Title: Transformation pathways of 2,4,6-trinitrobenzoic acid in the aqueous-phase hydrogenation over Pd/C catalyst

Author: Olga B. Belskaya Valentin P. Talsi Roman M. Mironenko Vladimir A. Rodionov Sergey V. Sysolyatin Vladimir A. Likholobov

PII: S1381-1169(16)30145-5
DOI: http://dx.doi.org/doi:10.1016/j.molcata.2016.04.014
Reference: MOLCAA 9858

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 11-3-2016
Revised date: 14-4-2016
Accepted date: 15-4-2016

Please cite this article as: Olga B.Belskaya, Valentin P.Talsi, Roman M.Mironenko, Vladimir A.Rodionov, Sergey V.Sysolyatin, Vladimir A.Likholobov, Transformation pathways of 2,4,6-trinitrobenzoic acid in the aqueous-phase hydrogenation over Pd/C catalyst, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2016.04.014

Transformation pathways of 2,4,6-trinitrobenzoic acid in the aqueous-phase hydrogenation over Pd/C catalyst

Olga B. Belskaya[a,b]*, Valentin P. Talsi[a], Roman M. Mironenko[a,c], Vladimir A. Rodionov[a], Sergey V. Sysolyatin[d], Vladimir A. Likholobov[a,b,e]

[a] Institute of Hydrocarbons Processing, Siberian Branch of the Russian Academy of Sciences, Neftezavodskaya st., 54, 644040 Omsk, Russia

[b] Omsk State Technical University, pr. Mira, 11, 644050 Omsk, Russia

[c] Dostoevsky Omsk State University, pr. Mira, 55a, 644077 Omsk, Russia

[d] Institute for Problems of Chemical and Energetic Technologies, Siberian Branch of the Russian Academy of Sciences, Socialisticheskaya st., 1, 659322, Biysk, Altai krai, Russia

[e] Omsk Scientific Center, Siberian Branch of the Russian Academy of Sciences, pr. Marksa, 15, 644024 Omsk, Russia

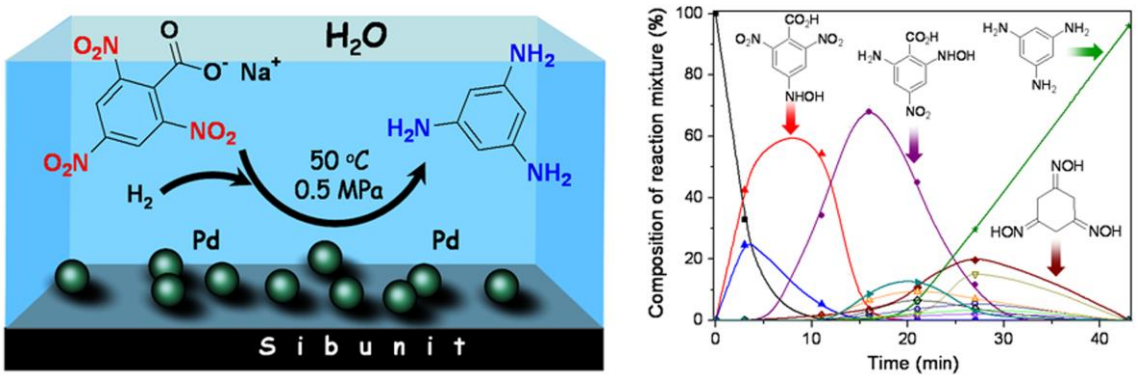
Corresponding author: Olga B. Belskaya

Present address: Institute of Hydrocarbons Processing, Siberian Branch of the Russian Academy of Sciences, Neftezavodskaya st., 54, 644040 Omsk, Russia

E-mail: obelska@ihcp.ru

Tel.: +7 (3812) 670 474, fax: +7 (3812) 646 156

Graphical abstract



Highlights

- Hydrogenation of 2,4,6-trinitrobenzoic acid over Pd/Sibunit catalyst.
- Identification of numerous reaction intermediates using NMR spectroscopy.
- Scheme of transformations of substrate and intermediates in an aqueous medium.

Abstract:

Results of the catalytic hydrogenation of 2,4,6-trinitrobenzoic acid (TNBA) in the presence of 1 % Pd/C catalyst with analysis of the reaction products at the steps corresponding to the consumption of 1, 3, 5, 6, 8 and 9 moles of hydrogen per mole of TNBA are presented. Numerous reaction intermediates were identified using the ^{1}H and ^{13}C NMR spectroscopy; the reaction mixture composition was assessed quantitatively at different steps of the hydrogenation. The data obtained were used to propose a scheme of TNBA transformations over the Pd/C catalyst in the aqueous-phase reaction conditions. The data on the component composition at different steps of TNBA hydrogenation are important to understand the process chemistry, to explore the possibility of selective formation of different types of intermediate nitroamino

compounds, and to synthesize high-performance catalysts for the hydrogenation of aromatic polynitro compounds.

Keywords: trinitrobenzoic acid, catalytic hydrogenation, aqueous-phase reaction, palladium catalyst

1. Introduction

The catalytic hydrogenation of aromatic nitro compounds is of interest not only as a model reaction in the development of theoretical bases for the liquid-phase hydrogenation of organic compounds, it is also of practical importance for chemical conversion of military high explosives into harmless products. Safe deactivation of 2,4,6-trinitrotoluene (TNT), which is among the most common explosives, by catalytic hydrogenation has substantial environmental advantages over its utilization by explosion, combustion, biological decomposition or chemical reduction [1-4]. So, optimization of conditions of the catalytic process and development of more efficient catalysts are the promising lines of investigation. The reduction of all nitro groups in TNT can produce 2,4,6-triaminotoluene (TAT), which is an important component in the synthesis of various commercial products [1-7]. The catalytic hydrogenation of aromatic trinitro compounds including TNT is usually performed in organic solvents with the use of bulk or supported catalysts containing nickel or platinum group metals [2-4, 7-33]. In the general case, the process scheme includes the delivery of hydrogen to the catalyst surface, its activation and interaction with nitro compound. Therewith, the hydrogen activation step is considered as the limiting one [16, 18].

Along with the works dealing with the exhaustive hydrogenation of all nitro groups in aromatic polynitro compounds, obtain of intermediate hydrogenation products is also important. A study of the hydrogenation of TNT on a palladium or Raney Ni catalysts in methanol and methanol/toluene medium demonstrated [4, 15, 19, 21] a complex chain of consecutive and parallel reactions. Analysis of products by ^{1}H NMR spectroscopy and mass spectrometry for the hydrogenation of TNT on a Pd/C catalyst in an alcohol solution made it possible to suggest scheme of transformations (Scheme 1) [21].

Along with TNT, among the most accessible and promising trinitro compounds is the product of TNT oxidation, 2,4,6-trinitrobenzoic acid (TNBA) [34-36]. Until now, only few works on catalytic hydrogenation of TNBA have been published [12, 37-42]. In view of environmental and green chemistry, the using of non-toxic and inexpensive solvent such as water is preferable, but the direct application of TNBA as the substrate for aqueous-phase hydrogenation is limited by its low solubility in water [38, 43]. However, as a component of a salt with alkaline metals, this compound has a good water solubility [38]. The literature provides no information about the effect of conditions of the aqueous-phase hydrogenation and catalyst composition on the process rate and depth and on the direction of TNBA transformations.

It should be noted that various methods were employed at different stages of studying the transformations of aromatic polynitro compounds for identification of hydrogenation products, in particular, the elemental analysis [7-10, 31], mass spectrometry [14, 21, 31], gas-liquid chromatography [4, 7, 15-18, 25, 29], high

performance liquid chromatography [7, 20, 29] and spectral methods [2, 3, 11, 14, 19, 21, 26, 28, 31]. Among them, one of the most efficient techniques is NMR spectroscopy. The non-destructive nature of the NMR is its doubtless advantage, which is most topical for investigation of unstable aromatic polynitro compounds and hydrogenation products.

In the present work, the catalytic hydrogenation of TNBA over Pd/C catalyst was conducted in an aqueous medium, and the products were analyzed at individual steps of the reaction. ^{1}H and ^{13}C NMR spectroscopy served as the main method of investigation. The study was aimed to reveal the directions of TNBA transformations in the aqueous-phase catalytic reaction. The choice of NMR is caused by not only a high informativity of this method but also a low efficiency or inability to use other techniques. So, we were not able to employ the capabilities of chromatography methods with mass detection. Obviously, these methods should be found to be unsuitable for the solution of our analytical task because of low stability of analyzed intermediates as well as lack of published mass spectra for most of these compounds.

2. Experimental

2.1. Catalyst preparation

The 1 % Pd/C catalyst was synthesized by the hydrolytic precipitation of palladium polyhydroxo complexes (PHC) on the surface of carbon material Sibunit [44-46]. The synthesis includes (1) the preparation of palladium PHC by slow introduction of the solution of $KHCO_3$ to the H_2PdCl_4 solution under stirring and pH controlling, (2) the impregnation of Sibunit by solution of PHC, (3) the reduction of palladium with sodium formate, (4) the washing of the samples [47]. Aqueous solution of H_2PdCl_4 with

desired Pd concentration was prepared by dissolution of $PdCl_2$ in concentrated hydrochloric acid. Before further experiments, no any pretreatments of obtained catalyst were performed and its moisture was about 50 %. Textural characteristics of the support, according to the low-temperature adsorption of nitrogen, were as follows: the specific surface area determined by the Brunauer-Emmett-Teller method was 422 m^2/g; the adsorption pore volume, 0.62 cm^3/g; and the mean pore diameter, 5.9 nm. Anchoring of palladium produced no changes in these parameters of the support.

