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Cyclopropanation of Alkenes, N–H and S–H Insertion of Ethyl Diazoacetate Catalysed by Ruthenium Porphyrin Complexes

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Abstract—Product yields, stereoselectivities and regioselectivities for cyclopropanation reactions of ethyl diazoacetate with styrene derivatives and α-heteroatom alkenes, catalysed by ruthenium porphyrins, are reported and compared with observed stereoselectivities for cyclopropanation reactions catalysed with other metalloporphyrin catalysts. Linear correlations are observed when the rates for competitive cyclopropanation or product stereoisomer ratio are plotted against Hammet constants of various ring-substituted groups on styrenes. Isomeric distribution for the cyclopropanation of isoprene and 1,3-pentadiene with ethyl diazoacetate and competition studies of the cyclopropanation and diazo insertion into heteroatom–hydrogen bonds are also reported. All these results agree with a major electronic and steric influence on both the regiochemical and stereochemical control in the catalytic cyclopropanation and diazo insertion reactions.

Introduction

Catalytic cyclopropanation reactions have become one of the most general and efficient methods available to the synthetic organic chemist.[1] There is also considerable interest in the development of effective catalytic systems for the enantioselective cyclopropanation of prochiral olefins.[2,3] The major advances have recently been achieved with various chiral rhodium derivatives[4] and with chiral ruthenium bis(oxazolinyl)pyridine catalysts, the latter developed by Nishiyama.[5] Although the accomplishments achieved thus far are quite impressive, exploration of new effective catalysts is still essential to extend the scope of these reactions.

The discovery that carbene complexes of hepatic cytochrome P450 iron(II) are important intermediates during the reductive metabolisation of polyhalogenated compounds[6a] has stimulated intense interest in the chemistry of carbene derivatives such as carbene ferrous porphyrin complexes.[6] Also of interest are precursor metalloporphyrins that can serve to catalyse carbene addition to unsaturated organic substrates. One strategy would be to employ ferrous porphyrins or ferric porphyrins under reducing conditions. Actually, such a system has been recently reported for the cyclopropanation of styrene.[7] However, the ferrous porphyrin precursors are too reactive towards dioxygen to be very promising for practical application in organic synthesis. It must also be underlined that a nice system with iron(III) porphyrin bearing electron-withdrawing pentafluorophenyl groups can be employed as precatalyst.[7] As a consequence, our attention turned to the use of ruthenium analogues, which were anticipated to be more stable.

Ruthenium porphyrins have been used frequently for oxidation reactions,[8,9] based on the greater stability of ruthenium compounds in various oxidation states, ranging from Ru(II) to Ru(VI). In contrast to these extensive investigations, only a few examples of catalytic reactions that proceed through ruthenium carbene complexes have been reported using Ru(II) porphyrins as catalysts.[10,11] This is quite unexpected since all the synthetic methods for the insertion of ruthenium into porphyrins yield ruthenium carbonyl complexes,[12] which are good precursors of carbene derivatives.[13] Other methods for the preparation of (porphyrin) ruthenium (carbene) complexes were also previously reported.[14] Our interest in the chemistry of ruthenium porphyrins prompted us to investigate the cyclopropanation reaction. We previously reported the preparation and the first X-ray structure of a (porphyrin) ruthenium (carbene) compound.[13] We now wish to report herein the details of the catalytic reaction of diazoesters with simple olefins catalysed with ruthenium porphyrins. Comparison with other rhodium,[15] osmium[16] and iron porphyrin catalytic systems[7] will also be discussed.

