Pergamon

Tetrahedron 58 (2002) 10043–10046

TETRAHEDRON

# *O*-Vinyldiaryl- and *O*-vinylaryl(hetaryl)ketoximes: a breakthrough in *O*-vinyloxime chemistry

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Received 19 July 2002; revised 18 September 2002; accepted 10 October 2002

**Abstract**—*O*-Vinyldiarylketoximes and *O*-vinylaryl(hetaryl)ketoximes, a novel family of stable *O*-vinyloximes, are synthesized by a straightforward, unusually fast vinylation of diarylketoximes and aryl(hetaryl)ketoximes with acetylene in a superbase system of KOH–DMSO (60–80°C, 5–7 min). Yields of up to 90% were obtained, thus introducing into organic synthesis a new group of highly promising building blocks and monomers. © 2002 Elsevier Science Ltd. All rights reserved.

Vinyl ethers of alcohols and phenols are well established monomers, building blocks and auxiliaries in organic synthesis, steadily expanding their scope of applications.[1–4] Vinyl ethers of oximes (*O*-vinyloximes) had been remaining almost unknown for a long time until their synthesis by the straightforward vinylation of oximes with acetylene was systematically developed,[5–9] although only ketoximes happened to enter the reaction, whereas aldoximes were found to dehydrate to nitriles.[5]

Recently,[10,11] *O*-vinylamidoximes were also synthesized. In spite of being unstable, both *O*-vinyldialkyl(alkylaryl)-ketoximes[5–9] and *O*-vinylamidoximes[10,11] are actively employed for the synthesis of a number of new unsaturated heteroatomic compounds (pyrroles,[5–8,12] hydroxypyrrolines,[5] 3*H*-pyrroles,[13] trifluoroacetyl derivatives[9–11]), and polymers,[5,6,14] as well as for theoretical and spectroscopic studies.[15–17] However, a drawback of the *O*-vinyldialkyl(alkylaryl)oximes so far synthesized is their chemical and thermal instability seriously limiting their broader use in organic synthesis. In fact, *O*-vinyldialkyl(alkylaryl)-ketoximes having a $CH_2$ group at the α-position to the oxime function are non-isolable intermediates in the Trofimov pyrrole synthesis,[5,6] while *O*-vinylacetoxime, *O*-vinylmethyl(*iso*- and *tert*-alkyl)ketoximes and *O*-vinylmethylarylketoximes explode above 143°C,[7] and hence should be handled with caution.[5,7]

To circumvent this obstacle for furthering *O*-vinyloxime chemistry, we have for the first time developed a facile vinylation of diaryl- and aryl(hetaryl)ketoximes which turned out to be a new family of entirely stable *O*-vinyloximes. Here, we briefly report on the results attained.

Diarylketoximes **2a–e** and phenyl(2-pyridyl)ketoxime **2f** were vinylated with acetylene in the KOH–DMSO system at 60–80°C for 5–7 min under pressure (initial pressure of 14 atm, maximum pressure of 30 atm), thus representing an unusually fast nucleophilic addition to the triple bond (Scheme 1).

The highest yields (80–90%) of *O*-vinylketoximes **3** were obtained at 70°C (Table 1). Both increasing and decreasing the reaction temperature by 10°C leads to a decrease in the product yield (Table 1).

Prior to use, the initial ketoximes **2a–f** were dried under vacuum and kept in hermetically sealed containers (benzophenone oxime, for example, is known to decompose in the presence of moisture and oxygen to give benzophenone and nitric acid[18]).

The distinction between the *E*- and *Z*-isomers of *O*-vinyldiarylketoximes was made based on the fact that the *ipso*-carbon resonance in the aryl substituent having a *syn*-orientation relative to the oxygen atom in the oxime function is ~3 ppm shifted to higher field compared to that with an *anti*-orientation.[17]

In order to attribute the $^1H$ and $^{13}C$ NMR spectroscopy, peaks of symmetrical diaryl- **3a**, **3c** and unsymmetrical phenyl(2-pyridyl)- **3f** ketoximes, 2D homonuclear COSY and NOESY routines, as well as 2D heteronuclear HSQC

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*Keywords*: vinylation; ketones; oximes; acetylene; superbase system.

