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Isomerisation of *N*-allyl-*N*-arylethanamides catalysed by ruthenium complexes

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Abstract

The isomerisation of *N*-allyl-*N*-arylethanamides having a general formula of AcN(Ar)allyl (Ar = Y–C_6H_4– where Y = H; *o*-, *m*-, *p*-OMe; *o*-, *p*-Br, Cl, Me, O_2N; Ar = 1- and 2-naphthyl) catalysed by ruthenium complexes—mostly by [RuClH(CO)(PPh_3)$_3$] has been studied. *N*-Allyl-*N*-arylethanamides were obtained by allylation of respective *N*-arylethanamides in the PTC conditions (excess of allyl chloride, 50% aq. NaOH, $NBu_4^+HSO_4^-$). The products of isomerisation (reaction conditions: 0.5% mol [RuClH(CO)(PPh_3)$_3$], 120 °C, 2–16 h) were mostly or practically solely (*E*)-*N*-aryl-*N*-(1-propenyl)-ethanamides. It is proposed that the observed selectivity of the double bond migration to (*E*)-enamides is a result of the interaction of the arene ring with the Ru atom in the transition states. Quantum calculations (PM5 method) done for *N*-allyl-*N*-arylethanamides and for (*E*)- and (*Z*)-*N*-aryl-*N*-(1-propenyl)ethanamides (aryl = Y–C_6H_4– where Y = H; *o*-, *m*-, *p*-OMe; *o*-, *p*-Br, Cl, Me, O_2N) as well as results of isomerisation of AcN(R)allyl (R = H or cyclohexyl) amides support this assumption. Moreover, the impact of substituents in Y–C_6H_4N(Ac)allyl and solvents on the rate of the double bond migration has been studied. The structure of the complexes forming in the course of the reaction and the reaction mechanism are also discussed.

Keywords: *N*-Allylamides; Selective isomerisation; Ruthenium complexes; (*E*)-enamides; Reaction mechanism

1. Introduction

N-Propenyl amides (in general: *N*-vinyl amides) are interesting substrates for, among others, synthesis of heterocyclic systems [1–3], cycloaddition reactions [4,5], reduction to enamines [6] and are thoroughly investigated as monomers and co-monomers [7,8]. Isomerisation of *N*-allyl to *N*-propenyl amides is also the key step of protection and following deprotection of amino groups [9]. The most convenient method of *N*-propenyl amides synthesis consists in a catalysed by LDA [10,11] and, particularly, by transition metals complexes isomerisation of appropriate *N*-allyl amides. Ruthenium [12–15], iron [12,15,16], cobalt [17] and rhodium [12,15,18], complexes were applied. Some enamides can also be synthesised via vinylation of amides by vinyl halides in the presence of nickel complexes [19] and by *N*-acylation of *N*-allyl imines [6]. *N*-Allyl amides (RCON(Ar)allyl) were synthesised from amides (RCONHAr) and allyl bromide in the PTC conditions [20,21], in the presence of NaH [22] or NaOH in acetone

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[23]. *N*-Acylation of *N*-allylaniline [12,24] was also used.

In our earlier papers, we described the synthesis of *O*-, *S*- and *N*-(1-propenyl) systems via isomerisation of respective allylic compounds catalysed by ruthenium and rhodium complexes [25–31]. In the present work, we describe a convenient and very selective method of synthesis of various (*E*)-*N*-aryl-*N*-(1-propenyl) amides by the isomerisation of appropriate *N*-allyl amides in the presence of [RuClH(CO)(PPh_3)$_3$] as the catalyst. The influence of solvents and substituents on the rate of the isomerisation of AcN(Y–C_6H_4)allyl amides is also discussed. The mechanism of the double bond migration and the reasons of the observed selectivity of the reaction are also analysed. We have announced some of the results described in the present work in our previous communication [32].

2. Results and discussion

N-Allylamides were obtained by allylation of respective amides by allyl chloride in the PTC conditions (Scheme 1).

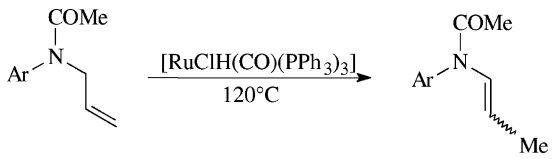
The purity of synthesised *N*-allyl amides (see Table 1) determined by ^{1}N NMR and GC–MS was higher than 99.5%. The method of *N*-allylamide synthesis described above is simple and much more effective than those already known. It can be also applied to allylation of other N–H acids, such as carbazole and phthalimide. Pure (recrystalised) *N*-allylcarbazole and *N*-allylphthalimide were prepared in the same conditions with yields of, respectively, 85 and 80%. *N*-Allyl-*N*-(4-nitrophenyl) and *N*-allyl-*N*-(2-nitrophenyl) ethanamide were obtained by allylation of appropriate amides by allyl bromide (in the presence of KOH) in acetone [23]. Allylation of *o*-O_2N- and *p*-$O_2NC_6H_4NHAc$ in the PTC conditions (as on Scheme 1) resulted in the formation of a mixture difficult to determine.

Table 1
Isolated yields of *N*-aryl-*N*-allylethanamides obtained via allylation of *N*-arylethanamides

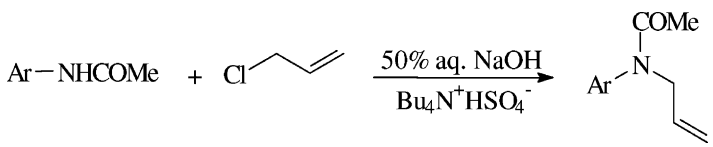
Number	Ar	Yield (%)
1	C_6H_5	80
2	*o*-Me–C_6H_4	78
3	*p*-Me–C_6H_4	75
4	*o*-MeO–C_6H_4	81
5	*m*-MeO–C_6H_4	75
6	*p*-MeO–C_6H_4	81
7	*o*-Cl–C_6H_4	74
8	*p*-Cl–C_6H_4	76
9	*o*-Br–C_6H_4	80
10	*p*-Br–C_6H_4	82
11	1-Naphthyl	82
12	2-Naphthyl	85

The synthesised *N*-aryl-*N*-allyl amides were isomerised to 1-propenyl derivatives in the presence of 0.5% mol [RuClH(CO)(PPh_3)$_3$] (Scheme 2).

The conversion of *N*-allyl amides to 1-propenyl derivatives has always been quantitative (determined by ^{1}H NMR and GC–MS) and no by-products were observed (see Table 2). Therefore, the yields given above are the yields of product separation. Moreover, in this reaction only (or almost only) (*E*)-enamides were formed. *N*-Allyl amides isomerisation is quantitative and selective even in the presence of a solvent (benzene or THF), also in temperatures as low as 60 °C. We think, however, that it is more convenient to carry out the reaction in a melted amide. The



Scheme 2. Isomerisation of *N*-aryl-*N*-allyl amides in the presence of [RuClH(CO)(PPh_3)$_3$].



Scheme 1. Allylation of *N*-arylethanamides in the PTC conditions.

Table 2
Isomerisation of *N*-allyl-*N*-arylethanamides-ArN(Ac)allyl in the presence of [RuClH(CO)(PPh_3)$_3$]

Number	Ar	τ (h)	Yield (%)[a]	*E*:*Z*
1	C_6H_5	2	92	99.0:1.0
2	*o*-Me–C_6H_4	2	95	99.8:0.1
3	*p*-Me–C_6H_4	2	93	98.9:1.1
4	*o*-MeO–C_6H_4	16	95	99.3:0.7
5	*m*-MeO–C_6H_4	2	92	99.0:1.0
6	*p*-MeO–C_6H_4	2	93	98.9:1.1
7	*o*-Cl–C_6H_4	2	95	99.8:0.2
8	*p*-Cl–C_6H_4	2	89	98.9:1.1
9	*o*-Br–C_6H_4	2	87	99.5:0.5
10	*p*-Br–C_6H_4	2	90	98.8:1.2
11	*o*-O_2N	3	95	81.0:19.0[b]
12	*p*-O_2N	2	95	99.3:0.7
13	1-Naphthyl	2	92	98.2:1.8[c]
14	2-Naphthyl	2	93	98.1:1.9[c]

Reaction conditions—substrate:catalyst = 200:1; temperature: 120 °C; without solvent; argon atmosphere.

[a] Isolated yields.

[b] After crystallisation from acetone *Z*:*E* = 98.1:1.9 (crystallisation yield, 52%).

[c] After crystallisation from acetone *Z*:*E* = 100:0.00 (crystallisation yield, 75%).

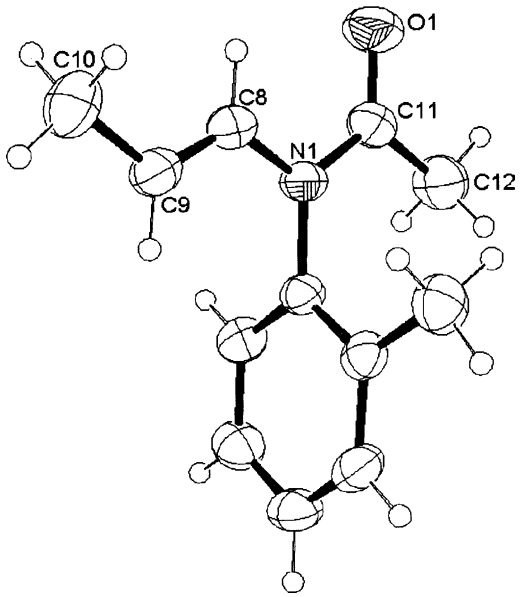
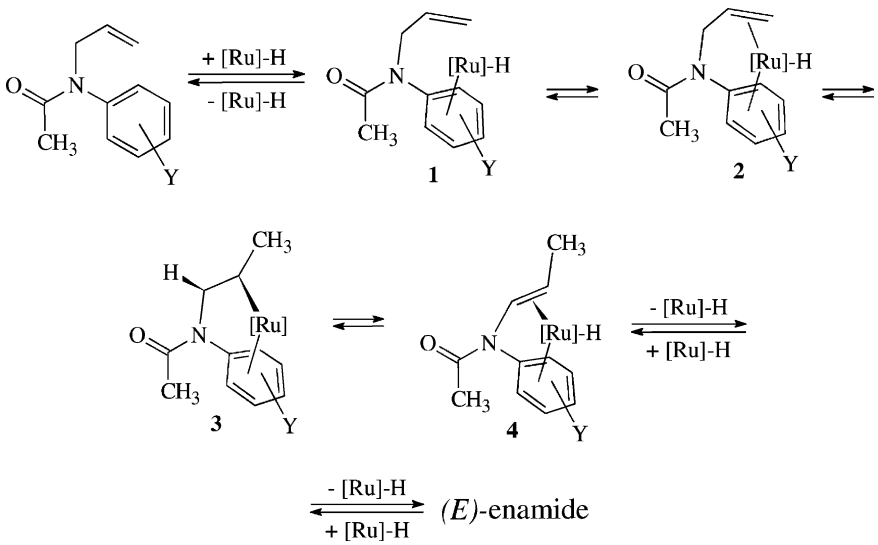


Fig. 1. An ortep view of the molecular structure of (*E*)-*N*-(*o*-methylphenyl)-*N*-(1-propenyl)ethanamide (40% displacement ellipsoids probability).

configuration (*E*) of synthesised enamides has been proved by X-ray crystallography, e.g. the structure of (*E*)-*N*-(*o*-methylphenyl)-*N*-(1-propenyl)ethanamide, see Fig. 1.

We claim that the observed high (*E*)-selectivity of the double bond migration cannot be explained by higher thermodynamical stability of the (*E*)-isomer. Quantum chemical calculations (see Section 4) using



Scheme 3. The formation of (*E*)-enamides as a result of coordination of the Ru atom by the aryl substituent. The step of PPh_3 dissociation leading to the formation of [Ru]–H has been omitted. The 1- or 2-naphthyl (but not *o*-O_2N–C_6H_4) may also take the place of Y–C_6H_4.

PM5 method show that the (*E*)- and (*Z*)- isomers of Y–C_6H_4N(Ac)CH=$CHCH_3$ differ in formation heat by 0.75 (Y = *m*-OMe), 2.68 (Y = H), 4.38 (Y = *o*-Cl), 4.50 (Y = *p*-OMe), 7.75 (Y = *o*-Br), 21.66 (Y = *o*-Me) and 22.67 kJ/mol (Y = *o*-MeO), respectively. The analysis of the shapes of molecular orbitals from HOMO − 2 to LUMO + 2 of the *N*-allyl-*N*-phenylethanamide and (*E*)-*N*-phenyl-*N*-(1-propenyl)ethanamide in the optimal conformation shows a possibility of coordination of the Ru atom in the reaction course, as depicted in Figs. 2 and 3. The substrate can coordinate the ruthenium atom mostly through the benzene ring (donor bonding) and benzene ring and double bond from allyl fragment (back bonding). The product coordinates through the double bond from the propenyl fragment and benzene ring (donor bonding) and through the benzene ring and double bond from propenyl fragment (back bonding).

