



## Research on a New Synthesis of LLM-105 Using N-Nitroso-bis(cyanomethyl)amine

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**Abstract:** A new three-step synthetic method was designed to prepare 2,6-diamino-3,5-dinitropyrazine 1-oxide (LLM-105) with an overall yield of 43.5%, using iminodiacetonitrile, triethylamine and hydroxylamine hydrochloride as the starting materials, and involved nitrosylation, cyclization and nitration. The structure of LLM-105 was characterized by FTIR, <sup>1</sup>H NMR spectroscopy and elemental analysis. The crucial factors and mechanism of the cyclization were explored. Thermal decomposition, mechanical sensitivity and the purity of the LLM-105 were determined by TG-DTA, an impact sensitivity instrument and high performance liquid chromatography (HPLC) respectively. The results showed that LLM-105 synthesised via 2,6-diamino-3,5-dinitropyrazine (ANPZ) was less sensitive to impact, but the LLM-105 synthesized by the new method had some obvious advantages in terms of purity, security and production costs. Moreover, the LLM-105 synthesized by this new method can be initiated reliably without recrystallization.

**Keywords:** LLM-105, energetic materials, synthesis, characterization, properties

### 1 Introduction

2,6-Diamino-3,5-dinitropyrazine 1-oxide (LLM-105) is a realistic high-performance energetic material [1]. LLM-105 has attracted substantial attention from researchers in the energetic materials field [2-7]. It is very thermally stable and insensitive to shock, spark and friction because of the extensive  $\pi$  conjugated system and the intra- and inter-molecular hydrogen bonds between molecules [8, 9]. Besides, LLM-105 is an energetic heterocyclic compound with a density

of 1.913 g/cm<sup>3</sup> and 25% more energy than TATB (81% of HMX). LLM-105 can be used in military and civil applications, such as insensitive boosters, main charge explosives and deep oil well exploration based on its excellent properties [10-13]. Although alternative routes for LLM-105 synthesis have been reported, most of them proceed through the intermediate compound 2,6-diamino-3,5-dinitropyrazine (ANPZ), which is then oxidized with trifluoroacetic acid and hydrogen peroxide to yield LLM-105. Over the years this route has been refined and optimized to give LLM-105 in a 65% [14] overall yield, but many problems still exist with this method, such as a complicated process, the existence of hidden danger and poor product purity (LLM-105 syntheses from ANPZ contains 3-10% ANPZ; it is difficult to separate ANPZ from LLM-105). In recent years, some new methods proceeding through 2,6-diaminopyrazine 1-oxide (AHAPO) [15] have been reported in some US patents, but they cannot be used because of their low production rates and expensive catalysts. The synthetic method using N-chloro-bis(cyanomethyl)amine and N-nitroso-bis(cyanomethyl)amine as starting materials was reported in two American patents [15, 16], but the yield was still unsatisfactory (less than 5%). LLM-105 is mainly used for the main charge explosive of detonating fuses, but LLM-105 synthesized through ANPZ cannot be initiated reliably by a detonator because of its insensitiveness. Therefore, attempts have been made to resolve this problem through recrystallization [17-19].

In the present work, LLM-105 was successfully synthesized and characterized using iminodiacetonitrile, hydroxylamine hydrochloride and N-nitroso-bis(cyanomethyl)amine as the starting materials. The study showed that the new method is simpler and less expensive, the final product can be initiated reliably and does not need to be recrystallized.

## 2 Experimental

### 2.1 Materials

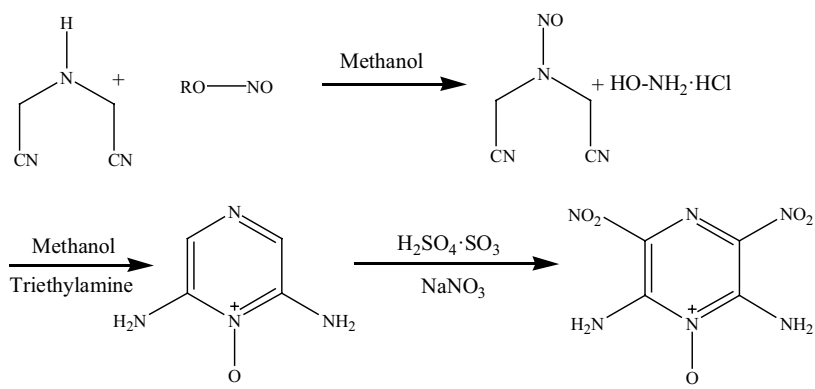
Iminodiacetonitrile (> 98%, CP), hydroxylamine hydrochloride (> 99%, AR), methanol (> 99%, AR), triethylamine (> 99%, AR) were used as the starting compounds for the preparation of 2,6-diaminopyrazine 1-oxide (DAPO). Fuming nitric acid (> 95%, LP) and concentrated sulfuric acid (> 98%, CP) were purchased from TianJin FuYu Corporation (China). RO-NO (99%) was supplied by the North University of China.

