

Palladium(0)-catalyzed synthesis of pyridines from β -acetoxy- γ,δ -unsaturated ketone oximes

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Dedicated to Professor Jim Coxon on his 65th birthday

Abstract

Pyridines are synthesized from β -acetoxy- γ,δ -unsaturated ketone *O*-acetyloximes by treatment with triethylamine and a catalytic amount of Pd(PPh₃)₄ in toluene at 120 °C.

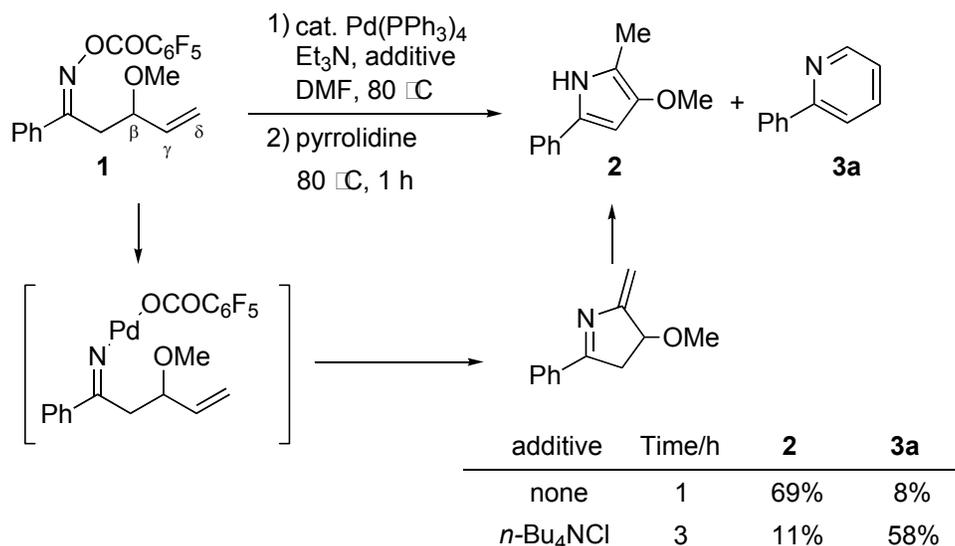
Keywords: Pyridines, palladium complex, intramolecular cyclization, oximes

Introduction

Metal-catalyzed amination reactions are an attractive topic in organic synthesis and various C-N bond formations have been developed by using transition metals. Especially, the amination of alkenes or alkynes¹ and the coupling reaction of aryl halides and amines² have been widely studied, and are now fully applied to the synthesis of aza-heterocycles. Two approaches have been employed in the former amination, such as alkene/alkyne or amine activation routes. Both protocols are achieved using early transition metal³ or f-element complexes⁴ as well as late transition metal catalysts.⁵ Though the coupling of aryl halides and amines has been known to proceed by using copper powder, these reactions required high temperature and the yields were not sufficiently good.⁶ Since Buchwald and Hartwig reported independently that the C-N coupling proceeds with palladium catalysts under mild conditions by employing bulky and electron rich phosphine ligands,⁷ the catalytic processes have been recognized as one of the secure amination reactions. In addition, the merit of Cu reagents was rediscovered recently as efficient catalysts of the coupling reaction.⁸

We have found that oxidative addition of oximes to Pd(0) complexes occurred to give alkylideneaminopalladium (II) species, which could react with internal olefinic moiety. Various γ,δ -unsaturated ketone *O*-pentafluorobenzoyl oximes cyclized in a 5-*exo* fashion to afford pyrroles by treatment with a Pd(0) complex (amino-Heck reaction).⁹ Recently, we have found that

the 6-*endo* cyclization product, pyridine, could be obtained as shown in scheme 1.



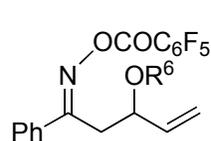
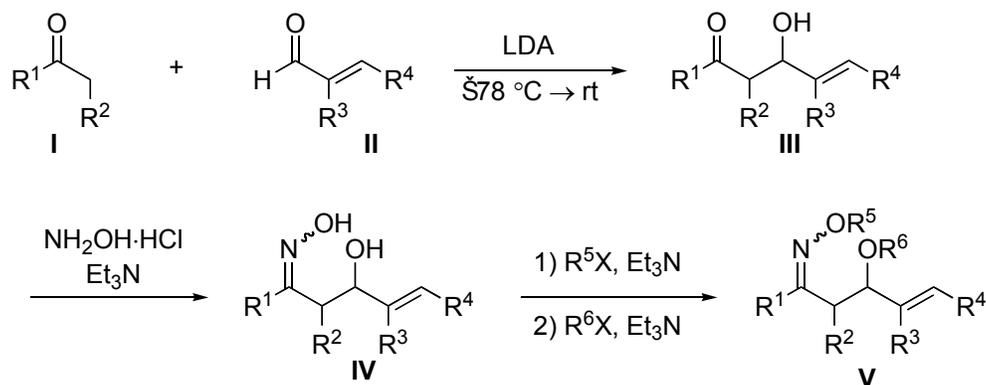
Scheme 1

That is, when a methoxy group was introduced at the β position of γ,δ -unsaturated ketone oxime **1**, a small amount of pyridine **3a** was obtained along with pyrrole **2** by the Pd-catalyzed amino-Heck reaction. In the presence of tetrabutylammonium chloride, the reaction became slower, and pyridine **3** was dominant instead of pyrrole **2**.¹⁰ The formation of pyridine via a 6-*endo* type cyclization was clearly due to the introduction of a methoxy group at the β -position, because the corresponding oxime lacking a β -methoxy substituent gave pyrrole exclusively under either reaction conditions. Generally, in the intramolecular Mizoroki-Heck reactions, 5-*exo* cyclization proceeded preferentially and the 6-*endo* cyclization products are rarely obtained.¹¹ Therefore, we became interested in the 6-*endo* mode cyclization of oximes, and examined the cyclization of several kinds of β -alkoxy or β -acyloxy oxime derivatives. Finally, β -acetoxy- γ,δ -unsaturated *O*-acetyl oximes were found to be converted to pyridines successfully.

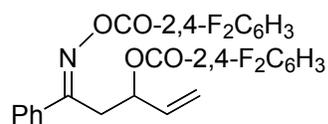
Results and Discussion

The starting materials, β -substituted- γ,δ -unsaturated oxime derivatives **V**, were prepared as outlined in scheme 2.¹² The aldol reaction of ketones **I** and alkenals **II**¹³ afforded β -hydroxyl ketones **III**, which were converted to oximes **IV**. Between the two kinds of hydroxyl groups in **IV**, the oxime hydroxy group was acylated and alkylated more preferentially, and the β -hydroxy group was then converted to an acyloxy or alkoxy group, affording **V** in good total yield. From aryl ketones ($R^1 = \text{aryl group}$), only *E*-isomers of oximes **IV** were isolated after purification by recrystallization, which were converted to their *O*-substituted *E*-oximes **V**. In the series of alkyl

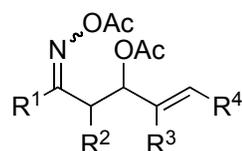
ketone oximes ($R^1 = \text{alkyl group}$), *tert*- and *sec*-alkyl ketone oximes **IV** ($R^1 = \textit{sec}$ - and *tert*-alkyl group) were isolated as *E*-isomers by recrystallization or column chromatography, whereas *prim*-alkyl and styryl ketone oximes **V** ($R^1 = \textit{prim}$ -alkyl and styryl) were isolated as a mixture of both *E* and *Z* isomers.



