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Palladium(0)-Catalyzed Tandem Cyclization of Allenenes: Direct Construction of Tricyclic Heterocycles through Aromatic C–H Activation

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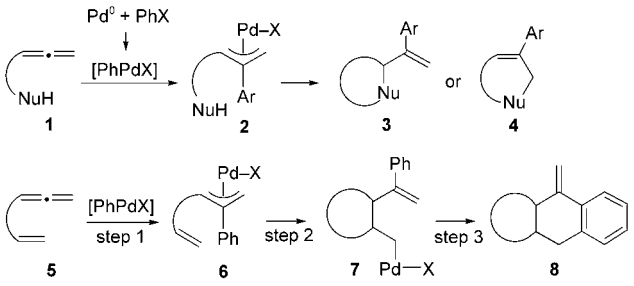
Abstract: Palladium(0)-catalyzed tandem cyclization of allenenes is described. Treatment of allenenes with an aryl halide, potassium carbonate, and catalytic [$Pd(PPh_3)_4$] in dioxane afforded tri- or tetracyclic heterocycles in moderate to good yields through insertion of arylpalladium(II) halide into the allenic moiety, intramolecular carbopalladation, and aromatic C–H bond activation. The substituent on the olefin terminus has proven to be essential for the success of the tandem cyclization. The reaction with heterocyclic aryl halides such as iodopyrazine or 4-bromo-1-methylindole afforded tri- or tetracyclic heteroaromatic products in good yields.

Keywords: allenes · C–H activation · heterocycles · palladium · tandem cyclization

Introduction

Palladium-catalyzed C–H activation of an aromatic group has received considerable attention in recent years due to the wide variety of reactions that afford condensed ring systems by using a nonfunctionalized aryl group.[1,2,3,4] In particular, tandem carbon–carbon bond formations through this process are useful in that complex molecules can be directly obtained in a single operation. Although palladium-catalyzed monocyclization onto an aryl ring forming two,[5] three,[6] or four carbon–carbon bonds[7] in a one-pot manner is well documented, the tandem reaction involving a bis-cyclization process is extremely rare. Grigg and co-workers reported that an aryl halide bearing a carbon–carbon multiple bond and an additional aryl group undergoes bis or tris cyclization when treated with a palladium(0) catalyst.[8] More recently, palladium(0)-catalyzed tandem cyclization of alkyne-substituted phenyl iodide with a terminal alkyne to form condensed aromatic rings was also reported.[9] In contrast, to the best of our knowledge, tandem carbon–carbon bond formation including C–H activation of aromatic rings by use of allenic compounds is unknown.

Currently, transition-metal-catalyzed cyclizations of allenes are becoming an attractive approach for the construction of heterocycles.[10] Cyclizations of allenes of type **1** with a nucleophilic functionality in the presence of a palladium catalyst to give **3** or **4** are well documented (Scheme 1).[11,12] Recently, cyclizations of bisallenes on treatment with silylstannane and palladium(0) were independently reported by two research groups.[13] Palladium(II)-catalyzed oxidative cyclization of allene-substituted alkenes and palladium(0)-catalyzed cyclization of allenes bearing an allyl ester moiety were reported by Bäckvall et al.[14,15] Furthermore, we recently reported a novel palladium(0)-catalyzed cyclization of allenenes giving 2,3-*cis*-pyrrolidines or 3-azabicyclo-[3.1.0]hexanes.[16] However, palladium(0)-catalyzed tandem



Scheme 1. Palladium(0)-catalyzed cyclization of allenes (Nu = nucleophile, X = halide).

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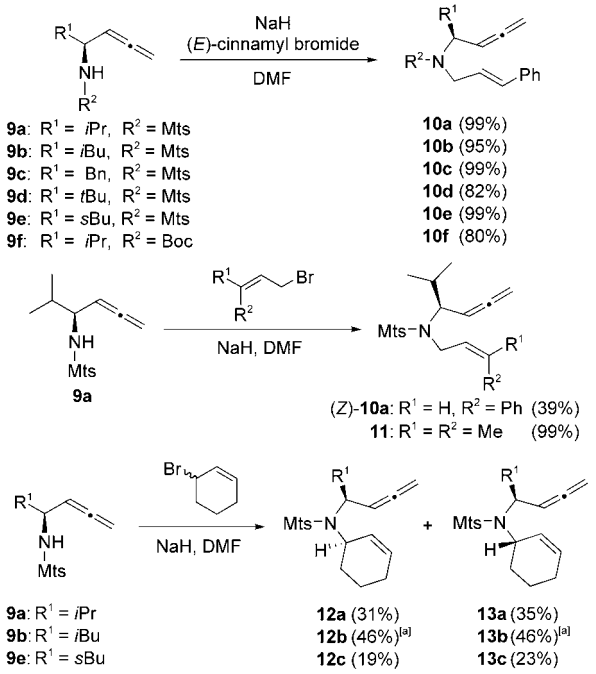
cyclizations of an allene that contains an additional multiple bond have scarcely been investigated.[17] We expected that allenene **5** could undergo a tandem cyclization of the type shown in Scheme 1, through insertion of arylpalladium(II) halide into an allenic moiety (step 1), carbopalladation onto a carbon–carbon double bond (step 2), and aromatic C–H activation of the resulting palladium(II) intermediate **7** (step 3). Herein we present a full account of our investigation into the palladium(0)-catalyzed tandem cyclization of allenenes.[18]

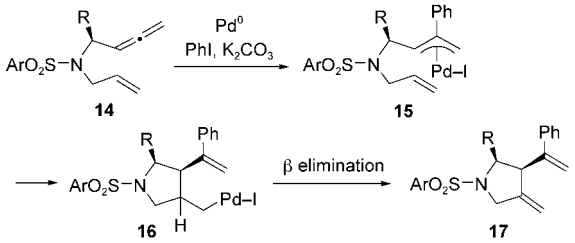
Results and Discussion

Synthesis of requisite allenenes for the palladium-catalyzed tandem cyclization: With a view to synthesizing nitrogen heterocycles, we prepared allenenes of type **10** by reaction of (*E*)-cinnamyl bromide with known amino allenes of type **9** (Scheme 2), which, in turn, were easily obtained from (*S*)-amino acids through the diethylzinc-mediated reductive synthesis of amino allenes catalyzed by palladium(0).[19] The corresponding isomer (*Z*)-**10a** and dimethylated allenene **11** were similarly prepared by treatment of **9a** with (*Z*)-cinnamyl bromide[20] or 4-bromo-2-methylbut-2-ene, respectively. Reaction of amino allenes of type **9** with racemic 3-bromocyclohexene followed by separation of the resulting diastereomixtures afforded (cyclohexenyl)amino allene derivatives of type **12** and **13** in moderate to good yields.[21]



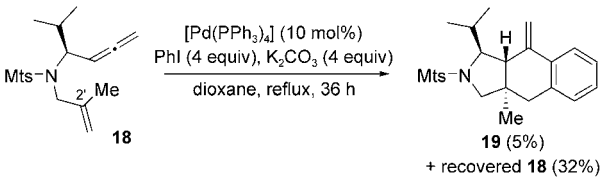
Scheme 2. Synthesis of requisite allenenes (Mts = 2,4,6-trimethylphenylsulfonyl). [a] Determined by ^{1}H NMR spectroscopy.

Tandem cyclization of allenenes with iodobenzene derivatives: We recently reported that treatment of amino allene derivatives of type **14** bearing an allyl group on the nitrogen atom with an aryl halide and potassium carbonate in the presence of $[Pd(PPh_3)_4]$ affords 2,3-*cis*-pyrrolidines of type **17** through carbocyclization on the double bond of **15** and subsequent β-hydride elimination of the resulting alkylpalladium intermediate **16** (Scheme 3).[16b] It is apparent that inhibition of the β-hydride elimination from **16** is essential for the success of the tandem cyclization and the aromatic C–H activation.



Scheme 3. Palladium(0)-catalyzed pyrrolidine formation through β-hydride elimination.

In an initial experiment, we investigated the reaction of known allenene **18**[16] bearing a methyl group on the double bond instead of the eliminative hydrogen atom (Scheme 4).

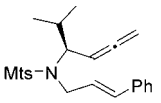
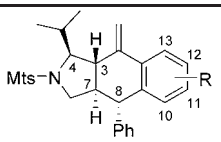
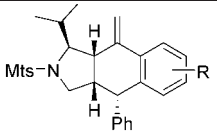
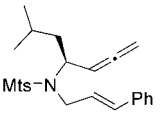
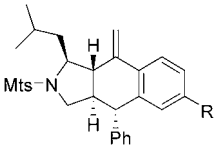
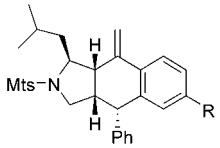
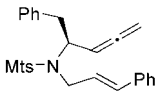
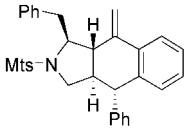
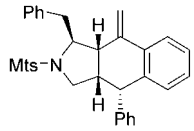
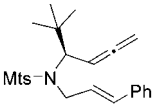
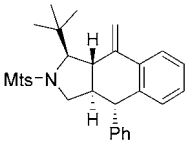
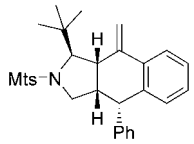
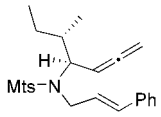
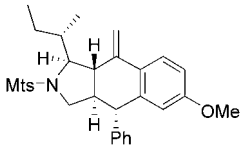
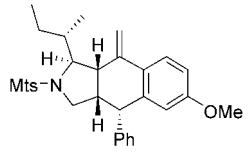
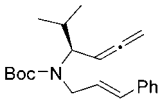
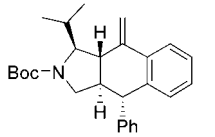
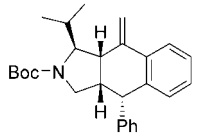
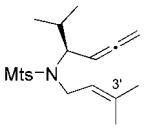
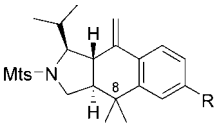


Scheme 4. Palladium(0)-catalyzed tandem cyclization of 2′-methylated allenene **18**.

Unfortunately, the reaction of **18** is extremely slow to afford the desired cyclized product **19** in only a 5% yield with recovery of the starting material. However, this result clearly shows that inhibition of the β-hydride elimination does promote the desired tandem cyclization onto an aryl group through C–H activation, although in a low yield.

We next investigated the cyclization of allenenes of type **10** with a phenyl substituent at the 3′-position, as the introduction of a substituent at the olefin terminus might impede the required arrangement of the palladium center relative to the hydrogen atom for β-hydride elimination to occur.[22,23] To our delight, allenene **10a** reacted with iodobenzene, potassium carbonate, and a catalytic amount of palladium(0) in dioxane to give a separable diastereomeric mixture of the benzoisoindole derivatives **20a** and **21a** in moderate yields (41 and 10%, respectively; Table 1, entry 1). This is the first example of a successful palladium(0)-catalyzed tandem cyclization of allenenes. Introduction of an electron-donating

Table 1. Palladium(0)-catalyzed tandem cyclization of allenenes with iodobenzene derivatives.[a]

Entry	Substrate	ArI	t [h]	Product (yield)	
					
1	**10a**	PhI	7.5	**20a**: R = H (41%)	**21a**: R = H (10%)
2	**10a**	4-MePhI	7	**20b**: R = 11-Me (37%)	**21b**: R = Me (18%)
3	**10a**	4-MeOPhI	3.5	**20c**: R = 11-OMe (43%)	**21c**: R = OMe (20%)
4	**10a**	3-MeOPhI	5	**20da**: R = 10-OMe (19%) **20db**: R = 12-OMe (17%)	**21da**: R = 10-OMe (trace) **21db**: R = 12-OMe (trace)
5	**10a**	2-MeOPhI	10	**20e**: R = 13-OMe (36%)	**21e**: R = 13-OMe (2%)
					
6[b]	**10b**	PhI	29	**22a**: R = H (21%)	**23a**: R = H (14%)
7	**10b**	4-MeOPhI	13	**22b**: R = OMe (32%)	**23b**: R = OMe (36%)
					
8	**10c**	PhI	23	**24** (30%)	**25** (24%)
					
9[b,c]	**10d**	PhI	6	**26** (34%)	**27** (7%)
					
10	**10e**	4-MeOPhI	3	**28** (34%)	**29** (31%)
					
11	**10f**	PhI	30	**30** (16%)	**31** (35%)
					
12[b]	**11**	PhI	28	**32a**: R = H (42%)	
13	**11**	4-MeOPhI	30	**32b**: R = OMe (45%)	

[a] Unless otherwise stated, reactions were carried out with $[Pd(PPh_3)_4]$ (10 mol%), ArI (2 equiv), and K_2CO_3 (2 equiv) in dioxane under reflux. [b] Increased amounts of ArI (4 equiv) and K_2CO_3 (4 equiv) were used. [c] Considerable amount of unidentified products were obtained.

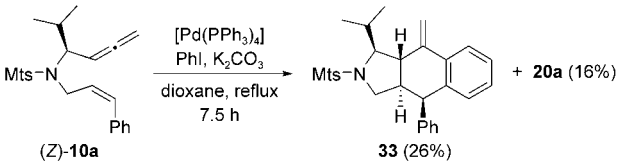
substituent such as a methyl and methoxy group at the 4-position of iodobenzene increased the reaction rate and slightly improved the yields of the tricyclic products (entries 2 and 3).[24] However, the reaction with 2-iodoanisole (entry 5) gave lower yields of the desired benzoisoindoles **20e** (36%) and **21e** (2%), presumably due to the steric hindrance of

the 2-anisyl group. It should be noted that, as we expected, the reaction with 3-iodoanisole (entry 4) yielded two regioisomeric products, 10- and 12-methoxy derivatives **20da** (19%) and **20db** (17%), respectively.

Similarly, other *N*-cinnamylamino allenes **10b** and **10c** (entries 6–8) in which the α substituent is smaller, also reacted to afford the expected tricyclic products **22**–**25**, although prolonged reaction times were required. When allenene **10d** with a bulky *tert*-butyl group on the α position to the allenic moiety was used, the corresponding benzoisoindoles **26** and **27** were obtained in a relatively lower combined yield (41%). Similar to allenene **10a** (entries 1–5), allenene **10e** bearing a branched alkyl group (*sec*-butyl) is more reactive and gives the desired tricyclic products **28** and **29** in good yields (65% combined yields, entry 10). A Boc group (Boc = *tert*-butoxycarbonyl) can also be used as the nitrogen-protecting group (entry 11). Interestingly, 3,7-*cis* isomer **31** predominated over its *trans* isomer **30** (**30**/**31** = 16:35), although the exact reason is unclear. Substituents other than a phenyl group at the olefin terminus can also promote the tandem cyclization. Thus, reaction of the *N*-(3,3-dimethylallyl)amino derivative **11** yielded the expected cyclized products of type **32** with geminal dimethyl substitution at C8 in a stereoselective manner (entries 12 and 13).

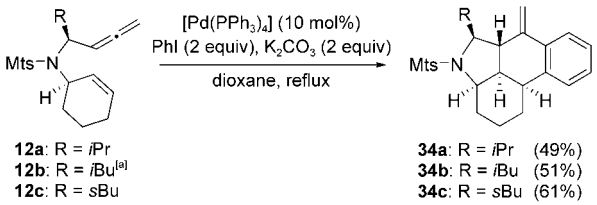
The cyclized products were fully characterized by ^{1}H NMR, ^{13}C NMR, NOE, and COSY spectroscopic analyses, and the structure of **21a** was also confirmed by HMQC and HMBC analyses. The configuration of the cyclized products were determined by NOE analyses (see the Supporting Information). Although the combined isolated yields are moderate (35–68%) due to the formation of some undesired byproducts, such as compounds **58** and **59**[25] (see the Experimental Section), the yields of the desired tricycic compounds are synthetically acceptable as three carbon–carbon bonds are successively formed in a single operation.

Next, the reaction of (*Z*)-cinnamyl derivative, (*Z*)-**10a**, was investigated (Scheme 5). Exposure of **10a** to the identical reaction conditions for 7.5 h yielded **33** (26%) and **20a** (16%). It should be mentioned that isomer **33** was not detected in the reaction of (*E*)-**10a** (Table 1, entry 1). The cyclization of (*Z*)-**10a** for a prolonged reaction time (15 h) gave **33** and **20a** in essentially the same product ratio (**33**/**20a** = 1.4:1), which strongly suggests that the reaction is kinetically controlled.



