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Synthesis of 2-amino-1,3-dienes by chromium-catalyzed addition of silylated propargyl bromides to imines

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ABSTRACT

(Silyl)methylallenic amines were synthesized by the chromium-catalyzed addition of (4-bromobutynyl) trimethylsilane to tosyl imines. Regioisomeric mixtures of the desired allene and the corresponding alkyne were obtained. Allenic imines were then treated with TBAF to afford 2-aminomethyl-1,3-dienes in good yields (62–92%). In the presence of a Lewis acid, silylallenic imines were added to benzaldehyde dimethylacetal to give highly functionalized dienes with excellent yields and good to excellent diastereomeric ratios.

1. Introduction

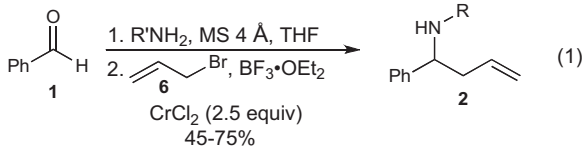
The addition of carbon nucleophiles to imines is a powerful and well-studied transformation for the preparation of nitrogen-containing organic compounds and for the synthesis of biologically active natural products.[1] However, methods for the preparation of 2-aminomethyl-1,3-dienes are still uncommon.

An early report describes the palladium-catalyzed coupling of amines with 2 equiv of propadiene gas to afford 2-aminomethyl-1,3-dienes along with bis(dienyl)amine byproducts.[2] Hosomi et al.[3] reported the Kumada cross-coupling of Grignard reagents prepared from 2-bromo-3-aminopropene to vinyl halides for the synthesis of 2-aminomethyl-1,3-dienes. This method proved to be efficient for the synthesis of 1,3-dienes, which were further used in Diels–Alder cycloaddition reactions. Unfortunately, the synthesis of the starting 2-bromo-3-aminopropene is not convenient. Although both methods afford the desired products with moderate to good yield, the substrate scope is limited. More recently, metathesis of aryl propargylic amines with ethylene, in the presence of Grubbs' catalyst, was utilized for the synthesis of 2-aminomethyl-1,3-dienes.[4] These dienes can also be obtained by a regioselective titanium-mediated cross-coupling of aryl imines with homoallenic alcohols.[5] One of the advantages of this method is the ability to use a range of protecting groups on nitrogen. Unfortunately, the use of excess titanium complex is required. Finally, 2-aminomethyl-1,3-dienes have been efficiently prepared by an indium mediated[6] reaction of imines with 1,4-dibromo-2-butyne. The scope of this method is broad and, in the presence of acid, imines can be formed in situ from aniline and the corresponding aldehyde to afford the desired dienes in a three-component reaction.

In view of the limited number of methods for the synthesis of 2-aminomethyl-1,3-dienes and aiming to expand the scope of the chromium-catalyzed[7–9] synthesis of substituted 1,3-butadienes from aldehydes and ketones previously developed in our laboratory,[10,11] we studied the reaction of imine electrophiles with (4-bromobut-2-yn-1-yl)trimethylsilane **8**.

2. Results and discussion

Metal-catalyzed additions to imines are well-known transformations (e.g., allylation, alkylation, propargylation, etc.)[1] Zinc, magnesium, tin, palladium,[12] and boron[13] are examples of metals used for this purpose. However, only one example of a stoichiometric chromium-mediated addition to imines has been reported (Eq. 1).[14] Therefore, we decided to first employ allyl bromide in a chromium-catalyzed synthesis of homoallylic amines to establish baseline reactivity in a catalytic process.



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When *N*-phenyl and *N*-benzyl imines **3a** or **4a** were combined with allyl bromide in the presence of a catalytic amount of $CrCl_3$, 2 equiv of Mn^0 and TMSCl, the desired product was not observed, albeit the imines were consumed as indicated by TLC (Table 1, entries 1 and 2). On the contrary, when *N*-tosyl imine **5a** was used, the desired product was obtained in 80% conversion. It was suspected that the product from the allylation of imines **3a** and **4a** was being formed but may be coordinating to the chromium salts present in the reaction mixture. If this were the case, the product would be lost after filtration of the reaction mixture though silica. In order to recover the desired adducts, an excess of Et_3N and DMF was added to the mixture prior to filtration, expecting the additives would coordinate to the chromium salts and release the desired products (entries 4–6). This procedure increased the yield in all cases, but we observed that tosyl imine **5a** (entry 7), activated by the presence of an electron-withdrawing group, afforded the corresponding adduct with higher conversion than the *N*-benzyl or *N*-phenyl derivatives.

Encouraged by these results, we directed our attention to the synthesis of (silylmethyl)allenic amines. The corresponding imines were mixed with (4-bromobut-2-yn-1-yl)trimethylsilane (**8**) in the presence of $CrCl_2$ (10 mol %), Mn^0 (2 equiv) and TMSCl. A considerable decrease in the reactivity of imines **3a** and **4a**, with respect to the allylation reaction, was observed (Table 2). In addition, after 36 h, only traces of product were observed when electron deficient **3b** was used. On the other hand, when tosyl imine **5a** was used, the desired adduct was obtained with 64% conversion. Thus, the presence of the electron withdrawing tosyl group appears to be necessary to increase the electrophilicity of the substrate under these reaction conditions. The conversion did not improve when the temperature of the reaction was increased to 60 °C. Furthermore, addition of excess propargyl bromide **8** after 12 h did not improve substrate conversion.

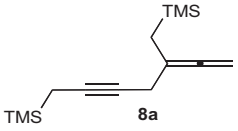
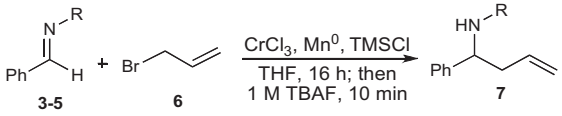


Table 1
Chromium-catalyzed allylation of imines[a]

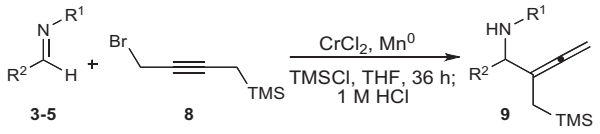


Entry	R	Imine	Additive[b]	Conversion[c] (%)
1	Ph	**3a**	—	—
2	Bn	**4a**	—	—
3	Ts	**5a**	—	80
4	Ph	**3a**	DMF	46
5	Bn	**4a**	DMF	36
6	Bn	**4a**	Et_3N	38
7	Ts	**5a**	Et_3N	88

[a] Imine (1 equiv), allyl bromide (1.5 equiv), $CrCl_3$ (10 mol %), Mn (2 equiv), TMSCl (1.1 equiv), 16 h.
[b] Added after 16 h; then TBAF (1 M in THF, 1 equiv).
[c] Determined by ^1H NMR spectroscopy.

The homo-coupled adduct, dienyne **8a**, derived from 2 equiv of **8**, was observed when unreactive substrates **3a**, **3b**, or **4a** were employed. A byproduct from the reaction of tosyl imine **5a** and propargyl bromide **8** was identified as the corresponding homopropargyl amine **10** (Table 2, entry 2). The mixture of regioisomers was observed in a 2.5:1 ratio. It is known that propargylic organometallic reagents exist as an equilibrium mixture of allenic and propargylic species.[15,16] Hence, the use of metal-catalyzed additions of propargylic reagents to electrophiles for the synthesis of allenic compounds has been previously limited by low regioselectivity. Interestingly, regioisomeric mixtures were never observed in our previous studies of the allenylation of aldehydes and ketones.[10,11]

Table 2
Allenylation of imines[a]

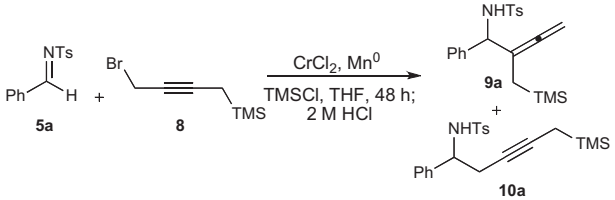


Entry	R^1	R^2	Imine	Conversion[b] (%)
1	Ph	Ph	**3a**	10
2	Ph	4-CF_3–C_6H_4	**3b**	—
3	Bn	Ph	**4a**	8
4	Ts	Ph	**5a**	64

[a] Imine (1 equiv), propargyl bromide **8** (1.5 equiv), $CrCl_2$ (10 mol %), Mn (2 equiv), TMSCl (1.1 equiv), 36 h; then 1 M HCl (2 mL).
[b] Determined by ^1H NMR spectroscopy.

