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Domino [4 + 1]-annulation of α,β-unsaturated δ-amino esters with Rh(II)–carbenoids – a new approach towards multi-functionalized *N*-aryl pyrrolidines†

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Catalytic decomposition of diazomalonates and other diazoesters using Rh(II)- and Cu(II)-complexes in the presence of α,β-unsaturated δ-(*N*-aryl)amino esters gives rise to the formation of multi-functionalized pyrrolidines with yields of up to 82%. The reaction apparently occurs as a domino process involving the initial *N*-ylide formation followed by intramolecular Michael addition to the conjugated system of amino esters to afford the pyrrolidine heterocycle. The whole process can also be classified as a [4 + 1]-annulation of the δ-amino α,β-unsaturated ester with the carbenoid intermediate.

Introduction

The pyrrolidine unit is an important heterocyclic element occurring in the structure of different natural and unnatural compounds that display a wide range of biological activities.[1,2] In pharmaceutical chemistry pyrrolidine is a structural element for many medicines.[3–5] Hence, the development of new methodologies towards the synthesis of functionalized pyrrolidines remains a highly valuable and actual research area for synthetic organic chemists.

Numerous methods are described in the literature for the creation of the pyrrolidine structure,[6] however to the best of our knowledge only a few catalytic reactions of diazo compounds have been used so far for this purpose.[7–9] These primarily involve intramolecular carbenoid N–H insertion reactions of γ-amino diazocarbonyl compounds,[7] ring enlargement of N-substituted azetidine derivatives during Cu(II)-catalyzed decomposition of diazocarbonyl compounds,[8] and others.[9]

Closely related to our investigations in this field is the research on the Rh-catalyzed three-component domino reaction of diazocarbonyl compounds with anilines and β,γ-unsaturated α-keto esters to produce pyrrolidines as a mixture of four diastereomers in moderate to good yields (Scheme 1).[9b]

Herein we present the results of the formal [4 + 1]-cycloaddition of carbenoids, generated by transition metal-catalyzed decomposition of diazomalonates and other diazoesters, with a variety of *N*-aryl substituted α,β-unsaturated δ-amino esters, which gives rise to multi-functionalized pyrrolidines. The products are obtained in one step with typically good yields as a mixture of two diastereomers.

Results

To elucidate the scope and limitations of the processes studied, a wide range of α,β-unsaturated δ-amino esters **1a–h** were employed in the study, which varied by the nature of *p*-substituents on the *N*-aryl group (**1a**, **1b**) and at the atom C-5 of the alkyl chain (**1c–1h**). With regard to diazo compounds typical representatives of the diazoesters were employed as precursors to carbenoids, namely diazomalonates **2a,b**, their cyclic analogue diazo Meldrum's acid **2c**, and diazoacetates **2d** and **2e** (Fig. 1).

Rh(II)-Complexes are currently believed to be among the most suitable catalysts for the reactions of diazo compounds with different substrates.[10] At the same time, it has been recently shown that Cu(II), Ru(II), and other transition metal complexes in many cases are no less efficient and selective catalysts for similar processes.[11–13] Accordingly, not only typical Rh(II)-catalysts were used for generation of metal–carbenes,

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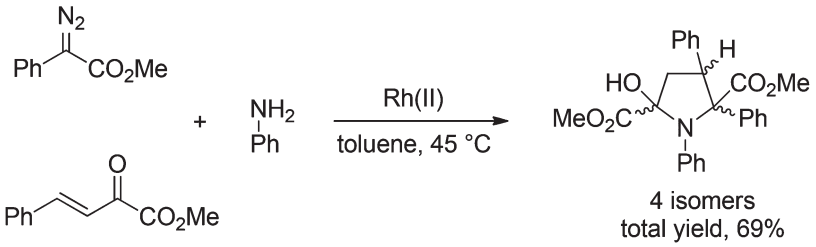


Scheme 1 Rh-catalyzed three-component domino reaction of diazo compounds with anilines and β,γ-unsaturated α-keto esters.[9b]

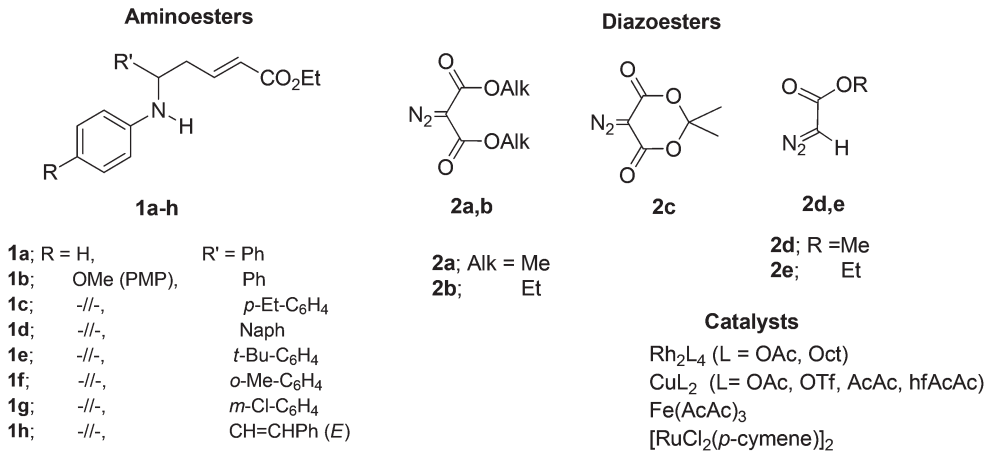


Fig. 1 The structures of amino esters **1**, diazo compounds **2** and catalysts used in this study.

but complexes of copper(II), iron(III), and ruthenium(II) were tested as well (Fig. 1).

*Reactions of diazomalonates **2a,b***. Preliminary experiments were carried out using amino ester **1a** and diazomalonate **2a** in methylene chloride at room temperature with dirhodium tetraacetate which is known as the standard catalyst for decomposition reactions of diazo compounds.[10] Based on universally known results of these reactions one might expect that in the presence of ester **1a** with a secondary N–H group, the principal direction of diazomalonate **2a** reaction should be insertion of the intermediate Rh(II)–carbenoid into the N–H-bond of the amino group.

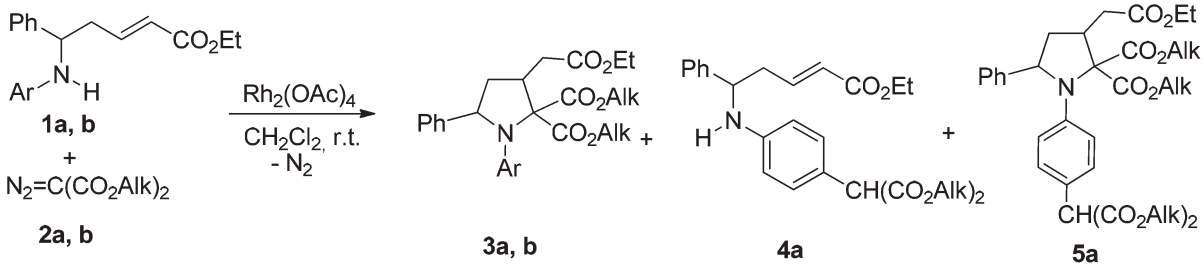
After work-up and chromatographic separation of the reaction mixture two main products were isolated in 56% combined yield (60% based on the recovered starting material) which by their composition were in fact consistent with the assumed insertion adduct. However, the detailed structural investigation revealed that none of them were the expected N–H-insertion product. In fact, these were pyrrolidine **3a** (as a mixture of two diastereomers) and the C–H-insertion product **4a** of carbenoid into the *p*-C–H-bond of the N–phenyl group (Table 1, entry 1).

In order to increase the conversion of amino ester **1a** and thus to enhance the yield of the principal reaction product **3a**, the proportion of diazomalonate **2a** was enhanced at first by 2 times and then by 4 times (entries 2 and 3). But instead of increasing the yield of pyrrolidine **3a** this resulted in the appearance of a new reaction product – a 1 : 2-adduct of the starting amino ester **1a** with di(alkoxycarbonyl)carbene, which had the structure of pyrrolidine **5a** (35% and 47% yield, respectively). Simultaneously, in the first case the yield of pyrrolidine **3a** decreased by almost two times (entry 2), while in the case of the 1 : 4 ratio of reagents the formation of pyrrolidine **3a** was not detected at all (entry 3).

