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Palladium(0)-Catalyzed Allylation of Highly Acidic and Non-nucleophilic Arenesulfonamides, Sulfamide, and Cyanamide. I.

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Abstract:

Arenesulfonamides, sulfamide, and cyanamide are efficiently allylated using allylic carbonates under Pd(0)-catalysis. *N*-Arenesulfonyl-2,5-dihydropyrroles are obtained by ruthenium-mediated ring closing metathesis of the corresponding *N*-diallylated compounds. A stereochemical study of the reactions of ethyl *cis*-(5-methyl-2-cyclohexenyl) carbonate with 2,4,6-triisopropylphenylsulfonamide was performed, clean overall retention of configuration being found with bidentate phosphines.

Keywords: Allylation; Catalysis; Palladium; Stereochemistry

The palladium(0)-catalyzed allylation of nucleophiles (the Tsuji-Trost reaction) is a synthetic method highly accepted due to its broad applicability and facile experimental procedure [1-13]. The catalytic cycle (Scheme 1) requires the formation of the cationic η^3-allylpalladium(II) complex, **2**, an intermediate which can be attacked by nucleophiles at both termini of the allylic system. Intermediate **2** is formed by reaction of Pd(0), **1**, generally stabilized by phosphine ligands, with an allyl system featuring a leaving group. Allylic carbonates are very useful as substrates since ethoxycarbonyloxy leaving group decomposes into CO_2 and ethoxide anion [14]. This is basic enough to take a proton from certain pronucleophiles generating *in situ* the actual nucleophilic species (Nu^-). Therefore, an allylation ensues taking place formally in neutral medium. Moreover, the reactions are usually carried out in THF solvent. Acidities in THF parallel acidities in other aprotic solvents such as DMSO and the order of acidities in DMSO is different from that in water [15-18]. Thus, in DMSO nitroanilines are more acidic than in methanol, and we have described the Pd-catalyzed allylation of acidic anilines using allylic carbonates [19] (pK_a values in DMSO of anilines [15]: diphenylamine: 24.95; phenothiazine: 22.7; 4-nitroaniline: 20.9; 2,4-dinitroaniline: 15.9, as compared with methanol: 29.0). The reactions are very efficient and take place with overall retention of configuration, two consecutive inversions each step of the catalytic cycle.

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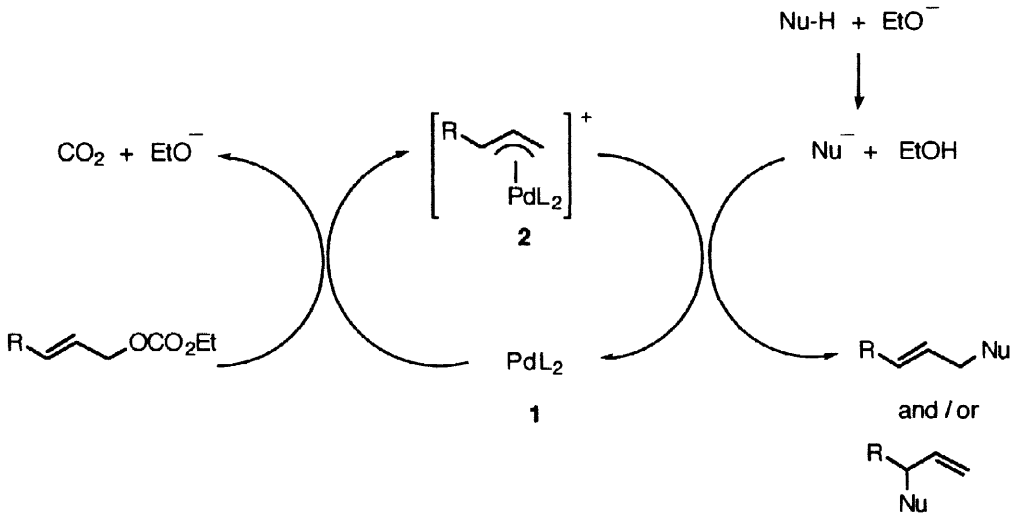
Scheme 1. General mechanistic scheme for the Pd(0)-catalyzed allylation of allylic carbonates.



Other N-H compounds are more acidic than alcohols in DMSO, and therefore in THF. Since as free bases they are only weakly or not at all nucleophilic, we decided to study their Pd-catalyzed reaction with allylic carbonates. The chosen nucleophiles were arenesulfonamides **3** (pK_a (DMSO) $PhSO_2NH_2$: 16.1 [15] or 15.16 [18], *p*-$MeC_6H_4SO_2NH_2$: 15.58 [18], *p*-$MeOC_6H_4SO_2NH_2$: 15.88 [18], and cyanamide **5**: 16.9 [15].

Some Pd-catalyzed allylations of *p*-toluenesulfonamide **3a** are known, mainly in the form of its sodium salt [20, 21, 22, 23], although the combination pronucleophile + allylic carbonate [24, 25, 26] or 2-allylisourea [27] has some precedents. Also the Pd-catalyzed reaction of several arenesulfonamides with allyl alcohol [28] and other allylic derivatives [29] have been described. 2-Methylene-1,3-propanediol biscarbonate has been reported to react with **3a** to afford polymers and cyclic oligomers [30] (see accompanying paper). The reactions with stereochemically defined allylic systems occur with overall retention of configuration [20, 22, 23, 24]. To the best of our knowledge no Pd-catalyzed allylations of sulfamide and cyanamide have been ever reported. Although reactions of sulfamide with carbonyl groups and with nitriles are well precedented [31, 32, 33, 34, 35], this is not so for alkylations, and substituted sulfamides are best prepared by nucleophilic attack of amines on the sulfur atom with elimination of ammonia [36, 37, 38]. Only few conventional alkylations of cyanamide have been described [39, 40, 41].

Double Pd-catalyzed allylations were performed with arenesulfonamides **3a-f** featuring both electron-donating and electron-withdrawing substituents at the aromatic ring. *N,N*-Diallylarenesulfonamides **11** were obtained in excellent yield in all cases (Scheme 2 and Table 1). Efficient allylation reaction were observed for the sterically demanding 2,4,6-triisopropylbenzenesulfonamide **3e** and for 1-naphthalenesulfonamide **3f**. The secondary cyclic mixed carbonate **9** was also very reactive towards **3a** and **3e**, the only arenesulfonamides tested, introduction of only one cyclohexenyl group being easily achieved. The reaction of **3e** with **9** is remarkable, as both nucleophile and electrophile are sterically hindered (Scheme 2).

Ring closing metathesis was performed on products **11** under catalysis by the Grubbs ruthenium carbene compound [42, 43, 44, 45, 46, 47]. In all cases *N*-arenesulfonyl-2,5-dihydropyrroles **12** were obtained in excellent yield (Scheme 2 and Table 1); these

compounds **12** could not be obtained by reaction of arenesulfonamides with butene-1,4-diol dicarbonate (see accompanying paper).

Scheme 2. Allylation of arenesulfonamides **3** and preparation of dihydropyrroles **12**

