# Reactions of diazo esters with electron-deficient alkenes in the presence of Lewis acids

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1,3-Dipolar cycloaddition reaction of diazo esters to electron-deficient dipolarophiles to yield the corresponding 1- or 2-pyrazolines was found to be significantly accelerated with Lewis acids ($Yb(OTf)_3$, $Sc(OTf)_3$, $GaCl_3$, $EtAlCl_2$). The use of $GaCl_3$ as the catalyst leads to the acceleration not only of the 1,3-dipolar cycloaddition reaction, but also subsequent insertion of the $CHCO_2Me$ electrophilic fragment of methyl diazoacetate into the N—H bond of 2-pyrazolines formed. Such Lewis acids as $SnCl_4$, $BF_3$, $TiCl_4$, and $In(OTf)_3$ are not efficient in the described processes, since they rapidly decompose starting diazo compounds.

**Key words:** diazo esters, pyrazolines, Lewis acids, 1,3-dipolar cycloaddition, N—H insertion, catalysis.

One of the most general reactions of aliphatic diazo compounds is their 1,3-dipolar cycloaddition to unsaturated compounds. In the case of alkenes and their derivatives, these reactions lead to the formation of 1- or 2-pyrazolines,[1] which are useful for the synthesis of various classes of compounds[2] including those possessing biological activity.[3] However, in the most cases reactions of diazo carbonyl compounds with alkenes require either long reaction time or heating, or use of alkenes with electron-withdrawing substituents or with a strained double bond. In a number of cases for acceleration of these reactions, heating in combination with catalysis with pyridine[4] or molybdenum hexacarbonyl is used.[5] There are also known several works, in which reactions of diazo esters with activated alkenes were studied in the presence of Lewis acids, such as titanium, nickel, magnesium compounds.[3,6,7] However, in this case the main attention has been paid to the study of enantioselectivity of the process, though, some acceleration of the reactions under influence of these catalysts has been noted. There is also report[8] on acceleration of 1,3-dipolar cycloaddition of diazoacetates to alkynes with the formation of pyrazoles upon catalysis with aqueous indium trichloride.

The absence of systematic studies on the influence of Lewis acids on the reactions of diazo esters with unsaturated compounds with a wide enough variation in the nature of substituents in them apparently is due to the instability of diazo carbonyl compounds themselves in the presence of Lewis acids,[9] which strongly complicates performing the 1,3-dipolar cycloaddition reaction.

## Results and Discussion

In the present work, we made an effort to estimate effect of various Lewis acids on acceleration of the reactions of diazo carbonyl compounds with unsaturated compounds and on a possibility of insertion of the electrophilic fragment of the diazo compounds into the N—H bond of 2-pyrazolines formed. The reaction of methyl diazoacetate (MDA) with methyl acrylate was chosen as a model reaction for this study, which at room temperature in the absence of a catalyst is fairly slow and leads to a high yield of 2-pyrazoline **1** (90—93%) at 25 °C only after 24 h. Addition of scandium or ytterbium triflates in catalytic amounts (5—6 mol.%) to a solution of MDA and methyl acrylate (molar ratio ~1 : 2) in $CH_2Cl_2$ leads to a considerable acceleration of the 1,3-dipolar cycloaddition reaction (about 50-fold), which results in virtually complete conversion of MDA already after 40 min. The presence of anhydrous $Yb(OTf)_3$ gives rise to expected pyrazoline **1** in up to 90% yield, whereas the presence of $Sc(OTf)_3$ yields, together with the major compound **1**, N-substituted pyrazoline **2** (Scheme 1, Table 1). The latter is obtained due to the partial dediazotization of MDA and insertion of the $CHCO_2Me$ electrophilic fragment into the N—H bond of the initially formed 2-pyrazoline **1**.

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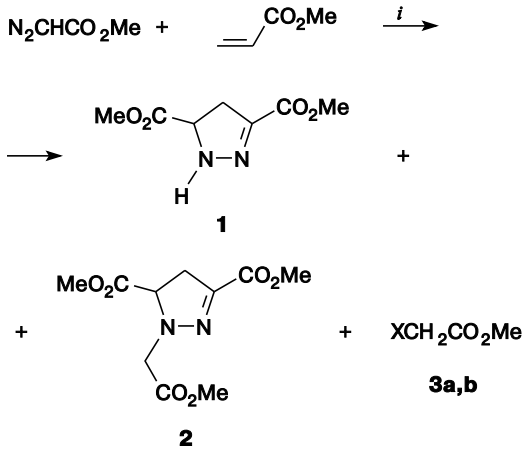
**Table 1.** Reaction products of MDA and methyl acrylate (the molar ratio 1 : 2) in the presence of Lewis acids ($CH_2Cl_2$, 20 °C)

