An Efficient and Convenient Bromination of BODIPY Derivatives with Copper(II) Bromide

Jia-Hai Ye,*[a] Guangpu Wang,[a] Chengmei Huang,[b] Zhengjuan Hu,[a] Whenchao Zhang,[a] Yan Zhang*[b]

[a] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. of China
Fax +86(25)84315857; E-mail: yejiahai@mail.njust.edu.cn

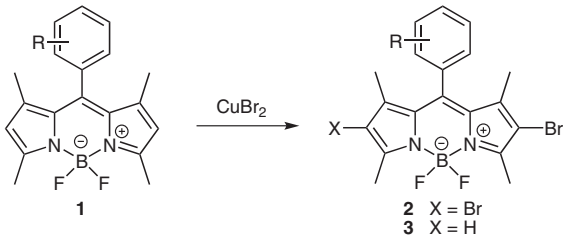
[b] School of Chemistry and Chemical Engineering, Key Laboratory of Analytical Chemistry for Life Science, Ministry of Education of China, Nanjing University, Nanjing 210093, P. R. of China

Received 19 September 2011; revised 8 November 2011

Abstract: Efficient and convenient methods for the mono- and dibromination of 1,3,5,7-tetramethyl-substituted BODIPYs were developed by using copper(II) bromide as the bromination reagent under mild reactions, in good to excellent yields. The selectivity of mono- or dibromination depends strongly on the additives of the reactions.

Key words: copper, bromination, selectivity, fluorescent dyes, 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes have received much interest in research areas, such as labeling reagents,[1] fluorescent switches,[2] chemosensors,[3] near-IR absorbing/emitting dyes, nonlinear optical materials, mesogenic materials,[4] supramolecular polymers,[5] light-harvesting systems,[6] photodynamic therapy,[7] molecular logic systems,[3e,8] and dye-sensitized solar cells,[9] owing to their many intriguing optical and chemical properties such as photostability, high absorption coefficients, long wavelength emission, relative insensitivity to environment, and high fluorescence quantum yields (typically 0.6–1.0).[4,10] In addition, functionalization of BODIPY dyes allows manipulation of the spectroscopic and electronic properties by introduction of suitable substituents to the BODIPY peripherals. Among synthetic precursors for functionalized BODIPYs, brominated BODIPYs are one of the most useful building blocks on the basis of a transition-metal-catalyzed cross-coupling strategy for the construction of extended π-electron conjugation affording red-shifted BODIPY derivatives[11] and can act as photodynamic therapy reagents.[7a] To the best of our knowledge, bromine, *N*-bromosuccinimide (NBS), and the NBS–AIBN [2,2′-azobis(isobutyronitrile)] system have been utilized for the bromination of BODIPYs;[7a,11,12] however, these methods suffer from some drawbacks and limitations: the use of expensive, toxic, or corrosive bromination reagents, high reaction temperature, and difficult handling of the reaction procedure. It is well known that copper(II) bromide can serve as an effective alternative of NBS and bromine for α-bromination of carbonyl compounds and bromination of alkenes, alkynes, aromatic systems, and heterocyclic compounds, including thiazoles, pyrroles, and indoles.[13] Herein, we wish to disclose an efficient and convenient mono- and dibromination of 1,3,5,7-tetramethyl-substituted BODIPYs at the 2- or 2,6-positions, which was carried out with copper(II) bromide as the inexpensive bromide source (Scheme 1).



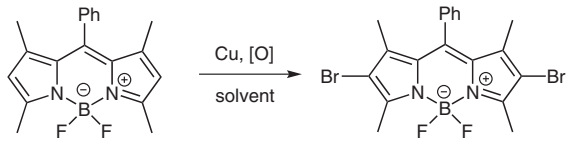
Scheme 1

First, we started our studies with the reaction of the 1,3,5,7-tetramethyl-BODIPY **1a** in the presence of copper salts to establish the reaction conditions for dibromination at the 2,6-positions (Table 1). Initially, the reaction of **1a** with copper(I) bromide (2.5 equiv) was conducted in toluene at 100 °C under air or oxygen atmosphere for more than 20 hours; unfortunately, the bromination barely occurred (Table 1, entries 1 and 2). Subsequently, the reaction of **1a** with copper(I) bromide (0.1 equiv) or copper(II) bromide (0.1 equiv) as the catalyst in the presence of potassium bromide as the bromide source was carried out (Table 1, entries 3 and 4). Similarly, no obvious amount of product **2a** was observed.

Thinking about the fact that copper(II) bromide is an efficient bromination reagent for many heterocyclic compounds,[13] we attempted to perform the bromination of **1a** with 2.5 equivalents of copper(II) bromide in different solvents at room temperature (Table 1, entries 5–9 and 12). To our delight, an excellent yield (94%) of dibromination product **2a** was obtained when the reaction mixture of **1a** with copper(II) bromide (2.5 equiv) was stirred in acetonitrile at room temperature in the presence of oxygen (1 atm, balloon). The amount of copper(II) bromide and the reaction atmosphere can also slightly affect the yield of the dibromination product **2a** (Table 1, entries 10 and 11). Based on the above research results, the optimized reaction conditions were obtained: reaction of **1a** with 2.5 equivalents of copper(II) bromide in acetonitrile carried out at room temperature in the presence of oxygen (bal-

