

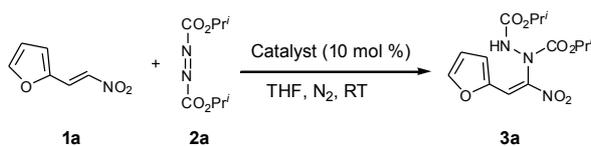
## Highly efficient hydrazination of conjugated nitroalkenes via imidazole or DMAP mediated Morita-Baylis-Hillman reaction

M. Dadwal, S. M. Mobin, I. N. N. Namboothiri \*

### Table of Contents

Entry		Page
1	Table S1. The MBH reaction of NVF <b>1a</b> with DIAD <b>2a</b> in the presence of 10 mol % of various catalysts	1
2	Table S2. The MBH reaction of NVF <b>1a</b> with DIAD <b>2a</b> in the presence of varying amounts of imidazole or DMAP in THF at room temperature	2
3	Table S3. The MBH reaction of NVF <b>1a</b> with DIAD <b>2a</b> mediated by imidazole (100 mol %) or DMAP (100 mol %) in different solvents	2
4	Table S4. The effect of NVF <b>1a</b> -DIAD <b>2a</b> ratio on the yield of MBH adduct <b>3a</b>	3
5	Table S5. The MBH reaction of NVF <b>1a</b> with DIAD <b>2a</b> in the presence of varying amounts of DMAP in acetonitrile at room temperature	3
6	Experimental section	3-11
7	Table S6. Crystallographic data for <b>3a</b>	4
8	References	11

**Table S1.** The MBH reaction of NVF **1a** with DIAD **2a**<sup>a</sup> in the presence of 10 mol % of various catalysts.



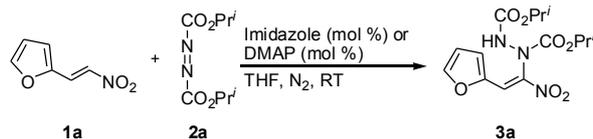
Entry	Catalyst	Time (h)	Yield (%) <sup>b</sup>
<b>1</b>	<b>Imidazole</b>	<b>24</b>	<b>13</b> <sup>c</sup>
<b>2</b>	<b>DMAP</b>	<b>24</b>	<b>4</b> <sup>c</sup>
3	DBU	1/4	<sup>d</sup>
4	DABCO	24	NR <sup>e</sup>
5	Et <sub>3</sub> N	24	NR <sup>e</sup>
6	L-proline	24	NR <sup>e</sup>
7	Ph <sub>3</sub> P	24	NR <sup>e</sup>

<sup>a</sup> 1.5 equiv of DIAD **2a** was used; <sup>b</sup> isolated yield of **3a** after column chromatography;

<sup>c</sup> reaction incomplete; <sup>d</sup> intractable mixture;

<sup>e</sup> NR = No Reaction.

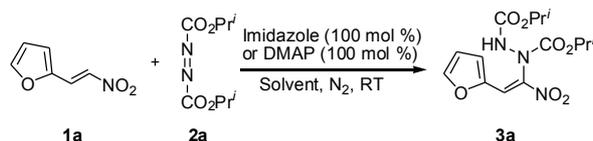
**Table S2.** The MBH reaction of NVF **1a** with DIAD **2a**<sup>a</sup> in the presence of varying amounts of imidazole or DMAP in THF at room temperature.



		Imidazole (a)		DMAP (b)	
Entry	Catalyst (mol %)	Time (h)	Yield (%) <sup>b</sup>	Time (h)	Yield (%) <sup>b</sup>
1	10	24	13 <sup>c</sup>	24	4 <sup>c</sup>
2	20	24	19 <sup>c</sup>	24	7 <sup>c</sup>
3	50	24	95	24	28 <sup>c</sup>
4	75	10	99	24	40 <sup>c</sup>
5	<b>100</b>	<b>4</b>	<b>98</b>	<b>24</b>	<b>43<sup>c</sup></b>

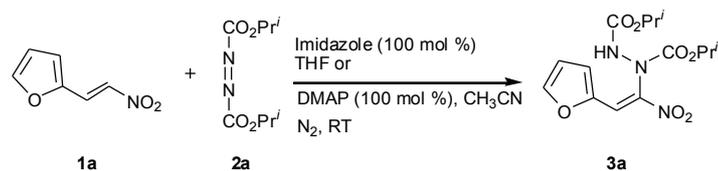
<sup>a</sup> 1.5 equiv of DIAD **2a** was used; <sup>b</sup> isolated yield of **3a** after column chromatography; <sup>c</sup> reaction incomplete.

