

# Supporting Information

for

## **A New Tool in the Quest for Biocompatible Phthalocyanines: Palladium Catalyzed Aminocarbonylation for Amide Substituted Phthalonitriles and Illustrative Phthalocyanines Thereof**

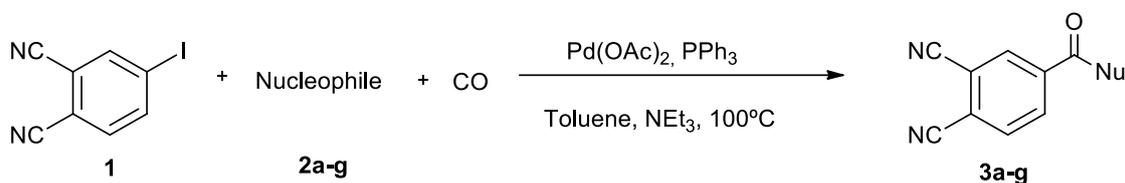
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1. Experimental procedures for the synthesis of phthalonitriles **3a-g** and copies of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and Mass Spectra



*General Procedure for synthesis of carboxamide substituted phthalonitriles **3a-g***

In a typical aminocarbonylation reaction, the catalyst precursor Pd(OAc)<sub>2</sub>, triphenylphosphine (PPh<sub>3</sub>) ligand, substrate 4-iodophthalonitrile and the nucleophile were directly introduced in a high pressure reactor having a magnetic stirrer inside. The reactor was sealed and 3 vacuum/CO gas cycles were performed. Under vacuum, the reaction solvent was then added (toluene) via cannula, followed by triethylamine as base. The reactor was then pressurized using 5 bar CO and the reaction mixture maintained at 100°C for the required period of time. After this period, the reactor was cooled to room temperature and depressurized. Palladium particles were filtered, the solvent rotary evaporated and the crude product was then purified according to the corresponding procedure and characterized by means of  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR and mass spectrometry.

1.1. Phthalonitrile **3a**

**Methyl 2-(3,4-dicyanobenzamido)acetate (glycine substituted phthalonitrile) (**3a**).**

Following the above described procedure, 6.75 mg (0.030 mmol) of Pd(OAc)<sub>2</sub>, 15.74 mg (0.060 mmol) of PPh<sub>3</sub>, 300 mg (1.18 mmol) of 4-iodophthalonitrile, 163.4 mg (1.30 mmol) glycine methyl ester hydrochloride (**2a**) and 1.1 mL Et<sub>3</sub>N were dissolved in 10 mL of toluene. The reaction was pressurized and maintained at 100 °C for 12 hours. The residue was dissolved in dichloromethane (20 mL), washed with brine (3x20 mL) and water (3x20 mL). The organic phase was dried with sodium sulfate and the solvent evaporated. The product was purified by recrystallization with ethyl acetate/*n*-hexane yielding (**3a**) in 65% yield (158 mg).  $^1\text{H}$  RMN (400.13 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (s, 1H), 8.15 (d,  $J=8.1\text{Hz}$ , 1H), 7.93 (d,  $J=8.1\text{Hz}$ , 1H), 6.77 (s, 1H), 4.27 (d,  $J=4.9\text{Hz}$ , 2H), 3.84 (s, 9H).  $^{13}\text{C}$  RMN (100.61 MHz, CDCl<sub>3</sub>)  $\delta$  170.0, 163.7, 138.4, 134.1, 132.4, 131.6,

118.6, 116.9, 114.8, 114.7, 53.0, 42.1. HRMS (ESI-TOF)  $m/z$  calcd for  $[M+Na]^+$ :  $C_{12}H_9N_3NaO_3$  266.0536; found 266.0532.

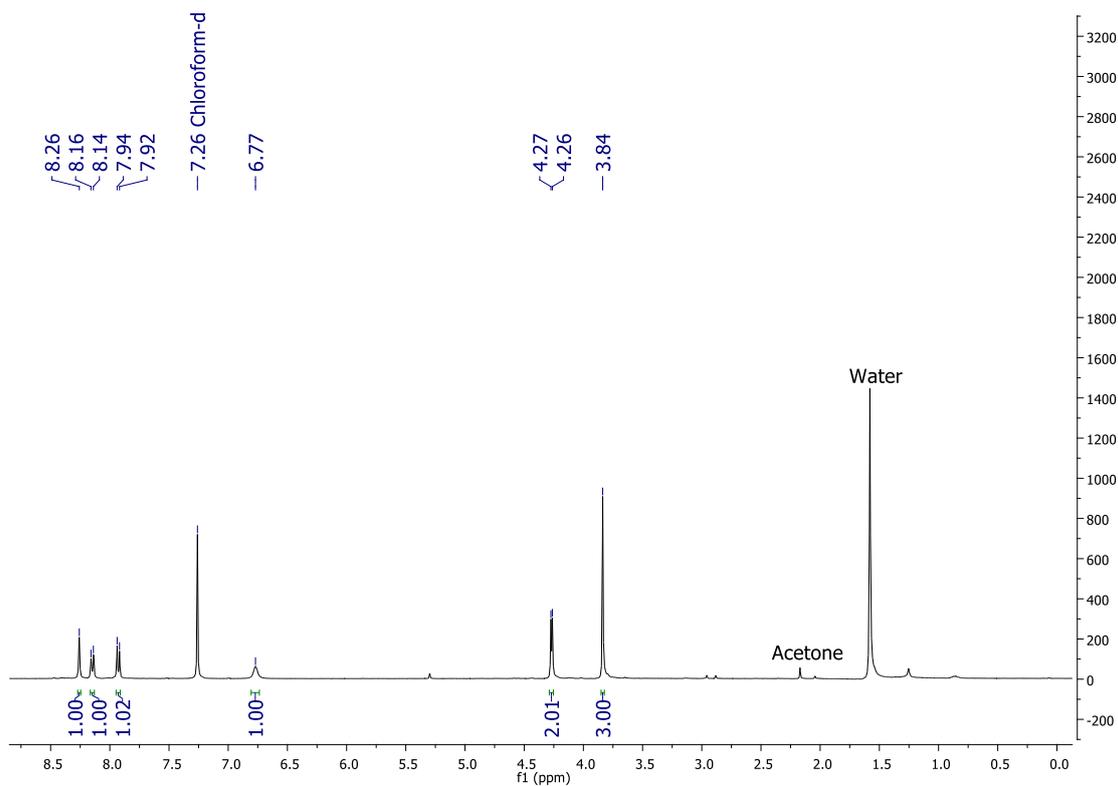


Fig. 1.  $^1H$ -NMR of Phthalonitrile **3a**, recorded in  $CDCl_3$ .

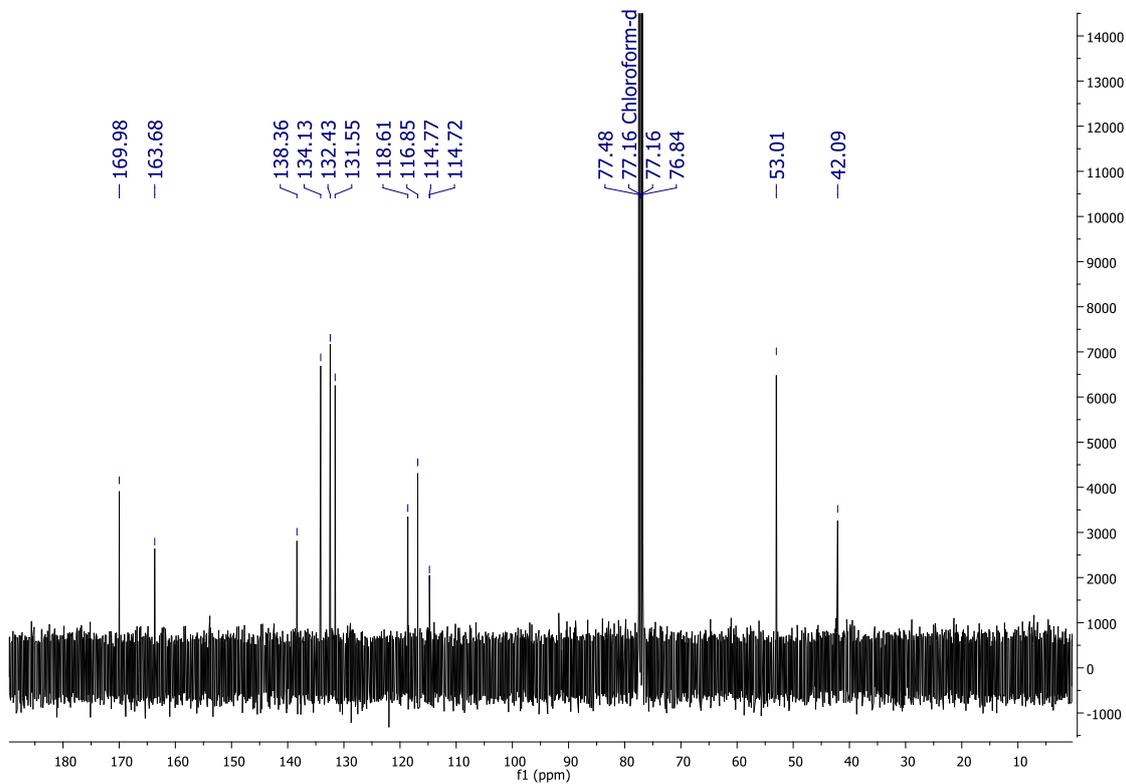


Fig. 2.  $^{13}C$ -NMR of Phthalonitrile **3a**, recorded in  $CDCl_3$ .

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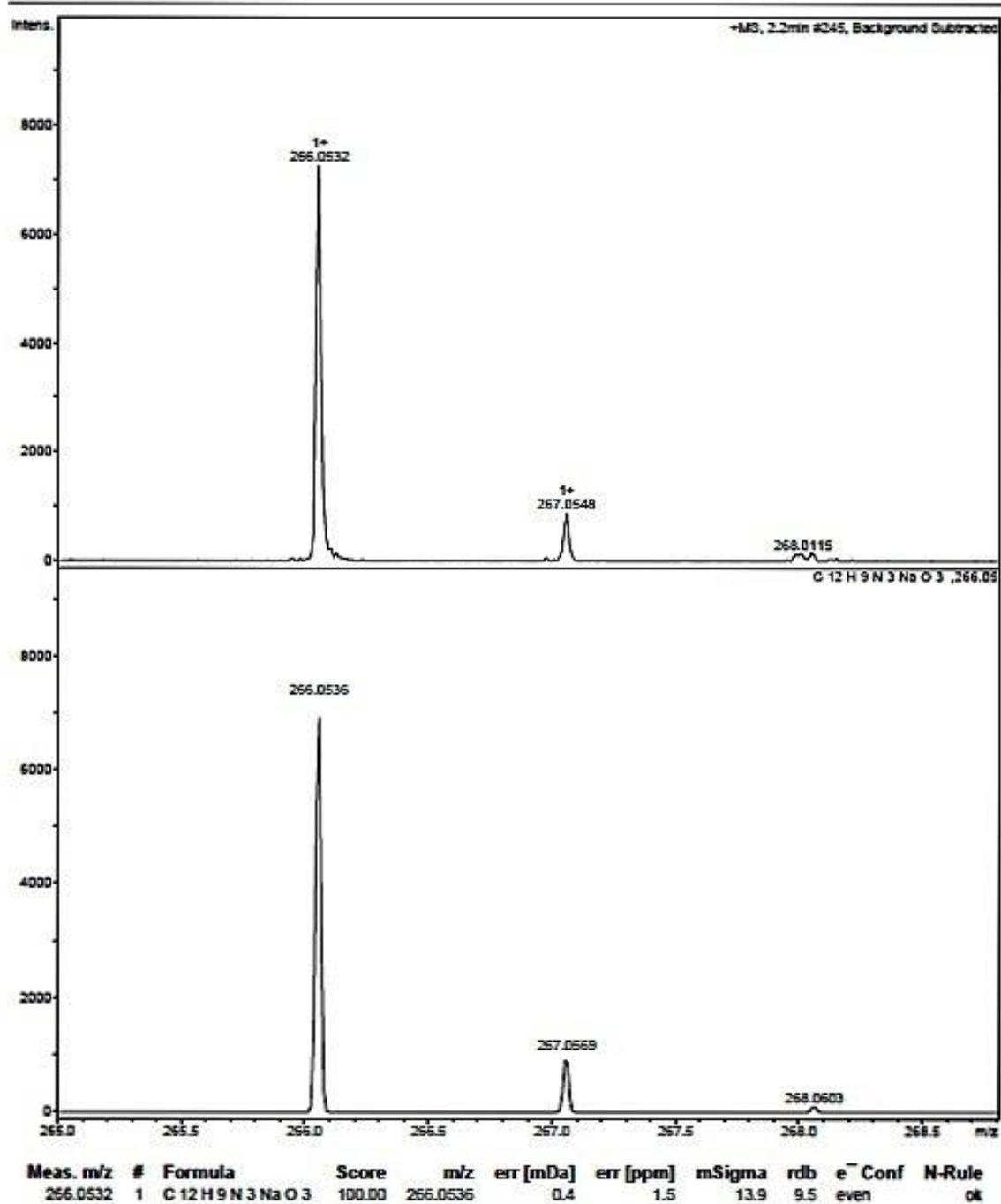
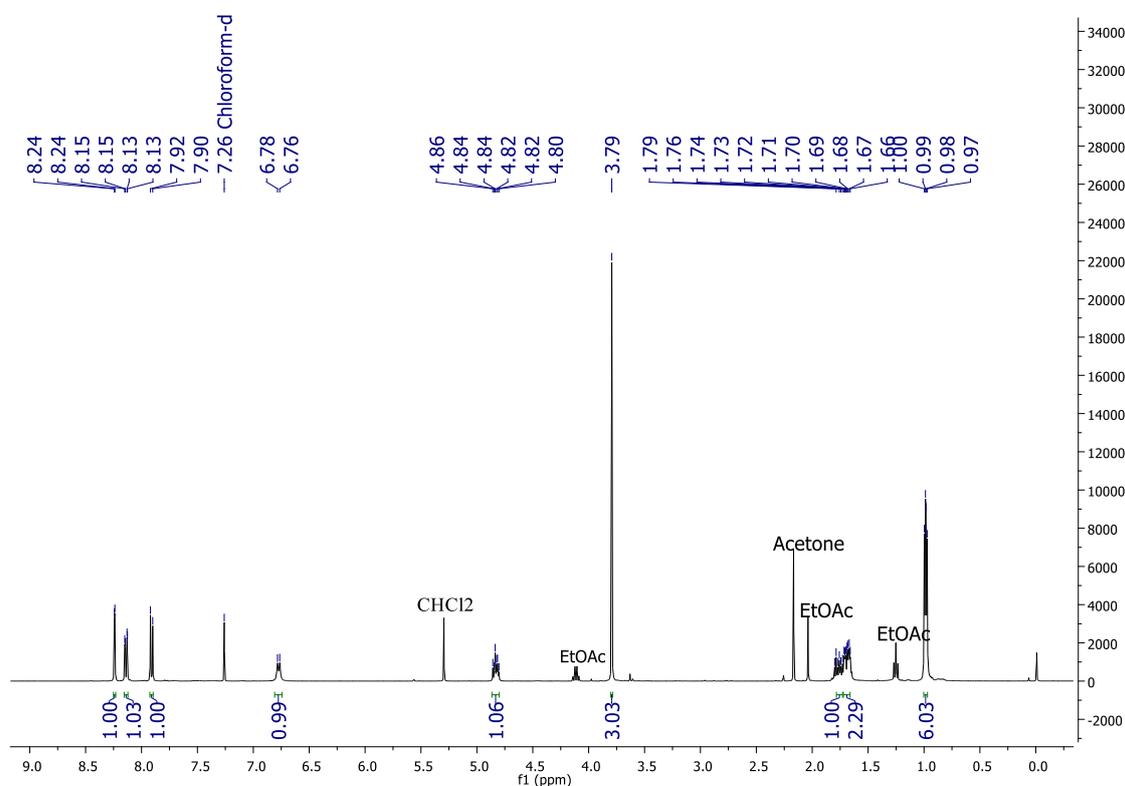


