Journal of Fluorine Chemistry 140 (2012) 49–53

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

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

Preparation and spectroscopic properties of some new diaroylmethanatoboron difluoride derivatives

Dun-Jia Wang *, Ben-Po Xu, Xian-Hong Wei, Jing Zheng

Hubei Key Laboratory of Pollutant and Reuse Technology, College of Chemistry and Environmental Engineering, Hubei Normal University, Huangshi 435002, PR China

ARTICLE INFO

Article history:
Received 9 February 2012
Received in revised form 18 April 2012
Accepted 19 April 2012
Available online 26 April 2012

Keywords:
Diaroylmethanatoboron difluoride
Preparation
Diaroylmethanes
Spectroscopic properties

ABSTRACT

Five diaroylmethanatoboron difluoride derivatives were prepared from aryl methyl ketones via Claisen condensation with aromatic esters and followed by complexation with boron trifluoride etherate. Their structures and spectroscopic properties were studied by elemental analysis, IR, NMR, ESI–MS, UV and fluorescence spectroscopy. The results showed that these boron complexes had strong fluorescent peaks in the 400–500 nm range in chloroform and high quantum yields. The emission peaks for boron complexes containing naphthyl group exhibited considerable red shift as compared to those of containing phenyl group.

1. Introduction

The boron difluoride β-diketonates, especially the diaroylmethanatoboron difluoride derivatives, are of great attention to the chemists because they exhibit high luminescence in the visible range of spectrum and can be used as fluorescent electroluminescent emitters, photoconductivity and fluorescent probes [1–3]. Boron difluoride β-diketonates have been known since 1924 and the methods of their preparation are considerably well known and systematized [3–6]. Recently, Ono et al. [7] and Zhang et al. [8,9] reported synthesis and photoluminescence properties of some new difluoroboron β-diketonates. In addition, a variety of solid state structures of difluoroboron complexes with 1,3-diketones are also studied [10,11]. With the purpose of investigation into the influence of aromatic substituent groups (including strong electron-withdrawing fluorophenyl, electron-donating *tert*-butyl phenyl and fused naphthalene ring) on the luminescene intensity, we report the preparation and spectroscopic properties of some new diaroylmethanatoboron difluoride derivatives. Structures and properties of the obtained compounds were established by means of the elemental analysis, IR, NMR, ESI–MS, UV and fluorescence spectroscopy.

2. Results and discussion

2.1. Preparation of diaroylmethanatoboron difluoride derivatives

Preparation of the title compounds is outlined in Scheme 1. The diaroylmethanatoboron difluoride derivatives were obtained by the reaction of boron trifluoride diethyl ether complex ($BF_3 \cdot Et_2O$) with the corresponding diaroylmethanes in dichloromethane. The diaroylmethanes were prepared from aryl methyl ketones via Claisen condensation with aromatic esters [12,13]. After recrystallization from ethanol, pure boron complexes were isolated in moderate to good yields. All products and intermediates were characterized by elemental analysis, FTIR, NMR, and mass spectroscopy.