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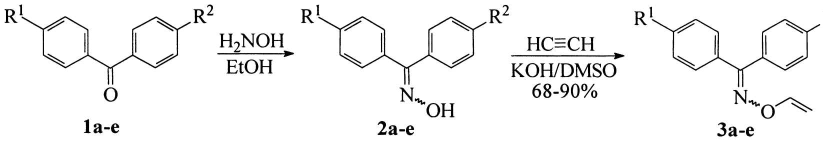
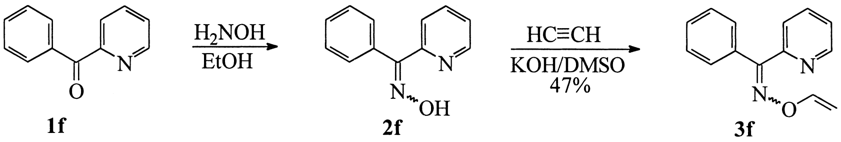
PII: S0040-4020(02)01304-2



**1a-e** **2a-e** **3a-e**

| 1-3 | R$^1$ | R$^2$ |
|---|---|---|
| **a** | H | H |
| **b** | H | Me |
| **c** | Me | Me |
| **d** | H | OMe |
| **e** | H | Br |



**1f** **2f** **3f**

**Scheme 1.**

**Table 1**. Vinylation of diarylketoximes and phenyl(2-pyridyl)ketoxime in the KOH–DMSO system under acetylene pressure

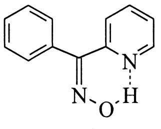
| *O*-Vinylketoxime | Reaction temperature[a] (°C) | Yield (%) | Isomer (*E*/*Z*) ratio |
|---|---|---|---|
| **3a** | 70 | 90 | 1:1[b] |
| **3b** | 70 | 83 | 1:1 |
| **3c** | 60 | 68 | 1:1[b] |
| **3c** | 70 | 82 | 1:1[b] |
| **3d** | 70 | 87 | 3:5 |
| **3e** | 70 | 80 | 1:1 |
| **3e** | 80 | 75 | 1:1 |
| **3f** | 70 | 47 | 2:1 |

[a] Reaction time at the given temperature is 5–7 min.

[b] Degeneration of the isomers due to the symmetric structure.

and HMBC techniques were used. For attribution of $^1$H and $^{13}$C NMR spectroscopy, peaks in the case of unsymmetrical oximes **3b**, **3d** and **3e**, the tabulated substituent chemical shifts[19] were analyzed in comparison with the corresponding parameters for oximes **3a** and **3c**.

A predominance of the *Z*-isomer for **3d** and the *E*-isomer for **3f** can most likely be accounted for by the repulsion of the lone pair of the oxygen atom and the more electron-rich 4-methoxyphenyl group (**3d**) and the lone pair of nitrogen atom (**3f**). In the initial oxime **2f**, there is an exactly opposite, but quite explainable, picture: the *Z*-isomer dominates (*E*/*Z*=~1:3) due to formation of a hydrogen bond between the nitrogen atom of the pyridine ring and the oxime function.



Z-**2f**

The *E*/*Z* ratio for ketoxime **2d** is ~1:1.

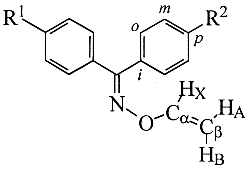
A study of the thermal stability of *O*-vinylbenzophenone oxime **3a** was performed using the previously described technique.[11] Upon heating to 220°C in a sealed ampoule, compound **3a** transforms without an explosion to a tarry viscous mass consisting of benzophenone and, probably, benzophenone imine ($^{13}$C NMR, $\delta$, ppm: 196.84 and 158.95, correspondingly) and products giving rise to a weak broad multiplet in the 7.1–7.5 ppm region of the $^1$H NMR spectrum (presumably, oligomers of benzophenone imine, acetaldehyde and acetylene). Higher-field peaks of probable products of polymerization involving the vinyl group are absent. Among gaseous and low-boiling decomposition products is acetaldehyde ($^1$H NMR, $\delta$, CDCl$_3$, ppm: 9.80 q, 2.20 d, $^3J$=2.9 Hz).

