decomposition of Diazo Meldrum's acid **2c** in the presence of amino ester **1b**. Preparation of pyrrolidines **3i** and indolineone **6**.

a) Catalytic decomposition of diazo Meldrum's acid **1c** (204 mg, 1.2 mmol, 4 eq) at 80 °C for 7.5 h in presence of amino ester **1b** (97.5 mg, 0.3 mmol, 1 eq) with 11 mg (2 mol%) of Rh<sub>2</sub>(OAc)<sub>4</sub> in 5 ml of benzene gave rise to pyrrolidine **3i** in the yield of 18 mg (13%) as a mixture of *trans*- and *cis*- isomers and indoline-2-one **6** in the yield of 15 mg (14%).

b) Catalytic decomposition of diazo Meldrum's acid **1c** (111 mg, 0.67 mmol, 2 eq) at 80 °C for 7.5 h in presence of amino ester **1b** (111.5 mg, 0.33 mmol, 1 eq) with 2 mg (0.7 mol%) of Rh<sub>2</sub>(OAc)<sub>4</sub> in 4 ml of benzene gave rise to pyrrolidine **3i** in the yield of 55 mg (35%) of as a mixture of *trans*- and *cis*- isomers and indoline-2-one **6** in the yield of 17 mg (14%).

c) Catalytic decomposition of diazo Meldrum's acid **1c** (153 mg, 0.9 mmol, 2 eq) at 80 °C for 7.5 h in presence of amino ester **1b** (146 mg, 0.45 mmol, 1 eq) with 14 mg (2 mol%) of Rh<sub>2</sub>(Oct)<sub>4</sub> in 10 ml of benzene gave rise to pyrrolidine **3i** in the yield of 71 mg (34%) of as a mixture of *trans*- and *cis*- isomers and indoline-2-one **6** in the yield of 51 mg (31%).

The combined mixtures of isomers **3i** from experiments a)-c) were subjected to preparative TLC to afford 35 mg of *trans*-**3i**, 21 mg of *cis*-**3i** and a quantity of the isomer mixture.

## VI. Rh(II)-Catalyzed reactions of diazoacetates **2d** and **2e** with amino ester **1b**.

a) Diazoacetate **2d** (102 mg, 1 mmol) was added in one portion to a solution of amino ester **1b** (82 mg, 0.25 mmol) in 2 ml of DCM with 0.9 mol% of Rh<sub>2</sub>(OAc)<sub>4</sub>, reaction mixture was stirred at -25 °C for 10 h to afford after standard work-up procedure starting amino ester **1b** (34 mg, 41%), N-H insertion product **8** (22 mg, 38%) and dimethyl fumarate **9** (14 mg, 10%).

b) Diazoacetate **2d** (124 mg, 1.24 mmol) was added dropwise during 2 h to a solution of amino ester **1b** (101 mg, 0.31 mmol) in 2 ml of DCM with 0.8 mol% of Rh<sub>2</sub>(OAc)<sub>4</sub>, reaction mixture was stirred at -10 °C for 22 h to afford after standard work-up procedure starting amino ester **1b** (70 mg, 69%), N-H insertion product **8** (10 mg, 29%) and mixture of dimethyl fumarate and maleate **9** (33 mg, 19%).

c) Diazoacetate **2d** (128 mg, 1.28 mmol) was added dropwise during 2 h to a solution of amino ester **1b** (104 mg, 0.32 mmol) in 15 ml of DCM with 0.7 mol% of Rh<sub>2</sub>(OAc)<sub>4</sub>, reaction mixture was stirred at -0 °C for 3 days to afford after standard work-up procedure starting amino ester **1b** (39 mg, 38%), N-H insertion product **8** (22 mg, 29%) and mixture of dimethyl fumarate and maleate **9** (11 mg, 6%).

d) Diazoacetate **2e** (869 mg, 4.92 mmol) in 4 ml of DCM was added by using syringe pump (1.0 ml/h) during 4 h to a solution of amino ester **1b** (200 mg, 0.62 mmol) in 4 ml of DCM with 1 mol% of Rh<sub>2</sub>(OAc)<sub>4</sub>, Additional 1 mol% of catalyst was added every hour (total 4 mol% of Rh(II)-catalyst). Reaction mixture was stirred at -0 °C for 4h to afford after standard work-up procedure pyrrolidine **7** (135 mg, 53%).

7.35  
7.32  
7.29  
7.27  
7.26  
7.24  
7.12  
7.08  
6.92  
6.88  
6.84  
6.81  
6.50  
6.46

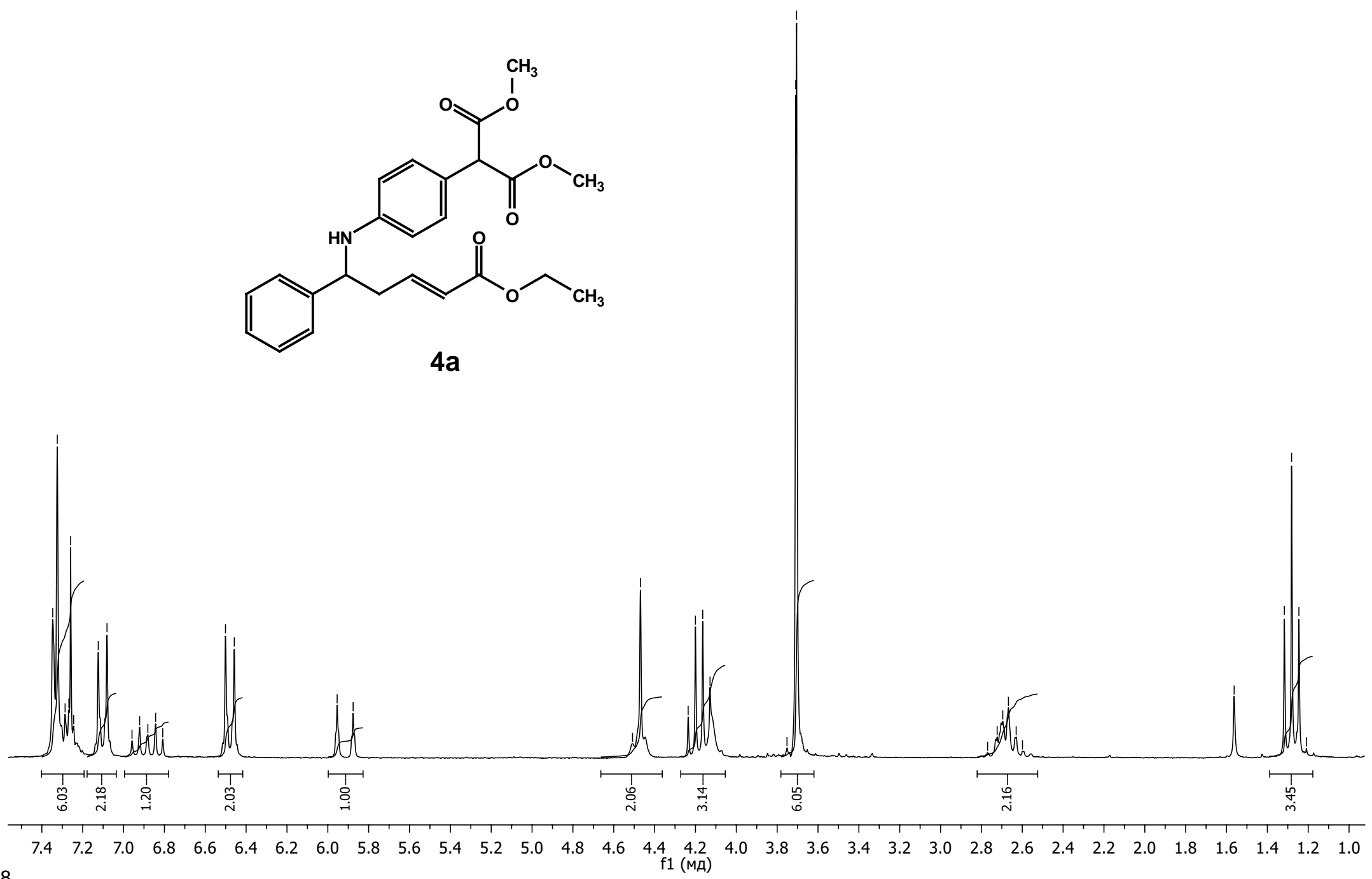
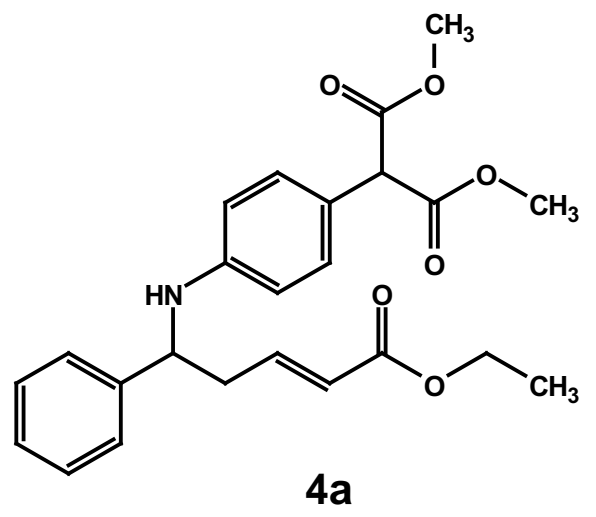
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5.88

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4.16  
4.13

3.75  
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2.77  
2.72  
2.70  
2.67  
2.63  
2.60

1.56  
1.32  
1.28  
1.25  
1.21



— 169.19  
— 166.08

— 146.93  
— 144.31  
— 142.57

— 130.14  
— 128.99  
— 127.62  
— 126.34  
— 124.52  
— 121.56

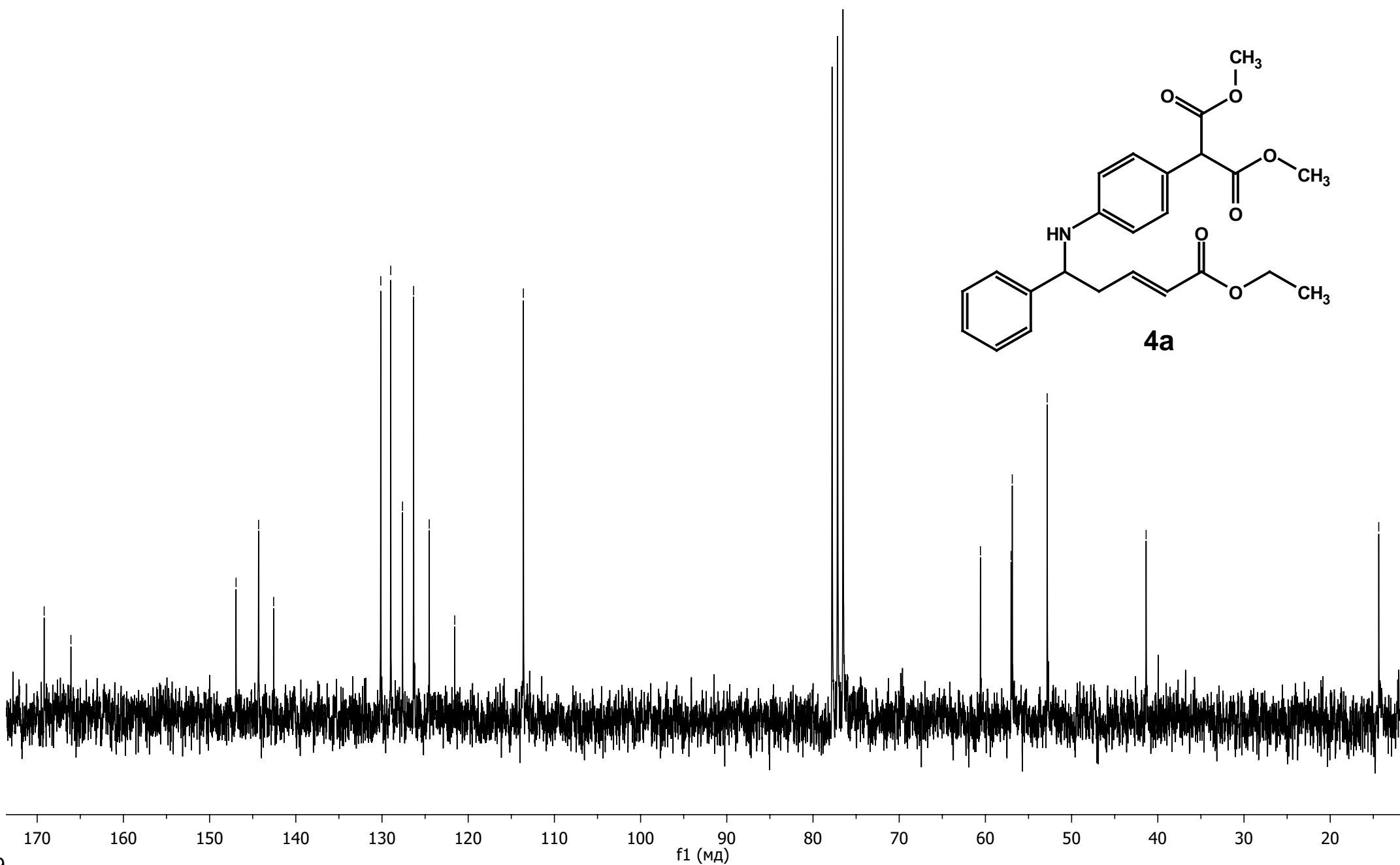
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— 57.02  
— 56.88

— 52.83

— 41.36

— 14.37



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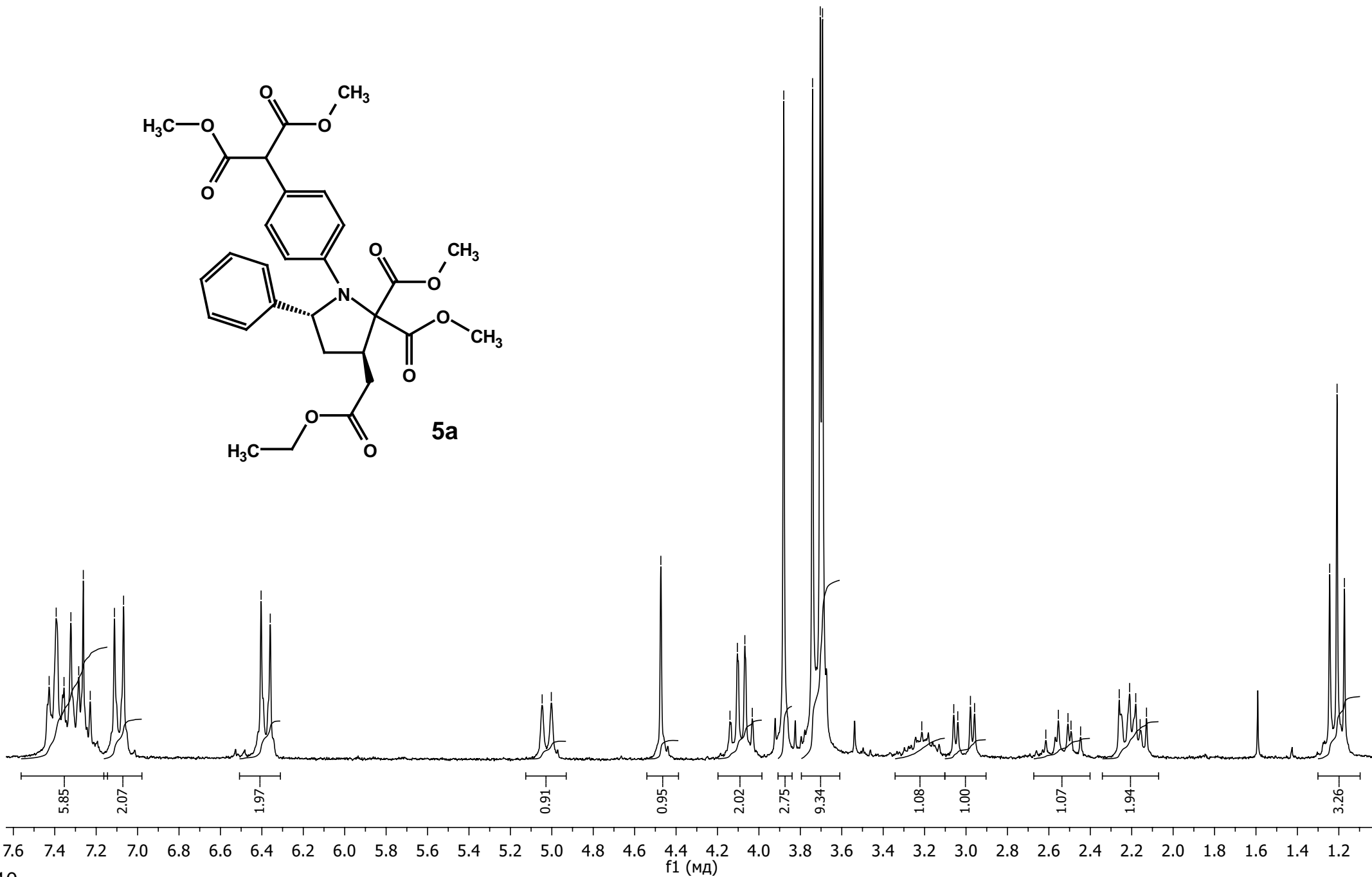
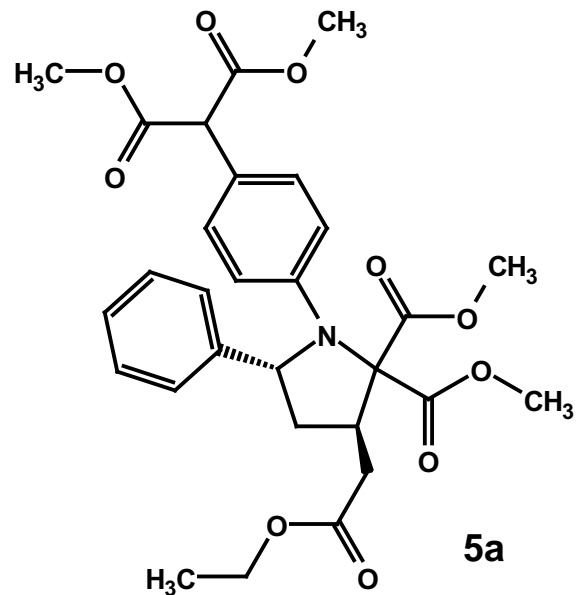
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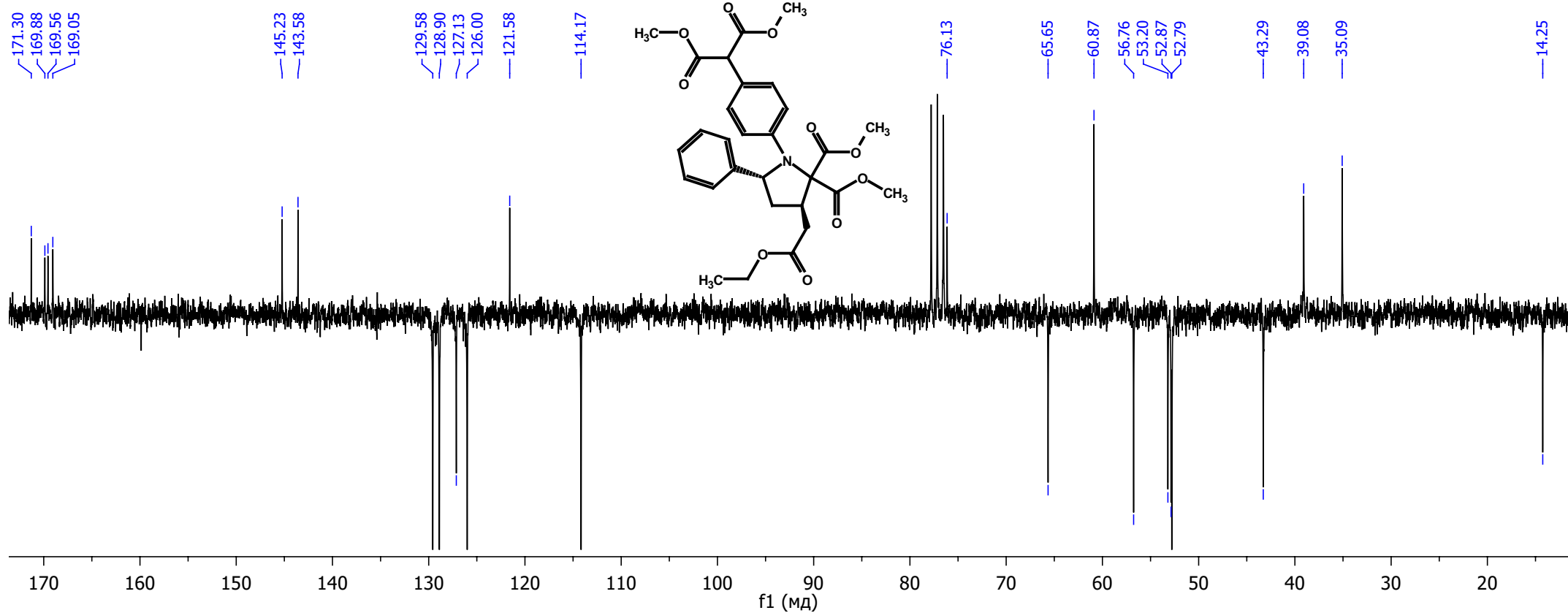
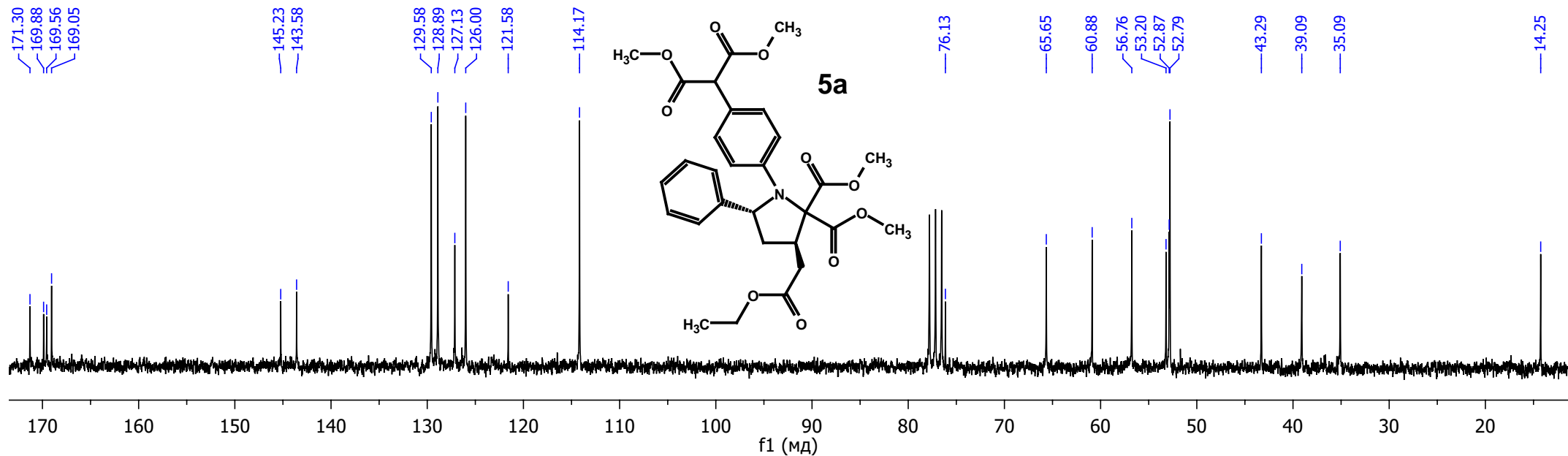
4.14  
4.10  
4.07  
4.03  
3.88  
3.74  
3.70  
3.69

3.21  
3.06  
3.04  
2.98  
2.96

2.61  
2.55  
2.51  
2.49  
2.45  
2.26  
2.21  
2.18  
2.16  
2.13

1.24  
1.21  
1.17





7.46  
7.45  
7.43  
7.35  
7.32  
7.30  
7.26  
7.11  
7.09  
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6.71  
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6.40

5.06  
5.03

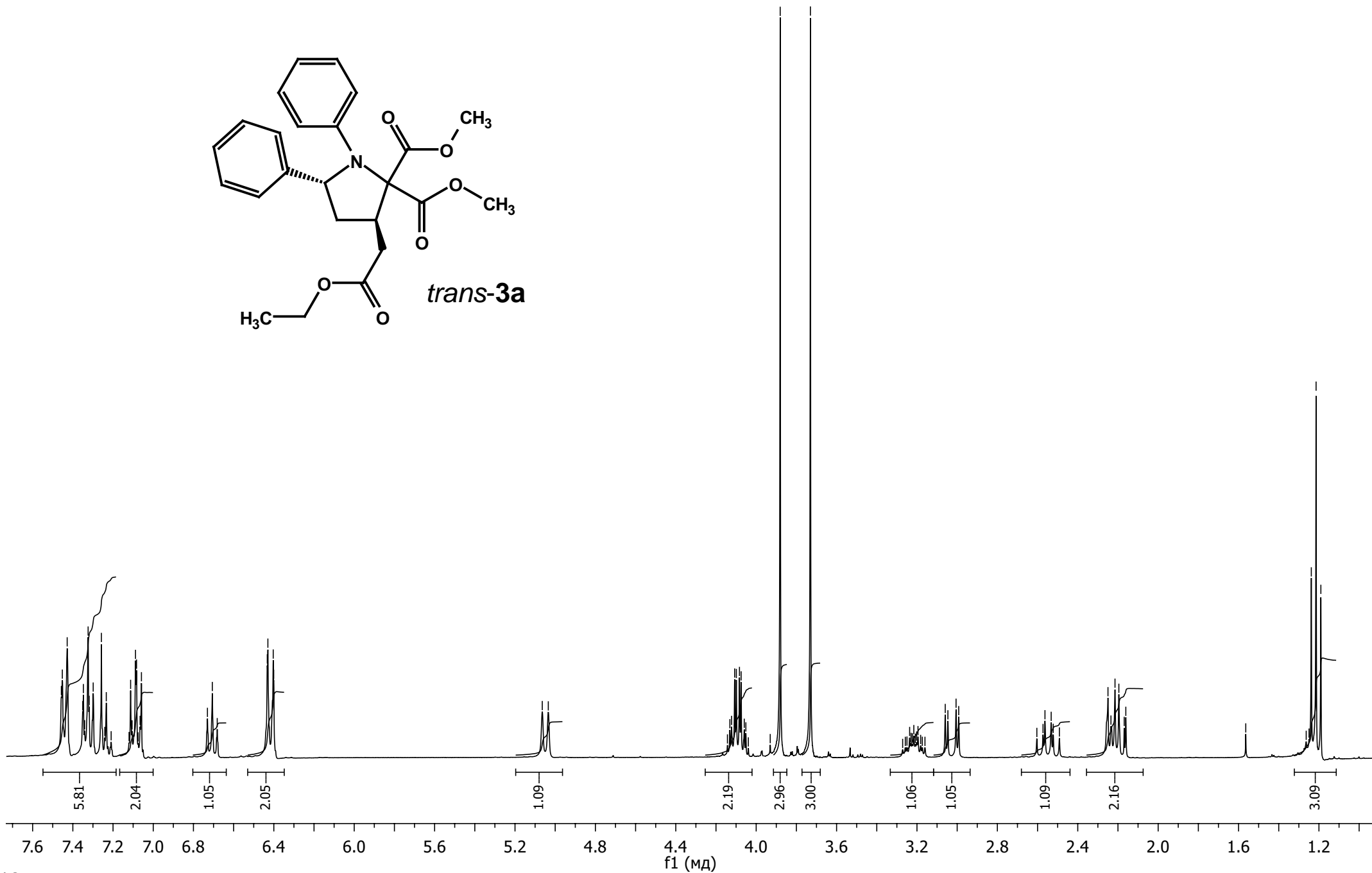
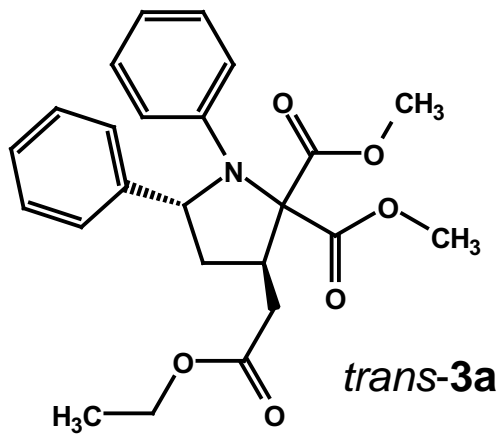
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4.13  
4.12  
4.11  
4.10  
4.08  
4.07  
4.06  
4.05  
4.04  
3.93  
3.88  
3.73

3.24  
3.22  
3.20  
3.19  
3.06  
3.05  
3.01  
2.99

2.57  
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2.48  
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2.16

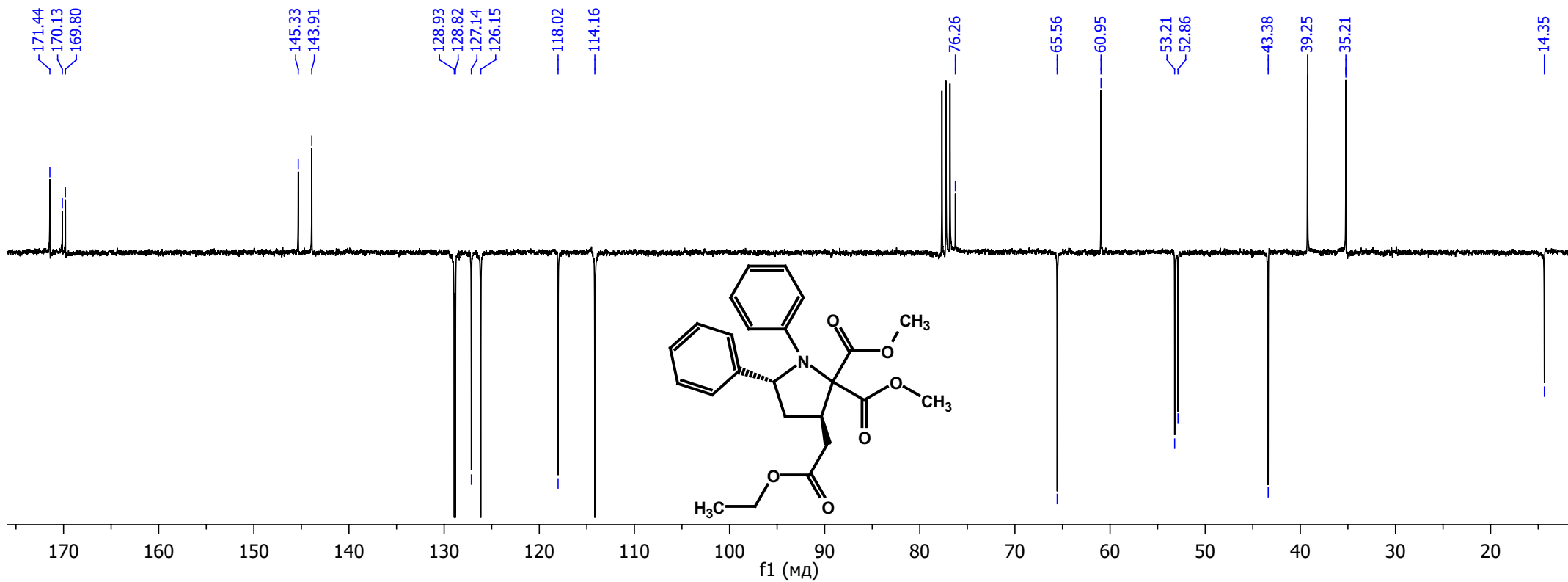
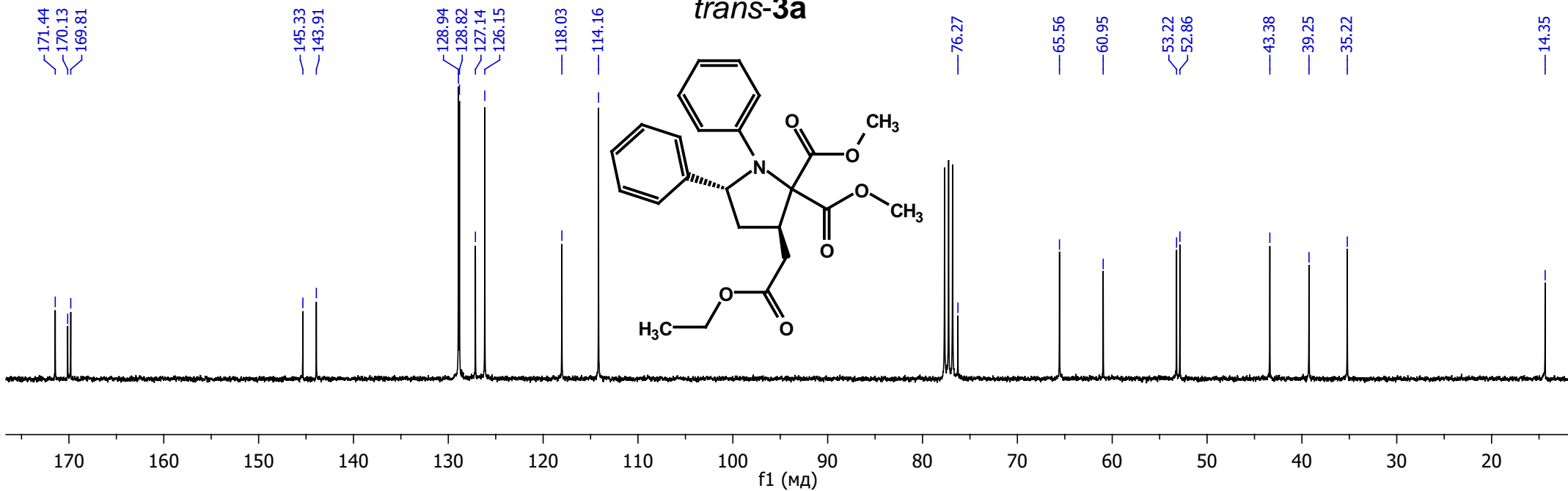
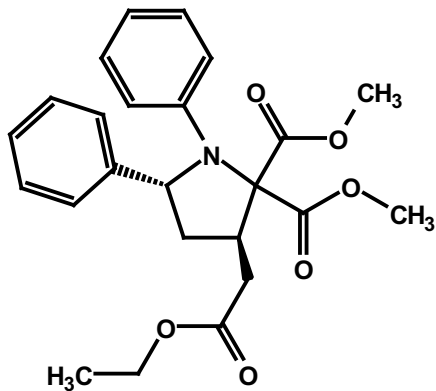
1.56

