

# Oxidative Cyclisation of 3-Oxopropanenitriles Mediated Manganese(III) Acetate with 2-Thienyl Substituted Alkenes

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The oxidative cyclisation of 3-oxopropanenitriles **1a-g** with alkenes **2a-c** containing 2-thienyl group by manganese(III) acetate was studied. Treatment of 3-oxopropanenitriles **1a-d** with 2-[(*E*)-2-phenylvinyl]thiophene **2a** gave 4-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitriles **3a-d** in moderate yields (52%-60%). 5-(2-thienyl) substituted 4,5-dihydrofuran-3-carbonitriles **3e-i** were obtained by the oxidative cyclisation of these 3-oxopropanenitriles with 2-[(*E*)-1-methyl-2-phenylvinyl]thiophene **2b** in good yields (54%-68%). In addition, the reactions of 2-(1-phenylvinyl)thiophene **2c** with various 3-oxopropanenitriles produced 4,5-dihydrofurans **3j-n** containing heterocycle in 77%-91% yields.

**Key Words:** Manganese(III) acetate, oxidative cyclisation, 4,5-dihydrofuran-3-carbonitrile, 3-oxopropanenitrile, conjugated alkene, radical addition.

## Introduction

The oxidative addition of carbon-centred radicals to alkenes mediated by transition metal salts (Mn<sup>+3</sup>, Ce<sup>+4</sup>, Co<sup>+3</sup>, Cu<sup>+2</sup>, etc.) in organic synthesis has received considerable attention for the construction of carbon-carbon bonds.<sup>1-6</sup> Among these, manganese(III) acetate<sup>3-5,7-22</sup> and cerium(IV) ammonium nitrate<sup>23-31</sup> are prominent and these salts have been used in the most efficient manner. Thus, they enable the formation of highly functionalised products such as furans,<sup>15-17,32,33</sup> dihydrofurans,<sup>9-14,18-22</sup>  $\gamma$ -lactones,<sup>34-41</sup>  $\beta$ -lactams,<sup>42-45</sup> and biologically active compounds and natural products.<sup>46-54</sup>

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We previously reported the synthesis of 4-cyano-2,3-dihydrofuran-3-carboxamides by the reaction of 3-oxopropanenitriles with unsaturated amides.<sup>22</sup> We also reported the formation of dihydrofuran and furan derivatives as a result of Mn(OAc)<sub>3</sub> mediated oxidative cyclisation of 1,3-dicarbonyl compounds with alkenes and alkynes.<sup>16,17</sup> Additionally, synthesis of 3-trifluoroacetyl-4,5-dihydrofurans and 3-(dihydrofuran-2(3*H*)-ylidene)-1,1,1-trifluoroacetones by the treatment of trifluoromethyl-1,3-dicarbonyl compounds with conjugated alkenes was described.<sup>20</sup> Previously, oxidative cyclisation of 3-oxopropanenitriles with alkenes containing phenyl and 2-thienyl groups was studied comparatively.<sup>21</sup>

In the present study, we examined oxidative cyclisation, using manganese(III) acetate, of conjugated alkenes **2a-c** containing 2-thienyl group with various 3-oxopropanenitriles **1a-g**. As a result of these reactions, we obtained 4,5-dihydrofuran-3-carbonitriles **3a-o** containing heterocycles such as 2-thienyl, 2-furyl, and 2-benzofuryl.

## Experimental

Melting points were determined on a Gallenkamp capillary melting point apparatus. IR spectra (KBr disc, CHCl<sub>3</sub>) were obtained with a Matson 1000 FT-IR in the 400-4000 cm<sup>-1</sup> range with 4 cm<sup>-1</sup> resolution. <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) spectra were recorded on a Bruker Avance DPX-400 MHz spectrophotometer and a Varian Mercury-400 high performance digital FT-NMR spectrophotometer. The mass spectra were measured on a Micromass UK LC/MS spectrophotometer (APCI, 100-150 eV), and a Shimadzu GC-17A/GC-MS-QP5000 (EIMS, 70 eV) spectrophotometer. Elemental analyses were performed on a Leco 932 CHNS-O instrument.

Thin layer chromatography (TLC) was performed on Merck aluminium-packed silica gel plates. Purification of products was performed by column chromatography on silica gel (Merck silica gel 60, 40-60 μm) or preparative TLC on silica gel of Merck (PF<sub>254-366nm</sub>). All reagents and 3-(4-chlorophenyl)-3-oxopropanenitril were purchased from Sigma-Aldrich.

### Synthesis of 2-[(*E*)-1-methyl-2-phenylvinyl]thiophene (**2b**).<sup>55</sup>

Benzyltriphenylphosphonium bromide (40 g, 92 mmol, obtained from benzyl bromide and triphenylphosphine in toluene) was added to a stirred suspension of NaH (3.68 g, 92 mmol, 60% in mineral oil) in THF and the mixture was stirred at 15 °C for 30 min. 2-Acetylthiophene (11.6 g, 92 mmol) was added to the orange solution and the mixture was heated under reflux for 3 h. The solvent was removed under reduced pressure and the residue was extracted with Et<sub>2</sub>O; the ether was then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was crystallised from MeOH to give 11.0 g (60%) of 2-[(*E*)-1-methyl-2-phenylvinyl]thiophene **2b** as a yellow solid, mp 47-48 °C.

### Synthesis of 3-(2-benzofuroyl)-3-oxopropanenitrile (**1g**).<sup>56</sup>

Suspension in 100 mL of dry toluene of methyl 1-benzofuran-2-carboxylate (17.6 g, 0.1 mole) that was synthesised by esterification of 1-benzofuran-2-carboxylic acid and MeOH in HCl according to the literature,<sup>57</sup> and NaH (8 g, 0.2 mol, 60 wt % in white oil) was heated up to 90 °C. Then under vigorous stirring it was dropped into acetonitrile (10.4 mL, 0.2 mol) within 2 h. Stirring was continued subsequently at this temperature until the end of the development of hydrogen (6 h). After cooling to room temperature, it

was filtered with suction, washed with ether, and dried. The solid material was solved in 100 mL of water and a cooling ice-salt mixture. After this, HCl 15% was added dropwise until the pH value of the solution became 2 and in a manner that ensured that its temperature did not exceed 5 °C. The precipitated solids were filtered off with suction, washed with water until they became neutral, and dried. Then they were recrystallised from acetone to give 17.2 g (93%), mp 148 °C (lit. mp 148.5 °C from acetone).<sup>56</sup>

