Rauhut–Currier type homo- and heterocouplings involving nitroalkenes and nitrodienes†

Pramod Shanbhag,[a] Pradeep R. Nareddy,[a] Mamta Dadwal,[a] Shaikh M. Mobin[b] and Irishi N. N. Namboothiri*[a]

Received 29th April 2010, Accepted 14th July 2010
DOI: 10.1039/c0ob00062k

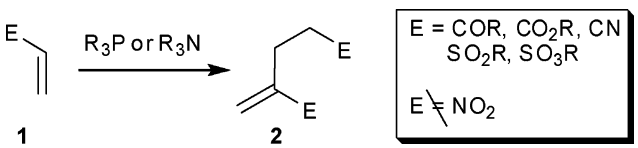
Reaction of nitroalkenes or nitrodienes with methyl vinyl ketone (MVK) or acrylate in the presence of the imidazole–LiCl catalyst system provides Rauhut–Currier (vinylogous Morita–Baylis–Hillman) adducts in moderate yield. Under similar conditions (imidazole–hydroquinone), nitroalkenes and nitrodienes undergo self-dimerization to afford the Rauhut–Currier adducts in varying yields. An alternative self-dimerization–nitro group elimination pathway in the presence tricyclohexylphosphine was observed with heteroaromatic nitroalkenes. A synthetically useful one-pot two step transformation of Rauhut–Currier adducts of nitroalkenes with MVK to 2,3-disubstituted cyclopentenones is also described.

Introduction

The phosphine-catalyzed dimerization of activated alkenes, first disclosed by Rauhut and Currier in their 1963 patent,[1] has set the stage for similar reactions of activated alkenes with other electrophiles, such as carbonyl compounds and imines, in the presence of phosphines, amines and analogous nucleophilic Lewis bases.[2] While the latter reaction, popularly known as the Morita–Baylis–Hillman (MBH) reaction, has developed into a highly efficient methodology of topical interest,[3,4] the homo- and heterodimerization of activated alkenes has not received much attention, primarily due to the limited substrate scope and poor selectivity.[5]

According to McClure,[6] Baizer and Anderson,[7] who investigated the phosphine-catalyzed dimerization of acrylonitrile, the mechanism of the Rauhut–Currier (RC) reaction involves reversible conjugate addition of the phosphine to the activated alkene followed by conjugate addition of the enolate to another molecule of activated alkene, proton transfer and elimination. Later on, Morita and Kobayashi[8] followed by McClure,[9] Hwu,[10] Basavaiah,[11] Miller[12] and Lee[13] reported the cross-coupling reaction of activated alkenes. Subsequently, phosphine/amine-catalyzed homodimerization of vinyl ketones,[14,15] acrylates,[15–17] acrylonitrile,[15,17,18] vinyl sulfone and vinyl sulfonate[15] has been reported by various research groups (Scheme 1). Intramolecular, including asymmetric versions[19] and their applications to natural product synthesis[20] have also been reported in recent years.[5]

We have reported the RC-type coupling of aromatic and heteroaromatic conjugated nitroalkenes with other activated alkenes such as vinyl ketone and acrylate for the first time in 2006.[21] Our reaction catalyzed by the imidazole–LiCl system provided



Scheme 1

the RC products in moderate yield. Many of our cross-coupled products exhibited tubulin binding anticancer activity at low micromolar concentrations. More recently, reports on a proline–NaN_3-mediated addition of β-alkyl nitroethylene to enone[22] and a Cinchona alkaloid-catalyzed coupling of β-substituted nitroethylene with cinnamate[23] have appeared in the literature. While the former is a Michael addition that provides a deconjugated RC product, the latter is a double Michael addition that provides formal RC products.

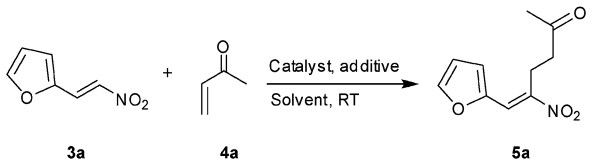
This paper, which is the full version of our preliminary results on the RC reaction we reported earlier,[21] describes for the first time our studies on similar reactions of aliphatic nitroalkenes and nitrodienes with enones and acrylates. Furthermore, the outcome of our attempts to subject nitroalkenes to self-coupling or RC dimerization is also presented here. A convenient one-pot transformation of the heterocoupled products to synthetically useful α,β-disubstituted cyclopentenones is also reported in this paper.

Results and discussion

First of all, we considered the cross-coupling of a nitroalkene with another activated alkene such as vinyl ketone. We envisaged that a nitroalkene, being a powerful acceptor, would undergo conjugate addition by the nucleophilic Lewis base and the resulting nitronate would add in a Michael fashion to the enone. Our extensive optimization studies using 2-nitrovinyl furan **3a** and MVK **4a** as the coupling partners in the presence of various nucleophilic Lewis bases such as DABCO, DBU, DMAP, imidazole *etc.* revealed that the desired product **5a** would indeed be isolable (Scheme 2). Although the superior catalytic activity of imidazole vis-à-vis other Lewis bases was amply evident from our experiments, there was further scope for improvement in the yield of the

[a]*Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076, India. E-mail: irishi@iitb.ac.in; Fax: +91-22-2576-7152; Tel: + 91-22-2576-7196*
[b]*National Single Crystal X-Ray Diffraction Facility, Indian Institute of Technology Bombay, Mumbai 400 076, India*

† Electronic supplementary information (ESI) available: Optimization tables, NMR and X-ray data tables, complete characterization data and copies NMR spectra. CCDC reference number 788174. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00062k



