JOC Article

Electrophilic Diamination of Alkenes by Using $FeCl_3-PPh_3$ Complex as the Catalyst

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The $FeCl_3-PPh_3$ complex was found to effectively catalyze the electrophilic diamination reaction of electron-deficient alkenes. Improvements on yields and stereoselectivity have been achieved for both α,β-unsaturated carboxylic esters and ketones. Under the new catalytic system, α,β-unsaturated carboxylic esters were found to be superior to their ketone counterparts, which is opposite to the previous $(C_3F_7CO_2)_2Rh\}_2$-catalyzed diamination. The reaction employs readily available *N*,*N*-dichloro-*p*-toluenesulfonamide ($TsNCl_2$) and acetonitrile as the nitrogen sources and is very easy to perform at room temperature without the special protection of inert gases. The resulting diamino products belong to imidazolidine analogue and can further strengthen the importance of the new reaction. Modest to good yields (52−84%) and high regio- and stereoselectivity have been achieved for 10 examples.

The vicinal diamine functionality is extremely important for organic synthesis, medicinal chemistry, and pharmaceutical research.[1,2] This functionality exists in many biologically important compounds. Enantiomerically pure diamines have been utilized as chiral auxiliaries and chiral ligands for asymmetric synthesis.[3,4] The development of efficient synthetic approaches to this functionality in regio- and stereoselective fashion represents a challenging topic, especially when the functionalized olefins such as cinnamic esters and α,β-unsaturated ketones are employed as the substrates. Recently, we have discovered two new diamination reactions of olefins which are electrophilic.[5] The first reaction was carried out in a tandem manner using *N*,*N*-dichloro-2-nitrobenzenesulfonamide ($2\text{-}NsNCl_2$) and acetonitrile as the nitrogen sources without using any catalysts.[5a] The diamination using alkyl cinnamates as substrates resulted in anti alkyl N^{α}-Ns, N^{β}-Ac diaminophenylpropionates. The latter diamination was achieved by using *N*,*N*-dichloro-*p*-toluenesulfonamide ($4\text{-}TsNCl_2$) and acetonitrile as the nitrogen sources in the presence of the catalytic complex of rhodium(II) heptafluorobutyrate and triphenylphosphine.[5b] The reaction afforded imidazoline products initially, which generated α,β-differentiated vicinal diamines after acidic hydrolysis (Scheme 1).

We also attempted to reduce to practice an asymmetric version of the latter diamination by using enantiomercially pure Doyle-type Rhodium catalysts which are commercially available.[6,7] But so far, the success has been limited. In fact, low enantiomeric excess (up to 30% ee) and poor yield (<35%) were obtained. To increase the chance of an asymmetric catalytic diamination reaction, a search for other transition metal catalysts is being conducted. In addition, some of the new transition metal−ligand complexes have the advantage of convenient handling since they are less hygroscopic. In this paper, we disclose our results using the $FeCl_3-PPh_3$ complex to catalyze the electrophilic diamination reaction of α,β-unsaturated carboxylic esters and α,β-unsaturated ketones.

Results and Discussion

Similar to our previous electrophilic aminohalogenation and diamination systems, the present reaction is also very easy to perform.[5,8−9] Essentially, it can be conducted at room temperature in any stopped or capped vessel of

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SCHEME 1

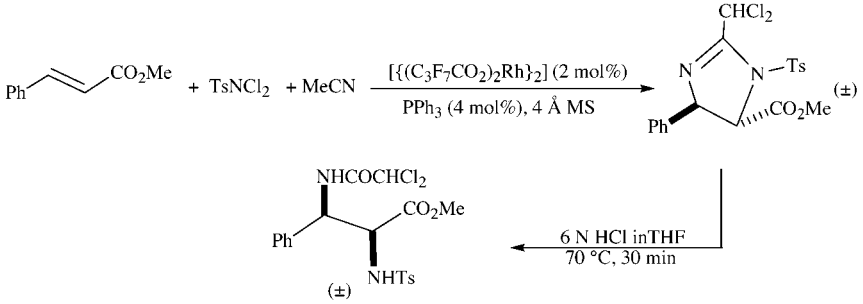
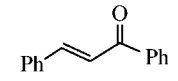
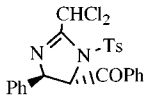
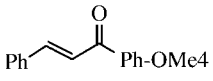
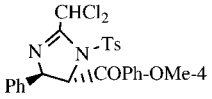
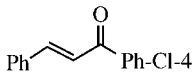
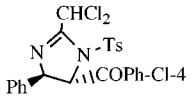
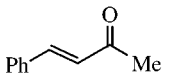
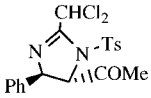
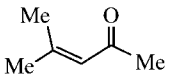
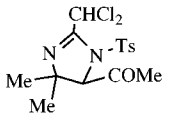


