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Highly selective isomerization of *N*-allylamides catalyzed by ruthenium and rhodium complexes

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Abstract

Isomerization of *N*-allylamides catalyzed by ruthenium and rhodium complexes to corresponding 1-propenyl derivatives is described. The first catalytic system containing a precursor ($\{[RuCl_2(1,5\text{-COD})]_x\}$), tris(2,4-di-*t*-butylphenyl)phosphite and CaH_2 for highly (*Z*)-selective isomerization of allylamides is presented. It has been shown that the double bond migration catalyzed by the investigated catalytic systems occurs according to the hydride mechanism. The participation of *ortho*-metallation from precursor and triphenylphosphine in the formation of hydride complex has been proved. It is proposed that the observed (*Z*)-selectivity of the isomerization of some allylamides is the result of the steric effect in the transition state. The application of siliceous mesoporous cellular foams for an effective removal of the catalyst from the post-reaction mixture is described.

Keywords: Double bond migration; *N*-Allylamides; Selective isomerization; Ruthenium complexes; Rhodium complexes; Siliceous mesoporous cellular foams

1. Introduction

Double bond migration of *N*-allyl derivatives (*N*-allyl: amines, amides, imides, imines, carbamates, oximes) has been studied extensively [1]. The products of these reactions: *N*-(1-propenyl) — in general: *N*-vinyl derivatives (e.g. enamines, enamides, azadienes) — are interesting intermediates in organic synthesis. Enamides are substrates in the synthesis of heterocyclic systems [2–4] and Diels–Alder cycloaddition [5–7]. Enamides have been also used for the formation of enamines [8–10], enamide-olefin ring-closing metathesis [11–13] and are thoroughly investigated monomers and co-monomers [14,15]. Ruthenium [16–22], iron [16,19,23,24], iridium [25], osmium [26], cobalt [27] and rhodium [16,23,28] complexes were applied for the isomerization of *N*-allyl compounds. In the present paper we describe isomerization of various *N*-allylamides catalyzed by ruthenium and rhodium complexes. The first catalytic system for (*Z*)-selective isomerization of some *N*-allylamides is presented. The mechanism of double bond migration and reasons for the observed (*Z*)-selectivity is also analyzed. Preliminary results of these investigations were described in our previous communication [22].

2. Results and discussion

The results of the isomerization of various *N*-allylamides catalyzed by $[RuClH(CO)(PPh_3)_3]$ have been summarized in Table 1. Reactions were carried out in benzene, 1,4-dioxane or THF or without a solvent. In such solvents as $CHCl_3$, CCl_4, tetrachloroethene, 2-butanone, ethyl acetate, 1,2-dimethoxyethane the reactions proceeded worse or did not proceed at all ($CHCl_3$ and CCl_4). The conversion of the allyl system was practically always quantita-

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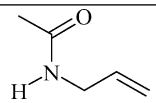
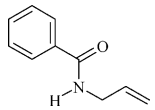
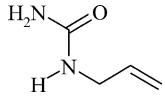
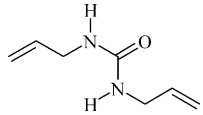
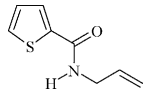
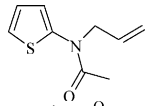
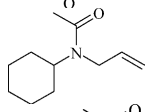
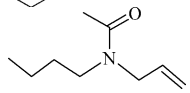
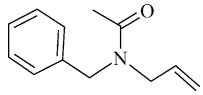
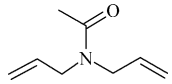
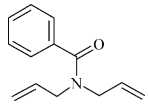
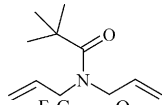
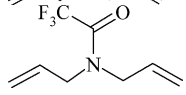
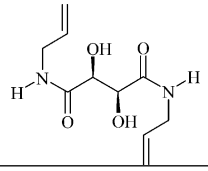
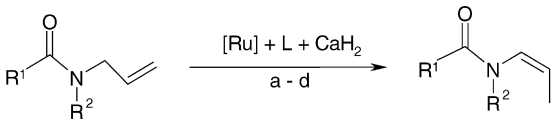
Table 1
Isomerization of *N*-allylamides to enamides catalyzed by [RuClH(CO)(PPh_3)$_3$] ([Ru]) and [RhH(CO)(PPh_3)$_3$] ([Rh])[a]

Entry	*N*-Allylamide	*t* (°C)	*τ* (h)	S/C	So (V)	Enamide	
						y[b] (%)	*E*/*Z*[c]
1		80	2	96 [Ru]	C_6H_6 (0.50)	100 (85[d])	59/41
		80	2	93 [Rh]	C_6H_6 (0.50)	100	58/42
2		80	3	59 [Ru]	C_6H_6 (0.50)	100 (84[d])	67/33
		100	2	54 [Rh]	C_6H_6 (0.50)	100	67/33
3		80	3	143	THF (1.00)	100 (60[e])	42/58
4		80	3	53	THF (2.50)	100 (50[e])	79/21/0[f]
5		70	3	57	C_6H_6 (0.84)	100	77/23
6		120	2	54	C_6H_6 (1.30)	95	83/17
7		120	2	200	–	100 (93[g])	85/15
8		100	2	63	THF (0.77)	100	87/13
9		120	2	100	–	100 (70[g])	91/9
10		120	2	98	–	100	44/66/0[f]
11		120	2	68	–	100 (70[g])	40/47/15[e]
12		120	2	53	–	100 (70[g])	53/47/15[f]
13		80	3	105	C_6H_6 (0.33)	98	55/45/0[f]
14		80	3	53	THF (2.5)	100 (60[g])	4/51/6[f]

[a] Experimental procedure as in our previous work [20]; S/C: substrate:catalyst; So (V): solvent, ([cm^3/1 mmol of substrate]); *y*: yield of the double bond migration product, determined by ^{1}H NMR.
[b] Conversion has always been quantitative (determined by ^{1}H NMR and GC–MS).
[c] Determined by ^{1}H NMR and GC–MS.
[d] Isolated yield after reduced pressure distillation.
[e] Recrystallized from methanol.
[f] *EE*/*EZ*/*ZZ*.
[g] Isolated yield after column chromatography.



a) $R^1 = CH_3$, $R^2 = H$, 80°C/2h, THF; b) $R^1 = Ph$, $R^2 = H$, 90°C/4h,THF; c) $R^1 = NH_2$, $R^2 = H$, 100°C/1h, 1,4-dioxane; d) $R^1 = CH_3$, $R^2 = Bu$, 110°C/2h, 1,4-dioxane; [Ru] = $\{[RuCl_2(1,5\text{-}COD)]_x\}$; L = tris(2,4-di-*t*-butylphenyl) phosphite; amide : [Ru] : L : CaH_2 = 100 : 1 : 1 : 10

Fig. 1. Stereoselective isomerization of *N*-allylamides to (*Z*)-enamides.

tive — only in the case of amide **6** a conversion of 95% was achieved, and for amide **13** 98% (this was, perhaps, an equilibrium conversion). It is important to note that the only products were 1-propenyl derivatives. As expected, the products consisted of a mixture of *E* and *Z* enamides. In our earlier papers we demonstrated that only *N*-allyl-*N*-aryl-amides can be isomerized selectively to (*E*)-enamides in the presence of $[RuClH(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$ or $[RhH(CO)(PPh_3)_3]$ [22]. This (*E*)-selectivity is the result of a specific coordination of the metal atom by the aryl substituent. It ought to be noted, that amide **13**, which contains unprotected hydroxyl groups, as well as amide **6** with a strongly coordinating thiophene fragment did isomerize. However, most interesting results were obtained when a new catalytic system containing a precursor — $\{[RuCl_2(1,5\text{-}COD)]_x\}$, a tri(2,4-di-*t*-butylphenyl)phosphite ligand and a hydride ligand donor (CaH_2) were employed. The application of this catalytic system enabled us to obtain, in some cases, exclusively (*Z*)-enamides, see Fig. 1.

To the best of our knowledge, this is the first example of a selective isomerization of allyl systems exclusively to (Z)-1-propenyl derivatives in the presence of transition metal complexes. The catalyst precursor $\{[RuCl_2(1,5\text{-}COD)]_x\}$ without an addition of phosphite and CaH_2 (or $NaBH_4$ or NaH) is catalytically inactive — due to the fact that it is completely insoluble in the solvent–substrate mixture. Moreover, the system $\{[RuCl_2(1,5\text{-}COD)]_x\}$ — phosphite without an addition of a hydride ligand donor is inactive too. This observation undoubtly indicates that the double bond migration complies with the hydride mechanism. In order to test this hypothesis, we carried out the isomerization of *N*-allylethanamide in the presence of the following catalytic systems: Ru^1 = $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + PPh_3 + $NaBD_4$, Ru^2 = $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + $P(OPh)_3$ + $NaBD_4$, Ru^3 = $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + PPh_3-d_{15}. In each case we observed a deuterium transfer

Table 2
Deuterium distribution in the isomerization of *N*-allylethanamide catalyzed by Ru^1, Ru^2 and Ru^3

Catalyst/(Ru:substrate)	Deuterium[a]		
	C^1	C^2	C^3
Ru^1 = $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + PPh_3 + $NaBD_4$ (1:1:10)/(1:50)	10	16	74
Ru^2 = $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + $P(OPh)_3$ + $NaBD_4$ (1:1:10)/(1:50)	24	41	35
Ru^3 = $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + PPh_3-d_{15} (1:1)/(1:20)	23	54	23

[a] The deuterium content in (*E*)- and (*Z*)-isomer was the same; error ±3%; reaction conditions: 120 °C, 3 h, argon, 1,4-dioxane.

to the product (i.e. the enamide), to both isomers (*E* and *Z*) to the same extent, see Fig. 2.

