DOI: 10.1002/adsc.201100731

Iron-Catalysed Markovnikov Hydrothiolation of Styrenes

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Received: September 20, 2011; Revised: November 14, 2011; Published online: February 23, 2012

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201100731.

Abstract: The bis(triflimide)iron(III) salt catalyzes the hydrothiolation of styrenes in a Markovnikov fashion with good selectivities and high yields. After isolation, different benzylic thioethers are obtained. This iron(III) catalyst is unique in terms of regioselectivity and represents a sustainable and economic alternative to those processes based on stoichiometric reagents.

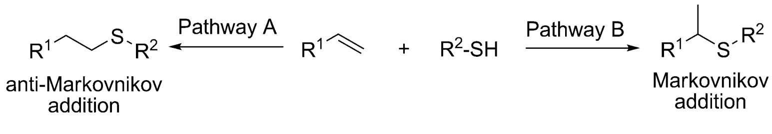
Keywords: benzylic thioethers; bis(triflimide)-iron(III); hydrothiolation; iron catalysis; Markovnikov addition; styrenes

Introduction

Carbon-sulfur bonds are present in compounds of industrial interest,[1] in many natural products,[2] and in pharmaceuticals with therapeutic activity such as cimetidine (antiulcer), 6-mercaptopurine (leukemia), and thorazine (antipsychotic).[1] Specifically, thioethers play an important role in organosulfur chemistry.[3] The synthesis of thioethers historically predates that of ethers and, as the latter, generally involves nucleophilic substitution of conveniently functionalized substrates (i.e., Williamson's or Mitsunobu's procedures). However, in the last years, the search for waste-free, environmentally-sustainable synthetic methods has stimulated chemists to explore the direct addition of X–H species (X = heteroatom) to unsaturated C–C bonds (hydroadditions). This strategy is 100% atom-economical since it allows both reactants to be fully incorporated in the final product. In fact, the hydration (H_2O), hydroalkoxylation (alcohols), and hydroesterification (esters) of alkenes are currently industrial processes.[4] Following Markovnikov's rule, the oxygen nucleophile adds onto the more positive carbon but, in contrast, the addition of thiols can proceed in two ways: free-radical (pathway A)[5] or electrophilic (pathway B, Scheme 1).

The addition of thiols to double bonds *via* a free-radical mechanism (pathway A) readily occurs under mild conditions and is fairly well described in the literature.[6–9] This process results exclusively in the formation of the anti-Markovnikov product and is generally carried out in the presence of a radical initiator (AIBN, light, etc.).[6–9] In contrast, the Markovnikov addition occurs when using over-stoichiometric amounts of Brønsted acids such as H_2SO_4 in AcOH,[10] *p*-TSA[11] and $HClO_4$[12] or Lewis acids ($TiCl_4$,[13] $AlCl_3$[14]). Very few examples of catalytic systems giving Markovnikov addition have been reported, and those include $In(OTf)_3$,[15] Fe(III) (as hemim complex[16] or as porphinato complex,[16b] using $NaBH_4$ as external reducing agent in over-stoichiometric amounts in both cases) and, finally, Montmorillonite (K10) clay.[17] In these works, the scope of substrates is limited[15] or the yields are poor.[16] Related examples with other metal catalysts have been reported.[18]

Because of its ability to activate C–C bonds,[19] several iron-catalyzed transformations of alkenes have appeared in recent years, including arylations,[20,21] 1,4



Scheme 1. Possible reaction pathways for the hydrothiolation of double bounds.

additions to dienes,[21] hydroaminations,[22] epoxidation of aromatic olefins and 1,3-dienes,[23] addition of 1,3-dicarbonyl nucleophiles,[24] dimerisation of styrenes,[25] as well as transformations of alkynes such as hydroarylation,[26] carbonylation,[27] aminocarbonylation,[28] and intramolecular alkyne-carbonyl metathesis.[29a] These highly efficient iron-catalysed processes involve soft nucleophiles, constituting therefore an attractive starting point to seek for a possible hydrothiolation of alkenes. According to the hardness-softness principle, a metal salt containing a hard cation and a very soft counteranion, such as the low-coordinating triflate or triflimide, would be a strong Lewis acid with reduced hardness. We envisaged that this kind of metal center could act as a soft, while strong, Lewis catalyst and could incorporate concomitantly the thiol and the alkene in its coordination sphere, then activating the Markovnikov position[29b] and minimising the radical anti-Markovnikov addition. It will be shown here that this strategy indeed works and allows the addition of thiols to styrenes with good conversion and selectivity and without polymerisation of styrene, contrary to what occurs with strong protic acids[10–12] or metal salts in over-stoichiometric amounts.[13,14]

Results and Discussion

Catalyst Screening

The reaction of 4-chlorostyrene **1** with thiophenol **2** in anhydrous 1,4-dioxane was chosen as a test reaction (Scheme 2).

The reactions were run at 80 °C after screening more than twenty metal species as triflate or triflimide salts [$M(OTf)_n$ or $M(NTf_2)_n$, $n = 1–4$], and the corresponding Brønsted acids HOTf and $HNTf_2$, as catalysts for the above reaction (Table 1). The corresponding chloride salts gave no Markovnikov product in any case. The results for reactions carried out at 50 °C are shown in parentheses.

