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The synthesis, characterization and optical properties of novel pyrido[1,2-*a*]benzimidazole derivatives

Yan Qing Ge [a,c,1], Jiong Jia [a,b,1], He Yang [a], Xu Tang Tao [b,*], Jian Wu Wang [a,*]

[a] School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong, 250100, PR China
[b] State Key Laboratory of Crystal Materials, Shandong University, Jinan, Shandong, 250100, PR China
[c] School of Chemistry and Chemical Engineering, Taishan Medical University, Taian, Shandong, 271016, PR China

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ABSTRACT

A series of novel, substituted, pyrido[1,2-*a*]benzimidazole derivatives were synthesized using a novel tandem annulation reaction between 2-acylbenzimidazole derivatives and 4-bromobut-2-enoic esters under mild conditions. The compounds were characterized using IR, ^{1}H NMR, ^{13}C NMR and HRMS; the crystal structure of 2,7,8-trimethyl-3-ethoxycarbonyl-4-phenylpyrido[1,2-*a*]benzimidazole was determined as orthorhombic. The absorbance and fluorescence spectra of the pyrido[1,2-*a*]benzimidazoles were measured in dichloromethane; an intense absorption maxima was observed at 250 nm and emission maxima were noted at 460 nm. The absorption spectra and fluorescence characteristics of the pyrido[1,2-*a*]benzimidazole derivatives revealed that a phenyl and a methyl group attached to the pyrido[1,2-*a*]benzimidazole ring markedly influenced maximum emission.

1. Introduction

Imidazo[1,2-*a*]pyridine derivatives (Ips) are common to several diverse classes of compounds with medicinal value [1]. They are also used as fluorescent ligands [2] and as components in organic light-emitting diodes (OLED) [3] and in organic field effect transistors (FET) [4]. In contrast, the related pyrido[1,2-*a*]benzimidazole ring system has not received much attention until the past two decades when some of its derivatives were found to have pharmaceutical applications [5–10]. Some of these compounds also display interesting photophysical and fluorescent properties [11–15]. However, as a class of compounds their spectroscopic properties have remained largely unexplored perhaps as a consequence of the lack of general synthetic methods to this class of heterocycle from easily accessible precursors.

It is promising that the introduction of additional π-systems into imidazo[1,2-*a*]pyridines influences their photophysical properties. Continuing our efforts on extending the scope and applications of the tandem reaction for the preparation of nitrogen-bridgehead heteroaromatics [16–18] and in order to search for novel fluorescent organic compounds, herein, pyrido[1,2-*a*]benzimidazole derivatives were conveniently synthesized by a novel tandem annulation reaction under very mild conditions and their structure and optical properties were described.

2. Experimental

2.1. General

Thin-layer chromatography (TLC) was conducted on silica gel 60 F_{254} plates (Merck KGaA). ^{1}H NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer, using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Melting points were determined on an XD-4 digital micro melting point apparatus. IR spectra were recorded with an IR spectrophotometer VERTEX 70 FT-IR (Bruker Optics). HRMS spectra were recorded on a Q-TOF6510 spectrograph (Agilent). UV–vis spectra were recorded on a U-4100 (Hitachi). Fluorescent measurements were recorded on a PerkineElmer LS-55 luminescence spectrophotometer.

* Corresponding authors. Tel.: +86 531 88362708; fax: +86 531 88364464.
E-mail addresses: txt@icm.sdu.edu.cn (X.T. Tao), jwwang@sdu.edu.cn (J.W. Wang).
[1] Equal contributors.

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2.2. Synthesis

The synthetic approach for the preparation of substituted pyrido [1,2-*a*]benzimidazole derivatives is shown in Fig. 1.

The hydroxybenzylimidazoles **5a**–**d** were synthesized by condensing diamines **4a**–**b** with an appropriate hydroxy acid via Phillips condensation [20].

2.2.1. Preparation of *1a*

The benzoimidazole-2-carbaldehyde **1a** was synthesized according to the literature [19], and was subjected to the following steps without purification.