## 2.2 Experimental

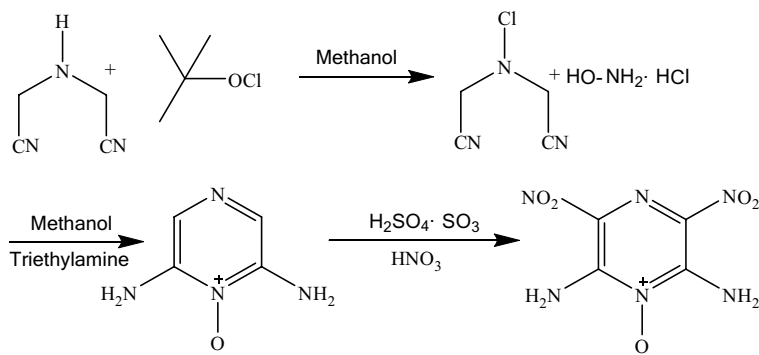
Melting points were determined in open capillaries. Densities were determined experimentally using Archimedes' principle. The IR spectra were recorded on a PerkinElmer Spectrum 100 (FTIR) instrument (America).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker-Avance DRX 500 MHz instrument (Switzerland). Elemental analyses were performed on a HERAEUS 1106 elemental analyzer (Germany). Thermo gravimetry and differential thermal analysis experiments were conducted in a  $\text{N}_2$  atmosphere using a STA 409 PC Luxx Thermo Gravimetry/ Differential Thermal Analysis instrument (NETZSCH Company, Germany). The test conditions were: sample mass 0.7 mg;  $\text{N}_2$  flow rate 15 mL/min and sample heating rate  $10 \text{ K}\cdot\text{min}^{-1}$ . The impact sensitivity of LLM-105 was tested at room temperature using an ERL type 12 drop hammer apparatus with a sample mass of  $35 \pm 1 \text{ mg}$  and a drop weight of  $5 \pm 0.002 \text{ kg}$ . Four groups of samples and 25 trials of the same sample from each group were tested. The results were obtained in terms of the critical drop-height of 50% explosion probability ( $H_{50}$ ) and the standard deviation (S).

## 2.3 Synthesis

The synthetic route is shown in Scheme 1, which is similar to the method of Pagoria and Mao [16] (Scheme 2). Some modifications were made in order to increase the yields in each step. Using RO-NO instead of t-butyl hypochlorite in step 1, the yield of DAPO was increased from 10.7 g (68.0%) to 12.8 g (81.2%), while the use of sodium nitrate instead of concentrated nitric acid caused the rate to be easier to control.



**Scheme 1.** The synthesis of LLM-105 with RO-NO.



**Scheme 2.** The synthesis of LLM-105 with t-butyl hypochlorite.

### 2.3.1 Synthesis of *N*-nitroso-bis(cyanomethyl)amine

Methanol (40 mL) was transferred to a 250 mL three-necked round-bottomed flask fitted with a mechanical stirrer, dropping funnel and reflux condenser, at 0-5 °C (ice-water cooling bath), and iminodiacetonitrile (6.5 g) was added with continuous stirring. Subsequently RO-NO (0.065 mol) was added via dropping funnel, the speed of addition being controlled so that the reaction temperature did not exceed 10 °C. One hour later, the mixture was allowed to warm to 20 °C for another hour. The mixture changed to a pale yellow solution. Yield: 98.6%. FTIR:  $\nu$  (cm<sup>-1</sup>): 3124, 3260, 1504, 1462, 1408, 1386, 1324, 1234, 1132, 981, 962, 922, 849, 733. Anal. calcd. for C<sub>4</sub>H<sub>4</sub>N<sub>4</sub>O: C 38.09, H 4.08, N 44.42; found C 38.22, H 4.05, N 44.37%; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz),  $\delta$ : 3.67 (s, 2H, CH<sub>2</sub>)

