

Synthesis of Primary Amines and *N*-Methylamines by the Electrophilic Amination of Grignard Reagents with 2-Imidazolidinone *O*-Sulfonyloxime

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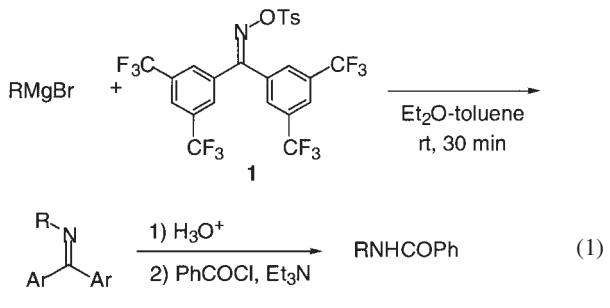
2-Imidazolidinone *O*-sulfonyloxime reacts with various aryl and alkyl Grignard reagents as an electrophilic amination reagent, giving *N*-alkylated imines. The resulting imines are transformed to primary amines and *N*-methyl secondary amines by hydrolysis with CsOH and $LiAlH_4$ reduction, respectively.

In general, primary amines are prepared by reduction of the corresponding nitro compounds,[1a] imines,[1b] and azides.[1c] Alkylation of nucleophilic amination reagents such as phthalimide and trifluoroacetamide is another common method for preparation of amino compounds,[2] whereas this method cannot be applied for the synthesis of aminoarene. Recently, a transition metal-mediated amination method has been developed, and this is now regarded as an efficient method for the preparation of arylamines.[3] While electrophilic amination has provided an alternative method,[4] this has rarely been utilized in organic synthesis, because electrophilic amination reagents such as chloramine and *O*-sulfonylhydroxylamine derivatives are not stable enough and not easy to handle due to their high reactivity.[5] Recently several electrophilic amination reactions such as *N*-metal hydroxylamine derivatives,[6] dialkyl azodicarboxylates,[7] oxaziridines,[8] and some oxime derivatives[9] have been reported.

Recently, we have reported substitution reactions on oxime nitrogen. One of the typical reaction is the electrophilic amination of Grignard reagents with benzophenone oxime derivatives.[10] For example, bis[3,5-bis(trifluoromethyl)phenyl] ketone *O*-tosyloxime (**1**) reacts with aryl and alkyl Grignard reagents at room temperature to give the corresponding imines, which are hydrolyzed to afford primary amines (Eq. 1).



(1)

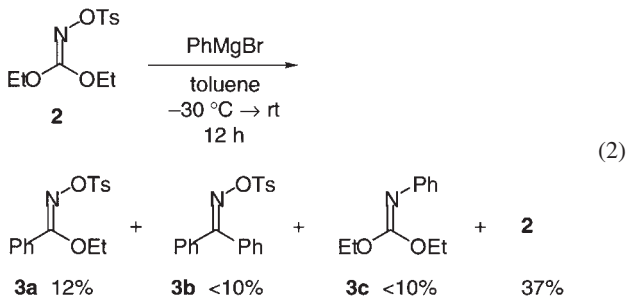
Ts = *p*-CH_3-C_6H_4-SO_2, Ar = 3,5-$(CF_3)_2C_6H_3$

This particular benzophenone oxime **1** was designed to meet the following conditions. There is no α-hydrogen to prevent Neber reaction,[11] and trifluoromethyl groups are introduced to suppress Beckmann rearrangement.[12] To apply this method to the preparation of primary amines, it was desired to employ simple oximes without bulky substituents like 3,5-bis(trifluoromethyl)phenyl group.

Since oximes of ureas and carbonates rarely undergo Beckmann rearrangement and Neber reaction, *O*-sulfonyl derivatives of these compounds were employed for electrophilic amination. We found that 1,3-dimethyl-2-imidazolidinone *O*-sulfonyloxime reacted smoothly with Grignard reagents, and the resulting *N*-alkylated imines were transformed to primary amines and secondary methylamines. In this paper, full accounts of these results are described.

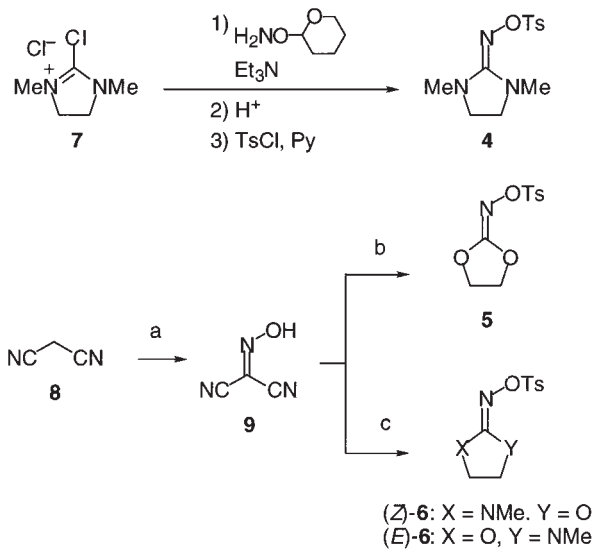
Results and Discussion

The reactions of phenyl Grignard reagent with *O*-sulfonyloximes of ureas and carbonates were screened. In the reaction with diethyl carbonate *O*-tosyloxime (**2**)[13] and phenylmagnesium bromide in toluene, the Grignard reagent attacked either oxime carbon or the nitrogen atom to give a mixture of **3a–c** and **2** (Eq. 2).



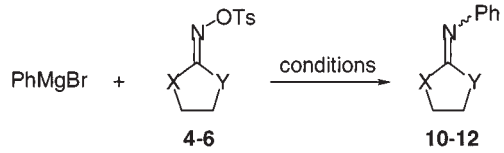
(2)

Cyclic *O*-sulfonyloximes such as 2-imidazolidinone *O*-tosyloxime **4**, 1,3-dioxolan-2-one *O*-tosyloxime (**5**), and 2-oxazolidinone *O*-tosyloxime **6** were prepared as described in the Scheme 1. Imidazolidinone oxime **4** was prepared from 2-chloro-1,3-dimethyl-1-imidazolinium chloride (**7**)[14] and *O*-tet-



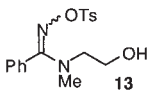
Scheme 1. Preparation of cyclic *O*-tosyloximes **4**–**6**. a) $NaNO_2$, AcOH, H_2O. b) TsCl, Pyridine; $HO(CH_2)_2OH$, NaH. c) BnBr, Et_3N; $HO(CH_2)_2NHMe$, NaH; H_2, $Pd(OH)_2$-C; TsCl, Et_3N.

