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## **Graphical Abstract**



# Unusual Manganese(III)-Mediated Oxidative Free-Radical Additions of Meldrum's acid and Dimethyl Malonate to Benzonorbornadiene and Oxabenzonorbornadiene

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Abstract: Benzonorbornadiene and 7-oxabenzonorbornadiene were reacted with Meldrum's acid and dimethyl malonate in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$  in acetic acid. The reaction of benzonorbornadiene with Meldrum's acid gave a naphthalene derivative whereas the reaction with dimethyl malonate formed rearranged products derived from a carbocation intermediate. However, the reaction of 7-oxabenzonorbornadiene with Meldrum's acid gave two nonrearranged products. On the other hand, the reaction with dimethyl malonate unexpectedly formed a dihydronapthalene derivative with an unusual structure. The mechanism for the formation of the products is discussed.

**Keywords:** Manganase(III) acetate; Copper(II) acetate; Cycloaddition; Oxidation; Dihydrofurans; Rearrangement; Benzonorbornadiene; Oxabenzonorbornadiene

### **1. Introduction**

The generation of carbon radicals using transition metal salts such as  $Mn(OAc)_3$ ,  $Cu(OAc)_2$ ,  $Pb(OAc)_4$ ,  $(NH_4)_2Ce(NO_3)_6$  and their addition to carbon-carbon double bonds is a valuable method for C- C bond formation.<sup>1</sup>  $Mn(OAc)_3$ , a one-electron oxidant, is considered one of the most popular reagents in the field of free-radical chemistry. It has found extensive use in the construction of a wide range of molecules with interesting properties.<sup>2</sup> It is well known that 1,3-dicarbonyl compounds undergo [3+2] cycloaddition to alkenes in the presence of  $Mn(OAc)_3$  to form dihydrofurans,<sup>3</sup> which are important building blocks of natural products and pharmaceuticals.

Generally, an oxidatively or reductively genareted radical **2** formed from a 1,3-dicarbonyl compound **1**, regioselectively attacks an electron-rich double bond forming a new radical **3** (Scheme 1).<sup>4</sup> The radical may be terminated or undergo a cyclization reaction.



Scheme 1. General mechanism for the formation of 2,3-dihydrofuran derivatives

Heiba and Dessau<sup>5</sup> proposed oxidation of radical **3** to a cation **4** followed by cyclization and proton loss to give dihydrofuran derivative **5**. However, Fristad *et al.*<sup>6</sup> proposed an alternative route where the radical **3** first undergoes a cyclization reaction to form a new radical **6** followed by oxidation and proton elimination to produce **5**. In order to address the question of at which stage the cyclization and oxidation take place we incorporated possible intermediates such as **3** and/or **4** in a bicyclic system.<sup>7</sup> It is well established that a radical intermediate of type **8** does not undergo rapid rearrangement.<sup>8</sup> However, a cation of type **9** has a great tendency to undergo rearrangement and to form rearranged products (Scheme 2).



Scheme 2. Possible structures formed by addition of a 1,3-dicarbonyl compound to a benzonorbornadiene system.

For this reason, benzonorbornadiene (7) and acetylacetone (10) were reacted in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$  (Scheme 3).<sup>7b</sup> The dihydrofuran adduct 11 was obtained as the major product whereas the rearranged product 12 was formed in 16% yield. The formation of 11 was rationalized by a fast intramolecular capture of the radical with a structure similar to 8. On the other hand, a nonclassical carbocation may also responsible for the formation of product 11. The reaction of homobenzonorbornadiene 13 with acetylacetone under the same reaction conditions resulted in the formation of a rearranged product 14 in 66% yield.<sup>7a</sup>



Scheme 3. Reaction of benzonorbornadiene (7) and homobenzonorbornadiene (13) with acetylacetone (10) in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ .

To gain more insight into the mechanism of the cycloaddition of 1,3-dicarbonyl compounds to bicyclic systems in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$  we reacted benzonorbornadiene (7) and oxabenzonorbornadiene (15) with Meldrum's acid (16) and dimethyl malonate (17). Herein we describe our results.

#### 2. Results and Discussion

The starting materials, benzonorbornadiene  $(7)^9$  and oxabenzonorbornadiene  $(15)^{10}$  were synthesized as described in the literature. The reaction of benzonorbornadiene (7) with 16 in the presence of Mn(OAc)<sub>3</sub> and Cu(OAc)<sub>2</sub> in acetic acid at 50 °C gave two separable products: a rearranged product 18 with a naphthalene skeleton and 1-naphthaldehyde (19) (Scheme 4). The structure of 18 was unambiguously characterized by NMR spectra. To test whether the minor product, 1-naphthaldehyde (19) is a primary or a secondary product, the rearranged product 18 was subjected to a Mn(OAc)<sub>3</sub>-oxidation reaction under the same reaction conditions. The rearranged product 18 was smoothly transferred into 1-naphthaldehyde (19) (Scheme 4).



Scheme 4. Reaction of benzonorbornadiene (7) with 16 in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ .

For the formation of rearranged product **18** we suggest the following mechanism as depicted in Scheme 5. The rearranged product **23** can be formed by the addition of the initially formed radical derived from **16** to the C=C double bond in **7** forming a new radical **20** followed by further oxidation, rearrangement, and loss of H<sup>+</sup> to give **23**. Further oxidation of **23** to **25** followed by a cleavage of the bridge carbon-carbon bond can result in the formation of a stable benzylic/allylic cation **26**. Aromatization of **26** can generate the final product **18** (Scheme 5). A similar tandem oxidation reaction with  $Mn(OAc)_3$  was recently observed by the reaction of homobenzonorbornadiene **13** with acetylacetone as depicted in Scheme 3. All this information indicates that a cation **21** is formed as an intermediate that has a great tendency for rearrangement.



Scheme 5. Proposed mechanism for the formation of 18.

When the scope of this reaction was expanded to oxabenzonorbornadiene **15** using the same methodology, a cyclopropane derivative<sup>11</sup> **27** was isolated as the major product in 52% yield besides the *exo*-cyclic methylene derivative **28** (Scheme 6).



Scheme 6. Reaction of oxabenzonorbornadiene (15) with 16 in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ .

The completely different behavior of the oxabenzonorbornadiene **15** may be attributed to the presence of the bridge oxygen atom. We assume that both of these products, **27** and **28**,

are formed from the initially formed classical carbocation **29**. Probably, this cation **29** has no tendency to undergo a Wagner-Meerwein type rearrangement due to the presence of an electron-withdrawing oxygen atom that retards the involvement of the neighboring  $\sigma$ -bond to form a nonclassical carbocation. Fast attack by the enol functionality of **29** results in the formation of cyclopropane derivative **27**. On the other hand, cation **29** can be further stabilized by a 1,2-hydrogen shift, thus forming a new cation **30**, which will form the *exo*-cyclic methylene derivative **28** (Scheme 7). and Wagner-Meerwein rearrangements, etc., are all sensible. In scheme 7, the pathway from cation **29** to final product **28** is shown as proceeding via a [1,2]-hydride shift to **30**. The final compound may also be formed by lost of H<sup>+</sup> from **29** to regenerate the endocyclic C=C double bond in the oxabenzonorbornadiene structure. In the next step alkene can tautomerize to final product **28** via an extended enol tautomer.



Scheme 7. Proposed mechanism for the formation of 27 and 28.

To gain more insight into the formation mechanism of the products we used dimethyl malonate (17) instead of a cyclic diester 16. The reaction of benzonorbornadiene (7) with dimethyl malonate (17) and  $Mn(OAc)_3$  in the presence of  $Cu(OAc)_2$  gave two separable products, 31 and 32, in yields of 45% and 36%, respectively (Scheme 8).



