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Chemoselective synthesis of multifunctional ferrocene-containing derivatives by the cross Rauhut–Currier reaction†

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A simple protocol has been developed for the chemoselective synthesis of ferrocene-containing Rauhut–Currier adducts from 1-ferrocenyl-2-nitroethene and vinyl ketones using 20 mol% of triphenylphosphine. Multifunctional ferrocene derivatives were obtained in moderate to high yields (51–92%) by the coupling between the α -position of vinyl ketones and the β -position of the nitroalkene. The study of the Rauhut–Currier reaction under the described conditions showed that the strong electron-donating group at the β -position of nitroalkenes plays a significant role in the reaction outcome due to prevention of polymerization and stabilization of the zwitterionic intermediate. Additionally, a preparative synthesis of 4-ferrocenyl-3-methylene-5-nitropentan-2-one was carried out and its synthetic transformations showed easy conversion to other useful building blocks.

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Introduction

The cross Rauhut–Currier (RC) reaction provides a new carbon–carbon bond formation between two different electron-deficient alkenes (Michael acceptors) in the presence of nucleophilic catalysts (Lewis bases).^{1,2} The RC transformation involves the coupling between the α -position of the alkene activated by the nucleophilic catalyst and the β -position of another Michael acceptor. According to the literature,^{1,2} the nucleophilic catalyst participates in the conjugate addition to one of Michael acceptors to give zwitterion. This zwitterionic intermediate, acting as a nucleophile, further undergoes the conjugate addition to the second electron-deficient alkene forming a new carbon–carbon bond. Although the RC reaction yields multifunctional compounds that are used for further synthetic transformation and/or total synthesis of natural products,^{1a,3–5} its application is limited due to problematic selectivity control and low reaction efficiency. In fact, the zwitterion can be trapped with other electrophiles present in the reaction, so the self-condensation of the alkenes is often a concurrent reaction under the same conditions.⁶ Therefore, the development of

efficient chemoselective synthetic cross RC protocols is a key challenge and of particular importance for organic chemistry.

Nitroalkenes are well-known electron-deficient olefins that are employed in the cross RC reaction.^{1b,7} Depending on the reaction conditions, the cross RC coupling is directed at the α -position or the β -position of nitroalkenes (Scheme 1).^{8–11} Accordingly, the reaction of nitroalkenes and methyl vinyl ketone (MVK) in the presence of an imidazole–LiCl catalytic system is described.⁸ This catalytic system is also able to promote the cross RC reaction between nitroalkenes and vinyl sulfones.⁹ Under the described conditions, the RC adducts are obtained by the coupling of nitroalkenes at the α -position with methyl vinyl ketone and vinyl sulfones (Scheme 1a). The intermolecular RC coupling at the β -position of nitroalkenes with ethyl allenolate is achieved under mild conditions in the presence of quinidine-derived β -isocupreidine (β -ICD) (Scheme 1b).¹⁰ The phosphine-catalyzed cross RC coupling at the β -position of nitroalkenes with trifluoromethyl-containing acrylonitrile is also reported (Scheme 1b).¹¹ Since the nitro RC products are useful building blocks for the synthesis of complex molecules,⁷ the synthesis of RC type adducts was achieved by the Mukaiyama reaction between nitroalkenes and silyl-diene enol ethers in the presence of bifunctional organocatalyst (Scheme 1c).¹² Although the synthetic protocols to the nitro RC adducts are reported, lack of substrate scope, as well as an explanation of the reactivity of electron-deficient alkenes in the cross RC reaction, requires more comprehensive research with an emphasis on chemoselectivity. In addition, the main problem to employ nitroalkenes in the RC reaction is their easy polymerization in the presence of Lewis bases.¹³ Therefore, constant efforts are made to develop chemoselective methods for the cross RC reaction.