SYNTHESIS 2012, 44, 104–110
Advanced online publication: 05.12.2011
DOI: 10.1055/s-0031-1289637; Art ID: H90011SS

Table 1 Optimization of the Reaction Conditions for Dibromination of **1a**[a]



1a **2a**

Entry	Metal salt	Solvent	[O]	Temp (°C)	Yield[a,b] (%)
1	CuBr (2.5 equiv)	toluene	air	100	n.r.
2	CuBr (2.5 equiv)	toluene	O_2	100	trace
3	CuBr (0.1 equiv), KBr (2.0 equiv)	toluene	air	100	n.r.
4	$CuBr_2$ (0.1 equiv), KBr (2.0 equiv)	toluene	O_2	100	trace
5	$CuBr_2$ (2.5 equiv)	DMF	O_2	r.t.	n.r.
6	$CuBr_2$ (2.5 equiv)	DMSO	O_2	r.t.	n.r.
7	$CuBr_2$ (2.5 equiv)	THF	O_2	r.t.	65
8	$CuBr_2$ (2.5 equiv)	toluene	O_2	r.t.	58
9	$CuBr_2$ (2.5 equiv)	xylene	O_2	r.t.	60
10	$CuBr_2$ (2.5 equiv)	MeCN	air	r.t.	91[c]
11	$CuBr_2$ (2.2 equiv)	MeCN	O_2	r.t.	86
12	**$CuBr_2$ (2.5 equiv)**	**MeCN**	**O_2**	**r.t.**	**94**

[a] Reaction time = 12 h unless otherwise specified.
[b] Isolated yield; n.r. = no reaction.
[c] Reaction time = 24 h.

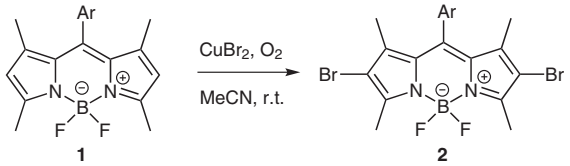
loon) for 12 hours gave 94% isolated yield of **2a**. The bromination efficiency of BODIPYs depends on parameters such as the reactants for the source of bromide, and the solvent.

With the optimized reaction results in hand, the scope of dibromination of BODIPYs was examined by using copper(II) bromide as the bromination reagent with a series of *meso*-aryl-1,3,5,7-tetramethyl-BODIPYs under the optimized reaction conditions; the full results are summarized in Table 2. All reactions proceeded smoothly to produce the products **2** in good to excellent yields. The results were not dependent on the nature of the substituent on the *meso*-aryl of the BODIPYs, but were dependent on the position of the aromatic substituent when the substituent was an electron-withdrawing group (see Table 2, entries 3–6, 8, 9, and 11).

Encouraged by the above results, we then investigated the monobromination of 1,3,5,7-tetramethyl-BODIPYs. Initially, the reaction of BODIPY **1a** with only one equivalent of copper(II) bromide was carried out under oxygen atmosphere in acetonitrile at room temperature. Surprisingly, the dibromination product **2a** was also observed together with the target monobromination product **3a** in 56% total yield (**2a**/**3a** = 39:61). This result may be attributed to hydrogen bromide (HBr) which is evolved from the reaction process and promotes the production of the dibromination product.[14] In an attempt to overcome this problem, we considered the possibility of addition of base. We rationalized that the employment of base, including inorganic and organic bases, could potentially help in neutralizing hydrogen bromide and thus promote the yield of the target products as well as inhibit the production of the dibromination products. The effects of various bases (such as K_3PO_4, K_2CO_3, KOAc, Na_2CO_3, Et_3N, and pyridine) were studied for this conversion. Of these bases, potassium carbonate was found to be effective in terms of the best conversion. The scope of the monobromination was explored using reaction conditions similar to the dibrominations as above, in the presence of 3.0 equivalents of potassium carbonate and 1.5 equivalents of copper(II) bromide under an oxygen atmosphere. Generally, the reaction proceeded in good yield for both electron-rich and electron-deficient aromatic groups at the *meso*-position of the BODIPYs. The scope and generality of this process is illustrated with respect to various *meso*-aryl-1,3,5,7-tetramethyl-BODIPYs; the results are presented in Table 3. In all cases, the di- and monobromination products **2** and **3** were characterized by ^1H NMR, ^{13}C NMR, and mass spectroscopy.

In summary, copper(II) bromide has proved to be a useful and highly efficient reagent for the bromination of

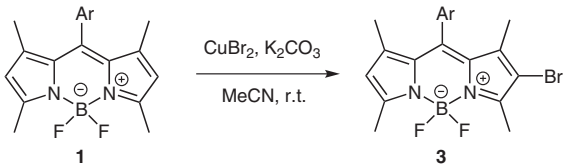
Table 2 Dibromination of BODIPYs **1** with Copper(II) Bromide



Entry	Ar	Product **2**	Yield[a] (%)
1	Ph	**2a**	94
2	4-Tol	**2b**	92
3	4-$MeOC_6H_4$	**2c**	86
4	3,4-$(MeO)_2C_6H_3$	**2d**	96
5	4-ClC_6H_4	**2e**	83
6	2-ClC_6H_4	**2f**	84
7	4-$(HC{\equiv}CCH_2O)C_6H_4$	**2g**	86
8	4-$O_2NC_6H_4$	**2h**	95
9	4-$F_3CC_6H_4$	**2i**	94
10	4-NCC_6H_4	**2j**	91
11	3-$F_3CC_6H_4$	**2k**	82
12	1-Naph	**2l**	89

[a] Isolated yield.