To prevent attack of the Rh(II)–carbenoid on the *p*-C–H-bond of the N–phenyl group of amino ester **1** and hence to avoid formation of the side products of the types **4** and **5**, the ensuing experiments were carried out with *p*-MeO-phenyl (PMP) amino esters **1b–h**. As one would expect, on decomposition of diazomalonates **2a,b** with $Rh_2(OAc)_4$ in the presence of the new amino ester **1b**, the yield of pyrrolidines **3b** and **3b′** increased considerably (up to 70%), while the parallel processes of C–H-insertion were completely suppressed (entries 4 and 5).

Thus it was established that the yields of pyrrolidines **3a,b** in catalytic reactions of diazomalonates **2a,b** in the presence of aminoesters **1** catalyzed by $Rh_2(OAc)_4$ did not exceed 70%. In an effort to elucidate the efficiency of other catalysts in these reactions, several alternative transition metal complexes were also tested for this purpose, namely $Rh_2(Oct)_4$ and a series of copper complexes, $Fe(acac)_3$ and $[RuCl_2(p\text{-cymene})]_2$ (Table 2). The reactions were carried out in dichloromethane, benzene or trifluoromethylbenzene at 25 °C (CH_2Cl_2), 80 °C (C_6H_6) or 103–104 °C ($CF_3C_6H_5$), using amino esters **1b,c** and dimethyl diazomalonate **2a** as the reagents in the ratio of 1 : 2 to 1 : 3.

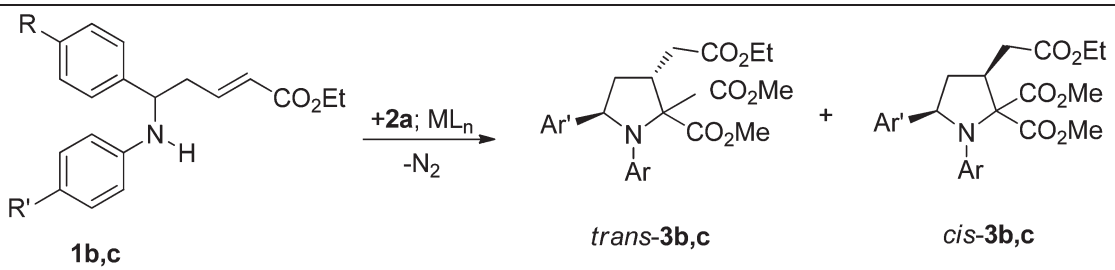
Table 1 Dirhodium tetraacetate-catalyzed reaction of diazomalonates **2a,b** with amino esters **1a,b**



Entry	Reagents	Ratio **1**/**2**	Yield[a] [%] **3**	**4a**	**5a**	Combined yield [%]
1	**1a**; **2a**	1/1.1	**3a**; 50	5.5	—	56
2	**1a**; **2a**	1/2	**3a**; 26	—	35	61
3	**1a**; **2a**	1/4	—	—	47	47
4	**1b**; **2a**	1/2	**3b**; 69	—	—	69
5	**1b**; **2b**	1/2	**3b′**; 70	—	—	70

[a] $Rh_2(OAc)_4$ (0.5–1.0 mol%), DCM, r.t., 12.5–16 h.

Table 2 Transition metal-catalyzed reactions of amino esters **1b**, **1c** with diazomalonate **2a**



Entry	Amine, no. R, R′	Catalyst (mol%)	Combined yield *trans* + *cis*-**3** [%]	d.r.; *trans*/*cis*
1	**1b**; H, OMe	$Rh_2(OAc)_4$ (2)	**3b**; 65[a]	1.75 : 1
2	**1b**; H, OMe	$Rh_2(Oct)_4$ (2)	**3b**; 68[a]	1.6 : 1
3	**1c**; Et, OMe	$Rh_2(OAc)_4$ (4)	**3c**; 72[a]	1.5 : 1
4	**1c**; Et, OMe	$Rh_2(Oct)_4$ (2)	**3c**; 82[a]	1.7 : 1
5	**1b**; H, OMe	$Cu(OAc)_2$ (5)	NR[a,b]	—
6	**1b**; H, OMe	$Cu(OAc)_2$ (10)	**3b**; 21[c]	1 : 1
7	**1b**; H, OMe	$Cu(acac)_2$ (5)	NR[b,c]	—
8	**1b**; H, OMe	$Cu(hfacac)_2$ (5)	**3b**; 51[c]	1 : 1
9	**1b**; H, OMe	$Cu(OTf)_2$ (10)	**3b**; 49[c]	1.9 : 1
10	**1b**; H, OMe	$Fe(acac)_3$ (5)	NR[b,d]	—
11	**1b**; H, OMe	$[RuCl_2(p\text{-cymene})]_2$ (2)	NR[a,b]	—

[a] DCM, r.t., 1.5–10 h. [b] No reaction. [c] C_6H_6, 80 °C, 3–7.5 h. [d] $PhCF_3$, 103.5 °C, 5 h.

The most efficient catalyst in this series of experiments was found to be $Rh_2(Oct)_4$ (Table 2). Its application under otherwise identical reaction conditions allowed us to increase the yield of the target pyrrolidines **3b** and **3c** up to 82% (entry 4), that is 10–15% more than that with dirhodium tetraacetate (entries 1 and 3).

When copper catalysts were used, the highest yields were obtained with copper(II) 1,1,1,5,5,5-hexafluoroacetylacetonate and copper(II) triflate in benzene at 80 °C (Table 2, entries 8 and 9). Decomposition of diazomalonate **2a** with Cu(II) acetate does not occur effectively at 25 °C and only by increasing the amount of the catalyst to 10 mol% and heating the reaction mixture to reflux for many hours we succeeded in the preparation of pyrrolidine **3b** in low yield (entries 5 and 6). Copper(II) acetylacetonate, $Fe(acac)_3$, and $[RuCl_2(p\text{-cymene})]_2$ were all found to be inefficient catalysts for the process studied (entries 7, 10, 11).

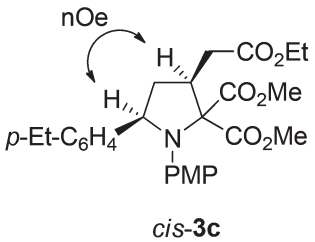
In these processes pyrrolidines **3a–c** were formed as a mixture of *cis*- and *trans*-stereoisomers in different ratios (Table 2). The separation of these mixtures was a challenging task but, nevertheless, in the majority of cases a quantity of both diastereomers of pyrrolidines **3** (*trans* and *cis*) was iso-

lated in their pure state using a combination of flash chromatography and preparative TLC. The structure of the isolated compounds **3a–c**, **4a**, and **5a** was unambiguously established using spectroscopy methods (^{1}H, ^{13}C NMR, IR, and UV), and their composition was confirmed by HRMS. The relative configuration of the *cis*-isomer **3c** was established based on nOe experiments (Fig. 2), and the structure and configuration of the *trans*-pyrrolidine **3b** was confirmed by X-ray crystal structure analysis (Fig. 3). The configurational assignment of the other pyrrolidines **3** was made by comparison and analogy of the related spectroscopy data of *cis*- or *trans*-diastereomers of pyrrolidine **3b** (see ESI,† p. S2 and S3).

Summing up the results of this part of research one can conclude that the best conditions found for the preparation of pyrrolidines **3a–c** from amino esters **1a–c** and diazomalonates **2a,b** are application of $Rh_2(Oct)_4$ and carrying out the catalytic reaction at room temperature in CH_2Cl_2.

In order to estimate further the scope and limitations of the process studied, a series of experiments with other amino esters **1d–h** was performed under the suitable conditions found for **1a–c** (Table 3). The reaction time was varied depending on the disappearance of amino esters **1** in the reaction mixture, which was monitored using TLC and ^{1}H NMR spectroscopy.

It was established that amino esters **1d–g** carrying 5-Ar′ or 5-Naph groups with different substituents at *p*-, *o*- or *m*-positions of the aryl ring furnished pyrrolidines **3d–g** in good yields (62–79%) as well (entries 3–6). A moderately lower yield of pyrrolidine **3h** (42%) was only obtained with the 5-(styryl)-substituted amino ester **1h** (entry 7). The origin of this might be the competitive cyclopropanation of the electron-rich styryl double bond.[15] In all experiments the *trans*-stereoisomer of pyrrolidines **3** was produced as the major stereoisomer.



cis-**3c**

Fig. 2 Configuration of the minor isomer *cis*-**3c** as revealed by NOESY experiments.