The reaction conditions were optimized as described in Table 3. It was observed that increasing the amount of chromium catalyst accelerates the reaction rate and favors the formation of the desired allene **9a** (entries 1–5) up to 30 mol % catalyst. When the reaction is cooled to 0 °C, alkyne **10a** is obtained as a single product albeit with low conversion (entry 6). Increasing the reaction temperature does not favor allene **9a** (entry 7). A large excess of propargyl bromide **8** reduces the reaction time to 16 h yet affords a 1:1.6 mixture of regioisomers (entry 10). It was also observed that using $CrCl_3$ in place of $CrCl_2$ or increasing the equiv of TMSCl have no effect on the regioisomeric ratio. Also, use of additives, including Et_3N and pyridine, does not improve the ratio however it does slow down the reaction. The reaction conditions can be tailored to afford the propargylic amine as the major product. The formation **10a** is favored when the amount of catalyst if reduced. Absence of TMSCl, the use of TESCl, or the use of large excess of Mn^0 all favors the formation of this regioisomer. This effect is equally observed when propargyl bromide **11,** containing a DMPS group in place of TMS, is utilized (Table 4).

Table 3
Optimization of allenylation conditions[a]



Entry	$CrCl_2$ (%)	T (°C)	Conversion[b] (%)	Ratio[b] (**9a**:**10a**)
1	5	rt	87	1:1
2	10	rt	99	2.5:1
3	15	rt	91	2.6:1
4[c]	30	rt	99	3.5:1
5	50	rt	99	3.5:1
6	10	0	27	0:1
7	10	70	99	2:1
8[d]	30	rt	23	2:1
9[e]	30	rt	82	2.5:1
10[f]	30	rt	91	1:1.6

[a] Imine **5a** (1 equiv), propargyl bromide **8** (1.5 equiv), $CrCl_2$ (30 mol %), Mn (2 equiv), TMSCl (1.1 equiv), 48 h; then 1 M HCl (2 mL).
[b] Determined by ^1H NMR spectroscopy.
[c] Propargyl bromide (2 equiv).
[d] Solvent: CH_3CN.
[e] Mn (5 equiv).
[f] Propargyl bromide **8** (3 equiv), reaction time: 16 h.

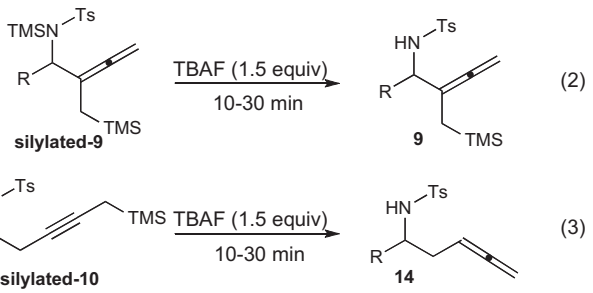
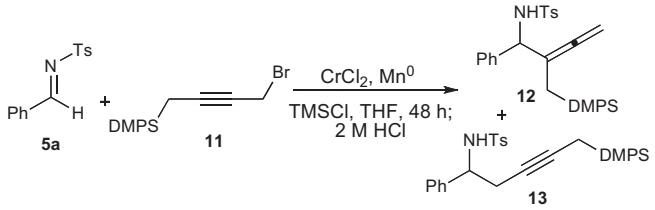


Table 4
Use of propargyl bromide **11**[a]



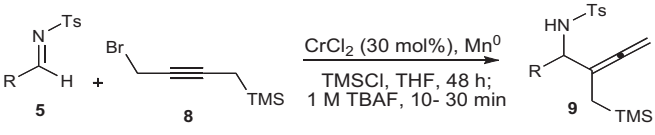
Entry	$CrCl_2$ (%)	Ratio[b] (**12**:**13**)	Yield[b] (%)
1	30	3:1	52
2[c]	10	1:3.3	42

[a] Imine **5a** (1 equiv), propargyl bromide **11** (1.5 equiv), Mn^0 (2 equiv), 16 h; then 2 M HCl (2 mL).
[b] Determined by ^1H NMR spectroscopy.
[c] No TMSCl added.

Due to the difficulty separating **9** from **10**, the unpurified *N*-silylated mixture of isomers was treated with 1.5 equiv of TBAF. After ~10 min, *silylated*-**10** reacted with TBAF to give the corresponding bis(desilylated) allene **14**. While mono(desilylation) of the more hindered *silylated*-**9** occurred quickly, reaction of the allylsilane was significantly slower. Hence, the resulting mixture of allenes **9** and **14** could be easily separated by column chromatography (Eqs. 2 and 3).

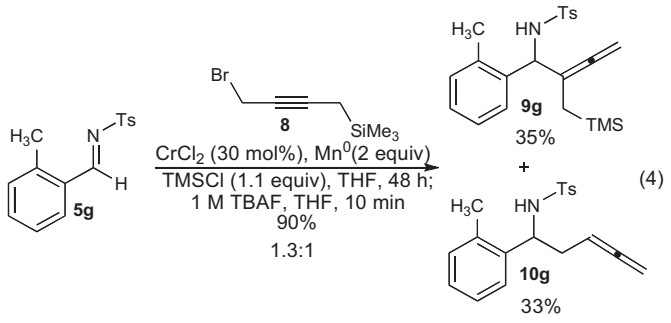
A sampling of tosyl imines was treated to the standard reaction conditions. Aromatic imines give the corresponding adducts in good yields (Table 5, entries 1 and 2). Imine **5c**, containing an electron withdrawing group, is consumed after 16 h under the reaction conditions albeit affording allene **9c** in low yield (entry 3). The presence of an electron donating group in the substrate increases the reaction time, thus allene **9d** was obtained in 53% yield after 3 days (entry 4). α,β-unsaturated imine **9e** is a poor substrate for the allenylation reaction giving the corresponding allene in only 16% yield (entry 5). On the contrary, aliphatic allene **9f** was obtained in excellent yield with 10:1 regioselectivity in favor of the desired allene (entry 6). When the more sterically hindered *ortho*-substituted imine **5g** is utilized, a 1.3:1 mixture of products **9g** and **10g** is observed (Eq. 4).

Table 5
Synthesis of allenic sulfonamides[a]



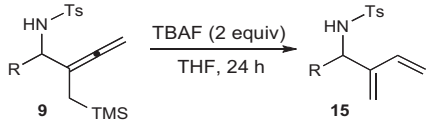
Entry	Imine	R	Product	Conversion[b] (%)	Yield[c] (%)
1	**5a**	Ph	**9a**	78	73
2	**5b**	*p*-Br–C_6H_4	**9b**	73	56
3	**5c**	*p*-CF_3–C_6H_4	**9c**	38	25
4[d]	**5d**	*p*-MeO–C_6H_4	**9d**	56	53
5	**5e**	*trans*-PhCH=CH	**9e**	—	16
6	**5f**	$PhCH_2CH_2$	**9f**	91	84

[a] Imine **5** (1 equiv), propargyl bromide **8** (2 equiv), $CrCl_3$ (30 mol %), Mn^0 (2 equiv), TMSCl (1.1 equiv), 48 h; then TBAF (1 M in THF, 1.5 equiv).
[b] Determined by ^1H NMR.
[c] Isolated yield.
[d] Reaction time: 3 days, propargyl bromide (3 equiv), 1 equiv added after 48 h.