1.26  
1.25  
1.24  
1.21  
1.19





*trans-3a*



7.42  
7.40  
7.40  
7.27  
7.26  
7.24  
7.03  
7.03  
6.90  
6.70  
6.68  
6.66  
6.56  
6.54

5.07  
5.05  
5.04  
5.03

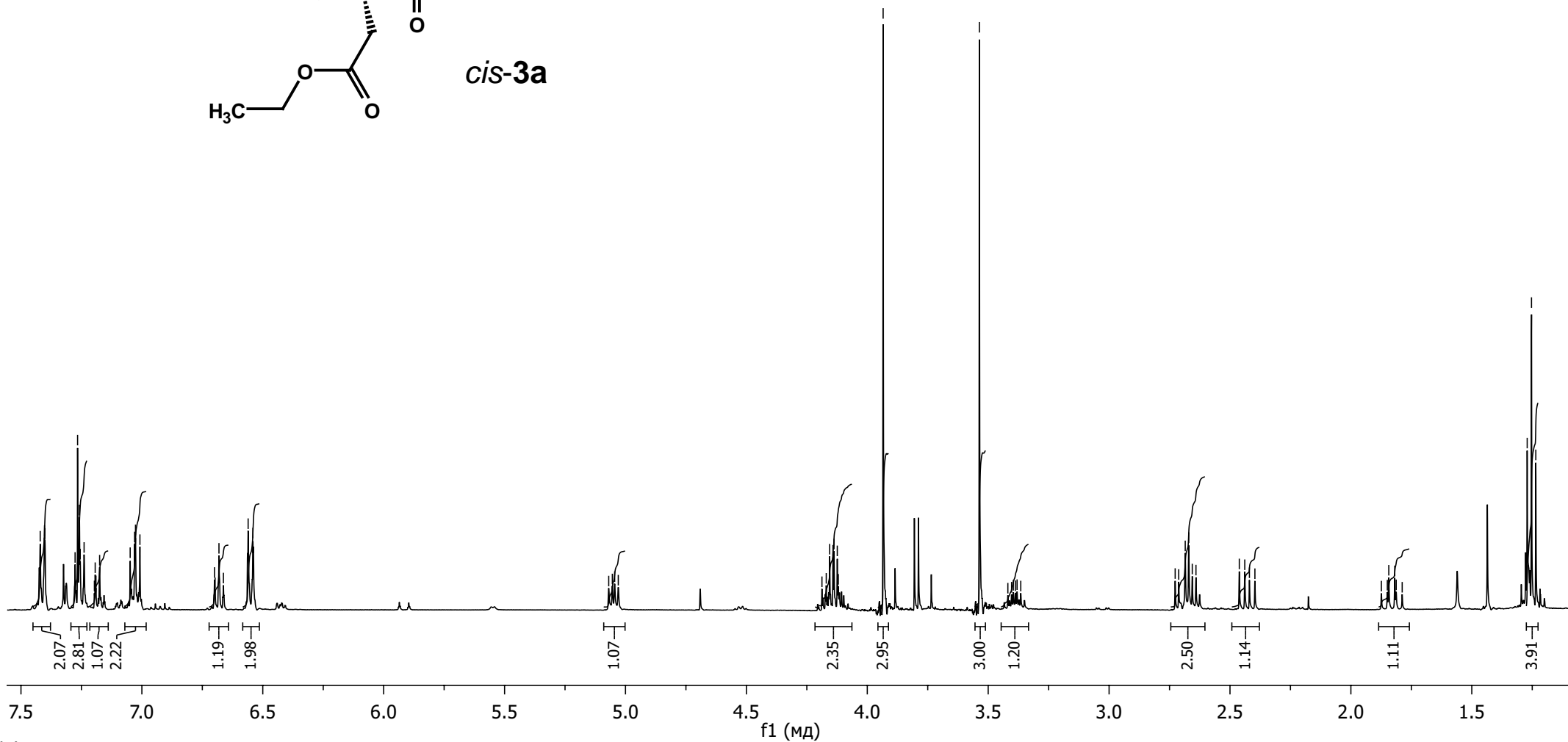
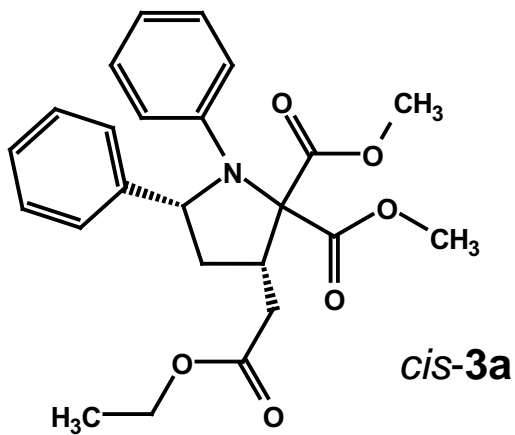
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4.14  
4.12  
4.12  
3.93

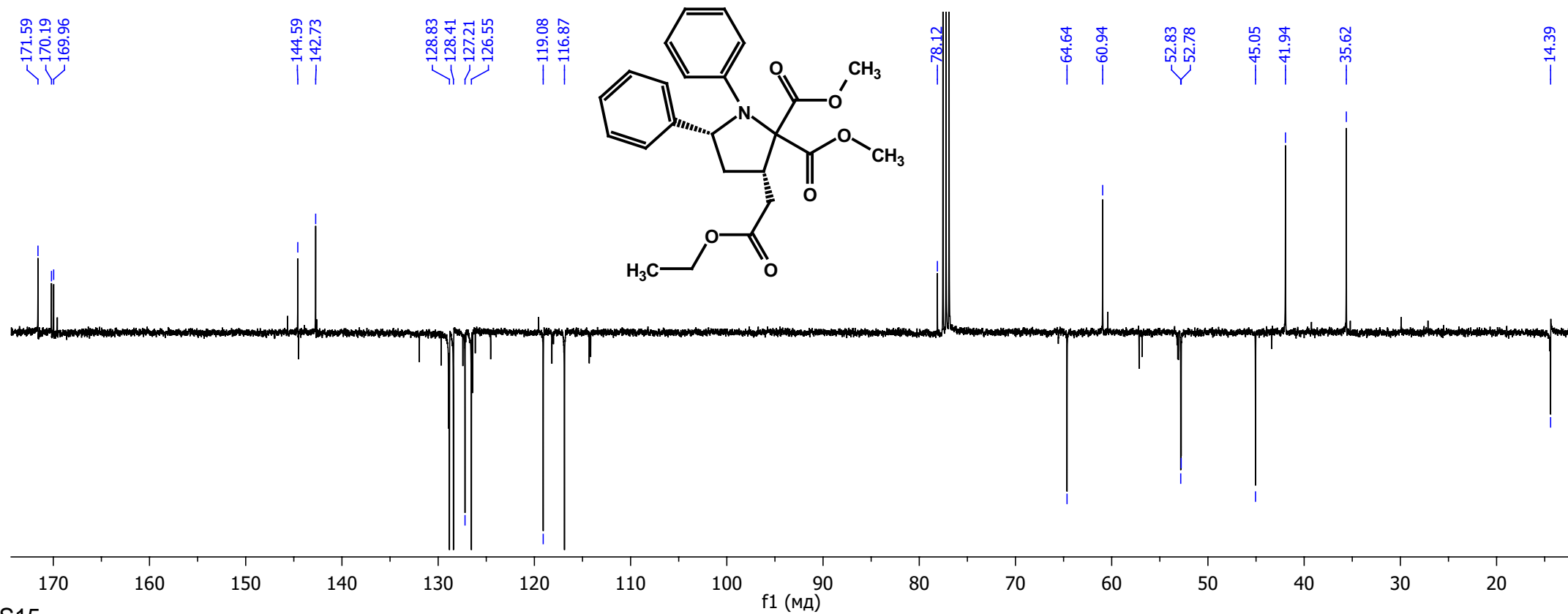
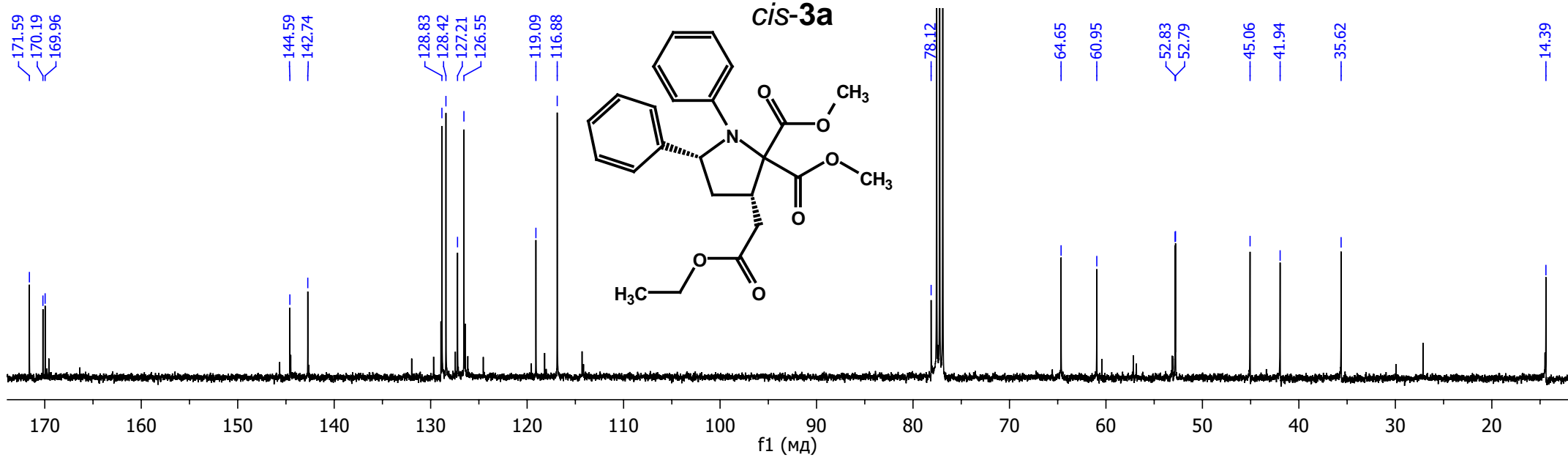
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3.38  
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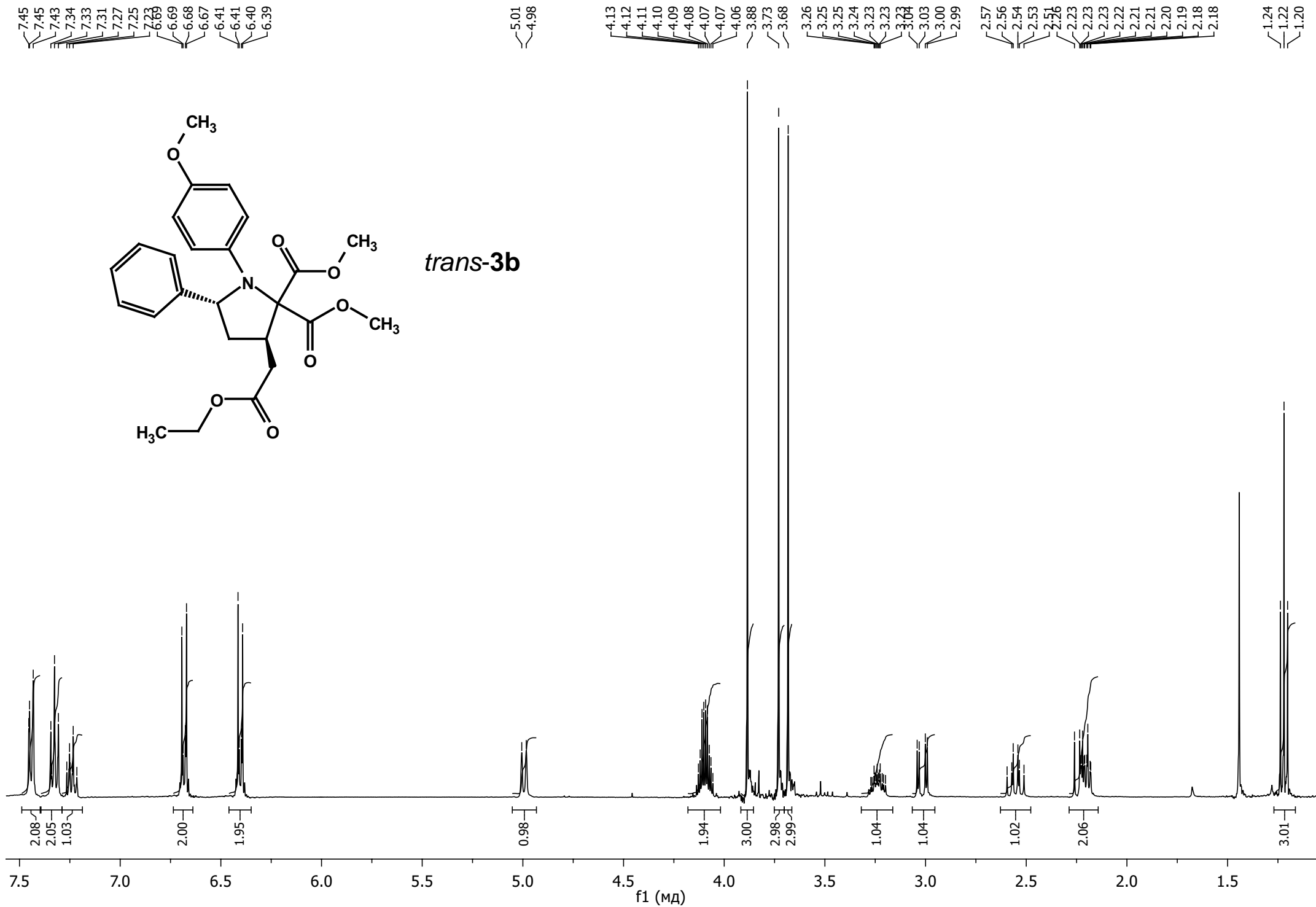
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2.66  
2.64  
2.46  
2.44  
2.42  
2.40

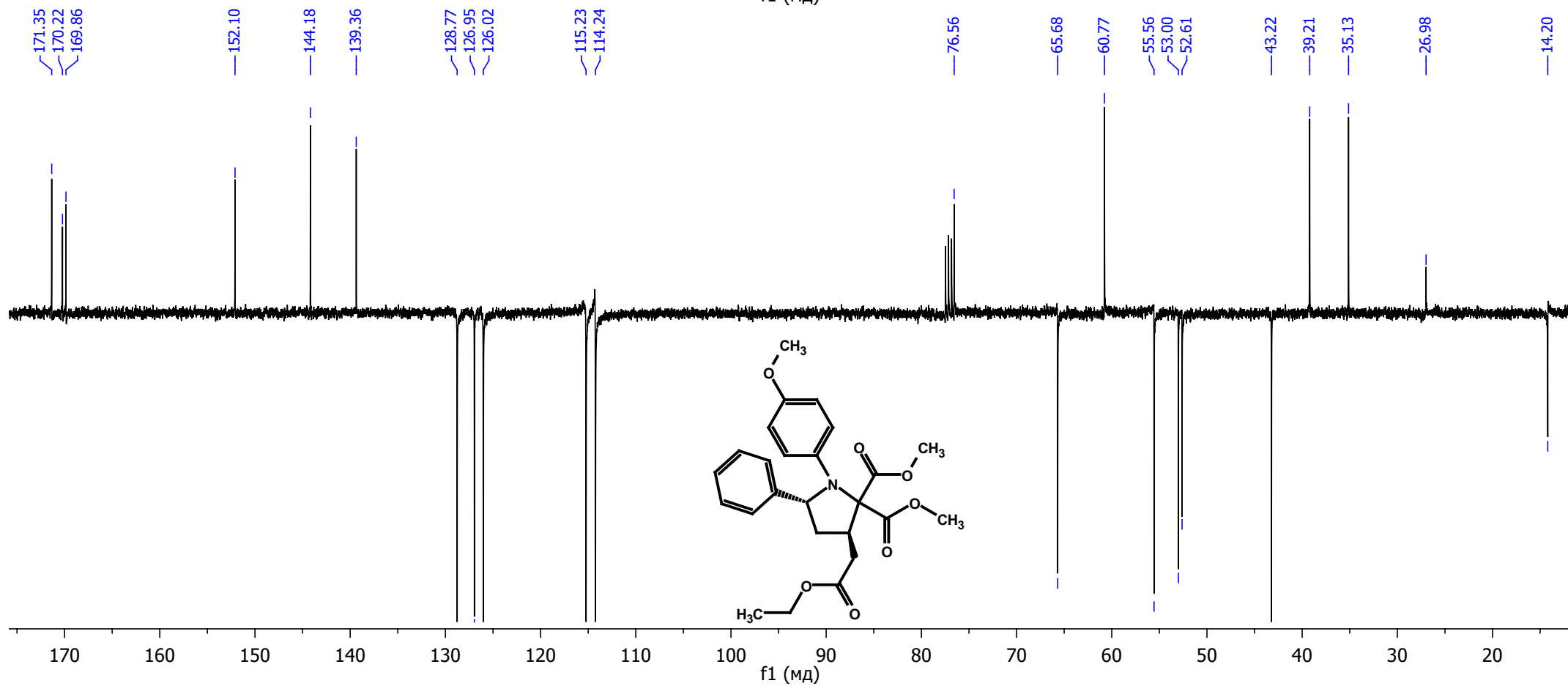
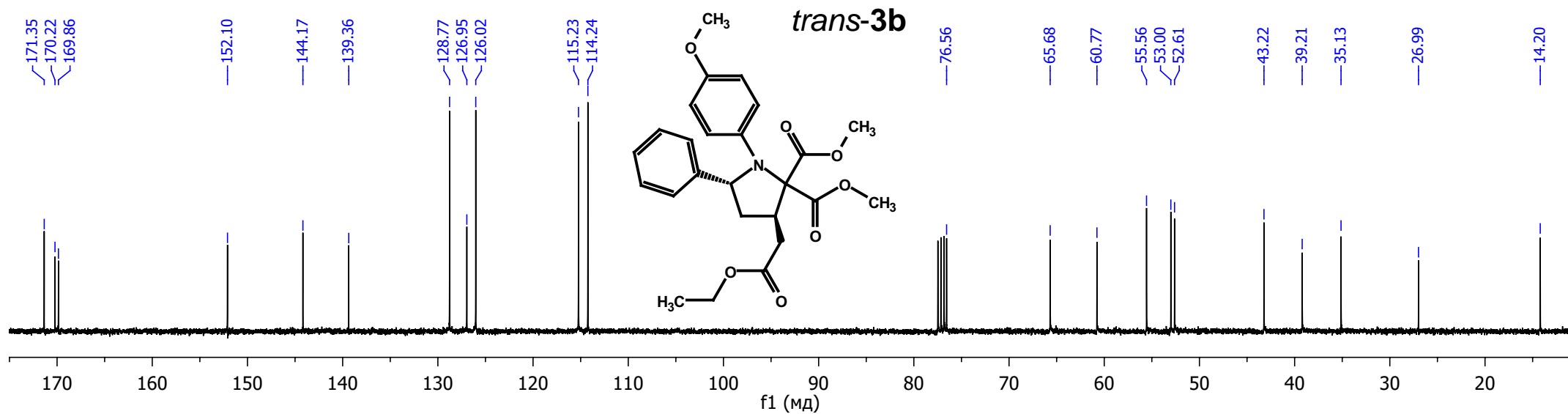
1.87  
1.85  
1.84  
1.82  
1.81  
1.79

1.27  
1.25  
1.24









7.44  
7.40  
7.32  
7.26  
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7.20  
7.19  
7.18  
7.15

6.61

5.00  
4.97  
4.95  
4.92

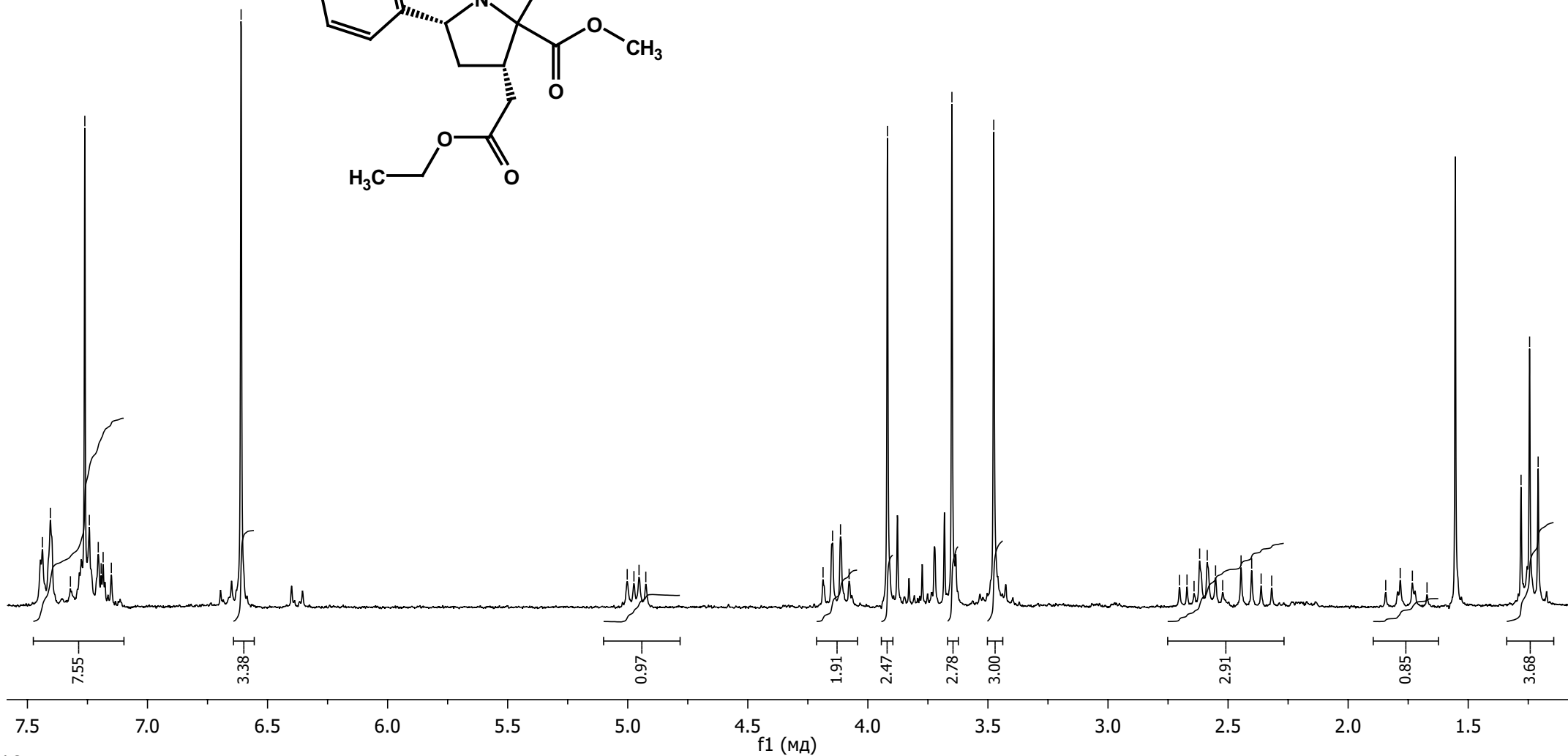
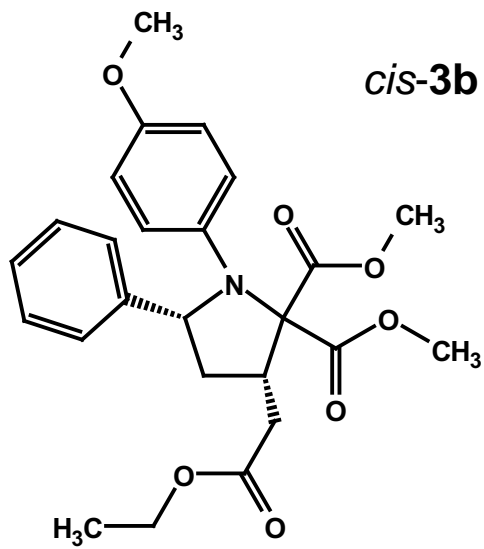
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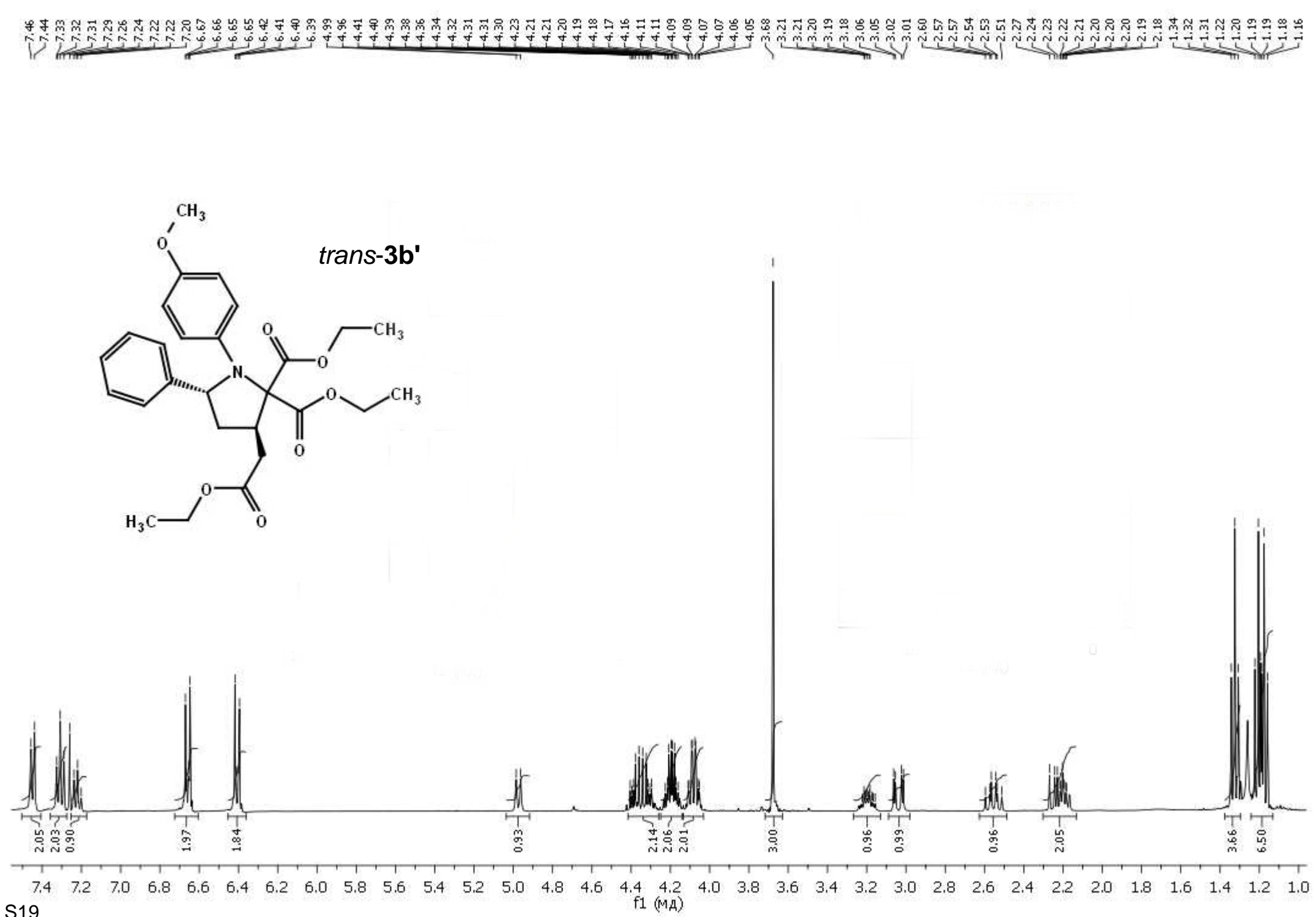
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2.52  
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2.40  
2.36  
2.32

1.84  
1.78  
1.73  
1.67

1.28  
1.24  
1.21





171.53  
169.72  
169.30

152.04

144.35

139.51

128.73  
126.95  
126.14

115.38  
114.13

76.53

65.63  
61.99  
61.83  
60.78

55.66

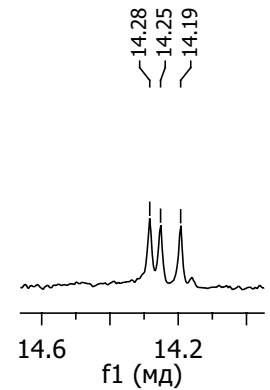
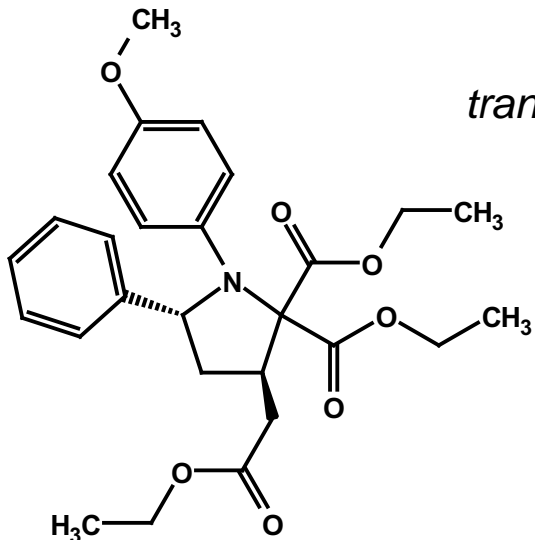
43.24

39.33

35.27

14.28  
14.25  
14.19

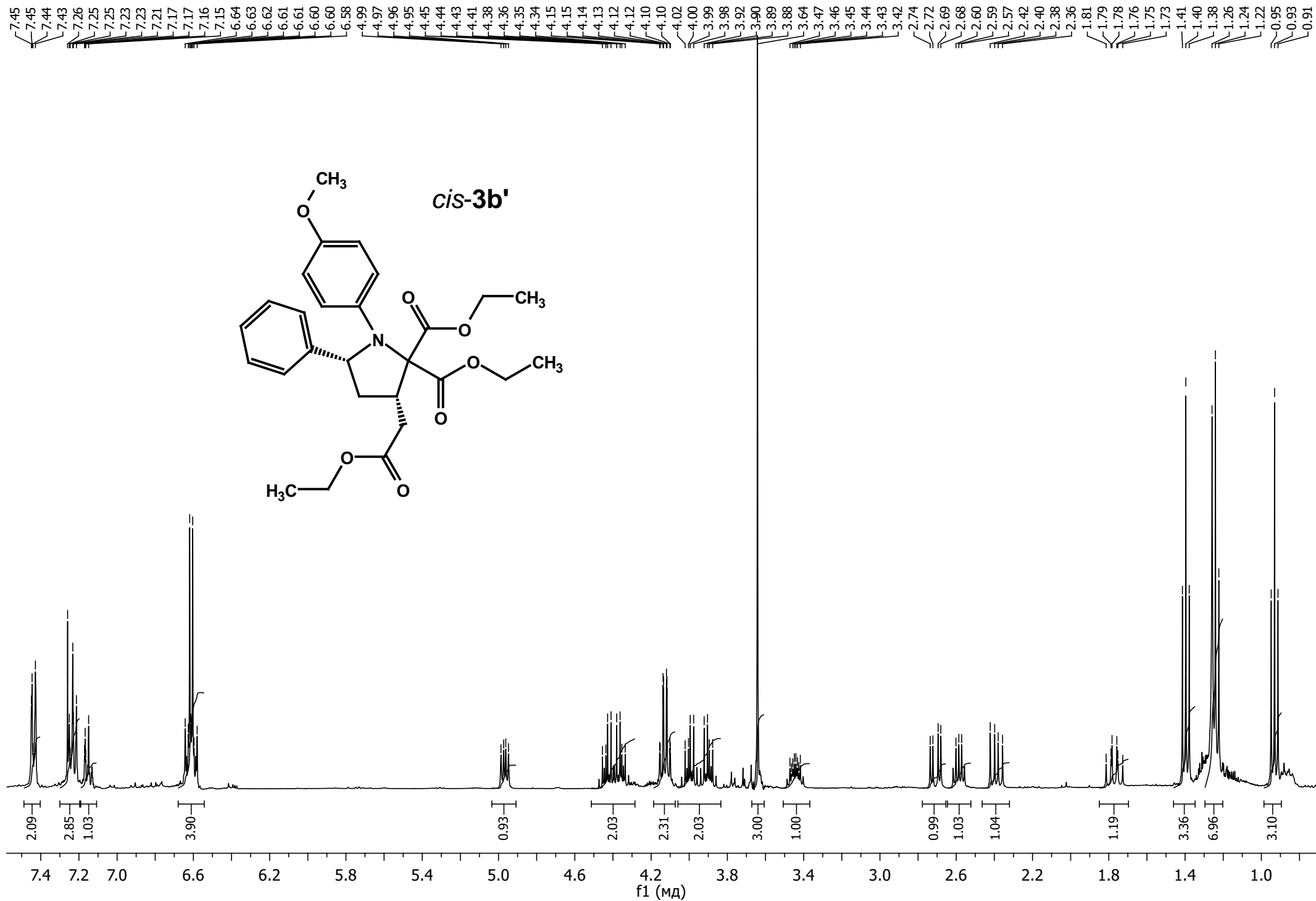
*trans-3b'*



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

f1 (MД)





