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Palladium(0)-Catalyzed Allylation of Highly Acidic and Non-nucleophilic Arenesulfonamides, Sulfamide, and Cyanamide. II. Formation of Medium and Large Heterocycles.

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Abstract:

Arenesulfonamides **10**, cyanamide **29**, and sulfamide **32** react with allylic bis-carbonates **8** (***Z*** and ***E***) and **9** under Pd(0)-catalysis to afford medium and large unsaturated heterocycles instead of three and/or five-membered ring compounds. Stable 15-membered palladium-containing rings were also isolated from arenesulfonamides and **8**, with three *trans* olefinic systems coordinated to the metal. NMR and MALDI-TOF MS experiments were used for structure elucidations. Suitable hydrogenation conditions to give the saturated macrocycles have been found.

Keywords: Allylation; Palladium Catalysis; Acidic *N*-nucleophiles; Macrocycles.

The palladium(0)-catalyzed allylation of nucleophiles (the Tsuji-Trost reaction) is a synthetic method very useful due to its broad applicability and facile experimental procedure [1-13]. The catalytic cycle requires the formation of the cationic η^3-allylpalladium(II) complex, an intermediate which can be attacked by nucleophiles at both termini of the allylic system. The cationic intermediate is formed by reaction of Pd(0), generally stabilized by phosphine ligands with an allyl system featuring a leaving group. Mixed carbonates are very useful as allylic substrates since an 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 [15-17]. Thus, in DMSO several N-H compounds are more acidic than methanol, and we have described the Pd-catalyzed allylation of acidic anilines, arenesulfonamides, sulfamide, and cyanamide using allylic carbonates [18, 19]. The reactions are very efficient and take place with overall retention of configuration, that is with consecutive inversions in both steps of the catalytic cycle.

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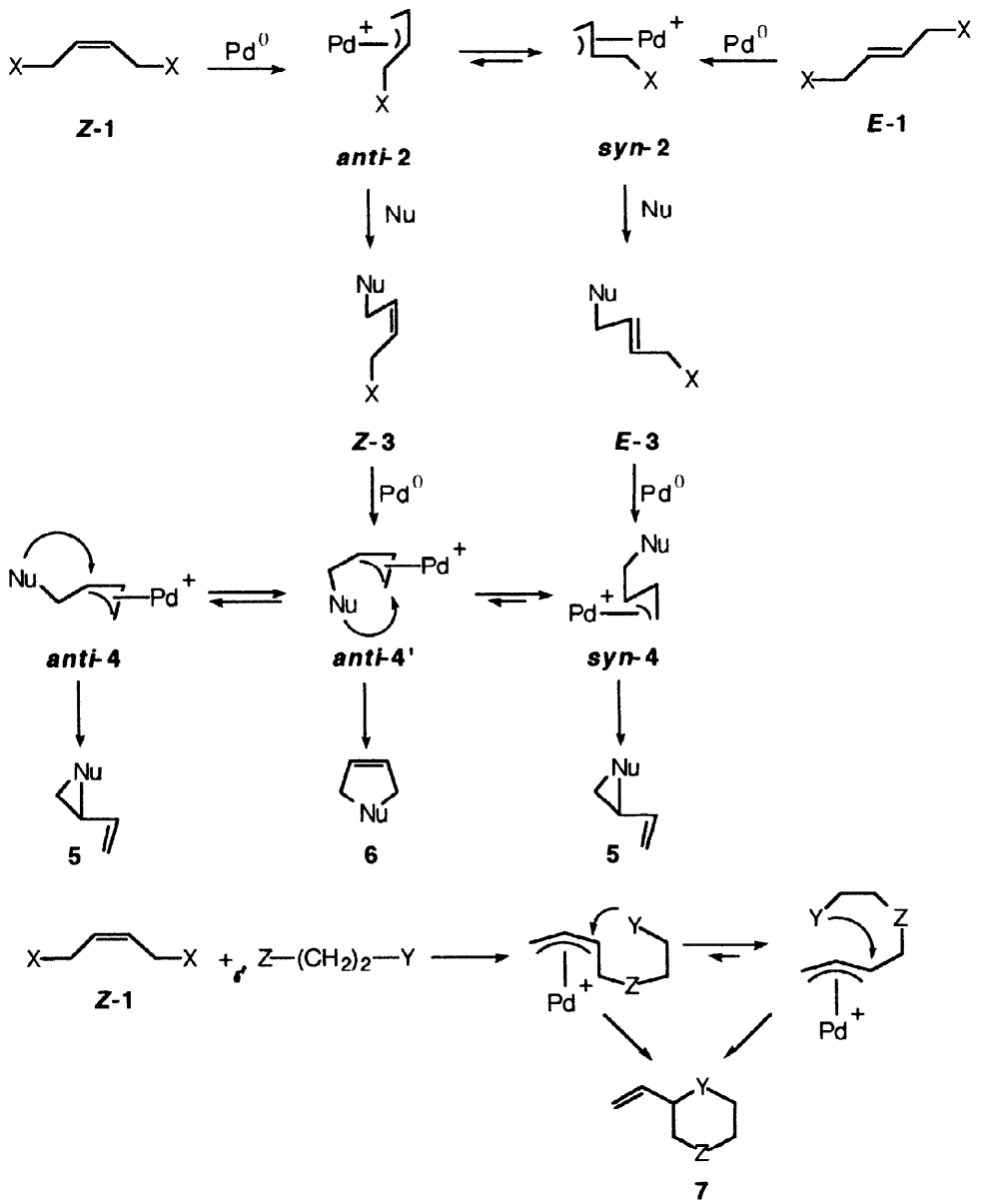
Pd(0)-catalyzed allylation of dinucleophiles with butene-1,4-diol derivatives **1** produces cyclic products (Scheme 1).

Scheme 1. Pd(0)- catalyzed reactions of butene-1,4-diol derivatives with dinucleophiles



The initially formed η^3-allylpalladium complex ***anti*-2** or ***syn*-2** can equilibrate before being attacked by the nucleophile, rendering the result independent of the stereochemistry of **1**. Nucleophilic attack affords **Z-3** and ***E*-3**. Dinucleophiles of type 1,1 (doubly nucleophilic reagents with a nucleophilic atom which may react twice, such as R-NH_2, RCO-CH_2-COR) can react again in an intramolecular way, the ***anti*-4** complex producing 3- or 5-membered rings (compounds of type **5** and **6** respectively) depending on the active conformation arising by rotation around a σ bond. On the other hand, complex ***syn*-4** leads only to 3-membered

rings **5**.

Ibuka and coworkers have reported the Pd(0)-catalyzed isomerization of *cis*- and *trans*-*N*-alkyl(or aryl)sulfonyl-2-alkyl-3-vinylaziridines [20, 21], without formation of 5-membered rings. In contrast, Oshima described the isomerization of *N*-tosyl-2-(1,3-butadienyl)aziridines into *N*-tosyl-2-vinyl-2,5-dihydropyrroles [22]. Strong electron-attracting *N*-sulfonyl groups are required in both cases for aziridine opening to occur. Moreover, 5-membered pyrroles and derivatives are formed directly from 1,4-difunctionalized butenes under Pd-catalysis [23, 24]. Dinucleophiles of type 1,4 (Y-C-C-Z) produce vinyl substituted 6-membered rings **7** where Z = Y = NHR [25-27], Z = NHR and Y = OH [25-29], and Z = Y = OH [30, 31] (Scheme 1). This includes highly acidic arenesulfonamide nucleophiles [25, 26, 29]. However, the reactions of type 1,5 and 1,6 dinucleophiles ($TsNH(CH_2)_nNHTs$ (n = 3,4) with butene-1,4-diol mixed bis-carbonate afford 8- and 9-membered rings rather than vinyl substituted 6- and 7-membered rings [25].

The 4-membered ring of *N*-(trifluoromethanesulfonyl)-2-vinylazetidine opens under Pd(0)-catalysis and dimerizes to the corresponding 12-membered ring rather than recyclising to the 6-membered ring [32].

We wish to present here a new reactivity pattern in the Pd(0)-catalyzed interaction of arenesulfonamides, sulfamide, and cyanamide with allylic bis-carbonates.

The results of the reactions of arenesulfonamides with bis-carbonates, ***E*-8** and ***Z*-8**, are in Scheme 2 and Table 1. The reaction of 2-methylbenzenesulfonamide **10a** with ***Z*-8** (entry 1 in Table 1) afforded a precipitate (mp 131-133°C) scarcely soluble in the usual solvents, and presenting IR and ^1H NMR spectra compatible with 2,5-dihydropyrrole **12a** (54% yield). Elemental analysis was also in agreement with **12a** . However, the signals of the ^1H NMR spectrum were not sharp, and the MS-EI was unclear.

