

## Grubbs Catalysts in Intramolecular Carbene C(sp<sup>3</sup>)-H Insertion Reactions from $\alpha$ -Diazoesters

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**General Methods.** All commercially available reagents were used without further purification. All reactions were carried out under an argon atmosphere. TLC was carried out on SiO<sub>2</sub> (silica gel 60 F<sub>254</sub>, Merck), and the spots were located with UV light or 1% aqueous KMnO<sub>4</sub>. Flash chromatography was carried out on SiO<sub>2</sub> (silica gel 60, SDS, 230–400 mesh ASTM). Drying of organic extracts during workup of reactions was performed over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of solvents was accomplished with a rotatory evaporator. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded using Me<sub>4</sub>Si as the internal standard, with a Varian Mercury 400 instrument. Chemical shifts are reported in ppm downfield (δ) from Me<sub>4</sub>Si for <sup>1</sup>H- and <sup>13</sup>C- NMR. HRMS were obtained using a LC/MSD TOF mass spectrometer.

### **Experimental procedures and characterization data for the starting materials**

#### **METHOD A: Methyl 4-(*N*-benzyl-*N*-*tert*-butylamino)-2-diazobutanoate (1a).**

Benzyl bromide (2.3 mL, 19.5 mmol) and K<sub>2</sub>CO<sub>3</sub> (3.5 g, 25.5 mmol) were added, under argon, to a solution of *N*-*tert*-butylethanolamine (1.5 g, 12.7 mmol) in CH<sub>3</sub>CN (26 mL). The resulting mixture was stirred at 80 °C for 24 h. The solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The combined organic extracts were dried, filtered and concentrated, and the residue was purified by chromatography (SiO<sub>2</sub>, from hexanes to hexanes-EtOAc 4:1) to give 2-(*N*-benzyl-*N*-*tert*-butylamino)ethanol (2.3 g, 86%) as a colorless oil.

2-(*N*-Benzyl-*N*-*tert*-butylamino)ethanol (2.3 g, 11.0 mmol) and triethylamine (2.3 mL, 16.4 mmols) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (22 mL), and methanesulfonyl chloride (1.8 mL, 23.3 mmols) was added dropwise at 0 °C. The resulting solution was stirred at room temperature for 3 h. The reaction mixture was poured into water and ice, basified with a saturated NaHCO<sub>3</sub> aqueous solution, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were washed with brine, dried, filtered and concentrated. The residue was dissolved in acetone (82 mL), and NaI (16.5 g, 111 mmols) was added. The mixture was stirred at reflux for 24 h, concentrated *in vacuo* and the residue was partitioned between water and Et<sub>2</sub>O. The organic extracts were washed with water, dried, filtered and concentrated to give *N*-benzyl-*N*-(2-iodoethyl)-*tert*-butylamine (3.4 g, quantitative), which was used in the next step without purification.

A solution of methyl 3-oxobutanoate (6.8 mL, 62.7 mmols) in dry THF (50 mL) was added dropwise, under an argon atmosphere, to a stirred suspension of NaH (1.5 g, 62.7 mmols) in dry THF (50 mL) at room temperature. After the mixture became clear (5 min), a solution of *N*-(2-iodoethyl)-*N*-benzyl-*tert*-butylamine (3.4 g) in dry THF (10 mL) was added dropwise, and the mixture was stirred at 80 °C for 96 h. The reaction mixture was poured into a mixture of saturated ammonium chloride aqueous solution and ice, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic

extracts were washed with brine, dried, filtered and concentrated. The resulting residue was purified by chromatography (SiO<sub>2</sub>, from hexanes to hexanes-EtOAc 9:1) to give methyl 2-acetyl-4-(*N*-benzyl-*N*-*tert*-butylamino)butanoate (1.53 g, 47% for two steps) as a colorless oil.

To a solution of methyl 2-acetyl-4-(*N*-benzyl-*N*-*tert*-butylamino)butanoate (1.53 g, 5.0 mmols) and DBU (1.12 mL, 7.3 mmols) in dry acetonitrile (25 mL) was added dropwise a solution of *p*-ABSA (1.56 g, 6.5 mmols) in dry acetonitrile (22 mL). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the resulting residue was purified by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) to give **1a** (0.9 g, 62%) as a yellow oil. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.14 (s, 9H), 1.99 (t, *J* = 7.0 Hz, 2H), 2.73 (t, *J* = 7.0 Hz, 2H), 3.65 (s, 3H), 3.68 (s, 2H), 7.20 (ddt, *J* = 8.0, 6.4 and 1.6 Hz, 1H), 7.25-7.35 (m, 4H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.4 (CH<sub>2</sub>), 27.4 (3 CH<sub>3</sub>), 49.4 (CH<sub>2</sub>), 51.8 (CH<sub>3</sub>), 55.4 (CH<sub>2</sub>), 55.5 (C), 68.1 (C), 126.6 (CH), 128.2 (2 CH), 128.4 (2 CH), 142.7 (C). One C was not observed. IR (NaCl) ν 2082, 1695 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>16</sub>H<sub>24</sub>N<sub>3</sub>O<sub>2</sub>: 290.1863 [M + H]<sup>+</sup>; found: 290.1867.

**METHOD B: Methyl 4-(*N*-[2-(2-bromophenyl)ethyl]-*N*-*tert*-butylamino)-2-diazobutanoate (3).**

A solution of 2-bromoacetaldehyde (1.3 g, 6.5 mmol) in methanol (14 mL) was cooled in an ice bath. *tert*-Butylamine (0.69 mL, 6.5 mmol) was added, and the mixture was stirred at room temperature for 3 h. Sodium borohydride (0.3 g, 7.79 mmol) was added slowly to the reaction mixture, which was maintained at 0 °C by using an ice bath. After the addition, the mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was dissolved in water, and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were dried, filtered and concentrated to give crude *N*-[2-(2-bromophenyl)ethyl]-*tert*-butylamine (1.35 g) as a colorless oil, which was used in the next step without purification.

A solution of *N*-[2-(2-bromophenyl)ethyl]-*tert*-butylamine (1.35 g), diisopropylethylamine (1.4 mL, 8.0 mmol), and methyl bromoacetate (1.3 mL, 13.8 mmol) in acetonitrile (34 mL) was refluxed for 24 h. The solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane and washed with saturated aqueous NaHCO<sub>3</sub> and brine. The organic layer was dried and concentrated. The residue was purified by chromatography (SiO<sub>2</sub>, from hexanes to 9:1 hexanes/EtOAc) to give methyl 2-(*N*-[2-(2-bromophenyl)ethyl]-*N*-*tert*-butylamino)acetate (1.0 g, 47% for two steps) as a colorless oil.

To a cooled (-30 °C) solution of methyl 2-(*N*-[2-(2-bromophenyl)ethyl]-*N*-*tert*-butylamino)acetate (1.0 g, 3.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 mL), DIBAL-H (5.2 mL of 25% solution in toluene, 7.8 mmol) was added dropwise. After 3 h at room temperature, the reaction mixture was poured into a saturated NH<sub>4</sub>Cl aqueous solution and stirring was continued for 1.5 h. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic layer was washed with saturated NaHCO<sub>3</sub> aqueous solution. The organic extracts were dried and the solvent was removed under vacuum

to give 2-(*N*-[2-(2-bromophenyl)ethyl]-*N*-*tert*-butylamino)ethanol (0.8 g), which was used in the next step without purification.

2-(*N*-[2-(2-Bromophenyl)ethyl]-*N*-*tert*-butylamino)ethanol (0.8 g) and triethylamine (0.56 mL, 4.1 mmols) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and methanesulfonyl chloride (0.26 mL, 3.4 mmols) was added dropwise at 0 °C. The resulting solution was stirred at room temperature for 3 h. The reaction mixture was poured into water and ice, basified with a saturated NaHCO<sub>3</sub> aqueous solution, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were washed with brine, dried, filtered and concentrated. The residue was dissolved in acetone (24 mL), and NaI (5 g, 31 mmols) was added. The mixture was stirred at reflux for 24 h, concentrated *in vacuo* and the residue was partitioned between water and Et<sub>2</sub>O. The organic extracts were washed with water, dried, filtered and concentrated to give *N*-[2-(2-bromophenyl)ethyl]-*N*-(2-iodoethyl)-*tert*-butylamine (0.87 g), which was used in the next step without purification.

A solution of methyl 3-oxobutanoate (1.4 mL, 12.7 mmols) in dry THF (11 mL) was added dropwise, under an argon atmosphere, to a stirred suspension of NaH (0.3 g, 12.7 mmols) in dry THF (11 mL) at room temperature. After the mixture became clear (5 min), a solution of *N*-[2-(2-bromophenyl)ethyl]-*N*-(2-iodoethyl)-*tert*-butylamine (0.87 g) in dry THF (11 mL) was added dropwise, and the mixture was stirred at 80 °C for 96 h. The reaction mixture was poured into a mixture of saturated ammonium chloride aqueous solution and ice, and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were washed with brine, dried, filtered and concentrated. The resulting residue was purified by chromatography (SiO<sub>2</sub>, from hexanes to hexanes-EtOAc 4:1) to give methyl 2-acetyl-4-(*N*-[2-(2-bromophenyl)ethyl]-*N*-*tert*-butylamino)butanoate (0.45 g, 37% for three steps) as a colorless oil.

To a solution of methyl 2-acetyl-4-(*N*-[2-(2-bromophenyl)ethyl]-*N*-*tert*-butylamino)butanoate (0.45 g, 1.1 mmols) and DBU (0.25 mL, 1.7 mmols) in dry acetonitrile (5 mL) was added dropwise a solution of *p*-ABSA (0.35 g, 1.5 mmols) in dry acetonitrile (5 mL). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the resulting residue was purified by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) to give **3** (324 mg, 75%) as a yellow oil. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.10 (s, 9H), 2.44 (t, *J* = 6.8 Hz, 2H), 2.69-2.74 (m, 2H), 2.79 (t, *J* = 6.8 Hz, 2H), 2.83-2.88 (m, 2H), 3.77 (s, 3H), 7.05 (ddd, *J* = 8.0, 6.0 and 3.2 Hz, 1H), 7.20-7.25 (m, 2H), 7.51 (dd, *J* = 8.0 and 0.8 Hz, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.3 (CH<sub>2</sub>), 27.5 (3 CH<sub>3</sub>), 38.6 (CH<sub>2</sub>), 49.0 (CH<sub>2</sub>), 51.4 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 55.4 (C), 124.6 (C), 127.7 (CH), 127.9 (CH), 131.1 (CH), 132.9 (CH), 140.2 (C). Two C were not observed. IR (NaCl) ν 2083, 1693 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>17</sub>H<sub>23</sub>BrN<sub>3</sub>O<sub>2</sub>: 382.1125 [M + H]<sup>+</sup>; found: 382.1133.

**Methyl 4-[*N*-*tert*-butyl-*N*-(4-chlorobenzyl)amino]-2-diazobutanoate (1b).** **1b** was obtained as a yellowish oil following Method A [(a) alkylation, 80%; (b) MsCl, Et<sub>3</sub>N; then NaI; (c)

CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 50% two steps; (d) *p*-ABSA, DBU, 60%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.12 (s, 9H), 2.05 (t, *J* = 6.8 Hz, 2H), 2.72 (t, *J* = 6.8 Hz, 2H), 3.63 (s, 2H), 3.65 (s, 3H), 7.22-7.29 (m, 4H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.5 (CH<sub>2</sub>), 27.4 (3 CH<sub>3</sub>), 49.2 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 54.7 (CH<sub>2</sub>), 55.6 (C), 66.4 (C), 128.3 (2 CH), 128.7 (C), 129.6 (2 CH), 141.3 (C). One C was not observed. IR (NaCl) ν 2083, 1694 cm<sup>-1</sup>.

**Methyl 4-[*N*-*tert*-butyl-*N*-(2-fluorobenzyl)amino]-2-diazobutanoate (1c).** **1c** was obtained as a yellowish oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 56% three steps; (d) *p*-ABSA, DBU, 80%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.13 (s, 9H), 2.06 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 3.66 (s, 3H), 3.75 (s, 2H), 6.97 (ddd, *J* = 10.8, 8.0 and 1.2 Hz, 1H), 7.08 (td, *J* = 7.6 and 1.2 Hz, 1H), 7.18 (dddd, *J* = 8.0, 7.6, 5.2 and 1.6 Hz, 1H), 7.50 (td, *J* = 7.6 and 1.6 Hz, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.3 (CH<sub>2</sub>), 27.3 (3 CH<sub>3</sub>), 47.7 (d, *J* = 2.7 Hz, CH<sub>2</sub>), 49.3 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 55.6 (C), 65.6 (C), 115.0 (d, *J* = 22.0 Hz, CH), 123.9 (d, *J* = 3.5 Hz, CH), 128.1 (d, *J* = 8.2 Hz, CH), 129.4 (d, *J* = 13.4 Hz, C), 130.9 (d, *J* = 4.6 Hz, CH), 160.9 (d, *J* = 245.1 Hz, C). One C was not observed. IR (NaCl) ν 2083, 1696 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>16</sub>H<sub>23</sub>FN<sub>3</sub>O<sub>2</sub>: 308.1774 [M + H]<sup>+</sup>; found: 308.1770.

**Methyl 4-[*N*-(2-bromobenzyl)-*N*-*tert*-butylamino]-2-diazobutanoate (1d).** **1d** was obtained as a brownish oil following Method A [(a) alkylation, 70%; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 25% two steps; (d) *p*-ABSA, DBU, 65%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.12 (s, 9H), 2.13 (t, *J* = 7.2 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 3.78 (s, 2H), 7.06 (ddd, *J* = 8.0, 7.6 and 1.6 Hz, 1H), 7.26 (td, *J* = 7.6 and 1.2 Hz, 1H), 7.47 (dd, *J* = 8.0 and 1.2 Hz, 1H), 7.67 (dd, *J* = 7.6 and 1.6 Hz, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.1 (CH<sub>2</sub>), 27.3 (3 CH<sub>3</sub>), 49.6 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 54.7 (CH<sub>2</sub>), 55.7 (C), 66.5 (C), 123.1 (C), 127.2 (CH), 128.0 (CH), 130.6 (CH), 132.4 (CH), 141.6 (C), 168.1 (C). IR (NaCl) ν 2082, 1696 cm<sup>-1</sup>.

**Methyl 4-[*N*-*tert*-butyl-*N*-(2-methoxybenzyl)amino]-2-diazobutanoate (1e).** **1e** was obtained as a brownish oil following Method A [(a) alkylation, 68%; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 23% two steps; (d) *p*-ABSA, DBU, 66%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.12 (s, 9H), 2.08 (t, *J* = 7.0 Hz, 2H), 2.76 (t, *J* = 7.0 Hz, 2H), 3.67 (s, 3H), 3.72 (s, 2H), 3.82 (s, 3H), 6.80 (dd, *J* = 8.0 and 1.2 Hz, 1H), 6.91 (td, *J* = 7.6 and 1.2 Hz, 1H), 7.17 (tdd, *J* = 8.0, 7.6 and 1.6 Hz, 1H), 7.52 (dd, *J* = 7.6 and 1.6 Hz, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.0 (CH<sub>2</sub>), 27.3 (3 CH<sub>3</sub>), 48.7 (CH<sub>2</sub>), 49.4 (CH<sub>2</sub>), 51.8 (CH<sub>3</sub>), 55.3 (CH<sub>3</sub>), 55.4 (C), 109.9 (CH), 120.4 (CH), 127.3 (CH), 129.9 (CH), 130.9 (C), 157.0 (C), 168.3 (C). One C was not observed. IR (NaCl) ν 2083, 1696 cm<sup>-1</sup>.

**Methyl 4-(*N*-[2-(benzyloxy)ethyl]-*N*-*tert*-butylamino)-2-diazobutanoate (5).** **5** was obtained from *N*-[2-(benzyloxy)ethyl]-*tert*-butylamine as a yellow oil following Method B [(a) BrCH<sub>2</sub>CO<sub>2</sub>Me; (b) DIBAL-H, 43% two steps; (c) MsCl, Et<sub>3</sub>N; then NaI; (d)

CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 18% two steps; (e) *p*-ABSA, DBU, 53%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.04 (s, 9H), 2.35 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 6.8 Hz, 2H), 2.76 (t, *J* = 6.8 Hz, 2H), 3.45 (t, *J* = 6.8 Hz, 2H), 3.74 (s, 3H), 4.50 (s, 2H), 7.26-7.33 (m, 5H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.0 (CH<sub>2</sub>), 27.2 (3 CH<sub>3</sub>), 50.1 (CH<sub>2</sub>), 50.7 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 55.2 (C), 72.1 (CH<sub>2</sub>), 73.3 (CH<sub>2</sub>), 127.7 (CH), 127.8 (2 CH), 128.5 (2 CH), 138.6 (C). Two C were not observed. IR (NaCl) ν 2083, 1693 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>18</sub>H<sub>28</sub>N<sub>3</sub>O<sub>3</sub>: 334.2131 [M + H]<sup>+</sup>; found: 334.2130.

**Methyl 4-(*N*-*tert*-butyl-*N*-[3-phenylpropyl]amino)-2-diazobutanoate (7).** 7 was obtained from 3-phenylpropanal as a yellowish oil following Method B [(a) <sup>t</sup>BuNH<sub>2</sub>; then NaBH<sub>4</sub>; (b) BrCH<sub>2</sub>CO<sub>2</sub>Me; (c) DIBAL-H; (d) MsCl, Et<sub>3</sub>N; then NaI, 44% four steps; (e) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 80% two steps; (f) *p*-ABSA, DBU, 68%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.03 (s, 9H), 1.71-1.79 (m, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 6.8 Hz, 2H), 3.71 (s, 3H), 7.14-7.19 (m, 3H), 7.24-7.29 (m, 2H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.6 (CH<sub>2</sub>), 27.3 (3 CH<sub>3</sub>), 32.9 (CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 49.1 (CH<sub>2</sub>), 50.7 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 55.2 (C), 125.8 (CH), 128.4 (2 CH), 128.5 (2 CH), 142.4 (C), 169.2 (C). One C was not observed. IR (NaCl) ν 2082, 1694 cm<sup>-1</sup>.

**Methyl 4-[*N*-benzyl-*N*-(2-iodobenzyl)amino]-2-diazobutanoate (9a).** 9a was obtained from *N*-(2-iodobenzyl)ethanolamine as a yellow oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI, 40% two steps; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 25%; (d) *p*-ABSA, DBU, 80%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 2.37 (t, *J* = 6.8 Hz, 2H), 2.65 (t, *J* = 6.8 Hz, 2H), 3.65 (s, 3H), 3.65 (s, 2H), 3.66 (s, 2H), 6.92 (td, *J* = 8.0 and 1.6 Hz, 1H), 7.20-7.35 (m, 6H), 7.50 (dd, *J* = 8.0 and 1.6 Hz, 1H), 7.80 (dd, *J* = 7.6 and 1.2 Hz, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 22.2 (CH<sub>2</sub>), 51.8 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 58.9 (CH<sub>2</sub>), 63.1 (CH<sub>2</sub>), 66.4 (C), 100.4 (C), 127.2 (CH), 128.3 (CH), 128.5 (2 CH), 128.9 (CH), 129.0 (2 CH), 130.2 (CH), 139.0 (C), 139.5 (CH), 141.4 (C), 167.9 (C). IR (NaCl) ν 2081, 1691 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>19</sub>H<sub>21</sub>I N<sub>3</sub>O<sub>2</sub>: 450.0673 [M + H]<sup>+</sup>; found: 450.0686.

**Methyl 4-[*N*-benzyl-*N*-(2-fluorobenzyl)amino]-2-diazobutanoate (9b).** 9b was obtained from *N*-(2-fluorobenzyl)ethanolamine as a yellow oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 55% three steps; (d) *p*-ABSA, DBU, 72%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 2.39 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 6.4 Hz, 2H), 3.60 (s, 2H), 3.64 (s, 2H), 3.66 (s, 3H), 7.01 (ddd, *J* = 10.4, 7.6 and 1.2 Hz, 1H), 7.10 (td, *J* = 7.6 and 1.2 Hz, 1H), 7.18-7.33 (m, 6H), 7.39 (td, *J* = 7.6 and 1.6 Hz, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 22.2 (CH<sub>2</sub>), 51.1 (d, *J* = 2.1 Hz, CH<sub>2</sub>), 51.7 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 58.9 (CH<sub>2</sub>), 115.4 (d, *J* = 22.3 Hz, CH), 124.1 (d, *J* = 3.6 Hz, CH), 125.9 (d, *J* = 14.4 Hz, C), 127.2 (CH), 128.4 (2 CH), 128.7 (d, *J* = 8.2 Hz, CH), 128.9 (2 CH), 131.2 (d, *J* = 4.5 Hz, CH), 139.3 (C), 161.6 (d, *J* = 245.8 Hz, C). Two C were not observed. IR (NaCl) ν 2082, 1692 cm<sup>-1</sup>.

**Methyl 4-(*N*-benzyl-*N*-isopropylamino)-2-diazobutanoate (11).** **11** was obtained from *N*-isopropylethanolamine as a yellow oil following Method A [(a) alkylation, 60%; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 58% two steps; (d) *p*-ABSA, DBU, 81%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.01 (d, *J* = 6.8 Hz, 2H), 2.25 (t, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 6.4 Hz, 2H), 2.93 (hept, *J* = 6.8 Hz, 1H), 3.56 (s, 2H), 3.67 (s, 3H), 7.18-7.30 (m, 5H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 17.9 (2 CH<sub>3</sub>), 23.4 (CH<sub>2</sub>), 47.9 (CH<sub>2</sub>), 50.1 (CH), 51.9 (CH<sub>3</sub>), 54.5 (CH<sub>2</sub>), 126.8 (CH), 128.3 (2 CH), 128.6 (2 CH), 140.9 (C). Two C were not observed. IR (NaCl) ν 2083, 1694 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>15</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>: 276.1707 [M + H]<sup>+</sup>; found: 276.1712.

**Methyl (*E*)-4-[*N*-(2-butenyl)-*N*-*tert*-butylamino]-2-diazobutanoate (14).** **14** was obtained from *E*-2-butenal as a brown oil following Method B [(a) <sup>t</sup>BuNH<sub>2</sub>; then NaBH<sub>4</sub>; (b) BrCH<sub>2</sub>CO<sub>2</sub>Me, 50% two steps; (c) DIBAL-H; (d) MsCl, Et<sub>3</sub>N; then NaI; (e) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 41% three steps; (f) *p*-ABSA, DBU, 60%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.06 (s, 9H), 1.66 (d, *J* = 5.2 Hz, 3H), 2.32 (broad t, *J* = 7.6 Hz, 2H), 2.67 (broad t, *J* = 7.6 Hz, 2H), 3.10 (broad s, 2H), 3.75 (s, 3H), 5.44-5.55 (broad signal, 2H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 17.9 (CH<sub>3</sub>), 25.1 (CH<sub>2</sub>), 27.4 (3 CH<sub>3</sub>), 47.9 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 52.5 (CH<sub>2</sub>), 55.1 (C), 126.4 (CH), 131.7 (CH). Two C were not observed. IR (NaCl) ν 2082, 1696 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>13</sub>H<sub>24</sub>N<sub>3</sub>O<sub>2</sub>: 254.1863 [M + H]<sup>+</sup>; found: 254.1872.

**Methyl 4-[*N*-*tert*-butyl-*N*-(2-methyl-2-propenyl)amino]-2-diazobutanoate (16a).** **16a** was obtained as a brown oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 65% three steps; (d) *p*-ABSA, DBU, 67%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.05 (s, 9H), 1.70 (dd, *J* = 1.2 and 0.8 Hz, 3H), 2.26 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.98 (broad s, 2H), 3.73 (s, 3H), 4.74 (q, *J* = 1.2 Hz, 1H), 4.93 (q, *J* = 0.8 Hz, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 20.6 (CH<sub>3</sub>), 25.4 (CH<sub>2</sub>), 27.2 (3 CH<sub>3</sub>), 49.5 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 55.1 (C), 57.7 (CH<sub>2</sub>), 111.4 (CH<sub>2</sub>), 146.4 (C), 168.4 (C). One C was not observed. IR (NaCl) ν 2082, 1697 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>13</sub>H<sub>24</sub>N<sub>3</sub>O<sub>2</sub>: 254.1863 [M + H]<sup>+</sup>; found: 254.1866.

**Methyl 4-[*N*-(2-bromo-2-propenyl)-*N*-*tert*-butylamino]-2-diazobutanoate (16b).** **16b** was obtained as a brown oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 46% three steps; (d) *p*-ABSA, DBU, 74%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.08 (s, 9H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 3.32 (m, 2H), 3.75 (s, 3H), 5.50 (m, 1H), 6.04 (m, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.3 (CH<sub>2</sub>), 27.2 (3 CH<sub>3</sub>), 49.6 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 55.4 (C), 60.0 (CH<sub>2</sub>), 116.6 (CH<sub>2</sub>), 136.0 (C), 168.0 (C). One C was not observed. IR (NaCl) ν 2084, 1694 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>12</sub>H<sub>21</sub>BrN<sub>3</sub>O<sub>2</sub>: 310.1945 [M + H]<sup>+</sup>; found: 310.1953.

**Methyl 4-[*N*-*tert*-butyl-*N*-(2-iodo-2-propenyl)amino]-2-diazobutanoate (16c).** **16c** was obtained as a brown oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c)

CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 40% three steps; (d) *p*-ABSA, DBU, 55%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.07 (s, 9H), 2.33 (m, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 3.27 (t, *J* = 1.6 Hz, 2H), 3.74 (s, 3H), 5.79 (m, 1H), 6.50 (m, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.3 (CH<sub>2</sub>), 27.3 (3 CH<sub>3</sub>), 49.4 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 55.4 (C), 63.9 (CH<sub>2</sub>), 124.9 (CH<sub>2</sub>), 150.5 (C), 173.4 (C). One C was not observed. IR (NaCl) ν 2083, 1693 cm<sup>-1</sup>.

**Methyl (Z)-4-(*N*-*tert*-butyl-*N*-propargylamino)-2-diazobutanoate (18a).** 18a was obtained as a brownish oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 35% two steps; (d) *p*-ABSA, DBU, 60%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.12 (s, 9H), 2.15 (t, *J* = 2.4 Hz, 1H), 2.41 (t, *J* = 6.8 Hz, 2H), 2.84 (t, *J* = 6.8 Hz, 2H), 3.47 (broad, 2H), 3.76 (s, 3H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 23.4 (CH<sub>2</sub>), 27.5 (3 CH<sub>3</sub>), 36.9 (CH<sub>2</sub>), 45.9 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 55.4 (C), 72.2 (CH), 82.7 (C), 168.3 (C). One C was not observed. IR (NaCl) ν 2083, 1693 cm<sup>-1</sup>.

**Methyl 4-[*N*-*tert*-butyl-*N*-(2-butyne)amino]-2-diazobutanoate (18b).** 18b was obtained as a yellowish oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 58% three steps; (d) *p*-ABSA, DBU, 79%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.10 (s, 9H), 1.78 (t, *J* = 2.4 Hz, 3H), 2.41 (t, *J* = 6.8 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H), 3.39 (q, *J* = 2.4 Hz, 2H), 3.76 (s, 3H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 3.7 (CH<sub>3</sub>), 23.7 (CH<sub>2</sub>), 27.5 (3 CH<sub>3</sub>), 37.4 (CH<sub>2</sub>), 46.1 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 55.2 (C), 77.6 (C), 79.4 (C), 168.4 (C). One C was not observed. IR (NaCl) ν 2083, 1694 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>13</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>: 252.1712 [M + H]<sup>+</sup>; found: 252.1717.

**Methyl 4-(*N*-*tert*-butyl-*N*-[3-(trimethylsilyl)-2-propynyl]amino)-2-diazobutanoate (18c).** 18c was obtained as a yellowish oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 24% three steps; (d) *p*-ABSA, DBU, 74%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 0.12 (s, 9H), 1.09 (s, 9H), 2.40 (t, *J* = 6.8 Hz, 2H), 2.81 (t, *J* = 6.8 Hz, 2H), 3.44 (s, 2H), 3.74 (s, 3H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 0.02 (3 CH<sub>3</sub>), 23.4 (CH<sub>2</sub>), 27.5 (3 CH<sub>3</sub>), 37.9 (CH<sub>2</sub>), 45.9 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 55.4 (C), 88.9 (C), 105.4 (C). Two C were not observed. IR (NaCl) ν 2084, 1694 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>15</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub>Si: 310.1945 [M + H]<sup>+</sup>; found: 310.1953.

**Methyl 4-[*N*-allyl-*N*-*tert*-butylamino]-2-diazobutanoate (20).** 20 was obtained as a brownish oil following Method A [(a) alkylation; (b) MsCl, Et<sub>3</sub>N; then NaI; (c) CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, NaH, 43% three steps; (d) *p*-ABSA, DBU, 80%]. <sup>1</sup>H RMN (CDCl<sub>3</sub>, 400 MHz) δ 1.06 (s, 9H), 2.32 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 3.18 (d, *J* = 6.4 Hz, 2H), 3.75 (s, 3H), 4.99 (dq, *J* = 11.6 and 1.6 Hz, 1H), 5.13 (dq, *J* = 17.2 and 1.6 Hz, 1H), 5.85 (ddt, *J* = 17.2, 11.6 and 6.4 Hz, 1H). <sup>13</sup>C RMN (CDCl<sub>3</sub>, 100.5 MHz) δ 25.0 (CH<sub>2</sub>), 27.4 (3 CH<sub>3</sub>), 48.3 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 53.6 (CH<sub>2</sub>), 55.2 (C), 115.3 (CH<sub>2</sub>), 139.5 (CH). Two C were not observed. IR (NaCl) ν 2082, 1694 cm<sup>-1</sup>.

**Representative procedure for the C-H insertion reaction (Table 1, Entry 1).** A mixture of diazoester **1a** (40 mg, 0.14 mmol) and Ru-1 (3.3 mg, 0.004 mmol) in dichloromethane (10 mL) was stirred at reflux under Argon atmosphere for 24 h. The solvent was removed *in vacuo*, and the residue was purified by chromatography (SiO<sub>2</sub>, from hexanes to hexanes-EtOAc 95:5) to give **2a** (32.5 mg, 90%).

#### Characterization data for the compounds of Tables 1-4 and Scheme 2

**Methyl *cis*-1-*tert*-butyl-2-phenylpyrrolidine-3-carboxylate (2a).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.98 (s, 9H), 1.85 (dtd, *J* = 12.4, 6.0 and 0.8 Hz, 1H), 2.29 (dddd, *J* = 13.2, 12.4, 12.0 and 6.8 Hz, 1H), 2.82 (ddd, *J* = 12.0, 9.0 and 6.0 Hz, 1H), 3.09 (ddd, *J* = 13.2, 9.0 and 6.0 Hz, 1H), 3.24 (ddd, *J* = 9.6, 6.8 and 0.8 Hz, 1H), 3.25 (s, 3H), 4.38 (d, *J* = 9.6 Hz, 1H), 7.14 (tt, *J* = 7.2 and 1.6 Hz, 1H), 7.19-7.25 (m, 2H), 7.31-7.35 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) δ 26.3 (CH<sub>2</sub>), 27.0 (3 CH<sub>3</sub>), 46.9 (CH<sub>2</sub>), 51.1 (CH), 51.2 (CH<sub>3</sub>), 53.8 (C), 62.9 (CH), 126.8 (CH), 127.5 (2 CH), 127.8 (2 CH), 145.5 (C), 172.3 (C). IR (film) 1743 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>16</sub>H<sub>24</sub>NO<sub>2</sub>: 262.1802 [M + H]<sup>+</sup>; found: 262.1805.

**Methyl *cis*-1-*tert*-butyl-2-(4-chlorophenyl)pyrrolidine-3-carboxylate (2b).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.97 (s, 9H), 1.86 (dtd, *J* = 12.4, 5.6 and 0.8 Hz, 1H), 2.24 (dddd, *J* = 12.8, 12.4, 11.6 and 6.8 Hz, 1H), 2.81 (ddd, *J* = 11.6, 9.6 and 5.6 Hz, 1H), 3.08 (ddd, *J* = 12.8, 9.6 and 5.6 Hz, 1H), 3.23 (ddd, *J* = 9.6, 6.8 and 0.8 Hz, 1H), 3.29 (s, 3H), 4.35 (d, *J* = 9.6 Hz, 1H), 7.17-7.21 (m, 2H), 7.26-7.30 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) δ 26.3 (CH<sub>2</sub>), 27.0 (3 CH<sub>3</sub>), 46.9 (CH<sub>2</sub>), 51.0 (CH), 51.4 (CH<sub>3</sub>), 53.8 (C), 62.2 (CH), 127.8 (2 CH), 129.2 (2 CH), 132.4 (C), 145.2 (C), 172.1 (C). IR (film) 1742 cm<sup>-1</sup>.

**Methyl *cis*-1-*tert*-butyl-2-(2-fluorophenyl)pyrrolidine-3-carboxylate (2c).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.98 (s, 9H), 1.90 (dddd, *J* = 12.0, 6.4, 5.6 and 1.2 Hz, 1H), 2.30 (dddd, *J* = 12.8, 12.0, 11.6 and 7.2 Hz, 1H), 2.83 (ddd, *J* = 11.6, 8.4 and 5.6 Hz, 1H), 3.14 (ddd, *J* = 12.8, 9.6 and 6.4 Hz, 1H), 3.25 (ddd, *J* = 8.4, 6.4 and 1.2 Hz, 1H), 3.31 (s, 3H), 4.79 (d, *J* = 9.6 Hz, 1H), 6.88 (dddd, *J* = 10.0, 7.6, 1.2 and 0.8 Hz, 1H), 7.07 (tdd, *J* = 7.6, 1.2 and 0.4 Hz, 1H), 7.10-7.16 (m, 1H), 7.64 (td, *J* = 7.6 and 2.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) δ 26.8 (3 CH<sub>3</sub>), 27.0 (CH<sub>2</sub>), 46.8 (CH<sub>2</sub>), 50.2 (CH), 51.3 (CH<sub>3</sub>), 53.9 (C), 54.9 (d, *J* = 3.2 Hz, CH), 114.2 (d, *J* = 22.5 Hz, CH), 123.7 (d, *J* = 3.3 Hz, CH), 128.1 (d, *J* = 8.3 Hz, CH), 131.0 (d, *J* = 4.3 Hz, CH), 132.6 (d, *J* = 12.5 Hz, C), 159.6 (d, *J* = 244.3 Hz, C), 172.4 (C). IR (film) 1743 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>16</sub>H<sub>23</sub>FN<sub>2</sub>O<sub>2</sub>: 280.1713 [M + H]<sup>+</sup>; found: 280.1715.

**Methyl *cis*-2-(2-bromophenyl)-1-*tert*-butylpyrrolidine-3-carboxylate (2d).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.97 (s, 9H), 1.91 (dddd, *J* = 12.0, 6.8, 5.6 and 1.6 Hz, 1H), 2.33 (qd, *J* = 12.0 and 6.8 Hz, 1H), 2.84 (ddd, *J* = 12.0, 8.8 and 5.6 Hz, 1H), 3.19 (ddd, *J* = 12.0, 9.6 and 6.8 Hz, 1H),

3.28 (ddd,  $J = 8.8, 6.8$  and  $1.6$  Hz, 1H), 3.26 (s, 3H), 4.83 (d,  $J = 9.6$  Hz, 1H), 7.02 (ddd,  $J = 8.0, 7.6$  and  $1.6$  Hz, 1H), 7.25 (ddd,  $J = 8.0, 7.6$  and  $1.2$  Hz, 1H), 7.39 (dd,  $J = 8.0$  and  $1.2$  Hz, 1H), 7.69 (dd,  $J = 8.0$  and  $1.6$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$  26.9 (3  $\text{CH}_3$ ), 27.5 ( $\text{CH}_2$ ), 47.1 ( $\text{CH}_2$ ), 49.9 (CH), 51.2 ( $\text{CH}_3$ ), 54.0 (C), 61.6 (CH), 123.0 (C), 127.0 (CH), 128.3 (CH), 131.6 (CH), 131.9 (CH), 144.4 (C), 172.4 (C). IR (film)  $1740\text{ cm}^{-1}$ .

**Methyl *cis*-1-*tert*-butyl-2-(2-methoxyphenyl)pyrrolidine-3-carboxylate (2e).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.97 (s, 9H), 1.87 (dddd,  $J = 12.0, 6.8, 5.6$  and  $1.6$  Hz, 1H), 2.23 (qd,  $J = 12.0$  and  $6.8$  Hz, 1H), 2.81 (ddd,  $J = 12.0, 8.8$  and  $5.6$  Hz, 1H), 3.07 (ddd,  $J = 12.0, 9.6$  and  $6.8$  Hz, 1H), 3.23 (ddd,  $J = 8.8, 6.8$  and  $1.2$  Hz, 1H), 3.26 (s, 3H), 3.79 (s, 3H), 4.87 (d,  $J = 9.6$  Hz, 1H), 6.73 (dd,  $J = 8.0$  and  $1.2$  Hz, 1H), 6.91 (td,  $J = 7.6$  and  $1.2$  Hz, 1H), 7.13 (ddd,  $J = 8.0, 7.6$  and  $1.6$  Hz, 1H), 7.64 (dd,  $J = 7.6$  and  $1.6$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$  26.8 (3  $\text{CH}_3$ ), 27.8 ( $\text{CH}_2$ ), 46.9 ( $\text{CH}_2$ ), 50.0 (CH), 51.2 ( $\text{CH}_3$ ), 53.8 (C), 55.3 (CH), 55.6 ( $\text{CH}_3$ ), 109.2 (CH), 120.2 (CH), 127.4 (CH), 130.2 (CH), 133.8 (C), 155.9 (C), 172.9 (C). IR (film)  $1737\text{ cm}^{-1}$ .

**Methyl *cis*-2-[(2-bromophenyl)methyl]-1-*tert*-butylpyrrolidine-3-carboxylate (*cis*-4).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.72 (s, 9H), 2.02 (dddd,  $J = 12.4, 8.0, 6.0$  and  $1.6$  Hz, 1H), 2.33 (qd,  $J = 12.0$  and  $8.0$  Hz, 1H), 2.50 (dd,  $J = 13.2$  and  $9.6$  Hz, 1H), 2.76 (dd,  $J = 13.2$  and  $4.8$  Hz, 1H), 2.78-2.86 (m, 2H), 3.10 (ddd,  $J = 10.0, 8.4$  and  $1.6$  Hz, 1H), 3.54 (s, 3H), 3.78 (ddd,  $J = 9.6, 8.0$  and  $4.8$  Hz, 1H), 7.01 (ddd,  $J = 8.0, 6.8$  and  $2.4$  Hz, 1H), 7.16-7.22 (m, 2H), 7.48 (d,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$  26.7 (3  $\text{CH}_3$ ), 27.0 ( $\text{CH}_2$ ), 40.1 ( $\text{CH}_2$ ), 46.0 ( $\text{CH}_2$ ), 48.3 (CH), 51.6 ( $\text{CH}_3$ ), 53.9 (C), 58.3 (CH), 125.7 (C), 126.6 (CH), 127.7 (CH), 132.4 (CH), 133.0 (CH), 139.3 (C), 173.2 (C). IR (film)  $1736\text{ cm}^{-1}$ . HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{25}\text{BrNO}_2$ : 354.1063 [ $\text{M} + \text{H}$ ] $^+$ ; found: 354.1070.

**Methyl *trans*-2-[(2-bromophenyl)methyl]-1-*tert*-butylpyrrolidine-3-carboxylate (*trans*-4).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.14 (s, 9H), 2.03 (broad, 1H), 2.13 (dddd,  $J = 8.8, 6.8, 5.6$  and  $2.4$  Hz, 1H), 2.67 (d,  $J = 6.8$  Hz, 1H), 2.83-2.90 (m, 2H), 3.01-3.08 (m, 2H), 3.53 (s, 3H), 3.83 (broad, 1H), 7.07 (td,  $J = 7.6$  and  $1.6$  Hz, 1H), 7.24 (td,  $J = 7.6$  and  $1.2$  Hz, 1H), 7.30 (dd,  $J = 7.6$  and  $1.6$  Hz, 1H), 7.53 (dd,  $J = 7.6$  and  $1.2$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$  27.4 ( $\text{CH}_2$ ), 27.6 (3  $\text{CH}_3$ ), 29.9 ( $\text{CH}_2$ ), 45.1 (C), 47.5 (CH), 47.6 ( $\text{CH}_2$ ), 51.9 ( $\text{CH}_3$ ), 61.3 (CH), 125.2 (C), 127.5 (CH), 128.1 (CH), 131.8 (CH), 133.0 (CH), 139.2 (C), 175.0 (C). IR (film)  $1736\text{ cm}^{-1}$ . HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{25}\text{BrNO}_2$ : 354.1063 [ $\text{M} + \text{H}$ ] $^+$ ; found: 354.1069.

**Methyl *cis*-2-(benzyloxymethyl)-1-*tert*-butylpyrrolidine-3-carboxylate (*cis*-6).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.05 (s, 9H), 1.91 (dt,  $J = 12.0$  and  $6.0$  Hz, 1H), 2.23 (qd,  $J = 12.4$  and  $7.2$  Hz, 1H), 2.59-2.68 (m, 1H), 2.69-2.80 (m, 1H), 2.94 (t,  $J = 8.0$  Hz, 1H), 3.29 (dd,  $J = 8.8$  and  $3.2$  Hz, 1H), 3.38 (ddd,  $J = 9.6, 6.4$  and  $3.2$  Hz, 1H), 3.43-3.48 (masked, 1H), 3.47 (s, 3H), 4.34 (d,  $J = 11.6$  Hz, 1H), 4.40 (d,  $J = 11.6$  Hz, 1H), 7.29-7.34 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6

MHz)  $\delta$  26.5 (3 CH<sub>3</sub>), 27.3 (CH<sub>2</sub>), 46.0 (CH), 46.6 (CH<sub>2</sub>), 51.6 (CH<sub>3</sub>), 53.6 (C), 58.7 (CH), 73.2 (2 CH<sub>2</sub>), 127.6 (CH), 128.0 (2 CH), 128.4 (2 CH), 138.3 (C), 173.0 (C). IR (film) 1737 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>18</sub>H<sub>28</sub>NO<sub>3</sub>: 306.2069 [M + H]<sup>+</sup>; found: 306.2060.

**Methyl *trans*-2-(benzyloxymethyl)-1-*tert*-butylpyrrolidine-3-carboxylate (*trans*-6).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a  $\approx$  5:1 mixture of *trans*-6 and *cis*-6)  $\delta$  1.06 (s, 9H), 1.96 (broad, 1H), 2.14 (dd,  $J$  = 12.8 and 5.6 Hz, 1H), 2.83 (td,  $J$  = 10.0 and 6.0 Hz, 1H), 2.90-3.00 (m, 1H), 2.99 (d,  $J$  = 7.2 Hz, 1H), 3.22 (broad, 1H), 3.42-3.50 (m, 1H), 3.41-3.56 (m, 1H), 3.69 (s, 3H), 4.52 (d,  $J$  = 12.4 Hz, 1H), 4.58 (d,  $J$  = 12.4 Hz, 1H), 7.26-7.34 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a  $\approx$  5:1 mixture of *trans*-6 and *cis*-6)  $\delta$  27.0 (3 CH<sub>3</sub>), 27.2 (CH<sub>2</sub>), 47.0 (CH), 47.4 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 54.2 (C), 60.5 (CH), 73.2 (CH<sub>2</sub>), 74.8 (CH<sub>2</sub>), 127.8 (CH), 127.9 (2 CH), 128.5 (2 CH), 138.4 (C), 175.2 (C). IR (film) 1736 cm<sup>-1</sup>.

**Methyl *cis*-1-*tert*-butyl-2-(2-phenylethyl)pyrrolidine-3-carboxylate (8).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.02 (s, 9H), 1.59 (broad, 1H), 1.75-1.85 (m, 1H), 1.93 (dt,  $J$  = 12.0 and 6.4 Hz, 1H), 2.22 (qd,  $J$  = 12.0 and 7.6 Hz, 1H), 2.43-2.57 (m, 2H), 2.68 (ddd,  $J$  = 11.2, 9.6 and 6.4 Hz, 1H), 2.79 (ddd,  $J$  = 12.4, 8.0 and 6.8 Hz, 1H), 3.00 (t,  $J$  = 8.8 Hz, 1H), 3.27-3.35 (m, 1H), 3.72 (s, 3H), 7.13-7.17 (m, 3H), 7.23-7.27 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz)  $\delta$  26.8 (3 CH<sub>3</sub>), 27.6 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 38.0 (CH<sub>2</sub>), 46.5 (CH<sub>2</sub>), 47.9 (CH), 51.7 (CH<sub>3</sub>), 54.2 (C), 58.7 (CH), 125.8 (CH), 128.4 (2 CH), 128.6 (2 CH), 142.7 (C), 173.5 (C). IR (film) 1737 cm<sup>-1</sup>.

**Methyl *cis*-1-(2-iodobenzyl)-2-phenylpyrrolidine-3-carboxylate (*cis*-10a).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a  $\approx$  12:1 mixture of *cis*-10a and *trans*-10a)  $\delta$  1.98 (dddd,  $J$  = 12.4, 8.4, 6.4 and 1.6 Hz, 1H), 2.28-2.48 (m, 2H), 3.10 (s, 3H), 3.27-3.39 (m, 2H), 3.38 (d,  $J$  = 14.8 Hz, 1H), 3.72 (d,  $J$  = 14.8 Hz, 1H), 3.98 (d,  $J$  = 9.6 Hz, 1H), 6.88-6.93 (m, 1H), 7.19-7.41 (m, 6H), 7.59 (dt,  $J$  = 7.6 and 1.2 Hz, 1H), 7.76 (dd,  $J$  = 7.6 and 1.6 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a  $\approx$  5:1 mixture of *cis*-10a and *trans*-10a)  $\delta$  26.5 (CH<sub>2</sub>), 49.7 (CH), 51.3 (CH<sub>3</sub>), 52.9 (CH<sub>2</sub>), 62.1 (CH<sub>2</sub>), 71.4 (CH), 99.6 (C), 127.7 (CH), 128.1 (2 CH), 128.4 (CH), 128.5 (2 CH), 128.6 (CH), 130.0 (CH), 139.2 (CH), 139.5 (C), 141.4 (C), 173.6 (C). IR (film) 1736 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>19</sub>H<sub>21</sub>INO<sub>2</sub>: 422.0611 [M + H]<sup>+</sup>; found: 422.0620.

**Methyl *trans*-1-(2-iodobenzyl)-2-phenylpyrrolidine-3-carboxylate (*trans*-10a).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, significant signals from a  $\approx$  5:1 mixture of *cis*-10a and *trans*-10a)  $\delta$  2.05-2.15 (m, 1H), 2.15-2.27 (m, 1H), 2.94 (ddd,  $J$  = 10.8, 8.4 and 5.6 Hz, 1H), 3.16 (ddd,  $J$  = 9.6, 8.4 and 2.0 Hz, 1H), 3.65 (s, 3H), 3.80 (d,  $J$  = 8.4 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a  $\approx$  5:1 mixture of *cis*-10a and *trans*-10a)  $\delta$  27.7 (CH<sub>2</sub>), 52.0 (CH<sub>3</sub>), 52.4 (CH<sub>2</sub>), 52.8 (CH), 62.0 (CH<sub>2</sub>), 72.7 (CH), 99.8 (C), 139.4 (CH), 141.5 (C), 141.6 (C), 175.2 (C).

**Methyl *cis*-1-(2-fluorobenzyl)-2-phenylpyrrolidine-3-carboxylate (*cis*-10b).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a  $\approx$  5:1 mixture of *cis*-10b and *trans*-10b)  $\delta$  1.90-1.97 (m, 1H), 2.29-2.48 (m, 2H), 3.08 (s, 3H), 3.20-3.32 (m, 2H), 3.37 (dd,  $J$  = 13.6 and 1.2 Hz, 1H), 3.78 (dt,

$J = 13.6$  and  $0.8$  Hz, 1H), 3.84 (d,  $J = 10.0$  Hz, 1H), 6.98 (m, 1H), 7.09 (td,  $J = 7.6$  and  $1.2$  Hz, 1H), 7.17-7.42 (m, 7H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz, signals from a  $\approx 5:1$  mixture of *cis*-10b and *trans*-10b)  $\delta$  26.4 ( $\text{CH}_2$ ), 49.7 (CH), 49.9 (d,  $J = 2.2$  Hz,  $\text{CH}_2$ ), 51.3 ( $\text{CH}_3$ ), 52.6 ( $\text{CH}_2$ ), 70.9 (CH), 115.2 (d,  $J = 22.1$  Hz, CH), 124.0 (d,  $J = 3.5$  Hz, CH), 125.6 (d,  $J = 14.9$  Hz, C), 127.7 (CH), 128.1 (2 CH), 128.6 (2 CH), 128.7 (d,  $J = 5.5$  Hz, CH), 131.4 (d,  $J = 4.8$  Hz, CH), 139.5 (C), 161.3 (d,  $J = 245.5$  Hz, C), 173.7 (C). IR (film)  $1738\text{ cm}^{-1}$ .

**Methyl *trans*-1-(2-fluorobenzyl)-2-phenylpyrrolidine-3-carboxylate (*trans*-10b).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, significant signals from a  $\approx 5:1$  mixture of *cis*-10b and *trans*-10b)  $\delta$  1.99-2.08 (m, 1H), 2.15-2.31 (m, 2H), 2.87-2.94 (m, 1H), 3.11-3.17 (m, 1H), 3.63 (s, 3H), 3.66-3.74 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz, significant signals from a  $\approx 5:1$  mixture of *cis*-10b and *trans*-10b)  $\delta$  27.4 ( $\text{CH}_2$ ), 50.3 (d,  $J = 2.2$  Hz,  $\text{CH}_2$ ), 51.9 ( $\text{CH}_3$ ), 52.4 ( $\text{CH}_2$ ), 52.5 (CH), 72.4 (CH), 115.3 (d,  $J = 21.8$  Hz, CH), 141.5 (C), 175.2 (C).

**Methyl *cis*-1-(benzyl)-2-(2-fluorophenyl)pyrrolidine-3-carboxylate (*cis*-10b').**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, signals from a  $\approx 3:1$  mixture of *cis*-10b' and *cis*-10b)  $\delta$  1.90-2.01 (m, 1H), 2.22-2.41 (m, 2H), 3.10 (s, 3H), 3.12 (d,  $J = 13.6$  Hz, 1H), 3.19-3.25 (m, 1H), 3.34-3.41 (m, 1H), 3.88 (d,  $J = 13.6$  Hz, 1H), 4.19 (d,  $J = 9.6$  Hz, 1H), 7.01 (m, 1H), 7.06-7.42 (m, 7H), 7.66 (td,  $J = 7.6$  and  $2.0$  Hz, 1H).

**Methyl *cis*-1-isopropyl-2-phenylpyrrolidine-3-carboxylate (*cis*-12).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, signals from a  $\approx 5.8:1$  mixture of *cis*-12 and *trans*-12)  $\delta$  0.89 (d,  $J = 6.4$  Hz, 3H), 1.02 (d,  $J = 6.4$  Hz, 3H), 1.82 (dddd,  $J = 12.4, 8.4, 6.4$  and  $1.6$  Hz, 1H), 2.35 (dddd,  $J = 12.4, 10.0, 9.6$  and  $7.6$  Hz, 1H), 2.64 (ddd,  $J = 10.0, 8.4$  and  $6.4$  Hz, 1H), 2.79 (hept,  $J = 6.4$  Hz, 1H), 3.11 (s, 3H), 3.18-3.23 (m, 2H), 4.09 (d,  $J = 9.6$  Hz, 1H), 7.16-7.40 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz, signals from a  $\approx 5.8:1$  mixture of *cis*-12 and *trans*-12)  $\delta$  15.8 ( $\text{CH}_3$ ), 22.2 ( $\text{CH}_3$ ), 26.2 ( $\text{CH}_2$ ), 46.3 ( $\text{CH}_2$ ), 49.2 (CH), 49.9 (CH), 50.9 ( $\text{CH}_3$ ), 66.7 (CH), 127.0 (CH), 127.6 (2 CH), 128.2 (2 CH), 141.5 (C), 173.1 (C). IR (film)  $1737\text{ cm}^{-1}$ .

**Methyl *trans*-1-isopropyl-2-phenylpyrrolidine-3-carboxylate (*trans*-12).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, significant signals from a  $\approx 5.8:1$  mixture of *cis*-12 and *trans*-12)  $\delta$  0.91 (d,  $J = 6.4$  Hz, 3H), 1.01 (d,  $J = 6.4$  Hz, 3H), 1.99-2.06 (m, 1H), 2.14-2.15 (m, 1H), 3.63 (s, 3H), 3.87 (d,  $J = 7.6$  Hz, 1H).

**Methyl 1-benzyl-2,2-dimethylpyrrolidine-3-carboxylate (13).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.90 (s, 3H), 1.35 (s, 3H), 1.88 (dddd,  $J = 13.2, 9.6, 9.2$  and  $5.6$  Hz, 1H), 2.18 (dddd,  $J = 13.2, 10.0, 9.2$  and  $4.8$  Hz, 1H), 2.49 (ddd,  $J = 10.0, 9.6$  and  $5.6$  Hz, 1H), 2.79 (td,  $J = 9.2$  and  $4.8$  Hz, 1H), 2.81 (t,  $J = 9.2$  Hz, 1H), 3.25 (d,  $J = 13.0$  Hz, 1H), 3.71 (s, 3H), 3.80 (d,  $J = 13.0$  Hz, 1H), 7.19-7.33 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$  15.9 ( $\text{CH}_3$ ), 23.9 ( $\text{CH}_2$ ), 26.3 ( $\text{CH}_3$ ), 49.5 ( $\text{CH}_2$ ), 51.7 ( $\text{CH}_3$ ), 52.8 ( $\text{CH}_2$ ), 54.5 (CH), 62.8 (C), 126.9 (CH), 128.4 (2 CH), 128.6 (2 CH),

140.5 (C), 174.2 (C). IR (film) 1736 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>15</sub>H<sub>22</sub>NO<sub>2</sub>: 248.1645 [M + H]<sup>+</sup>; found: 248.1650.

**Methyl (*E*)-*cis*-1-*tert*-butyl-2-(1-propenyl)pyrrolidine-3-carboxylate (*cis*-15).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a ≈ 8:1 mixture of *cis*-15 and *trans*-15) δ 1.06 (s, 9H), 1.61 (ddd, *J* = 6.0, 1.6 and 0.4 Hz, 3H), 1.89 (dtd, *J* = 12.4, 6.4 and 1.2 Hz, 1H), 2.20 (tdd, *J* = 12.4, 10.8 and 7.6 Hz, 1H), 2.70 (ddd, *J* = 11.2, 8.8 and 6.0 Hz, 1H), 2.89 (ddd, *J* = 12.4, 8.8 and 6.8 Hz, 1H), 3.02 (t, *J* = 8.8 Hz, 1H), 3.61 (s, 3H), 3.74 (d, *J* = 8.4 Hz, 1H), 5.35-5.52 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 8:1 mixture of *cis*-15 and *trans*-15) δ 17.8 (CH<sub>3</sub>), 26.4 (CH<sub>2</sub>), 27.0 (3 CH<sub>3</sub>), 46.4 (CH<sub>2</sub>), 49.5 (CH), 51.5 (CH<sub>3</sub>), 54.2 (C), 61.5 (CH), 125.8 (CH), 133.1 (CH), 172.8 (C). IR (film) 1742 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>13</sub>H<sub>24</sub>NO<sub>2</sub>: 226.1802 [M + H]<sup>+</sup>; found: 226.1810.

**Methyl *cis*-1-*tert*-butyl-2-(1-methylvinyl)pyrrolidine-3-carboxylate (*cis*-17a).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.03 (s, 9H), 1.72 (dd, *J* = 1.6 and 1.2 Hz, 3H), 1.85 (dddd, *J* = 12.0, 6.4, 5.6 and 0.8 Hz, 1H), 2.22 (dtd, *J* = 13.2, 12.0 and 7.2 Hz, 1H), 2.71 (ddd, *J* = 12.0, 8.4 and 5.6 Hz, 1H), 2.93 (ddd, *J* = 13.2, 9.6 and 6.4 Hz, 1H), 3.08 (ddd, *J* = 8.4, 7.2 and 0.8 Hz, 1H), 3.61 (s, 3H), 3.81 (d, *J* = 9.6 Hz, 1H), 4.74 (dd, *J* = 1.2 and 0.8 Hz, 1H), 4.83 (dd, *J* = 1.6 and 0.8 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) δ 20.2 (CH<sub>3</sub>), 26.6 (3 CH<sub>3</sub>), 27.7 (CH<sub>2</sub>), 46.8 (CH<sub>2</sub>), 50.3 (CH), 51.5 (CH<sub>3</sub>), 53.9 (C), 64.6 (CH), 111.9 (CH<sub>2</sub>), 150.0 (C), 173.0 (C). IR (film) 1743 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>13</sub>H<sub>24</sub>NO<sub>2</sub>: 226.1802 [M + H]<sup>+</sup>; found: 226.1808.

**Methyl *trans*-1-*tert*-butyl-2-(1-methylvinyl)pyrrolidine-3-carboxylate (*trans*-17a).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a ≈ 4:1 mixture of *trans*-17a and *cis*-17a) δ 1.02 (s, 9H), 1.75 (dd, *J* = 1.6 and 0.8 Hz, 3H), 1.90-2.00 (m, 2H), 2.59 (dt, *J* = 7.6 and 4.0 Hz, 1H), 2.86 (dddd, *J* = 10.0, 8.8, 6.4 and 0.8 Hz, 1H), 2.99 (ddd, *J* = 9.2, 6.4 and 2.8 Hz, 1H), 3.63 (dd, *J* = 4.0 and 0.8 Hz, 1H), 3.69 (s, 3H), 4.73 (m, 1H), 5.10 (dt, *J* = 2.4 and 0.8 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 4:1 mixture of *trans*-17a and *cis*-17a) δ 19.1 (CH<sub>3</sub>), 27.1 (3 CH<sub>3</sub>), 27.8 (CH<sub>2</sub>), 47.5 (CH<sub>2</sub>), 50.0 (CH), 51.9 (CH<sub>3</sub>), 53.7 (C), 66.5 (CH), 110.7 (CH<sub>2</sub>), 150.7 (C), 177.7 (C).

**Methyl *cis*-2-(1-bromovinyl)-1-*tert*-butylpyrrolidine-3-carboxylate (*cis*-17b).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a ≈ 11:1 mixture of *cis*-17b and *trans*-17b) δ 1.05 (s, 9H), 1.87 (dddd, *J* = 12.0, 6.0, 5.6 and 0.8 Hz, 1H), 2.26 (dtdd, *J* = 13.2, 12.0, 7.2 and 0.4 Hz, 1H), 2.71 (ddd, *J* = 12.0, 8.4 and 5.6 Hz, 1H), 2.86 (ddd, *J* = 13.2, 8.8 and 6.0 Hz, 1H), 3.10 (ddd, *J* = 8.4, 7.2 and 0.8 Hz, 1H), 3.69 (s, 3H), 3.95 (dd, *J* = 8.8 and 0.8 Hz, 1H), 5.63 (d, *J* = 1.2 Hz, 1H), 6.14 (t, *J* = 1.2 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 11:1 mixture of *cis*-17b and *trans*-17b) δ 26.7 (3 CH<sub>3</sub>), 26.8 (CH<sub>2</sub>), 46.3 (CH<sub>2</sub>), 48.9 (CH), 51.9 (CH<sub>3</sub>), 53.9 (C), 66.5 (CH), 119.1 (CH<sub>2</sub>), 137.8 (C), 172.0 (C). IR (film) 1743 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>12</sub>H<sub>21</sub>BrNO<sub>2</sub>: 290.0750 [M + H]<sup>+</sup>; found: 290.0758.

