Preliminary Communication

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Synthesis of 7-cyanoindolizine derivatives via a tandem reaction

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Abstract: A series of 2-substituted and 2,3-disubstituted 5-cyanoindolizine derivatives were conveniently synthesized by a one-pot tandem reaction under mild conditions in moderate yields. The reaction mechanism was proposed.

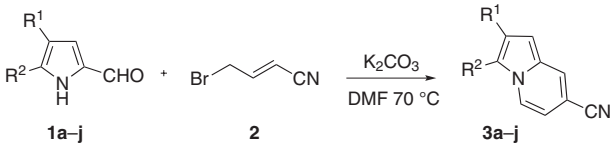
Keywords: 4-bromobut-2-enenitrile; indolizine; one-pot; pyrrole-2-carboxaldehyde.

Indolizine (pyrrolo[1,2-*a*]pyridine), one of the most important *N*-fused heterocycles, plays key roles in medicinal and materials chemistry [1–3]. The partially or more often wholly hydrogenated derivatives of indolizine can be frequently found as backbones in many bioactive natural products such as swainsonine or cryptowoline [4, 5]. Synthetic indolizines are potential inhibitors of vascular endothelial growth factor (VEGF), calcium entry blockers, potential central nervous system depressants, 5-HT3 receptor antagonists, phosphodiesterase V inhibitors, histamine H3 receptor antagonists, cardiovascular agents, and PLA2 inhibitors [6–13]. They have also drawn much attention owing to their possible usage as dyes for dye-sensitized solar cells (DSSC) or organic light-emitting devices (OLEDs) [14–22].

During the last decade, many methods for the synthesis of indolizines had been explored [1–3]. Most strategies are still based on pyridine derivatives as starting materials because the pyridines are easily available via synthetic methods and more than 2000 of them are commercial products. In principle, the alternative approach toward assembling the indolizine core starting from a pyrrole derivative and building a six-membered ring is simply a mirror image of the previous concept. However, such a synthesis has been a challenge to realize. Numerous difficulties, including significantly fewer commercially available pyrrole derivatives, their low oxidation potential and, hence, their stability, are reflected in an overall smaller number of such synthetic strategies.

Cyano-substituted indoles are key building units embedded in lead compounds currently being developed as estrogen receptor ligands, hepatitis C virus inhibitors, or therapeutic agents for cardiovascular diseases [23–25]. Thus, the synthesis of compounds containing a cyano group is important. Previously, we reported a novel tandem reaction of α,β-unsaturated esters with aldehydes to synthesize indolizine, imidazo[1,2-*a*]pyridine, imidazo[1,5-*a*]pyridine, and pyrido[1,2-*a*]benzimidazole derivatives [26–35]. Herein, we expand the tandem reaction to synthesize 2-substituted and 2,3-disubstituted 7-cyanoindolizines under mild conditions.

4,5-Disubstituted 1*H*-pyrrole-2-carbaldehydes **1a–j** were prepared per a literature method (Scheme 1) [28]. The desired 2-substituted and 2,3-disubstituted 7-cyanoindolizines **3a–j** were obtained by the reaction of pyrrole-2-carbaldehydes **1a–j** and 4-bromobut-2-enenitrile **2** in the presence of K_2CO_3 in dry DMF at 70°C for 6–10 h. A variety of products **3a–j** were obtained in good yields starting



1a–j **2** **3a–j**

a: R^1 = propionyl; R^2 = H
b: R^1 = benzoyl; R^2 = H
c: R^1 = 4-nitrobenzoyl; R^2 = H
d: R^1 = 4-methylbenzoyl; R^2 = H
e: R^1 = 4-methoxybenzoyl; R^2 = H
f: R^1 = 4-fluorobenzoyl; R^2 = H
g: R^1 = 4-chlorobenzoyl; R^2 = H
h: R^1 = 2-fluorobenzoyl; R^2 = H
i: R^1 = 2,4-dichlorobenzoyl; R^2 = H
j: R^1 = Br; R^2 = Br