2.2. Hydrogenation of TNBA

TNBA (98 % purity) was synthesized by oxidation of TNT as described by Clarke and Hartman [34]. The sodium salt of TNBA was obtained by the addition of sodium bicarbonate to the aqueous suspension of TNBA under careful stirring [38]. The catalytic hydrogenation of the obtained salt (100 mL of 2 % aqueous solution) was performed at a temperature of 323 K and pressure of 0.5 MPa in the presence of 1.00 g catalyst (loading was about 400 g of TNBA per 1 g of Pd). The reaction was conducted in a 180 mL steel autoclave equipped with a valve for hydrogen input and an external thermostatted jacket. The reaction mixture was stirred by a magnetic stirrer at 1400 rpm to prevent external diffusion limitations. The progress of the reaction was monitored by measuring the volume of consumed hydrogen with a mass flow meter. The reaction was stopped when the required amount of hydrogen was consumed. After cooling, the sampling was carried out with a syringe.

2.3. Analysis of hydrogenation products by ^1H and ^{13}C NMR spectroscopy

Spectra were recorded on an Avance-400 (Bruker) NMR spectrometer using standard ampoules 5 mm in diameter at the Larmor frequency of 400 MHz (^{1}H) or 100.6 MHz (^{13}C) at a temperature of 303 K in a pulsed mode. The signals from residual protons (δ_H of 3.30 ppm, a quintet) or carbon nuclei in methyl groups (δ_C of 49.0 ppm, a septet) of methanol-d_4 were used as the internal standard for the chemical shifts. A signal from water at ~4.9 ppm in the ^{1}H NMR spectra was suppressed by presaturation method using the pulse sequence program (zgpr) provided with the Bruker software. The *J*-modulated (JMOD) pulse sequence [48] was employed for recording all of the ^{13}C NMR spectra. In the JMOD ^{13}C NMR spectra, the methine and methyl signals have opposite phase to those of quaternary and methylene resonances. NMR spectra were simulated with the ACD/Labs 6.00 (Advanced Chemistry Development Inc.) software. Simulation was especially useful in the absence of published spectra. The quantitative composition of reaction mixture was assessed by ^{1}H NMR from the integral intensity corresponding to the signals of individual components non-overlapping with other resonances. Bearing in mind that none of the signals of studied compounds was saturated in the NMR registration conditions, it was admitted that the integral intensity of signals is directly proportional to the number of molecules of a component in the solution and to the number of protons in the molecules generating these signals.

3. Results and discussion

3.1. Obtaining of TNBA hydrogenation products

The hydrogenation of the sodium salt of TNBA under the chosen conditions resulted in the consumption of 1500 mL hydrogen (reduced to normal conditions), which is close to the stoichiometric value (9 mole per mole of TNBA) at a complete

hydrogenation of all nitro groups in trinitro compound. The obtained hydrogen consumption curve (Fig. 1a) does not have the pronounced steps, which testifies to the absence of selective consecutive reduction of nitro groups with a strongly different rate and suggests that the reduction involves all nitro groups. Such a process leads to a great number of the reaction products and complicates their identification [4, 19, 21].

To examine the composition of products resulting from the hydrogenation of TNBA, points ii-vii, corresponding to the consumption of 1, 3, 5, 6, 8 and 9 moles of hydrogen per mole of TNBA, were distinguished on the curve of consumption rate versus the amount of consumed hydrogen (Fig. 1b). Further experiments consisted in the hydrogenation of six identical solutions of the substrate with termination of the reaction in one of the chosen points. This gave the subjects of inquiry represented by aqueous solutions of the sodium salt of TNBA (sample i), products of complete transformation (sample vii), and products of consecutive incomplete hydrogenation of TNBA (samples ii-vi).

3.2. NMR study of the composition of TNBA hydrogenation products

The ^{1}H NMR spectra of the starting compound, final and intermediate hydrogenation products of TNBA corresponding to samples i-vii (Fig. 1), which were obtained by the stepwise hydrogenation, are depicted in Fig. 2. It should be noted that in some cases intermediate compounds were identified using the ^{13}C and ^{1}H NMR spectra that were obtained in our similar studies on the hydrogenation of more concentrated solutions of the substrate (10 wt. %) with the catalysts of different activity.

The ^{1}H NMR spectrum of the starting solution (sample i) in addition to the signal from the solvent shows only a singlet at 9.25 ppm corresponding to the aromatic

protons of TNBA (Fig. 2a). At the initial step of hydrogenation (sample ii) with the consumption of 1 mole of H_2 per mole of TNBA, three main compounds were identified in the solution (Fig. 2b). Along with the signal from unreacted TNBA, the spectrum has a singlet at 7.87 ppm and two doublets at 8.27 and 8.33 ppm with long range couplings of 2.2 Hz (the splitting typical of *meta* protons), which can be assigned to aromatic protons of 4-(hydroxyamino)-2,6-dinitrobenzoic acid (**1**) and 6-(hydroxyamino)-2,4-dinitrobenzoic acid (**2**), respectively (Table 1). As a single alternative to compounds **1** and **2** we considered their analogs containing the amino groups instead of hydroxyamino ones. However, such compounds give signals of their aromatic protons in a noticeably stronger field (Δδ 0.4-0.7 ppm) [49, 54]. In addition, a weak signal possibly corresponding to 4-amino-2,6-dinitrobenzoic acid (**3**) is observed at the next hydrogenation steps (Fig. 2c and d) along with the signal from compound **1**. The chemical shifts of the signals that were attributed to TNBA and compounds **1** and **2** in the ^{13}C NMR spectrum of sample ii (Fig. S1 in the Supplementary materials) agree satisfactorily with the similar values in the simulated spectra of individual compounds (Table 2).

In the solution obtained by the consumption of 3 moles of H_2 per mole of TNBA (sample iii), the starting compound is absent, and compound **1** gives the most intense signal in the ^1H NMR spectrum (Fig. 2c). This spectrum has also the next high-intensity group of signals in the region of 7.0-7.1 ppm, which is a overlapping of the singlet at 7.09 ppm with two doublets at ~7.06 and ~7.10 ppm. The validity of this fact was confirmed by the analysis of spectra of the samples in which only a singlet or only two doublets are observed in the region under consideration (Figs. 2d and 2f; Fig. S2). The singlet at 7.09 ppm can be assigned to aromatic protons of 2,6-*bis*(hydroxyamino)-4-

nitrobenzoic acid (**4**), while the two doublets (7.06, 7.10 ppm) to 2-amino-6-(hydroxyamino)-4-nitrobenzoic acid (**5**). The correctness of identification of compound **5** is undeniable. Since this compound is the main component of sample iv (the consumption of 5 moles of H_2 per mole of TNBA) (Figs. 2d and 3), the corresponding signals in the ^{13}C NMR spectrum can clearly be determined (Fig. 4). The signals that correspond to compound **5** in the ^{1}H and ^{13}C NMR spectra can belong only to the reduction product of TNBA that contains one nitro group and two nonequivalent *meta* protons (H-3 and H-5) in the benzene ring. As shown by the analysis of simulated ^{13}C NMR spectra for all possible locations of amino, hydroxyamino and nitro groups in the *ortho* and *para* positions of benzoic acid, the ^{13}C NMR spectrum depicted in Fig. 4 can belong only to compound **5** in which the nitro group places in the *para* position to the carboxyl group. After identification of compound **5**, the structure of compound **4** also becomes well established, although it could be validated only by the simulated ^{1}H NMR spectrum of the mixture of compounds **4** and **5**, which demonstrates the experimentally observed overlapping of the signals.

The ^{1}H NMR spectrum of sample iii (Fig. 2c) also has proton signals in the saturated region. The intensity of these signals monotonically increases in the spectra of samples iii-vi (Figs. 2c-f; see also Fig. 3). The compounds that give singlets in the region of 3.2-3.7 ppm were assigned, regarding the published ^{1}H NMR spectra of individual compounds [50, 55, 56], to methylene protons of (1*Z*)-cyclohexane-1,3,5-trione trioxime (**6**) (three singlets at 3.22, 3.46, 3.70 ppm) and (1*E*,3*E*,5*E*)-cyclohexane-1,3,5-trione trioxime (**7**) (one singlet at 3.50 ppm). Additionally, the identification of these compounds was based on the spectra of the samples obtained by hydrogenation of more concentrated (10 wt. %) solutions of TNBA where the content of compounds **6**

and **7** was ~50 %. The ^{1}H NMR spectrum of one of such samples is depicted in Fig. 5, and the JMOD ^{13}C NMR spectrum – in Fig. S3. The experimental and simulated ^{13}C NMR spectra of trioximes **6** and **7** are virtually identical (Table 2).

It should be noted that a singlet at 5.75 ppm assigned to aromatic protons of 1,3,5-triaminobenzene (**8**), which is the product of complete hydrogenation of TNBA, was observed for the first time in the spectrum of sample iv (Fig. 2d). Later, upon consumption of 8 and 9 moles of H_2 per mole of TNBA (Figs. 2f and 2g), compound **8** became the main product (Fig. 3).

Before starting the identification of minor reduction products of TNBA, let us consider the main route of the reaction, which can be derived from quantitative assessment of the composition of reaction mixture at different hydrogenation steps by ^{1}H NMR spectroscopy (Figs. 2 and 3). First, TNBA is reduced to **1** and **2**, a further hydrogenation of which leads to **4** and then to **5**. The resulting compound **5** transforms into trioximes **6** and **7** which, in their turn, are hydrogenated to **8** (Scheme 2).

It should be noted that the formation of compound **5** cannot be attributed only to the consecutive hydrogenation of TNBA through the formation of compounds **2** and **4**. Even at the first step upon consumption of 1 mole of H_2 per mole of TNBA (Figs. 2b and 3), compound **1** predominates in the mixture of hydrogenation products, and at the next steps (Figs. 2c, d and 3) the observed substantial increase in the content of **5** can occur mainly via the reduction of **1**. Hence, along with consecutive hydrogenation, the formation of compound **5** should include a step at which the carboxyl group migrates to form a symmetric molecule of intermediate **4**. Perhaps, such migration occurs via decarboxylation of **9** and subsequent carboxylation of formed carbanion, i.e. in the same

way as described for the Henkel process (also referred to as the Raecke rearrangement) which is the isomerization of potassium phthalate to terephthalate [57, 58].

