## **Radical C–H Arylation of the BODIPY Core with Aryldiazonium** Salts: Synthesis of Highly Fluorescent Red-Shifted Dyes\*\*

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**Abstract:** We describe herein the first radical C–H arylation of BODIPY dyes. This novel, general, one-step synthetic procedure uses ferrocene to generate aryl radical species from aryldiazonium salts and allows the straightforward synthesis of brightly fluorescent ( $\Phi > 0.85$ ) 3,5-diarylated and 3-monoarylated boron dipyrrins in up to 86% yield for a broad range of aryl substituents. In this way, new and complex dyes with redshifted spectra can be easily prepared.

Over the last two decades, BODIPY dyes (4,4-difluoro-4bora-3a,4a-diaza-s-indacenes)<sup>[1,2]</sup> have become increasingly valuable fluorophores. The growing success of this class of compounds is attributed to their many excellent characteristics, including bright fluorescence and their vast potential for functionalization leading to sophisticated dyes with finetuned properties.<sup>[3]</sup> The numerous applications being reported for these dyes illustrate the importance of these interesting compounds.<sup>[4]</sup>

Most derivation strategies for synthesizing new boron dipyrrins either start from suitably functionalized pyrroles<sup>[5]</sup> or use reactive BODIPY dyes<sup>[6,7]</sup> (Scheme 1). However, these two methodologies tend to suffer from the use of unstable intermediates and/or the need for a long synthetic route. A more efficient method of introducing functional groups is by C–H functionalization reactions,<sup>[8,9]</sup> allowing the synthesis of new dyes in a single atom economical step. A few examples of such direct derivatization reactions for these fluorophores are currently known,<sup>[10,11]</sup> most of which require rather forcing reaction conditions to overcome the inertness of the C–H bond which limits the scope and the obtained yield.

In contrast, radical C–H functionalization can occur under mild conditions, owing to the high reactivity of radicals.<sup>[9,12]</sup> However, radical functionalization of boron dipyrromethenes is virtually unknown. Up to this point only one example, proposed to occur through an electrophilic radical species, has been reported in a low yield.<sup>[13]</sup> Until now, radical arylation of boron dipyrrins has not been described, despite the obviously desirable bathochromic spectral shift it



**Scheme 1.** Summary of synthetic pathways toward arylated BODIPY dyes.

can introduce. Aryldiazonium salts are one of the well-known sources of aryl radicals through a homolytic dediazoniation mechanism, mostly achieved by means of a reduction (Scheme S1, Supporting Information, SI).<sup>[14]</sup> Likewise, the use of aryldiazonium salts for the arylation of readily available *meso*-substituted BODIPY dyes **1** could prove to be an interesting alternative for synthesizing new derivatives of this fluorophore. Hence, we set out to investigate the feasibility of this novel radical reaction.

As an initial experiment 8-(2,6-dichlorophenyl)-BODIPY 1 was reacted with excess benzenediazonium tetrafluoroborate 2a and one equivalent of copper(I) chloride at room temperature. After 25 h the desired diphenylated compound **3a** was obtained in a low yield of 13% (Table S1, entry 2). Characterization of the formed products showed that the phenyl radicals reacted exclusively at the 3,5-positions of the boron dipyrromethene core. This selectivity can be compared with the exclusive 2-addition of radical species to electrondeficient alkenes, in which the electron-withdrawing group is stabilizing the newly formed radical species. In this case, after addition to the 3-position of one pyrrole moiety, and delocalization over several double bonds, the imine part of the adjacent pyrroline, aided by the complexed boron, is causing an increased stability of the formed radical (Scheme S1). Moreover, such a high selectivity in radical reactions is also known for protonated heteroaromatic bases.<sup>[12]</sup> This is accounted for by the strong increase in polarity of these heteroaromatic bases when protonated, causing polar effects to determine the outcome of the reaction. A similar reason can be used to rationalize the observed selectivity in the radical C-H arylation of the BODIPY core, because the BF2 group can be seen as a strongly polarizing Lewis acid complexed with a dipyrromethene base.

