Experimental Data and Optimization Tables
For

The Morita-Baylis-Hillman adducts of β-aryl nitroethylenes with other activated alkenes: synthesis and anticancer activity studies

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Experimental Section

General

The melting points are uncorrected. IR spectra were recorded on an Impact 400/Nicolet FT spectrometer. NMR spectra (^{1}H & ^{13}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. High resolution mass spectra were recorded at 60-70 eV on a Waters Micromass Q-TOF spectrometer (ESI) or VG-Fisons "Autospec" spectrometer (DCI in CH_4 or *i*-butane). All the nitroalkenes were prepared in the laboratory by standard nitroaldol (Henry) reaction.

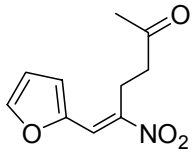
Cell culture and cell proliferation assay.[1] HeLa cells were cultured in Eagle's minimal essential medium (Himedia) supplemented with 10 % (v/v) fetal bovine serum, 1.5 g/L sodium bicarbonate and 1 % antibiotic antimycotic solution containing streptomycin, amphotericin B and penicillin. Cells were maintained at 37 ºC in a humidified atmosphere of 5 % carbon dioxide and 95 % air. Cells were seeded at a density of 1×10^5 cells/ml on 96-well plates and the inhibition of cell proliferation was determined using the standard sulforhodamine B assay as described previously.[1] Cells were incubated with different concentrations of MBH compounds for one cell cycle. DMSO was used as a vehicle control. The cells were stained with 0.4 % sulforhodamine B and the protein-bound dye was detected by measuring the absorbance at 560 nm. For all the compounds, the percentage inhibition of proliferation was calculated for 5 μM and 25 μM. The results are the average of three independent experiments. Each experiment was done in duplicate.

Binding of MBH adducts 3 and 5 to tubulin. Binding of MBH adducts **3** and **5** to purified goat brain tubulin was determined by measuring the intrinsic tubulin fluorescence quenching as described previously.[2] Tubulin (1 μM) was incubated with 10 μM each of the 14 tested MBH compounds in PEM buffer (25 mM pipes (pH 6.8), 3 mM $MgSO_4$, and 1 mM EGTA) for 30 min at room temperature. Fluorescence measurements were taken on a JASCO FP-750 spectrofluorometer using a 0.3 cm path length cuvette with excitation and emission wavelengths of 280 and 335 nm, respectively. The tested compounds quenched the intrinsic tryptophan fluorescence of tubulin.

General experimental procedure for the MBH reaction

To a stirred solution of nitroalkene **1** (1 mmol) in THF (2 ml) was added imidazole (0.068 mg, 1 mmol), lithium chloride (0.042 mg, 1 mmol), followed by MVK **2** or ethyl acrylate **4** (3 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_2SO_4 and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography (10 % EtOAc:hexane) to afford pure product **3** or **5**.

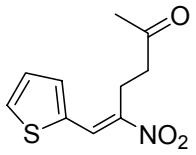
(*E*)-6-(Furan-2-yl)-5-nitrohex-5-en-2-one (3a).



3a

Yield 44 %; yellow solid; mp 57-58 °C; ν_{max} (KBr)/cm^{-1} 1709m, 1494m, 1294s; δ_H ($CDCl_3$) 2.20 (3H, s), 2.76 (2H, t, *J* 7.8), 3.30 (2H, t, *J* 7.8), 6.59 (1H, dd, *J* 3.3, 1.8), 6.87 (1H, d, *J* 3.3), 7.64 (1H, d, *J* 1.8), 7.85 (1H, s); δ_C ($CDCl_3$) 22.1, 29.8, 41.4, 113.1, 120.2, 121.2, 146.8, 146.9, 147.5, 206.8; *m/z* (ESI) 232 (MNa^+, 25 %), 164 (100), 159 (23); HRMS (ESI) calcd. for $C_{10}H_{11}NO_4Na$ (MNa^+) 232.0586, found 232.0579.

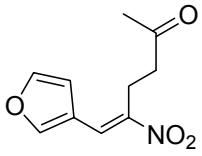
(*E*)-6-(Thien-2-yl)-5-nitrohex-5-en-2-one (3b).



