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Synthesis, X-ray crystal structure and optical properties of novel 2-aryl-3-ethoxycarbonyl-4-phenylpyrido[1,2-a]benzimidazoles

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ABSTRACT: A series of novel 2-aryl-3-ethoxycarbonyl-4-phenylpyrido[1,2-a]benzimidazole derivatives were synthesized by the tandem reaction of 2-benzoyl benzimidazole and (*Z*)-ethyl 4-bromo-3-arylbut-2-enoate in the presence of potassium carbonate. The compounds were characterized using IR, ^{1}H-NMR, ^{13}C-NMR, HRMS and the structure of 6f was further determined by X-ray crystallography. Both absorption and fluorescence spectra characteristics of the compounds were investigated in acetonitrile and dichloromethane. The results showed that the absorption maxima of the compounds varied from 220 to 284 nm, depending on the structure of 2-aryl group. The fluorescence results revealed that these compounds exhibited blue-green fluorescence (463–475 nm) in dilute solutions and showed acceptable fluorescence quantum yields (Φ_{PL} = 0.13–0.73) in dichloromethane.

Supporting information may be found in the online version of this article.

Keywords: pyrido[1,2-a]benzimidazole; synthesis; X-ray; absorption; fluorescence

Introduction

Nitrogen bridge-head heterocycles are of special interest, due to their wide variety biological activities and optical/electrical properties, and many of attractive methods have been developed for synthesizing this class of compounds. Of these heterocycles, compounds containing imidazo[1,2-a]pyridine ring systems (1–3) and related structures such as imidazo[1,2-a]pyrimidine, imidazo[1,2-a]quinoxaline or imidazo[2,1-a]isoquinoline (4–6) have been reported to possess a wide variety of biological and pharmacological properties. In contrast, the related pyrido[1,2-a]benzimidazole ring system has not received much attention until the past two decades (7–11) when some of its derivatives found pharmaceutical applications, based on their anti-anxiety (12), anti-tumour (13–15) and antiviral activities (16). Furthermore, some of these compounds were also found to display interesting photophysical and fluorescent properties (17–19). However, as a class of compounds their spectroscopic properties and biological activity have remained largely unexplored, which in part can be attributed to the lengths of the preparative routes, the formation of regioisomeric mixtures of products, limited substrate scope and unsatisfactory yields (20).

Recently, there is a great interest to vary the structure of conjugated molecules in order to tune and acquire more favourable physical properties and functional properties (21). In previous work, we have reported the synthesis of pyrido[1,2-a]benzimidazole containing different substituents, which emit blue-green fluorescence and have acceptable fluorescence quantum yields (22,23). In order to investigate in detail the photophysical properties of compounds containing the pyrido[1,2-a]benzimidazole moiety and extend the conjugated π-electron system, a series of aromatic rings, such as a phenyl ring, a naphthyl ring and a thiophene ring, were introduced to the C-2 position of the pyrido[1,2-a]benzimidazole ring. Herein, we report the synthesis, X-ray crystal structure and optical properties of novel 2-aryl-3-ethoxycarbonyl-4-phenylpyrido[1,2-a]benzimidazoles.

Experimental

Thin-layer chromatography (TLC) was conducted on silica gel GF_{254} plates (Merck KGaA). ^{1}H-NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer, using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the 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 Perkin-Elmer LS-55 luminescence spectrophotometer.

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General experimental procedure for the synthesis of α,β-unsaturated esters 3a–h

As shown in Fig. 1, compounds **3a–h** were synthesized according to the literature method (24,25). To a suspension of sodium hydride (0.24 g, 10 mmol) in dry THF (100 mL) was added dropwise triethyl phosphonoacetate (2.34 g, 10 mmol) at 0 °C under nitrogen atmosphere. The mixture was stirred for 1 h at 0 °C and then the appropriate ketone (6.76 mmol) in 15 mL THF was added dropwise. After stirring at room temperature for 2 days and then cooled with a water bath, a saturated aqueous ammonium chloride solution (20 mL) was added dropwise to the cold mixture. The aqueous phase was extracted with ethyl acetate (3 × 40 mL) and the combined organic phase was washed with brine (3 × 30 mL), dried over sodium sulphate and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel to afford compounds **3a–h** in 70–85% yield. Here only the *E*-isomer of the products were isolated and characterized.

(*E*)-Ethyl 3-phenylbut-2-enoate (3a)

Colourless oil, yield 85%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.33–7.45 (m, 5H), 6.13–6.14 (q, 1H, J = 1.5 Hz), 4.18–4.25 (q, 2H, J = 7.2 Hz), 2.58 (d, 3H, J = 1.5 Hz), 1.29–1.34 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.3, 156.0, 142.7, 129.5, 129.0, 126.8, 117.7, 78.0, 77.6, 77.2, 60.3, 18.4, 14.8; HRMS calcd for $[M+H]^+$ $C_{12}H_{15}O_2$, 191.1072; found, 191.1065.

(*E*)-Ethyl 3-(4-fluorophenyl)but-2-enoate (3b)

Colourless oil, yield 80%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.44–7.48 (m, 2H), 7.02–7.08 (m, 2H), 6.09 (d, 1H, J = 1.2 Hz), 4.18–4.25 (q, 2H, J = 7.2 Hz), 2.55–2.56 (d, 3H, J = 1.2 Hz), 1.29–1.34 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.2, 165.4, 162.1, 154.7, 138.7, 128.6, 117.6, 60.4, 18.4, 14.8; HRMS calcd for $[M+H]^+$ $C_{12}H_{14}FO_2$ 209.0978; found, 209.0968.

(*E*)-Ethyl 3-(4-chlorophenyl)but-2-enoate (3c)

Colourless oil, yield 70%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.32–7.42 (m, 4H), 6.10–6.12 (q, 1H, J = 1.2 Hz), 4.18–4.25 (q, 2H, J = 7.2 Hz), 2.55 (d, 3H, J = 1.2 Hz), 1.29–1.34 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.1, 154.5, 141.1, 135.5, 129.2, 128.1, 118.0, 60.4, 18.3, 14.8; HRMS calcd for $[M+H]^+$ $C_{12}H_{14}ClO_2$, 225.0682; found, 225.0679.

