Facile Regioselective Synthesis of 5-Hydroxy-4,5-dihydroisoxazoles from Acetylenic Ketones

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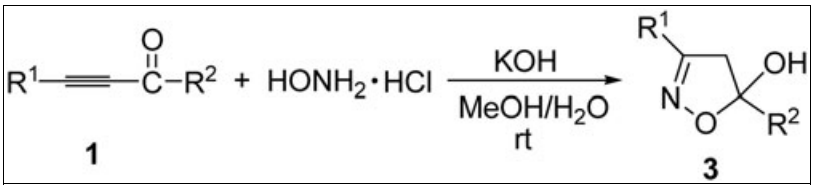

5-Hydroxy-4,5-dihydroisoxazoles were synthesized conveniently in good yields by tandem conjugate addition-cyclization reaction of acetylenic ketones and hydroxylamine hydrochloride salt.

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INTRODUCTION

In recent years, considerable efforts have been prompted toward the synthesis of heterocycles because many of them are biologically active and have found applications as pharmaceuticals [1]. 4,5-Dihydroisoxazoles are important heterocycles in medicinal chemistry. They are important constituent of a variety of biologically active molecules such as the antitumor drug Acivicin and the antithrombotic agent DMP802 [2]. In organic chemistry, they are highly useful synthetic intermediates due to the fact that the N–O bond can be cleaved under mild reducing conditions. For example, cleavage of 4,5-dihydroisoxazole can give rise to several useful synthetic units such as β-hydroxyketones, β-hydroxynitriles, γ-amino alcohols, and α,β-unsaturated oximes [3]. Therefore, many synthetic methods have been developed to prepare 4,5-dihydroisoxazoles. Among them, the 1,3-dipolar cycloaddition of nitrile oxides to olefins [4] and the reaction of α,β-unsaturated-ketones with hydroxylamine [5] are most common synthetic methods. However, these transformations have some disadvantages arising from the dimerization of nitrile oxide and the poor cycloaddition regioselectivity. Thus, the development of facile and regioselective methods for the synthesis of this kind of compounds is an area of considerable ongoing interest and significant effort continues to be directed toward the new methods for their construction. Recently, She et al. prepared 4,5-dihydroisoxazole regioselectively from the reaction of α,β-unsaturated ketones with *N*-hydroxyl-4-toluenesulfonamide [6]. Knight et al. reported the synthesis of 4,5-dihydroisoxazoles by silver nitrate-catalyzed intramolecular cyclization of *O*-propargylic hydroxylamines [7]. Mosher et al. reported the synthesis of differently substituted 4,5-dihydroisoxazoles by the cyclization of β,γ-unsaturated oximes under different reaction conditions [8].

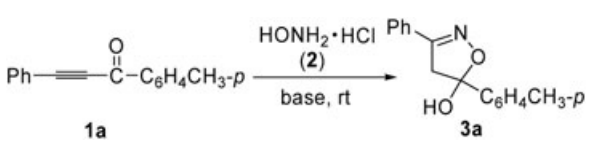
Acetylenic ketones are useful compounds in organic synthesis. Perumal et al. [9] recently reported stepwise synthesis of isoxazoles by oximation of acetylenic ketones and a subsequent gold-catalyzed cycloisomerization of the resulting α,β-acetylenic oximes. Müller et al. [10] synthesized isoxazoles from 1,3-dipolar cycloaddition of acetylenic ketones and nitrile oxides. However, to the best of our knowledge, one pot synthesis of 4,5-dihydroisoxazole directly from the reaction of acetylenic ketones with hydroxylamine has not been reported. Herein,we wish to report a facile regioselective procefor the synthesis of 5-hydroxyl-4,5-dihydroisoxazoles by one-pot tandem conjugate addition-cyclization reaction of acetylenic ketones and hydroxylamine hydrochloride salt.