- 4a** $R^6 = \text{Et}$
4b $R^6 = \text{CH}_3\text{OCH}_2$
4c $R^6 = \text{C}_6\text{H}_5\text{CH}_2$
4d $R^6 = \text{Ac}$
4e $R^6 = \text{C}_6\text{H}_5\text{CO}$
4f $R^6 = 2,4\text{-F}_2\text{C}_6\text{H}_3\text{CO}$
4g $R^6 = \text{C}_6\text{F}_5\text{CO}$



5



- | | R^1 | R^2 | R^3 | R^4 |
|-----------|------------------------------------|-------|-------|-------|
| 6a | Ph | H | H | H |
| 6b | 4-MeOC ₆ H ₄ | H | H | H |
| 6c | 4-ClC ₆ H ₄ | H | H | H |
| 6d | Ph | H | H | Me |
| 6e | Ph | H | H | Ph |
| 6f | Ph | H | Me | H |
| 6g | Ph | Me | H | H |
| 6h | (<i>E</i>)-Ph-CH=CH | H | H | H |
| 6i | cyclo-hexyl | H | H | H |
| 6j | PHCH ₂ CH ₂ | H | H | H |
| 6k | <i>tert</i> -butyl | H | H | H |

Scheme 2

In the cyclization reaction of 2-alkoxy-3-butenyl phenyl ketone *O*-penafluorobenzoyloximes **4a-c**, 6-*endo* cyclization products were preferably formed, while the yield of pyridine **3a** was lower (for **4a**, 46%; for **4b**: 40%; for **4c**: 27%) than that from β -methoxy oxime **1**. Then, we focused on the reaction of β -acyloxy oximes (Table 1). The reaction of β -acetoxy *O*-penafluorobenzoyloximes **4d** proceeded to afford pyridine **3a** in 39% yield in the absence of *n*-Bu₄NCl, and the addition of *n*-Bu₄NCl made this reaction slower and gave pyridine **3a** in lower yield (Run 1). These results revealed that β -substituent having better leaving ability enabled the

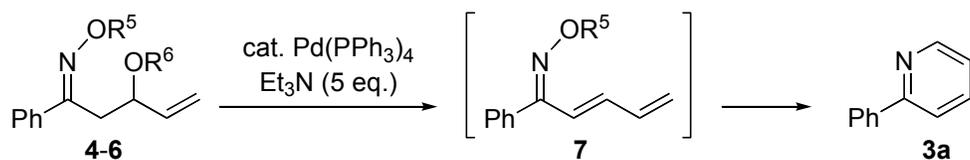
6-*endo* cyclization even in the absence of tetrabutylammonium chloride. In toluene, the yield of pyridine **3a** was increased to 60% (Run 1-4). After several investigations, pyridine was obtained in 70% by the reaction at 120 °C in toluene (Run 5). Various β -acyloxy *O*-penafluorobenzoyloximes **4e-g** gave pyridine **3a** in good yield under these conditions (Runs 6-8), especially β -2,4-difluorobenzoyloxime which was converted to pyridine **3a** in 83% yield (Run 7).

Although β -acyloxy *O*-pentafluorobenzoyl oxime was found to be suitable for pyridine preparation, it was desirable to simplify the preparation of the oxime derivatives by introducing a similar leaving group on either site of the oxime nitrogen (OR⁵) and the β -position (OR⁶). Bis-2,4-difluorobenzoylated oxime **5** was transformed to pyridine **3a** in a disappointing yield (Run 9), while bis-acetyl oxime **6a** cyclized to 2-phenylpyridine **3a** in 78% yield, which was competitive to the yield of *O*-pentafluorobenzoyl oxime **4f** (Run 10).

In all the Pd-catalyzed reactions of β -acyloxy oxime in Table 1, oximes **4-6** were disappeared in the early stage of the reaction and dienone oximes **7** was detected. Then, the resulting dienone oximes **7** disappeared gradually to give pyridine **3a**. These observations strongly suggest dienone oximes **7** as intermediates.

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Table 1. Optimization of the synthesis of pyridines from β -acyloxy- γ,δ -unsaturated ketone oximes



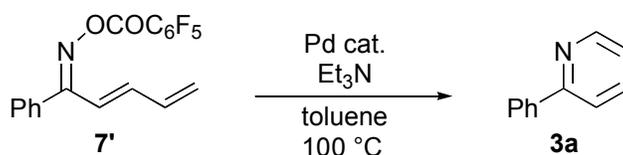
Run	R ⁵	R ⁶		Solvent	$\text{Pd}(\text{PPh}_3)_4$ /mol%	Temp /°C	Time /h ^a	Yield /% ^a
1	C ₆ F ₅ CO	Ac	4d	DMF	10	100	1 (5)	39 (10)
2	C ₆ F ₅ CO	Ac	4d	THF	10	reflux	5	42
3	C ₆ F ₅ CO	Ac	4d	CH ₃ CN	10	reflux	2	5
4	C ₆ F ₅ CO	Ac	4d	Toluene	10	80	2	60
5	C ₆ F ₅ CO	Ac	4d	Toluene	20	120	0.75	70
6	C ₆ F ₅ CO	C ₆ H ₅ CO	4e	Toluene	10	80-110	3.5	44
7	C ₆ F ₅ CO	2,4-F ₂ C ₆ H ₃ CO	4f	Toluene	20	120	0.5	83
8	C ₆ F ₅ CO	C ₆ F ₅ CO	4g	Toluene	20	120	0.5	61
9	2,4-F ₂ C ₆ H ₃ CO	2,4-F ₂ C ₆ H ₃ CO	5	Toluene	20	120	3.5	20
10	Ac	Ac	6a	Toluene	20	120	0.5	78

a) The result with *n*-Bu₄NCl is shown in parenthesis.

Generally, conjugated trienes and azatrienes are relatively unstable and suffer from 6π electronic cyclization under thermal or photo-irradiation conditions.¹⁴ Moreover, dienyl ketone oximes are known to be transformed to pyridines by treatment with an equimolar amount of Pd(II) complexes such as PdCl₂ and PdCl₂(PPh₃)₂.¹⁵

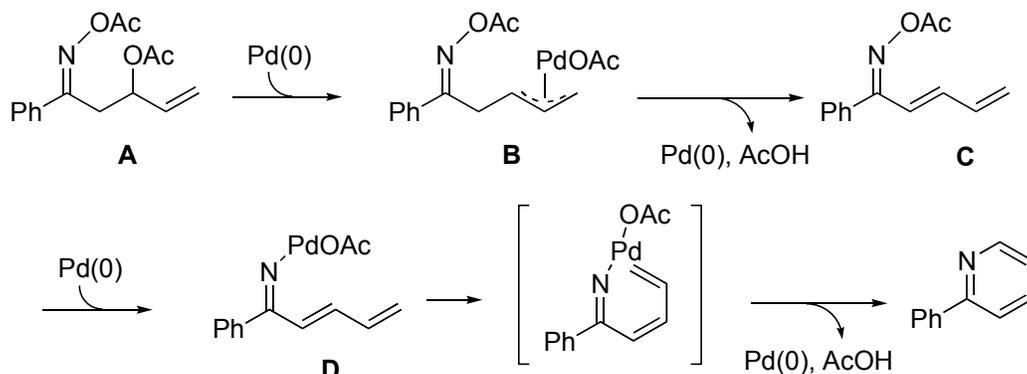
Then, to confirm the hypothesis that dienone oxime **7** is the reaction intermediate of this Pd-catalyzed cyclization of β -acyloxy *O*-acyloximes, dienone *O*-pentafluorobenzoyloxime **7'** was isolated and the cyclization was examined (Table 2). The cyclization of **7'** did not proceed smoothly with PdCl₂ or with heating at 100 °C (run 1 and 2), while the cyclization proceeded to afford pyridine **3a** in 43% yield by treatment with Pd(PPh₃)₄ (run 3). Thus, Pd(PPh₃)₄ clearly catalyzes the cyclization of **7'** to pyridine **3a**.

