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A Mild and Effective Synthesis of α,β-unsaturated Carboxamides and Sulfonamides by Electrophilic Substitution of Alkenylstannanes with Isocyanates

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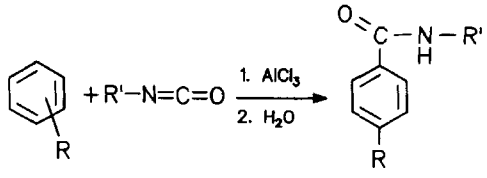
A new and effective method for the preparation of a variety of olefinic carboxamides **6a–k** and *N*-(4-methylphenylsulfonyl)carboxamides **7a–d** is described. The reaction of aryl and alkyl isocyanates **4a–c** or 4-methylphenylsulfonyl isocyanate **5** with 1-alkenyltrialkylstannanes **1a–e** and di-1-alkenyldibutylstannanes **2a–c** in the presence of aluminium trichloride provides the corresponding *N*-aryl-substituted olefinic carboxamides **6a–k** or the *N*-(4-methylphenylsulfonyl)-substituted olefinic carboxamides **7a–d** in good yields. The stannyl moiety is superior to hydrogen as a leaving group and enables electrophilic *ipso* substitution at the vinylic system. In the case of di-1-alkenyldibutylstannanes the substitutions are also stereospecific, whereas the reactions of 1-alkenyltrialkylstannanes with isocyanates proceed with partial isomerisation.

Trialkylarylstannanes have become of considerable importance in the field of electrophilic aromatic substitution. Their use makes it possible to introduce electrophiles into the aromatic system in an *ipso*-specific manner. This has been demonstrated for Friedel-Crafts acylations[2], amidations with various isocyanates[3–5], sulfonations[6] etc., which lead in a regioselective manner under mild conditions to the aromatic substitution products. Even the strong directing effect of the methoxy group is overcompensated by the effectiveness of the trialkylstannyl moiety as a leaving group[2–6]. This methodology thus provides an elegant route to substitution patterns which could previously not be obtained by conventional electrophilic aromatic substitution.

The normal reaction of olefins with electrophiles involves addition to the double bond. Electrophilic vinylic substitutions have been observed only in a few special cases[7]. Thus the acylation of olefins under Friedel-Crafts conditions[7] is an example of this unusual type of reaction at the vinylic system. An addition-elimination sequence is normally necessary to introduce functional groups into olefins. However, normally this mechanism entails no stereo- or regioselectivity. This disadvantage can be eliminated by using the trialkylstannyl group as a leaving group in such reactions, as has been shown by a various number of proto-[8,9] and halodestannylations[10,11]. These reactions take place both regio- and stereospecifically. Nevertheless, destannylation reactions at vinyltin compounds have previously been limited to acylations[12] and nitrations[13].

Methods developed for the synthesis of aromatic carboxamides[14] are often not applicable to α,β-unsaturated carboxamides. The amidation of dicyclohexyldiimide adducts of acrylic acids[15] yields only small amounts of the corresponding amides. The reaction of aromatic hydrocarbons with isocyanates in the presence of aluminium trichloride results in *para* isomers of *N*-substituted arylamides[16].



We have enlarged the synthetic potential of this method by using trialkylarylstannanes[3a]. A number of aromatic amides which are not obtainable by conventional electrophilic substitution have been synthesized in high yields in a regioselective manner. As has been shown in a few cases, this reaction can be extended to other unsaturated systems, such as vinyl- or alkynyltin compounds. In this paper we discuss the reaction of isocyanates (**4** and **5**) with 1-alkenylstannanes (**1** and **2**) which leads to the corresponding previously unaccessible *N*-substituted 1-alkenecarboxamides.

Results and Discussion

1-Alkenyltrialkylstannanes **1** react readily under mild conditions with aryl isocyanates **4a,b** in the presence of aluminium trichloride to yield the corresponding *N*-substituted 1-alkenecarboxamides **6a–k** (45 to 78% yield). Only the *ipso*-substitution products are obtained, eq. (2). The reac-

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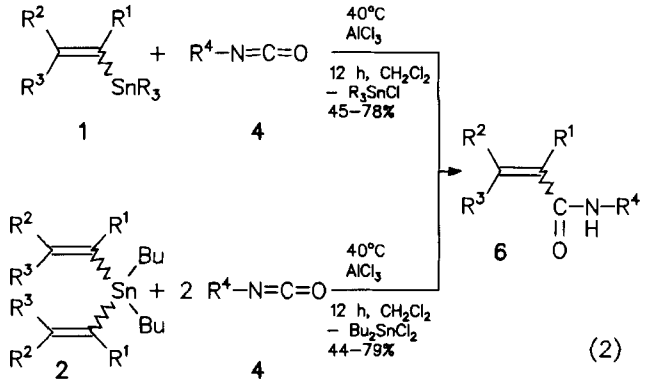
tions do not proceed stereospecifically, as the *E* isomer of the carboxamide is formed preferentially (for *E*/*Z* distribution of **1a-e, 2a-c**, see Table 1), even though the *E* and *Z* isomers of **1a** show almost the same reactivity in electrophilic halodestannylations[9]. The amount of *E* isomer increases at longer reaction times. A comparison of the yields of the amides obtained from **1a** and **1d** shows that the toxicologically much less problematic tributylstannyl group is just as effective as a leaving group as the trimethylstannyl moiety.



