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ONE-POT SYNTHESIS OF 2-IMINO-1,3-OXASELENOLANES BY REACTION OF ISOSELENOCYANATES WITH 2-BROMOETHANOL

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Abstract – One-pot synthesis of 2-imino-1,3-oxaselenolanes has been achieved by reactions of isoselenocyanates with 2-bromoethanol in good to excellent yields. The structure of the 2-imino-1,3-oxaselenolanes was confirmed by spectroscopic and X-ray analysis. The thermal rearrangement of 2-imino-1,3-oxaselenolanes to 1,3-selenazolidin-2-one is observed for the first time.

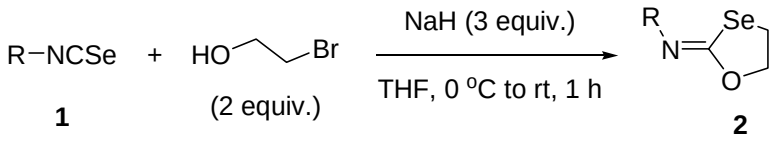
INTRODUCTION

In recent years, interest in the synthesis of compounds containing selenium has increased because of their interesting reactivities[1] and their potential biological activity. The biological and medicinal properties of selenium and organoselenium compounds are increasingly appreciated, mainly due to their antioxidant, antitumor, antimicrobial, and antiviral properties.[2] The 1,3-selenolanes have been found to have anticancer activity.[3] From the result of the investigation of structure-biological activity relationships, 1,3-selenolane skeleton bearing specific substituent groups has been indicated to influence strongly the activity. Therefore the preparation of many kinds of 1,3-selenolane derivatives has been desired for the development of potential agents. On the other hand, there are some drawbacks of the syntheses of selenium heterocycles as they often involve the use of toxic selenium reagents, which are difficult to handle and to store. In this context, isoselenocyanates have been emerged as a powerful tool for the synthesis of selenium-containing heterocycles, since they are easy to prepare and store and are safe to handle.[4] Our group has shown the utility of isoselenocyanates as building blocks for the synthesis of selenium heterocycles.[5] Recently we have reported the synthesis of 2-imono-1,3-oxaselenolanes *via* iodocyclization reaction of *O*-allylselenocarbamates,[6] whereas Kambe et al. reported the synthesis of

2-imono-1,3-selenolanes *via* intramolecular cycloaddition reaction of selenolates to carbon-carbon triple bonds.[7] By way of contrast, no report on the synthesis of 2-imono-1,3-oxaselenolanes by the reaction of 2-bromoethanol with isoselenocyanates in the literature. Herein, we report the one-pot synthesis of 2-imino-1,3-oxaselenolanes and their rearrangement to 1,3-selenazolidin-2-one.

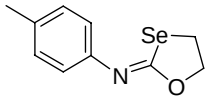
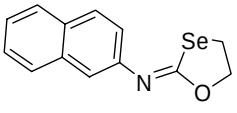
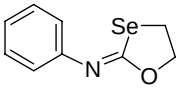
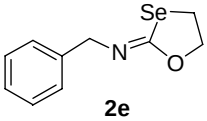
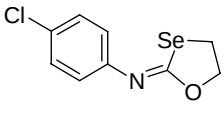
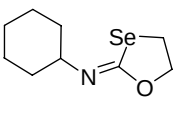
RESULTS AND DISCUSSION