Results

Cyclopropanation of styrene derivatives

meso-Tetraphenylporphyrin carbonyl ruthenium (TPP)Ru(CO) (Fig. 1) catalysed decomposition of ethyl diazoacetate

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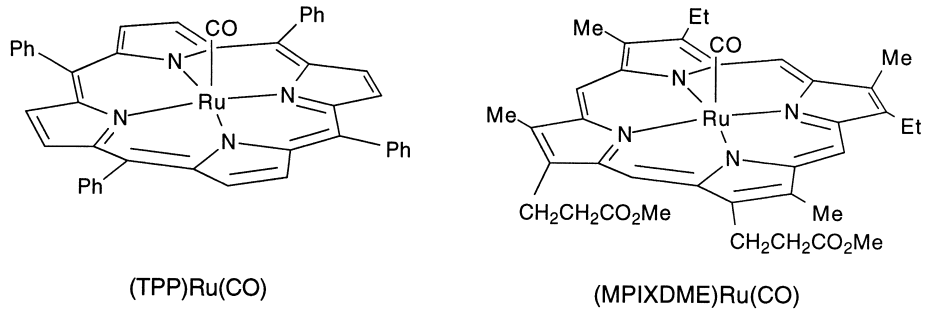
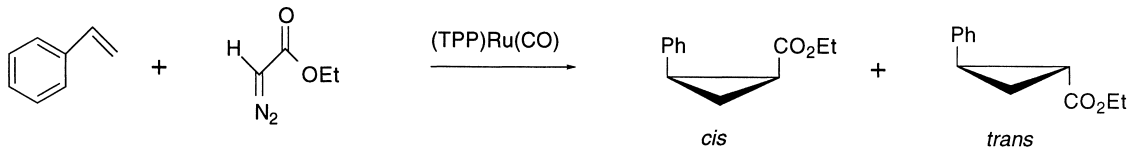


Figure 1. Catalysts used in this study.



(EDA) in the presence of styrene resulted in the formation of the corresponding cyclopropane in 93% yield with more than 500 turnover (Eq. 1).[11a]

Proton NMR and GC analysis of the crude reaction mixture indicated a *trans*/*cis* stereoselectivity of 13/1.

Table 1. Competition studies of the cyclopropanation of various substituted styrenes (substrate A) and styrene (substrate B) with EDA catalysed by (TPP)Ru(CO) (catalyst: 0.0027 mmol; styrenes: 2.70 mmol; EDA: 0.270 mmol; 4 h; RT)

Substrate A	Ratio of products derived from A/B
4-Methoxystyrene	3.2
4-Methylstyrene	2.8
4-Chlorostyrene	0.9
4-Trifluoromethylstyrene	0.3
α-Methylstyrene	10.1
2,4-Dimethylstyrene	2.9

To examine the scope of this cyclopropanation, the reaction of a number of styrene derivatives and conjugated alkenes with EDA in the presence of (TPP)Ru(CO) at 25°C in toluene was studied (Tables 1–3). First, cyclopropanation competition experiments were conducted with a large excess of each substrate and limiting quantities of ethyl diazoacetate (substrate/EDA=10/1) (Table 1). The relative reactivities were measured by the molar ratio in GC/MS of cyclopropyl esters derived from styrene and from the other substrates. In all these experiments, cyclopropanes are the major products, usually obtained with diethyl maleate and fumarate as by-products. Electron-rich styrenes (*4*-X=OMe and Me; α-methyl styrene; 2,4-dimethyl styrene) are cyclopropanated more efficiently than alkenes bearing electron-withdrawing groups (*4*-X=Cl and CF_3).

The data were fit to a Hammett plot (Fig. 2), with a good correlation (r^2=0.991) which allowed us to calculate a ρ value of -1.29 ± 0.08. Analogous preferences for electron rich alkenes were observed in the corresponding cyclopropanation reactions catalysed by iron porphyrins.[7]

Table 2. Isomeric distribution (%) for the cyclopropanation of isoprene with EDA catalysed by (TPP)Ru(CO) (catalyst: 0.0027 mmol; olefin: 2.70 mmol; EDA: 0.270 mmol; 4 h; RT)

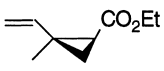
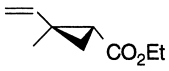
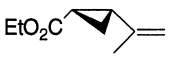
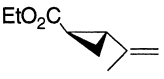
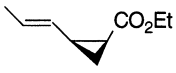
				
