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Synthesis of Conjugated BODIPYs via the Wittig Reaction

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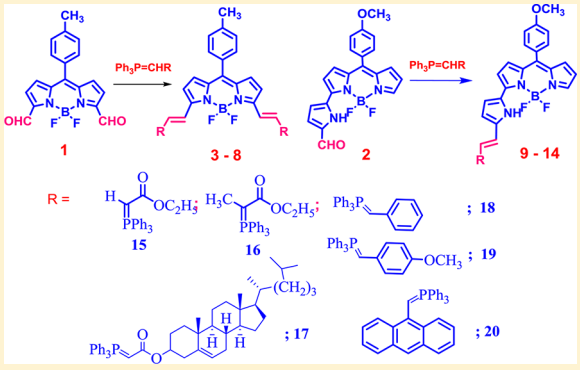
Supporting Information

ABSTRACT: A Wittig reaction was employed to synthesize conjugated BODIPYs in high yields by treating formylated BODIPYs with alkyl/aryl ylides under simple room temperature conditions. Treatment of 3,5-diformyl BODIPYs or α-formyl 3-pyrrolyl BODIPY with different alkyl/aryl ylides in CH_2Cl_2 at room temperature for 2 h followed by straightforward column chromatographic purification on silica afforded conjugated BODIPYs in ~65−90% yields. This is an alternate method to Knoevenagel and Heck reactions which have been used to synthesize such conjugated BODIPYs. The method works very efficiently, and we prepared 12 substituted BODIPYs including cholesterol-substituted BODIPYs to demonstrate the versatility of the reaction. The spectral, electrochemical, and fluorescence properties of these conjugated BODIPYs are also described.



INTRODUCTION

Among the numerous classes of highly fluorescent dyes, 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) is known to be a versatile and robust fluorophore due to its novel characteristic features and numerous useful applications. The novel features of BODIPY include the robustness against light and chemicals, the relatively high molar absorption coefficients and fluorescence quantum yields, negligible triplet formation, narrow emission bandwidths with high peak intensities, good solubility, resistance toward self-aggregation in solution,[1] excitation/emission wavelengths in the visible spectral region (>500 nm), and fluorescence lifetimes in the nanosecond range.[2] BODIPY dyes have been shown as promising for a variety of applications including biological labeling,[1,3] as electroluminescent devices, as tunable laser dyes,[4] as potential candidates for solid-state solar concentrators,[5] as fluorescent switches[6] and fluorophores in sensors, and as potential photosensitizers in photodynamic therapy of cancer.[1,7] Moreover, the spectroscopic and photophysical properties of BODIPYs can be fine-tuned by attachment of ancillary residues at the appropriate positions of the BODIPY core[8] by carrying out various synthetic reactions on BODIPYs. The various synthetic strategies available for the modification of the BODIPY core are electrophilic substitution,[9] condensation reactions,[10] substitution of the fluorine atoms,[11] direct substitution of the hydrogen atoms,[12] and transition-metal-catalyzed reactions through the use of halogenated systems.[13] Knoevenagel condensation is the popular approach used to date to obtain conjugated BODIPYs such as styryl-substituted BODIPYs, which absorb at long wavelengths.[14] Since the methyl-substituted BODIPYs are readily available and the methyl groups can be activated easily by reacting with aromatic aldehydes under Knoevenagel reaction conditions, Ziessel, Akkayya, and other research groups successfully prepared several monostyryl- to tetrastyryl-substituted BODIPYs.[14] Although the Knoevenagel condensation reaction is very convenient, the product yields are moderate and require longer reaction times. In addition to the Knoevenagel reaction, the conjugated BODIPY systems were also synthesized by using halogenated BODIPYs under Heck coupling conditions.[15,22] Alternate approaches to the above-mentioned two methods are highly desirable which allow us to synthesize new conjugated BODIPYs with interesting properties and applications. Recently, we reported 3,5-diformyl BODIPYs and demonstrated their use as a pH sensor,[16] cyanide sensor,[17] and for other applications.[18] The formyl groups at the BODIPY core are very useful functional groups to prepare a variety of BODIPY derivatives.[16−19] In this paper, we report the synthesis of conjugated BODIPYs by carrying out a reaction between formyl BODIPYs and alkyl or aryl ylides under the Wittig reaction conditions. Prior to this work, Rurack et al. synthesized extended pyrroles from 2-formyl pyrroles using Wittig conditions, and the extended pyrroles were then employed to synthesize conjugated BODIPYs.[20] Here, we used 3,5-diformyl BODIPY **1**[16] as well as α-formyl-substituted 3-pyrrolyl BODIPY **2**[21] to prepare conjugated BODIPYs including cholesterol-substituted BODIPYs **3**−**14**. The spectral, electrochemical, and photophysical properties of the conjugated BODIPYs **3**−**14** are also described.