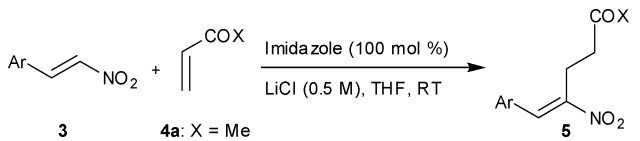
Scheme 2

coupled product **5a** under imidazole-catalyzed conditions. Therefore, various additives that are capable of activating the enone *via* iminium formation, activating the enone and/or nitroalkene *via* hydrogen bonding and minimizing the polymerization of these coupling partners were screened. Since we had only limited success with hydroquinone as additive, we employed LiCl (0.5 M) in conjunction with a stoichiometric amount of imidazole in THF for the cross-coupling of **3a** with **4a**. This was inspired by the recent reports on the application of salt to catalyze MBH reactions.[24] This catalyst system, which is also reminiscent of the Et_3N–LiCl combination of the Masamune–Roush variant[25] of the Horner–Wadsworth–Emmons reaction, provided the coupled product **5a** in satisfactory (44%) yield in 48 h.[21]

The above optimized conditions were successfully employed for the cross-coupling of other heteroaromatic nitroalkenes **3b–3d** and aromatic nitroalkenes **3e–3j** with MVK **4a** (Table 1, entries 2–10). It may be noted that although the yields are only moderate in most cases (28–60%), the reaction was reasonably clean causing no difficulty whatsoever in the purification and characterization of the desired products. Since prolonging the reaction time in many cases caused considerable decomposition of the products, the reactions were worked up after the specified time, although some amount of nitroalkene remained.

Having performed the cross-coupling of various aromatic and heteroaromatic nitroalkenes **3a–j** with MVK **4a**, we explored the possibility of reacting selected nitroalkenes **3** with ethyl acrylate **4b** in a Rauhut–Currier fashion (Table 1, entries 11–14). Although these efforts were curtailed by prolonged reaction times and low yields, we were pleased to isolate and characterize the γ-nitroesters **5k–5n** which are immediate precursors to γ-keto acids and biologically relevant γ-amino acids.

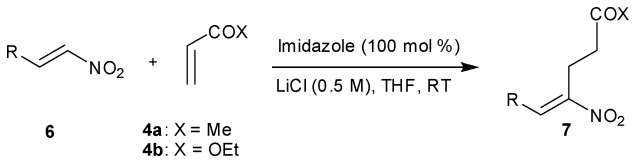
Table 1 The RC reaction of aromatic nitroalkenes **3** with MVK **4a** and ethyl acrylate **4b** in the presence of 100 mol% imidazole, and 0.5 M LiCl in THF at room temperature[a]



Entry	**3**, Ar	**4**	**5**	Time/h	Yield (%)[b,c]
1	**3a**, 2-furyl	**4a**	**5a**	48	44
2	**3b**, 2-thienyl	**4a**	**5b**	50	40
3	**3c**, 3-furyl	**4a**	**5c**	80	36
4	**3d**, 3-thienyl	**4a**	**5d**	20	34
5	**3e**, Ph	**4a**	**5e**	72	39
6	**3f**, 4-OMe–Ph	**4a**	**5f**	48	41
7	**3g**, 4-Cl–Ph	**4a**	**5g**	48	42
8	**3h**, 3,4-OCH_2O–Ph	**4a**	**5h**	48	47
9	**3i**, 3,4-$(OMe)_2$Ph	**4a**	**5i**	56	60
10	**3j**, 4-CF_3–Ph	**4a**	**5j**	6	28
11	**3a**, 2-furyl	**4b**	**5k**	56	21
12	**3e**, Ph	**4b**	**5l**	34	18
13	**3h**, 3,4-(OCH_2O)Ph	**4b**	**5m**	88	21
14	**3i**, 3,4-$(OMe)_2$Ph	**4b**	**5n**	90	24

[a] 3 equiv. of **4** was used. [b] Isolated yield after purification by silica gel column chromatography. [c] 5–23% of **3** was recovered.

Table 2 The RC reaction of aliphatic nitroalkenes **6** with MVK **4a** and ethyl acrylate **4b** in the presence of 100 mol% imidazole, and 0.5 M LiCl in THF at room temperature[a]



Entry	**6**, R	**4**	**7**	Time/h	Yield (%)[b,c]
1	**6a**, *i*-propyl	**4a**	**7a**	10	40
2	**6b**, *n*-butyl	**4a**	**7b**	16	29
3	**6c**, *n*-hexyl	**4a**	**7c**	14	35
4	**6d**, cyclohexyl	**4a**	**7d**	10	44
5	**6e**, norbornenyl	**4a**	**7e**	8	49[d]
6	**6f**, *n*-butyl	**4b**	**7f**	20	22
7	**6g**, *n*-hexyl	**4b**	**7g**	36	27
8	**6h**, cyclohexyl	**4b**	**7h**	24	25

[a] 3 equiv. of **4** was used. [b] Isolated yield after purification by silica gel column chromatography. [c] 10–20% of **6** was recovered. [d] $E:Z = 1:5$.

