Experimental Data and Optimization Tables
For

Hydroxyalkylation of Conjugated Nitroalkenes with Activated Non-enolizable Carbonyl Compounds

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Table S1. The MBH reaction of *p*-methoxynitrostyrene **1a** with ethyl glyoxylate **2a**^a in THF at room temperature in the presence of 100 mol % of various catalysts.

entry	catalyst (100 mol %)	time	yield (%) ^b
1	DABCO	3 d	30 ^c
2	DBU	3 d	^d
3	DMAP	2 h	70
4	Imidazole	16 h	68
5	HMTA	3 d	^e
6	Bu ₃ P	3 d	^e

^a 4 equiv as a 50 % solution in toluene; ^b Isolated yield of **3a** after column chromatography; ^c reaction incomplete; ^d complex mixture; ^e traces

Table S2. The MBH reaction of *p*-methoxynitrostyrene **1a** with ethyl glyoxylate **2a**^a in THF at room temperature in the presence of varying amounts of DMAP or imidazole.

entry	catalyst (mol %)	DMAP (a)		imidazole (b)	
		time	yield (%) ^b	time	yield (%) ^b
1	100	2 h	70	16 h	68
2	50	5 h	70	29 h	58
3	40	7 h	78	48 h	40
4	30	12 h	60	-	-
5	20	15 h	54	-	-
6	10	2 d	33 ^c	-	-
7	150	-	-	13 h	68

^a 4 equiv as a 50 % solution in toluene; ^b Isolated yield of **3a** after column chromatography; ^c reaction incomplete

Table S3. The effect of *p*-methoxynitrostyrene **1a**/ethyl glyoxylate **2a**^a ratio on the DMAP (40 mol %) and imidazole (100 mol %) catalyzed MBH reaction in THF.

entry	2a (equiv)	DMAP (a)		imidazole (b)	
		time	yield (%) ^b	time	yield (%) ^b
1	1	2 d	20 ^c	34 h	25 ^b
2	2	2 d	28 ^c	29 h	34
3	3	12 h	65	26 h	52
4	4	7 h	78	16 h	68
5	5	6 h	66	15 h	45

^a As a 50 % solution in toluene; ^b Isolated yield of **3a** after column chromatography; ^c reaction incomplete

Table S4. The solvent effect on the DMAP (40 mol %) or imidazole (100 mol %) catalyzed MBH reaction of *p*-methoxynitrostyrene **1a** with ethyl glyoxylate **2a**^a at room temperature.

entry	solvent	DMAP (a)		imidazole (b)	
		time	yield (%) ^b	time	yield (%) ^b
1	THF	7 h	78	16 h	68
2	DMF	1 h	73	40 h	58
3	1,4-Dioxan	5 h	63	34 h	60
4	MeOH	24 h	48 ^c	19 h	66
5	MeCN	10 min	81	15 h	58
6	CH ₃ COCH ₃	1½ h	53	1¾ h	52
7	CHCl₃	25 min	60	2¾ h	73
8	CH ₂ Cl ₂	30 min	46	3 h	60
9	Toluene	35 min	55	3.5 h	60

^a 4 equiv as a 50 % solution in toluene for both DMAP and imidazole catalyzed reactions; ^b Isolated yield of **3a** after column chromatography; ^c reaction incomplete

Table S5. The MBH reaction of *p*-methoxynitrostyrene **1a** with ethyl glyoxylate **2a**^a in the presence of varying amounts of DMAP in CH₃CN and imidazole in CHCl₃ at room temperature.

entry	catalyst (mol %)	DMAP		imidazole	
		time	yield (%) ^b	time	yield (%) ^b
1	10	90 min	51	5 d	10
2	20	10 min	55	5 d	25
3	30	10 min	62	5 d	30
4	40	10 min	81	24 h	40
5	50	10 min	63	8 h	55
6	100	-	-	2¾ h	73

^a 4 equiv as a 50 % solution in toluene for both DMAP and imidazole catalyzed reactions (see Table S2); ^b Isolated yield of **3a** after column chromatography

Table S6. The effect of *p*-methoxynitrostyrene **1a**/ethyl glyoxylate **2a**^a ratio on the MBH reaction catalyzed by DMAP (40 mol %) in CH₃CN at room temperature.

entry	2a (equiv)	DMAP		imidazole	
		time	yield (%) ^b	time	yield (%) ^b
1	2	25 min	63	34 h	50
2	3	10 min	69	5 h	65
3	4	10 min	81	2 ¾	73
4	5	10 min	80	2 ½	70

^a As a 50 % solution in toluene

^b 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 (^1H and ^{13}C) were recorded on an AMX-400 or VXR-300S spectrometer with TMS as the internal standard. ^{19}F NMR spectra with CFCl_3 as internal standard and ^1H - ^1H NOESY spectra were recorded on an AMX-400 NMR spectrometer. 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). All the nitroalkenes were prepared in the laboratory by the standard nitroaldol (Henry) reaction.¹

General experimental procedures

Procedure A

To a stirred solution of nitroalkene **1** (0.5 mmol) in MeCN (1 ml), was added DMAP² (25 mg, 40 mol % or 62.5 mg, 100 mol %) followed by activated carbonyl compound **2** (4 equiv) 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 (5 ml) and the aqueous layer was extracted with ethyl acetate (3×5 ml), the combined organic layers were washed with brine (10 ml), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography by eluting with EtOAc:hexane (gradient elution).