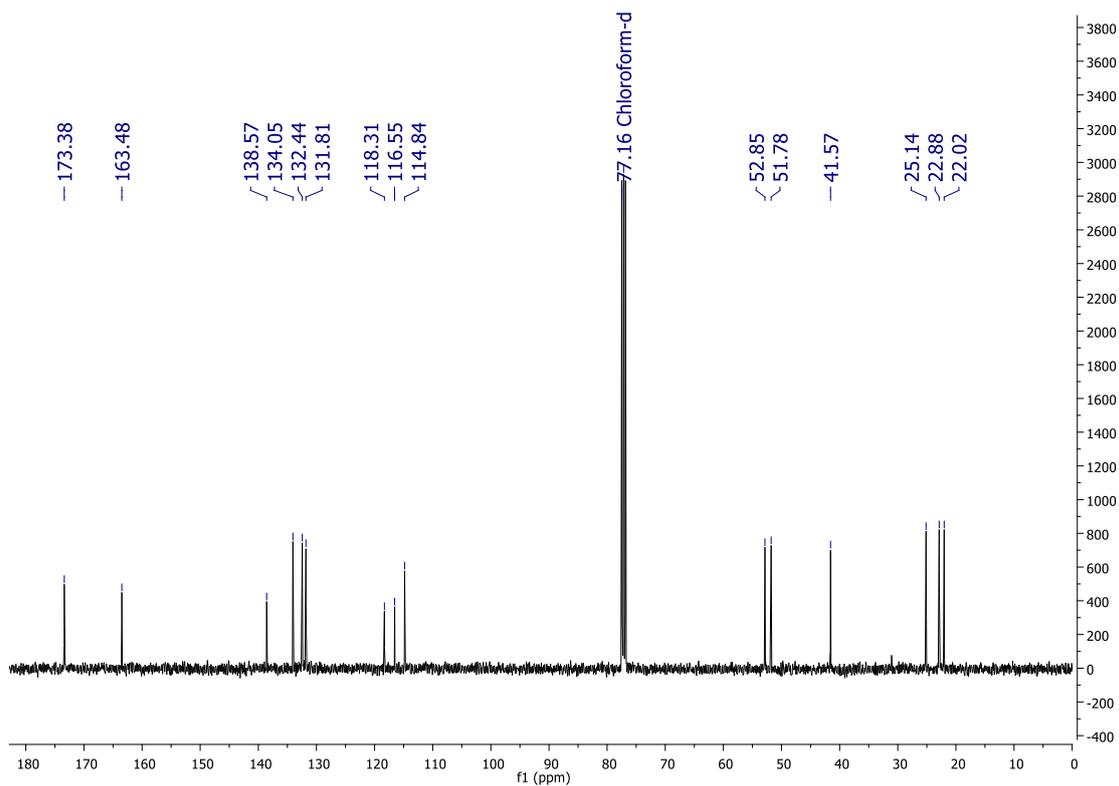
Fig. 3. Mass spectrum of Phthalonitrile 3a.

## 1.2. Phthalonitrile **3b**

**(S)-Methyl 2-(3,4-dicyanobenzamido)-4-methylpentanoate (leucine substituted phthalonitrile) (3b)**. Following the above described procedure, 6.75 mg (0.030 mmol) of Pd(OAc)<sub>2</sub>, 15.74 mg (0.06 mmol) of PPh<sub>3</sub>, 300 mg (1.18 mmol) of 4-iodophthalonitrile, 236.6 mg (1.30 mmol) leucine methyl ester hydrochloride (**2b**) and 1.1 mL Et<sub>3</sub>N were dissolved in 10 mL toluene. The reaction was pressurized and maintained at 100 °C for 12 hours. The residue was dissolved in dichloromethane (20 mL), washed with brine (3x20 mL) and water (3x20 mL). The organic phase was dried with sodium sulfate and the solvent evaporated. The product (**3b**) was purified by column chromatography on silica gel (stationary phase) first using chloroform and then a mixture of chloroform/ethyl acetate (20/1) and obtained in 54% yield (120 mg), after being washed with *n*-hexane. <sup>1</sup>H RMN (400.13 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J*=1.7Hz, 1H), 8.14 (dd, *J*=8.1, 1.7 Hz, 1H), 7.91 (d, *J*=8.1Hz, 1H), 6.77 (br s, 1H), 4.86-4.80 (m, 1H), 3.79 (s, 3H), 1.80-1.66 (2 m, 3H), 1.00-0.97 (m, 6H). <sup>13</sup>C RMN (100.61 MHz, CDCl<sub>3</sub>) δ 173.4, 163.5, 138.6, 134.1, 132.4, 131.9, 118.3, 116.6, 114.9, 52.9, 51.8, 41.6, 25.1, 22.9, 22.0. HRMS (ESI-TOF) *m/z* calcd for [M+Na]<sup>+</sup>: C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>NaO<sub>3</sub> 322.1162; found 322.1153.



**Fig. 4.** <sup>1</sup>H-NMR of Phthalonitrile **3b**, recorded in CDCl<sub>3</sub>.



**Fig. 5.**  $^{13}\text{C}$ -NMR of Phthalonitrile **3b**, recorded in  $\text{CDCl}_3$ .

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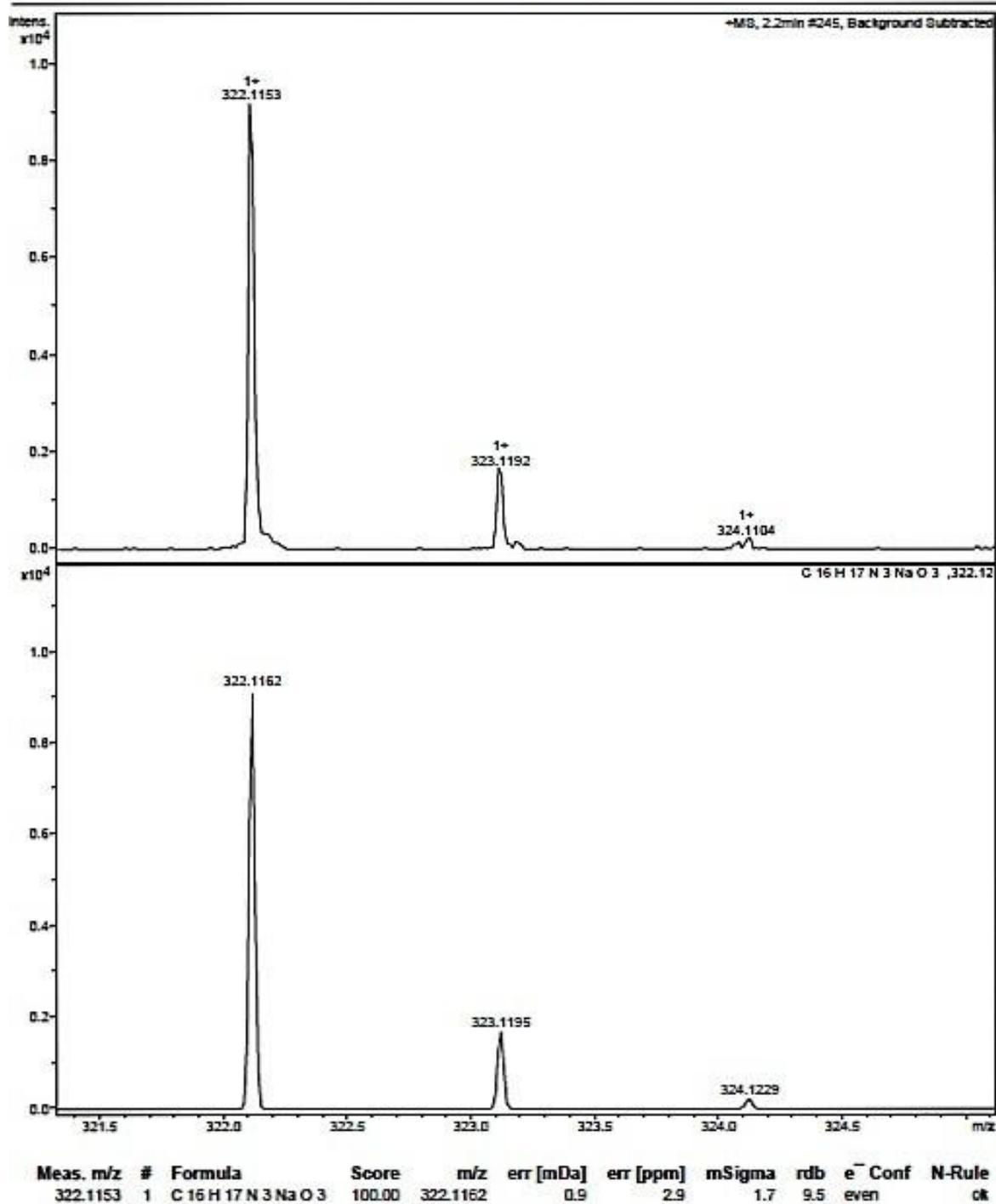
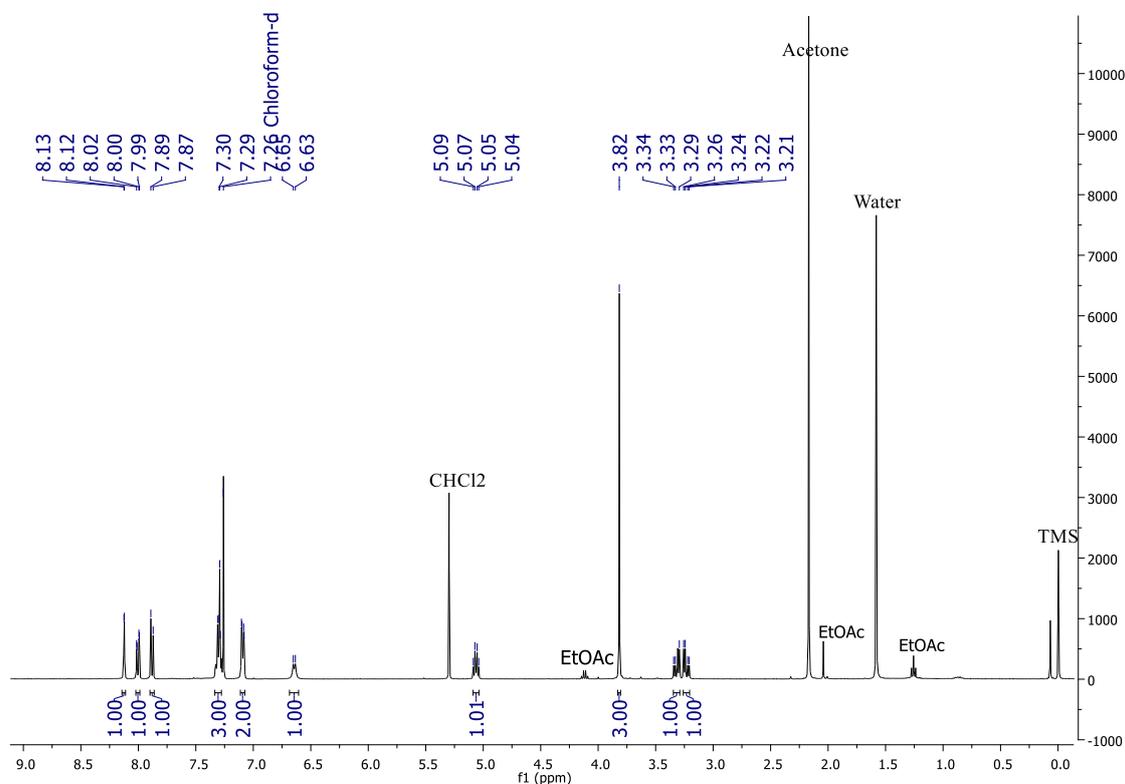