TABLE 1. Results of $FeCl_3$-PPh_3-Catalyzed Cyclic Diamination of α,β-Unsaturated Ketones

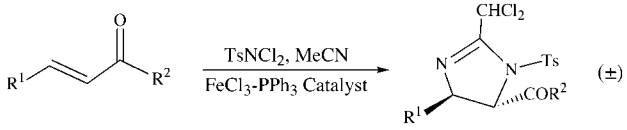
entry	substrates	product (±)		stereoselectivty[a] (*anti:syn*)	yield (%)[b]
1[c]			**1**	>95	79
2			**2**	>95	73
3			**3**	>95	60
4			**4**	>95	52
5			**5**	—	84

[a] Estimated by crude ^{1}H NMR determination. >95% means no minor isomer was detected. [b] The yields after purification via column chromatography. [c] Previous results: 66% yield, 26:1 anti/syn stereoselectivity.

convenient size without the need of inert atmosphere protection. In the previous Rh-catalyzed diamination, *N*,*N*-dichloro-*p*-toluenesulfonamide (4-$TsNCl_2$) was added into the reaction mixture in two portions at different times to optimize the yield. But in the present system, 4-$TsNCl_2$ was added in one portion to make the procedure simpler. In addition, as compared with the $\{(C_3F_7CO_2)_2Rh\}_2$ catalyst, the ferric chloride catalyst is inexpensive and is much easier to handle because it is less hygroscopic.

Since α,β-unsaturated ketones were proven to be superior to their carboxylic ester counterparts as electrophilic diamination substrates in our previous $\{(C_3F_7CO_2)_2Rh\}_2$-catalyzed reaction,[5b] chalcone was thus chosen as the first substrate for the initial study (Scheme 2, R_1, R_2 = Ph). It was found that the catalytic complex of $FeCl_3-PPh_3$ worked much better than the rhodium(II) heptafluorobutyrate and triphenylphosphine combination. The reaction was complete in 24 h instead of 44 h. The chemical yield was also increased to 79% with the

SCHEME 2



complete control of anti/syn stereoselectivity as compared to the previous results (66% and 26:1 anti/syn stereoselectivty) (Table 1). Similar improvements were also observed for *p*-methoxychalcone and the terminal disubstituted substrates. Only in one case (entry 4 of Table 1) was the yield slightly diminished to 52%, but the anti/syn stereoselectivity was completely controlled.

Interestingly, it was later found that the α,β-unsaturated esters were better substrates than α,β-unsaturated ketones for this $FeCl_3/PPh_3$-catalyzed diamination (Scheme 3), which is in contrast to the previous reaction using $\{(C_3F_7CO_2)_2Rh\}_2-PPh_3$ as the catalyst. Furthermore, the improvements on both yields and anti/syn stereoselectivty were observed for all five examples (6−10 of Table 2). For ethyl cinnamate substrate, the original chemical yield of 49% was improved to 60%. Similar enhancement was observed even for terminal disubstituted α,β-

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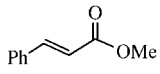
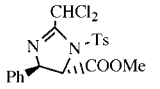
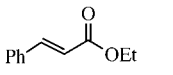
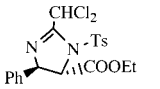
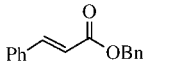
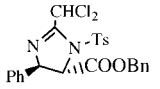
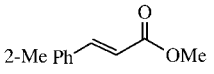
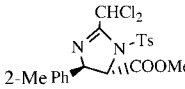
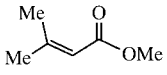
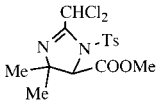
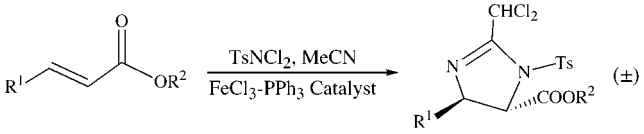
TABLE 2. Results of $FeCl_3$-PPh_3-Catalyzed Cyclic Diamination of α,β-unsaturated Esters

entry	substrates	product (±)		stereoselectivty[a] (*anti:syn*)	yield (%)[b]
6			**6**[c]	>95	63
7			**7**	>95	60
8			**8**	>95	65
9			**9**	>95	47
10			**10**	—	77