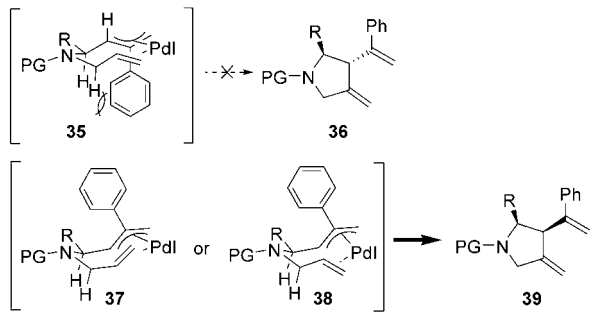
Scheme 5. Palladium(0)-catalyzed tandem cyclization of (*Z*)-**10a** (see Scheme 1 for abbreviations).

In order to examine the scope of the tandem cyclization as a useful synthetic method of various polycyclic compounds, we investigated the reaction of *N*-cyclohexenyl derivatives of type **12** (Scheme 6). Treatment of **12a** under the standard cyclization conditions led to the formation of the desired tetracyclic compound **34a** in a 49% yield as a single isomer. The structure of **34a** was confirmed by NMR analysis, including NOE and COSY experiments. It is worth noting that three stereogenic centers are newly created with complete stereoselectivity. In contrast, the reaction of **13a** (Scheme 2), the corresponding C1′ epimer to **12a**, gave a complex mixture of unidentified products when exposed to identical cyclization conditions, presumably due to steric reasons. Allenenes **12b** and **12c** were cyclized into tetracyclohexadecatriene derivatives **34b** and **34c**, respectively, also in a stereoselective manner. These results clearly demonstrate the utility of our tandem cyclization as a novel method for the synthesis of complex heterocycles.



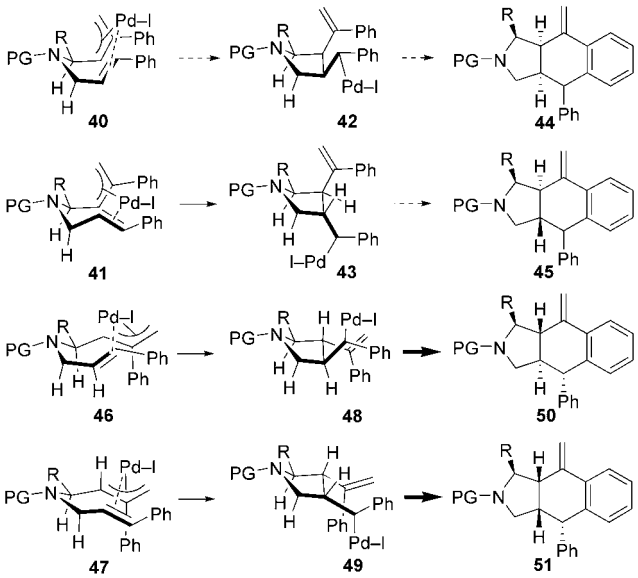
Scheme 6. Palladium(0)-catalyzed tandem cyclization of **12**. [a] A mixture of **12b** and **13b** (1:1) was used. Yield of **34** (51%) is based on **12b** (see Scheme 1 for abbreviations).

Stereoselectivity and mechanism of the tandem cyclization: In all cases listed in Table 1, the stereochemistry of the first cyclization (which dictates the relative configuration at C3 and C4 in the product) was the opposite of that observed in the pyrrolidine formation. As we have already described,[16b] the observed 2,3-*cis* selectivity in the pyrrolidination is attributed to an unfavorable steric interaction between pseudo-axial protons and the phenyl group in **35** (Scheme 7). Thus, the ring formation would proceed preferentially from the more abundant conformers **37** and/or **38** to yield *cis*-pyrrolidine **39** as the sole isolable isomer.



Scheme 7. Stereoselectivity of the monocyclization (PG = protecting group = SO_2Ar).

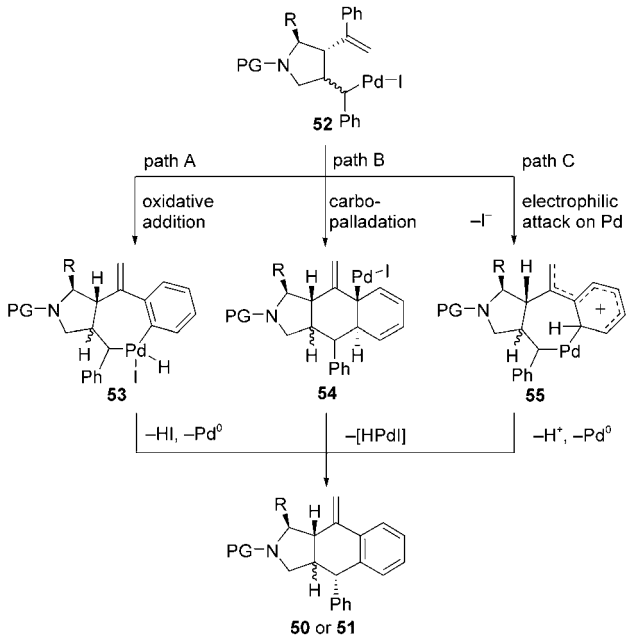
Although the exact reason for the opposite stereoselectivity at the C3 position in the tandem cyclization is not clear, it is apparent that the substituent at the olefin terminus plays an important role in the stereoselectivity of the first cyclization, not only in the inhibition of the β-hydride elimination. If the first cyclization proceeded with the same stereoselectivity as the pyrrolidine formation, tricyclic compounds **44** or **45** would be obtained through intermediate **40** or **41** (Scheme 8). In sharp contrast to intermediate **37** in the



Scheme 8. Stereoselectivity of the tandem cyclization.

pyrrolidination (Scheme 7), the upper side of intermediate **40** is highly sterically hindered because of the existence of a phenyl group on the double bond. Furthermore, if the first cyclization proceeded through intermediate **41**, the second cyclization step might be hampered by the relatively long distance between the reaction sites, as shown in **43**. The 2,3-*cis* configuration of the minor products generated by the β-hydride elimination[25] also supports the theory of the poor reactivity of the alkylpalladium intermediate of type **43** toward the second cyclization. Accordingly, predominant formation of the two diastereomers **50** and **51** through **46** and **47** is understandable.

Three possible mechanistic pathways for the final C–H activation are shown in Scheme 9: 1) Intramolecular oxidative addition of an aromatic C–H bond to palladium(II) to form palladium(IV) intermediate **53**,[1] which gives the benzoisoindoles **50** and **51** on loss of HI and subsequent reductive elimination (path A); 2) Carbopalladation onto the aryl group in **52** would give the palladium(II) intermediate **54**, in which the β hydrogen has an *anti* configuration to the palladium atom. In most cases, the subsequent β-hydride elimination proceeds with the *syn* stereochemistry.[23] Accordingly, the rearomatization to **50**/**51** might proceed through a facile



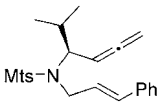
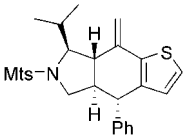
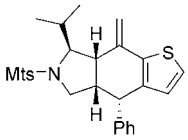
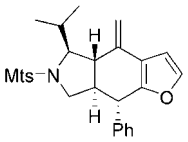
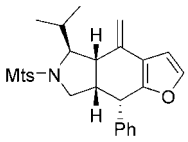
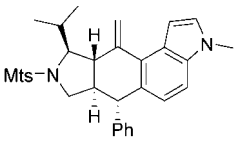
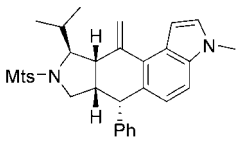
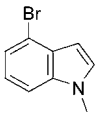
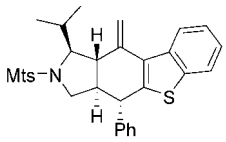
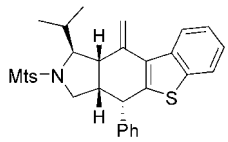
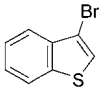
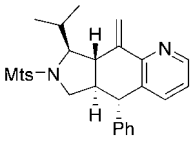
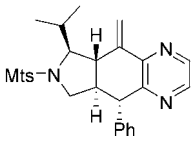
Scheme 9. Possible reaction pathways for the C–H functionalization.

stereomutation furnishing the required *syn* elimination,[26] presumably by the η^3–η^1–η^3 mechanism of the allylpalladium(II) species.[27] In addition, the *anti* elimination might be one rationalization for the rearomatization of **54** (path B);[28] 3) Alternatively, electrophilic attack by the palladium(II) intermediate **52** onto the aromatic carbon would give cationic intermediate **55**, deprotonation of which and subsequent reductive elimination would afford **50** or **51** (path C).[2]

If path C is the major reaction pathway, an electron-donating methoxy substituent on the 3-position of the aryl halide would strongly promote the second cyclization by stabilizing the cationic intermediate **55**. However, the tandem cyclization with 3- and 4-iodoanisole gave similar results (Table 1, entries 4 and 5), which indicates that the cation-stabilizing effect of the methoxy group is relatively unimportant and that path C will not be the major reaction pathway. At the present stage of our understanding, it is difficult to determine which is the most favorable reaction course in this case, as well as in related reactions.[3]

Tandem cyclization of allenenes with heteroaryl halides: Finally, we investigated the direct synthesis of tri- or tetracyclic heterocycles by using the tandem cyclization with heteroaromatic halides. The results are summarized in Table 2. The reaction of allenene **10a** with 2-bromothiophene yielded tricyclic products **56a** and **57a** in 59% combined isolated yields (entry 1). The cyclization using 3-bromofuran afforded tricyclic furan **56b** as a single isolable diastereomer (entry 2). The relatively low yield (31%) is due to instability of **56b**. We next investigated the reaction with bicyclic heteroaryl halides such as 4-bromo-1-methylindole and 3-bromobenzothiophene and found that these halides are good partners for the tandem cyclization of allenene **10a** (entries 3

Table 2. Palladium(0)-catalyzed tandem cyclization of allenene **10a** with heteroaryl halides.[a]

Entry	Substrate	ArX	*t* [h]	Product (yield)	
					
1	**10a**		8	**56a** (47%)	**57a** (12%)
					
2	**10a**		5	**56b** (31%)	**57b** (trace)
					
3	**10a**		12	**56c** (43%)	**57c** (6%)
					
4	**10a**		6	**56d** (45%)	**57d** (trace)
					
5[b]	**10a**		10	**56e** (49%)	
					
6	**10a**		8	**56f** (62%)	

[a] Unless otherwise stated, reactions were carried out with $[Pd(PPh_3)_4]$ (10 mol%), ArI (2 equiv), and K_2CO_3 (2 equiv) in dioxane under reflux. [b] Increased amount of $[Pd(PPh_3)_4]$ (20 mol%) was used.

and 4). In most cases using heteroaryl halides, the reaction proceeded smoothly to give the desired products even with aryl bromides, presumably due to the electron-rich nature of these heteroaryl rings. This trend is in good agreement with the results for electron-rich iodobenzene derivatives (see Table 1). In contrast, our results suffered from lower reactivities of 2-bromopyridine and chloropyrazine in the reaction with **10a**, affording the desired products in lower yields (30–42%) with some undesired byproducts after a prolonged reaction time (30 h). This problem has been overcome by using 2-iodopyridine (entry 5) and iodopyrazine (entry 6) to give **56e** and **56f**, respectively, in moderate yields (49 and 62%, respectively).

Conclusion

In conclusion, we have developed a novel tandem-cyclization reaction of allenenes for the synthesis of tri- and tetracyclic heterocycles. We found that inhibition of the β-hydride elimination of the monocyclized alkylpalladium(II) intermediate by introducing a substituent on the double bond efficiently promotes the second cyclization onto an aromatic ring. This study demonstrates that allenenes can undergo a tandem cyclization involving C–H activation of benzene or heteroaromatic rings such as thiophene, furan, and indole, in the presence of a palladium(0) catalyst. The tandem cyclization forming three carbon–carbon bonds is synthetically useful in that complex heterocyclic skeletons can be constructed from readily prepared allenenes.

Experimental Section

General methods: All reactions were carried out under a positive pressure of argon, and glassware and syringes were dried in an electric oven at 100°C prior to use. THF was distilled from sodium benzophenone ketyl under N_2. Other solvents and reagents were used without further purification. Melting points are uncorrected. ^1H NMR spectra (270, 300, or 500 MHz) were recorded using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million downfield from internal Me_4Si (s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublet, t = triplet, m = multiplet). For flash chromatography, silica gel 60 (230—400 mesh, Merck) was employed. Known compounds **9a**,[19b] **9b**,[16b] **9c**,[19b] **9d**,[16b] **9e**,[16b] **9f**,[16b] **18**,[16b] and (*Z*)-cinnamyl bromide[20] were synthesized according to the literature.

General procedure for the synthesis of allenenes

***N*-[(1*S*)-1-Isopropylbuta-2,3-dienyl]-2,4,6-trimethyl-*N*-[(*E*)-3-phenyl-2-propenyl]phenylsulfonamide (10a)**: A solution of **9a** (250 mg, 0.852 mmol) in DMF (2 mL) at 0 °C was added to a stirred suspension of 60% NaH (117 mg, 2.90 mmol) in DMF (3 mL), and the mixture was stirred for 10 min. (*E*)-Cinnamyl bromide (572 mg, 2.90 mmol) was added to the mixture at 0 °C, and the mixture was stirred for 2 h at this temperature, followed by quenching with saturated NH_4Cl (1 mL). All of this was extracted with Et_2O and the extract was washed with water and brine, and dried over $MgSO_4$. Concentration of the filtrate under reduced pressure followed by flash column chromatography over silica gel with *n*-hexane/EtOAc (40:1) gave allenene **10a** as colorless crystals (372 mg, 99%). M.p. 73–74 °C; $[\alpha]_D^{22}=+14.7$ ($c=0.075$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.92$ (d, $J=6.3$ Hz, 3H; CMe), 0.93 (d, $J=6.3$ Hz, 3H; CMe), 1.89–2.01 (m, 1H; Me_2CH), 2.22 (s, 3H; $PhCH_3$), 2.63 (s, 6H; $2\times PhCH_3$), 3.88–3.95 (m, 1H; 1-H), 3.98 (dd, $J=6.9$, 1.5 Hz, 2H; 1′-CH_2), 4.71 (dd, $J=6.9$, 1.5 Hz, 2H; 4-CH_2), 5.24 (dt, $J=7.8$, 6.9 Hz, 1H; 2-H), 6.03 (dt, $J=15.9$, 6.9 Hz, 1H; 2′-H), 6.34 (d, $J=15.9$ Hz, 1H; 3′-H), 6.88 (s, 2H; Ph), 7.17–7.30 ppm (m, 5H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=20.1$, 20.7, 20.8, 23.3 (2C), 30.5, 45.8, 63.2, 76.1, 88.9, 126.3 (2C), 126.9, 127.5, 128.4 (2C), 131.6, 131.9 (2C), 133.9, 136.5, 140.1 (2C), 142.2, 209.2 ppm; IR (KBr): $\tilde{\nu}=1955$ (C=C=C), 1322 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 410 (24) [M^++H], 366 (100); HRMS (FAB): calcd for $C_{25}H_{32}NO_2S$ [M^++H]: 410.2154; found: 410.2150.

***N*-[(1*S*)-1-Isobutylbuta-2,3-dienyl]-2,4,6-trimethyl-*N*-[(*E*)-3-phenyl-2-propenyl]phenylsulfonamide (10b)**: By using a procedure identical to that described for the synthesis of **10a**, amino allene **9b** (200 mg, 0.651 mmol) was converted into allenene **10b** (263 mg, 95%). Colorless oil; $[\alpha]_D^{27}=-39.2$ ($c=3.00$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.74$ (d, $J=6.1$ Hz, 3H; CMe), 0.78 (d, $J=6.1$ Hz, 3H; CMe), 1.43–1.49 (m, 1H; Me_2CH), 1.56–1.61 (m, 2H; Me_2CHCH_2), 2.23 (s, 3H; $PhCH_3$), 2.63 (s, 6H; $2\times PhCH_3$), 3.91 (dd, $J=17.0$, 6.7 Hz, 1H; 1′-C*H*H), 4.00 (dd, $J=17.0$, 6.7 Hz, 1H; 1′-CH*H*), 4.31–4.35 (m, 1H; 1-H), 4.73–4.80 (m, 2H; 4-CH_2), 5.29 (dt, $J=6.1$, 6.1 Hz, 1H; 2-H), 6.01 (dt, $J=15.9$, 6.7 Hz, 1H; 2′-H), 6.33 (d, $J=15.9$ Hz, 1H; 3′-H), 6.90 (s, 2H; Ph), 7.05–7.29 ppm (m, 5H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta=20.9$, 22.1, 22.6, 23.1 (2C), 24.7, 41.6, 45.3, 53.5, 77.0, 90.5, 126.2 (2C), 127.0, 127.4, 128.3 (2C), 131.6, 131.8 (2C), 133.3, 136.5, 140.1 (2C), 142.3, 208.7 ppm; IR (KBr): $\tilde{\nu}=1954$ (C=C=C), 1319 (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 424 (14) [M^++H], 117 (100); HRMS (FAB): calcd for $C_{26}H_{34}NO_2S$ [M^++H]: 424.2310; found: 424.2308.

