



The synthesis of diethyl 2-(2,2'-bipyridin-4-ylmethylene)malonate and diethyl 3,3'-(2,2'-bipyridine-4,4'-diyl)diacrylate

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Abstract. The new acrylic acid derivatives diethyl 2-(2,2'-bipyridin-4-ylmethylene)malonate and diethyl 3,3'-(2,2'-bipyridine-4,4'-diyl)diacrylate which may be used for the introduction of metal coordination sites in polyacrylates were synthesized and characterized. Intermediates of the syntheses were prepared by improved synthetic protocols working under microwave conditions whenever it was advantageous for the resulting product in terms of reaction time and/or chemical yield. In addition, the crystal structure of one of the intermediates, 4,4'-dibromo-2,2'-bipyridine (**6**), is reported, in which molecules are arranged into infinite chains by C-H—Br interactions.

Keywords. Bromination; crystal structure; microwave assisted synthesis; bipyridine ligands; Wittig reaction.

1. Introduction

Bipyridine ligands are a commonly used class of ligands in the synthesis of transition metal complexes. In the last decades, photochemically active transition metal complexes with 2,2'-bipyridine ligands and their applications were in the focus of scientific interest. The prototype of this class of compounds is $[\text{Ru}(\text{bipy})_3]^{2+}$, but other metals as Ir, Re, Os, and even first-row transition metals as e.g. Fe have caused considerable attention. A number of recent reviews summarize results concerning the photophysical properties of $[\text{Ru}(\text{bipy})_3]^{2+}$ derivatives,^{1–3} their application in photocatalysis^{4–8} as well as for the construction of dye-sensitized solar cells^{9–14} and the potential use of iron instead of ruthenium.^{15,16}

Recently, we reported a new 2,2'-bipyridine derivative with an acrylate related side chain.¹⁷ Compounds containing acrylate related side chains might be used as co-monomers in the synthesis of polyacrylates as a potential pathway to integrate coordination sites for transition metals into the surfaces of polymeric materials.

In the meantime we were able to further develop the synthetic methodology applying microwave technology whenever it was advantageous for the synthesis of two new 2,2'-bipyridine derivatives with acrylate related side chains. We therefore report herein the synthesis of diethyl 2-(2,2'-bipyridin-4-ylmethylene)malonate and diethyl 3,3'-(2,2'-bipyridine-4,4'-diyl)diacrylate.

2. Experimental

2.1 Materials and physical measurements

Reagents and solvents were purchased from Aldrich, Carl Roth and Laachner and used without further purification. Diethyl ether, THF and toluene were dried over sodium/benzophenone. Silica gel 60 from Machery-Nagel was used for column chromatography. Nitrogen was used as inert gas if needed.

For microwave assisted reactions a MLS Ethos.Lab microwave oven with pressure vessels in a monorack and internal ATC-FO sensor was used. Melting points were determined with a Melting Point Meter MPM-HV2, GC-MS spectra were recorded with a Finnigan Mat GCQ. IR spectra were recorded

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with a Shimadzu IR Prestige-21 FTIR spectrometer. UV-Vis Data were obtained with a WTW photolab 6600 UV-Vis spectrometer. NMR data were recorded on a Bruker DRX 400 spectrometer (^1H : 400.13 MHz; ^{13}C : 100.62 MHz; CDCl_3 as internal standard).

2.2 Synthesis of diethyl

2-(2,2'-bipyridin-4-ylmethylene)malonate (3)