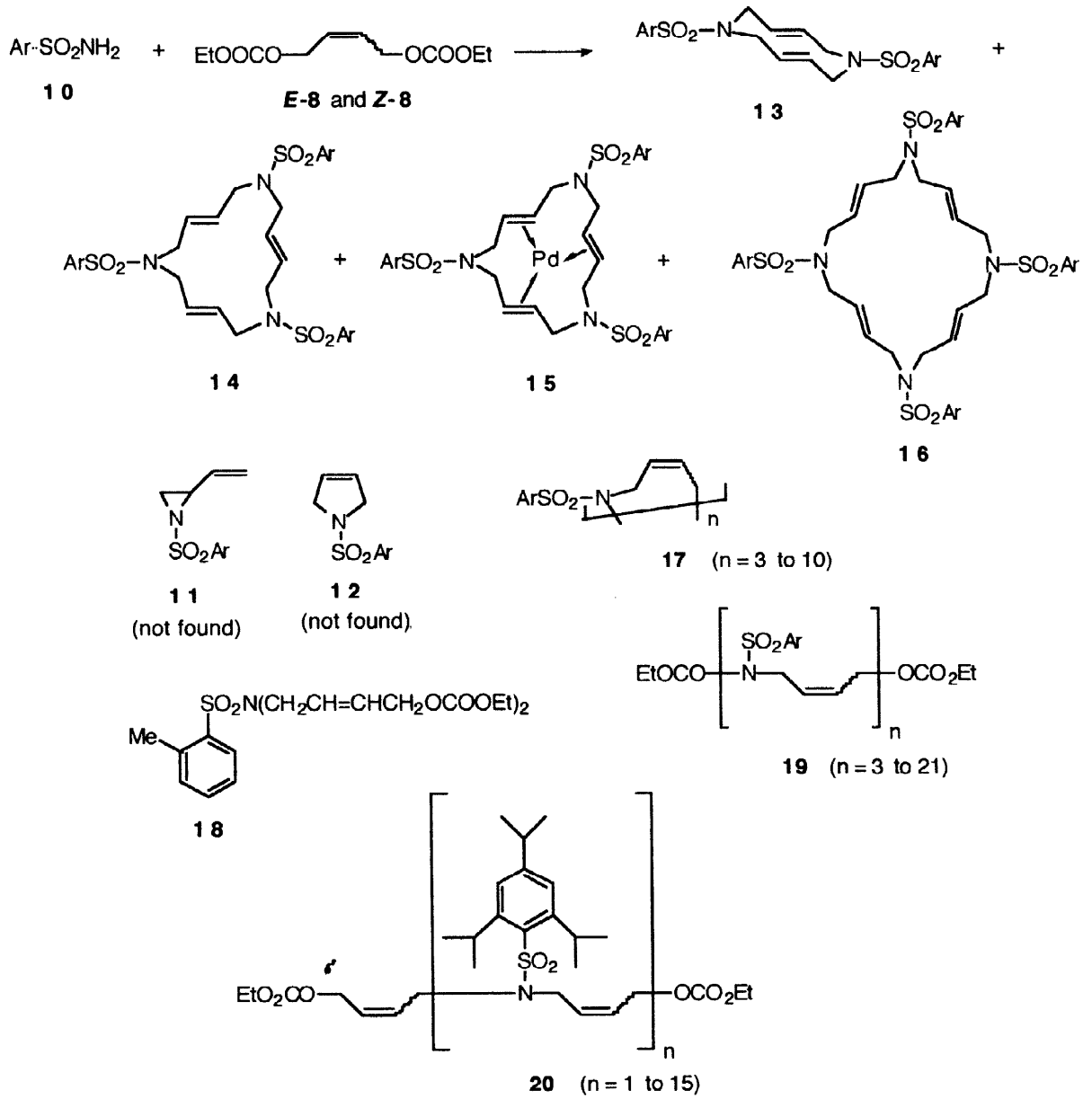
Similarly, the reaction of 4-methylbenzenesulfonamide **10b** (entry 5 in Table 1) afforded a precipitate (mp 109-111°C), again quite insoluble, featuring IR and ^1H NMR spectra compatible with dihydropyrrole **12b** (57% yield). Moreover, the MS-EI presented a peak at *m/z* 221(55) corresponding to the mass M - 2, which is reasonable considering that loss of hydrogen leads to an aromatic structure; other peaks were at *m/z* 155(55, $C_7H_7SO_2^+$) and 91(100, $C_7H_7^+$). Dihydropyrrole **12b** had been prepared by a different method and reported to have mp 117-119°C [33], not identical to ours but not far from it. Again the signals in the ^1H NMR spectrum were broader than expected. In the same reaction another impure product was isolated (mp 212-217°C) and structure **13b** (*trans,trans* stereochemistry) was assigned to it on the basis of MS-EI. The 10-membered ring **13b** with *cis,cis* double bonds had been described in the literature [34], having a melting point (mp 226°C) similar (but not exactly the same) to that of our product, but the ^1H NMR spectrum was not coincident (see below for a detailed discussion on the stereochemistry of double bonds in these compounds).

Then, the reaction of **10a** with ***E*-8** was studied (entry 2 in Table 1); a precipitate (34% yield) was also formed exhibiting similar, but not exactly the same, melting point (mp 137-138°C) and the same spectroscopic behaviour as the precipitate of entry 1. This solid was studied by MALDI-TOF MS and presented peaks for molecular ions corresponding to a mixture of linear oligomers **19a**. The 10-membered ring compound **13a** was isolated (11% yield) from the filtrate.

The precipitate of entry 5 was shown by MALDI-TOF MS to be a mixture of cycles **17b** and **15b** (Scheme 2).

In summary, compounds **11** or **12** could never be isolated. Independent preparation of compounds **12a-b** was achieved by double allylation followed by metathesis [19] to confirm that they were different from the precipitates obtained in entries 1, 2 and 5.

Scheme 2. Pd(0)-catalyzed reactions of arenesulfonamides **10** with bis-carbonates **8**.



Reactions performed in DMF were slower and heating was required in order to obtain the macrocycles. The reaction of **10a** with ***Z*-8** in DMF at room temperature (entry 3 in Table 1) led to partial recovery of arenesulfonamide and to the isolation of compound **18**, an intermediate in the formation of cycles **13**-**17**. Reactions performed at 85°C (entry 4 in Table 1) afforded 15-membered palladium complex **15a** in 24% maximum yield and starting sulfonamide **10a** was partially recovered.

Two reactions were studied in DMF between **10b** and both isomers ***Z*-8** and ***E*-8** (entries 6 and 7 in Table 1), the results being similar. In both cases the 10-membered ring **13b** was

isolated in 15-20% yield.

Similar results were obtained for arenesulfonamides **10c-d** (entries 8 and 9 in Table 1). The reaction of **10c** with **Z-8** afforded a mixture of macrocycles **17c** in 70% yield (MALDI-TOF MS analysis). Analogously the reaction of **10d** with **Z-8** yielded the mixture of cycles **17d** together with 10-membered ring **13d** (69% overall yield).

The reactions of 1-naphthalenesulfonamide **10e** with both isomers **Z-8** and ***E*-8** were also independent of the stereochemistry of the bis-carbonate (entries 10 and 11 in Table 1). In these cases a mixture of macrocycles **17e** was separated by filtration and from the filtrate pure 20-membered ring **16e** could be isolated. These compounds were identified by MALDI-TOF MS analysis.

Table 1.
Pd(0)-catalyzed reactions of arenesulfonamides **10** with bis-carbonates **8**.[a]

Entry	**10**[b]	Ar	**8**	[**10**] M	Temp (°C)	Time (h)	**Products** (%)
1	**10a**	2-MeC_6H_4-	*Z*	0.68	rt	24	**19a** (54)
2	**10a**	2-MeC_6H_4-	*E*	0.24	rt	12	**13a** (11), **19a** (34)
3[c]	**10a**	2-MeC_6H_4-	*Z*	0.24	rt	12	**18a** (12)[d]
4[c]	**10a**	2-MeC_6H_4-	*Z*	0.24	85	12	**15a** (24)[d,e]
5	**10b**	4-MeC_6H_4-	*Z*	0.20	60	24	**13b** (5), **17b** + **15b** (57)
6[c]	**10b**	4-MeC_6H_4-	*Z*	0.24	85	12	**13b** (15)[d]
7[c]	**10b**	4-MeC_6H_4-	*E*	0.24	85	12	**13b** (20)[d]
8	**10c**	2-$NO_2C_6H_4$-	*Z*	0.50	rt	15	**17c** (70)
9	**10d**	4-$MeOC_6H_4$-	*Z*	0.18	rt	19	**13d** + **17d** (69)
10	**10e**	1-Naphthyl	*Z*	0.24	rt	12	**13e**[f], **16e** (12), **17e** (39)
11	**10e**	1-Naphthyl	*E*	0.24	rt	12	**13e**[f], **16e** (17), **17e** (30)

[a] All reactions were carried out using 5% of $Pd(PPh_3)_4$ in THF unless otherwise stated.
[b] **10/8** = 0.8.
[c] Reaction was carried out in DMF.
[d] Partial recovery of starting arenesulfonamide **10** (12-20% yield).
[e] Erratic yield.
[f] Traces detected by ^1H NMR spectrum (< 5% yield).

In summary, several macrocyclic compounds are formed in the aforementioned reactions, independently of the stereochemistry of the starting bis-carbonate, indicating isomerization of intermediate complexes. In a separate experiment we noticed that **Z-8** equilibrates with ***E*-8** under $Pd(PPh_3)_4$ catalysis in THF at room temperature. No conclusions could be drawn with respect to the factors favoring one or another type of macrocycle since insolubility prevented a quantitative evaluation.

Seeking for more soluble compounds we moved to arenesulfonamide **10f** (R = 2,4,6-triisopropyl) and we made a deeper study of the formation of compounds **13f-16f** (Scheme 2, Table 2).

The three isopropyl groups conferred higher solubility on all reaction products which were more easily separated by column chromatography. Under a broad variety of experimental conditions (Table 2) some differences in the ratios of products **13f-16f** were observed. The higher isolated yield of 10-membered ring **13f** was obtained by high dilution, high temperature, and $Pd(dba)_2$/dppf (bis(dibenzylideneacetone)palladium(0)/1,1'-bis(diphenylphosphino)ferrocene) as a catalytic system (entry 7 in Table 2), whereas 20-

membered ring **16f** seems to be favoured by high concentration and $Pd(PPh_3)_4$ as a catalyst (entries 3 and 6 in Table 2). Low temperature (0°C) (entry 8 in Table 2) prevented the formation of macrocycles and linear oligomers **19f** and **20** were isolated instead.

Table 2.
Pd(0)-catalyzed reactions of 2,4,6-triisopropylbenzenesulfonamide **10f** with bis-carbonate ***Z*-8**.[a]