| Lewis acid | *c* (mol.%) | *t*/ min | Yield (%) | | |
|---|---|---|---|---|---|
| | | | **1** | **2** | **3** |
| $Yb(OTf)_3$ | 5 | 40 | 90 | — | 4 |
| $Sc(OTf)_3$ | 6 | 40 | 74 | 15 | 4 |
| $Sn(OTf)_2$ | 10 | 30 | 35 | 7 | 10 |
| $GaCl_3$ | 10 | 5 | 9 | 45 | 4 |
| $GaCl_3$ | 20 | 5 | 15 | 76 | 5 |
| $EtAlCl_2$ | 100 | 4 | >90 | — | 5 |
| $SnCl_4$ | 100 | 2 | 10 | — | 85 |
| $TiCl_4$ | 100 | 2 | — | — | 96 |
| $In(OTf)_3$ | 20 | 2 | — | — | 94 |

Anhydrous dichloromethane should be used as the solvent for the maximum yield of pyrazolines to be achieved.

Tin(II) triflate acts similarly to scandium triflate giving rise, along with pyrazoline **1**, to the insertion product into the N—H bond of pyrazoline **2** (see Table 1). However, $Sn(OTf)_2$ itself actively enough reacts with diazo ester, losing the catalytic activity. After a work-up of the reaction mixture with 5% aqueous HCl, significant amount of triflate anions is found as compound **3b**.

**Scheme 1**




X = Cl (**a**), OTf (**b**)

**Reagents and conditions:** Lewis acid, $CH_2Cl_2$.

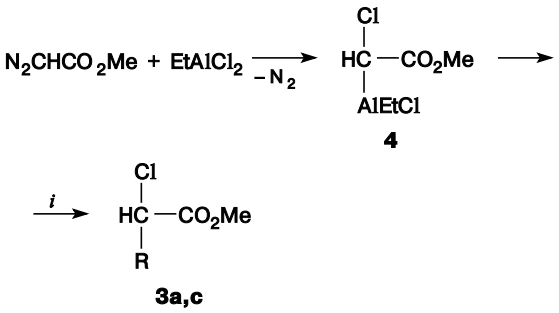
Anhydrous gallium trichloride, which itself decomposes diazo esters slowly enough, is an interesting catalyst accelerating the reaction of MDA with methyl acrylate. Addition of 20 mol.% of $GaCl_3$ to a solution of MDA and methyl acrylate in $CH_2Cl_2$ at 20 °C is accompanied by a noticeable gas evolution and complete conversion of the diazo ester already after 5 min. N-Substituted 2-pyrazoline **2** was the major product, which was isolated in 76% yield (after decomposition of the reaction mixture with dilute HCl), 2-pyrazoline **1** was the minor product (Scheme 1, see Table 1). When 10 mol.% of $GaCl_3$ has been used, the yields of pyrazolines were reduced (see Table 1), whereas a part of the diazo ester remains unreacted even after 30 min, which apparently is due to the involvement of $GaCl_3$ in complexation with pyrazoline **1**. Thus, gallium trichloride is very specific catalyst, which efficiently accelerates not only the 1,3-dipolar cycloaddition reaction, but also the insertion reaction of the $CHCO_2M$ fragment into the N—H bond of the initially formed 2-pyrazoline **1**.

Significant overall yield of pyrazolines **1** and **2** when 10—20 mol.% of $GaCl_3$ is used indicates that the latter has time to be involved into several catalytic cycles before it is removed from the reaction in the form of the complex with 2-pyrazoline **1**. Such complexation, in particular, is due to its good absorption with silica gel, as a result virtually all the pyrazoline **1** formed in the reaction remains on the sorbent. This property of the complex can be used for the isolation of pure N-substituted 2-pyrazoline **2** from the reaction mixture, which is enough to be passed through a short layer of silica gel before work-up with HCl.

Ethylaluminum dichloride used as a 0.8 *M* solution in hexane is an efficient reagent significantly accelerating the 1,3-dipolar addition of MDA to methyl acrylate with low amount of side products. Ethylaluminum dichloride itself fairly rapidly decomposes the diazo ester with evolution of nitrogen, giving rise to the low stable organoaluminum compound **4**. Its decomposition with water or methanol gives methyl chloroacetate **3a**, whereas in the case when $D_2O$ or MeOD are used, monodeuterated chloroacetate **3c** is formed (Scheme 2). Analogous transformations apparently takes place in the case of other Lewis acids, resulting in the transformations of diazo esters to chloroacetates **3** as well.