### 2.3.2 Preparation of DAPO

Hydroxylamine hydrochloride (5.0 g) was added to the solution of *N*-nitroso-bis(cyanomethyl)amine (6.5 g) in methanol (100 mL) at 0-5 °C. Triethylamine (30 mL) was also added via dropping funnel and the speed of addition was controlled so that the reaction temperature did not exceed 15 °C. After the addition was complete, the reaction mixture was stirred in the cooling bath for 30 min. The mixture was then stirred at room temperature for 3 h. The precipitate was collected by filtration, and washed with methanol to give DAPO (4.32 g, 68.0%). m.p.: 295-296 °C; FTIR:  $\nu$  (cm<sup>-1</sup>): 3399, 3260, 3117, 1609, 1542, 1485, 1641, 1394, 1312, 1266, 1229, 1162, 1069, 836, 810, 733, 710. Anal. calcd. for C<sub>4</sub>H<sub>6</sub>N<sub>4</sub>O: C 38.09, H 4.08, N 44.42; found C 38.22, H 4.05, N 44.37%; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz),  $\delta$ : 6.68 (s, 4H, NH<sub>2</sub>), 7.32 (s, 2H, CH); ESI-MS, m/z: 127 [M+H]<sup>+</sup>.

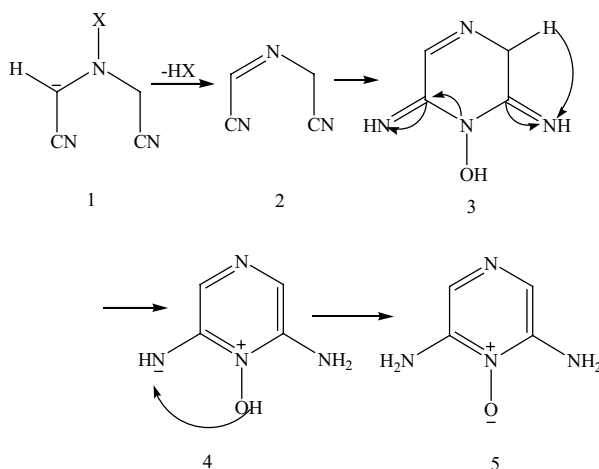
### 2.3.3 Preparation of 2,6-diamino-3,5-dinitropyrazine 1-oxide (LLM-105)

Into a 500 mL three-necked round-bottomed flask, equipped with a mechanical stirrer, thermometer and dropping funnel, was added 15% oleum (105 mL) followed by portion-wise addition of DAPO (5.0 g) with continuous stirring. Sodium nitrate (13.5 g) was added slowly at 15 °C whilst the DAPO dissolved completely. The reaction mixture was stirred at 5-10 °C for 0.5 h and then warmed to 23 °C for 4 h. Finally, the mixture was poured into water (800 mL) to yield a voluminous yellow solid. The precipitate was collected by filtration, washed with water and methanol to yield LLM-105 (4.96 g, 64.1%). m. p.: 274-275 °C; FTIR:  $\nu$  (cm<sup>-1</sup>): 3432, 3404, 3883, 3229, 1647, 1566, 1491, 1378, 1338, 1248, 815, 562, 534. Anal. calcd for C<sub>4</sub>H<sub>4</sub>N<sub>6</sub>O<sub>5</sub>: C 22.23, H 1.87, N 38.89; found C 22.29, H 1.87, N 39.02%; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz),  $\delta$ : 8.78 (s, 2H, NH<sub>2</sub>), 9.06 (s, 2H, NH<sub>2</sub>); ESI-MS, m/z: 215 [M-H]<sup>-</sup>.

## 3 Results and Discussion

### 3.1 Condensation mechanism of DAPO

In the presence of an appropriate base, DAPO can be prepared directly from iminodiacetonitrile derivatives (compound 1 in Scheme 3), where X is a leaving group such as chlorine, bromine, nitroso, nitro group *etc.*



**Scheme 3.** The mechanism of the cyclization reaction.

The X unites with a hydrogenion from the ortho-position to form HX and compound 1 loses HX to become compound 2. Compound 2 then combines with

hydroxylamine hydrochloride to form compound 3. Because of the instability of the two double bonds between carbon and nitrogen, electron transfer, proton transfer and aromatization occur in compounds 3 and 4. Finally, compound 4 is transformed into compound 5.

