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ARTICLE

Microwave-assisted reduction of *F*-BODIPYs and dipyrrins to generate dipyrromethanes

Jennifer A. Melanson, Deborah A. Smithen, T. Stanley Cameron, and Alison Thompson

Abstract: The reduction of BODIPYs and dipyrrins to dipyrromethanes, via a reaction involving ethylene glycol and sodium methoxide, is reported. When benzyl alcohol is used in place of ethylene glycol, the addition of 2,4-dinitrophenylhydrazine to the reaction mixture after microwave irradiation results in the production of 1-benzylidene-2-(2,4-dinitrophenyl)hydrazone, indicating concomitant production of aldehyde alongside the dipyrromethane.

Key words: F-BODIPY, dipyrrin reduction, dipyrromethane formation, microwave-assisted.

Résumé : On décrit la réduction de BODIPYs et de dipyrrines en dipyrrométhanes par une réaction faisant intervenir de l'éthylène glycol et du méthanolate de sodium. Si l'on remplace l'éthylène glycol par l'alcool benzylique, l'ajout de 2,4-dinitrophénylhydrazine au mélange réactionnel après irradiation par micro-ondes donne de la 1-benzylidène-2-(2,4-dinitrophényl) hydrazone, ce qui indique la production concomitante d'un aldéhyde et du dipyrrométhane. [Traduit par la Rédaction]

Mots-clés : réduction des dipyrrines, *F*-BODIPY, formation de dipyrrométhane, assistée par mico-ondes.

Introduction

Dipyrrins present a useful ligand scaffold, with significant interest being devoted to dipyrrinato complexes of transition metals and boron.[1,2] There are limited reports regarding the chemical manipulation of dipyrrins, and indeed, one strategy that is often used to overcome the problems associated with the relative instability of free-base dipyrrins involves protection by means of complexation, particularly with $-BF_2$, thus giving rise to *F*-BODIPYs (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes).[3–5] *F*-BODIPYs have been a popular research focus in recent times due to the many applications of these compounds courtesy of their stability and intense fluorescence.[6] For example, *F*-BODIPYs have been used as dyes to label proteins[7–10] and DNA.[11–13] We herein report upon the reduction of *F*-BODIPYs and dipyrrins to the corresponding dipyrromethanes using an alcohol as the REDOX partner.

Results and discussion

Preliminary observations

For an ongoing project involving the dipyrrinato framework, we required an *F*-BODIPY featuring an ester to react with an alcohol. Given a report that tris[5-(4-methoxycarbonylphenyl)-dipyrrinato]Co(III) was hydrolyzed to its carboxylate and then esterified via the acyl chloride,[14] we utilized the analogous *F*-BODIPY **1** that features an ester at the 4-position of the *meso*-phenyl group. To replace the electrophilic methyl carboxylate functionality with a nucleophilic hydroxyl group, **1** was reacted with excess ethylene glycol with the expectation that the corresponding ester **2** would be produced. Instead, under microwave-assisted transesterification conditions,[15] and using NaOMe as the base, dipyrromethane **3** was produced with no traces of the anticipated *F*-BODIPY **2** or the corresponding dipyrrin (Scheme 1). Given that the dipyrromethane **3** is likely produced via reduction of the corresponding dipyrrin, following removal of the $-BF_2$ moiety, we further investigated this reaction to gain an understanding of its scope, limitations, and REDOX partner.

Generation of dipyrromethanes

To the best of our knowledge, there are no reports of dipyrromethanes being produced via the reduction of *F*-BODIPYs. However, there is reference to the removal of other metal ions from dipyrrinato complexes, followed by reduction of the resulting dipyrrin, using $NaBH_4$.[16] Indeed, dipyrrins may be reduced to dipyrromethanes via hydrogenolysis (H_2/Pd) or through the use of $NaBH_4$, although most reported examples feature a stabilizing group either in the way of a *meso*-aryl substituent or an alpha carbonyl group.[17–19] Related systems such as biliverdins[20–23] are routinely reduced to bilirubins upon reaction with $NaBH_4$: similarly, tripyrrenes may be reduced to tripyrranes,[24] and conjugated tetrapyrrolic systems may be reduced to the corresponding phlorins.[25,26] There is one example of a dipyrrin reacting with $BH_3{\cdot}SMe_2$ to form a dipyrrinato–BH_2 adduct that isomerizes to effectively deliver hydride to the *meso*-position, thus generating a –BH complex of a dipyrromethane.[27] Although shaking an organic solution of a dipyrrin with an aqueous solution of sodium dithionite removes the colour of the dipyrrin (and hence, dipyrromethane formation is assumed), we report herein that the strategy does not give a reasonable yield of the anticipated dipyrromethane. When **6** was exposed to an aqueous/THF solution[10] of sodium dithionite, the respective dipyrromethane **5** was isolated in only 10% yield, alongside significant decomposition products including an unstable tetrapyrrolic material. When **6** was shaken with dithionite (phosphate buffered, aqueous $Na_2S_2O_4$ pH 7.0/CH_2Cl_2), comparable results were obtained. Complete conversion of the dipyrrin to baseline material was observed within 20 min (TLC analysis) with dilute solutions of aqueous dithionite (0.2 mol/L), and the use of saturated aqueous dithionite solution resulted in complete decomposition within 5 min.

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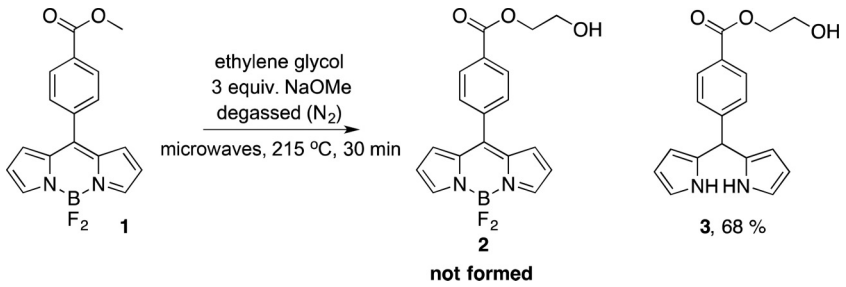
Scheme 1. Reaction of **1** with ethylene glycol.



We first wanted to assess the general scope of the production of dipyrromethanes via reduction using our new methodology. Working with the unfunctionalized system, *F*-BODIPY **4** was found to generate 5-phenyldipyrromethane (**5**) upon treatment with ethylene glycol and NaOMe (Scheme 2), indicating that the ester functionality of **1** is unnecessary for the curious reduction of the dipyrrinato unit to the dipyrromethane. More interestingly, the free-base dipyrrin (**6**) evidently also serves as a substrate for the reduction. Given our recent work using alkoxides to remove the $-BF_2$ moiety from *F*-BODIPYs,[28,29] presumably the initial transformation of **4** involves decomplexation followed by reduction of the resultant dipyrrin.

