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RESEARCH ARTICLE

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Synthesis, characterization and crystal structure of 1-ferrocenesulfonyl-2-long carbon chain alkyl benzimidazole

Abstract Six new 1-ferrocenesulfonyl-2-benzimidazole derivatives were prepared by the reaction of ferrocenesulfonyl chloride with benzimidazole derivatives in the presence of dichloromethane and n-tetrabutylammonia bromide. The yields of these six new ferrocenesulfonyl benzimidazole derivatives were about 80%. The structures characteristic were confirmed by IR, ^{1}H-NMR, Elemental analysis and MS. The crystal structure of compound $\mathbf{a_2}$ was determined *via* X-ray single crystal diffraction and it belongs to monoclinic system with space group C2/c, and the unit cell parameters are $\alpha = 2.8252(2)$ nm, $b = 0.97696(7)$ nm, $c = 1.64828(12)$ nm, $\alpha = 90°$, $\beta = 92.053(2)°$, $\gamma = 90°$, $V = 4.5466(6)\ \mathrm{nm}^3$, $Z = 8$, $F(000) = 2024$, $Mr = 481.40$, $Dc = 1.407\ \mathrm{g/cm}^3$, $\mu = 0.784\ \mathrm{mm}^{-1}$, $R_1 = 0.0495$, $wR_2 = 0.1517$. The results show that the reactions of 2-alkylbenzimidazoles containing active hydrogen with ferrocenesulfonyl chloride gave 1-ferrocenesulfonyl-2-alkylbenzimidazoles in good yields.

Keywords ferrocenesulfonyl benzimidazol, synthesis, characteristic, crystal structure

In recent years, benzimidazole derivatives, in particular 2-alkyl benzimidazole, have widespread applications [1] in high-performance composite materials, metal surface treatment, biological and medical fields, *etc*. 2-alkyl benzimidazole can form the stable and orderly L-B film [2] on the silver nitrate subfacies, short-chain derivatives can form a regular layered structure, its single-layer L-B film have the uniform and smooth appearance, and the substituted long carbon chain benzimidazole can only form multilayered LB film, which is a new type of metal surface treatment agent [3]. It can form a dense protective film on the surface of copper to prevent the corrosion of copper surface [4], and possess a good thermal stability [5–7], with a high mechanical strength and heat distortion temperature. It can be also used for heat resistance of the printed circuit board and electrical wiring insulation material. It can used as epoxy curing agents [8,9], as the length of 2-alkyl imidazole substituted carbon chain increase, the gelatination time of the mixture of epoxy resin markedly increase and the application period is extended. As a corrosion inhibitor [10,11], it played an extremely important role in the fields of chemical, oil, electricity, machinery, metal processing, transportation, nuclear energy and astronautics, *etc*. [12]. Benzimidazole compounds possess low toxicity [13] and can be used as pesticides, with the growth of 2-substituted carbon chain, the insecticide activity increased. However, its activity drops as the growth of carbon chain when the substituted carbon chain is more than 6 C atoms [14]. Ferrocene and its derivatives is concerned with applications in the field of polymer, electrochemical, liquid crystal materials [15,16], anti-cancer, sterilization, insecticide, anti-inflammatory and regulate plant growth [17] *etc*.

The long-term use will cause drug-resistance [18], So it is some of import to find efficient and new fungicides.

It has been reported that the reaction of the indole, morpholine, midazole, benzotriazole, piperazine, *etc*. of nitrogen heterocyclic compounds and 2-substituted methyl-, ethyl-, propyl-, butyl-benzimidazole with ferrocenesulfonyl chloride [19] , can prepare the corresponding nitrogen heterocyclic ring ferrocenesulfuryl amine compounds by a conventional route and microwave radiation system, respectively, and some of the compounds have good biological activity. To deal with the problems of 2-substituted benzimidazole and ferrocene and its derivatives in the application, in this article we will show that the reaction of 2-substituted benzimidazole derivatives with ferrocenesulfonyl chloride to prepare 1-ferrocenesulfonyl-2-long carbon chain alkyl benzimidazole compounds and its structures were characterized. The synthetic route as shown in Scheme 1.