171.64  
170.10  
169.27

153.30

142.82

138.53

128.57

127.08

126.76

119.61

113.69

78.35

64.81

61.83

61.64

60.77

55.47

44.40

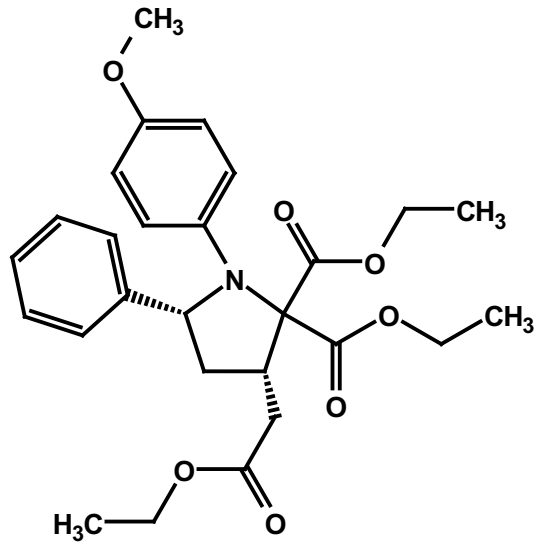
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35.79

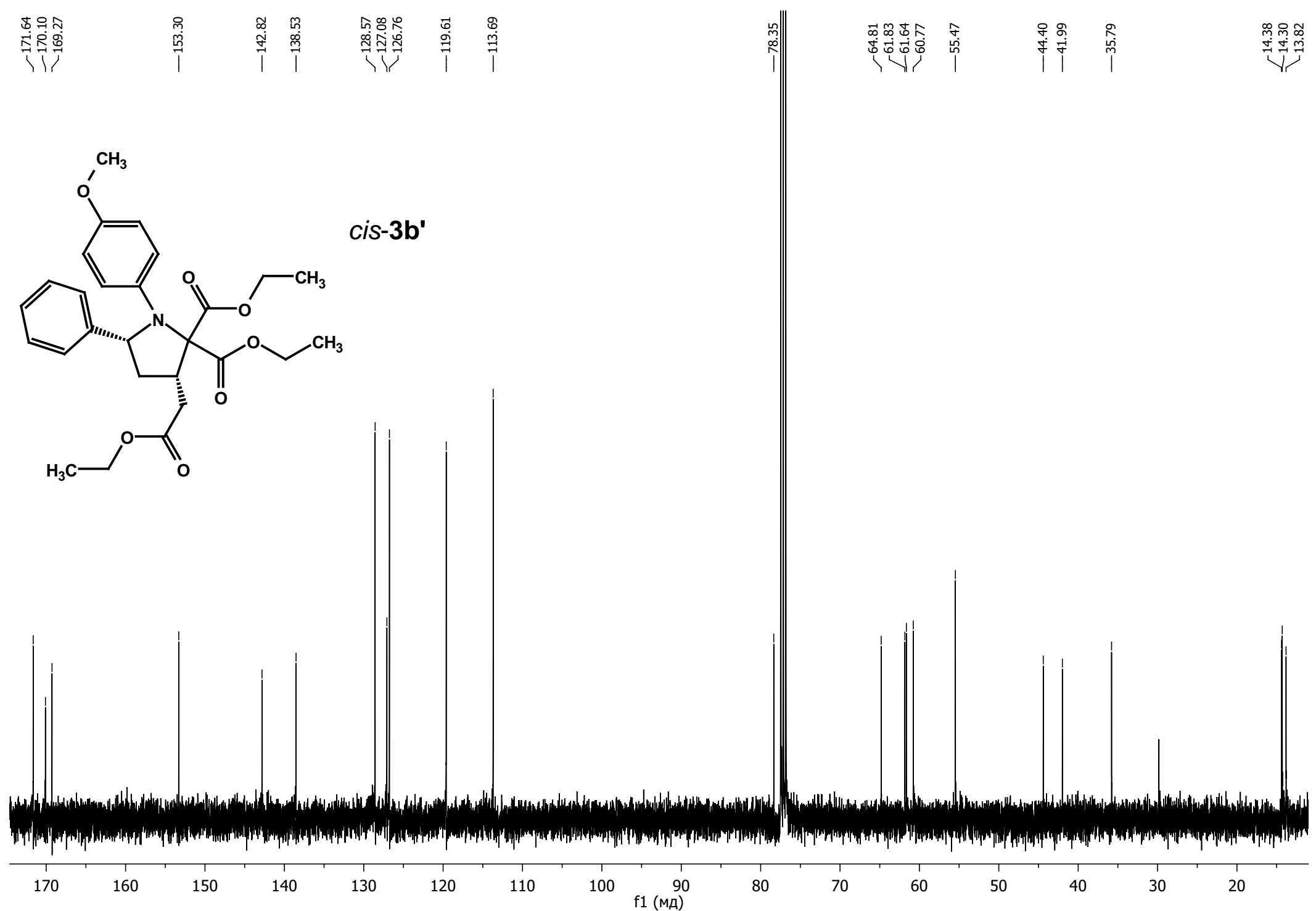
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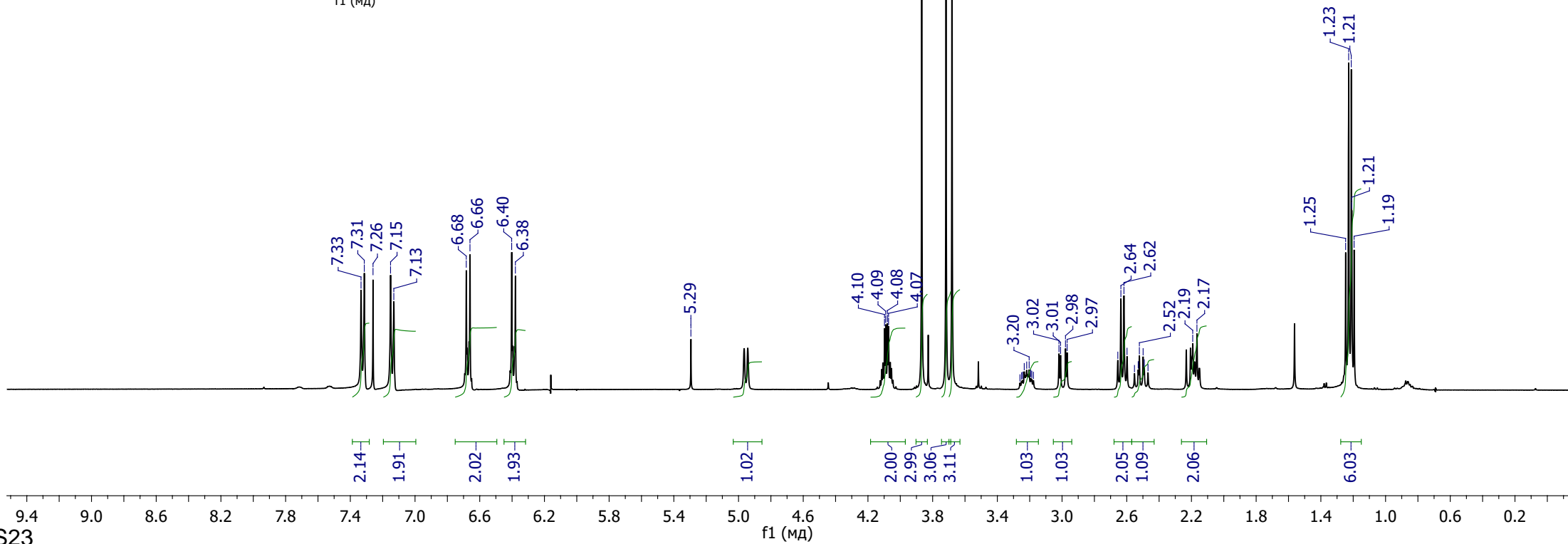
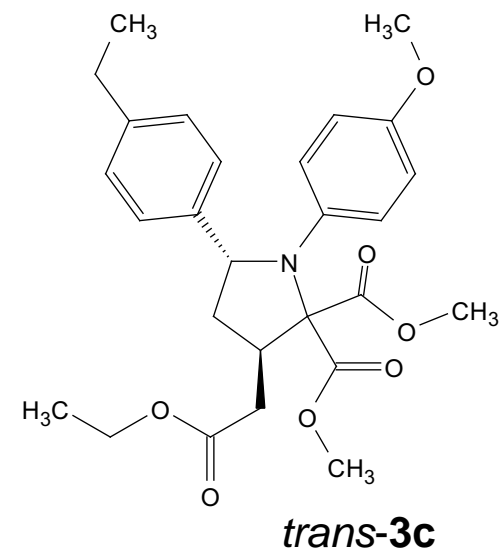
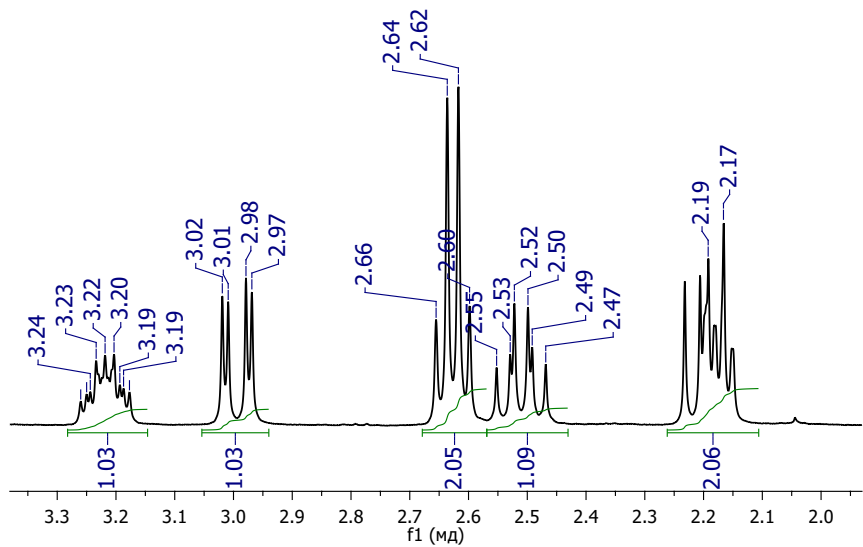
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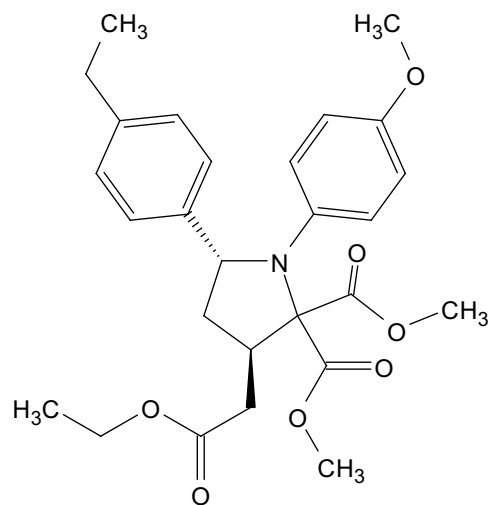
13.82



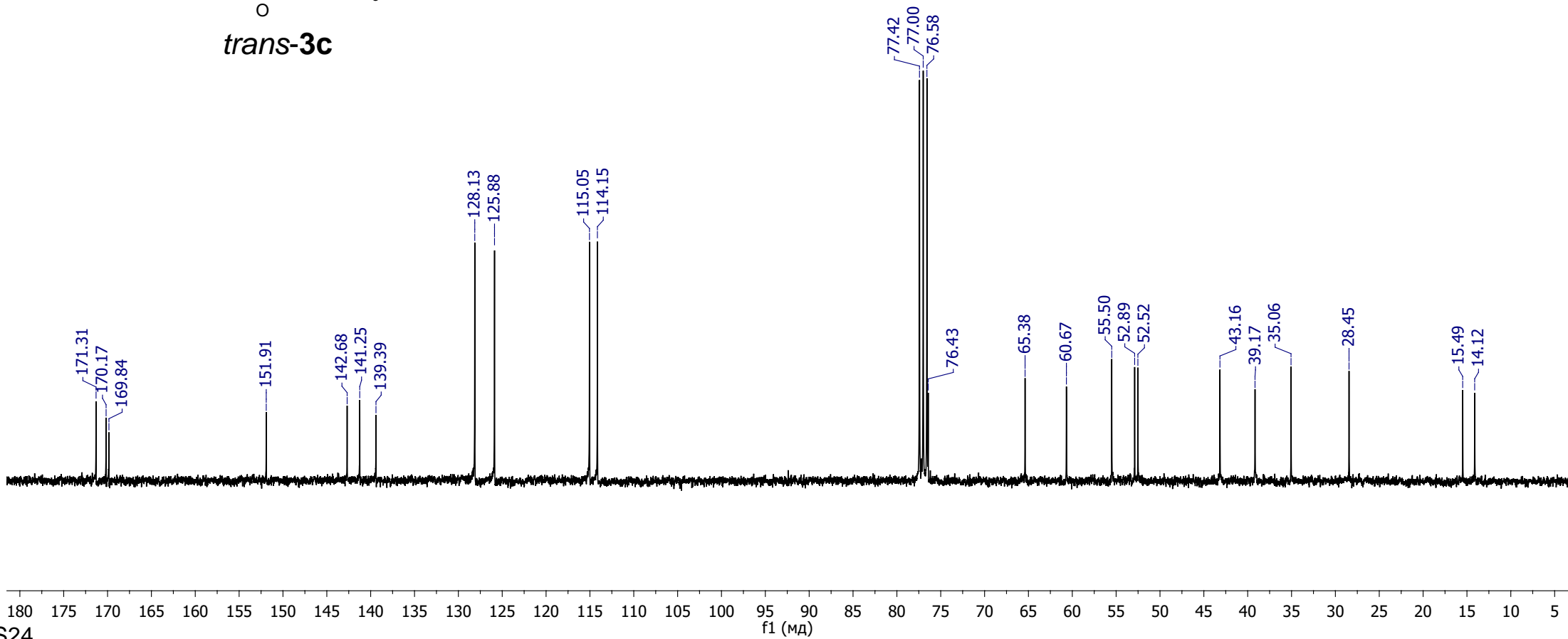
*cis-3b'*





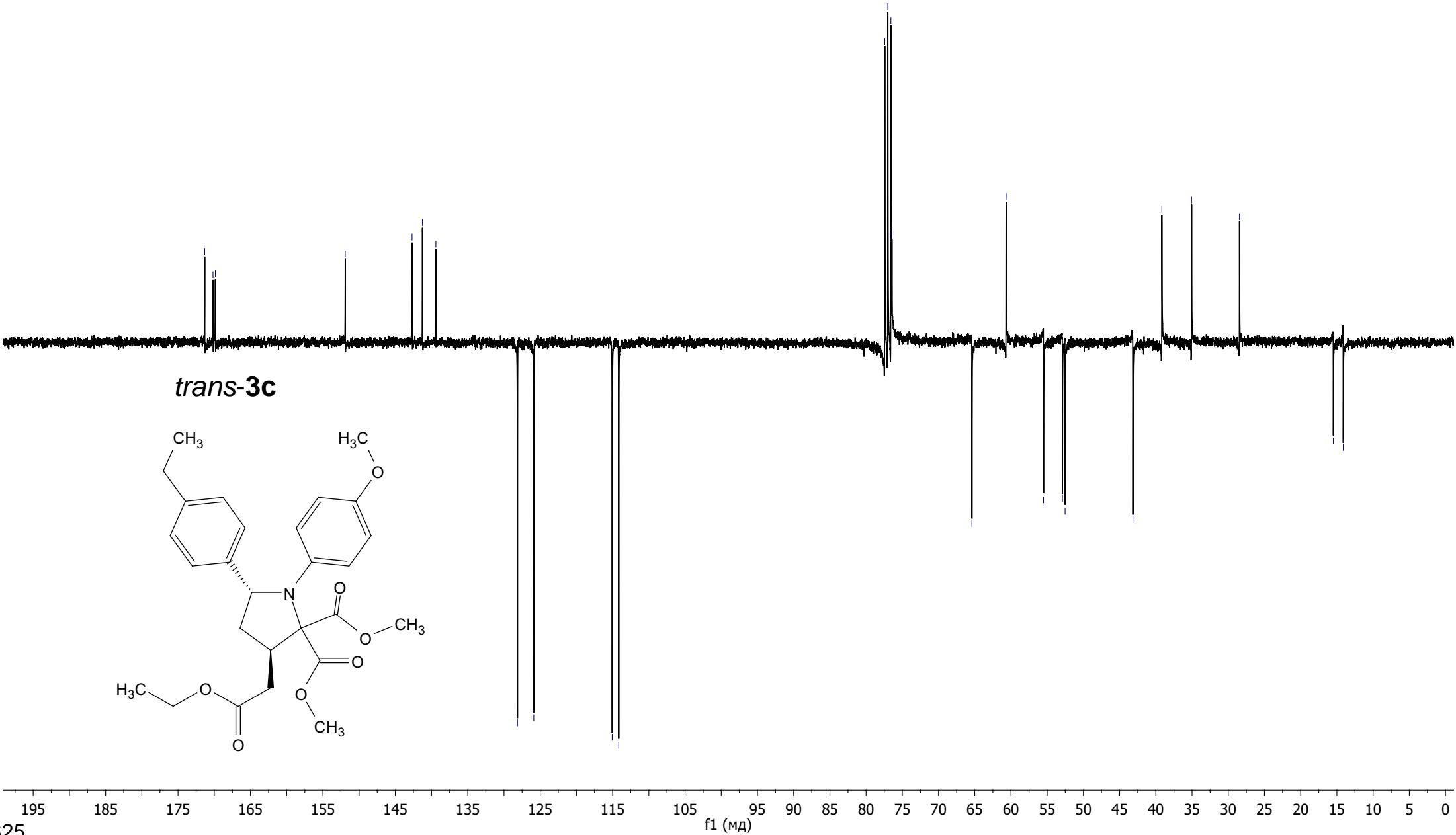
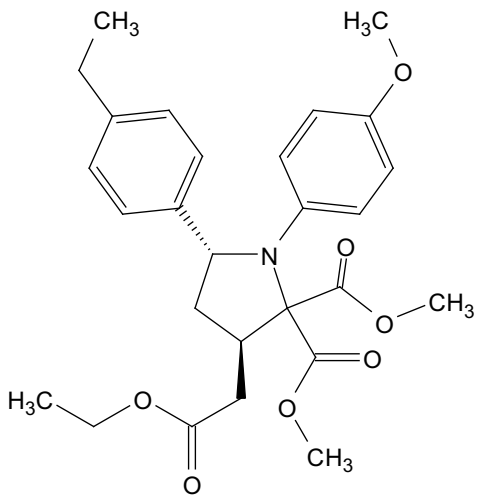


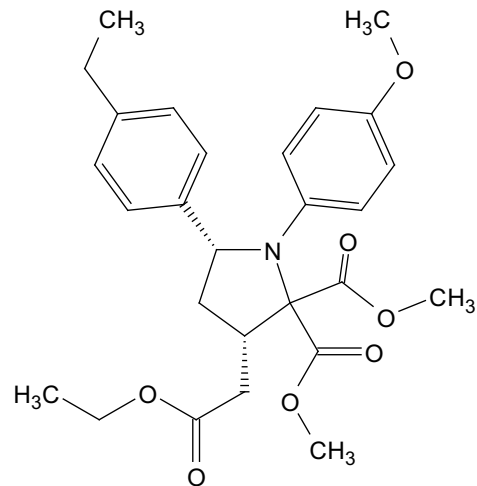
*trans-3c*



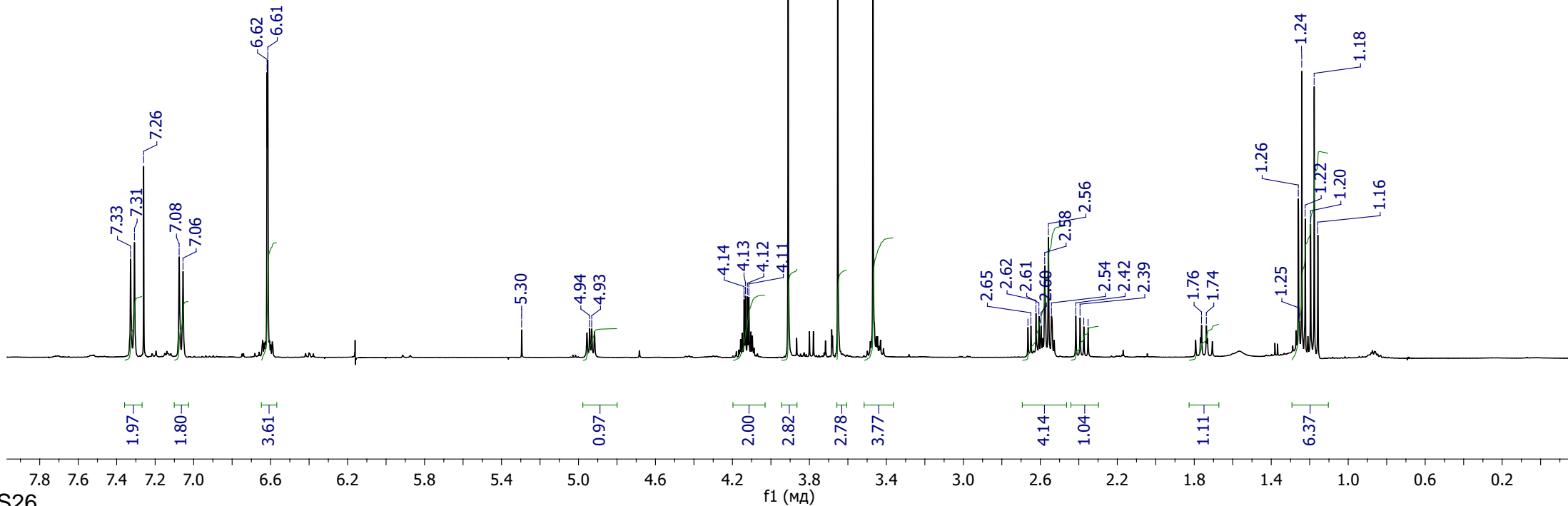
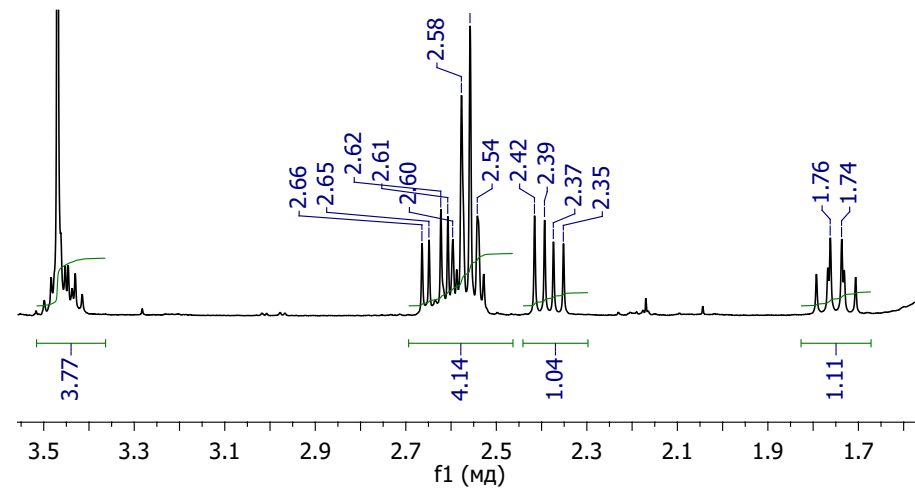
171.32 170.17 169.85  
151.92 142.69 141.25 139.40  
128.14 125.88 115.05 114.15  
77.42 77.00 76.58 76.43  
65.39 60.67 55.51 52.89 52.53  
43.17 39.17 35.06  
28.45  
15.49 14.12

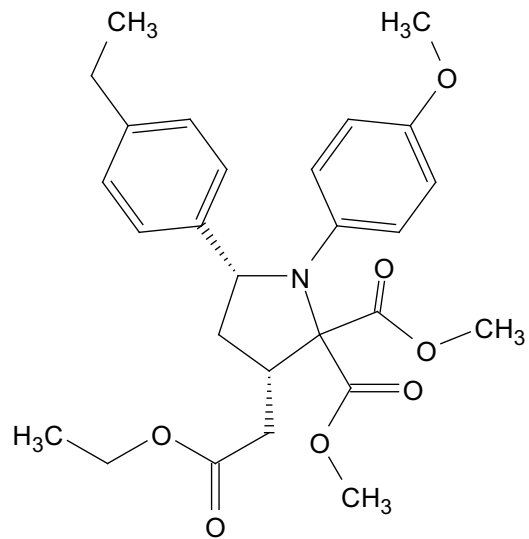
*trans-3c*



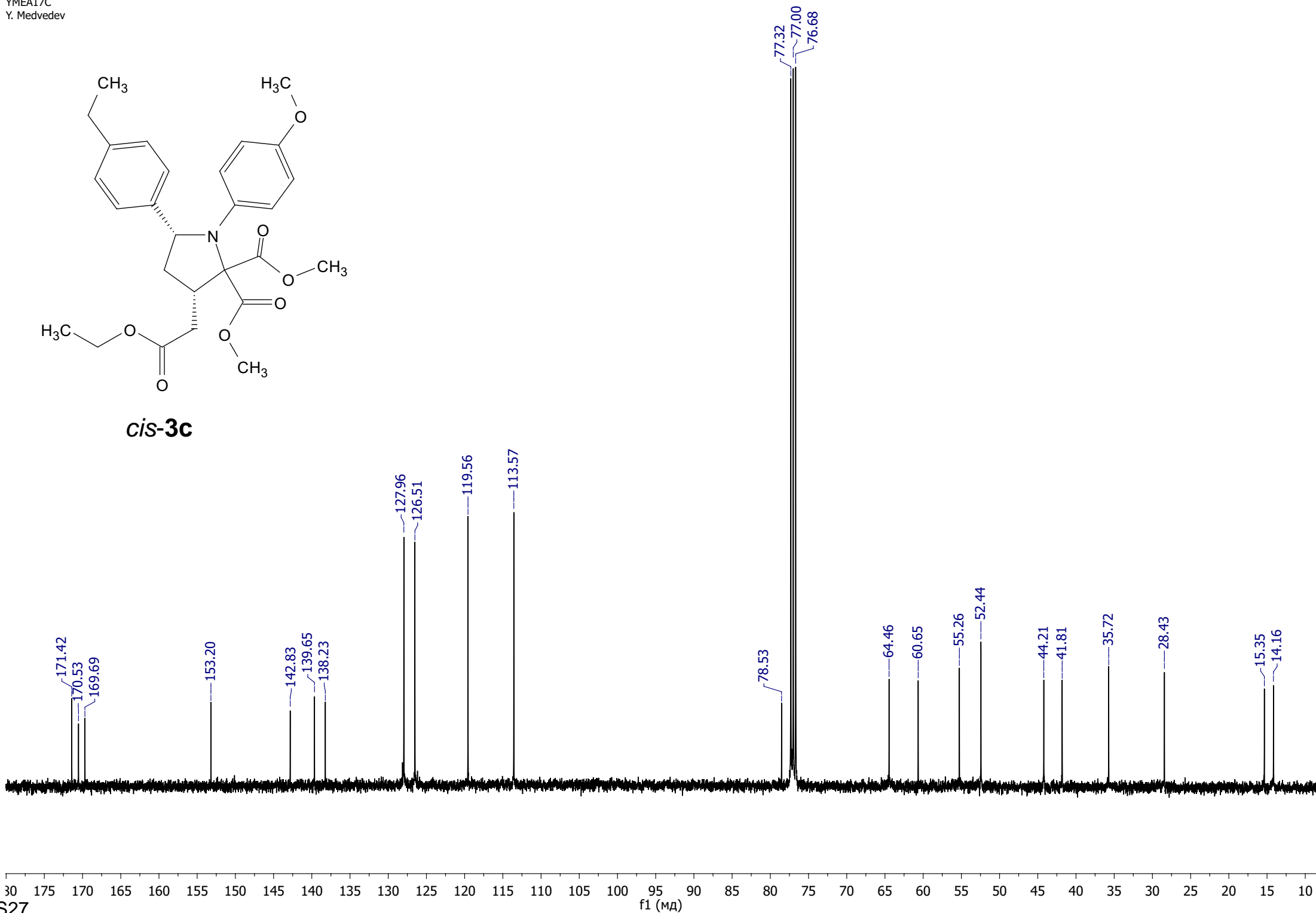


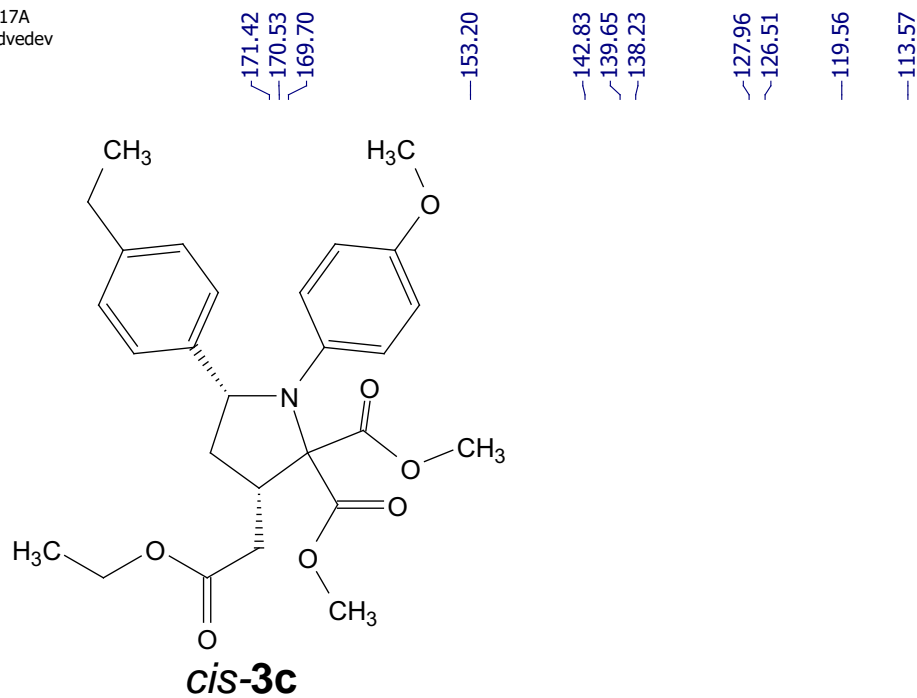
*cis*-3c





*cis*-3c





171.42  
170.53  
169.70

153.20

142.83  
139.65  
138.23

127.96  
126.51

119.56

113.57

78.53  
77.32  
77.00  
76.68

64.47

60.65

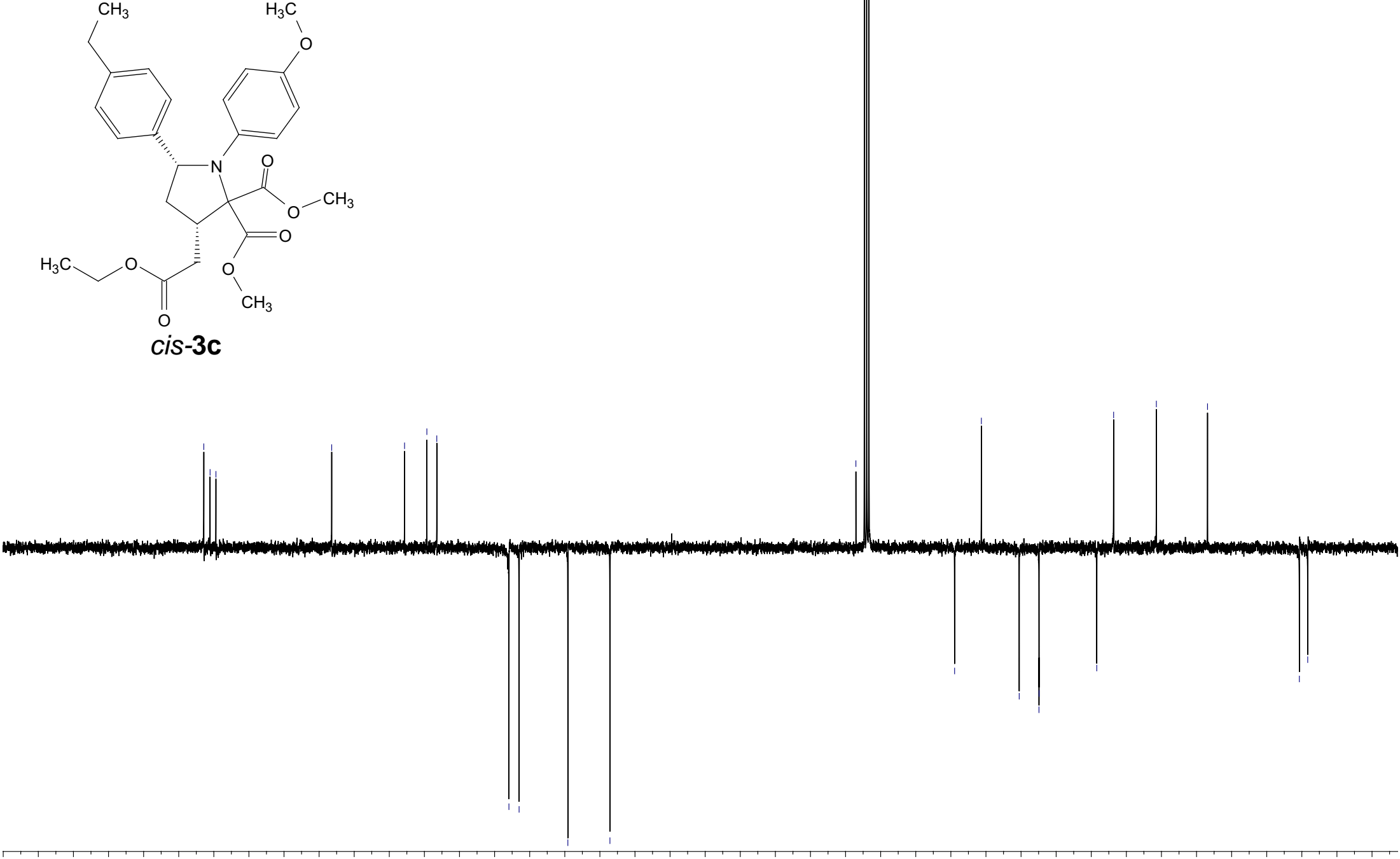
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44.22  
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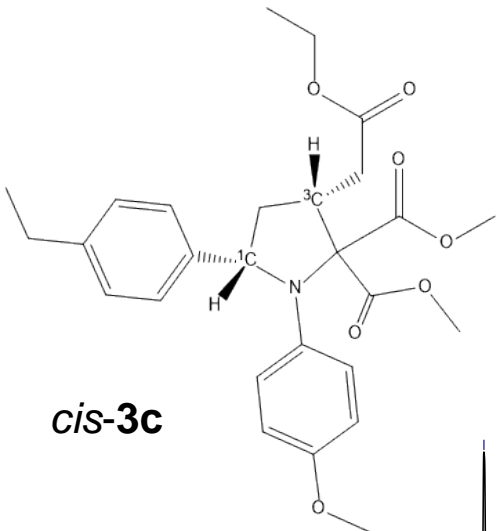
35.72