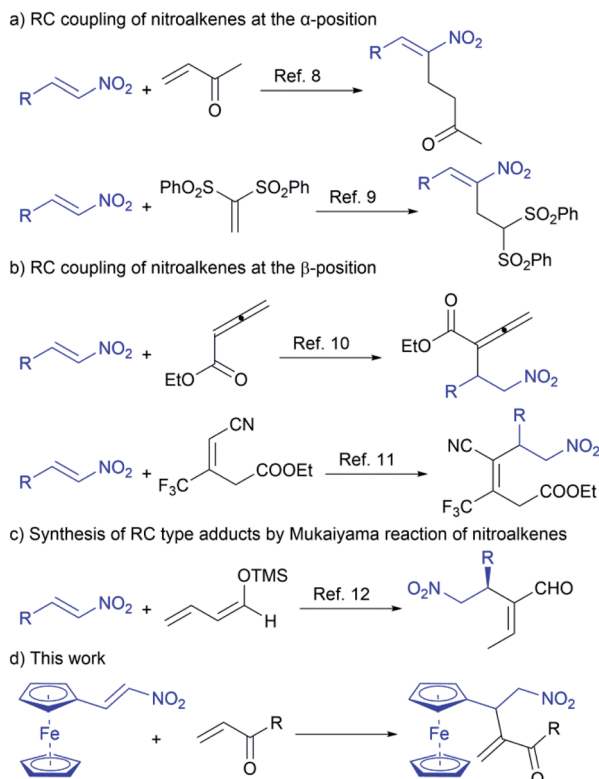
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Scheme 1 Synthetic protocols to the Rauhut–Currier adducts from nitroalkenes.

Our constant research interest in the functionalization of ferrocene, the synthetic transformation of its derivatives as well as the role of this metallocene in the reaction outcomes,¹⁴ has inspired us to employ ferrocene-containing electron-deficient olefin in the cross RC reaction. Herein we report a useful method for the cross RC reaction of ferrocene-containing nitroalkene with vinyl ketones affording multifunctional ferrocene-containing RC products in good yield with complete chemoselectivity (Scheme 1d).

Results and discussion

Our investigation began with a screening of nucleophilic catalysts for their ability to promote the RC reaction between nitroalkene **1** and MVK (**2a**) in DCM (Table 1, entries 1–7). When the nucleophilic tertiary amines (30 mol%) were used as a Lewis base catalyst, the results were not encouraging (Table 1, entries 1–5). Actually, the reactions catalyzed by triethylamine, diazabicyclo[2.2.2]octane (DABCO), and imidazole afforded the mixtures without the products (Table 1, entries 1, 2, and 5). The use of 4-(dimethylamino)pyridine (DMAP) as the nucleophilic catalyst of the RC reaction resulted in traces of product **3a** after stirring at room temperature for 48 hours (Table 1, entry 3), while the reactions with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,1,3,3-tetramethylguanidine (TMG) gave the complex mixtures where are observed the product **3a'** in traces (Table 1, entries 4 and 6). An optimistic yield of 48% is obtained in the triphenylphosphine-catalyzed reaction after stirring for

Table 1 Optimization of the conditions of the cross RC reaction between nitroalkene **1** and MVK (**2a**)^a

Entry	Catalyst (mol%)	Solvent	Time (h)	3a yield ^b (%)
1	Et ₃ N (30)	DCM	24	NR ^{c,d}
2	DABCO (30)	DCM	24	NR ^{c,d}
3	DMAP (30)	DCM	48	<5
4	DBU (30)	DCM	24	Complex mixture ^e
5	Imidazole (30)	DCM	24	NR ^{c,d}
6	TMG (30)	DCM	24	Complex mixture ^e
7	PPh ₃ (30)	DCM	24	48
8	PPh ₃ (30)	MeCN	48	18
9	PPh ₃ (30)	Toluene	72	28
10	PPh ₃ (30)	THF	120	23
11	PPh ₃ (30)	AcOEt	120	20
12	PPh ₃ (30)	CHCl ₃	24	90
13	PPh₃ (20)	CHCl₃	24	92
14	PPh ₃ (10)	CHCl ₃	24	75