To verify that the product was stable under the reaction conditions, dipyrromethane **5** was submitted to the microwave-assisted conditions in ethylene glycol, with and without NaOMe. These reactions yielded essentially quantitative return of the dipyrromethane.

Solvent effects

With the goal being to identify both the optimum reaction conditions as well as the REDOX partner for the reduction of **6**, we explored the use of several solvents and compared their effectiveness with that of ethylene glycol (Table 1). The use of 2-methoxyethanol, under identical conditions to those used previously, returned a comparable yield of the dipyrromethane **5** (compare entries 1 and 2). However, the use of 1,2-dimethoxyethane (DME) (entry 3) resulted in only decomposition products: clearly the solvent choice is crucial for the success of the reaction, with a hydroxyl functionality being essential for reduction of the dipyrrin to the dipyrromethane. The use of simple alcohols was largely unsuccessful (entries 4 and 5), perhaps due to the fact that solvents with lower boiling points tended to reach elevated system pressures during the reactions, promoting decomposition. Pleasingly, the use of benzyl alcohol (entry 6) resulted in the production of dipyrromethane **5** in acceptable yield, as did the use of 4-methoxybenzyl alcohol (entry 7).

Maintaining the use of ethylene glycol, we also explored the effects of reducing the amount of NaOMe. Using 1 and 2 equiv. of NaOMe resulted in slightly lower yields of **5** compared with the use of 3 equiv.; furthermore, significantly lower yields were obtained if substoichiometric amounts of NaOMe were employed. Consequently, we maintained our use of 3 equiv. of NaOMe for the remainder of our investigations.

We next investigated the role of water in the reaction. Using ^{1}H NMR spectroscopy and a relaxation time of 15 s, we confirmed the <0.2% water content of commercial anhydrous ethylene glycol by spiking with a known quantity of water and comparing the quantitative integrals of the –O*H* signals.[30] Given the hygroscopic properties of ethylene glycol, we similarly determined that our reagent-grade ethylene glycol contained 1.3% water. Anhydrous ethylene glycol and anhydrous reaction conditions were subsequently employed for the transformation of **6** to **5**. Furthermore, two parallel reactions were run whereby reactions using anhydrous ethylene glycol were doped with 10 and 100 equiv. of water, respectively: the yields remained consistent throughout all three experiments and matched the yield obtained when reagent-grade (i.e., 1.3% water, wet) ethylene glycol was used. As such, we concluded that water does not play a significant role in the reaction and that precautions to exclude water from the reaction mixture are unnecessary.

Effects of temperature and time

In an effort to reduce both the temperature and time required for reduction of the dipyrrin to the dipyrromethane, we evaluated the effects of varying these reactions conditions (Table 2). The time was successfully reduced to 10 min, with a slightly elevated yield of **5** compared with that seen after 30 min (compare entries 1 and 3). Further reducing the reaction time returned a lower yield (entry 4). Employing the optimized 10 min reaction time and reducing the temperature from 215 °C resulted in significantly lower yields despite consumption of the dipyrrin (entries 5 and 6): this implies that decomposition competes with the production of the desired dipyrromethane. As such, the optimized reaction conditions emerged as 215 °C for 10 min.

Exploring substrate scope

Satisfied that we had identified a reasonable set of reaction conditions, we then explored the scope of the substrate. In particular, we were interested in whether other *meso*-aryl functionalities would be tolerated and also whether *meso*-unsubstituted (i.e., *meso*-H) *F*-BODIPYs and dipyrrins would undergo reduction as per their *meso*-aryl-substituted counterparts. Furthermore, we were interested in the influence of substituents about the pyrrolic units.

First, we investigated *F*-BODIPYs bearing a variety of substituted phenyl groups at the *meso*-position (Table 3). Both electron-withdrawing and electron-donating moieties were tolerated (entries 2–7). The requisite dipyrromethanes were obtained in moderate yields in all cases except for the 4-nitro derivative (entry 8), which presumably undergoes decomposition facilitated by the nitro functionality. Nevertheless, the use of aryl halides, aryl amines, and aryl ethers all returned good yields of the corresponding *meso*-aryl dipyrromethanes.

A series of *meso*-unsubstituted substrates (**13–17**, Fig. 1) were also explored using the optimized reaction conditions (10 min, 215 °C, microwaves, 3 equiv. of NaOMe, ethylene glycol): these substrates all featured alkyl chains and functional groups on the pyrrolic units. These *meso*-H *F*-BODIPYs yielded only decomposition products under the reaction conditions: dipyrromethane was not obtained. As the *meso*-phenyl substituent seems to offer stability to the dipyrrolic unit, substrates **18** and **19** were also investigated: these *F*-BODIPYs feature a *meso*-phenyl group as well as substituents about the pyrrolic framework. These two substrates also yielded decomposition products under the reaction conditions, as did the analogue **20** that is unsubstituted adjacent to the *meso*-position. Of course, alkyl-substituted dipyrromethanes are prone to auto-oxidation (to the dipyrrins), but nevertheless, we saw no sign of these compounds.

The scope of this reduction of *F*-BODIPYs and dipyrrins to the corresponding dipyrromethanes is thus limited to dipyrrinato units that are unsubstituted about the dipyrrolic framework and that feature an aryl group at the *meso*-position.

Scheme 2. Production of 5-phenyldipyrromethane (**5**).

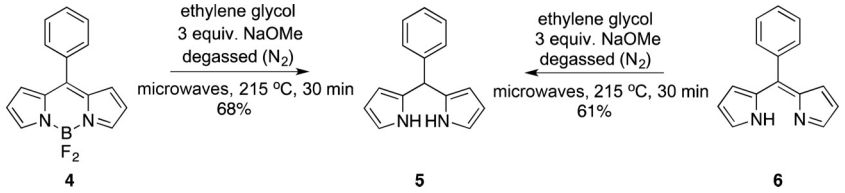


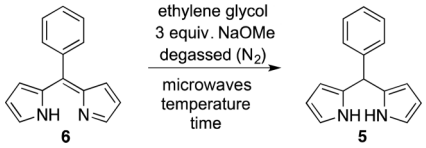
Table 1. The role of the solvent in the reduction of **6**.