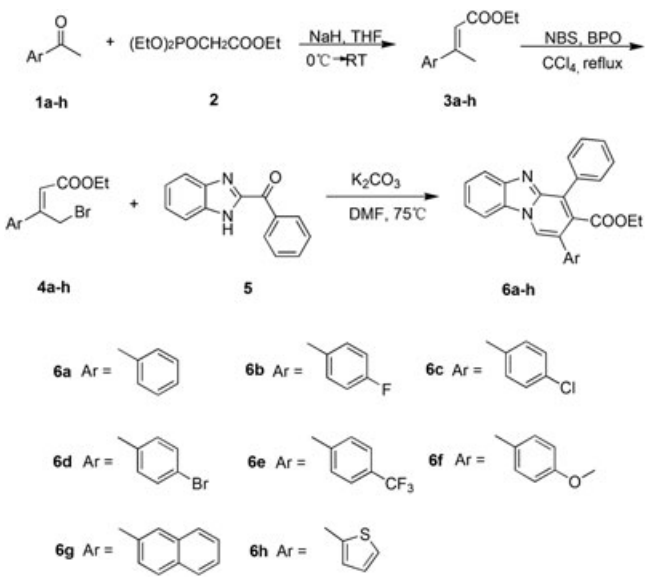

Figure 1. Synthesis of 2-aryl-3-ethoxycarbonyl-4-phenylpyrido[1,2-a]benzimidazoles.

(*E*)-Ethyl 3-(4-bromophenyl)but-2-enoate (3d)

Colourless oil, yield 82%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.47–7.50 (m, 2H), 7.32–7.34 (m, 2H), 6.11 (d, 1H, J = 1.2 Hz), 4.18–4.25 (q, 2H, J = 7.2 Hz), 2.54 (d, 3H, J = 1.2 Hz), 1.29–1.34 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.1, 154.5, 141.5, 132.1, 128.4, 123.7, 118.1, 60.4, 18.2, 14.8; HRMS calcd for $[M+H]^+$ $C_{12}H_{14}BrO_2$, 269.0177; found, 269.0148.

(*E*)-Ethyl 3-(4-(trifluoromethyl)phenyl)but-2-enoate (3e)

Colourless oil, yield 80%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.55–7.64 (m, 4H), 6.15 (d, 1H, J = 1.5 Hz), 4.20–4.27 (q, 2H, J = 7.2 Hz), 2.58 (d, 3H, J = 1.2 Hz), 1.30–1.35 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.9, 154.2, 146.3, 127.1, 126.2, 125.9, 122.6, 119.5, 60.6, 18.4, 14.8; HRMS calcd for $[M+H]^+$ $C_{13}H_{14}F_3O_2$, 259.0946; found, 259.0935.

(*E*)-Ethyl 3-(4-methoxyphenyl)but-2-enoate (3f)

Colourless oil, yield 75%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.43–7.46 (m, 2H), 6.87–6.90 (m, 2H), 6.10–6.11 (d, 1H, J = 1.2 Hz), 4.17–4.24 (q, 2H, J = 7.2 Hz), 3.81 (s, 3H), 2.56 (d, 3H, J = 1.2 Hz), 1.28–1.33 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.5, 160.9, 155.3, 134.8, 128.1, 115.8, 114.3, 60.2, 55.8, 18.1, 14.9; HRMS calcd for $[M+H]^+$ $C_{13}H_{17}O_3$, 221.1178; found, 221.1176.

(*E*)-Ethyl 3-(naphthalen-2-yl)but-2-enoate (3g)

Colourless oil, yield 85%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.93–7.79 (m, 4H), 7.60–7.56 (m, 1H), 7.50–7.45 (m, 2H), 6.28 (s, 1H), 4.27–4.20 (q, 2H, J = 7.2 Hz), 2.68 (s, 3H), 1.35–1.30 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 155.7, 139.9, 134.0, 133.6, 129.0, 128.7, 128.1, 127.2, 127.0, 126.4, 124.5, 118.0, 60.4, 18.4, 14.9; HRMS calcd for $[M+H]^+$ $C_{16}H_{17}O_2$, 241.1229; found, 241.1228.

(*E*)-Ethyl 3-(thiophen-2-yl)but-2-enoate (3h)

Colourless oil, yield 80%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.31–7.26 (m, 2H), 7.05–7.02 (m, 1H), 6.25 (s, 1H), 4.24–4.16 (q, 2H, J = 7.2 Hz), 2.61 (s, 3H), 1.33–1.29 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.2, 148.2, 146.1, 128.4, 127.5, 127.2, 114.8, 78.0, 77.6, 77.1, 60.3, 17.8, 14.8; HRMS calcd for $[M+H]^+$ $C_{10}H_{13}O_2S$, 197.0636; found, 197.0632.

General experimental procedure for the synthesis of γ-bromo-α,β-unsaturated esters 4a–h

A solution of α,β-unsaturated ester **3** (1 mmol), NBS (1.05 mmol) and benzoyl peroxide (0.04 mmol) in dry CCl_4 (35 mL) was refluxed for 8–10 h. The resulting reaction mixture was cooled to room temperature and then filtered through a sintered funnel to separate succinimide formed during the reaction. The filtrate was concentrated under reduced pressure to obtain crude products, which were then purified by column chromatography on silica gel to afford compounds **4a–h** in 70–80% yield.