**Methyl *trans*-2-(1-bromovinyl)-1-*tert*-butylpyrrolidine-3-carboxylate (*trans*-17b).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, significant signals from a ≈ 11:1 mixture of *cis*-17b and *trans*-17b) δ 1.04 (s, 9H), 1.95-2.08 (m, 2H), 2.82-2.92 (m, 1H), 3.03 (ddd, *J* = 8.8, 6.8 and 2.0 Hz, 1H), 3.71 (s, 3H), 5.51 (t, *J* = 1.2 Hz, 1H), 6.22 (t, *J* = 1.2 Hz, H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 11:1 mixture of *cis*-17b and *trans*-17b) δ 27.2 (3 CH<sub>3</sub>), 29.9 (CH<sub>2</sub>), 47.3 (CH<sub>2</sub>), 49.6 (CH), 52.1 (CH<sub>3</sub>), 53.6 (C), 68.0 (CH), 116.6 (CH<sub>2</sub>), 140.2 (C). One C was not observed.

**Methyl 1-bromo-3-(*tert*-butyl)-3-azabicyclo[4.1.0]heptane-6-carboxylate.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.01 (s, 9H), 1.58 (d, *J* = 5.6 Hz, 1H), 1.70 (ddd, *J* = 13.6, 12.0 and 6.4 Hz, 1H), 1.90 (d, *J* = 5.6 Hz, 1H), 2.08 (td, *J* = 12.0 and 4.8 Hz, 1H), 2.62 (ddd, *J* = 13.6, 4.8 and 2.0 Hz, 1H), 2.74 (d, *J* = 11.2 Hz, 1H), 2.85 (ddt, *J* = 12.0, 6.4 and 2.0 Hz, 1H), 3.47 (dd, *J* = 11.2 and 2.0 Hz, 1H), 3.74 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) δ 24.2 (CH<sub>2</sub>), 26.4 (3 CH<sub>3</sub>), 28.7 (CH<sub>2</sub>), 30.1 (C), 40.6 (C), 44.2 (CH<sub>2</sub>), 52.4 (CH<sub>3</sub>), 53.8 (C), 54.5 (CH<sub>2</sub>), 172.2 (C). IR (film) 1739 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>12</sub>H<sub>21</sub>BrNO<sub>2</sub>: 290.0750 [M + H]<sup>+</sup>; found: 290.0753.

**Methyl *cis*-1-*tert*-butyl-2-(1-iodovinyl)pyrrolidine-3-carboxylate (*cis*-17c).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a ≈ 14:1 mixture of *cis*-17c and *trans*-17c) δ 1.06 (s, 9H), 1.87 (dtd, *J* = 12.0, 6.0 and 0.8 Hz, 1H), 2.39 (dtd, *J* = 13.2, 12.0 and 7.2 Hz, 1H), 2.73 (ddd, *J* = 12.0, 8.4 and 6.0 Hz, 1H), 2.92 (ddd, *J* = 13.2, 9.2 and 6.0 Hz, 1H), 3.13 (ddd, *J* = 8.4, 7.2 and 0.8 Hz, 1H), 3.69 (s, 3H), 3.77 (dd, *J* = 9.2 and 0.8 Hz, 1H), 5.92 (d, *J* = 1.2 Hz, 1H), 6.50 (t, *J* = 1.2 Hz, H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 14:1 mixture of *cis*-17c and *trans*-17c) δ 26.7 (CH<sub>2</sub>), 27.0 (3 CH<sub>3</sub>), 46.5 (CH<sub>2</sub>), 49.8 (CH), 51.9 (CH<sub>3</sub>), 53.7 (C), 67.9 (CH), 120.3 (C), 126.7 (CH<sub>2</sub>), 172.0 (C). IR (film) 1742 cm<sup>-1</sup>.

**Methyl *trans*-1-*tert*-butyl-2-(1-iodovinyl)pyrrolidine-3-carboxylate (*trans*-17c).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, significant signals from a ≈ 14:1 mixture of *cis*-17c and *trans*-17c) δ 1.04 (s, 9H), 1.98-2.05 (m, 2H), 2.63-2.68 (m, 1H), 2.80-2.86 (m, 1H), 3.03-3.08 (m, 1H), 3.71 (s, 3H), 5.79 (t, *J* = 0.8 Hz, 1H), 6.63 (t, *J* = 1.2 Hz, H).

**Methyl *cis*-1-*tert*-butyl-2-ethynylpyrrolidine-3-carboxylate (*cis*-19a).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a ≈ 6:1 mixture of *cis*-19a and *trans*-19a) δ 1.16 (s, 9H), 1.99 (dtddd, *J* = 12.8, 7.2, 6.8 and 3.2 Hz, 1H), 2.27 (d, *J* = 2.0 Hz, 1H), 2.34 (ddt, *J* = 12.8, 11.6 and 8.4 Hz, 1H), 2.79 (td, *J* = 8.4 and 6.8 Hz, 1H), 3.01-3.09 (m, 2H), 3.72 (s, 3H), 4.13 (dd, *J* = 8.4 and 2.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 6:1 mixture of *cis*-19a and *trans*-19a) δ 25.7 (CH<sub>2</sub>), 26.9 (3 CH<sub>3</sub>), 44.9 (CH<sub>2</sub>), 49.4 (CH), 50.6 (CH), 52.0 (CH<sub>3</sub>), 53.8 (C), 73.0 (CH), 84.2 (C), 171.9 (C). IR (film) 1744 cm<sup>-1</sup>.

**Methyl *trans*-1-*tert*-butyl-2-ethynylpyrrolidine-3-carboxylate (*trans*-19a).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, significant signals from a ≈ 6:1 mixture of *cis*-19a and *trans*-19a) δ 1.16 (s, 9H), 2.08 (ddt, *J* = 12.4, 6.8 and 3.6 Hz, 1H), 2.16-2.24 (m, 1H), 2.29 (d, *J* = 2.4 Hz, 1H), 2.74-2.81 (masked, 1H), 2.96-3.12 (m, 2H), 3.72 (s, 3H), 4.07 (dd, *J* = 3.6 and 2.4 Hz, 1H). <sup>13</sup>C NMR

(CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 6:1 mixture of *cis*-19a and *trans*-19a) δ 27.2 (3 CH<sub>3</sub>), 28.0 (CH<sub>2</sub>), 45.8 (CH<sub>2</sub>), 51.1 (CH), 51.7 (CH), 52.3 (CH<sub>3</sub>), 53.9 (C), 71.2 (CH), 174.1 (C). One C was not observed.

**Methyl *cis*-1-*tert*-butyl-2-(1-propynyl)pyrrolidine-3-carboxylate (*cis*-19b).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, signals from a ≈ 4:1 mixture of *cis*-19b and *trans*-19b) δ 1.14 (s, 9H), 1.75 (d, *J* = 2.4 Hz, 3H), 1.87 (dtd, *J* = 12.8, 6.8 and 3.2 Hz, 1H), 2.32 (dddd, *J* = 12.8, 11.2, 8.4 and 8.0 Hz, 1H), 2.74 (td, *J* = 8.4 and 6.8 Hz, 1H), 2.95-3.06 (m, 2H), 3.70 (s, 3H), 4.08 (ddt, *J* = 8.4, 2.4 and 2.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 4:1 mixture of *cis*-19b and *trans*-19b) δ 3.8 (CH<sub>3</sub>), 25.8 (CH<sub>2</sub>), 26.9 (3 CH<sub>3</sub>), 45.0 (CH<sub>2</sub>), 49.6 (CH), 50.9 (CH), 51.9 (CH<sub>3</sub>), 53.6 (C), 79.0 (C), 80.5 (C), 172.3 (C). IR (film) 1744 cm<sup>-1</sup>.

**Methyl *trans*-1-*tert*-butyl-2-(1-propynyl)pyrrolidine-3-carboxylate (*trans*-19b).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, significant signals from a ≈ 4:1 mixture of *cis*-19b and *trans*-19b) δ 1.15 (s, 9H), 1.78 (d, *J* = 2.4 Hz, 3H), 2.03 (ddt, *J* = 12.4, 7.2 and 4.0 Hz, 1H), 2.17 (dtd, *J* = 12.4, 8.8 and 7.6 Hz, 1H), 3.70 (s, 3H), 3.97 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, signals from a ≈ 4:1 mixture of *cis*-19b and *trans*-19b) δ 4.0 (CH<sub>3</sub>), 27.2 (3 CH<sub>3</sub>), 28.0 (CH<sub>2</sub>), 46.1 (CH<sub>2</sub>), 51.5 (CH), 52.0 (CH<sub>3</sub>), 52.2 (CH), 53.9 (C), 78.7 (C), 82.4 (C), 174.5 (C).

**Methyl *cis*-1-*tert*-butyl-2-[2-(trimethylsilyl)ethynyl]pyrrolidine-3-carboxylate (*cis*-19c).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.11 (s, 9H), 1.16 (s, 9H), 1.96 (m, 1H), 2.32 (dddd, *J* = 12.0, 10.4, 9.2, and 8.0 Hz, 1H), 2.78 (q, *J* = 9.2 Hz, 1H), 2.98-3.08 (m, 2H), 3.69 (s, 3H), 4.13 (d, *J* = 8.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) δ 0.1 (9 CH<sub>3</sub>), 25.4 (CH<sub>2</sub>), 27.0 (3 CH<sub>3</sub>), 44.6 (CH<sub>2</sub>), 49.5 (CH), 51.5 (CH), 51.9 (CH<sub>3</sub>), 53.7 (C), 89.6 (C), 106.1 (C), 171.9 (C). IR (film) 1747 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd for C<sub>15</sub>H<sub>28</sub>NO<sub>2</sub>Si: 282.1884 [M + H]<sup>+</sup>; found: 282.1887.

**Methyl *trans*-1-*tert*-butyl-2-[2-(trimethylsilyl)ethynyl]pyrrolidine-3-carboxylate (*trans*-19c).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, significant signals from a ≈ 3:1 mixture of *cis*-19c and *trans*-19c) δ 0.10 (s, 9H), 1.15 (s, 9H), 3.69 (s, 3H), 4.05 (d, *J* = 3.2 Hz, 1H).

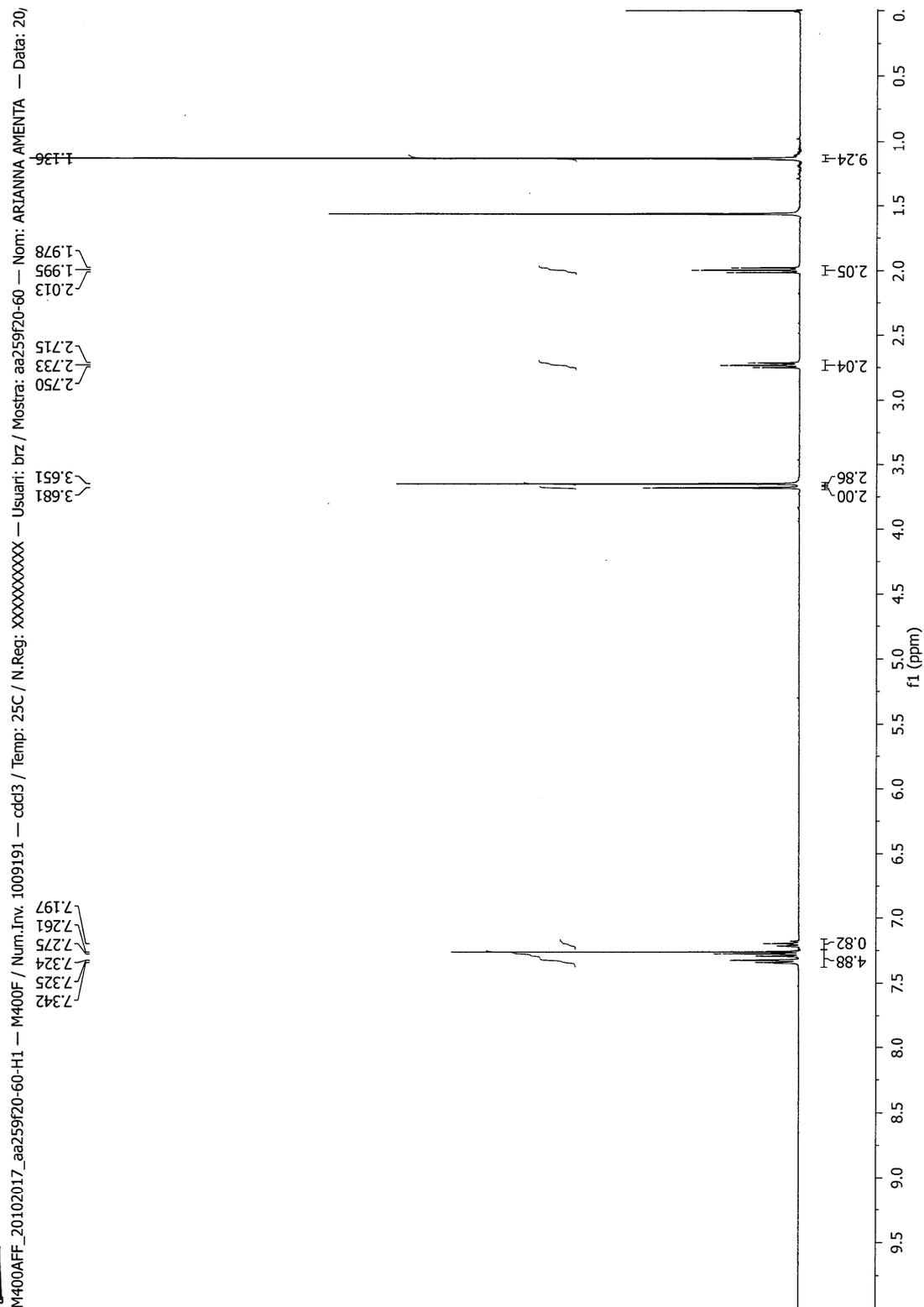
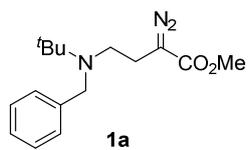
**Methyl *cis*-5-(*tert*-butyl)-3,3a,4,5,6,7-hexahydro-7aH-pyrazolo[4,3-*c*]pyridine-7a-carboxylate (21).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.00 (s, 9H), 1.90-1.98 (m, 1H), 2.35-2.64 (m, 6H), 3.78 (s, 3H), 4.43 (dd, *J* = 17.2 and 6.4 Hz, 1H), 4.63 (dd, *J* = 17.2 and 7.6 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) δ 26.2 (3 CH<sub>3</sub>), 30.0 (CH<sub>2</sub>), 36.3 (CH), 42.0 (CH<sub>2</sub>), 44.6 (CH<sub>2</sub>), 52.9 (CH<sub>3</sub>), 53.7 (C), 80.5 (CH<sub>2</sub>), 91.9 (C), 171.2 (C). HRMS (ESI-TOF) calcd for C<sub>12</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>: 240.1707 [M + H]<sup>+</sup>; found: 240.1705.

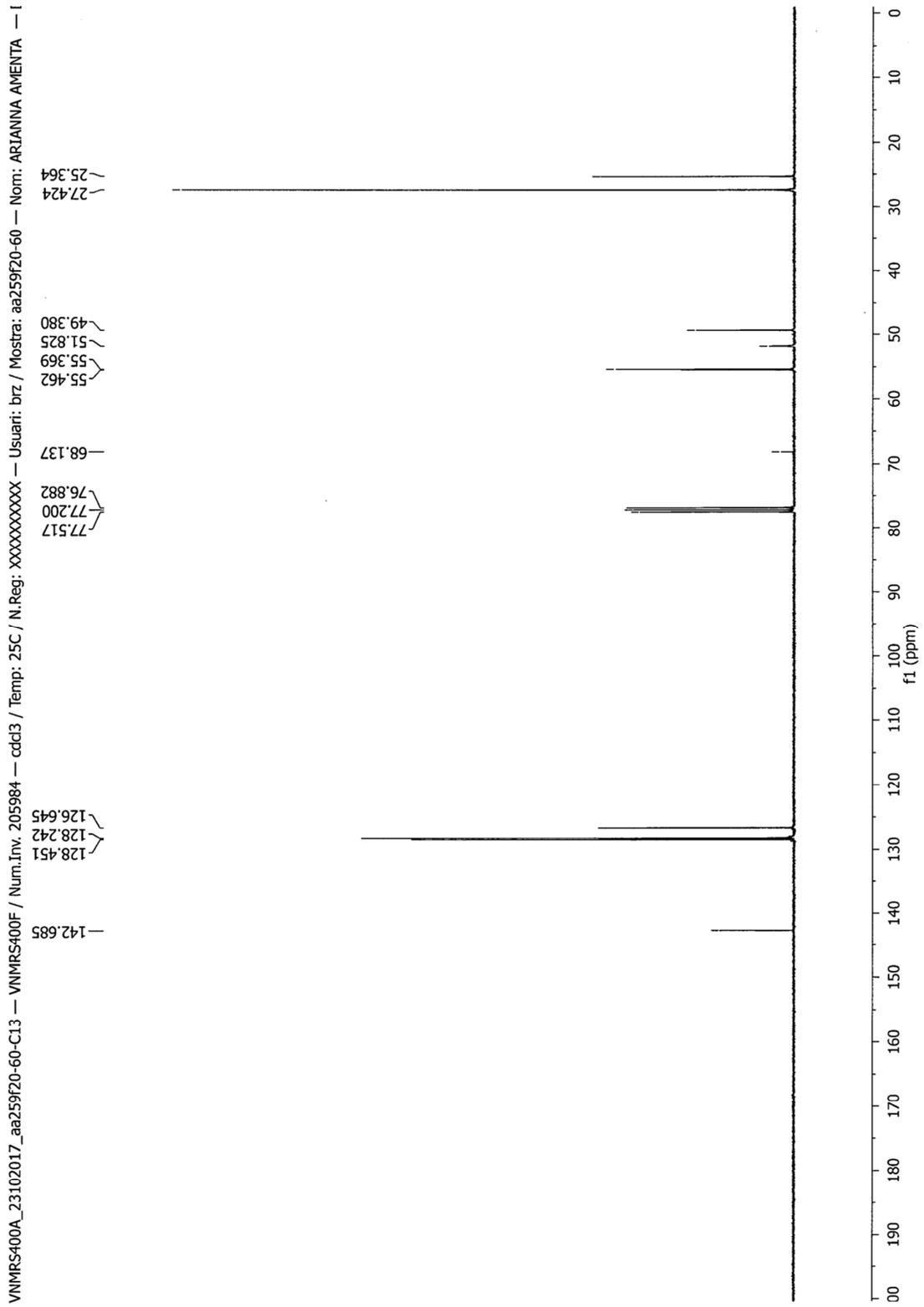
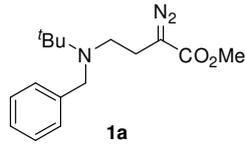
**Methyl *cis*-5-(*tert*-butyl)-1,3a,4,5,6,7-hexahydro-7aH-pyrazolo[4,3-*c*]pyridine-7a-carboxylate (22).** **22** was isolated as a brown oil (35%) from the crude reaction mixture of the reaction of **20** with **Ru-1** (Scheme 1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.06 (s, 9H), 1.87 (ddd, *J* = 14.0, 4.8 and 3.2 Hz, 1H), 2.02 (dtd, *J* = 14.0, 10.0 and 4.4 Hz, 1H), 2.13 (dd, *J* = 11.6 and 9.2

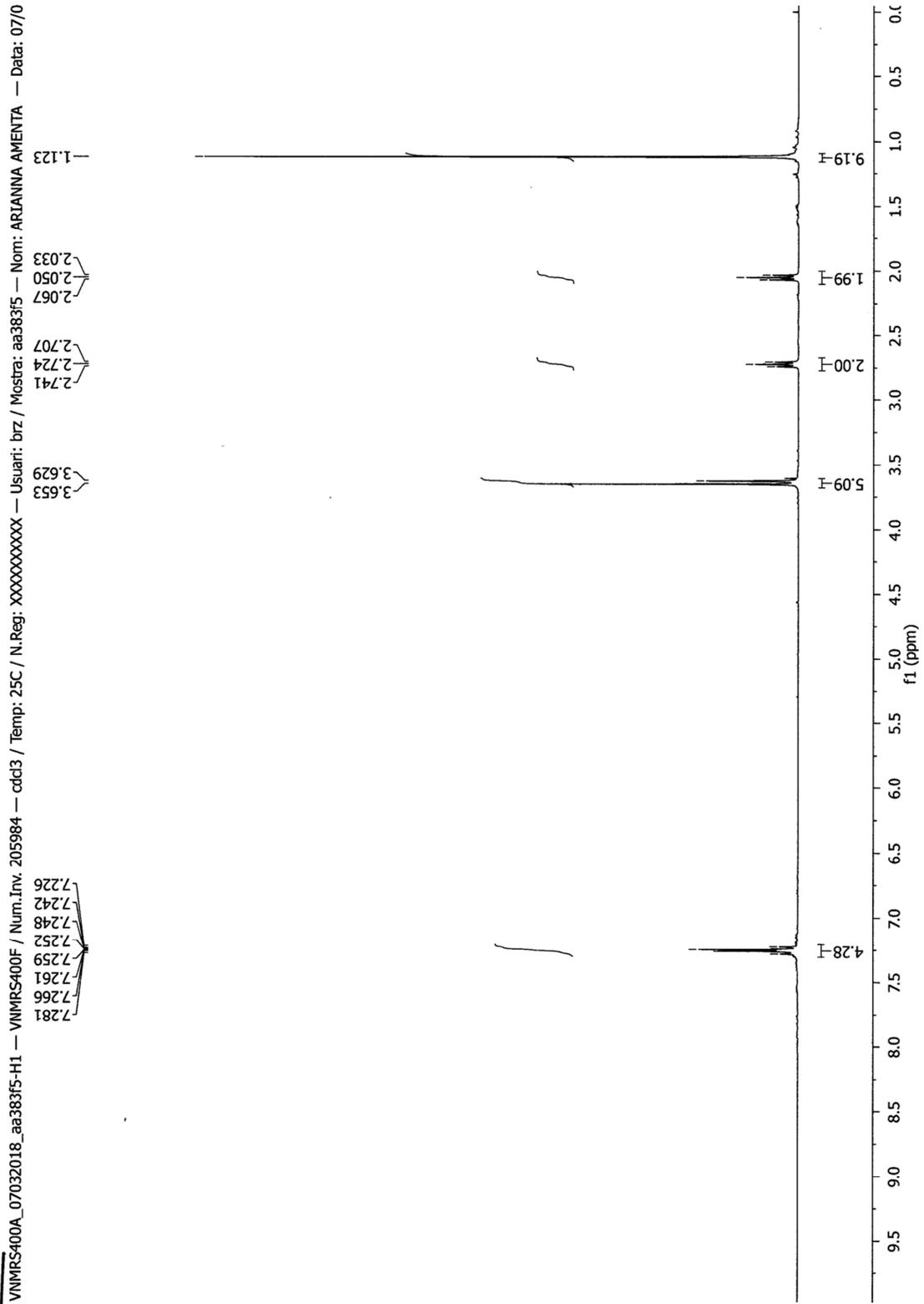
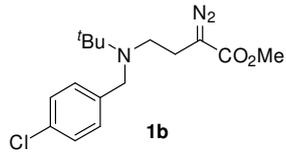
Hz, 1H), 2.45 (ddd,  $J = 12.0, 10.0$  and  $3.2$  Hz, 1H), 2.67 (ddd,  $J = 12.0, 4.8$  and  $4.4$  Hz, 1H), 2.95 (ddd,  $J = 11.6, 6.0$  and  $1.6$  Hz, 1H), 3.31 (dd,  $J = 9.2$  and  $6.0$  Hz, 1H), 3.73 (s, 3H), 6.16 (s, 1H), 6.79 (dd,  $J = 1.6$  and  $0.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz)  $\delta$  26.3 (3  $\text{CH}_3$ ), 30.9 ( $\text{CH}_2$ ), 42.1 ( $\text{CH}_2$ ), 45.4 ( $\text{CH}_2$ ), 47.2 (CH), 52.8 ( $\text{CH}_3$ ), 54.2 (C), 68.3 (C), 147.8 (CH), 175.7 (C). IR (film)  $1732\text{ cm}^{-1}$ . HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{22}\text{N}_3\text{O}_2$ : 240.1707  $[\text{M} + \text{H}]^+$ ; found: 240.1709.

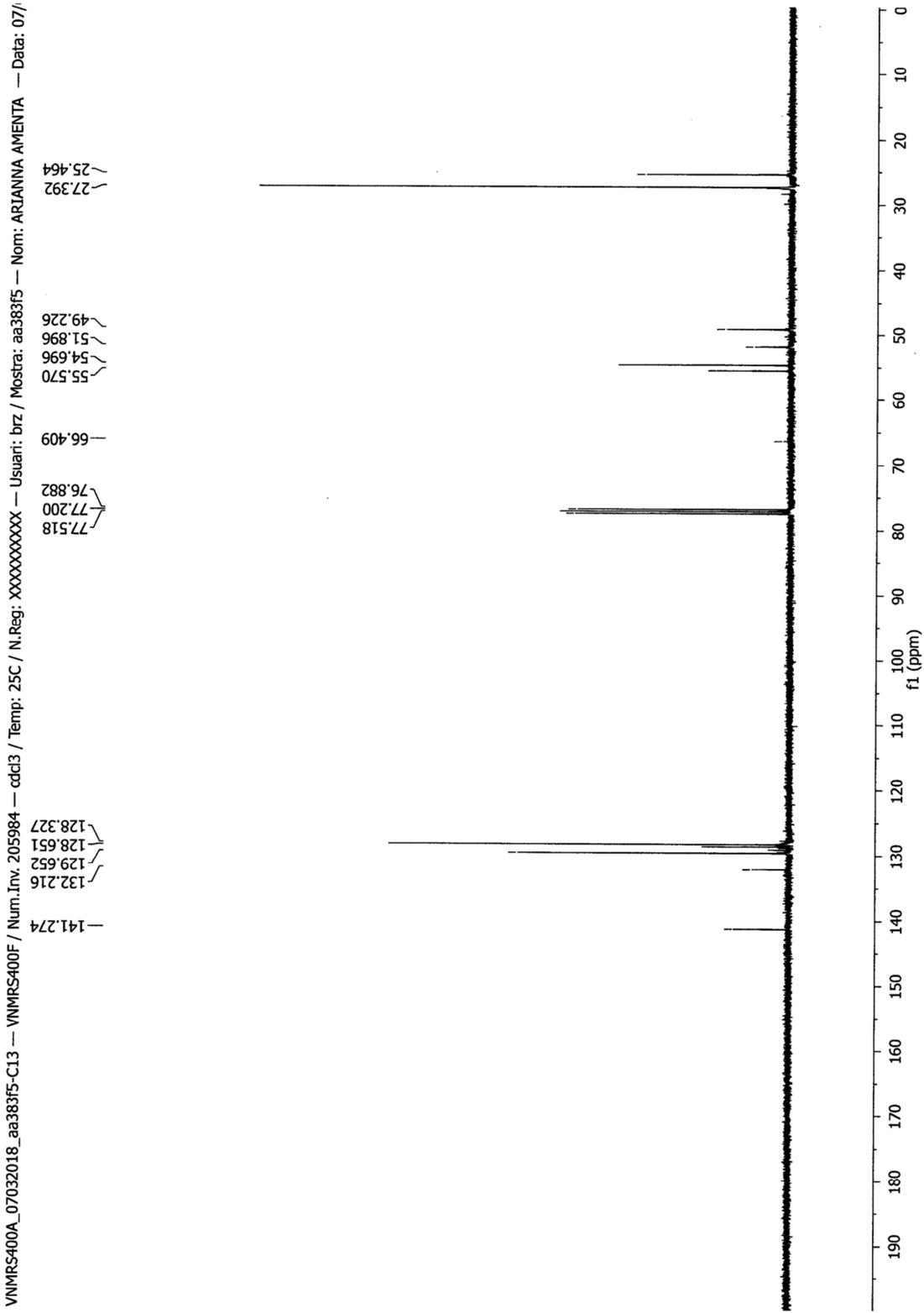
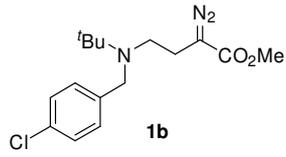
**Methyl (*E*)-*cis*-1-*tert*-butyl-2-vinylpyrrolidine-3-carboxylate (23).** **23** was isolated as a brown oil (15%) from the crude reaction mixture of the reaction of **20** with **Ru-1** (Scheme 1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.09 (s, 9H), 1.90 (dtd,  $J = 12.4, 6.0$  and  $1.2$  Hz, 1H), 2.18 (tdd,  $J = 12.4, 11.2$  and  $7.6$  Hz, 1H), 2.72 (ddd,  $J = 11.2, 8.8$  and  $6.0$  Hz, 1H), 2.92 (ddd,  $J = 12.4, 8.8$  and  $6.0$  Hz, 1H), 3.04 (ddd,  $J = 8.8, 7.6$  and  $1.2$  Hz, 1H), 3.63 (s, 3H), 3.78 (t,  $J = 8.8$  Hz, 1H), 4.98 (ddd,  $J = 10.0, 2.0$  and  $1.2$  Hz, 1H), 5.12 (ddd,  $J = 17.2, 2.0$  and  $1.2$  Hz, 1H), 5.76 (ddd,  $J = 17.2, 10.0$  and  $8.8$  Hz, 1H). IR (film)  $1744\text{ cm}^{-1}$ . HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{22}\text{NO}_2$ : 212.1651  $[\text{M} + \text{H}]^+$ ; found: 212.1649.

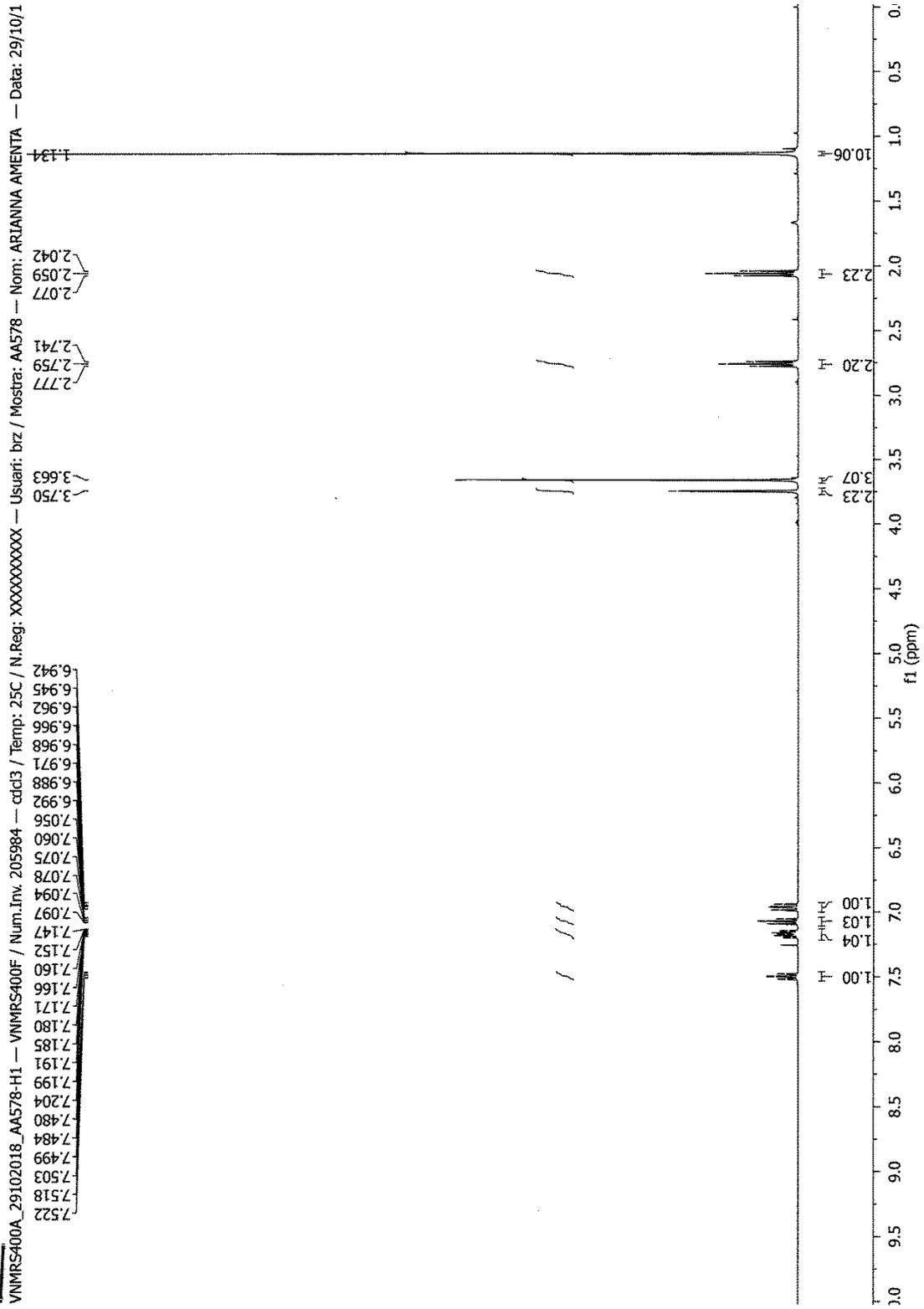
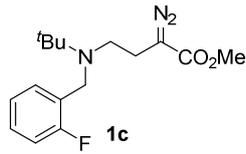
Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of new compounds

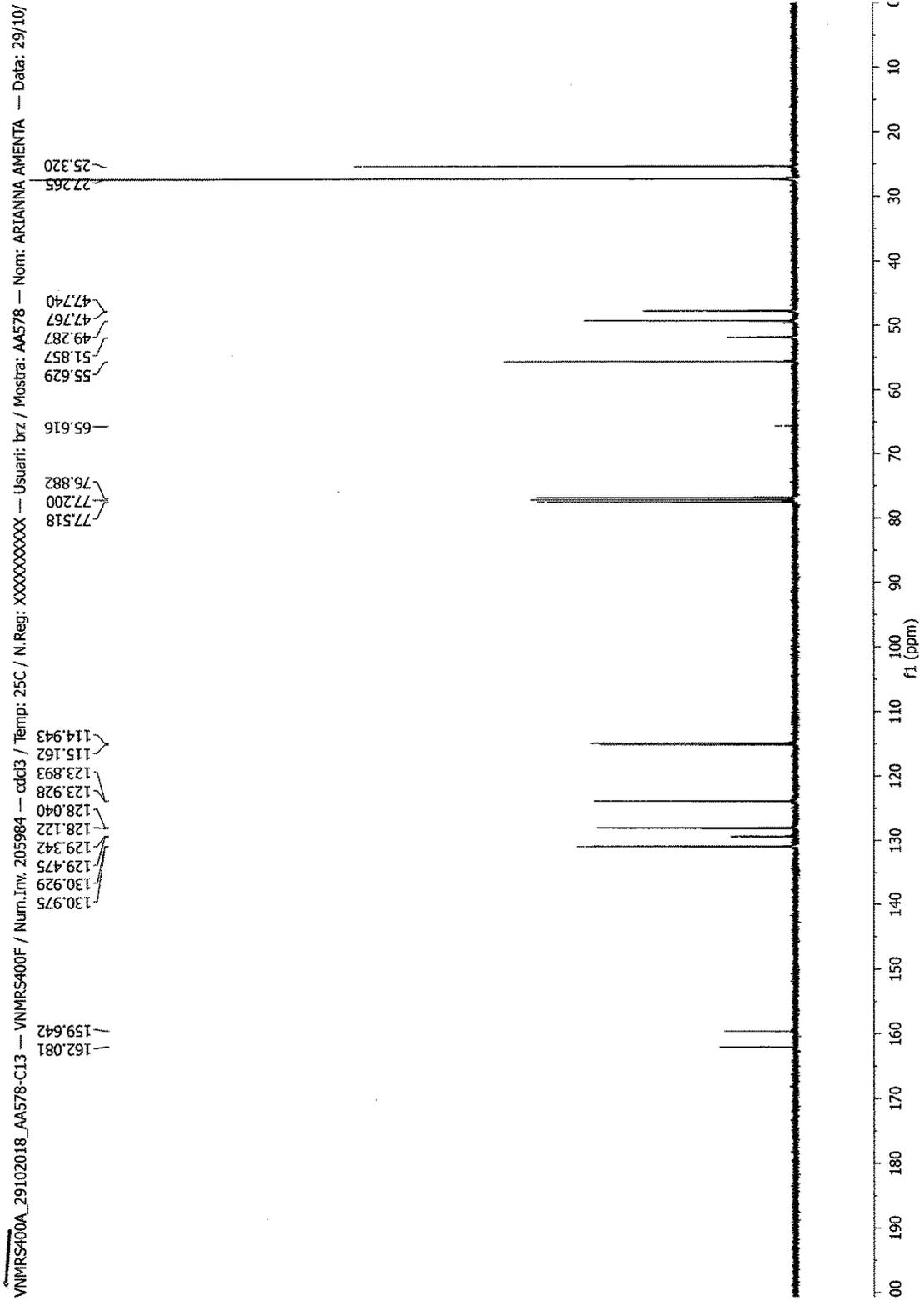
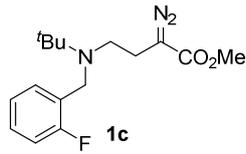


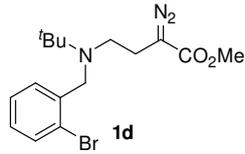




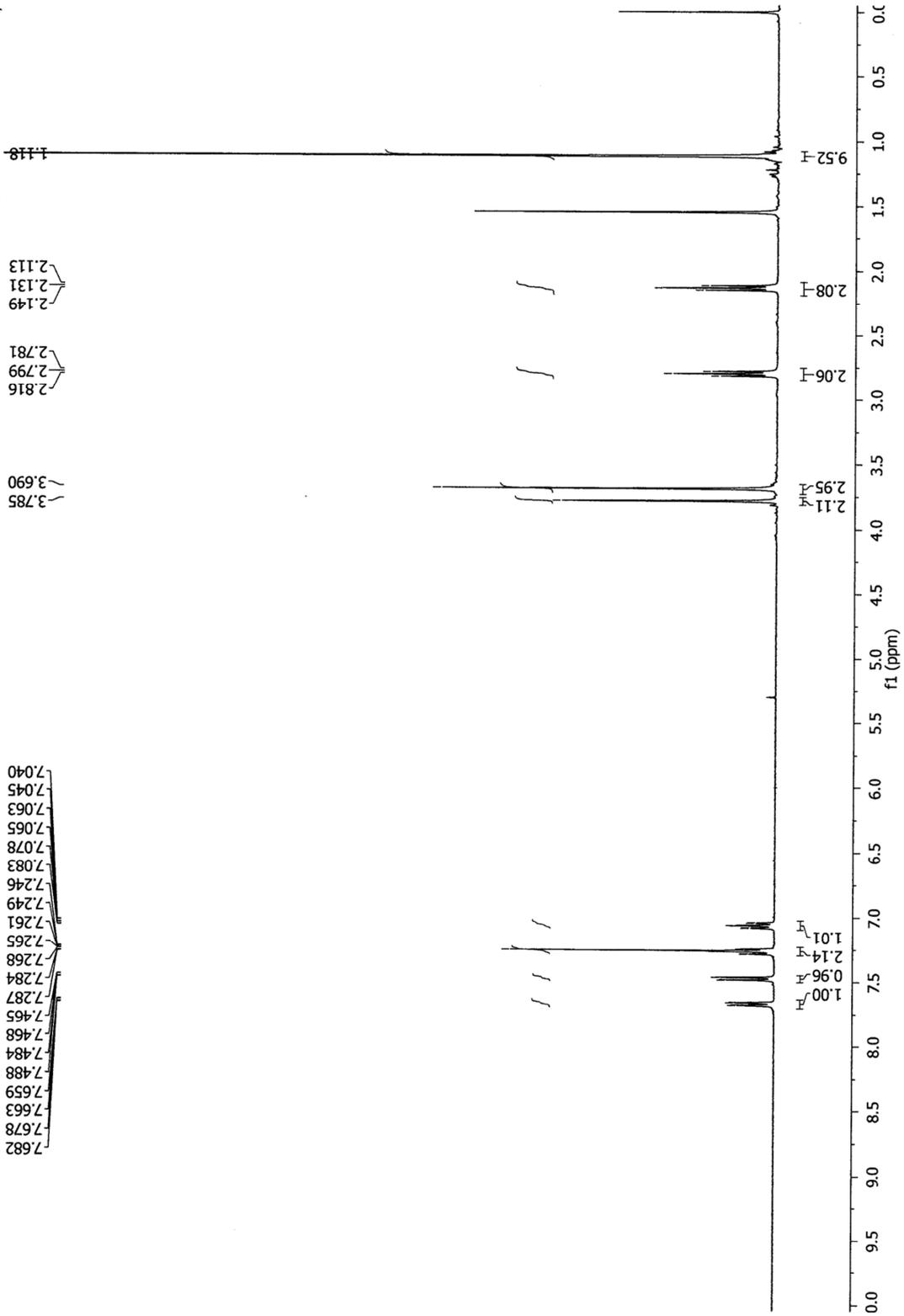


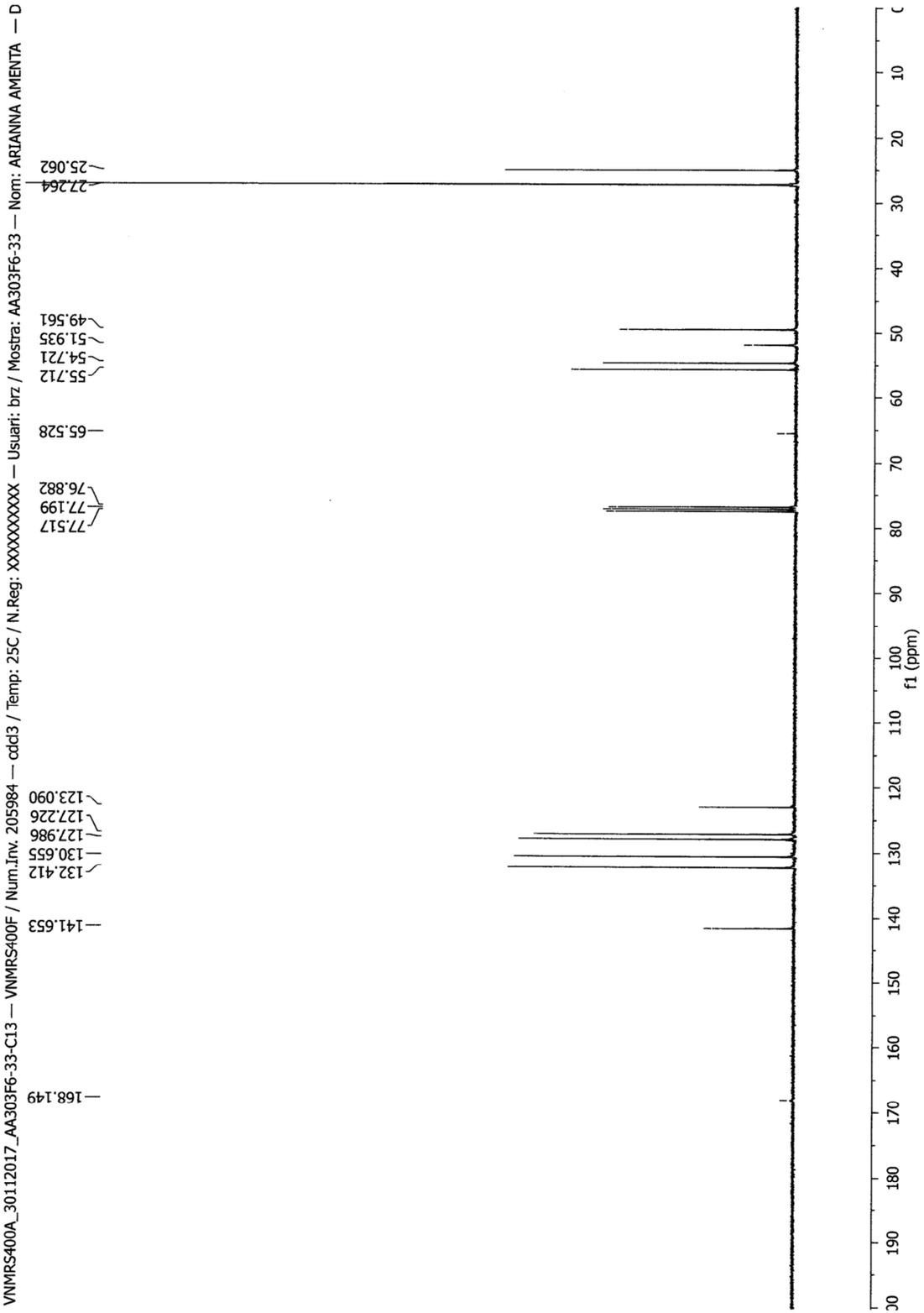
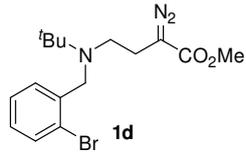


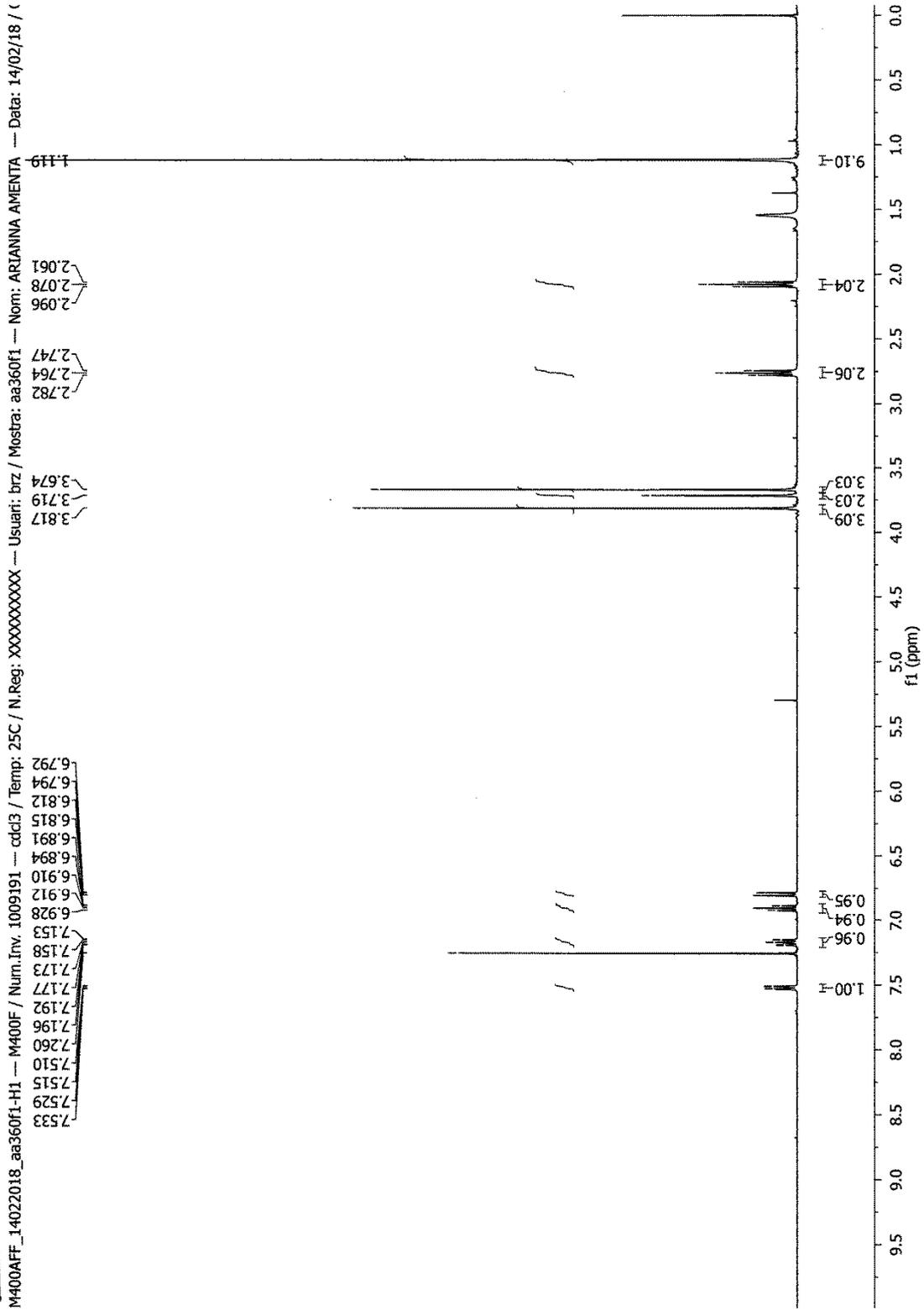
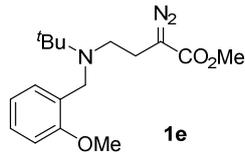


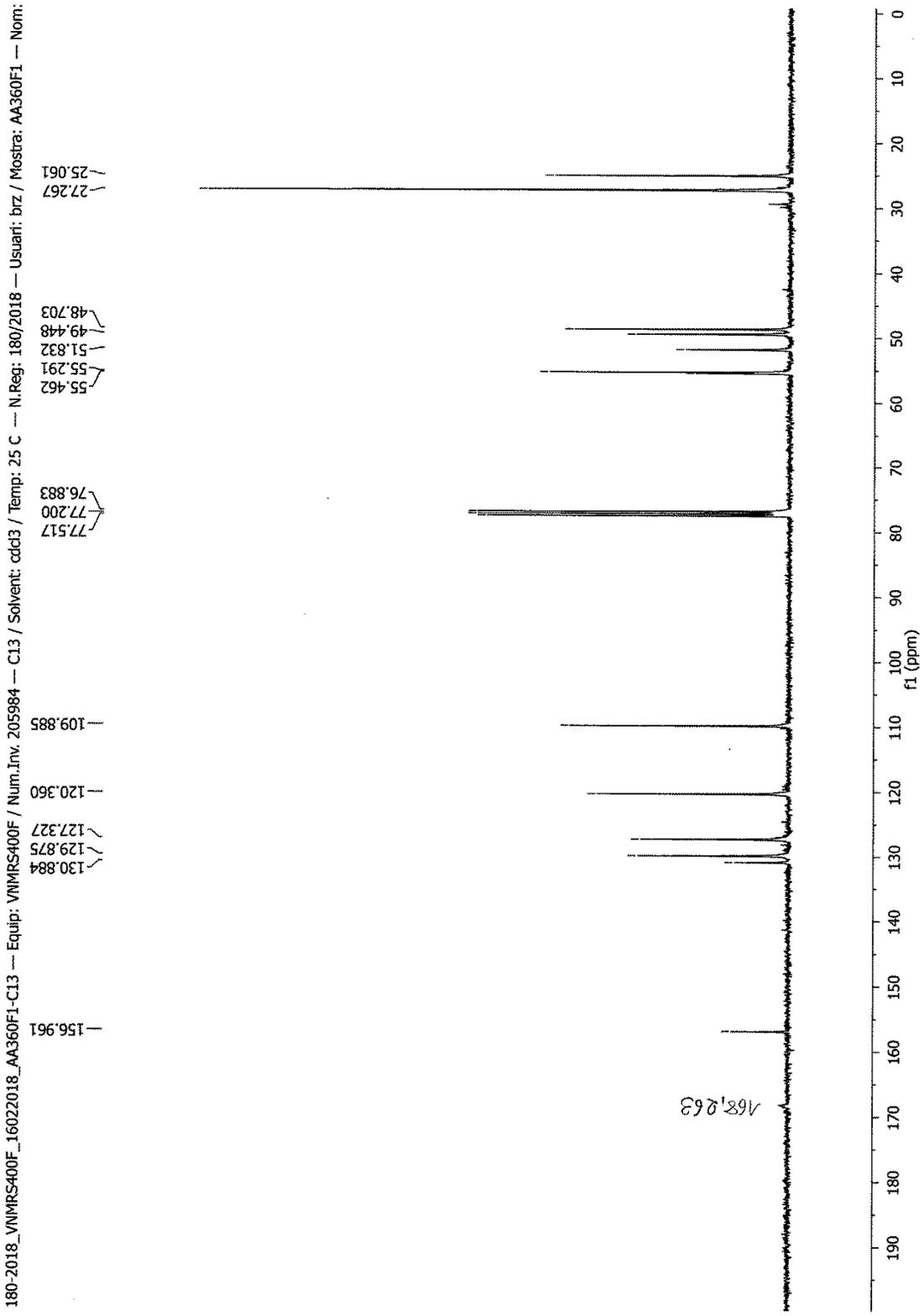
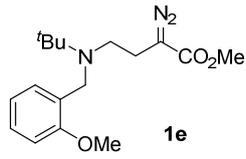


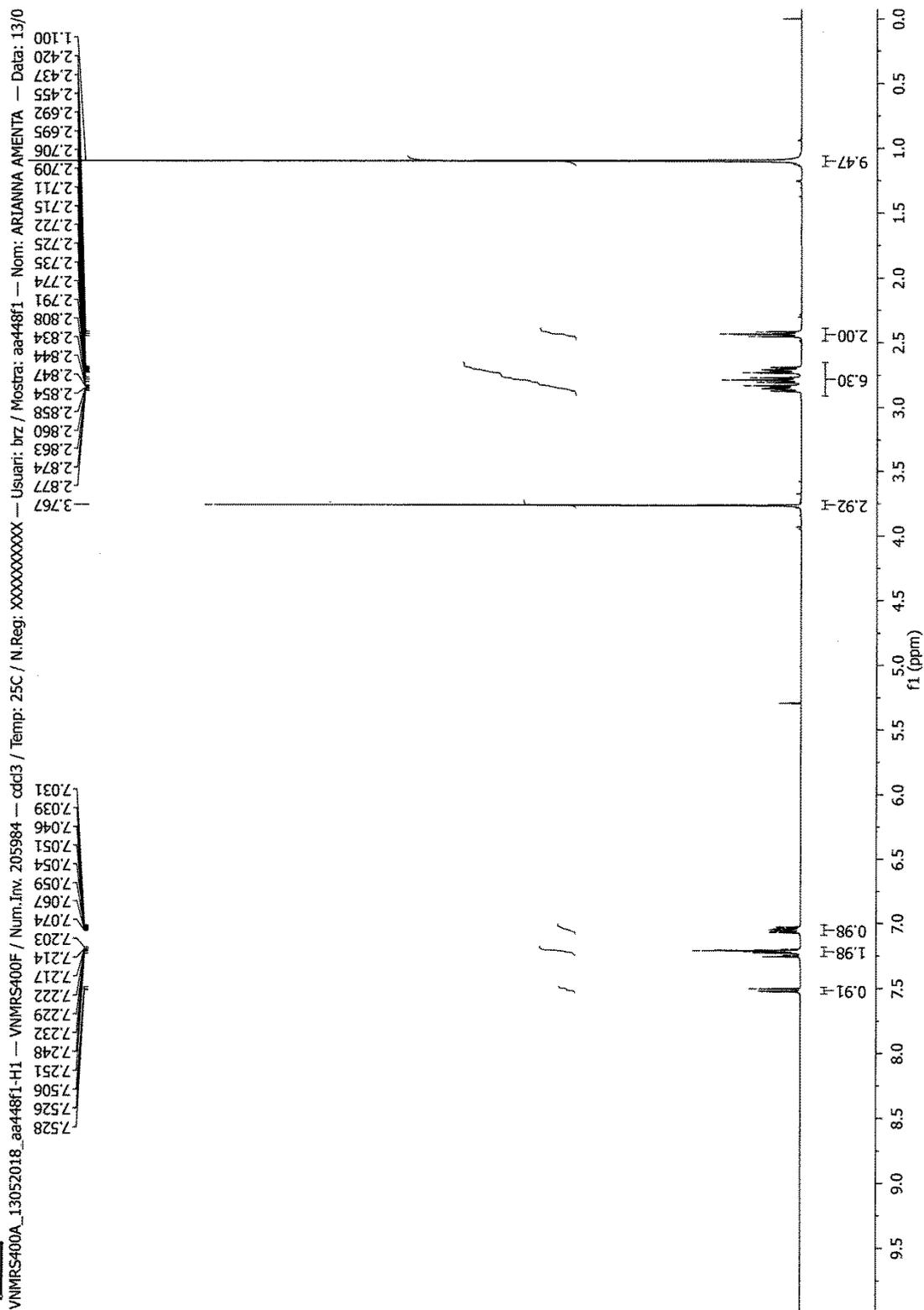
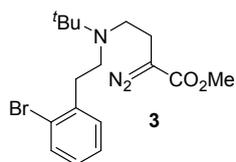
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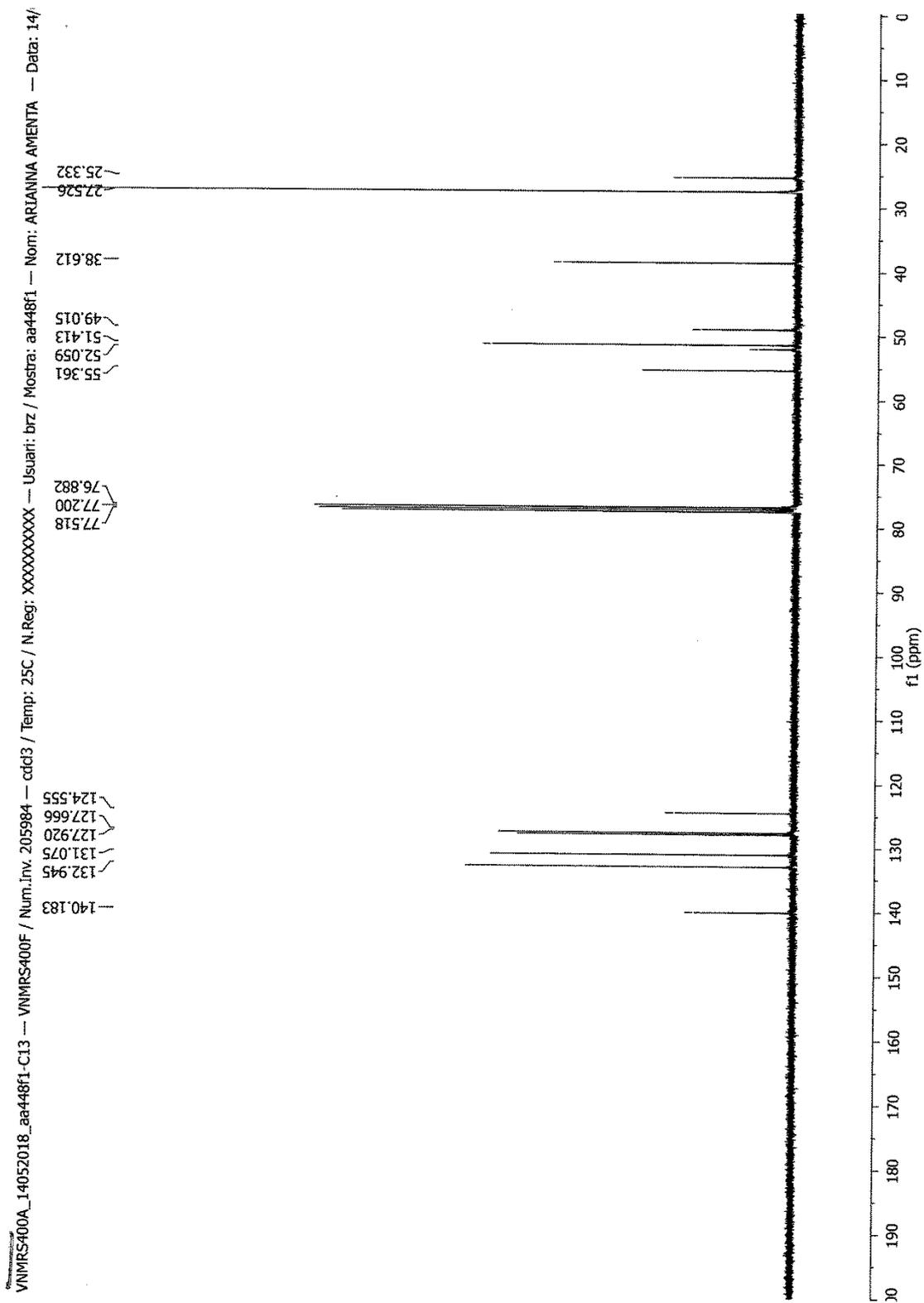
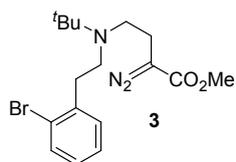