2.2.2. General procedure for the preparation of *1b*–*e*

A solution of chromium trioxide (caution: Stable. Very strong oxidant; reacts with most organic material in a violent and often explosive fashion; moisture sensitive: 0.60 g, 6.00 mmol) in water (2 mL) was added dropwise to a solution of hydroxybenzylimidazoles **5** (8.00 mmol) in glacial acid (20 mL) at 90 °C. The reaction mixture was heated at 100 °C for a further 5 min and then poured into water (100 mL) and filtered. The filtrate was extracted with dichloromethane (3 × 30 mL). The combined extracts were washed with brine (2 × 20 mL), dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The crude products **1b**–**e** were purified by recrystallization from ethyl acetate.

*2.2.2.1. 1-(1H-Benzo[d]imidazol-2-yl)ethanone (**1b**).* White solid (80% yield): mp 187–188 °C (lit. 186–188 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.85 (s, 1H), 7.91 (d, J = 7.2 Hz, 2H), 7.36–7.55 (m, 3H), 2.85 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 192.2, 147.8, 143.5, 133.8, 126.6, 123.9, 121.9, 112.2, 26.0; IR (KBr) ν = 3290, 3060, 2924, 1675, 1578, 1507, 1485, 1442, 1420, 1313, 1236, 950, 733 cm^{-1}; HRMS: *m/z* calcd for $C_9H_9N_2O$ $[M + H]^+$ 161.1715, found 161.1704.

*2.2.2.2. (1H-Benzo[d]imidazol-2-yl)(phenyl)methanone (**1c**).* White solid (85% yield): mp 213–215 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.53 (s, 1H), 8.59 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 8.1 Hz, 2H), 7.75 (t, J = 7.2 Hz, 1H), 7.61–7.66 (m, 3H), 7.44 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 183.5, 147.9, 143.2, 135.6, 134.1, 133.6, 130.8, 128.4, 125.7, 123.1, 121.3, 112.8; IR (KBr) ν = 3302, 3051, 2854, 1657, 1593, 1514, 1486, 1431, 1318, 1262, 919, 739 cm^{-1}; HRMS: *m/z* calcd for $C_{14}H_{11}N_2O$ $[M + H]^+$ 233.0871, found 233.0869.

*2.2.2.3. 1-(5,6-Dimethyl-1H-benzo[d]imidazol-2-yl)ethanone (**1d**).* Yellow solid (75% yield): mp 179–180 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.39 (s, 1H), 7.64 (s, 1H), 7.29 (s, 1H), 2.80 (s, 3H), 2.39 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 191.9, 147.2, 142.3, 136.6, 133.3, 132.4, 121.5, 111.9, 107.5, 25.8, 20.8, 20.4; IR (KBr) ν = 3307, 2981, 2919, 1670, 1572, 1509, 1441, 1414, 1352, 1236, 1001, 667 cm^{-1}; HRMS: *m/z* calcd for $C_{11}H_{13}N_2O$ $[M + H]^+$ 189.1028, found 189.1034.

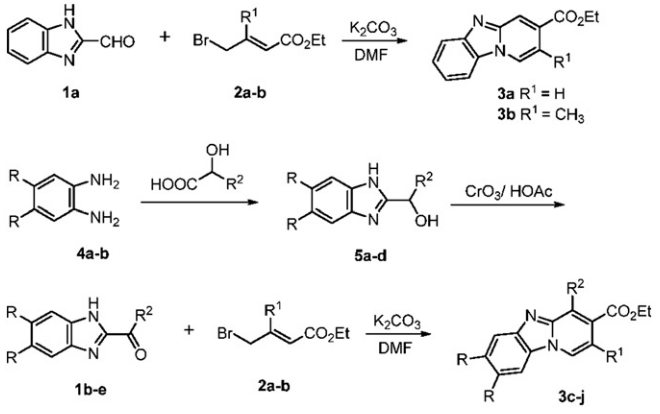

Fig. 1. Synthesis of substituted pyrido[1,2-*a*]benzimidazole derivatives.

