



# Iron pentacarbonyl assisted photochemical route to 2,5- and 2,6-divinyl-substituted 1,4-benzoquinones from 1-ene-3-yne

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## ABSTRACT

Photochemical reaction between the enynes, (Z)-1-methoxybut-1-ene-3-yne, **1** or isopropenyl acetylene, **2** with CO in presence of Fe(CO)<sub>5</sub> yields the 2,6- and 2,5-divinyl-substituted 1,4-benzoquinones: 2,6-bis((Z)-2-methoxyvinyl)-1,4-benzoquinone (**3**, 42%), 2,5-bis((Z)-2-methoxyvinyl)-1,4-benzoquinone (**4**, 31.5%), [η<sup>2</sup>,η<sup>2</sup>:2,6-di(prop-1-en-2-yl)-1,4-benzoquinone]tricarbonyliron (**5**, 45%), and [η<sup>2</sup>,η<sup>2</sup>:2,5-di(prop-1-en-2-yl)-1,4-benzoquinone]tricarbonyliron (**6**, 65%).

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## 1. Introduction

Alkynes and alkenes exhibit a rich organometallic chemistry. In recent times, there has been much interest in organometallic chemistry of polyenes and polyenyne.<sup>1–13</sup> Although several examples exist of metal ene-yne complexes, their chemistry, in general, has been much less studied than that of metal alkynes and metal alkene complexes.

The ene-yne, (Z)-1-methoxybut-1-ene-3-yne, **1** (Fig. 1) has been used in a number of interesting organic transformations. For instance, addition of lithium acetylide of **1** to lactones followed by acid hydrolysis yields dihydropyrone spiroketal systems, while addition of inactivated aldehydes to the lithium salt of **1** followed

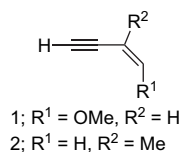


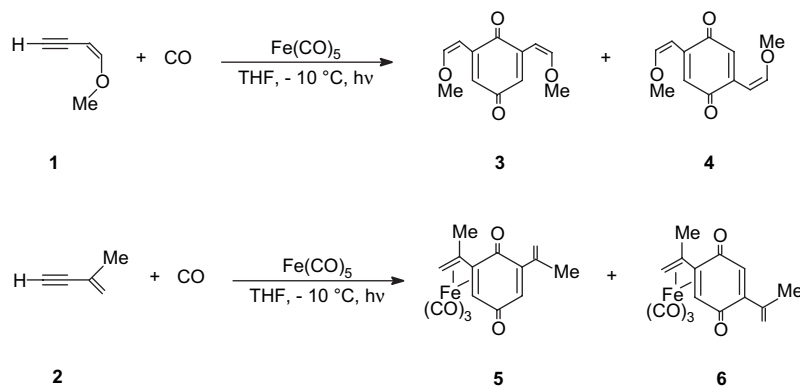
Figure 1.

by treatment of isolated acetylenic alcohol with HClO<sub>4</sub> or with a PTSA gives dihydropyrane.<sup>14</sup> Organometallic chemistry of some metal complexes of isopropenyl acetylene (IPA) **2** (Fig. 1) has been reported; thermal reaction of Co<sub>2</sub>(CO)<sub>8</sub> with **2** leads to cyclo-trimerization of the ligand to give the 2,4,6-substituted benzene.<sup>15</sup> Isopropenyl acetylide cluster Cp\*WRe<sub>2</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-η<sup>2</sup>-IPA) reacts with methanol to form an open chain complex bridged by OMe.<sup>16</sup> Reaction of (Cp)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>4</sub> with lithiated isopropenyl acetylide followed by acidic hydrolysis gives a carbyne-vinylidene derivative and Cp<sub>2</sub>Mo<sub>3</sub>(CO)<sub>4</sub>(μ<sub>3</sub>-η<sup>2</sup>-IPA).<sup>17</sup>

