Dual Intermolecular Allylic C-H Functionalization within the Tetrasubstituted Alkene Scaffold

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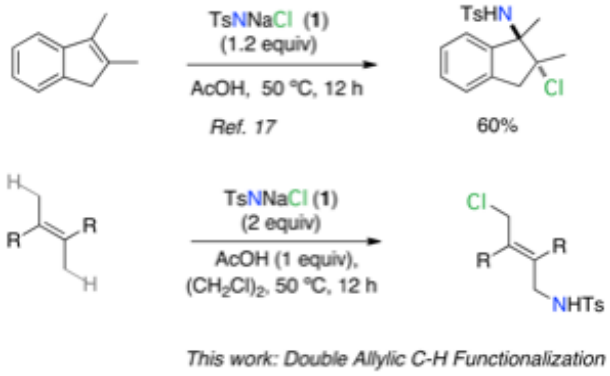
Dedicated to the memory of Professor Ricardo Llavona

Abstract: Activation of chloramine-T (TsNNaCl) with Brønstedt acid generates an active reagent for the double allylic C-H functionalization of tetrasubstituted alkenes under intermolecular reaction control. The reaction generates a carbon-nitrogen and a carbon-chlorine bond, respectively, and proceeds with complete regio- and chemoselectivity. A total of 14 examples demonstrate the applicability of the dual C-H functionalization process. The mechanism involves the intermediary participation of a 1,3-butadiene derivative, which can also be employed directly as substrates.

Introduction

Intermolecular carbon-heteroatom bond formation through direct oxidative C-H functionalization at the allylic position represents a versatile strategy for the refinement of unsaturated hydrocarbon compounds.[1] Such reactions are widely sought after, and particularly well-designed, metal-based innovative C-H oxidation reactions[2] have emerged over recent years. Despite these broad advances, reactions that can be conducted without the requirement of a metal promoter constitute a strategic alternative of conceptual importance,[3,4] both for economical and ecological reasons. Examples of such practical transformations include selenium-mediated allylic oxygenation[5] and amination,[6] hypervalent iodine mediated processes,[7] and related radical-based oxidations.[8] Within this context, *N*-halo amines represent powerful alternative oxidants for metal-free oxidation,[9,10] which is well illustrated by the versatile Wohl-Ziegler reaction for allylic halogenation[11] and the prominent Hofmann-Löffler reaction[12] The latter is a particularly instructive reaction, since the involved *N*-halogenated amines usually promote highly selective C-H functionalization.[13] In the broader *N*-halo amine area, commercially available chloramine-T (**1**)[14] has attracted significant interest in the field of alkene oxidation.[15,16] Despite the mature state in the area of expertise, it appears that the exploration of innovative and practical reactivity based on **1** may still be possible. We here report such a case of an unprecedented double allylic C-H functionalization within a metal-free reaction manifold. We recently reported conditions for a metal-free aminochlorination of alkenes through an operationally convenient Brønstedt acid activation of chloramine-T **1**.[17] This reaction is characterized by an unusually broad substrate scope, which tolerates all different alkene classes. For cyclic tetrasubstituted alkenes, clean vicinal aminochlorination was observed (Scheme 1). However, this outcome was found to change entirely in case of the corresponding class of acyclic tetrasubstituted alkenes. We here report conditions for a dual allylic amination/chlorination reaction through a selective oxidation manifold under metal-free conditions.



Scheme 1. Oxidation of tetrasubstituted alkenes with the TsNHCl reagent.

Results and Discussion

The reaction was discovered and optimized for 2-phenyl-3-methyl but-2-ene **2a**. Treatment of this tetrasubstituted alkene with 1.2 equivalents of **1** and pivalic acid in dichloroethane did not provide the expected corresponding vicinal aminochlorination product, but gave rise to an unexpected formation of **3a**, which resembles a regioselective aminochlorination at two of the allylic positions (Table 1, entry 1). Since this product **3a** requires two formal allylic oxidation events, the yield increased with the enhancement of chloramine reagent to 2.4 equivalents (entry 2). No reaction takes place at room temperature (entry 3). With acetic acid as activating agent, a room temperature process was again not possible, however, a reaction temperature of 40 ºC led to formation of **3a** (entries 4,5). An an increased yield was observed at 50 ºC (entry 6), and finally, product **3a** could be isolated in 64% from a reaction with 2 equivalents of **1** in combination with 1 equivalent of acetic acid (entry 7). Solvents other than dichloroethane gave inferior results (CH_2Cl_2, 51%, C_6H_5Cl, 45%, EtOAc, 42%).

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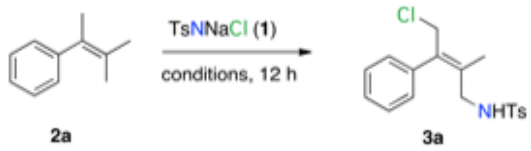
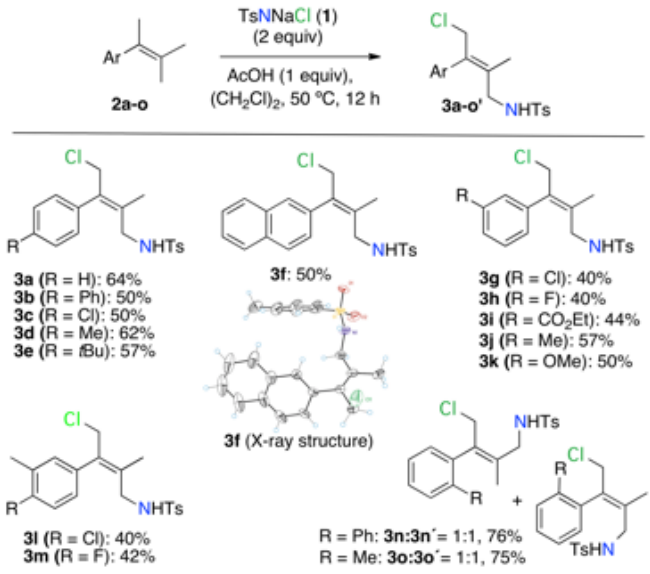


Table 1. Optimization of Reaction Conditions.

