

4-Aryl-2, 6-di(pyren-1-yl)pyridines: A facile procedure for synthesis and studying of fluorescence properties

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Abstract

Pyrene and its derivatives exhibit thermal stability, high extinction coefficients, excimer formation, high photoluminescence, long fluorescence lifetime, fluorophoric properties and enhanced charge carrier mobility which make them find applications in optoelectronic area and are useful as large planar synthetic building blocks in supramolecular chemistry. One of the approaches to overcome this downside is the introduction of bulky aryl/alkyl substituents or incorporation heteroatoms into the π -extended conjugated system of pyrene. In this work, Some new derivatives of 4-Aryl-2, 6-di(pyren-1-yl)pyridines have been synthesized through one-pot reaction and were formed with cyclization of arylaldehydes, 1-acetylpyrene and ammonium acetate in acetic acid. The products were confirmed by FT-IR, Mass, ¹H-NMR, ¹³C-NMR and elemental analysis. These new compounds were subsequently studied for their fluorescence properties.

Keywords: 4-Aryl-2,6-di(pyren-1-yl)pyridines; 1-actylpyrene multicomponent reactions; fluorescence.

Introduction

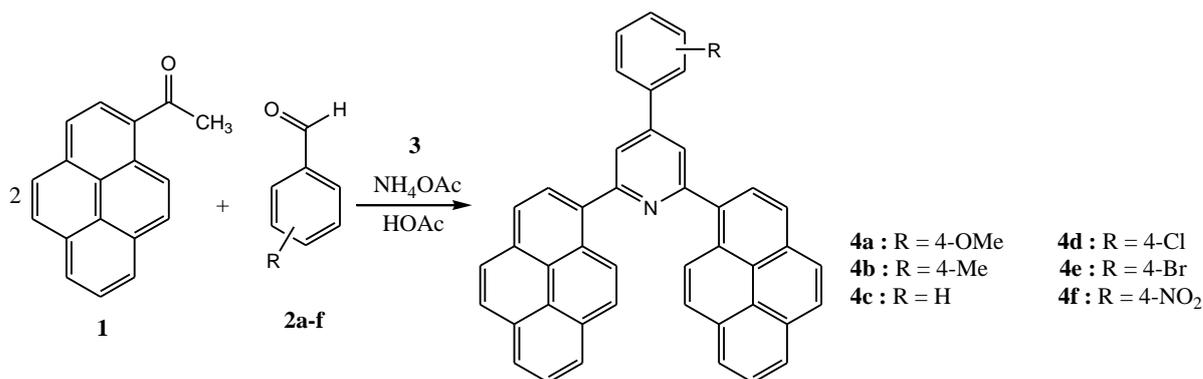
The increasing attention during the last decades for environmental protection has led both modern academic and high-wrought platoons to expand chemical activities with superlative efficiency and minimum cost whenever exerting non-poisonous reagents, solvents, and catalysts or solvent-free condition [1-2]. One of the tools used to combine economic aspects with the environmental ones is the multi component reaction (MCR) strategy.

MCRs have attracted much interest and are highly regarded in modern organic synthesis and pharmaceutical chemistry insomuch they are single-pot procedures that fetch three or more components and show high atom economy and wide selectivity [3-4]. MCRs have been widely used in the convergent synthesis of complex and significant organic molecules from easy and useful inception substances, and have emerged as powerful tools for drug discovery [5-6].