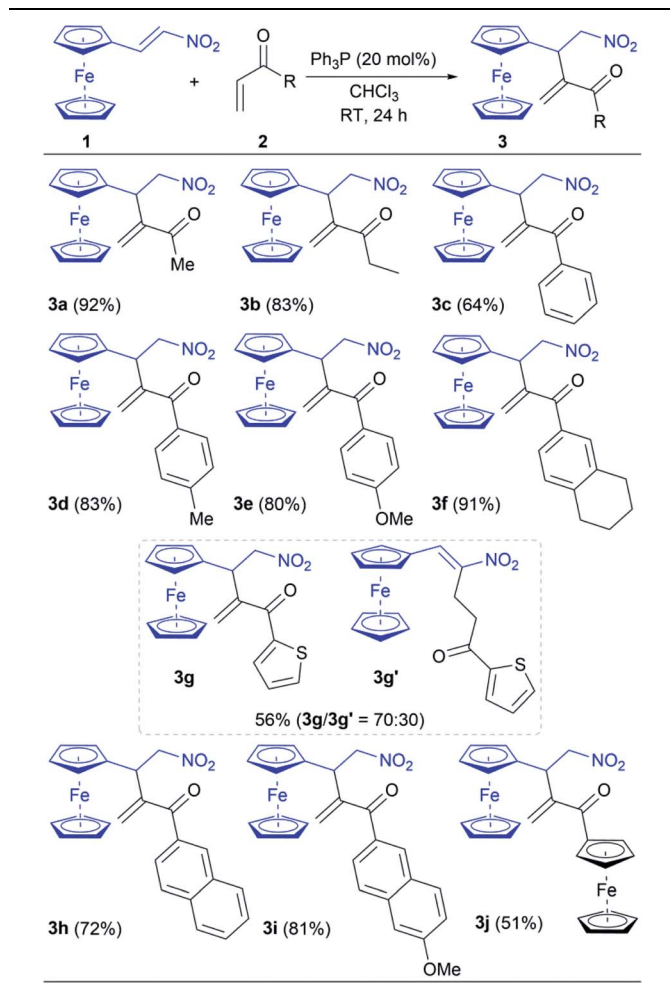
^a All reactions were carried out with **1** (0.2 mmol) and **2a** (0.24 mmol) in solvent (1 mL) at room temperature. ^b Isolated yield by flash column chromatography on silica gel. ^c NR: no reaction. ^d **1** is completely recovered by flash column chromatography. ^e **3a'** was observed and isolated in traces.

24 hours at room temperature (Table 1, entry 7). Therefore, triphenylphosphine was selected as a convenient catalyst for the RC reaction, after which solvent screening was performed (Table 1, entries 8–12). Further attempts to increase the yield performing reactions in several solvents afforded **3a** in 90% yield in CHCl₃ (Table 1, entry 12), while the other solvents gave a poor yield (Table 1, entries 8–11). The catalyst loading was also investigated (Table 1, entries 12–14). We found that the use of 20 mol% of triphenylphosphine in CHCl₃ led to a high yield of RC adduct **3a** in the intermolecular reaction between nitroalkene **1** and **2a** (Table 1, entry 13). RC adduct **3a'** was not observed in the phosphine-catalyzed reactions indicating that the phosphine carries out the nucleophilic attack on **2a** generating the corresponding zwitterion for the RC coupling with **1**. The established protocol offers the chemoselective synthesis of ferrocene-containing RC adduct **3a**, and the reaction is conducted under an air atmosphere demonstrating the ease of operation and practicality.

After optimization of reaction conditions (Table 1, entry 13), the scope of phosphine-catalyzed intermolecular RC reaction between nitroalkene **1** and vinyl ketones **2** was investigated (Table 2). The obtained results, listed in Table 2, show that the reaction of **1** with vinyl ketones **2** is easily completed under the established conditions giving the corresponding product **3** in



Table 2 Substrate scope of the intermolecular RC reaction between nitroalkene **1** and vinyl ketones **2**



51–92% yields. These conditions provide the synthetic pathway with complete chemoselectivity since the cross RC coupling at the β -position of nitroalkene **1** was only achieved, except for the reaction with **2g**. While products **3a** and **3b** were obtained in high yields (92% and 83%, respectively) employing the corresponding alkyl vinyl ketones **2a** and **2b**, the yields of reactions with aromatic vinyl ketones **2c–j** are varied from moderate to excellent due to the different electron-donating and steric effects of aromatic groups. Thus, aryl vinyl ketones **2c–f** reacted with **1** under the optimal conditions giving the corresponding products **3c–f** in 64–91% yields (Table 2). Notably, substituents on the phenyl group of **2c–f** affected the reaction outcomes. Utilizing phenyl vinyl ketone (**2c**) in the RC reaction with **1** led to **3c** in a 64% yield, while vinyl ketones **2d–f** with the electron-donating substituted phenyl group increased the yield up to 91% (Table 2). Heteroaryl vinyl ketone **2g** smoothly gave a product mixture with lower efficiency. It is found that the reaction of **2g** provided the desired product **3g** as well as product **3g'** in a total yield of 56% (the ratio was 70 : 30 for **3g** and **3g'**, respectively; see ESI†). Therefore, the catalyst participated in the conjugate addition to both of the Michael