Entry	Conditions	Yield [%][a]
1	**1** (1.2 equiv.), *t*BuCO$_2$H (1.2 equiv.), (CH$_2$Cl)$_2$, 50 °C	34
2	**1** (2.4 equiv.), *t*BuCO$_2$H (2.4 equiv.), (CH$_2$Cl)$_2$, 50 °C	43
3	**1** (2.4 equiv.), *t*BuCO$_2$H (2.4 equiv.), (CH$_2$Cl)$_2$, 25 °C	n.c.[b]
4	**1** (2.0 equiv.), AcOH (2.0 equiv.), (CH$_2$Cl)$_2$, 25 °C	n.c.[b]
5	**1** (2.0 equiv.), AcOH (2.0 equiv.), (CH$_2$Cl)$_2$, 40 °C	40
6	**1** (2.0 equiv.), AcOH (2.0 equiv.), (CH$_2$Cl)$_2$, 50 °C	63
7	**1** (2.0 equiv.), AcOH (1.0 equiv.), (CH$_2$Cl)$_2$, 50 °C	64

[a] Isolated yield of **3a** after purification. [b] n.c. = no conversion.



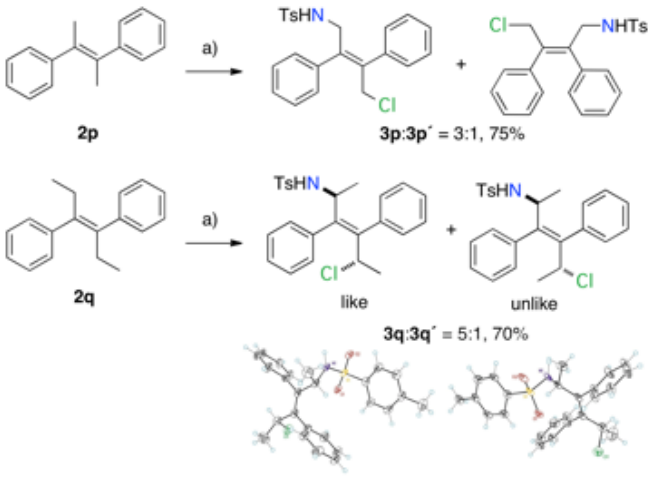
Scheme 2. Aminochlorination of alkenes **2a-o**.

This reaction outcome represents an attractive new synthetic strategy through direct intermolecular double allylic oxidation involving participation of two different heteronucleophiles. In addition, the two allylic carbon-heteroatom bond instalments take place with complete regioselectivity and, the resulting double bond geometry was installed with complete (*E*)-selectivity. The reaction was found to be operative for a series of substrates **2a-o** with different substitution pattern at the aryl group. Para-substitued products **3a-e**, meta-substituted products **3g-k** and higher-substituted products **3l,m** were formed as single regioisomers and with exclusive (E)-double bond geometry. The regioselectivity regarding the allylic carbon-heteroatom bonds was assured from X-ray analysis[18,19] of naphthyl derivative **3f** (Scheme 2).

Only for substrates **2n** and **2o** with their sterically more demanding *ortho*-substituted arenes did the products form as 1:1-(*E*):(*Z*)-isomers regarding the double bond geometry.

However, complete regioselectivity was preserved for the two allylic oxidations.

The scope could be further extended to the 1,2-dialkyl-(*E*)-stilbenes **2p** and **2q** (Scheme 3). The former undergoes the selective 1,4-functionalization and provides the product as a 3:1-mixture with respect to the double bond geometry. The more challenging situation of the diethyl-substituted stilbene **2q** once more exemplified the power of the current transformation: first, an (*E*)-configured double bond was obtained selectively together with a reasonably high diastereomeric excess regarding the two newly formed stereogenic allylic centers. The relative configurations for **3q** and **3q´** were established by X-ray analysis.[19]



Scheme 3. Aminochlorination of tetrasubstituted alkenes **2p,q** and X-ray structural assignment of **3q**, **3q'**. Conditions: a) chloramine-T **1** (2 equiv), acetic acid (1 equiv), dichloroethane, 50°C, 14 h.

At first sight, the reaction outcome appears counterintuitive, since the two allylic C-H functionalization events would be expected to result from radical reactivity, while the ionic reactivity of the *in situ* generated TsNHCl reagent should exclusively address oxidation at the alkene.[17] However, the unexpected double allylic C-H functionalization can be rationalized by the assumption of an initial oxidation at the internal double bond to form a chloronium intermediate, which undergoes elimination to furnish the allylic chloride **A**. This intermediate could alternatively be accessed directly from **2** within an ene reaction.[20] A subsequent elimination event generates a 1,3-butadiene **4**, which undergoes a second regioselective oxidation with TsNHCl followed by an S_N2'-opening of the initial chloronium intermediate **B** or a nucelophilic addition to the corresponding allylic cation **B'** (Figure 1). It is important to note that the overall process liberates additional amounts of acid, which explains why an initial 2:1-ratio between TsNClNa and HOAc (Table 1, entry 5) is sufficient for full

conversion of the chloramine salt. Based on this current understanding, an alternative radical mechanism can be ruled out. No reaction proceeds in the dark laboratory.[21]

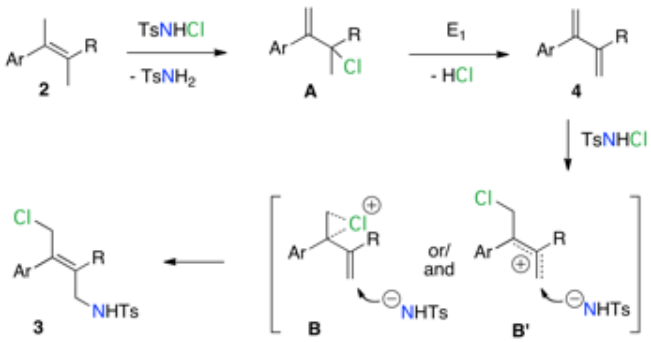
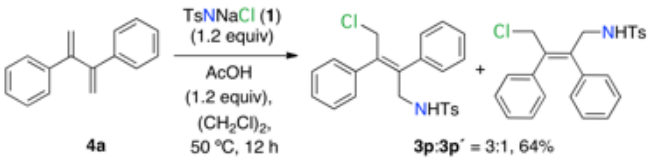


Figure 1. Mechanistic rationale.

