This journal is © The Royal Society of Chemistry 2010

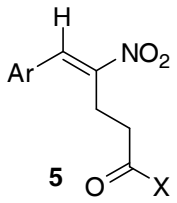
Electronic Supplementary Information for **Rauhut-Currier type homo- and heterocouplings involving nitroalkenes and nitrodienes**

Pramod Shanbhag, Pradeep R. Nareddy, Mamta Dadwal, Irishi N. N. Namboothiri*

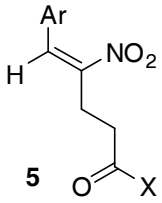
Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076, India

This journal is © The Royal Society of Chemistry 2010

Table S1. ^{1}H NMR chemical shift of H β to NO_2 group in RC adducts **5** (see Table 1, main text).



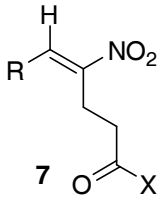
(*E*)



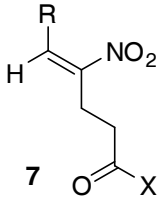
(*Z*)

Entry	**5**, Ar	X	β-H (*E*)	β-H (*Z*)
1	**5a,** 2-furyl	Me	7.85	-
2	**5b,** 2-thienyl	Me	8.30	-
3	**5c,** 3-furyl	Me	7.94	-
4	**5d,** 3-thienyl	Me	8.08	-
5	**5e,** Ph	Me	8.10	-
6	**5f,** 4-OMe-Ph	Me	8.07	-
7	**5g,** 4-Cl-Ph	Me	8.02	-
8	**5h,** 3,4-OCH_2O-Ph	Me	8.05	-
9	**5i,** 3,4-$(OMe)_2$Ph	Me	8.05	-
10	**5j,** 4-CF_3-Ph	Me	8.07	-
11	**5a,** 2-furyl	OEt	7.88	-
12	**5e,** Ph	OEt	8.11	-
13	**5k,** 3,4-(OCH_2O)Ph	OEt	8.04	-
14	**5l,** 3,4-$(OMe)_2$Ph	OEt	8.00	-

Table S2. ^{1}H NMR chemical shift of H β to NO_2 group in RC adducts **7** (see Table 2, main text).



(*E*)

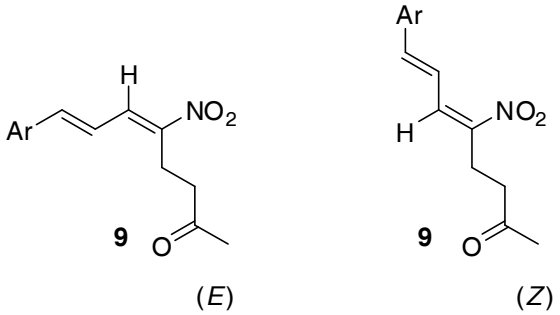


(*Z*)

Entry	**6**, R	X	β-H (*E*)	β-H (*Z*)
1	**7a,** *i*-propyl	Me	6.95	-
2	**7b,** *n*-butyl	Me	7.16	-
3	**7c,** *n*-hexyl	Me	7.15	-
4	**7d,** cyclohexyl	Me	6.95	-
5	**7e,** norbornenyl	Me	7.12	6.71
6	**7f,** *n*-butyl	OEt	7.16	-
7	**7g,** *n*-hexyl	OEt	7.19	-
8	**7h,** cyclohexyl	OEt	7.01	-

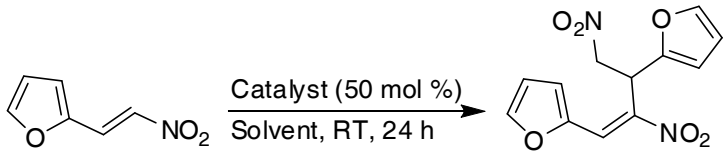
This journal is © The Royal Society of Chemistry 2010

Table S3. ^{1}H NMR chemical shift of H β to NO_2 group in RC adducts **9** (see Table 3, main text).



Entry	**6**, Ar	β-H (*E*)	β-H (*Z*)
1	**9a,** Ph	7.78	-
2	**9b,** 2-OMe-Ph	7.81	-
3	**9c,** 2-NO_2-Ph	7.79	-
4	**9d,** 2-furyl	7.70	-

Table S4. The Rauhut-Currier homo-dimerization of nitroalkene **3a** in the presence of various nucleophilic Lewis bases (50 mol %) as catalysts.[a]

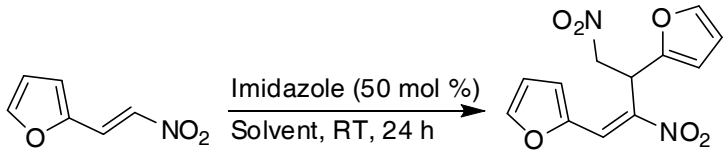


3a **10a**

Entry	Catalyst	Yield of **10a** (%)[a]	Recovered **3a** (%)[b]
1	**Imidazole**	**28**	**18**
2	DMAP	-	< 5
3	DBU	-	>60
4	DABCO	-	>60
5	Triethylamine	-	>60
6	Hünig's base	-	>60
7	Pyridine	-	>60

[a]Isolated yield after purification by silica gel column chromatography.
[b]Trimerized product (see ref 29, main text) and polymeric material were also isolated.

Table S5. The Rauhut-Currier homo-dimerization of nitroalkene **3a** in the presence of imidazole (50 mol %) in different solvents.[a]

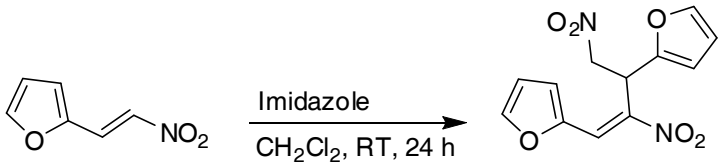


3a **10a**

Entry	Solvent	Yield of **10a** (%)[a]	Recovered **3a** (%)[a]
1	THF	38	40
2	1,4-dioxan	11	40
3	Ether	< 5	50
4	Acetone	None	10
5	DMF	7	20
6	DMSO	< 5	>60
7	Acetonitrile	< 5	>60
8	Chloroform	12	>60
9	**CH_2Cl_2**	**58**	**20**
10	CCl_4	15	40

[a]Isolated yield after purification by silica gel column chromatography.