0.5 cm³ (2.5 mmol) diethyl malonate, one drop of piperidine, one drop of acetic acid and 0.46 g (2.5 mmol) 2,2'-bipyridine-4-carbaldehyde¹⁷ were dissolved in 10 cm³ n-heptane. The reaction mixture was heated to reflux for 17 h. After cooling to room temperature 10 cm³ distilled water and 10 cm³ methyl *tert*-butyl ether were added. The organic layer was separated and washed with 10 cm³ water and 10 cm³ brine. The organic layer was dried over sodium sulfate and the solvent was evaporated. The crude product was purified by column chromatography using alumina as stationary phase and a mixture of diethyl ether and toluene (1:2) as eluent. The product was recrystallized from an ethanol water mixture by dissolving the product first in ethanol and adding water until the solution turned cloudy. Yield: 14% (0.12 g, 0.35 mmol). IR (298 K) [cm⁻¹]: 2995w, 2970w, 2936w, 1715vs, 1697s, 1643m, 1589m, 1547m, 1450m, 1364s, 1317s, 1206s, 1177vs, 1028m, 982m, 839s; MS (EI), *m/z* (%): 327 (1) [MH⁺], 297 (65) [M⁺ - C₂H₅], 282 (62) [MH⁺ - C₂H₅O], 269 (65) [M⁺ - 2 C₂H₅], 253 (80) [MH⁺ - C₂H₅O - C₂H₅], 235 (30) [MH⁺ - 2 C₂H₅OH], 225 (100) [MH⁺ - C₃H₅O₂ - C₂H₅], 210 (100) [C₁₃H₁₀N₂O⁺], 182 (95) [C₁₀H₉N₂⁺], 156 (15) [C₁₀H₈N₂⁺]; $^1\text{H-NMR}$ (CDCl_3): δ [ppm] = 1.32 (t, J = 7.07 Hz, 3 H), 1.36 (t, J = 7.20 Hz, 3 H), 4.34 (q, J = 1.00 Hz, 2 H), 4.39 (q, J = 1.00 Hz, 2 H), 7.31–7.36 (m, 2 H), 7.76 (s, 1 H), 7.83 (td, J = 7.77, 1.89 Hz, 1 H), 8.40 (dt, J = 7.89, 0.98 Hz, 1 H), 8.48–8.51 (m, 1 H), 8.66–8.69 (m, 1 H), 8.71 (d, J = 5.31 Hz, 1 H); $^{13}\text{C-NMR}$ (CDCl_3): δ [ppm] = 13.8, 14.1, 62.0, 120.6, 121.0, 122.4, 124.0, 130.5, 136.9, 139.3, 141.3, 149.2, 149.7, 155.3, 157.0, 163.4, 165.6; M.p.: 65–67 °C; elemental analysis: calc. (%) for C₁₈H₁₈N₂O₄: C 66.25, H 5.56, N 8.58; found: C 67.94, H 5.65, N 8.85.

2.3 Synthesis of 2,2'-bipyridine-*N,N'*-dioxide (4)

4 was synthesized according to a modified literature procedure.¹⁸ 2 g (12.8 mmol) 2,2'-bipyridine were suspended in 15 cm³ concentrated acetic acid in a microwave vessel and 5 cm³ (49 mmol) of 30% H₂O₂ were added dropwise. The microwave vessel was sealed and heated to 100 °C within 20 min using a maximum power of 1000 MW. The temperature was held for one hour and forty minutes. After cooling to room temperature, the mixture was mixed with 170 cm³ acetone leading to the immediate formation of a white precipitate. The mixture was cooled for an additional hour in an ice bath before the precipitate was collected, washed with acetone and air dried. Yield: 97% (2.39 g, 12.7 mmol); melting point: 303 °C (decomp.), literature: 307–309 °C.¹⁹

2.4 Synthesis of 4,4'-dinitro-2,2'-bipyridine-*N,N'*-dioxide (5) and 4,4'-dinitro-2,2'-bipyridine (5a)

5 and **5a** were synthesized according to a modified literature procedure.^{18,19} 1.0 g (5.3 mmol) **4** was dissolved in a mixture of 0.4 cm³ oleum and 4.2 cm³ concentrated sulfuric acid and cooled to 0 °C in an ice bath. 2.2 cm³ fuming nitric acid were added carefully. The reaction mixture was heated to 100 °C overnight. Subsequently the reaction mixture was cooled to 0 °C using an ice bath before it was poured on 20 g crushed ice. Liquid nitrogen was added immediately to freeze the reaction mixture. After warming to room temperature, liquid nitrogen was added again. While warming to room temperature a slightly yellow precipitate formed, which was collected and washed with water. The crude product consisted of a mixture of **5** and **5a** and was used for further reactions without purification. Yield: 40% (0.6 g, 2.16 mmol).