acceptors, whereby nucleophilic coupling partners were generated and subsequently cross-reacted with the present electrophile. The outcome indicated that the electron-donating effect of the 2-thienyl group significantly reduces the electrophilicity of **2g** leading to the unfavoured addition to **1**. Hence, the result of the reaction between **1** and **2g** was the cross RC coupling at the β -position of nitroalkene **1** as well as the coupling at α -position. In the case of vinyl ketones **2h** and **2i**, the corresponding products **3h** and **3i** were obtained in a good yield of 72% and 81%, respectively. The influence of the steric effect was evident in the reaction between **1** and acryloylferrocene (**2j**) due to the presence of two bulky ferrocene units which definitely affect the reaction outcome. Product **3j** was suitable for single-crystal X-ray diffraction analysis (Fig. 1).¹⁵ The analysis showed that two ferrocene units in the compound are mutually almost perfectly orthogonal. Thus a dihedral angle between two adjacent cyclopentadienyl rings (the C11–C15 and C16–C20 rings) is $86.4(2)^\circ$. This molecular geometry is clearly caused by a relatively strong intramolecular C–H \cdots π interaction¹⁶ shown in Fig. 1 with the dotted green line. Namely, the C11–H group is directed to the midpoint (Cg) of the C16–C20 ring with an H \cdots Cg distance of 2.84 Å (this distance for the position of H atoms normalized to neutron values is only 2.70 Å). The C11–H \cdots Cg angle also has a desirable value of 151° . Selected bond lengths in **3j** are given in Table S1† (see ESI†).

The potential impact of this method would be expanded if other α,β -unsaturated compounds with an electron-withdrawing group (Michael acceptors) could be used as a partner in the cross RC reaction with nitroalkenes **1**. Thus, our investigation is directed to employ Michael acceptors **2k–m** in the RC reaction under the optimal conditions (Scheme 2). Unfortunately, cyclic enone **2k** did not cross-react with **1** under the conditions as well as vinyl Michael acceptors – methyl

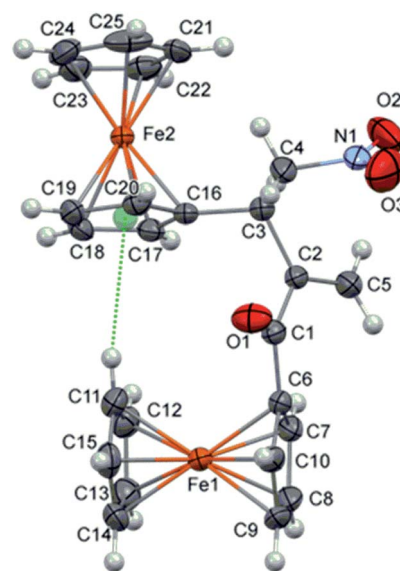
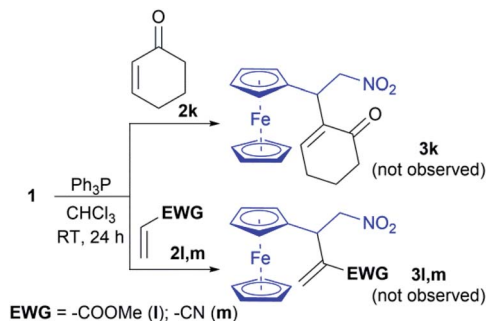


Fig. 1 Crystal structure of molecules **3j** (thermal ellipsoids are shown at the 40% probability level). Dotted green line represents intramolecular C–H \cdots π interaction.





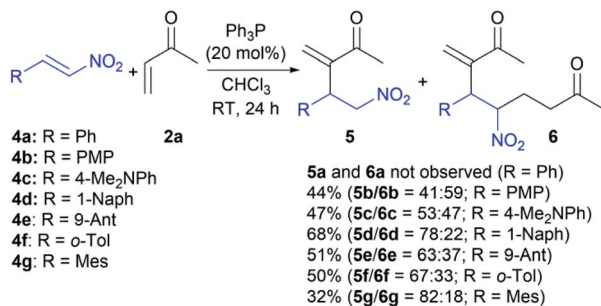
Scheme 2 Cross RC reaction between nitroalkene **1** and Michael acceptors **2k–m**.

acrylate (**2l**) and acrylonitrile (**2m**). Therefore, we can define that the developed method of the intermolecular RC reaction with **1** is specific for vinyl ketones **2a–j**.