In addition, the main route of the reaction under consideration implies the transformation of compound **5** into trioximes **6** and **7**, which cannot result from the direct reduction. Most likely, there occurs the intramolecular redox transformation of compound **5** into symmetric 2,4,6-*tris*(hydroxyamino)benzoic acid (**10**) whose decarboxylation gives 1,3,5-*tris*(hydroxyamino)benzene (**11**), which is able to isomerize into oximes **6** and **7** (Scheme 2). Although the identification of intermediates **10** and **11** has failed, some of the ^{1}H NMR spectra of reaction mixtures (samples iv and v) showed a singlet with the chemical shift at about 6.30 ppm, which can belong, according to the simulated spectrum (Table 1), to aromatic protons of compound **11**. Earlier it was assumed that trioxime **6** or **7** exists in tautomeric equilibrium with **11** [59]. However, more recent investigations by NMR have been established that compound **11** always transforms into trioximes, among of which unsymmetric isomer **6** prevails [50, 55]. The ratio of isomers **6** and **7** estimated from ^{1}H NMR data (about 90 % of **6**, see Fig. 3) is close to those determined in [50]. It is important that upon catalytic hydrogenation of trioxime, aromatic structure is restored [55].

To determine the composition of components of samples ii-vi, which are characterized by less intense signals in the ^{1}H NMR spectra (Figs. 2b-f), we analyzed also the ^{1}H and ^{13}C NMR spectra of the solutions obtained earlier in the experiments with a higher content of the substrate (10 wt. %) and shown in Figs. 5, 6 and S4. Therewith, Fig. 6 shows the spectra of the same solution with different holding time,

which allows observing transformation of the solution components with time. The ^{1}H NMR spectrum displayed in Fig. 5 shows not only the resonances relating to compounds **5**-**8** but also two relatively intense doublet-triplet pairs of signals at 6.10 (doublet), 6.14 (triplet) and 5.88 (triplet), 5.94 (doublet) ppm, which are present in Figs. 2d-f, too. These signals can be assigned to aromatic protons of 3,5-*bis*(hydroxyamino)aniline (**12**) and 5-(hydroxyamino)benzene-1,3-diamine (**13**), respectively. Correctness of the attribution is confirmed by good agreement between parameters of the experimental and simulated ^{1}H NMR spectra of these compounds (Table 1) and by the results of analysis of the corresponding JMOD ^{13}C NMR spectrum (Table 2, Fig. S3). Compounds **12** and **13** are present in samples iv-vi, reach a maximum content at the consumption of 8 moles of H_2 per mole of TNBA, and are absent in sample vii (Fig. 3). As shown in Scheme 2, compounds **12** and **13** are the intermediate reduction products of oximes **6** and **7**; however, other routes of their formation (e.g. from compound **11**) also cannot be ruled out.

A singlet with the chemical shift at ~5.86 ppm, which is seen in Figs. 2d-g, can be assigned to aromatic protons of 2,4,6-triaminobenzoic acid (**14**). In the spectra depicted in Fig. 6, this signal is relatively intense (second in the intensity after the signal from compound **8**), and its assignment to **14** is unambiguous, taking into account the simulated spectrum (Table 1) and the analysis of the JMOD ^{13}C NMR spectrum (Table 2, Fig. S4). Other signals in the spectra shown in Fig. 6 are the two doublets at 6.64, 6.88 ppm and two doublets at 6.39, 6.63 ppm, which were possibly attributed to aromatic protons of 4-amino-2-(hydroxyamino)-6-nitrobenzoic acid (**15**) and 2,4-diamino-6-nitrobenzoic acid (**16**), respectively. Therewith, a less stable **15** converts into **16** upon holding of the sample.

The spectra in Figs. 2d-f, in addition to the indicated signals of compounds **15** and **16**, show another two doublets at about 6.77 and 6.87 ppm, which was probably attributed to aromatic protons of 2-amino-4-(hydroxyamino)-6-nitrobenzoic acid (**17**). One can see in a detailed fragment of the spectrum in Fig. 2f (Fig. S5) that all the pairs of doublets for compounds **15**-**17** are well enough resolved and do not overlap, in distinction to the spectra in Figs. 2d and 2e. Parameters of the experimental and simulated spectra of compounds **15**-**17**, especially the relative positions of the corresponding pairs of doublets, are consistent with each other. Correctness of the identification of compound **16** is confirmed also by JMOD ^{13}C NMR spectrum (Table 2, Fig. S4). Signals corresponding to compounds **15** and **17** were not detected in the ^{13}C NMR spectra, probably due to their insufficient stability during the long-term (12 h) recording of the ^{13}C NMR spectrum.

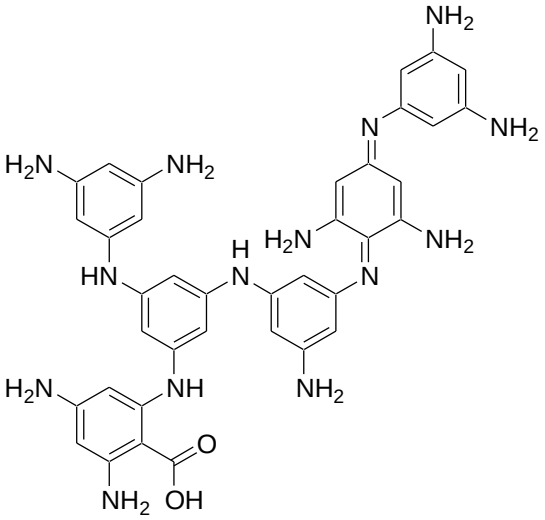
Thus, the identification of compounds and the assessment of their contents at consecutive hydrogenation steps give grounds to suggest that the reduction of TNBA produces not only the main intermediate **5** but also its isomers **15** and **17**. Similar to compound **5**, isomers **15** and **17** seem to be capable of transforming into the final triamine **8** through oximes **6** and **7** and compounds **12** and **13** according to Scheme 2. At the same time, isomers **5**, **15** and **17** can be reduced to compound **16**, which then lead to the formation of triamine **8**, probably via the decarboxylation of intermediate **14** (Scheme 3).

Some very weak and poorly resolved signals in the ^{1}H NMR spectra under consideration can be attributed to aromatic protons of 3,5-diaminophenol (**18**), 5-aminobenzene-1,3-diol (**19**) and benzene-1,3,5-triol (**20**), which can be produced by the

consecutive hydrolysis of compound **8** (Scheme 4) when the reaction is carried out in an aqueous medium [42, 60]. A singlet at 5.89 ppm corresponding to **20** overlaps with the signals from other compounds in most of the spectra. In some spectra, pairs of the signals (doublet-triplet) attributed to compounds **18** and **19** are not clearly seen due to overlapping with other resonances. The ^{1}H NMR spectrum of the sample of reaction mixture with an increased content of one of the tested compounds, which gives doublet at 5.78 and triplet at 5.83 ppm (Fig. S6), showed that the indicated signals belong to aromatic protons of **18** (Table 1). In addition, identification of **18** was validated by JMOD ^{13}C NMR (Fig. S7, Table 2). Compound **19** was identified less reliably.

Fig. 2g depicts the ^{1}H NMR spectrum of sample vii that was obtained by the exhaustive hydrogenation of all nitro groups of TNBA (about 9 mole of H_2 per mole of TNBA was consumed). The content of **8** in the reaction mixture, according to ^{1}H NMR, was above 95 % (see Fig. 3). To provide a correct identification of low intensity signals, more concentrated solutions (10 wt. %) with a close composition of products were also examined. In the ^{1}H NMR spectrum displayed in Fig. S8, very weak signals corresponding to aromatic protons of compounds **18**-**20** are observed.

Probably, the side hydrolysis reactions enhance the polycondensation of hydrogenation products. In many ^{1}H and JMOD ^{13}C NMR spectra, a number of weak signals may be observed. Taking into account the simulated ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) and the literature data [61, 62], these signals were assigned to the oxidative polycondensation product that may be represented by the structural fragment shown below.



21

There is a satisfactory agreement between parameters of the ^{1}H NMR spectrum (Fig. S8) that were attributed to the aromatic protons of oxidative polycondensation product of **8** and the corresponding parameters of the simulated ^{1}H NMR spectrum of structure **21** (Table 1). Generally speaking, the respective parameters of experimental and simulated ^{13}C NMR spectra (Fig. S9, Table 2) are also close to each other.

4. Conclusions

The suggested conditions of the hydrogenation of TNBA as a component of the sodium salt in an aqueous medium in the presence of 1 % Pd/C catalyst made it possible to perform a complete hydrogenation of all nitro groups with simultaneous decarboxylation and to selectively produce 1,3,5-triaminobenzene at a stoichiometric hydrogen consumption.

At the same time, the NMR analysis of reaction mixtures at consecutive steps of the reaction allowed us to obtain unique information on the composition of intermediate transformation products and to propose a scheme of consecutive and parallel reactions

occurring in the hydrogenation. Systematization of the large body of experimental data acquired by the ^{1}H and ^{13}C NMR investigation of the solutions with different and sometimes predominant content of individual components allowed for a reliable identification of numerous intermediates, although experimental spectral information reported in the literature is quite scarce.

The data on the component composition at different steps of TNBA hydrogenation, which were obtained in the study, are important to understand the process chemistry, to explore the possibility of selective formation of different types of intermediate nitroamino compounds, and to synthesize high-performance catalysts for the hydrogenation of aromatic trinitro and in general polynitro compounds.

Acknowledgements

The authors are grateful to S. Vysotskii for participation in the catalyst preparation and testing. In the work, the equipment of the Omsk Regional Center of Collective Usage, Siberian Branch of the Russian Academy of Sciences was used. The support from the Russian Foundation for Basic Research (Project No. 16-03-00601) is gratefully acknowledged.

References

[1] V.A. Tartakiovsky, S.A. Shevelev, M.D. Dutov, A.Kh. Shakhnes, A.L. Rusanov, L.G. Komarova, A.M. Andrievsky, in: H. Krause (Ed.), Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Kluwer Academic Publishers, Dordrecht, 1997, pp. 137-149.

[2] P. Wanninger, Chem. Unserer Zeit 29 (1995) 135-140.