RESULTS AND DISCUSSION

Initially, the reaction of 1-(*p*-methylphenyl)-3-phenyl-2-propyn-1-one (**1a**) with excess hydroxylamine hydrochloride salt (**2**) was investigated and the results are summarized in Table 1. The results show that **3a** was obtained in 52% yield when **1a** react with 2 equiv **2** in methanol for 24 h in the presence of potassium hydroxide (2 equiv). Gratifyingly, the desired product **3a** was obtained in 93% yield when 4 equiv hydroxylamine hydrochloride salts and potassium hydroxide were used. The yield of **3a** was increased to 98%, and the reaction time was dramatically decreased to 8 h when a small amount of water was added to methanol (entry 4, Table 1). Using sodium hydroxide or potassium carbonate as bases resulted in lower yields (entries 5 and 6, Table 1). Further investigations show that the solvents have apparent effect on the

Table 1

Reaction of acetylenic ketone **1a** with hydroxylamine hydrochloride salt **2**.



1a **3a**

Entry	Molar ratio of 2:1	Base	Solvent	Yield[a]
1	2	KOH	MeOH	52
2	3	KOH	MeOH	82
3	4	KOH	MeOH	93
4[b]	4	KOH	MeOH/H_2O	98
5[b]	4	NaOH	MeOH/H_2O	91
6[b]	4	K_2CO_3	MeOH/H_2O	86
7	4	KOH	EtOH	24
8	4	KOH	CH_2Cl_2	28
9[c]	4	KOH	Toluene	0
10	4	KOH	THF	34

[a]Isolated yields based on **1a**.
[b]MeOH/H_2O (v/v) = 9/1.
[c]No reaction was happened and the starting material was recovered.

reaction. Among various solvents tested, methanol/H_2O was the most suitable (entries 7–10, Table 1). Therefore, the general reaction conditions were 1.0 equiv of acetylenic ketone **1**, 4.0 equiv of hydroxylamine hydrochloride salt **2**, and 4.0 equiv of potassium hydroxide in methanol/H_2O (v/v 9:1) at room temperature.

With the optimal reaction conditions in hand, we next examined the scope and generality of the reaction. The results are compiled in Table 2.

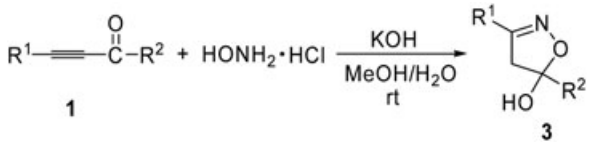
As shown in Table 2, various 3,5-disubstituted 5-hydroxyl-4,5-dihydroisoxazoles can be readily synthesized in good to excellent yields from acetylenic ketones and hydroxylamine hydrochloride salt. R^1 can be phenyl or *n*-butyl. R^2 can be phenyl, electron-rich phenyl or electron-poor phenyl. All products were characterized by spectral data and the molecular structure of compound **3a** was further confirmed by X-ray diffraction analysis (Fig. 1) [11]. However, no reaction occurred under the same reaction conditions when hydroxylamine was replaced by *N*-methylhydroxylamine and a complex mixture was obtained when R^2 is an alkyl group.

The plausible mechanism was suggested as following (Scheme 1): first, conjugate addition adduct **I** was formed through the reaction of hydroxylamine and acetylenic ketone; then intramolecular cyclization of **I** generated intermediate **II**; finally, product **3** was obtained by the isomerization of the enamine **II** to the more stable imine. The reaction is highly regioselective and no regioisomers were formed in all cases.

In summary, a regioselective synthesis of 5-hydroxy-4,5-dihydroisoxazoles from direct reaction of acetylenic ketones with hydroxylamine hydrochloride salt was

Table 2

Synthesis of 5-hydroxy-4,5-dihydroisoxazoles.



1 **3**

Entry	R^1	R^2	Product	Yield (%)[a]
1	Ph	*p*-$CH_3C_6H_4$	**3a**	98
2	Ph	Ph	**3b**	87
3	Ph	*p*-BrC_6H_4	**3c**	83
4	Ph	*p*-ClC_6H_4	**3d**	95
5	Ph	*p*-$O_2NC_6H_4$	**3e**	81
6	Ph	*p*-$CH_3OC_6H_4$	**3f**	85
7	Ph	2,4-$(CH_3O)_2C_6H_3$	**3g**	84
8	Ph	2,4-$Cl_2C_6H_3$	**3h**	92
9	*n*-C_4H_9	*p*-$O_2NC_6H_4$	**3i**	75
10	*n*-C_4H_9	Ph	**3j**	78
11	*n*-C_4H_9	*p*-$CH_3C_6H_4$	**3k**	81

[a]Isolated yield based on **1**.

reported. The procedure involves tandem conjugate addition, intramolecular cyclization and isomerization. The method has the advantages such as readily available starting materials, mild reaction conditions, high efficiency and high regioselectivity.