Table 2. The cyclization of dienyl ketone oxime **7'**



Run	Pd cat.	Time	Yield (3a)	Recovery (7)
1	none	1.5 h	0%	80%
2	10 mol% PdCl ₂	4.5 h	7%	54%
3	10 mol% Pd(PPh ₃) ₄	2 h	43%	0%

A possible reaction pathway is depicted in Scheme 3. First, the allylic ester moiety of oxime **A** reacts with Pd(PPh₃)₄ to give π -allylpalladium complex **B**, which undergoes β -hydrogen elimination to afford dienyl ketone oxime **C** along with the regenerated Pd(0) complex. Then, dienyl ketone *O*-acetyloxime **C** reacts with the Pd(0) complex to form alkylideneaminopalladium **D**, and isomerization¹⁶ of the α,β -carbon-carbon double bond from *trans* to *cis* induces the successive cyclization to pyridine. For the last cyclization step, other processes such as a 6π -electron cyclization, aminopalladation, or any others cannot be excluded.

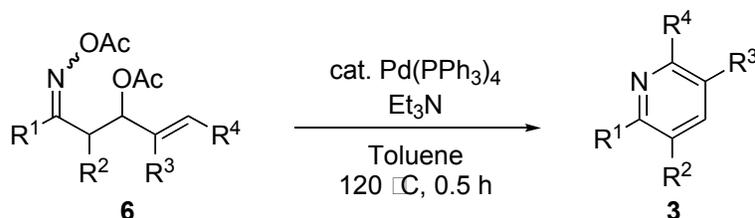


Scheme 3. Proposed reaction pathway.

By this Pd-catalyzed cyclization, various β -acetoxy- γ,δ -unsaturated *O*-acetoxyoximes were transformed to pyridines (Table 3). In the cyclization of aryl ketone oximes (runs 1-6), the nature of *p*-substituents on the aryl group did not influence the reaction and 2-arylpyridines were obtained in good yield (Runs 1 and 2). Introduction of substituents on the olefin moiety exhibited no significant effect on the product yield (Runs 3-5). Only in the cyclization of α -substituted oxime **6g**, the yield was slightly decreased (Run 6). As a complementary example, a conjugated ketone oxime such as styryl ketone **6h** also cyclized to pyridine in 63% yield.

Although *t*-butyl ketone oxime did not give the product, primary and secondary alkyl ketone oximes gave the corresponding pyridines in moderate yield (Runs 8-10). Interestingly, in the reaction of phenethyl ketone oxime **6j**, a dehydrogenated product, 2-cinnamylpyridine **3h** was isolated in 16% yield along with 44% of 2-phenethylpyridine **3j** (Run 9). The dehydrogenation probably occurred by a C-H activation of oxime derivatives **6j**¹⁷ or pyridine **3j**.

Table 3. Synthesis of pyridines from β -acetoxy *O*-acetyl oximes^a



Run	R ¹	R ²	R ³	R ⁴		Yield/%
1	4-MeO-C ₆ H ₄	H	H	H	6b	3b 76
2	4-Cl-C ₆ H ₄	H	H	H	6c	3c 71
3	Ph	H	H	Me	6d	3d 70
4	Ph	H	H	Ph	6e	3e 55
5	Ph	H	Me	H	6f	3f 73
6	Ph	Me	H	H	6g	3g 46
7	(<i>E</i>)-Ph-CH=CH-	H	H	H	6h	3h 63
8	<i>cyclo</i> -hexyl	H	H	H	6i	3i 44
9	PhCH ₂ CH ₂ -	H	H	H	6j	3j 44 ^b
10	<i>tert</i> -Butyl	H	H	H	6k	3k 0

a) Reaction conditions: 20 mol% Pd(PPh₃)₄, 5 eq. Et₃N.

b) 2-styrylpyridine **3h** was obtained in 16% yield.

Experimental Section

General Procedures. ^1H NMR (500, 400, and 270 MHz) spectra were recorded on Bruker DRX 500, Bruker AVANCE 500, JEOL AL 400, and JEOL AL 270 spectrometers in CDCl_3 [using CHCl_3 (δ 7.24) as an internal standard]. ^{13}C NMR (125 and 100 MHz) spectra were recorded on Bruker DRX 500, Bruker AVANCE 500, and JEOL AL 400 in CDCl_3 [using CHCl_3 (δ 77.0) as an internal standard]. IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-700M 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, Silica gel 60N (spherical, neutral) or Fuji Sylicia PSQ-100B]. Preparative thin-layer chromatography was carried out using Wakogel B-5F. *N,N*-Dimethylformamide (DMF) was distilled under reduced pressure from CaH_2 , and stored over molecular sieves 4A under argon atmosphere. Dichloromethane was distilled from P_2O_5 and then from CaH_2 , and was stored over molecular sieves 4A. Tetrahydrofuran was purchased from Kanto Chemical and was used without purification. Toluene was distilled from CaCl_2 , and was stored over molecular sieves 4A. Triethylamine was distilled from NaH and stored over KOH. $\text{Pd}(\text{PPh}_3)_4$ was prepared according to literature procedure.¹⁸ Pentafluorobenzoyl chloride was purchased from Tokyo Chemical Industry and used without purification.

Preparation of β -alkoxy or acyloxy γ,δ -unsaturated ketone *O*-substituted oximes 4-6: Experimental procedures were shown below as a typical example for the synthesis of (*E*)-1-[2-(pentafluorobenzoyloxy)imino-2-phenylethyl]prop-2-enyl acetate (4d)

To a solution of 3-hydroxy-1-phenyl-4-penten-1-one¹³ (510 mg, 2.89 mmol) in EtOH was added hydroxylamine hydrochloride (400 mg, 5.77 mmol) and triethylamine (0.60 mL, 4.3 mmol), and the mixture was stirred for 1 h at room temperature, then for 1 h at 50 °C. After the reaction was quenched with water, the mixture was extracted three times with ethyl acetate. The combined extracts were washed with water and brine. Ethyl acetate was removed under vacuum, and the crude material was purified by recrystallization (hexane/ethyl acetate/ether) to afford (*E*)-3-hydroxy-1-phenyl-4-penten-1-one oxime (254 mg, 46%).

To an ice cold solution of (*E*)-3-hydroxy-1-phenyl-4-penten-1-one oxime (1.10 g, 5.7 mmol) in CH_2Cl_2 was added triethylamine (0.90 mL, 6.5 mmol) and pentafluorobenzoyl chloride (0.90 mL, 6.3 mmol) and stirred for 10 min under an argon atmosphere. After quenching with water, the mixture was extracted twice with ethyl acetate. The combined extracts were washed with water and brine and then, dried over sodium sulfate. The solvent was removed under vacuum, and the crude materials were purified by flash column chromatography (hexane/ethyl acetate = 92/8 to 8/2) to give (*E*)-3-hydroxy-1-phenyl-4-penten-1-one *O*-pentafluorobenzoyloxime (1.37 g, 62%).

To a solution of (*E*)-3-hydroxy-1-phenyl-4-penten-1-one *O*-pentafluorobenzoyloxime (0.83 g, 2.2 mmol) in CH_2Cl_2 was added acetic anhydride (0.29 mL, 3.1 mmol), pyridine (0.26 mL, 3.3 mmol) and a catalytic amount of *N,N*-dimethylaminopyridine (DMAP), and the mixture was

stirred for 45 min at 0 °C, then stirred for 1.5 h at room temperature. After quenching the reaction with saturated NH₄Cl aq., the mixture was extracted twice with diethyl ether, and the combined extracts were washed with water and brine, and dried over sodium sulfate. After the solvent was removed under vacuum, the crude product was purified by recrystallization from hexane/ethyl acetate to give (*E*)-1-[2-(pentafluorobenzoyloxy)imino-2-phenylethyl]prop-2-enyl acetate (**4d**) (749 mg, 81%).