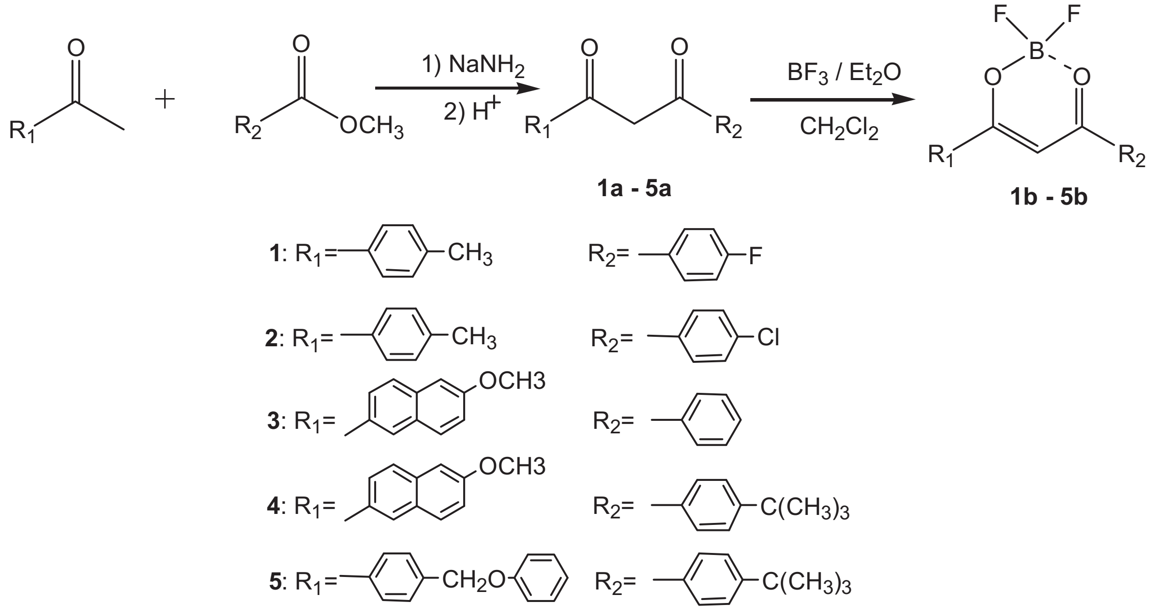
2.2. IR spectra

The IR spectra of diaroylmethanatoboron difluoride derivatives show marked changes in comparison with those of the diaroylmethanes. The characteristic, strong bands of the diaroylmethanes and their boron complexes are summarized in Table 1. Their IR spectra showed several weak vibrations in the range of 3100–2800 cm^{-1} assigned to the stretching vibrations for saturated C–H and unsaturated C–H. In the range of 1650–500 cm^{-1}, their spectra are substantially different. The strong absorption bands in the regions of 1629–1599 cm^{-1} and 1546–1500 cm^{-1} belonged to the C=O and enolic C=C stretching vibrations [14,15]. However, the C=O and C=C stretching frequencies of the boron complexes were

---

* Corresponding author. Tel.: +86 714 6515602; fax: +86 714 6573832.
E-mail address: dunjiawang@163.com (D.-J. Wang).

0022-1139/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jfluchem.2012.04.010



Scheme 1. Synthetic routes for compounds **1b**–**5b**.

red-shifted 1–5 cm^{-1} with respect to those of the corresponding diaroylmethanes. These results indicated that the C=O bond in the diaroylmethanes was weakened due to boron complex formation arising from the withdraw of electronic density from the chelate ring by the fluorine atoms, and the vibration frequency was decreased. The strong absorptions of the boron complexes in the region of 1371–1366 cm^{-1} were due to the B–O stretching vibrations and those in the region of 1203–1180 cm^{-1} were attributed to the B–F stretching vibrations [14,16]. Obviously, there were no strong absorptions in these regions for the diaroylmethane compounds.

2.3. ^{1}H NMR spectra

In the ^{1}H NMR spectra of the diaroylmethanes and their boron complexes, their chemical shifts of the phenyl and naphthenyl ring protons were very similar. However, the chemical shifts of the enolic OH proton, the keto-CH$_2$ proton and the vinylic proton in enol exhibited pronounced difference (Table 2). In the diaroylmethanes, the enolic protons displayed a single peak at δ = 16.98–17.10 ppm and the keto-CH$_2$ protons also revealed a single peak at δ = 4.56–4.70 ppm. But in the boron complexes, they did not show the presence of not only the enolic proton but also the keto-CH$_2$ proton signals. The vinylic protons for the diaroylmethanes and their boron complexes exhibited a single peak at δ = 6.78–6.99 ppm, whereas the vinylic proton signal for boron complexes was shifted 0.24–0.34 ppm to lower field with respect to the corresponding vinylic signal in the parent enol [14,15]. This is also explained by the effect of electronegative fluorine atoms on the electron density of the quasiaromatic cycle of the boron complex.