RESULTS AND DISCUSSION

The key precursors, 3,5-diformyl BODIPY **1** and α-formyl 3-pyrrolyl BODIPY **2**, were prepared by following our reported

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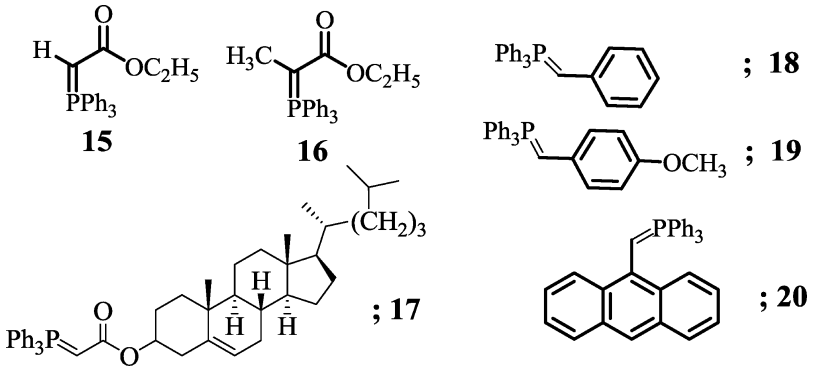
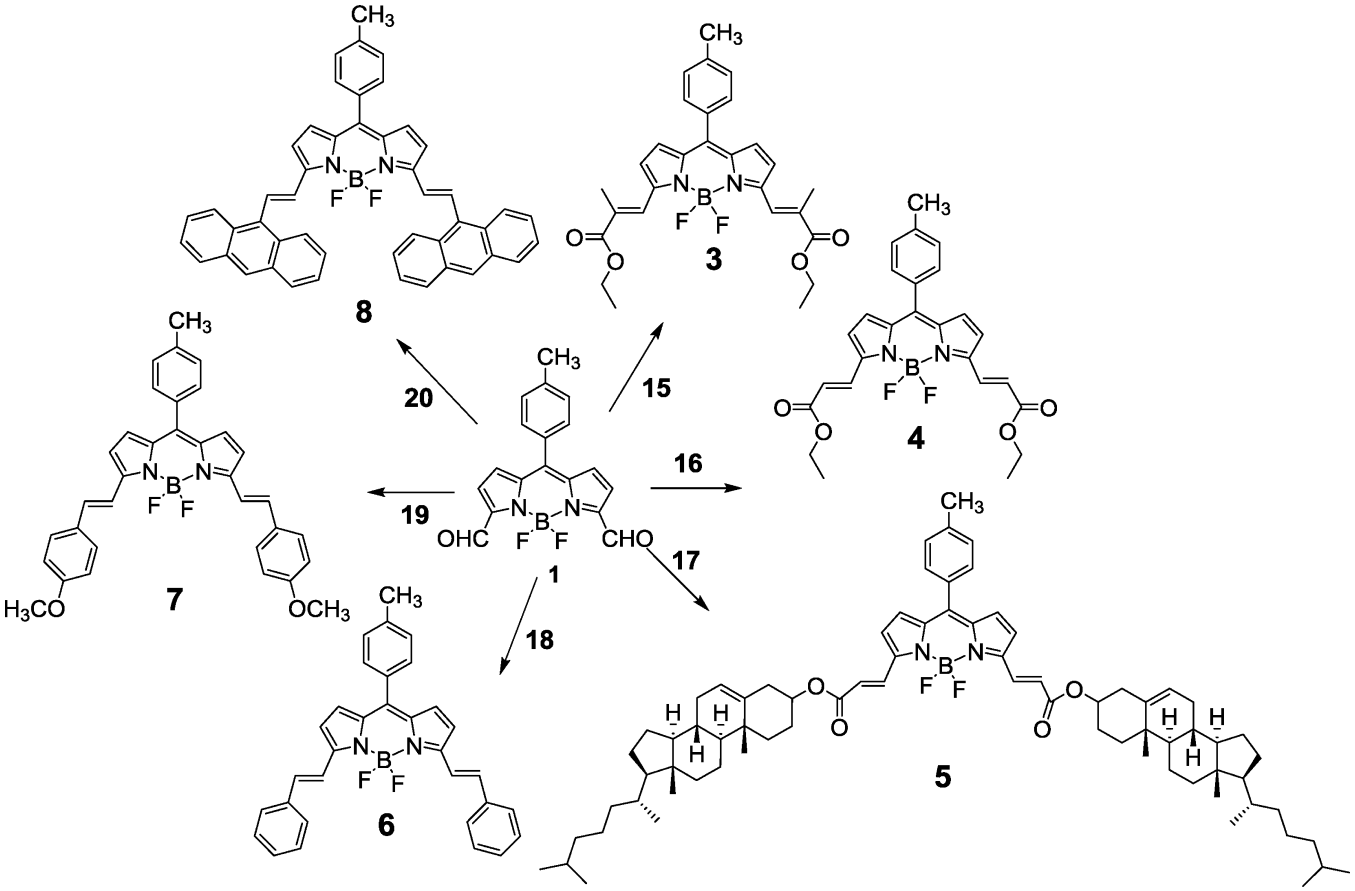
Chart 1. Different Types of Ylides