3-Ethoxy-1-phenylpent-4-en-1-one (*E*)-*O*-pentafluorobenzoyloxime (4a**).** Colorless crystals; mp 44-46 °C; IR (ZnSe, cm⁻¹) 2978, 1863, 1653, 1523, 1496, 1421, 1325, 1190, 1093, 1003, 931, 876; ¹H NMR (500 MHz, CDCl₃) δ 1.03 (3H, t, *J* = 7.2 Hz), 3.09 (1H, dd, *J* = 6.0, 13.2 Hz), 3.14 (1H, dd, *J* = 8.1, 13.2 Hz), 3.17 (1H, dt, *J* = 7.2, 16.2 Hz), 3.46 (1H, dt, *J* = 7.2, 16.2 Hz), 3.96 (1H, ddd, *J* = 6.0, 7.5, 8.1 Hz), 5.13 (1H, d, *J* = 17.3 Hz), 5.14 (1H, d, *J* = 10.0 Hz), 5.68 (1H, ddd, *J* = 7.5, 10.0, 17.3 Hz), 7.34-7.49 (3H, m), 7.76 (2H, m); ¹³C NMR (125 MHz, CDCl₃) δ 14.9, 35.6, 64.2, 78.2, 107.0 (m), 117.6, 127.9, 128.6, 130.8, 133.8, 137.5, 137.8 (dm), 143.4 (dm), 145.5 (dm), 156.4, 166.4; Anal. Found: C, 58.04; H, 4.14; N, 3.14%. Calcd for C₂₀H₁₆F₅NO₃: C, 58.12; H, 3.90; N, 3.39%.

3-(Methoxymethyl)oxy-1-phenylpent-4-en-1-one (*E*)-*O*-pentafluorobenzoyloxime (4b**).** Yellow powder; mp 72 °C; IR (ZnSe, cm⁻¹) 1763, 1523, 1495, 1419, 1325, 1188, 999, 873; ¹H NMR (500 MHz, CDCl₃) δ 3.10 (1H, dd, *J* = 5.5, 13.5 Hz), 3.17 (3H, s), 3.21 (1H, dd, *J* = 8.8, 13.5 Hz), 4.35-4.40 (1H, m), 4.40 (1H, d, *J* = 6.8 Hz), 4.58 (1H, d, *J* = 6.8 Hz), 5.19 (1H, d, *J* = 17.3 Hz), 5.20 (1H, d, *J* = 9.7 Hz), 5.68 (1H, ddd, *J* = 7.6, 9.7, 17.3 Hz), 7.40-7.48 (3H, m), 7.80 (2H, m); ¹³C NMR (125 MHz, CDCl₃) δ 35.1, 55.4, 74.3, 93.6, 107.0 (m), 118.5, 127.8, 128.7, 131.1, 133.5, 136.5, 137.9 (dm), 143.4 (dm), 145.5 (dm), 156.3, 165.8; Anal. Found: C, 55.71; H, 3.82; N, 3.05%. Calcd for C₂₀H₁₆F₅NO₄: C, 55.95; H, 3.76; N, 3.26%.

3-Benzoyloxy-1-phenylpent-4-en-1-one (*E*)-*O*-pentafluorobenzoyloxime (4c**).** Colorless crystals; mp 48-50 °C; IR (ZnSe, cm⁻¹) 1763, 1653, 1523, 1496, 1325, 1190, 1093, 1070, 1003; ¹H NMR (500 MHz, CDCl₃) δ 3.12 (1H, dd, *J* = 5.8, 13.3 Hz), 3.22 (1H, dd, *J* = 8.1, 13.3 Hz), 4.10 (1H, ddd, *J* = 5.8, 7.6, 8.1 Hz), 4.22 (1H, d, *J* = 11.9 Hz), 4.51 (1H, d, *J* = 11.9 Hz), 5.18 (1H, d, *J* = 17.2 Hz), 5.24 (1H, d, *J* = 10.0 Hz), 5.74 (1H, ddd, *J* = 7.6, 10.0, 17.2 Hz), 7.10-7.13 (2H, m), 7.18-7.22 (3H, m), 7.35-7.49 (3H, m), 7.73-7.76 (2H, m); ¹³C NMR (125 MHz, CDCl₃) δ 35.4, 70.3, 77.5, 106.9 (m), 118.6, 127.5, 127.6, 127.9, 128.2, 128.6, 130.9, 133.6, 137.0, 137.7, 137.7 (dm, *J* = 255 Hz), 143.5 (dm, *J* = 259 Hz), 145.5 (dm, *J* = 251 Hz), 156.4, 166.1; HRMS (FAB⁺) Found: *m/z* 476.1284. Calcd for C₂₅H₁₈F₅NO₃: (M+H)⁺, 476.1280.

(*E*)-1-[2-(Pentafluorobenzoyloxy)imino-2-phenylethyl]prop-2-enyl acetate (4d**).** Colorless crystal; mp 81 °C; IR (ZnSe, cm⁻¹) 1765, 1496, 1327, 1194, 1003, 881; ¹H NMR (500 MHz, CDCl₃) δ 1.87 (3H, s), 3.23 (1H, dd, *J* = 7.0, 13.5 Hz), 3.29 (1H, dd, *J* = 7.6, 13.5 Hz), 5.17 (1H, d, *J* = 10.5 Hz), 5.21 (1H, d, *J* = 17.5 Hz), 5.50 (1H, ddd, *J* = 6.6, 7.0, 7.6 Hz), 5.77 (1H, ddd, *J* = 6.6, 10.5, 17.5 Hz), 7.39-7.51 (3H, m), 7.75 (2H, m); ¹³C NMR (125 MHz, CDCl₃) δ 20.7, 33.5, 71.7, 106.8 (m), 118.0, 127.7, 128.8, 131.2, 133.1, 134.6, 137.8 (dm, *J* = 250 Hz), 143.6 (dm, *J* = 250 Hz), 145.5 (dm, *J* = 255 Hz), 156.2, 164.7, 169.7; Anal. Found: C, 56.23; H, 3.47; N, 3.10%. Calcd for C₂₀H₁₄F₅NO₄: C, 56.21; H, 3.30; N, 3.28%.

(E)-1-[2-(Pentafluorobenzoyloxy)imino-2-phenylethyl]prop-2-enyl benzoate (4e). Colorless crystals; mp 96-98 °C; IR (ZnSe, cm^{-1}) 1763, 1718, 1523, 1495, 1325, 1267, 1186, 1001, 989, 879; ^1H NMR (400 MHz, CDCl_3) δ 3.41 (1H, dd, $J = 6.0, 13.2$ Hz), 3.45 (1H, dd, $J = 7.2, 13.2$ Hz), 5.21 (1H, d, $J = 10.3$ Hz), 5.30 (1H, d, $J = 17.0$ Hz), 5.74 (1H, ddd, $J = 6.0, 7.0, 7.2$ Hz), 5.86 (1H, ddd, $J = 7.0, 10.3, 17.0$ Hz), 7.30-7.52 (8H, m), 7.74-7.77 (2H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 33.6, 72.3, 106.7 (m), 118.1, 127.7, 128.2, 128.9, 129.4, 129.5, 131.2, 133.2, 133.3, 134.5, 137.8 (dm), 143.5 (dm), 145.5 (dm), 156.2, 164.8, 165.2; Anal. Found: C, 61.28; H, 3.38; N, 2.78%. Calcd for $\text{C}_{25}\text{H}_{16}\text{F}_5\text{NO}_4$: C, 61.36; H, 3.30; N, 2.86%.

