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Ligandless Iron-Catalyzed Desulfinylative C–C Allylation Reactions using Grignard Reagents and Alk-2-enesulfonyl Chlorides

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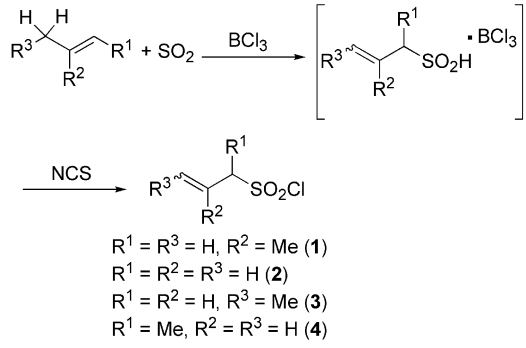
Alk-2-enesulfonyl chlorides **1**–**4** were synthesized by the BCl_3-promoted ene reaction of alkenes with SO_2. These sulfonyl chlorides were then used as electrophilic partners in iron-catalyzed desulfinylative cross-coupling reactions with different Grignard reagents (aromatic, aliphatic, and heteroaromatic). The reaction can be catalyzed with even 2 mol-% of the simple iron salt $Fe(acac)_3$. The regioselectivity of these allylations was studied by using sulfonyl chlorides **3** and **4** with aryl Grignard reagents. The scope of these allylations was further extended by the coupling of ester-substituted alk-2-enesulfonyl chloride **10** with aromatic Grignard reagents. Symmetrical products were synthesized by double C–C allylation with the use of 2-methylidenepropane-1,3-disulfonyl chloride (**12**).

Introduction

Carbon–carbon cross-coupling reactions are very important in the areas of material sciences and medicinal chemistry.[1] Transition-metal-catalyzed cross-coupling of organometallic reagents (nucleophiles) with halides or triflates (electrophiles) constitutes one of the most powerful methods to construct C–C bonds.[2] Arene- and alkanesulfonyl chlorides are inexpensive and readily available compounds. We have shown that Stille, carbonylative Stille,[3] Suzuki–Miyaura,[4] Sonogashira–Hagihara,[5] Mizoroki–Heck,[6] and Negishi[7] type cross-couplings can be carried out by using sulfonyl chlorides as electrophilic partners under desulfinylative conditions.[8] We have shown also that 2-methylprop-2-ene- (**1**), prop-2-ene- (**2**), 1-methylprop-2-ene- (**3**), and (*E*)-but-2-enesulfonyl chloride (**4**) are useful electrophilic partners in desulfinylative palladium-catalyzed C–C coupling reactions with inexpensive Grignard reagents and sodium salts of malonic esters and methyl acetoacetate.[9] As these sulfonyl chlorides can now be prepared in one-pot operations (Scheme 1) through a BCl_3-promoted ene reaction of the corresponding simple monoalkenes with sulfur dioxide,[10] substrates **1**–**4** have become now powerful electrophilic allylating agents (without BCl_3, the ene reaction of simple monoalkenes with SO_2 is endergonic above –100 °C).[11] Previously, we have shown that iron catalysts can be used in the desulfinylative C–C cross-coupling reaction of Grignard reagents with alkane-, alkene-, and arenesulfonyl chlorides.[12] Here we demonstrate that sulfonyl chlorides **1**–**4** can also be coupled with Grignard reagents by using simple iron salts under ligandless conditions.



Scheme 1. One-pot synthesis of alk-2-enesulfonyl chlorides.[27]

Results and Discussion

In 1954, Kharasch and Reinmuth,[13] and in 1971, Tamura and Kochi,[14] proposed to use of iron catalysts for the C–C cross-coupling reactions of Grignard reagents with alkyl halides. In the meantime, iron catalysts have become very popular for related reactions.[15–25] Recently, Sonogashira–Hagihara,[26,27] Mizoroki–Heck[28] and Suzuki–Miyaura C–C cross-coupling reactions[29] have been catalyzed by iron salts or iron complexes.

Screening of the iron catalysts was carried out by using *o*-tolylmagnesium chloride (**5a**) and 2-methylprop-2-enesulfonyl chloride (**1**) at room temperature. Our results are summarized in Table 1. As for the desulfinylative C–C cross-coupling reactions of alkane- and alkenylsulfonyl chlorides

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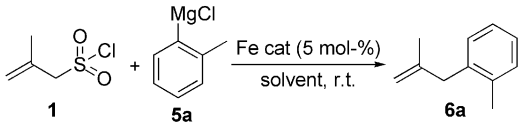
with Grignard reagents,[12] air-stable $Fe(acac)_3$ in THF appears to be a better catalyst than $FeCl_3$ or FeF_3 (Table 1, Entry 1 vs. 7). The use of a cosolvent like NMP (*N*-methylpyrrolidone) did not improve the reaction (Table 1, Entry 3). Contrary to aliphatic sulfonyl chlorides, which require refluxing temperatures for the successful reaction, these allylations occur smoothly at room temperature with good yields. Interestingly, the reaction can be run with only 2 mol-% of $Fe(acac)_3$ in THF, although it takes longer time for completion.

Table 1. Screening of iron salts for the coupling of 2-methylprop-2-enesulfonyl chloride (**1**) with *o*-tolylmagnesium chloride (**5a**).[a]



1 **5a** **6a**

Entry	Fe catalyst	Solvent	Time [h]	Yield[b] [%]
1	$Fe(acac)_3$	THF	3	82
2	$Fe(acac)_3$	DME	2	75
3	$Fe(acac)_3$	THF/NMP (4:1)[c]	2	78
4	$Fe(acac)_3$	THF	2	73[d]
5	$Fe(acac)_3$	THF	8	61[e]
6	$FeCl_3$	THF	3	78
7	FeF_3	THF	4	58

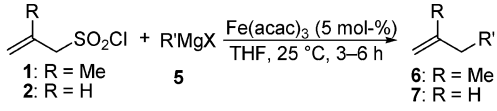
[a] Sulfonyl chloride (1.0 equiv.) with the Grignard reagent (1.5 equiv.) in the presence of the iron salt (5 mol-%) in the given solvent (5 mL). [b] Yield of isolated product after column chromatography on silica gel. [c] A mixture of THF (4 mL) and NMP (1 mL) was used as solvent. [d] Reaction was done under reflux instead of at room temperature. [e] Reaction was done with 2 mol-% of $Fe(acac)_3$. THF = tetrahydrofuran, DME = dimethoxyethane, NMP = *N*-methylpyrrolidone.