Table 1. Reaction of PhMgBr with Cyclic Oximes **4**–**6**



Run	X	Y		Solvent	Conditions		Yield/%
1	NMe	NMe	**4**	toluene	0 °C, 15 min	**10a**	98[a]
2	NMe	NMe	**4**	THF	0 °C, 2 days	**10a**	92[b,c]
3	O	O	**5**	toluene	0 °C, 1 h	**11**	66[b,d]
4	O	O	**5**	CH_2Cl_2	0 °C, 1 h	**11**	66[b]
5	NMe	O	(*Z*)-**6**	toluene	rt, 30 min	**12**	97[a,e]
6	O	NMe	(*E*)-**6**	CH_2Cl_2	0 °C, 30 min	**12**	0[f]

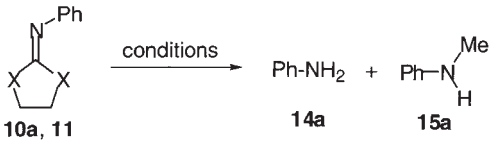
a) Isolated yield. b) NMR yield. c) **4** was recovered in 6% yield. d) **5** was recovered in 19% yield. e) See Ref. 17. f) **13** was isolated in 70% yield.



rahydropyranylhydroxylamine[15] by 3 steps.[16] It was stable enough to be stored at least for 3 months at 0 °C. 1,3-Dioxolan-2-one oxime **5** and 2-oxazolidinone oxime **6** were synthesized from malononitrile (**8**) according to a modified literature procedure.[13]

The results of the reactions of phenylmagnesium bromide and cyclic urea and carbonate *O*-sulfonyloximes **4**–**6** are summarized in Table 1. 2-Imidazolidinone *O*-tosyloxime **4** reacted smoothly with an equimolar amount of phenylmagnesium bromide (Et_2O solution) in toluene at 0 °C, giving *N*-phenylimine **10a** in 98% yield (run 1). In THF, the reaction became much slower (run 2). Thus, 2-imidazolidinone oxime **4** was found to be more reactive in toluene as compared to bis[3,5-bis(trifluoromethyl)phenyl] ketone oxime **1**, the reaction of which proceeded at room temperature.[10] 1,3-Dioxolan-2-one oxime **5** was insoluble in toluene and less reactive as compared to 2-imidazolidinone oxime **4**, the reaction of which with phenylmagnesium bromide in toluene gave imine **11** in 66% yield with the recovery of 19% of the starting material **5** (run 3). By the reaction in CH_2Cl_2 in which 1,3-dioxolan-2-one oxime **5** was completely soluble, **5** was consumed within 1 h, but the yield of *N*-phenylimine **11** was 66%. (*Z*)-*N*-Methyloxazolidinone *O*-sulfonyloxime **6** was scarcely soluble in toluene, but the reaction with phenylmagnesium bromide in toluene yielded the corresponding imine **12**[17] in high yield (97%, run 5). Strangely in the reaction of stereoisomer (*E*)-*N*-methyloxazolidinone oxime **6**, Grignard reagent attacked the oxime carbon instead of the nitrogen to yield amidoxime **13** in 70% yield (run 6).

Table 2. Transformation of Imine **10a**, **11** to Amines



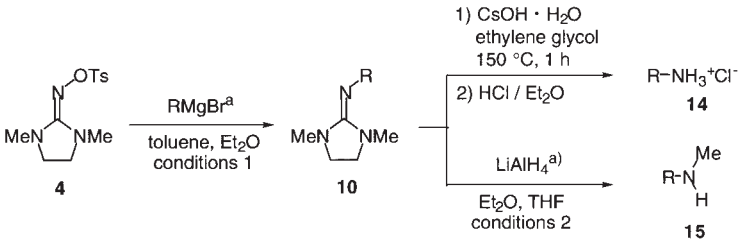
Run	X		Conditions	Yield/%	
				14a	**15a**
1	NMe	**10a**	$CsOH \cdot H_2O$, ethylene glycol 150 °C, 1 h; HCl/Et_2O	95[a]	0
2	NMe	**10a**	$LiAlH_4$, Et_2O, THF, rt, 12 h	0	93[b]
3	NMe	**10a**	DIBAL-H, CH_2Cl_2 −78 °C→rt, 12 h	50[c]	38[c]
4	O	**11**	1 M HCl, MeOH rt, 30 min	41[c,d]	0

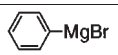
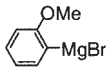
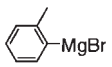
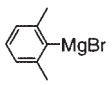
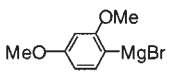
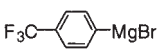
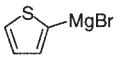
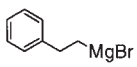
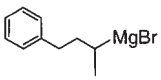
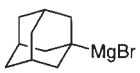
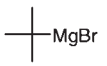
a) Isolated as a HCl salt. b) Isolated yield. c) NMR yield. d) 2 steps yield from **5** [amination (Table 1, Run 4) and hydrolysis].

Then, the transformations of the resulting imines to amines were investigated under various conditions as shown in Table 2. The hydrolysis of **10a** under acidic conditions failed. Treatment of **10a** with various hetero nucleophiles such as NH_2NH_2, H_2O_2 under neutral or basic conditions, did not give the desired amine **14a** at all. Imidazolidinone imine **10a** was hydrolyzed by the treatment of $CsOH \cdot H_2O$ in ethylene glycol at 150 °C for 1 h to give aniline (**14a**) in 95% yield (run 1). The reduction of **10a** proceeded smoothly with $LiAlH_4$, and *N*-methylaniline (**15a**) was obtained as the sole product in 93% yield (run 2), whereas diisobutylaluminum hydride (DIBAL-H) reduction gave a mixture of aniline (**14a**) and *N*-methylaniline (**15a**) (run 3). The results show that imines formed by the reaction of **4** with Grignard reagents could be selectively transformed to primary amines or monomethyl secondary amines.[18] The imine **11** was hydrolyzed under acidic conditions to give aniline (**14a**) in moderate yield (run 4). Although imine **11** was hydrolyzed more easily under acidic conditions as compared with imine **10a**, the yield of imine **11** (66%) could not be improved (vide supra). The hydrolysis of **12** was as difficult as that of **10a**. Thus, it was concluded that 2-imidazolidinone oxime **4** is most suitable for electrophilic amination among **4**–**6**, and we examined further by using **4** or its addition product **10**.