(2)

1	R	R^1	R^2	R^3
a	Me	H	H	Me
b	Bu	H	H	Me
c	Me	Me	H	Me
d	Bu	H	Ph	H
e	Me	$-[CH_2]_6-$		H

2	R^1	R^2	R^3
a	H	H	Me
b	Me	H	Me
c	$-[CH_2]_6-$		H

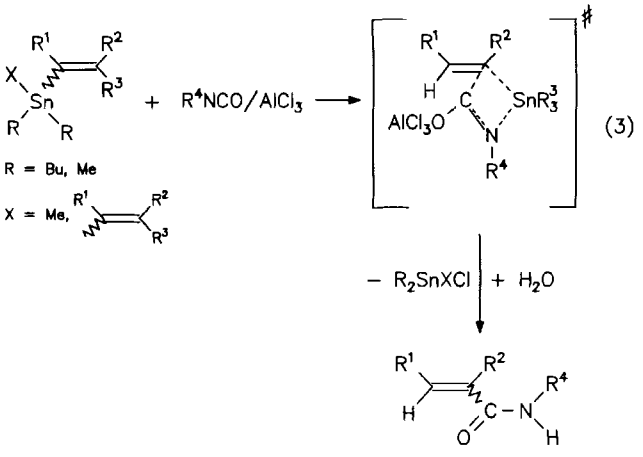
4	R^4
a	Ph
b	3-ClC_6H_4
c	n-Bu

6	R^1	R^2	R^3	R^4	E:Z (from 1)	E:Z (from 2)	Yield (from 1)	Yield (from 2)
a	H	H	Me	Ph	4.9 : 1.0	1.0 : 0.66	50 %	74 %
b	Me	H	Me	Ph	3.9 : 1.0	1.0 : 3.5	45 %	68 %
c	$-[CH_2]_6-$		H	Ph	only Z	only Z	–	50 %
d	H	H	Me	3-ClC_6H_4	4.2 : 1.0	1.0 : 0.66	74 %	78 %
e	Me	H	Me	3-ClC_6H_4	1.0 : 4.2	1.0 : 3.5	78 %	73 %
f	$-[CH_2]_6-$		H	3-ClC_6H_4	only Z	only Z	69 %	56 %
g	Ph	H	H	3-ClC_6H_4	only E	–	76 %	–
h	H	H	Me	n-Bu	2.0 : 1.0	1.0 : 0.66	69 %	49 %
i	Me	H	Me	n-Bu	3.8 : 1.0	1.0 : 3.5	58 %	47 %
j	$-[CH_2]_6-$		H	n-Bu	only Z	only Z	53 %	44 %
k	Ph	H	H	n-Bu	only E	–	53 %	–

This electrophilic substitution can also be extended to di-1-alkenyldibutylstannanes **2**. The yields of the corresponding *N*-substituted carboxamides **6** are in the same range as those obtained from **1**. Yields higher than 50% demonstrate that electrophilic substitution occurs at both vinylic systems of the stannane **2**. An additional advantage of this variant of electrophilic substitution at vinyltin compounds is the formation of Bu_2SnCl_2 as the tin byproduct. Bu_2SnCl_2 can be considered as almost non-toxic in comparison with trialkyltin chlorides. Moreover, it can readily be converted to the insoluble $(Bu_2SnO)_n$. A further advantage is the regio- and stereoselective nature of the reaction of **2**. In contrast to reactions of **1**, isomerization of the amides **6** was not be observed.

Although alkyl isocyanates are less reactive than their aryl counterparts in electrophilic substitution at aromatic hydrocarbons[16], the reaction of **4c** with vinylstannanes **1** and **2** in the presence of aluminium trichloride indicates only slight differences in the reactivity of aryl and alkyl isocyanates. The yields of the corresponding *N*-butyl-substituted 1-alkenecarboxamides **6h–k** are in the same range as those of the aryl derivatives **6a–g**.

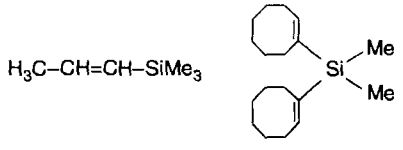
The weakness of the tin-carbon bond promotes electrophilic substitutions at vinylic systems, so that the amide function can be introduced directly into an olefinic system. The regio- and in the case of **2** stereoselective course of the reaction leads us to assume that a close complex between the electrophile and the stannane under extension of the coordination sphere of the tin atom by the lone electron pair of the nitrogen atom is responsible for this result.



(3)

Due to this four-centered transition state, suggested as well for other destannylations at vinyltin compounds[17], cleavage of the double bond during the substitution does not occur. The stereochemistry of the vinylstannane is thus preserved in the product.

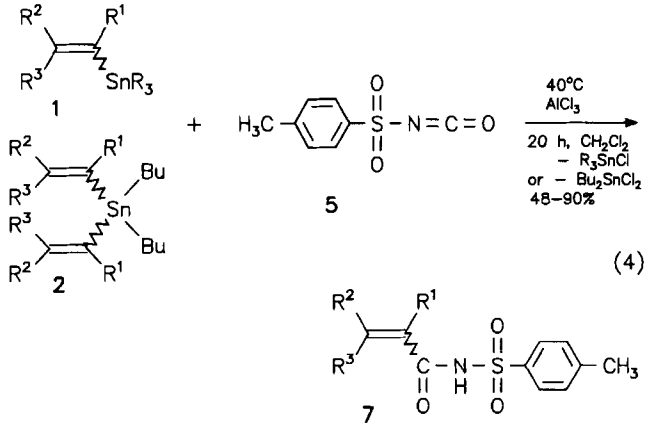
The superior leaving ability of the stannyl group is demonstrated by the fact that the corresponding silanes, eg. 1-(trimethylsilyl)-1-propene (**3a**) or di-1-cycloocten-1-yldimethylsilane (**3b**), do not react with isocyanates in the presence of aluminium trichloride. The silyl group, which also has been used in electrophilic demetallation reactions[18], is too unreactive because the coordination ability of the silicon atom is too low and the Si–C bond too strong to facilitate a reaction with the weakly electrophilic isocyanates.



3a **3b**

The amidation of olefins via vinyltin compounds is not restricted to simple aryl and alkyl isocyanates **4**. 4-Methylphenylsulfonyl isocyanate (TSI) (**5**) also reacts with **1** and **2** in the presence of aluminium trichloride under mild conditions to give *N*-*p*-tosyl-substituted 1-alkenecarboxamides **7** in yields between 48 and 92%, eq. (4). The formation of **7** proceeds in an *ipso*-specific manner. The stereochemistry of the stannanes **1** and **2** is retained in the products, and no

isomerization is observed. In the case of **1** the use of the Lewis acid is not necessary, although TSI is only a weak electrophile. A decrease of the yield is however observed in reactions carried out in the absence of a Lewis acid, so that extended reaction times are needed to obtain yields similar to those obtained with catalyst. Reactions of **2** with TSI without aluminium trichloride as a catalyst afford yields lower than 50%. This suggests that only one of the vinylic substituents at the tin is cleaved. TSI shows also no reactions with the less reactive silanes **3a** or **3b**.