28.43

15.35  
14.16







7.33  
7.31

6.62

6.16  
6.16

4.96  
4.94  
4.93  
4.92

3.48  
3.47  
3.45

2.59  
2.57  
2.56  
2.54  
2.53

<sup>1</sup>C - H

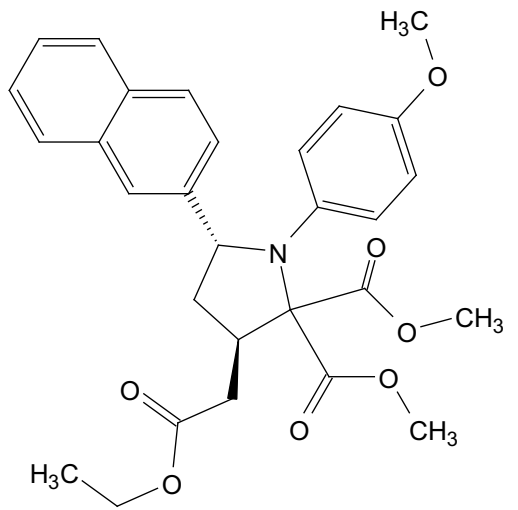
<sup>1</sup>CH - <sup>3</sup>CH

7.51  
7.50  
7.49  
7.48  
7.47  
7.46  
7.45  
7.44  
7.43  
7.43  
7.42  
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6.44  
6.44  
6.42  
6.41

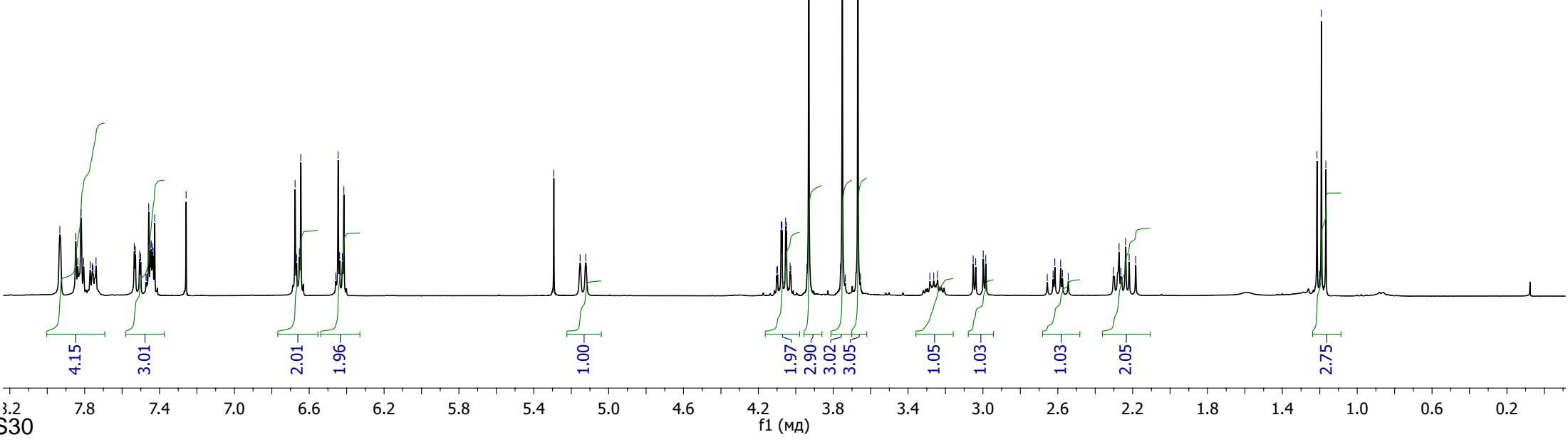
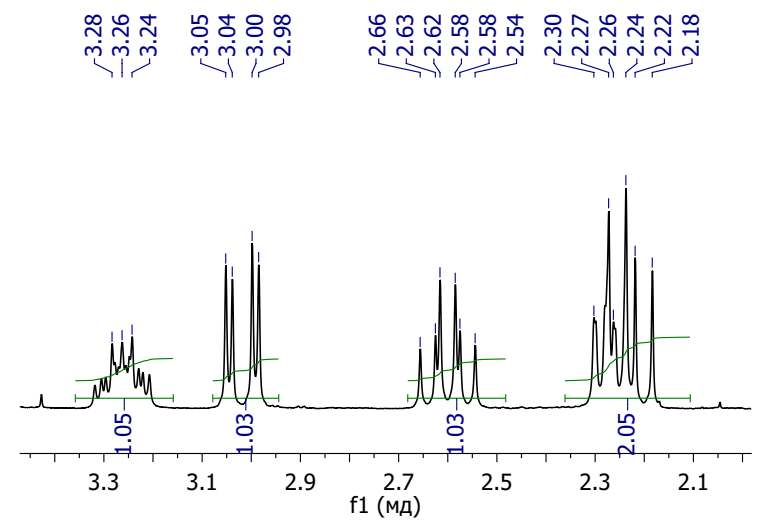
5.29  
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4.10  
4.10  
4.08  
4.07  
4.05  
4.05  
4.03  
4.03  
3.94  
3.93  
3.76  
3.75  
3.74  
3.67  
3.65

3.26  
3.24  
3.05  
3.04  
3.00  
2.98  
2.62  
2.58  
2.58  
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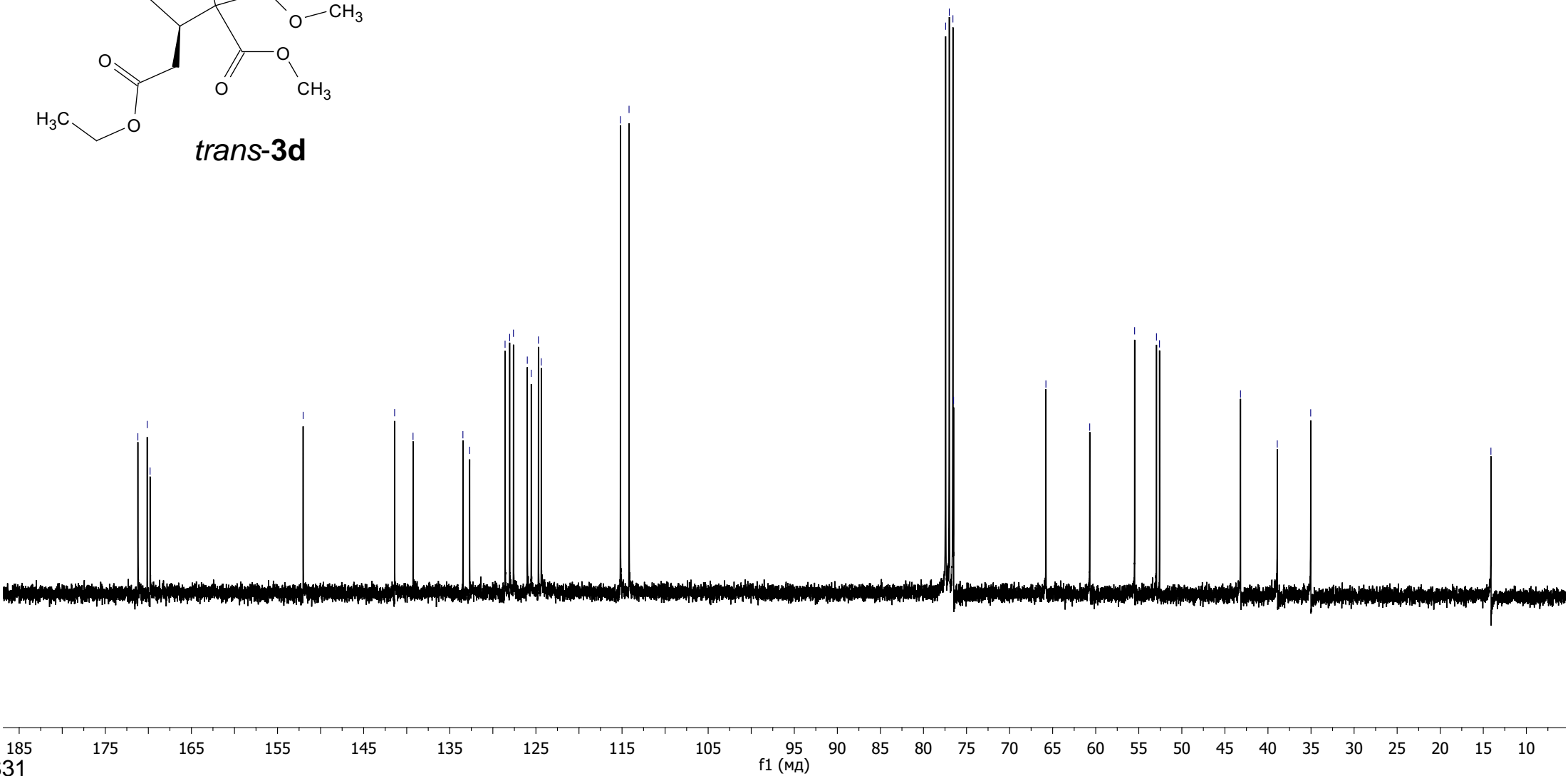
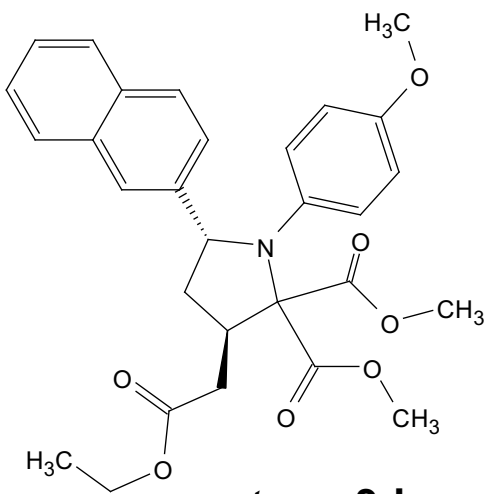


*trans*-3d

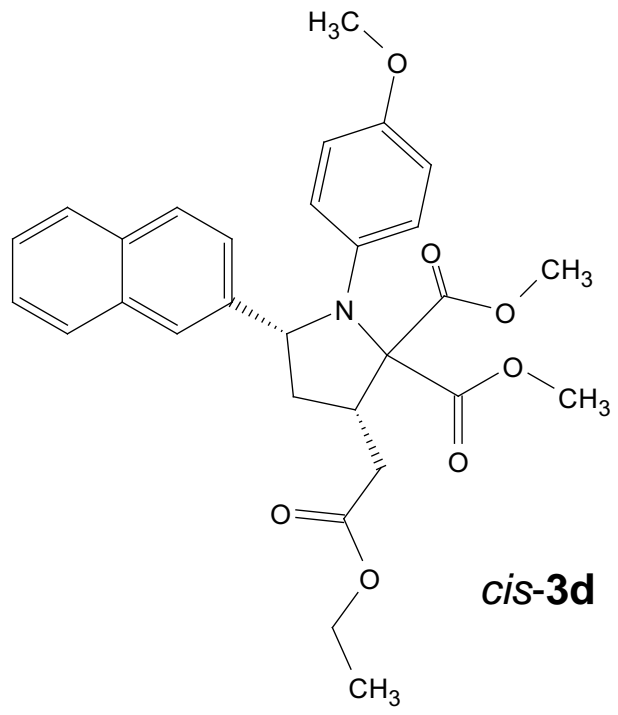


171.22  
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169.80  
152.03  
141.41  
139.27  
133.48  
132.69  
128.58  
128.05  
127.61  
126.00  
125.54  
124.71  
124.38  
115.19  
114.19

77.43  
77.00  
76.58  
76.50  
65.78  
60.69  
55.48  
52.94  
52.59  
43.19  
38.92  
35.04  
14.11



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5.08  
5.07  
5.06  
5.04

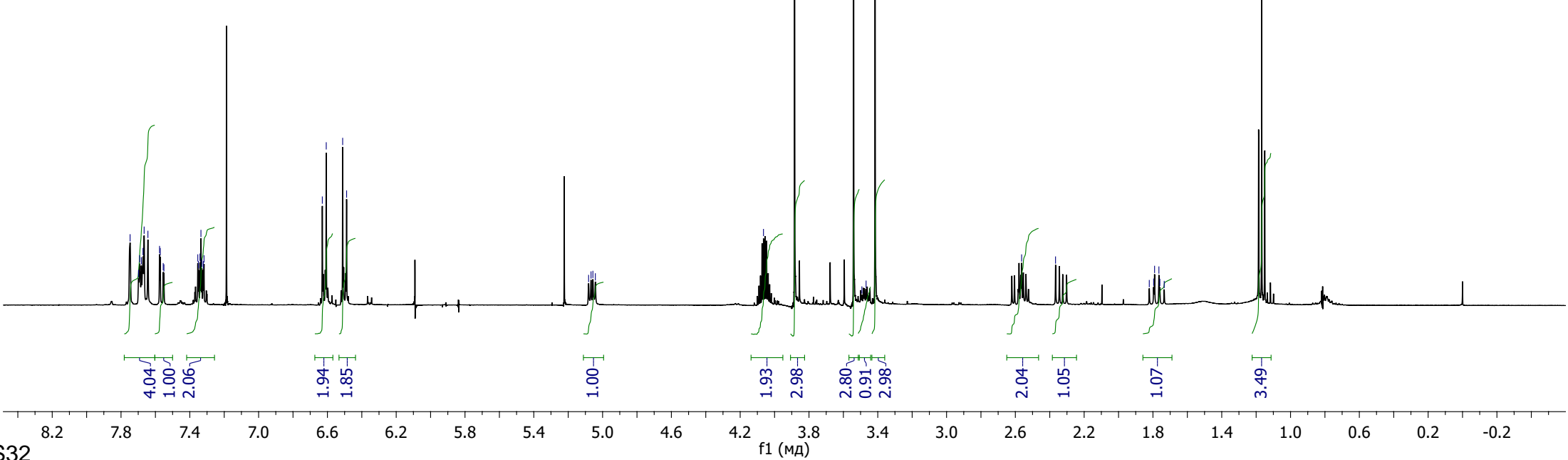
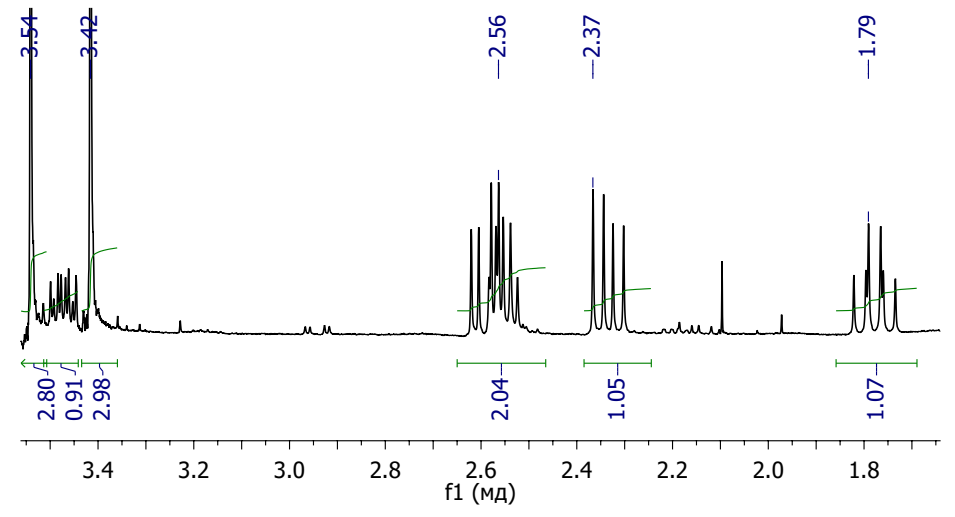
4.06  
3.88

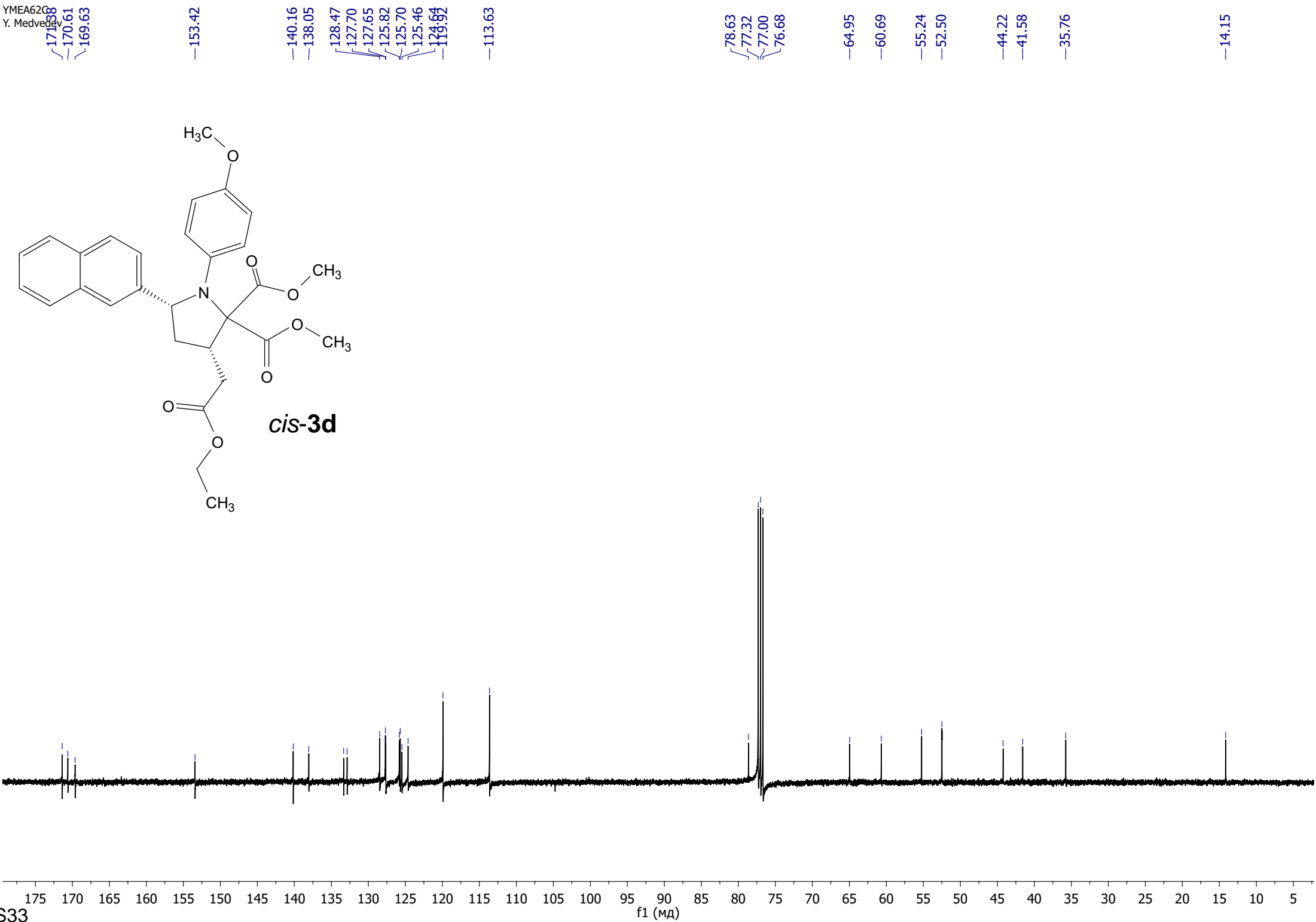
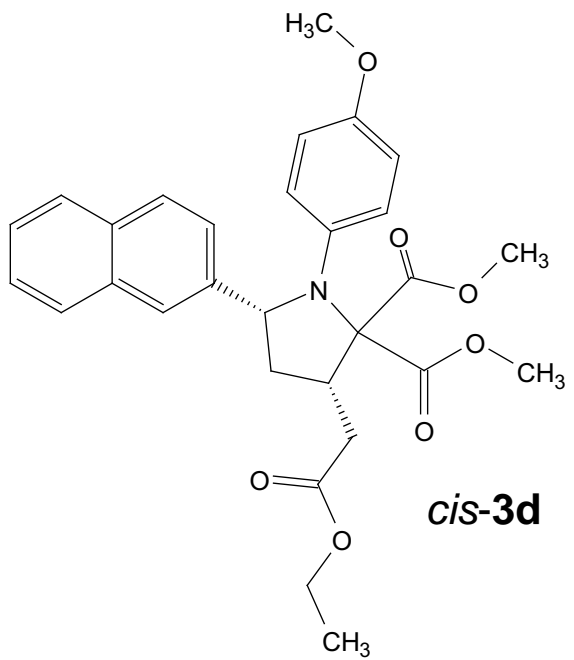
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3.47  
3.42

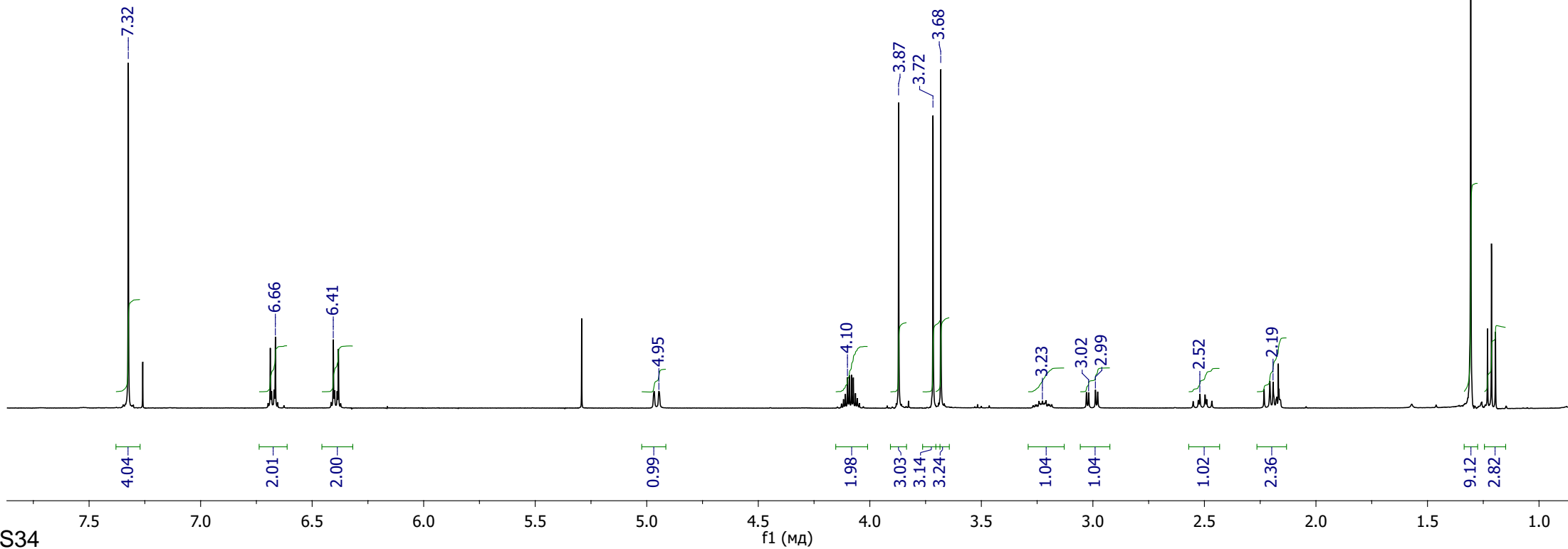
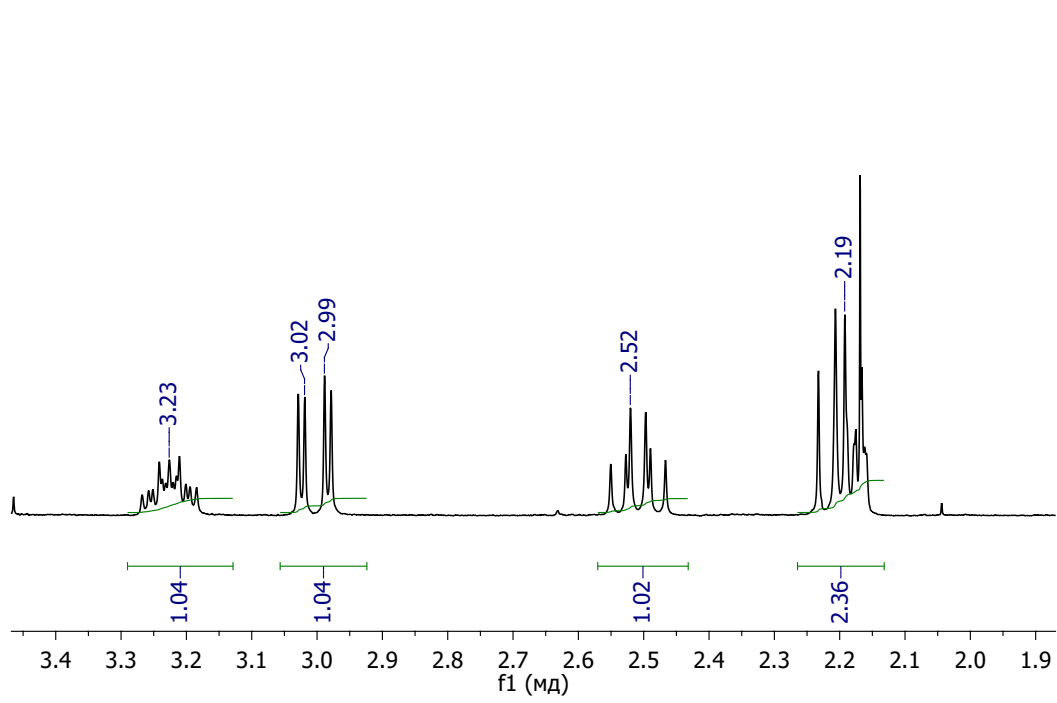
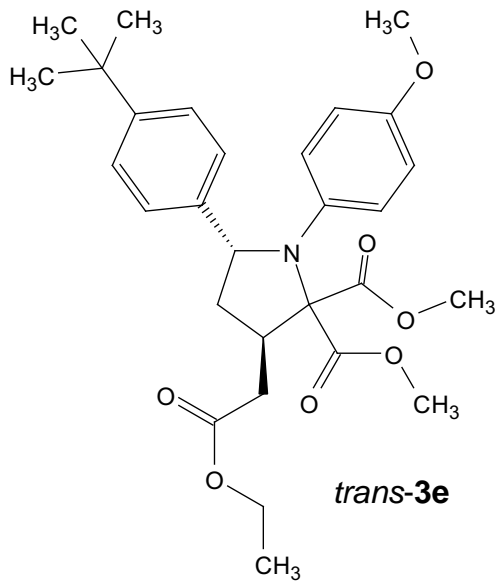
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1.82  
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1.79  
1.77  
1.76  
1.73

1.17







171.36  
170.16  
169.87

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125.54

115.01  
114.14

77.32  
77.00  
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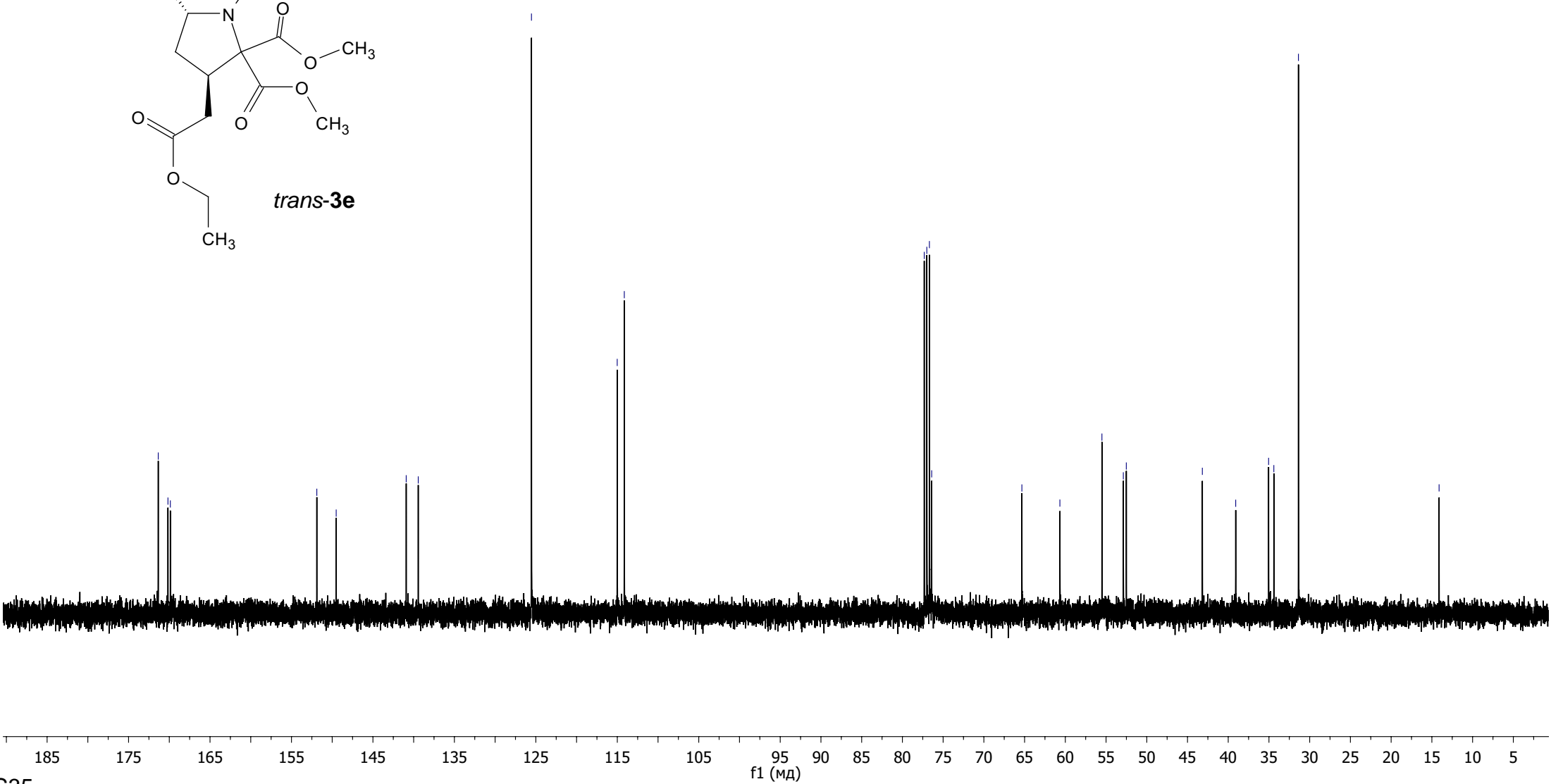
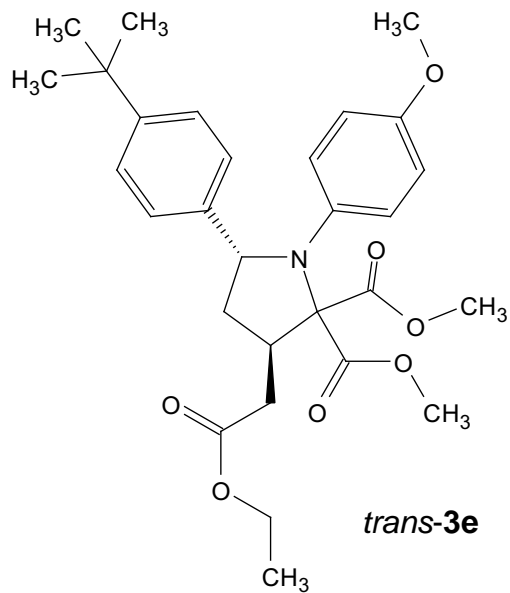
65.33