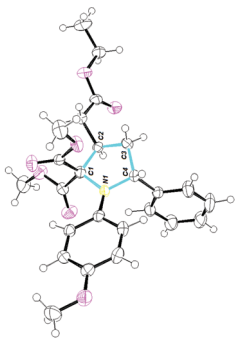
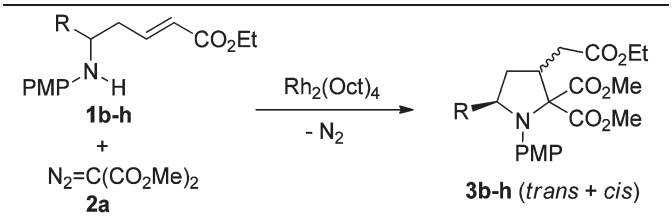


Fig. 3 ORTEP-generated[14] structure of the major isomer of pyrrolidine *trans*-**3b**.

Table 3 $Rh_2(Oct)_4$-catalyzed reaction of diazomalonate **2a** with amino esters **1b–h**



3b-h (*trans* + *cis*)

Entry	Amine; R	Combined yield[a] [%]	d.r.; (*trans*/*cis*)
1	**1b**; Ph	68	1.6 : 1
2	**1c**; *p*-Et-C_6H_4	82	1.7 : 1
3	**1d**; Naph	79	1.8 : 1
4	**1e**; *p*-*t*-Bu-C_6H_4	62	2.1 : 1
5	**1f**; *o*-Me-C_6H_4	76	2.4 : 1
6	**1g**; *m*-Cl-C_6H_4	75	1.8 : 1
7	**1h**; CH=CHPh (*E*)	42	2.4 : 1

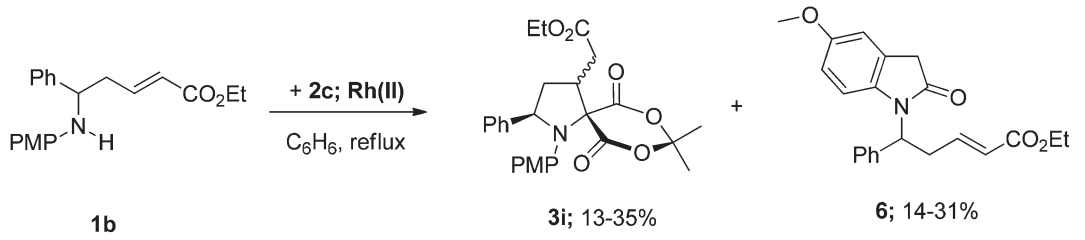
[a] $Rh_2(Oct)_4$ (2 mol%), DCM, r.t., 2–23 h.

Reactions of diazo Meldrum's acid ***2c*** (the cyclic analogue of diazomalonates **2a,b**) with amino ester **1b** were carried out using $Rh_2(OAc)_4$ and $Rh_2(Oct)_4$ in boiling benzene due to the high thermo-catalytic stability of this diazo compound. As the main products in these reactions spirocyclic pyrrolidine **3i** and indoline-2-one **6** were obtained (Scheme 2).

The yields of pyrrolidine **3i** and indolineone **6** were rather low, however, and could not be significantly improved, neither by an increase of the amount of the diazo compound nor by changing the catalyst from $Rh_2(OAc)_4$ to $Rh_2(Oct)_4$. A two-fold increase of the diazo compound/amino ester ratio (4 : 1) reduced the yield of pyrrolidine **3i** (from 35 to 13%) and slowed down the rate of the process. Replacement of $Rh_2(OAc)_4$ with $Rh_2(Oct)_4$ notably accelerated the decomposition process but did not increase the yield of pyrrolidine **3i** (34%), while the yield of indolineone **6** markedly enhanced on changing the catalyst (from 14 to 31%). The structure of compounds **3i** and **6** was assigned using a set of spectroscopy methods including two-dimensional NMR-techniques such as ^{1}H–^{1}H-COSY and HMBC (see ESI,† p. S2 and S3).

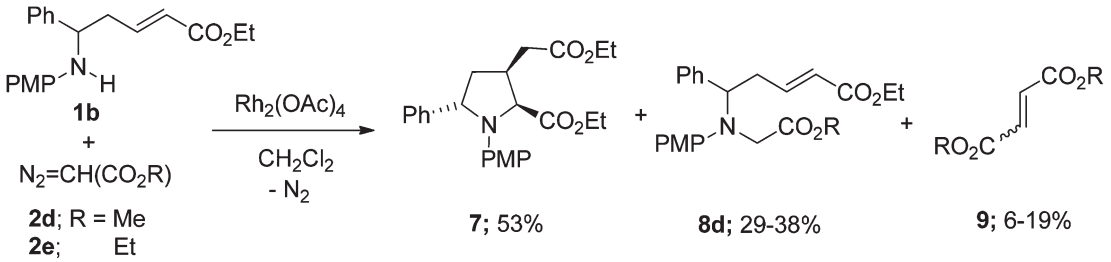
Catalytic decomposition of methyl diazoacetate ***2d***, contrary to diazomalonates **2a,b** and diazoisopropylidene malonic acid **2c**, occurred at room temperature very fast. Accordingly, reactions of diazoacetate **2d,e** with amino ester **1b** were carried out at 0, −15 and −25 °C by slow addition of the diazo compound to a solution of the amino ester-substrate **1b** and the catalyst in CH_2Cl_2.

It was found that with diazoester **2e** at 0 °C and using 4 mol% of Rh(II)-catalyst, pyrrolidine **7** was formed in 53% yield as a homogenous 2,3-*cis*-2,5-*trans*-stereoisomer (Table 4). At the same time, in the experiments at 0–25 °C with diazoester **2d** the N–H-insertion product **8d** (29–38%) was isolated



Scheme 2 Rh(II)-catalyzed reaction of diazo Meldrum's acid **2c** with amino ester **1b**.

Table 4 Rh(II)-catalyzed reaction of diazoacetates **2d,e** with unsaturated amino ester **1b**



			Yield[a] [%]			
Entry	Diazoester	Temp. [°C]	7[b]	**8d**	**9**	**1b** (recovered)
1[c]	**2e**	0	53	—	—	—
2	**2d**	0	—	29	6	38
3	**2d**	−15	—	29	19	69
4	**2d**	−25	—	38	10	41

[a] **2d**/**1b** = 4/1, $Rh_2(OAc)_4$ (0.7–0.9 mol%), DCM, 10 h – **3d**. [b] Solely the 2,5-*trans*-isomer was obtained. [c] **2e**/**1b** = 8/1, $Rh_2(OAc)_4$ (4 mol%), DCM, 4 h.

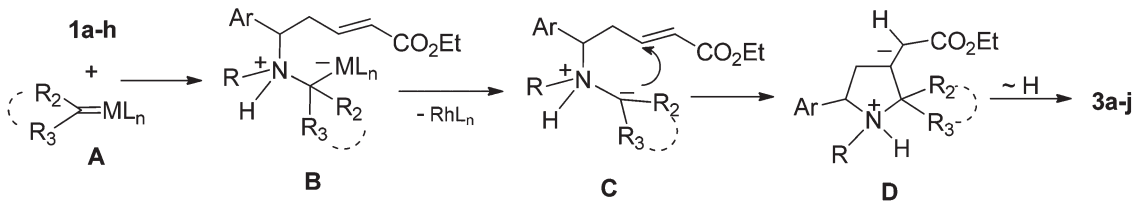
along with a mixture of methyl maleate–fumarate **9** (6–19%) and amino ester **1b** was recovered.

Discussion

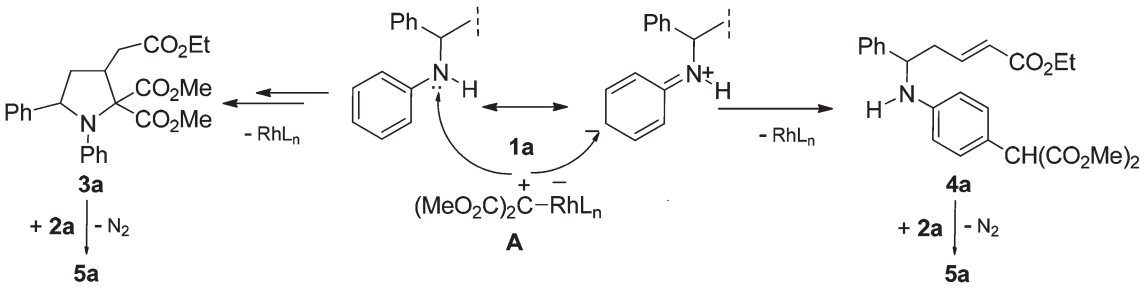
This study has revealed that the catalytic decomposition of diazoesters **2a–e** in the presence of α,β-unsaturated δ-amino esters **1a–h** gives rise in one stage to the formation of pyrrolidines **3** and **7** in moderate to good yields. The following mechanistic rationale can be put forth to account for the outcome of the reaction by analogy with literature data (Scheme 3).