EXPERIMENTAL

All reagents and solvents were purchased from commercial sources and were used without further purification. All solid products were recrystallized from ethyl acetate and hexane, and the melting points were obtained with a XT4A micromelting point apparatus and uncorrected. Infrared spectra were recorded as KBr plates on an FT IR-8400 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker Avance 300 MHz NMR spectrometer in $CDCl_3$ or in DMSO-d_6. HRMS (EI, 70 eV) were determined on a CA 064 mass spectrometer. X-ray crystallographic analysis was carried out on a Bruker SMART 1000 CCD diffractometer. Acetylenic ketones were prepared according to literature procedures [12].

General procedure for the synthesis of 5-hydroxy-4,5-dihydroisoxazoles 3. To a solution of acetylenic ketone (0.5 mmol) and hydroxylamine hydrochloride salt (2.0 mmol) in 4.0 mL methanol/water (v:v = 9:1) was added potassium hydroxide (2.0 mmol) at room temperature. The reaction mixture was stirred at room temperature and the progress was monitored by TLC. When the reaction was completed, the reaction

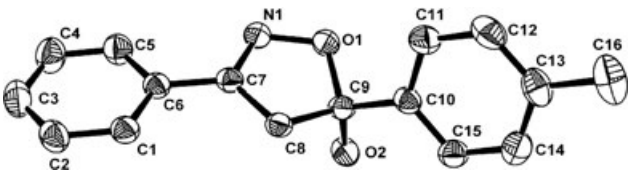
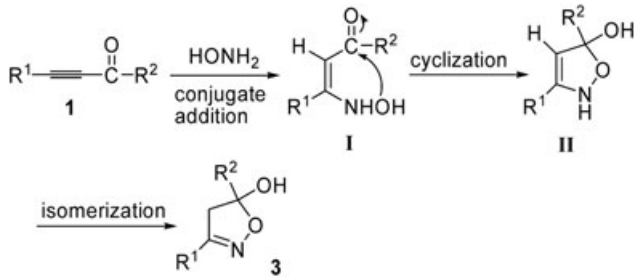


Figure 1. The molecular structure of compound **3a**.

Scheme 1. Plausible mechanism.



mixture was added 5 mL saturated ammonium chloride and extracted with ethyl acetate (3 × 10 mL). The organic extract was combined and dried over anhydrous sodium sulfate. The crude product was purified by flash chromatography on silica gel (10/1 hexane/ethyl acetate) to afford products **3**.

3-Phenyl-5-p-tolyl-4,5-dihydroisoxazol-5-ol (3a). White solid, mp 176−177 °C; IR (KBr): ν (cm^{-1}) 3300, 1595, 1446, 1045; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.77−7.66 (m, 2H), 7.53 (d, J = 7.7 Hz, 2H), 7.45−7.28 (m, 3H), 7.23−7.20 (m, 2H), 3.66 (d, J = 17.4 Hz, 1H), 3.46 (d, J = 17.4 Hz, 1H), 3.17 (s, 1H), 2.37 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.4, 138.7, 137.7, 130.3, 129.2, 129.1, 128.7, 126.7, 125.4, 107.5, 48.8, 21.1; HRMS (EI) calcd for $C_{16}H_{15}NO_2$ [M^+]: 253.1103, found: 253.1111.

3,5-Diphenyl-4,5-dihydroisoxazol-5-ol (3b). White solid, mp 172−173°C; IR (KBr): ν (cm^{-1}) 3309, 1597, 1448, 1043; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67−7.64 (m, 4H), 7.50−7.31 (m, 6H), 3.68 (d, J = 17.4 Hz, 1H), 3.48 (d, J = 17.4 Hz, 1H), 3.26 (s, 1H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 157.0, 142.2, 130.4, 130.0, 129.1, 128.5, 128.4, 126.9, 126.1, 107.9, 48.8; HRMS (EI) calcd for $C_{15}H_{13}NO_2$ [M^+]: 239.0946, found: 239.0939.