The coordination of the benzene ring has, in our opinion, a great impact on the stereoselectivity of the reaction: it forces (*E*)-configuration in the product of the double bond migration. Formation of an (*Z*)-enamide is much less probable due to steric effects. In the complexes **3** and **4** (see Scheme 3) there is an increase in steric repulsion of the methyl group of the propenyl moiety and the ligands bound to the ruthenium atom. According to the authors, the oxygen atom from the acetyl group is unlikely to

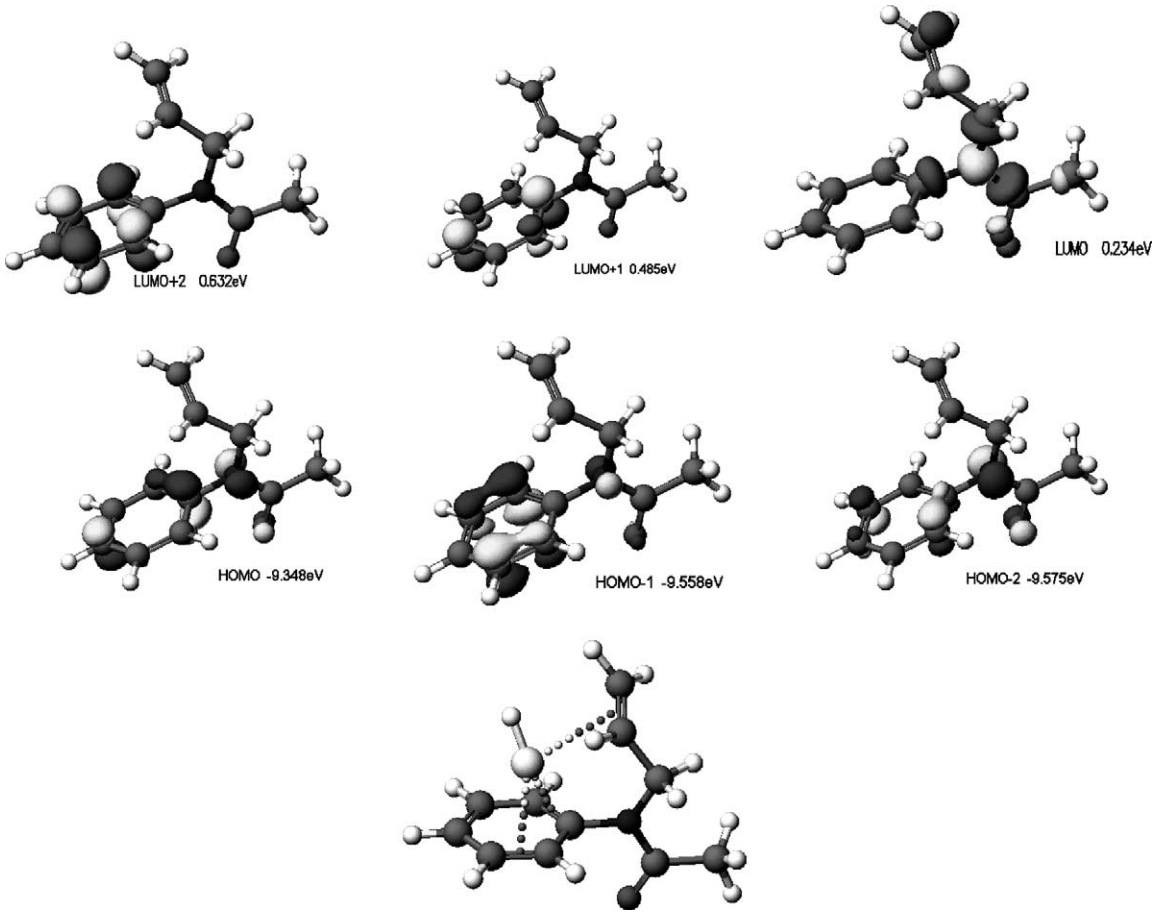


Fig. 2. The shapes of molecular orbitals from HOMO − 2 to LUMO + 2 of *N*-allyl-*N*-phenylethanamide determined by PM5 method. A suggestion of the coordination of the ruthenium atom ([Ru]–H) by the substrate. In this and further suggestions of the structures of the complexes the amide is in its optimal conformation. Changes in bond lengths and angles resulting from the coordination are neglected.

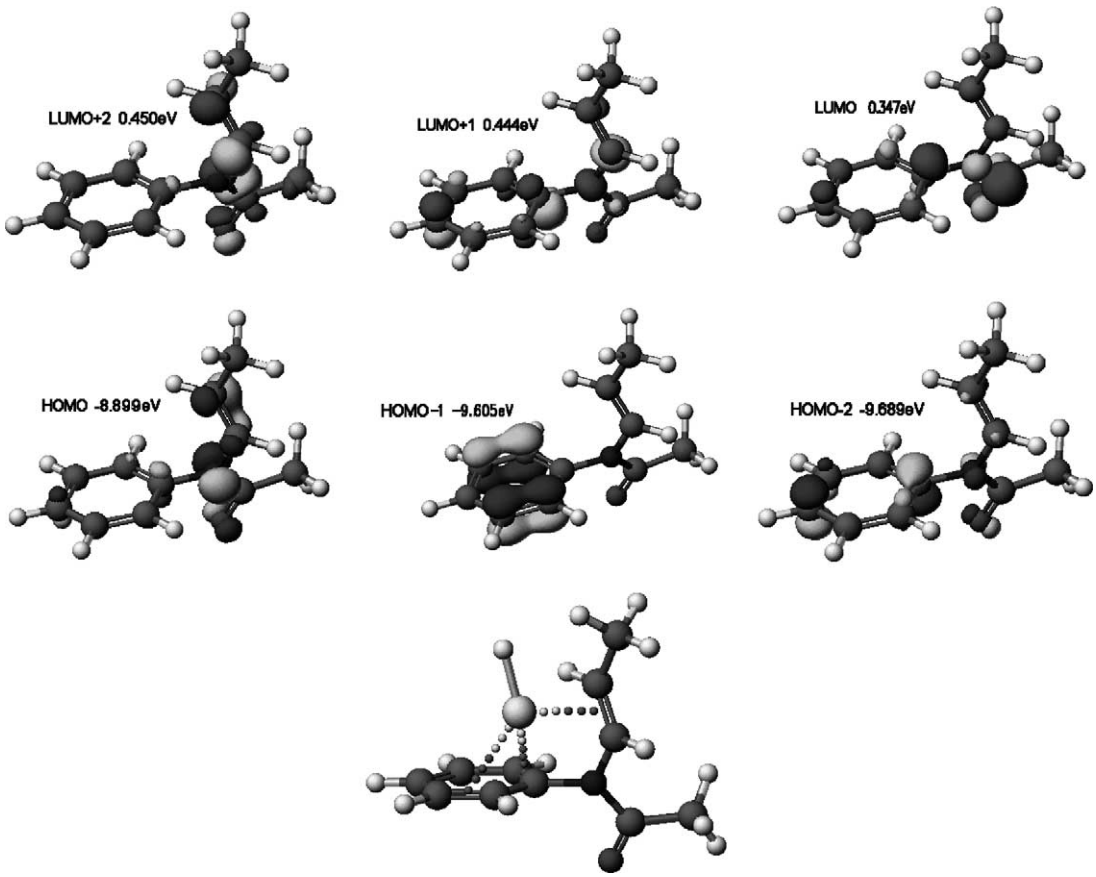


Fig. 3. The shapes of molecular orbitals from HOMO − 2 to LUMO + 2 of (*E*)-*N*-phenyl-*N*-(1-propenyl)ethanamide determined by PM5 method. A suggestion of the coordination of the ruthenium atom ([Ru]–H) by the product.

participate in the coordination of the ruthenium atom by ArN(Ac)allyl or ArNAc(1-propenyl). The nitrogen atom, however, can contribute to the coordination of the ruthenium atom, but with no impact on the stereochemistry of the reaction. It is noteworthy that this interpretation of the cause of the high (*E*)-selectivities observed can be applied to every system studied which is of *o*-Y–C_6H_4N(Ac)allyl type, except those where Y = *o*-O_2N. It is clearly indicated by the results of PM5 calculations for Y–C_6H_4N(Ac)$CH_2CH{=}CH_2$ and Y–C_6H_4N(Ac)$CH{=}CHCH_3$ (where Y = H; *o*-Br, Cl, Me, MeO; *m*-MeO; *p*-MeO).

The analysis of the shapes and energies of the molecular orbitals (from HOMO − 2 to LUMO + 2) suggests that the Ru atom is coordinated in the same manner in each case (as in Figs. 2 and 3)—without the participation of Y substituent. In our opinion, the strong decrease in (*E*)-selectivity for Y = *o*-O_2N is a result of the participation of the nitro group in the coordination. The substrate forms a donor bonding via the nitrogen atom and, to a lesser degree, via the benzene ring, see Fig. 4.

The product forms a donor bonding through the nitrogen atom and the double bond from the propenyl fragment (and probably to some extent through the benzene ring as the substrate), see Fig. 5. The back bonding is formed (by the substrate and by the product) through the nitro group, and not through the benzene ring, as in the case of the amides which do not contain an *o*-NO_2 moiety. The influence of the interaction of the methyl group from the propenyl fragment of the amide with other ligands on the stereochemistry

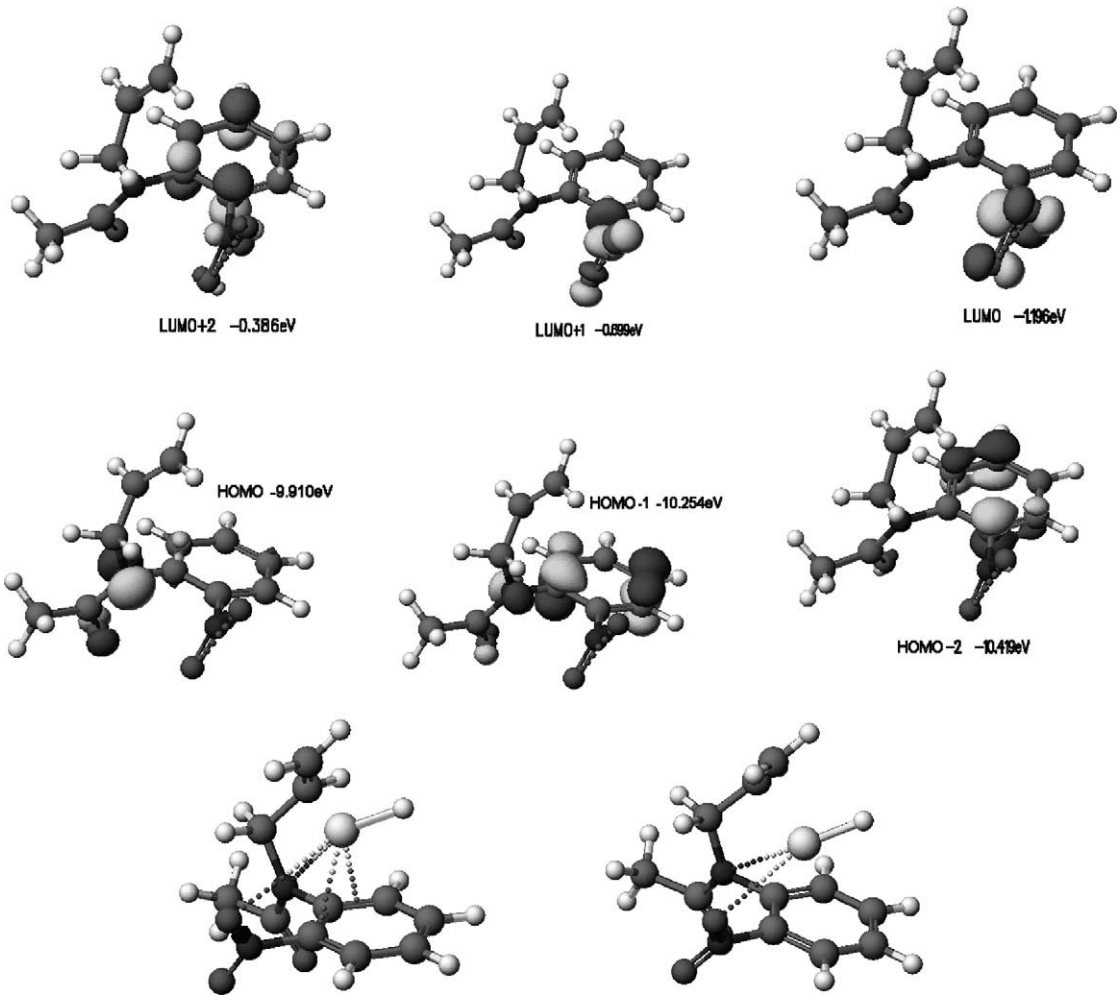


Fig. 4. The shapes of molecular orbitals from HOMO − 2 to LUMO + 2 of *N*-allyl-*N*-(*o*-nitrophenyle)ethanamide determined by PM5 method. A suggestion of the coordination of the ruthenium atom ([Ru]–H) by substrate.

of the double bond migration is least in the case of the amide containing *o*-nitro moiety. Therefore, a mixture of (*E*)- and (*Z*)-enamides is formed in that case.