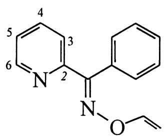
*O*-Vinyldiarylketoximes **3** do not explode even on contact with open flames. Instead, they smoothly inflame and evenly burn out. Storing compound **3a** at a temperature of 10°C in air for 8 months has not led to formation of any noticeable amounts of admixtures (by $^1$H NMR spectroscopy).

To conclude, the present paper for the first time describes a simple and efficient method for the synthesis of a novel family of stable and safe in handling *O*-vinyldiaryl- and aryl(hetaryl)ketoximes, thus opening opportunities for their broader use in organic synthesis, polymer chemistry and the design of advanced materials.

## 1. Experimental

$^1$H and $^{13}$C NMR spectra were taken on a Bruker DPX 400 spectrometer (400.13 and 100.61 MHz, respectively) in CDCl$_3$ using HMDS as an internal standard. For assignment of the signals the following designation was used.





IR spectra were recorded on a Bruker IFS 25 instrument. Oximes **2a–e** were prepared from commercial benzophenones **1a–e** using literature procedure[18] in nearly quantitative yields, oxime **2f** was synthesized by our own improved technique[20] allowing to increase the yield from 50 to 87%.

### 1.1. Oximation of phenyl(2-pyridyl)ketone (1f)

10.00 g (55 mmol) of phenyl(2-pyridyl)ketone and 5.98 g (86 mmol) of $NH_2OH\cdot HCl$ was mixed with 40 mL of 95% ethanol and 4 mL of water. To the mixture, 11.00 g (275 mmol) of fine-powdered NaOH was gradually added upon shaking. After introduction of the whole NaOH amount, the mixture was stirred for 1 h at room temperature, and 50 mL of water was added. The obtained homogeneous solution was neutralized with excess of dry ice, the precipitate formed was filtered off and washed with water. After drying in vacuum and recrystallization from chloroform, 9.51 g (48 mmol) of oxime **2f** was obtained in 87% yield. The product represents slightly pink crystals, mp 149–151°C (lit.:[20] mp 150–152°C).

### 1.2. General procedure: vinylation of benzophenone oxime (2a)

Into a steel 0.5-liter rotating autoclave, 2.00 g (10 mmol) of benzophenone oxime **2a**, 1.14 g (17.5 mmol) of $KOH\cdot 0.5H_2O$ (15% water content) and 50 mL of DMSO were loaded. The mixture was saturated with acetylene to 14 atm and heated up to 70°C during 30 min (the maximum acetylene pressure in the autoclave thus reached ~30 atm), with the following instant removal of heating and opening the autoclave oven (time of the reaction at maximum temperature made ~5–7 min). After cooling to room temperature the reaction mixture was unloaded, diluted with water up to 100 mL and extracted with diethyl ether (30 mL×4). The ether extracts were washed with water (20 mL×3), dried over anhydrous $K_2CO_3$ and filtered. Distilling off ether and vacuuming produced raw product (>90% purity, $^1H$ NMR), which was additionally purified using column chromatography ($Al_2O_3$, petroleum ether). As a result, 2.04 g (9 mmol) of *O*-vinylbenzophenone oxime **3a** in 90% yield was obtained.