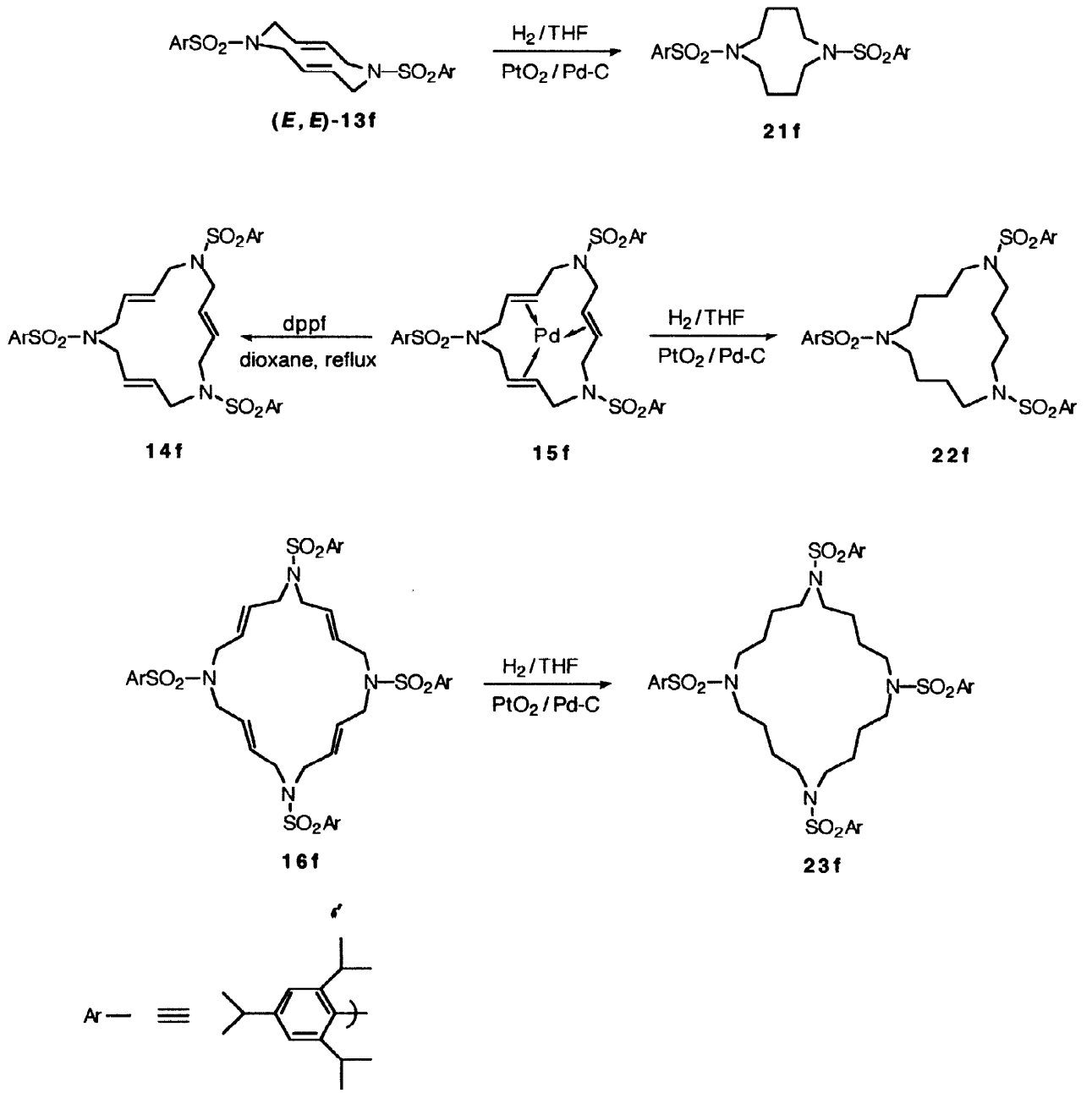
Entry	**10f/8**	[**10f**] M	Catalyst (%)	Temp (°C)	Time (h)	**Products** (%)
1[b]	1.00	0.22	$Pd(PPh_3)_4$ (5)	rt	36	**13f**, **15f**, **16f** (2:3:4)[b]
2[c]	0.91	0.22	$Pd(PPh_3)_4$ (5)	reflux	20	**13f** (21)[c], **16f** (29)[c]
3[c]	0.91	0.50	$Pd(PPh_3)_4$ (5)	rt	72	**13f** (11)[c], **16f** (47)[c]
4[b]	0.89	0.09	$Pd(PPh_3)_4$ (5)	reflux	24	**13f**, **14f**, **16f** (3:3:1)[b]
5[c]	0.76	0.17	$Pd(PPh_3)_4$ (5)	reflux	40	**13f** (15)[c], **16f** (12)[c], **15f** (17)[c], **14f** (8)[d]
6[b]	0.76	0.64	$Pd(PPh_3)_4$ (5)	reflux	70	**14f**, **15f**, **16f** (1:4:5)[b]
7[c]	0.76	0.12	$Pd(dba)_2$ (5) dppf (10)	reflux	60	**13f** (35)[c], **16f** (6)[c]
8[c]	1.00	0.43	$Pd(PPh_3)_4$ (5)	0	24	**13f** (1.5)[c], **16f** (8)[c], **14f** (7)[c], **19f** (15)[c], **20** (16)[c]

[a] All reactions were carried out in anhydrous THF.
[b] Ratio of compounds by ^1H NMR integration.
[c] Yields of isolated products.
[d] Yield estimated by ^1H NMR integration.

Isolation of substantial amounts of the above products enabled us to perform the reactions outlined in Scheme 3. A sample of the free ligand **14f** was obtained after prolonged refluxing of complex **15f** in dioxane in the presence of stoichiometric amounts of dppf. After some experimentation, suitable conditions could be found for the hydrogenation of macrocycles **13f**, **14f**, and **16f** to afford the fully saturated **21f**, **22f**, and **23f**.

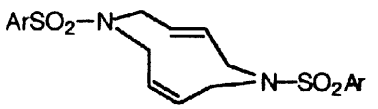
trans,trans-Stereochemistry was assigned to compounds **13** by a detailed comparative study of selective 1D TOCSY experiments with *trans,cis*-**13f** (Scheme 4). The *trans,cis*-10-membered ring (***E*,*Z*)-13f** was prepared in a similar manner as for the *cis,cis*-10-membered ring (***Z*,*Z*)-13b** reported in the literature [34]. Moreover, compound (***E*,*E*)-13f** presented in the ^1H NMR spectrum olefinic protons at δ 5.49 and methylene protons as a multiplet at δ 3.66 and a clean doublet at δ 4.39 (J = 14.6 Hz, 4H) (spectrum D, Scheme 4). The reported (***Z*,*Z*)-13b** showed two multiplets at δ 3.88 and δ 5.40 for the methylene (8H) and olefinic protons (4H) respectively. The ^1H NMR spectrum of (***E*,*Z*)-13f** presented methylene protons at 3.51 (m, 2H), 3.66 (dd, J =15.4 and 5.9 Hz, 2H), 3.95 (dd, J = 15.4 and 5.9 Hz, 2H) and 4.12 (m, 2H + 4H), and olefinic protons as a multiplets at δ 5.58 and δ 5.64 (spectrum C, Scheme 4). From selective 1D TOCSY to the olefinic proton at 5.64 ppm (spectrum A, Scheme 4) methylene protons of the same spin system were assigned (a multiplet at δ 3.51 and a doublet at δ 4.12 ppm). On the other hand, irradiation of olefinic protons at δ 5.58 (spectrum B, Scheme 4) gave the methylene protons at δ 3.66 and 3.95 belonging to the same spin system. Two symmetric and different olefinic systems could, thus, be identified.

Scheme 3. Hydrogenation and decomplexation reactions performed with compounds **13f**, **15f**, and **16f**.



By comparing the ^{1}H NMR spectrum of compound **13f** obtained in our Pd-catalyzed reactions (spectrum D, Scheme 4) with that of **(*E*,*Z*)-13f** (spectrum C, Scheme 4) and also with that reported in the literature [34] for **(Z,Z)-13b**, *trans,trans* stereochemistry for ten-membered ring compounds could be assigned.

Scheme 4. ^{1}H NMR partial spectra of (*E*,*Z*)-**13f** and (*E*,*E*)-**13f** and some selective 1D TOCSY experiments on (*E*,*Z*)-**13f**.



(*E*,*Z*)-**13f**

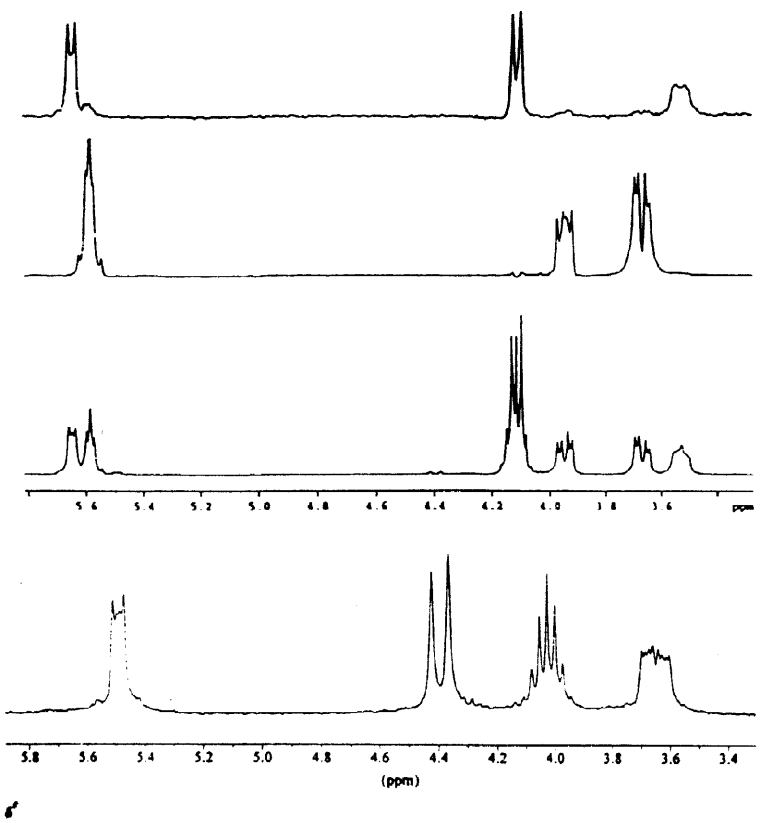
(*E*,*E*)-**13f**

Spectrum A
Selective 1D TOCSY at δ 5.64
of (*E*,*Z*)-**13f**

Spectrum B
Selective 1D TOCSY at δ 5.58
of (*E*,*Z*)-**13f**

Spectrum C
^{1}H NMR ($CDCl_3$, 400 MHz)
of (*E*,*Z*)-**13f**

Spectrum D
^{1}H NMR ($CDCl_3$, 250 MHz)
of (*E*,*E*)-**13f**

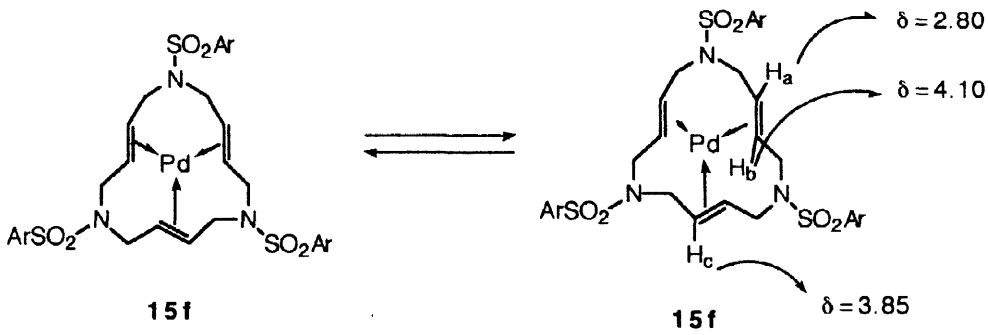


Selective 1D TOCSY experiments performed on **15f** showed that this compound has an averaged plane of symmetry or a C_2 symmetry axis rather than a C_3 symmetry axis, due to the presence of one palladium atom. ^{1}H and ^{13}C chemical shifts were unambiguously assigned by concerted use of 2D COSY, HSQC and HMBC experiments. Compound **15f** presented two magnetically equivalent olefinic systems with non magnetically equivalent protons at δ 2.80 (apparent t, J = 12.4 Hz, 2H) and δ 4.10 (dd, J = 12.4 Hz and 11.1 Hz, 2H) (spectrum B, Scheme 5) plus a different olefinic system with equivalent protons at δ 3.85 (apparent d, J = 9.5 Hz, 2H) (spectrum C, Scheme 5). The strong upfield shift of olefinic signals as well as the *trans* coupling constant value of *ca.* 12 Hz are normal for olefin-Pd(0) complexes such as palladium bis(dibenzylidene)acetone [35]. A 2D NOESY experiment confirmed the *trans*-stereochemistry assignment of the asymmetric olefinic part. Clearly the third olefinic system in the ring is also coordinated to Pd but in a different way. The above data are compatible with the *cis* stereochemistry for this third double bond as well as with a *trans* stereochemistry with a dynamic process rendering equivalent both ends of the third double bond and giving

an averaged plane of symmetry to the molecule. However, compound **14f**, the free ligand obtained from **15f**, presented only one olefinic signal at δ 5.79 for the six olefinic protons and one signal at δ 3.77 for the twelve methylene protons (spectrum D, Scheme 5) consistent with the all-*trans* stereochemistry for **14f** and **15f**, and also for 20-membered **16f** (spectrum E, Scheme 5) since this macrocycle presents the corresponding olefinic and methylene signals at δ 5.67 and 3.77 with multiplicities similar to those found in **14f**.