Table 3 Monobromination of BODIPYs **1** with Copper(II) Bromide



Entry	Ar	Product **3**	Yield[a] (%)
1	Ph	**3a**	81
2	4-Tol	**3b**	75
3	4-$MeOC_6H_4$	**3c**	76
4	3,4-$(MeO)_2C_6H_3$	**3d**	80
5	4-ClC_6H_4	**3e**	86
6	2-ClC_6H_4	**3f**	84
7	4-$(HC{\equiv}CCH_2O)C_6H_4$	**3g**	80
8	4-$O_2NC_6H_4$	**3h**	78
9	4-$F_3CC_6H_4$	**3i**	81
10	4-NCC_6H_4	**3j**	79
11	3-$F_3CC_6H_4$	**3k**	74
12	1-Naph	**3l**	87

[a] Isolated yield.

BODIPYs at their 2-/2,6-positions, in combination with different additives, under mild conditions. In addition to its simplicity and efficiency, this method selectively produces mono- or dibrominated BODIPYs in good to excellent yields. This method provides an easy access to a wide range of potentially valuable *meso*-aryl-1,3,5,7-tetramethyl-BODIPYs. The use of readily available and inexpensive copper(II) bromide makes this method simple, convenient, cost-effective, and practical.

All chemicals were obtained from commercial suppliers and used without further purification except for CH_2Cl_2 which was distilled from P_2O_5 and MeCN which was distilled from CaH_2. Column chromatography was carried out over silica gel (BDH 200–300 mesh) and TLC was performed using silica gel GF_{254} (Merck) plates. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Avance III 500-MHz spectrometer. Mass spectra (EI and ESI) were measured with Jeol JMS-DX300 and Thermo Fisher LCQ instruments. Elemental analyses were obtained using a Perkin-Elmer 240C analyzer. Melting points were measured with a Shanghai WRS-1B digital melting-point apparatus and are uncorrected. The substrates **1** were prepared according to the literature.[3a]

Dibromides 2a–l; General Procedure

A mixture of the 1,3,5,7-tetramethyl-BODIPY **1** (0.2 mmol) and $CuBr_2$ (0.5 mmol) in anhyd MeCN (20 mL) was stirred under O_2 atmosphere (balloon) at r.t. for 12 h. The residue obtained after the removal of the solvent by rotary evaporation was extracted with EtOAc (3 × 40 mL), and the extracts were washed with H_2O (3 × 30 mL), dried (anhyd Na_2SO_4), and concentrated under reduced pressure. The crude product was further purified using column chromatography (EtOAc–petroleum ether) to afford the dibromide **2**.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (2a)[12]

Yield: 90.6 mg (94%); red solid; mp 229–231 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 6 H, CH_3), 2.63 (s, 6 H, CH_3), 7.26–7.28 (m, 2 H, ArH), 7.54–7.55 (m, 3 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.9, 141.0, 139.6, 133.3, 129.3, 128.5, 128.4, 126.7, 110.7, 12.6.

EI-MS: *m*/*z* = 482 $[M]^+$.

Anal. Calcd for $C_{19}H_{17}BBr_2F_2N_2$: C, 47.35; H, 3.56; N, 5.81. Found: C, 47.39; H, 3.64; N, 5.76.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-*s*-indacene (2b)

Yield: 91.3 mg (92%); red solid; mp 191–193 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.41 (s, 6 H, CH_3), 2.48 (s, 3 H, CH_3), 2.62 (s, 6 H, CH_3), 7.14 (d, *J* = 7.95 Hz, 2 H, ArH), 7.34 (d, *J* = 7.8 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7, 142.6, 140.7, 139.6, 131.3, 130.5, 130.1, 127.6, 111.6, 21.5, 13.8, 13.7.

EI-MS: *m*/*z* = 496 $[M]^+$.

Anal. Calcd for $C_{20}H_{19}BBr_2F_2N_2$: C, 48.43; H, 3.86; N, 5.65. Found: C, 48.39; H, 3.90; N, 5.63.

2,6-Dibromo-4,4-difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2c)

Yield: 88.1 mg (86%); red solid; mp 236–238 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.47 (s, 6 H, CH_3), 2.62 (s, 6 H, CH_3), 3.91 (s, 3 H, OCH_3), 7.06 (d, *J* = 8.65 Hz, 2 H, ArH), 7.16 (d, *J* = 8.65 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.6, 153.7, 142.3, 140.6, 130.9, 130.8, 129.1, 128.8, 126.3, 114.8, 111.7, 55.4, 13.9, 13.7.

EI-MS: *m*/*z* = 512 $[M]^+$.

Anal. Calcd for $C_{20}H_{19}BBr_2F_2N_2O$: C, 46.96; H, 3.74; N, 5.47. Found: C, 47.02; H, 3.72; N, 5.50.