Procedure B

To a stirred solution of nitroalkene **1** (0.5 mmol) in dry CHCl_3 or THF (1 ml), was added imidazole³ (34 mg, 100 mol %) followed by activated carbonyl compound **2** 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 (5 ml) and the aqueous layer was extracted with ethyl acetate (3×5 ml), the combined organic layers were washed with brine (10 ml), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography by eluting with EtOAc: hexane (gradient elution).

(*E*)-Ethyl 2-hydroxy-4-(4-methoxyphenyl)-3-nitrobut-3-enoate (**3a**)

Bright yellow solid; Yield 81 % (Method A), 68 % (Method B); mp. 68 °C; IR (KBr, cm^{-1}) 3461 (br s), 2926 (w), 1765 (m), 1642 (m), 1602 (s), 1511 (s), 1310 (m), 1257 (s), 1179 (m); ^1H NMR (CDCl_3) δ 1.26 (t, J = 6.9 Hz, 3H), 3.70 (br s, 1H), 3.87 (s, 3H), 4.30 (ABqq, J = 10.8, 7.2 Hz, 2H), 5.24 (s, 1H), 7.00 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 8.3 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 55.4, 62.8, 66.0, 114.8, 123.0, 132.1, 139.4, 145.9, 162.2, 170.6; MS (ESI) m/e (rel. intensity) 304 (MNa^+ , 30), 218 (5), 177 (100); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_6\text{Na}$ (MNa^+) 304.0797, found 304.0833.

(E)-Ethyl 2-hydroxy-4-(2,4-dimethoxyphenyl)-3-nitrobut-3-enoate (3b)

Bright yellow solid; Yield 95 % (Method A), 70 % (Method B); mp. 130 °C; IR (KBr, cm^{-1}) 3445 (br m), 2980 (w), 2939 (w), 1751 (m), 1605 (s), 1500 (m), 1267 (s), 1101 (w); ^1H NMR (CDCl_3) δ 1.26 (t, $J = 7.3$ Hz, 3H), 3.65 (br s, 1H), 3.87 (s, 3H), 3.89 (s, 3H), 4.29 (ABqq, $J = 10.6, 7.3$ Hz, 2H), 5.21 (s, 1H), 6.50 (d, $J = 2.3$ Hz, 1H), 6.57 (dd, $J = 8.7, 2.3$ Hz, 1H), 7.54 (d, $J = 8.7$ Hz, 1H), 8.56 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.8, 55.5, 55.6, 62.6, 66.2, 98.3, 105.6, 112.7, 131.5, 135.7, 145.3, 160.4, 164.2, 170.8; MS (ESI) m/e (rel. intensity) 334 (MNa^+ , 20), 248 (100); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_7\text{Na}$ (MNa^+) 334.0903, found 334.0911.

(E)-Ethyl 2-hydroxy-4-(2,5-dimethoxyphenyl)-3-nitrobut-3-enoate (3c)

Bright yellow solid; Yield 99 % (Method A), 71 % (Method B); mp. 145 °C; IR (KBr, cm^{-1}) 3492 (br s), 2979 (w), 2937 (w), 1757 (s), 1639 (w), 1516 (m), 1338 (m), 1295 (s), 1070 (m); ^1H NMR (CDCl_3) δ 1.27 (t, $J = 7.0$ Hz, 3H), 3.64 (d, $J = 6.0$ Hz, 1H), 3.79 (s, 3H), 3.86 (s, 3H), 4.30 (ABqq, $J = 10.8, 7.3$ Hz, 2H), 5.25 (d, $J = 6.0$ Hz, 1H), 6.89 (d, $J = 9.2$ Hz, 1H), 7.02 (dd, $J = 9.2, 3.1$ Hz, 1H), 7.15 (d, $J = 3.1$ Hz, 1H), 8.51 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 55.7, 56.0, 62.8, 66.1, 112.0, 115.2, 118.4, 120.3, 135.8, 147.3, 152.9, 153.5, 170.6; MS (ESI) m/e (rel. intensity) 334 (MNa^+ , 25), 248 (10), 220 (45), 177 (100), 159 (45); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_7\text{Na}$ (MNa^+) 334.0903, found 334.0906.

(E)-Ethyl 4-(4-dimethylamino)phenyl)-2-hydroxy-3-nitrobut-3-enoate (3d)

Bright red solid; Yield 98 % (Method A), 80 % (Method B); mp. 151 °C; IR (KBr, cm^{-1}) 3458 (br s), 2923 (w), 1746 (m), 1596 (s), 1533 (m), 1483 (m), 1376 (w), 1289 (m); ^1H NMR (CDCl_3) δ 1.24 (t, $J = 7.1$ Hz, 3H), 3.08 (s, 6H), 3.75 (br s, 1H), 4.27 (ABqq, $J = 11.2, 10.0$ Hz, 2H), 5.31 (s, 1H), 6.74 (d, $J = 9.0$ Hz, 2H), 7.52 (d, $J = 9.0$ Hz, 2H), 8.30 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.8, 39.7, 62.3, 66.3, 111.8, 117.5, 132.8, 140.7, 142.5, 152.5, 170.9; MS (ESI) m/e (rel. intensity) 317

(MNa⁺, 15), 295 (100), 231 (20), 177 (5), 159 (20); HRMS (ESI) calcd for C₁₄H₁₈N₂O₅Na (MNa⁺) 317.1113, found 317.1112. Selected X-ray crystallographic data for **3d**. C₁₄H₁₈N₂O₅, M = 294.30, Monoclinic, P 2₁/c, a = 6.0200(7) Å, b = 15.0800(13) Å, c = 16.3710(11) Å, α = 90, β = 92.672(3), γ = 90, V = 1484.6(2) Å³, Z = 4, D_{calc} = 1.317 g cm⁻³, μ = 0.101 mm⁻¹, 2866 reflections measured, R₁ = 0.1566, R_w = 0.1383.