Isomeric distribution	34.1	40.1	2.6	23.2

Table 3. Isomeric distribution (%) for the cyclopropanation of *trans*-1-3-pentadiene with EDA (catalyst: 0.0027 mmol; olefin: 2.70 mmol; EDA: 0.270 mmol; 4 h; RT)

				
Isomeric distribution	5.7	6.4	40.8	47.1

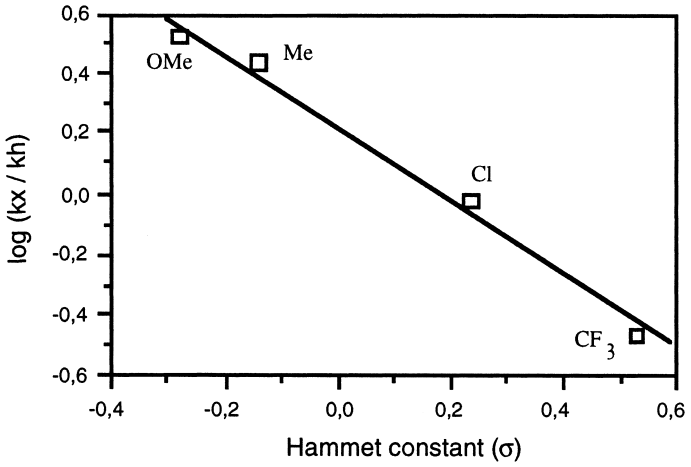


Figure 2. Hammet plot for the competitive cyclopropanation of styrene derivatives with EDA.

Table 4. Diastereoselectivity in the cyclopropanation of 4-substituted styrene derivatives catalysed by (MPIXDME)Ru(CO) (catalyst: 0.0027 mmol; styrene: 0.540 mmol; EDA: 0.270 mmol; 4 h; RT)

X	*trans*/*cis* Ratio
OMe	4.3
Me	5.4
H	9.3
Cl	12.0

To complete these data, we also studied the cyclopropanation of isoprene and *trans*-1,3-pentadiene. Isomeric distributions reported in Tables 2 and 3, respectively, emphasise the pronounced electronic and shape preference of the catalyst previously reported.[11a] Thus the results indicate that the cycloaddition of isoprene preferentially occurred (>74%) at the electron-rich double bond and confirm the results obtained with substituted styrenes. The regioisomer distribution is also influenced by steric effects. Terminal linear olefins were cyclopropanated with high yields. Accordingly the cycloaddition preferentially occurred at the terminal double bond with *trans*-1-3-pentadiene (>87%).

The influence of olefin structure on observed stereoselectivity (*trans*/*cis* ratio) is surprisingly weak for cyclopropanation of *trans*-1-3-pentadiene, the selectivity being close to one (Table 3). However, increasing the steric bulk of the olefinic substituents results in an enhancement of the relative percentage of the less encumbered cyclopropane product with isoprene, and changes the *trans*/*cis* ratios from 1.1 to 8.9 for the two different regioisomers (Table 2).

We then investigated the relation between the diastereoselectivity of the reaction and the electronic effect of the *para*-substituent of styrenes. We used the mesoporphyrin dimethyl ester carbonyl ruthenium complex[17] (MPIXDME)Ru(CO) (Fig. 1) as catalyst to avoid steric interactions between the *meso*-substituents of the porphyrin ring and the olefin. Data are shown in Table 4.

The plot of the log(*trans*/*cis*) against the Hammet constant is displayed in Fig. 3 and gives $\rho=+0.93\pm0.07$ ($r^2=0.957$). The *trans*/*cis* ratio is strongly affected by the electronic effect of the alkene substituents; the reaction with 4-chlorostyrene is almost three times more selective than the reaction with 4-methoxystyrene.