The interaction of a catalyst with the carbon atom of the diazo group generates metal–carbene **A** followed by nitrogen elimination.[10a,16] The highly electrophilic carbenoid **A** subsequently attacks the electron-rich amino group and furnishes the intermediate complex **B** which further breaks down with the formation of the metal-free ylide **C** and regeneration of the catalyst.[17] The ylide **C** formed easily undergoes intramolecular conjugate addition to the pendant enoate giving rise to pyrrolidines **3** and **7** upon ring-closure followed by 1,4-*H*-migration within zwitterion **D**.[18]

Hence in the course of the catalytic process studied, two sites within the δ-unsaturated amino ester **1** structure were involved, namely the N–H- and C=C-bonds. However, other functional groups may react as well as was observed with **1a** and **1h**. For example, even at about an equimolar ratio of diazomalonate **2a** and amine **1a** (1 : 1.1), the product **4a** of metal–carbene **A** insertion into the *p*-CH-bond of the phenyl group of amino ester **1a** was formed along with pyrrolidine **3a** (Scheme 4). It is quite evident[10a,19] that the insertion product **4a** was produced due to competitive attack of the Rh(II)–carbe-



Scheme 3 Mechanistic rationale for the synthesis of pyrrolidines **3a–j** from amino esters **1a–h** and carbenoids **A**.



Scheme 4 Competitive carbenoid **A** insertion into NH- and CH-bonds of aminoester **1a** followed by formation of pyrrolidine **5a** from compounds **3a** and **4a**.

noid **A** onto the electron-rich *p*-CH-bond of the aromatic ring (Scheme 4, right pathway).

Based on the ratio of reaction products **3a**/**4a** formed (9 : 1; Table 1, entry 1) one can conclude that with the ratio of reactants 1.1 : 1 the interaction of carbenoid **A** with the N–H group (Scheme 4, left pathway) occurs at about 9 times faster than insertion into the *p*-C–H-bond of the phenyl group (right pathway). At the same time, in the presence of a large excess of diazomalonate **2a** (up to 4 : 1; entry 3) the initially formed pyrrolidine **3a** and *p*-CH$(CO_2Me)_2$-substituted amino ester **4a** both further react with one more equivalent of diazomalonate **2a**/carbenoid **A** producing pyrrolidine **5a** as the sole final reaction product (Scheme 4).

Essentially, in all experiments using rhodium catalysts, pyrrolidines **3a–i** were formed as a mixture of *trans*- and *cis*-isomers in the ratio 1.5–2.4 : 1, while on usage of Cu-complexes this ratio was ~1 : 1, except for $Cu(OTf)_2$, where it was 1.9 : 1. The reason for the notable diastereoselectivity of the processes studied when employing achiral rhodium complexes and copper(II) triflate still remains unclear.

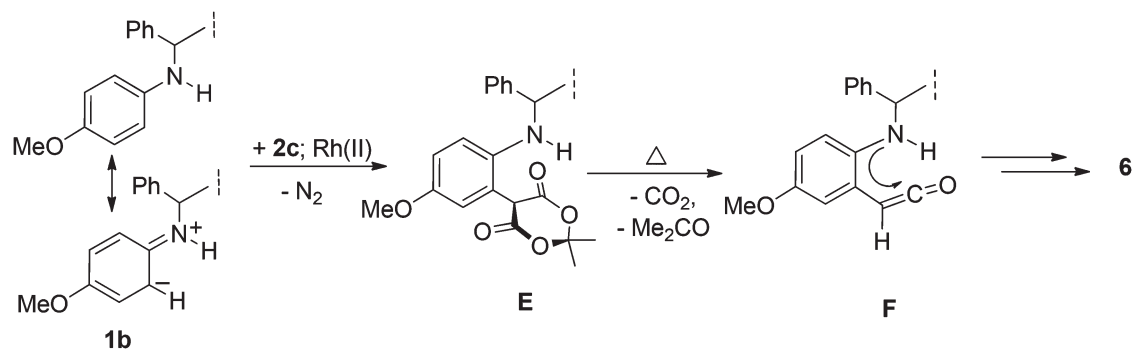
Similar to the formation of **4a** a competitive process apparently takes place in the course of catalytic decomposition of diazo Meldrum's acid **2c** in the presence of amino ester **1b** (Scheme 5) which results in the isolation of indole **6** along with pyrrolidine **3i**.

It is suggested that during this process electrophilic attack of the carbenoid **A** onto the *o*-CH-bond of the aromatic (PMP) ring initially takes place to furnish the C–H-insertion product **E**. On heating the latter eliminates CO_2 and acetone[20] giving rise to β-amino ketene **F** followed by intramolecular acylation of the N–H-group to produce indole **6**. Similar acylations are well precedented in the chemistry of ketenes.[21]

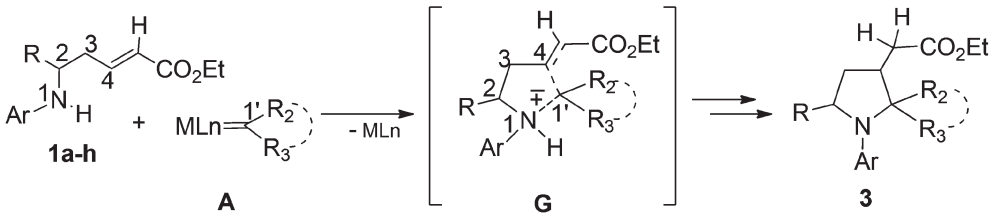
In contrast to reactions of diazomalonates **2a,b** and diazo Meldrum's acid **2c**, on catalytic decomposition of diazoacetic ester **2d** in the presence of amine **1b** the formation of tertiary amine **8d** was observed as well, which formally arises from insertion of carbenoid **A** into the N–H-bond of amino ester **1b**. The key intermediate of this reaction most likely is also a metal-free *N*-ylide of type **C** (Scheme 3),[17] which can undergo either 1,2-proton migration to produce N–CH_2CO_2Me-substituted amine **8d**, or can experience intramolecular cyclization into pyrrolidine **7**. Apparently, *N*-ylide **C** carrying only one ester group is less stabilized than other ylides, derived from β-dicarbonyl compounds, and is more rapidly converted into tertiary amine **8d**.

The considered catalytic reactions of diazomalonates and other diazoesters **2** in the presence of unsaturated amino esters **1** with production of pyrrolidines **3** can be classified as a [4 + 1]-annulation process. Metal–carbenes **A** formed during the decomposition process interact with the α,β-unsaturated δ-NH-system of ester **1** which may be schematically illustrated through transition state **G** although it apparently proceeds as a domino process (Scheme 6).

Until the present time similar catalytic processes with diazo compounds, which formally take place *via* transition state **G**, have essentially not been studied. There is in fact only one report on [4 + 1]-cycloaddition of carbenoids which was demonstrated by the example of catalytic decomposition of



Scheme 5 The proposed pathway to indolineone **6**.



Scheme 6 [4 + 1]-Annulation of **1** with carbenoid A *via* proposed transition state G to furnish pyrrolidines **3** and **7**.

diazocarbonyl compounds in the presence of homopropargylic alcohols to produce the corresponding tetrahydrofurans.[22] In this respect, further investigations of catalytic reactions of diazocarbonyl compounds of different types with α,β-unsaturated δ-N-substituted amino esters are undeniably of great importance and interest.

Conclusions

In conclusion, we have described herein for the first time a catalytic reaction of diazomalonates and other diazoesters with α,β-unsaturated δ-(*N*-aryl)amino esters. In the case of diazomalonates they provide a good way for the synthesis of multisubstituted functionalized *N*-aryl pyrrolidines. Among eight transition metal-complexes tested on Rh(II)-, Cu(II)-, Fe(III)- and Ru(II)-basis, the most efficient catalyst was found to be $Rh_2(Oct)_4$. Generally, *N*-aryl pyrrolidines are formed as a mixture of two diastereomers with the *trans*-isomer being the major one. There was only one case, employing ethyl diazoacetate, when the 2,5-*trans*-isomer was obtained exclusively. The main side process amounting up to 6–31% yield in these catalytic reactions was an insertion of the electrophilic metal–carbene into the electron-rich *p*- or *o*-C–H-bond of the *N*-aryl group.