5-(4-Bromophenyl)-3-phenyl-4,5-dihydroisoxazol-5-ol (3c). White solid, mp 204−205°C; IR (KBr): ν (cm^{-1}) 3269, 1595, 1446, 1039; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71−7.67 (m, 2H), 7.54 (s, 4H), 7.44−7.42 (m, 3H), 3.68 (d, J = 17.4 Hz, 1H), 3.45 (d, J = 17.4 Hz, 1H), 3.15 (s, 1H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 157.2, 141.7, 131.5, 130.6, 129.9, 129.3, 128.6, 127.0, 122.0, 107.6, 48.8; HRMS (EI) calcd for $C_{15}H_{12}BrNO_2$ [M^+] (^{79}Br): 317.0051, found: 317.0056.

5-(4-Chlorophenyl)-3-phenyl-4,5-dihydroisoxazol-5-ol (3d). White solid, mp 204−206°C; IR (KBr): ν (cm^{-1}) 3273, 1598, 1446, 1045; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.45−7.27 (m, 3H), 7.26 (s, 2H), 3.68 (d, J = 17.4 Hz, 1H), 3.46 (d, J = 17.4 Hz, 1H), 3.25 (s, 1H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 157.1, 141.2, 133.3, 130.5, 129.9, 129.2, 128.4, 128.2, 126.9, 107.5, 48.8; HRMS (EI) calcd for $C_{15}H_{12}ClNO_2$ [M^+] (^{35}Cl): 273.0557, found: 273.0553.

5-(4-Nitrophenyl)-3-phenyl-4,5-dihydroisoxazol-5-ol (3e). >Yellow solid, mp: 155−157°C; IR (KBr): ν (cm^{-1}) 3228, 1660, 1517, 1450, 1346, 1037; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.26 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.75−7.67 (m, 2H), 7.50−7.32 (m, 3H), 3.74 (d, J = 17.5 Hz, 1H), 3.51-3.46 (m, 2H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 157.3, 148.8, 147.7, 130.8, 129.3, 129.2, 127.7 126.9, 123.7, 107.1, 48.7; HRMS (EI). calcd for $C_{15}H_{12}N_2O_4$ [M^+]: 284.0797, found: 284.0802.

5-(4-Methoxyphenyl)-3-phenyl-4,5-dihydroisoxazol-5-ol (3f). White solid, mp 156−158°C; IR (KBr): ν (cm^{-1}) 3278, 1614, 1462, 1031; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 3.9 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.42 (s, 3H), 6.93 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H), 3.66 (d, J = 17.4 Hz, 1H), 3.46 (d, J = 17.4 Hz, 1H), 3.20 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.8, 157.4, 132.7, 130.3, 129.2, 128.7, 126.9, 126.7, 113.7, 107.6, 55.2, 48.8; HRMS (EI): calcd for $C_{16}H_{15}NO_3$ [M^+]: 269.1052, found: 269.1057.

5-(3,4-Dimethoxyphenyl)-3-phenyl-4,5-dihydroisoxazol-5-ol (3g). White solid, mp 134−135 °C; IR (KBr): ν (cm^{-1}) 3506, 1591, 1456, 1022; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.72−7.68 (m, 2H), 7.44−7.41 (m, 3H), 7.23-7.15 (m, 2H), 6.89 (d, J = 8.4 Hz, 1H), 3.91 (s, 6H), 3.66 (d, J = 17.4 Hz, 1H), 3.47 (d, J = 17.4 Hz, 1H), 3.24 (s, 1H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 157.1, 149.0, 148.6, 134.5, 130.4, 130.1, 129.2, 126.9, 118.6, 111.5, 110.0, 107.9, 55.9, 55.8, 48.6; HRMS (EI) calcd for $C_{17}H_{17}NO_4$ [M^+]: 299.1158, found: 299.1152.

