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Organocatalyzed regio- and stereoselective diamination of functionalized alkenes

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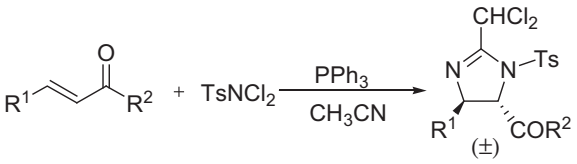
ABSTRACT

The first organocatalyzed diamination reaction of alkenes with *N*,*N*-dichlorotoluenesulfonamide ($TsNCl_2$) and acetonitrile as nitrogen sources was reported. The catalytic diamination reaction was convenient to carry out, resulting in imidazoline products with good yields and excellent regio- and stereoselectivities. Several other organic molecules were also tried as catalyst for this reaction and good results were achieved. A new one-pot synthesis of vicinal diamines via the current PPh_3-catalyzed diamination and the hydrolysis of resulting imidazoline products with $SnCl_4$ as promoter was also established.

1. Introduction

The vicinal diamines represent a class of organic compound,[1] which is extremely important for organic synthesis, medicinal chemistry, and pharmaceutical research.[2,3] This functionality also exists in many biologically important compounds. The vicinal diamines have been used as organocatalyst or chiral ligands for asymmertric synthesis.[4,5] Despite their extensive value and utility, the approaches to this vicinal diamine functionality in regio- and stereoselective still remain great challenges.[6] In the recent years, direct catalytic oxidative alkenes diamination presents an attractive access for generation of vicinal diamines. These intermolecular or intramolecular oxidative diamination systems were usually catalyzed by palladium or copper with alkyl ureas[7–9] or di-*tert*-butyldiaziridinone[10] as nitrogen resources. Electrophilic diamination reactions also gave an alternative methodology for the preparation of vicinal diamines.[11,12] Rhodium or iron complex was used as catalyst for these electrophilic diamination systems, to convert functionalized alkenes into imidazoline dimaine functionalitis.[11] Although oxidative diamination and electrophilic diamination have achieved success in the formation of vicinal diamines, there still exist limitations in yield, product diversification, reaction rates, chemoselectivity, and stereoselectivity.[7] So, the development of new efficient diamination methods becomes very urgent.

Triphenylphosphine is a commercially available reagent and tertiary phosphines are known as organocatalyst for many catalytic organic reactions.[13] In our previous reported electrophilic diamination reaction, the metal complexes with triphenylphosphine were found to be efficient catalysts for this electrophilic diamination reaction.[11b,c] In our continuous work about diamiantion reaction, we become interested in investigating whether phosphine can catalyze the diamination reaction of alkenes. Herein, we reported our results about the first organocatalyzed diamination reaction of alkenes with $TsNCl_2$ and acetonitrile as nitrogen resource (Scheme 1).



Scheme 1. Diamination of alkenes catalyzed by PPh_3.

2. Results and discussion

Initially, PPh_3 was used as catalyst for the diamination of chalcone **1a** under the previous reported diamination conditions.[11b] The reaction was performed in acetonitrile catalyzed by 20 mol %

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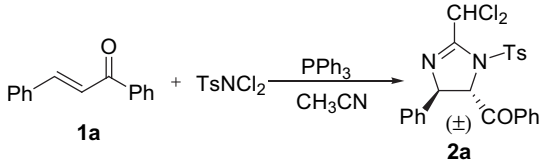
of triphenylphosphine with $TsNCl_2$ as nitrogen resource, and the expected diamine product **2a** was observed by ^1H NMR after 24 h.

To improve the yield, the reaction conditions were optimized, and the results were listed in Table 1. Slightly more diamine product was obtained when increasing the loading amount of triphenylphosphine from 20% to 30% (Table 1, entries 1–2). Acetonitrile seemed to be the best choice of solvent, as the use of other cosolvents, such as CH_2Cl_2, DMF, THF, and toluene together with acetonitrile, gave none or only a trace amount of the desired product (Table 1, entries 3–6). Increase of the loading amount of $TsNCl_2$ failed to give any improvement in chemical yield (Table 1, entry 7). The temperature appeared to have some influence on the chemical yields. The best yield was obtained when the reaction was performed at 30 °C (Table 1, entries 8–10). Similar to our previous catalytic system that 4 Å molecular sieve could promote the formation of product, the yield decreased to 70% when no 4 Å molecular sieve was used in the reaction (Table 1, entry 11). Extension the reaction time to 48 h almost had no effect on the completion of the reaction, but a lower yield would be obtained when the reaction was stopped at 12 h (Table 1, entries 12–13). If no triphenylphosphine catalyst was used in the diamination reaction, only 57% yield was obtained (Table 1, entry 14).