Even more interestingly, for reactions done at room temperature no sulfone was formed. This is not the case with non-allylic sulfonyl chlorides. This suggests that the low-valent iron species generated upon reaction of the Grignard reagent with $Fe(acac)_3$[25,30,31] coordinates to the alkene quickly, which accelerates the oxidative addition on the C–S bond, leading to an allyliron-type of intermediate.

We then explored the scope of this new iron-catalyzed electrophilic allylation by using sulfonyl chlorides **1** and **2** with various aryl and alkyl Grignard reagents. Good yields for products **6** and **7** were obtained in most cases, as shown in Table 2. Differently substituted aromatic Grignard reagents and a heteroaromatic Grignard reagent coupled nicely under the optimized conditions with alk-2-enesulfonyl chlorides. The successful application of aliphatic Grignard reagents as the coupling partners will increase the scope of these iron-catalyzed coupling reactions (Table 2, Entries 7, 8, and 11).

Using *o*-tolylmagnesium chloride (**5a**), we examined the regioselectivity of its cross-coupling with a 3:1 mixture of (*E*)- and (*Z*)-but-2-enesulfonyl chloride (**3**; Table 3). Applying our standard conditions [5 mol-% of $Fe(acac)_3$, THF, r.t.], the product ratio was found to be 86:14 (**8a** vs. **9a**). Changing solvent from THF to toluene did not improve this regioselectivity (Table 3, Entry 2). In 1,2-dimethoxyethane (DME) and acetonitrile the ratio was slightly better (9:1 and 88:12, respectively). Using iron salts other than $Fe(acac)_3$ such as $FeCl_3$ in THF or $FeBr_3$ in THF led to the best regioselectivity (9:1). $FeCl_3$/DME was not as good as $FeCl_3$/THF. No improvement could be observed with $FeCl_2$ (Table 3, Entry 8), $Fe(ClO_4)_2$ (Table 3, Entry 9), $FeBr_2$ (Table 3, Entry 12), and FeF_3 (Table 3, Entry 10) in THF, but interestingly, all these iron salts did catalyze the desulfinylative C–C cross-coupling reaction requiring somewhat longer reactions times than with $Fe(acac)_3$. With Fe_2O_3 in THF (Table 3, Entry 13) only trace amounts of product **10a** + **11a** were formed, probably because of the low solubility of iron oxide.

Table 2. Iron-catalyzed allylation of Grignard reagents with allylsulfonyl chlorides.



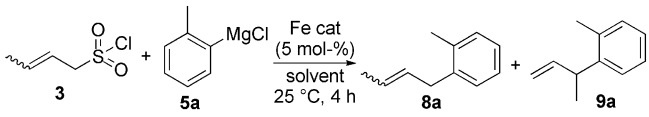
1: R = Me
2: R = H
5
6: R = Me
7: R = H

Entry	RSO_2Cl	R'	Product	Time [h]	Yield[a] [%]
1	**1**	*o*-tolyl (**5a**)	**6a**	3	82
2	**1**	*p*-tolyl (**5b**)	**6b**	3	79
3	**1**	*p*-methoxyphenyl (**5c**)	**6c**	3	87
4	**1**	*p*-fluorophenyl (**5d**)	**6d**	4	74
5	**1**	*p*-dimethylphenyl (**5e**)	**6e**	3	76
6	**1**	2-thiophenyl (**5f**)	**6f**	4	64
7	**1**	cyclohexyl (**5g**)	**6g**	6	61
8	**1**	2-phenethyl (**5h**)	**6f**	6	56
9	**2**	phenyl (**5i**)	**7a**	3	78
10	**2**	*p*-methoxyphenyl (**5c**)	**7b**	3	91
11	**2**	*n*-octyl (**5j**)	**7c**	6	75

[a] Yield of isolated product after flash column chromatography on silica gel.

We explored the scope of the allylation reaction with **3** for *p*-tolylmagnesium bromide (**5b**) and *p*-methoxyphenylmagnesium bromide (**5c**) by using $Fe(acac)_3$ (5 mol-%) as catalyst in DME at 25 °C. After 4 h, 88:12 and 85:15 mixtures of products **8b/9b** and **8c/9c** were obtained in 82 and 85% yield, respectively (Table 4). Interestingly, nearly the

Table 3. Regioselectivity of the allylation of *o*-tolylmagnesium chloride (**5a**) with a 3:1 mixture of (*E*)- and (*Z*)-but-2-enesulfonyl chloride (**3**).



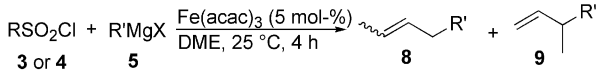
3 5a 8a 9a

Entry	Fe catalyst	Solvent	Ratio[a] (% yield)[b]
1	$Fe(acac)_3$	THF	86:14 (78)
2	$Fe(acac)_3$	toluene	85:15
3	$Fe(acac)_3$	DME	90:10 (75)
4	$Fe(acac)_3$	CH_3CN	88:12 (57)
5	$Fe(OAc)_2$	THF	85:15
6	$FeCl_3$	THF	90:10 (68)
7	$FeCl_3$	DME	84:16 (71)
8	$FeCl_2$	THF	87:13
9	$Fe(ClO_4)_2$	THF	83:17
10	FeF_3	THF	80:20
11	$FeBr_3$	THF	90:10
12	$FeBr_2$	THF	85:15
13	Fe_2O_3	THF	traces

[a] The **8/9** product ratio was determined by analysis of the ^1H NMR spectrum of the crude reaction mixture. [b] Yield of **8** + **9** determined after column chromatography on silica gel.

same mixtures of **8a/9a**, **8b/9b**, and **8c/9c** were obtained when using 2-methylprop-2-enesulfonyl chloride (**4**) as electrophilic allylating agent (Table 4) in comparable yields.

Table 4. Scope of the iron-catalyzed coupling of sulfonyl chlorides with Grignard reagents.