(*Z*)-Ethyl 4-bromo-3-phenylbut-2-enoate (4a)

Yellow oil, yield 80%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.52–7.57 (m, 2H), 7.39–7.44 (m, 3H), 6.21 (s, 1H), 4.98 (s, 2H), 4.23–4.30 (q, 2H, J = 7.2 Hz), 1.31–1.36 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.0, 153.7,

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139.0, 130.2, 129.3, 127.1, 126.8, 120.3, 61.0, 27.1, 14.7; HRMS calcd for $[M+H]^+$ $C_{12}H_{14}BrO_2$, 269.0099; found, 269.0174.

(*Z*)-Ethyl 4-bromo-3-(4-fluorophenyl)but-2-enoate (4b)

Yellow oil, yield 78%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.39–7.54 (m, 2H), 7.01–7.13 (m, 2H), 6.16 (s, 1H), 4.95 (s, 2H), 4.18–4.30 m, 2H), 1.29–1.36 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 138.7, 135.0, 129.1, 128.6, 120.2, 117.6, 116.5, 115.8, 61.1, 26.9, 18.4, 14.8; HRMS calcd for $[M+H]^+$ $C_{12}H_{13}BrFO_2$, 287.0083; found, 287.0092.

(*Z*)-Ethyl 4-bromo-3-(4-chlorophenyl)but-2-enoate (4c)

Yellow oil, yield 75%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.46–7.51 (m, 2H), 7.32–7.42 (m, 2H), 6.18 (s, 1H), 4.94 (s, 2H), 4.18–4.30 (m, 2H), 1.29–1.36 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 165.8, 152.4, 137.4, 136.3, 129.5, 129.2, 128.4, 128.1, 120.6, 61.2, 26.7, 14.8; HRMS calcd for $[M+H]^+$ $C_{12}H_{13}BrClO_2$, 302.9787; found, 302.9788.

(*Z*)-Ethyl 4-bromo-3-(4-bromophenyl)but-2-enoate (4d)

Yellow oil, yield 75%. ^{1}H-NMR (300 MHz,$CDCl_3$): δ 7.48–7.57 (m, 2H), 7.32–7.44 (m, 2H), 6.18 (s, 1H), 4.93 (s, 2H), 4.18–4.30 (m, 2H), 1.29–1.36 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 165.8, 152.5, 137.9, 132.5, 128.7, 124.6, 120.6, 118.1, 61.2, 26.7, 18.3, 14.8; HRMS calcd for $[M+H]^+$ $C_{12}H_{13}Br_2O_2$, 346.9282; found, 346.9268.

(*Z*)-Ethyl 4-bromo-3-(4-(trifluoromethyl)phenyl) but-2-enoate (4e)

Yellow oil, yield 73%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.55–7.70 (m, 4H), 6.21 (s, 1H), 4.20–4.32 (m, 2H), 2.58 (d, 2H, J = 1.2 Hz), 1.30–1.37 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.9, 165.6, 154.2, 131.1, 127.1, 126.2, 122.0, 119.5, 60.6, 26.6, 18.4; HRMS calcd for $[M+H]^+$ $C_{12}H_{13}BrF_3O_2$, 337.0051; found, 337.0042.

(*Z*)-Ethyl 4-bromo-3-(4-methoxyphenyl)but-2-enoate (4f)

Yellow solid, yield 78%, mp 84–85 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.44–7.55 (m, 2H), 6.88–6.95 (m, 2H), 6.18 (s, 1H), 4.98 (s, 2H), 4.19–4.29 (m, 2H), 3.83–3.84 (d, 3H, J = 1.2 Hz), 1.31–1.35 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.3, 161.5, 153.0, 130.9, 128.5, 118.2, 114.7, 60.9, 55.9, 26.9, 14.7; HRMS calcd for $[M+H]^+$ $C_{13}H_{16}BrO_3$, 299.0283; found, 299.0271.

(*Z*)-Ethyl 4-bromo-3-(naphthalen-2-yl)but-2-enoate (4g)

Yellow oil, yield 70%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.93–7.80 (m, 4H), 7.60–7.56 (m, 1H), 7.50–7.46 (m, 2H), 6.33 (s, 1H), 5.08 (s, 2H), 4.27–4.20 (q, 2H, J = 7.2 Hz), 1.35–1.30 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.4, 155.7, 139.9, 134.0, 129.2, 128.2, 127.6, 127.1, 126.4, 124.5, 120.5, 118.1, 61.1, 27.0, 18.4, 14.9; HRMS calcd for $[M+H]^+$ $C_{16}H_{16}BrFO_2$, 319.0334; found, 319.0336.

(*Z*)-Ethyl 4-bromo-3-(thiophen-2-yl)but-2-enoate (4h)

Yellow oil, yield 75%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.45–7.44 (m, 1H), 7.37–7.35 (m, 1H), 7.10–7.07 (m, 1H), 6.29 (s, 1H), 4.96 (s, 2H), 4.29–4.22 (q, 2H, J = 7.2 Hz), 1.35–1.31 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.0, 146.9, 142.2, 128.4, 116.8, 61.0, 25.9, 14.7; HRMS calcd for $[M+H]^+$ $C_{10}H_{12}BrO_2S$, 274.9741; found, 274.9734.

General procedure for the synthesis of compounds 6a–h

A mixture of compound **5** (1 mmol), compound **4** (1.2 mmol) and potassium carbonate (0.28 g, 2.05 mmol) in DMF (10 mL) was stirred at 75 °C for 12–14 h and then filtered. The filtrate was poured into water (40 mL) and extracted with ethyl acetate (3 × 30 mL). The combined extracts were washed with brine, dried over sodium sulphate, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel to afford compounds **6a–h** in 60–78% yield.