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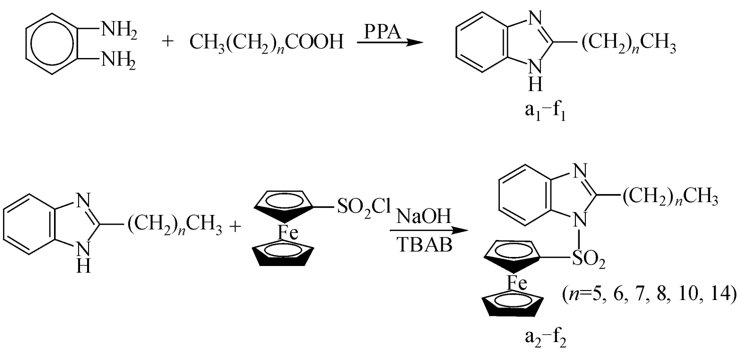

Scheme 1 The synthetic route of 1-ferrocenesulfonyl-2-alkylbenzimidazole

1 Experiments

1.1 Instruments and reagents

The melting point(mp) was measured on a XT-4 microscopic melting point apparatus which is uncorrected. IR spectra were measured on a German BRUKER EQUINOX-55 infrared spectrometer in a KBr matrix. The element analysis was carried on a German VARIOELCHNOS III element analysis instrument. ^{1}H-NMR spectra were recorded on an American VARIAN INOVA-400 NMR spectrometer in $CDCl_3$ with TMS as the internal standard: MS was measured on a MALDI-TOF mass spectrometer. The column chromatography used here is with the particle size in 90–120 µm of silica gel. The reaction process was monitored by TLC. Solvents and reagents used are both commercial analytical reagent.

1.2 The synthesis of ferrocenesulfonyl chloride

Ferrocenesulfonyl chloride was prepared according to the literature method [20], to a suspension of 12.4 g (0.067 mol) ferrocene stirred in 100 mL anhydrous ether, and then dropped into 4.7 mL (0.073 mol) chlorosulfonic acid for about 2.5 h in an ice bath. It was stirred 40 h at room temperature after dropping and produced a dark blue reaction solution. 13.5 mL (0.15 mol) phosphorus trichloride was introduced and was placed for about 2 h in an ice bath. The reaction mixture was stirred for 24 h at room temperature. The solvent was evaporated under reduced pressure and the residual solid was extracted with boiling petroleum ether (b.p. 60－90°C) to get orange red needle-like crystals. It was recrystallized in petroleum ether (30－60°C) to afford 10.9 g ferrocenesulfonyl chloride inorange-red needle-like crystals with the yield of 56%, m.p. 99－101°C.

1.3 The synthesis of 2-substitute-n-alkyl benzimidazole

2-substitute-n-alkyl benzimidazole was prepared as follows. The mixture of 5.4 g (0.05 mol) o-phenylenediamine, 6.5 g (0.05 mol) heptanoic acid and 10 mL polyphosphoric acid (PPA) was stirred in a 100 mL three-necked round-bottomed flask in an oil bath. The temperature was slowly raised to 170°C and the solution was stirred for about 1 h at this temperature, and then warm up to 220°C and kept for 1.5 h. After that, heating was stopped and ethanol was dropped when the temperature was down to 80°C. NaOH (10%) was added and the solution pH was adjusted to 8 to 9. The crystals were precipitated when it dropped to the room temperature, solution filtration, recrystallized by ethanol–water solution, decolorized by activated carbon, at last, the colorless tabular crystal $\mathbf{a_1}$ was produced. The synthesis of $\mathbf{b_1}$, $\mathbf{c_1}$, $\mathbf{d_1}$, $\mathbf{e_1}$ and $\mathbf{f_1}$ is in the similar method. The melting point is consistent with the literature value [21].

1.4 The synthesis of 1-ferrocenesulfonyl-2-long chain alkylbenzimidazole

1-ferrocenesulfonyl-2-long chain alkylbenzimidazole was synthesized as follows. The mixture of 10 mL chloroform, 30 mg n-tetrabutylammonia bromide (TBAB) and 0.5 g sodium hydroxide (NaOH) was stirred in an ice bath, and then 1.2 g (6 mmol) 2-hexylbenzimidazole was added with stirring, 1.4 g (5 mmol) ferrocenesulfonyl chloride dissolved in 5 mL chloroform was slowly added, after continual stirring for 25 min, 5 mL chloroform was added and the mixture was stirred for 5 h at 40°C. Chloroform was evaporated from the reaction mixture. The residual solid was washed and extracted with chloroform from the aqueous phase, chloroform was evaporated from the organic phase, and then a dark brown sticky residue was produced. The residue purified by column chromatography eluted with chloroform. At last, the product was obtained as a orange yellow crystal of $\mathbf{a_2}$. The synthesis of $\mathbf{b_2}$, $\mathbf{c_2}$, $\mathbf{d_2}$, $\mathbf{e_2}$ and $\mathbf{f_2}$ were obtained in the similar method as the above.

