DOI: 10.1002/ejoc.200601119

An Improved Ring-Closing Metathesis Approach to Fluorinated and Trifluoromethylated Nitrogen Heterocycles

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Keywords: Ring-closing metathesis / Fluorinated heterocycles / Trifluoromethylated heterocycles / Sulfonamides / Trifluoromethylated pyrrole

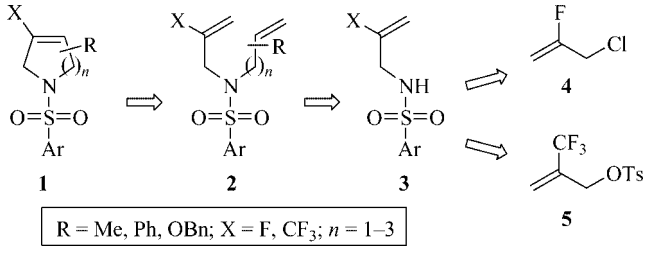
The synthesis of fluoro- and trifluoromethyl-containing *N*-sulfonylated nitrogen heterocycles is described. A first crucial step is a Mitsunobu functionalization of intermediate sulfonamides using commercially available unsaturated alcohols, which gives efficient access to fluorinated ring-closing metathesis (RCM) precursors. Key step is an RCM reaction of these precursors leading to the corresponding fluoro- and trifluoromethyl-containing heterocyclic building blocks. Furthermore, aminopalladation of the same sulfonamide intermediates provides access to trifuoromethyl-containing pyrrole derivatives.

Introduction

There is a strongly increasing interest in fluorine-containing biologically active compounds for potential application as agrochemicals and pharmaceuticals.[1] This is due to the fact that incorporation of fluorine or fluorine-containing groups such as trifluoromethyl in organic molecules often leads to improved pharmacological properties of the parent compound.[2,3] Consequently, in the last few years much research has been aimed at developing general methodology for the straightforward introduction of fluorine or trifluoromethyl substituents in non-aromatic heterocyclic systems.[4]

In developing such general methods, one strategy is application of proven ring-closure methodology to appropriate fluorine-containing precursor molecules. This is exemplified by work of the Brown group who successfully applied ring-closing metathesis (RCM) on vinyl fluoride-containing substrates to prepare fluorinated analogues of seven-membered heterocyclic HIV protease inhibitors,[5] and related work from the Haufe group.[6] At the same time, we were developing a similar RCM approach to prepare small libraries of fluorinated[7] and trifluoromethylated[8] nitrogen heterocycles, including the development of a route to a new trifluoromethyl-containing allylating reagent.[9]

Inspired by these successful approaches, we aimed to extend this methodology to a complementary pathway, which is retrosynthetically outlined in Scheme 1. The targeted sulfonylated heterocycles **1** are accessible through RCM from the precursors **2**, which are now envisaged to be prepared in a different way from the alkylating agents **4** and **5** in a Mitsunobu process. While Mitsunobu reactions are normally restricted to aromatic sulfonamides containing electron-withdrawing nitro substituents, we hoped that the strongly electron-withdrawing fluorine substituents would be beneficial in making this process possible for a wider range of (biologically relevant) sulfonyl groups.



Scheme 1. Retrosynthetic approach to fluorinated and trifluoromethylated nitrogen heterocycles.

Besides the fact that this will lead to a general process that can be applied on both olefins **4** and **5**, the Mitsunobu reaction will allow for use of commercially available unsaturated alcohols as reaction partners, whereas previous alkylation strategies had to rely on less well accessible olefinic halides. Furthermore, the sulfonamides **3** can be subjected to aminopalladation with alkoxyallenes, a reaction that has been developed in our group,[10] which will give access to an even greater variety of fluorinated heterocycles.

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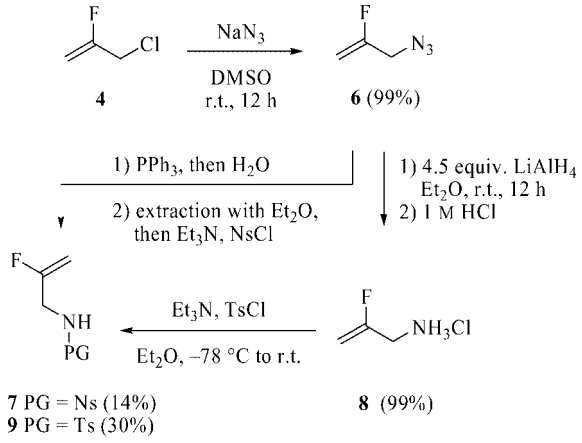
Results and Discussion

The investigation started with exploring the possibility of transforming the commercially available fluoride **4** in a nucleophilic amine that may then provide the sulfonamides **7** and **9** (Scheme 2). Compound **4** was reacted at room temp. with sodium azide in DMSO for 12 h. Initially, the reaction was performed in deuterated DMSO to monitor the conversion by ^{1}H NMR, which indicated that the reaction was complete in 12 h giving rise to azide **6** as a single product. Initial attempts to reduce the azide via Staudinger reduction with triphenylphosphane, followed by sulfonylation provided low yields (<30%) of the corresponding sulfonamides (exemplified for **7**), both on small and on larger scale.



Scheme 2. Synthesis of vinyl fluoride-containing sulfonamides.

In a modified pathway, azide **6** was first extracted into diethyl ether, dried ($MgSO_4$), filtered and then directly treated with 4.5 equiv. of $LiAlH_4$. Precipitation of the aluminum salts via sodium sulfate treatment, followed by filtration and extraction with 1 M aqueous HCl provided upon freeze-drying amine **8** as its hydrochloride. The salt was suspended in diethyl ether, treated with excess triethylamine and tosyl chloride at –78 °C, stirred for 12 h at room temp. and worked up to provide sulfonamide **9**. Although this procedure could be readily scaled up to larger quantities, the last step reproducibly proceeded in a rather modest 30% yield (Scheme 2). However, the procedure still compares favorably to a known procedure in which **4** is heated in ammonia in a steel bomb to provide **9** in 30%.[11]

Having sulfonamides **7** and **9** in hand, the feasibility of the Mitsunobu approach was probed. To this end, the required RCM precursors **11–20** were either prepared via a regular alkylation reaction (method A, entries 1, 4 and 5) or via Mitsunobu conditions (method B, entries 2, 3 and 6–10). Method A involved addition of sulfonamide **8** to a suspension of NaH in DMF and subsequent treatment with the bromide followed by stirring for 12 h. Method B comprised the successive treatment of a solution of sulfonamide **8** in toluene with triphenylphosphane, the appropriate alcohol and diethyl azodicarboxylate (DEAD). The mixture was then heated at 50 °C for 12 h and worked up. Although most of the yields were fairly good, it was obvious that the Mitsunobu sequence worked more reliably in case of non-activated substrates (e.g. compare the low alkylation yield in entries 4 and 5 with the good Mitsunobu yields in entries 2, 3 and 6–10). Hence we concluded that the Mitsunobu approach allows the use of commercially available unsaturated alcohols to prepare a variety of RCM precursors in a straightforward manner.

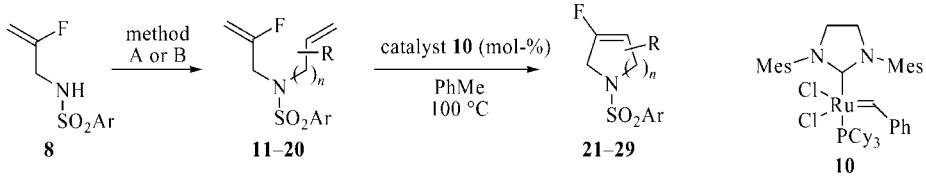
Precursor molecules **11–20** were then subjected to the RCM reaction. The second-generation Grubbs catalyst **10** was added portionwise over a period of 2 h to the reaction mixture, which was heated in toluene at 100 °C. Most of these precursors led to the corresponding fluoro-substituted cyclic building blocks in good to excellent yields (Table 1). There are some exceptions, however. Compound **11**, whichs lacks a substituent adjacent to the nitrogen atom, does not give any cyclization product, even on prolonged heating and larger amounts of catalyst (entry 1). Introduction of a methyl substituent at the 2-position (**12**) surprisingly led to the five-membered ring **22** in 72% yield, using similar conditions (entry 2). To further investigate the influence of a substituent in this position, precursor **13** containing a phenyl group was synthesized, but unfortunately did not provide any cyclized product (entry 3). These results suggest that there is an optimum in the size of the 2-substituent with respect to cyclization. We then moved on to prepare six-and seven-membered ring building blocks as shown in entries 4–7. These cyclizations proceeded readily in good yields ranging from 72 to 97% to provide rings **24–27**, although in case of **27** a larger amount of catalyst was required. Remarkably, subjection of compound **18** to the metathesis conditions did not provide the eight-membered ring, but instead gave the corresponding seven-membered ring system (entry 8). This must be due to isomerization of the terminal olefin to the internal position, possibly as a result of a relatively slow cyclization process, followed by ring closure and expulsion of propene.[12,13]

We have also investigated the possibility of forming larger rings via this process. Precursors **19** and **20** were conveniently prepared via the newly developed Mitsunobu sequence in 78 and 99%, respectively. Exposure of **19** to the RCM catalyst led to a complex mixture of unidentifiable products rather than the desired twelve-membered ring **28**. Moreover, all attempts to form a thirteen-membered vinyl fluoride ring (**29**) from precursor **20** failed.