### General procedure for synthesis of 4,5-dihydrofuran-3-carbonitriles

A solution of manganese(III) acetate dihydrate (3 mmol, 0.83 g) in 15 mL of glacial acetic acid was heated under nitrogen atmosphere at 80 °C until it dissolved. After Mn(OAc)<sub>3</sub> dissolved completely, the solution was cooled to 60 °C. A solution of 3-oxopropanenitrile (2 mmol) and alkene (1 mmol) in acetic acid was added to this mixture. The reaction was completed when the dark brown colour of the solution disappeared (in 10-30 min). Water was added to this solution and extracted with CHCl<sub>3</sub> (3 × 20 mL). The combined organic phases were neutralised with saturated NaHCO<sub>3</sub> solution, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated. Crude products were purified by column chromatography on silica gel or preparative TLC (20 × 20 cm plates, 2 mm thickness) using n-hexane/EtOAc (5:1) as eluent.

#### 2-(4-Methoxyphenyl)-4-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3a).

Yield 58% (208 mg) as a colourless solid mp 85-86 °C; [Found C, 73.6; H, 4.7; N, 4.0; S, 9.2. C<sub>22</sub>H<sub>17</sub>NO<sub>2</sub>S requires C, 73.5; H, 4.8; N, 3.9; S, 8.9%];  $\nu_{max}$ (KBr disc) 2194 (CN), 1606 (C=C), 1508, 1348, 1257 (C-O-C), 1178, 702;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.93 (2 H, d,  $J = 7.0$  Hz, arom.), 7.33-6.88 (10 H, m, arom.), 5.69 (1 H, d,  $J = 7.3$  Hz, H-5), 4.45 (1 H, d,  $J = 7.3$  Hz, H-4), 3.80 (3 H, s, -OMe);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 166.5 (C-2), 162.6, 112.1, 139.5, 129.6, 129.5, 128.4, 127.8, 127.3, 126.7, 126.3, 120.4, 117.8 (CN), 114.4, 88.1 (C-3), 82.5 (C-5), 59.0 (C-4), 55.7 (OMe); m/z (EI, 70 eV) 360 (MH<sup>+</sup>, 17.21), 359 (M<sup>+</sup>, 79.05), 344 (M<sup>+</sup> -CH<sub>3</sub>, 5.11), 328 (M<sup>+</sup> -OCH<sub>3</sub>, 7.77), 282 (M<sup>+</sup> -C<sub>6</sub>H<sub>5</sub>, 7.25), 204 (M<sup>+</sup> -PhCH<sub>2</sub>-C<sub>4</sub>H<sub>2</sub>N, 9.41), 135 (C<sub>8</sub>H<sub>7</sub>O<sub>2</sub><sup>+</sup>, 100.00), 111 (C<sub>5</sub>H<sub>3</sub>SO<sup>+</sup>, 10.06), 91 (PhCH<sub>2</sub><sup>+</sup>, 15.92), 83 (C<sub>4</sub>H<sub>3</sub>S<sup>+</sup>, 0.57), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 19.86).

#### 2-(4-Chlorophenyl)-4-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3b).

Yield 60% (218 mg) as a pale yellow oil; [Found C, 69.1; H, 4.2; N, 4.0; S, 8.7. C<sub>21</sub>H<sub>14</sub>ClNOS requires C, 69.3; H, 3.9; N, 3.85; S, 8.8%];  $\nu_{max}$ (KBr disc) 2205 (CN), 1621 (C=C), 1236 (C-O-C), 1099 (C-O-C), 835, 704;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.95 (2 H, d,  $J = 8.6$  Hz, arom.), 7.40-7.18 (8 H, m, arom.), 7.01 (1 H, d,  $J = 3.3$  Hz, arom.), 6.95 (1 H, dd,  $J = 5.0, 3.6$  Hz, arom.), 5.79 (1 H, d,  $J = 7.6$  Hz, H-5), 4.57 (1 H, d,  $J = 7.6$  Hz, H-4);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 165.3 (C-2), 141.6, 138.9, 138.2, 129.6, 129.3, 128.9, 128.6, 127.8, 127.4, 126.9, 126.6, 126.3, 116.9 (CN), 88.5 (C-3), 85.2 (C-5), 59.1 (C-4); m/z (EI, 70 eV) 364 (MH<sup>+</sup>, 11.60), 363 (M<sup>+</sup>, 42.25), 328 (M<sup>+</sup> -Cl, 5.72), 224 (M<sup>+</sup> -C<sub>7</sub>H<sub>4</sub>OCl, 6.13), 139 (C<sub>7</sub>H<sub>4</sub>OCl<sup>+</sup>, 100.00), 111 (C<sub>5</sub>H<sub>3</sub>SO<sup>+</sup>, 31.32), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 5.19).

#### 4-Phenyl-2,5-di-2-thienyl-4,5-dihydrofuran-3-carbonitrile (3c).

Yield 55% (184 mg) as a colourless solid mp 79-80 °C; [Found C, 67.7; H, 4.0; N, 4.1; S, 19.4. C<sub>19</sub>H<sub>13</sub>NOS<sub>2</sub> requires C, 68.0; H, 3.9; N, 4.2; S, 19.1%];  $\nu_{max}$ (KBr disc) 2207 (CN), 1646 (C=C), 1174 (C-O-C), 758, 706;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 8.21 (1 H, dd,  $J = 3.8, 1.0$  Hz, arom.), 7.82 (1 H, dd,  $J = 5.0, 1.1$  Hz, arom.), 7.66-7.54 (6 H, m, arom.), 7.43 (1 H, dd,  $J = 5.0, 3.85$  Hz, arom.), 7.34 (1 H, dt,  $J = 3.4, 0.6$  Hz, arom.),

7.29 (1 H, dd,  $J = 5.0, 3.5$  Hz arom.), 6.05 (1 H, d,  $J = 7.45$  Hz, H-5), 4.83 (1 H, d,  $J = 7.45$  Hz, H-4);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 161.8 (C-2), 141.5, 139.0, 130.6, 129.9, 129.5, 128.6, 128.5, 127.8, 127.3, 126.9, 126.6, 116.8 (CN), 89.1 (C-3), 82.8 (C-5), 58.8 (C-4); m/z (EI, 70 eV) 336 (MH<sup>+</sup>, 15.43), 335 (M<sup>+</sup>, 76.33), 140 (C<sub>10</sub>H<sub>6</sub>N<sup>+</sup>, 15.69), 111 (C<sub>5</sub>H<sub>3</sub>SO<sup>+</sup>, 100.00), 92 (C<sub>5</sub>H<sub>5</sub>S<sup>+</sup>, 5.36), 83 (C<sub>4</sub>H<sub>3</sub>S<sup>+</sup>, 9.36), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 2.73), 39 (C<sub>2</sub>HN<sup>+</sup>, 37.85).