The starting alkyl and aryl isoselenocyanates (**1**) for our approach were prepared by reactions of *N*-substituted formamides with an excess of triphosgene, selenium and triethylamine according to the previous literature.[8] First, the reaction of isoselenocyanates (R = *p*-CH_3-C_6H_4) **1a** with 2-bromoethanol using 1.1 equiv. of NaH in THF was examined, to our delight the reaction took place readily at room temperature and the cyclization product **2a** was obtained in 52% yield after work-up of the reaction mixture. To improve the yield of reaction, different conditions were then screened. As shown in Scheme 1, 2.0 equiv. of 2-bromoethanol was a suitable for the cyclization reaction, furthermore the reaction was influenced by the amount of base used and the best result was obtained when 3.0 equiv. of NaH was used (92%, Table 1). The structure of **2a** was elucidated by studies of IR, ^{1}H-, ^{13}C-, ^{77}Se-NMR, correlation spectroscopy (COSY), hetero-nuclear multiple quantum coherence (HMQC), hetero-nuclear multiple-bond connectivity (HMBC), MS, elemental analysis and X-ray analysis.



Scheme 1

Table 1. Reaction of isoselenocyanates with 2-bromoethanol

Product (**2**)	Yield (%)[a]	^{77}Se NMR (δ)	Product (**2**)	Yield (%)[a]	^{77}Se NMR (δ)
 **2a**	92	285.6	 **2d**	79	291.3
 **2b**	93	286.9	 **2e**	78	269.0
 **2c**	96	290.6	 **2f**	45	255.2

a: Isolated yield.

Under the similar reaction conditions, the reactions of six kinds of isoselenocyanates **1** with 2-bromoethanol gave the 2-imino-1,3-oxaselenolanes (**2**) in good to excellent yields (Table 1). Both alkyl and aryl isoselenocyanates provided the corresponding 2-imino-1,3-oxaselenolanes (**2**). The structures of products (**2b-2f**) were determined by comparing the spectral data with those of **2a**. In the ^{77}Se NMR spectra of the 1,3-oxaselenolanes **2**, ^{77}Se signals were observed in the range of δ 273.3±18.1, which are at a higher field as compared with ^{77}Se signals of selenocarbonyl compounds (δ 1420-2131).[9] The values are typical for a C-Se single bond with an sp^3 selenium atom not for a C=Se double bond with an sp^2 selenium atom.[10] Recently, Heimgartner et al. reported the synthesis of 2-imimo-1,3-oxaselenanes by the reaction of chloropropanol with the isoselenocyanates in CH_2Cl_2, in which their attempts to synthesize 2-imino-1,3-oxaselenolanes (**2**) was failed.[11] Our current report allows the synthesis of 2-imino-1,3-oxaselenolanes (**2**) in good to excellent yields.

In order to confirm the structure of **2a**, we carried out the X-Ray analysis of this compound. An ORTEP drawing, depicted in Figure 1, shows the molecular structure of the **2a**.[12] The bond angle of the selenium atom C1-Se1-C3 was 86.24(13)°, consistent with the previous reported value.[13] The bond angle the selenium atom C1-O1-C2 was 114.3(2)°. The bond length of C1-N2 in **2a** is 1.258(4) A˚ clearly shows that it is double bonds. Compound **2a** possesses an exocyclic carbon-nitrogen double bond with *Z*-configuration.

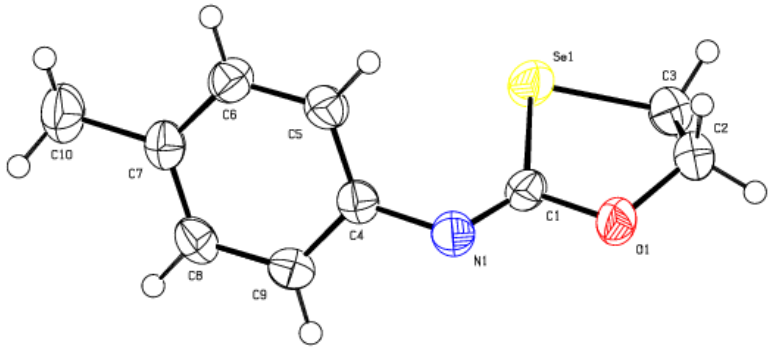
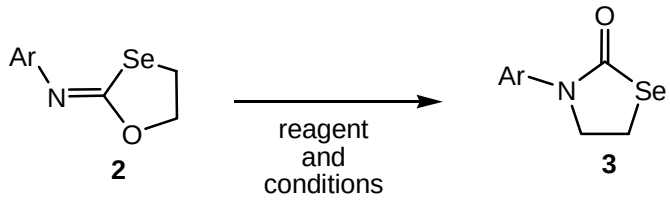


