Tetrahedron 64 (2008) 6294–6299

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# An efficient synthesis of (*E*)-nitroalkenes catalyzed by recoverable diamino-functionalized mesostructured polymers

Shaoyu Yan, Yuan Gao, Rong Xing, Yali Shen, Yueming Liu, Peng Wu *, Haihong Wu *

*Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China*

ARTICLE INFO

*Article history:*
Received 26 February 2008
Received in revised form 22 April 2008
Accepted 25 April 2008
Available online 30 April 2008

*Keywords:*
Nitroalkene
Heterogeneous catalyst
Mesoporous polymer
Hydrophobicity
Nitroaldol condensation

ABSTRACT

A clean, efficient, and simple method has been developed for synthesis of (*E*)-nitroalkenes using FDU–ED as an efficient catalyst. The reactions proceeded with moderate to high yields (60–96%) under mild conditions. The catalyst FDU–ED is recyclable and can be reused more than seven times without significant loss of activity and selectivity.



## 1. Introduction

Nitroalkenes are valuable intermediates for preparation of numerous products including insecticides,[1] fungicides,[2] and pharmacologically active substances.[3] Because the nitro group can be easily transformed into a variety of groups with different functionalities, such as amine, carbonyl groups, etc., nitroalkenes are considered to be particularly versatile in organic synthesis.[4] Moreover, they are powerful dienophiles in Diels–Alder reactions, and readily undergo addition reactions with many different nucleophiles.[5] They are also very useful substrates in asymmetric reactions.[6]

Conjugated nitroalkenes are usually synthesized via Henry reaction of nitroalkanes with carbonyl derivatives followed by dehydration of the resultant nitroalcohols. Different base catalysts have been used in the classical synthetic procedure for nitroalcohols, such as alkali metal hydroxides, metal oxides, carbonates, bicarbonates, alkoxides, magnesium and aluminum alkoxides, alkaline earth hydroxides, and rhodium complex.[7] Furthermore, the organic amines such as primary and tertiary amines have also been proven to be useful.[7] For the dehydration step, several reagents, such as basic alumina,[8] phthalic anhydride,[4b] dicyclohexylcarbodiimide (DCC),[9] $MeSO_2Cl$,[10] and $Me_3CCOCl$,[11] are commonly utilized to perform the reaction. These methods suffer from several disadvantages such as rigorous experimental conditions, use of stoichiometric amounts of reagents, long reaction time, tedious working-up procedures, large amounts of acids to neutralize bases, salts formed on neutralization of soluble base, lack of recoverability and sometimes high temperature for the second step.[12] Thus, the design and development of new catalysts and procedures for synthesis of nitroalkenes with high efficiency under mild conditions has been constantly in focus.

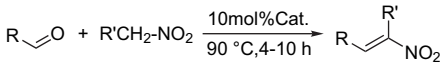
Presently, the use of eco-friendly heterogeneous catalysts has become an important research target for clean processes in fine chemical industries. Use of heterogeneous base catalysts, which are more stable and easier to be recycled, can offer a process solving the problems in classical methods. Several articles have reported the use of heterogeneous catalysts for one or two steps. The catalysts used were alumina,[13] alumina-KF,[14] Amberlyst A-21,[15] Mg–Al hydrotalcites,[16] Envirocat EPZG,[17] zeolite,[18] and amines supported on siliceous materials.[19] In order to achieve the maximum yield, high selectivity, and better process efficiency, there is still much work for researchers to accomplish and novel solid base materials with superior performance in catalytic activity and selectivity are expected.

In the present paper, we choose FDU-type mesoporous phenolic resins to immobilize the base catalysts, since the abundant aromatic rings contained in their structure are facile for further modification. FDU-mesoporous phenolic resin is a class of advanced materials possessing the advantages of both mesoporous materials (high surface area, large pore volume, and tunable mesostructure) and organic polymers (high hydrophobicity and containing aromatic sections).[20] Great advances in direct hydrothermal syntheses

* Corresponding authors.
*E-mail address:* hhwu@chem.ecnu.edu.cn (H. H. Wu).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.04.100

of mesoporous polymers make new solid catalysts promising. We have a continuing interest in the field of new solid catalysts. We recently reported a new method for the preparation of $SO_3H$-functionalized FDU-type mesoporous polymers (FDU–$SO_3H$).[21] Based on the previous work, we are now developing different series of new FDU-type solid base catalysts. Among those catalysts diamino-functionalized FDU-mesoporous polymers has proven to be the most efficient solid base catalyst. Herein, we report the efficient and eco-friendly application of diamino-functionalized FDU-mesoporous polymers (FDU–ED) for the synthesis of nitroalkenes under mild conditions (Scheme 1).




**Scheme 1.** The synthesis of (*E*)-nitroalkenes catalyzed by FDU–ED.

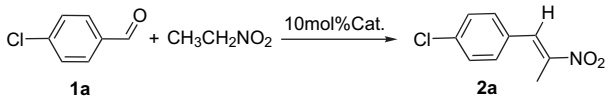
## 2. Results and discussion

The diamino-functionalized FDU-mesoporous polymers were easily prepared in two steps using 1,2-ethylenediamine (EDA). The solid base catalyst FDU–ED is then prepared (Scheme 2).