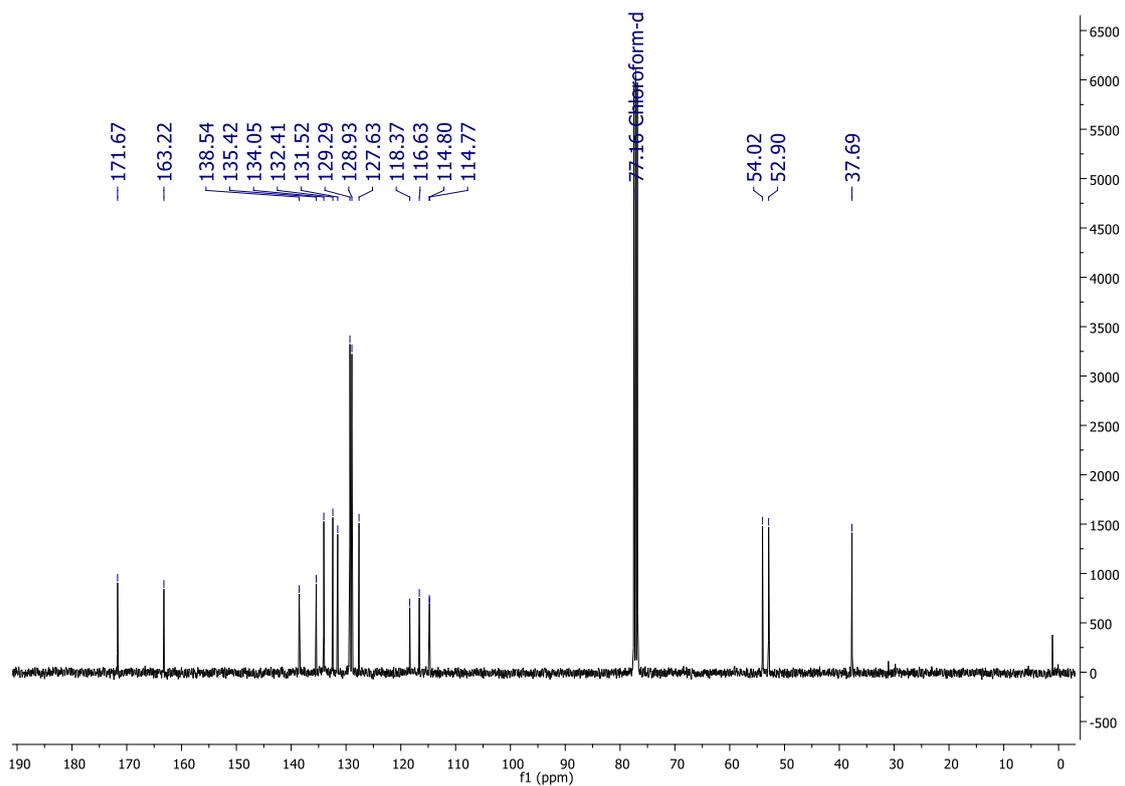
Fig. 6. Mass spectrum of Phthalonitrile **3b**.

### 1.3. Phthalonitrile **3c**

**(S)-Methyl 2-(3,4-dicyanobenzamido)-3-phenylpropanoate (phenyl alanine substituted phthalonitrile) (3c)**. Following the above described procedure, 6.75 mg (0.030 mmol) of Pd(OAc)<sub>2</sub>, 15.74 mg (0.06 mmol) of PPh<sub>3</sub>, 300 mg (1.18 mmol) of 4-iodophthalonitrile, 280.4 mg (1.30 mmol) phenyl alanine methyl ester hydrochloride (**2c**) and 1.1 mL Et<sub>3</sub>N were dissolved in 10 mL toluene. The reaction was pressurized and maintained at 100 °C for 12 hours. The residue was dissolved in dichloromethane (20 mL), washed with brine (3x20 mL) and water (3x20 mL). The organic phase was dried with sodium sulfate and the solvent evaporated. The product (**3c**) was purified by column chromatography on silica gel (stationary phase) first using chloroform and then a mixture of chloroform/ethyl acetate (10/1) and obtained in 59.0% yield (192 mg), after being washed with *n*-hexane. <sup>1</sup>H RMN (400.13 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J*=1.7 Hz, 1H), 8.00 (dd, *J*=8.1,1.7 Hz, 1H), 7.88 (d, *J*=8.1 Hz, 1H), 7.30-7.29 (m, 3H), 7.10-7.08 (m, 2H), 6.64 (br s, 1H), 5.09-5.04 (m, 1H), 3.82 (s, 3H), 3.34-3.21 (m, 2H). <sup>13</sup>C RMN (100.61 MHz, CDCl<sub>3</sub>) δ 171.7, 163.3, 138.6, 135.4, 134.1, 132.4, 131.6, 129.3, 128.9, 127.6, 118.4, 116.6, 114.8, 114.8, 54.0, 52.9, 37.7. HRMS (ESI-TOF) *m/z* calcd for [M+Na]<sup>+</sup>: C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>NaO<sub>3</sub> 356.1003; found 356.1006.

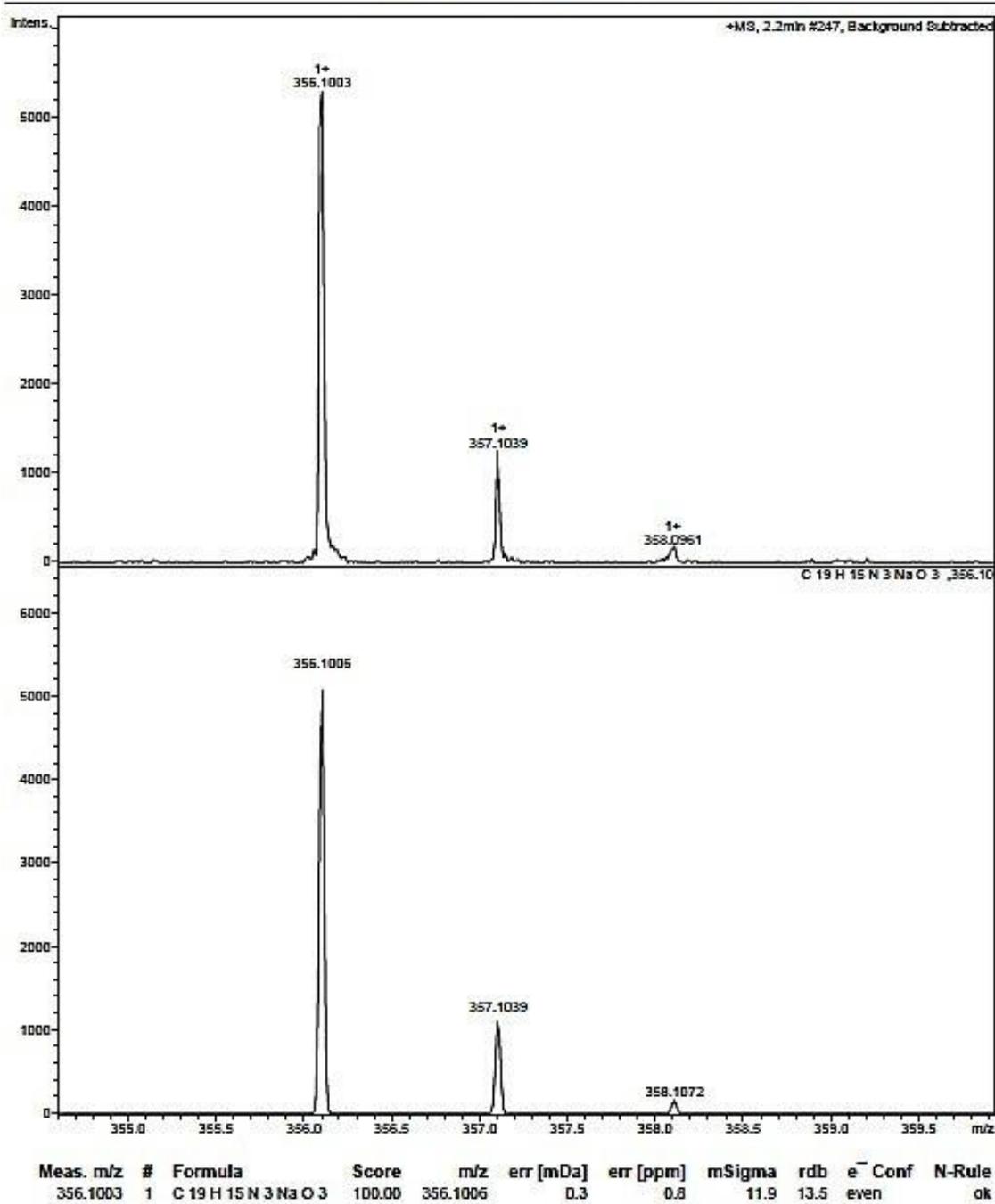


**Fig. 7.** <sup>1</sup>H-NMR of Phthalonitrile **3c**, recorded in CDCl<sub>3</sub>.



**Fig. 8.**  $^{13}\text{C}$ -NMR of Phthalonitrile **3c**, recorded in  $\text{CDCl}_3$ .

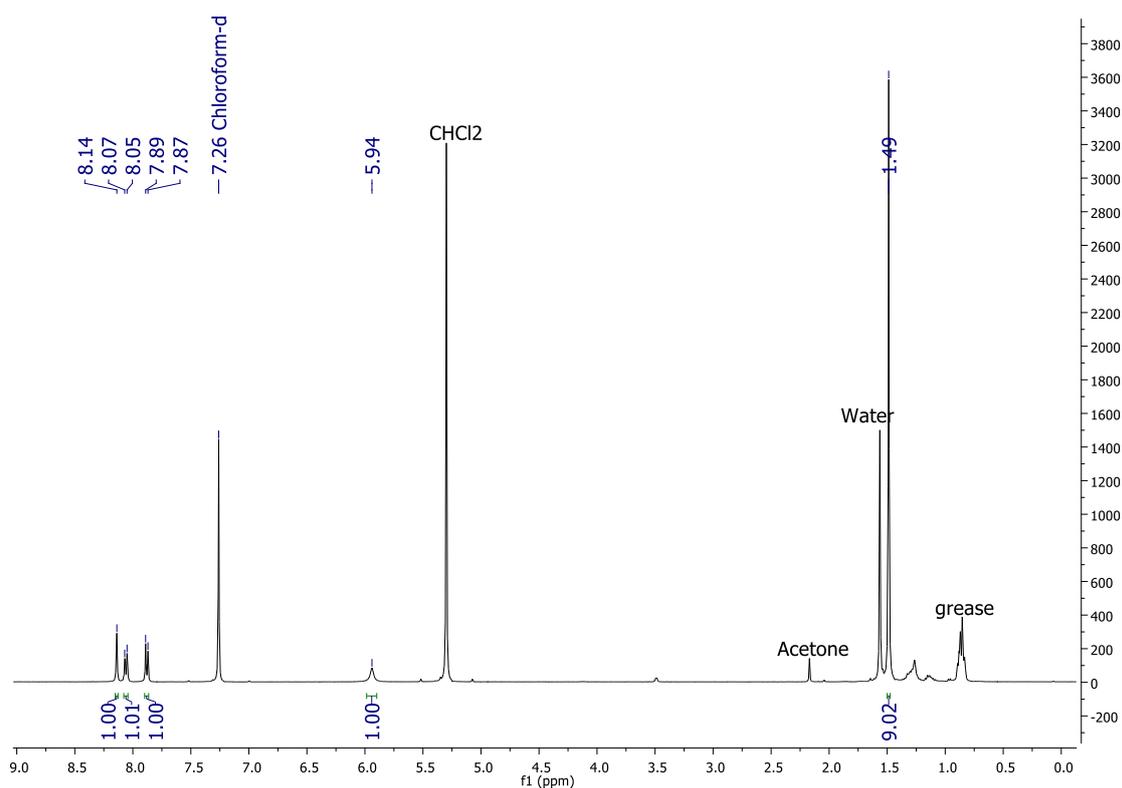
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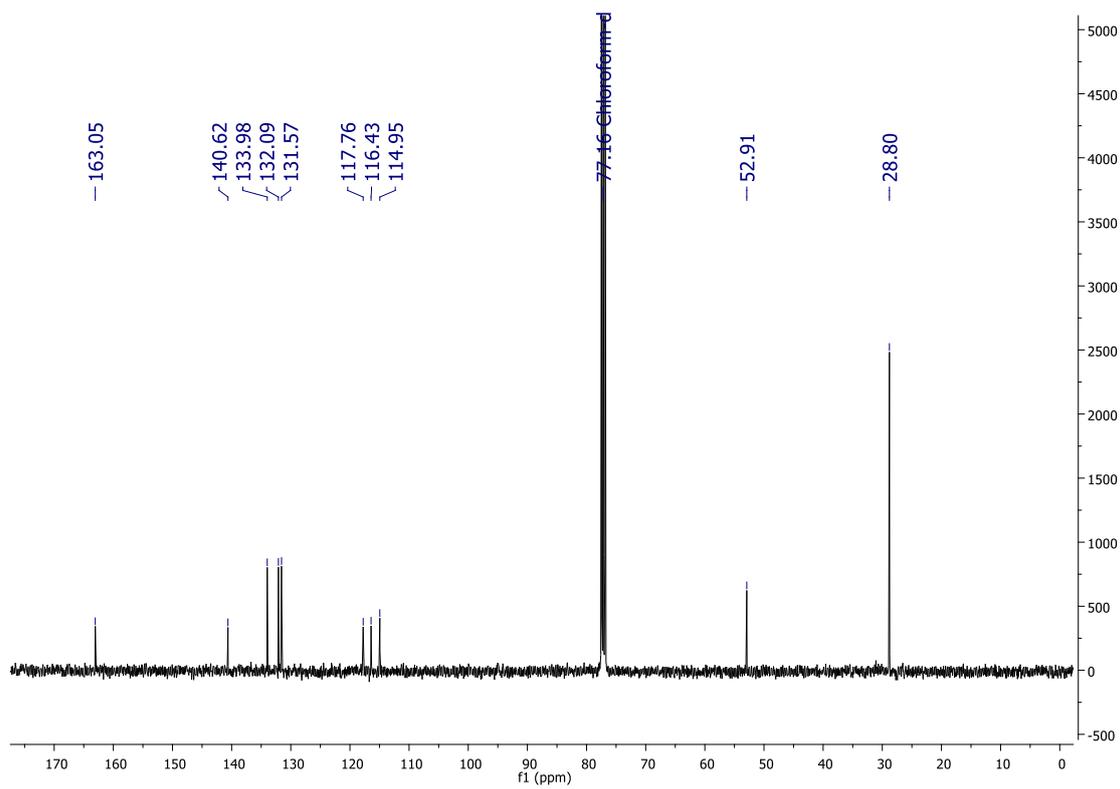
**Fig. 9.** Mass spectrum of Phthalonitrile **3c**.