Figure 1. Crystal structure of 2-(4-methylphenyl)imino-1,3-oxaselenolane (**2a**)

Next, we attempted the thermal rearrangement of 1,3-oxaselenolane **2** (Scheme 2). The reaction of 1,3-oxaselenolane **2** in THF or toluene was carried out to get the rearranged product 1,3-selenazolidin-2-one **3** (Table 2, entries 1 and 2), but the reaction not resulted in the formation of the required product even after 4 days (entry 2). Thermal rearrangement of 2-imino-1,3-oxathiolane to 1,3-thiazolidin-2-one using Bu_3SnI was reported by Sakai *et al.*[14] But the use of Bu_3SnI in the present reaction in toluene at 80 °C for 5 days also not resulted in the formation of required product.

Indium reagent catalysed cycloisomerization reactions of enynes has recently been reported by Chatani et

al.[15] This prompted us to examine its use of indium as a catalyst in the thermal rearrangement reaction. No rearrangement reaction was observed when the In metal (1 equiv.) was used in the reaction and the 2-(4-methylphenyl)imino-1,3-oxaselenolane (**2a**) was recovered in quantitative (entry 3). When the reaction of 1,3-oxaselenolane **2** with ethyl bromoacetate (2.0 equiv.) in the presence of indium metal (2.2 equiv.) using THF as the solvent produced the rearranged product **3a** in 27 % yield (entry 4). Toluene was found to be good solvent for the rearrangement reaction (entry 5) and best results were obtained when the reaction time was shortened to 9 h (Table 2, entries 6 and 7). To the best of our knowledge there is no report on the rearrangement of 2-imino-1,3-oxaselenolane in the literature. In the present reaction indium as well as ethyl bromoacetate is needed for the rearrangement reaction.



Scheme 2

Table 2. Reaction of 1,3-oxaselenolanes **2** with indium and ethyl bromoacetate

Entry	Ar	In (equiv.)	$BrCH_2CO_2Et$ (equiv.)	Solvent	Temp.	Time	Yield (%)[a]
1	*p*-MeC_6H_4	—	—	THF	reflux	16 h	0 (**3a**)
2	*p*-MeC_6H_4	—	—	Toluene	100 °C	4 days	0 (**3a**)
3	*p*-MeC_6H_4	1.0	—	THF	reflux	26 h	0 (**3a**)
4	*p*-MeC_6H_4	2.2	2.0	THF	reflux	24 h	27 (**3a**)[b]
5	*p*-MeC_6H_4	2.2	2.0	Toluene	100 °C	24 h	26 (**3a**)
6	*p*-MeC_6H_4	2.2	2.0	Toluene	100 °C	9 h	30 (**3a**)
7	C_6H_5	2.2	2.0	Toluene	100 °C	9 h	37 (**3b**)

[a]Isolated yield. [b]Reaction results are not consistant.

In conclusion, we have demonstrated one-pot synthesis of 2-imino-1,3-oxaselenolane (**2**) by reactions of the isoselenocyanates (**1**) with 2-bromoethanol. The rearrangement of 2-imino-1,3-oxaselenolanes (**2**) to 1,3-selenazolidin-2-one (**3**) is observed for the first time. Further expansion of current strategies is in progress.

EXPERIMENTAL

General

The chemical shifts of ^{77}Se NMR were expressed in ppm deshielded with respect to neat Me_2Se in $CDCl_3$. $^2J(^{77}Se\text{-}^1H)$ values are the satellites of the ^{1}H NMR spectra. Melting points were measured by a Yanagimoto micromelting point apparatus (uncorrected).