[3] P. Wanninger, in: K.K. Kuo (Ed.), Challenges in Propellants and Combustion, 100 Years after Nobel, Begell House, New York, 1997, pp. 155-166.

[4] E.F. Litvin, V.Z. Sharf, Ross. Khim. Zhurnal 44 (2000) 90-98.

[5] A.L. Rusanov, L.G. Komarova, D.Yu. Likhatchev, S.A. Shevelev, V.A. Tartakovsky, Russ. Chem. Rev. 72 (2003) 899-911.

[6] V.I. Ushkarov, K.I. Kobrakov, A.I. Alafinov, S.A. Shevelev, A.Kh. Shakhnes, Theor. Found. Chem. Eng. 41 (2007) 671-674.

[7] V.A. Kashaev, G.Kh. Khisamutdinov, S.A. Shevelev, S.I. Valeshnii, A.Kh. Shakhnes, A.P. Bavrina, Theor. Found. Chem. Eng. 42 (2008) 650-656.

[8] F. Hein, F. Wagner, Ber. Dtsch. Chem. Ges. 68 (1935) 856-864.

[9] S.S. Voris, P.E. Spoerri, J. Am. Chem. Soc. 60 (1938) 935-936.

[10] J.E. Gill, R. MacGillivray, J. Munro, J. Chem. Soc. (1949) 1753-1754.

[11] T. Yamaoka, H. Hosoya, S. Nagakura, Tetrahedron 24 (1968) 6203-6213.

[12] E. Vero, J.N. Vickers, GB Patent 1 106 088 (1968), to Fisons Industrial Chemicals Ltd.

[13] W.A. Freeman, C.F. Liu, Inorg. Chem. 14 (1975) 2120-2124.

[14] B. Kohne, K. Praefcke, T. Derz, T. Gondro, F. Frolow, Angew. Chem. Int. Ed. Engl. 25 (1986) 650-651.

[15] K.B. van Gelder, J.K. Damhof, P.J. Kroijenga, K.R. Westerterp, Chem. Eng. Sci. 45 (1990) 3159-3170.

[16] U. Kürschner, H. Ehwald, G. Alscher, Chem. Tech. 45 (1993) 448-452.

[17] H. Ehwald, G. Alscher, Chem. Tech. 47 (1995) 297-301.

[18] U. Kürschner, H. Ehwald, G. Alscher, Catal. Lett. 34 (1995) 191-199.

[19] W. Chuntiag, V.G. Dorokhov, G.A. Boiko, B.S. Bal'zhinimaev, V.V. Barelko, Dokl. Chem. 402 (2005) 111-113.

[20] M.E. Fuller, C.E. Schaefer, J.M. Lowey, Chemosph. 67 (2007) 419-427.

[21] V.G. Dorokhov, V.I. Savchenko, in: A.A. Berlin, N.A. Khalturinskiy, A.A. Voshkin (Eds.), International Conference on Chemical Technology, LENAND, Moscow, 2007, pp. 383-385.

[22] A.I. Kozlov, V.L. Zbarskij, N.V. Khodov A.F. Kuimov, RU Patent 2 333 795 (2008), to ZAO Russkij katalizator.

[23] A.V. Gavrikov, V.G. Dorokhov, A.S. Ivanov, A.F. Pal, O.F. Petrov, A.N. Ryabinkin, V.I. Savchenko, A.O. Serov, E.A. Skryleva, A.N. Starostin, V.E. Fortov, Yu.M. Shul'ga, Dokl. Phys. 55 (2010) 55-57.

[24] Z.-Y. Xiao, X. Zhao, X.-K. Jiang, Z.-T. Li, Langmuir 26 (2010) 13048-13051.

[25] F. Cárdenas-Lizana, S. Gómez-Quero, G. Jacobs, Y. Ji, B.H. Davis, L. Kiwi-Minsker, M.A. Keane, J. Phys. Chem. C 116 (2012) 11166-11180.

[26] G.J. Merten, C. Neis, S. Stucky, V. Huch, E. Rentschler, H. Natter, R. Hempelmann, K. Stöwe, K. Hegetschweiler, Eur. J. Inorg. Chem. (2012) 31-35.

[27] Z.-G. Tao, X. Zhao, X.-K. Jiang, Z.-T. Li, Tetrahedron Lett. 53 (2012) 1840-1842.

[28] A.D. Pomogailo, G.I. Dzhardimalieva, J. Catalysts (2013) 276210.

[29] G. Dormán, L. Kocsis, R. Jones, F. Darvas, J. Chem. Health Saf. 20 (2013) 3-8.

[30] D.V. LaBarbera, E.B. Skibo, J. Org. Chem. 78 (2013) 11887-11895.

[31] J. Mahmood, D. Kim, I.-Y. Jeon, M.S. Lah, J.-B. Baek, Synlett 24 (2013) 246-248.

[32] K. Hermann, M. Nakhla, J. Gallucci, E. Dalkilic, A. Dastan, J.D. Badjić, Angew. Chem. 125 (2013) 11523-11526.

[33] T. Trzeciak, L. Niedzicki, G. Groszek, P. Wieczorek, M. Marcinek, W Wieczorek, J. Power Sources 252 (2014) 229-234.

[34] H.T. Clarke, W.W. Hartman, Org. Synth. 2 (1922) 95-97.

[35] M.L. Kastens, J.F. Kaplan, Ind. Eng. Chem. 42 (1950) 402-413.

[36] B.J. Kim, J.M. Choi, J.G. Cho, E.Y. Lee, S.Y. Kim, D.H. Lee, KR Patent 10-2011-0123222 (2011), to Korea Institute of Industrial Technology.

[37] G.S. Samuelsen, V.L. Garik, G.B.L. Smith, J. Am. Chem. Soc. 72 (1950) 3872-3874.

[38] J. Miller, M. Searle, US Patent 3 678 114 (1972), to Fisons Ltd.

[39] Y. Chen, D. Zhao, Ranliao Gongye 38 (2001) 24-25.

[40] Q.-H. Yang, Y.-S. Feng, L. Chen, Zhongguo Yiyao Gongye Zazhi 36 (2005) 735-736.

[41] V.A. Kuz'mina, Yu.T. Lapina, S.V. Sysolyatin, Polzunovsky Vestnik (2008) 129-131.

[42] Z.-L. Yao, R.-B. Wang, H.-L. Liu, Yingyong Huagong 38 (2009) 1153-1155.

[43] L. Desvergnes, Monit. Sci. 16 (1926) 201-208.

[44] V.A. Semikolenov, Russ. Chem. Rev. 61 (1992) 168-174.

[45] V.F. Surovikin, G.V. Plaxin, V.A. Semikolenov, V.A. Likholobov, I.J. Tiunova, US Patent 4 978 649 (1990).

[46] V.F. Surovikin, Yu.V. Surovikin, M.S. Tsekhanovich, Russ. J. Gen. Chem. 77 (2007) 2301-2310.

[47] P.A. Simonov, S.Yu. Troitskii, V.A. Likholobov, Kinet. Catal. 41 (2000) 255-269.

[48] C. Le Cocq, J.-Y. Lallemand, J. Chem. Soc. Chem. Commun. (1981) 150-152.

[49] A. Preiss, M. Elend, S. Gerling, S. Tränckner, Magn. Reson. Chem. 43 (2005) 736-746.

[50] J.C. Bottaro, R. Malhotra, A. Dodge, Synth. (2004) 499-500.

[51] B.-S. Liao, S.-T. Liu, J. Org. Chem. 77 (2012) 6653-6656.

[52] M. Peterca, M.R. Imam, C.-H. Ahn, V.S.K. Balagurusamy, D.A. Wilson, B.M. Rosen, V. Percec, J. Am. Chem. Soc. 133 (2011) 2311-2328.

[53] J.-Y. Park, J.H. Kim, J.M. Kwon, H.-J. Kwon, H.J. Jeong, Y.M. Kim, D. Kim, W.S. Lee, Y.B. Ryu, Bioorg. Med. Chem. 21 (2013) 3730-3737.

[54] R. Bhadra, R.J. Spanggord, D.G. Wayment, J.B. Hughes, J.V. Shanks, Environ. Sci. Technol. 33 (1999) 3354-3361.

[55] I. Arai, Y. Sei, I. Muramatsu, J. Org. Chem. 46 (1981) 4597-4599.

[56] A. Calvo Mateo, M. Esteban Morales, T. Gallego Camara, M. Muñoz Mouton, Int. Patent WO 91/12231 (1991), to Rhone-Poulenc Farma, S.A.E.

[57] Y. Ogata, M. Hojo, M. Morikawa, J. Org. Chem. 25 (1960) 2082-2087.

[58] Z. Wang, Comprehensive Organic Name Reactions and Reagents, John Wiley & Sons, New York, 2010.

[59] N. Tokura, I. Shirai, T. Sugahara, Bull. Chem. Soc. Jpn. 35 (1962) 722-725.

[60] W.H. Lee, J.S. Kim, S.C. Kim, Bull. Korean Chem. Soc. 30 (2009) 3105-3106.

[61] J.B. Torrance, S. Oostra, A. Nazzal, Synth. Met. 19 (1987) 709-714.

[62] I. Johannsen, J.B. Torrance, A. Nazzal, Macromol. 22 (1989) 566-570.

Figure captions

Fig. 1. Hydrogen consumption curve (a) and hydrogen consumption rate versus the amount of consumed hydrogen (b) for the hydrogenation of TNBA (in the form of sodium salt) in aqueous solution at a temperature of 323 K and pressure of 0.5 MPa over the 1 % Pd/C catalyst (400 g of TNBA per 1 g of Pd).

Fig. 2. The ^{1}H NMR spectra (303 K, 400 MHz, H_2O) of samples i (a), ii (b), iii (c), iv (d), v (e), vi (f), and vii (g).