**Table S3.** The MBH reaction of NVF **1a** with DIAD **2a**<sup>a</sup> mediated by imidazole (100 mol %) or DMAP (100 mol %) in different solvents.



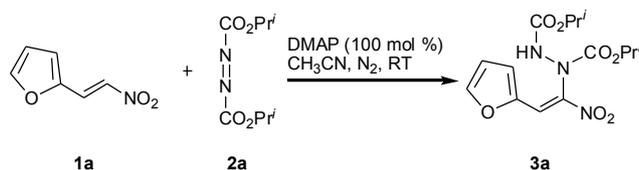
		Imidazole (a)		DMAP (b)	
Entry	Solvent	Time (h)	Yield (%) <sup>b</sup>	Time (h)	Yield (%) <sup>b</sup>
<b>1</b>	<b>THF</b>	<b>4</b>	<b>98</b>	24	43 <sup>c</sup>
2	CH <sub>3</sub> OH	3¼	7 <sup>d</sup>	½	16 <sup>d</sup>
3	DMF	3	85	5	83
4	DMSO	3½	53	1	29 <sup>e</sup>
<b>5</b>	<b>CH<sub>3</sub>CN</b>	1	94	<b>3¼</b>	<b>85</b>
6	1,4-Dioxan	4½	78	24	49 <sup>f</sup>
7	Acetone	½	83	24	25 <sup>g</sup>
8	CH <sub>2</sub> Cl <sub>2</sub>	½	85	24	17 <sup>e</sup>
9	Toluene	2	91	24	28 <sup>e</sup>
10	Ethyl acetate	1	90	24	34 <sup>h</sup>

<sup>a</sup> 1.5 equiv of DIAD **2a** was used; <sup>b</sup> isolated yield of **3a** after column chromatography; <sup>c</sup> 44 % of **1a** was recovered; <sup>d</sup> DIAD decomposed; <sup>e</sup> complete consumption of **1a** was observed; <sup>f</sup> 38 % of **1a** was recovered; <sup>g</sup> 10 % of **1a** was recovered; <sup>h</sup> 18 % of **1a** was recovered.

**Table S4.** The effect of NVF **1a**-DIAD **2a** ratio on the yield of MBH adduct **3a**.

Entry	<b>1a:2a</b>	Imidazole (a)		DMAP (b)	
		Time (h)	Yield (%) <sup>a</sup>	Time (h)	Yield (%) <sup>a</sup>
1	1:1.0	3¼	89	3¼	80
2	<b>1:1.3</b>	3	93	<b>3¼</b>	<b>85</b>
3	<b>1:1.5</b>	<b>3</b>	<b>98</b>	3¼	85

<sup>a</sup> isolated yield of **3a** after column chromatography

**Table S5.** The MBH reaction of NVF **1a** with DIAD **2a** in the presence of varying amounts of DMAP in acetonitrile at room temperature.

Entry	Catalyst (mol %)	Time (h)	DMAP	
			Time (h)	Yield (%) <sup>a</sup>
1	10	24	20	
2	20	24	22	
3	50	6½	71	
4	75	4½	75	
5	<b>100</b>	<b>3¼</b>	<b>85</b>	

<sup>a</sup> Isolated yield of **3a** after column chromatography

## Experimental Section

### General

The melting points are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum One FT spectrometer. NMR spectra (<sup>1</sup>H & <sup>13</sup>C) were recorded on an AMX-400 or VXR-300S spectrometer with TMS as the internal standard. The coupling constants (*J* values) are given in Hz. The <sup>1</sup>H-<sup>1</sup>H NOESY spectrum was recorded on an AMX-400 NMR spectrometer. High resolution mass spectra were recorded at 60-70 eV on a Waters Micromass Q-TOF spectrometer (ESI). All the nitroalkenes were prepared in the laboratory by the standard nitroaldol (Henry) reaction.<sup>1</sup>