Table 1
Diamination of chalcone **1a** with $TsNCl_2$ under various conditions[a]

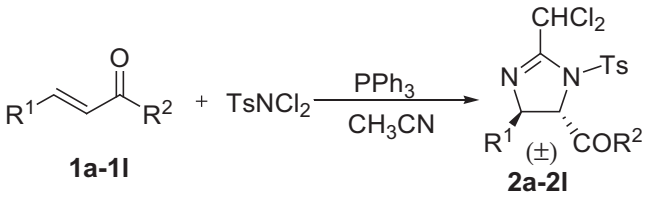


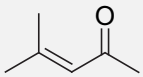
Entry	$TsNCl_2$ (mmol)	Solvent	Cat. (mol %)	Time (h)	T (°C)	Yield[b] (%)
1	3	CH_3CN	20	30	30	80
2	3	CH_3CN	30	30	30	83
3	3	CH_2Cl_2[c]	20	30	30	<10
4	3	DMF[c]	20	30	30	<10
5	3	THF[c]	20	30	30	<10
6	3	Toluene[c]	20	30	30	<10
7	4	CH_3CN	20	30	30	75
8	3	CH_3CN	20	30	5	40
9	3	CH_3CN	20	30	25	77
10	3	CH_3CN	20	30	50	76
11	3	CH_3CN	20	30	30	70[d]
12	3	CH_3CN	20	12	30	53
13	3	CH_3CN	20	48	30	85
14	3	CH_3CN	0	30	30	57

[a] Reactions were carried out using 1 mmol **1a** in 6 mL solvent with 0.5 g 4 Å molecular sieves.
[b] Isolated yields.
[c] Solvent of 5 mL and 1 mL acetonitrile was used together.
[d] No 4 Å molecular sieves was used.

Using the above optimized reaction condition, we next investigated the scope and limitations of this new PPh_3-based catalytic system (Table 2). It was found that both α,β-unsaturated ketone and α,β-unsaturated ester work well in this system. Good to excellent yield was obtained for all the substrates, even for the substrate with strong electron-withdrawing group on the aromatic ring (Table 2, entry 12). Especially for aliphatic substrate, the highest yield was obtained (88% yield) (Table 2, entry 7). The obvious improvement on chemical yield was observed comparing to the previous reported transition metal catalyzed diamination system (Table 2, entries 1, 2, 7–9).[11b,c] Furthermore, these substrates showed excellent stereoselectivities, only the *anti* isomers were found. Also, only one regioisomer was detected for all these twelve cases.

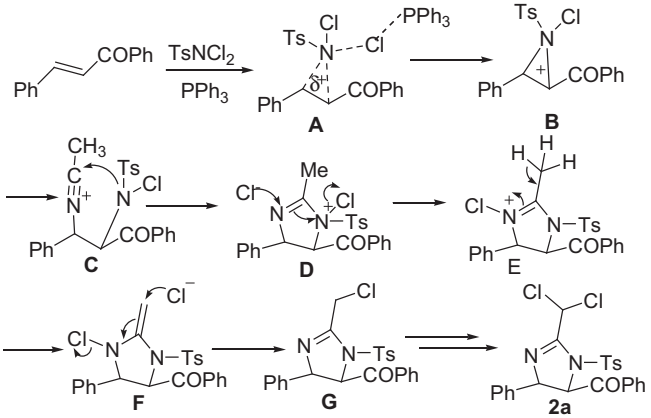
Table 2
Results of triphenylphosphine-catalyzed diamination of alkenes[a]