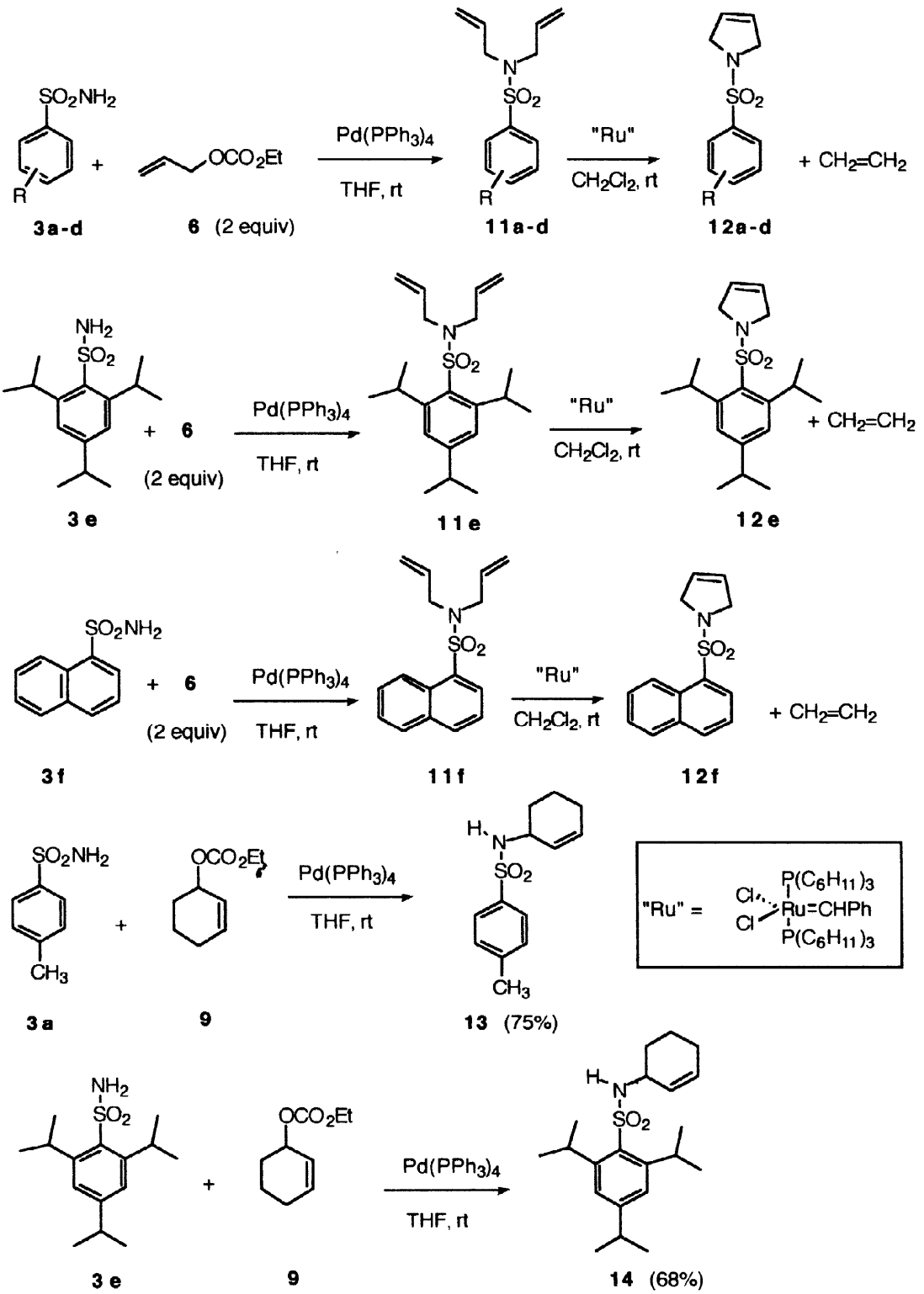


Table 1.
Compounds **11** and **12**.

Entry	R	**11** (%)[a]	**12** (%)[a]
1	4-Me	**11a** (93)	**12a** (91)
2	2-Me	**11b** (90)	**12b** (92)
3	4-MeO	**11c** (87)	**12c** (82)
4	2-NO_2	**11d** (75)	**12d** (94)
5	see Scheme 2	**11e** (89)	**12e** (91)
6	see Scheme 2	**11f** (88)	**12f** (77)

[a] Yield of isolated pure compounds.

Depending on the nature of the nucleophile, two different types of stereochemical behavior have been identified in Pd-catalyzed allylations; thus, the first step is the formation of the cationic η^3-allylpalladium(II) intermediate which occurs with inversion of configuration on the allyl system as a rule [48, 49] but not without exception [50, 51, 52]. Many common nucleophiles attack the cationic palladium intermediate with a second inversion of configuration, thus affording the final product with overall retention of configuration [1-13]. On the other hand, nucleophiles such as organometallics of the type C-Metal (Metal = Mg, Al, Zr, Sn, B) bind to the palladium in a transmetallation step followed by intramolecular delivery or reductive elimination which takes place with retention of configuration. This results in overall inversion of configuration [1-13]. 5-Substituted cyclohexenyl systems of type **10** have been used as stereochemical probes in Pd-catalyzed allylations [53, 54]. However, a correct interpretation of the results should take into account, apart from any possible retention of configuration in the second step, two different mechanisms of isomerization of starting materials and cationic intermediates:

1. Equilibration of the isomeric starting materials (Pathway A in Scheme 3). The leaving group X^- from *cis* cyclohexene isomer attaches to Pd in the *trans* cationic intermediate to give a neutral *trans* complex, which by reductive elimination completes the isomerization to *trans* cyclohexene. Of course this process works in the other direction. Isomerization of cyclic allylic acetates (X = OAc) [48, 55, 56, 57, 58, 59, 60] and carbonates (X = OCO_2R) [19, 61] have been proved.

2. Cationic intermediate isomerization by nucleophilic attack of Pd, or rather PdL_2, to *trans* cationic complex with inversion of configuration (S_N2 type mechanism) to afford *cis* cationic complex and the other way around (Pathway B in Scheme 3). Convincing evidence for the operation of this mechanism has been given by Bäckvall [55, 56] and the cationic intermediate equilibration mechanism has been invoked by us [59] and others [62, 63, 64].

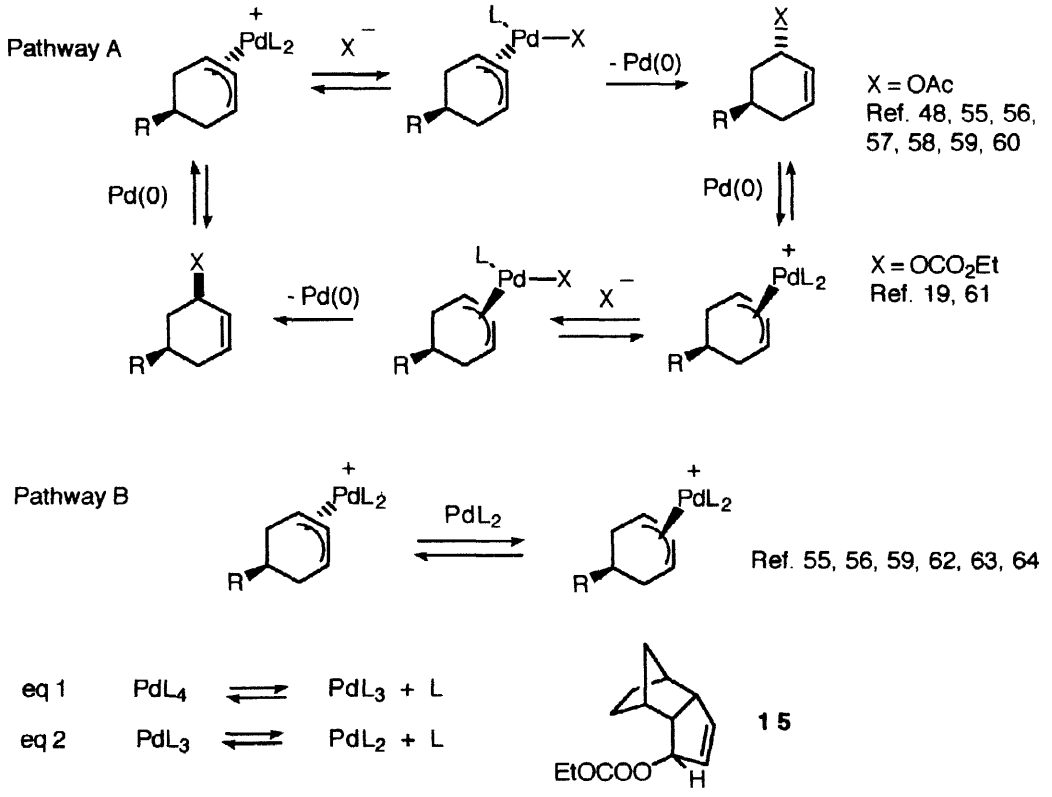
Other important factors to consider concerning the stereochemical outcome of the Pd-catalyzed allylation of nucleophiles are the nature (mono- or bidentate) of the stabilizing phosphine, the leaving group ability, and the nucleophilic strength. A summary of the situation is as follows:

1. Bidentate phosphines give much clearer overall retention of stereochemistry, since they do not easily permit bonding of the leaving group or of the incoming nucleophile to the palladium atom. This militates against starting material equilibration and against retention of configuration in the second step [55, 56, 57, 59, 63, 64, 65, 66]. On the other hand, the cationic intermediate equilibration is slow with bidentate phosphines [56]. For monodentate phosphines a high phosphine:Pd ratio has the same effect [48, 59].