### *Crystal structure determination of 3a*

Suitable X-ray quality crystals of **3a** were grown and X-ray diffraction studies were undertaken. Relevant crystallographic data and details of measurements are given in Table S6. X-ray crystallographic data were collected from single crystal samples of volume  $0.40 \times 0.15 \times 0.15$  mm<sup>3</sup>. Unit cell dimensions were obtained using 25 centered reflections in  $\theta$  range 5.1600-10.4600° mounted on a Nonius MACH 3 diffractometer equipped with graphite monochromated Mo K $\alpha$  radiation (0.71073 Å). The intensity data were collected by  $\omega$ -2 $\theta$  scan mode, and corrected by Lorentz Polarization and absorption effects using Psi-Scan ( $\psi$ -scan). Three standard reflections monitored after every 200 reflections and 3 intensity control reflections monitored every hour showed no significant changes (<3%). The structure was solved by direct methods shelxs97 and refined by full-matrix least squares against F<sup>2</sup> using shelxl97 software. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

**Table S6.** Crystallographic Data for **3a**

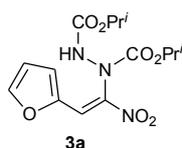
Identification code	<b>3a</b> (iin22b)
Empirical formula	C14 H19 N3 O7
Formula weight	341.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.6000(6) Å    alpha = 67.342(8) deg. b = 10.0870(12) Å    beta = 89.563(6) deg c = 10.8430(9) Å    gamma = 89.466(8) deg.
Volume	867.97(14) Å <sup>3</sup>
Z, Calculated density	2, 1.306 Mg/m <sup>3</sup>
Absorption coefficient	0.106 mm <sup>-1</sup>
F(000)	360
Crystal size	0.40 x 0.15 x 0.15 mm
Theta range for data collection	2.04 to 24.97 deg.
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 0, -12 ≤ l ≤ 11
Reflections collected / unique	3192 / 3004 [R(int) = 0.0184]

Absorption correction	Psi-scan
Max. and min. transmission	0.9843 and 0.9589
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3004 / 0 / 237
Goodness-of-fit on F <sup>2</sup>	1.02
Final R indices [I > 2σ(I)]	R1 = 0.0495, wR2 = 0.1233
R indices (all data)	R1 = 0.1194, wR2 = 0.1468
Largest diff. peak and hole	0.289 and -0.225 e.Å <sup>-3</sup>

### General procedure for the MBH reaction of nitroalkenes **1** and enones **4-6** with azo compounds **2**

To a stirred solution of nitroalkene **1** or enone **4**, **5** or **6** (1 mmol) in THF or acetonitrile (2 ml), under N<sub>2</sub> and protected from light, was added imidazole (68 mg, 1 mmol, Method a) or DMAP (122 mg, 1 mmol, Method b) followed by diazo compound **2** (1.5 mmol) and the reaction mixture was stirred at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was diluted with water (10 ml) and acidified with 5 N HCl (10 ml). The aqueous layer was extracted with ethyl acetate (3 × 10 ml), the combined organic layers were washed with brine (20 ml), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography (0-10 % EtOAc/hexane, gradient elution).

#### (*E*)-Diisopropyl 1-(2-(furan-2-yl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (**3a**).



Yield 98 % (Method a), 85 % (Method b); yellow solid; mp 138 °C;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3478br m, 3130m, 2983w, 1752m, 1721s, 1654m, 1533w, 1400s, 1385s, 1312s, 1247m;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.06-1.29 (12H, broad unresolved doublets), 4.99 (2H, two overlapped septets, *J* 6.3), 6.66 (1H, d, *J* 1.8), 6.97 (1H, br s), 7.72 (2H, unresolved m), 7.98 (1H, s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 21.7, 21.9, 70.4, 72.7, 114.1, 120.3, 121.9, 140.0, 146.0, 148.0, 153.7, 155.4; *m/z* (ESI, Ar) 364 (MNa<sup>+</sup>, 100 %), 167 (1), 107 (4), 106 (12); HRMS (ESI, Ar) calcd for C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>O<sub>7</sub>Na (MNa<sup>+</sup>) 364.1121, found 364.1134.