When no catalyst is added, only the anti-Markovnikov addition occurs (entry 1). When the Brønsted acids HOTf and $HNTf_2$ are added in catalytic amounts (10 mol%), the results show very low selectivity for the Markovnikov product (entries 2 and 3). This indicates that protons do not activate efficiently the benzylic position of the styrene. In contrast, a combined high yield and good Markovnikov selectivity (**3**) was obtained when iron(III)-based salts were used as catalysts (entries 6, 7, 9, 10–13). For instance, $Fe(NTf_2)_3$ (preformed from reaction of $FeCl_3 + 3\,AgNTf_2$) gave an 84% yield of **3** (entry 9), and $Fe(OTf)_3$ (preformed from $FeCl_3 + 3\,AgOTf$) gave 74% (entry 6). The possible catalytic activity of metal impurities in the iron salt is negligible since ultrapure iron(III) gives similar results (entries 7 and 10),[30] and $FeCl_3$ does not give any product (entry 4). These re-

Table 1. Catalyst screening for the hydrothiolation of 4-chlorostyrene **1** with thiophenol **2**.

Entry[a]	Cation	Anion	Conv. [%][b]	**3** [%][b]	**4** [%][b]
1	none	none	89 (65)	1 (0)	81 (60)
2	H^+	^-OTf	80 (84)	5 (1)	70 (79)
3		$^-NTf_2$	83 (91)	24 (0)	57 (86)
4	**Fe^{3+}**	^-Cl	6 (4)	1 (0)	2 (3)
5		^-OTf	82	48	28
6[c]			85 (41)	74 (17)	3 (14)
7[c,d]			77	65	5
8[e]			9 (18)	1 (0)	6 (4)
9[c]		**$^-NTf_2$**	**98 (70)**	**84 (55)**	**9(5)**
10[c,d]			81	63	11
11[c,f]			94	85	2
12[c,f,g]			97	82	6
13[c,h]			**95**	**88**	**1**
14[e]			44 (23)	19 (2)	20 (4)
15[c]		$^-PF_6$	97	79	11
16[c]		$^-BF_4$	86	20	58
17[c]		$^-SbF_6$	94	61	6

[a] *Standard reaction conditions:* 4-chlorostyrene (0.25 mmol, 30 μL), thiophenol (0.25 mmol, 26 μL), catalyst (0.025 mmol, 10 mol%), anhydrous 1,4-dioxane (0.5 mL) at 80 °C for 24 h.

[b] Conversion and yields to **3** and **4** calculated by GC. Small amounts of the dimer of thiophenol were found, which completed mass balance.

[c] Catalyst was preformed as [MCl_n (10 mol%) + n Ag (salt) (30 mol%)] in anhydrous 1,4-dioxane (0.5 mL) for 30 min at room temperature.

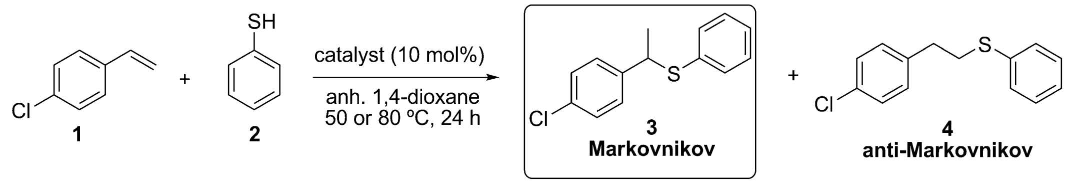
[d] $FeCl_3$ (99.99%) was used.

[e] Catalyst was preformed as [MCl_n (10 mol%) + n Li (salt) (30 mol%)] in anhydrous 1,4-dioxane (0.5 mL) for 30 min at room temperature.

[f] Run with 4-*tert*-butylcatechol (0.25 mmol, 41.6 mg) as radical inhibitor.

[g] Catalyst 5 mol%.

[h] Under an N_2 atmosphere.



Scheme 2. Hydrothiolation of 4-chlorostyrene **1** with thiophenol **2** using 10 mol% of catalyst.