Table S6. The Rauhut-Currier homo-dimerization of nitroalkene **3a** in the presence of varying amounts of imidazole.[a]



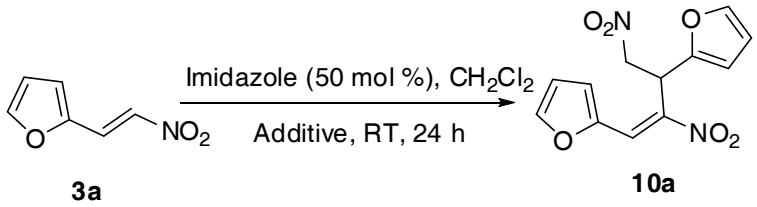
3a **10a**

Entry	Imidazole (mol %	Yield of **10a** (%)	Recovered **3a** (%)
1	25	17	72
2	**50**	**58**	**20**
3	75	30	22
4	100	28	18

[a]Isolated yield after purification by silica gel column chromatography.

This journal is © The Royal Society of Chemistry 2010

Table S7. The Rauhut-Currier homo-dimerization of nitroalkene **3a** in the presence of imidazole (50 mol %) and various co-catalysts.[a]

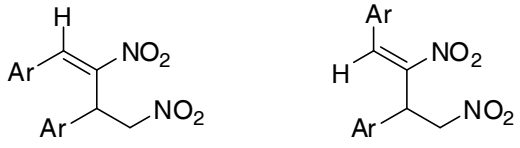


3a **10a**

Entry	Additives (mol %)	Yield of **10a** (%	Recovered **3a** (%)
1	LiCl	16	40
2	**Hydroquinone**	**59**	**17**
3	4-methoxyphenol	45	33
4	Anthranilic acid	5	60
5	L-Proline	30	25

[a]Isolated yield after purification by silica gel column chromatography.

Table S8. ^{1}H NMR chemical shift of H β to NO_2 group in RC adducts **10** (see Table 4, main text).



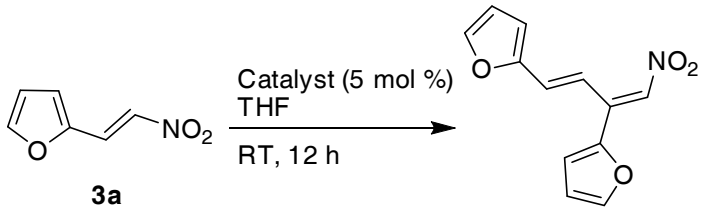
10 **10**

(*E*) (*Z*)

Entry	**10**, Ar	β-H (*E*)	β-H (*Z*)
1	**10a,** 2-furyl	7.99	-
2	**10b,** 2-thienyl	8.41	-
3	**10c,** 3-furyl	8.03	-
4	**10f,** 4-OMe-Ph	8.22	-

This journal is © The Royal Society of Chemistry 2010

Table S9. Various phosphines as catalysts

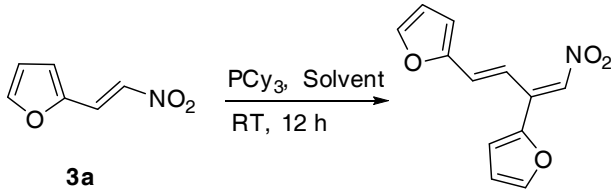


3a **12a**

Entry	Catalyst	Yield of **12a** (%)[a]	Recovered **3a** (%)
1	PMe_3	16	64
2	PBu_3	77	16
3	PPh_3	8	73
4	**PCy_3**	**78**	**17**
5	$P(C_{12}H_9)_3$	-[b]	-
6	$AsPh_3$	-[b]	-

[a]Isolated yield after purification by silica gel column chromatography,[b] Polymerization

Table S10. Solvent optimization



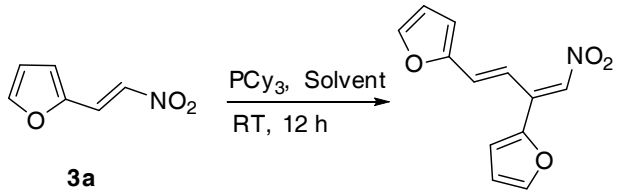
3a **12a**

Entry	Solvent	Yield of **12a** (%)[a]	Recovered **3a** (%)
1	**THF**	**77**	**16**
2	1,4 dioxan	10	17
3	Et_2O	8	<5
4	Toluene	14	40

[a] Isolated yield after purification by silica gel column chromatography

This journal is © The Royal Society of Chemistry 2010

Table S11. Optimisation of the amount of catalyst



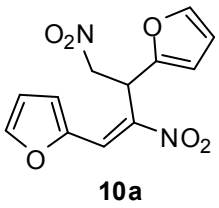
3a **12a**

Entry	PCy_3 (mol %)	Yield of **12a** (%)[a]	Recovered **3a** (%)
1	**5**	**78**	**16**
2	10	76	16
3	20	62	9
4	50	35	Traces [b]

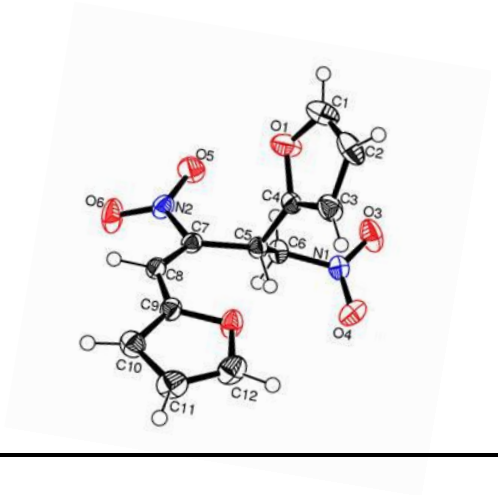
[a] Isolated yield after purification by silica gel column chromatography. [b] Nitroalkene polymerized

This journal is © The Royal Society of Chemistry 2010

Table S12. X-ray data for 10a



10a



Empirical formula	$C_{12}H_{10}N_2O_6$
Formula weight	278.22
Wavelength	0.71073 A
Temperature	150 (2)
Crystal system	Triclinic
Space group	P -1
a, Å	9.0724 (4)
b, Å	9.7915 (4)
c, Å	14.0849 (7)
α deg	89.657 (3)
β deg	77.662 (4)
γ deg	82.933 (3)
Volume $Å^3$	1212.75 (9)
Z	2
Density (calcd), mg/m^{-3}	1.524
Absorption coefficient, mm^{-1}	0.125
F(000)	576
Crystal size, mm	0.23 x 0.21 x 0.19
θ range, deg	2.92 to 25.00
Index ranges	-10<=h<=10, -11<=k<=11, -15<=l<=16
Reflections collected / unique	10904 / 4233 [R(int) = 0.0271]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9767 and 0.9719
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4233 / 0 / 441
Goodness-of-fit on F^2	1.014
Final R indices [I>2σ(I)]	R1 = 0.0374, wR2 = 0.0818
R indices (all data)	R1 = 0.0594, wR2 = 0.0922
Largest diff. peak and hole $e.A^{-3}$	0.246 and -0.211