2,4-Diphenyl-3-ethoxycarbonylpyrido[1,2-a] benzimidazole (6a)

Yellow solid, yield 75%, mp 182–184 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.97–8.00 (d, 1H, J = 8.4 Hz), 7.88–7.90 (d, 1H, J = 8.1 Hz), 7.64–7.68 (m, 2H), 7.35–7.54 (m, 10H), 3.84–3.91 (q, 2H, J = 7.2 Hz), 0.79–0.84 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.9, 134.9, 134.8, 130.2, 129.6, 129.5, 129.4, 129.3, 129.1, 129.0, 128.7, 126.4, 124.1, 124.0, 122.4, 121.3, 111.1, 78.0, 77.6, 77.1, 61.9, 13.9; IR (KBr) ν/cm^{-1}: 3053, 2985, 1727, 1481, 1463, 1321, 1253, 1121, 1018, 847, 736, 699; HRMS calcd for $[M+H]^+$ $C_{26}H_{20}N_2O_2$, 393.1603; found, 393.1598.

4-Phenyl-2-(4-fluorophenyl)-3-ethoxycarbonylpyrido[1,2-a] benzimidazole (6b)

Yellow solid, yield 60%, mp 156–158 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.98–8.01 (d, 1H, J = 8.4 Hz), 7.89–7.92 (d, 1H, J = 8.4 Hz), 7.63–7.67 (m, 2H), 7.37–7.55 (m, 7H), 7.10–7.18 (m, 2H), 3.85–3.92 (q, 2H, J = 7.2 Hz), 0.82–0.87 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.4, 165.0, 161.7, 147.1, 145.8, 134.8, 132.8, 131.3, 131.2. 130.1, 129.6, 129.4, 129.0, 126.5, 124.0, 123.0, 122.5, 121.3, 116.2, 111.1, 62.0, 14.0; IR (KBr) ν/cm^{-1}: 3052, 2979, 1731, 1483, 1461, 1318, 1244, 1118, 1015, 841, 746, 700; HRMS calcd for $[M+H]^+$ $C_{26}H_{19}FN_2O_2$, 411.1509; found, 411.1513.

4-Phenyl-2-(4-chlorophenyl)-3-ethoxycarbonylpyrido[1,2-a] benzimidazole (6c)

Yellow solid, yield 72%, mp 248–250 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.99–8.02(d, 1H, J = 8.1 Hz), 7.91–7.94 (d, 1H, J = 8.1 Hz), 7.64–7.67 (m, 2H), 7.39–7.57 (m, 9H), 3.86–3.93 (q, 2H, J = 7.2 Hz), 0.83–0.87 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.3, 147.0, 145.7, 135.3, 135.0, 134.7, 134.5, 130.8, 130.2, 130.1, 129.8, 129.4, 129.0, 128.7, 126.6, 124.0, 123.0, 122.6, 121.4, 111.1, 62.1, 14.0; IR (KBr) ν/cm^{-1}: 3010, 2982, 1729, 1480, 1462, 1319, 1247, 1120, 1019, 832, 739, 697; HRMS calcd for $[M+H]^+$ $C_{26}H_{19}ClN_2O_2$, 427.1213; found, 427.1202.

4-Phenyl-2-(4-bromophenyl)-3-ethoxycarbonylpyrido[1,2-a] benzimidazole (6d)

Yellow solid, yield 63%, mp 206–207 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.99–8.02 (d, 1H, J = 8.4 Hz), 7.91–7.94 (d, 1H, J = 8.4 Hz), 7.63–7.67 (m, 2H), 7.42–7.61 (m, 7H), 7.36–7.40 (m, 2H), 3.86–3.93 (q, 2H, J = 7.2 Hz), 0.83–0.88 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.3, 151.0, 147.0, 145.7, 135.8, 134.6, 134.4, 132.3, 131.1, 130.5, 130.1, 129.8, 129.4, 129.0, 126.6, 123.9, 123.2, 122.6, 121.4, 111.1, 62.1, 14.0; IR (KBr) ν/cm^{-1}: 3012, 2981, 1730, 1478, 1462, 1320, 1248, 1120, 1017, 829, 738, 696; HRMS calcd for $[M+H]^+$ $C_{26}H_{19}BrN_2O_2$, 471.0708; found, 471.0696.

4-Phenyl-2-(4-(trifluoromethyl)phenyl)-3-ethoxycarbonylpyrido [1,2-a]benzimidazole (6e)

Yellow solid, yield 74%, mp 330–332 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.02–8.05 (d, 1H, J = 8.1 Hz), 7.92–7.95 (d, 1H, J = 8.1 Hz), 7.72–7.75 (d, 2H, J = 8.1 Hz), 7.62–7.66 (m, 4H), 7.42–7.59 (m, 5H), 3.86–3.93 (q, 2H, J = 7.2 Hz), 0.80–0.85 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.1, 140.5, 134.4, 131.2, 130.8, 130.0, 129.8, 129.6, 129.3, 129.1, 126.9, 126.3, 126.2, 126.1, 126.0, 124.3, 123.1, 122.9, 122.7, 121.3, 111.2, 62.2, 13.9; IR (KBr) ν/cm^{-1}: 3057, 3011, 1726, 1486, 1464, 1322, 1251, 1127, 1066, 845, 739, 697; HRMS calcd for $[M+H]^+$ $C_{27}H_{19}F_3N_2O_2$, 461.1477; found, 461.1467.

4-Phenyl-2-(4-methoxyphenyl)-3-ethoxycarbonylpyrido [1,2-a]benzimidazole (6f)

Yellow solid, yield 78%, mp 130–132 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.97–8.00 (d, 1H, J = 8.4 Hz), 7.88–7.91 (d, 1H, J = 8.4 Hz), 7.64–7.68 (m, 2H), 7.35–7.53 (m, 7H), 6.95–6.99 (m, 2H), 3.86–3.93 (q, 2H, J = 7.2 Hz), 3.85 (s, 3H), 0.83–0.87 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.6, 160.2, 147.1, 145.7, 135.1, 134.9, 130.6, 130.2, 129.5, 129.3, 129.1, 128.9, 126.4, 123.8, 123.7, 122.3, 121.2, 114.5, 111.1, 61.9, 55.9, 14.0; IR (KBr) ν/cm^{-1}: 3044, 2981, 2961, 1727, 1483, 1461, 1344, 1246, 1181, 1040, 836, 748, 701; HRMS calcd for $[M+H]^+$ $C_{27}H_{22}N_2O_3$, 423.1709; found, 423.1697.