Scheme 8. Reaction of benzonorbornadiene (7) with dimethyl malonate (17) in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ .

It was interesting to note that no trace of the expected dihydrofuran derivatives was formed. The initially formed radical **33**, formed by the addition of dimethyl malonate, undergoes fast oxidation with  $Cu(OAc)_2$  to form a nonclassical cation **34**, which can be stabilized by the nucleophilic attack of the acetate anion to form **31**. The rearrangement of the nonclassical cation **34** to the classical cation **35** followed by H<sup>+</sup> elimination results in the formation of **32** (Scheme 9).



Scheme 9. Proposed mechanism for the formation of 30 and 31.

Finally, the reaction of oxabenzonorbornadiene (15) with dimethyl malonate (17) in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$  gave the rearranged product 36 in a yield of 56% (Scheme 10). The exact structure of 36 was determined by X-ray crystallographic analysis (Figure 1). The mechanism for the formation of this compound is not known.



Scheme 10. Reaction of oxabenzonorbornadiene (15) with dimethyl malonate (17) in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ .

All these experiments show that 1,3-dicarbonyl compounds such as Meldrum's acid and dimethyl malonate having ester carbonyl functionalities do not undergo a cyclization reaction to form dihydrofuran derivatives, at least in these bicyclic systems.<sup>12</sup> Radicals can be classified as electrophilic/nucleophilic. The initially formed radicals such as **20** and **33** are nucleophilic.<sup>13</sup> Since the carbonyl oxygen atoms in **16** and **17** are also nucleophilic, cyclization is not likely. The carbocations formed after oxidation of the radicals can form cyclization products. However, the fact that cyclization products with dihydrofuran structure are not observed can be attributed to the increased tendency of the formed cations for Wagner-Meerwein type rearrangement.



Figure 1. Thermal ellipsoid drawings of compound 36.

#### **3.** Conclusion

The primary goal of this work was to examine the reactivity of 1,3-dicarbonyl compounds having ester functionalities by the addition to bicyclic olefins in the presence of Mn(OAc)<sub>3</sub> and Cu(OAc)<sub>2</sub>. 1,3-Dicarbonyl compounds with ketone functional groups form mainly rearranged or nonrearranged dihydrofuran derivatives. The reaction of benzonorbornadiene (7) with Meldrum's acid (16) gave a naphthalene derivative 18 after tandem oxidation reaction. On the other hand, the reaction of 7 with 17 gave rearranged products indicating that the initially formed radical first undergoes oxidation before undergoing further reactions. However, the reaction of 7-oxabenzonorbornadiene (15) with Meldrum's acid (16) gave nonrearranged products 27 and 28. On the other hand, the reaction with dimethyl malonate unexpectedly formed the compound 36 with an unusual structure. The mechanism for the formation of this compound is not known. Generally speaking, 1,3-dicarbonyl compounds with ester functionalities do not have a tendency to generate dihydrofuran addition products, at least in these chosen systems.

#### 4. Experimental Section

**4.1. General Methods**. NMR spectra were recorded on a 400 MHz spectrometer. Infrared (IR) spectra were recorded in the range 4000-600 cm-1 via ATR diamond. Melting points were determined using a melting point apparatus and were uncorrected. Column chromatography was performed on silica gel (60-mesh), TLC was carried out on 0.2 mm silica gel 60 F254 analytical aluminum plates.

**4.2.** General procedure for addition of 1,3-dicarbonyl compounds to alkenes. A solution of 1,3-diketone (5 mmol) and olefin (5 mmol) in 20 mL of a glacial acetic acid in a flame-dried flask was heated to 50 °C under nitrogen. Then 10 mmol of  $Mn(OAc)_3 \cdot 2H_2O$  and 2 mmol of  $Cu(OAc)_2$  were added to the solution. The dark brown solution became lighter as the Mn(III)

was reduced. When the reaction was complete, the solution was colorless to light blue-green with a variable amount of white precipitate present. Water was added to the reaction mixture and the precipitate was dissolved. The solution was extracted with methylene chloride. The combined organic layers were washed several times with saturated NaHCO<sub>3</sub> solution and then water and dried (MgSO<sub>4</sub>). Evaporation of the solvent gave the crude compound, which was purified by crystallization or column chromatography.