#### 1.4. Phthalonitrile **3d**

***N*-tert-butyl-3,4-dicyanobenzamide (3d)**. Following the above described procedure, 4.4 mg (0.020 mmol) of Pd(OAc)<sub>2</sub>, 10.5 mg (0.040 mmol) of PPh<sub>3</sub>, 200 mg (0.79 mmol) of 4-iodophthalonitrile, 0.28 mL (2.6 mmol) of *tert*-butyl amine (**2d**) and 0.8 mL Et<sub>3</sub>N were dissolved in 6 mL of toluene. The reaction was pressurized and maintained at 100 °C for 4 hours. The residue was dissolved in dichloromethane (20 mL), washed with brine (3x20 mL) and water (3x20 mL). The organic phase was dried with sodium sulfate and the solvent evaporated. The product (**3d**) was purified by column chromatography on silica gel (stationary phase) using a mixture of dichloromethane/ethyl acetate (20/1) and obtained in 74% yield (132.9 mg). <sup>1</sup>H-RMN (400.13 MHz, CDCl<sub>3</sub>) δ 8.14 (sl, 1H), 8.06 (d, *J*=8.1Hz, 1H), 7.88 (d, *J*=8.1Hz, 1H), 5.94 (br s, 1H), 1.49 (s, 9H). <sup>13</sup>C-RMN (100.61 MHz, CDCl<sub>3</sub>) δ 163.1, 140.6, 134.0, 132.1, 131.6, 117.8, 116.4, 115.0, 53.0, 28.8. HRMS (EI) *m/z* calcd for [M]<sup>+</sup>: C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O 227.1059; found: 227.1060.



**Fig. 10.** <sup>1</sup>H-NMR of Phthalonitrile **3d**, recorded in CDCl<sub>3</sub>.



**Fig. 11.**  $^{13}\text{C}$ -NMR of Phthalonitrile **3d**, recorded in  $\text{CDCl}_3$ .

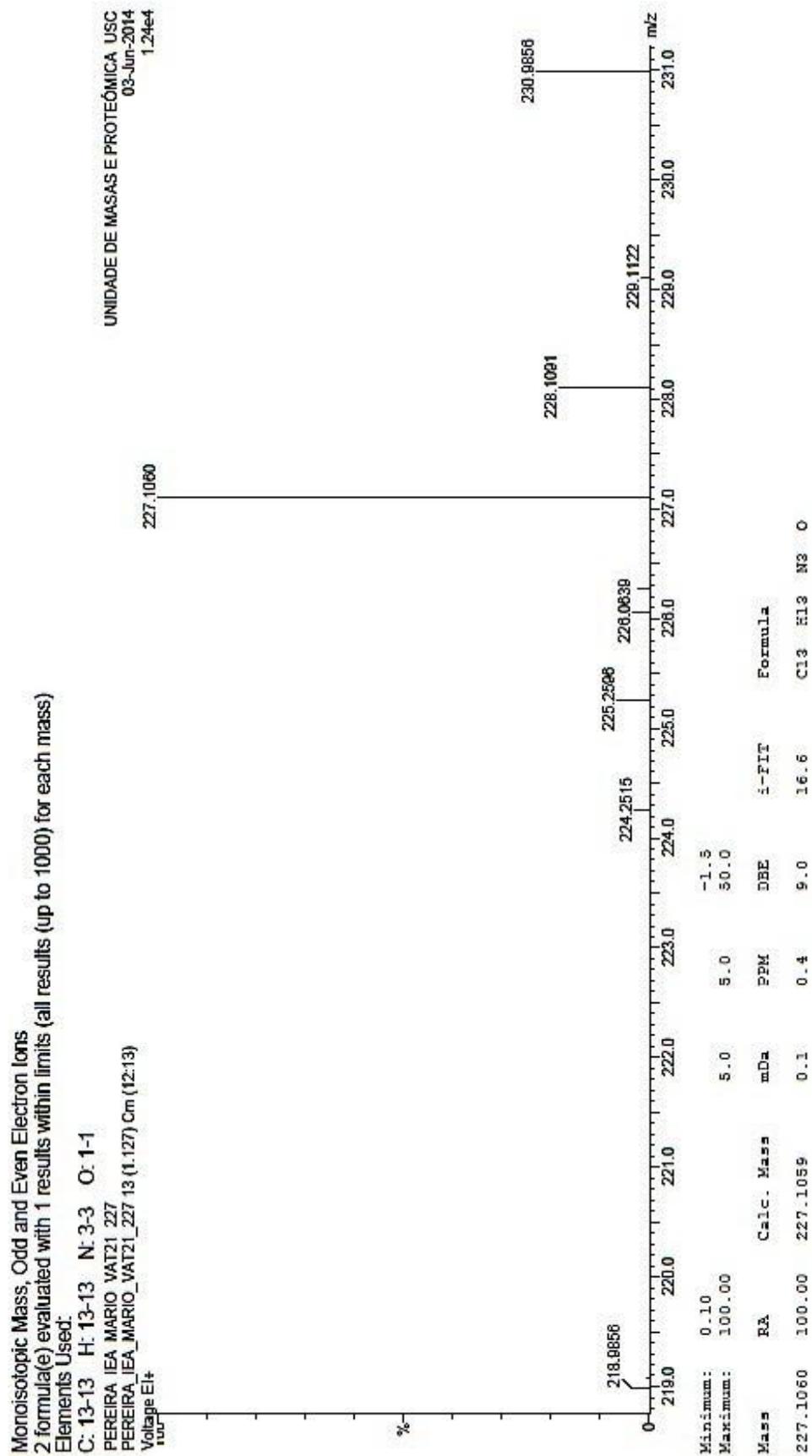
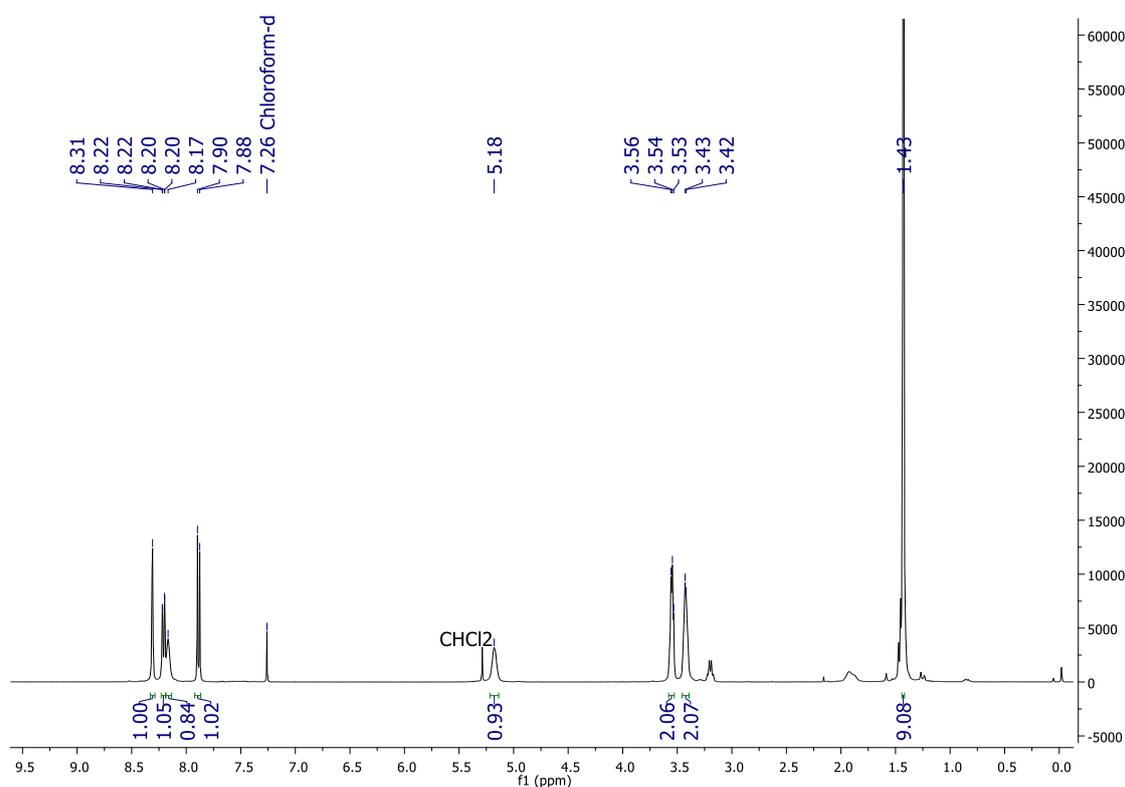


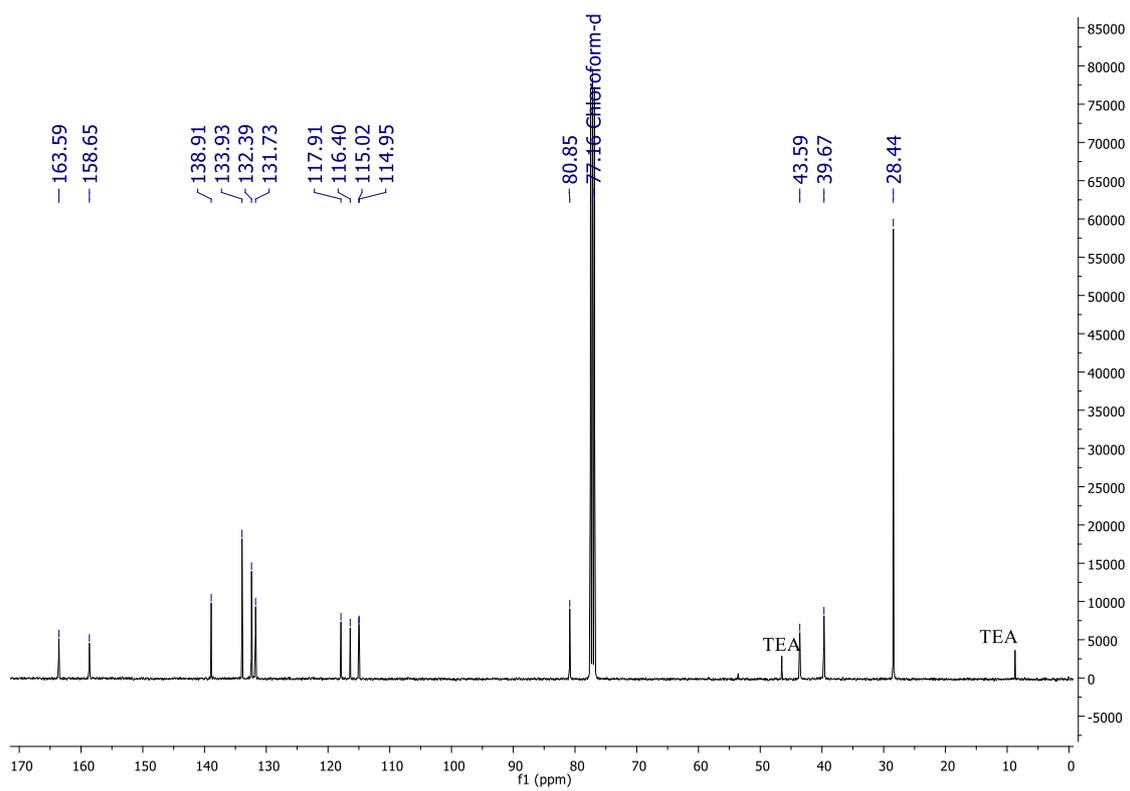
Fig. 12. Mass spectrum of Phthalonitrile 3d.