Experimental section

General methods

All reactions were carried out under an argon atmosphere in the solvents dried and purified before use by common methods. Monitoring of the reaction course was accomplished by thin-layer chromatography (TLC) on precoated silica gel SIL G/UV254 plates (Marchery, Nagel & Co.) Flash chromatography was performed using Merck silica gel 60 230–400 mesh. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using Varian Gemini 200 and 2000 (200 MHz), Varian Gemini 300BB (300 MHz) and Brucker Avance DRX 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm, and coupling constants are given in Hz. All signals in NMR spectra were normalized relative to signals of $CDCl_3$ (δ = 7.26 ppm in ^{1}H NMR and δ = 77.0 in ^{13}C NMR spectra). A single crystal of the *trans*-isomer of pyrrolidine **3b** was selected from the analytical sample; the supplementary crystallographic data for **3b** (CCDC 1039286) are provided in the ESI.† IR spectra were obtained with a FT IR spectrometer (Genesis ATIMattson/Unicam). UV spectra were recorded on a UV spectrometer (DU-650 Beckmann). Melting points are uncorrected. All the ESI/HR mass spectra were recorded on a Brucker APEX II FT-ICR. Amino esters **1a–h** and diazo compounds **2a–e** were prepared using previously described protocols.[10a,23,24]

General procedure for $Rh_2(OAc)_4$-catalyzed reactions of diazomalonate 2a with aminoester 1a. Preparation of pyrrolidines 3a, 5a and insertion product 4a

Dimethyl diazomalonate **2a** was added in one portion or dropwise to a solution of amino ester **1a** and $Rh_2(OAc)_4$ in CH_2Cl_2. The reaction mixture was stirred overnight, the solvent was removed *in vacuo*, and then the residue was separated by silica gel flash chromatography to afford a quantity of starting amine **1a**, a mixture of *trans*- and *cis*-isomers of pyrrolidine **3a**, as well as insertion products **4a**, **5a** in separate experiments. The mixture of isomers **3a** was further subjected to preparative TLC to give pure *trans*- and *cis*-diastereomers of **3a**. (The detailed description of these experiments is given in ESI,† p. S4–S7).

(3*R,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1,5-diphenylpyrrolidine-2,2-dicarboxylate (*trans*-3a).** Colorless solid; m.p. 124–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.49 (m, 2H), 7.18–7.38 (m, 3H), 7.12–7.05 (m, 2H), 6.71 (d, J = 7.3, 1.0 Hz, 1H), 6.36–6.48 (m, 2H), 5.05 (d, J = 9.0 Hz, 1H), 4.04–4.14 (m, 2H), 3.88 (2, 3H), 3.73 (s, 3H), 3.22 (dddd, J = 12.4, 10.4, 6.5, 3.9 Hz, 1H), 3.03 (dd, J = 16.1, 4.0 Hz, 1H), 2.55 (td, J = 12.2, 9.2 Hz, 1H), 2.16–2.25 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.1, 168.9, 169.9, 145.1, 143.4, 129.4, 128.7, 127.0, 125.8, 121.4, 114.0, 75.6, 65.5, 60.7, 56.6, 53.0, 52.7, 43.1, 38.9, 34.9, 14.1; HRMS (ESI) calcd for $C_{24}H_{27}NO_6$ $[M + H]^+$ 426.1917, found 426.1915.

(3*S,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1,5-diphenylpyrrolidine-2,2-dicarboxylate (*cis*-3a).** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.43 (m, 2H), 7.13–7.33 (m, 3H), 6.98–7.04 (m, 2H), 6.64–6.70 (m, 1H), 6.50–6.59 (m, 2H), 5.04 (dd, J = 9.8, 6.0 Hz, 1H), 4.02–4.22 (m, 2H), 3.93 (s, 3H), 3.53 (s, 3H), 3.27–3.43 (m, 1H), 2.53–2.75 (m, 2H), 2.42 (dd, J = 16.8, 9.1 Hz, 1H), 1.82 (t d, J = 12.3, 9.9 Hz, 1H), 1.24 (t, J = 7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 170.0, 169.7, 144.4, 142.5, 128.6, 128.2, 127.0, 126.3, 118.9, 116.6, 77.9, 64.4, 60.7, 52.6, 52.6, 44.8, 41.7, 35.4, 14.2; HRMS (ESI) calcd for $C_{24}H_{27}NO_6$ $[M + H]^+$ 426.1917, found 426.1915.

(*E*)-Dimethyl 2-(4-((5-ethoxy-5-oxo-1-phenylpent-3-en-1-yl)-amino)phenyl)malonate (4a). Colorless oil; ^{1}H NMR

(200 MHz, $CDCl_3$) δ 7.19–7.38 (m, 5H), 7.03–7.16 (m, 2H), 6.88 (dt, J = 14.7, 7.2 Hz, 1H), 6.42–6.56 (m, 2H), 5.92 (dt, J = 15.6, 1.5 Hz, 1H), 4.47 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 4.11 (broad, 1H), 3.71 (s, 6H), 2.45–2.87 (m, 2H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.0; 165.9, 146.8, 144.2, 142.4, 130.0, 128.8, 127.5, 126.2, 124.4, 113.4, 60.4, 56.9, 56.7, 52.7, 41.2, 14.2; HRMS (ESI) calcd for $C_{24}H_{27}NO_6$ $[M + Na]^+$ 448.1736, found 448.1735.

Dimethyl 1-(4-(1,3-dimethoxy-1,3-dioxopropan-2-yl)phenyl)-3-(2-ethoxy-2-oxoethyl)-5-phenylpyrrolidine-2,2-dicarboxylate (*trans*-5a). Colorless solid; m.p. 143–144 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.19–7.46 (m, 5H), 7.09 (d, J = 8.8 Hz, 2H), 6.38 (d, J = 8.8 Hz, 2H), 5.02 (d, J = 8.9 Hz, 1H), 3.98–4.19 (m, 2H), 3.74 (s, 3H), 3.88 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.10–3.37 (m, 1H), 3.01 (dd, J = 16.1, 4.0 Hz, 1H), 2.53 (td, J = 12.2, 9.0 Hz, 1H), 2.05–2.32 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.1, 169.7, 168.9, 145.1, 143.4, 129.4, 128.7, 127.0, 125.8, 121.4, 114.0, 76.0, 65.5, 60.7, 56.6, 53.0, 52.7, 52.6, 43.1, 38.9, 34.9, 14.1; HRMS (ESI) calcd for $C_{29}H_{33}NO_{10}$ $[M + Na]^+$ 578.2002, found 578.2001.

General procedure for Rh(II)-catalyzed decomposition of diazomalonates 2a and 2b in the presence of aminoesters 1b–h. Preparation of pyrrolidines 3b–h

A solution of diazomalonate **2a** or **2b** in DCM was added in one portion to a solution of amino ester **1b–h** in DCM with the Rh(II)-catalyst and the reaction mixture was stirred at room temperature until the disappearance of the starting amino ester **1**. Then, DCM was removed *in vacuo* and the residue was purified by silica gel flash chromatography to afford pyrrolidines **3b–h** as the mixtures of *trans*- and *cis*-isomers which were thereafter subjected to preparative TLC to give pure *trans*- and *cis*-diastereoisomers. (The detailed description of these experiments is given in ESI,† p. S4–S7).

(3*R,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine-2,2-dicarboxylate (*trans*-3b).** Colorless solid; m.p. 153–155 °C; IR (KBr) ν_{max} 3052, 2989, 2946, 2927, 2879, 2827, 1735, 1602, 1514, 1454, 1437, 1420, 1380, 1351, 1297 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.3, 1H), 6.66 (d, J = 9.2 Hz, 2H), 6.39 (d, J = 9.2 Hz, 2H), 4.98 (d, J = 9.0 Hz, 1H), 3.71 (s, 3H), 3.87 (s, 3H), 3.11–3.27 (m, 1H), 3.66 (s, 3H), 3.00 (dd, J = 16.2, 4.0 Hz, 1H), 2.54 (td, J = 12.1, 9.3 Hz, 1H), 2.10–2.28 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 170.1, 169.7, 151.9, 144.0, 139.2, 128.6, 126.8, 125.9, 115.1, 114.1, 76.4, 65.5, 60.6, 55.4, 52.9, 52.5, 43.1, 39.0, 35.0, 14.0; HRMS (ESI) calcd $C_{25}H_{29}NO_7$ $[M + Na]^+$ 478.1836, found 478.1834.