2.4. UV–vis spectra

The UV–vis spectra data for compounds **1a**–**5a** and **1b**–**5b** in chloroform are summarized in Table 3. The results showed that there were a strong broad absorption bands at 364–370 nm and 392–422 nm in compounds **1a**–**5a** and **1b**–**5b**, respectively, which assigned to $\pi-\pi^*$ transitions in the conjugated ring system. The UV spectra of the boron complexes are similar to those of the corresponding diaroylmethanes, but bands are red-shifted about 40–50 nm, which indicated that the boron complex forms an effective π-conjugation between the two aryl groups via the BF$_2$-chelating moiety.

2.5. Fluorescence spectra and quantum yields

The fluorescence spectra of compounds **1b**–**5b** were recorded in chloroform at a concentration of 2.0×10^{-5} mol L^{-1} (Fig. 1 and Table 4). The results showed that the boron complexes **1b**–**5b** are strong fluorescent in the range of 400–500 nm and their quantum yields are good-to-excellent, attributed to their extended π-conjugated molecules. The emission maxima, intensity and quantum yield of **1b** were much analogous to those of **2b**, assigned to their similar structure and substituents. As for **5b**, its emission

Table 1
Comparison of the characteristic IR data for compounds **1a**–**5a** and **1b**–**5b**.

Compound	ν (C=O), cm^{-1}	ν (C=C), cm^{-1}	ν (B–O), cm^{-1}	ν (B–F), cm^{-1}
1a	1602 (s)	1505 (s)	–	–
1b	1599 (s)	1500 (s)	1368 (s)	1180 (s)
2a	1605 (s)	1509 (s)	–	–
2b	1600 (s)	1506 (s)	1366 (s)	1186 (s)
3a	1628 (s)	1541 (s)	–	–
3b	1627 (s)	1537 (s)	1371 (s)	1203 (s)
4a	1629 (s)	1545 (s)	–	–
4b	1625 (s)	1541 (s)	1369 (s)	1198 (s)
5a	1605 (s)	1506 (s)	–	–
5b	1600 (s)	1501 (s)	1370 (s)	1184 (s)

Table 2
Comparison of ^{1}H NMR parameters for compounds **1a**–**5a** and **1b**–**5b**.

Compound	δ (keto-CH$_2$), ppm	δ (C=C–H), ppm	δ (O–H), ppm
1a	4.56	6.78	17.06
1b	–	7.02	–
2a	4.61	6.78	17.03
2b	–	7.05	–
3a	4.70	6.99	17.05
3b	–	7.25	–
4a	4.70	6.97	17.10
4b	–	7.25	–
5a	4.65	6.78	16.98
5b	–	7.12	–

Table 3
UV–vis spectra data for compounds **1a**–**5a** and **1b**–**5b**.

Compound	λ_{max} (nm)	$\log \varepsilon_{max}$
1a	358	4.73
2a	360	4.75
3a	368	4.35
4a	370	4.30
5a	364	4.58
1b	400	4.63
2b	402	4.65
3b	420	4.21
4b	422	4.18
5b	404	4.54

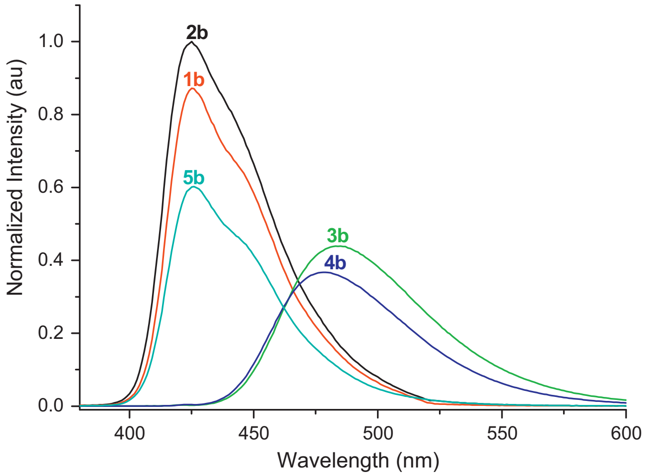


Fig. 1. Normalized emission spectra for compounds **1b**–**5b**.