Previously, we have reported photochemical reactions between Fe(CO)<sub>5</sub> and ferrocenylacetylene, which yield ferrocenyl substituted quinones.<sup>18,19</sup> Our continuing interest in metal mediated preparation of quinones results from the existing vast synthetic utility of benzoquinones on the one hand and their biological significance on the other. Benzoquinones primin, verapliquinone A, B, shikonin, and alkanin are used as skin sensitizer and human telomerase inhibitors.<sup>20,21</sup> Asterriquinones have been recognized for their anti-HIV properties and are used as anti-diabetic agents.<sup>22</sup> Compounds containing the benzoquinone moiety have several applications in dye and pharmaceutical industries and their electrochemical properties are of significance in materials science. For a synthetic chemist, use of quinones as dienophiles in Diels–Alder reactions and in synthesis of chiral derivatives is very important.<sup>23</sup> Naturally occurring 1,4-benzoquinones mainly have a nucleus functionalized at 2,5 positions.<sup>24</sup> However, reports of facile one-pot synthesis of 2,5-disubstituted-1,4-benzoquinones are limited.<sup>25</sup>

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Scheme 1.

In this paper, we report a photochemically promoted one-step synthesis of 1,4-benzoquinones, which bear vinyl substituents in 2,5- and 2,6-position.

## 2. Results and discussion

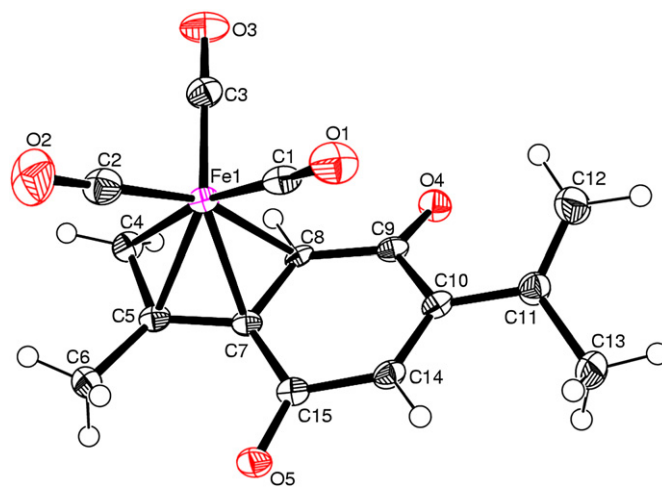
Low temperature photolysis of THF solution containing  $\text{Fe}(\text{CO})_5$  and ene-yne **1** or **2** with a constant bubbling of CO through the solution leads to a rapid formation of the vinyl-substituted compounds **3/4** and **5/6**, respectively (Scheme 1).

Compounds **3–6** were characterized by IR,  $^1\text{H}$  NMR, and mass spectral methods, and their compositions were confirmed by elemental analysis. The infrared and NMR spectra of **3** were similar to that of **4** and likewise, the spectral features observed for **5** were similarly present in the spectra of **6**. The IR spectra confirmed the presence of ketone carbonyl in all four compounds, and of terminally bonded metal carbonyls in **5** and **6**.  $^1\text{H}$  NMR spectra of all are consistent with the presence of a 2,6-substituted and 2,5-substituted 1,4-benzoquinone ring, the presence of equivalent methoxyvinyl groups in **3** and **4**, and of two non-equivalent substituents in each of **5** and **6**. In order to unequivocally establish the identity of the new compounds, molecular structure determinations by single crystal X-ray diffraction methods were carried out on two representative compounds, **3** and **6**.

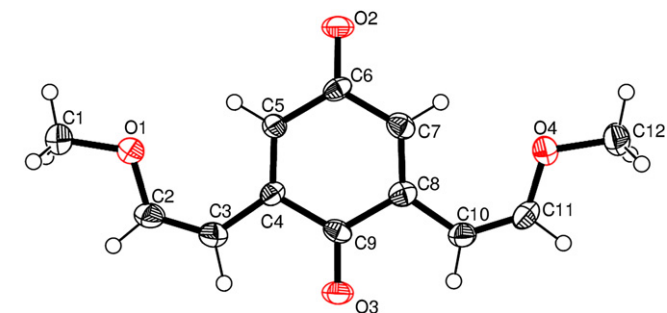
Molecular structure of **3** (Fig. 2) consists of a 1,4-benzoquinone ring with methoxyvinyl substituents at 2- and 6-position. The bond metrics are within expected values. Notably, methoxyvinyl substituents are in *syn* orientation. The molecular structure of **6** (Fig. 3) has isopropenyl substituents at 2- and 5-position of the 1,4-benzoquinone ring. In contrast to the planar quinone ring in **3**, the one in **6** has a bowed conformation with the oxygen-bearing carbon