Despite that the diazo ester is readily decomposed by $EtAlCl_2$, it accelerates the reaction of MDA with methyl

**Scheme 2**




R = H (**a**), D (**c**)

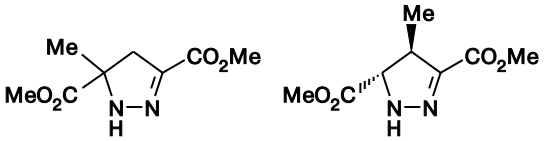
*i*. ROH or ROMe

acrylate so strong, that pyrazoline **1** is obtained in more than 90% yield just for several minutes (see Table 1). Successful progress of the target reaction apparently is promoted by the coordination of $EtAlCl_2$ with the ester group of the substrate, which, from the one hand, activates the C=C bond and, from the other hand, reduces electrophilicity of $EtAlCl_2$ with respect to the diazo ester. It should be noted that in this reaction, $EtAlCl_2$ is taken in the equimolar ratio to diazo ester, since 2-pyrazoline **1** formed tightly coordinates $EtAlCl_2$ thus removing it from the reaction. For the isolation of target pyrazoline, the reaction mixture is treated with dilute aqueous HCl. If the reaction is performed thoroughly (in particular, a dry atmosphere is used), the formation of undesirable chloroacetate can be reduced to trace amounts.

Our efforts to use a number of other Lewis acids, such as $TiCl_4$, $SnCl_4$, or $In(OTf)_3$, proved unsuccessful, since all of them actively decomposed MDA with major formation (after hydrolysis) of methyl chloroacetate (**3a**) or methyl (trifluoromethylsulfonyl)acetate (**3b**).

To sum up, among compounds studied only ytterbium triflate and ethylaluminum dichloride allow to significantly accelerate the 1,3-dipolar cycloaddition of methyl diazoacetate to methyl acrylate with the formation of 2-pyrazoline **1** in high yields. Gallium trichloride not only allows to accelerate this reaction, but promotes efficient insertion of the $CHCO_2Me$ fragment of the diazo ester into the N—H bond of forming 2-pyrazoline as well.

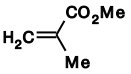
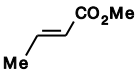
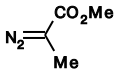
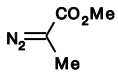
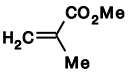
The regularities found were used in the reactions of other diazo carbonyl and unsaturated compounds. For instance, it turned out that the reaction of MDA with methyl methacrylate at 20 °C in the presence of equimolar amount of $EtAlCl_2$ proceeds similarly to the reaction with methyl acrylate and just for 4 minutes (instead of 48 h) leads to 2-pyrazoline **5** in 85% yield (Table 2). Ethylaluminum dichloride significantly accelerates the reaction of MDA with methyl crotonate as well, giving rise to *trans*-4-methyl-2-pyrazolinedicarboxylate **6** in 55% yield (see Table 2). Since methyl crotonate is less reactive than methyl acrylate, the reaction time in this case considerably increases, which facilitates a competing reaction of $EtAlCl_2$ with MDA and, in the end after hydrolysis, the side formation of chloroacetate **3a**.




**5** **6**

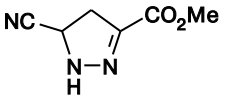
Ethylaluminum dichloride cannot be used in the reaction of MDA with acrylonitrile, since it itself readily adds to the acrylonitrile double bond. On the contrary, the use of ytterbium triflate in amount of 5 mol.% is successful in activating the 1,3-dipolar cycloaddition of MDA to acrylonitrile and when the reaction is performed in

**Table 2.** Reaction of diazo esters with electron-deficient alkenes (the molar ratio ~1 : 2) in the presence of Lewis acids in $CH_2Cl_2$ as the solvent

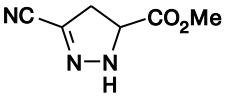
| Diazo ester | Unsaturated compound | Lewis acid | *c* (mol.%) | Reaction conditions* | | Reaction products | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | | | *t* | *T*/°C | | |
| $N_2CHCO_2Me$ |  | $EtAlCl_2$ | 100 | 4 min (48 h) | 20 | **5** | 85 |
| $N_2CHCO_2Me$ |  | $EtAlCl_2$ | 100 | 15 min | 10 | **6** | 55 |
| $N_2CHCO_2Me$ |  | $Yb(OTf)_3$ | 5 | 30 min | 40 | **7a** : **7b** (4 : 1) | 82 |
| $N_2CHCO_2Me$ |  | $GaCl_3$ | 50 | 15 min | 5—10 | **7b** : **8** (1 : 1) | 72 |
| $N_2CHCO_2Me$ |  | $EtAlCl_2$<br>$Yb(OTf)_3$<br>$GaCl_3$ | 100<br>6<br>20 | 15 min<br>2 h<br>2 h | 20<br>20<br>10 | **9** (see Ref. 10) | — |
|  |  | $EtAlCl_2$<br>$GaCl_3$ | 100<br>10 | 4 min (36 h)<br>5 min | 20<br>20 | **5** | 85<br>82 |
|  |  | $Yb(OTf)_3$ | 5 | 30 min (80 h) | 20 | **10** ($E$ : $Z$ = 3.7 : 1) | 85 |
| $N_2C(CO_2Me)_2$ |  | $GaCl_3$ | 50 | 12 h | 20 | **11** | ~30 |