**1.2.1. *O*-Vinylbenzophenone oxime (3a).** A transparent viscous liquid, $n_D^{20}=1.6050$. [Found: C 80.72; H 5.88; N 6.24. $C_{15}H_{13}NO$ requires C 80.69; H 5.87; N 6.27%]; $\nu_{max}$ (liquid film) 3060 ($\nu$CH), 1634 ($\nu_{trans}$C=C), 1610, 1591, 1493 ($\nu_{cis}$C=C in benzene ring), 1444, 1381 ($\delta CH_2$), 1325, 1305, 1179 ($\nu$C–O), 1145, 988 ($\nu$N–O), 945 ($\delta_{trans}$CH), 864 ($\gamma$C–C–C), 838 ($\gamma CH_2$), 774, 694, 667, 650 $cm^{-1}$; $\delta_H$ 7.51 (d, 2H, $H_o$-*anti*, $^3J_{H_oH_m}$=7.0 Hz,), 7.30–7.45 (m, 8H, $H_o$-*syn*, $H_m$-*syn*, $H_p$-*syn*, $H_m$-*anti*, $H_p$-*anti*), 6.99 (dd 1H, $H_X$, $^3J_{AX}$=6.6 Hz, $^3J_{BX}$=14.2 Hz), 4.63 (dd, 1H, $H_B$, $^2J_{AB}$=1.4 Hz, $^3J_{BX}$=14.2 Hz), 4.15 (dd, 1H, $H_A$, $^2J_{AB}$=1.4 Hz, $^3J_{AX}$=6.6 Hz); $\delta_C$=159.47 (C=N), 152.72 ($C_\alpha$), 135.75 ($C_i$-*anti*), 132.81 ($C_i$-*syn*), 130.03 ($C_p$-*anti*), 129.29 ($C_o$-*syn*, $C_p$-*syn*), 128.39 ($C_o$-*anti*, $C_m$-*anti*), 128.20 $C_m$-*syn*), 88.56 ($C_\beta$).

**1.2.2. *O*-Vinyl-*p*-methylbenzophenone oxime (3b).** A transparent viscous liquid, $n_D^{20}=1.6000$. [Found: C 81.05; H 6.39; N 6.80. $C_{16}H_{15}NO$ requires C 80.98; H 6.37; N 6.74%]; $\nu_{max}$ (liquid film) 3058 ($\nu$CH), 1636 ($\nu_{trans}$C=C), 1325, 1305, 1179 ($\nu$C–O), 1147, 988 ($\nu$N–O), 947 ($\delta_{trans}$=CH), 865 ($\gamma$C–C–C), 837, 824 ($\gamma CH_2$), 774, 696 $cm^{-1}$; $\delta_H$ (*E*-isomer) 7.49 (d, 2H, $H_o$-*anti*, $^3J_{H_oH_m}$=7.9 Hz), 7.40–7.20 (m, 5H, $H_o$-*syn*, $H_m$-*syn*, $H_p$-*syn*), 7.11 (d, 2H, $H_m$-*anti*, $^3J_{H_oH_m}$=7.9 Hz), 6.95 (dd, 1H, $H_X$, $^3J_{AX}$= 6.8 Hz, $^3J_{BX}$=14.2 Hz), 4.59 (dd, 1H, $H_B$, $^2J_{AB}$=1.9 Hz, $^3J_{BX}$=14.2 Hz), 4.11 (dd, 1H, $H_A$, $^2J_{AB}$=1.9 Hz, $^3J_{AX}$=6.8 Hz), 2.35 (s, 3H, Me). $\delta_C$ (*E*-isomer) 158.93 (C=N), 152.62 ($C_\alpha$), 139.91 ($C_p$-*anti*), 133.02 ($C_i$-*anti*), 132.92 ($C_i$-*syn*), 129.14 ($C_o$-*syn*), 128.98 ($C_p$-*syn*), 128.96 ($C_m$-*anti*), 128.41 ($C_o$-*anti*), 128.00 ($C_m$-*syn*), 88.29 ($C_\beta$), 21.35 (Me); $\delta_H$ (*Z*-isomer) 7.40–7.20 (m, 9H, $H_o$-*syn*, $H_m$-*syn*, $H_o$-*anti*, $H_m$-*anti*, $H_p$-*anti*), 6.97 (dd, 1H, $H_X$, $^3J_{AX}$=6.8 Hz, $^3J_{BX}$=14.2 Hz), 4.61 (dd, 1H, $H_B$, $^2J_{AB}$= 1.6 Hz, $^3J_{BX}$=14.2 Hz), 4.13 (dd, 1H, $H_A$, $^2J_{AB}$=1.6 Hz, $^3J_{AX}$=6.8 Hz), 2.40 (s, 3H, $CH_3$); $\delta_C$ (Z-isomer)=159.25 (C=N), 152.65 ($C_\alpha$), 139.06 ($C_p$-*syn*), 135.98 ($C_i$-*anti*), 129.86 ($C_i$-*syn*), 129.74 ($C_p$-*anti*), 129.29 ($C_o$-*syn*), 128.73 ($C_m$-*syn*), 128.23 ($C_m$-*anti*), 128.18 ($C_o$-*anti*), 88.37 ($C_\beta$), 21.47 (Me).