The reaction of 4-chlorobenzaldehyde **1a** with nitroethane over FDU–ED (10 mol %) was studied as a model reaction. The results listed in Table 1 show the effect of reaction temperature and solvent. When the reaction was carried out at 40 °C no product was detected. The reaction was completed in 4 h at 90 °C and gave a yield for product **2a** as high as 93%. However, prolonged reaction times are required for the reactions proceeded at lower temperatures such as 60 °C and 70 °C. When nitroethane was used as both nucleophile and solvent, high yield and high stereoselectivity (>95%) of product **2a** were realized in the reaction (entries 1–4). Other solvents such as tetrahydrofuran and water were also tested (entries 5 and 6). The results of the reactions proceeded in water were quite attractive, since it may lead to a more environmentally benign process for the synthesis, albeit the selectivity is low at the present stage.

With the best reaction conditions obtained, we further investigated the reactivity of various substituted benzaldehydes (**1b**–**1r**) over solid base catalyst FDU–ED and the results were summarized in Table 2. Table 2 shows that the corresponding nitroalkenes (**2b**–**2r**) are generally obtained in moderate to high yields, however, the reactions of all the substituted benzaldehydes proceed in a lower rate than that of 4-chlorobenzaldehyde. When the reactions of 2-chloro and 3-chlorobenzaldehyde proceed for 6 h, the corresponding product yields attained 77% and 80%, respectively (entries 1–2). The reactions of other halogen substituted aldehydes, such as 4-bromo, 2-bromo, and 4-fluorobenzaldehyde were also resulted in product yields of 80–89% (entries 3–5). Moderate product yields were obtained for the reactions of 3-nitro and 4-cyanobenzaldehyde with nitroethane (entries 6–7). Furthermore, the reaction of benzaldehyde also gave the product in moderate (76%) yield (entry 8). The reactions of derivatives of aromatic

**Table 1**
Influence of the reaction temperature and solvent on the reactivity and selectivity for the model reaction of **1a** and nitroethane

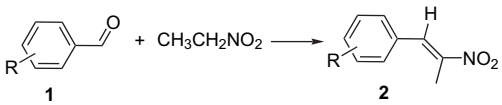



**1a** **2a**

| Entry | Time (h) | Temperature (°C) | Solvent | Conversion (%) | Selectivity[c] (%) |
|---|---|---|---|---|---|
| 1 | 4 | 40 | — | 6 | — |
| 2 | 4 | 60 | — | 37 | 100 |
| 3 | 4 | 70 | — | 51 | 96 |
| 4 | 4 | 90 | — | 100 (93[d]) | 100 |
| 5 | 8[a] | 60 | THF[b] | 100 | 60 |
| 6 | 4 | 90 | $H_2O$[b] | 89 | 90 |

Reaction conditions: 4-chlorobenzaldehyde (1 mmol), nitroethane 2 mL.
[a] Detected by TLC.
[b] Nitroethane 4 mmol, solvent 2 mL.
[c] Selectivity of (*E*)-1-(4-chlorophenyl)-2-nitropropene.
[d] Isolated yield.

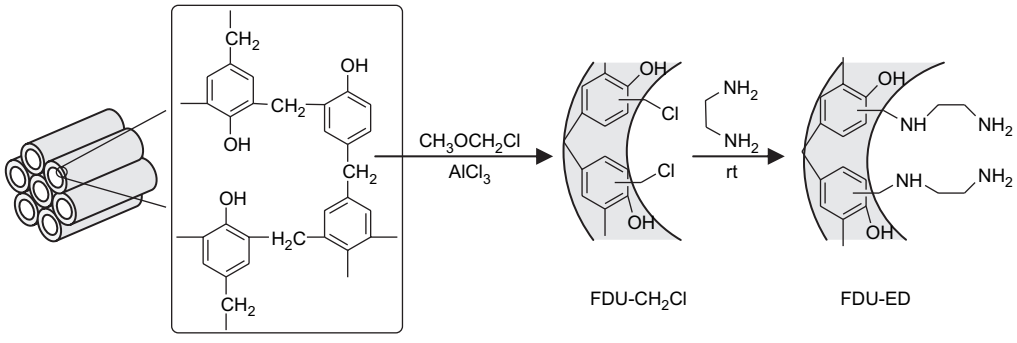
**Table 2**
Synthesis of (*E*)-nitrostyrenes catalyzed by FDU–ED




**1** **2**

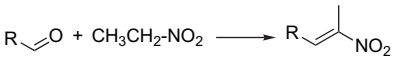
| Entry | R | Time[a] (h) | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 | **1b**: 2-Cl | 6 | **2b** | 77 |
| 2 | **1c**: 3-Cl | 6 | **2c** | 80 |
| 3 | **1d**: 4-Br | 6 | **2d** | 85 |
| 4 | **1e**: 2-Br | 6 | **2e** | 89 |
| 5 | **1f**: 4-F | 6 | **2f** | 80 |
| 6 | **1g**: 3-$NO_2$ | 6 | **2g** | 70 |
| 7 | **1h**: 4-CN | 6 | **2h** | 72 |
| 8 | **1i**: H | 6 | **2i** | 76 |
| 9 | **1j**: 4-$CH_3$ | 6 | **2j** | 84 |
| 10 | **1k**: 4-OMe | 6 | **2k** | 84 |
| 11 | **1l**: 3-OMe | 6 | **2l** | 85 |
| 12 | **1m**: 2-OMe | 6 | **2m** | 88 |
| 13 | **1n**: 2,3-OMe | 6 | **2n** | 83 |
| 14 | **1o**: 3,4,5-OMe | 6 | **2o** | 81 |
| 15 | **1p**: 4-OH | 6 | **2p** | 93 |
| 16 | **1q**: 3-OH | 6 | **2q** | 71 |
| 17 | **1r**: 4-$(CH_3)_2N$ | 10 | **2r** | 96 |

Reaction conditions: aldehyde (1 mmol), nitroethane 2 mL, catalyst (10 mol %), 90 °C.
[a] Detected by TLC.
[b] Isolated yield.