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

(E)-Ethyl 4-(benzo[d][1,3]dioxol-6-yl)- 2-hydroxy-3-nitrobut-3-enoate (3e)

Bright yellow liquid; Yield 65 % (Method A), 67 % (Method B); mp. 90 °C; IR (film, cm⁻¹) 3513 (br w), 3020 (s), 1748 (s), 1527 (m), 1490 (w), 1448 (m), 1334 (m), 1216 (s), 1041 (m); ¹H NMR (CDCl₃) δ 1.26 (t, *J* = 7.0 Hz, 3H), 4.29 (ABqq, *J* = 10.8, 7.3 Hz, 2H), 5.24 (s, 1H), 6.06 (s, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 1.8 Hz, 1H), 7.13 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.24 (s, 1H); ¹³C NMR (CDCl₃) δ 13.8, 62.7, 65.8, 101.9, 109.0, 109.4, 124.4, 126.0, 139.3, 146.2, 148.4, 150.4, 170.4; MS (ESI) *m/e* (rel. intensity) 318 (MNa⁺, 35), 232 (85), 188 (70), 158 (55), 141 (50), 124 (100); HRMS (ESI) calcd for C₁₃H₁₃NO₇Na (MNa⁺) 318.0590, found 318.0584.

(E)-Ethyl 4-(4-chlorophenyl)- 2-hydroxy-3-nitrobut-3-enoate (3f)

Light yellow solid; Yield 45 % (Method A), 43 % (Method B), mp. 102 °C; IR (KBr, cm⁻¹) 3473 (br s), 2925 (m), 1768 (s), 1651 (w), 1589 (w), 1516 (m), 1338 (m); ¹H NMR (CDCl₃) δ 1.26 (t, *J*

= 7.0 Hz, 3H), 3.76 (d, J = 5.2 Hz, 1H), 4.30 (ABqq, J = 10.7, 7.0 Hz, 2H), 5.15 (d, J = 5.2 Hz, 1H), 7.49 (ABq, J = 8.2 Hz, 4H), 8.27 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 63.1, 65.7, 129.2, 129.6, 131.1, 137.5, 137.9, 148.1, 170.2; MS (ESI) m/e (rel. intensity) 308 (MNa^+ , 100), 194 (30), 158 (30), 141 (80), 124 (95); HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{12}\text{NO}_5\text{ClNa}$ (MNa^+) 308.0302, found 308.0289.

(*E*)-Ethyl 2-hydroxy-3-nitro-4-phenylbut-3-enoate (3g)

Light yellow viscous liquid; Yield 33 % (Method A), 31 (Method B); IR (film, cm^{-1}) 3476 (br s), 2984 (w), 1749 (s), 1649 (m), 1558 (w), 1529 (s), 1449 (w), 1338 (m), 1105 (s); ^1H NMR (CDCl_3) δ 1.27 (t, J = 7.0 Hz, 3H), 3.70 (d, J = 5.0 Hz, 1H), 4.30 (ABqq, J = 10.7, 7.3 Hz, 2H), 5.23 (d, J = 5.0 Hz, 1H), 7.53 (m, 5H), 8.33 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 62.9, 65.8, 129.2, 129.8, 130.8, 131.0, 139.3, 147.7, 170.5; MS (ESI) m/e (rel. intensity) 274 (MNa^+ , 100), 214 (18), 166 (7), 159 (48), 158 (35), 141 (18); HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_5\text{Na}$ (MNa^+) 274.0691, found 274.0700.

(*E*)-Ethyl 4-(2-(allyloxy)phenyl)-2-hydroxy-3-nitrobut-3-enoate (3h)

Yellow solid; Yield 69 % (Method A), 62 % (Method B); mp. 53 °C; IR (film, cm^{-1}) 3475 (br w), 3020 (s), 1747 (s), 1649 (w), 1600 (w), 1527 (m), 1487 (w), 1337 (w), 1216 (s); ^1H NMR (CDCl_3) δ 1.27 (t, J = 7.0 Hz, 3H), 3.73 (br s, 1H), 4.25 (ABqq, J = 10.7, 7.0 Hz, 2H), 4.64 (d, J = 4.9 Hz, 2H), 5.24 (s, 1H), 5.33 (dABq, J = 10.5, 1.5 Hz, 1H), 5.43 (dABq, J = 17.2, 1.5 Hz, 1H), 6.02-6.14 (m, 1H), 6.94-7.08 (m, 2H), 7.42-7.58 (m, 2H), 8.5 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.8, 62.7, 66.0, 69.1, 112.1, 117.8, 120.1, 121.0, 130.1, 132.3, 132.8, 135.8, 147.1, 157.5, 170.6; MS (ESI) m/e (rel. intensity) 330 (MNa^+ , 100), 216 (6), 171 (4), 124 (7); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_6\text{Na}$ (MNa^+) 330.0954, found 330.0958.