These (silylmethyl)allenic amines were successfully transformed to the desired 2-aminomethyl-1,3-dienes by treatment with TBAF in good to excellent yields (Table 6). This method was equally efficient for desilylation of aromatic and aliphatic allenic amines. 2-aminomethyl-1,3-diene **15b** was obtained in 62% yield albeit a 74% conversion (entry 2). This reaction was not allowed to go to completion to avoid decomposition of the product. Electron rich diene **15d** was obtained in 84% yield (entry 3). Aliphatic allene was successfully transformed to the diene in excellent yield (entry 4). Finally, allenic imine **9g** afforded the desired diene in the presence of an *ortho*-substituent (entry 5).

Table 6
Synthesis of 2-aminomethyl-1,3-dienes[a]



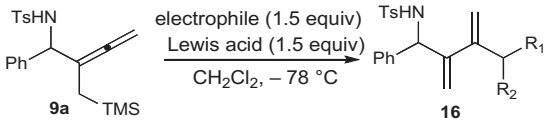
Entry	Allene	R	Product	Yield[b] (%)
1	**9a**	Ph	**15a**	81
2	**9b**	*p*-Br–C_6H_4	**15b**	62
3	**9d**	*p*-MeO–C_6H_4	**15d**	84
4	**9f**	$PhCH_2CH_2$	**15f**	92
5	**9g**	*o*-Me–C_6H_4	**15g**	73

[a] Allene **9** (1 equiv) TBAF (1 M in THF, 1 equiv and 1 more equiv after 3 h).
[b] Isolated yields.

(Silylmethyl)allenes are known to react with several electrophiles including acyl iminium ions,[17] halogens,[18,19] aldehydes, and acetals[20] to afford highly functionalized dienes. To further illustrate the usefulness of (silylmethyl)allenes **9** for the synthesis of highly functionalized 1,3-dienes, allenic amine **9a** was mixed with different electrophiles in the presence of a Lewis acid (Table 7). The corresponding dienes were not obtained in the presence of benzaldehyde or 3-phenylpropanal (entries 1 and 2). However, the desired product was formed in 46% conversion using benzaldehyde dimethylacetal with $TiCl_4$ as a Lewis acid (entry 3). To increase the yield of the reaction and avoid the formation of byproducts, the milder Lewis acid $BF_3{\cdot}OEt_2$ was successfully employed to deliver diene **16a** with 100% conversion.

To study the scope of this dienylation reaction, we exposed several allenic sulfonamides to benzaldehyde dimethylacetal in the presence of 1 equiv of $BF_3{\cdot}OEt_2$ at −78 °C (Table 8). The desired products were obtained after 2–3 h in excellent yields for both

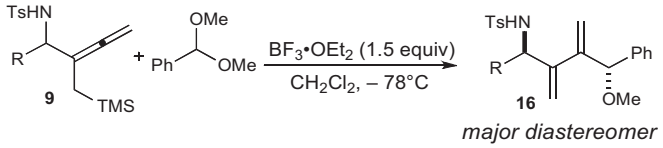
Table 7
Synthesis of highly functionalized 1,3-dienes[a]



Entry	Electrophile	Lewis acid	R^1	R^2	Yield[b] (%)
1	PhCHO	$TiCl_4$	Ph	OH	—
2	$PhCH_2CH_2CHO$	$TiCl_4$	CH_2CH_2Ph	OH	—
3	$PhCH(OMe)_2$	$TiCl_4$	Ph	OMe	46
4	$PhCH(OMe)_2$	$BF_3{\cdot}OEt_2$	Ph	OMe	100

[a] Imine **9a** (1 equiv), electrophile (1.6 equiv), $TiCl_4$ (1.5 equiv), −78 °C, 16 h.
[b] Determined by ^{1}H NMR spectroscopy.

Table 8
Dienylation with benzaldehyde dimethylacetal[a]



major diastereomer

Entry	Allene	R	Product	Yield[b] (%)	dr[c]
1	**9a**	Ph	**16a**	92	1:3
2	**9b**	*p*-Br−C_6H_4	**16b**	93	1:3
3	**9d**	*p*-MeO−C_6H_4	**16c**	95	1:3
4	**9f**	$PhCH_2CH_2$	**16d**	78	1:9

[a] Imine (1 equiv), aldehyde/acetal (1.6 equiv), $BF_3{\cdot}OEt_2$ (1.5 equiv), −78 °C.
[b] Isolated yields.
[c] *syn*/*anti*; determined by ^{1}H NMR spectroscopy.

aromatic and aliphatic substrates. A 1:3 diastereomeric mixture was obtained for the aromatic substrates (entries 1–3), while aliphatic substrate **9f** afforded the desired diene in a 1:9 dr (entry 4). We have tentatively assigned the major diastereomer as the anti isomer, based on the strong precedent provided by several studies of chiral allylsilane additions to aldehydes in the presence of $BF_3{\cdot}OEt_2$.[21,22]

3. Conclusions

The presence of an electron withdrawing tosyl group is fundamental to increase the reactivity of the imines toward nucleophilic additions catalyzed by chromium. Interestingly, the regioselectivity of the allenylation reaction was drastically affected by the presence of a bulky tosyl group in the substrate leading to the formation of regioisomeric mixtures not observed with aldehydes or ketones. The nature of the substituent on the imine affects the isomer ratio, with smaller substituents favoring the formation of the desired allenic amine. Allenic imines can be desilylated to deliver of 2-aminomethyl-1,3-dienes and furthermore, benzaldehyde dimethylacetal can be used in the preparation of more complex 1,3-dienes in excellent yields. The development of this methodology provided a novel route for the preparation of a variety of highly functionalized 1,3-dienes, making this transformation a valuable tool for the synthesis of complex organic compounds.

4. Experimental section

4.1. General information

All reactions were performed under an argon atmosphere in oven-dried glassware with magnetic stirring. TMSCl was distilled from CaH_2 before use. THF and CH_2Cl_2 were dried with a solvent purification system. Other commercially available reagents were used as received. Reactions were monitored by analytical thin layer chromatography using 0.25 mm glass-backed silica gel plates. Flash column chromatography was performed using silica gel (230–400 mesh). Visualization was accomplished by UV light and potassium permanganate.

^{1}H NMR spectra were recorded at 300 MHz and referenced to $CDCl_3$ (δ 7.27). ^{1}H NMR coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dt (doublet of triplets), td (triplet of doublets), tt (triplet of triplets), dq (doublet of quadruplets), br (broad), dd (doublet of doublets). Proton-decoupled ^{13}C NMR spectra were recorded at 75 MHz and reported relative to $CDCl_3$ (δ 77). Infrared spectra were obtained as thin film on NaCl plates.

4.2. Preparation of tosyl imines

*4.2.1. N-Benzylideneaniline (**3a**)*[23]. Prepared following the procedure described for the synthesis of compound **3b**. Product obtained as a light yellow solid (3 g, 16.5 mmol, 60%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.50 (s, 1H), 7.99 (m, 2H), 7.55–7.49 (m, 3H), 7.47–7.40 (m, 2H), 7.28–7.22 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 160.4, 152.0, 136.2, 131.3, 129.1, 128.8, 128.7, 125.9, 120.8.

*4.2.2. N-(4-(Trifluoromethyl)benzylidene)aniline (**3b**)*[24]. *p*-(Trifluoromethyl)benzaldehyde (1.36 mL, 10 mmol) and aniline (0.8 mL, 9 mmol) were dissolved in toluene (100 mL) and stirred under reflux for 16 h. The solution was cooled to rt and toluene was removed under reduced pressure. After recrystallization from hexanes the product was obtained as a white solid (1.93 g, 7.75 mmol, 77%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.54 (s, 1H), 8.06 (d, J=8.0 Hz, 2H), 7.77 (d, J=8.2 Hz, 2H), 7.49–7.41 (m, 2H), 7.34–7.29 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 158.5, 129.2, 128.9, 126.5, 125.6 (q, J=4.3 Hz), 120.8.