2 Results and discussion

2.1 The characterization of the compound

Compound $\mathbf{a_2}$ 1-ferrocenesulfonyl-2-hexylbenzimidazole was obtained with the yield of 80%; as orange yellow crystals. m.p. 110–113°C; IR (KBr) υ/cm^{-1}: 2951, 1377, 1134; ^{1}H-NMR (CDCl3), δ: 0.90 (t, 3H, CH_3, J = 6.8 Hz), 1.34 (t, 4H, CH_2, J = 3.6 Hz), 1.47 (s, 2H, CH_2), 1.90 (t, 2H, CH_2, J = 7.4 Hz), 3.12 (t, 2H, CH_2, J = 7.6 Hz), 4.42–4.77 (s, 9H, Fc), 7.30 (t, 2H, C_6H_4, J = 4.2 Hz), 7.63 (t, 1H, C_6H_4, J = 4.2 Hz), 7.93 (t, 1H, C_6H_4, J = 4.6 Hz); MS, m/z: 450 (M^+); Elemental analysis $C_{23}H_{26}FeN_2O_2S$, Measured (Calculated)/%: C 61.39 (61.33), H 5.86 (5.78), N 6.01 (6.22).

Compound $\mathbf{b_2}$ 1-ferrocenesulfonyl-2-heptylbenzimidazole is obtained with the yield of 78% as orange yellow crystals. m.p. 109–110°C; IR (KBr) υ/cm^{-1}: 2950, 1377, 1141, ^{1}H-NMR ($CDCl_3$), δ: 0.90 (t, 3H, CH_3, J = 7.2 Hz), 1.34 (m, 6H, CH_2, J = 5.2 Hz), 1.46 (s, 2H, CH_2), 1.91 (s, 2H, CH_2), 3.12 (t, 2H, CH_2, J = 7.2 Hz), 4.22–4.77 (s, 9H, Fc), 7.30 (t, 2H, C_6H_4, J = 3.8 Hz), 7.64 (d, 1H, C_6H_4, J = 8 Hz), 7.93 (t, 1H, C_6H_4, J = 4.6 Hz); MS, m/z: 464(M^+); Elemental analysis $C_{24}H_{28}FeN_2O_2S$, Measured (Calculated)/%: C 62.17 (62.07), H 6.01 (6.03), N 6.11 (6.03).

Compound $\mathbf{c_2}$ 1-ferrocenesulfonyl-2-octylbenzimidazole was synthesized with the yield of 87% as orange yellow crystals. m.p. 96–97°C; IR (KBr) υ/cm^{-1}: 2955, 1377, 1141; ^{1}H-NMR ($CDCl_3$), δ: 0.89 (s, 3H, CH_3), 1.29 (s, 8H, CH_2), 1.46 (s, 2H, CH_2), 1.90 (s, 2H, CH_2), 3.12 (s, 2H, CH_2), 4.42–4.77 (s, 9H, Fc), 7.30 (s, 2H, C_6H_4), 7.64 (s, 1H, C_6H_4), 7.93 (d, 1H, C_6H_4, J = 6.4 Hz); MS, m/z: 478 (M^+); Elemental analysis $C_{25}H_{30}FeN_2O_2S$, Measured (Calculated)/%: C 62.83(62.76), H 6.42 (6.28), N 5.65 (5.86).

Compound $\mathbf{d_2}$ 1-ferrocenesulfonyl-2-nonylbenzimidazole was prepared with the yield of 85% as orange yellow crystals. m.p. 95–97°C; IR (KBr) υ/cm^{-1}: 2951, 1377, 1137; ^{1}H-NMR ($CDCl_3$), δ: 0.89 (t, 3H, CH_3, J = 6.6 Hz), 1.28 (m, 10H, CH_2, J = 10 Hz), 1.46 (d, 2H, CH_2, J = 6.8 Hz), 1.90 (t, 2H, CH_2, J = 6.6 Hz), 3.12 (t, 2H, CH_2, J = 7.6 Hz), 4.40–4.77 (m, 9H, Fc), 7.30 (m, 2H, C_6H_4, J = 2.3 Hz), 7.63 (m, 1H, C_6H_4, J = 2.8 Hz), 7.93 (m, 1H, C_6H_4, J = 2.9 Hz); MS, m/z: 492 (M^+); Elemental analysis $C_{26}H_{32}FeN_2O_2S$, Measured (Calculated)/%: C 63.52 (63.41), H 6.42 (6.50), N 5.35 (5.69).