Entry	Solvent	Isolated yield (%)
1	Ethylene glycol	68
2	2-Methoxyethanol	59
3	DME	0[a]
4	Ethanol	0[a]
5	*n*-Butanol	0[a]
6	Benzyl alcohol	59
7	4-Methoxybenzyl alcohol	47

Note: Reaction conditions: 30 min, 215 °C, microwaves, 3 equiv. of NaOMe, solvent.

[a]Only decomposition products observed.

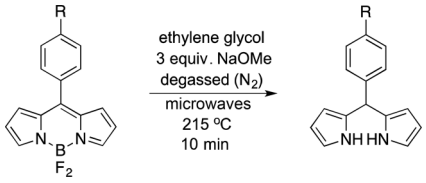
Table 2. The effects of temperature and time on consumption and yield.



Entry	Time (min)	Temperature (°C)	Consumption of **6** (%)[a]	Isolated yield of **5** (%)
1	30	215	100	61
2	20	215	100	63
3	10	215	100	71
4	5	215	89	54
5	10	200	80	34
6	10	150	5	2

[a]Obtained from the ratio of **6** to **5** via integration of NMR signals.

Table 3. Deprotection and reduction of *meso*-aryl *F*-BODIPYs.



Entry	R	Isolated yield (%)
1	–H (**4**)	68
2	–COOMe (**1**)	68
3	$-CF_3$ (**7**)	53
4	$-CH_3$ (**8**)	63
5	$-OCH_3$ (**9**)	76
6	–Br (**10**)	61
7	$-NMe_2$ (**11**)	47
8	$-NO_2$ (**12**)	0[a]

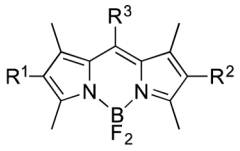
[a]Only decomposition products observed.

Probing the REDOX partner

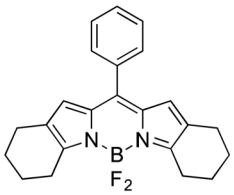
Since the reaction results in reduction of a dipyrrin to a dipyrromethane, we sought to identify the concomitant REDOX partner: we hypothesized that ethylene glycol was being oxidized to generate 2-hydroxyacetaldehyde (glycolaldehyde).[31] Similarly, when benzyl alcohol was used as solvent, benzaldehyde would be produced. As such, we anticipated that the addition of 2,4-dinitrophenylhydrazine (2,4-DNPH)[32] would lead to formation of the yellow 2,4-DNP hydrazone. After our optimized microwave irradiation of **6** and NaOMe in ethylene glycol, solutions of 2,4-DNPH (2.5 and 80 equiv.)[33] in acidic methanol were added directly to the reaction mixture: the respective hydrazone was not detected, even after heating to 65 °C.[34] Likewise, in trying to identify the REDOX partner for the reduction in ethylene glycol, matters are complicated by the fact that glycolaldehyde has been reported to be a product of the air-oxidation of ethylene glycol at high temperatures.[35] Furthermore, glycolaldehyde is a better reducing agent than ethylene glycol, as demonstrated by its use in the polyol synthesis of metal colloids.[36] However, our reaction protocol incorporates a degassing step to remove oxygen from the reaction mixture, and so we are confident that significant concentrations of glycolaldehyde are not generated via this alternative mechanism.

Regardless, when benzyl alcohol was used as solvent, the addition of 2,4-DNPH to the reaction mixture post-microwave irradiation of **6** resulted in the formation of 1-benzylidene–2-(2,4-dinitrophenyl)hydrazone in 66% isolated yield, alongside an equivalent yield of the requisite dipyrromethane **5**. In a parallel reaction, without 2,4-DNPH, column chromatography enabled the isolation of benzaldehyde in a comparable yield. As such, we hypothesize that the alcohol effectively transfers hydrogen to the dipyrrinato core under the reaction conditions. Of course, given the high temperatures and the presence of base, interference via a Cannizzaro-type hydride transfer cannot be ruled out once some benzaldehyde has formed.

Fig. 1. Further investigation into substrate tolerance.



13: $R^1 = R^2 =$ ethyl, $R^3 = H$
14: $R^1 = R^2 = (CH_2)_3OH$, $R^3 = H$
15: $R^1 = R^2 =$ *n*-pentyl, $R^3 = H$
16: $R^1 = CH(OH)CF_3$, $R^2 =$ ethyl, $R^3 = H$
17: $R^1 = H$, $R^2 =$ *n*-hexyl, $R^3 = H$
18: $R^1 = R^2 =$ Et, $R^3 =$ phenyl
19: $R^1 = R^2 =$ Et, $R^3 =$ methoxycarbonylphenyl



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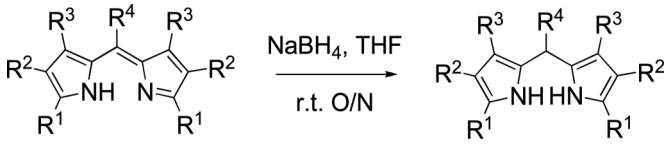
Mechanistic insight

To draw some parallel between our methodology and the reduction of dipyrrins via hydride delivery, dipyrrins **6**, **21**, **22**, and **22·HBr** were reacted with $NaBH_4$ (Table 4).

Meso-phenyl substrates were successfully reduced (unoptimized, entries 1 and 2), although the alkyl-substituted dipyrromethane obtained from **21** readily oxidizes in air and so isolation is fraught with the practicalities of timeliness and maintaining oxygen-free conditions during chromatography, both of which likely contribute to the rather low yield. Reactions involving *meso*-H dipyrrins (entries 3 and 4) were unsuccessful, presumably due to this position being both less electrophilic and less able to afford resonance

Table 4. Reduction of dipyrrins using $NaBH_4$.



Entry (compound)	R¹	R²	R³	R⁴	Isolated yield (%)
1 (**6**)	H	H	H	Ph	60
2 (**21**)	Me	Et	Me	Ph	20[a]
3 (**22**)	Me	Et	Me	H	0[b]
4 (**22·HBr**)	Me	Et	Me	H	0[b]

[a]Dipyrromethane product auto-oxidizes to dipyrrin; compound isolated under N_2.

[b]Complete return of starting material.

stabilization to the consequent intermediate upon hydride attack. Based on the similar reactivity of dipyrrin **6** and *F*-BODIPY **4** in our reductive methodology ($(CH_2OH)_2$, NaOMe), we were surprised that a very low product yield, alongside decomposition products, was observed when **4** was reacted with $NaBH_4$.