In the next step, we submitted various β -aryl nitroalkenes **4a–g** in the RC reaction with vinyl ketone **2a** under the established conditions (Scheme 3). The reaction of β -nitrostyrene (**4a**) and MVK (**2a**) in chloroform in the presence of 20 mol% of Ph_3P at room temperature for 24 h resulted in a complete polymerization of nitroalkene **4a**¹³ and self-condensation of MVK (**2a**).⁶ Actually, the product of the self-condensation was only isolated in a yield of 95%. The same reaction conditions were applied in the RC reaction between nitroalkene **4b** and **2a**. Since the ferrocenyl group has a stronger electron-donating effect than the phenyl group,¹⁷ we expected that the methoxy group at the para-position on the benzene ring of nitroalkene **4b** could affect the reaction outcome. In fact, the strong electron-donating effect of the methoxy group should prevent rapid polymerization due to decreasing electrophilicity at the β -position of the nitroalkene¹³ and allow cross-reacting of **4b** with partner **2a**. Indeed, the reaction gave the product mixture followed by the polymerization of **4b**, as well as the self-condensation of **2a** (*ca.* 40%). The products were identified as desired RC adduct **5b** and another **6b** with a total yield of 44% (Scheme 3). In this case, the reaction conditions favored the formation of product **6b** (the ratio is 41 : 59 for **5b** and **6b**, respectively). A similar trend was remarked in the reactions of nitroalkenes bearing stronger electron-donating groups at the β -position such as **4c** and **4d** because the product mixture was formed in a variable product ratio (Scheme 3). Also, polymerization of **4** and self-

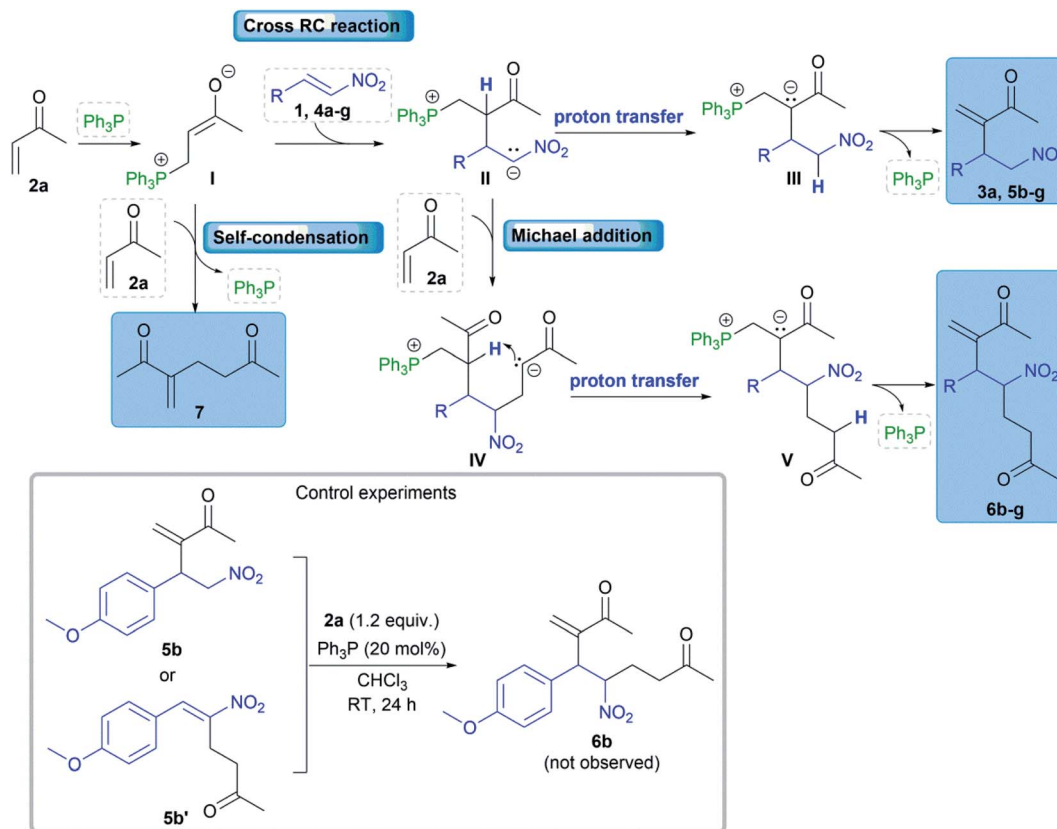
condensation of **2a** were observed in these reactions, but to a lesser extent. Nitroalkene **4c** with the dimethylamino group at the para-position on the benzene ring in the reaction with **2a** gave both **5c** and **6c** in a total yield of 47% with an almost equal ratio of the products (Scheme 3). On the other hand, nitroalkene **4d** reacted with **2a** giving both products with a good efficacy (68% yields) and dominantly RC adduct **5d** (Scheme 3). The steric effect of the bulky substituent at the β -position of nitroalkene **4d** could affect this reaction outcome. Hence, nitroalkenes **4e–g** with large aryl groups (9-anthracenyl, *o*-tolyl, and mesityl) at the β -position were employed to determine the influence of steric effect on the reaction efficiency. The reaction outcomes indicated that the efficiency decreases with increasing the group voluminosity and that nitroalkenes **4e–g** mostly form RC product **5**. While nitroalkenes **4e** and **4f** provided similar results in terms of the reaction efficiencies (51% and 50%, respectively) and product distribution (the ratios are 63 : 37 for **5e** and **6e** and 67 : 33 for **5f** and **6f**, respectively), nitroalkene **4g** gave the low efficiency (32%) with dominant RC adduct **5g** (the ratio is 82 : 18 for **5g** and **6g**, respectively). These results showed that both the electronic and steric effects of the substituent at the β -position of nitroalkenes impact the outcome of the cross RC coupling, and the nitroalkenes with stronger electron-donating substituents at the β -position allow to obtain the corresponding RC adducts **5**.

