Tetrahedron Letters 52 (2011) 2299–2301

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Solvent-free reaction between acenaphthoquinone, various benzils and ammonium acetate: synthesis of 9,10-diaryl-7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones

Mehdi Adib [a,*], Bagher Mohammadi [b], Samira Ansari [a], Hamid Reza Bijanzadeh [c], Long-Guan Zhu [d]

[a] School of Chemistry, University College of Science, University of Tehran, PO Box 14155–6455, Tehran, Iran
[b] Member of Young Researchers Club, Islamic Azad University, Takestan Branch, Takestan, Iran
[c] Department of Chemistry, Tarbiat Modarres University, PO Box 14115–175, Tehran, Iran
[d] Chemistry Department, Zhejiang University, Hangzhou 310027, PR China

ARTICLE INFO

Article history:
Received 25 August 2010
Revised 5 January 2011
Accepted 21 January 2011
Available online 27 January 2011

Keywords:
Acenaphthoquinone
Benzils
9,10-Diaryl-7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones
Imidazole synthesis

ABSTRACT

A simple synthesis of benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolines is described. Heating a mixture of acenaphthoquinone, a benzil, and ammonium acetate under solvent-free conditions afforded 9,10-diaryl-7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones in good to excellent yields.

Imidazoles, an important class of heterocyclic compounds, are of both biological and chemical interest, and their involvement in catalytic processes at the active sites of enzymes have been well documented. They are part of a large number of highly significant biomolecules such as the essential amino acid histidine, biotin, and imidazole alkaloids.[1–4] The potency and wide applicability of the imidazole pharmacophore can be attributed to its hydrogen bond donor–acceptor ability, as well as its high affinity for metals present in many protein active sites.[5] Some imidazole derivatives act as p38 mitogen activated protein kinase inhibitors,[6a] B-Raf kinase inhibitors,[6b] transforming growth factor β1 type 1 activin receptor-like kinase inhibitors,[6c] and cyclooxygenase-2 inhibitors.[6d] Appropriately substituted imidazoles are used extensively as glucagon receptors,[7a] CB_1 cannabinoid receptor antagonists,[7b] modulators of P-glycoprotein mediated multidrug resistance,[7c] antibacterials,[7d] antitumor agents,[7e] and pesticides.[7f] Recent advances in green chemistry and organometallic catalysis have extended the application of imidazoles as precursors to ionic liquids[8] and *N*-heterocyclic carbenes.[9]

The most common synthetic routes reported for the preparation of imidazole derivatives involve: (i) cyclizations, classified on the basis of the number of ring atoms in each of the components being cyclized: (a) single bond formation, (b) formation of two bonds, from [4+1] or [3+2] atom fragments, (c) formation of three or four bonds; (ii) transformation of an existing heterocyclic ring, including expansion of smaller rings, contraction of larger rings, and transformation of other five-membered rings.[3]

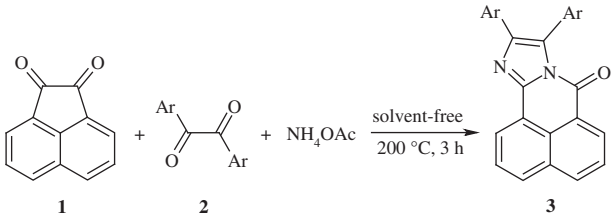
There are several methods for the syntheses of highly substituted imidazoles. The most frequently used methods involve: synthesis via hetero-Cope rearrangement,[10] four-component condensation of arylglyoxals, primary amines, carboxylic acids, and isocyanides on Wang resin,[11] reaction of *N*-(2-oxo)amides with $NH_4O_2CCF_3$[12] and reaction of *N*-alkyl-*N*-(β-keto)amides with NH_4OAc.[13] The synthesis of tri-/tetra-substituted imidazoles via condensation of aldehydes, benzils, and NH_4OAc/primary amines is also a well established procedure.[14]