(*E*)-Ethyl 2-hydroxy-3-nitro-4-(2-(prop-2-ynyloxy)phenyl)but-3-enoate (3i)

Pale yellow solid; Yield 52 % (Method A), 53 % (Method B); mp. 84 °C; IR (KBr, cm^{-1}) 3503 (br s), 3456 (br s), 3070 (w), 2976 (m), 2936 (w), 2118 (w), 1762 (s), 1649 (m), 1600 (m), 1527 (s), 1485 (w), 1341 (w), 1226 (w), 1107 (w); ^1H NMR (CDCl_3) δ 1.27 (t, $J = 7.0$ Hz, 3H), 2.57 (t, $J = 2.4$ Hz, 1H), 3.67 (br s, 1H), 4.30 (ABqq, $J = 10.8, 7.2$ Hz, 2H), 4.81 (d, $J = 2.4$ Hz, 2H), 5.20 (s, 1H), 7.08-7.27 (m, 2H), 7.48-7.54 (m, 2H), 8.5 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.8, 56.1, 62.7, 65.9, 76.3, 77.5, 112.4, 120.4, 121.7, 130.2, 132.7, 135.5, 147.3, 156.3, 170.5; MS (ESI) m/e (rel. intensity) 328 (MNa^+ , 100) 214 (5), 141 (6); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_6\text{Na}$ (MNa^+) 328.0797, found 328.0802.

(E)-Ethyl 4-(furan-2-yl)-2-hydroxy-3-nitrobut-3-enoate (3j)

Bright yellow solid; Yield 63 % (Method A), 65 % (Method B); mp. 50 °C; IR (KBr, cm^{-1}) 3482 (br s), 2928 (w), 1745 (s), 1643 (m), 1515 (w), 1470 (w), 1322 (s), 1223 (m); ^1H NMR (CDCl_3) δ 1.26 (t, $J = 7.2$ Hz, 3H), 3.75 (br s, 1H), 4.28 (ABqq, $J = 10.7, 7.3$ Hz, 2H), 6.01 (s, 1H), 6.64 (dd, $J = 3.4, 1.8$ Hz, 1H), 7.05 (d, $J = 3.4$ Hz, 1H), 7.71 (d, $J = 1.8$ Hz, 1H), 7.97 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.7, 62.4, 66.1, 113.3, 122.9, 124.1, 143.6, 146.1, 147.8, 170.6; MS (ESI) m/e (rel. intensity) 264 (MNa^+ , 100); HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_6\text{Na}$ (MNa^+) 264.0484, found 264.0487.

(E)-Ethyl 2-hydroxy-3-nitro-4-(thiophen-2-yl)but-3-enoate (3k)

Bright yellow liquid; Yield 64 % (Method A), 65 % (Method B); IR (film, cm^{-1}) 3513 (br m), 3020 (m), 1748 (s), 1639 (m), 1525 (m), 1421 (w), 1316 (m), 1216 (s), 1100 (m); ^1H NMR (CDCl_3) δ 1.26 (t, $J = 7.3$ Hz, 3H), 3.74 (br s, 1H), 4.30 (ABqq, $J = 10.7, 7.0$ Hz, 2H), 5.58 (s, 1H), 7.22 (dd, $J = 4.9, 3.6$ Hz, 1H), 7.57 (d, $J = 3.6$ Hz, 1H), 7.72 (d, $J = 4.9$ Hz, 1H), 8.39 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.7, 62.6, 65.9, 128.6, 131.8, 132.5, 133.5, 136.2, 144.2, 170.1; MS (ESI) m/e (rel. intensity) 280 (MNa^+ , 75), 194 (15), 168 (18), 150 (100); HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_5\text{SNa}$ (MNa^+) 280.0256, found 280.0243.

(E)-Ethyl 4-(furan-3-yl)-2-hydroxy-3-nitrobut-3-enoate (3l)

Light yellow liquid; Yield 60 % (Method A), 55 % (Method B); IR (film, cm^{-1}) 3508 (br m), 3020 (m), 1751 (s), 1655 (m), 1527 (m), 1333 (m), 1217 (m), 1168 (m), ^1H NMR (CDCl_3) δ 1.25 (t, $J = 7.2$ Hz, 3H), 3.70 (br s, 1H), 4.30 (ABqq, $J = 11.0, 7.3$ Hz, 2H), 5.33 (s, 1H), 6.71 (d, $J = 1.5$ Hz, 1H), 7.58 (d, $J = 0.7$ Hz, 1H), 7.93 (dd, $J = 1.5, 0.7$ Hz, 1H), 8.12 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 63.0, 65.9, 109.8, 117.6, 130.1, 145.3, 146.1, 147.1, 170.4; MS (ESI) m/e (rel. intensity) 264 (MNa^+ , 40), 198 (3), 178 (25), 141 (60), 124 (100), HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_6\text{Na}$ (MNa^+) 264.0484, found 264.0489.