7	R¹	R²	R³	E:Z (from 1)	E:Z (from 2)	Yield (from 1)	Yield (from 2)
a	H	H	Me	1.0 : 1.1	1.0 : 0.66	90 %	72 %
b	Me	H	Me	1.0 : 3.7	1.0 : 3.5	74 %	74 %
c	–[CH₂]₆–		H	only Z	only Z	48 %	67 %
d	Ph	H	H	only E	–	91 %	–

Because of the efficiency, regioselectivity and in some cases stereospecificity of the reactions described, further work is in progress to extend this methodology to other vinylic stannanes and electrophiles.

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Experimental

Melting points: Büchi SMP 20. – IR: Shimadzu 3283. – NMR: Varian EM 360 (60 MHz, ^{1}H), Bruker AC 200 (200 MHz, ^{1}H), and Bruker AM 300 (300 MHz, ^{1}H; 75.47 MHz, ^{13}C; 59.63 MHz ^{29}Si, and 111.92 MHz ^{119}Sn). – MS: Finnigan MAT 8230, 70 eV. – GC: Carlo Erba 4260. – Elemental analyses: Carlo Erba MOD 1106.

The 1-alkenyltrialkylstannanes **1a–f** were prepared according to published procedures[3a,17b,19,20].

Table 1. Isomers of the compounds **1** and **2**

Compound	*E*:*Z*	Compound	*E*:*Z*
1a	1.00:1.10	**2a**	1.00:0.66
1b	1.00:1.10	**2b**	1.00:3.5
1c	1.0:3.7	**2c**	only *Z*
1d	only *Z*		
1e	only *E*		

Di-1-alkenyldibutylstannanes (**2a–c**). – *General Procedure I:* A solution of dibutyltin dichloride in 50 ml of anhydrous diethyl ether is added under Ar during 1 h to the vinyllithium reagent, prepared from the 1-bromo-1-alkenes and lithium in 250 ml of anhydrous diethyl ether. After stirring under reflux for 12 h the reaction mixture is hydrolysed with 100 ml of a saturated aqueous NH_4Cl solution. Twofold extraction of the aqueous layer with 100 ml of diethyl ether, drying of the combined organic layers with $MgSO_4$, and removal of the solvent afforded the crude product which was fractionated.

Dibutyldi-1-propenylstannane (**2a**): 21.4 g (68%) of **2a** is obtained from 3.7 g (0.53 mmol) of lithium, 32.7 g (0.27 mol) of 1-bromo-1-propene (mixture of *E* and *Z* isomers), and 30.4 g (0.10 mol) of Bu_2SnCl_2 as a mixture of three isomers [35% (*E*,*E*); 49% (*E*,*Z*); 16% (*Z*,*Z*)] according to the general procedure I; b.p. 73°C/0.5 Torr. – ^{1}H NMR ($CDCl_3$): δ = 0.91 (t, 6H, $CH_2CH_2CH_2CH_3$), 1.55 (m, 12H, CH_2), 1.80 (dd, 6H, CH_{3Z}, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.7 Hz), 1.88 (dd, 6H, CH_{3E}, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.7 Hz), 5.86 (qd, 2H, CH_Z, $^3J_{HH}$ = 12.2, $^4J_{HH}$ = 1.7 Hz), 5.91 (qd, 2H, CH_E, $^3J_{HH}$ = 15.7, $^4J_{HH}$ = 1.7 Hz), 6.02 (qd, 2H, CH_Z, $^3J_{HH}$ = 12.2, $^4J_{HH}$ = 1.7 Hz), 6.61 (qd, 2H, CH_E, $^3J_{HH}$ = 15.7, $^4J_{HH}$ = 1.7 Hz). – ^{13}C NMR ($CDCl_3$): δ = 11.0 ($SnCH_{2E}$), 11.7 ($SnCH_{2Z}$), 14.0 (CH_3), 21.7 (CH_3), 23.5 (CH_3), 27.2 (CH_2), 29.2 (CH_2), 128.7 (CH), 129.2 (CH), 144.0 (CH), 145.7 (CH). – ^{119}Sn NMR ($CDCl_3$): δ = –90.2 (*E*,*E*), –101.6 (*E*,*Z*), –115.5 (*Z*,*Z*). – MS, *m/z* (%): 316 (2) [M^+], 275 (100) [M^+ – $CH{=}CHCH_3$], 259 (87) [M^+ – C_4H_9], 219 (14) [$(H_3CCH{=}CH)_2SnH^+$], 203 (73) [$(C_4H_9)CH_3(CH{=}CH)SnH^+$], 57 (16) [$C_4H_9$]. – $C_{14}H_{28}Sn$ (315.1): calcd. C 53.37, H 8.96; found C 53.8, H 9.4.

Dibutylbis(1-methyl-1-propenyl)stannane (**2b**): 32.3 g (94%) of **2b** is obtained from 4.0 g (0.57 mol) of lithium, 40.5 g (0.30 mol) of 2-bromo-2-butene (mixture of *E* and *Z* isomers), and 30.4 g (0.10 mol) of Bu_2SnCl_2 as a mixture of three isomers [1% (*E*,*E*); 42% (*E*,*Z*); 57% (*Z*,*Z*)] according to the general procedure I, b.p. 90°C/0.5 Torr. – ^{1}H NMR ($CDCl_3$): δ = 1.07 (t, 6H, CH_3), 1.57 (m, 12H, CH_2), 1.70 (d, 6H, CH_{3E}, $^4J_{HH}$ = 1.8 Hz), 1.72 (d, 6H, CH_{3Z}, $^4J_{HH}$ = 1.8 Hz), 1.90 (d, 6H, CH_{3E}, $^3J_{HH}$ = 5.0 Hz), 1.96 (d, 6H, CH_{3Z}, $^3J_{HH}$ = 5.0 Hz), 5.74 (qd, 2H, CH_E, $^3J_{HH}$ = 5.0, $^4J_{HH}$ = 1.8 Hz), 6.16 (qd, 2H, CH_Z, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1.8 Hz). – ^{13}C NMR ($CDCl_3$): δ = 10.2 (CH_2Sn_E), 10.7 (CH_2Sn_Z), 14.0 (CH_3), 18.6 (CH_{3E}), 19.8 (CH_{3Z}), 26.6 (CH_{3Z}), 26.9 (CH_{3E}), 27.5 (CH_2), 29.3 (CH_2), 134.8 (CH_E), 135.2 (CH_Z), 138.5 (C_E), 138.8 (C_Z). – ^{119}Sn NMR ($CDCl_3$): δ = –70.8 (*E*,*E*), –83.1 (*E*,*Z*), –98.7 (*Z*,*Z*). – MS, *m/z* (%): 343 (23) [M^+ – H], 287 (51) [M^+ – C_4H_9], 231 (100) [$(H_3CCH{=}CCH_3)_2SnH^+$], 177 (40) [M^+ – (C_4H_9) – 2 C_4H_7], 57 (4) [C_4H_9], 55 (20) [C_4H_7]. – $C_{16}H_{32}Sn$ (343.1): calcd. C 56.01, H 9.40; found C 56.6, H 9.4.