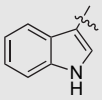



**Scheme 2.** The synthesis of solid base catalyst FDU–ED.

**Table 3**
Synthesis of (*E*)-nitroalkenes by the reactions of aliphatic aldehydes and heterocyclic aldehyde with nitroethane in the presence of FDU–ED




3 4

| Entry | R | Time[a] (h) | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  | 6 | **4a** | 89 |
| 2 |  | 6 | **4b** | 70 |
| 3 |  | 6 | **4c** | 70 |
| 4 | $CH_3CH_2CH_2$ | 6 | **4d** | 60 |
| 5 | $(CH_3)_2CH$ | 10 | **4e** | 85 |

Reaction conditions: aldehyde (1 mmol), nitroethane 2 mL, catalyst (10 mol %), 90 °C.
[a] Detected by TLC.
[b] Isolated yield.

aldehydes bearing electron-donating groups, such as methoxy, methyl, and hydroxyl, all gave satisfactory yields within 6 h, whereas the reaction of *p*-dimethylaminobenzaldehyde gave a good product yield after 10 h (entries 9–17). The results listed in Table 2 clearly demonstrate that the FDU–ED catalyst is efficient, with nearly quantitative results in most cases. Excellent regioselectivity has also been observed, where the (*E*)-stereoisomer is the sole product detected.[22]

The reaction of heterocyclic aldehyde and aliphatic aldehydes with nitroethane were also studied. The results are summarized in Table 3. The reaction of indole-3-carboxaldehyde gave the corresponding product **4a** in 89% yield after 6 h. The yields of the products **4b** and **4c** of the reactions of pyridine-3-carboxaldehyde and 2-furaldehyde, respectively, were both 70%. For aliphatic aldehydes, *n*-butyraldehyde gave a moderate yield for product **4d** because of the self-condensation, whereas the reaction of isobutyraldehyde afforded the corresponding product **4e** in 85% yield in 10 h.

When nitromethane was used as the nucleophile instead of the nitroethane, we were surprised to find that the reaction of 4-chlorobenzaldehyde **1a** with nitromethane in the presence of 10 mol % catalyst gave the corresponding (*E*)-1-(4-chlorophenyl)-2-nitroethene **5** in only 40% yield, and the main by-product was 2-phenyl-1,3-dinitropropane **6** via a subsequent Michael addition of the second molecular of nitromethane to product **5**. When the reaction proceeded continuously, the by-product **6** could attain a yield of 99% in 12 h. After further optimizing the reaction condition, we were pleased to find that 91% of **5** was afforded with a lower catalyst loading (5 mol %) (Scheme 3).

The reusability of FDU–ED in the reaction of 4-chlorobenzaldehyde **1a** and nitroethane was studied (Fig. 1). The catalyst was recovered by simple filtration and washing with acetone.

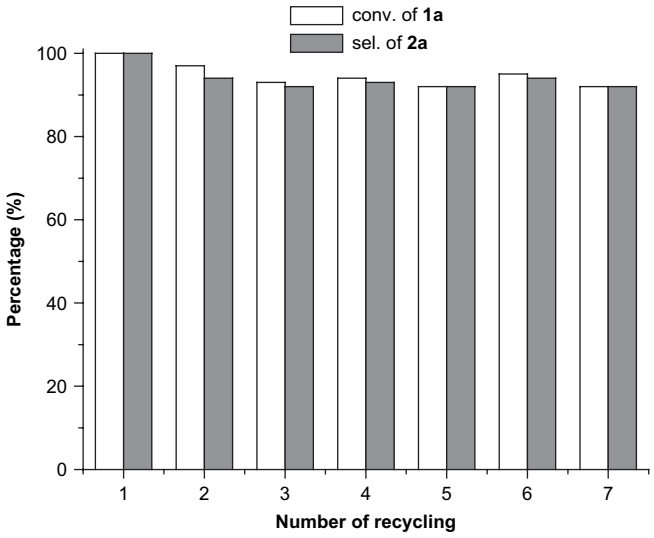



**Figure 1.** The **1a** conversion (blank) and **2a** (gray) selectivity when FDU–ED was reused in the model reaction. Reaction conditions: aldehyde (1 mmol), nitroethane 2 mL, catalyst (10 mol %), 90 °C, 4 h.

After being reused seven times, FDU–ED still showed high activity with 92% conversion and high selectivity, which was slightly lower than that of the fresh catalyst (100%). During the recycling of the catalyst, the high selectivity for **2a** was constantly maintained.

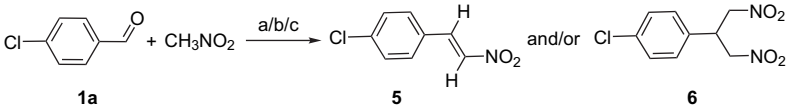
## 3. Conclusion

In summary, we have demonstrated that the mesoporous FDU–ED is a highly efficient solid basic catalyst for the nitroaldol condensation. Only (*E*)-nitroalkenes are obtained in moderate to high yields in the reaction of nitroethane with aldehydes, especially those aromatic aldehydes. The reaction using FDU–ED catalysts is eco-friendly, which minimizes harmful reagents, simplifies the work-up procedure, avoids the use of acids for neutralizing bases and the other problems associated with the salts formed on neutralization. The catalyst is recyclable, easily separable from the liquid reaction mixtures and can be reused more than seven times without noticeable decrease in reactivity and selectivity.