sults reflect the high impact on the catalytic activity when low-coordinating counteranions are used in combination with Fe(III). The better yield obtained with the bis(triflimide) ($^-NTf_2$) group compared to the triflate (^-OTf) group is related to the stronger Lewis acidity that the former confers to Fe(III).[31] When other low-coordinating anions ($AgPF_6$, $AgBF_4$ and $AgSbF_6$) were employed (entries 15, 16 and 17) the selectivity to the Markovnikov regioisomer could not be improved, although a nearly comparable selectivity to that of $^-NTf_2$ was obtained with the anion $^-PF_6$ (79%). Some changes in selectivity depending on the compensating anion ($^-NTf_2$, ^-OTf, $^-PF_6$, $^-BF_4$ or $^-SbF_6$) can be observed. The catalytic activity for 18 more metals in different oxidation states was tested (Supporting Information, Table S1). The effect of the anion is also observed in the case of other metals such as Mn^{2+} (entries 9 and 25), Cu^+ (entries 10 and 26), Rh^{3+} (entries 16 and 31), Ni^{2+} (entries 18 and 33), Pd^{2+} (entries 19 and 34) and Hg^+ (entries 20 and 35). In all cases, the metal salt with $^-NTf_2$ shows better selectivity than that in the case of ^-OTf. Bi^{3+}, Cu^+, Cu^{2+}, Au^{3+}, Rh^{3+}, Ru^{3+} and Hg^+ metal salts show some Markovnikov selectivity (42–69%; entries 8, 11, 14, 17, 26, 27, 29, 31, 32, 35, respectively), albeit in any case below those obtained with bis(triflimide)iron(III). Therefore the result obtained for bis(triflimide)iron(III) is the best out of all metal species tested here. When the reaction is carried out under anaerobic conditions, the Markovnikov selectivity increases slightly (+4%) since oxygen removal from the reaction medium allows a further minimisation of the radical process (entry 13). The same effect

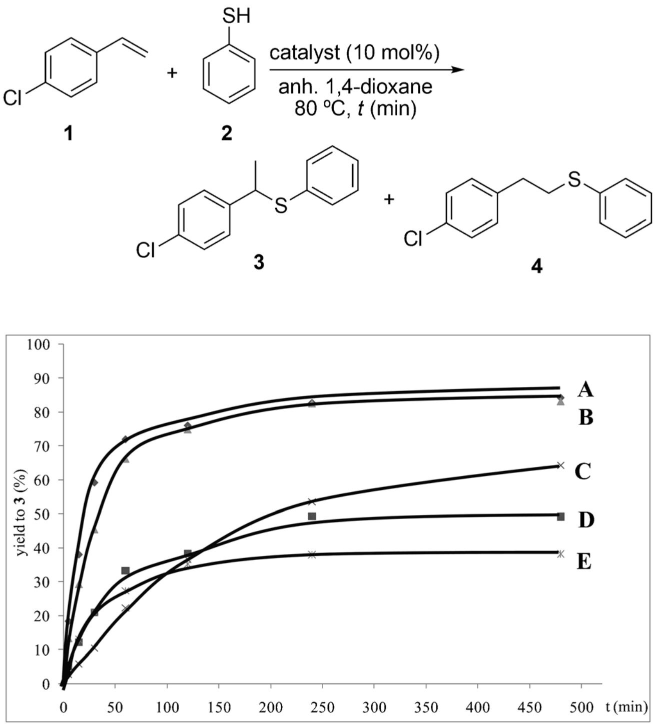


Figure 1. Plot-time yield for the reaction of **1** with **2** at 80 °C catalysed by 10 mol%: A) $FeCl_3 + 3\,AgNTf_2$; B) $RuCl_3 + 3\,AgNTf_2$; C) $Bi(OTf)_3$; D) $CuCl_2 + 2\,AgNTf_2$; E) $AuCl_3 + 3\,AgNTf_2$.

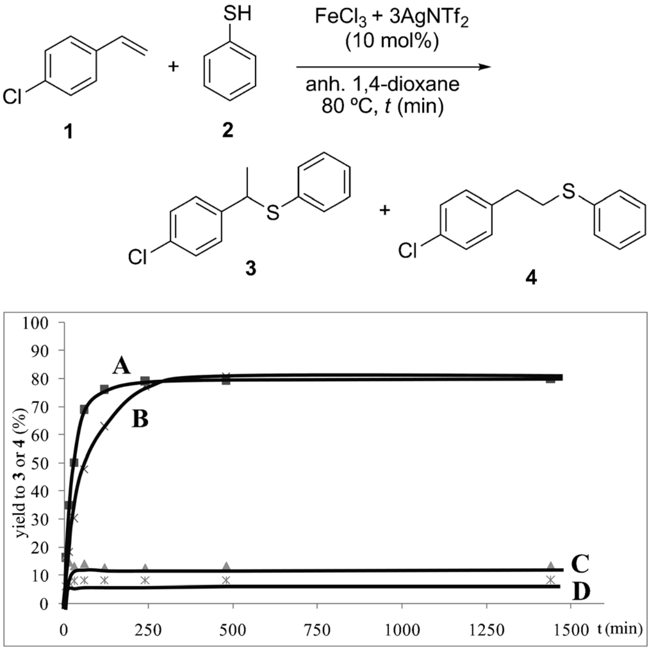


Figure 2. Plot-time yield for the reaction of **1** with **2** catalysed by 10 mol% of $FeCl_3 + 3\,AgNTf_2$ at 80 °C in anhydrous 1,4-dioxane. A) Yield to **3** without 4-*tert*-butylcatechol; B) yield to **3** with (1 equiv.) of 4-*tert*-butylcatechol; C) yield to **4** without 4-*tert*-butylcatechol; D) yield to **4** with (1 equiv.) of 4-*tert*-Butylcatechol.