### 1.5. Phthalonitrile **3e**

***N*-BOC-ethylenediamine-3,4-dicyanobenzamide (**3e**)**. Following the above described procedure, 4.4 mg (0.020 mmol) of Pd(OAc)<sub>2</sub>, 10.5 mg (0.040 mmol) of PPh<sub>3</sub>, 200 mg (0.79 mmol) of 4-iodophthalonitrile, 151 mg (0.94 mmol) of *N*-BOC-ethylenediamine (**2e**) and 0.8 mL Et<sub>3</sub>N were dissolved in 6 mL toluene. The reaction was pressurized and maintained at 100 °C for 3 hours. The product (**3e**) precipitated in the middle of the reaction and then was washed with *n*-hexane and obtained in 80% yield (198.5 mg). <sup>1</sup>H-RMN (400.13 MHz, CDCl<sub>3</sub>) δ 8.31 (sl, 1H), 8.21 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.17 (br s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 5.18 (br s, 1H), 3.56-3.53 (m, 2H), 3.43-3.41 (m, 2H), 1.43 (s, 9H). <sup>13</sup>C RMN (100.61 MHz, CDCl<sub>3</sub>) δ 163.6, 158.7, 138.9, 133.9, 132.4, 131.7, 117.9, 116.4, 115.0, 114.9, 80.9, 43.6, 39.7, 28.4. HRMS (ESI-TOF) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>NaO<sub>3</sub> 337.1271; found 337.1271.



**Fig. 13.** <sup>1</sup>H-NMR of Phthalonitrile **3e**, recorded in CDCl<sub>3</sub>.



**Fig. 14.**  $^{13}\text{C}$ -NMR of Phthalonitrile **3e**, recorded in  $\text{CDCl}_3$ .

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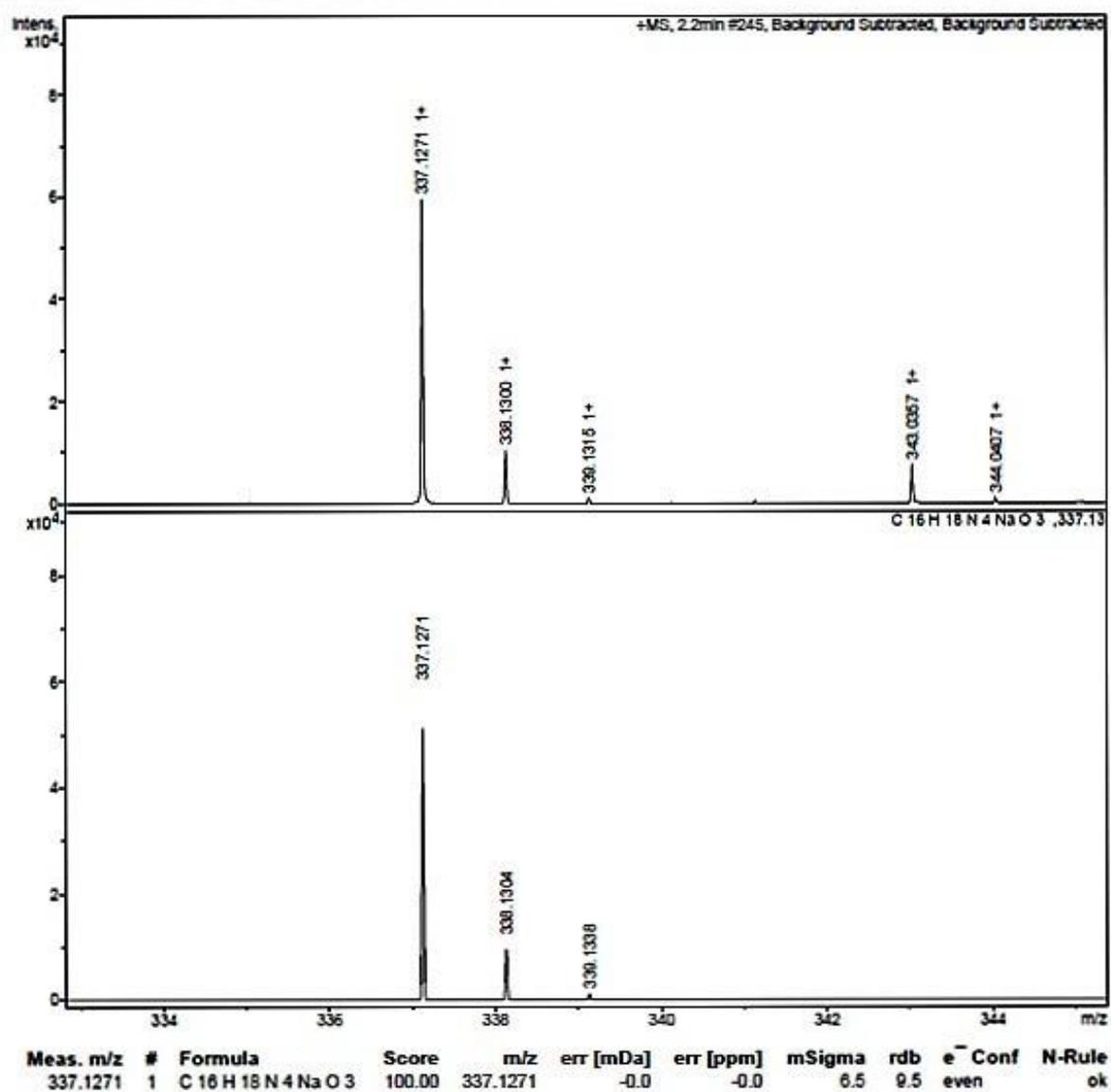
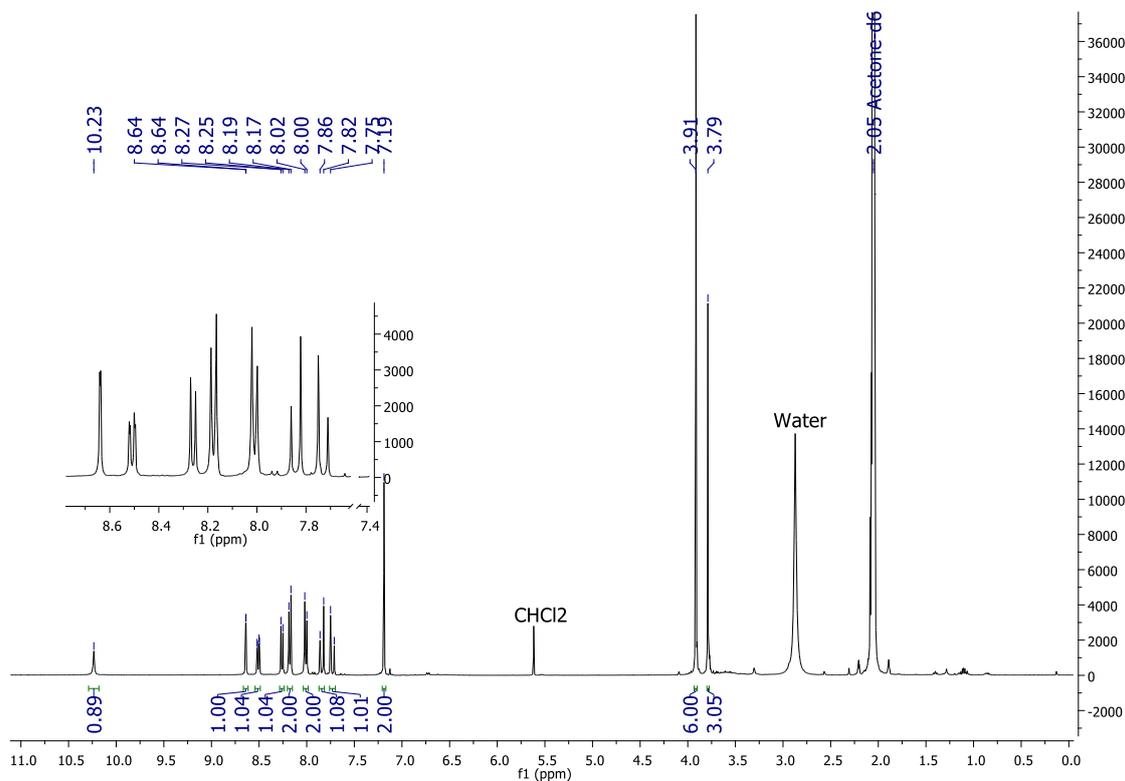


Fig. 15. Mass spectrum of Phthalonitrile **3e**

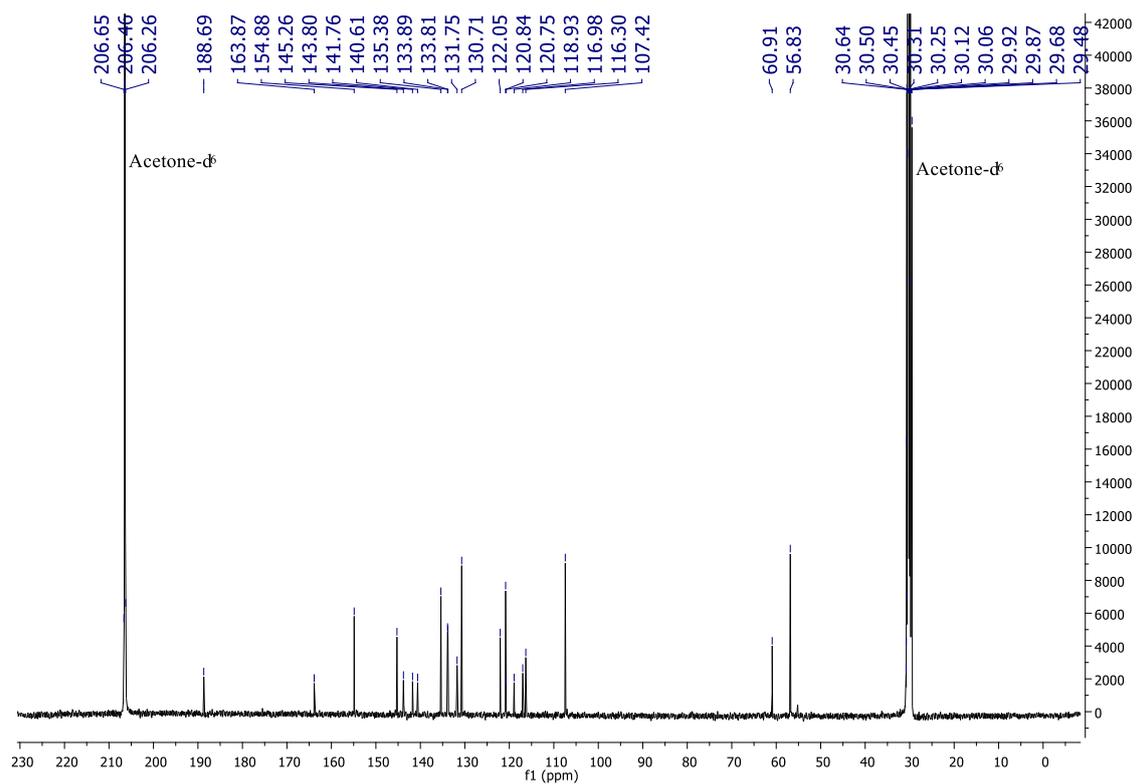
### 1.6. Phthalonitrile **3f**

#### **(E)-3,4-dicyano-N-(4-(3-(3,4,5-trimethoxyphenyl)acryloyl)phenyl)benzamide (3f).**

Following the above described procedure, 4.4 mg (0.020 mmol) of Pd(OAc)<sub>2</sub>, 10.5 mg (0.040 mmol) of PPh<sub>3</sub>, 200 mg (0.79 mmol) of 4-iodophthalonitrile, 296 mg (0.94 mmol) of (*E*)-1-(4-aminophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (**2f**) and 0.8 mL Et<sub>3</sub>N were dissolved in 6 mL toluene. The reaction was pressurized and maintained at 100°C for 25 hours. The product (**3f**) precipitated in the middle of reaction and was washed with methanol and cyclohexane and obtained in 70% yield (256 mg). <sup>1</sup>H NMR (400.13 MHz, acetone-d<sub>6</sub>) δ 10.23 (s, 1H), 8.64 (d, *J* = 1.5 Hz, 1H), 8.51 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.18 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 15.5 Hz, 1H), 7.73 (d, *J* = 15.5 Hz, 1H), 7.19 (s, 2H), 3.91 (s, 6H), 3.79 (s, 3H). <sup>13</sup>C NMR (100.61 MHz, acetone-d<sub>6</sub>) δ 188.7, 163.9, 154.9, 145.3, 143.8, 141.8, 140.6, 135.4, 133.9, 133.8, 131.8, 130.7, 122.1, 120.8, 120.7, 118.9, 117.0, 116.3, 107.4, 60.9, 56.8. HRMS (ESI-TOF) *m/z* calcd for [M]<sup>+</sup>: C<sub>27</sub>H<sub>21</sub>N<sub>3</sub>O<sub>5</sub> 468.1554; found 468.1555.