Table 4
Fluorescence spectra data and quantum yields for compounds **1b**–**5b**.

Compound	λ_{ex} (nm)	λ_{em} (nm)	ϕ_F
1b	400	425	0.68
2b	402	425	0.76
3b	420	485	0.33
4b	422	483	0.29
5b	404	426	0.46

intensity and quantum yield were lower than that of **1b** and **2b**, owing to steric hindrance of benzyl and *tert*-butyl groups. However, the emission maxima for **3b** and **4b** were red-shifted about 60 nm as compared to those of compounds **1b**, **2b** and **5b**, because of their much larger π-conjugated systems. On the contrary, their fluorescent intensities and quantum yields were much lower than those of compounds **1b** and **2b**, these results in accordance with the literature [3].

3. Conclusions

In summary, some new diaroylmethanatoboron difluoride compounds were prepared, and their structures and spectroscopic properties were investigated by UV–vis, IR, NMR and fluorescence spectroscopy. These boron complexes exhibited intense fluorescence in the 400–500 nm range and high quantum yields. The absorption and emission maxima of compounds **3b** and **4b** were considerably red-shifted as compared to those of compounds **1b**, **2b** and **5b**, suggesting a much extended π-conjugation in complexes **3b** and **4b**. They could be used as fluorescent electroluminescent materials because of their strong fluorescent property and high quantum yields. The further investigation of their potential application is in progress.

4. Experimental

4.1. Chemicals and methods

Melting points were determined using X-4 digital melting point apparatus and uncorrected. Elemental analysis (C, H, N) was performed using a Perkin-Elmer 2400 elemental analyzer. ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury-Plus 400 NMR nuclear magnetic resonance instrument in $CDCl_3$ solution with TMS as internal standard. Infrared spectra were recorded at 1 cm^{-1} resolution on a Nicolet FTIR 5700 spectrophotometer with KBr pellets. Low-resolution electrospray ionization mass spectra (ESI–MS) were determined with a Finnigan LCQ ADVANTAGE MAX spectrometer. Reagents were of analytical grade and were used without further purification.

The UV–vis spectra were obtained with Hitachi U-3010 spectrometer. The emission spectra of the sample were carried out on a Varian Cary Eclipse fluorescence spectrometer. The ϕ values were determined according to literature method using quinine sulfate in 0.1 mol L^{-1} sulfuric acid ($\phi_{ST} = 0.55$, $\lambda_{ex} = 366$ nm, at room temperature) as a standard [17]. The fluorescence quantum yields ϕ were calculated from the relation shown in Eq. (1):

$$\Phi_F = \frac{D_X \times A_{ST} \times n_X^2}{D_{ST} \times A_X \times n_{ST}^2} \times \Phi_{ST} \qquad (1)$$

where the subscripts X and ST denote test and standard respectively, ϕ is the fluorescence quantum yield, A is the absorbance at the excitation wavelength, D is the integrated emission spectrum, and n is the refractive index for the solvent.

4.2. Preparation of dibenzoylmethanes

The mixture of aryl methyl ketones (0.04 mol), aromatic esters (0.04 mol), $NaNH_2$ (1.95 g, 0.05 mol) and toluene (50 mL) was stirred at 80 °C for 6 h. The reaction mixture was cooled to room temperature, acidified with dilute hydrochloric acid and then stirred until all solids dissolved. The toluene layer was separated, washed with a saturated $NaHCO_3$ solution, dried over anhydrous $MgSO_4$ and the solvent was removed by evaporation. The residual oil solidified on standing and the solid was recrystallized from ethanol to obtain the dibenzoylmethanes.