Entry	Substrates	R^1	R^2	Product (±)	*anti*/*syn*[b]	Yield[c] (%)
1	**1a**	Ph	Ph	**2a**	>95:1	83
2	**1b**	Ph	4-Cl–Ph	**2b**	>95:1	80
3	**1c**	Ph	4-Br–Ph	**2c**	>95:1	78
4	**1d**	Ph	4-Me–Ph	**2d**	>95:1	75
5	**1e**	4-Cl-Ph	Ph	**2e**	>95:1	68
6	**1f**	2-Cl-Ph	Ph	**2f**	>95:1	59
7	**1g**			**2g**	N/A	88
8	**1h**	Ph	OMe	**2h**	>95:1	72
9	**1i**	Ph	OEt	**2i**	>95:1	70
10	**1j**	Ph	OPh	**2j**	>95:1	69
11	**1k**	4-F-Ph	OMe	**2k**	>95:1	71
12	**1l**	4-Cl-Ph	OMe	**2l**	>95:1	70

[a] Carried out at 30 °C for 30 h in CH_3CN with alkenes as limiting reagent (alkenes/$TsNCl_2$=1:3) using 20 mol % PPh_3 in the presence of 4 Å molecular sieves.
[b] Estimated by crude ^1H NMR determination. >95% means no minor isomer was detected.
[c] Isolated yields.

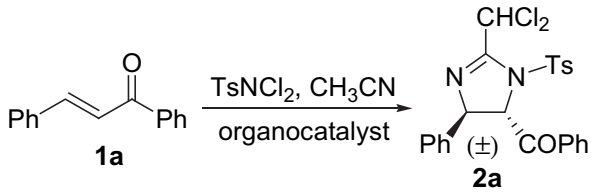
The mechanism of this catalytic system is believed to be similar to that of our previous reported metal complex catalyzed reactions.[11] In the initial step of the catalytic process, PPh_3 is assumed to active the nitrogen source ($TsNCl_2$), followed by reaction with chalcone, resulting in **A**. Then is the key step, which involves the formation of *N*-tosyl,*N*-chloroaziridinium intermediate **B**. And this aziridinium intermediate is next subjected to [2+3] cycloaddition with acetonitrile to form the 1*N*-tosyl,1*N*-chloroimidazolinium **D**. The following steps involve S_N2' and elimination reactions prior to forming the final product **2a** (Scheme 2).[11]



Scheme 2. Possible mechanism for the triphenylphosphine-catalyzed diamination process.

After triphenylphosphine was found to be an efficient catalyst for diamination reaction, the scope of organocatalyst for this reaction was then explored. Base on the assumption that triphenylphosphine can active N–Cl bond of nitrogen source, several regular organic compounds, which are expected to be able to react with $TsNCl_2$ are employed as catalysts for the current catalytic system, and the results were shown in Table 3. Diphenylsulfane, tributylamine, dibutylamine, and aminoalcohol

Table 3
Organocatalyzed electrophilic diamination of chalcone[a]



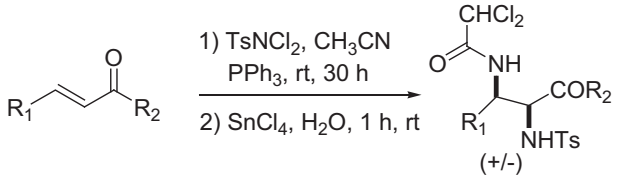
Entry	Catalyst	Amount (mmol%)	Time (h)	*anti*/*syn*[b]	Yield[c] (%)
1	Diphenylsulfane	20	30	>95:1	79
2	Bu_3N	20	30	>95:1	61
3	Bu_2NH	20	30	>95:1	65
4	2-Aminoethanol	20	30	>95:1	77

[a] Carried out at 30 °C in CH_3CN with alkenes as limiting reagent (alkenes/$TsNCl_2$=1:3) in the presence of 4 Å molecular sieves.
[b] Regio- and stereoselectivity >95:1 for all these reactions, and estimated by crude ^1H NMR.
[c] Isolated yields.

were tried, and all of these compounds can efficiently catalyze the diamination reaction to give desired diamine products in good yields, high regio- and stereoselectivities.