***N*-[(1*S*)-1-Benzylbuta-2,3-dienyl]-2,4,6-trimethyl-*N*-[(*E*)-3-phenyl-2-propenyl]phenylsulfonamide (10c)**: By using a procedure identical to that described for the synthesis of **10a**, amino allene **9c** (250 mg, 0.732 mmol) was converted into allenene **10c** (338 mg, 99%). Colorless oil; $[\alpha]_D^{28}=-95.0$ ($c=1.38$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=2.23$ (s, 1H; $PhCH_3$), 2.64 (s, 6H; $2\times PhCH_3$), 2.96–3.05 (m, 2H; $PhCH_2$), 4.03–4.13 (m, 2H; 1′-CH_2), 4.56–4.59 (m, 1H; 1-H), 4.77–4.79 (m, 2H; 4-CH_2), 5.35 (dt, $J=6.7$, 6.7 Hz, 1H; 2-H), 6.07 (dt, $J=15.9$, 6.7 Hz, 1H; 2′-H), 6.41 (d, $J=15.9$ Hz, 1H; 3′-H), 6.83 (s, 2H; Ph), 7.00–7.31 ppm (m, 10H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta=20.9$, 22.9 (2C), 39.2, 45.7, 56.9, 77.7, 90.0, 126.2, 126.3 (2C), 126.9, 127.5, 128.1 (2C), 128.4 (2C), 129.1 (2C), 131.9 (3C), 132.9, 136.5, 138.0, 140.3 (2C), 142.3, 209.0 ppm; IR (KBr): $\tilde{\nu}=1954$ (C=C=C), 1317 (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 458 (14) [M^++H], 117 (100); HRMS (FAB): calcd for $C_{29}H_{32}NO_2S$ [M^++H]: 458.2154; found: 458.2162.

***N*-[(1*S*)-1-(*tert*-Butyl)buta-2,3-dienyl]-2,4,6-trimethyl-*N*-[(*E*)-3-phenyl-2-propenyl]phenylsulfonamide (10d)**: By using a procedure identical to that described for the synthesis of **10a**, amino allene **9d** (200 mg, 0.651 mmol) was converted into allenene **10d** (227 mg, 82%). Colorless crystals; m.p. 86–88 °C; $[\alpha]_D^{21}=+77.0$ ($c=0.865$, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=1.01$ (s, 9H; $3\times$CMe), 2.16 (s, 3H; $PhCH_3$), 2.61 (s, 6H; $2\times PhCH_3$), 4.01 (dd, $J=17.0$, 7.1 Hz, 1H; 1′-C*H*H), 4.11 (dd, $J=17.0$, 5.8 Hz, 1H; 1′-CH*H*), 4.27 (dt, $J=8.9$, 1.6 Hz, 1H; 1-H), 4.69 (dd, $J=6.8$, 1.6 Hz, 2H; 4-CH_2), 5.32 (dt, $J=8.9$, 6.8 Hz, 1H; 2-H), 5.92 (ddd, $J=16.0$, 7.1, 5.8 Hz, 1H; 2′-H), 6.83 (s, 2H; Ph), 7.09–7.27 ppm (m, 5H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta=20.8$, 23.5 (2C), 28.1 (2C), 37.3, 47.2, 65.9, 75.5, 86.6, 126.2 (2C), 126.9, 127.3, 128.2 (2C), 130.9, 131.8 (2C), 134.1, 136.4, 140.1 (2C), 142.1, 209.1 ppm; IR (KBr): $\tilde{\nu}=1956$ (C=C=C), 1323, 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 366 (33) [M^++H], 117 (100); HRMS (FAB): calcd for $C_{26}H_{34}NO_2S$ [M^++H]: 424.2310; found: 424.2319.

***N*-{(1*S*)-1-[(1*S*)-1-Methylpropyl]buta-2,3-dienyl}-2,4,6-trimethyl-*N*-[(*E*)-3-phenyl-2-propenyl]phenylsulfonamide (10e)**: By using a procedure identical to that described for the synthesis of **10a**, amino allene **9e** (100 mg, 0.325 mmol) was converted into allenene **10e** (137 mg, 99%). Colorless oil; $[\alpha]_D^{22}=+2.49$ ($c=1.00$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.79$ (t, $J=7.3$ Hz, 3H; CMe), 0.88 (d, $J=6.1$ Hz, 3H; CMe), 0.90–0.91 (m, 1H; 2″-C*H*H), 1.66–1.71 (m, 1H; 1″-H), 1.75–1.80 (m, 1H; 2″-CH*H*), 2.22 (s, 3H; $PhCH_3$), 2.62 (s, 6H; $2\times PhCH_3$), 3.91–4.04 (m, 3H; 1-H and 1′-CH_2), 4.64–4.71 (m, 2H; 4-CH_2), 5.19 (ddd, $J=7.4$, 6.7, 6.7 Hz, 1H; 2-H), 6.04 (ddd, $J=15.9$, 7.3, 7.3 Hz, 1H; 2′-H), 6.34 (d, $J=15.9$ Hz, 1H; 3′-H), 6.89 (s, 2H; Ph), 7.19–7.29 ppm (m, 5H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta=11.4$, 16.7, 20.9, 23.4 (2C), 25.7, 37.1, 46.1, 62.1, 76.0, 88.6, 126.2 (2C), 126.8, 127.5, 128.3 (2C), 131.6, 131.9 (2C), 133.8, 136.4, 140.0 (2C), 142.2, 209.0 ppm; IR (KBr): $\tilde{\nu}=1952$ (C=C=C), 1315 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 424 (100) [M^++H]; HRMS (FAB): calcd for $C_{26}H_{34}NO_2S$ [M^++H]: 424.2310; found: 424.2304.

***N*-[(1*S*)-1-Isopropylbuta-2,3-dienyl]-*N*-[(*E*)-3-phenyl-2-propenyl]-*tert*-butylcarbamate (10f)**: By using a procedure identical to that described for the synthesis of **10a**, amino allene **9f** (100 mg, 0.473 mmol) was converted into allenene **10f** (124 mg, 80%). Colorless oil; $[\alpha]_D^{26}=-19.9$ ($c=1.31$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 328 K): $\delta=0.89$–0.96 (m, 6H; $2\times$CMe), 1.44–1.49 (m, 9H; CMe_3), 1.99–2.11 (m, 1H; Me_2CH), 3.89–3.91 (m, 3H; 1-H and 1′-CH_2), 4.71 (dd, $J=6.6$, 1.5 Hz, 2H; 4-CH_2), 5.26 (dd, $J=13.1$, 6.6 Hz, 1H; 2-H), 6.14–6.24 (m, 1H; 2′-H), 6.42–6.48 (m, 1H; 3′-H), 7.17–7.34 ppm (m, 5H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$, 328 K): $\delta=19.7$, 20.6, 28.6 (3C), 30.9, 47.8, 62.9, 75.7, 79.7, 90.0, 126.2 (2C), 127.2, 127.3, 128.1 (2C), 131.4, 137.2, 155.4, 209.2 ppm; IR (KBr): $\tilde{\nu}=1955$ (C=C=C), 1693 cm^{-1} (C=O); MS (FAB): *m*/*z* (%): 328 (23) [M^++H], 272 (100); HRMS (FAB): calcd for $C_{21}H_{30}NO_2$ [M^++H]: 328.2277; found: 328.2269.

***N*-[(1*S*)-1-(Isopropyl)buta-2,3-dienyl]-2,4,6-trimethyl-*N*-[(*Z*)-3-phenyl-2-propenyl]phenylsulfonamide ((*Z*)-10a)**: By using a procedure similar to that described for the synthesis of **10a**, amino allene **9a** (200 mg, 0.682 mmol) was converted into, in the order of elution, (*Z*)-**10a** (107 mg, 39%) and (*E*)-**10a** (18 mg, 6%), by use of (*Z*)-cinnamyl bromide (268 mg, 1.36 mmol). Compound (*Z*)-**10a**: Colorless oil; $[\alpha]_D^{25}=-16.7$ ($c=0.425$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.82$ (d, $J=6.6$ Hz, 3H; CMe), 0.87 (d, $J=6.6$ Hz, 3H; CMe), 1.62–1.74 (m, 1H; Me_2CH), 2.30 (s, 3H; $PhCH_3$), 2.58 (s, 6H; $2\times PhCH_3$), 3.79–3.86 (m, 1H; 1-H), 4.07 (ddd, $J=17.4$, 6.0, 2.1 Hz, 1H; 1′-C*H*H), 4.21 (ddd, $J=17.4$, 6.0, 2.1 Hz, 1H; 1′-CH*H*), 4.46 (ddd, $J=11.4$, 6.6, 1.5 Hz, 1H; 4-C*H*H), 4.61 (ddd, $J=11.4$, 6.6, 1.5 Hz, 1H; 4-CH*H*), 5.08 (ddd, $J=6.6$, 6.6, 6.6 Hz, 1H; 2-H), 5.67 (ddd, $J=11.7$, 6.0, 6.0 Hz, 1H; 2′-H), 6.34 (d, $J=11.7$ Hz, 1H; 3′-H), 6.91 (s, 2H; Ph), 7.12–7.36 ppm (m, 5H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=20.2$, 20.6, 20.9, 23.3 (2C), 30.2, 41.4, 63.1, 76.0, 88.6, 127.1, 128.2 (2C), 128.8 (2C), 129.7, 130.2, 132.0 (2C), 133.6, 136.4, 140.1 (2C), 142.2, 209.2 ppm; IR (KBr): $\tilde{\nu}=1956$ (C=C=C), 1323 (SO_2N), 1157 cm^{-1} (SO_2N).

***N*-[(1*S*)-1-(2-Isopropyl)buta-2,3-dienyl]-2,4,6-trimethyl-*N*-(3-methyl-2-butenyl)phenylsulfonamide (11)**: By using a procedure similar to that described for the synthesis of **10a**, amino allene **9a** (200 mg, 0.682 mmol) was converted into allenene **11** (250 mg, 99%) by use of 4-bromo-2-methylbut-2-ene. Colorless oil; $[\alpha]_D^{23}=-20.4$ ($c=0.89$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.89$ (d, $J=6.1$ Hz, 3H; CMe), 0.90 (d, $J=6.1$ Hz, 3H; CMe), 1.58 (m, 6H; $2\times$CMe), 1.81–1.89 (m, 1H; Me_2CH), 2.28 (s, 3H; $PhCH_3$), 2.61 (s, 6H; $2\times PhCH_3$), 3.76–3.86 (m, 3H; 1-H and 1′-CH_2), 4.66–4.72 (m, 2H; 4-CH_2), 5.10 (t, $J=6.7$ Hz, 1H; 2′-H), 5.18 (dt, $J=6.7$, 6.7 Hz, 1H; 2-H), 6.91 ppm (s, 2H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=17.7$, 20.1, 20.8, 20.9, 23.2 (2C), 25.6, 30.6, 41.6, 63.1, 75.9, 88.9, 122.0, 131.8 (2C), 133.4 (2C), 134.0, 140.1 (2C), 142.0, 209.1 ppm; IR (KBr): $\tilde{\nu}=1956$ (C=C=C), 1323 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 362 (16) [M^++H], 119 (100); HRMS (FAB): calcd for $C_{21}H_{32}NO_2S$ [M^++H]: 362.2154; found: 362.2134.

***N*-[(1*R*)-Cyclohex-2-en-1-yl]-*N*-[(1*R*)-1-isopropylbuta-2,3-dienyl]-2,4,6-trimethylphenylsulfonamide (12a) and its [(1*S*)-cyclohex-2-en-1-yl] isomer (13a)**: By using a procedure similar to that described for the synthesis of **10a**, amino allene **9a** (400 mg, 1.36 mmol) was converted into, in the order of elution, **12a** (159 mg, 31%) and **13a** (178 mg, 35%) by use of racemic 3-bromocyclohexene.

*Compound **12a***: Colorless oil; $[\alpha]_D^{24} = -11.9$ ($c = 2.75$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.80$ (d, $J = 6.7$ Hz, 3H; CMe), 0.84 (d, $J = 6.7$ Hz, 3H; CMe), 1.45–2.08 (m, 7H; Me_2CH, 4′-CH_2, 5′-CH_2, and 6′-CH_2), 2.27 (s, 3H; $PhCH_3$), 2.64 (s, 6H; 2×$PhCH_3$), 3.55 (dd, $J = 9.8$, 9.2 Hz, 1H; 1-H), 4.10 (m, 1H; 1′-H), 4.66–4.74 (m, 2H; 4-CH_2), 5.54 (dt, $J = 8.5$, 6.7 Hz, 1H; 2-H), 5.62 (d, $J = 10.4$ Hz, 1H; 2′-H), 5.69–5.72 (m, 1H; 3′-H), 6.91 ppm (s, 2H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 20.7$, 21.0, 21.3, 23.0, 23.3 (2C), 24.6, 29.0, 31.6, 55.5, 64.1, 75.5, 90.5, 129.3, 130.2, 131.9 (2C), 134.1, 140.0 (2C), 142.1, 208.7 ppm; IR (KBr): $\tilde{\nu} = 1956$ (C=C=C), 1319 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 374 (28) [M^++H], 119 (100); HRMS (FAB): calcd for $C_{22}H_{31}NO_2S$ [M^++H] 374.2154; found: 374.2145.

*Compound **13a***: Colorless crystals; m.p. 63–65 °C; $[\alpha]_D^{25} = -73.8$ ($c = 2.94$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.75$ (d, $J = 6.7$ Hz, 3H; CMe), 0.84 (d, $J = 6.7$ Hz, 3H; CMe), 1.49–2.32 (m, 7H; Me_2CH, 4′-CH_2, 5′-CH_2, and 6′-CH_2), 2.29 (s, 3H; $PhCH_3$), 2.68 (s, 6H; 2×$PhCH_3$), 3.38 (dd, $J =$ 9.2, 9.2 Hz, 1H; 1-H), 3.98 (m, 1H; 1′-H), 4.73 (dd, $J = 11.0$, 6.7 Hz, 1H; 4-CHH), 4.77 (dd, $J = 11.0$, 6.7 Hz, 1H; 4-CHH), 5.53 (ddd, $J = 8.5$, 6.7, 6.7 Hz, 1H; 2-H), 5.73–5.75 (m, 1H; 3′-H), 5.95 (d, $J = 10.4$ Hz, 1H; 2′-H), 6.95 ppm (s, 2H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 20.5$, 21.0 (2C), 23.1, 23.3 (2C), 24.6, 29.7, 31.1, 55.6, 64.0, 75.6, 89.5, 129.0, 129.5, 131.8 (2C), 133.3, 140.4 (2C), 142.2, 209.0 ppm; IR (KBr): $\tilde{\nu} = 1956$ (C=C=C), 1317 (SO_2N), 1155 cm^{-1} (SO_2N); elemental analysis calcd (%) for $C_{22}H_{31}NO_2S$: C 70.74, H 8.36, N 3.75; found: C 70.70, H 8.31, N 3.75.

***N*-[(1*R*)-Cyclohex-2-en-1-yl]-*N*-[(1*R*)-1-isobutylbuta-2,3-dienyl]-2,4,6-trimethylphenylsulfonamide (12b) and its [(1*S*)-cyclohex-2-en-1-yl] isomer (13b)**: By using a procedure similar to that described for the synthesis of **10a**, amino allene **9b** (300 mg, 0.976 mmol) was converted into an inseparable mixture of **12b** and **13b** (1:1; 347 mg, 92%) by use of racemic 3-bromocyclohexene. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.71$ (d, $J = 6.3$ Hz, 3H; CMe), 0.72 (d, $J = 6.0$ Hz, 3H; 3×CH), 1.81–2.05 (m, 6H; 6×CH), 2.29 (s, 3H; $PhCH_3$), 2.67 (s, 6H; 2×$PhCH_3$), 3.86–3.93 (m, 1H; NCH), 3.98–4.01 (m, 1H; NCH), 4.74 (dd, $J = 6.9$, 3.6 Hz, 2H; 4-CH_2), 5.55 (dt, $J = 6.9$, 6.9 Hz, 1H; 2-H), 5.66–5.86 (m, 2H; 2×C=CH), 6.93 ppm (s, 2H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 20.9$, 21.1 (0.5C), 21.3 (0.5C), 22.5 (0.5C), 22.6 (0.5C), 22.90, 22.93, 23.0 (0.5C), 23.3 (0.5C), 24.5, 25.1 (0.5C), 25.4 (0.5C), 28.7 (0.5C), 29.3 (0.5C), 43.2 (0.5C), 43.6 (0.5C), 55.0 (0.5C), 55.2 (0.5C), 55.3 (0.5C), 55.5 (0.5C), 75.9 (0.5C), 76.0 (0.5C), 91.4 (0.5C), 91.8 (0.5C), 129.3 (0.5C), 129.4 (0.5C), 129.9 (0.5C), 130.6 (0.5C), 131.9 (2C), 133.3 (0.5C), 133.6 (0.5C), 140.4, 140.5, 142.37 (0.5C), 142.41 (0.5C), 208.5 (0.5C), 208.6 ppm (0.5C); IR (KBr): $\tilde{\nu} = 1953$ (C=C=C), 1315 (SO_2N), 1157 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 388 (38) [M^++H], 268 (100), 119 (100); HRMS (FAB): calcd for $C_{23}H_{34}NO_2S$ [M^++H]: 388.2310; found: 388.2308.