Scheme 1. Synthesis of Compounds 3−8



procedures.[16,21] The selected ylides **15**−**20** (Chart 1) were prepared by following the standard procedures.[22] The synthesis of various conjugated 3,5-disubstituted BODIPYs **3**−**8** prepared via the Wittig reaction is presented in Scheme 1. The reactions were carried out by treating 3,5-diformyl BODIPY **1** with an excess amount of appropriate ylide in CH_2Cl_2 at 0 °C, which was then slowly brought to room temperature and stirred for 2 h. The progress of the reaction was followed by TLC analysis, which showed the complete disappearance of the spot corresponding to compound **1** and appearance of one minor spot (R_f = 0.78) corresponding to the monosubstituted compound followed by a major spot corresponding to the desired disubstituted products (R_f = 0.53) **3**−**8**. The solvent was removed on a rotary evaporator, and the crude compound was subjected to silica gel column chromatography. The trace amount of monosubstituted product was removed first, and the desired products **3**−**8** were then collected as a major band. The solvent was removed on a rotary evaporator to afford the conjugated disubstituted BODIPYs **3**−**8** in 65−80% yields. All reactions worked smoothly and required simple column chromatographic purifications to afford the desired conjugated BODIPYs **3**−**8** in high yields. To show the versatility of the Wittig reaction, we prepared the dicholesterol-substituted BODIPY **5** under simple reaction conditions to afford 74% yield.