Finally, a new one-pot reaction condition for the highly stereoselective synthesis of α,β-differentiated 1,2-vicinal diamines was also established, which contains the current triphenylphosphine-catalyzed diamination reaction and the hydrolysis of the resulting imidazoline products with $SnCl_4$ as promoter (Table 4).[11e,14] As shown in Table 4, the highly stereoselecitive one-pot reaction was convenient to carry out, and moderate to good chemical yields were obtained. The stereochemistry of this reaction was unambiguously confirmed by X-ray

Table 4
One-pot synthesis of α,β-differentiated 1,2-vicinal diamines



Entry	Substrates	R^1	R^2	Product[a] (±)	Yield[b] (%)
1	**1a**	Ph	Ph	**3a**	74
2	**1c**	Ph	4-Br–Ph	**3c**	60
3	**1h**	Ph	OMe	**3h**	51
4	**1k**	4-F–Ph	OMe	**3k**	45

[a] Regio- and stereoselectivity >95:1 for all these reactions, and estimated by crude ^1H NMR.
[b] Isolated yields.

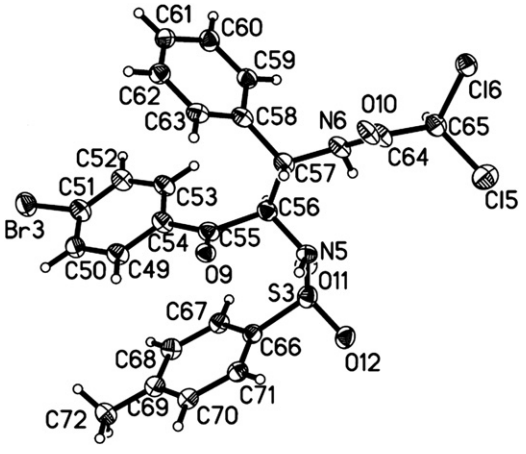


Figure 1. ORTEP diagram showing **3c**.

structural analysis (Fig. 1). This one-pot reaction provides an easy access to the synthesis of α,β-differentiated 1,2-vicinal diamines starting from readily available and inexpensive olefins.

3. Conclusion

In summary, triphenylphospine found to be efficient organocatalysts for diamination of olefins with $TsNCl_2$ the nitrogen source, resulting in imidazoline derivatives in high chemical yields and excellent regio- and stereoselectives. The reaction provides an easy way to synthesize the α,β-differentiated 1,2-vicinal diamines. In addition, various regular organic compounds can also be used as catalyst for this reaction. A new one-pot synthesis of vicinal diamines via the current PPh_3-catalyzed diamination and the hydrolysis of resulting imidazoline products with $SnCl_4$ as promoter was also established.

4. Experimental section

4.1. General

Melting points were uncorrected. IR spectra were collected on Bruker Vector 22 in KBr pellets. ^1H NMR, ^{13}C NMR (TMS used as internal standard) spectra were recorded on Bruker ARX-300 spectrometer. Elemental analyses were performed on a Perkin–Elmer 240 elemental analysis instrument. Mass spectrum was done by Finnigan TSQ7000 Electrospray Mass Spectrometer. Thin layer chromatography was carried out on Silica Gel 60 F-254 TLC plates. 20×20 cm Gel 60 F-254 TLC plates were used for Isolation.

4.2. General procedure for electrophilic diamination

Into a dry vial was added triphenylphosphine (5.2 mg, 0.2 mmol), 4 Å molecular sieves (0.5 g), and freshly distilled acetonitrile (6 mL). Then α,β-unsaturated ketone or carboxylic ester (1 mmol) was added to the stirred mixture. $TsNCl_2$ (0.72 g, 3 mmol) was added as solid for 5 min, shortly after $TsNCl_2$ was added. The resulting slurry was stirred at 30 °C for 30 h in the capped vial without argon protection. The 4 Å molecular sieves and other solid precipitates were filtered off and washed with EtOAc (3×15 mL). The organic solution was directly concentrated without quenching and then purified via TLC plate (petroleum ether/EtOAc=5:1) to give 1-*p*-toluenesulfonyl-2-dichloromethyl-imidazoline **2a**–**l**.