***N*-[(1*R*)-Cyclohex-2-en-1-yl]-*N*-{(1*S*)-1-[(1*S*)-1-methylpropyl]buta-2,3-dienyl}-2,4,6-trimethylphenylsulfonamide (12c) and its *N*-[(1*S*)-cyclohex-2-en-1-yl] isomer (13c)**: By using a procedure similar to that described for the synthesis of **10a**, amino allene **9a** (100 mg, 0.325 mmol) was converted into, in the order of elution, **12c** (23.4 mg, 19%) and **13c** (28.4 mg, 23%) by use of racemic 3-bromocyclohexene.

*Compound **12c***: Colorless crystals; m.p. 76–78 °C (*n*-hexane/Et_2O); $[\alpha]_D^{23} = +3.38$ ($c = 0.87$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.64$ (t, $J = 7.3$ Hz, 3H; CMe), 0.73–0.76 (m, 1H; CH), 0.84 (d, $J = 6.7$ Hz, 3H; CMe), 1.52–2.07 (m, 8H; 8×CH), 2.23 (s, 3H; $PhCH_3$), 2.65 (s, 6H; 2×$PhCH_3$), 3.64 (dd, $J = 9.8$, 9.2 Hz, 1H; 1-H), 4.19–4.22 (m, 1H; 1′-H), 4.67–4.75 (m, 2H; 4-CH_2), 5.57–5.76 (m, 2H; 2′-H and 3′-H), 5.73–5.77 (m, 1H; 2-H), 6.93 ppm (s, 2H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta =$ 11.5, 17.0, 21.0, 23.0, 23.3 (2C), 24.7, 26.5, 29.2, 38.1, 56.0, 63.2, 75.2, 90.6, 129.8 (2C), 131.9 (2C), 134.6, 139.9 (2C), 142.0, 208.8 ppm; IR (KBr): $\tilde{\nu} =$ 1956 (C=C=C), 1319 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 388 (100) [M^++H]; HRMS (FAB): calcd for $C_{23}H_{34}NO_2S$ [M^++H]: 388.2310; found: 388.2328.

*Compound **13c***: Colorless oil; $[\alpha]_D^{25} = -5.91$ ($c = 1.11$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.60$–0.68 (m, 1H; CH), 0.69 (d, $J = 6.1$ Hz, 3H; CMe), 0.83 (d, $J = 6.7$ Hz, 3H; CMe), 1.42–2.26 (m, 8H; 8×CH), 2.23 (s, 3H; $PhCH_3$), 2.67 (s, 6H; 2×$PhCH_3$), 3.50 (dd, $J = 9.2$, 9.2 Hz, 1H; 1-H), 4.00–4.05 (m, 1H; 1′-H), 4.69–4.77 (m, 2H; 4-CH_2), 5.52 (ddd, $J = 8.5$, 6.7, 6.7 Hz, 1H; 2-H), 5.72–5.77 (m, 1H; CH=CH), 5.95 (d, $J = 10.4$ Hz, 1H; CH=CH), 6.92 ppm (s, 2H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 11.4$, 16.7, 21.0, 23.1, 23.2 (2C), 24.6, 26.2, 29.6, 37.8, 55.8, 62.9, 75.4, 89.4, 129.1, 129.6, 131.8 (2C), 133.5, 140.4 (2C), 142.2, 209.1 ppm; IR (KBr): $\tilde{\nu} = 1956$ (C=C=C), 1317 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 388 (100) [M^++H]; HRMS (FAB): calcd for $C_{23}H_{34}NO_2S$ [M^++H]: 388.2310; found: 388.2314.

(3*R*,4*S*,7*R*)-5-Aza-4-isopropyl-7-methyl-2-methylene-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (19): A stirred mixture of allenene **18** (50.0 mg, 0.144 mmol), [$Pd(PPh_3)_4$] (16.2 mg, 0.014 mmol), iodobenzene (0.065 mL, 0.584 mmol), and K_2CO_3 (80.7 mg, 0.584 mmol) in dioxane (3 mL) was heated under reflux for 36 h. Water was added to the mixture, and it was extracted with Et_2O. The extract was washed with water and brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to leave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane/EtOAc (50:1) to give **19** (2.8 mg, 5%) and recovered starting material (15.8 mg, 32%). Compound **19**: Colorless oil; $[\alpha]_D^{23} = -71.9$ ($c = 0.69$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.63$ (d, $J = 7.3$ Hz, 3H; CMe), 0.76 (d, $J = 6.7$ Hz, 3H; CMe), 0.89 (s, 3H; CMe), 1.78–1.84 (m, 1H; Me_2CH), 2.30 (s, 3H; $PhCH_3$), 2.64 (d, $J = 9.2$ Hz, 1H; 3-H), 2.66 (s, 6H; 2×$PhCH_3$), 2.81 (d, $J = 15.9$ Hz, 1H; 8-CHH), 2.90 (d, $J = 15.9$ Hz, 1H; 8-CHH), 3.09 (d, $J = 10.4$ Hz, 1H; 6-CHH), 4.20 (d, $J = 10.4$ Hz, 1H; 6-CHH), 4.32 (dd, $J = 9.2$, 3.1 Hz, 1H; 4-H), 5.02 (d, $J = 1.8$ Hz, 1H; C=CHH), 5.60 (d, $J = 1.8$ Hz, 1H; C=CHH), 6.93 (s, 2H; Ph), 7.13 (d, $J =$ 7.3 Hz, 1H; Ph), 7.18–7.24 (m, 2H; Ph), 7.57 ppm (dd, $J = 7.9$, 1.2 Hz, 1H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 17.4$, 17.8, 19.2, 21.0, 23.1 (2C), 31.5, 41.1, 41.3, 52.0, 62.8, 63.9, 108.4, 124.9, 126.0, 128.0, 130.0, 131.8 (2C), 134.7, 136.1, 136.4, 138.7 (2C), 141.6, 142.5 ppm; IR (KBr): $\tilde{\nu} = 1324$ (SO_2N), 1147 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 424 (100) [M^+ +H]; HRMS (FAB): calcd for $C_{26}H_{34}NO_2S$ [M^++H]: 424.2310; found: 424.2332.

General procedure for the palladium(0)-catalyzed tandem cyclization

(3*S*,4*S*,7*R*,8*S*)-5-Aza-4-isopropyl-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (20a) and its (3*S*,4*S*,7*S*,8*S*) isomer (21a, Table 1, entry 1): A stirred mixture of allenene **10a** (100 mg, 0.244 mmol), [$Pd(PPh_3)_4$] (27.7 mg, 0.024 mmol), iodobenzene (0.055 mL, 0.488 mmol), and K_2CO_3 (67.4 mg, 0.488 mmol) in dioxane (3 mL) was heated under reflux for 7.5 h. Water was added to the mixture and it was extracted with Et_2O. The extract was washed with water and brine, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to leave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane/EtOAc (50:1) to give, in the order of elution, **20a** (48.4 mg, 41%) and **21a** (12.4 mg, 10%).

*Compound **20a***: Colorless oil; $[\alpha]_D^{25} = +12.0$ ($c = 1.33$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.90$ (d, $J = 7.3$ Hz, 3H; CMe), 0.92 (d, $J = 7.3$ Hz, 3H; CMe), 2.02–2.16 (m, 1H; Me_2CH), 2.26 (s, 3H; $PhCH_3$), 2.33–2.41 (m, 1H; 7-H), 2.53 (s, 6H; 2×$PhCH_3$), 2.64–2.68 (m, 1H; 3-H), 2.77 (dd, $J = 11.6$, 11.6 Hz, 1H; 6-CHH), 3.47 (dd, $J = 11.6$, 6.1 Hz, 1H; 6-CHH), 3.88 (d, $J = 11.6$ Hz, 1H; 8-H), 4.45 (dd, $J = 7.9$, 4.3 Hz, 1H; 4-H), 5.11 (s, 1H; C=CHH), 5.57 (s, 1H; C=CHH), 6.79–7.61 (m, 9H; Ph), 6.87 ppm (s, 2H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 17.3$, 19.4, 20.9, 22.9 (2C), 32.6, 48.4, 51.5, 51.9, 53.2, 64.1, 106.0, 125.4, 126.5, 126.9, 128.1, 128.5 (2C), 128.7 (2C), 129.8, 131.9 (2C), 133.1, 136.7, 139.5, 140.1 (2C), 142.3, 143.9, 145.4 ppm; IR (KBr): $\tilde{\nu} = 1315$ (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 486 (100) [M^++H]; HRMS (FAB): calcd for $C_{31}H_{36}NO_2S$ [M^++H]: 486.2467; found: 486.2471.

*Compound **21a***: Colorless crystals; $[\alpha]_D^{24} = -1.05$ ($c = 1.39$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.81$ (d, $J = 7.3$ Hz, 3H; CMe), 0.92 (d, $J = 7.3$ Hz, 3H; CMe), 2.00–2.04 (m, 1H; Me_2CH), 2.28 (s, 3H; $PhCH_3$), 2.52 (s, 6H; 2×$PhCH_3$), 2.81 (ddd, $J = 12.8$, 6.1, 6.1 Hz, 1H; 7-H), 3.07–3.09 (m, 1H; 3-H), 3.22 (dd, $J = 9.8$, 6.1 Hz, 1H; 6-CHH), 3.36 (dd, $J =$ 9.8, 6.1 Hz, 1H; 6-CHH), 3.96–3.99 (m, 2H; 4-H and 8-H), 5.11 (s, 1H;

C=C*H*H), 5.58 (s, 1H; C=CH*H*), 6.86 (s, 2H; Ph), 7.01–7.50 ppm (m, 9H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ=17.1, 19.8, 21.0, 23.2 (2C), 32.0, 44.1, 45.2, 46.2, 52.9, 72.1, 113.1, 125.0, 126.3, 126.9, 128.1, 128.4 (4C), 129.5, 131.7 (2C), 133.9, 134.8, 136.7, 139.4 (2C), 141.8, 143.7, 144.9 ppm; IR (KBr): $\tilde{\nu}$=1317 (SO_2N), 1157 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 486 (70) [M^++H], 442 (100); HRMS (FAB): calcd for $C_{31}H_{36}NO_2S$ [M^++H]: 486.2467; found: 486.2459.

(3*S*,4*S*,7*R*,8*S*)-5-Aza-4-isopropyl-11-methyl-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (20b) and its (3*S*,4*S*,7*S*,8*S*) isomer (21b) (Table 1, entry 2): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (80.0 mg, 0.195 mmol) was converted into, in the order of elution, **20b** (35.9 mg, 37%) and **21b** (18.0 mg, 18%), by use of 4-iodotoluene.

Compound ***20b***: Colorless oil; $[\alpha]_D^{24}$=−6.03 (*c*=1.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.89 (d, *J*=7.3 Hz, 3H; CMe), 0.91 (d, *J*=7.3 Hz, 3H; CMe), 1.99–2.06 (m, 1H; Me_2CH), 2.17 (s, 3H; $PhCH_3$), 2.27 (s, 3H; $PhCH_3$), 2.34 (dddd, *J*=11.6, 11.6, 11.0, 6.1 Hz, 1H; 7-H), 2.53 (s, 6H; 2×$PhCH_3$), 2.60–2.65 (m, 1H; 3-H), 2.75 (dd, *J*=11.6, 11.6 Hz, 1H; 6-C*H*H), 3.44 (dd, *J*=11.6, 6.1 Hz, 1H; 6-CH*H*), 3.83 (d, *J*=11.0 Hz, 1H; 8-H), 4.43 (dd, *J*=7.9, 4.3 Hz, 1H; 4-H), 5.05 (d, *J*=1.8 Hz, 1H; C=C*H*H), 5.51 (d, *J*=1.8 Hz, 1H; C=CH*H*), 6.59 (s, 1H; Ph), 6.87 (s, 2H; Ph), 7.01 (d, *J*=7.9 Hz, 1H; Ph), 7.06 (d, *J*=6.7 Hz, 2H; Ph), 7.22–7.29 (m, 3H; Ph), 7.50 ppm (d, *J*=7.9 Hz, 1H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ=17.4, 19.5, 21.0, 21.2, 23.0 (2C), 32.6, 48.5, 51.4, 52.0, 53.2, 64.2, 105.1, 125.2, 126.7, 127.4, 128.4 (2C), 128.6 (2C), 130.1, 131.8 (2C), 133.0, 134.0, 137.9, 139.2, 139.9 (2C), 142.2, 143.8, 145.1 ppm; IR (KBr): $\tilde{\nu}$=1315 (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 500 (98) [M^++H], 456 (100); HRMS (FAB): calcd for $C_{32}H_{38}NO_2S$ [M^++H]: 500.2623; found: 500.2635.

Compound ***21b***: Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.79 (d, *J*=6.7 Hz, 3H; CMe), 0.90 (d, *J*=6.7 Hz, 3H; CMe), 1.96–2.02 (m, 1H; Me_2CH), 2.22 (s, 3H; $PhCH_3$), 2.28 (s, 3H; $PhCH_3$), 2.52 (s, 6H; 2×$PhCH_3$), 2.76–2.81 (m, 1H; 7-H), 3.04–3.06 (m, 1H; 3-H), 3.21 (dd, *J*=9.8, 6.7 Hz, 1H; 6-C*H*H), 3.36 (dd, *J*=9.8, 6.7 Hz, 1H; 6-CH*H*), 3.93 (d, *J*=5.5 Hz, 1H; 8-H), 3.96 (dd, *J*=4.3, 4.3 Hz, 1H; 4-H), 5.04 (s, 1H; C=C*H*H), 5.54 (s, 1H; C=CH*H*), 6.68 (s, 1H; Ph), 6.85 (s, 2H; Ph), 7.03 (d, *J*=6.7 Hz, 2H; Ph), 7.17–7.29 (m, 4H; Ph), 7.39 ppm (d, *J*=7.9 Hz, 1H; Ph).

(3*S*,4*S*,7*R*,8*S*)-5-Aza-4-isopropyl-11-methoxy-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (20c) and its (3*S*,4*S*,7*S*,8*S*) isomer (21c) (Table 1, entry 3): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (80.0 mg, 0.195 mmol) was converted into, in the order of elution, **20c** (43.8 mg, 43%) and **21c** (20.4 mg, 20%), by use of 4-iodoanisole.

Compound ***20c***: Colorless crystals; m.p. 185–187 °C; $[\alpha]_D^{23}$=−14.7 (*c*=0.38, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.90 (d, *J*=7.3 Hz, 3H; CMe), 0.91 (d, *J*=7.3 Hz, 3H; CMe), 2.00–2.06 (m, 1H; Me_2CH), 2.27 (s, 3H; $PhCH_3$), 2.36 (dddd, *J*=11.6, 11.6, 11.6, 6.1 Hz, 1H; 7-H), 2.53 (s, 6H; 2×$PhCH_3$), 2.61–2.65 (m, 1H; 3-H), 2.75 (dd, *J*=11.6, 11.6 Hz, 1H; 6-C*H*H), 3.44 (dd, *J*=11.6, 6.1 Hz, 1H; 6-CH*H*), 3.62 (s, 3H; OMe), 3.83 (d, *J*=11.6 Hz, 1H; 8-H), 4.43 (dd, *J*=7.9, 4.3 Hz, 1H; 4-H), 5.00 (s, 1H; C=C*H*H), 5.44 (s, 1H; C=CH*H*), 6.29 (d, *J*=2.4 Hz, 1H; Ph), 6.76 (dd, *J*=9.2, 2.4 Hz, 1H; Ph), 6.87 (s, 2H; Ph), 7.06 (d, *J*=7.3 Hz, 2H; Ph), 7.21–7.28 (m, 3H; Ph), 7.55 ppm (d, *J*=9.2 Hz, 1H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ=17.4, 19.5, 21.0, 23.0 (2C), 32.6, 48.5, 51.6, 51.7, 53.2, 55.2, 64.1, 104.3, 112.4, 114.5, 126.5, 126.9, 128.4 (2C), 128.6 (2C), 129.6, 131.8 (2C), 132.9, 139.9 (2C), 140.9, 142.2, 143.4, 144.7, 159.2 ppm; IR (KBr): $\tilde{\nu}$=1313 (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 516 (70) [M^++H], 472 (100); HRMS (FAB): calcd $C_{32}H_{38}NO_3S$ [M^++H]: 516.2572; found: 516.2572.