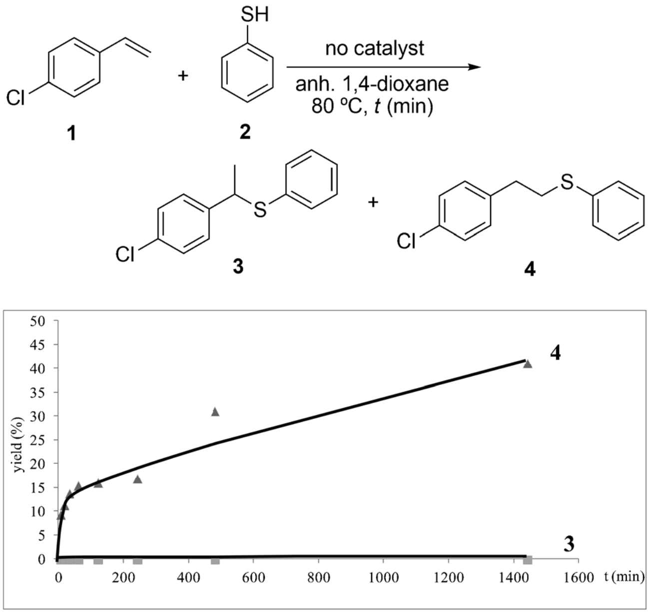


Figure 3. Plot-time yield for hydrothiolation of 4-chlorostyrene **1** with thiophenol **2** without catalyst at 80 °C.

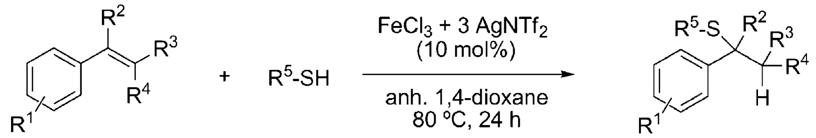
is observed when the reaction is carried out by adding 4-*tert*-butylcatechol (1 equiv.) as radical inhibitor (entries 11 and 12). Nevertheless, for experimental convenience, experiments have been carried out under ambient conditions unless otherwise indicated.

Kinetic studies for the more active metal species were performed and also showed that iron(III) is the most active catalyst (Figure 1).

It can be seen that the activity of the group VIII transition metals Fe(III) and Ru(III) are one order of magnitude higher than those of the group XI metals Cu(II) and Au(III), and also than Bi(III) (for initial rates at three different temperatures see Supporting Information, Figure S2–S6). The latter shows a particular kinetic behaviour, since, although it is the less active, it deactivates more slowly under the reactions conditions. In view of the results in Figure 1 and Table 1, we can say that $Fe(NTf_2)_3$, generated *in situ* from $FeCl_3 + 3\,AgNTf_2$, is the most active and selective catalyst for the hydrothiolation of styrenes.

Kinetic experiments performed with $Fe(NTf_2)_3$ as catalyst in the presence or absence of a radical inhibitor are shown (Figure 2). In the presence of 4-*tert*-butylcatechol the progressive formation of the Markovnikov adduct can be observed (curve B), while the anti-Markovnikov product is early formed and rapidly inhibited (curve D). Both initial rates diminished when 4-*tert*-butylcatechol is used as the radical inhibitor but the differences between both adducts are more pronounced (curves C and D). These results confirm that the Markovnikov product is obtained through a non-radical mechanism. As expected, when no catalyst is used, the anti-Markovnikov product is produced from a radical process (Figure 3).

Table 2. Markovnikov hydrothiolation of styrenes with different thiols catalyzed by $Fe(NTf_2)_3$.