The limited yield of the test reaction might be caused by the reductant used, because copper(I) chloride can react with diazonium salts in a Sandmeyer reaction.<sup>[15]</sup> To improve the yield, other common reducing agents were tried (Table S1, entries 1–11) and the most notable of these experiments was

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the use of ferrocene (FeCp<sub>2</sub>), because it gave an immediate reaction although in a moderate yield. The yield in this case was limited due to a significant arylation of the formed ferricinium cation,<sup>[16]</sup> resulting in the formation of phenyl-ferrocene and diphenylferrocene. To counter this, the ferrocene concentration has to be low (Table S1, entry 12). However, due to insufficient regeneration of the ferrocene catalyst (Table S1, entry 13), this can only be achieved by continuous addition of this reducing agent (Table S1, entries 14–17). The best result was obtained with an addition speed of 0.2 mmol h<sup>-1</sup> providing the diphenylated product **3a** in less than an hour in an excellent yield of 84 %. Further optimization tests afforded no improvement (Table S1, entries 18–25).

Using this optimized condition, the radical C–H arylation was executed with different BODIPY substrates and a range of aryldiazonium tetrafluoroborates (Scheme 2), illustrating the broad scope of this reaction. Different *meso*-substituted



Scheme 2. Generality of the radical C-H diarylation of BODIPY dyes.

boron dipyrromethenes were reactive in this type of arylation providing the phenylated product **3a-c** in good to excellent yields. The three isomers of nitrobenzenediazonium tetrafluoroborate 2d-f all yielded the desired compounds 3d-f, with the directly conjugated 4-nitro and 2-nitro substituents resulting in higher yields in comparison to the cross-conjugated 3-nitro group. Other electron-poor diazonium salts **2g-i** were also reactive under these conditions and gave up to 86% yield. Of particular interest are the bromo 3h and carboxy products 3i, because both functionalities allow further derivatization through transition-metal-catalyzed cross-coupling and esterification/amidation reactions, respectively. Moreover, 3,5-bis(4'-carboxyphenyl)-BODIPY 3i is a water-soluble fluorophore in its deprotonated form, highlighting the capabilities of this C-H arylation, because it provides easy access to water-soluble dyes with red-shifted UV/Vis absorption and emission spectra. Not only electronpoor diazonium salts can be used, because both the ring-fused naphthalene-2-diazonium tetrafluoroborate 2j and the sterically hindered 2,4,6-trimethylbenzenediazonium tetrafluoroborate 2k resulted in the 3,5-diarylated compounds 3j-k. However, the steric hindrance of the latter made this reaction less effective. A three times longer reaction time was needed to give the product 3k in a low yield of 19%. Lastly, 4methoxybenzenediazonium salt 21 gave product 31 in a moderate yield. This lower yield was probably caused by a reduced reactivity of the more electron-rich monoarylated intermediate, hindering the second arvlation step. The 4-(dimethylamino)benzenediazonium salt 2 m proved to be too electronrich to be reduced by ferrocene. By using the more reducing decamethylferrocene, reaction did occur. However, after complete reaction only a trace amount of diarylated compound was formed and the monoarylated product **5h** was isolated instead in 35% yield.

These results demonstrate the vast improvement of the present radical C–H arylation compared to previous arylation protocols.<sup>[5,11]</sup> This new method provides easy access to new compounds in a much shorter reaction time, because most of these radical reactions are completed within one hour. Furthermore, our new procedure supplies compounds in a higher yield in one atom-economical step avoiding the use of multistep synthesis, high reaction temperatures, and unstable pyrrole intermediates.