**1.2.3. *O*-Vinyl(di-*p*,*p*′-methyl)benzophenone oxime (3c).** White crystals, mp 54–56°C. [Found: C 81.19; H 6.80; N 5.53. $C_{17}H_{17}NO$ requires C 81.24; H 6.82; N 5.57%]; $\nu_{max}$ (KBr) 1637 ($\nu_{trans}$C=C), 1612, 1510 ($\nu_{cis}$C=C in benzene ring), 1323, 1176 ($\nu$C–O), 983 ($\nu$N–O), 947 ($\delta_{trans}$=CH), 863 ($\gamma$C–C–C), 826 ($\gamma CH_2$) $cm^{-1}$; $\delta_H$ 7.38 (d, 2H, $H_o$-*anti*, $^3J_{H_oH_m}$=7.9 Hz), 7.22 (s, 4H, $H_o$-*syn*, $H_m$-*syn*), 7.12 (d, 2H, $H_m$-*anti*, $^3J_{H_oH_m}$=7.9 Hz), 6.96 (dd, 1H, $H_X$, $^3J_{AX}$=6.7 Hz, $^3J_{BX}$=14.1 Hz), 4.61 (dd, 1H, $H_B$, $^2J_{AB}$=1.7 Hz, $^3J_{BX}$= 14.1 Hz), 4.12 (dd, 1H, $H_A$, $^2J_{AB}$=1.7 Hz, $^3J_{AX}$=6.7 Hz), 2.40 (s, 3H, Me-*syn*), 2.35 (s, 3H, Me-*anti*); $\delta_C$ 159.37 (C=N), 152.81 ($C_\alpha$), 139.93 ($C_p$-*anti*), 139.06 ($C_p$-*syn*), 133.29 ($C_i$-*anti*), 130.15 ($C_i$-*syn*), 129.41 ($C_o$-*syn*), 129.05 ($C_m$-*anti*), 128.83 ($C_m$-*syn*), 128.49 ($C_o$-*anti*), 88.33 ($C_\beta$), 21.64 (Me-*syn*), 21.51 (Me-*anti*).

**1.2.4. *O*-Vinyl-*p*-methoxybenzophenone oxime (3d).** A transparent viscous liquid, $n_D^{20}=1.6074$. [Found: C 75.86; H 5.94; N 5.57. $C_{16}H_{15}NO_2$ requires C 75.87; H 5.97; N 5.53%]; $\nu_{max}$ (liquid film) 1637 ($\nu_{trans}$C=C), 1607, 1510, ($\nu_{cis}$C=C in benzene ring), 1326, 1305, 1251 ($\nu$C–O), 1174 ($\nu$C–O), 1147, 1033, 988 ($\nu$N–O), 947 ($\delta_{trans}$=CH), 865 ($\gamma$C–C–C), 835 ($\gamma CH_2$), 774 $cm^{-1}$; $\delta_H$ (*E*-isomer) 7.43–7.27 (m, 7H, $H_o$-*syn*, $H_m$-*syn*, $H_p$-*syn*, $H_o$-*anti*), 6.92 (dd, 1H, $H_X$, $^3J_{AX}$=6.7 Hz, $^3J_{BX}$=14.2 Hz), 6.80 (d, 2H, $H_m$-*anti*, $^3J_{H_oH_m}$=6.8 Hz), 4.57 (dd, 1H, $H_B$, $^2J_{AB}$=1.7 Hz, $^3J_{BX}$= 14.2 Hz), 4.09 (dd, 1H, $H_A$, $^2J_{AB}$=1.7 Hz, $^3J_{AX}$=6.7 Hz), 3.76 (s, 3H, OMe); $\delta_C$ (*E*-isomer) 161.04 ($C_p$-*anti*), 158.85 (C=N), 152.69 ($C_\alpha$), 133.11 ($C_i$-*syn*), 129.65 ($C_o$-*syn*, $C_o$-*anti*), 128.14 ($C_i$-*anti*), 127.98 ($C_p$-*syn*), 113.63 ($C_m$-*anti*), 88.11 ($C_\beta$), 55.05 (OMe); $\delta_H$ (*Z*-isomer) 7.43–7.27 (m, 5H, $H_o$-*syn*, $H_m$-*anti*, $H_p$-*anti*), 7.48 (d, 2H, $H_o$-*anti*, $^3J_{H_oH_m}$=6.8 Hz), 6.96 (dd, 1H, $H_X$, $^3J_{AX}$=6.7 Hz, $^3J_{BX}$=14.2 Hz), 6.89 (d, 2H, $H_m$-*syn*, $^3J_{H_oH_m}$=7.0 Hz), 4.61 (dd, 1H, $H_B$, $^2J_{AB}$=1.7 Hz, $^3J_{BX}$=14.2 Hz), 4.11 (dd, 1H, $H_A$, $^2J_{AB}$=1.7 Hz, $^3J_{AX}$=6.7 Hz), 3.80 (s, 3H, OMe); $\delta_C$ (*Z*-isomer) 160.18 ($C_p$-*syn*), 158.79 (C=N), 152.69 ($C_\alpha$), 136.22 ($C_i$-*anti*), 131.17 ($C_o$-*syn*), 129.05 ($C_p$-*anti*), 128.57 ($C_o$-*anti*, $C_m$-*anti*), 124.85 ($C_i$-*syn*), 113.36 ($C_m$-*syn*), 88.30 ($C_\beta$), 55.05 (OMe).