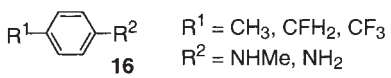
The results of the amination of various Grignard reagents with **4** are listed in Table 3. 2-Imidazolidinone *O*-tosyloxime

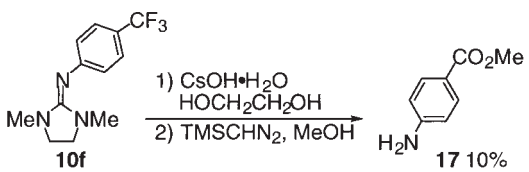
Table 3. Preparation of Various Primary Amines **14** and Mono-*N*-methylamines **15** by the Reaction of **4** with Grignard Reagents



Run	RMgBr	Conditions 1	Conditions 2	Yield/%					
				10[b)]		**14**[c)]		**15**[c)]	
1		0 °C, 15 min	rt, 12 h	**10a**	98	**14a**	95	**15a**	93
2		0 °C–rt, 30 min	rt, 12 h	**10b**	99	**14b**	98	**15b**	81
3		0 °C, 15 min	reflux, 8 h	**10c**	96	**14c**	36[d),e)]	**15c**	89
4		0 °C–rt, 30 min	reflux, 24 h	**10d**	85	**14d**	0[f)]	**15d**	0[f)]
5		0 °C–rt, 30 min	reflux, 3 h	**10e**	96	**14e**	55[g)]	**15e**	70
6		0 °C, 15 min	rt, 12 h	**10f**	88	**14f**	0[h)]	**15f**	0[i)]
7		0 °C, 30 min	reflux, 9 h	**10g**	> 99	**14g**	84[d)]	**15g**	92
8		0 °C, 15 min	reflux, 1.5 h	**10h**	84	**14h**	0[f)]	**15h**	68[j)]
9		−78 °C, 15 min	rt, 12 h	**10i**	94	**14i**	93	**15i**	73
10		−78 °C, 15 min	rt, 12 h	**10j**	96	**14j**	96	**15j**	84
11		−78 °C, 15 min	reflux, 24 h	**10k**	—[k)]	**14k**	71	**15k**	55[d),l)]
12		−78 °C, 15 min		**10l**	—[m)]	**14l**	0		

a) Oxime: Grignard reagent = 1:1. b) Isolated yield. c) Isolated yield (2 steps from **4**). d) NMR yield. e) Hydrolysis was carried out for 7.5 h, and 50% of imine **10c** was recovered. f) Imine **10** was recovered. g) Hydrolysis was carried out for 3 h. h) See Eq. 3. i) A mixture of **16** was isolated. j) 2-Aminothiophene **14h** was isolated in 2%. When the reaction was carried out at room temperature for 12 h, 2-methylaminothiophene **15h** and 2-aminothiophene **14h** were obtained in 63% and 15%, respectively. k) Imine **10k** was not isolated. l) Imine **10k** was recovered in 15%. m) Imine **10l** is detected to be formed in low yield (< 8%) by NMR, but could not be isolated and characterized.





(3)

4 reacted with aryl Grignard reagents smoothly at 0 °C–room temperature (run 1–8), even with sterically hindered 2,6-dimethylphenylmagnesium bromide, giving the corresponding *N*-arylimines in high yields. The resulting imines **10**, except 2,6-dimethylphenylimine **10d** and *p*-trifluoromethylphenylimine **10f**, were hydrolyzed with CsOH to anilines and/or reduced with $LiAlH_4$ to *N*-methylanilines. The difficulty of the hydrolysis of 2,6-dimethylphenylimine **10d** is due to the sterical hindrance. 2-Thienyl Grignard reagent also reacted with **4** to give imine **10h**, which was converted to 2-*N*-methy-

laminothiophene **15h** in 68% yield, but was not hydrolyzed at all and **10h** was recovered (run 7).

As compared with aryl Grignard reagents, alkyl Grignard reagents reacted with **4** at lower temperature, −78 °C, within 15 min, giving *N*-alkylimines **10** in high yields, regardless of the primary, secondary, or tertiary alkyl Grignard reagents except *tert*-butylmagnesium bromide (run 9–12). Hydrolysis under alkali conditions and the reduction with LAH of primary and secondary-alkylimines **10** proceeded in high yields (run 9, 10), whereas the yield of adamantylamine was moderate (run 11).

In conclusion, various primary amines and *N*-methyl secondary amines are prepared by the reaction of 2-imidazolidinone *O*-tosyloxime with aryl and alkyl Grignard reagents and the successive hydrolysis and $LiAlH_4$ reduction, respectively.

Experimental

General. ^{1}H NMR (500 and 270 MHz) spectra were recorded on Bruker DRX 500, Bruker AVANCE 500, and JEOL AL 270 spectrometers in $CDCl_3$ [using tetramethylsilane (for ^{1}H, $\delta = 0$) as internal standard] or DMSO-d_6 [using DMSO (for ^{1}H, $\delta = 2.49$) as internal standard]. ^{13}C NMR (125 and 67.5 MHz) spectra were recorded on Bruker DRX 500, Bruker AVANCE 500, and JEOL AL 270 spectrometers in $CDCl_3$ [using $CHCl_3$ (for ^{13}C, $\delta = 77.00$) as internal standard] or DMSO-d_6 [using DMSO (for ^{13}C, $\delta = 39.70$) as internal standard]. IR spectra were recorded on a Horiba FT 300-S by ATR method. High-resolution mass spectra were obtained with a JEOL MS-700P mass spectrometer. The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, the University of Tokyo. Flash column chromatography was performed on silica gel [Kanto Chemical Co., Inc. Silica gel 60N (spherical, neutral)] and preparative thin-layer chromatography was carried out using Wakogel B-5F. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purchased from Kanto Chemical Co., Inc and used without purification. Toluene was distilled, and water was azeotropically removed. Dichloromethane was distilled twice from P_2O_5 then from CaH_2, and stored over molecular sieves 4A. Triethylamine was distilled from CaH_2 and stored over KOH. 2-Chloro-1,3-dimethyl-1-imidazolinium chloride was purchased from Nacalai Tesque, Inc., Japan. *t*-Butylmagnesium chloride was purchased from Aldrich Chemical Co., Inc., and was titrated by the literature procedure.[19] Phenylmagnesium bromide, 1-naphthylmagnesium bromide, 2-methylphenylmagnesium bromide, 2,6-dimethylphenylmagnesium bromide, 2-methoxyphenylmagnesium bromide, 2,4-dimethoxyphenylmagnesium bromide, 4-trifluoromethylphenylmagnesium bromide, 2-thienylmagnesium bromide, phenethylmagnesium bromide, 1-methyl-3-phenylpropylmagnesium bromide, and 1-adamantylmagnesium bromide[20] were prepared according to the references and titrated by the literature procedure.[19]

1,3-Dimethyl-2-imidazolidinone *O*-Tetrahydropyranyloxime: To a solution of *O*-tetrahydropyranylhydroxylamine[15] (10.2 g, 87.2 mmol) and triethylamine (35.0 mL, 251 mmol) in acetonitrile (75 mL) was slowly added 2-chloro-1,3-dimethyl-1-imidazolinium chloride (14.1 g, 83.1 mmol) in acetonitrile (75 mL) at −20 °C under an argon atmosphere, and this mixture was stirred at room temperature for 30 min. After the reaction was quenched with water, the mixture was extracted three times with dichloromethane. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The dichloromethane was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel; hexane/acetone = 7/3) to give 1,3-dimethyl-2-imidazolidinone *O*-tetrahydropyranyloxime (15.5 g, 88%). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52–1.68 (4H, m), 1.75–1.81 (2H, m), 2.65 (3H, s), 3.16 (3H, s), 3.05–3.22 (4H, m), 3.58–3.63 (1H, m), 3.92–3.97 (1H, m), 4.93–4.95 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.3, 25.4, 29.3, 34.8, 38.1, 49.5, 51.2, 62.8, 100.8, 158.2.