*4.2.1. Compound **2a**.* Compound **2a** was isolated as white solid. Mp 144–145 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.67–7.81 (m, 4H), 7.62–7.67 (m, 1H), 7.45–7.50 (m, 2H), 7.25–7.33 (m, 6H), 6.90 (d, *J*=6.77 Hz, 2H), 5.57 (d, *J*=4.87 Hz, 1H), 5.02 (d, *J*=4.79 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 157.1, 146.1, 139.0, 134.7, 134.7, 133.8, 130.5, 129.5, 129.4, 129.2, 129.1, 128.3, 126.9, 72.6, 72.2, 61.8, 22.0; IR (KBr): 1691; MS (ESI): calcd for $[C_{24}H_{20}Cl_2N_2O_3S]$ ($[M+H]^+$): 487.06, found: 487.00. Anal. Calcd for $C_{24}H_{20}Cl_2N_2O_3S$: C 59.14, H 4.14, N 5.75 Found: C 59.28, H 4.08, N 5.86.

*4.2.2. Compound **2b**.* Compound **2b** isolated as white solid. Mp 124–125 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J*=8.32 Hz, 2H), 7.69 (d, *J*=8.57 Hz, 2H), 7.44 (d, *J*=8.53 Hz, 2H), 7.22–7.34 (m, 6H), 6.90 (d, *J*=6.76 Hz, 2H), 5.49 (d, *J*=5.11 Hz, 1H), 5.02 (d, *J*=5.07 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.7, 157.1, 146.2, 141.4, 138.9, 134.6, 132.1, 130.5, 129.7, 129.5, 129.3, 129.2, 128.3, 126.9, 72.7, 72.3, 61.7, 22.1; IR (KBr): 1698; MS (ESI): calcd for $[C_{24}H_{19}Cl_3N_2O_3S]$ ($[M+H]^+$): 521.02, found: 520.95. Anal. Calcd for $C_{24}H_{19}Cl_3N_2O_3S$: C 55.24, H 3.67, N 5.37. Found: C 55.25, H 3.52, N 5.25.

*4.2.3. Compound **2c**.* Compound **2c** was isolated as white solid. Mp 132–133 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J*=8.29 Hz, 2H),

7.62 (s, 4H), 7.22–7.34 (m, 6H), 6.89 (d, J=6.87 Hz, 2H), 5.49 (d, J=5.10 Hz, 1H), 5.02 (d, J=5.05 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.9, 157.1, 146.3, 138.9, 134.6, 132.7, 132.5, 130.6, 130.5, 130.2, 129.5, 129.2, 128.3, 126.9, 72.6, 72.3, 61.7, 22.1; IR (KBr): 1700; MS (ESI): calcd for [$C_{24}H_{19}BrCl_2N_2O_3S$] ([M+H]$^+$): 564.97, found: 564.93. Anal. Calcd for $C_{24}H_{19}BrCl_2N_2O_3S$: C 50.90, H 3.38, N 4.95. Found: C 50.83, H 3.30, N 5.05.

*4.2.4. Compound **2d**.* Compound **2d** was isolated as white solid. Mp 159–161 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J=8.37 Hz, 2H), 7.66 (d, J=8.15 Hz, 2H), 7.24–7.34 (m, 8H), 6.91 (d, J=6.81 Hz, 2H), 5.55 (d, J=4.84 Hz, 1H), 5.02 (d, J=4.78 Hz, 1H), 2.46 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 157.1, 146.1, 145.9, 139.1, 134.8, 131.2, 130.5, 130.1, 129.4, 129.3, 129.0, 128.3, 127.0, 72.7, 72.1, 61.8, 22.2, 22.1; IR (KBr): 1697; MS (ESI): calcd for [$C_{25}H_{22}Cl_2N_2O_3S$] ([M+H]$^+$): 501.07, found: 501.02. Anal. Calcd for $C_{25}H_{22}Cl_2N_2O_3S$: C 59.88, H 4.42, N 5.59. Found: C 59.83, H 4.56, N 5.61.

*4.2.5. Compound **2e**.* Compound **2e** was isolated as white solid. Mp 124–125 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74–7.78 (m, 4H), 7.64–7.68 (m, 1H), 7.46–7.51 (m, 2H), 7.23–7.32 (m, 5H), 6.84 (d, J=8.41 Hz, 2H), 5.50 (d, J=4.87 Hz, 1H), 5.02 (d, J=4.85 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 157.6, 146.3, 137.7, 135.0, 134.8, 134.6, 133.8, 130.5, 129.6, 129.4, 129.1, 128.2, 72.0, 71.9, 61.7, 22.0; IR (KBr): 1693; MS (ESI): calcd for [$C_{24}H_{19}Cl_3N_2O_3S$] ([M+H]$^+$): 521.02, found: 520.96. Anal. Calcd for $C_{24}H_{19}Cl_3N_2O_3S$: C 55.24, H 3.67, N 5.37. Found: C 55.28, H 3.66, N 5.25.