To further investigate the mechanism of reduction, and to probe for an intermediate tertiary radical, 10 equiv. of 2-propanol-2-D_1 was added to a reaction mixture featuring **6**, ethylene glycol, and NaOMe. No deuterated product was observed and the 71% yield of the undeuterated dipyrromethane (**5**) was consistent with reactions conducted in the absence of 2-propanol. Our mechanistic hypothesis thus leans towards a more reasonable formal hydride-transfer approach. When deuterated ethylene glycol ($DOCH_2CH_2OD$) was employed as a solvent under the optimized conditions, incorporation of deuterium occurred throughout the dipyrrolic framework and mirrored that of deuterium incorporation via hydrogen/deuterium exchange, as previously noted for pyrroles.[37] Consequently, deuterated benzyl alcohol was used to track the fate of deuterium incorporation from the alcohol. When **6** was reacted with NaOMe in benzyl alcohol-OD-d_1[38] (BnOD), incorporation of deuterium was not observed. However, when benzyl alcohol-d_2[39] ($PhCD_2OH$) was used as the solvent, ^{1}H NMR spectroscopy revealed that incorporation of deuterium occurred solely at the *meso*-position, as expected if formal hydride delivery occurs via nucleophilic attack at the *meso*-position. We similarly observed selective *meso*-D incorporation when **6** was reacted with $NaBD_4$ in ethylene glycol.

In all, our preliminary investigations resulted in evidence that supports our mechanistic hypothesis. We present this work as both a useful method to prepare select dipyrromethanes and a caution with regard to a previously unobserved reaction of dipyrrins.

Conclusions

In conclusion, it has been demonstrated that *meso*-aryl *F*-BODIPYs and dipyrrins undergo reduction to produce the corresponding dipyrromethane in basic, microwave-assisted conditions in the presence of excess ethylene glycol, benzyl alcohol, 4-methoxybenzyl alcohol, or 2-methoxyethanol. The REDOX partner appears to be the hydroxyl-containing solvent, thus generating the corresponding aldehyde. Although the formation of dipyrromethanes via the condensation of pyrrole with aryl aldehydes can be high-yielding,[40] a viscous and difficult-to-manipulate reaction mixture is often received and this is complicated by the fact that pyrrole is often used as the reaction solvent.[41–43] Alternatively, making *F*-BODIPYs can be a simple one-pot process:[4,44] the method described in this article can therefore be used as a strategy by which to produce dipyrromethanes via the respective *F*-BODIPY.

Experimental section

General experimental

All ^{1}H and ^{13}C NMR spectra were obtained using a 500 MHz NMR spectrometer (operating at 500 and 125 MHz, respectively) and $CDCl_3$ as solvent. Chemical shifts were recorded in parts per million (ppm) with reference to $CDCl_3$ (^{1}H NMR at 7.26 ppm, ^{13}C NMR at 77.16 ppm). ^{11}B{^{1}H} NMR spectra were obtained using a 500 MHz NMR instrument (operating at 160 MHz). Coupling constants (*J*) are reported in units of hertz (Hz). High- and low-resolution ESI$^+$ mass spectra were recorded using a microTOF instrument. All microwave-promoted reactions were performed using a Biotage Initiator 8 laboratory microwave apparatus, 0–400 W power, 2.45 GHz. Column chromatography was performed using Silicycle 230–400 mesh ultrapure silica or Brockman (III) basic alumina, as indicated. The following compounds were prepared according to literature procedures: 5-(4-methoxycarbonylphenyl) phenyldipyrrin,[14] 5-(4-trifluoromethyl)phenyldipyrromethane,[45] 1,3,7,9-tetramethyl-2,8-dipentyl-dipyrrin·HBr,[46] **4**,[47] **8**,[48] **9**,[49] **10**,[50] **11**,[50] **12**,[48] **13**,[28] **15**,[46] **16**,[29] **17**,[29] **18**,[29] and **19**.[51] Measurements for the crystal structure of **1** were made using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated M_o-K_α radiation. The structures were solved by direct method[52] and expanded using Fourier techniques.[53] The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Calculations were performed using the CrystalStructure[54,55] crystallographic software package.

General procedure (GP1) for the synthesis of *F*-BODIPYs

The appropriate dipyrrin or HBr dipyrrin salt was treated with 6 equiv. of NEt_3 and 9 equiv. of $BF_3{\cdot}OEt_2$ while stirring at room temperature in anhydrous dichloromethane (~0.04 mol/L). Upon complete consumption of the dipyrrin, according to analysis using TLC, the solvent was removed from the reaction mixture in vacuo. The crude dark red solid was dissolved in diethyl ether and washed twice with an equal volume of 1 mol/L HCl (to remove excess $BF_3{\cdot}OEt_2$) followed by distilled water and then brine. The organic fraction was then reduced in vacuo, and the compound was purified using column chromatography (silica). Removal of the organic solvent in vacuo gave the product as a red/orange solid.

General procedure (GP2) for the synthesis of *F*-BODIPYs

The appropriate dipyrromethane was treated with 1.1 equiv. of DDQ while stirring at room temperature in anhydrous dichloromethane (~0.12 mol/L). Upon complete consumption of the dipyrromethane, according to analysis using TLC (i.e., conversion to the dipyrrin, typically within 30–45 min), the reaction mixture was treated with 6 equiv. of NEt_3 and 9 equiv. of $BF_3{\cdot}OEt_2$. Upon complete consumption of the dipyrrin, according to analysis using TLC, the solvent was removed from the reaction mixture in vacuo. The crude dark red solid was dissolved in diethyl ether and washed twice with 1 mol/L HCl (equal parts, to remove excess $BF_3{\cdot}OEt_2$) followed by distilled water and then brine. The organic fraction was then reduced in vacuo, and the compound was purified using column chromatography (silica). Removal of the organic solvent in vacuo gave the product as a red/orange solid.

4,4-Difluoro-8-(4-methoxycarbonylphenyl)-4-bora-3a,4a-diaza-s-indacene (1)

Using GP1, the title compound was synthesized from 5-(4-methoxycarbonylphenyl)phenyldipyrrin (542 mg, 1.94 mmol) in 5.5 h. The title compound was isolated as a red solid (483 mg, 76% yield) after column chromatography (silica–DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.19 (d, 2H, *J* = 8), 7.96 (s, 2H), 7.64 (d, 2H, *J* = 8), 6.88 (d, 2H, *J* = 4), 6.56 (d, 2H, *J* = 4), 3.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.3, 145.9, 145.0, 138.1, 134.8, 132.3, 131.6, 130.5, 129.7, 119.1, 52.7. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ: 0.24 (t, *J* = 27.2). HRMS-ESI (*m*/*z*): $[M + Na]^+$ calcd. for $C_{17}H_{13}B_1F_2N_2O_2Na$: 349.0936; found:

349.0930. Crystal data for **1**: $C_{17}H_{13}N_2BF_2O_2$, MM = 326.11 g/mol, dark red needle, 0.90 mm × 0.33 mm × 0.15 mm; primitive triclinic, space group *P*1 (#2), *a* = 7.5380(7) Å, *b* = 7.8407(7) Å, *c* = 13.3682(7) Å, β = 77.62(4)°, *V* = 740.0(2) Å^3, *Z* = 2, ρ = 1.463 g/cm^3, μ(MoKα) = 1.127 cm^{-1}, 53727 reflections (20535 unique, R_{int} = 0.029), *R*(*F*) = 0.0350, *Rw*(*F*) = 0.0487, GOF = 0.933; CCDC 949267.