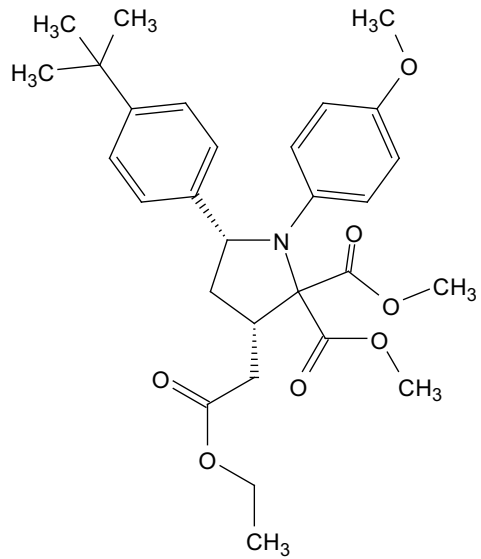
60.67

55.50  
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52.51

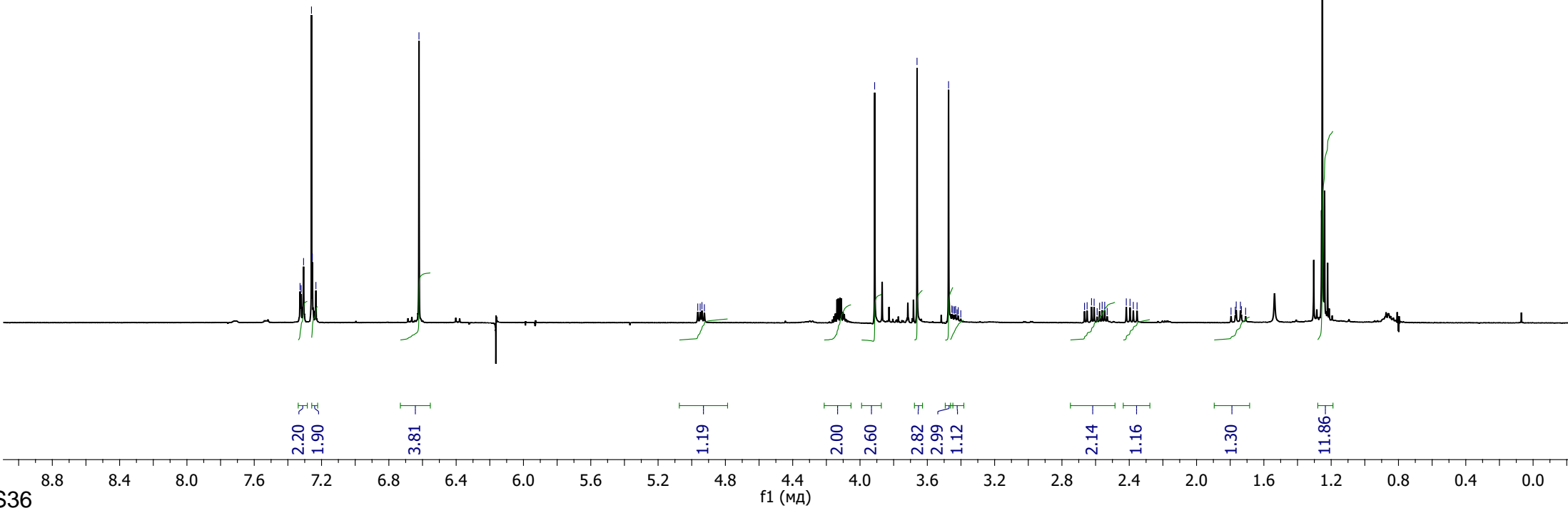
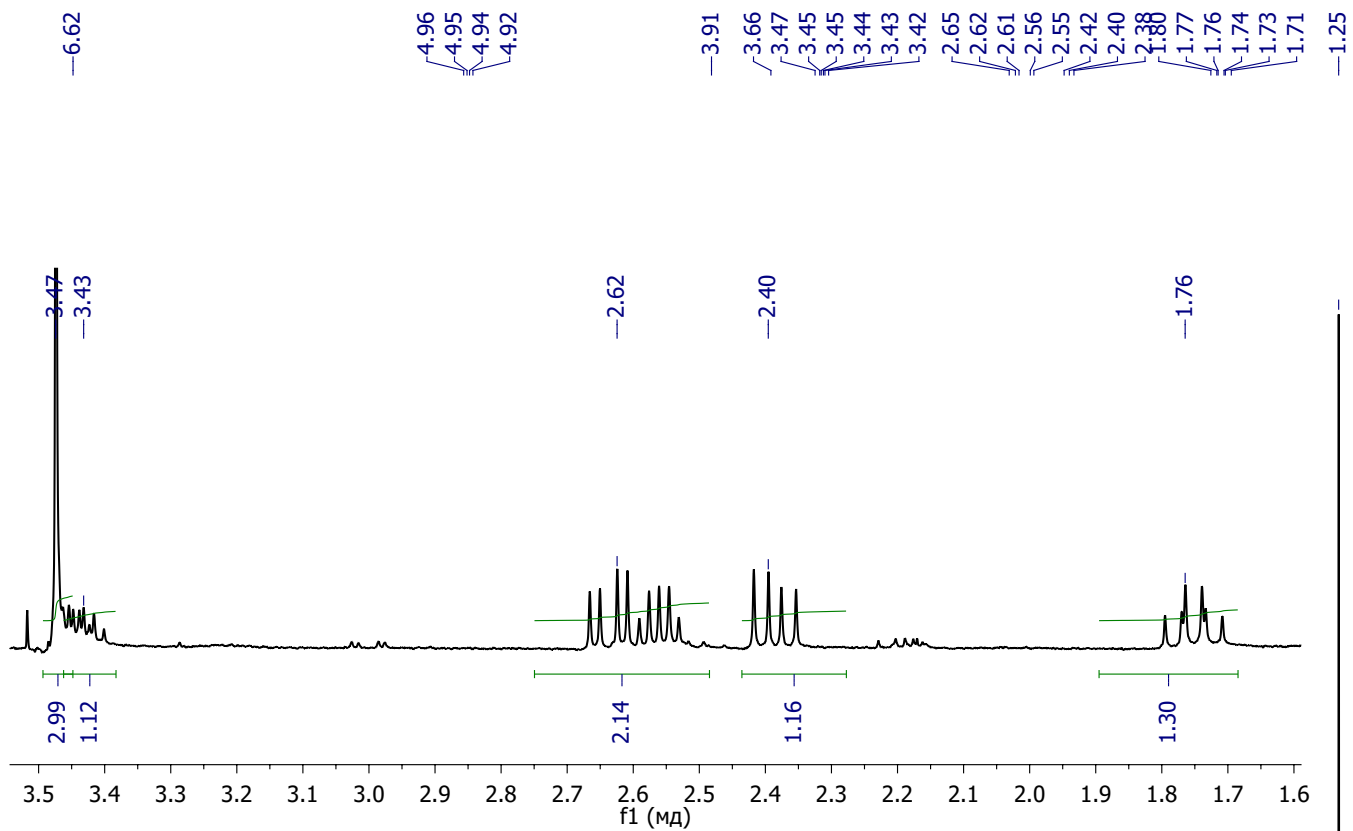
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31.38

14.11

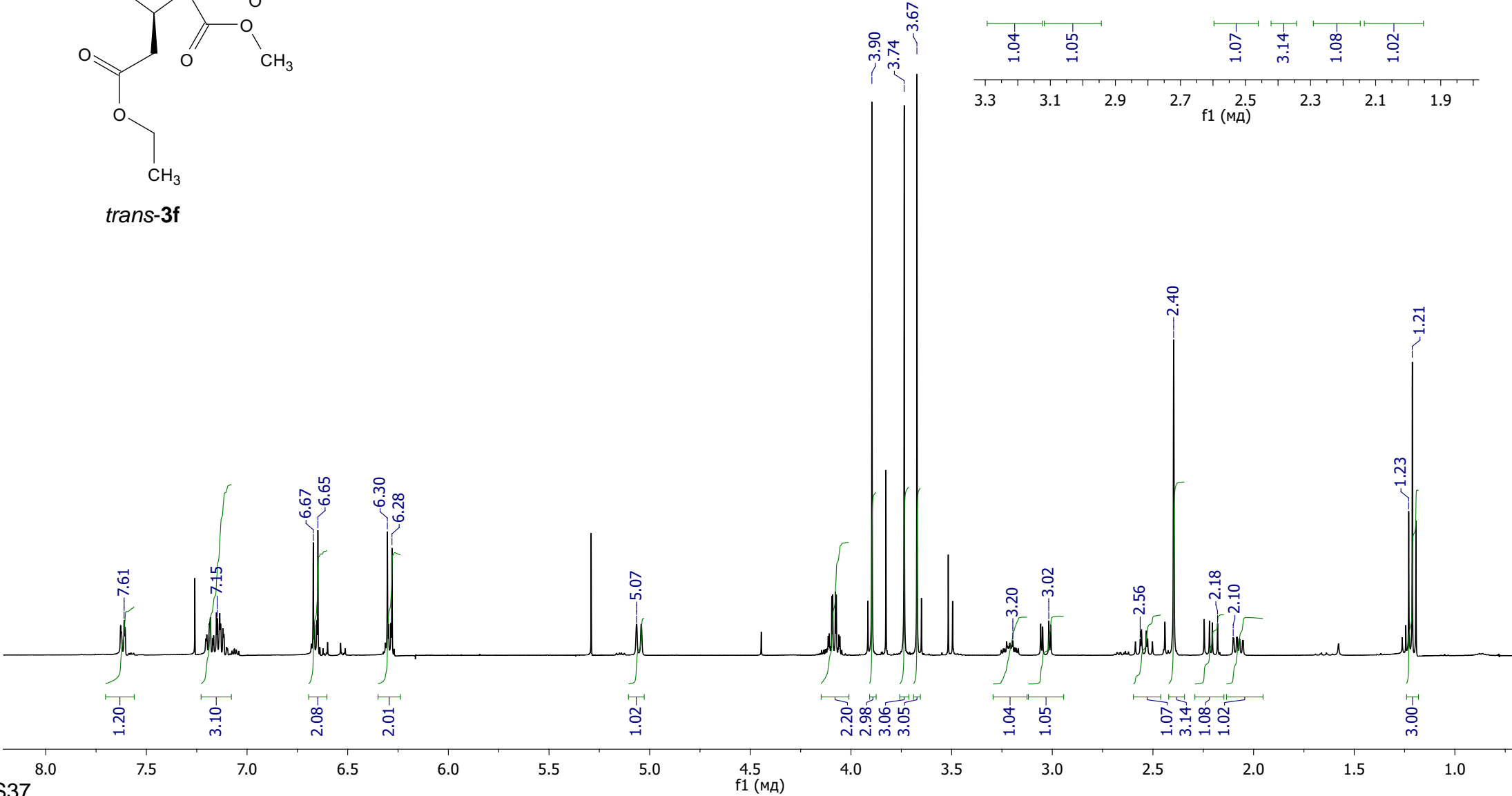
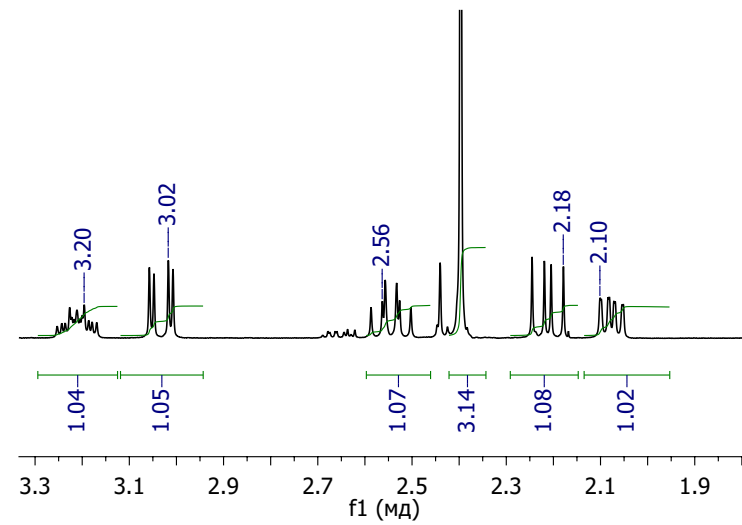
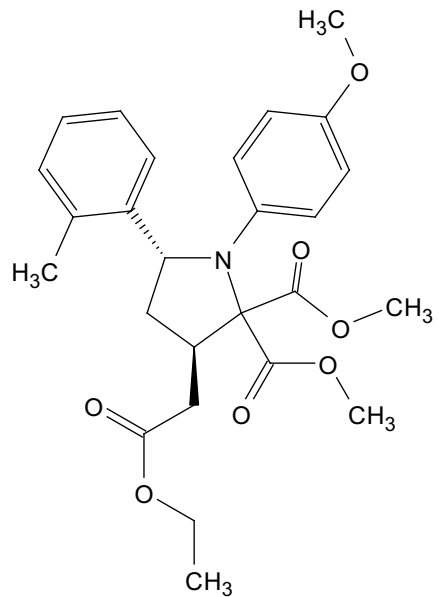


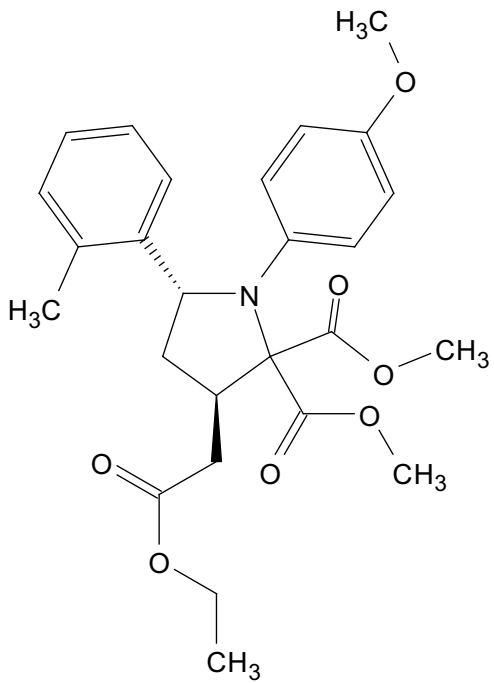


*cis*-3e

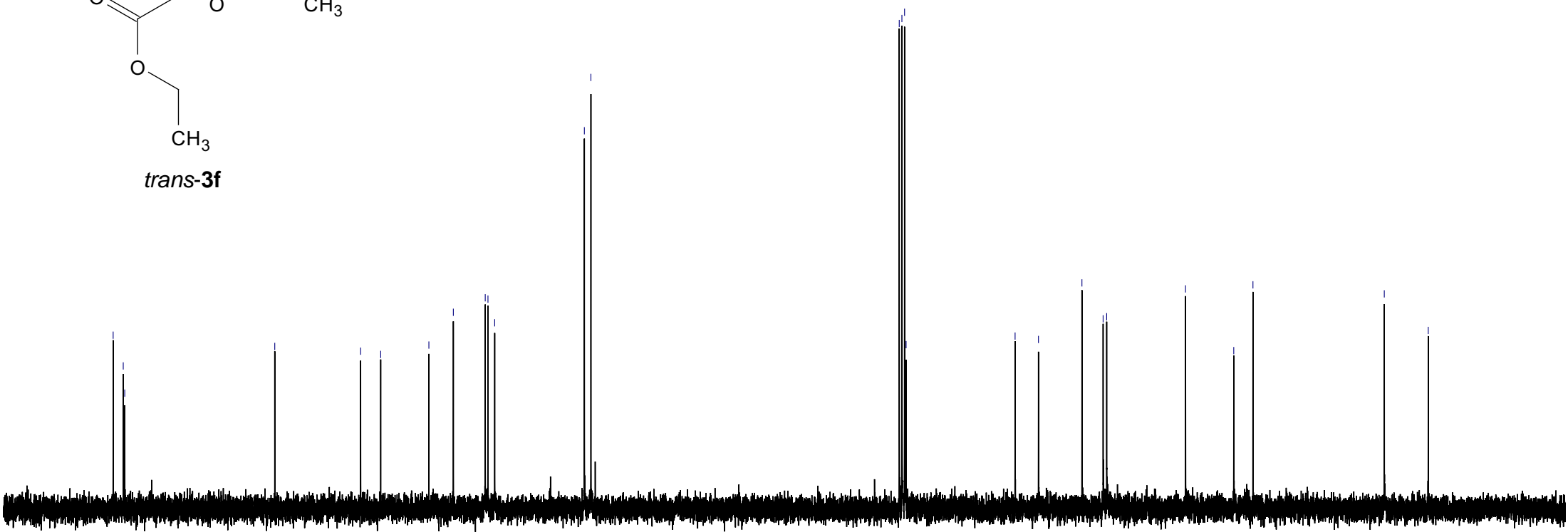


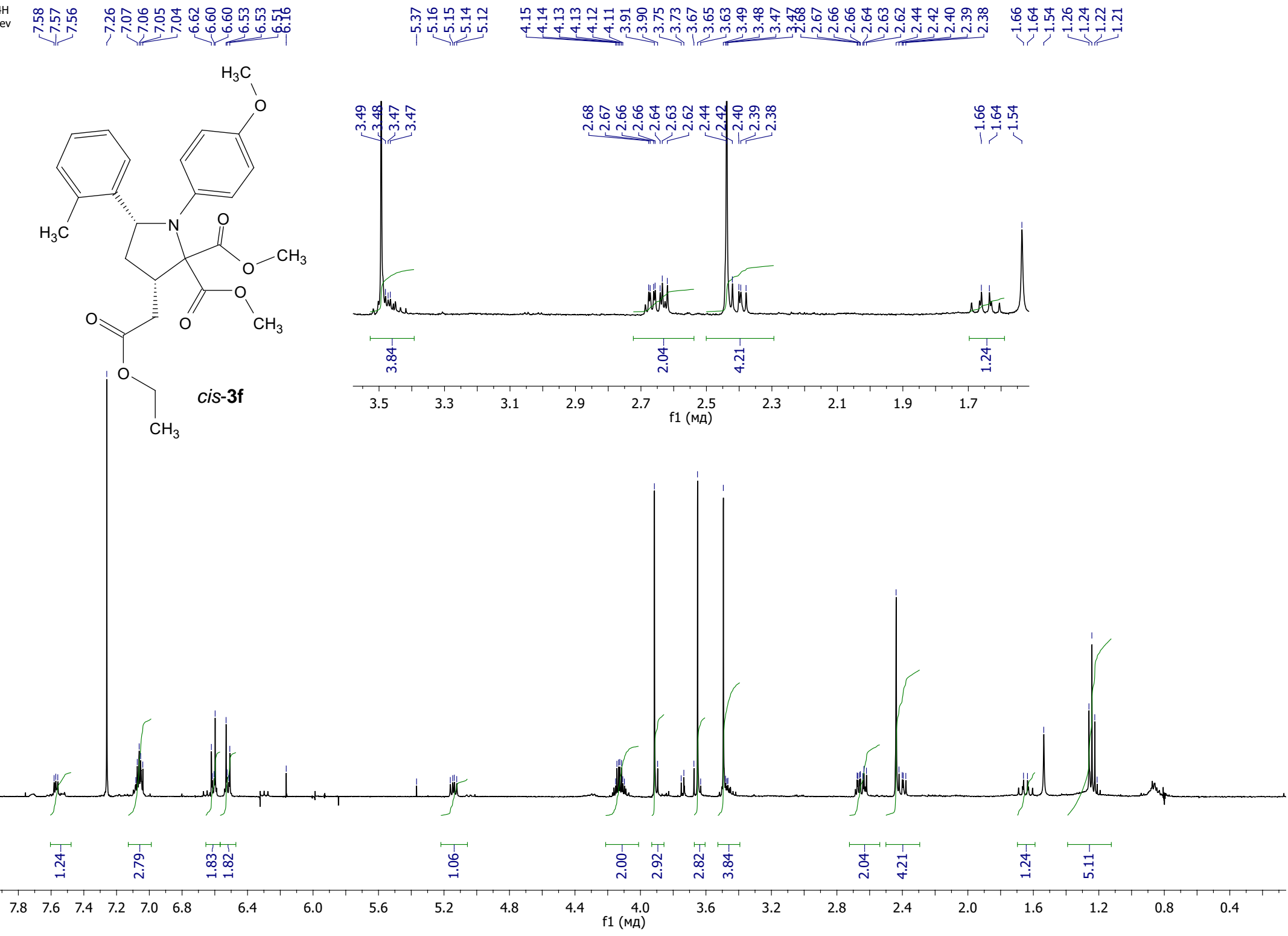
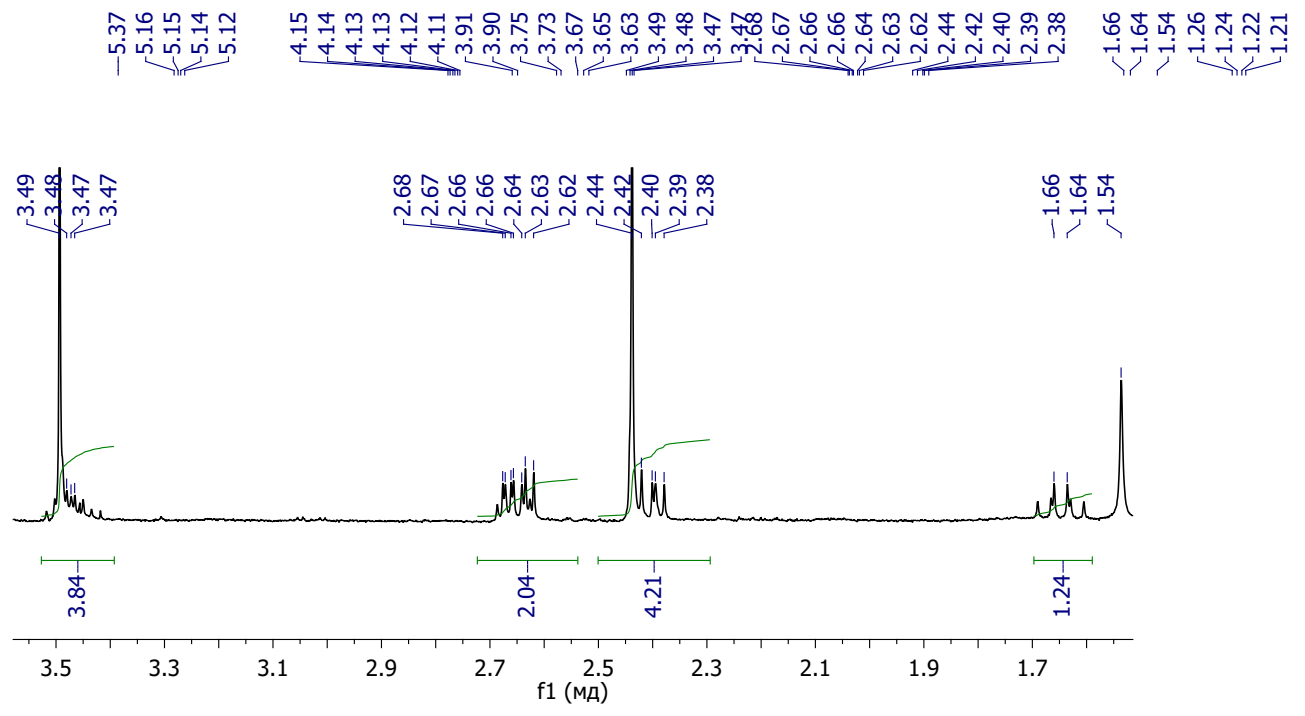
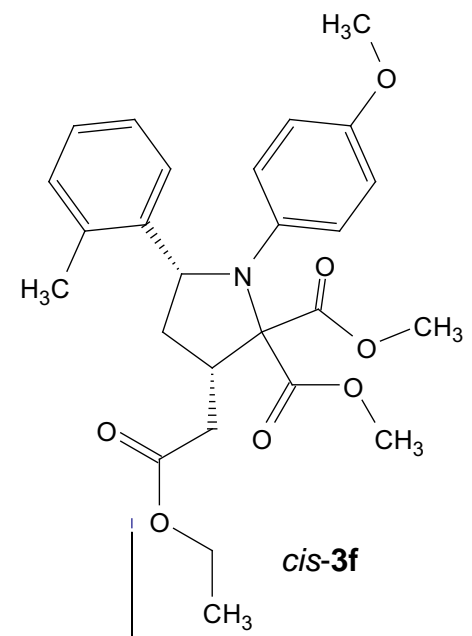






171.26  
170.05  
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125.67  
114.95  
114.17  
77.32  
77.00  
76.69  
76.50  
63.48  
60.68  
55.49  
52.96  
52.53  
43.11  
37.35  
35.05  
19.36  
14.10





7.46  
7.45  
7.32  
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7.23  
7.22  
7.21

6.70  
6.68  
6.67  
6.37  
6.35

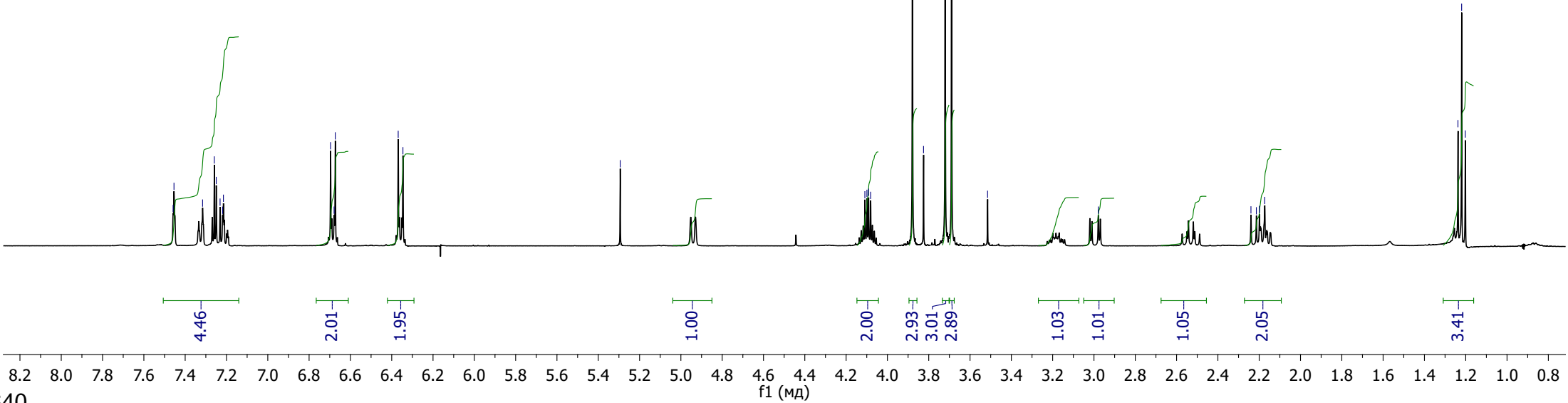
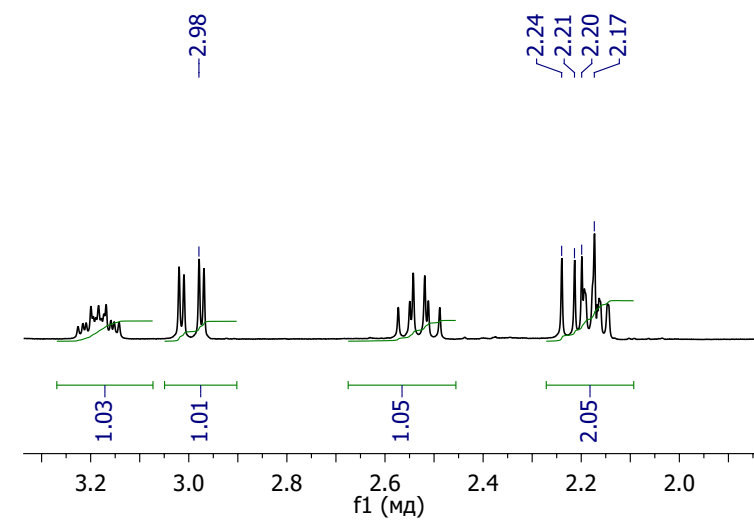
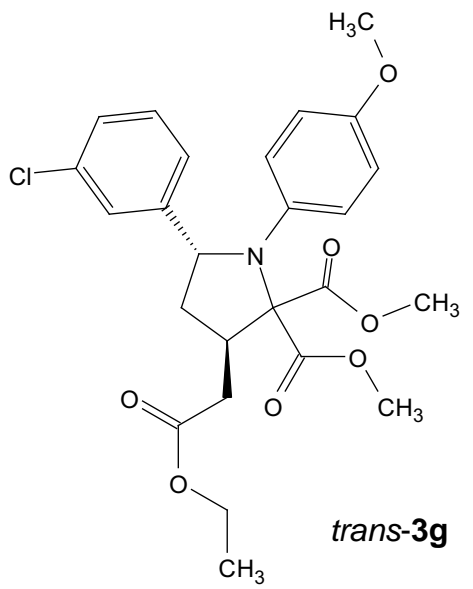
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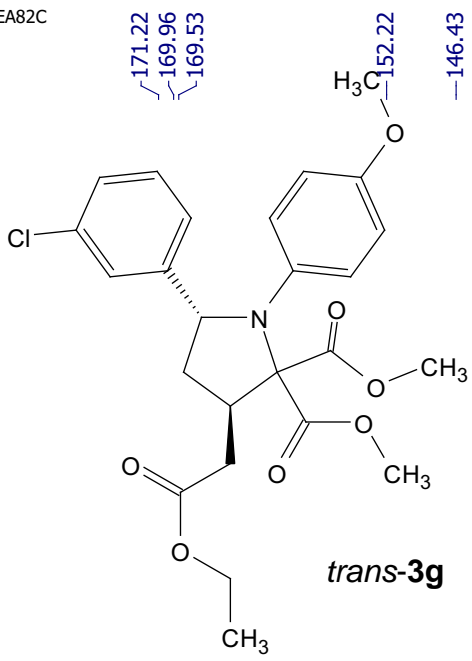
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3.52

2.98

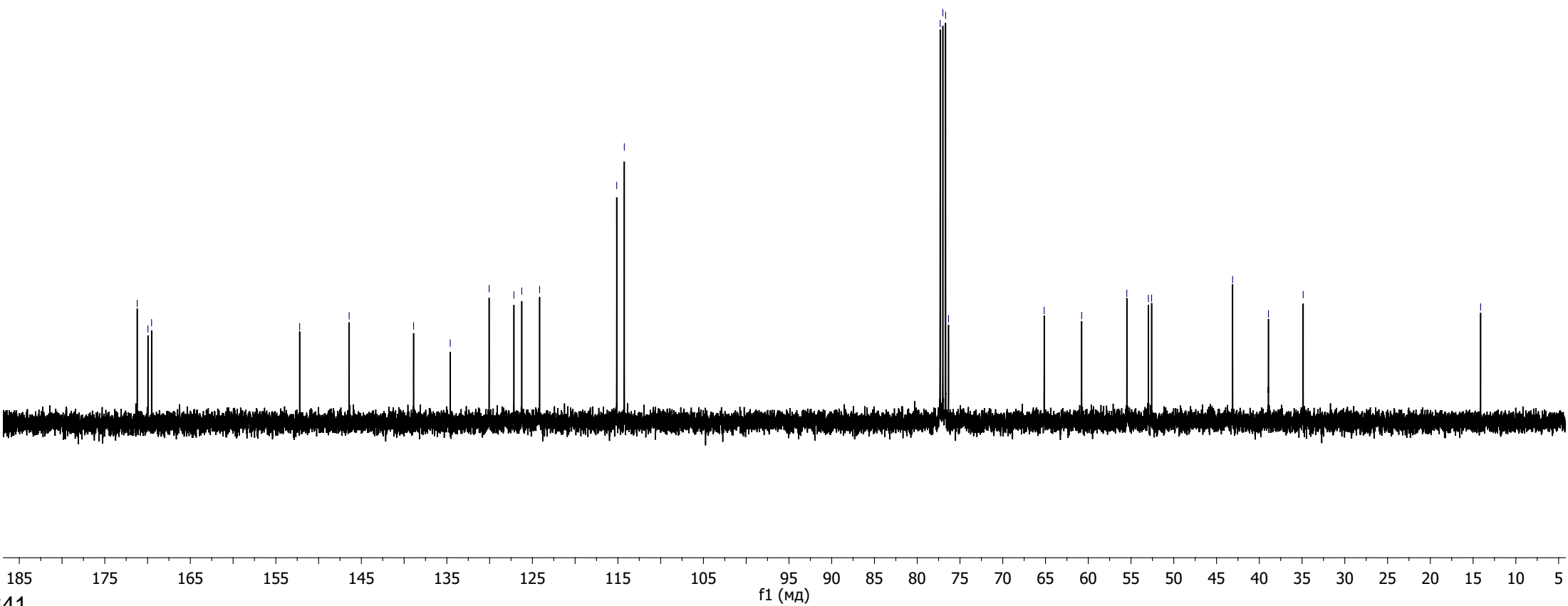
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2.20  
2.17

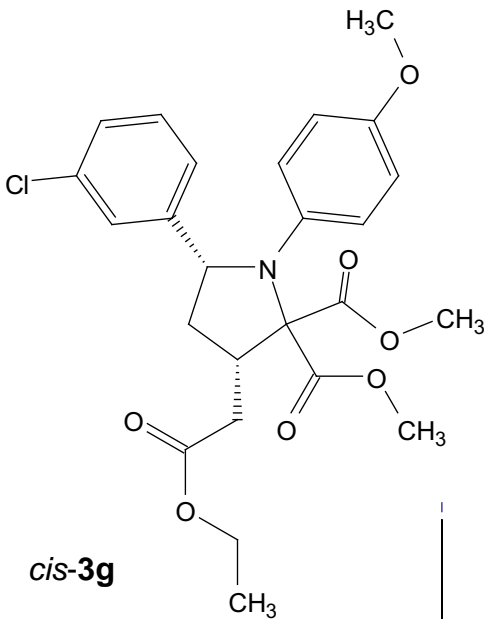
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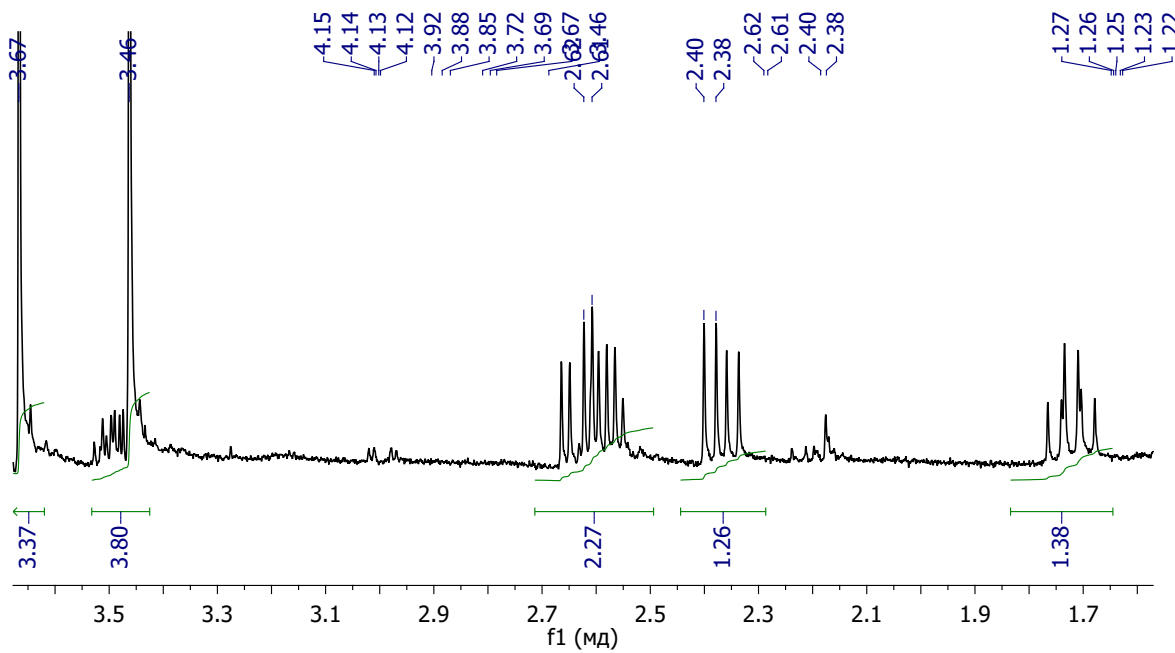