The procedure developed for diarylation can be modified to allow radical C–H monoarylation (Scheme 3). This is achieved by using one equivalent of diazonium salt instead of



**Scheme 3.** Generality of the radical C<sup>--</sup>H monoarylation of BODIPY dyes (Ar=2,6-dichlorophen-1-yl).

an excess and simultaneously reducing the amount of ferrocene. In this way, the monoarylated product 5a, formed by reaction between BODIPY 1 and benzenediazonium tetrafluoroborate 4a, could be isolated in 58% yield. Similarly, electron-poor diazonium salts reacted in good yields, e.g., up to 74% in the case of 4-cyanobenzenediazonium tetrafluoroborate 4c. Ring-fused and sterically hindered diazonium salts also resulted in the formation of the desired products with comparable yields. In the case of electron-rich diazonium salts, the resulting yields were unfortunately somewhat lower. Due to the identical reactivity of the 3- and the 5-hydrogens some overarylation occurs in all these examples, producing the diarylated compound 3 as a side product in an estimated yield between 5 and 15%, depending on the used diazonium salt.

Finally, to illustrate the potential of this novel reaction, two asymmetrically substituted dyes (6 and 7) were synthesized according to our developed methodology (Scheme 4). The 3-phenylBODIPY **5a** was reacted with excess 4-cyanobenzenediazonium tetrafluoroborate **4c**. Unfortunately, starting compound **5a** was insufficiently soluble in the reaction solvent, causing an incomplete reaction and hence a low yield. When the reaction order was reversed and 3-(4-cyanophenyl)-BODIPY **5c** was combined with benzenediazonium tetrafluoroborate **4a**, this problem was avoided. Thus, the desired 3-(4-cyanophenyl)-5-phenyl-BODIPY **6** was isolated in a good yield of 73%. Compound 3-(4-cyanophenyl)-BODIPY **5c** could also be used in the synthesis of 3-(4-

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**Scheme 4.** Synthesis of asymmetrical 3,5-diarylated BODIPY dyes through radical C<sup>-</sup>H arylation (Ar = 2,6-dichlorophen-1-yl).

cyanophenyl)-5-(4-methoxyphenyl)-BODIPY 7 through reaction with 4-methoxybenzenediazonium tetrafluoroborate 4g. The separation of compound 7 from a small amount of starting material 5c proved very tedious: thus 54% of the product was isolated as pure compound and the rest was lost as mixed column chromatography fractions. The same asymmetrical dye 7 was also prepared from 3-(4-methoxyphenyl)-BODIPY 5g. However, in analogy with the synthesis of 3,5di(4-methoxyphenyl)-BODIPY 31, compound 5g was not reactive enough to give a complete conversion resulting in a lower yield. Both synthesized asymmetrical fluorophores described here are compounds that are a challenge to prepare with previously reported methodologies. Hence, the current radical C-H arylation allows the synthesis of sophisticated BODIPY dyes in a straightforward fashion.

BODIPY dyes are generally characterized by narrow absorption and emission bandwidths covering the entire visible spectral range<sup>[3,17]</sup> with high peak intensities, small Stokes shifts, and high fluorescence quantum yields  $\Phi$ .<sup>[3,11b]</sup> The majority of the fluorophores synthesized for the present study show these properties. The versatility of the described radical C–H arylation is shown in its ability to create a library of compounds, which can greatly assist in creating a dye with fine-tuned spectroscopic and photophysical properties (Figure 1). The key spectroscopic and photophysical data of these BODIPY derivatives are compiled in Tables S4–S6.

For each dye, the absorption maxima are slightly bathochromically shifted with increasing solvent polarizability (from methanol/acetonitrile to toluene). The visible absorption band is assigned to the strong  $S_1 \leftarrow S_0$  transition. An additional, much weaker, broad absorption band can be observed in the UV spectral range (see Figures  $S_1$  and  $S_2$ ), attributed to the  $S_2 \leftarrow S_0$  transition. All the derivatives also show the typical emission features of boron dipyrrins: that is, a narrow, slightly Stokes-shifted band of mirror image shape, whose maximum  $\lambda_{em}(max)$  is somewhat red-shifted with increasing solvent polarizability. Although the shapes of the spectra of all the investigated difluoroboron dipyrrins are similar, their absorption and emission maxima  $[\lambda_{abs}(max)]$ ,  $\lambda_{em}(max)$ ], Stokes shifts  $(\Delta \bar{\nu})$ , absorption and emission bandwidths [measured by the full width at half-height of the maximum of the absorption (fwhm<sub>abs</sub>) and the fluorescence