## 4. Experimental

### 4.1. General

All reagents were commercially available (Aldrich, Alfa Aesar) and were directly used without further purification. All reactions were carried out in Argonaut advantage series™ 2410 personal screening synthesizer. $^1H$ and $^{13}C$ NMR spectra were acquired on a Bruker DRX500 spectrometer at 500 MHz and 125 MHz, respectively, in $CDCl_3$. TMS was used as an internal standard for $^1H$ and $^{13}C$ NMR spectra. Flash column chromatography was performed using silica gel 60 (230–400 mesh). The X-ray diffraction




1a 5 6

a. 10mol%Cat., 4 h, **5** 40% yield
b. 10mol%Cat. 12 h, **6** 99% yield
c. 5mol%Cat., 10 h, **5** 91% yield

**Scheme 3.** Reaction of **1a** with nitromethane catalyzed by FDU–ED. Reaction conditions: aldehyde (1 mmol), nitromethane 2 mL, 90 °C.

(XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu Kα radiation (λ=1.5418 Å) at 40 kV and 40 mA. Nitrogen adsorption–desorption isotherms were recorded on a Quancachrome Autosorb-3B instrument. The specific surface areas were evaluated using Brunauer–Emmett–Teller (BET) method. The TEM images were recorded using a JEOL-JEM-2010 microscope. N elemental analyses were performed on an Elementar VarioEL III CHN elemental analyzer, while the amount of basic sites was quantified by a back titration method. When the reaction conditions were optimized, the conversion and selectivity of products were quantified on a Shimadzu 14B gas chromatograph equipped with an OV-1 capillary column using dodecane as an internal standard.

### 4.2. The preparation and characterization of solid base catalyst FDU–ED

The FDU-type mesoporous polymer was prepared following the literature procedures.[20a] Phenol (28 g, 0.3 mol) and aqueous solution of formaldehyde (38 wt %, 71.0 g, 1 mol) were added to 0.1 M NaOH solution (690 mL) to form a partially transparent solution after heating at 70 °C for 1.5 h. The mixture was then cooled at room temperature and mixed well with a clear solution of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, MW=5800, 67.2 g, 11.5 mmol) and deionized water (700 mL). It was then stirred continuously at 65 °C for 120 h and at 70 °C for 48 h in turn. The products of brown particles were collected by filtration and dried at 80 °C in air. After the removal of surfactant template by thermal decomposition under vacuum at 350 °C for 6 h, the FDU-type mesoporous polymer was obtained.

#### 4.2.1. The chloromethylation of FDU-type mesoporous polymers

Anhydrous $AlCl_3$ (12 g, 90 mmol) was added to a suspension of FDU-type mesoporous polymer (3 g) in chloromethyl methyl ether (30 mL) at room temperature. The reaction mixture was stirred and kept at room temperature for 10 h. The resulting suspension was treated with distilled water and filtered. The residue was washed repeatedly with distilled water and acetone to give corresponding FDU–$CH_2Cl$.

#### 4.2.2. The synthesis of solid base catalyst FDU–ED

FDU–$CH_2Cl$ (1 g) was mixed with ethylenediamine (10 mL) and the mixture was stirred at 60 °C for 6 h. The resulting suspension was filtered and washed repeatedly with distilled water, ethanol, and acetone to give the novel solid base mesoporous polymer FDU–ED.

#### 4.2.3. Characterization of FDU–ED

The powder XRD pattern FDU–ED showed well-resolved four reflection peaks (Fig. 2), which could be indexed as the [211], [220], [420], and [332] planes of a 3D bicontinuous cubic structure with an $Ia\bar{3}d$ space group. High resolution transmission electron microscopy (HRTEM) consistently verified that FDU–ED had a well-ordered mesostructure (Fig. 3). Moreover, $N_2$ adsorption isotherm indicated that FDU–ED had a specific surface area of 385 $m^2\,g^{-1}$ and a narrowed pore distribution centered at 3.0 nm. These results verified that the ordered mesostructure and mesopores were well preserved after the functionalizations. The nitrogen content of FDU–ED determined by elemental analysis was 4 mmol $g^{-1}$.

### 4.3. General procedure for the synthesis of conjugated nitroalkenes with various aldehyde and nitroalkanes

In a typical experiment, a mixture of the aldehyde (1 mmol) and FDU–ED 50 mg in nitroalkane (2 mL) was stirred at 90 °C. The reaction was monitored by TLC. After the completion of the reaction, the catalyst was filtered off and washed with dichloromethane and acetone. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (hexane/EtOAc) affording the products. The *E* geometry was readily assigned on the basis of $^1H$ NMR spectra. The catalyst was washed with acetone, dried, and reused without any further activation. The structures of the known products were characterized by comparison with data shown in literature.

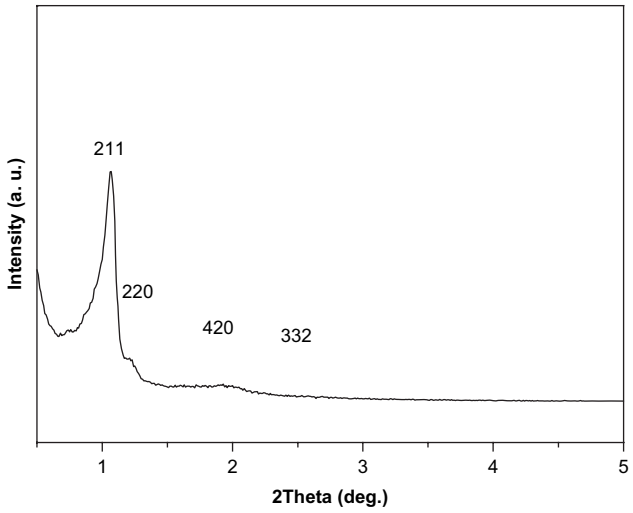



**Figure 2.** Powder XRD patterns of FDU–ED.

#### 4.3.1. (E)-1-(4-Chlorophenyl)-2-nitropropene (**2a**)[6a]

$^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 7.38 (d, 2H, *J*=9.0 Hz), 7.44 (d, 2H, *J*=9.0 Hz), 8.03 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 148.07, 136.07, 132.18, 131.14, 130.83, 129.23, 13.99.