We extended the Wittig reaction approach to prepare conjugated substituted 3-pyrrolyl BODIPYs **9**−**14**, as shown in Scheme 2. All reactions were carried out by treating α-formyl 3-pyrrolyl BODIPY **2** with a slight excess of appropriate ylide under simple room temperature reaction conditions. The TLC

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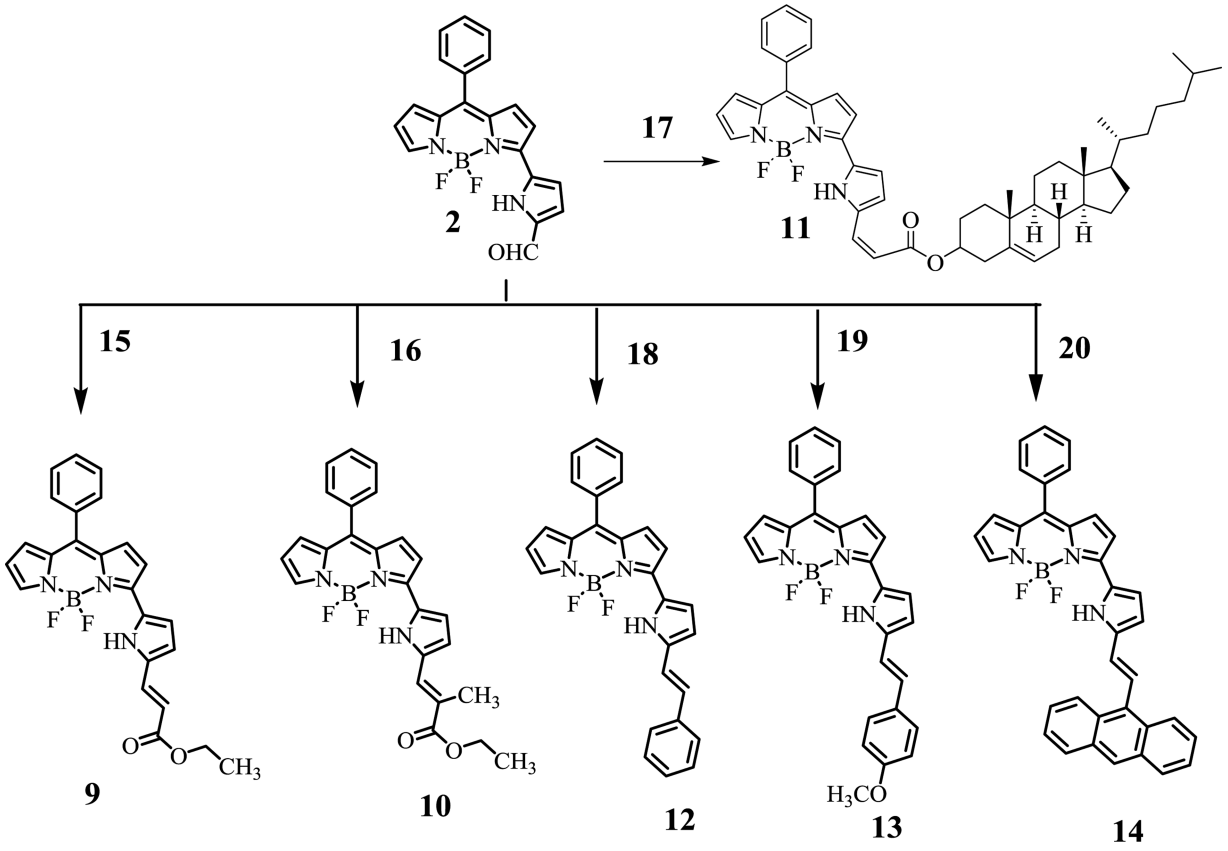
Scheme 2. Synthesis of Compounds 9−14