Dibutyldi-1-cycloocten-1-ylstannane (**2c**): According to the general procedure I 42.0 g (93%) of **2c** is obtained from 5.5 g (0.79 mol) of lithium, 75.7 g (0.40 mol) of 1-bromo-1-cyclooctene, and 30.4 g (0.10 mol) of Bu_2SnCl_2, b.p. 140°C/0.01 Torr. – ^{1}H NMR ($CDCl_3$): δ = 0.92 (t, 6H, CH_3), 1.37 (m, 12H, $CH_2CH_2CH_2CH_3$), 1.50 (m, 16H, CH_2), 2.24 (m, 4H, $CH_{2allylic}$), 2.41 (m, 4H, $CH_{2allylic}$), 5.86 (t, 2H, CH, $^3J_{HH}$ = 8.2 Hz). – ^{13}C NMR ($CDCl_3$): δ = 9.9 (CH_2Sn), 13.7 (CH_3), 26.1, 26.5, 27.2, 27.6, 29.2, 29.3, 30.9 (all CH_2), 141.5 (CH), 147.0 (C). – ^{119}Sn NMR ($CDCl_3$): δ = –76.2. – MS, *m/z* (%): 395 (14) [M^+ – C_4H_9], 343 (5%) [M^+ – cyclooctene], 339 (8) [$(cyclooctene)_2SnH^+$], 109 (45) [cyclooctene – H], 95 (45) [C_7H_{11}], 81 (55) [C = $CH(CH_2)_4$], 67 (100) [$C{=}CH(CH_2)_3$], 57 (9) [C_4H_9]. – $C_{24}H_{44}Sn$ (451.3): calcd. C 63.87, H 9.83; found C 64.1, H 10.2.

Di-1-cycloocten-1-yldimethylsilane (**3b**): From 5.5 g (0.79 mol) of lithium, 75.6 g (0.40 mol) of 1-bromo-1-cyclooctene, and 12.9 g (0.10 mol) of Me_2SiCl_2 25.4 g (92%) of **3b** is obtained according to the general procedure I, b.p. 105°C/0.02 Torr. – ^{1}H NMR

($CDCl_3$): δ = 0.13 (s, 6H, CH_3, $^3J_{SiH}$ = 58.7 Hz), 1.45 (m, 12H, CH_2), 2.20 (m, 8H, $CH_{2allylic}$), 6.00 (t, 2H, CH, $^3J_{HH}$ = 8.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = −3.0 (CH_3), 26.3, 26.5, 27.0, 27.6, 29.0, 29.9 (all CH_2), 140.5 (CH), 140.6 (C). – ^{29}Si NMR ($CDCl_3$): δ = −9.5. – MS, *m/z* (%): 276 (76) [M^+], 261 (35) [$M^+ - CH_3$], 167 (85) [M^+ – cyclooctene], 109 (39) [cyclooctene – H], 67 (48) [C_5H_7], 59 (100) [$HSiMe_2^+$]. – $C_{18}H_{32}Si$ (276.5): calcd. C 78.18, H 11.66; found C 78.0, H 12.0.

N-Aryl- and N-Alkyl-1-alkenecarboxamides **6a–k**. – *General Procedure II:* The isocyanate **4a–c** is added to $AlCl_3$ in 20 ml of anhydrous dichlormethane and the mixture is stirred for 30 min. After addition of the 1-alkenyltrialkylstannane **1** or di-1-alkenyldibutylstannane **2** the mixture is stirred at 40°C for 12 h. The solution is then poured on ca. 50 g of ice and stirred for 30 min. Separation of the organic layer is followed by twofold extraction of the aqueous layer with 15 ml of dichloromethane. In the case of the reactions of 1-alkenyltrialkylstannanes the combined organic layers are treated with 10 ml of a saturated solution of KF in water, stirred vigorously for 3 h, and the precipated R_3SnF is filtered off. The filtrate is extracted twice with 10 ml of dichloromethane. In the case of **1** and **2** the combined organic layers are dried with $MgSO_4$ and concentrated in vacuo. The residue is purified by distillation or recrystallized from the appropriate solvent.

N-Phenyl-2-butenamide (**6a**): From 1.4 g (7.0 mmol) of **1a** (mixture of *E* and *Z* isomers, 1:1.1), 0.80 g (7.0 mmol) of **4a**, and 0.90 g (7.0 mmol) of $AlCl_3$ according to the general procedure II 0.56 g (50%) of **6a** is obtained (mixture of *E* and *Z* isomers 4.9:1), b.p. 130°C/0.02 Torr. From 0.90 g (3 mmol) of **2a**, 1.4 g (8 mmol) of **4a**, and 1.1 g (8 mmol) of $AlCl_3$ 0.70 g (74%) of **6a** (*E*/*Z* = 1:0.66) is obtained, b.p. 130°C/0.02 Torr. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1}, 1648, 1550. – ^1H NMR ($CDCl_3$): δ = 1.88 (dd, 3H, CH_{3E}, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.0 Hz), 2.02 (d, 3H, CH_{3Z}, $^3J_{HH}$ = 7.0 Hz), 5.90 (d, 1H, CH_Z, $^3J_{HH}$ = 12 Hz), 6.00 (qd, 1H, CH_E, $^3J_{HH}$ = 15, $^4J_{HH}$ = 1 Hz), 6.87 (qd, 1H, CH_{3E}, $^3J_{HH}$ = 15, $^3J_{HH}$ = 7 Hz), 7.01 (qd, 1H, $^3J_{HH}$ = 12, $^3J_{HH}$ = 7 Hz), 7.50 (m, 5H, aromatic H), 8.23 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 16.5 (CH_3), 18.3 (CH_3), 120.4, 124.3, 128.6, 129.4, 129.8, 131.3 (all CH), 134.9 (C), 137.3 (CH), 168.9 (C=O). – $C_{10}H_{11}NO$ (161.2): calcd. C 74.51, H 6.88, N 8.69; found C 74.3, H 6.8, N 8.8.