#### (*E*)-Diisopropyl 1-(2-(thiophene-2-yl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (**3b**).



Yield 94 % (Method a), 86 % (Method b); yellow solid; mp 135-137 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3477br m, 3300m, 3114m, 2981m, 1754s, 1731s, 1537m, 1400s, 1301s, 1244m;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.05-1.27 (12H, broad unresolved doublets), 4.99 (2H, two overlapped septets,  $J$  6.2), 7.00 (1H, br s), 7.20 (1H, dd collapsed to t,  $J$  4.5), 7.77 (1H, d,  $J$  4.5), 7.88 (1H, unresolved m), 8.25 (1H, s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.8 ( $\times 2$ ), 70.3, 72.9, 126.3, 128.3, 132.2, 135.6, 137.2, 140.6, 153.9, 155.1;  $m/z$  (ESI, Ar) 380 ( $\text{MNa}^+$ , 100 %), 358 (3), 269 (2), 228 (1), 122 (3); HRMS (ESI, Ar) calcd for  $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_6\text{SNa}$  ( $\text{MNa}^+$ ) 380.0892, found 380.0895.

**(E)-Diisopropyl 1-(2-(furan-3-yl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3c).**



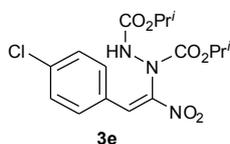
Yield 100 % (Method a), 87 % (Method b); yellow solid; mp 85 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3472br s, 3276w, 3137w, 2985m, 1759s, 1727s, 1531m, 1399s, 1317m, 1234m;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.05-1.33 (12H, broad unresolved doublets), 5.00 (2H, two overlapped septets,  $J$  6.2), 6.97 (1H, br s), 7.40 (1H, unresolved m), 7.52 (1H, unresolved m), 7.99 (1H, unresolved m), 8.14 (1H, s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.7, 21.9, 70.5, 72.8, 110.5, 117.6, 124.4, 142.0, 144.9, 149.7, 154.0, 155.6;  $m/z$  (ESI, Ar) 364 ( $\text{MNa}^+$ , 50 %), 253 (2), 214 (3), 159 (10), 158 (4), 99 (100); HRMS (ESI, Ar) calcd for  $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_7\text{Na}$  ( $\text{MNa}^+$ ) 364.1121, found 364.1137.

**(E)-Diisopropyl 1-(2-(thiophene-3-yl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3d).**



Yield 98 % (Method a), 83 % (Method b); yellow solid; mp 108 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3471br s, 3298m, 3113w, 2981w, 1754s, 1732s, 1536m, 1390s, 1301s, 1243s;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.96-1.33 (12H, broad unresolved doublets), 5.01 (2H, two overlapped septets,  $J$  6.4), 7.00 (1H, br s), 7.41 (1H, dd,  $J$  5.0, 3.0), 7.93 (1H, unresolved m), 8.07 (1H, unresolved m), 8.37 (1H, s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.6, 21.9, 70.5, 72.8, 126.3, 126.8, 129.4, 131.3, 135.5, 141.8, 153.9, 155.7;  $m/z$  (ESI, Ar) 380 ( $\text{MNa}^+$ , 19 %), 158 (13), 156 (22), 122 (82), 99 (100); HRMS (ESI, Ar) calcd for  $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_6\text{SNa}$  ( $\text{MNa}^+$ ) 380.0892, found 380.0885.

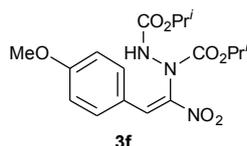
**(E)-Diisopropyl 1-(2-(4-chlorophenyl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3e).**



Yield 93 % (Method a), 70 % (Method b); yellow solid; mp 85-86 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3293br m, 2984m, 1741br s, 1541m, 1322m, 1233m, 1104m;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.98-1.28 (12H, broad unresolved doublets), 4.99 (2H, two overlapped septets,  $J$  6.2), 6.97 (1H, br s), 7.45 (2H, d,  $J$  8.3), 7.96 (1H,

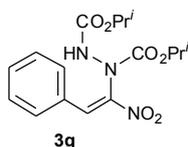
s), 8.06 (2H, d expected, unresolved);  $\delta_C$  (CDCl<sub>3</sub>) 21.0, 21.3, 69.9, 72.3, 127.6, 128.7, 129.9, 133.3, 137.9, 142.9, 153.2, 155.2;  $m/z$  (ESI, Ar) 408 (MNa<sup>+</sup>, 100 %), 211 (5), 152 (11), 150 (95), 99 (29); HRMS (ESI, Ar) calcd for C<sub>16</sub>H<sub>20</sub>N<sub>3</sub>O<sub>6</sub>ClNa (MNa<sup>+</sup>) 408.0938, found 408.0929.