Prompted by the successful Mitsunobu reaction and subsequent RCM results, we aimed to apply this protocol in a similar fashion on our previously developed trifluoromethyl-containing allylating reagent **5**.[8,9] (Scheme 3).

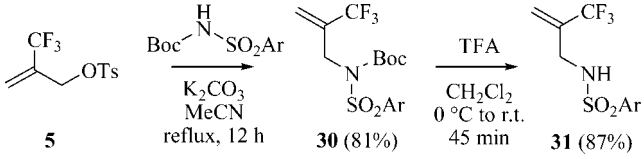
The sequence proceeded via initial alkylation of *tert*-butyl tosylcarbamate[14] with tosylate **5**[8] in refluxing acetonitrile, followed by TFA-mediated liberation of sulfonamide **31** in good overall yield. Compound **31** was alkylated under Mitsunobu conditions (triphenylphosphane, diethyl azodicarboxylate, toluene, 50 °C) with several unsaturated alcohols in generally good yields to provide the RCM precursors **32–35**, which in turn, were subjected to the aforementioned RCM conditions (Table 2).

Table 1. Synthesis of fluoride-containing RCM precursors and products.[a]



Entry	Reagent/method	Precursor	cat (mol-%)	Time (h)	Product (yield)	Entry	Reagent/method	Precursor	cat (mol-%)	Time (h)	Product (yield)
1	A	**11** (54%)	25	10	**21** (0%)	5	A	**15** (19%)	5	1	**25** (80%)
2	B	**12** (79%)	20	3	**22** (72%)	6	B	**16** (68%)	5	1	**26** (94%)
3	B	**13** (33%)	25	4	**23** (0%)	7	B	**17** (60%)	20	3	**27** (72%)
4	A	**14** (60%)	5	1	**24** (97%)	8	$n = 4$ B	$n = 4$ **18** (77%)	10	2	$n = 3$ **25** (41%)
						9	$n = 8$ B	$n = 8$ **19** (78%)	40	48	$n = 8$ **28** (0%)
						10	$n = 9$ B	$n = 9$ **20** (99%)	15	3	$n = 9$ **29** (0%)

[a] *Conditions:* Method A: (i) NaH, DMF, then add sulfonamide **8**, 15 min, room temp., (ii) alkylating agent, 12 h room temp. Method B: PPh_3, alcohol, DEAD, 50 °C, 12 h.

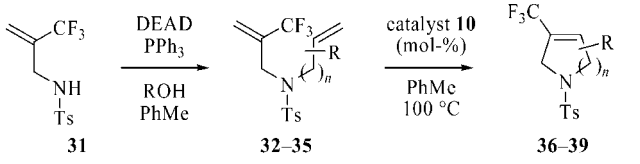


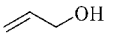
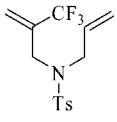
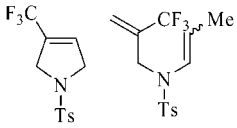
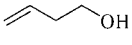
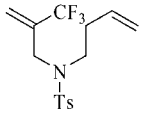
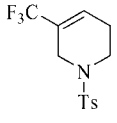
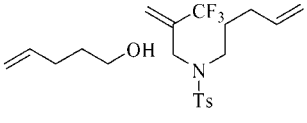
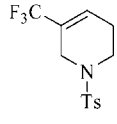
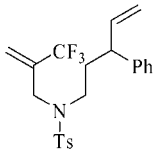
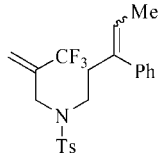
Scheme 3. Synthesis of trifluoromethyl-containing sulfonamides.

Starting from **32**, pyrroline **36** was obtained in 57% together with the isomerized product **37** (23%, entry 1). This sharply contrasts with the fluoride-containing precursor **11**, which failed to cyclize under identical conditions. The homologous six-membered ring **38** was also readily formed in one hour from precursor **33** in 98% yield. Precursors **34** and **35**, however, behaved in a different manner. In both cases, isomerization took place, which was either followed by cyclization to the corresponding six-membered ring **38** in 65% yield (entry 3), or led to the stable product **39** (entry 4). In the latter case, we hoped that the phenyl substituent would suppress the isomerization process, but instead a good yield of the isomerized linear product was obtained.

Comparison of Table 1 and Table 2 clearly shows that the fluoro and trifluoromethyl substituents play an important role in the RCM process. The fluorinated precursors readily afford six- and seven-membered ring products without any isomerization. The trifluoromethylated precursors on the other hand suffered from isomerization processes, which were only absent using the six-membered ring precursors. Recently, the Grubbs group reported that addition of benzoquinone could efficiently suppress undesired isomerization processes.[15] We also applied these conditions to precursors **34** and **35** to see if this would be beneficial for our RCM processes. In case of precursor **34** (20 mol-% of catalyst **10**, 0.4 equiv. of benzoquinone, toluene, 100 °C) the

Table 2. Synthesis of CF_3-containing RCM precursors and products.

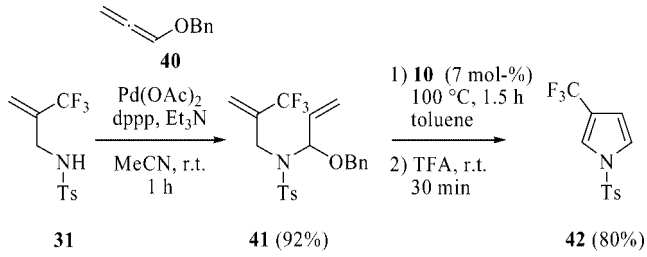


Entry	Reagent	Precursor	cat (mol-%)	Time (min)	Product (yield)
1		 **32** (99%)	5	45	 **36** (57%) **37** (23%)
2		 **33** (64%)	5	60	 **38** (98%)
3	 **34** (60%)	7	90	 **38** (65%)	
4		 **35** (74%)	10	120	 **39** (68%)

isomerization was partially suppressed. GC-MS analysis revealed the presence of the seven-membered ring product, together with the isomerized precursor and the six-membered ring **38** in a ratio of 1.3:1.1:1, respectively. In contrast, precursor **35** was reacted under identical conditions, but solely provided the isomerized product **39**, which led us to conclude that benzoquinone addition in these particular cases is not very useful.

Another interesting application of sulfonamide **31** lies in the synthesis of trifluoromethylated pyrrole derivatives. These compounds represent an industrially relevant compound class, which is poorly accessible via published methods.[16] Inspired by recent work by Donohue et al.,[17] we decided to use our recently developed aminopalladation involving alkoxyallenes[10] to open up new entries to such compounds (Scheme 4).

Thus, benzyloxyallene **40**[18] was treated with sulfonamide **31** in the presence of Et_3N, catalytic $Pd(OAc)_2$ and dppp in acetonitrile to provide N,O-acetal **41** in excellent yield. The RCM precursor **41** was subjected to the previously described RCM conditions using 7 mol-% of catalyst **10** in toluene at 100 °C. Once TLC indicated that the conversion was complete, TFA was added and after stirring for 30 min the mixture was worked up. Concentration and



Scheme 4. Synthesis of a trifluoromethyl-substituted pyrrole.

chromatography then provided pyrrole **42** in 80% yield. This example clearly shows that the aminopalladation pathway provides an efficient and straightforward entry into the synthesis of trifluoromethylated pyrroles that may be further exploited in a general sense.

Conclusions

In conclusion, we have shown that sulfonylated fluoro- and trifluoromethyl-containing RCM precursors can be readily synthesized via a Mitsunobu reaction applied on the corresponding fluorinated sulfonamides involving suitable olefins. The first class of compounds was obtained from commercially available 3-chloro-2-fluoropropene, whereas for the second compound class a trifluoromethyl-containing allylating reagent – previously developed in our group – served as the starting material. We also demonstrated that RCM on these olefins led to fluoro- and trifluoromethyl-containing five-, six- and seven-membered ring heterocyclic building blocks. Furthermore, a straightforward synthetic pathway to prepare trifluoromethylated pyrrole derivatives has been developed.