(3*S,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine-2,2-dicarboxylate (*cis*-3b).** Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.09–7.49 (m, 7H), 6.34–6.81 (m, 2H), 4.96 (dd, J = 9.9, 5.6 Hz, 1H), 4.08–4.18 (m, 2H), 3.92 (s, 3H), 3.65 (s, 3H), 3.43–3.52 (m, 4H), 2.27–2.78 (m, 3H), 1.76 (td, J = 12.1, 10.0 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H); HRMS (ESI) calcd for $C_{25}H_{29}NO_7$ $[M + Na]^+$ 478.1836, found 478.1834.

(3*R,5*R**)-Diethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine-2,2-dicarboxylate (*trans*-3b′).** Orange oil; IR (film) ν_{max} 3060, 2981, 2932, 1735, 1603, 1582, 1513, 1450, 1380, 1295, 1250, 1180 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 2H), 7.17–7.34 (m, 3H), 6.66 (d, J = 9.2 Hz, 2H), 6.40 (d, J = 9.2 Hz, 2H), 4.97 (d, J = 9.0 Hz, 1H), 4.29–4.40 (m, 2H), 4.12–4.24 (m, 2H), 4.01–4.13 (m, 2H), 3.67 (s, 3H), 3.11–3.28 (m, 1H), 3.04 (dd, J = 16.0, 3.8 Hz), 2.55 (td, J = 12.1, 9.3 Hz, 1H), 2.11–2.30 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 5.8 Hz, 3H), 1.17 (t, J = 5.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 169.6, 169.2, 151.9, 144.2, 139.4, 128.6, 126.8, 126.0, 115.2, 114.0, 76.4, 65.5, 61.8, 61.7, 60.6, 55.5, 43.1, 39.2, 35.1, 14.1, 14.1, 14.0; HRMS (ESI) calcd for $C_{27}H_{33}NO_7$ $[M + Na]^+$ 506.2155, found 506.2152.

(3*S,5*R**)-Diethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine-2,2-dicarboxylate (*cis*-3b′).** Yellow oil; IR (film) ν_{max} 2931, 2853, 1732, 1604, 1582, 1511, 1455, 1388, 1244, 1082 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.48 (m, 2H), 7.19–7.28 (m, 2H), 7.08–7.19 (m, 1H), 6.51–6.68 (m, 4H), 4.97 (dd, J = 10.1, 5.6 Hz), 4.28–4.49 (m, 2H), 4.06–4.18 (m, 2H), 3.81–4.03 (m, 2H), 3.64 (s, 3H), 3.44 (ddt, J = 11.9, 9.2, 5.9 Hz, 1H), 2.71 (dd, J = 16.6, 5.7 Hz, 1H), 2.54–2.63 (m, 1H), 2.39 (dd, J = 16.6, 9.2 Hz, 1H), 1.77 (td, J = 12.3, 10.2 Hz, 1H), 1.40 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 169.9, 169.1, 153.2, 142.7, 138.4, 128.4, 126.9, 126.6, 119.5, 113.5, 78.2, 64.7, 61.7, 61.5, 60.6, 55.3, 44.3, 41.8, 35.6, 14.2, 14.1, 13.7; HRMS (ESI) calcd for $C_{27}H_{33}NO_7$ $[M + Na]^+$ 506.2155, found 506.2153.

(3*R,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-5-(4-ethylphenyl)-1-(4-methoxyphenyl)pyrrolidine-2,2-dicarboxylate (*trans*-3c).** Colorless oil; IR (film) ν_{max} 2988, 2962, 2952, 2932, 2907, 2879, 1750, 1742, 1733, 1517, 1459, 1433, 1374, 1291, 1271, 1253, 1227, 1189, 1152 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.63–6.74 (m, 2H), 6.35–6.43 (m, 2H), 4.96 (d, J = 8.9 Hz, 1H), 4.04–4.14 (m, 2H), 3.87 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 3.16–3.27 (m, 1H), 2.99 (dd, J = 16.1, 4.0 Hz, 1H), 2.63 (q, J = 7.6 Hz, 2H), 2.51 (td, J = 12.1, 9.2 Hz, 1H), 2.03–2.29 (m, 2H), 1.05–1.33 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 170.2, 169.8, 151.9, 142.7, 141.3, 139.4, 128.1, 125.9, 115.1, 114.2, 76.4, 65.4, 60.7, 55.5, 52.9, 52.5, 43.2, 39.2, 35.1, 28.5, 15.5, 14.1; HRMS (ESI) calcd for $C_{27}H_{33}NO_7$ $[M + Na]^+$ 506.2155, found 506.2154.

(3*S,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-5-(4-ethylphenyl)-1-(4-methoxyphenyl)pyrrolidine-2,2-dicarboxylate (*cis*-3c).** Colorless oil; IR (film) ν_{max} 2960, 2934, 2873, 2837, 1737, 1513, 1463, 1456, 1435, 1247, 1219, 1181, 1060, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.58–6.66 (m, 4H), 4.94 (dd, J = 10.0, 5.7 Hz), 4.05–4.20 (m, 2H), 3.91 (s, 3H), 3.65 (s, 3H), 3.40–3.51 (m, 4H), 2.50–2.68 (m, 4H), 2.38 (dd, J = 16.7, 8.9 Hz, 1H), 1.75 (td, J = 12.3, 10.1 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 170.5, 169.7, 153.2, 142.8, 139.7, 138.2, 128.0, 126.5, 119.6, 113.6, 78.5, 64.5, 60.7, 55.3, 52.4, 44.2, 35.7, 28.4, 15.4, 14.2; HRMS (ESI) calcd for $C_{27}H_{33}NO_7$ $[M + H]^+$ 484.2335, found 484.2335.

(3*R,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-(naphthalen-2-yl)pyrrolidine-2,2-dicarboxylate (*trans*-3d).** Bright yellow oil; IR (film) ν_{max} 3051, 2982, 2952, 2905, 2835, 1737, 1463, 1454, 1433, 1380, 1334, 1295, 1295, 1250, 1216, 1193, 1179, 1147 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.70–7.87 (m, 3H), 7.40–7.56 (m, 3H), 6.59–6.71 (m, 2H), 6.37–6.48 (m, 2H), 5.14 (d, J = 9.0 Hz, 1H), 4.00–4.12 (m, 2H), 3.93 (s, 3H), 3.75 (s, 3H), 3.67 (s, 3H), 3.26 (tdd, J = 12.1, 6.6, 4.0 Hz, 1H), 3.02 (dd, J = 16.1, 4.0 Hz, 1H), 2.60 (td, J = 12.1, 9.3 Hz, 1H), 2.19–2.30 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 170.1, 169.8, 152.0, 141.4, 139.3, 133.5, 132.7, 128.6, 128.0, 127.6, 126.0, 125.5, 124.7, 124.4, 115.2, 114.2, 76.5, 65.8, 60.7, 55.5, 52.9, 52.6, 43.2, 38.9, 35.0, 14.1; HRMS (ESI) for $C_{29}H_{31}NO_7$ $[M + Na]^+$ 528.1998, found 528.1998.

(3*S,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-(naphthalen-2-yl)pyrrolidine-2,2-dicarboxylate (*cis*-3d).** Bright yellow oil; IR (film) ν_{max} 3056, 2934, 2953, 2934, 2871, 2837, 1736, 1512, 1464, 1456, 1435, 1384, 1247, 1218, 1181, 1152, 1058, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.68–7.78 (m, 3H), 7.64 (dd, J = 8.5, 1.7 Hz, 1H), 7.34–7.46 (m, 2H), 6.63–6.73 (m, 2H), 6.53–6.61 (m, 2H), 5.13 (dd, J = 10.0, 5.7 Hz, 1H), 4.05–4.18 (m, 2H), 3.96 (s, 3H), 3.61 (s, 3H), 3.50–3.58 (m, 1H), 3.49 (s, 3H), 2.58–2.74 (m, 2H), 2.41 (dd, J = 16.7, 8.9 Hz, 1H), 1.85 (td, J = 12.3, 10.1 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 170.6, 169.6, 153.4, 140.2, 138.1, 133.3, 132.9, 128.5, 127.7, 127.6, 125.8, 125.7, 125.5, 124.6, 119.9, 113.6, 78.6, 65.0, 60.7, 55.2, 52.5, 44.2, 41.6, 35.8, 14.2; HRMS (ESI) calcd for $C_{29}H_{31}NO_7$ $[M + Na]^+$ 528.1998, found 528.1990.