Fig. 3. (a) The change of composition of reaction mixture during the hydrogenation of TNBA (in the form of sodium salt) in aqueous solution at a temperature of 323 K and pressure of 0.5 MPa over the 1 % Pd/C catalyst (400 g of TNBA per 1 g of Pd). The consumption of 0, 1, 3, 5, 6, 8 and 9 moles of hydrogen per mole of TNBA corresponds to samples i-vii. The main components (TNBA, compounds **1**, **2**, **5**, **6**, **8** and **17**) detected by ^{1}H NMR in samples i-vii are indicated; (b) The isolated fragment of Fig. 3a for components with a lower concentration: **6**, **7**, **12**-**17**.

Fig. 4. The $^{13}C\{^{1}H\}$ JMOD NMR spectrum (303 K, 100.6 MHz, H_2O) of sample iv, whose ^{1}H NMR spectrum is depicted in Fig. 2d. The assignment of signals to compound **5** is shown in Table 2.

Fig. 5. The ^{1}H NMR spectrum (303 K, 400 MHz, H_2O) of reaction mixture obtained by hydrogenation of TNBA (in the form of sodium salt) in aqueous solution (concentration

of TNBA is 10 wt. %) at a temperature of 343 K and pressure of 0.5 MPa. The content of compounds **6** and **7** is 48 %. The other signals in the spectrum belong to compounds **5**, **8**, **12**, **13**, **15** and **21** (see Table 1). The JMOD ^{13}C NMR spectrum of this solution, which was used for identification of compounds **6**-**8** and **14**, is displayed in Fig. S3 (in the Supplementary materials).

Fig. 6. (a) The ^{1}H NMR spectrum (303 K, 400 MHz, H_2O) of the reaction mixture obtained by hydrogenation of TNBA (in the form of sodium salt) in aqueous solution (concentration of TNBA is 10 wt. %) at a temperature of 343 K and pressure of 0.5 MPa. The spectrum was recorded immediately after sampling. (b) The ^{1}H NMR spectrum of the same reaction mixture after holding in an NMR ampoule for 12 h. The attribution of signals can be found in Table 1.

Figure 1

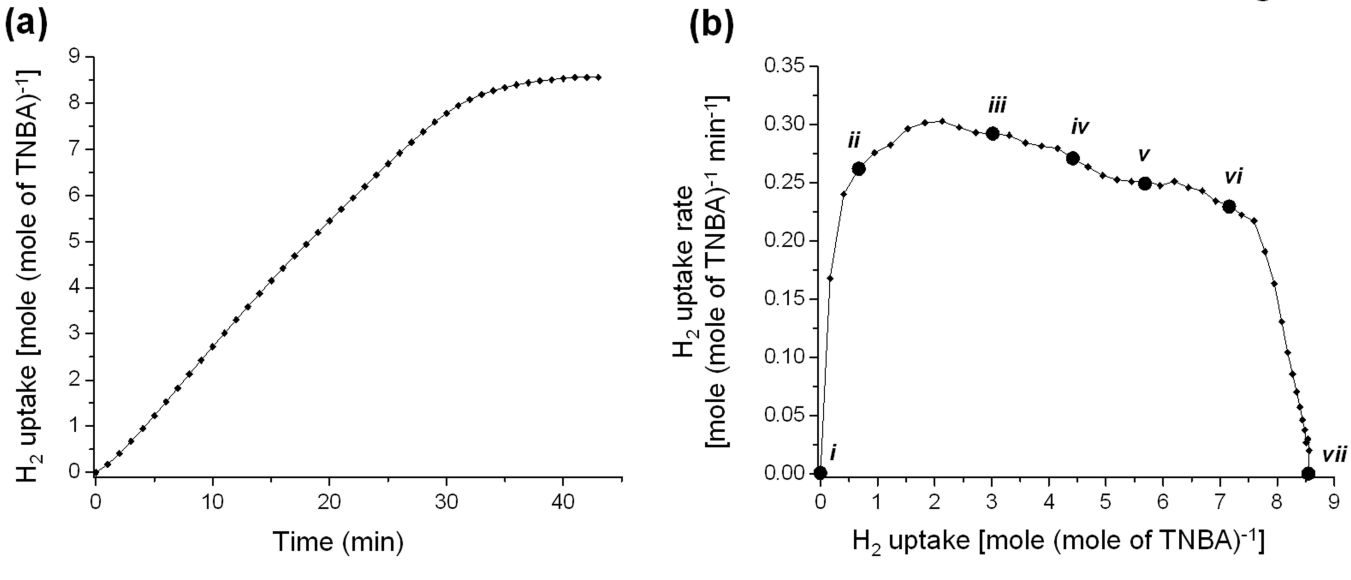

(a)
H2 uptake [mole (mole of TNBA)-1]
Time (min)
0
1
2
3
4
5
6
7
8
9
0
10
20
30
40
(b)
H2 uptake rate
[mole (mole of TNBA)-1 min-1]
H2 uptake [mole (mole of TNBA)-1]
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0
1
2
3
4
5
6
7
8
9
i
ii
iii
iv
v
vi
vii

Figure 2

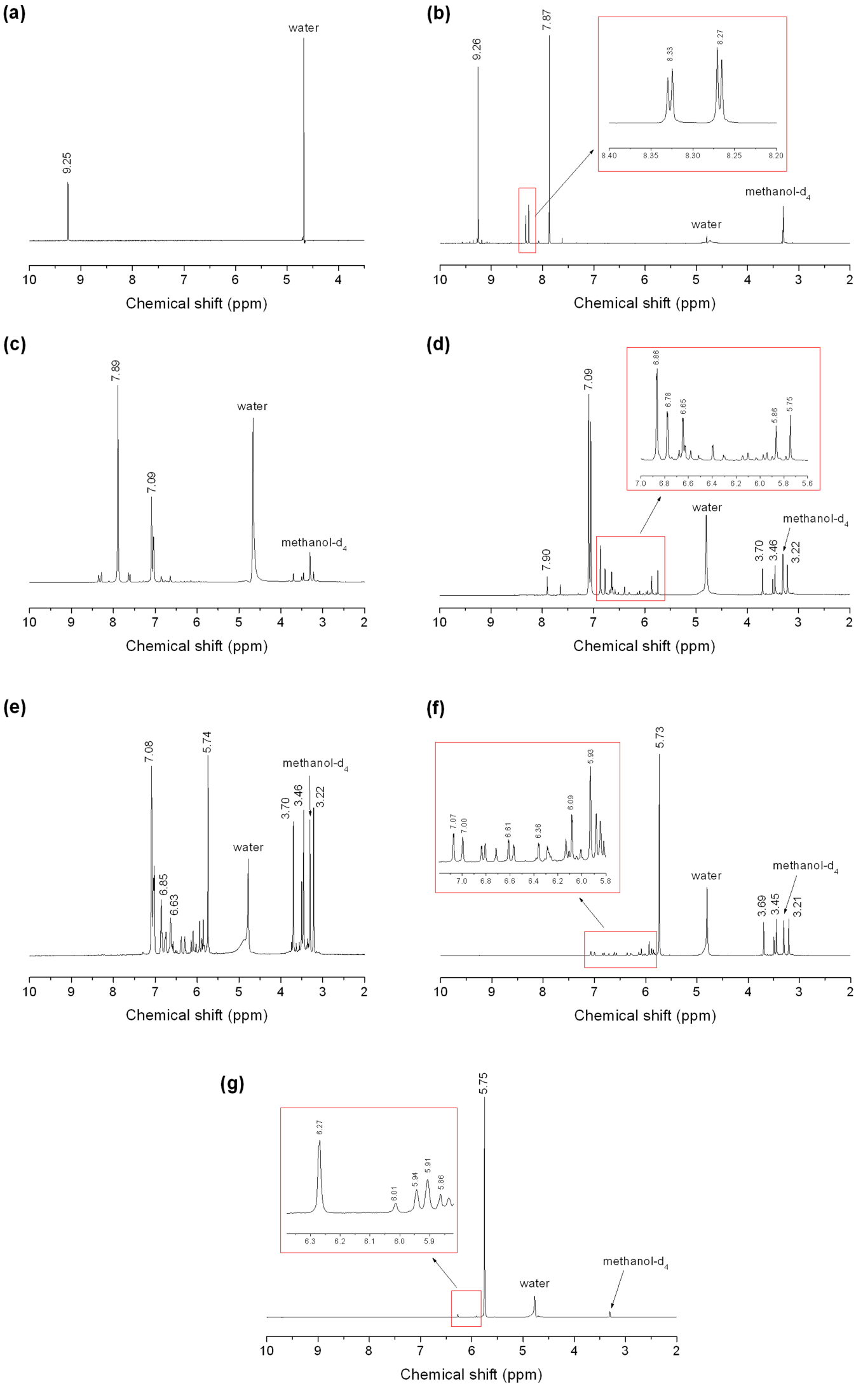
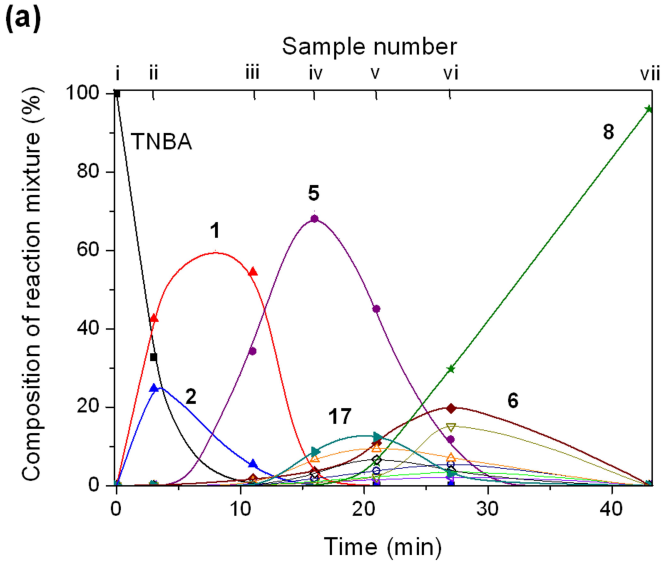