2,6-Dibromo-8-(3,4-dimethoxyphenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2d)
Yield: 104.1 mg (96%); red solid; mp 230–232 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.49 (s, 6 H, CH_3), 2.62 (s, 6 H, CH_3), 3.88 (s, 3 H, OCH_3), 3.98 (s, 3 H, OCH_3), 6.76 (d, *J* = 1.85 Hz, 1 H, ArH), 6.82 (dd, *J* = 1.9, 8.15 Hz, 1 H, ArH), 7.01 (d, *J* = 8.15 Hz, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7, 150.1, 142.0, 140.6, 130.7, 126.4, 120.3, 111.7, 110.8, 56.1, 56.0, 13.8, 13.7.

ESI-MS: *m*/*z* = 541 $[M - H]^+$.

Anal. Calcd for $C_{21}H_{21}BBr_2F_2N_2O_2$: C, 46.53; H, 3.91; N, 5.17. Found: C, 46.49; H, 3.89; N, 5.23.

2,6-Dibromo-8-(4-chlorophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2e)
Yield: 85.7 mg (83%); red solid; mp 212–214 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43 (s, 6 H, CH_3), 2.63 (s, 6 H, CH_3), 7.24 (d, *J* = 8.35 Hz, 2 H, ArH), 7.55 (d, *J* = 8.35 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 140.4, 140.3, 135.9, 132.8, 130.3, 129.9, 124.4, 120.1, 120.0, 13.9, 13.7.

ESI-MS: *m*/*z* = 517 $[M + H]^+$.

Anal. Calcd for $C_{19}H_{16}BBr_2ClF_2N_2$: C, 44.19; H, 3.12; N, 5.42. Found: C, 44.22; H, 3.09; N, 5.41.

2,6-Dibromo-8-(2-chlorophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2f)
Yield: 86.7 mg (84%); red solid; mp >300 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 7.29 (d, *J* = 5.0 Hz, 1 H, ArH), 7.46 (t, *J* = 7.4 Hz, 1 H, ArH), 7.50 (t, *J* = 7.4 Hz, 1 H, ArH), 7.57 (d, *J* = 7.9 Hz, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.5, 140.0, 138.2, 133.4, 132.9, 131.1, 130.8, 130.0, 129.9, 129.7, 128.8, 127.9, 111.8, 13.8, 12.9.

ESI-MS: *m*/*z* = 515 $[M - H]^+$.

Anal. Calcd for $C_{19}H_{16}BBr_2ClF_2N_2$: C, 44.19; H, 3.12; N, 5.42. Found: C, 44.20; H, 3.16; N, 5.37.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-[4-(prop-2-ynyloxy)phenyl]-4-bora-3a,4a-diaza-*s*-indacene (2g)
Yield: 92.2 mg (86%); red solid; mp 221–223 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44 (s, 6 H, CH_3), 2.59 (t, *J* = 2.4 Hz, 1 H, CH), 2.62 (s, 6 H, CH_3), 4.79 (d, *J* = 2.35 Hz, 2 H, CH_2), 7.13 (d, *J* = 8.65 Hz, 2 H, ArH), 7.18 (d, *J* = 8.65 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.5, 153.9, 141.9, 140.6, 130.7, 129.1, 127.3, 116.0, 111.7, 77.8, 76.1, 56.1, 13.9, 13.7.

ESI-MS: *m*/*z* = 537 $[M + H]^+$.

Anal. Calcd for $C_{22}H_{19}BBr_2F_2N_2O$: C, 49.30; H, 3.57; N, 5.23. Found: C, 49.32; H, 3.54; N, 5.28.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-nitrophenyl)-4-bora-3a,4a-diaza-*s*-indacene (2h)
Yield: 100.1 mg (95%); red solid; mp >300 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 7.55 (d, *J* = 8.6 Hz, 2 H, ArH), 8.44 (d, *J* = 8.65 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.3, 148.7, 141.2, 140.0, 138.6, 129.6, 124.6, 112.5, 14.0, 13.8.

ESI-MS: *m*/*z* = 527 $[M]^+$.

Anal. Calcd for $C_{19}H_{16}BBr_2F_2N_3O_2$: C, 43.31; H, 3.06; N, 7.97. Found: C, 43.27; H, 3.12; N, 7.95.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-[4-(trifluoromethyl)phenyl]-4-bora-3a,4a-diaza-*s*-indacene (2i)
Yield: 103.4 mg (94%); red solid; mp 227–229 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 7.47 (d, *J* = 8.0 Hz, 2 H, ArH), 7.84 (d, *J* = 8.0 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.8, 140.2, 139.8, 138.2, 132.0 (q, $^2J_{C-F}$ = 32.9 Hz), 131.9, 130.0, 128.7, 126.4, 123.7 (q, $^1J_{C-F}$ = 270.0 Hz, CF_3), 112.2, 13.8, 13.7.

ESI-MS: *m*/*z* = 551 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{16}BBr_2F_5N_2$: C, 43.68; H, 2.93; N, 5.09. Found: C, 43.70; H, 3.01; N, 5.05.

2,6-Dibromo-8-(4-cyanophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2j)
Yield: 92.3 mg (91%); red solid; mp >300 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 6 H, CH_3), 2.63 (s, 6 H, CH_3), 7.47 (d, *J* = 8.3 Hz, 2 H, ArH), 7.87 (d, *J* = 8.3 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.1, 140.0, 139.3, 138.9, 133.1, 129.7, 129.2, 117.8, 113.9, 112.4, 13.9, 13.7.