atoms being bent by about  $8^\circ$  out of the carbocyclic diene plane. A  $\text{Fe}(\text{CO})_3$  unit is attached in  $\eta^2:\eta^2$  fashion with the *cis*-diene system, which comprises a double bond of the ring and the olefinic bond of one of the isopropenyl substituents. Consequently, the double bond of the isopropenyl group, which is part of the *cis*-diene unit and is coordinated to the iron atom,  $\text{C}(4)\text{--}\text{C}(5)=1.422(3)$  Å, is lengthened with respect to the double bond of the uncoordinated isopropenyl group,  $\text{C}(11)\text{--}\text{C}(12)=1.336(4)$  Å. Similarly, the quinonoid ring double bond, which is coordinated,  $\text{C}(7)\text{--}\text{C}(8)=1.445(3)$  Å, is longer than the uncoordinated double bond of the ring,  $\text{C}(10)\text{--}\text{C}(14)=1.352(3)$  Å. Whereas the original stereochemistry of (*Z*)-1-methoxy-1-butene-3-yne is retained during the formation of **3** and **4**, use of a non-geometrically isomeric 2-methyl-1-butene-3-yne gives compounds **5** and **6** in which the two substituents on the benzoquinone ring adopt *cis* and *trans* geometries, the *cis* geometry of one of the isopropenyl substituents in each compound resulting from the presence of the coordinated  $\text{Fe}(\text{CO})_3$  group. Indeed, the diene- $\text{Fe}(\text{CO})_3$  groups in **5** and **6** are very stable; attempts to demetallate under thermal and oxidizing conditions have been unsuccessful.<sup>26</sup>

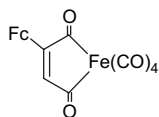
Although the exact mechanism of formation of **3–6** is not known at present, some parallels can be drawn from the related photochemical preparation of ferrocenyl-1,4-benzoquinones. In the reaction of  $\text{Fe}(\text{CO})_5$  with ferrocenylacetylene in presence of CO, the ferrole,  $\text{Fe}(\text{CO})_4\{(\text{CO})_2\text{HCCFc}\}$  (**7**) (Fig. 4), is formed. Compound **7** is



**Figure 3.** ORTEP view of the molecular structure of **6** with 50% probability. Selected bond distances (Å) and bond angles ( $^\circ$ ),  $\text{C}(4)\text{--}\text{C}(5)=1.422(3)$ ,  $\text{C}(5)\text{--}\text{C}(6)=1.510(3)$ ,  $\text{C}(5)\text{--}\text{C}(7)=1.416(3)$ ,  $\text{C}(7)\text{--}\text{C}(8)=1.445(3)$ ,  $\text{C}(8)\text{--}\text{C}(9)=1.462(3)$ ,  $\text{C}(9)\text{--}\text{O}(4)=1.225(3)$ ,  $\text{C}(10)\text{--}\text{C}(14)=1.352(3)$ ,  $\text{C}(10)\text{--}\text{C}(11)=1.472(3)$ ,  $\text{C}(11)\text{--}\text{C}(12)=1.336(4)$ ,  $\text{C}(11)\text{--}\text{C}(13)=1.499(3)$ ,  $\text{Fe}(1)\text{--}\text{C}(4)=2.131(2)$ ,  $\text{Fe}(1)\text{--}\text{C}(5)=2.095(2)$ ,  $\text{Fe}(1)\text{--}\text{C}(7)=2.049(2)$ ,  $\text{Fe}(1)\text{--}\text{C}(8)=2.106(2)$ ,  $\text{C}(10)\text{--}\text{C}(11)\text{--}\text{C}(12)=122.1(2)$ ,  $\text{C}(10)\text{--}\text{C}(11)\text{--}\text{C}(13)=117.2(2)$ .



