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Direct Electrophilic Diamination of Functionalized Alkenes without the Use of Any Metal Catalysts

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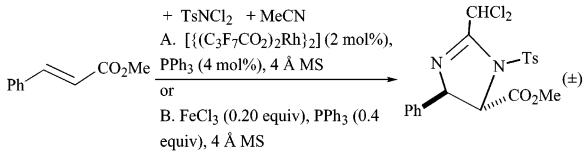
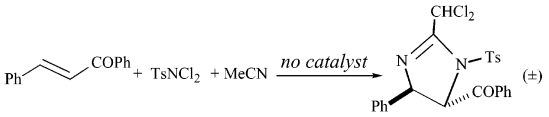
Abstract: A new direct electrophilic diamination reaction of α,β-unsaturated ketones and esters has been established without the use of any metal catalysts. Three types of nitriles (CH_3CN, CH_3CH_2CN, and $CH_3CH_2CH_2CN$) were employed as nucleophilic nitrogen sources. A new mechanism has also been proposed to explain the resulting regio- and stereoselectivity.

The development of regio- and strereoselective diamination of alkenes has been a challenging and important topic in organic chemistry because the resulting vicinal diamine products are extremely important for medicinal chemistry and pharmaceutical research.[1,2] Enantiomerically pure diamine derivatives are often utilized as chiral auxiliaries and ligands for asymmetric synthesis and catalysis.[3−6] So far, most olefinic diaminations have been achieved by using nonfunctionalized alkenes as the starting materials in the presence of various metal promoters derived from metals such as thallium, palladium, osmium, and mercury.[7,8] Recently, we have established novel diamination methods for the synthesis of α,β-differentiated diamines and imidazolines.[9,10] These reactions can employ electron-deficient alkenes as the substrates and take the advantage of readily available *N*,*N*-dichloro-*p*-toluenesulfonamide (4-$TsNCl_2$) as electrophilic nitrogen source and acetonitrile as the nucleophilic nitrogen source in the presence of the catalytic complexes of rhodium(II) heptafluorobutyrate or iron(III) trichloride with triphenylphosphine (Scheme 1).

SCHEME 1



SCHEME 2



During our initial study of catalytic diamination, methyl cinnamate was employed as the substrate and did not result in either haloamine or diamine products in the absence of any catalyst at room temperature even after 2 days. However, we later found that when the reaction temperature was increased to 50 °C, the diamination did occur in a further prolonged period (3 days) in the absence of any metal catalysts to give 1-*p*-toluesulfonyl-3-dichloromethyl-4,5-imidazoline in a chemical yield of 35%.

This new finding prompted us to reexamine the noncatalyzed dimination of another substrate series, α,β-unsaturated ketones, to explore if higher yields and faster reaction rate can be achieved. In fact, it has been shown that in our previous catalytic systems α,β-unsaturated ketones are more effective for diamination than α,β-unsaturated esters under some conditions. Surprisingly, when we subjected α,β-unsaturated ketones to the above direct diamination without the use of any metal catalysts in prolonged reaction time, we found that the diamination can proceed to completion at room temperature, although the yields are decreased in comparison with the previous yields of catalytic diamination using rhodium(II) heptafluorobutyrate and iron(III) trichloride as catalysts. In this paper, we report our preliminary results of the direct electrophilic diamination of α,β-unsaturated ketones without the use of any catalysts (Scheme 2). In addition to acetonitrile as the nucleophilic nitrogen source, two new nitrogen sources, EtCN and PrCN, were also studied for the first time for diamination reaction of alkenes.

As shown in the typical procedure in the Experimental Section, it is very convenient to carry out the present diamination reaction simply by mixing reactants in a one-pot operation at room temperature. Since there are no sensitive catalysts involved, the reaction can thus be performed without the special protection from inert gases. The diamination results are summarized in Table