*2.2.2.4. (5,6-Dimethyl-1H-benzo[d]imidazol-2-yl)(phenyl) methanone (**1e**).* Yellow solid (78% yield): mp 190 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.50 (s, 1H), 8.68 (d, J = 8.1 Hz, 2H), 7.71 (s, 1H), 7.52–7.66 (m, 3H), 7.33 (s, 1H), 2.40 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.9, 147.2, 142.9, 136.6, 135.6, 133.7, 133.6, 133.2, 131.9, 131.3, 128.4, 121.8, 111.7, 20.8, 20.4; IR (KBr) ν = 3305, 2968, 2902, 1629, 1596, 1570, 1505, 1433, 1407, 1328, 1264, 993, 734 cm^{-1}; HRMS: *m/z* calcd for $C_{16}H_{15}N_2O$ $[M + H]^+$ 251.1184, found 251.1178.

2.2.3. General procedure for the preparation of *3a*–*j*

To a 50-mL round-bottomed flask were added **1** (1.00 mmol), α, β-unsaturated ester **2** (2.00 mmol), potassium carbonate (0.28 g, 2.05 mmol) and dry DMF (10 mL). The mixture was stirred at r.t for 3 h and then filtered. The filtrate was poured into water (100 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with water, dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The crude products were purified by column chromatography to afford compound **3** in 42–88%.

*2.2.3.1. 3-Ethoxycarbonylpyrido[1,2-a]benzimidazole (**3a**).* Yellow solid (55% yield): mp 203–204 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (d, J = 7.2 Hz, 1H), 8.45 (s, 1H), 8.01(d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.59 (t, J = 4.8 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 4.46 (q, J = 7.2 Hz, 2H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 147.3, 145.5, 130.8, 128.7, 126.3, 124.9, 122.4, 120.9, 120.7, 110.8, 109.3, 61.9, 14.3; IR (KBr) ν = 3415, 3031, 2981, 1720, 1519, 1474, 1330, 1230, 1082, 743 cm^{-1}; HRMS: *m/z* calcd for $C_{14}H_{13}N_2O_2$ $[M + H]^+$ 241.0977, found 241.0976.

*2.2.3.2. 2-Methyl-3-ethoxycarbonylpyrido[1,2-a]benzimidazole (**3b**).* Yellow solid (42% yield): mp 134–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (s, 1H), 8.28 (s, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 3.0 Hz, 1H), 7.41 (t, J = 3.0 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 2.61 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.7, 146.7, 145.4, 132.2, 128.4, 126.0, 124.1, 122.0, 121.2, 120.5, 119.4, 110.8, 61.6, 18.5, 14.3; IR (KBr) ν = 3451, 3050, 2980, 1690, 1638, 1506, 1454, 1430, 1333, 1277, 1258, 1013, 748 cm^{-1}; HRMS: *m/z* calcd for $C_{15}H_{15}N_2O_2$ $[M + H]^+$ 255.1134, found 255.1134.

*2.2.3.3. 3-Ethoxycarbonyl-4-methylpyrido[1,2-a]benzimidazole (**3c**).* Yellow solid (85% yield): mp 129–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, J = 7.2 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.57 (m, 1H), 7.43 (m, 1H), 7.32 (d, J = 7.2 Hz, 1H), 4.44 (q, J = 7.2 Hz, 2H), 3.04 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 148.8, 144.7, 132.2, 129.3, 128.0, 126.0, 122.2, 121.9, 120.5, 110.8, 110.6, 61.6, 15.3, 14.3; IR (KBr) ν = 3391, 3126, 2991, 1709, 1478, 1328, 1244, 1170, 1058, 746 cm^{-1}; HRMS: *m/z* calcd for $C_{15}H_{15}N_2O_2$ $[M + H]^+$ 255.1134, found 255.1134.

*2.2.3.4. 2,4-Dimethyl-3-ethoxycarbonylpyrido[1,2-a]benzimidazole (**3d**).* Yellow solid (79% yield): mp 140–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.50 (m, 1H), 7.36 (m, 1H), 4.47 (q, J = 7.2 Hz, 2H), 2.70 (s, 3H), 2.36 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 147.6, 144.6, 134.3, 129.0, 125.6, 125.2, 121.5, 121.1, 120.2, 110.6, 61.7, 16.9, 14.8, 14.3; IR (KBr) ν = 3425, 2975, 1724, 1490, 1468, 1450, 1338, 1255, 1153, 1038, 756 cm^{-1}; HRMS: *m/z* calcd for $C_{16}H_{17}N_2O_2$ $[M + H]^+$ 269.1290, found 269.1293.