We have found that isomerisation of AcN(R)allyl (where R = H or cyclohexyl) catalysed by [RuClH-(CO)(PPh_3)$_3$] leads to a mixture of (*Z*)- and (*E*)-enamides (isomerisation conditions as before; quantitative conversion). Recently, we observed that in the isomerisation of Me_3CCONHallyl and RCONallyl$_2$ (R = Me or Me_3C) also a mixture of isomers forms [25,31].

It means that the increase of the steric effect of acyl group has no influence on the selectivity. The result of the isomerisation of *N*-allyl-*N*-cyclohexylethanamide was particularly important for the explanation of the observed double bond migration selectivity. The fact that (*E*)- and (*Z*)-enamides are formed (60:40) proves that the selectivity is not a result of the steric effect but of the coordination. Quantum calculations show that amides with a cyclohexyl fragment (both the allyl substrate and the product of its isomerisation) can co-ordinate the ruthenium atom, as depicted in Fig. 6. The cyclohexyl fragment is so far away from the reaction

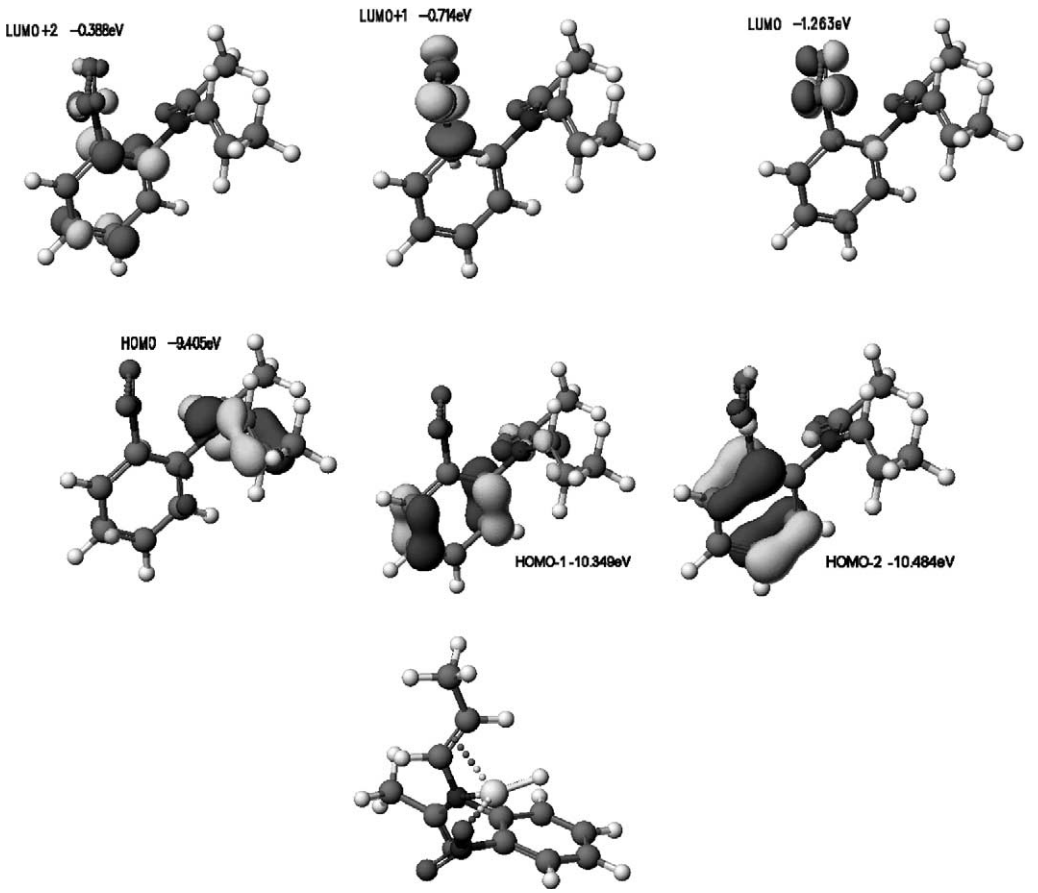


Fig. 5. The shapes of molecular orbitals from HOMO − 1 to LUMO + 1 of (*E*)-*N*-(*o*-nitrophenyl)-*N*-(1-propenyl)ethanamide determined by PM5 method. A suggestion of the coordination of the ruthenium atom ([Ru]–H) by the product of the reaction.

centre (compared to Ar) that its steric interaction is weak and, therefore, both isomeric enamides are formed. It is now clear that the isomerisation of $RCONR^1$(allyl) is selective (i.e. (*E*)-enamides are formed) if and only if R^1 is an aryl (except R^1 = *o*-$O_2NC_6H_4$).

We have assumed that the double bond migration catalysed by [$RuClH(CO)(PPh_3)_3$] occurs according

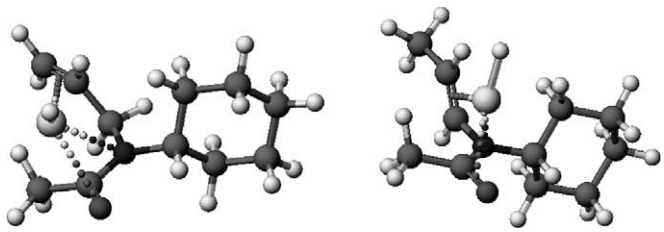
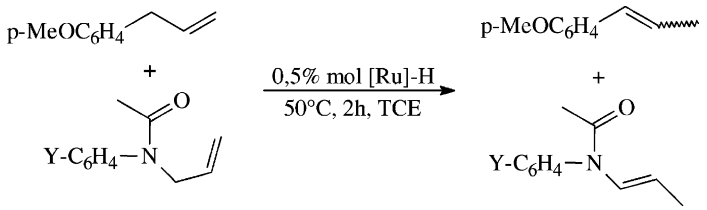


Fig. 6. The coordination of the ruthenium atom by *N*-allyl-*N*-cyclohexylethanamide, (*E*)- and (*Z*)-*N*-cyclohexyl-*N*-(1-propenyl)ethanamide (a suggestion). Donor bonding through: nitrogen atom, oxygen atom and double bond. Back bonding through: C=O and C=C bonds.



Scheme 4. An outline of the method used for determining relative reactivities of Y–C_6H_4N(Ac)allyl.

to the hydride mechanism, as in the case of alkenes [25] and allyl ethers [25].

Furthermore, it has been determined that the substituents in Y–C_6H_4N(Ac)allyl amides have limited influence on the double bond migration rate. Only *o*-substituents decrease the reaction rate, but to an extent much lower than expected. It is important that the interaction of Y cannot be modelled by any correlation equation (like that of Hammett, Taft, etc.). In order to eliminate any external influences and the influence of impurities (present in the substrates), the relative reactivity rates of the amides have been determined by carrying out the reactions in parallel (Scheme 4 and Table 3).

The results imply hydride mechanism of the isomerisation with an addition of [Ru]–H to the double bond (transformation of complex **2** into complex **3**, see Scheme 3) as the step limiting the reaction rate. The reason is that in this step the substituents are mostly distant from the reaction centre and therefore have no important impact on the rate. We have observed a similar effect in the isomerisation of allyl-aryl ethers—Y–C_6H_4–Oallyl—catalysed by [RuClH(CO(PPh_3)$_3$] as well (hydride mechanism) [25]. On the other hand, when [Ru(acac)$_3$] was used as the catalyst of Y–C_6H_4–Oallyl isomerisation, the Y moiety had a great importance on the reaction rate [25,26]. It that case, however, the mechanism was hydride–π-allyl, therefore the Y substituents were much closer to the reaction centre. The rate-limiting step of that reaction is an oxidative addition leading to a hydride–π-allyl complex [26].

An important impact of the solvents on the rate of *N*-allylamide isomerisation has been observed. The solvent, however, has no influence on the selectivity (Table 4). The migration rate is highest in benzene. This fact supports the assumption that arenes are capable of stabilising complexes formed in the reaction

Table 3
Influence of substituents on the isomerisation rate of Y–C_6H_4-N(Ac)allyl (at 60 °C)

Y	k_1:k_2[a] (±0.05)
H	1.4
o-CH_3	2.0
p-CH_3	1.4
o-CH_3O	2.3
m-CH_3O	1.4
p-CH_3O	1.5
o-Cl	1.7
p-Cl	1.0
o-Br	1.2
p-Br	1.0
o-O_2N	2.3
p-O_2N	1.0

[a] k_1:k_2 = *kp*-MeOC_6H_4allyl:*k*Y–C_6H_4(Ac)allyl; calculated assuming quasi-first-order kinetics; a mean value of three independent measurements.

Table 4
Influence of solvents on the isomerisation of *N*-allyl-*N*-(*p*-methylphenyl)ethanamide[a]

Solvent	ε (%)
$CDCl_3$	0
CD_3OD	19
CD_2Cl_2	46
CD_3COCD_3	52
CCl_4	71
$Cl_2C{=}CCl_2$	90
1,4-Dioxane-*d*8	94
THF-*d*8	100
THF-*d*8	66[b]
Benzene-*d*6	100
Benzene-*d*6	96[b]

ε: substrate conversion.
[a] 0.1 M allyl amide; 0.001 [RuClH(CO)(PPh_3)$_3$].
[b] 80 °C, 2 h or 60 °C, 2 h.

course. Nevertheless, the reaction cannot be carried out in solvents containing active hydrogen. This would lead to a transformation of [Ru]–H into catalytically inactive complexes not containing a hydride ligand [25].

We have found that $[RuClH(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, $[RuH_2PPh_3)_3]$, $[Ru(CO)_3(PPh_3)_2]$, $[RuCl_2(COD)]_x$, $[RuCl_2(p\text{-cymene})]_2$ are much less active as catalysts of the *N*-allylamide isomerisation studied.

3. Conclusions

The isomerisation of *N*-allyl-*N*-arylethanamides—ArN(Ac)allyl (Ar = Y–C_6H_4– where Y = H; *o*-, *m*-, *p*-OMe; *o*-, *p*-Br, Cl, Me; *p*-O_2N; Ar = 1- or 2-naphthyl)—catalysed by $[RuClH(CO)(PPh_3)_3]$ leads mainly or exclusively to (*E*)-enamides. This selectivity is a result of the coordination of the Ru atom by the aryl substituent. It is clearly implied by the shapes of the molecular orbitals (from HOMO − 2 to LUMO + 2) of *N*-allyl-*N*-arylethanamides and (*E*)- and (*Z*)-*N*-aryl-*N*-(1-propenyl)ethanamides calculated according to PM5 method. The decrease in the (*E*)-selectivity of the reaction in the case of the isomerisation of *o*-O_2N–$C_6H_4N(Ac)CH_2CH{=}CH_2$ is due to the participation of the nitro moiety (instead of the benzene ring) in the coordination (back bonding) of the ruthenium atom. Reaction (*E*)-selectivity decreases also when the aryl substituent is replaced with a non-coordinative cyclohexyl moiety.

4. Experimental

4.1. Materials

Aniline derivatives, allyl chloride, allyl bromide—from Aldrich. Solvents (benzene, THF, deuterated solvents and others) were dried with sodium, CaH_2, or molecular sieves (3A or 4A) and distilled prior to use.

4.2. Synthesis of N-aryl-N-allylethanamides (general method)

An amide (0.2 mol), 50% aq. NaOH (50 cm^3), $Bu_4N^+HSO_4^-$ (0.002 mol) and excess of allyl chloride (50 cm^3) has been intensively stirred and refluxed in a water bath for 4 h. After cooling, 100 cm^3 of water was added and excess of allyl was removed by distillation from the water bath. The residue has been extracted two times with 100 cm^3 of hexane (or pentane). The combined extract has been dried with anhydrous magnesium sulfate and decolourised by active coal. After distilling all volatiles off (with a vacuum evaporator), the residue was then distilled under reduced pressure (0.5–1 mmHg).