3b

Yield 40 %; yellow solid; mp 71 °C; ν_{max}(KBr)/cm^{-1} 1704m, 1494m, 1295s; δ_H ($CDCl_3$) 2.22 (3H, s), 2.80 (2H, t, *J* 8.0), 3.25 (2H, t, *J* 8.0), 7.19 (1H, dd, *J* 5.1, 3.7), 7.46 (1H, d, *J* 3.7), 7.65 (1H, d, *J* 5.1), 8.30 (1H, s) ; δ_C ($CDCl_3$) 22.2, 29.8, 40.3, 127.9, 128.3, 132.2, 134.3, 135.5, 146.9, 206.3; *m/z* (DCI, CH_4) 226 (MH^+, 19 %), 180 (37), 179 (100), 163 (20), 135 (20), 121 (39); HRMS (DCI, CH_4) calcd. for $C_{10}H_{12}NO_3S$ (MH^+) 226.0538, found 226.0543.

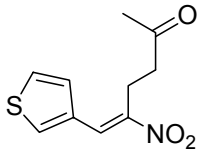
(*E*)-6-(Furan-3-yl)-5-nitrohex-5-en-2-one (3c).



3c

Yield 42 %; yellow solid; mp 65-66 °C; ν_{max}(KBr)/cm^{-1} 1719s, 1505s, 1322s; δ_H ($CDCl_3$) 2.21 (3H, s), 2.79 (2H, t, *J* 7.8), 3.12 (2H, t, *J* 7.8), 6.68 (1H, dd, *J* 1.6, 0.8), 7.54 (1H, dd, *J* 1.6, 0.8), 7.83 (1H, t, *J* 0.8), 7.94 (1H, s); δ_C ($CDCl_3$) 21.9, 29.9, 40.8, 109.5, 118.6, 125.3, 145.1, 146.9, 148.7, 206.6; *m/z* (ESI) 232 (MNa^+, 6 %), 189 (20), 158 (100); HRMS (ESI) calcd. for $C_{10}H_{11}NO_4Na$ (MNa^+) 232.0586, found 232.0588.

(*E*)-6-(Thien-3-yl)-5-nitrohex-5-en-2-one (3d).

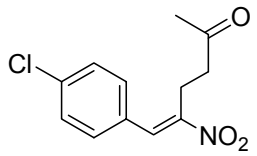


3d

Yield 41 %; yellow solid; mp 78-79 °C; ν_{max}(KBr)/cm^{-1} 1714s, 1520s, 1317s; δ_H ($CDCl_3$) 2.22 (3H, s), 2.82 (2H, t, *J* 7.7), 3.18 (2H, t, *J* 7.7), 7.28 (1H, dd, *J* 5.1, 1.1), 7.45 (1H, dd, *J* 5.1, 1.8), 7.69 (1H, dd, *J* 1.8, 1.1), 8.08 (1H, s); δ_C ($CDCl_3$) 21.9, 30.0, 40.8, 127.5, 127.9, 128.4, 130.9,

133.0, 148.7, 206.7; *m/z* (ESI) 248 (MNa^+, 5 %), 189 (30), 159 (100), 143 (26), 140 (15); HRMS (ESI) calcd. for $C_{10}H_{11}NO_3SNa$ (MNa^+) 248.0357, found 248.0358.

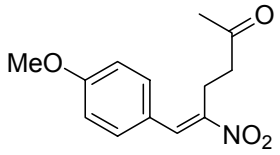
(*E*)-6-(4-Chlorophenyl)-5-nitrohex-5-en-2-one (3e).



3e

Yield 39 %; yellow solid; mp 73-74 °C; ν_{max}(KBr)/cm^{-1} 1708m, 1507s, 1309s; δ_H ($CDCl_3$) 2.19 (3H, s), 2.80 (2H, t, *J* 7.5), 3.10 (2H, t, *J* 7.5), 7.40 (4H, ABq, *J* 8.8), 8.02 (1H, s); δ_C ($CDCl_3$) 21.4, 29.8, 40.8, 129.4, 130.2, 130.9, 133.3, 136.4, 150.8, 206.0; *m/z* (DCI, CH_4) 254 (MH^+, 10 %), 207 (100), 191 (19), 165 (35), 149 (30), 128 (34), 115 (30), 99 (10), 84 (16); HRMS (DCI, CH_4) calcd. for $C_{12}H_{12}ClNO_3$ 254.0498, found 254.05078.

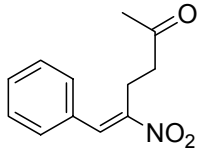
(*E*)-6-(4-Methoxyphenyl)-5-nitrohex-5-en-2-one (3f).