To get more information about the alkenes that are electronically tolerated by the ruthenium catalyst, we investigated the cyclopropanation of some vinyl compounds having an α-heteroatom. The results are summarised in

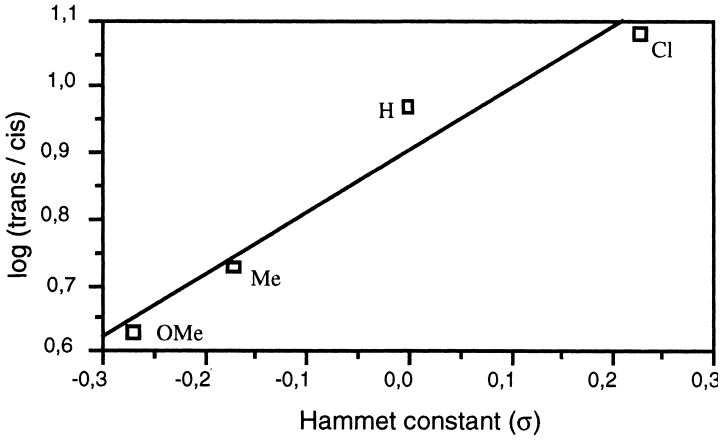


Figure 3. *trans*/*cis* Ratio against Hammet parameters for the cyclopropanation of styrene derivatives with EDA.

Table 5. Cyclopropanation of vinyl compounds with α-Heteroatoms catalysed by (TPP)Ru(CO) (catalyst: 0.0027 mmol; olefin: 0.270 mmol; EDA: 0.270 mmol; 6 h; RT)

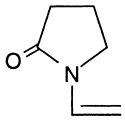
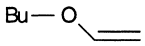
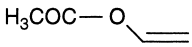
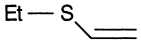
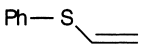
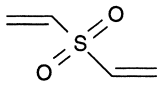
Vinyl compound	Yield (%)	*trans*/*cis* Ratio
	74	11.5
	61	2.1
	0	–
	67	3.6
	61	1.8
	0	–
	0	–

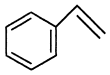
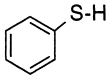
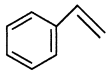
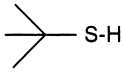
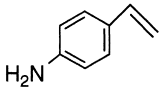
Table 5. Alkenes bearing electron-donating groups (S–R; O–R) are efficiently cyclopropanated with a weak stereoselectivity (an equimolar ratio of alkene to EDA was used for these reactions). In contrast, alkenes bearing electron-withdrawing groups (O–C=O; Br; SO_2) show a dramatic loss of reactivity, only the dimeric by-products, diethyl maleate and fumarate, being observed. Simple olefins such as 4-vinyl-1-cyclohexene or allylbenzene are also very poor substrates.[11a] Thus heteroatom substituents such as oxygen in vinyl ether and sulphur in vinyl thioether offer advantages in reactivity but not in selectivity. However, increasing the steric bulk of the olefinic substituent such as in 1-vinyl-2-pyrrolidinone, does result in enhancement of the relative percentage of the less encumbered cyclopropane product with a ratio of *trans*/*cis*=11.5. These data confirm the very strong sensitivity of the catalyst to both electronic and steric effects of the alkene substituents.

Competition between cyclopropanation and insertion into N–H or S–H bonds

To fully characterise the catalytic property of the ruthenium porphyrin compound, an investigation of the competition between the cyclopropanation of alkenes with EDA and the insertion of the diazo compound into heteroatom–hydrogen bond was also undertaken. In a typical experiment, 1 equiv. of EDA was added to a mixture of 10 equiv. of styrene and 10 equiv. of a thiol or an amine in toluene (see Section 4). Results are displayed in Table 6.

All the data show that the major reaction is the insertion of EDA into a heteroatom bond to give either an α-thio ethyl ester or an *N*-substituted glycine ester. For example, only the insertion compound is observed by GC/MS and ^{1}H NMR when 4-aminostyrene is the substrate. It should be noted that a preference for insertion has already been observed in the rhodium-catalysed reaction of diazoesters with unsaturated alcohols.[18]

Table 6. Competition studies of the cyclopropanation and diazo insertion into heteroatom–hydrogen bond (catalyst: 0.0027 mmol; substrates A and B: 2.70 mmol; EDA: 0.270 mmol; 4 h; RT)