4,4-Difluoro-8-(4-trifluoromethylphenyl)-4-bora-3a,4a-diaza-s-indacene (7)

Using GP2, the title compound was synthesized from 5-(4-trifluoromethyl)phenyldipyrromethane (300 mg, 1.03 mmol). The title compound was isolated as a red solid (166 mg, 48% yield) after column chromatography (silica – 20% Et_2O/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (s, 2H), 7.77 (d, 2H, *J* = 8), 7.65 (d, 2H, *J* = 8), 6.83 (d, 2H, *J* = 4), 6.53 (d, 2H, *J* = 4). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.2, 137.4, 134.9, 132.9, 132.7, 131.6, 130.8, 130.1, 125.7, 119.3. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ: 1.20 (t, *J* = 27.5). HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd. for $C_{16}H_{10}B_1F_5N_2O_2Na$: 359.0755; found: 359.0749.

4,4-Difluoro-1,3,5,7-tetramethyl-2,6-di-3-hydroxypropyl-4-bora-3a,4a-diaza-s-indacene (14)

Using GP1, the title compound was synthesized from 1,3,7,9-tetramethyl-2,8-di(hydroxypropyl)-dipyrrin·HCl (450 mg, 1.29 mmol) in 3 h. The title compound was isolated as a red solid (90 mg, 18% yield) after column chromatography (silica – 5% MeOH/DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.92 (s, 1H), 3.62 (t, 4H), 2.46 (s, 6H), 2.43 (t, 4H), 2.14 (s, 6H), 1.64–1.70 (m, 4H), 1.24 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.6, 137.9, 133.0, 129.8, 119.4, 62.7, 33.4, 20.7, 13.2, 10.2. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ: 0.86 (t, *J* = 34.2). HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd. for $C_{19}H_{27}B_1F_2N_2O_2Na$: 387.2031; found: 387.2026.

***4,4-Difluoro-1,3,5,7-tetramethyl-2,6-dipentyl-4-bora-3a,4a-diaza-s-indacene (15)*[46]**

Using GP1, the title compound was synthesized from 1,3,7,9-tetramethyl-2,8-di(hydroxypropyl)-dipyrrin·HBr (250 mg, 0.59 mmol) in 4 h. The title compound was isolated as a red solid (122 mg, 71% yield) after column chromatography (silica–DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.94 (s, 1H), 2.48 (s, 6H), 2.34 (t, 4H), 2.15 (s, 6H), 1.40–1.46 (m, 4H), 1.27–1.36 (m, 8H), 0.90 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.0, 137.1, 132.6, 130.4, 118.7, 31.8, 30.0, 24.2, 22.7, 14.2, 12.8, 9.7. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ: 0.76 (t, *J* = 34.6). HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd. for $C_{23}H_{35}B_1F_2N_2Na$: 411.2759; found: 411.2754.

***4,4-Difluoro-1,3,5,7-tetramethyl–2,6-diethyl-8-(4-methoxycarbonylphenyl)-4-bora-3a,4a-diaza-s-indacene (19)*[51]**

Using GP2, the title compound was synthesized from 1,3,7,9-tetramethyl-2,8-diethyl-5-(4-methoxycarbonylphenyl)dipyrromethane (2.39 g, 6.10 mmol) stepwise. Following GP2, the dipyrrin formed in 45 min and was converted to the BODIPY in an additional 2 h. The title compound was isolated as a dark green solid (589 mg, 22% yield) after column chromatography (silica–DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.17 (d, 2H, *J* = 8), 7.40 (d, 2H, *J* = 8), 3.98 (s, 3H), 2.53 (s, 6H), 2.29 (q, 4H), 1.25 (s, 6H), 0.98 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.7, 154.4, 140.8, 138.8, 138.2, 133.2, 130.7, 130.4, 128.8, 52.5, 17.2, 14.7, 12.7, 12.0. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ: 0.65 (t, *J* = 33.3). HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd. for $C_{25}H_{29}B_1F_2N_2Na$: 461.2188; found: 461.2182.

5,5-Difluoro-11-phenyl-5-bora-4b,5adiaza-s-1,2,3,4,6,7,8,9-octahydroindeno[2,1-b]fluorene (20)

Tetrahydroindole (429 mg, 3.54 mmol) and benzoyl chloride (205 μL, 1.77 mmol) were heated and stirred at reflux temperature in anhydrous dichloroethane (55 mL) for 48 h. The solution was allowed to cool to room temperature, and then the in situ generated dipyrrin was treated with 6 equiv. of NEt_3 and 9 equiv. of BF_3·OEt_2. Upon consumption of the dipyrrin (monitored via TLC, 1 h), the solvent was removed from the reaction mixture in vacuo. The crude dark red solid was dissolved in diethyl ether and washed twice with 1 mol/L HCl (equal parts) to remove excess BF_3·OEt_2 followed by distilled water and then brine. The organic solvent volume was then reduced in vacuo, and the compound was purified using column chromatography (silica – 2% Et_2O/hexanes). Removal of the organic solvent in vacuo gave the title compound as a red/orange solid (106 mg, 16% yield). Upon NMR analysis, it was noted that the compound was not pure. Purification was attempted via column chromatography (silica – 10% EtOAc/hexanes, alumina – 10% DCM/hexanes): these attempts proved to be unsuccessful and the sample was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45–7.50 (m, 5H), 6.42 (s, 2H), 3.09 (t, 4H), 2.50 (t, 4H), 1.83–1.88 (m, 4H), 1.71–1.76 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.5, 141.1, 134.8, 133.9, 130.4, 129.7, 129.4, 129.3, 128.2, 126.6, 24.8, 23.3, 23.0, 22.5. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ: 0.58 (t, *J* = 32.6). HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd. for $C_{23}H_{23}B_1F_2N_2Na$: 399.1820; found: 399.1815.