**(E)-Diisopropyl 1-(2-(4-methoxyphenyl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3f).**



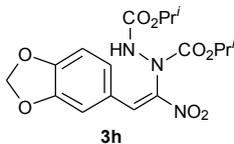
Yield 98 % (Method a), 84 % (Method b); yellow solid; mp 95-96 °C;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3307br m, 2984m, 1743br s, 1532m, 1515m, 1376m, 1307m, 1178m;  $\delta_H$  (CDCl<sub>3</sub>) 1.00-1.33 (12H, broad unresolved doublets), 3.87 (3H, s), 4.99 (2H, two overlapped septets, *J* 6.2), 6.99 (2H, d, *J* 8.9), 7.20 (1H, br s), 8.00 (1H, s), 8.09 (2H, d expected, unresolved);  $\delta_C$  (CDCl<sub>3</sub>) 21.3, 21.5, 55.05 (55.08, rotamer), 69.9, 72.21 (72.24, rotamer), 114.2, 121.6, 131.9, 134.7, 141.0, 153.8, 155.2, 162.9;  $m/z$  (ESI, Ar) 404 (MNa<sup>+</sup>, 48 %), 324 (6), 208 (8), 178 (8), 147 (33), 146 (100), 99 (9); HRMS (ESI, Ar) calcd for C<sub>17</sub>H<sub>23</sub>N<sub>3</sub>O<sub>7</sub>Na (MNa<sup>+</sup>) 404.1434, found 404.1428.

**(E)-Diisopropyl 1-(1-nitro-2-phenylvinyl)hydrazine-1,2-dicarboxylate (3g).**



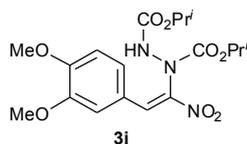
Yield 83 % (Method a), 78 % (Method b); yellow liquid;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3310br w, 3055w, 2986w, 1744br s, 1536m, 1376w, 1321m, 1266m;  $\delta_H$  (CDCl<sub>3</sub>) 0.92-1.26 (12H, broad unresolved doublets), 5.00 (2H, two overlapped septets, *J* 6.2), 6.96 (1H, br s), 7.47-7.50 (3H, m), 8.00 (1H, s), 8.09 (2H, unresolved m);  $\delta_C$  (CDCl<sub>3</sub>) 21.7, 21.9, 70.5, 72.9, 129.0, 129.4, 132.0, 132.4, 132.5, 143.0, 153.9, 155.5;  $m/z$  (ESI, Ar) 374 (MNa<sup>+</sup>, 28 %), 177 (2), 156 (37), 99 (100); HRMS (ESI, Ar) calcd for C<sub>16</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub>Na (MNa<sup>+</sup>) 374.1328, found 374.1337.

**(E)-Diisopropyl 1-(2-(benzo[d][1,3]dioxol-5-yl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3h).**



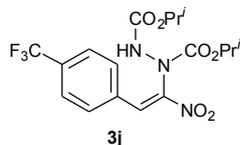
Yield 92 % (Method a), 82 % (Method b); yellow solid; mp 98-99 °C;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3401br s, 1739br s, 1543m, 1325s, 1266s;  $\delta_H$  (CDCl<sub>3</sub>) 1.03-1.33 (12H, broad unresolved doublets), 5.02 (2H, two overlapped septets, *J* 6.2), 6.07 (2H, s), 6.85 (1H, d, *J* 6.1), 7.05 (1H, br s), 7.40 (1H, d expected, unresolved), 7.95 (1H, s), 8.03 (1H, unresolved m);  $\delta_C$  (CDCl<sub>3</sub>) 21.4, 21.7, 70.2, 72.5, 101.9, 108.4, 110.7, 123.3, 130.2, 132.2, 141.3, 148.4, 151.4, 153.9, 155.3;  $m/z$  (ESI, Ar) 418 (MNa<sup>+</sup>, 18 %), 313 (2), 221 (1), 161 (15), 160 (30), 99 (100); HRMS (ESI, Ar) calcd for C<sub>17</sub>H<sub>21</sub>N<sub>3</sub>O<sub>8</sub>Na (MNa<sup>+</sup>) 418.1226, found 418.1224.