N-Allyl-*N*-phenylethanamide: bp = 113–114 °C/1 mmHg: MS (70 eV) *m/e* (int[%]): 175 (15) M^+; 160 (7); 132 (63); 118 (16); 106 (44); 77 (43); 51 (30); 43 (100); 39 (53). ^{1}H NMR (C_6D_6): δ = 7.19–7.01 (m, 3H, $H_{3\text{-arom}}$, $H_{5\text{-arom}}$, and $H_{4\text{-arom}}$), 6.84 (d, 2H, $J_{2-3} = J_{5-6}$ = 7.1 Hz, $H_{2\text{-arom}}$ and $H_{6\text{-arom}}$), 5.87 (ddt, 1H, J = 14.4, 10.2, 5.9 Hz, $-CH_2C\underline{H}{=}CH_2$), 4.94 (ddt, 1H, J = 10.2, 1.5, <0.9 Hz, $-CH_2CH{=}C\underline{H}_2$-*cis*) 4.92 (ddt, 1H, J = 14.4, 1.5, <0.9 Hz, $-CH_2CH{=}C\underline{H}_2$-*trans*), 4.27 (ddd, 2H, J = 5.9, <0.9, <0.9 Hz, $-C\underline{H}_2CH{=}CH_2$), 1.73 (s, 3H, $-COC\underline{H}_3$). ^{13}C NMR (C_6D_6): δ = 168.6 ($-\underline{C}OCH_3$); 143.7 ($C_{1\text{-arom}}$); 134.2 ($-CH_2\underline{C}H{=}CH_2$); 129.5 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 128.4 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 127.7 ($C_{4\text{-arom}}$); 117.3 ($-CH_2CH{=}\underline{C}H_2$); 52.0 ($-\underline{C}H_2CH{=}CH_2$); 22.5 ($-CO\underline{C}H_3$).

N-Allyl-*N*-(2-chlorophenyl)ethanamide: bp = 141–142 °C/1 mmHg: MS (70 eV) *m/e* (int[%]): 209 (92) M^+; 174 (100); 167 (24); 166 (18); 165 (9); 152 (10); 132 (62); 130 (28); 117 (8); 105 (5); 63 (3); 43 (6); 39 (17). ^{1}H NMR (C_6D_6): δ = 7.18 (d, 2H, $J_{2-3} = J_{5-6}$ = 7.2 Hz, $H_{2\text{-arom}}$ and $H_{6\text{-arom}}$), 6.85 (m, 3H, $H_{3\text{-arom}}$, $H_{5\text{-arom}}$, and $H_{a4\text{-arom}}$), 5.86 (dddd, 1H, J = 17.1, 10.7, 7.2, 5.70 Hz, $-CH_2C\underline{H}{=}CH_2$), 4.91 (dddd, 1H, J = 10.7, 1.5, 1.2, 1.0 Hz, $H_2C{-}CH{=}C\underline{H}_2$-*cis*), 4.85 (dddd, 1H, J = 17.1, 1.5, 1.2, 1.0 Hz, $-CH_2CH{=}C\underline{H}_2$-*trans*), 4.78 (dddd, 1H, J = 14.7, 5.7, 1.2, 1.2 Hz, $-C\underline{H}_2CH{=}CH_2$), 3.82 (dddd, 1H, J = 14.7, 7.2, 1.0, 1.0 Hz, $-C\underline{H}_2CH{=}CH_2$), 1.68 (s, 3H, $-COC\underline{H}_3$). ^{13}C NMR (C_6D_6): δ = 168.8 ($-\underline{C}OCH_3$); 141.9 ($C_{1\text{-arom}}$); 133.7 ($-CH_2\underline{C}H{=}CH_2$); 133.6 ($C_{4\text{-arom}}$); 131.3 ($C_{5\text{-arom}}$); 130.6 ($C_{4\text{-arom}}$); 129.4 ($C_{6\text{-arom}}$); 128.3 ($C_{2\text{-arom}}$); 118.0 ($-CH_2CH{=}\underline{C}H_2$); 50.9 ($-\underline{C}H_2CH{=}CH_2$); 22.6 ($-CO\underline{C}H_3$).

N-Allyl-*N*-(2-bromophenyl)ethanamide:157–158 °C/1 mmHg: MS (70 eV) *m/e* (int[%]): 255 (2) M^+; 253 (3); 213 (9); 184 (19); 174 (100); 157 (5); 132

(28); 130 (21); 117 (11); 105 (18); 91 (12); 77 (22); 63 (10); 51 (9); 43 (65); 39 (18). ^{1}H NMR (C_6D_6): δ = 7.39 (dd, 1H, $J_{3–4}$ = 8.1 Hz, $J_{3–5}$ = 1.5 Hz, $H_{3\text{-arom}}$), 6.96 (ddd, 1H, $J_{3–4}$ = 8.1 Hz, $J_{4–5}$ = 7.5 Hz, $J_{4–6}$ = 1.8 Hz, $H_{4\text{-arom}}$), 6.87 (dd, 1H, $J_{5–6}$ = 7.5 Hz, $J_{4–6}$ = 1.8 Hz, $H_{6\text{-arom}}$), 6.80 (ddd, 1H, $J_{4–5}$ = 7.5 Hz, $J_{5–6}$ = 7.8 Hz, $J_{3–5}$ = 1.5 Hz, $H_{5\text{-arom}}$), 5.88 (dddd, 1H, J = 18.3, 10.2, 7.7, 5.7 Hz, –$CH_2C\underline{H}$=CH_2), 4.91 (dddd, 1H, J = 10.2, 1.5, 1.2, 1.0 Hz, –CH_2CH=$C\underline{H}_2$-*cis*), 4.87 (dddd, 1H, J = 14.7, 5.7, 1.2, 1.2 Hz, –$C\underline{H}_2CH$=CH_2), 4.85 (dddd, 1H, J = 18.3, 1.5, 1.2, 1.0 Hz, –CH_2CH=$C\underline{H}_2$-*trans*), 3.70 (dddd, 1H, J = 14.7, 7.7, 1.0, 1.0 Hz, –$C\underline{H}_2CH$=CH_2), 1.69 (s, 3H, –$COC\underline{H}_3$). ^{13}C NMR (C_6D_6): δ = 168.6 (–$\underline{C}OCH_3$); 141.9 ($C_{1\text{-arom}}$); 133.8 (–$CH_2\underline{C}H$=CH_2); 133.7 ($C_{3\text{-arom}}$); 131.5 ($C_{4\text{-arom}}$); 129.7 ($C_{5\text{-arom}}$); 129.5 ($C_{6\text{-arom}}$); 124.3 ($C_{2\text{-arom}}$); 118.0 (–CH_2CH=$\underline{C}H_2$); 50.9 (–$\underline{C}H_2CH$=CH_2); 22.9 (–$CO\underline{C}H_3$).

N-Allyl-*N*-(2-methylphenyl)ethanamide:120–121°C/1 mmHg: MS (70 eV) *m/e* (int[%]): 189 (100) M^+; 174 (8); 148 (8); 147 (21); 130 (17); 118 (19); 106 (14); 91 (5); 82 (6); 51 (2); 43 (9); 39 (14). ^{1}H NMR (C_6D_6): δ = 7.03–7.01 (m, 3H, $H_{3\text{-arom}}$, $H_{4\text{-arom}}$, and $H_{5\text{-arom}}$), 6.84 (d, 1H, $J_{5–6}$ = 6.8 Hz, $H_{6\text{-arom}}$), 5.92 (dddd, 1H, J = 17.1, 7.5, 7.3, 6.0 Hz, –$CH_2C\underline{H}$=CH_2), 4.92 (dddd, 1H, J = 7.3, 1.7, 1.4, 1.0 Hz, –CH_2CH=$C\underline{H}_2$-*cis*), 4.88 (dddd, 1H, J = 17.1, 1.7, 1.4, 1.0 Hz, –CH_2CH=$C\underline{H}_2$-*trans*), 4.67 (dddd, 1H, J = 14.1, 6.0, 1.4, 1.4 Hz, –$C\underline{H}_2CH$=CH_2), 3.70 (dddd, 1H, J = 14.1, 7.5, 1.0, 1.0 Hz, –$C\underline{H}_2CH$=CH_2), 1.97 (s, 3H, *o*-C_6H_4–$C\underline{H}_3$), 1.63 (s, 3H, –$COC\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 170.9 (–$\underline{C}OCH_3$); 141.4 ($C_{1\text{-arom}}$); 135.6 (–$CH_2\underline{C}H$=CH_2); 132.9 ($C_{2\text{-arom}}$); 131.4 ($C_{3\text{-arom}}$); 129.1 ($C_{4\text{-arom}}$); 128.3 ($C_{5\text{-arom}}$); 127.1 ($C_{6\text{-arom}}$); 118.2 (–CH_2CH=$\underline{C}H_2$); 51.2 (–$\underline{C}H_2$-CH=CH_2); 22.2 (–$CO\underline{C}H_3$); 17.6 (*o*-C_6H_4–$\underline{C}H_3$).

N-Allyl-*N*-(2-methoxyphenyl)ethanamide: 138–139 °C/1 mmHg: MS (70 eV) *m/e* (int[%]): 255 (20) M^+; 205 (82); 200 (9); 174 (26); 163 (26); 148 (68); 134 (40); 120 (39); 108 (26); 91 (42); 82 (63); 77 (100); 65 (71); 51 (33); 43 (83). ^{1}H NMR (C_6D_6): δ = 7.08 (ddd, 1H, $J_{3–4}$ = 7.5 Hz, $J_{4–5}$ = 7.8 Hz, $J_{4–6}$ = 0.9 Hz, $H_{4\text{-arom}}$), 6.92 (dd, 1H, $J_{3–4}$ = 7.5 Hz, $J_{3–5}$ = 1.2 Hz, $H_{3\text{-arom}}$), 6.78 (ddd, 1H, $J_{5–6}$ = 8.4 Hz, $J_{4–5}$ = 7.8 Hz, $J_{3–5}$ = 1.2 Hz, $H_{5\text{-arom}}$), 6.61 (dd, 1H, $J_{5–6}$ = 8.4 Hz, $J_{4–6}$ = 0.9 Hz, $H_{6\text{-arom}}$), 5.91 (dddd, 1H, J = 16.8, 10.2, 6.9, 6.0 Hz, –$CH_2C\underline{H}$=CH_2), 4.92 (dddd, 1H, J = 16.8, 1.5, 1.5, 1.4 Hz, –CH_2CH=$C\underline{H}_2$-*trans*), 4.91 (dddd, 1H, J = 10.2, 1.5, 1.5, 1.4 Hz, –CH_2CH=$C\underline{H}_2$-*cis*), 4.70 (dddd, 1H, J = 14.7, 6.0, 1.5, 1.5 Hz, –$C\underline{H}_2CH$=CH_2), 4.05 (dddd, 1H, J = 14.7, 6.9, 1.5, 1.5 Hz, –$C\underline{H}_2CH$=CH_2), 3.33 (s, 3H, *o*-C_6H_4–$OC\underline{H}_3$), 1.78 (s, 3H, –$COC\underline{H}_3$). ^{13}C NMR (C_6D_6): δ = 169.7 (–$\underline{C}OCH_3$); 155.7 ($C_{2\text{-arom}}$); 134.7 (–$CH_2\underline{C}H$=CH_2); 132.0 ($C_{1\text{-arom}}$); 130.3 ($C_{4\text{-arom}}$); 129.3 ($C_{6\text{-arom}}$); 121.0 ($C_{5\text{-arom}}$); 117.0 (–CH_2CH ndbond$\underline{C}H_2$); 112.2 ($C_{3\text{-arom}}$); 55.2 (*o*-C_6H_4–OCH_3); 51.1 (–$\underline{C}H_2CH$=CH_2); 22.9 (–$CO\underline{C}H_3$).