*4.2.3. N-Benzylidene-1-phenylmethanamine (**4a**)*[25]. A mixture of benzaldehyde (2.6 mL, 25.6 mmol), benzylamine (2.8 mL, 25.6 mmol), and $MgSO_4$ (7 g) in 25 mL of benzene was stirred at rt for 24 h. After this time, $MgSO_4$ was removed by filtration and rinsed with CH_2Cl_2. The solution was then concentrated under reduced pressure to give a yellow oil. The residue was distilled under reduced pressure (105–120 °C at 320 mTorr) to afford a clear oil (2.6 g, 13.3 mmol, 51%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.44 (t, J=1.4 Hz, 1H), 7.85–8.81 (m, 2H), 7.49–7.44 (m, 3H), 7.40–7.38 (m, 4H), 7.32 (m, 1H), 4.87 (d, J=1.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 162.0, 139.2, 136.1, 130.7, 128.6, 128.4, 128.2, 127.9, 126.9, 65.0.

*4.2.4. N-Benzylidene-4-methylbenzenesulfonamide (**5a**)*[26]. Following the procedure reported by Wynne et al., *p*-toluenesulfonamide (4.5 g, 26.3 mmol) was mixed with dry toluene (70 mL). Next, benzaldehyde (2.4 mL, 26.3 mmol) was added via syringe and the mixture was heated to reflux with a Dean–Stark trap for 24 h or until completion of the reaction as judged by ^{1}H NMR. After the solution was cooled down, toluene was removed under reduced pressure to afford a white solid. The compound was recrystallized from diethyl ether to afford the pure imine as white (6.16 g, 23.7 mmol, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.02 (s, 1H), 7.91 (m, 4H), 7.6 (t, J=7.0 Hz, 1H), 7.48 (t, J=7.6 Hz, 2H), 7.34 (d, J=8.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 144.5, 134.4, 132.3, 131.2, 129.7, 129.1, 128.0, 126.2, 21.6.

*4.2.5. N-(4-Bromobenzylidene)-4-methylbenzenesulfonamide (**5b**)*[27]. Following a modification of the procedure reported by Duguet et al.,[27] *p*-toluenesulfonamide (1.4 g, 7.78 mmol) was mixed with dry toluene (70 mL). Next aldehyde (7.78 mmol) and $BF_3{\cdot}OEt_2$ (300 μl) were sequentially added to the reaction mixture via

syringe. Mixture was heated to reflux with a Dean–Stark trap for 24 h or until completion of the reaction as judged by ^{1}H NMR. After the solution was cooled down, EtOAc was added to completely dissolve the newly formed precipitate (if any). The solution was washed with 1 M NaOH and brine. The organic phase was dried over Mg_2SO_4 and concentrated under reduced pressure. The solid was recrystallized from a mixture of EtOAc and hexanes to afford the pure imine. Obtained as a white solid (1.4 g, 4.18 mmol, 53%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.98 (s, 1H), 7.89 (d, J=8.7 Hz, 2H), 7.79 (d, J=8.7 Hz, 2H), 7.65 (d, J=8.3 Hz, 2H), 7.65 (d, J=8.5 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 144.8, 134.8, 132.5, 132.3, 131.2, 130.2, 129.8, 128.1, 21.6.

*4.2.6. 4-Methyl-N-(4-(trifluoromethyl)benzylidene)benzenesulfonamide (**5c**)*[28]. Obtained as a white solid (1.95 g, 5.9 mmol, 31%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.1 (s, 1H), 8.06 (d, J=8.5 Hz, 2H), 7.91 (d, J=8.2 Hz, 2H), 7.76 (d, J=8.5 Hz, 2H), 7.38 (d, J=7.9 Hz, 2H), 2.4 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 145.1, 134.4, 131.3, 129.9, 128.3, 126.2 (q, J=3.9 Hz), 19.4; MS (ESI) calcd for $C_{15}H_{12}F_3NO_2S$ 237.0541, found 237.9835.

*4.2.7. N-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide (**5d**)*[29]. Obtained as white crystals (4.1 g, 14 mmol, 85%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.95 (s, 1H), 7.9 (d, J=8.1 Hz, 2H), 7.8 (d, J=8.4 Hz, 2H), 7.34 (d, J=8.2 Hz, 2H), 6.78 (d, J=9.1 Hz, 2H), 3.9 (s, 3H), 2.4 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 165.2, 144.5, 135.8, 133.7, 129.7, 127.9, 125.2, 114.6, 55.6, 21.7; HRMS (ESI) calcd for $C_{15}H_{15}NO_3S$ (M+H) 290.0851, found 290.0860.

*4.2.8. 4-Methyl-N-((E)-3-phenylallylidene)benzenesulfonamide (**5e**)*[27]. Obtained as light brown crystals (0.83 g, 1.33 mmol, 25%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.78 (d, J=9.4 Hz, 1H), 7.86 (d, J=8.8 Hz, 2H), 7.58–7.51 (m, 2H), 7.47–7.41 (m, 4H), 7.34 (d, J=8.0 Hz, 2H) 6.99 (dd, J=9.4, 15.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 153.8, 144.5, 135.3, 134.1, 131.7, 129.8, 129.2, 128.6, 128.0, 124.7, 21.7; HRMS (ESI) calcd for $C_{16}H_{15}NO_2S$ (M+H) 286.0902, found 286.0913.

*4.2.9. 4-Methyl-N-(3-phenylpropylidene)benzenesulfonamide (**5f**)*[30]. Prepared following the procedure described for the preparation of compound **5g** as previously described by Wipf.[30] Obtained as a white solid after recrystallization from hexanes (1.4 g, 4.9 mmol, 49%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.62 (t, J=4.1 Hz, 1H), 7.77 (d, J=8.5 Hz, 2H), 7.33 (J=8.1 Hz, 2H), 7.28–7.10 (m, 5H), 2.98–2.92 (m, 2H), 2.88–2.80 (m, 2H), 2.4 (s, 3H); 177.4, 144.7, 139.6, 134.3, 129.8, 128.6, 128.3, 128.1, 126.4, 37.3, 30.6, 21.6; IR (thin film) 2925, 1629, 1453, 1090 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}NO_2S$ (M+Li) 294.1140, found 294.1127.

*4.2.10. 4-Methyl-N-(2-methylbenzylidene)benzenesulfonamide (**5g**)*[31]. Prepared following the procedure described by Chemla et al.[32] Sodium *p*-toluenesulfinate (1.78 g, 10 mmol), *p*-toluenesulfonamide (1.71 g, 10 mmol), and *o*-methylbenzaldehyde (1.15 mL, 10 mmol) were dissolved in a 1:1 solution of formic acid/H_2O (30 mL). The mixture was stirred at rt for 1 week until the aldehyde was consumed as judged by TLC. After this time, the white precipitate was collected by filtration and rinsed with water and hexanes. The white solid was dissolved in CH_2Cl_2 (50 mL), a saturated solution of $NaHCO_3$ (50 mL) was added and the mixture was stirred for 2 h. The aqueous layer was extracted with CH_2Cl_2. The combined organic phases were washed with brine dried over $MgSO_4$ and concentrated under reduced pressure. The desired imine was obtained as a white solid and was used without further purification (2.02 g, 7.4 mmol, 74%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.95 (s, 1H), 7.9 (d, J=8.1 Hz, 2H), 7.8 (d, J=8.4 Hz, 2H), 7.34 (d, J=8.2 Hz, 2H), 6.78 (d, J=9.1 Hz, 2H), 3.9 (s, 3H), 2.4 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 144.4, 142.2, 135.4, 134.5, 131.4, 130.46, 130.4, 129.7, 128.0, 126.5, 21.5, 19.6.