2.5 Synthesis of 4,4'-dibromo-2,2'-bipyridine (6)

6 was synthesized according to a modified literature procedure.²⁰ 0.9 g (3.2 mmol) of a mixture consisting of **5** and **5a** were suspended in 20 cm³ glacial acetic acid in a microwave vessel and 3 cm³ (40.5 mmol) acetyl bromide were added. The mixture turned yellow immediately and the microwave vessel was sealed before it was heated to 130 °C within ten minutes and a maximum power of 1000 MW. The reaction temperature then was maintained for 2 h after which the vessel was allowed to cool to room temperature. The reaction mixture was basified with a concentrated K₂CO₃ solution so that a brownish precipitate formed. The precipitate was collected, washed with water and dried. For purification, the crude product was dissolved in dichloromethane and filtered. After the solvent was evaporated product was further purified by distillation under reduced pressure to obtain as white solid. Single crystals of (**6**) were obtained by dissolving a sample of the compound in the minimum amount of ethanol, adding water until a low haze was observed and storing the solution in a refrigerator (4 °C) overnight. Yield: 81% (0.825 g, 2.6 mmol); melting point: 141–142 °C, literature: 135–136 °C.²¹

2.6 Synthesis of 2,2'-bipyridine-4,4'-dicarbaldehyde (7)

7 was synthesized before by applying other methodologies.^{22,23} 0.9 g of **6** (2.9 mmol) were dissolved in 25 cm³ anhydrous diethyl ether and 25 cm³ anhydrous toluene under a nitrogen atmosphere at -78 °C. Butyl lithium in hexane (5 cm³, 2.5 mol/L) was added dropwise. The solution was stirred at -78 °C for 90 min before 8.0 cm³ anhydrous dimethyl formamide were added. The resulting solution was then stirred for another 90 min at the same temperature. To stop the reaction 50 cm³ 2 N hydrochloric acid were added at -78 °C and the solution was then allowed to reach room temperature. The organic phase was separated and the aqueous phase was neutralized with diluted sodium hydroxide solution. A smooth

white precipitate formed that was three times extracted with CH_2Cl_2 . The solvent was evaporated under reduced pressure and a pale brown oil that solidified to a pale brown solid was obtained. Yield: 35% (0.215 g, 1.01 mmol); M.p.: 194–196 °C, literature 192 °C.²⁴

2.7 Synthesis of diethyl 3,3'-(2,2'-bipyridine-4,4'-diyl)diacrylate (**8**)

Dry potassium carbonate (1.7 g, 12.3 mmol) and 2.1 g triethylphosphonoacetate were suspended in 10 cm³ of anhydrous THF and stirred at room temperature for 15 min before the suspension was refluxed for 20 min. After cooling the suspension to room temperature it was transferred into a microwave vessel and 1.0 g (4.7 mmol) of (**7**) in 2 cm³ anhydrous THF were added. The vessel was sealed and heated to 110 °C within 10 min using a maximum power of 1000 MW. The reaction temperature then was maintained for 2 h after which the vessel was allowed to cool down to room temperature. After cooling, 20 cm³ of a 10% potassium carbonate solution was added. The mixture was extracted three times with ethyl acetate. The organic phase was dried over sodium sulfate and the solvent was evaporated under reduced pressure. The remaining triethylphosphonoacetate was removed by distillation *in vacuo*. The crude product was purified by column chromatography on silica gel using a diethyl ether: light petroleum (40–60) 1 : 1 mixture as the eluent. After the solvent mixture was evaporated a white solid was obtained which was recrystallized from ethanol/water by first dissolving the crude product in ethanol and then adding water until the solution misted. For complete crystallization the solution was placed in the refrigerator. Yield: 40% (0.66 g, 1.88 mmol).

IR (298 K) [cm⁻¹]: 2980w, 2936vw, 1726vs, 1697vs, 1584m, 1545w, 1458m, 1443m, 1377s, 1294s, 1263s, 1217vs, 1063vs, 1011s, 991m, 930w, 880w, 860w, 843m, 791s, 770w, 746m; MS (EI) m/z (%): 352 (10) [M⁺]; 323 (5) [M⁺-C₂H₅]; 308 (70) [M⁺-C₂H₅-CH₃]; 280 (100) [M⁺-C₄H₉O]; 261 (20) [M⁺-C₄H₁₁O₂]; 233 (25) [M⁺-C₆H₁₅O₂]; 208 (70) [M⁺-C₈H₁₈O₂]; ¹H NMR (CDCl₃) δ ppm 1.36 (t, *J* = 7.07 Hz, 6 H) 4.30 (q, *J* = 7.16 Hz, 4 H) 6.73 (s, 1 H) 6.77 (s, 1 H) 7.41 (dd, *J* = 5.05, 1.77 Hz, 2 H) 7.73 (s, 1 H) 7.69 (s, 1 H) 8.55–8.58 (m, 2 H) 8.73 (d, *J* = 5.05 Hz, 2 H); ¹³C-NMR (CDCl₃): δ [ppm] = 14.2, 61.0, 119.3, 122.2, 123.1, 141.8, 142.8, 150.0, 156.4, 166.1; M.p.: 139 °C; elemental analysis: calc. (%) for C₂₀H₂₀N₂O₄: C 68.17, H 5.72, N 7.95; found: C 67.30, H 5.66, N 8.03.