It is worth noting, that deuterium was present in all the three carbon atoms of the propenyl system, as well as in the nitrogen atom. The distribution of deuterium observed in the studied systems has been summarized in Table 2. Therefore, there is no doubt that in the case of all the catalytic systems in our study the hydride mechanism operates. Moreover, if triphenylphosphine is a ligand, the active form is also formed via *ortho*-metallation — therefore in the case of Ru^3 deuteration of the enamide was observed too.

Therefore, the results of our study imply that polymeric $\{[RuCl_2(1,5\text{-}COD)]_x\}$ undergoes a transformation to a complex containing a hydride ligand and a coordinated phosphite in situ. Furthermore, we have found that the addition of a greater amount of phosphite to the catalytic system results in a quick decrease of the catalytic activity. When the ratio Ru:P is 1:2 the system is completely inactive towards isomerization. This means that in the active form only one molecule of the phosphite is coordinated. A suggestion of the structure of this complex and of the key step determining the (*Z*)-selectivity is demonstrated in Fig. 3.

In our opinion, steric interactions in the β-elimination step are responsible for the high (*Z*)-selectivity. These repulsive interactions are weakest when Q and CH_3 are on the same side of the plane in which β-elimination takes place, and the bulky phosphite ligand is on the other side. However, when the ligand was sterically less demanding (triphenylphosphite) we observed a mixture of isomeric (*E*)- and (*Z*)-enamides.

In order to remove [Ru] from the post-reaction mixture, siliceous mesoporous cellular foams (MCFs) were used, which constitute a new class of materials with well-defined

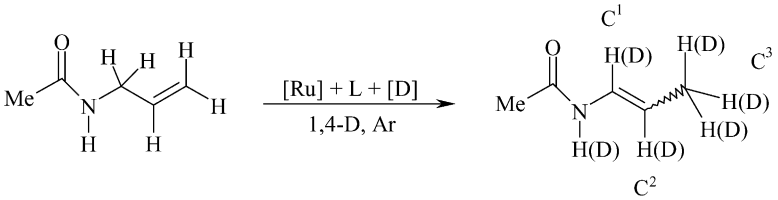


Fig. 2. Isomerization of *N*-allylethanamide in the presence of Ru^1 (Ru^1 = $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + PPh_3 + $NaBD_4$), Ru^2 ($\{[RuCl_2(1,5\text{-}COD)]_x\}$ + $P(OPh)_3$ + $NaBD_4$) and Ru^3 ($\{[RuCl_2(1,5\text{-}COD)]_x\}$ + PPh_3-d_{15}). Reaction conditions are quoted in Table 2.

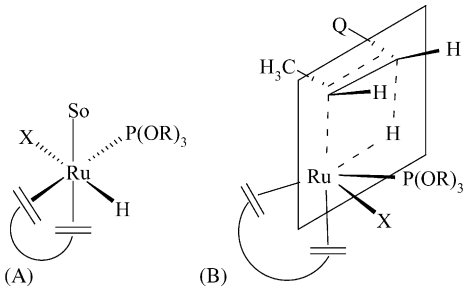
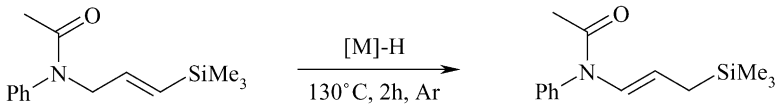


Fig. 3. (A) Postulated structure of the active form of the ruthenium catalyst. (B) Postulated transition structure for the (*Z*)-selective isomerization of *N*-allylamides (R = 2,4-di-*t*-butylphenyl; X = H or Cl).

uniform ultra-large mesopores [29,30]. We have found that the efficiency of [Ru] separation using a column with MCFs was significantly higher compared with a typical silica gel (200–400 mesh, Aldrich). MCFs were used to separate the catalyst from the (*Z*)-enamides.

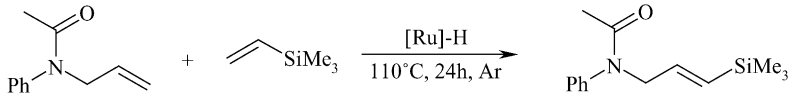
Moreover, it was demonstrated that isomerization of an *N*-allylamide containing a trimethylsilyl group at the double bond is possible, see Fig. 4. This finding broadens the scope of applications of these isomerization reactions in organic syntheses. It is worth noting that in the case of amide **24** a high (*E*)-selectivity of double bond migration was observed. This also confirms our earlier statement that *N*-allyl-*N*-aryl systems isomerize to (*E*)-1-propenyl derivatives [22].

Silylated amide was obtained via silylative coupling of *N*-allyl-*N*-phenylethanamide with trimethylvinylsilane in the presence of a ruthenium catalyst, see Fig. 5.



[M]-H = 3% mol $[RuClH(CO)(PPh_3)_3]$, conversion = 96%

Fig. 4. Isomerization of silylated *N*-allylamide.



[Ru]-H = 0.2% mol $[RuClH(CO)(PCy_3)_2]$, isolated yield = 50%

Fig. 5. Synthesis of silylated *N*-allylamide.

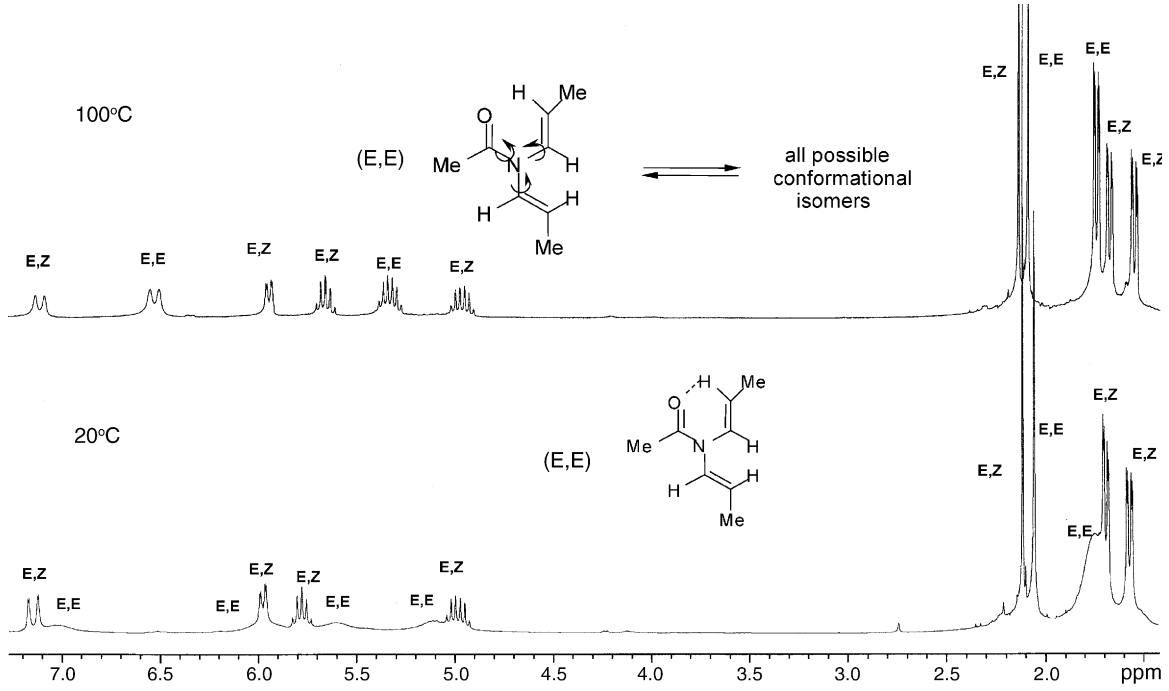


Fig. 6. ^1H NMR spectrum of (*E*,*E*)- and (*E*,*Z*)-*N*,*N*-di(1-propenyl)ethanamides at 20 and 100 °C (in nitrobenzene-d_5).

The silylative coupling reaction was also highly (*E*)-selective.

During the NMR analysis of *N*,*N*-di(1-propenyl) ethonamide in the ^{1}H NMR spectrum recorded at room temperature broad separate lines of methyl and methine protons of the *E*,*E*-isomer were observed likewise they are in non-equivalent environments (Fig. 1a). The *E*,*Z*-isomer retained the expected characteristic spin–spin coupling multiplets of those protons in these conditions. As the temperature of measurements is raised, the separate signals coalesce to single peaks which become narrow at 100 °C (Fig. 1b). Probably this phenomenon is caused by inhibited rotation of molecule at room temperature and possible intramolecular hydrogen bond (C=O · · · H–C) formation as a consequence of the more planar form of the *E*,*E*-isomer in comparison with the *E*,*Z*-isomer, see Fig. 6.

An analogous effect was observed in the case of (*E*,*E*)-*N*,*N*-di(1-propenyl)-1,1,1-trifluorethanamide and (*E*,*E*)-*N*,*N*-di(1-propenyl)benzamide. But this phenomenon did not occur in the case of (*E*,*E*)-2,2-dimethyl-*N*,*N*-di(1-propenyl)propanamide. It is likely that the presence of the bulky Me_3CCO group at the nitrogen atom precludes planarization of the molecule, thus hindering the formation of an intramolecular hydrogen bond.

3. Conclusions

Isomerization of *N*-allylamides catalyzed by [RuClH(CO)$(PPh_3)_3$] leads to (*E*)- and (*Z*)-enamides with a yield of practically 100%. The application of a novel catalytic system consisting of a precursor—{[$RuCl_2$(1,5-COD)]$_x$}, tri(2,4-di-*t*-butylphenyl)phosphite and CaH_2 for the isomerization of some *N*-allylamides allows to obtain (*Z*)-enamides with 100% selectivity. The double bond migration catalyzed by this new system complies with the hydride mechanism. The high (*Z*)-selectivity is a result of steric effects.