Table 1
Crystal data and structure refinement for **3j**.

Empirical formula	$C_{23}H_{22}N_2O_2$
Formula weight	358.43
Temperature	293(2)K
Wavelength	0.71973 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	$a = 16.4809(12)$ Å $\alpha = 99$ deg. $b = 12.4963(9)$ Å $\beta = 99$ deg. $c = 19.1780(14)$ Å $\gamma = 90$deg.
Volume	3949.7(5) A^3
Z	8
Calculated density	1.206 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	1520
Crystal size	0.29 × 0.15 × 0.19 mm
θ range for data collection	2.12–27.54°
Limiting indices	$-29 \le h \le 21$, $-16 \le k \le 14$, $-12 \le 1 \le 24$
Reflections collected/unique	21955/4518 [R(int) = 0.0263]
Completeness to $\theta = 27.54°$	99.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9923 and 0.9847
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4518/0/245
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0658$, $wR_2 = 0.2054$
R indices (all data)	$R_1 = 0.0884$, $wR_2 = 0.2307$
Largest diff. peak and hole	0.536 and −0.352 e. $Å^{-3}$

*2.2.3.5. 3-Ethoxycarbonyl-4-phenylpyrido[1,2-a]benzimidazole (**3e**).* Yellow solid (88% yield): mp 165–166 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (d, J = 7.2 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.41–7.54 (m, 7H), 7.28 (d, J = 7.2 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 147.8, 145.4, 135.4, 132.7, 130.1, 129.4, 129.0, 128.5, 128.3, 126.0, 123.9, 122.2, 121.0, 110.7, 110.3, 61.6, 13.6; IR (KBr) ν = 3410, 3031, 2984, 1717, 1468, 1369, 1327, 1257, 1135, 1011, 768, 697 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{17}N_2O_2$ $[M + H]^+$ 317.1290, found 269.1294.

*2.2.3.6. 2-Methyl-3-ethoxycarbonyl-4-phenylpyrido[1,2-a]benzimidazole (**3f**).* Yellow solid (77% yield): mp 136–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.61–7.64 (m, 2H), 7.35–7.52 (m, 5H), 4.10 (q, J = 7.2 Hz, 2H), 2.43 (s, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 146.7, 145.1, 134.9, 134.7, 129.6, 129.1, 128.8, 128.7, 128.5, 125.6, 122.5, 121.6, 120.7, 117.1, 110.5, 61.6, 16.8, 13.7; IR (KBr) ν = 3438, 3051, 3010, 2927, 1730, 1641, 1640, 1490, 1340, 1244, 1182, 1087, 1016, 741, 697 cm^{-1}; HRMS: *m/z* calcd for $C_{21}H_{19}N_2O_2$ $[M + H]^+$ 331.1447, found 331.1445.

*2.2.3.7. 3-Ethoxycarbonyl -4,7,8-trimethylpyrido[1,2-a]benzimidazole (**3g**).* Yellow solid (82% yield): mp 159–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, J = 7.2 Hz, 1H), 7.76 (s, 1H), 7.61 (s, 1H), 7.24 (d, J = 7.2 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 3.01 (s, 3H), 2.47 (s, 3H), 2.46 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 148.3, 143.6, 135.5, 132.1, 131.9, 127.8, 127.0, 121.5, 120.2, 110.5, 110.2, 61.4, 20.8, 20.7, 15.3, 14.3; IR (KBr) ν = 3407, 2979, 2920, 2853, 1719, 1490, 1470, 1309, 1235, 1147, 1055, 737 cm^{-1}; HRMS: *m/z* calcd for $C_{17}H_{19}N_2O_2$ $[M + H]^+$ 283.1447, found 283.1448.

*2.2.3.8. 2,4,7,8-Tetramethyl-3-ethoxycarbonylpyrido[1,2-a]benzimidazole (**3h**).* Yellow solid (70% yield): mp 84.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.71 (s, 1H), 7.58 (s, 1H), 4.47 (q, J = 7.2 Hz, 2H), 2.68 (s, 3H), 2.46 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 147.0, 143.3, 135.0, 133.4, 131.1, 127.5, 125.1, 120.9, 119.9, 116.3, 110.4, 61.6, 20.7, 20.6, 16.8, 14.8, 14.3; IR (KBr) ν = 3444, 3038, 2983, 2926, 1729, 1629, 1499, 1473, 1384, 1266, 1245, 1180, 1145, 1064, 1007, 852 cm^{-1}; HRMS: *m/z* calcd for $C_{18}H_{21}N_2O_2$ $[M + H]^+$ 297.1603, found 297.1606.