2-Methyl-N-phenyl-2-butenamide (**6b**): From 1.5 g (7.0 mmol) of **1c** (mixture of *E* and *Z* isomers, 1:3.7), 0.80 g (7.0 mmol) of **4a**, and 0.90 g (7.0 mmol) of $AlCl_3$ 0.60 g (45%) of **6b** (*E*:*Z* = 3.9:1) is obtained, b.p. 140°C/0.02 Torr. From 1.0 g (3 mmol) of **2b**, 1.4 g (8 mmol) of **4a**, and 1.1 g (8 mmol) of $AlCl_3$, 0.80 g (68%) of **6b** (*E*:*Z* = 1:3.5) is obtained, m.p. 71–72°C (pentane). – IR (KBr): $\tilde{\nu}$ = 3265 cm^{-1}, 1640, 1535. – ^1H NMR ($CDCl_3$): δ = 1.78 (d, 3H, CH_{3E}, $^3J_{HH}$ = 7.0 Hz), 1.92 (d, 3H, CH_{3Z}, $^3J_{HH}$ = 7.0 Hz), 2.00 (s, 3H, CH_3), 5.78 (q, 1H, CH_E, $^3J_{HH}$ = 7.0 Hz), 7.48 (m, 5H, aromatic), 8.07 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 15.1 (CH_3), 20.7 (CH_3), 120.4, 124.2, 127.0, 129.3 (all CH), 134.8 (C), 140.0 (CH), 169.0 (C=O). – MS, *m/z* (%): 175 (72) [M^+], 93 (25) [$PhNH_2^+$], 83 (100) [$C_4H_7CO^+$], 55 (100) [$C_4H_7^+$]. – $C_{11}H_{13}NO$ (175.2): calcd. C 75.40, H 7.48, N 7.99; found C 75.5, H 7.3, N 8.1.

N-Phenyl-1-cyclooctene-1-carboxamide (**6c**): According to the general procedure II from 1.4 g (3 mmol) of **2c**, 1.4 g (8 mmol) of **4a**, and 1.1 g (8 mmol) of $AlCl_3$ 0.70 g (50%) of **6c** is obtained, m.p. 95°C (pentane) (ref.[3a] 96°C). – ^1H NMR ($CDCl_3$): δ = 1.65 (m, 8H, CH_2), 2.37 (m, 2H, $CH_{2allylic}$), 2.58 (m, 2H, $CH_{2allylic}$), 6.56 (t, 1 CH, $^3J_{HH}$ = 8.3 Hz), 7.45 (m, 5H, aromatic), 8.48 (s, 1H, NH).

N-(3-Chlorophenyl-2-butenamide (**6d**): From 1.5 g (7.0 mmol) of **1a**, 1.1 g (7.0 mmol) of **4b**, and 0.90 g (7.0 mmol) of $AlCl_3$ in 1,2-dichloromethane 1.0 g (74%) of **6d** (*E*:*Z* = 4.2:1) is obtained, b.p. 120°C/0.01 Torr. From 0.90 g (3 mmol) of **2a**, 1.2 g (8 mmol) of **4b**, and 1.1 g (8 mmol) of $AlCl_3$ 0.90 g (78%) of **6d** (*E*:*Z* = 1:0.66) is obtained. – IR (KBr): $\tilde{\nu}$ = 3302 cm^{-1}, 1665, 1565. – ^1H NMR ($CDCl_3$): δ = 0.95 (d, 3H, CH_{3E}, $^3J_{HH}$ = 7.0 Hz), 1.10 (d, 3H, CH_{3Z}, $^3J_{HH}$ = 7.0 Hz), 6.00 (m, 1H, CH_E), 6.70 (qd, 1H, CH_E), 6.70 (qd, 1H, CH_Z, $^3J_{HH}$ = 12, $^3J_{HH}$ = 7.0 Hz), 7.11 (qd, 1H, CH_E, $^3J_{HH}$ = 15.0, $^3J_{HH}$ = 7.0 Hz), 7.50 (m, 4H, aromatic), 8.33 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 15.6 (CH_3), 17.8 (CH_3), 118.3, 120.4, 124.2, 125.2, 129.7 (all CH), 134.3 (C), 139.2 (C), 142.0 (CH), 164.7 (C=O). – $C_{10}H_{10}ClNO$ (195.6): calcd. C 61.39, H 5.15, N 7.16; found C 61.2, H 5.3, N 7.0.

N-(3-Chlorophenyl)-2-methyl-2-butenamide (**6e**): From 1.5 g (7.0 mmol) of **1b**, 1.1 g (7.0 mmol) of **4b**, and 0.90 g (7.0 mmol) of $AlCl_3$ in 1,2-dichloroethane 1.0 g (78%) of **6e** (*E*:*Z* = 4.2:1) is obtained, b.p. 130°C/0.01 Torr. From 1.0 g (3 mmol) of **2b**, 1.2 g (8 mmol) of **4b**, and 1.1 g (8 mmol) of $AlCl_3$ 0.90 g (73%) of **6e** (*E*:*Z* = 1:3.5) is obtained, b.p. 130°C/0.01 Torr. – IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1}, 1670, 1555. – ^1H NMR ($CDCl_3$): δ = 1.67 (m, 3H, CH_3), 1.87 (m, 3H, CH_3), 5.17 (q, 1H, CH_Z, $^3J_{HH}$ = 7 Hz), 5.77 (q, 1H, CH_E, $^3J_{HH}$ = 7 Hz), 7.13 (m, 4H, aromatic), 7.58 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 14.5 (CH_3), 15.8 (CH_3), 18.5 (CH_3), 20.1 (CH_3), 118.5, 120.3, 123.9, 125.4, 129.5 (all CH), 134.4 (C), 138.4 (C), 139.4 (CH), 166.8 (C=O). – $C_{11}H_{12}ClNO$ (209.7): calcd. C 63.01, H 5.77, N 6.68; found C 62.7, H 5.9, N 6.9.