General procedure (GP3) for the microwave-assisted deprotection and reduction of *F*-BODIPYs

F-BODIPY (50 mg) was added to a solution of NaOMe (3 equiv.) and ethylene glycol (3 mL). The reaction mixture was degassed by bubbling with N_2 for 15 mins, and then it was then heated and stirred at 215 °C for 10 min in a Biotage microwave system. The reaction mixture was dissolved in DCM (50 mL) and washed with water (50 mL × 3). The organic layer was dried with anhydrous Na_2SO_4, concentrated, and purified via column chromatography (alumina) to give a semisolid.

5-((4-(2-Hydroxy)ethoxycarboxy)phenyl)dipyrromethane (3)

Using GP3, the title compound was synthesized from 4,4-difluoro-8-(4-methoxycarbonylphenyl)-4-bora-3a,4a-diaza-*s*-indacene (**1**). The title compound was isolated as a dark semisolid (29 mg, 68% yield) after column chromatography (alumina – 0%–10% MeOH/DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12 (s, 2H), 7.99 (d, 2H, *J* = 8), 7.29 (d, 2H, *J* = 8), 6.72 (s, 2H), 6.15 (quintet, 2H), 5.88 (s, 2H), 5.53 (s, 1H), 4.45 (t, 2H), 3.95 (t, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.9, 147.9,131.7, 130.1, 128.60, 128.56, 117.7, 108.6, 107.6, 66.7, 61.4, 44.1. HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd. for $C_{18}H_{18}N_2O_3Na$: 333.1215; found: 333.1210.

5-Phenyldipyrromethane (5)

Using GP3, the title compound was synthesized from 4,4-difluoro-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (**4**). The title compound was isolated as a dark beige solid (28 mg, 68% yield) after column chromatography (alumina – 10% Et_2O/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (br s, 1H), 7.20–7.35 (m, 5H), 6.70 (d, 2H, *J* = 6), 6.17 (d, 2H, *J* = 7) 5.92 (d, 2H, *J* = 6), 5.48 (s, 1H). Data comparable with previously reported data.[40]

5-(4-Trifluoromethylphenyl)dipyrromethane

Using GP3, the title compound was synthesized from 4,4-difluoro-8-(4-trifluoromethylphenyl)-4-bora-3a,4a-diaza-*s*-indacene (**7**). The title compound was isolated as a dark beige semisolid (21 mg, 53% yield) after column chromatography (alumina–DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (s, 2H), 7.59 (d, 2H, *J* = 8), 7.35 (d, 2H, *J* = 8), 6.74 (s, 2H), 6.17 (s, 2H), 5.53 (s, 1H). Data comparable with previously reported data.[56]

5-(4-Methylphenyl)dipyrromethane

Using GP3, the title compound was synthesized from 4,4-difluoro-8-(4-methylphenyl)-4-bora-3a,4a-diaza-*s*-indacene (**8**). The title compound was isolated as a dark beige solid (26 mg, 63% yield) after column chromatography (alumina – 5%–10% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (s, 2H), 7.26 (d, 2H, *J* = 9), 6.80 (s, 2H), 6.30 (q, 2H), 6.06 (s, 2H), 5.56 (s, 1H), 2.49 (s, 3H). Data comparable with previously reported data.[40]

5-(4-Methoxyphenyl)dipyrromethane

Using GP3, the title compound was synthesized from 4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (**9**). The title

compound was isolated as a dark beige solid (34 mg, 76% yield) after column chromatography (alumina – 10% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (s, 2H), 7.14 (d, 2H, J = 9), 6.86 (d, 2H, J = 9), 6.68 (d, 2H, J = 4), 6.16 (d, 2H, J = 4), 5.92 (s, 1H), 3.80 (s, 3H). Data comparable with previously reported data.[40]

5-(4-Bromophenyl)dipyrromethane

Using GP3, the title compound was synthesized from 4,4-difluoro-8-(4-bromophenyl)-4-bora-3a,4a-diaza-*s*-indacene (**10**). The title compound was isolated as a dark beige solid (23 mg, 61% yield) after column chromatography (alumina – 10%–20% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (s, 2H), 7.44 (d, 2H, J = 9), 7.19 (d, 2H, J = 9), 6.70–6.72 (m, 2H), 6.17 (q, 2H), 5.87–5.91 (m, 2H), 5.43 (s, 1H). Data comparable with previously reported data.[56]

5-(4-Dimethylamino)dipyrromethane

Using GP3, the title compound was synthesized from 4,4-difluoro-8-(4-dimethylaminophenyl)-4-bora–3a,4a-diaza-*s*-indacene (**11**). The title compound was isolated as a dark beige solid (20 mg, 47% yield) after column chromatography (alumina – 10%–20% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (s, 2H), 7.09 (d, 2H, J = 9), 6.70 (d, 2H, J = 9), 6.66–6.72 (m, 2H), 6.16 (q, 2H), 5.93–5.96 (m, 2H), 5.39 (s, 1H), 2.94 (s, 6H). Data comparable with previously reported data.[57]

1-Benzylidene-2-(2,4-dinitrophenyl)hydrazone

After microwave irradiation (10 min, 215 °C) of 5-phenyldipyrrin (**6**) (50 mg, 0.23 mmol) and NaOMe (37 mg, 0.68 mmol) in benzyl alcohol (3 mL), a solution of 2,4-DNPH (2.5 equiv.) in acidic methanol (Brady's test, 25:1 MeOH/sulfuric acid) was added directly to the reaction mixture which was then stirred at room temperature for 3 h. The resulting yellow precipitate was isolated via suction filtration (35 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.32 (s, 1H), 9.16 (s, 1H), 8.37 (d, 1H, J = 10), 8.13 (d, 1H, J = 10), 8.09 (s, 1H), 7.75–7.80 (m, 2H), 7.46–7.50 (m, 3H). Data comparable with previously reported data.[58]

General procedure (GP4) for the reduction of dipyrrins to dipyrromethanes using $NaBH_4$

$NaBH_4$ (1 equiv.) was added under a flow of N_2 to a solution of dipyrrin (50 mg, 1 equiv.) in anhydrous THF (1.5 mL). The reaction mixture was stirred at room temperature overnight and then quenched with dilute aqueous HCl (30 mL). The resulting solution was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic phases were washed with water (90 mL) and brine (90 mL) and then dried over anhydrous Na_2SO_4 and the solvent removed in vacuo. Purification was achieved using column chromatography to produce a solid.