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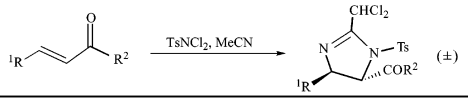
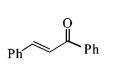
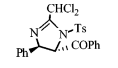
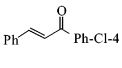
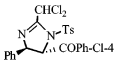
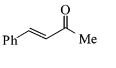
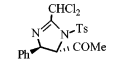
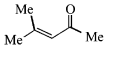
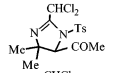
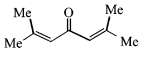
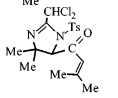
TABLE 1. Results of Non Catalyst-involved Diamination of α,β-Unsaturated Ketones



entry	substrates	product (±)		stereoselectivty[a]	time (h)	yield (%)[b]
1			**1**	>95	32	60
2			**2**	>95	32	63
3			**3**	>95	40	48
4			**4**	—	8	80
5			**5**	—	8	81

[a] Estimated by crude ^{1}H NMR determination. >95% means no minor isomer was detected. [b] The yields after purification via column chromatography.

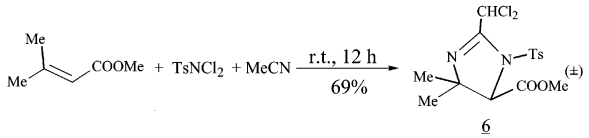
1 for acetonitrile and in Table 2 for propionitrile and butyronitrile.

Chalcone was chosen as the substrate for the initial study (entry 1 of Table 1). It was found that the reaction can be finished within 32 h at room temperature to give a chemical yield of 60%. As compared to the previous catalytic conditions, the yields of 79% and 66% were obtained for $FeCl_3/PPh_3$ and $[(C_3F_7CO_2)_2Rh]_2$-catalyzed diamination, respectively, for the same α,β-unsaturated ketone. However, the excellent stereoselectivity was retained for all relevant cases as shown in Table 1. In fact, only one stereo- and regioisomer was detected in each of these cases, which is similar to our previous two catalytic systems. Interestingly, as compared to chalcone, β,β-disubstituted α,β-unsaturated ketones needed shortened reaction period (entries 4 and 5, Table 1). The reaction went to completion within 8 h at room temperature to give yields similar to those of catalytic systems.

This is the first example of the use of dienone for the diamination reaction (entry 5, Table 1). The diamination of phorone only had one carbon−carbon double bond reacted, even when 3 equiv of $TsNCl_2$ was used over a prolonged period (more than 32 h). New diamination conditions will be studied for this substrate so as to get two C═C bonds reacted.

These reactivity difference between β-monosubstituted and β,β-disubstituted α,β-unsaturated ketones could be explained by the mechanism hypothesis in which aziridinium is formed as the key intermediate during the reaction process (Scheme 5). The two methyl groups on the terminal of α,β-unsaturated ketones could stabilize the aziridinium intermediate more efficiently than their monosubstituted counterparts. The stabilization can decrease the reaction activation energy and, therefore, enhance the reaction rate. This explanation is supported by the observation that monoaromatic α,β-unsaturated ketones worked much better than their aliphatic counterparts. For example, 3-penten-2-one gave only 10% of diamine product in 3 days under the same conditions.

SCHEME 3



6

In the previous procedures,[9,10a,b] unknown side products often accompanied the major products, which made column chromatography purification difficult sometimes. These unknown side products could involve 1-*p*-toluesulfonyl-3-trichloromethyl-4,5-imidazoline or different isomers of vicinal haloamino compounds.[11,12] In the current diamination system, the generated crude mixtures are much easier to be purified via column chromatography to give pure 1-*p*-toluesulfonyl-3-dichloromethyl-4,5-imidazoline product.

At the current stage, β-monosubstituted α,β-unsaturated esters have not shown their effectiveness for this noncatalyst involved direct diamination. However, some promising results were obtained for β,β-disubstituted α,β-unsaturated esters. For example, methyl 3,3-dimethylacrylate effected the diamination within 12 h under this new condition and afforded imidazoline product in a chemical yield of 69% (Scheme 3), whereas, as mentioned earlier, methyl cinnamate only gave 35% yield when the reaction was conducted at higher temperature (50 °C) and over a prolonged period (3 days).