N-(3-Chlorophenyl)-1-cyclooctene-1-carboxamide (**6f**): From 1.9 g (7.0 mmol) of **1e**, 1.0 g (7.0 mmol) of **4b**, and 0.90 g (7.0 mmol) of $AlCl_3$ in 1,2-dichloroethane 1.3 g (69%) of **6f** is obtained, b.p. 150°C/0.01 Torr. From 1.4 g (3 mmol) of **2c**, 1.2 g (8 mmol) of **4b**, and 1.1 g (8 mmol) of $AlCl_3$ 0.90 g (56%) of **6f** is obtained. – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1}, 1653, 1565. – ^1H NMR ($CDCl_3$): δ = 1.33 (m, 8H, CH_2), 1.67 (m, 2H, $CH_{2allylic}$), 2.27 (m, 2H, $CH_{2allylic}$), 5.87 (t, 1H, CH, $^3J_{HH}$ = 7.0 Hz), 6.68 (m, 4H, aromatic), 7.90 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 25.1, 25.7, 26.2, 26.6, 28.7, 29.2 (all CH_2), 118.3, 123.7, 127.7, 129.3 (all CH), 133.8 (C), 135.7 (CH), 137.1 (C), 139.4 (C), 167.3 (C=O). – $C_{15}H_{18}ClNO$ (263.8): calcd. C 68.30, H 6.88, N 5.31; found C 68.1, H 6.83, N 5.4.

N-(3-Chlorophenyl)-(E)-β-styrenecarboxamide (**6g**): From 2.7 g (7.0 mmol) of **1d**, 1.0 g (7.0 mmol) of **4b**, and 0.90 g (7.0 mmol) of $AlCl_3$ in 1,2-dichloroethane 1.4 g (76%) of **6g** is obtained according to the general procedure II, m.p. 124°C (ref.[21] 125–126°C). – IR (KBr): $\tilde{\nu}$ = 3210 cm^{-1}, 1652, 1540. – ^1H NMR ($CDCl_3$): δ = 6.67 (d, 1H, CH, $^3J_{HH}$ = 15.0 Hz), 7.68 (m, 9H, aromatic), 7.89 (d, 1H, CH, $^3J_{HH}$ = 15.0 Hz), 8.53 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 117.7, 117.8, 120.0, 123.8, 128.7, 128.9, 129.2, 129.7 (all CH), 133.4, 134.3, 139.5 (all C), 144.5 (CH), 169.2 (C=O).

N-Butyl-2-butenamide (**6h**): From 1.4 g (7.0 mmol) of **1a** (mixture of *E*/*Z* isomers 1:1.2), 0.70 (7.0 mmol) of **4c**, and 0.90 g (7.0 mmol) of $AlCl_3$ 0.70 g (69%) of **6h** (*E*:*Z* = 2:1) is obtained, b.p. 120°C/0.01 Torr. From 0.90 g (3 mmol) of **2a**, 0.80 g (8 mmol) of **4c**, and 1.1 g (8 mmol) of $AlCl_3$ 0.50 g (49%) of **6h** (*E*:*Z* = 1:0.66) is obtained. – IR (KBr): $\tilde{\nu}$ = 3340 cm^{-1}, 1675, 1545. – ^1H NMR ($CDCl_3$): δ = 1.01 (m, 7H, C_3H_7), 1.76 (dd, 3H, CH_{3E}, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.0 Hz), 1.93 (d, 3H, CH_{3Z}, $^3J_{HH}$ = 7.0 Hz), 3.30 (m, 2H, CH_2), 5.91 (qd, 1H, CH_E, $^3J_{HH}$ = 15.0, $^4J_{HH}$ = 1.0 Hz), 6.10 (d, 1H, CH_Z, $^3J_{HH}$ = 11 Hz), 7.00 (m, 1H, CH), 8.76 (s, 1H, NH), 9.10 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 13.5, 15.8, 17.7 (all CH_3), 20.1, 31.5, 39.2 (all CH_2), 123.4 (CH), 137.2 (CH), 165.9 (C=O). – MS, *m/z*: 141 [M^+], 126 [M^+ – NH], 98 [M^+ – HNCO], 84 [$C_3H_5CONH^+$], 69 [$C_3H_5CO^+$]. – $C_8H_{15}NO$ (141.2): calcd. C 68.04, H 10.71, N 9.92; found C 67.9, H 10.7, N 9.9.

N-Butyl-2-methyl-2-butenamide (**6i**): From 1.5 g (7.0 mmol) of **1c**, 0.70 g (7.0 mmol) of **4c**, and 0.90 g (7.0 mmol) of $AlCl_3$ 0.60 g (58%) of **6i** (*E*:*Z* = 3.8:1) is obtained, b.p. 130°C/0.01 Torr. From 1.0 g (3 mmol) of **2b**, 0.80 g (8 mmol) of **4c**, and 1.1 g (8 mmol) of $AlCl_3$ 0.50 g (47%) of **6i** (*E*:*Z* = 1:3.5) is obtained. – IR (KBr): $\tilde{\nu}$ = 3290 cm^{-1}, 1668, 1551. – ^1H NMR ($CDCl_3$): δ = 0.85 (3H, CH_{3E}, $^3J_{HH}$ = 8.0 Hz), 1.76 (dd, 3H, CH_{3E}, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.0 Hz), 0.90 (d, 3H, CH_{3Z}, $^3J_{HH}$ = 8.0 Hz), 1.58 (m, 10H, CH_3, C_3H_7), 3.28 (m, 2H, CH_2), 5.58 (q, 1H, CH_Z, $^3J_{HH}$ = 8.0 Hz), 6.27 (q, 1H, CH_E, $^3J_{HH}$ = 8.0 Hz), 8.90 (s, 1H, NH), 9.27 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 13.4, 14.3, 15.8, 18.2 (all CH_3), 19.7 (CH_2), 20.3 (CH_3), 31.1 (CH_2), 39.5 (CH_2), 120.8 (CH), 135.7 (C), 164.9 (C=O). – $C_9H_{17}NO$ (155.2): calcd. C 69.63, H 11.04, N 9.02; found C 69.7, H 11.1, N 8.9.