### 3.2 Effect of different catalysts on the yield of 2,6-diaminopyrazine1-oxide

Iminodiacetonitrile derivatives can be reacted with hydroxylamine derivatives in the presence of an appropriate base, which can be divided into two types, organic and inorganic bases. The yield of DAPO is in the range 0-60%, the effect of the different catalysts on the yield of 2, 6-diaminopyrazine1-oxide is shown in Table 1.

**Table 1.** Effect of different catalysts on the yield of 2,6-diaminopyrazine 1-oxide

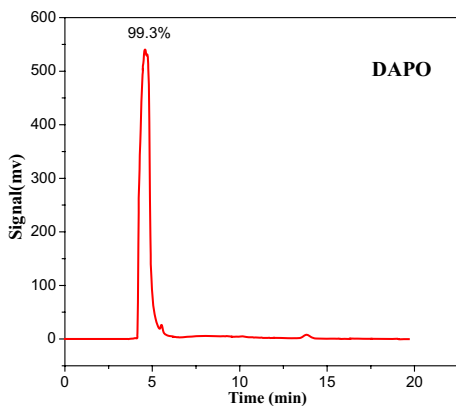
Catalyst	Product, [g]	Yield, [%]
CH <sub>3</sub> CH <sub>2</sub> ONa	1.24 <sup>a</sup>	14.6
CH <sub>3</sub> ONa	1.82 <sup>a</sup>	21.3
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	4.80 <sup>a</sup>	68.0
C <sub>4</sub> H <sub>11</sub> N	2.43 <sup>a</sup>	28.6
Na <sub>2</sub> CO <sub>3</sub>	0 <sup>a</sup>	0
NaHCO <sub>3</sub>	0 <sup>a</sup>	0
NaOH	0 <sup>a</sup>	0

<sup>a</sup> The mass ratio of hydroxylamine hydrochloride and N-nitroso-bis(cyanomethyl)amine was 5.0 g:6.5 g. The reaction temperature was 25 °C.

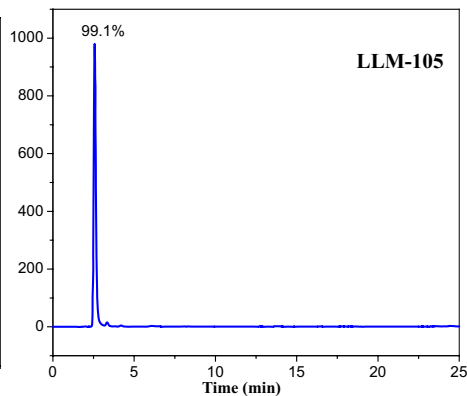
As is shown in Table 1, iminodiacetonitrile derivatives can be reacted with hydroxylamine derivatives in the presence of organic bases, the highest DAPO yield was 68.0% when triethylamine was used as the catalyst.

### 3.3 Purity analysis of DAPO and LLM-105

The purity of DAPO was analyzed by high-performance liquid chromatography (HPLC) with an initial mobile phase of acetonitrile-water (3:2). From Figure 1, it can be seen that the purity of DAPO was 99.3%. The purity of LLM-105 was also analyzed by HPLC with an initial mobile phase of methanol-trifluoroacetate (99.97:0.03). From Figure 2, it can be seen that the purity of LLM-105 synthesized via DAPO was 99.1%, while the purity of LLM-105 synthesized via ANPZ was 89-97% [16].



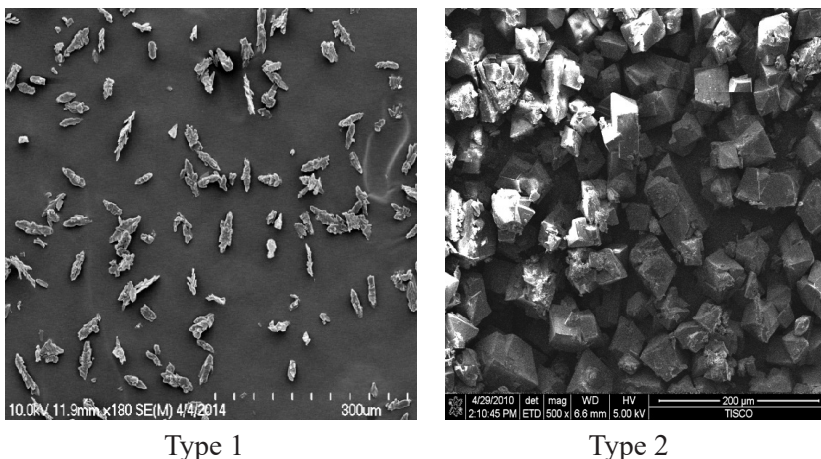
**Figure 1.** HPLC chromatogram of DAPO.