*4.2.6. Compound **2f**.* Compound **2f** was isolated as white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J=7.46 Hz, 2H), 7.71 (d, J=7.46 Hz, 2H), 7.60–7.65 (m, 1H), 7.43–7.48 (m, 2H), 7.23–7.28 (m, 5H), 7.13–7.17 (m, 1H), 6.84 (d, J=7.53 Hz, 1H), 5.61 (d, J=5.18 Hz, 1H), 5.53 (d, J=5.18 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.8, 157.9, 146.1, 136.9, 134.5, 132.7, 130.4, 130.1, 130.0, 129.2, 129.1, 128.7, 128.2, 127.8, 69.9, 69.6, 61.8, 22.0; IR (KBr): 1684; MS (ESI): calcd for [$C_{24}H_{19}Cl_3N_2O_3S$] ([M+H]$^+$): 521.02, found: 520.96. Anal. Calcd for $C_{24}H_{19}Cl_3N_2O_3S$: C 55.24, H 3.67, N 5.37. Found: C 55.31, H 3.50, N 5.47.

*4.2.7. Compound **2g**.* Compound **2g** was isolated as white solid. Mp 95–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J=8.25 Hz, 2H), 7.40 (d, J=8.04 Hz, 2H), 7.21 (s, 1H), 4.00 (s, 1H), 2.48 (s, 3H), 2.23 (s, 3H), 1.22 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.0, 153.9, 146.5, 133.5, 130.8, 128.0, 76.9, 70.8, 62.1, 31.1, 28.2, 23.6, 22.1; IR (KBr): 1718; MS (ESI): calcd for [$C_{15}H_{18}Cl_2N_2O_3S$] ([M+H]$^+$): 377.04, found: 376.96. Anal. Calcd for $C_{15}H_{18}Cl_2N_2O_3S$: C 47.75, H 4.81, N 7.42. Found: C 47.60, H 4.92, N 7.31.

*4.2.8. Compound **2h**.* Compound **2h** was isolated as white solid. Mp 125–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J=8.28 Hz, 2H), 7.18–7.27 (m, 6H), 6.89 (d, J=7.19 Hz, 2H), 5.22 (d, J=4.31 Hz, 1H), 4.57 (d, J=4.38 Hz, 1H), 3.82 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 157.0, 146.1, 139.6, 134.1, 130.5, 129.1, 128.4, 128.0, 126.2, 72.4, 69.5, 61.8, 53.5, 22.0; IR (KBr): 1758; MS (ESI): calcd for [$C_{19}H_{18}Cl_2N_2O_4S$] ([M+H]$^+$): 441.04, found: 440.97. Anal. Calcd for $C_{19}H_{18}Cl_2N_2O_4S$: C 51.71, H 4.11, N 6.35. Found: C 51.57, H 4.08, N 6.42.

*4.2.9. Compound **2i**.* Compound **2i** was isolated as white solid. Mp 99–101 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J=8.33 Hz, 2H), 7.18–7.27 (m, 6H), 6.90 (d, J=6.47 Hz, 2H), 5.22 (d, J=4.24 Hz, 1H), 4.57 (d, J=4.31 Hz, 1H), 4.25 (q, J=7.13 Hz, 2H), 2.43 (s, 3H), 1.31 (t, J=7.13 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 157.0, 146.1, 139.6, 134.3, 130.4, 129.2, 128.4, 128.0, 126.2, 72.5, 69.6, 62.7, 61.8, 22.0, 14.4; IR (KBr): 1751; MS (ESI): calcd for [$C_{20}H_{20}Cl_2N_2O_4S$] ([M+H]$^+$): 455.05, found: 454.97. Anal. Calcd for $C_{20}H_{20}Cl_2N_2O_4S$: C 52.75, H 4.43, N 6.15. Found: C 52.84, H 4.32, N 6.02.