*2.2.3.9. 3-Ethoxycarbonyl-4-phenyl-7,8-dimethylpyrido[1,2-a]benzimidazole (**3i**).* Yellow solid (83% yield): mp 179–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (d, J = 7.2 Hz, 1H), 7.74 (s, 1H), 7.68 (s, 1H), 7.44–7.56 (m, 5H), 7.23 (d, J = 7.2 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 2.48 (s, 3H), 2.43 (s, 3H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 147.2, 144.2, 135.6, 135.5, 132.6, 131.9, 129.4, 129.2, 128.3, 128.2, 127.5, 123.6, 120.7, 110.4, 110.0, 61.4, 20.8, 20.7, 13.5; IR (KBr) ν = 3452, 2974, 1706, 1644, 1618, 1564, 1462, 1326, 1212, 1157, 1026, 847, 687 cm^{-1}; HRMS: *m/z* calcd for $C_{22}H_{21}N_2O_2$ $[M + H]^+$ 345.1603, found 345.1607.

*2.2.3.10. 2,7,8-Trimethyl-3-ethoxycarbonyl-4-phenylpyrido[1,2-a]benzimidazole (**3j**).* Yellow solid (74% yield): mp 163–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.71 (s, 1H), 7.63–7.60 (m, 3H), 7.39–7.50 (m, 3H), 4.08 (q, J = 7.2 Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 146.2, 144.0, 135.0, 134.9, 133.9, 131.2, 129.6, 128.9, 128.5, 128.4, 127.3, 122.4, 120.4, 116.6, 110.3, 61.4, 20.7, 20.6, 16.8, 13.7; IR

Table 2
Selected bond lengths and angles for **3j**.

Bond lengths							
N(l)-C(9)	1.372(2)	N(l)-C(8)	1.389(2)	N(l)-C(17)	1.391(3)	C(9)-C(10)	1.349(3)
C(10)-C(12)	1.438(3)	C(8)-N(2)	1.330(3)	C(8)-C(7)	1.422(3)	C(7)-C(12)	1.367(3)
C(7)-C(l)	1.491(3)	N(2)-C(16)	1.387(3)	C(16)-C(23)	1.399(3)	C(13)-O(l)	1.188(3)
C(13)-O(2)	1.334(3)	O(2)-C(14)	1.466(4)	C(21)-C(19)	1.424(4)	C(14)-C(15)	1.431(6)
Bond angles							
C(9)-N(l)-C(8)			123.58(17)	C(19)-C(18)-C(17)			117.5(2)
C(18)-C(17)-C(16)			123.0(2)	C(8)-N(l)-C(17)			106.34(16)
N(2)-C(16)-C(17)			111.54(19)	C(10)-C(9)-N(l)			119.84(18)
C(9)-N(l)-C(17)			129.91(16)	C(9)-C(10)-C(12)			118.24(18)
N(2)-C(16)-C(23)			129.9(2)	N(2)-C(8)-N(l)			112.84(18)
C(17)-C(16)-C(23)			118.6(2)	N(2)-C(8)-C(7)			129.46(18)
C(7)-C(12)-C(10)			122.49(19)	N(l)-C(8)-C(7)			117.64(17)
C(7)-C(12)-C(13)			118.59(18)	C(12)-C(7)-C(8)			118.21(18)
C(10)-C(12)-C(13)			118.89(18)	C(12)-C(7)-C(l)			122.59(19)
C(6)-C(l)-C(2)			118.7(2)	C(8)-C(7)-C(l)			119.17(18)
C(6)-C(l)-C(7)			120.5(2)	N(l)-C(17)-C(18)			131.82(19)
C(8)-N(2)-C(16)			104.18(17)	N(l)-C(17)-C(16)			105.06(17)
O(l)-C(13)-O(2)			124.9(2)	O(2)-C(13)-C(12)			110.9(2)
O(l)-C(13)-C(12)			124.2(2)	C(21)-C(23)-C(16)			119.9(2)