II. Experimental Section

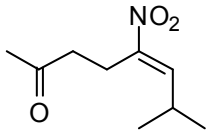
General

The melting points were recorded on Thermonik melting point apparatus. IR spectra were recorded on an Impact 400/Nicolet or Perkin Elmer Spectrum One FT spectrometer. NMR spectra (^{1}H, ^{13}C, ^{19}F, ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY) were recorded on an AMX-400 (Varian Mercury Plus OXFORD, broad band, auto switchable and inverse probe) or VXR-300S spectrometer. TMS was the internal standard for ^{1}H and ^{13}C and $CFCl_3$ was the internal standard for ^{19}F. The coupling constants (*J* values) are given in Hz. Mass spectra (LR and HR) were recorded at 60-70 eV on a Micromass Q-TOF mass spectrometer under ESI mode. Elemental analysis was performed on a Thermo Finnigan Flash EA 1112 Analyzer. The structure was solved by direct methods shelxs97 and refined by full-matrix least squares against F^2 using shelxl97 software. Nitroalkenes[1] were prepared following literature protocols. For the experimental data for **5a-n** see our preliminary communication (Ref. 21, main text).

General Procedure for the Rauhut-Currier heterocoupling of nitroalkenes or dienes with MVK or acrylate (see Tables 1-3, main text)

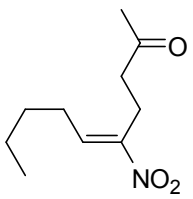
To a stirred solution of nitroalkene **3**, **6** or nitrodiene **8** (1 mmol) in THF (2 ml) was added imidazole (0.068 mg, 1 mmol), lithium chloride (0.042 mg, 1 mmol), followed by MVK **4a** or ethyl acrylate **4b** (3 mmol) and the reaction mixture was stirred at room temperature. After the completion 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 **5**, **7** or **9**.

(*E*)-7-Methyl-5-nitrooct-5-en-2-one (7a)



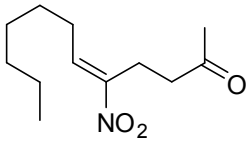
Yellow oil; Yield 74 mg (40%); ν_{max} (KBr)/cm^{-1} 2965w, 2918m, 2850w, 1715s, 1523m, 1363m; δ_H ($CDCl_3$, 400 MHz) 1.11 (6H, d, *J* 6.7), 2.17 (3H, s), 2.70 (1H, dseptet, *J* 10.7, 6.7), 2.71 (2H, t, *J* 7.6), 2.84 (2H, t, *J* 7.6), 6.95 (1H, d, *J* 10.7); δ_C ($CDCl_3$, 100 MHz) 20.7, 22.1, 28.0, 29.9, 41.4, 143.9, 148.7, 206.6; m/z (QTOF ES+, Ar) 208 (MNa^+, 100), 205 (7), 149 (10), 99 (7); HRMS (QTOF ES+, Ar) calcd for $C_9H_{15}NO_3Na$ (MNa^+) 208.0950, found 208.0952.

(*E*)-5-Nitrodec-5-en-2-one (7b)



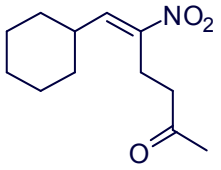
Yellow oil; Yield 58 mg (29%); ν_{max} (KBr)/cm^{-1} 2958m, 2932m, 2873w, 1717s, 1521m, 1336m; δ_H ($CDCl_3$, 400 MHz) 0.94 (3H, t, *J* 7.3), 1.39 (2H, dq, *J* 14.6, 7.3), 1.45-1.51 (2H, m), 2.17 (3H, s), 2.30 (2H, dt collapsed to q, *J* 7.8) 2.69 (2H, t, *J* 7.3), 2.84 (2H, t, *J* 7.3), 7.16 (1H, t, *J* 7.8); δ_C ($CDCl_3$, 100 MHz) 14.0, 20.7, 22.6, 28.0, 30.1, 30.7, 41.3, 138.4, 150.3, 206.8; m/z (QTOF ES+, Ar) 222 (MNa^+, 100); HRMS (QTOF ES+, Ar) calcd for $C_{10}H_{17}NO_3Na$ (MNa^+) 222.1106, found 222.1106.

(*E*)-5-Dodec-5-en-2-one (7c)



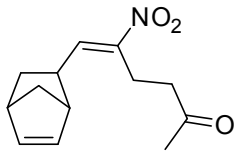
Yellow oil; Yield 79 mg (35%); ν_{max} (KBr)/cm^{-1} 2957s, 2928s, 2858s, 1721s, 1520s, 1336m; δ_H ($CDCl_3$, 400 MHz) 0.89 (3H, t, *J* 6.8), 1.22-1.38 (6H, m), 1.46-1.68 (2H, m), 2.16 (3H, s), 2.29 (2H, dt collapsed to q, *J* 7.7), 2.69 (2H, t, *J* 7.2), 2.84 (2H, t, *J* 7.2), 7.15 (1H, t, *J* 7.7); δ_C ($CDCl_3$, 100 MHz) 14.1, 20.7, 22.6, 28.2, 28.5, 29.1, 30.0, 31.6, 41.3, 138.4, 150.4, 206.7; m/z (QTOF ES+, Ar) 250 (MNa^+, 42), 228 (100), 180 (14), 168 (2), 99 (15); HRMS (QTOF ES+, Ar) calcd for $C_{12}H_{21}NO_3Na$ (MNa^+) 250.1419, found 250.1416.

(*E*)-6-Cyclohexyl-5-nitrohex-5-en-2-one (7d)

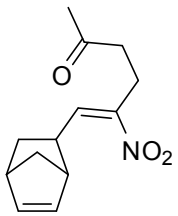


Yellow oil; Yield 110 mg (49%); ν_{max} (KBr)/cm^{-1} 3021m, 2932s, 2856m, 1719s, 1523m, 1335m; δ_H ($CDCl_3$, 400 MHz) 1.18-1.34 (5H, m), 1.63-1.77 (5H, m), 2.15 (3H, s), 2.31-2.43 (1H, m), 2.67 (2H, t, *J* 7.3), 2.81 (2H, t, *J* 7.3), 6.95 (1H, d, *J* 10.7); δ_C ($CDCl_3$, 100 MHz) 20.6, 25.1, 25.4, 29.8, 31.8, 37.4, 41.5, 142.4, 148.8, 206.7; m/z (QTOF ES+, Ar) 248 (MNa^+, 100), 206 (30), 166 (30), 95 (20); HRMS (QTOF ES+, Ar) calcd for $C_{12}H_{19}NO_3Na$ (MNa^+) 248.1263, found 248.1259.