(E)-Ethyl 2-hydroxy-3-nitro-4-(thiophen-2-yl)but-3-enoate (3m)

Bright yellow liquid; Yield 60 % (Method A), 76 % (Method B); IR (film, cm^{-1}) 3508 (br m), 3019 (m), 1745 (s), 1648 (w), 1528 (m), 1334 (m), 1216 (m), 1108 (m); ^1H NMR (CDCl_3) δ 1.26 (t, $J = 7.0$ Hz, 3H), 4.29 (ABqq, $J = 10.6, 6.9$ Hz, 2H), 5.35 (s, 1H), 7.34 (d, $J = 4.9$ Hz, 1H), 7.48 (dd, $J = 4.9, 2.1$ Hz, 1H), 7.80 (d, $J = 2.1$ Hz, 1H), 8.25 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.8, 62.8, 65.9, 127.7, 128.0, 131.3, 131.8, 133.1, 146.4, 170.4; MS (ESI) m/e (rel. intensity) 280 (MNa^+ , 100), 194 (3), 150 (50), 122 (15); HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_5\text{SNa}$ (MNa^+) 280.0256, found 280.0251.

(E)-Methyl 2-(trifluoromethyl)-2-hydroxy-4-(4-methoxyphenyl)-3-nitrobut-3-enoate (4c)

Bright yellow solid; Yield 70 %; mp. 75 °C; IR (KBr, cm^{-1}) 3512 (br s), 3012 (w), 1757 (s), 1656 (w), 1610 (m), 1531 (s), 1452 (w), 1433 (w), 1349 (m), 1298 (s), 1260 (s), 1182 (s), 1134 (s), 1105 (m), 1032 (m); ^1H NMR (acetone- d_6) δ 3.04 (br s, 1H), 3.84 (s, 3H), 3.95 (s, 3H), 7.00 (d, $J = 9.0$ Hz, 2H), 7.22 (s, 1H), 7.38 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (acetone- d_6) δ 54.8, 55.9, 77.9 (q, $J_{\text{C-F}} = 30.8$ Hz), 115.4, 123.3, 123.6 (q, $J_{\text{C-F}} = 284.5$ Hz), 129.2, 131.6, 142.8, 162.6, 166.8; ^{19}F NMR (acetone- d_6) δ -75.3 (CF_3); MS (ESI) m/e (rel. intensity) 358 (MNa^+ , 12), 272 (25), 252 (100), 189 (3), 143 (4); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{NO}_6\text{F}_3\text{Na}$ (MNa^+) 358.0514, found 358.0528.

(E)-Methyl 2-(trifluoromethyl)-2-hydroxy-4-(2,5-methoxyphenyl)-3-nitrobut-3-enoate (4d)

Light orange solid; Yield 71 %; mp. 78 °C; IR (KBr, cm^{-1}) 3452 (br, m), 2962 (m), 2843 (w), 1757 (s), 1544 (s), 1499 (m), 1372 (w), 1291 (s), 1234 (s); ^1H NMR (acetone- d_6) δ 3.73 (s, 3H), 3.79 (s, 3H), 3.95 (s, 3H), 6.80 (m, 1H), 7.02 (m, 2H), 7.42 (s, 1H); ^{13}C NMR (acetone- d_6) δ 54.8, 56.0, 56.6, 78.1 (q, $J_{\text{C-F}} = 28.9$ Hz), 113.5, 114.6, 117.8, 121.0, 123.6 (q, $J_{\text{C-F}} = 285.2$ Hz), 126.6, 145.5, 152.6, 154.5, 166.8; ^{19}F NMR (acetone- d_6) δ -74.8 (CF_3); MS (ESI) m/e (rel. intensity) 388 (MNa^+ , 5), 302 (100), 156 (4); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_7\text{F}_3\text{Na}$ (MNa^+) 388.0620, found 388.0626.

(E)-Methyl 4-(4-dimethylamino)phenyl)-2-(trifluoromethyl)-2-hydroxy-3-nitrobut-3-enoate (4e)

Bright red solid; Yield 80 %; mp 138 °C; IR (KBr, cm^{-1}) 3454 (m), 1766 (m), 1531 (m), 1437 (w), 1346 (w), 1287 (m), 1257 (m), 1133 (m); ^1H NMR (CDCl_3) δ 3.0 (s, 6H), 3.99 (s, 3H), 6.61 (d, $J = 9.2$ Hz, 2H), 6.93 (s, 1H), 7.28 (d, $J = 9.2$ Hz, 2H); ^{13}C NMR (acetone- d_6) δ 40.0, 54.4, 77.9 (q, $J_{\text{C-F}} = 29.7$ Hz), 112.4, 117.6, 123.7 (q, $J_{\text{C-F}} = 285.2$ Hz), 131.0, 132.4, 139.1, 153.2, 167.1; ^{19}F NMR (acetone- d_6) δ 71.0 (CF_3); MS (ESI) m/e (rel. intensity) 349 (MH^+ , 60), 273 (3), 197 (2), 156 (100); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_5\text{F}_3$ (MH^+), 349.1011, 349.1004.