5-(2,4-Dichlorophenyl)-3-phenyl-4,5-dihydroisoxazol-5-ol (3h). White solid, mp 158−160 °C; IR (KBr): ν (cm^{-1}) 3190, 1587, 1465, 1020; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.87 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 4.3 Hz, 2H), 7.47−7.44(m, 4H), 7.31−7.28 (m, 1H), 3.83 (d, J = 17.7 Hz, 1H), 3.70 (d, J = 17.7 Hz, 1H), 3.45 (s, 1H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 157.0, 138.0, 134.3, 133.12, 130.6, 130.5, 123.0, 129.6, 129.2, 127.2, 126.9, 106.1, 47.1; HRMS (EI) calcd for $C_{15}H_{11}Cl_2NO_2$ [M^+](^{35}Cl): 307.0167, found: 307.0162.

3-Butyl-5-(4-nitrophenyl)-4,5-dihydroisoxazol-5-ol (3i). Yellow solid, mp: 68−70 °C; IR (KBr): ν (cm^{-1}) 3167, 1600, 1454, 1028; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.23 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 3.36 (s, 1H), 3.27 (d, J = 17.7 Hz, 1H), 3.06 (d, J = 17.7 Hz, 1H), 2.43 (t, J = 6.9 Hz, 2H), 1.63–1.59 (m, 2H), 1.44–1.39 (m, 2H), 0.94 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.3, 147.9, 147.7, 126.8, 123.5, 105.7, 51.4, 28.2, 27.3, 22.2, 13.6; HRMS (EI) calcd for: $C_{13}H_{16}N_2O_4$ [M^+]: 264.1110, found: 264.1104.

3-Butyl-5-phenyl-4,5-dihydroisoxazol-5-ol (3j). White solid, mp: 122–124°C; IR (KBr): ν (cm^{-1}) 3238, 2953, 1469, 1444, 1049; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67−7.64 (m, 2H), 7.42−7.36 (m, 3H), 3.49 (d, J = 17.5 Hz, 1H), 3.21 (d, J = 17.5 Hz, 1H), 1.84 (m, 2H), 1.46-1.35 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.0, 130.1, 129.5, 128.5, 126.5, 102.6, 39.4, 35.0, 25.9, 22.8, 13.9; HRMS (EI) calcd for $C_{13}H_{17}NO_2$ [M^+]: 219.1259, found: 219.1276.

3-Butyl-5-p-tolyl-4,5-dihydroisoxazol-5-ol (3k). White solid, m. p. 82–83°C; IR (KBr): ν (cm^{-1}) 3460, 3242, 2953, 1597, 1419, 1047; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.54 (d, J = 8.2 Hz, 2H), 7.2 (m, 2H), 3.45 (d, J = 17.5 Hz, 1H), 3.19 (d, J = 17.5 Hz, 1H), 2.37 (s, 3H), 1.86–1.82 (m, 2H), 1.46–1.28 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.0, 140.3, 129.2, 126.7, 126.5, 102.4, 39.6, 34.9, 25.9, 22.8, 21.4, 13.9; HRMS (EI) calcd for $C_{14}H_{19}NO_2$ [M^+]: 233.1416, found: 233.1421.

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REFERENCES AND NOTES

[1] (a) Gulevich, A. V.; Zhdanko, A. G.; Orru, R. V. A.; Nenajdenko, V. G. Chem Rev 2010, 110, 5235; (b) Álvarez-Corral, M.; Munoz-Dorado, M.; Rodríguez-García, I. Chem Rev 2008, 108, 3174.

[2] (a) Mouradzadegun, A.; Dianat S. J Heterocycl Chem 2009, 46, 778; (b) Antczak, C.; Bauvois, B.; Monneret, C.; Florent, J.-C. Bioorg Med Chem 2001, 9, 2843; (c) Hwang, I. T.; Kim, H. R.; Jeon, D. J.; Hong,

K. S.; Song, J. H.; Cho, K. Y. J Agric Food Chem 2005, 53, 8639; (d) Olson, R. E.; Sielecki, T. M.; Wityak, J.; Pinto, D. J.; Batt, D. G.; Frietze, W. E.; Liu, J.; Tobin, A. E.; Orwat, M. J.; Di Meo, S. V.; Houghton, G. C.; Lalka, G. K.; Mousa, S. A.; Racanelli, A. L.; Hausner, E. A.; Kapil, R. P.; Rabel, S. R.; Thoolen, M. J.; Reilly, T. M.; Anderson, P. S.; Wexler, R. R. J Med Chem 1999, 42, 1178.