Experimental Section

General Information: All reactions were carried out under an inert atmosphere of dry nitrogen. Solvents were distilled from the appropriate drying agents immediately prior to use. Infrared (IR) spectra were recorded on an ATI Mattson Genesis Series FTIR spectrometer and absorptions are reported in cm^{-1}. NMR spectra were recorded at 298 K using a Bruker DMX300 (300 MHz) spectrometer from $CDCl_3$ solutions using TMS as internal standard unless otherwise reported. Mass spectra and accurate mass measurements were carried out using a Fisons (VG) Micromass 7070E or a Finnigan MAT900S instrument. Melting points were determined with a Büchi melting point B-545 apparatus.

***N*-(2-Fluoroallyl)-4-nitrobenzenesulfonamide (7):** To a solution of **4** (252 mg, 2.68 mmol) in DMSO (24 mL) NaN_3 (720 mg, 11.3 mmol) was added and the resulting mixture was vigorously stirred for 12 h at room temp. To the gelly mixture containing **6** was added PPh_3 (992 mg, 3.78 mmol) and the solution was stirred for 12 h at room temp. The reaction was slowly quenched with water (24 mL) and extracted with Et_2O (5 × 20 mL). The ether layer was dried ($MgSO_4$), filtered and directly treated with Et_3N (0.60 mL, 3.78 mmol). After stirring for 15 min at room temp., the mixture was cooled to –78 °C, NsCl (838 mg, 3.78 mmol) was added and the mixture was stirred for 12 h thereby slowly reaching

room temp. The solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 10:1 to 3:1) to give **7** (100 mg, 14%) as a yellow solid. **7**: IR (neat): $\tilde{\nu}$ = 3291, 3105, 2924, 2867, 1688, 1528, 1437, 1346, 1156, 1091, 849, 737 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 9.0 Hz, 2 H, Ar), 8.04 (d, J = 9.0 Hz, 2 H, Ar), 5.28 (br. t, J = 6.0 Hz, 1 H, N*H*), 4.57 (dd, J = 3.3, 28.5 Hz, 1 H CH_{2cis}=C*F*), 4.47 (dd, J = 3.6, 60.1 Hz, 1 H, CH_{2trans}=C*F*), 3.86–3.79 (m, 2 H, CFCH_2NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7 (d, J = 256.2 Hz, *C*F), 150.0, 145.8, 128.3, 124.3, 93.7 (d, J = 17.2 Hz, *C*=CF), 43.8 (d, J = 32.2 Hz, *C*H_2CF) ppm. HRMS (EI): calcd. for $C_9H_9FN_2O_4S$ (M^+) 260.0267, found 260.0274.

***N*-(2-Fluoroallyl)-4-methylbenzenesulfonamide (9):** To a solution of **4** (252 mg, 2.68 mmol) in DMSO (24 mL) NaN_3 (720 mg, 11.34 mmol) was added and the resulting mixture was vigorously stirred for 12 h at room temp. It was diluted with water (10 mL), extracted with Et_2O (3× 20 mL), dried ($MgSO_4$) and filtered. The filtrate was carefully treated with $LiAlH_4$ (458 mg, 12.1 mmol) at room temp., after which a strong evolution of gas started. The reaction mixture was stirred overnight, a few drops of EtOAc were added, followed by aqueous saturated Na_2SO_4 (a few drops) and solid Na_2SO_4. After stirring for a few minutes, the resulting suspension was filtered and the filtrate was extracted with 1 M HCl (3× 20 mL). The aqueous layer was freeze-dried to give **8** (297 mg, 99%) in crude form, which was used for the next step without further purification. IR (neat): $\tilde{\nu}$ = 2876, 2625, 1692, 1593, 1502, 1403, 1251, 1100, 927, 879 cm^{-1}. ^{1}H NMR (300 MHz, D_2O): δ = 5.0 (dd, J = 4.2, 16.8 Hz, 1 H, CH_{2cis}=C*F*), 4.87 (dd, J = 3.9, 49 Hz, 1 H, CH_{2trans}=C*F*), 3.8 (d, J = 16.2 Hz, 2 H, CFCH_2N) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 157.8 (d, J = 252.5 Hz, *C*F), 97.4 (d, J = 15.8 Hz, *C*=CF), 39.9 (d, J = 31.3 Hz, *C*H_2CF) ppm. Crude **8** was suspended in Et_2O (10 mL), treated with Et_3N (0.6 mL, 3.78 mmol) for 15 min at room temp., followed by addition of TsCl (721 mg, 3.78 mmol) at –78 °C and stirring for 12 h thereby allowing the mixture to warm up to room temp. The solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 10:1 to 6:1) to give **9** (185 mg, 30%) as a white solid. **9**: M.p. 89–90 °C. IR (neat): $\tilde{\nu}$ = 3279, 2927, 2852, 1680, 1593, 1428, 1320, 1154, 1092, 856, 806, 707, 661 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.4 Hz, 2 H, Ar), 7.27 (d, J = 8.1 Hz, 2 H, Ar), 5.31 (br. s, 1 H, N*H*), 4.56 (dd, J = 3.6, 33.6 Hz, 1 H, CH_{2cis}=C*F*), 4.46 (dd, J = 3.3, 64.8 Hz, 1 H, CH_{2trans}=C*F*), 3.70–3.64 (m, 2 H, CFCH_2NH), 2.41 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.5 (d, J = 255.3 Hz, *C*F), 143.6, 136.6, 129.6, 127.9, 92.6 (d, J = 16.9 Hz, *C*=CF), 43.4 (d, J = 33.9 Hz, *C*H_2CF), 21.8 ppm. HRMS (EI): calcd. for $C_{10}H_{12}FNO_2S$ (M^+) 229.0573, found 229.0580.

***N*-Allyl-*N*-(2-fluoroallyl)-4-methylbenzenesulfonamide (11):** A suspension of NaH (25 mg, 1.05 mmol) in DMF (6 mL) was treated with compound **9** (162 mg, 0.70 mmol). After stirring for 30 min, 3-bromopropene (73 μL, 0.84 mmol) was added dropwise at room temp. The reaction was stirred for 12 h, quenched with water (6 mL) and extracted with Et_2O (3 × 6 mL). The ether layers were dried ($MgSO_4$), evaporated and the residue was purified using column chromatography (heptane/EtOAc, 10:1 to 6:1) to give **11** (152 mg, 54%) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3071, 3015, 2954, 2920, 1679, 1597, 1346, 1161, 1096, 927, 798, 659 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.1 Hz, 2 H, Ar), 7.27 (d, J = 7.8 Hz, 2 H, Ar), 5.68–5.55 (m, 1 H, CH_2=C*H*), 5.19–5.13 (m, 2 H, CH_2=CH), 4.61 (dd, J = 3.0, 51.7 Hz, 1 H, CH_{2cis}=C*F*), 4.51 (dd, J = 3.0, 82.9 Hz, 1 H, CH_{2trans}=C*F*), 3.91 (d, J = 13.5 Hz, 2 H, CFCH_2N), 3.83 (d, J = 6.3 Hz, 2 H, NCH_2CH), 2.41 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.3 (d, J = 258.5 Hz, *C*F), 143.3, 136.9, 132.0, 129.5, 127.1, 119.6, 93.9 (d, J = 17.2 Hz, *C*=CF), 49.9, 46.4 (d, J = 31.9 Hz, *C*H_2CF), 21.7 ppm. HRMS (EI): calcd. for $C_{13}H_{16}FNO_2S$ (M^+) 269.0886, found 269.0895.

***N*-(2-Fluoroallyl)-4-methyl-*N*-(1-methylallyl)benzenesulfonamide (12):**[19] To a solution of compound **9** (100 mg, 0.38 mmol) in toluene (5 mL) were added PPh_3 (202 mg, 0.77 mmol), 3-buten-2-ol (40 μL, 0.46 mmol) and diethyl azodicarboxylate (80 μL, 0.61 mmol). The mixture was heated at 50 °C for 12 h, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **12** (86 mg, 79%) as a pink oil. **12**: IR (neat): $\tilde{\nu}$ = 3088, 3023, 2980, 2924, 1675, 1593, 1338, 1152, 1092, 1014, 901, 845, 815, 659, 547 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, J = 8.1 Hz, 2 H, Ar), 7.27 (d, J = 8.1 Hz, 2 H, Ar), 5.68–5.57 (m, 1 H, CH_2=C*H*), 5.14–5.5 (m, 2 H, CH_2=CH), 4.71–4.48 (m, 3 H, NC*H*CH_3, CH_2=C*F*), 3.89 (dd, J = 11.7, 16.8 Hz, 1 H, CFCH_2N), 3.73 (dd, J = 11.7, 16.8 Hz, 1 H, CFCH_2N), 2.42 (s, 3 H, ArCH_3), 1.25 (d, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.1 (d, J = 257.6 Hz, *C*F), 143.3, 136.9, 129.5, 127.13, 127.12, 117.3, 93.0 (d, J = 17.5 Hz, *C*=CF), 55.13, 43.5 (d, J = 34.5 Hz, *C*H_2CF), 21.8, 17.5 ppm. HRMS (EI): calcd. for $C_{14}H_{18}FNO_2S$ (M^+) 283.1042, found 283.1034.