#### 4.3.2. (E)-1-(2-Chlorophenyl)-2-nitropropene (**2b**)[6a]

$^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 2.37 (s, 3H), 7.29–7.41 (m, 3H), 7.51 (dd, 1H, *J*=2.0, 7.0 Hz), 8.21 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 149.22, 134.78, 131.27, 130.82, 130.61, 130.18, 129.99, 126.89, 13.91.

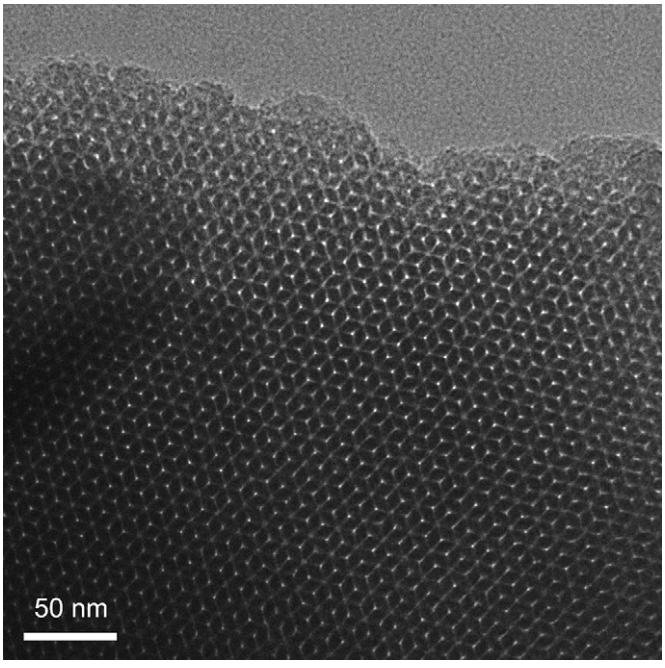



**Figure 3.** TEM micrograph of FDU–ED along [111].

*4.3.3. (E)-1-(3-Chlorophenyl)-2-nitropropene (**2c**)*[6a]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.47 (s, 3H), 7.32–7.34 (m, 1H), 7.42–7.44 (m, 3H), 8.03 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 148.74, 134.89, 134.17, 131.85, 130.16, 129.83, 129.58, 127.94, 13.97.

*4.3.4. (E)-1-(4-Bromophenyl)-2-nitropropene (**2d**)*[4e]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.46 (s, 3H), 7.33 (d, 2H, $J$=8.5 Hz), 7.62 (d, 2H, $J$=8.5 Hz), 8.04 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 148.13, 132.25, 132.19, 131.32, 131.28, 128.65, 124.38, 14.01.

*4.3.5. (E)-1-(2-Bromophenyl)-2-nitropropene (**2e**)*[4g]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.35 (s, 3H), 7.28–7.35 (m, 2H), 7.43 (t, 1H, $J$=8.0 Hz), 7.70 (d, 2H, $J$=8.0 Hz), 8.15 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 149.02, 133.17, 132.77, 130.92, 130.26, 127.51, 124.67, 13.84.

*4.3.6. (E)-1-(4-Fluorophenyl)-2-nitropropene (**2f**)*[3d]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.48 (s, 3H), 7.19 (t, 2H, $J$=8.5 Hz), 7.62 (dd, 2H, $J$=5.5, 8.5 Hz), 8.08 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 164.39, 162.39, 147.53, 132.39, 132.03, 131.96, 128.49, 116.26, 116.08, 13.94.

*4.3.7. (E)-1-(3-Nitrophenyl)-2-nitropropene (**2g**)*[12c]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.51 (s, 3H), 7.70 (t, 1H, $J$=8.0 Hz), 7.77 (d, 2H, $J$=8.0 Hz), 8.15 (s, 1H), 8.32 (d, 2H, $J$=7.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 149.84, 148.46, 135.44, 134.11, 130.65, 130.08, 124.32, 124.25, 13.95.

*4.3.8. (E)-1-(4-Cyanophenyl)-2-nitropropene (**2h**)*[4f]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.44 (s, 3H), 7.52 (d, 2H, $J$=8.0 Hz), 7.76 (dd, 2H, $J$=2.0, 8.0 Hz), 8.05 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 149.87, 136.98, 132.55, 131.44, 130.23, 118.05, 114.06, 14.01.

*4.3.9. (E)-1-Phenyl-2-nitropropene (**2i**)*[4e]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.49 (s, 3H), 7.28–7.35 (m, 5H), 8.12 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 147.75, 133.49, 132.42, 129.93, 129.88, 128.88, 14.00.

*4.3.10. (E)-1-(4-Methylphenyl)-2-nitropropene (**2j**)*[6a]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.44 (s, 3H), 2.49 (s, 3H), 7.29 (d, 2H, $J$=8.0 Hz), 7.38 (d, 2H, $J$=8.0 Hz), 8.11 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 146.93, 140.49, 133.67, 130.09, 129.64, 129.51, 21.43, 14.07.