Scheme 1

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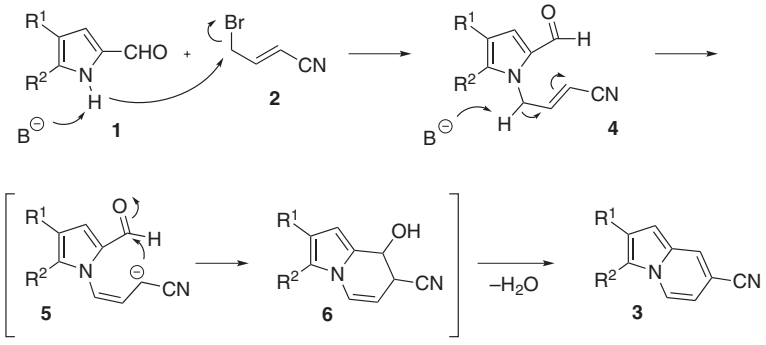

Scheme 2

with substituted pyrrole-2-carbaldehydes **1a–j** (Scheme 1). The structures of products **3** were characterized by ^{1}H NMR, ^{13}C NMR, IR and HR-MS.

The suggested mechanism is shown in Scheme 2. First, in the presence of base B^-, an intermolecular displacement reaction occurs between pyrrole-2-carbaldehyde **1** and 4-bromobut-2-enenitrile **2**. Then, deprotonation of the resultant adduct **4** followed by cyclization of the anion **5** generate intermediate product **6**, which is a direct precursor to the final indolizine **3**.

Experimental

All reagents and solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. Thin-layer chromatography (TLC) was conducted on silica gel GF254 plates (Merck KGaA). ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded on a Bruker Avance 300 spectrometer, using $CDCl_3$ or DMSO-d_6 as solvents and tetramethylsilane (TMS) as an internal standard. IR spectra were recorded with an Avtar 370 FT-IR spectrophotometer (Termo Nicolet). Elemental analyses were performed on a Vario EL III (Elementar Analysensysteme GmbH) analyzer. Mass spectra were recorded on a Trace DSQ mass spectrometer. The high resolution mass spectra (HRMS) were recorded on an Agilent Q-TOF6510 spectrometer. Pyrrole-2-carbaldehydes **1a–j** were prepared per the literature [36, 37].

General procedure for the synthesis of 3a–j

To a 100-mL round-bottom flask were added **1a–j** (6.0 mmol), enoate **2** (7.2 mmol), potassium carbonate (1.60 g, 12.5 mmol), and DMF (30 mL). The mixture was stirred at 70°C for 6–10 h and then filtered. The filtrate was concentrated by rotary evaporation. The crude products were purified by column chromatography eluting with EtOAc/hexane (1:5).

2-Propionylindolizine-7-carbonitrile (3a) Yellow solid; mp 161–162°C; yield 68%; ^{1}H NMR ($CDCl_3$): δ 7.97–7.89 (m, 2H), 7.84 (s, 1H), 7.09 (s, 1H), 6.65 (dd, 1H, J = 7.3, 1.7 Hz), 2.95 (q, 2H, J = 7.3 Hz), 1.24 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$): δ 197.2, 130.8, 129.9, 128.1, 126.1, 118.2, 117.7, 111.9, 104.7, 101.4, 33.4, 8.2: IR (neat): ν (cm^{-1}) 3425, 3140, 2979, 2934, 2218, 1673, 1628, 1521, 1467, 1414, 1333, 1202, 1167, 901, 797, 613, 558, 478, 419. HR-MS. Calcd for $(C_{12}H_{10}N_2O+H)^+$: *m/z* 199.0871. Found: *m/z* 199.0862.