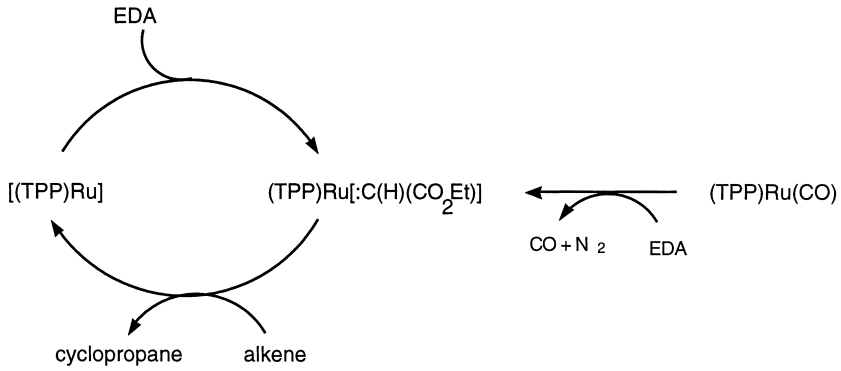
Substrate A	Substrate B	% of Insertion
		>99
		>99
	–	>99

Discussion

The data in Tables 1–6 clearly show that the chemical reactivity of alkenes in the cyclopropanation catalysed by ruthenium–porphyrin complexes is strongly dependent upon the electronic nature of the substrate. These results are in agreement with our precedent studies[13] showing that a porphyrin ruthenium carbene complex can be an intermediate of the cyclopropanation reaction, the limiting step being the attack of the double bond on the electrophilic carbene. When the rate of the carbene transfer from the ruthenium complex to the olefin is too low, the competitive formation of diethyl maleate and fumarate by attack of EDA on the electrophilic carbon becomes the major process. Electron-releasing groups increase the nucleophilic behaviour of the alkene, and so increase the rate of cyclopropanation, whereas the presence of electron-withdrawing groups decreases this rate. The same trend has already been reported by Kodadeck[7] and Woo[16] using iron and osmium porphyrins, respectively. In contrast, no electronic influence was detected for rhodium porphyrin catalysed cyclopropanation.[15c]

When there are no (or weak) steric interactions between the substrate and the *meso*-substituents of the macrocycle, the diastereoselectivity (*trans*/*cis* ratio) is also influenced by electronic effects. As shown by data in Table 4, the *trans* isomer is very predominant when electron-withdrawing groups are in the *para*-position of the styrene. Thus decreasing the reactivity of the double bond results in an enhancement of the *trans*/*cis* ratio. In contrast, it must be noted that we have recently shown that the enantioselectivity of the cyclopropanation with chiral ruthenium porphyrin complexes is not affected by such electronic effects.[11b] The selectivity is also strongly dependent upon the metalloporphyrin used as catalyst. Osmium and iron,[7,16] as well as ruthenium derivatives, provide the *trans* cyclopropyl ester as the major product. In contrast rhodium usually leads to a *trans*/*cis* ratio close to 1, and sometimes to the *cis* isomer as main product.[15]

The second main characteristic of ruthenium porphyrin catalyst is its strong shape selectivity. Only alk-1-enes and 1,1-disubstituted alkenes react efficiently with EDA. This is



Scheme 1. Catalytic cycle for the cyclopropanation of alkenes with (TPP)Ru(CO).

shown by data in Table 3, the more activated double bond being cyclopropanated more slowly than the less hindered. Thus the ruthenium is still similar to iron and osmium based catalysts, and contrasts with the broader substrate compatibility of rhodium porphyrins.[15]

Based on our previous results[13] and on other work,[7] we propose a catalytic cycle to rationalise these data (Scheme 1). The first step of this cycle is the formation of a ruthenium carbene complex. After the liberation of the cyclopropane, a highly reactive bare ruthenium(II) complex [(TPP)Ru] (possibly coordinated by nitrogen[19]) is released in solution, and can react with a new molecule of EDA. A tri-centre late transition state with a small cationic charge $\delta+$ on the double bond,[7] which is consistent with the fact that porphyrin ruthenium(II) carbene complexes are isolable and with the moderate negative ρ value obtained from the Hammet plot, is probably involved in the formation of the cyclopropane. This scheme is supported by the strong shape selectivity observed with tri- or tetra-substituted alkenes. This is explained by severe steric interactions between the porphyrin ring and the olefin substituents in the transition state. Such interactions would be reduced in the early transition state proposed for rhodium-catalysed cyclopropanation.[7]

This model and the data in Table 4 showing that the *trans*/*cis* ratio is inversely proportional to the reactivity of the olefin also support the proposal of Kodadek and co-workers[7] that the diastereoselectivity of the cyclopropanation is the result of a late transition state.