(*E*)-6-(Bicyclo [2.2.1] hept-5-en-2-yl)-5-nitrohex-5-en-2-one (*E*-7e, Minor) and (*Z*)-6-(Bicyclo [2.2.1] hept-5-en-2-yl)-5-nitrohex-5-en-2-one (*Z*-7e, Major)



Minor isomer



Major isomer

Yellow oil; Yield 118 mg (50%); inseparable mixture of (*Z*) and (*E*) isomers in 5:1 ratio; ν_{max} (KBr)/cm^{-1} 2971m, 2943m, 2872w, 1718s, 1519s, 1336s

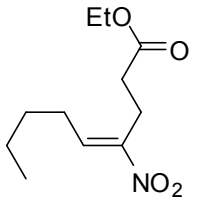
Major + minor: δ_H ($CDCl_3$, 400 MHz) 0.88 (1H, ddd, *J* 11.9, 4.3, 2.4), 1.37-1.40 (1H, m), 1.51-1.55 (1H, m), 2.08-2.15 (2H, m), 2.91-3.09 (6H, m); δ_C ($CDCl_3$, 100 MHz) 21.0, 30.0, 33.6, 38.0, 41.5, 42.9, 48.0, 49.8, 132.3, 138.8, 143.8, 149.2, 206.9

Major (peaks appearing separately): 2.18 (3H, major isomer, s), 6.03 (1H, dd, *J* 5.8, 2.9), 6.29 (1H, dd, *J* 5.8, 2.9), 6.71 (1H, d, *J* 11.0);

Minor (peaks appearing separately): 2.16 (3H, s), 6.17 (2H, dd, *J* 5.5, 3.1), 7.12 (1H, d, *J* 10.7)

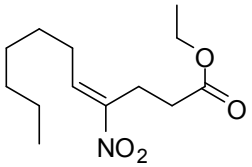
m/z (QTOF ES+, Ar) 236 (MH^+, 100); HRMS (QTOF ES+, Ar) calcd for $C_{13}H_{18}NO_3$ (MH^+) 236.1287, found 236.1283.

(*E*)-Ethyl 4-nitronon-4-enoate (7f)



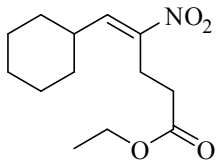
Yellow oil; Yield 50 mg (22%); ν_{max} (KBr)/cm^{-1} 2960m, 2934m, 2874w, 1736s, 1523m, 1337m, 1181m; δ_H ($CDCl_3$, 400 MHz) 0.94 (3H, t, *J* 7.1), 1.26 (3H, t, *J* 6.3), 1.38 (2H, tq, *J* 14.3, 7.1), 1.46-1.53 (2H, m), 2.31 (2H, dt collapsed to q, *J* 7.3), 2.55 (2H, t, *J* 7.5), 2.92 (2H, t, *J* 7.5), 4.14 (2H, q, *J* 7.1), 7.16 (1H, t, *J* 8.1); δ_C ($CDCl_3$, 100 MHz) 13.9, 14.3, 22.1, 22.6, 28.0, 30.7, 32.3, 60.9, 138.7, 149.9, 172.2; m/z (QTOF ES+, Ar) 252 (MNa^+, 100); HRMS (QTOF ES+, Ar) calcd for $C_{11}H_{19}NO_4Na$ (MNa^+) 252.1212, found 252.1189.

(*E*)-Ethyl 4-nitroundec-4-enoate (7g)



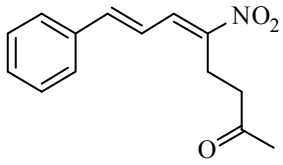
Red oil; Yield 70 mg (27%); ν_{max} (KBr)/cm^{-1} 2926s, 2854s, 1736s, 1524s, 1336m, 1181m; δ_H ($CDCl_3$, 400 MHz) 0.90 (3H, t, *J* 6.8), 1.26 (3H, t, *J* 7.0), 1.30-1.39 (6H, m), 1.42-1.54 (2H, m), 2.30 (2H, dt collapsed to q, *J* 7.5), 2.55 (2H, t, *J* 7.5), 2.92 (2H, t, *J* 7.5), 4.14 (2H, q, *J* 7.0), 7.19 (1H, t, *J* 8.1); δ_C ($CDCl_3$, 100 MHz) 14.1, 14.3, 22.0, 22.6, 28.2, 28.5, 29.1, 31.7, 32.3, 60.9, 138.8, 149.9, 172.2; m/z (QTOF ES+, Ar) 280 (MNa^+, 100), 194 (4), 149 (8), 102 (2); HRMS (QTOF ES+, Ar) calcd for $C_{13}H_{23}NO_4Na$ (MNa^+) 280.1525, found 280.1536.

(*E*)-Ethyl 5-cyclohexyl-4-nitropent-4-enoate (7h)



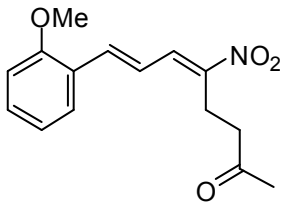
Yellow oil; Yield 71 mg (28%); ν_{max} (KBr)/cm^{-1} 2928s, 2850m, 1736s, 1522s, 1335m, 1182m; δ_H ($CDCl_3$, 400 MHz) 1.18-1.42 (5H, m), 1.27 (3H, t, *J* 7.2), 1.66-1.80 (5H, m), 2.15-2.21 (1H, m), 2.54 (2H, t, *J* 7.6), 2.92 (2H, t, *J* 7.6), 4.14 (2H, q, *J* 7.2), 7.01 (1H, d, *J* 10.7); δ_C ($CDCl_3$, 100 MHz) 14.3, 22.3, 25.3, 25.6, 32.1, 32.7, 37.7, 60.9, 142.8, 148.6, 172.2; m/z (QTOF ES+, Ar) 295 (MK^+,46), 278 (MNa^+,100), 263 (5), 223 (1), 210 (85); HRMS (QTOF ES+, Ar) calcd for $C_{13}H_{21}NO_4Na$ (MNa^+) 278.1368, found 278.1378.