The same stereochemistry is assumed for other macrocycles **13-16** of Table 1 on the basis of similar NMR spectra.

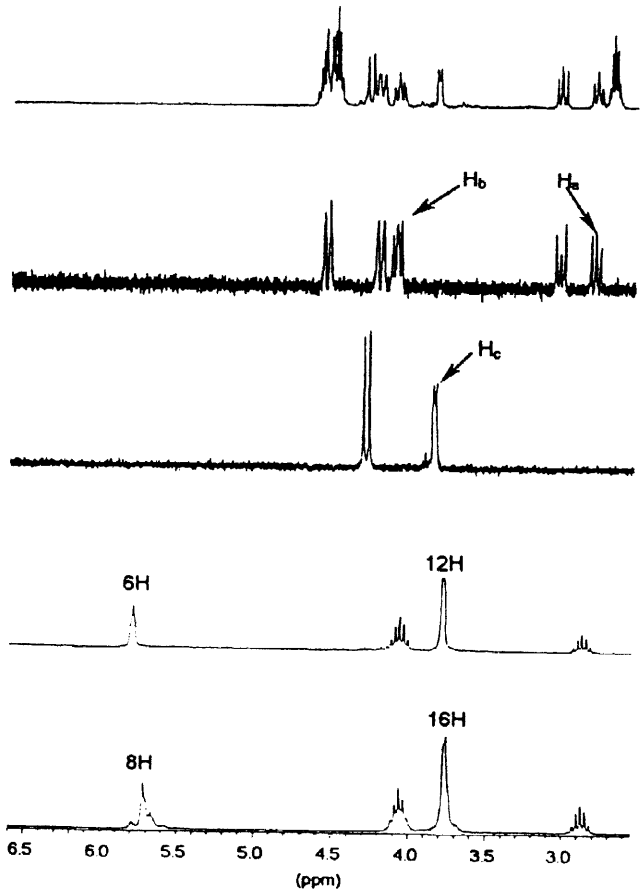
Scheme 5. ^{1}H NMR partial spectra of olefinic part of **15f**, **14f** and **16f** and some selective 1D TOCSY experiments on **15f**.



Spectrum A
^{1}H NMR (toluene-d_8, 400 MHz)
of **15f**

Spectrum B
Selective 1D TOCSY at δ 3.05
of **15f**

Spectrum C
Selective 1D TOCSY at δ 3.85
of **15f**



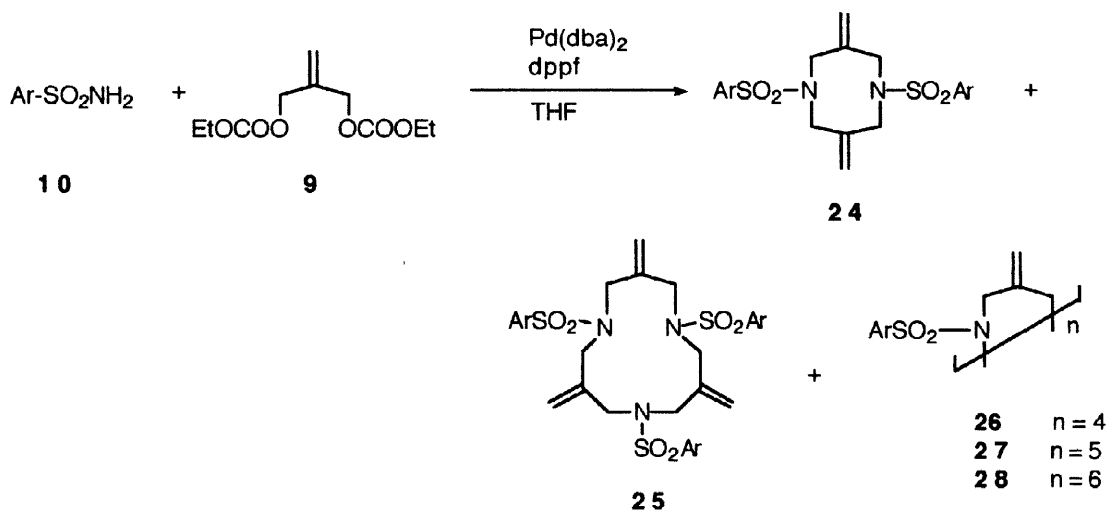
Spectrum D
^{1}H NMR ($CDCl_3$, 250 MHz)
of **14f**

Spectrum E
^{1}H NMR ($CDCl_3$, 250 MHz)
of **16f**

No defined results were obtained in the reactions of cyanamide **29** and sulfamide **32** with **Z-8**.

On the other hand, the reaction of 4-methylbenzenesulfonamide **10b** with dimethyl 2-methylene-1,3-propanediol biscarbonate under Pd(0) catalysis had been reported [36] to afford 8-membered ring **24b** and 12-membered ring **25b** (32% overall yield, 66:36 ratio) along with linear polymers (47% yield). The same bis-carbonate reacted with ditosylated diamines to afford mixtures of cyclic oligomers. Since the authors were more interested in polymers than in monomers, we reinvestigated the first reaction. The results of the reaction of arenesulfonamides **10** with bis-carbonate **9** are in Scheme 6 and Table 3. In all cases 8-membered ring **24** was the major product. Minor quantities of other macrocycles were isolated or detected.

Scheme 6. Pd(0)-catalyzed reactions of arenesulfonamides **10** with bis-carbonate **9**.



10 **9** **24** **25** **26** n = 4, **27** n = 5, **28** n = 6

Table 3.
Pd(0)-catalyzed reactions of arenesulfonamides **10** with bis-carbonate **9**.[a]

Entry	**10**	Ar	Temp	Time (h)	**Products** (%)[b]
1	**10b**	4-MeC_6H_4-	rt	14	**24b** (51), **25b** (13), **26b** (8), **27b** (3), **28b** (1)
2	**10f**	2,4,6-$iPrC_6H_2$-	reflux	48	**24f** (51), **25f**[c], **26f**[c], **27f**[c]
3	**10g**	2,3,4,5,6-MeC_6-	rt	14	**24g** (30), **25g** (11)

[a] All reactions were carried out using $Pd(dba)_2$ (5% molar)/dppf (5% molar) in THF at [**10**] = 0.10 M.

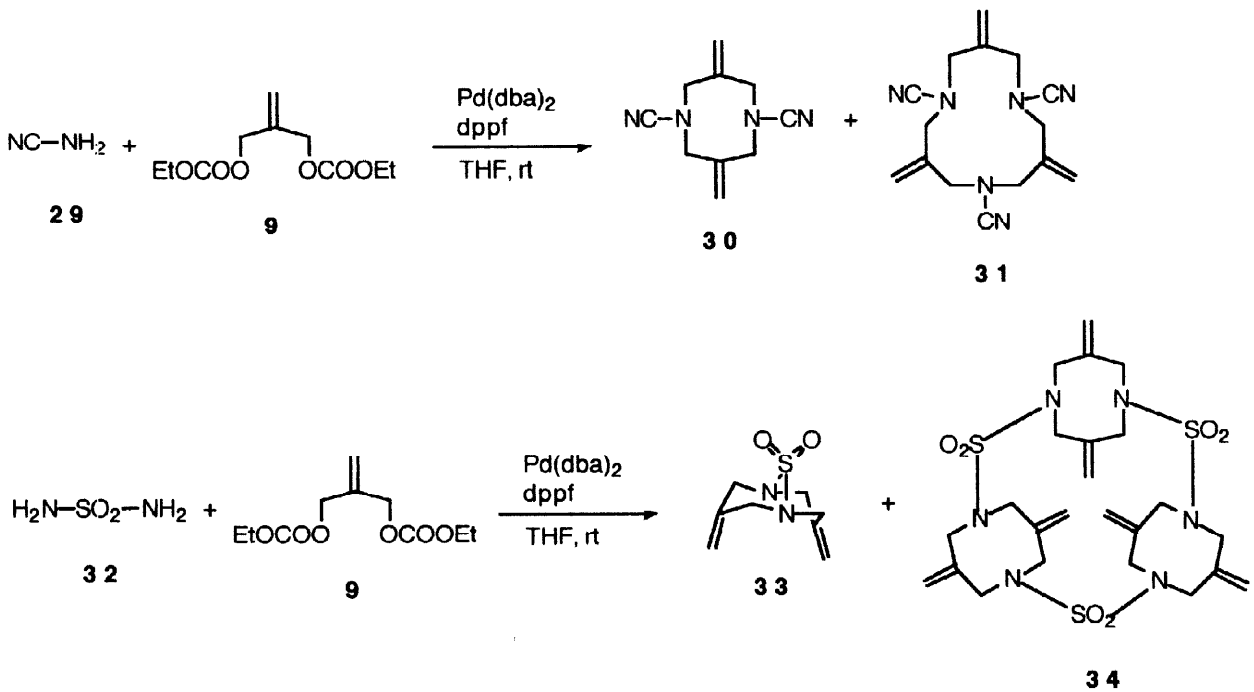
[b] Yields of isolated products unless otherwise stated.

[c] Yield not determined. Identification of products by MALDI-TOF.

Similar results were obtained for cyanamide **29** using the same catalytic system as for arenesulfonamides **10** (Scheme 7). The reaction of **29** with bis-carbonate **9** gave the 8-membered ring **30** (47% yield) together with 12-membered ring **31** (17%). The reaction of sulfamide **32** with bis-carbonate **9** afforded the bicyclic **33** as the major product (68%) along with traces (5% yield) of compound **34** (Scheme 7). All other catalytic systems tested ($Pd(PPh_3)_4$, $Pd(dppe)_2$, $PdCl_2(dppf)$, $PdCl_2(dppf)$/dppf/*n*-BuLi, $PdCl_2(dppf)$/DIBAL,

$Pd(OAc)_2/PPh_3$ and $Pd(OAc)_2$/dppf) in this reaction failed to give **33**.

Scheme 7. Pd(0)-catalyzed reactions of cyanamide **29** and sulfamide **32** with bis-carbonate **9**.



In summary, medium and large unsaturated heterocycles are obtained by reaction of arenesulfonamides **10**, cyanamide **29** and sulfamide **32** with allylic bis-carbonates **8** (*Z* and *E*) and **9** under Pd(0)-catalysis, 3- or 5-membered ring compounds not being detected. MALDI-TOF MS (molecular weight, ring size) and NMR techniques (double bond stereochemistry) were used for structural assignment of macrocycles. From arenesulfonamides and bis-carbonate **8** stable 15-membered rings containing palladium were also isolated, featuring three *trans* olefinic systems coordinated to the metal. We continue to search for more selective preparations of the more interesting heterocyclic compounds.