A plausible reaction mechanism could be explained by the influence of electro-donating substituents at the β -position of nitroalkenes (Scheme 4). The cross RC reaction certainly includes the generation of zwitterion **I** by the conjugate addition of nucleophilic catalyst to methyl vinyl ketone (**2a**) and the subsequent addition of **I** to the corresponding nitroalkene **1**, **4a–g** to form a new zwitterion **II** (Scheme 4).¹ An alternative pathway of zwitterion **I** is the addition to another molecule of methyl vinyl ketone (**2a**). The corresponding cross RC adduct **3a**, **5a–g** as well as homo RC adduct **7** are formed by proton transfer following the regeneration of the nucleophilic catalyst (Scheme 4). The study showed that zwitterion **II** generated from **1** (ferrocenyl group at the β -position of the nitroalkene) exclusively undergoes proton transfer leading to the RC adduct. The reactions with β -aryl nitroalkenes **4a–g** gave the product mixtures. The RC adduct **5** is obtained together with the product **6** formed by the Michael addition of the zwitterion **II** to another molecule of **2a** (Scheme 4). The key intermediate in the mechanism is zwitterion **II** which can follow two possible pathways. The first pathway is proton transfer followed by elimination of the phosphine providing RC adduct **5**, and the second is the Michael addition of formed **II** to **2a** which processes to product **6** *via* intramolecular proton transfer and the elimination of the catalyst (Scheme 4). The second pathway is defined by control experiments that confirmed the formation of product **6** *via* zwitterion **II** (Scheme 4). The first control experiment was performed between RC adduct **5b** and **2a** and showed that product **5b** could not be converted to **6b** under the RC reaction conditions. Although product **5b'** was not observed after the reaction between **4b** and **2a** in the presence of the phosphine, a possible synthetic pathway to **6** could be double RC reaction. The second control experiment was performed assuming that product **5b'** is



Scheme 3 Cross RC reaction between nitroalkenes **4** and MVK (**2a**).