(E)-1-[2-(Pentafluorobenzoyloxy)imino-2-phenylethyl]prop-2-enyl 2,4-difluorobenzoate (4f). Colorless crystals; mp 88 °C; IR (ZnSe, cm^{-1}) 1766, 1614, 1523, 1496, 1325, 1268, 1186, 1118; ^1H NMR (400 MHz, CDCl_3) δ 3.37 (1H, dd, $J = 6.2, 13.4$ Hz), 3.46 (1H, dd, $J = 7.6, 13.4$ Hz), 5.23 (1H, d, $J = 10.4$ Hz), 5.32 (1H, d, $J = 16.9$ Hz), 5.74 (1H, ddd, $J = 6.2, 6.2, 7.6$ Hz), 5.86 (1H, ddd, $J = 6.2, 10.4, 16.9$ Hz), 6.77 (1H, dd, $J = 2.4, 9.2$ Hz), 6.82 (1H, dd, $J = 2.4, 8.0$ Hz), 7.36-7.46 (3H, m), 7.63-7.69 (1H, m), 7.73-7.78 (2H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 33.5, 72.7, 105.2 (t, $J = 26$ Hz), 106.7 (m), 111.5 (dd, $J = 4, 22$ Hz), 114.5 (dd, $J = 4, 10$ Hz), 118.4, 127.7, 128.8, 131.2, 133.0, 133.8 (dd, $J = 2, 11$ Hz), 134.2, 137.8 (dm, $J = 250$ Hz), 143.6 (dm, $J = 259$ Hz), 145.6 (dm, $J = 255$ Hz), 156.2, 162.1 (d, $J = 4$ Hz), 162.8 (dd, $J = 13, 263$ Hz), 164.5, 165.8 (dd, $J = 12, 256$ Hz); Anal. Found: C, 57.12; H, 2.84; N, 2.60%. Calcd for $\text{C}_{25}\text{H}_{14}\text{F}_7\text{NO}_4$: C, 57.15; H, 2.69; N, 2.67%.

(E)-1-[2-(Pentafluorobenzoyloxy)imino-2-phenylethyl]prop-2-enyl pentafluorobenzoate (4g). Colorless crystals; mp 78 °C; IR (ZnSe, cm^{-1}) 1765, 1739, 1650, 1523, 1493, 1323, 1223, 1184, 995, 937, 885; ^1H NMR (270 MHz, CDCl_3) δ 3.33 (1H, dd, $J = 6.3, 13.8$ Hz), 3.48 (1H, dd, $J = 7.6, 13.8$ Hz), 5.27 (1H, d, $J = 10.3$ Hz), 5.34 (1H, d, $J = 17.0$ Hz), 5.74 (1H, ddd, $J = 6.3, 7.0, 7.6$ Hz), 5.84 (1H, ddd, $J = 7.0, 10.3, 17.0$ Hz), 7.37-7.49 (3H, m), 7.71-7.75 (2H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 33.3, 74.3, 106.6 (m), 107.4 (m), 119.5, 127.6, 128.9, 131.4, 132.6, 133.3, 137.7 (overlapped, dm), 143.3 (dm), 143.5 (dm), 145.6 (overlapped, dm), 156.1, 157.8, 163.9; Anal. Found: C, 51.56; H, 2.12; N, 2.38%. Calcd for $\text{C}_{25}\text{H}_{11}\text{F}_{10}\text{NO}_4$: C, 51.83; H, 1.91; N, 2.42%.

(E)-1-[2-(2,4-Difluorobenzoyloxy)imino-2-phenylethyl]prop-2-enyl 2,4-difluorobenzoate (5). Colorless crystal; mp 76 °C; IR (ZnSe, cm^{-1}) 1736, 1612, 1502, 1430, 1259, 1230, 1147, 1119, 1105, 1080, 973, 854, 760; ^1H NMR (400 MHz, CDCl_3) δ 3.47 (2H, d, $J = 6.8$ Hz), 5.23 (1H, d, $J = 10.4$ Hz), 5.35 (1H, d, $J = 16.8$ Hz), 5.84 (1H, dt, $J = 6.8, 6.4$ Hz), 5.93 (1H, ddd, $J = 6.4, 10.4, 16.8$ Hz), 6.76 (2H, t, $J = 8.0$ Hz), 6.94 (1H, ddd, $J = 2.4, 8.8, 11.0$ Hz), 7.00 (1H, m), 7.34-7.44 (3H, m), 7.58-7.64 (1H, m), 7.80 (1H, d, $J = 8.0$ Hz), 7.78 (1H, d, $J = 6.8$ Hz), 8.12 (1H, dt, $J = 6.8, 8.6$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 33.6, 72.9, 105.1 (t, $J = 26$ Hz), 105.2 (t, $J = 26$ Hz), 111.4 (dd, $J = 5, 21$ Hz), 112.2 (dd, $J = 4, 21$ Hz), 113.7 (dd, $J = 4, 11$ Hz), 114.6 (dd, $J = 4, 10$ Hz), 118.1, 127.7, 128.7, 130.8, 133.7, 133.8 (m), 134.6, 134.7 (dd, $J = 2, 11$ Hz), 161.1 (d, $J = 4$ Hz), 162.1 (d, $J = 4$ Hz), 162.5 (dd, $J = 13, 260$ Hz), 163.8 (dd, $J = 13, 260$ Hz), 163.6, 165.6 (dd, $J = 12, 255$ Hz), 166.1 (dd, $J = 12, 255$ Hz); Anal. Found: C, 63.78; H, 3.85; N, 2.77%. Calcd for $\text{C}_{25}\text{H}_{17}\text{F}_4\text{NO}_4$: C, 63.70; H, 3.63; N, 2.97%.

(E)-1-[2-(Acetoxy)imino-2-phenylethyl]prop-2-enyl acetate (6a). Colorless oil; IR (ZnSe,

cm⁻¹) 1768, 1735, 1376, 1230, 1190; ¹H NMR (400 MHz, CDCl₃) δ 1.86 (3H, s), 2.25 (3H, s), 3.21 (2H, d, *J* = 7.2 Hz), 5.18 (1H, dt, *J* = 10.4, 1.0 Hz), 5.24 (1H, dt, *J* = 17.2, 1.0 Hz), 5.54 (1H, dt, *J* = 6.7, 7.2 Hz), 5.80 (1H, ddd, *J* = 6.7, 10.4, 17.2 Hz), 7.37-7.45 (3H, m), 7.72 (2H, d, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.9, 20.9, 33.2, 71.8, 117.6, 127.4, 128.6, 130.6, 133.9, 134.8, 162.0, 168.4, 169.6; Anal. Found: C, 65.34; H, 6.21; N, 4.88%. Calcd for C₁₅H₁₇NO₄: C, 65.44; H, 6.22; N, 5.09%.

(E)-1-[2-(Acetoxy)imino-2-(4-methoxyphenyl)ethyl]prop-2-enyl acetate (6b). Colorless oil; IR (ZnSe, cm⁻¹) 1763, 1736, 1604, 1514, 1367, 1200 (br), 1022, 999, 928, 833; ¹H NMR (500 MHz, CDCl₃) δ 1.91 (3H, s), 2.23 (3H, s), 3.14 (1H, dd, *J* = 7.5, 13.2 Hz), 3.18 (1H, dd, *J* = 6.7, 13.2 Hz), 3.80 (3H, s), 5.14 (1H, d, *J* = 10.5 Hz), 5.20 (1H, d, *J* = 17.2 Hz), 5.50 (1H, ddd, *J* = 6.6, 6.7, 7.5 Hz), 5.77 (1H, ddd, *J* = 6.6, 10.5, 17.2 Hz), 6.89 (2H, d, *J* = 8.9 Hz), 7.68 (2H, d, *J* = 8.9 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 19.8, 20.9, 32.8, 55.3, 72.0, 113.9, 117.6, 126.0, 129.0, 134.8, 161.3, 161.6, 168.6, 169.8; Anal. Found: C, 62.73; H, 6.43; N, 4.29%. Calcd for C₁₆H₁₉NO₅: C, 62.94; H, 6.27; N, 4.59%.