(1*E*,3*E*)-4-(Nitrobut-1,3-dienyl)benzene (9a)



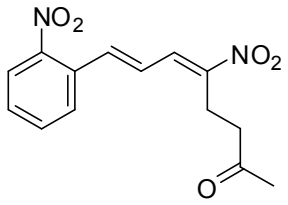
Yellow solid; Yield 81 mg (33%); mp 78 ˚C; ν_{max} (KBr)/cm^{-1} 1717m, 1508m, 1313m, 1167m, 975 w, 738s; δ_H($CDCl_3$, 400 Hz) 2.20 (3H, s), 2.78 (2H, t, *J* 7.2), 3.10 (2H, t, *J* 7.2), 7.10 (2H, m), 7.34-7.44 (3H, m), 7.52-7.58 (2H, m), 7.78 (1H, dd, *J* 9.5, 1.3); δ_C($CDCl_3$, 100 Hz) 21.0, 30.1, 41.3, 121.3, 127.8, 129.1, 130.1, 135.2, 135.7, 145.0, 148.8, 207.0; MS (QTOF ES+, Ar) m/e (rel intensity) 246 (35), 200 (100), HRMS (QTOF ES+, Ar) calcd for $C_{14}H_{16}NO_3$ (MH^+) 246.1130, found 246.1137. Confirmed by ^{1}H-^{1}H 2D COSY and NOESY experiments.

(5*E*, 7*E*)-8-(2-Methoxyphenyl)-5-nitroocta-5, 7-dien-2-one (9b)



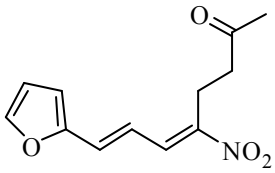
Yellow solid; Yield 96 mg (35%); mp 70-73 ^{o}C; ν_{max} (KBr)/cm^{-1} 1716s, 1627m, 1596m, 1504m, 1304vs; δ_H ($CDCl_3$, 400 MHz) 2.18 (3H, s), 2.78 (2H, t, *J* 7.3), 3.03 (2H, t, *J* 7.3), 3.90 (3H, s), 6.92 (1H, d, *J* 8.3), 6.99 (1H, t, *J* 7.5), 7.10 (1H, dd, *J* 15.3, 11.6), 7.34 (1H, td, *J* 8.3, 1.5), 7.47 (1H, d, *J* 15.3), 7.59 (1H, dd, *J* 7.9, 1.5), 7.81 (1H, d, *J* 11.6); δ_C ($CDCl_3$, 100 MHz) 20.9, 29.6, 41.3, 55.5, 111.1, 120.9, 121.6, 124.6, 128.0, 131.3, 136.1, 140.4, 148.1, 157.9, 206.8; m/z (QTOF ES+, Ar) 298 (MNa^+, 15), 276 (MH^+, 25), 246 (93), 230 (100), 172 (13), 99 (10), 91 (33); HRMS (QTOF ES+, Ar) calcd for $C_{15}H_{18}NO_4$ (MH^+) 276.1236, found 276.1244.

(5*E*,7*E*)-5-Nitro-8-phenylocta-5,7-dien-2-one (9c)



Yellow solid; Yield 110 mg (38%); 82-84 ^{o}C; ν_{max} (KBr)/cm^{-1} 2924m, 2852w, 1715m, 1520s, 1343m, 1314s; δ_H ($CDCl_3$, 400 MHz) 2.18 (3H, s), 2.82 (2H, t, *J* 6.9), 3.05 (2H, t, *J* 6.9), 7.12 (1H, dd, *J* 15.3, 11.6), 7.58 (1H, td, *J* 7.3, 1.1), 7.60 (1H, d, *J* 15.3), 7.69 (1H, t, *J* 7.3), 7.79 (1H, d, *J* 11.6), 7.83 (1H, d, *J* 7.9), 8.04 (1H, dd, *J* 7.9, 1.1); δ_C ($CDCl_3$, 400 MHz) 20.9, 30.1, 41.1, 125.1, 126.2, 129.0, 130.0, 131.5, 133.6, 133.9, 138.8, 148.1, 150.8, 206.8. m/z (QTOF ES+, Ar) 313 (MNa^+, 100), 244 (78), 226 (40), 197 (22), 179 (18), 146 (15); HRMS (QTOF ES+, Ar) calcd for $C_{14}H_{14}N_2O_5Na$ (MH^+) 313.0800, found 313.0799.

(5E, 7E)-8-(8-furan-2-yl)-5-nitroocta-5,7-dien-2-one (9d)

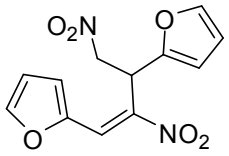


Red viscous liquid; yield 94 mg (40%); ν_{max} (KBr)/cm^{-1} 2922s, 2852m, 1715m, 1633m, 1520s, 1344m, 1313m, 1168m; δ_H ($CDCl_3$, 400Hz) δ 2.20 (3H, s), 2.78 (2H, t, *J* 7.3), 3.11 (2H t, *J* 7.3), 6.49 (1H, dd, *J* 1.8), 6.59 (1H, d, *J* 3.3), 6.80-7.0 (2H, m), 7.50 (1H, d, *J* 1.6), 7.70 (1H, d, *J* 10.6); δ_C ($CDCl_3$, 100 MHz) δ 21.2, 30.0, 41.4, 112.7, 114.2, 119.4, 130.8, 134.9, 144.9, 148.8, 152.2, 206; m/z (QTOF ES+, Ar) 258 (MNa^+, 100), 236 (M+, 98), 192 (96); HRMS (QTOF ES+, Ar) calcd for $C_{12}H_{13}NO_4Na$ (MH^+) 258.0742, found 258.0735.

General Procedure for the Rauhut-Currier homocoupling of nitroalkenes or dienes (see Table 4, main text)

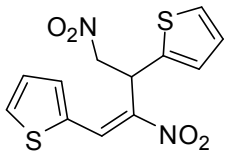
To a stirred solution of nitroalkene **3** or nitrodiene **8** (0.5 mmol) in CH_2Cl_2 (1 mL), imidazole (0.017 g, 0.25 mmol, 50 mol %) and hydroquinone (5 mg, 0.05 mmol, 10 mol %) was added in one portion. Stirring was continued at room temperature for the specified time (see Table 4). The crude product was purified by silica gel column chromatography (5% EtOAc:hexane) to afford the pure dimer **10** or **11.**

2, 2´-(2, 4-Dinitrobut-1-ene-1, 3-diyl) difuran (10a)