(E)-Methyl 2-(trifluoromethyl)-4-(furan-3-yl)-2-hydroxy-3-nitrobut-3-enoate (4f)

Bright yellow viscous liquid; Yield 40 %; IR (KBr, cm^{-1}) 3465 (w), 3055 (m), 1757 (m), 1702 (m), 1540 (m), 1422 (w), 1265 (s); ^1H NMR (acetone- d_6) δ 3.94 (s, 3H), 4.57 (br s, 1H), 6.50 (unresolved m, 1H), 6.97 (unresolved m, 1H), 7.46, (unresolved m, 1H), 7.85 (s, 1H); ^{13}C NMR (acetone- d_6) δ 54.6, 77.9 (q, $J_{\text{C-F}} = 30.5$ Hz), 109.1, 118.1, 122.1, 123.5 (q, $J_{\text{C-F}} = 285.2$ Hz), 142.3, 146.2, 149.3, 166.6; ^{19}F NMR (acetone- d_6) δ -75.3 (CF_3); MS (ESI) m/e (rel. intensity) 318 (MNa^+ , 98), 268 (100), 208 (25), 149 (15); HRMS (ESI) calcd for $\text{C}_{10}\text{H}_8\text{NO}_6\text{F}_3\text{Na}$ (MNa^+) 318.0201, found 318.0189.

(E)-3-hydroxy-5-(4-methoxyphenyl)-4-nitropent-4-en-2-one (5b)

Viscous bright yellow liquid; Yield 26 % (Method A), 20 % (Method B); IR (film, cm^{-1}) 3464 (br w), 3055 (m), 2987 (w), 1730 (w), 1604 (w), 1422 (m), 1265 (s); ^1H NMR (CDCl_3) δ 2.16 (s, 3H), 3.88 (s, 3H), 4.29 (d, $J = 4.1$ Hz, 1H), 5.05 (d, $J = 4.1$ Hz, 1H), 7.01 (d, $J = 8.6$ Hz, 2H), 7.59 (d, $J = 8.6$ Hz, 2H), 8.38 (s, 1H); ^{13}C NMR (CDCl_3) δ 24.7, 55.5, 72.8, 115, 122.9, 132.4, 141.0, 145.9, 162.5, 202.6; MS (ESI) m/e (rel. intensity) 274 (MNa^+ , 18), 202 (15), 188 (42), 145 (5); HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_5\text{Na}$ (MNa^+) 274.0691, found 274.0680.

(E)-3-hydroxy-5-(2,4-dimethoxyphenyl)-4-nitropent-4-en-2-one (5c)

Yellow solid; Yield 32 % (Method A), 30 % (Method B); mp. 119-120 °C IR (film, cm^{-1}) 3467 (br s), 2941 (w), 1725 (s), 1633 (m), 1611 (s), 1503 (m), 1454 (m), 1302 (m), 1272 (s), 1212 (m); ^1H NMR (CDCl_3) δ 2.11 (s, 3H), 3.87 (s, 3H), 3.90 (s, 3H), 4.27 (d, $J = 3.7$ Hz, 1H), 5.0 (d, $J = 3.7$ Hz, 1H), 6.51 (d, $J = 2.4$ Hz, 1H), 6.59 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.57 (d, $J = 8.8$ Hz, 1H), 8.6 (s, 1H); ^{13}C NMR (CDCl_3) δ 24.6, 55.6, 55.7, 73.1, 98.4, 105.7, 112.7, 131.7, 137.4, 145.4, 160.5, 164.5, 202.9; MS (ESI) m/e (rel. intensity) 304 (MNa^+ , 45), 218 (100), 175 (48); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_6\text{Na}$ (MNa^+) 304.0797, found 304.0797.

(E)-3-hydroxy-5-(2,5-dimethoxyphenyl)-4-nitropent-4-en-2-one (5d)

Yellowish red solid; Yield 30 % (Method A), 28 % (Method B); mp. 80 °C; IR (film, cm^{-1}) 3471 (br s), 2923 (m), 2847 (w), 1721 (s), 1643 (m), 1521 (m), 1497 (s), 1335 (m), 1299 (s); ^1H NMR (CDCl_3) δ 2.17 (s, 3H), 3.79 (s, 3H), 3.87 (s, 3H), 4.22 (d, $J = 4.1$ Hz, 1H), 5.02 (d, $J = 4.1$ Hz, 1H), 6.91 (d, $J = 9.1$ Hz, 1H), 7.03 (dd, $J = 9.1, 2.7$ Hz, 1H), 7.13 (d, $J = 2.7$ Hz, 1H), 8.5 (s, 1H); ^{13}C NMR (CDCl_3) δ 24.6, 55.8, 56.1, 72.9, 112.1, 114.9, 118.7, 120.3, 137.4, 147.7, 152.8, 153.6, 202.7; MS (ESI) m/e (rel. intensity) 304 (MNa^+ , 75), 218 (70), 214 (5), 189 (30), 159 (25); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_6\text{Na}$ (MNa^+) 304.0797, found 304.0790.

(E)-5-(furan-2-yl)-3-hydroxy-4-nitropent-4-en-2-one (5e)

Light yellow viscous liquid; Yield 33 % (Method A), 25 % (Method B); IR (film, cm^{-1}) 3470 (br, w), 3055 (m), 1729 (m), 1649 (m), 1520 (m), 1421 (m), 1266 (s); ^1H NMR (CDCl_3) δ 2.25 (s, 3H), 5.88 (s, 1H), 6.67 (dd, $J = 3.5, 1.8$ Hz, 1H), 7.07 (d, $J = 3.5$ Hz, 1H), 7.73 (d, $J = 1.8$ Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (CDCl_3) δ 24.7, 72.9, 113.6, 123.4, 124.5, 143.8, 146.2, 148.0, 203.2; MS (ESI) m/e (rel. intensity) 234 (MNa^+ , 30), 148 (100); HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{NO}_5\text{Na}$ (MNa^+) 234.0378, found 234.0374.