2. Good leaving groups (*eg* trifluoroacetoxy *vs* acetoxy) cause all palladium to be present in the form of cationic complex, no palladium remaining outside the allylic framework as PdL_n, and therefore rendering the S_N2 type mechanism less operative [55, 56, 57, 62].

3. Active nucleophiles reacting fast give less opportunity for starting materials and/or cationic intermediates equilibration to occur [48, 58].

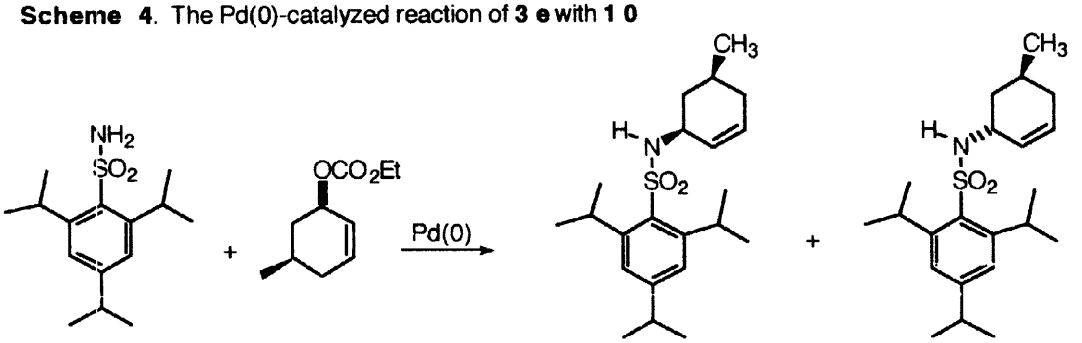
Scheme 3. Equilibration pathways leading to stereochemical scrambling



The stereochemical results obtained with arenesulfonamide **3e** and the stereochemically defined **10** are in Scheme 4 and Table 2. Clean overall retention of configuration was observed when using bidentate phosphine (entries 5-7). When using triphenylphosphine stereochemical scrambling was observed. Carbonate **10** equilibrates fast with its *trans* isomer in THF at room temperature (Pathway A in Scheme 3) [19]. However, the ratio overall retention/overall inversion increases with the ratio phosphine/Pd (entries 1-4), thus indicating the participation of pathway B. Concentration of PdL_2 required in Pathway B depends on the position of equilibria in eq 1 and 2 (Scheme 3) and it is diminished by increasing the overall quantity of L. Indeed, a low concentration of PdL_2 will also slow down the formation of *trans* cationic intermediate but simple kinetic considerations lead to the conclusion that equilibration of cationic intermediates should be more sensitive to $[PdL_2]$ since PdL_2 acts consecutively twice for the equilibrium of intermediates to be reached [59]. Then, we prepared carbonate **15**; its related acetate has been reported to react only by the overall inversion pathway (inversion + retention) since an inversion in the second step is hampered by steric constraints [67]. Carbonate **15** did not react with arenesulfonamides **3a,e** under a wide range of forcing experimental conditions with temperatures up to 120 °C,

including mono- and bidentate phosphines, giving further evidence that the overall retention pathway is predominant if not exclusive.

Scheme 4. The Pd(0)-catalyzed reaction of **3 e** with **1 0**



3 e **1 0** ***cis*-16** ***trans*-16**

Table 2.
Stereochemical study of the Pd-catalyzed reactions of **3 e** with **1 0**.[a]

Entry	**1 0/3 e**	Catalyst (%)	Total P (%)	Temp (°C)	Time (h)	% **16**[b]	***cis*-16/*trans*-16**[b]
1[c]	1.6	$Pd(PPh_3)_4$ (5)	20[d]	rt	24	82[c]	0.8
2	1.6	$Pd(PPh_3)_4$ (5)	40[d]	rt	72	65	1.8
3	1.6	$Pd(PPh_3)_4$ (5)	100[d]	rt	72	50	4.6
4	1.6	$Pd(PPh_3)_4$ (5)	140[d]	rt	72	40	12.3
5	1.6	$Pd(dba)_2$ (5)	10[e]	rt	72	73	19.0
6[c]	1.6	$Pd(dba)_2$ (5)	10[e]	rt	48	72[c]	27.0
7	1.6	$Pd(dba)_2$ (5)	20[e]	rt	72	76	13.0

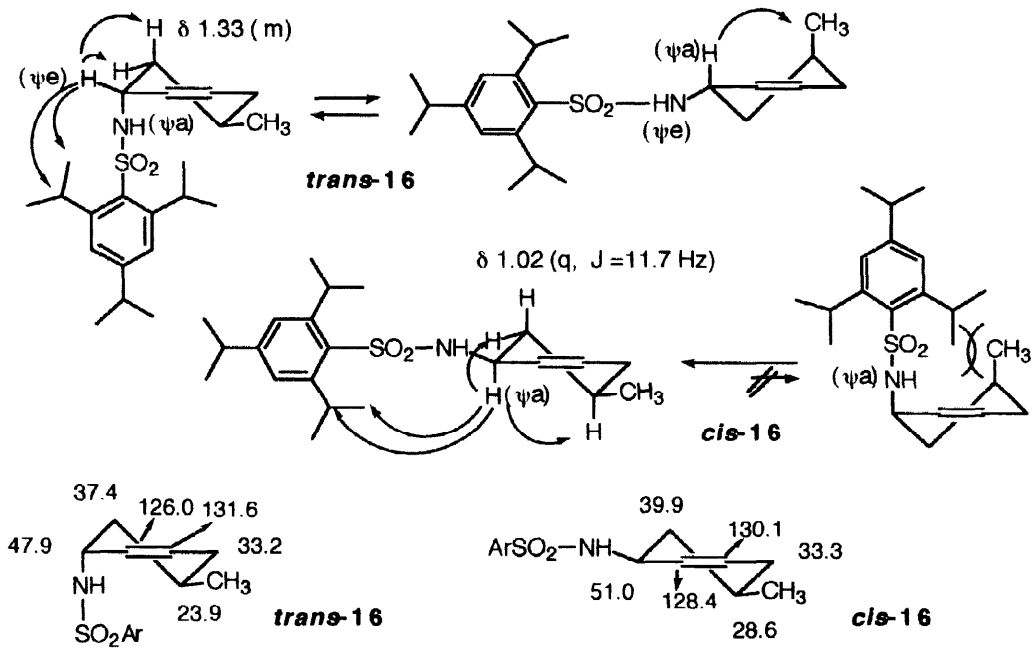
[a] [**3 e**] = 0.56 M in THF in all cases.
[b] GLC areas, sulfonamide **3 e** and possible diallylation products account for the difference to 100%.
[c] Preparative reactions. Yields of isolated products.,
[d] Added PPh_3 + catalyst.
[e] In the form of dppe (5% dppe = 10% P).

The mechanistic conclusions rely upon the correct assignment of configuration to pairs of isomers ***cis*-16** and ***trans*-16**. This was done by standard NMR correlations to assign all signals in each isomer, and by NOE measurements. The results are summarized in Scheme 5, and are in agreement with the reported conformational behavior of substituted cyclohexenes [58, 59, 68, 69, 70] and with previous stereochemical assignments to pairs of *cis*- and *trans*-3,5-disubstituted cyclohexenes [48, 53, 56, 59, 63, 71, 72].

Sulfamide **4** reacts also with allylic carbonates without addition of external base (Scheme 6 and Table 3). However, the reactions are difficult to control and, if ratios carbonate/sulfamide <4 are used, mixtures of many possible alkylation products are produced (**17-19**). Tetrasubstituted sulfamides **17e** and **19e** were efficiently prepared by adding an excess of alkylating reagent. The nucleophile has to be added to the mixture of allylic carbonate, palladium catalyst and solvent. Sulfamide forms an insoluble complex with the catalyst, which prevents further allylation if allylic carbonate is the last reagent added.