4. Experimental

4.1. Materials

Allyl chloride and allyl bromide were from Aldrich. Solvents were dried with appropriate drying agents (molecular sieves (3Å or 4Å), Na, CaH_2) and distilled prior to use. *N*-Allylurea (**3**) were purchased from Fluka, 1,3-diallylurea (**4**) and *N*,*N*-diallyl-2,2,2-trifluoroethanamide (**13**), (+)-*N*,*N*-diallyltartardiamide (**14**), *N*-allylcyclohexylamine were from Aldrich.

4.2. General procedures of synthesis of N-allylamides

Method A. *N*-Allylethanamide (**1**), *N*,*N*-diallylethanamide (**10**).

These *N*-allylethanamides were obtained by a typical acylation of allyl or diallylamine with acetic anhydride [16]. After the reaction the mixture was fractionally distilled under reduced pressure.

Method B. *N*-Allylbenzamide (**2**),*N*-allyl-2- thiophenecarboxamide (**5**), *N*-allyl-*N*-cyclohexylethanamide (**7**), *N*,*N*-diallylbenzamide (**11**) and 2,2-dimethyl-*N*,*N*-diallylpropionamide (**12**).

The procedure was run according to Carnahan and Hurd [31]. Appropriate allylamine was mixed with acidic chloride. Crude amides were distilled under reduced pressure or crystallized from ethanol.

Method C. *N*-Allyl-*N*-(2-thienyl)ethanamide (**6**) and *N*-allyl-*N*-benzylethanamide (**9**).

We used the procedure described in our earlier paper [21] for the allylation of *N*-allyl-*N*-arylethanamides. 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) were intensively stirred and refluxed in a water bath for 4 h. After cooling, 100 cm^3 of water were added and the excess of allyl chloride was removed by distillation from the water bath. The residue was extracted two times with 100 cm^3 of hexane (or pentane). The combined extract was dried with anhydrous magnesium sulphate and decolorized by active coal. After distilling the whole volatiles off (by means of a vacuum evaporator), the residue was distilled under reduced pressure (0.5–1 mmHg) or recrystallized.

N-Allyl-N-butylethanamide (**8**). *N*-Allylethanamide (30 mmol), powdered NaOH (150 mmol), $Bu_4N^+HSO_4^-$ (10 mmol) and 1-chlorobutane (150 mmol) were intensively stirred and refluxed in a water bath for 2 h. After cooling, 60 cm^3 of petrol ether and 60 cm^3 of water were added. The extract was washed with water and dried with anhydrous magnesium sulphate. The volatile matter was distilled off with a vacuum evaporator.

(E)-N-phenyl-N-(3-trimethylsilyl-2-propenyl)ethanamide. [RuHCl(CO)$(PCy)_2$] (30 mg; 0.041 mmol), vinyl trimethylsilane (0.41 g; 4.1 mmol), *N*-phenyl-*N*-allylethanamide (3.59 g; 20.5 mmol) and 0.5 cm^3 of toluene were heated for 24 h at 110 °C under argon in a 20 cm^3 sealed ampoule. The mixture was chromatographed in a column containing silica sand with hexane–methyl acetate (50:1) as eluent. The crude amine was distilled under reduced pressure yielding 0.51 g (50% yield) of the title compound.

N-Allyl-2-thiophenecarboxamide. MS (70 eV), *m*/*e* (int [%]): 167 (10) M^+; 152 (11); 139 (4); 134 (13); 12 (11); 111 (100); 97 (2); 83 (3); 56 (5); 45 (2). ^{1}H NMR ($CDCl_3$), δ: 7.54 (dd, 1H, J = 3.9, <1.0 Hz, –S–C*H*=CH–), 7.47 (dd, 1H, J = 4.8, <1.0 Hz, –S–C=C*H*–), 7.07 (dd, 1H, J = 4.8, 3.9 Hz; –S–CH=C*H*–), 6.26 (s, 1H, –N*H*–CH_2–CH=CH_2), 5.76 (ddt, 1H, J = 17.1, 10.5, 5.7 Hz, –NH–CH_2C*H*=CH_2), 5.25 (ddt, 1H, J = 17.1, <0.9, <0.9 Hz, –NH–CH_2CH=CH_2-*trans*), 5.18 (ddt, 1H, J = 10.5, <0.9, <0.9 Hz, –CH_2CH=CH_2-*cis*), 4.06 (ddd, 2H, J = 5.7, <0.9, <0.9 Hz, –CH_2CH=CH_2). ^{13}C NMR ($CDCl_3$), δ: 158.3 (–*C*ONH–); 134.0 (–S–*C*=CH–); 129.9 (–S–C=*C*H–);

129.9 (–CH_2–*C*H=CH_2); 128.1 (–S–*C*H=CH–); 127.6 (–S–CH=*C*H–); 116.8 (–CH_2–CH=*C*H_2) and 42.4 (–*C*H_2–CH=CH_2).

N-Allyl-N-(2-thienyl)ethanamide. MS (70 eV), *m/e* (int [%]): 181 (27) M^+; 178 (10); 139 (64); 129 (11); 119 (13); 115 (15); 110 (15); 105 (24); 98 (89); 91 (50); 81 (24); 69 (29); 63 (100); 55 (71); 51 (23). ^{1}H NMR (C_6D_6): *δ*: 6.64 (dd, 1H, *J* = 4.8, 1.0 Hz, –S–C*H*=CH–), 6.46 (dd, 1H, *J* = 4.8, 3.9 Hz, –S–CH=C*H*–), 6.30 (dd, 1H, *J* = 3.9, 1.0 Hz, –S–C=C*H*–), 5.76 (ddt, 1H, *J* = 17.1, 10.5, 6.0 Hz, –CH_2C*H*=CH_2), 4.92 (ddt, 1H, *J* = 9.6, 1.2, <0.9 Hz, –CH_2CH=CH_2-*cis*), 4.91 (ddt, 1H, *J* = 21.0, 1.2, <0.9 Hz, –CH_2CH=CH_2-*trans*), 4.13 (ddd, 2H, *J* = 6.0, <0.9, <0.9 Hz, –CH_2CH=CH_2), 1.76 (s, 3H, –COCH_3). ^{13}C NMR (C_6D_6): *δ*: 169.9 (–*C*OCH_3–), 145.3 (–S–*C*=CH–), 132.5 (–CH_2–*C*H=CH_2), 125.4 (–S–C=*C*H–CH=), 124.9 (–S–*C*H=CH–), 124.4 (–S–CH=*C*H–), 117.9 (–CH_2CH=*C*H_2), 52.4 (–*C*H_2CH=CH_2) and 21.9 (–CO*C*H_3).

N-Allyl-N-butylethanamide. MS (70 eV), *m/e* (int [%]): 155 (16) M^+; 140 (51); 126 (31); 112 (58); 98 (16); 84 (34); 70 (100); 56 (35); 43 (60). ^{1}H NMR ($CDCl_3$), *δ*: 5.76 (ddt, 1H, *J* = 17.7, 9.3, 6.0 Hz, –CH_2C*H*=CH_2), 5.19 (ddt, 1H, *J* = 17.7, 1.2, <0.9 Hz, –CH_2CH=CH_2-*trans*), 5.17 (ddt, 1H, *J* = 9.3, 1.2, <0.9 Hz, –CH_2CH=CH_2-*cis*), 3.98 (ddd, 2H, *J* = 6.0, <0.9, <0.9 Hz, –CH_2CH=CH_2-rotamer 2), 3.89 (ddd, 2H, *J* = 6.0, <0.9, <0.9 Hz, –CH_2CH=CH_2-rotamer 1), 3.32 (t, 2H, *J* = 7.5 Hz, –*CH*$_2$–CH_2–CH_2–CH_3-rotamer 1), 3.23 (t, 2H, *J* = 7.5 Hz, –CH_2–CH_2–CH_2–CH_3-rotamer 2), 2.12 (s, 3H, –COCH_3-rotamer 2), 2.06 (s, 3H, –COCH_3-rotamer 1), 1.51 (tt, 2H, *J* = 8.7, 7.5 Hz, –CH_2–CH_2–CH_2–CH_3), 1.32 (tq, 2H, *J* = 8.7, 8.7 Hz, –CH_2–CH_2–CH_2–CH_3), 0.92 (t, 3H, *J* = 8.7 Hz, –CH_2–CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$), *δ*: 178.2 (–$COCH_3$-rotamer 1), 168.3 (–$COCH_3$-rotamer 1), 133.4 (–CH_2CH=CH_2-rotamer 2), 132.8 (–CH_2CH=CH_2-rotamer 1), 116.3 (–CH_2CH=CH_2-rotamer 2), 115.9 (–CH_2CH=CH_2-rotamer 1), 50.6 (–CH_2–CH=CH_2-rotamer 1), 47.6 (–CH_2–CH=CH_2-rotamer 2), 47.4 (–CH_2–CH_2–CH_2–CH_3-rotamer 1), 45.3 (–CH_2–CH_2–CH_2–CH_3-rotamer 2), 30.4 (–CH_2–CH_2–CH_2–CH_3-rotamer 2), 29.5 (–CH_2–CH_2–CH_2–CH_3-rotamer 1), 21.1 (–CH_2–CH_2–CH_2–CH_3-rotamer 1), 20.9 (–CH_2–CH_2–CH_2–CH_3-rotamer 2), 19.8 (–$COCH_3$-rotamer 1), 19.6 (–$COCH_3$-rotamer 2), 13.5 (–CH_2–CH_2–CH_2–CH_3-rotamer 1) and 13.4 (–CH_2–CH_2–CH_2–CH_3-rotamer 2).