**(E)-Diisopropyl 1-(2-(3,4-dimethoxyphenyl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3i).**



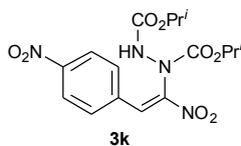
Yield 99 % (Method a), 81 % (Method b); yellow solid; mp 115-117 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3478br s, 3321m, 2984m, 1728br s, 1518m, 1400s, 1310m, 1267s;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.97-1.33 (12H, broad unresolved doublets), 3.95 (3H, s), 3.98 (3H, s), 4.98 (2H, two overlapped septets,  $J$  6.3), 6.93 (1H, d,  $J$  8.6), 7.03 (1H, br s), 7.46 (1H, d,  $J$  8.6), 7.99 (1H, s), 8.09 (1H, s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.4, 21.6, 55.7, 56.0, 70.0, 72.4, 110.4, 113.2, 122.0, 128.7, 132.4, 140.8, 149.1, 152.9, 154.0, 155.2;  $m/z$  (ESI, Ar) 434 ( $\text{MK}^+$ , 12 %), 366 (22), 313 (17), 297 (5), 177 (100), 176 (80), 99 (92); HRMS (ESI, Ar) calcd for  $\text{C}_{18}\text{H}_{27}\text{N}_4\text{O}_6\text{K}$  ( $\text{MK}^+$ ) 434.1568, found 434.1570.

**(E)-Diisopropyl 1-(1-nitro-2-(4-(trifluoromethyl)phenyl)vinyl)hydrazine-1,2-dicarboxylate (3j).**



Yield 93 % (Method a), 43 % (Method b); yellow solid; mp 65 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3381w, 3054w, 2986m, 1744br s, 1543m, 1376w, 1323m, 1266s;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.88-1.26 (12H, broad unresolved doublets), 5.00 (2H, two overlapped septets,  $J$  6.2), 6.98 (1H, br s), 7.74 (2H, d,  $J$  8.0), 7.99 (1H, s), 8.24 (2H, d expected, unresolved);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.3, 21.7, 70.6, 73.0, 123.5 (q,  $J$  271.0), 125.7 (q,  $J$  4.8), 129.6, 132.2, 132.6 (q,  $J$  32.0), 132.8, 144.3, 153.4, 155.4;  $m/z$  (ESI, Ar) 442 ( $\text{MNa}^+$ , 15 %), 245 (12), 218 (100), 174 (27), 99 (37); HRMS (ESI, Ar) calcd for  $\text{C}_{17}\text{H}_{20}\text{N}_3\text{O}_6\text{F}_3\text{Na}$  ( $\text{MNa}^+$ ) 442.1202, found 442.1201.

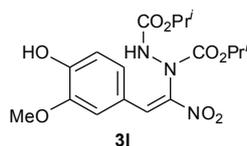
**(E)-Diisopropyl 1-(1-nitro-2-(4-nitrophenyl)vinyl)hydrazine-1,2-dicarboxylate (3k).**



Yield 84 % (Method a), 68 % (Method b); yellow solid; mp 83-84 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3373w, 3055m, 2986m, 1745br s, 1546s, 1527s, 1350m, 1326m, 1266m;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.08-1.33 (12H, broad unresolved doublets), 5.00 (2H, two overlapped septets,  $J$  6.2), 7.08 (1H, s), 8.02 (1H, s), 8.33 (4H, unresolved m);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.4, 21.7, 70.7, 73.3, 123.71, 128.6, 132.8, 135.4, 144.9, 149.1, 153.2, 155.5;  $m/z$  (ESI, Ar) 419 ( $\text{MNa}^+$ , 9 %), 308 (8), 222 (100), 156 (25), 99 (90); HRMS (ESI, Ar) calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_8\text{Na}$  ( $\text{MNa}^+$ ) 419.1179, found 419.1181.