**2-tert-Butyl-4-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3d).**

Yield 52% (160 mg) as a colourless solid mp 105-107 °C; [Found C, 74.1; H, 6.3; N, 4.2; S, 9.9. C<sub>19</sub>H<sub>19</sub>NOS requires C, 73.75; H, 6.2; N, 4.5; S, 10.35%];  $\nu_{max}$ (KBr disc) 2205 (CN), 1616 (C=C), 1244 (C-O-C), 729, 702;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.65-7.57 (7 H, m, arom.), 7.25 (1 H, t,  $J = 3.5$  Hz, arom.), 5.89 (1 H, d,  $J = 6.2$  Hz, H-5), 4.56 (1 H, d,  $J = 6.2$  Hz, H-4), 1.64 (9 H, s, 3 × Me); m/z (EI, 70 eV) 310 (MH<sup>+</sup>, 1.56), 309 (M<sup>+</sup>, 6.82), 252 (M<sup>+</sup>-C(Me)<sub>3</sub>, 7.21), 224 (M<sup>+</sup>-C<sub>5</sub>H<sub>9</sub>O, 16.13), 141 (M<sup>+</sup>-C<sub>4</sub>H<sub>3</sub>S-C<sub>5</sub>H<sub>9</sub>O, 10.15), 111 (C<sub>5</sub>H<sub>3</sub>SO<sup>+</sup>, 3.14), 83 (C<sub>4</sub>H<sub>3</sub>S<sup>+</sup>, 1.38), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 5.24), 57 (C(Me)<sub>3</sub><sup>+</sup>, 100.00), 41 (C<sub>3</sub>H<sub>5</sub><sup>+</sup>, 49.59).

**5-Methyl-2,4-diphenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3e).**

Yield 68% (233 mg) as a colourless solid mp 103-104 °C; [Found C, 76.6; H, 4.8; N, 4.2; S, 9.4. C<sub>22</sub>H<sub>17</sub>NOS requires C, 76.9; H, 5.0; N, 4.1; S, 9.3%];  $\nu_{max}$ (KBr disc) 2207 (CN), 1629 (C=C), 1259 (C-O-C), 714, 696;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 8.14 (2 H, dd,  $J = 7.1, 1.6$  Hz, arom.), 7.64-7.24 (10 H, m, arom.), 7.08 (1 H, dd,  $J = 5.0, 3.6$  Hz, arom.), 4.80 (1 H, s, H-4), 1.42 (3 H, s, Me);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 166.5 (C-2), 150.2, 136.1, 132.0, 129.2, 129.1, 129.0, 128.6, 128.1, 127.7, 127.2, 125.1, 123.3, 117.5 (CN), 91.5 (C-3), 84.0 (C-5), 62.1 (C-4), 25.6 (Me); m/z (EI, 70 eV) 344 (MH<sup>+</sup>, 3.83), 343 (M<sup>+</sup>, 18.45), 238 (M<sup>+</sup>-PhCO, 3.16), 217 (M<sup>+</sup>-C<sub>6</sub>H<sub>6</sub>SO, 4.84), 126 (C<sub>6</sub>H<sub>6</sub>SO<sup>+</sup>, 4.74), 105 (PhCO<sup>+</sup>, 44.86), 111 (C<sub>5</sub>H<sub>3</sub>SO<sup>+</sup>, 16.3), 97 (C<sub>5</sub>H<sub>5</sub>S<sup>+</sup>, 13.44), 83 (C<sub>4</sub>H<sub>3</sub>S<sup>+</sup>, 19.17), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 52.94), 43 (CH<sub>3</sub>CO<sup>+</sup>, 100.00), 41 (C<sub>3</sub>H<sub>5</sub><sup>+</sup>, 67.22).

**2-(4-Methoxyphenyl)-5-methyl-4-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3f).**

Yield 63% (235 mg) as a colourless solid mp 128-129 °C; [Found C, 74.2; H, 4.9; N, 3.8; S, 8.4. C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>S requires C, 74.0; H, 5.1; N, 3.75; S, 8.6%];  $\nu_{max}$ (KBr disc) 2203 (CN), 1612 (C=C), 1251 (C-O-C), 712;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 8.11 (2 H, dd,  $J = 7.0, 2.85$  Hz, arom.), 7.42-7.01 (10 H, m, arom.), 4.77 (1 H, s, H-4), 3.91 (3 H, s, -OMe), 1.40 (3 H, s, Me); m/z (EI, 70 eV) 374 (MH<sup>+</sup>, 5.62), 373 (M<sup>+</sup>, 21.75), 358 (M<sup>+</sup>-CH<sub>3</sub>, 1.73), 247 (M<sup>+</sup>-C<sub>6</sub>H<sub>6</sub>SO, 9.29), 232 (M<sup>+</sup>-C<sub>6</sub>H<sub>6</sub>SO-CH<sub>3</sub>, 9.76), 135 (C<sub>8</sub>H<sub>7</sub>O<sub>2</sub><sup>+</sup>, 100.00), 126 (C<sub>6</sub>H<sub>6</sub>SO<sup>+</sup>, 4.87), 91 (PhCH<sub>2</sub><sup>+</sup>, 16.16), 83 (C<sub>4</sub>H<sub>3</sub>S<sup>+</sup>, 1.47), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 33.21), 64 (C<sub>4</sub>H<sub>2</sub>N<sup>+</sup>, 8.58).