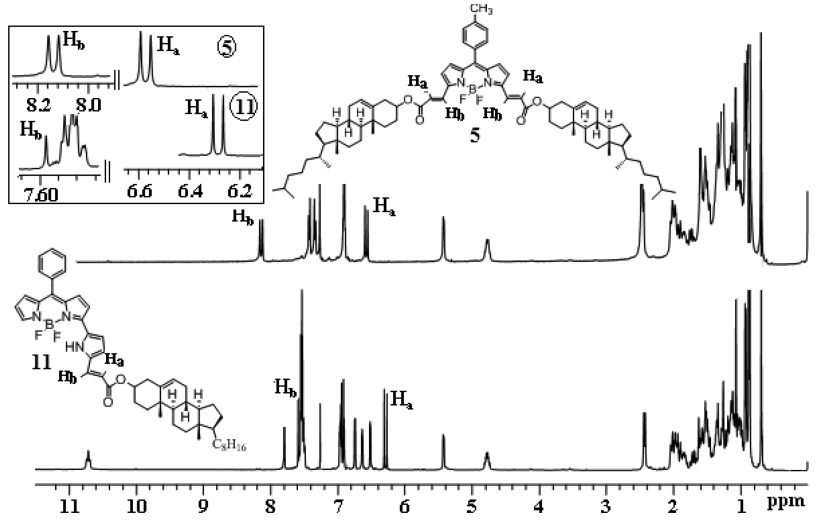


Figure 1. Comparison of ^{1}H NMR spectra of compounds **5** and **11**. The inset shows the expansion of H_a and H_b protons.

analysis clearly indicated the formation of desired products. Simple column chromatographic purification on silica of crude compounds afforded the desired substituted 3-pyrrolyl BODIPYs **9−14** as bluish solids in 75−90% yields. Thus, the conjugated 3,5-disubstituted BODIPYs **3−8** and α-pyrrolyl-substituted BODIPYs **9−14** can be obtained in good yields under simple Wittig reaction conditions.

All compounds are freely soluble in common organic solvents, and the identities of the compounds were confirmed by HRMS, ^{1}H, ^{19}F, and ^{11}B NMR spectroscopies. Figure 1 shows the ^{1}H NMR spectra of cholesterol-substituted BODIPY **5** and cholesterol-substituted 3-pyrrolyl BODIPY **11**. Compounds **5** and **11** showed NMR features of both constituted components. The main feature of these ^{1}H NMR spectra is the presence of two doublets (H_a and H_b) with a coupling constant of ∼17 Hz, which indicates the *trans* arrangement of the olefin in compounds **5** and **11**. Similar observations were made in all other compounds. This kind of *trans* configuration was also recently discussed by Akkayya and co-workers[14e] in styryl-substituted BODIPYs that were prepared by the Knoevenagel condensation reaction.

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Table 1. Photophysical Data of Compounds 1−14 Recorded in CH_2Cl_2

compound	λ_{abs} (nm)	log ε_{max} [b] ($mol^{-1}dm^3$ cm^{-1})	λ_{em} (nm)	$\Delta\nu_{st}$ (cm^{-1})	ϕ_f [c]	τ_f [d] (ns)	k_f (10^8 s^{-1})	k_{nr} (10^8 s^{-1})
1	546	4.09	556	329	0.31	5.9	0.53	1.17
4	590	4.61	601	310	0.38	3.82	0.99	1.62
3	595	4.97	610	414	0.67	6.85	1.17	0.48
5	593	4.93	604	307	0.72	6.23	1.16	0.45
6	635	4.99	650	363	0.46	6.42	0.72	0.84
7	656	4.98	679	516	0.22	7.16	0.31	1.09
8	643	4.46						
2	585	4.86	601	455	0.39	5.09	0.77	1.20
9	621	4.76	643	551	0.26	4.34	0.60	1.95
10	625	4.87	650	615	0.20	3.80	0.53	2.11
11	622	4.86	644	549	0.28	2.48	1.13	2.90
12	648	4.78	684	812	0.03	2.64	0.11	3.67
13	658	4.67	713	1173	0.009			
14	634	4.66	700[a]	1487				

[a]Excited at 350 nm. [b]Molar absorption (log ε_{max}, ±0.1). [c]Fluorescence quantum yields were measured using sulforhodamine in ethanol (ϕ, ±0.05). [d]Fluorescence lifetime (τ, ±0.05 ns).