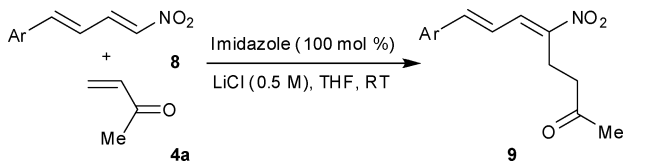
The *E* geometry of the nitroalkenyl double bond in the RC adducts **5a–n** was evident from the appearance of the proton β to the NO_2 group in the range δ 7.85–8.30 in the ^{1}H NMR (Table S1, see the ESI†). This was further confirmed by a ^{1}H–^{1}H 2D-NOESY experiment on a representative compound, **5e**. Strong NOEs observed between the CH_3 groups and one of the CH_2 groups with the aromatic protons together with weak NOEs observed between the former and the benzylic olefinic proton supported the above assignment. The structure and geometry of **5e** were further unambiguously established by single crystal X-ray analysis.[21]

Our subsequent endeavors to introduce aliphatic nitroalkenes **6** for the first time as RC coupling partners with MVK **4a** and acrylate **4b** provided similar results (Table 2). Since the aliphatic nitroalkenes were less amenable for prolonged reactions due to their propensity to undergo polymerization, the reactions in most cases were performed for less than 24 h. As in the case of aromatic nitroalkenes **3**, RC coupling of aliphatic ones **6** with MVK **4a** (Table 2, entries 1–5) was more impressive than that with acrylate **4b** (entries 6–8).

Analogous to the RC adducts **5** arising from aromatic nitroalkenes **3**, the RC adducts **7** of aliphatic nitroalkenes **6** also possessed *E* geometry with the proton β to the nitro group resonating in the range of δ 6.95–7.19 (Table S2, see the ESI†). A mixture of isomers (1 : 5) was isolated only in the case of RC adduct **7e**. Interestingly, the major isomer in this case was assigned *Z* geometry based on the shielding of the proton β to the nitro group in the major isomer as compared to that in the minor isomer by ~0.4 ppm.

Although nitroalkenes have been extensively employed as substrates in Michael addition, cycloadditions[26] and other reactions such as MBH reaction,[4] conjugated nitrobutadienes have been

Table 3 The RC reaction of nitrodienes **8** with MVK **4a** at room temperature in the presence of imidazole (100 mol%) and 0.5 M LiCl in THF at room temperature[a]



Entry	8, Ar	9	Time/h	Yield (%)[b]
1	**8a**, Ph	**9a**	24	33
2	**8b**, 2-OMe–Ph	**9b**	10	44
3	**8c**, 2-NO_2–Ph	**9c**	20	38
4	**8d**, 2-furyl	**9d**	18	40

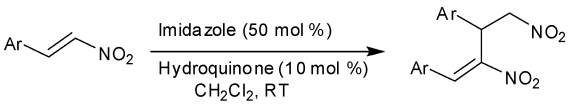
[a] 3 equiv. of **4a** was used. [b] Isolated yield after purification by silica gel column chromatography.

seldom employed in a similar capacity.[27] This is despite the fact that nitrodienes are conveniently accessible *via* Henry reaction of α,β-unsaturated aldehydes with nitromethane.[28] Therefore, we decided to investigate the RC cross-coupling of selected nitrodienes **8**, under the optimized conditions, with MVK **4a** and were pleased to isolate the products **9** in moderate yield (Table 3). It may be noted that the nature of the aromatic ring appears to have some effect on the yield of the RC product, in that nitrodienes with relatively electron donating aromatic rings furnished the products in better yield at shorter reaction times (Table 3, entries 2 and 4).

The geometries of the double bonds in **9a–d** were assigned *E*,*E* based on detailed NMR analysis. The protons β to the nitro group in these isomerically pure products resonated in the range δ 7.70–7.81, suggesting that the α,β-double bond has *E* configuration (Table S3, see the ESI†). These protons coupled with the γ-protons with *J* values in the range of 9.5–11.6 Hz. *J* values of 15–16 Hz for the coupling between γ- and δ-protons suggested that the γ,δ-double bond also has *E* configuration. These assignments were confirmed by ^{1}H–^{1}H 2D NOESY analysis of a representative compound **9a**. For instance, there was strong NOE between one of the CH_2 groups and the proton γ to the nitro group.

Our next objective was to investigate the more challenging self- or homocoupling of nitroalkenes. Although cyclotrimerization of nitroalkenes is reported in the literature,[29] there has been no report, to our knowledge, on the dimerization of nitroalkenes presumably because the major pathway is either cyclotrimerization or linear oligomerization or polymerization. Our preliminary screening of various amine-based catalysts such as imidazole, DMAP, DBU, DABCO, Et_3N, Hünig's base and pyridine for the RC dimerization of nitrovinyl furan **3a** revealed that imidazole was still the only catalyst that provided the dimer in isolable quantities (Table S4, see the ESI†). Subsequent solvent screening proved useful as the reaction proceeded well in CH_2Cl_2 affording the dimer **10a** in 58% yield in 24 h (Table S5, see the ESI†). The optimum amount of imidazole was 50 mol% as the reaction was sluggish with lower quantities and polymerization of nitroalkene **3a** was observed with higher quantities (Table S6, see the ESI†). Further attempts to improve the yield by screening co-catalysts had only marginal effect. However, the reaction was cleaner in the presence of 10 mol% of hydroquinone (Table S7, see the ESI†).

Table 4 Dimerization of nitroalkenes **3** at room temperature in the presence of imidazole (50 mol%) and hydroquinone (10 mol%) in CH_2Cl_2 at room temperature



Entry	3, Ar	10	Time/h	Yield (%)[a,b]
1	**3a**, 2-furyl	**10a**	24	58
2	**3b**, 2-thienyl	**10b**	24	38[c]
3	**3c**, 3-furyl	**10c**	72	14[c]
4	**3f**, 4-OMe–Ph	**10f**	48	7[c]

[a] Isolated yield after purification by silica gel column chromatography. [b] 11–32% of **3** was recovered. [c] Substantial amounts of trimeric/oligomeric/polymeric materials were also isolated in these cases.