3f

Yield 36 %; yellow solid; mp 74-75 °C; ν_{max}(KBr)/cm^{-1} 1710m, 1502m, 1306s; δ_H ($CDCl_3$) 2.21 (3H, s), 2.81 (2H, t, *J* 7.7), 3.15 (2H, t, *J* 7.7), 3.86 (3H, s), 6.97 (2H, d, *J* 8.8), 7.41 (2H, d, *J* 8.8), 8.07 (1H, s); δ_C ($CDCl_3$) 21.8, 30.1, 41.1, 55.5, 114.7, 124.0, 131.9, 134.5, 148.2, 161.3, 206.3; *m/z* (DCI, CH_4) 250 (MH^+, 11 %), 203 (100), 187 (34), 161 (32), 145 (47), 115 (10), 102 (5), 84 (8); HRMS (DCI, CH_4) calcd for $C_{13}H_{15}NO_4$ 250.1079, found 250.1052.

(*E*)-6-(Phenyl)-5-nitrohex-5-en-2-one (3g).



3g

Yield 34 %; yellow solid; mp 76-77 °C; ν_{max}(KBr)/cm^{-1} 1713s, 1512s, 1401s, 1327s; δ_H ($CDCl_3$) 2.20 (3H, s), 2.82 (2H, t, *J* 7.9), 3.13 (2H, t, *J* 7.9), 7.27-7.47 (5H, m), 8.10 (1H, s); δ_C ($CDCl_3$) 21.6, 30.0, 41.2, 129.2, 129.8, 130.4, 132.0, 134.8, 150.5, 206.4; *m/z* (ESI) 242 (MNa^+, 2 %), 227 (2), 189 (20), 159 (100), 140 (48); HRMS (ESI) calcd. for $C_{12}H_{13}NO_3Na$ (MNa^+) 242.0793, found 242.0801.

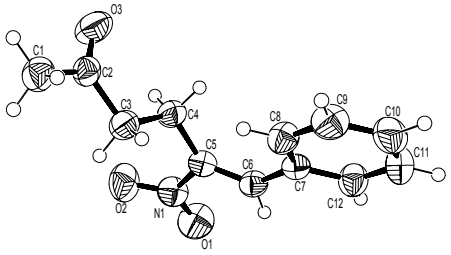
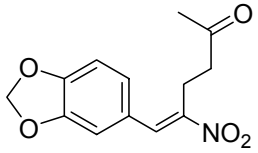


Figure S1. X-Ray crystal structure of **3g**.

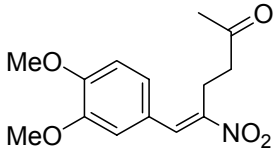
(*E*)-6-(Benzo[d][1,3]dioxol-6-yl)-5-nitrohex-5-en-2-one (3h).



3h

Yield 47 %; yellow solid; mp 102-104 ^{o}C; ν_{max}(KBr)/cm^{-1} 1714m, 1510m, 1317m, 1245s; δ_H ($CDCl_3$) 2.21 (3H, s), 2.81 (2H, t, *J* 7.7), 3.13 (2H, t, *J* 7.7), 6.05 (2H, s), 6.92 (2H, ABq, *J* 8.1; the low field half of ABq is further split into d, *J* 1.8), 6.98 (1H, d, *J* 1.8), 8.05 (1H, s); δ_C ($CDCl_3$) 21.6, 29.9, 40.9, 102.0, 109.0, 109.3, 125.6, 126.1, 134.7, 148.5, 148.8, 149.7, 206.6; *m/z* (ESI) 286 (MNa^+, 20 %), 218 (100), 189 (6), 161 (22), 159 (42), 145 (13); HRMS calcd. for $C_{13}H_{13}NO_5Na$ (MNa^+) 286.0691, found 286.0685.

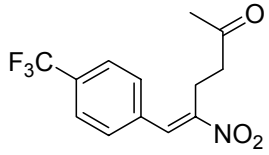
(*E*)-6-(3,4-Dimethoxyphenyl)-5-nitrohex-5-en-2-one (3i).



3i

Yield 60 %; yellow solid; mp 103-105 ^{o}C; ν_{max}(KBr)/cm^{-1} 1724m, 1520m, 1317m, 1276s; δ_H ($CDCl_3$) 2.22 (3H, s), 2.84 (2H, t, *J* 7.7), 3.19 (2H, t, *J* 7.7), 3.91 (3H, s), 3.94 (3H, s), 6.94 (1H d, *J* 8.4), 7.02 (1H, d, *J* 1.8), 7.08 (1H, dd, *J* 8.4, 1.8), 8.05 (1H, s); δ_C ($CDCl_3$) 21.9, 30.0, 41.1, 56.2 (× 2), 111.6, 112.9, 124.4, 124.5, 134.8, 148.7, 149.5, 151.4, 206.6; *m/z* (ESI) 302 (MNa^+, 100 %), 234 (89), 177 (7), 159 (13); HRMS (ESI) calcd. for $C_{14}H_{17}NO_5Na$ (MNa^+) 302.1004, found 302.1011.