Absorption, Electrochemical, and Fluorescence Properties. The absorption spectra of compounds **3**−**14** were studied in chloroform, and the data for all compounds are presented in Table 1. All compounds **3**−**14** exhibited typical strong $S_0 \rightarrow S_1$ transition with a vibronic component at the higher energy side with a maximum above 590 nm and a weaker, broad absorption band at a shorter wavelength corresponding to $S_0 \rightarrow S_2$ transition. Comparisons of absorption spectra of 3,5-diformyl BODIPY **2**, the dicholesterol-substituted BODIPY **5**, and distyryl-substituted BODIPY **6** are shown in Figure 2a. The 3,5-diformyl BODIPY **1** showed a

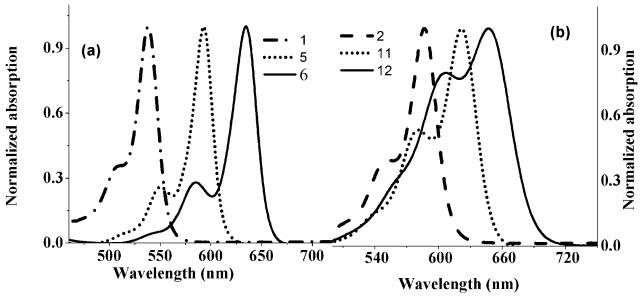

Figure 2. Comparison of normalized absorption spectra of compounds (a) **5** and **6** along with **1** and (b) **11** and **12** along with **2**.

$S_0 \rightarrow S_1$ transition at 546 nm, which was shifted to longer wavelengths in the Wittig products **3**−**8**. The absorption spectra of the alkyl-substituted BODIPYs **3**−**5** are bathochromically shifted by 45 nm, whereas the absorption spectra of more conjugated aryl-substituted BODIPYs **6**−**8** are bathochromically shifted by 90 nm compared to compound **1**. Similar observations were made in substituted 3-pyrrolyl BODIPYs. The comparison of absorption spectra of formylated 3-pyrrolyl BODIPY **2**, cholesterol-substituted 3-pyrrolyl BODIPY **11**, and styryl-substituted 3-pyrrolyl BODIPY **12** is shown in Figure 2b.

Here also the more conjugated styryl-substituted 3-pyrrolyl BODIPY **12** showed a more bathochromically shifted absorption band compared to cholesterol-substituted BODIPY **11**, which in turn showed a bathochromically shifted absorption band compared to formylated 3-pyrrolyl BODIPY **2**. Thus, absorption studies showed a bathochromically shifted absorption band due to an increase in the conjugation in the Wittig products **3**−**14**.

The electrochemical properties of compounds **3**−**14** were investigated by cyclic voltammetry and differential pulse voltammetry at a scan rate of 50 mV/s using tetrabutylammonium perchlorate as supporting electrolyte. A comparison of the first reduction wave of compounds **1**, **5**, and **6** is shown in Figure 3a and compounds **2**, **11**, and **12** are shown in Figure

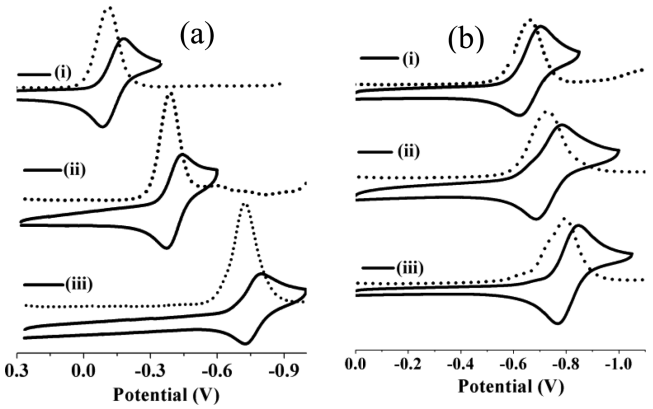

Figure 3. Comparison of first reduction waves of the cyclic voltammogram (solid line) and differential pulse voltammogram (dotted line) of compounds (a) (i) **1**, (ii) **5**, and (iii) **6**; (b) (i) **2**, (ii) **11**, and (iii) **12**.