[a] Estimated by crude ^{1}H NMR determination. >95% means no minor isomer was detected. [b] The yields after purification via column chromatography. [c] X-ray structure was obtained. Hydrolysis of **6**: Into a 10 mL round-bottom flask equipped with a magnetic stir bar was added 110 mg (0.25 mmol) of **6**, 3 mL of THF and 0.5 mL of 6 N aqueous HCl. After being stirred at 70 °C for 30 min, the reaction mixture was poured into 5 mL of cold water. The aqueous solution was extracted with EtOAc (3 × 5 mL), and the combined organic layers were washed with brine (10 mL), dried by Na_2SO_3, and concentrated in vacuo to give the α,β-diamino carboxylic ester (111 mg, quant.) which is nearly pure indicated by its crude NMR spectrum (see Supporting Information).

SCHEME 3

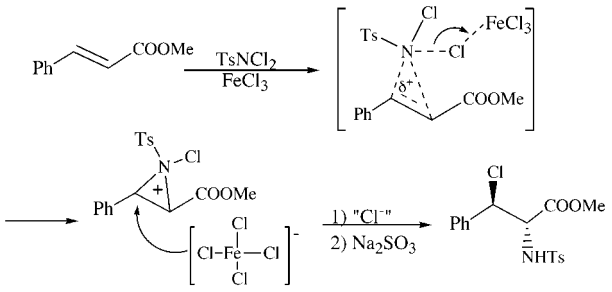


unsaturated carboxylic esters (entry 10 of Table 2) in which the yield was increased to 77% from 69%. Only one limitation has been encountered so far, i.e., the reaction proceeded extremely slowly for those substrates with a strong electron-withdrawing group (NO_2) on the aromatic rings at the olefin terminus.

Triphenylphosphine was found to play a critical role for the current diamination. Triphenylphosphine apparently inhibit the formation of vicinal haloamine side-products which are generated from aminochlorination. This reaction can proceed in competition with the main diamination reaction. Both of these reactions proceed via the formation of novel aziridinium intermediates as described below. In fact, only a trace amount of diamination products was detected if triphenylphosphine was not utilized. Iron(III) chloride itself can catalyze aminochlorination but gives incomplete conversion and a poor yield (<30%). More diamine product was formed when the amount of triphenylphosphine was increased, and the turnover was observed when the ratio of PPh_3 to $FeCl_3$ reached 2:1. Similar to our previous catalytic system, addition of 4 Å molecular sieves slightly improved yields (~5−10%). The use of other cosolvents, such as toluene, benzene, CH_2Cl_2, $CHCl_3$, $EtNO_2$, and THF together with acetonitrile failed to give any improvement.

Besides three known metals (zinc, copper, and rhodium),[5b,8−9] iron has become the fourth metal which can effectively catalyze the formation of *N*-(*p*-tosyl),*N*-chloroaziridinium intermediate as described in Scheme 4.[5,8−9]

SCHEME 4



In the case of the aminohalogenation side reaction, the aziridinium intermediate is directly opened by chloride to give the haloamine product whose structure has been confirmed by comparison with a known sample. This hypothesis is also supported by our initial diamination reaction,[5a] although *N*,*N*-dichloro-*p*-nitrobenzenesulfonamide instead of *N*,*N*-dichloro-*p*-toluenesulfonamide was employed as the nitrogen source. At the initial step of this mechanism, the iron metal center of $FeCl_3$ is coordinated to the *N*-chlorine instead of the oxygen moiety of *N*,*N*-dichloro-*p*-toluenesulfonamide. This interaction weakens the N−Cl bond, which is necessary to remove chlorine anion to form "Ts-$N^{\delta+}$-Cl" type of electrophilic species for subsequent electrophilic addition. The Fe-associated "Cl^-" near the carbonium reactive site acts as the nucleophile to open the three-member ring of the *N*-tosyl *N*-chloro aziridinium intermediate. The S_N2 mechanism of this aziridinium ring opening is responsible for the high anti stereoselectivty. The regioselectivity can be explained by the fact that the β-position of the aziridinium intermediate has more positive charge than α-position because of the stabilization effect from the β-phenyl ring.