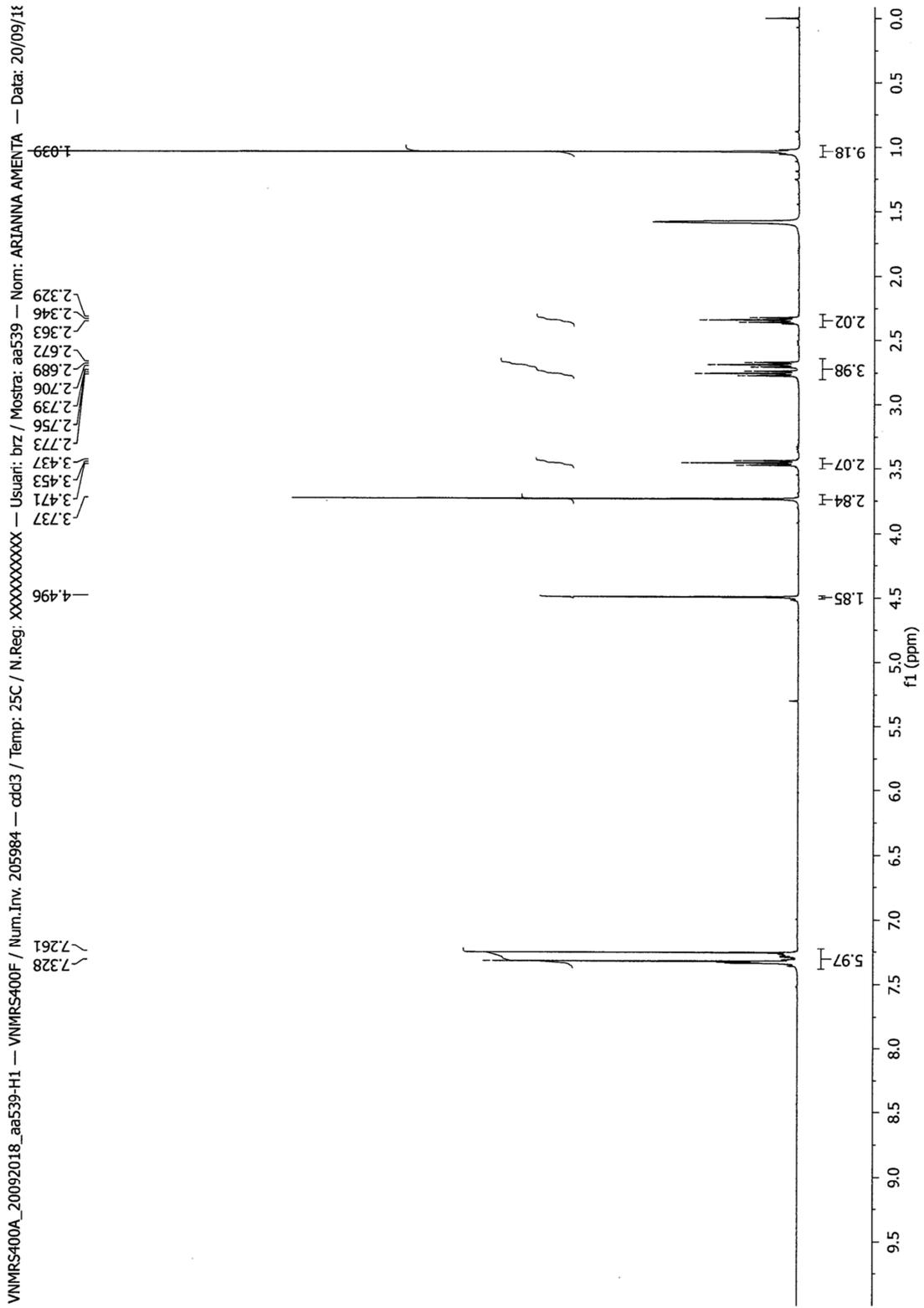
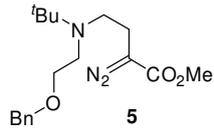


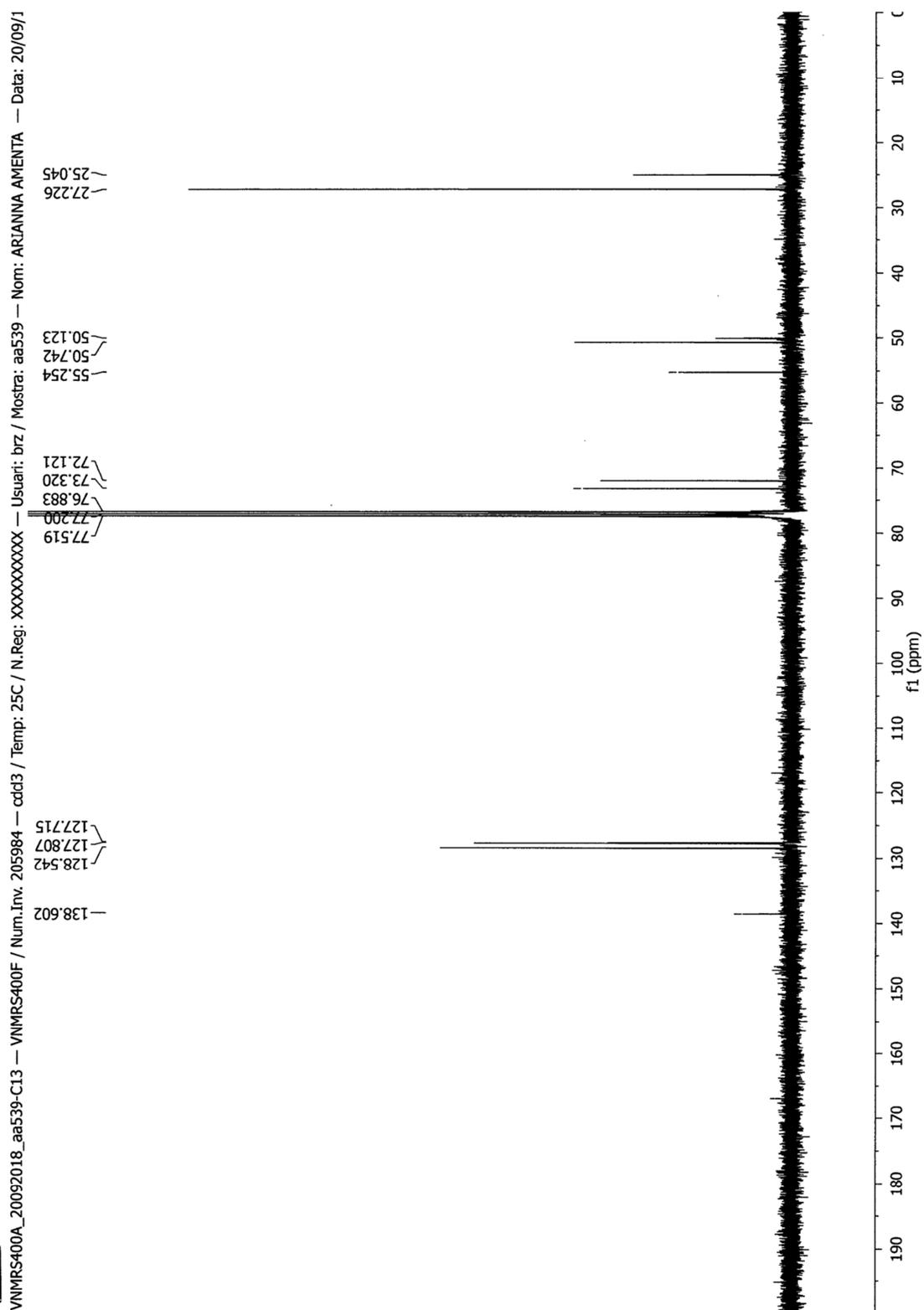
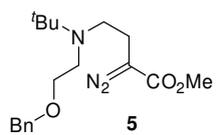


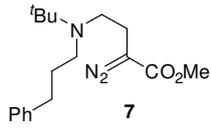






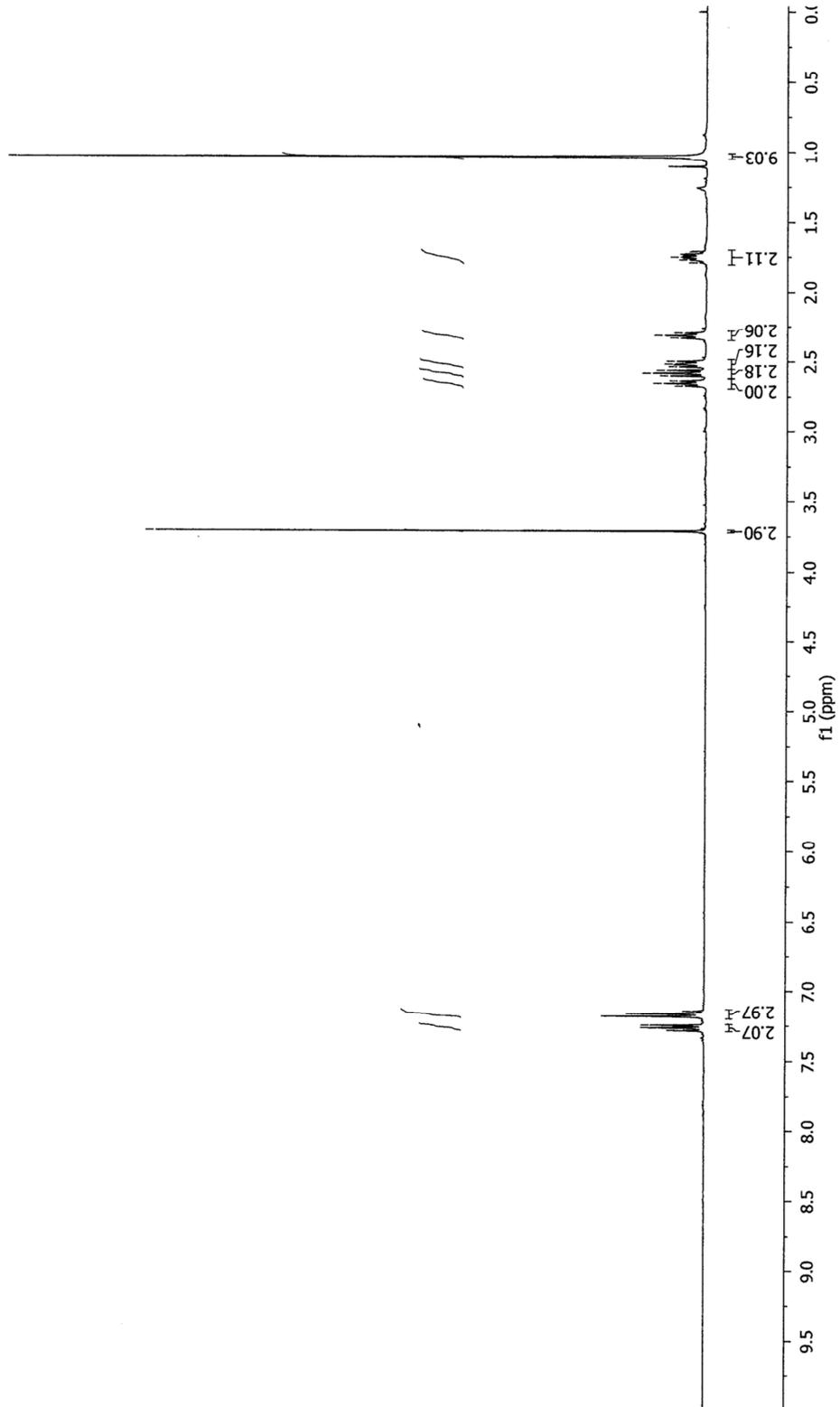


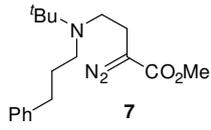




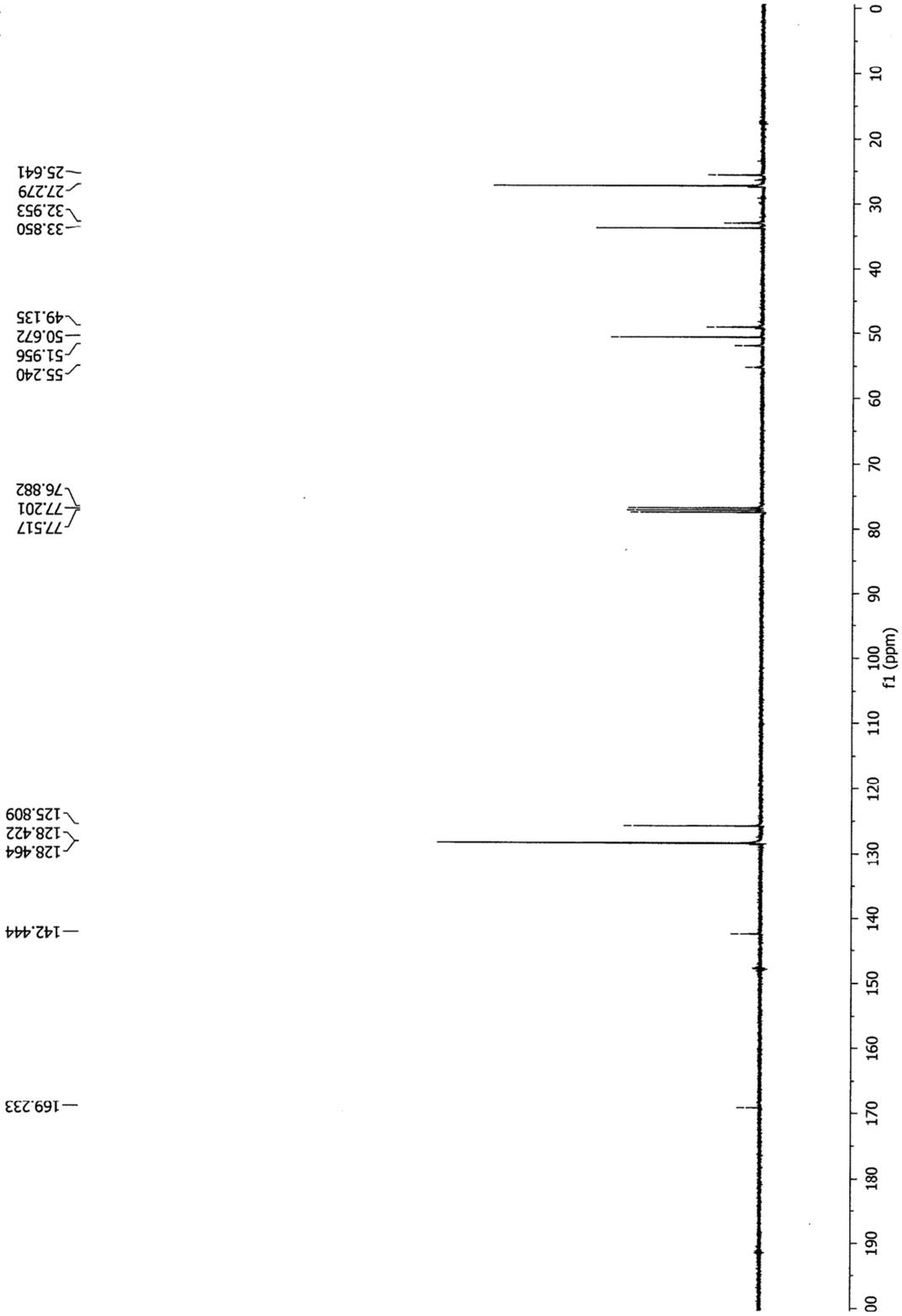
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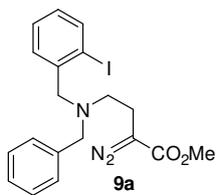
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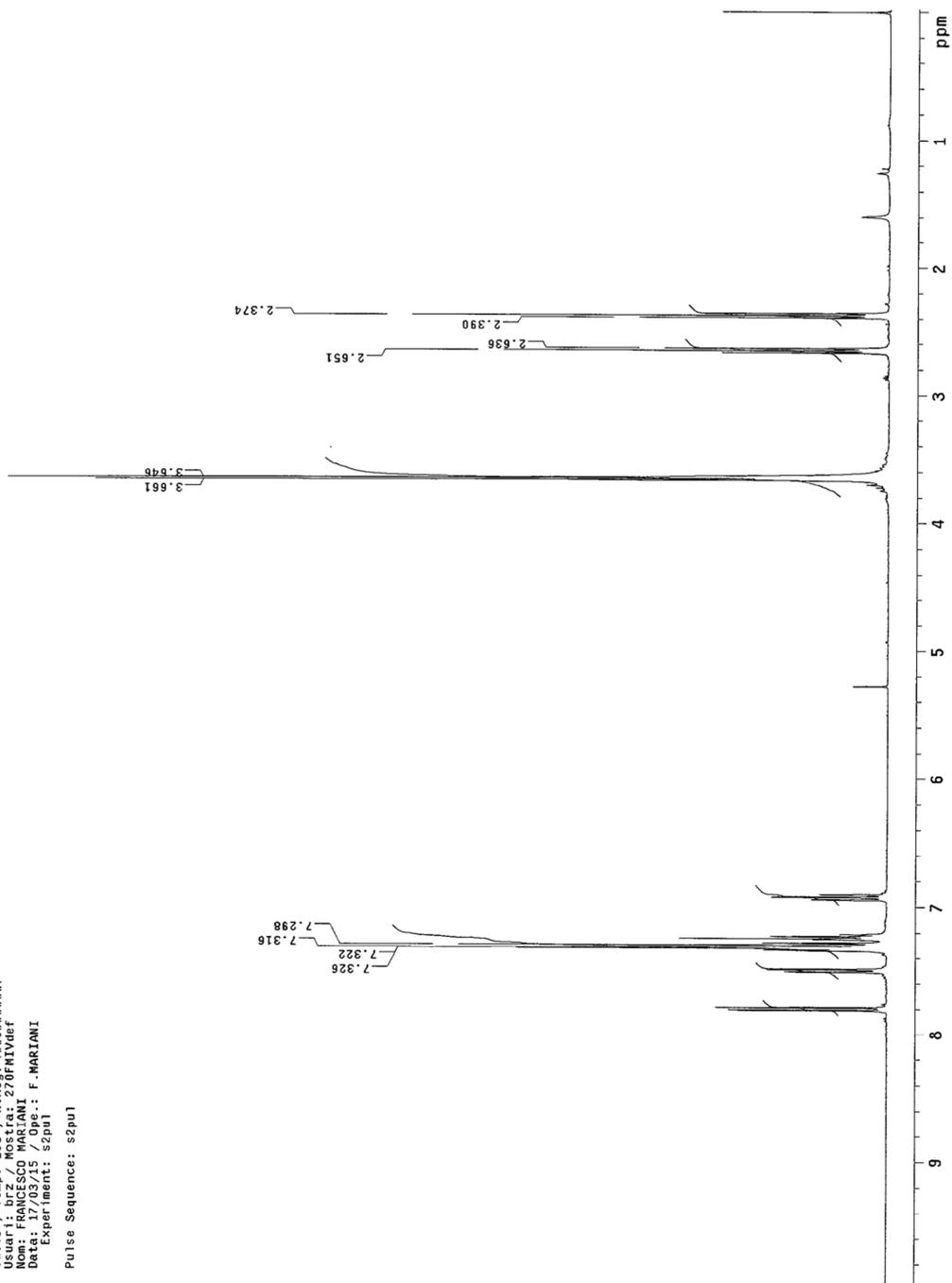


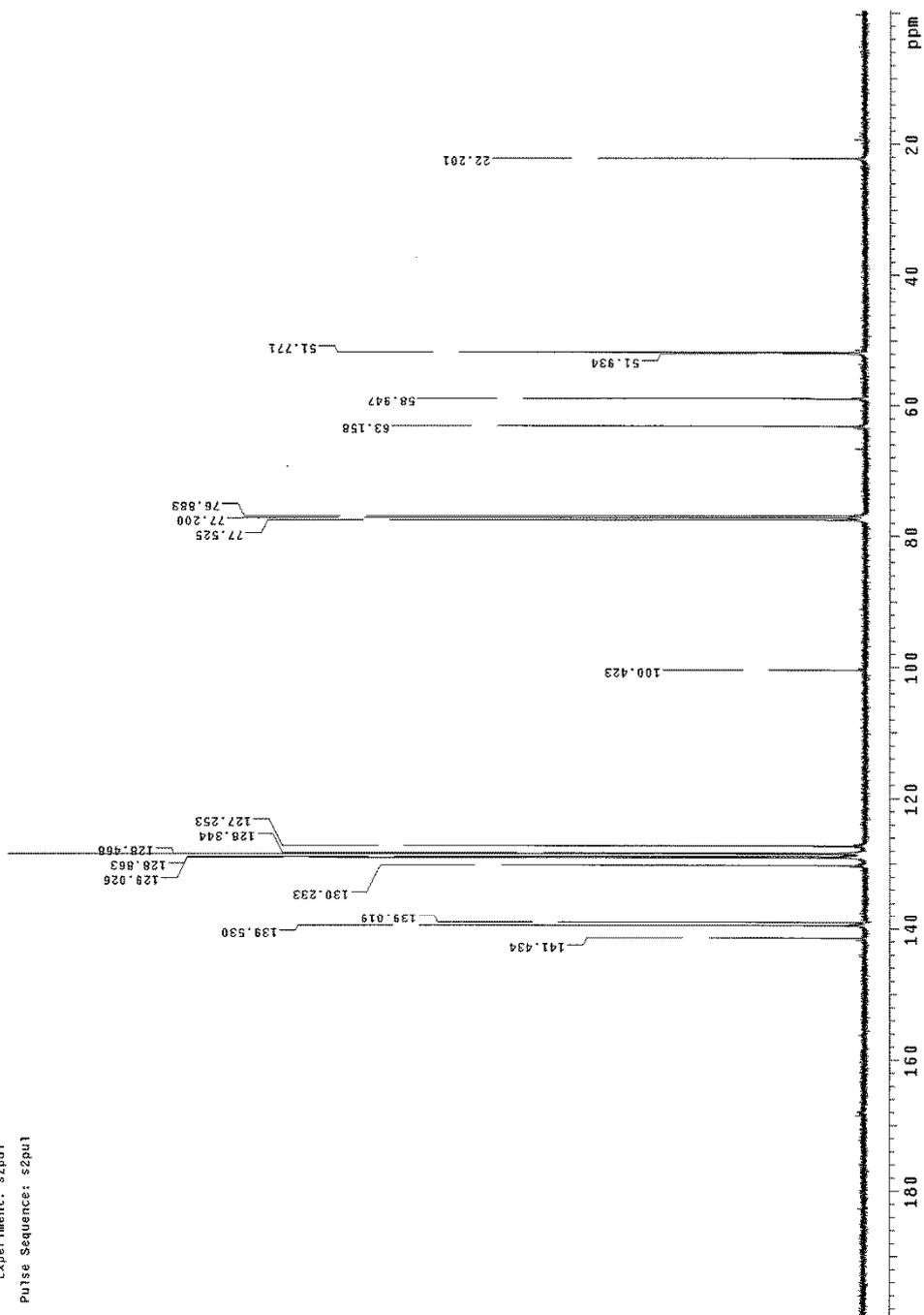
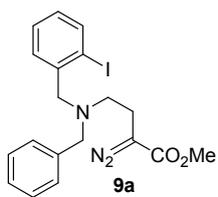
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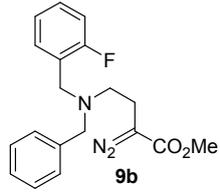


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 Usuari: bfz / Mostra: 270FIVdef  
 Nom: FRANCESCO MARIANI  
 Data: 17/03/15 / Ope.: F. MARIANI  
 Experiment: szpa1  
 Pulse Sequence: szpu1

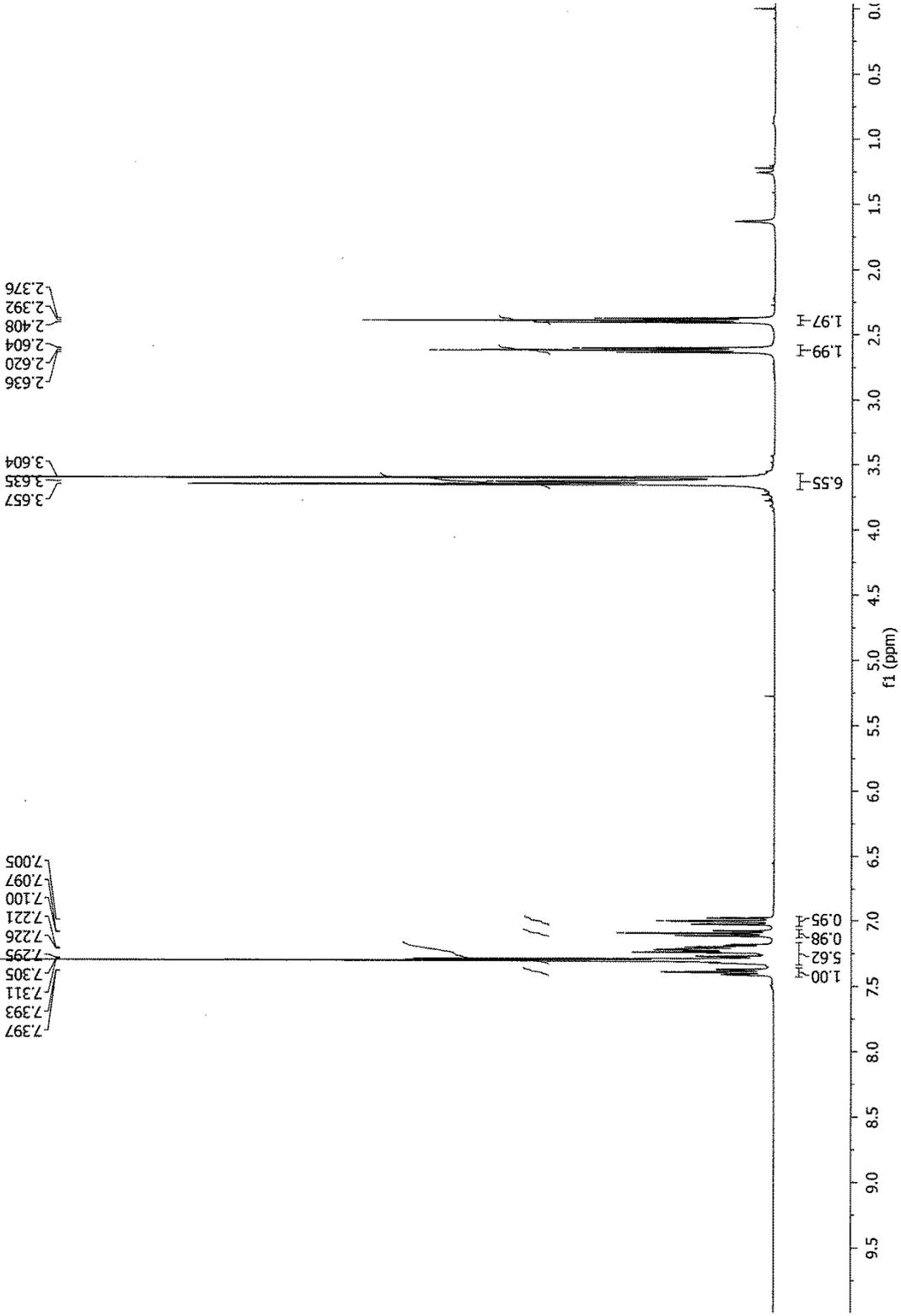


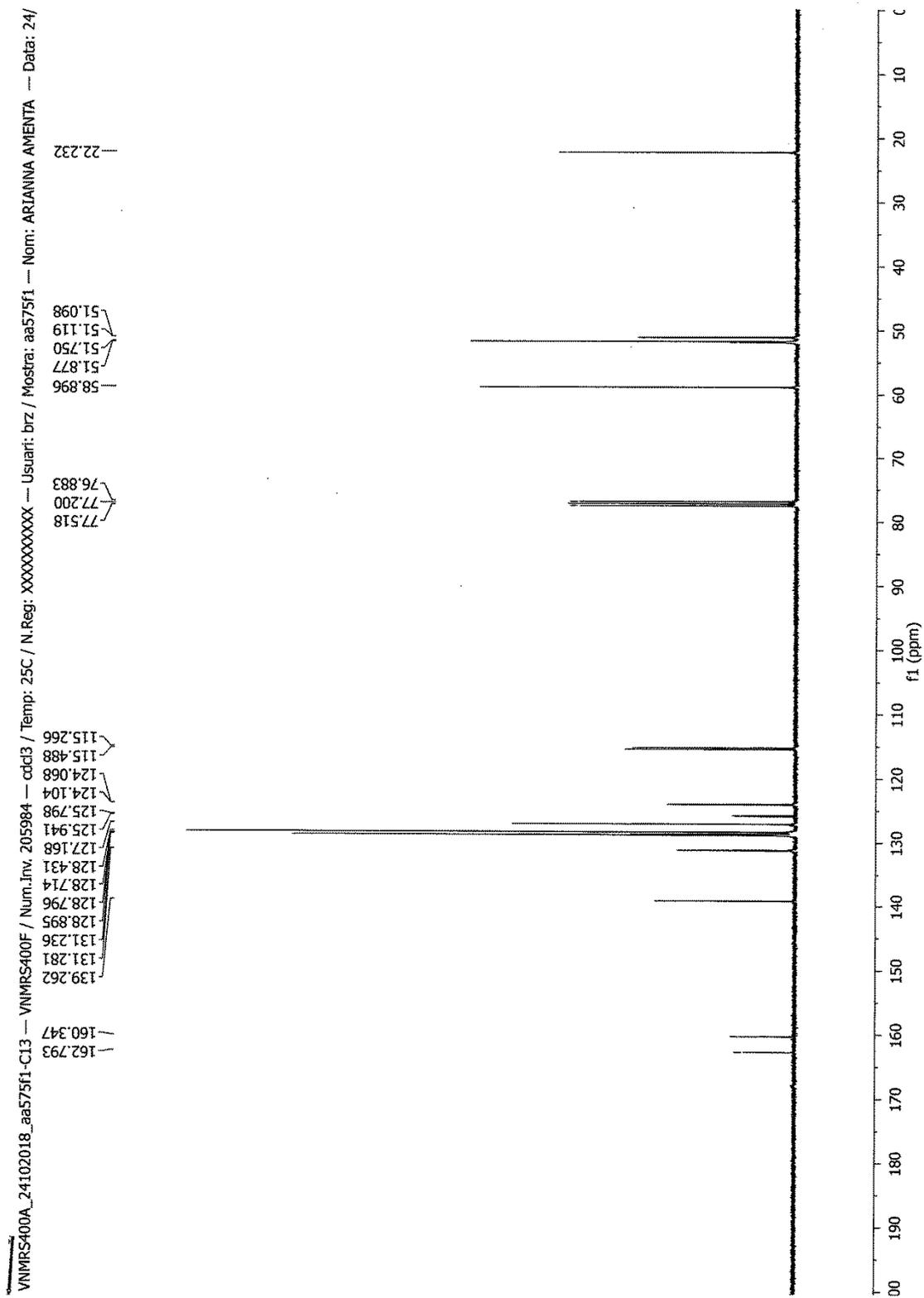
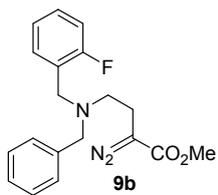


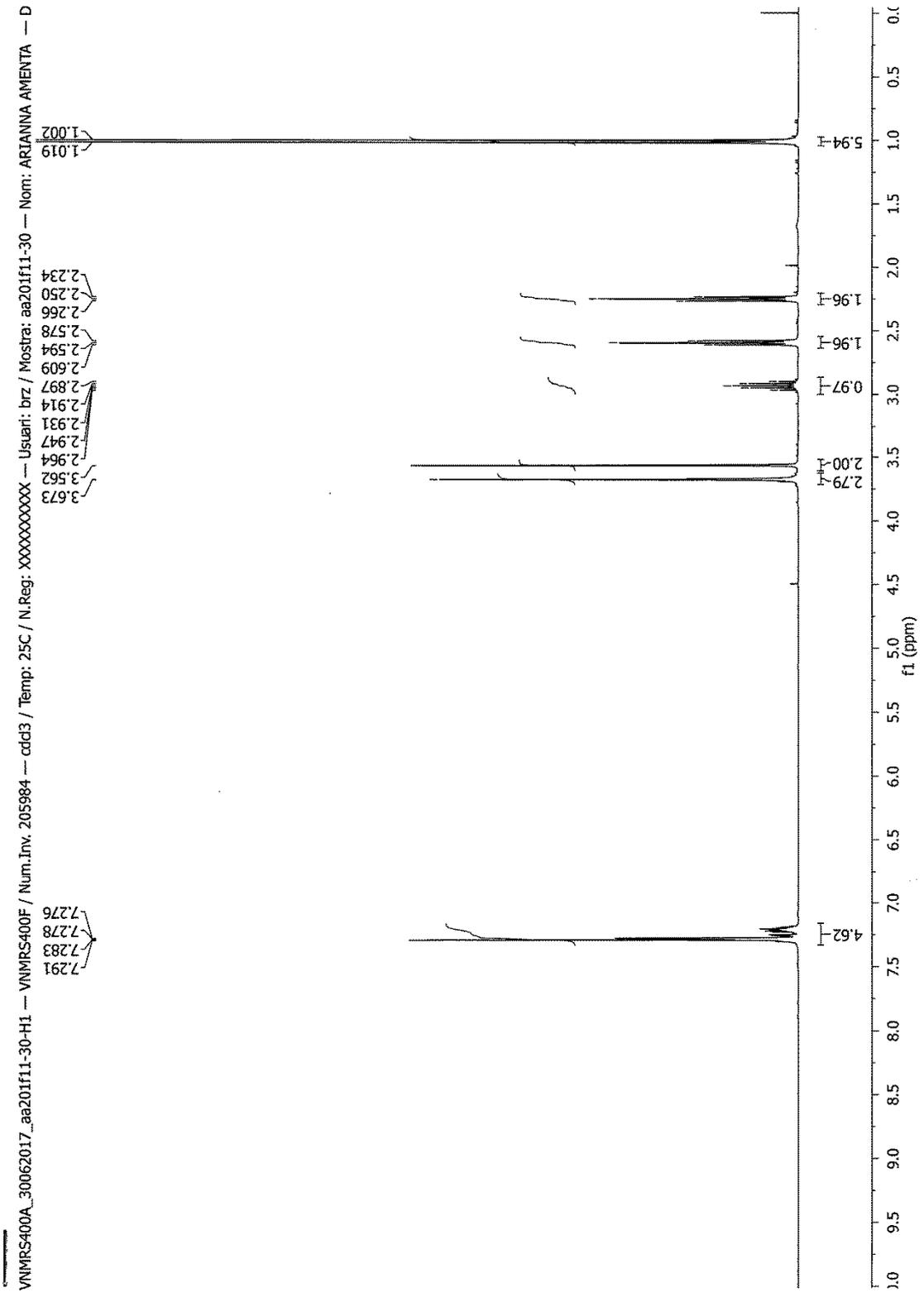
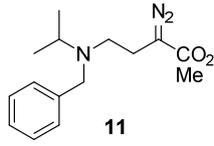
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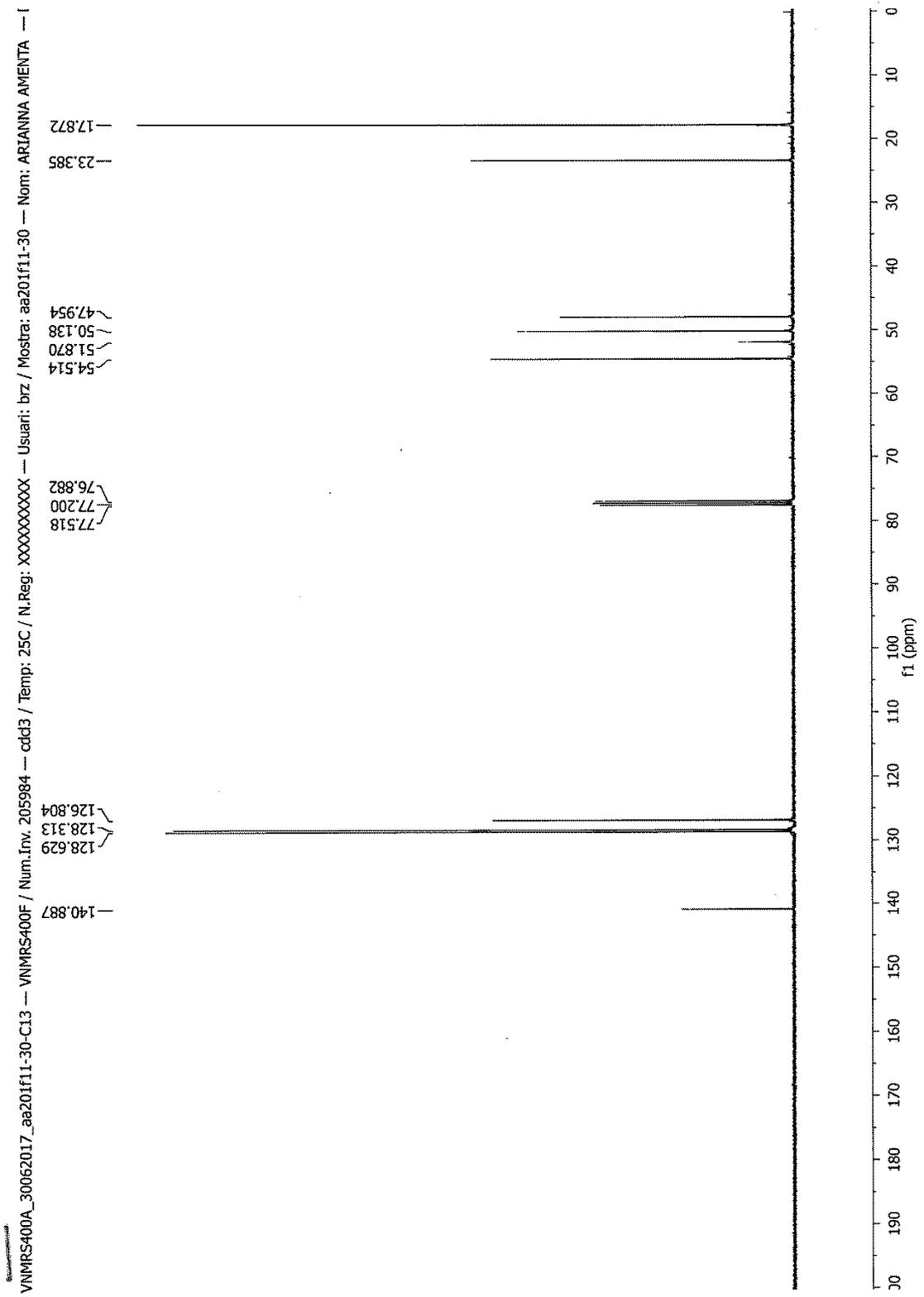
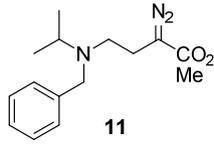


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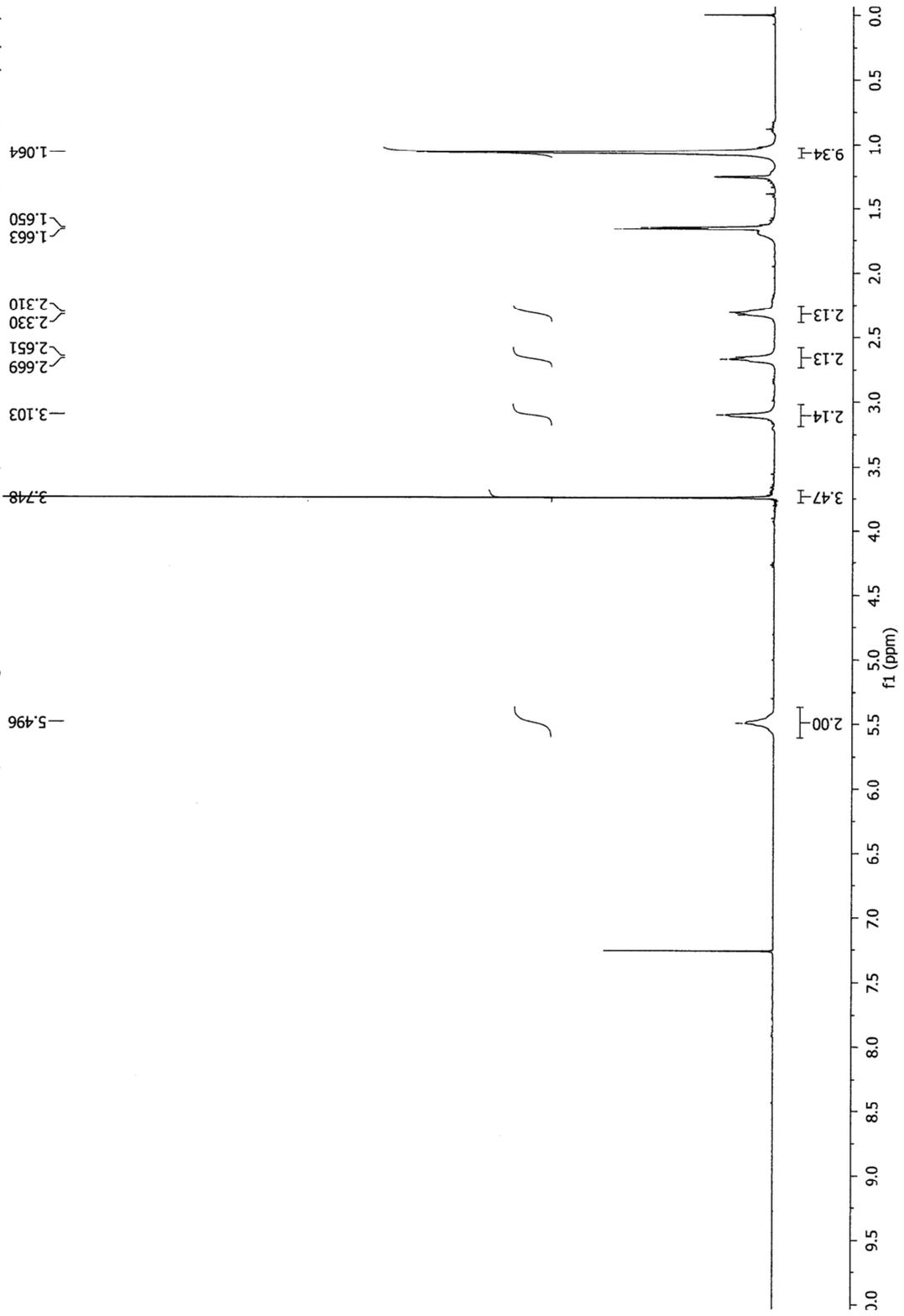
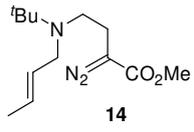


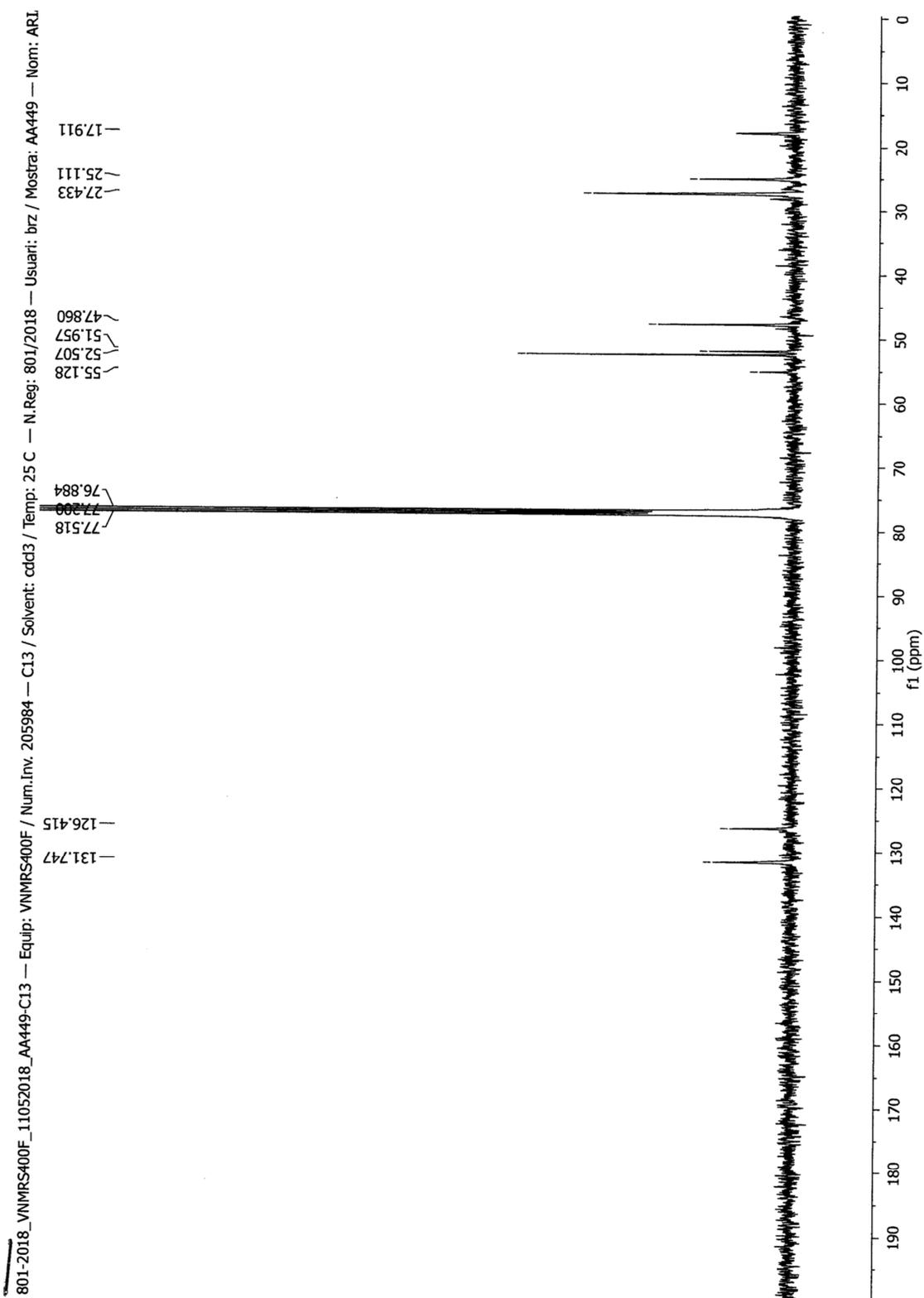
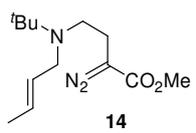


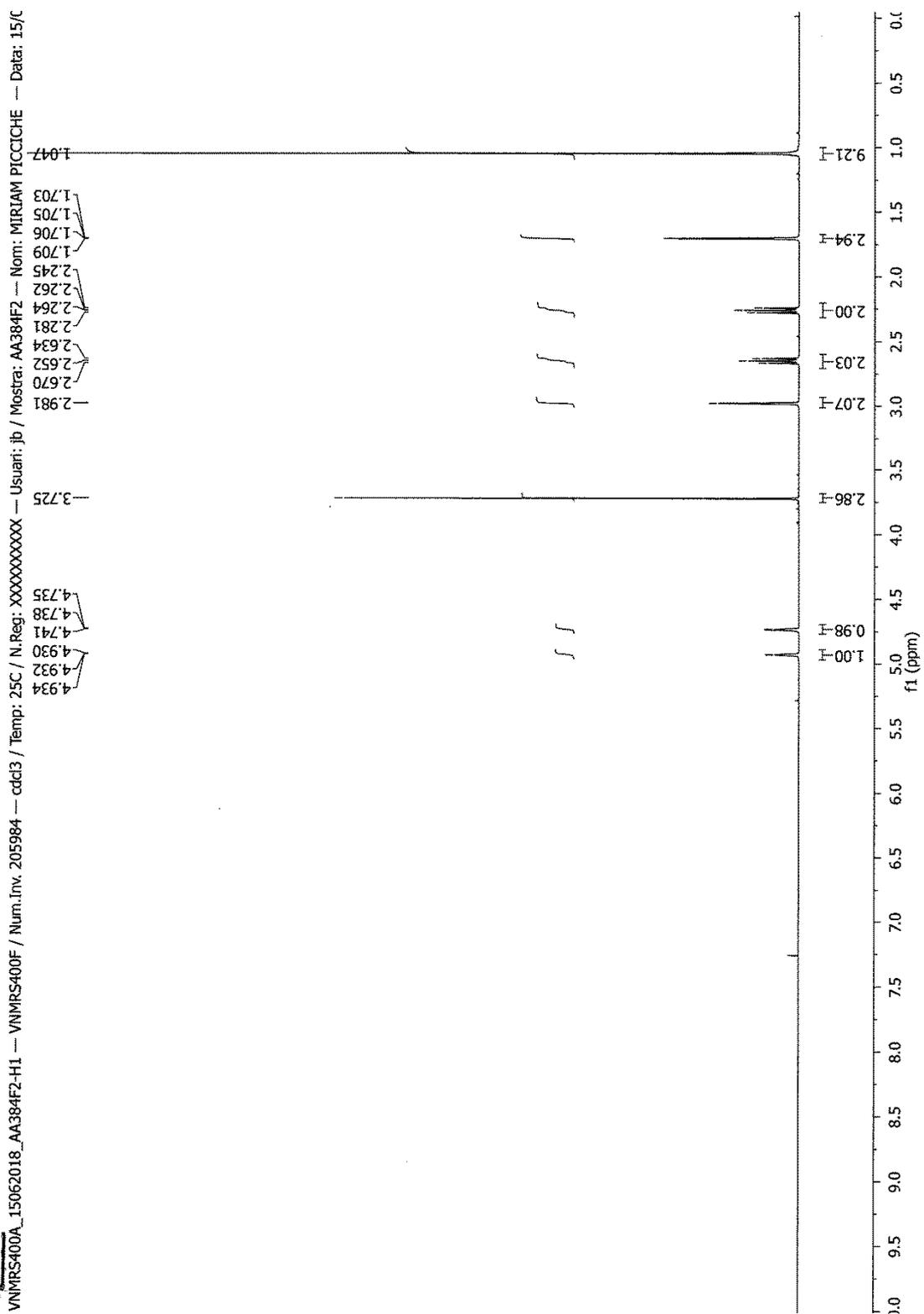
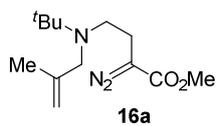


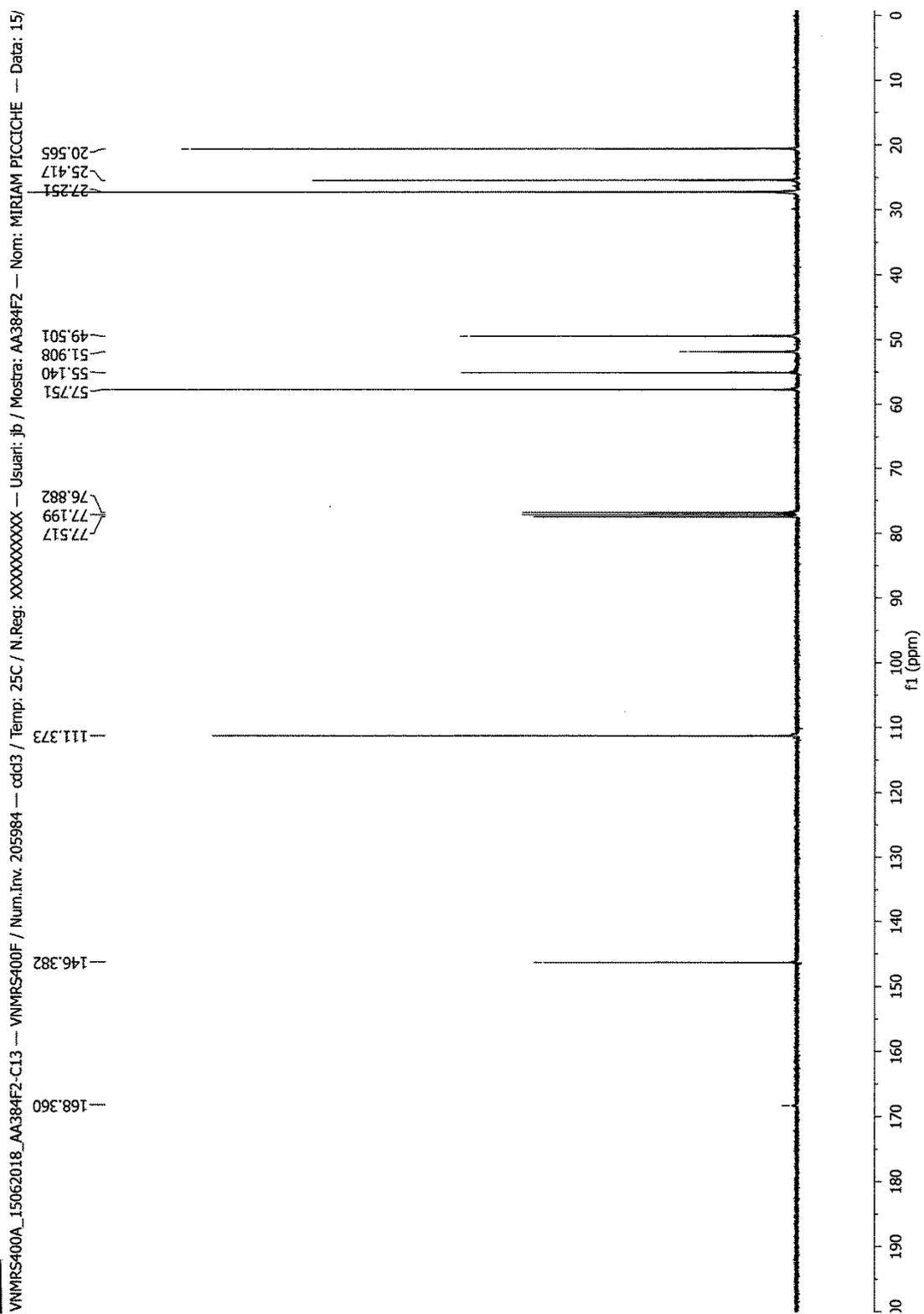
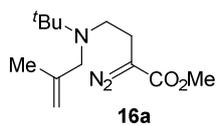


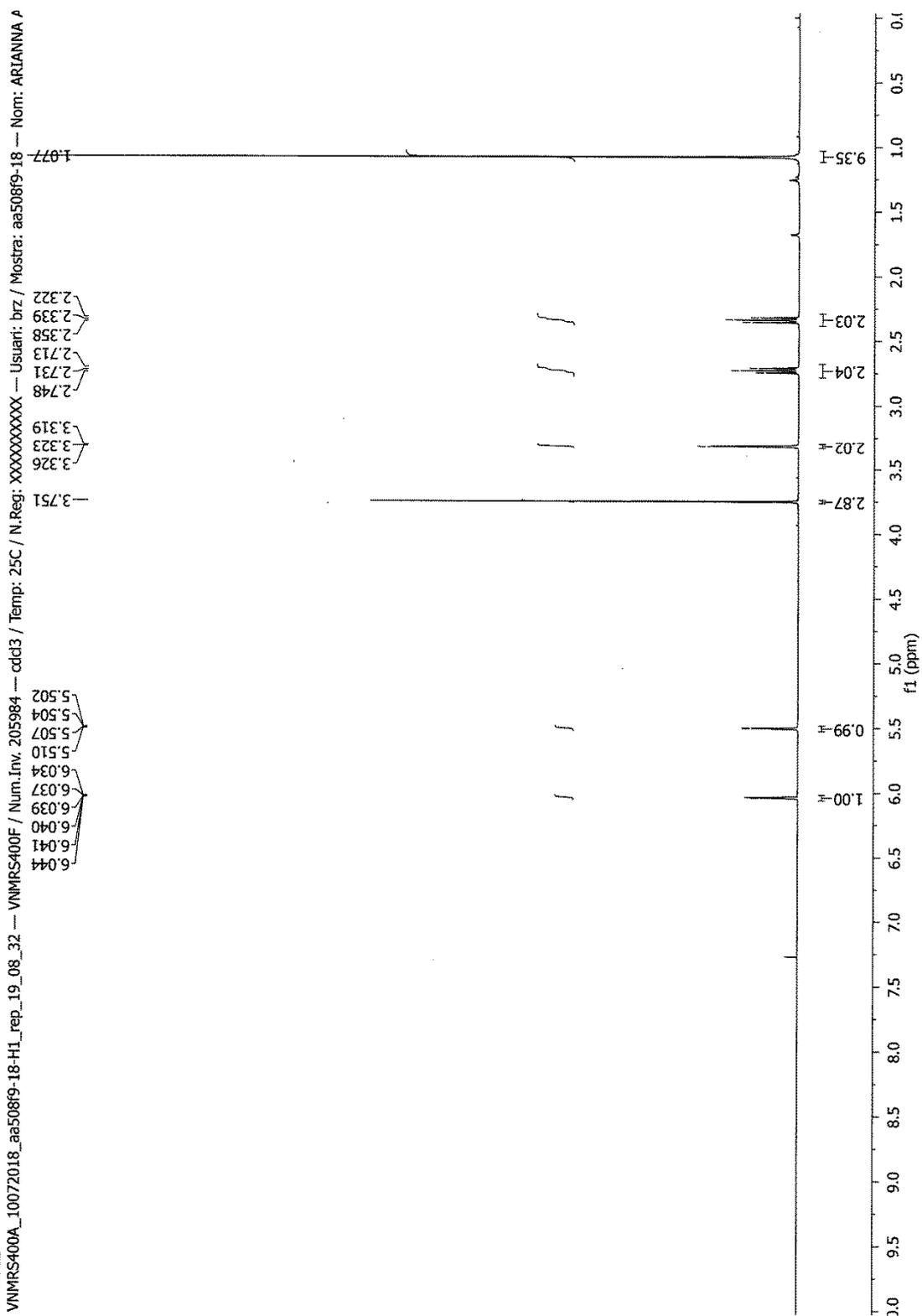
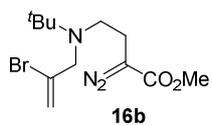
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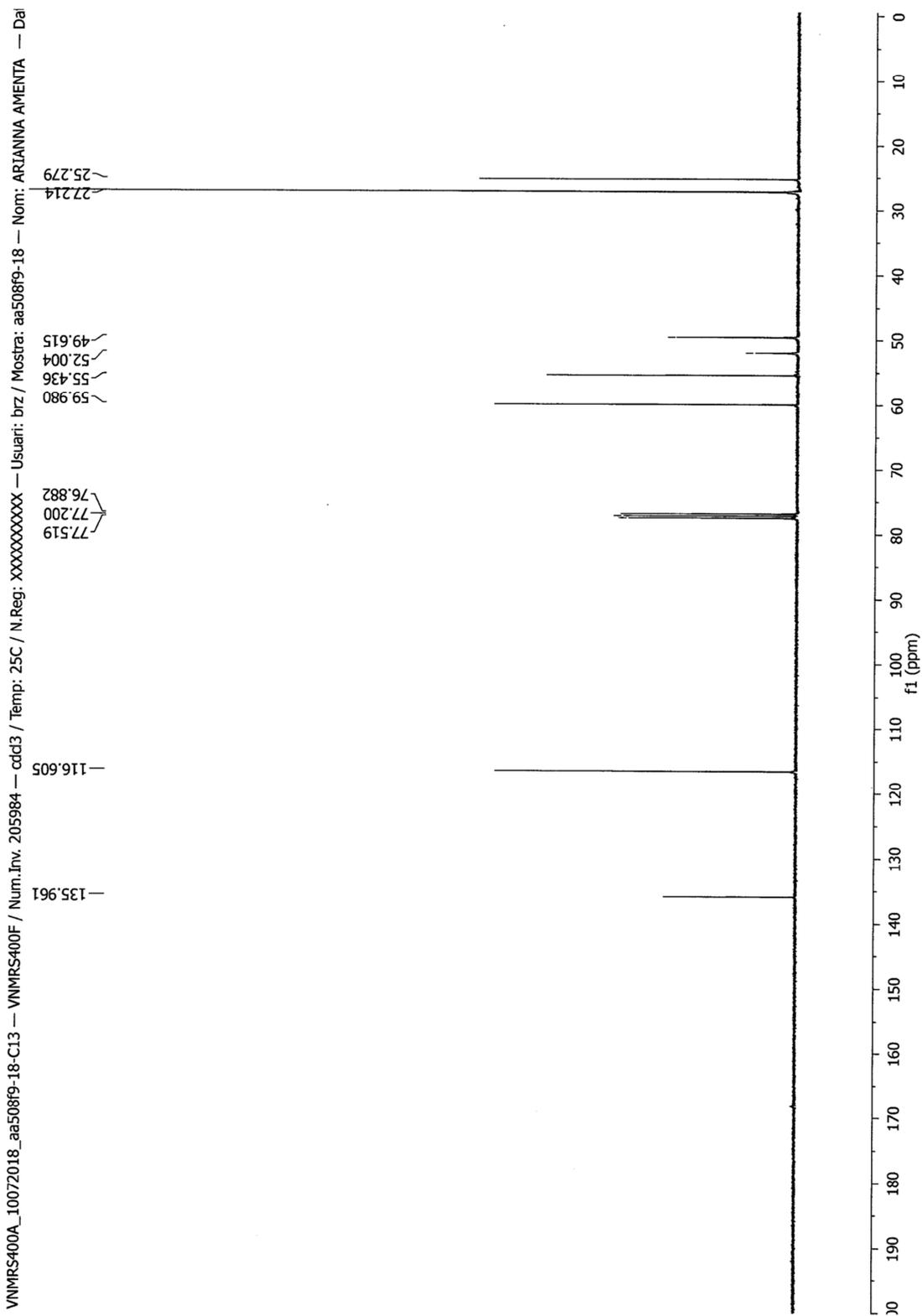
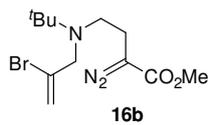