In summary, highly efficient cyclopropanations have been developed by reaction of ethyl diazoacetate with alkenes using a commercially available ruthenium porphyrin catalyst. The success of this methodology rests on the excellent stereoselectivity and high turnovers that are observed in the cyclopropanation and also the easy extension to chiral ruthenium porphyrins.

Experimental

General procedures

NMR spectra were recorded in $CDCl_3$ on a Bruker 200 DPX and chemical shifts are referenced to internal TMS. GC/MS analyses were performed on a CE GC8000 coupled with a Finnigan Mat AutomassII. High-Resolution Mass Spectrometry (EI) was performed at the Centre de Mesures Physiques de l'Ouest, Rennes on a Varian MAT311 spectrometer (2980 V, 30°) coupled with a GC. Toluene was distilled under sodium/benzophenone. The porphyrins were synthesised by literature methods: $TPPH_2$[20] and MPIXDME-H_2.[21] The corresponding ruthenium carbonyl complexes were obtained by refluxing the porphyrins in *o*-dichlorobenzene[22] with Ru_3CO_{12}.[23] Ethyl diazoacetate, styrenes and vinyl derivatives were purchased from Aldrich, Acros Organics or Lancaster.

Stereochemistry of cyclopropyl esters was assigned by ^1H NMR spectroscopy by comparison with published data when previously described.[24,25] The stereochemical assignments for the new cyclopropyl esters were based on a combination of NOE enhancement studies and determination of coupling constants on the cyclopropane ring. Once the major isomer was assigned by NMR, product ratios were then determined by GC/MS.

Cyclopropanation of styrene derivatives using (MPIXDME)Ru(CO). In a typical experiment 2.7 μmol of catalyst, 0.54 mmol of olefin were placed in a schlenk tube under argon, and dissolved in 300 μl of toluene. Ethyl diazoacetate (28 μl, 0.27 mmol) was then slowly added (16 μl h^{-1}) at room temperature. After 3 h of stirring, GC/MS analysis was performed to determine yields.

Cyclopropanation of vinyl compounds using (TPP)Ru(CO). In a typical experiment 2.7 μmol of catalyst and 0.27 mmol of olefin were placed in a schlenk tube under argon and dissolved in 300 μl of toluene. Ethyl diazoacetate (28 μl, 0.27 mmol, in 92 μl of toluene) was then slowly added (9 μl h^{-1}) at room temperature. After 3 h of stirring, GC/MS analysis was performed to determine yields. Products were purified by silica gel chromatography (pentane/ether, 5:1).

Competition studies. In a typical experiment 2.7 μmol of catalyst, 2.70 mmol of thiol (or styrene derivative) and 2.70 mmol of styrene were placed in a schlenk tube under argon, and dissolved in 300 μl of toluene. Ethyl diazoacetate (28 μl, 0.27 mmol) was then slowly added (20 μl h^{-1}) at room temperature. After 3 h of stirring, GC/MS analysis was performed to determine yields.