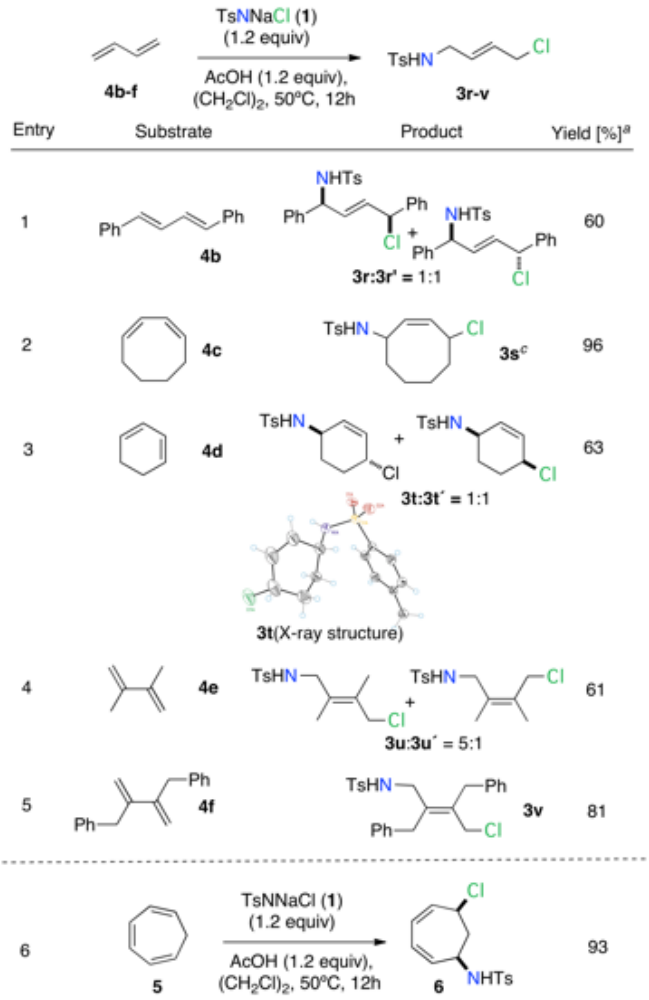
In order to verify the intermediacy of a 1,3-butadiene derivative, the reaction between 2,3-diphenyl-1,3-butadiene **4a** and TsNHCl was investigated. Indeed, the two products **3p** and **3p´** were formed in 64% yield and in an identical 3:1 isomeric ratio (Scheme 4), identical to the outcome from oxidation of the tetrasubstituted alkene **2q** from Scheme 3.



Scheme 4. Aminochlorination of butadiene **4a**.

We realized the aditional attractiveness of this transformation as it should give general access to those products **3** that cannot be accessed through the direct allylic C-H oxidation strategy. Indeed, treatment of several 1,3-butadienes **4b-f** with the TsNHCl reagent was studied more systematically and provided selective 1,4-oxidation products **3r-v** (Scheme 5). First, 1,4-Disubstituted 1,3-butadiene **4b** again follows the general reactivity and provides the 1,4-aminochlorination product as a 1:1-diastereomeric mixture of **3r/3r´** due to the configurational lability of the benzylic chloride (entry 1).[17]

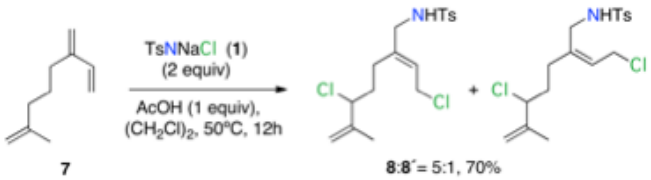
Minakata and Kumatsu reported previously the single pioneering example of an aminochlorination of 1,3-cyclooctadiene **4c** with chloramine-T under carbon dioxide pressure.[15] The yield of **3s** using our methodology compares well with the reported 70% for the only precedence of this transformation under the previous conditions. The related 1,3-cyclohexadiene **4d** forms aminochlorination derivatives **3t/3t'** in good yield as a 1:1-diastereomeric mixture (entries 2,3). The X-ray structure of **3t** allowed for a definite structural assignment of the isomers.§ Isoprene **4j** and 2,3-dimethyl-1,3-butadiene **4e** undergo clean aminochlorination reaction as well forming products **3u/3u'** in a 5:1-mixture of the corresponding double bond isomers (entry 4). For the dibenzyl derivative **4f**, steric reasons lead to the formation of a single product **3v** in high yield (entry 5). The reaction also proceeds for higher conjugated substrates as demonstrated for the case of 1,3,5-cycloheptatriene **7**, which forms the 1,6-aminochlorination product **8** as a single isomer in 93% isolated yield, and again demonstrates the inherent possibilities resulting from the **1**/HOAc reagent combination.



Scheme 5. Regioselective 1,4-aminochlorination of 1,3-butadienes (entries 1-5) and 1,3,5-heptatriene (entry 6). [a]Isolated yield after purification. [b]10:1 ratio of regioisomers. [c]10:1 diastereomeric mixture.

Finally, the reaction could also be conducted for the 1,3-butadiene unit of myrcene **7**. In addition to the expected regioselective aminochlorination reaction at the butadiene site of this molecule, the product displayed an additional carbon chlorine bond derived from an unexpected allylic chlorination following a Wohl-Ziegler pathway (Scheme 6). This triple allylic C-H functionalization within a single oxidative transformation

adds to a recent impressive study by Braddock on full oxidative saturation of myrcene.[22]



Scheme 6. Triple C-H oxidation of myrcene (**7**) with the **1**/HOAc reagent combination.

Conclusions

In summary, we have reported a new intermolecular allylic oxidation reaction that converts tetrasubstituted alkenes into the corresponding 4-chloro-but-2-enyl amine derivatives within a double allylic amination process. This process proceeds with excellent regio- and chemoselectivity under mild conditions and without the requirement of any promoter or catalyst. It exemplifies that efficient protocols for unprecedented oxidative C-H functionalization from rather unexpected pathways may readily derive exploring the reactivity pattern of well-established haloamine reagents.