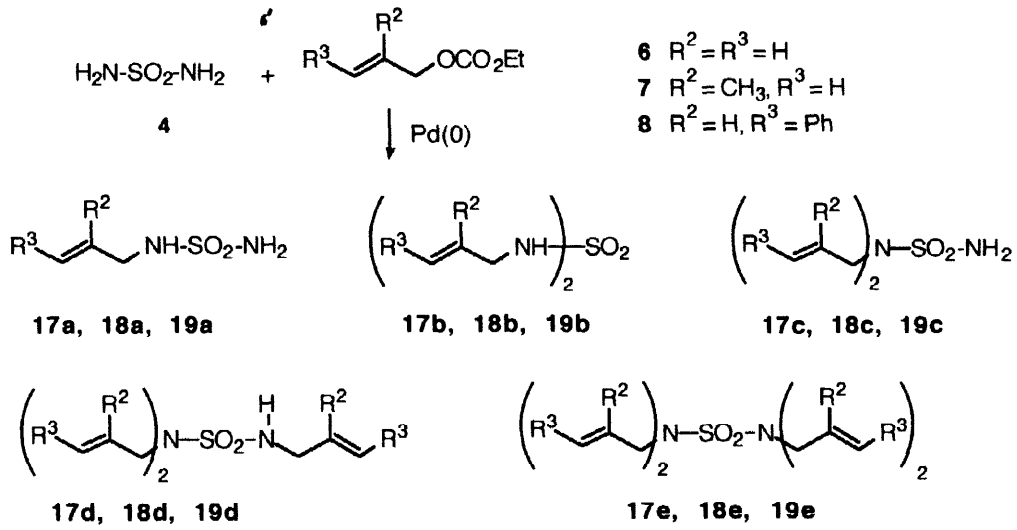
Similar results are observed for cyanamide **5**. By adding no less than two equivalents of allylic carbonate, disubstituted cyanamides **20**, **21**, and **22** can be efficiently prepared (Scheme 7 and Table 3).

Scheme 5. Main spectroscopic data for ***cis*-16** and ***trans*-16**. Curved arrows indicate positive NOE.



Two palladium catalytic systems have been successfully used for this nucleophile: $Pd(PPh_3)_4$ (entries 8, 9, 11, 12, and 13 in Table 3) and $Pd(dba)_2$/dppf (entry 10 in Table 3). When the reaction of **5** with carbonate **7** was performed in refluxing tetrahydrofuran instead of at room temperature as in other cases, *N*,*N*'-di(2-methylallyl)carbodiimide **23** was also obtained (11%) together with **21** (80%) (entry 12, Table 3). Minor amounts of monoallylated compounds **24** and **25** were also detected even when excess of cinnamyl ethyl carbonate was used. For an efficient preparation of **22** and minimization of the amount of monoallylation products the order of addition was crucial. A solution containing the cyanamide **5** has to be added to the mixture of allylic carbonate, palladium catalyst, and solvent (entry 13, Table 3).

Scheme 6. Pd(0)-catalyzed allylations of sulfamide **4** with allylic carbonates



Scheme 7. Pd(0)-catalyzed allylations of cyanamide **5** with allylic carbonates

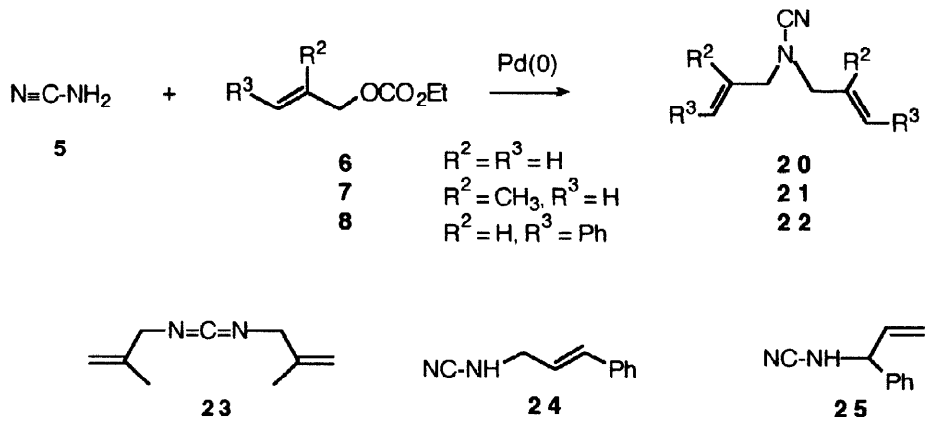


Table 3
Pd(0)-catalyzed allylation of sulfamide **4** and cyanamide **5**.[a]

Entry	Nucleophile [ ]	Carbonate	Ratio carbonate/ nucleophile	Catalyst (%)	Temp (°C)	Time (h)	Products (%)[b]
1	**4** (0.1 M)	**6**	2.0	$Pd(PPh_3)_4$ (4)	rt	4	**17a** (11); **17b** (5); **17c** (15); **17d** (9); **17e** (22)
2	**4** (0.1 M)	**6**	4.0	$Pd(PPh_3)_4$ (4)	rt	24	**17b** (2); **17c** (4); **17d** (8); **17e** (58)
3	**4** (0.5 M)	**6**	5.0	$Pd(PPh_3)_4$ (4)	rt	24	**17b** (2); **17c** (4); **17d** (5); **17e** (64)
4	**4** (0.13 M)	**7**	4.4	$Pd(PPh_3)_4$ (5)	rt	15	**18e** (75)
5	**4** (0.08 M)	**8**	1.0	$Pd(PPh_3)_4$ (5)	rt	8	**19a** (33); **19b** (17); **19e** (3)
6	**4** (0.08 M)	**8**	2.0	$Pd(PPh_3)_4$ (4)	rt	24	**19a** (5); **19b** (3); **19e** (73)
7	**4** (0.25 M)	**8**	5.0	$Pd(PPh_3)_4$ (3)	rt	24	**19e** (85)
8	**5** (0.1 M)	**6**	5.0	$Pd(PPh_3)_4$ (5)	rt	5	**20** (79)
9	**5** (0.1 M)	**6**	3.0	$Pd(PPh_3)_4$ (5)	rt	15	**20** (69)
10	**5** (0.1 M)	**6**	2.4	$Pd(dba)_2$ (5) dppf (5)	rt	15	**20** (87)
11	**5** (0.1 M)	**7**	3.0	$Pd(PPh_3)_4$ (4)	rt	72	**21** (88)
12	**5** (0.1 M)	**7**	2.9	$Pd(PPh_3)_4$ (4)	reflux	15	**21** (80); **23** (11)
13	**5** (0.13 M)	**8**	2.3	$Pd(PPh_3)_4$ (4)	rt	14	**22** (65); **24** (5); **25** (6)

[a] THF was the solvent used in all experiments.
[b] Yiels of isolated compounds calculated with respect to initial amount of nucleophile.

Experimental

All reactions were carried out under nitrogen atmosphere. The solvents were distilled and stored under nitrogen. ^1H NMR (^{13}C NMR) spectra were recorded at 250 MHz (62.5 MHz) using Me_4Si as internal standard. NOE spectra were recorded at 400 MHz. Chemical shifts are given in δ units. Mass spectra were recorded under electron impact at 70 eV. The carbonates were prepared using known procedures.