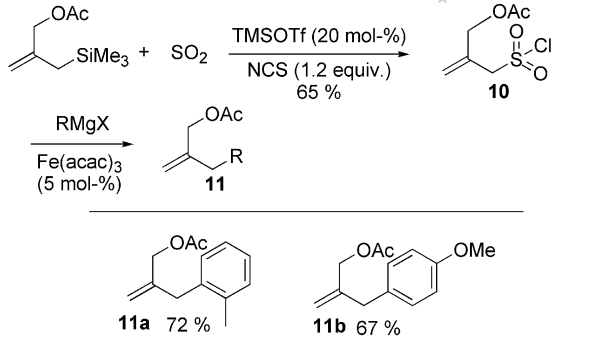


3 or 4 5 8 9

Entry	RSO_2Cl	R′	Yield[a] [%]	Ratio (product)[b]	Ratio (*E*)-**8**/(*Z*)-**8**
1	**3**	*o*-tolyl (**5a**)	75	90:10 (**8a+9a**)	10: 1
2	**3**	*p*-tolyl (**5b**)	82	88:12 (**8b+9b**)	6:1
3	**3**	*p*-methoxyphenyl (**5c**)	85	85:15 (**8c+9c**)	8:1
4	**4**	*o*-tolyl (**5a**)	72	88:12 (**8a+9a**)	10:1
5	**4**	*p*-tolyl (**5b**)	77	87:13 (**8b+9b**)	6:1
6	**4**	*p*-methoxyphenyl (**5c**)	79	84:16 (**8c+9c**)	8:1

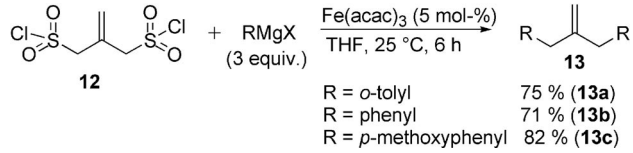
[a] Yield of **8a** + **9a** determined after column chromatography on silica gel. [b] The **8/9** product ratio was determined by analysis of the ^1H NMR spectrum of the crude reaction mixture.

We have already demonstrated that coupling of sulfonyl chlorides with Grignard reagents tolerates a wide range of functional groups, including carbonyl groups which are prone to react with Grignard reagents. To further expand the scope of these coupling reactions, we prepared allyl sulfonyl chloride **10** containing an allyl ester group (Scheme 2).[32] As proof of principle, **10** was treated with Grignard reagents and to our delight the coupling reaction tolerated the ester functional group to give the corresponding products **11**. This reaction shows that (a) ester groups are tolerated in the coupling reaction and (b) alk-2-enesulfonyl chloride was more reactive than allyl ester towards the Grignard reagent.



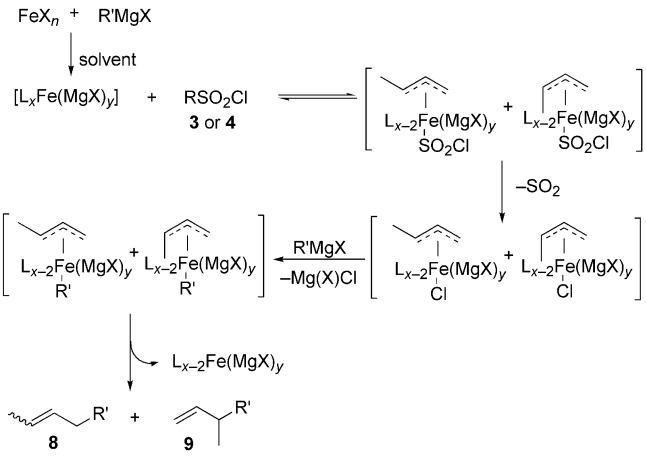
Scheme 2. Iron-catalyzed coupling of a functionalized alk-2-ene-1-sulfonyl chloride with Grignard reagents.

The scope of the iron-catalyzed cross-coupling reaction was further tested by using disulfonyl dichloride **12**. It reacted with different aromatic Grignard reagents under our standard conditions with the use of $Fe(acac)_3$ (5 mol-%). The reactions were completed in 6 h to give the symmetrically substituted coupling products **13** in good yields (Scheme 3).



Scheme 3. Coupling of disulfonyl dichlorides with Grignard reagents.

The same regioselectivity was obtained starting either with sulfonyl chloride **3** or **4**. This suggests that the same type of 1-methylallyl iron intermediate was formed independently from **3** and **4** and that they coupled with the Grignard reagents with nearly the same regioselectivity, independent of the nature of the initial iron salt and the nature of the arylmagnesium reagent. The preference for non-branched products **8** can be attributed to a steric effect that renders the insertion of the aryl group easier at the unsub-



Scheme 4. Proposed mechanism for the iron-catalyzed desulfinylative allylation of Grignard reagents with alk-2-enesulfonyl chlorides.

stituted end of the allyl moiety than at the substituted end. The mechanism shown in Scheme 4 interprets the data presented.

Conclusion

In conclusion, we have developed a new iron-catalyzed desulfinylative coupling of alk-2-enesulfonyl chlorides (which can be prepared easily from alkenes) with Grignard reagents in THF. A variety of nucleophilic reagents like aromatic, aliphatic, and heteroaromatic Grignard reagents were coupled with alk-2-enesulfonyl chlorides under mild conditions (room temperature, no ligand, harmless solvent) to give the C–C cross-coupling products in high yields. Allylations with the use of but-2-ene-1-sulfonyl and but-3-ene-2-sulfonyl chloride and aryl Grignard reagents led to the same mixture of regioisomers (85:15 to 9:1), favoring linear products. Preliminary experiments showed that our C–C cross-coupling conditions are tolerant towards allylic ester moieties (Scheme 2). Symmetrical products resulting from the double C–C coupling of 2-methylidenepropane-1,3-disulfonyl dichloride were also obtained in good yields. This new chemistry takes special value knowing that alk-2-enesulfonyl chlorides can be prepared by the BCl_3-promoted ene reaction of alkenes with SO_2 (Scheme 1).