*4.2.11. 4-Methyl-N-(1-phenylbut-3-en-1-yl)benzenesulfonamide (**7**)*[12]. Inside a nitrogen atmosphere drybox, a mixture of $CrCl_3$ (4.5 mg, 0.03 mmol) and Mn powder 325-mesh (33 mg, 0.66 mmol) were added to a 2-dram vial. The vial was capped with a Teflon lid and it was removed from the drybox. Tosyl imine 5a (77 mg, 0.3 mmol) was added to the mixture and the vial was flushed with argon. Dry THF (2 mL) was added via syringe and a brown suspension was formed. This was followed by addition of TMSCl (42 μl, 0.33 mmol) and freshly distilled allyl bromide (40 μL, 0.45 mmol). The mixture was stirred at rt for 16 h. EtOAc (1–2 mL) was added to the gray suspension and the mixture was filtered through a path of silica to remove solids. The resulting clear solution was concentrated under reduced pressure and the residue was redissolved in THF (3 mL). TBAF (1 M in THF, 0.3 mL, 0.3 mmol) was added and the mixture was stirred for 10 min. A saturated solution of NH_4Cl was added and the mixture was extracted with EtOAc. The organic phases were dried over Mg_2SO_4, filtered though a path of silica and concentrated under reduced pressure. The residue was purified by flash chromatography using a gradient of EtOAc in hexanes (15–20%) to afford the desired product as a clear oil (80 mg, 0.27 mmol, 88%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57 (d, J=7.6 Hz, 2H), 7.20–7.05 (m, 7H), 5.51 (m, 1H), 5.23 (d, J=7.0 Hz, 1H), 5.13 (m, 2H), 4.46 (q, J=6.8 Hz, 1H), 2.46 (q, J=6.2 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 140.3, 137.5, 133.1, 129.2, 128.3, 127.3, 127.1, 126.5, 119.1, 57.2, 41.8, 21.4.

4.3. General method for the preparation of (silylmethyl) allenic amines (9)

Inside a nitrogen atmosphere drybox, a mixture of $CrCl_2$ (11 mg, 0.09 mmol) and Mn powder 325-mesh (33 mg, 0.66 mmol) were added to a 2-dram vial. The vial was capped with a Teflon lid and it was removed from the drybox. The tosyl imine (0.3 mmol) was added to the mixture and the vial was flushed with argon. Dry THF (2 mL) was added via syringe and a brown suspension was formed. This was followed by addition of TMSCl (42 μL, 0.33 mmol) and (4-bromo-2-butyn-1-yl)trimethylsilane (120 mg, 0.6 mmol). The mixture was stirred at rt for 48 h Et_3N (1 mL) and EtOAc (1–2 mL) were added to the gray suspension and the brown mixture was filtered trough a path of silica using EtOAc as eluent. The resulting clear solution was concentrated under reduced pressure and the residue was redissolved in THF (3 mL). TBAF (1 M in THF, 0.45 mL, 0.45 mmol) was added to the solution in two parts over 10 min. The mixture was stirred for a maximum of 30 min or until the majority of propargylamine is consumed to afford the corresponding homoallenic amine as judged by TLC (eluent 20% EtOAc in hexanes). The yellow solution was again filtered through a path of silica using EtOAc as eluent. The resulting solution was concentrated under reduced pressure to give a yellow oil. The residue was purified by flash chromatography using a gradient of EtOAc in hexanes (0–10%).

*4.3.1. 4-Methyl-N-(1-phenyl-2-((trimethylsilyl)methyl)buta-2,3-dien-1-yl)benzenesulfonamide (**9a**).* Obtained as a white solid (83 mg, 22 mmol, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60 (d, 2H), 7.25–7.13 (m, 7H), 5.06 (d, J=8.0 Hz, 1H), 4.95–4.88 (dq, J=2.84, 9.8 Hz, 1H), 4.84–4.77 (dq, J=3.0, 9.8 Hz, 1H), 4.64 (dt, J=2.5, 7. 7 Hz, 1H), 2.39 (s, 3H), 1.07 (dt, J=3.0, 15.1 Hz, 1H), 0.99 (dt, J=2.99, 15.1 Hz, 1H), −0.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.9, 142.99, 139.3, 137.7, 129.2, 128.4, 127.7, 127.6, 127.1, 102.7, 80.5, 59.3, 21.4, 18.3, −1.3; IR (thin film) 3277, 2954, 1955, 1330, 1162 cm^{-1};

HRMS (MALDI) calcd for $C_{21}H_{27}NO_2SSi$ (M+Na) 408.1429, found 408.1439.

*4.3.2. N-(1-(4-Bromophenyl)-2-((trimethylsilyl)methyl)buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide (**9b**).* Obtained as a clear oil (81 mg, 0.17 mmol, 58%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.4 Hz, 2H), 7.17 (d, J=8.0 Hz, 2H), 7.06 (d, J=8.4 Hz, 2H), 5.14 (d, J=8.1 Hz, 1H), 4.9 (dq, J=2.9, 10.0 Hz, 1H), 4.8 (dq, J=2.9, 10.1 Hz, 1H), 4.59 (dt, J=3.2, 7.4 Hz, 1H), 2.39 (s, 3H), 1.15 (dt, J=3.2, 15.0 Hz, 1H), 0.9 (dt, J=2.9, 15.1 Hz, 1H), −0.7 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 143.2, 138.3, 137.5, 131.4, 129.4, 129.3, 127.1, 121.7, 102.3, 80.9, 58.8, 21.4, 18.3, −1.2; IR (thin film) 3277, 1958, 1334, 1163 cm^{-1}; HRMS (MALDI) calcd for $C_{21}H_{26}NO_2SSi$ (M+Na) 486.0535, found 486.0552.

*4.3.3. 4-Methyl-N-(1-(4-(trifluoromethyl)phenyl)-2-((trimethylsilyl) methyl)buta-2,3-dien-1-yl)benzenesulfonamide (**9c**).* Obtained as a clear oil (27 mg, 0.06 mmol, 20%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50 (d, J=8.3 Hz, 2H), 7.48 (d, J=7.9 Hz, 2H), 7.21 (d, J=8.1 Hz, 2H), 7.11 (d, J=8.1 Hz, 2H), 5.16 (d, J=7.2 Hz, 1H), 4.93 (dq, J=2.9, 10.2 Hz, 1H), 4.87 (dq, J=3.0, 10.2 Hz, 1H), 4.67 (dt, J=3.0, 7.3 Hz, 1H), 2.34 (s, 3H), 1.16 (dt, J=2.9, 15.1 Hz, 1H), 0.96 (dt, J=2.7, 15.1 Hz, 1H), −0.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 143.2, 137.3, 129.2, 128.0, 127.0, 125.1 (q, J=3.6 Hz) 102.2, 81.0, 58.9, 21.3, 18.3, −1.3; IR (thin film) 2956, 1956, 1326, 1162 cm^{-1}; HRMS (MALDI) calcd for $C_{22}H_{26}F_3NO_2SSi$ (M+Na) 476.1303, found 476.1292.

*4.3.4. N-(1-(4-Methoxyphenyl)-2-((trimethylsilyl)methyl)buta-2,3-dien-1-yl)-4-methyl benzenesulfonamide (**9d**).* Obtained as a clear oil (66 mg, 0.16 mmol, 53%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59 (d, J=8.45 Hz, 2H), 7.18 (d, J=7.74 Hz, 2H), 7.06 (d, J=9.45 Hz, 2H), 6.47 (d, J=8.80 Hz, 2H), 5.09 (d, J=7.60 Hz, 1H), 4.9 (dq, J=3.0, 9.71 Hz, 1H), 4.7 (dq, J=3.0, 9.78 Hz, 1H), 4.59 (dt, J=3.18, 7.54 Hz, 1H), 3.77 (s, 3H), 2.38 (s, 3H), 1.16 (dt, J=2.95, 15.21 Hz, 1H), 0.89 (dt, J=2.71, 15.2 Hz, 1H), −0.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 159.1, 142.8, 137.8, 131.4, 129.2, 128.8, 127.2, 113.7, 102.7, 80.4, 58.8, 55.2, 21.4, 18.4, −1.2; IR (thin film) 3277, 3033, 2898, 1956, 1328, 1161 cm^{-1}; HRMS (MALDI) calcd for $C_{22}H_{29}NO_2SSi$ (M+Na) 438.1535, found 438.1555.