(E)-1-[2-(Acetoxy)imino-2-(4-chlorophenyl)ethyl]prop-2-enyl acetate (6c). Colorless oil; IR (ZnSe, cm⁻¹) 1772, 1736, 1367, 1228, 1188, 1093, 999, 928, 831; ¹H NMR (500 MHz, CDCl₃) δ 1.89 (3H, s), 2.23 (3H, s), 3.13 (1H, dd, *J* = 7.6, 13.3 Hz), 3.18 (1H, dd, *J* = 6.6, 13.3 Hz), 5.15 (1H, d, *J* = 10.5 Hz), 5.20 (1H, d, *J* = 17.1 Hz), 5.47 (1H, dt, *J* = 7.6, 6.6 Hz), 5.75 (1H, ddd, *J* = 6.6, 10.5, 17.1 Hz), 7.35 (2H, d, *J* = 8.5 Hz), 7.66 (2H, d, *J* = 8.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 19.7, 20.8, 32.9, 71.7, 117.8, 128.7, 128.8, 132.3, 134.6, 136.9, 160.9, 168.2, 169.7; HRMS (FAB⁺) Found: *m/z* 290.1411. Calcd for C₁₆H₁₉NO₄: (M+H)⁺, 290.1392.

(E)-1-[2-(Acetoxy)imino-2-phenylethyl]but-2-enyl acetate (6d). Colorless crystals; mp 80 °C; IR (ZnSe, cm⁻¹) 1770, 1739, 1734, 1367, 1232, 1196; ¹H NMR (400 MHz, CDCl₃) δ 1.63 (3H, d, *J* = 1.2 Hz), 1.87 (3H, s), 2.26 (3H, s), 3.18 (2H, d, *J* = 6.8 Hz), 5.34-5.49 (2H, m), 5.66 (1H, dt, *J* = 14.4, 6.4 Hz), 7.36-7.45 (3H, m), 7.65-7.71 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 17.6, 19.8, 21.0, 33.5, 72.0, 127.4, 128.0, 128.5, 130.2, 130.5, 134.0, 162.3, 168.4, 169.7; Anal. Found: C, 66.46; H, 6.65; N, 4.69%. Calcd for C₁₆H₁₉NO₄: C, 66.42; H, 6.62; N, 4.84%.

(E)-1-[2-(Acetoxy)imino-2-phenylethyl]-3-phenylprop-2-enyl acetate (6e). Colorless crystals; mp 79 °C; IR (ZnSe, cm⁻¹) 1768, 1734, 1365, 1227, 1192, 1018, 999, 966, 930, 891, 764, 748, 692; ¹H NMR (400 MHz, CDCl₃) δ 1.93 (3H, s), 2.25 (3H, s), 3.33 (2H, d, *J* = 6.8 Hz), 5.70 (1H, dt, *J* = 7.2, 6.8 Hz), 6.09 (1H, dd, *J* = 7.2, 16.0 Hz), 6.55 (1H, d, *J* = 16.0 Hz), 7.21-7.34 (5H, m), 7.39-7.47 (3H, m), 7.70-7.76 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 19.9, 21.0, 33.6, 71.9, 125.8, 126.5, 127.5, 128.2, 128.5, 128.6, 130.6, 133.1, 134.0, 135.7, 161.9, 168.6, 169.7; Anal. Found: C, 71.68; H, 6.00; N, 3.83%. Calcd for C₂₁H₂₁NO₄: C, 71.78; H, 6.02; N, 3.99%.

(E)-1-[2-(Acetoxy)imino-2-phenylethyl]-2-methylprop-2-enyl acetate (6f). Colorless oil; IR (ZnSe, cm⁻¹) 1768, 1736, 1365, 1228, 1190, 997, 930, 897, 764, 694; ¹H NMR (400 MHz, CDCl₃) δ 1.76 (3H, s), 1.86 (3H, s), 2.24 (3H, s), 3.16 (1H, dd, *J* = 8.0, 13.4 Hz), 3.26 (1H, dd, *J* = 5.8, 13.4 Hz), 4.88 (2H, d, *J* = 7.3 Hz), 5.43 (1H, dd, *J* = 5.8, 8.0 Hz), 7.37-7.43 (3H, m), 7.68-7.70 (2H, m); ¹³C NMR (500 MHz, CDCl₃) δ 18.0, 19.8, 20.7, 32.1, 74.2, 113.5, 127.5, 128.3, 130.6, 134.0, 141.9, 162.5, 168.5, 169.7; Anal. Found: C, 66.29; H, 6.82; N, 4.69%. Calcd for

C₁₆H₁₉NO₄: C, 66.42; H, 6.62; N, 4.84%.

1-[2-(Acetoxy)imino-1-methyl-2-phenylethyl]prop-2-enyl acetate (6g) (4 isomers). Colorless oil; IR (ZnSe, cm⁻¹) 1766, 1736, 1367, 1228, 1194, 912, 773, 698; ¹H NMR (400 MHz, CDCl₃) δ 1.17-1.34 (3H, m), 1.89 (0.30H, s), 1.91 (1.95H, s), 1.98 (2.10H, s), 2.01 (0.15H, s), 2.05 (0.60H, s), 2.24 (0.30H, s), 2.27 (0.60H, s), 3.10-3.17 (0.70 H, m), 3.43-3.53 (0.30 H, m), 5.13-5.40 (2.95H, m), 5.55 (0.05H, dd, *J* = 7.4, 8.0 Hz), 5.65-5.87 (1H, m), 7.16-7.55 (5H, m); ¹³C NMR (500 MHz, CDCl₃) δ 13.1, 13.8, 14.0, 14.2, 19.5 (overlapped), 19.6, 19.7, 20.7, 20.8, 20.9, 21.0, 40.8, 41.5, 43.6, 44.1, 74.4, 74.7, 75.5, 75.7, 118.2, 118.3, 119.6, 120.2, 126.9, 126.9, 127.7, 127.9, 128.1, 128.2, 128.4 (overlapped), 129.1, 129.2, 129.8, 130.0, 132.2, 133.0, 133.4, 134.0, 134.0, 134.3, 134.4, 134.7, 166.5, 167.2, 167.3, 167.5, 167.9, 168.1, 168.5, 168.6, 169.2, 169.7, 169.8, 169.9; HRMS (FAB⁺) Found: *m/z* 304.1544. Calcd for C₁₇H₂₁NO₄: (M+H)⁺, 304.1549.