2-Benzoylindolizine-7-carbonitrile (3b) Yellow solid; mp 192–193°C; yield 76%; ^{1}H NMR ($CDCl_3$): δ 7.98–7.84 (m, 5H), 7.66–7.57 (m, 1H), 7.57–7.47 (m, 2H), 7.14 (s, 1H), 6.68 (dd, 1H, J = 7.3, 1.7 Hz; ^{13}C NMR ($CDCl_3$) δ 191.0, 138.6, 132.5, 130.6, 129.4, 129.1, 128.5, 128.1, 126.0, 119.6, 118.2, 112.0, 106.7, 101.5; IR (neat): ν (cm^{-1}) 3075, 2227, 1633, 1528, 1478, 1402, 1359, 1328, 1243, 1113, 883, 796, 717, 684, 424. HR-MS. Calcd for $(C_{16}H_{10}N_2O+H)^+$: *m/z* 247.0871. Found: *m/z* 247.0861.

2-(4-Nitrobenzoyl)indolizine-7-carbonitrile (3c) Yellow solid; mp > 220°C; yield 65%; ^{1}H NMR (DMSO-d_6): δ 8.49–8.29 (m, 5H), 8.15–8.05 (m, 2H), 7.18 (s, 1H), 6.95 (dd, 1H, J = 7.3, 1.7 Hz); ^{13}C NMR (DMSO-d_6): δ 189.0, 149.4, 143.6, 130.5, 130.1, 128.4, 127.4, 127.1, 123.7, 121.5, 118.4, 111.6, 105.8, 101.0; IR (neat): ν (cm^{-1}) 3444, 3124, 2927, 2852, 2220, 1651, 1600, 1519, 1350, 1236, 1110, 1007, 848, 720, 622, 428. HR-MS. Calcd for $(C_{16}H_9N_3O_3+H)^+$: *m/z* 292.0722. Found: *m/z* 292.0726.

2-(4-Methylbenzoyl)indolizine-7-carbonitrile (3d) Yellow solid; mp 215–216°C; yield 66%; ^{1}H NMR ($CDCl_3$): δ 7.98–7.89 (m, 2H), 7.89–7.79 (m, 3H), 7.32 (d, 2H, J = 7.9 Hz), 7.13 (s, 1H), 6.71–6.63 (m, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 190.6, 143.3, 136.0, 130.6, 129.6, 129.4, 129.2, 128.1, 126.0, 119.5, 118.3, 111.9, 106.7, 101.4, 21.7; IR (neat): ν (cm^{-1}) 2222, 1631, 1526, 1471, 1328, 1247, 1114, 885, 744. HR-MS. Calcd for $(C_{17}H_{12}N_2O+H)^+$: *m/z* 261.1028. Found: *m/z* 261.1023.

2-(4-Methoxybenzoyl)indolizine-7-carbonitrile (3e) Yellow solid; mp 216–217°C; yield 65%; ^{1}H NMR ($CDCl_3$) δ 8.00–7.83 (m, 5H), 7.12 (s, 1H), 7.00 (d, 2H, J = 8.9 Hz), 6.67 (dd, 1H, J = 7.3, 1.6 Hz), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 189.5, 163.3, 131.8, 131.3, 130.5, 129.5, 128.0, 126.0, 119.3, 118.3, 113.8, 111.8, 106.6, 101.3, 55.5; IR (neat): ν (cm^{-1}) 3445, 3127, 3074, 2227, 1628, 1465, 1394, 1321, 1250, 1174, 1112, 885, 846, 806, 706, 471. HR-MS. Calcd for $(C_{17}H_{12}N_2O_2+H)^+$: *m/z* 277.0977. Found: *m/z* 277.0977.