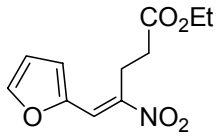
(*E*)-6-(4-(Trifluoromethyl)phenyl)-5-nitrohex-5-en-2-one (3j).



3j

Yield 28 %; yellow solid; mp 75-76 ^{o}C; ν_{max}(KBr)/cm^{-1} 1724s, 1536s, 1337s; δ_H ($CDCl_3$) 2.19 (3H, s), 2.80 (2H, t, *J* 7.6), 3.09 (2H, t, *J* 7.6), 6.97 (2H, d, *J* 8.6), 7.41 (2H, d, *J* 8.6), 8.07 (1H s); δ_C ($CDCl_3$) 21.4, 29.7, 40.8, 125.0, 125.9 (q, *J* 4.0), 129.7, 131.8 (q, *J* 32.8), 132.6, 135.5, 152.3, 205.7; *m/z* (ESI) 310 (MNa^+, 100 %), 238 (3); HRMS (ESI) calcd for $C_{13}H_{12}NO_3F_3Na$ (MNa^+) 310.0670, found 310.0667.

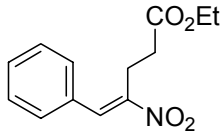
(*E*)-Ethyl-5-(furan-2-yl)-4-nitropent-4-enoate (5a).



5a

Yield 21 %; yellow liquid; ν_{max}(KBr)/cm^{-1} 1734s, 1520s, 1322s; δ_H ($CDCl_3$) 1.25 (3H, t, *J* 7.3), 2.64 (2H, t, *J* 7.6), 3.39 (2H, t, *J* 7.6), 4.14 (2H, q, *J* 7.3), 6.60 (1H, dd, *J* 3.4, 1.8), 6.90 (1H, d, *J* 3.4), 7.67 (1H, d, *J* 1.8), 7.88 (s, 1H); δ_C ($CDCl_3$) 14.1, 23.3, 32.3, 60.6, 113.0, 120.1, 121.3, 146.5, 146.7, 147.4, 172.0; *m/z* (ESI) 262 (MNa^+, 100 %), 189 (3), 166 (11), 120 (14), 106 (30); HRMS (ESI) calcd. for $C_{11}H_{13}NO_5Na$ (MNa^+) 262.0691, found 262.0687.

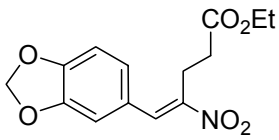
(*E*)-Ethyl-5-phenylpent-4-enoate (5g).



5g

Yield 18 %; yellow liquid; ν_{max}(KBr)/cm^{-1} 1739s, 1525s, 1332s; δ_H ($CDCl_3$) 1.24 (3H, t, *J* 7.3), 2.66 (2H, t, *J* 8.0), 3.09 (2H, t, *J* 8.0), 4.14 (2H, q, *J* 7.3), 7.45 (5H, m), 8.11 (1H, s); δ_C ($CDCl_3$) 14.1, 22.9, 32.1, 60.8, 129.1, 129.6, 130.2, 131.8, 134.8, 150.1, 171.7; *m/z* (ESI) 272 (MNa^+, 100 %), 269 (57), 216 (13), 213 (2), 176 (22), 154 (20); HRMS (ESI) calcd. for $C_{13}H_{15}NO_4Na$ (MNa^+) 272.0899, found 272.0907.

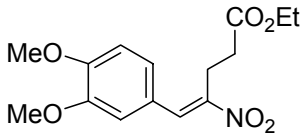
(*E*)-Ethyl-5-((benzo[*d*][1,3]dioxol-6-yl)-4-nitropent-4-enoate (5h).



5h

Yield 21 %; yellow solid; mp 72-73 °C; ν_{max}(KBr)/cm^{-1} 1739s, 1525s, 1322s; δ_H ($CDCl_3$) 1.26 (3H, t, *J* 7.3), 2.66 (2H, t, *J* 7.9), 3.20 (2H, t, *J* 7.9), 4.16 (2H, q, *J* 7.3), 6.06 (2H, s), 6.96 (2H, ABq, *J* 8.8), 6.99 (1H, s), 8.04 (1H, s); δ_C ($CDCl_3$) 14.2, 23.0, 32.0, 60.9, 101.9, 109.0, 109.2, 125.5, 126.1, 135.0, 148.3, 148.5, 149.7, 171.9; *m/z* (ESI) 316 (MNa^+, 100 %), 248 (40); HRMS (ESI) calcd for $C_{14}H_{15}NO_6Na$ (MNa^+) 316.0797, found 316.0786.