**4.3.** Oxidative addition of Meldrum's acid (16) to benzonorbornadiene (7) in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ . Meldrum's acid (16) (0.72 g, 5 mmol), benzonorbornadiene (7) (0.71 g, 5 mmol), Mn(OAc)\_3·2H\_2O (2.7 g, 10 mmol), and Cu(OAc)\_2·2H\_2O (0.18 g, 1 mmol) in 30 mL of glacial acetic acid were reacted for 2 h as described above. The chromatography of the residue on silica gel (37.4 g, hexane/EtOAc; 4:1) gave 0.81 g of **18** (58%) and 0.085 g of **19** (11%).

4.3.1. Data for 2,3-dimethyl-5-(1-naphthylmethylene)1,3-dioxane-4,6-dione (18): Yellow crystals, mp 130–132 °C (Lit. mp, 125–126 °C<sup>14</sup>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ9.15 (s, 1H) 8.02-7.90 (m, 3H), 7.62-7.50 (m, 4H), 1.79 (s, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 162.7, 159.4, 156.4, 133.3, 133.2, 131.7, 129.9, 129.1, 129, 127.7, 126.6, 124.9, 123.6, 117.7, 104.8, 27.8.

**4.4.** Oxidative addition of Meldrum's acid (16) to 7-oxabenzonorbornadiene (15) in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ . Meldrum's acid (16) (0.72 g, 5 mmol), 7-oxabenzonorbornadiene (15) (0.72 g, 5 mmol),  $Mn(OAc)_3 \cdot 2H_2O$  (2.7 g, 10 mmol), and  $Cu(OAc)_2 \cdot 2H_2O$  (0.18 g, 1 mmol) in 30 mL of glacial acetic acid were reacted for 2 h as described above. The chromatography of the residue on silica gel (82.5 g, 4:1 hexane/EtOAc) gave 0.743 g of **27** (52%) and 0.242 g of **28** (17%).

**4.4.1.** *rel-(1aS(R),2R(S),7S(R),7aS(R))-2',2'-dimethyl-1a,2,7,7a-tetrahydrospiro[2,7-epoxy-cyclopropa-[b]-naphthalene-1,5'-[1,3]dioxane]-4',6'-dione* (**27**). Colorless crystals, mp 132-133 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.35 (A-part of AA'BB' system, 2H), 7.12 (B-part of AA'BB' system, 2H), 5.62 (s, 2H), 2.52 (s, 2H), 1.82 (s, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 165.1, 162.4, 145.4, 126.0, 121.1, 105.2, 78.6, 43.2, 41.3, 27.1; IR (KBr, cm<sup>-1</sup>) 3117, 2925, 2854, 1736, 1705, 1664, 1471, 1285, 1017, 951, 741, 498; HRMS-TOF [M - H]<sup>-</sup>: Calcd for C<sub>16</sub>H<sub>13</sub>O<sub>5</sub> 285.0768, found: 285.0769.

