Tetrahedron 66 (2010) 6895–6900

Contents lists available at ScienceDirect

Tetrahedron

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

# Synthesis of π-expanded BODIPYs and their fluorescent properties in the visible–near–infrared region

Tetsuo Okujima *, Yuya Tomimori, Jun Nakamura, Hiroko Yamada, Hidemitsu Uno, Noboru Ono

*Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan*

ARTICLE INFO

*Article history:*
Received 12 May 2010
Received in revised form 16 June 2010
Accepted 17 June 2010
Available online 22 June 2010

*Keywords:*
Dyes–pigments
Boron
Dipyrromethene
Fluorescent dye
Fluoranthene

ABSTRACT

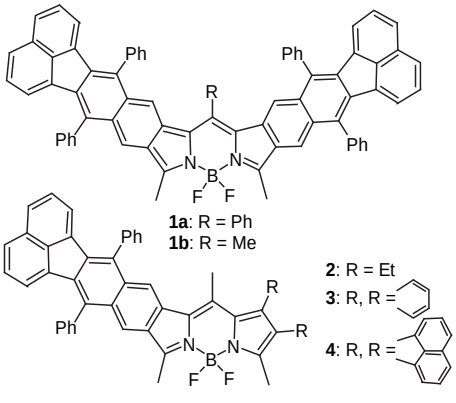
A series of π-expanded boron–dipyrromethenes (BODIPYs) fused with aromatic rings at β,β-positions, such as benzene, acenaphthylene, and benzofluoranthene were prepared by the reaction of $BF_3 \cdot OEt_2$ with bicyclo[2.2.2]octadiene-fused dipyrromethene and the subsequent retro Diels–Alder reaction. These BODIPYs exhibited the absorptions and the fluorescence emissions over wide range of visible–near–infrared region at 500–800 nm. BODIPYs composed of two fluoranthо[8,9-*f*]isoindoles absorbed and emitted at red-region over 750 nm with absolute fluorescence quantum yield ($\Phi_f$) of ca. 0.3, although they are unstable under air in room light. BODIPY composed fluoranthо[8,9-*f*]isoindole and acenaphthо[1,2-c]pyrrole was stable and showed a bright fluorescence emission at 695 nm with high $\Phi_f$ of 0.70.



## 1. Introduction

Boron–dipyrromethene (BODIPY) derivatives have attracted much attention as fluorescent dyes because of their stability, sharp absorption and emission spectra, and high fluorescence quantum yield. Thus, extensive studies have been reported for the application of this dye to chemosensors, biological probes, organic light-emitting diodes, and dye-sensitized solar cells.[1–5] The BODIPY properties can be easily modified by the substituents. Synthetic methods of BODIPY derivatives have been developed in order to tune the absorption and emission wavelength since the end of 1980s. These methods enable us to access a variety of BODIPY derivatives.[5–12] π-Expanded BODIPYs show red-shifted absorptions and emissions. However, most of them with absorptions at over 650 nm are relatively unstable and show emission with low quantum yields. Little is known about long-wavelength fluorescent BODIPYs with high quantum yield over 0.50.

Recently, we have reported the synthesis of benzofluoranthene-fused porphyrins by the retro Diels–Alder reaction of the bicyclo[2.2.2]octadiene(BCOD)-fused precursors.[13] These porphyrins were stable and exhibited intense absorptions and emissions at 700–800 nm with the absolute quantum yield ($\Phi_f$) of 0.1–0.3 although linearly π-expanded porphyrins are usually unstable, such as tetraanthra[2,3-*b*]porphyrin.[14] We have also reported the preparation of BODIPYs composed of isoindoles or acenaphthо[1,2-*c*]pyrroles by the retro Diels–Alder strategy.[10b–d] The benzene- or acenaphthylene–fused BODIPYs show the absorptions at 560–657 nm. Thus, the π-expanded pyrrole component was expected to afford the BODIPYs with absorption and emission at over 700 nm. In this paper, we described the synthesis of a series of linearly π-expanded BODIPYs **1**–**4** with exocyclic rings at β,β-positions and their photochemical properties.

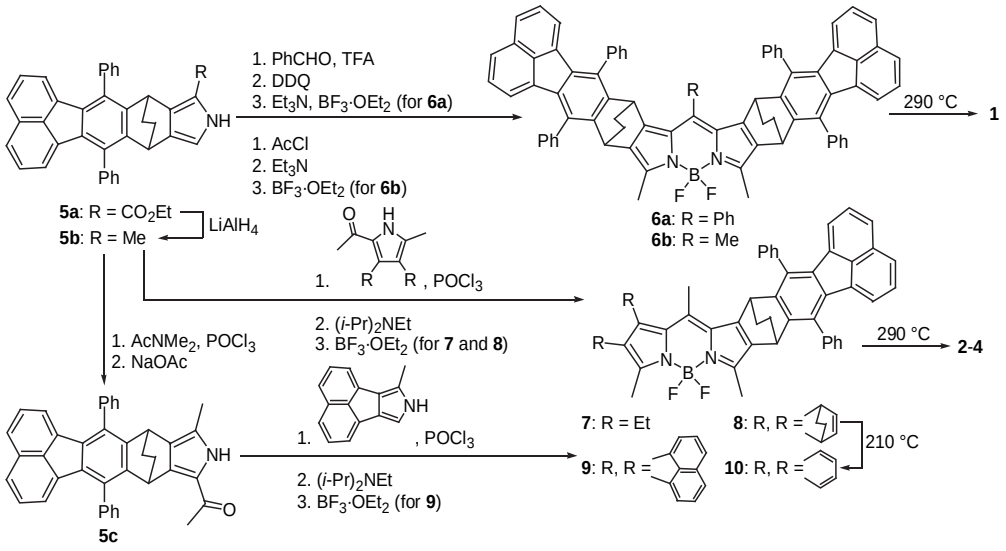



## 2. Results and discussion

The synthesis of BCOD-fused BODIPYs is shown in Scheme 1. BCOD-fused BODIPYs **6**–**9** were synthesized and converted into