Experimental Section

General. All solvents, reagents and all deuterated solvents were purchased from Aldrich and TCI. Column chromatography was performed with silica gel (Merck, type 60, 0.063-0.2 mm). NMR spectra were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometers, respectively. All chemical shifts in NMR experiments were reported as ppm downfield from TMS. The following calibrations were used: $CDCl_3$ δ = 7.26 and 77.0 ppm. MS (ESI-LCMS) experiments were performed using an Agilent 1100 HPLC with a Bruker micro-TOF instrument (ESI). A Supelco C8 (5 cm x 4.6 mm, 5 µm particles) column was used with a linear elution gradient from 100% H_2O (0.5% HCO_2H) to 100% MeCN in 13 min at a flow rate of 0.5 mL/min. MS (EI) and HRMS experiments were performed on a Kratos MS 50 within the service centers at ICIQ. IR spectra were taken in a Bruker Alpha instrument in the solid state. The following compounds were commercially available and directly used as received: 2,3-dimethylbuta-1,3-diene, cycloocta-1,3-diene, cyclohexa-1,3-diene, cyclohepta-1,3,5-triene, (1*E*, 3*E*)-1,4-diphenylbuta-1,3-diene, myrcene, (2,3-dimethylenebutane-1,4-diyl)dibenzene and (*E*)-but-2-ene-2,3-diyldibenzene.

Synthesis of tetrasubstituted alkenes 2. The synthesis of tetrasubstituted alkenes was adapted from a previously reported procedure.[23] A representative example is as follows: 2-bromo-3-methylbut-2-ene (1.0 equiv) and $Pd(PPh_3)_4$ (5 mol%) are added to a Schlenk tube. The tube is evacuated and refilled with Argon three times, and DME (31 mL) is added. The reaction mixture is then stirred at room temperature for 20 min. Sodium carbonate (1 equiv), water (8 mL) and the boronic acid (2.1 equiv) are added, and the reaction is heated at reflux for 18 h. The reaction mixture is cooled to room temperature, and the solvent is removed under reduced pressure. The product is extracted with diethylether (3x), washed with brine, and concentrated. Column chromatography on silica gel (100% hexane) gives the tetrasubstituted alkene products in good yields.

1-(*tert*-Butyl)-4-(3-methylbut-2-en-2-yl)benzene (2e): Obtained as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 9H), 1.61 (s, 3H), 1.82 (s, 3H), 1.96 (s, 3H), 7.06 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.8, 22.3, 31.6, 34.5, 124.9, 127.1, 128.2, 129.9, 142.3, 148.5. IR ν = 2692, 2910, 2864, 1508, 1460, 1396, 1363, 1269, 1133, 1112, 1017, 834, 758, 616 cm^{-1}. HRMS: calcd for $C_{15}H_{23}$: 203.1794; found: 203.1796.

General procedure for the dual C-H functionalization: A Pyrex tube equipped with a stirrer bar is charged with 73 mg chloramine-T (0.22 mmol, 2.0 equiv), 0.01 mL acetic acid (0.11 mmol, 1.0 equiv) and the alkene (0.11 mmol, 1.0 equiv) in 0.6 mL of absolute dichloroethane. The solution is stirred at 50 ºC for 20 h. After cooling down to room temperature, CH_2Cl_2 is added and the resulting solution is washed three times with saturated aqueous solution of $NaHCO_3$. The solvent is evaporated under reduced pressure and the crude product is purified by chromatography (silica gel, *n*-hexane/ethyl acetate, 4/1, v/v) to give the pure product.

(*E*)-*N*-(4-Chloro-2-methyl-3-phenylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3a): Obtained as white foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 2.40 (s, 3H), 3.38 (d, *J* = 6.3 Hz, 2H), 4.26 (s, 2H), 4.29 (t, *J* = 6.3 Hz, 1H, NH), 7.04-7.06 (m, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.26-7.28 (m, 3H), 7.55 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5, 21.6, 45.6, 46.9, 127.1, 127.6, 128.5, 128.6, 129.8, 134.3, 136.6, 139.4, 143.5. IR ν = 3275, 2956, 2925, 2856, 1708, 1598, 1492, 1442, 1323, 1156, 1092, 1053, 908, 813 cm^{-1}. HRMS: calcd for $C_{18}H_{20}ClNNaO_2S$: 372.0796; found: 372.0795.

(*E*)-*N*-(3-([1,1'-Biphenyl]-4-yl)-4-chloro-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3b): Obtained as white foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s, 3H), 2.26 (s, 3H), 3.43 (d, *J* = 5.1 Hz, 2H), 4.30 (s, 2H), 4.42 (br t, *J* = 8.9 Hz, 1H, NH), 7.12 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.36-7.39 (m, 1H), 7.45-7.48 (m, 4H), 7.55-7.58 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.6, 21.5, 45.5, 47.1, 127.0, 127.1, 127.2, 127.6, 128.9, 129.7, 134.5, 136.5, 138.3, 140.5, 140.6, 143.6. IR ν =3275, 2960, 2956, 2925, 2856, 1492, 1442, 1323, 1156, 1092, 1053, 909, 813 cm^{-1}. HRMS: calcd for $C_{24}H_{24}ClNNaO_2S$: 448.1109; found: 448.1108.

(*E*)-*N*-(4-Chloro-3-(4-chlorophenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3c): Obtained as white foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 2.43 (s, 3H), 3.33 (d, *J* = 5.6 Hz, 2H), 4.22 (s, 2H), 4.46 (t br, *J* = 6.1 Hz, 1H, NH), 6.97 (d, *J* = 8.4 Hz, 2H), 7.21 (dd, *J* = 9.2, 8.1 Hz, 4H), 7.54 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5, 21.7, 45.3, 46.9, 127.1, 128.9, 129.8, 129.9, 133.7, 134.9, 135.7, 136.3, 137.7, 143.8. IR: ν = 3276, 2953, 2922, 2854, 1490, 1325, 1159, 1092, 831 cm^{-1}. HRMS: calcd. for $C_{18}H_{19}Cl_2NNaO_2S$: 406.0404; found: 406.0406.