Figure 1. Normalized, visible absorption spectra and corresponding normalized fluorescence emission spectra of a selection of *meso*-(2,6-dichlorophenyl)-substituted BODIPY dyes (5b, 5e, 6, 3d, 3j) in MeCN.

emission (fwhm<sub>em</sub>) bands], and fluorescence quantum yields  $(\Phi)$  may vary considerably.

Most of the synthesized compounds have high  $\Phi$ -values, an important exception to this is 8-phenyl BODIPY **3b**, due to the rotation of the 8-phenyl substituent being a major nonradiative deactivation pathway of the singlet excited state S<sub>1</sub>. Rotation of the 8-(2,6-dichlorophenyl) group and 8mesityl group (in **3a** and **3c**) is restricted by steric hindrance between the Cl atoms and methyl groups, respectively, and the 1,7-hydrogens of the BODIPY nucleus. The higher  $\Phi$ values of **3a** with a *meso*-2,6-dichlorophenyl group<sup>[11b]</sup> compared to those of **3c** with a *meso*-mesityl substituent indicate that the 2,6-dichlorophenyl group is the more efficient rotation-blocking group.

The symmetrically 3,5-disubstituted products **3** have bathochromically absorption and emission spectra compared to their asymmetrically 3-substituted counterparts **5** (Figure 1).<sup>[3a]</sup> These shifts reflect the better  $\pi$ -conjugation in the 3,5-diaryl dyes compared to their 3-aryl analogues and evidently to the starting material **1**. Introduction of one phenyl group at the 3-position (in **5a**) produces a bathochromic shift of approximately 29 nm in  $\lambda_{abs}(max)$  and ca. 35 nm in  $\lambda_{em}(max)$  compared to starting compound **1**, which serves as reference. Incorporating a second phenyl group (in **3a**) entails an additional red shift of approximately 27 nm in  $\lambda_{abs}(max)$  and ca. 40 nm in  $\lambda_{em}(max)$  relative to dye **5a**.<sup>[3a,11b]</sup>

Replacing the 3,5-phenyl (in **3a** and **5a**) substituents by the electron-donating *p*-anisyl groups (in **31** and **5g**) results in a further red-shifted spectra for both the mono- and diarylated compound.<sup>[3a,11b]</sup> In contrast, the bulky mesityl group (in 3k and 5f) introduces only a small bathochromic shift, suggesting a severely restricted electronic coupling caused by steric hindrance twisting the mesityl group out of the BODIPY plane. Furthermore, 3,5-dimesityl dye 3k has very small Stokes shifts ( $\Delta \bar{\nu} \approx 600 \text{ cm}^{-1}$ ), combined with high  $\Phi$ values (up to 0.98), suggesting a very rigid structure. Compound 3-[4-(dimethylamino)phenyl]-BODIPY 5h shows no fluorescence in the more polar solvents; it is quenched by the electron-rich 3-[4-(dimethylamino)-phenyl] substituent. Addition of acid (H<sup>+</sup>) blocks the lone electron pair of the nitrogen donor and hence decreases the electron-donating

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ability of the amine. This leads to inhibition of the quenching process, resulting in the "switching on" of the fluorescence, which renders this molecule an extremely sensitive probe for pH (Table S4).