4-Phenyl-2-(naphthalen-2-yl)-3-ethoxycarbonylpyrido[1,2-a] benzimidazole (6g)

Yellow solid, yield 67%, mp 198–200 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.00–8.02 (d, 1H, J = 8.4 Hz), 7.91–7.95 (m, 2H), 7.84–7.88 (m, 3H), 7.76–7.70 (m, 2H), 7.36–7.59(m, 7H), 7.24 (s, 1H), 3.81–3.88 (q, 2H, J = 7.2 Hz), 0.74–0.79 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.6, 147.2, 145.8, 134.9, 134.3, 133.7, 133.3, 130.2, 129.7, 129.6, 129.3, 129.0, 128.8, 128.5, 128.3, 127.2, 127.1, 127.0, 124.3, 124.1, 122.4, 121.3, 111.2, 62.0, 14.0; IR (KBr) ν/cm^{-1}: 3052, 2975, 1733, 1490, 1460, 1314, 1247, 1111, 1014, 854, 744, 698; HRMS calcd for $[M+H]^+$ $C_{30}H_{22}N_2O_2$, 443.1760; found, 443.1754.

4-Phenyl-2-(thiophen-2-yl)-3-ethoxycarbonylpyrido[1,2-a] benzimidazole (6h)

Yellow solid, yield 70%, mp: 157–159 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.98–8.01 (d, 1H, J = 8.1 Hz), 7.92–7.94 (d, 1H, J = 8.1 Hz), 7.65–7.68 (m, 2H), 7.39–7.56 (m, 6H), 7.19–7.20 (m, 1H), 7.10–7.13 (m, 1H), 3.94–4.01 (q, 2H, J = 7.2 H), 0.88–0.93 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 167.2, 147.1, 145.6, 137.2, 134.9, 134.5, 130.2, 129.4, 129.0, 128.3, 128.2, 127.0, 126.6, 124.5, 122.6, 121.3, 116.8, 114.1, 62.1, 14.0; IR (KBr) ν/cm^{-1}: 3051, 3003, 2922, 1731, 1484, 1461, 1313, 1247, 1110, 1019, 839, 740, 698; HRMS calcd for $[M+H]^+$ $C_{24}H_{18}N_2O_2S$, 399.1167; found, 399.1167.

X-ray crystallography

Suitable single crystals of **6f** for X-ray structure analysis were obtained by slow evaporation of a solution of the solid in ethyl acetate. The diffraction data were collected with a Bruker–Nonius SMART APEX IICCD diffractometer using a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 295(2) K. The structures were solved by direct methods using the SHELXS-97 program and refinements on F^2 were performed with the SHELXL-97 program by full-matrix least-squares techniques, with anisotropic thermal parameters for the non-hydrogen atoms. All H atoms were initially located in a difference Fourier map and were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq} (C). A summary of the crystallographic data and structure refinement details is given in Table 1 (see also Supporting information).

Results and discussion

Synthesis

The synthetic route to the target heterocycles is shown in Fig. 1. Firstly, the α,β-unsaturated esters **3a–h** were obtained from the reaction of aryl ketones **1a–h** and triethyl phosphonoacetate **2**, which were readily available, in the presence of sodium hydride from 0 °C to room temperature (24,25). After that, allylic bromination of compounds **3a–h** with NBS afforded the brominated derivatives **4a–h** in good yields after work-up, which was the key step in the synthesis of these target products. Finally, compounds **4a–h** reacted with 2-benzoyl benzimidazole **5** in the presence of K_2CO_3 at 75 °C for 12–14 h to afford pyrido[1,2-a]benzimidazole derivatives in good yield via the tandem reaction we reported before (26) It should be noted that the reaction between compound **5** and (*Z*)-ethyl 4-bromo-3-arylbut-2-enoate requires a higher temperature than that between compound **5** with (*E*)-ethyl 4-bromobut-2-enoate we previously reported. Within the (*Z*)-ethyl 4-bromo-3-arylbut-2-enoate derivatives, the bromomethyl and

Table 1. Crystal data and structure refinement for **6f**

	6f
Empirical formula	$C_{27}H_{22}N_2O_3$
Formula weight	422.48
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 13.0331(17) Å, α = 90.00°
	b = 15.9620(2) Å, β = 104.169(2)°
	c = 12.4647(17) Å, γ = 90.00°
Volume	2514.2(6) Å^3
Z	4
Calculated density	1.214 mg/m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	972
Crystal size	0.28 × 0.18 × 0.14 mm
θ range for data collection	2.06 to 25.50°
Limiting indices	$-15 \le h \le 15$, $-19 \le k \le 8$, $-15 \le l \le 14$
Reflections collected/ unique	12674/4646 [R (int) = 0.0266]
Completeness to θ = 25.50°	99.5%
Absorption correction	None
Max. and min. transmission	0.9889 and 0.9779
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4646/3/314
Goodness-of-fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0641, wR_2 = 0.1871
R indices (all data)	R_1 = 0.0905, wR_2 = 0.2090
Extinction coefficient	0.006(2)
Largest diff. peak and hole	0.683 and −0.363 e. Å^{-3}

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ester group adopt a *syn* configuration, resulting in certain degree of steric effect, which may hinder the reaction between compound **5** and the brominated ester derivatives.