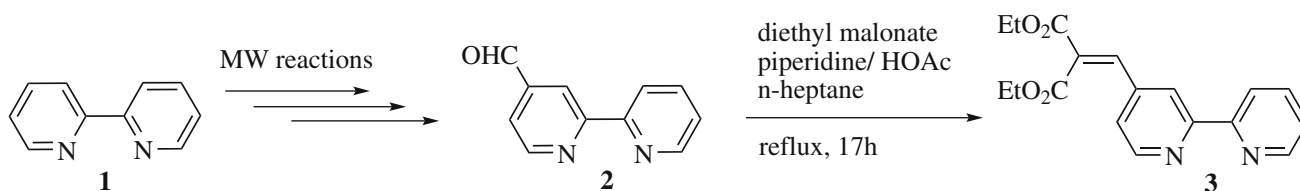
3. X-ray crystal structure analysis of **6**

Intensity data were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.^{25–27} The structure was solved by direct methods (SHELXS²⁸) and refined by full-matrix least squares techniques against F_o² (SHELXL-97²⁸). Hydrogen atoms of compound **6** were located by difference Fourier synthesis and refined isotropically.²⁸ Molecular illustrations were drawn using the programs ORTEP-3 for Windows and Mercury.^{29,30} Crystal Data for **6**: C₁₀H₆Br₂N₂, M_r = 313.99 g mol⁻¹, colourless prism, size 0.122 x 0.082 x 0.080 mm³, monoclinic, space group P2₁/n, a = 3.9307(2), b = 15.7655(7), c = 7.8915(3) Å, β = 93.706(2)°, V = 488.01(4) Å³, T = -140 °C, Z = 2, ρ_{calcd} = 2.137 g cm⁻³, μ (Mo-K_α) = 82.61 cm⁻¹, multi-scan, Trans_{min}: 0.4599, Trans_{max}: 0.7456, F(000) = 300, 5553 reflections in h(-5/5), k(-20/19), l(-10/9), measured in the range 2.58° ≤ 2θ ≤ 27.48°, completeness Θ_{max} = 99.8%, 1110 independent reflections, R_{int} = 0.0323, 1031 reflections with F_o > 4σ(F_o), 76 parameters, 0 restraints, R_{1obs} = 0.0215, wR_{2obs} = 0.0456, R_{1all} = 0.0243, wR_{2all} = 0.0471, GOOF = 1.110, largest difference peak and hole: 0.351 / -0.499 e Å⁻³.