5-Phenyldipyrromethane (5)

Using GP4, the title compound was synthesized from 5-phenyldipyrrin (**6**) and isolated as a beige solid (30 mg, 60% yield) after column chromatography (silica–CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (br s, 2H), 7.20–7.35 (m, 5H), 6.70 (d, 2H, J = 6), 6.17 (d, 2H, J = 7) 5.92 (d, 2H, J = 6), 5.48 (s, 1H). Data comparable with previously reported data.[40]

2,8-Diethyl-1,3,7,9-tetramethyl-dipyrromethane[59]

Using GP4, the title compound was synthesized from 2,8-diethyl-1,3,7,9-tetramethyl-dipyrrin (**18**). The title compound was isolated as a pale pink solid (10 mg, 20% yield despite auto-oxidation upon running the column) after column chromatography (silica–CH_2Cl_2). HRMS-ESI (m/z): $[M + Na]^+$ calcd. for $C_{23}H_{30}N_2Na$: 357.2301; found: 357.2305. Note: this compound readily oxidizes to the corresponding dipyrrin (orange/red solid) and therefore, full characterization was not possible.

Sodium dithionite-mediated reduction[60]

5-Phenyldipyrrin (**6**, 50 mg, 0.227 mmol) was added under a flow of N_2 to a stirring solution of aqueous $Na_2S_2O_4$/THF (395 mg in 1 mL of H_2O and 3 mL of THF). The reaction mixture was allowed to stir at room temperature for 10 min, where the solvent was removed azeotropically using toluene (2 × 50 mL) and the resulting oil was separated between DCM (50 mL) and water (50 mL). The aqueous layer was extracted using DCM (50 mL × 2) and then the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was then purified over neutral Brockman III alumina – 10%–20% Et_2O/hexanes. 5-Phenyldipyrromethane was isolated as a beige solid (5 mg, 10% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (br s, 2H), 7.20–7.35 (m, 5H), 6.70 (d, 2H, J = 6), 6.17 (d, 2H, J = 7) 5.92 (d, 2H, J = 6), 5.48 (s, 1H). Data comparable with previously reported data.[40]

Supplementary data

Supplementary data (copies of NMR spectra) are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0341. CCDC 949267 contains the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 33603, e-mail: deposit@ccdc.cam.ac.uk).

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References

(1) Wood, T. E.; Thompson, A. *Chem. Rev.* **2007**, *107*, 1831. doi:10.1021/cr050052c.
(2) Wood, T. E.; Uddin, I. M.; Thompson, A. In *Handbook of Porphyrin Science*; Kadish, K. M., Smith, K., Guilard, R., Eds.; World Scientific: Singapore, 2010.
(3) Benstead, M.; Mehl, G. H.; Boyle, R. W. *Tetrahedron* **2011**, *67*, 3573. doi:10.1016/j.tet.2011.03.028.
(4) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. doi:10.1021/cr078381n.
(5) Ziessel, R.; Ulrich, G.; Harriman, A. *New J. Chem.* **2007**, *31*, 496. doi:10.1039/b617972j.
(6) Boens, N.; Leen, V.; Dehaen, W. *Chem. Soc. Rev.* **2012**, *41*, 1130. doi:10.1039/c1cs15132k.
(7) Karolin, J.; Johansson, L. B.-A.; Strandberg, L.; Ny, T. *J. Am. Chem. Soc.* **1994**, *116*, 7801. doi:10.1021/ja00096a042.
(8) Tan, K.; Jaquinod, L.; Paolesse, R.; Nardis, S.; Di Natale, C.; Di Carlo, A.; Prodi, L.; Montalti, M.; Zaccheroni, N.; Smith, K. M. *Tetrahedron* **2004**, *60*, 1099. doi:10.1016/j.tet.2003.11.072.
(9) Yee, M.-C.; Fas, S. C.; Stohlmeyer, M. M.; Wandless, T. J.; Cimprich, K. A. *J. Biol. Chem.* **2005**, *280*, 29053. doi:10.1074/jbc.M504730200.
(10) Wagner, R. W.; Lindsey, J. S. *Pure Appl. Chem.* **1996**, *68*, 1373. doi:10.1351/pac199668071373.
(11) Metzker, M. L.; Lu, J.; Gibbs, R. A. *Science* **1996**, *271*, 1420. doi:10.1126/science.271.5254.1420.
(12) Metzker, M. L. In *WO Patent*; Patent, W., Ed. 2003; Vol. WO/2003/066812.
(13) Wang, J.; Hou, Y.; Lei, W.; Zhou, Q.; Li, C.; Zhang, B.; Wang, X. *Chem. Phys. Chem.* **2012**, *13*, 2739. doi:10.1002/cphc.201200224.
(14) Brückner, C.; Zhang, Y.; Rettig, S. J.; Dolphin, D. *Inorg. Chim. Acta* **1997**, *263*, 279. doi:10.1016/S0020-1693(97)05700-9.
(15) Regourd, J.; Comeau, I. M.; Beshara, C. S.; Thompson, A. *J. Heterocycl. Chem.* **2006**, *43*, 1709. doi:10.1002/jhet.5570430645.
(16) Yu, L.; Muthukumaran, K.; Muthukumaran, K.; Sreedharan, P.; Lindsey, J. S. 2012, US2012/0126,214, US13/359,668.
(17) Brückner, C.; Karunaratne, V.; Rettig, S. J.; Dolphin, D. *Can. J. Chem.* **1996**, *74* (11), 2182. doi:10.1139/v96-245.
(18) Gossauer, A.; Engel, J. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. I, Chap. 7.
(19) Paine, J. B. III. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. I, Chap. 4.
(20) Boiadjiev, S. E.; Lightner, D. A. *Tetrahedron Asymmetry* **2001**, *12*, 2551. doi:10.1016/S0957-4166(01)00455-4.