*4.3.11. (E)-1-(4-Methoxyphenyl)-2-nitropropene (**2k**)*[6a,23a]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.48 (s, 3H), 3.87 (s, 3H), 6.98 (d, 2H, $J$=9.0 Hz), 7.43 (d, 2H, $J$=8.0 Hz), 8.05 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 161.08, 145.87, 133.57, 132.06, 124.71, 114.46, 55.41, 14.10.

*4.3.12. (E)-1-(3-Methoxyphenyl)-2-nitropropene (**2l**)*[6a,23a]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.48 (s, 3H), 3.87 (s, 3H), 6.98 (d, 1H, $J$=7.0 Hz), 7.00 (d, 1H, $J$=2.0 Hz), 7.05 (d, 1H, $J$=8.0 Hz), 7.40 (t, 1H, $J$=8.0 Hz), 8.08 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 159.75, 147.95, 133.68, 133.40, 129.92, 122.25, 115.44, 115.36, 55.34, 14.06.

*4.3.13. (E)-1-(2-Methoxyphenyl)-2-nitropropene (**2m**)*[6a,23a]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.42 (s, 3H), 3.91 (s, 3H), 6.98 (d, 1H, $J$=8.5 Hz), 7.04 (t, 1H, $J$=7.5 Hz), 7.33 (d, 1H, $J$=7.0 Hz), 7.43 (t, 1H, $J$=7.0 Hz), 8.31 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 158.10, 147.51, 131.52, 129.97, 129.79, 121.51, 120.47, 110.82, 55.55, 14.11.

*4.3.14. (E)-1-(2,3-Dimethoxyphenyl)-2-nitropropene (**2n**)*[4e]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.41 (s, 3H), 3.88 (s, 3H), 3.93 (s, 3H), 6.94 (d, 1H, $J$=8.0 Hz), 7.02 (d, 1H, $J$=7.5 Hz), 7.14 (t, 1H, $J$=8.0 Hz), 8.25 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 152.87, 148.42, 148.26, 129.44, 126.81, 124.06, 121.40, 114.05, 61.27, 55.88, 14.17.

*4.3.15. (E)-1-(3,4,5-Trimethoxyphenyl)-2-nitropropene (**2o**)*[3e]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.47 (s, 3H), 3.88 (s, 6H), 3.90 (s, 3H), 6.65 (s, 2H), 8.02 (s, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ (ppm): 152.90, 146.92, 139.16, 133.48, 127.32, 108.11, 60.09, 56.02, 13.92.

*4.3.16. (E)-1-(4-Hydroxyphenyl)-2-nitropropene (**2p**)*[7h]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.47 (s, 3H), 5.30 (s, 1H), 6.93 (d, 2H, $J$=9.0 Hz), 7.39 (d, 2H, $J$=8.0 Hz), 8.07 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 157.38, 145.73, 133.79, 132.33, 124.87, 116.05, 14.10.

*4.3.17. (E)-1-(3-Hydroxyphenyl)-2-nitropropene (**2q**)*[7i]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.45 (s, 3H), 5.07 (s, 1H), 6.91 (d, 2H, $J$=7.0 Hz), 7.01 (d, 1H, $J$=7.0 Hz), 7.33 (t, 1H, $J$=7.0 Hz), 8.03 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 157.38, 145.73, 133.79, 132.33, 124.87, 116.05, 14.10.

*4.3.18. (E)-1-(4-Dimethylaminophenyl)-2-nitropropene (**2r**)*[12c]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.49 (s, 3H), 3.05 (s, 6H), 6.73 (d, 2H, $J$=9.0 Hz), 7.41 (d, 2H, $J$=9.0 Hz), 8.09 (s, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ (ppm): 151.55, 141.89, 134.79, 132.86, 118.55, 111.80, 39.69, 14.11.

*4.3.19. 3-(2-Nitro-propenyl)-1H-indole (**4a**)*[23b]

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm): 2.49 (s, 3H), 7.20 (t, 1H, $J$=7.5 Hz), 7.26 (t, 1H, $J$=7.5 Hz), 7.51 (d, 1H, $J$=8.0 Hz), 7.84 (d, 1H, $J$=8.0 Hz), 8.02 (s, 1H), 8.47 (s, 1H), 12.21 (br, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ (ppm): 141.04, 136.13, 130.01, 127.44, 126.57, 122.91, 120.98, 118.22, 112.32, 108.16, 14.61.

*4.3.20. (E)-1-(3-Pyridyl)-2-nitropropene (**4b**)*[12c]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.45 (s, 3H), 7.40 (dd, 1H, $J$=4.0, 8.0 Hz), 7.74 (d, 1H, $J$=8.0 Hz), 8.03 (s, 1H), 8.64 (d, 1H, $J$=4.0 Hz), 8.68 (s, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ (ppm): 150.82, 150.41, 149.04, 137.07, 129.97, 128.32, 123.74, 13.86.

*4.3.21. (E)-1-(2-Furyl)-2-nitropropene (**4c**)*[3f]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 2.58 (s, 3H), 6.57 (dd, 1H, $J$=1.0, 3.0 Hz), 6.81 (d, 1H, $J$=3.0 Hz), 7.63 (s, 1H), 7.84 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 147.98, 146.18, 120.56, 119.14, 112.83, 13.99.

*4.3.22. (E)-2-Nitro-2-hexene (**4d**)*[22b]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 0.98 (t, 3H, $J$=7.0 Hz), 1.53–1.57 (m, 2H), 2.17 (s, 3H), 2.22 (q, 2H, $J$=8.0 Hz), 7.14 (t, 1H, $J$=8.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 147.69, 136.08, 29.98, 21.61, 13.69, 12.43.