**Fig. 16.** <sup>1</sup>H-NMR of Phthalonitrile **3f**, recorded in CD<sub>3</sub>COCD<sub>3</sub>.



**Fig. 17.**  $^{13}\text{C}$ -NMR of Phthalonitrile **3f**, recorded in  $\text{CD}_3\text{COCD}_3$ .

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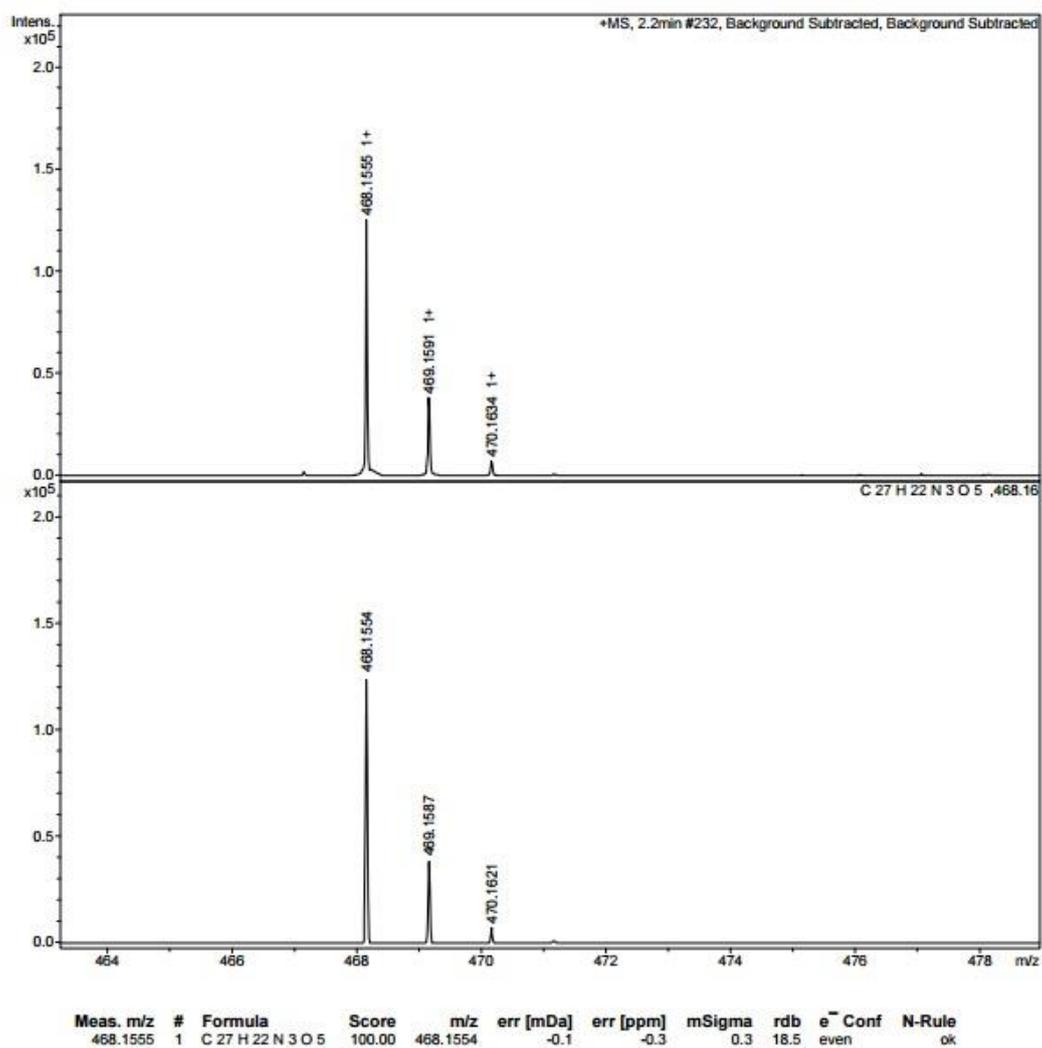
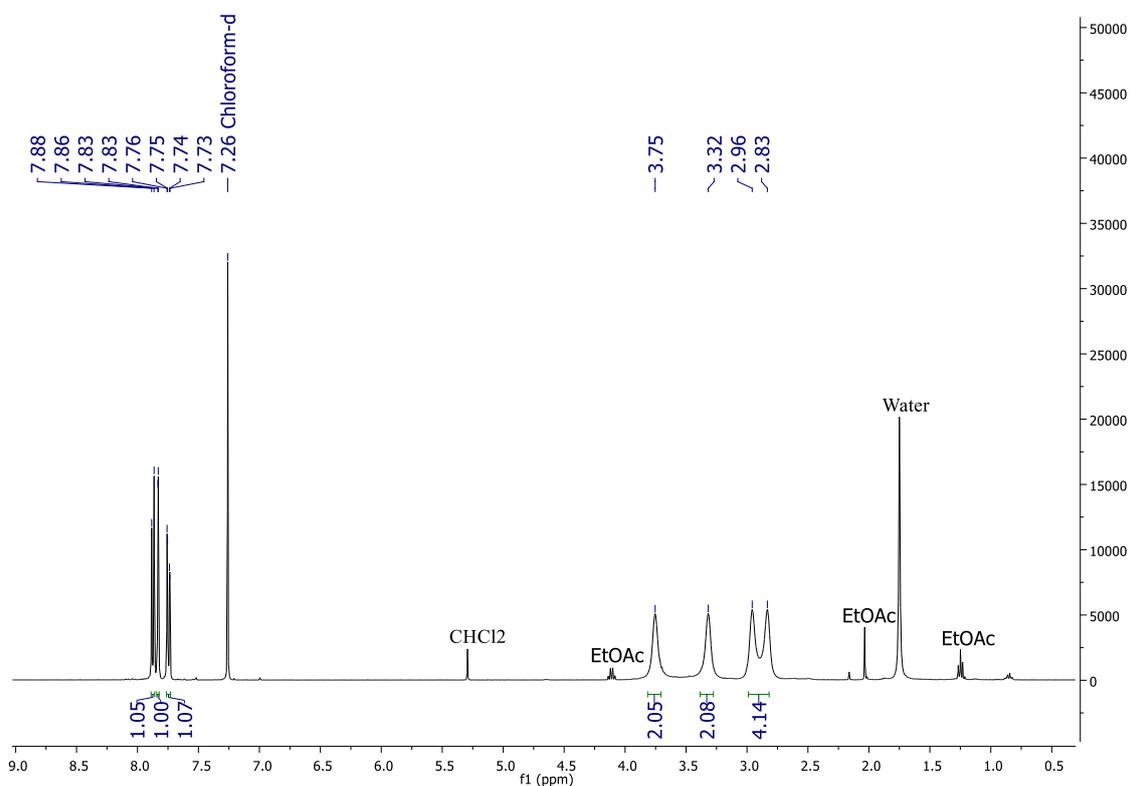


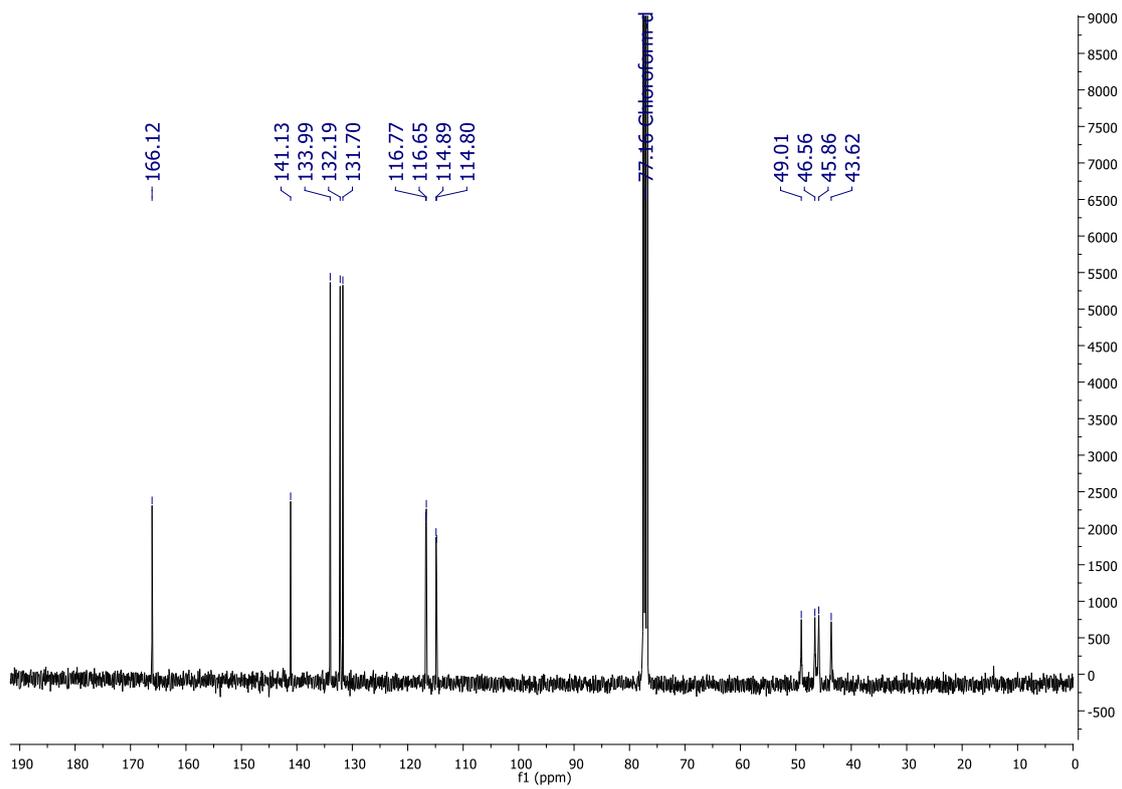
Fig. 18. Mass spectrum of Phthalonitrile 3f.

### 1.7. Phthalonitrile **3g**

***N*-piperazine-3,4-dicyanobenzamide (**3g**)**. Following the above described procedure, 4.4 mg (0.020 mmol) of Pd(OAc)<sub>2</sub>, 10.5 mg (0.040 mmol) of PPh<sub>3</sub>, 200 mg (0.79 mmol) of 4-iodophthalonitrile, 407 mg (4.72 mmol) piperazine (**2g**) and 0.8 mL Et<sub>3</sub>N were dissolved in 6 mL toluene. The reaction was pressurized and maintained at 100 °C for 7 hours. The product (**3g**) was purified by column chromatography on silica gel (stationary phase) using ethanol as eluent and obtained in 77% yield (146 mg). <sup>1</sup>H RMN (400.13 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 1.3 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.75 (s, 2H), 3.32 (s, 2H), 2.90 (d, *J* = 49.8 Hz, 4H). <sup>13</sup>C RMN (100.61 MHz, CDCl<sub>3</sub>) δ 166.1, 141.1, 134.0, 132.2, 131.7, 116.8, 116.7, 114.9, 114.8, 49.0, 46.6, 45.9, 43.6. HRMS (ESI-TOF) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>13</sub>H<sub>13</sub>N<sub>4</sub>O 241.1084; found 241.1081.