**Figure 2.** ORTEP view of the molecular structure of **3** with 50% probability. Selected bond distances (Å) and bond angles ( $^\circ$ ):  $\text{C}1\text{--}\text{O}1=1.451(4)$ ,  $\text{C}2\text{--}\text{C}3=1.332(5)$ ,  $\text{C}2\text{--}\text{O}1=1.347(4)$ ,  $\text{C}3\text{--}\text{C}4=1.445(4)$ ,  $\text{C}4\text{--}\text{C}5=1.355(5)$ ,  $\text{C}4\text{--}\text{C}9=1.499(4)$ ,  $\text{C}5\text{--}\text{C}6=1.461(4)$ ,  $\text{C}6\text{--}\text{O}2=1.243(3)$ ,  $\text{C}(3)\text{--}\text{C}(4)\text{--}\text{C}(5)=126.2(3)$ ,  $\text{C}(3)\text{--}\text{C}(4)\text{--}\text{C}(9)=115.6(3)$ ,  $\text{C}(2)\text{--}\text{C}(3)\text{--}\text{C}(4)=128.6(3)$ .



**Figure 4.** The ferrole, **7** formed from photolysis of ferrocenylacetylene and  $\text{Fe}(\text{CO})_5$  in presence of CO.

sufficiently stable to have been isolated and its molecular structure to have been determined crystallographically. Further, exchange of the  $\text{Fe}(\text{CO})_4$  group of **7** by a second ferrocenylacetylene molecule was demonstrated, resulting in the formation of 2,5- and 2,6-diferrocenyl-1,4-benzoquinone.

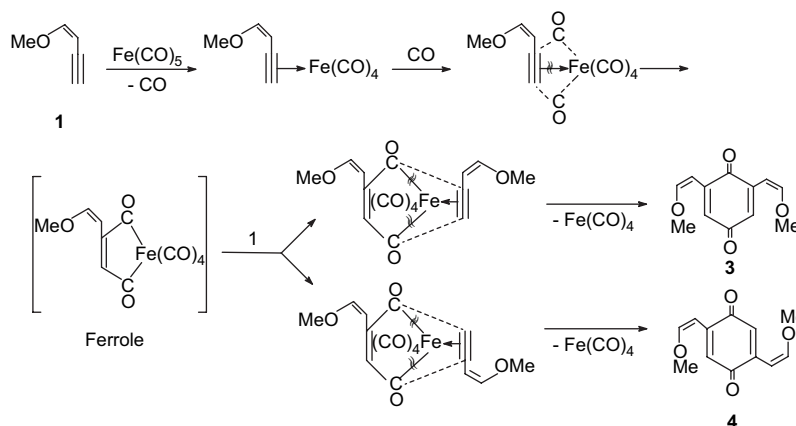
It is quite likely that in our present reaction of **1** or **2** with  $\text{Fe}(\text{CO})_5$ , an intermediate similar to **7**, is initially formed, which rapidly undergoes a  $\text{Fe}(\text{CO})_4$ /enyne exchange to form **3–6** (Scheme 2). Formation of two isomers, **3** and **4** can be thought to result from two possible orientations of the second molecule of **1** as it approaches to formally substitute the  $\text{Fe}(\text{CO})_4$  group of the intermediate ferrole. Likewise, two uncoordinated precursors to **5** and **6** can be thought to form via an intermediacy of a ferrole followed by two possibilities for a second enyne, **2**, to substitute the iron tetracarbonyl group (Scheme 3). In this reaction however, the presence of iron carbonyl fragments in solution leads to coordination of one  $\text{Fe}(\text{CO})_3$  group to a *cis*-diene system formed from the double bond of one of the isopropenyl substituents and one of the two ring double bonds.

In summary, we have demonstrated a one-pot synthesis of vinyl-substituted 1,4-benzoquinone derivatives by employing iron pentacarbonyl as a template in presence of carbon monoxide. Significantly, formation of the 2,6- and 2,5-disubstituted derivatives is easily understood, and therefore, our method of synthesis may find general utility in the rational design of vinyl-substituted quinone derivatives.