(a)
water
9.25
Chemical shift (ppm)
(b)
9.26
7.87
8.33
8.27
methanol-d4
water
Chemical shift (ppm)
(c)
7.89
7.09
water
methanol-d4
Chemical shift (ppm)
(d)
7.09
6.86
6.78
6.65
5.86
5.75
water
methanol-d4
7.90
3.70
3.46
3.22
Chemical shift (ppm)
(e)
7.08
5.74
methanol-d4
3.70
3.46
3.22
6.85
6.63
water
Chemical shift (ppm)
(f)
5.73
5.93
7.07
7.00
6.61
6.36
6.09
water
methanol-d4
3.69
3.45
3.21
Chemical shift (ppm)
(g)
5.75
6.27
6.01
5.94
5.91
5.86
methanol-d4
water
Chemical shift (ppm)

Figure 3


(a)
Sample number
i
ii
iii
iv
v
vi
vii
Composition of reaction mixture (%)
Time (min)
TNBA
1
2
5
6
8
17

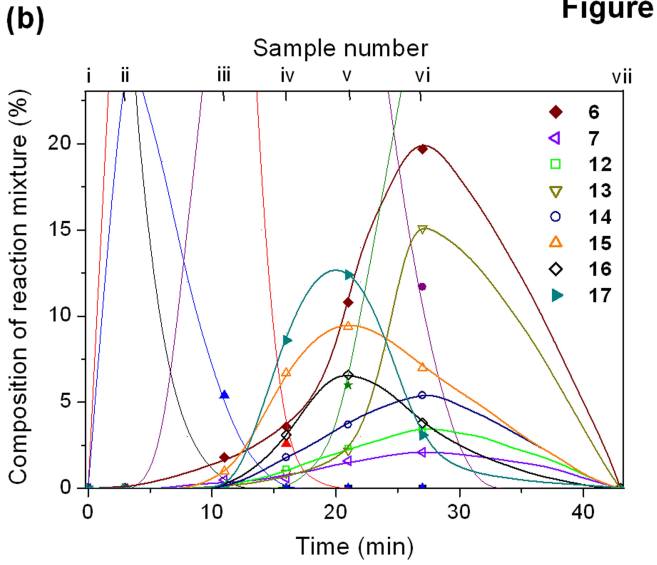

(b)
Sample number
i
ii
iii
iv
v
vi
vii
Composition of reaction mixture (%)
Time (min)
6
7
12
13
14
15
16
17

Figure 4

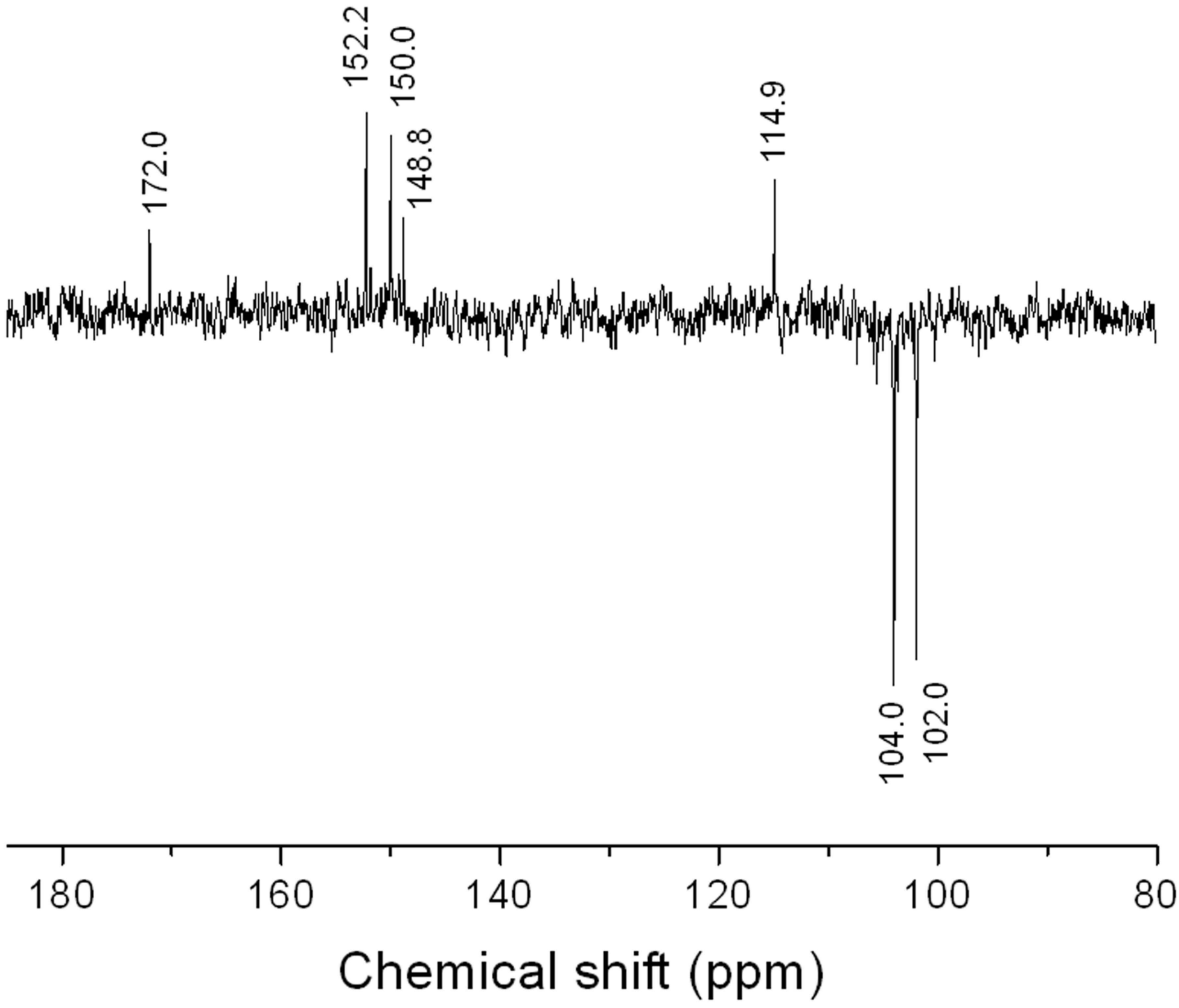

172.0
152.2
150.0
148.8
114.9
104.0
102.0
180
160
140
120
100
80
Chemical shift (ppm)