(*E*)-*N*-(4-Chloro-2-methyl-3-(*p*-tolyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3d): Obtained as white foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3H), 2.33 (s, 3H), 2.40 (s, 3H), 3.39 (d, *J* = 6.2 Hz, 2H), 4.24 (s, 2H), 4.48 (t, *J* = 6.2 Hz, 1H, NH), 6.93 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5, 21.3, 21.6, 45.7, 46.9, 127.2, 128.4, 129.2, 129.7, 134.0, 136.4, 136.7, 137.3, 143.4. IR ν = 3273, 3024, 2923, 2855, 1598, 1442, 1323, 1256, 1184, 1157, 1092, 1052, 950, 813, 662 cm^{-1}. HRMS: calcd for $C_{19}H_{22}ClNNaO_2S$: 386.0952; found: 386.0957.

(*E*)-*N*-(3-(4-(*tert*-Butyl)phenyl)-4-chloro-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3e): Obtained as white foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 9H), 1.92 (s,

3H), 2.39 (s, 3H), 3.40 (d, *J* = 6.3 Hz, 2H), 4.25 (s, 2H), 4.49 (t, *J* = 6.3 Hz, 1H, NH), 6.99 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.26-7.28 (m, 2H), 7.59 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5, 21.6, 31.4, 34.6, 45.8, 47.0, 125.4, 127.2, 128.2, 129.7, 134.1, 136.4, 136.6, 136.8, 143.4, 150.5. IR ν = 3273, 2961, 2926, 2867, 1598, 1401, 1266, 1158, 1092, 1054, 837, 813, 704 cm^{-1}. HRMS: calcd for $C_{22}H_{28}ClNNaO_2S$: 428.1417; found: 428.1421.

(*E*)-*N*-(4-Chloro-2-methyl-3-(naphthalen-2-yl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3f): Obtained as a white solid following the general procedure. m.p: 128-129 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3H), 2.24 (s, 3H), 3.39 (d, *J* = 6.2 Hz, 2H), 4.34 (s, 2H), 4.45 (t, *J* = 8.0 Hz, 1H, NH), 6.94 (d, *J* = 8.4 Hz, 2H), 7.16 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.49-7.52 (m, 3H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.75-7.78 (m, 1H), 7.80-7.84 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7, 21.5, 45.6, 47.1, 126.3, 126.5, 126.6, 126.9, 127.5, 127.8, 128.1, 128.4, 129.6, 132.7, 133.2, 134.7, 136.2, 136.8, 136.9, 143.4. IR ν = 3266, 3055, 2953, 2923, 2853, 1597, 1496, 1184, 1155, 1091, 1051, 812, 750, 721, 705, 683, 663, 573 cm^{-1}. HRMS: calcd for $C_{22}H_{22}ClNNaO_2S$: 422.0905; found: 422.0934.

(*E*)-*N*-(4-Chloro-3-(3-chlorophenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3g): Obtained as yellow foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 3H), 2.40 (s, 3H), 3.35 (d, *J* = 6.2 Hz, 2H), 4.22 (s, 2H), 4.39 (brt, *J* = 6.9 Hz, 1H, NH), 6.94 (dt, *J* = 7.3, 1.5 Hz, 1H), 7.06 (t, *J* = 1.8 Hz, 1H), 7.18-7.25 (m, 4H), 7.56 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.4, 21.7, 45.2, 46.8, 127.0, 127.1, 127.9, 128.6, 129.8, 129.9, 143.5, 135.3, 135.4, 136.4, 141.2, 143.7. IR ν = 3270, 2958, 2918, 2849, 1594, 1406, 1324, 1158, 1093, 813, 750, 663 cm^{-1}. HRMS: calcd for $C_{18}H_{19}Cl_2NNaO_2S$: 406.0406; found: 406.0406.

(*E*)-*N*-(4-Chloro-3-(3-fluorophenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3h): Obtained as yellow foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 2.40 (s, 3H), 3.36 (d, *J* = 6.2 Hz, 2H), 4.22 (s, 2H), 4.51 (t, *J* = 6.3 Hz, 1H, NH), 6.77 (ddd, *J* = 9.5, 2.6, 1.5 Hz, 1H), 6.83 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.95 (tdd, *J* = 8.5, 2.6, 1.0 Hz, 1H), 7.20-7.24 (m, 3H), 7.57 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.3, 21.5, 45.1, 46.7, 114.5 (d, $J_{C\text{-}F}$ = 20.9 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.3 Hz), 124.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 126.9, 129.7, 130.0 (d, $J_{C\text{-}F}$ = 8.5 Hz), 134.9, 135.3, 136.3, 141.4 (d, $J_{C\text{-}F}$ = 7.6 Hz), 143.6, 162.5 (d, $J_{C\text{-}F}$ = 247.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -112.4. IR ν = 3269, 2959, 2929, 2850, 1580, 1431, 1322, 1151, 1092, 663, 551 cm^{-1}. HRMS: calcd for $C_{18}H_{19}ClFNNaO_2S$: 390.0701; found: 390.0690.

(*E*)-Ethyl 3-(1-chloro-3-methyl-4-(4-methylphenylsulfonamido)but-2-en-2-yl)benzoate (3i): Obtained as yellow foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.1 Hz, 3H), 1.96 (s, 3H), 2.38 (s, 3H), 3.33 (d, *J* = 6.2 Hz, 2H), 4.26 (s, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 4.50 (brt, 1H, NH), 7.17 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.72 (s, 1H), 7.94 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.5, 16.5, 21.6, 45.3, 46.9, 61.3, 127.1, 128.8, 129.5, 129.7, 130.9, 133.2, 135.1, 135.8, 136.4, 139.6, 143.6, 166.3. IR ν = 3260, 3021, 2982, 2959, 2926, 1717, 1431, 1303, 1251, 1158, 1092, 751 cm^{-1}. HRMS: calcd for $C_{21}H_{24}ClNNaO_4S$: 444.1007; found: 444.0993.