*4.3.5. 4-Methyl-N-(1-phenyl-4-((trimethylsilyl)methyl)hexa-1,4,5-trien-3-yl)benzenesulfonamide (**9e**).* Obtained as a clear oil (20 mg, 0.05 mmol, 16%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (d, J=8.5 Hz, 2H), 7.30–7.14 (m, 7H), 6.33 (d, J=15.7 Hz, 1H), 5.76 (dd, J=7.8, 15.6 Hz, 1H), 4.83 (m, 2H), 4.77 (d, J=8.1 Hz, 1H), 4.21 (m, 1H), 2.34 (s, 3H), 1.29 (dt, J=1.3, 15.0 Hz, 1H), 1.16 (dt, J=2.7, 15.1 Hz, 1H), −0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.07, 143.2, 136.1, 132.2, 129.4, 128.4, 127.8, 127.3, 127.2, 126.4, 101.1, 80.1, 58.0, 21.3, 18.07, −1.2; IR (thin film) 3272, 2953, 1953, 1329, 1161 cm^{-1}; HRMS (ESI$^-$) calcd for $C_{23}H_{29}NO_2SSi$ (M−H) 440.1610, found 440.1623.

*4.3.6. 4-Methyl-N-(1-phenyl-4-((trimethylsilyl)methyl)hexa-4,5-dien-3-yl)benzenesulfonamide (**9f**).* Obtained as a clear oil (103 mg, 0.25 mmol, 84%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, J=8.26 Hz, 2H), 7.32–7.08 (m, 7H), 4.82–4.63 (m, 3H), 3.6 (m, 1H), 2.63 (dt, J=5.8, 9.6 Hz, 2H), 2.42 (s, 3H), 1.96 (m, 1H), 1.73 (m, 1H), 1.14 (dt, J=3.1, 15.3 Hz, 1H), 0.9 (dt, J=3.0, 15.2 Hz, 1H), −0.1 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.4, 143.2, 141.4, 137.9, 129.4, 128.4, 128.3, 127.3, 125.8, 101.7, 79.3, 55.9, 36.1, 31.6, 21.4, 17.6, −1.3; IR (thin film) 3278, 1955.9, 1333, 1163 cm^{-1}; HRMS (MALDI) calcd for $C_{23}H_{31}NO_2SSi$ (M+Na) 436.1743, found 436.1750.

*4.3.7. 4-Methyl-N-(1-(o-tolyl)-2-((trimethylsilyl)methyl)buta-2,3-dien-1-yl)benzenesulfonamide (**9g**).* Obtained as a white solid (35 mg, 0.09 mmol, 30%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59 (d, J=8.4 Hz, 2H), 7.16 (J=8.3 Hz, 2H), 7.13–7.03 (m, 4H), 4.96 (s, 2H), 4.86 (m, 1H) 4.62 (m, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 1.16 (dt, J=3.0, 15.1 Hz, 1H), 0.89 (dt, J=2.8, 15.2 Hz, 1H), −0.05 (s, 0H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.3, 142.8, 137.9, 137.1, 136.4, 130.6, 129.1, 127.6, 127.3, 127.1, 126.0, 102.5, 80.3, 56.1, 21.4, 19.1, 18.2, −1.3; IR (thin film) 3280, 1955, 1599, 1331, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{21}NO_2S$ (M+Na) 422.1586, found 422.1598.

*4.3.8. 4-Methyl-N-(1-(o-tolyl)penta-3,4-dien-1-yl)benzenesulfonamide (**14g**).* Obtained as a white solid (34 mg, 0.10 mmol, 35%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, J=8.3 Hz, 2H), 7.12 (d, J=7.9 Hz, 2H), 7.09–6.98 (m, 4H), 4.87 (d, J=6.3 Hz, 1H), 4.85 (quint, J=7.0 Hz, 1H), 4.65 (m, 3H), 2.38 (m, 2H), 2.36 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 143.1, 138.2, 137.4, 134.8, 130.3, 129.2, 127.2, 127.0, 126.1, 124.9, 85.1, 75.3, 53.5, 36.0, 21.4, 19.1; IR (thin film) 3276, 1956, 1331, 1158 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{19}H_{21}NO_2S$ (M+H) 328.1371, found 328.1360.

*4.3.9. 4-Methyl-N-(1-phenyl-5-(trimethylsilyl)pent-3-yn-1-yl)benzenesulfonamide (**10a**).* Obtained as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61 (d, J=8.3 Hz, 2H), 7.22–7.14 (m, 7H), 5.15 (d, J=7.1 Hz, 1H), 4.42 (q, J=6.0 Hz, 1H), 2.58 (dt, J=2.7, 5.9 Hz, 2H), 2.39 (s, 3H), 1.38 (t, J=2.7 Hz, 2H), −0.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 139.7, 137.3, 129.3, 128.3, 128.2, 127.6, 127.5, 127.1, 126.6, 82.1, 72.8, 56.0, 27.6, 21.4, 6.9, −2.1; IR (thin film) 3257, 3032, 2223, 1330, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{27}NO_2SSi$ (M+Na) 408.1429, found 408.1204.

*4.3.10. N-(2-((Dimethyl(phenyl)silyl)methyl)-1-phenylbuta-2,3-dien-1-yl)-4-methylbenzenesulfonamide (**12**).* After the reaction mixture was stirred for 48 h as described in the general procedure, HCl (2 M, 1 mL) and EtOAc (1–2 mL) were added to the gray suspension and the green mixture was stirred for 1 h. The resulting mixture was extracted with three portions of EtOAc. Combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography using a gradient of EtOAc in hexanes (0–10%) to give the desired product as a white solid (69 mg, 0.15 mmol, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (d, J=8.4 Hz, 2H), 7.42–7.31 (m, 5H), 7.20–7.12 (m, 5H), 7.01 (m, 2H), 4.99 (d, J=7.6 Hz, 1H), 4.83 (dq, J=2.6, 9.9 Hz, 1H), 4.7 (dq, J=3.0, 10.0 Hz, 1H), 4.57 (dt, J=3.2, 7.7 Hz, 1H), 2.38 (s, 3H), 1.43 (dt, J=2.7, 15.2 Hz, 1H), 1.17 (dt, J=2.8, 15.1 Hz, 1H), 0.23 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.0, 142.8, 139.1, 138.2, 137.6, 133.5, 129.2, 129.1, 128.3, 127.7, 127.6, 127.5, 127.1, 102.2, 80.5, 59.1, 21.4, 17.5, −2.7, −3.0; IR (thin film) 3774, 2955, 1955, 1329, 1161 cm^{-1}; HRMS (MALDI) calcd for $C_{26}H_{29}NO_2SSi$ (M+Na) 470.1586, found 470.1601.

*4.3.11. N-(5-(Dimethyl(phenyl)silyl)-1-phenylpent-3-yn-1-yl)-4-methyl-benzenesulfonamide (**13**).* Inside a nitrogen atmosphere drybox, a mixture of $CrCl_2$ (3.6 mg, 0.03 mmol) and Mn powder 325-mesh (33 mg, 0.66 mmol) were added to a 2-dram vial. The vial was capped with a Teflon lid and it was removed from the drybox. The tosyl imine (0.3 mmol) was added to the mixture and the vial was flushed with argon. Dry THF (2 mL) was added via syringe and a brown suspension was formed. This was followed of (4-bromobut-2-yn-1-yl)dimethyl(phenyl)silane (120 mg, 0.45 mmol). The mixture was stirred at rt for 48 h. HCl (2 M, 1 ml) and EtOAc (1–2 mL) were added to the gray suspension and the green mixture was stirred for 1 h. The resulting mixture was extracted with three portions of EtOAc. Combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to give a tan oil. The residue was purified by flash chromatography using a gradient of EtOAc in hexanes (0–10%) to give the desired product as a yellow oil (56 mg, 0.12 mmol, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 (d, J=8.2 Hz, 2H), 7.49 (m, 2H), 7.39 (m, 3H),

7.20–7.15 (m, 5H), 7.09–7.05 (m, 2H), 5.05 (d, *J*=7.1 Hz, 1H), 4.42 (q, *J*=5.7, 11.8 Hz, 1H), 2.57 (dt, *J*=2.6, 2.6, 5.6 Hz, 2H), 2.39 (s, 3H), 1.63 (t, *J*=2.5 Hz, 2H), 0.29 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 143.1, 140.9, 136.9, 133.0, 132.9, 132.8, 131.7, 131.4, 130.9, 130.5, 130.1; IR (thin film) 3277, 3068, 2223, 1331, 1161 cm^{-1}; HRMS (MALDI) calcd for $C_{26}H_{29}NO_2SSi$ (M+Na) 470.1586, found 470.3550.