***N*-(2-Fluoroallyl)-4-methyl-*N*-(1-phenylallyl)benzenesulfonamide (13):** To a solution of compound **9** (158 mg, 0.60 mmol) in toluene (8 mL) were added PPh_3 (315 mg, 1.20 mmol), vinyl benzyl alcohol (95 μL, 0.72 mmol) and diethyl azodicarboxylate (0.13 mL, 0.96 mmol). The mixture was heated at 50 °C for 12 h, the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **13** (68 mg, 33%) as a colorless oil. **13**: IR (neat): $\tilde{\nu}$ = 3019, 2963, 2920, 2868, 1679, 1593, 1493, 1446, 1342, 1260, 1156, 1096, 1018, 914, 811, 741, 664, 616, 543 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.1 Hz, 2 H, SO_2Ar), 7.30–7.20 (m, 7 H, 2H SO_2Ar, 5H Ph), 6.45 (d, J = 15.9 Hz, 1 H, CH_2=CH); 6.02–5.92 (m, 1 H, CH_2=C*H*), 4.65 (dd, J = 3.0, 53.1 Hz, 1 H, CH_{2cis}=C*F*), 4.55 (dd, J = 3.0, 84.7 Hz, 1 H, CH_{2trans}=C*F*), 4.00–3.95 (m, 4 H, 1H CH_2=CH, CFCH_2N, NC*H*Ph), 2.42 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7 (d, J = 259.9 Hz, *C*F), 143.6, 137.2, 136.1, 134.8, 129.8, 128.7, 128.2, 127.4, 126.6, 123.3, 94.1 (d, J = 17.2 Hz, *C*=CF), 49.5, 46.5 (d, J = 31.9 Hz, *C*H_2CF), 21.6 ppm. HRMS (EI): calcd. for $C_{19}H_{20}FNO_2S$ (M^+) 345.1199, found 345.1210.

***N*-(But-3-enyl)-*N*-(2-fluoroallyl)-4-nitrobenzenesulfonamide (14):** A suspension of NaH (13 mg, 0.52 mmol) in DMF (4 mL) was treated with compound **9** (90 mg, 0.35 mmol). After stirring for 30 min, 4-bromo-1-butene (42 μL, 0.42 mmol) was added dropwise at room temp. The reaction was stirred for 12 h, quenched with water (4 mL) and extracted with Et_2O (3 × 4 mL). The ether layers were dried ($MgSO_4$), evaporated and the residue was purified using column chromatography (heptane/EtOAc, 10:1 to 6:1) to give **14** (65 mg, 60%) as a white solid. **14**: M.p. 77–79 °C. IR (neat): $\tilde{\nu}$ = 3110, 3071, 2928, 2868, 1718, 1679, 1528, 1346, 1165, 1091, 923, 858 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (d, J = 9.0 Hz, 2 H, Ar), 7.98 (d, J = 8.7 Hz, 2 H, Ar), 5.76–5.63 (m, 1 H, CH_2=C*H*), 5.11–5.04 (m, 2 H, CH_2=CH), 4.66 (dd, J = 3.6, 44.1 Hz, 1 H, CH_{2cis}=C*F*), 4.56 (dd, J = 3.6, 75.4 Hz, 1 H, CH_{2trans}=C*F*), 4.05 (d, J = 15.9 Hz, 2 H, CFCH_2N), 3.30 (t, J = 7.5 Hz, 2 H, NC$H_2$$CH_2$), 2.39–2.32 (m, 2 H, NC$H_2CH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5 (d, J = 259.0 Hz, *C*F), 149.8, 145.6, 133.7, 128.4, 124.1, 117.7, 95.2 (d, J = 17.2 Hz, *C*=CF), 47.7 (d, J = 30.2 Hz, *C*H_2CF), 46.9, 32.9 ppm. HRMS (EI): calcd. for $C_{13}H_{15}FN_2O_4S$ (M^+) 314.0737, found 314.0733.

***N*-(2-Fluoroallyl)-4-methyl-*N*-(pent-4-enyl)benzenesulfonamide (15):** A suspension of NaH (33 mg, 1.38 mmol) in DMF (10 mL) was treated with compound **9** (210 mg, 0.92 mmol). After stirring for 30 min, 5-bromo-1-pentene (0.13 mL, 1.10 mmol) was added dropwise at room temp. The reaction was stirred for 12 h, quenched with water (10 mL) and extracted with Et_2O (3 × 10 mL). The ether layers were dried ($MgSO_4$), evaporated and the residue was purified using column chromatography (heptane/EtOAc, 10:1 to 6:1) to give **15** (53 mg, 19%) as a yellow oil. **15**: IR (neat): $\tilde{\nu}$ = 3075, 2963, 2924, 2863, 1679, 1597, 1442, 1342, 1156, 1087, 914, 811 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.4 Hz, 2 H, Ar), 7.28 (d, J = 8.7 Hz, 2 H, Ar), 5.80–5.66 (m, 1 H, CH_2=C*H*), 5.02–4.93 (m, 2 H, CH_2=CH), 4.63 (dd, J = 3.3, 44.1 Hz, 1 H, CH_{2cis}=C*F*), 4.53 (dd, J = 3.3, 75.7 Hz, 1 H, CH_{2trans}=C*F*), 3.91 (d, J = 13.8 Hz, 2 H, CFCH_2N), 3.16 (t, J = 7.5 Hz, 2 H, NCH_2CH_2), 2.41 (s, 3 H, CH_3), 2.06–1.99 (m, 2 H, NCH$_2$CH$_2$CH_2), 1.70–1.60 (m, 2 H, NCH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7 (d, J = 258.8 Hz, *C*F), 143.2, 137.2, 136.7, 129.5, 127.2, 115.3, 94.0 (d, J = 17.2 Hz, *C*=CF), 47.8 (d, J = 31.9 Hz, *C*H$_2$CF), 47.6, 30.9, 27.5, 21.8 ppm. HRMS (EI): calcd. for $C_{15}H_{20}FNO_2S$ (M^+) 297.1199, found 297.1203.

***N*-(2-Fluoroallyl)-4-methyl-*N*-(3-methylpent-4-enyl)benzenesulfonamide (16):** To a solution of compound **9** (90 mg, 0.40 mmol) in toluene (4 mL) were added PPh_3 (210 mg, 0.80 mmol), 3-methyl-4-pentenol (48 mg, 0.48 mmol) and diethyl azodicarboxylate (0.12 mL, 0.64 mmol). The mixture was heated at 50 °C for 12 h, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **16** (85 mg, 68%) as a colorless oil. **16**: IR (neat): $\tilde{\nu}$ = 3075, 2958, 2928, 2863, 1679, 1593, 1450, 1346, 1156, 1091, 923, 849, 815, 664 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.4 Hz, 2 H, Ar), 7.29 (d, J = 9.3 Hz, 2 H, Ar), 5.68–5.56 (m, 1 H, CH_2=C*H*), 5.99–4.91 (m, 2 H, CH_2=CH), 4.65 (dd, J = 3.3, 43.5 Hz, 1 H, CH_{2cis}=C*F*), 4.55 (dd, J = 3.3, 75.4 Hz, 1 H, CH_{2trans}=C*F*), 3.99–3.83 (m, 2 H, CFCH_2N), 3.23–3.07 (m, 2 H, NCH_2CH$_2$), 2.41 (s, 3 H, CH_3), 2.16–2.07 (m, 1 H, C*H*CH$_3$), 1.59–1.51 (m, 2 H, NCH$_2$CH_2), 0.98 (d, J = 6.6 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.0 (d, J = 259.6 Hz, *C*F), 143.4, 143.3, 136.8, 129.7, 127.3, 113.6, 94.0 (d, J = 17.2 Hz, *C*=CF), 47.7 (d, J = 32.2 Hz, *C*H$_2$CF), 46.2, 35.6, 34.6, 21.6, 20.3 ppm. HRMS (EI): calcd. for $C_{16}H_{22}FNO_2S$ (M^+) 311.1355, found 311.1349.