The mechanism of this catalytic system is believed to be similar to that of our previous rhodium-catalyzed reaction,[5b] where the first step is to form the aziridinium intermediate. This positively charged intermediate is then attacked by MeCN to give nitrilium intermediate, which belongs to the Ritter class of the nucleophilic substitutions.[10,11] The opening of the aziridinium ring by acetonitrile occurring on the β-position is reponsible for the complete regioselective control. Since the anti configuration of methylcinnamate was retained in the product, the coordination of MeCN to the iron center is suggested to occur prior to the aziridinium ring opening. For this coordination, the Lewis basic moieties could be either *N*-chlorine or the sulfonyl oxygen of the Ts group. At this moment, it is not clear how triphenylphosphine plays the crucial role to inhibit the formation of haloamine products. It is possible that the secondary structure generated from the coordination of triphenylphosphine ligand to the iron center favors the formation of the five-membered ring intermediate.

In summary, the $FeCl_3-PPh_3$ complex has been found to be an effective catalyst for the regio- and stereoselective electrophilic diamination of α,β-unsaturated carboxylic esters and ketones. By using this catalyst, improved chemical yields and stereoselectivity were obtained for most cases which were examined. The reaction is easier to handle due to the fact that the catalyst is much less hygroscopic and *N*,*N*-dichloro-*p*-toluenesulfonamide can be added in one portion. The catalytic conditions for the conversion of the $CHCl_2$ group of the imidazoline into the CCl_3 are being studied for easier deprotection purposes.

Experimental Section

General Procedure. All reactions were conducted without inert gas protection. Acetonitrile was dried and freshly distilled from calcium hydride under the nitrogen atmosphere. Other commercial chemicals were used without purification, and their stoichiometries were calculated based on the reported purities from the manufacturers. Flash chromatography was performed on silica gel 60 (230−400 mesh). ^{1}H NMR (200 MHz) and ^{13}C NMR (125 MHz) were acquired in deuterated chloroform ($CDCl_3$). High-resolution mass spectral analysis was conducted by the mass spectroscopy laboratory of the Scripps Research Institute.

General Procedure for Electrophilic Diamination. Into a dry vial was added iron(II) chloride (109 mg, 0.10 mmol, 0.20 equiv), triphenylphosphine (56.0 mg, 0.20 mmol, 0.40 equiv), and freshly distilled acetonitrile (3.0 mL). The mixture was stirred at room temperature for 30 min before 4 Å molecular sieves (200 mg, predried in the oven at 200 °C overnight) was added. The resulting brownish yellow mixture was stirred for 10 min and was loaded with α,β-unsaturated carboxylic ester or ketone (0.50 mmol) and *N*,*N*-dichloro-*p*-tolunesulfonamide (360 mg, 1.50 mmol, 3.0 equiv). Shortly after *N*,*N*-dichloro-*p*-tolunesulfonamide was added, the reaction became exothermic with the color changed to bright yellow. The resulting bright yellow slurry was stirred at room temperature for 24 h in the capped vial without argon protection. The 4 Å molecular sieves and other solid precipitates were filtered off and washed with EtOAc (3 × 5 mL). The organic solution was directly concentrated without quenching and then purified via flash chromatography with hexane and EtOAc as the eluent to give 1-*p*-toluenesulfonyl-2-dichloromethyl-imidazoline.