- 171.22
- 169.96
- 169.53
- 152.22
- 146.43
- 138.89
- 134.61
- 130.06
- 127.16
- 126.24
- 124.16
- 115.14
- 114.25
- 77.32
- 77.00
- 76.68
- 76.34
- 65.16
- 60.77
- 55.49
- 52.97
- 52.59
- 43.12
- 38.93
- 34.87
- 14.12



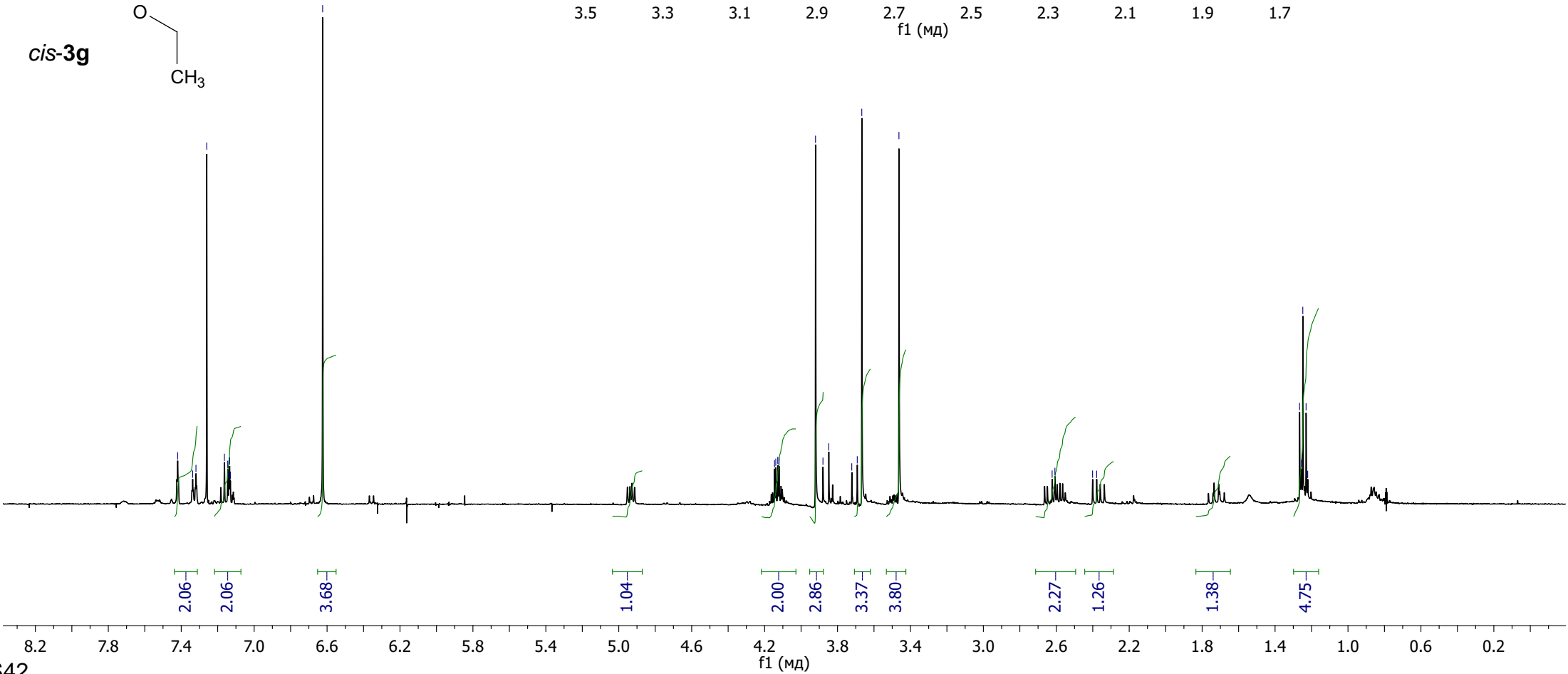


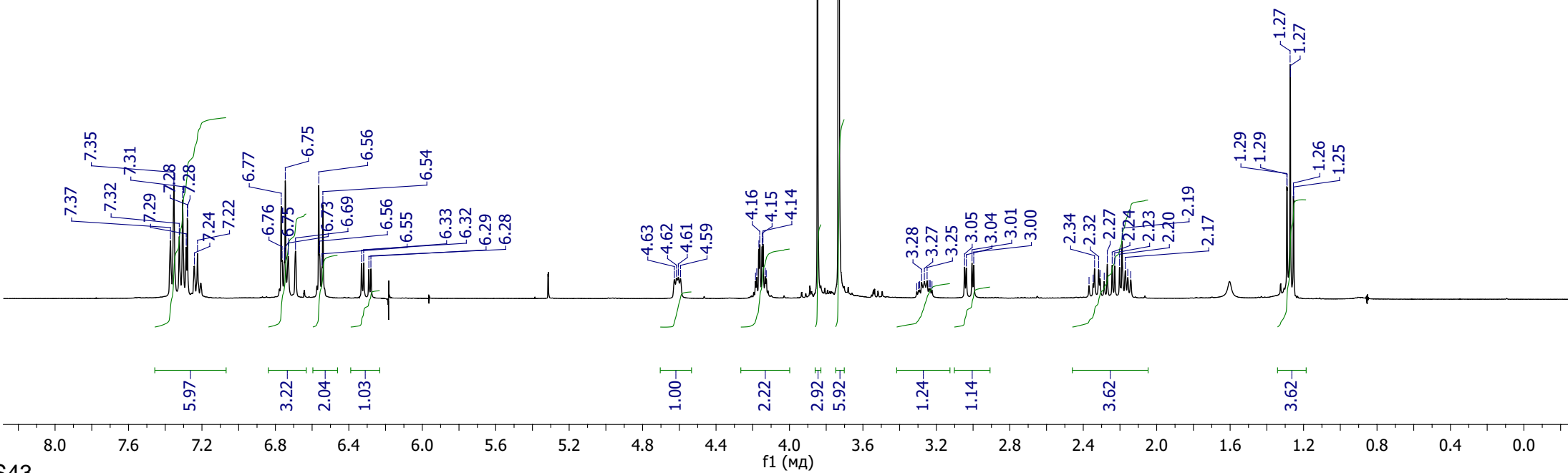
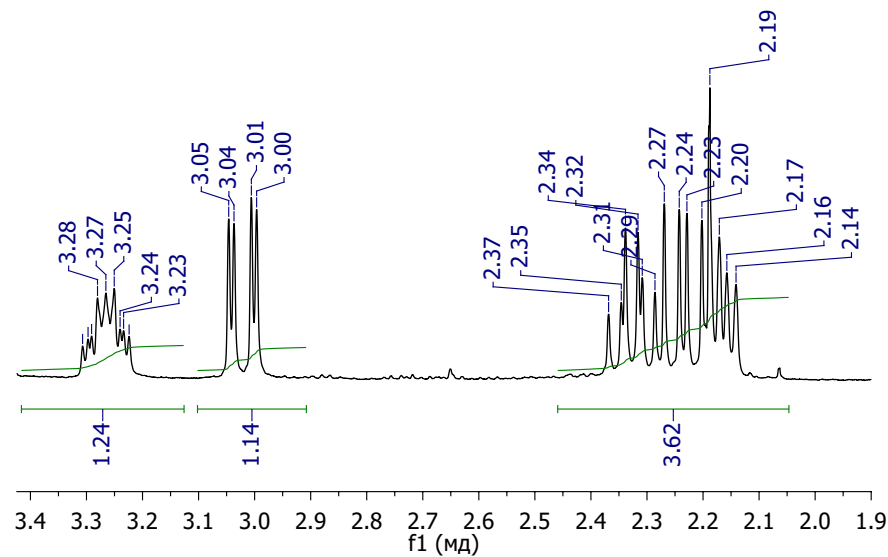
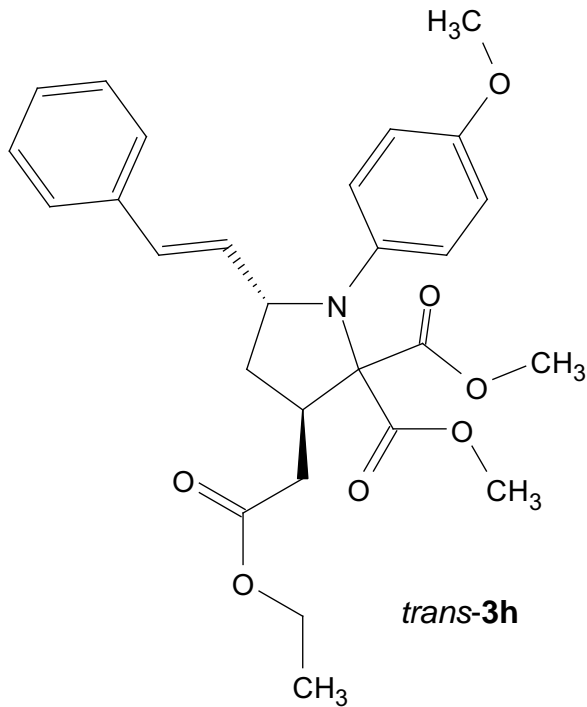
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7.32  
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7.14  
7.14  
7.13  
7.13  
6.62

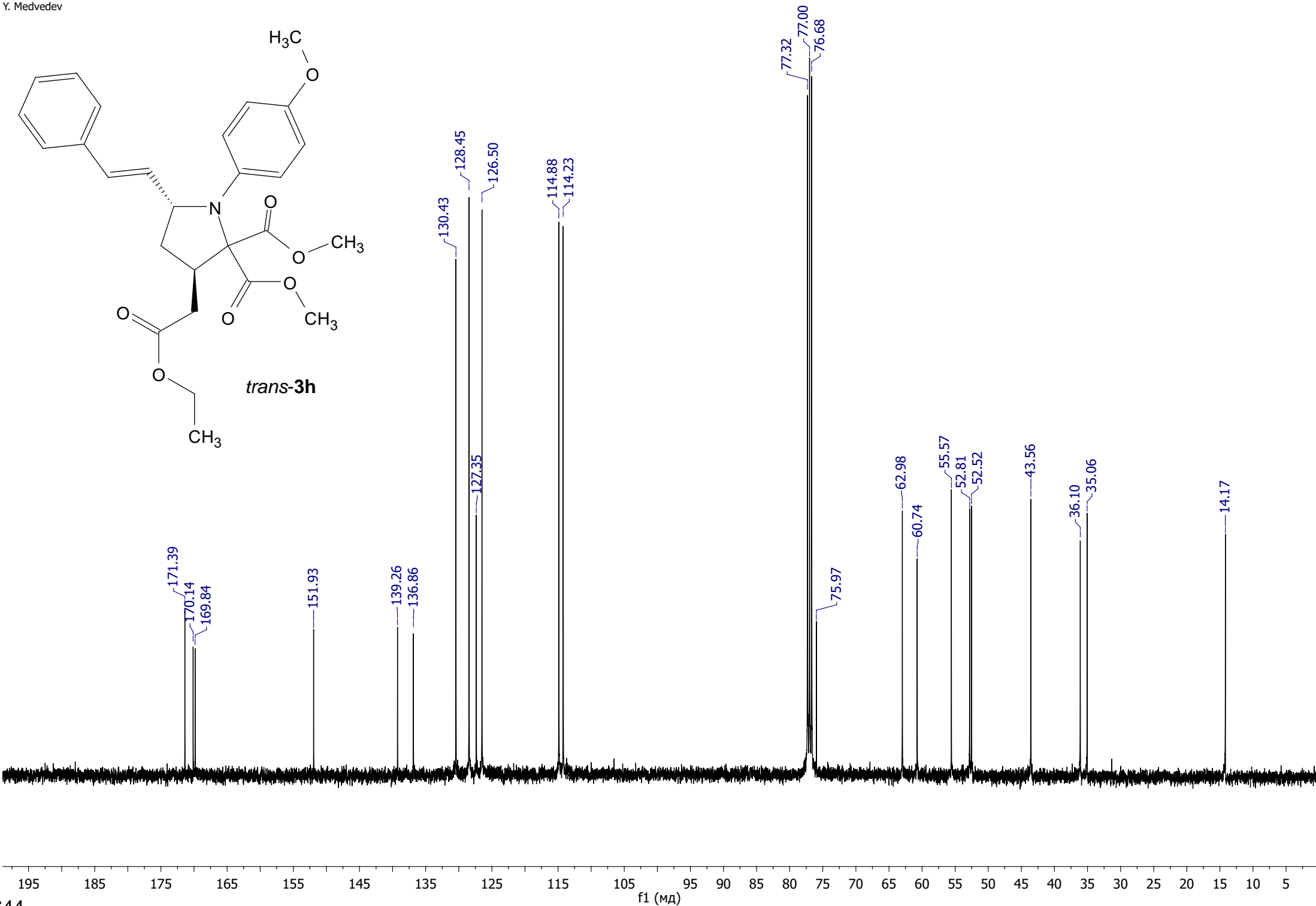
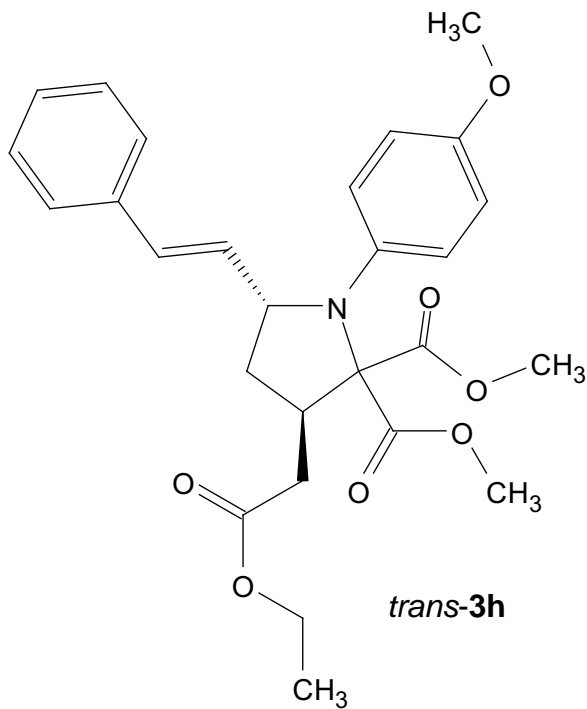


4.15  
4.14  
4.13  
4.12  
3.92  
3.88  
3.85  
3.72  
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2.64  
2.46  
2.40  
2.38  
2.62  
2.61  
2.40  
2.38

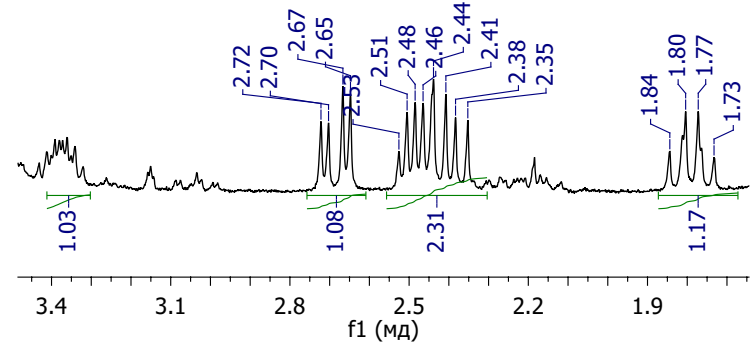
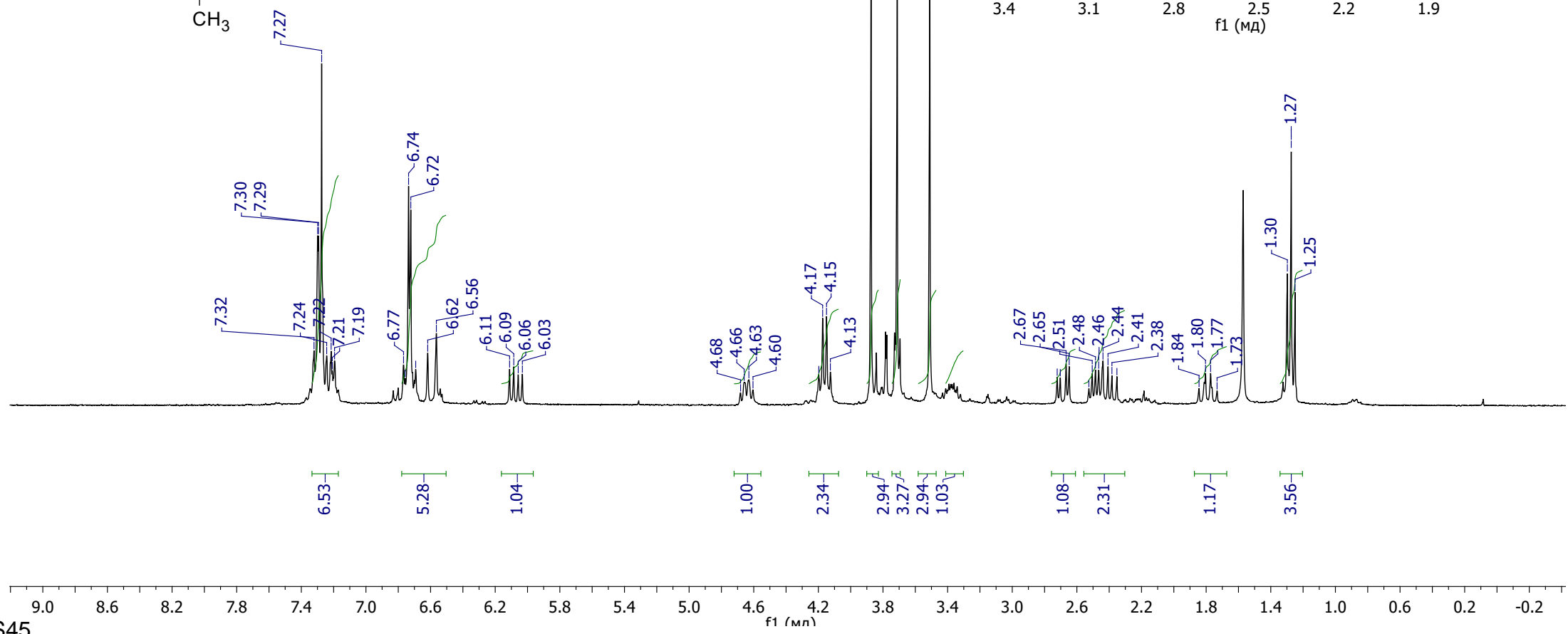
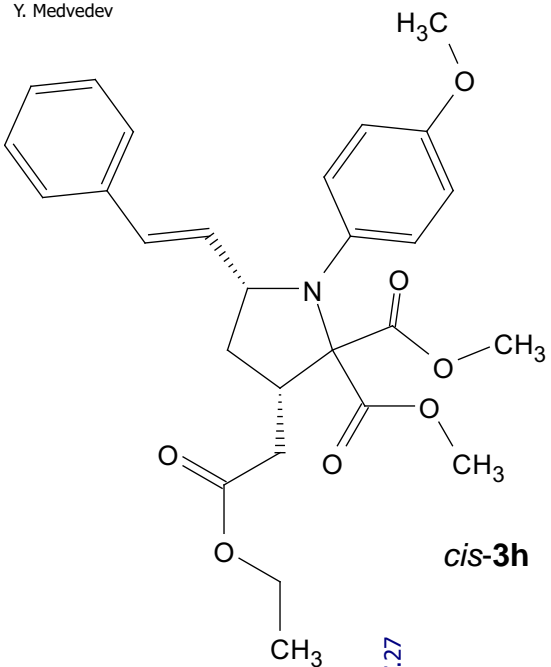
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1.25  
1.23  
1.22











7.54  
7.54  
7.52

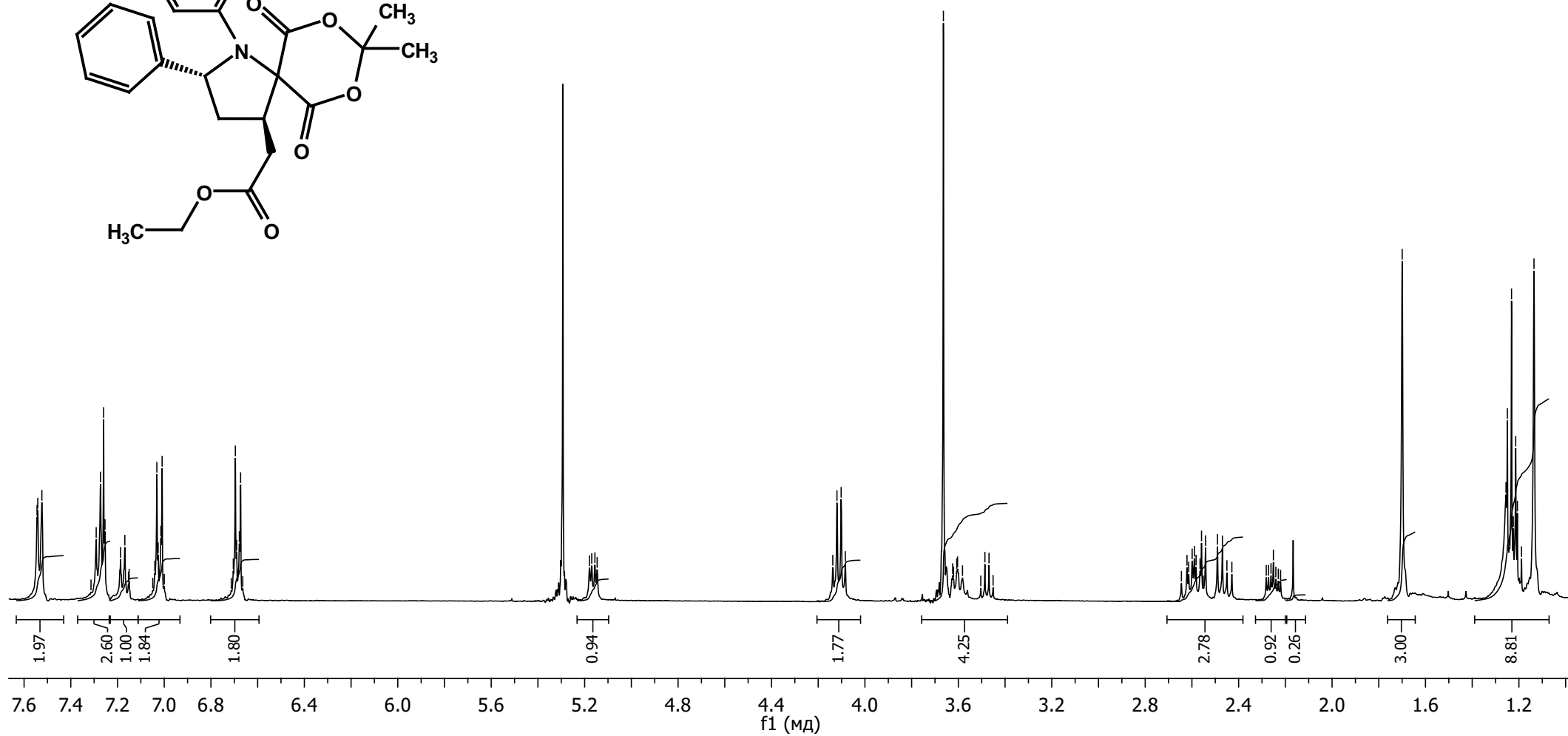
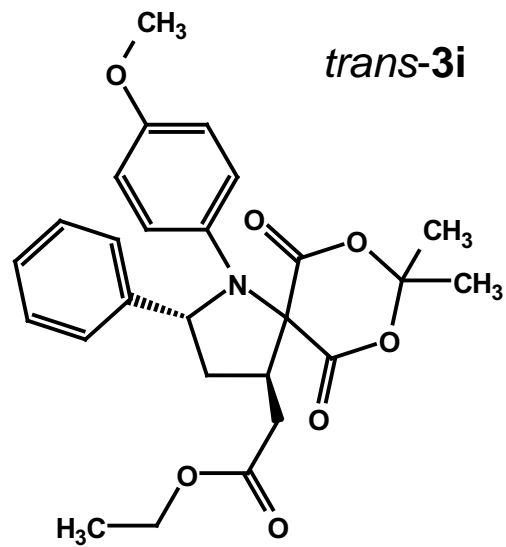
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7.25  
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6.70  
6.70  
6.69  
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6.67  
6.66

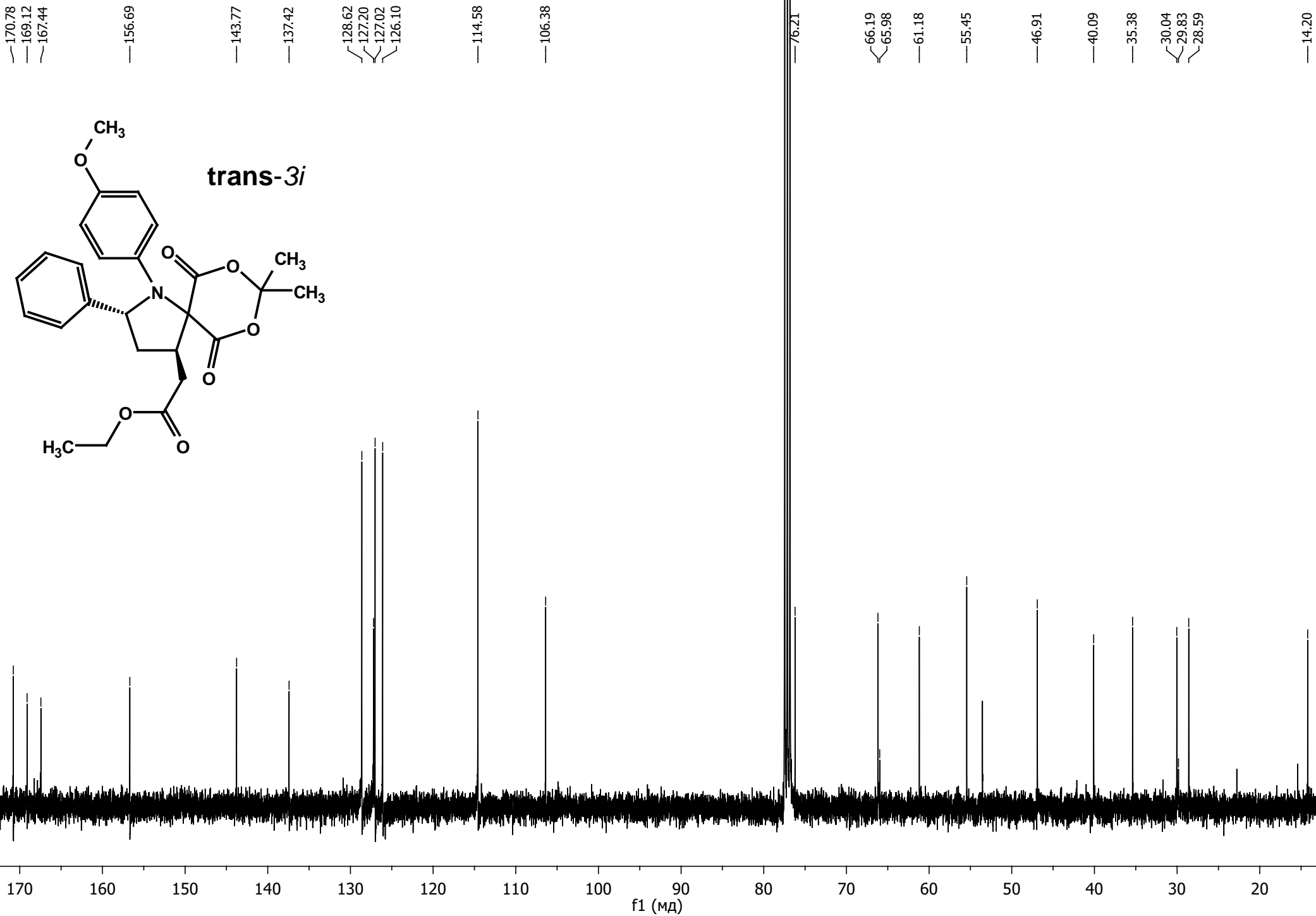
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4.14  
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4.10  
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3.61  
3.60  
3.58  
3.50  
3.49  
3.47  
3.45

2.62  
2.61  
2.60  
2.59  
2.58  
2.57  
2.56  
2.54  
2.49  
2.47  
2.45  
2.43  
2.28  
2.27  
2.26  
2.25

1.26  
1.25  
1.24  
1.23  
1.22  
1.21  
1.21  
1.14





7.48  
7.47  
7.45  
7.31  
7.29  
7.29  
7.27  
7.23  
7.21

6.63  
6.62  
6.61

6.28  
6.26

5.03  
5.02  
5.01  
4.99

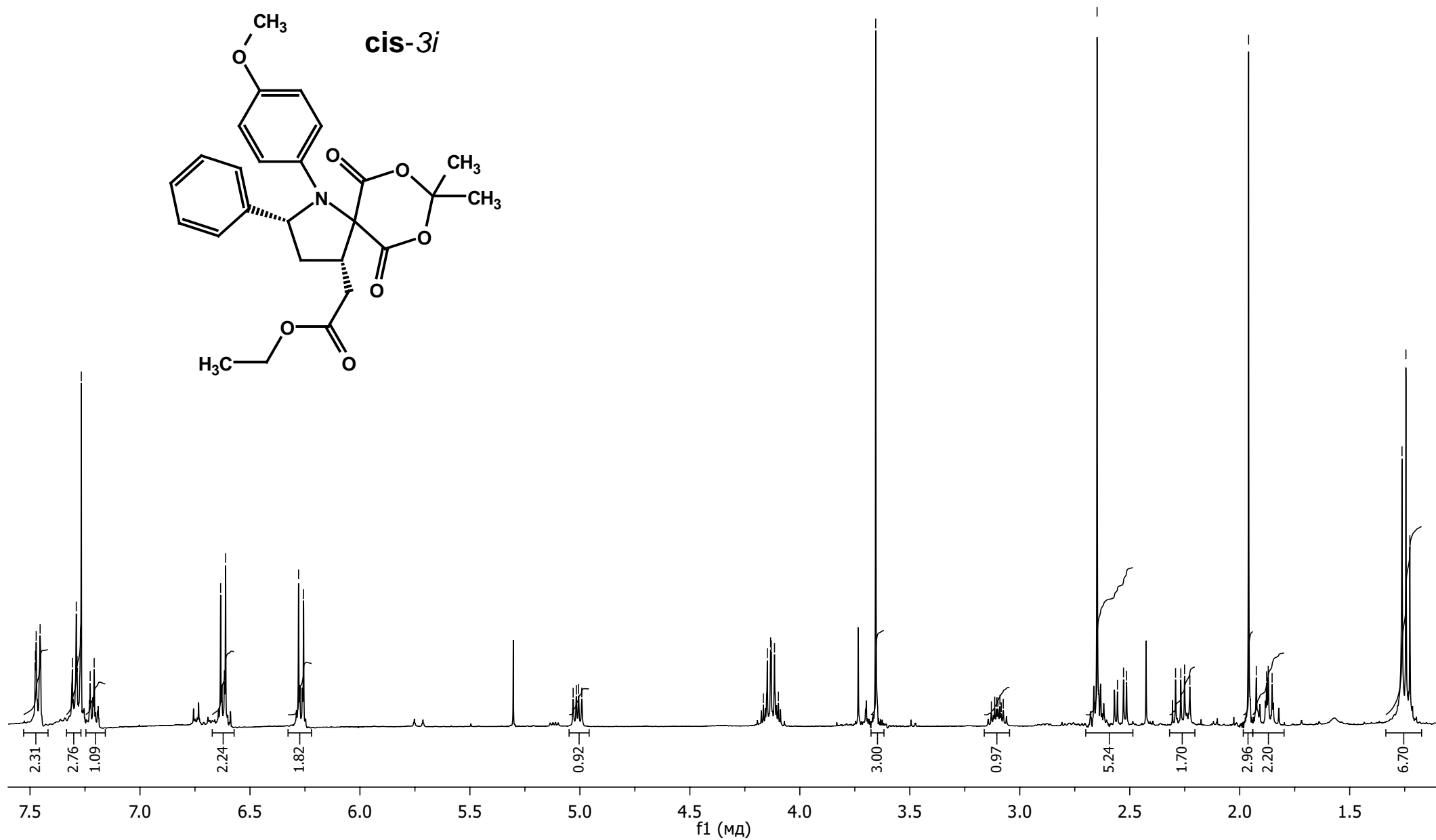
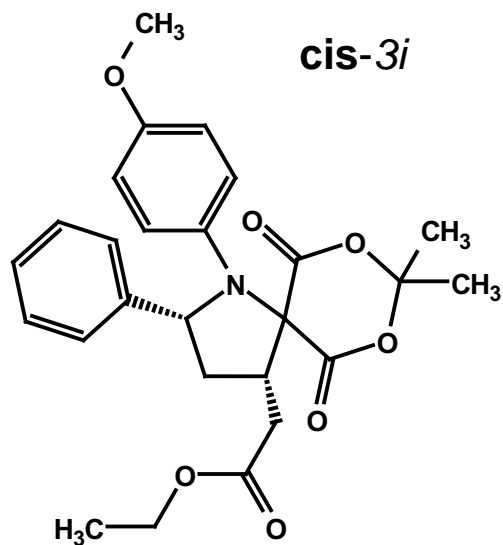
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4.13  
4.12  
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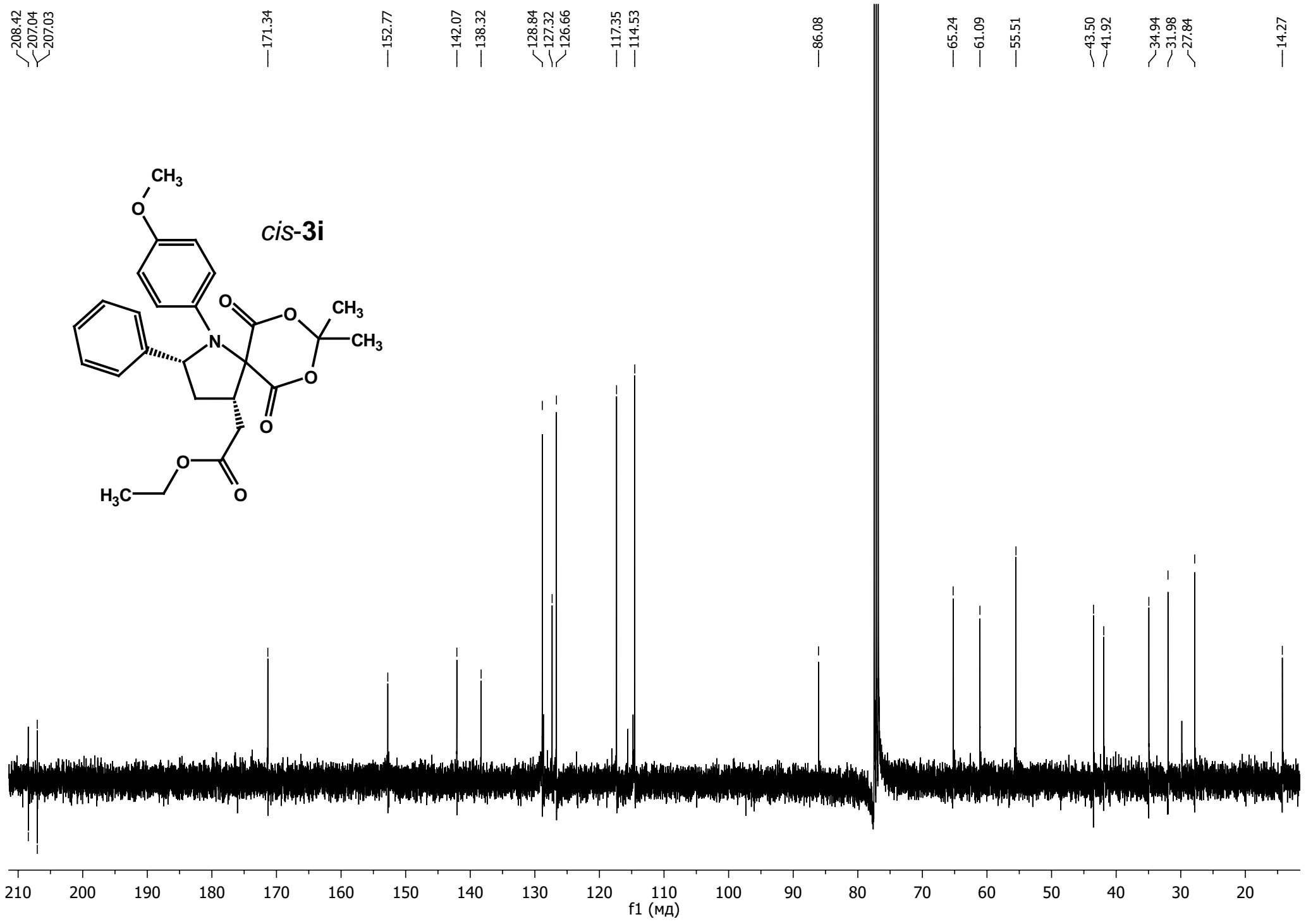
3.65