* Corresponding author. Tel./fax: +81 89 927 9615; e-mail address: tetsuo@chem.sci.ehime-u.ac.jp (T. Okujima).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.06.045




**Scheme 1.**

symmetrical π-expanded BODIPYs **1** and unsymmetrical ones **2**–**4** and **10** by the retro Diels–Alder reaction in order to compare their photochemical properties depending on the structure of the BODIPYs. Pyrrole **5a** was prepared from BCOD-fused pyrrole according to the literature procedure.[13,15] α-Methylpyrrole **5b** was obtained by the reduction of **5a** with $LiAlH_4$. The subsequent reaction of **5b** with benzaldehyde in the presence of TFA followed by treatment with DDQ, $BF_3 \cdot OEt_2$, and $Et_3N$ gave BCOD-fused BODIPY **6a** in a 37% yield from **5a**. *meso*-Methylbodipy **6b** was also prepared by the similar reaction of **5b** with acetyl chloride. Unsymmetrical BODIPYs **7** and **8** were obtained by the reaction of **5b** with α-acetyl-β-diethyl-[16] and α-acetyl-β-BCODpyrroles[10c,d] in the presence of $POCl_3$, followed by treatment with $(i\text{-}Pr)_2NEt$ and $BF_3 \cdot OEt_2$. The Vilsmeier–Haack-type reaction of **5b** with *N*,*N*-dimethylacetamide gave **5c** in a 39% yield from **5a**, which reacted with α-methylacenaphtho[1,2-*c*]pyrrole[10c,17] followed by treatment with $(i\text{-}Pr)_2NEt$ and $BF_3 \cdot OEt_2$ to give **9** in a 5% yield.

The crystal structure of **6a** and **7** was determined by X-ray diffraction analysis.[18] Single crystals for the X-ray structural determination were obtained by recrystallization from MeOH–$CHCl_3$ for **6a** and **7**. The crystallographic data are summarized in Table S1. BODIPY **6a** was crystallized with two molecules of $CHCl_3$ in a monoclinic cell, space group *C*2/*c*, and *Z*=4. The BODIPY molecule occupied the *C*2 axis of *C*2/*c*. Boron and *meso*-carbon were found in the *C*2 axis. The ORTEP drawing of **6a** is shown in Figure 1. Three phenyl groups at the *meso*-position of BODIPY core and 7-positions of the fluoranthene moiety were treated as a disordered structure. The stereochemistry of two fluoranthenes is *anti*. The dihedral angles between BODIPY core and fluoranthene moieties are 111.21°. The single crystals of *anti*-**6a** were selectively precipitated by recrystallization, while **6a** was obtained as a 1:1 mixture of diastereomers in the reaction of **5b** with benzaldehyde. The BODIPY core was slightly distorted and the dihedral angle of two pyrrole moieties was 11.43°. On the other hand, **7** was crystallized in a triclinic cell and the dihedral angle of pyrrole moieties was 6.03°. The dihedral angles between BODIPY core and fluoranthene moieties are slightly large (130.34°) compared that of **6a**. In the molecular packing, **7** adopts a parallelogram-shaped configuration with two molecules as shown in Figure 2. The distance between fluoranthene moieties is 4.497 Å.

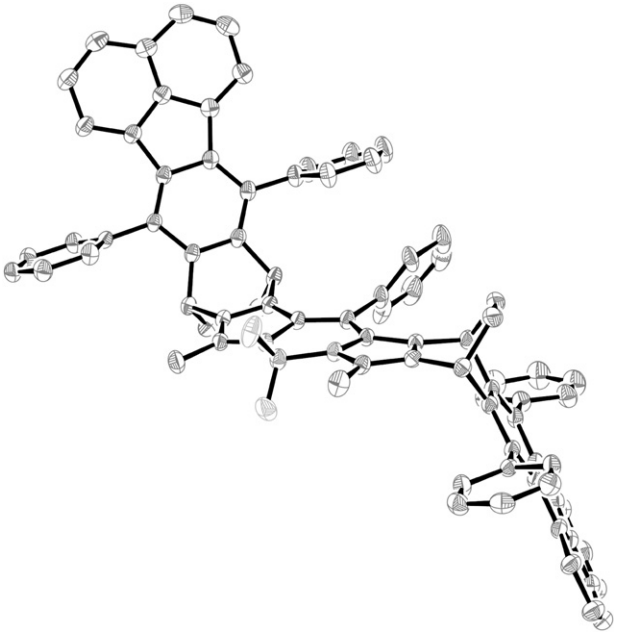


**Figure 1.** ORTEP drawing of **6a**. Solvent, hydrogen and disordered (less popular) atoms are omitted for clarity.

Thermogravimetric analysis (TGA) of **6**–**9** was carried out in order to estimate the temperature of the retro Diels–Alder reaction. TGA curve of **8** showed the stepwise weight loss corresponding to removal of two ethylene molecules at around 200 °C and 300 °C (Fig. 3). The weight loss of the other BODIPYs started at 270 °C and ceased after 310 °C. The reaction temperature of inner BCOD moiety of **8** was expected to be around 300 °C while that of another BCOD was around 200 °C. BCOD-fused pyrrole moiety of **8** was converted into isoindole to give **10** in a nearly quantitative yield by heating at 210 °C. When the BODIPYs **6**–**9** were heated as a solid at 290 °C for 2 h under reduced pressure, benzofluoranthene–fused BODIPYs **1**–**4** were formed with change of the color in nearly quantitative yields without purification. The BODIPYs **2**, **4**, and **6**–**10** are stable and fully characterized by physical and spectral methods including the X-ray crystallographic analysis in