* In parentheses is given the reaction time without Lewis acid.

boiling $CH_2Cl_2$ leads to a mixture of isomeric pyrazolines **7a** and **7b** (the ratio ~4 : 1) in the overall yield of 82% (see Table 2).



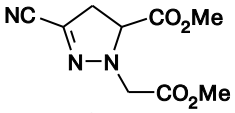
**7a**



**7b**

Formation of the isomeric mixture distinguishes this process from the reaction of ethyl diazoacetate with acrylonitrile in the presence of pyridine (the molar ratio 1 : 10 : 5, 60 °C, 3 h) described in the literature,[4] which results in the formation of only single isomer, *viz.*, pyrazoline with the conjugated ethoxycarbonyl group analogous to **7a**. In this connection, we studied behavior of pyrazolines **7a** and **7b** upon the action of pyridine directly in the NMR tube, analyzing isomeric composition from the integral intensities of nonoverlapped signals of the methine and methoxy protons. Keeping the mixture of pyrazolines **7a** and **7b** (~4 : 1) in pyridine-$d_5$ for 1.5 h at 25 °C virtually produces no changes. However, when this mixture is heated at 60 °C for 20 min, the fraction of isomer **7a** decreases two-fold and after another 5 min at 100 °C, the ratio of isomers becomes equal to about 1 : 1. Further keeping this mixture at 100 °C for another 12 min makes the ratio **7a** and **7b** equal to 1 : 2.9, which further virtually remains unchanged.

Gallium trichloride shows significant acceleration of the reaction of MDA with acrylonitrile as well. Gradual addition of 50 mol.% $GaCl_3$ in dichloromethane over 15 min at 5—10 °C leads to a regioselective formation of pyrazoline **7b**, which, like in the reaction of MDA with methyl acrylate, is further readily transformed to N-substituted pyrazoline **8** (see Table 2). Despite a two-fold excess of acrylonitrile, both pyrazolines were obtained in the ratio about 1 : 1. We have shown that pyrazoline **8** can be obtained in ~70% yield also by the insertion of the methoxycarbonylcarbene fragment into the N—H bond of pyrazoline **7b** under conditions of dediazoniation of MDA upon the action of $Rh_2(OAc)_4$ in boiling dioxane.

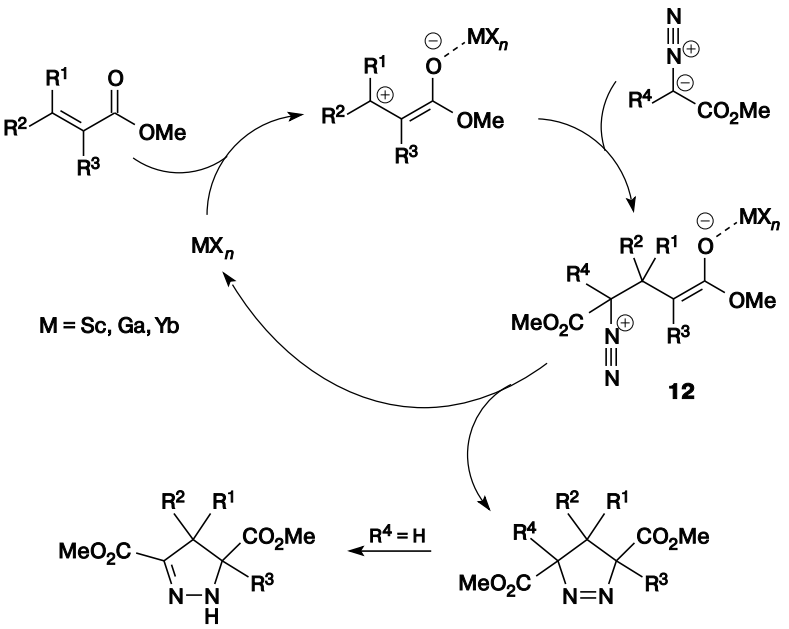


**8**

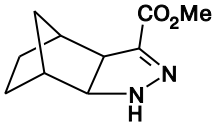
The same-type position of substituents in pyrazolines **7b** and **8** was inferred from their $^{13}C$ NMR spectra, according to which in both pyrazolines the signals for the carbon atoms C(3), CN, and COO are found at $\delta_C$ 121—124, 113.7, and 169—171, respectively, whereas in pyrazoline **7a** analogous signals of C atoms are found, respectively, at $\delta_C$ 142.7, 117.9, and 161.6.