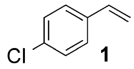
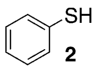
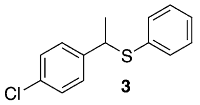
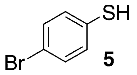
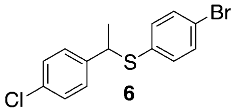
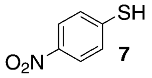
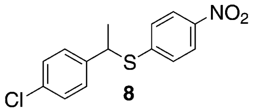
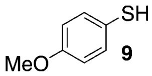
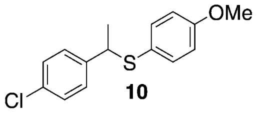
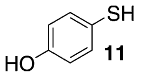
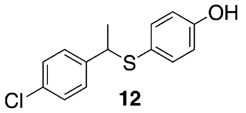
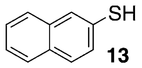
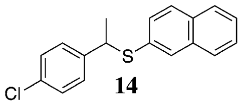
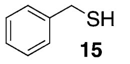
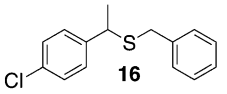
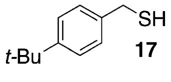
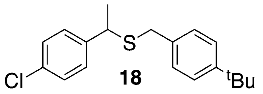
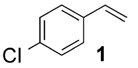
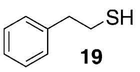
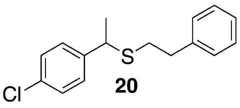
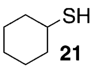
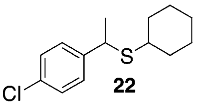
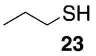
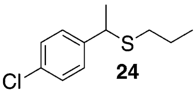
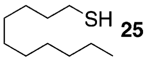
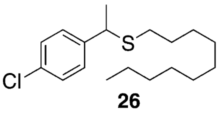
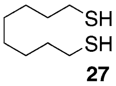
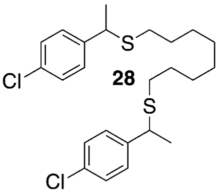
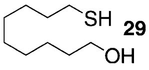
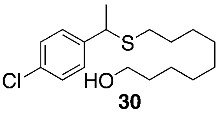
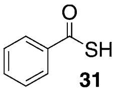
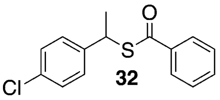
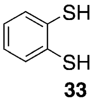
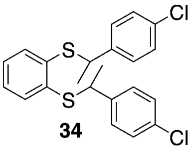
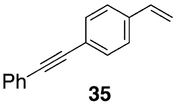
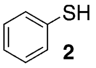
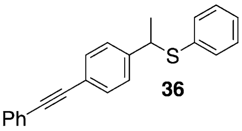
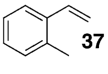
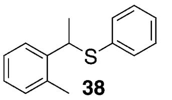
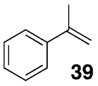
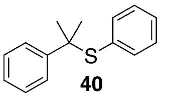
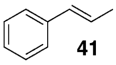
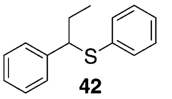
Entry[a]	Alkene	Thiol	Main product	Yield [%][b]
1	 **1**	 **2**	 **3**	88 [83]
2[c,d]		 **5**	 **6**	80 [69]
3		 **7**	 **8**	89 [81]
4		 **9**	 **10**	97 [90]
5[c]		 **11**	 **12**	68 [49]
6		 **13**	 **14**	53 [47]
7[c]		 **15**	 **16**	82 [71]
8[c,d]		 **17**	 **18**	86 [75]

Table 2. (Continued)

Entry[a]	Alkene	Thiol	Main product	Yield [%][b]
9	 **1**	 **19**	 **20**	87 [80]
10		 **21**	 **22**	87 [83]
11		 **23**	 **24**	90 [82]
12[c]		 **25**	 **26**	83 [75]
13[e]		 **27**	 **28**	91 [86]
14		 **29**	 **30**	92 [84]
15		 **31**	 **32**	83 [76]
16[e]		 **33**	 **34**	87 [79]
17	 **35**	 **2**	 **36**	86 [83]
18	 **37**		 **38**	85 [79]
19[f]	 **39**		 **40**	76 [58]
20[c]	 **41**		 **42**	79 [70]

[a] *Standard reaction conditions:* styrene (0.25 mmol), thiophenol (0.25 mmol), $FeCl_3$ (0.025 mmol, 4 mg), $AgNTf_2$ (0.075 mmol, 30 mg), anhydrous 1,4-dioxane (0.5 mL) at 80 °C for 24 h.

[b] GC yield; between brackets isolated yields.

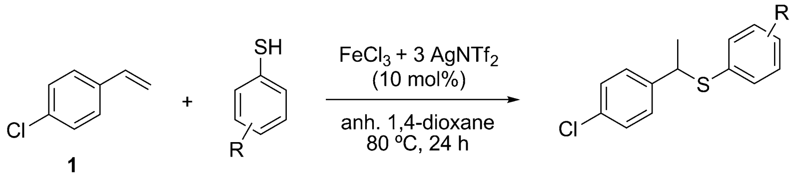
[c] 50 h reaction time.

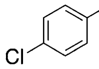
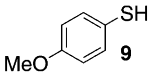
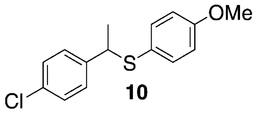
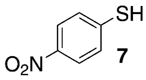
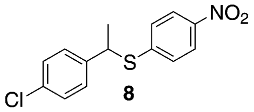
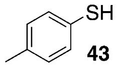
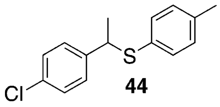
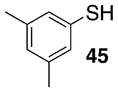
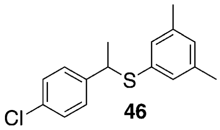
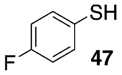
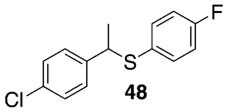
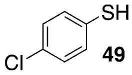
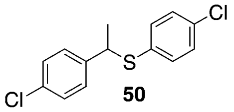
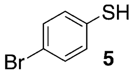
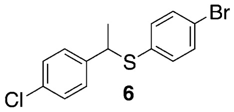
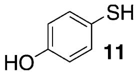
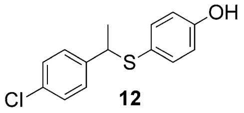
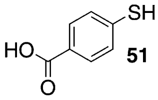
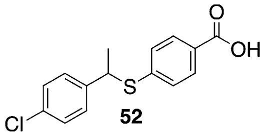
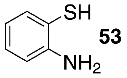
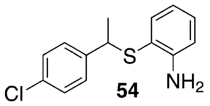
[d] With 4-*tert*-butylcatechol (1 equiv.).