Structure characterization

The assumed structures of target products were proved by IR, ^{1}H-NMR and HRMS spectra. For example, compound **6f**, obtained as yellow solid, gave an [M + H]-ion peak at *m/z* 423.1697 in the HRMS, in accord with the molecular formula $C_{27}H_{22}N_2O_3$. The IR spectra of compound **6f** showed the characteristic absorption bands at 3044 (ArH), 1721 (C = O), 1483 (C = C), 1246 (C–O–C). The ^{1}H-NMR spectra of compound **6f** revealed two singlet peaks at δ 3.93 (3H, CH_3) and 8.39 (1H, pyridine moiety) which were readily assigned to the hydrogen of methoxy and pyridine moiety, respectively. Moreover, compound **6f** showed peaks at δ 0.85 (t, 3H, J = 7.2 Hz) and 3.90 (q, 2H, J = 7.2 Hz), assigned to the protons of ethoxycarbonyl group. Compound **6f** also showed peaks between δ 6.95–8.00 (13H), assigned to the protons on aromatic rings. All other signals are consistent with the structure of **6f**.

Crystal structure

The spatial structures of compound **6f** were determined by using X-ray diffraction analysis. A summary of crystallographic data collection parameters and refinement parameters for **6f** are compiled in Table 1.

The single crystal structure and packing diagram of **6f** are shown in Figs 2 and 3. The structure of compound **6f** is crystallized in monoclinic space group $P2_1/c$. One benzene moiety and one *p*-methoxy phenyl moiety are bonded to the pyrido [1,2-a]benzimidazole ring at the atoms of C8 and C10, respectively. Consistent with a pronounced electronic interaction, the bond lengths of C8–C12 and C10–C21 are significantly shorter as would be expected for a normal carbon-carbon single bond. The dihedral angle between the N1/C7/N2/C6/C1 ring and N1/C7/C8/C9/C10/C11 ring is 1.985°, and 0.693° for the C1/C2/C3/C4/C5/C6 ring; thus, the three rings in **6f** are nearly in the same plane and this coplanar conformation provides a large conjugated system. In contrast, the pyridine moiety makes dihedral angles with benzene ring and *p*-methoxyphenyl ring of 61.963° and 53.111°, respectively. The torsion angles apparently result from the steric effect between the aryl rings and ester group.

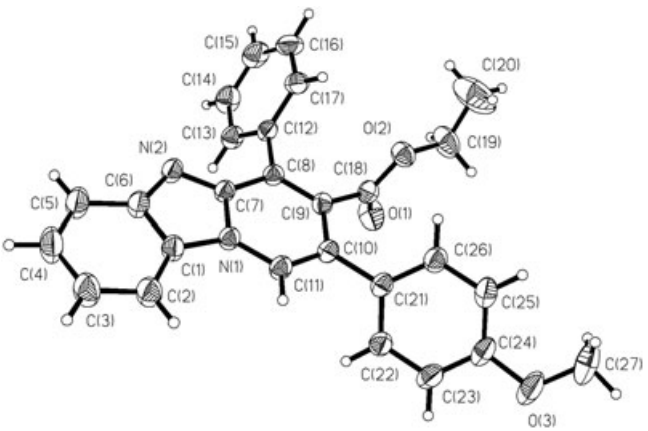

Figure 2. The molecular strcture of **6f** with displacement ellipsoids drawn at the 30% probability level.

Absorption spectra

The absorption spectra of the compounds **6a-h** measured in acetonitrile solution with the concentration of 5×10^{-6} mol/L are shown in Fig. 4. And the optical characteristics are summarized in Table 2. As shown in Fig. 4, compounds **6a–h** display similar absorption characteristics, with absorption peaks in the range 220–284 nm, which are attributed to the π–π^* transition of conjugate backbone.

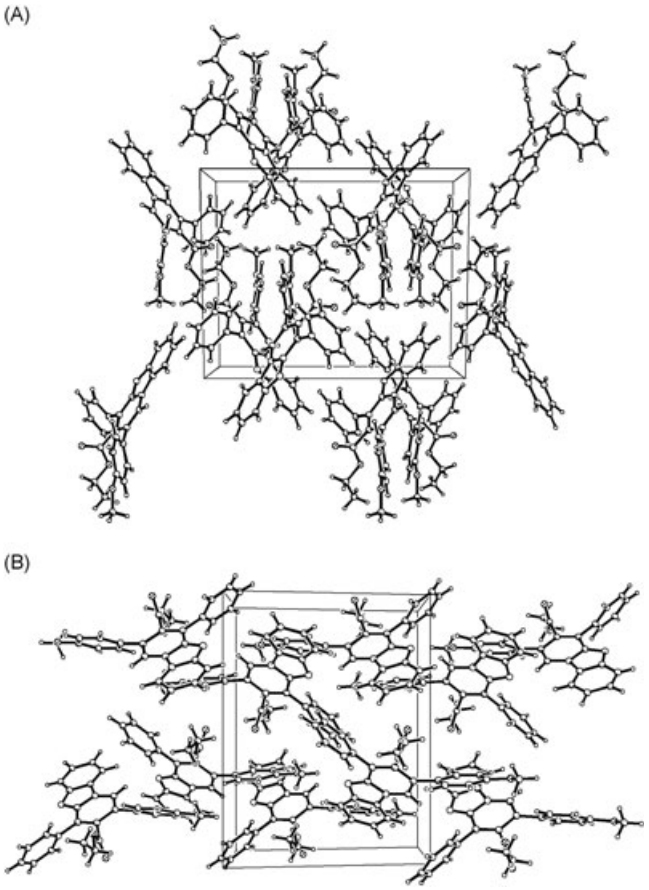

Figure 3. Crystal packing diagram of **6f** along the *a* axis (A) and the *c* axis (B).

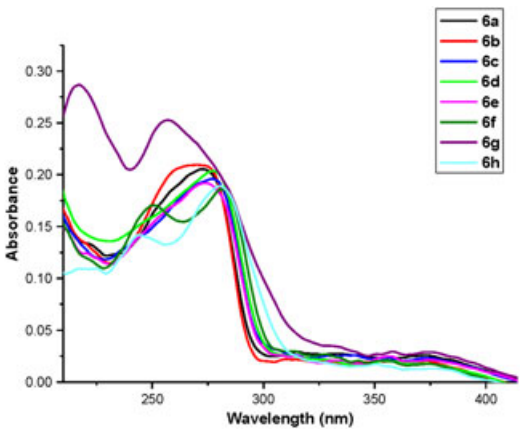

Figure 4. UV-vis absorbtion spectrum of compounds **6a–h** in dilute (5×10^{-6} mol/L) acetonitrile solution.