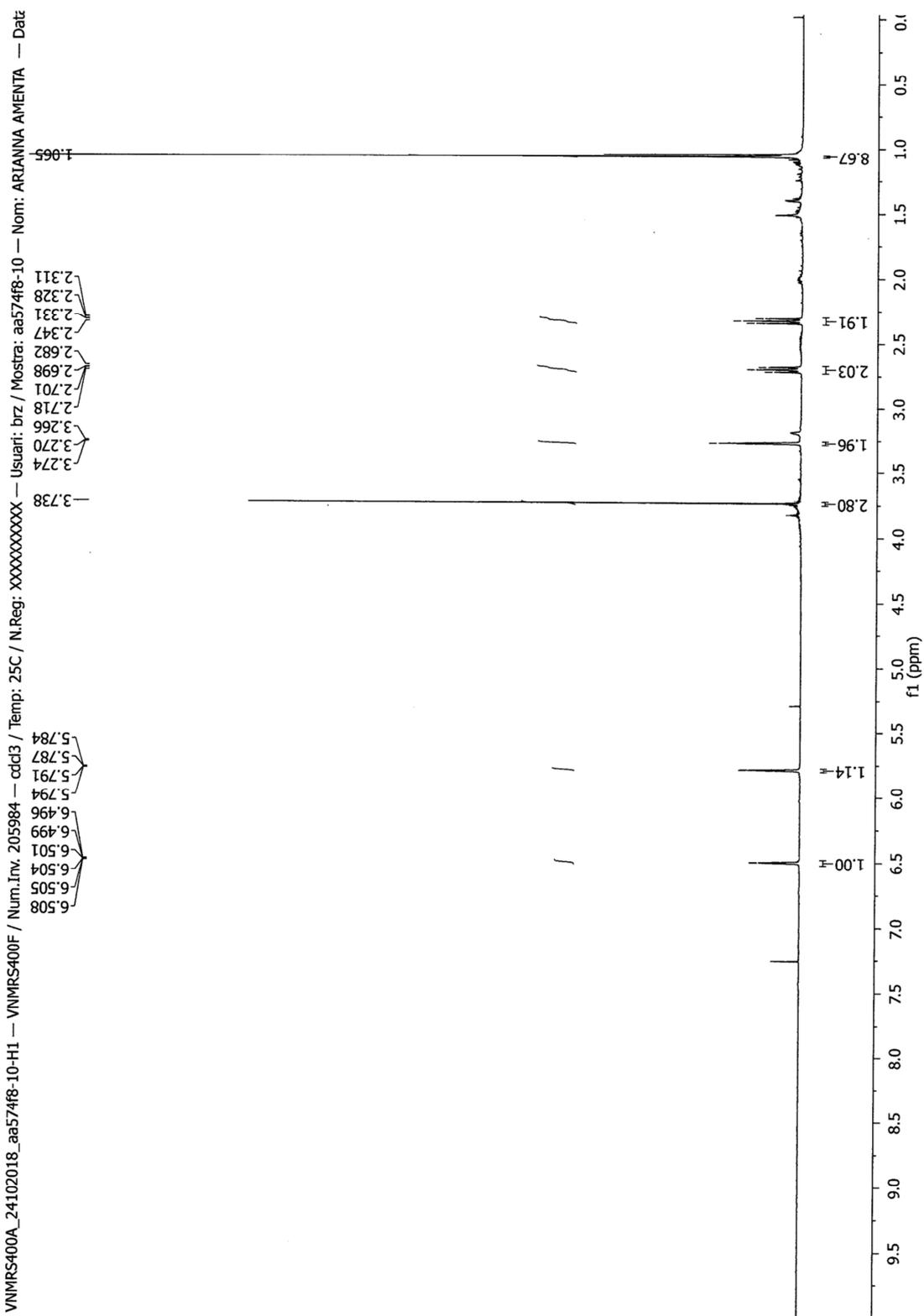
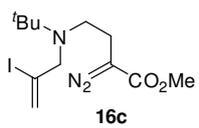


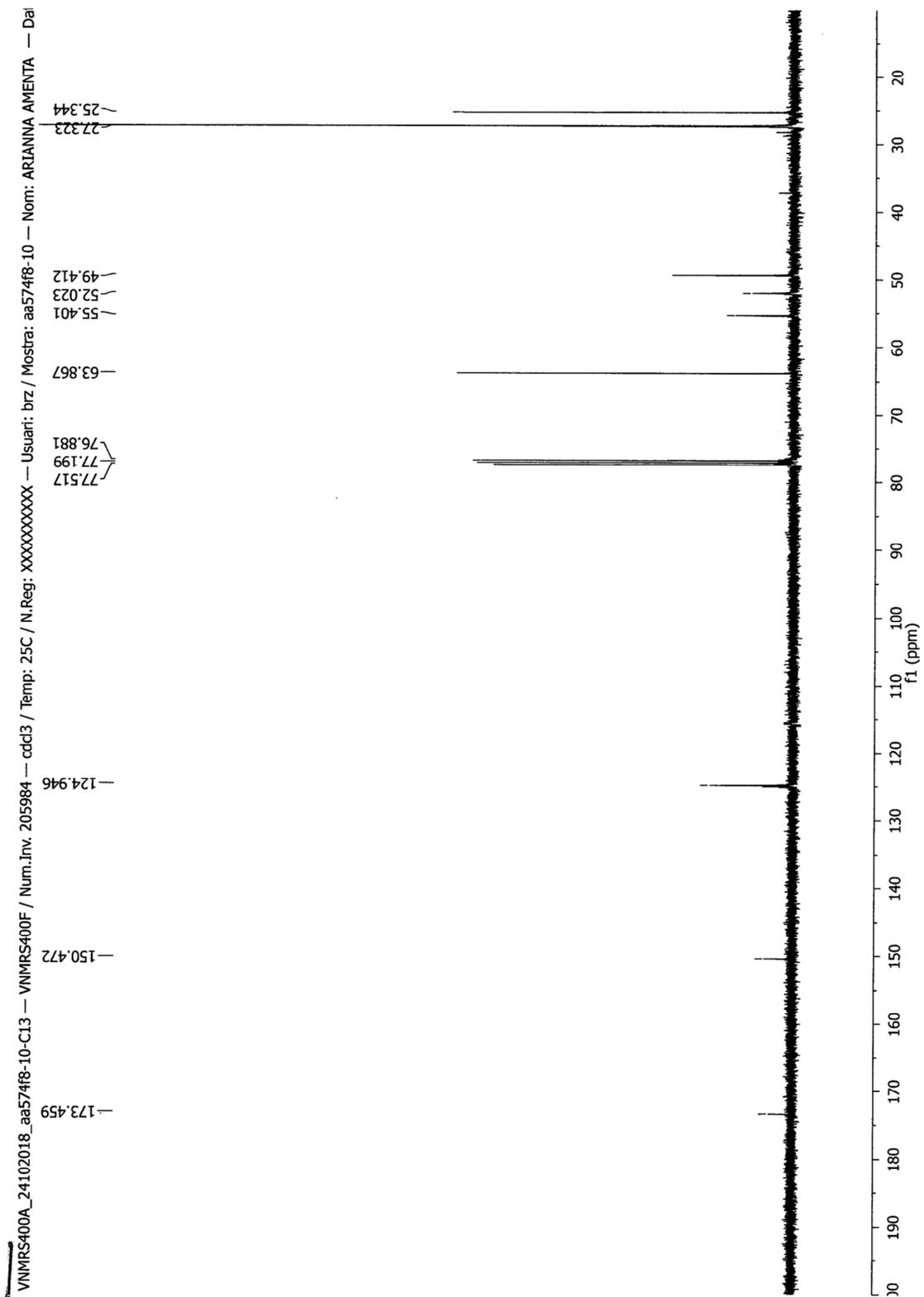
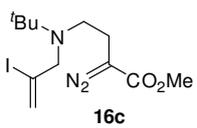


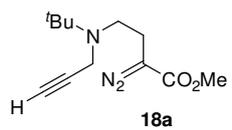




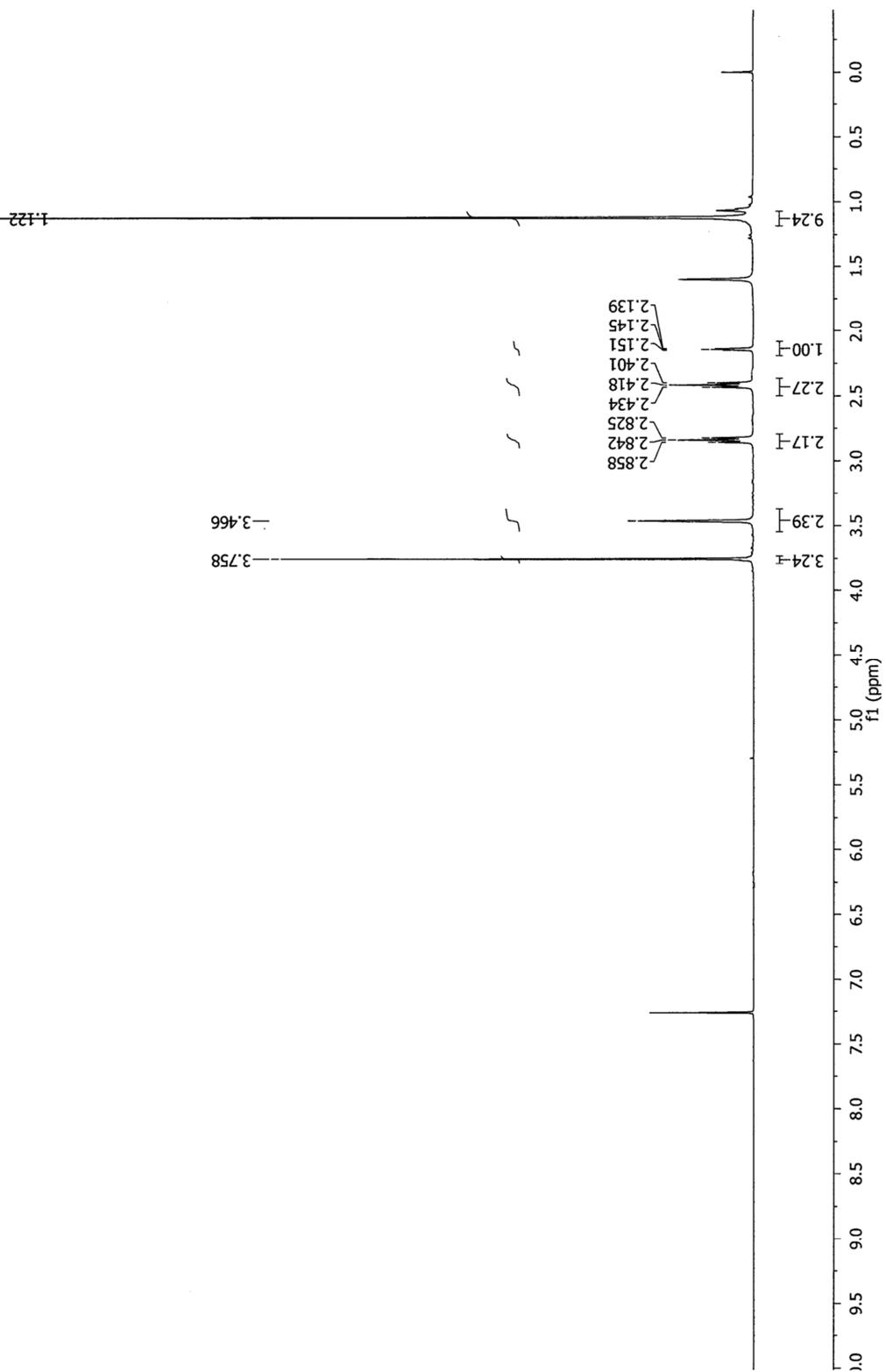


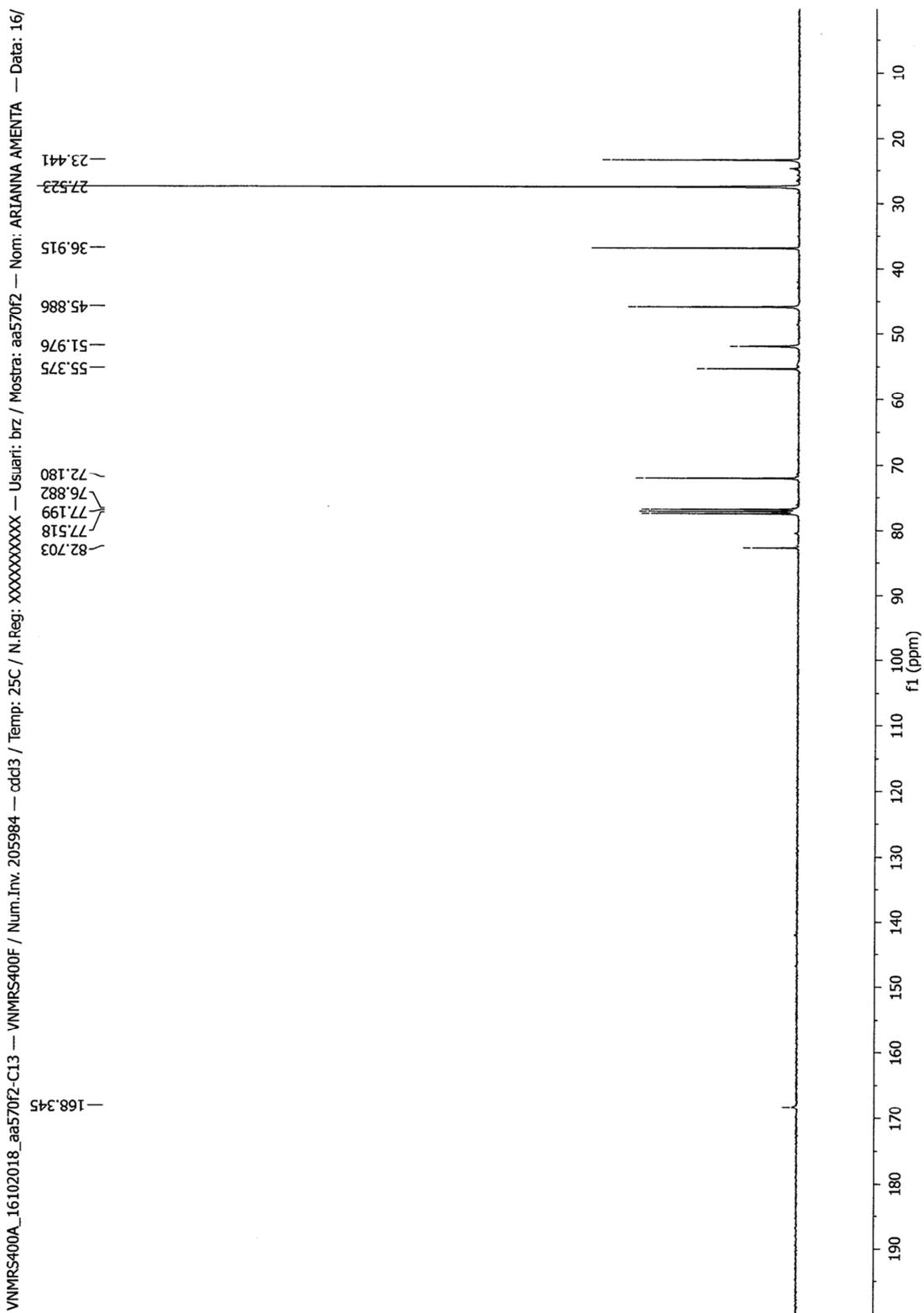
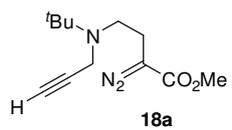


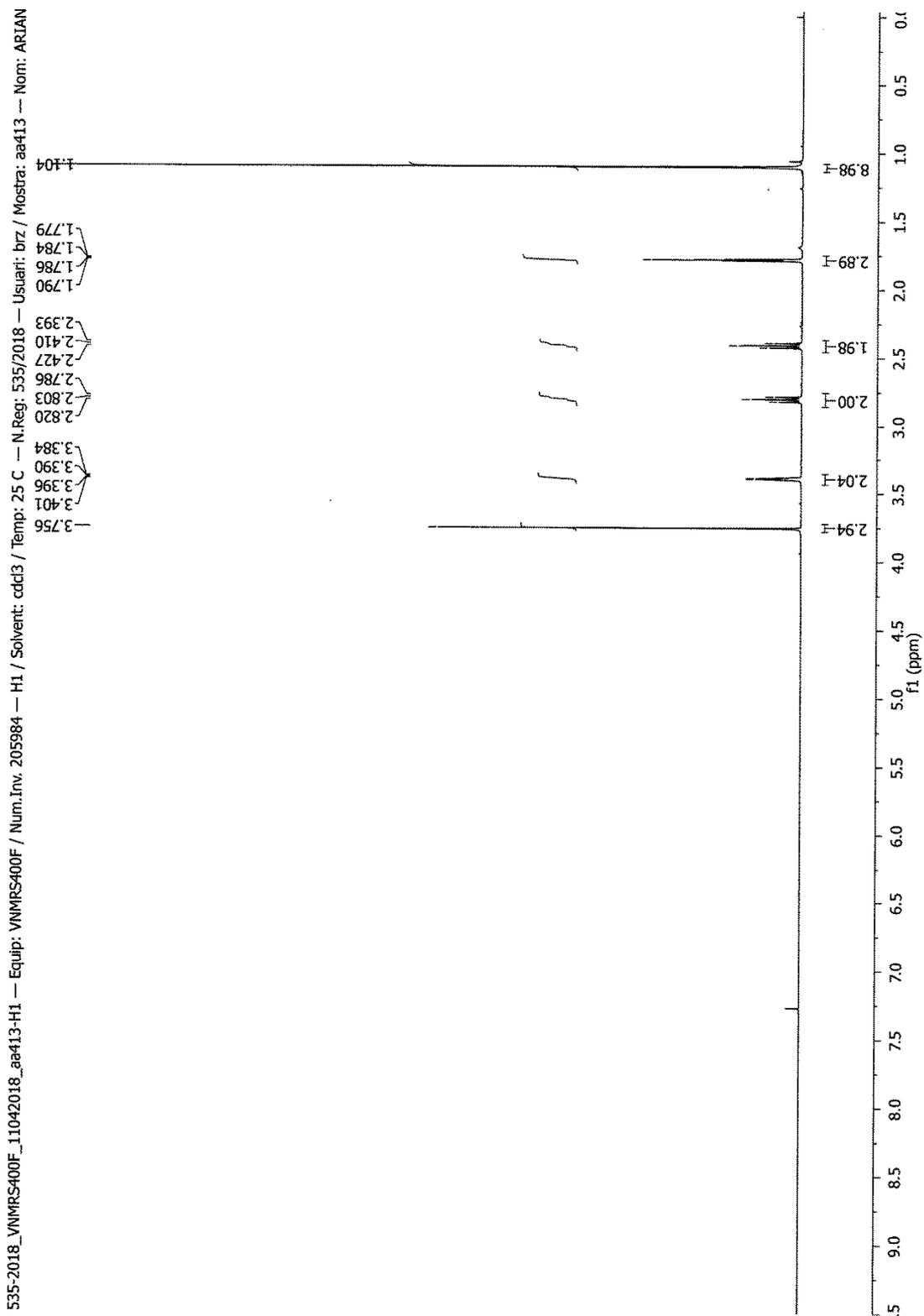
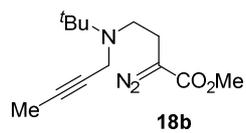


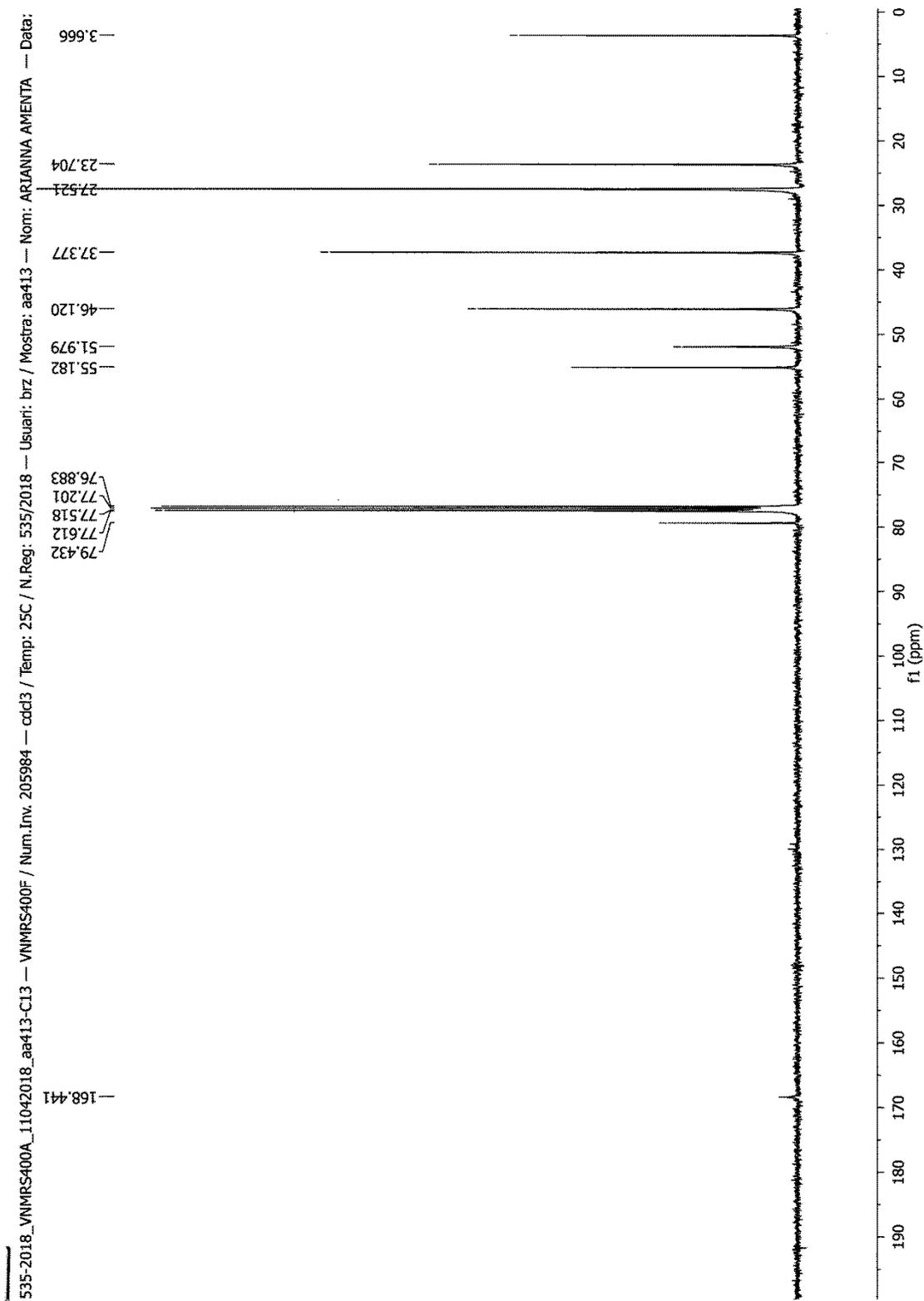
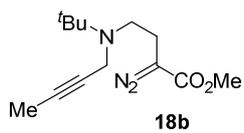


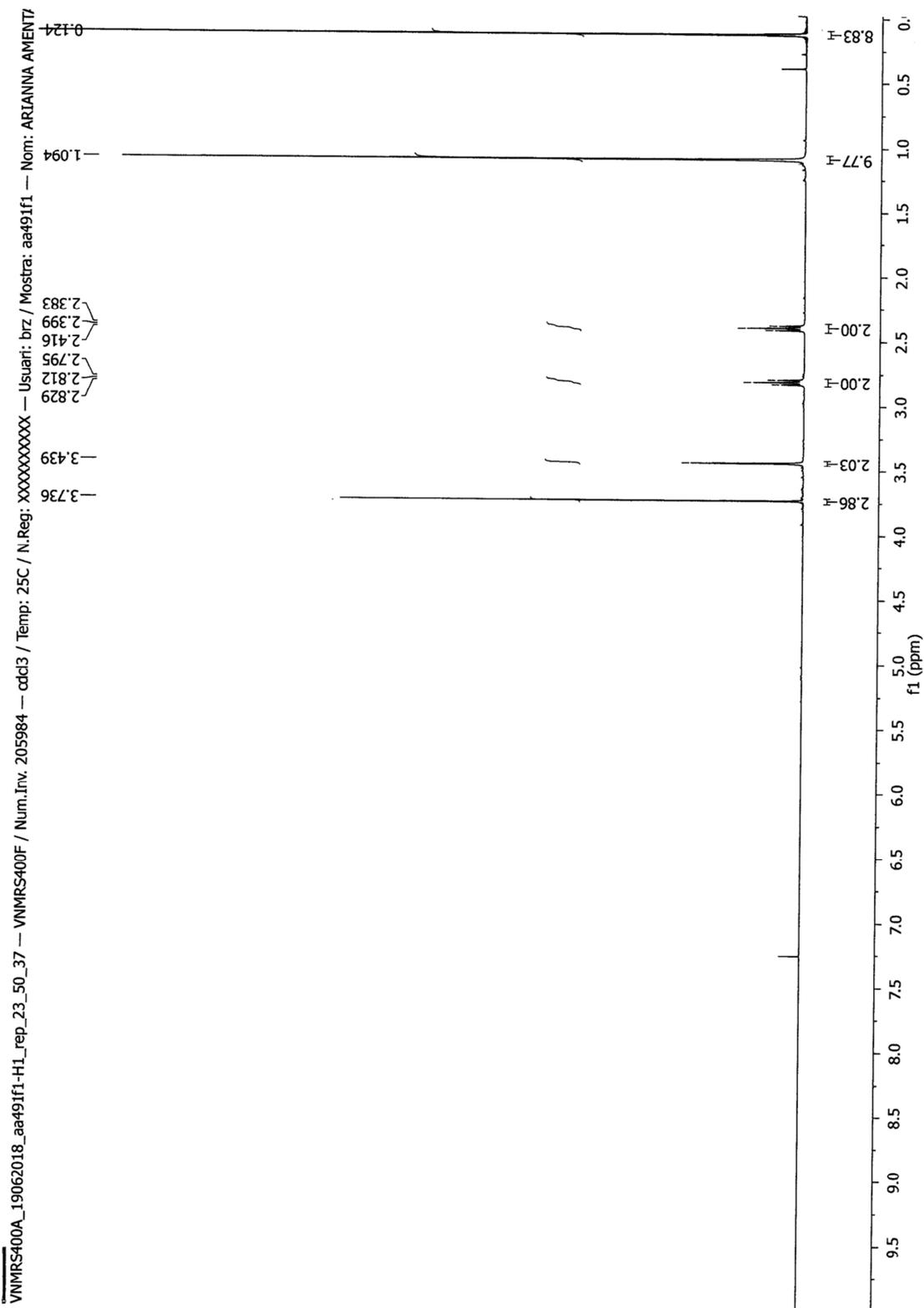
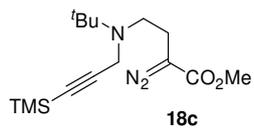
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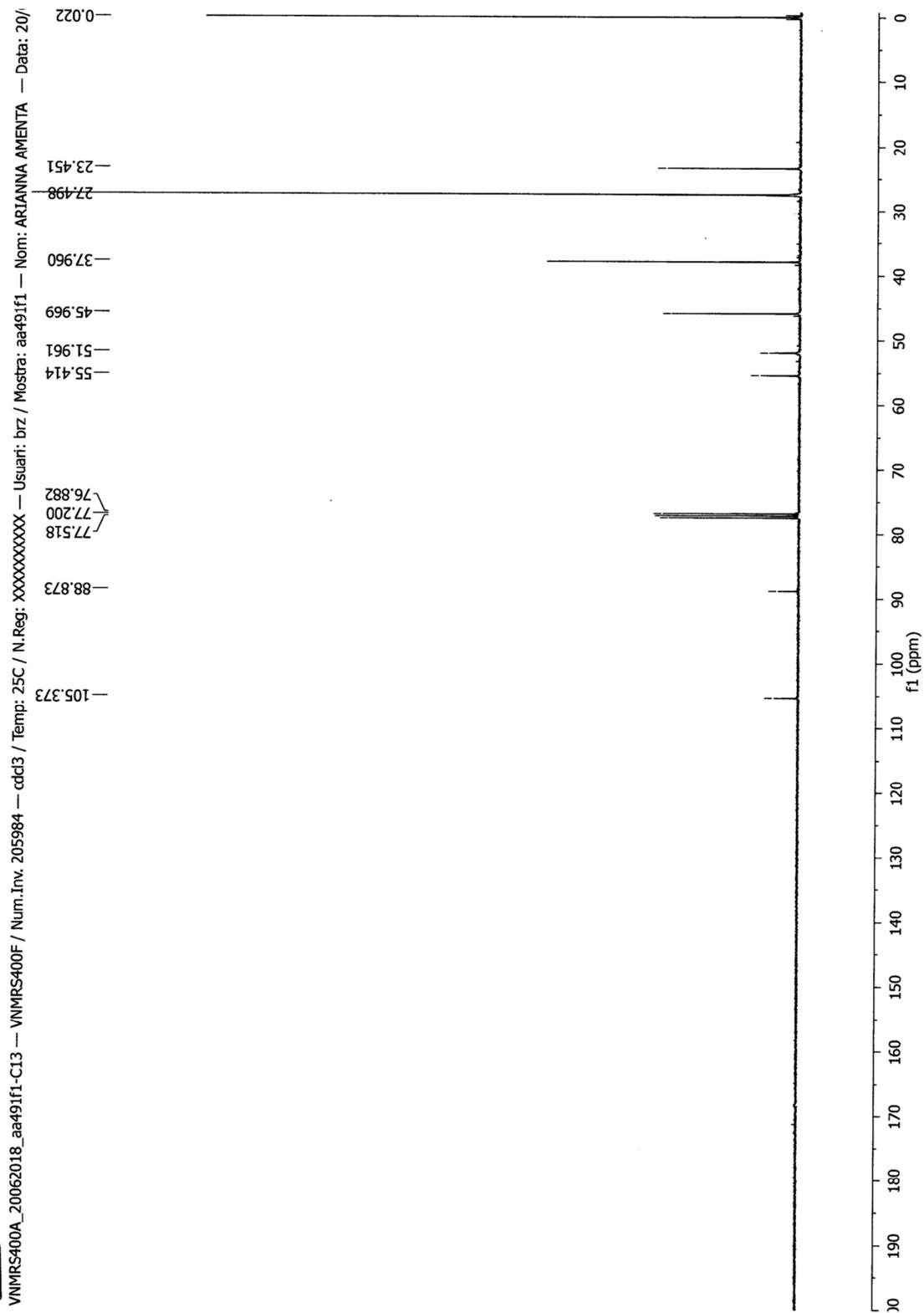
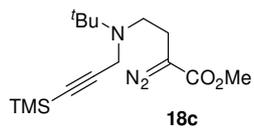




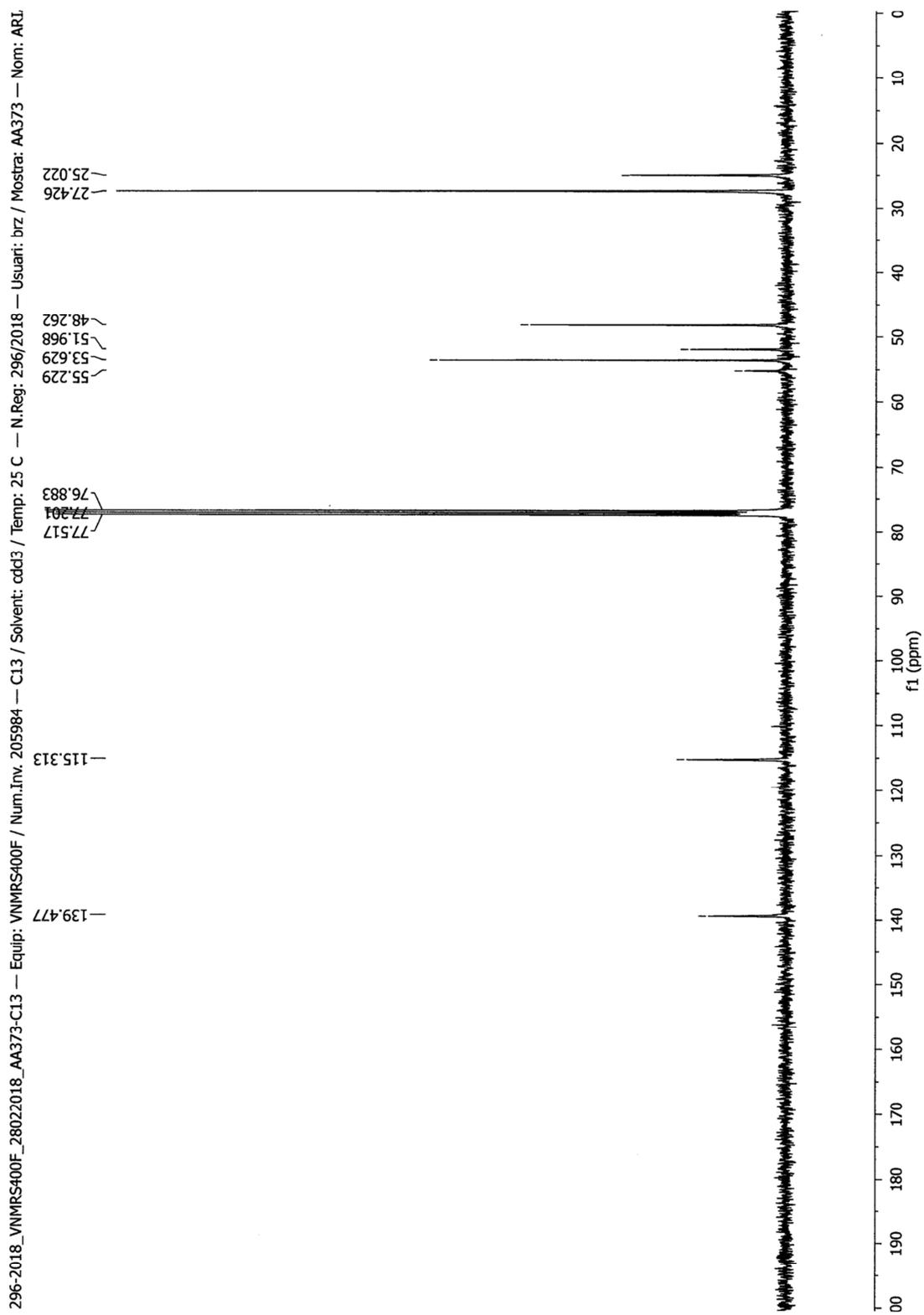
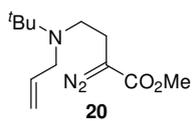


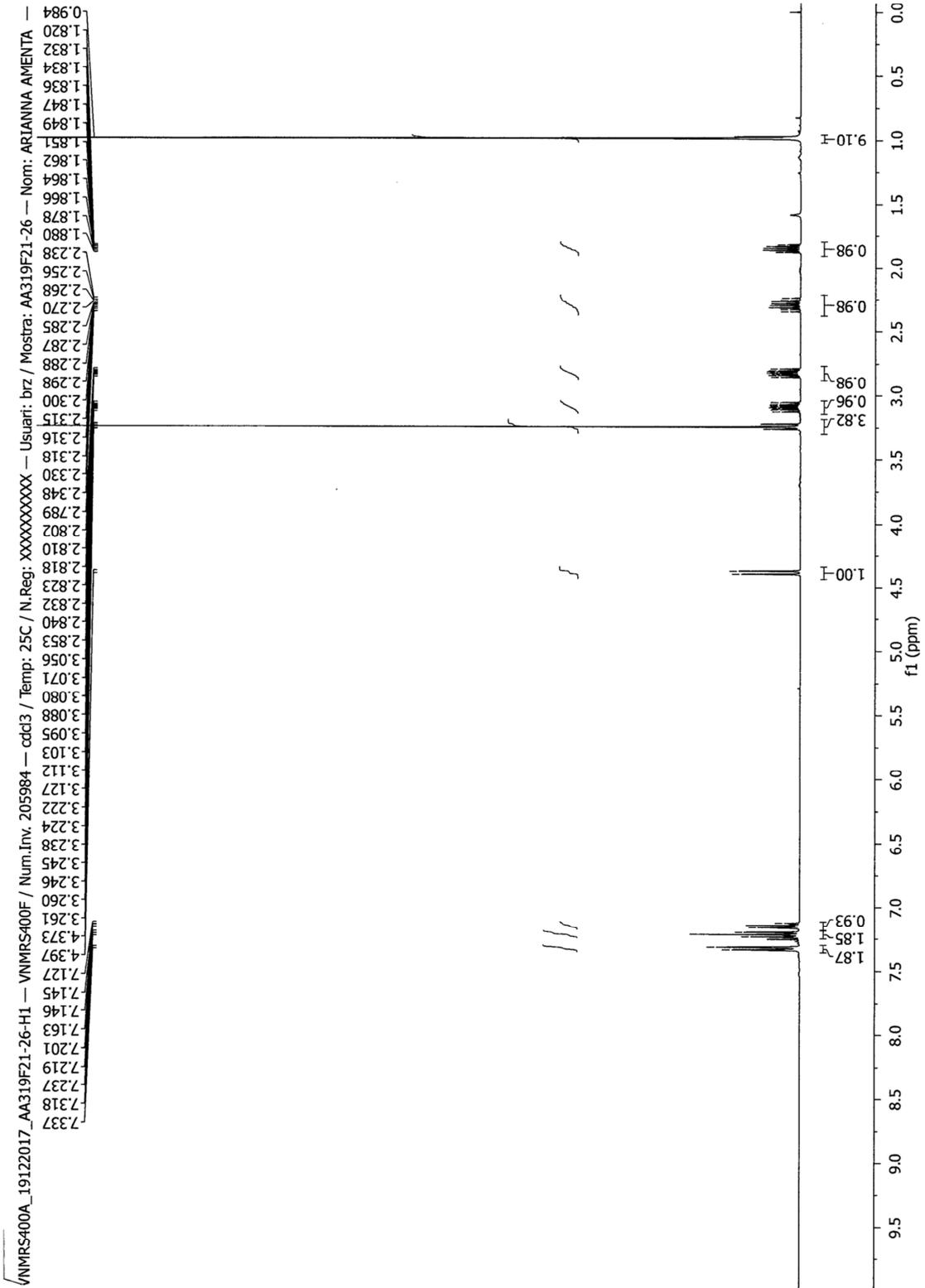
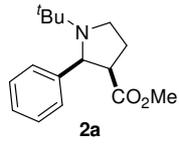


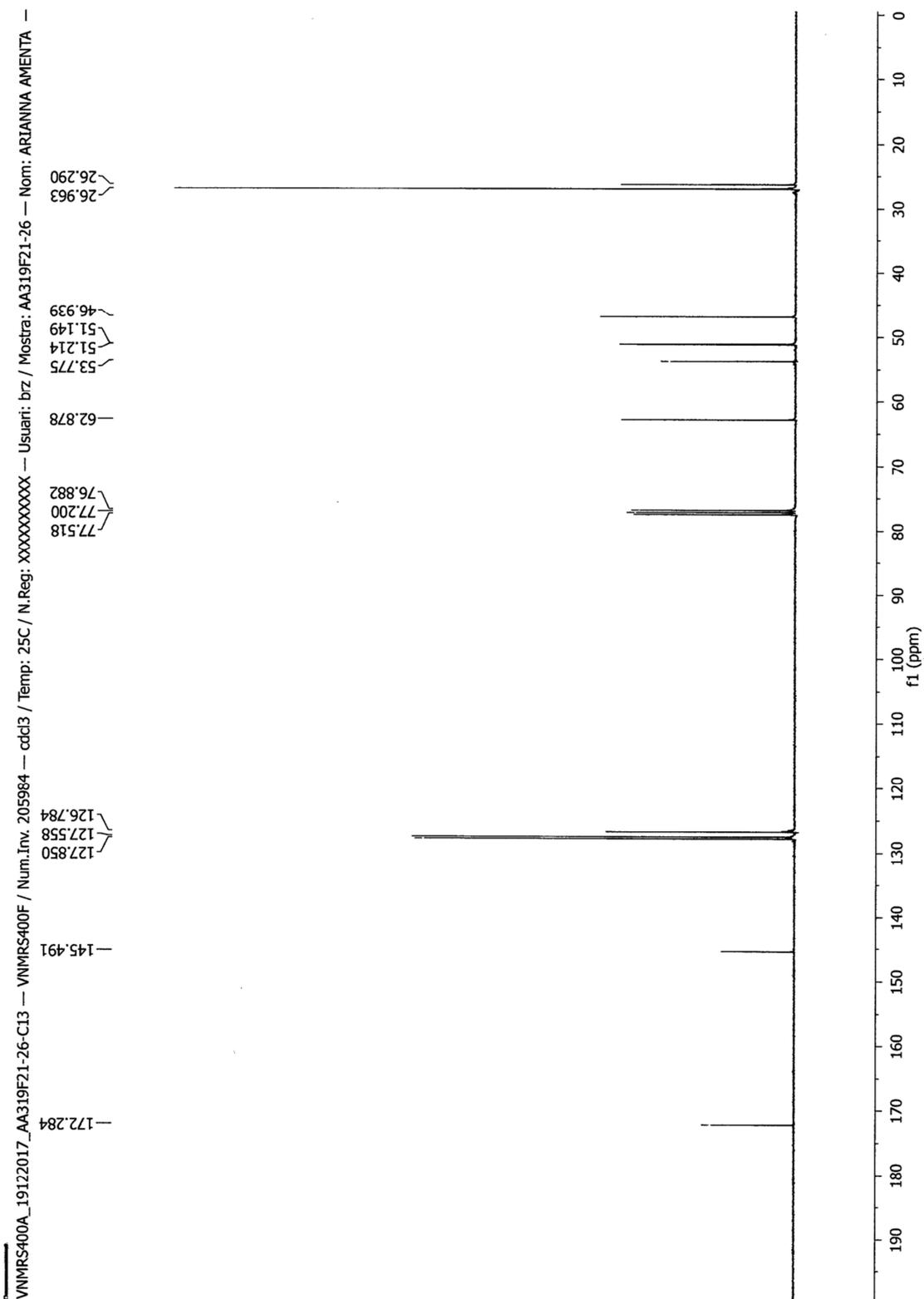
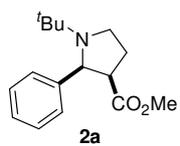


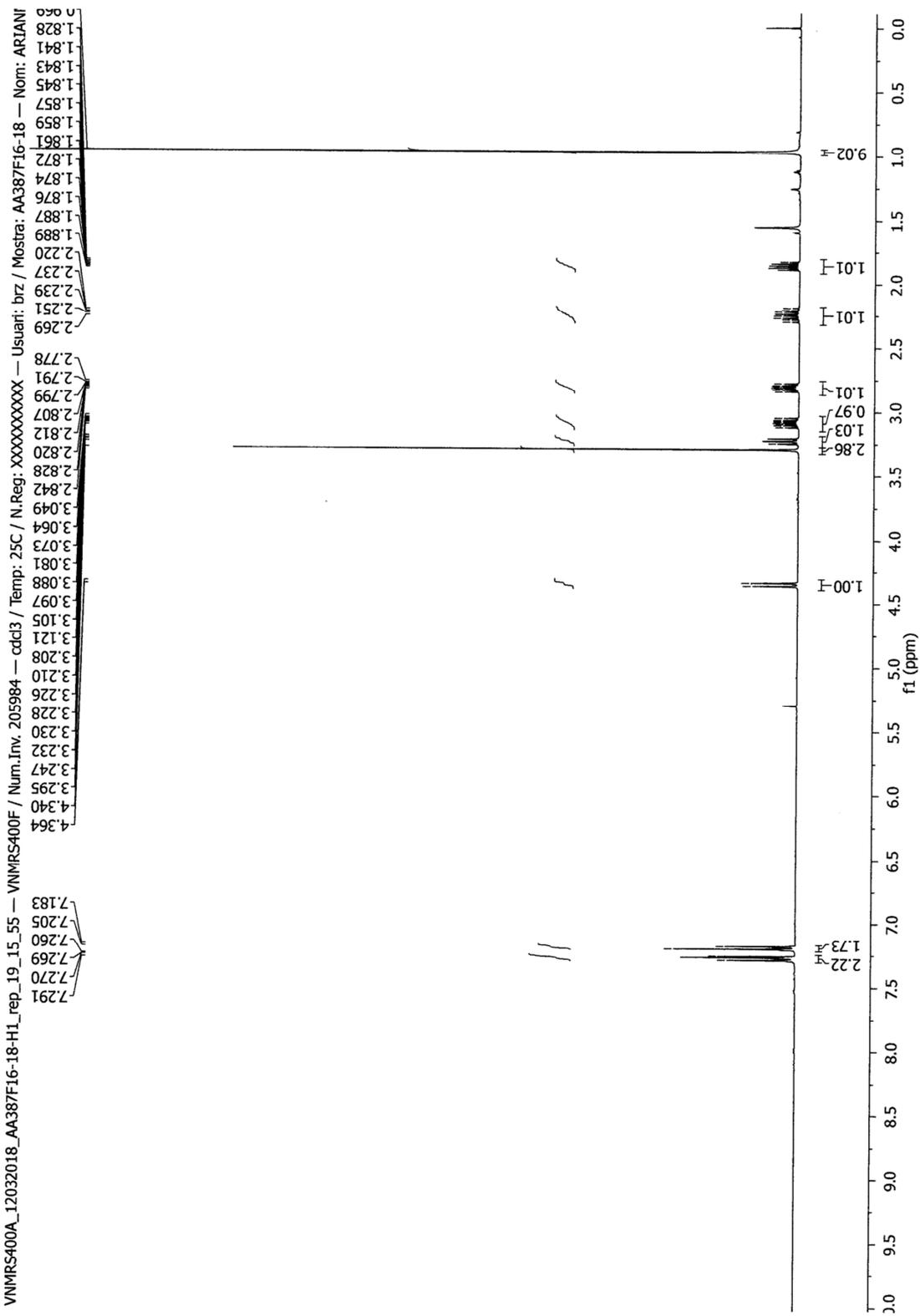
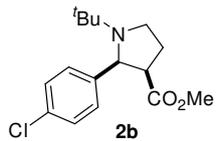


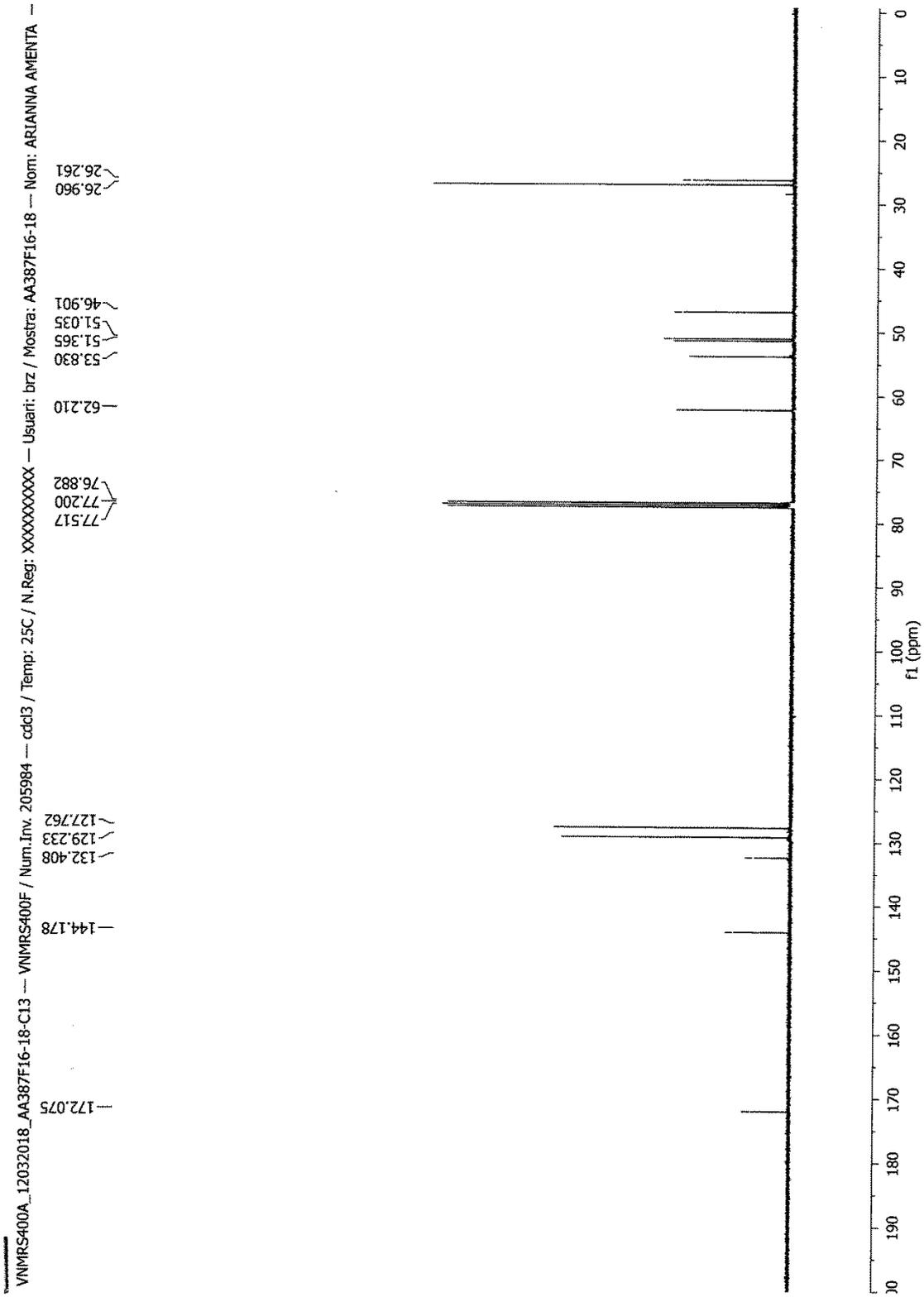
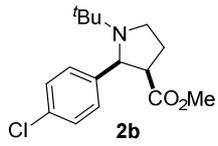


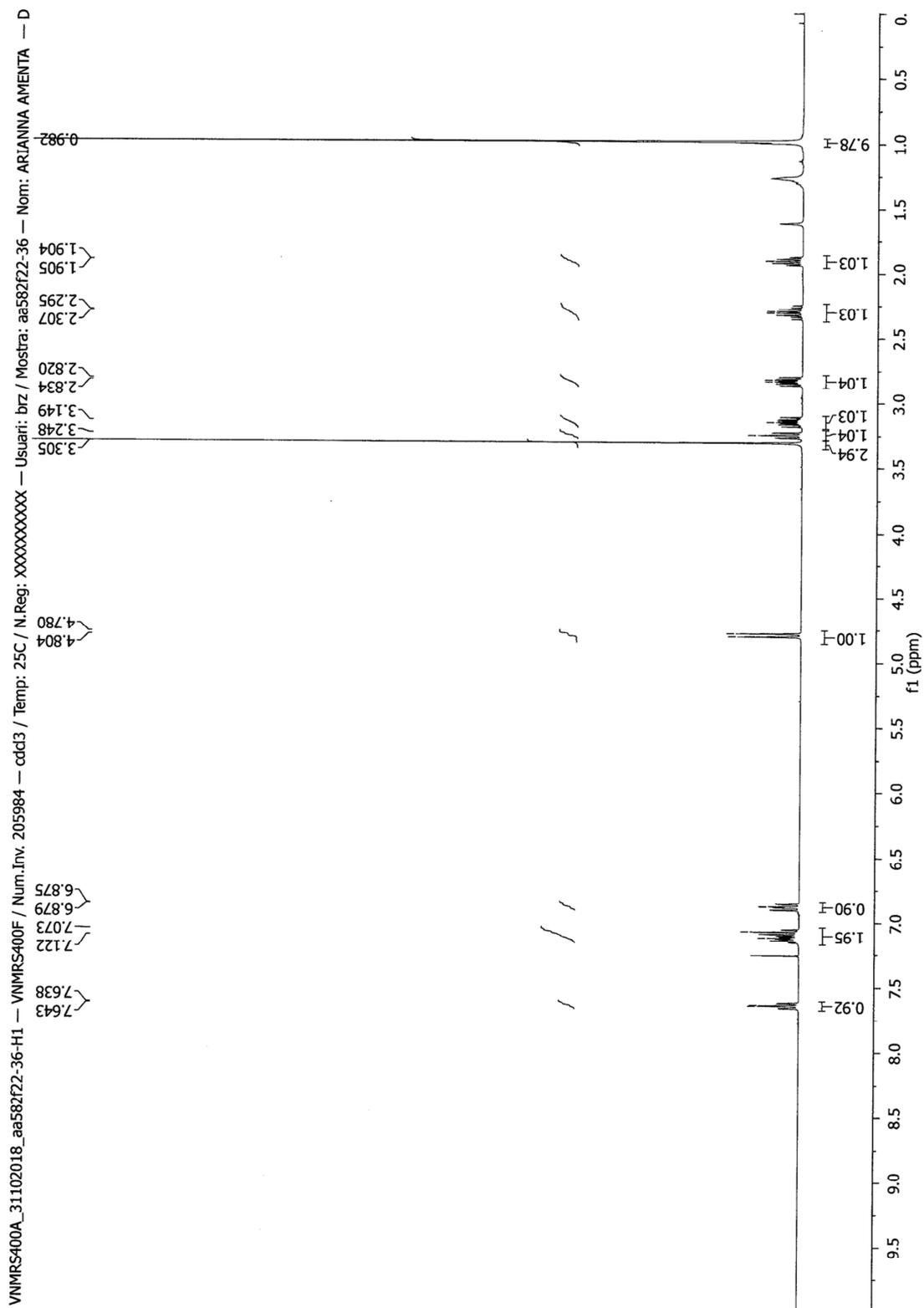
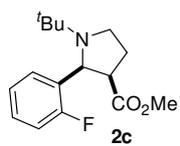


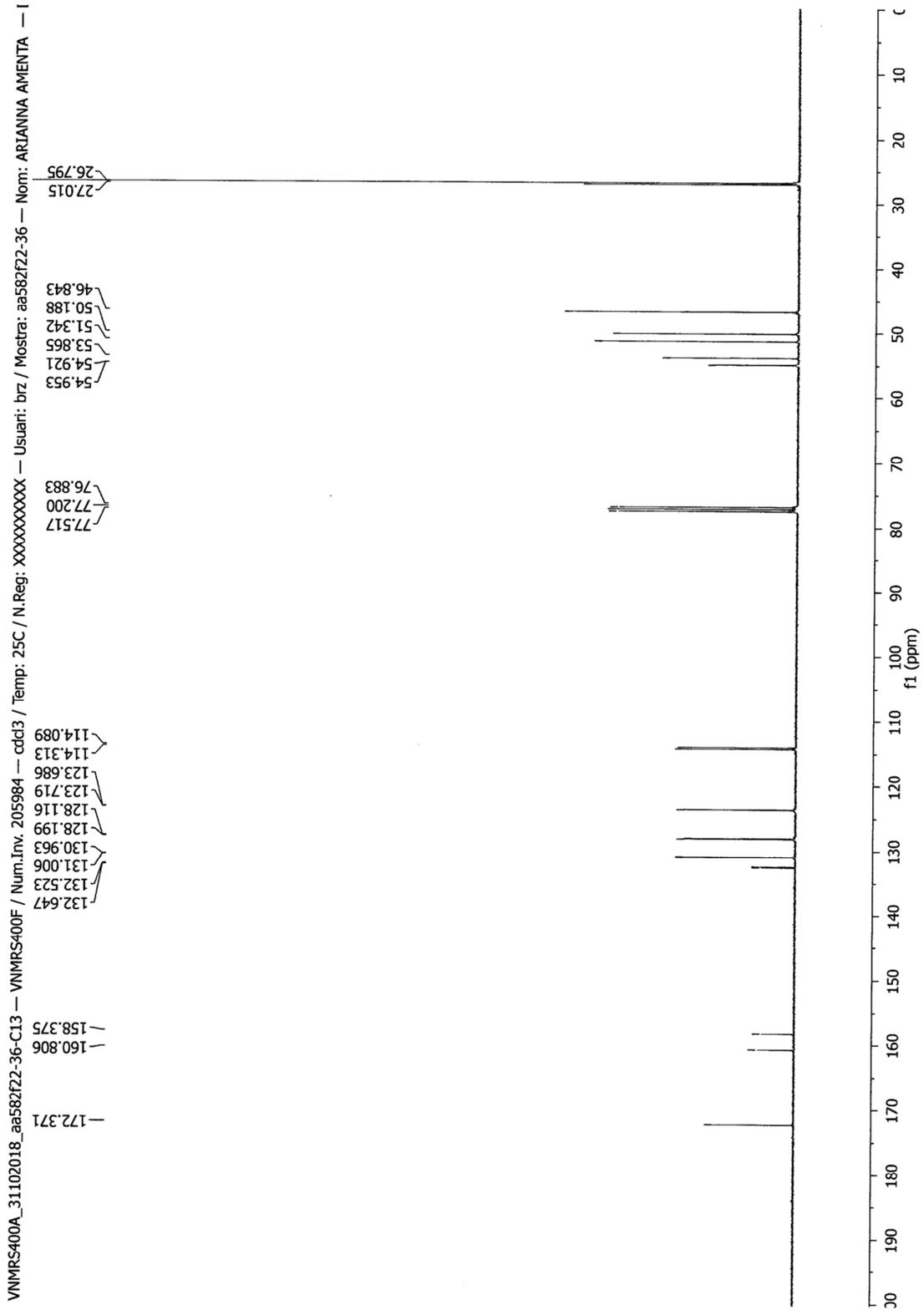
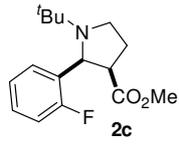