N-Allyl-*N*-(3-methoxyphenyl)ethanamide: 141–142 °C/1 mmHg: MS (70 eV) *m/e* (int[%]): 205(19) M^+; 190 (3); 163 (38); 162 (22); 148 (24); 136 (21); 108 (10); 92 (18); 43 (100); 41 (36). ^{1}H NMR (C_6D_6): δ = 7.21 (s, 1H, $H_{2\text{-arom}}$), 7.09 (dd, 1H, $J_{4–5}$ = 8.1 Hz, $J_{5–6}$ = 8.1 Hz, $H_{5\text{-arom}}$), 6.73 (dd, 1H, $J_{4–5}$ = 8.1 Hz, $J_{4–6}$ = 1.8 Hz, $H_{4\text{-arom}}$), 6.59 (d, 1H, $J_{5–6}$ = 8.1 Hz, $H_{6\text{-arom}}$), 5.86 (ddt, 1H, J = 21.0, 10.8, 6.0 Hz, –$CH_2C\underline{H}$=CH_2), 4.99 (dd, 1H, J = 21.0, 1.5 Hz, –CH_2CH=$\underline{C}H_2$-*trans*), 4.96 (dd, 1H, J = 10.8, 1.5 Hz, –CH_2CH=$C\underline{H}_2$-*cis*), 4.30 (d, 1H, J = 6.0 Hz, –$C\underline{H}_2CH$=CH_2), 3.45 (s, 3H, *m*-C_6H_4–$OC\underline{H}_3$), 1.80 (s, 3H, –$COC\underline{H}_3$). ^{13}C NMR (C_6D_6): δ = 169.3 (–$\underline{C}OCH_3$); 158.0 ($C_{3\text{-arom}}$); 133.4 ($C_{1\text{-arom}}$); 134.5 (–$CH_2\underline{C}H$=CH_2); 129.7 ($C_{5\text{-arom}}$); 117.3 (–CH_2CH=$\underline{C}H_2$); 112.7 ($C_{6\text{-arom}}$); 110.0 ($C_{4\text{-arom}}$); 105.7 ($C_{2\text{-arom}}$); 55.1 (*m*-C_4H_6–OCH_3); 51.9 (–$\underline{C}H_2CH$=CH_2); 22.7 (–$CO\underline{C}H_3$).

N-Allyl-*N*-(4-methoxyphenyl)ethanamide: 125–126 °C/0.8 mmHg: MS (70 eV) *m/e* (int[%]): 205(53) M^+; 190 (5); 163 (78); 148 (80); 122 (55); 95 (29); 82 (33); 43 (100); 41 (36). ^{1}H NMR (C_6D_6): δ = 6.77 (AA′XX′, 2H, –C_6H_4–), 6.66 (AA′XX′, 2H, –C_6H_4–), 5.90 (ddt, 1H, J = 16.5, 10.5, 6.6 Hz, –$CH_2C\underline{H}$=CH_2), 4.97 (ddt, 1H, J = 10.5, 1.5, 1.0 Hz, –CH_2CH=$C\underline{H}_2$-*cis*), 4.95 (ddt, 1H, J = 16.5, 1.5, 1.2 Hz, –CH_2CH=$C\underline{H}_2$-*trans*), 4.30 (ddd, 2H, J = 6.6, 1.2, 1.0 Hz, –$C\underline{H}_2CH$=CH_2), 3.33 (s, 3H, *p*-C_6H_4–$OC\underline{H}_3$), 1.77 (s, 3H, –$COC\underline{H}_3$). ^{13}C NMR (C_6D_6): δ = 169.1 (–$\underline{C}OCH_3$); 159.1 ($C_{4\text{-arom}}$); 136.4 ($C_{1\text{-arom}}$); 134.4 (–$CH_2\underline{C}H$=CH_2); 129.5 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 117.4 (–CH_2CH=$\underline{C}H_2$); 114.8 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 55.0 (*p*-C_6H_4–$O\underline{C}H_3$); 52.0 (–$\underline{C}H_2CH$=CH_2); 22.5 (–$CO\underline{C}H_3$).

N-Allyl-*N*-(4-methylphenyl)ethanamide:111-112 °C/0.9 mmHg: MS (70 eV) *m/e* (int[%]): 189 (62) M^+;

174 (9); 146 (100); 132 (52); 120 (90); 118 (41); 91 (92); 84 (35); 77 (55); 65 (62); 51 (18); 43 (83). ^{1}H NMR (C_6D_6): δ = 6.97 (AA′XX′, 2H, –C_6H_4–), 6.86 (AA′XX′, 2H, –C_6H_4–), 5.89 (ddt, 1H, J = 16.5, 10.1, 6.3 Hz, –$CH_2C\underline{H}$=CH_2), 4.97 (dd, 1H, J = 10.1, 1.4 Hz, –CH_2CH=$C\underline{H_2}$-*cis*), 4.96 (dd, 1H, J = 16.5, 1.4 Hz, –CH_2CH=$C\underline{H_2}$-*trans*), 4.31 (dd, 2H, J = 6.1, 1.2 Hz, –$C\underline{H_2}CH$=CH_2), 2.12 (s, 3H, *p*-C_6H_4–$C\underline{H_3}$), 1.78 (s, 3H, –$COC\underline{H_3}$). ^{13}C NMR ($CDCl_3$): δ = 169.7 (–$\underline{C}OCH_3$); 140.5 ($C_{1\text{-arom}}$); 137.5 ($C_{4\text{-arom}}$); 133.4 (–$CH_2\underline{C}H$=CH_2); 130.1 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 127.8 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 117.5 (–CH_2CH=$\underline{C}H_2$); 51.9 (–$\underline{C}H_2CH$=CH_2); 22.5 (–$CO\underline{C}H_3$); 21.0 (*p*-C_6H_4–$\underline{C}H_3$).

N-Allyl-*N*-(4-chlorophenyl)ethanamide: 145–146 °C/1 mmHg: MS (70 eV) *m/e* (int[%]): 211 (11) M^+; 209 (31); 169 (34); 167 (90); 152 (12); 142 (15); 140 (69); 130 (29); 111 (27); 105 (17); 99 (17); 84 (21); 82 (23); 77 (38); 75 (64); 63 (31); 56 (19); 43 (100); 39 (22). ^{1}H NMR ($CDCl_3$): δ = 7.38 (AA′XX′, 2H, –C_6H_4–), 7.16 (AA′XX′, 2H, –C_6H_4–), 5.85 (ddt, 1H, J = 17.1, 10.8, 6.3 Hz, –$CH_2C\underline{H}$=CH_2), 5.11 (dd, 1H, J = 10.8, 1.1 Hz, –CH_2CH=$C\underline{H_2}$-*cis*), 5.05 (dd, 1H, J = 17.1, 1.1 Hz, –CH_2CH=$C\underline{H_2}$-*trans*), 4.28 (dd, 2H, J = 6.3, 1.1 Hz, –$C\underline{H_2}CH$=CH_2), 1.87 (s, 3H, –$COC\underline{H_3}$). ^{13}C NMR (C_6D_6): δ = 169.6 (–$\underline{C}OCH_3$); 141.5 ($C_{1\text{-arom}}$); 133.6 ($C_{4\text{-arom}}$); 132.9 (–$CH_2\underline{C}H$=CH_2); 129.7 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 129.5 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 118.1 (–CH_2CH=$\underline{C}H_2$); 51.9 (–$\underline{C}H_2CH$=CH_2); 22.6 (–$CO\underline{C}H_3$).

N-Allyl-*N*-(4-bromophenyl)ethanamide: 161–163 °C/1 mmHg: MS (70 eV) *m/e* (int[%]): 255 (20) M^+; 253 (19); 238 (2); 210 (70); 186 (25); 184 (38); 157 (10); 130 (33); 105 (11); 90 (9); 82 (10); 76 (18); 50 (11); 43 (100). ^{1}H NMR ($CDCl_3$) δ = 7.54 (AA′XX′, 2H, –C_6H_4–), 7.08 (AA′XX′, 2H, –C_6H_4–), 5.89 (ddt, 1H, J = 18.3, 11.2, 6.2 Hz, –$CH_2\underline{C}H$=CH_2), 5.11 (dd, 1H, J = 11.2, 1.2 Hz, –CH_2CH=$C\underline{H_2}$-*cis*), 5.06 (dd, 1H, J = 18.3, 1.2 Hz, –CH_2CH=$C\underline{H_2}$-*trans*), 4.28 (dd, 2H, J = 6.2, 1.1 Hz, –$C\underline{H_2}CH$=CH_2), 1.87 (s, 3H, –$COC\underline{H_3}$). ^{13}C NMR (C_6D_6): δ = 169.5 (–$\underline{C}OCH_3$); 141.9 ($C_{1\text{-arom}}$); 132.9 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 132.7 (–$CH_2\underline{C}H$=CH_2); 129.8 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 121.6 ($C_{4\text{-arom}}$); 118.1 (–CH_2CH=$\underline{C}H_2$); 51.8 (–$\underline{C}H_2CH$=CH_2); 22.6 (–$CO\underline{C}H_3$).

N-allyl-*N*-(1-naphthyl)ethanamide: 175–176 °C/0.6 mmHg: MS (70 eV) *m/e* (int[%]): 225 (73) M^+; 210 (5); 183 (100); 168 (71); 166 (11); 154 (20); 141 (14); 127 (39); 115 (7); 82 (47); 77 (18); 75 (10); 63 (9); 51 (7); 43 (38); 39 (7). ^{1}H NMR ($CDCl_3$): δ = 7.98–7.34 (m, 7H, H_{arom}); 5.98 (dddd, 1H, J = 17.9, 10.8, 7.5, 6.5 Hz, –$CH_2C\underline{H}$=CH_2), 5.23 (dddd, 1H, J = 10.8, 1.2, 1.0, 1.0 Hz, –CH_2CH=$C\underline{H_2}$-*cis*), 5.11 (dddd, 1H, J = 17.9, 1.2, 1.0, 1.0 Hz, –CH_2CH=$C\underline{H_2}$-*trans*), 4.91 (dddd, 1H, J = 14.1, 6.5, 1.2, 1.2 Hz, –$C\underline{H_2}CH$=CH_2), 3.77 (dddd, 1H, J = 14.1, 7.5, 1.0, 1.0 Hz, –$C\underline{H_2}CH$=CH_2), 1.82 (s, 3H, –$COC\underline{H_3}$). ^{13}C NMR ($CDCl_3$): δ = 171.0 (–$\underline{C}OCH_3$); 138.9 ($C_{1\text{-arom}}$); 134.8 ($C_{10\text{-arom}}$); 133.2 (–$CH_2\underline{C}H$=CH_2); 130.5 ($C_{9\text{-arom}}$); 128.7 ($C_{5\text{-arom}}$); 128.6 ($C_{3\text{-arom}}$); 127.4 ($C_{6\text{-arom}}$); 126.7 ($C_{7\text{-arom}}$), 126.6 ($C_{8\text{-arom}}$); 125.6 ($C_{4\text{-arom}}$); 122.5 ($C_{2\text{-arom}}$); 118.4 (–CH_2CH=$\underline{C}H_2$); 51.8 (–$\underline{C}H_2CH$=CH_2); 22.3 (–$CO\underline{C}H_3$).

N-Allyl-*N*-(2-naphthyl)ethanamide: 175–177 °C/0.6 mmHg: MS (70eV) *m/e* (int[%]): 225 (63) M^+; 210 (4); 183 (58); 168 (32); 156 (23); 142 (27); 127 (32); 115 (28); 101 (4); 82 (100); 77 (10); 63 (6); 51 (3); 43 (29); 39 (7). ^{1}H NMR ($CDCl_3$): δ = 7.98–7.28 (m, 7H, H_{arom}); 5.88 (ddt, 1H, J = 17.6, 10.3, 6.3 Hz, –$CH_2C\underline{H}$=CH_2), 5.11 (dd, 1H, J = 10.3, 1.0 Hz, –CH_2CH=$C\underline{H_2}$-*cis*), 5.09 (dd, 1H, J = 17.6, 1.0 Hz, –CH_2CH=$C\underline{H_2}$-*trans*), 4.37 (dd, 2H, J = 6.3, 1.2 Hz, –$C\underline{H_2}CH$=CH_2), 1.88 (s, 3H, –$COC\underline{H_3}$). ^{13}C NMR (C_6D_6): δ = 149.7 (–$\underline{C}OCH_3$); 134.2 (–$CH_2\underline{C}H$=CH_2); 123.3 ($C_{9\text{-arom}}$); 132.2 ($C_{2\text{-arom}}$); 131.6 ($C_{10\text{-arom}}$); 129.2 128.5, 128.4, 116.8 and 115.8 ($C_{1\text{-arom}}$, $C_{3\text{-arom}}$, $C_{4\text{-arom}}$, $C_{5\text{-arom}}$, $C_{6\text{-arom}}$, $C_{7\text{-arom}}$ and $C_{8\text{-arom}}$);112.8 (–CH_2CH=$\underline{C}H_2$); 112.2 ($C_{3\text{-arom}}$); 55.2 (–$\underline{C}H_2CH$=CH_2); 37.7 (–$CO\underline{C}H_3$).