Compound ***21c***: Colorless oil; $[\alpha]_D^{22}$=−5.45 (*c*=1.05, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.80 (d, *J*=7.3 Hz, 3H; CMe), 0.90 (d, *J*=7.3 Hz, 3H; CMe), 1.97–2.03 (m, 1H; Me_2CH), 2.28 (s, 3H; $PhCH_3$), 2.53 (s, 6H; 2×$PhCH_3$), 2.76–2.81 (m, 1H; 7-H), 3.02–3.05 (m, 1H; 3-H), 3.23 (dd, *J*=9.8, 6.1 Hz, 1H; 6-C*H*H), 3.37 (dd, *J*=9.8, 6.7 Hz, 1H; 6-CH*H*), 3.69 (s, 3H; OMe), 3.94 (d, *J*=5.5 Hz, 1H; 8-H), 3.96 (dd, *J*=4.3, 4.3 Hz, 1H; 4-H), 5.00 (s, 1H; C=C*H*H), 5.47 (s, 1H; C=CH*H*), 6.38 (d, *J*=2.4 Hz, 1H; Ph), 6.77 (dd, *J*=8.5, 2.4 Hz, 1H; Ph), 6.86 (s, 2H; Ph), 7.03 (d, *J*=7.3 Hz, 2H; Ph), 7.17–7.26 (m, 3H; Ph), 7.44 ppm (d, *J*=8.5 Hz, 1H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=17.1, 19.6, 20.9, 23.1 (2C), 31.9, 44.0, 45.0, 46.4, 52.9, 55.2, 72.4, 111.2, 113.4, 114.1, 126.4, 126.5, 127.7, 128.5 (5C), 131.8 (2C), 134.1, 138.1, 139.6 (2C), 141.9, 143.7, 144.4 ppm; IR (KBr): $\tilde{\nu}$=1315 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 516 (53) [M^++H], 136 (100); HRMS (FAB): calcd for $C_{32}H_{38}NO_3S$ [M^++H]: 516.2572; found: 516.2571.

(3*S*,4*S*,7*R*,8*S*)-5-Aza-4-isopropyl-10-methoxy-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (20da) and (3*S*,4*S*,7*R*,8*S*)-5-aza-4-isopropyl-12-methoxy-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (20db) (Table 1, entry 4): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (213 mg, 0.520 mmol) was converted into **20da** (50.0 mg, 19%) and **20db** (45.0 mg, 17%) by use of 3-iodoanisole.

Compound ***20da***: Colorless powder; m.p. 163–165 °C; $[\alpha]_D^{23}$=+6.70 (*c*=1.035, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (d, *J*=6.2 Hz, 3H; CMe), 0.91 (d, *J*=6.9 Hz, 3H; CMe), 2.01–2.04 (m, 1H; Me_2CH), 2.27 (s, 3H; $PhCH_3$), 2.27–2.40 (m, 1H; 7-H), 2.53 (s, 6H; 2×$PhCH_3$), 2.62–2.70 (m, 1H; 3-H), 2.77 (dd, *J*=11.8, 11.8 Hz, 1H; 6-C*H*H), 3.45 (dd, *J*=11.8, 6.2 Hz, 1H; 6-CH*H*), 3.81 (s, 3H; OMe), 3.82 (d, *J*=8.7 Hz, 1H; 8-H), 4.44 (dd, *J*=8.1, 4.4 Hz, 1H; 4-H), 5.12 (d, *J*=1.2 Hz, 1H; C=C*H*H), 5.56 (d, *J*=1.2 Hz, 1H; C=CH*H*), 6.70 (s, 2H; Ar), 6.88 (s, 2H; Ar), 7.05 (d, *J*=8.1 Hz, 2H; Ar), 7.11 (s, 1H; Ar), 7.22–7.30 ppm (m, 3H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=17.2, 19.5, 20.9, 22.9 (2C), 32.5, 48.3, 50.8, 52.2, 53.1, 55.3, 64.0, 106.2, 109.7, 114.5, 126.8, 128.4 (2C), 128.7 (2C), 130.9, 131.9 (3C), 133.0, 137.8, 140.0 (2C), 142.4, 144.0, 145.4, 158.0 ppm; IR (KBr): $\tilde{\nu}$=1311 (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 516 (86) [M^++H], 472 (100); HRMS (FAB): calcd for $C_{32}H_{38}NO_3S$ [M^++H]: 516.2572; found: 516.2550.

Compound ***20db***: Colorless powder; m.p. 202–204 °C; $[\alpha]_D^{22}$=−27.5 (*c*=1.01, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.85 (d, *J*=7.5 Hz, 3H; CMe), 0.88 (d, *J*=7.5 Hz, 3H; CMe), 1.99–2.18 (m, 2H; Me_2CH and 7-H), 2.27 (s, 3H; $PhCH_3$), 2.49 (s, 6H; 2×$PhCH_3$), 2.48–2.57 (m, 1H; 3-H), 2.85 (dd, *J*=11.8, 11.2 Hz, 1H; 6-C*H*H), 3.31 (s, 3H; OMe), 3.61 (dd, *J*=11.8, 6.2 Hz, 1H; 6-CH*H*), 3.91 (d, *J*=10.6 Hz, 1H; 8-H), 4.37 (dd, *J*=8.1, 4.4 Hz, 1H; 4-H), 5.10 (s, 1H; C=C*H*H), 5.57 (s, 1H; C=CH*H*), 6.72 (dd, *J*=6.9, 2.5 Hz, 1H; Ar), 6.87 (s, 2H; Ar), 6.91 (d, *J*=6.9 Hz, 2H; Ar), 7.08–7.24 ppm (m, 5H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=16.8, 19.6, 20.9, 22.8 (2C), 32.3, 47.2, 47.3, 53.2, 53.3, 55.3, 63.5, 105.7, 111.3, 118.3, 125.5, 126.5 (2C), 127.6, 128.0 (2C), 128.2, 131.9 (2C), 133.0, 139.6, 140.0 (2C), 142.3, 146.0, 146.6, 158.1 ppm; IR (KBr): $\tilde{\nu}$=1313 (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 516 (99) [M^++H], 472 (100); HRMS (FAB): calcd for $C_{32}H_{38}NO_3S$ [M^++H]: 516.2572; found: 516.2567.

(3*S*,4*S*,7*R*,8*S*)-5-Aza-4-isopropyl-13-methoxy-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (20e), its (3*S*,4*S*,7*S*,8*S*) isomer (21e) (Table 1, entry 5), and (2*S*,3*S*)-4-[(*Z*)-benzylidene]-2-isopropyl-3-[1-(2-methoxyphenyl)vinyl]-1-(2,4,6-trimethylphenylsulfonyl)pyrrolidine (58):[25] By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (100 mg, 0.244 mmol) was converted into **20e** (45.2 mg, 36%), **21e** (3 mg, 2%), and **58** (18.0 mg, 14%) by use of 2-iodoanisole.

Compound ***20e***: Colorless powder; m.p. 221–222 °C; $[\alpha]_D^{23}$=+24.0 (*c*=1.06, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.86 (d, *J*=6.9 Hz, 3H; CMe), 0.92 (d, *J*=7.5 Hz, 3H; CMe), 1.97–2.05 (m, 1H; Me_2CH), 2.27 (s, 3H; $PhCH_3$), 2.27–2.41 (m, 1H; 7-H), 2.53 (s, 6H; 2×$PhCH_3$), 2.53–2.59 (m, 1H; 3-H), 2.77 (dd, *J*=11.8, 11.2 Hz, 1H; 6-C*H*H), 3.54 (dd, *J*=11.2, 5.6 Hz, 1H; 6-CH*H*), 3.85 (s, 3H; OMe), 3.88 (d, *J*=11.2 Hz, 1H; 8-H), 4.48 (dd, *J*=8.1, 3.8 Hz, 1H; 4-H), 5.46 (s, 1H; C=C*H*H), 6.04 (s, 1H; C=CH*H*), 6.44 (d, *J*=7.5 Hz, 1H; Ar), 6.78 (d, *J*=8.1 Hz, 1H; Ar), 6.88 (s, 2H; Ar), 7.00–7.07 (m, 3H; Ar), 7.19–7.29 ppm (m, 3H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=17.2, 19.5, 20.9, 22.9 (2C), 32.3, 49.5, 52.0, 52.2, 53.8, 55.6, 63.5, 109.3, 111.8, 122.6, 126.2, 126.7, 127.8, 128.4 (2C), 128.6 (2C), 131.9 (2C), 133.2, 139.7, 140.0 (2C), 141.7, 142.3, 144.6, 157.5 ppm; IR (KBr): $\tilde{\nu}$=1309 (SO_2N), 1153 cm^{-1} (SO_2N); elemental analysis calcd

(%) for $C_{32}H_{37}NO_3S$: C 74.53, H 7.23, N 2.72; found: C 74.38, H 7.27, N 2.74.

Compound ***58***: Colorless oil; $[\alpha]_D^{22}=-102$ ($c=1.165$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.41$ (d, $J=6.9$ Hz, 3H; CMe), 0.68 (d, $J=6.9$ Hz, 3H; CMe), 1.62–1.70 (m, 1H; Me_2CH), 2.30 (s, 3H; $PhCH_3$), 2.62 (s, 6H; $2\times PhCH_3$), 3.59 (d, $J=3.7$ Hz, 1H; 2-H), 3.87 (s, 3H; OMe), 4.00 (s, 1H; 3-H), 4.32 (d, $J=15.0$ Hz, 1H; 5-CHH), 4.62 (d, $J=15.0$ Hz, 1H; 5-CHH), 5.10 (s, 1H; C=CHH), 5.20 (s, 1H; C=CHH), 6.49 (s, 1H; C=CHPh), 6.87 (dd, $J=8.1$, 7.5 Hz, 2H; Ar), 6.93 (s, 2H; Ar), 7.07 (d, $J=7.5$ Hz, 1H; Ar), 7.21–7.40 ppm (m, 6H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=16.3$, 18.7, 20.9, 23.1 (2C), 32.2, 50.8, 51.4, 55.3, 67.4, 110.1, 115.2, 120.5, 125.5, 126.9, 128.2 (2C), 128.5 (2C), 128.9, 130.8, 131.7 (2C), 131.8, 133.5, 136.9, 139.8, 140.1 (2C), 142.3, 150.1, 156.0 ppm; IR (KBr): $\tilde{\nu}=1319$ (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 516 (97) [M^++H], 472 (100); HRMS (FAB): calcd for $C_{32}H_{38}NO_3S$ [M^++H]: 516.2572; found: 516.2584.

(3*S*,4*S*,7*R*,8*S*)-5-Aza-4-isobutyl-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (22a) and its (3*S*,4*S*,7*S*,8*S*) isomer (23a) (Table 1, entry 6): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **10b** (150 mg, 0.354 mmol) was converted into, in the order of elution, **22a** (38.0 mg, 21%) and **23a** (25.0 mg, 14%).

Compound ***22a***: Colorless oil; $[\alpha]_D^{28}=+14.9$ ($c=1.22$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=0.82$ (d, $J=6.7$ Hz, 3H; CMe), 0.83 (d, $J=6.7$ Hz, 3H; CMe), 1.25–1.49 (m, 2H; Me_2CHCH_2), 1.68–1.74 (m, 1H; Me_2CH), 2.27 (s, 3H; $PhCH_3$), 2.34–2.43 (m, 1H; 7-H), 2.51–2.54 (m, 1H; 3-H), 2.55 (s, 6H; $2\times PhCH_3$), 2.87 (dd, $J=12.2$, 11.6 Hz, 1H; 6-CHH), 3.55 (dd, $J=12.2$, 6.1 Hz, 1H; 6-CHH), 3.85 (d, $J=11.0$ Hz, 1H; 8-H), 4.38 (ddd, $J=6.7$, 6.7, 6.7 Hz, 1H; 4-H), 5.06 (d, $J=1.8$ Hz, 1H; C=CHH), 5.58 (d, $J=1.8$ Hz, 1H; C=CHH), 6.77–7.64 (m, 9H; Ph), 6.89 ppm (s, 2H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=20.9$, 22.9 (2C), 23.2, 23.4, 24.2, 45.9, 51.4, 51.6, 52.2, 54.8, 59.1, 105.5, 125.1, 126.6, 126.9, 128.2, 128.6 (2C), 128.7 (2C), 129.8, 131.9 (2C), 133.3, 136.1, 139.5, 140.1 (2C), 142.3, 143.8, 144.7 ppm; IR (KBr): $\tilde{\nu}=1313$ (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 500 (100) [M^++H]; HRMS (FAB): calcd for $C_{32}H_{38}NO_2S$ [M^++H]: 500.2623; found: 500.2626.

Compound ***23a***: Colorless solid; $[\alpha]_D^{28}=-5.78$ ($c=1.88$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=0.77$ (d, $J=6.1$ Hz, 3H; CMe), 0.80 (d, $J=6.1$ Hz, 3H; CMe), 1.37–1.48 (m, 2H; Me_2CHCH_2), 1.57–1.62 (m, 1H; Me_2CH), 2.27 (s, 3H; $PhCH_3$), 2.53 (s, 6H; $2\times PhCH_3$), 2.82–2.87 (m, 1H; 7-H), 2.93–2.95 (m, 1H; 3-H), 3.10 (dd, $J=9.8$, 6.1 Hz, 1H; 6-CHH), 3.38 (dd, $J=9.8$, 6.7 Hz, 1H; 6-CHH), 3.97–4.02 (m, 2H; 4-H and 8-H), 5.13 (s, 1H; C=CHH), 5.65 (s, 1H; C=CHH), 6.86 (s, 2H; Ph), 6.87–7.55 ppm (m, 9H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta=21.0$, 21.7, 23.2 (2C), 23.8, 25.4, 44.1 (2C), 46.3, 48.5, 51.2, 65.6, 112.8, 124.7, 126.4, 126.9, 128.1, 128.4 (2C), 129.7, 131.6 (4C), 133.7, 134.5, 136.5, 139.7 (2C), 141.9, 143.7, 143.8 ppm; IR (KBr): $\tilde{\nu}=1315$ (SO_2N), 1157 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 500 (80) [M^++H], 91 (100); HRMS (FAB): calcd for $C_{32}H_{38}NO_2S$ [M^++H]: 500.2623; found: 500.2621.

(3*S*,4*S*,7*R*,8*S*)-5-Aza-4-isobutyl-11-methoxy-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (22b) and its (3*S*,4*S*,7*S*,8*S*) isomer (23b) (Table 1, entry 7): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **10b** (122 mg, 0.288 mmol) was converted into, in the order of elution, **22b** (48.0 mg, 32%) and **23b** (54.7 mg, 36%), by use of 4-iodoanisole.

Compound ***22b***: Colorless crystals; m.p. 145–148°C (*n*-hexane/EtOAc); $[\alpha]_D^{20}=-0.92$ ($c=1.00$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=0.76$ (d, $J=6.1$ Hz, 3H; CMe), 0.79 (d, $J=6.7$ Hz, 3H; CMe), 1.35–1.45 (m, 2H; 1′-CH_2), 1.48–1.70 (m, 1H; 2′-H), 2.28 (s, 3H; $PhCH_3$), 2.53 (s, 6H; $2\times PhCH_3$), 2.79–2.86 (m, 1H; 7-H), 2.88–2.92 (m, 1H; 3-H), 3.11 (dd, $J=9.8$, 6.1 Hz, 1H; 6-CHH), 3.38 (dd, $J=9.8$, 6.7 Hz, 1H; 6-CHH), 3.68 (s, 3H; OMe), 3.92–4.00 (m, 2H; 4-H and 8-H), 5.01 (s, 1H; C=CHH), 5.54 (s, 1H; C=CHH), 6.38 (d, $J=2.4$ Hz, 1H; 10-H), 6.77 (dd, $J=8.5$, 2.4 Hz, 1H; 12-H), 6.87 (s, 2H; Ph), 7.03–7.04 (m, 2H; Ph), 7.17–7.26 (m, 3H; Ph), 7.49 ppm (d, $J=8.5$ Hz, 1H; 13-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=20.9$, 21.6, 23.0 (2C), 23.7, 25.3, 43.97, 44.00, 46.4, 48.4, 51.2, 55.1, 65.7, 110.8, 113.5, 114.2, 126.2, 126.5, 127.4, 128.5 (2C), 128.5 (2C), 131.7 (2C), 133.9, 138.0, 139.8 (2C), 142.0, 143.2, 143.8, 159.5 ppm; IR (KBr): $\tilde{\nu}=1313$ (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 530 (100) [M^++H]; HRMS (FAB): calcd for $C_{33}H_{40}NO_3S$ [M^++H]: 530.2729; found: 530.2727.