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Scheme 1. Synthesis of 4-aryl-2,6-di(pyren-1-yl)pyridines

Pyrene and its derivatives are π -extended conjugated polyaromatic systems. They exhibit thermal stability, high extinction coefficients, excimer formation, high photoluminescence, long fluorescence lifetime, fluorophoric properties and enhanced charge carrier mobility which make them find applications in optoelectronic area and are useful as large planar synthetic building blocks in supramolecular chemistry [7]. However, the blue light emitting properties of pyrene are greatly diminished due to its high tendency to aggregate by virtue of intermolecular π - π stacking in the solid state or at higher concentrations, and eventually leading to quenching of fluorescence emission. One of the approaches to overcome this downside is the introduction of bulky aryl/alkyl substituents or incorporation heteroatoms into the π -extended conjugated system of pyrene. Furthermore, the pyridine ring systems are also useful due to the incidence of their saturated and partially saturated derivatives in biologically strenuous combinations and natural yields such as NAD nucleotides, pyridoxol (vitamin B6), and pyridine alkaloids [8]. Due to their π -stacking capability, some pyridines are used in supramolecular chemistry [9]. Some instances are used as medicals, pigmentations,

increasables (as antioxidant), agrochemicals, veterinary [8,10–13].

There have been many procedures for the procurement of pyridines [14]. Formerly, 2, 4, 6-triarylpyridines have been generated by the condensation of 1,5-diketones with formamide-formic acid [15] and by other synthetic methods containing the Chichibabin procedure [16–19]. These combinations have also been synthesized *via* the reaction of Pyridinium salts with α,β -unsaturated ketones in the attendance of ammonium acetate [20]. Lately, many corrected procedures for generation of 2,4,6-triarylpyridines have been reported for example reaction of α -ketoketenedithioacetals with methyl ketones in the attendance of ammonium acetate [21], reaction of N-phosphinyloethanimines with aldehydes [22], addition of lithiated benaminophosphonates to chalcones [23]. In some of these methods, which is used to provide triarylpyridine derivatives, acetophenones, benzaldehydes and NH₄OAc are condensed together in the presence of NaOH or Ionic liquids under solvent-free conditions [24-25]. We have used these methods to synthesis of Aryl (pyren-1-yl) pyridine derivatives in the similar way. Thus, in this article, we report an appropriate synthesis of some 4-Aryl-2, 6-di(pyren-1-yl)pyridines **4a-**

f by a one-pot three-component reaction of 1-Acetylpyrene **1**, arylaldehydes **2a-f** and ammonium acetate **3** in refluxing glacial acetic acid (Scheme 1).

Experimental

All the chemicals were purchased from Merck Company. 1-acetylpyrene were prepared according to the literature procedures. Melting points were measured on Stuart SMP3 apparatus. FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer on KBr discs. ^1H and ^{13}C NMR spectra were determined on a Bruker 300 DRX Avance instrument using DMSO-*d*₆ as solvent and tetramethylsilane as an internal standard. Elemental analysis was performed on a ThermoFinnigan Flash EA microanalyzer. Absorption and fluorescence spectra were recorded on a Varian 50-bio UV-Vis spectrophotometer and a Varian Cary Eclipse spectrofluorometer, respectively. UV-Vis and fluorescence scans were recorded from 350 to 600 nm.

Synthesis of 4-aryl-2, 6-di(pyren-1-yl)pyridines **4a-f**; (general procedure).

A mixture of 1-actylpyrene **1** (2 mmol), an arylaldehyde **2a-f** (1 mmol), and ammonium acetate **3** (1.2 mmol) in glacial acetic acid (5 mL) was heated under reflux for 6 hours. After the completion of the reaction, the solvent was evaporated in vacuum. The crude product was gathered and recrystallized in DMSO to give compounds **4a-f** in 68-86% yields.

4-(4-Methoxyphenyl)-2,6-di(pyren-1-yl)pyridine (**4a**)

Yield 68%, brown powder, mp 140-143 °C, IR spectrum, ν , cm^{-1} : 3038 (arom-CH), 1593, 1514, 1249, 1178, 1032, 840; ^1H NMR spectrum (DMSO-*d*₆), δ , ppm (J, Hz): 3.85 (s, 3H, OCH₃), 7.11-

8.68 (m, 12H, arom-H); ^{13}C NMR (DMSO-*d*₆), δ , ppm: 55.80, 115.15, 121.42, 124.45, 124.68, 125.39, 125.68, 126.04, 126.91, 127.85, 128.45, 128.63, 129.22, 129.93, 130.82, 131.38, 131.41, 136.23, 148.89, 159.65, 160.97; Mass spectrum (EI, 70 eV), m/z : 585.2[M]⁺; Found, %: C 89.18; H 4.38; N 2.31. C₄₄H₂₇NO. Calculated, %: C, 90.23; H, 4.65; N, 2.39; O, 2.73.