Figure 5

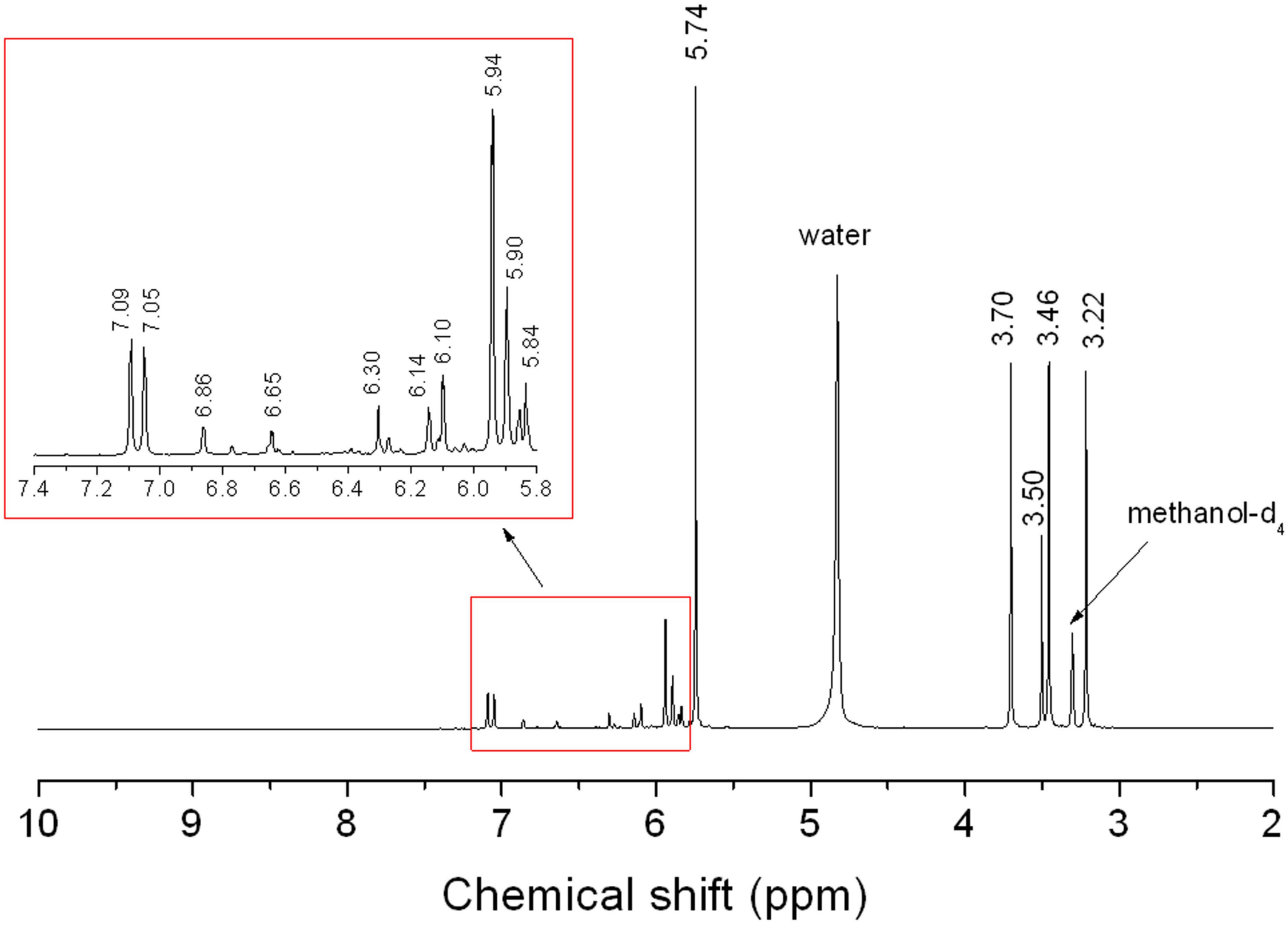
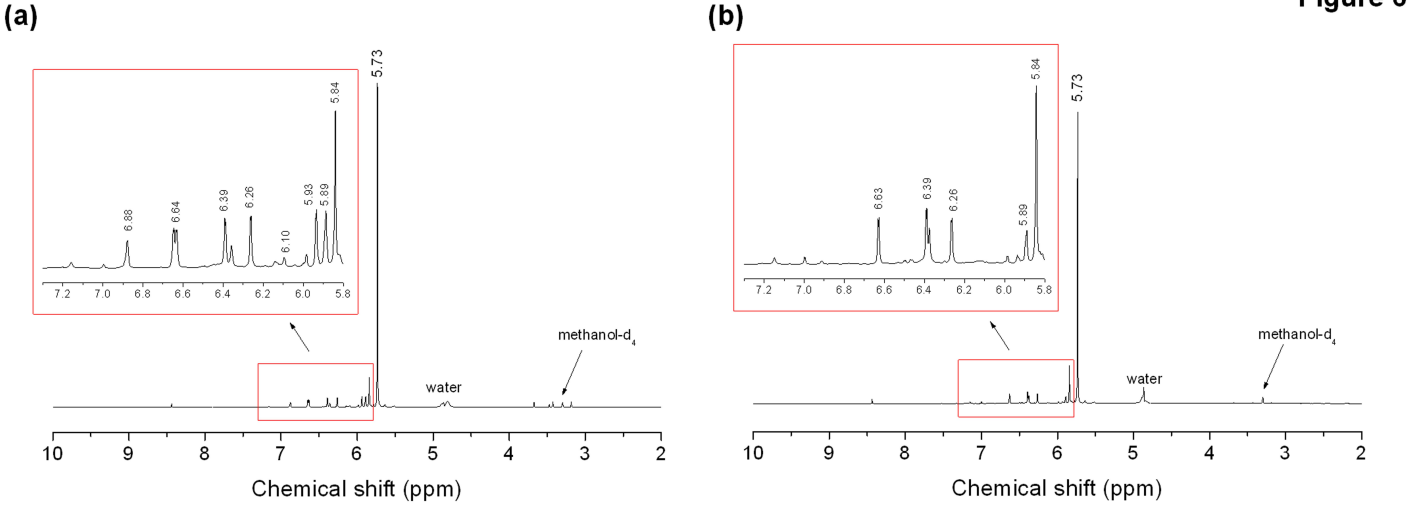
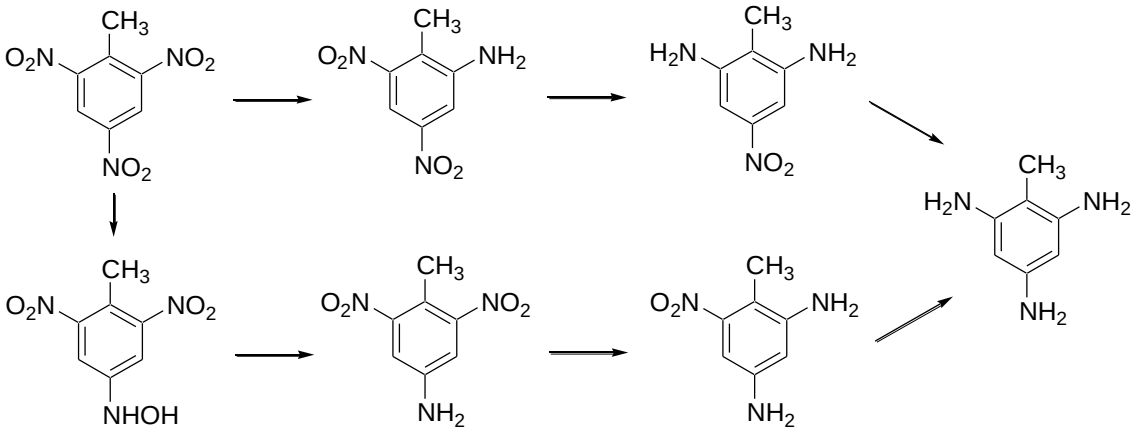
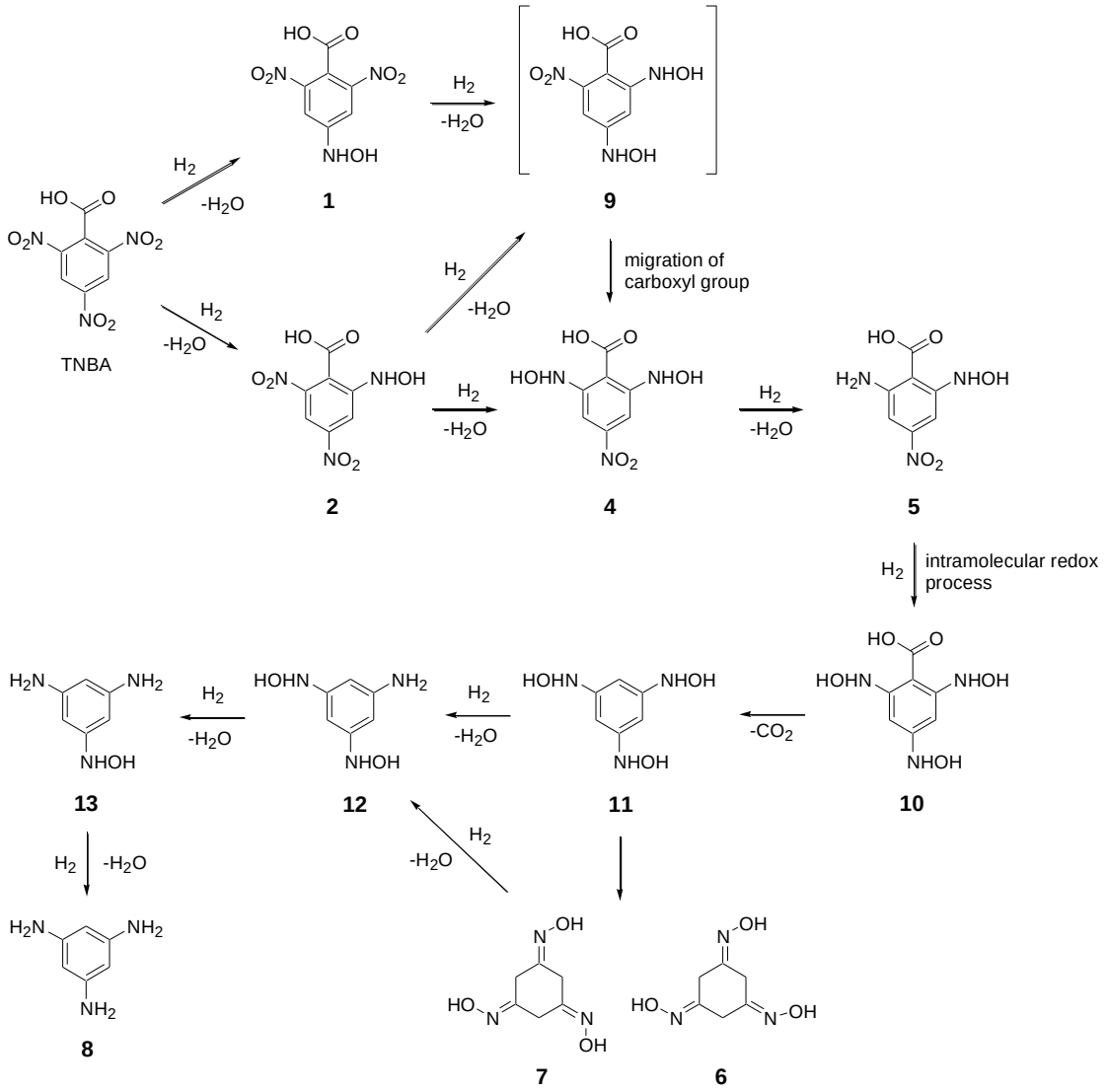

5.74
water
3.70
3.46
3.22
3.50
methanol-d4
7.09
7.05
6.86
6.65
6.30
6.14
6.10
5.94
5.90
5.84
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
10
9
8
7
6
5
4
3
2
Chemical shift (ppm)