4.2.1. 1-(4-Methyl-phenyl)-3-(4-fluoro-phenyl)-propane-1,3-dione (1a)

Colorless crystals, yield 72%, mp 125–126 °C; IR (KBr): ν 3452 (w), 3078 (m), 2961 (m), 2870 (w), 1602 (s), 1540 (m), 1505 (s), 1456 (m), 1365 (w), 1226 (s), 1158 (s), 1104 (m), 1011 (m), 850 (s), 794 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 4.56 (s, 0.14H, keto CH_2), 6.78 (s, 1H, enol CH), 7.10–7.13 (m, 2H), 7.50 (d, 2H, Ar–H, J = 8.4 Hz), 7.81 (d, 2H, Ar–H, J = 8.4 Hz), 7.96–7.99 (m, 2H), 17.06 (br s, 1H, enol OH) ppm; ESI–MS: m/z 257.11 $[M+1]^+$; Anal. calcd. for $C_{16}H_{13}FO_2$: C, 74.99; H, 5.11; found: C, 75.46; H, 5.03.

4.2.2. 1-(4-Methyl-phenyl)-3-(4-chloro-phenyl)-propane-1,3-dione (2a)

Colorless crystals, yield 78%, mp 136–137 °C; IR (KBr): ν 3469 (w), 3065 (m), 2952 (m), 2860 (w), 1605 (s), 1545 (m), 1509 (s), 1463 (m), 1369 (w), 1231 (m), 1150 (m), 1100 (s), 1021 (s), 856 (s), 798 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 4.61 (s, 0.16H, keto CH_2), 6.78 (s, 1H, enol CH), 7.06–7.09 (m, 2H), 7.48

(d, 2H, Ar–H, J = 8.4 Hz), 7.90 (d, 2H, Ar–H, J = 8.4 Hz), 7.99–8.02 (m, 2H), 17.03 (br s, 1H, enol OH) ppm; ESI–MS: m/z 273.68 [M + 1]$^{+}$; Anal. calcd. for $C_{16}H_{13}ClO_{2}$: C, 70.46; H, 4.80; found: C, 70.93; H, 4.75.

4.2.3. 1-(6-Methoxy-naphthalen-2-yl)-3-phenyl-propane-1,3-dione (3a)

Pale yellow crystals, yield 52%, mp 143–144 °C; IR (KBr): ν 3490 (w), 3063 (w), 2975 (w), 2852 (w), 1628 (s), 1599 (m), 1541 (s), 1480 (m), 1391 (s), 1267 (s), 1234 (s), 1197 (s), 1022 (s), 857 (s), 770 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3}$): δ 3.96 (s, 3H, OCH_{3}), 4.70 (s, 0.14H, keto CH_{2}), 6.99 (s, 1H, enol CH), 7.17–7.18 (m, 2H), 7.51–7.53 (m, 3H), 7.81 (d, 1H, Ar–H, J = 8.4 Hz), 7.88 (d, 1H, Ar–H, J = 9.6 Hz), 7.99–8.04 (m, 3H), 8.48 (s, 1H), 17.05 (br s, 1H, enol OH) ppm; ESI–MS: m/z 305.03 [M + 1]$^{+}$; Anal. calcd. for $C_{20}H_{16}O_{3}$: C, 78.93; H, 5.30; found: C, 79.18; H, 5.16.

4.2.4. 1-(4-tert-Butyl-phenyl)-3-(6-methoxy-naphthalen-2-yl)-propane-1,3-dione (4a)

Pale yellow crystals, yield 48%, mp 146–147 °C; IR (KBr): ν 3473 (w), 3071 (w), 2950 (s), 2865 (w), 1629 (s), 1608 (m), 1545 (s), 1526 (m), 1481 (m), 1459 (m), 1362 (m), 1300 (m), 1269 (s), 1199 (s), 1111 (s), 1028 (s), 913 (s), 855 (s), 808 (s), 786 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3}$): δ 1.37 (s, 9H, $C(CH_{3})_{3}$), 3.96 (s, 3H, OCH_{3}), 4.70 (s, 0.14H, keto CH_{2}), 6.97 (s, 1H, enol CH), 7.17–7.23 (m, 2H), 7.53 (d, 2H, Ar–H, J = 8.0 Hz), 7.82 (d, 1H, Ar–H, J = 8.4 Hz), 7.88 (d, 1H, Ar–H, J = 9.2 Hz), 7.96–8.01 (m, 3H), 8.47 (s, 1H), 17.10 (br s, 1H, enol OH) ppm; ESI–MS: m/z 361.06 [M + 1]$^{+}$; Anal. calcd. for $C_{24}H_{24}O_{3}$: C, 79.97; H, 6.71; found: C, 80.45; H, 6.62.