Fused imidazoles, for example, 7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones, have been used as electron acceptor molecules in organic photovoltaic devices,[15] discotic and lyotropic liquid crystal systems,[16,17] organic *n*-channel field-effect transistors,[18] and as new dyes and pigments.[19,20] Some derivatives modulate interaction of nerve growth factor with neurotrophic receptors,[21] and some examples have been polymerized and used in industrial water systems.[22]

The most common synthesis of 7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones involves condensation of the corre-

* Corresponding author. Tel./fax: +98 21 66495291.
E-mail address: madib@khayam.ut.ac.ir (M. Adib).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.01.091



Scheme 1.

sponding 1,8-naphthalenedicarboxylic anhydrides and vicinal diamines.[18,19,23]

As part of our current studies on the development of efficient and simple syntheses of biologically active heterocyclic compounds,[24] we herein describe a new synthesis of 7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones. Thus a mixture of acenaphthoquinone (**1**), benzil **2** and excess ammonium acetate underwent a 1:1:2 addition reaction, under solvent-free conditions, to produce the corresponding 7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones, **3a**–**k** in 80–92% yields (Scheme 1 and Table 1). All the reactions proceeded at 200 °C and reached completion within 3 h. TLC analysis of the reaction mixtures clearly indicated the formation of the corresponding highly fluorescent 7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones **3**.[25]

The structures of the isolated products **3** were deduced on the basis of IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The mass spectrum of **3c** displayed the molecular ion (M^+) peak at m/z = 400, which was consistent with the 1:1:2 adduct of acenaphthoquinone, 1,2-bis(4-methylphenyl)-1,2-ethanedione and ammonia with loss of three H_2O molecules. The IR spectrum of **3c** showed an absorption at 1695 cm^{-1} indicating the presence of an amide. The ^{1}H NMR spectrum of **3c** exhibited two sharp singlets at 2.34 and 2.49 ppm due to the methyl groups of the two aryl substituents along with characteristic signals with appropriate chemical shifts and coupling constants for the 14 aromatic H atoms. The ^{1}H-decoupled ^{13}C NMR spectrum of **3c** showed characteristic signals at 21.25 and 21.59 ppm (due to the two methyl substituents), a deshielded signal at 160.40 ppm (due to the amide carbonyl group), as well as 21 other distinct resonances (10 CH and 11 C) in agreement with the proposed structure.[25]

Single-crystal X-ray analysis of product **3k** confirmed conclusively its structure, and by analogy, those of the other isolated products. An ORTEP diagram of **3k** is shown in Figure 1.[26]

In conclusion, we have reported a novel reaction for the preparation of 7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones from an addition reaction between acenaphthoquinone, various benzils, and ammonium acetate. Solvent-free conditions, good to excellent yields of the products, the use of simple and readily available starting materials and fairly short reaction times are the main advantages of this reaction. The highly fluorescent 7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones prepared may find useful applications in bioorganic and medicinal chemistry, and also in light-emitting devices. Further investigations on the reaction mechanism, the scope and the limitations of this reaction are underway.

Table 1
Synthesis of 7*H*-benzo[*d*,*e*]imidazo [2,1-*a*]isoquinolin-7-ones **3a**–**k**

Product	Ar	Yield[a] (%)
3a	C_6H_5	92
3b	3-$CH_3C_6H_4$	85
3c	4-$CH_3C_6H_4$	88
3d	3-$CH_3OC_6H_4$	83
3e	4-$CH_3OC_6H_4$	80
3f	4-$O_2NC_6H_4$	89
3g	4-ClC_6H_4	87
3h	4-BrC_6H_4	86
3i	4-FC_6H_4	89
3j	2-Furyl	80
3k	2-Pyridyl	86

[a] Isolated yield.