Figure 6

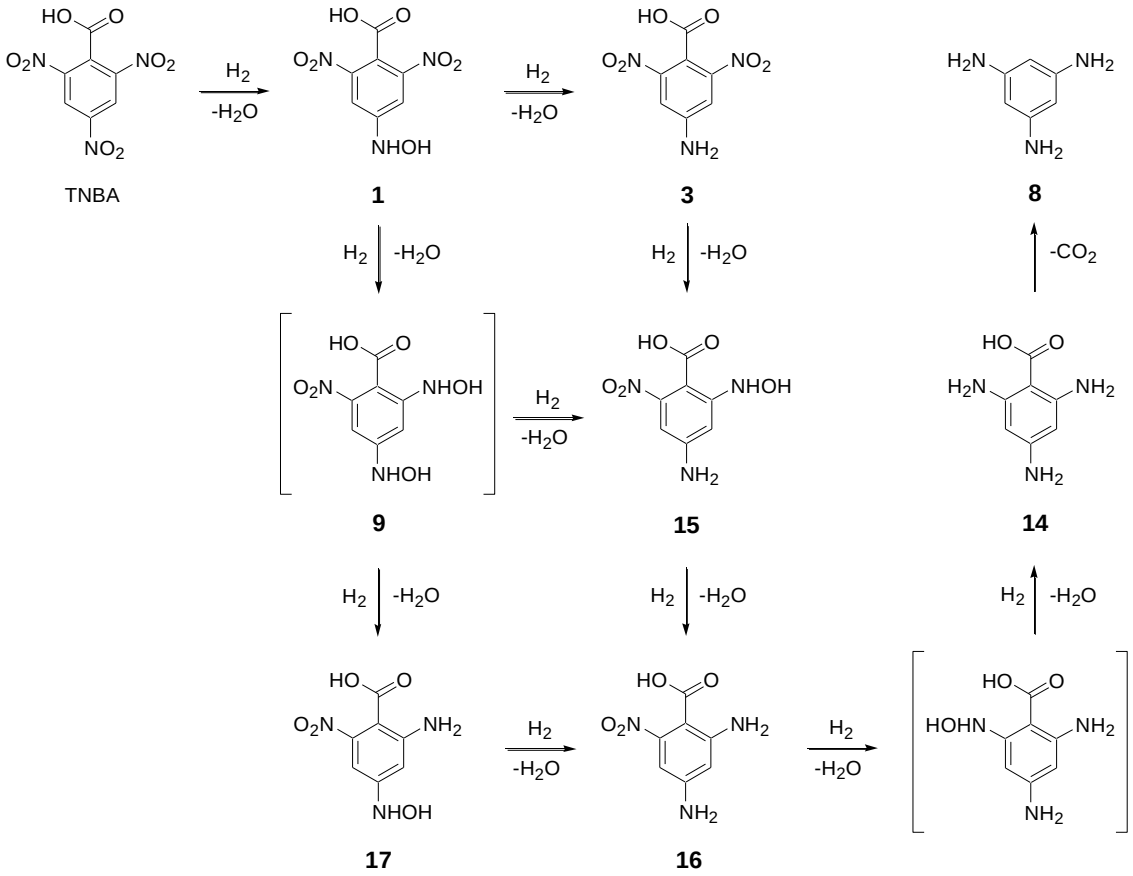

(a)
5.73
5.84
6.88
6.64
6.39
6.26
6.10
5.93
5.89
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
methanol-d4
water
10
9
8
7
6
5
4
3
2
Chemical shift (ppm)
(b)
5.84
5.73
6.63
6.39
6.26
5.89
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
methanol-d4
water
10
9
8
7
6
5
4
3
2
Chemical shift (ppm)



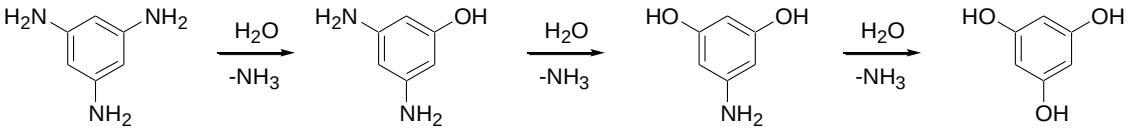
Scheme 1. Reaction pathways of TNT hydrogenation over Pd/C catalyst in an alcohol solution. Based on ^{1}H NMR and mass spectrometry data [21].



Scheme 2. Possible reaction pathways of aqueous-phase TNBA hydrogenation over Pd/C catalyst. The formation of main reaction products is presented.



Scheme 3. Possible reaction pathways of aqueous-phase TNBA hydrogenation over Pd/C catalyst. The formation of minor intermediates is presented.



8 **18** **19** **20**

Scheme 4. Side hydrolysis reactions possibly occurred during aqueous-phase catalytic hydrogenation of TNBA.

Table captions

Table 1. Assignment of signals in ^{1}H NMR spectra of TNBA and its hydrogenation products[a].

Compound	Experimental spectrum	Simulated spectrum[b]	Literature spectral data
TNBA	δ 9.25 (s)	δ 8.86 (s, 2H, H-3, H-5)	δ 9.11 (s, H-3, H-5) [49]
1	δ 7.87 (s)	δ 8.08 (s, 2H, H-3, H-5)	
2	δ 8.27 (d, *J* = 2.2), 8.33 (d, *J* = 2.2)	δ 8.01 (d, ^{4}J = 2.3, 1H, H-3), 8.08 (d, ^{4}J = 2.3, 1H, H-5)	
3	δ 7.64 (s)	δ 7.82 (s, 2H, H-3, H-5)	δ 7.50 (s, H-3, H-5) [49]
4	δ 7.09 (s)	δ 6.80 (s, 2H, H-3, H-5)	
5	δ 7.06 (d, *J* = 2), 7.10 (d, *J* = 2)	δ 6.63 (d, ^{4}J = 2.3, 1H, H-3), 6.80 (d, ^{4}J = 2.3, 1H, H-5)	
6	δ 3.22 (s), 3.46 (s), 3.70 (s)	δ 3.0 (m, 6H, 3CH_2)	δ 3.1 (s, CH_2), 3.3 (s, CH_2), 3.5 (s, CH_2) [50]
7	δ 3.50 (s)	δ 3.15 (m, 6H, 3CH_2)	δ 3.33 (s, CH_2) [50]
8	δ 5.74 (s)	δ 5.24 (s, 3H, H-2, H-4, H-6)	δ 1.50 (br.s, 6H), 5.52 (s, 3H) [51]
11	δ 6.30 (s)	δ 6.18 (s, 3H, H-2, H-4, H-6)	
12	δ 6.10 (d), 6.14 (t)	δ 6.02 (d, ^{4}J = 2.3, 2H, H-2, H-6), 6.18 (dd, ^{4}J = 2.3, 1H, H-4)	
13	δ 5.88 (t), 5.94 (d)	δ 5.25 (t, ^{4}J = 2.3, 1H, H-2), 6.02 (d, ^{4}J = 2.3, 2H, H-4, H-6)	
14	δ 5.86 (s)	δ 5.61 (s, 2H, H-3, H-5)	
15	δ 6.64 (d, *J* = 2), 6.88 (d, *J* = 2)	δ 6.54 (d, ^{4}J = 2.3, 1H, H-5), 7.21 (d, ^{4}J = 2.3, 1H, H-3)	
16	δ 6.39 (d, *J* = 2), 6.63 (d, *J* = 2)	δ 6.54 (d, ^{4}J = 2.3, 1H, H-5), 6.95 (d, ^{4}J = 2.3, 1H, H-3)	

17	δ 6.77 (d, *J* = 2), 6.87 (d, *J* = 2)	δ 6.80 (d, ^4J = 2.3, 1H, H-5), 7.21 (d, ^4J = 2.3, 1H, H-3)	
18	δ 5.78 (d, *J* = 2), 5.83 (t, *J* = 2)	δ 5.20 (t, ^4J = 1.9, 1H, H-4), 5.80 (d, ^4J = 1.9, 2H, H-2, H-6)	
19	δ 5.92 (t), 5.99 (d)	δ 5.93 (d, ^4J = 2.1, 2H, H-4, H-6), 6.14 (t, ^4J = 2.1, 1H, H-2)	δ 4.72 (s, 2H, OH), 5.43 (t, *J* = 1.8, 1H, H-2), 5.48 (t, *J* = 1.8, 2H, H-4, H-6), 8.61 (s, 2H, NH_2) [52]
20	δ 5.89 (s)	δ 5.56 (s, 3H, H-2, H-4, H-6)	δ 5.80 (s, 3H, H-2, H-4, H-6) [53]
21	Main signals: δ 5.63 (s), 6.26 (d, *J* = 1.8) Minor signals: δ 5.53 (t), 7.16 (s)	Main signals: δ 6.10 (s, 2H), 6.18 (d, 2H), 6.32 (d, 2H) Minor signals: δ 5.28 (t, 1H), 5.65 (d, 1H), 5.70 (t, 1H), 6.50 (t, 1H), 6.52 (dd, 1H), 6.54 (d, 1H), 6.61 (t, 1H), 6.66 (t, 1H), 6.68 (t, 1H), 7.01 (dd, 1H)	

[a] Chemical shifts are expressed in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants (*J*) are given in Hz.

[b] Simulation of spectra were performed with the ACD/Labs 6.00 (Advanced Chemistry Development Inc.) software. The signals of exchangeable protons (such as NH and OH) are not presented.

Table 2. Assignment of signals in JMOD ^{13}C NMR spectra of TNBA and its hydrogenation products[a].

Compound	Experimental spectrum							Simulated spectrum[b]						
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-1	C-2	C-3	C-4	C-5	C-6	C-7
TNBA	136.4	146.1	126.1	146.1	126.1	146.1	167.1	126.9	146.5	125.8	144.0	125.8	146.5	169.3
1	124.0	147.5	114.0	151.9	114.0	147.5	170.0	115.1	152.0	117.6	156.6	117.6	152.0	169.3
2	126.8	146.6	111.3	150.3	113.0	148.2	169.7	118.9	152.0	114.1	154.3	117.6	153.0	167.4
5	114.9	148.8	104.0	152.2	102.0	150.0	172.0	110.1	153.6	105.4	162.0	102.9	155.5	165.7
6	154.0	35.7	153.9	31.0	153.9	25.8		158.9	36.3	156.3	30.3	156.3	24.3	
7	154.0	30.4	154.0	30.4	153.9	30.4		158.9	30.3	158.9	30.3	156.3	30.3	
8	149.1	96.9	149.1	96.9	149.1	96.9		149.4	97.4	149.4	97.4	149.4	97.4	
13	149.0	95.0	149.0	99.3	152.8	99.3		149.6	97.8	149.6	101.9	153.3	101.9	
14	106.7	147.0	96.1	147.7	96.1	147.0	161.4	95.7	154.1	98.6	164.0	98.6	154.1	165.9
16	110.5	148.5	107.4	151.4	102.3	149.4	173.5	104.1	153.4	112.9	159.3	104.9	154.7	167.6
18	158.4	95.6	149.6	97.6	149.6	95.6		156.9	96.9	146.5	101.3	146.5	96.9	
21	Main signals: 96.2, 96.3, 99.6, 148.6, 161.2							Main signals: 89.2, 90.1, 90.4, 91.0, 94.3, 96.4, 100.2, 101.2, 101.6, 102.1, 102.2, 102.9, 105.8						
	Minor signals: 92.9, 95.4, 95.6, 108.4, 143.5, 147.1, 148.1, 161.0, 162.2							Minor signals: 94.0, 143.9, 144.1, 145.7, 145.8, 146.1, 146.7, 147.1, 147.8, 148.0, 150.3, 150.5, 153.9, 157.0, 160.1, 162.0, 165.6						

[a] Chemical shifts are expressed in ppm.
[b] Simulation of spectra were performed with the ACD/Labs 6.00 (Advanced Chemistry Development Inc.) software.