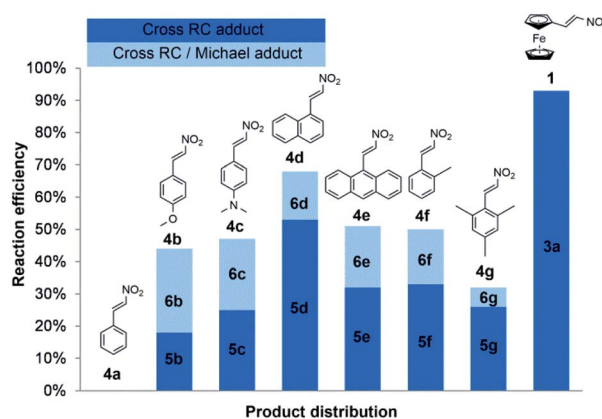


Scheme 4 Proposed reaction mechanism.

formed by the RC coupling at the α -position of **4b** and then **5b'** cross-reacts with **2a** as a partner in the subsequent RC reaction (Scheme 4).¹⁸ This experiment eliminated the double RC reaction as the pathway to product **6** due to the absence of **6b** in the reaction mixture after 24 hours. Based on the obtained results, zwitterion **II** generated from nitroalkenes with a stronger electron-donating substituent at the β -position has favored the formation of RC adducts rather than the products of the Michael addition. In addition, nitroalkenes with the large aryl groups at the β -position predominantly provided the cross RC adducts presumably due to the steric hindrance that blocked the Michael addition. Therefore, the substituents affect the stability of zwitterion **II**, and their electron-donating properties could be crucial for the chemoselectivity and regioselectivity of the cross RC reactions.

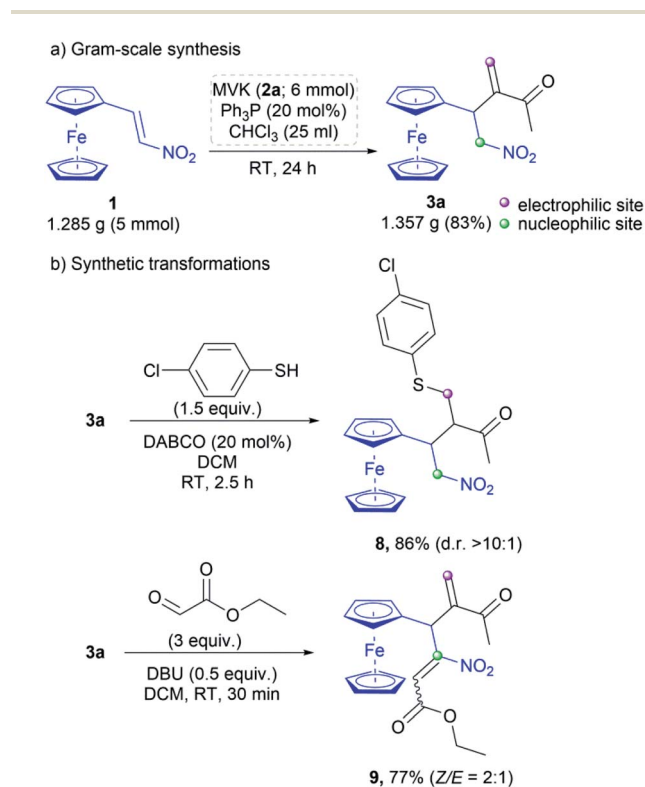
We obtained comparable results in terms of electron and steric effects of substituents at the β -position of nitroalkenes and their ability to be used in the cross RC reaction (Fig. 2). The results indicated that the electron-donating effect of the ferrocenyl group is significantly stronger than the effects of *p*-anisyl, 4-dimethylamino phenyl, and 1-naphthyl groups, while the weakest effect shows the phenyl group. These observations are consistent with the previous reports.¹⁷ Nitroalkenes **4a**, **4b**, and **4f** with weak electron-donating substituents at the β -position easily undergo polymerization, while nitroalkenes **1**, **4d**, **4e**, and **4g**, with stronger electron-donating effect of substituents and/or large aryl groups, are more stable under the reaction conditions.

Thus, the reaction between **4a** and **2a** does not give the cross-product due to an easy polymerization of **4a**. The generation of zwitterion **I** is probably a slower reaction than polymerization of **4a** and thus zwitterion **I** only has the opportunity to react with another molecule of **2a** giving **7** (Scheme 4). On the other hand, more stable nitroalkenes smoothly react with **2a** in the cross RC reaction. The results showed that the reaction efficiency, as well as the distribution of products, depends on the electronic and steric properties of nitroalkenes (Fig. 2). The reactions of

Fig. 2 Influence of electronic and steric effects of substituents at the β -position of nitroalkenes on chemoselectivity.

nitroalkene **4b–g** gave the RC product **5** together with the product **6** while **1** only formed the corresponding RC adduct. Therefore, the reactivity of **1** in the RC reaction is directly related to the strong electron-donating and steric effects of the ferrocenyl group. The ratio of **5** and **6** suggests that fine-tuning the electronic and/or steric properties of nitroalkenes can achieve the chemoselective protocol. Briefly, the electron-donating and steric effects of the substituents at the β -position of nitroalkenes could play a double role in the cross RC reaction: (i) prevent the polymerization of nitroalkenes and (ii) contribute to the stabilization of zwitterion **II** during the RC transformation.