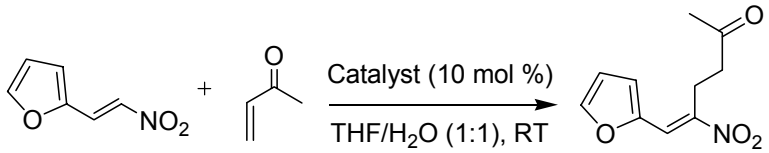
(*E*)-Ethyl-5-(3,4-dimethoxyphenyl)-4-nitropent-4-enoate (5i).



5i

Yield 24 %; yellow solid; mp 69-70 °C; ν_{max}(KBr)/cm^{-1} 1739m, 1525s, 1322m; δ_H ($CDCl_3$) 1.18 (3H, t, *J* 7.3), 2.61 (2H, t, *J* 8.0), 3.18 (2H, t, *J* 8.0), 3.84 (3H, s), 3.86 (3H, s), 4.07 (2H, q, *J* 7.3), 6.88 (1H, d, *J* 8.6), 6.97 (1H, d, *J* 2.3), 7.04 (1H, dd, *J* 8.6, 2.3), 8.00 (1H, s); δ_C ($CDCl_3$) 14.2, 23.3, 32.2, 56.1 (× 2), 61.0, 111.4, 112.6, 124.3, 124.5, 135.3, 148.0, 149.4, 151.3, 172.1; *m/z* (ESI) 332 (MNa^+, 100 %); HRMS (ESI) calcd. for $C_{15}H_{19}NO_6Na$ (MNa^+) 332.1110, found 332.1125.

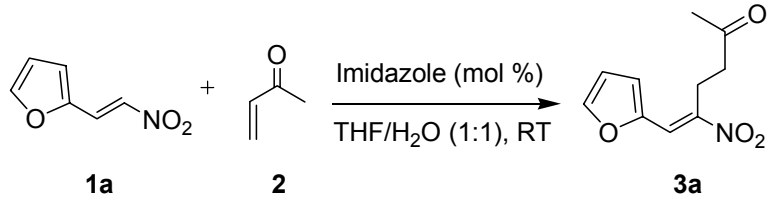
Table S1. The MBH reaction of NVF **1a** with MVK **2** in the presence of 10 mol % of various catalysts.



1a **2** **3a**

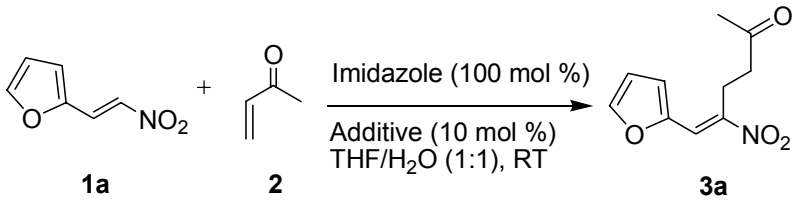
Entry	Catalyst (10 mol %)	Time (d)	Isolated Yield (%) of **3a**
1	**Imidazole**[3]	**4**	**8**
2	DMAP[4]	5	5
3	DABCO	7	None
4	DBU	7	None
5	Pyridine	7	None
6	Et_3N	7	None
7	Benzimidazole	7	None
8	Histidine	7	None

Table S2. The MBH reaction of NVF **1a** with MVK **2** in the presence of varying amounts of imidazole.



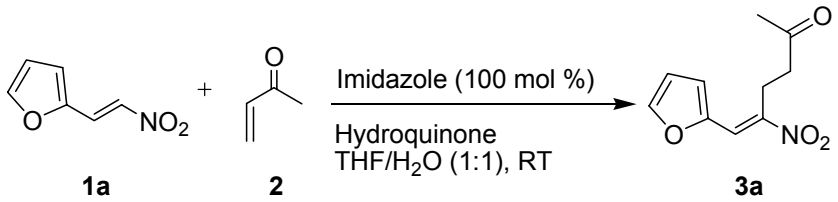
Entry	Imidazole (mol %)	Time (h)	Isolated Yield (%) of **3a**
1	10	96	8
2	30	24	11
3	50	8	16
4	**100**	**1**	**27**
5	200	¼	28
6	300	¼	24

Table S3. The MBH reaction of NVF **1a** with MVK **2** in the presence of 100 mol % of imidazole and various co-catalysts.