Table 2. The absorption characteristics of compounds **6a-h**

Compounds	λ_{max} (nm)		
6a–h	Cyclohexane	Dichloromethane	Acetonitrile
6a	274	277	274
6b	272	275	273
6c	275	277	275
6d	276	281	281
6e	274	275	272
6f	283	284	284
6g	215	223	220
	259	260	261
6h	283	281	283

The data indicated that the structure of 2-aryl ring has definite effects on the absorption bands. The absorption maximum of compound **6a** with the 2-phenyl ring is at 274 nm. As the steric hindrance of the 2-aryl ring increased, the maximum absorption of compound **6g** with the 2-naphthyl ring is blue-shifted to 261 nm compared to compound **6a**, which indicates that the conjugated π-system between the 2-aryl ring and pyrido[1,2-a] benzimidazole ring decreases due to steric hindrance effect. Compound **6h** with the 2-thienyl exhibits the maximum absorption wavelength at 283 nm, resulting in a 9 nm red shift compared to compound **6a**. This result may be attributed to the enhancement of conjugation between the 2-aryl ring and pyrido [1,2-a]benzimidazole ring and the strong electron-donating effect of 2-thienyl moiety. In addition, compound **6g** also displays the absorption peak at 220 nm, which is attributed to π–π* transition of the naphthyl ring.

Furthermore, it is noted that when an electron-donating substituent, such as a bromo group or a methoxyl group is located on the 2-phenyl ring, the absorption peaks of **6d** and **6f** are at longer wavelengths (281 and 284 nm) than that of compound **6a**. In contrast, the electron-withdrawing substituent located on the 2-phenyl ring could not obviously affect the absorption spectra of compounds **6**.

Possible influence of the solvent on the absorption behaviour was investigated. The absorption spectra of **6a**, **6c**, **6e** and **6g**, as examples, in three different solvents of cyclohexane, dichloromethane and acetonitrile, at a concentration of 5×10^{-6} mol/L are shown in Fig. 5. It was observed that the absorption spectra changed very little with the increase of solvent polarity although there was a tendency of a shorter λ_{max} in acetonitrile, indicating that there was no charge transfer in the ground state.

Comparing with the 3-ethoxycarbonyl-4-phenylpyrido [1,2-a]benzimidazole derivatives (22) the absorption maxima of compounds **6**, in which an aryl group is bonded to the C-2 position of pyrido[1,2-a]benzimidazole ring, are red-shifted, with the maximum shift of 53 nm. The difference in absorption spectra is due to the fact that there is an aryl group in the C-2 position of pyrido[1,2-a]benzimidazole ring. The aryl group enhances the extent of conjugation in compounds **6** and thus shifts the absorption spectra to longer wavelengths.

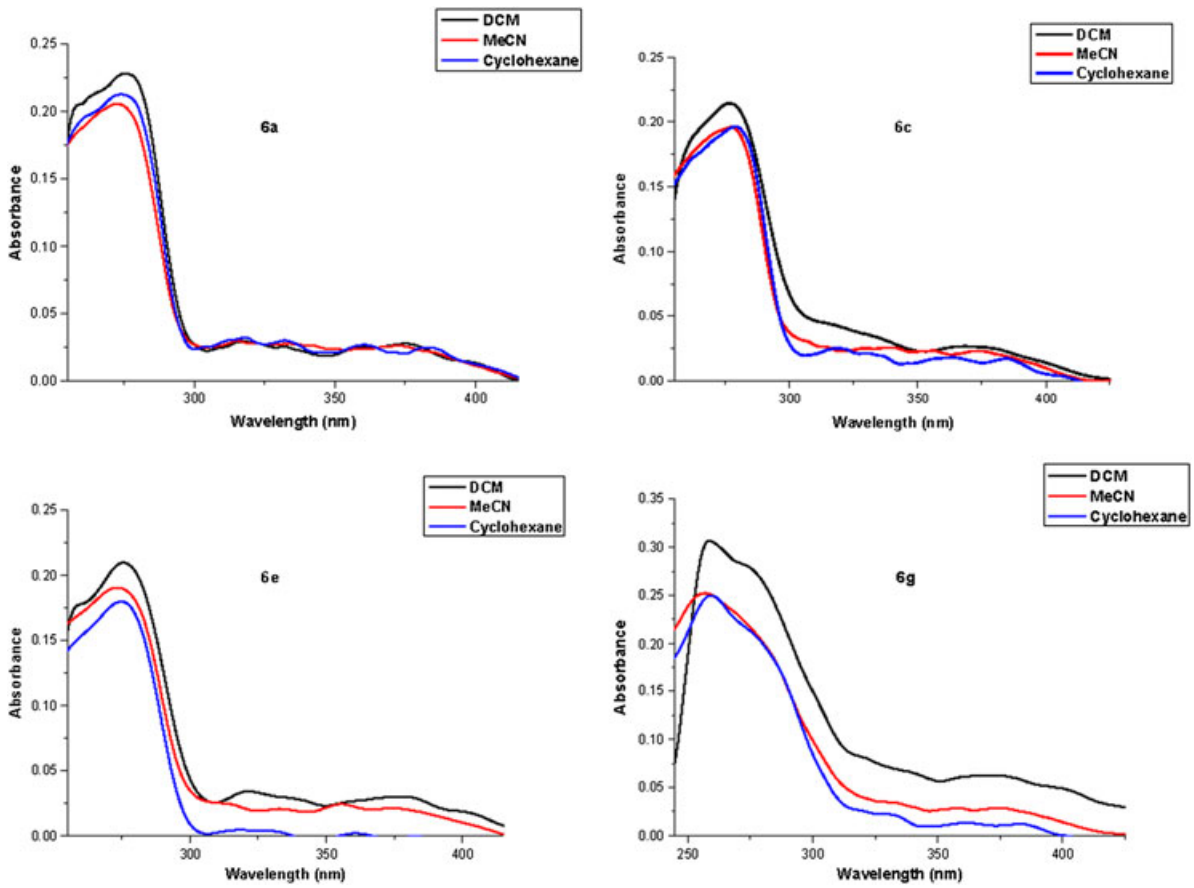

Figure 5. UV-vis absorption spectrum of compounds **6a**, **6c**, **6e**, **6g** in different solvents.