N-Allyl-*N*-(2-nitrophenyl)ethanamide and *N*-allyl-*N*-(4-nitrophenyl)ethanamide were obtained by allylation of respective amides by allyl bromide (in KOH) in acetone [23]. *N*-Allylethanamide was obtained by a typical acylation of *N*-allylamine by acetic anhydride [12]. *N*-Allyl-*N*-cyclohexylethanamide was synthesised via a typical acylation of allylcyclohexylamine by acetyl chloride [33]. Crude amide was distilled under reduced pressure and crystallised from ethanol afterwards. Pure *N*-allyl-*N*-cyclohexylethanamide was obtained with a yield of 50%. The bp = 115 °C/0.5 mmHg; mp = 61–62 °C.

N-Allyl-*N*-(2-nitrophenyl)ethanamide (major rotamer): MS (70 eV) *m/e* (int[%]): 220 (1) M^+; 190 (7); 178 (9); 174 (12); 147 (8); 131 (26); 119 (8);

105 (49); 92 (12); 77 (26); 65 (8); 55 (23); 43 (100); 39 (22). ^{1}H NMR ($CDCl_3$): δ = 8.02 (dd, 1H, $J_{3–4}$ = 7.8 Hz, $J_{3–5}$ = 1.2 Hz, $H_{3\text{-arom}}$), 7.75 (ddd, 1H, $J_{3–4}$ = $J_{4–5}$ = 7.8 Hz, $J_{4–6}$ = 1.5 Hz, $H_{4\text{-arom}}$), 7.65 (ddd, 1H, $J_{4–5}$ = $J_{5–6}$ = 7.8 Hz, $J_{3–5}$ = 1.2 Hz, $H_{5\text{-arom}}$), 7.39 (dd, 1H, $J_{5–6}$ = 7.8 Hz, $J_{4–6}$ = 1.5 Hz, $H_{6\text{-arom}}$), 5.81 (dddd, 1H, J = 15.6, 10.1, 7.1, 6.6 Hz, $–CH_2C\underline{H}=CH_2$), 5.10 (dddd, 1H, J = 10.2, 1.4, 1.0, 0.8 Hz, $–CH_2CH=C\underline{H}_2$-*cis*), 5.02 (dddd, 1H, J = 17.1, 1.4, 1.0, 0.8 Hz, $–CH_2CH=C\underline{H}_2$-*trans*), 4.51 (dddd, 1H, J = 14.7, 6.4, 1.0, 1.0 Hz, $–C\underline{H}_2CH=CH_2$), 3.96 (dddd, 1H, J = 14.7, 7.1, 0.8, 0.8 Hz, $–C\underline{H}_2CH=CH_2$), 1.87 (s, 3H, $–COC\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 169.7 ($–\underline{C}OCH_3$); 147.2 ($C_{2\text{-arom}}$); 135.7 ($C_{1\text{-arom}}$); 133.9, 132.4, 129.6 and 128.3 ($C_{1\text{-arom}}$); 125.5 ($–CH_2\underline{C}H=CH_2$); 119.3 ($–CH_2CH=\underline{C}H2$); 51.9 ($–\underline{C}H_2CH=CH_2$); 22.5 ($–CO\underline{C}H_3$).

N-Allyl-*N*-(4-nitrophenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 220 (4) M^+; 190 (5); 179 (9); 174 (19); 131 (54); 119 (8); 105 (66); 92 (8); 78 (26); 59 (16); 51 (23); 43 (100); 39 (32). ^{1}H NMR ($CDCl_3$): δ = 8.29 (AA′XX′, 2H, $–C_6H_4–$), 7.40 (AA′XX′, 2H, $–C_6H_4–$), 5.85 (ddt, 1H, J = 17.0, 10.4, 5.9 Hz, $–CH_2C\underline{H}=CH_2$), 5.21 (dd, 1H, J = 10.4, 0.8 Hz, $–CH_2CH=C\underline{H}_2$-*cis*), 5.14 (dd, 1H, J = 17.2, 0.8 Hz, $–CH_2CH=C\underline{H}_2$-*trans*), 4.28 (dd, 2H, J = 6.0, 0.8 Hz, $–C\underline{H}_2CH=CH_2$), 2.01 (s, 3H, $COC\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 169.5 ($–\underline{C}OCH_3$); 148.7 ($C_{1\text{-arom}}$); 146.6 ($C_{4\text{-arom}}$); 132.6 ($–CH_2\underline{C}H=CH_2$); 128.4 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 124.9 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 118.4 ($–CH_2CH=\underline{C}H2$); 52.3 ($–\underline{C}H_2CH=CH_2$); 22.8 ($–CO\underline{C}H_3$).

N-Allyl-*N*-cyclohexylethanamide (major rotamer): MS (70 eV) *m/e* (int[%]): 181 (33) M^+; 166 (9); 138 (19); 124 (11); 110 (5); 100 (27); 96 (100); 83 (33); 67 (34); 56 (78); 41 (71). ^{1}H NMR ($CDCl_3$): δ = 5.80 (ddt, 1H, J = 17.6, 10.2, 5.5 Hz, $–CH_2C\underline{H}=CH_2$); 5.19 (dtd, 1H, J = 10.2, 1.8, −1.7 Hz, $–CH_2CH=C\underline{H}_2$-*cis*); 5.18 (ddt, 1H, J = 17.6, −1.7, 1.2 Hz, $–CH_2CH=C\underline{H}_2$-*trans*); 4.44 (dddd, 1H, Jaa = 11.7, Jaa′ = 11.7, Jae = 3.7, Jae′ = 3.7, CH-cyclohexyl); 3.84 (ddd, 2H, J = 5.5, 1.8, 1.2 Hz, $–C\underline{H}_2CH=CH_2$); 2.06 (s, 3H, $–COC\underline{H}_3$); 1.9–1.0 (m, 10H, $C\underline{H}_2$-cyclohexyl). ^{13}C NMR ($CDCl_3$): δ = 170.8 ($–\underline{C}OCH_3$); 135.4 ($–CH_2\underline{C}H=CH_2$); 116.1 ($–CH_2CH=\underline{C}H_2$); 53.1 ($–\underline{C}H_2CH=CH_2$); 46.3 ($C_{1\text{-cyclohexyl}}$); 30.7 ($C_{2\text{-cyclohexyl}}$ and $C_{6\text{-cyclohexyl}}$); 25.8 ($C_{3\text{-cyclohexyl}}$ and $C_{5\text{-cyclohexyl}}$); 25.6 ($C_{4\text{-cyclohexyl}}$); 22.2 ($–CO\underline{C}H_3$).

4.3. Ruthenium complexes

$[RuCl_2(p\text{-cymene})]_2$ and $[RuH_2(CO)(PPh_3)_3]$ from STREM. $[RuClH(CO)(PPh_3)_3]$ [34], $[RuCl_2(PPh_3)_3]$ [35], $[RuH_2(PPh_3)_4]$ [36], $[RuClH(PPh_3)_3]$ [37], $[Ru(CO)_3(PPh_3)_2]$ [38], $[RuCl_2(COD)]_x$ [39] obtained according to methods known in literature.

4.4. Synthesis of (E)-N-(1-propenyl)ethanamides (general method)

A total of 0.1 mol *N*-aryl-*N*-allyl amides and 0.5% mol $[RuClH(CO)(PPh_3)_3]$ were heated at 120 °C for 2 h (*o*-MeO 16 h) under argon atmosphere. After cooling to room temperature, 300 cm^3 hexane (or benzene–hexane 1:1 when aryl = *o*- and *p*-$O_2N–C_6H_4$) was added and the mixture was cooled to 0 °C. Precipitated ruthenium compounds and PPh_3 were filtered off. The filtrate was chromatographed in a column containing 5g (20 g when aryl = *o*- and *p*-$O_2N–C_6H_4$) of silica gel (200–400 mesh). Hexane was evaporated from the eluate in a vacuum evaporator. Pure enamides (purity > 99.5 determined by GC–MS) were obtained in 87–95% yields.

N-Phenyl-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 175 (43) M^+; 157 (32); 132 (71); 130 (43); 117 (22); 105 (11); 91 (6); 77 (24); 63 (12); 50 (17); 43 (100). ^{1}H NMR ($CDCl_3$): δ = 7.89 (dq, 1H, J = 14.4, 1.5 Hz, $–C\underline{H}=CHCH_3$), 7.11–6.71 (m, 5H, H_{arom}), 4.32 (dq, 1H, J = 14.4, 6.9 Hz, $–CH=C\underline{H}CH_3$), 1.63 (s, 3H, $–COC\underline{H}_3$), 1.43 (dd, 3H, J = 6.9, 1.5 Hz, $–CH=CHC\underline{H}_3$). ^{13}C NMR (C_6D_6): δ = 168.4 ($–\underline{C}OCH_3$); 144.7 ($C_{1\text{-arom}}$); 129.0 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 128.8 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 127.7 ($C_{4\text{-arom}}$); 129.2 ($–\underline{C}H=CHCH_3$); 115.1 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 108.7 ($–CH=\underline{C}HCH_3$); 23.1 ($–CO\underline{C}H_3$); 15.0 ($–CH=CH\underline{C}H_3$).

N-(2-Chlorophenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 209 (10) M^+; 174 (15); 169 (13); 167 (40); 166 (13); 132 (23); 132 (85); 111 (13); 105 (10); 77 (14); 75 (38); 63 (9); 50 (18); 43 (100); 39 (25). ^{1}H NMR (C_6D_6): δ = 7.78 (dq, 1H, J = 14.6, 1.5 Hz, $–C\underline{H}=CHCH_3$), 7.19–6.82 (m, 4H, H_{arom}), 4.23 (dq, 1H, J = 14.6, 6.8 Hz, $–CH=C\underline{H}CH_3$), 1.66 (s, 3H, $–COC\underline{H}_3$), 1.41 (dd, 3H,

J = 6.8, 1.5 Hz, –CH=CHC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 168.4 (–$\underline{C}OCH_3$); 139.4 ($C_{2\text{-arom}}$); 139.5 ($C_{1\text{-arom}}$); 130.9 ($C_{3\text{-arom}}$ and $C_{6\text{-arom}}$); 130.1 ($C_{4\text{-arom}}$); 128.4 (–$\underline{C}H$=CHCH$_3$); 127.3 ($C_{5\text{-arom}}$); 108.4 (–CH=$\underline{C}$HCH$_3$); 22.6 (–CO$\underline{C}H_3$); 15.0 (–CH=CH$\underline{C}H_3$).

N-(2-Bromophenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 255 (4) M^+; 253 (3); 213 (20); 211 (20); 184 (5); 182 (4); 155 (7); 132 (44); 130 (30); 117 (18); 105 (7); 91 (5); 77 (20); 75 (18); 63 (7); 50 (16); 43 (100); 39 (34). ^{1}H NMR (C_6D_6): δ = 7.83 (dq, 1H, J = 14.4, 1.5 Hz, –C$\underline{H}$=CHCH$_3$), 7.82 (dd, 1H, $J_{3–4}$ = 7.8 Hz, $J_{3–5}$ = 1.2 Hz, $H_{3\text{-arom}}$), 6.76 (ddd, 1H, $J_{3–4}$ = $J_{4–5}$ = 7.8 Hz, $J_{4–6}$ = 1.5 Hz, $H_{4\text{-arom}}$), 6.63 (dd, 1H, $J_{5–6}$ = 7.8 Hz, $J_{4–6}$ = 1.2 Hz, $H_{6\text{-arom}}$), 6.59 (ddd, 1H, $J_{4–5}$ = $J_{5–6}$ = 7.8 Hz, $J_{3–5}$ = 1.5 Hz, $H_{5\text{-arom}}$), 4.21 (dq, 1H, J = 14.4, 6.6 Hz, –CH=C$\underline{H}$CH$_3$), 1.63 (s, 3H, –COC$\underline{H}_3$), 1.42 (dd, 3H, J = 6.6, 1.5 Hz, –CH=CHC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 166.7 (–$\underline{C}OCH_3$); 139.7 ($C_{2\text{-arom}}$); 134.1 ($C_{1\text{-arom}}$); 131.3 ($C_{3\text{-arom}}$ and $C_{6\text{-arom}}$); 139.8, 128.8 ($C_{4\text{-arom}}$ and $C_{5\text{-arom}}$; 124.5 (–$\underline{C}$H=CHCH$_3$); 107.1 (–CH=$\underline{C}$HCH$_3$); 22.6 (–CO$\underline{C}H_3$); 15.0 (–CH=CH$\underline{C}H_3$).