Experimental Section

Methods: Unless stated otherwise, reactions were conducted in flame-dried glassware under a vacuum. THF was distilled before use from sodium and benzophenone. Solvents after reactions and extraction were evaporated in a rotary evaporator under vacuum (solvents were removed by cooling at –20 °C for low-boiling or low-molecular-mass compounds). TLC for reaction monitoring was performed on 60 F_{254} (Merck) with detection by UV light and charring with $KMnO_4$ or Pancaldi reagent. ^1H and ^{13}C NMR spectra were recorded with Bruker-DPX-400 or Bruker-ARX-400 spectrometer at 400 MHz and 100.6 MHz, respectively, and are reported relative to Me_4Si (δ = 0.0 ppm) or to the solvents residual ^1H signal ($CHCl_3$, δ_H = 7.27 ppm). Data for ^1H NMR spectra are reported as follows: chemical shift, multiplicity, coupling constant, and integration. Data for ^{13}C NMR spectra reported in terms of chemical shift. IR spectra were recorded with a Perkin–Elmer-1420 spectrometer and are reported in frequency of absorption (cm^{-1}). High-resolution MALDI-TOF mass spectra were obtained from the Institute of Molecular and Biology Chemistry, Swiss Institute of Technology Mass Spectral Facility, EPFL, Lausanne. 1,3-Bischlorsulfonyl-2-methylenepropane was prepared from a known procedure.

2-Methylprop-2-ene-1-sulfonyl Chloride (1):[33] In a two-necked, 100–mL, round-bottomed flask was placed a solution of BCl_3 (1.0 M in DCM, 36 mL, 35.7 mmol, 1 equiv.) under an argon atmosphere. Sulfur dioxide (0.71 mol, 20 equiv.), dried through a column packed with phosphorus pentoxide and aluminum oxide, was transferred on the vacuum line to the solution frozen at –196 °C. The mixture was allowed to melt and to warm to –40 °C. After 30 min at this temperature, 2-methylpropene (2.0 g, 35.7 mmol, 1 equiv.) was transferred to the solution frozen at –196 °C. The mixture was stirred at –20 °C for 6 h. After cooling to –78 °C, the excess amount of SO_2 and the solvent were evaporated under reduced pressure (10^{-3} Torr) to dryness (ca. 1 h). NCS (5.7 g, 42.8 mmol, 1.2 equiv.) dissolved in DCM was added to the reaction mixture at –20 °C, and the mixture was allowed to reach room temperature in 3 h. The reaction mixture was quenched with water, and the aqueous layer was extracted with DCM (3 × 100 mL). The combined organic phase was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude mixture was filtered through a pad of silica gel to obtain **1** (4.67 g, 30.3 mmol, 85%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.01 (s, 3 H, Me), 4.34 (s, 2 H, CH_2), 5.32 (br. s, 1 H, olefinic), 5.41 (br. s, 1 H, olefinic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.2, 73.2, 124.2, 132.0 ppm. MS (CI, NH_3): *m*/*z* (%) = 172 (4) $[M + 18]^+$, 154 (1) $[M + 1]^+$, 90 (10) $[M – 64]^+$, 72 (100) $[M – 82]^+$.

Prop-2-ene-1-sulfonyl Chloride (2):[34] Using the same procedure as that used for **1**, starting from 1-propene (2.0 g, 47.6 mmol, 1 equiv.) in the presence of a solution of BCl_3 (1.0 M in DCM, 47.6 mL), product **2** (5.4 g, 38.6 mmol, 81%) was obtained as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.34 (d, *J* = 7.4 Hz, 2 H, CH_2), 5.71 (m, 2 H, olefinic), 6.05 (m, 1 H, olefinic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 69.0, 123.4, 128.1 ppm. MS (CI, NH_3): *m*/*z* (%) = 158 (16) $[M + 18]^+$, 140 (22) $[M]^+$, 76 (100) $[M – 64]^+$.

2-Butene-1-sulfonyl Chloride (3):[35] Using the same procedure as that used for **1**, starting from 1-butene (2.0 g, 35.7 mmol, 1 equiv.) in the presence of a solution of BCl_3 (1.0 M in DCM, 36 mL), product **3** (4.78 g, 31.0 mmol, 87%) was obtained as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.72 (d, *J* = 6.8 Hz, 3 H, Me), 4.26 (m, 1 H, CH), 5.62 (m, 1 H, olefinic), 5.98 (m, 1 H, olefinic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.4, 77.5, 127.9, 132.5 ppm. MS (CI, NH_3): *m*/*z* (%) = 154 (27) $[M]^+$, 98 (100) $[M – 55]^+$.

3-Butene-2-sulfonyl Chloride (4):[9] Using the same procedure as that for **1**, starting from 2-butene (2.0 g, 35.7 mmol, 1 equiv.) in the presence of a solution of BCl_3 (1.0 M in DCM, 36 mL), product **4** (4.34 g, 28.2 mmol, 79%) was obtained as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.65 (d, *J* = 6.5 Hz, 3 H, Me), 3.54 (d, *J* = 7.4 Hz, 2 H, CH_2), 5.52 (m, 1 H, olefinic), 5.81 (m, 1 H, olefinic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.6, 68.9, 116.0, 140.6 ppm. MS (CI, NH_3): *m*/*z* (%) = 155 (47) $[M + 1]^+$, 88 (100) $[M – 66]^+$.

2-[(Chlorosulfonyl)methyl]allyl Acetate (10): TMSOTf (2.16 mmol, 20 mol-%) in anhydrous CH_3CN (10 mL) was degassed by freeze–thaw cycles on the vacuum line. Sulfur dioxide (0.21 mol, 20 equiv.), dried through a column packed with phosphorus pentoxide and aluminum oxide, was transferred on the vacuum line to the CH_3CN solution frozen at –196 °C. The mixture was allowed to melt and to warm to –40 °C. After 30 min at this temperature, 2-(trimethylsilylmethyl)allyl acetate (10.8 mmol, 1 equiv.) was added slowly. The mixture was stirred at –20 °C for 12 h. After cooling to –78 °C, the excess amount of SO_2 and the solvent were evaporated under reduced pressure (10^{-3} Torr) to dryness (ca. 1 h). Halogenating agent (NCS 16.2 mmol, 1.2 equiv., dissolving in CH_3CN) was added to the reaction mixture at –20 °C. After 3 h at this temperature, the reaction mixture was quenched with water, and the aqueous layer was extracted with DCM (3 × 100 mL). The combined organic phase was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ether, 9:1) to obtain **10** (1.49 g, 7.0 mmol, 65%) as a light yellow oil. IR (film): $\tilde{\nu}$ = 2922, 1736, 1369, 1223, 1168, 1035, 941, 677, 632, 602 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, Me), 4.44 (s, 2 H, CH_2), 4.76 (s, 2 H, OCH_2), 5.66 (s, 1 H, olefinic), 5.75 (s, 1 H, olefinic)

ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.7, 65.1, 68.3, 126.7, 131.2, 170.2 ppm. HRMS (ESI-TOF): calcd. for $C_6H_9ClO_4S$ 212.9988; found 212.9985.