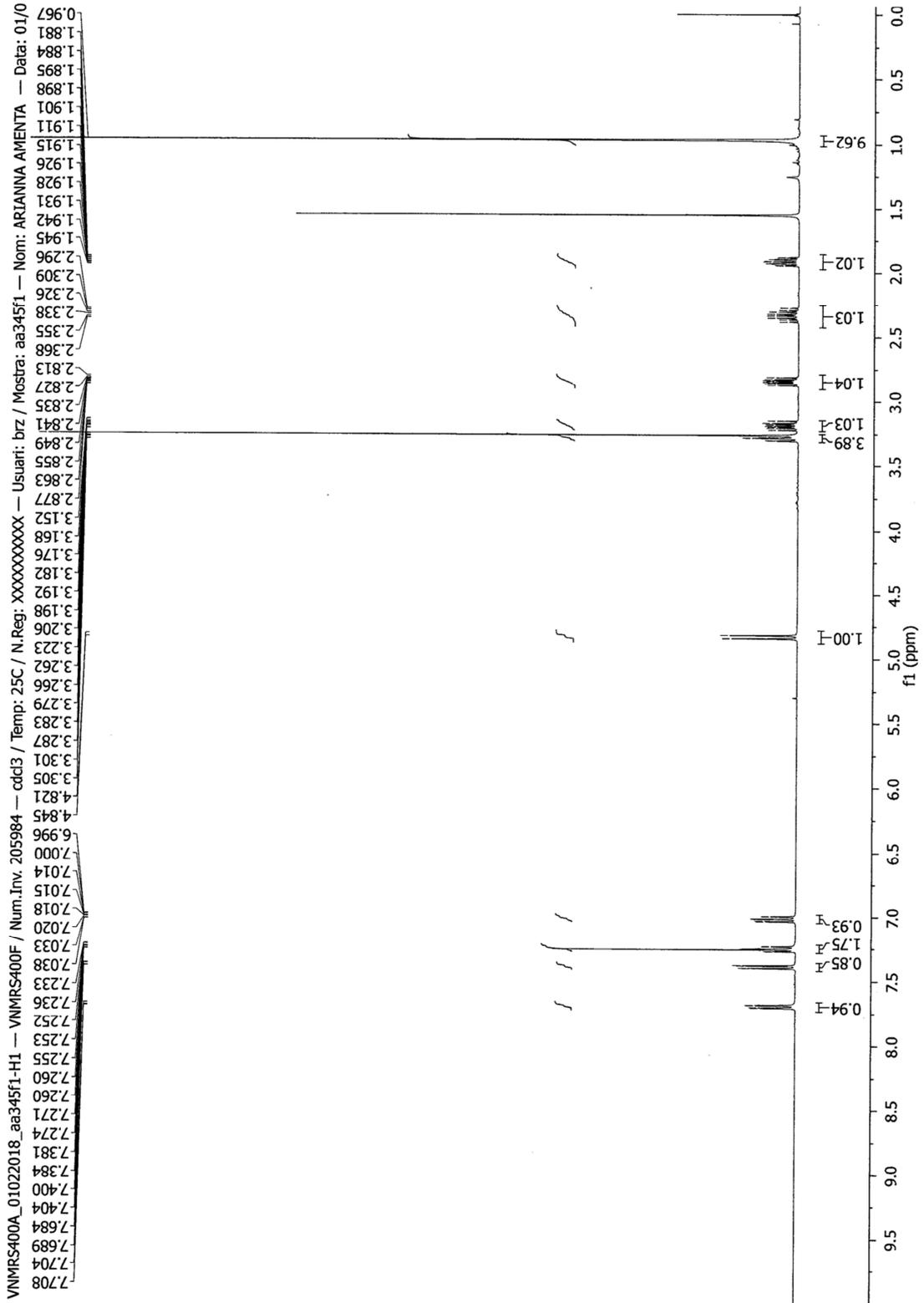
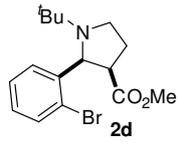


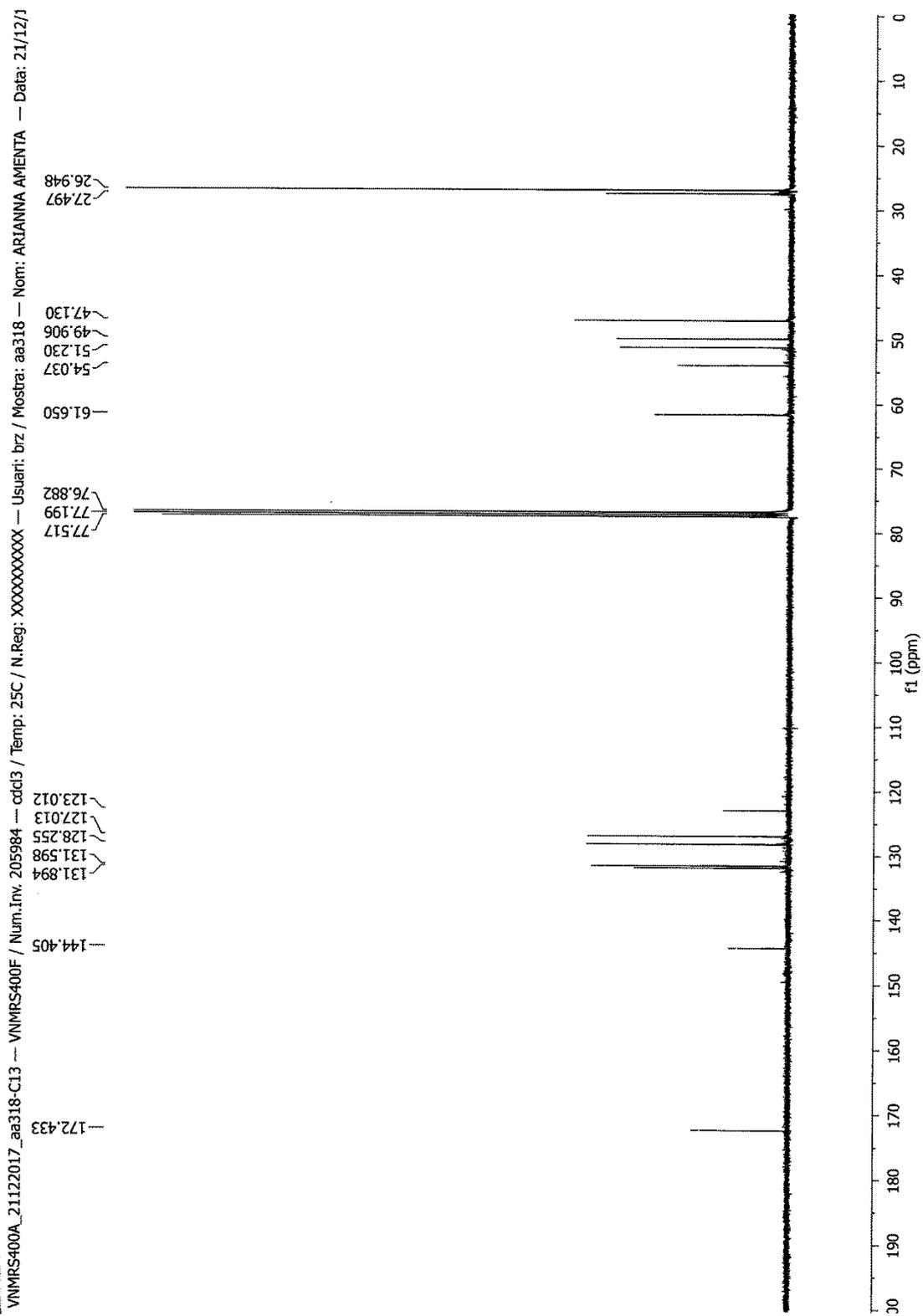
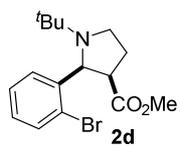




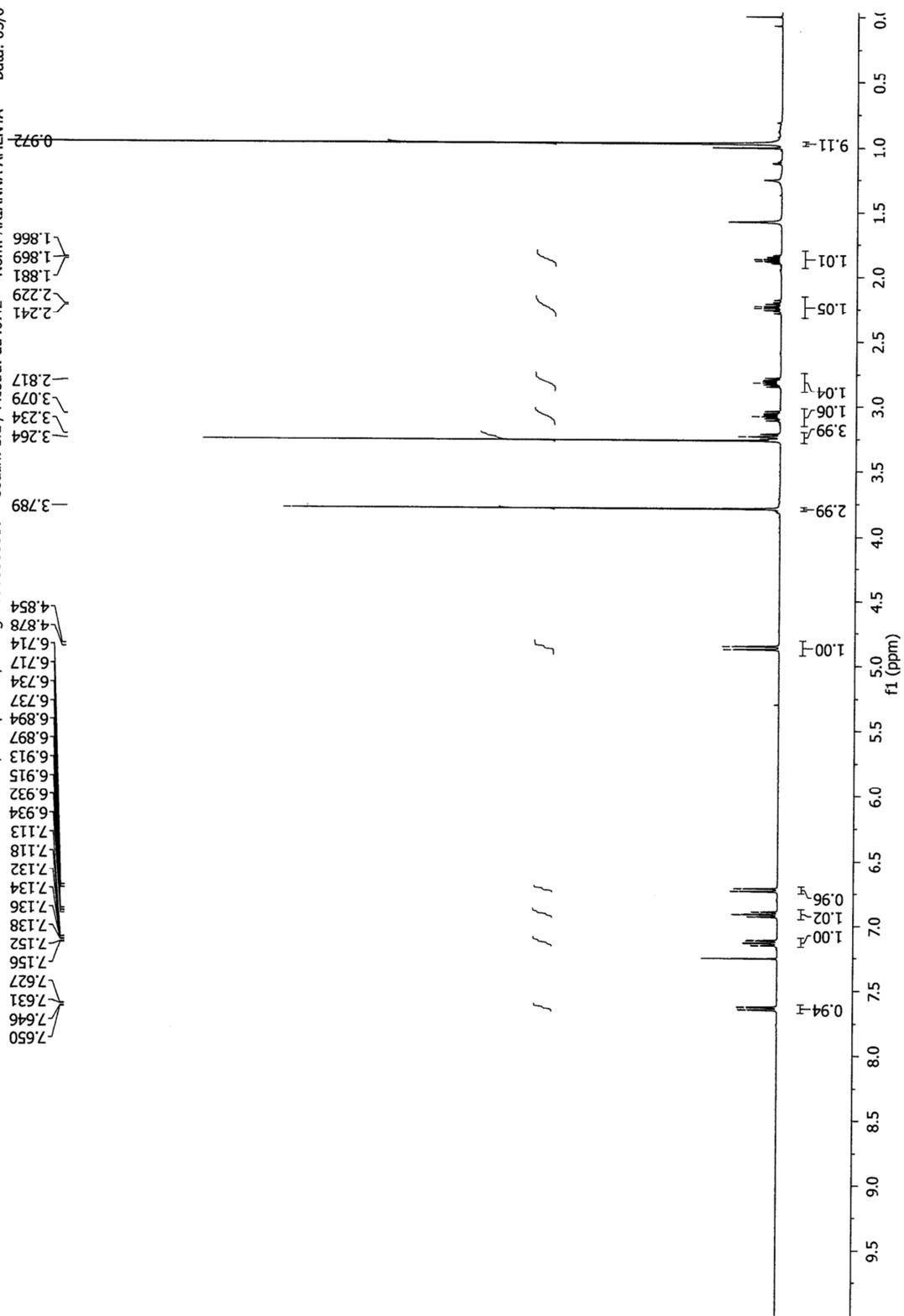
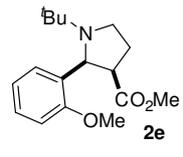


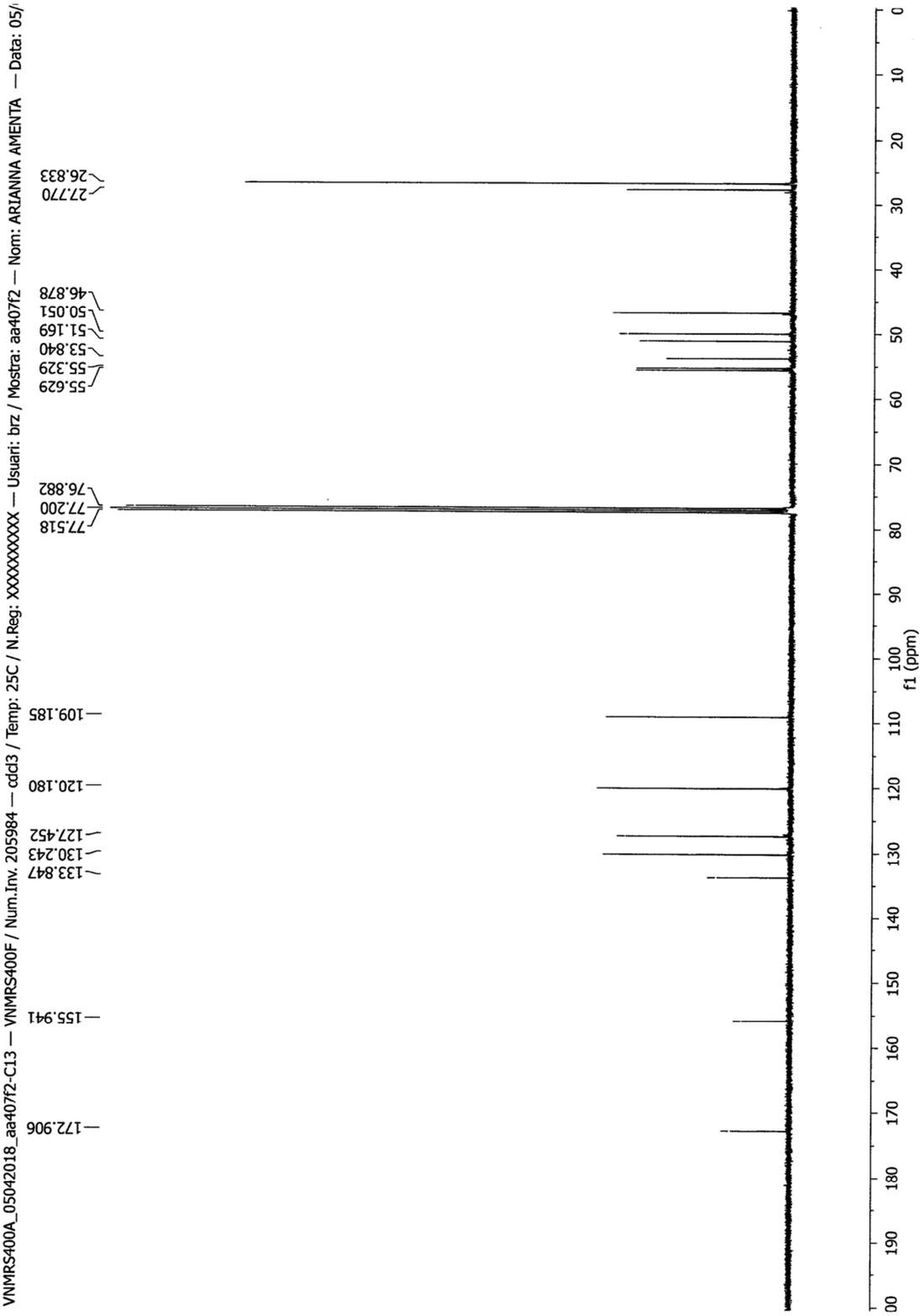
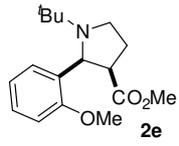


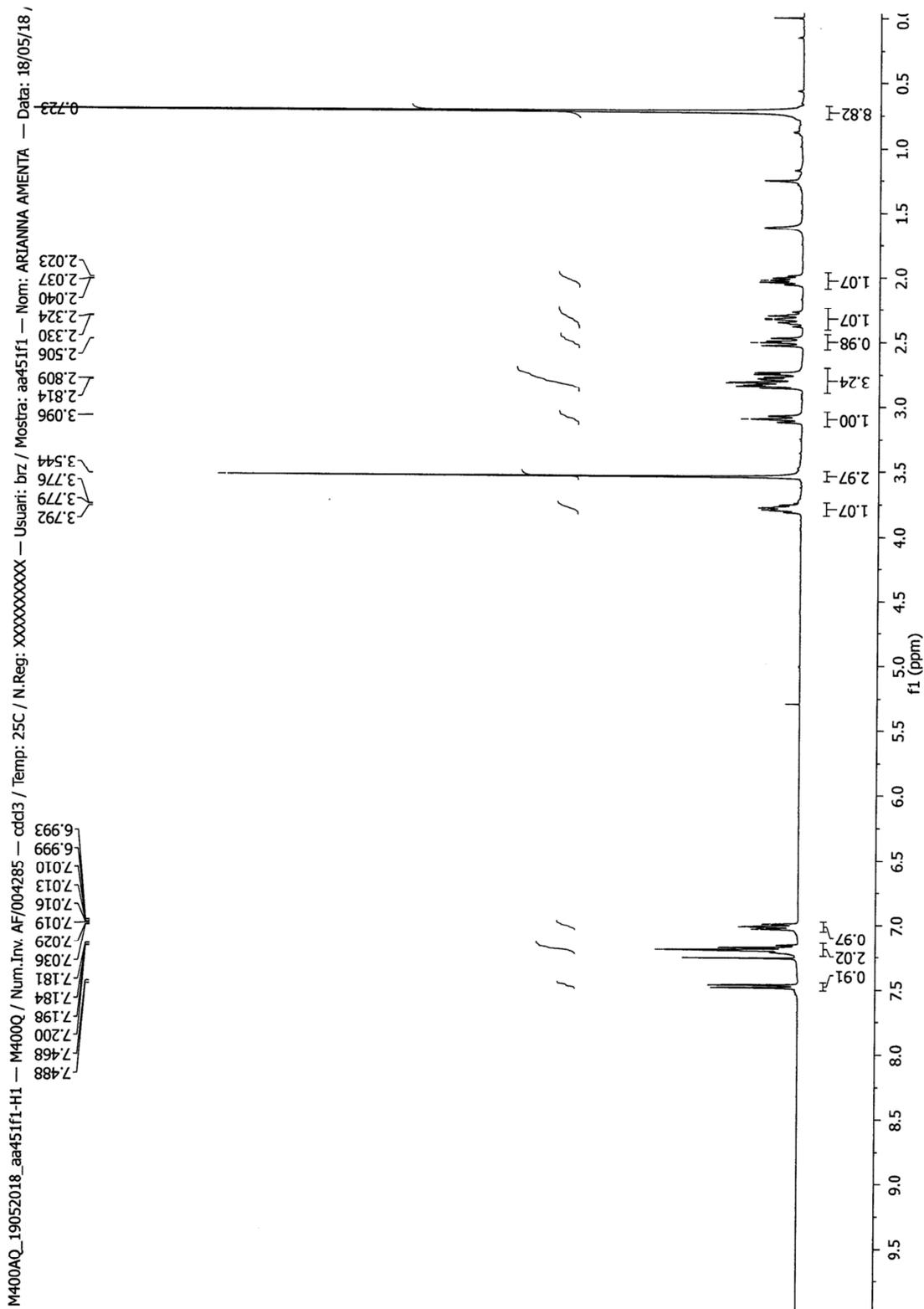
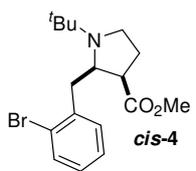


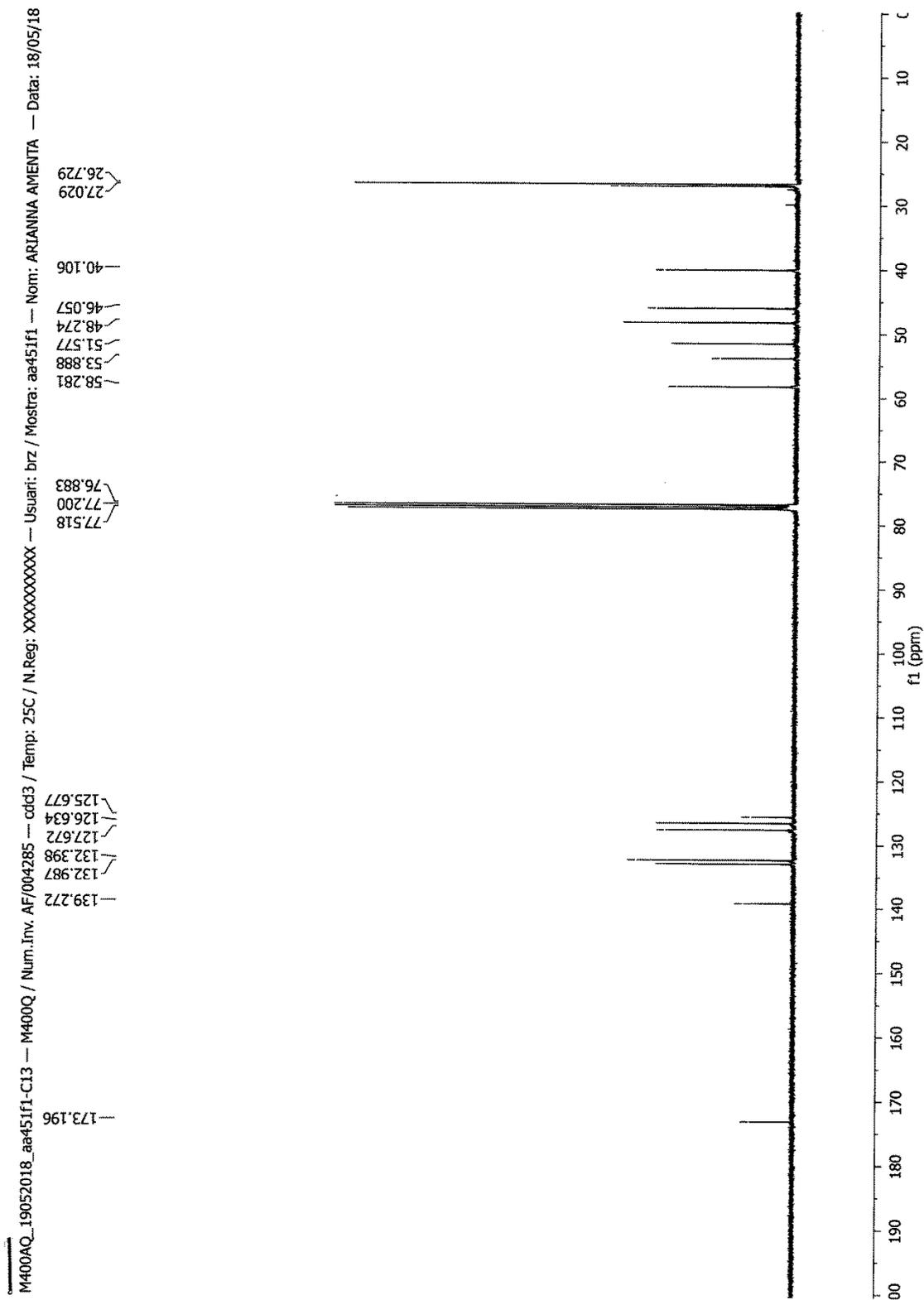
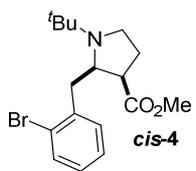


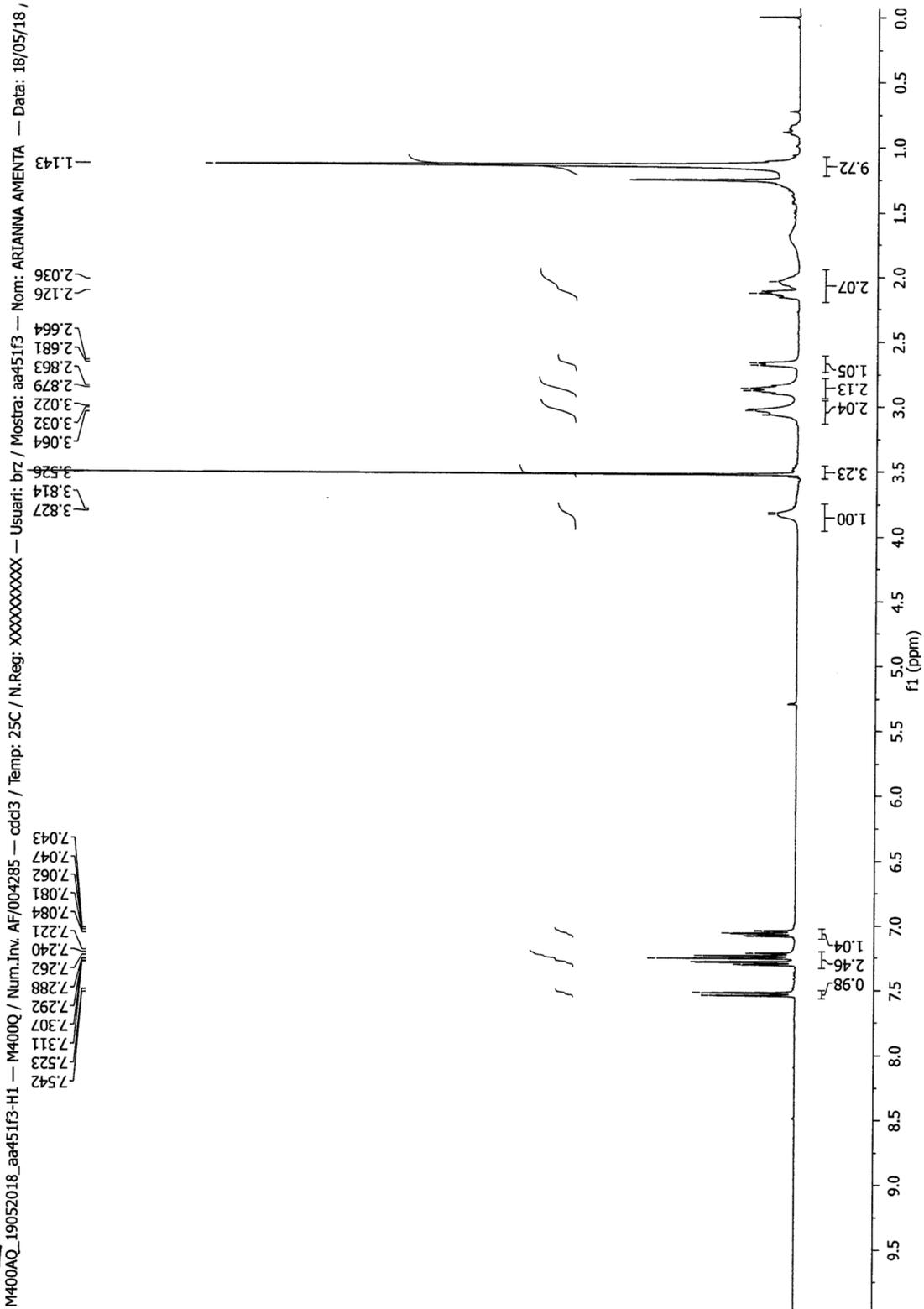
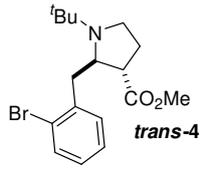
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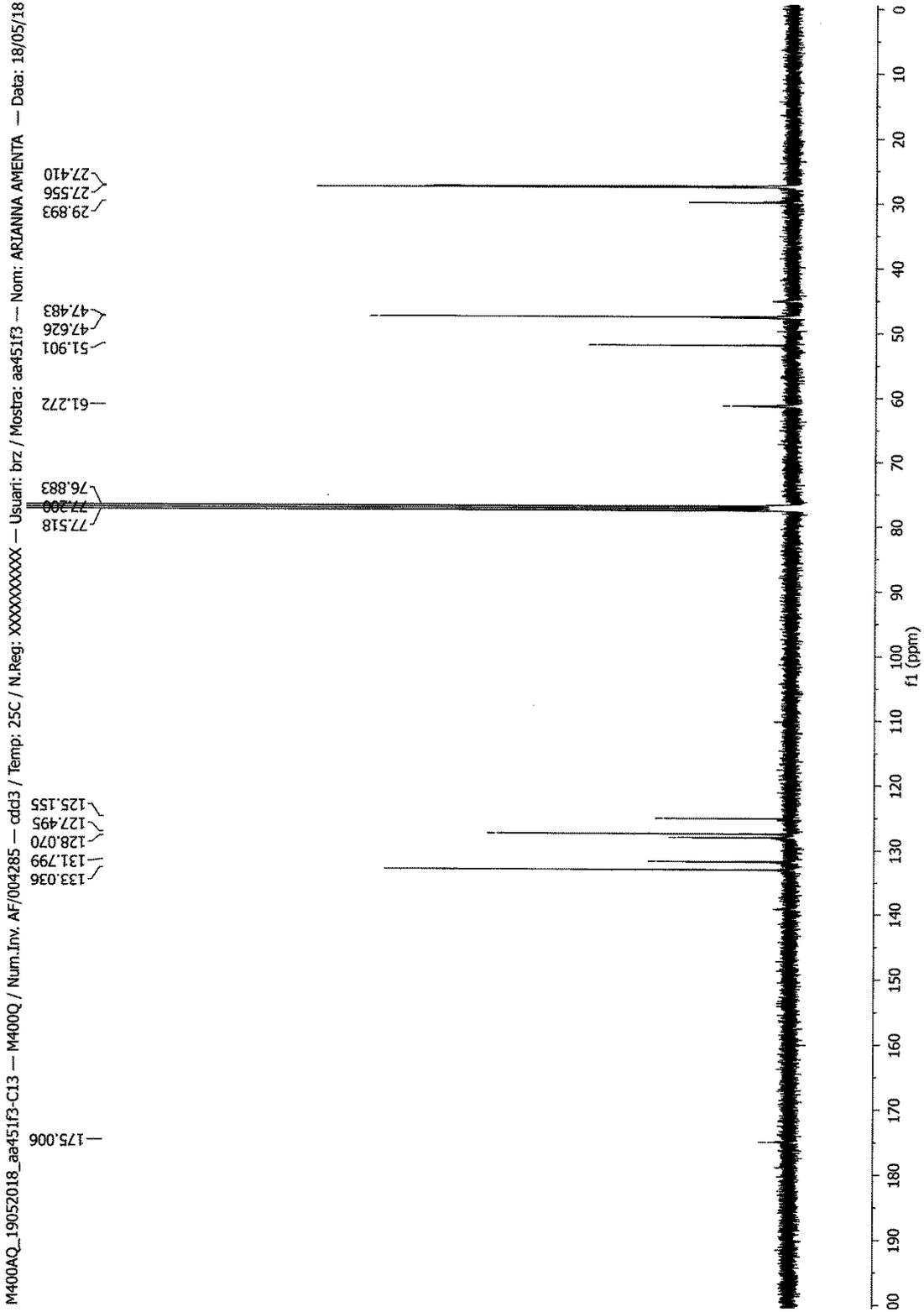
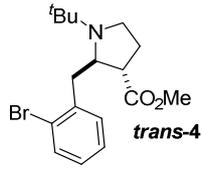


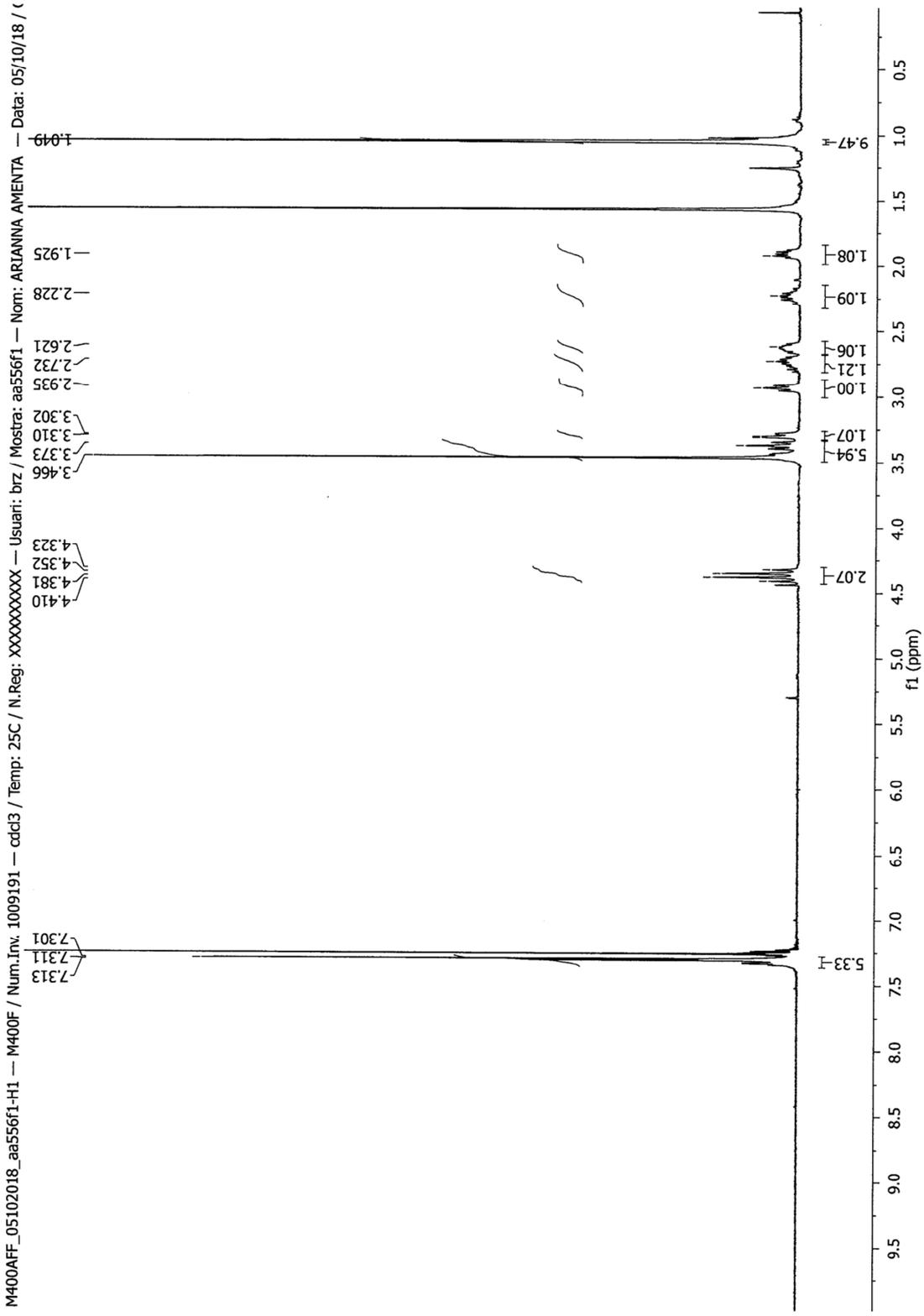
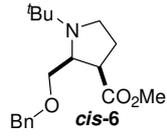


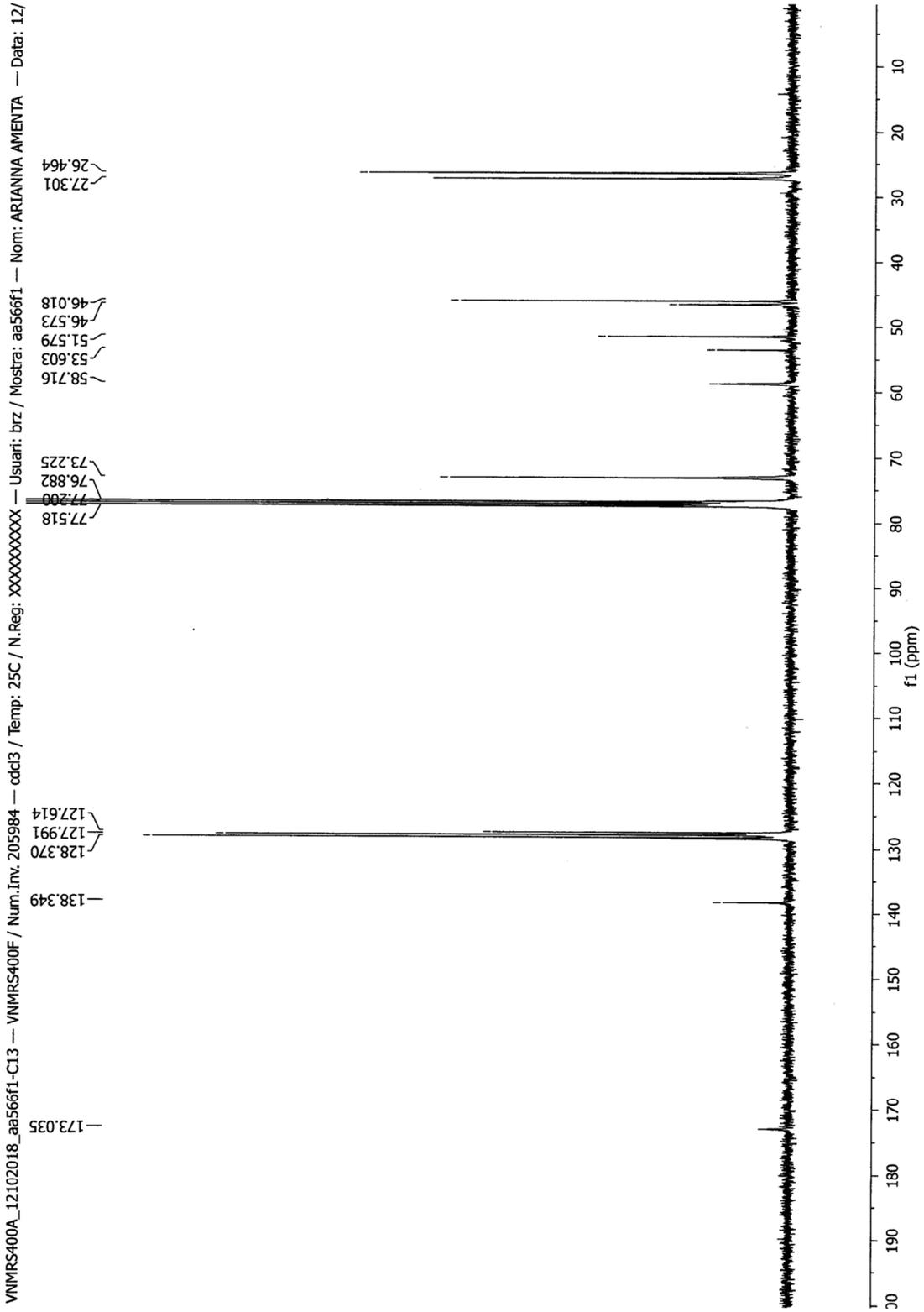
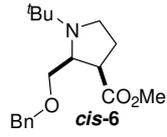


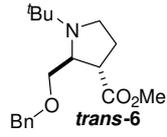




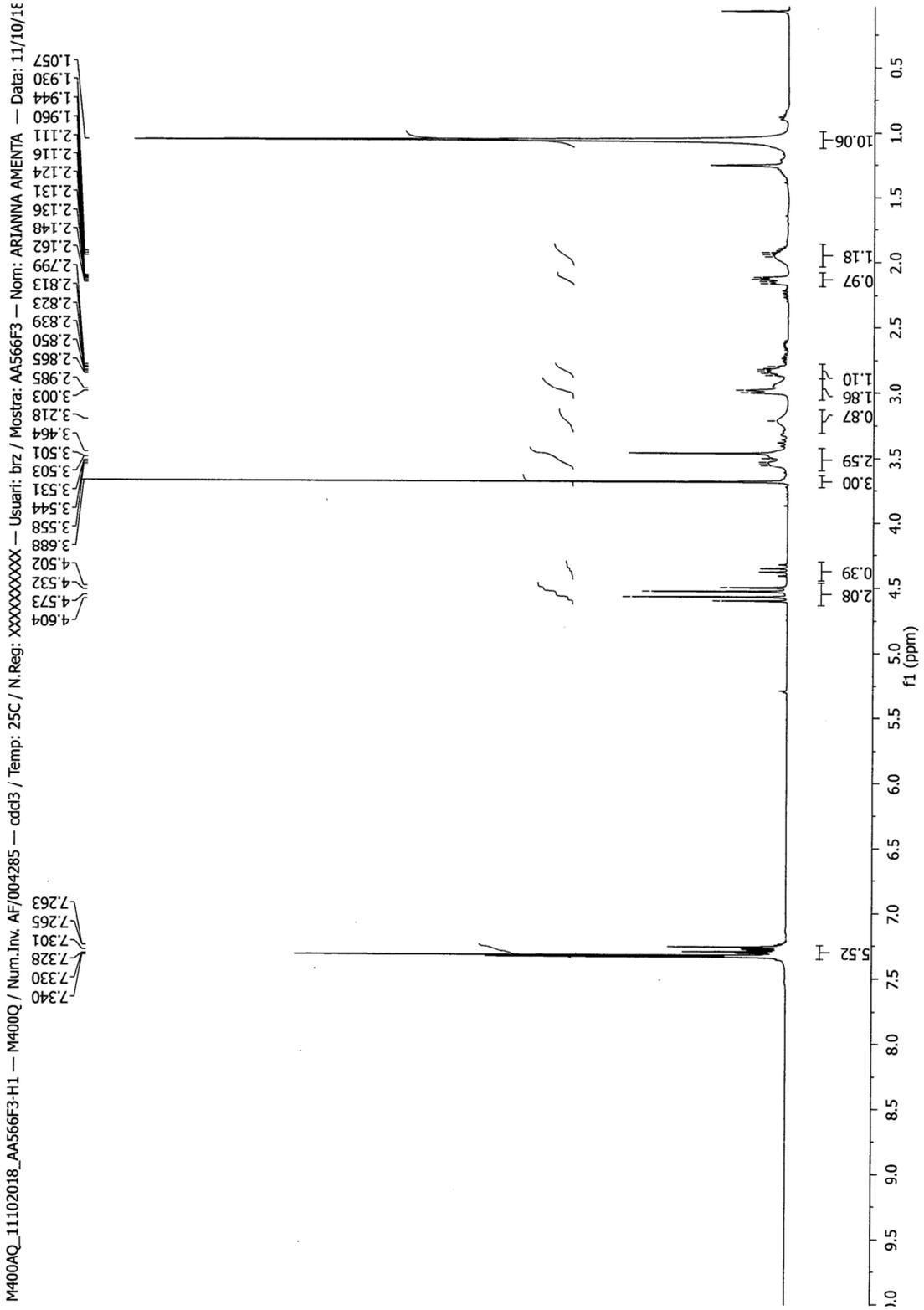


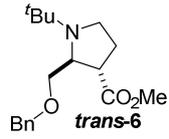




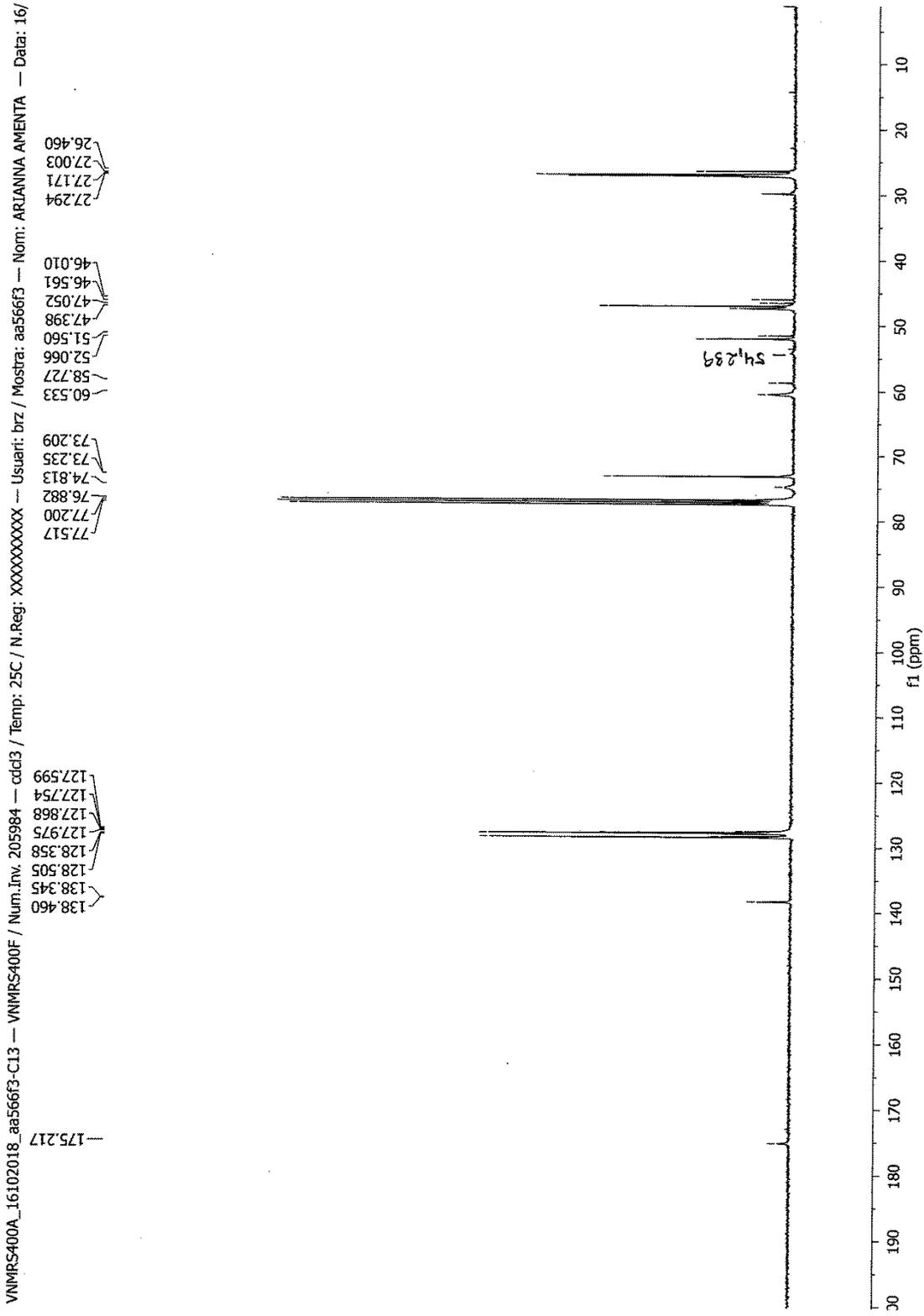


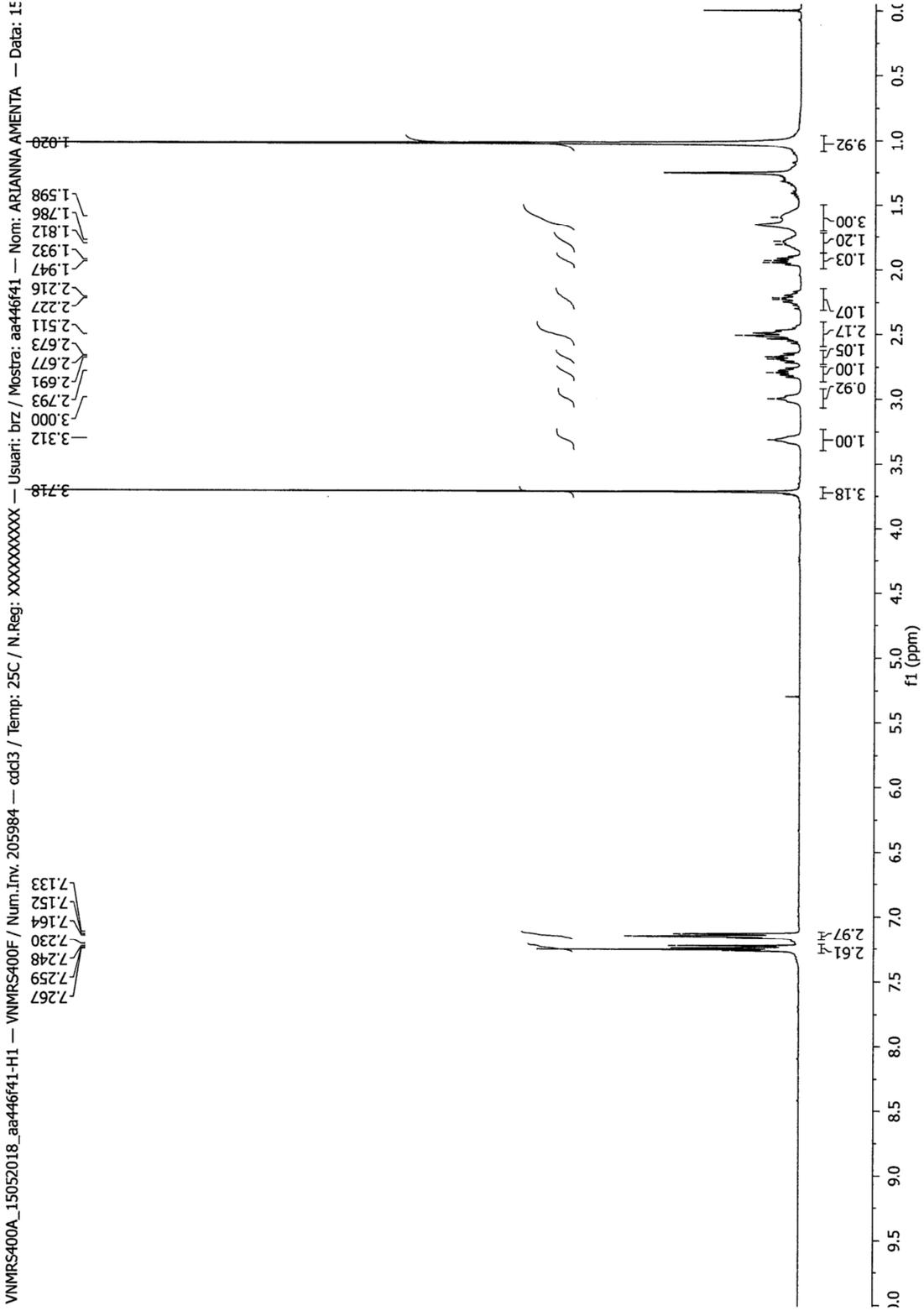
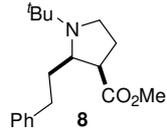
5:1 mixture of *trans-6* and *cis-6*

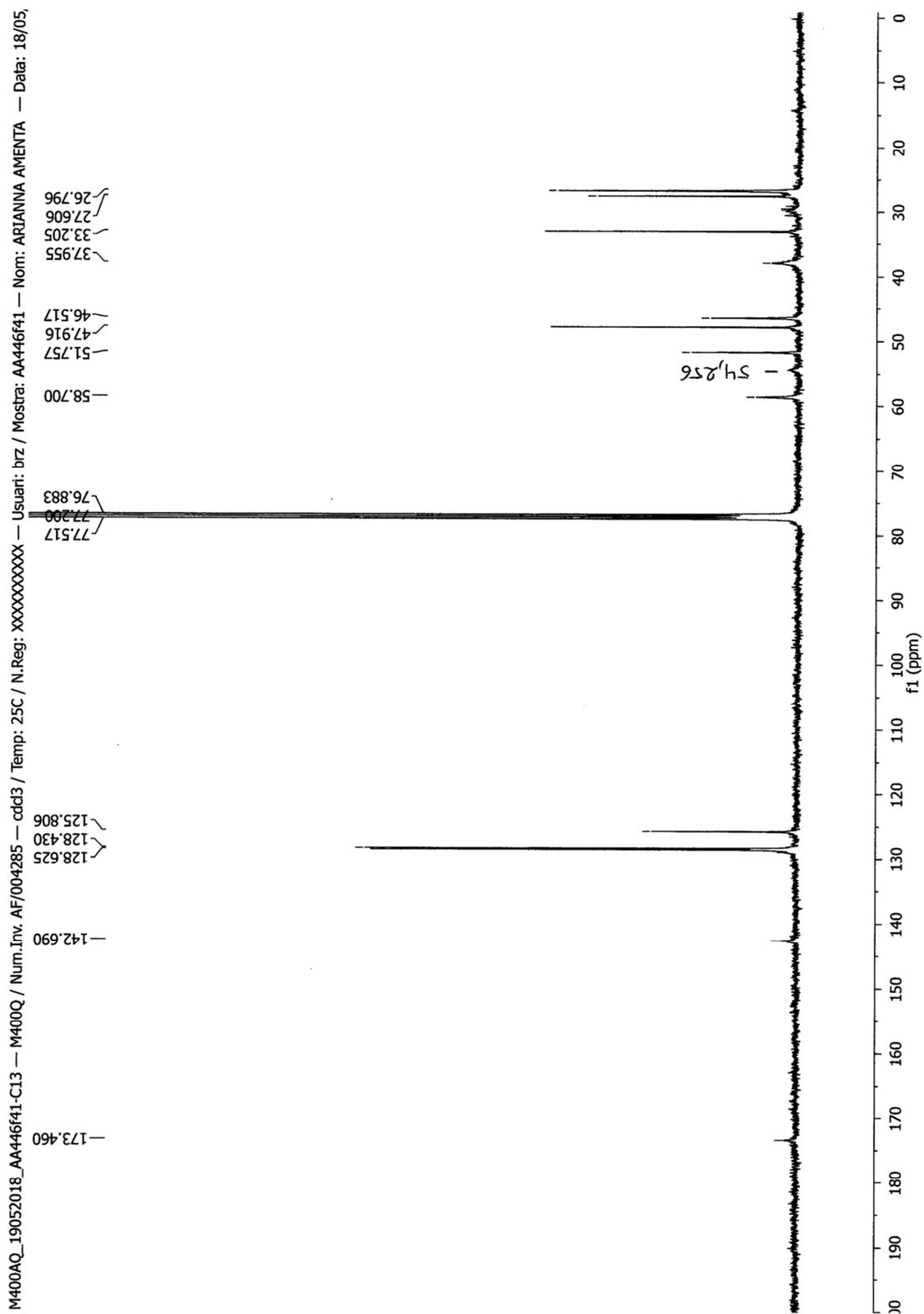
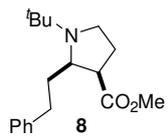


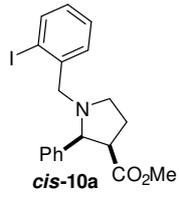


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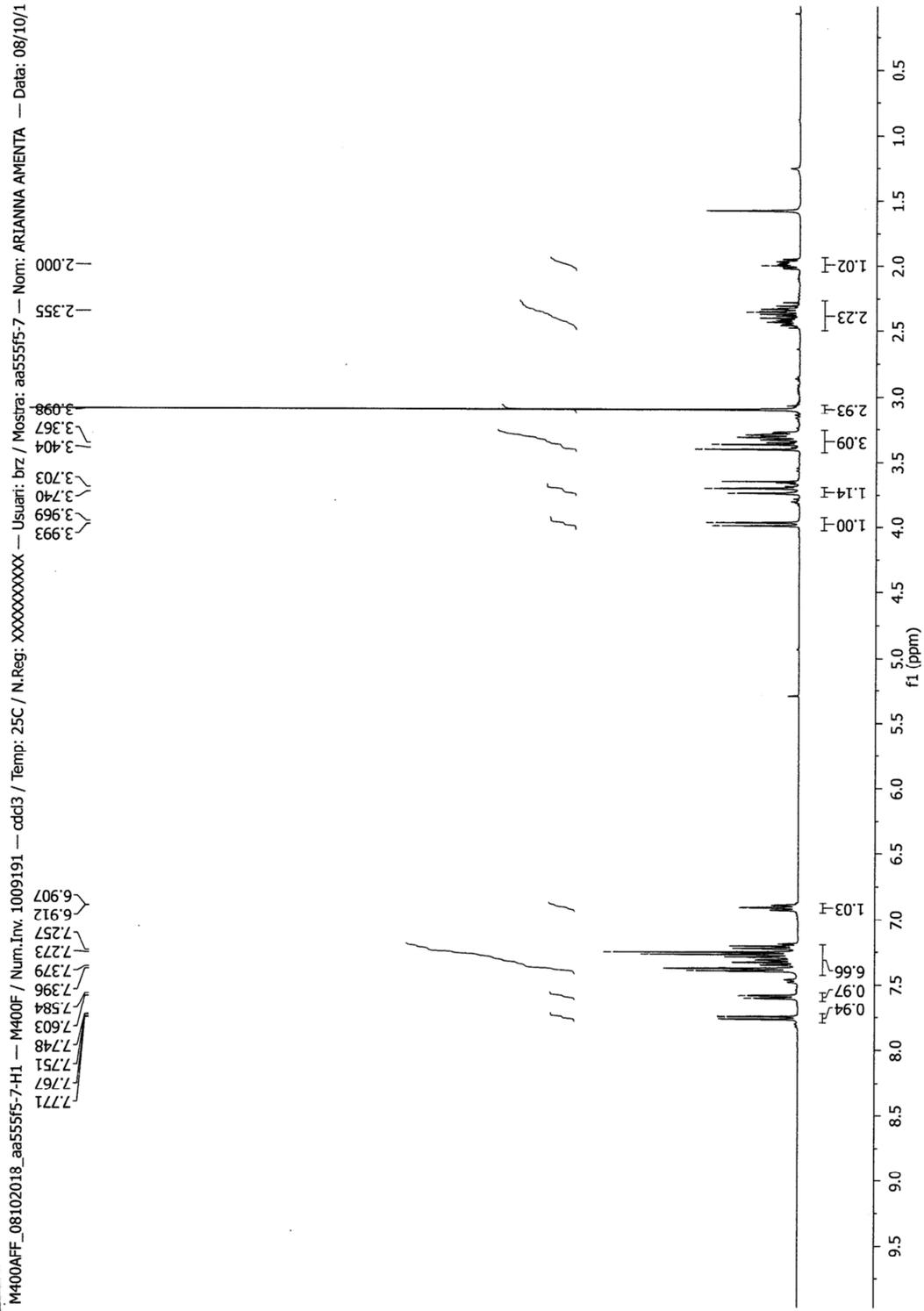


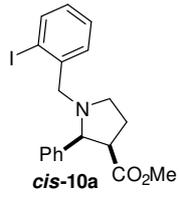




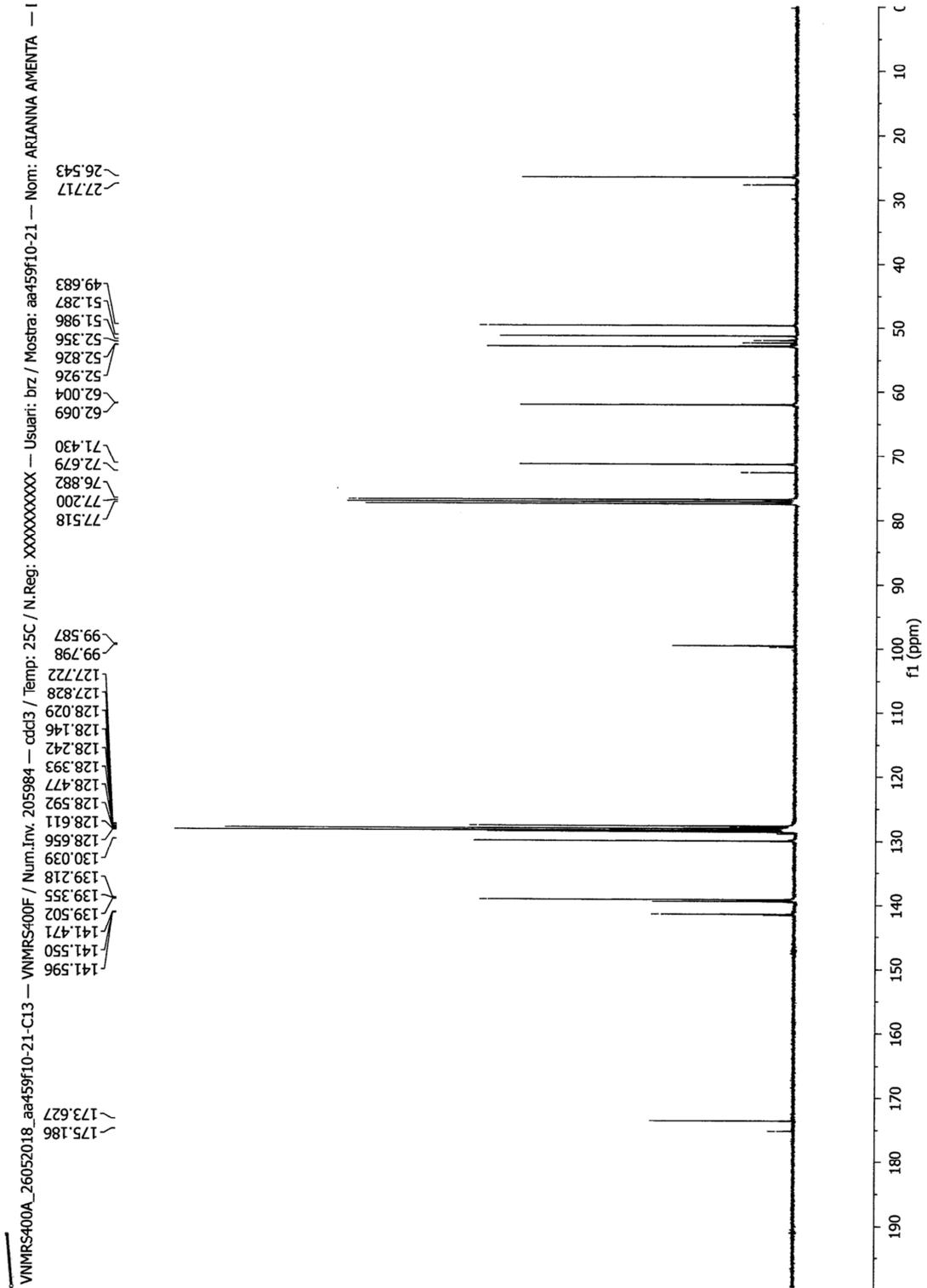


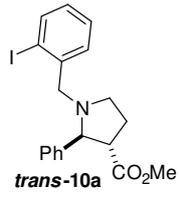
12:1 mixture of *cis-10a* and *trans-10a*