N-Allyl-N-benzylethanamide. bp = 120 °C/2 mmHg. MS (70 eV), *m/e* (int [%]): 189 (29) M^+; 173 (11); 148 (75); 129 (20); 116 (9); 105 (100); 90 (95); 79 (30); 65 (43); 55 (67). ^{1}H NMR ($CDCl_3$), *δ*: 7.37–7.15 (m, 5H, H_{arom}), 5.76 (ddt, 1H, *J* = 17.7, 10.2, 6.0 Hz, –CH_2C*H*=CH_2), 5.20 (ddt, 1H, *J* = 10.2, 1.2, <0.9 Hz, –CH_2CH=CH_2-*cis*), 5.08 (ddt, 1H, *J* = 17.7, 1.2, <0.9 Hz, –CH_2CH=CH_2-*trans*), 4.58 (s, 2H, –CH_2-rotamer 1), 4.49 (s, 2H, –CH_2-rotamer 2), 3.98 (ddd, 2H, *J* = 6.0, <0.9, <0.9 Hz, –CH_2CH=CH_2-rotamer 2), 3.80 (ddd, 2H, *J* = 6.0, <0.9, <0.9 Hz, –CH_2CH=CH_2-rotamer 1), 2.14 (s, 3H, –COCH_3-rotamer 2), 2.13 (s, 3H, –COCH_3-rotamer 2). ^{13}C NMR ($CDCl_3$), *δ*: 170.8 (–$COCH_3$-rotamer 1), 170.6 (–$COCH_3$-rotamer 1), 137.6 (–CH_2CH=CH_2-rotamer 1), 136.7 (–CH_2CH=CH_2-rotamer 2), 132.9 ($C_{1\text{-arom}}$, rotamer 2), 132.4 ($C_{1\text{-arom}}$, rotamer 1), 128.9 ($C_{4\text{-arom}}$ rotamer 2), 128.5 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$, rotamer 2), 128.1 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$, rotamer 1), 127.5 ($C_{4\text{-arom}}$, rotamer 1), 127.3 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$ rotamer 2), 126.3 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$ rotamer 1), 117.4 (–CH_2CH=CH_2-rotamer 2), 116.7 (–CH_2CH=CH_2-rotamer 1), 50.9 (–CH_2CH=CH_2-rotamer 2), 49.8 (–CH_2CH=CH_2-rotamer 1), 48.0 (–CH_2-rotamer 1), 47.7 (–CH_2-rotamer 2), 21.6 (–$COCH_3$-rotamer 2) and 21.4 (–$COCH_3$-rotamer 1).

(E)-N-Phenyl-N-(3-trimethylsilyl-2-propenyl)ethanamide: bp = 140–145 °C/1 mmHg. MS (70 eV), *m/e* (int [%]): 247 (81) M^+; 232 (100); 218 (5); 204 (14); 190 (32); 174 (29); 156 (38); 132 (97); 118 (84); 106 (45); 93 (16); 73 (94); 59 (15). ^{1}H NMR (C_6D_6), *δ*: 7.54 (ddd, 2H, $J_{2-3} = J_{5-6} = 6.9$, $J_{3-4} = J_{4-5} = 7.5$, $J_{3-5} = >1.0$ Hz, $H_{3\text{-arom}}$ and $H_{5\text{-arom}}$), 7.31 (dd, 1H, $J_{3-4} = J_{4-5} = 7.5$, $J_{2-4} = J_{4-6} = >1.0$ Hz, $H_{4\text{-arom}}$), 7.31 (dd, 2H, $J_{2-3} = J_{5-6} = 7.5$, $J_{2-4} = J_{4-6} = 1.0$ Hz, $H_{2\text{-arom}}$ and $H_{6\text{-arom}}$), 6.21 (dt, 1H, *J* = 18.6, 5.4 Hz, –CH_2C*H*=CH–), 5.84 (dt, 1H, *J* = 18.6, >1.0 Hz, –CH_2CH=C*H*–), 4.50 (dd, 2H, *J* = 5.4, >1.0 Hz, –CH_2CH=CH–), 2.04 (s, 3H, –COCH_3), 0.20 (s, 9H, –$Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$), *δ*: 169.5 (–*C*OCH_3), 146.2 ($C_{1\text{-arom}}$), 140.2 (–CH_2*C*H=CH–), 133.1 (–CH_2CH=*C*H–), 129.1 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$), 127.8 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$), 127.5 ($C_{4\text{-arom}}$), 53.8 (–*C*H_2CH=CH–), 21.3 (–CO*C*H_3) and −1.7 (–$Si(CH_3)_3$).

4.3. Ruthenium and rhodium complexes

[RuClH(CO)(PPh_3)$_3$] [32], {[$RuCl_2$(COD)]$_x$} [33], [RhH(CO)(PPh_3)$_3$] [34] were obtained according to the methods known in literature. Tris(2,4-di-*t*-butylphenyl) phosphite was from Aldrich.

4.4. (E)- and (Z)-enamides (general procedure)

N-Allyl amides were heated with [RuClH(CO)(PPh_3)$_3$] (with or without a solvent) under argon atmosphere in high-pressure glass ampoules, which were put in a thermostat (±0.1 °C). The proportions of the substrate, the catalyst and the solvent have been presented in Table 1. After the reaction had been completed, the crude amide was chromatographed in a column containing silica gel (200–400 mesh) and hexane as eluent, distilled under reduced pressure or recrystallized from methanol (see Table 1). Pure enamides were obtained with yields of 55–95%.

4.5. (Z)-Enamides (general procedure)

N-Allyl amide (0.01 mol), {[$RuCl_2$(1,5-COD)]$_x$} (1 mol%), tris(2,4-di-*t*-butylphenyl)phosphite (1 mol%) and CaH_2 (10 mol%) in 5 cm^3 THF were heated at 80 °C for 2 h

(*N*-allylbenzamide: 90 °C for 4 h, *N*-allylurea: 100 °C for 1 h) under argon atmosphere. After cooling down to room temperature, 10 cm^3 of benzene–hexane mixture (1:3) were added. The precipitated ruthenium compounds and phosphine were filtered off. The filtrate was chromatographed in a column containing 0.6 g of siliceous mesoporous cellular foams. After evaporating the solvent in a vacuum evaporator, the residue was distilled under reduced pressure. (*N*-(1-Propenyl)urea was recrystallized from methanol:

1. *(E)-N-(1-Propenyl)ethanamide*. MS (70 eV), *m/e* (int [%]): 99 (33) M^+; 84 (3); 56 (100); 52 (3). ^{1}H NMR ($CDCl_3$), *δ*: 8.21 (d, *J* = 6.9 Hz, –N*H*–CH=CHCH$_3$), 6.73 (ddq, 1H, *J* = 14.1, 6.9, 1.5 Hz, –NH–C*H*=CHCH$_3$), 5.21 (dq, 1H, *J* = 14.1, 6.6 Hz, –NH–CH=C*H*CH$_3$), 2.02 (s, 3H, –C*H*$_3$), 1.62 (dd, 3H, *J* = 6.6, 1.5 Hz, –NH–CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$), *δ*: 167.9 (–*C*OCH$_3$), 123.5 (–*C*H=CHCH$_3$), 108.0 (–CH=*C*HCH$_3$), 22.9 (–CO*C*H$_3$) and 14.9 (–CH=CH*C*H$_3$).
   (Z)-N-(1-Propenyl)ethanamide. MS (70 eV), *m/e* (int [%]): 99 (13) M^+; 84 (3); 56 (100); 52 (2). ^{1}H NMR ($CDCl_3$), *δ*: 8.37 (d, *J* = 6.9 Hz, –N*H*–CH=CHCH$_3$), 6.66 (ddq, 1H, *J* = 7.2, 6.9, 1.5 Hz, –NH–C*H*=CHCH$_3$), 4.79 (dq, 1H, *J* = 7.2, 6.6 Hz, –NH–CH=C*H*CH$_3$), 2.10 (s, 3H, –C*H*$_3$) and 1.62 (dd, 3H, *J* = 6.6, 1.5 Hz, –NH–CH=CH*C*H$_3$). ^{13}C NMR ($CDCl_3$), *δ*: 168.5 (–*C*OCH$_3$), 122.0 (–*C*H=CHCH$_3$), 106.0 (–CH=*C*HCH$_3$), 23.0 (–CO*C*H$_3$) and 11.1 (–CH=CH*C*H$_3$).
2. *(E)-N-(1-Propenyl)benzamide*. MS (70 eV), *m/e* (int [%]): 161 (41) M^+; 146 (11); 144 (10); 105 (100); 77 (10); 56 (2); 51 (5). ^{1}H NMR ($CDCl_3$), *δ*: 7.80 (d, 1H, *J* = 7.5 Hz, –N*H*–CH=CHCH$_3$), 7.53–7.23 (m, 5H, H_{arom}), 6.90 (ddq, 1H, *J* = 14.1, 7.5, 1.5 Hz, –NH–C*H*=CHCH$_3$), 5.41 (dq, 1H, *J* = 14.1, 6.9 Hz, –NH–CH=C*H*CH$_3$), 1.67 (dd, 3H, *J* = 6.9, 1.5 Hz, –NH–CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$), *δ*: 164.5 (–*C*O–), 131.4 ($C_{4\text{-arom}}$), 133.7 ($C_{1\text{-arom}}$), 128.2 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$), 127.1 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$), 123.6 (–*C*H=CHCH$_3$), 109.1 (–CH=*C*HCH$_3$) and 14.9 (–CH=CH*C*H$_3$).
   (Z)-N-(1-Propenyl)benzamide. MS (70 eV), *m/e* (int [%]): 161 (30) M^+; 146 (13); 105 (100); 77 (12); 56 (3); 51 (6). ^{1}H NMR ($CDCl_3$), *δ*: 8.14 (d, 1H, *J* = 7.2 Hz, –NH–CH=C*H*CH$_3$), 7.53–7.23 (m, 5H, H_{arom}), 6.90 (ddq, 1H, *J* = 7.5, 7.2, 1.5 Hz, –NH–C*H*=CHCH$_3$), 4.92 (dq, 1H, *J* = 7.5, 6.9 Hz, –NH–CH=C*H*CH$_3$) and 1.70 (dd, 3H, *J* = 6.9, 1.5 Hz, –NH–CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$), *δ* = 164.7 (–*C*O–), 131.7 ($C_{4\text{-arom}}$), 134.5 ($C_{1\text{-arom}}$), 128.5 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$), 126.9 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$), 122.0 (–*C*H=CHCH$_3$), 106.8 (–CH=*C*HCH$_3$) and 10.9 (–CH=CH*C*H$_3$).
3. *(E)-(1-Propenyl)urea*. MS (70 eV), *m/e* (int [%]): 100 (40) M^+;82 (1); 60 (2); 56(100); 54 (8). ^{1}H NMR (CD_3OD), *δ*: 6.48 (ddq, 1H, *J* = 13.5, 1.5 Hz, –C*H*=CHCH$_3$), 4.94 (dq, 1H, *J* = 13.5, 6.6 Hz, –CH=C*H*CH$_3$), 1.62 (dd, 3H, *J* = 6.6, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (CD_3OD), *δ* = 158.8 (–*C*ONH$_2$), 125.7 (–*C*H=CHCH$_3$), 104.4 (–CH=*C*HCH$_3$) and 15.0 (–CH=CH*C*H$_3$).
   (Z)-(1-Propenyl)urea. MS (70 eV), *m/e* (int [%]): 100 (40) M^+; 82 (1); 60 (2); 56 (100); 54 (8). ^{1}H NMR (CD_3OD), *δ*: 6.44 (ddq, 1H, *J* = 8.7, 1.5 Hz, –C*H*=CHCH$_3$), 4.54 (dq, 1H, *J* = 8.7, 6.9 Hz, –CH=C*H*CH$_3$), 1.53 (dd, 3H, *J* = 6.9, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (CD_3OD), *δ*: 158.8 (–*C*ONH$_2$), 124.1 (–*C*H=CHCH$_3$), 102.2 (–CH=*C*HCH$_3$) and 10.7 (–CH=CH*C*H$_3$).
4. *(E,Z)-1,3-Di(1-propenyl)urea*. MS (70 eV), *m/e* (int [%]): 140 (27) M^+; 117 (1); 111 (64); 105 (2); 91 (6); 84 (8); 63 (11); 56 (100); 51 (3). ^{1}H NMR (CD_3OD), *δ*: 6.48 (dq, 1H, *J* = 13.8, 1.5 Hz, –C*H*=CHCH$_3$-*trans*), 6.47 (dq, 1H, *J* = 7.5, 1.5 Hz, –C*H*=CHCH$_3$-*cis*), 4.98 (dq, 1H, *J* = 13.8, 6.9 Hz, –CH=C*H*CH$_3$-*trans*), 4.60 (dq, 1H, *J* = 7.2, 6.9 Hz, –CH=C*H*CH$_3$-*cis*), 1.64 (dd, 3H, *J* = 6.9, 1.5 Hz, –CH=CHC*H*$_3$-*trans*), 1.58 (dd, 3H, *J* = 6.9, 1.5 Hz, –CH=CHC*H*$_3$-*cis*). ^{13}C NMR (CD_3COCD_3), *δ*: 152.1 (–*C*ONH$_2$), 125.8 (–*C*H=CHCH$_3$-*cis*), 124.4 (–*C*H=CHCH$_3$-*trans*), 103.0 (–CH=*C*HCH$_3$-*cis*), 100.7 (–CH=*C*HCH$_3$-*trans*), 15.2 (–CH=CH*C*H$_3$-*trans*) and 11.0 (–CH=CH*C*H$_3$-*cis*).
   (Z,Z)-1,3-Di(1-propenyl)urea. MS (70 eV), *m/e* (int [%]): 140 (27) M^+; 117 (1); 111 (64); 105 (2); 91 (6); 84 (8); 63 (11); 56 (100); 51 (3). ^{1}H NMR (CD_3OD), *δ*: 6.48 (dq, 1H, *J* = 7.3, 1.5 Hz, –C*H*=CHCH$_3$), 4.59 (dq, 1H, *J* = 7.3, 6.9 Hz, –CH=C*H*CH$_3$), 1.60 (dd, 3H, *J* = 6.9, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (CD_3COCD_3), *δ*: 152.1 (–*C*ONH$_2$), 125.9 (–*C*H=CHCH$_3$), 103.2 (–CH=*C*HCH$_3$) and 11.0 (–CH=CH*C*H$_3$).
5. *(E)-N-(1-Propenyl)-2-thiophenecarboxamide*. MS (70 eV), *m/e* (int [%]): 167 (22) M^+; 152 (11); 139 (4); 124 (11); 111 (100); 83 (3); 56 (5); 45 (2). ^{1}H NMR (DMSO), *δ*: 10.24 (dd, 1H, *J* = 9.9, >1.0 Hz; –N*H*–CH=CHCH$_3$), 7.97 (dd, 1H, *J* = 3.7, 1.0 Hz, –S–C*H*=CH–), 7.78 (dd, 1H, *J* = 4.9, 1.0 Hz, –S–C=C*H*–CH=), 7.19 (dd, 1H, *J* = 4.9, 3.7 Hz; –S–CH=C*H*–), 6.87 (ddq, 1H, *J* = 14.1, 9.9, 1.5 Hz; –NH–C*H*=CHCH$_3$), 5.44 (dqd, 1H, *J* = 14.1, 6.8, >1.0 Hz, –NH–CH=C*H*CH$_3$), 1.71 (dd, 3H, *J* = 6.8, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (DMSO), *δ*: 158.3 (–*C*ONH–), 139.36 (–S–*C*=CH–), 130.5 (–S–C=*C*H–), 128.7 (–S–*C*H=CH–), 127.9 (–S–CH=*C*H–), 124.1 (–*C*H=CHCH$_3$), 107.9 (–CH=*C*HCH$_3$) and 15.0 (–CH=CH*C*H$_3$).
   (Z)-N-(1-Propenyl)-2-thiophenecarboxamide: MS (70 eV), *m/e* (int [%]): 167 (29) M^+; 152 (7); 134 (10); 124 (6); 111 (100); 83 (4); 56 (2); 45 (2). ^{1}H NMR (DMSO), *δ*: 9.60 (dd, 1H, *J* = 9.6, >1.0 Hz; –N*H*–CH=CHCH$_3$), 8.09 (dd, 1H, *J* = 3.7, 1.0 Hz, –S–C*H*=CH), 7.82 (dd, 1H, *J* = 4.9, 1.0 Hz, –S–C=C*H*–), 7.20 (dd, 1H, *J* = 4.9, 3.7 Hz, –S–CH=C*H*–), 6.71 (ddq, 1H, *J* = 9.6, 7.5, 1.2 Hz;

–NH–C*H*=CHCH$_3$), 4.88 (dqd, 1H, *J* = 7.5, 6.8, >1.0 Hz, –NH–CH=C*H*CH$_3$), 1.76 (dd, 3H, *J* = 6.8, 1.2 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (DMSO), *δ*: 159.5 (–*C*ONH–), 139.0 (–S–*C*=CH–), 131.6 (–S–C=*C*H–), 129.5 (–S–*C*H=CH–), 128.3 (–S–CH=*C*H–), 122.4 (–*C*H=CHCH$_3$), 107.5 (–CH=*C*HCH$_3$) and 11.722 (–CH=CH*C*H$_3$).

6. *(E)-N-(1-Propenyl)-N-(2-thienyl)ethanamide*. MS (70 eV), *m*/*e* (int [%]): 181 (38) M^+; 152 (11); 139 (100); 129 (10); 124 (14); 115 (12); 111 (23); 105 (28); 98 (64); 91 (47); 77 (45); 69 (25); 63 (91); 57 (61); 51 (33). ^{1}H NMR (CDCl$_3$), *δ*: 6.95–6.45 (m, 3H, H$_{arom}$), 7.66 (dq, 1H, *J* = 14.1, 1.5 Hz, –C*H*=CHCH$_3$), 4.45 (dq, 1H, *J* = 14.1, 6.9 Hz, –CH=C*H*CH$_3$), 1.69 (s, 3H, –COC*H*$_3$) and 1.21 (dd, 3H, *J* = 6.9, 1.8 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (C$_6$H$_6$), *δ*: 168.0 (–*C*OCH$_3$–), 142.2 (–S–*C*=CH–), 133.9 (–S–C=*C*H–), 132.2 (–S–*C*H=CH–), 129.7 (–S–CH=*C*H–), 128.6 (–*C*H=CHCH$_3$), 107.3 (–CH=*C*HCH$_3$), 22.7 (–COCH$_3$) and 15.1 (–CH=CH*C*H$_3$).
(Z)-N-(1-Propenyl)-N-(2-thienyl)ethanamide. MS (70 eV), *m*/*e* (int [%]): 181 (38) M^+; 152 (11); 139 (100); 129 (10); 124 (14); 115 (12); 111 (23); 105 (28); 98 (64); 91 (47); 77 (45); 69 (25); 63 (91); 57 (61); 51 (33). ^{1}H NMR (CDCl$_3$), *δ*: 6.89 (dd, 1H, *J* = 5.4, 1.0 Hz, –S–C*H*=CH–), 6.40 (dd, 1H, *J* = 5.4, 3.6 Hz, –S–CH=C*H*–), 6.30 (dd, 1H, *J* = 3.6, 1.0 Hz, –S–C=C*H*–), 7.12 (dq, 1H, *J* = 6.9, 1.5 Hz; –C*H*=CHCH$_3$), 4.45(dq, 1H, *J* = 7.2, 6.9 Hz, –CH=C*H*CH$_3$), 1.78 (s, 3H, –COC*H*$_3$), 1.46 (dd, 3H, *J* = 7.2, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (C$_6$H$_6$), *δ*: 168.0 (–*C*OCH$_3$–), 142.2 (–S–*C*=CH–), 134.2 (–S–C=*C*H–), 132.4 (–S–*C*H=CH–), 129.7 (–S–CH=*C*H–), 128.8 (–*C*H=CHCH$_3$), 108.5 (–CH=*C*HCH$_3$), 22.6 (–COCH$_3$) and 14.9 (–CH=CH*C*H$_3$).