Apparently, the presence of an electron-withdrawing group on the double bond, capable to coordinate Lewis acids and significantly polarize the C=C bond, is the major reason for the significant acceleration of the 1,3-dipolar cycloaddition reaction (Scheme 3). When the C=C bond is not enough activated, the reaction of a Lewis acid with a diazo ester leading to its dediazotization becomes predominant. This suggestion is confirmed by the absence of the catalytic effect by the Lewis acids studied above on the cycloaddition of MDA to norbornene

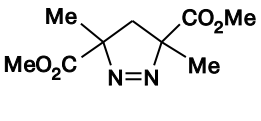
**Scheme 3**



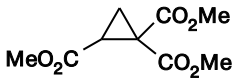
containing no electron-withdrawing groups on the double bond. When the catalyst is absent, its reaction with MDA[10] proceeds upon reflux in benzene for 8 h and gives *exo*-5-methoxycarbonyl-3,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-4-ene (**9**) in 67% yield. The use of Lewis acids ($EtAlCl_2$, $Yb(OTf)_3$, $GaCl_3$) independent on the reaction conditions leads only to various side transformations of MDA.




**9**




**10**




**11**

Effect of Lewis acids on the behavior of diazo esters in the reactions with electron-deficient alkenes was also studied using the reaction of methyl diazopropionate and dimethyl diazomalonate with acrylates as an example. The use of $EtAlCl_2$ in equimolar amount accelerates the reaction of methyl diazopropionate with methyl acrylate almost 500-fold and expected 2-pyrazoline **5** was obtained as a major product in up to 85% yield (see Table 2), which is identical to the reaction product of MDA with methyl methacrylate. Gallium trichloride also successfully accelerates the 1,3-dipolar cycloaddition reaction, in this case catalytic (~10 mol.%) amount of $GaCl_3$ is enough for the reaction to be successful and the reaction itself stops on the step of N-unsubstituted pyrazoline **5** formation. The absence of the N—H insertion product in this case apparently is due to both the steric factor and the higher stability of methyl diazopropionate to $GaCl_3$.

The reaction of methyl diazopropionate with methyl methacrylate in the absence of a catalyst proceeds at 20 °C for 3—4 days and leads to a mixture of isomeric 1-pyrazolines **10** with the overall yield of 85—90%. Addition of $EtAlCl_2$ or $GaCl_3$ to the reaction mixture is accompanied by a rapid enough transformation of the starting reagents, which, however, results in the obtaining a complex mixture of compounds containing only 25—30% of pyrazolines **10**. The use of softer Lewis acid, *viz.*, 5 mol.% of ytterbium triflate, proved more efficient: the reaction time is reduced to 30 min, whereas the overall yield of pyrazolines *E*- and *Z*-**10** reaches 85% (see Table 2). It should be noted that the accelerating effect of $Yb(OTf)_3$ virtually has no influence on the stereoisomeric composition of pyrazolines formed.

Dimethyl diazomalonate is very stable and low active diazo compound. It virtually does not give the 1,3-dipolar cycloaddition reaction even with methyl acrylate. Such Lewis acid as $EtAlCl_2$, $SnCl_4$ and $TiCl_4$ had no positive effect right up to 80 °C. Only the presence of $GaCl_3$ (the molar ratio methyl acrylate : diazomalonate : $GaCl_3$ = = 2 : 1 : 0.5) made dimethyl diazomalonate to slowly react with methyl acrylate at 20 °C providing ~50% conversion of diazomalonate after 12 h. However, in this case cyclopropanetricarboxylate **11** was isolated from the reaction mixture in ~30% yield instead of pyrazoline. Further keeping the reaction mixture or performing the reaction at elevated temperatures gave no positive result due to the increase in the amount of side transformations and formation of a complex mixture of compounds. Apparently, the presence of two geminal electron-withdrawing groups on the α-C atom leads to elimination of nitrogen molecule from the intermediate **12** (see Scheme 3; $R^1 = R^2 = R^3 = H$, $R^4 = CO_2Me$) before it cyclizes to pyrazoline.