(*E*)-*N*-(4-Chloro-2-methyl-3-(*m*-tolyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3j): Obtained as yellow foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 2.30 (s, 3H), 2.40 (s, 3H), 3.39 (d, *J* = 6.1 Hz, 2H), 4.24 (s, 2H), 4.32 (brt, 1H, NH), 6.83 (d, *J* = 7.7 Hz, 1H), 6.87 (s, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5, 21.5, 21.6, 125.6, 127.1, 128.4, 128.5, 129.1, 129.7, 134.1, 136.7, 136.9, 138.3, 139.4, 143.5. IR ν = 3277, 2956, 2922, 2852, 1455, 1322, 1157, 1092, 1053, 662, 551 cm^{-1}. HRMS: calcd for $C_{19}H_{22}ClNNaO_2S$: 386.0941; found: 386.0952.

(*E*)-*N*-(4-Chloro-3-(3-methoxyphenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3k): Obtained as yellow foam following the general procedure**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 2.40 (s, 3H), 3.39 (d, *J* = 6.3 Hz, 2H), 3.77 (s, 3H), 4.24 (s, 2H), 4.44 (brt, 1H, NH), 6.61-6.63 (m, 2H), 6.80 (d, *J* = 8.3 Hz, 1H), 7.15-7.21 (m, 3H), 7.56 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5, 21.6, 45.5, 46.9, 55.3, 113.3, 114.2, 120.9, 127.1, 129.6, 129.7, 134.4, 136.5, 136.6, 140.8, 143.5, 159.7. IR ν =: 3276, 3020, 2958, 2925, 2854, 1320, 1304, 1215, 1159, 746 cm^{-1}. HRMS: calcd for $C_{19}H_{22}ClNNaO_3S$: 402.0901; found: 402.0895.

(*E*)-*N*-(4-Chloro-3-(3-chloro-4-methylphenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3l): Obtained as yellow foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 2.35 (s, 3H), 2.40 (s, 3H), 3.36 (d, *J* = 6.2 Hz, 2H), 4.21 (s, 2H), 4.45 (brt, *J* = 6.3 Hz, 1H, NH), 6.84 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.6, 19.9, 21.7, 45.4, 46.9, 127.0, 127.2, 128.9, 129.7, 131.0, 134.5, 134.9, 135.4, 135.5, 136.5, 138.4, 143.6. IR ν = 3276, 2956, 2923, 2851, 1436, 1321, 1158, 1050, 813, 550 cm^{-1}. HRMS: calcd for $C_{19}H_{21}Cl_2NNaO_2S$: 420.0562; found: 420.0553.

(*E*)-*N*-(4-Chloro-3-(3-fluoro-4-methylphenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3m): Obtained as yellow foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3H), 2.25 (s, 3H), 2.40 (s, 3H), 3.37 (d, *J* = 5.8 Hz, 2H), 4.21 (s, 2H), 4.51 (brt, 1H, NH), 6.69-6.72 (m, 2H), 7.06 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.5, 16.4, 21.7, 45.4, 46.9, 115.2 (d, $J_{C\text{-}F}$ = 22.3 Hz), 124.1 (d, $J_{C\text{-}F}$ = 3.5 Hz), 126.6, 127.2, 129.7, 131.6 (d, $J_{C\text{-}F}$ = 5.7 Hz), 134.7, 135.6, 136.5, 138.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 143.6, 161.1 (d, $J_{C\text{-}F}$ = 246.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -116.8. IR ν = 3271, 2958, 2925, 2853, 1406, 1323, 1159, 812, 663 cm^{-1}. HRMS: calcd for $C_{19}H_{21}ClFNNaO_2S$: 404.0858; found: 404.0846.

(*E*)-*N*-(3-([1,1'-Biphenyl]-2-yl)-4-chloro-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3n) and (*Z*)-*N*-(3-([1,1'-Biphenyl]-2-yl)-4-chloro-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3n´): Obtained as yellow foams following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.80 (s, 6H), 2.41 (s, 6H), 3.15-3.17 (m, 2H), 3.28-3.30 (m, 2H), 3.48 (brt, 2H, NH), 3.87-3.89 (m, 2H), 4.28-4.30 (m, 2H), 7.16-7.18 (m, 3H), 7.19-7.21 (m, 2H), 7.24 (d, *J* = 8.3 Hz, 4H), 7.29 (dd, *J* = 7.2, 1.5 Hz, 4H), 7.33-7.37 (m, 9H), 7.57 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.9, 21.7, 45.7, 47.2, 127.1, 127.6, 127.7, 128.2, 128.5, 129.2, 129.7, 130.1, 130.3, 134.6, 135.4, 136.8, 137.5, 140.2, 140.9, 143.5. IR ν = 3275, 3060, 3022, 2925, 2855, 1495, 1156, 1119, 1092, 1052, 1009, 813, 746, 721, 701, 663 cm^{-1}. HRMS: calcd for $C_{24}H_{24}ClNNaO_2S$: 448.1108; found: 448.1108.

(*E*)-*N*-(4-Chloro-2-methyl-3-(*o*-tolyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3o) and (*Z*)-*N*-(4-Chloro-2-methyl-3-(*o*-tolyl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3o´): Obtained as white foams following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 6H), 2.12 (s, 6H), 2.42 (s, 6H), 3.22-3.24 (m, 2H), 3.31-3.33 (m, 2H), 4.12-4.14 (m, 2H), 4.21 (brt, *J* = 6.4 Hz, 2H, NH), 4.36-4.38 (m, 2H), 6.97 (m, 2H), 7.11-7.16 (m, 4H), 7.19-7.22 (m, 6H), 7.55 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.1, 19.8, 21.6, 45.2, 46.9, 126.0, 127.0, 127.8, 129.4, 129.8, 130.4, 134.7, 135.5, 136.6, 138.6, 143.5. IR ν = 3274, 2957, 29221, 2853, 1598, 1488, 1400, 1166, 1056, 982 cm^{-1}. HRMS: calcd for $C_{19}H_{22}ClNNaO_2S$: 386.0952; found: 386.0941.