***N*-(2-Fluoroallyl)-4-methyl-*N*-(3-phenylpent-4-enyl)benzenesulfonamide (17):** To a solution of compound **9** (90 mg, 0.40 mmol) in toluene (4 mL) were added PPh_3 (210 mg, 0.80 mmol), 3-phenyl-4-penten-1-ol (78 mg, 0.48 mmol) and diethyl azodicarboxylate (0.12 mL, 0.64 mmol). The mixture was heated at 50 °C for 12 h, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **17** (90 mg, 60%) as a pink oil. **17**: IR (neat): $\tilde{\nu}$ = 3084, 3058, 3028, 2976, 2928, 2863, 1675, 1597, 1489, 1455, 1342, 1156, 1087, 927, 810, 759, 707, 664, 547 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.4 Hz, 2 H, SO_2Ar), 7.31–7.13 (m, 7 H, 2H SO_2Ar, 5H Ph), 5.94–5.83 (m, 1 H, CH_2=C*H*), 5.05–4.99 (m, 2 H, CH_2=CH), 4.58 (dd, J = 3.3, 57.9 Hz, 1 H, CH_{2cis}=C*F*), 4.47 (dd, J = 3.3, 89.5 Hz, 1 H, CH_{2trans}=C*F*), 3.88 (d, J = 14.4 Hz, 2 H, CFCH_2N), 3.26–3.12 (m, 2 H, 1H NCH_2CH$_2$, C*H*Ph), 3.06–2.96 (m, 1 H, NCH_2CH$_2$), 2.40 (s, 3 H, CH_3), 2.04–1.96 (m, 2 H, NCH$_2$CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.8 (d, J = 259.6 Hz, *C*F), 143.5, 143.1, 141.2, 136.7, 129.7, 128.7, 127.6, 127.4, 126.6, 114.8, 94.2 (d, J = 17.2 Hz, *C*=CF), 48.0 (d, J = 31.9 Hz, *C*H$_2$CF), 47.3, 46.4, 33.6, 21.6 ppm. HRMS (EI): calcd. for $C_{21}H_{24}FNO_2S$ (M^+) 373.1512, found 373.1497.

***N*-(2-Fluoroallyl)-*N*-(hex-5-enyl)-4-methylbenzenesulfonamide (18):** To a solution of compound **9** (70 mg, 0.27 mmol) in toluene (3 mL) were added PPh_3 (141 mg, 0.54 mmol), 5-hexenol (39 μL, 0.33 mmol) and diethyl azodicarboxylate (78.7 μL, 0.43 mmol). The mixture was heated at 50 °C for 12 h, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 10:1) to give **18** (65 mg, 77%) as a colorless oil. **18**: IR (neat): $\tilde{\nu}$ = 3071, 2971, 2924, 2863, 1675, 1593, 1442, 1338, 1161, 1091, 909, 810, 664, 547 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.4 Hz, 2 H, Ar), 7.26 (d, J = 8.4 Hz, 2 H, Ar), 5.79–5.66 (m, 1 H, CH_2=C*H*), 4.99–4.91 (m, 2 H, CH_2=CH), 4.63 (dd, J = 3.3, 44.2 Hz, 1 H, CH_{2cis}=C*F*), 4.52 (dd, J = 3.3, 75.7 Hz, 1 H, CH_{2trans}=C*F*), 3.91 (d, J = 14.1 Hz, 2 H, CFCH_2N), 3.16 (t, J = 7.5 Hz, 2 H, NCH_2CH$_2$), 2.41 (s, 3 H, CH_3), 2.05–1.99 (m, 2 H, CH$_2$=CHCH_2), 1.66–1.50 (m, 2 H, NCH$_2$CH_2CH$_2$), 1.42–1.25 (m, 2 H, NCH$_2$CH$_2$CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7 (d, J = 258.8 Hz, *C*F), 143.2, 138.1, 136.7, 129.5, 127.2, 114.8, 93.9 (d, J = 17.5 Hz, *C*=CF), 47.9, 47.6 (d, J = 27.3 Hz, *C*H$_2$CF), 33.4, 27.6, 26.0, 21.8 ppm. HRMS (EI): calcd. for $C_{16}H_{23}FNO_2S$ [M + H]$^+$ 312.1433, found 312.1437.

***N*-Decyl-*N*-(2-fluoroallyl)-4-methylbenzenesulfonamide (19):** To a solution of compound **9** (110 mg, 0.42 mmol) in toluene (5 mL) was added PPh_3 (222 mg, 0.85 mmol), 9-decenol (91 μL, 0.51 mmol) and diethyl azodicarboxylate (0.13 mL, 0.67 mmol). The mixture was heated at 50 °C for 12 h, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **19** (121 mg, 78%) as a yellow oil. **19**: IR (neat): $\tilde{\nu}$ = 3071, 2971, 2928, 2855, 1779, 1675, 1636, 1593, 1467, 1342, 1234, 1156, 1087, 914, 815, 659, 547 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.4 Hz, 2 H, Ar), 7.26 (d, J = 8.7 Hz, 2 H, Ar), 5.85–5.71 (m, 1 H, CH_2=C*H*), 5.00–4.88 (m, 2 H, CH_2=CH), 4.63 (dd, J = 3.0, 41.2 Hz, 1 H, CH_{2cis}=C*F*), 4.52 (dd, J = 3.0, 72.7 Hz, 1 H, CH_{2trans}=C*F*), 3.90 (d, J = 13.5 Hz, 2 H, CFCH_2N), 3.14 (t, J = 7.5 Hz, 2 H, NCH_2CH$_2$), 2.40 (s, 3 H, CH_3), 2.06–1.99 (m, 2 H, CH$_2$=CHCH_2), 1.54–1.24 (m, 12 H, NCH$_2$(CH_2)$_6$CH$_2$CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7 (d, J = 258.8 Hz, *C*F), 143.1, 138.9, 136.7, 129.4, 127.1, 114.1, 93.8 (d, J = 17.2 Hz, *C*=CF), 47.9, 47.6 (d, J = 31.8 Hz, *C*H$_2$CF), 33.9, 29.5, 29.3, 29.2, 29.1, 28.2, 26.8 ppm. HRMS (EI): calcd. for $C_{20}H_{30}FNO_2S$ (M^+) 367.1981, found 367.1967.

***N*-(2-Fluoroallyl)-4-methyl-*N*-(undec-10-enyl)benzenesulfonamide (20):** To a solution of compound **9** (90 mg, 0.35 mmol) in toluene (4 mL) were added PPh_3 (181 mg, 0.69 mmol), 10-decen-1-ol (83.1 μL, 0.42 mmol) and diethyl azodicarboxylate (72 μL, 0.55 mmol). The mixture was heated at 50 °C for 12 h, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **20** (130 mg, 99%) as a yellow oil. **20**: IR (neat): $\tilde{\nu}$ = 3075, 2924, 2855, 1779, 1675, 1636, 1593, 1463, 1342, 1156, 1087, 919, 811, 664, 543 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.4 Hz, 2 H, Ar), 7.28 (d, J = 7.8 Hz, 2 H, Ar), 5.87–5.74 (m, 1 H, CH_2=C*H*), 5.02–4.90 (m, 2 H, CH_2=CH), 4.65 (dd, J = 3.0, 41.4 Hz, 1 H, CH_{2cis}=C*F*), 4.54 (dd, J = 3.0, 73.3 Hz, 1 H, CH_{2trans}=C*F*), 3.92 (d, J = 13.5 Hz, 2 H, CFCH_2N), 3.15 (t, J = 7.5 Hz, 2 H, NCH_2CH$_2$), 2.41 (s, 3 H, CH_3), 2.07–1.99 (m, 2 H, CH$_2$=CHCH_2), 1.32–1.24 (m, 14 H, NCH$_2$(CH_2)$_7$CH$_2$CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.0 (d, J = 259.9 Hz, *C*F), 143.3, 139.2, 136.9, 129.6, 127.3, 114.2, 93.8 (d, J = 17.5 Hz, *C*=CF), 47.8, 47.5 (d, J = 32.2 Hz, *C*H$_2$CF), 33.8, 29.5, 29.4, 29.2, 29.1, 28.9, 28.0, 26.8 ppm. HRMS (EI): calcd. for $C_{21}H_{32}FNO_2S$ (M^+) 381.2138, found 381.2133.

General Procedure for the RCM Reactions

To a 0.01 M solution of the diolefin in dry toluene under an inert atmosphere was added the second-generation Grubbs catalyst **10** at 100 °C in small portions over 30 min. Stirring was continued until the reaction was complete (indicated by TLC or GC), followed by concentration of the reaction mixture and subsequent purification with column chromatography.

4-Fluoro-2-methyl-1-(4-tolylsulfonyl)-2,5-dihydro-1*H*-pyrrole (22): RCM was carried out following the general procedure with compound **12** (76 mg, 0.27 mmol) and was completed in 3 h. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **22** (50 mg, 72%) as a yellow oil. **22**: IR (neat): $\tilde{\nu}$ = 3101, 3062, 3028, 2963, 2920, 2872, 1701, 1597, 1450, 1351, 1161, 1091, 1035, 936, 815, 664, 577, 547 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.4 Hz, 2 H, Ar), 7.31 (d, J = 8.7 Hz, 2 H, Ar), 4.92–4.89 (m, 1 H, FC=C*H*CH), 4.46–4.44 (m, 1 H, NC*H*CH$_3$), 4.16–3.98 (m, 2 H, NCH_2CF), 2.42 (s, 3 H, ArCH_3), 1.44 (d, J = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7 (d, J = 273.4 Hz, *C*F), 143.7, 143.1, 129.8, 127.4, 104.4 (d, J = 7.5 Hz, *C*=CF), 59.9 (d, J = 6.9 Hz, *C*HCH=CF), 50.0 (d, J = 30.7 Hz, *C*H$_2$CH=CF), 23.6, 21.8 ppm. HRMS (CI) calcd. for $C_{12}H_{15}FNO_2S$ [M + H]$^+$ 256.0807, found 256.0809.