*4.2.10. Compound **2j**.* Compound **2j** was isolated as white solid. Mp 118–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J=8.34 Hz, 2H), 7.40–7.42 (m, 2H), 7.24–7.31 (m, 7H), 7.14 (dd, J=1.14, 8.68 Hz, 2H), 6.99 (dd, J=1.67, 7.76 Hz, 2H), 5.42 (d, J=4.48 Hz, 1H), 4.79 (d, J=4.55 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 157.1, 150.5, 146.3, 139.4, 134.2, 130.6, 129.9, 129.3, 128.7, 128.2, 126.9, 126.3, 121.4, 72.7, 69.7, 61.8, 22.0; IR (KBr): 1759; MS (ESI): calcd for [$C_{24}H_{20}Cl_2N_2O_4S$] ([M+H]$^+$): 503.05, found: 502.99. Anal. Calcd for $C_{24}H_{20}Cl_2N_2O_4S$: C 57.26, H 4.00, N 5.56. Found: C 57.12, H 4.05, N 5.48.

*4.2.11. Compound **2k**.* Compound **2k** was isolated as white solid. Mp 123–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J=8.32 Hz, 2H), 7.25 (d, J=8.08 Hz, 2H), 7.20 (s, 1H), 6.88 (d, J=6.88 Hz, 4H), 5.22 (d, J=4.23 Hz, 1H), 4.52 (d, J=4.28 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 164.4, 161.1, 157.4, 146.3, 135.6, 134.1, 130.5, 128.0, 127.9, 116.2, 115.9, 71.6, 69.5, 61.7, 53.5, 21.9; IR (KBr): 1762; MS (ESI): calcd for [$C_{19}H_{17}Cl_2FN_2O_4S$] ([M+H]$^+$): 459.03, found: 458.93. Anal. Calcd for $C_{19}H_{17}Cl_2FN_2O_4S$: C 49.68, H 3.73, N 6.10. Found: C 49.66, H 3.74, N 6.29.

*4.2.12. Compound **2l**.* Compound **2l** was isolated as white solid. Mp 105–106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J=8.37 Hz, 2H), 7.14–7.27 (m, 5H), 6.83 (d, J=8.33 Hz, 2H), 5.20 (d, J=4.07 Hz, 1H), 4.50 (d, J=4.16 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 157.6, 146.4, 138.3, 134.4, 134.0, 130.4, 129.3, 127.9, 127.5, 71.5, 69.5, 61.7, 53.6, 22.0; IR (KBr): 1759; MS (ESI): calcd for [$C_{19}H_{17}Cl_3N_2O_4S$] ([M+H]$^+$): 475.00, found: 474.99. Anal. Calcd for $C_{19}H_{17}Cl_3N_2O_4S$: C 47.96, H 3.60, N 5.89. Found: C 47.92, H 3.63, N 5.92.

4.3. General procedure for the one-pot synthesis of vicinal diamines

Into a dry vial was added triphenylphosphine (5.2 mg, 0.2 mmol), 4 Å molecular sieves (0.5 g) and freshly distilled acetonitrile (6 mL). Then α,β-unsaturated ketone or carboxylic ester (1 mmol) was added to the stirred mixture. $TsNCl_2$ (0.72 g, 3 mmol) was added as solid for 5 min, shortly after $TsNCl_2$ was added. The resulting slurry was stirred at room temperature for 30 h in the capped vial without argon protection. Then, H_2O (5.0 mL) and $SnCl_4 \cdot 5H_2O$ (1.75 g, 5.0 mmol) were added with strong stirring. After 1 h, the 4 Å molecular sieves and other solid precipitates were filtered off and washed with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3×30 mL), and the combined organic solution was concentrated and then purified via TLC plate (petroleum ether/EtOAc=2.5:1) to give products **3**.

*4.3.1. Compound **3a**.* Compound **3a** was isolated as white solid. Mp 157–159 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.58 (m, 5H), 7.25–7.36 (m, 8H), 7.04 (d, J=8.00 Hz, 2H), 6.03 (d, J=8.93 Hz, 1H), 5.91 (s, 1H), 5.20–5.31 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 164.3, 144.3, 136.6, 136.5, 134.7, 134.5, 130.0, 129.4, 129.0, 128.6, 127.4, 127.3, 66.5, 60.7, 56.1, 21.7; IR (KBr) 3367, 3269, 3064, 1677, 1342, 1165; MS (ESMS/[M+H]$^+$) calcd for $C_{24}H_{22}Cl_2N_2O_4SH$: 505.1, found: 504.8. $C_{24}H_{22}Cl_2N_2O_4S$: calcd C 57.03, H 4.39, N 5.54, found C 57.23, H 4.33, N 5.45.