2-(4-Fluorobenzoyl)indolizine-7-carbonitrile (3f) Yellow solid; mp 233–234°C; yield 62%; ^{1}H NMR ($CDCl_3$): δ 7.99–7.93 (m, 3H), 7.92–7.88 (m, 2H), 7.23–7.17 (m, 2H), 7.11 (s, 1H), 6.69 (dd, 1H, J = 7.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$): δ 189.4, 134.8, 132.0, 131.9, 130.7, 128.9, 128.1, 126.0, 119.4, 118.1, 115.8, 115.5, 112.1, 106.6, 101.7; IR (neat): ν (cm^{-1}) 3072, 2227, 1633, 1603, 1510, 1478, 1404, 1359, 1329, 1246, 1154, 1113, 891, 843, 801, 742, 702, 607, 426. HR-MS. Calcd for $(C_{16}H_9N_2OF+H)^+$: *m/z* 265.0777. Found: *m/z* 265.0780.

2-(4-Chlorobenzoyl)indolizine-7-carbonitrile (3g) Yellow solid; mp 230–231°C; yield 72%; ^{1}H NMR ($CDCl_3$): δ 8.05–7.78 (m, 5H), 7.50 (d, 2H, J = 8.4 Hz), 7.11 (s, 1H), 6.70 (d, 1H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 189. 7, 139.0, 136.9, 130.8, 130.7, 128.8, 128.8, 128.1, 126.1, 119.5, 118.1, 112.1, 106.6, 101.8; IR (neat): ν (cm^{-1}) 3328, 3069, 2928, 2852, 2229, 1631, 1587, 1527, 1478, 1401, 1355, 1329, 1242, 1095, 1009, 884, 746, 696, 573, 477, 424. HR-MS. Calcd for $(C_{16}H_9N_2OCl + H)^+$: *m/z* 281.0482. Found: *m/z* 281.0485.

2-(2-Fluorobenzoyl)indolizine-7-carbonitrile (3h) Yellow solid; mp 204–205°C; yield 76%; ^{1}H NMR ($CDCl_3$): δ 7.95–7.81 (m, 3H), 7.66–7.49 (m, 2H), 7.33–7.27 (m, 1H), 7.26–7.15 (m, 1H), 7.09 (d, 1H, J = 0.9 Hz), 6.66 (dd, 1H, J = 7.3, 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 188.0, 161.5, 158.2, 133.1, 133.0, 130.8, 130.4, 130.4, 129.8, 128.3, 126.1, 124.3, 124.3, 119.7, 119.7, 118.1, 116.6, 116.3, 112.1, 106.3, 106.3, 101.7; IR (neat): ν (cm^{-1}) 3134, 3077, 2225, 1644, 1527, 1482, 1444, 1400, 1359, 1327, 1234, 1148, 1094, 891, 819, 744, 712, 662, 600, 423. HR-MS. Calcd for $(C_{16}H_9N_2OF + H)^+$: *m/z* 265.0777. Found: *m/z* 265.0775.

2-(2,4-Dichlorobenzoyl)indolizine-7-carbonitrile (3i) Yellow solid; mp 198–199°C; yield 71%; ^{1}H NMR ($CDCl_3$): δ 7.90 (d, 1H, J = 7.3 Hz), 7.84 (s, 1H), 7.77 (d, 1H, J = 0.8 Hz), 7.52 (d, 1H, J = 1.7 Hz), 7.44–7.34 (m, 2H), 7.01 (s, 1H), 6.67 (dd, 1H, J = 7.3, 1.7 Hz); ^{13}C NMR ($CDCl_3$): δ 189.1, 137.4, 136.9, 132.2, 131.1, 130.3, 129.8, 129.2, 128.3, 127.1, 126.2, 119. 8, 118.0, 112.4, 106.2, 102.0; IR (neat): ν (cm^{-1}) 3446, 3137, 2219, 1655, 1583, 1521, 1466, 1371, 1330, 1230, 1109, 885, 825, 775, 595, 512, 416. HR-MS. Calcd for $(C_{16}H_8N_2OCl_2 + H)^+$: *m/z* 315.0092. Found: *m/z* 315.0095.