Under the above optimized conditions, *i.e.* 50 mol% of imidazole and 10 mol% of hydroquinone in CH_2Cl_2, several other nitroalkenes **3a–c** and **3f** were allowed to dimerize and the results are summarized in Table 4. It may be noted that although the yield of the dimer was good (58%) when nitroalkene **3a** was used as the substrate (Table 4, entry 1), it dropped substantially with other heteroaromatic nitroalkenes **3b** and **3c** (Table 4, entries 2 and 3, respectively). The above optimized conditions were ineffective for aromatic nitroalkenes such as **3f** (Table 4, entry 4).

The *E* geometry of the double bond in **10a–c** and **f** was evident from the NMR chemical shift of the ^{1}H β to the nitro group (Table S8, see the ESI†). The structure and geometry of **10** were further unambiguously established by single crystal X-ray analysis of a representative system, **10a** (Fig. 1, see also the Experimental Section).

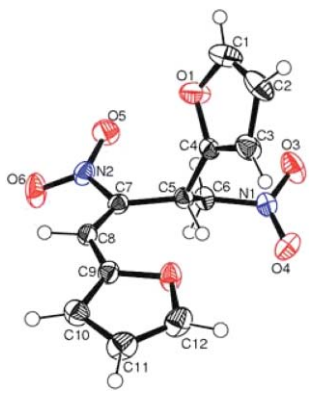
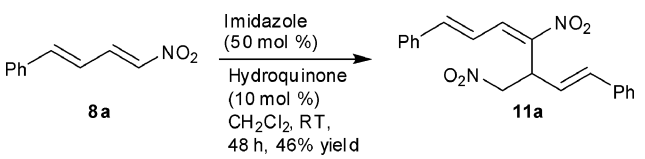


Fig. 1 Single crystal X-ray structure of dimer **10a**.

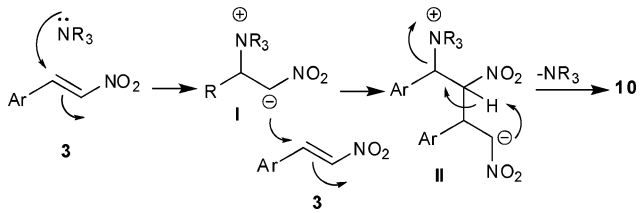
The RC homocoupling of a representative nitrodiene, **8a**, proceeded satisfactorily to provide the dimer **11a** in moderate yield (46%, Scheme 3). The structure and geometry of **11a** were determined by ^{1}H and ^{13}C NMR. The *E* geometry of the C6–C7



Scheme 3

double bond was confirmed from the ^{1}H–^{1}H coupling constant of 15.8 Hz. ^{1}H–^{1}H J values of 11.7 and 11.2 Hz, respectively, were indicative of the *E* geometry for the electron deficient conjugated double bonds C1–C2 and C3–C4 as well.

The proposed mechanism for the RC homocoupling involves initial conjugate addition of amine to nitroalkene **3** followed by a second conjugate addition of the nitronate **I** to another molecule of **3** to form intermediate **II** (Scheme 4). Intramolecular proton transfer and elimination of the amine would provide the RC product **10**.

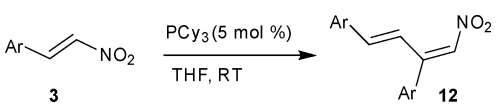


Scheme 4 Formation of RC homocoupled adducts **10** from nitroalkenes **3**.

Since the scope of RC homocoupling of nitroalkenes under imidazole-catalyzed conditions appeared limited, we screened various phosphines and an arsine as catalysts, again by taking nitroalkene **3a** as the model substrate (Table S9, see the ESI†). Interestingly, instead of the RC dimer, we observed the formation of an unexpected product which was later identified as nitrodiene **12a** (*vide infra*). Among the catalysts screened, tributyl phosphine (TBP) and tricyclohexyl phosphine (TCHP) provided the nitrodiene **12a** in comparable yields 77% and 78%, respectively) in 12 h. Further solvent screening and optimization of the amount of catalyst suggested that the reaction works well in THF with 5 mol% TCHP (Tables S10–S11, see the ESI†). Substantial polymerization of nitroalkene **3a** was observed when larger quantities of TCHP were used (Table S11, see the ESI†).

Subsequently, we subjected other aromatic and heteroaromatic nitroalkenes to the above optimized conditions. The results presented in Table 5 show that while heteroaromatic nitroalkenes, with the exception of **3d**, smoothly undergo the dimerization–elimination reaction, nitrostyrene **3e** and other aromatic nitroalkenes are not amenable for such a transformation.

Table 5 Dimerization of nitroalkenes **3** at room temperature in the presence of tricyclohexyl phosphine (TCHP) (5 mol%) in THF at room temperature[a]



Entry	3	Ar	Time	Yield (%)[a]
1	**3a**	2-furyl	12 h	79
2	**3b**	2-thienyl	20 h	69[b]
3	**3c**	3-furyl	12 h	58[b]
4	**3d**	3-thienyl	48 h	—[c]
5	**3e**	Ph	48 h	—[d]

[a] Isolated yield after purification by silica gel column chromatography. [b] Decomposes slowly on repeated purification. [c] Inseparable mixture of **12d** and **3d**. [d] Complex mixture.

The structure and stereochemistry of nitrodienes **12** were unambiguously established by extensive NMR studies on a representative system **12a** (Fig. 2). A coupling of J = 16.4 Hz between the γ- and δ-protons confirmed that the γ,δ double bond has *E* geometry. That the α,β double bond is also *E*, as is evident from the chemical shift of the γ-proton, which experiences a deshielding effect due to the anisotropic effect of the nitro group. Unfortunately, appreciable NOE is seen only between the vicinal γ- and δ-protons, which is expected. HSQC and HMBC experiments further confirmed the structure through H–C connectivity (see the ESI†).