Experimental

All reactions under Pd(0) catalysis 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. Chemical shifts are given in δ units. NMR experiments were performed at 400 MHz on a spectrometer equipped with an inverse probehead and gradient capabilities. NMR assignments were made by concerted use of gradient-based 2D COSY [37], 2D multiplicity-edited HSQC [38], 2D HMBC [39], 2D NOESY [40] and selective 1D TOCSY [41] experiments. EI mass spectra were recorded under electron impact at 70 eV. MALDI-TOF mass spectra were obtained on an instrument equipped with a pulsed nitrogen laser (337 nm). The instrument was operated in the reflectron, positive-ion, high voltage (19 kV) mode. α-Cyano-4-hydroxycinnamic acid was

used as a matrix. Samples were prepared by mixing a solution of the matrix (THF) and the studied compound (THF, $CHCl_3$, DMSO). The mixture was left to dry at room temperature. LSI mass spectra were recorded on a VG-Autospec mass spectrometer. 3-Nitrobenzyl alcohol (3-NBA) was used as LSI MS matrix and the standard Cs^+ gun was operated at 30 kV. The allylic carbonates were prepared using standard procedures.

Reaction of 2-methylbenzenesulfonamide 10a with bis-carbonate *Z*-8 under $Pd(PPh_3)_4$ catalysis (entry 1, Table 1) (General Method).
A solution of bis-carbonate **Z-8** (2.50 g, 10.80 mmol) in degassed anhydrous THF (3 mL) was added to a mixture of **10a** (1.50 g, 8.80 mmol), $Pd(PPh_3)_4$ (0.50 g, 0.43 mmol) and degassed anhydrous THF (10 mL) kept under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h (TLC monitoring). The precipitate was filtered and washed with ethyl acetate and ethanol to afford a colorless solid (1.05 g, 54%) which was characterized by MALDI-TOF MS as a mixture of linear oligomers **19a** (n = 8 to 21); IR (KBr): 1315, 1159 cm^{-1}; ^1H NMR ($CDCl_3$): 2.52 (s, 3nH), 3.66 (broad s, 4nH), 5.38 (broad s, 2nH), 7.25 (m, 2nH), 7.40 (m, 1nH), 7.87 (m, 1nH); ^{13}C NMR ($CDCl_3$): 20.3, 47.1, 126.1, 129.1, 129.8, 132.8, 132.9, 137.7, 137.8; MALDI-TOF MS (*m/z*, %): 4852.7 (M^+ + 1, n = 21, 10), 4630.7 (M^+ + 2, n = 20, 12), 4406.3 (M^+ + 1, n = 19, 10), 4182.7 (M^+ + 1, n = 18, 20), 3959.4 (M^+ + 1, n = 17, 25), 3735.8 (M^+ + 1, n = 16, 30), 3512.5 (M^+, n = 15, 40), 3289.0 (M^+, n = 14, 50), 3065.5 (M^+, n = 13, 68), 2842.0 (M^+, n = 12, 90), 2618.3 (M^+, n = 11, 100), 2394.4 (M^+, n = 10, 100), 2170.3 (M^+ - 1, n = 9, 85), 1947.5 (M^+ - 1, n = 8, 45).

Under the conditions described in Table 1 (entries 2, 3 and 4) different reaction products were obtained:

Entry 2, Table 1. The precipitate **19a** (34% yield) was filtered from the crude mixture. The solvent from the filtrate was evaporated and the residue was chromatographed through a column of silica gel with hexanes-ethyl acetate (4:6) to give **(*E*,*E*)-1,6-bis[(2-methylphenyl)sulfonyl]-1,2,5,6,7,10-hexahydro-1,6-diazecine 13a** (11% yield) as a colorless solid; mp 165-167 °C (dichloromethane); IR (KBr): 1313, 1158 cm^{-1}; ^1H NMR ($CDCl_3$): 2.57 (s, 6H), 3.66 (m, 4H), 4.45 (d, J = 13.9 Hz, 4H), 5.45 (m, 4H), 7.29 (m, 4H), 7.44 (m, 2H), 7.88 (m, 2H); ^{13}C NMR ($CDCl_3$): 20.2, 52.8, 126.1, 129.6, 132.7, 132.8, 133.2, 133.8, 137.5; MALDI-TOF MS (*m/z*): 469 ([M + Na]$^+$), 446 (M^+). Anal.: Calcd. for $C_{22}H_{26}N_2O_4S_2$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.08 and 58.97; H, 6.15 and 6.19; N, 6.07 and 6.00.

Entry 3, Table 1. Purification of the crude reaction mixture by column chromatography (hexanes-ethyl acetate (2:1)) gave **18** (12% yield) as a colorless oil; IR (film): 1744, 1257, 1158 cm^{-1}; ^1H NMR ($CDCl_3$): 1.25 (m, 6H), 2.56 (s, 3H), 3.81 (d, J = 5.1 Hz, 4H), 4.18 (q, J = 7.3 Hz, 4H), 4.52 (d, J = 4.4 Hz, 4H), 5.63 (m, 4H), 7.30 (m, 2H), 7.40 (m, 1H), 7.91 (m, 1H); ^{13}C NMR ($CDCl_3$): 14.2, 20.3, 47.4, 64.1, 66.9, 126.1, 127.4, 128.5, 129.3, 130.0, 132.7, 132.8, 154.9; MS (*m/z*, %): 366 (M^+ - OCO_2Et, 5), 276 (21), 155 (26), 143 (40), 120 (64), 91 (100).

Entry 4, Table 1. Purification of the crude reaction mixture by column chromatography (hexanes-ethyl acetate (1:1)) afforded **(*E*,*E*,*E*)-1,6,11-tris[(2-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) 15a** (24% yield) as a colorless solid; mp 113-116 °C (methanol); IR (KBr): 1320, 1158 cm^{-1}; ^1H NMR ($CDCl_3$):

2.08 (m, 4H), 2.60 (s, 6H), 2.62 (s, 3H), 3.05-3.29 (m, 4H), 3.94 (m, 2H), 4.01-4.23 (m, 2H), 4.53-4.73 (m, 6H), 7.34 (m, 6H), 7.42 (m, 3H), 7.92 (m, 3H); ^{13}C NMR ($CDCl_3$): 20.3, 44.5, 47.4, 48.7, 79.4, 79.5, 83.5, 126.1, 126.2, 129.6, 129.8, 132.8, 137.5; MALDI-TOF MS (*m/z*): 775 (M^+), 692 ([M - Pd + Na]$^+$). Anal.: Calcd. for $C_{33}H_{39}N_3O_6PdS_3$: C, 51.09; H, 5.07; N, 5.42. Found: C, 51.75; H, 5.39; N, 5.23.

Reaction of 4-methylbenzenesulfonamide 10b with bis-carbonate *Z*-8 under $Pd(PPh_3)_4$ catalysis (entry 5, Table 1).

Purification of the crude reaction mixture by column chromatography (hexanes-ethyl acetate (2:1)) gave an inseparable mixture of cycles **17b** (n = 3 to 5) + **15b** (57% yield); IR (KBr): 1338, 1158 cm^{-1}; ^1H NMR ($CDCl_3$): 2.38 (s, 3nH), 3.60 (s, 4nH), 5.36 (m, 2nH), 7.26 (d, J = 6.6 Hz, 2nH), 7.60 (d, J = 6.6 Hz, 2nH); ^{13}C NMR ($CDCl_3$): 21.5, 48.4, 49.1, 49.5, 78.7, 78.9, 82.9, 127.2, 128.9, 129.8, 136.7, 143.5; MALDI-TOF MS (*m/z*): 1138 ([M + Na]$^+$, n = 5), 915 ([M + Na]$^+$, n = 4), 775.0 (M^+, **15b**), 692 ([M + Na]$^+$, n = 3).

(*E,E*)-1,6-Bis[(4-methylphenyl)sulfonyl]-1,2,5,6,7,10-hexahydro-1,6-diazecine 13b was eluted later (5% yield); mp 212-217 °C (THF-hexanes); IR (KBr): 1330, 1160 cm^{-1}; ^1H NMR ($CDCl_3$): 2.45 (s, 6H), 3.37 (m, 4H), 4.55 (d, J = 13.2 Hz, 4H), 5.29 (m, 4H), 7.33 (d, J = 8.0 Hz, 4H), 7.65 (d, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$): 21.5, 53.5, 127.0, 129.9, 133.4, 139.2, 146.9; MS (*m/z*, %): 446 (M^+, 1), 291 (40), 155 (49), 91 (100).

Reaction of 2-nitrobenzenesulfonamide 10c with bis-carbonate *Z*-8 under $Pd(PPh_3)_4$ catalysis (entry 8, Table 1).

The precipitate was filtered to afford a pale yellow solid (70% yield) which was characterized by MALDI-TOF MS as a mixture of cycles **17c** (n=3 to 6); IR (KBr): 1543, 1372, 1348, 1163 cm^{-1}; ^1H NMR (DMSO-d_6): 3.69 (broad s, 4nH), 5.37 (broad s, 2nH), 7.70-8.00 (m, 4nH); MALDI-TOF MS (*m/z*): 1547 ([M + Na]$^+$, n = 6), 1293 ([M + Na]$^+$, n = 5), 1039 ([M + Na]$^+$, n = 4), 785 ([M + Na]$^+$, n = 3).

Reaction of 4-methoxybenzenesulfonamide 10d with bis-carbonate *Z*-8 under $Pd(PPh_3)_4$ catalysis (entry 9, Table 1).

The crude reaction mixture was chromatographed through a column of silica gel with hexanes-ethyl acetate (1:1) to afford a colorless solid (69% yield), which was identified as an inseparable mixture of **13d** and **17d** (n = 3 to 10); ^1H NMR ($CDCl_3$): 3.30-3.45 (m, 4H, **13d**), 3.63 (broad s, 4nH, **17d**), 3.86 (broad s, 3nH, **17d**), 3.89 (s, 6H, **13d**), 4.55 (d, J = 13.2 Hz, 4H, **13d**), 5.25-5.32 (m, 4H, **13d**), 5.41 (broad s, 2nH, **17d**), 6.99 (m, 4H of **13d**, 2nH of **17d**), 7.68 (m, 4H of **13d**, 2nH of **17d**).

(*E,E*)-1,6-Bis[(4-methoxyphenyl)sulfonyl]-1,2,5,6,7,10-hexahydro-1,6-diazecine 13d was characterized by HPLC-MS (*m/z*, %): 478 (M^+, 2), 307 (50), 171 (100), 107 (63).