N,N-Diallyl-2-methylbenzenesulfonamide 11b (General Method).
A solution of allyl ethyl carbonate **6** (1.05 g, 8.08 mmol) in degassed anhydrous THF (3 mL) was added to a mixture of 2-methylbenzenesulfonamide **3b** (0.63 g, 3.68 mmol), $Pd(PPh_3)_4$ (0.25 g, 0.22 mmol) and degassed anhydrous THF (2 mL) kept under nitrogen atmosphere. The mixture was stirred at room temperature for 5 h (TLC monitoring). The solvent was evaporated to give a residue which was chromatographed through a column of silica gel with hexanes-ethyl acetate (9:1) to afford **11b** (0.83 g, 90%) [27] as a colorless oil; bp 175-180 °C (bulb-to-bulb distillation)/3 mm Hg; IR (film): 1322, 1158 cm^{-1}; ^1H NMR ($CDCl_3$): 2.61 (s, 3H), 3.83 (d, J = 6.6 Hz, 4H), 5.11-5.20 (m, 4H), 5.65 (ddt, J = 16.8 Hz, 10.2 Hz, 6.6 Hz, 2H), 7.27-7.34 (m, 2H), 7.40-7.49 (m, 1H), 7.93-7.99 (m, 1H); ^{13}C NMR ($CDCl_3$): 20.2, 48.3, 119.1, 125.9, 129.7, 132.4, 132.5, 137.4, 138.0; MS (*m/z*, %): 251 (M^+, 1), 155 (21), 96 (41), 91 (100), 41 (52). Anal.: Calcd. for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57; Found: C, 62.14 and 62.31; H, 6.74 and 6.58; N, 5.63 and 5.66.

N,N-Diallyl-4-methylbenzenesulfonamide 11a.
It was obtained in 93% yield (colorless oil) from 4-methylbenzenesulfonamide **3a** and allyl ethyl carbonate **6** as for **11b**. Bp 190 °C (bulb-to-bulb distillation)/3-4 mm Hg (Lit. [73] bp 85-87 C°/0.01 mm Hg); IR (film): 1345, 1160 cm^{-1}; ^1H NMR ($CDCl_3$): 2.39 (s, 3H), 3.77 (d, J = 6.6 Hz, 4H), 5.10 (m, 4H), 5.58 (ddt, J = 17.5 Hz, 10.2 Hz, 6.6 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): 21.4, 49.2, 118.8, 127.1, 129.6, 132.6, 137.3, 143.1; MS (*m/z*, %): 251 (M^+, 8), 155 (55), 91 (100), 41 (53). Anal.: Calcd. for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57; Found: C, 61.87 and 62.17; H, 6.28 and 6.36; N, 5.58 and 5.45.

N,N-Diallyl-4-methoxybenzenesulfonamide 11c.
It was obtained in 87% yield (colorless oil) from 4-methoxybenzenesulfonamide **3c** and allyl ethyl carbonate **6** as for **11b**. Bp 200-220 °C (bulb-to-bulb distillation)/3 mm Hg; IR (film): 1344, 1260, 1154 cm^{-1}; ^1H NMR ($CDCl_3$): 3.75 (d, J = 5.8 Hz, 4H), 3.83 (s, 3H), 5.00-5.15 (m, 4H), 5.59 (ddt, J = 17.5 Hz, 9.5 Hz, 5.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): 49.3, 55.5, 114.1, 118.8, 129.2, 132.0, 132.7, 162.7; MS (*m/z*, %): 267 (M^+, 12), 240 (9), 171 (100), 107 (64), 96 (99).

N,N-Diallyl-2-nitrobenzenesulfonamide 11d.
It was obtained in 75% yield (colorless oil) from 2-nitrobenzenesulfonamide **3d** and allyl ethyl carbonate **6** as for **11b**. Bp 220-230 °C (bulb-to-bulb distillation)/0.5 mm Hg (Lit. [74] bp 200 °C/0.12 mm Hg); IR (film): 1544, 1370, 1352, 1161 cm^{-1}; ^1H NMR ($CDCl_3$): 3.93 (d, J = 6.6 Hz, 4H), 5.10-5.23 (m, 4H), 5.66 (ddt, J = 16.1 Hz, 10.2 Hz, 6.6 Hz, 2H), 7.62-7.72 (m, 3H), 8.00-8.10 (m, 1H); ^{13}C NMR ($CDCl_3$): 49.1, 119.4, 124.1, 130.8, 131.7, 132.1, 133.5, 133.7, 147.8; MS (*m/z*, %): 283 (M^+ + 1, 0.3), 255 (1), 209 (25), 186 (59), 96 (45), 41 (100).

N,N-Diallyl-2,4,6-triisopropylbenzenesulfonamide 11e.
It was obtained in 89% yield (colorless oil) from 2,4,6-triisopropylbenzenesulfonamide **3e** and allyl ethyl carbonate **6** as for **11b**. Bp 230 °C (bulb-to-bulb distillation)/3-4 mm Hg; IR (film): 1317, 1152 cm^{-1}; ^1H NMR ($CDCl_3$): 1.23 (d, J = 6.6 Hz, 18H), 2.87 (septet, J = 6.6 Hz, 1H), 3.77 (d, J = 6.6 Hz, 4H), 4.13 (septet, J = 6.6 Hz, 2H), 5.10-5.20 (m, 4H), 5.70 (ddt, J = 16.8 Hz, 10.2 Hz, 6.6 Hz, 2H), 7.13 (s, 2H); ^{13}C NMR ($CDCl_3$): 23.5, 24.8, 29.2,

34.1, 47.7, 119.4, 123.8, 131.3, 132.7, 151.4, 153.0; MS (*m/z*, %): 267 (M^+ - 96, 24), 187 (13), 97 (100), 82 (60). Anal.: Calcd. for $C_{21}H_{33}NO_2S$: C, 69.38; H, 9.15; N, 3.85; Found: C, 69.45 and 69.73; H, 8.85 and 8.83; N, 4.02 and 4.09.

N,N-Diallyl-1-naphthalenesulfonamide 11f.
It was obtained in 88% yield (colorless oil) from 1-naphthalenesulfonamide **3f** and allyl ethyl carbonate **6** as for **11b**. Bp 230-240 °C (bulb-to-bulb distillation)/3 mm Hg; IR (film): 1324, 1160, 1131 cm^{-1}; ^1H NMR ($CDCl_3$): 3.90 (d, J = 6.6 Hz, 4H), 5.00-5.14 (m, 4H), 5.57 (ddt, J = 17.5 Hz, 10.9 Hz, 6.6 Hz, 2H), 7.45-7.68 (m, 3H), 7.92 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 7.3 Hz, 1H), 8.63 (d, J = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): 48.5, 119.2, 124.0, 124.9, 126.8, 128.0, 128.5, 128.9, 130.1, 132.5, 134.2, 135.0; MS (*m/z*, %): 287 (M^+, 7), 191 (10), 127 (100), 96 (89). Anal.: Calcd. for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87; Found: C, 66.79 and 67.13; H, 5.84 and 5.89; N, 4.63 and 4.58.

2,5-Dihydro-1-[(2-methylphenyl)sulfonyl]-1*H*-pyrrole 12b (General Method).
A solution of **11b** (0.50 g, 1.99 mmol) in anhydrous CH_2Cl_2 (15 mL) was added to a homogeneous orange-red solution of $RuCl_2(=CHPh)(PCy_3)_2$ (0.06 g, 0.07 mmol) in anhydrous CH_2Cl_2 (25 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 6 h (TLC monitoring). The reaction mixture was quenched by exposure to air for 2 h. The solvent was evaporated to give a residue which was chromatographed through a column of silica gel with hexanes-ethyl acetate (9:1) to afford **12b** (0.41 g, 92%) as a colorless solid; mp 81-82 °C (pentane); IR (KBr): 1318, 1155 cm^{-1}; ^1H NMR ($CDCl_3$): 2.66 (s, 3H), 4.20 (s, 4H), 5.78 (s, 2H), 7.29-7.48 (m, 3H), 7.80 (d, J = 8.0 Hz, 1H); ^{13}C ($CDCl_3$): 20.4, 54.5, 125.4, 126.0, 128.5, 132.5, 132.8, 137.3, 137.8; MS (*m/z*, %): 223 (M^+, 4), 155 (9), 91 (69), 68 (100). Anal.: Calcd. for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27; S, 14.36; Found: C, 59.14 and 58.97; H, 6.10 and 6.05; N, 6.26 and 6.01; S, 14.25 and 14.17.

2,5-Dihydro-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrrole 12a.
It was obtained in 91% yield (colorless solid) from **11a** as for **12b**. Mp 130-131°C (hexane) (Lit. [75] mp 117-118°C); IR (KBr): 1338, 1161 cm^{-1}; ^1H NMR ($CDCl_3$): 2.42 (s, 3H), 4.12 (s, 4H), 5.65 (s, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): 21.5, 54.8, 125.4, 127.4, 129.7, 134.3, 143.4; MS (*m/z*, %): 223 (M^+, 18), 155 (27), 91 (76), 68 (100); Anal.: Calcd. for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27; S, 14.36; Found: C, 59.15 and 59.17; H, 5.83 and 6.02; N, 6.33 and 6.31; S, 14.15 and 14.12.