N-Butyl-1-cyclooctene-1-carboxamide (**6j**): From 1.9 g (7.0 mmol) of **1e**, 0.70 g (7.0 mmol) of **4c**, and 0.90 g (7.0 mmol) of $AlCl_3$ 0.80 g (53%) of **6j** is obtained, b.p. 150°C/0.01 Torr. From 1.4 g (3 mmol) of **2c**, 0.80 g (8 mmol) of **4c**, and 1.1 g (8 mmol) of $AlCl_3$ 0.70 g (44%) of **6j** is obtained. – IR (KBr): $\tilde{\nu}$ = 3310 cm^{-1}, 1671, 1542. – ^1H NMR ($CDCl_3$): δ = 1.27 (m, 15H, CH_3, CH_2), 2.43 (m, 4H, $CH_{2allylic}$), 3.36 (m, 2H, CH_2), 6.53 (t, CH, $^3J_{HH}$ = 8.0 Hz), 8.86 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 13.8 (CH_3), 20.0, 25.0, 25.7, 26.3, 26.6, 28.8, 29.2, 31.2, 39.7 (all CH_2), 135.7 (CH), 137.1 (C), 166.8 (C=O). – MS, *m/z* (%): 209 (36) [M^+], 194 (31) [M^+ – NH], 180 (23) [M^+ – HCO], 166 (18) [M^+ – HNCO], 152 (19) [$C_8H_{13}CONH_2^+$], 137 (33) [$C_8H_{13}COH^+$], 109 (30) [$C_8H_{13}^+$], 100 (16) [$C_4H_9CO^+$], 67 (100) [$C_5H_7^+$]. – $C_{13}H_{23}NO$ (209.3): calcd. C 74.59, H 11.07, N 6.69; found C 74.3, H 11.0, N 6.6.

N-Butyl-(E)-β-styrenecarboxamide (**6k**): From 2.7 g (7.0 mmol) of **1d**, 0.70 g (7.0 mmol) of **4c**, and 0.90 g (7.0 mmol) of $AlCl_3$ 0.80 g (53%) of **6k** is obtained, b.p. 150°C/0.01 Torr. – IR (KBr): $\tilde{\nu}$ = 3364 cm^{-1}, 1672, 1539. – ^1H NMR ($CDCl_3$): δ = 1.17 (m, 7H, C_3H_7), 3.34 (m, 2H, CH_2), 6.63 (d, 1H, CH, $^3J_{HH}$ = 15.8 Hz), 7.34 (m, 5H, aromatic), 8.01 (d, 1H, CH, $^3J_{HH}$ = 15.8 Hz), 8.34 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 13.5 (CH_3), 19.9, 31.4, 39.3 (all CH_2), 121.3, 127.3, 128.3, 129.0 (all CH), 134.7 (C), 139.7 (CH), 166.2 (C=O). – MS, *m/z* (%): 203 (86) [M^+], 161 (16) [M^+ – NCO], 146 (15) [M^+ – C_4H_9], 131 (100) [PhCH=CHCOH$^+$], 103 (56) [PhCH=CH$^+$], 77 (31) [$C_6H_5^+$]. – $C_{13}H_{17}NO$ (203.3): calcd. C 76.81, H 8.43, N 6.89; found C 76.8, H 8.5, N 6.8.

General Procedure III: A solution of 4-methylphenylsulfonyl isocyanate (**5**) in 20 ml of anhydrous dichloromethane is treated under argon with aluminium trichloride at 20°C for 30 min. After adding the alkenyltrialkylstannane (**1d**–**f**) or the di-1-alkenyldibutylstannane (**2a**–**c**) the mixture is stirred under reflux for 20 h. The solution is hydrolysed with 50 ml of a cold saturated aqueous NH_4Cl solution. Separation of the organic layer is followed by twofold extraction of the aqueous layer with 20 ml of dichloromethane. After drying with $MgSO_4$ the solvent is removed in vacuo, and the crude product is recrystallized from the appropriate solvent.

N-(4-Methylphenylsulfonyl)-2-butenamide (**7a**): According to the general procedure III from 1.2 g (5.7 mmol) of **1a**, 1.1 g (5.5 mmol) of **5**, and 0.70 g (5.5 mmol) of $AlCl_3$ 1.2 g (90%) of **7a** (*E*/*Z* = 1.1:1) is obtained, b.p. 110°C/0.01 Torr. From 0.90 g (3.0 mmol) of **2a**, 1.5 g (8.0 mmol) of **5**, and 1.1 g (8 mmol) of $AlCl_3$ 1.0 g (72%) of **7a** (*E*/*Z* = 1:0.66) is obtained, m.p. 58–60°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1}, 1690, 1599, 1343, 1163. – ^1H NMR ([D_6]acetone): δ = 1.46 (dd, 3H, CH_{3E}, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.7 Hz), 1.70 (dd, 3H, CH_{3Z}, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.8 Hz), 2.04 (s, 3H, CH_3), 5.61 (qd, 1H, CH_Z, $^3J_{HH}$ = 11.4, $^4J_{HH}$ = 1.8 Hz), 5.71 (qd, 1H, CH_E, $^3J_{HH}$ = 15.3, $^4J_{HH}$ = 1.7 Hz), 6.01 (qd, 1H, CH_Z, $^3J_{HH}$ = 11.4, $^3J_{HH}$ = 7.3 Hz), 6.60 (qd, 1H, CH_E, $^3J_{HH}$ = 15.3, $^3J_{HH}$ = 7.0 Hz), 7.54 (m, 4H, aromatic), 10.27 (s, 1H, NH). – ^{13}C NMR ([D_6]acetone): δ = 15.3, 17.8, 21.3 (all CH_3), 120.0, 122.5, 127.9, 129.2 (all CH), 134.9 (C), 135.5 (C), 146.0 (CH), 147.5 (CH), 163.4 (C=O). – MS, *m/z* (%): 239 (3) [M^+], 175 (18) [M^+ – SO_2], 171 (22) [$TosNH_2^+$], 155 (45) [$H_3CC_6H_4SO_2^+$], 108 (100) [$H_3CC_6H_4NH_3^+$], 91 (90) [$CH_3C_6H_4^+$]. – $C_{11}H_{13}NO_3S$ (239.3): calcd. C 55.21, H 5.48, N 5.85; found C 55.1, H 5.6, N 6.0.