Typical Experimental Procedure for the Iron-Catalyzed Desulfinylative Allylations: In a glove box under a nitrogen atmosphere, a round-bottomed flask, dried under vacuum, was charged with the corresponding sulfonyl chloride (1 equiv.) and $Fe(acac)_3$ (5 mol-%). Then, the flask was connected to a vacuum line and filled with argon (3×) and solvent (5 mL). The corresponding Grignard reagent (1.5 equiv.) was added dropwise over 5–10 min by syringe. The reaction mixture was stirred until complete disappearance of the starting material. The mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and diluted with diethyl ether. The aqueous layer was extracted again with diethyl ether (3 × 20 mL). The combined organic phase was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluting with pentane.

1-Methyl-2-(2-methylallyl)benzene (Table 2, Entry 1):[7] Following the typical experimental procedure, sulfonyl chloride **1** (0.1 g, 0.65 mmol, 1 equiv.) and *o*-tolylmagnesium chloride (**5a**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the product (78 mg 82%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, Me), 2.31 (s, 3 H, Me-arom.), 3.35 (s, 2 H, CH_2), 4.56 (s, 1 H, olefinic), 4.84 (s, 1 H, olefinic), 7.15–7.19 (m, 4 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.3, 22.7, 41.8, 111.5, 125.8, 126.3, 129.8, 130.1, 136.8, 137.9, 144.2 ppm. MS (CI, NH_3): *m*/*z* (%) = 147 (8) $[M + 1]^+$, 146 (68) $[M]^+$, 131 (100) [M – 15], 105 (19) $[M – 41]^+$, 91 (33) $[M – 55]^+$.

1-Methyl-4-(2-methylallyl)benzene (Table 2, Entry 2):[36] Following the typical experimental procedure, sulfonyl chloride **1** (0.1 g, 0.65 mmol, 1 equiv.) and *p*-tolylmagnesium bromide (**5b**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the product (75 mg, 79%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (s, 3 H, Me), 2.40 (s, 3 H, Me-arom.), 3.32 (s, 2 H, CH_2), 4.47 (s, 1 H, olefinic), 4.83 (s, 1 H, olefinic), 7.12–7.15 (m, 4 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.0, 22.1, 44.2, 111.7, 128.8, 129.0,135.5, 136.7, 145.4 ppm. MS (CI, NH_3): *m*/*z* (%) = 147 (7) $[M + 1]^+$, 146 (63) $[M]^+$, 131 (100) [M – 15], 105 (29) $[M – 41]^+$, 91 (43) $[M – 55]^+$.

1-Methoxy-4-(2-methylallyl)benzene (Table 2, Entry 3):[37] Following the typical experimental procedure, sulfonyl chloride **1** (0.1 g, 0.65 mmol, 1 equiv.) and 4-methoxyphenylmagnesium bromide (**5c**; 0.5 M in THF, 2.0 mL, 1.0 mmol, 1.5 equiv.) gave the product (91 mg, 87%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (s, 3 H, Me), 3.31 (s, 2 H, CH_2), 3.85 (s, 3 H, OMe), 4.76 (s, 1 H, olefinic), 4.83 (s, 1 H, olefinic), 6.88 (d, *J* = 8.7 Hz, 2 H, arom.), 7.15 (d, *J* = 8.7 Hz, 2 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.0, 43.7, 55.3, 111.5, 113.7, 129.8, 131.9, 145.6, 158.0 ppm. MS (CI, NH_3): *m*/*z* (%) = 163 (13) $[M + 1]^+$, 162 (98) $[M]^+$, 147 (100) [M – 15], 121 (70) $[M – 41]^+$, 91 (29) $[M – 71]^+$.

1-Fluoro-4-(2-methylallyl)benzene (Table 2, Entry 4): Following the typical experimental procedure, sulfonyl chloride **1** (0.1 g, 0.65 mmol, 1 equiv.) and 4-fluorophenylmagnesium bromide (**5d**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the product (72 mg, 74%) as a light yellow oil. IR (film): $\tilde{\nu}$ = 2972, 2909, 1601, 1506, 1220, 1156, 1093, 1016, 891, 806, 776, 632, 567 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3 H, Me), 3.31 (s, 2 H, CH_2), 4.73 (s, 1 H, olefinic), 4.82 (s, 1 H, olefinic), 6.96–7.02 (m, 2 H, arom.), 7.13–7.19 (m, 2 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.4, 43.6, 112.0, 115.0 (d, *J* = 20.8 Hz), 130.1 (d, *J* = 8.0 Hz), 135.3 (d, *J* = 2.9 Hz), 145.1, 161.4 (d, *J* = 244.2 Hz) ppm. MS (CI, NH_3): *m*/*z* (%) = 151 (7) $[M + 1]^+$, 150 (61) $[M]^+$, 135 (100) $[M – 15]^+$, 115 (20) $[M – 35]^+$, 109 (60) $[M – 41]^+$.

***N*,*N*-Dimethyl-4-(2-methylallyl)benzenamine (Table 2, Entry 5):**[38] Following the typical experimental procedure, sulfonyl chloride **1** (0.1 g, 0.65 mmol, 1 equiv.) and 4-(*N*,*N*-dimethyl)aniline magnesium bromide (**5e**; 0.5 M in THF, 2.0 mL, 1.0 mmol, 1.5 equiv.) gave the product (86 mg, 76%) as a dark brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (s, 3 H, Me), 2.95 [s, 6 H, $N(CH_3)_2$], 3.26 (s, 2 H, CH_2), 4.75 (s, 1 H, olefinic), 4.81 (s, 1 H, olefinic), 6.73 (d, *J* = 8.8 Hz, 2 H, arom.), 7.09 (d, *J* = 8.8 Hz, 2 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.1, 40.9, 43.7, 111.2, 112.9, 127.9, 129.5, 146.0, 149.2 ppm. HRMS (ESI-TOF): calcd. for $C_{12}H_{17}N$ 176.1439; found 176.1440.