**2-(4-Chlorophenyl)-5-methyl-4-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3g).**

Yield 65% (245 mg) as a colourless solid mp 149-150 °C; [Found C, 70.0; H, 4.7; N, 3.6; S, 8.65. C<sub>22</sub>H<sub>16</sub>CINOS requires C, 69.9; H, 4.3; N, 3.7; S, 8.5%];  $\nu_{max}$ (KBr disc) 2207 (CN), 1643 (C=C), 1180 (C-O-C), 748, 700;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.69 (1 H, d,  $J = 7.8$  Hz, arom.), 7.65 (1 H, dd,  $J = 8.4, 0.6$  Hz, arom.), 7.51-7.28 (8 H, m, arom.), 7.12 (1 H, dd,  $J = 3.6, 1.2$  Hz, arom.), 7.04 (1 H, dd,  $J = 7.8, 3.65$  Hz arom.), 4.77 (1 H, s, H-4), 1.45 (3 H, s, Me);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 157.5 (C-2), 155.6, 149.2, 144.5, 135.4, 128.9, 128.5, 127.3, 127.0, 125.2, 123.9, 122.3, 118.9 (CN), 112.2, 110.8, 92.6 (C-3), 85.3 (C-5), 61.5 (C-4), 25.1 (Me); m/z (APCI, 150 eV) 379 (MH<sup>+</sup>, 11.2), 377.5 (M<sup>+</sup>, 44.3), 266 (M<sup>+</sup>-C<sub>5</sub>H<sub>3</sub>SO, 4.3), 239 (M<sup>+</sup>-C<sub>7</sub>H<sub>4</sub>OCl,

32.5), 223 ( $M^+ - CH_3 - C_7H_4OCl$ , 7.8), 199 ( $C_{13}H_{11}S^+$ , 7.3), 165 ( $C_9H_8NCl^+$ , 25.8), 141 ( $C_7H_5SO^+$ , 34.0), 139 ( $C_7H_4OCl^+$ , 100.00), 115 ( $C_9H_7^+$ , 25.8), 111 ( $C_5H_3SO^+$ , 8.60).

#### 5-Methyl-4-phenyl-2,5-di-2-thienyl-4,5-dihydrofuran-3-carbonitrile (3h).

Yield 66% (230 mg) as a colourless solid mp 83-84 °C; [Found C, 70.1; H, 4.5; N, 3.85; S, 18.5.  $C_{20}H_{15}NOS_2$  requires C, 68.7; H, 4.3; N, 4.0; S, 18.35%];  $\nu_{max}$ (KBr disc) 3101, 2988, 2930, 2201 (CN), 1616 (C=C), 1457, 1247 (C-O-C), 1062, 856, 752, 710;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 8.02 (1 H, d,  $J = 4.0$  Hz), 7.59 (1 H, d,  $J = 4.8$  Hz), 7.43-7.36 (4 H, m, arom.), 7.3 (1 H, d,  $J = 4.8$  Hz), 7.26 (1 H, d,  $J = 6.8$  Hz), 7.19 (1 H, d,  $J = 4.4$  Hz), 7.09 (1 H, dd,  $J = 3.6, 0.8$ , Hz), 7.02 (1 H, dd,  $J = 5.2, 0.8$ , Hz), 4.17 (1 H, s, H-4), 1.28 (3 H, s, Me);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 161.8 (C-2), 149.8, 136.1, 130.8, 130.6, 130.2, 129.2, 129.0, 128.6, 128.5, 127.3, 125.3, 123.5, 117.2 (CN), 92.4 (C-3), 82.3 (C-5), 61.85 (C-4), 25.5 (Me); m/z (EI, 70 eV) 349 ( $M^+$ , 23.47), 334 ( $M^+ - CH_3$ , 1.58), 266 ( $M^+ - C_4H_3S$ , 4.12), 238 ( $M^+ - C_5H_3SO$ , 5.85), 223 ( $M^+ - C_6H_6SO$ , 24.71), 189 ( $M^+ - C_4H_3S - C_6H_5$ , 13.53), 126 ( $C_6H_6SO^+$ , 5.99), 111 ( $C_5H_3SO^+$ , 100.00), 83 ( $C_4H_3S^+$ , 10.03), 77 ( $C_6H_5^+$ , 8.76).

#### 2-tert-Butyl-5-methyl-4-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3i).

Yield 54% (174 mg) as a colourless solid mp 80-81 °C; [Found C, 74.5; H, 6.2; N, 4.4; S, 9.8.  $C_{20}H_{21}NOS$  requires C, 74.3; H, 6.5; N, 4.3; S, 9.9%];  $\nu_{max}$ (KBr disc) 2203 (CN), 1619 (C=C), 1195 (C-O-C), 706;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 7.44-7.36 (5 H, m, arom.), 7.31 (1 H, dd,  $J = 3.8, 2.5$ , Hz, arom.), 7.04 (1 H, d,  $J = 2.5$  Hz, arom.), 7.02 (1 H, d,  $J = 3.6$  Hz, arom.), 4.56 (1 H, s, H-4), 1.47 (9 H, s,  $C(Me)_3$ ), 1.31 (3 H, s, Me);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 178.8 (C-2), 150.4, 136.1, 128.8, 128.7, 128.2, 126.9, 124.6, 122.8, 117.0 (CN), 90.6 (C-3), 84.5 (C-5), 61.2 (C-4), 34.9 (Me), 28.2 ( $\underline{C}(Me)_3$ ), 25.3 (3  $\times$  Me); m/z (EI, 70 eV) 323 ( $M^+$ , 8.29), 266 ( $M^+ - C_4H_9$ , 29.13), 238 ( $M^+ - C_5H_9O$ , 22.87), 223 ( $M^+ - C_5H_9O - CH_3$ , 8.79), 197 ( $M^+ - C_6H_6SO$ , 2.47), 182 ( $M^+ - C_6H_6SO - CH_3$ , 3.09), 126 ( $C_6H_6SO^+$ , 6.48), 111 ( $C_5H_3SO^+$ , 11.24), 97 ( $C_5H_5S^+$ , 3.87), 91 ( $PhCH_2^+$ , 5.21), 77 ( $C_6H_5^+$ , 10.70), 57 ( $C_4H_9^+$ , 100.00).