(E)-5-(furan-3-yl)-3-hydroxy-4-nitropent-4-en-2-one (5f)

Light yellow viscous liquid; Yield: 35 % (method A), 36 % (Method B); IR (film, cm^{-1}) 3451 (br m), 3054 (m), 2987 (m), 1729 (m), 1653 (m), 1525 (m), 1421 (m), 1337 (w), 1266 (s), 1169 (m), 1109 (w); ^1H NMR (CDCl_3) δ 2.20 (s, 3H), 4.27 (br s, 1H), 5.16 (s, 1H), 6.72 (d, $J = 1.5, 0.6$ Hz, 1H), 7.59 (dd, $J = 1.5, 0.9$ Hz, 1H), 7.95 (dd, $J = 0.9, 0.6$ Hz, 1H), 8.2 (s, 1H); ^{13}C NMR (CDCl_3) δ 24.6, 72.6, 109.4, 117.6, 131.2, 145.6, 146.1, 147.8, 202.5; MS (ESI) m/e (rel. intensity) 250 (MK^+ , 35), 222 (35), 176 (5), 148 (100); HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{NO}_5\text{K}$ (MK^+) 250.0118, found 250.0109.

2-Hydroxy-2-[(Z)-2-(4-methoxyphenyl)-1-nitrovinyl]-2H-indene-1,3-dione (6c) and 2-hydroxy-2-[(E)-2-(4-methoxyphenyl)-1-nitrovinyl]-2H-indene-1,3-dione (7c)

Yellow solid; Yield 55 % (inseparable mixture of isomers, 56:44 ratio, Method a), 61 % (inseparable mixture of isomers, 65:35 ratio, Method b); mp 162 $^{\circ}\text{C}$; IR (KBr, cm^{-1}) 3415 (br s), 3125 (br m), 1716 (s), 1637 (w), 1603 (m), 1511 (m), 1400 (s), 1308 (m), 1250 (m), 1181 (m); ^1H NMR (acetone d_6) δ 3.00 (br s expected, presumably overlapping with H_2O in solvent peak, 2H, Major + minor), 3.88 (s, 3H, minor isomer), 3.89 (s, 3H, Major isomer), 6.99 (d, $J = 9.1$ Hz, 2H, minor), 7.03 (d, $J = 9.1$ Hz, 2H, Major), 7.62 (d, $J = 9.1$ Hz, 2H, minor), 7.65 (d, $J = 9.1$ Hz, 2H, Major), (8.00 (s, 1H, Major), 8.02 (s, 1H, minor), 8.12-8.13 (m, 8H, Major + minor); ^{13}C NMR (acetone d_6) δ 55.8, 55.9, 76.9, 77.0, 78.1, 78.2, 114.1, 115.0, 123.2, 124.0, 125.1, 125.3, 133.6, 135.4, 136.3, 137.5, 137.6, 140.7, 141.2, 143.5, 144.2, 145.1, 162.8, 163.3, 196.0, 196.1 (CHOH carbon 76.9, 77.0, 78.1, 78.2 is unusually split); MS (ESI) m/e (rel. intensity) 362 (MNa^+ , 100),

340 (28), 322 (26), 276 (98); HRMS (ESI) calcd for $C_{18}H_{13}NO_6Na$ (MNa^+) 362.0641, found 362.0653.

2-Hydroxy-2-[(Z)-1-nitro-2-phenylvinyl]-2H-indene-1,3-dione (6d) and 2hydroxy-2-[(E)-1-nitro-2-phenylvinyl]-2H-indene-1,3-dione (7d)

Yellow solid; Yield 44 % (inseparable mixture of isomers, 64:36 ratio, Method a), 53 % (inseparable mixture of isomers, 72:28 ratio, Method b); mp 184 °C; IR (KBr, cm^{-1}) 3414 (br w), 3133 (br s), 1707 (s), 1643 (w), 1526 (m), 1400 (s), 1326 (m); 1H NMR (acetone d_6) δ 3.00 (br s expected, presumably overlapping with H_2O in solvent peak, 2H, Major + minor), 7.43-7.51 (m, 5H), 7.51-7.53 (m, 5H), 7.94 (s, 1H), 7.95 (s, 1H), 8.12-8.16 (m, 8H). ^{13}C NMR (acetone d_6) δ 76.9, 78.3, 125.2, 125.4, 128.5, 129.5, 130.1, 131.0, 131.1, 131.5, 132.2, 132.3, 136.1, 137.6, 137.8, 140.7, 141.3, 144.1, 146.3, 147.1, 195.7 ($\times 2$); MS (ESI) m/e (rel. intensity) 332 (MNa^+ , 100), 263 (7), 246 (24), 245 (8); HRMS (ESI) calcd for $C_{17}H_{11}NO_5Na$ (MNa^+) 332.0535, found 332.0539.