2-(2-Methylallyl)thiophene (Table 2, Entry 6): Following the typical experimental procedure, sulfonyl chloride **1** (0.1 g, 0.65 mmol, 1 equiv.) and thiophen-2-yl-magnesium bromide (**5f**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the product (57 mg, 64%) as a colorless oil. IR (film): $\tilde{\nu}$ = 2977, 1383, 1111, 904, 727, 650, 632, 544, 532 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, Me), 3.54 (s, 2 H, CH_2), 4.86 (br. s, 2 H, olefinic), 6.83–6.86 (m, 1 H, arom.), 6.96 (dd, *J* = 5.1, 3.3 Hz, 1 H, arom.), 7.17 (dd, *J* = 5.1, 1.2 Hz, 1 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8, 38.5, 112.1, 123.7, 125.3, 126.7, 142.6, 144.5 ppm. MS (CI, NH_3): *m*/*z* (%) = 139 (11) $[M + 1]^+$, 138 (98) $[M]^+$, 123 (100) [M – 15], 97 (93) $[M – 41]^+$. HRMS (ESI-TOF): calcd. for $C_8H_{10}S$ 139.0581; found 139.0583.

(2-Methylallyl)cyclohexane (Table 2, Entry 7):[39] Following the typical experimental procedure, sulfonyl chloride **1** (0.1 g, 0.65 mmol, 1 equiv.) and cyclohexylmagnesium chloride (**5g**; 2.0 M in Et_2O, 0.5 mL, 1.0 mmol, 1.5 equiv.), gave the product (55 mg, 61%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0. 84 (m, 2 H, cyclohexyl), 1.21–1.50 (m, 8 H, cyclohexyl), 1.52 (m, 1 H, cyclohexyl), 1.71 (s, 3 H, Me), 1.91 (d, *J* = 7.3 Hz, 2 H, CH_2), 4.65 (br. s, 1 H, olefinic), 4.74 (br. s, 1 H, olefinic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.3, 26.4, 26.6, 33.3, 35.4, 46.2, 111.1, 144.6 ppm. MS (CI, NH_3): *m*/*z* (%) = 138 (7) $[M]^+$, 123 (2) $[M – 15]^+$, 82 (49) $[M – 56]^+$, 67 (49) $[M – 71]^+$, 55 (100) $[M – 83]^+$.

(4-Methylpent-4-enyl)benzene (Table 2, Entry 8):[40] Following the typical experimental procedure, sulfonyl chloride **1** (0.1 g, 0.65 mmol, 1 equiv.) and 2-phenethylmagnesium chloride (**5h**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the product (58 mg, 56%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74 (s, 3 H, Me), 1.75–1.82 (m, 2 H, CH_2), 2.07 (t, *J* = 7.5 Hz, 2 H, CH_2), 2.62 (t, *J* = 7.8 Hz, 2 H, CH_2), 4.71 (br. s, 1 H, olefinic), 4.74 (br. s, 1 H, olefinic), 7.18–7.22 (m, 2 H, arom.), 7.27–7.31 (m, 3 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.4, 29.4, 35.5, 37.4, 110.1, 125.7, 128.2, 128.5, 142.6, 145.7 ppm. MS (CI, NH_3): *m*/*z* (%) = 160 (9) $[M]^+$, 144 (4) [M – 26], 104 (100) $[M – 56]^+$.

Allylbenzene (Table 2, Entry 9): Following the typical experimental procedure, sulfonyl chloride **2** (0.1 g, 0.71 mmol, 1 equiv.) and phenylmagnesium chloride (**5i**; 1.8 M in THF, 0.6 mL, 1.1 mmol, 1.5 equiv.) gave the product (65 mg, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.41 (d, *J* = 6.5 Hz, 2 H, CH_2), 5.06–5.14 (m, 2 H, olefinic), 5.94–6.06 (m, 1 H, olefinic), 7.24–7.32 (m, 3 H, arom.), 7.34–7.42 (m, 2 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 40.5, 115.8, 126.2, 128.4, 128.6, 137.5, 140.1 ppm. MS (CI, NH_3): *m*/*z* (%) = 118 (81) $[M]^+$, 117 (100) $[M – 1]^+$, 103 (8) $[M – 15]^+$, 91 (38) $[M – 27]^+$.

1-Allyl-4-methoxybenzene (Table 2, Entry 10): Following the typical experimental procedure, sulfonyl chloride **2** (0.1 g, 0.71 mmol, 1 equiv.) and 4-methoxyphenylmagnesium bromide (**5c**; 1.0 M in THF, 1.1 mL, 1.1 mmol, 1.5 equiv.) gave the product (96 mg, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.39 (d, J = 6.6 Hz, 2 H, CH_2), 3.84 (s, 3 H, OMe), 5.08–5.16 (m, 2 H, olefinic), 5.96–6.07 (m, 1 H, olefinic), 6.90 (d, J = 8.6 Hz, 2 H, arom.), 7.16 (d, J = 8.6 Hz, 2 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 39.4, 55.3, 113.8, 115.4, 129.5, 132.1, 137.9, 158.0 ppm. MS (CI, NH_3): m/z (%) = 149 (8) $[M + 1]^+$, 148 (100) $[M]^+$, 133 (23) $[M - 15]$, 117 (41) $[M - 31]^+$, 91 (31) $[M - 57]^+$.