In our previous catalytic systems,[9,10a,b] molecular sieves were found to play important roles. The yields can be increased up to 10% if molecular sieves were used to minimize the formation of 1-*p*-toluesulfonyl-3-trichloromethyl-4,5-imidazoline. Molecular sieves were also found to play even more important roles in the present system. For most ketone cases, if no molecular sieves were used, the mixture products consisting both 1-*p*-toluesulfonyl-3-trichloromethyl-4,5-imidazoline and 1-*p*-toluesulfonyl-3-dichloromethyl-4,5-imidazoline were produced with the latter as the major product. But for 3-methyl 3-penten-2-one substrate (entry 4, Table 1), 1-*p*-toluesulfonyl-3-trichloromethyl-4,5-imidazoline became the predominant product if no molecular sieves were added into the reaction system.

For most substrates, the formation of 1-*p*-toluesulfonyl-3-trichloromethyl-4,5-imidazoline can be increased by increasing the reaction temperature and further extending the reaction time after the starting material is consumed. As anticipated, the diamination occurred at a faster rate as anticipated at higher temperature. The diamination of 4-phenyl-3-buten-2-one needed 40 h to finish at room temperature but only 8 h at 50 °C.

After acetonitrile was successfully utilized for this direct diamination, two other nitriles, CH_3CH_2CN and $CH_3CH_2CH_2CN$, were also used as the nucleophilic nitrogen sources (Scheme 4, Table 2). It was found that for both β,β-disubstituted α,β-unsaturated ketones the reaction went to completion within 8 h to give good yields. Interestingly, only monochlorinated product, 1-*p*-toluesulfonyl-3-chloromethyl-4,5-imidazoline, was predomi-

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SCHEME 4

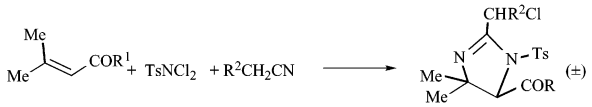
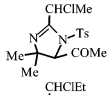
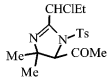
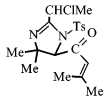
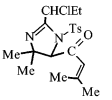
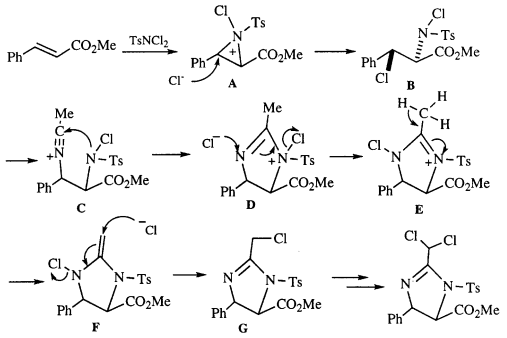


TABLE 2. Diamination Using CH_3CH_2CN and $CH_3CH_2CH_2CN$ as the Nitrogen Sources

entry	R^1	R^2	product		regioselectivty[a]	yield (%)[b]
1	Me—	Me—		**7**	3.6	82
2	Me—	Et—		**8**	3.4	70
3		Me—		**9**	4.0	74
4		Et—		**10**	3.5	81

[a] Determined by crude ^{1}H NMR determination. No regioisomer was detected for each case. [b] The combined yields of two individual isomers after column chromatography. The reaction was carried out for 8 h for all four cases.

SCHEME 5



nantly generated with no 1-*p*-toluesulfonyl-3-dichloromethyl-4,5-imidazoline observed at all. This observation could be attributed to the steric effects from alkyl substitutions (Me- and Et-) in these nitrogen sources. The stereochemistry was generated by the 3-chloromethyl carbon center and the 5-position of imidazoline, which made the products more complex. Fortunately, the two individual stereoisomers for each case can be separated via flash column chromatography in combined yields arranged from 70% to 82% (Table 2). The regioselectivity was readily measured by ^{1}H NMR for the four cases of Table 2.

The resulting regio- and stereochemistry (entries 1−3, Table 1) from this nonmetal catalyzed diamination (entries 1−3, Table 1) suggests that the previous mechanism hypothesis should be modified (Scheme 5). The first step of this reaction is believed to be the same as that of the metal-catalyzed diamination through the electrophilic addition for the formation of *N*-*p*-tosyl-*N*-chloroaziridinium intermediate (**A**).[9−12] The second step involves the aziridinium ring opening by chlorine anion instead of acetonitrile to form *N*-chloro haloamine intermediate (**B**). This step is then followed by another S_N2 displacement with acetonitrile to afford a nitrinium intermediate (**C**) to afford the overall syn stereochemistry. The following steps are the same as previously suggested;[9] i.e., the cyclization of intermediate **C** gives rise to 1*N*-*p*-tosyl-1*N*-chloroimidazolinium (**D**) followed by 1,3-displacement of 1*N*-chlorine leading to 1*N*-*p*-tosyl-3*N*-chloroimidazolinium (**E**). Deprotonation of the 2-methyl group of **E** gives methylene scaffold **F**, which enables the second S_N2' type displacement to afford 1-*p*-toluenesulfonyl-2-chloromethyl-4-phenyl-5-methyloxycarbonylimidazoline (**G**), which is then converted into the final imidazoline product through further similar steps from **D** to **G**.