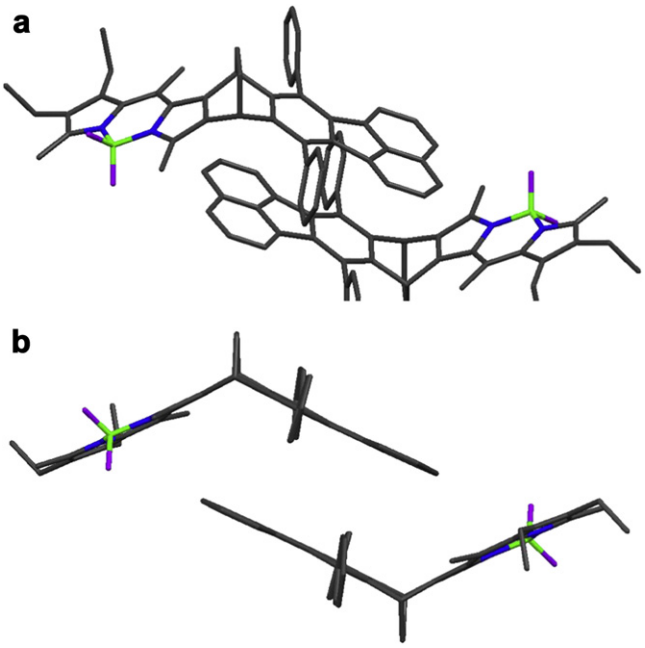



**Figure 2.** (a) Molecular packing and (b) side view of **7**. Hydrogen atoms are omitted for clarity.

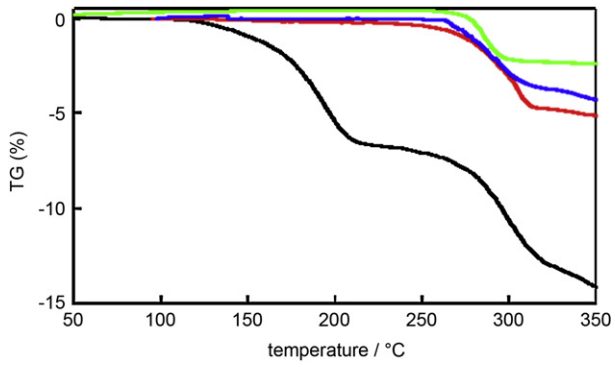



**Figure 3.** TGA of **6a** (red), **7** (blue), **8** (black), and **9** (green line).

the case of **6a** and **7**. However, **1** and **3** are unstable under air in room light to give decomposed products.

In order to identify the decomposed product, a solution of **1b** in $CHCl_3$ was irradiated by using a Xe lamp at 762 nm under air. The color of the solution was changed from red to yellow. In UV–vis absorption of this green-fluorescent solution (Fig. S1 in Supplementary data), three absorptions at 436, 464, and 499 nm appeared and the strong absorption at 761 nm disappeared. The MALDI–TOF MS showed a strong peak at *m*/*z* 986 corresponding to the molecular ion peak of **1b** and small peaks with the difference of ca. 16 at *m*/*z* 1000–1050. These results indicated that **1b** was oxidized under air in room light to give the BODIPY without π-expansion. The photoreaction was performed in $CDCl_3$ in an NMR tube under an $O_2$ atmosphere (Fig. S2 in Supplementary data). During the irradiation of the light of 762 nm, two signals at 5.5 and 6.0 ppm, which were assigned to bridge head protons in a bicyclic ring, were observed. After 4 h, the signals of **1b** disappeared completely. On the other hand, **1b** was stable under an $O_2$ atmosphere in a shaded vessel. Thus, these results suggested that the endoperoxide or further oxidized structure was formed by the photoreaction of benzofluoranthene moieties with $^1O_2$ although the structure of the products was not determined, yet.

The UV–vis absorption spectra of the BODIPYs **1a**, **2**–**4**, **6a**, and **7**–**10** are shown in Figure 4. Preparation of the solutions of **1** and **3** was carried out under a $N_2$ atmosphere in a glove box. Their absorption bands were observed over wide range of visible–near–IR region. The BODIPYs without π-conjugation **6**–**8** showed sharp absorptions around 530 nm similar to those of typical BODIPYs. Absorptions of BODIPYs with acenaphtho[1,2-*c*]pyrrole **9** and isoindole **10** were consistent with the reported values of another acenaphthoBODIPYs.[10c] Benzofluoranthene–fused BODIPYs showed a remarkable bathochromic shift after heating the BCOD-fused precursors. An absorption band of **1a** was observed at 765 nm, which was red-shifted by 230 nm compared to that of the corresponding precursor **6a**. Among the air-stable BODIPYs, **4** showed the most red-shifted absorption with broadening at 658 nm.

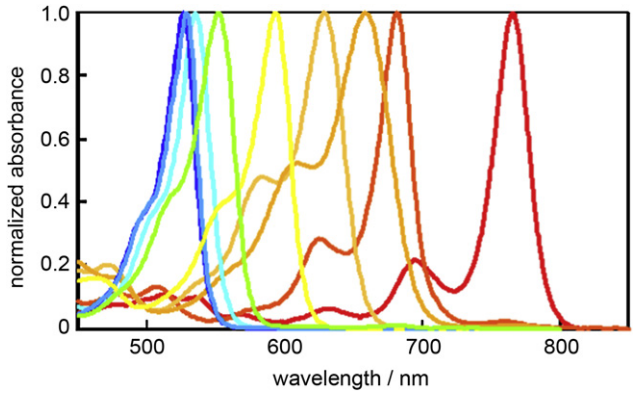



**Figure 4.** Normalized UV–vis absorption spectra of **7**, **8**, **6a**, **10**, **9**, **2**, **4**, **3**, and **1a** (from left to right).