2,6-Di(pyren-1-yl)-4-*p*-tolylpyridine (**4b**)

Yield 65%, brown powder, mp 129-131 °C, IR spectrum, ν , cm^{-1} : 3038 (arom-CH), 1591, 1535, 1393, 1185, 842; ^1H NMR spectrum (DMSO-*d*₆), δ , ppm (J, Hz): 2.41 (s, 3H, CH₃), 7.39-8.69 (m, 12H, arom-H); ^{13}C NMR (DMSO-*d*₆), δ , ppm: 21.18, 119.27, 122.49, 124.17, 124.38, 125.80, 126.59, 126.76, 127.31, 127.66, 129.57, 130.69, 132.77, 132.92, 133.18, 139.01, 139.70, 149.95, 159.02; Mass spectrum (EI, 70 eV), m/z : 569.2[M]⁺; Found, %: C90.08; H4.53; N2.36. C₄₄H₂₇N. Calculated, %: C, 92.76; H, 4.78; N, 2.46.

4-Phenyl-2,6-di(pyren-1-yl)pyridine (**4c**)

Yield 79%, light green powder, mp 199-202 °C, IR spectrum, ν , cm^{-1} : 3036 (arom-CH), 1589, 1538, 1396, 840, 757, 716; ^1H NMR spectrum (DMSO-*d*₆), δ , ppm (J, Hz): 7.56-8.71 (m, 10H, arom-H); ^{13}C NMR (DMSO-*d*₆), δ , ppm: 122.10, 124.46, 124.70, 125.41, 125.70, 126.07, 126.93, 127.85, 127.94, 128.43, 128.52, 128.64, 129.76, 129.96, 130.83, 131.39, 131.47, 136.08, 137.94, 149.43, 159.76; Mass spectrum (EI, 70 eV), m/z : 555.1[M]⁺; Found, %: C90.87; H4.46; N 2.45. C₄₃H₂₅N. Calculated, %: C, 92.94; H, 4.53; N, 2.52.

4-(4-Chlorophenyl)-2,6-di(pyren-1-yl)pyridine (**4d**)

Yield 82%, yellow powder, mp 160-163 °C, IR spectrum, ν , cm^{-1} : 3041

(arom-CH), 1593, 1537, 1493, 1386, 1093, 838; ^1H NMR spectrum (DMSO- d_6), δ , ppm (J, Hz): 7.62-8.69 (m, 12H, arom-H); ^{13}C NMR (DMSO- d_6), δ , ppm: 121.95, 124.42, 124.67, 125.38, 125.70, 126.07, 126.92, 127.83, 128.44, 128.51, 128.63, 128.68, 129.67, 129.77, 130.80, 131.36, 131.48, 134.89, 135.93, 136.69, 148.10, 159.81; Mass spectrum (EI, 70 eV), m/z : 589.1[M] $^+$; Found, %: C86.14; H3.97; N 2.29. $\text{C}_{43}\text{H}_{24}\text{ClN}$. Calculated, %: C, 87.52; H, 4.10; Cl, 6.01; N, 2.37.