General procedure for the synthesis of 2-(4-methylphenyl)imino-1,3-oxaselenolane (2a) To a stirred solution of NaH (60%, 59.5 mg, 1.49 mmol) in dry THF (1.5 mL) was added 4-methylphenyl isoselenocyanate (98.1 mg, 0.50 mmol) at 0 °C. After 10 min 2-bromoethanol (95%, 74.5 μL, 1.00 mmol) was added and stirring was continued for 1 h at rt. The reaction mixture was quenched with saturated aqueous NH_4Cl solution, extracted with Et_2O, washed with water and brine. The combined organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with Et_2O / *n*-hexane (1/1) as the eluent to give **2a** (110.5 mg, yield 92%) mp (n-Hexane/EtOAc) 95 °C; IR (KBr): 1646, 1503 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (3H, s, CH_3) 3.43 (2H, t, *J* = 6.4 Hz, $^2J(^{77}Se\text{-}^1H)$ = 26.1 Hz, CH_2), 4.50 (2H, t, *J* = 6.4 Hz, CH_2), 6.85 (2H, d, *J* = 8.2 Hz, Ar), 7.12 (2H, d, *J* = 8.2 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9 (q), 26.6 (t), 71.1 (t), 120.6 (d), 129.8 (d), 134.0 (s), 148.0 (s), 162.2 (s); ^{77}Se NMR (95 MHz, $CDCl_3$): δ 285.2; MS (EI): *m/z* = 241 [M^+]; Anal. Calcd for $C_{10}H_{11}NOSe$: C, 50.01; H, 4.62; N, 5.83. Found: C, 49.65; H, 4.64; N, 5.79.

2-Phenylimino-1,3-oxaselenolane (2b) mp (n-Hexane/EtOAc) 91 °C; IR (KBr): 1651, 1590 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.44 (2H, t, *J* = 6.4 Hz, $^2J(^{77}Se\text{-}^1H)$ = 24.7 Hz, CH_2), 4.51 (2H, t, *J* = 6.4 Hz, CH_2), 6.97 (2H, dd, *J* = 7.8, 7.8 Hz, Ar), 7.15 (1H, t, *J* = 7.8 Hz, Ar), 7.33 (2H, t, *J* = 7.8 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6 ($^1J(^{77}Se\text{-}^{13}C)$ = 54.6 Hz, t), 71.0 (t), 120.6 (d), 124.3 (d), 129.0 (d), 150.3 (s), 162.4 (s); ^{77}Se NMR (95 MHz, $CDCl_3$): δ 286.9; MS (EI): *m/z* = 227 [M^+]; Anal. Calcd for C_9H_9NOSe: C, 47.80; H, 4.01; N, 6.19. Found: C, 47.46; H, 3.83; N, 6.17.

2-(4-Chlorophenyl)imino-1,3-oxaselenolane (2c) mp (n-Hexane/EtOAc) 97 °C; IR (KBr): 1645, 1589, 841 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.44 (2H, t, *J* = 6.4 Hz, $^2J(^{77}Se\text{-}^1H)$ = 24.6 Hz, CH_2), 4.50 (2H, t, *J* = 6.4 Hz, CH_2), 6.88 (2H, d, *J* = 8.7 Hz, Ar), 7.27 (2H, d, *J* = 8.7 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.8 ($^1J(^{77}Se\text{-}^{13}C)$ = 53.6 Hz, t), 71.3 (t), 122.2 (d), 129.2 (d), 129.7 (s), 148.9 (s), 163.1 (s); ^{77}Se NMR (95 MHz, $CDCl_3$): δ 290.6; MS (EI): *m/z* = 261 [M^+]; Anal. Calcd for $C_9H_8ClNOSe$: C, 41.48; H, 3.09; N, 5.38. Found: C, 41.29; H, 3.16; N, 5.31.