Absorption and fluorescence emission data, absolute fluorescence quantum yields, and fluorescence lifetime ($\tau_f$) are summarized in Table 1, and the fluorescence emission spectra are shown in Figure 5. The fluorescence emission peaks appeared at 547–783 nm. Their fluorescence lifetimes are determined to be 4–5 ns. No difference was observed owing to their π-conjugation structures. BCOD–fused BODIPYs **6**, **7**, **8**, and **10** showed a strong and sharp emission peak at 550–570 nm with high $\Phi_f$ values of 0.8–1.0. The emission peaks of these BODIPYs are observed in a similar region to the parent BODIPYs because they have a similar π-conjugation, a BODIPY core or a BODIPY core fused with a benzene ring. BODIPY **4** showed a bright red fluorescence emission at

**Table 1**
Absorbance, Fluorescence, Absolute Quantum Yields, and Fluorescence Lifetimes of BODIPYs

| | $\lambda_{abs}$/nm[a] (log $\varepsilon$) | $\lambda_{em}$/nm[b] | $\Phi_f$[b] ($\lambda_{ex}$/nm) | $\tau_f$/ns[c,d] |
|---|---|---|---|---|
| **7** | 526 (4.91) | 547 | 0.96 (492) | 5.0 |
| **8** | 529 (4.86) | 546 | 0.83 (495) | 5.0 |
| **6b** | 531 (4.92) | 547 | 0.87 (505) | 4.6 |
| **6a** | 535 (4.92) | 557 | 0.92 (501) | 5.0 |
| **10** | 552 (4.86) | 573 | 1.00 (513) | 4.6 |
| **9** | 593 (4.96) | 613 | 0.76 (552) | 4.7 |
| **2** | 629 (4.89) | 652 | 0.70 (586) | 4.4 |
| **4** | 658 (4.90) | 695 | 0.70 (610) | 3.8 |
| **3** | 681 (4.96) | 697 | 0.36 (627) | —[e] |
| **1b** | 761 (5.22) | 777 | 0.35 (695) | —[e] |
| **1a** | 765 (5.30) | 783 | 0.32 (700) | —[e] |

[a] In $CH_2Cl_2$ at $10^{-6}$ M.
[b] In $CH_2Cl_2$ at $10^{-7}$ M.
[c] In toluene.
[d] Excited at 532 nm.
[e] Fluorescence lifetimes of **1** and **3** could not be measured due to their instability.

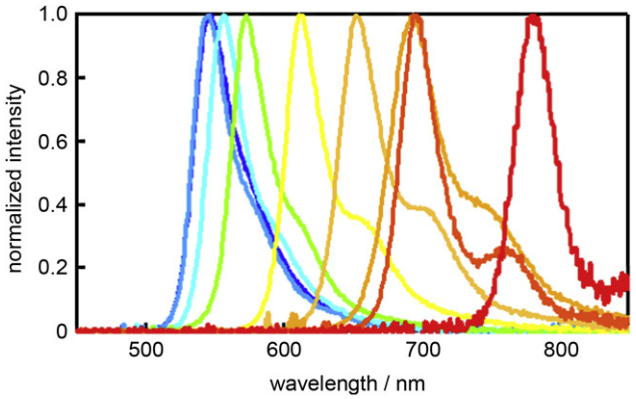



**Figure 5.** Normalized fluorescence emission spectra of **7**, **8**, **6a**, **10**, **9**, **2**, **4**, **3**, and **1a** (from left to right).

695 nm, which was red-shifted by 80 nm compared to the corresponding BCOD-fused precursor **9**. The $\Phi_f$ value (0.70) of **4** is relatively high compared to those of other BODIPYs with the emission in the same region.[22] BODIPYs composed of two fluorantho[8,9-*f*]isoindole moieties **1a** and **1b** showed fluorescence emission at 783 and 777 nm with $\Phi_f$ values of 0.32 and 0.35, respectively, although they were unstable. Their $\Phi_f$ values were similar to the known BODIPYs with over 750-nm emission.[22b–c,23]

## 3. Conclusion

We have synthesized a series of π-expanded BODIPYs fused with aromatic rings at β-positions, such as benzene, acenaphthylene, and benzo[*k*]fluoranthene by the retro Diels–Alder reaction of the corresponding BCOD-fused precursors. These BODIPYs exhibited the absorptions and the fluorescence emissions over wide range of visible–near–IR region at 500–800 nm. It is well known that linearly acene–fused BODIPYs at β-positions are unstable compared to those at α,β-positions. BODIPY **4** is stable and showed a bright fluorescence emission at 695 nm with high $\Phi_f$ value of 0.70. BODIPYs composed of two fluorantho[8,9-*f*]isoindoles **1** absorbed and emitted at red-region over 750 nm with $\Phi_f$ value of ca. 0.3. Therefore, π-expansion with the combination of benzene and acenaphthylene without isoindole moiety has an advantage for the preparation of stable linearly π-expanded BODIPYs with a bright fluorescence emission at near–IR region. These findings would be important for the modification of BODIPY structure.

## 4. Experimental section

### 4.1. General

Melting points were determined on a Yanaco micro melting point apparatus MP500D and are uncorrected. DI–EI and FAB mass spectra were measured on a JEOL JMS-700. MALDI–TOF mass spectra were measured on an Applied Biosystems Voyager de Pro. UV–vis spectra were measured on a JASCO V-570 spectrophotometer. $^1$H NMR spectra were recorded on a JEOL AL-400 at 400 MHz. The fluorescence emission spectra and the $\Phi_f$ values were measured on a Hamamatsu Photonics K.K. absolute PL quantum yield measurement system C9920–03. The fluorescence decay was measured, using a C7990-01 near–infrared fluorescence lifetime measurements system, consisting of a Hamamatsu Photonics K.K. using a 1 ns (FWHM) pulse laser light at 532 nm (45 mW, 14 kHz) from a CrsLas FTSS355–Q YAG laser and a NIR region R5509-43 PMT. Elemental analyses were performed at Integrated Center for Sciences, Ehime University.