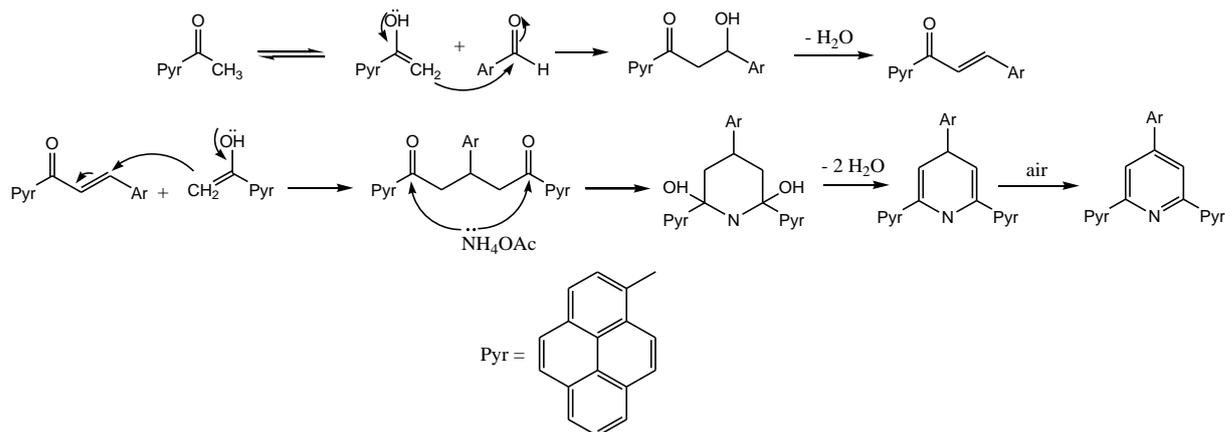
4-(4-Bromophenyl)-2,6-di(pyren-1-yl)pyridine (**4e**)

Yield 86%, orang powder, mp 217-219 $^\circ\text{C}$, IR spectrum, ν , cm^{-1} : 3037 (arom-CH), 1592, 1536, 1490, 1380, 1011, 837; ^1H NMR spectrum (DMSO- d_6), δ , ppm (J, Hz): 7.77-8.69 (m, 12H, arom-H); ^{13}C NMR (DMSO- d_6), δ , ppm: 121.93, 123.64, 124.42, 124.66, 125.40, 125.73, 126.10, 126.96, 127.85, 128.16,

128.47, 128.54, 128.63, 128.70, 130.09, 130.81, 131.26, 131.37, 131.49, 132.42, 132.63, 135.93, 137.10, 148.21, 159.84; Mass spectrum (EI, 70 eV), m/z : 633.1[M] $^+$; Found, %: C80.24; H3.75; N 2.13. $\text{C}_{43}\text{H}_{24}\text{BrN}$. Calculated, %: C, 81.39; H, 3.81; Br, 12.59; N, 2.21.

4-(4-Nitrophenyl)-2,6-di(pyren-1-yl)pyridine (**4f**)

Yield 72%, dark green powder, mp 206-209 $^\circ\text{C}$, IR spectrum, ν , cm^{-1} : 3043 (arom-CH), 1590, 1520, 1344, 1112, 846; ^1H NMR spectrum (DMSO- d_6), δ , ppm (J, Hz): 7.82-8.71 (m, 12H, arom-H); ^{13}C NMR (DMSO- d_6), δ , ppm: 117.23, 119.29, 122.47, 124.20, 124.41, 125.38, 125.76, 126.63, 126.81, 127.66, 130.69, 132.77, 132.92, 133.20, 138.98, 140.43, 149.82, 159.15; Mass spectrum (EI, 70 eV), m/z : 600.1[M] $^+$; Found, %: C84.88; H3.95; N 4.53. $\text{C}_{43}\text{H}_{24}\text{N}_2\text{O}_2$. Calculated, %: C, 85.98; H, 4.03; N, 4.66; O, 5.33.