(*E*)-*N*-(4-Chloro-2,3-diphenylbut-2-en-1-yl)-4-methylbenzenesulfonamide 3p and (*Z*)-*N*-(4-Chloro-2,3-diphenylbut-

2-en-1-yl)-4-methylbenzenesulfonamide (3p´): Obtained as white foams following the general procedure. *Major diastereomer:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 3.75 (d, *J* = 6.1 Hz, 2H), 4.11 (s, 2H), 4.24 (t, *J* = 6.3 Hz, 1H, NH), 7.18 (d, *J* = 8.3 Hz, 2H), 7.22-7.27 (m, 4H), 7.37-7.40 (m, 6H), 7.43 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 46.5, 46.9, 127.2, 128.1, 128.4, 128.5, 128.6, 128.7, 128.9, 129.6, 136.3, 137.4, 138.1, 138.2, 138.3, 143.4. IR ν = 3227, 3023, 2949, 2934, 2885, 2854, 1425, 1345, 1185, 1029, 940, 790, 767, 699 cm^{-1}. HRMS: calcd for $C_{23}H_{21}ClNO_2S$: 410.0987; found: 410.0987.

(±)-*N*-(*E*)-5-Chloro-3,4-diphenylhex-3-en-2-yl)-4-methylbenzenesulfon-amides (3q) and (3q´): Obtained as white foam following the general procedure. *Major diastereomer:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 6.3 Hz, 3H), 1.23 (d, *J* = 6.7 Hz, 3H), 2.46 (s, 3H), 3.99-4.04 (m, 1H), 4.56 (q, *J* = 6.7 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.36-7.50 (m, 10H), 7.57 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 22.3, 24.0, 50.8, 57.6, 127.3, 127.9, 128.2, 129.7, 135.2, 135.5, 137.8, 139.5, 141.4, 143.4. IR ν = 3286, 2964, 2924, 2854, 1598, 1494, 1421, 1185, 1161, 814, 753, 701, 660, 622, 585, 566 cm^{-1}. HRMS: calcd for $C_{25}H_{25}ClNO_2S$: 438.1306; found: 438.1300. *Minor diastereomer:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 6.7 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H), 2.42 (s, 3H), 3.93-3.99 (m, 1H), 4.61 (q, *J* = 6.7 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.36-7.50 (m, 10H), 7.56 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 22.3, 23.5, 50.7, 58.2, 127.3, 127.7, 128.1, 129.6, 135.3, 135.5, 137.6, 139.4, 141.7, 143.4.

General procedure for the aminochlorination of 1,3-butadienes: A Pyrex tube equipped with a stirrer bar is charged with 44 mg chloramine-T (0.22 mmol, 1.2 equiv), 0.013 mL acetic acid (0.13 mmol, 1.2 equiv) and the butadiene (0.11 mmol, 1.0 equiv) in 0.5 mL of absolute dichloroethane. The solution is stirred at 50 ºC for 20 h. After cooling down to room temperature, CH_2Cl_2 is added and the resulting solution is washed three times with saturated aqueous solution of $NaHCO_3$. The solvent is evaporated under reduced pressure and the crude product is purified by chromatography (silica gel, *n*-hexane/ethyl acetate, 4/1, v/v) to give the pure product.

***N*-((1*S*,4*S*,*E*)-4-Chloro-1,4-diphenylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3r) and *N*-((1*S*,4*R*,*E*)-4-Chloro-1,4-diphenylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3r´):** Obtained as a 1:1-mixture as white foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 2.33 (s, 3H), 4.69-4.72 (m, 1H), 4.74 (dd, *J* = 8.0 Hz, 2H), 4.82 (dd, *J* = 8.9, 50 Hz, 1H), 5.63 (d, *J* = 7.4 Hz, 1H, NH), 5.68 (d, *J* = 8.4 Hz, 1H, NH), 5.87 (dd, *J* = 15.7, 9.0 Hz, 1H), 6.06-6.12 (m, 1H), 6.56 (dd, *J* = 15.7, 2.2 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 4H), 7.10-7.31 (m, 22H), 7.54-7.58 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 62.1, 62.4, 66.3, 66.7, 125.1, 125.4, 126.9, 127.0, 127.1, 127.2, 127.5, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 129.4, 129.5, 143.6, 134.8, 135.4, 135.5, 136.1, 137.0, 137.2, 137.3, 143.3, 143.4. IR ν = 3270, 3060, 3029, 2958, 2922, 2865, 1494, 1324, 1155, 1118, 1066, 964, 811, 748, 694, 665, 600 cm^{-1}. HRMS: calcd for $C_{23}H_{21}ClNO_2S$: 410.0987; found: 410.0985.

(*Z*)-*N*-(4-Chlorocyclooct-2-en-1-yl)-4-methylbenzenesulfonamide (3s):[15] Obtained as a yellow oil following the general procedure. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31-1.88 (m, 6H), 1.98-2.13 (m, 2H), 2.43 (s, 3H), 4.45 (d, *J* = 7.2 Hz, 1H, NH), 4.59-4.65 (m, 1H), 4.69 (ddd, *J* = 10.4, 6.6, 4.6 Hz, 1H), 5.17 (ddd, *J* = 11.9, 7.2, 0.8 Hz, 1H), 5.66 (ddd, *J* = 11.9, 6.5, 1.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 22.8, 23.7, 34.9, 37.4, 51.5, 57.6, 127.5, 129.8, 131.1, 132.1, 137.6, 146.6. Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31-1.88 (m, 6H), 1.98-2.13 (m, 2H), 2.43 (s, 3H), 4.45 (d, *J* = 7.2 Hz, 1H, NH), 4.59-4.65 (m, 1H), 4.69 (ddd, *J* = 10.4, 6.6, 4.6 Hz, 1H), 5.11 (ddd, *J* = 10.9, 8.4, 1.5 Hz, 1H), 5.52 (ddd, *J* = 10.9, 7.9, 1.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 22.8, 23.7, 34.9, 37.4, 51.5, 57.6, 127.5, 129.8, 131.1, 132.1, 137.6, 146.6.

***N*-(4-Chlorocyclohex-2-en-1-yl)-4-methylbenzenesulfonamide (3t):** Obtained as an inseparable 1:1 diasteromeric mixture as yellow oil following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76-1.80 (m, 2H), 1.98-2.02 (m, 2H), 2.43 (s, 3H), 3.87-3.92 (m, 1H), 4.45-4.46 (m, 1H), 5.52 (dd, *J* = 9.9, 2.6 Hz, 1H), 5.84 (dtd, *J* = 8.3, 4.3, 2.0 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 26.2, 30.4, 49.5, 53.1, 127.1, 129.9, 131.0, 131.1, 131.2, 131.3, 138.3, 143.7. IR ν = 3247, 2958, 2923, 2866, 1494, 1433, 1080, 979, 810, 663, 582 cm^{-1}. HRMS: calcd for $C_{13}H_{16}ClNNaO_2S$: 308.0482; found: 308.0480.