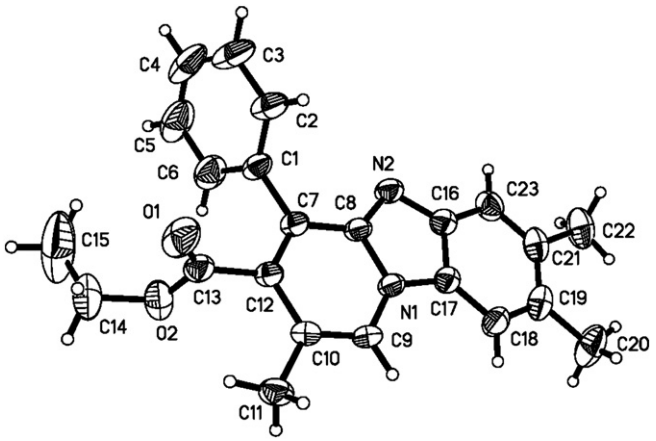

Fig. 2. The molecular structures of **3j**, H atoms and the molecular structures of solvents are omitted for clarity.

(KBr) ν = 3448, 3017, 2974, 1735, 1621, 1492, 1468, 1424, 1313, 1240, 1172, 1116, 1019, 857, 699 cm^{-1}; HRMS: *m/z* calcd for $C_{23}H_{23}N_2O_2$ $[M + H]^+$ 359.1760, found 359.1766.

2.3. X-ray crystallography

Single crystals of compound **3j** suitable for X-ray diffraction were obtained by slow evaporation of a solution of the solid in ethyl acetate at room temperature for 5 days. A crystal with approximate dimension of 0.20 mm × 0.15 mm × 0.10 mm was mounted on a Bruker Smart Apex II CCD equipped with a graphite monochromated MoKα radiation (λ = 0.71073Å) by using Φ and ω scan modes and the data were collected at 293(2) K. The structure of the crystal was solved by direct methods and refined by full-matrix least-squares techniques implemented in the SHELXTL-97 crystallographic software. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms bound to carbon were located by geometrical calculations, with their position and thermal parameters being fixed during the structure refinement. A summary of the crystallographic data and structure refinement details is given in Table 1, and the selected bond lengths and angles are presented in Table 2. The crystal structure and cell structure of **3j** are shown in Figs. 2 and 3, respectively.

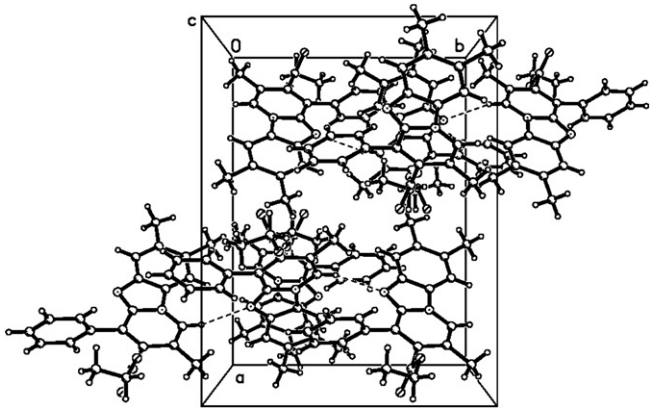

Fig. 3. A packing diagram for **3j**, H atoms and the molecular structures of solvents are omitted for clarity.

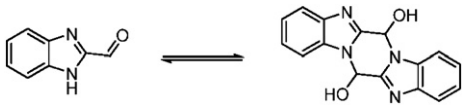

Fig. 4. The dimeric structure of **1a**.