#### 2,5-Diphenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3j).

Yield 91% (300 mg) as a colourless solid mp 115-116 °C; [Found C, 76.5; H, 4.4; N, 4.2; S, 9.8.  $C_{21}H_{15}NOS$  requires C, 76.6; H, 4.6; N, 4.25; S, 9.7%];  $\nu_{max}$ (KBr disc) 2200 (CN), 1623 (C=C), 1249 (C-O-C), 773, 702;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 8.15 (2 H, dd,  $J = 8.0, 1.6$  Hz), 7.54-7.30 (11 H, m, arom.), 3.95 (1 H, d,  $J = 14.9$  Hz, Hb-4), 3.77 (1 H, d,  $J = 14.9$  Hz, Ha-4);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 165.4 (C-2), 148.1, 143.7, 131.9, 129.5, 128.8, 128.6, 128.1, 127.5, 127.0, 126.1, 125.5, 117.4 (CN), 111.5, 90.9 (C-3), 79.3 (C-5), 47.3 (C-4); m/z (EI, 70 eV) 329 ( $M^+$ , 25.17), 252 ( $M^+ - C_6H_5$ , 2.99), 224 ( $M^+ - C_7H_5O$ , 4.47), 198 ( $M^+ - C_7H_5O - CN$ , 4.33), 171 ( $M^+ - C_7H_5O - C_3H_3N$ , 8.39), 105 ( $C_7H_5O^+$ , 100.00), 77 ( $C_6H_5^+$ , 74.76).

#### 2-(4-Methoxyphenyl)-5-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3k).

Yield 82% (294 mg) as a colourless solid mp 99-101 °C; [Found C, 73.6; H, 4.7; N, 3.8; S, 9.3.  $C_{22}H_{17}NO_2S$  requires C, 73.5; H, 4.8; N, 3.9; S, 8.9%];  $\nu_{max}$ (KBr disc) 2201 (CN), 1621 (C=C), 1253 (C-O-C), 723, 698, 650;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 8.05 (2 H, dd,  $J = 6.8, 2.0$  Hz), 7.49-7.34 (6 H, m, arom.), 7.29 (1 H, dd,  $J = 4.4, 1.6$  Hz, arom.), 6.97 (3 H, m), 3.86 (3 H, s, OMe), 3.86 (1 H, d,  $J = 14.8$  Hz, Hb-4), 3.67 (1 H, d,  $J = 15.2$  Hz, Ha-4);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 165.3 (C-2), 162.3, 148.2, 143.8, 129.4, 128.8, 128.6, 127.0, 126.5,

126.0, 125.5, 120.65, 118.0 (CN), 114.4, 90.7 (C-3), 65.2 (C-5), 55.7 (OMe), 47.2 (C-4); m/z (APCI, 100 eV) 360 (MH<sup>+</sup>, 62.26), 276 (M<sup>+</sup> -C<sub>4</sub>H<sub>3</sub>S, 7.40), 252 (M<sup>+</sup>-C<sub>7</sub>H<sub>7</sub>O, 11.30), 135 (C<sub>8</sub>H<sub>7</sub>O<sub>2</sub><sup>+</sup>, 100.00).

**5-Phenyl-2,5-di-2-thienyl-4,5-dihydrofuran-3-carbonitrile (3l).**

Yield 84% (281 mg) as a colourless solid mp 111-112 °C; [Found C, 68.1; H, 4.1; N, 4.2; S, 19.4. C<sub>19</sub>H<sub>13</sub>NOS<sub>2</sub> requires C, 68.0; H, 3.9; N, 4.2; S, 19.1%];  $\nu_{max}$ (KBr disc) 2201 (CN), 1619 (C=C), 1259 (C-O-C), 847, 706;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.95 (1 H, dd,  $J = 3.15, 0.6$  Hz), 7.57 (1 H, dd,  $J = 4.9, 0.8$  Hz), 7.50 (2 H, dd,  $J = 8.5, 1.45$  Hz), 7.45-7.33 (4 H, m, arom.), 7.19 (1 H, d,  $J = 3.9$  Hz), 6.98 (2 H, dd,  $J = 5.5, 0.6$  Hz), 3.89 (1 H, d,  $J = 14.8$  Hz, Hb-4), 3.73 (1 H, d,  $J = 14.85$  Hz, Ha-4);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 161.6 (C-2), 148.4, 144.1, 131.1, 130.9, 130.8, 129.4, 129.3, 129.0, 127.6, 127.3, 126.9, 126.0, 117.6 (CN), 92.1 (C-3), 78.0 (C-5), 47.1 (C-4); m/z (EI, 70 eV) 335 (M<sup>+</sup>, 20.94), 251 (M<sup>+</sup>-C<sub>4</sub>H<sub>3</sub>S, 4.40), 224 (M<sup>+</sup>-C<sub>5</sub>H<sub>3</sub>SO, 7.23), 140 (C<sub>10</sub>H<sub>6</sub>N<sup>+</sup>, 5.52), 111 (C<sub>5</sub>H<sub>3</sub>SO<sup>+</sup>, 100.00), 97 (C<sub>5</sub>H<sub>5</sub>S<sup>+</sup>, 2.76), 83 (C<sub>4</sub>H<sub>3</sub>S<sup>+</sup>, 9.52), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 5.57).

**5-Phenyl-5-(2-thienyl)-4,5-dihydro-2,2'-bifuran-3-carbonitrile (3m).**

Yield 77% (246 mg) as a yellow solid mp 132-134 °C; [Found C, 71.7; H, 4.2; N, 4.1; S, 10.3. C<sub>19</sub>H<sub>13</sub>CINO<sub>2</sub>S requires C, 71.45; H, 4.1; N, 4.4; S, 10.0%];  $\nu_{max}$ (KBr disc) 3152, 2200 (CN), 1648 (C=C), 1473, 1273 (C-O-C), 1184, 924, 831, 740, 741;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.65 (1 H, d,  $J = 1.4$  Hz), 7.49-7.39 (5 H, m, arom.), 7.34 (1 H, dd,  $J = 6.8, 2.0$  Hz), 7.11 (1 H, d,  $J = 3.5$  Hz), 6.99 (2 H, t,  $J = 2.1$  Hz), 6.58 (1 H, dd,  $J = 3.5, 1.8$  Hz), 3.88 (1 H, d,  $J = 15.0$  Hz, Hb-4), 3.67 (1 H, d,  $J = 15.0$  Hz, Ha-4);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 157.4 (C-2), 148.2, 146.5, 144.4, 144.0, 129.4, 129.3, 127.6, 127.4, 127.1, 126.1, 116.9 (CN), 115.1, 112.7, 92.3 (C-3), 78.5 (C-5), 46.7 (C-4); m/z (EI, 70 eV) 320 (MH<sup>+</sup>, 5.36), 319 (M<sup>+</sup>, 23.72), 252 (M<sup>+</sup>-C<sub>4</sub>H<sub>3</sub>O, 3.01), 236 (M<sup>+</sup>-C<sub>4</sub>H<sub>3</sub>S, 3.56), 224 (M<sup>+</sup>-C<sub>5</sub>H<sub>3</sub>O<sub>2</sub>, 11.40), 209 (M<sup>+</sup>-C<sub>5</sub>H<sub>3</sub>SO, 4.59), 170 (C<sub>11</sub>H<sub>6</sub>S<sup>+</sup>, 7.62), 140 (C<sub>10</sub>H<sub>6</sub>N<sup>+</sup>, 13.43), 111 (C<sub>5</sub>H<sub>3</sub>SO<sup>+</sup>, 3.85), 95 (C<sub>5</sub>H<sub>3</sub>O<sub>2</sub><sup>+</sup>, 100.00), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 7.66), 67 (C<sub>4</sub>H<sub>3</sub>O<sup>+</sup>, 4.07).