7. *(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$_3$), *δ*: 5.98 (dd, 1H, *J* = 13.6, 1.8 Hz, –C*H*=CHCH$_3$); 5.52 (dq, 1H, *J* = 13.6, 6.8 Hz, CH=C*H*CH$_3$), 4.23 (dddd, 1H, J_{aa} = 11.8, J'_{aa} = 10.8, *J*ae = 3.5, J'_{ae} = 3.5 Hz, C*H*-cyclohexyl), 1.96 (s, 3H, –COC*H*$_3$), 1.76 (dd, 3H, *J* = 6.8, 1.8 Hz, –CH=CHC*H*$_3$), 1.78–0.95 (m, 10 H, H-cyclohexyl). ^{13}C NMR (CDCl$_3$), *δ*: 169.3 (–*C*OCH$_3$), 128.0 (–*C*H=CHCH$_3$), 126.3 (–CH=*C*HCH$_3$), 53.1 (C$_1$-cyclohexyl), 30.3 (C$_2$-cyclohexyl and C$_6$-cyclohexyl), 25.5 (C$_3$-cyclohexyl and C$_5$-cyclohexyl), 25.4 (C$_4$-cyclohexyl), 23.0 (–CO*C*H$_3$), 14.8 (–CH=CH*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$_3$), *δ*: 5.98 (dd, 1H, *J* = 7.0, 1.8 Hz, –C*H*=CHCH$_3$), 5.69 (dq, 1H, *J* = 7.0, 7.0 Hz, –CH=C*H*CH$_3$), 4.44 (dddd, 1H, J_{aa} = 11.8, J'_{aa} = 10.7, *J*ae = 3.7, J'_{ae} = 3.7 Hz, C*H*-cyclohexyl), 2.02 (s, 3H, –COC*H*$_3$), 1.60 (dd, 3H, *J* = 6.8, 1.8 Hz, –CH=CHC*H*$_3$), 1.78–0.95 (m, 10 H, H-cyclohexyl). ^{13}C NMR (CDCl$_3$), *δ*: 169.1 (–*C*OCH$_3$), 128.2 (–*C*H=CHCH$_3$), 126.8 (–CH=*C*HCH$_3$), 53.2 (C$_1$-cycloheksyl), 30.0 (C$_2$-cyclohexyl and C$_6$-cyclohexyl), 25.3 (C$_3$-cyclohexyl and C$_5$-cyclohexyl), 25.3 (C$_4$-cyclohexyl), 22.0 (–CO*C*H$_3$) and 12.2 (–CH=CH*C*H$_3$).

8. *(E)-N-Butyl-N-(1-propenyl)ethanamide*. MS (70 eV), *m*/*e* (int [%]): 155 (70) M^+; 140 (74); 126 (16); 113 (71); 98 (13); 84 (79); 70 (100); 57 (25). ^{1}H NMR (CDCl$_3$), *δ*: 6.45 (dq, 1H, *J* = 13.5, 1.2 Hz, –C*H*=CHCH$_3$), 5.05 (dq, 1H, *J* = 13.5, 6.9 Hz, –CH=C*H*CH$_3$), 3.57 (t, 2H, *J* = 7.5 Hz, –C*H*$_2$–CH$_2$–CH$_2$–CH$_3$), 2.16 (s, 3H, –COC*H*$_3$), 1.73 (dd, 3H, *J* = 6.9, 1.2 Hz, –CH=CHC*H*$_3$), 1.50 (tt, 2H, *J* = 7.5, 6.9 Hz, –CH$_2$–C*H*$_2$–CH$_2$–CH$_3$), 1.33 (tq, 2H, *J* = 7.5, 6.9 Hz, –CH$_2$–CH$_2$–C*H*$_2$–CH$_3$), 0.92 (t, 3H, *J* = 7.5 Hz, –CH$_2$–CH$_2$–CH$_2$–C*H*$_3$). ^{13}C NMR (CDCl$_3$), *δ*: 168.3 (–*C*OCH$_3$), 128.3 (–*C*H=CHCH$_3$), 107.2 (–CH=*C*HCH$_3$), 42.4 (–*C*H$_2$–CH$_2$–CH$_2$–CH$_3$), 28.7 (–CH$_2$–*C*H$_2$–CH$_2$–CH$_3$), 21.7 (–CH$_2$–CH$_2$–*C*H$_2$–CH$_3$), 19.9 (–CO*C*H$_3$), 15.2 (–CH=CH*C*H$_3$) and 13.5 (–CH$_2$–CH$_2$–CH$_2$–*C*H$_3$).
(Z)-N-Butyl-N-(1-propenyl)ethanamide. MS (70 eV), *m*/*e* (int [%]): 155 (11) M^+; 140 (70); 126 (10); 112 (6); 84 (44); 70 (100); 57 (11). ^{1}H NMR (CDCl$_3$), *δ*: 6.03 (dq, 1H, *J* = 7.8, 1.5 Hz, –C*H*=CHCH$_3$), 5.53 (dq, 1H, *J* = 7.8, 7.8 Hz, –CH=C*H*CH$_3$), 3.34 (t, 2H, *J* = 7.5 Hz, –C*H*$_2$–CH$_2$–CH$_2$–CH$_3$), 2.00 (s, 3H, –COC*H*$_3$), 1.62 (dd, 3H, *J* = 7.8, 1.5 Hz, –CH=CHC*H*$_3$), 1.50 (tt, 2H, *J* = 7.5, 6.9 Hz, –CH$_2$–C*H*$_2$–CH$_2$–CH$_3$), 1.33 (tq, 2H, *J* = 7.5, 6.9 Hz, –CH$_2$–CH$_2$–C*H*$_2$–CH$_3$), 0.95 (t, 3H, *J* = 7.5 Hz, –CH$_2$–CH$_2$–CH$_2$–C*H*$_3$). ^{13}C NMR (CDCl$_3$), *δ*: 168.3 (–*C*OCH$_3$), 125.9 (–*C*H=CHCH$_3$), 105.4 (–CH=*C*HCH$_3$), 45.4 (–*C*H$_2$–CH$_2$–CH$_2$–CH$_3$), 29.4 (–CH$_2$–*C*H$_2$–CH$_2$–CH$_3$), 21.9 (–CH$_2$–CH$_2$–*C*H$_2$–CH$_3$), 19.8 (–CO*C*H$_3$), 13.5 (–CH=CH*C*H$_3$) and 13.4 (–CH$_2$–CH$_2$–CH$_2$–*C*H$_3$).

9. *(E)-N-Benzyl-N-(1-propenyl)ethanamide*. MS (70 eV), *m*/*e* (int [%]): 189 (36) M^+; 173 (21); 146 (40); 132 (31); 98 (18); 91 (100); 89 (12); 65 (30); 62 (9). ^{1}H NMR (CDCl$_3$), *δ*: 7.39–7.13 (m, 5H, H$_{arom}$), 6.54 (dq, 1H, *J* = 13.8, 1.5 Hz, –C*H*=CHCH$_3$), 5.00 (dq, 1H, *J* = 13.8, 7.2 Hz, –CH=C*H*CH$_3$), 4.85 (s, 2H, –C*H*$_2$–), 2.29 (s, 3H, –COC*H*$_3$), 1.63 (dd, 3H, *J* = 7.2, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (CDCl$_3$), *δ*: 168.5 (–*C*OCH$_3$), 137.3 (C$_{1\text{-arom}}$), 128.9 (C$_{4\text{-arom}}$), 128.4 (C$_{3\text{-arom}}$ and C$_{5\text{-arom}}$), 126.8 (C$_{2\text{-arom}}$ and C$_{6\text{-arom}}$), 125.5 (–*C*H=CHCH$_3$), 108.9 (–CH=*C*HCH$_3$), 46.7 (–*C*H$_2$–), 22.2 (–COCH$_3$) and 15.5 (–CH=CH*C*H$_3$).
(Z)-N-Benzyl-N-(1-propenyl)ethanamide. MS (70 eV), *m*/*e* (int [%]): 189 (18) M^+; 173 (21); 146 (40); 132 (29); 98 (18); 91 (100); 70 (6); 65 (30); 56 (7). ^{1}H NMR (CDCl$_3$), *δ*: 7.39–7.13 (m, 5H, H$_{arom}$), 4.98 (dq, 1H, *J* = 7.8, 1.8 Hz, –C*H*=CHCH$_3$), 5.49 (dq,

1H, J = 7.8, 6.9 Hz, –CH=C*H*CH$_3$), 4.74 (s, 2H, –C*H*$_2$–), 2.13 (s, 3H, –COC*H*$_3$) and 1.65 (dd, 3H, J = 7.2, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$), δ: 168.5 (–*C*OCH$_3$), 136.5 ($C_{1\text{-arom}}$), 128.7 ($C_{4\text{-arom}}$), 128 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$), 127.3 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$), 126.3 (–*C*H=CHCH$_3$), 107.1 (–CH=*C*HCH$_3$), 49.7 (–*C*H$_2$–), 25.6 (–COCH$_3$) and 12.2 (–CH=CH*C*H$_3$).