2-(2-Naphthyl)imino-1,3-oxaselenolane (2d) mp (n-Hexane/EtOAc) 106 °C; IR (KBr): 1653, 1619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (2H, t, *J* = 6.4 Hz, $^2J(^{77}Se\text{-}^1H)$ = 25.7 Hz, CH_2), 4.55 (2H, t, *J* = 6.4 Hz, CH_2), 7.16 (1H, dd, *J* = 1.9, 8.7 Hz, Ar), 7.34 (1H, s, Ar), 7.38-7.48 (2H, m, Ar), 7.75-7.83 (3H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.7 (t), 71.3 (t), 116.7 (d), 121.9 (d), 124.9 (d), 126.2 (d), 127.5 (d), 127.7 (d), 129.2 (d), 131.0 (s), 134.1 (s), 148.4 (s), 162.8 (s); ^{77}Se NMR (95 MHz, $CDCl_3$): δ 291.3; MS (EI): *m/z* = 277 [M^+]; Anal. Calcd for $C_{13}H_{11}NOSe$: C, 56.53; H, 4.01; N, 5.07. Found: C, 56.09; H, 4.00;

N, 5.12.

2-Benzylimino-1,3-oxaselenolane (2e) Yellow oil; IR (KBr): 1666, 1560 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.42 (2H, t, *J* = 6.4 Hz, $^2J(^{77}Se\text{-}^1H)$ = 23.4 Hz, CH_2), 4.30 (2H, s, CH_2), 4.32 (2H, t, *J* = 6.4 Hz, CH_2), 7.20-7.35 (5H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.1 ($^1J(^{77}Se\text{-}^{13}C)$ = 47.9 Hz, t), 60.8 (t), 70.1 (t), 126.8 (d), 127.5 (d), 128.2 (d), 139.0 (s), 160.8 (s); ^{77}Se NMR (95 MHz, $CDCl_3$): δ 269.0; MS (EI): *m/z* = 241 [M^+]; Anal. Calcd for $C_{11}H_{12}N_2Se$: C, 50.10; H, 4.62; N, 5.83. Found: C, 49.63; H, 4.97; N, 5.76.

2-Cyclohexylimino-1,3-oxaselenolane (2f) Colorless oil; IR (KBr): 1669, 1544 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.16-1.47 (5H, m, ringCH_2), 1.57-1.65 (1H, m, ringCH), 1.70-1.80 (4H, m, ringCH_2), 2.46-2.54 (1H, m, ringCH), 3.42 (2H, t, *J* = 6.4 Hz, $^2J(^{77}Se\text{-}^1H)$ = 25.7 Hz, CH_2), 4.29 (2H, t, *J* = 6.4 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6 (t), 25.5 (t), 26.5 (t), 33.7 (t), 67.2 (d), 69.5 (t), 157.0 (s); ^{77}Se NMR (95 MHz, $CDCl_3$): δ 255.2; MS (EI): *m/z* = 233 [M^+]; Anal. Calcd for $C_9H_{15}NOSe$: C, 46.56; H, 6.51; N, 6.03. Found: C, 46.50; H, 6.56; N, 5.87.