(21) Boiadjiev, S. E.; Lightner, D. A. *J. Org. Chem.* **2003**, *68*, 7591. doi:10.1021/jo030091t.
(22) Holmes, D. L.; Lightner, D. A. *J. Heterocycl. Chem.* **1995**, *32*, 113. doi:10.1002/jhet.5570320120.
(23) Hölzl, M.; Klampfl, C.; Grubmayr, K. *Monatsh. Chem.* **2005**, *136*, 755. doi:10.1007/s00706-004-0269-4.
(24) Aoyama, Y.; Saita, K.; Toi, H.; Ogoshi, H. *Tetrahedron Lett.* **1987**, *28*, 4853. doi:10.1016/S0040-4039(00)96643-7.
(25) Krattinger, B.; Callot, H. J. *Tetrahedron Lett.* **1996**, *37*, 7699. doi:10.1016/0040-4039(96)01827-8.
(26) Setsune, J.; Ikeda, M.; Iida, T.; Kitao, T. *J. Am. Chem. Soc.* **1988**, *110*, 6572. doi:10.1021/ja00227a053.
(27) Bonnier, C.; Piers, W. E.; Al-Sheikh Ali, A.; Thompson, A.; Parvez, M. *Organometallics* **2009**, *28*, 4845. doi:10.1021/om900402e.
(28) Crawford, S. M.; Thompson, A. *Org. Lett.* **2010**, *12*, 1424. doi:10.1021/ol902908j.
(29) Smithen, D. A.; Baker, A. E. G.; Offman, M.; Crawford, S. M.; Cameron, T. S.; Thompson, A. *J. Org. Chem.* **2012**, *77*, 3439. doi:10.1021/jo3002003.
(30) Burton, I. W.; Quilliam, M. A.; Walter, J. A. *Anal. Chem.* **2005**, *77*, 3123. doi:10.1021/ac048385h.
(31) Butler, R. A.; De Lucia, F. C.; Petkie, D. T.; Mollendal, H.; Horn, A.; Herbst, E. *Astrophys. J. Suppl. Ser.* **2001**, *134*, 319. doi:10.1086/320859.
(32) Neuenfeldt, P. D.; Drawanz, B. B.; Siqueira, G. M.; Gomes, C. R. B.; Wardell, S. M. S. V.; Flores, A. F. C.; Cunico, W. *Tetrahedron Lett.* **2010**, *51*, 3106. doi:10.1016/j.tetlet.2010.04.026.
(33) Guan, X. R., E.; Anni, H. *Alcohol. Clin. Exp. Res.* **2012**, *36*, 398. doi:10.1111/j.1530-0277.2011.01612.x.
(34) Anderson, S. E.; Wells, J. R.; Fedorowicz, A.; Butterworth, L. F.; Meade, B. J.; Munson, A. E. *J. Toxicol. Sci.* **2007**, *97*, 355. doi:10.1093/toxsci/kfm043.
(35) Skrabalak, S. E.; Wiley, B. J.; Kim, M.; Formo, E. V.; Xia, Y. *Nano Lett.* **2008**, *8*, 2077. doi:10.1021/nl800910d.
(36) Xiong, Y.; Washio, I.; Chen, J.; Cai, H.; Li, Z.-Y.; Xia, Y. *Langmuir* **2006**, *22*, 8563. doi:10.1021/la061323x.
(37) Muir, D. M.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1316. doi:10.1039/P29750001316.
(38) Kang, P.; Bobyr, E.; Dustman, J.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Stack, T. D. P. *Inorg. Chem.* **2010**, *49*, 11030. doi:10.1021/ic101515g.
(39) Bejot, R.; Tisserand, S.; Li, D. R.; Falck, J. R. *Tetrahedron Lett.* **2007**, *48*, 3855. doi:10.1016/j.tetlet.2007.03.150.
(40) Rohand, T.; Dolusic, E.; Ngo, T. H.; Maes, W.; Dehaen, W. *Arkivoc* **2007**, 307. doi:10.3998/ark.5550190.0008.a20.
(41) Laha, J. K.; Dhanalekshmi, S.; Taniguchi, M.; Ambroise, A.; Lindsey, J. S. *Org. Proc. Res. Dev.* **2003**, *7*, 799. doi:10.1021/op034083q.
(42) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427. doi:10.1016/S0040-4020(01)89282-6.
(43) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864. doi:10.1021/jo982452o.
(44) Wu, L.; Burgess, K. *Chem. Commun.* **2008**, 4933. doi:10.1039/B810503K.
(45) Temelli, B.; Unaleroglu, C. *Tetrahedron* **2006**, *62*, 10130. doi:10.1016/j.tet.2006.08.047.
(46) Yutanovaa, S. L.; Berezina, M. B.; Semeikinb, A. S.; Antinaa, E. V.; Gusevaa, G. B.; V'yugina, A. I. *Russ. J. Gen. Chem.* **2013**, *83*, 545. doi:10.1134/S1070363213030237.
(47) Lundrigan, T.; Baker, A. E. G.; Longobardi, L. E.; Wood, T. E.; Smithen, D. A.; Crawford, S. M.; Cameron, T. S.; Thompson, A. *Org. Lett.* **2012**, *14*, 2158. doi:10.1021/ol300681w.
(48) Cui, A.; Peng, X.; Fan, J.; Chen, X.; Wu, Y.; Guo, B. *J. Photochem. Photobiol., A* **2007**, *186*, 85. doi:10.1016/j.jphotochem.2006.07.015.
(49) Yu, C.; Jiao, L.; Yin, H.; Zhou, J.; Pang, W.; Wu, Y.; Wang, Z.; Yang, G.; Hao, E. *Eur. J. Org. Chem.* **2011**, 5460. doi:10.1002/ejoc.201100736.
(50) Lager, E.; Liu, J.; Aguilar-Aguilar, A.; Tang, B. Z.; Pena-Cabrera, E. *J. Org. Chem.* **2009**, *74*, 2053. doi:10.1021/jo802519b.
(51) Eggenspiller, A.; Takai, A.; El-Khouly, M. E.; Ohkubo, K.; Gros, C. P.; Bernhard, C.; Goze, C.; Denat, F.; Barbe, J. M.; Fukuzumi, S. *J. Phys. Chem. A* **2012**, *116*, 3889. doi:10.1021/jp300415a.
(52) Sheldrick, G. M. *SHELX97*, 1997.
(53) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *DIRDIF99*; The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
(54) Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W.; Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. *CRYSTALS Issue 11*; Chemical Crystallography Laboratory, Oxford, UK, 1999.
(55) *CrystalStructure 3.8: Crystal Structure Analysis Package*; Rigaku and Rigaku/MSC, 9009 New Trails Dr., The Woodlands, TX 77381, USA, 2000–2006.
(56) Temelli, B.; Unaleroglu, C. *Tetrahedron* **2006**, *62*, 10130. doi:10.1016/j.tet.2006.08.047.
(57) Verma, S.; Kumar, S.; Jain, S. L.; Sain, B. *Org. Biomol. Chem.* **2011**, *9*, 6943. doi:10.1039/c1ob05818e.
(58) Mohapatra, S. C.; Hundal, M. S.; Mathur, P. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2011**, *79*, 1634. doi:10.1016/j.saa.2011.05.024.
(59) Berini, C.; Minassian, F.; Pelloux-Leon, N.; Vallee, Y. *Tetrahedron Lett.* **2005**, *46*, 8653. doi:10.1016/j.tetlet.2005.10.061.
(60) Matsuo, T.; Ito, K.; Kanehisa, N.; Hayashi, T. *Org. Lett.* **2007**, *9*, 5303. doi:10.1021/ol7025087.