1-Undecene (Table 2, Entry 11): Following the typical experimental procedure, sulfonyl chloride **2** (0.1 g, 0.71 mmol, 1 equiv.) and *n*-octylmagnesium bromide (**5j**; 2.0 M in Et_2O, 0.55 mL, 1.1 mmol, 1.5 equiv.) gave the product (82 mg, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0. 88–0.93 (m, 3 H, Me), 1.24–1.35 (m, 12 H, 6 CH_2), 1.36–1.44 (m, 2 H, CH_2), 2.07–2.10 (m, 2 H, CH_2), 4.92–5.06 (m, 2 H, olefinic), 5.78–5.90 (m, 1 H, olefinic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.9, 29.2, 29.3, 29.5, 29.6, 31.9, 33.8, 114.07, 139.3 ppm. MS (CI, NH_3): m/z (%) = 154 (3) $[M]^+$, 126 (6) $[M - 28]^+$, 111 (14) $[M - 43]^+$, 97 (31) $[M - 57]^+$, 83 (55) $[M - 71]^+$, 69 (68) $[M - 85]^+$, 55 (100) $[M - 99]^+$.

1-(But-2-enyl)-2-methylbenzene[9] and 1-(But-3-en-2-yl)-2-methylbenzene (Table 4, Entries 1 and 4)[9]

Method A: Following the typical experimental procedure, sulfonyl chloride **3** (0.1 g, 0.65 mmol, 1 equiv.) and *o*-tolylmagnesium chloride (**5a**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the mixture of products (71 mg, 75%) as a colorless oil.

Method B: Following the typical experimental procedure, sulfonyl chloride **4** (0.1 g, 0.65 mmol, 1 equiv.) and *o*-tolylmagnesium chloride (**5a**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the mixture of products (68 mg, 72%) as a colorless oil.

1-(But-2-enyl)-2-methylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (dq, J = 6.2, 1.4 Hz, 3 H, Me), 2.34 (s, 3 H, Me-arom.), 3.35 (dt, J = 6.3, 1.3 Hz, 2 H, CH_2), 5.43–5.54 (m, 1 H, olefinic), 5.57-5.66 (m, 1 H, olefinic), 7.14–7.21 (m, 4 H, arom.) ppm.

1-(But-3-en-2-yl)-2-methylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (d, J = 6.8 Hz, 3 H, Me), 2.39 (s, 3 H, Me-arom.), 3.70–3.78 (m, 1 H, CH), 5.03–5.12 (m, 2 H, olefinic), 5.98- 6.10 (m, 1 H, olefinic), 7.14–7.21 (m, 4 H, arom.) ppm. MS (CI, NH_3): m/z (%) = 147 (8), $[M + 1]^+$, 146 (54) $[M]^+$, 105 (100), $[M - 41]^+$, 91 (36) $[M - 55]^+$.

1-(But-2-enyl)-4-methylbenzene[41] and 1-(But-3-en-2-yl)-4-methylbenzene (Table 4, Entries 2 and 5):[42]

Method A: Following the typical experimental procedure, sulfonyl chloride **3** (0.1 g, 0.65 mmol, 1 equiv.) and *p*-tolylmagnesium chloride (**5b**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the mixture of products (78 mg, 82%) as a colorless oil.

Method B: Following the typical experimental procedure, sulfonyl chloride **4** (0.1 g, 0.65 mmol, 1 equiv.) and *p*-tolylmagnesium chloride (**5b**; 1.0 M in THF, 1.0 mL, 1.0 mmol, 1.5 equiv.) gave the mixture of products (73 mg, 77%) as a colorless oil.

1-(But-2-enyl)-4-methylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (dq, J = 6.0, 1.2 Hz, 3 H, Me), 2.35 (s, 3 H, Me-arom.), 3.31 (d, J = 6.3 Hz, 2 H, CH_2), 5.47–5.66 (m, 2 H, olefinic), 7.09–7.15 (m, 4 H, arom.).

1-(But-3-en-2-yl)-4-methylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (d, J = 7.0 Hz, 3 H, Me), 2.36 (s, 3 H, Me-arom.), 3.42–3.51 (m, 1 H, CH), 5.02–5.10 (m, 2 H, olefinic), 5.97- 6.07 (m, 1 H, olefinic), 7.09–7.15 (m, 4 H, arom.). MS (CI, NH_3): m/z (%) = 147 (7) $[M + 1]^+$, 146 (62) $[M]^+$, 131 (100) $[M - 15]$, 115 (18) $[M - 31]^+$, 91 (34) $[M - 55]^+$.

1-(But-2-enyl)-4-methoxybenzene and 1-(But-3-en-2-yl)-4-methoxybenzene (Table 4, Entries 3 and 6):[43]

Method A: Following the typical experimental procedure, sulfonyl chloride **3** (0.1 g, 0.65 mmol, 1 equiv.) and 4-methoxyphenylmagnesium bromide (**5c**; 0.5 M in THF, 2.0 mL, 1.0 mmol, 1.5 equiv.) gave the mixture of products (90 mg, 85%) as a colorless oil.

Method B: Following the typical experimental procedure, sulfonyl chloride **4** (0.1 g, 0.65 mmol, 1 equiv.) and 4-methoxyphenylmagnesium bromide (**5c**; 0.5 M in THF, 2.0 mL, 1.0 mmol, 1.5 equiv.) gave the mixture of products (83 mg, 79%) as a colorless oil.

1-(But-2-enyl)-4-methoxylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (dq, J = 6.1, 1.2 Hz, 3 H, Me), 3.31 (d, J = 6.4 Hz, 2 H, CH_2), 3.83 (s, 3 H, OMe), 5.47–5.68 (m, 2 H, olefinic), 6.88 (d, J = 8.6 Hz, 2 H, arom.), 7.14 (d, J = 8.6 Hz, 2 H, arom.).

1-(But-3-en-2-yl)-4-methoxylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (d, J = 7.1 Hz, 3 H, Me), 3.43–3.51 (m, 1 H, CH), 5.04–5.11 (m, 2 H, olefinic), 6.00- 6.09 (m, 1 H, olefinic), 6.90 (d, J = 8.7 Hz, 2 H, arom.), 7.18 (d, J = 8.7 Hz, 2 H, arom.) ppm. MS (CI, NH_3): m/z (%) = 163 (13) $[M + 1]^+$, 162 (99) $[M]^+$, 147 (100) $[M - 15]$, 131 (45) $[M - 31]^+$, 115 (50) $[M - 47]^+$, 91 (79) $[M - 71]^+$.