### 4.2. Synthesis

*4.2.1. General procedure for the synthesis of **5b**.* To a solution of **5a** (3.0 mmol) in dry THF (70 ml) was added slowly $LiAlH_4$ (15 mmol) at 0 °C under an Ar atmosphere. The resulting mixture was refluxed for 6 h. After slow addition of water at 0 °C, the mixture was filtrated with Celite. The filtrate was extracted with $CHCl_3$. The organic layer was separated, washed successively with water and brine, and dried over $Na_2SO_4$. The solvent was removed under reduced pressure to give **5b** in a nearly quantitative yield. The obtained **5b** was used without further purification: pale yellow powder; mp 189.5–191.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=7.62–7.53 (m, 10H), 7.47 (m, 2H), 7.22 (m, 2H), 6.63 (d, *J*=7.1 Hz, 1H), 6.59 (d, *J*=7.1 Hz, 1H), 6.33 (d, *J*=2.2 Hz, 1H), 4.21 (m, 2H), 2.13 (s, 3H), and 1.75–1.65 (m, 4H).

*4.2.2. Fluorantho[8,9-f]isoindole **5c**.* The general procedure was followed by using **5a** (272 mg, 0.499 mmol), $LiAlH_4$ (97 mg, 2.5 mmol), and dry THF (12.5 ml) to give **5b**. $POCl_3$ (0.06 ml) was added dropwise to *N*,*N*-dimethylacetamide (0.04 ml) at 0 °C under an Ar atmosphere. After the mixture was stirred at the same temperature for 30 min, the resulting solid was dissolved in dry $CH_2Cl_2$ (3 ml). To this solution was added dropwise a solution of **5b** in dry $CH_2Cl_2$ (1.5 ml) at 0 °C. The resulting mixture was refluxed for 1 h under an Ar atmosphere. After addition of aqueous NaOAc (336 mg/0.9 ml) to the reaction mixture at 0 °C, the mixture was refluxed for 30 min. The organic layer was separated; washed successively with aqueous $NaHCO_3$, water, and brine; dried over $Na_2SO_4$; and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to give **5c** (104 mg, 39% from **5a**): yellow crystals; mp >300 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=8.48 (br s, 1H), 7.64–7.56 (m, 10H), 7.44 (m, 2H), 7.24 (m, 2H), 6.65 (d, *J*=7.3 Hz, 1H), 6.63 (d, *J*=7.1 Hz, 1H), 4.61 (m, 1H), 4.22 (m, 1H), 2.15 (s, 3H), 2.14 (s, 3H), and 1.85–1.60 (m, 4H); IR (KBr disk) $\nu_{max}$ 3261, 3056, 2937, 2861, and 1614 cm$^{-1}$; MS (70 eV) *m*/*z* (relative intensity) 527 ($M^+$, 13) and 499 ($M^+-C_2H_4$, 100). Anal. Calcd for $C_{11}H_{17}NO$: C, 88.77; H, 5.54; N, 2.65. Found: C, 88.51; H, 5.73; N, 2.62.

*4.2.2.1. BODIPY **6a**.* The general procedure was followed by using **5a** (925 mg, 1.70 mmol), $LiAlH_4$ (327 mg, 8.62 mmol), and dry THF (41 ml) to give **5b**. To a solution of **5b** in dry $CH_2Cl_2$ (90 ml) were added benzaldehyde (85 μl, 0.84 mmol) and a drop of TFA at room temperature under an Ar atmosphere in a shaded vessel. The resulting mixture was stirred for 2 h. The reaction mixture was treated with a solution of DDQ (188 mg, 0.827 mmol) in dry $CH_2Cl_2$ (18 ml) for 30 min with stirring at room temperature. After addition of $Et_3N$ (2.60 ml) and $BF_3\cdot OEt_2$ (2.60 ml), the mixture was stirred at room temperature for 30 min. The reaction mixture was filtrated with Celite. The filtrate was washed successively with satd aqueous $NaHCO_3$, water, and brine; dried over $Na_2SO_4$; and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and flash column chromatography with 50% $CHCl_3$–hexane followed by recrystallization from $CHCl_3$–MeOH to give **6a** (345 mg, 37%): orange crystals; mp 300 °C (decomp.); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=7.76–7.40 (m, 22H), 7.26–6.85 (m, 11H), 6.61 (m, 2H), 6.23 (m, 2H), 4.17 (m, 2H), 3.25 (m, 2H), 2.44 (s, 6H), and 1.62–1.45 (m, 8H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 374 (4.42) and 535 (4.93); MS (FAB) *m*/*z* 1105 $[M+H]^+$, 1086 $[M+H-F]^+$, 1077 $[M+H-C_2H_4]^+$, and 1049 $[M+H-2C_2H_4]^+$; HRMS calcd for $C_{81}H_{56}N_2BF_2$, 1105.4505; found 1105.4506.

*4.2.2.2. BODIPY **6b**.* The general procedure was followed by using **5a** (813 mg, 1.50 mmol), $LiAlH_4$ (285 mg, 7.51 mmol), and dry THF (37.5 ml) to give **5b**. To a solution of **5b** in dry $CH_2Cl_2$ (40 ml)

were added acetyl chloride (0.24 ml) at room temperature under an Ar atmosphere. The resulting mixture was refluxed for 3 h. After evaporation, the residue was dissolved in toluene (80 ml). The mixture was treated with $Et_3N$ (0.54 ml) for 30 min with stirring at room temperature. After addition of $BF_3\cdot OEt_2$ (0.70 ml), the mixture was stirred at 80 °C for 30 min. The reaction mixture was filtrated with Celite. The filtrate was washed successively with water and brine; dried over $Na_2SO_4$; and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$–MeOH to give **6b** (198 mg, 25%): red crystals; mp 300 °C (decomp.); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=7.74–7.41 (m, 24H), 7.25 (m, 4H), 6.66 (m, 4H), 4.65 (m, 2H), 4.23 (m, 2H), 2.39 (s, 6H), 2.03 (s, 3H), and 1.85–1.54 (m, 8H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 374 (4.41) and 531 (4.92); MS (FAB) *m*/*z* 1043 $[M+H]^+$, 1024 $[M+H-F]^+$, 1015 $[M+H-C_2H_4]^+$, and 987 $[M+H-2C_2H_4]^+$. Anal. Calcd for $C_{76}H_{53}N_2BF_2\cdot H_2O\cdot CHCl_3$: C, 78.35; H, 4.78; N, 2.37. Found: C, 78.06; H, 5.06; N, 2.46.