[e] Styrene (0.5 mmol), thiol (0.25 mmol).

[f] Catalyst 20 mol%.

Table 3. Additional scope for the hydrothiolation of 4-chlorostyrene **1** with various thiophenols.



Entry[a]	Alkene	Thiol	Main product	Yield [%][b]
1	 **1**	 **9**	 **10**	97 [90]
2		 **7**	 **8**	89 [81]
3		 **43**	 **44**	81
4		 **45**	 **46**	71
5		 **47**	 **48**	67
6		 **49**	 **50**	64
7[c,d]		 **5**	 **6**	80[69]
8[c]		 **11**	 **12**	68[49]
9[c]		 **51**	 **52**	19
10		 **53**	 **54**	n.r.

[a] *Standard reaction conditions:* styrene (0.25 mmol), thiophenol (0.25 mmol), $FeCl_3$ (0.025 mmol, 4 mg), $AgNTf_2$ (0.075 mmol, 30 mg), anhydrous 1,4-dioxane (0.5 mL) at 80 °C for 24 h; n.r. = no reaction.

[b] GC yield; between brackets isolated yields.

[c] 50 h reaction time.

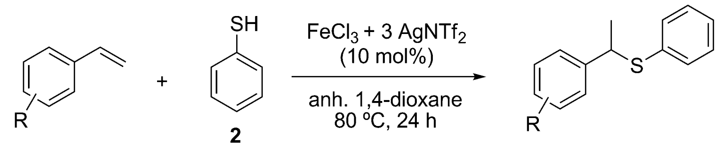
[d] With 4-*tert*-butylcatechol (1 equiv.).

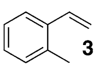
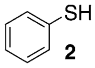
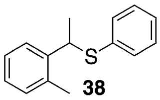
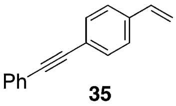
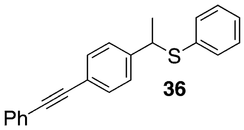
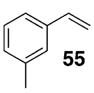
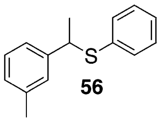
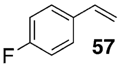
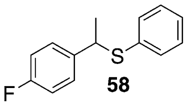
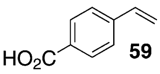
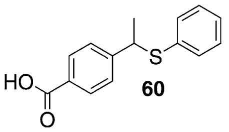
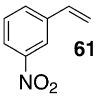
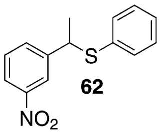
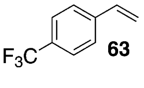
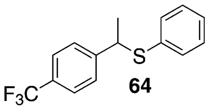
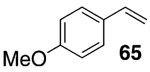
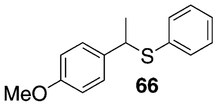
Scope of the Reaction

The hydrothiolation of different styrenes and alkynes is shown in Table 2. A wide array of sulfur derivatives (entries 1–9), alkylic thiols (entries 10–14), and a thioacid (entry 15) can be added to 4-chlorostyrene **1** in high yields and selectivities. There is a thiol complementarily, i.e., a variety of styrene derivatives including *para*- (entry 17), *ortho*- (entry 18), α- (entry 19), and β-substituted (entry 20) substrates can engage with thiophenol.[32]

Results of a further study on the influence of electron-poor and electron-rich substituents on the aryl ring of various thiophenols and styrenes are shown in Table 3 and Table 4. For substituted thiophenols, both electron-rich (methoxy, Table 3, entry 1) and electron-poor (nitro, Table 3, entry 2) groups are compatible and give excellent yields of isolated product (90%). Other substituents such as methyl and halogens F, Cl, and Br give also good yields (Table 3, entries 3–7). However, groups having labile hydrogens such as alcohol, carboxylic acid and amine give lower yields (entries 8–10). For substituted styrenes, methyl, fluoro, and alkynyl substituents give good yields (Table 4, entries 1–4), regardless of the position on the ring (Table 4, entry 3). However, the presence of both electron-poor and electron-rich substituents,

Table 4. Additiional scope for the hydrothiolation of various styrenes with thiophenol **2**.



Entry[a]	Alkene	Thiol	Main product	Yield [%][b]
1	 **37**	 **2**	 **38**	85 [79]
2	 **35**		 **36**	86 [83]
3	 **55**		 **56**	69
4	 **57**		 **58**	73
5	 **59**		 **60**	49
6[c]	 **61**		 **62**	40
7[d,e]	 **63**		 **64**	36
8	 **65**		 **66**	29

[a] *Standard reaction conditions:* styrene (0.25 mmol), thiophenol (0.25 mmol), $FeCl_3$ (0.025 mmol, 4 mg), $AgNTf_2$ (0.075 mmol, 30 mg), anhydrous 1,4-dioxane (0.5 mL) at 80 °C for 24 h.