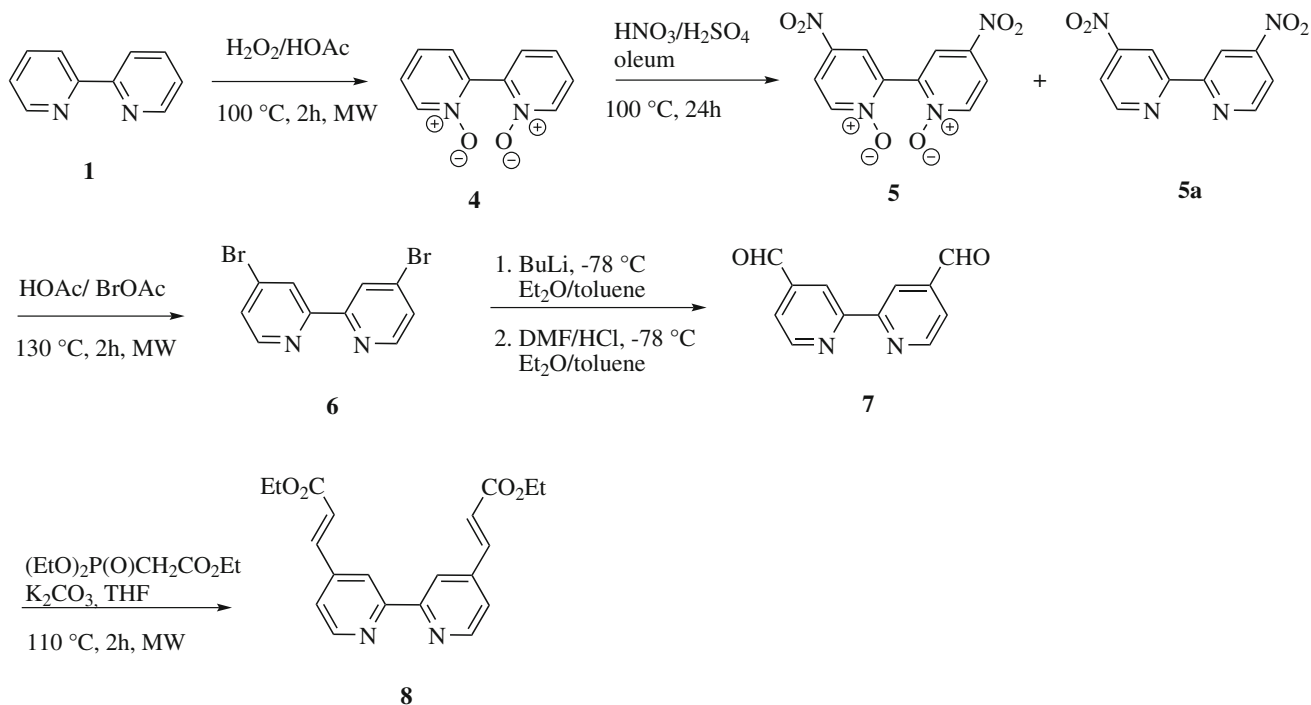
4. Results and Discussion

4.1 Synthesis and characterization

Scheme 1 shows the synthetic pathway synthesizing diethyl 2-(2,2'-bipyridin-4-ylmethylene)malonate **3** from 2,2'-bipyridine via the key intermediate 4-formyl-2,2'-bipyridine **2**. The synthesis of the latter was published by us earlier since **2** also is the key intermediate in the synthesis of ethyl 3-(2,2'-bipyridin-4-yl)acrylate.¹⁷ The formation of **3** from **2** is achieved by a Knoevenagel condensation with considerably low yield which was not improved if microwave activation was used instead of a classical thermal reaction regime.



Scheme 1. Synthesis of **3**.

Scheme 2. Synthesis of **8**.

Scheme 2 shows the complete reaction scheme producing diethyl 3,3'-(2,2'-bipyridine-4,4'-diyl)diacrylate **8**. The use of laboratory microwave technique led to significant improvement of several individual reactions. We expected that working under microwave conditions would lead to shortening of reaction times as well as to improved yields and less side products, providing the compounds are stable under these conditions.^{31,32} In the reaction sequence depicted in Scheme 2, the reaction time of the *N*-oxidation of 2,2'-bipyridine leading to the formation of **4** could be significantly shortened to two hours instead of 19 hours. Synthesizing 4,4'-dinitro-2,2'-bipyridine-(*N*, *N'*-oxide) **5** could not be improved by using microwave technique and was therefore performed thermally. This synthetic step only provides a yield of 40% of a mixture of both products **5** and **5a**. The following bromination could be effectively carried out under microwave conditions and provided 4,4'-dibromo-2,2'-bipyridine **6** as the sole product due to the bromination and the reduction of the *N*-oxide functions taking place at the same time. The following step is a one-pot synthesis which is characterized by a halogen-metal exchange reaction followed by a formylation with DMF to produce 2,2'-bipyridine-4,4'-dicarbaldehyde **7**. In the last reaction step a Horner-Wadsworth-Emmons reaction is used to build up the acrylate related side chains.

The new compounds **3** and **8** are fully characterized by mass spectrometry, IR- and NMR-spectroscopy as

well as by elemental analysis. The NMR spectra of **3** as expected show two different ester groups whereas the acrylic acid ester substituents in **8** are identical on the NMR time scale (*cf.* Supporting Information).