In conclusion, a new direct electrophilic diamination reaction of α,β-unsaturated ketones and esters has been established. Three types of nitriles (CH_3CN, CH_3CH_2CN, and $CH_3CH_2CH_2CN$) were found to be effective as nucleophilic nitrogen sources. The electrophilic nitrogen source, *N*,*N*-dichloro-*p*-toluenesulfonamide (4-$TsNCl_2$), can be readily synthesized from inexpensive starting materials, *p*-toluenesulfonamide and commercial bleach, which makes this synthesis inexpensive.

Experimental Section

Typical Procedure for Direct Diamination. Into a dry vial were added olefin (1.0 mmol), 4 Å molecular sieves (0.50 g), and 4-$TsNCl_2$ (480 mg, 2.0 mmol). Newly distilled acetonitrile (4.0 mL) was then added into the above mixture. The resulting solution was stirred at room temperature until the reaction was finished as revealed by TLC or GC. The reaction times are indicated in Tables 1 and 2. The reaction was quenched by 5.0 mL of saturated aqueous Na_2SO_3 solution. The 4 Å molecular sieves and other solid precipitates were filtered off and washed with EtOAc (3 × 5 mL). The two phases were separated, and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phase was washed with brine and dried with anhydrous sodium sulfate. Purification by flash chromatography (EtOAc/hexane, v/v, 1/4) provided pure product.

1. Compound **1**, a white solid (293 mg, 60%) obtained from the electrophilic addition reaction of chalcone (208 mg, 1.0 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (480 mg, 2.0 mmol) in the presence of 4 Å molecular sieves (500 mg) in 4.0 mL of acetonitrile: 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.

2. Compound **2**, a white solid (330 mg, 63%) obtained from the electrophilic addition reaction of 4′-chlorochalcone (243 mg, 1.0 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (480 mg, 2.0 mmol) in the presence of 4 Å molecular sieves (500 mg) in 4.0 mL of acetonitrile: mp 96−98 °C; 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.

3. Compound **3**, a white solid (204 mg, 48%) obtained from the electrophilic addition reaction of *trans*-4-phenylbuten-2-one (146 mg, 1.0 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (480 mg, 2.0 mmol) in the presence of 4 Å molecular sieves (500 mg) in 4 mL of acetonitrile: mp 86−88 °C; 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.

4. Compound **4**, a white solid (452 mg, 80%) obtained from the electrophilic addition reaction of 3-methyl 3-penten-2-one (0.17 mL, 1.5 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (720 mg, 3.0 mmol) in the presence of 4 Å molecular sieves (750 mg) in 6.0 mL of acetonitrile: mp 95−97 °C; 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.

5. Compound **5**, a white solid (249 mg, 81%) obtained from the electrophilic addition reaction of phorone (138 mg, 1.0 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (480 mg, 2.0 mmol) in the presence of 4 Å molecular sieves (500 mg) in 4.0 mL of acetonitrile: mp 138−140 °C; IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1685 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78−7.74 (m, 2H), 7.38−7.34 (m, 2H), 7.21 (s, 1H), 6.13 (s, 1H), 4.10 (s, 1H), 2.45 (s, 1H), 2.09 (d, J = 1 Hz, 3H), 1.88 (d, J = 1 Hz, 3H), 1.20 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.1, 160.6, 153.4, 145.6, 133.9, 130.1, 127.8, 120.1, 76.7, 70.5, 62.0, 30.7, 28.2, 23.4, 21.7, 21.2; HRMS (MALDI-FTMS) m/z (M^+ + 1) found 417.0804, calcd for $C_{18}H_{22}N_2O_3SCl$ 417.0801.