5-Fluoro-1-(4-nitrophenylsulfonyl)-1,2,3,6-tetrahydropyridine (24): RCM was carried out following the general procedure with compound **14** (40 mg, 0.13 mmol) and was completed in 1 h. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **24** (36 mg, 97%) as a white solid. **24**: M.p. 116–118 °C. IR (neat): $\tilde{\nu}$ = 3101, 2963, 2920, 2859, 2790, 1713, 1576, 1528, 1455, 1351, 1260, 1169, 1091, 1009, 824, 798 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (d, J = 8.7 Hz, 2 H, Ar), 7.97 (d, J = 8.4 Hz, 2 H, Ar), 5.31 (dt, J = 5.7, 17.1 Hz, 1 H, FC=C*H*CH$_2$), 3.75–3.73 (m, 2 H, CFCH_2N), 3.25 (t, J = 5.7 Hz, 2 H, NCH_2CH$_2$), 2.25–2.19 (m, 2 H, NCH$_2$CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4 (d, J = 251.6 Hz, *C*F), 150.5, 142.6, 128.6, 124.5, 100.9 (d, J = 13.2 Hz, *C*=CF), 43.9 (d, J = 39.9 Hz, *C*H$_2$CF), 42.8 (d, J = 1.4 Hz, *C*H$_2$CH=CF), 22.7 ppm. HRMS (EI): calcd. for $C_{11}H_{11}FN_2O_4S$ (M$^+$) 286.0424, found 286.0417.

6-Fluoro-1-(4-tolylsulfonyl)-2,3,4,7-tetrahydro-1*H*-azepine (25): RCM was carried out following the general procedure with compound **15** (46 mg, 0.15 mmol) and was completed in 1 h. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **25** (32 mg, 80%) as a colorless oil. **25**: IR (neat): $\tilde{\nu}$ = 3058, 2980, 2933, 2872, 2846, 1701, 1597, 1450, 1342, 1161, 1091, 1044, 914, 811, 664, 551 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.1 Hz, 2 H, Ar), 7.27 (d, J = 8.1 Hz, 2 H, Ar), 5.28 (dt, J = 5.7, 19.8 Hz, 1 H, FC=C*H*CH$_2$), 4.00 (d, J = 6.6 Hz, 2 H, CFCH_2N), 3.38 (t, J = 6.0 Hz, 2 H, NCH_2CH$_2$), 2.42 (s, 3 H, CH_3), 2.04–1.97 (m, 2 H, NCH$_2$CH$_2$CH_2), 1.85–1.77 (m, 2 H, NCH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2 (d, J = 251.0 Hz, *C*F), 143.4, 135.9, 128.6, 127.1, 106.9 (d, J = 18.7 Hz, *C*=CF), 49.0, 47.4 (d, J = 43.9 Hz, *C*H$_2$CF), 27.2, 21.8, 21.4 (d, J = 9.8 Hz, *C*H$_2$CH=CF) ppm. HRMS (EI): calcd. for $C_{13}H_{16}FNO_2S$ (M$^+$) 269.0886, found 269.0889.

6-Fluoro-4-methyl-1-(4-tolylsulfonyl)-2,3,4,7-tetrahydro-1*H*-azepine (26): RCM was carried out following the general procedure with compound **16** (73 mg, 0.23 mmol) and was completed in 1 h. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **26** (62 mg, 94%) as a colorless oil. **26**: IR (neat): $\tilde{\nu}$ = 3028, 2963, 2924, 2872, 1692, 1597, 1489, 1446, 1342, 1161, 1100, 923, 879, 815, 754, 655, 590, 547 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.4 Hz, 2 H, Ar), 7.31 (d, J = 7.8 Hz, 2 H, Ar), 5.13 (dd, J = 3.9, 21.0 Hz, 1 H, FC=C*H*CHPh), 4.16–4.07 (m, 1 H, CFCH_2N), 3.91–3.83 (m, 1 H, CFCH_2N), 3.44–3.28 (m, 2 H, NCH_2CH$_2$), 2.42 (s, 3 H, ArCH_3), 2.39–2.37 (br. m, 1 H, C*H*CH$_3$), 1.87–1.77 (m, 1 H, NCH$_2$CH_2), 1.69–1.56 (m, 1 H, NCH$_2$CH_2), 1.01 (d, J = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2 (d, J = 252.3 Hz, *C*F), 143.7, 135.9, 129.8, 127.3, 113.4 (d, J = 16.9 Hz, *C*=CF), 47.3, 47.1 (d, J = 44.5 Hz, *C*H$_2$CF), 34.9 9 (d, J = 0.6 Hz, NCH$_2$*C*H$_2$), 27.7 (d, J = 9.2 Hz, CF=CH*C*HCH$_3$), 22.1, 21.6 ppm. HRMS (EI): calcd. for $C_{14}H_{18}FNO_2S$ (M$^+$) 283.1042, found 283.1036.

6-Fluoro-4-phenyl-1-(4-tolylsulfonyl)-2,3,4,7-tetrahydro-1*H*-azepine (27): RCM was carried out following the general procedure with compound **17** (60 mg, 0.16 mmol) and was completed in 3 h. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **27** (40 mg, 72%) as a colorless oil. **27**: IR (neat): $\tilde{\nu}$ = 3062, 3028, 2924, 2859, 1697, 1593, 1489, 1446, 1338, 1161, 1091, 936, 815, 754, 698, 659, 547 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.4 Hz, 2 H, SO_2Ar), 7.34–7.11 (m, 5 H, SO_2Ar, Ph), 7.10 (d, J = 6.9 Hz, 2 H, Ph), 5.38 (dd, J = 3.6, 21.0 Hz, 1 H, FC=C*H*CHPh), 4.29–4.20 (m, 1 H, CFCH_2N), 4.05–3.96 (m, 1 H, CFCH_2N), 3.51–3.49 (m, 1 H, C*H*Ph), 3.43–3.28 (m, 2 H, NCH_2CH$_2$), 2.44 (s, 3 H, CH_3), 2.07–1.99 (m, 2 H, NCH$_2$CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1 (d, J = 253.3 Hz, *C*F), 144.4, 143.8, 135.8, 129.9, 128.8, 127.36, 127.35, 126.8, 111.7 (d, J = 19.8 Hz, *C*=CF), 46.9 (d, J = 44.2 Hz, *C*H$_2$CF), 46.8, 39.6 (d, J = 9.5 Hz, CF=CH*C*HPh), 35.6, 21.6 ppm. HRMS (EI): calcd. for $C_{19}H_{20}FNO_2S$ (M$^+$) 345.1199, found 345.1190.

6-Fluoro-1-(4-tolylsulfonyl)-2,3,4,7-tetrahydro-1*H*-azepine (25) from Precursor 18: RCM was carried out following the general procedure with compound **18** (57 mg, 0.18 mmol) and was completed in 2 h. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **25** (20 mg, 41%) as a colorless oil.

***tert*-Butyl *N*-Tosyl-*N*-[2-(trifluoromethyl)allyl]carbamate (30):** A solution of compound **5** (461 mg, 1.64 mmol) and *tert*-butyl *N*-tosylcarbamate[14] (0.536 g, 1.98 mmol) in MeCN (70 mL) was treated with K_2CO_3 (2.76 g, 2.0 mmol) and the suspension refluxed for 18 h. After cooling to room temp., K_2CO_3 was filtered off and the solvent evaporated. The crude product was purified by flash chromatography (ethyl acetate/heptane, 1:25 to 1:15) to give **30** (0.505 g, 81%) as a white solid. **30**: M.p. 89–91 °C. IR (neat): $\tilde{\nu}$ = 2981, 2933, 1734, 1597, 1144 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.83 (m, 1 H), 7.30–7.33 (m, 1 H), 5.87–5.88 (m, 1 H), 5.61–5.62 (m, 1 H), 4.61–4.62 (m, 2 H), 2.45 (s, 3 H), 1.36 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.4, 144.8, 136.7, 134.6 (q, J = 29.5 Hz, *C*CF$_3$), 129.5, 128.4, 123.0 (q, J = 273.7 Hz, *C*F$_3$), 119.2 (q, J = 5.2 Hz, *C*=CCF$_3$) 85.1, 45.3, 27.9, 21.8 ppm. HRMS (ESI) calcd. for $C_{16}H_{20}F_3NNaO_4S$ [M + Na]$^+$ 402.0963, found 402.0960.