*4.3.2. Compound **3c**.* Compound **3c** was isolated as white solid. Mp 144–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J=8.00 Hz, 2H), 7.44 (d, J=8.36 Hz, 2H), 7.28–7.36 (m, 8H), 7.06 (d, J=7.87 Hz, 2H), 6.01 (d, J=9.16 Hz, 1H), 5.92 (s, 1H), 5.24–5.29 (m, 1H), 5.12–5.15 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 164.5, 144.5,

136.5, 136.4, 133.5, 132.3, 130.0, 130.0, 129.8, 129.4, 129.1, 127.4, 127.4, 66.5, 60.6, 56.0, 21.8; IR (KBr): 3313, 3267, 3032, 1680, 1343, 1072; MS (ESMS/$[M+H]^+$) calcd for $C_{24}H_{21}BrCl_2N_2O_4SH$: 582.9, found: 583.0. $C_{24}H_{21}BrCl_2N_2O_4S$: calcd C 49.33, H 3.62, N 4.79, found C 49.19, H 3.42, N 4.92; crystal data for **3c**: 3 ($C_{24}H_{21}BrCl_2N_2O_4S$), H_2O; formula weight, 1770.91; monoclinic, space group $P2(1)/c$; a=20.8165(19), b=17.2483(16), c=21.723(2) Å; β=97.026(2); V=7741.1(12) Å^3; Z=4; D_{calcd}=1.520 g cm^{-3}; $F(000)$=3592; crystal size=0.32×0.26×0.24 mm; $2\theta_{max}$=52.0°; reflections collected, 15,171; reflections used, 10,507; $R1$=0.0586; $wR2$=0.1181; GOF=1.02. CCDC number, 627034.

*4.3.3. Compound **3h**.* Compound **3h** was isolated as white solid. Mp 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J=8.22 Hz, 2H), 7.46 (d, J=8.07 Hz, 1H), 7.24–7.35 (m, 7H), 5.92 (s, 1H), 5.42 (d, J=9.33 Hz, 1H), 5.27–5.32 (m, 1H), 4.34–4.39 (m, 1H), 3.49 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 164.2, 144.4, 136.6, 135.9, 130.1, 129.3, 129.1, 127.5, 127.2, 66.5, 59.7, 55.9, 53.3, 21.9; IR (KBr): 3320, 3264, 3066, 1744, 1672, 1345, 1162; MS (ESMS/$[M+H]^+$) calcd for $C_{19}H_{20}Cl_2N_2O_5SH$: 459.0, found: 458.8. $C_{19}H_{20}Cl_2N_2O_5S$: calcd C 49.68, H 4.39, N 6.10, found C 49.60, H 4.52, N 6.31.

*4.3.4. Compound **3k**.* Compound **3k** was isolated as white solid. Mp 172–174 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J=8.26 Hz, 2H), 7.44 (d, J=8.25 Hz, 1H), 7.22–7.29 (m, 4H), 6.99–7.05 (m, 2H), 5.93 (s, 1H), 5.46–5.49 (m, 1H), 5.28–5.33 (m, 1H), 4.29–4.34 (m, 1H), 3.51 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.9, 164.2, 160.8, 143.4, 138.4, 134.1, 130.1, 129.8, 129.6, 127.1, 116.0, 115.7, 67.6, 60.6, 54.7, 52.8, 21.7; IR (KBr) 3325, 3203, 1745, 1655, 1345, 1145; MS (ESMS/$[M+Na]^+$) calcd for $C_{19}H_{19}Cl_2FN_2O_5SNa$: 499.0, found: 498.8. $C_{19}H_{19}Cl_2FN_2O_5S$: calcd C 47.81, H 4.01, N 5.87, found C 47.76, H 4.12, N 5.68.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.04.054. These data include MOL files and InChIKeys of the most important compounds described in this article.

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