N-(2-Methylphenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 189 (10) M^+; 174 (5); 160 (3); 147 (14); 132 (11); 130 (12); 118 (100); 106 (3); 91 (20); 89 (5); 82 (3); 77 (8); 65 (23); 51 (7); 43 (100); 39 (21). ^{1}H NMR (C_6D_6): δ = 7.45 (dq, 1H, J = 14.1, 1.8 Hz, –C$\underline{H}$=CHCH$_3$), 7.35–7.07 (m, 4H, H_{arom}), 6.59 (ddd, 1H, $J_{4–5}$ = $J_{5–6}$ = 7.8 Hz, $J_{3–5}$ = 1.5 Hz, $H_{5\text{-arom}}$), 4.33 (dq, 1H, J = 14.1, 6.9 Hz, –CH=C$\underline{H}$CH$_3$), 2.16 (s, 3H, *o*-C_6H_4–C$\underline{H}_3$), 1.78 (s, 3H, –COC$\underline{H}_3$), 1.61 (dd, 3H, J = 6.9, 1.8 Hz, –CH=CHC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 168.3 (–$\underline{C}OCH_3$); 138.4 ($C_{1\text{-arom}}$); 137.5 (–$\underline{C}$H=CHCH$_3$); 130.5, 129.0, 128.5 and 128.5 ($C_{2,3,4,5,6\text{-arom}}$); 108.9 (–CH=$\underline{C}HCH_3$); 23.1 (–CO$\underline{C}H_3$); 21.1 (*o*-$C_4H_6$–$\underline{C}H_3$); 15.0 (–CH=CH$\underline{C}H_3$).

N-(2-Methoxyphenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 205 (34) M^+; 163 (81); 148 (31); 146 (15); 134 (67); 132 (32); 130 (21); 120 (80); 117 (13); 108 (15); 92 (20); 77 (42); 65 (30); 51 (32); 43 (100); 39 (52). ^{1}H NMR (C_6D_6): δ = 7.57 (dq, 1H, J = 14.4, 1.5 Hz, –C$\underline{H}$=CHCH$_3$), 7.21–6.60 (m, 4H, H_{arom}), 4.41 (dq, 1H, J = 14.2, 6.8 Hz, –CH=C$\underline{H}$CH$_3$), 3.28 (s, 3H, *o*-C_6H_4–OC$\underline{H}_3$), 1.74 (s, 3H, –COC$\underline{H}_3$), 1.43 (dd, 3H, J = 6.8, 1.5 Hz, –CH=CHC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 168.5 (–$\underline{C}OCH_3$); 155.9 ($C_{3\text{-arom}}$); 132.8 ($C_{1\text{-arom}}$); 131.2 (–$\underline{C}$H=CHCH$_3$); 131.2, 129.9, 121.4 and 116.3 ($C_{2,4,5,6\text{-arom}}$); 55.1 (*o*-C_4H_6–O$\underline{C}H_3$) 113.5 (–CH=$\underline{C}$HCH$_3$); 22.4 (–CO$\underline{C}H_3$); 15.2 (–CH=CH$\underline{C}H_3$).

N-(2-Nitrophenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 220 (1) M^+; 148 (2); 138 (3); 134 (6); 130 (7); 118 (5); 106 (19); 91 (6); 83 (5); 79 (19); 65 (9); 59 (10); 52 (7); 43 (100); 39 (30). ^{1}H NMR ($CDCl_3$): δ = 8.08 (dd, 1H, $J_{4–3}$ = 8.1, $J_{3–5}$ = 1.5 Hz, $H_{3\text{-arom}}$), 7.82 (ddd, 1H, $J_{3–4}$ = $J_{4–5}$ = 8.1 Hz, $J_{4–6}$ = 1.5 Hz, $H_{4\text{-arom}}$), 7.70 (ddd, 1H, $J_{4–5}$ = $J_{5–6}$ = 8.1 Hz, $J_{3–5}$ = 1.5, $H_{5\text{-arom}}$), 7.42 (dd, 1H, $J_{5–6}$ = 8.1, $J_{4–6}$ = 1.5 Hz, $H_{6\text{-arom}}$), 7.45 (dd, 1H, J = 14.4. 1.5 Hz, –C$\underline{H}$=CHCH$_3$), 4.30 (dq, 1H, J = 14.4, 6.8 Hz, –CH=C$\underline{H}$CH$_3$), 1.92 (s, 3H, –COC$\underline{H}_3$), 1.56 (dd, 3H, J = 6.8, 1.5 Hz, –CH=CHC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 167.8 (–$\underline{C}OCH_3$); 136.0, 133.5, 132.2 and 128.5 ($C_{1,2,3,4,5,6\text{-arom}}$); 130.6; 128.7 (–$\underline{C}$H=CHCH$_3$); 108.8 (–CH=$\underline{C}HCH_3$); 22.9 (–CO$\underline{C}H_3$); 15.0 (–CH=CH$\underline{C}H_3$).

N-(3-Methoxyphenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 205 (48) M^+; 190 (8); 163 (61); 162 (61); 148 (23); 132 (23); 118 (10); 103 (10); 91 (6); 77 (25); 65 (14); 51 (14); 43 (100); 39 (27). ^{1}H NMR (C_6D_6): δ = 7.82 (dq, 1H, J = 14.2. 1.5 Hz, –C$\underline{H}$=CHCH$_3$), 7.08 (dd, 1H, $J_{5–6}$ = $J_{4–5}$ = 8.1 Hz, $H_{5\text{-arom}}$), 6.76 (ddd, 1H, $J_{4–5}$ = 8.1 Hz, $J_{4–6}$ = 2.6 Hz, $J_{2–4}$ = 0.9 Hz, $H_{4\text{-arom}}$), 6.61 (dd, 1H, $J_{2–4}$ = $J_{2–6}$ = 0.9 Hz, $H_{2\text{-arom}}$), 6.53 (ddd, 1H, $J_{5–6}$ = 8.1, $J_{4–6}$ = 2.6, $J_{2–6}$ = 0.9 Hz, $H_{6\text{-arom}}$), 4.44 (dq, 1H, J = 14.2, 6.7 Hz, –CH=C$\underline{H}$CH$_3$), 3.35 (s, 3H, *m*-C_6H_4–OC$\underline{H}_3$), 1.73 (s, 3H, –COC$\underline{H}_3$), 1.47 (dd, 3H, J = 6.7, 1.5 Hz, –CH=CHC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ = 168.1 (–$\underline{C}OCH_3$); 160.7 ($C_{3\text{-arom}}$); 141.2 ($C_{1\text{-arom}}$); 130.6 ($C_{5\text{-arom}}$); 128.7 (–$\underline{C}$H=CHCH$_3$); 121.0 ($C_{6\text{-arom}}$); 114.6 ($C_{4\text{-arom}}$); 114.0 ($C_{2\text{-arom}}$); 109.2 (–CH=$\underline{C}$HCH$_3$); 55.4 (*m*-C_6H_4–O$\underline{C}H_3$); 23.1 (–CO$\underline{C}H_3$); 15.0 (–CH=CH$\underline{C}H_3$).

N-(4-Methoxyphenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 205 (67) M^+; 163 (100); 148 (65); 134 (10); 121 (17); 93 (6); 91 (33); 82 (20); 77 (35); 64 (31); 51 (8); 43 (40); 39 (11). ^{1}H NMR ($CDCl_3$): δ = 7.42 (dq, 1H, J = 14.3, 1.5 Hz, –C$\underline{H}$=CHCH$_3$), 7.07 (AA′XX′, 2H, –C_6H_4–), 6.97 (AA′XX′, 2H, –C_6H_4–), 4.42 (dq,

1H, J = 14.1, 6.8 Hz, –CH=C<u>H</u>–CH_3), 3.85 (s, 3H, *p*-C_6H_4–O<u>C</u>H_3), 1.84 (s, 3H, –CO<u>C</u>H_3), 1.61 (dd, 3H, J = 6.8, 1.5 Hz, –CH=CHC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$): δ = 168.5 (–<u>C</u>OCH$_3$); 159.4 ($C_{4\text{-arom}}$); 132.7 ($C_{1\text{-arom}}$); 129.8 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 129.2 (–<u>C</u>H=CHCH$_3$); 115.1 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 108.7 (–CH=<u>C</u>HCH$_3$); 55.4 (*p*-C_6H_4–O<u>C</u>H$_3$); 23.1 (–CO<u>C</u>H$_3$); 15.0 (–CH=CH<u>C</u>H$_3$).

N-(4-Methylphenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 189 (35) M^+; 174 (9); 147 (80); 132 (68); 118 (21); 105 (13); 91 (35); 77 (12); 65 (37); 51 (15); 43 (100); 39 (48). ^{1}H NMR ($CDCl_3$): δ = 7.46 (dq, 1H, J = 14.1, 1.5 Hz, –C<u>H</u>=CHCH$_3$), 7.26 (AA′XX′, 2H, –C_6H_4–), 7.05 (AA′XX′, 2H, –C_6H_4–), 4.42 (dq, 1H, J = 14.1, 6.8 Hz, –CH=C<u>H</u>CH$_3$), 3.30 (s, 3H, *p*-C_6H_4–C<u>H</u>$_3$), 1.75 (s, 3H, –COC<u>H</u>$_3$), 1.43 (dd, 3H, J = 6.8, 1.5 Hz, –CH=CHC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$): δ = 168.3 (–<u>C</u>OCH$_3$); 138.4 ($C_{1\text{-arom}}$); 137.5 ($C_{4\text{-arom}}$); 130.5 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 129.0 (–<u>C</u>H=CHCH$_3$); 128.5 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 108.9 (–CH=<u>C</u>HCH$_3$); 23.1 (–CO<u>C</u>H$_3$); 21.1 (*p*-C_6H_4–<u>C</u>H$_3$); 15.0 (–CH=CH<u>C</u>H$_3$).

N-(4-Nitrophenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 220 (1) M^+; 160 (1); 147 (1); 134 (100); 119 (9); 105 (17); 94 (49); 77 (25); 65 (12); 51 (19). ^{1}H NMR ($CDCl_3$): δ = 8.35 (AA′XX′, 2H, –C_6H_4–), 7.41 (AA′XX′, 2H, –C_6H_4–), 7.25 (dd, 1H, J = 14.1, 1.5 Hz, –C<u>H</u>=CHCH$_3$), 4.30 (dq, 1H, J = 14.1, 6.6 Hz, –CH=C<u>H</u>CH$_3$), 1.97 (s, 3H, –COC<u>H</u>$_3$), 1.65 (dd, 3H, J = 6.6, 1.5 Hz, –CH=CHC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$): δ = 168.0 (–<u>C</u>OCH$_3$); 147.1 ($C_{1\text{-arom}}$); 146.9 ($C_{4\text{-arom}}$); 128.8 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 125.9 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 129.5 (–<u>C</u>H=CHCH$_3$); 109.5 (–CH=<u>C</u>HCH$_3$); 23.3 (–CO<u>C</u>H$_3$); 15.2 (–CH=CH<u>C</u>H$_3$).

N-(4-Chlorophenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 199 (18); 183 (19);163 (10); 151 (12); 138 (12); 123 (23); 119 (33); 97 (51); 81 (59); 64 (77); 57 (100); 41 (70). ^{1}H NMR ($CDCl_3$): δ = 7.43 (dq, 1H, J = 13.5, 1.5 Hz, –C<u>H</u>=CHCH$_3$), 7.46 (AA′XX′, 2H, –C_6H_4–), 7.14 (AA′XX′, 2H, –C_6H_4–), 4.41 (dq, 1H, J = 13.5, 6.6 Hz, –CH=C<u>H</u>CH$_3$), 1.85 (s, 3H, –COC<u>H</u>$_3$), 1.62 (dd, 3H, J = 6.6, 1.5 Hz, –CH=CHC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$): δ = 167.9 (–<u>C</u>OCH$_3$); 138.6 ($C_{1\text{-arom}}$); 132.1 (–<u>C</u>H=CHCH$_3$); 130.3 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 138.9 and 128.6 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 128.6 ($C_{4\text{-arom}}$); 109.4 (–CH=<u>C</u>HCH$_3$); 23.1 (–CO<u>C</u>H$_3$); 15.1 (–CH=CH<u>C</u>H$_3$).

N-(4-Bromophenyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 255 (3) M^+; 253 (4); 213 (15); 211 (16); 184 (5); 167 (4); 157 (4); 155 (4); 132 (13); 130 (21); 115 (5); 105 (7); 91 (2); 78 (54); 56 (11); 50 (25); 43 (100); 39 (30). ^{1}H NMR ($CDCl_3$): δ = 7.62 (AA′XX′, 2H, –C_6H_4–), 7.42 (dq, 1H, J = 13.5, 1.5 Hz, –C<u>H</u>=CHCH$_3$), 7.08 (AA′XX′, 2H, –C_6H_4–), 4.40 (dq, 1H, J = 13.5, 6.6 Hz, –CH=C<u>H</u>CH$_3$), 1.85 (s, 3H, –COC<u>H</u>$_3$), 1.62 (dd, 3H, J = 6.6, 1.5 Hz, –CH=CHC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$): δ = 167.8 (–<u>C</u>OCH$_3$); 139.2 ($C_{1\text{-arom}}$); 133.2 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 130.6 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 128.9 (–<u>C</u>H=CHCH$_3$); 122.5 ($C_{4\text{-arom}}$); 109.5 (–CH=<u>C</u>HCH$_3$); 23.1 (–CO<u>C</u>H$_3$); 15.1 (–CH=CH<u>C</u>H$_3$).