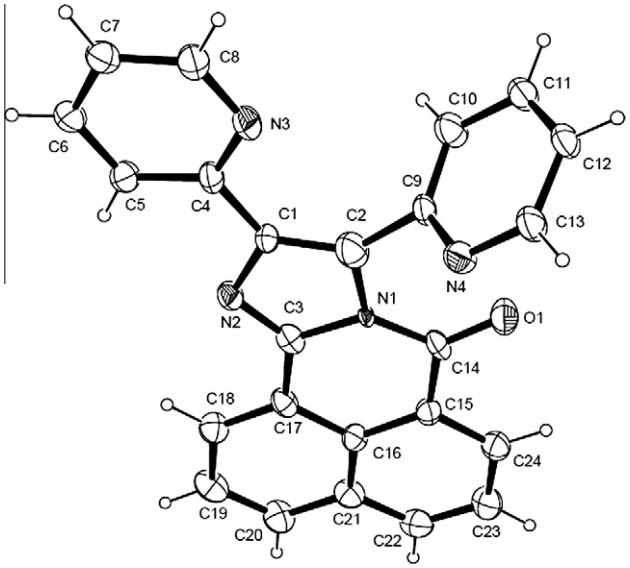


Figure 1. ORTEP diagram of the molecular structure of **3k**.

Acknowledgment

This research was supported by the Research Council of the University of Tehran as research project (6102036/1/03).

References and notes

1. Grimmett, M. R. In *Comprehensive Heterocyclic Chemistry I*; Katritzky, A. R., Rees, C. W., Potts, K. T., Eds.; Pergamon Press: New York, 1984; Vol. 5, pp 457–497.
2. Grimmett, M. R. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon Press: New York, 1996; Vol. 3, pp 77–220.
3. Xi, N.; Huang, Q.; Liu, L. In *Comprehensive Heterocyclic Chemistry III*; Katritzky, A. R., Ramsden, C. A., Scriven, E. F. V., Taylor, R. J. K., Eds.; Elsevier Science: Oxford, 2008; Vol. 4, pp 143–348. and references therein.
4. De Luca, L. *Curr. Med. Chem.* **2006**, *13*, 1–23.
5. Rotstein, D. M.; Kertesz, D. J.; Walker, K. A. M.; Swinney, D. C. *J. Med. Chem.* **1992**, *35*, 2818–2825.
6. (a) Lee, J. C.; Laydon, J. T.; McDonnell, P. C.; Gallagher, T. F.; Kumar, S.; Green, D.; McNulty, D.; Blumenthal, M. J.; Keys, J. R.; Vatter, S. W. L.; Strickler, J. E.; McLaughlin, M. M.; Siemens, I. R.; Fisher, S. M.; Livi, G. P.; White, J. R.; Adams, J. L.; Young, P. R. *Nature* **1994**, *372*, 739–746; (b) Takle, A. K.; Brown, M. J. B.; Davies, S.; Dean, D. K.; Francis, G.; Gaiba, A.; Hird, A. W.; King, F. D.; Lovell, P. J.; Naylor, A.; Reith, A. D.; Steadman, J. G.; Wilson, D. M. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 378–381; (c) Khanna, I. K.; Weier, R. M.; Yu, Y.; Xu, X. D.; Koszyk, F. J.; Collins, P. W.; Koboldt, C. M.; Veenhuizen, A. W.; Perkins, W. E.; Casler, J. J.; Masferrer, J. L.; Zhang, Y. Y.; Gregory, S. A.; Seibert, K.; Isakson, P. C. *J. Med. Chem.* **1997**, *40*, 1634–1647; (d) Lange, J. H. M.; Van Stuivenberg, H. H.; Coolen, H. K. A. C.; Adolfs, T. J. P.; McCreary, A. C.; Keizer, H. G.; Wals, H. C.; Veerman, W.; Borst, A. J. M.; de Looff, W.; Verveer, P. C.; Kruse, C. G. *J. Med. Chem.* **2005**, *48*, 1823–1838.
7. (a) de Laszlo, S. E.; Hacker, C.; Li, B.; Kim, D.; MacCoss, M.; Mantlo, N.; Pivnichny, J. V.; Colwell, L.; Koch, G. E.; Cascieri, M. A.; Hagmann, W. K. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 641–646; (b) Eyers, P. A.; Craxton, M.; Morrice, N.; Cohen, P.; Goedert, M. *Chem. Biol.* **1998**, *5*, 321–328; (c) Newman, M. J.; Rodarte, J. C.; Benbatoul, K. D.; Romano, S. J.; Zhang, C.; Krane, S.; Moran, E. J.; Uyeda, R. T.; Dixon, R.; Guns, E. S.; Mayer, L. D. *Cancer Res.* **2000**, *60*, 2964–2972; (d) Antolini, M.; Bozzoli, A.; Ghiron, C.; Kennedy, G.; Rossi, T.; Ursini, A. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1023–1028; (e) Wang, L.; Woods, K. W.; Li, Q.; Barr, K. J.; McCroskey, R. W.; Hannick, S. M.; Gherke, L.; Credo, R. B.; Hui, Y.-H.; Marsh, K.; Warner, R.; Lee, J. Y.; Zielinsky-Mozng, N.; Frost, D.; Rosenberg, S. H.; Sham, H.