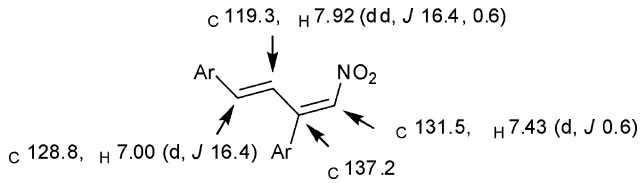
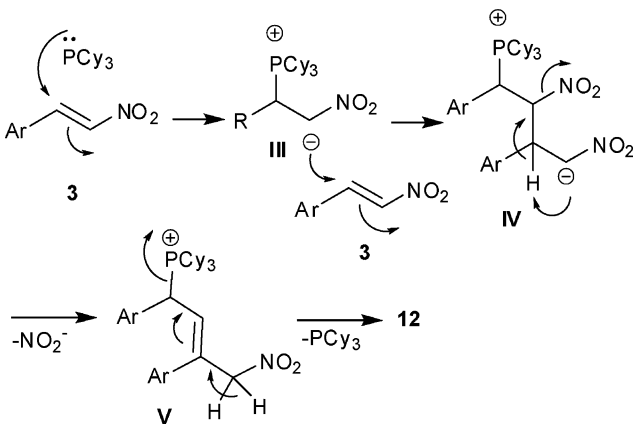


Fig. 2 Structure and stereochemistry of **12a** (Ar = 2-furyl) by ^{1}H, ^{13}C, APT, ^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY, HSQC and HMBC experiments.

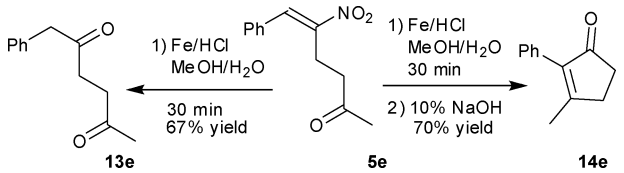
It is important to note that while the imidazole-mediated reaction furnished the homodimers **10** and **11** (Table 4, Schemes 3 and 4), the corresponding reaction mediated by phosphine delivered the elimination product **12**. This dichotomous behavior of nitroalkenes is explained in terms of an alternative elimination pathway available for the intermediate **IV** (Scheme 5) which is analogous to intermediate **II** in Scheme 4. Here, the elimination of HNO_2 prior to the elimination of phosphine from the intermediate **IV** is key to the formation of nitrodiene **12**.



Scheme 5 Formation of nitrodienes **12** *via* RC homocoupling and elimination.

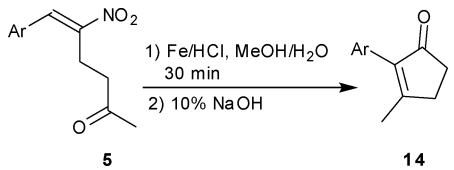
Finally, we investigated some of the possible applications of our RC adducts. When RC adduct **5e** was subjected to tandem metal–acid reduction–hydrolysis,[30] the 1,4-diketone **13e** was isolated in 67% yield (Scheme 6). Much to our delight, basic workup of the reaction mixture containing **13e** led to the formation of cyclopentenone **14e** *via* intramolecular aldol reaction in 70% yield.

The scope of the above one-pot transformation of RC adduct **5e** to substituted cyclopentenone **14e**, which involves reduction, hydrolysis, aldol reaction and dehydration, was subsequently extended to other RC adducts (Table 6). Thus, selected RC adducts arising from heteroaromatic and aromatic nitroalkenes **5b**, **5f**, **5h**



Scheme 6 Formation of 1,4-diketone **13e** and cyclopentenone **14e** from the RC adduct of nitroalkene **5e**.

Table 6 Synthesis of substituted cyclopentenones **14** from the RC adducts of nitroalkenes **5**



Entry	Ar	14	Yield (%)[a]
1	**5b**, Thienyl	**14b**	68
2	**5e**, Phenyl	**14e**	70
3	**5f**, 4-OMe–Ph	**14f**	74
4	**5h**, 3,4-(OCH_2O)–Ph	**14h**	75
5	**5i**, 3,4-$(OMe)_2$–Ph	**14i**	72

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

and **5i** were subjected to the one-pot transformation to afford cyclopentenones **14b**, **14f**, **14h** and **14i**, respectively, in good yield (Table 6, entries 1, 3–5).

Although such 1,2-disubstituted cyclopentenones possessing a quaternary benzylic chiral center have been synthesized from 1,4-diketones,[31] a one-pot transformation involving generation of 1,4-diketone and its intramolecular aldol condensations is hitherto unreported.[32] This is also a convenient alternative to various other existing methods[33,34] for the synthesis of 1,2-disubstituted cyclopentenones.

Conclusions

β-Substituted nitroethylenes and δ-substituted nitrodienes undergo facile coupling at the α-position with methyl vinyl ketone (MVK) and ethyl acrylate in the presence of the imidazole–LiCl catalyst system at room temperature. The nitroalkene–MVK adducts were transformed to 1,2-disubstituted cyclopentenones through a one-pot three step sequence involving reduction of the nitro group, hydrolysis of the enamine and aldol condensation of the 1,4-diketone. Homocoupling of nitroalkenes and nitrodienes under similar conditions (imidazole–hydroquinone) provides 1,3-dinitro compounds, the immediate precursors to 1,3-diamines. A tandem self-dimerization–elimination providing nitrodienes was observed when heteroaromatic nitroalkenes were treated with phosphine catalysts.

Experimental section

General procedure for the Rauhut–Currier heterocoupling of nitroalkenes or dienes with MVK or acrylate (see Tables 1–3)

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) and 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**.