General procedure for the synthesis of 3-(4-Methylphenyl)-1,3-selenazolidin-2-one (3a) To a stirred solution of 2-(4-methylphenyl)imino-1,3-oxaselenolane **(2a)** (48.6 mg, 0.20 mmol) in toluene (2 mL) was added indium (51.2 mg, 0.44 mmol) and ethyl bromoacetate (44.3 μL, 0.40 mmol) at rt and stirring was continued for 9 h at 100 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and filtered through bed of celite, extracted with CH_2Cl_2. The combined organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with EtOAc / *n*-hexane (1/10) as the eluent to give **3a** (14.4 mg, yield 30%) mp (n-Hexane/EtOAc) 97 °C; IR (KBr): 1667, 1544 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.33 (3H, s, CH_3), 3.44 (2H, t, *J* = 6.9 Hz, $^2J(^{77}Se\text{-}^1H)$ = 25.7 Hz, CH_2), 4.09 (2H, t, *J* = 6.9 Hz, CH_2), 7.17 (2H, d, *J* = 8.2 Hz, Ar), 7.22 (2H, d, *J* = 8.2 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7 (t), 20.9 (q), 52.7 (t), 123.2 (d), 129.6 (t), 135.9 (s), 136.8 (s), 168.9 (s); ^{77}Se NMR (95 MHz, $CDCl_3$): δ 323.2; MS (EI): *m/z* = 241 [M^+]; Anal. Calcd for $C_{10}H_{11}NOSe$: C, 50.01; H, 4.62; N, 5.83. Found: C, 50.05; H, 4.69; N, 5.76.

3-Phenyl-1,3-selenazolidin-2-one (3b) mp (n-Hexane/EtOAc) 72 °C; IR (KBr): 1662 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.45 (2H, t, *J* = 6.8 Hz, $^2J(^{77}Se\text{-}^1H)$ = 26.6 Hz, CH_2), 4.13 (2H, t, *J* = 6.4 Hz, CH_2), 7.18-7.2 (1H, m, Ar), 7.33-7.40 (4H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7 (t), 52.4 (t), 123.1 (d), 125.9 (d), 129.1 (d), 139.4 (s), 169.0 (s); ^{77}Se NMR (95 MHz, $CDCl_3$): δ 326.4; MS (EI): *m/z* = 227 [M^+]; Anal. Calcd for C_9H_9NOSe: C, 47.80; H, 4.01; N, 6.19. Found: C, 48.15; H, 4.26; N, 5.97.