ESI-MS: *m*/*z* = 508 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{16}BBr_2F_2N_3$: C, 47.38; H, 3.18; N, 8.29. Found: C, 47.41; H, 3.15; N, 8.26.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-[3-(trifluoromethyl)phenyl]-4-bora-3a,4a-diaza-*s*-indacene (2k)
Yield: 90.2 mg (82%); red solid; mp 227–229 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 7.53 (d, *J* = 7.7 Hz, 1 H, ArH), 7.62 (s, 1 H, ArH), 7.72 (t, *J* = 7.7 Hz, 1 H, ArH), 7.85 (d, *J* = 7.85 Hz, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.8, 140.2, 139.5, 135.3, 132.2 (q, $^2J_{C-F}$ = 32.7 Hz), 131.2, 130.1, 126.3 (q, $^3J_{C-F}$ = 3.65 Hz), 125.2 (q, $^3J_{C-F}$ = 3.70 Hz), 123.5 (q, $^1J_{C-F}$ = 271.0 Hz, CF_3), 112.3, 13.8, 13.7.

ESI-MS: *m*/*z* = 551 $[M + H]^+$.

Anal. Calcd for $C_{20}H_{16}BBr_2F_5N_2$: C, 43.68; H, 2.93; N, 5.09. Found: C, 43.72; H, 2.92; N, 5.13.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-(1-naphthyl)-4-bora-3a,4a-diaza-*s*-indacene (2l)
Yield: 94.7 mg (89%); red solid; mp 248–250 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (s, 6 H, CH_3), 2.67 (s, 6 H, CH_3), 7.38–7.42 (m, 1 H, ArH), 7.45–7.50 (m, 1 H, ArH), 7.54–7.58 (m, 1 H, ArH), 7.59–7.64 (m, 1 H, ArH), 7.74 (d, *J* = 8.25 Hz, 1 H, ArH), 7.94 (d, *J* = 8.2 Hz, 1 H, ArH), 8.03 (d, *J* = 8.25 Hz, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.1, 140.7, 140.5, 133.6, 131.7, 131.4, 130.9, 129.8, 128.4, 127.6, 126.9, 125.9, 125.8, 124.6, 111.8, 13.7, 13.1.

ESI-MS: m/z = 531 $[M - H]^+$.

Anal. Calcd for $C_{23}H_{19}BBr_2F_2N_2$: C, 51.92; H, 3.60; N, 5.27. Found: C, 51.96; H, 3.58; N, 5.22.

Monobromides 3a–l; General Procedure

To a soln of the 1,3,5,7-tetramethyl-BODIPY **1** (0.2 mmol) and K_2CO_3 (0.6 mmol) in anhyd MeCN (20 mL) was slowly added a soln of $CuBr_2$ (0.3 mmol) in MeCN (25 mL). The mixture was stirred under an O_2 atmosphere (balloon) at r.t. for 24 h. The residue obtained after the removal of the solvent by rotary evaporation was extracted with EtOAc (3 × 40 mL), and the extracts were washed with H_2O (3 × 30 mL), dried (anhyd Na_2SO_4), and concentrated under reduced pressure. The crude product was further purified using column chromatography (EtOAc–petroleum ether) to afford the monobromide **3**.

2-Bromo-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (3a)

Yield: 65.3 mg (81%); red solid; mp 183–185 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 6.05 (s, 1 H, pyrrole-H), 7.25–7.30 (m, 2 H, ArH), 7.49–7.55 (m, 3 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.9, 151.4, 145.1, 141.8, 138.8, 134.7, 132.0, 129.8, 129.3, 127.9, 122.2, 14.8, 14.5, 13.4.

EI-MS: m/z = 402 $[M - H]^+$.

Anal. Calcd for $C_{19}H_{18}BBrF_2N_2$: C, 56.62; H, 4.50; N, 6.95. Found: C, 56.60; H, 4.55; N, 6.91.

2-Bromo-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-*s*-indacene (3b)

Yield: 62.6 mg (75%); red solid; mp 193–195 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 6.04 (s, 1 H, pyrrole-H), 7.14 (d, J = 8.0 Hz, 2 H, ArH), 7.32 (d, J = 7.5 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.7, 151.2, 145.1, 142.3, 139.2, 138.8, 132.2, 131.6, 129.9, 127.7, 122.0, 110.5, 21.4, 14.7, 14.6, 13.5.

ESI-MS: m/z = 416 $[M - H]^+$.

Anal. Calcd for $C_{20}H_{20}BBrF_2N_2$: C, 57.59; H, 4.83; N, 6.72. Found: C, 57.64; H, 4.90; N, 6.68.

2-Bromo-4,4-difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (3c)

Yield: 65.8 mg (76%); red solid; mp 163–165 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 6.05 (s, 1 H, pyrrole-H), 7.04 (d, J = 9.0 Hz, 2 H, ArH), 7.17 (d, J = 8.5 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.4, 157.7, 151.2, 145.1, 142.0, 138.8, 130.2, 129.1, 128.8, 126.6, 122.0, 114.7, 110.5, 55.3, 14.7, 13.6, 13.4.

EI-MS: m/z = 432 $[M - H]^+$.