*4.2.2.3. BODIPY **7**.* The general procedure was followed by using **5a** (820 mg, 1.51 mmol), $LiAlH_4$ (294 mg, 7.74 mmol), and dry THF (38 ml) to give **5b**. To a solution of **5b** and 2-acetyl-3,4-diethyl-5-methylpyrrole (195 mg, 1.09 mmol) in dry $CHCl_3$ (50 ml) was added $POCl_3$ (0.18 ml) under an Ar atmosphere. The resulting mixture was refluxed for 14 h. The mixture was treated with (*i*-Pr)$_2$EtN (0.80 ml) for 1.5 h with stirring at reflux. After addition of $BF_3\cdot OEt_2$ (0.60 ml), the mixture was refluxed for 5 h. The reaction mixture was filtrated with Celite. The filtrate was washed successively with satd aqueous $NaHCO_3$, water, and brine; dried over $Na_2SO_4$; and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and 50% $CHCl_3$–hexane followed by recrystallization from $CHCl_3$–MeOH to give **7** (326 mg, 31%): red crystals; mp 245.0–246.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=7.66–7.55 (m, 10H), 7.45 (m, 2H), 7.25 (m, 2H), 6.68 (d, 1H, *J*=7.1 Hz), 6.61 (d, 1H, *J*=7.1 Hz), 4.71 (m, 1H), 4.24 (m, 1H), 2.70 (q, 2H, *J*=7.5 Hz), 2.48 (s, 3H), 2.40 (s, 3H), 2.37 (m, 2H), 2.35 (s, 3H), 1.84–1.60 (m, 4H), 1.16 (t, 3H, *J*=7.5 Hz), and 1.05 (t, 3H, *J*=7.5 Hz); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 374 (4.22) and 526 (4.91); MS (FAB) *m*/*z* 694 $M^+$, 675 $[M-F]^+$, and 666 $[M-C_2H_4]^+$. Anal. Calcd for $C_{48}H_{41}N_2BF_2\cdot H_2O$: C, 80.89; H, 6.08; N, 3.93. Found: C, 80.72; H, 5.98; N, 4.02.

*4.2.2.4. BODIPY **8**.* The general procedure was followed by using **5a** (202 mg, 0.371 mmol), $LiAlH_4$ (77 mg, 2.0 mmol), and dry THF (20 ml) to give **5b**. To a solution of **5b** and 1-acetyl-4,7-ethano-3-methyl-4,7-dihydro-2*H*-isoindole (78 mg, 0.39 mmol) in dry $CHCl_3$ (25 ml) was added $POCl_3$ (0.05 ml) at room temperature under an Ar atmosphere. The resulting mixture was refluxed for 12 h. The mixture was treated with (*i*-Pr)$_2$EtN (0.30 ml) for 2 h with stirring at reflux. After addition of $BF_3\cdot OEt_2$ (0.25 ml), the mixture was refluxed for 6 h. The reaction mixture was filtrated with Celite. The filtrate was washed successively with water and brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to give **8** (95 mg, 36%). red crystals: mp 200 °C (decomp.); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=7.67–7.55 (m, 10H), 7.48–7.43 (m, 2H), 7.27–7.22 (m, 2H), 6.68 (d, 1H, *J*=7.6 Hz), 6.63 (d, 1H, *J*=7.6 Hz), 6.52–6.36 (m, 2H), 4.69 (m, 1H), 4.32 (m, 1H), 4.23 (m, 1H), 3.86 (m, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.38 (m, 3H), and 1.83–1.36 (m, 8H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 374 (4.23) and 529 (4.86); MS (FAB) *m*/*z* 716 $M^+$, 697 $[M-F]^+$, 688 $[M-C_2H_4]^+$, and 660 $[M-2C_2H_4]^+$; HRMS calcd for $C_{50}H_{40}N_2BF_2$, 717.3253; found 717.3254. Anal. Calcd for $C_{50}H_{39}N_2BF_2\cdot 2H_2O$: C, 79.78; H, 5.76; N, 3.72. Found: C, 79.95; H, 5.38; N, 3.67.

*4.2.2.5. BODIPY **9**.* To a solution of **5c** (277 mg, 0.526 mmol) and 7-methyl-8*H*-acenaphtho[1,2-*c*]pyrrole (104 mg, 0.506 mmol) in dry $CHCl_3$ (25 ml) was added $POCl_3$ (0.05 ml) at room temperature under an Ar atmosphere. The resulting mixture was refluxed for 13 h. The mixture was treated with (*i*-Pr)$_2$EtN (0.38 ml) for 2 h with stirring at reflux. After addition of $BF_3\cdot OEt_2$ (0.30 ml), the mixture was refluxed for 6 h. The reaction mixture was filtrated with Celite. The filtrate was washed successively with satd aqueous $NaHCO_3$, water, and brine; dried over $Na_2SO_4$; and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and flash column chromatography with 50% $CHCl_3$–hexane and 10% EtOAc–hexane to give **9** (21 mg, 5%): dark blue crystals; mp 300 °C (decomp.); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=7.86 (m, 2H), 7.747–7.54 (m, 14H), 7.48 (m, 2H), 7.26 (m, 2H), 6.69 (d, 1H, *J*=7.1 Hz), 6.64 (d, 1H, *J*=7.1 Hz), 4.83 (m, 1H), 4.31 (m, 1H), 2.86 (s, 3H), 2.67 (s, 3H), 2.51 (s, 3H), and 19.1–1.63 (m, 4H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 594 (4.96); MS (FAB) *m*/*z* 762 $M^+$, 743 $[M-F]^+$, and 734 $[M-C_2H_4]^+$; HRMS (FAB) calcd for $C_{54}H_{38}N_2BF_2$, 763.3096; found 763.3093.

*4.2.3. Retro Diels–Alder reaction of BCOD–fused BODIPYs.* BODIPYs **6**–**9** (ca. 10 mg each) were heated at 210 °C (for **10**) or 290 °C (for **1**–**4**) under reduced pressure for 2 h in a glass tube to give BODIPYs **1**–**4** and **10** in quantitative yields.