1,3-Dimethyl-2-imidazolidinone Oxime: To a solution of 1,3-dimethyl-2-imidazolidinone *O*-tetrahydropyranyloxime (15.5 g, 72.7 mmol) in methanol (50 mL) was added 1.0 M HCl (75 mL, 75 mmol), and this mixture was stirred at 80 °C for 30 min. After the reaction was quenched with 1.0 M NaOH (100 mL, 100 mmol) at 0 °C, the mixture was extracted five times with dichloromethane and washed with brine. The extracts were dried over anhydrous sodium sulfate, and the dichloromethane was removed in vacuo to give 1,3-dimethyl-2-imidazolidinone oxime (7.7 g, 82%). White powder; mp 121–122 °C; IR (ZnSe) 3249, 3176, 2940, 2867, 1664, 1497, 1438, 1390, 1288, 1039, 971, 927, 761, 688 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.60 (3H, s), 3.13–3.17 (4H, m), 3.18 (3H, s), 7.79 (1H, br); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.5, 37.6, 49.5, 51.1, 157.5; Anal. Found: C, 46.42; H, 8.58; N, 32.50%. Calcd for $C_5H_{11}N_3O$: C, 46.50; H, 8.58; N, 32.53%.

1,3-Dimethyl-2-imidazolidinone *O*-*p*-Tosyloxime (4): To an ice cold solution of 1,3-dimethyl-2-imidazolidinone oxime (2.02 g, 15.7 mmol) and triethylamine (7.0 mL, 50.2 mmol) in dichloromethane (20 mL) was slowly added *p*-toluenesulfonyl chloride (3.06 g, 16.1 mmol), and this mixture was stirred at the same temperature for 10 min. After the reaction was quenched with water, the mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel; hexane/acetone = 7/3) to give 1,3-dimethyl-2-imidazolidinone *O*-tosyloxime (4.21 g, 95%). White powder; mp 70–75 °C (dec.); IR (ZnSe) 2950, 2857, 1596, 1494, 1353, 1292, 1172, 1095, 1037, 875, 825, 757, 665 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (3H, s), 2.57 (3H, s), 3.13 (3H, s), 3.16 (2H, t, J = 7.7 Hz), 3.24 (2H, t, J = 7.7 Hz), 7.31 (2H, d, J = 8.2 Hz), 7.87 (2H, d, J = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 33.6, 37.2, 48.7, 51.0, 128.8, 129.1, 132.6, 144.1, 161.6; Anal. Found: C, 50.86; H, 5.95; N, 14.87%. Calcd for $C_{12}H_{17}N_3O_3S$: C, 50.87; H, 6.05; N, 14.83%.

Typical Procedure for the Preparation of Imine by the Reaction of 2-Imidazolidinone Oxime 4 with Grignard Reagents (Table 1, Run 1): To a solution of 1,3-dimethyl-2-imidazolidinone *O*-tosyloxime (**4**, 843 mg, 2.98 mmol) in toluene (20 mL) was added dropwise an ether solution of phenylmagnesium bromide (1.00 M, 3.0 mL) at 0 °C under an argon atmosphere, and this mixture was stirred at the same temperature for 15 min. After the reaction was quenched with pH 9 buffer at 0 °C, the mixture was extracted three times with ethyl acetate, and the combined extracts were washed with brine. The solution was dried over anhydrous sodium sulfate, and the ethyl acetate was removed in vacuo. To the crude imine was added aqueous 1.0 M HCl (5 mL, 5 mmol), and the mixture was washed with ether. To the aqueous layer was added 1.0 M NaOH (8 mL, 8 mmol), and the mixture was extracted twice with dichloromethane. The combined extracts were washed with brine and dried over anhydrous sodium

sulfate; then the dichloromethane was removed in vacuo to give 1,3-dimethyl-2-(phenylimino)imidazolidine (**10a**, 553 mg, 98%).

Spectral Data. 1,3-Dimethyl-2-(phenylimino)imidazolidine (10a): Pale yellow oil; IR (ZnSe) 2937, 2850, 1629, 1581, 1479, 1390, 1270, 1226, 1031, 966, 775, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.64 (6H, s), 3.28 (4H, s), 6.84 (1H, t, $J = 7.4$ Hz), 6.87 (2H, d, $J = 7.4$ Hz), 7.17 (2H, t, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.4, 48.6, 120.1, 122.5, 128.5, 150.0 155.8; Anal. Found: C, 69.82; H, 8.10; N, 22.06%. Calcd for $C_{11}H_{15}N_3$: C, 69.81; H, 7.99; N, 22.20%.

1,3-Dimethyl-2-(2-methoxyphenylimino)imidazolidine (10b): Pale yellow oil; IR (ZnSe) 2937, 2834, 1635, 1583, 1484, 1436, 1390, 1276, 1234, 1110, 1024, 966, 740, 694, 646 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.64 (6H, s), 3.27 (4H, s), 3.82 (3H, s), 6.78–6.85 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.9, 48.5, 55.6, 110.9, 120.6, 120.8, 123.3, 139.4, 151.8, 155.8; FABHRMS Found: m/z 220.1448. Calcd for $C_{12}H_{18}ON_3$: $(M + H)^+$, 220.1450.

1,3-Dimethyl-2-(2-methylphenylimino)imidazolidine (10c): Pale yellow oil; IR (ZnSe) 2937, 2844, 2362, 1635, 1590, 1479, 1436, 1388, 1276, 1228, 1027, 966, 769, 728, 647 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.15 (3H, s), 2.59 (6H, s), 3.25 (4H, s), 6.77–6.82 (2H, m), 7.02 (1H, t, $J = 7.5$ Hz), 7.06 (1H, d, $J = 7.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.5, 35.0, 48.6, 120.5, 122.4, 125.9, 129.6, 129.7, 148.6, 154.2; Anal. Found: C, 70.99; H, 8.44; N, 20.55%. Calcd for $C_{12}H_{17}N_3$: C, 70.90; H, 8.43; N, 20.67%.