[3] (a) Kim, D.; Lee, J.; Shim, P. J.; Lim, J. I.; Jo, H.; Kim, S. J Org Chem 2002, 67, 764; (b) Bode, J. W.; Carreira, E. M. J Org Chem 2001, 66, 6410; (c) Kambe, M.; Arai, E.; Suzuki, M.; Tokuyama, H.; Fukuyama, T. Org Lett 2001, 3, 2575; (d) Nicolaou, K. C.; Dai, W. M.; Guy, R. K. Angew Chem Int Ed Engl 1994, 33, 15; (e) Kozikowski, A. P. Acc Chem Res 1984, 17, 410.

[4] (a) Bujak, P.; Krompiec, S.; Malarz, J.; Krompiec, M.; Filapek, M.; Danikiewicz, W.; Kania, M.; Gębarowska, K.; Grudzka, I. Tetrahedron 2010, 66, 5972; (b) De Almeida, V. M.; Dos Santos, R. J.; Da Silva Góes, A. J.; De Lima, J. G.; Correia, C. R. D.; De Faria, A. R. Tetrahedron Lett 2009, 50, 684; (c) Feuer, H. Nitrile Oxides, Nitrones, and Nitronates in Organic Synthesis; Wiley-Interscience: New Jersey, 2007; (d) Cecchi, L.; De Sarlo, F.; Machetti, F. Synlett 2007, 2451; (e) Gothelf, K. V.; Jorgensen, K. A. Chem Rev 1998, 98, 863.

[5] (a) Matoba, K.; Kawai, H.; Furukawa, T.; Kusuda, A.; Tokunaga, E.; Nakamura, S.; Shiro, M.; Shibata, N. Angew Chem Int Ed Engl 2010, 49, 5762; (b) Kumar, V.; Aggarwal, R.; Singh, S. P. J Fluorine Chem 2006, 127, 880; (c) Sutharchanadevi, M.; Muragan, R. In Comprehensive Heterocyclic Chemistry II; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V., Eds.; Pergamon Press: Oxford, 1996; Vol. 6, p 221; (d) Lang, S. A.; Lin, Y. I. In Comprehensive Heterocyclic Chemistry; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon Press: Oxford, 1984.

[6] Tang, S. B.; He, J. M.; Sun, Y. Q.; He, L. E.; She X. G. J Org Chem 2010, 75, 1961.

[7] Knight, D. W.; Proctor, A. J.; Clough, J. M. Synlett 2010, 628.

[8] (a) Mosher, M. D.; Norman, A. L.; Shurrush, K. A. Tetrahedron Lett 2009, 50, 5647; (b) Norman, A. L.; Mosher, M. D. Tetrahedron Lett 2008, 49, 4153; (c) Norman, A. L.; Shurrush, K. A.; Calleroz, A. T.; Mosher, M. D. Tetrahedron Lett 2007, 48, 6849.

[9] Praveen, C.; Kalyanasundaram, A.; Perumal, P. T. Synlett 2010, 777.

[10] Willy, B.; Rominge, F.; Müller, T. Synthesis 2008, 293.

[11] X-ray data for **3a** have been deposited at the Cambridge Crystallographic Data Centre, deposition number CCDC 805384. Crystal data for **3a**: $C_{16}H_{15}NO_2$, MW = 253.29, monoclinic, space group *P2(1)/c*, a = 10.1203(9), b = 9.4778(8), c = 14.0262(13) Å; α = 90, β = 99.8160 (10), γ = 90°. V = 1325.7(2) Å^3, T = 293 K, Z = 4, Dc = 1.269 g cm^{-1}, μ = 0.087 mm^{-1}, λ = 0.71073 Å; F(000) 536, 3063 independent reflections (R_{int} = 0.0280), 11145 reflections collected; refinement method, Full-matrix least-squares on F^2; goodness-of-fit on F^2 = 1.022; Final R indices [$I > 2\sigma(I)$]. R_1 = 0.0374, wR_2 = 0.1033.

[12] (a) Stork, G.; Tomasz, M. J Am Chem Soc 1962, 84, 310; (b) Goldman I. M. J Org Chem 1969, 34, 1979.