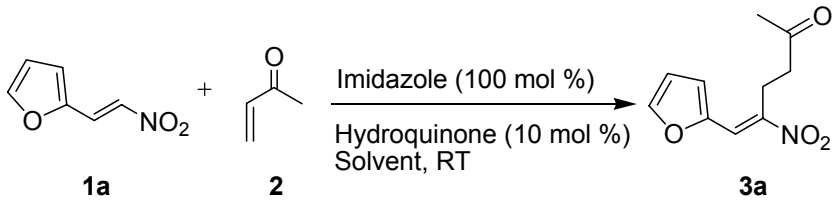
Entry	Additive (10 mol %)	Time (h)	Isolated Yield (%) of **3a**
1	-	1	27
2	Anthranilic acid	6	15
3	L-Proline	3	26
4	o-Aminophenol	1	24
5	m-Aminobenzoic acid	1	14
6	Morpholine	¾	15
7	**Hydroquinone**	**1**	**39**
8	**p-Methoxyphenol**	**1**	**41**
9	β-Cyclodextrin	1	15
10	Urea	1	24
11	Thiourea	1	19
12	Bis-thiourea[5]	1	28

Table S4. The MBH reaction of NVF **1a** with MVK **2** in the presence of 100 mol % imidazole and varying amounts of hydroquinone.



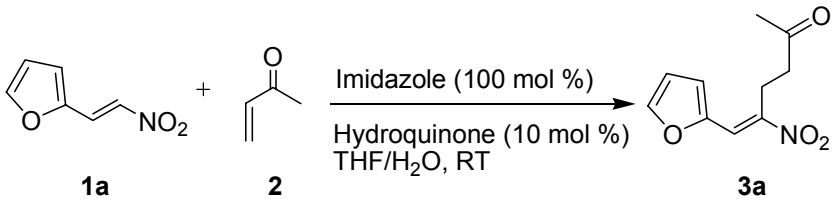
Entry	Hydroquinone (mol %)	Time (h)	Isolated Yield (%) of **3a**
1	5	1	38
2	**10**	**1**	**39**
3	20	1¼	33

Table S5. The MBH reaction of NVF **1a** with MVK **2** in the presence of 100 mol % imidazole and 10 mol % of hydroquinone in different solvents.



Entry	Solvent	Time (h)	Isolated Yield (%) of **3a**
1	**THF/H_2O (1:1)**	**1**	**39**
2	DMF/H_2O (1:1)	½	5
3	Dioxan/H_2O (1:1)	12	12
4	MeOH/ H_2O (1:1)	¼	15
5	THF	24	11
6	Dioxan	12	12
7	MeOH	2	22
8	CH_2Cl_2	2	10
9	H_2O	1	6
10	-	½	10

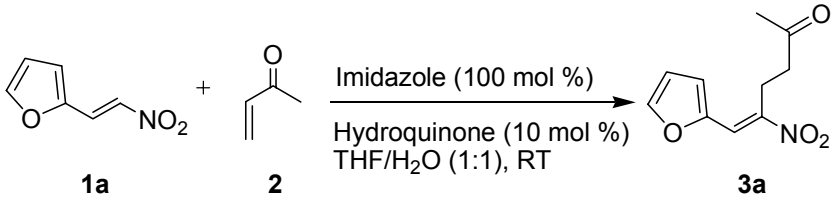
Table S6. The MBH reaction of NVF **1a** with MVK **2** in the presence of 100 mol % imidazole and 10 mol % hydroquinone in different ratios of THF and H_2O.



1a **2** **3a**

Entry	THF:H_2O	Time (h)	Isolated Yield (%) of **3a**
1	**1:1**	**1**	**39**
2	2:1	1	17
3	10:1	¾	7

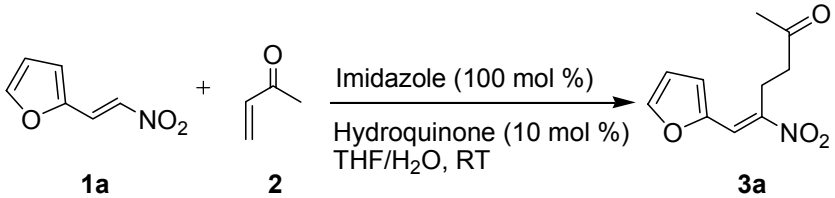
Table S7. The effect of NVF **1a**-MVK **2** ratio on the MBH reaction in the presence of 100 mol % imidazole and 10 mol % hydroquinone.