1,3-Dimethyl-2-(2,6-dimethylphenylimino)imidazolidine (10d): Pale yellow crystals; mp 65–66 °C; IR (ZnSe) 2935, 2844, 1652, 1587, 1482, 1434, 1386, 1274, 1238, 1029, 966, 757, 713, 622 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.13 (6H, s), 2.56 (6H, s), 3.22 (4H, s), 6.73 (1H, t, $J = 7.4$ Hz), 6.93 (1H, d, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.9, 34.4, 48.6, 120.4, 127.2, 129.3, 147.2, 152.8; Anal. Found: C, 71.76; H, 8.69; N, 19.17%. Calcd for $C_{13}H_{19}N_3$: C, 71.85; H, 8.81; N, 19.34%.

1,3-Dimethyl-2-(2,4-dimethoxyphenylimino)imidazolidine (10e): Pale yellow oil; IR (ZnSe) 2937, 2832, 1633, 1498, 1488, 1434, 1390, 1274, 1199, 1151, 1122, 1025, 966, 829, 713, 636 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.63 (6H, s), 3.24 (4H, s), 3.77 (3H, s), 3.80 (3H, s), 6.37 (1H, dd, $J = 8.5$, 2.7 Hz), 6.43 (1H, d, $J = 2.7$ Hz), 6.73 (1H, d, $J = 8.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.9, 48.6, 55.4, 55.6, 110.9, 120.6, 120.8, 123.3, 139.4, 151.8, 155.8; FABHRMS Found: m/z 250.1556. Calcd for $C_{13}H_{20}N_3O_2$: $(M + H)^+$, 250.1556.

1,3-Dimethyl-2-(4-trifluoromethylphenylimino)imidazolidine (10f): Pale yellow oil; IR (ZnSe) 2940, 2861, 1639, 1585, 1317, 1278, 1153, 1097, 1058, 1029, 968, 840, 728, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.66 (6H, s), 3.33 (4H, s), 6.90 (2H, d, $J = 8.4$ Hz), 7.40 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.3, 48.5, 121.4 (q, $J = 32$ Hz), 122.0, 125.0 (q, $J = 269$ Hz), 125.7 (q, $J = 4$ Hz), 153.8, 156.6; Anal. Found: C, 56.25; H, 5.64; N, 16.27%. Calcd for $C_{12}H_{14}F_3N_3$: C, 56.03; H, 5.49; N, 16.33%.

1,3-Dimethyl-2-(1-naphthylimino)imidazolidine (10g): Pale yellow oil; IR (ZnSe) 3046, 2937, 2844, 1623, 1567, 1482, 1386, 1276, 1226, 1139, 1072, 1024, 962, 773, 696, 653 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.59 (6H, s), 3.31 (4H, s), 6.90 (1H, d, $J =$ 7.4 Hz), 7.31 (1H, dd, $J = 7.4$, 7.4 Hz), 7.37–7.43 (3H, m), 7.76 (1H, d, $J = 7.4$ Hz), 8.09 (1H, d, $J = 7.4$ Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.0, 48.6, 116.6, 120.2, 124.4, 124.6, 125.5, 126.0, 127.6, 129.0, 134.3, 146.8, 155.1; FABHRMS Found: m/z 240.1467. Calcd for $C_{15}H_{18}N_3$: $(M + H)^+$, 240.1501.

1,3-Dimethyl-2-(2-thienylimino)imidazolidine (10h): Pale purple oil; IR (ZnSe) 3396, 3062, 2937, 2854, 1635, 1496, 1440, 1276, 1139, 1025, 966, 844, 806, 786, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.74 (6H, s), 3.30 (4H, s), 6.21 (1H, dd, $J = 3.3$, 0.8 Hz), 6.63 (1H, dd, $J = 5.0$, 0.8 Hz), 6.72 (1H, dd, $J = 5.0$, 3.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.0, 48.4, 112.9, 114.7, 125.5, 154.9, 157.0; Anal. Found: C, 55.46; H, 6.83; N, 21.38%. Calcd for $C_9H_{13}N_3S$: C, 55.35; H, 6.71; N, 21.52%.

1,3-Dimethyl-2-(phenethylimino)imidazolidine (10i): Pale yellow oil; IR (ZnSe) 2931, 2834, 1652, 1481, 1436, 1382, 1353, 1263, 1022, 956, 748, 723, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.79 (6H, br), 2.86 (2H, t, $J = 7.9$ Hz), 3.14 (4H, s), 3.60 (2H, t, $J = 7.9$ Hz), 7.16–7.20 (1H, m), 7.25–7.29 (4H, m); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C) δ 35.5 (br), 39.4, 48.3, 48.6 (br), 125.1, 127.5, 128.5, 141.1, 155.4; Anal. Found: C, 71.63; H, 8.79; N, 19.16%. Calcd for $C_{13}H_{19}N_3$: C, 71.85; H, 8.81; N, 19.34%.

1,3-Dimethyl-2-(1-methyl-3-phenylpropylimino)imidazolidine (10j): Pale yellow oil; IR (ZnSe) 2923, 2844, 1652, 1479, 1452, 1378, 1259, 1197, 1035, 746, 698, 636 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.18 (3H, d, $J = 6.2$ Hz), 1.65–1.68 (2H, m), 2.55 (1H, ddd, $J = 14.5$, 9.3, 6.6 Hz), 2.68 (1H, ddd, $J = 14.5$, 9.3, 6.6 Hz), 2.77 (6H, br), 3.20–3.26 (2H, m), 3.02–3.08 (2H m), 3.66 (1H, ddq, $J = 6.2$, 6.2, 6.2 Hz), 7.15 (1H, t, $J = 7.3$ Hz), 7.19 (2H, d, $J = 6.9$ Hz), 7.25 (2H, dd, $J = 7.3$, 6.9 Hz); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C) δ 23.6, 32.1, 35.7 (br), 41.8, 48.2, 48.6 (br), 124.9, 127.7, 127.9, 142.7; FABHRMS Found: m/z 246.1990. Calcd for $C_{15}H_{24}N_3$: $(M+H)^+$, 246.1970.

1,3-Dimethyl-2-(1-adamantylimino)imidazolidine (10k): ^1H NMR (500 MHz, $CDCl_3$) δ 1.67 (6H, s), 2.03 (6H, s), 2.14 (3H, s), 3.22 (6H, s), 3.75 (4H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.7, 35.6, 37.5, 43.5, 48.5, 58.4, 161.8.