4.2.5. 1-(4-Benzyloxy-phenyl)-3-(4-tert-butyl-phenyl)-propane-1,3-dione (5a)

White crystals, yield 62%, mp 99–101 °C; IR (KBr): ν 3425 (m), 3010 (w), 2961 (m), 2843 (m), 1605 (s), 1506 (s), 1481 (m), 1452 (s), 1379 (w), 1264 (s), 1230 (s), 1174 (s), 1109 (m), 1027 (m), 895 (m), 790 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3}$): δ 1.36 (s, 9H, $C(CH_{3})_{3}$), 4.65 (s, 0.10H, keto CH_{2}), 5.15 (s, 2H, OCH_{2}), 6.78 (s, 1H, enol CH), 7.06 (d, 2H, Ar–H, J = 8.8 Hz), 7.39–7.46 (m, 5H), 7.50 (d, 2H, Ar–H, J = 8.4 Hz), 7.91 (d, 2H, Ar–H, J = 8.4 Hz), 7.97 (d, 2H, Ar–H, J = 8.8 Hz), 16.98 (br s, 1H, enol OH) ppm; ESI–MS: m/z 387.12 [M + 1]$^{+}$; Anal. calcd. for $C_{26}H_{26}O_{3}$: C, 80.80; H, 6.78; found: C, 81.38; H, 6.70.

4.3. Preparation of diaroylmethanatoboron difluoride

Boron trifluoride diethyl etherate (1 mL, 7 mmol) was added to a solution of dibenzoylmethanes (5 mmol) in dry dichloromethane (10 mL). The reaction mixture was stirred at 40 °C for 3 h. After removal of the solvent, the residue was filtered and crystallized from ethanol. The solid was sublimation at 200 °C under 10^{-3} mmHg to provide the boron complexes.

4.3.1. Boron difluoride 1-(4-methyl-phenyl)-3-(4-fluoro-phenyl)-propane-1,3-dionate (1b)

Yellow microcrystalline powder, yield 69%, mp 223–224 °C; IR (KBr): ν 3070 (w), 2965 (w), 2866 (w), 1599 (s), 1548 (s), 1500 (s), 1478 (m), 1368 (s), 1316 (s), 1279 (s), 1245 (s), 1180 (s), 1038 (m), 845 (s), 791 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3}$): δ 2.37 (s, 3H, CH_{3}), 7.02 (s, 1H, C=CH), 7.13–7.16 (m, 2H), 7.52 (d, 2H, Ar–H, J = 8.4 Hz), 7.90 (d, 2H, Ar–H, J = 8.4 Hz), 8.02–8.05 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_{3}$): δ 20.6, 92.8, 116.0/115.7, 128.3, 128.9, 131.9/131.8, 132.5, 135.2, 145.1, 167.1/163.7, 184.5, 185.1 ppm; ESI–MS: m/z 305.02 [M + 1]$^{+}$; Anal. calcd. for $C_{16}H_{12}BF_{3}O_{2}$: C, 63.20; H, 3.98; found: C, 63.36; H, 3.95.

4.3.2. Boron difluoride 1-(4-methyl-phenyl)-3-(4-chloro-phenyl)-propane-1,3-dionate (2b)

Yellow green powder, yield 65%, mp 23–239 °C; IR (KBr): ν 3032 (w), 2953 (m), 2865 (w), 1600 (s), 1553 (s), 1506 (s), 1458 (m), 1366 (s), 1243 (m), 1186 (s), 1102 (s), 1023 (s), 850 (s), 796 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3}$): δ 2.36 (s, 3H, CH_{3}), 7.05 (s, 1H, C=CH), 7.10–7.12 (m, 2H), 7.51 (d, 2H, Ar–H, J = 8.4 Hz), 7.96 (d, 2H, Ar–H, J = 8.4 Hz), 8.05–8.08 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_{3}$): δ 20.6, 92.5, 128.2, 128.9, 129.2, 130.6, 134.5, 135.7, 138.7, 145.3, 183.6, 184.2 ppm; ESI–MS: m/z 321.45 [M + 1]$^{+}$; Anal. calcd. for $C_{16}H_{12}BClF_{2}O_{2}$: C, 59.96; H, 3.77; found: C, 60.12; H, 3.75.