2-Methyl-N-(4-methylphenylsulfonyl)-2-butenamide (**7b**): According to the general procedure III from 1.2 g (5.5 mmol) of **1c**, 1.1 g (5.5 mmol) of **5**, and 0.70 g (5.5 mmol) of $AlCl_3$ 1.0 g (74%) of **7b** (*E*/*Z* = 1:3.7) is obtained, m.p. 62–63°C (*n*-pentane). From 1.0 g (3.0 mmol) of **2b**, 1.5 g (8.0 mmol) of **5**, and 1.1 g (8 mmol) of $AlCl_3$ 1.1 g (74%) of **7b** (*E*/*Z* = 1:3.5) is obtained, m.p. 62–64°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 3255 cm^{-1}, 1692, 1599, 1338, 1170. – ^1H NMR ([D_6]acetone): δ = 1.28 (d, 3H, CH_{3E}, $^3J_{HH}$ = 7.2 Hz), 1.36 (s, 3H, CH_{3E}), 1.37 (d, 3H, CH_{3Z}, $^3J_{HH}$ = 7.6 Hz), 1.45 (s, 3H, CH_{3Z}), 1.95 (s, 3H, CH_3), 5.35 (q, 1H, CH_E, $^3J_{HH}$ = 7.2 Hz), 6.28 (q, 1H, CH_Z, $^3J_{HH}$ = 7.6 Hz), 7.31 (m, 4H, aromatic), 10.05 (s, 1H, NH). – ^{13}C NMR ([D_6]acetone): δ = 11.6, 14.2, 15.2, 19.2, 21.4 (all CH_3), 128.2, 129.3 (all CH), 130.1 (C), 134.6 (CH), 135.5 (C), 144.8 (C), 166.4 (C=O). – MS, *m/z* (%): 235 (11) [M^+], 189 (29) [M^+ – SO_2], 155 (30) [$H_3CC_6H_4SO_2^+$], 108 (100) [$H_3CC_6H_4NH_3^+$], 91 (86) [$C_6H_5CH_2^+$], 83 (86) [$C_4H_7CO^+$], 55 (94) [C_4H_7]. – $C_{12}H_{15}NO_3S$ (253.3): calcd. C 56.90, H 5.97, N 5.53; found C 57.0, H 5.8, N 5.6.

N-(4-Methylphenylsulfonyl)-1-cyclooctene-1-carboxamide (**7c**): According to the general procedure III from 1.5 g (5.6 mmol) of **1e**, 1.1 g (5.5 mmol) of **5**, and 0.70 g (5.5 mmol) of $AlCl_3$ 0.80 g (48%) of **7c** is obtained, m.p. 126°C (*n*-pentane). From 1.4 g (3.0 mmol) of **2c**, 1.5 g (8.0 mmol) of **5**, and 1.1 g (8 mmol) of $AlCl_3$ 1.2 g (67%) of **7c** is obtained, m.p. 126°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 3245 cm^{-1}, 1694, 1599, 1342, 1161. – ^1H NMR ($CDCl_3$): δ = 1.38 (m, 8H, CH_2), 1.37 (m, 4H, $CH_{2allylic}$), 2.33 (s, 3H, CH_3), 6.68 (t, 1H, CH, $^3J_{HH}$ = 8.6 Hz), 7.56 (m, 4H, aromatic), 9.23 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 21.5 (CH_3), 24.6, 25.6, 26.2, 27.1, 28.6, 29.0 (all CH_2), 128.2 (CH), 129.4 (CH), 135.0 (C), 135.7 (C), 141.2 (CH), 144.6 (C), 165.8 (C=O). – MS, *m/z* (%): 307 (3) [M^+], 243 (1) [M^+ – SO_2], 152 (12) [$C_8H_{13}CONH^+$], 136 (16) [$C_8H_{12}CO^+$], 108 (100) [$C_8H_{12}^+$], 91 (35) [$PhCH_2^+$]. – $C_{16}H_{21}NO_3S$ (307.4): calcd. C 62.52, H 6.89, N 4.56; found C 62.5, H 6.8, N 4.5.

N-(4-Methylphenylsulfonyl)-3-phenyl-2-propenamide (**7d**): According to the general procedure III from 2.3 g (5.6 mmol) of **1d**, 1.1 g (5.5 mmol) of **5**, and 0.70 g (5.5 mmol) of $AlCl_3$ 1.5 g (91%) of **7d** is obtained, m.p. 118°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 3245 cm^{-1}, 1630, 1579, 1347, 1177. – ^1H NMR ($CDCl_3$): δ = 2.43 (s, 3H, CH_3), 6.50 (d, 1H, CH, $^3J_{HH}$ = 15.9 Hz), 7.55 (m, 9H, aromatic), 7.71 (d, 1H, CH, $^3J_{HH}$ = 15.9 Hz), 9.50 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 21.4 (CH_3), 117.6, 126.2, 128.2, 128.7, 129.5, 130.6 (all CH), 133.6, 135.6, 144.8 (all C), 145.7 (CH), 164.0 (C=O). – MS; *m/z* (%): 301 (6) [M^+], 237 (39) [M^+ – SO_2], 131 (91) [C_6H_5CH=CHCO$^+$], 108 (100) [$H_3CC_6H_4NH_3^+$], 103 (80) [C_6H_5CH=CH$^+$], 91 (66) [$H_3CC_6H_5^+$], 77 (71) [$C_6H_5^+$]. – $C_{16}H_{15}NO_2S$ (301.4): calcd. C 63.77, H 5.02, N 4.65; found C 63.8, H 5.0, N 4.5.

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