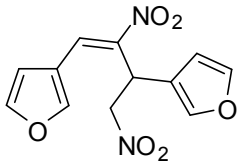
Yellow solid; Yield 40 mg (58%); mp 85-86 ^{o}C; ν_{max} (KBr)/cm^{-1} 2927m, 2351w, 1647m, 1559w, 1371w, 1325m, 1023s; δ_H ($CDCl_3$, 400 MHz) 5.10 (1H, dd, *J* 13.7, 6.9), 5.33 (1H, dd, *J* 13.7, 7.8), 6.14 (1H, dd collapsed to t, *J* 6.9), 6.23 (1H, d, *J* 3.2), 6.32 (1H, d, *J* 1.8), 6.65 (1H, dd collapsed to t, *J* 1.6), 7.03 (1H, d, *J* 3.2), 7.33 (1H, s), 7.74 (1H, s), 7.99 (1H, s); δ_C ($CDCl_3$, 100 MHz) 36.6, 75.5, 107.2, 110.9, 113.4, 123.0, 124.2, 142.1, 142.3, 146.4, 147.8, 148.6; m/z (QTOF ES+, Ar) 301 (MNa^+, 100), 232 (42), 218 (35), 186 (5), 79 (8). HRMS (QTOF ES+, Ar) calcd for $C_{12}H_{10}N_2O_6Na$ (MNa^+) 301.0437, found 301.0442.

2,2'-(2,4-Dinitrobut-1-ene-1,3-diyl)dithiophene (10b)



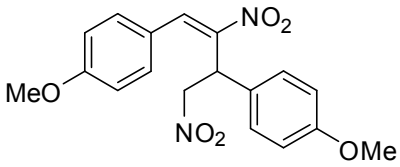
Yellow solid; Yield 29 mg (38%); mp 122-124 ^{o}C; ν_{max} (KBr)/cm^{-1}2923m, 2852w, 1621s, 1553s, 1508m, 1375m, 1300s; δ_H ($CDCl_3$, 400 MHz) 5.20 (1H, dd, *J* 13.7, 6.4), 5.33 (1H, d, *J* 13.7, 7.3), 5.94 (1H, dd collapsed to t, *J* 6.8), 6.97 (1H, dd, *J* 5.0, 3.7), 7.11 (1H, d, *J* 3.7), 7.24-7.26 (2H, m), 7.59 (1H, d, *J* 3.7), 7.76 (1H, d, *J* 5.0), 8.41 (1H, s); δ_C ($CDCl_3$, 100 MHz) 38.2, 77.6, 126.0, 126.8, 127.3, 128.9, 131.3, 133.1, 133.6, 137.1, 137.5, 144.4. m/z (QTOF ES+, Ar) 333 (MNa^+, 46 %), 298 (8), 251 (8), 250 (100), 159 (10), 157 (7), 59 (5). HRMS (QTOF ES+, Ar) calcd for $C_{12}H_{10}N_2O_4NaS_2$ (MNa^+) 332.9980, found 332.9971.

(E)-3,3'-(2,4-Dinitrobut-1-ene-1,3-diyl)difuran (10c)



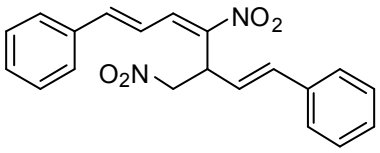
Yellow oil; Yield 9 mg (14%); ν_{max} (KBr)/cm^{-1} 2924s, 2853m, 1645m, 1555s, 1515m, 1378m, 1322w, 1024m; δ_H ($CDCl_3$, 400 MHz) 5.04 (1H, dd, *J* 13.2, 6.2), 5.20 (1H, dd, *J* 13.2, 7.7), 5.30 (1H, dd collapsed to t, *J* 7.0), 6.32 (1H, d, *J* 1.8), 6.79 (1H, d, *J* 1.4), 7.38 (1H, d, *J* 1.8), 7.39 (1H, d, *J* 1.8), 7.61 (1H, d, *J* 1.4), 7.91 (1H, s), 8.03 (1H, s); δ_C ($CDCl_3$, 100 MHz) 34.4, 77.2, 109.1, 109.5, 117.7, 120.0, 128.4, 140.3, 143.9, 145.7, 146.3, 147.8; m/z (QTOF ES+, Ar) 317 (MK^+, 5%), 280 (32), 267 (100), 242 (4); HRMS (QTOF ES+, Ar) calcd for $C_{12}H_{10}N_2O_6K$ (MK^+) 317.0176, found 317.0179.

3, 4'-(2, 4-Dinitrobut-1-ene-1, 3-diyl) bis (methoxybenzene) (10f)



Yellow oil; Yield 6 mg (7%); ν_{max} (KBr)/cm^{-1} 2928m, 2846w, 1605m, 1556m, 1513s, 1374w, 1300w, 1029m; δ_H ($CDCl_3$, 400 MHz) 3.78 (3H, s), 3.88 (3H, s), 5.15 (1H, dd, *J* 12.8, 6.4), 5.36 (1H, dd, *J* 12.8, 7.8), 5.43 (1H, dd collapsed to t, *J* 6.9),6.85 (2H, d, *J* 8.7), 7.01 (2H, d, *J* 8.7), 7.13 (2H, d, *J* 8.7), 7.47 (2H, d, *J* 8.7), 8.22 (1H, s); δ_C ($CDCl_3$, 400 MHz) 40.8, 55.4, 55.6, 114.4, 114.6, 114.9, 115.1, 128.3, 128.9, 130.4, 131.8, 137.8, 159.5 (× 2); m/z (QTOF ES+, Ar) 381 (MNa^+, 25), 365 (6), 332 (12), 316 (18), 294 (31), 280 (39), 267 (100); HRMS (QTOF ES+, Ar) calcd for $C_{18}H_{18}N_2O_6$ (MNa^+) 381.1080, found 381.1063.

4-Nitro-5-(nitromethyl)hepta-1,3,6-triene-1,7-diyl)dibenzene (11a)



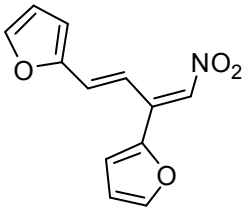
Yellow crystalline solid; Yield 79 mg (46%); mp 117-119 ^oC; ν_{max} (KBr)/cm^{-1} 1624s, 1553s, 1509m, 1449w, 1376m, 1312vs, 1170m, 972m, 752m; δ_H ($CDCl_3$, 400 MHz) 4.76 (1H, ABqd, *J* 16.1, 7.5), 4.97 (2H, ABqd, *J* 12.8, 7.5), 6.35 (1H, dd, *J* 16.1, 15.8), 6.64 (1H, d, *J* 15.8), 7.13 (1H, dd, *J* 11.7, 11.2), 7.20-7.40 (7H, m), 7.42-7.44 (2H, m), 7.52-7.59 (2H, m), 7.89 (1H, d, *J* 11.2); δC ($CDCl_3$, 100 MHz) 40.5, 41.7, 119.5, 122.5, 126.6, 128.1, 128.5, 128.7, 129.0, 129.1, 130.7, 135.2, 135.6, 137.9, 145.8, 147.8; m/z (QTOF ES+, Ar) 373 (MNa^+, 100), 351 (55), 301 (48), 245 (35), 179 (36), 149 (30); HRMS (QTOF ES+, Ar) calcd for C20H19N2O4 (MH+) 351.1345, found 351.1331.