3.13  
3.11  
3.10  
3.10  
3.09  
3.08  
3.08

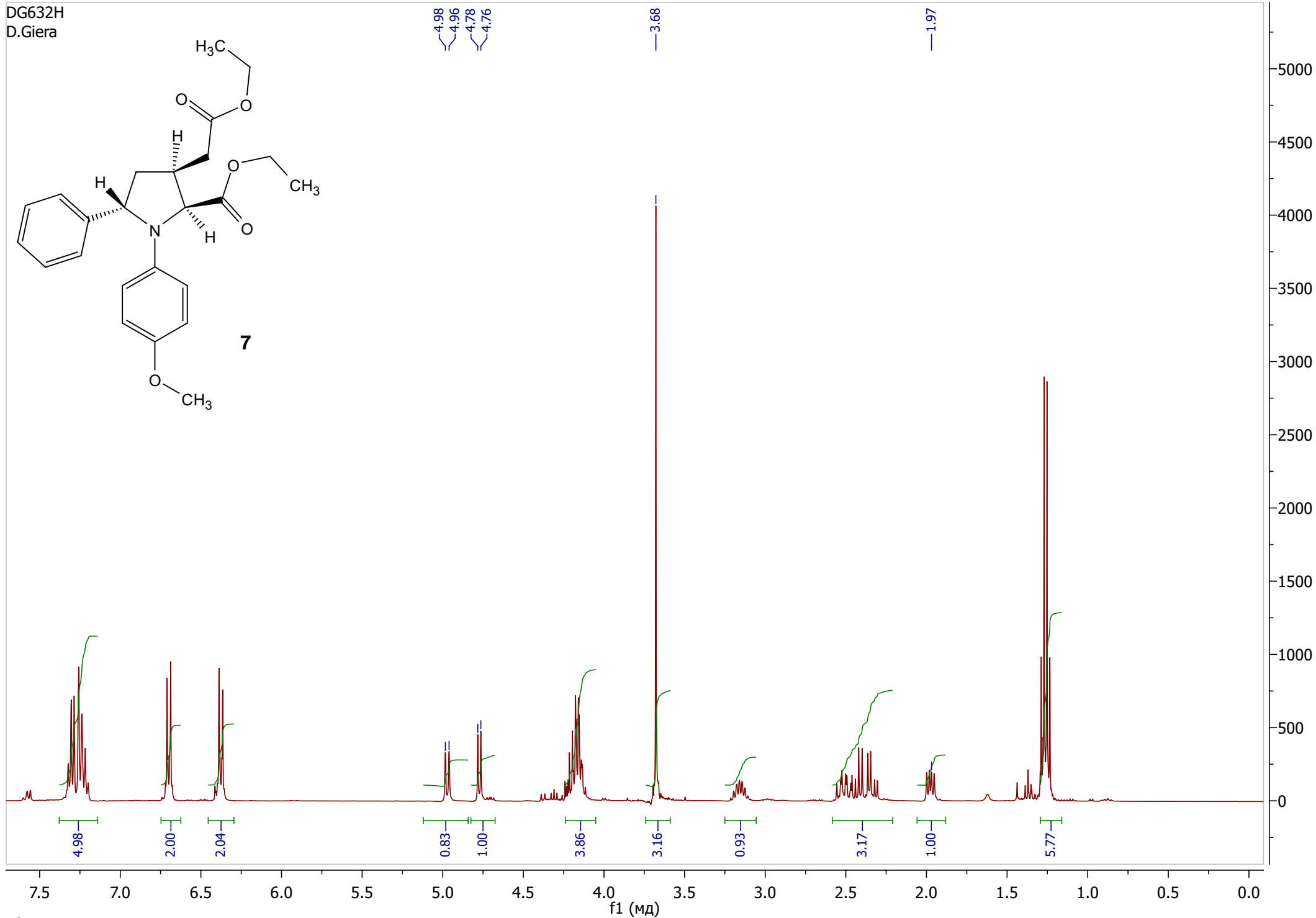
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2.56  
2.53  
2.51  
2.29  
2.27  
2.25  
2.23  
1.96  
1.92  
1.88  
1.87  
1.85

1.26  
1.24  
1.23

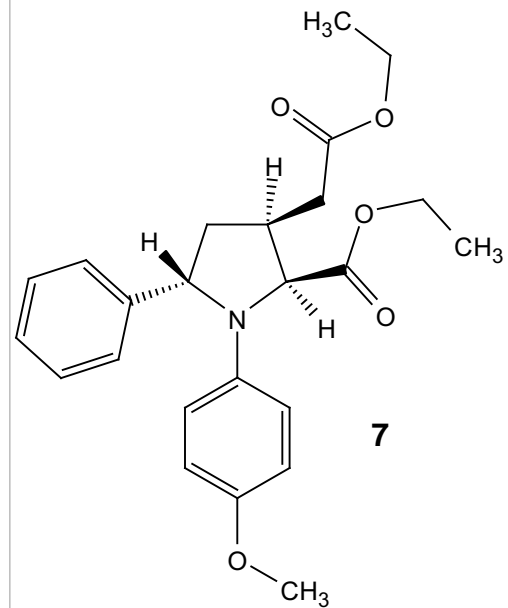




DG632H  
D.Giera



DG632C  
D.Giera



172.82  
171.46

151.37

144.37

139.87

128.61

126.76

125.76

114.73

113.50

77.32

77.00

76.68

64.94

62.67

60.78

60.61

55.57

39.35

35.39

34.82

14.25

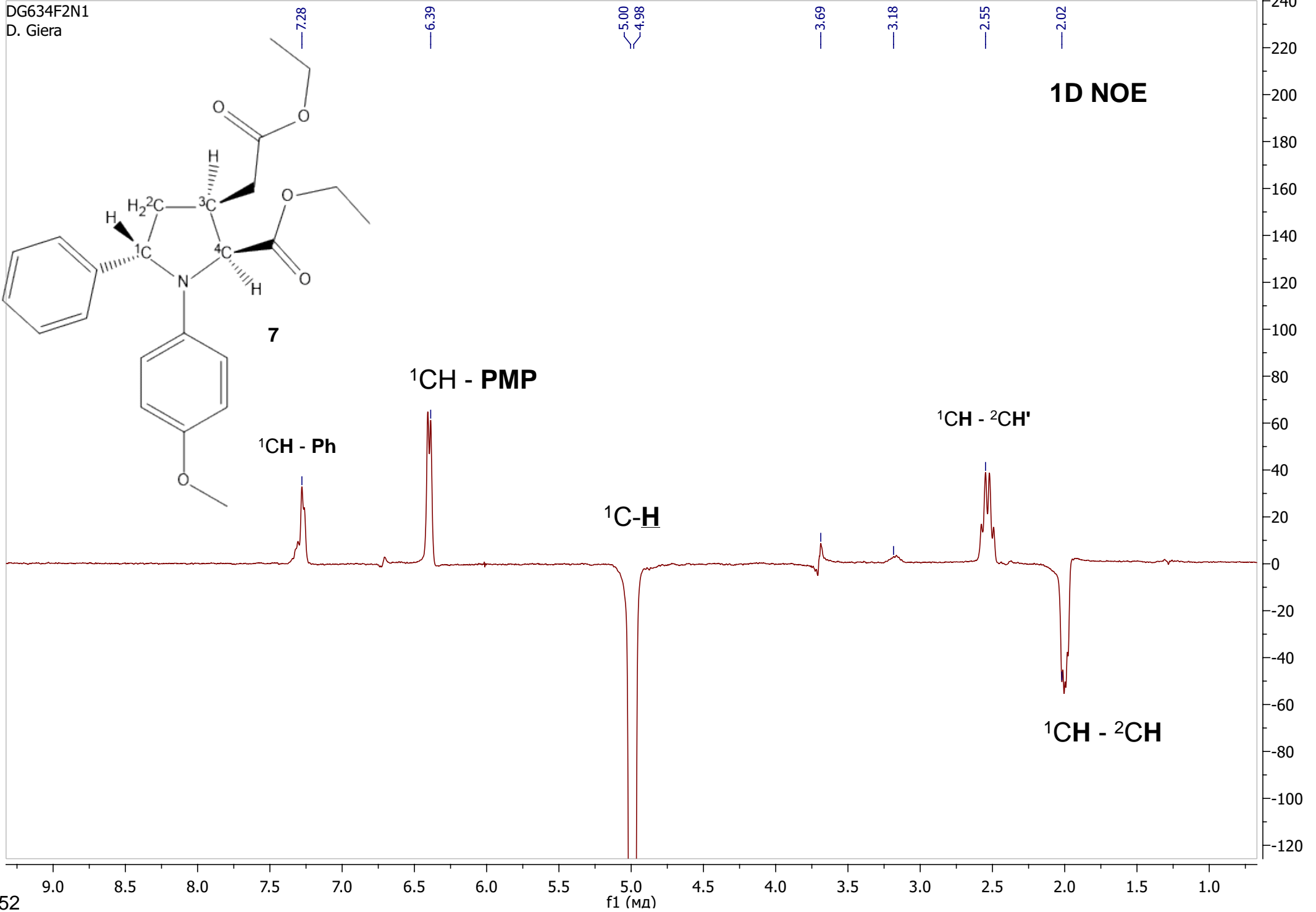
14.16

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

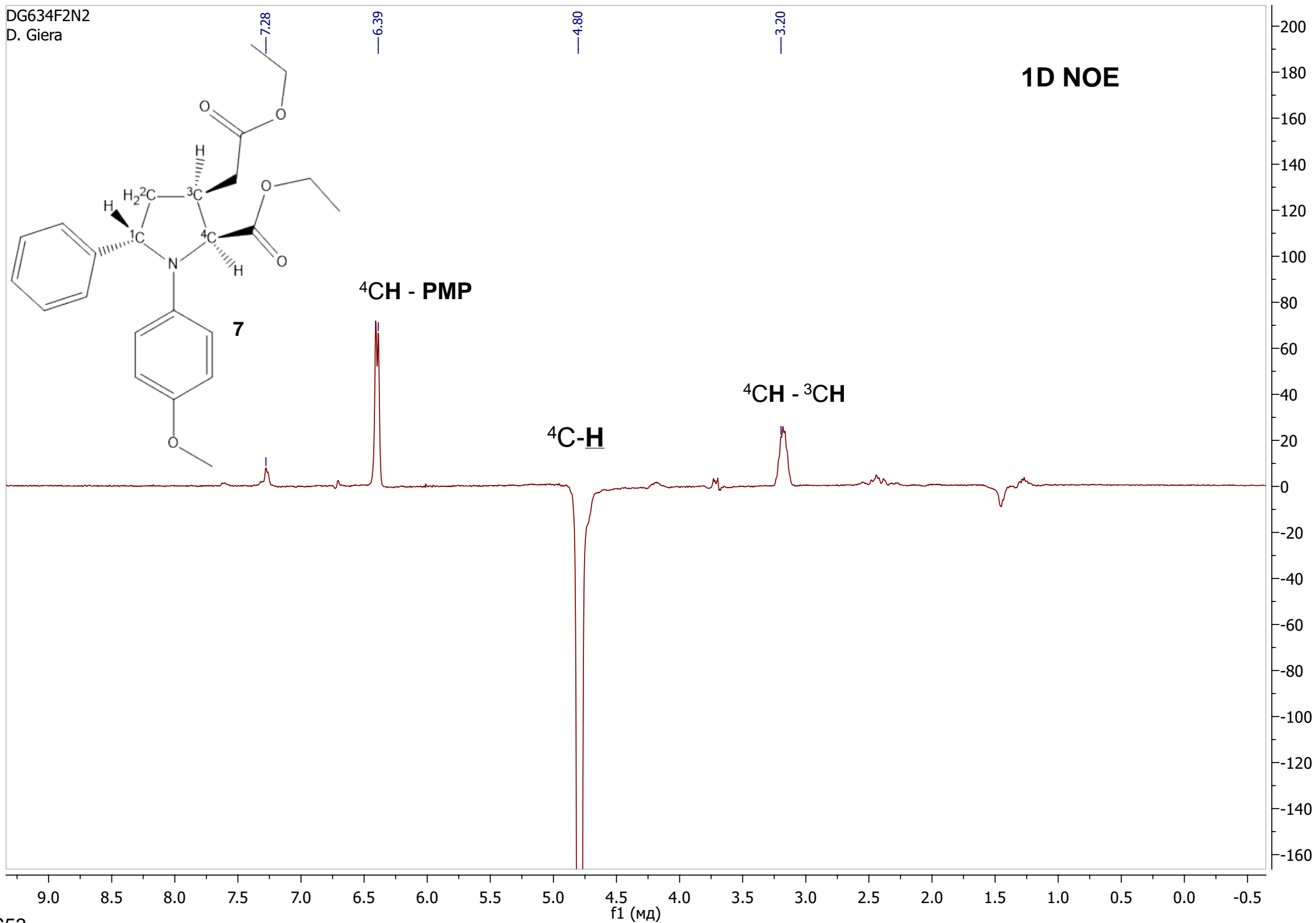
f1 (MД)

50000  
45000  
40000  
35000  
30000  
25000  
20000  
15000  
10000  
5000  
0

DG634F2N1  
D. Giera







ESI positiv, Galkina OG-1F1 in MeOH, 28/09/10

a.i.

2.5e+07

2.0e+07

1.5e+07

1.0e+07

5.0e+06

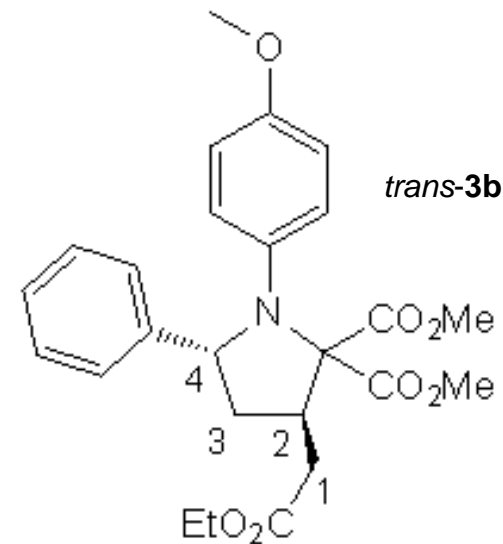
0.

236.07163

478.18339

691.26769

933.37838



Calculated exact mass  
OG-1F1

[M + Na]<sup>+</sup> 478,18362

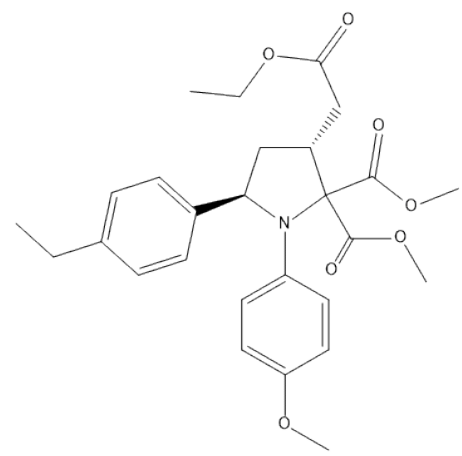
[2M + Na]<sup>+</sup> 933,37803

S54

100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 m/z

ESI positiv, Medvedev XMEA-16 in MeOH , 08/11/13

a.i.



3.5e+07  
3.0e+07  
2.5e+07  
2.0e+07  
1.5e+07  
1.0e+07  
5.0e+06  
0.

506.21538

989.44132

990.44459

991.44886

507.21911

508.22163

503

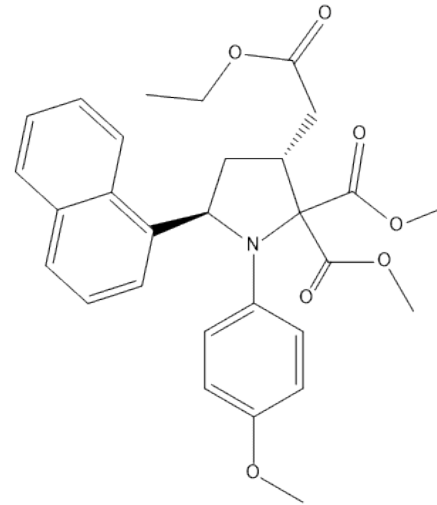
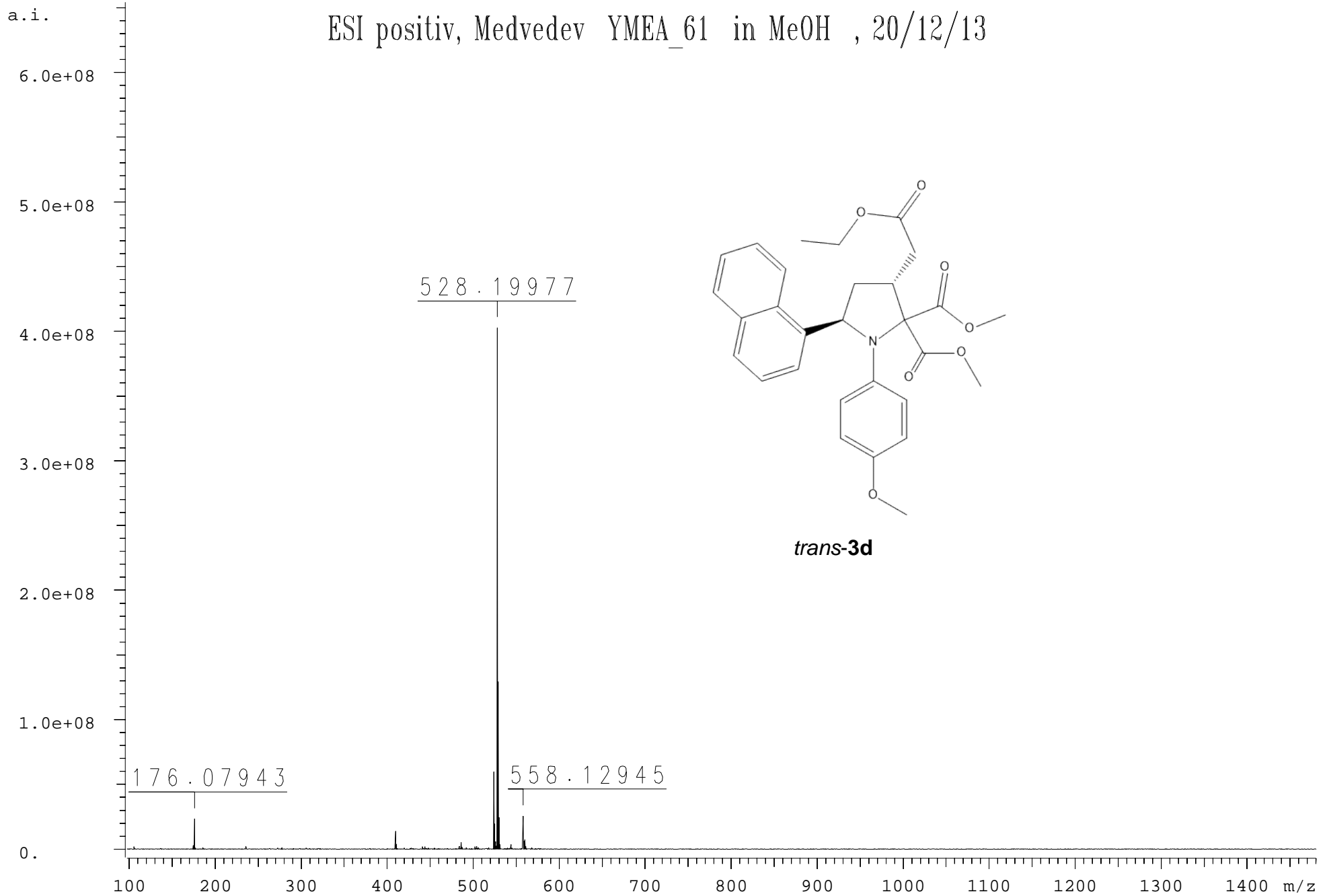
508

513

m/z

S55

ESI positiv, Medvedev YMEA\_61 in MeOH , 20/12/13



*trans*-3d

ESI positiv, Medvedev YMEA\_80 in MeOH , 20/12/13

a.i.

7.0e+08

6.0e+08

5.0e+08

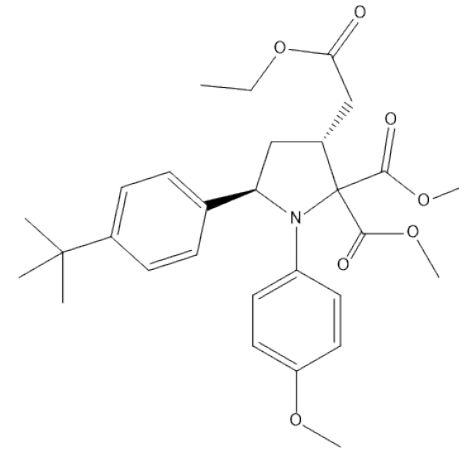
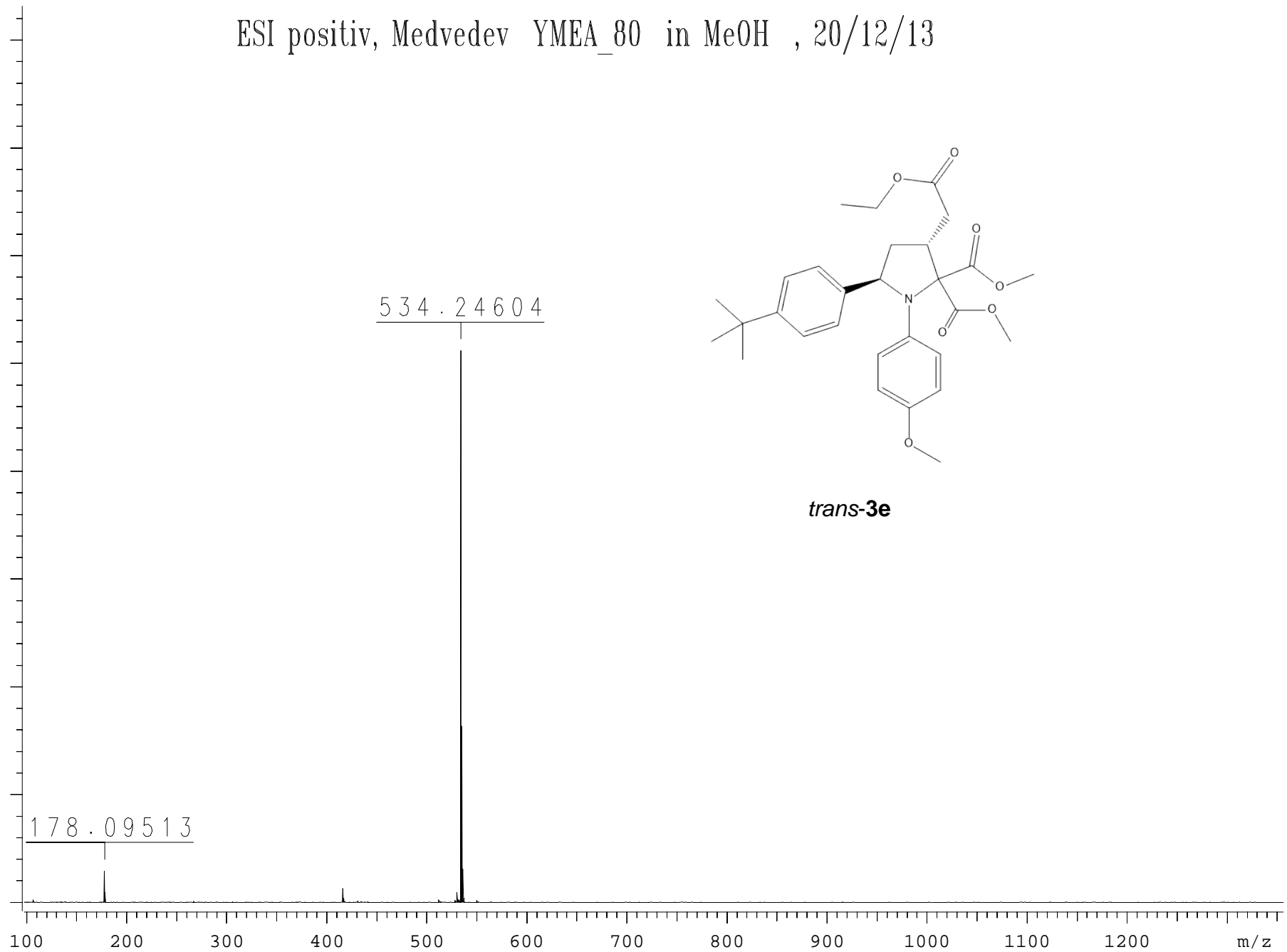
4.0e+08

3.0e+08

2.0e+08

1.0e+08

0.



*trans-3e*

ESI positiv, Medvedev YMEA\_81 in MeOH , 20/12/13

a.i.

5.0e+08

4.0e+08

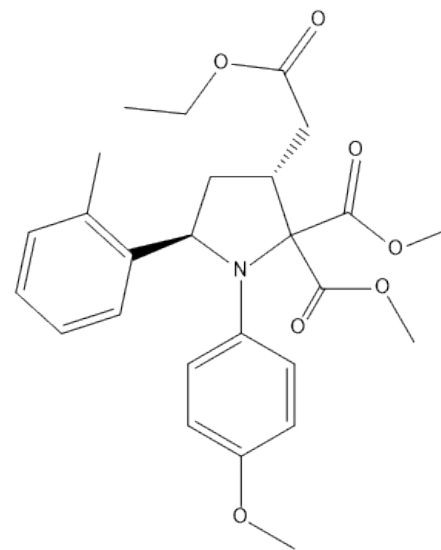
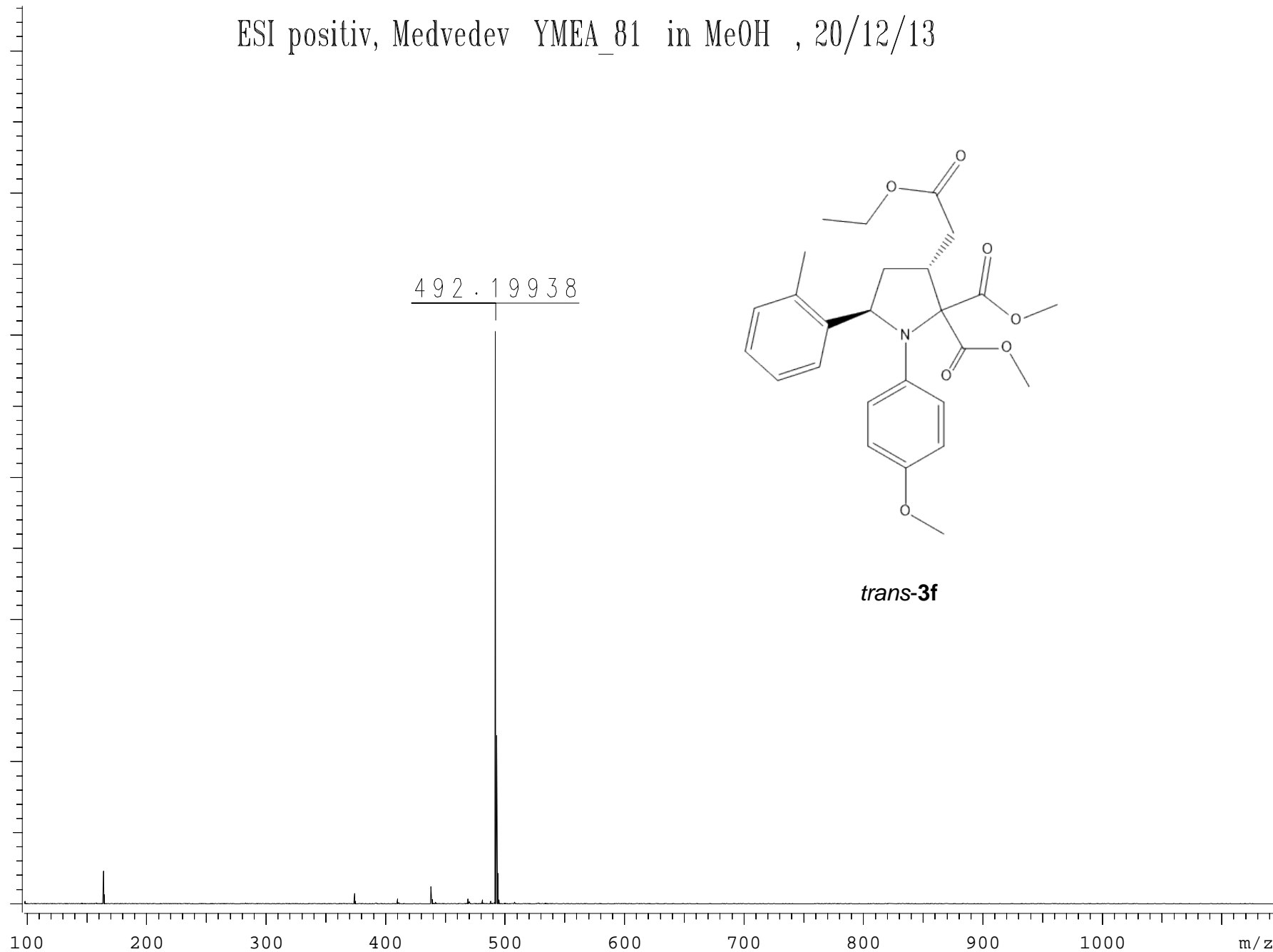
3.0e+08

2.0e+08

1.0e+08

0.