2-(2-Methylbenzyl)-2-propenyl Acetate (11a): Following the typical experimental procedure, sulfonyl chloride **10** (0.3 g, 1.4 mmol, 1 equiv.) and *o*-tolylmagnesium chloride (**5a**; 1.0 M in THF, 2.2 mL, 2.2 mmol, 1.5 equiv.) gave the product (205 mg, 72%) as a light yellow oil. IR (film): $\tilde{\nu}$ = 2926, 1737, 1372, 1225, 1028, 908, 743, 631, 604, 530 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, Me), 2.27 (s, 3 H, Me-arom.), 3.39 (s, 2 H, CH_2), 4.54 (s, 2 H, OCH_2), 4.75 (br. s, 1 H, olefinic), 5.12 (br. s, 1 H, olefinic), 7.12–7.17 (m, 4 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.5, 20.8, 37.3, 67.0, 114.3, 125.9, 126.7, 129.9, 130.2, 136.5, 136.8, 142.4, 170.7 ppm. MS (CI, NH_3): m/z (%) = 204 (9) $[M]^+$, 162 (8) $[M - 42]^+$, 144 (70) $[M - 60]^+$, 129 (100) $[M - 75]^+$, 91 (15) $[M - 133]^+$. HRMS (ESI-TOF): calcd. for $C_{13}H_{16}O_2$ 205.1228; found 205.1238.

2-(4-Methoxybenzyl)-2-propenyl Acetate (11b): Following the typical experimental procedure, sulfonyl chloride **10** (0.3 g, 1.4 mmol, 1 equiv.) and 4-methoxyphenylmagnesium bromide (**5c**; 0.5 M in THF, 4.4 mL, 2.2 mmol, 1.5 equiv.) gave the product (206 mg, 67%) as a light yellow oil. IR (film): $\tilde{\nu}$ = 2933, 1740, 1510, 1373, 1245, 1177, 1035, 902, 808, 632, 574 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, Me), 3.35 (s, 2 H, CH_2), 3.81 (s, 3 H, OMe), 4.48 (s, 2 H, OCH_2), 4.96 (br. s, 1 H, olefinic), 5.11 (br. s, 1 H, olefinic), 6.84 (d, J = 8.9 Hz, 2 H, arom.), 7.10 (d, J = 8.9 Hz, 2 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.1, 39.5, 55.4, 66.4, 113.8, 113.9, 129.8, 130.5, 143.6, 158.2, 170.8 ppm. MS (CI, NH_3): m/z (%) = 221 (4) $[M + 1]^+$, 220 (34) $[M]^+$, 159 (100) $[M - 61]^+$, 145 (80) $[M - 75]$, 129 (63) $[M - 91]^+$, 91 (25) $[M - 129]^+$. HRMS (ESI-TOF): calcd. for $C_{13}H_{16}O_3$ 221.1178; found 221.1182.

2-Methylene-1,3-di*o*-tolylpropane (13a): Following the typical experimental procedure, sulfonyl chloride **12** (0.2 g, 0.8 mmol, 1 equiv.) and *o*-tolylmagnesium chloride (**5a**; 1.0 M in THF, 2.4 mL, 2.4 mmol, 3.0 equiv.) gave the product (142 mg, 75%) as a light yellow oil. IR (film): $\tilde{\nu}$ = 2921, 1644, 1493, 1460, 1378, 896, 741, 633, 541 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 6 H, Me-arom.), 3.34 (s, 4 H, 2CH_2), 4.60 (s, 2 H, olefinic), 7.11–7.17 (m, 8

H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.3, 40.2, 112.4, 125.8, 126.4, 129.9, 130.1, 136.8, 137.6, 146.4 ppm. MS (CI, NH_3): *m/z* (%) = 254 (14) $[M + 18]^+$, 236 (44) $[M]^+$, 221 (11) $[M – 15]^+$, 144 (25) $[M – 92]^+$, 130 (100) $[M – 106]^+$, 105 (59) $[M – 121]^+$, 91 (42) $[M – 145]^+$.

2-Methylene-1,3-diphenylpropane (13b):[44] Following the typical experimental procedure, sulfonyl chloride **12** (0.2 g, 0.8 mmol, 1 equiv.) and phenylmagnesium chloride (**5i**; 1.8 M in THF, 1.35 mL, 2.4 mmol, 3.0 equiv.) gave the product (118 mg, 71%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.31 (s, 4 H, $2CH_2$), 4.87 (s, 2 H, olefinic), 7.30–7.35 (m, 10 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 42.3, 113.4, 126.4, 128.4, 129.1, 139.6, 148.5 ppm. MS (CI, NH_3): *m/z* (%) = 209 (9) $[M + 1]^+$, 208 (52) $[M]^+$, 193 (25) [M – 15], 129 (33) $[M – 79]^+$, 117 (100) $[M – 91]^+$, 115 (84) $[M – 93]^+$, 91 (67) $[M – 117]^+$.

1,3-Bis(4-methoxyphenyl)-2-methylenepropane (13c): Following the typical experimental procedure, sulfonyl chloride **12** (0.2 g, 0.8 mmol, 1 equiv.) and 4-methoxyphenylmagnesium bromide (**5c**; 0.5 M in THF, 4.8 mL, 2.4 mmol, 3.0 equiv.) gave the product (176 mg, 82%) as a colorless oil. IR (film): $\tilde{\nu}$ = 2932, 1609, 1508, 1463, 1300, 1242, 1174, 1035, 907, 818, 732, 631 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.29 (s, 4 H, $2CH_2$), 3.86 (s, 6 H, OMe), 4.87 (s, 2 H, olefinic), 6.90 (d, *J* = 8.9 Hz, 4 H, arom.), 7.13 (d, *J* = 8.9 Hz, 2 H, arom.) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 41.2, 55.3, 112.7, 113.8, 130.1, 131.7, 149.2, 158.1 ppm. MS (CI, NH_3): *m/z* (%) = 268 (91) $[M]^+$, 253 (14) [M – 15], 160 (81) $[M – 108]^+$, 145 (65) $[M – 123]^+$, 121 (100) $[M – 147]^+$, 91 (31) $[M – 177]^+$. HRMS (ESI-TOF): calcd. for $C_{18}H_{20}O_2$ 269.1541; found 269.1538.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra of the compounds.

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