3. Results and discussion

3.1. Synthesis

The desired pyrido[1,2-*a*]benzimidazole **3** was obtained by the reactions of compounds **1** and the bromomethyl substituted esters **2** in the presence of K_2CO_3 at room temperature. Because of the low solubility of the benzoimidazole-2-carbaldehyde **1a** in DMF and the formation of the dimeric structure (Fig. 4) [21], the yields of **3a**–**b** are low compared to those of other products. It is interesting to note that the presence of a benzoyl or acetyl substituent of benzimidazole did not show any significant influence on the outcome of the reaction but the presence of a methyl substituent on the α, β-unsaturated ester interfered with the reaction because of the inductive effect. Additionally, increased temperature (50 °C) and extended reaction time (up to 9 h) were required to obtain the desired product when 2-benzoylbenzoimidazoles **1b**–**e** were reacted with ethyl 4-bromo-3-methylbut-2-enoate **2b**. On the basis of the above results and our previous work [16,17,18], we believe that this reaction proceeds by an S_N2 displacement of bromide ion, deprotonation resulting in an ester stabilised anion which facilitates cyclisation and a subsequent dehydration as shown in Fig. 5.

3.2. Structure characterization

The structures of products **3a-j** were characterized by spectroscopic methods (^1H and ^{13}C NMR, IR, and HRMS). For example, compound **3j**, obtained as yellow crystals, gave an [M + H]-ion peak at *m/z* 359.1766 in the HRMS, in accord with the molecular formula $C_{23}H_{23}N_2O_2$. The IR spectra of compound **3j** showed the characteristic absorption bands at 1715 (C═O), 1621 (C═C), 1240 (C–O–C) and the ^1H NMR spectra ($CDCl_3$) revealed five distinct singlets at δ 2.40 (3H, CH_3), 2.42 (3H, CH_3), 2.47 (3H, CH_3), 7.71 (1H, benzimidazole moiety) and 8.20 (1H, pyridine moiety). Moreover, compound **3j** showed peaks at δ 0.97 (t, 3H, J = 7.2 Hz), 4.08 (q, 2H, J = 7.2 Hz), assigned to the protons of ethoxycarbonyl group. All other signals are consistent with the structure of **3j**.

3.3. Crystal structure

From Fig. 2 and from Table 1, the bond length of C1–C7 is, as expected, shorter than a normal carbon–carbon single bond due to

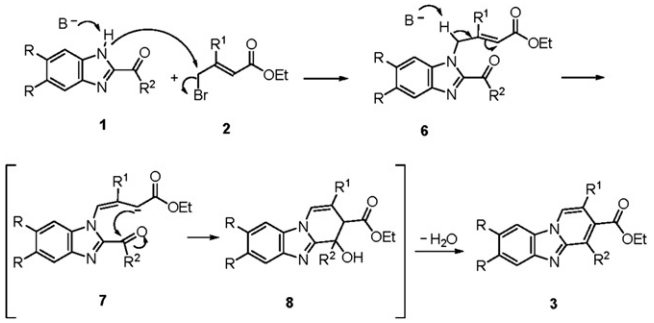

Fig. 5. The mechanism of the tandem reaction.

Table 3
The optical characteristics of the compounds **3a**–**j** in dichloromethane.

Compounds	λ_{max} (nm)	λ_{ex} (nm)	ϵ_{max} (L mol^{-1} cm^{-1})	F_{max} (nm)	Stokes shift (nm)
3a	248	335	42213	457	122
3b	253	335	49202	465	130
3c	250	335	40822	447	112
3d	250	335	55090	451	116
3e	256	335	45612	472	137
3f	253	335	48410	473	138
3g	252	335	38855	457	122
3h	251	335	47854	461	126
3i	228	340	33071	443	103
3j	258	335	46168	494	149

the conjugation effect. The dihedral angle between the N1/C8/N2/C16/C17 ring and N1/C9/C10/C12/C7/C8 ring is 3.38°, and 3.44° for the C16/C174/C18/C19/C21/C23 ring, thus the three rings in **3j** are nearly in the same plane and this coplanar conformation provides a large conjugated system. However, the dihedral angle between the N1/C9/C10/C12/C7/C8 ring and C16/C17/C18/C19/C21/C23 ring is 6.62°, and 71.32° for the C1/C2/C3/C4/C5/C6 ring thus overall from the dihedral angle data compound **3j** is not a planar molecule.