10. *(E,E)-N,N-di(1-Propenyl)ethanamide*. MS (70 eV), *m*/*e* (int [%]): 139 (88) M^+; 124 (7); 110 (5); 97 (83); 94 (13); 82 (100); 68 (76); 55 (9). ^{1}H NMR ($C_6D_5NO_2$, 80 °C), δ: 7.03 (dq, 2H, J = 14.3, 1.8 Hz, –C*H*=CHCH$_3$), 5.81 (dq, 2H, J = 13.8, 7.2 Hz, –CH=C*H*CH$_3$), 2.59 (s, 3H, –C*H*$_3$), 2.19 (dd, 6H, J = 7.7, 1.8 Hz, –CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$), δ: 167.5 (–*C*O–), 126.5 (–*C*H=CHCH$_3$), 109.4 (–CH=*C*HCH$_3$), 22.4 (–*C*H$_3$) and 14.5 (–CH=CH*C*H$_3$).
(E,Z)-N,N-Di(1-propenyl)ethanamide. MS (70 eV), *m*/*e* (int [%]): 139 (100) M^+; 124 (9); 97 (95); 82 (91); 68 (52); 54 (7). ^{1}H NMR ($C_6D_5NO_2$, 80 °C), δ: 7.63 (dq, 1H, J = 14.1, 1.5 Hz, –C*H*=CHCH$_3$-*trans*), 6.43 (dq, 1H, J = 7.2, 2.1 Hz, –C*H*=CHCH$_3$-*cis*), 6.16 (dq, 1H, J = 7.2, 7.2 Hz, –CH=C*H*CH$_3$-*cis*), 5.43 (dq, 1H, J = 14.1, 6.6 Hz, –CH=C*H*CH$_3$-*trans*), 2.55 (s, 3H, –C*H*$_3$), 2.16 (dd, 3H, J = 6.6, 1.5 Hz, –CH=CHC*H*$_3$-*trans*), 2.01 (dd, 3H, J = 7.2, 2.1 Hz, –CH=CHC*H*$_3$-*cis*). ^{13}C NMR ($CDCl_3$), δ: 167.7 (–*C*O–), 127.8 (–*C*H=CHCH$_3$-*trans*), 125.8 (–*C*H=CHCH$_3$-*cis*), 125.2 (–CH=*C*HCH$_3$-*cis*), 107.4 (–CH=*C*HCH$_3$-*trans*), 21.5 (–*C*H$_3$), 14.5 (–CH=CH*C*H$_3$-*trans*) and 11.3 (–CH=CH*C*H$_3$-*cis*).

11. *(E,E)-N,N-Di(1-propenyl)benzamide*. MS (70 eV), *m*/*e* (int [%]): 201 (24) M^+; 186 (2); 172 (2); 144 (2); 105 (100); 96 (2); 77 (37); 68 (3); 51 (10). ^{1}H NMR ($C_6D_5NO_2$, 100 °C), δ: 7.60–7.36 (m, 5H, H_{arom}), 6.58 (dq, 2H, J = 14.1, 1.5 Hz, –C*H*=CHCH$_3$), 5.28 (dq, 2H, J = 14.1, 6.9 Hz, –CH=C*H*CH$_3$), 1.61 (dd, 6H, J = 6.9, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$), δ: 168.7 (–*C*O–), 136.0 ($C_{1\text{-arom}}$), 130.2 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$), 130.0 ($C_{4\text{-arom}}$), 128.8 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$), 127.9 (–*C*H=CHCH$_3$), 109.8 (–CH=*C*HCH$_3$) and 15.1 (–CH=CH*C*H$_3$).
(E,Z)-N,N-Di(1-propenyl)benzamide. MS (70 eV), *m*/*e* (int [%]): 201 (22) M^+; 186 (2); 172 (2); 144 (2); 105 (100); 77 (34); 68 (3); 51 (9). ^{1}H NMR ($C_6D_5NO_2$, 100 °C), δ: 7.60–7.36 (m, 5H), 7.10 (dq, 2H, J = 14.1, 1.5 Hz, –C*H*=CHCH$_3$-*trans*), 6.04 (dq, 2H, J = 6.9, 1.5 Hz, –C*H*=CHCH$_3$-*cis*), 5.39 (dq, 2H, J = 6.9, 6.9 Hz, –CH=C*H*CH$_3$-*cis*), 5.14 (dq, 2H, J = 14.1, 6.9 Hz, –CH=C*H*CH$_3$-*trans*), 1.68 (dd, 6H, J = 6.9, 1.5 Hz, –CH=CHC*H*$_3$-*trans*), 1.35 (dd, 6H, J = 6.9, 1.5 Hz, –CH=CHC*H*$_3$-*cis*). ^{13}C NMR ($CDCl_3$), δ: 168.7 (–*C*O–), 135.8 ($C_{1\text{-arom}}$), 128.3 ($C_{4\text{-arom}}$), 130.2 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$), 127.9 (–*C*H=CHCH$_3$-*trans*), 128.8 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$), 126.8 (–*C*H=CHCH$_3$-*cis*), 118.6 (–CH=*C*HCH$_3$-*cis*), 109.8 (–CH=*C*HCH$_3$-*trans*), 15.1 (–CH=CH*C*H$_3$-*trans*) and 12.3 (–CH=CH*C*H$_3$-*trans*).

12. *(E,E)-2,2-Dimethyl-N,N-di(1-propenyl)propanamide*. MS (70 eV), *m*/*e* (int [%]): 181 (30) M^+; 166 (3); 124 (2); 96 (11); 85 (14); 82 (49); 68 (33); 57 (100). ^{1}H NMR ($CDCl_3$), δ: 6.51 (dq, 2H, J = 14.1, 1.4 Hz, –C*H*=CHCH$_3$), 5.31 (dq, 2H, J = 14.1, 6.9 Hz, –CH=C*H*CH$_3$), 1.74 (dd, 6H, J = 6.9, 1.4 Hz, –CH=CHC*H*$_3$), 1.26 (s, 9H, –C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$), δ: 176.0 (–*C*O–), 128.6 (–*C*H=CHCH$_3$), 107.2 (–CH=*C*HCH$_3$), 40.3 (–*C*(CH$_3$)$_3$), 28.7 (–C(*C*H$_3$)$_3$) and 15.0 (–CH=CH*C*H$_3$).
(E,Z)-2,2-Dimethyl-N,N-di(1-propenyl)propanamide. MS (70 eV), *m*/*e* (int [%]): 181 (340) M^+; 166 (5); 124 (7); 96 (8); 85 (25); 82 (60); 68 (31); 57 (100). ^{1}H NMR ($CDCl_3$), δ: 7.12 (dq, 1H, J = 14.2, 1.5 Hz, –C*H*=CHCH$_3$-*trans*), 6.12 (dq, 1H, J = 7.1, 1.5 Hz, –C*H*=CHCH$_3$-cis), 5.71 (dq, 1H, J = 7.1, 6.8 Hz, –CH=C*H*CH$_3$-*cis*), 4.98 (dq, 1H, J = 14.2, 7.6 Hz, –CH=C*H*CH$_3$-*trans*), 1.68 (dd, 3H, J = 6.8, 1.5 Hz, –CH=CHC*H*$_3$-*cis*), 1.52 (dd, 3H, J = 7.6, 1.5 Hz, –CH=CHC*H*$_3$-*trans*), 1.26 (s, 3H, –C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$), δ: 175.9 (–*C*O–), 128.6 (–*C*H=CHCH$_3$-*trans*), 128.2 (–*C*H=CHCH$_3$-*cis*), 127.5 (–CH=*C*HCH$_3$-*cis*), 127.3 (–CH=*C*HCH$_3$-*trans*), 40.3 (–*C*(CH$_3$)$_3$-*trans*), 40.1 (–*C*(CH$_3$)$_3$-*cis*), 28.7 (–C(*C*H$_3$)$_3$-*trans*), 27.7 (–C(*C*H$_3$)$_3$-*cis*), 15.2 (–CH=CH*C*H$_3$-*trans*) and 12.5 (–CH=CH*C*H$_3$-*cis*).

13. *(E,E)-N,N-Di(1-propenyl)-2,2,2-trifluoroethanamide*. MS (70 eV), *m*/*e* (int [%]): 193 (100) M^+; 178 (23); 136 (5); 124 (33); 108 (13); 96 (17); 81 (18); 68 (21); 56 (3). ^{1}H NMR ($C_6D_5NO_2$, 100 °C), δ: 6.43 (dq, 2H, J = 14.1, 1.4 Hz, –C*H*=CHCH$_3$), 5.62 (dq, 2H, J = 14.1, 6.9 Hz, –CH=C*H*CH$_3$), 1.74 (dd, 6H, J = 6.9, 1.4 Hz, –CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$), δ: 128.4 (–*C*H=CHCH$_3$), 115.1 (–CH=*C*HCH$_3$), 22.4 (–CF$_3$) and 15.1 (–CH=CH*C*H$_3$).
(E,Z)-N,N-Di(1-propenyl)-2,2,2-trifluoroethanamide. MS (70 eV), *m*/*e* (int [%]): 193 (100) M^+; 178 (27); 136 (6); 124 (38); 104 (12); 96 (18); 81 (18); 68 (23); 56 (4). ^{1}H NMR ($C_6D_5NO_2$, 100 °C), δ: 9.94 (dq, 1H, J = 14.2, 1.5 Hz, –C*H*=CHCH$_3$-*trans*), 6.00 (dq, 1H, J = 6.9, 1.5 Hz, –C*H*=CHCH$_3$-*cis*), 5.90 (dq, 1H, J = 6.9, 6.6 Hz, –CH=C*H*CH$_3$-*cis*), 5.36 (dq, 1H, J = 13.8, 6.9 Hz, –CH=C*H*CH$_3$-*trans*), 1.68 (dd, 3H, J = 6.9, 1.5 Hz, –CH=CHC*H*$_3$-*cis*) and 1.54 (dd, 3H, J = 6.9, 1.5 Hz, –CH=CHC*H*$_3$-*trans*). ^{13}C NMR ($CDCl_3$), δ: 168.8 (–*C*O–), 132.6 (–*C*H=CHCH$_3$-*trans*), 124.9 (–*C*H=CHCH$_3$-*cis*), 122.6 (–CH=*C*HCH$_3$-*cis*), 113.0 (–CH=*C*HCH$_3$-*trans*), 34.3 (–*C*F$_3$-*cis*), 25.9 (–CF$_3$-*trans*), 15.2 (–CH=CH*C*H$_3$-*trans*) and 12.3 (–CH=CH*C*H$_3$-*trans*).