(3*R,5*R**)-Dimethyl 5-(4-(*tert*-butyl)phenyl)-3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)pyrrolidine-2,2-dicarboxylate (*trans*-3e).** Bright yellow oil; IR (film) ν_{max} 2954, 2905, 2871, 2834, 1738, 1514, 1464, 1444, 1434, 1295, 1252, 1218, 1193, 1178, 1157, 1060, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.35 (m, 4H), 6.63–6.73 (m, 2H), 6.35–6.43 (m, 2H), 4.96 (d, J = 8.6 Hz, 1H), 4.02–4.16 (m, 2H), 3.87 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 3.16–3.29 (m, 1H), 3.00 (dd, J = 16.1, 4.0 Hz, 1H), 2.51 (td, J = 12.1, 9.2 Hz, 1H), 2.14–2.26 (m, 2H), 1.31 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 170.2, 169.9, 151.9, 149.5, 140.9, 139.4, 125.5, 115.0, 114.1, 76.4, 65.3, 60.7, 55.5, 52.9, 52.5, 43.2, 39.1, 35.0, 34.4, 31.4, 14.1; HRMS (ESI) m/z calcd for $C_{29}H_{37}NO_7$ $[M + Na]^+$ 534.2468, found 534.2460.

(3*S,5*R**)-Dimethyl 5-(4-(*tert*-butyl)phenyl)-3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)pyrrolidine-2,2-dicarboxylate (*cis*-3e).** Bright yellow oil; IR (film) ν_{max} 3047, 2954, 2907, 2869, 2837, 1739, 1732, 1514, 1464, 1444, 1435, 1287, 1246, 1218, 1194, 1194, 1182, 1171, 1057, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.38 (m, 4H), 6.60–6.66 (m, 4H), 4.94 (dd, J = 10.0, 5.7 Hz, 1H), 4.03–4.18 (m, 2H), 3.91 (s, 3H), 3.66 (s, 3H), 3.37–3.49 (m, 4H), 2.52–2.69 (m, 2H), 2.39 (dd, J = 16.7, 8.9 Hz, 1H), 1.75 (td, J = 12.3, 10.1 Hz, 1H), 1.21–1.27 (m, 12H); HRMS (ESI) calcd for $C_{29}H_{37}NO_7$ $[M + Na]^+$ 534.2468, found 534.2464.

(3*R,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-(o-tolyl)pyrrolidine-2,2-dicarboxylate (*trans*-3f).** Bright yellow oil; IR (film) ν_{max} 3047, 2981, 2952, 2907, 2835, 1735, 1514, 1462, 1435, 1382, 1295, 1250, 1218, 1194, 1177, 1062, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.65 (m, 1H), 7.02–7.21 (m, 3H), 6.66 (d, J = 9.2 Hz, 2H), 6.29 (d, J = 9.2 Hz, 2H), 5.05 (d, J = 9.2 Hz, 1H), 4.04–4.12 (m, 2H), 3.90 (s, 3H), 3.74 (s, 3H), 3.67 (s, 3H), 3.14–3.28 (m, 1H), 3.03 (dd, J = 16.1, 3.9 Hz, 1H), 2.55 (td, J = 12.1, 9.5 Hz, 1H), 2.40 (s, 3H), 2.21 (dd, J = 16.2, 10.5, 1H), 2.08 (ddd, J = 11.8, 6.9, 1.0 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 170.1, 169.9, 151.9, 141.7, 139.3, 133.5, 130.6, 126.8, 126.5, 125.7, 114.9, 114.2, 76.5, 63.5, 60.7, 55.5, 53.0, 52.5, 43.1, 37.3, 35.1, 19.4, 14.1; HRMS (ESI) calcd for $C_{26}H_{31}NO_7$ $[M + Na]^+$ 492.1998, found 492.1994.

(3*S,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-(o-tolyl)pyrrolidine-2,2-dicarboxylate (*cis*-3f).** Bright yellow oil; IR (film) ν_{max} 3048, 2952, 2926, 2871, 2850, 1734, 1509, 1489, 1458, 1436, 1384, 1246, 1217, 1105, 1058, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.62 (m, 1H), 7.04–7.10 (m, 3H), 6.61 (d, J = 9.2 Hz, 2H), 6.52 (d, J = 9.2 Hz, 2H), 5.14 (dd, J = 9.8, 5.9 Hz, 1H), 4.04–4.20 (m, 2H), 3.91 (s, 3H), 3.65 (s, 3H), 3.40–3.53 (m, 4H), 2.57–2.70 (m, 2H), 2.36–2.47 (m, 4H), 1.65 (td, J = 12.1, 9.8 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H); HRMS (ESI) calcd for $C_{26}H_{31}NO_7$ $[M + Na]^+$ 492.1998, found 492.1997.

(3*R,5*R**)-Dimethyl 5-(3-chlorophenyl)-3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)pyrrolidine-2,2-dicarboxylate (*trans*-3g).** Bright yellow oil; IR (film) ν_{max} 3051, 2983, 2952, 2907, 2835, 1768, 1747, 1732, 1597, 1574, 1521, 1470, 1464, 1455, 1382, 1339, 1295, 1021 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.47 (m, 1H), 7.15–7.37 (m, 3H), 6.69 (d, J = 9.2 Hz, 2H), 6.36 (d, J = 9.2 Hz, 2H), 4.94 (d, J = 9.1 Hz, 1H), 3.98–4.19 (m, 2H), 3.88 (s, 3H), 3.72 (s, 3H), 3.69 (s, 3H), 3.11–3.27 (m, 1H), 3.00 (dd, J = 16.3, 4.0 Hz, 1H), 2.53 (td, J = 12.2, 9.3 Hz, 1H), 2.15–2.24 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 170.0, 169.5, 152.2, 146.4, 138.9, 134.6, 130.1, 127.2, 126.2, 124.2, 115.1, 114.3, 76.3, 65.2, 60.8, 55.5, 53.0, 52.6, 43.1, 38.9, 34.9, 14.1; HRMS (ESI) calcd for $C_{25}H_{28}ClNO_7$ $[M + Na]^+$ 512.1452, 512.1422, found 512.1451, 514.1424.

(3*R,5*R**)-Dimethyl 5-(3-chlorophenyl)-3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)pyrrolidine-2,2-dicarboxylate (*cis*-3g).** Bright yellow oil; IR (film) ν_{max} 3047, 2953, 2934, 2871, 2838, 1737, 1513, 1466, 1457, 1434, 1248, 1216, 1181, 1078, 1057, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.45 (m, 2H), 7.10–7.20 (m, 2H), 6.56–6.74 (m, 4H), 4.93 (dd, J = 10.0, 5.7 Hz, 1H), 4.07–4.20 (m, 2H), 3.67 (s, 3H), 3.47–3.54 (m, 1H), 3.46 (s, 3H), 2.55–2.66 (m, 2H), 2.37 (dd, J = 16.7, 8.9 Hz, 1H), 1.72 (td, J = 12.3, 10.1 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H); HRMS (ESI) calcd for $C_{25}H_{28}ClNO_7$ $[M + Na]^+$ 512.1452, 512.1422, found 512.1450, 514.1423.

(3*R,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-((*E*)-styryl)pyrrolidine-2,2-dicarboxylate (*trans*-3h).** Bright yellow oil; IR (film) ν_{max} 3081, 3052, 3025, 2982, 2952, 2906, 2834, 1736, 1514, 1463, 1448, 1434, 1380, 1350, 1296, 1250, 1214, 1193, 1179, 1096, 1081, 1073, 1055, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.13–7.40 (m, 5H), 6.62–6.80 (m, 3H), 6.45–6.59 (m, 2H), 6.22–6.36 (m, 1H), 4.59 (dd, J = 8.6, 4.7 Hz,

1H), 4.02–4.22 (m, 2H), 3.83 (s, 3H), 3.71 (s, 6H), 3.11–3.32 (m, 1H), 3.00 (dd, J = 16.2, 3.8 Hz, 1H), 2.06–2.39 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 170.1, 169.8, 151.9, 139.3, 136.9, 130.4, 128.5, 127.4, 126.5, 114.9, 114.2, 76.0, 63.0, 60.7, 55.6, 52.8, 52.5, 43.6, 36.1, 35.1, 14.2; HRMS (ESI) calcd for $C_{27}H_{31}NO_7$ $[M + Na]^+$ 504.1998, found 504.1989.