1a **2** **3a**

Entry	**1a**:**2**	Time (h)	Isolated Yield (%) of **3a**
1	1:1	1	27
2	1:2	1	32
3	**1:3**	**1**	**39**
4	1:4	1	37
5	1:5	1½	39

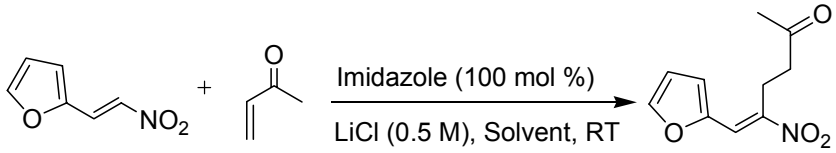
Table S8. The effect of concentration on the MBH reaction of NVF **1a** with MVK **2** in the presence of 100 mol % imidazole and 10 mol % hydroquinone in THF:H_2O (1:1).



1a **2** **3a**

Entry	Concentration (M)	Time (h)	Isolated Yield (%) of **5a**
1	0.25	24	Polymerization
2	0.5	2	30
3	1	1½	33
4	**2**	**1**	**39**

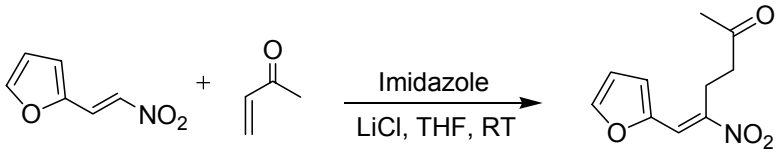
Table S9. The MBH reaction of NVF **1a** with MVK **2** in the presence of 100 mol % imidazole and 0.5 M LiCl in different solvents.



1a **2** **3a**

Entry	Solvent	Time (h)	Isolated Yield (%) of **3a**
1	THF/H_2O	1	22
2	**THF**	**48**	**44**
3	DMF	24	24
4	CH_3CN	32	29
5	1,4-Dioxan	40	33

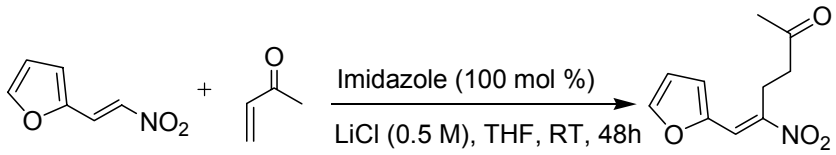
Table S10. The effect of imidazole-LiCl ratio on the MBH reaction of NVF **1a** with MVK **2**.



1a **2** **3a**

Entry	Imidazole (mol %)	LiCl (M)	Time (h)	Isolated Yield (%) of **3a**
1	**100**	**0.5**	**48**	**44**
2	100	1.0	37	43
3	100	2.0	39	41
4	100	3.0	40	42
5	50	0.5	134	18
6	200	0.5	39	42

Table S11. The effect of NVF **1a**-MVK **2** ratio on the MBH reaction in the presence of 100 mol % imidazole and 0.5 M LiCl.



1a **2** **3a**

Entry	**1a:2**	Isolated Yield (%)[a] of **3a**
1	1:1	34
2	1:2	37
3	**1:3**	**44**
4	1:4	43
5	1:5	44

[a] 15-20 % of **1a** was recovered

Table S12. The % inhibition of HeLa cell proliferation by MBH adducts **3** and **5.**

Entry	**3, 5**	Ar	% Inhibition of HeLa Cell Proliferation by **3** and **5**	
			5 μM	25 μM
1	**3a**	2-Furyl	33 ± 11	73 ± 7
2	**3b**	2-Thienyl	52 ± 3	91 ± 6
3	**3c**	3-Furyl	33 ± 9	70 ± 7
4	**3d**	3-Thienyl	42 ± 4	95 ± 3
5	**3e**	(4-Cl)Ph	75 ± 12	98 ± 1
6	**3f**	(4-OMe)Ph	80 ± 4	95 ± 2
7	**3g**	Ph	72 ± 10	95 ± 2
8	**3h**	3,4-(OCH_2O)Ph	30 ± 3	82 ± 5
9	**3i**	3,4-$(OMe)_2$Ph	34 ± 8	82 ± 2
10	**3j**	4-CF_3Ph	43 ± 8	65 ± 8
11	**5a**	2-Furyl	25 ± 5	67 ± 6
12	**5g**	Ph	58 ± 6	76 ± 5
13	**5h**	3,4-(OCH_2O)Ph	32 ± 7	94 ± 1
14	**5i**	3,4-$(OMe)_2$Ph	58 ± 3	76 ± 5

Table S13. Quenching of intrinsic tryptophan fluorescence by MBH adducts **3** and **5** (control intensity 40.6).