4-Methyl-*N*-[2-(trifluoromethyl)allyl]benzenesulfonamide (31): TFA (10 mL) was added to a solution of compound **30** (0.445 g, 1.17 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After 5 min the reaction was warmed to room temp. and stirred for an additional 40 min. Subsequently, the reaction mixture was evaporated and the crude product purified by column chromatography to give **31** (0.285 g, 87%) as a white solid. **31**: M.p. 69 °C. IR (neat): $\tilde{\nu}$ = 3280, 2925, 2856, 1672, 1598, 1321 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.74 (m, 1 H), 7.74–7.71 (m, 1 H), 7.33–7.32 (m, 1 H), 7.31–7.29 (m, 1 H), 5.78–5.75 (m, 1 H), 5.63 (dd, J = 2.8, 1.4 Hz, 1 H), 4.87–4.77 (m, 1 H), 3.74 (d, J = 6.6 Hz, 2 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.9, 136.6, 134.1 (q, J = 29.0 Hz, *C*CF$_3$), 129.8, 127.1, 122.7 (q, J = 273.5 Hz, *C*F$_3$), 120.6 (q, J = 5.2 Hz, *C*=CCF$_3$), 41.7, 21.5 ppm. HRMS (EI): calcd. for $C_{11}H_{12}F_3NO_2S$ (M$^+$) 279.0541, found 279.05379.

***N*-Allyl-4-methyl-*N*-[2-(trifluoromethyl)allyl]benzenesulfonamide (32):** To a solution of compound **31** (50 mg, 0.179 mmol) in toluene (4 mL) were added PPh_3 (94 mg, 0.36 mmol), 2-propenol (12.5 mg, 0.214 mmol) and diethyl azodicarboxylate (49.8 mg, 0.286 mmol). The mixture was heated at 50 °C for 40 min, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **32** (57 mg, 99%) as a colorless oil. **32**: IR (neat): 2985, 2924, 2858, 1347, 1321. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.72 (m, 2 H, Ar), 7.29–7.32 (m, 2 H, Ar), 5.85–5.87 (m, 1 H, C*H*=CCF$_3$), 5.66–5.68 (m, 1 H, C*H*=CCF$_3$), 5.50 (ddt, *J* = 6.7, 6.7, 10.1 Hz, 1 H, C*H*=CH$_2$), 5.06–5.15 (m, 1 H, CH=C*H*$_2$), 5.10–5.13 (m, 1 H, CH=C*H*$_2$), 3.90 (s, 2 H, NC*H*$_2$CH), 3.78–3.81 (m, 2 H, NC*H*$_2$CCF$_3$), 2.42 (s, 3 H, C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.9, 136.9, 133.9 (q, *J* = 29.1 Hz, *C*CF$_3$), 131.8, 130.0, 127.4, 123.1 (q, *J* = 273.6 Hz, *C*F$_3$), 120.6, (q, *J* = 5.3 Hz, *C*=CCF$_3$), 120.5, 50.6, 44.9, 21.7 ppm. HRMS (EI): calcd. for $C_{14}H_{16}F_3NO_2S$ (M^+) 319.0854, found 319.0854.

***N*-(But-3-enyl)-4-methyl-*N*-(2-trifluoromethylallyl)benzenesulfonamide (33):** To a solution of compound **31** (50 mg, 0.179 mmol) in toluene (4 mL) were added PPh_3 (94 mg, 0.36 mmol), 3-butenol (18.4 μL, 0.214 mmol) and diethyl azodicarboxylate (52.2 μL, 0.286 mmol). The mixture was heated at 50 °C for 40 min, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **33** (38 mg, 64%) as a colorless oil. **33**: IR (neat): $\tilde{\nu}$ = 3071, 2976, 2855, 1455, 1407, 1346, 1321, 1156, 1122, 1091, 953, 919, 811, 754, 664, 543 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.1 Hz, 2 H, Ar), 7.32 (d, *J* = 8.1 Hz, 2 H, Ar), 5.88–5.87 (m, 1 H, F$_3$CC=C*H*), 5.73–5.70 (m, 1 H, F$_3$CC=C*H*) 5.68–5.56 (m, 1 H, CH$_2$=C*H*), 5.05–4.97 (m, 2 H, C*H*$_2$=CH), 3.93 (s, 2 H, NC*H*$_2$CCF$_3$), 3.22 (t, *J* = 7.7 Hz, 2 H, NC*H*$_2$CH$_2$), 2.43 (s, 3 H, C*H*$_3$), 2.25–2.17 (m, 2 H, NCH$_2$C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.9, 136.6, 134.3, 134.2 (q, *J* = 29 Hz, *C*CF$_3$), 129.9, 127.3, 123.1 (q, *J* = 272 Hz, *C*F$_3$), 120.7 (q, *J* = 5.2 Hz, *C*=CCF$_3$), 117.6, 48.3, 46.5, 32.6, 21.6 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}F_3NO_2S$ $[M+H]^+$ 334.1089, found 334.1077.

4-Methyl-*N*-(pent-4-enyl)-*N*-(2-trifluoromethylallyl)benzenesulfonamide (34): To a solution of compound **31** (50 mg, 0.179 mmol) in toluene (4 mL) were added PPh_3 (94 mg, 0.36 mmol), 4-pentenol (22 μL, 0.21 mmol) and diethyl azodicarboxylate (52.2 μL, 0.286 mmol). The mixture was heated at 50 °C for 40 min, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **34** (37 mg, 60%) as a colorless oil. **34**: IR (neat): $\tilde{\nu}$ = 3067, 2963, 2924, 2855, 1645, 1597, 1455, 1346, 1325, 1161, 1117, 1091, 1048, 949, 910, 811, 664, 551 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.4 Hz, 2 H, Ar), 7.32 (d, *J* = 8.4 Hz, 2 H, Ar), 5.88 (s, 1 H, F$_3$CC=C*H*), 5.73 (s, 1 H, F$_3$CC=C*H*), 5.77–5.64 (m, 1 H, CH$_2$=C*H*), 5.02–4.95 (m, 2 H, C*H*$_2$=CH), 3.90 (s, 2 H, F$_3$CCC*H*$_2$N), 3.13 (t, *J* = 7.7 Hz, 2 H, NC*H*$_2$CH$_2$), 2.43 (s, 3 H, C*H*$_3$), 2.02–1.95 (m, 2 H, NCH$_2$CH$_2$C*H*$_2$), 1.61–1.51 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.8, 137.2, 136.6, 134.4 (q, *J* = 28.7 Hz, *C*CF$_3$), 129.9, 127.3, 123.1 (q, *J* = 272 Hz, *C*F$_3$), 120.6 (q, *J* = 5.2 Hz, *C*=CCF$_3$), 115.7, 48.8, 46.5, 30.9, 27.2, 21.7 ppm. HRMS (EI): calcd. for $C_{16}H_{20}F_3NO_2S$ (M^+) 347.1167, found 347.1169.

4-Methyl-*N*-(3-phenylpent-4-enyl)-*N*-[2-(trifluoromethyl)allyl]benzenesulfonamide (35): To a solution of compound **31** (28 mg, 0.1 mmol) in toluene (3 mL) were added PPh_3 (52.6 mg, 0.20 mmol), 3-phenyl-4-pentenol (19.5 mg, 0.12 mmol) and diethyl azodicarboxylate (28 mg, 0.16 mmol). The mixture was heated at 50 °C for 40 min, then the solvent was evaporated and the residue was purified using column chromatography (heptane/EtOAc, 20:1) to give **35** (31 mg, 74%) as a colorless oil. **35**: IR (neat): $\tilde{\nu}$ = 3060, 3027, 2924, 2867, 1637, 1598, 1492, 1452, 1341, 1321, 1158, 1121, 955, 701 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.2 Hz, Ar), 7.08–7.31 (m, 7 H, Ar), 5.84 (ddd, *J* = 17.1, 10.3, 7.5 Hz C*H*=CH$_2$), 5.83 (dd, *J* = 2.8, 1.4 Hz, 1 H, C*H*=CCF$_3$), 5.64 (dd, *J* = 2.8, 1.4 Hz, C*H*=CCF$_3$), 5.00 (dt, *J* = 25.5, 1.4 Hz, 1 H, CH=C*H*$_2$), 5.00–5.02 (m, 1 H, CH=C*H*$_2$), 3.87 (br. s, 2 H, NC*H*$_2$), 3.09–3.20 (m, 2 H, NC*H*$_2$CCF$_3$), 2.91–3.01 (m, 1 H, C*H*Ph), 2.42 (s, 3 H, C*H*$_3$), 1.85–1.93 (m, 2 H, NCH$_2$C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 142.9, 141.7, 136.4, 134.3 (q, *J* = 30.0 Hz, *C*CF$_3$), 129.9, 128.8, 127.6, 127.4, 126.8, 123.1 (q, *J* = 277 Hz, *C*F$_3$), 120.8 (q, *J* = 7.5 Hz, *C*=CCF$_3$), 115.0, 47.6, 47.5, 46.8, 33.4, 21.7 ppm.