Representative experimental data.

*(E)-7-Methyl-5-nitrooct-5-en-2-one (**7a**).* Yellow oil; Yield 74 mg (40%); ν_{max} (KBr)/cm^{-1} 2965w, 2918 m, 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.

General Procedure for the Rauhut–Currier homocoupling of nitroalkenes or dienes (see Table 4)

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%) were 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**.

Representative experimental data.

*2,2′-(2,4-Dinitrobut-1-ene-1,3-diyl) difuran (**10a**).* Yellow solid; Yield 40 mg (58%); mp 85–86 °C; ν_{max} (KBr)/cm^{-1} 2927 m, 2351w, 1647 m, 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; Selected X-ray data (CCDC 788174†) $C_{24}H_{20}N_4O_{12}$, *M* = 556.44, Triclinic, space group $P\bar{1}$, *a* = 9.0724(4) Å, *b* = 9.7915(4) Å, *c* = 14.0849(7) Å, α = 89.657(3), β = 77.662(4), γ = 82.933(3)°, U = 2040.2(4) $Å^3$, D_c = 1.524 Mg/m3, *Z* = 2, *F*(000) = 576, λ = 0.71073 Å, μ = 0.125 mm^{-1}, Total/Unique Reflections = 10904/4233 [R(int) = 0.0271], *T* = 150(2) K θ range = 2.92 to 25.00°, Final *R* indices [$I > 2\sigma(I)$] R_1 = 0.0374, wR_2 = 0.0818, *R* indices (all data) R_1 = 0.0594, wR_2 = 0.0922 (see also Table S12, ESI†).

General procedure for the homocoupling–elimination of nitroalkenes 3 (see Table 5)

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 4). 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**.

Representative experimental data.

2-((1E,3E)-3-(Furan-2-yl)-4-nitrobuta-1,3-dienyl)furan (***12a***). Yellow crystalline solid; Yield 90 mg (79%); mp 52–54 °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 ($CDCl_3$, 100 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.

General procedure for the synthesis of substituted cyclopentenone 14 (see Table 6)

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 through 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 layers were washed with brine (10 ml), concentrated *in vacuo* and the residue was purified by silica gel column chromatography by eluting with a 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).

Representative experimental data.

2-(3,4-Dimethoxyphenyl)-3-methylcyclopent-2-enone (***14i***). 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.

Acknowledgements

The authors thank DST, India for funding, SAIF, IIT Bombay and Mr Uday Prabhu, IISc Bangalore for selected NMR data. PS and MD thank CSIR, India for research fellowship.