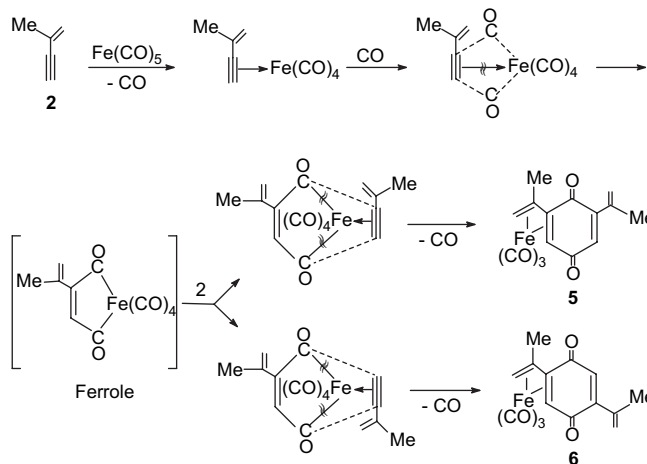
### 3. Experimental section

#### 3.1. General

Reactions and manipulations were performed using standard Schlenk techniques under argon with a slightly positive pressure. Photochemical reactions were carried out in cold double-walled quartz vessel having a 125-W immersion type mercury lamp manufactured by Applied Photophysics Ltd. Infrared spectra were recorded on Nicolet Impact 400 FT spectrometer as hexane solutions in 0.1 mm path length of NaCl cells and NMR spectra on Varian VXRO-400S spectrometer in  $\text{CDCl}_3$ . Elemental analysis was performed on a Carlo-Erba automatic analyzer. Iron pentacarbonyl was purchased from Fluka. (*Z*)-1-Methoxy-2-butene-3-yne was purchased from Aldrich and isopropenyl acetylene was purchased from Merck. All compounds were used without further purification. Solvents were purchased from Merck and used after purification and drying under argon atmosphere.



**Scheme 2.** Proposed mechanism of formation of **3** and **4**.  $\lambda$ —Bond cleavage. ———=New bond formation.



**Scheme 3.** Proposed mechanism of formation of **5** and **6**.  $\lambda$ —Bond cleavage. ———=New bond formation.

### 3.1.1. Preparation of 2,6-bis((Z)-2-methoxyvinyl)-1,4-benzoquinone (**3**) and 2,5-bis((Z)-2-methoxyvinyl)-1,4-benzoquinone (**4**)

To a solution of compound **1** (0.205 g, 2.5 mmol) in THF (70 ml), Fe(CO)<sub>5</sub> (0.60 g, 3.1 mmol) was added. Reaction mixture was subjected to photolysis for 15 min at –10 °C in a photochemical reaction vessel with continuous bubbling of CO through the solution. After removal of the volatiles, the residue was extracted with dichloromethane and passed through a Celite pad to remove insoluble material. Filtrate was concentrated and subjected to chromatographic work-up on silica gel TLC plates. Elution with a dichloromethane and *n*-hexane (85:15 v/v) mixture yielded two major bands: reddish orange band of compound **3** (*R<sub>f</sub>* 0.67) and yellowish orange band of compound **4** (*R<sub>f</sub>* 0.33) along with few minor bands.

**3**: 60 mg (42%). IR ( $\nu$ (CO), cm<sup>-1</sup>, *n*-hexane): 1738 (s), 1643 (s), 1619 (vs), 1562 (vs), 1259 (vs), 1068 (vs). Mass (*m/z*)=220 (M<sup>+</sup>). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 6.80 (s, 2H, OCC=CH), 5.28 (d, *J*=6 Hz, 2H, HC=CHOCH<sub>3</sub>), 6.42 (d, *J*=6 Hz, 2H, C=CHOCH<sub>3</sub>), 3.60 (s, 6H, 2-OCH<sub>3</sub>). Mp (°C) 190–192. Found (calcd for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>): C 65.58 (65.45), H 5.6 (5.45).

**4**: 45 mg (31.5%). IR ( $\nu$ (CO), cm<sup>-1</sup>, *n*-hexane): 1740 (br), 1643 (s), 1619 (vs), 1563 (vs), 1259 (vs), 1068 (vs). Mass (*m/z*)=220 (M<sup>+</sup>). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 6.8 (s, 2H, OCC=CH), 5.28 (d, *J*=6 Hz, 2H, HC=CHOCH<sub>3</sub>), 6.42, 6.42 (d, *J*=6 Hz, 2H, C=CHOCH<sub>3</sub>), 3.6 (s, 6H, 2-OCH<sub>3</sub>). Mp (°C) 185–188. Found (calcd for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>): C 65.58 (65.45), H 5.6 (5.45).