2,3-Dibromoindolizine-7-carbonitrile (3j) White solid; mp 186–187°C; yield 62%; ^{1}H NMR ($CDCl_3$): δ 7.98 (d, 1H, J = 7.3 Hz), 7.73 (s, 1H), 6.91 (s, 1H), 6.76 (dd, 1H, J = 7.3, 1.6 Hz); ^{13}C NMR ($CDCl_3$): δ 131.6, 124.9, 123.9, 118.2, 111.4, 108.9, 107.2, 100.9, 99.6; IR (neat): ν (cm^{-1}) 3424, 3121, 3073, 2222, 1628, 1511, 1460, 1425, 1345, 1285, 1246, 1142, 990, 898, 757, 697, 599, 480, 420. HR-MS. Calcd for $(C_9H_4N_2Br_2 + H)^+$: *m/z* 298.8819. Found: *m/z* 298.8820.

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References

[1] Borrow, E. T.; Holland, D. O. The chemistry of the pyrrocolines and the octahydropyrrocolines. *Chem. Rev.* **1948**, *42*, 611–643.

[2] Uchida, T.; Matsumoto, K. Methods for the comstruction of the indolizine nucleus. *Synthesis* **1976**, *7*, 209–236.

[3] Sadowski, B.; Klajn, J.; Gryko, D. T. Recent advances in the synthesis of indolizines and their π-expanded analogues. *Org. Biomol. Chem.* **2016**, *14*, 7804–7828.

[4] Michael, J. P. Indolizidine and quinolizidine alkaloids. *Nat. Prod. Rep.* **2008**, *25*, 139–165.

[5] Lebceuf, M.; Cave, A.; Ranaivo, A.; Moskowitz, H. New alkaloids of the dibenzopyrrocoline type. *Can. J. Chem.* **1989**, *67*, 947–952.

[6] Gubin, J.; Vogelaer, H.; Inion, H.; Houben, C.; Lucchetti, J.; Mahaux, J.; Rosseels, G.; Peiren, M.; Clinet, M.; Polster, P.; et al. Novel heterocyclic analogs of the new potent class of calcium entry blockers: 1-[[4-(aminoalkoxy)phenyl]- sulfonyl]indolizines. *J. Med. Chem.* **1993**, *36*, 1425–1433.

[7] Gupta, S. P.; Mathur, A. N.; Nagappa, A. N.; Kumar, D.; Kumaran, S. A quantitative structure-activity relationship study on a novel class of calcium-entry blockers: 1-[(4-(aminoalkoxy) phenyl)sulphonyl]indolizines. *Eur. J. Med. Chem.* **2003**, *38*, 867–873.

[8] Chen, P.; Chaikuad, A.; Bamborough, P.; Bantscheff, M.; Bountra, C.; Chung, C. W.; Fedorov, O.; Grandi, P.; Jung, D.; Lesniak, R.; et al. Discovery and characterization of GSK2801, a selective chemical probe for the bromo domains BAZ2A and BAZ2B. *J. Med. Chem.* **2016**, *59*, 1410–1424.

[9] Bedjeguelal, K.; Bienayme, H.; Dumoulin, A.; Poigny, S.; Schmitt, P.; Tam, E. Discovery of protein-protein binding disruptors using multi-component condensations small molecules. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 3998–4001.

[10] Chai, W.; Breitenbucher, J. G.; Kwok, A.; Li, X.; Wong, V.; Carruthers, N. I.; Lovenberg, T. W.; Mazur, C.; Wilson, S. J.; Axe, F. U.; et al. Non-imidazole heterocyclic histamine H_3 receptor antagonists. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 1767–1770.

[11] Gubin, J.; Descamps, M.; Chatelain, P.; Nisato, D. Indolizine derivatives, process for their preparation and compositions containing them. *Eur. Pat. Appl. EP.* **1987**, 235111.

[12] Gundersen, L. L.; Charnock, C.; Negussie, A. H.; Rise, F.; Teklu, S. Synthesis of indolizine derivatives with selective antibacterial activity against mycobacterium tuberculosis. *Eur. J. Pharm. Sci.* **2007**, *30*, 26–35.