3-(Acetoxy)imino-1-ethenyl-5-phenylpent-4-enyl acetate (6h) (E : Z = 0.7 : 0.3). Yellow oil; IR (ZnSe, cm⁻¹) 1763, 1736, 1367, 1230, 1194, 1022, 991, 968, 933, 910, 872, 754, 731, 692; ¹H NMR (400 MHz, CDCl₃) δ 1.95 (2.1H, s), 1.98 (0.9H, s), 2.17 (3H, s), 2.80 (0.3H, dd, *J* = 6.6, 10.8 Hz), 2.98 (0.3H, dd, *J* = 6.6, 10.2 Hz), 2.95-3.04 (1.4H, m), 5.13 (0.7H, d, *J* = 9.6 Hz), 5.15 (0.3H, d, *J* = 8.8 Hz), 5.22 (1H, d, *J* = 17.0 Hz), 5.47 (0.7H, q, *J* = 6.6 Hz), 5.50 (0.3H, q, *J* = 6.6 Hz), 5.77 (0.7H, ddd, *J* = 6.6, 9.6, 17.0 Hz), 5.83 (0.3H, ddd, *J* = 6.6, 8.8, 17.0 Hz), 6.90 (0.7H, d, *J* = 16.6 Hz), 7.15 (0.7H, d, *J* = 16.6 Hz), 7.20-7.35 (3.6H, m), 7.43 (1.4H, d, *J* = 6.8 Hz), 7.49 (0.6H, dd, *J* = 1.8, 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.5, 19.7, 20.9, 21.0, 30.8, 35.5, 71.9, 72.4, 115.5, 117.4, 117.6, 123.2, 127.0, 127.6, 128.7, 129.2, 129.8, 134.5, 134.7, 135.0, 135.2, 138.2, 140.0, 158.5, 161.3, 167.8, 168.3, 169.6, 169.9; HRMS (FAB⁺) Found: *m/z* 302.1397. Calcd for C₁₇H₁₉NO₄: (M+H)⁺, 302.1387.

(E)-1-[2-(Acetoxy)imino-2-cyclohexyl]prop-2-enyl acetate (6i). Colorless oil; IR (ZnSe, cm⁻¹) 3460(br), 2929, 1763, 1736, 1645, 1450, 1429, 1228, 1205; ¹H NMR (400 MHz, CDCl₃) δ 1.15-1.47 (6H, m), 1.70-1.76 (1H, m), 1.80-1.89 (3H, m), 2.05 (3H, s), 2.19 (3H, s), 2.34 (1H, tt, *J* = 2.8, 11.6 Hz), 2.65 (1H, dd, *J* = 6.4, 13.2 Hz), 2.76 (1H, dd, *J* = 8.0, 13.2 Hz), 5.21 (1H, d, *J* = 10.4 Hz), 5.28 (1H, d, *J* = 16.8 Hz), 5.62 (1H, ddd, *J* = 6.4, 6.4, 8.0 Hz), 5.79 (1H, ddd, *J* = 6.4, 10.4, 16.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 19.7, 21.0, 25.7, 26.0, 26.0, 29.9, 30.2, 33.5, 44.3, 71.4, 117.3, 135.1, 168.0, 168.4, 169.5; Anal. Found: C, 64.00; H, 8.29; N, 4.83%. Calcd for C₁₅H₂₃NO₄: C, 64.03; H, 8.24; N, 4.98%.

3-(Acetoxy)imino-1-ethenyl-5-phenylpentyl acetate (6j) (E : Z = 0.5 : 0.5). Colorless oil; IR (ZnSe, cm⁻¹) 1763, 1736, 1367, 1228, 1198, 1022, 995, 927, 748, 700; ¹H NMR (400 MHz, CDCl₃) δ 2.02 (s, 1.5H), 2.04 (s, 1.5H), 2.11 (1.5H, s), 2.17 (1.5H, s), 2.44-2.93 (6H, m), 5.20 (1H, dm, *J* = 10.4 Hz), 5.26 (1H, dm, *J* = 16.8 Hz), 5.48-5.56 (1H, m), 5.75 (0.5H, ddd, *J* = 6.4, 10.4, 16.8 Hz), 5.79 (0.5H, ddd, *J* = 6.4, 10.4, 16.8 Hz), 7.10-7.31 (5H, m); ¹³C NMR (125 MHz, CDCl₃) δ 19.6, 19.6, 21.0, 21.1, 31.5, 31.8, 32.2, 34.5, 36.8, 38.9, 71.1, 71.2, 117.6, 117.8, 126.3, 126.5, 128.2, 128.3, 128.5, 128.6, 134.9, 135.0, 140.0, 140.4, 164.4, 165.1, 168.4, 168.5, 169.7, 170.1; HRMS (FAB⁺) Found: *m/z* 310.0865. Calcd for C₁₅H₁₆ClNO₄: (M+H)⁺, 310.0846.

(E)-1-[2-(acetoxy)imino-3,3-dimethylbutyl]prop-2-enyl acetate (6k). Yellow oil; IR (ZnSe cm⁻¹) 1770, 1736, 1367, 1230, 1196; ¹H NMR (400 MHz, CDCl₃) δ 1.14 (9H, s), 1.96 (3H, s),

2.12 (3H, s), 2.60 (1H, dd, $J = 6.0, 13.5$ Hz), 2.68 (1H, dd, $J = 8.0, 13.5$ Hz), 5.12 (1H, d, $J = 10.4$ Hz), 5.19 (1H, d, $J = 16.8$ Hz), 5.67 (1H, ddd, $J = 6.0, 6.8, 8.0$ Hz), 5.74 (1H, ddd, $J = 6.8, 10.4, 16.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 19.8, 21.0, 27.7, 32.3, 38.3, 71.6, 116.9, 135.5, 168.5, 169.4, 169.9; Anal. Found: C, 61.21; H, 8.37; N, 5.33%. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_4$: C, 61.16; H, 8.29; N, 5.49%

1-Phenyl-2,4-pentadiene-1-one (*E*)-*O*-pentafluorobenzoyloxime (7). Yellow plate; mp 99 °C; IR (ZnSe, cm^{-1}) 1749(b), 1651, 1597, 1522, 1492, 1323, 1188, 1080, 1001, 868; ^1H NMR (270 MHz, CDCl_3) δ 5.34 (1H, d, $J = 9.2$ Hz), 5.35 (1H, d, $J = 17.0$ Hz), 6.33 (1H, dd, $J = 10.3, 15.3$ Hz), 6.51 (1H, ddd, $J = 9.2, 10.3, 17.0$ Hz), 6.70 (1H, d, $J = 15.3$ Hz), 7.24-7.47 (5H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 107.0 (dt, $J = 1.0, 6.5$ Hz), 120.9, 126.3, 128.6, 129.7, 130.5, 132.1, 135.8, 137.8 (dm, $J = 250$ Hz), 143.5 (dm, $J = 245$ Hz), 144.9, 145.5 (dm, $J = 250$ Hz), 156.4, 165.5; Anal. Found: C, 58.67; H, 2.94; N, 3.71%. Calcd for $\text{C}_{18}\text{H}_{10}\text{F}_5\text{NO}_2$: C, 58.86; H, 2.74; N, 3.81%.

Synthesis of pyridines from α -alkoxy or acyloxy γ,δ -unsaturated ketone *O*-substituted oximes: Experimental procedures were shown below as a typical example for the synthesis of 2-phenylpyridine (3a) from (*E*)-1-[2-(acetoxy)imino-2-phenylethyl]prop-2-enyl acetate (6a)

To a solution of (*E*)-1-[2-(acetyloxy)imino-2-phenylethyl]prop-2-enyl acetate (6a) (87.2 mg, 0.317 mmol) in toluene (20 mL) at 50 °C, $\text{Pd}(\text{PPh}_3)_4$ (74.7 mg, 0.070 mmol) and triethylamine (0.22 mL, 1.6 mmol) were added, and the mixture was warmed and stirred for 30 min at 120 °C. After cooling to room temperature, the mixture was passed through celite pad. The filtrate was evaporated under vacuum, and the red-black organic residue was purified by column chromatography (hexane/acetone = 8/2) to afford 2-phenylpyridine 3a (40.4 mg, 82%).