Compound $\mathbf{e_2}$ 1-ferrocenesulfonyl-2-undecylbenzimidazole was obtained with the yield of 83% as orange yellow crystals. m.p. 79–81°C; IR (KBr) υ/cm^{-1}: 2958, 1377, 1140; ^{1}H-NMR ($CDCl_3$), δ: 0.89 (s, 3H, CH_3), 1.27 (s, 14H, CH_2), 1.46 (s, 2H, CH_2), 1.90 (s, 2H, CH_2), 3.12 (s, H, CH_2), 4.42–4.77 (s, 9H, Fc), 7.30 (s, 2H, C_6H_4), 7.65 (s, 1H, C_6H_4), 7.93 (d, 1H, C_6H_4, J = 6.0 Hz); MS, m/z: 520 (M^+); Elemental analysis $C_{28}H_{36}FeN_2O_2S$, Measured (Calculated)/%: C 64.36 (64.62), H 6.75 (6.92), N 5.35 (5.39).

Compound $\mathbf{f_2}$ 1-ferrocenesulfonyl-2-pentadecylbenzimidazole was synthesized with the yield of 85% as orange yellow crystals. m.p. 76–78°C; IR (KBr) υ/cm^{-1}: 2959, 1377, 1140; ^{1}H-NMR ($CDCl_3$), δ: 0.88 (t, 3H, CH_3, J = 6.4 Hz), 1.26 (s, 22H, CH_2), 1.46 (s, 2H, CH_2), 1.90 (s, 2H, CH_2), 3.12 (s, 2H, CH_2), 4.36–4.77 (m, 9H, Fc), 7.30 (d, 2H, C_6H_4, J = 8.0 Hz), 7.63 (s, 1H, C_6H_4), 7.93 (d, 1H, C_6H_4, J = 8.0 Hz); MS, m/z: 576 (M^+); Elemental analysis $C_{32}H_{44}FeN_2O_2S$, Measured(Calculated) /%: C 66.23 (66.67), H 7.38 (7.64), N 4.93 (4.86).

2.2 Melting point analysis

As the length of 2-substituted carbon chain of benzimidazole increased, the melting point dropped. The reason possibly is that the association of hydrogen bonds between the imidazole rings became weakened along with the increase of substituted carbon atom number [22].

2.3 The crystal structure of compound $\mathbf{a_2}$ ($C_{23}H_{26}FeN_2O_2S$)

Compound $\mathbf{a_2}$ was purified by column chromatography on silica gel and then dissolved in ethyl acetate. Ethanol and petroleum ether were finally added. The yellow single crystals were obtained by slow evaporation of the solvent at room temperature after 6 weeks. The measurement of the crystal (in size of 0.34 mm×0.26 mm×0.18 mm) was carried on a Bruker Smart APEX Ⅱ X-ray diffraction with graphite-monochrome MoK^{a} ray (λ = 0.071073 nm) used as photo source. 11048 diffraction points were collected within $4.42° \leqslant \theta \leqslant 50.10°$ by the scanning way of ω (2^{θ}) at the room temperature 296(2) K, 4022 [R (int) = 0.0301] independent points existed. All calculations were solved by the SHELXL297 routine package. The coordinates of non-hydrogen atoms and the factors of aeolotropic temperature were refined by the full-matrix least-squares method. The data was corrected by the LP factor and the experience absorption. The crystal structure was solved by the Direct Method and refined on Fourier. The final R_1 = 0.0495, wR_2= 0.1517, GOF = 1.066. The intensive parameter is 283. The final margin of the biggest residual peak on Fourier is 0.336×10^3 e/nm^3. The smallest residual peak is -0.570×10^3 e/nm^3.

The compound belongs to the monoclinic system with space group C2/c, and the unit cell parameters are a = 2.8252(2) nm, b = 0.97696(7) nm, c = 1.64828(12) nm, α = 90°, β = 92.053(2)°, γ = 90°, V = 4.5466(6) nm^3, Z = 8, F(000) = 2024, Mr = 481.40, Dc = 1.407 g/cm^3, μ = 0.784 mm^{-1}, R_1= 0.0495, wR_2= 0.1517.