*4.2.3.1. BODIPY **10**.* Purple crystals; mp 300 °C (decomp.); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=7.90 (d, *J*=8.3 Hz, 1H), 7.73 (d, *J*=7.8 Hz, 1H), 7.69–7.56 (m, 10H), 7.49 (m, 3H), 7.32–7.22 (m, 3H), 6.68 (d, 1H, *J*=7.1 Hz), 6.62 (d, 1H, *J*=7.1 Hz), 4.75 (m, 1H), 4.25 (m, 1H), 2.90 (s, 3H), 2.54 (s, 3H), 2.42 (s, 3H), and 1.86–1.66 (m, 4H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 355 (4.14), 373 (4.14), and 552 (4.84); MS (FAB) *m*/*z* 688 $M^+$, 669 $[M-F]^+$, and 660 $[M-C_2H_4]^+$. Anal. Calcd for $C_{48}H_{35}N_2BF_2\cdot 3-2H_2O$: C, 80.56; H, 5.35; N, 3.91. Found: C, 80.69; H, 5.26; N, 3.97.

*4.2.3.2. BODIPY **1a**.* Dark purple crystals; mp >300 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=7.90 (s, 2H), 7.78–7.51 (m, 25H), 7.29–7.14 (m, 6H), 6.90 (m, 2H), 6.58 (s, 2H), 6.48 (d, 2H, *J*=7.1 Hz), 6.18 (d, 2H, *J*=7.3 Hz), and 2.92 (s, 6H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 765 (5.31); MS (FAB) *m*/*z* 1065 $[M+H+16]^+$, 1049 $[M+H]^+$, and 1030 $[M+H-F]^+$; HRMS calcd for $C_{77}H_{48}N_2BF_2$, 1049.3879; found 1049.3878.

*4.2.3.3. BODIPY **1b**.* Dark purple crystals; mp >300 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=8.14 (s, 2H), 7.97 (s, 2H), 7.76–7.24 (m, 28H), 6.62 (d, 2H, *J*=7.1 Hz), 6.56 (d, 2H, *J*=7.1 Hz), 2.88 (s, 6H), and 2.53 (s, 3H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 761 (5.22); MS (FAB) *m*/*z* 987 $[M+H]^+$; HRMS calcd for $C_{72}H_{46}N_2BF_2$, 987.3722; found 987.3721.

*4.2.3.4. BODIPY **2**.* Green crystals; mp 259.7–261.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=8.15 (s, 1H), 8.04 (s, 1H), 7.75–7.66 (m, 8H), 7.62–7.58 (m, 4H), 7.36–7.31 (m, 2H), 6.63 (d, 1H, *J*=6.8 Hz), 6.60 (d, 1H, *J*=6.8 Hz), 2.90 (s, 3H), 2.73 (q, 2H, *J*=7.6 Hz), 2.57 (s, 3H), 2.46 (s, 3H), 2.38 (q, 2H, *J*=7.6 Hz), 1.20 (t, 3H, *J*=7.6 Hz), and 1.08 (t, 3H, *J*=7.6 Hz); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 325 (4.58), 584 (4.57), and 629 (4.89); MS (FAB) *m*/*z* 666 $M^+$. Anal. Calcd for $C_{46}H_{37}N_2BF_2$: C, 82.88; H, 5.59; N, 4.20. Found: C, 82.65; H, 5.69; N, 4.24.

*4.2.3.5. BODIPY **3**.* Green crystals; mp >300 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=8.21 (s, 1H), 8.02 (s, 1H), 7.91 (d, 1H, *J*=8.1 Hz), 7.76–7.14 (m, 17H), 6.64 (d, 1H, *J*=6.8 Hz), 6.58 (d, 1H, *J*=7.1 Hz), 2.92 (s, 3H), 2.88 (s, 3H), and 2.80 (s, 3H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 681 (4.96); MS (FAB) *m*/*z* 660 $M^+$; HRMS calcd for $C_{46}H_{32}N_2BF_2$, 661.2627; found 661.2629.

*4.2.3.6. BODIPY **4**.* Green crystals; mp >300 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=8.28 (s, 1H), 8.10 (s, 1H), 7.87–7.25 (m, 20H), 6.68 (d, 1H, *J*=7.3 Hz), 6.64 (d, 1H, *J*=7.3 Hz), 2.96 (s, 3H), 2.87 (s, 3H), and 2.82 (s, 3H); UV–vis ($CH_2Cl_2$) $\lambda_{max}$, nm (log $\varepsilon$) 610 (4.62) and 658

(4.90); MS (MALDI–TOF) $m/z$ 734 $M^+$ and 715 $[M-F]^+$; HRMS calcd for $C_{52}H_{34}N_2BF_2$, 735.2783; found 735.2784.

## Acknowledgements

The authors thank Venture Business Laboratory, Ehime University, for assistance in obtaining the MALDI–TOF mass spectra. We used ethyl isocyanoacetate for the preparation of the pyrroles by Barton–Zard reaction from the Nippon Synthetic Chem. Ind. (Osaka Japan). This work was partially supported by Grants-in-Aid for the Scientific Researches on Innovative Areas (No 21108517, π-Space to H. U.) and C (No 20550047 to H.U.) from the Japanese Ministry of Education, Culture, Sports, Science and Technology and PRESTO (Photon on soft materials to H.Y.) from Japan Science and Technology Agency.

## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.06.045. These data include MOL files and InChIKeys of the most important compounds described in this article.