BODIPY dyes with electron-withdrawing groups (4-nitrophenyl in 3d and 5b, 4-cyanophenyl in 3g and 5c, 4bromophenyl in **3h**, and 4-carboxyphenyl in **3i** and **5d**) show smaller bathochromic spectral shifts compared to the phenyl derivatives (3a and 5a), but the influence on the fluorescence quantum yields is minimal. The 3,5-di(4-nitrophenyl)-substituted 3d shows rather small bathochromic shifts compared to the 3,5-di(3-nitrophenyl) derivative 3e, but much larger red shifts compared to the 3,5-di(2-nitrophenyl) compound 3 f. The quantum yields and Stokes shifts of 3d and 3e are comparable, whereas the sterically hindered 2-nitro variant 3f barely shows any fluorescence. Negligible fluorescence has previously also been observed for 8-(4nitrophenyl)-3-phenylBODIPY and 8-(4-nitrophenyl)-3,5diphenylBODIPY.<sup>[11b]</sup> Products 3i and 5d, containing two and one carboxylic acid groups, respectively, are soluble in slightly basic water. Combined with their moderate to good quantum yields  $\Phi$  (up to 0.85), these compounds are promising candidates as the basis for constructing labeling dves.

 $\lambda_{abs}(max)$  and  $\lambda_{em}(max)$  of **5e** and **3j**, with one and two 2naphthyl groups, respectively, are bathochromically shifted compared to those of the corresponding phenyl-substituted analogues **5a** and **3a**, respectively. This reflects the improved  $\pi$ -conjugation in the 2-naphthyl-substituted derivatives relative to their phenyl counterparts.<sup>[3a]</sup>

The absorption and emission maxima of **6** and **7** correspond to the average between their corresponding symmetrical analogues. Likewise,  $\lambda_{abs}(max)$  and  $\lambda_{em}(max)$  of product **6** are the average between **3a** and **3g**, whereas those of product **7** are the average between **31** and **3g**.

In conclusion, a versatile, general method for the synthesis of brightly fluorescent ( $\Phi > 0.85$ ) 3,5-diarylated and 3-monoarylated BODIPY dyes with UV/Vis absorption and fluorescence emission spectra, which are bathochromically shifted compared to those of the starting boron dipyrrins, has been developed and investigated. The present radical C–H arylation, based on the ferrocene-catalyzed reduction of aryldiazonium salts, is a fast and high yielding reaction displaying a broad scope. In this way, new interesting fluorophores can be synthesized, such as asymmetrically substituted dyes, thus avoiding the tedious synthesis of substituted pyrrole building blocks and unstable intermediates.

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- A. Treibs, F.-H. Kreuzer, *Liebigs Ann. Chem.* 1968, 718, 208– 223.
- [2] The trade name BODIPY (acronym of *bo*ron *dipy*rrin or *bo*ron *dipy*rromethene), has become the common name for this class of fluorophores.