Compound ***23b***: Colorless crystals; m.p. 163–165°C (*n*-hexane/EtOAc); $[\alpha]_D^{20}=-11.3$ ($c=1.03$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=0.82$ (d, $J=6.7$ Hz, 3H; CMe), 0.84 (d, $J=6.7$ Hz, 3H; CMe), 1.38–1.50 (m, 2H; 1′-CH_2), 1.69–1.75 (m, 1H; 2′-H), 2.27 (s, 3H; $PhCH_3$), 2.33–2.40 (m, 1H; 7-H), 2.47–2.52 (m, 1H; 3-H), 2.55 (s, 6H; $2\times PhCH_3$), 2.85 (dd, $J=11.6$, 11.6 Hz, 1H; 6-CHH), 3.52 (dd, $J=11.6$, 5.5 Hz, 1H; 6-CHH), 3.62 (s, 3H; OMe), 3.80 (d, $J=11.0$ Hz, 1H; 8-H), 4.37 (ddd, $J=7.9$, 6.1, 6.1 Hz, 1H; 4-H), 4.94 (s, 1H; C=CHH), 5.44 (s, 1H; C=CHH), 6.28 (d, $J=2.4$ Hz, 1H; 10-H), 6.76 (dd, $J=8.5$, 2.4 Hz, 1H; 12-H), 6.89 (s, 2H; Ph), 7.06–7.07 (m, 2H; Ph), 7.22–7.29 (m, 3H; Ph), 7.57 ppm (d, $J=8.5$ Hz, 1H; 13-H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta=21.0$, 23.0 (2C), 23.3, 23.4, 24.3, 46.0, 51.3, 51.8, 52.2, 54.9, 55.2, 59.1, 103.6, 112.5, 114.5, 126.3, 126.9, 128.5 (2C), 128.6 (2C), 129.0, 131.8 (2C), 133.2, 140.0 (2C), 140.9, 142.2, 143.4, 144.1, 159.3 ppm; IR (KBr): $\tilde{\nu}=1319$ (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 530 (87) [M^++H], 472 (100); HRMS (FAB): calcd for $C_{33}H_{40}NO_3S$ [M^++H]: 530.2729; found: 530.2736.

(3*S*,4*S*,7*R*,8*S*)-5-Aza-4-benzyl-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (24) and its (3*S*,4*S*,7*S*,8*S*) isomer (25) (Table 1, entry 8): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **10c** (150 mg, 0.328 mmol) was converted into, in the order of elution, **24** (52.6 mg, 30%) and **25** (42.7 mg, 24%).

Compound ***24***: Colorless oil; $[\alpha]_D^{28}=+32.7$ ($c=2.00$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=2.22$–2.32 (m, 1H; 7-H), 2.29 (s, 3H; $PhCH_3$), 2.56–2.65 (m, 1H; 3-H), 2.62 (s, 6H; $2\times PhCH_3$), 2.70 (dd, $J=11.6$, 11.6 Hz, 1H; 6-CHH), 2.88 (dd, $J=13.4$, 6.7 Hz, 1H; Ph–CHH), 2.95 (dd, $J=13.4$, 6.1 Hz, 1H; Ph–CHH), 3.63 (dd, $J=11.6$, 6.1 Hz, 1H; 6-CHH), 3.70 (d, $J=11.0$ Hz, 1H; 8-H), 4.51–4.54 (m, 1H; 4-H), 4.58 (d, $J=1.8$ Hz, 1H; C=CHH), 5.38 (d, $J=1.8$ Hz, 1H; C=CHH), 6.71–7.54 ppm (m, 16H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=20.9$, 23.2 (2C), 40.6, 50.9, 51.2, 51.6, 52.7, 61.7, 106.1, 125.0, 126.5 (2C), 126.9, 128.1, 128.3 (2C), 128.5 (2C), 128.7 (2C), 129.8, 130.0 (2C), 132.1 (2C), 133.5, 135.7, 137.0, 139.3, 139.9 (2C), 142.6, 143.4, 143.7 ppm; IR (KBr): $\tilde{\nu}=1311$ (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 534 (20) [M^++H], 136 (100); HRMS (FAB): calcd for $C_{35}H_{36}NO_2S$ [M^++H]: 534.2467; found: 534.2470.

Compound ***25***: Colorless oil; $[\alpha]_D^{28}=+6.35$ ($c=1.81$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=2.28$ (s, 3H; $PhCH_3$), 2.57 (s, 6H; $2\times PhCH_3$), 2.70–2.77 (m, 2H; Ph–CHH and 7-H), 2.97–2.99 (m, 1H; 3-H), 3.07 (dd, $J=14.0$, 3.7 Hz, 1H; Ph–CHH), 3.11 (dd, $J=9.8$, 6.1 Hz, 1H; 6-CHH), 3.34 (dd, $J=9.8$, 6.7 Hz, 1H; 6-CHH), 3.92 (d, $J=6.1$ Hz, 1H; 8-H), 4.25 (ddd, $J=7.9$, 3.7, 3.7 Hz, 1H; 4-H), 4.61 (d, $J=1.2$ Hz, 1H; C=CHH), 5.43 (s, 1H; C=CHH), 6.65–7.44 ppm (m, 16H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=20.9$, 23.2 (2C), 40.7, 43.6, 45.9, 46.2, 51.7, 68.3, 113.0, 124.8, 126.4 (2C), 127.0, 128.1, 128.4 (4C), 128.5 (2C), 129.6 (2C), 129.7, 131.9 (2C), 133.7, 134.4, 136.5, 137.9, 139.8 (2C), 142.2, 143.0, 143.7 ppm; IR (KBr): $\tilde{\nu}=1317$ (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 534 (70) [M^++H], 442 (100); HRMS (FAB): calcd for $C_{35}H_{36}NO_2S$ [M^++H]: 534.2467; found: 534.2457.

(3*S*,4*R*,7*R*,8*S*)-5-Aza-4-(*tert*-butyl)-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (26) and its (3*S*,4*R*,7*S*,8*S*) isomer (27) (Table 1, entry 9): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **10d** (45.0 mg, 0.106 mmol) was converted into, in the order of elution, **26** (18.0 mg, 34%) and **27** (3.6 mg, 7%).

Compound ***26***: Colorless oil; $[\alpha]_D^{23}=+31.9$ ($c=1.62$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=0.97$ (s, 3H; CMe_3), 2.24 (s, 3H; $PhCH_3$), 2.24–2.34 (m, 1H; 7-H), 2.50 (s, 6H; $2\times PhCH_3$), 2.69 (dd, $J=12.2$, 7.3 Hz, 1H; 3-H), 2.75 (dd, $J=12.2$, 12.2 Hz, 1H; 6-CHH), 3.30 (dd, $J=12.2$, 6.1 Hz, 1H; 6-CHH), 3.87 (d, $J=11.6$ Hz, 1H; 8-H), 4.40 (d, $J=7.3$ Hz, 1H; 4-H), 5.19 (s, 1H; C=CHH), 5.61 (s, 1H; C=CHH), 6.79 (d, $J=7.9$ Hz, 1H; Ph), 6.82 (s, 2H; Ph), 6.97–6.98 (m, 2H; Ph), 7.10 (t, $J=7.3$ Hz, 1H; Ph), 7.18–7.25 (m, 4H; Ph), 7.62 ppm (d, $J=7.9$ Hz, 1H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=20.9$, 23.3 (2C), 27.2 (3C), 36,4, 50.0, 51.5, 52.0,

53.5, 68.1, 105.9, 125.6, 126.5, 126.8, 128.0, 128.5 (2C), 128.6 (2C), 129.9, 131.9 (2C), 133.0, 137.0, 139.6, 140.1 (2C), 142.2, 143.9, 145.4 ppm; IR (KBr): $\tilde{\nu}$ = 1309 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m/z* (%): 500 (100) [M^++H]; HRMS (FAB): calcd for $C_{32}H_{38}NO_2S$ [M^++H]: 500.2623; found: 500.2591.

Compound ***27***: Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (s, 3H; CMe_3), 2.26 (s, 3H; $PhCH_3$), 2.48 (s, 6H; 2×$PhCH_3$), 2.99–3.05 (m, 1H; 7-H), 3.19 (dd, *J* = 11.0, 6.1 Hz, 1H; 6-C*H*H), 3.22–3.24 (m, 1H; 3-H), 3.37 (dd, *J* = 11.0, 8.5 Hz, 1H; 6-CH*H*), 3.80 (d, *J* = 6.7 Hz, 1H; 8-H), 4.14 (s, 1H; 4-H), 5.22 (s, 1H; C=C*H*H), 5.58 (s, 1H; C=CH*H*), 6.75 (d, *J* = 7.3 Hz, 1H; Ph), 6.81 (s, 2H; Ph), 6.95 (d, *J* = 7.9 Hz, 2H; Ph), 7.10 (t, *J* = 7.3 Hz, 1H; Ph), 7.19–7.26 (m, 4H; Ph), 7.47 ppm (d, *J* = 7.9 Hz, 1H; Ph).

(3*S*,4*S*,7*R*,8*S*)-5-Aza-11-methoxy-2-methylene-4-[(1*S*)-1-methylpropyl]-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (28) and its (3*S*,4*S*,7*S*,8*S*) isomer (29) (Table 1, entry 10): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **10e** (141 mg, 0.332 mmol) was converted into, in the order of elution, **28** (60.4 mg, 34%) and **29** (53.9 mg, 31%), by use of 4-iodoanisole.

Compound ***28***: Colorless crystals; m.p. 105–108°C (*n*-hexane/Et_2O); $[\alpha]_D^{19}$ = +13.3 (*c* = 0.95, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.76 (d, *J* = 6.7 Hz, 3H; CMe), 0.79 (t, *J* = 7.3 Hz, 3H; CMe), 1.10–1.17 (m, 1H; 2′-C*H*H), 1.36–1.42 (m, 1H; 2′-CH*H*), 1.59–1.63 (m, 1H; 1′-H), 2.28 (s, 3H; $PhCH_3$), 2.54 (s, 6H; 2×$PhCH_3$), 2.74–2.79 (m, 1H; 7-H), 3.05 (dd, *J* = 6.1, 5.5 Hz, 1H; 3-H), 3.32–3.40 (m, 2H; 6-CH_2), 3.69 (s, 3H; OMe), 3.98 (d, *J* = 6.1 Hz, 1H; 8-H), 4.02 (dd, *J* = 5.5, 3.7 Hz, 1H; 4-H), 4.98 (s, 1H; C=C*H*H), 5.45 (s, 1H; C=CH*H*), 6.39 (d, *J* = 2.4 Hz, 1H; 10-H), 6.77 (dd, *J* = 8.5, 2.4 Hz, 1H; 12-H), 6.87 (s, 2H; Ph), 7.04–7.07 (m, 2H; Ph), 7.18–7.26 (m, 3H; Ph), 7.45 ppm (d, *J* = 8.5 Hz, 1H; 13-H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 12.5, 14.2, 21.0, 23.1 (2C), 27.0, 38.9, 44.5, 45.5, 46.5, 53.2, 55.2, 70.3, 111.3, 113.4, 114.1, 126.3, 126.4, 127.5, 128.4 (2C), 128.5 (2C), 131.6 (2C), 134.2, 138.1, 139.4 (2C), 141.8, 143.9, 144.3, 159.4 ppm; IR (KBr): $\tilde{\nu}$ = 1317 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): *m/z* (%): 530 (46) [M^++H], 472 (100); HRMS (FAB): calcd for $C_{33}H_{40}NO_3S$ [M^++H]: 530.2729; found: 530.2715.

Compound ***29***: Colorless crystals; m.p. 167–169°C (*n*-hexane/Et_2O); $[\alpha]_D^{22}$ = −7.47 (*c* = 1.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.3 Hz, 3H; CMe), 0.86 (d, *J* = 6.7 Hz, 3H; CMe), 0.98–1.08 (m, 1H; 2′-C*H*H), 1.47–1.56 (m, 1H; 2′-CH*H*), 1.69–1.72 (m, 1H; 1′-H), 2.27 (s, 3H; $PhCH_3$), 2.32–2.41 (m, 1H; 7-H), 2.54 (s, 6H; 2×$PhCH_3$), 2.64 (dd, *J* = 12.2, 7.9 Hz, 1H; 3-H), 2.77 (dd, *J* = 12.2, 11.6 Hz, 1H; 6-C*H*H), 3.47 (dd, *J* = 11.6, 6.1 Hz, 1H; 6-CH*H*), 3.62 (s, 3H; OMe), 3.84 (d, *J* = 12.2 Hz, 1H; 8-H), 4.44 (dd, *J* = 7.9, 4.3 Hz, 1H; 4-H), 5.01 (s, 1H; C=C*H*H), 5.41 (s, 1H; C=CH*H*), 6.29 (d, *J* = 1.8 Hz, 1H; 10-H), 6.76 (dd, *J* = 9.2, 1.8 Hz, 1H; 12-H), 6.88 (s, 2H; Ph), 7.05–7.07 (m, 2H; Ph), 7.21–7.28 (m, 3H; Ph), 7.53 ppm (d, *J* = 9.2 Hz, 1H; 13-H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 12.4, 14.0, 21.0, 23.0 (2C), 26.4, 39.8, 48.5, 51.7, 52.1, 53.1, 55.2, 63.6, 104.2, 112.4, 114.5, 126.6, 126.9, 128.4 (2C), 128.6 (2C), 129.8, 131.8 (2C), 132.9, 140.0 (2C), 140.9, 142.3, 143.5, 145.0, 159.2 ppm; IR (KBr): $\tilde{\nu}$ = 1309 (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): *m/z* (%): 530 (87) [M^++H], 472 (100); HRMS (FAB): calcd for $C_{33}H_{40}NO_3S$ [M^++H]: 530.2729; found: 530.2736.

(3*S*,4*S*,7*R*,8*S*)-5-Aza-5-(*tert*-butoxycarbonyl)-4-isopropyl-2-methylene-8-phenyltricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (30) and its (3*S*,4*S*,7*S*,8*S*) isomer (31) (Table 1, entry 11): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **10f** (45.2 mg, 0.138 mmol) was converted into, in the order of elution, **30** (8.7 mg, 16%) and **31** (19.4 mg, 35%).

Compound ***30***: Colorless oil; $[\alpha]_D^{24}$ = −17.9 (*c* = 1.40, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 328 K): δ = 0.93 (d, *J* = 6.6 Hz, 3H; CMe), 0.95 (d, *J* = 6.9 Hz, 3H; CMe), 1.36 (s, 9H; CMe_3), 1.97–2.09 (br s, 1H; Me_2CH), 2.81–2.90 (m, 1H; 7-H), 2.99–3.01 (m, 1H; 3-H), 3.28–3.29 (br s, 1H; 6-C*H*H), 3.40 (dd, *J* = 11.4, 7.5 Hz, 1H; 6-CH*H*), 3.75–3.77 (br s, 1H; 4-H), 3.93 (d, *J* = 4.5 Hz, 1H; 8-H), 5.10 (s, 1H; C=C*H*H), 5.56 (s, 1H; C=CH*H*), 6.96 (d, *J* = 7.2 Hz, 1H; Ph), 7.05 (d, *J* = 6.9 Hz, 2H; Ph), 7.14–7.28 (m, 5H; Ph), 7.54 ppm (dd, *J* = 7.5, 1.2 Hz, 1H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$, 328 K): δ = 18.9, 19.3, 28.5 (3C), 31.8, 44.1, 47.5, 51.5, 71.1, 77.1, 79.1, 112.3, 125.0, 126.4, 127.1, 128.2, 128.4 (2C), 128.5 (2C), 129.9, 135.8, 137.0, 144.3, 145.8, 155.0 ppm; IR (KBr): $\tilde{\nu}$ = 1691 cm^{-1} (C=O); MS (FAB): *m/z* (%): 404 (8) [M^++H], 348 (100); HRMS (FAB): calcd for $C_{27}H_{34}NO_2$ [M^++H]: 404.2590; found: 404.2607.

Compound ***31***: Colorless oil; $[\alpha]_D^{24}$ = −7.14 (*c* = 1.47, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 333 K): δ = 0.92 (d, *J* = 6.9 Hz, 3H; CMe), 0.95 (d, *J* = 6.9 Hz, 3H; CMe), 1.40–1.44 (m, 9H; CMe_3), 2.12–2.20 (m, 1H; 7-H), 2.40–2.66 (br s, 2H; Me_2CH and 3-H), 2.90 (dd, *J* = 11.1, 11.1 Hz, 1H; 6-C*H*H), 3.60–3.80 (br s, 1H; 6-CH*H*), 3.98 (d, *J* = 11.1 Hz, 1H; 8-H), 4.13–4.21 (br s, 1H; 4-H), 5.08 (s, 1H; C=C*H*H), 5.55 (d, *J* = 1.8 Hz, 1H; C=CH*H*), 6.81 (d, *J* = 7.5 Hz, 1H; Ph), 7.08–7.30 (m, 7H; Ph), 7.59–7.61 ppm (m, 1H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$, 333 K): δ = 17.5, 19.4, 28.7 (3C), 29.8, 48.7, 51.3, 52.1, 62.4, 77.2, 79.4, 105.5, 125.3, 126.4, 126.8, 128.0, 128.6 (4C), 130.0, 137.0, 139.7, 144.4, 146.3, 154.5 ppm; IR (KBr): $\tilde{\nu}$ = 1693 cm^{-1} (C=O); MS (FAB): *m/z* (%): 404 (6) [M^++H], 348 (100); HRMS (FAB): calcd for $C_{27}H_{34}NO_2$ [M^++H]: 404.2590; found: 404.2590.