## References and notes

1. Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184–1201.
2. Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891–4932.
3. Qi, X.; Jun, E. J.; Xu, L.; Kim, S.-J.; Hong, J. S. J.; Yoon, Y. J.; Yoon, J. *J. Org. Chem.* **2006**, *71*, 2881–2884.
4. Hepp, A.; Ulrich, G.; Schmechel, R.; von Seggern, H.; Ziessel, R. *Synth. Met.* **2004**, *146*, 11–15.
5. (a) Kumaresan, D.; Thummel, R. P.; Bura, T.; Ulrich, G.; Ziessel, R. *Chem.—Eur. J.* **2009**, *15*, 6335–6339; (b) Rousseau, T.; Cravino, A.; Bura, T.; Ulrich, G.; Ziessel, R.; Roncali, J. *Chem. Commun.* **2009**, 1673–1675; (c) Erten-Ela, S.; Yilmaz, M. D.; Icli, B.; Dede, Y.; Icli, S.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 3299–3302; (d) Hattori, S.; Ohkubo, K.; Urano, Y.; Sunahara, H.; Nagano, T.; Wada, Y.; Tkachenko, N. V.; Lemmetyinen, H.; Fukuzumi, S. *J. Phys. Chem. B* **2005**, *109*, 15368–15375.
6. (a) Chen, J.; Mizumura, M.; Shinokubo, H.; Osuka, A. *Chem.—Eur. J.* **2009**, *15*, 5942–5949; (b) Rurack, K.; Kollmannsberger, M.; Daub, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 385–387.
7. (a) Wakamiya, A.; Sugita, N.; Yamaguchi, S. *Chem. Lett.* **2008**, *37*, 1094–1095; (b) Burghart, A.; Kim, H.; Welch, M. B.; Thoresen, L. H.; Reibenspies, J.; Burgess, K.; Bergström, F.; Johansson, L. B. -Å *J. Org. Chem.* **1999**, *64*, 7813–7819.
8. (a) Umezawa, K.; Nakamura, Y.; Makino, H.; Citterio, D.; Suzuki, K. *J. Am. Chem. Soc.* **2008**, *130*, 1550–1551; (b) Umezawa, K.; Matsui, A.; Nakamura, Y.; Citterio, D.; Suzuki, K. *Chem.—Eur. J.* **2009**, *15*, 1096–1106.
9. Chen, J.; Burghart, A.; Derecskei-Kovacs, A.; Burgess, K. *J. Org. Chem.* **2000**, *65*, 2900–2906.
10. (a) Descalzo, A. B.; Xu, H.-J.; Xue, Z.-L.; Hoffmann, K.; Shen, Z.; Weller, M. G.; You, X.-Z.; Rurack, K. *Org. Lett.* **2008**, *10*, 1581–1584; (b) Shen, Z.; Röhr, H.; Rurack, K.; Uno, H.; Spieles, M.; Schulz, B.; Reck, G.; Ono, N. *Chem.—Eur. J.* **2004**, *10*, 4853–4871; (c) Ono, N.; Yamamoto, T.; Shimada, N.; Kuroki, K.; Wada, M.; Utsunomiya, R.; Yano, T.; Uno, H.; Murashima, T. *Heterocycles* **2003**, *61*, 433–447; (d) Wada, M.; Ito, S.; Uno, H.; Murashima, T.; Ono, N.; Urano, T.; Urano, Y. *Tetrahedron Lett.* **2001**, *42*, 6711–6713.
11. (a) Harriman, A.; Mallon, L. J.; Goeb, S.; Ulrich, G.; Ziessel, R. *Chem.—Eur. J.* **2009**, *15*, 4553–4564; (b) Goeb, S.; Ziessel, R. *Org. Lett.* **2007**, *9*, 737–740.
12. (a) Buyukcakir, O.; Bozdemir, O. A.; Kolemen, S.; Erbas, S.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 4644–4647; (b) Atilgan, S.; Ozdemir, T.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 4065–4067.
13. Nakamura, J.; Okujima, T.; Tomimori, Y.; Komobuchi, N.; Yamada, H.; Uno, H.; Ono, N. *Heterocycles* **2010**, *80*, 1165–1175.
14. (a) Yamada, H.; Kuzuhara, D.; Takahashi, T.; Shimizu, Y.; Uota, K.; Okujima, T.; Uno, H.; Ono, N. *Org. Lett.* **2008**, *10*, 2947–2950; (b) Kobayashi, N.; Konami, H. *J. Porphyrins Phthalocyanines* **2001**, *5*, 233–255; (c) Mack, J.; Asano, Y.; Kobayashi, N.; Stillman, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 17697–17711.
15. Okujima, T.; Komobuchi, N.; Uno, H.; Ono, N. *Heterocycles* **2006**, *67*, 255–267.
16. Tang, J.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 7793–7802.
17. (a) Ono, N.; Hironaga, H.; Shimizu, K.; Ono, K.; Kuwano, K.; Ogawa, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1019–1020; (b) Lash, T. D.; Novak, B. H.; Lin, Y. *Tetrahedron Lett.* **1994**, *35*, 2493–2494.
18. The diffraction data were processed with Crystal Clear, solved with SIR-97[19] or DIRDIF-99,[20] and refined with SHELXL-97.[21] The data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
19. A Package for Crystal Structure Solution and Refinement, Istituto di Gristallografia, Italy Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
20. Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M. *Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 2008.
21. Scheldrick, G.; Schneider, T. *SHELXL-97, Program for Refinement of Crystal Structures from Diffraction Data*. Methods Enzymol.; University of Göttingen: Göttingen (Germany), 1997; 277; 319–343.
22. (a) Killoran, J.; O'Shea, D. F. *Chem. Commun.* **2006**, 1503–1505; (b) Dost, Z.; Atilgan, S.; Akkaya, E. U. *Tetrahedron* **2006**, *62*, 8484–8488; (c) Ulrich, G.; Goeb, S.; De Nicola, A.; Retailleau, P.; Ziessel, R. *Synlett* **2007**, 1517–1520.
23. (a) Zhao, W.; Carreira, E. M. *Chem.—Eur. J.* **2006**, *12*, 7254–7263; (b) Yu, Y.-H.; Descalzo, A. B.; Shen, Z.; Röhr, H.; Liu, Q.; Wang, Y.-W.; Spieles, M.; Li, Y.-Z.; Rurack, K.; You, X.-Z. *Chem.—Asian. J.* **2006**, *1*, 176–187.