In conclusion, the use of Lewis acids allows one in a number of cases to significantly accelerate the 1,3-dipolar cycloaddition reactions of diazo esters to olefins activated with an electron-withdrawing substituent and carry out them at room temperature for several minutes instead of several hours or days. Dichloromethane was found to be the most appropriate solvent, whereas such Lewis acids as $EtAlCl_2$, $GaCl_3$ (acceleration by 300—500 times), $Yb(OTf)_3$, and $Sc(OTf)_3$ (acceleration by 50—100 times) are acceptable catalysts. In these reactions, $EtAlCl_2$ is necessary to use in equimolar amount with respect to diazo ester, whereas $GaCl_3$, together with the 1,3-dipolar cycloaddition reaction, significantly activates insertion of the electrophilic fragment of the diazo ester into the N—H bond of 2-pyrazolines as well. On the whole, accelerating effect of Lewis acids in the reactions of diazo compounds with unsaturated substrates apparently is due to the coordination of the Lewis acid with the hetero atom of the electron-withdrawing substituent, which causes a strong polarization of the double bond.

## Experimental

$^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker Avance II 300 (300 and 75.5 MHz, respectively) and Bruker AMX-400 spectrometers (400 and 100.7 MHz, respectively) for solutions in $CDCl_3$ containing 0.05% of $Me_4Si$ as an internal standard. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct injection). Merck silica gel 60 (0.040—0.063 mm) was used for chromatography. Methyl diazoacetate, methyl diazopropionate, and dimethyl diazomalonate were synthesized according to the described procedures.[11—13] In this work we used Lewis acids $Sc(OTf)_3$ and $Sn(OTf)_2$ purchased from Acros Organics; $EtAlCl_2$ (0.8 *M* solution in hexane), $GaCl_3$, $Yb(OTf)_3$, and $In(OTf)_3$ from Aldrich. Dichloromethane was first kept over granulated KOH to bound HCl and then distilled over $P_2O_5$ under dry argon.

**Reaction of methyl diazoacetate with unsaturated compounds in the presence of Lewis acids (general procedure).** A Lewis acid (5—10 mol.%) was added either in one portion for the solid $Sc(OTf)_3$, $Yb(OTf)_3$, or $GaCl_3$ or dropwise for solutions of

$EtAlCl_2$ in hexane (0.8 *M*, 100 mol.%) or $GaCl_3$ in dichloromethane (0.5—1 mL) (20—50 mol.%) to a stirred solution of methyl diazoacetate (2 mmol) and unsaturated compound (4 mmol) in dichloromethane (5 mL) under argon at 5—20 °C. The reaction mixture was stirred over period of time indicated in Tables 1 and 2, then treated with 5% aq. HCl at 0 °C to pH 3, and extracted with dichloromethane (3×10 mL). The organic extracts were combined, dried with anhydrous $MgSO_4$, the solvent was evaporated *in vacuo*, and the residue was analyzed by $^1$H NMR spectroscopy. The reaction products were isolated by column chromatography on silica gel using a mixture of benzene and AcOEt with the gradient from 4 : 1 to 2 : 1 as an eluent, unless otherwise is specified.

**Dimethyl 4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (1).** Methyl diazoacetate (0.20 g, 2 mmol), methyl acrylate (0.35 g, 4 mmol), and 0.8 *M* solution of $EtAlCl_2$ in hexane (2.5 mL, 2 mmol), which was added over 1 min, yielded pyrazoline **1** (0.34 g, 91%) with the purity >95%. $^1$H NMR spectrum agrees with that described earlier.[14] Pyrazoline **1** (0.17 g, 90%) was obtained similarly from methyl diazoacetate (0.10 g, 1 mmol), methyl acrylate (0.17 g, 2 mmol), and $Yb(OTf)_3$ (36 mg, 0.06 mmol).

**Dimethyl 1-(2-methoxy-2-oxoethyl)-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (2).** Methyl diazoacetate (0.20 g, 2 mmol), methyl acrylate (0.26 g, 3.0 mmol), and $GaCl_3$ (70 mg, 20 mol.%) in $CH_2Cl_2$ (0.5 mL) yielded pyrazoline **1** (56 mg, 15%) and pyrazoline **2** (195 mg, 76%). $^1$H NMR, δ: 3.30 (dd, 1 H, $H_aC(4)$, $^2J$ = 17.8 Hz, $^3J$ = 11.6 Hz); 3.40 (dd, 1 H, $H_bC(4)$, $^2J$ = 17.8 Hz, $^3J$ = 13.2 Hz); 3.71, 3.77, and 3.82 (all s, 3 H each, 3 OMe); 4.21 and 4.46 (both d, 1 H each, $H_2CN$, $^2J$ = 18.2 Hz); 4.66 (dd, 1 H, H(5), $^3J$ = 11.6 Hz and 13.2 Hz). $^{13}$C NMR, δ: 36.2 (C(4)); 52.1, 52.3 and 52.8 (3 OMe); 52.5 ($NCH_2$); 65.2 (C(5)); 139.7 (C(3)); 162.3 (COO at C(3)); 169.9 and 170.3 (2 COO). If the reaction mixture before treatment with dilute HCl was passed through a layer of silica gel, individual pyrazoline **2** was isolated in 72% yield.