(3*S*,4*S*,7*S*)-5-Aza-4-isopropyl-8,8-dimethyl-2-methylene-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (32a) (Table 1, entry 12): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **11** (40.0 mg, 0.110 mmol) was converted into **32a** (20.1 mg, 42%). Colorless oil; $[\alpha]_D^{22}$ = −42.9 (*c* = 2.86, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.7 Hz, 3H; CMe), 0.88 (d, *J* = 6.7 Hz, 3H; CMe), 1.21 (s, 3H; CMe), 1.34 (s, 3H; CMe), 2.04–2.17 (m, 2H; Me_2CH and 7-H), 2.30 (s, 3H; $PhCH_3$), 2.69 (s, 6H; 2×$PhCH_3$), 2.67–2.71 (m, 1H; 3-H), 2.96 (dd, *J* = 11.6, 11.6 Hz, 1H; 6-C*H*H), 3.72 (dd, *J* = 11.6, 6.7 Hz, 1H; 6-CH*H*), 4.41 (dd, *J* = 7.3, 4.3 Hz, 1H; 4-H), 5.06 (d, *J* = 1.8 Hz, 1H; C=C*H*H), 5.47 (d, *J* = 1.8 Hz, 1H; C=CH*H*), 6.96 (s, 2H; Ph), 7.16–7.19 (m, 1H; Ph), 7.26–7.29 (m, 1H; Ph), 7.33–7.35 (m, 1H; Ph), 7.52–7.54 ppm (m, 1H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.3, 19.4, 20.9, 23.1 (2C), 25.2, 30.2, 32.8, 37.1, 43.2, 49.2, 53.6, 63.9, 105.4, 125.6, 126.2, 126.6, 128.4, 131.9 (2C), 133.3, 135.2, 140.1 (2C), 142.4, 145.7, 146.4 ppm; IR (KBr): $\tilde{\nu}$ = 1315 (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m/z* (%): 438 (100) [M^++H]; HRMS (FAB): calcd for $C_{27}H_{36}NO_2S$ [M^++H]: 438.2467; found: 438.2468.

(3*S*,4*S*,7*S*)-5-Aza-4-isopropyl-11-methoxy-8,8-dimethyl-2-methylene-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (32b) (Table 1, entry 13): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **11** (50.0 mg, 0.138 mmol) was converted into **32b** (29.0 mg, 45%) by use of 4-iodoanisole. Colorless oil; $[\alpha]_D^{20}$ = −49.2 (*c* = 0.92, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.876 (d, *J* = 6.7 Hz, 3H; CMe), 0.882 (d, *J* = 6.7 Hz, 3H; CMe), 1.20 (s, 3H; CMe), 1.32 (s, 3H; CMe), 2.02–2.15 (m, 2H; Me_2CH and 7-H), 2.30 (s, 3H; $PhCH_3$), 2.64–2.71 (m, 1H; 3-H), 2.69 (s, 6H; 2×$PhCH_3$), 2.95 (dd, *J* = 11.6, 11.6 Hz, 1H; 6-C*H*H), 3.70 (dd, *J* = 11.6, 6.7 Hz, 1H; 6-CH*H*), 3.81 (s, 3H; OMe), 4.39 (dd, *J* = 7.3, 4.3 Hz, 1H; 4-H), 4.94 (d, *J* = 1.2 Hz, 1H; C=C*H*H), 5.34 (d, *J* = 1.8 Hz, 1H; C=CH*H*), 6.75 (dd, *J* = 8.5, 2.4 Hz, 1H; Ph), 6.85 (d, *J* = 2.4 Hz, 1H; Ph), 6.96 (s, 2H; Ph), 7.48 ppm (d, *J* = 8.5 Hz, 1H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.4, 19.3, 20.9, 23.1 (2C), 25.1, 30.2, 32.9, 37.2, 43.3, 49.2, 53.5, 55.3, 63.9, 103.7, 111.8, 111.9, 126.8, 128.2, 131.9 (2C), 133.3, 140.1 (2C), 142.4, 145.8, 147.3, 159.7 ppm; IR (KBr): $\tilde{\nu}$ = 1367 (NSO_2), 1153 cm^{-1} (NSO_2); MS (FAB): *m/z* (%): 468 (80) [M^++H], 424 (100); HRMS (FAB): calcd for $C_{28}H_{38}NO_3S$ [M^++H]: 468.2572; found: 468.2580.

(3*S*,4*S*,7*R*,8*R*)-5-Aza-4-isopropyl-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (33): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene (*Z*)-**10a** (50.0 mg, 0.122 mmol) was converted into, in the order of elution, **20a** (9.3 mg, 16%) and **33** (15.2 mg, 26%).

Compound ***33***: Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.53 (d, *J* = 6.7 Hz, 3H; CMe), 0.74 (d, *J* = 6.7 Hz, 3H; CMe), 1.86–1.92 (m, 1H; Me_2CH), 2.20 (dd, *J* = 12.2, 11.6 Hz, 1H; 6-C*H*H), 2.29 (s, 3H; $PhCH_3$), 2.49–2.56 (m, 1H; 7-H), 2.63 (s, 6H; 2×$PhCH_3$), 2.79 (dd, *J* = 12.8, 7.3 Hz, 1H; 3-H), 3.61 (dd, *J* = 11.6, 6.1 Hz, 1H; 6-CH*H*), 4.31 (dd, *J* = 7.3, 4.3 Hz, 1H; 4-H), 4.45 (d, *J* = 5.5 Hz, 1H; 8-H), 5.12 (d, *J* = 1.8 Hz, 1H; C=C*H*H), 5.62 (d, *J* = 1.8 Hz, 1H; C=CH*H*), 6.90 (d, *J* = 6.7 Hz, 2H; Ph), 6.93 (s, 2H; Ph), 6.98 (d, *J* = 7.3 Hz, 1H; Ph), 7.17–7.25 (m, 5H; Ph), 7.70 ppm (d, *J* = 7.3 Hz, 1H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 17.3,

19.2, 21.1, 23.1 (2C), 32.9, 41.2, 46.5, 46.7, 51.0, 63.5, 106.4, 125.0, 126.6, 126.7, 128.0 (2C), 128.3, 129.8 (2C), 131.0, 131.8 (2C), 133.1, 136.3, 138.2, 140.0 (2C), 141.0, 142.3, 144.9 ppm; IR (KBr): $\tilde{\nu}$ = 1315 (SO_2N), 1153 cm^{-1} (SO_2N).

(1*S*,9*S*,10*S*,12*R*,16*R*)-11-Aza-10-isopropyl-8-methylene-11-(2,4,6-trimethylphenylsulfonyl)tetracyclo[7.6.1.0^{2,7}.0^{12,16}]hexadeca-2(3),4,6-triene (34a): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **12a** (80 mg, 0.214 mmol) was converted into **34a** (47.0 mg, 49%). Colorless solid; $[\alpha]_D^{28} = -12.9$ (c = 1.59, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.01 (d, J = 6.7 Hz, 3H; CMe), 1.03 (d, J = 6.7 Hz, 3H; CMe), 1.19–1.40 (m, 3H; 3×CH), 1.47–1.48 (m, 1H; CH), 1.65–1.68 (m, 1H; CH), 1.88–1.91 (m, 1H; CH), 2.17–2.22 (m, 1H; Me_2CH), 2.31 (s, 3H; $PhCH_3$), 2.31–2.36 (m, 1H; 16-H), 2.70 (s, 6H; 2×$PhCH_3$), 2.84 (dd, J = 13.4, 8.5, Hz, 1H; 9-H), 3.01 (ddd, J = 11.6, 6.1, 6.1 Hz, 1H; 1-H), 3.67 (ddd J = 13.4, 6.7, 6.7 Hz, 1H; 12-H), 4.35 (dd, J = 8.5, 4.9 Hz, 1H; 10-H), 5.11 (d, J = 1.8 Hz, 1H; C=C*H*H), 5.41 (d, J = 1.8 Hz, 1H; C=CH*H*), 6.95 (s, 2H; Ph), 7.13–7.52 ppm (m, 4H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 18.7, 21.1 (2C), 23.2 (2C), 23.8, 28.5, 30.7, 32.7, 38.9, 40.9, 45.9, 58.7, 64.8, 107.1, 125.6, 126.2, 127.9, 128.7, 131.8 (3C), 132.6, 136.1, 140.3 (2C), 142.4, 146.8 ppm; IR (KBr): $\tilde{\nu}$ = 1306 (SO_2N), 1149 cm^{-1} (SO_2N); MS (FAB): m/z (%): 450 (100) [M^++H]; HRMS (FAB): calcd for $C_{28}H_{36}NO_2S$ [M^++H]: 450.2467; found: 450.2470.

(1*S*,9*S*,10*S*,12*R*,16*R*)-11-Aza-10-isobutyl-8-methylene-11-(2,4,6-trimethylphenylsulfonyl)tetracyclo[7.6.1.0^{2,7}.0^{12,16}]hexadeca-2(3),4,6-triene (34b): By using a procedure identical to that described for the synthesis of **20a** and **21a**, a diastereomixture of allenene **12b** and **13b** (1:1; 80 mg, 0.206 mmol) was converted into **34b** (24.3 mg, 51% based on **12b**). Colorless oil; $[\alpha]_D^{24} = -6.02$ (c = 1.40, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (d, J = 6.7 Hz, 3H; CMe), 0.88 (d, J = 6.7 Hz, 3H; CMe), 1.20–1.38 (m, 3H; 3×CH), 1.46–1.69 (m, 4H; 4×CH), 1.81–1.90 (m, 2H; 2×CH), 2.32 (s, 3H; $PhCH_3$), 2.35–2.40 (m, 1H; 16-H), 2.71 (s, 6H; 2×$PhCH_3$), 2.74–2.78 (m, 1H; 9-H), 3.04 (ddd, J = 11.6, 6.1, 5.5 Hz, 1H; 1-H), 3.76–3.80 (m, 1H; 12-H), 4.24 (ddd, J = 11.0, 11.0, 4.8 Hz, 1H; 10-H), 5.02 (d, J = 1.8 Hz, 1H; C=C*H*H), 5.44 (d, J = 1.8 Hz, 1H; C=CH*H*), 6.96 (s, 2H; Ph), 7.14 (d, J = 7.3 Hz, 1H; Ph), 7.18 (dd, J = 7.3, 7.3 Hz, 1H; Ph), 7.23 (dd, J = 7.3, 7.3 Hz, 1H; Ph), 7.56 ppm (d, J = 7.3 Hz, 1H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.0, 22.8, 23.1 (2C), 23.7, 23.8, 24.5, 29.0, 30.3, 38.8, 45.8, 46.9, 48.8, 58.3, 58.6, 105.7, 125.4, 126.4, 128.1, 129.0, 131.9 (3C), 132.5, 135.3, 140.6 (2C), 142.6, 146.3 ppm; IR (KBr): $\tilde{\nu}$ = 1301 (SO_2N), 1157 cm^{-1} (SO_2N); MS (FAB): m/z (%): 464 (100) [M^++H]; HRMS (FAB): calcd for $C_{29}H_{38}NO_2S$ [M^++H]: 464.2623; found: 464.2612.

(1*S*,9*S*,10*S*,12*R*,16*R*)-11-Aza-8-methylene-10-[(1*S*)-1-methylpropyl]-5-(2,4,6-trimethylphenylsulfonyl)tetracyclo[7.6.1.0^{2,7}.0^{12,16}]hexadeca-2(3),4,6-triene (34c): By using a procedure identical to that described for the synthesis of **20a** and **21a**, allenene **12c** (39.3 mg, 0.101 mmol) was converted into **34c** (28.4 mg, 61%). Colorless oil; $[\alpha]_D^{24} = -17.2$ (c = 0.72, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 3H; CMe), 0.97 (d, J = 6.7 Hz, 3H; CMe), 1.02–1.68 (m, 7H; 7×CH), 1.86–1.91 (m, 2H; CH_2), 2.31 (s, 3H; $PhCH_3$), 2.32–2.37 (m, 1H; 16-H), 2.70 (s, 6H; 2×$PhCH_3$), 2.82–2.87 (m, 1H; 9-H), 2.99–3.04 (m, 1H; 1-H), 3.70 (ddd, J = 11.6, 5.5, 5.5 Hz, 1H; 12-H), 4.35 (dd, J = 8.5, 4.3 Hz, 1H; 10-H), 5.11 (s, 1H; C=C*H*H), 5.38 (s, 1H; C=CH*H*), 6.95 (s, 2H; Ph), 7.13–7.26 (m, 3H; Ph), 7.49 ppm (d, J = 7.3 Hz, 1H; Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 12.6, 14.6, 21.0, 23.1 (2C), 23.7, 27.4, 28.6, 30.8, 38.8, 39.4, 40.8, 46.0, 58.4, 64.4, 107.1, 125.5, 126.1, 127.8, 128.5, 131.7 (3C), 136.2, 140.1, 140.2 (2C), 142.3, 146.9 ppm; IR (KBr): $\tilde{\nu}$ = 1307 (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): m/z (%): 464 (100) [M^++H]; HRMS (FAB): calcd for $C_{29}H_{38}NO_2S$ [M^++H]: 464.2623; found: 464.2622.

(1*S*,8*S*,9*R*,12*S*)-11-Aza-12-isopropyl-2-methylene-8-phenyl-4-thia-11-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.3.0.0^{3,7}]dodeca-3(7),5-diene (56a) and its (1*S*,8*S*,9*S*,12*S*) isomer (57a) (Table 2, entry 1): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (155 mg, 0.378 mmol) was converted into **56a** (88.1 mg, 47%) and **57a** (23.0 mg, 12%) by use of 2-bromothiophene.

Compound ***56a***: Colorless oil; $[\alpha]_D^{25} = +7.63$ (c = 1.04, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, J = 6.9 Hz, 6H; 2×CMe), 1.99–2.04 (m, 1H; Me_2CH), 2.26 (s, 3H; $PhCH_3$), 2.52 (s, 6H; 2×$PhCH_3$), 2.52–2.60 (m, 1H; 9-H), 2.74–2.82 (m, 2H; 1-H and 10-C*H*H), 3.39 (dd, J = 11.8, 5.6 Hz, 1H; 10-CH*H*), 3.75 (d, J = 11.2 Hz, 1H; 8-H), 4.38 (dd, J = 8.1, 4.4 Hz, 1H; 12-H), 4.93 (s, 1H; C=C*H*H), 5.35 (s, 1H; C=CH*H*), 6.38 (d, J = 5.0 Hz, 1H; Ar), 6.87 (s, 2H; Ar), 7.01 (d, J = 5.0 Hz, 1H; Ar), 7.08 (d, J = 7.5 Hz, 2H; Ar), 7.23–7.30 ppm (m, 3H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.0, 19.0, 20.9, 22.9 (2C), 33.0, 48.4, 49.4, 52.1, 52.4, 64.0, 105.4, 124.0, 127.1, 127.8 (2C), 127.9, 128.6 (2C), 131.9 (2C), 132.9, 138.8, 140.1 (2C), 140.4, 141.2, 142.4 ppm (2C); IR (KBr): $\tilde{\nu}$ = 1313 (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): m/z (%): 492 (58) [M^++H], 307 (100); HRMS (FAB): calcd for $C_{29}H_{34}NO_2S_2$ [M^++H]: 492.2031; found: 492.2061.

Compound ***57a***: Pale-yellow oil; $[\alpha]_D^{23} = +7.83$ (c = 1.06, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (d, J = 6.9 Hz, 3H; CMe), 0.86 (d, J = 6.9 Hz, 3H; CMe), 1.92–1.99 (m, 1H; Me_2CH), 2.29 (s, 3H; $PhCH_3$), 2.60 (s, 6H; 2×$PhCH_3$), 2.89–3.07 (m, 1H; 9-H), 3.11 (dd, J = 6.9, 6.2 Hz, 1H; 1-H), 3.25 (dd, J = 10.0, 5.0 Hz, 1H; 10-C*H*H), 3.79 (dd, J = 10.0, 3.7 Hz, 1H; 10-CH*H*), 4.01–4.05 (m, 2H; 8-H and 12-H), 4.98 (s, 1H; C=C*H*H), 5.46 (s, 1H; C=CH*H*), 6.43 (d, J = 5.0 Hz, 1H; Ar), 6.91 (s, 2H; Ar), 7.04 (d, J = 5.0 Hz, 1H; Ar), 7.15–7.18 (m, 2H; Ar), 7.18–7.30 ppm (m, 3H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.8, 18.6, 20.9, 22.9 (2C), 30.9, 42.3, 45.9, 46.8, 53.4, 69.4, 110.7, 124.2, 126.7, 128.6 (3C), 128.7 (2C), 131.8 (2C), 135.4, 135.5, 138.3, 138.8, 139.3 (2C), 142.0, 144.1 ppm; IR (KBr): $\tilde{\nu}$ = 1315 (SO_2N), 1155 cm^{-1} (SO_2N); MS (FAB): m/z (%): 492 (100) [M^++H]; HRMS (FAB): calcd for $C_{29}H_{34}NO_2S_2$ [M^++H]: 492.2031; found: 492.2037.