14. *(+)-(E,E)-N,N-Di(1-propenyl)tartardiamide*. MS (70 eV), *m*/*e* (int [%]): 228 (33) M^+; 172 (6); 144 (55); 126 (7); 115 (8); 98 (10); 84 (75); 78 (16); 71 (20); 61 (23); 56 (100). ^{1}H NMR (CD_3OD), δ: 6.70 (ddq, 1H, J = 14.4, 1.5, Hz, –C*H*=CHCH$_3$), 5.44 (dqd, 1H, J = 14.4, 6.9, Hz, –CH=C*H*CH$_3$), 1.68 (dd, 3H, J =

6.9, 1.5 Hz, –CH=CHCH_3). ^{13}C NMR ($CDCl_3$), δ: 171.5 (–*C*O–), 123.8 (–*C*H=CHCH$_3$), 111.1 (–CH=*C*HCH$_3$), 74.0 (–*C*(OH)–) and 15.2 (–CH=CH*C*H$_3$).

(+)-(E,Z)-N,N-Di(1-propenyl)tartardiamide. MS (70 eV), *m/e* (int [%]): 228 (33) M^+; 172 (6); 144 (55); 126 (7); 115 (8); 98 (10); 84 (75); 78 (16); 71 (20); 61 (23); 56 (100). ^{1}H NMR (CD_3OD), δ: 6.70 (dq, 1H, J = 14.4, 1.5 Hz, –C*H*=CHCH$_3$-*trans*), 6.63 (dq, 1H, J = 6.9, 1.5 Hz, –C*H*=CHCH$_3$-*cis*), 5.43 (dq, 1H, J = 14.4, 6.9 Hz, –CH=C*H*CH$_3$-*trans*), 4.94 (dq, 1H, J = 6.9, 6.9 Hz, –CH=C*H*CH$_3$-*cis*), 1.68 (dd, 3H, J = 6.9, 1.5 Hz, –CH=CHCH_3). ^{13}C NMR ($CDCl_3$), δ: 171.7 (–*C*O-*cis*), 171.6 (–*C*O-*trans*), 123.8 (–*C*H=CHCH$_3$-*trans*), 121.9 (–*C*H=CHCH$_3$-*cis*), 111.2 (–CH=*C*HCH$_3$-*trans*), 108.8 (–CH=*C*HCH$_3$-*cis*), 74.1 (–*C*(OH)-*trans*), 74.0 (–*C*(OH)-*cis*), 15.2 (–CH=CH*C*H$_3$-*trans*) and 10.9 (–CH=CH*C*H$_3$-*cis*).

(+)-(Z,Z)-N,N-Di(1-propenyl)tartardiamide. MS (70 eV), *m/e* (int [%]): 228 (33) M^+; 172 (6); 144 (55); 126 (7); 115 (8); 98 (10); 84 (75); 78 (16); 71 (20); 61 (23); 56 (100). ^{1}H NMR (CD_3OD), δ: 6.63 (dq, 1H, J = 6.9, 1.5, Hz, –C*H*=CHCH$_3$), 4.95 (dq, 1H, J = 6.9, 6.9 Hz, –CH=C*H*CH$_3$), 1.68 (dd, 3H, J = 6.9, 1.5 Hz, –CH=CHCH_3). ^{13}C NMR ($CDCl_3$), δ: 171.6 (–*C*O–), 121.8 (–*C*H=CHCH$_3$), 108.8 (–CH=*C*HCH$_3$), 73.9 (–*C*(OH)–) and 10.9 (–CH=CH*C*H$_3$).

(E)-N-Phenyl-N-(3-trimethylsilyl-1-propenyl)ethanamide. MS (70 eV), *m/e* (int [%]): 247 (100) M^+; 232 (55); 204 (11); 192 (12); 174 (8); 156 (32); 132 (87); 117 (16); 106 (8); 73 (92); 43 (39). ^{1}H NMR ($CDCl_3$), δ: 7.55 (dd, 2H, $J_{2–3}$ = $J_{5–6}$ = 6.9 Hz, $J_{2–4}$ = $J_{4–6}$ < 0.9 Hz, $H_{2\text{-arom}}$ and $H_{6\text{-arom}}$), 7.54 (dt, 1H, J = 14.4, 1.2 Hz, –C*H*=CHCH$_2$–), 7.46 (dd, 1H, $J_{3–4}$ = $J_{4–5}$ = 6.9 Hz, $J_{2–4}$ = $J_{4–6}$ < 0.9 Hz, $H_{4\text{-arom}}$), 7.25 (ddd, 2H, $J_{2–3}$ = $J_{5–6}$ = 6.9, $J_{3–4}$ = $J_{4–5}$ = 6.9, $J_{3–5}$ = 1.2 Hz, $H_{3\text{-arom}}$ and $H_{5\text{-arom}}$), 4.75 (dt, 1H, J = 14.4, 8.4 Hz, –CH=C*H*CH$_2$–), 1.92 (s, 3H, –COCH_3), 1.46 (dd, 2H, J = 8.40, 1.2 Hz, –CH=CHCH_2–), 0.09 (s, 9H, –Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$), δ: 167.5 (–*C*OCH$_3$), 142.5 ($C_{1\text{-arom}}$), 129.6 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$), 127.7 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$), 126.8 ($C_{4\text{-arom}}$), 128.6 (–*C*H=CHCH$_3$), 111.5 (–CH=*C*HCH$_2$–), 22.9 (–CO*C*H$_3$), 19.2 (–CH=CH*C*H–) and –1.6 (–Si(CH_3)$_3$).

4.6. Mechanistic investigation

N-Allylethanamide (2.00 mmol) was heated with Ru^1, Ru^2 or Ru^3 in 1,4-dioxane at 120 °C for 3 h in high-pressure glass ampoules, which were put in a thermostat (±0.1 °C). The proportions of the substrate, the catalyst and the solvent have been quoted in Fig. 2. Before the reaction, the system had been saturated with argon. After the reaction was completed, the solvent was removed in vacuo and the crude mixture was investigated on ^{1}H and ^{2}H NMR.

Deuterated (E)-N-(1-propenyl)ethanamide. ^{2}H NMR (THF), δ: 9.55 (–N*D*–), 7.00 (–ND–C*D*=CDCDH$_2$), 5.45 (–ND–CD=C*D*CDH$_2$) and 1.79 (–ND–CD=CDC*D*H$_2$).

Deuterated (Z)-N-(1-propenyl)ethanamide. ^{2}H NMR (THF), δ: 9.26 (–N*D*–), 7.00 (–ND–C*D*=CDCDH$_2$), 4.97 (–ND–CD=C*D*CDH$_2$) and 1.93 (–ND–CD=CDC*D*H$_2$).

4.7. Spectroscopic measurements

^{1}H, ^{2}H and ^{13}C NMR spectra were measured on a Varian Unity 300 MHz spectrometer. ^{1}H NMR spectra at 40, 60, 80 and 100 °C were measured on Varian VXR-300. GC–MS were run on: (a) a Varian 3300 gas chromatograph equipped with a 30 m long DB 1701 fused silica capillary column and a Finnigan MAT 800 AT ion trap detector; (b) a Varian Saturn 2100T gas chromatograph equipped with a 30 m long DB-5 capillary column and TCD detector; (c) Thermo Finnigan equipped with a 30 m long MDN 5S column and Mass Detector (EI, 70 eV). HPLC–MS spectra were recorded on HPLC–MS Waters Integrity Systems with a Termabeam Mass Detector (EI, 70 eV), a Photodiode Array detector on a cartridge column; methanol–water mixture (70:25; flow 0.25 ml/min) used as the solvent.

4.8. Preparation of MCFs

In a typical procedure, surfactant Pluronic PE 9600 (0.4 mmol) was dissolved in 1.6 M HCl (75 ml) at room temperature. 1,3,5-Trimethylbenzene (17 mmol) and NH_4F (0.6 mmol) were added under vigorous stirring and the mixture was heated to 60 °C. After 1 h of stirring tetraethoxysilane was added (4.4 g). The mixture was stirred for 2 h and subsequently stored at 60 °C for 20 h and at 100 °C for 24 h. After cooling to room temperature, the precipitate was isolated by filtration, dried at room temperature for 4 days and calcinated at 500 °C for 8 h. The preparation procedure was the same as proposed in [29]. The texture parameters (specific surface area, S_{BET}; pore volume, V_p; diameter of the cells, d_s and diameter of interconnected windows, d_w) of calcinated materials were obtained by means of the nitrogen adsorption method. The nitrogen isotherms were measured by a Micromeritics ASAP 2000 instrument at −196 °C. Typical texture parameters of the calcined MCFs were: S_{BET} ca. 650 m^2/g, V_p ca. 2.5 cm^3/g, d_s ca. 30 nm and d_w ca. 15 nm.

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