Scheme 2. Plausible mechanism for the formation of 4-Aryl-2,6-di(pyren-1-yl)pyridines

Results and discussion

The new 2,6-di(pyrene-1-yl)pyridine derivatives **4a-f** were synthesized by an Aldol condensation of 1-acetylpyrene **1** with carbonyl group of Arylaldehydes **2a-f** and after losing of water, generating a conjugated enone. The Michael addition of the second mole of 1-acetylpyrene to a conjugated enone, leading to 1,3,5-diaryl-1,5-

diketone. The subsequent cyclization through the ring closure with ammonium acetate **3** is followed by air oxidation to form the products **4a-f** (Scheme 2). The structures of the productions were concluded from their spectral and microanalytical data. For example, the ^1H NMR spectrum of **4a** which this is a symmetrical produce, exhibited one singlet signal at δ 3.85

ppm for methyl group, connected with Oxygen, as well as, the signals in the aromatic area, δ 7.11-8.68 ppm, due to 12 aromatic protons demonstrating the organization of the combination 4a. The IR spectrum of 4a demonstrated strong absorptions at 3055 and 2994 cm^{-1} due to the aromatic and aliphatic protons respectively. The MS (APCI) of 4b displayed a peak at m/z 327.26 ($[\text{M}+\text{H}]^+$) corresponding to the

molecular formula $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$. This production also gave proton decoupled ^{13}C NMR information in 21.22 (CH₃), 118.89, 120.76, 125.27, 126.60, 127.44, 127.48, 128.05, 128.68, 128.84, 128.89, 129.00, 129.97, 130.07, 131.02, 135.54, 138.33, 153.14 (C=O) (see experimental section). The reaction conditions and the melting point of all products are illustrated in Table 1.

Table 1. Synthesis of 4-Aryl-2,6-di(pyren-1-yl)pyridine 4a-f

Product ^b	R	Time(hr)	Yield(%) ^c	m.p.(°C)
4a	4-OMe	6	68	140-143
4b	4-Me	6	65	129-131
4c	H	6	79	199-202
4d	4-Cl	6	82	160-163
4e	4-Br	6	86	217-219
4f	4-NO ₂	6	72	206-209

^aReaction conditions : 1-Actylpyrene **1** (2 mmol), an Arylaldehyde **2a-f** (1 mmol), ammonium acetate **3** (1.2 mmol), glacial acetic acid (5 mL), reflux, 6h.

^bAll the products were characterized according to their spectral and microanalytical data.

^cIsolated yields.

In order to study the fluorescence properties of these compositions, we investigated the fluorescence absorption and emission spectra of combinations 4a-f. The λ_{abs} , amounts of extinction coefficient (ϵ), λ_{ex} , λ_{flu} and fluorescence quantum efficiency (Φ_{F}) information of these compounds are reported in Table 2. Values of the extinction coefficient (ϵ) were computed from the inclination of the plan of absorbance against condensation. The fluorescence quantum yields (Φ_{F}) of combinations 4a-f were characterized using comparison procedures, with fluorescein as a standard sample in 0.1 M NaOH and MeOH solution [26]. It can be received from the information in

Table 2 that these combinations are fluorescent. Scheme 3 has shown that the overlap of the electron donors groups attached to the phenylene ring such as chlorine and bromine with the π -system in pyridine ring generates a highly conjugated system as a result fluorescence has increased and in the NO₂ group, electron acceptor, fluorescence dropped (Scheme 3). The fluorescence absorption and of compound 4d were measured at the concentration of $1 \times 10^{-6} \text{ mol L}^{-1}$ in several solvents (Scheme 4). As is illustrated in these schemes, the fluorescence absorption and emission spectra of 4d in polar solvents accomplished a solvatochromic red shift with increasing solvent polarity.

Solvent effects shift the emission to lower energy owing to stabilization of the excited state by the polar solvent molecules (Table 2). This type of treatment is observed for most of the

dyes. For example, in Table 2, one can see that in the absorption spectrum for **4d**, λ_{abs} shifts from 446 to 464 nm as the solvent is changed from ethanol to acetone.