(1*S*,2*S*,9*S*,10*S*)-11-Aza-10-isopropyl-8-methylene-4-oxa-2-phenyl-11-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.3.0.0^{3,7}]dodeca-3(7),5-diene (56b) (Table 2, entry 2): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (158 mg, 0.386 mmol) was converted into **56b** (56.3 mg, 31%) by use of 3-bromofuran. Colorless oil; $[\alpha]_D^{20} = +24.2$ (c = 1.04, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, J = 7.5 Hz, 6H; 2×CMe), 1.96–2.05 (m, 1H; Me_2CH), 2.27 (s, 3H; $PhCH_3$), 2.41–2.53 (m, 1H; 1-H), 2.51 (s, 6H; 2×$PhCH_3$), 2.51–2.74 (m, 1H; 9-H), 2.82 (dd, J = 12.5, 11.8 Hz, 1H; 12-C*H*H), 3.44 (dd, J = 11.8, 5.6 Hz, 1H; 12-CH*H*), 3.86 (d, J = 10.6 Hz, 1H; 2-H), 4.37 (dd, J = 8.1, 4.4 Hz, 1H; 10-H), 4.92 (s, 1H; C=C*H*H), 5.21 (s, 1H; C=CH*H*), 6.49 (d, J = 1.9 Hz, 1H; Ar), 6.87 (s, 2H; Ar), 7.04 (d, J = 8.1 Hz, 2H; Ar), 7.22–7.30 ppm (m, 4H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.2, 18.9, 20.9, 22.9 (2C), 33.0, 46.5, 49.4, 51.7, 52.4, 63.6, 105.1, 106.9, 122.8, 127.4, 127.7 (2C), 128.7 (2C), 131.9 (2C), 132.9, 138.5, 139.4, 140.2 (2C), 142.4, 142.9, 152.9 ppm; IR (KBr): $\tilde{\nu}$ = 1313 (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): m/z (%): 476 (96) [M^++H], 432 (100); HRMS (FAB): calcd for $C_{29}H_{34}NO_3S$ [M^++H]: 476.2259; found: 476.2253.

(10*S*,11*R*,14*S*,15*S*)-5,13-Diaza-14-isopropyl-5-methyl-16-methylene-10-phenyl-13-(2,4,6-trimethylphenylsulfonyl)tetracyclo[7.7.0.0^{2,6}.0^{11,15}]hexadeca-1(9),2(6),3,7-tetraene (56c) and its (10*S*,11*S*,14*S*,15*S*) isomer (57c) (Table 2, entry 3): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (150 mg, 0.366 mmol) was converted into **56c** (84.3 mg, 43%) and **57c** (12.2 mg, 6%) by use of 4-bromo-1-methylindole.

Compound ***56c***: Colorless powder; m.p. 223–225 °C; $[\alpha]_D^{20} = +65.3$ (c = 1.005, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, J = 6.9 Hz, 3H; CMe), 0.95 (d, J = 6.9 Hz, 3H; CMe), 2.03–2.08 (m, 1H; Me_2CH), 2.27 (s, 3H; $PhCH_3$), 2.37–2.46 (m, 1H; 11-H), 2.54 (s, 6H; 2×$PhCH_3$), 2.73 (dd, J = 11.8, 8.7 Hz, 1H; 15-H), 2.84 (dd, J = 11.8, 11.2 Hz, 1H; 12-C*H*H), 3.57 (dd, J = 11.8, 6.2 Hz, 1H; 12-CH*H*), 3.75 (s, 3H; CMe), 4.00 (d, J = 10.6 Hz, 1H; 10-H), 4.52 (dd, J = 8.7, 4.4 Hz, 1H; 14-H), 5.43 (s, 1H; C=C*H*H), 5.84 (s, 1H; C=CH*H*), 6.68 (d, J = 8.1 Hz, 1H; Ar), 6.83 (d, J = 3.1 Hz, 1H; Ar), 6.88 (s, 2H; Ar), 7.07–7.11 (m, 4H; Ar), 7.21–7.27 ppm (m, 3H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.8, 19.7, 20.9, 22.9 (2C), 32.3, 32.9, 48.8, 51.6, 53.5, 53.6, 63.5, 101.3, 108.6, 109.3, 123.7, 125.2, 126.6, 128.5 (2C), 128.6 (2C), 129.1, 130.0, 130.7, 131.9 (2C), 133.3, 135.8, 140.0 (2C), 142.2, 145.1, 145.4 ppm; IR (KBr): $\tilde{\nu}$ = 1311 (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): m/z (%): 539 (100) [M^++H]; HRMS (FAB): calcd for $C_{34}H_{39}N_2O_2S$ [M^++H]: 539.2732; found: 539.2744.

Compound ***57c***: Pale-yellow powder; m.p. 194–196 °C; $[\alpha]_D^{25} = -15.7$ (c = 0.735, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, J = 6.9 Hz, 3H; CMe), 0.95 (d, J = 6.9 Hz, 3H; CMe), 2.04–2.13 (m, 1H; Me_2CH), 2.23 (s,

3H; $PhCH_3$), 2.44 (s, 6H; $2\times PhCH_3$), 2.86–2.90 (m, 1H; 11-H), 3.12–3.22 (m, 2H; 12-C*H*H and 15-H), 3.44 (dd, $J=10.0$, 6.9 Hz, 1H; 12-CH*H*), 3.79 (s, 3H; NMe), 3.98–4.03 (m, 2H; 10-H and 14-H), 5.34 (s, 1H; C=C*H*H), 5.79 (s, 1H; C=CH*H*), 6.74 (s, 2H; Ar), 6.70–6.90 (m, 2H; Ar), 7.00–7.28 ppm (m, 7H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=16.5$, 19.8, 20.9, 23.1 (2C), 32.0, 32.9, 45.7, 45.8, 47.1, 53.3, 72.1, 101.3, 109.2, 114.7, 123.6, 125.2, 126.1, 127.2, 127.5, 128.3 (2C), 128.5 (2C), 129.0, 131.6 (2C), 134.0, 136.2, 139.5 (2C), 141.5, 144.5, 144.9 ppm; IR (KBr): $\tilde{\nu}=1317$ (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 539 (100) [M^++H]; HRMS (FAB): calcd for $C_{34}H_{39}N_2O_2S$ [M^++H]: 539.2732; found: 539.2744.

(10*S*,11*S*,14*S*,15*S*)-13-Aza-14-isopropyl-16-methylene-10-phenyl-8-thia-13-(2,4,6-trimethylphenylsulfonyl)tetracyclo[7.7.0.0^{2,7}.0^{11,15}]hexadeca-1(9),2(7),3,5-tetraene (56d) (Table 2, entry 4): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (150 mg, 0.366 mmol) was converted into **56d** (90.0 mg, 45%) by use of 3-bromobenzothiophene. Colorless powder; m.p. 201–202 °C; $[\alpha]_D^{25}=+75.8$ ($c=1.015$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.92$ (d, $J=6.9$ Hz, 3H; CMe), 0.97 (d, $J=7.5$ Hz, 3H; CMe), 2.03–2.10 (m, 1H; Me_2CH), 2.28 (s, 3H; $PhCH_3$), 2.56 (s, 6H; $2\times PhCH_3$), 2.62–2.73 (m, 1H; 11-H), 2.80–2.89 (m, 2H; 12-C*H*H and 15-H), 3.55 (dd, $J=11.8$, 5.6 Hz, 1H; 12-CH*H*), 4.05 (d, $J=10.6$ Hz, 1H; 10-H), 4.52 (dd, $J=8.1$, 4.4 Hz, 1H; 14-H), 5.38 (s, 1H; C=C*H*H), 5.77 (s, 1H; C=CH*H*), 6.90 (s, 2H; Ar), 7.17–7.22 (m, 2H; Ar), 7.28–7.33 (m, 4H; Ar), 7.38 (m, 1H; Ar), 7.68 (d, $J=8.1$ Hz, 1H; Ar), 8.10 ppm (d, $J=8.1$ Hz, 1H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=17.3$, 19.4, 20.9, 22.9 (2C), 32.6, 49.3, 49.8, 52.6, 53.2, 62.9, 107.6, 122.7, 122.9, 124.2, 124.5, 127.7, 127.9 (2C), 128.8 (2C), 131.9 (2C), 132.2, 133.0, 136.7, 140.1 (2C), 140.3, 140.9, 142.1, 142.5, 145.0 ppm; IR (KBr): $\tilde{\nu}=1313$ (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 542 (55) [M^++H], 136 (100); HRMS (FAB): calcd $C_{33}H_{36}NO_2S_2$ [M^++H]: 542.2187; found: 542.2205.

(2*S*,3*R*,6*S*,7*S*)-5,10-Diaza-6-isopropyl-8-methylene-2-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (56e) and (2*S*,3*S*)-4-[(*Z*)-benzylidene]-2-isopropyl-3-[1-(2-pyridyl)vinyl]-1-(2,4,6-trimethylphenylsulfonyl)pyrrolidine (59) (Table 2, entry 5): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (100 mg, 0.244 mmol) was converted into **56e** (57.8 mg, 49%) and **59** (12.5 mg, 11%) by use of 2-iodopyridine.

Compound ***56e***: Colorless oil; $[\alpha]_D^{26}=+41.7$ ($c=1.04$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.91$ (d, $J=6.9$ Hz, 3H; CMe), 0.94 (d, $J=7.5$ Hz, 3H; CMe), 2.00–2.07 (m, 1H; Me_2CH), 2.27 (s, 3H; $PhCH_3$), 2.40–2.54 (m, 1H; 3-H), 2.54 (s, 6H; $2\times PhCH_3$), 2.60 (m, 1H; 7-H), 2.77 (dd, $J=11.8$, 11.8 Hz, 1H; 4-C*H*H), 3.46 (dd, $J=11.8$, 5.6 Hz, 1H; 4-CH*H*), 3.88 (d, $J=11.2$ Hz, 1H; 2-H), 4.46 (dd, $J=8.1$, 4.5 Hz, 1H; 6-H), 5.29 (s, 1H; C=C*H*H), 6.34 (s, 1H; C=CH*H*), 6.89 (s, 2H; Ar), 7.01–7.10 (m, 4H; Ar), 7.12–7.31 (m, 3H; Ar), 8.46 ppm (d, $J=3.7$ Hz, 1H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=17.5$, 19.3, 20.9, 22.9 (2C), 32.6, 48.2, 50.1, 50.6, 52.8, 64.6, 110.6, 122.7, 127.3, 128.4 (2C), 128.9 (2C), 131.9 (2C), 132.9, 134.6, 137.7, 140.1 (2C), 142.4, 142.5, 144.5, 147.7, 153.1 ppm; IR (KBr): $\tilde{\nu}=1315$ (SO_2N), 1153 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 487 (100) [M^++H]; HRMS (FAB): calcd for $C_{30}H_{35}N_2O_2S$ [M^++H]: 487.2419; found: 487.2407.

Compound ***59***: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.67$ (d, $J=7.5$ Hz, 3H; CMe), 0.79 (d, $J=6.9$ Hz, 3H; CMe), 1.71–1.85 (m, 1H; Me_2CH), 2.29 (s, 3H; CMe), 2.54 (s, 6H; $2\times$CMe), 3.59 (d, $J=4.5$ Hz, 1H; 2-H), 4.30 (d, $J=15.0$ Hz, 1H; 5-C*H*H), 4.43 (s, 1H; 3-H), 4.64 (d, $J=15.0$ Hz, 1H; 5-CH*H*), 5.28 (s, 1H; C=C*H*H), 5.56 (s, 1H; C=CH*H*), 6.52 (s, 1H; C=C*H*Ph), 6.90 (s, 2H; Ar), 6.93 (m, 1H; Ar), 7.17–7.27 (m, 3H; Ar), 7.37 (m, 2H; Ar), 7.49 (d, $J=8.1$ Hz, 1H; Ar), 7.65 (t, $J=6.5$ Hz, 1H; Ar), 8.57 ppm (d, $J=3.0$ Hz, 1H; Ar).

(3*S*,4*S*,7*S*,8*S*)-5,10,13-Triaza-4-isopropyl-2-methylene-8-phenyl-5-(2,4,6-trimethylphenylsulfonyl)tricyclo[7.4.0.0^{3,7}]trideca-1(9),10,12-triene (56f) (Table 2, entry 6): By using a procedure similar to that described for the synthesis of **20a** and **21a**, allenene **10a** (150 mg, 0.366 mmol) was converted into **56f** (110 mg, 62%) by use of iodopyrazine. Colorless oil; $[\alpha]_D^{24}=+85.3$ ($c=1.035$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.94$ (d, $J=6.9$ Hz, 3H; CMe), 0.95 (d, $J=6.9$ Hz, 3H; CMe), 2.03–2.10 (m, 1H; Me_2CH), 2.28 (s, 3H; $PhCH_3$), 2.54 (s, 6H; $2\times PhCH_3$), 2.50–2.58 (m, 1H; 7-H), 2.70–2.78 (m, 1H; 3-H), 2.81 (dd, $J=11.8$, 11.8 Hz, 1H; 6-C*H*H), 3.48 (dd, $J=11.8$, 5.6 Hz, 1H; 6-CH*H*), 4.06 (d, $J=11.2$ Hz, 1H; 8-H), 4.48 (dd, $J=8.1$, 4.4 Hz, 1H; 4-H), 5.39 (d, $J=1.9$ Hz, 1H; C=C*H*H), 6.39 (d, $J=1.9$ Hz, 1H; C=CH*H*), 6.89 (s, 2H; Ar), 7.01 (d, $J=8.1$ Hz, 2H; Ar), 7.24–7.30 (m, 3H; Ar), 8.38 (d, $J=1.9$ Hz, 1H; Ar), 8.40 ppm (d, $J=1.9$ Hz, 1H; Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=17.6$, 19.3, 20.9, 22.8 (2C), 32.7, 47.7, 50.2, 52.7 (2C), 64.3, 112.4, 127.2, 128.4 (2C), 128.8 (2C), 131.9 (2C), 132.7, 140.2 (2C), 141.7, 142.2, 142.6, 142.8, 143.6, 148.9, 153.6 ppm; IR (KBr): $\tilde{\nu}=1315$ (SO_2N), 1151 cm^{-1} (SO_2N); MS (FAB): *m*/*z* (%): 488 (41) [M^++H], 307 (100); HRMS (FAB): calcd for $C_{29}H_{34}N_3O_2S$ [M^++H]: 488.2372; found: 488.2353.

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[21] As separation of **12b** and **13b** was extremely difficult, an almost 1:1 diastereomixture of **12b** and **13b** was used directly for the palladium-catalyzed cyclization without further purification. Other diastereomixtures (**12a**/**13a** and **12c**/**13c**) were readily separated by flash column chromatography.

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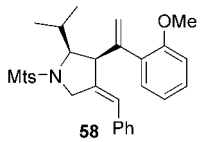
[23] Although the *syn*-β elimination generally predominates, a base-induced *anti* elimination by an E2 mechanism can occur in limited cases. See, for examples: a) J. M. Takacs, E. C. Lawson, F. Clement, *J. Am. Chem. Soc.* **1997**, *119*, 5956–5957; b) I. Schwarz, M. Braun, *Chem. Eur. J.* **1999**, *5*, 2300–2305, and references therein.

[24] The reaction with iodobenzene bearing an electron-withdrawing substitutent has not been examined, because, in our previous study of pyrrolidine formation, the reaction with 1-iodo-4-nitrobenzene afforded a lower yield of the corresponding pyrrolidine (36%).[16b]

[25] For example, in the reaction of allenene **10a** with 2-iodoanisole (Table 1, entry 5), 14% of the β-elimination product **58** was isolated. In other cases, the yields of this type of elimination product were lower (<5%) and isolation of these compounds was difficult.



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[26] For related stereomutations of the palladium(II) intermediate in the carbopalladation onto an aryl ring, see: a) R. Grigg, V. Sridharan, P. Stevenson, S. Sukirthalingam, T. Worakun, *Tetrahedron* **1990**, *46*, 4003–4018; b) M. S. McClure, B. Glover, E. McSorley, A. Millar, M. H. Osterhout, F. Roschangar, *Org. Lett.* **2001**, *3*, 1677–1680.

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