4.4. General method for the preparation of 2-aminomethyl-1,3-dienes

Allene (0.21 mmol) was dissolved in THF (2 mL). TBAF (1 M in THF, 0.21 mL, 0.21 mmol) was added and the solution. After 3 h one extra equivalent of TBAF (1 M in THF, 0.21 mL, 0.21 mmol) was added and the mixture was stirred for 21 h at rt. The yellow solution was filtered though a path of silica using EtOAc as eluent. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography using a gradient of EtOAc in hexanes (0–12%) to afford the desired diene.

*4.4.1. 4-Methyl-N-(2-methylene-1-phenylbut-3-en-1-yl)benzenesulfonamide (**15a**).* Obtained as a white solid (53 mg, 0.17 mmol, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68 (d, *J*=8.4 Hz, 2H), 7.23 (m, 5H) 7.16 (m, 2H), 6.18 (dd, *J*=11.4, 17.7 Hz, 1H), 5.26–5.22 (m, 3H), 5.13 (d, *J*=0.8 Hz, 1H), 5.08 (d, *J*=18.0 Hz, 1H), 5.02 (d, *J*=11.5 Hz, 1H), 4.84 (d, *J*=7.9 Hz, 1H), 2.4 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 143.2, 139.0, 137.4, 135.5, 129.4, 128.5, 127.7, 127.2, 127.1, 118.2, 116.0, 58.6, 21.5; IR (thin film) 3283, 1637, 1599, 1326, 1160 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}NO_2S$ (M+Na) 336.1034, found 336.1028.

*4.4.2. N-(1-(4-Bromophenyl)-2-methylenebut-3-en-1-yl)-4-methylbenzenesulfonamide (**15b**).* Obtained as a white solid (49 mg, 0.13 mmol, 65%, 74% conversion). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61 (d, *J*=8.3 Hz, 2H), 7.33 (d, *J*=8.6 Hz, 2H), 7.21 (d, *J*=8.6 Hz, 2H), 7.02 (d, *J*=8.6 Hz, 2H), 6.18 (dd, *J*=11.3, 17.7 Hz, 1H), 5.24–4.99 (m, 6H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 143.5, 138.0, 135.2, 131.5, 129.4, 128.9, 127.2, 121.6, 118.6, 116.3, 58.0, 21.5; IR (thin film) 3277, 1597, 1328, 1184 cm^{-1}; HRMS (ESI$^-$) calcd for $C_{18}H_{18}BrNO_2S$ (M−H) 390.0163, found 390.0175.

*4.4.3. N-(1-(4-Methoxyphenyl)-2-methylenebut-3-en-1-yl)-4-methylbenzenesulfonamide (**15d**).* Obtained as a white solid (53 mg, 0.16 mmol, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 (d, *J*=8.5 Hz, 2H), 7.21 (d, *J*=8.14 Hz, 2H), 7.02 (d, *J*=9.3 Hz, 2H), 6.72 (d, *J*=8.5 Hz, 2H), 6.19 (dd, *J*=11.3, 18.0 Hz, 1H), 5.22 (s, 1H), 5.17 (d, *J*=7.7 Hz, 1H), 5.15 (s, 1H), 5.05 (d, *J*=17.9 Hz, 1H), 5.00 (d, *J*=11.4 Hz, 1H) 4.88 (d, *J*=7.0 Hz, 1H), 3.79 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 144.5, 143.2, 137.5, 135.6, 131.1, 129.3, 128.4, 127.2, 117.8, 115.8, 113.9, 58.0, 55.2, 21.5; IR (thin film) 3435, 1611, 1511, 1323, 1158 cm^{-1}; HRMS (ESI$^-$) calcd for $C_{19}H_{21}NO_3S$ (M+Li) 350.1402, found 350.1408.

*4.4.4. 4-Methyl-N-(4-methylene-1-phenylhex-5-en-3-yl)benzenesulfonamide (**15f**).* Obtained as a white solid (78 mg, 0.23 mmol, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, *J*=8.3 Hz, 2H), 7.31–7.20 (m, 5H), 7.11 (d, *J*=6.8 Hz, 2H), 6.15 (dd, *J*=10.9, 17.8 Hz, 1H), 5.17 (d, *J*=8.1 Hz, 1H), 5.05 (d, *J*=18.0 Hz, 1H), 5.03 (s, 1H), 5.0 (d, *J*=12.0 Hz, 1H), 4.89 (s, 1H), 4.09 (q, *J*=7.2 Hz, 1H), 2.62 (m, 2H), 2.44 (s, 3H), 1.92 (m. 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 142.2, 141.0, 137.7, 135.5, 129.4, 128.5, 128.4, 127.2, 126.0, 115.7, 114.8, 54.4, 37.1, 31.9, 21.5; IR (thin film) 3276, 2864, 1597, 1318, 1162 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{20}H_2NO_2S$ (M+H) 342.1528, found 342.1537.

*4.4.5. 4-Methyl-N-(2-methylene-1-(o-tolyl)but-3-en-1-yl)benzenesulfonamide (**15g**).* Obtained as a white solid (24 mg, 0.073 mmol, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59 (d, *J*=8.5 Hz, 2H), 7.16 (d, *J*=8.3 Hz, 2H), 7.11–6.94 (m, 4H), 6.26 (dd, *J*=11.18, 17.9 Hz, 1H), 5.52 (d, *J*=7.0 Hz, 1H), 5.19 (d, *J*=17.6 Hz, 1H), 5.19 (s, 1H), 5.04 (d, *J*=11.1 Hz, 1H), 4.88 (s, 1H), 4.74 (d, *J*=7.1 Hz, 1H), 2.37 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 143.1, 137.7, 136.7, 135.9, 135.7, 130.6, 129.6, 127.6, 127.1, 126.6, 125.9, 118.6, 115.3, 54.6, 21.4, 18.9; IR (thin film) 3271, 3064, 1596, 1319, 1186 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{19}H_{21}NO_3S$ (M+H) 328.1371, found 328.1379.

4.5. General method for the preparation of 2,3-disubstituted-1,3-butadienes

The allene (0.15 mmol) was dissolved in CH_2Cl_2 (1 mL) and cooled to −78 °C. Then, a solution of benzaldehyde dimethylacetal (0.16 mmol) and $BF_3\cdot Et_2O$ (0.16 mmol) in CH_2Cl_2 (1 mL) was added to the allene solution dropwise. The mixture was stirred at −78 °C for 1 h. After this time, one more portion of benzaldehyde dimethylacetal (0.15 mmol) and $BF_3\cdot Et_2O$ (0.16 mmol) were added to the reaction mixture. Reaction was monitored by TLC and after completion, a saturated solution of $NaHCO_3$ (1 mL) and EtOAc (1 mL) were added to the red solution. The mixture was extracted with three portions of EtOAc. The combined organic phased were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (0–12% EtOAc in hexanes) to give the desired diene.