(3*S,5*R**)-Dimethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-((*E*)-styryl)pyrrolidine-2,2-dicarboxylate (*cis*-3h).** Bright yellow oil; IR (film) ν_{max} 3026, 2982, 2952, 2934, 2836, 1735, 1513, 1463, 1447, 1434, 1246, 1216, 1194, 1181, 1075, 1056, 1034 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08–7.39 (m, 5H), 6.44–6.81 (m, 5H), 6.06 (dd, J = 7.72, 15.99 Hz, 1H), 4.59–4.67 (m, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.70 (s, 3H), 3.50 (s, 3H), 3.29–3.42 (m, 1H), 2.67 (dd, J = 16.6, 5.7 Hz, 1H), 2.25–2.55 (m, 2H), 1.77 (td, J = 11.9, 9.6 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H); HRMS (ESI) calcd for $C_{27}H_{31}NO_7$ $[M + Na]^+$ 504.1998, found 504.1994.

General procedure for Cu(II)-catalyzed decomposition of diazomalonate 2a in the presence of amino ester 1b. Preparation of pyrrolidines 3b

The description of these experiments is given in ESI,† p. S4–S7.

Attempts to carry out catalytic decomposition of diazomalonate 2a using Cu(II), Fe(III) and Ru(II)-complexes in the presence of amino ester 1b

The description of these experiments is given in ESI,† p. S4–S7.

Rh(II)-catalyzed decomposition of diazo Meldrum's acid 2c in the presence of amino ester 1b. General procedure for preparation of pyrrolidines 3i and indolineone 6

A solution of amino ester **1b** and diazo Meldrum's acid **2c** with the Rh(II)-catalyst in anhydrous benzene was refluxed until the disappearance of the starting amino ester. Then the solvent was removed *in vacuo*, and the residue was purified by silica gel flash chromatography to afford pyrrolidines **3i** as a mixture of *trans*- and *cis*-isomers, which were further separated using preparative thin-layer chromatography, and indoline-2-one **6**. The detailed description of these experiments is given in ESI,† p. S4–S7.

(3*R,5*R**)-Diethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine-2,2-dicarboxylate (*trans*-3i).** Bright yellow oil; IR (film) ν_{max} 3062, 2933, 2852, 1780, 1735, 1604, 1580, 1511, 1452, 1418, 1381, 1247, 1105 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.58 (m, 2H), 7.10–7.42 (m, 3H), 6.96–7.06 (m, 2H), 6.62–6.73 (m, 2H), 5.16 (dd, J = 9.3, 3.9 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.66 (s, 3H), 3.53–3.63 (m, 1H), 2.37–2.68 (m, 3H), 2.21–2.28 (m, 1H), 1.70 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 169.0, 167.3, 156.5, 143.6, 137.3, 128.5, 127.1, 126.9, 126.0, 114.4, 106.2, 76.1, 66.0, 61.0, 55.3, 46.8, 39.9, 35.3, 29.9, 28.4, 14.1; HRMS (ESI) calcd for $C_{26}H_{29}NO_7$ $[M + K]^+$ 506.1581, found 506.1579.

(3*S,5*R**)-Diethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine-2,2-dicarboxylate (*cis*-3i).** Bright yellow oil; IR (film) ν_{max} 2926, 2853, 1733, 1663, 1604, 1511, 1454, 1355, 1289, 1246, 1179, 1094, 1033 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.50 (m, 2H), 7.14–7.34 (m, 3H), 6.62 (d, J = 9.1 Hz, 2H), 6.26 (d, J = 9.1 Hz, 2H), 5.00 (dd, J = 10.0, 5.8 Hz, 1H), 3.99–4.22 (m, 2H), 3.65 (s, 3H), 3.03–3.14 (m, 1H), 2.61–2.68 (m, 4H), 2.54 (dd, J = 16.5, 5.5 Hz, 1H), 2.20–2.31 (m, 1H), 1.95 (s, 3H), 1.83–1.92 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 207.0, 171.3, 152.8, 142.0, 138.3, 128.8, 127.3, 126.7, 117.3, 114.5, 86.1, 65.2, 61.1, 55.5, 43.5, 41.9, 34.9, 32.0, 27.8, 14.3; HRMS (ESI) calcd for $C_{26}H_{29}NO_7$ $[M + K]^+$ 506.1581, found 506.1578.

(*E*)-Ethyl 5-(5-methoxy-2-oxoindolin-1-yl)-5-phenylpent-2-enoate 6. Bright yellow oil; IR (film) ν_{max} 2934; 1710; 1655; 1599; 1490; 1486; 1436; 1390; 1367; 1331; 1289; 1227; 1189; 1160; 1095; 1035 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.41 (m, 5H), 6.78–6.97 (m, 2H), 6.60 (dd, J = 9.8, 6.1 Hz, 1H), 6.49 (d, J = 8.6 Hz, 1H), 5.82 (dt, J = 15.6, 1.4 Hz, 1H), 5.69 (dd, J = 9.8, 6.1 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.73 (s, 3H), 3.56 (s,2H), 3.08–3.37 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 165.9, 155.6, 143.9, 137.9, 136.4, 128.8, 127.8, 127.0, 125.9, 124.3, 111.9, 111.9, 110.4, 60.3, 55.7, 53.4, 36.0, 33.1, 14.2; HRMS (ESI) calcd for $C_{22}H_{23}NO_4$ $[M + Na]^+$ 388.1525, found 388.1518.

Rh(II)-catalyzed reactions of diazoacetates 2d and 2e with amino ester 1b. General procedure

Diazoacetate **2d** or **2e** was added to a solution of amine **1b** at the relevant temperature (0 °C, −10 °C, −25 °C) in DCM with $Rh_2(OAc)_4$. The reaction mixture was stirred for an appropriate period of time keeping the temperature of the reaction mixture constant. Then the solvent was removed *in vacuo* and the residue was purified by silica gel flash chromatography to afford starting amine **1b**, a mixture of dimethyl fumarate and maleate **9**, N–H insertion product **8**, and pyrrolidine **7** (in the case of reaction with diazo acetate **2e**). The detailed description of these experiments is given in ESI,† p. S4–S7.

Ethyl (*E*)-5-((2-methoxy-2-oxoethyl)(4-methoxyphenyl)-amino)-5-phenylpent-2-enoate (8d). Bright yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.38 (m, 7H), 6.75–6.98 (m, 3H), 5.81 (dt, J = 15.7, 1.5 Hz, 1H), 4.91 (dd, J = 8.0, 6.4 Hz, 1H), 3.97–4.22 (m, 2H), 3.76 (s, 3H), 3.69 (d, J = 7.2 Hz, 2H), 3.60 (s, 3H), 2.59–2.97 (m, 2H), 1.24 (t, J = 7.13 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 166.2, 153.8, 145.6, 142.2, 139.5, 128.6, 128.0, 127.7, 123.3, 118.9, 114.6, 62.9, 60.2, 55.6, 51.7, 50.7, 35.4, 14.2; HRMS (ESI) calcd for $C_{23}H_{27}NO_5$ $[M + Na]^+$ 420.1787, found 420.1792.

(2*R,3*R**,5*R**)-ethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-5-phenylpyrrolidine-2-carboxylate (7).** Colorless oil; IR (film) ν_{max} 2981, 1736, 1620, 1513, 1450, 1363, 1242, 1178, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.33 (m, 5H), 6.70 (d, J = 9.0 Hz, 2H), 6.38 (d, J = 9.0 Hz, 2H), 4.98 (d, J = 9.0 Hz, 1H), 4.78 (d, J = 7.5 Hz, 1H), 4.14–4.23 (m, 4H), 3.68 (s, 3H), 3.09–3.22 (m, 1H), 2.52 (ddd, J = 9.5, 12.0, 12.0 Hz, 1H), 2.43 (dd, J = 8.5, 17.0 Hz, 1H), 2.34 (dd, J = 7.0, 17.0 Hz, 1H),

1.98 (dd, J = 6.5, 12.0 Hz, 1H), 1.24–1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 171.5, 151.4, 144.4, 139.9, 128.6, 126.8, 125.8, 114.7, 113.5, 64.9, 62.7, 60.8, 60.6, 55.6, 39.4, 35.4, 34.8, 14.3, 14.2; MS (ESI) calcd for $C_{24}H_{29}NO_5$ $[M + H]^+$ 412, found 412; HRMS (ESI) calcd for $C_{24}H_{29}NO_5$ $[M + Na]^+$ 434.1943, found 434.1946.

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