L. *J. Med. Chem.* **2002**, *45*, 1697–1711; (f) Maier, T.; Schmierer, R.; Bauer, K.; Bieringer, H.; Buerstell, H.; Sachse, B. U.S. Patent 4820335, 1989; *Chem. Abstr.* **1989**, *111*, 19494w.
8. (a) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692; (b) Chowdhury, S.; Mohan, R. S.; Scott, J. L. *Tetrahedron* **2007**, *63*, 2363–2389.
9. (a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–92; (b) Arnold, P. L.; Liddle, S. T. *Chem. Commun.* **2006**, 3959–3971; (c) Kühl, O. *Chem. Soc. Rev.* **2007**, *36*, 592–607.
10. Lantos, I.; Zhang, W. Y.; Shui, X.; Eggleston, D. S. *J. Org. Chem.* **1993**, *58*, 7092–7095.
11. (a) Zhang, C.; Moran, E. J.; Woiwode, T. F.; Short, K. M.; Mjalli, A. M. M. *Tetrahedron Lett.* **1996**, *37*, 751–754; (b) Sarshar, S.; Siev, D.; Mjalli, A. M. M. *Tetrahedron Lett.* **1996**, *37*, 835–838.
12. Claiborne, C. F.; Liverton, N. J.; Nguyen, K. T. *Tetrahedron Lett.* **1998**, *39*, 8939–8942.
13. Lee, H. B.; Balasubramanian, S. *Org. Lett.* **2000**, *2*, 323–326.
14. Das Sharma, S.; Hazarika, P.; Konwar, D. *Tetrahedron Lett.* **2008**, *49*, 2216–2220. and references cited therein.
15. Shin, W. S.; Jeong, H. H.; Kim, M. K.; Jin, S. H.; Kim, M. R.; Lee, J. K.; Lee, J. W.; Gal, Y. S. *J. Mater. Chem.* **2006**, *16*, 384–390.
16. Wicklein, A.; Kohn, P.; Ghazaryan, L.; Thurn-Albrecht, T.; Thelakkat, M. *Chem. Commun.* **2010**, *46*, 2328–2330.
17. Nazarov, V. V.; Sidorenko, E. N. U.S. Patent 215,015 A1, 2004; *Chem. Abstr.* **2004**, *141*, 386740m.
18. Ortiz, R. P.; Herrera, H.; Blanco, R.; Huang, H.; Facchetti, A.; Marks, T. J.; Zheng, Y.; Segura, J. L. *J. Am. Chem. Soc.* **2010**, *132*, 8440–8452.
19. Graciet, J. C. Eur. Patent 1,422,267 A1, 2004; *Chem. Abstr.* **2004**, *140*, 408230d.
20. Flatt, T. U.S. Patent 139,813 A1, 2008; *Chem. Abstr.* **2008**, *149*, 33650k.
21. Vohra, R.; Dube, G.; Gan, Z.; Gill, N.; Cui, X. U.S. Patent 82,368 A1, 2009; *Chem. Abstr.* **2009**, *150*, 351920d.
22. Morris, J. D.; Moriarty, B. E. Wei, M.; Murray, P. G.; Reddinger, J. L. U.S. Patent 135,124 A1, 2004; *Chem. Abstr.* **2004**, *141*, 76327n.
23. Feiler, L.; Langhals, H.; Polborn, K. *Liebigs Ann.* **1995**, 1229–1244.