When an amine was used as substrate, the amine was added together with EDA to avoid catalyst poisoning.[11e]

Ethyl 2-butoxycyclopropanecarboxylate (*E* isomer). ^{1}H NMR ($CDCl_3$, δ): 4.11 (q, 2H, J=7.1 Hz, CH_2); 3.57 (d of d of d, 1H, J=1.9 Hz, 4.3 Hz, 6.1 Hz, OCH); 3.52 (m, 2H, CH_2O); 1.72 (d of d of d, 1H, J=2.1 Hz, 6.2 Hz, 9.4 Hz, $CHCO_2$); 1.28 (m, 2H, CH_2); 1.55–0.82 (10H, CH_3+$CH_3CH_2CH_2$). IR (cm^{-1}): 1725 (ν_{CO}). Mass (*m*/*z*) (relative intensity): 186 (3), 129 (8), 101 (22), 85 (17), 57 (69), 41 (46), 19 (100); HR-MS (*m*/*z*): calcd for $C_{10}H_{18}O_3$ (M^+): 186.1256, found: 186.1263.

Ethyl 2-pyrrolidinonecyclopropanecarboxylate (*E* isomer). ^{1}H NMR ($CDCl_3$, δ): 4.19 (q, 2H, J=7.2 Hz, CH_2); 3.35 (t, 2H, 7.0 Hz, CH_2CO); 3.21 (m, 1H, NCH); 2.43 (t, 2H, J=8.0 Hz, CH_2N); 2.06 (m, 2H, CH_2); 1.89 (d of d of d, 1H, J=3.0 Hz, 5.9 Hz, 9.1 Hz, $CHCO_2$); 1.50 (m, 2H, CH_2); 1.29 (t, 3H, J=7.2 Hz, CH_3). IR (cm^{-1}): 1713 (ν_{COO}), 1704 (ν_{CO}). Mass (*m*/*z*) (relative intensity): 197 (8), 168 (10), 151 (16), 140 (8), 124 (100), 112 (64), 96 (21), 84 (27), 69 (35), 56 (31), 41 (79), 28 (34), 18 (39); HR-MS (*m*/*z*): calcd for $C_{10}H_{15}NO_3$ (M^+): 197.1052, found: 197.1046.

Ethyl 2-ethylmercaptocyclopropanecarboxylate (*E* isomer). ^{1}H NMR ($CDCl_3$, δ): 4.15 (q, 2H, J=7.1 Hz, CH_2); 2.63 (q, 2H, J=7.4 Hz, CH_2S); 2.45 (d of d of d; 1H, J=3.6 Hz, 5.7 Hz, 8.3 Hz; SCH); 1.77 (d of d of d; 1H; J=3.6 Hz, 5.2 Hz, 8.7 Hz; $CHCO_2$); 1.48 (d of d of d; 1H; J=4.6 Hz, 5.3 Hz, 8.3 Hz; CH); 1.29 (m; 6H; CH_3); 1.12 (d of d of d; 1H; J=4.6 Hz, 5.7 Hz, 8.6 Hz; CH). IR (cm^{-1}): 1716 (ν_{COO}). Mass (*m*/*z*) (relative intensity): 174 (25), 145 (12), 128 (30), 101 (48), 73 (12), 45 (30), 29 (23), 18 (100); HR-MS (*m*/*z*): calcd for $C_8H_{14}O_2S$ (M^+): 174.0714, found: 174.0712.

Ethyl 2-(4-vinylphenylamino)acetate. ^{1}H NMR ($CDCl_3$, δ): 7.33 (d, 2H, J=8.4 Hz, Ph); 6.68 (m, 1H, C*H*=CH_2); 6.63 (d, 2H, J=8.4 Hz, Ph); 5.61 (d, 1H, J=17.0 Hz, CH=C*H*$_2$); 5.10 (d, 1H, J=10.8 Hz, CH=C*H*$_2$); 4.41 (q, 2H, J=7.2 Hz, CH_2); 3.97 (d, 2H, J=5.0 Hz, NCH_2); 1.37 (t, 3H, 7.1 Hz, CH_3). IR (cm^{-1}): 1739 (ν_{COO}), 1611 ($\nu_{C=C}$). Mass (*m*/*z*) (relative intensity): 205 (25), 132 (100), 103 (12), 119 (31), 91 (9), 77 (15), 65 (3), 39(2), 29 (7), 18 (9); HR-MS (*m*/*z*): calcd for $C_{12}H_{15}NO_2$ (M^+): 205.1103, found: 205.1099.

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