Typical Procedure for the Preparation of Amine Hydrochloride by the Reaction of Imidazolidinone Oxime 4 with Grignard Reagents (Table 2, Run 1): To a solution of 1,3-dimethyl-2-imidazolidinone *O*-tosyloxime (**4**, 283 mg, 1.00 mmol) in toluene (8 mL) was added dropwise an ether solution of phenylmagnesium bromide (1.00 M, 1.0 mL) at 0 °C under an argon atmosphere, and this mixture was stirred at the same temperature for 15 min. After the reaction was quenched with pH 9 buffer at 0 °C, the mixture was extracted three times with ethyl acetate, and the combined extracts were washed with brine. The solution was dried over anhydrous sodium sulfate, and the ethyl acetate was removed in vacuo. The crude imine was dissolved in ethylene glycol (3 mL); then cesium hydroxide monohydrate (1.52 g, 9.05 mmol) was added to the solution. After the suspension was stirred at 150 °C for 1 h under an argon atmosphere, the mixture was cooled to 0 °C. After 4.0 M HCl (3 mL, 12.0 mmol) was added to the solution, the mixture was extracted with ether. To the aqueous phase was added 2.0 M NaOH (2 mL, 4.0 mmol) and the mixture was extracted twice with dichloromethane. The combined extracts were washed with brine and dried over anhydrous magnesium sulfate. After the dichloromethane was removed in vacuo, the resulting crude materials were dissolved in ether (3 mL). To the solution was added 2.0 M HCl in ether (1.0 mL, 2.0 mmol) to form a white precipitate, which was collected by filtration to give aniline hydrochloride (**14a**, 123 mg, 95%).

Spectral Data. *o*-Toluidine and Naphthylamine are known compounds, and their spectral data are in good agreement with those of authentic samples.[21]

Aniline Hydrochloride (14a):[21] White powder; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.36–7.39 (3H, m), 7.47 (2H, t, $J = 7.5$ Hz), 10.37 (3H, br); ^{13}C NMR (125 MHz, DMSO-d_6) δ 123.3, 128.0, 129.9, 132.5; Anal. Found: C, 55.67; H, 6.38; N, 10.76%. Calcd for C_6H_8ClN: C, 55.61; H, 6.22; N, 10.81%.

2-Methoxyaniline Hydrochloride (14b): White powder; mp 228–230 °C (dec.); IR (ZnSe) 2794, 2618, 2360, 1629, 1496, 1324, 1294, 1263, 1025, 643 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.82 (3H, s), 6.99 (1H, dd, $J = 7.6$, 7.5 Hz), 7.16 (1H, d, $J = 8.2$ Hz), 7.34 (1H, dd, $J = 8.2$, 7.6 Hz), 7.53 (1H, d, $J = 7.5$ Hz), 10.35 (3H, br); ^{13}C NMR (125 MHz, DMSO-d_6) δ 56.4, 112.8, 120.7, 121.0, 124.5, 129.7, 152.7; Anal. Found: C, 52.87; H, 6.35; N, 8.54%. Calcd for $C_7H_{10}ClNO$: C, 52.67; H, 6.31; N, 8.78%.

2,4-Dimethoxyaniline Hydrochloride (14e):[21] White powder; ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.77 (3H, s), 3.86 (3H, s), 6.58 (1H, dd, $J = 8.6$, 2.4 Hz), 6.74 (1H, d, $J = 2.4$ Hz), 7.38 (1H, d, $J = 8.6$ Hz), 9.98 (3H, br); ^{13}C NMR (125 MHz, DMSO-d_6) δ 56.0, 56.6, 100.0, 105.4, 113.4, 125.0, 153.8, 160.5; Anal. Found: C, 50.48; H, 6.39; N, 7.26%. Calcd for $C_8H_{12}ClNO_2$: C, 50.67; H, 6.38; N, 7.39%.

Phenethylammonium Chloride (14i):[21] White powder; ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.89 (2H, t, $J = 7.8$ Hz), 2.99 (2H, br), 7.22–7.26 (3H, m), 7.32 (2H, t, $J = 7.4$ Hz), 8.20 (3H, br); ^{13}C NMR (125 MHz, DMSO-d_6) δ 33.1, 40.1, 126.9, 128.81, 128.84, 137.7; Anal. Found: C, 61.18; H, 7.72; N, 8.70%. Calcd for $C_8H_{12}ClN$: C, 60.95; H, 7.67; N, 8.89%.

1-Methyl-3-phenylpropylammonium Chloride (14j): White powder; mp 139–141 °C (dec.); IR (ZnSe) 2879, 2373, 2318, 1716, 1540, 1508, 765, 744, 700 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.22 (3H, d, $J = 6.5$ Hz), 1.67–1.75 (1H, m), 1.85–1.93 (1H, m), 2.58–2.69 (2H, m), 3.08–3.12 (1H, m), 7.17–7.21 (3H, m), 7.29 (2H, t, $J = 7.5$ Hz), 8.05 (3H, br); ^{13}C NMR (125 MHz, DMSO-d_6) δ 18.2, 31.0, 36.1, 46.6, 126.2, 128.4, 128.7, 141.2; Anal. Found: C, 64.76; H, 8.74; N, 7.35%. Calcd for $C_{10}H_{16}ClN$: C, 64.68; H, 8.68; N, 7.54%.

1-Adamantylammonium Chloride (14k):[10b] White powder; ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.57 (3H, d, $J = 12.1$ Hz), 1.66 (3H, d, $J = 12.1$ Hz), 1.81 (6H, s), 2.08 (3H, s), 8.09 (3H, br); ^{13}C NMR (125 MHz, DMSO-d_6) δ 28.5, 35.3, 40.2, 51.2; Anal. Found: C, 63.77; H, 9.46; N, 7.17%. Calcd for $C_{10}H_{18}ClN$: C, 63.99; H, 9.67; N, 7.46%.

Typical Procedure for the Preparation of *N*-Methylamine (Table 3, Run 2): To a solution of 1,3-dimethyl-2-imidazolidinone *O*-tosyloxime (**4**, 283 mg, 1.00 mmol) in toluene (8 mL) was added dropwise an ether solution of 2-methoxyphenylmagnesium bromide (1.22 M, 0.82 mmol) at 0 °C under an argon atmosphere, and this mixture was stirred at the same temperature for 15 min. After the reaction was quenched with pH 9 buffer at 0 °C, the mixture was extracted three times with ethyl acetate, and the combined extracts were washed with brine. The solution was dried over anhydrous sodium sulfate, and the ethyl acetate was removed in vacuo. The crude imine was dissolved in ether (3 mL); then lithium aluminum hydride in tetrahydrofuran (1.0 M, 1.0 mL) was added to the solution at 0 °C. After the resulting solution was stirred at room temperature for 12 h, the mixture was quenched with 1.0 M HCl (5 mL, 5.0 mmol) at 0 °C. After the mixture was washed with ether, to the resulting aqueous layer was added 2 M NaOH (3 mL, 6.0 mmol). The mixture was extracted twice with ether and washed with brine. The ether solution was dried over anhydrous magnesium sulfate, and ether was removed in vacuo. The crude materials were purified by flash column chromatography (silica gel, hexane/ethyl acetate = 9/1) to give 2-methoxy-*N*-methylaniline (**15b**, 111 mg, 81%).