Anal. Calcd for $C_{20}H_{20}BBrF_2N_2O$: C, 55.46; H, 4.65; N, 6.47. Found: C, 55.47; H, 4.70; N, 6.49.

2-Bromo-8-(3,4-dimethoxyphenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (3d)

Yield: 74.1 mg (80%); red solid; mp 162–164 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.47 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 3.86 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3), 6.05 (s, 1 H, pyrrole-H), 6.77 (d, J = 1.5 Hz, 1 H, ArH), 6.81–6.83 (m, 1 H, ArH), 6.99 (d, J = 8.5 Hz, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.9, 151.4, 149.9, 149.7, 145.1, 141.7, 138.7, 132.3, 130.1, 126.7, 122.1, 120.4, 111.6, 110.9, 110.5, 56.1, 55.9, 14.7, 14.6, 13.5, 13.4.

ESI-MS: m/z = 464 $[M + H]^+$.

Anal. Calcd for $C_{21}H_{22}BBrF_2N_2O_2$: C, 54.46; H, 4.79; N, 6.05. Found: C, 54.49; H, 4.82; N, 6.01.

2-Bromo-8-(4-chlorophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (3e)

Yield: 75.3 mg (86%); red solid; mp 197–199 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 6.06 (s, 1 H, pyrrole-H), 7.23 (d, J = 8.5 Hz, 2 H, ArH), 7.52 (d, J = 8.5 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 151.9, 144.8, 140.2, 138.5, 135.5, 133.1, 131.9, 129.7, 129.5, 128.8, 122.4, 110.8, 14.8, 13.7, 13.5.

ESI-MS: m/z = 437 $[M]^+$.

Anal. Calcd for $C_{19}H_{17}BBrClF_2N_2$: C, 52.16; H, 3.92; N, 6.40. Found: C, 52.15; H, 3.88; N, 6.45.

2-Bromo-8-(2-chlorophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (3f)

Yield: 73.5 mg (84%); red solid; mp 218–220 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 6.07 (s, 1 H, pyrrole-H), 7.28–7.31 (m, 1 H, ArH), 7.42–7.50 (m, 2 H, ArH), 7.53–7.56 (m, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.7, 151.9, 144.6, 138.2, 138.0, 133.7, 132.9, 131.7, 130.9, 130.3, 129.8, 129.3, 127.8, 122.3, 110.7, 14.9, 13.8, 13.6, 12.6.

ESI-MS: m/z = 437 $[M]^+$.

Anal. Calcd for $C_{19}H_{17}BBrClF_2N_2$: C, 52.16; H, 3.92; N, 6.40. Found: C, 52.13; H, 3.96; N, 6.39.

2-Bromo-4,4-difluoro-1,3,5,7-tetramethyl-8-[4-(prop-2-ynyloxy)phenyl]-4-bora-3a,4a-diaza-*s*-indacene (3g)

Yield: 73.1 mg (80%); red solid; mp 203–204 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 2.58 (s, 3 H + 1 H, CH_3 + CH), 2.61 (s, 3 H, CH_3), 4.78 (d, J = 2.5 Hz, 2 H, CH_2), 6.05 (s, 1 H, pyrrole-H), 7.12 (d, J = 8.5 Hz, 2 H, ArH), 7.20 (d, J = 9.0 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.3, 157.8, 151.4, 145.1, 141.6, 138.7, 132.4, 130.2, 129.2, 128.8, 127.6, 122.1, 115.8, 110.6, 77.9, 75.9, 56.0, 14.7, 13.6.

ESI-MS: m/z = 457 $[M]^+$.

Anal. Calcd for $C_{22}H_{20}BBrF_2N_2O$: C, 57.80; H, 4.41; N, 6.13. Found: C, 57.85; H, 4.43; N, 6.08.

2-Bromo-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-nitrophenyl)-4-bora-3a,4a-diaza-*s*-indacene (3h)

Yield: 69.9 mg (78%); red solid; mp >300 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 6.09 (s, 1 H, pyrrole-H), 7.56 (d, J = 9.0 Hz, 2 H, ArH), 8.42 (d, J = 8.5 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.2, 152.8, 148.5, 144.4, 141.5, 138.4, 138.2, 131.3, 129.6, 129.0, 124.5, 122.8, 111.3, 14.9, 13.8, 13.6.

ESI-MS: m/z = 447 $[M - H]^+$.

Anal. Calcd for $C_{19}H_{17}BBrF_2N_3O_2$: C, 50.93; H, 3.82; N, 9.38. Found: C, 50.98; H, 3.86; N, 9.32.

2-Bromo-4,4-difluoro-1,3,5,7-tetramethyl-8-[4-(trifluoromethyl)phenyl]-4-bora-3a,4a-diaza-*s*-indacene (3i)
Yield: 76.3 mg (81%); red solid; mp 203–205 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 6.08 (s, 1 H, pyrrole-H), 7.47 (d, *J* = 8.0 Hz, 2 H, ArH), 7.82 (d, *J* = 8.0 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.7, 152.3, 144.7, 139.6, 138.6, 131.9, 131.7 (q, $^2J_{C-F}$ = 32.5 Hz), 129.4, 128.7, 126.3, 123.8 (q, $^1J_{C-F}$ = 280.0 Hz, CF_3), 122.6, 111.1, 14.8, 14.7, 13.6.