492.19938

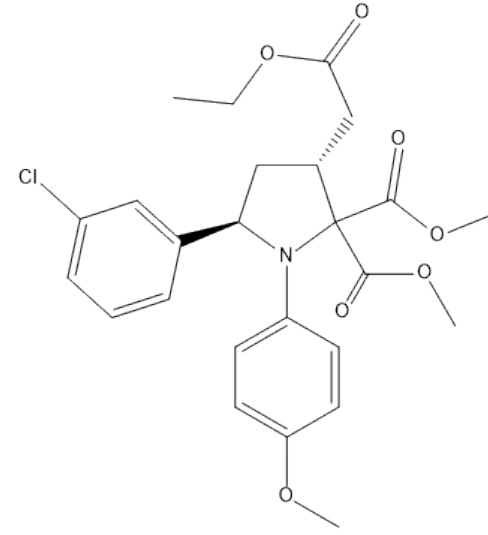
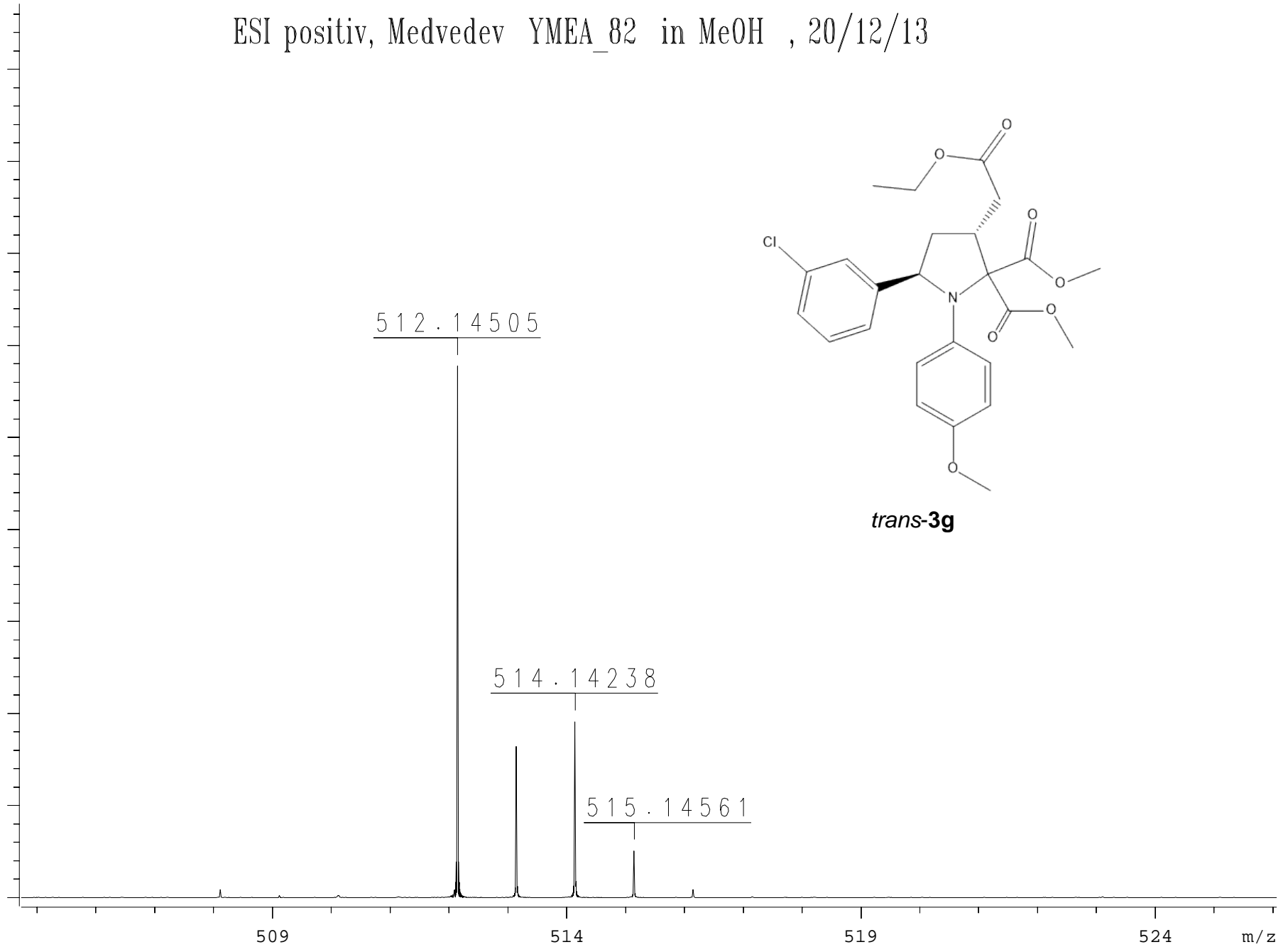


*trans*-3f

ESI positiv, Medvedev YMEA\_82 in MeOH , 20/12/13

a.i.

8.0e+08  
7.0e+08  
6.0e+08  
5.0e+08  
4.0e+08  
3.0e+08  
2.0e+08  
1.0e+08  
0.



**trans-3g**

ESI positiv, Medvedev YMEA\_86 in MeOH , 19/12/13

a.i.

4.5e+07

4.0e+07

3.5e+07

3.0e+07

2.5e+07

2.0e+07

1.5e+07

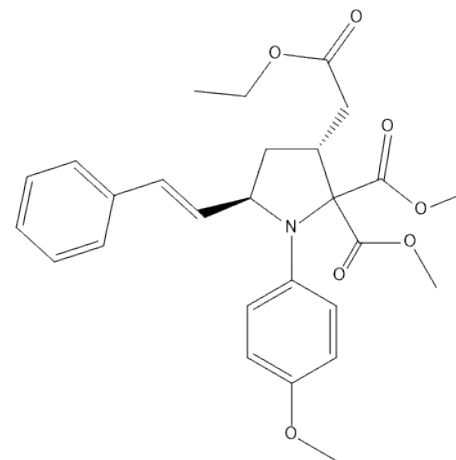
1.0e+07

5.0e+06

0.

504.19890

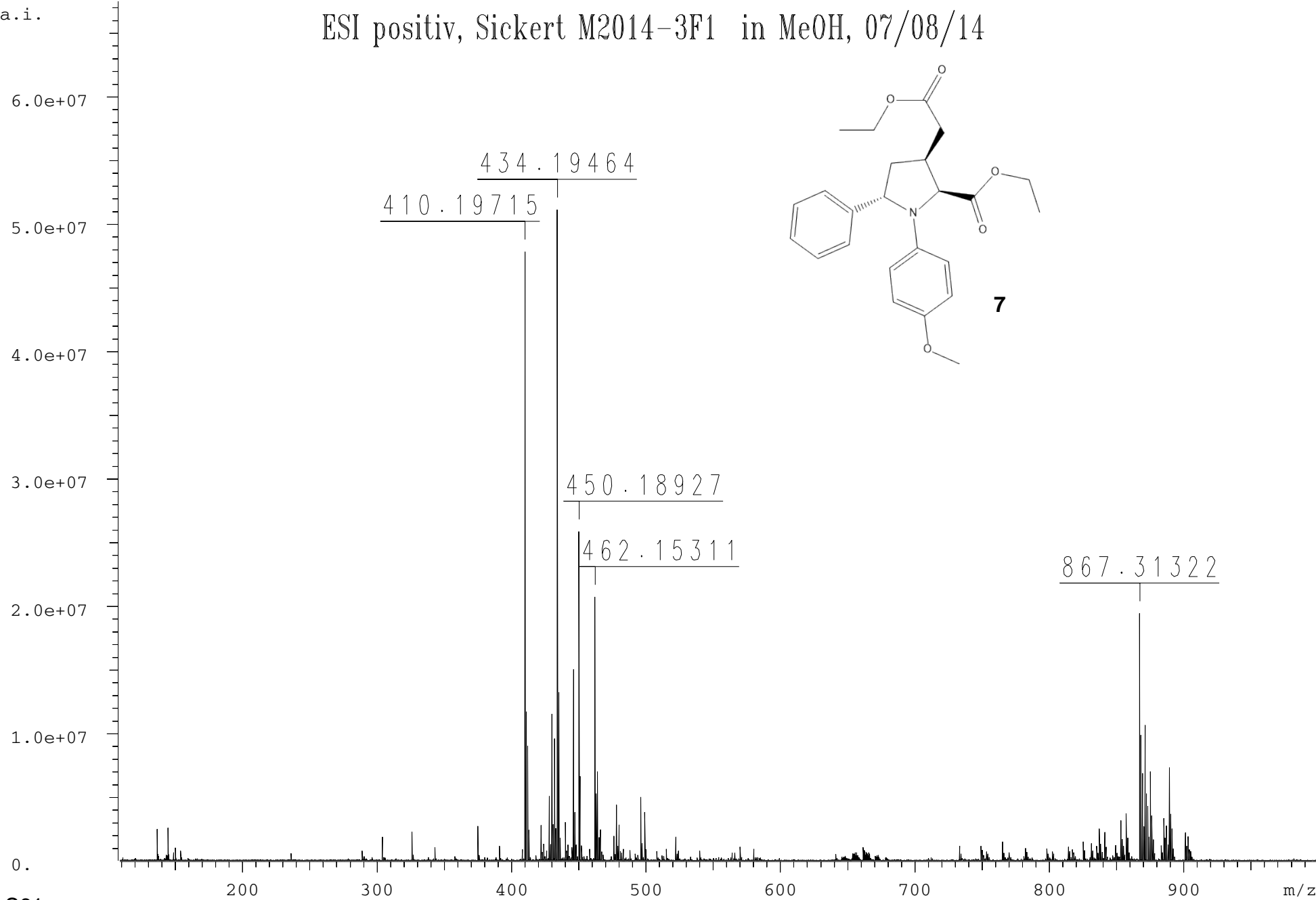
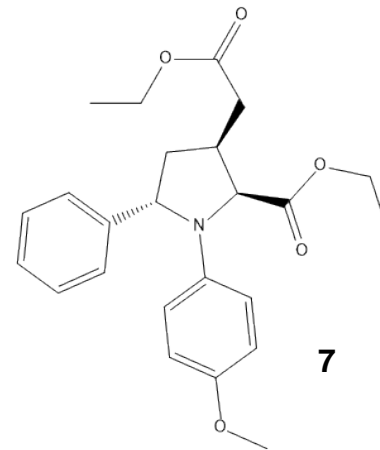
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 m/z



**trans-3h**



# ESI positiv, Sickert M2014-3F1 in MeOH, 07/08/14



S61

## Crystallographic data for compound *trans*-3b

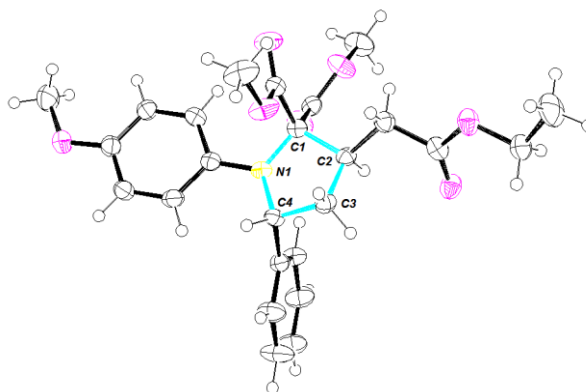
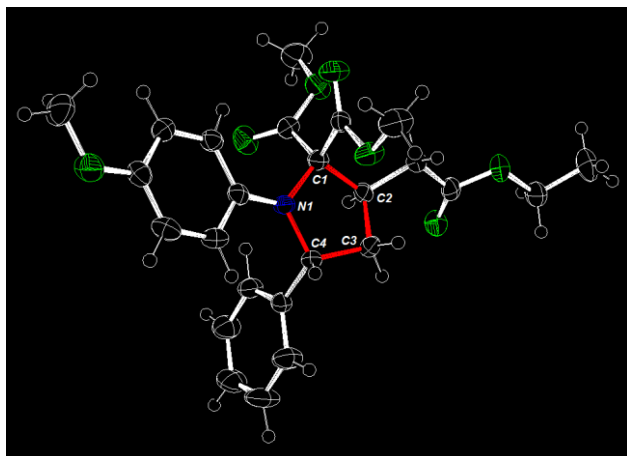


Table 1. Crystal data and structure refinement for compounds *trans*-3b (x1113fin.)

Identification code	x1113fin	
Empirical formula	C <sub>25</sub> H <sub>29</sub> N O <sub>7</sub>	
Formula weight	455.49	
Temperature	130(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 1214.83(4) pm	∠ = 90°.
	b = 1395.59(4) pm	∠ = 90.921(2)°.
	c = 1375.85(4) pm	∠ = 90°.
Volume	2.33232(12) nm <sup>3</sup>	
Z	4	
Density (calculated)	1.297 Mg/m <sup>3</sup>	
Absorption coefficient	0.095 mm <sup>-1</sup>	
F(000)	968	
Crystal size	0.4 x 0.3 x 0.1 mm <sup>3</sup>	
Theta range for data collection	2.92 to 28.28°.	
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -18 ≤ l ≤ 14	
Reflections collected	22890	
Independent reflections	5788 [R(int) = 0.0444]	
Completeness to theta = 28.28°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.99202	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5788 / 17 / 391	
Goodness-of-fit on F <sup>2</sup>	0.891	
Final R indices [I > 2σ(I)]	R1 = 0.0418, wR2 = 0.0890	
R indices (all data)	R1 = 0.0812, wR2 = 0.0964	
Largest diff. peak and hole	0.345 and -0.183 e.Å <sup>-3</sup>	

**Comments:** Structure solution with SIR92. One substituent and parts of the five-membered ring were found to be disordered (ratio: 0.885(3):0.115(3)). Anisotropic refinement of all non-hydrogen atoms with SHELXL (Exception: The minor disordered part of the molecule). With the exception of disordered parts of the molecule, all H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement.

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for x1113fin.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
O(1)	6834(1)	2995(1)	10197(1)	47(1)
O(2)	1620(1)	3157(1)	9070(1)	43(1)
O(3)	1068(1)	4288(1)	8016(1)	41(1)
O(4)	3114(1)	4839(1)	7281(1)	40(1)
O(5)	3690(1)	3671(1)	6307(1)	39(1)
N(1)	3147(1)	2431(1)	7782(1)	27(1)
C(1)	2419(1)	3198(1)	7472(1)	26(1)
C(5)	4065(1)	2600(1)	8387(1)	26(1)
C(6)	4943(1)	1946(1)	8439(1)	32(1)
C(7)	5840(1)	2103(1)	9043(1)	36(1)
C(8)	5906(1)	2904(1)	9625(1)	33(1)
C(9)	5047(1)	3557(1)	9593(1)	31(1)
C(10)	4152(1)	3411(1)	8980(1)	30(1)
C(11)	6937(2)	3819(2)	10796(2)	55(1)
C(12)	1677(1)	3543(1)	8296(1)	29(1)
C(13)	280(2)	4666(1)	8702(1)	50(1)
C(14)	3092(1)	4024(1)	7024(1)	26(1)
C(15)	4373(2)	4353(2)	5804(2)	51(1)
C(4)	3163(2)	1601(2)	7128(2)	26(1)
C(3)	2360(2)	1896(1)	6303(1)	30(1)
C(2)	1642(2)	2676(1)	6732(1)	26(1)
C(16)	1101(2)	3333(1)	5978(1)	30(1)
C(17)	179(2)	2836(2)	5434(1)	29(1)
O(6)	-249(2)	2098(2)	5674(2)	36(1)
O(7)	-111(3)	3347(3)	4652(2)	36(1)
C(18)	-943(2)	2895(2)	4023(1)	41(1)
C(19)	-1150(2)	3580(2)	3214(2)	57(1)
C(4F)	2889(16)	1706(14)	7020(15)	26(1)
C(3F)	1722(12)	1811(9)	6580(10)	33(4)
C(2F)	1653(13)	2895(11)	6470(14)	26(1)
C(16F)	526(13)	3309(10)	6310(11)	44(4)
C(17F)	-132(14)	2743(14)	5570(12)	29(1)
O(6F)	-507(17)	1950(15)	5592(17)	36(1)
O(7F)	-220(20)	3310(30)	4789(17)	36(1)
C(18F)	-1198(13)	3371(14)	4171(10)	42(4)
C(19F)	-970(20)	3090(18)	3152(13)	72(8)
C(20)	2851(1)	679(1)	7624(1)	28(1)
C(21)	3242(2)	-177(1)	7261(1)	44(1)
C(22)	2951(2)	-1042(1)	7675(2)	57(1)
C(23)	2258(2)	-1054(1)	8461(1)	52(1)
C(24)	1862(2)	-210(1)	8825(1)	47(1)
C(25)	2158(1)	655(1)	8412(1)	35(1)

Table 3. Bond lengths [pm] and angles [°] for x1113fin.

---

O(1)-C(8)	136.96(18)
O(1)-C(11)	141.9(2)
O(2)-C(12)	119.77(16)
O(3)-C(12)	132.87(17)
O(3)-C(13)	145.43(17)
O(4)-C(14)	119.09(16)
O(5)-C(14)	132.98(16)
O(5)-C(15)	144.64(19)
N(1)-C(5)	140.11(19)
N(1)-C(1)	144.84(18)
N(1)-C(4)	146.75(19)
N(1)-C(4F)	148.7(9)
C(1)-C(12)	153.59(18)
C(1)-C(14)	154.66(19)
C(1)-C(2)	155.8(2)
C(1)-C(2F)	170.4(19)
C(5)-C(10)	139.8(2)
C(5)-C(6)	140.5(2)
C(6)-C(7)	137.7(2)
C(6)-H(6)	95.6(14)
C(7)-C(8)	137.7(2)
C(7)-H(7)	94.8(18)
C(8)-C(9)	138.6(2)
C(9)-C(10)	138.1(2)
C(9)-H(9)	97.7(15)
C(10)-H(10)	94.6(16)
C(11)-H(11A)	98.2(19)
C(11)-H(11B)	96(2)
C(11)-H(11C)	101(2)
C(13)-H(13A)	98.00
C(13)-H(13B)	98.00
C(13)-H(13C)	98.00
C(13)-H(13D)	98.00
C(13)-H(13E)	98.00
C(13)-H(13F)	98.00
C(15)-H(15A)	98(2)
C(15)-H(15B)	97(2)
C(15)-H(15C)	92(2)
C(4)-C(20)	150.7(3)
C(4)-C(3)	154.1(3)
C(4)-H(4)	100.00
C(3)-C(2)	152.0(2)
C(3)-H(3A)	99.00
C(3)-H(3B)	99.00
C(2)-C(16)	152.6(2)
C(2)-H(2)	100.00
C(16)-C(17)	150.5(3)
C(16)-H(16A)	99.00
C(16)-H(16B)	99.00
C(17)-O(6)	120.2(2)
C(17)-O(7)	133.4(3)
O(7)-C(18)	146.4(3)
C(18)-C(19)	148.5(3)
C(18)-H(18A)	99.00
C(18)-H(18B)	99.00

C(19)-H(19A)	98.00
C(19)-H(19B)	98.00
C(19)-H(19C)	98.00
C(4F)-C(3F)	154.0(16)
C(4F)-C(20)	166(3)
C(4F)-H(4F)	100.00
C(3F)-C(2F)	152.3(15)
C(3F)-H(3F1)	99.00
C(3F)-H(3F2)	99.00
C(2F)-C(16F)	150.0(15)
C(2F)-H(2F)	100.00
C(16F)-C(17F)	150.8(15)
C(16F)-H(16C)	99.00
C(16F)-H(16D)	99.00
C(17F)-O(6F)	119.6(16)
C(17F)-O(7F)	133.8(16)
O(7F)-C(18F)	145.1(17)
C(18F)-C(19F)	148.7(16)
C(18F)-H(18C)	99.00
C(18F)-H(18D)	99.00
C(19F)-H(19D)	98.00
C(19F)-H(19E)	98.00
C(19F)-H(19F)	98.00
C(20)-C(21)	138.2(2)
C(20)-C(25)	138.3(2)
C(21)-C(22)	138.4(2)
C(21)-H(21)	94.1(17)
C(22)-C(23)	138.0(3)
C(22)-H(22)	96(2)
C(23)-C(24)	137.0(2)
C(23)-H(23)	95.3(18)
C(24)-C(25)	138.5(2)
C(24)-H(24)	96.1(17)
C(25)-H(25)	100.1(15)
C(8)-O(1)-C(11)	118.25(14)
C(12)-O(3)-C(13)	117.76(11)
C(14)-O(5)-C(15)	115.78(12)
C(5)-N(1)-C(1)	121.80(11)
C(5)-N(1)-C(4)	118.58(13)
C(1)-N(1)-C(4)	114.68(12)
C(5)-N(1)-C(4F)	133.6(7)
C(1)-N(1)-C(4F)	100.1(7)
C(4)-N(1)-C(4F)	15.2(7)
N(1)-C(1)-C(12)	112.14(11)
N(1)-C(1)-C(14)	110.13(11)
C(12)-C(1)-C(14)	112.36(11)
N(1)-C(1)-C(2)	101.92(11)
C(12)-C(1)-C(2)	105.82(12)
C(14)-C(1)-C(2)	113.99(11)
N(1)-C(1)-C(2F)	112.1(5)
C(12)-C(1)-C(2F)	110.8(6)
C(14)-C(1)-C(2F)	98.5(5)
C(2)-C(1)-C(2F)	15.9(5)
C(10)-C(5)-N(1)	122.31(13)
C(10)-C(5)-C(6)	116.49(14)
N(1)-C(5)-C(6)	121.19(13)

C(7)-C(6)-C(5)	121.35(14)
C(7)-C(6)-H(6)	119.2(9)
C(5)-C(6)-H(6)	119.4(9)
C(6)-C(7)-C(8)	121.22(15)
C(6)-C(7)-H(7)	120.0(10)
C(8)-C(7)-H(7)	118.8(10)
O(1)-C(8)-C(7)	116.70(14)
O(1)-C(8)-C(9)	124.73(14)
C(7)-C(8)-C(9)	118.57(15)
C(10)-C(9)-C(8)	120.54(14)
C(10)-C(9)-H(9)	122.5(9)
C(8)-C(9)-H(9)	117.0(9)
C(9)-C(10)-C(5)	121.82(15)
C(9)-C(10)-H(10)	114.6(9)
C(5)-C(10)-H(10)	123.5(9)
O(1)-C(11)-H(11A)	108.3(11)
O(1)-C(11)-H(11B)	105.2(11)
H(11A)-C(11)-H(11B)	111.9(15)
O(1)-C(11)-H(11C)	106.8(11)
H(11A)-C(11)-H(11C)	112.4(16)
H(11B)-C(11)-H(11C)	111.7(16)
O(2)-C(12)-O(3)	124.71(13)
O(2)-C(12)-C(1)	123.95(14)
O(3)-C(12)-C(1)	111.23(11)
O(3)-C(13)-H(13A)	109.5
O(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(3)-C(13)-H(13D)	109.5
H(13A)-C(13)-H(13D)	141.1
H(13B)-C(13)-H(13D)	56.3
H(13C)-C(13)-H(13D)	56.3
O(3)-C(13)-H(13E)	109.5
H(13A)-C(13)-H(13E)	56.3
H(13B)-C(13)-H(13E)	141.1
H(13C)-C(13)-H(13E)	56.3
H(13D)-C(13)-H(13E)	109.5
O(3)-C(13)-H(13F)	109.5
H(13A)-C(13)-H(13F)	56.3
H(13B)-C(13)-H(13F)	56.3
H(13C)-C(13)-H(13F)	141.1
H(13D)-C(13)-H(13F)	109.5
H(13E)-C(13)-H(13F)	109.5
O(4)-C(14)-O(5)	124.37(13)
O(4)-C(14)-C(1)	127.06(12)
O(5)-C(14)-C(1)	108.54(11)
O(5)-C(15)-H(15A)	109.7(14)
O(5)-C(15)-H(15B)	109.7(11)
H(15A)-C(15)-H(15B)	109.7(17)
O(5)-C(15)-H(15C)	102.7(13)
H(15A)-C(15)-H(15C)	114.2(18)
H(15B)-C(15)-H(15C)	110.7(18)
N(1)-C(4)-C(20)	112.99(18)
N(1)-C(4)-C(3)	103.07(13)
C(20)-C(4)-C(3)	113.66(17)

N(1)-C(4)-H(4)	109.0
C(20)-C(4)-H(4)	109.0
C(3)-C(4)-H(4)	109.0
C(2)-C(3)-C(4)	105.39(13)
C(2)-C(3)-H(3A)	110.7
C(4)-C(3)-H(3A)	110.7
C(2)-C(3)-H(3B)	110.7
C(4)-C(3)-H(3B)	110.7
H(3A)-C(3)-H(3B)	108.8
C(3)-C(2)-C(16)	114.20(15)
C(3)-C(2)-C(1)	104.13(14)
C(16)-C(2)-C(1)	114.42(15)
C(3)-C(2)-H(2)	107.9
C(16)-C(2)-H(2)	107.9
C(1)-C(2)-H(2)	107.9
C(17)-C(16)-C(2)	111.75(14)
C(17)-C(16)-H(16A)	109.3
C(2)-C(16)-H(16A)	109.3
C(17)-C(16)-H(16B)	109.3
C(2)-C(16)-H(16B)	109.3
H(16A)-C(16)-H(16B)	107.9
O(6)-C(17)-O(7)	124.8(2)
O(6)-C(17)-C(16)	125.39(18)
O(7)-C(17)-C(16)	109.8(2)
C(17)-O(7)-C(18)	114.7(3)
O(7)-C(18)-C(19)	105.8(2)
O(7)-C(18)-H(18A)	110.6
C(19)-C(18)-H(18A)	110.6
O(7)-C(18)-H(18B)	110.6
C(19)-C(18)-H(18B)	110.6
H(18A)-C(18)-H(18B)	108.7
N(1)-C(4F)-C(3F)	113.3(11)
N(1)-C(4F)-C(20)	104.0(13)
C(3F)-C(4F)-C(20)	104.3(15)
N(1)-C(4F)-H(4F)	111.6
C(3F)-C(4F)-H(4F)	111.6
C(20)-C(4F)-H(4F)	111.6
C(2F)-C(3F)-C(4F)	100.5(12)
C(2F)-C(3F)-H(3F1)	111.7
C(4F)-C(3F)-H(3F1)	111.7
C(2F)-C(3F)-H(3F2)	111.7
C(4F)-C(3F)-H(3F2)	111.7
H(3F1)-C(3F)-H(3F2)	109.5
C(16F)-C(2F)-C(3F)	116.5(13)
C(16F)-C(2F)-C(1)	120.5(12)
C(3F)-C(2F)-C(1)	98.0(10)
C(16F)-C(2F)-H(2F)	106.9
C(3F)-C(2F)-H(2F)	106.9
C(1)-C(2F)-H(2F)	106.9
C(2F)-C(16F)-C(17F)	111.7(13)
C(2F)-C(16F)-H(16C)	109.3
C(17F)-C(16F)-H(16C)	109.3
C(2F)-C(16F)-H(16D)	109.3
C(17F)-C(16F)-H(16D)	109.3
H(16C)-C(16F)-H(16D)	107.9
O(6F)-C(17F)-O(7F)	122.8(19)
O(6F)-C(17F)-C(16F)	131.7(17)

O(7F)-C(17F)-C(16F)	105.4(15)
C(17F)-O(7F)-C(18F)	124(2)
O(7F)-C(18F)-C(19F)	111.8(19)
O(7F)-C(18F)-H(18C)	109.3
C(19F)-C(18F)-H(18C)	109.3
O(7F)-C(18F)-H(18D)	109.3
C(19F)-C(18F)-H(18D)	109.3
H(18C)-C(18F)-H(18D)	107.9
C(18F)-C(19F)-H(19D)	109.5
C(18F)-C(19F)-H(19E)	109.5
H(19D)-C(19F)-H(19E)	109.5
C(18F)-C(19F)-H(19F)	109.5
H(19D)-C(19F)-H(19F)	109.5
H(19E)-C(19F)-H(19F)	109.5
C(21)-C(20)-C(25)	118.67(14)
C(21)-C(20)-C(4)	118.91(14)
C(25)-C(20)-C(4)	122.39(14)
C(21)-C(20)-C(4F)	123.6(6)
C(25)-C(20)-C(4F)	115.8(7)
C(4)-C(20)-C(4F)	13.1(7)
C(20)-C(21)-C(22)	120.90(15)
C(20)-C(21)-H(21)	119.2(10)
C(22)-C(21)-H(21)	119.9(10)
C(23)-C(22)-C(21)	119.77(17)
C(23)-C(22)-H(22)	122.3(12)
C(21)-C(22)-H(22)	117.8(12)
C(24)-C(23)-C(22)	119.81(16)
C(24)-C(23)-H(23)	117.2(11)
C(22)-C(23)-H(23)	123.0(11)
C(23)-C(24)-C(25)	120.35(16)
C(23)-C(24)-H(24)	123.3(10)
C(25)-C(24)-H(24)	116.4(10)
C(20)-C(25)-C(24)	120.51(15)
C(20)-C(25)-H(25)	118.9(8)
C(24)-C(25)-H(25)	120.5(8)

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Symmetry transformations used to generate equivalent atoms:



Table 4. Anisotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for x1113fin. 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
O(1)	37(1)	41(1)	62(1)	-3(1)	-16(1)	4(1)
O(2)	44(1)	52(1)	34(1)	11(1)	16(1)	6(1)
O(3)	47(1)	42(1)	35(1)	6(1)	17(1)	18(1)
O(4)	49(1)	26(1)	47(1)	-5(1)	15(1)	-3(1)
O(5)	49(1)	31(1)	36(1)	-5(1)	23(1)	-11(1)
N(1)	32(1)	21(1)	27(1)	-2(1)	3(1)	0(1)
C(1)	28(1)	25(1)	26(1)	0(1)	4(1)	0(1)
C(5)	28(1)	24(1)	25(1)	4(1)	5(1)	-2(1)
C(6)	33(1)	23(1)	40(1)	-2(1)	6(1)	-1(1)
C(7)	29(1)	28(1)	52(1)	4(1)	2(1)	2(1)
C(8)	30(1)	32(1)	36(1)	6(1)	-2(1)	-1(1)
C(9)	32(1)	31(1)	30(1)	-2(1)	1(1)	-1(1)
C(10)	32(1)	28(1)	31(1)	0(1)	3(1)	6(1)
C(11)	48(1)	57(1)	57(1)	-13(1)	-21(1)	4(1)
C(12)	27(1)	30(1)	29(1)	-1(1)	5(1)	-3(1)
C(13)	50(1)	47(1)	53(1)	-3(1)	26(1)	13(1)
C(14)	28(1)	26(1)	23(1)	1(1)	1(1)	2(1)
C(15)	64(1)	42(1)	49(1)	-2(1)	33(1)	-15(1)
C(4)	30(1)	22(1)	25(1)	-2(1)	1(1)	4(1)
C(3)	35(1)	28(1)	25(1)	-3(1)	-2(1)	-2(1)
C(2)	30(1)	23(1)	24(1)	4(1)	1(1)	-3(1)
C(16)	33(1)	29(1)	28(1)	2(1)	-1(1)	1(1)
C(17)	29(1)	37(1)	22(1)	2(1)	6(1)	5(1)
O(6)	32(1)	40(1)	36(1)	6(1)	0(1)	-10(1)
O(7)	34(1)	47(1)	28(1)	8(1)	-3(1)	-2(1)
C(18)	42(1)	42(1)	36(1)	2(1)	-12(1)	3(1)
C(19)	59(2)	68(2)	43(1)	16(1)	-16(1)	5(1)
C(4F)	30(1)	22(1)	25(1)	-2(1)	1(1)	4(1)
C(2F)	30(1)	23(1)	24(1)	4(1)	1(1)	-3(1)
C(17F)	29(1)	37(1)	22(1)	2(1)	6(1)	5(1)
O(6F)	32(1)	40(1)	36(1)	6(1)	0(1)	-10(1)
O(7F)	34(1)	47(1)	28(1)	8(1)	-3(1)	-2(1)
C(20)	30(1)	24(1)	29(1)	-1(1)	-2(1)	-1(1)
C(21)	52(1)	32(1)	48(1)	-6(1)	14(1)	5(1)
C(22)	77(2)	24(1)	72(1)	-3(1)	16(1)	8(1)
C(23)	70(1)	27(1)	60(1)	8(1)	6(1)	-6(1)
C(24)	62(1)	34(1)	45(1)	3(1)	14(1)	-7(1)
C(25)	45(1)	26(1)	36(1)	-3(1)	7(1)	-1(1)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for x1113fin.

	x	y	z	U(eq)
H(13A)	-113	5209	8407	74
H(13B)	671	4881	9292	74
H(13C)	-248	4165	8870	74
H(13D)	320	4294	9305	74
H(13E)	-464	4622	8421	74
H(13F)	455	5338	8842	74
H(4)	3918	1532	6858	31
H(3A)	2768	2142	5738	35
H(3B)	1906	1343	6090	35
H(2)	1045	2358	7106	31
H(16A)	807	3907	6307	36
H(16B)	1661	3547	5510	36
H(18A)	-1627	2777	4385	49
H(18B)	-670	2277	3769	49
H(19A)	-1426	4185	3477	85
H(19B)	-1698	3310	2761	85
H(19C)	-463	3698	2871	85
H(4F)	3461	1696	6505	31
H(3F1)	1652	1482	5944	40
H(3F2)	1155	1564	7024	40
H(2F)	2097	3069	5890	31
H(16C)	594	3980	6085	53
H(16D)	131	3315	6934	53
H(18C)	-1484	4035	4180	50
H(18D)	-1774	2945	4431	50
H(19D)	-1644	3132	2759	108
H(19E)	-688	2431	3140	108
H(19F)	-411	3523	2885	108
H(6)	4915(12)	1376(11)	8054(10)	32(4)
H(7)	6422(15)	1650(12)	9070(11)	49(5)
H(9)	5107(12)	4113(11)	10022(10)	32(4)
H(10)	3594(13)	3881(11)	9024(10)	36(4)
H(11A)	6310(17)	3834(13)	11237(13)	58(6)
H(11B)	7622(17)	3739(12)	11141(13)	55(5)
H(11C)	6952(17)	4390(15)	10351(14)	74(7)
H(15A)	3916(19)	4870(17)	5540(15)	84(8)
H(15B)	4918(18)	4615(14)	6250(14)	66(7)
H(15C)	4703(18)	3979(15)	5338(15)	77(7)
H(21)	3719(15)	-166(12)	6729(12)	51(5)
H(22)	3219(17)	-1621(14)	7380(13)	73(6)
H(23)	2043(16)	-1630(13)	8778(12)	57(5)
H(24)	1386(15)	-177(12)	9374(12)	54(5)
H(25)	1882(13)	1274(11)	8684(10)	34(4)