General procedure for the homocoupling-elimination of nitroalkenes 3 (see Table 5, main text)

To a stirred solution of nitroalkene **3** (1 mmol) in THF (2 mL), tricyclohexylphosphine (14 mg, 5 mol %) was added in one portion. Stirring was continued at room temperature for the specified time (Table 5, main text). The reaction mixture was concentrated in vacuo and the crude product was purified by silica gel column chromatography (0-5% EtOAc:hexane) to obtain the nitrodienes **12a-c**.

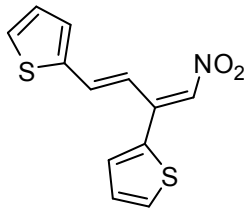
This journal is © The Royal Society of Chemistry 2010

2-((1*E*,3*E*)-3-(furan-2-yl)-4-nitrobuta-1,3-dienyl)furan (12a)



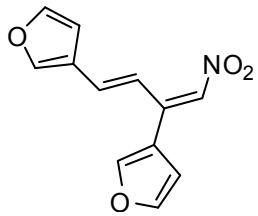
Yellow crystalline solid; Yield 90 mg (79%); mp 52-54 ^{o}C; ν_{max} (KBr)/cm^{-1} 2921s, 1613m, 1586m,1556w, 1318m, 1092m, 1021s, 804m; δ_H ($CDCl_3$, 400 MHz) 6.49 (1H, dd, *J* 3.4, 1.8), 6.58 (2H, dd, *J* 3.4, 1.8), 6.86 (1H, d, *J* 3.4), 7.00 (1H, d, *J* 16.4), 7.43 (1H, d, *J* 0.6), 7.54 (1H, d, *J* 1.5), 7.61 (1H, d, *J* 1.5), 7.92 (1H, dd, *J* 16.4, 0.6); δ_C ($CDCl_3$, 400 MHz) 112.6, 112.9, 113.9, 117.4, 119.3, 128.8, 131.5, 137.2, 144.9, 145.9, 148.8, 152.0; m/z (QTOF ES+, Ar) 232 (MH^+, 100%), 187 (44), 185 (38), 158 (10), 129 (3); HRMS (QTOF ES+) calcd for $C_{12}H_{10}NO_4$ (MH^+) 232.0610, found 232.0600. Confirmed by COSY, NOESY, HSQC and HMBC.

2-((1*E*,3*E*)-4-nitro-3-(thiophen-2-yl)buta-1,3-dienyl)thiophene (12b)



Yellow sticky solid; Yield 89 mg (69%); ν_{max} (KBr)/cm^{-1} 3107m, 2962m, 2926m, 2854w, 1564s, 1515m, 1411m, 1333s, 1081m, 1056s, 817m, 711s; δ_H ($CDCl_3$, 400 MHz) 7.06 (1H, dd, *J* 5.1, 3.7), 7.18 (1H, dd, *J* 5.1, 3.7), 7.20-7.24 (2H, m), 7.25-7.27 (1H, m), 7.36 (1H, dd, *J* 3.7, 1.1), 7.41-7.47 (1H, m), 7.54 (1H, dd, *J* 5.1, 1.1), 8.10 (1H, dd, *J* 15.8, 0.7); δ_C ($CDCl_3$, 75 MHz) 122.4, 128.21, 128.23, 128.8, 128.9, 129.5, 130.4, 130.7, 131.6, 132.3, 137.1, 141.1, 142.6; m/z (QTOF ES+, Ar) 264 (MH^+, 42%), 247 (33), 217 (100), 216 (6), 175 (7), 145 (8), 68 (8); HRMS (QTOF ES+, Ar) calcd for $C_{12}H_{10}NO_2S_2$ (MH^+) 264.0153, found 264.0146. Decomposes slowly on repeated purification.

3-((1*E*,3*E*)-3-(furan-3-yl)-4-nitrobuta-1,3-dienyl)furan (12c)



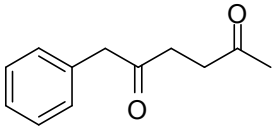
Yellow sticky solid; Yield 65 mg (58%); ν_{max} (KBr)/cm^{-1} 3148w, 2924w, 1558s, 1367m, 1161m, 1025m, 874m, 799m, 739m, 601m; δ_H ($CDCl_3$, 400 MHz) 6.54 (1H, dd, *J* 1.8, 0.9), 6.57 (1H, dd, *J* 1.2, 0.6), 6.75 (1H, dd, *J* 1.2, 0.6), 7.01 (1H, s), 7.05 (1H, s), 7.11 (1H, s), 7.37 (1H, s), 7.40 (1H,

s), 7.46 (1H, m), 7.52 (1H, m), 7.54 (1H, t, *J* 1.8), 7.57 (1H, dd, *J* 1.5, 0.9), 7.60 (1H, d, *J* 0.6), 7.67 (1H, t, *J* 0.9), 7.83 (1H, s), 7.91 (1H, s), 7.95 (1H, s), 7.99 (1H, s); δ_C ($CDCl_3$, 100 MHz) 107.5, 110.8, 122.4, 124.1, 132.0, 133.4, 141.1, 143.3, 144.1, 144.2, 144.6, 145.3; m/z (QTOF ES+, Ar) 254 (MNa^+, 55%), 232 (MH^+, 58), 215 (100), 187 (42), 158 (55), 149 (10); HRMS (QTOF ES+, Ar) calcd for $C_{12}H_{10}NO_4$ (MH^+) 232.0610, found 232.0601. Decomposes slowly on repeated purification.

General procedure for the synthesis of substituted cyclopentenones 14

To a solution of RC adduct **5** (1 mmol) in a mixture of MeOH (1.7 ml), H_2O (0.7 ml), and conc. HCl (0.7 ml), iron dust (112 mg, 2 mmol) was added in portions and the resulting reaction mixture was heated over a water bath for 30 min. After complete disappearance of starting material (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with MeOH (10 ml) and filtered over a bed of celite. The filtrate was concentrated in vacuo, the residue was diluted with water (10 ml), basified with 10% NaOH (10 ml) and extracted with ethyl acetate (3 × 10 ml). The combined organic layer was washed with brine (10 ml), concentrated in vacuo and the residue was purified by silica gel column chromatography by eluting with ethyl acetate/pet ether mixture (10-20%) to afford pure cyclopentenone **14.** Note: neutral workup of the reaction mixture, i.e. without using 10% NaOH (10 ml) provided 1,4-diketone **13** (see Scheme 6).