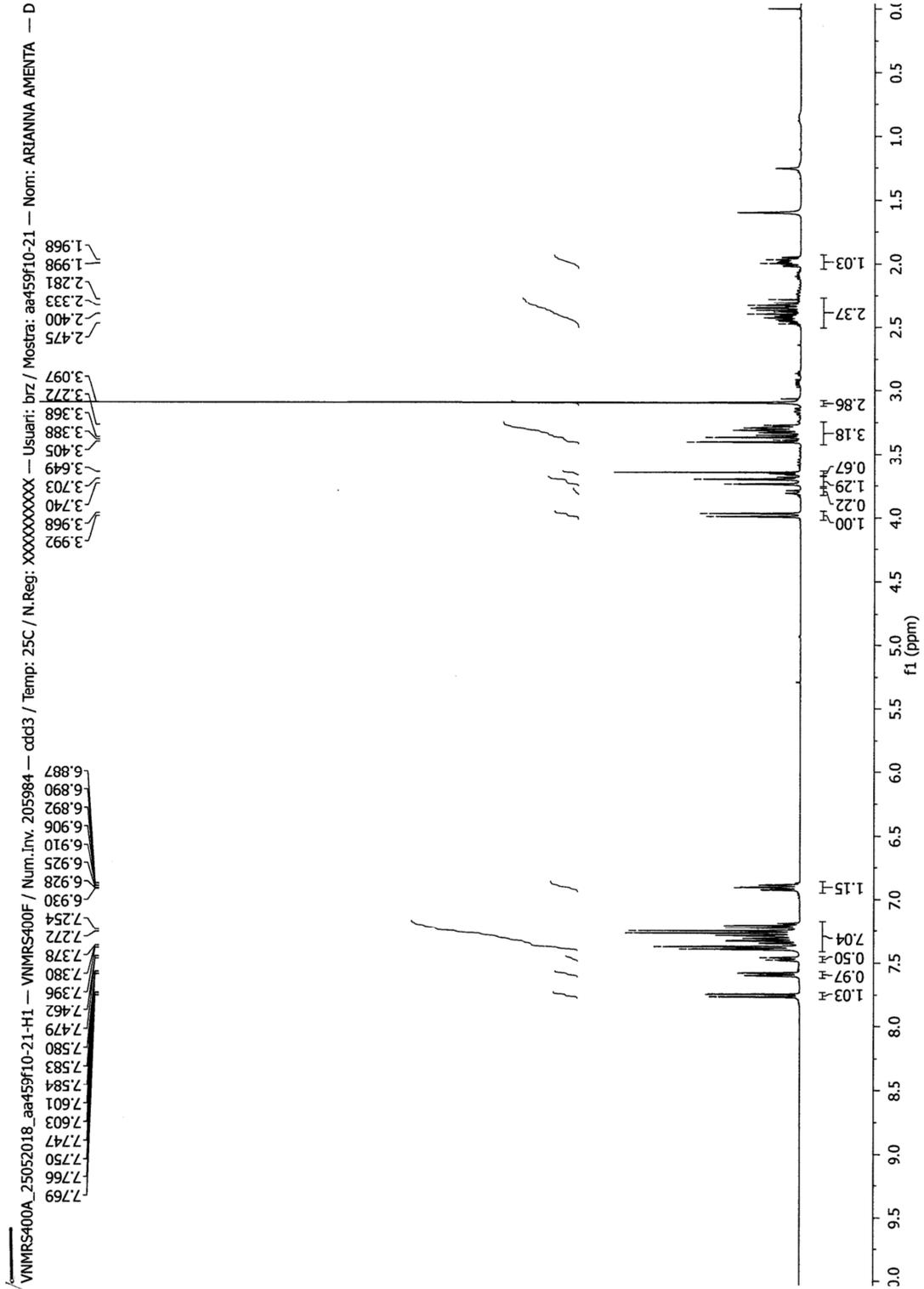


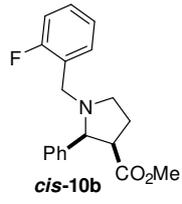
5:1 mixture of *cis*-10a and *trans*-10a



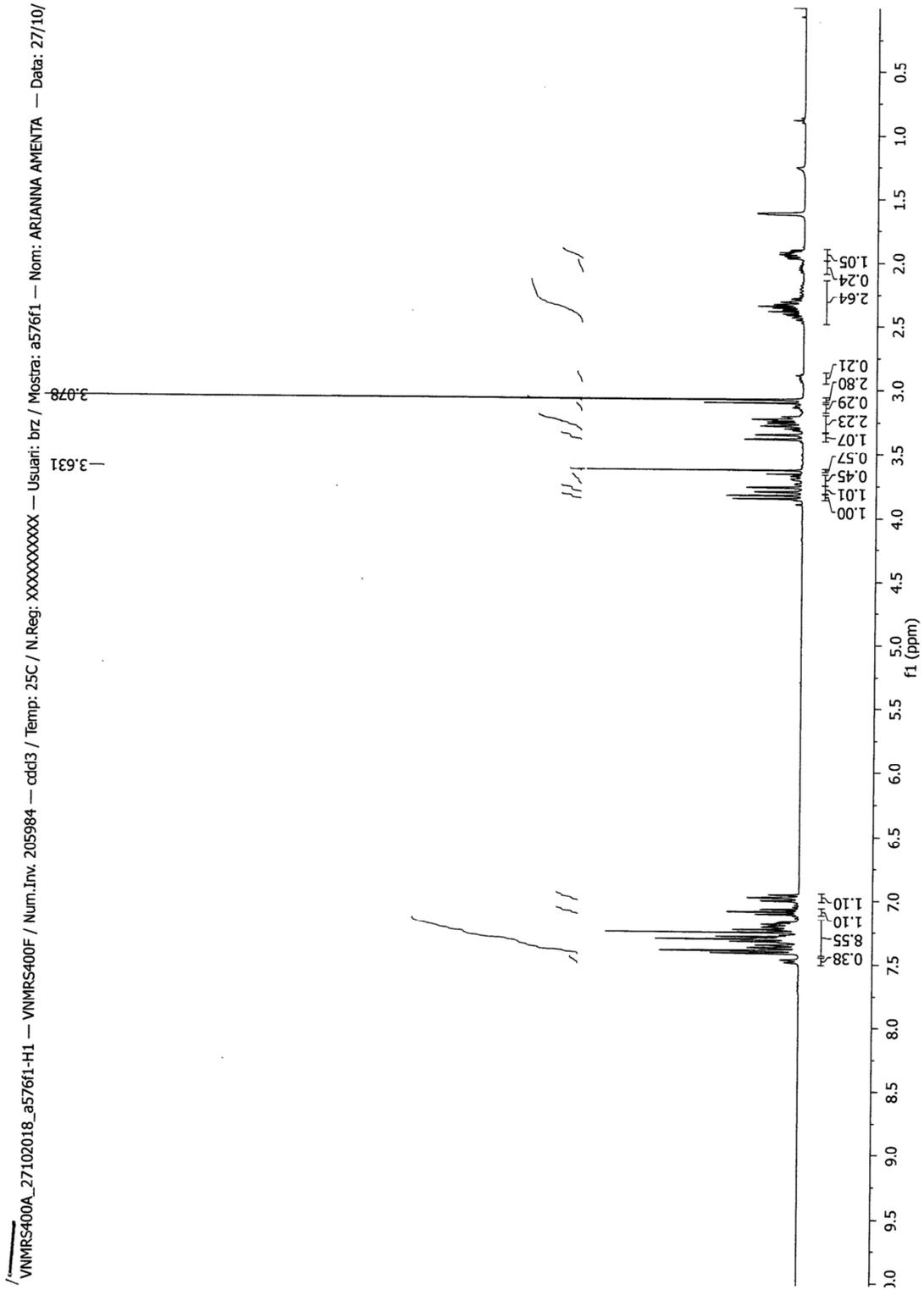


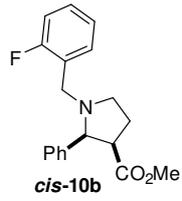
5:1 mixture of *cis*-10a and *trans*-10a



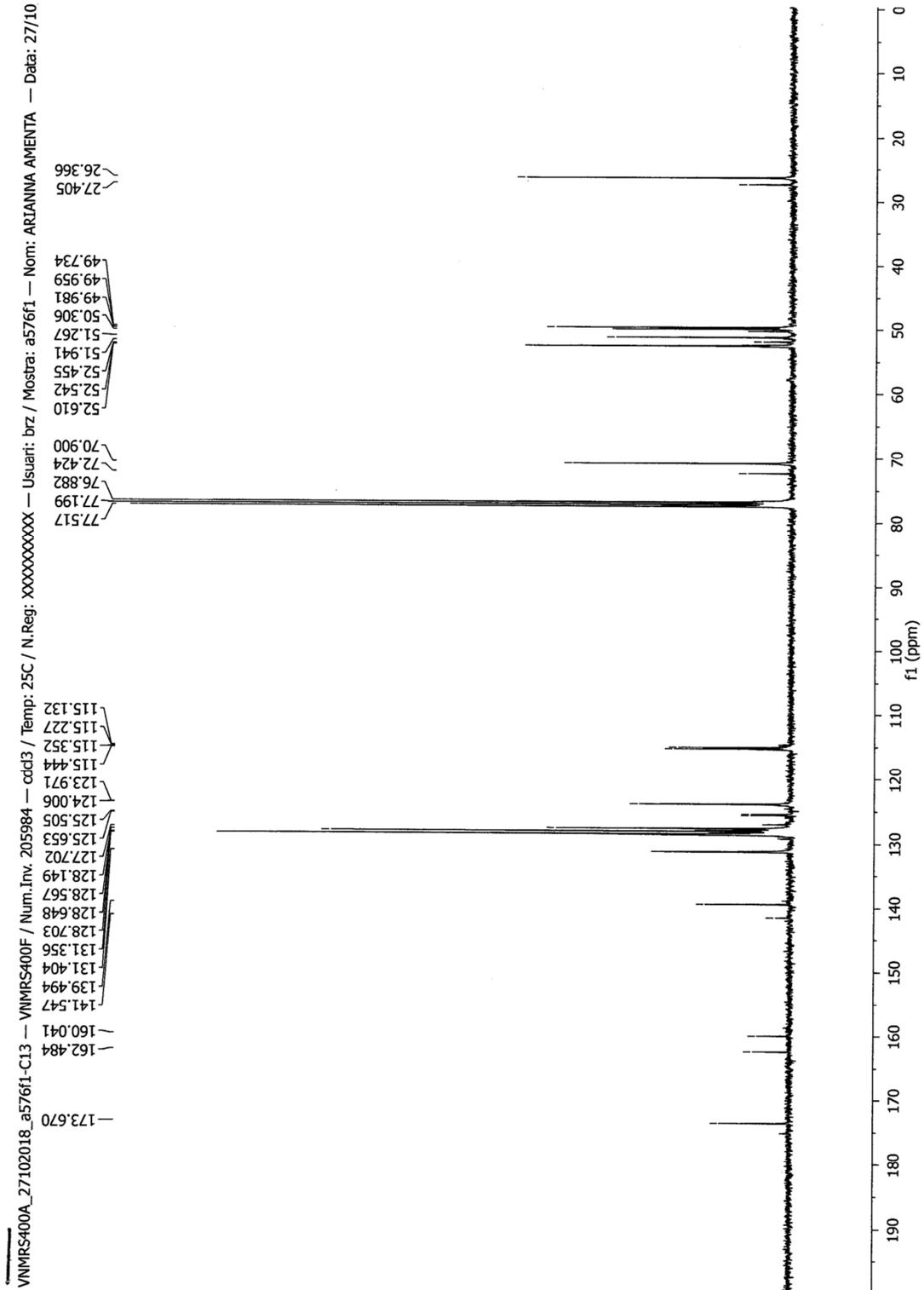


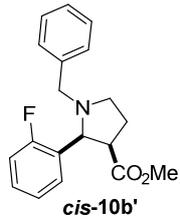
5:1 mixture of **cis-10b** and **trans-10b**



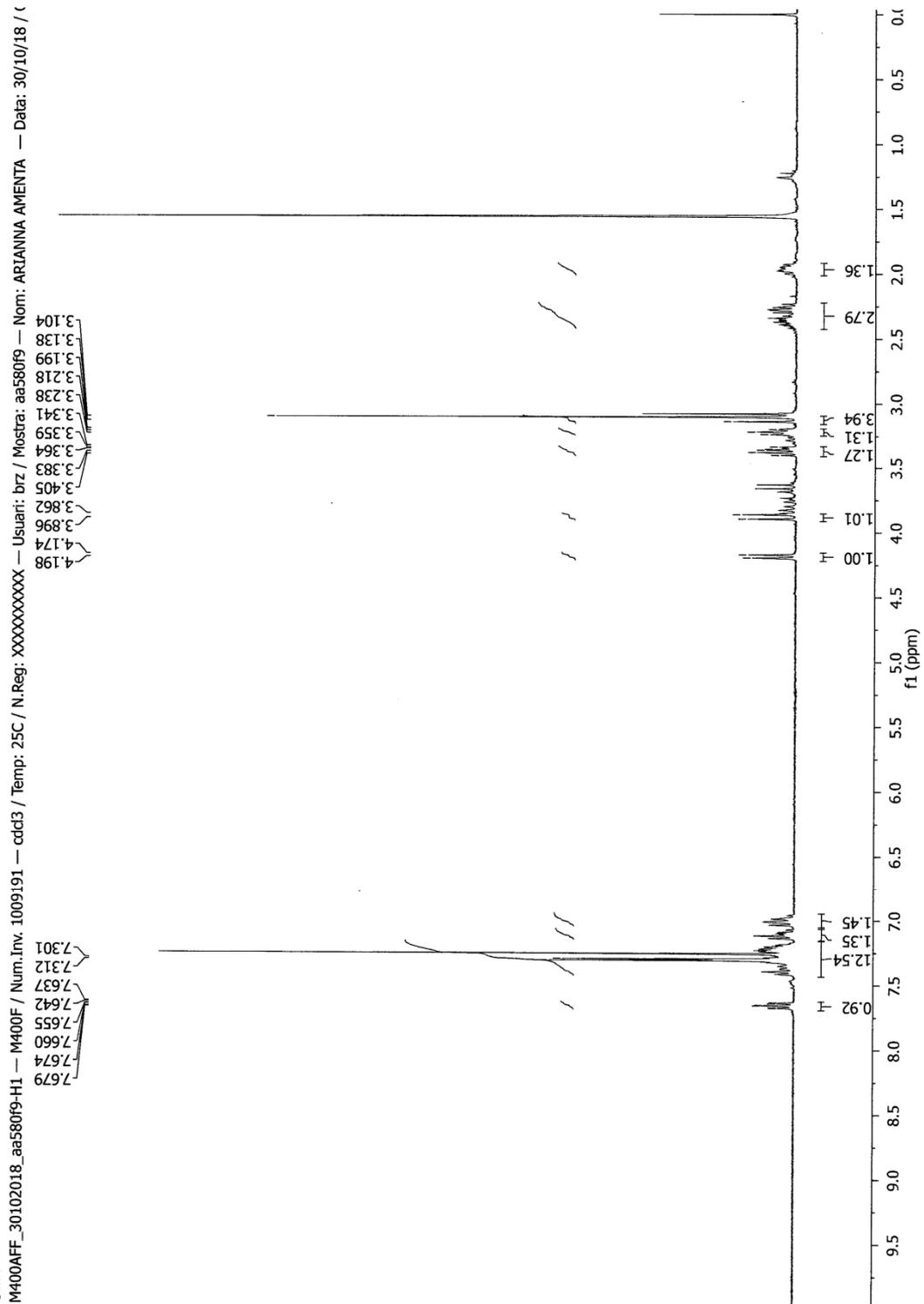


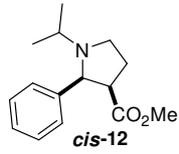
5:1 mixture of *cis-10b* and *trans-10b*



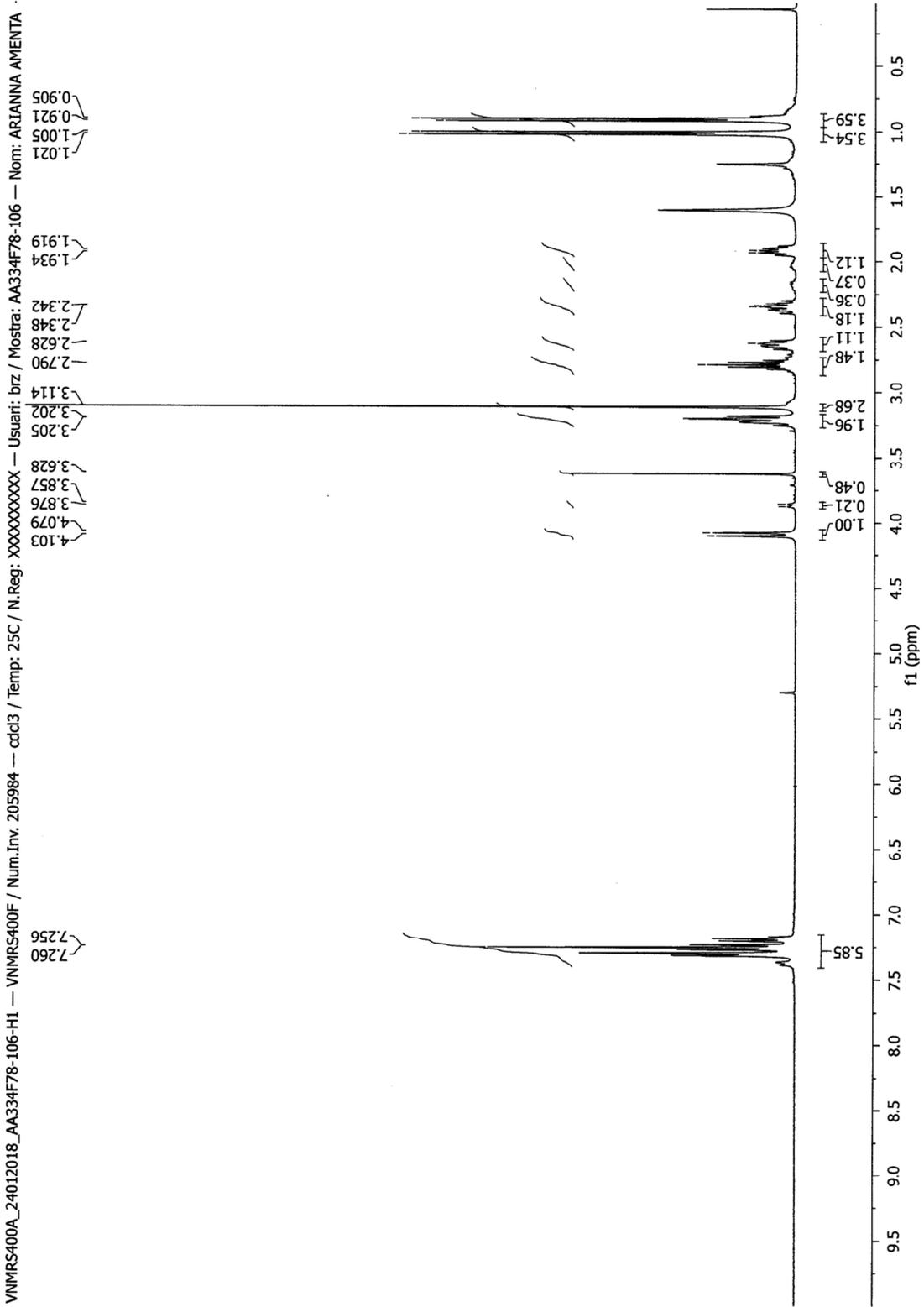


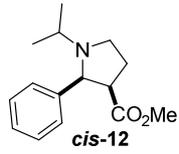
3:1 mixture of *cis-10b'* and *cis-10b*



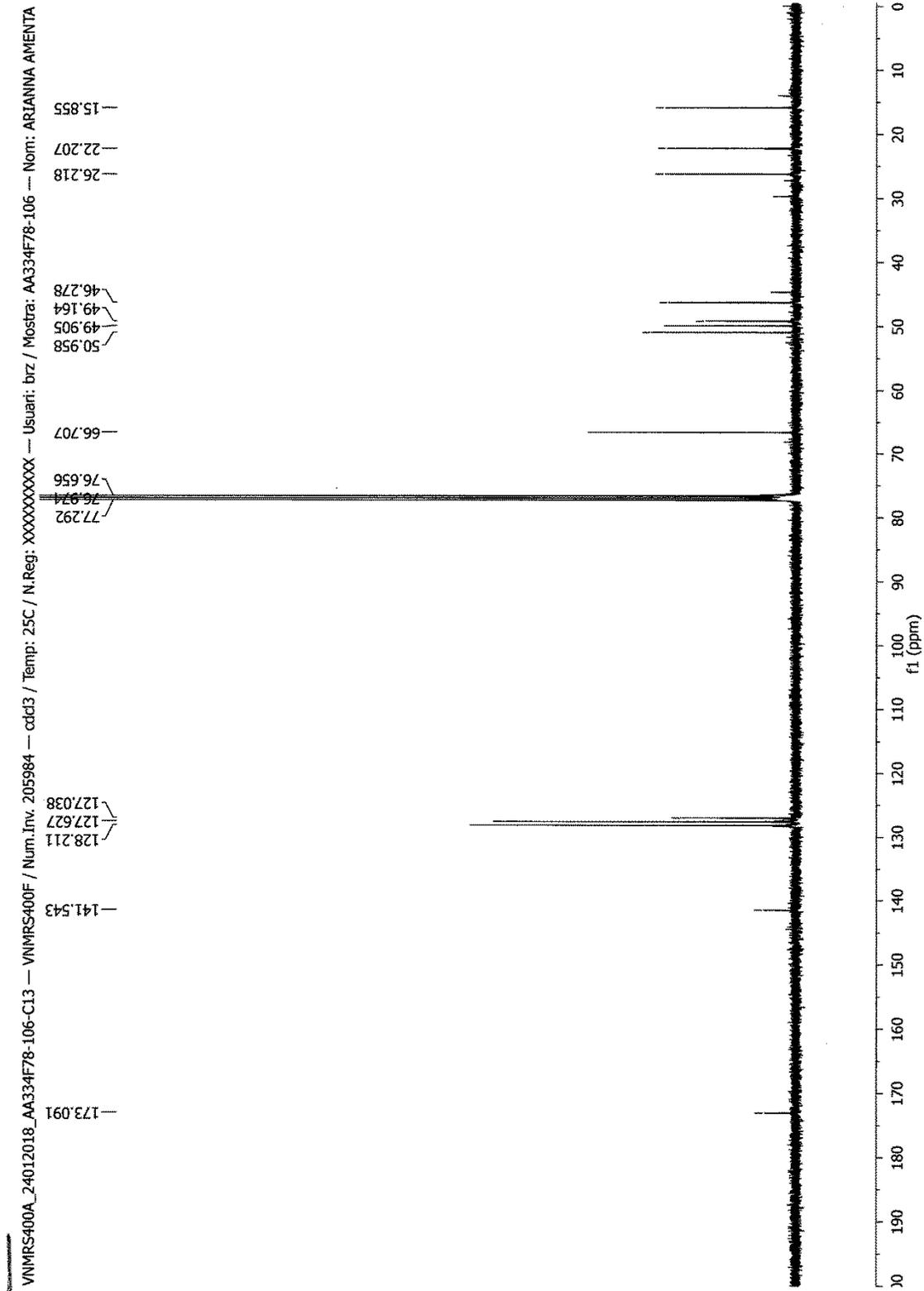


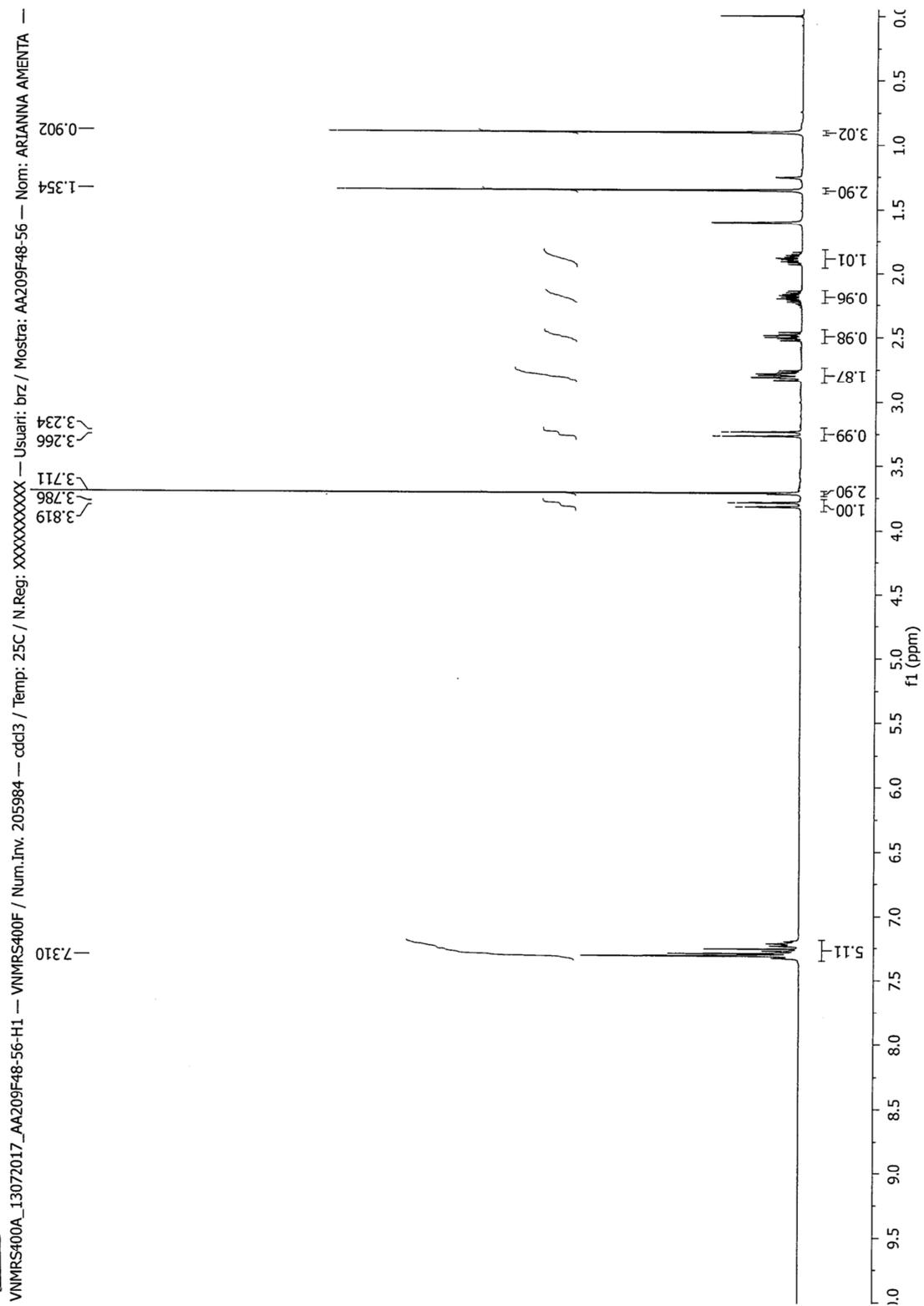
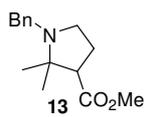
5.8:1 mixture of *cis*-12 and *trans*-12

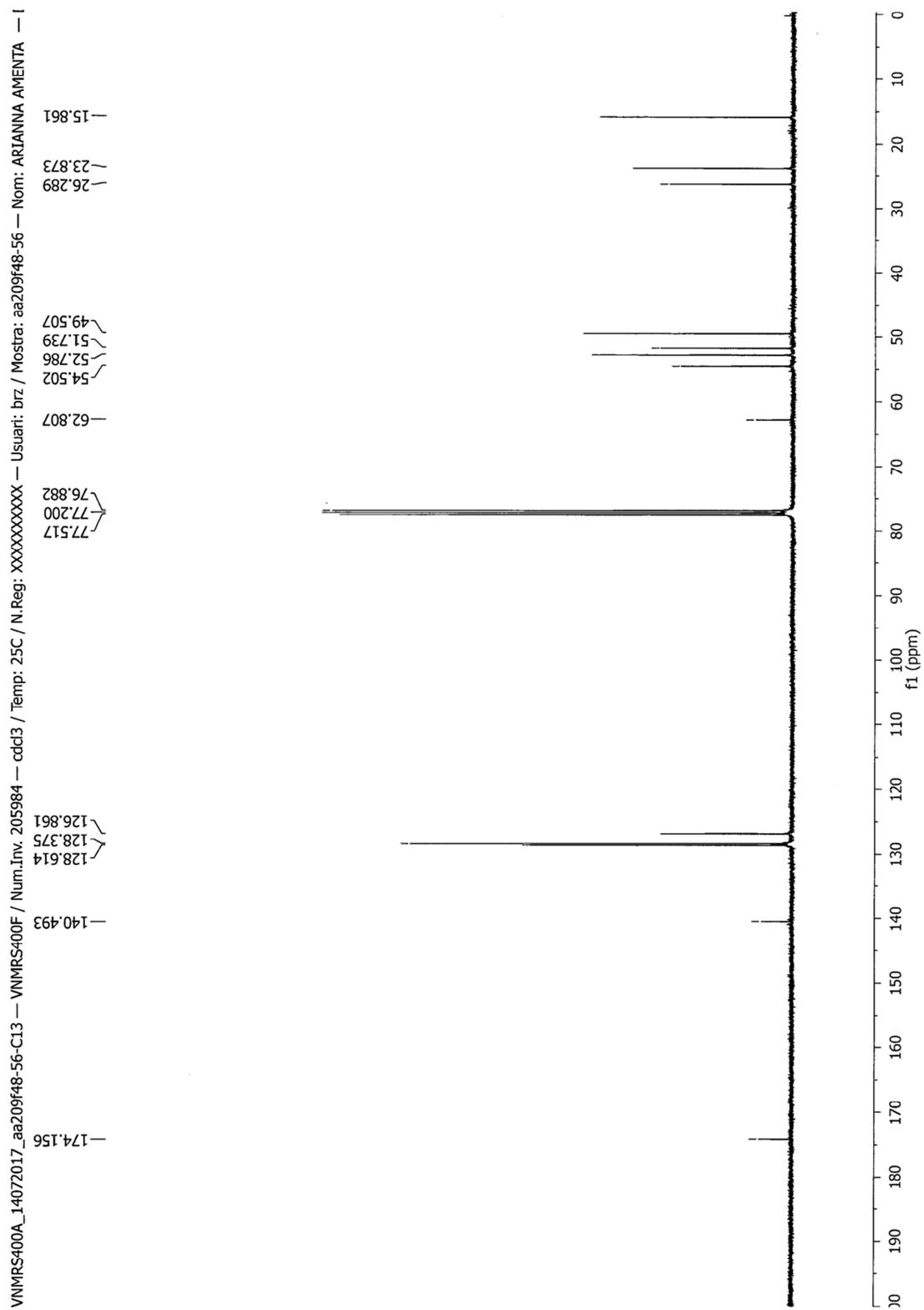
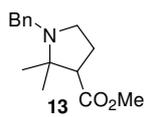


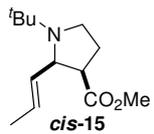


5.8:1 mixture of *cis*-12 and *trans*-12

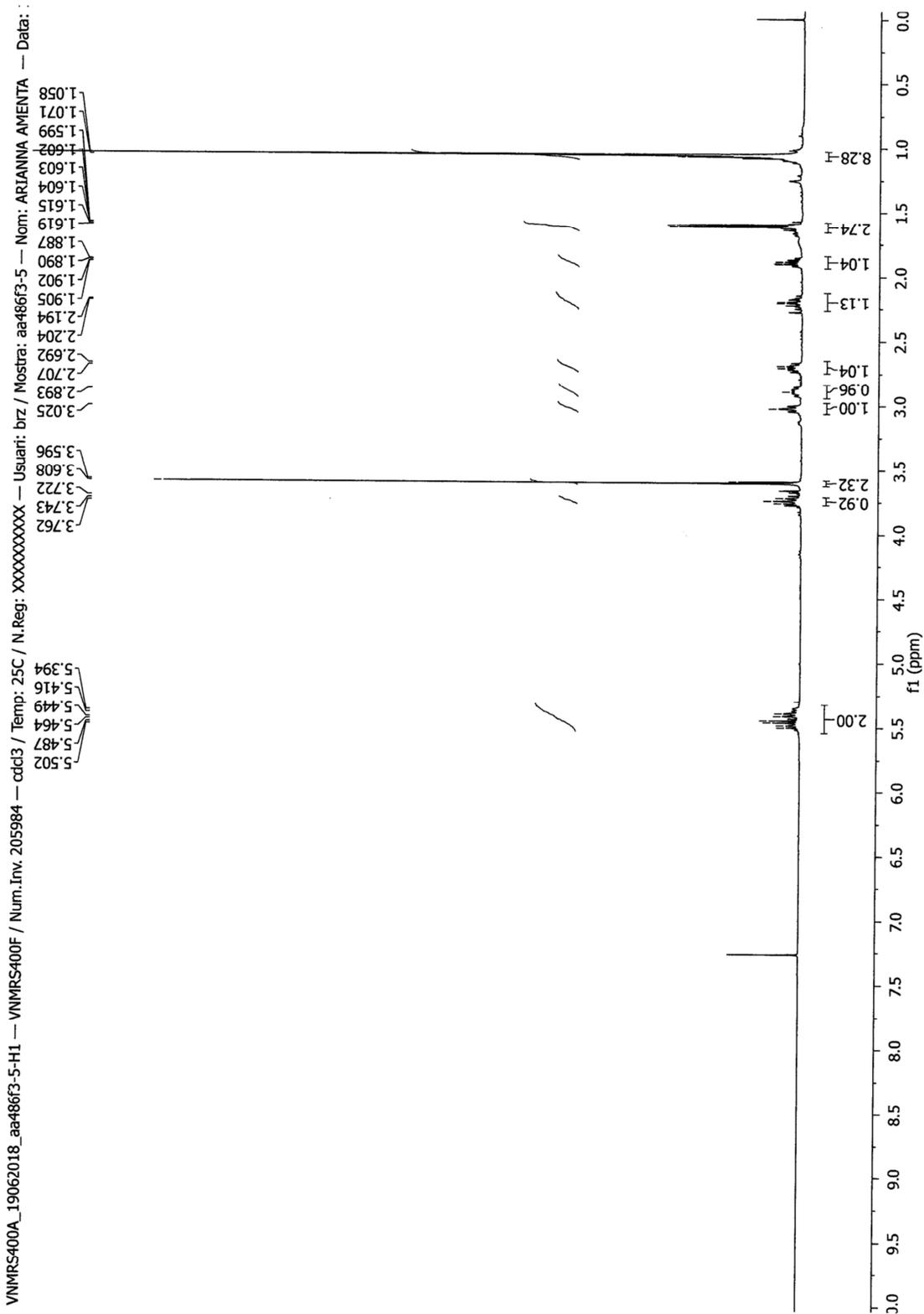


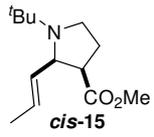




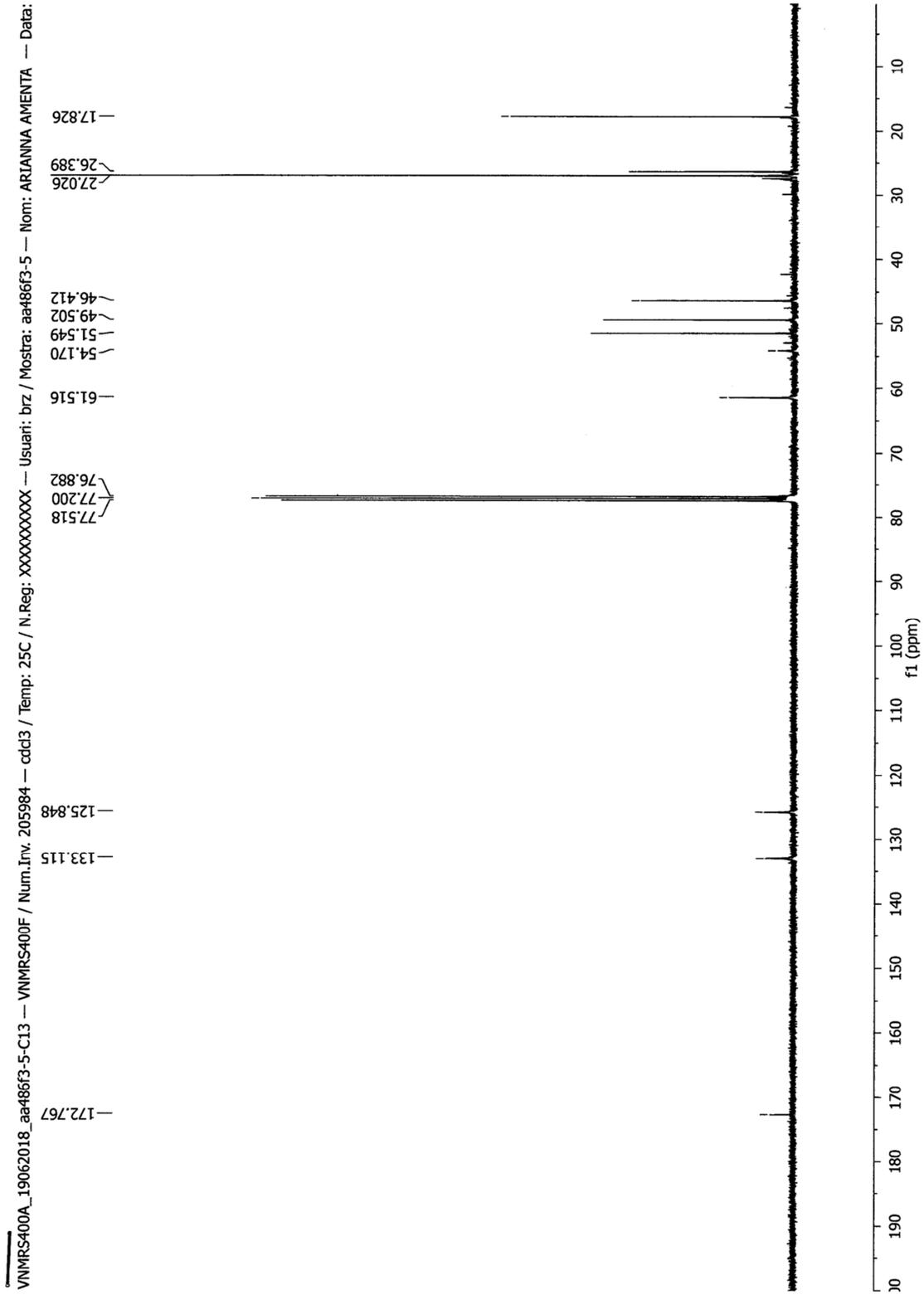


8:1 mixture of *cis*-15 and *trans*-15

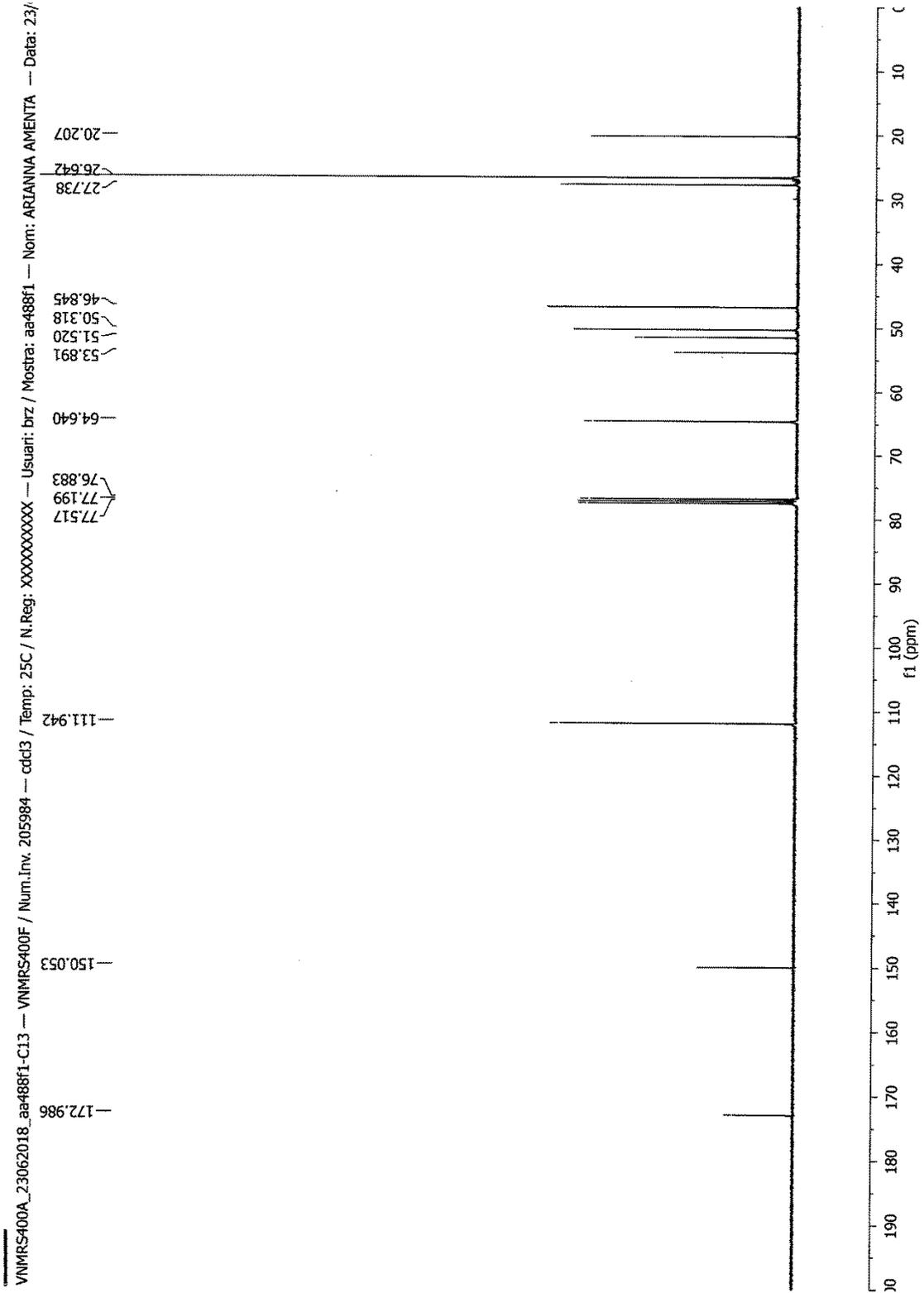
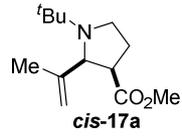


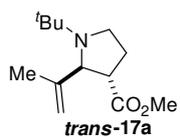


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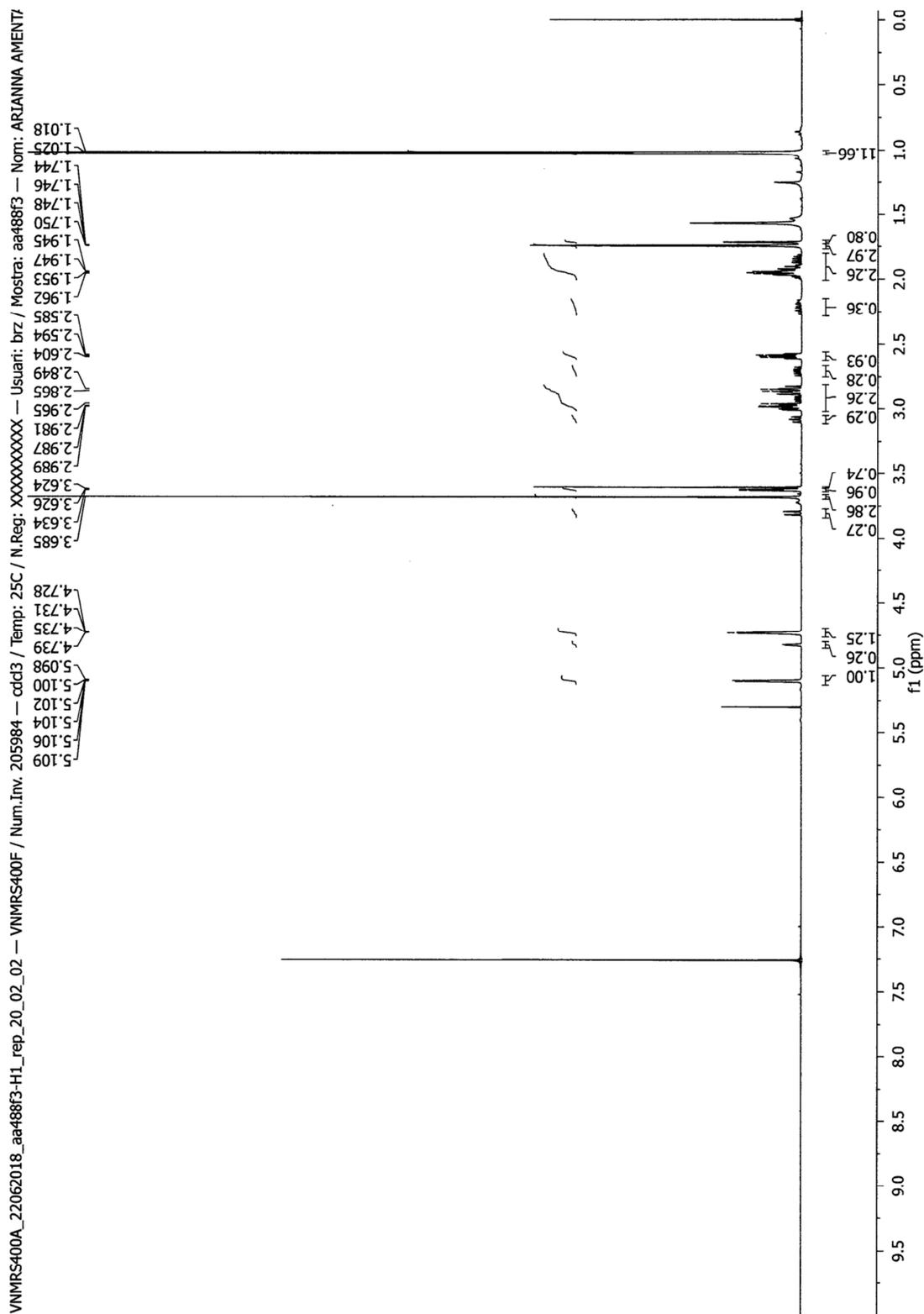


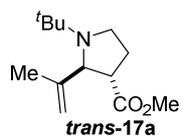




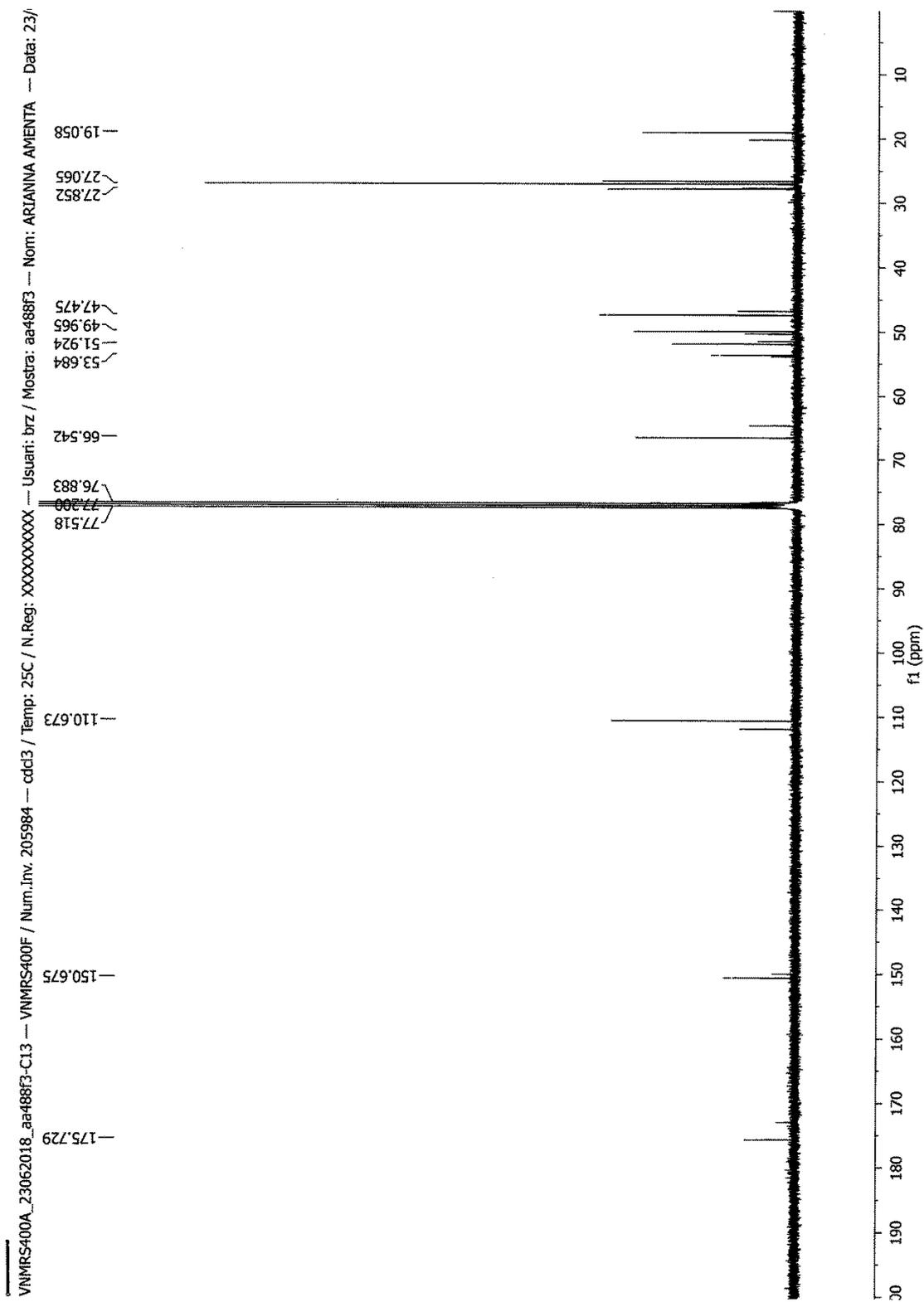


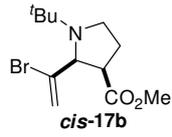
4:1 mixture of *trans-17a* and *cis-17a*



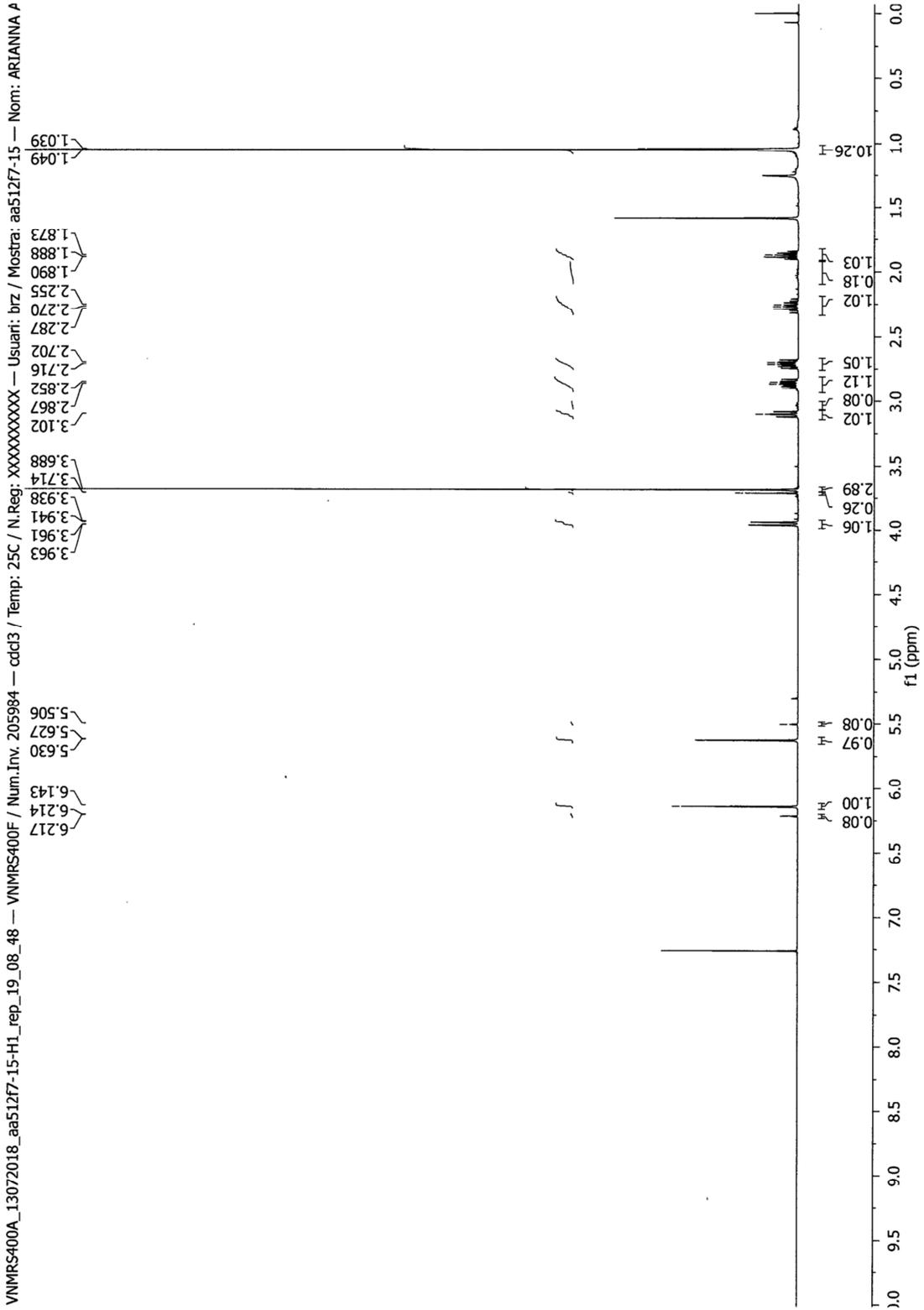


4:1 mixture of *trans-17a* and *cis-17a*



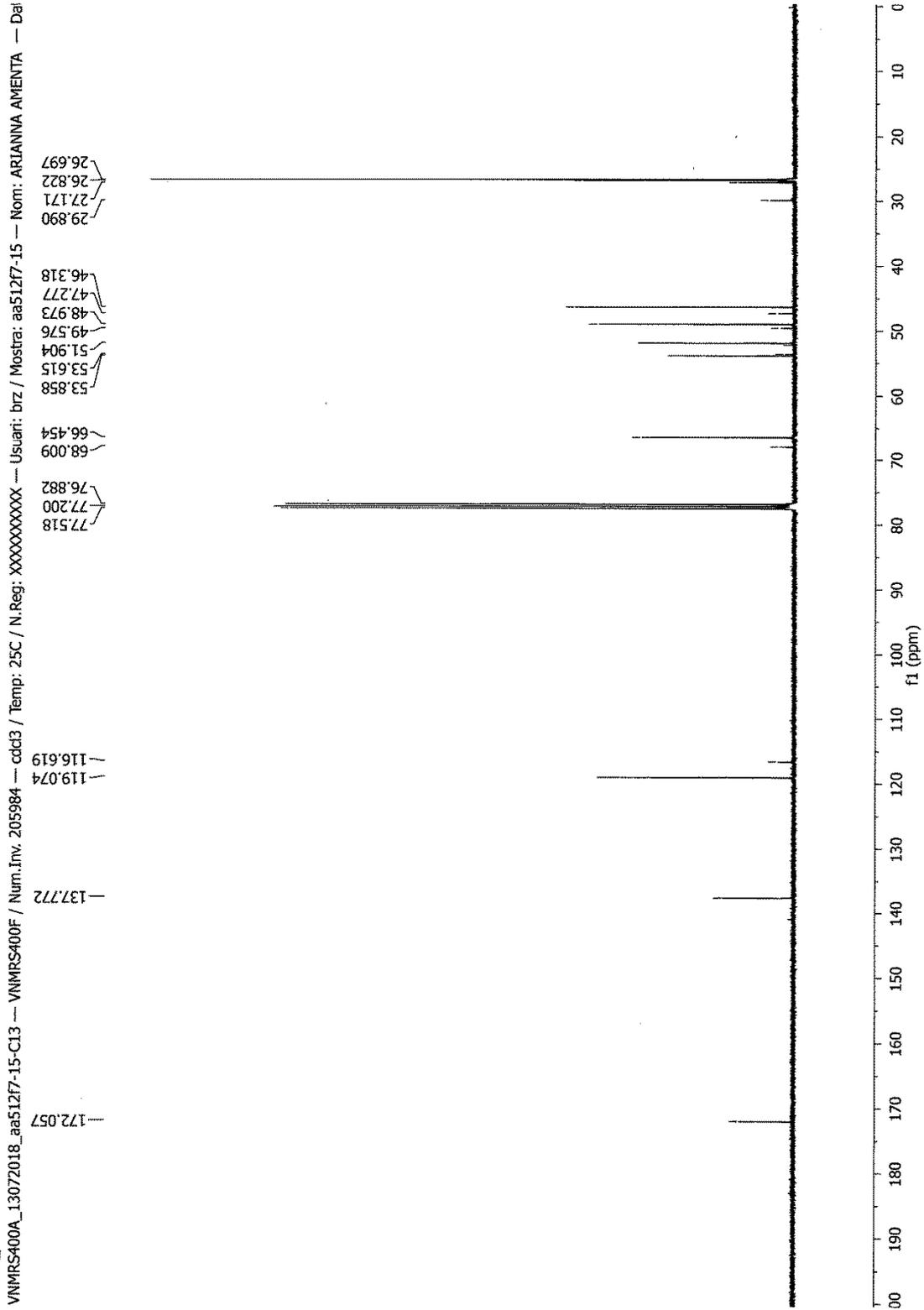


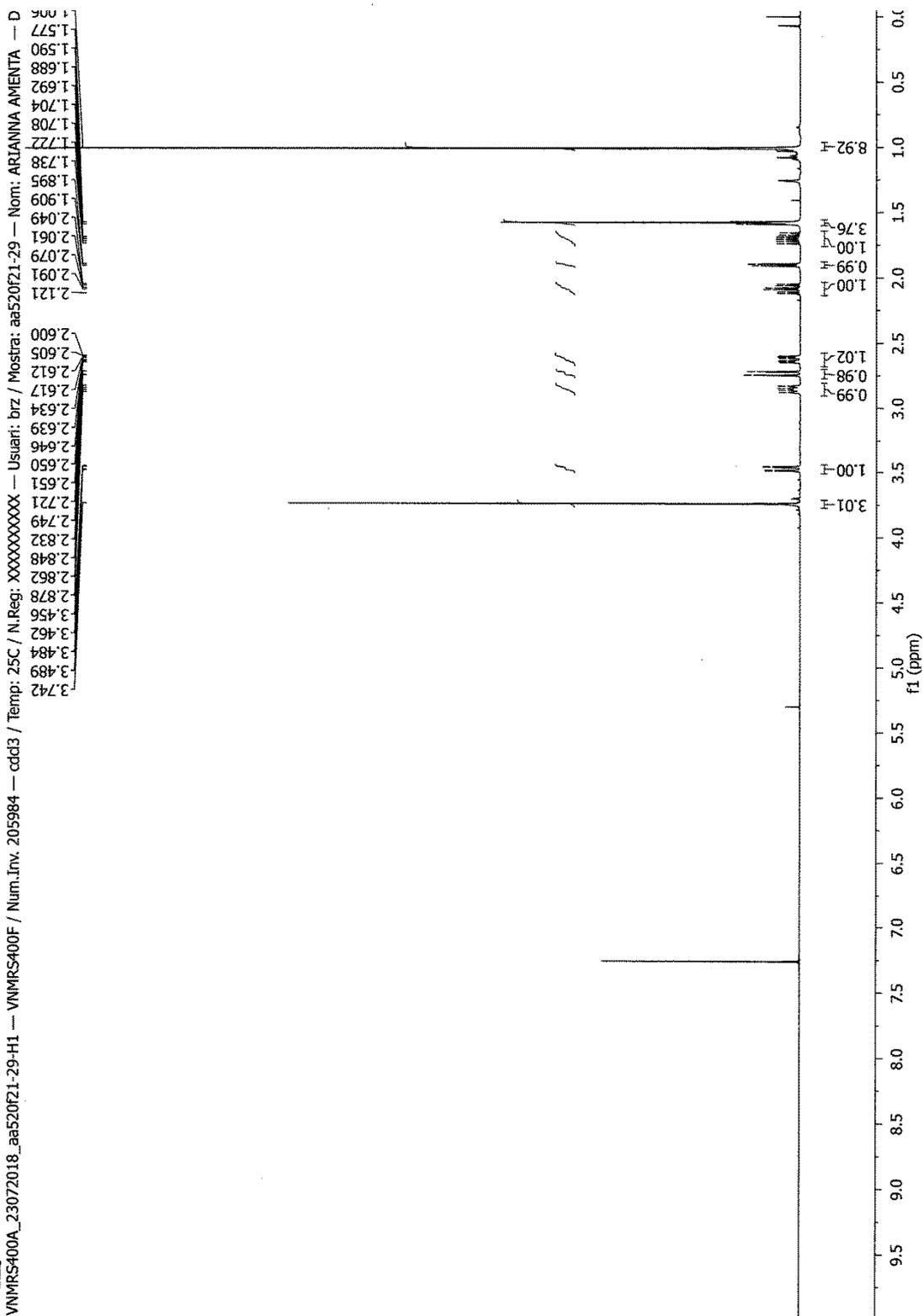
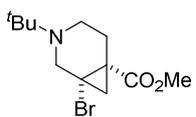
11:1 mixture of *cis-17b* and *trans-17b*