[13] Hagishita, S.; Yamada, M.; Shirahase, K.; Okada, T.; Murakami, Y.; Ito, Y.; Matsuura, T.; Wada, M.; Kato, T.; Ueno, M.; et al. Potent inhibitors of secretory phospholipase A2: synthesis and inhibitory activities of indolizine and indene derivatives. *J. Med. Chem.* **1996**, *39*, 3636–3658.

[14] Surpateanu, G. G.; Becuwe, M.; Lungu, N. C.; Dron, P. I.; Fourmentin, S.; Landy, D.; Surpateanu, G. Photochemical behaviour upon the inclusion for some volatile organic compounds in new fluorescent indolizine β-cyclodextrin sensors. *J. Photochem. Photobiol. A.* **2007**, *185*, 312–320.

[15] Delattre, F.; Oisel, P.; Surpateanu, G.; Cazier, F.; Blach, P. Photochemical behaviour upon the inclusion for some volatile organic compounds in new fluorescent indolizine β-cyclodextrin sensors. *Tetrahedron* **2005**, *61*, 3939–3945.

[16] Rotaru, A. V.; Druta, L. D.; Oeser, T.; Mueller, T. J. J. Novel coupling 1,3-dipolar cycloaddition sequence as a three-component approach to highly fluorescent indolizines. *Helv. Chim. Acta* **2005**, *88*, 1798–1812.

[17] Sonnenschein, H.; Henrich, G.; Resch-Genger, V.; Schulz, B. Fluorescence and UV/Vis spectroscopic behaviour of novel biindolizines. *Dyes Pigments* **2000**, *46*, 23–27.

[18] Saeva, F. D.; Luss, H. R. Cheminform abstract: novel synthesis of the 2,3-benzindolizine ring system. Mechanism of formation, redox, electronic absorption, and fluorescence behavior. *J. Org. Chem.* **1988**, *53*, 1804–1806.

[19] Weidner, C. H.; Wadsworth, D. H.; Bender, S. L.; Beltman, D. J. Indolizines. 4. dyes derived from oxoindolizinium ions and active methylene compounds. *J. Org. Chem.* **1989**, *54*, 3660–3664.

[20] Delcamp, J. H.; Yella, A.; Holcombe, T. W.; Nazeeruddin, M. K.; Grätzel, M. The molecular engineering of organic sensitizers for solar-cell applications. *Angew. Chem., Int. Ed.* **2013**, *52*, 376–380.

[21] Wan, J.; Zheng, C. J.; Fung, M. K.; Liu, X. K.; Lee, C. S.; Zhang, X. H. Multifunctional electron-transporting indolizine derivatives

for highly efficient blue fluorescence, orange phosphorescence host and two-color based white OLEDs. *J. Mater. Chem.* **2012**, *22*, 4502–4510.

[22] Song, Y. R.; Lim, C. W.; Kim, T. W. Synthesis and photophysical properties of 1,2-diphenylindolizine derivatives: fluorescent blue-emitting materials for organic light-emitting device. *Luminescence* **2015**, *31*, 364–371.

[23] Patil, S. A.; Patil, R.; Miller, D. D. Microwave-assisted synthesis of medicinally relevant indoles. *Curr. Med. Chem.* **2011**, *18*, 615–637.

[24] Murali Dhar, T. G.; Shen, Z.; Gu, H. H.; Chen, P.; Norris, D.; Watterson,S. H.; Ballentine, S. K.; Fleener,C. A.; Rouleau,K. A.; Barrish,J. C.; et al. 3-Cyanoindole-based inhibitors of inosine monophosphate dehydrogenase: synthesis and initial structure-activity relationships. *Bioorg. Med. Chem. Lett.,* **2003**, *13*, 3557–3560.