3.4. Absorption spectral characteristics of the compounds *3a–j*

For UV–visible absorption measurements, the dye concentration was 1×10^{-5} mol L^{-1}, and the absorption data are summarized in Table 3. The UV–visible absorption spectra of compounds **3a**–**j** are given in Fig. 6. Several absorption peaks could be observed in the wavelength range from 225 to 425 nm, while almost no absorption was observed beyond 425 nm. It is noted that **3a**–**j** display very similar absorptions with a strong absorption band at ca. 250 nm, which should originate from the benzene ring and pyrido[1,2-*a*]benzimidazole ring and should be assigned to the π–π^* electronic transition. The relatively weak absorption bands between 300 and 425 nm are assigned to the n–π^* electronic transition (Fig. 7).

3.5. Fluorescence spectral characteristics

The emission spectra of compounds **3a**–**j** in dichloromethane solution (1×10^{-5} mol L^{-1}) are presented in Fig. 7 and their excitation wavelengths are shown in Table 3. The fluorescence intensity and maximum emission bands of **3a**–**j** are dependent on the groups bonded to pyrido[1,2-*a*]benzimidazole rings. Emission maxima of compounds **3a**–**j** range from 443 to 494 nm. The emission maxima of **3e** and **3f**, in which a phenyl group is bonded

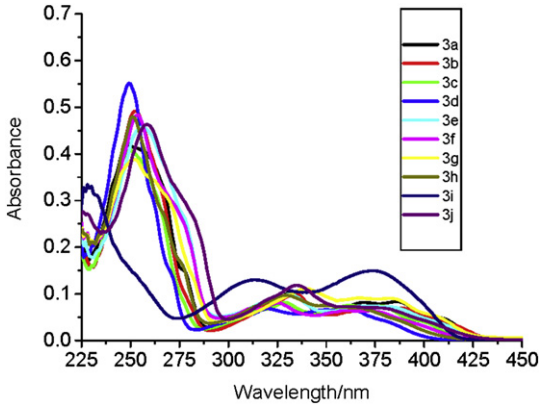

Fig. 6. The UV–vis spectra of the compounds **3a**–**j** in dichloromethane.

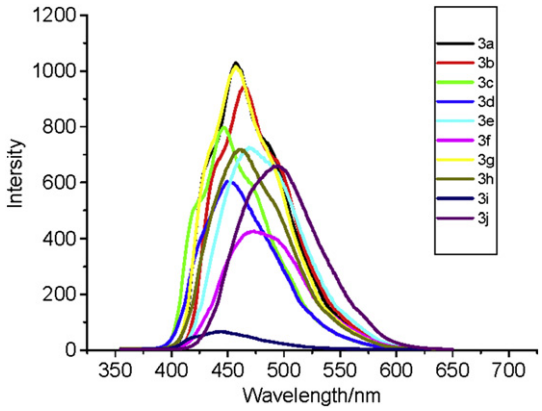

Fig. 7. The Fluorescence spectra of the compounds **3a**–**j** in dichloromethane.

to the pyrido[1,2-*a*]benzimidazole ring, are red-shifted by 15 and 8 nm, respectively, compared to **3a** and **3b**. The position of the methyl groups has a different effect on the emission maxima: **3b** is red-shifted 8 nm while **3c** is blue-shifted 10 nm compared to **3a**. Both **3g** and **3h** are red-shifted by 10 nm compared to **3c** and **3d**, respectively. Stokes shifts of compounds **3a**–**j** (Table 3) are also dependent on the groups bonded to pyrido[1,2-*a*]benzimidazole ring. Fluorescence quantum yields (Φ_F) in CH_2Cl_2 were determined by a comparative method, using quinine sulfate (purchased from Sigma-Aldrich) as a standard sample with $\Phi_F = 0.577$ in 0.1 mol L^{-1} H_2SO_4 as the reference. The Φ_F values for **3a**–**j** were listed in Table 3.

4. Conclusion

This paper describes the use of a novel tandem annulation reaction to prepare pyrazolo[1,5-*a*]pyridine derivatives under mild conditions in good yields. The structures of compounds obtained were determined by IR, ^{1}H NMR, ^{13}C NMR and HRMS spectra, and the spatial structure of compound **3j** was conformed by X-ray crystallography. Absorption and fluorescence spectral characteristics of the compounds were investigated in dichloromethane solution by UV–vis absorption and emission spectra. The absorption spectra and fluorescence characteristics were correlated with substituents on pyrido[1,2-*a*]benzimidazole rings.

5. Supplementary material

CCDC 747673 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

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