Table 2. Photophysical data for absorption and fluorescence of **4a-f**

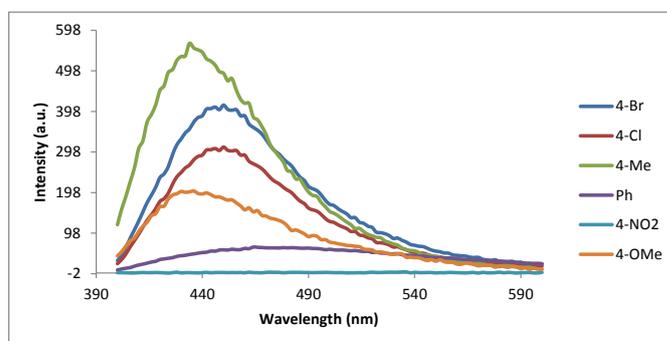
Compound	4a	4b	4c	4d	4e	4f
$\lambda_{\text{abs}}/\text{nm}^{\text{a}}$	405	401	411	398	395	406
$\epsilon \times 10^{-7} / \text{mol}^{-1} \text{L cm}^{-1\text{b}}$	8.05	8.10	8.26	8.59	8.38	8.15
$\lambda_{\text{fl}}/\text{nm}^{\text{c}}$	436	434	464	446	446	462
$\Phi_{\text{F}}^{\text{d}}$	12.8	12.2	12.1	16.7	15.3	10.1

^aWavelengths of maximum absorbance.

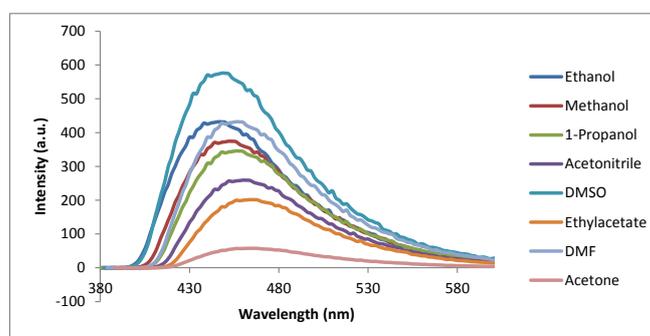
^bExtinction coefficient.

^cWavelengths of fluorescence emission.

^dFluorescence quantum yield (%).



Scheme 3. Emission spectrum of compound **4a-f** in DMSO/MeOH solvent ($5 \times 10^{-5} \text{mol L}^{-1}$)



Scheme 4. Emission spectrum of compound **4d** in several solvents ($1 \times 10^{-6} \text{mol L}^{-1}$)

Conclusion

In conclusion, we have found that the one-pot three-component reaction of Arylaldehydes, 1-acetylpyrene and ammonium acetate in acetic acid leads to a facile synthesis of 4-Aryl-2,6-di(pyren-1-yl)pyridine. A plausible mechanism for the formation of the products has been also suggested.