6. Compound **6**, a white solid (410 mg, 69%) obtained from the electrophilic addition reaction of methyl 3,3-dimethylacrylate (0.2 mL, 1.5 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (720 mg, 3.0 mmol) in the presence of 4 Å molecular sieves (750 mg) in 6 mL of acetonitrile: mp 134−136 °C; IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1755 (C=O), 1292 (C−O) cm^{-1}; ^{1}H 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.

7a. Compound **7a**, a white solid (336 mg, 64%) obtained from the electrophilic addition reaction of mesityl oxide (0.17 mL, 1.5 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (720 mg, 3.0 mmol) in the presence of 4 Å molecular sieves (750 mg) in 4.5 mL of propionitrile: mp 91−93 °C; IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1716 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76−7.71 (m, 2H), 7.40−7.35 (m, 2H), 5.44 (q, J = 7.0 Hz, 1H), 4.04 (s, 1H), 2.46 (s, 3H), 2.17 (s, 3H), 1.81 (d, J = 7.0 Hz, 3H), 1.15 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.6, 156.3, 145.4, 134.3, 130.2, 127.5, 76.0, 69.8, 48.6, 30.8, 27.8, 23.4, 21.9, 21.7; HRMS (MALDI-FTMS) m/z (M^+ + 1) found 357.1038, calcd for $C_{16}H_{21}N_2O_3SCl$ 357.1034.

7b. Compound **7b**, a colorless oil (94 mg, 18%) obtained from the electrophilic addition reaction of mesityl oxide (0.17 mL, 1.5 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (720 mg, 3.0 mmol) in the presence of 4 Å molecular sieves (750 mg) in 4.5 mL of propionitrile: IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1718 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84−7.79 (m, 2H), 7.41−7.36 (m, 2H), 5.50 (q, J = 7.0 Hz, 1H), 3.96 (s, 1H), 2.46 (s, 3H), 2.26 (s, 3H), 1.88 (d, J = 7.0 Hz, 3H), 1.17 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 156.7, 145.6, 133.9, 130.2, 127.7, 76.1, 69.2, 48.4, 30.9, 27.9, 24.4, 23.5, 21.7.

8a. Compound **8a**, a white solid (316 mg, 54%) obtained from the electrophilic addition reaction of mesityl oxide (0.17 mL, 1.5 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (720 mg, 3.0 mmol) in the presence of 4 Å molecular sieves (750 mg) in 4.5 mL of butyronitrile: mp 105−107 °C; IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1717 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76−7.71 (m, 2H), 7.41−7.35 (m, 2H), 5.18 (t, J = 7.5 Hz, 1H), 4.04 (s, 1H), 2.46 (s, 3H), 2.28−2.20 (m, 1H), 2.20 (s, 3H), 2.14−2.04 (m, 1H), 1.15 (s, 3H), 1.09 (t, J = 7.5 Hz, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.6, 155.4, 145.4, 134.5, 130.1, 127.4, 75.8, 69.7, 54.3, 30.9, 28.7, 27.8, 23.3, 21.7, 11.4; HRMS (MALDI-FTMS) m/z (M^+ + 1) found 371.1195, calcd for $C_{17}H_{23}N_2O_3SCl$ 371.1191.

8b. Compound **8b**, a white solid (94 mg, 16%) obtained from the electrophilic addition reaction of mesityl oxide (0.17 mL, 1.5 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (720 mg, 3.0 mmol) in the presence of 4 Å molecular sieves (750 mg) in 4.5 mL of butyronitrile: mp 99−101 °C; IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1718 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85−7.80 (m, 2H), 7.41−7.36 (m, 2H), 5.31 (dd, J = 6.0, 7.5 Hz, 1H), 3.97 (s, 1H), 2.46 (s, 3H), 2.32−2.22 (m,1H), 2.28 (s, 3H), 2.14−2.04 (m, 1H), 1.17 (s, 3H), 1.14 (t, J = 7.5 Hz, 3H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 155.8, 145.6, 133.8, 130.2, 127.7, 76.0, 69.4, 54.3, 31.1, 30.9, 28.0, 23.7, 21.7, 10.9.