ESI-MS: *m*/*z* = 471 $[M]^+$.

Anal. Calcd for $C_{20}H_{17}BBrF_5N_2$: C, 50.09; H, 3.64; N, 5.95. Found: C, 50.06; H, 3.63; N, 5.91.

2-Bromo-8-(4-cyanophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (3j)
Yield: 67.6 mg (79%); red solid; mp 229–231 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 6.09 (s, 1 H, pyrrole-H), 7.48 (d, *J* = 8.5 Hz, 2 H, ArH), 7.85 (d, *J* = 8.0 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.0, 152.7, 144.4, 139.7, 138.7, 138.2, 133.0, 131.4, 129.3, 129.1, 122.7, 117.9, 113.6, 111.2, 14.8, 14.7, 13.7, 13.6.

ESI-MS: *m*/*z* = 427 $[M - H]^+$.

Anal. Calcd for $C_{20}H_{17}BBrF_2N_3$: C, 56.11; H, 4.00; N, 9.82. Found: C, 56.16; H, 4.02; N, 9.79.

2-Bromo-4,4-difluoro-1,3,5,7-tetramethyl-8-[3-(trifluoromethyl)phenyl]-4-bora-3a,4a-diaza-*s*-indacene (3k)
Yield: 69.7 mg (74%); red solid; mp 186–188 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 6.08 (s, 1 H, pyrrole-H), 7.53 (d, *J* = 7.7 Hz, 1 H, ArH), 7.62 (s, 1 H, ArH), 7.69 (t, *J* = 7.75 Hz, 1 H, ArH), 7.81 (d, *J* = 7.85 Hz, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.7, 152.3, 144.6, 139.3, 138.4, 135.6, 132.1, 131.9 (q, $^2J_{C-F}$ = 32.9 Hz), 131.6, 129.9, 129.5, 126.0 (q, $^3J_{C-F}$ = 3.75 Hz), 125.3 (q, $^3J_{C-F}$ = 3.35 Hz), 123.6 (q, $^1J_{C-F}$ = 271.0 Hz, CF_3), 122.6, 111.1, 14.8, 14.7, 13.6, 13.5.

ESI-MS: *m*/*z* = 471 $[M]^+$.

Anal. Calcd for $C_{20}H_{17}BBrF_5N_2$: C, 50.09; H, 3.64; N, 5.95. Found: C, 50.14; H, 3.61; N, 5.99.

2-Bromo-4,4-difluoro-1,3,5,7-tetramethyl-8-(1-naphthyl)-4-bora-3a,4a-diaza-*s*-indacene (3l)
Yield: 78.8 mg (87%); red solid; mp 209–211 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 2.63 (s, 3 H, CH_3), 2.66 (s, 3 H, CH_3), 6.02 (s, 1 H, pyrrole-H), 7.40 (d, *J* = 7.0 Hz, 1 H, ArH), 7.44–7.49 (m, 1 H, ArH), 7.52–7.57 (m, 1 H, ArH), 7.57–7.62 (m, 1 H, ArH), 7.78 (d, *J* = 8.4 Hz, 1 H, ArH), 7.93 (d, *J* = 8.2 Hz, 1 H, ArH), 8.00 (d, *J* = 8.3 Hz, 1 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.1, 151.6, 144.9, 140.4, 138.6, 133.5, 132.6, 132.1, 131.6, 130.3, 129.6, 128.3, 127.4, 126.8, 125.9, 125.8, 124.7, 122.1, 110.6, 14.8, 14.0, 13.5, 12.9.

ESI-MS: *m*/*z* = 453 $[M]^+$.

Anal. Calcd for $C_{23}H_{20}BBrF_2N_2$: C, 60.96; H, 4.45; N, 6.18. Found: C, 60.93; H, 4.46; N, 6.15.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

Acknowledgment

We thank the Analysis and Testing Center of the School of Chemical Engineering, Nanjing University of Science and Technology, and Mrs. R. Yi for assistance with the NMR experiments.