1-Tosyl-3-(trifluoromethyl)-2,5-dihydro-1*H*-pyrrole (36): RCM was carried out following the general procedure with compound **32** (40 mg, 0.125 mmol) and was completed in 45 min. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **36** (21 mg, 57%) as a white solid and **37** (9.1 mg, 23%) as an amorphous solid. **36**: M.p. 63–64 °C. IR (neat): $\tilde{\nu}$ = 3060, 3027, 2956, 2923, 2856, 1679, 1597, 1379 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.2 Hz, 2 H, Ar), 7.35 (d, *J* = 8.0 Hz, 2 H, Ar), 6.19–6.20 (m, 1 H), 4.26 (s, 4 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 133.8, 130.2, 129.8 (q, *J* = 4.8 Hz, *C*=CCF$_3$), 129.3 (q, *J* = 35.5 Hz, *C*CF$_3$), 127.6, 120.8 (q, *J* = 269.3 Hz, *C*F$_3$), 54.9, 52.2, 21.7 ppm. HRMS (EI): calcd. for $C_{12}H_{12}F_3NO_2S$ (M^+) 291.0541, found 291.0539. **37**: IR (neat): $\tilde{\nu}$ = 3060, 3027, 2959, 2924, 2860, 1662, 1597, 1360, 1322, 1165, 1121, 1051, 972, 943 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.8 Hz, 2 H, Ar), 7.31 (d, *J* = 7.8 Hz, 2 H, Ar), 6.56 (d, *J* = 14.1 Hz, 1 H, NC*H*=CH), 5.79 (m, 1 H, C*H*=CCF$_3$), 5.55 (m, 1 H, C*H*=CCF$_3$), 4.72 (m, 1 H, NCH=C*H*CH$_3$), 4.02 (s, 2 H, NC*H*$_2$), 2.42 (s, 3 H, ArC*H*$_3$), 1.64 (dd, *J* = 6.6, 1.5 Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1, 135.7, 131.8 (q, *J* = 29.3 Hz, *C*CF$_3$), 129.9, 126.9, 125.5, 122.9 (q, *J* = 271.8 Hz, *C*F$_3$), 119.2, 107.8, 44.2, 21.6, 15.2 ppm.

1-(4-Tolylsulfonyl)-5-(trifluoromethyl)-1,2,3,6-tetrahydropyridine (38): RCM was carried out following the general procedure with compound **33** (30 mg, 0.09 mmol) and the reaction was completed in 1 h. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **38** (27 mg, 98%) as a colorless oil. **38**: M.p. 90–93 °C. IR (neat): $\tilde{\nu}$ = 3036, 2954, 2920, 2846, 1459, 1394, 1342, 1316, 1169, 1117, 1091, 966, 879, 746 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.1 Hz, 2 H, Ar), 7.35 (d, *J* = 8.1 Hz, 2 H, Ar), 5.39 (t, *J* = 1.8 Hz, 1 H, F$_3$CC=C*H*CH$_2$), 3.72 (s, 2 H, F$_3$CCC*H*$_2$N), 3.21 (t, *J* = 5.7 Hz, 2 H, NC*H*$_2$CH$_2$), 2.44 (s, 3 H, CH$_3$), 2.35–2.32 (m, 2 H, NCH$_2$C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.2, 133.3, 130.0, 129.1 (q, *J* = 5.4 Hz, *C*=CCF$_3$), 127.8, 125.5 (q, *J* = 31.0 Hz, *C*CF$_3$), 122.7 (q, *J* = 270.3 Hz, *C*F$_3$), 42.1, 41.9, 24.5, 21.7 ppm. HRMS (EI): calcd. for $C_{13}H_{14}F_3NO_2S$ (M^+) 305.0697, found 305.0696.

1-(4-Tolylsulfonyl)-5-(trifluoromethyl)-1,2,3,6-tetrahydropyridine (38) from Precursor 34: RCM was carried out following the general procedure with compound **34** (20 mg, 0.06 mmol) and the reaction was completed in 1 h. The mixture was purified using column chromatography (heptane/EtOAc, 10:1) to give **38** (12 mg, 65%) as a colorless oil.

4-Methyl-*N*-(3-phenyl-3-pentenyl)-*N*-(2-trifluoromethylallyl)benzenesulfonamide (39): RCM was carried out following the general procedure with compound **35** (22 mg, 0.05 mmol) and the reaction was completed in 2 h. The mixture was purified using column

chromatography (heptane/EtOAc, 10:1) to give **39** (15 mg, 68%) as a colorless oil. **39** (major isomer): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.4 Hz, Ar), 7.34–7.18 (m, 7 H, Ar), 5.88–5.86 (m, 1 H, C*H*=CCF_3), 5.83–5.81 (m, 1 H, C*H*=CCF_3), 5.66 (q, J = 1.2 Hz, 1 H, PhC=C*H*CH_3), 3.99 (s, 2 H, N$CH_2$$CCF_3$), 3.12–3.05 (m, 2 H, N$CH_2$), 2.74–2.69 (m, 2 H, N$CH_2$$CH_2$), 2.45 (s, 3 H, CH_3), 1.76 (d, J = 7.2 Hz, 3 H, =CH_3) ppm.

***N*-[1-(Benzyloxy)allyl]-4-methyl-*N*-[2-(trifluoromethyl)allyl]benzenesulfonamide (41):** Compound **41** was prepared according to a general literature procedure for amidopalladation of tosylamides.[10] To a 0.1 M solution of compound **31** (103 mg, 0.36 mmol) in MeCN were added Et_3N (54 mg, 0.54 mmol), $Pd(OAc)_2$ (4 mg, 5 mol-%), dppp (7.4 mg, 5 mol-%) and benzyloxyallene **40** (57.6 mg, 0.39 mmol). After stirring at room temp. for one hour, the solvent was evaporated and the crude residue purified by column chromatography (heptane/EtOAc, 6:1 to 4:1) to give product **41** (0.144 g, 92%)as a colorless oil. **41**: IR (neat): $\tilde{\nu}$ = 3066, 3031, 2926, 2868, 1347, 1321, 1160 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.68 (m, 2 H, Ar), 7.36–7.18 (m, 7 H, Ar), 5.80 (dd, J = 2.9, 1.5 Hz, 1 H, C*H*=CCF_3), 5.73 (dd, J = 3.0, 1.5 Hz, 1 H, C*H*=CCF_3), 5.67 (dd, J = 3.1, 1.3 Hz, 1 H, *CH*=CH), 5.50–5.45 (m, 2 H, HC=CH_2), 5.28 (ddd, J = 6.7, 2.6, 1.1 Hz, 1 H, HC=CH_2), 4.52 (dd, J = 11.8, 3.8 Hz, 2 H, OCH_2), 3.94 (q, J = 18.2 Hz, 2 H, NCH_2), 2.42 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1, 137.2, 137.0, 135.0 (q, J = 28.8 Hz, *C*CF_3), 133.0, 129.9, 128.5, 127.9, 127.7, 127.6, 123.2 (q, J = 273.8 Hz, *C*F_3), 120.3 (q, J = 5.2 Hz, *C*=CCF_3), 119.9, 87.0, 70.0, 41.4, 21.7 ppm. HRMS (EI): calcd. for $C_{21}H_{22}F_3NO_3S$ (M^+) 426.1351, found 426.1352.

1-Tosyl-3-(trifluoromethyl)-1*H*-pyrrole (42): To a solution of **41** (0.358 g, 0.842 mmol) in toluene (150 mL) at 100 °C was added catalyst **10** (6.5 mol%) in two portions with an interval of 30 min. After completion of the RCM (1.5 h), the reaction was cooled to room temp. and TFA (5.5 mL) was added. After stirring for 30 min at room temp., the solvent was evaporated and the crude product purified by flash chromatography (heptane/EtOAc, 40:1) to give **42** (0.195 g, 80%) as a white solid. **42**: M.p. 57 °C. IR (neat): $\tilde{\nu}$ = 3066, 3031, 2957, 2922, 2852, 1583, 1479, 1378, 1122, 1057 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–7.81 (m, 1 H, Ar), 7.77–7.78 (m, 1 H, Ts), 7.45–7.49 (m, 1 H, Ts), 7.35–7.36 (m, 1 H, Ar), 7.32–7.33 (m, 1 H, Ts), 7.16–7.18 (m, 1 H, Ts), 6.43–6.44 (m, 1 H, Ar), 2.43 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 135.1, 130.3, 127.2, 126.0 (q, J = 267.1 Hz, *C*F_3), 121.6, 119.9 (q, J = 5.0 Hz, *C*=CCF_3), 119.4 (q, J = 37.5 Hz, *C*CF_3), 110.2 (m, F_3C*C*H=C), 21.7 ppm. HRMS (EI): calcd. for $C_{12}H_{10}F_3NO_2S$ (M^+) 289.0384, found 289.0387.

Acknowledgments

Bayer CropScience GmbH (Frankfurt am Main, Germany) is gratefully acknowledged for financial support.

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Received: December 22, 2006
Published Online: March 14, 2007