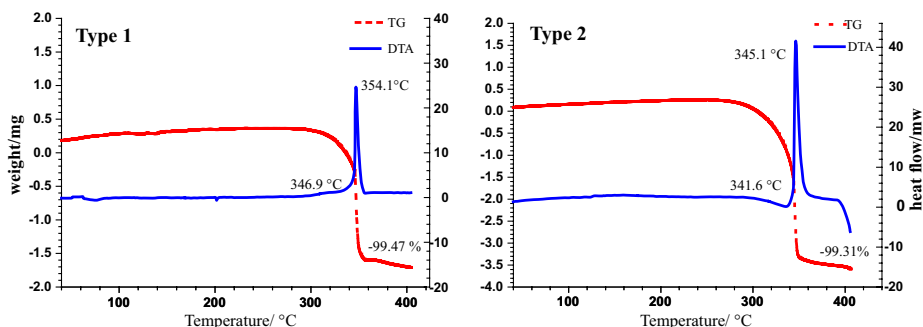
**Figure 2.** HPLC chromatogram of LLM-105.

### 3.4 Morphology characteristics and thermal stability analysis for LLM-105 synthesized by different methods

Figure 3 shows micrograph images of the LLM-105; Type 1 and Type 2 are LLM-105 samples synthesized from DAPO and ANPZ, respectively. Figure 3 (Type 1) shows that the sample particle size ranges from 5 to 60  $\mu\text{m}$ . The samples exhibit incomplete crystal structure and uneven grain size. By contrast, Type 2 crystals have uniform and smooth surfaces, its particle size ranges from 20 to 80  $\mu\text{m}$ .



**Figure 3.** SEM images of different LLM-105 samples.



**Figure 4.** TG-DTA curves of LLM-105 at a heating rate of 10 K/min.

The TG-DTA curves of LLM-105 at a heating rate of 10 K/min under a nitrogen atmosphere are shown in Figure 4. These indicate that the thermal decomposition of LLM-105 consists of one stage only. The TG-DTA curve of Type 1 LLM-105 shows that at  $10\text{ }^{\circ}\text{C min}^{-1}$ , its thermal decomposition process starts at  $345.1\text{ }^{\circ}\text{C}$  with a peak maximum at  $346.9\text{ }^{\circ}\text{C}$ , and is almost complete by  $\sim 349\text{ }^{\circ}\text{C}$ , the total mass loss being 99.47%. The TG-DTA curve of Type 2 LLM-105 shows that the exothermic peak begins at  $341.6\text{ }^{\circ}\text{C}$ , which is caused by the sublimation of the ANPZ contained within the Type 2 LLM-105. This is followed by a single exothermic peak with a peak maximum at  $346.4\text{ }^{\circ}\text{C}$ . The TG curve of Type 2 LLM-105 shows no weight loss until about  $341.6\text{ }^{\circ}\text{C}$ . Beyond  $341.6\text{ }^{\circ}\text{C}$ , the weight loss is slow up to  $345.5\text{ }^{\circ}\text{C}$ , and after that the rate of weight loss increases and is almost complete by  $\sim 351\text{ }^{\circ}\text{C}$ , the total weight loss being 99.31%.

### 3.5 Impact sensitivity and performance

**Table 2.** Impact sensitivity of Type 1 and Type 2 LLM-105

Sample	Impact sensitivity $H_{50}$ , [cm] (standard deviation S)				Average
	Experiment				
	1	2	3	4	
Type 1	47.4 (0.07)	48.4 (0.05)	46.9 (0.09)	47.1 (0.06)	47.2
Type 2	52.1 (0.05)	53.1 (0.06)	51.4 (0.06)	51.8 (0.07)	52.1
Type 3	38.4 (0.07)	39.6 (0.06)	38.9 (0.05)	37.8 (0.05)	38.7

From Table 2, it can be seen that the drop height for Type 2 and Type 3 LLM-105 are higher than that for Type 1 LLM-105 from four replicate experiments. Because the length/diameter ratio of Type 1 is larger than that of



Type 2; particles of Type 1 might be more easily broken under intense impact than those of Type 2.

The performance of braided detonating cord using various types of LLM-105 as the charge is shown in Table 3. Type 3 LLM-105 is recrystallized from dimethyl sulfoxide (DMSO) and water. Type 2 cannot be initiated by a detonator. The velocity of detonation and the density of Type 1 are better than those of Type 3 because of the grading distribution. It is difficult to obtain braided detonating cord with a high density using Type 3 as the charge because of the uniform size.