**1.2.5. *O*-Vinyl-*p*-bromobenzophenone oxime (3e).** Keeping the liquid mixture of *E*- and *Z*-isomers (*E*/*Z*~1:1) of ketoxime **3e** for 2 days resulted in crystallization of *Z*-isomer. The liquid phase thus became enriched with the *E*-isomer. Washing the crystals with a small amount of hexane allowed to isolate the *Z*-isomer, which represents white crystals, mp 83–84°C. [Found: 59.68; H 4.02; Br 26.34; N 4.67. $C_{15}H_{12}BrNO$ requires C 59.62; H 4.00; Br 26.44; N 4.64%]; $\nu_{max}$ (KBr) 1636 ($\nu_{trans}$C=C), 1486 ($\nu_{cis}$C=C in benzene ring), 1179 ($\nu$C–O), 1145, 1071, 991 ($\nu$N–O), 947 ($\delta_{trans}$=CH), 829 ($\gamma CH_2$), 775, 697 cm$^{-1}$; $\delta_H$ (*E*-isomer) 7.55–7.15 (m, 9H, $H_o$-*syn*, $H_m$-*syn*, $H_p$-*syn*, $H_o$-*anti*, $H_m$-*anti*), 6.94 (dd, 1H, $H_X$, $^3J_{AX}$=6.7 Hz, $^3J_{BX}$=14.2 Hz), 4.59 (dd, 1H, $H_B$, $^2J_{AB}$=1.9 Hz, $^3J_{BX}$=14.2 Hz), 4.13 (dd, 1H, $H_A$, $^2J_{AB}$=1.9 Hz, $^3J_{AX}$=6.7 Hz); $\delta_C$ (*E*-isomer) 161.04 ($C_p$-*anti*), 158.03 (C=N), 152.43 ($C_\alpha$), 134.57 ($C_i$-*anti*), 132.24 ($C_i$-*syn*), 131.34 ($C_m$-*anti*), 129.68 ($C_o$-*anti*), 129.24 ($C_p$-*syn*), 129.02 ($C_m$-*syn*), 128.49 ($C_o$-*syn*), 124.38 ($C_p$-*anti*), 88.78 ($C_\beta$); $\delta_H$ (*Z*-isomer) 7.55–7.15 (m, 9H, $H_o$-*syn*, $H_m$-*syn*, $H_o$-*anti*, $H_m$-*anti*, $H_p$-*anti*), 6.93 (dd, 1H, $H_X$, $^3J_{AX}$=6.7 Hz, $^3J_{BX}$=14.2 Hz), 4.58 (dd, 1H, $H_B$, $^2J_{AB}$=1.9 Hz, $^3J_{BX}$=14.2 Hz), 4.12 (dd, 1H, $H_A$, $^2J_{AB}$=1.9 Hz, $^3J_{AX}$=6.7 Hz); $\delta_C$ (*Z*-isomer) 157.94 (C=N), 152.43 ($C_\alpha$), 135.17 ($C_i$-*anti*), 131.51 ($C_i$-*syn*), 131.42 ($C_m$-*syn*), 130.84 ($C_o$-*syn*), 129.98 ($C_p$-*anti*), 128.17 ($C_m$-*anti*), 128.14 ($C_o$-*anti*), 123.48 ($C_p$-*syn*), 88.78 ($C_\beta$).