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References

- [1] M. Poliakoff, J.M. Fitzpatrick, T.R. Farren, P.T. Anastas, *Science*, **2002**, 297, 807-810.
- [2] A. Khojastehnezhad, A. Davoodnia, M. Bakavoli, N. Tavakoli-Hoseini, M. Zeinali-Dastmalbaf, *Chin. J. Chem.*, **2011**, 29, 297-302.
- [3] I. Ugi, *Pure Appl. Chem.*, **2001**, 187, 73, 187-191.
- [4] A. Domling, *Chem. Rev.*, **2006**, 106, 17-89.
- [5] L. Weber, *Drug Discov. Today*, **2002**, 7, 143-147.
- [6] C. Hulme, V. Gore, *Curr. Med. Chem.*, **2003**, 10, 51-80.
- [7] T. M. Figueira-Duarte, K. Mullen, *Chem. Rev.*, **2011**, 111, 7260-7314.
- [8] M. Balasubramanian, J.G. Keay, In *Comprehensive Heterocyclic Chemistry II*, A. R. Katritzky, C. W. Rees, E. V. F. Scriven, Eds.; Pergamon Press: London, **1996**; Vol. 5, Chapter 6, pp 245-300.
- [9] (a) E.C. Constable, C.E. Housecroft, M. Neuburger, D. Phillips, P.R. Raithby, E. Schofield, E. Sparr, D.A. Tocher, M. Zehnder, Y. Zimmermann, *J. Chem. Soc., Dalton Trans.*, **2001**, 2864-2871; (b) G.W.V. Cave, M.J. Hardie, B.A. Roberts, C.L. Raston, *Eur. J. Org Chem.*, **2001**, 17, 3227-3231; (c) R.K.R. Jetti, A. Nagia, F. Xue, T.C.W. Mak, *Chem. Commun.*, **2001**, 10, 919-920; (d) Z.C. Watson, N. Bampos, J.K.M. Sanders, *New J. Chem.*, **1998**, 22, 1135-1138.
- [10] B.Y. Kim, J.B. Ahn, H.W. Lee, S.K. Kang, J.H. Lee, J.S. Shin, S.K. Ahn, C.I. Hong, S.S. Yoon, *Eur. J. Med. Chem.*, **2004**, 39, 433-447.
- [11] I.J. Enyedy, S. Sakamuri, W.A. Zaman, K.M. Johnson, S. Wang, *Bioorg. Med. Chem. Lett.*, **2003**, 13, 513-517.
- [12] A.D. Pillai, P.D. Rathod, P.X. Franklin, M. Patel, M. Nivsarkar, K.K. Vasu, H. Padh, V. Sudarsanam, *Biochem Biophys. Res. Commun.*, **2003**, 301, 183-186.
- [13] V. Klimes`ova`, M. Svoboda, K. Waisser, M. Pour, Kaustova`, J. IL. *Farmaco.*, **1999**, 54, 666-672.
- [14] F. Kro`hnke, *Synthesis*, **1976**, 1, 1-24.
- [15] F. Chubb, A.S. Hay, R.B. Sandin, *J. Am. Chem. Soc.*, **1953**, 75, 6042-6044.
- [16] W. Dilthey, G. Bauriedel, B. Burger, G. Geisselbrecht, F. von Ibach, F. Kiefer, A. Seeger, O. Simon, R. Taucher, J. Winkler, *J. Prakt. Chem.*, **1921**, 102, 8-10, 209 Wiley Online Library.
- [17] R. Lombard, J.P. Stephen, *Bull. Soc. Chim. Fr.*, **1958**, 6, 1458-1461.
- [18] W. Zecher, F. Krohnke, *Chem. Ber.*, **1961**, 94, 690-697.
- [19] R.L. Frank, R.P. Seven, *J. Am. Chem. Soc.*, **1949**, 71, 2629-2635.
- [20] F. Kro`hnke, W. Zecher, *Angew. Chem. Int. Ed.*, **1962**, 1, 626-630.
- [21] (a) K.T. Potts, M.J. Cipullo, P. Ralli, G. Theodoridis, *J. Am. Chem. Soc.*, **1981**, 103, 3584-3585; (b) K.T. Potts, M.J. Cipullo, P. Ralli, G. Theodoridis, *J. Am. Chem. Soc.*, **1981**, 103, 3585-3586.
- [22] T. Kobayashi, H. Kakiuchi, H. Kato, *Bull. Chem. Soc. Jpn.*, **1991**, 64, 392-395.

[23] F. Palacios, A.M. O. de Retana, J. Oyarzabal, *Tetrahedron Lett.*, **1996**, 37, 4577-4580.

[24] S. Tu, T. Li, F. Shi, F. Fang, S. Zhu, X. Wei, Z. Zong, *Chem Lett.*, **2005**, 34, 732-733.

[25] H. Behmadi, Sh. Naderipour, S.M. Saadati, M. Barghamadi, M. Shaker, N. Tavakoli Hoseini. *J. Heterocyclic Chem.*, **2011**, 48, 1117-1121.

[26] V. Pakjoo, M. Roshani, M. Pordel, T. Hoseini, *ARKIVOC*, **2012**, 195-203.

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