(*E*)-*N*-(4-Chloro-2,3-dimethylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3u) and (*Z*)-*N*-(4-Chloro-2,3-dimethylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3u´): Obtained as a 5:1 diasteromeric mixture as yellow oil following the general procedure. *Major diastereomer:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (s, 3H), 1.73 (s, 3H), 2.46 (s, 3H), 3.64 (d, *J* = 6.0 Hz, 2H), 3.99 (s, 2H), 4.41 (t, *J* = 6.0 Hz, 1H, NH), 7.33 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.7, 16.8, 21.7, 45.9, 46.2, 127.3, 129.9, 130.3, 130.5, 136.9, 143.7. IR ν(cm^{-1}): 3296, 2969, 2923, 2865, 1493, 1419, 1255, 1184, 1151, 839, 812, 661, 550. HRMS: calcd for $C_{13}H_{17}ClNO_2S$: 286.0677; found: 286.0674. *Minor diastereomer:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (s, 3H), 1.76 (s, 3H), 2.46 (s, 3H), 3.62 (d, *J* = 6.0 Hz, 2H), 3.97 (s, 2H), 4.46 (t, *J* = 6.0 Hz, 1H, NH), 7.34 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.7, 17.8, 21.7, 45.4, 45.5, 127.3, 129.9, 130.3, 130.5, 136.9, 143.7.

(*E*)-*N*-(2,3-Dibenzyl-4-chlorobut-2-en-1-yl)-4-methylbenzenesulfonamide (3v): Obtained as a white foam following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 3.54-3.56 (m, 4H), 3.60 (s, 2H), 4.11 (s, 2H), 7.06-7.11 (m, 4H), 7.22-7.31 (m, 8H), 7.56-7.58 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 35.8, 36.5, 43.7, 43.8, 126.8, 126.9, 127.3, 128.6, 128.8, 129.9, 135.2, 135.8, 136.4, 138.1, 138.9, 143.7. IR ν = 3277, 3061, 3027, 2924, 1493, 1254, 1121, 1053, 843, 698, 665, 550 cm^{-1}. HRMS: calcd for $C_{25}H_{26}ClNNaO_2S$: 462.1265; found: 462.1268.

***N*-(6-Chlorocyclohepta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (6):** Obtained as yellow oil following the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (ddd, *J* = 7.1, 5.5, 3.2 Hz, 2H), 2.43 (s, 3H), 4.28-4.33 (m, 1H), 4.60-4.64 (m, 1H), 4.69 (d, *J* = 8.3 Hz, 1H, NH), 5.74-5.76 (m, 2H), 5.78-5.83 (m, 1H), 5.89-5.93 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 41.6, 50.6, 55.7, 123.7, 125.2, 127.4, 129.9, 133.3, 137.2, 137.4, 143.8. IR ν = 3270, 3029, 2925, 2858, 1493, 1325, 1217, 1155, 691 cm^{-1}. HRMS: calcd for $C_{14}H_{16}ClNNaO_2S$: 320.0482; found: 320.0477.

(*E*)-*N*-(5-Chloro-2-(2-chloroethylidene)-6-methylhept-6-en-1-yl)-4-methylbenzenesulfonamide (8) and (*Z*)-*N*-(5-Chloro-2-(2-chloroethylidene)-6-methylhept-6-en-1-yl)-4-methylbenzenesulfonamide (8´): Obtained as a 5:1 diasteromeric mixture as yellow oil following the general procedure. *Major regioisomer:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 3H), 1.84 (m, 2H), 2.10-2.16 (m, 1H), 2.18-2.24 (m, 1H), 2.43 (s, 3H), 3.52 (d, *J* = 6.3 Hz, 2H), 4.02 (d, *J* = 7.9 Hz, 2H), 4.25 (t, *J* = 7.1 Hz, 1H), 4.82 (brt, 1H, NH), 4.90 (d, *J* = 1.3 Hz, 1H), 5.00 (d, *J* = 1.3 Hz, 1H), 5.60 (t, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.3, 21.6, 25.6, 34.8, 39.5, 48.3, 66.0, 114.6, 125.2, 127.2, 129.9, 136.8, 139.3, 143.8, 143.9. IR ν = 3250, 2960, 2922, 2874, 1494, 1093, 662, 552, 479 cm^{-1}. HRMS: calcd for $C_{17}H_{23}Cl_2NNaO_2S$: 398.0719; found: 398.0719. *Minor regioisomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 3H), 1.84 (m, 2H), 2.10-2.16 (m, 1H), 2.18-2.24 (m, 1H), 2.43 (s, 3H),

3.52 (d, *J* = 6.3 Hz, 2H), 3.93 (d, *J* = 2.7 Hz, 1H), 3.97 (m, 1H), 4.82 (brt, 1H, NH), 4.89 (d, *J* = 1.2 Hz, 1H), 4.98 (d, *J* = 1.2 Hz, 1H), 5.31 (t, *J* = 6.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.3, 21.6, 25.6, 34.8, 39.5, 48.3, 66.0, 114.6, 125.2, 127.2, 129.9, 136.8, 139.3, 143.8, 143.9.

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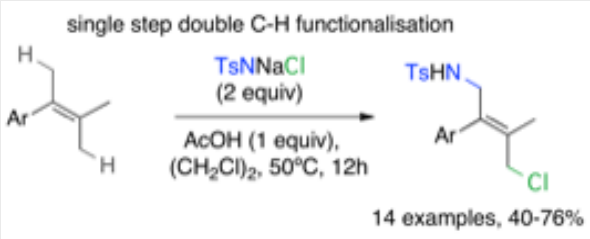

C-H Functionalisation

*Claudio Martínez, Kilian Muñiz**

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Dual Intermolecular Allylic C-H Functionalization within the Tetrasubstituted Alkene Scaffold

A simple activation of chloramine-T by Brønstedt acid generates N-chlorotosylamide, which serves as a unique reagent for the selective double C-H functionalization in allylic position of tetrasubstituted alkenes.