**(E)-diisopropyl  
dicarboxylate (3l).**

**1-(2-(4-hydroxy-3-methoxyphenyl)-1-nitrovinyl)hydrazine-1,2-**



Yield 97 % (Method a), 79 % (Method b); yellow solid; mp 120 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3419br s, 3270w, 3125w, 2985m, 1761m, 1725s, 1587m, 1512m, 1400s, 1283m;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.98-1.33 (12H, broad unresolved doublets), 4.00 (3H, s), 4.98 (2H, two overlapped septets,  $J$  6.3), 6.29 (1H, br s), 6.96 (1H, d,  $J$  8.2), 7.03 (1H, s), 7.30 (1H, unresolved m), 7.98 (1H, s), 8.26 (1H, unresolved m);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.4, 21.7, 56.3, 70.1, 72.5, 113.3, 114.6, 121.5, 129.5, 132.9, 140.6, 147.2, 150.5, 154.2, 155.4;  $m/z$  (ESI, Ar) 420 ( $\text{MNa}^+$ , 12 %), 352 (6), 163 (32), 99 (100); HRMS (ESI, Ar) calcd for  $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_8\text{Na}$  ( $\text{MNa}^+$ ) 420.1383, found 420.1375.

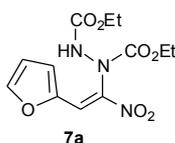
**(E)-Diisopropyl  
(3m).**

**1-(1-nitro-2-(4-N,N-dimethylphenyl)vinyl)hydrazine-1,2-dicarboxylate**



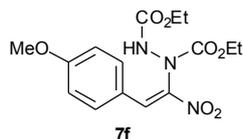
Yield 86 % (Method a), 46 % (Method b); red solid; mp 122-124 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3475br s, 3154s, 1722br s, 1593s, 1536m, 1503m, 1398s, 1279s, 1175s;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.02-1.33 (12H, broad unresolved doublets), 3.09 (6H, s), 5.00 (2H, two overlapped septets,  $J$  6.3), 6.72 (2H, d,  $J$  8.6), 7.05 (1H, br s), 8.03 (3H, d + s, expected, unresolved);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.3, 21.5 (21.6, rotamer), 39.4, 69.5, 71.8, 111.2, 116.0, 133.7, 135.1, 138.2, 152.9, 154.4, 155.3;  $m/z$  (ESI, Ar) 395 ( $\text{M}^+$ , 12 %), 349 (24), 246 (4), 159 (57), 99 (100); HRMS (ESI, Ar) calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_6$  ( $\text{M}^+$ ) 395.1931, found 395.1944.

**(E)-Diethyl 1-(2-(furan-2-yl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (7a).**



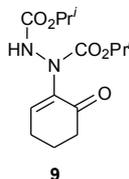
Yield 95 % (Method a), 75 % (Method b); yellow solid mp 128 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3475br m, 3286m, 3146w, 2986m, 1759s, 1729s, 1652m, 1534m, 1463m, 1308s, 1241m;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.12-1.26 (6H, broad unresolved triplets), 4.20 (4H, two overlapped q,  $J$  7.0), 6.66 (1H, unresolved m), 7.11 (1H, br s), 7.74 (2H, unresolved m), 8.00 (1H, s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 13.9, 14.0, 62.2, 64.0, 113.8, 120.1, 121.9, 139.6, 145.7, 148.0, 154.0, 155.5;  $m/z$  (ESI, Ar) 336 ( $\text{MNa}^+$ , 10 %), 159 (9), 99 (100); HRMS (ESI, Ar) calcd. for  $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_7\text{Na}$  ( $\text{MNa}^+$ ) 336.0808, found 336.0795.

**(E)-Diethyl 1-(2-(4-methoxyphenyl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (7f).**



Yield 94 % (Method a), 87 % (Method b); yellow solid; mp 110-112 °C;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3386br w, 3020s, 1745br s, 1602s, 1514m, 1305s, 1216s;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.07-1.35 (6H, broad unresolved triplets, for two rotamers), 3.85, 3.88 (3H, s, minor and major rotamers, respectively), 4.20 (4H, two overlapped q,  $J$  7.0), 6.99 (2H, d,  $J$  8.9), 7.13 (1H, br s), 8.04 (1H, s), 8.10 (2H, d expected, unresolved);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 13.9, 14.0, 55.2, 62.1, 64.0, 114.3, 121.5, 132.3, 134.8, 140.9, 154.5, 155.6, 163.1;  $m/z$  (ESI, Ar) 376 ( $\text{MNa}^+$ , 5 %), 149 (5), 146 (12), 99 (100); HRMS (ESI, Ar) calcd for  $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_7\text{Na}$  ( $\text{MNa}^+$ ) 376.1121, found 376.1118.