The mixture of cycles **17d** was characterized by MALDI-TOF MS (*m/z*): 2414 ([M + Na]$^+$, n = 10), 2174 ([M + Na]$^+$, n = 9), 1935 ([M + Na]$^+$, n = 8), 1696 ([M + Na]$^+$, n = 7), 1457 ([M + Na]$^+$, n = 6), 1218 ([M + Na]$^+$, n = 5), 979 ([M + Na]$^+$, n = 4), 740 ([M + Na]$^+$, n = 3).

Reaction of 1-naphthalenesulfonamide 10e with bis-carbonate *Z*-8 under $Pd(PPh_3)_4$ catalysis (entry 10, Table 1).

The precipitate was filtered to afford a colorless solid (39% yield) which was characterized by MALDI TOF MS as a mixture of cycles **17e** (n=3 to 6); IR (KBr): 1309, 1158, 1130 cm^{-1}; ^1H NMR (C_6D_6 + TFA): 3.60 (broad s, 4nH), 5.30 (broad s, 2nH), 7.10-7.30 (m, 2nH),

7.35-7.60 (m, 3nH), 8.12 (m, 1nH), 8.56 (m, 1nH); ^{13}C NMR ($CDCl_3$ + TFA): 47.2, 124.2, 127.3, 128.2, 128.6, 129.3, 130.6, 133.0, 134.5, 135.4; MALDI TOF MS (*m/z*): 1577 ([M + Na]$^+$, n = 6), 1318 ([M + Na]$^+$, n = 5), 1059 ([M + Na]$^+$, n = 4), 800 ([M + Na]$^+$, n = 3).
The solvent from the filtrate was evaporated and the residue chromatographed through a column of silica gel with hexanes-ethyl acetate (1:1) to give **(*E,E,E,E*)-1,6,11,16-tetrakis(1-naphthalenesulfonyl)-1,6,11,16-tetraazacycloicosa-3,8,13,18-tetraene 16e** (12% yield) as a colorless solid; mp 237-240 °C (hexane-ethyl acetate); IR (KBr): 1315, 1157, 1127 cm^{-1}; ^{1}H NMR ($CDCl_3$ + TFA): 3.74 (broad s, 16H), 5.41 (broad s, 8H), 7.40-7.78 (m, 12H), 7.95 (d, J = 7.3 Hz, 4H), 8.08 (d, J = 8.0 Hz, 4H), 8.15 (d, J = 7.3 Hz, 4H), 8.41 (d, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$ + TFA): 48.6, 124.1, 124.2, 127.4, 128.8, 129.4, 129.9, 130.8, 132.3, 134.6, 135.7; MALDI-TOF MS (*m/z*): 1075 ([M + K]$^+$), 1059 ([M + Na]$^+$). Anal.: Calcd. for $C_{56}H_{52}N_4O_8S_4.2H_2O$: C, 62.67; H, 5.26; N, 5.22; S, 11.95. Found: C, 62.75 and 62.74; H, 5.06 and 5.19; N, 5.19 and 5.19; S, 11.58 and 11.72.

Reaction of 2,4,6-triisopropylbenzenesulfonamide 10f with bis-carbonate *Z*-8 under Pd(PPh$_3$)$_4$ catalysis (Table 2).
An analogous procedure as for **10a** was followed for **10f**. For variations of experimental conditions see Table 2. The crude reaction mixtures were purified by column chromatography through silica gel using hexanes-ethyl acetate mixtures of increasing polarity. The following compounds were obtained. (See Table 2 for products and yields).

(*E,E*)-1,6-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,2,5,6,7,10-hexahydro-1,6-diazecine 13f. Mp 262-263 °C (pentane); IR (KBr): 1316, 1146 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.13-1.40 (m, 36H), 2.87 (septet, J = 6.6 Hz, 2H), 3.66 (m, 4H), 4.03 (septet, J = 6.6 Hz, 4H), 4.39 (d, J = 14.6 Hz, 4H), 5.49 (m, 4H), 7.13 (s, 4H); ^{13}C NMR ($CDCl_3$): 23.5, 24.7, 29.2, 34.2, 51.8, 123.9, 130.8, 133.7, 151.3, 153.1; MS (*m/z*, %): 403 (M$^+$ - SO_2Ar, 8), 267 (15), 137 (100), 108 (43). Anal.: Calcd. for $C_{38}H_{58}N_2O_4S_2$: C, 68.02; H, 8.71; N, 4.17. Found: C, 67.85; H, 8.41; N, 4.00.

(*E,E,E*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene 14f. Mp >290 °C; IR (KBr): 1316, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.17-1.25 (m, 54H), 2.86 (septet, J = 6.6 Hz, 3H), 3.77 (broad s, 12H), 4.07 (septet, J = 6.6 Hz, 6H), 5.79 (apparent s, 6H), 7.13 (s, 6H); ^{13}C NMR ($CDCl_3$): 23.6, 24.8, 29.2, 31.2, 49.2, 123.9, 130.2, 131.0, 151.5, 153.2; MS (*m/z*, %): 739 (M$^+$ - SO_2Ar, 3), 472 (44), 267 (13), 204 (35), 91 (60), 43 (100).

(*E,E,E*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-trienepalladium(0) 15f. Mp >280 °C; IR (KBr): 1316, 1151 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.55 (m, 54H), 2.10 (dd, J = 14.6 and 10.2 Hz, 4H), 2.88 (septet, J = 6.6 Hz, 3H), 3.17 (m, 4H), 3.94 (m, 2H), 4.07-4.28 (m, 8H), 4.37-4.56 (m, 6H), 7.15 (s, 6H); ^{13}C NMR ($CDCl_3$): 23.6, 24.8, 29.2, 34.1, 43.8, 46.5, 47.9, 78.9, 79.1, 83.7, 123.9, 131.3, 151.2, 153.2; MS (*m/z*, %): 739 (M$^+$ - $ArSO_2$ - Pd, 4), 472 (56), 267 (50), 187 (55), 91 (78), 43 (100); LSI MS (*m/z*, %): 1113 (M$^+$, 50), 844 (51), 578 (43), 442 (36); MALDI-TOF MS (*m/z*, %): 1113 (M$^+$, 100), 1029 ([M - Pd + Na]$^+$, 36), 846 (27), 446 (16). Anal.: Calcd. for $C_{57}H_{87}N_3O_6PdS_3$: C, 61.52; H, 7.88; N, 3.78; S, 8.64. Found: C, 61.74 and 61.88; H, 7.67 and 7.59; N, 3.76 and 3.76; S, 8.67 and 8.68.

(*E,E,E,E*)-1,6,11,16-Tetrakis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11,16-tetraazacycloicosa-3,8,13,18-tetraene 16f. Mp 233-236 °C; IR (KBr): 1315, 1152 cm^{-1}; ^1H NMR ($CDCl_3$): 1.08-1.35 (m, 72H), 2.89 (m, 4H), 3.77 (s, 16H), 4.07 (m, 8H), 5.67 (m, 8H), 7.14 (s, 8H); ^{13}C NMR ($CDCl_3$): 23.5, 24.8, 29.2, 34.2, 47.5, 123.9, 130.1, 130.9, 151.5, 153.2; MS (*m/z*, %): 807 (M^+ - 2[SO_2Ar], 15), 539 (20), 267 (75), 175 (85), 91 (100); MALDI-TOF MS (*m/z*, %): 1380 ([M + K]$^+$, 10), 1364 ([M + Na]$^+$, 46), 1341 (M^+, 10), 1113 (10), 1097 (21), 1073 (100). Anal.: Calcd. for $C_{76}H_{116}N_4O_8S_4$: C, 68.02; H, 8.71; N, 4.17. Found: C, 67.56 and 67.54; H, 8.36 and 8.53; N, 4.08 and 4.10.

Mixture of linear oligomers 19f. IR (KBr): 1748, 1601, 1316, 1153 cm^{-1}; ^1H NMR ($CDCl_3$): 1.16-1.23 (m, 300H), 2.86 (m, 14H), 3.70 (broad s, 52H), 4.04 (m, 28H), 4.50 (d, J = 5.8 Hz, 1H), 5.57 (m, 26H), 7.11 (broad s, 85H); ^{13}C NMR ($CDCl_3$): 23.5, 24.8, 29.2, 34.1, 46.2, 123.8, 129.3, 131.2, 151.3, 153.1; MALDI-TOF MS (*m/z*, %): 5889.7 ([M + Na + 1]$^+$, n = 17, 15), 5554.1 ([M + Na + 1]$^+$, n = 16, 20), 5218.4 ([M + Na + 1]$^+$, n = 15, 21), 4883.5 ([M + Na + 1]$^+$, n = 14, 24), 4547.6 ([M + Na + 1]$^+$, n = 13, 27), 4212.0 ([M + Na + 1]$^+$, n = 12, 29), 3876.0 ([M + Na]$^+$, n = 11, 32), 3540.2 ([M + Na]$^+$, n = 10, 39), 3204.4 ([M + Na]$^+$, n = 9, 44), 2868.4 ([M + Na]$^+$, n = 8, 58), 2532.3 ([M + Na - 1]$^+$, n = 7, 75), 2196.3 ([M + Na - 2]$^+$, n = 6, 89), 1861.2 ([M + Na - 1]$^+$, n = 5, 100), 1524.9 ([M + Na - 2]$^+$, n = 4, 80), 1189.3 ([M + Na - 2]$^+$, n = 3, 61).

Mixture of linear oligomers 20. IR (KBr): 1748, 1601, 1316, 1152 cm^{-1}; ^1H NMR ($CDCl_3$): 1.10-1.24 (m, 71H), 2.85 (m, 4H), 3.70 (broad s, 12H), 4.00-4.20 (m, 8H), 4.50 (m, 1H), 5.56 (m, 6H), 7.10 (broad s, 6H); ^{13}C NMR ($CDCl_3$): 14.2, 23.5, 24.8, 29.2, 34.1, 46.3, 64.0, 66.9, 123.9, 129.3, 131.3, 151.4, 153.0; MALDI-TOF MS (*m/z*, %): 5291.9 ([M + Na + 4]$^+$, n = 15, 5), 4957.7 ([M + Na + 5]$^+$, n = 14, 7), 4620.1 ([M + Na + 3]$^+$, n = 13, 10), 4284.3 ([M + Na + 3]$^+$, n = 12, 13), 3948.9 ([M + Na + 3]$^+$, n = 11, 17), 3612.7 ([M + Na + 2]$^+$, n = 10, 23), 3276.5 ([M + Na + 2]$^+$, n = 9, 28), 2940.8 ([M + Na + 1]$^+$, n = 8, 32), 2604.9 ([M + Na + 1]$^+$, n = 7, 36), 2268.8 ([M + Na]$^+$, n = 6, 35), 1933.0 ([M + Na]$^+$, n = 5, 34), 1597.0 ([M + Na]$^+$, n = 4, 35), 1260.7 ([M + Na - 1]$^+$, n = 3, 43), 925.3 ([M + Na - 1]$^+$, n = 2, 52), 590.0 ([M + Na]$^+$, n = 1, 100).

1,6-Bis[(2,4,6-triisopropylphenyl)sulfonyl]perhydrodiazecine 21f (General Method).