*4.5.1. N-(3-(Methoxy(phenyl)methyl)-2-methylene-1-phenylbut-3-en-1-yl)-4-methylbenzenesulfonamide (**16a**).* Obtained as a clear oil (60 mg, 0.13 mmol, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, *J*=7.5 Hz, 2H), 2.33–7.12 (m, 10H), 7.01 (m, 2H), 5.19–4.85 (m, 6H), 4.70 (s, 1H), 3.24 (d, *J*=0.6 Hz, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145. 4, 145.0, 143.0, 139.0, 139.1, 137.4, 129.3, 128.3, 127.8, 127.5, 127.4, 127.3, 117.4, 116.5, 85.0, 60.4, 56.9, 21.5; IR (thin film) 3278, 3062, 1599, 1328, 1186 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{26}H_{27}NO_3S$ (M+Li) 440.1872, found 440.1861.

*4.5.2. N-(1-(4-Bromophenyl)-3-(methoxy(phenyl)methyl)-2-methylenebut-3-en-1-yl)-4-methylbenzenesulfonamide (**16b**).* Obtained as a clear oil (43 mg, 0.084 mmol, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.5 (d, *J*=8.21 Hz, 2H), 7.33–7.12 (m, 10H), 6.88 (d, *J*=8.4 Hz, 2H), 5.17–5.91 (m, 5H), 4.81 (s, 1H), 4.70 (s, 1H), 3.26 (s, 3H), 2.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 144.8, 143.33, 139.1, 138.1, 137.2, 131.3, 129.3, 129.2, 129.0, 128.3, 127.9, 127.2, 127.1, 117.8, 116.9, 85.2, 60.0, 56.9, 21.5; IR (thin film) 3278, 3089, 1600, 1332, 1187 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{26}H_{26}BrNO_3S$ (M+Li) 518.0977 found 518.0971.

*4.5.3. N-(3-(Methoxy(phenyl)methyl)-1-(4-methoxyphenyl)-2-methylenebut-3-en-1-yl)-4-methylbenzenesulfonamide (**16c**).* Obtained as a clear oil (49 mg, 0.10 mmol, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (d, *J*=8.2 Hz, 2H), 7.39–7.15 (m, 8H), 6.95 (d, *J*=8.7 Hz, 2H), 6.72 (d, *J*=8.7 Hz, 2H), 5.20–4.93 (m, 6H), 4.73 (s, 1H), 3.78 (s, 3H), 3.28 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 145.4, 145.4, 145.1, 143.0, 139.5, 139.5, 137.5, 131.2, 129.3, 128.3, 127.8, 127.3, 127.2, 116.5, 113.7, 85.1, 59.8, 56.9, 55.2, 21.5; IR (thin film) 3280, 3062, 1599, 1325, 1160 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{27}H_{29}NO_4S$ (M+Li) 470.1977 found 470.1971.

*4.5.4. N-(5-(Methoxy(phenyl)methyl)-4-methylene-1-phenylhex-5-en-3-yl)-4-methylbenzenesulfonamide (**16d**).* Obtained as a clear oil (79 mg, 0.17 mmol, 78%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62 (d, *J*=8.3 Hz, 2H), 7.35–7.18 (m, 10H), 7.07 (d, *J*=8.9 Hz, 2H), 5.30 (d, *J*=7.8 Hz, 1H), 5.16 (s, 1H), 5.04 (s, 1H), 4.9 (s, 1H), 4.83 (s, 1H), 4.7 (s, 1H), 4.0 (q, *J*=7.2 Hz, 1H), 3.3 (s, 3H), 2.51 (m, 2H), 2.43 (s, 3H), 1.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 146.1, 143.0, 141.2, 139.2, 137.8, 129.4, 128.5, 128.3, 128.2, 127.8, 127.3, 127.2, 125.9, 115.7, 115.3, 84.7, 56.9, 56.2, 36.7, 31.8, 21.5; IR (thin film) 3282.7, 3085.7, 1599.5,

1323.5, 1158.4 cm^{-1}; HRMS (ESI^+) calcd for $C_{28}H_{31}NO_3S$ (M+Li) 468.2185 found 468.2177.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.08.010.

References and notes

1. Bloch, R. *Chem. Rev.* **1998**, *98*, 1407–1438.
2. Coulson, D. R. *J. Org. Chem.* **1973**, *38*, 1483–1490.
3. Hosomi, A.; Masunari, T.; Tominaga, Y.; Hojo, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1051–1053.
4. Castagnolo, D.; Renzulli, M. L.; Galletti, E.; Corelli, F.; Botta, M. *Tetrahedron: Asymmetry* **2005**, *16*, 2893–2896.
5. McLaughlin, M.; Shimp, H. L.; Navarro, R.; Micalizio, G. C. *Synlett* **2008**, 735–738.
6. Seomoon, D. A. ,J.; Lee, P. H. *Org. Lett.* **2009**, *11*, 2401–2404.
7. Furstner, A. *Chem. Rev.* **1999**, *99*, 991–1046.
8. Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 12349–12357.
9. Fürstner, A. *Chem.—Eur. J.* **1998**, *4*, 567–570.
10. Durán-Galván, M.; Hemmer, J. R.; Connell, B. T. *Tetrahedron Lett.* **2010**, *51*, 5080–5082.
11. Durán-Galván, M.; Worlikar, S. A.; Connell, B. T. *Tetrahedron* **2010**, *66*, 7707–7719.
12. Solin, N.; Wallner, O. A.; Szabo, K. J. *Org. Lett.* **2005**, *7*, 689–691.
13. Barker, T. J.; Jarvo, E. R. *Org. Lett.* **2009**, *11*, 1047–1049.
14. Giammaruco, M.; Taddei, M.; Ulivi, P. *Tetrahedron Lett.* **1993**, *34*, 3635–3638.
15. Kobayashi, S.; Nishio, K. *J. Am. Chem. Soc.* **1995**, *117*, 6392–6393.
16. Xia, G. Y. ,H. *J. Am. Chem. Soc.* **2007**, *129*, 496–497 and the references within.
17. Mentink, G.; van Maarseveen, J. H.; Hiemstra, H. *Org. Lett.* **2002**, *4*, 3497–3500.
18. Pacheco, M. C.; Gouverneur, V. R. *Org. Lett.* **2005**, *7*, 1267–1270.
19. Yu, C.-M.; Yoon, S.-K.; Lee, S.-J.; Lee, J.-Y.; Kim, S. S. *Chem. Commun.* **1998**, 2749–2750.
20. Ogasawara, M.; Ueyama, K.; Nagano, T.; Mizuhata, Y.; Hayashi, T. *Org. Lett.* **2003**, *5*, 217–219.
21. Nishigaichi, Y.; Takuwa, A.; Jodai, A. *Tetrahedron Lett.* **1991**, *32*, 2383–2386.
22. Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293–1316.
23. Nongkunsarn, P.; Ramsden, C. A. *Tetrahedron* **1997**, *53*, 3805–3830.
24. Rosa, J. O. N.; Santos, A. G.; Afonso, C. A. M. *J. Mol. Catal. A: Chem* **2004**, *214*, 161–165.
25. Ramalingam, B.; Seayad, A. M.; Chuanzhao, L.; Garland, M.; Yoshinaga, K.; Wadamoto, M.; Nagata, T.; Chai, C. L. L. *Adv. Synth. Catal.* **2010**, *352*, 2153–2158.
26. Wynne, J. H.; Price, S. E.; Rorer, J. R.; Stalick, W. M. *Synth. Commun.* **2003**, *33*, 341–352.
27. Duguet, N.; Campbell, C. D.; Slawin, A. M. Z.; Smith, A. D. *Org. Biomol. Chem.* **2008**, *6*, 1108–1113.
28. Wu, X.-F.; Vovard-Le Bray, C.; Bechki, L.; Darcel, C. *Tetrahedron* **2009**, *65*, 7380–7384.
29. Sivakumar, A. V.; Babu, G. S.; Bhat, S. V. *Tetrahedron: Asymmetry* **2001**, *12*, 1095–1099.
30. Wipf, P.; Kendall, C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2002**, *125*, 761–768.
31. Ueno, S.; Ohtsubo, M.; Kuwano, R. *J. Am. Chem. Soc.* **2009**, *131*, 12904–12905.
32. Chemla, F.; Hebbe, V.; Normant, J.-F. *Synthesis* **2000**, *1*, 75–77.