4.3.3. Boron difluoride 1-(6-methoxy-naphthalen-2-yl)-3-phenyl-propane-1,3-dionate (3b)

Earth yellow powder, yield 51%, mp 230–231 °C; IR (KBr): ν 3011 (w), 2949 (w), 2845 (w), 1627 (s), 1599 (m), 1537 (s), 1491 (s), 1390 (s), 1371 (s), 1273 (s), 1203 (s), 1131 (s), 1035 (s), 845 (m), 820 (m), 776 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3}$): δ 3.99 (s, 3H, OCH_{3}), 7.20 (s, 1H, Ar–H), 7.25 (s, 1H, C=CH), 7.31 (s, 1H, Ar–H), 7.56–7.60 (m, 2H, Ar–H), 7.70 (m, 1H, Ar–H), 7.85 (d, 1H, Ar–H, J = 9.2 Hz), 7.92 (d, 1H, Ar–H, J = 8.8 Hz), 8.08 (d, 1H, Ar–H, J = 8.8 Hz), 8.19 (d, 2H, Ar–H, J = 7.6 Hz), 8.72 (s, 1H, Ar–H) ppm; ^{13}C NMR (100 MHz, $CDCl_{3}$): δ 56.1, 94.7, 106.8, 120.7, 125.0, 126.5, 128.0, 128.2, 129.5, 129.8, 132.0, 132.4, 132.7, 136.0, 139.0, 161.2, 181.6, 182.9 ppm; ESI–MS: m/z 353.09 [M + 1]$^{+}$; Anal. calcd. for $C_{20}H_{15}BF_{2}O_{3}$: C, 68.22; H, 4.29; found: C, 68.41; H, 4.27.

4.3.4. Boron difluoride1-(4-tert-butyl-phenyl)-3-(6-methoxy-naphthalen-2-yl)-propane-1,3-dionate (4b)

Bright yellow needles, yield 68%, mp 243–244 °C; IR (KBr): ν 3022 (w), 2960 (w), 2865 (w), 1625 (s), 1606 (m), 1541 (s), 1388 (s), 1369 (s), 1269 (s), 1198 (s), 1029 (s), 848 (s), 788 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3}$): δ 1.38 (s, 9H, $C(CH_{3})_{3}$), 3.98 (s, 3H, OCH_{3}), 7.18–7.23 (m, 2H, Ar–H), 7.25 (s, 1H, C=CH), 7.56 (d, 2H, Ar–H, J = 8.8 Hz), 7.82 (d, 1H, Ar–H, J = 8.8 Hz), 7.90 (d, 1H, Ar–H, J = 8.8 Hz), 8.05 (d, 1H, Ar–H, J = 8.4 Hz), 8.11 (d, 2H, Ar–H, J = 8.4 Hz), 8.68 (s,1H, Ar–H) ppm; ^{13}C NMR (100 MHz, $CDCl_{3}$): δ 31.0, 35.4, 55.5, 92.9, 105.9, 120.4, 124.3, 126.2, 126.8, 127.6, 127.9, 128.8, 129.3, 131.3, 131.7, 138.5, 159.4, 160.8, 181.2, 182.5 ppm; ESI–MS: m/z 409.06 [M + 1]$^{+}$; Anal. calcd. for $C_{24}H_{23}BF_{2}O_{3}$: C, 70.61; H, 5.68; found: C, 70.78; H, 5.65.