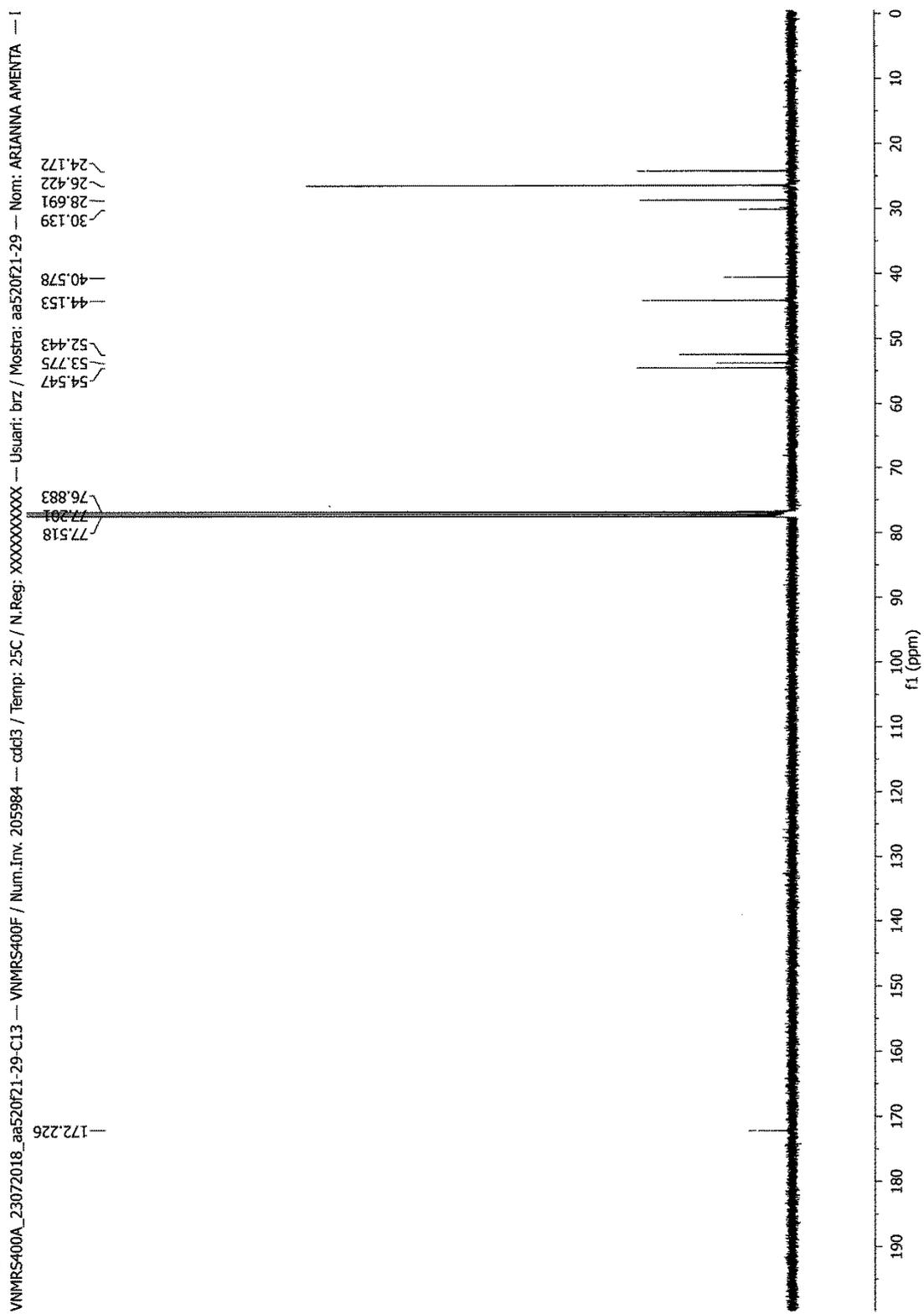
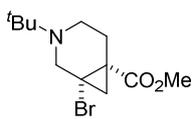




11:1 mixture of *cis*-17b and *trans*-17b

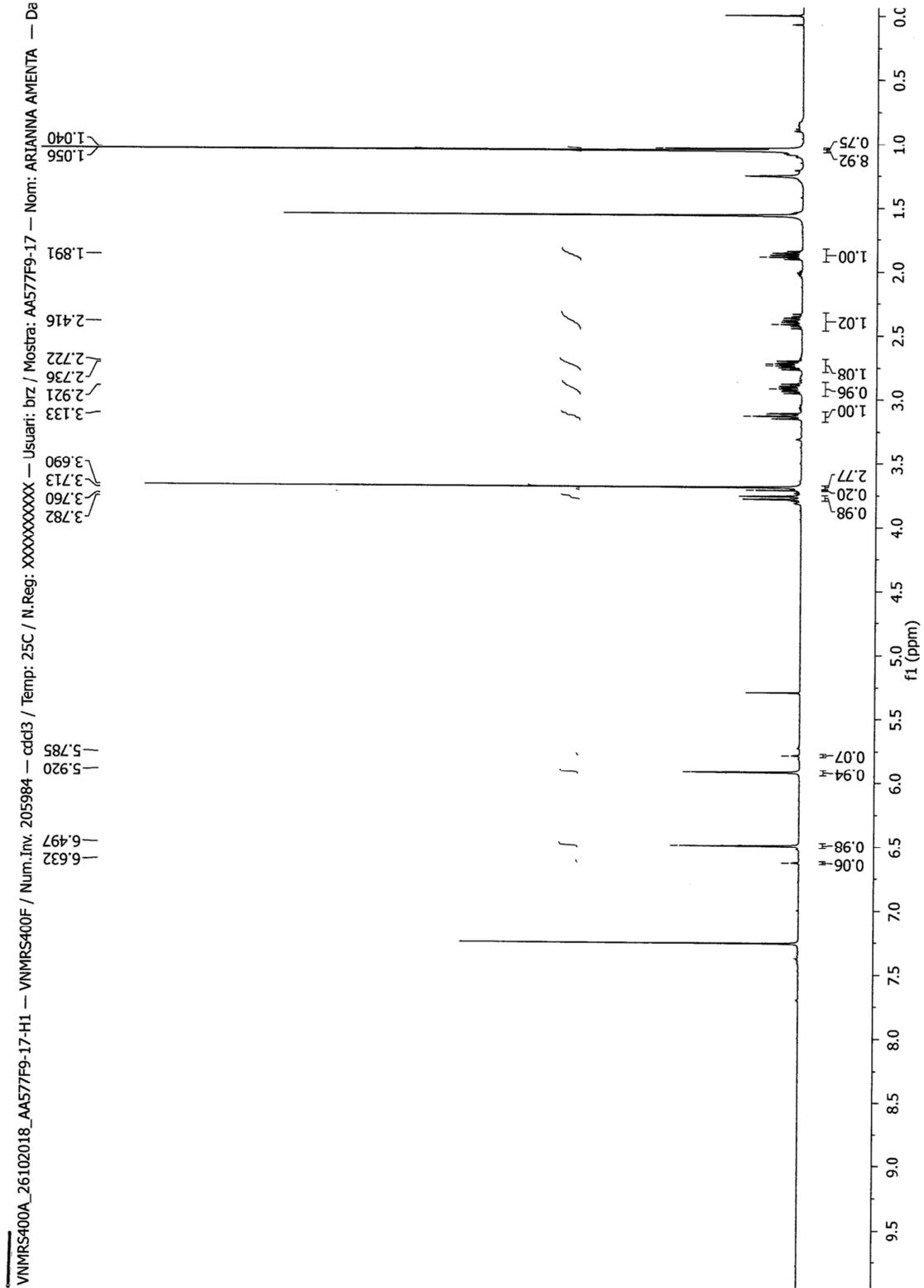


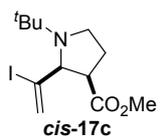




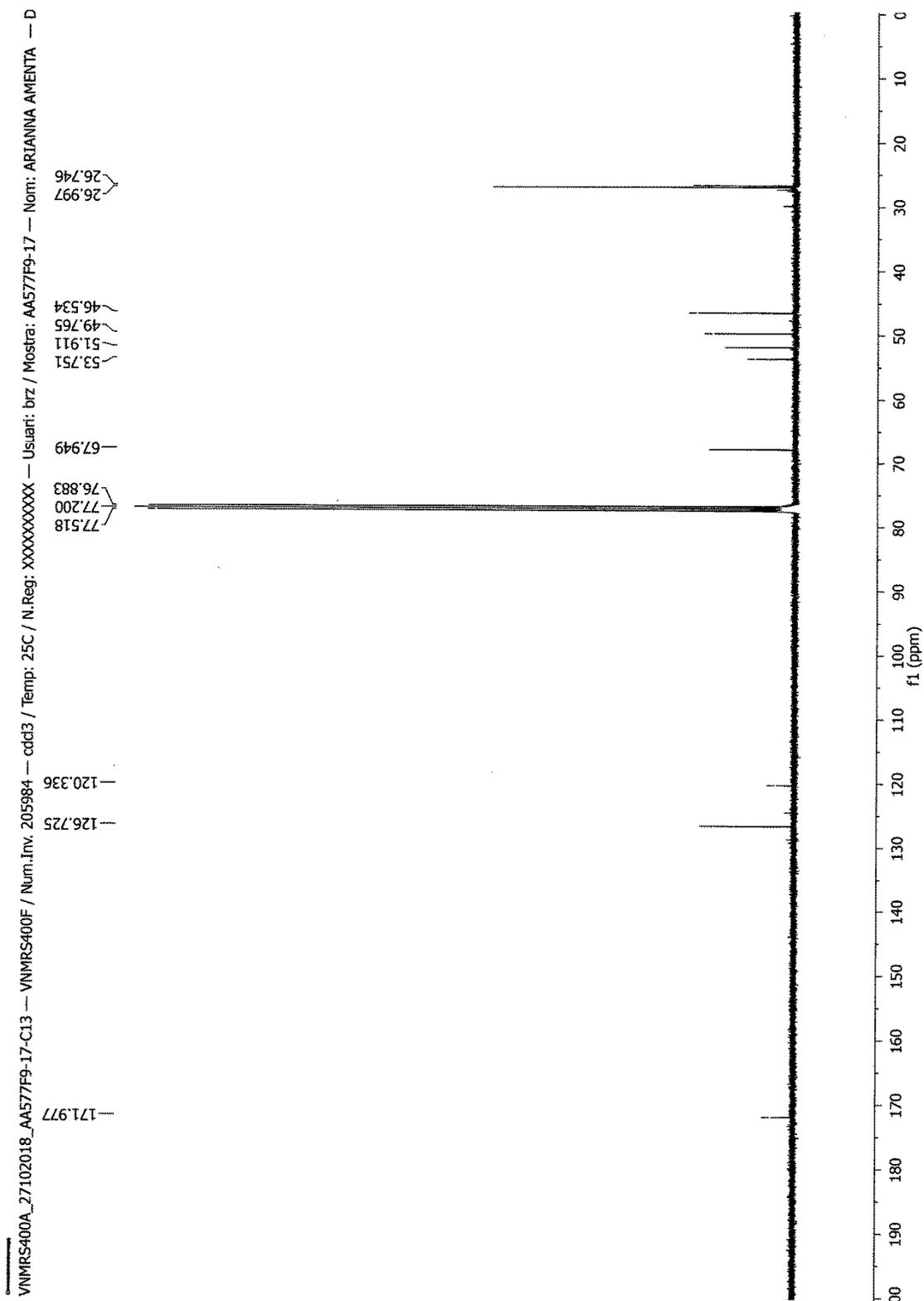


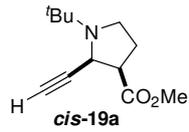
14:1 mixture of *cis*-17c and *trans*-17c



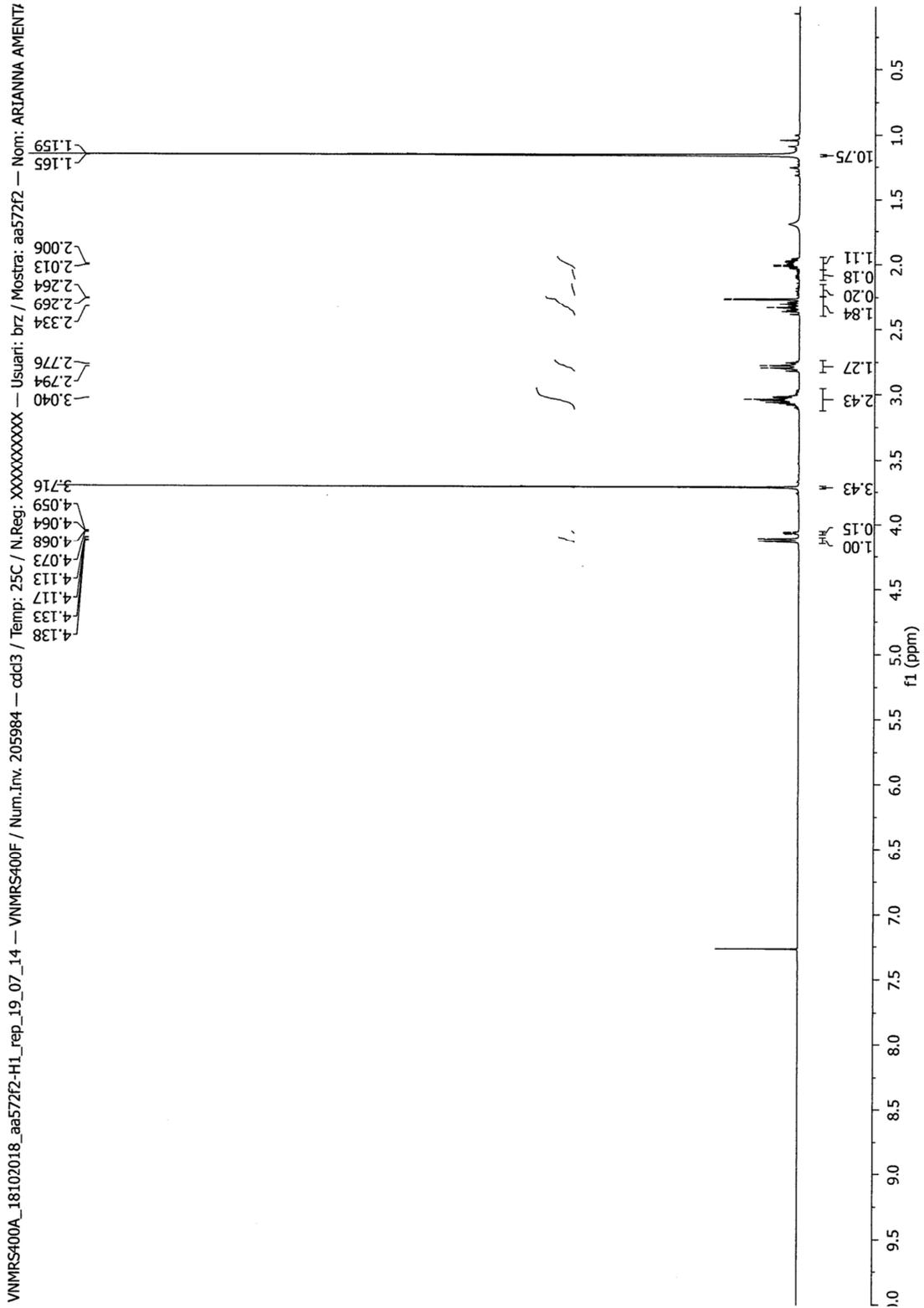


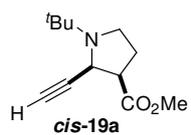
14:1 mixture of *cis*-17c and *trans*-17c



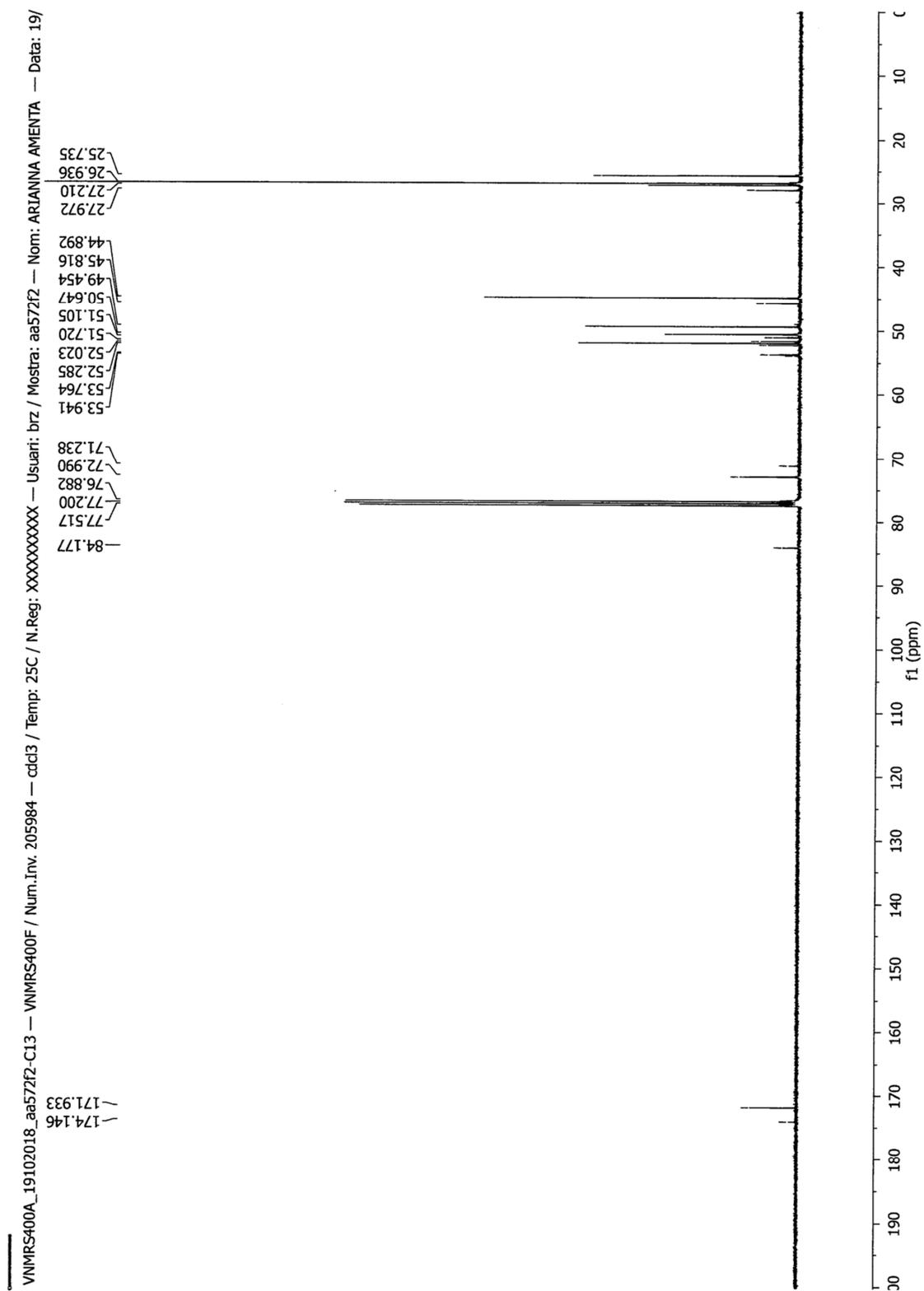


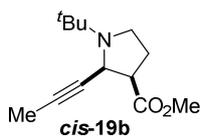
6:1 mixture of *cis-19a* and *trans-19a*



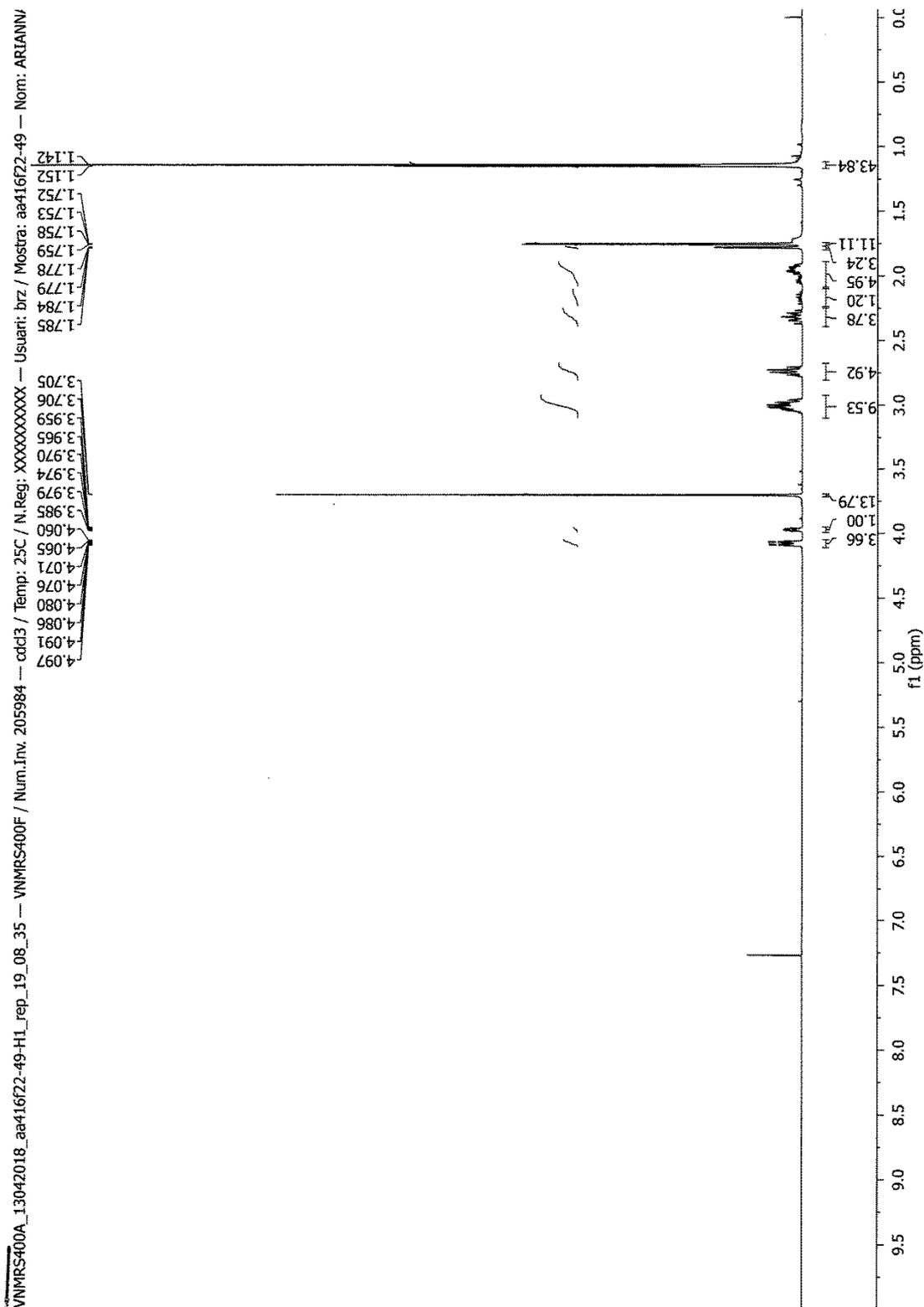


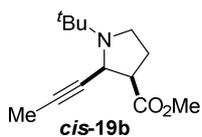
6:1 mixture of *cis-19a* and *trans-19a*



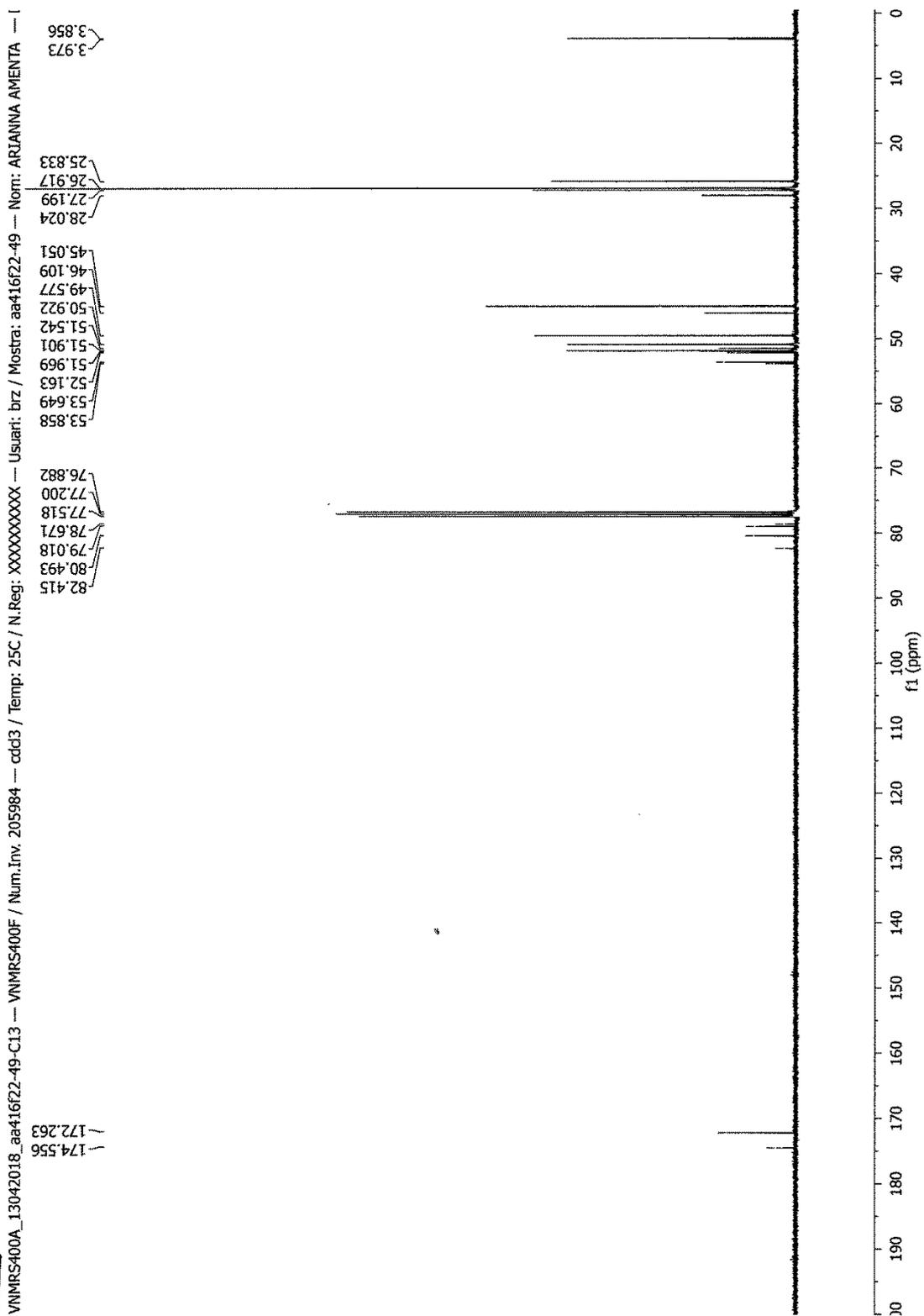


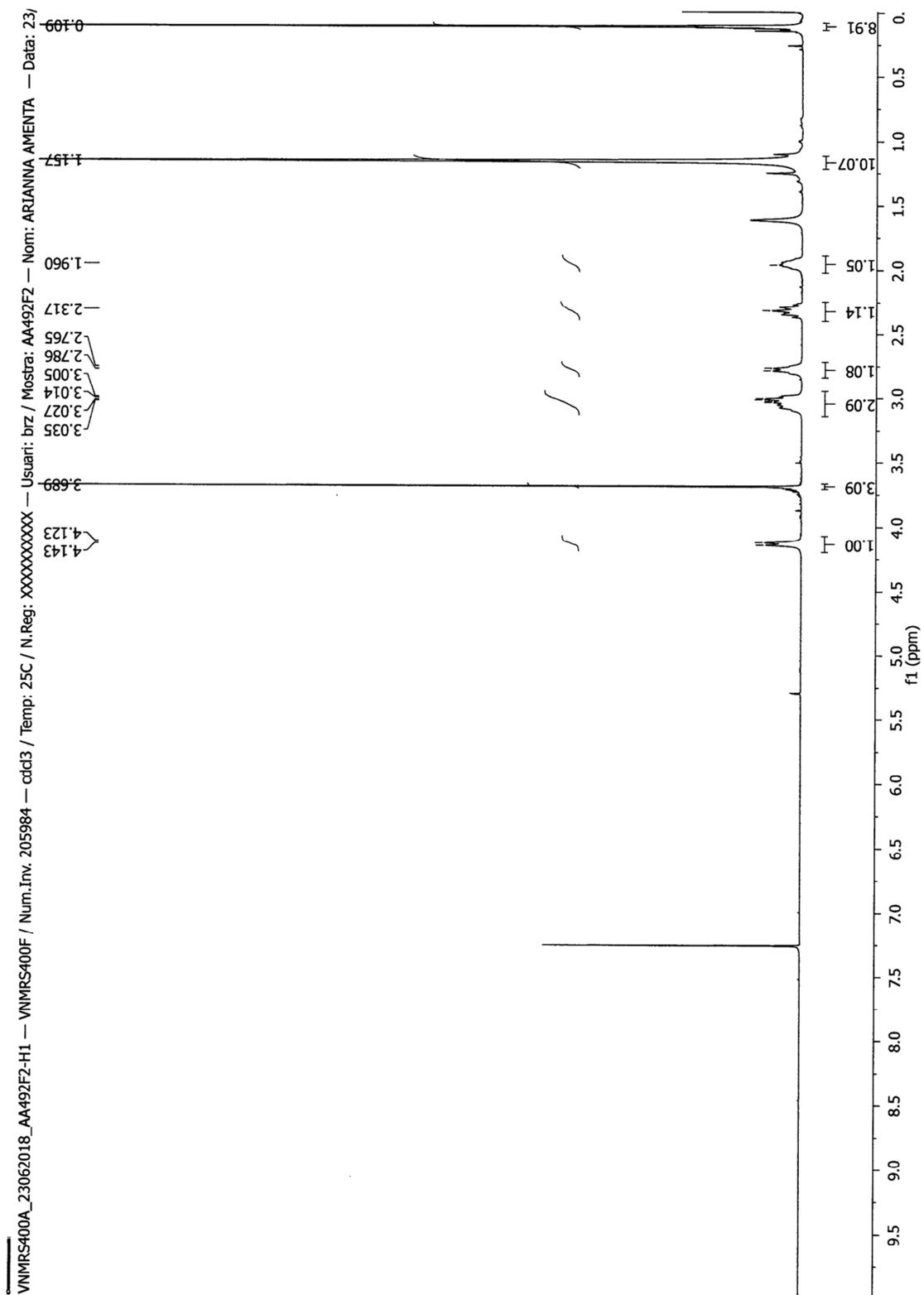
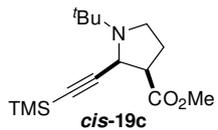
4:1 mixture of *cis-19b* and *trans-19b*

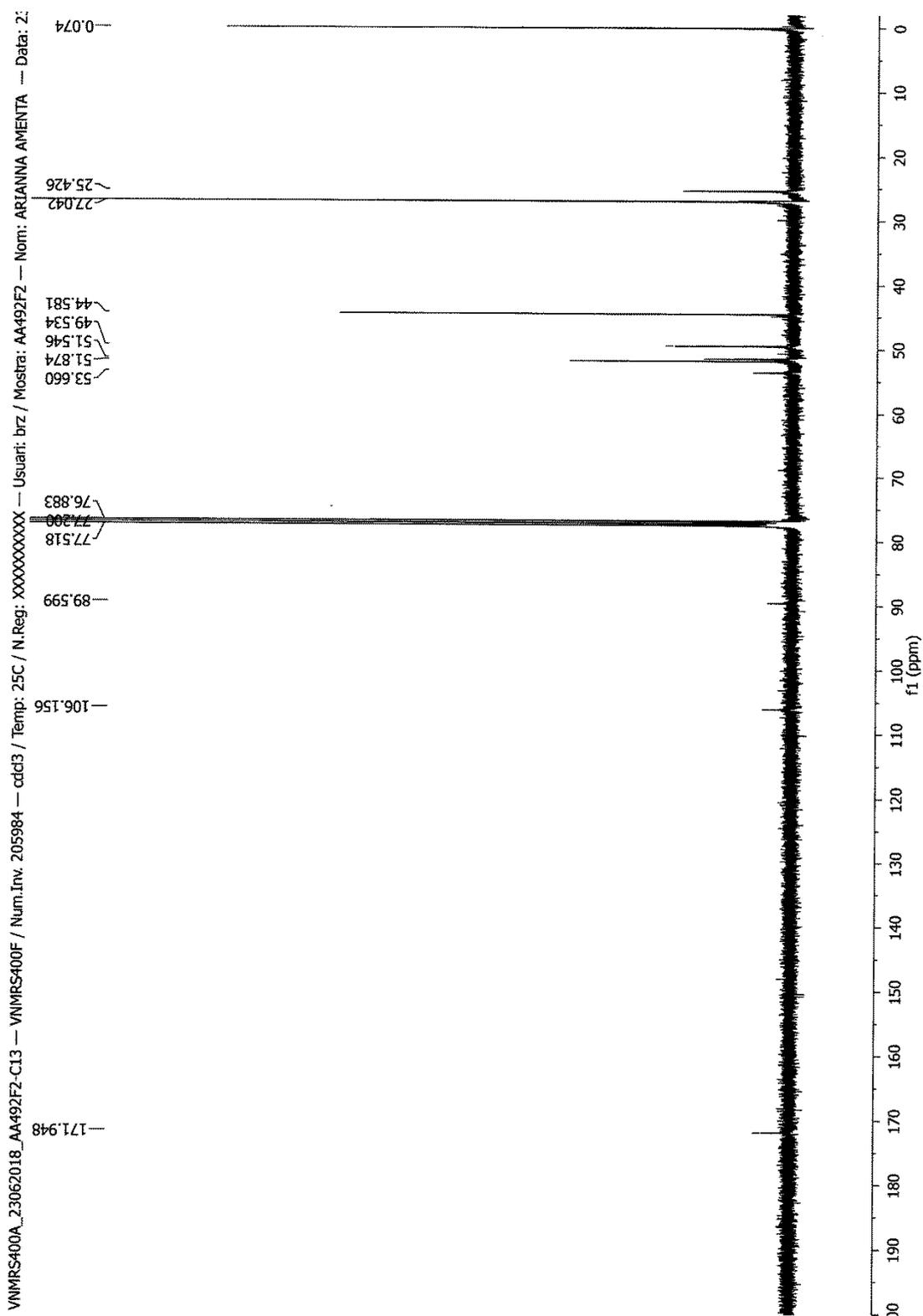
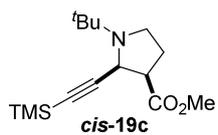


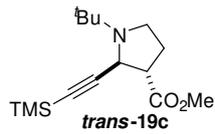


4:1 mixture of *cis*-19b and *trans*-19b

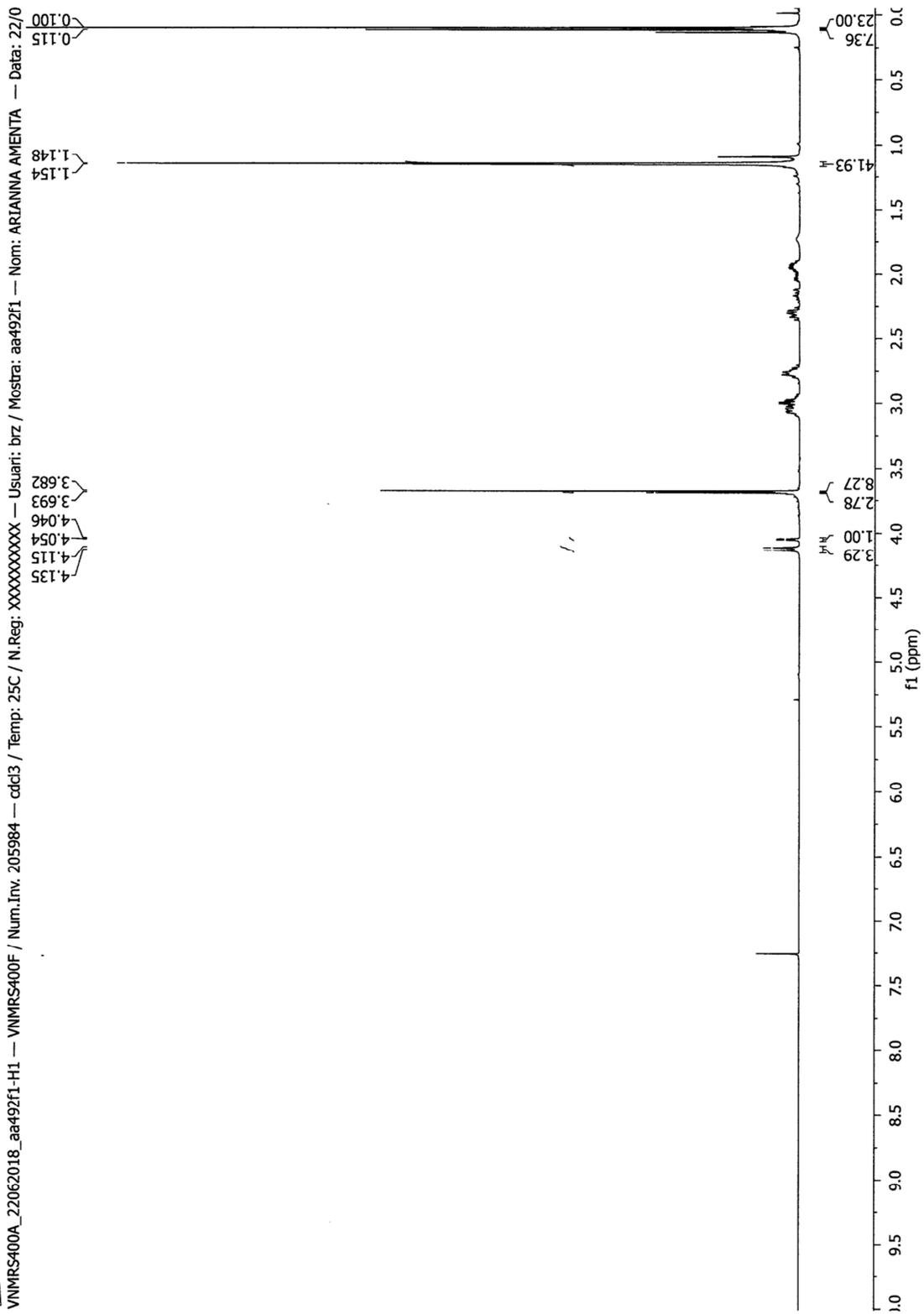


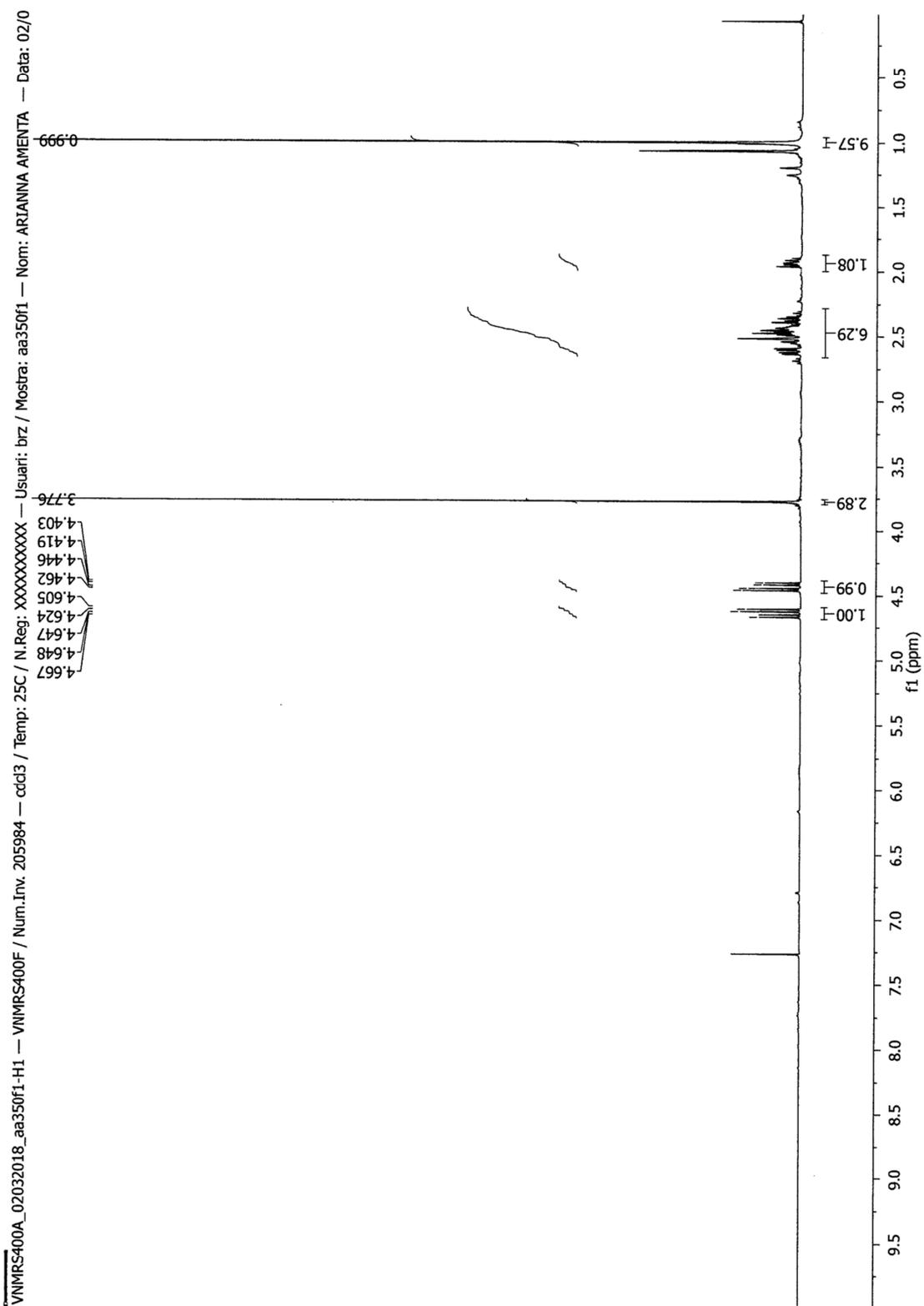
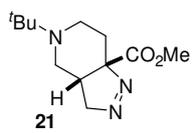




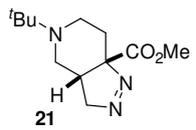
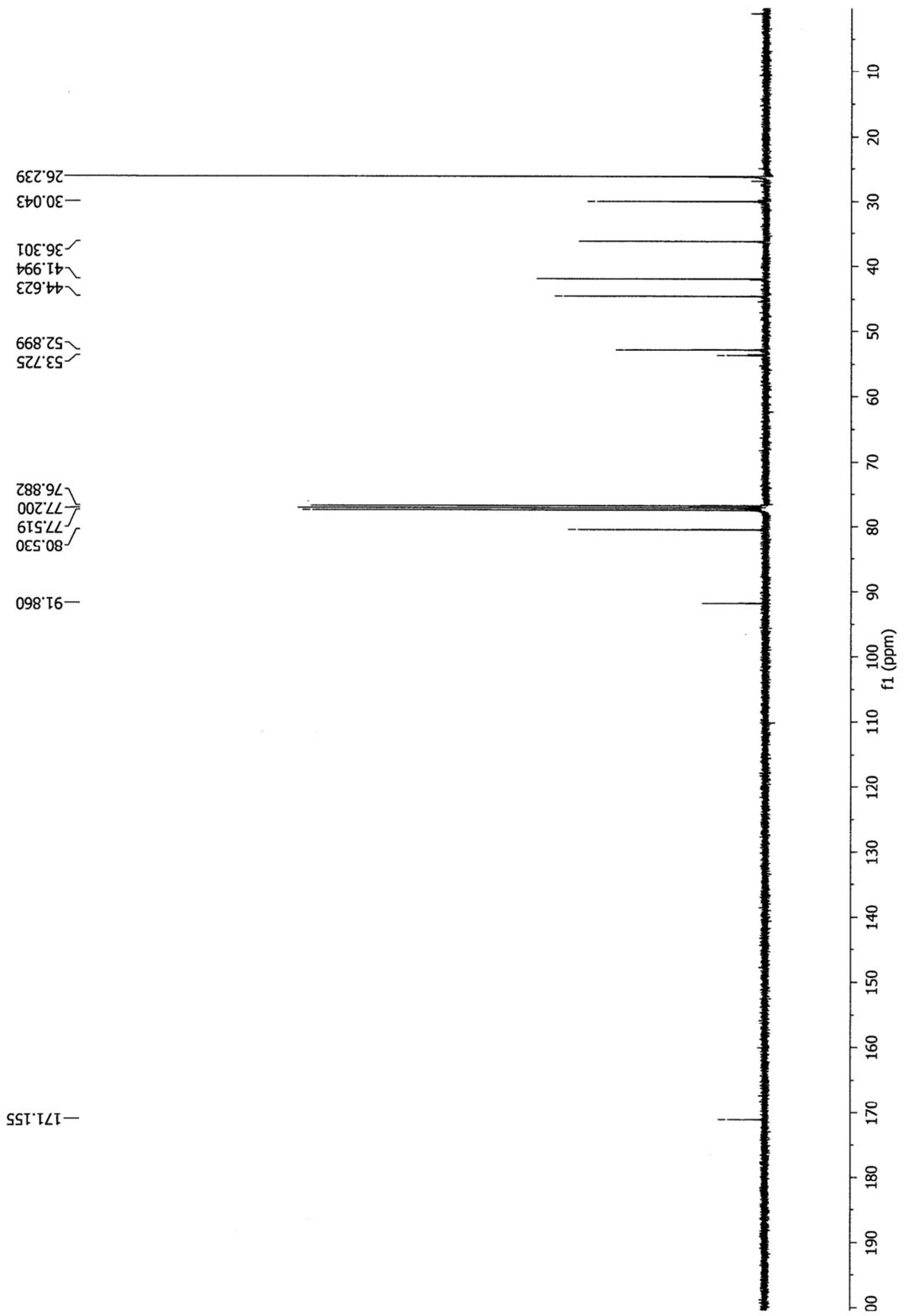


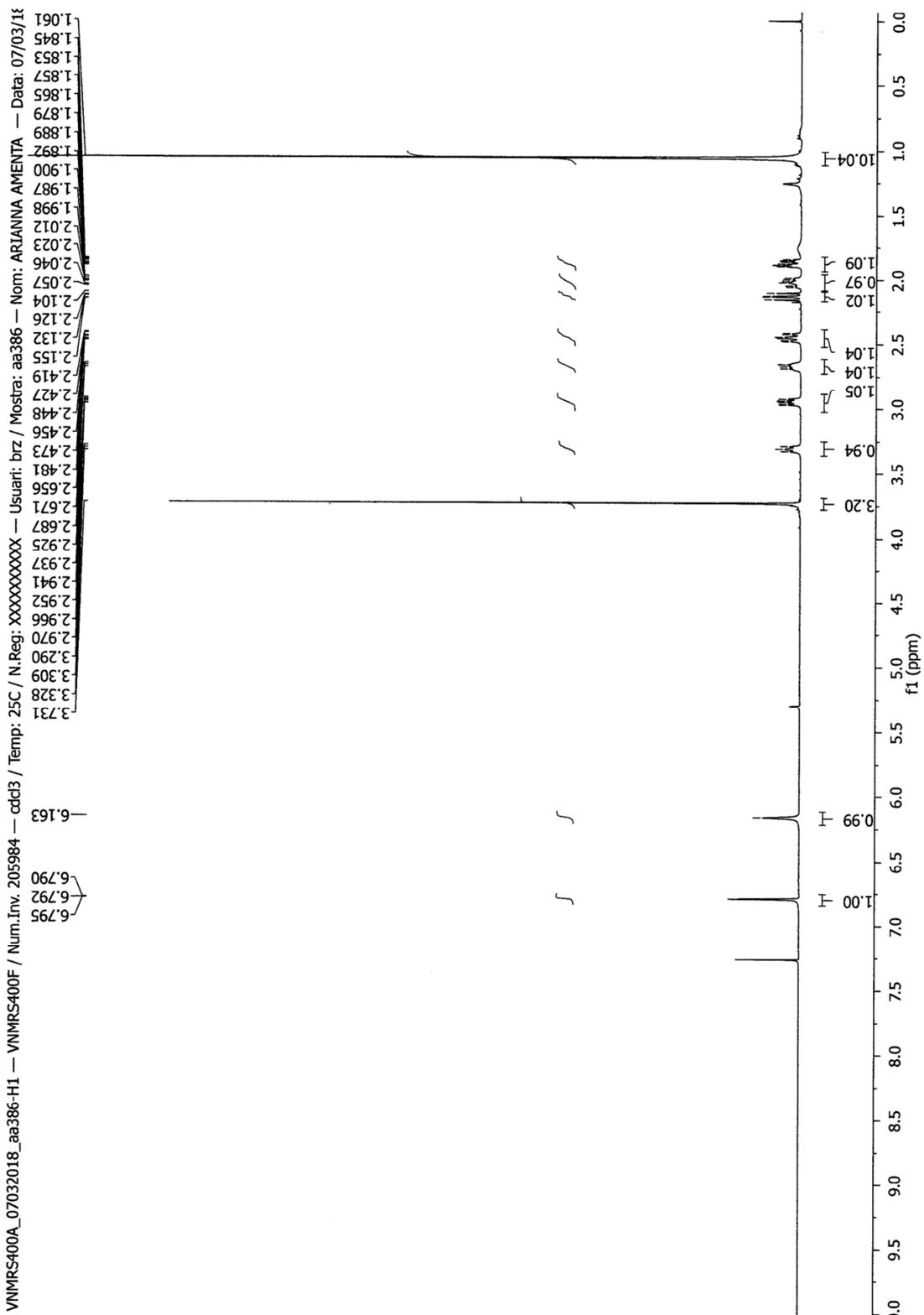
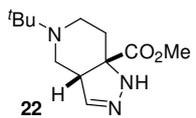
3:1 mixture of *cis*-19c and *trans*-19c

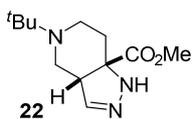




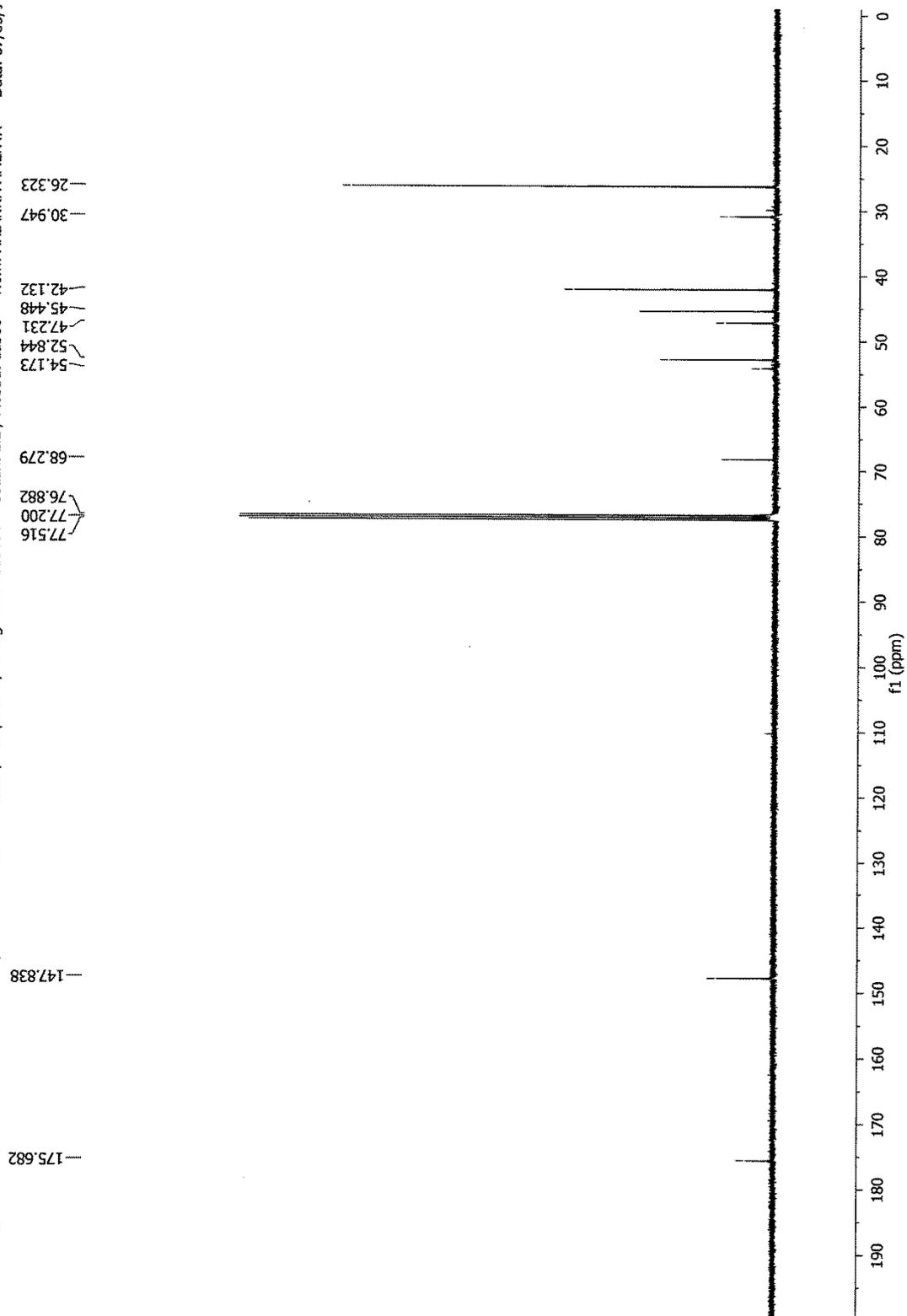
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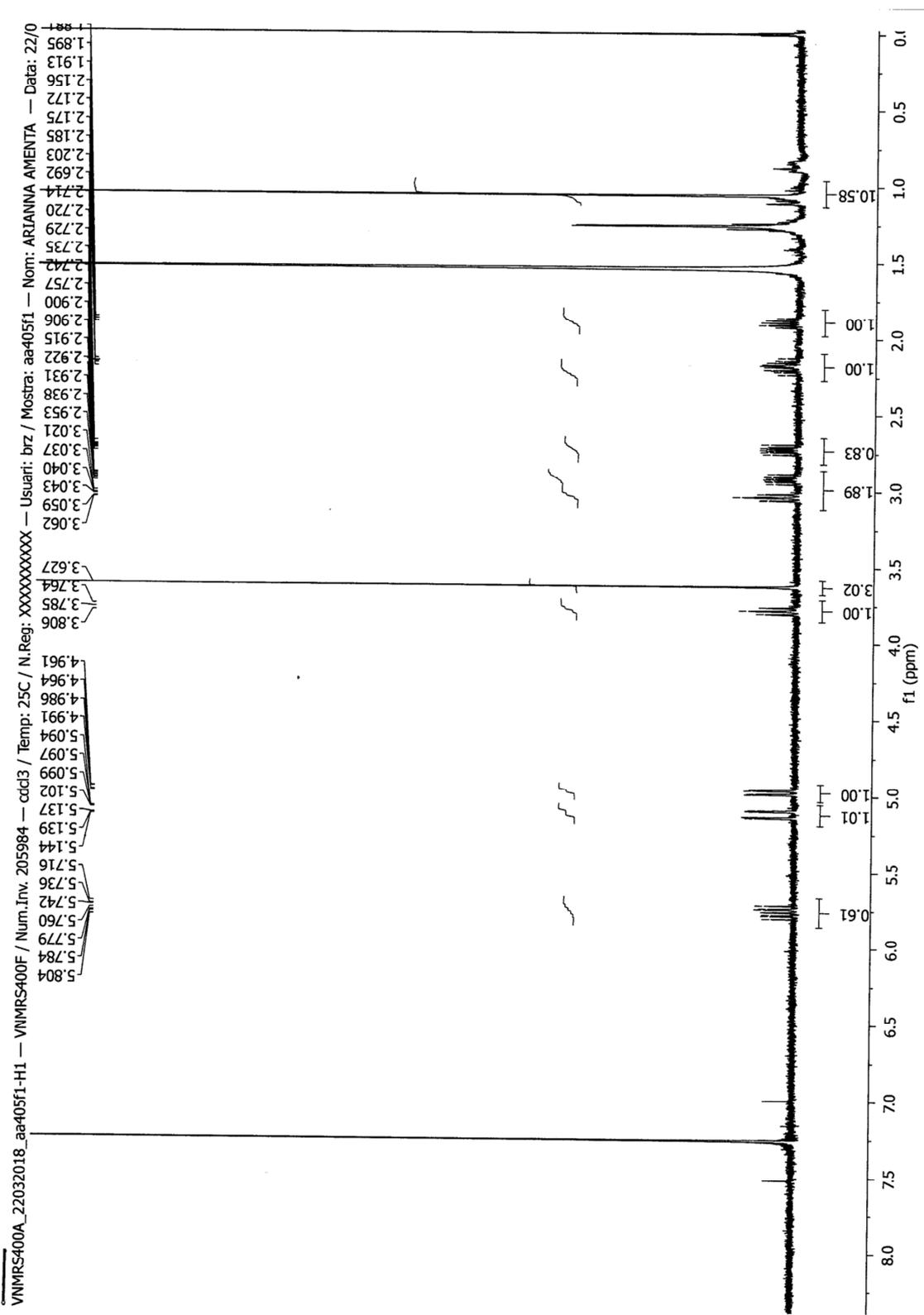
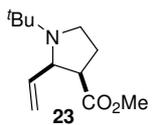


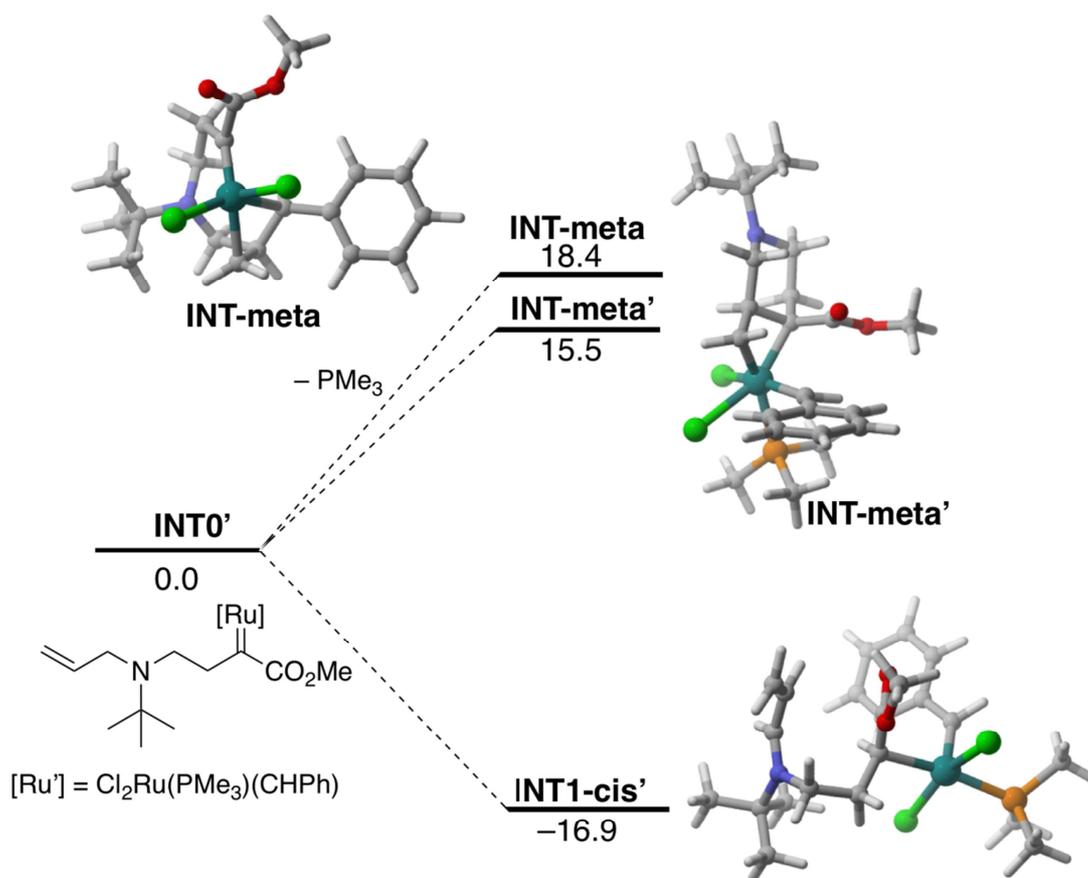




VNMR5400A\_07032018\_aa386-C13 — VNMR5400F / Num.Inv. 205984 — cdd3 / Temp: 25C / N.Reg: XXXXXXXXXXXX — Usuari: brz / Mostra: aa386 — Nom: ARIANNA AMENTA — Data: 07/03/1







**Figure S1.** Comparative computed reaction profile for the metathesis versus C–H activation reaction from the ruthenacarbene formed upon reaction of **20** (see main text) and **Ru-1'**. Relative free energies ( $\Delta G$ , at 298 K) and bond lengths are given in kcal/mol and angstroms, respectively. All data have been computed at the PCM( $\text{CH}_2\text{Cl}_2$ )-B3LYP-D3/def2-TZVPP//PCM( $\text{CH}_2\text{Cl}_2$ )-B3LYP-D3/def2-SVP level.