**2-(1-Benzofuran-2-yl)-5-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3n).**

Yield 81% (299 mg) as a colourless solid mp 145-147 °C; [Found C, 75.1; H, 3.8; N, 4.0; S, 8.3. C<sub>23</sub>H<sub>15</sub>NO<sub>2</sub>S requires C, 74.8; H, 4.1; N, 3.8; S, 8.6%];  $\nu_{max}$ (KBr disc) 2200 (CN), 1648 (C=C), 1211 (C-O-C), 829, 750, 698;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.68 (1 H, d,  $J = 7.8$  Hz), 7.64 (1 H, d,  $J = 8.35$  Hz), 7.54-7.29 (9 H, m, arom.), 7.01 (2 H, d,  $J = 4.6$  Hz), 3.94 (1 H, d,  $J = 15.2$  Hz, Hb-4), 3.75 (1 H, d,  $J = 15.25$  Hz, Ha-4);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 157.4 (C-2), 156.6, 148.1, 145.5, 143.9, 129.5, 129.4, 128.0, 127.9, 127.7, 127.5, 127.2, 126.1, 124.7, 123.1, 116.5 (CN), 112.8, 111.1, 92.5 (C-3), 81.5 (C-5), 47.0 (C-4); m/z (EI, 70 eV) 369 (M<sup>+</sup>, 33.95), 224 (M<sup>+</sup>-C<sub>9</sub>H<sub>5</sub>O<sub>2</sub>, 9.47), 209 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>-C<sub>4</sub>H<sub>3</sub>S, 3.95), 197 (M<sup>+</sup>-C<sub>11</sub>H<sub>8</sub>S, 7.66), 172 (C<sub>11</sub>H<sub>8</sub>S<sup>+</sup>, 5.65), 145 (C<sub>9</sub>H<sub>5</sub>O<sub>2</sub><sup>+</sup>, 5.65), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 8.43).

**2-tert-Butyl-5-phenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile (3o).**

Yield 73% (226 mg) as a yellow oil; [Found C, 73.9; H, 6.3; N, 4.35; S, 10.3. C<sub>19</sub>H<sub>19</sub>NOS requires C, 73.75; H, 6.2; N, 4.5; S, 10.4%];  $\nu_{max}$ (KBr disc, CHCl<sub>3</sub>) 2207 (CN), 1627 (C=C), 1263 (C-O-C), 935, 700;  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.43-7.37 (4 H, m, arom.), 7.34 (1 H, dd,  $J = 6.0, 3.2$  Hz, arom.), 7.28 (1 H, dd,  $J = 5.2, 1.2$  Hz, arom.), 6.94 (1 H, dd,  $J = 5.2, 4.4$  Hz, arom.), 6.88 (1 H, dd,  $J = 3.6, 1.2$  Hz, arom.), 3.67 (1 H, d,  $J = 14.4$  Hz, Hb-4), 3.53 (1 H, d,  $J = 14.0$  Hz, Ha-4), 1.36 (9 H, s, C(Me)<sub>3</sub>);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 177.3

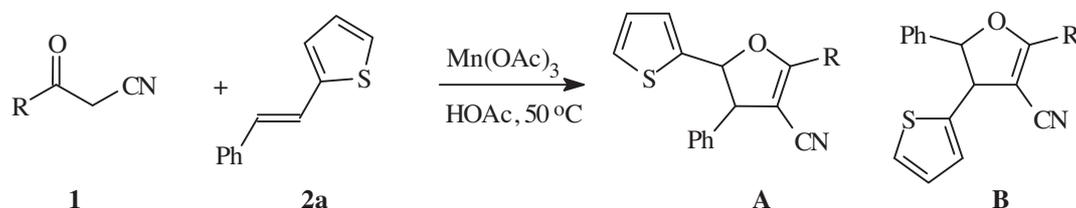
(C-2), 148.7, 144.1, 128.7, 128.4, 126.8, 126.3, 125.6, 125.4, 117.0 (CN), 90.3 (C-3), 78.0 (C-5), 47.4 (C-4), 35.1 (C(Me)<sub>3</sub>), 28.2 (3 × Me); m/z (EI, 70 eV) 309 (M<sup>+</sup>, 10.39), 294 (M<sup>+</sup>-CH<sub>3</sub>, 13.47), 252 (M<sup>+</sup>-C<sub>4</sub>H<sub>9</sub>, 38.51), 224 (M<sup>+</sup>-C<sub>5</sub>H<sub>9</sub>O, 16.37), 141 (M<sup>+</sup>-C<sub>5</sub>H<sub>3</sub>SO-C<sub>4</sub>H<sub>9</sub>, 21.09), 111 (C<sub>5</sub>H<sub>3</sub>SO<sup>+</sup>, 4.88), 97 (C<sub>5</sub>H<sub>5</sub>S<sup>+</sup>, 5.42), 85 (C<sub>5</sub>H<sub>9</sub>O<sup>+</sup>, 6.25), 83 (C<sub>4</sub>H<sub>3</sub>S<sup>+</sup>, 1.24), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 8.43), 57 (C<sub>4</sub>H<sub>9</sub><sup>+</sup>, 100.00), 41 (C<sub>3</sub>H<sub>6</sub><sup>+</sup>, 75.06).