Spectral Data. *N*-Methylaniline (15a):[21] Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.83 (3H, s), 3.68 (1H, br), 6.61 (2H, dd, $J = 8.5$, 0.8 Hz), 6.71 (1H, tt, $J = 7.3$, 0.8 Hz), 7.19 (2H, dd, $J = 8.5$, 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.7, 112.4, 117.2, 129.2, 149.3.

2-Methoxy-*N*-methylaniline (15b): Pale yellow oil; IR (ZnSe) 3432, 2892, 2813, 1606, 1585, 1513, 1471, 1301, 1263, 1166, 1043, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.86 (3H, s), 3.84 (3H, s), 4.23 (1H, br), 6.60 (1H, dd, $J = 7.7$, 1.0 Hz), 6.67 (1H, ddd, $J = 7.7$, 7.7, 1.0 Hz), 6.76 (1H, dd, $J = 7.7$, 1.0 Hz), 6.89 (1H, ddd, $J = 7.7$, 7.7, 1.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.3, 55.3, 109.2, 109.3, 116.2, 121.3, 139.3, 146.8; Anal. Found: C, 70.13; H, 8.08; N, 10.07%. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21%.

2-Methyl-*N*-methylaniline (15c): Pale yellow oil; IR (ZnSe) 3432, 2910, 2813, 1606, 1585, 1513, 1471, 1446, 1427, 1301, 1263, 1166, 1043, 742, 715 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (3H, s), 2.89 (3H, s), 3.55 (1H, br), 6.61 (1H, d, $J = 8.0$ Hz), 6.66 (1H, dd, $J = 7.6$, 7.4 Hz), 7.05 (1H, d, $J = 7.4$ Hz), 7.06 (1H, dd, $J = 8.0$, 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.4, 30.7, 109.1, 116.8, 121.9, 127.2, 129.9, 147.2; Anal. Found: C, 79.02; H, 9.15; N, 11.41%. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56%.

2,4-Dimethoxy-*N*-methylaniline (15e): Pale purple oil; IR (ZnSe) 3415, 2937, 2930, 1594, 1511, 1452, 1284, 1228, 1201, 1029, 917, 829, 788, 617 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.83 (3H, s), 3.76 (3H, s), 3.82 (3H, s), 3.88 (1H, br), 6.44 (1H, dd, $J = 8.3$, 2.7 Hz), 6.45 (1H, d, $J = 2.7$ Hz), 6.51 (1H, d, $J = 8.3$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 55.4, 55.8, 99.0, 103.6, 109.5, 133.8, 148.0, 151.8; Anal. Found: C, 64.61; H, 7.89; N, 8.15%. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38%.

***N*-Methyl-1-naphthylamine (15g):**[22] Pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.99 (3H, s), 4.40 (1H, br), 6.59 (1H, d, $J = 7.0$ Hz), 7.23 (1H, d, $J = 8.2$ Hz), 7.36 (1H, d, $J = 8.2$ Hz), 7.37–7.46 (2H, m), 7.73–7.80 (2H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 31.0, 103.7, 117.2, 119.7, 123.3, 124.6, 125.7, 126.6, 128.6, 134.2, 144.5.

2-Methylaminothiophene (15h):[23] Purple oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.87 (3H, s), 6.00 (1H, dd, $J = 3.6$, 1.3 Hz), 6.45 (1H, dd, $J = 5.4$, 1.3 Hz), 6.73 (1H, dd, $J = 5.4$, 3.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.3, 103.1, 110.2, 126.3, 156.4.

***N*-Methylphenethylamine (15i):**[21] Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 (3H, s), 2.78–2.89 (4H, m), 7.20–7.33 (5H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 36.1, 36.3, 53.1, 126.1, 128.5, 128.7, 140.0.

***N*-Methyl-(1-methyl-3-phenylpropyl)amine (15j):** Colorless oil; IR (ZnSe) 3303, 2964, 2933, 2856, 1658, 1494, 1454, 1376, 1155, 1078, 1029, 786, 746, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (3H, d, $J = 6.2$ Hz), 1.61 (1H, dddd, $J = 6.6$, 6.6, 10.1, 13.4 Hz), 1.78 (1H, dddd, $J = 5.9$, 5.9, 9.9, 13.4 Hz), 2.41 (3H, s), 2.57 (1H, ddq, $J = 5.9$, 6.6, 6.2 Hz), 2.60–2.69 (2H, m), 7.16–7.20 (3H, m), 7.28 (2H, t, $J = 7.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.8, 32.3, 33.8, 38.5, 54.4, 125.7, 128.29, 128.32, 142.4; FABHRMS Found: m/z 164.1461. Calcd for $C_{11}H_{18}N$: $(M + H)^+$, 164.1439.

1-(*N*-Methylamino)adamantane (15k):[24] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66–1.70 (12H, m), 2.09 (3H, brs), 2.36 (3H, s), 2.55 (1H, br).

2-Benzyloxyiminomalononitrile: To a solution of malononi-

trile (906 mg, 13.7 mmol) in acetic acid (2 mL) and water (5mL) was slowly added sodium nitrite (1.42 g, 20.6 mmol) at 0 °C, and this mixture was stirred at the same temperature for 30 min. After quenching the reaction with 2 M HCl (10 mL), the mixture was extracted three times with ether. The extracts were dried over anhydrous sodium sulfate, and the ether was removed in vacuo. To a solution of the crude materials and benzyl bromide (1.8 mL, 15 mmol) in dichloromethane (10 mL) was slowly added triethylamine (5.7 mL, 41 mmol) at 0 °C. This mixture was stirred at the same temperature for 15 min, and the reaction was quenched with water. The mixture was extracted three times with ethyl acetate, and the combined extracts were washed with brine and dried over anhydrous sodium sulfate. Volatile materials were removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel; hexane/ethyl acetate = 95/5) to give 2-benzyloxyiminomalononitrile (1.66 g, 65%). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (2H, s), 7.35–7.40 (2H, m), 7.41–7.44 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.4, 105.6, 108.5, 109.0, 129.0, 129.3, 129.8, 133.2.

1,3-Dioxolan-2-one *O*-Tosyloxime (5):[13] Color needles; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (3H, s), 4.52–4.54 (2H, m), 4.58–4.60 (2H, m), 7.33 (2H, d, $J = 8.1$ Hz), 7.85 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.9, 66.1, 66.9, 122.8, 123.4, 125.6, 137.6, 156.1.

2-(Phenylimino)-1,3-dioxolane (11): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.49 (4H, brs), 7.06 (1H, t, $J = 7.4$ Hz), 7.09 (2H, d, $J = 8.2$ Hz), 7.28 (2H, dd, $J = 7.4$, 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.8, 66.6, 123.0, 123.4, 128.6, 145.3, 153.5.