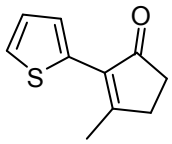
1-Phenylhexane-2,5-dione (13e)[1]



13e

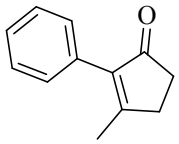
Yellow oil; Yield 127 mg (67%); ν_{max} (KBr)/cm^{-1} 3027w, 2912m, 1713vs, 1602w, 1399m, 1360m, 1175w, 1093w, 741m, 701m; δ_H ($CDCl_3$, 400 MHz) 2.15 (3H, s), 2.68-2.72 (4H, m), 3.74 (2H, s), 7.19-7.32 (5H, m); δ_C ($CDCl_3$, 100 MHz) 30.0, 35.6, 37.1, 50.1, 127.2, 128.8, 129.6, 134.3, 207.1, 207.3. In agreement with the data reported in the literature.[1]

3-Methyl-2-(thiophen2-yl) cyclopent-2-enone (14b)



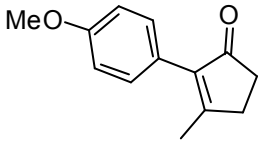
Yellow solid; Yield 118 mg (68%); ν_{max} (KBr)/cm^{-1} 2919m, 1691s, 1614w, 1295m, 1216m, 1127m, 761m, 720m; δ_H ($CDCl_3$, 400 MHz) 2.37 (3H, s), 2.53-2.56 (2H, m), 2.68-2.71 (2H, m), 7.11 (1H, dd, *J* 5.2, 3.7), 7.38 (1H, dd, *J* 5.2, 1.2), 7.46 (1H, dd, *J* 3.7, 1.2); δ_C ($CDCl_3$, 100 MHz) 19.4, 32.5, 34.7, 125.9, 126.7, 126.9, 132.9, 133.3, 170.1, 206.7; m/z (QTOF ES+) 179 (MH^+, 100), 149 (11); HRMS (ES+) calcd for $C_{10}H_{11}OS$ 179.0531, found 179.0528.

3-Methyl-2-phenylcyclopent-2-enone[1-2] **(14e)**



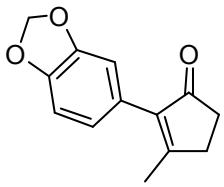
Red oil; Yield 119 mg (70%); ν_{max} (film)/cm^{-1} 2922m, 1696s, 1133m, 701m, δ_H ($CDCl_3$, 400 MHz) 2.20 (3H, s), 2.45 (2H, m), 2.64 (2H, m), 7.21-7.48 (5H, m); δ_C ($CDCl_3$, 100 MHz) 18.4, 31.9, 34.9, 127.7, 128.3, 129.2, 131.9, 140.4, 172.1, 207.8. IR, ^{1}H NMR and ^{13}NMR data are consistent with those reported in the literature.[1]

2-(4-methoxyphenyl)-3-methylcyclopent-2-enone[3-4] (14f)



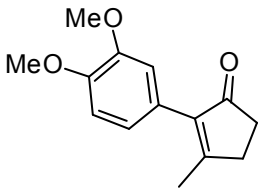
Red oil; Yield 149 mg (74%); ν_{max} (film)/cm^{-1} 2924m, 1696s, 1607m, 1513s, 1249s, 1033m, 834; δ_H ($CDCl_3$, 400 MHz) 2.18 (3H, s), 2.28-2.38 (2H, m), 2.41-2.48 (2H, m), 3.81 (3H, s), 6.94 (2H, shielded half of AA'XX' collapsed to dt, *J* 8.9, 2.2), 7.23 (2H, deshielded half of AA'XX' collapsed to dt, *J* 8.9, 2.2); δ_C ($CDCl_3$, 100 MHz) 18.5, 31.8, 34.9, 55.4, 113.9, 124.2, 130.4, 139.9, 159.1, 171.1, 208.2. The experimental data are consistent with those reported in the literature.[3]

2-(benzo[d][1,3]dioxo-5-yl)-3-methylcyclopent-2-enone[3] (14h)



Red liquid; Yield 162 mg (75%); ν_{max} (film)/cm^{-1} 2909w, 1696vs, 1503m, 1491s, 1239vs, 1039s, 933m; δ_H ($CDCl_3$, 400 MHz) 2.20 (3H, s), 2.48-2.54 (2H, m), 2.58-2.68 (2H, m), 5.95 (2H, s), 6.80 (2H, ABq, *J* 7.9, the upper half further split into d, *J* 1.5), 6.79 (1H, d, *J* 1.5); δ_C ($CDCl_3$, 100 MHz) 18.5, 31.8, 34.8, 101.1, 108.4, 109.7, 122.9, 125.5, 140.0, 147.1, 147.6, 171.6, 207.9. The experimental data are consistent with those reported in the literature.[3]

2-(3,4-dimethoxyphenyl)-3-methylcyclopent-2-enone (14i)



This journal is © The Royal Society of Chemistry 2010

Red liquid; Yield 167 mg (72%); ν_{max} (film)/cm^{-1} 2964s, 2939s, 2879s, 1725s, 1516w, 1466w, 1376w, 1257s, 1053m, 1017w, 968m; δ_H ($CDCl_3$, 400 MHz) 2.20 (3H, s), 2.48-2.60 (2H, m), 2.60-2.72 (2H, m), 3.90 (3H, s), 3.92 (3H, s), 6.82-6.95 (3H, m); δ_C ($CDCl_3$, 100 MHz) 18.6, 31.9, 35.0, 56.0 (× 2), 111.2, 112.5, 121.9, 124.6, 140.1, 148.7, 148.8, 171.5, 208.2; m/z (QTOF ES+) 233 (MH^+, 100); HRMS (QTOF ES+, Ar) calcd for $C_{14}H_{17}O_3$ (MH^+) 233.1178, found 233.1174.

References

1. Ref. 31b, main text.
2. Ref. 31, main text.
3. Ref. 31c, main text.
4. K. Itami, K. Mitsudo, K. Fujita, Y. Ohashi and J. Yoshida, *J. Am. Chem. Soc.*, 2004, **126**, 11058.