## Computational details

All the calculations reported in this paper were performed with the Gaussian 09 suite of programs.<sup>1</sup> Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP<sup>2</sup> in conjunction with the D3 dispersion correction suggested by Grimme et al.<sup>3</sup> using the standard double- $\zeta$  quality def2-SVP<sup>4</sup> basis set for all atoms. The Polarizable Continuum Model (PCM)<sup>5</sup> was used to model the effects of the solvent (CH<sub>2</sub>Cl<sub>2</sub>). This level is denoted PCM(CH<sub>2</sub>Cl<sub>2</sub>)-B3LYP-D3/def2-SVP. Geometries were fully optimized in solution without any geometry or symmetry constraints. Reactants, intermediates, and products were characterized by frequency calculations,<sup>6</sup> and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.<sup>7</sup> Frequency calculations were also used to determine the difference between the potential (E) and Gibbs (G) energies,  $G - E$ , which contains the zero-point, thermal, and entropy energies. Potential energies were refined,  $E_{\text{sol}}$ , by means of single point (SP) calculations at the same level with a larger basis set, def2-TZVPP,<sup>4</sup> where all elements were described with a triple- $\zeta$  plus polarization quality basis set. This level is denoted PCM(CH<sub>2</sub>Cl<sub>2</sub>)-B3LYP-D3/def2-TZVPP//PCM(CH<sub>2</sub>Cl<sub>2</sub>)-B3LYP-D3/def2-SVP. The  $\Delta G$  and  $\Delta G^\ddagger$  values given in the text were obtained from the Gibbs energy in solution,  $G_{\text{sol}}$ , which was calculated by adding the thermochemistry corrections,  $G - E$ , to the refined SP energies,  $E_{\text{sol}}$ , i.e.,  $G_{\text{sol}} = E_{\text{sol}} + G - E$ .

**Cartesian coordinates** (in Å) and **total energies** (in a.u.) of all the stationary points discussed in the text. All calculations have been performed at the PCM(dichloroethane)-M06L/def2-TZVP//PCM-(dichloroethane)-B3LYP-D3/def2-SVP.

**1a:** E= -938.625210

C	1.411295000	1.048336000	0.521201000
C	2.669694000	0.343815000	0.068585000
H	1.637911000	2.107840000	0.707688000
H	1.108658000	0.608861000	1.483216000
N	-1.061677000	1.332874000	-0.082997000
C	0.260662000	0.905507000	-0.508271000
H	0.550415000	1.420715000	-1.434505000
H	0.189372000	-0.161452000	-0.768929000
C	-1.668592000	0.426730000	0.882269000
H	-2.615714000	0.865454000	1.229406000
H	-1.058131000	0.293363000	1.799426000
C	2.862148000	-1.108366000	0.045096000
O	3.852413000	-1.690021000	-0.355596000
O	1.773156000	-1.734156000	0.536179000
C	1.811204000	-3.163334000	0.548832000
H	2.016915000	-3.556671000	-0.457923000
H	2.591047000	-3.526402000	1.235845000
H	0.820122000	-3.487856000	0.885363000
N	3.668094000	1.039987000	-0.415124000
C	-1.372177000	2.778664000	0.075095000
C	-2.863827000	2.998030000	-0.257013000
H	-3.528187000	2.440951000	0.420370000
H	-3.126892000	4.063649000	-0.166331000
H	-3.074978000	2.669914000	-1.286332000
C	-0.553295000	3.612927000	-0.924952000
H	0.524142000	3.600120000	-0.703831000
H	-0.703183000	3.257464000	-1.956035000
H	-0.882444000	4.661555000	-0.877881000
C	-1.087842000	3.296522000	1.505450000
H	-1.696798000	2.768719000	2.255281000
H	-0.029939000	3.165738000	1.777049000
H	-1.326262000	4.369356000	1.583592000
C	-1.981999000	-0.944974000	0.308128000
C	-1.746917000	-2.106250000	1.056667000
C	-2.542872000	-1.071986000	-0.972210000
C	-2.076411000	-3.367769000	0.546907000
H	-1.291558000	-2.022704000	2.047873000
C	-2.868031000	-2.329298000	-1.487819000
H	-2.704993000	-0.168320000	-1.564682000
C	-2.637866000	-3.483613000	-0.728684000
H	-3.302370000	-2.411084000	-2.488025000
H	-2.890308000	-4.467685000	-1.132105000
N	4.534009000	1.649294000	-0.823894000
H	-1.885416000	-4.262849000	1.145210000

**Ru-1:** E= -3381.123383

Ru	-0.046259000	0.025778000	-0.097773000
Cl	0.056032000	-0.651980000	-2.474638000
Cl	-0.053751000	0.244258000	2.345190000
C	-0.407264000	1.743070000	-0.667463000
H	-0.527734000	1.794264000	-1.766187000

C	-0.632814000	3.062738000	-0.070536000
C	-1.098432000	4.082407000	-0.935395000
C	-0.405121000	3.397440000	1.284157000
C	-1.347171000	5.373221000	-0.468002000
H	-1.267890000	3.847059000	-1.989633000
C	-0.644611000	4.689168000	1.747335000
H	-0.037926000	2.624437000	1.958659000
C	-1.120076000	5.681022000	0.877611000
H	-1.712326000	6.141261000	-1.154307000
H	-0.459085000	4.929227000	2.797386000
H	-1.307598000	6.691996000	1.248489000
P	-2.341581000	-0.683622000	-0.062204000
P	2.430219000	-0.037176000	-0.176032000
C	-3.388880000	-0.211955000	1.409798000
C	-3.286462000	1.288747000	1.751527000
C	-4.871988000	-0.633014000	1.373479000
H	-2.882626000	-0.761425000	2.224132000
C	-3.954747000	1.584921000	3.099396000
H	-3.778249000	1.885773000	0.966631000
H	-2.236697000	1.592582000	1.777612000
C	-5.545983000	-0.345141000	2.723861000
H	-5.391400000	-0.060179000	0.587294000
H	-4.992299000	-1.692739000	1.118904000
C	-5.419088000	1.130612000	3.118715000
H	-3.880455000	2.662812000	3.322476000
H	-3.394819000	1.059672000	3.894920000
H	-6.607249000	-0.643212000	2.681107000
H	-5.073316000	-0.974173000	3.500578000
H	-5.866843000	1.303106000	4.112064000
H	-5.995935000	1.744350000	2.402029000
C	-2.062802000	-2.539259000	-0.005077000
C	-0.792653000	-2.832727000	0.821394000
C	-3.202728000	-3.461690000	0.460837000
H	-1.826886000	-2.763260000	-1.061109000
C	-0.377393000	-4.303957000	0.724011000
H	-0.953329000	-2.549738000	1.874209000
H	0.057539000	-2.213090000	0.477946000
C	-2.793764000	-4.938823000	0.353387000
H	-3.441521000	-3.233707000	1.513917000
H	-4.119169000	-3.287560000	-0.119283000
C	-1.519239000	-5.231999000	1.152615000
H	0.521102000	-4.478033000	1.338632000
H	-0.094294000	-4.528228000	-0.319845000
H	-3.622152000	-5.579308000	0.699352000
H	-2.624397000	-5.188041000	-0.710120000
H	-1.221981000	-6.287102000	1.032784000
H	-1.724139000	-5.080935000	2.228304000
C	-3.258821000	-0.322239000	-1.647213000
C	-4.358081000	-1.309716000	-2.083456000
C	-3.766765000	1.130947000	-1.710904000
H	-2.435408000	-0.411307000	-2.375036000
C	-4.865390000	-0.956347000	-3.491103000
H	-5.203388000	-1.285797000	-1.376190000
H	-3.972374000	-2.340081000	-2.089019000
C	-4.262521000	1.472223000	-3.122163000
H	-4.600519000	1.267334000	-1.001942000
H	-2.976302000	1.833418000	-1.407054000
C	-5.352295000	0.494627000	-3.577310000
H	-5.670437000	-1.651969000	-3.782113000
H	-4.042624000	-1.105573000	-4.213858000
H	-4.637685000	2.509162000	-3.146451000

H	-3.410425000	1.426506000	-3.824529000
H	-5.677596000	0.729613000	-4.604657000
H	-6.240256000	0.617712000	-2.929583000
C	3.236804000	-0.037908000	1.507073000
C	2.979468000	-1.367359000	2.246951000
C	4.719123000	0.363680000	1.638948000
H	2.632360000	0.726981000	2.024888000
C	3.357144000	-1.239997000	3.728117000
H	3.584023000	-2.167976000	1.787847000
H	1.922965000	-1.655963000	2.153458000
C	5.094024000	0.505148000	3.122542000
H	5.364421000	-0.400500000	1.180958000
H	4.926904000	1.305098000	1.112143000
C	4.811927000	-0.785899000	3.901138000
H	3.190449000	-2.201126000	4.243523000
H	2.678820000	-0.506259000	4.198984000
H	6.157058000	0.785181000	3.215293000
H	4.509803000	1.333415000	3.563825000
H	5.048598000	-0.649288000	4.969898000
H	5.484044000	-1.581920000	3.529767000
C	3.113891000	-1.472303000	-1.179031000
C	4.624975000	-1.744529000	-1.035918000
C	2.332401000	-2.788011000	-0.985166000
H	2.908723000	-1.135798000	-2.210285000
C	5.090041000	-2.800571000	-2.049087000
H	4.828134000	-2.122717000	-0.020946000
H	5.216170000	-0.827438000	-1.150967000
C	2.801353000	-3.862487000	-1.974944000
H	2.461258000	-3.156089000	0.046299000
H	1.263662000	-2.608771000	-1.141700000
C	4.310266000	-4.109986000	-1.886701000
H	6.172418000	-2.977716000	-1.931198000
H	4.943685000	-2.409427000	-3.072755000
H	2.243220000	-4.797438000	-1.797281000
H	2.543958000	-3.532191000	-2.997995000
H	4.627305000	-4.846056000	-2.644624000
H	4.548359000	-4.549821000	-0.900372000
C	2.957506000	1.518132000	-1.089790000
C	2.850411000	2.757578000	-0.179620000
C	4.282591000	1.539977000	-1.872179000
H	2.148245000	1.582014000	-1.836979000
C	2.935752000	4.046526000	-1.004671000
H	3.673228000	2.750648000	0.553441000
H	1.919715000	2.736396000	0.398571000
C	4.385497000	2.836627000	-2.693799000
H	5.139430000	1.476896000	-1.180281000
H	4.351999000	0.677212000	-2.551171000
C	4.232196000	4.089636000	-1.822515000
H	2.866436000	4.923526000	-0.339593000
H	2.063660000	4.096541000	-1.681582000
H	5.346489000	2.858727000	-3.234739000
H	3.591541000	2.831510000	-3.462837000
H	4.265395000	4.996573000	-2.449429000
H	5.091537000	4.154800000	-1.129575000

**INTO:** E= -3162.641247

C	2.780168000	0.157021000	-1.030310000
C	1.669852000	1.154284000	-0.980490000
H	2.424709000	-0.882841000	-0.962851000
H	3.284869000	0.272802000	-2.004752000

C	3.805243000	0.412985000	0.112824000
H	4.086258000	1.478016000	0.120313000
C	2.057423000	2.560359000	-1.268357000
O	2.139874000	2.995445000	-2.396749000
O	2.280417000	3.271764000	-0.160701000
C	2.539738000	4.674857000	-0.328483000
H	3.424429000	4.832365000	-0.962032000
H	1.669041000	5.166231000	-0.786976000
H	2.708463000	5.071339000	0.678771000
Ru	-0.110111000	0.628588000	-0.644981000
Cl	-0.681767000	0.358481000	-2.978419000
Cl	0.406077000	0.174097000	1.701570000
C	-0.918817000	2.292259000	-0.626521000
H	-1.550084000	2.469312000	-1.514890000
C	-0.883189000	3.452736000	0.249540000
C	-1.609180000	4.597148000	-0.166007000
C	-0.160184000	3.522694000	1.464536000
C	-1.607505000	5.765915000	0.593560000
H	-2.174274000	4.556654000	-1.100923000
C	-0.168490000	4.688568000	2.224489000
H	0.399343000	2.650340000	1.796089000
C	-0.886013000	5.813256000	1.792280000
H	-2.168840000	6.639633000	0.254272000
H	0.392858000	4.727622000	3.161154000
H	-0.882361000	6.727232000	2.391758000
P	-2.213736000	-0.768536000	-0.060324000
H	3.267512000	0.247436000	1.057327000
N	4.973997000	-0.452260000	0.044704000
C	6.230425000	0.161439000	-0.470829000
C	5.091781000	-1.291803000	1.234721000
H	6.093919000	-1.738981000	1.260515000
H	4.995364000	-0.707669000	2.173375000
C	6.855094000	1.132835000	0.554711000
H	7.778038000	1.584931000	0.158399000
H	6.161314000	1.952155000	0.802253000
H	7.112178000	0.609974000	1.489203000
C	5.937734000	0.917670000	-1.781337000
H	5.242882000	1.759089000	-1.644649000
H	6.873497000	1.334949000	-2.182244000
H	5.516174000	0.238361000	-2.538017000
C	7.243188000	-0.948904000	-0.814192000
H	8.118216000	-0.514251000	-1.321054000
H	7.617801000	-1.476486000	0.075042000
H	6.783521000	-1.689418000	-1.487008000
C	4.084389000	-2.426232000	1.247647000
C	3.145147000	-2.565137000	2.276652000
C	4.105517000	-3.382901000	0.218463000
C	2.265668000	-3.655863000	2.300569000
C	3.238721000	-4.475861000	0.242294000
C	2.321233000	-4.620738000	1.292112000
H	3.098749000	-1.811669000	3.067608000
H	4.816453000	-3.260126000	-0.602750000
H	1.535242000	-3.748290000	3.108611000
H	3.273839000	-5.219402000	-0.558304000
H	1.644772000	-5.478171000	1.311626000
C	-2.967753000	-0.400012000	1.612593000
C	-2.976968000	1.105857000	1.941881000
C	-4.359609000	-1.004676000	1.886470000
H	-2.236705000	-0.869115000	2.294351000
C	-3.413018000	1.352140000	3.392019000
H	-3.659369000	1.635895000	1.255169000

H	-1.978109000	1.524601000	1.788541000
C	-4.775109000	-0.774333000	3.346907000
H	-5.100839000	-0.519180000	1.230049000
H	-4.388663000	-2.077165000	1.653547000
C	-4.772613000	0.716769000	3.701349000
H	-3.434883000	2.436509000	3.593207000
H	-2.647768000	0.923692000	4.065289000
H	-5.771954000	-1.212429000	3.523454000
H	-4.072365000	-1.311293000	4.010408000
H	-5.035626000	0.861772000	4.762745000
H	-5.554912000	1.227987000	3.110010000
C	-3.520160000	-0.741932000	-1.387586000
C	-4.575344000	-1.865048000	-1.432848000
C	-4.197135000	0.639591000	-1.481600000
H	-2.892550000	-0.844707000	-2.288616000
C	-5.405945000	-1.755307000	-2.721691000
H	-5.249857000	-1.796249000	-0.566135000
H	-4.099368000	-2.854492000	-1.384501000
C	-5.030569000	0.748841000	-2.764864000
H	-4.856658000	0.791041000	-0.609621000
H	-3.443805000	1.439733000	-1.450087000
C	-6.066474000	-0.377980000	-2.856036000
H	-6.168742000	-2.551820000	-2.741996000
H	-4.745253000	-1.928894000	-3.590785000
H	-5.525852000	1.733373000	-2.809899000
H	-4.349246000	0.696046000	-3.633312000
H	-6.625507000	-0.311027000	-3.804439000
H	-6.807240000	-0.253123000	-2.044298000
C	-1.518359000	-2.504982000	0.042595000
C	-2.291363000	-3.567091000	0.846535000
C	-1.149797000	-3.033664000	-1.360099000
H	-0.575990000	-2.318402000	0.589108000
C	-1.480516000	-4.868850000	0.935856000
H	-3.263761000	-3.775084000	0.370244000
H	-2.502533000	-3.203867000	1.863236000
C	-0.342893000	-4.333376000	-1.263595000
H	-2.071905000	-3.226043000	-1.934727000
H	-0.590534000	-2.275825000	-1.929340000
C	-1.086131000	-5.397990000	-0.448276000
H	-2.057266000	-5.628853000	1.489345000
H	-0.567908000	-4.674194000	1.524963000
H	-0.120182000	-4.710003000	-2.276125000
H	0.627248000	-4.117570000	-0.786259000
H	-0.467532000	-6.306105000	-0.347825000
H	-2.000045000	-5.699104000	-0.993344000

**INTO' : E= -3939.786802**

C	1.480150000	-1.536630000	-0.227929000
C	0.349006000	-0.952708000	0.564386000
H	1.445785000	-1.179657000	-1.261214000
H	2.397251000	-1.131969000	0.232679000
C	1.635857000	-3.067371000	-0.224158000
H	1.667672000	-3.434871000	0.815688000
C	0.214419000	-1.490260000	1.972442000
O	-0.726378000	-2.106684000	2.425214000
O	1.315834000	-1.210797000	2.682752000
C	1.272342000	-1.506478000	4.082236000
H	0.415528000	-0.996797000	4.546481000
H	1.184241000	-2.590643000	4.246891000
H	2.214406000	-1.133769000	4.498528000

Ru	-0.668462000	0.474793000	0.049615000
Cl	-0.938930000	1.268073000	2.343698000
Cl	-0.822025000	0.164422000	-2.380048000
P	1.205230000	2.098250000	-0.314469000
P	-2.896104000	-0.583348000	0.014051000
H	0.745627000	-3.529795000	-0.669044000
N	2.852063000	-3.463195000	-0.934938000
C	3.879352000	-3.973271000	-0.034546000
H	3.543612000	-4.865891000	0.537257000
H	4.745658000	-4.295619000	-0.626732000
C	2.663702000	-4.150736000	-2.239321000
C	4.016796000	-4.271056000	-2.966527000
H	4.525643000	-3.294775000	-2.995208000
H	4.689941000	-5.002278000	-2.495370000
H	3.852940000	-4.606796000	-4.001669000
C	1.749251000	-3.287024000	-3.132314000
H	0.751690000	-3.128875000	-2.700020000
H	2.199436000	-2.298215000	-3.304642000
H	1.608288000	-3.777439000	-4.107385000
C	2.052462000	-5.559266000	-2.065997000
H	2.700269000	-6.192205000	-1.438539000
H	1.059550000	-5.511835000	-1.592619000
H	1.932671000	-6.060633000	-3.039565000
C	4.355924000	-2.915435000	0.947486000
C	4.925366000	-1.720419000	0.473664000
C	4.222314000	-3.089322000	2.329875000
C	5.350533000	-0.729923000	1.360253000
C	4.653899000	-2.101184000	3.224307000
C	5.215151000	-0.916930000	2.742621000
H	5.014142000	-1.568050000	-0.604994000
H	3.765473000	-4.006023000	2.713789000
H	5.786185000	0.195885000	0.976696000
H	4.540041000	-2.255997000	4.300208000
H	5.541634000	-0.138557000	3.436702000
C	2.740289000	1.482653000	-1.217757000
C	2.452078000	1.010163000	-2.656161000
C	3.991685000	2.388888000	-1.189518000
H	2.996919000	0.589020000	-0.626506000
C	3.668458000	0.307563000	-3.270634000
H	2.183594000	1.878813000	-3.282300000
H	1.579132000	0.349186000	-2.677642000
C	5.199572000	1.688164000	-1.832721000
H	3.795207000	3.332171000	-1.721945000
H	4.253696000	2.657377000	-0.159154000
C	4.905748000	1.208500000	-3.256490000
H	3.429957000	-0.015451000	-4.297831000
H	3.878440000	-0.612700000	-2.695427000
H	6.066951000	2.369384000	-1.820823000
H	5.478544000	0.816779000	-1.214348000
H	5.780014000	0.679797000	-3.672370000
H	4.725128000	2.083884000	-3.907463000
C	1.809655000	2.838451000	1.290767000
C	2.644059000	1.799088000	2.066138000
C	2.482328000	4.224907000	1.303895000
H	0.860038000	2.939076000	1.839765000
C	2.905004000	2.264110000	3.502863000
H	3.612844000	1.635057000	1.565524000
H	2.129253000	0.830509000	2.082572000
C	2.737093000	4.673633000	2.752675000
H	3.439725000	4.210131000	0.761605000
H	1.850566000	4.969581000	0.799685000

C	3.566574000	3.646352000	3.532963000
H	3.532080000	1.521138000	4.024721000
H	1.941694000	2.302207000	4.042570000
H	3.238523000	5.656374000	2.754684000
H	1.765623000	4.814567000	3.261069000
H	3.714867000	3.984036000	4.572735000
H	4.572629000	3.574748000	3.078414000
C	0.394105000	3.451801000	-1.324131000
C	-0.665845000	4.201676000	-0.484691000
C	1.296852000	4.449773000	-2.074648000
H	-0.143840000	2.858675000	-2.084814000
C	-1.500116000	5.139790000	-1.365613000
H	-0.164483000	4.797071000	0.296513000
H	-1.325765000	3.503472000	0.051733000
C	0.455927000	5.399428000	-2.941678000
H	1.892613000	5.038423000	-1.358510000
H	2.011373000	3.915465000	-2.715554000
C	-0.609953000	6.133060000	-2.120485000
H	-2.241952000	5.672269000	-0.747205000
H	-2.071233000	4.536417000	-2.093550000
H	1.116936000	6.120871000	-3.450807000
H	-0.040129000	4.811860000	-3.735892000
H	-1.220116000	6.780059000	-2.772820000
H	-0.111384000	6.798904000	-1.391985000
C	-3.680839000	-0.833845000	1.691843000
C	-4.193351000	0.480389000	2.320824000
C	-4.754143000	-1.930727000	1.838628000
H	-2.797248000	-1.147727000	2.271112000
C	-4.500747000	0.268669000	3.808373000
H	-5.116613000	0.803884000	1.814762000
H	-3.452367000	1.279280000	2.200420000
C	-5.087589000	-2.147461000	3.324078000
H	-5.669919000	-1.639588000	1.297589000
H	-4.418793000	-2.881452000	1.403297000
C	-5.529904000	-0.849835000	4.010598000
H	-4.863837000	1.209867000	4.255433000
H	-3.561363000	0.012624000	4.330716000
H	-5.868631000	-2.920545000	3.423009000
H	-4.188643000	-2.540201000	3.833619000
H	-5.706524000	-1.026139000	5.085345000
H	-6.497358000	-0.527723000	3.581877000
C	-2.820295000	-2.221017000	-0.924530000
C	-2.113414000	-3.346135000	-0.150925000
C	-4.114214000	-2.741516000	-1.584997000
H	-2.143830000	-1.922844000	-1.742396000
C	-1.842894000	-4.559707000	-1.048856000
H	-2.722564000	-3.666445000	0.709472000
H	-1.175732000	-2.980952000	0.276342000
C	-3.831664000	-3.970095000	-2.464996000
H	-4.857678000	-3.013710000	-0.817643000
H	-4.569206000	-1.964746000	-2.214143000
C	-3.130637000	-5.086203000	-1.686412000
H	-1.340236000	-5.349246000	-0.465240000
H	-1.141951000	-4.267618000	-1.851373000
H	-4.776920000	-4.333842000	-2.902124000
H	-3.190593000	-3.663310000	-3.311865000
H	-2.916760000	-5.943617000	-2.346440000
H	-3.804513000	-5.457272000	-0.892005000
C	-4.039412000	0.466453000	-1.060696000
C	-5.553641000	0.211433000	-0.897730000
C	-3.744393000	1.978739000	-0.974150000

H	-3.736855000	0.149431000	-2.073785000
C	-6.362604000	0.990448000	-1.943908000
H	-5.875963000	0.539092000	0.101726000
H	-5.791946000	-0.857080000	-0.960972000
C	-4.585443000	2.778000000	-1.980848000
H	-3.936305000	2.343717000	0.048809000
H	-2.685973000	2.168728000	-1.198917000
C	-6.083848000	2.493539000	-1.847506000
H	-7.438143000	0.785839000	-1.809534000
H	-6.095987000	0.630386000	-2.954802000
H	-4.382940000	3.854406000	-1.856064000
H	-4.255286000	2.512845000	-3.002121000
H	-6.649831000	3.044884000	-2.617123000
H	-6.439066000	2.863400000	-0.867817000

**TS1-cis:** E= -3162.627583

C	2.227052000	-1.801116000	-1.396788000
C	1.900978000	-0.371161000	-1.062091000
H	1.451759000	-2.467326000	-0.991869000
H	2.218652000	-1.908083000	-2.492202000
N	3.784963000	-2.011684000	0.518401000
C	3.625832000	-2.293875000	-0.893828000
H	3.734624000	-3.366876000	-1.089068000
H	4.392377000	-1.767526000	-1.477173000
C	3.668066000	-0.659948000	0.813230000
H	3.303401000	-0.450567000	1.821298000
H	2.647185000	-0.260121000	0.147191000
C	2.640482000	0.691524000	-1.850407000
O	2.458379000	1.885490000	-1.759008000
O	3.582195000	0.172720000	-2.658821000
C	4.406416000	1.105621000	-3.367778000
H	4.992515000	1.705914000	-2.655793000
H	5.072547000	0.505424000	-3.998992000
H	3.791262000	1.775906000	-3.985610000
Ru	-0.007306000	-0.081229000	-0.518739000
Cl	-0.449392000	-0.221122000	-2.935516000
Cl	0.468826000	-0.612160000	1.814734000
C	3.534316000	-3.101212000	1.516200000
C	3.530297000	-2.531524000	2.942144000
H	2.664771000	-1.877028000	3.116457000
H	3.465150000	-3.366527000	3.654863000
H	4.457099000	-1.977539000	3.158408000
C	4.703416000	-4.099577000	1.392970000
H	4.763192000	-4.538479000	0.385653000
H	5.660712000	-3.600369000	1.608496000
H	4.570870000	-4.926294000	2.107955000
C	2.195446000	-3.821809000	1.261127000
H	1.359593000	-3.110607000	1.311765000
H	2.180656000	-4.327239000	0.284013000
H	2.043178000	-4.595572000	2.029130000
C	4.764551000	0.288038000	0.410502000
C	4.542790000	1.672155000	0.505960000
C	6.021246000	-0.173571000	-0.010279000
C	5.553392000	2.576046000	0.173953000
H	3.564199000	2.041058000	0.820242000
C	7.031412000	0.731873000	-0.346143000
H	6.206546000	-1.248559000	-0.058293000
C	6.800203000	2.109323000	-0.258887000
H	5.363270000	3.649640000	0.246079000
H	8.005878000	0.359193000	-0.671996000

H	7.589922000	2.816847000	-0.523499000
C	-0.089689000	1.749169000	-0.544096000
H	-0.447334000	2.159684000	-1.507102000
C	0.106242000	2.808779000	0.448008000
C	-0.511687000	4.056064000	0.195361000
C	0.860965000	2.668830000	1.633373000
C	-0.411241000	5.109427000	1.105104000
H	-1.085629000	4.187635000	-0.726115000
C	0.978723000	3.729181000	2.530685000
H	1.335581000	1.712708000	1.844687000
C	0.337521000	4.949308000	2.276522000
H	-0.908914000	6.059816000	0.896373000
H	1.572766000	3.604371000	3.439689000
H	0.427137000	5.774788000	2.987400000
P	-2.491696000	-0.287120000	-0.106841000
C	-3.471419000	1.227610000	-0.631454000
C	-3.419263000	1.469331000	-2.152503000
C	-4.919015000	1.357964000	-0.114804000
H	-2.884969000	2.033012000	-0.152878000
C	-4.019720000	2.833128000	-2.519333000
H	-3.989224000	0.675534000	-2.667370000
H	-2.389610000	1.388809000	-2.522421000
C	-5.511472000	2.725883000	-0.487603000
H	-5.547957000	0.561539000	-0.542918000
H	-4.959458000	1.236387000	0.974891000
C	-5.452283000	2.981006000	-1.996629000
H	-3.988947000	2.971279000	-3.613201000
H	-3.388764000	3.631027000	-2.084801000
H	-6.550457000	2.792152000	-0.122940000
H	-4.943145000	3.516314000	0.036978000
H	-5.851684000	3.981304000	-2.234922000
H	-6.102394000	2.250370000	-2.512897000
C	-2.847467000	-0.544758000	1.709903000
C	-2.581817000	0.757483000	2.495856000
C	-4.165579000	-1.207021000	2.153528000
H	-2.034023000	-1.236592000	1.982142000
C	-2.564947000	0.485457000	4.004279000
H	-3.368822000	1.498619000	2.275764000
H	-1.625537000	1.198415000	2.181479000
C	-4.145589000	-1.463145000	3.669414000
H	-5.029496000	-0.571714000	1.903126000
H	-4.316526000	-2.160950000	1.629022000
C	-3.865907000	-0.183157000	4.465516000
H	-2.397401000	1.426935000	4.554538000
H	-1.706468000	-0.171927000	4.230496000
H	-5.102678000	-1.912359000	3.984578000
H	-3.359317000	-2.207054000	3.894775000
H	-3.825207000	-0.405451000	5.545353000
H	-4.705464000	0.522484000	4.321312000
C	-3.088856000	-1.774455000	-1.063067000
C	-2.433453000	-3.054805000	-0.500190000
C	-4.600474000	-1.970651000	-1.284512000
H	-2.630173000	-1.583322000	-2.049438000
C	-2.714487000	-4.265066000	-1.399578000
H	-2.823476000	-3.261767000	0.511444000
H	-1.345985000	-2.916003000	-0.385365000
C	-4.866759000	-3.193099000	-2.176800000
H	-5.118517000	-2.102767000	-0.321314000
H	-5.035044000	-1.077304000	-1.754898000
C	-4.219745000	-4.462969000	-1.612876000
H	-2.262495000	-5.170864000	-0.961493000

H	-2.224402000	-4.106883000	-2.377514000
H	-5.953705000	-3.334635000	-2.300350000
H	-4.457861000	-2.996630000	-3.184917000
H	-4.404479000	-5.319238000	-2.283094000
H	-4.692957000	-4.711932000	-0.644818000

**TS1-trans:** E= -3162.617648

C	1.714453000	-2.505079000	-0.925710000
C	1.532954000	-1.073160000	-1.327074000
H	1.137495000	-2.734126000	-0.019978000
H	1.336416000	-3.134933000	-1.745995000
N	3.888134000	-2.060034000	0.229100000
C	3.217458000	-2.937473000	-0.699440000
H	3.242314000	-3.978442000	-0.360492000
H	3.723176000	-2.896012000	-1.678650000
C	3.873341000	-0.762475000	-0.314916000
H	2.704043000	-0.478074000	-0.502911000
C	2.049620000	-0.672241000	-2.681895000
O	2.499963000	0.417979000	-2.963042000
O	1.939254000	-1.670701000	-3.573103000
C	2.201233000	-1.337359000	-4.940549000
H	1.493268000	-0.566806000	-5.280609000
H	3.228190000	-0.962593000	-5.062105000
H	2.059621000	-2.261809000	-5.512912000
Ru	-0.106813000	-0.173744000	-0.635434000
Cl	-1.113424000	-0.583024000	-2.864370000
Cl	0.790969000	-0.118244000	1.606534000
C	4.005866000	-2.490356000	1.663871000
C	5.201106000	-3.462457000	1.728584000
H	6.124292000	-2.954203000	1.410258000
H	5.341280000	-3.832941000	2.756384000
H	5.045890000	-4.334559000	1.074298000
C	2.726595000	-3.204518000	2.153349000
H	1.864966000	-2.525038000	2.116133000
H	2.497242000	-4.111699000	1.576408000
H	2.872527000	-3.517799000	3.198039000
C	4.260548000	-1.316481000	2.619759000
H	5.210625000	-0.808315000	2.419100000
H	3.444973000	-0.583646000	2.573555000
H	4.306053000	-1.716516000	3.643903000
H	4.213187000	-0.830156000	-1.361209000
C	0.289681000	1.538033000	-1.173110000
H	0.304059000	1.656674000	-2.269624000
C	0.675218000	2.767314000	-0.480653000
C	1.357545000	3.744902000	-1.243420000
C	0.423728000	3.043958000	0.882590000
C	1.806286000	4.930267000	-0.661676000
H	1.551245000	3.549555000	-2.301105000
C	0.856590000	4.237345000	1.457195000
H	-0.108554000	2.309607000	1.483459000
C	1.556478000	5.180756000	0.692307000
H	2.347819000	5.662719000	-1.265332000
H	0.649385000	4.435566000	2.511768000
H	1.899468000	6.112031000	1.150276000
P	-2.487075000	-0.081823000	0.120946000
C	4.556008000	0.439196000	0.282806000
C	3.829470000	1.531204000	0.769616000
C	5.958960000	0.508599000	0.246444000
C	4.494108000	2.670691000	1.235374000
C	6.623062000	1.640335000	0.723939000

C	5.890639000	2.726586000	1.220924000
H	2.742318000	1.479622000	0.796522000
H	6.530038000	-0.335359000	-0.150248000
H	3.908297000	3.515532000	1.605448000
H	7.715256000	1.679228000	0.701057000
H	6.410185000	3.615789000	1.587321000
C	-3.199145000	-1.746828000	-0.367397000
C	-2.131042000	-2.856106000	-0.241859000
C	-4.523565000	-2.188956000	0.283617000
H	-3.369295000	-1.599903000	-1.448460000
C	-2.630686000	-4.184882000	-0.821047000
H	-1.849878000	-2.992321000	0.815702000
H	-1.220568000	-2.554394000	-0.787888000
C	-5.014490000	-3.513046000	-0.320616000
H	-4.375806000	-2.329875000	1.365940000
H	-5.297620000	-1.417251000	0.172654000
C	-3.958434000	-4.616350000	-0.188236000
H	-1.862686000	-4.964363000	-0.682679000
H	-2.767400000	-4.065521000	-1.911189000
H	-5.955616000	-3.818051000	0.166957000
H	-5.248154000	-3.357614000	-1.389908000
H	-4.317969000	-5.551821000	-0.648681000
H	-3.796224000	-4.833914000	0.883873000
C	-2.771304000	0.222156000	1.943918000
C	-4.174449000	0.670956000	2.398171000
C	-2.288848000	-0.960042000	2.811877000
H	-2.075397000	1.059886000	2.132635000
C	-4.159249000	1.057191000	3.885978000
H	-4.897477000	-0.145408000	2.237655000
H	-4.529350000	1.526411000	1.807626000
C	-2.257466000	-0.563487000	4.292912000
H	-2.977199000	-1.811981000	2.687975000
H	-1.293800000	-1.290938000	2.488909000
C	-3.630665000	-0.077474000	4.771164000
H	-5.172831000	1.354712000	4.203766000
H	-3.516119000	1.947363000	4.014480000
H	-1.917420000	-1.417667000	4.902489000
H	-1.509470000	0.238631000	4.429663000
H	-3.581213000	0.249759000	5.823484000
H	-4.342985000	-0.922725000	4.737857000
C	-3.428777000	1.192499000	-0.875169000
C	-4.946082000	1.005653000	-1.061187000
C	-3.086276000	2.625394000	-0.424755000
H	-2.964103000	1.039362000	-1.864016000
C	-5.503809000	2.058647000	-2.032265000
H	-5.470054000	1.090487000	-0.095261000
H	-5.162358000	0.001696000	-1.455451000
C	-3.658432000	3.663268000	-1.398913000
H	-3.495804000	2.815586000	0.581784000
H	-1.997929000	2.748245000	-0.348484000
C	-5.169588000	3.485148000	-1.582321000
H	-6.594557000	1.929651000	-2.133950000
H	-5.071024000	1.885125000	-3.034549000
H	-3.427519000	4.680005000	-1.039192000
H	-3.154832000	3.552081000	-2.376626000
H	-5.560122000	4.218245000	-2.307997000
H	-5.677182000	3.690877000	-0.621411000

**INT1-cis:** E= -3162.658101

C	2.490858000	-1.338284000	-1.446919000
C	2.233987000	0.144722000	-1.185058000
H	1.660843000	-1.967796000	-1.092019000
H	2.539573000	-1.516509000	-2.529878000
N	3.776982000	-1.987443000	0.632693000
C	3.799272000	-1.901780000	-0.853413000
H	3.992091000	-2.910868000	-1.232840000
H	4.639266000	-1.276579000	-1.164331000
C	4.032035000	-0.969398000	1.395684000
H	3.785027000	-1.091299000	2.448397000
H	2.684302000	0.500811000	-0.260453000
C	2.634511000	1.104632000	-2.232109000
O	2.750141000	2.310420000	-2.073979000
O	2.888909000	0.540153000	-3.442971000
C	3.117133000	1.435646000	-4.523277000
H	2.227711000	2.059995000	-4.705034000
H	3.972751000	2.099632000	-4.322620000
H	3.321442000	0.814871000	-5.405806000
Ru	0.145064000	0.248247000	-0.639133000
Cl	-0.385944000	0.173113000	-3.025473000
Cl	1.007837000	-0.328097000	1.647153000
C	3.341016000	-3.323065000	1.245160000
C	3.102594000	-3.194509000	2.755236000
H	2.306520000	-2.468652000	2.974396000
H	2.776989000	-4.175892000	3.126516000
H	4.015136000	-2.928851000	3.309326000
C	4.492563000	-4.313715000	0.994402000
H	4.673559000	-4.484691000	-0.076213000
H	5.424929000	-3.956347000	1.457146000
H	4.231974000	-5.282837000	1.444343000
C	2.037166000	-3.810495000	0.592220000
H	1.237290000	-3.071667000	0.737758000
H	2.149291000	-4.024055000	-0.478722000
H	1.741143000	-4.749690000	1.080395000
C	4.655429000	0.314927000	1.057042000
C	4.124733000	1.470422000	1.665925000
C	5.791923000	0.425091000	0.234622000
C	4.675379000	2.719913000	1.392041000
H	3.236208000	1.378819000	2.293163000
C	6.356633000	1.677536000	-0.009406000
H	6.256030000	-0.465879000	-0.190966000
C	5.790284000	2.827005000	0.551721000
H	4.231929000	3.614549000	1.834222000
H	7.242589000	1.754997000	-0.643456000
H	6.223099000	3.807500000	0.340003000
C	-0.118798000	2.054029000	-0.600302000
H	-0.150121000	2.505182000	-1.611177000
C	-0.392827000	3.055341000	0.439917000
C	-0.997608000	4.268653000	0.033897000
C	-0.116865000	2.884929000	1.814613000
C	-1.345026000	5.252812000	0.960845000
H	-1.204887000	4.425790000	-1.028060000
C	-0.447466000	3.876967000	2.737987000
H	0.367699000	1.964619000	2.138661000
C	-1.071577000	5.060109000	2.320008000
H	-1.824858000	6.174876000	0.622131000
H	-0.219677000	3.726076000	3.796822000
H	-1.336930000	5.830298000	3.049037000
P	-2.144813000	-0.444168000	-0.054386000

C	-3.371452000	0.970887000	-0.150893000
C	-3.465949000	1.544843000	-1.577664000
C	-4.779696000	0.767091000	0.441662000
H	-2.860860000	1.729450000	0.468636000
C	-4.260376000	2.857689000	-1.590823000
H	-3.968045000	0.812022000	-2.234548000
H	-2.461996000	1.693142000	-1.997936000
C	-5.566726000	2.086774000	0.429706000
H	-5.331605000	0.013134000	-0.140695000
H	-4.725713000	0.387287000	1.470301000
C	-5.655276000	2.681330000	-0.980041000
H	-4.334769000	3.240265000	-2.622934000
H	-3.702673000	3.616436000	-1.012477000
H	-6.575691000	1.923810000	0.845304000
H	-5.063410000	2.809839000	1.098070000
H	-6.193621000	3.644153000	-0.959391000
H	-6.248052000	2.002308000	-1.621028000
C	-2.283662000	-1.164744000	1.670054000
C	-2.214991000	-0.048735000	2.732582000
C	-3.412407000	-2.159851000	1.997517000
H	-1.330781000	-1.716621000	1.740534000
C	-2.016067000	-0.636068000	4.133806000
H	-3.149543000	0.536397000	2.723699000
H	-1.401222000	0.645842000	2.493869000
C	-3.223497000	-2.738698000	3.409555000
H	-4.395474000	-1.665179000	1.932743000
H	-3.429198000	-2.984379000	1.271682000
C	-3.121810000	-1.642104000	4.475886000
H	-1.987219000	0.174861000	4.881635000
H	-1.030935000	-1.134875000	4.169607000
H	-4.051268000	-3.429347000	3.644480000
H	-2.297005000	-3.342376000	3.424307000
H	-2.947642000	-2.088926000	5.469589000
H	-4.088228000	-1.107452000	4.536819000
C	-2.659519000	-1.752372000	-1.289266000
C	-1.748399000	-2.991432000	-1.160828000
C	-4.140454000	-2.154210000	-1.417775000
H	-2.373802000	-1.253258000	-2.230891000
C	-1.967339000	-3.968496000	-2.322658000
H	-1.944091000	-3.511867000	-0.206875000
H	-0.690580000	-2.686638000	-1.136922000
C	-4.338837000	-3.139507000	-2.580629000
H	-4.506279000	-2.615316000	-0.487002000
H	-4.761545000	-1.264639000	-1.593309000
C	-3.440420000	-4.373555000	-2.444063000
H	-1.329298000	-4.858912000	-2.190912000
H	-1.642805000	-3.480667000	-3.259679000
H	-5.399347000	-3.437813000	-2.639995000
H	-4.102705000	-2.625200000	-3.530344000
H	-3.584462000	-5.051844000	-3.301999000
H	-3.735950000	-4.940107000	-1.541028000

**INT1-trans:** E= -3162.651247

C	1.748766000	-2.387567000	-0.420739000
C	1.645415000	-0.906023000	-0.748367000
H	1.393471000	-2.544758000	0.605811000
H	1.099168000	-2.984552000	-1.081137000
N	4.197419000	-2.188411000	0.104157000
C	3.162181000	-3.004763000	-0.585618000
H	3.202278000	-4.031415000	-0.213181000

H	3.424560000	-3.023260000	-1.649460000
C	4.691457000	-1.230209000	-0.615714000
H	2.182264000	-0.284375000	-0.022582000
C	2.032011000	-0.488596000	-2.103132000
O	2.443855000	0.616603000	-2.429135000
O	1.920059000	-1.488912000	-3.021611000
C	2.044445000	-1.112679000	-4.390251000
H	1.224558000	-0.432603000	-4.667377000
H	3.007010000	-0.614778000	-4.584560000
H	1.974902000	-2.039752000	-4.974392000
Ru	-0.413158000	-0.214663000	-0.341569000
Cl	-1.054522000	-0.242833000	-2.722838000
Cl	0.062046000	-0.670833000	2.024561000
C	4.400121000	-2.355889000	1.623979000
C	5.897555000	-2.523157000	1.928457000
H	6.440830000	-1.575708000	1.864538000
H	6.002510000	-2.891707000	2.958758000
H	6.363239000	-3.258512000	1.255104000
C	3.673949000	-3.616290000	2.119032000
H	2.590256000	-3.579178000	1.954295000
H	4.083977000	-4.534866000	1.675001000
H	3.831871000	-3.676889000	3.204666000
C	3.813065000	-1.122968000	2.328516000
H	4.282496000	-0.191188000	1.987932000
H	2.726292000	-1.053544000	2.178689000
H	4.002891000	-1.220068000	3.407704000
H	4.363913000	-1.240991000	-1.660099000
C	-0.008263000	1.562016000	-0.478611000
H	-0.521005000	2.084682000	-1.309302000
C	0.965339000	2.451069000	0.167916000
C	1.121999000	3.749688000	-0.374435000
C	1.782577000	2.095500000	1.264815000
C	2.054761000	4.647830000	0.145036000
H	0.499295000	4.046232000	-1.223095000
C	2.712318000	2.994698000	1.785423000
H	1.659784000	1.110292000	1.710325000
C	2.857156000	4.272245000	1.229250000
H	2.158222000	5.642569000	-0.296319000
H	3.337357000	2.694392000	2.630636000
H	3.591410000	4.971149000	1.638566000
P	-2.819379000	0.020225000	0.063856000
C	5.567759000	-0.088981000	-0.281101000
C	4.979761000	1.188909000	-0.352833000
C	6.950173000	-0.213436000	-0.066335000
C	5.760416000	2.321938000	-0.117794000
C	7.725316000	0.930241000	0.142059000
C	7.130629000	2.196100000	0.134651000
H	3.919544000	1.290061000	-0.593951000
H	7.424797000	-1.194799000	-0.084307000
H	5.287588000	3.305846000	-0.139475000
H	8.800159000	0.827977000	0.307860000
H	7.739374000	3.086558000	0.308862000
C	-3.775671000	-1.251738000	-0.935464000
C	-3.050250000	-2.615353000	-0.982507000
C	-5.266236000	-1.466539000	-0.605220000
H	-3.697717000	-0.824571000	-1.950258000
C	-3.710419000	-3.555760000	-2.000210000
H	-3.066846000	-3.082903000	0.016425000
H	-1.996951000	-2.473284000	-1.262383000
C	-5.925325000	-2.391075000	-1.640173000
H	-5.358818000	-1.932411000	0.389389000

H	-5.811507000	-0.514858000	-0.554487000
C	-5.205966000	-3.742250000	-1.722685000
H	-3.193793000	-4.530696000	-2.000057000
H	-3.574446000	-3.127929000	-3.010407000
H	-6.990110000	-2.535319000	-1.389727000
H	-5.897365000	-1.900667000	-2.630683000
H	-5.666447000	-4.378574000	-2.497424000
H	-5.331883000	-4.275116000	-0.761683000
C	-3.375984000	-0.081743000	1.849401000
C	-4.750115000	0.502330000	2.233978000
C	-3.242315000	-1.515153000	2.406878000
H	-2.596573000	0.523026000	2.346912000
C	-4.931619000	0.492486000	3.760113000
H	-5.554016000	-0.091042000	1.770755000
H	-4.867255000	1.529217000	1.862503000
C	-3.415407000	-1.526189000	3.930849000
H	-4.018281000	-2.157539000	1.958452000
H	-2.265442000	-1.937168000	2.136029000
C	-4.758085000	-0.913058000	4.346593000
H	-5.923208000	0.899323000	4.022060000
H	-4.183813000	1.169534000	4.212646000
H	-3.328813000	-2.558057000	4.312158000
H	-2.587819000	-0.951384000	4.384381000
H	-4.848058000	-0.885170000	5.445880000
H	-5.577473000	-1.559380000	3.980129000
C	-3.340731000	1.693266000	-0.610481000
C	-4.792593000	1.907362000	-1.077872000
C	-2.891746000	2.840359000	0.317291000
H	-2.715243000	1.730622000	-1.519308000
C	-4.938962000	3.276258000	-1.763062000
H	-5.486952000	1.851393000	-0.223213000
H	-5.089840000	1.118872000	-1.784863000
C	-3.031288000	4.198101000	-0.380882000
H	-3.511292000	2.847095000	1.229386000
H	-1.854687000	2.688080000	0.650328000
C	-4.468698000	4.425465000	-0.863806000
H	-5.987898000	3.429812000	-2.068418000
H	-4.338078000	3.275598000	-2.690970000
H	-2.718551000	5.006447000	0.301319000
H	-2.342868000	4.230613000	-1.245282000
H	-4.550710000	5.387682000	-1.397015000
H	-5.136749000	4.494733000	0.015016000

**TS2-cis:** E= -3162.642010

C	2.133913000	2.092086000	0.398051000
C	2.111070000	0.597544000	0.418245000
H	1.547250000	2.472412000	-0.448924000
H	1.706199000	2.510845000	1.322029000
N	4.243973000	1.905222000	-0.800222000
C	3.605241000	2.617192000	0.297341000
H	3.658566000	3.701732000	0.165526000
H	4.101791000	2.369015000	1.241631000
C	4.304142000	0.564619000	-0.618069000
H	4.120047000	-0.041557000	-1.508766000
H	1.860628000	0.025205000	-0.473958000
C	2.471459000	-0.163284000	1.599332000
O	2.524022000	-1.379270000	1.694546000
O	2.844951000	0.645930000	2.630539000
C	3.214433000	-0.010782000	3.837722000
H	3.458434000	0.781698000	4.557549000

H	2.380426000	-0.620592000	4.217252000
H	4.091799000	-0.657917000	3.682293000
Ru	-0.430506000	0.065121000	0.251462000
Cl	-0.463890000	-0.158266000	2.657247000
Cl	-0.337974000	1.037508000	-1.969129000
C	4.181847000	2.414720000	-2.221953000
C	3.945267000	3.930415000	-2.232663000
H	4.703896000	4.465785000	-1.642185000
H	4.013609000	4.288307000	-3.270043000
H	2.945575000	4.196749000	-1.859201000
C	3.070145000	1.734211000	-3.041070000
H	3.221026000	0.648934000	-3.138057000
H	2.077657000	1.895569000	-2.602666000
H	3.069760000	2.148360000	-4.060594000
C	5.557454000	2.120486000	-2.848686000
H	6.357673000	2.610027000	-2.272525000
H	5.765062000	1.039733000	-2.871450000
H	5.590923000	2.491439000	-3.884320000
C	5.089041000	-0.133743000	0.397567000
C	5.033252000	-1.543613000	0.415203000
C	5.939730000	0.520573000	1.313231000
C	5.791002000	-2.274501000	1.329076000
H	4.373489000	-2.060156000	-0.285017000
C	6.695179000	-0.213892000	2.224866000
H	6.030824000	1.607349000	1.288493000
C	6.618653000	-1.613829000	2.242359000
H	5.727215000	-3.365212000	1.333548000
H	7.355762000	0.306501000	2.922778000
H	7.210555000	-2.185370000	2.961644000
C	-0.215227000	-1.739460000	0.025755000
H	-0.787867000	-2.398790000	0.704182000
C	0.777149000	-2.477894000	-0.758099000
C	1.155766000	-3.762015000	-0.303370000
C	1.408869000	-1.965936000	-1.914288000
C	2.165062000	-4.481568000	-0.941331000
H	0.665925000	-4.177693000	0.581004000
C	2.406437000	-2.695411000	-2.560923000
H	1.100547000	-0.994610000	-2.302646000
C	2.799285000	-3.947495000	-2.070227000
H	2.460204000	-5.462097000	-0.559500000
H	2.884495000	-2.283692000	-3.453815000
H	3.590895000	-4.510142000	-2.571597000
P	-2.761906000	0.040777000	-0.009850000
C	-3.293507000	1.811948000	-0.368928000
C	-4.796374000	2.137799000	-0.239246000
C	-2.455098000	2.845803000	0.416683000
H	-3.003755000	1.913175000	-1.429388000
C	-5.092142000	3.566767000	-0.718267000
H	-5.104012000	2.051462000	0.814124000
H	-5.412894000	1.424866000	-0.801261000
C	-2.765976000	4.276669000	-0.044604000
H	-2.655419000	2.748560000	1.496495000
H	-1.378507000	2.664405000	0.272031000
C	-4.260506000	4.597875000	0.051479000
H	-6.169079000	3.778155000	-0.608712000
H	-4.863547000	3.642265000	-1.797341000
H	-2.175238000	4.994480000	0.548685000
H	-2.436383000	4.387259000	-1.093998000
H	-4.460620000	5.615066000	-0.324993000
H	-4.566438000	4.587893000	1.113907000
C	-3.764604000	-0.634311000	1.422954000

C	-3.794281000	0.320226000	2.637077000
C	-5.195115000	-1.122667000	1.111684000
H	-3.161770000	-1.513440000	1.715109000
C	-4.401141000	-0.373685000	3.862802000
H	-4.406824000	1.202412000	2.393362000
H	-2.783114000	0.672457000	2.869994000
C	-5.811251000	-1.812711000	2.338731000
H	-5.825472000	-0.267357000	0.819667000
H	-5.203475000	-1.821306000	0.265868000
C	-5.809642000	-0.902158000	3.570965000
H	-4.421668000	0.328494000	4.713368000
H	-3.743256000	-1.210085000	4.162318000
H	-6.836932000	-2.142364000	2.101765000
H	-5.230808000	-2.726793000	2.562048000
H	-6.213323000	-1.439085000	4.445924000
H	-6.484534000	-0.045474000	3.387235000
C	-3.194446000	-0.923053000	-1.573541000
C	-3.065834000	-2.449997000	-1.403542000
C	-4.498329000	-0.559667000	-2.311258000
H	-2.365420000	-0.602736000	-2.225554000
C	-3.151155000	-3.164962000	-2.758711000
H	-3.864212000	-2.832950000	-0.746607000
H	-2.114305000	-2.703735000	-0.919542000
C	-4.580476000	-1.291986000	-3.660337000
H	-5.376826000	-0.826123000	-1.701477000
H	-4.549364000	0.522942000	-2.493348000
C	-4.444389000	-2.809047000	-3.498507000
H	-3.075750000	-4.255027000	-2.609092000
H	-2.281831000	-2.869768000	-3.374332000
H	-5.530186000	-1.038648000	-4.160810000
H	-3.770237000	-0.924014000	-4.316076000
H	-4.475746000	-3.305589000	-4.482879000
H	-5.307881000	-3.192740000	-2.923881000

**2a:** E= -829.128743

C	-1.096605000	2.307513000	0.926212000
C	0.102828000	1.399610000	1.228908000
H	-1.785863000	2.266624000	1.784362000
H	-0.817203000	3.359224000	0.765661000
N	-1.459043000	0.222059000	-0.193561000
C	-1.752218000	1.660684000	-0.297740000
H	-2.833414000	1.861188000	-0.311275000
H	-1.333254000	2.078378000	-1.228590000
C	-0.433062000	-0.018326000	0.823872000
H	-0.873543000	-0.443146000	1.747164000
H	0.375243000	1.398304000	2.291948000
C	1.380418000	1.768151000	0.499252000
O	2.479959000	1.763728000	1.004741000
O	1.169964000	2.081132000	-0.789637000
C	2.331021000	2.337475000	-1.586096000
H	2.919241000	3.166378000	-1.165457000
H	2.963835000	1.438108000	-1.633967000
H	1.964758000	2.597658000	-2.586394000
C	-2.611377000	-0.711931000	-0.248511000
C	-3.346713000	-0.502000000	-1.585702000
H	-2.652041000	-0.648783000	-2.427439000
H	-4.173547000	-1.222651000	-1.684413000
H	-3.776983000	0.506830000	-1.669869000
C	-3.590401000	-0.490673000	0.928494000
H	-3.087791000	-0.647840000	1.896142000

H	-4.008475000	0.528035000	0.922401000
H	-4.434724000	-1.195879000	0.873765000
C	-2.117727000	-2.169873000	-0.214642000
H	-1.410455000	-2.365727000	-1.032824000
H	-2.976809000	-2.849385000	-0.325286000
C	0.694191000	-0.947572000	0.388999000
C	1.421195000	-1.661078000	1.351673000
C	1.075796000	-1.046964000	-0.956164000
C	2.508845000	-2.458489000	0.981287000
H	1.130912000	-1.593586000	2.404685000
C	2.164171000	-1.840028000	-1.330680000
H	0.498929000	-0.496063000	-1.700370000
C	2.885676000	-2.549166000	-0.362908000
H	3.063112000	-3.011487000	1.744339000
H	2.448884000	-1.908859000	-2.384226000
H	3.734735000	-3.172415000	-0.655483000
H	-1.617864000	-2.422186000	0.731694000

## References

- (1) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- (2) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
- (3) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
- (4) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- (5) (a) Miertuš, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.*, 1981, **55**, 117. (b) Pascual-Ahuir, J. L.; Silla, E.; Tuñón, I. *J. Comp. Chem.*, 1994, **15**, 1127. (c) Barone, V.; Cossi, M. *J. Phys. Chem. A*, 1998, **102**, 1995.
- (6) McIver, J. W.; Komornicki, A. K. *J. Am. Chem. Soc.* **1972**, *94*, 2625.
- (7) González, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.