- [3] a) A. Loudet, K. Burgess, *Chem. Rev.* 2007, *107*, 4891–4932;
  b) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem. Int. Ed.* 2008, *47*, 1184–1201; *Angew. Chem.* 2008, *120*, 1202–1219.
- [4] a) M. Benstead, G. H. Mehl, R. W. Boyle, *Tetrahedron* 2011, 67, 3573-3601; b) N. Boens, V. Leen, W. Dehaen, *Chem. Soc. Rev.* 2012, 41, 1130-1172, and references therein; c) S. G. Awuah, Y. You, *RSC Adv.* 2012, 2, 11169-11183; d) A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung, K. Burgess, *Chem. Soc. Rev.* 2013, 42, 77-88; e) A. Bessette, G. S. Hanan, *Chem. Soc. Rev.* 2014, 43, 3342-3405; f) S. P. Singh, T. Gayathri, *Eur. J. Org. Chem.* 2014, 4689-4707.
- [5] a) A. Burghart, H. Kim, M. B. Welch, L. H. Thoresen, J. Reibenspies, K. Burgess, J. Org. Chem. 1999, 64, 7813-7819;
  b) A. B. Zaitsev, R. Méallet-Renault, E. Y. Schmidt, A. I. Mikhaleva, S. Badré, C. Dumas, A. M. Vasil'tsov, N. V. Zorina, R. B. Pansu, *Tetrahedron* 2005, 61, 2683-2688; c) L. N. Sobenina, A. M. Vasil'tsov, O. V. Petrova, K. B. Petrushenko, I. A. Ushakov, G. Clavier, R. Meallet-Renault, A. I. Mikhaleva, B. A. Trofimov, Org. Lett. 2011, 13, 2524-2527.
- [6] a) M. Baruah, W. Qin, R. A. L. Vallée, D. Beljonne, T. Rohand, W. Dehaen, N. Boens, Org. Lett. 2005, 7, 4377-4380; b) T. Rohand, M. Baruah, W. Qin, N. Boens, W. Dehaen, Chem. Commun. 2006, 266-268; c) T. Rohand, W. Qin, N. Boens, W. Dehaen, Eur. J. Org. Chem. 2006, 4658-4663; d) V. Leen, E. Braeken, K. Luckermans, C. Jackers, M. Van der Auweraer, N. Boens, W. Dehaen, Chem. Commun. 2009, 4515-4517; e) L. Jiao, J. Li, S. Zhang, C. Wei, E. Hao, M. G. H. Vicente, New J. Chem. 2009, 33, 1888-1893; f) T. K. Khan, M. R. Rao, M. Ravikanth, Eur. J. Org. Chem. 2010, 2314-2323; g) V. Leen, D. Miscoria, S. Yin, A. Filarowski, J. M. Ngongo, M. Van der Auweraer, N. Boens, W. Dehaen, J. Org. Chem. 2011, 76, 8168-8176; h) V. Leen, T. Leemans, N. Boens, W. Dehaen, Eur. J. Org. Chem. 2011, 4386-4396; i) Y. Hayashi, S. Yamaguchi, W. Y. Cha, D. Kim, H. Shinokubo, Org. Lett. 2011, 13, 2992-2995; j) G. Ulrich, A. Haefele, P. Retailleau, R. Ziessel, J. Org. Chem. 2012, 77, 5036-5048; k) V. Leen, P. Yuan, L. Wang, N. Boens, W. Dehaen, Org. Lett. 2012, 14, 6150-6153.
- [7] a) T. V. Goud, A. Tutar, J.-F. Biellmann, *Tetrahedron* 2006, 62, 5084–5091; b) E. Peña-Cabrera, A. Aguilar-Aguilar, M. González-Domínguez, E. Lager, R. Zamudio-Vázquez, J. Godoy-Vargas, F. Villanueva-García, Org. Lett. 2007, 9, 3985–3988; c) J. Han, O. Gonzalez, A. Aguilar-Aguilar, E. Peña-Cabrera, K. Burgess, Org. Biomol. Chem. 2009, 7, 34–36; d) I. J. Arroyo, R. Hu, B. Z. Tang, F. I. López, E. Peña-Cabrera, *Tetrahedron* 2011, 67, 7244–7250; e) C. F. A. Gómez-Durán, I. García-Moreno, A. Costela, V. Martin, R. Sastre, J. Bañuelos, F. López Arbeloa, I. López Arbeloa, E. Peña-Cabrera, *Chem. Commun.* 2010, 46, 5103–5105; f) J. O. Flores-Rizo, I. Esnal, C. A. Osorio-Martínez, C. F. A. Gómez-Durán, J. Bañuelos, I. López Arbeloa, K. H. Pannell, A. J. Metta-Magaña, E. Peña-Cabrera, *J. Org. Chem.* 2013, 78, 5867–5877.
- [8] L. Ackermann, R. Vicente, A. R. Kapdi, Angew. Chem. Int. Ed. 2009, 48, 9792–9826; Angew. Chem. 2009, 121, 9976–10011.
- [9] a) A. Wetzel, G. Pratsch, R. Kolb, M. R. Heinrich, *Chem. Eur. J.* 2010, *16*, 2547–2556; b) A. Honraedt, M.-A. Raux, E. Le Grognec, D. Jacquemin, F.-X. Felpin, *Chem. Commun.* 2014, *50*, 5236–5238.
- [10] a) C. Thivierge, R. Bandichhor, K. Burgess, Org. Lett. 2007, 9, 2135–2138; b) J. Chen, M. Mizumura, H. Shinokubo, A. Osuka, Chem. Eur. J. 2009, 15, 5942–5949; c) V. Leen, V. Z. Gonzalvo, W. M. De Borggraeve, N. Boens, W. Dehaen, Chem. Commun. 2010, 46, 4908–4910; d) V. Leen, M. Van der Auweraer, N. Boens, W. Dehaen, Org. Lett. 2011, 13, 1470–1473.
- [11] a) B. Verbelen, V. Leen, L. Wang, N. Boens, W. Dehaen, *Chem. Commun.* 2012, 48, 9129–9131; b) L. Wang, B. Verbelen, C. Tonnelé, D. Beljonne, R. Lazzaroni, V. Leen, W. Dehaen, N. Boens, *Photochem. Photobiol. Sci.* 2013, 12, 835–847.