4.3.5. Boron difluoride 1-(4-benzyloxy-phenyl)-3-(4-tert-butyl-phenyl)-propane-1,3-dionate (5b)

Yellow green powder, yield 79%, mp 219–220 °C; IR (KBr): ν 3068 (w), 3030 (w), 2960 (m), 2867 (m), 1600 (s), 1562 (m), 1501 (s), 1370 (s), 1321 (s), 1260 (s), 1184 (s), 1129 (s), 1030 (s), 800 (s), 819 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3}$): δ 1.37 (s, 9H, $C(CH_{3})_{3}$), 5.20 (s, 2H, OCH_{2}), 7.09 (d, 2H, Ar–H, J = 6.4 Hz), 7.12 (s, 1H, C=CH), 7.42–7.44 (m, 5H, Ar–H), 7.55 (d, 2H, Ar–H, J = 8.4 Hz), 8.06 (d, 2H, Ar–H, J = 8.4 Hz), 8.15(d, 2H, Ar–H, J = 8.8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_{3}$): δ 31.0, 35.4, 70.4, 92.2, 115.4, 124.5, 126.1, 127.5, 128.5, 128.7, 128.8, 129.4, 131.5, 135.6, 159.2, 164.6, 180.5, 181.2 ppm; ESI–MS: m/z 435.17 [M + 1]$^{+}$; Anal. calcd. for $C_{26}H_{25}BF_{2}O_{3}$: C, 71.86; H, 5.80; found: C, 72.09; H, 5.79.

Acknowledgment

Financial support for this work from the Natural Science Foundation of the Educational Commission of Hubei Province, PR China (No. CXY2009B029).

References

[1] H.D. Ilge, E. Birckner, D. Fassler, Journal of Photochemistry 32 (1986) 177–189.

[2] A.G. Mirochink, E.V. Fedorenko, G. Kh Gizzatulina, V.E. Karasev, Russian Journal of Physical Chemistry A 81 (2007) 1880–1883.

[3] E. Cogné-Laage, J.-F. Allemand, O. Ruel, J.-B. Baudin, V. Croquette, M. Blanchard-Desce, L. Julien, Chemistry: A European Journal 10 (2004) 1445–1455.

[4] G.T. Morgan, R.B. Tunstall, Journal of the Chemical Society Transactions 125 (1924) 1963–1967.

[5] V.A. Reutov, E.V. Gukhman, Russian Journal of General Chemistry 69 (1999) 1603–1607.

[6] H. Maeda, Y. Ito, Inorganic Chemistry 45 (2006) 8205–8210.

[7] K. Ono, K. Yoshikawa, Y. Tsuji, H. Yamaguchi, R. Uozumi, M. Tomura, K. Taga, K. Saito, Tetrahedron 63 (2007) 9354–9358.

[8] G. Zhang, J. Chen, S.J. Payne, S.E. Kooi, J.N. Demas, C.L. Fraser, Journal of the American Chemical Society 129 (2007) 8942–8943.

[9] G. Zhang, J. Lu, M. Sabat, C.L. Fraser, Journal of the American Chemical Society 132 (2010) 2160–2162.

[10] B.V. Bukvetskii, E.V. Fedorenko, A.G. Mirochnik, A.Y. Beloliptsev, Journal of Structural Chemistry 51 (2010) 545–551.

[11] B.V. Bukvetskii, E.V. Fedorenko, A.G. Mirochnik, V.E. Karasev, Journal of Structural Chemistry 47 (2006) 56–62.

[12] J.M. Sprague, L.J. Beckham, H. Adkins, Journal of the American Chemical Society 56 (1934) 2665–2668.

[13] C.Y. Zheng, J. Zheng, L. Fan, D.J. Wang, Huaxue Shiji 28 (2006) 538–540 (in Chinese).

[14] N.M.D. Brown, P. Bladon, Journal of the Chemical Society A (1969) 526–532.

[15] O.A. Turanova, A.N. Turanov, D.V. Lapaev, O.I. Gnezdilov, S.V. Lobkov, Yu.G. Galyametdinov, Russian Journal of General Chemistry 76 (2006) 730–732.

[16] V.A. Reutov, E.V. Gukhman, E.E. Kafitulova, Russian Journal of General Chemistry 73 (2003) 1141–1444.

[17] J.N. Demas, G.A. Croby, Journal of Physical Chemistry 75 (1971) 991–1024.