4.4.2. 5-((1S(R),4R(S))-5-(3,4-dihydro-1,4-epoxynaphthalen-2(1H)-2,2-dimethyl-1,3-dioxane-4,6-dione (28):
Colorless crystals, mp 117-118 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ7.6-7.2 (m, aromatic, 4H),
6.64 (s, 1H), 5.59 (d, J = 4.2 Hz, 1H), 3.19 (dd, A-part of AB system, J = 18.4 and 4.2 Hz,
1H), 3.07 (d, B-part of AB system, J = 18.4 Hz, 1H), 1.78 (s, 3H), 1.69 (s, 3H); <sup>13</sup>C-NMR
(100 MHz, CDCl<sub>3</sub>) δ 178.8, 159.7, 159.5, 144.8, 137.8, 127.4, 126.7, 121.3, 118.8, 109.6,
103.7, 81.7, 76.8, 39.8, 26.6, 26.4; IR (KBr, cm<sup>-1</sup>) 3114, 2958, 2796, 1741, 1667, 1425, 1219,
1058, 760, 692, 548; HRMS Calcd for (C<sub>16</sub>H<sub>13</sub>O<sub>5</sub>) [M - H]: 285.0768; Found: 285.0770.

**4.5.** Oxidative addition of dimethyl malonate (17) to benzonorbornadiene (7) in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ . Dimethyl malonate (17) (0.66 g, 5 mmol), benzonorbornadiene (7) (0.71 g, 5 mmol),  $Mn(OAc)_3 \cdot 2H_2O$  (2.7 g, 10 mmol), and  $Cu(OAc)_2 \cdot 2H_2O$  (0.18 g, 1 mmol) in 30 mL of glacial acetic acid were reacted for 16 h as described above. The chromatography of the residue on silica gel (37.5 g, 4:1 hexane/EtOAc) gave 0.489 g of **31** (45%) and 0.597 g of **32** (36%).

**4.5.1.** Dimethyl 2-(1,4-dihydro-1,4-methanonaphthalen-9-yl)malonate (32). Pale yellow oil; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.11 (A-part of AA'BB' system, 2H), 6.86 (B- part of AA'BB' system, 2H), 6.55 (s, 2H), 3.75 (s, 2H), 3.72 (d, J = 11.6 Hz, 1H), 3.68 (s, 6H), 3.10 (d, J = 11.6 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.80, 151.2, 140.3, 125.28, 122.4, 77.1

(Overlapping CDCl3 peaks), 53.7, 53.1. 52.9; IR (KBr, cm<sup>-1</sup>): 3044, 2961, 2870, 1726, 1682, 1453, 1383, 1275, 1089, 759, 711; HRMS-TOF [M + Na]<sup>+</sup>- Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>Na 295.0946, found: 295.0952.

**4.5.2.** Data for Dimethyl 2[(1R(S), 2R(S), 4S(R), 9S(RS))-2-(acetyloxy)-1,2,3,4-tetrahydro-1,4- methanonaphthalen -9-yl]malonate (31): Colorless crystals, mp 103-105 °C ; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.30-7.01 (m, Aromatic, 4H), 4.68 (dd, J = 7.2 and 3.1 Hz, 1H), 3.95 (d, J = 12.2 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 6H), 3.47 (s, 1H), 3.33 (bs, 1H), 2.73 (d, J = 12.2 Hz, 1H), 2.07 (s, 3H), 1.95 (dt, A-part of AB system, J = 13.4 and 3.1 Hz, 1H), 1.95 (dd, B-part of AB system, J = 13.4 and 7.2 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.4, 168.9, 168.7, 148.1, 143.0, 126.7, 126.1, 122.4, 120.8, 75.7, 57.6, 52.5, 52.4, 51.2, 51.1, 45.2, 33.7, 21.1; IR (KBr, cm<sup>-1</sup>) : 3054, 2961, 2875, 1720, 1451, 1403, 1375,1250, 1160, 754; HRMS Calcd for (C<sub>18</sub>H<sub>21</sub>O<sub>6</sub>) [M + H]<sup>+</sup>: 333.1338; Found: 333.1338.