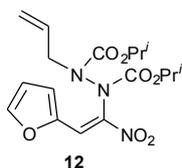
**(E)-Diisopropyl 2-(6-oxocyclohex-1-enyl)hydrazine-1,2-dicarboxylate (9).**



Yield 52 % (Method a), 38 % (Method b); colourless liquid;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3390br m, 3301br m, 2984s, 1721br s, 1486m, 1380s, 1266s, 1108s;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.25-1.27 (12H, two overlapped doublets,  $J$  5.8, 6.4), 2.03-2.09 (2H, m), 2.50-2.55 (4H, m), 4.95 (2H, two overlapped septets,  $J$  5.8, 6.4), 6.5 (1H, unresolved m), 7.0 (1H, br s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.77, 21.84, 21.9, 22.2, 25.2, 25.5, 37.9, 69.6, 69.9, 70.7 ( $\times 2$ ), 138.3, 148.6, 154.4, 155.0, 155.6, 156.3, 195.1 (all the peaks corresponding to the hydrazino moiety appear twice in  $^{13}\text{C}$  NMR indicating the anisotropy exerted by the carbonyl groups);  $m/z$  (ESI, Ar) 337 ( $\text{MK}^+$ , 5 %), 321 (13), 297 (100), 99 (7); HRMS (ESI, Ar) calcd for  $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_5\text{K}$  ( $\text{MK}^+$ ) 337.1166, found 337.1164.

**(E)-Diisopropyl-N-allyl-1-(2-(furan-2-yl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (12).**

To a stirred solution of sodium hydride (17 mg, 0.75 mmol, obtained after removal of paraffin oil by rinsing with pet ether) in THF (5 ml) at 0 °C, under  $\text{N}_2$ , the MBH adduct **3a** (171 mg, 0.5 mmol) was added portionwise. The solution was allowed to stir for another 10 min at the same temperature, followed by slow addition of dilute solution of allyl bromide (45 mg, 0.75 mmol) in THF (2 ml). The reaction mixture was stirred at 0 °C for another 15 min and then quenched by slow addition of saturated  $\text{NH}_4\text{Cl}$  solution. The aqueous layer was extracted with ethyl acetate (3  $\times$  10 ml), the combined organic layers were washed with brine (20 ml), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography (0-20 % EtOAc/hexane, gradient elution) to afford **12**.



Yield 57 %; yellow liquid;  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$  3056m, 2978m, 1743br s, 1531m, 1265s;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.15-1.30 (9H, six overlapped unresolved doublets), 1.34-1.40 (3H, two overlapped doublets,  $J$  6.2 for both) 4.05-4.31 (2H, unresolved m), 4.91-5.08 (4H, m), 5.81-5.92 (1H, ddt,  $J$  12.1, 6.2, 5.8), 6.62 (1H, dd,  $J$  3.6, 1.8), 7.60-7.85 (2H, unresolved m), 7.66 (1H, s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 21.58, 21.67, 21.7, 21.8, 70.6, 70.7, 72.0, 113.4, 116.7, 116.9, 122.0, 133.3, 133.5, 145.9, 147.5, 147.6, 152.3 (the Me groups in the hydrazino moiety appear twice in  $^{13}\text{C}$  NMR indicating the anisotropy exerted by the carbonyl groups;  $m/z$  (ESI, Ar) 420 ( $\text{MK}^+$ , 58 %), 404 (100); HRMS (ESI, Ar) calcd for  $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_7\text{K}$  ( $\text{MK}^+$ ) 420.1173, found 420.1132.

## References

- 1 Vogel's Text Book of Practical Organic Chemistry, Addison Wesley Longman Ltd., Essex, England, 5<sup>th</sup> Ed., 1989, p 1035.