The developed protocol is validated through the gram-scale synthesis of **3a** (Scheme 5a). RC adduct **3a** was obtained in 83% yield by the reaction of 1.285 g (5 mmol) of nitroalkene **1** under the optimal conditions. Further synthetic transformations of **3a** were also performed to demonstrate the importance of the RC product as a building block due to the presence of both nucleophilic and electrophilic centers (Scheme 5b). The RC product was subjected to the thia-Michael addition with 4-chlorothiophenol in the presence of DABCO (20 mol%).¹⁹ The corresponding product **8** was obtained in 86% yield with high diastereoselectivity (d. r. > 10 : 1). Under Henry conditions,²⁰ **3a** was reacted with ethyl glyoxylate to afford product **9** in 77% yield as a mixture of *Z/E* isomers (Scheme 5b). The isomers were separated by column chromatography on silica gel and the ratio was 2 : 1 for *Z* and *E* isomers, respectively.



Scheme 5 (a) Gram-scale synthesis of RC adduct **3a**; (b) synthetic transformations of RC adduct **3a**.

Conclusions

The chemoselective synthesis of multifunctional ferrocene derivatives by the cross Rauhut–Currier reaction between 1-ferrocenyl-2-nitroethene and vinyl ketones has been reported. The established reaction conditions provided the RC coupling of the nitroalkene at the β -position giving the corresponding products in moderate to high yields with complete chemoselectivity, except for the reaction with 2-thienyl vinyl ketone. Based on the results, we observed that the ferrocenyl group plays a significant role in this coupling process. The present study showed that the reaction efficiency directly depends on the electronic and steric properties of substituents at the β -position of nitroalkenes and the strong electron-donating bulky ferrocenyl group at the β -position certainly contributes to a more successful protocol. Reducing electrophilicity at the β -position of nitroalkenes ensures the conjugate addition of the catalyst to the vinyl ketone that is the more electrophilic partner in the reaction. The developed method overcomes the typical challenges associated with nitroalkene instability, limited selectivity, and low reaction efficiency, providing building blocks that can be used in further synthesis.

Experimental

General procedure for the cross Rauhut–Currier reaction

To a solution of nitroalkene **1** (51.4 mg, 0.2 mmol, 1 equiv.) and the corresponding vinyl ketone **2a–j** (0.24 mmol, 1.2 equiv.) in chloroform (1 mL) at room temperature, triphenylphosphine (10.5 mg, 20 mol%) was added. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel with *n*-hexane/ethyl acetate as eluent. Following the general procedure for the RC reaction, **3a** was obtained as a yellow solid in 92% yield (60.2 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9 : 1); mp 82–83 °C; IR (KBr, cm^{-1}) 1674 (C=O), 1549 (NO_2), 1381 (NO_2); ^1H NMR (200 MHz, CDCl_3) δ 6.12 (s, 1H, $\text{CH}_2=\text{C}$), 5.81 (s, 1H, $\text{CH}_2=\text{C}$), 5.06–4.74 (m, 2H, CH_2), 4.64–4.42 (m, 1H, CH), 4.17–4.13 (overlapped m, 2H, C_5H_4), 4.15 (overlapped s, 5H, C_5H_5), 4.11–4.06 (m, 1H, C_5H_4), 4.06–4.01 (m, 1H, C_5H_4), 2.34 (s, 3H, CH_3); ^{13}C NMR (50 MHz, CDCl_3) δ 198.0, 147.8, 127.6, 87.2, 78.7, 69.3, 68.3, 68.2, 66.8, 39.5, 26.2. Anal. calcd for $\text{C}_{16}\text{H}_{17}\text{FeNO}_3$: C, 58.74; H, 5.24; Fe, 17.07; N, 4.28; O, 14.67. Found: C, 58.81; H, 5.25; N, 4.28.

Conflicts of interest

There are no conflicts to declare.

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