*4.3.23. (E)-4-Methyl-2-nitro-2-pentene (**4e**)*[6a]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 1.11 (d, 6H, $J$=6.0 Hz), 2.17 (s, 3H), 2.55–7.60 (m, 1H), 6.95 (d, 1H, $J$=10.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 146.31, 142.20, 27.99, 21.79, 12.44.

*4.3.24. (E)-1-(4-Chlorophenyl)-2-nitroethene (**5**)*[6e]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 7.44 (dd, 2H, $J$=2.0, 8.0 Hz), 7.49 (dd, 2H, $J$=1.5, 7.0 Hz), 7.65 (d, 1H, $J$=14.0 Hz), 7.97 (d, 1H, $J$=14.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 138.30, 137.63, 137.40, 130.22, 129.73, 128.51.

*4.3.25. 2-(4-Chlorophenyl)-1,3-dinitro-propane (**6**)*[16b]

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): 4.29–4.32 (m, 1H), 4.71–4.80 (m, 4H), 7.18 (d, 2H, $J$=8.5 Hz), 7.37 (dd, 2H, $J$=2.0, 8.5 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 136.61, 133.93, 131.21, 130.09, 77.84, 42.51.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20602012), Shanghai Phosphor Project of Science and Technology for Excellent Young Researcher (No. 07QA14017), the Research Fund for the Doctoral Program of Higher Education (20070269023) and Shanghai Leading Academic Discipline Project (No. B409).