2-[(Z)-2-(Furan-2-yl)-1-nitrovinyl]-2-hydroxy-2H-indene-1,3-dione (6e)

Yellow solid; Yield 79 % (single isomer, Method a), 74 % (single isomer, Method b); mp 178 °C; IR (KBr, cm^{-1}) 3408 (br, s), 2925 (w), 1718 (s), 1642 (m), 1508 (m), 1461 (w), 1398 (w), 1335 (w), 1307 (w); 1H NMR (acetone d_6) δ 2.50 (br s, 1H), 6.85 (ddd, $J = 3.7, 1.7, 0.6$ Hz, 1H), 7.71 (s, 1H), 7.88 (dd, $J = 3.7, 0.6$ Hz, 1H), 8.02 (dd, $J = 1.7, 0.6$ Hz, 1H), 8.10 (s, 1H), 8.11 (s, 4H); ^{13}C NMR (acetone d_6) δ 76.5, 115.0, 123.7, 125.0, 125.1, 137.5, 140.3, 141.1, 148.6, 149.3, 196.1; MS (ESI) m/e (rel. intensity) 322 (MNa^+ , 79), 319 (4), 282 (21), 254 (12), 236 (100), 214 (5), 158 (11), 141 (8), 73 (53); HRMS (ESI) calcd for $C_{15}H_9NO_6Na$ (MNa^+) 322.0328, found 322.0328.

2-[(Z)-2-(Thien-2-yl)-1-nitrovinyl]-2-hydroxy-2H-indene-1,3-dione (6f)

Yellow solid; Yield 73 % (single isomer, Method a), 71 % (single isomer, Method b); mp 190-192 °C; IR (KBr, cm^{-1}) 3403 (br s), 3117 (br s), 1714 (s), 1637 (m), 1497 (m), 1401 (s), 1295 (s); ^1H NMR (acetone d_6) δ 2.83 (s, 1H), 7.37 (dd, $J = 5.1, 3.8$ Hz, 1H), 8.05 (d, $J = 3.8$ Hz, 1H), 8.10 (m, 4H), 8.14 (d, $J = 5.1$ Hz, 1H), 8.18 (s, 1H); ^{13}C NMR (acetone d_6) δ 76.5, 125.0, 128.9, 133.0, 134.9, 137.5, 138.6, 141.0, 143.3, 196.3 (125.0 or 137.5 is presumably for 2C); MS (ESI) m/e (rel. intensity) 338 (MNa^+ , 63), 270 (7), 252 (100), 158 (3), 141 (12), 77 (12); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_9\text{NO}_5\text{NaS}$ (MNa^+) 338.0099, found 338.0100.

2-[(Z)-2-(Furan-3-yl)-1-nitrovinyl]-2-hydroxy-2H-indene-1,3-dione (6g) and 2-[(E)-2-(furan-3-yl)-1-nitrovinyl]-2-hydroxy-2H-indene-1,3-dione (7g)

Total Yield 68 % (mixture of isomers, 59:41 ratio, Method a), 70 % (mixture of isomers, 74:26 ratio, Method b); The two isomers **6g** and **7g** were separated by column chromatography.

6g: Yellow solid (R_f 0.37, 25 % ethyl acetate/ pet. ether); mp 155 °C; IR (KBr, cm^{-1}) 3404 (br s), 1708 (s), 1649 (s), 1587 (m), 1495 (s), 1315 (s), 1253 (m), 1165 (s); ^1H NMR (acetone d_6) δ 2.60 (br s, 1H), 7.02, 7.78, 8.55 (AMX, $J = 1.3, 0.8, 0.5$ Hz, 3H), 7.70 (s, 1H), 8.10-8.12 (m, 4H); ^{13}C NMR (acetone d_6) δ 76.5, 76.6, 112.7, 119.5, 125.0, 129.0, 137.5, 141.1, 142.7, 145.4, 151.8, 196.1; MS (ESI) m/e (rel. intensity) 322 (MNa^+ , 100), 254 (75); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_9\text{NO}_6\text{Na}$ (MNa^+) 322.0328, found 322.0338; Selected X-ray crystallographic data for **6g**, $\text{C}_{15}\text{H}_9\text{NO}_6$, $M = 299.23$, monoclinic, $P 2_1/m$, $a = 7.4374(4)$, $b = 8.0243(6)$, $c = 11.3999(15)$, $\alpha = 90.00$, $\beta = 92.670(7)$, $\gamma = 90.00$, $V = 679.61(11) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.462 \text{ g cm}^{-3}$, $\mu = 0.116 \text{ mm}^{-1}$, 1340 reflections measured, $R_1 = 0.0412$, $R_w = 0.1034$.

Figure S2. X-Ray crystal structure of **6g**

7g: Light yellow solid (R_f 0.40, 25 % ethyl acetate/ pet. ether); mp 152-153 °C; IR (KBr, cm^{-1}) 3370 (br s), 1710 (s), 1644 (m), 1516 (s), 1324 (m), 1258 (m), 1165 (s); ^1H NMR (acetone d_6) δ 2.70 (br s, 1H), 7.22 (d, J = 1.5 Hz, 1H), 7.68 (dd, J = 1.5, 0.8 Hz, 1H), 8.10-8.13 (m, 4H), 8.38 (d, J = 0.8 Hz, 1H), 8.50 (s, 1H); ^{13}C NMR (acetone d_6) δ 77.6, 114.3, 118.7, 125.3, 134.5, 137.6, 140.8, 145.2, 145.4, 152.0, 195.7; MS (ESI) m/e (rel. intensity) 322 (MNa^+ , 100), 284 (10), 254 (57), 158 (8), 73 (43); HRMS calcd for $\text{C}_{15}\text{H}_9\text{NO}_6\text{Na}$ (MNa^+) 322.0328, found 322.0324.

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