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1: Isolated as a white solid (194 mg, 79% yield). Obtained from the electronphilic addition reaction of chalcone (106 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-tolunesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). Mp 130−131 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1698 (C═O) cm^{-1}. ^{1}H NMR (300 MHZ, $CDCl_3$) δ 7.80−7.74 (m, 4H), 7.64−7.61 (m, 1H), 7.49−7.44 (m, 2H), 7.32−7.23 (m, 6H), 6.90 (dd, J = 1.40, 8.02 Hz, 2H), 5.56 (d, J = 4.86 Hz, 1H), 5.01 (d, J = 4.86 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 156.7, 145.7, 138.7, 134.4, 134.3, 133.5, 130.1, 129.0(2), 128.8, 128.7, 128.0, 126.6, 72.3, 71.9, 61.4, 21.7. HRMS (MALDI−FTMS) *m*/*z* ($M^+ + 1$) found 487.0644, calcd for $C_{24}H_{20}O_3N_2SCl_2$ 487.0644.

2: Isolated as a white solid (189 mg, 73% yield). Obtained from the electronphilic addition reaction of 4′-methyoxychalcone (120 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-tolunesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). Mp 58−59 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1688 (C═O), 1248 (C−O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.65 Hz, 2H), 7.74 (d, J = 8.84 Hz, 2H), 7.22 (s, 1H), 6.92 (dd, J = 2.00, 6.76 Hz, 4H), 5.53 (d, J = 4 0.96 Hz, 1H), 5.01 (d, J = 4.96 Hz, 1H), 3.88 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 164.5, 156.7, 145.6, 138.8, 134.5, 131.2, 130.0, 129.0, 128.6, 128.0, 126.6, 126.4, 114.2, 72.6, 71.5, 61.5, 55.6, 21.7. HRMS (MALDI−FTMS) *m*/*z* ($M^+ + 1$) found 517.0768, calcd for $C_{25}H_{22}O_4N_2SCl_2$ 517.0750.

3: Isolated as a colorless oil (156 mg, 60% yield). Obtained from the electronphilic addition reaction of chalcone (106 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-tolunesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1869 (C═O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.50 Hz, 2H), 7.69 (d, J = 8.99 Hz, 2H), 7.44 (d, J = 8.99 Hz, 2H), 7.33−7.26 (m, 5H), 7.21 (s, 1H), 6.89 (d, J = 8.50 Hz, 2H), 5.48 (d, J = 5.00 Hz, 1H), 5.00 (d, J = 5.00 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 156.7, 145.9, 141.0, 138.5, 134.3, 131.8, 132.0, 132.1, 129.4, 129.1, 128.8, 127.9, 126.5, 72.3, 72.0, 61.4, 21.7.

4: Isolated as a colorless oil (110 mg, 52% yield). Obtained from the electronphilic addition reaction of *trans*-4-phenyl-3-buten-2-one (75.0 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-tolunesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1719 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.41 Hz, 2H), 7.32 (s, 1H), 7.18−7.14 (m, 3H), 7.10−7.08 (m, 2H), 6.69 (d, J = 8.41 Hz, 2H), 5.14 (d, J = 4.26 Hz, 1H), 4.28 (d, J = 4.26 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.0, 156.8, 146.0, 139.6, 132.6, 130.3, 128.6, 127.5, 127.4, 125.6, 75.5, 71.5, 61.8, 26.6, 21.6. HRMS (MALDI−FTMS) *m*/*z* ($M^+ + 1$) found 425.0500, calcd for $C_{19}H_{18}O_3N_2SCl_2$ 425.0488.

5: Isolated as a colorless oil (142 mg, 84% yield). Obtained from the electronphilic addition reaction of 4,4-dimethyl-3-buten-2-one (50.0 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-tolunesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1715 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.46 Hz, 2H), 7.41 (d, J = 8.46 Hz, 2H), 7.21 (s, 1H), 3.99 (s, 1H), 2.47 (s, 3H), 2.23 (s, 3H), 1.21 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 153.5, 146.1, 133.2, 130.4, 127.6, 70.4, 61.7, 30.7, 27.8, 23.2, 21.7. HRMS (MALDI−FTMS) *m*/*z* ($M^+ + 1$) found 337.0484, calcd for $C_{15}H_{18}O_3N_2SCl_2$ 337.0488.