Notes and references

1 M. M. Rauhut and H. Currier, *U.S. Patent*, 1963, 3074999; *Chem. Abstr.*, 1963, **58**, 11224a.
2 (*a*) K. Morita, Z. Suzuki and H. Hirose, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2815; (*b*) A. B. Baylis, M. E. D. Hillman, *Ger. Offen.*, 1972, DE 2155113; *Chem. Abstr.*, 1972, **77**, 434174; M. E. D. Hillman, A. B. Baylis, *US Pat.*, 1973, US 3743669.
3 Reviews: (*a*) V. Singh and S. Batra, *Tetrahedron*, 2008, **64**, 4511; (*b*) D. Basavaiah, K. V. Rao and R. J. Reddy, *Chem. Soc. Rev.*, 2007, **36**, 1581; (*c*) K. Y. Lee, S. Gowrisankar and J. N. Kim, *Bull. Korean Chem. Soc.*, 2005, **26**, 1481; (*d*) D. Basavaiah, A. J. Rao and T. Satyanarayana, *Chem. Rev.*, 2003, **103**, 811; (*e*) S. E. Drewes and G. H. P. Roos, *Tetrahedron*, 1988, **44**, 4653; (*f*) D. Basavaiah, P. D. Rao and R. S. Hyma, *Tetrahedron*, 1996, **52**, 8001; (*g*) E. Ciganek, *Organic Reactions*, ed. L. A. Paquette, John Wiley and Sons, Inc., 1997, Vol. 51.; (*h*) Y.-L. Shi and M. Shi, *Eur. J. Org. Chem.*, 2007, 2905; (*i*) V. Declerck, J. Martinez and F. Lamaty, *Chem. Rev.*, 2009, **109**, 1; (*j*) G. Masson, C. Housseman and J. Zhu, *Angew. Chem., Int. Ed.*, 2007, **46**, 4614; (*k*) C. Limberakis, *Morita–Baylis–Hillman Reaction. Name Reactions for Homologations*, ed. Ji Jack Li, 2009, Pt. 1, p 350; (*l*) V. Carrasco-Sanchez, M. J. Simirgiotis and L. S. Santos, *Molecules*, 2009, **14**, 3989; (*m*) G.-N. Ma, J.-J. Jiang, M. Shi and Y. Wei, *Chem. Commun.*, 2009, 5496; (*n*) Y. Wei and M. Shi, *Acc. Chem. Res.*, 2010, **43**, 1005.
4 For our reports on the MBH reaction of nitroalkenes with various electrophiles. Formaldehyde: (*a*) N. Rastogi, I. N. N. Namboothiri and M. Cojocaru, *Tetrahedron Lett.*, 2004, **45**, 4745; (*b*) R. Mohan, N. Rastogi, I. N. N. Namboothiri, S. M. Mobin and D. Panda, *Bioorg. Med. Chem.*, 2006, **14**, 8073. Other carbonyl compounds: (*c*) I. Deb, M. Dadwal, S. M. Mobin and I. N. N. Namboothiri, *Org. Lett.*, 2006, **8**, 1201; (*d*) I. Deb, P. Shanbhag, S. M. Mobin and I. N. N. Namboothiri, *Eur. J. Org. Chem.*, 2009, 4091. Activated imines/iminiums: (*e*) N. Rastogi, R. Mohan, D. Panda, S. M. Mobin and I. N. N. Namboothiri, *Org. Biomol. Chem.*, 2006, **4**, 3211; (*f*) K. Rajesh, P. Shambhag, M. Raghavendra, P. Bhardwaj and I. N. N. Namboothiri, *Tetrahedron Lett.*, 2010, **51**, 846. Azodicarboxylates: (*g*) M. Dadwal, S. M. Mobin and I. N. N. Namboothiri, *Org. Biomol. Chem.*, 2006, **4**, 2525.
5 For the only comprehensive review: (*a*) C. E. Aroyan, A. Dermenci and S. J. Miller, *Tetrahedron*, 2009, **65**, 4069 and the references cited therein. See also: (*b*) J. L. Methot and W. R. Roush, *Adv. Synth. Catal.*, 2004, **346**, 1035.
6 J. D. McClure, *U.S. Patent*, 1965, 3225083.
7 M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, 1965, **30**, 1357.
8 Between methyl acrylate and acrylonitrile with fumaric/maleic esters: K. Morita and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2732.
9 Between ethyl acrylate and acrylonitrile: J. D. McClure, *J. Org. Chem.*, 1970, **35**, 3045.
10 Enone with acrylate, acrylonitrile and sulfone: J. R. Hwu, G. H. Hakimelahi and C.-T. Chou, *Tetrahedron Lett.*, 1992, **33**, 6469. The same authors proposed a Michael addition of the dienoate generated from the β-alkyl enone by the base to the desired activated alkene as the pathway, rather than the RC pathway.
11 Acrylonitrile with α-halomethyl acrylate and vinyl ketone: (*a*) D. Basavaiah, N. Kumaragurubaran and D. S. Sharada, *Tetrahedron Lett.*, 2001, **42**, 85. Acrylate, acrylonitrile and vinyl ketone with α-bromomethyl acrylate: (*b*) D. Basavaiah, D. S. Sharada, N. Kumaragurubaran and R. M. Reddy, *J. Org. Chem.*, 2002, **67**, 7135.
12 Allenoate with enone: C. A. Evans and S. J. Miller, *J. Am. Chem. Soc.*, 2003, **125**, 12394.
13 MVK and acrylate with dihalonaphthoquinones: C. H. Lee and K.-J. Lee, *Synthesis*, 2004, 1941.
14 (*a*) H. Amri and J. Villieras, *Tetrahedron Lett.*, 1986, **27**, 4307; (*b*) D. Basavaiah, V. V. L. Gowriswari and T. K. Bharathi, *Tetrahedron Lett.*, 1987, **28**, 4591; (*c*) S. E. Mc Dougal and S. E. Schaus, *Angew. Chem., Int. Ed.*, 2006, **45**, 3117.
15 P. T. Kaye and X. W. Nocanda, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1318.
16 (*a*) H. Amri, M. Rambaud and J. Villieras, *Tetrahedron Lett.*, 1989, **30**, 7381; (*b*) S. E. Drewes, N. D. Emslie and N. Karodia, *Synth. Commun.*, 1990, **20**, 1915.
17 G. Jenner, *Tetrahedron Lett.*, 2000, **41**, 3091.
18 D. Basavaiah, V. V. L. Gowriswari, P. Dharma Rao and T. K. Bharathi, *J. Chem. Res. (S)*, 1995, 267.
19 Intramolecular: (*a*) J. K. Erguden and H. W. Moore, *Org. Lett.*, 1999, **1**, 375; (*b*) P. M. Brown, N. Kappel and P. J. Murphy, *Tetrahedron Lett.*, 2002, **43**, 8707; (*c*) P. M. Brown, N. Kappel, P. J. Murphy, S. J. Koles and M. B. Hursthouse, *Tetrahedron*, 2007, **63**, 1100; (*d*) L. C. Wang, A. L. Luis, K. Agapiou, H. Y. Jang and M. J. Krische, *J. Am. Chem. Soc.*, 2002, **124**, 2402; (*e*) A. L. Luis and M. J. Krische, *Synthesis*, 2004, **15**, 2579; (*f*) S. A. Frank, D. J. Mergott and W. R. Roush, *J. Am. Chem. Soc.*, 2002, **124**, 2404; (*g*) R. K. Thalji and W. R. Roush, *J. Am. Chem. Soc.*, 2005, **127**, 16778; (*h*) F. O. Seidel and J. A. Gladysz, *Adv. Synth. Catal.*, 2008, **350**, 2443. Intramolecular asymmetric: (*i*) C. E. Aroyan and S. J. Miller, *J. Am. Chem. Soc.*, 2007, **129**, 256; (*j*) F. O. Seidel and J. A. Gladysz, *Synlett*, 2007, 986.

20 For recent selected examples: (*a*) P. Webber and M. J. Krische, *J. Org. Chem.*, 2008, **73**, 9379; (*b*) S. M. Winbush, D. J. Mergott and W. R. Roush, *J. Org. Chem.*, 2008, **73**, 1818; (*c*) L. M. Stark, K. Pekari and E. J. Sorensen, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 12064.

21 M. Dadwal, R. Mohan, D. Panda, S. M. Mobin and I. N. N. Namboothiri, *Chem. Commun.*, 2006, 338. Although we called this reaction a Morita–Baylis–Hillman (MBH) reaction, according to the present classification (see ref. 5), this vinylogous MBH reaction is more appropriately called a Rauhut–Currier (RC) reaction.