**Dimethyl 5-methyl-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (5).** ***A.*** Methyl diazoacetate (0.20 g, 2 mmol), methyl methacrylate (0.40 g, 4 mmol), and 0.8 *M* solution of $EtAlCl_2$ in hexane (2.5 mL, 2 mmol) yielded pyrazoline **5** (0.35 g, 85%) as a colorless oil. $^1$H NMR, δ: 1.53 (s, 3 H, Me); 2.80 and 3.49 (both d, 1 H each, $H_2C(4)$, $^2J$ = 17.8 Hz); 3.75 and 3.81 (both s, 3 H each, 2 $CO_2$Me); 6.70 (br.s, 1 H, NH). $^{13}$C NMR, δ: 24.1 (Me); 41.3 (C(4)); 52.2 and 53.0 (2 OMe); 69.9 (C(5)); 142.2 (C(3)); 162.5 (COO at C(3)); 174.2 (COO at C(5)).

***B.*** Pyrazoline **5** (131—136 mg, 82—85%) was obtained from methyl diazopropionate (115 mg, 2 mmol), methyl acrylate (0.35 g, 4 mmol), and 0.8 *M* solution of $EtAlCl_2$ in hexane (2.5 mL, 2 mmol) or $GaCl_3$ (35 mg, 0.2 mmol) in dichloromethane (0.5 mL), which was identical to the sample obtained in method *A*.

**Dimethyl *trans*-4-methyl-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (6).** Pyrazoline **6** (0.22 g, 55%) was obtained from methyl diazoacetate (0.20 g, 2 mmol), methyl (*E*)-crotonate (0.40 g, 4 mmol), and a 0.8 *M* solution of $EtAlCl_2$ (2.5 mL, 2 mmol) at 10 °C as a colorless oil. Found (%): C, 48.22; H, 6.19; N, 13.77. $C_8H_{12}N_2O_4$. Calculated (%): C, 48.00; H, 6.04; N, 13.99. MS, $m/z$ ($I_{rel}$ (%)): 200 (14) $[M]^+$, 169 (10), 141 (100), 109 (54), 59 (34). $^1$H NMR, δ: 1.36 (d, 3 H, Me, $^3J$ = 7.2 Hz); 3.59 (dq, 1 H, H(4), $^3J$ = 4.1 Hz and 7.2 Hz); 3.76 and 3.84 (both s, 3 H each, 2 OMe); 4.04 (d, 1 H, H(5), $^3J$ = 4.1 Hz); 6.66 (br.s, 1 H, NH). $^{13}$C NMR, δ: 17.2 (Me); 43.2 (C(4)); 52.2 and 52.9 (2 OMe); 69.1 (C(5)); 146.4 (C(3)); 162.2 (COO at C(3)); 171.9 (COO at C(5)).

**Methyl 5-cyano-4,5-dihydro-1*H*-pyrazole-3-carboxylate (7a) and methyl 3-cyano-4,5-dihydro-1*H*-pyrazole-5-carboxylate (7b).** A mixture of pyrazolines **7a** and **7b** (0.25 g, 82%, the ratio ~4 : 1) was obtained from methyl diazoacetate (0.20 g, 2 mmol), acrylonitrile (0.21 g, 4 mmol), and $Yb(OTf)_3$ (62 mg, 0.1 mmol) as a colorless oil. Found (%): C, 47.35; H, 4.79; N, 27.27. $C_6H_7N_3O_2$. Calculated (%): C, 47.06; H, 4.61; N, 27.44. Isomer **7a**. $^1$H NMR, δ: 3.30 (m, 2 H, $H_2C(4)$); 3.87 (s, 3 H, OMe); 4.72 (dd, 1 H, H(5), $^3J$ = 8.9 Hz and 9.5 Hz); 6.99 (br.s, 1 H, NH). $^{13}$C NMR, δ: 36.7 (C(4)); 49.3 (C(5)); 52.5 (OMe); 117.9 (C≡N); 142.7 (C(3)); 161.6 (COO). Isomer **7b**. $^1$H NMR, δ: 3.18 (dd, 1 H, $H_a(4)$, $^2J$ = 17.3 Hz, $^3J$ = 12.0 Hz); 3.25 (dd, 1 H, $H_b(4)$, $^2J$ = 17.3 Hz, $^3J$ = 6.3 Hz); 3.81 (s, 3 H, OMe); 4.52 (dd, 1 H, H(5), $^3J$ = 6.3 Hz and 12.0 Hz); 7.00 (br.s, 1 H, NH). $^{13}$C NMR, δ: 36.5 (C(4)); 53.1 (OMe); 60.8 (C(5)); 113.7 (C≡N); 123.8 (C(3)); 170.9 (COO). $^1$H NMR spectrum of ethyl 5-cyano-4,5-dihydro-1*H*-pyrazole-3-carboxylate, a homologue of pyrazoline **7a**, is given in Ref. 4.