2,5-Dihydro-1-[(4-methoxyphenyl)sulfonyl]-1*H*-pyrrole 12c.
It was obtained in 82% yield (colorless solid) from **11c** as for **12b**. Mp 105-106 °C (cyclohexane); IR (KBr): 1340, 1262, 1160 cm^{-1}; ^1H NMR ($CDCl_3$): 3.87 (s, 3H), 4.11 (s, 4H), 5.65 (s, 2H), 6.98 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): 54.8, 55.5, 114.2, 125.4, 128.9, 129.4, 162.9; MS (*m/z*, %): 239 (M^+, 17), 171 (65), 123 (36), 107 (46), 77(38), 68 (100); Anal.: Calcd. for $C_{11}H_{13}NO_3S$: C, 55.21; H, 5.47; N, 5.85; S, 13.40; Found: C, 55.13 and 55.17; H, 5.63 and 5.71; N, 5.83 and 5.81; S, 13.22 and 13.25.

2,5-Dihydro-1-[(2-nitrophenyl)sulfonyl]-1*H*-pyrrole 12d.

It was obtained in 94% yield (colorless solid) from **11d** as for **12b**. Mp 125-126 °C (hexane-ethyl acetate); IR (KBr): 1538, 1362, 1335, 1163, 1138 cm^{-1}; ^1H NMR ($CDCl_3$): 4.30 (s, 4H), 5.77 (s, 2H), 7.60-7.74 (m, 3H), 7.95-8.00 (m, 1H); ^{13}C NMR ($CDCl_3$): 54.9, 124.1, 125.2, 130.2, 131.6, 132.1, 133.5, 148.3; MS (*m/z*, %): 255 (M^+ + 1, 1), 219 (34), 186 (33), 77 (54), 68 (100), 41 (71). Anal.: Calcd. for $C_{10}H_{10}N_2O_4S$: C, 47.24; H, 3.96; N, 11.02; S, 12.61; Found: C, 46.89 and 46.86; H, 3.86 and 3.95; N, 10.89 and 10.87; S, 12.48 and 12.42.

2,5-Dihydro-1-[(2,4,6-triisopropylphenyl)sulfonyl]-1*H*-pyrrole 12e.
It was obtained in 91% yield (colorless solid) from **11e** as for **12b**. Mp 97-98 °C (hexane); IR (KBr): 1316, 1160 cm^{-1}; ^1H NMR ($CDCl_3$): 1.24 (d, J = 6.6 Hz, 12H), 1.25 (d, J = 6.6 Hz, 6H), 2.90 (septet, J = 6.6 Hz, 1H), 4.10 (s, 4H), 4.23 (septet, J = 6.6 Hz, 2H), 5.75 (s, 2H), 7.16 (s, 2H); ^{13}C NMR ($CDCl_3$): 23.5, 24.8, 29.3, 34.1, 53.5, 123.8, 125.3, 131.6, 151.2, 152.9; MS (*m/z*, %): 267 (M^+ - 68, 22), 69 (100); Anal.: Calcd. for $C_{19}H_{29}NO_2S$: C, 68.02; H, 8.71; N, 4.17; S, 9.55; Found: C, 68.22 and 68.14; H, 8.69 and 8.63; N, 4.30 and 4.19; S, 9.28 and 9.30.

2,5-Dihydro-1-(naphthalenesulfonyl)-1*H*-pyrrole 12f.
It was obtained in 77% yield (colorless solid) from **11f** as for **12b**. Mp 128-129 °C (hexane-ethyl acetate); IR (KBr): 1325, 1177, 1100 cm^{-1}; ^1H NMR ($CDCl_3$): 4.24 (s, 4H), 5.72 (s, 2H), 7.45-7.71 (m, 3H), 7.92 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.13 (dd, J = 7.3 Hz, 1.5 Hz, 1H), 8.83 (d, J = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): 54.5, 124.0, 125.0, 125.2, 126.8, 127.9, 128.5, 128.7, 128.9, 134.0, 134.3; MS (*m/z*, %): 259 (M^+, 20), 191 (6), 127 (80), 68 (100). Anal.: Calcd. for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40; S, 12.36; Found: C, 65.08 and 65.23; H, 5.28 and 5.20; N, 5.50 and 5.57; S, 11.91 and 12.07.

***N*-(2-Cyclohexenyl)-4-methylbenzenesulfonamide 13.**
A solution of 2-cyclohexenyl ethyl carbonate **9** (1.23 g, 7.2 mmol) in degassed anhydrous THF (4 mL) was added to a mixture of 4-toluenesulfonamide **3a** (1.03 g, 6.0 mmol), $Pd(PPh_3)_4$ (0.35 g, 0.3 mmol) and degassed anhydrous THF (8 mL) kept under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h (TLC monitoring). The solvent was evaporated to give a residue which was chromatographed through a column of silica gel with hexanes-ethyl acetate (8:2) to recover 19% of starting material **3a** and to afford **13** (1.13 g, 75%); Mp 108-109 °C (pentane); IR (KBr): 3273, 1321, 1159 cm^{-1}; ^1H NMR ($CDCl_3$): 1.43-1.80 (m, 4H), 1.89 (apparent s, 2H), 2.40 (s, 3H), 2.79 (m, 1H), 4.68 (d, J = 16.3 Hz, 1H, NH), 5.31 (dd, J = 10.2 Hz, 3.7 Hz, 1H), 5.72 (m, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): 19.2, 21.4, 24.3, 30.0, 48.8, 126.8, 126.9, 129.5, 131.3, 138.2, 143.1. Anal.: Calcd. for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.27 and 62.24; H, 6.35 and 6.45; N, 5.46 and 5.46.

***N*-(2-Cyclohexenyl)-2,4,6-triisopropylbenzenesulfonamide 14.**
Obtained in 68% yield from **3e** and **9** as for **13**. Mp 124-125 °C (pentane); IR (KBr): 3311, 1320, 1149 cm^{-1}; ^1H NMR ($CDCl_3$): 1.21-1.28 (m, 18H), 1.56 (m, 3H), 1.78 (m, 1H), 1.93 (apparent s, 2H), 2.88 (septet, J = 6.6 Hz, 1H), 3.89 (m, 1H), 4.14 (septet, J = 6.6 Hz, 2H), 4.33 (d, J = 8.0 Hz, 1H, NH), 5.42 (dd, J = 9.5 Hz, 2.2 Hz, 1H), 5.76 (m, 1H), 7.13 (s, 2H); ^{13}C NMR ($CDCl_3$): 19.4, 23.5, 24.5, 24.8, 29.6, 30.3, 34.1, 48.6, 123.7, 127.5, 131.3,

133.7, 150.0, 152.6. Anal.: Calcd. for $C_{21}H_{33}NO_2S$: C, 69.38; H, 9.15; N, 3.85. Found: C, 69.68 and 69.41; H, 8.86 and 8.97; N, 3.84 and 3.84.