**1.2.6. *O*-Vinyl(2-pyridyl)phenylketoxime (3f).** A transparent viscous liquid, $n_D^{20}$=1.6070. [Found: C 74.94; H 5.46; N 12.41. $C_{14}H_{12}N_2O$ requires C 74.98; H 5.39; N 12.49%]; $\nu_{max}$ (liquid film) 1637 ($\nu_{trans}$C=C), 1183, 1168 ($\nu$C–O), 1144, 982 ($\nu$N–O), 947 ($\delta_{trans}$=CH), 696 cm$^{-1}$; $\delta_H$ (*E*-isomer) 8.65 (d, 1H, $H_6$, $^3J_{H_5H_6}$=4.7 Hz), 7.85 (d, 1H, $H_3$, $^3J_{H_3H_4}$=7.5 Hz), 7.72 (t, 1H, $H_4$, $^3J_{H_3H_4}$=$^3J_{H_4H_5}$=7.5 Hz), 7.47 (s, 5H, $H_o$, $H_m$, $H_p$), 7.29 (dd, 1H, $H_5$, $^3J_{H_4H_5}$=7.5 Hz, $^3J_{H_5H_6}$=4.7 Hz), 7.14 (dd, 1H, $H_X$, $^3J_{AX}$=6.9 Hz, $^3J_{BX}$=14.2 Hz), 4.72 (dd, 1H, $H_B$, $^2J_{AB}$=1.9 Hz, $^3J_{BX}$=14.2 Hz), 4.22 (dd, 1H, $H_A$, $^2J_{AB}$=1.9 Hz, $^3J_{AX}$=6.9 Hz); $\delta_C$ (*E*-isomer) 158.56 (C=N), 153.85 ($C_2$), 152.58 ($C_\alpha$), 149.34 ($C_6$), 136.25 ($C_4$), 131.58 ($C_i$), 129.29 ($C_o$), 129.21 ($C_p$), 127.84 ($C_m$), 123.90 ($C_5$), 123.09 ($C_3$), 89.03 ($C_\beta$); $\delta_H$ (*Z*-isomer) 8.77 (d, 1H, $H_6$, $^3J_{H_5H_6}$=4.7 Hz), 7.80 (t, 1H, $H_4$, $^3J_{H_3H_4}$=$^3J_{H_4H_5}$=7.5 Hz), 7.57 (d, 2H, $H_o$, $^3J_{H_oH_m}$=7.4 Hz), 7.53 (d, 1H, $H_3$, $^3J_{H_3H_4}$=7.5 Hz), 7.40 (m, 1H, $H_p$), 7.37 (m, 2H, $H_m$), 7.34 (dd, 1H, $H_5$, $^3J_{H_4H_5}$=7.5 Hz, $^3J_{H_5H_6}$=4.7 Hz), 7.05 (dd, 1H, $H_X$, $^3J_{AX}$=6.7 Hz, $^3J_{BX}$=14.2 Hz), 4.68 (dd, 1H, $H_B$, $^2J_{AB}$=1.7 Hz, $^3J_{BX}$=14.2 Hz), 4.23 (dd, 1H, $H_A$, $^2J_{AB}$=1.7 Hz, $^3J_{AX}$=6.7 Hz); $\delta_C$ (*Z*-isomer) 157.92 (C=N), 152.37 ($C_\alpha$), 151.72 ($C_2$), 149.59 ($C_6$), 135.95 ($C_4$), 134.13 ($C_i$), 129.93 ($C_p$), 128.23 ($C_m$), 127.79 ($C_o$), 125.00 ($C_3$), 123.51 ($C_5$), 88.76 ($C_\beta$).

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