### 3.1.2. Preparation of [( $\eta^2, \eta^2$ :2,6-di(prop-1-en-2-yl)-1,4-benzoquinone)tricarbonyliron] (**5**) and [( $\eta^2, \eta^2$ :2,5-di(prop-1-en-2-yl)-1,4-benzoquinone)tricarbonyliron] (**6**)

To a solution of compound **2** (0.165 g, 2.5 mmol) in THF (70 ml), Fe(CO)<sub>5</sub> (0.60 g, 3.1 mmol) was added. Reaction mixture was subjected to photolysis for 15 min at –10 °C in a photochemical reaction vessel with continuous bubbling of CO through the solution. After removal of the volatiles, the residue was extracted with dichloromethane and passed through a Celite pad to remove insoluble material. Filtrate was concentrated and subjected to chromatographic work-up on silica gel TLC plates. Elution with a dichloromethane and *n*-hexane (85:15 v/v) mixture yielded two yellow bands, compounds **5** (*R<sub>f</sub>* 0.55) and **6** (*R<sub>f</sub>* 0.4).

**5**: 92 mg (45%). IR ( $\nu$ (CO), cm<sup>-1</sup>, *n*-hexane): 2060 (s), 2012 (vw), 1980 (vs), 1742 (br), 1740 (br), 1652 (s), 1613 (br). Mass (*m/z*)=328 (M<sup>+</sup>), 66. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 6.62 (s, 1H, OCC=CH Fe), 6.28 (s, 1H, OCC=CH), 5.19–5.24 (m, 4H, CH<sub>3</sub>C=CH<sub>2</sub>Fe and CH<sub>3</sub>C=CH<sub>2</sub>), 2.62 (s, 3H, CH<sub>3</sub>C=CHFe), 2.14 (s, 3H, CH<sub>3</sub>C=CH). Mp (°C) 144–146 (dec). Found (calcd for C<sub>15</sub>H<sub>12</sub>O<sub>5</sub>Fe): C 54.98 (54.88), H 3.6 (3.01).

**6**: 134 mg (65%). IR ( $\nu$ (CO), cm<sup>-1</sup>, *n*-hexane): 2060 (s), 2012 (vw), 1998 (vs), 1740 (br), 1643 (s), 1619 (vs), 1562 (vs), 1259 (vs), 1068 (vs). Mass (*m/z*)=328 (M<sup>+</sup>). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 6.62 (s, 1H, OCC=CH Fe), 6.28 (s, 1H, OCC=CH), 5.20–5.24 (m, 4H, CH<sub>3</sub>C=CH<sub>2</sub>Fe and CH<sub>3</sub>C=CH<sub>2</sub>), 2.62 (s, 3H, CH<sub>3</sub>CCHFe), 2.14 (s, 3H, CH<sub>3</sub>C=CH). Mp (°C) 132–134 (dec). Anal. Found (calcd for C<sub>15</sub>H<sub>12</sub>O<sub>5</sub>Fe): C 55.02 (54.88), H 3.2 (3.01).

### 3.2. Crystal structure determination of **3** and **6**

Suitable X-ray quality crystals of **3** and **6** were grown by slow evaporation of dichloromethane and *n*-hexane solvent mixture at 5 °C and X-ray crystallographic data were collected from single crystal samples of **3** (0.25×0.17×0.15 mm<sup>3</sup>) and **6** (0.43×0.28×0.23 mm<sup>3</sup>) mounted on a glass fibers. Oxford diffraction XCALIBUR-S CCD was used for the cell determination and intensity data collection for compounds **3** and **6**. The structures were solved by direct methods (SHELXS) and refined by full-matrix least squares against *F*<sup>2</sup> using SHELXL-97 (SHELX-TL for **1**) software.<sup>27</sup> Non-hydrogen atoms were refined with anisotropic

thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

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### Supplementary data

CCDC 681312 and 681313 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.06.059.

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