## Results and Discussion

The conjugated alkenes, 2-[(*E*)-2-phenylvinyl]thiophene **2a**<sup>58,59</sup> and 2-[(*E*)-1-methyl-2-phenylvinyl]thiophene **2b** were synthesised via the Wittig method with benzyltriphenylphosphonium bromide and suitable carbonyl compounds. 2-(1-Phenylvinyl)thiophene **2c**<sup>60</sup> was prepared by removing water from the carbinole formed during the Grignard reaction of phenylmagnesium bromide and 2-acetylthiophene. All 3-oxopropanenitriles (except **1b**) were prepared according to the literature.<sup>61</sup>

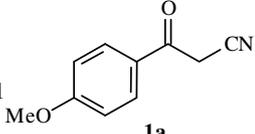
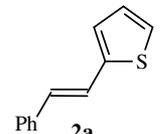
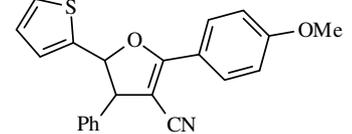
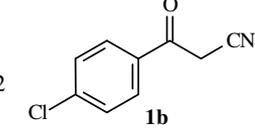
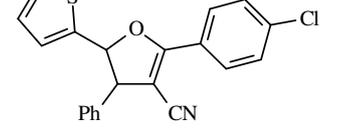
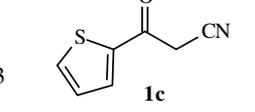
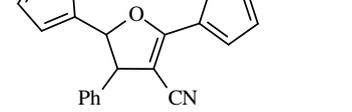
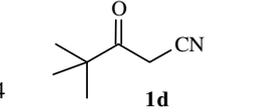
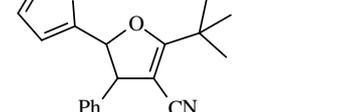
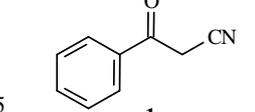
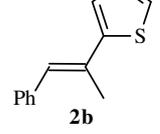
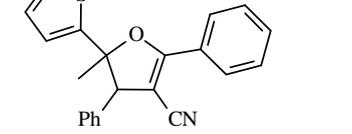
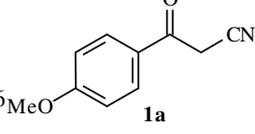
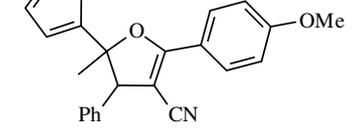
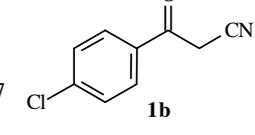
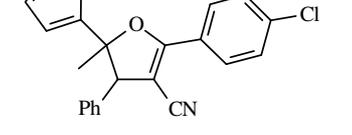
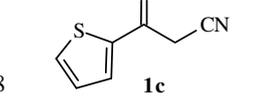
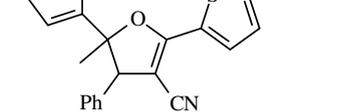
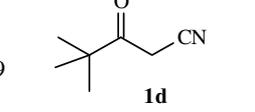
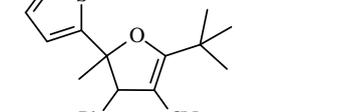
Oxidative cyclisation reactions were performed in 2:1:3 molar ratio (**1**:**2**:Mn(OAc)<sub>3</sub>, respectively) under nitrogen, at 60 °C in HOAc. After the workup procedure, all compounds were purified by column chromatography or preparative TLC and characterised by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, MS, and microanalysis.

The oxidative cyclisation of 3-oxopropanenitriles with 1,1-diarylethylenes and their reaction mechanism have been reported by Nishino et al.<sup>62</sup> Previously, we described the mechanism of the radical cyclisation of 3-oxopropanenitriles with 2-[(*E*)-2-phenylvinyl]thiophene **2a**.<sup>22</sup> According to the mechanism, the α-carbon radical formed on the 3-oxopropanenitrile by Mn(OAc)<sub>3</sub> was added to **2a** in 2 ways and, as we have mentioned before, as a result 2 types of cyclisation products, **A** or **B**, could be produced as shown in the **Figure**. We have explained that only 5-(2-thienyl) substituted 4,5-dihydrofurans **A** were formed by deriving the advantage of chemical shift values of H5 protons in the <sup>1</sup>H-NMR spectrum; however, the other cyclisation products were not isolated.



In this study, radical cyclisation of various 3-oxopropanenitriles with conjugated alkenes containing 2-thienyl group via manganese(III) acetate was studied. The results of the oxidative cyclisation of **1a-g** with **2a** and **2b** using manganese(III) acetate are given in Table 1. Treatments of 3-(4-methoxyphenyl)-3-oxopropanenitrile **1a** and 3-(4-chlorophenyl)-3-oxopropanenitrile **1b** with **2a** gave 4,5-dihydrofuran-3-carbonitriles **3a** (58%) and **3b** (60%), respectively, in good yields. 2,5-Di(2-thienyl) substituted 4,5-dihydrofuran **3c** was obtained in 55% yield by treatment of **1a** with **2b**. Additionally, the radical cyclisation of 4,4-dimethyl-3-oxopropanenitrile **1d** with **2a** afforded compound **3d** in 52% yield. In the <sup>1</sup>H-NMR spectrum, the coupling constants of H-4 and H-5 protons of **3a-d** are 6.2-7.6 Hz. The coupling constant between cis protons in the same structures was given as  $J_{cis} = 8-9$  Hz in the literature.<sup>63-65</sup> Moreover, very recently, we obtained a cis and trans isomer mixture of 4,5-dihydrofurans in the reaction of 3-oxopropanenitriles with (2*E*, 4*E*)-5-phenylpenta-2,4-dienamide by manganese(III) acetate.<sup>22</sup> While the coupling constant between the relevant protons of cis-dihydrofurans is 9.6-10.0 Hz, that of trans-dihydrofurans is 6.0-7.5 Hz. According to these data, we concluded that the phenyl and thienyl groups in compounds **3a-d** are in the trans position.