2-Phenylpyridine (3a).¹⁹ Brown oil; IR (ZnSe, cm^{-1}) 1585, 1579, 1564, 1468, 1448, 1423, 736, 690; ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.24 (1H, m), 7.37-7.48 (3H, m), 7.70-7.76 (2H, m), 7.96-7.99 (2H, m), 8.68 (1H, d, $J = 4.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 120.5, 122.0, 126.8, 128.7, 128.9, 136.6, 139.3, 149.6, 157.4.

2-(4-Methoxyphenyl)pyridine (3b).²⁰ Colorless oil; IR (ZnSe, cm^{-1}) 1601, 1585, 1560, 1512, 1456, 1244, 1022, 839, 775, 737, 717; ^1H NMR (400 MHz, CDCl_3) δ 3.85(3H, s), 6.98 (2H, d, $J = 8.8$ Hz), 7.15 (1H, ddd, $J = 1.6, 4.9, 6.4$ Hz), 7.64 (3H, m), 7.94 (2H, d, $J = 8.8$ Hz), 8.63 (1H, dm, $J = 4.9$ Hz).

2-(4-Chlorophenyl)pyridine (3c).²¹ Colorless oil; IR (ZnSe, cm^{-1}) 1585, 1462, 1433, 1398, 766, 735; ^1H NMR (500 MHz, CDCl_3) δ 7.21 (1H, ddd, $J = 0.8, 4.5, 7.2$ Hz), 7.42 (2H, d, $J = 8.5$ Hz), 7.67 (1H, d, $J = 8.0$ Hz), 7.72 (1H, dt, $J = 2.0, 8.0$ Hz), 7.92 (2H, d, $J = 8.5$ Hz), 8.66 (1H, d, $J = 4.5$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 120.3, 122.4, 128.1, 128.9, 135.1, 136.9, 137.8, 149.7, 156.2; Anal. Found: C, 69.86; H, 4.42; N, 7.15%. Calcd for $\text{C}_{11}\text{H}_8\text{ClN}$: C, 69.67; H, 4.25; N, 7.39%.

2-Methyl-6-phenylpyridine (3d).²² Brown oil; IR (ZnSe, cm^{-1}) 1593, 1572, 1458, 1446, 754, 692; ^1H NMR (400 MHz, CDCl_3) δ 2.62 (3H, s), 7.18 (1H, d, $J = 7.6$ Hz), 7.35-7.40 (1H, m), 7.47

(2H,m), 7.50 (1H, d, $J = 7.6$ Hz), 7.62 (1H, t, $J = 7.6$ Hz), 7.94-7.97 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 24.8, 117.6, 121.5, 126.9, 128.6, 136.8, 139.7, 156.9, 158.2.

2,6-Diphenylpyridine (3e).²³ White crystals; mp 80-81 °C (lit. 80-81°C); IR (ZnSe, cm^{-1}) 3060-2820(br), 2360, 2341, 1564, 1452, 1439, 1055, 1032, 1018, 748, 690; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (2H, t, $J = 7.6$ Hz), 7.49 (4H, t, $J = 7.6$ Hz), 7.68 (2H, d, $J = 7.6$ Hz), 7.80 (1H, t, $J = 7.6$ Hz), 8.15 (4H, d, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 118.5, 126.9, 128.6, 128.9, 137.4, 139.4, 156.7.

5-Methyl-2-phenylpyridine (3f).²⁴ Colorless oil; IR (ZnSe, cm^{-1}) 1475, 833, 773, 734, 690; ^1H NMR (400 MHz, CDCl_3) δ 2.34 (3H, s), 7.33-7.39 (1H, m), 7.44 (2H, t, $J = 7.6$ Hz), 7.51 (1H, dd, $J = 1.6, 8.0$ Hz), 7.59 (1H, d, $J = 8.0$ Hz), 7.93-7.97 (2H, m), 8.50 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 18.1, 120.0, 126.6, 128.5, 128.6, 131.5, 137.2, 139.3, 150.0, 154.7; Anal. Found: C, 85.03; H, 6.75; N, 8.00%. Calcd for $\text{C}_{12}\text{H}_{11}\text{N}$: C, 85.17; H, 6.55; N, 8.28%.

3-Methyl-2-phenylpyridine (3g).²⁵ Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 2.34 (3H, s), 7.16 (1H, dd, $J = 4.8, 7.5$ Hz), 7.35-7.39 (1H, m), 7.43 (2H, t, $J = 7.5$ Hz), 7.49-7.51 (2H, m), 7.56 (1H, d, $J = 7.5$ Hz), 8.51 (1H, d, $J = 4.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.1, 122.0, 127.8, 128.0, 128.8, 130.7, 138.3, 140.4, 146.8, 158.5.

2-Styrylpyridine (3h).²⁶ Brown oil; IR (ZnSe, cm^{-1}) 1581, 1560, 1493, 1466, 1448, 1433, 1153, 987, 970, 777, 735, 690, 552, 532; ^1H NMR (400 MHz, CDCl_3) δ 7.11-7.14 (1H, m), 7.15 (1H, d, $J = 16.4$ Hz), 7.28 (1H, tm, $J = 7.4$ Hz), 7.36 (3H, d, $J = 7.6$ Hz), 7.57 (2H, d, $J = 7.6$ Hz), 7.62 (1H, d, $J = 16.4$ Hz), 7.64 (1H, dt, $J = 2.0, 7.4$ Hz), 8.59 (1H, d, $J = 4.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 122.0, 122.1, 127.1, 127.9, 128.3, 128.7, 132.7, 136.5, 136.6, 149.6, 155.5.

2-(Cyclohexyl)pyridine (3i). Orange oil; IR (ZnSe, cm^{-1}) 2924, 2850, 1589, 1570, 1471, 1450, 1433, 746; ^1H NMR (400 MHz, CDCl_3) δ 1.27 (1H, tt, $J = 3.2, 12.4$ Hz), 1.39 (2H, tq, $J = 3.2, 12.4$ Hz), 1.50 (2H, dq, $J = 3.2, 12.4$ Hz), 1.72 (1H, dm, $J = 10.8$ Hz), 1.83 (2H, dm, $J = 13.0$ Hz), 1.92 (2H, dm, $J = 13.0$ Hz), 2.67 (1H, tt, $J = 3.4, 11.6$ Hz), 7.06 (1H, ddd, $J = 1.0, 4.8, 7.6$ Hz), 7.12 (1H, d, $J = 7.6$ Hz), 7.56 (1H, dt, $J = 2.0, 7.6$ Hz), 8.50 (1H, dm, $J = 4.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 26.1, 26.6, 33.0, 46.6, 120.9, 136.2, 148.9, 166.4; HRMS (FAB⁺) Found: m/z 294.0280. Calcd for $\text{C}_{10}\text{H}_{15}\text{N}$: (M+Cs)⁺, 294.0259.

2-Phenethylpyridine (3j).²⁷ Brown oil; IR (ZnSe, cm^{-1}) 1589, 1568, 1473, 1454, 1434, 773, 744, 696; ^1H NMR (400 MHz, CDCl_3) δ 3.06 (4H, m), 7.06 (1H, d, $J = 8.0$ Hz), 7.10 (1H, ddd, $J = 0.8, 4.8, 7.6$ Hz), 7.14-7.19 (3H, m), 7.26 (2H, tm, $J = 7.2$ Hz), 7.55 (1H, dt, $J = 1.6, 7.6$ Hz), 8.55 (1H, dm, $J = 4.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 36.1, 40.3, 121.1, 122.9, 125.9, 128.3, 128.4, 136.2, 141.5, 149.2, 161.1; Anal. Found: C, 84.94; H, 7.38; N, 7.41%. Calcd for $\text{C}_{13}\text{H}_{13}\text{N}$: C, 85.21; H, 7.15; N, 7.64%.

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