9a. Compound **9a**, a white solid (234 mg, 59%) obtained from the electrophilic addition reaction of phorone (138 mg, 1.0 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (480 mg, 2.0 mmol) in the presence of 4 Å molecular sieves (500 mg) in 3.0 mL of propionitrile: mp 149−151 °C; IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1681 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79−7.75 (m, 2H), 7.34−7.29 (m, 2H), 6.17−6.14 (m, 1H), 5.47 (q, J = 7.0 Hz, 1H), 4.15 (s, 1H), 2.43 (s, 3H), 2.04−2.03 (m, 3H), 1.84−1.80 (m, 6H), 1.15 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 159.7, 156.1, 144.9, 134.9, 129.8, 127.8, 120.4, 76.1, 69.9, 48.9, 30.9, 27.9, 23.5, 22.0, 21.6, 21.1; HRMS (MALDI-FTMS) m/z (M^+ + 1) found 397.1347, calcd for $C_{19}H_{25}N_2O_3SCl$ 397.1351.

9b. Compound **9b**, a colorless oil (59 mg, 15%) obtained from the electrophilic addition reaction of phorone (138 mg, 1.0 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (480 mg, 2.0 mmol) in the presence of 4 Å molecular sieves (500 mg) in 3.0 mL of propionitrile: IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1690 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84−7.79 (m, 2H), 7.39−7.35 (m, 2H), 6.08−6.11 (m, 1H), 5.49 (q, J = 7.0 Hz, 1H), 4.04 (s, 1H), 2.45 (s, 3H), 2.19 (s, 3H), 1.96 (s, 3H), 1.87 (d, J = 7.0 Hz, 3H), 1.16 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 160.0, 156.8, 145.2, 134.6, 130.1, 127.6, 120.6, 76.2, 69.3, 48.7, 30.9, 28.3, 24.5, 23.7, 21.7, 21.3.

10a. Compound **10a**, a white solid (259 mg, 63%) obtained from the electrophilic addition reaction of phorone (138 mg, 1.0 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (480 mg, 2.0 mmol) in the presence of 4 Å molecular sieves (500 mg) in 3.0 mL of butyronitrile: mp 99−101 °C; IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1683 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79−7.75 (m, 2H), 7.35−7.20 (m, 2H), 6.20−6.16 (m, 1H), 5.21 (dd, J = 6.5, 7.5 Hz, 1H), 4.14 (s, 1H), 2.43 (s, 3H), 2.31−2.21 (m, 1H), 2.17 (s, 3H), 2.13−2.06 (m, 1H), 2.06−2.09 (m, 3H), 1.84−1.82 (m, 3H), 1.15 (s, 3H), 1.09 (t, J = 7.5 Hz, 3H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 159.7, 155.4, 144.9, 135.1, 129.8, 127.8, 120.5, 75.9, 69.8, 54.6, 30.9, 28.8, 28.0, 23.4, 21.6, 21.1, 11.4; HRMS (MALDI-FTMS) m/z (M^+ + 1) found 411.1487, calcd for $C_{20}H_{27}N_2O_3SCl$ 411. 1504.

10b. Compound **10b**, a white solid (74 mg, 18%) obtained from the electrophilic addition reaction of phorone (138 mg, 1.0 mmol) with *N*,*N*-dichloro-*p*-toluenesulfonamide (480 mg, 2.0 mmol) in the presence of 4 Å molecular sieves (500 mg) in 3.0 mL of butyronitrile: IR (deposit from CH_2Cl_2 solution on a NaCl plate) 1689 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85−7.80 (m, 2H), 7.40−7.35 (m, 2H), 6.16−6.12 (m, 1H), 5.30 (dd, J = 6.5, 7.5 Hz, 1H), 4.04 (s, 1H), 2.46 (s, 3H), 2.31−2.21 (m, 1H), 2.20 (s, 3H), 2.13−2.06 (m, 1H), 1.97−1.94 (m, 3H), 1.16 (s, 3H), 1.13 (t, J = 7.5 Hz, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 159.9, 155.8, 145.2, 134.5, 130.1, 127.7, 120.6, 76.0, 69.4, 54.4, 31.1, 31.0, 28.2, 23.8, 21.7, 21.3, 10.8.

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Supporting Information Available: General procedure of direct diamination, HR-MS, and ^{1}H and ^{13}C NMR spectra of all pure products. This material is available free of charge via the Internet at http://pubs.acs.org.

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