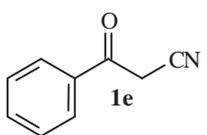
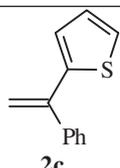
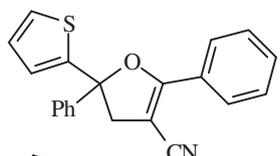
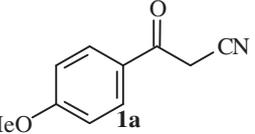
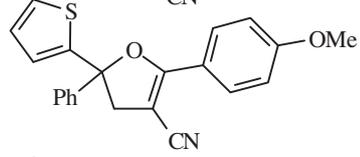
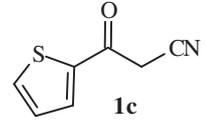
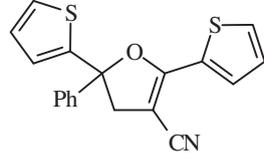
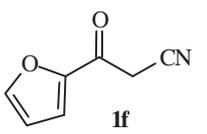
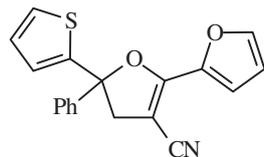
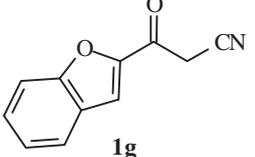
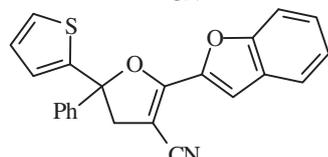
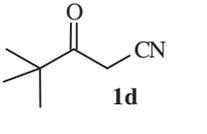
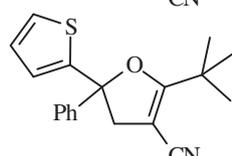
**Table 1.** The oxidative cyclisation of 3-oxopropanenitriles with **2a** and **2b**.

entry	3-oxopropanenitrile	alkene	4,5-dihydrofuran-3-carbonitrile	yield (%) <sup>a</sup>
1	 <b>1a</b>	 <b>2a</b>		<b>3a</b> (58)
2	 <b>1b</b>	<b>2a</b>		<b>3b</b> (60)
3	 <b>1c</b>	<b>2a</b>		<b>3c</b> (55)
4	 <b>1d</b>	<b>2a</b>		<b>3d</b> (52)
5	 <b>1e</b>	 <b>2b</b>		<b>3e</b> (68)
6	 <b>1a</b>	<b>2b</b>		<b>3f</b> (63)
7	 <b>1b</b>	<b>2b</b>		<b>3g</b> (65)
8	 <b>1c</b>	<b>2b</b>		<b>3h</b> (66)
9	 <b>1d</b>	<b>2b</b>		<b>3i</b> (54)

a: Yield of isolated product based on the alkene

While **3e** was produced in 68% yield by the reaction of 1,1,2-tri substituted alkene 2-[(*E*)-1-methyl-2-phenylvinyl]thiophene **2b** with 3-oxo-3-phenylpropanenitrile **1e**, the reactions of **2b** with **1a** and **1b** yielded **3f** (63%) and **3g** (65%), respectively. Furthermore, 2,5-di(2-thienyl) substituted 4,5-dihydrofuran **3h** was formed in 66% yield in the oxidative cyclisation of **1c** with **2b**. 4,5-Dihydrofurans in the cyclisation of 3-oxopropanenitriles with 1,1,2-tri substituted alkene **2b** was obtained in better yields than the reactions of 1,2-disubstituted alkene **2a**. The cyclisation of more stable intermediate products form 4,5-dihydrofuran-3-carbonitriles in higher yields. Similarly, the tertiary radical intermediate product formed as a result of the addition of this  $\alpha$ -carbon radical to 2-(1-phenylvinyl)thiophene **2c** gains stability since it is conjugated with both phenyl and thienyl groups. Consequently, cyclisation reactions of **2c** gave higher yields than those of **2a** and **2b** (Table 2).

**Table 2.** The oxidative cyclisation of 3-oxopropanenitriles with **2c**.

entry	3-oxopropanenitrile	alkene	4,5-dihydrofuran-3-carbonitrile	yield (%) <sup>a</sup>
1	 <b>1e</b>	 <b>2c</b>		<b>3j</b> (91)
2	 <b>1a</b>	<b>2c</b>		<b>3k</b> (82)
3	 <b>1c</b>	<b>2c</b>		<b>3l</b> (84)
4	 <b>1f</b>	<b>2c</b>		<b>3m</b> (77)
5	 <b>1g</b>	<b>2c</b>		<b>3n</b> (81)
6	 <b>1d</b>	<b>2c</b>		<b>3o</b> (73)

a: Yield of isolated product based on the alkene

2,5-Diphenyl-5-(2-thienyl)-4,5-dihydrofuran-3-carbonitrile **3j** was obtained in excellent yield (91%) by the cyclisation reaction of **2c** with **1e** via manganese(III) acetate. While treatments of **1a** with **2a**

and **2b** formed 5-(2-thienyl) substituted products **3a** (58%) and **3f** (63%) in Table 1 (entries 1 and 6), respectively, **3k** was obtained in 82% yield in the radical cyclisation of **1a** with 1,1-disubstituted alkene **2c**. Similarly, the reaction of 3-(2-thienyl)-3-oxopropanenitrile **1c** with **2e** yielded 2,5-di(2-thienyl) substituted 4,5-dihydrofuran-3-carbonitrile **3l**, and treatments of 3-oxopropanenitriles containing 2-furyl **1f** and 2-benzofuryl **1g** with **2e** produced **3m** and **3n** in good yields (entries 4 and 5). Moreover, compound **3o** was synthesised in 73% yield by the reaction of **1d** with **2c**.

In conclusion, the oxidative cyclisation of 3-oxopropanenitriles with 2-thienyl substituted alkenes using manganese(III) acetate was studied in mild conditions. As a result of these cyclisation reactions, various 4,5-dihydrofuran-3-carbonitriles were obtained in good yields. While the reactions of alkene **2b** with 3-oxopropanenitriles are compared to reactions with that of 1,2-diphenyl-1-pentene,<sup>21</sup> and similarly reactions of **2c** with 3-oxopropanenitriles are compared to reactions with that of 1,1-diphenylethylene,<sup>62</sup> it is seen that there is a noteworthy increase in product yields because of replacement of the phenyl group with a thienyl group.

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