22 X. Sun, S. Sengupta, J. L. Peterson, H. Wang, J. P. Lewis and X. Shi, *Org. Lett.*, 2007, **9**, 4495.

23 J. Wang, H. Xie, L. Zu and W. Wang, *Angew. Chem., Int. Ed.*, 2008, **47**, 4177.

24 (*a*) V. K. Aggarwal, D. K. Dean, A. Mereu and R. Williams, *J. Org. Chem.*, 2002, **67**, 510; (*b*) A. Kumar and S. S. Pawar, *Tetrahedron*, 2003, **59**, 5019.

25 (*a*) M. A. Blanchette, W. Choy, J. T. Davis, A. P. Essenfeld, S. Masamune, W. R. Roush and T. Sakai, *Tetrahedron Lett.*, 1984, **25**, 2183. See also: (*b*) J. J. Li, *Name Reactions*, Springer (India) Pvt. Ltd., New Delhi, 2nd edn, 2003.

26 For selected reviews: (*a*) I. N. N. Namboothiri and N. Rastogi, *Top. Heterocycl. Chem.*, 2008, **12**, 1; (*b*) R. Ballini, L. Barboni, G. Bosica, D. Fiorini and A. Palmieri, *Pure Appl. Chem.*, 2006, **78**, 1857; (*c*) O. M. Berner, L. Tedeschi and D. Enders, *Eur. J. Org. Chem.*, 2002, 1877; (*d*) I. N. N. Namboothiri and A. Hassner, *Top. Curr. Chem.*, 2001, **216**, 1; (*e*) S. E. Denmark and A. Thorarensen, *Chem. Rev.*, 1996, **96**, 137; (*f*) V. V. Perekalin, E. S. Lipina, V. M. Berestovitskaya, and D. A. Efremov, *Nitroalkenes: Conjugated Nitro Compounds*, Wiley, Chichester, UK, 1994, p 1; (*g*) Nitroalkanes and Nitroalkenes in Synthesis, Tetrahedron Symposia-in-Print, No. 41, ed. A. G. M. Barrett, in: *Tetrahedron*, 1990, **46**, 285; (*h*) G. W. Kabalka and R. S. Varma, *Org. Prep. Proced. Int.*, 1987, **19**, 283; (*i*) D. Seebach, E. W. Colvin, F. Lehr and T. Weller, *Chimia*, 1979, **33**, 1.

27 For the Michael addition of aldehydes to nitrodienes: (*a*) S. Belot, A. Massaro, A. Tenti, A. Mordini and A. Alexakis, *Org. Lett.*, 2008, **10**, 4557; (*b*) For the MBH reaction of nitrodienes with carbonyl compounds: see ref. 4d.

28 (*a*) C. Dockendorff, S. Sahhli, M. Olsen, L. Milhau and M. Lautens, *J. Am. Chem. Soc.*, 2005, **127**, 15028; (*b*) N. K. Kochetkov and N. V. Dubikina, *J. Gen. Chem. USSR*, 1958, **28**, 2473.

29 (*a*) T. Y. Kim, H. S. Kim, K. Y. Lee and J. N. Kim, *Bull. Kor. Chem. Soc.*, 1999, **20**, 1255; (*b*) T. Y. Kim, H. S. Kim, K. Y. Lee and J. N. Kim, *Bull. Kor. Chem. Soc.*, 2000, **21**, 521.

30 For a recent procedure: P. K. Pradhan, Sumit Dey, P. Jaisankar and V. S. Giri, *Synth. Commun.*, 2005, **35**, 913.

31 (*a*) M. Yuguchi, M. Tokuda and K. Orito, *J. Org. Chem.*, 2004, **69**, 908; (*b*) A. Pecunioso and R. Menicagli, *J. Org. Chem.*, 1988, **53**, 2614; (*c*) H. Stetter and G. Lorenz, *Chem. Ber.*, 1985, **118**, 1115.

32 For a one-pot synthesis of cyclopentenones *via* conjugate addition of primary nitroalkanes to α,β-unsaturated ketones followed by Nef reaction and aldol condensation: R. Ballini, L. Barboni, G. Bosica and D. Fiorini, *Synthesis*, 2002, 2725.

33 By Pauson–Khand reaction, selected reviews: (*a*) N. E. Schore, *Organic Reactions*, 1991, 40; (*b*) T. Shibata, *Adv. Synth. Catal.*, 2006, **348**, 2328; (*c*) S. Laschat, A. Becheanu, T. Bell and A. Baro, *Synlett*, 2005, 2547; (*d*) S. E. Gibson and N. Mainolfi, *Angew. Chem., Int. Ed.*, 2005, **44**, 3022; (*e*) J. Blanco-Urgoiti, L. Anorbe, L. Perez-Serrano, G. Dominguez and J. Perez-Castells, *Chem. Soc. Rev.*, 2004, **33**, 32; (*f*) M. R. Rivero, J. Adrio and J. C. Carretero, *Eur. J. Org. Chem.*, 2002, 2881; (*g*) T. Sugihara, M. Yamaguchi and M. Nishizawa, *Chem.–Eur. J.*, 2001, **7**, 1589.

34 By zirconium promoted intermolecular coupling of an alkyne, EtMgBr or ethylene, and CO: (*a*) T. Takahashi, Z. Xi, Y. Nishihara, S. Huo, K. Kasai, K. Aoyagi, V. Denisov and E. Negishi, *Tetrahedron*, 1997, **53**, 9123. By Ramberg-Bäcklund reaction: (*b*) G. Casy and R. J. K. Taylor, *Tetrahedron*, 1989, **45**, 455. By cycloreversion reaction: (*c*) G. Stork, G. L. Nelson, F. Rouessac and O. Gringore, *J. Am. Chem. Soc.*, 1971, **93**, 3091.