A thick-walled hydrogenation bottle was charged with **13f** (0.48 g, 0.72 mmol), $PtO_2.H_2O$ (0.04 g), 10% Pd-C (0.015 g) and THF (15 mL). The mixture was hydrogenated (1 atm. H_2) at room temperature for 2 h (TLC monitoring). The crude reaction mixture was filtered through celite and then evaporated *in vacuo* to afford **21f** (0.49 g, 100%) as a colorless solid which was washed several times with pentane; mp 188-189 °C (THF-pentane); IR (KBr): 1317, 1151 cm^{-1}; ^1H NMR ($CDCl_3$): 1.22 (apparent d, J = 6.6 Hz, 36H), 1.92 (broad s, 8H), 2.87 (septet, J = 6.6 Hz, 2H), 3.30 (broad s, 8H), 4.08 (septet, J = 6.6 Hz, 4H), 7.13 (s, 4H); ^{13}C NMR ($CDCl_3$): 23.5, 24.4, 25.0, 29.6, 30.1, 48.1, 124.1, 131.6, 151.1, 152.8; MS (*m/z*, %): 675 (M^+, 1), 407 (100), 267 (8), 141 (81), 140 (59), 139 (84), 91 (27), 72 (67), 70 (48), 43 (55); LSI MS (*m/z*, %): 675 (M^+, 55), 407 (100). Anal.: Calcd. for $C_{38}H_{62}N_2O_4S_2$: C, 67.61; H, 9.26; N, 4.15; S, 9.50. Found: C, 67.80 and 67.77; H, 8.98 and 8.94; N, 4.47 and 4.41; S, 9.09 and 9.08. **Caution: severe damage of the rubber cap of the hydrogenation bottle was observed due to the THF solvent.**

1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadecane 22f.
It was obtained in 100% yield (colorless solid) from **15f** as for **21f**. Mp 165-169 °C (THF-pentane); IR (KBr): 1315, 1152 cm^{-1}; ^1H NMR ($CDCl_3$): 1.21 (m, 54H), 1.63 (broad s, 12H), 2.87 (septet, J = 6.6 Hz, 3H), 3.14 (broad s, 12H), 4.07 (septet, J = 6.6 Hz, 6H), 7.11 (s, 6H); ^{13}C NMR ($CDCl_3$): 23.5, 24.9, 26.5, 29.3, 34.1, 47.5, 124.0, 131.0, 151.4, 153.0; MS (*m/z*, %): 745 (M^+ - $ArSO_2$, 2), 478 (100), 267 (8), 43 (34); LSI MS (*m/z*, %): 1013 (M^+, 25), 745 (30), 479 (100). Anal.: Calcd. for $C_{57}H_{93}N_3O_6S_3$: C, 67.61; H, 9.26; N, 4.15; S, 9.50. Found: C, 67.58 and 67.51; H, 8.99 and 8.96; N, 4.12 and 4.04; S, 9.17 and 9.06.

1,6,11,16-Tetrakis[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11,16-tetraazacycloicosane 23f.
It was obtained in 100% yield (colorless solid) from **16f** as for **21f**. Mp 207-208 °C (THF-pentane); IR (KBr): 1314, 1150 cm^{-1}; ^1H NMR ($CDCl_3$): 1.17-1.24 (m, 72H), 1.54 (broad s, 16H), 2.87 (septet, J = 6.6 Hz, 4H), 3.15 (broad s, 16H), 4.03 (septet, J = 6.6 Hz, 8H), 7.11 (s, 8H); ^{13}C NMR ($CDCl_3$): 23.5, 24.8, 25.7, 29.2, 34.0, 45.8, 123.9, 131.3, 151.2, 153.0; MS (*m/z*, %): 1083 (M^+ - $ArSO_2$, 1), 816 (21), 547 (4), 267 (25), 84 (100), 43 (60); LSI MS (*m/z*, %): 1350 (M^+, 15), 1082 (33), 816 (100), 548 (15). Anal.: Calcd. for $C_{76}H_{124}N_4O_8S_4$: C, 67.61; H, 9.26; N, 4.15; S, 9.50. Found: C, 67.69 and 67.48; H, 8.97 and 8.90; N, 4.33 and 4.12; S, 9.13 and 9.09.

Preparation of 14f from 15f.
1,1'-Bis(diphenylphosphino)ferrocene (0.15 g, 0.27 mmol) was added to a solution of **15f** (0.54 g, 0.05 mmol) in degassed anhydrous dioxane (10 mL). The mixture was refluxed with stirring under nitrogen atmosphere for 48 h (TLC monitoring). The solvent was evaporated to give a residue which was chromatographed through a column of silica gel with hexanes-ethyl acetate (6:1) to afford **14f** (0.03 g, 61%) as a colorless solid. Recovered starting material **15f** (0.02 g, 33%) was eluted later.

Preparation of (*E,Z*)-1,6-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,2,5,6,7,10-hexahydro-1,6-diazecine (*E,Z*)-13f.
(*Z*)-1,4-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,4-diamine-2-butene. This compound was prepared in 9% overall yield (not optimized) from (*Z*)-2-butene-1,4-diol following a procedure reported in the literature for a similar compound [34]. Mp 162-164 °C; IR (KBr): 1321, 1154 cm^{-1}; ^1H NMR ($CDCl_3$): 1.21 (d, J = 6.6 Hz, 36H), 2.88 (septet, J = 6.6 Hz, 2H), 3.58 (apparent t, J = 5.8 Hz, 4H), 4.06 (septet, J = 6.6 Hz, 4H), 4.37 (t, J = 5.8 Hz, 2H), 5.47 (t, J = 5.8 Hz, 2H), 7.13 (s, 4H).
(*E,Z*)-1,6-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,2,5,6,7,10-hexahydro-1,6-diazecine. (*Z*)-1,4-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-1,4-diamine-2-butene (0.19 g, 0.31 mmol) was added to a solution of NaOEt (0.04 g, 0.65 mmol) in ethanol (15 mL) at 60 °C. Then, after 1 h at reflux the solvent was evaporated to give a residue which was dissolved in DMF (10 mL). To this solution prewarmed at 90 °C was added (*E*)-1,4-dibromo-2-butene (0.08 g, 0.37 mmol) and the mixture was stirred for 12 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 the 10-membered ring (0.13 g, 60%) as a colorless solid, mp 246-247 °C (pentane); IR (KBr): 1321, 1147 cm^{-1}; ^1H NMR ($CDCl_3$): 1.23 (d, J = 6.6 Hz, 36H), 2.88 (septet, J = 6.6 Hz, 2H), 3.51 (m, 2H), 3.66 (dd, J = 15.4 and 5.9 Hz, 2H), 3.95 (dd, J = 15.4 and 5.9 Hz, 2H), 4.12 (m, 6H), 5.58 (t, J = 5.1 Hz, 2H), 5.64 (m, 2H), 7.14

(s, 4H); ^{13}C NMR ($CDCl_3$): 23.5, 24.8, 29.3, 34.2, 41.7 (broad signal), 50.0 (broad signal), 124.0, 128.9-129.1 (broad signal), 130.5, 133.7, 151.5, 153.3; MALDI-TOF MS (*m/z*): 709 ([M + K]$^+$), 693 ([M + Na]$^+$), 670 (M$^+$). Anal.: Calcd. for $C_{38}H_{58}N_2O_4S_2$: C, 68.02; H, 8.71; N, 4.17. Found: C, 68.17 and 67.97; H, 8.98 and 8.91; N, 4.12 and 4.12.

(*E*)-1,4-Dibromo-2-butene was prepared in 65% yield by treatment of (*E*)-2-butene-1,4-diol with PBr_3. (*E*)-2-Butene-1,4-diol was obtained in 87% yield by reduction of 2-butyne-1,4-diol with $LiAlH_4$/THF.

Reaction of 4-methylbenzenesulfonamide 10b with bis-carbonate 9 under Pd(dba)$_2$/dppf catalysis (entry 1, Table 3) (General Method).
A solution of bis-carbonate **9** (0.58 g, 2.49 mmol) in degassed anhydrous THF (10 mL) was added to a mixture of **10b** (0.35 g, 2.00 mmol), $Pd(dba)_2$ (0.05 g, 0.10 mmol), dppf (0.05 g, 0.10 mmol) and degassed anhydrous THF (10 mL). The stirred mixture was kept at room temperature under nitrogen atmosphere for 14 h (GLC monitoring). The solvent was evaporated and the residue chromatographed through a silica gel column, eluting with mixtures of increasing polarity from hexanes-ethyl acetate, (9:1 to 65:35). The following compounds were obtained in the order:

3,7-Dimethylene-1,5-bis[(4-methylphenyl)sulfonyl]perhydro-1,5-diazocine 24b (0.199 g, 51%) as a colorless solid; mp 200-201 °C (hexane-ethyl acetate) (Lit. [42] mp 194-197 °C); IR (KBr): 1337, 1157 cm^{-1}; ^1H NMR ($CDCl_3$): 2.43 (s, 6H), 3.82 (s, 8H), 5.19 (s, 4H), 7.31 (d, J = 8.8 Hz, 4H), 7.67 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$): 21.4, 53.0, 118.1, 127.1, 129.7, 135.9, 141.8, 143.5; MALDI-TOF MS (*m/z*): 485 ([M + K]$^+$), 470 ([M + 1 + Na]$^+$), 447 (M$^+$ + 1). Anal.: Calcd. for $C_{22}H_{26}N_2O_4S_2$: C, 59.17; H, 5.87; N, 6.27; S, 14.36. Found: C, 58.84 and 58.67; H, 5.92 and 5.95; N, 6.27 and 6.23; S, 13.92 and 13.98.

3,7,11-Trimethylene-1,5,9-tris[(4-methylphenyl)sulfonyl]-1,5,9-triazacyclododecane 25b (0.086 g, 13%); ^1H NMR ($CDCl_3$): 2.43 (s, 9H), 3.75 (s, 12H), 5.03 (s, 6H), 7.31 (d, J = 8.0 Hz, 6H), 7.65 (d, J = 8.0 Hz, 6H); MALDI-TOF MS (*m/z*): 692 ([M + Na]$^+$), 515 (M$^+$ + 1 - $ArSO_2$).

3,7,11,15-Tetramethylene-1,5,9,13-tetrakis[(4-methylphenyl)sulfonyl]-1,5,9,13-tetraazacyclohexadecane 26b (0.037 g, 8%); ^1H NMR ($CDCl_3$): 2.43 (s, 12H), 3.75 (s, 16H), 5.03 (s, 8H), 7.31 (d, J = 8.8 Hz, 8H), 7.65 (d, J = 8.8 Hz, 8H); MALDI-TOF MS (*m/z*): 931 ([M + K]$^+$), 915 ([M + Na]$^+$).