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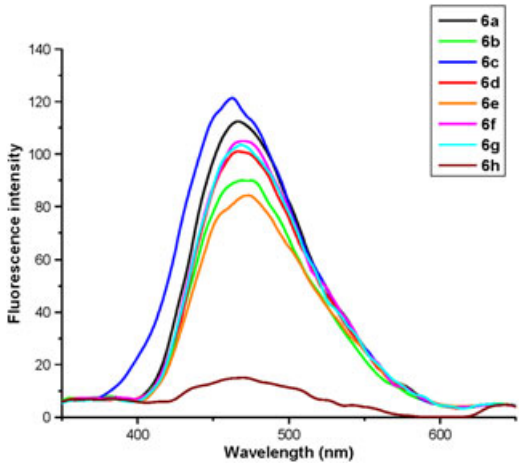

Figure 6. Emission spectrum of compounds **6a–h** in dilute (5×10^{-6} mol/L) dichloromethane solution.

Table 3. Fluorescence spectral data for **6a–h** in dichloromethane

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Stokes' shift (nm)	Φ_{PL}
6a	317	466	149	0.73
6b	315	475	160	0.33
6c	317	463	146	0.61
6d	321	467	146	0.30
6e	315	471	156	0.50
6f	324	475	151	0.54
6g	300	469	169	0.27
6h	321	470	149	0.13

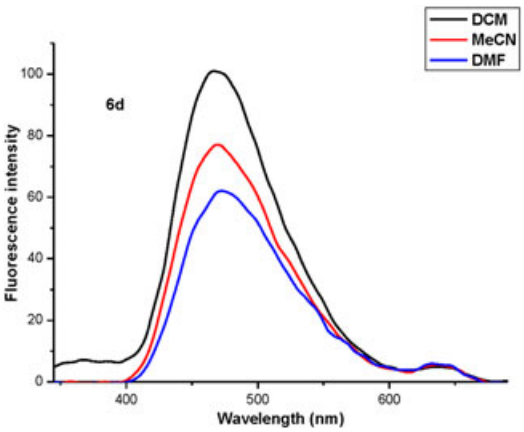

Figure 7. The fluoroscence spectra of compound **6d** in different solvents.

Fluorescence

Figure 6 displayed the emission spectra of compounds **6a–h** in dichloromethane solution (5×10^{-6} mol/L). These compounds showed a blue-green fluorescence with the maximum emission peaks varying in the range 463–475 nm. Their maximum emission peaks and the intensity of fluorescence are dependent on 2-aryl ring bonded to pyrido[1,2-a]benzimidazole ring. The emission maximum of **6f**, in which a methoxyl group bonded to 2-phenyl ring, is red-shifted by 9 nm compared to **6a**, which might be attributed to the different conjugation degree and different electronic effects in these compounds. Moreover, the trifluoromethyl on the 2-phenyl ring is an electron-attracting group, which causes a shift of fluorescence band to longer wavelengths.

Fluorescence quantum yields (Φ_{PL}) of **6a–h** in dichloromethane were measured using quinine sulphate ($\Phi = 0.55$) as standard (27) The highest Φ_{PL} value of 0.73 is observed for **6a**, which is higher than that of other compounds. The fluorescence quantum yields of the other compounds are in the range of 0.13–0.61. This difference of quantum yields might be due to the change of the electronic push–pull substitution of the conjugated part in the molecules. From Table 3, it can be also seen that the Stokes' shifts of compounds **6a–h** between absorption and emission maximum are significant. The efficient π-conjugation in molecule is known to be responsible for the charge-transfer nature of the emissive excited state and causing the observed relatively large Stokes' shifts.

Moreover, the solvent effect on the fluorescence characteristics was also observed (Fig. 7). The emission peaks of compound **6d** were red-shifted from 467 nm in dichloromethane to 469 nm, 472 nm in acetonitrile and in DMF, respectively, which indicated that the emission wavelength of the compound was red-shifted with the increase of solvent polarity (Fig. 7).

Conclusion

A series of novel 2-aryl-3-ethoxycarbonyl-4-phenylpyrido[1,2-a] benzimidazole derivatives have been synthesized by the tandem reaction of 2-benzoyl benzimidazole and γ-bromo-α,2β-unsaturated esters in the presence of potassium carbonate at 75 °C. The structures of the compounds obtained were determined by IR, ^{1}H-NMR, ^{13}C-NMR and HRMS spectra, and the spatial structure of compound **6f** was confirmed by X-ray crystallography. It can be concluded that the absorption and fluorescence characteristics of compounds **6a–h** show a significant dependence on the structure of 2-aryl ring in the C-2 position of pyrido[1,2-a] benzimidazole. These compounds exhibited blue-green fluorescence (463–475 nm) in dilute solutions and showed acceptable quantum yields of fluorescence in dichloromethane, with the highest Φ_{PL} value of 0.73 for compound **6a**. These observations indicate that the high conjugated molecule structure enhances the light absorption and the fluorescence emission ability of compounds **6a–h** due to the contribution of 2-aryl ring.

Supplementary information

The following supplementary information (file CCDC 813941) may be found in the online version of this article:

Supplementary crystallographic data for this paper (these data can be obtained free of charge via http://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 CB2 1EZ, UK; fax: +44 1223 336033).

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