References

(1) Haugland, R. P. *The Handbook: A Guide to Fluorescent Probes and Labeling Technologies*, 10th ed.; Invitrogen Corp.: Eugene (OR, USA), **2005**.
(2) (a) Golovkova, T. A.; Kozlov, D. V.; Neckers, D. C. *J. Org. Chem.* **2005**, *70*, 5545. (b) Trieflinger, C.; Rurack, K.; Daub, J. *Angew. Chem. Int. Ed.* **2005**, *44*, 2288.
(3) (a) Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2005**, *127*, 10464. (b) Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968. (c) Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2006**, *128*, 14474. (d) Zeng, L.; Miller, E. W.; Pralle, A.; Isacoff, E. Y.; Chang, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 10. (e) Coskun, A.; Deniz, E.; Akkaya, E. U. *Org. Lett.* **2005**, *7*, 5187. (f) Saki, N.; Dinc, T.; Akkaya, E. U. *Tetrahedron* **2006**, *62*, 2721. (g) Coskun, A.; Turfan, B. T.; Akkaya, E. U. *Tetrahedron Lett.* **2003**, *44*, 5649. (h) Ekmekci, Z.; Yilmaz, M. D.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 461.
(4) (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (b) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 1184. (c) Loudet, A.; Burgess, K. In *Handbook of Porphyrin Science*, Vol. 8; Kadish, K. M.; Smith, K. M.; Guilard, K. R., Eds.; World Scientific: Hackensack, **2010**, 1. (d) Ziessel, R.; Ulrich, G.; Harriman, A. *New J. Chem.* **2007**, *31*, 496. (e) Buyukcakir, O.; Bozdemir, O. A.; Kolemen, S.; Erbas, S.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 4644.
(5) Bozdemir, Ö. A.; Büyükcakir, O.; Akkaya, E. U. *Chem. Eur. J.* **2009**, *15*, 3830.
(6) (a) Li, F.; Yang, S. I.; Ciringh, Y. Z.; Seth, J.; Martin, C. H.; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 10001. (b) Yilmaz, M. D.; Bozdemir, O. A.; Akkaya, E. U. *Org. Lett.* **2006**, *8*, 2871.
(7) (a) Atilgan, S.; Ekmekci, Z.; Dogan, A. L.; Guc, D.; Akkaya, E. U. *Chem. Commun.* **2006**, 4398. (b) Lim, S. H.; Thivierge, C.; Nowak-Sliwinska, P.; Han, J.; van den Bergh, H.; Wagniéres, G.; Burgess, K.; Lee, H. B. *J. Med. Chem.* **2010**, *53*, 2865.
(8) Yuan, M.; Zhou, W.; Liu, X.; Zhu, M.; Li, J.; Yin, X.; Zheng, H.; Zuo, Z.; Ouyang, C.; Liu, H.; Li, Y.; Zhu, D. *J. Org. Chem.* **2008**, *73*, 5008.
(9) (a) Hattori, S.; Ohkubo, K.; Urano, Y.; Sunahara, H.; Nagano, T.; Wada, Y.; Tkachenko, T. V.; Lemmetyinen, H.; Fukuzumi, S. *J. Phys. Chem. B* **2005**, *109*, 15368. (b) Erten-Ela, S.; Yilmaz, M. D.; Icli, B.; Dede, Y.; Icli, S.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 3299.
(10) (a) Sameiro, M.; Gonçalves, T. *Chem. Rev.* **2009**, *109*, 190. (b) Kuimova, M. K.; Yahioglu, G.; Levitt, J. A.; Suhling, K. *J. Am. Chem. Soc.* **2008**, *130*, 6672.

(11) (a) Bonardi, L.; Ulrich, G.; Ziessel, R. *Org. Lett.* **2008**, *10*, 2183. (b) Hayashi, Y.; Yamaguchi, S.; Cha, W. Y.; Kim, D.; Shinokubo, H. *Org. Lett.* **2011**, *13*, 2992. (c) Dost, Z.; Atilgan, S.; Akkaya, E. U. *Tetrahedron* **2006**, *62*, 8484. (d) Cihaner, A.; Algi, F. *React. Funct. Polym.* **2009**, *69*, 62. (e) Algi, F.; Cihaner, A. *Org. Electron.* **2009**, *10*, 453. (f) Xiao, Y.; Zhang, D. Faming Zhuanli Shenqing Gongkai Shuomingshu CN 101302353, **2008**; *Chem. Abstr.* **2008**, *150*, 21133.

(12) Deniz, E.; Isbasar, G. C.; Bozdemir, Ö. A.; Yildirim, L. T.; Siemiarczuk, A.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 3401.

(13) (a) Narender, N.; Srinivasu, P.; Prosad, M. R. S.; Karani, J. K.; Raghavan, K. V. *Synth. Commun.* **2002**, *32*, 2313. (b) Mauathen, H. A. *Helv. Chim. Acta* **2003**, *86*, 164. (c) Kovacic, P.; Davis, K. E. *J. Am. Chem. Soc.* **1964**, *86*, 427. (d) Gallou, F.; Reeves, J. T.; Tan, Z.; Song, J. J.; Yee, N. K.; Harcken, C.; Liu, P.; Thomson, D.; Senanayake, C. H. *Synlett* **2007**, 211. (e) Peng, A.-Y.; Hao, F.; Li, B.; Wang, Z.; Du, Y. *J. Org. Chem.* **2008**, *73*, 9012. (f) Kalyani, D.; Satterfield, A. D.; Sanford, M. S. *J. Am. Chem. Soc.* **2010**, *132*, 8419. (g) Shen, Z.; Lu, X. *Adv. Synth. Catal.* **2009**, *351*, 3107. (h) Siméon, F. G.; Wendahl, M. T.; Pike, V. W. *J. Org. Chem.* **2009**, *74*, 2578. (i) Tang, S.; Li, J.-H.; Xie, Y.-X.; Wang, N.-X. *Synthesis* **2007**, 1535. (j) Bedford, R. B.; Engelhart, J. U.; Haddow, M. F.; Mitchell, C. J.; Webster, R. L. *Dalton Trans.* **2010**, *39*, 10464. (k) Bhatt, S.; Nayak, S. K. *Synth. Commun.* **2007**, *37*, 1381. (l) Jia, X.; Yang, D.; Wang, W.; Luo, F.; Cheng, J. *J. Org. Chem.* **2009**, *74*, 9470. (m) Petruso, S.; Caronna, S. *J. Heterocycl. Chem.* **1992**, *29*, 355.

(14) King, L. C.; Ostrum, G. K. *J. Org. Chem.* **1964**, *29*, 3459.