**Methyl 3-cyano-5-(2-methoxy-2-oxoethyl)-4,5-dihydro-1*H*-pyrazole-5-carboxylate (8).** ***A.*** Methyl diazoacetate (0.20 g, 2 mmol), acrylonitrile (0.21 g, 4 mmol), and $GaCl_3$ (0.17 g, 1 mmol) dissolved in dichloromethane (4 mL) yielded colorless oily liquid (0.19 g), from which pyrazoline **7b** (115 mg, 37%) ($R_f$ 0.4) and pyrazoline **8** (80 mg, 35%) ($R_f$ 0.7) were isolated by preparative TLC on $SiO_2$ (eluent: $CH_2Cl_2$—MeOH, 10 : 1). Found (%): C, 48.21; H, 5.02; N, 18.50. $C_9H_{11}N_3O_4$. Calculated (%): C, 48.00; H, 4.92; N, 18.66. MS, $m/z$ ($I_{rel}$ (%)): 225 (16) $[M]^+$, 193 (3), 166 (86), 138 (10), 106 (100). $^1$H NMR, δ: 3.34 (d, 2 H, $H_2C(4)$, $^3J$ = 12.4 Hz); 3.75 and 3.81 (both s, 3 H each, 2 OMe); 4.23 and 4.43 (both d, 1 H each, $CH_2N$, $^2J$ = 18.1 Hz); 4.69 (t, 1 H, H(5), $^3J$ = 12.4 Hz). $^{13}$C NMR, δ: 37.7 (C(4)); 52.1 and 53.0 (2 OMe); 52.2 ($CH_2N$); 64.3 (C(5)); 113.7 (C≡N); 120.9 (C(3)); 169.2 and 169.4 (2 COO).

***B.*** Methyl diazoacetate (0.15 g, 1.5 mmol) in dioxane (2 mL) was added to a boiling solution of pyrazoline **7b** (0.23 g, 1.5 mmol) and $Rh_2(OAc)_4$ (3.5 mg, 0.008 mmol) in dioxane (5 mL) over 1 h with stirring and the mixture was refluxed for another 4 h. Then dioxane was evaporated *in vacuo* and the residue was subjected to chromatography on silica gel with $CH_2Cl_2$ as an eluent to obtain pyrazoline **8** (0.51 g, 70%), which was identical to the sample obtained in method *A*.

**Dimethyl *E,Z*-3,5-dimethyl-4,5-dihydro-3*H*-pyrazole-3,5-dicarboxylate (10).** Stereoisomeric pyrazolines **10** (*E*/*Z* = 3.7 : 1) (146 mg, 85%) were obtained from methyl diazopropionate (91 mg, 0.8 mmol), methyl metacrylate (200 mg, 2 mmol), and $Yb(OTf)_3$ (24 mg, 0.04 mmol). Found (%): C, 50.74; H, 6.77; N, 12.95. $C_9H_{14}N_2O_6$. Calculated (%): C, 50.46; H 6.59; N, 13.08. $^1$H NMR, δ, *E*-isomer: 1.66 (s, 6 H, 2 Me); 2.01 (s, 2 H, $H_2C(4)$); 3.80 (s, 6 H, 2 $CO_2$Me); *Z*-isomer: 1.72 (s, 6 H, 2 Me); 1.32 and 2.77 (both d, 1 H each, $H_2C(4)$, $^2J$ = 13.5 Hz); 3.76 (s, 6 H, 2 $CO_2$Me). $^{13}$C NMR, δ, *E*-isomer: 22.8 (2 Me); 38.5 (C(4)); 53.0 (2 OMe); 98.1 (C(3), C(5)); 170.6 (2 COO); *Z*-isomer: 24.0 (2 Me); 39.0 (C(4)); 52.4 (2 OMe); 97.3 (C(3), C(5)); 170.8 (2 COO).

**Trimethyl 1,1,2-cyclopropanetricarboxylate (11).** Cyclopropane **11** (65 mg, 30%) was obtained as a colorless oil from dimethyl diazomalonate (0.16 g, 1 mmol), methyl acrylate (0.17 g, 2 mmol), and $GaCl_3$ (88 mg, 0.5 mmol), which was

added in one portion, after usual work-up and chromatography on $SiO_2$ (eluent: benzene—AcOEt, 50 : 1). $^1$H NMR spectrum agrees with that described earlier.[15]

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