**Fig. 19.** <sup>1</sup>H-NMR of Phthalonitrile **3g**, recorded in CDCl<sub>3</sub>.



**Fig. 20.**  $^{13}\text{C}$ -NMR of Phthalonitrile **3g**, recorded in  $\text{CDCl}_3$ .

## Medida De Masas Exactas

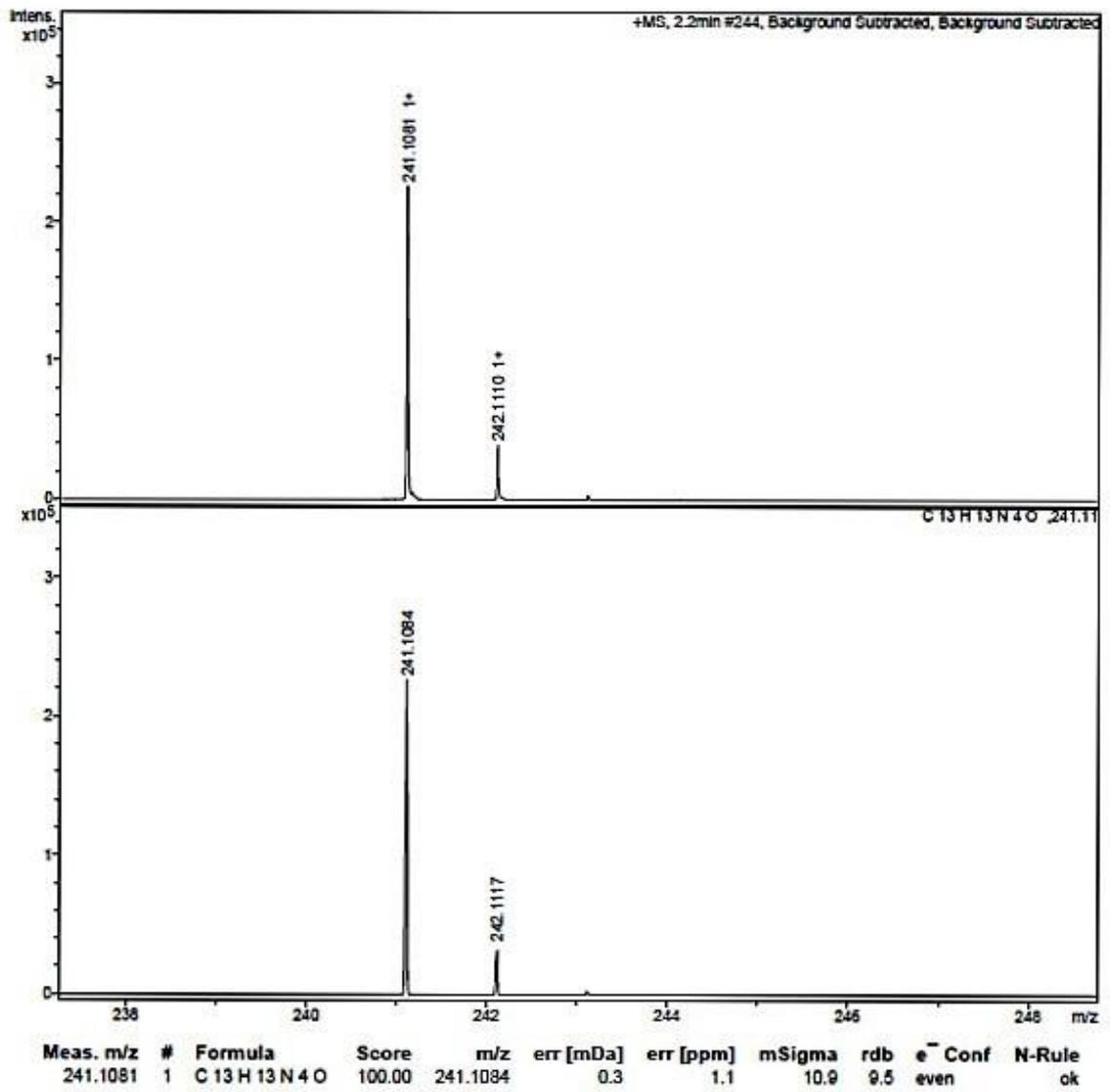
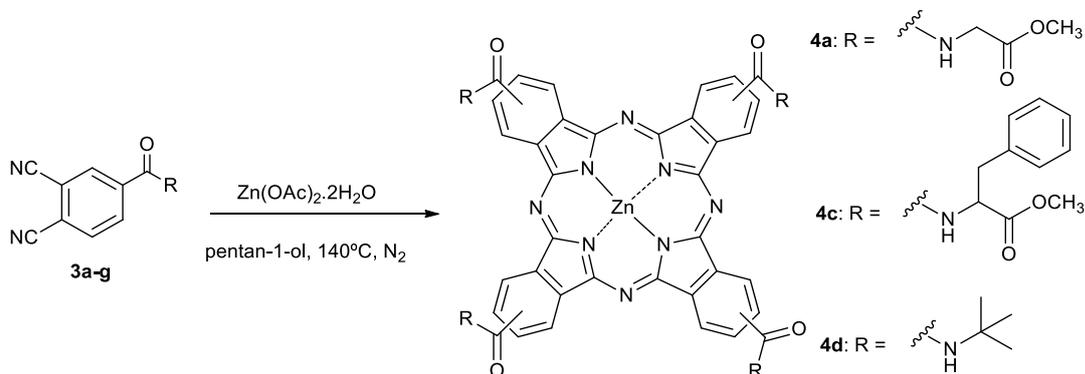


Fig. 21. Mass spectrum of Phthalonitrile 3g.

## 2. Experimental procedures for the synthesis of phthalocyanines and copies of $^1\text{H}$ NMR and Mass Spectra



**General procedure for synthesis of carboxamide substituted phthalocyanines.** In a typical experiment, the desired phthalonitrile and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  were dissolved in high boiling solvent pentan-1-ol and the mixture heated to reflux temperature for the required time for total consumption of the substrate (checked by TLC) under nitrogen atmosphere. After distilling off most of the solvent, the mixture was cooled to room temperature, and *n*-hexane was added to precipitate the crude compound. The solid was filtered, washed with water and purified according to the corresponding procedure and characterized by means of  $^1\text{H}$  NMR, UV-vis, fluorescence and mass spectrometry.

### 2.1. Phthalocyanine 4a

**2(3)-Tetra-(keto-*N*-glyciny) phthalocyaninato zinc(II) (4a).** Following the procedure described above, 100 mg of phthalonitrile **3a** (0.41 mmol) and 29.7 mg  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.14 mmol) were dissolved in 1 mL of pentan-1-ol. The mixture was heated to  $140^\circ\text{C}$  and stirred for 20 hours. After workup procedure, the zinc(II) phthalocyanine complex **4a** was purified by column chromatography on silica gel first using dichloromethane/ethyl acetate (1/1) and then a mixture of dichloromethane /ethanol (20/1) as eluent to obtain 62 mg of **4a** (58% yield), as a waxy dark blue solid. UV-vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 350 (4.52), 611 (4.22), 676 (4.87).  $^1\text{H}$ -RMN (400.13 MHz, acetone- $d_6$ ,  $30^\circ\text{C}$ )  $\delta$  8.46 (br s, 4H), 8.34 (d,  $J=7.7$  Hz, 4H), 8.29 (s, 4H), 7.94 (d,  $J=7.7$ Hz, 4H), 4.04-3.94 (m, 8H), 2.76 (s, 12H). MS (MALDI-TOF-INFUSION)  $m/z$  calcd for  $[\text{M}+\text{Li}]^+$ :  $\text{C}_{48}\text{H}_{36}\text{N}_{12}\text{O}_{12}\text{LiZn}$  1043.2023; found 1043.2050. EA calcd for  $\text{C}_{48}\text{H}_{36}\text{N}_{12}\text{O}_{12}\text{Zn} \cdot 2\text{C}_5\text{H}_{12}\text{O} \cdot 2\text{H}_2\text{O}$  C, 55.70; H, 5.16; N, 13.44; found C, 55.55; H, 5.35; N, 13.50.

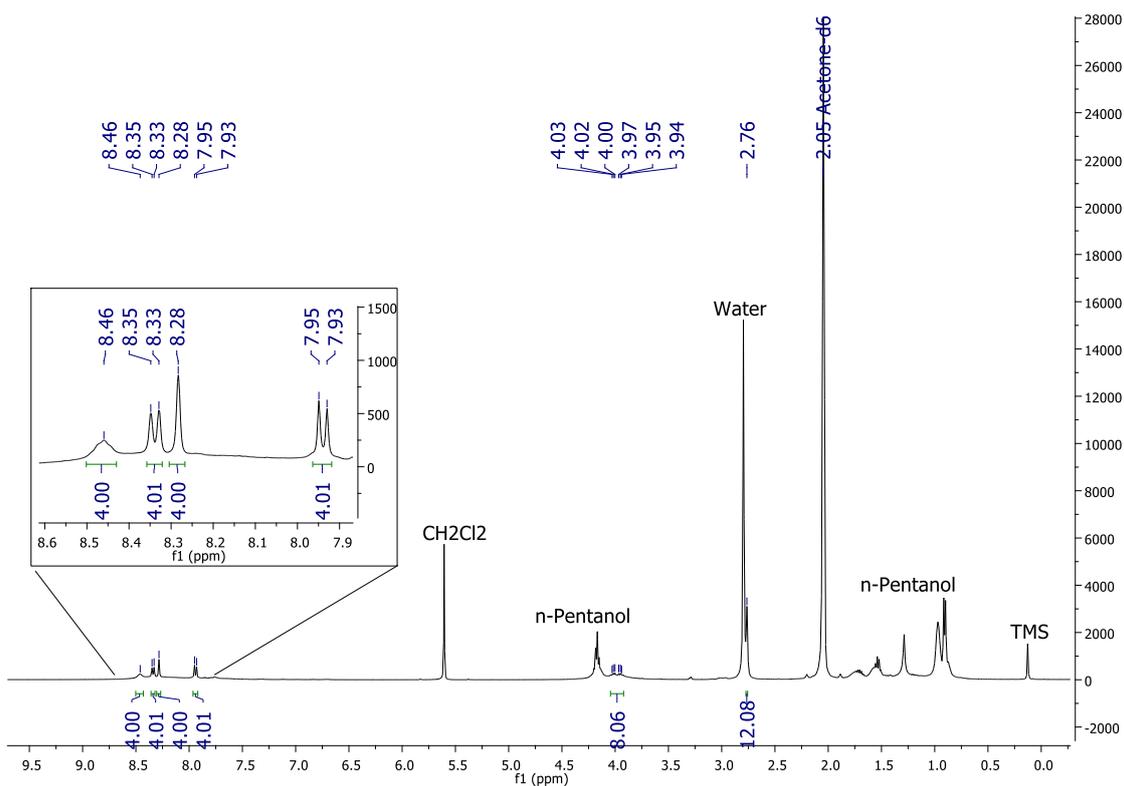
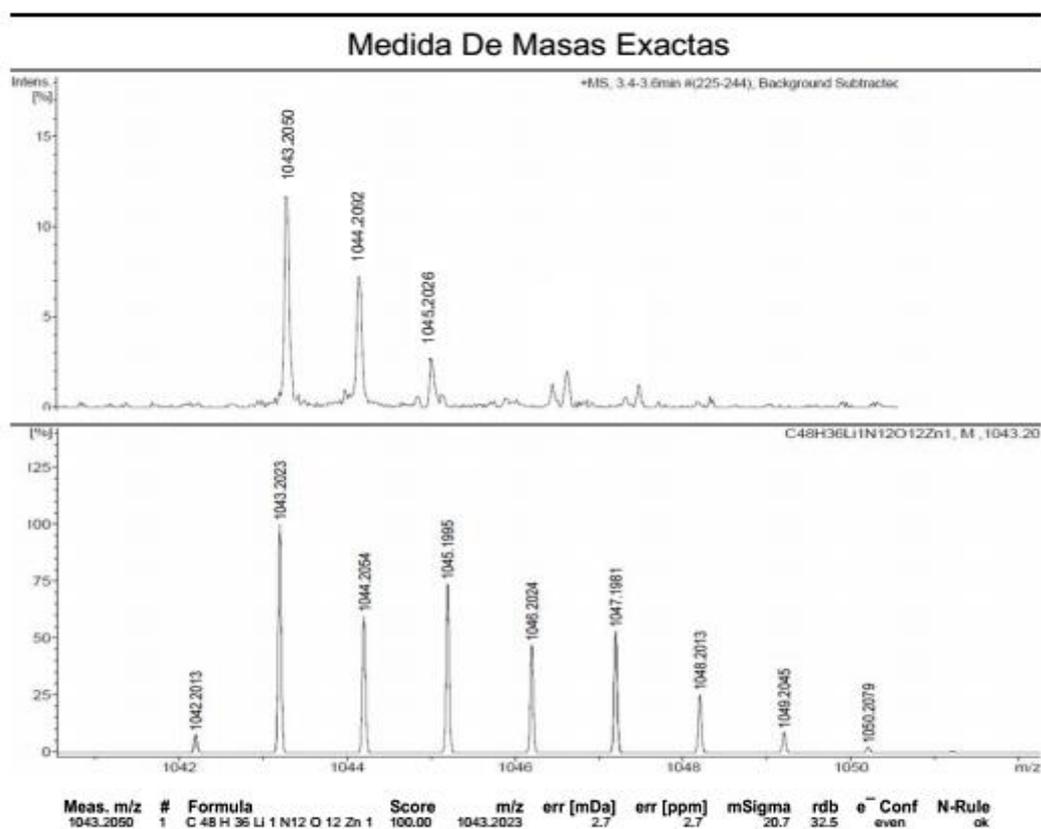


Fig. 22.  $^1\text{H-NMR}$  of Phthalocyanine **4a**, recorded in  $\text{CD}_3\text{COCD}_3$ .