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REFERENCES

1. A. Ogawa and N. Sonoda, In *Comprehensive Organic Synthesis*; ed. by B. M. Trost and Fleming, Pergamon Press: Oxford, 1991; Vol. 6, p. 461; A. Ogawa and N. Sonoda, *Rev. Heteroat. Chem*., 1994, **10**, 43; F. S. Guziec Jr. and L. J. Guziec, In *Comprehensive Organic Functional Group Transformations*; ed. by A. R. Katritzky, O. Meth-Cohn, and C. W. Rees, Pergamon: Oxford, 1995; Vol. 6, p. 587; C. P. Dell, In *Comprehensive Organic Functional Group Transformations*; ed. by A. R. Katritzky, O. Meth-Cohn, and C. W. Rees, Pergamon: Oxford, 1995; Vol. 5, p. 565; A. Krief, In *Comprehensive Organometallic Chemistry*; ed. by W. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon: Oxford, 1995; Vol. 11, p. 515; *Organoselenium Chemistry: A Practical Approach*; ed. by T. G. Back, Oxford University Press: Oxford, 1999.
2. M. Koketsu, H. Ishihara, W. Wu, K. Murakami, and I. Saiki, *Eur. J. Pharm. Sci.*, 1999, **9**, 157; W. Wu, K. Murakami, M. Koketsu, Y. Yamada, and I. Saiki, *Anticancer Res*., 1999, **19**, 5375; S. I. Cho, M. Koketsu, H. Ishihara, M. Matsushita, A. C. Nairn, H. Fukazawa, and Y. Uehara, *Biochim. Biophys. Acta*, 2000, **1475**, 207; G. Mugesh, W.-W. du Mont, and H. Sies, *Chem. Rev*., 2001, **101**, 2125; T. G. Back and Z. Moussa, *J. Am. Chem. Soc*., 2003, **125**, 13455; K. B. Gutzkow, H. U. Låhne, S. Naderi, K. M. Torgersen, B. Skålhegg, M. Koketsu, Y. Uehara, and H. K. Blomhoff, *Cell. Signal*., 2003, **15**, 871; A. Nishina, A. Sekiguchi, R. Fukumoto, M. Koketsu, and S. Furukawa, *Biochem. Biophys. Res. Commun*., 2007, **352**, 360; K.-N. Nam, M. Koketsu, and E. H. Lee, *Eur. J. Pharmacol*., 2008, **589**, 53.
3. J. Du, S. Surzhykov, J. S. Lin, M. G. Newton, Y. C. Cheng, R. F. Schinazi, and C. K. Chu, *J. Med. Chem*., 1997, **40**, 2991; C. K. Chu, L. Ma, S. Olgen, C. Pierra, J. Du, G. Gumina, E. Gullen, Y. C. Cheng, and R. F. Schinazi, *J. Med. Chem*., 2000, **43**, 3906.
4. See the review: D. R. Garud, M. Koketsu, and H. Ishihara, *Molecules*, 2007, **12**, 504.
5. M. Koketsu, Y. Yamamura, and H. Ishihara, *Heterocycles*, 2006, **68**, 1191; M. Koketsu, Y. Yamamura, H. Ando, and H. Ishihara, *Heterocycles*, 2006, **68**, 1267; M. Koketsu, T. Otsuka, and H. Ishihara, *Heterocycles*, 2006, **68**, 2107; M. Koketsu, T. Sakai, T. Kiyokuni, D. R. Garud, H. Ando, and H. Ishihara, *Heterocycles*, 2006, **68**, 1607; M. Koketsu, Y. Yamamura, and H. Ishihara, *Synthesis*, 2006, 2738; M. Koketsu, A. Takahashi, and H. Ishihara, *J. Heterocycl. Chem*., 2007, **44**, 79; M. Koketsu, T. Otsuka, D. Swenson, and H. Ishihara, *Org. Biomol. Chem*., 2007, **5**, 613; D. R. Garud and M. Koketsu, *Org. Lett.*, 2008, **10**, 3319.
6. D. R. Garud, M. Makimura, H. Ando, H. Ishihara, and M. Koketsu, *Tetrahedron Lett*., 2007, **48**, 7764.
7. Y. Asanuma, S. Fujiwara, T. Shin-ike, and N. Kambe, *J. Org. Chem*., 2004, **69**, 4845.

8. D. H. R. Barton, S. I. Parekh, M. Tajbakhsh, E. A. Theodorakis, and C.-L. Tse, *Tetrahedron*, 1994, **50**, 639.
9. T. Murai, K. Kakami, A. Hayashi, T. Komuro, H. Takada, M. Fujii, T. Kanda, and S. Kato, *J. Am. Chem. Soc.*, 1997, **119**, 8592; T. C. Wong, F. S. Guziec Jr., and C. A. Moustakis, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1471; E. R. Cullen, F. S. Guziec Jr., C. J. Murphy, T. C. Wong, and K. K. Andersen, *J. Am. Chem. Soc.*, 1981, **103**, 7055.
10. T. C. Wong and E. M. Engler, *J. Mol. Struct.*, 1980, **67**, 279; J. R. Bartels-Keith, M. T. Burgess, and J. M. Stevenson, *J. Org. Chem.*, 1977, **42**, 3725; M. Garreau, G. J. Martin, M. L. Martin, J. Morel, and C. Paulmier, *Org. Magn. Reson.*, 1974, **6**, 648.
11. G. L. Sommen and H. Heimgartner, *Pol. J. Chem.*, 2007, **81**, 1413.
12. CCDC 679392 for **2a** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.
13. V. Barba, C. Hernandez, S. Rojas-Lima, N. Farfan, and R. Santillan, *Can. J. Chem.*, 1999, **77**, 2025.
14. S. Sakai, H. Niimi, Y. Kobayashi, and Y. Ishii, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 3271.
15. Y. Miyanohana and N. Chatani, *Org. Lett.*, 2006, **8**, 2155.