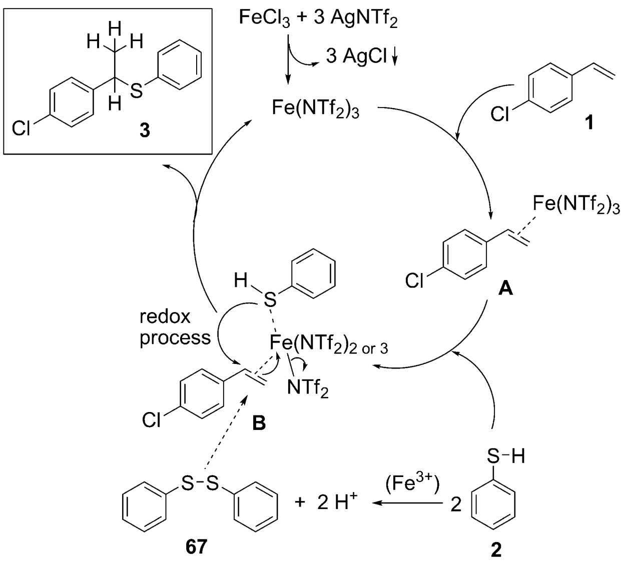
[b] GC yield; between brackets isolated yields.

[c] Catalyst 20 mol%.

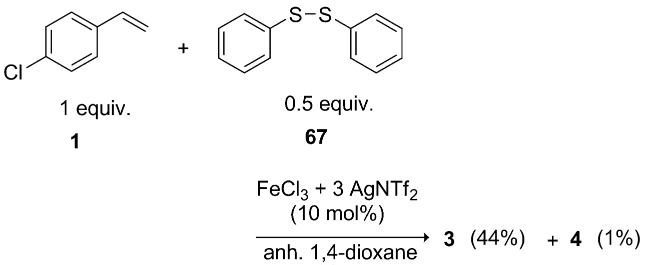
[d] 50 h reaction time.

[e] With 4-*tert*-butylcatechol (1 equiv.).

having or not having labile hydrogens, lowered the yield to <50% (Table 4, entries 5–8).



Scheme 3. Plausible mechanism for the Markovnikov hydrothiolation of 4-chlorostyrene **1** with thiophenol **2** by using Fe(NTf$_2$)$_3$ as catalyst.

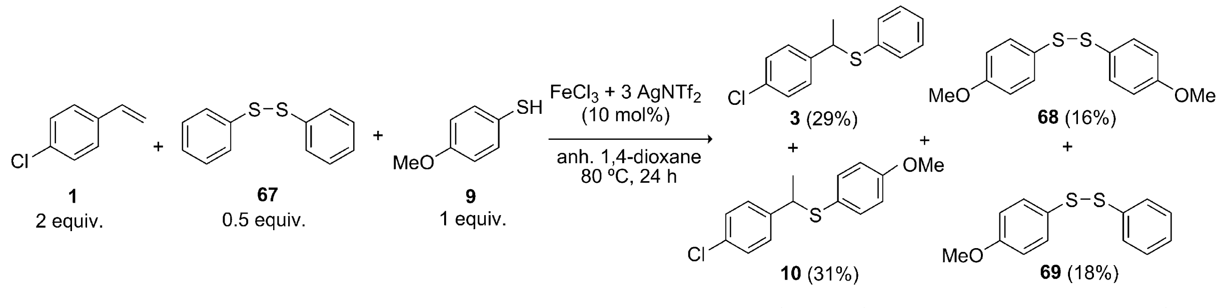


Scheme 4. Hydrothiolation of 4-chlorostyrene **1** with diphenyl disulfide **67** in different reaction conditions. GC yields are given in parentheses.

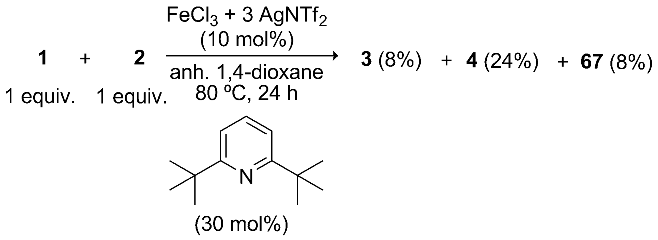
Reaction Mechanism Studies

A possible mechanism for the Fe(III)-catalysed Markovnikov hydrothiolation of styrenes is depicted in Scheme 3. This mechanistic proposal is based on the well-known capability of iron(III) to activate concomitantly the benzylic position of double bonds[20] and soft nucleophiles toward additions.[33a] The first step would consist in the formation of an iron-olefin complex (intermediate **A**). In the second step, the thiol adds onto the benzylic position. At this point, the mechanism of the thiol addition is uncertain. Although an outer-sphere attack is feasible, thiol coordination and nucleophilic attack can also occurs (intermediate **B**). We presume that the thiol is coordinated to the iron Lewis acid since it becomes more nucleophilic if coordinated to the metal.[15] The interaction between thiol and the iron(III) site is inferred from the fact that styrene does not dimerise at all[25] and, in contrast, dimers of the thiol are systematically observed during the reaction.