Reaction of 2,4,6-triisopropylbenzenesulfonamide 3e with ethyl *cis*-5-methyl-2-cyclohexenyl carbonate 10 with $Pd(PPh_3)_4$ as catalyst (entry 1, Table 2).
A solution of **10** [59] (0.83 g, 4.51 mmol) in degassed anhydrous THF (1 mL) was added to a mixture of **3e** (0.80 g, 2.82 mmol), $Pd(PPh_3)_4$ (0.161 g, 0.14 mmol) and degassed anhydrous THF (4 mL). The stirred mixture was kept at room temperature under nitrogen atmosphere for 24 h (GLC monitoring). The solvent was evaporated and the residue chromatographed through a silica gel column, eluting with mixtures of increasing polarity, from hexanes to hexanes-ethyl acetate (8:2). The following fractions were obtained in that order: 0.13 g (10%) of a mixture of diallylation products; 0.23 g (21%) of *trans*-*N*-(5-methyl-2-cyclohexenyl)-2,4,6-triisopropylbenzensulfonamide, ***trans*-16**; 0.65 g (61%) of a 2:3 mixture of ***trans*-16** and ***cis*-16**. Data for isomer ***trans*-16**: mp 75-78 °C; IR (KBr): 3306, 1318, 1153 cm^{-1}; ^1H NMR ($CDCl_3$): 0.85 (d, J = 6.6 Hz, 3H), 1.15-1.40 (m, 18H+1H+1H), 1.55 (m, 1H), 1.72 (apparent d, J = 14.6 Hz, 1H), 2.05 (apparent d, J = 17.6 Hz, 1H), 2.88 (septet, J = 6.6 Hz, 1H), 3.89 (m, 1H), 4.14 (septet, J = 6.6 Hz, 2H), 4.36 (d, J = 8.8 Hz, 1H, NH), 5.44 (m, 1H), 5.77 (m, 1H), 7.13 (s, 2H).; ^{13}C NMR ($CDCl_3$): 21.2, 23.6, 23.9, 24.8, 29.7, 33.2, 34.1, 37.4, 47.9, 123.7, 126.0, 131.6, 133.7, 150.0, 152.6. Anal.: Calcd. for $C_{22}H_{35}NO_2S$: C, 69.98; H, 9.34; N, 3.71. Found: C, 69.82; H, 9.22; N, 3.38.

Reaction of 3e with 10, using $Pd(dba)_2$/dppe as catalyst (entry 6, Table 2).
A solution of **10** (0.83 g, 4.5 mmol) in degassed anhydrous THF (2 mL) was added to a mixture of **3e** (0.80 g, 2.82 mmol), $Pd(dba)_n$ ($1.5 < n < 2.0$) (0.073 g, 0.13-0.16 mmol), 1,2-bis(diphenylphosphino)ethane (0.11 g, 0.3 mmol), and degassed anhydrous THF (3 mL). The stirred mixture was kept at room temperature under nitrogen atmosphere for 48 h (GLC monitoring). The solvent was evaporated and the residue chromatographed trough a silica gel column, eluting with mixtures of increasing polarity, from hexanes to hexanes-ethyl acetate (8:2), to afford ***cis*-16** (0.79 g, 72%); mp 116-118 °C; IR (KBr): 3286, 1306, 1153 cm^{-1}; ^1H NMR ($CDCl_3$): 0.88 (d, J = 6.6 Hz, 3H), 1.00 (q, J = 11.7 Hz, 1H), 1.18-1.30 (m, 18H), 1.48-1.73 (m, 1H+1H), 1.90-2.02 (m, 1H+1H), 2.87 (septet, J = 6.6 Hz, 1H), 3.99 (m, 1H), 4.03-4.23 (m, 2H+1H (NH)), 5.38 (apparent d, J = 10.2 Hz, 1H), 5.69 (m, 1H), 7.13 (s, 2H); ^{13}C NMR ($CDCl_3$): 21.8, 23.6, 24.8, 28.6, 29.6, 33.3, 34.1, 39.9, 51.0, 123.8, 128.4, 130.1, 133.8, 150.0, 152.6. Anal.: Calcd. for $C_{22}H_{35}NO_2S$: C, 69.98; H, 9.34; N, 3.71. Found: C, 70.15; H, 9.30; N, 3.50.

Reaction of sulfamide 4 with allyl ethyl carbonate 6 (entry 1, Table 3).
A solution of **4** (0.20 g, 2.1 mmol) in degassed anhydrous THF (10 mL) was slowly added under nitrogen to a stirred mixture of **6** (0.54 g, 4.2 mmol), $Pd(PPh_3)_4$ (0.188 g, 0.16 mmol), and degassed anhydrous THF (10 mL). The mixture was stirred at room temperature under nitrogen atmosphere for 4 h, the formation of a precipitate being observed. The solid was filtered off (0.080 g) and the solvent from filtrate was evaporated. The residue was chromatographed through a silica gel column eluting with mixtures of increasing polarity, from hexane to hexanes-ethyl acetate (1:1). Carbonate **6** was partially recovered (0.060 g, 11%) and the following fractions were eluted in the order:
N,N,N',N'-Tetraallylsulfamide **17e** (0.060 g, 22%); oil; IR (film): 1342, 1144 cm^{-1}; ^1H NMR ($CDCl_3$): 3.73 (d, J = 6.5 Hz, 8H), 5.18 (d, J = 17.5 Hz, 4H), 5.19 (d, J = 10.2 Hz,

4H), 5.68-5.85 (m, 4H); ^{13}C NMR ($CDCl_3$): 49.4, 118.9, 132.9; MS (*m/z*, %): 229 (M^+ - vinyl, 1), 96 (17), 41 (100).

N,N,N'- Triallylsulfamide **17d** (0.025 g, 9%); oil; IR (film): 3282, 1324, 1149 cm^{-1}; ^1H NMR ($CDCl_3$): 3.60 (t, J = 5.9 Hz, 2H), 3.78 (d, J = 5.9 Hz, 4H), 4.15 (broad s, 1H), 5.14-5.27 (m, 6H), 5.73-5.84 (m, 3H); ^{13}C NMR ($CDCl_3$): 45.7, 49.6, 117.5, 119.0, 132.9, 133.5; MS (*m/z*, %): 189 (M^+ - vinyl, 2), 56 (29), 41 (100).

N,N' -Diallylsulfamide **17b** (0.019 g, 5%); oil; IR (film): 3281, 1316, 1149 cm^{-1}; ^1H NMR ($CDCl_3$): 3.65 (tt, J = 5.9 Hz, 1.5 Hz, 4H), 4.40 (broad s, 2H), 5.17 (dd, J = 10.2 Hz, 1.5 Hz, 2H), 5.26 (dt, J = 17.5 Hz, 1.5 Hz, 2H), 5.84 (ddt, J = 17.5 Hz, 10.2 Hz, 5.9 Hz, 2H); ^{13}C NMR ($CDCl_3$): 45.7, 117.8, 133.3; MS (*m/z*, %): 135 (M^+ - allyl, 1), 56 (100), 41 (65).

N,N-Diallylsulfamide **17c** (0.055 g, 15%); oil; IR (film): 3373, 3283, 1381, 1158 cm^{-1}; ^1H NMR ($CDCl_3$): 3.81 (d, J = 6.6 Hz, 4H), 4.39 (broad s, 2H), 5.25 (d, J = 17.5 Hz, 2H), 5.28 (d, J = 10.2 Hz, 2H), 5.85 (ddt, J = 17.5 Hz, 10.2 Hz, 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): 49.9, 119.3, 132.5; MS (*m/z*, %): 176 (M^+, 1), 149 (5), 96 (5), 41 (100).

N-Allylsulfamide **17a** (0.061 g, 11%); oil; IR (film): 3528, 3284 (broad), 1327, 1159 cm^{-1}; ^1H NMR ($CDCl_3$): 3.69 (tt, J = 5.9 Hz, 1.5 Hz, 2H), 4.92 (broad t, J = 5.9 Hz, 1H), 5.01 (s, 2H), 5.17 (dt, J = 10.2 Hz, 1.5 Hz, 1H), 5.27 (apparent dq, J = 17.5 Hz, 1.5 Hz, 1H), 5.88 (ddt, J = 17.5 Hz, 10.2 Hz, 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): 46.0, 117.8, 133.4; MS (*m/z*, %): 136 (M^+, 1), 109 (8), 80 (14), 56 (100), 41 (50).

***N,N,N',N'*-Tetra(2-methylallyl)sulfonamide 18e.**

It was obtained in 75% yield from **4** and **7** under the conditions specified in Table 3 (entry 4); oil; IR (film): 1349, 1150 cm^{-1}; ^1H NMR ($CDCl_3$): 1.74 (s, 12H), 3.73 (s, 8H), 4.92 (s, 8H); ^{13}C NMR ($CDCl_3$): 20.4, 53.6, 114.2, 140.4; MS (*m/z*, %): 312 (M^+, 2), 124 (27), 110 (18), 84 (16), 82 (29), 70 (15), 56 (15), 55 (100). Anal.: Calcd. for $C_{16}H_{28}N_2O_2S$: C, 61.50; H, 9.03; N, 8.96; S, 10.26. Found: C, 61.60 and 61.66; H, 9.10 and 9.17; N, 8.78 and 9.01; S, 9.51 and 9.80.