5. X-ray crystal structure analysis of **6**

By recrystallization of **6** from ethanol/water we obtained crystals suitable for X-ray diffraction. The molecular structure is shown in Figure 1, the most important bond lengths and angles are summarized in Table 1, crystal and intensity data are presented in the experimental

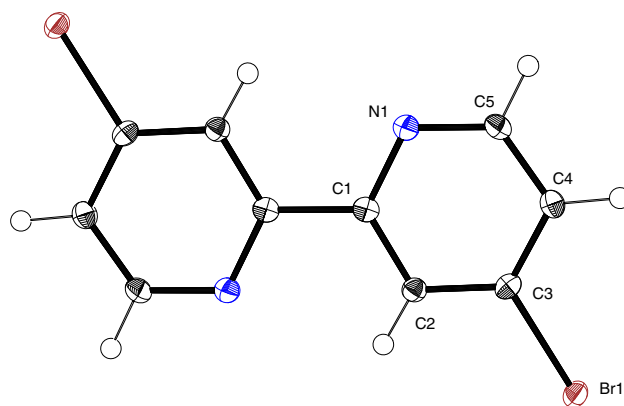
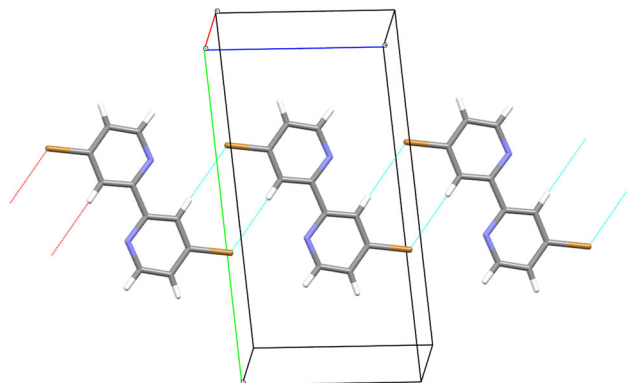


Figure 1. Molecular structure of **6**. Thermal ellipsoids are depicted on the 50% probability level.

Table 1. Selected bond lengths [pm] and angles [°] of (**6**).

N1-C1	135.5(3)	N1-C5	134.6(3)	Br1-C3	189.8(2)
C1-N1-C5	116.7(2)	C4-C3-Br1	120.5(2)	C2-C3-Br1	119.3(2)
Br1—H2	292.8	C2-H2—Br1	162.1		

**Figure 2.** Crystal structure of **6**.

part. The center of the carbon carbon bond that connects the two pyridine rings represents a crystallographic center of inversion, therefore also determining the *s*-trans conformation of the compound. The most significant intermolecular interactions are weak hydrogen bonds of the C-H—Br type which connect molecules into infinite chains along the *c* axis (Figure 2).³³

6. Conclusions

A synthetic procedure yielding two new 2,2'-bipyridine derivatives functionalized by acrylate substituents is presented herein. These compounds may be used for the introduction of metal coordination sites in polyacrylates. The reaction sequences proceed *via* the key intermediates 2,2'-bipyridine-4-carbaldehyde **2** and 2,2'-bipyridine-4,4'-dicarbaldehyde **7** which are prepared from the corresponding bromo derivatives. A Knoevenagel reaction of **2** with diethylmalonate produces diethyl 2-(2,2'-bipyridin-4-ylmethylene)malonate **3** in comparatively low yields whereas a Horner-Wadsworth-Emmons reaction of **7** leads to the formation of diethyl 3,3'-(2,2'-bipyridine-4,4'-diyl)diacrylate **8** in reasonable yields. Moreover, working under microwave conditions led to shortened reaction times and improved the yields for a considerable number of synthetic steps.

Supplementary Information (SI)

Crystallographic data were deposited at the Cambridge Crystallographic Data Centre under CCDC-1810667 for **6** and

contain supplementary crystallographic data excluding structure factors. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). CIF and CHECK CIF files of the structure analysis of **6**, additional analytic properties of **4**, **5**, **5a**, **6** and **7** which were used to prove the identity of the compounds next to their melting points and NMR spectra of **3** and **8** are available at www.ias.ac.in/chemsci.

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