3,7,11,15,19-Pentamethylene-1,5,9,13,17-pentakis[(4-methylphenyl)sulfonyl]-1,5,9,13,17-pentaazacycloicosane 27b (0.012 g, 3%); ^1H NMR ($CDCl_3$): 2.43 (s, 15H), 3.60 (s, 20H), 4.97 (s, 10H), 7.28-7.31 (m, 10H), 7.63 (d, J = 8.0 Hz, 10H); MALDI-TOF MS (*m/z*): 1138 ([M + Na]$^+$).

3,7,11,15,19,23-Hexamethylene-1,5,9,13,17,21-hexakis[(4-methylphenyl)sulfonyl]-1,5,9,13,17,21-hexaazacyclotetracosane 28b (0.006 g, 1%); ^1H NMR ($CDCl_3$): 2.41 (s, 18H), 3.62 (broad s, 24H), 4.97 (broad s, 12H), 7.28 (d, J = 8.8 Hz, 12H), 7.64 (d, J = 8.8 Hz, 12H); MALDI-TOF MS (*m/z*): 1361 ([M + Na]$^+$).

Reaction of 2,4,6-triisopropylbenzenesulfonamide 10f with bis-carbonate 9 under Pd(dba)$_2$/dppf catalysis (entry 2, Table 3)
The crude mixture was chromatographed through a column of silica gel eluting with mixtures of increasing polarity from hexanes-ethyl acetate (9:1 to 8:2). The following compounds were obtained in the order:

1,5-Bis[(2,4,6-triisopropylphenyl)sulfonyl]-3,7-dimethyleneperhydro-1,5-diazocine 24f (51% yield) as a colorless solid; mp 202-203 °C (cyclohexane); IR (KBr): 1317, 1154 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.25 (apparent t, J = 6.5 Hz, 36H), 2.90 (septet, J = 6.6 Hz, 2H), 3.95 (s, 8H), 4.07 (septet, J = 6.6 Hz, 4H), 5.10 (s, 4H), 7.17 (s, 4H); ^{13}C NMR ($CDCl_3$): 23.5, 24.9, 29.3, 34.2, 52.2, 118.4, 124.0, 130.9, 142.5, 151.5, 153.3; MALDI-TOF MS (*m/z*): 709 ([M + K]$^+$), 693 ([M + Na]$^+$), 671 (M$^+$ + 1), 669 (M$^+$ - 1), 403 (M$^+$ - $ArSO_2$). Anal.: Calcd. for $C_{38}H_{58}N_2O_4S_2$: C, 68.02; H, 8.71; N, 4.17; S, 9.56. Found: C, 68.13 and 67.95; H, 8.58 and 8.59; N, 4.24 and 4.13; S, 9.35 and 9.36.

The following compounds could not be separated by chromatography. They were eluted together and identified by MALDI-TOF MS:
1,5,9-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-3,7,11-trimethylene-1,5,9-triazacyclododecane 25f; ^{1}H NMR ($CDCl_3$): 1.25 (apparent t, J = 6.5 Hz, 54H), 2.90 (septet, J = 6.6 Hz, 3H), 3.91 (s, 12H), 4.07 (septet, J = 6.6 Hz, 6H), 5.22 (s, 6H), 7.17 (s, 6H); MALDI-TOF MS (*m/z*): 748 (M$^+$ - $ArSO_2$).
1,5,9,13-Tetrakis[(2,4,6-triisopropylphenyl)sulfonyl]-3,7,11,15-tetramethylene-1,5,9,13-tetraazacyclohexadecane 26f; ^{1}H NMR ($CDCl_3$): 1.25 (apparent t, J = 6.5 Hz, 72H), 2.90 (septet, J = 6.6 Hz, 4H), 3.82 (s, 16H), 4.07 (septet, J = 6.6 Hz, 8H), 5.17 (s, 8H), 7.17 (s, 8H); MALDI-TOF MS (*m/z*): 1073 (M$^+$ - $ArSO_2$).
1,5,9,13,17-Pentakis[(2,4,6-triisopropylphenyl)sulfonyl]-3,7,11,15,19-pentamethylene-1,5,9,13,17-pentaazacycloicosane 27f; ^{1}H NMR ($CDCl_3$): 1.25 (apparent t, J = 6.5 Hz, 90H), 2.90 (septet, J = 6.6 Hz, 5H), 3.96 (s, 20H), 4.07 (septet, J = 6.6 Hz, 10H), 5.11 (s, 10H), 7.17 (s, 10H); MALDI-TOF MS (*m/z*): 1408 (M$^+$ - $ArSO_2$).

Reaction of 2,3,4,5,6-pentamethylbenzenesulfonamide 10g with bis-carbonate 9 under Pd(dba)$_2$/dppf catalysis (entry 3, Table 3).
The crude mixture was chromatographed through a column of silica gel eluting with mixtures of increasing polarity from hexanes-ethyl acetate (9:1 to 7:3). The following compounds were obtained in the order:

3,7-Dimethylene-1,5-bis[(2,3,4,5,6-pentamethylphenyl)sulfonyl]perhydro-1,5-diazocine 24g (30% yield) as a colorless solid; mp 218-220 °C (hexane-ethyl acetate); IR (KBr): 1308, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$): 2.24 (s, 12H), 2.29 (s, 6H), 2.53 (s, 12H), 3.88 (s, 8H), 5.07 (s, 4H); ^{13}C NMR ($CDCl_3$): 17.1, 17.9, 18.8, 51.9, 118.8, 134.1, 135.0, 135.6, 140.1, 142.1; MALDI-TOF MS (*m/z*): 597 ([M + K]$^+$), 582 ([M + 1 + Na]$^+$), 559 (M$^+$ + 1). Anal.: Calcd. for $C_{30}H_{42}N_2O_4S_2$: C, 64.48; H, 7.58; N, 5.01; S, 11.47. Found: C, 64.39 and 64.31; H, 7.31 and 7.48; N, 5.03 and 5.06; S, 11.32 and 11.33.

3,7,11-Trimethylene-1,5,9-tris[(2,3,4,5,6-pentamethylphenyl)sulfonyl]-1,5,9-triazacyclododecane 25g (11% yield) as a colorless solid; mp 239-241 °C (hexane-ethyl acetate); IR (KBr): 1316, 1146 cm^{-1}; ^{1}H NMR ($CDCl_3$): 2.23 (s, 18H), 2.28 (s, 9H), 2.51 (s, 18H), 3.73 (s, 12H), 5.13 (s, 6H); ^{13}C NMR ($CDCl_3$): 17.1, 17.9, 19.1, 49.4, 118.3, 134.3,

135.0, 135.4, 138.4, 140.3; MALDI-TOF MS (*m/z*): 876 ([M + K]$^+$), 860 ([M + Na]$^+$), 836 (M$^+$ - 1), 626 (M$^+$ - $ArSO_2$). Anal.: Calcd. for $C_{45}H_{63}N_3O_6S_3$: C, 64.48; H, 7.58; N, 5.01; S, 11.47. Found: C, 64.40 and 64.46; H, 7.71 and 7.61; N, 5.14 and 5.12; S, 11.49 and 11.56.

Reaction of cyanamide 29 with bis-carbonate 9 under Pd(dba)$_2$/dppf catalysis. An analogous procedure as for **10b** was followed for **29**. The crude mixture was chromatographed through a column of silica gel eluting with mixtures of increasing polarity from hexanes-ethyl acetate (9:1 to 1:1). The following compounds were obtained in the order:

1,5-Dicyano-3,7-dimethyleneperhydro-1,5-diazocine 30 (47% yield) as a colorless solid; mp 96-98 °C (hexane-ethyl acetate); IR (KBr): 2206 cm^{-1}; ^{1}H NMR ($CDCl_3$): 3.83 (s, 8H), 5.32 (s, 4H); ^{13}C NMR ($CDCl_3$): 55.4, 116.3, 121.1, 138.1; MS (*m/z*, %): 188 (M$^+$, 100), 160 (59), 147 (79), 95 (78), 93 (67), 55 (97). Anal.: Calcd. for $C_{10}H_{12}N_4$: C, 63.81; H, 6.43. Found: C, 63.74 and 63.77; H, 6.26 and 6.23. HRMS: Calcd. for $C_{10}H_{12}N_4$: 188.105697. Found: 188.106197.

1,5,9-Tricyano-3,7,11-trimethylene-1,5,9-triazacyclododecane 31 (17% yield) as a colorless solid; mp 178-179 °C (ethyl acetate); IR (KBr): 2218 cm^{-1}; ^{1}H NMR ($CDCl_3$): 3.67 (s, 12H), 5.54 (s, 6H); ^{13}C NMR ($CDCl_3$): 52.4, 116.5, 122.7, 134.6; MALDI-TOF MS (*m/z*): 321 ([M + K]$^+$), 305 ([M + Na]$^+$), 282 (M$^+$). Anal.: Calcd. for $C_{15}H_{18}N_6$: C, 63.81; H, 6.43; N, 29.76. Found: C, 63.70 and 63.58; H, 6.20 and 6.18; N, 29.38 and 29.35.

Reaction of sulfamide 32 with bis-carbonate 9 under Pd(dba)$_2$/dppf catalysis. An analogous procedure as for **10b** was followed for **32**. The crude mixture was chromatographed through a column of silica gel eluting with hexanes-ethyl acetate (9:1). The following compounds were obtained in the order:

3,7-Dimethylene-9,9-dioxo-1,5,9-diazathiabicyclo[3.3.1]nonane 33 (68% yield) as a colorless solid; mp 180-182 °C (pentane); IR (KBr): 1362, 1171 cm^{-1}; ^{1}H NMR ($CDCl_3$): 3.83 (d, J = 16 Hz, 4H), 4.75 (d, J = 16 Hz, 4H), 4.93 (s, 4H); ^{13}C NMR ($CDCl_3$): 58.9, 114.8, 133.0; MS (*m/z*, %): 200 (M$^+$, 69), 108 (54), 95 (35), 68 (44), 42 (100). Anal.: Calcd. for $C_8H_{12}N_2O_2S$: C, 47.98; H, 6.04; N, 13.99; S, 16.01. Found: C, 47.90 and 47.91; H, 6.20 and 6.21; N, 13.65 and 13.71; S, 15.77 and 15.88.

Trimer 34 (5% yield) as a colorless solid; mp 248-249 °C (ethyl acetate); IR (KBr): 1340, 1164 cm^{-1}; ^{1}H NMR ($CDCl_3$): 3.63 (s, 12H), 3.78 (m, 12H), 5.12 (s, 6H), 5.33 (s, 6H); ^{13}C NMR ($CDCl_3$): 48.7, 50.9, 52.4, 53.0, 54.7, 113.8, 115.4, 116.3, 117.9, 118.8, 120.4, 133.6, 137.5; MALDI-TOF MS (*m/z*): 639 ([M + K]$^+$), 623 ([M + Na]$^+$), 600 (M$^+$). Anal.: Calcd. for $C_{24}H_{36}N_6O_6S_3$: C, 47.98; H, 6.04; N, 13.99; S, 16.01. Found: C, 47.55; H, 6.15; N, 13.39; S, 15.61.

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