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- [12] F. Minisci, E. Vismara, F. Fontana, G. Morini, M. Serravalle, C. Giordano, J. Org. Chem. 1986, 51, 4411–4416.
- [13] N. Santschi, J. Cvengroš, C. Matthey, E. Otth, A. Togni, Eur. J. Org. Chem. 2014, 6371–6375.
- [14] C. Galli, Chem. Rev. 1988, 88, 765-792.
- [15] J. K. Kochi, J. Am. Chem. Soc. 1957, 79, 2942-2948.
- [16] A. L. J. Beckwith, R. J. Leydon, *Tetrahedron Lett.* **1963**, *4*, 385– 388.
- [17] a) see Ref. [7e]; b) J. Bañuelos, V. Martín, C. F. A. Gómez-Durán, I. J. A. Córdoba, E. Peña-Cabrera, I. García-Moreno, A. Costela, M. E. Pérez-Ojeda, T. Arbeloa, I. L. Arbeloa, *Chem. Eur. J.* 2011, *17*, 7261–7270; c) I. Esnal, A. Urías-Benavides, C. F. A. Gómez-Durán, C. A. Osorio-Martínez, I. García-

Moreno, A. Costela, J. Bañuelos, N. Epelde, I. López Arbeloa, R. Hu, B. Zhong Tang, E. Peña-Cabrera, *Chem. Asian J.* 2013, *8*, 2691–2700; d) R. I. Roacho, A. Metta-Magaña, M. M. Portillo, E. Peña-Cabrera, K. H. Pannell, *J. Org. Chem.* 2013, *78*, 4245– 4250; e) N. Boens, L. Wang, V. Leen, P. Yuan, B. Verbelen, W. Dehaen, M. Van der Auweraer, W. D. De Borggraeve, L. Van Meervelt, J. Jacobs, D. Beljonne, C. Tonnelé, R. Lazzaroni, M. J. Ruedas-Rama, A. Orte, L. Crovetto, E. M. Talavera, J. M. Alvarez-Pez, *J. Phys. Chem. A* 2014, *118*, 1576–1594.

[18] H. L. Kee, C. Kirmaier, L. Yu, P. Thamyongkit, W. J. Youngblood, M. E. Calder, L. Ramos, B. C. Noll, D. F. Bocian, W. R. Scheidt, R. R. Birge, J. S. Lindsey, D. Holten, *J. Phys. Chem. B* 2005, *109*, 20433–20443.



## **Communications**

## C–H Arylation

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Radical C-H Arylation of the BODIPY Core with Aryldiazonium Salts: Synthesis of Highly Fluorescent Red-Shifted Dyes



A one-step procedure for the first radical C-H arylation of BODIPY dyes has been developed. This method uses ferrocene (FeCp<sub>2</sub>) to generate aryl radical species from aryldiazonium salts and allows the synthesis of brightly fluorescent ( $\Phi$  >

0.85) 3,5-diarylated and 3-monoarylated boron dipyrrins in up to 86% yield for a broad range of aryl substituents. In this way, new and complex dyes with redshifted spectra can be easily prepared.

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