Since the dimers of the thiol are observed in the reaction medium (Supporting Information, Scheme S1), we have studied the influence of the pair[33b] thiol-dimer on the reaction, by performing two different experiments. When the dimer was used as starting reactant, the hydrothiolation proceeds (Scheme 4, see also Supporting Information, Table S2 and Table S3). These results indicate that the disulfide can act as nucleophile under iron(III)-catalysed conditions, although less efficiently than the corresponding thiol. In fact, some dithiolation can be observed (Supporting Information, Table S2). However, protodemetalation preferentially occurs and thus thioether **3** is the main product formed. Reduction of diphenyl disulfide **67** to thiophenol **2** does not occur directly if any alkene is not present in the reaction medium (Supporting Information, Table S3). However, a possible redox reaction between the thiol and the iron center ($2\,\mathrm{RSH} + 2\,\mathrm{Fe}^{3+} \rightarrow \mathrm{RSSR} + 2\,\mathrm{H}^{+} + 2\,\mathrm{Fe}^{2+}$) should not be discarded. A second experiment was conducted by adding *p*-methoxythiophenol **9** (1 equiv.) along with 4-chlorostyrene **1** and diphenyl disulfide **67** (0.5 equiv.;



Scheme 5. Hydrothiolation of 4-chlorostyrene **1** with *p*-methoxythiophenol **9** (1 equiv.) and diphenyl disulfide **67** (0.5 equiv.) using Fe(NTf$_2$)$_3$ as catalyst. GC yields are given in parentheses.



Scheme 6. Hydrothiolation of 4-chlorostyrene **1** with thiophenol **2** using $Fe(NTf_2)_3$ as catalyst in the presence of 2,6-di-*tert*-butylpyridine (30 mol%). GC yields are given in parentheses.

Scheme 5) and it was found that thiol exchange indeed occurs, even in the absence of iron(III) or alkene (Supporting Information, Scheme S2). Finally, the reaction was performed in the presence of a hindered base such as 2,6-di-*tert*-butylpyridine (30 mol%) and formation of the Markovnikov product was almost completely inhibited (Scheme 6). This result accounts for the important role of H^+ in the reaction.

Conclusions

It can be said that the iron-catalysed Markovnikov hydrothiolation of styrene derivatives has been accomplished. The metal salt $Fe(NTf_2)_3$ is a superior catalyst when compared to twenty different metal species and the corresponding Brønsted acids. Benzyl thioethers having a variety of substituents have been obtained in good to excellent yields after isolation. Since a new stereogenic centre (the benzylic carbon) is formed, the use of a chiral anion[34] might allow enantioselective induction. Studies in this sense are currently underway.

Experimental Section

Typical Reaction Procedure for [1-(4-Chlorophenyl)ethyl] Phenyl Sulfide (3) (Table 2, entry 1)

$FeCl_3$ (4.0 mg, 10 mol%) and $AgNTf_2$ (30.0 mg, 30 mol%) were placed in a 2-mL vial. Then, 1,4-dioxane (0.5 mL) was added and the mixture was magnetically stirred at room temperature for 30 min. Then, 4-chlorostyrene (30 μL, 0.25 mmol) and thiophenol (26 μL, 0.25 mmol) were added and the mixture was placed in a pre-heated oil bath at 80 °C and magnetically stirred for 24 h. After cooling, *n*-hexane (1 mL) was added, observing the precipitation of the catalyst. The liquid was passed through a microfilter syringe and the filtrates were isolated by TLC preparative and [1-(4-chlorophenyl)ethyl] phenyl sulfide **3** was obtained as a yellow oil; yield: 52 mg (83%). R_f (*n*-hexane): 0.48. IR: ν = 3073 (m, arC–H), 3058 (m, arC–H), 2968 (m, C–H), 2924 (m, C–H), 2864 (m, C–H), 2000–1600 (l, overtones), 1490 (vi, arC–C), 1479 (m, arC–C), 1439 (l, $-CH_3$), 1093 (vi, arC–Cl), 828 (vi), 791 (m), 690 cm^{-1} (m, C–S); GC-MS ($M^{+\cdot}$ 248, major peaks given): m/z = 248 (46%), 233 (2%), 197 (4%), 141 (100%), 103 (100%), 77 (46%); ^1H NMR: δ = 7.31–7.29 (9H, mult), 4.33 (1H, q, J = 7.1 Hz), 1.64 (3H, d, J = 7.1 Hz). ^{13}C NMR: δ = 141.8 (C), 132.7 (2×C), 128.7 (4×CH), 128.6 (3×CH), 128.5 (CH), 127.4 (CH), 47.4 (CH), 22.2 (CH_3).

Supporting Information

Supporting information for this article, including additional schemes, figure and tables, reaction procedures, compound characterization, and NMR spectra, is available.

Acknowledgements

The work have been supported by Consolider-Ingenio 2010 (proyecto MULTICAT), and PROMETEO from Generalitat Valenciana. J.R.C.-A. thanks MCIINN for the provision of a doctoral grant. A.L.-P. thanks ITQ for financial support. We thank Dr. M. Domine for the HR-MS measurements.

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