The crystal data and structure refinement of the compound are shown in Table 1 and the experimental results for the bond lengths and bond angles of the compound are shown in Table 2. The molecular structure of the compound is shown in Fig. 1 and the molecular packing of the compound is shown in Fig. 2 (All hydrogen atoms and their number are not defined). From the Table 2, we can see that the two cyclopentadienyl rings in the ferrocene unit are not completely parallel and the distances out of plane are 0.00146 nm (C14–C18) and 0.00091 nm (C19–C23) in ferrocene. The bond angle of ∠C14-S-N1 is 103.19° and the twist angle of S-N1-C7-N2 with S-C14-C15-C16 are 169.2° and –179.0°, all those shown that the

Table 1 Crystal data and structure refinement for the compound $\mathbf{a_2}$

Empirical formula	$C_{23}H_{26}FeN_2O_2S$	Crystal size/mm	0.34 × 0.26 × 0.18
Formula weight	450.13	Theta range for data collection	2.21°–25.05°
Temperature/K	296(2) K	Limiting indices	$-30 \leqslant h \leqslant 33$, $-11 \leqslant k \leqslant 8$, $-18 \leqslant l \leqslant 19$
Wavelength/nm	0.071073	Reflections collected/unique	11048/4022 [R(int) = 0.0301]
Crystal system	Monoclinic	Completeness to $\theta = 25.05$	99.9%
Space group	C2/c	Absorption correction	None
Unit cell dimensions	$a = 0.28252(2)$ nm, $\alpha = 90°$	Max. and min. Transmission	0.8705 and 0.7760
	$b = 0.97696(7)$ nm, $\beta = 92.053(2)°$	Data/restraints/parameters	4022/0/283
	$c = 1.64828(12)$ nm, $\gamma = 90°$	Goodness-of-fit on F^2	1.066
Volume/nm^3	4546.6(6)	Final R indices $[I > 2^{\theta}(I)]$	$R_1 = 0.0495$, $wR_2 = 0.1517$
Z	8	R indices (all data)	$R_1 = 0.0658$, $wR_2 = 0.1687$
Dc /(g/cm^{-3})	1.407	Refinement method	Full-matrix least-squares on F^2
Absorption coefficient/mm^{-1}	0.784	Extinction coefficient	0.00008(13)
F(000)	2024	Largest diff. peak/hol (e/nm^3)	0.336 and – 0.570

ring of ferrocene and benzimidazole is almost parallel. The crystal structure shows that inter-molecular interaction is by Van der Waals force.

2.4 The effect of reaction conditions on the yield

It is required to heat the system to keep the reaction going. According to the literature [19], the nitrogen heterocyclic ferrocene sulfonamide can be prepared by combining ferrocenesulfonyl chloride and nitrogen heterocyclic compounds in an ice bath and the reaction would take 16–24 h to end with stirring. We found that the reaction of 2-substituted long carbon chain benzimidazole with ferrocenesulfonyl chloride almost did not carry on in the ice bath. But when the temperature rose up to 40–50°C, the reaction was completed in about 4–4.5 h with good yields. Compared with the nitrogen heterocyclic compounds, it is difficult for the reaction of 2-substituted long carbon chain benzimidazole. However, the rapid reaction can carry on at an appropriate temperature.