6: Isolated as a white solid (139 mg, 63% yield). Obtained from the electronphilic addition reaction of *trans*-methyl cinnamate (82.0 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-tolunesulfonamide (360 mg, 1.50 mmol) in the presence of triphen-

ylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). Mp 126−127 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1760 (C═O), 1291 (C−O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.41 Hz, 2H), 7.26−7.18 (m, 6H), 6.88 (d, J = 8.41 Hz, 2H), 5.21 (d, J = 4.39 Hz, 1H), 4.56 (d, J = 4.39 Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 156.6, 145.7, 139.2, 133.8, 130.1, 128.8, 128.0, 127.7, 125.8, 72.0, 69.2, 61.4, 53.1, 21.6. HRMS (MALDI−FTMS) m/z ($M^+ + 1$) found 441.0446, calcd for $C_{19}H_{18}O_4N_2SCl_2$ 441.0437.

7: Isolated as a white solid (137 mg, 60% yield). Obtained from the electronphilic addition reaction of *trans*-ethyl cinnamate (90.0 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). Mp 102−104 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1755 (C═O), 1292 (C−O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.41 Hz, 2H), 7.26−7.19 (m, 6H), 6.90 (d, J = 8.41 Hz, 2H), 5.20 (d, J = 4.28 Hz, 1H), 4.55 (d, J = 4.28 Hz, 1H), 4.23 (q, J = 7.13 Hz, 2H), 2.42 (s, 3H), 1.29 (t, J = 7.13 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 156.6, 145.7, 139.3, 133.9, 130.0, 128.8, 128.0, 127.7, 125.8, 72.1, 69.3, 62.3, 61.5, 21.6, 14.0. HRMS (MALDI−FTMS) m/z ($M^+ + 1$) found 455.0587, calcd for $C_{20}H_{20}O_4N_2SCl_2$ 455.0594.

8: Isolated as a colorless solid (168 mg, 65% yield). Obtained from the electronphilic addition reaction of *trans*-benzyl cinnamate (120 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1760 (C═O), 1227 (C−O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.46 Hz, 2H), 7.26 (d, J = 8.46 Hz, 2H), 7.19 (s, 1H), 6.88 (d, J = 6.74 Hz, 4H), 5.20 (d, J = 4.29 Hz, 1H), 4.51 (d, J = 4.29 Hz, 1H), 3.81 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 157.0, 145.9, 135.3, 135.2, 133.8, 130.1, 127.7, 127.6, 115.9, 71.3, 69.2, 61.4, 53.2, 52.0, 21.6.

9: Isolated as a colorless solid (104 mg, 47% yield). Obtained from the electronphilic addition reaction of *trans*-methyl 2-methylcinnamate (90.0 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-tolunesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1682 (C═O), 1252 (C−O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.73−7.69 (dd, J = 1.86, 6.60 Hz, 2H), 7.28−7.22 (dd, J = 1.86, 6.60 Hz, 2H), 7.22 (s, 1H), 7.12 (dd, J = 0.87, 4.87 Hz, 2H), 6.89−6.86 (m, 1H), 6.37 (d, J = 7.60 Hz, 1H), 5.42 (d, J = 4.23 Hz, 1H), 4.47 (d, J = 4.23 Hz, 1H), 3.79 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 156.6, 145.7, 137.0, 134.7, 134.1, 130.7, 130.1, 128.0, 127.7, 126.4, 125.5, 68.8, 68.7, 61.4, 53.1, 21.6, 19.4.

10: Isolated as a white solid (151 mg, 77% yield). Obtained from the electrophilic addition reaction of methyl 3,3-dimethylacrylate (59.0 mg, 0.50 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (360 mg, 1.50 mmol) in the presence of triphenylphosphine (56.0 mg, 0.20 mmol) and iron(II) chloride (109 mg, 0.10 mmol). Mp 134−136 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): 1755 (C═O), 1292 (C−O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (dd, J = 1.88, 6.65 Hz, 2H), 7.38 (dd, J = 1.88, 6.65 Hz, 2H), 7.05 (s, 1H), 4.33 (s, 1H), 3.68 (s, 3H), 2.46 (s, 3H), 1.26 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168. 5, 153.3, 145.6, 134.3, 130.0, 127.8, 70.9, 69.5, 61.4, 52.3, 29.3, 23.1, 21.7. HRMS (MALDI−FTMS) m/z ($M^+ + 1$) found 393.0437, calcd for $C_{15}H_{18}O_4N_2SCl_2$ 393.0449.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of all pure products, the X-ray structure of **6**, and the ^1H NMR spectrum of the hydrolysis product of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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