3-Methyl-2-oxazolidinone *O*-Benzyloxime: To an ice cold solution of sodium hydride (485 mg, 20.2 mmol) in tetrahydrofuran (10 mL) was slowly added 2-(methylamino)ethanol (1.44 g, 19.2 mmol) in tetrahydrofuran (10 mL) and this mixture was stirred at 0 °C for 20 min. To the solution was added *O*-benzylhydroxyiminomalononitrile at −78 °C, and the mixture was stirred at 60 °C for 5 h. The reaction was quenched with water at 0 °C, and the mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. Volatile materials were removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel; hexane/acetone = 7/3) to give 3-methyl-2-oxazolidinone *O*-benzyloxime (372 mg, 22%). Pale yellow oil; IR (ZnSe) 2910, 2852, 1654, 1494, 1452, 1402, 1363, 1282, 1045, 825, 736, 696, 592 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.74 (3H, s), 3.37 (2H, t, $J = 7.1$ Hz), 4.33 (2H, t, $J = 7.1$ Hz), 7.27 (1H, tt, $J = 7.2$, 1.4 Hz), 7.33 (2H, dd, $J = 7.2$, 7.1 Hz), 7.41 (2H, dd, $J = 7.1$, 1.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.7, 49.7, 66.1, 127.5, 127.8, 128.1, 128.5, 138.0, 157.8; FABHRMS Found: m/z 207.1149. Calcd for $C_{11}H_{15}N_2O_2$: $(M + H)^+$, 207.1134.

N*-Methyl-2-oxazolidinone *O*-Tosyloxime (6):** In the presence of palladium hydroxide (119 mg, 20 wt% Pd on carbon), a suspension of 3-methyl-2-oxazolidinone *O*-benzyloxime (372.7 mg, 1.81 mmol) in ethanol (5 mL) was stirred at room temperature under hydrogen atmosphere for 5 h. After purging with argon, the mixture was filtered through a celite pad, and the solvent was removed in vacuo. To a solution of the crude materials and triethylamine (0.75 mL, 5.4 mmol) in dichloromethane (4 mL) was slowly added tosyl chloride (360 mg, 1.89 mmol) at 0 °C. After the mixture was stirred for 30 min, the reaction was quenched with water. The mixture was extracted three times with ethyl acetate, and the combined extracts were washed with brine and dried over anhydrous sodium sulfate. The ethyl acetate was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel; hexane/acetone = 1/1) to give 3-methyl-2-oxazolidinone *O*-tosyloxime. The configuration of (Z***)-**6** was determined by the X-ray analysis (Fig. 1).

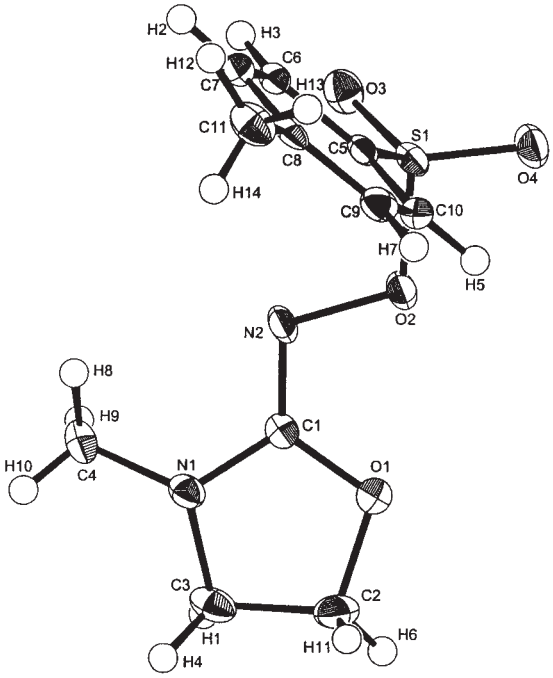


Fig. 1. X-ray analysis of (***Z***)-**6**.

(***Z***)-**6** (278 mg, 57%); Colorless crystal; mp 125–126 °C; IR (ZnSe) 2973, 2358, 1637, 1500, 1351, 1292, 1186, 1172, 1043, 900, 804, 669, 566 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (3H, s), 2.73 (3H, s), 3.48 (2H, ddd, $J = 7.7$, 7.4, 1.1 Hz), 4.36 (2H, ddd, $J = 7.7$, 7.4, 1.1 Hz), 7.31 (2H, d, $J = 8.2$ Hz), 7.86 (2H, d, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 31.9, 49.5, 66.8, 128.9, 129.2, 132.8, 144.3; Anal. Found: C, 49.14; H, 5.33; N, 10.15%. Calcd for $C_{11}H_{14}N_2O_4S$: C, 48.88; H, 5.22; N, 10.36%.

(***E***)-**6** (49.8 mg, 10%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (3H, s), 2.95 (3H, s), 3.63 (2H, dd, $J = 9.3$, 8.3 Hz), 4.52 (2H, dd, $J = 9.3$, 8.3 Hz), 7.25 (2H, d, $J = 8.1$ Hz), 7.85 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 31.8, 47.4, 66.3, 126.9, 129.0, 140.1, 142.2, 158.5.

3-Methyl-2-(phenylimino)oxazolidine (12):[17] To a solution of (*Z*)-3-methyl-2-oxazolidinone *O*-tosyloxime (113 mg, 0.418 mmol) in toluene (5 mL) was added dropwise an ether solution of phenylmagnesium bromide (1.00 M, 0.42 mL) at room temperature under an argon atmosphere, and this mixture was stirred at the same temperature for 30 min. After the reaction was quenched with pH 9 buffer at 0 °C, the mixture was extracted three times with ethyl acetate, and the combined extracts were washed with brine and dried over anhydrous sodium sulfate. After the volatile material was removed in vacuo, the residues were purified by the flash column chromatography (silica gel; hexane/acetone = 7/3) to give *N*-methyl-2-(phenylimino)oxazolidine (71.7 mg, 97%). Pale yellow oil; IR (ZnSe) 2906, 2865, 1660, 1585, 1477, 1400, 1265, 1213, 1024, 962, 748, 709 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.98 (3H, s), 3.50 (2H, t, $J = 7.6$ Hz), 4.30 (2H, t, $J = 7.6$ Hz), 6.96 (1H, t, $J = 8.1$ Hz), 7.04 (2H, d, $J = 7.7$ Hz), 7.24 (2H, dd, $J = 8.1$, 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.4, 48.3, 64.2, 122.0, 123.4, 128.5, 147.9,

153.8; FABHRMS Found: m/z 177.1011. Calcd for $C_{10}H_{13}N_2O$: $(M + H)^+$, 177.1028.

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