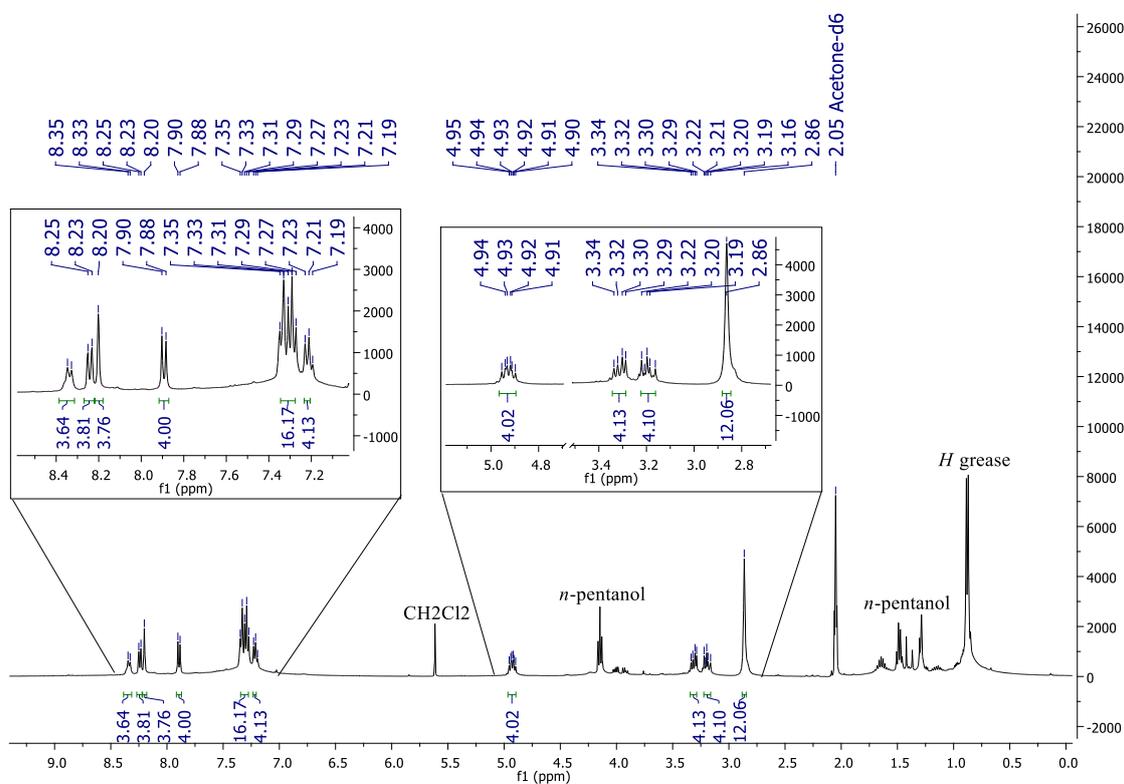


**Fig. 23.** Mass spectrum of Phthalocyanine **4a**.

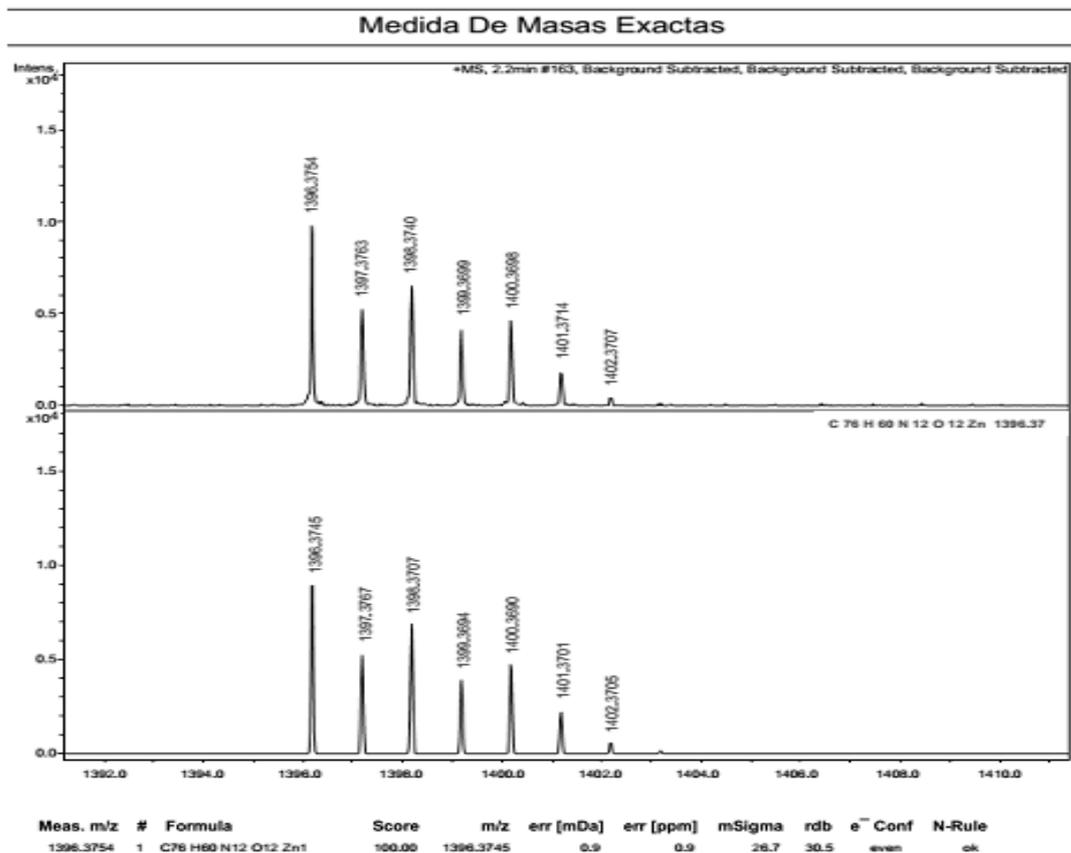
## 2.2. Phthalocyanine **4c**

### **(S,S,S,S)-2(3)-Tetra-(keto-N-phenyl alaninyl) phthalocyaninato zinc(II) (4c).**

Following the procedure described above, 45 mg of phthalonitrile **3c** (0.14 mmol) and 11 mg  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.05 mmol) were dissolved in 0.5 mL of pentan-1-ol. The mixture was heated to 140 °C and stirred for 20 hours. After workup procedure, the zinc(II) phthalocyanine complex **4c** was purified by column chromatography on silica gel first using dichloromethane/ethyl acetate (5/1) and then a mixture of dichloromethane/ethanol (20/1) as eluent to obtain 32 mg of **4c** (65% yield), as a waxy dark blue solid. UV-Vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 350 (4.14), 610 (3.81), 675 (4.48).  $^1\text{H}$  RMN (400.13 MHz, acetone- $d_6$ )  $\delta$  8.34 (br s, 4H), 8.24 (d,  $J=7.8\text{Hz}$  4H), 8.20 (s, 4H), 7.89 (d,  $J=7.7\text{Hz}$ , 4H), 7.27 (2m, 20H), 4.93 (m, 4H), 3.31 (m, 4H), 3.19 (m, 4H), 2.86 (s, 12H). MS (ESI-TOF-INFUSION)  $m/z$  calcd for  $[\text{M}]^+$ :  $\text{C}_{76}\text{H}_{60}\text{N}_{12}\text{O}_{12}\text{Zn}$  1396.3745; found 1396.3754. EA calcd for  $\text{C}_{76}\text{H}_{60}\text{N}_{12}\text{O}_{12}\text{Zn} \cdot 2\text{C}_5\text{H}_{12}\text{O} \cdot \text{H}_2\text{O}$  C, 64.84; H, 5.44; N, 10.55; found C, 64.59; H, 5.75; N, 10.83.



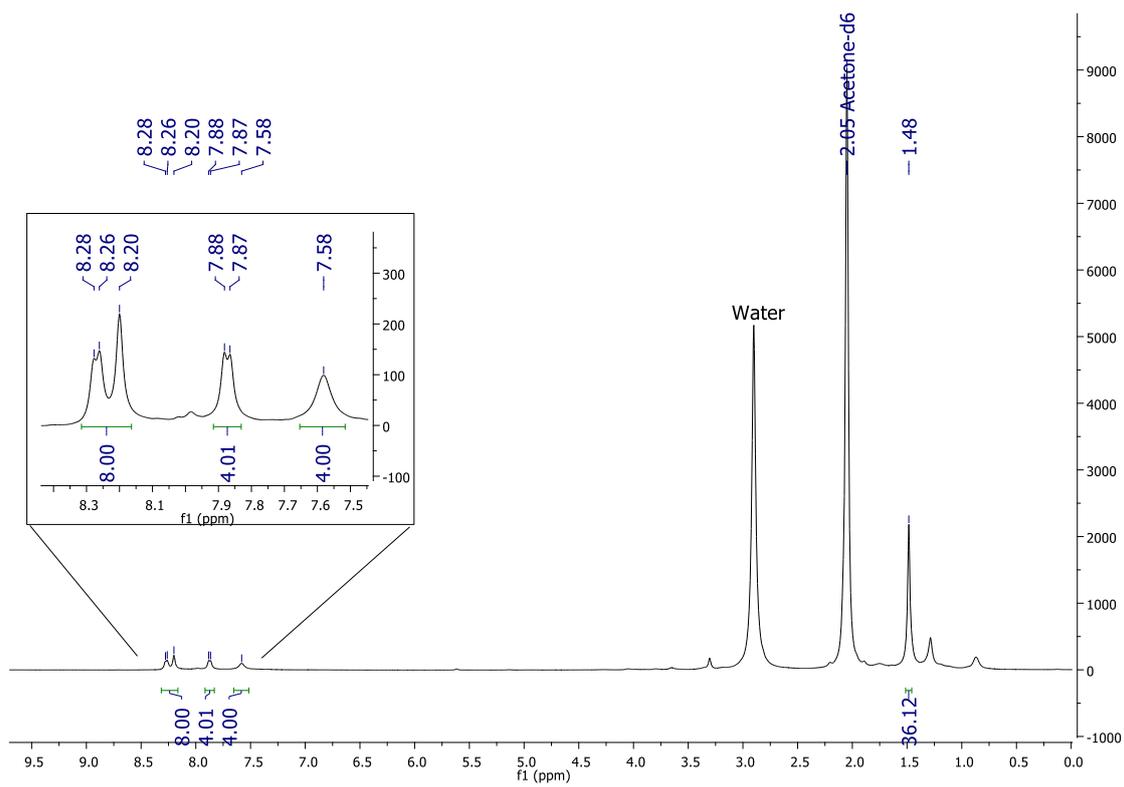
**Fig. 24.**  $^1\text{H}$ -NMR of Phthalocyanine **4c**, recorded in acetone- $d_6$ .



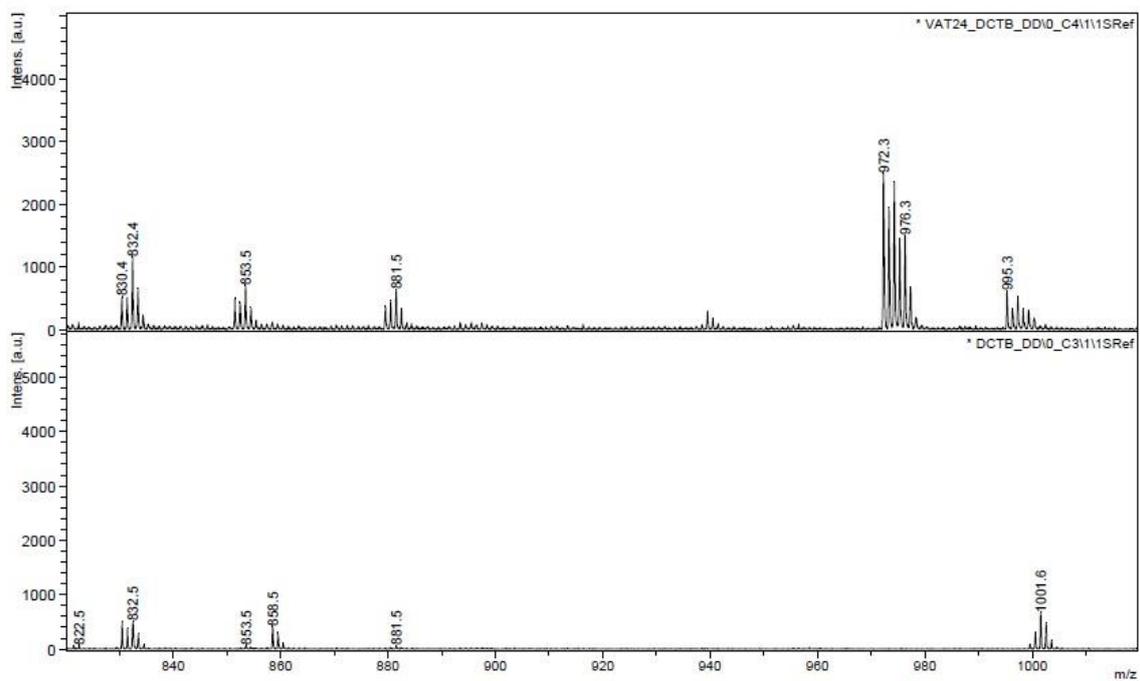
**Fig. 25.** Mass spectrum of Phthalocyanine **4c**.

### 2.3. Phthalocyanine **4d**

**2(3)-Tetra(*tert*-butyl-carboxamidyl) phthalocyaninato zinc(II) (**4d**).** Following the procedure described above, 100 mg of phthalonitrile **3d** (0.44 mmol) and 32.9 mg Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.15 mmol) were dissolved in 0.5 mL of pentan-1-ol. The mixture was heated to 140 ° C and stirred for 20 hours. After workup procedure, the zinc(II) phthalocyanine complex (**4d**) was purified by column chromatography on silica gel using a mixture dichloromethane/methanol (20/1) as eluent to obtain 74 mg of (**4d**) (68% yield), as a dark blue solid. UV-Vis (THF)  $\lambda_{\max}$  (log  $\epsilon$ ) 351 (4.41), 610 (4.49), 676 (5.10). <sup>1</sup>H RMN (400.13 MHz, acetone-*d*<sub>6</sub>)  $\delta$  8.26-8.20 (br s, 8H), 7.88-7.86 (br s, 4H), 7.58 (sl, 4H), 1.48 (s, 36H). MS (MALDI-TOF) *m/z* calcd for [M]<sup>+</sup>: C<sub>52</sub>H<sub>52</sub>N<sub>12</sub>O<sub>4</sub>Zn 972.3; found 972.3; [M+Na]<sup>+</sup>, *m/z*: 995.3. EA calcd for C<sub>52</sub>H<sub>52</sub>N<sub>12</sub>O<sub>4</sub>Zn\*2H<sub>2</sub>O C, 61.81; H, 5.59; N, 16.63; found C, 62.06; H, 5.50; N, 16.43.



**Fig. 26.**  $^1\text{H-NMR}$  of Phthalocyanine **4d**, recorded in  $\text{CD}_3\text{COCD}_3$ .



**Fig. 27.** Mass spectrum of Phthalocyanine **4d**.