24. (a) Adib, M.; Ansari, S.; Feizi, S.; Bijanzadeh, H. R. *Synlett* **2010**, 921–923; (b) Adib, M.; Ansari, S.; Fatemi, S.; Bijanzadeh, H. R.; Zhu, L. G. *Tetrahedron* **2010**, *66*, 2723–2727; (c) Adib, M.; Ansari, S.; Mohammadi, A.; Bijanzadeh, H. R. *Tetrahedron Lett.* **2010**, *51*, 30–32; (d) Adib, M.; Ansari, S.; Feizi, S.; Asgarian Damavandi, J.; Mirzaei, P. *Synlett* **2009**, 3263–3266; (e) Adib, M.; Mahdavi, M.; Ansari, S.; Malihi, F.; Zhu, L. G.; Bijanzadeh, H. R. *Tetrahedron Lett.* **2009**, *50*, 7246–7248; (f) Adib, M.; Sheibani, E.; Bijanzadeh, H. R.; Zhu, L. G. *Tetrahedron* **2008**, *64*, 10681–10686; (g) Adib, M.; Sayahi, M. H.; Ziyadi, H.; Zhu, L. G.; Bijanzadeh, H. R. *Synthesis* **2008**, 3289–3294; (h) Adib, M.; Mohammadi, B.; Bijanzadeh, H. R. *Synlett* **2008**, 3180–3182; (i) Adib, M.; Mohammadi, B.; Bijanzadeh, H. R. *Synlett* **2008**, 177–180; (j) Adib, M.; Sayahi, M. H.; Ziyadi, H.; Bijanzadeh, H. R.; Zhu, L. G. *Tetrahedron* **2007**, *63*, 11135–11140.
25. *General procedure for the preparation of compounds* **3a–k**: A mixture of acenaphthoquinone (1 mmol), the appropriate benzil (1 mmol), and ammonium acetate (4 mmol) was heated at 200 °C for 3 h. The reaction mixture was cooled to room temperature and the product was purified by column chromatography using *n*-hexane–EtOAc (3:1) as eluent. *9,10-Diphenyl-7H-benzo[d,e]imidazo[2,1-a]isoquinolin-7-one* (**3a**): Yield: 0.34 g (92%); yellow crystals, mp 390–393 °C. IR (KBr) (ν_{max}/cm^{-1}): 1698 (C=O), 1600, 1556, 1485, 1388, 1293, 1170, 1158, 1091, 1028, 997, 898, 825, 770, 742, 706. EI–MS, *m*/*z* (%): 372 (M$^+$, 100), 332 (37), 295 (19), 281 (22), 269 (14), 247 (10), 217 (9), 207 (19), 196 (15), 179 (46), 105 (74), 91 (38), 77 (52), 57 (60), 43 (18). Anal. Calcd for $C_{26}H_{16}N_2O$ (372.42): C, 83.85; H, 4.33; N, 7.52. Found: C, 84.04; H, 4.47; N, 7.26. ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 7.22–7.29 (m, 3H, 3CH), 7.44–7.51 (m, 7H, 7CH), 7.85 (t, *J* = 7.8 Hz, 1H, CH), 7.86 (t, *J* = 7.7 Hz, 1H, CH), 8.26 (d, *J* = 8.2 Hz, 1H, CH), 8.47 (d, *J* = 8.2 Hz, 1H, CH), 8.48 (d, *J* = 7.2 Hz, 1H, CH), 8.62 (d, *J* = 7.2 Hz, 1H, CH). ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 120.34 and 122.79 (2C), 125.00 (CH), 125.14 and 126.62 (2C), 127.09, 127.16, 127.42, 127.57, 128.05, 128.12, 128.35, 130.69 and 130.70 (9CH), 131.09 (C), 131.64 (CH), 131.71 and 133.06 (2C), 135.67 (CH), 139.83 and 144.78 (2C) 159.47 (C=O). *9,10-Bis(4-methylphenyl)-7H-benzo[d,e]imidazo[2,1-a]isoquinolin-7-one* (**3c**): Yield: 0.35 g (88%); yellow crystals, mp 400–402 °C. IR (KBr) (ν_{max}/cm^{-1}): 1695 (C=O), 1605, 1548, 1494, 1448, 1378, 1344, 1300, 1240, 1172, 1113, 1023, 965, 908, 876, 824, 770, 728, 682. EI–MS, *m*/*z* (%): 400 (M$^+$, 28), 384 (4), 371 (2), 343 (5), 254 (7), 177 (2), 119 (100), 91 (14), 65 (14), 55 (9), 43 (9). Anal. Calcd for $C_{28}H_{20}N_2O$ (400.47): C, 83.97; H, 5.03; N, 7.00. Found: C, 83.81; H, 5.23; N, 6.85. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.34 and 2.49 (2s, 6H, 2CH_3), 7.11 (d, *J* = 8.1 Hz, 2H, 2CH), 7.31 (d, *J* = 8.0 Hz, 2H, 2CH), 7.42 (d, *J* = 8.0 Hz, 2H, 2CH), 7.55 (d, *J* = 8.1 Hz, 2H, 2CH), 7.72 (t, *J* = 7.8 Hz, 1H, CH), 7.76 (t, *J* = 7.8 Hz, 1H, CH), 8.03 (d, *J* = 8.1 Hz, 1H, CH), 8.22 (d, *J* = 8.0 Hz, 1H, CH), 8.60 (d, *J* = 6.7 Hz, 1H, CH), 8.77 (d, *J* = 7.2 Hz, 1H, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 21.25 and 21.59 (2CH_3), 121.18 and 123.50 (2C), 125.57 (CH), 125.93 (C), 126.68, 127.39 and 127.67 (3CH), 128.46 (C), 128.96 and 129.13 (2CH), 129.74 (C), 130.16 (CH), 130.59 (C), 130.74 and 131.99 (2CH), 132.05 (C), 135.27 (CH), 137.23, 138.34, 141.20 and 145.23 (4C), 160.40 (C=O). *9,10-Bis(4-chlorophenyl)-7H-benzo[d,e]imidazo[2,1-a]isoquinolin-7-one* (**3g**): Yield: 0.38 g (87%); yellow crystals, mp 441–444 °C. IR (KBr) (ν_{max}/cm^{-1}): 1703 (C=O), 1585, 1551, 1472, 1392, 1345, 1303, 1231, 1168, 1129, 1088, 1015, 965, 910, 836, 775, 740. EI–MS, *m*/*z* (%): 444 (M$^+$ $^{37}Cl_2$, <1), 442 (M$^+$ $^{37}Cl^{35}Cl$, 3), 440 (M$^+$ $^{35}Cl_2$, 4), 380 (58), 363 (18), 349 (19), 315 (17), 293 (18), 273 (47), 179 (43), 149 (22), 111 (20), 97 (31), 83 (43), 69 (51), 57 (100), 43 (78). Anal. Calcd for $C_{26}H_{14}Cl_2N_2O$ (441.31): C, 70.76; H, 3.20; N, 6.35. Found: C, 70.70; H, 3.24; N, 6.34. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.6 Hz, 2H, 2CH), 7.44 (d, *J* = 8.6 Hz, 2H, 2CH), 7.47 (d, *J* = 8.6 Hz, 2H, 2CH), 7.53 (d, *J* = 8.6 Hz, 2H, 2CH), 7.78 (dd, *J* = 7.8, 7.6 Hz, 1H, CH), 7.81 (dd, *J* = 7.9, 7.5 Hz, 1H, CH), 8.11 (d, *J* = 8.2 Hz, 1H, CH), 8.29 (d, *J* = 8.0 Hz, 1H, CH), 8.64 (d, *J* = 7.3 Hz, 1H, CH), 8.79 (d, *J* = 7.3 Hz, 1H, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 120.83 and 123.14 (2C), 125.97 (CH), 126.00 (C), 126.86, 127.50, 128.58, 128.80 and 129.08 (5CH), 129.09 and 129.53 (2C), 130.72 (CH), 131.56 and 132.12 (2C), 132.22 and 132.31 (2CH), 133.71 and 134.98 (2C), 135.70 (CH), 140.61 and 145.81 (2C) 160.44 (C=O). *9,10-Di(2-pyridyl)-7H-benzo[d,e]imidazo[2,1-a]isoquinolin-7-one* (**3k**): Yield: 0.32 g (86%); red crystals; mp 374–376 °C. IR (KBr) (ν_{max}/cm^{-1}): 1696 (C=O), 1584, 1469, 1423, 1384, 1342, 1298, 1224, 1156, 1087, 1034, 992, 908, 838, 777, 742, 710, 681. EI–MS, *m*/*z* (%): 374 (M$^+$, 100), 345 (40), 317 (5), 197 (12), 187 (13), 172 (15), 152 (11), 126 (8), 78 (16), 57 (13), 43 (13). Anal. Calcd for $C_{24}H_{14}N_4O$ (374.39): C, 76.99; H, 3.77; N, 14.96. Found: C, 76.76; H, 3.88; N, 14.72. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.13 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H, CH), 7.41 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H, CH), 7.59 (dt, *J* = 1.8, 7.8 Hz, 1H, CH), 7.62 (d, *J* = 7.8 Hz, 1H, CH), 7.66 (d, *J* = 7.9 Hz, 1H, CH), 7.73 (dd, *J* = 7.8, 7.6 Hz, 1H, CH), 7.77 (dd, *J* = 7.8, 7.6 Hz, 1H, CH), 7.81 (dt, *J* = 1.8, 7.7 Hz, 1H, CH), 8.07 (d, *J* = 8.1 Hz, 1H, CH), 8.25 (d, *J* = 8.1 Hz, 1H, CH), 8.54 (dd, *J* = 4.1, 0.9 Hz, 1H, CH), 8.60 (dd, *J* = 7.3, 0.9 Hz, 1H, CH), 8.81 (d, *J* = 4.2 Hz, 1H, CH), 8.87 (dd, *J* = 7.3, 0.8 Hz, 1H, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 120.75 (C), 122.37, 122.67 and 123.15 (3CH), 126.14 (C), 126.48, 126.56, 126.72 and 127.40 (4CH), 127.59 (C), 130.81 (CH), 132.09 (C), 132.33, 135.70, 135.96 and 136.08 (4CH), 138.12, 141.76 and 148.30 (3C), 149.28 and 149.59 (2CH), 151.06 and 152.11 (2C), 160.15 (C=O).
26. *Selected X-ray crystallographic data for compound* **3k**: $C_{24}H_{14}N_4O$, orthorhombic, space group = *P*na2$_1$, *a* = 10.5295(20) Å, *b* = 9.7580(18) Å, *c* = 17.3399(33) Å, *V* = 1781.62(6) Å^3, *T* = 295(2) K, *Z* = 4, D_{calcd} = 1.396 g cm^{-3}, μ = 0.089 mm^{-1}, 1684 observed reflections, final R_1 = 0.072, wR_2 = 0.173 and for all data R_1 = 0.125, wR_2 = 0.205. CCDC 782758 contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.