Entry	Compound	Fluorescence Intensity at 335 nm
1	control	40.6
2	**3a**	24.3
3	**5a**	21.9
4	**3f**	10.0
5	**3e**	10.7
6	**3b**	13.7
7	**3g**	12.8
8	**3i**	8.5
9	**3d**	11.5
10	**3h**	7.2
11	**3c**	15.0
12	**3j**	10.1
13	**5g**	10.5
14	**5i**	7.1
15	**5h**	6.2

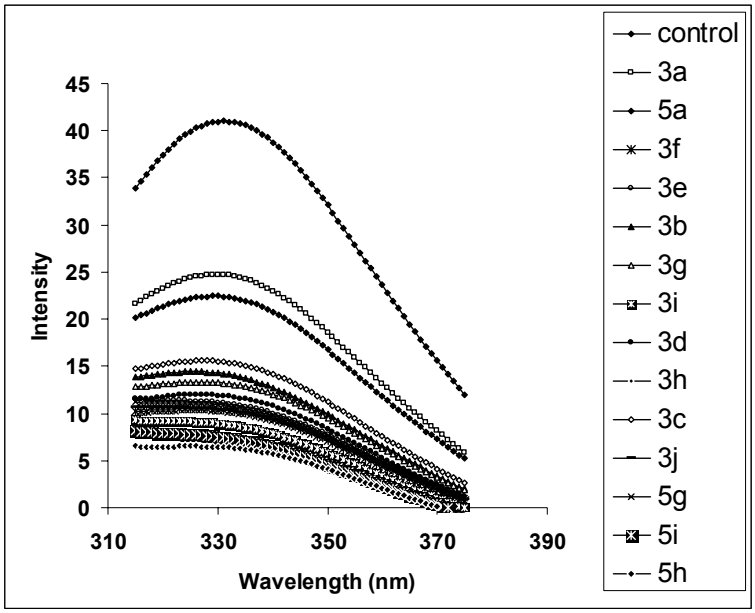


Figure S2. Decrease in intrinsic tryptophan fluorescence by MBH adducts **3** and **5** (control intensity 40.6).

Table S14. Quenching of intrinsic tryptophan fluorescence by MBH adducts **3** and **5** (control intensity 60.6).

Entry	Sample	Fluorescence Intensity at 335 nm
1	control	60.6
2	**3a**	52.5
3	**5a**	49.0
4	**3f**	42.7
5	**3e**	32.5
6	**3b**	45.5
7	**3g**	40.3
8	**3i**	39.1
9	**3d**	41.7
10	**3h**	34.4
11	**3c**	48.2
12	**3j**	32.7
13	**5g**	34.0
14	**5i**	24.3
15	**5h**	22.0

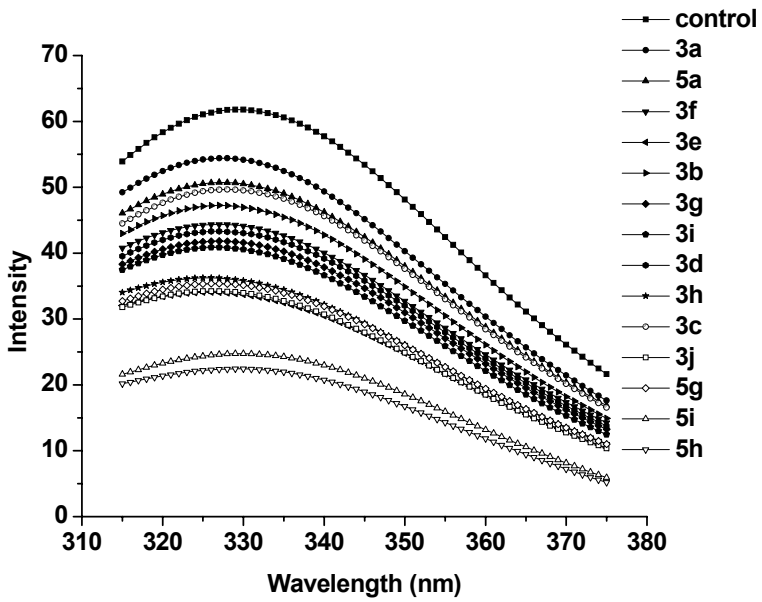


Figure S3. Decrease in intrinsic tryptophan fluorescence by MBH adducts **3** and **5** (control intensity 60.6).

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