Reaction of sulfamide 4 with cinnamyl ethyl carbonate 8 (see conditions, products and yields in entries 5, 6 and 7 of Table 3).

N-Cinnamylsulfamide **19a**: mp 112 °C (THF-pentane); IR (KBr): 3328, 3288, 3270, 1388, 1153 cm^{-1}; ^1H NMR ($CDCl_3$): 3.90 (broad t, J = 6.2 Hz, 2H), 4.46 (broad s, 1H), 4.58 (broad s, 2H), 6.22 (dt, J = 15.7 Hz, 6.2 Hz, 1H), 6.57 (d, J = 15.7 Hz, 1H), 7.22-7.49 (m, 5H); ^{13}C NMR ($CDCl_3$): 45.9, 124.2, 126.5, 128.1, 128.7, 133.5, 136.0. Anal.: Calcd. for $C_9H_{12}N_2O_2S$: C, 50.93; H,5.70; N, 13.20. Found: C, 50.61 and 50.52; H, 5.54 and 5.58; N, 12.83 and 12.86.

N,N'-Dicinnamylsulfamide **19b**: mp 172-174 °C (THF-pentane); IR (KBr): 3346, 3276, 1341, 1145 cm^{-1}; ^1H NMR ($CDCl_3$): 3.87 (t, J = 6.2 Hz, 4H), 4.30 (t, J = 6.2 Hz, 2H), 6.22 (dt, J = 16.0 Hz, 6.2 Hz, 2H), 6.58 (d, J = 16.0 Hz, 2H), 7.22-7.40 (m, 10H); ^{13}C NMR ($CDCl_3$): 45.6, 124.3, 126.5, 128.1, 128.6, 133.4, 136.0. Anal.: Calcd. for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.71 and 65.82; H, 5.84 and 5.90; N, 8.34 and 8.39.

N,N,N',N'-Tetracinnamylsulfamide **19e**: mp 92-92.5 °C (THF-pentane); IR (KBr): 1340, 1142 cm^{-1}; ^1H NMR ($CDCl_3$): 4.02 (d, J = 6.6 Hz, 8H), 6.23 (dt, J = 16.1 Hz, 6.6 Hz, 4H), 6.55 (d, J = 16.1 Hz, 4H), 7.21-7.44 (m, 20H); ^{13}C NMR ($CDCl_3$): 49.4, 124.3, 126.5, 127.9, 128.6, 134.1, 136.2. Anal.: Calcd. for $C_{36}H_{36}N_2O_2S$: C, 77.11; H, 6.47; N, 4.99; S, 5.71. Found: C, 77.29 and 77.31; H, 6.24 and 6.27; N, 4.93 and 4.80; S, 5.37 and 5.33.

N,N-Diallylcyanamide 20.
It was prepared under the conditions and yields indicated in Table 3 (entries 8, 9, and 10); oil; IR (film): 2213 cm^{-1}; ^1H NMR ($CDCl_3$): 3.62 (d, J = 6.5 Hz, 4H), 5.32 (d, J ca 17 Hz, 2H), 5.34 (d, J ca 10 Hz, 2H), 5.85 (m, 2H); ^{13}C-NMR ($CDCl_3$): 53.2, 117.4, 120.4, 130.8; MS (*m/z*, %): 122 (M^+, 7), 81 (7), 55 (14), 54 (7), 41 (100).

Reaction of cyanamide 5 with ethyl 2-methylallyl carbonate 7 (entry 12, Table 3).
A solution of **5** (0.135 g, 3.21 mmol) in degassed anhydrous THF (15 mL) was added under nitrogen atmosphere to a stirred mixture of **7** (1.340 g, 9.30 mmol), $Pd(PPh_3)_4$ (0.168 g, 0.145 mmol) and degassed anhydrous THF (15 mL). The mixture was refluxed for 15 h, the solvent was evaporated and the residue chromatographed on silica gel under pressure, eluting with hexanes-ethyl acetate (8:2). The following compounds were obtained in the order:
N,N-Di(2-methylallyl)cyanamide **21** (0.386 g, 80%): oil; IR (film): 2214 cm^{-1}; ^1H NMR ($CDCl_3$): 1.81 (s, 6H), 3.54 (s, 4H), 4.97 (s, 2H), 5.03 (s, 2H); ^{13}C NMR ($CDCl_3$): 19.8, 56.6, 115.8, 118.1, 138.6; MS (*m/z*, %): 150 (M^+, 3), 135 (15), 110 (12), 95 (15), 82 (9), 68 (8), 56 (16), 55 (100), 41 (9). Anal.: Calcd. for $C_9H_{14}N_2$: H, 9.39; N, 18.65. Found: H, 9.39; N, 18.57.
N,N' -Di(2-methylallyl)carbodiimide **23** (0.054 g, 11%): oil; IR (film): 2175 cm^{-1}; ^1H NMR ($CDCl_3$): 1.70 (s, 6H), 3.84 (s, 4H), 4.90 (s, 2H), 4.98 (s, 1H); ^{13}C NMR ($CDCl_3$): 20.2, 54.8, 114.9, 139.5; MS (*m/z*, %): 150 (M^+, 9), 95 (13), 82 (11), 70 (10), 55 (100), 53 (10), 41 (9). Anal.: Calcd. for $C_9H_{14}N_2$: C, 71.96; H, 9.39. Found: C, 72.09; H, 9.66.

Reaction of cyanamide 5 with cinnamyl ethyl carbonate 8 (entry 13, Table 3).
A solution of **5** (0.162 g, 3.81 mmol) in degassed anhydrous THF (15 mL) was added under nitrogen to a stirred mixture of **8** (1.778 g, 8.62 mmol), $Pd(PPh_3)_4$ (0.168 g, 0.145 mmol), and degassed anhydrous THF (15 mL). The stirred mixture was kept under nitrogen at room temperature for 14 h (GLC monitoring). The solvent was evaporated and the residue (1.402 g) chromatographed on silica gel under pressure using hexanes-ethyl acetate (9:1) as eluent. The following compounds were obtained in the order:
N-(1-phenyl-2-propenyl)cyanamide **25** (0.035 g, 6%): ^1H NMR ($CDCl_3$): 3.74 (d, J = 10.2 Hz, 1H), 5.29 (d, J = 16.8 Hz, 1H), 5.41 (d, J = 10.2 Hz, 1H), 6.11 (dt, J = 16.8 Hz, 10.2 Hz, 1H), 7.28-7.40 (m, 5H); MS (*m/z*, %): 132 (M^+ - CN, 49), 131 (M^+ - $CH{=}CH_2$, 100), 104 (23), 103 (55), 78 (34), 77 (45), 35 (51).
N,N-Dicinnamylcyanamide **22** (0.677 g, 65%): mp 79-80 °C (ethyl acetate-hexane); IR (KBr): 2213 cm^{-1}; ^1H NMR ($CDCl_3$): 3.82 (dd, J = 7.0 Hz, 1.5 Hz, 4H), 6.21 (dt, J = 16.0 Hz, 7.0 Hz, 2H), 6.62 (d, J = 16.0 Hz, 2H), 7.28-7.41 (m, 10H); ^{13}C NMR ($CDCl_3$): 52.9, 121.8, 126.7, 128.3, 128.7, 135.6; MS (*m/z*, %): 273 (M^+ -1, 3), 117 (100), 115 (31), 91 (14). Anal.: Calcd. for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.22 and 83.10; H, 6.95 and 6.94; N, 10.15 and 10.16.
N-Cinnamylcyanamide **24** (0.029 g, 5%): ^1H NMR ($CDCl_3$): 4.28 (broad d, J = 5.1 Hz, 2H), 6.33 (dt, J ca 16 Hz, ca 5 Hz, 1H), 6.62 (d, J ca 16 Hz, 1H), 7.20-7.42 (m, 5H); MS (*m/z*, %): 117 (M^+ - 41, 100), 115 (30), 91 (13).

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