**4.6.** Oxidative addition of dimethyl malonate (17) to 7-oxabenzonorbornadiene in the presence of  $Mn(OAc)_3$  and  $Cu(OAc)_2$ . Dimethyl malonate (17) (0.66 g, 5 mmol), 7-oxabenzonorbornadiene (15) (0.72 g, 5 mmol),  $Mn(OAc)_3 \cdot 2H_2O$  (2.7 g, 10 mmol), and  $Cu(OAc)_2 \cdot 2H_2O$  (0.18 g, 1 mmol) in 30 mL of glacial acetic acid were reacted for 12 h as described above. The chromatography of the residue on silica gel (82.4 g, 4:1 hexane/EtOAc) gave 0.811 g of **36** (56%).

**4.6.1.** *Dimethyl* 3-formyl-1-hydroxynaphthalene-2,2(1H)dicarboxylate (**36**). Colorless crystals, mp 145-147 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.62 (s, 1H), 7.79-7.65 (m, 1H), 7.55-7.45 (m, 1H), 7.40-7.35 (s, 1H), 7.35 (m, 2H), 5.45 (s, 1H), 4.51 (bs, 1H), 3.77 (s, 3H), 3.65 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  189.7, 170.3, 169.9, 146.2, 139.5, 136.1, 132.6, 129.3, 129.2, 128.4, 124.7, 74.3, 58.8, 53.5, 53.2; IR (KBr, cm<sup>-1</sup>) 3539, 3027, 2974, 2699, 1728, 1682, 1657, 1410, 1366, 1255, 1124, 796, 532; HRMS-TOF [M + Na]<sup>+</sup>: Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>6</sub>Na 313.0688, found: 313.0697.

**4.7.** *X-ray crystal structure analysis of* **36**. For the crystal structure determination, a singlecrystal of the compound **36** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphitemonochromated Mo-K<sub>a</sub> radiation ( $\lambda = 0.71073$  Å) and oscillation scans with  $\Delta w = 5^{\circ}$  for one image were used for data collection. The lattice parameters were determined by the leastsquares methods on the basis of all reflections with  $F^2 > 2\sigma(F^2)$ . Integration of the intensities, correction for Lorentz and polarization effects and cell refinement were performed using CrystalClear (Rigaku/MSC Inc., 2005) software.<sup>15</sup> The structures were solved by direct methods using SHELXS-97 and refined by a full-matrix least-squares procedure using the same program.<sup>16</sup> All nonhydrogen atoms were refined anisotropically and H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance.

**4.6.1.** *Crystal data for* (**36**): C<sub>15</sub>H<sub>14</sub>O<sub>6</sub>, crystal system, space group: monoclinic, *P*2<sub>1</sub>/n; (no:14); unit cell dimensions: a = 10.4059 (6), b = 6.2340(3), c = 21.6724(12) Å,  $\alpha = 90$ ,  $\beta = 103.195(2)$ ,  $\gamma = 90^{\circ}$ ; volume: 1368.78 (7) Å<sup>3</sup>; Z = 4; calculated density: 1.41 g/cm<sup>3</sup>; absorption coefficient: 0.110 mm<sup>-1</sup>; *F*(000): 608;  $\theta$ -range for data collection 3.4–28.3°; refinement method: full matrix least-square on *F*<sup>2</sup>; data/parameters: 2453/193; goodness-of-fit on *F*<sup>2</sup>: 1.056; final *R*-indices [*I* > 2 $\sigma$ (*I*)]: *R*<sub>1</sub> = 0.052, w*R*<sub>2</sub> = 0.134; largest diff. peak and hole:

0.260 and -0.200 e Å<sup>-3</sup>. Crystallographic data that were deposited in CSD under CCDC-1484154 registration numbers contain the supplementary crystallographic data for this Letter. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data\_request/cif and are upon request to CCDC, 12 Union Road, Cambridge, UK (fax: +441223 336033, e-mail: <u>deposit@ccdc.cam.ac.uk</u>).

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#### Supplementary data

Supplementary data related to this article (1D and 2D NMR spectra of the products and (17 pages)) can be found in the online version, at http://dx.doi.org/.....

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