The reaction activity reduced with the growth of

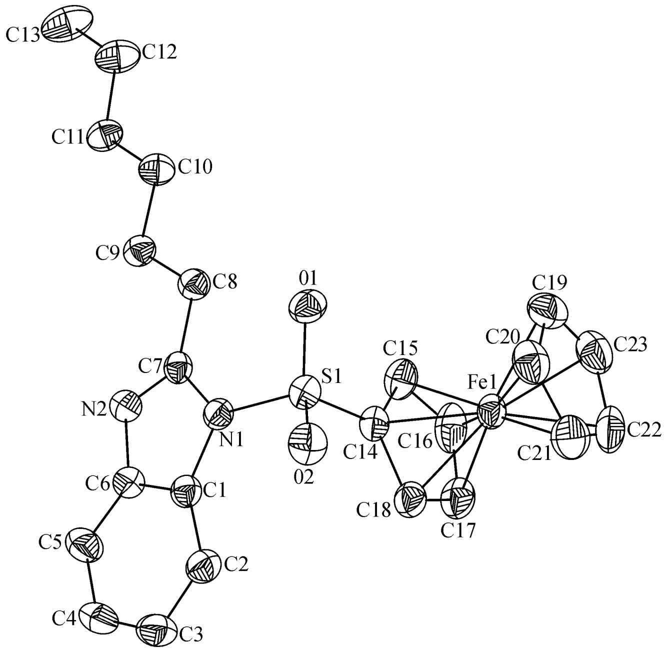

Fig. 1 Crystal structure of compound $\mathbf{a_2}$

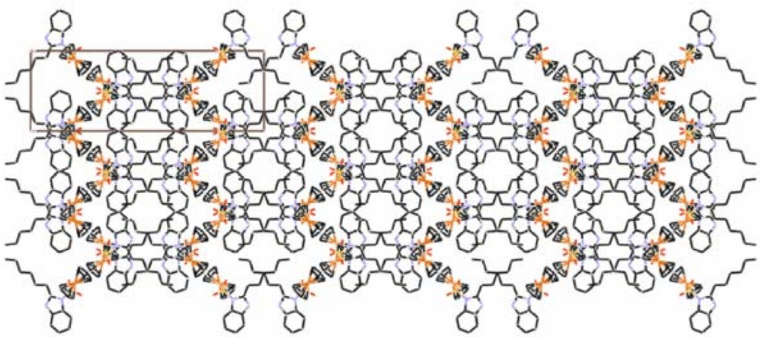

Fig. 2 Molecular packing of the title compound $\mathbf{a_2}$

Table 2 Selected bond lengths (nm) and angles (°) for the compound $\mathbf{a_2}$

Fe(1)-C(14)	0.1997(4)	Fe(1)-C(19)	0.2048(4)
Fe(1)-C(15)	0.2035(4)	Fe(1)-C(20)	0.2036(4)
Fe(1)-C(16)	0.2042(4)	Fe(1)-C(21)	0.2024(5)
Fe(1)-C(17)	0.2055(4)	Fe(1)-C(22)	0.2015(4)
Fe(1)-C(18)	0.2038(4)	Fe(1)-C(23)	0.2030(4)
S(1)-O(1)	0.1418(3)	S(1)-O(2)	0.1424(3)
N(1)-S(1)-C(14)	103.19(16)	C(7)-N(1)-S(1)	128.5(2)
C(1)-N(1)-S(1)	123.8(2)	C(6)-C(1)-N(1)	104.3(3)
C(2)-C(1)-C(6)	122.1(4)	C(2)-C(3)-C(4)	121.3(4)
C(3)-C(2)-C(1)	117.0(4)	C(4)-C(5)-C(6)	117.7(4)
C(5)-C(4)-C(3)	121.6(4)	C(1)-C(6)-N(2)	111.2(3)
C(1)-C(6)-C(5)	120.3(4)	C(18)-C(14)-C(15)	109.0(4)
N(2)-C(7)-N(1)	111.8(3)	C(17)-C(16)-C(15)	110.4(4)
C(16)-C(15)-C(14)	104.8(4)	C(17)-C(18)-C(14)	107.3(4)
C(16)-C(17)-C(18)	108.5(4)	C(19)-C(20)-C(21)	108.7(4)
C(20)-C(19)-C(23)	108.4(4)	C(21)-C(22)-C(23)	107.5(4)
C(20)-C(21)-C(22)	107.9(5)	C(19)-C(23)-C(22)	106.6(4)

2-substituted carbon chain. At the same time, synthetic compounds $\mathbf{a_2}$ require that the temperature be at 40°C. Synthetic compounds $\mathbf{f_2}$ required a temperature of 45°C. The probable reason is: (1) With the growth of carbon chain, the size of the substituting group volume increases and the space effect increases, and so the active centre would be deactivated; (2) In the reaction process, its active center is positively charged. As the number of alkyl carbon chain increases, the ability of electron donation increases and so the active center is deactivated. Along with the growth of 2-substituted carbon chain, both the temperature of reaction and the product yield increases.

3 Conclusion

These results show that 1-ferrocenesulfonyl-2-long chain alkylbenzimidazoles could obtain by the reaction of benzimidazole derivatives containing active hydrogen with ferrocenesulfonyl chloride in good yields. The as-synthesized six compounds were characterized by nuclear magnetic resonance, infrared spectra element analysis and flight mass spectrometry. The data were basically consistent with theoretical values. The crystal structure of $\mathbf{a_2}$ compound was also studied.

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