## References and notes

1. Boelle, J.; Schneider, R.; Gerardin, P.; Loubinoux, B.; Maienfisch, P.; Rindlisbacher, A. *Pestic. Sci.* **1998**, *54*, 304–307.
2. (a) Brian, P. W.; Grove, J. F.; McGowan, J. C. *Nature* **1946**, *158*, 876–877; (b) McGowan, J. C.; Brian, P. W.; Hemming, H. G. *Ann. Appl. Biol.* **1948**, *35*, 25–36.
3. (a) Schales, O.; Graefe, H. A. *J. Am. Chem. Soc.* **1952**, *74*, 4486–4490; (b) Dann, O.; Moller, E. F. *Chem. Ber.* **1949**, *82*, 76–92; (c) Zee-Cheng, K.-Y.; Cheng, C. C. *J. Med. Chem.* **1969**, *12*, 157–161; (d) Plenevaux, A.; Dewey, S. L.; Fowler, J. S.; Guillaume, M.; Wolf, A. P. *J. Med. Chem.* **1990**, *33*, 2015–2019; (e) Rosowsky, A.; Mota, C. E.; Wright, J. E.; Freisheim, J. H.; Heusner, J. J.; McCormack, J. J.; Queener, S. F. *J. Med. Chem.* **1993**, *36*, 3103–3112; (f) Vallejos, G.; Fierro, A.; Rezende, M. C.; Sepulveda-Boza, S.; Reyes-Parada, M. *Bioorg. Med. Chem.* **2005**, *13*, 4450–4457.
4. (a) Barratt, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751–762; (b) Barratt, A. G. M. *Chem. Soc. Rev.* **1991**, *20*, 95–127; (c) Kabalka, G. W.; Varma, R. S. *Org. Prep. Proced. Int.* **1987**, *19*, 283–328; (d) Gorczynski, M. J.; Huang, J.; Lee, H.; King, S. B. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 2013–2017; (e) Mourad, M. S.; Varma, R. S.; Kabalka, G. W. *J. Org. Chem.* **1985**, *50*, 133–135; (f) Bak, R. R.; Mcanda, A. F.; Smallridge, A. J.; Trewhella, M. A. *Aust. J. Chem.* **1996**, *49*, 1257–1260; (g) Takeshita, M.; Yoshida, S.; Kohno, Y. *Heterocycles* **1994**, *37*, 553–562.
5. (a) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137–166; (b) Fringuelli, F.; Matteucci, M.; Piermatti, O.; Pizzo, F.; Burla, M. C. *J. Org. Chem.* **2001**, *66*, 4661–4666.
6. (a) Kawai, Y.; Inaba, Y.; Tokitoh, N. *Tetrahedron: Asymmetry* **2001**, *12*, 309–318; (b) McAnda, A. F.; Roberts, K. D.; Smallridge, A. J.; Ten, A.; Trewhella, M. A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 501–504; (c) Ji, J. G.; Barnes, D. M.; Zhang, J.; King, S. A.; Wittenberger, S. J.; Morton, H. E. *J. Am. Chem. Soc.* **1999**, *121*, 10215–10216; (d) Okino, T.; Hoashi, Y.; Furukawa, T.; Xu, X.; Takemoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 119–125; (e) Andrey, O.; Alexakis, A.; Bernardinelli, G. *Org. Lett.* **2003**, *5*, 2559–2561; (f) Mampreian, D. M.; Hoveyda, A. H. *Org. Lett.* **2004**, *6*, 2829–2832; (g) Cote, A.; Lindsay, V. N. G.; Charette, A. B. *Org. Lett.* **2007**, *9*, 85–87.
7. (a) Bulbule, V. J.; Jnaneshwara, G. K.; Deshmukh, R. R.; Borate, H. B.; Deshpande, V. H. *Synth. Commun.* **2001**, *31*, 3623–3626; (b) Sasai, H.; Suzuki, T.; Arai, S.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1992**, *114*, 4418–4420; (c) Kumar, H. M. S.; Reedy, B. V. S.; Yadav, J. S. *Chem. Lett.* **1998**, 637–638; (d) Ballini, R.; Bosica, G. *J. Org. Chem.* **1997**, *62*, 425–427; (e) Nunan, J. G.; Himelfarb, P. B.; Herman, R. G.; Klier, K.; Bogdan, C. E.; Simmons, G. W. *Inorg. Chem.* **1989**, *28*, 3868–3874; (f) Kisanga, P. B.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 4298–4303; (g) Kiyooka, S.; Tsutsui, T.; Maeda, H.; Kaneko, Y.; Isobe, K. *Tetrahedron Lett.* **1995**, *36*, 6531–6534; (h) Varma, R. S.; Dahiya, R.; Kumar, S. *Tetrahedron Lett.* **1997**, *38*, 5131–5134; (i) Somasekhara, S.; Desai, D. M.; Upadhyaya, U. V. US3985761, 1976.
8. Ballini, R.; Castagnani, R.; Petrini, M. *J. Org. Chem.* **1992**, *57*, 2160–2162.
9. Knochel, P.; Seebach, D. *Synthesis* **1982**, 1017–1018.
10. Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*, 2138–2139.
11. Seebach, D.; Knochel, P. *Helv. Chim. Acta* **1984**, *67*, 261–283.
12. (a) Rosini, G.; Ballini, R.; Petrini, M.; Sorrenti, P. *Synthesis* **1985**, 515–517; (b) Saikia, A. K.; Barua, N. C.; Sharma, R. P.; Ghosh, A. C. *Synthesis* **1994**, 685–686; (c) Agafonov, N. E.; Sedishev, I. P.; Dudin, A. V.; Kutin, A. A.; Stashina, G. A.; Zhulin, V. M. *Bull. Acad. Sci. Russ. Div. Chem. Sci. (Engl. Transl.)* **1991**, *40*, 366–372.
13. Rosini, G.; Ballini, R.; Sorrenti, P. *Synthesis* **1983**, 1014–1016.
14. Melot, J. M.; Texier-Boullet, F.; Foucaud, A. *Tetrahedron Lett.* **1986**, *27*, 493–496.
15. Ballini, R.; Bosica, G.; Forconi, P. *Tetrahedron* **1996**, *52*, 1677–1684.
16. (a) Bulbule, V. J.; Deshpande, V. H.; Velu, S.; Sudalai, A.; Sivasankar, S.; Sathe, V. T. *Tetrahedron* **1999**, *55*, 9325–9332; (b) Cwik, A.; Fuchs, A.; Hell, Z.; Clecens, J. M. *Tetrahedron* **2005**, *61*, 4015–4021; (c) Choudary, B. M.; Kantam, M. L.; Reddy, V. Ch.; Rao, K. K.; Figueras, F. *Green. Chem.* **1999**, *1*, 187–189; (d) Choudary, B. M.; Kantam, M. L.; Kavita, B. *J. Mol. Catal. A: Chem.* **2001**, *169*, 193–197.
17. Bandgar, B. P.; Zirange, M. B.; Wadgaonkar, P. P. *Synlett* **1996**, 149–150.
18. Ballini, R.; Bigi, F.; Gogni, E.; Maggi, R.; Sartori, G. *J. Catal.* **2000**, *191*, 348–353.
19. (a) Demicheli, G.; Maggi, R.; Mazzacani, A.; Righi, P.; Sartori, G.; Bigi, F. *Tetrahedron Lett.* **2001**, *42*, 2401–2403; (b) Sharma, K. K.; Asefa, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 2879–2882; (c) Kantam, M. L.; Sreekanth, P. *Catal. Lett.* **1999**, *57*, 227–231; (d) Macquarie, D. J.; Maggi, R.; Mazzacani, A.; Sartori, G.; Sartorio, R. *Appl. Catal. A: Gen.* **2003**, *246*, 183–188; (e) Sartori, G.; Bigi, F.; Maggi, R.; Sartorio, R.; Macquarrie, D. J.; Lenarda, M.; Storaro, L.; Coluccia, S.; Martra, G. *J. Catal.* **2004**, *222*, 410–418.
20. (a) Zhang, F.; Meng, Y.; Gu, D.; Yan, Y.; Yu, C.; Tu, B.; Zhao, D. *J. Am. Chem. Soc.* **2005**, *127*, 13508–13509; (b) Meng, Y.; Gu, D.; Zhang, F.; Shi, Y.; Yang, H.; Li, Z.; Yu, C.; Tu, B.; Zhao, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 7053–7059; (c) Meng, Y.; Gu, D.; Zhang, F.; Shi, Y.; Cheng, L.; Feng, D.; Wu, Z.; Chen, Z.; Wan, Y.; Stein, A.; Zhao, D. *Chem. Mater.* **2006**, *18*, 4447–4464.
21. Xing, R.; Liu, N.; Liu, Y.; Wu, H.; Jiang, Y.; Chen, L.; He, M.; Wu, P. *Adv. Funct. Mater.* **2007**, *17*, 2455–2461.
22. (a) Ono, D.; Kamimura, A.; Kawai, T.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1550–1551; (b) Peter Stanetty, P.; Kremslehner, M. *Tetrahedron Lett.* **1998**, *39*, 811–812.
23. (a) Dawson, B. A.; By, A. W.; Avdovich, H. W. *Magn. Reson. Chem.* **1991**, *29*, 188–189; (b) Bakhmutov, V. I.; Kochetkov, K. A.; Burmistrov, V. A.; Babievskii, K. K.; Belikov, V. M. *Bull. Acad. Sci. Russ. Div. Chem. Sci. (Engl. Transl.)* **1977**, *26*, 1520–1521.