[25] Li, B.; Zhang, B. B.; Zhang, X. Y.; Fan, X. S. Synthesis of 3-cyano-1*H*-indoles and their 2′-deoxyribonucleoside derivatives through one-pot cascade reactions. *J. Org. Chem*. **2016**, *81*, 9530–9538.

[26] Ge, Y. Q.; Jia, J.; Yang, H.; Tao, X. T.; Wang, J. W. The synthesis, characterization and optical properties of novel pyrido[1,2-*a*] benzimidazole derivatives. *Dyes Pigments* **2011**, *88*, 344–349.

[27] Ge, Y. Q.; Jia, J.; Li, Y.; Yin, L.; Wang, J. W. ChemInform abstract: a novel and efficient approach to pyrazolo[1,5-*a*]pyridine derivatives via one-pot tandem reaction. *Heterocycles* **2009**, *78*, 197–206.

[28] Ge, Y. Q.; Jia, J.; Yang, H.; Zhao, G. L.; Zhan, F. X.; Wang, J. W. A facile approach to indolizines via tandem reaction. *Heterocycles* **2009**, *78*, 725–736.

[29] Jia, J.; Ge, Y. Q.; Tao, X. T.; Wang, J. W. Facile synthesis of imidazo[1,2-*a*]pyridines via tandem reaction. *Heterocycles* **2010**, *81*, 185–194.

[30] Ge, Y. Q.; Hao, B. Q.; Duan, G. Y.; Wang, J. W. The synthesis, characterization and optical properties of novel 1,3,4-oxadiazole-containing imidazo[1,5- a]pyridine derivatives. *J. Lumin.* **2011**, *131*, 1070–1076.

[31] Cao, X. Q.; Lin, X. H.; Zhu, Y.; Ge, Y. Q. The optical properties, synthesis and characterization of novel 5-aryl-3-benzimidazolyl -1-phenyl-pyrazoline derivatives. *Spectrochim. Acta A* **2012**, *98*, 76–80.

[32] Ge, Y. Q.; Gong, X. Y.; Song, G. J.; Cao X. Q.; Wang, J. W. The synthesis, characterization and optical properties of novel 2-acyl 6- arylindolizines. *Spectrochim. Acta A* **2015**, *135*, 7–13.

[33] Ge, Y. Q.; Wang, T.; Duan, G. Y.; Dong, L. H.; Cao, X. Q.; Wang, J. W. Synthesis, characterization, optical properties and theoretical studies of novel substituted imidazo[1,5-*a*] pyridinyl-1,3,4-oxadiazole derivatives. *J. Fluoresc.* **2012**, *22*, 1531–1538.

[34] Ge, Y. Q.; Li, F. R.; Zhang, Y. J.; Bi, Y. S.; Cao, X. Q.; Duan, G. Y.; Wang, J. W.; Liu, Z. L. Synthesis, crystal structure, optical properties and antibacterial evaluation of novel imidazo[1,5-*a*] pyridine derivatives bearing a hydrazone moiety. *Luminescence* **2014**, *29*, 293–300.

[35] Ge, Y. Q.; Jia, J.; Wang, T.; Sun, H. W.; Duan, G. Y.; Wang, J. W. The synthesis, characterization and optical properties of novel 5-(3-aryl-1H-pyrazol-5-yl)-2-(3- butyl-1-chloroimidazo[1,5-*a*] pyridin-7-yl)-1,3,4-oxadiazole. S*pectrochim. Acta A.* **2014**, *123*, 336–341.

[36] Sonnet, P. E. Preparation and properties of ternary iminium salts of pyrrole aldehydes and ketones. Synthesis of 4-substituted pyrrole-2-carboxaldehydes. *J. Org. Chem*. **1972**, *37*, 925–929.

[37] Anderson, H. J.; Loader, C. E.; Foster, A. Pyrrole chemistry. XXII. A 'one-pot' synthesis of some 4-acylpyrrole-2-carboxaldehydes from pyrrole. *Can. J. Chem.* **1980**, *58*, 2527–2530.