**Table 3.** Performance of braided detonating cord using different types of LLM-105

Experiment	Velocity of detonation, [ $\text{m}\cdot\text{s}^{-1}$ ] (density, [ $\text{g}\cdot\text{cm}^{-3}$ ])	
	Type 1	Type 3
1	6768 (1.51)	6337 (1.45)
2	6724 (1.50)	6493 (1.45)
3	6733 (1.51)	6291 (1.44)
4	6751 (1.51)	6488 (1.45)
5	6773 (1.51)	6383 (1.45)
Average	6749.5 (1.51)	6399 (1.45)

### 3.6 Cost of LLM-105 synthesized by different methods

We have achieved the scale-up of LLM-105 by ANPZ and DAPO methods respectively, the cost of synthesizing and recrystallizing LLM-105 are showed in Table 4, 5 and 6.

**Table 4.** The cost of synthesizing 1 kg LLM-105 by the ANPZ method

	Material	Amount used/kg	Price (US dollar/kg) <sup>b</sup>
1	methyl alcohol	10 L <sup>b</sup>	0.57 <sup>c</sup>
2	Na	0.81 kg <sup>b</sup>	16 <sup>c</sup>
3	dichloropyrazine	1.3 kg <sup>b</sup>	32 <sup>c</sup>
4	fuming sulphuric acid	15 kg <sup>b</sup>	2.4 <sup>c</sup>
5	nitrosonitric acid	3 kg <sup>b</sup>	0.8 <sup>c</sup>
6	ammonium hydroxide	5 L <sup>b</sup>	1.2 <sup>c</sup>
7	acetonitrile	5 L <sup>b</sup>	2.4 <sup>c</sup>
8	H <sub>2</sub> O <sub>2</sub>	3 L <sup>b</sup>	0.8 <sup>c</sup>
9	trifluoroacetic acid	23 kg <sup>b</sup>	14.4 <sup>c</sup>
10	concentrated sulfuric acid	33 kg <sup>b</sup>	0.8 <sup>c</sup>

<sup>b</sup>Amount of materials of synthesizing 1 kg LLM-105;

<sup>c</sup>The materials were purchased from the company in chapter 2.1.

**Table 5.** The cost of synthesizing 1 kg LLM-105 by the DAPO method

	Material	Amount used/kg	Price (US dollar/kg)
1	methyl alcohol	10 L <sup>d</sup>	0.57 <sup>e</sup>
2	iminodiacetonitrile	1.4 kg <sup>d</sup>	12 <sup>e</sup>
3	RO-NO	1.7 kg <sup>d</sup>	32 <sup>e</sup>
4	fuming sulphuric acid	3 L <sup>d</sup>	2.4 <sup>e</sup>
5	nitrosonitric acid	1 L <sup>d</sup>	0.8 <sup>e</sup>
6	triethylamine	3 L <sup>d</sup>	2.4 <sup>e</sup>
7	hydroxylamine hydrochloride	1.2 kg <sup>d</sup>	2.4 <sup>e</sup>

<sup>d</sup> Amount of materials of synthesizing 1 kg LLM-105;

<sup>e</sup> The materials were purchased from the company in chapter 2.1.

**Table 6.** The cost of recrystallizing 1 kg LLM-105

	Material	Amount used/kg	Price (US dollar/kg)
1	LLM-105	1.12 kg <sup>f</sup>	-
2	DMSO	1.6 kg <sup>f</sup>	40 <sup>g</sup>

<sup>f</sup> Amount of materials of recrystallizing 1 kg LLM-105;

<sup>g</sup> The materials were purchased from the company mentioned in chapter 2.1.

As is shown in Tables 4 and 5, the cost of synthesizing LLM-105 by the traditional method is 465 US dollars/kg, and only 81 US dollars/kg by the new method. Besides, the DAPO method lead to a lower cost of labor and energy consumption because of the featuring simplicity in operation, mild reaction condition and simplicity in purification of the products.

## 4 Conclusions

We have developed an efficient and straight forward procedure for the synthesis of LLM-105. Compared with the traditional method, the new method has the characteristics of security, high purity, efficiency and low cost. The results of thermal decomposition and mechanical sensitivity tests show that LLM-105 synthesized by the new method is more sensitive to impact.

**S.I.** available at <http://www.wydawnictwa.ipo.waw.pl/CEJEM/contents.html>

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