N-(1-Naphthyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 225 (93) M^+; 210 (4); 183 (100); 180 (19); 168 (47); 156 (42); 142 (12); 115 (30); 101 (4); 82 (36); 77 (11); 63 (4); 51 (4); 43 (38); 39 (6). ^{1}H NMR ($CDCl_3$): δ = 7.94–7.34 (m, 7H, H_{arom}), 7.64 (dq, 1H, J = 14.3, 1.5 Hz, –C<u>H</u>=CHCH$_3$) 4.30 (dq, 1H, J = 14.3, 6.6 Hz, –CH=C<u>H</u>CH$_3$), 1.75 (s, 3H, –COC<u>H</u>$_3$), 1.56 (dd, 3H, J = 6.6, 1.50 Hz, –CH=CHC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$): δ = 169.0 (–<u>C</u>OCH$_3$); 136.5 ($C_{10\text{-arom}}$); 134.8 ($C_{1\text{-arom}}$); 130.4 ($C_{9\text{-arom}}$); 129.2 (–<u>C</u>H=CHCH$_3$); 128.5, 127.6, 127.1, 126.8, 125.8 and 122.7 ($C_{2\text{-arom}}$, $C_{3\text{-arom}}$, $C_{4\text{-arom}}$, $C_{5\text{-arom}}$, $C_{6\text{-arom}}$, $C_{7\text{-arom}}$ and $C_{8\text{-arom}}$); 109.3 (–CH=<u>C</u>HCH$_3$); 22.7 (–CO<u>C</u>H$_3$); 15.0 (–CH=CH<u>C</u>H$_3$).

N-(2-Naphthyl)-*N*-(1-propenyl)ethanamide: MS (70 eV) *m/e* (int[%]): 225 (13) M^+; 183 (30); 180 (6); 169 (32); 154 (8); 141 (8); 127 (23); 115 (6); 101 (6); 91 (4); 85 (11); 82 (32); 78 (100); 63 (12); 55 (10); 51 (36); 43 (70); 39 (45). ^{1}H NMR ($CDCl_3$): δ = 8.54 (dq, 1H, J = 14.1, 1.6 Hz, –C<u>H</u>=CHCH$_3$), 7.94–23 (m, 7H, H_{arom}), 4.45 (dq, 1H, J = 14.1, 6.9 Hz, –CH=C<u>H</u>CH$_3$), 1.89 (s, 3H, –COC<u>H</u>$_3$), 1.55 (dd, 3H, J = 6.9, 1.60 Hz, –CH=CHC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$): δ = 148.0 (–<u>C</u>OCH$_3$); 128.9 (–<u>C</u>H=CHCH$_3$); 123.5 ($C_{9\text{-arom}}$); 132.0 ($C_{2\text{-arom}}$); 131.8 ($C_{10\text{-arom}}$); 128.1 128.2, 128.4, 116.7 and 115.4 ($C_{1\text{-arom}}$, $C_{3\text{-arom}}$, $C_{4\text{-arom}}$, $C_{5\text{-arom}}$, $C_{6\text{-arom}}$, $C_{7\text{-arom}}$ and $C_{8\text{-arom}}$); 112.6 ($C_{3\text{-arom}}$); 109.5, 109.2 (–<u>C</u>H=CHCH$_3$ and –CH=<u>C</u>HCH$_3$); 22.9 (–CO<u>C</u>H$_3$); 15.1 (–CH=CH<u>C</u>H$_3$).

4.5. Isomerisation of N-allyl-N-cyclohexylethanamide and N-allylethanamide

A total of 0.05 mol of *N*-allylethanamide and 0.5% mol of [RuClH(CO)(PPh_3)$_3$] were heated at 120 °C for 2 h under argon atmosphere. After this time substrate conversion was found to be quantitative. The obtained mixture of (*E*)- and (*Z*)-enamides was distilled from the post-reaction mixture under reduced pressure, thus being separated from the catalyst, triphenylphosphine and its oxide. The (*E*)- and (*Z*)-*N*-1-propenylethanamides were obtained with a yield of 92% (isolated yield). Physical and spectroscopic properties of the products were consistent with those described in the [12]. The isomerisation of *N*-allyl-*N*-cyclohexylethanamide was carried out in 0.05 mol scale according to the routine described in Section 4.4 of the present work. A mixture of (*E*)- and (*Z*)-*N*-cyclohexyl-*N*-(1-propenyl)ethanamides has been obtained with a yield of 93%.

(*E*)-*N*-cyclohexyl-*N*-(1-propenyl)ethanamide: MS (70 eV) *m*/*e* (int[%]): 181 (12) M^+; 166 (11); 138 (5); 110 (5); 100 (27); 96 (28); 83 (20); 67 (5); 57 (100); 43 (49); 39 (19). ^{1}H NMR ($CDCl_3$): $\delta = 5.98$ (dd, 1H, $J = 13.6$, 1.8 Hz, –C$\underline{H}$=CHCH$_3$); 5.52 (dq, 1H, $J = 13.6$, 6.8 Hz, CH=C$\underline{H}$CH$_3$), 4.23 (dddd, 1H, Jaa = 11.8, Jaa′ = 10.8, Jae = 3.5, Jae′ = 3.5 Hz, C$\underline{H}_{cyclohexyl}$) 1.96 (s, 3H, –COC$\underline{H}_3$), 1.76 (dd, 3H, $J = 6.8$, 1.8 Hz, –CH=CHC$\underline{H}_3$), 1.78–0.95 (m, 10H, $H_{cyclohexyl}$). ^{13}C NMR ($CDCl_3$): $\delta = 169.3$ (–$\underline{C}$OCH$_3$); 128.0 (–$\underline{C}$H=CHCH$_3$); 126.3 (–CH=$\underline{C}$HCH$_3$); 53.1 ($C_{1\text{-cyclohexyl}}$); 30.3 ($C_{2\text{-cyclohexyl}}$ and $C_{6\text{-cyclohexyl}}$); 25.5 ($C_{3\text{-cyclohexyl}}$ and $C_{5\text{-cyclohexyl}}$); 25.4 ($C_{4\text{-cyclohexyl}}$); 23.0 (–CO$\underline{C}$H$_3$); 14.8 (–CH=CH$\underline{C}$H$_3$).

(*Z*)-*N*-Cyclohexyl-*N*-(1-propenyl)ethanamide: MS (70 eV) *m*/*e* (int[%]): 181 (9) M^+; 166 (8); 138 (3); 110 (5); 100 (19); 96 (27); 83 (40); 68 (8); 57 (100); 43 (58); 39 (22). ^{1}H NMR ($CDCl_3$): $\delta = 5.98$ (dd, 1H, $J = 7.0$, 1.8 Hz, –C$\underline{H}$=CHCH$_3$); 5.69 (dq, 1H, $J = 7.0$, 7.0 Hz, –CH=C$\underline{H}$CH$_3$), 4.44 (dddd, 1H, Jaa = 11.8, Jaa′ = 10.7, Jae = 3.7, Jae′ = 3.7 Hz, C$\underline{H}_{cyclohexyl}$) 2.02 (s, 3H, –COC$\underline{H}_3$), 1.60 (dd, 3H, $J = 6.8$, 1.8 Hz, –CH=CHC$\underline{H}_3$), 1.78–0.95 (m, 10H, $H_{cyclohexyl}$). ^{13}C NMR ($CDCl_3$): $\delta = 169.1$ (–$\underline{C}$OCH$_3$); 128.2 (–$\underline{C}$H=CHCH$_3$); 126.8 (–CH=$\underline{C}$HCH$_3$); 53.2 ($C_{1\text{-cyclohexyl}}$); 30.0 ($C_{2\text{-cyclohexyl}}$ and $C_{6\text{-cyclohexyl}}$); 25.3 ($C_{3\text{-cyclohexyl}}$ and $C_{5\text{-cyclohexyl}}$); 25.3 ($C_{4\text{-cyclohexyl}}$); 22.0 (–CO$\underline{C}$H$_3$); 12.2 (–CH=CH$\underline{C}$H$_3$).

4.6. Investigation of the impact of the substituents on the isomerisation rate (competitive reactions method)

In a twisted-cap ampoule 1.5 mmol *N*-allylamide (Y–C_6H_4NAc(allyl)), 3 cm^3 0.5 M *p*-methoxyallylbenzene in tetrachloroethylene and 12 mg [RuClH(CO)(PPh_3)$_3$] was introduced. Having been saturated with argon, the mixture was heated and stirred for 2 h at 50 °C and analysed by ^{1}H NMR afterwards.

4.7. Investigation of the influence of the solvent

In a twisted-cap ampoule 1.0 mmol *N*-allyl-*N*-(*p*-methylphenyl)ethanamide, 3 cm^3 of solvent and 12 mg [RuClH(CO)(PPh_3)$_3$] was introduced. Having been saturated with argon, the mixture was heated and stirred for 2 h at 80 °C (or 60 °C) and analysed by ^{1}H NMR afterwards.

4.8. Spectroscopic measurements

^{1}H and ^{13}C NMR spectra were measured on a Varian Unity 300 MHz spectrometer. GC–MS analyses were run on a 30 m long DB 1701 fused silica capillary column, using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800 AT ion trap detector. Diethylene glycol dimethyl ether was used as the internal standard for the yield measurement.

4.9. Quantum calculations

Semi-empirical quantum calculations have been carried out using PM5 method of MOPAC 2002 [40] accompanied by CAChe graphical interface [41]. The stop criterion was to achieve a gradient less than 0.01, by eigenvector following method.

4.10. Crystallographic data of (E)-N-(o-methylphenyl)-N-(1-propenyl)ethanamide

The measurements of diffraction intensities were performed on a KUMA KM4 four-circle

diffractometer, Mo Kα radiation, $\omega/2\Theta$ scan mode [42]. The structure were solved by direct methods using the program SHELXS-97 [43] and refined by full-matrix least-squares with the aid of the program SHELXL97 [44]. All non-hydrogen atoms were refined anisotropically. The hydrogen positions were calculated according to the standard geometry, and refined as a riding model with isotropic thermal parameters [44]. Software used to prepare material for publication: Ortep-3 [45].

The crystal chosen for X-ray analysis was a clear colourless block with the approximate dimensions 0.3 mm × 0.4 mm × 0.65 mm. $C_{12}H_{15}NO$ (189.25 g/mol) crystallises in the monoclinic system, space group $P2_1/n$, with $a = 10.191$ Å (**3**), $b = 7.347$ Å (**2**), $c = 15.187$ Å (**3**), $\beta = 107.07^\circ$ (**3**), $V = 1087.1$ Å^3 (**4**), $Z = 4$, μ(Mo Kα) = 0.07 mm^{-1}, and $D_{calcd} = 1.156$ g/cm^3. The e.s.d. unit cell parameters were determined by least-squares refinement using 34 centred reflections within $9.67^\circ < \Theta < 28.95^\circ$. A total of 2753 reflections were collected to $2\Theta_{max} = 46.99^\circ$ (h: $-9 \rightarrow 11$, k: $0 \rightarrow 8$, l: $-5 \rightarrow 17$), of which 1566 were unique. The intensity decay of the reference reflections was 72%. In refinements, weights were used according to the scheme $w = 1/[\sigma^2(F_0^2) + (0.1003P)^2 + 0.20P]$, where $P = (F_0^2 + 2F_c^2)/3$. The refinement of 128 parameters (data-to-parameter ratio being 12.23) converged to the final agreement factors $R = 0.0504$, $R_w = 0.1542$, and $S = 1.00$ for 1157 observed reflections with $F > 4\sigma(F_0)$. The electron density of the largest difference peak was found to be 0.29 e/Å^3, while that of the largest difference hole was 0.25 e/Å^3.

Tables of bond distances and angles, atomic coordinates, and anisotropic thermal parameters for of (*E*)-*N*-(*o*-methylphenyl)-*N*-(1-propenyl)ethanamide (CCDC 162489) have been deposited with the Cambridge Crystallographic Data Centre.[1]

[1] A complete listing of the atomic coordinates of (*E*)-*N*-(*p*-methylphenyl)-*N*-(1-propenyl)ethanamide can be obtained free of charge, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk), on quoting the depository numbers, the names of the authors, and the journal citation.

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