3b, and the data for all compounds **1**−**14** are presented in Table 2. All compounds **1**−**14** exhibited ill-defined one or two oxidations and one reversible reduction and one irreversible reduction. The 3,5-diformyl BODIPY **1**, which is very electron-deficient due to the presence of formyl groups, showed two reversible reductions at −0.13 and −1.04 V.[12] However, in all disubstituted BODIPYs **3**−**8**, we observed one clear reversible reduction and one irreversible reduction that were shifted toward more negative potential, indicating that the disubstituted BODIPYs **3**−**8** are difficult to reduce compared to compound **1**. Furthermore, the diaryl-substituted BODIPYs **6**−**8** are relatively more difficult to reduce compared to dialkyl-substituted BODIPYs **3**−**5**, which is clearly evident from Figure 3a and data presented in Table 2. We also observed an irreversible oxidation and a quasi-reversible oxidation for only

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Table 2. Electrochemical Data of Compounds 1−14 in CH_2Cl_2 Containing 0.1 M TBAP as Supporting Electrolyte Recorded at 50 mV/s Scan Speed

	E_{ox} (V vs SCE)			
compound	I[a]	II	I	II[c]
1			−0.13	−1.04
3	1.46		−0.51	−1.30
4	1.46		−0.51	−1.30
5	1.52		−0.41	−1.18
6	1.03	0.50	−0.72	−1.55
7	1.16	0.88	−0.79	−1.62
8	1.33	0.80	−0.72	−1.71
2	1.37		−0.67	−1.56
9	1.33	1.06[b]	−0.69	−1.49
10	1.37	1.06[b]	−0.76	−1.55
11	1.32	1.05[b]	−0.71	−1.50
12		0.86	−0.76	−1.64
13	1.05	0.79	−0.81	−1.63
14	0.91	0.52	−0.74	−1.62

[a]Ill-defined oxidation. [b]Quasi-reversible. [c]Irreversible.

diaryl-substituted BODIPYs **6**−**8**. Thus, the diaryl-substituted BODIPYs **6**−**8** are relatively electron-rich compared to dialkyl-substituted BODIPYs **3**−**5**, which in turn possess more electron-rich nature compared to diformyl BODIPY **1**. Similar observations were also noted in alkyl/aryl-substituted 3-pyrrolyl BODIPYs **9**−**14** compared to formylated 3-pyrrolyl BODIPY **2** (Figure 3b).

The fluorescence properties of compounds **3**−**14** were investigated in CH_2Cl_2 by both steady-state and time-resolved fluorescence techniques. The comparison of fluorescence spectra of disubstituted BODIPYs **5** and **6** along with diformyl BODIPY **1** is shown in Figure 4a, and comparison of

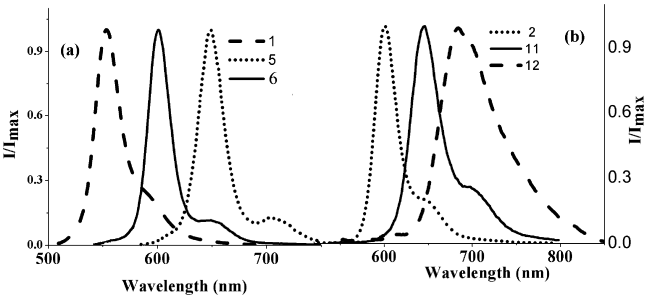

Figure 4. Comparison of normalized emission spectra of compounds (a) **5**, **6**, along with **1** and (b) **11**, **12**, along with **2**.

fluorescence spectra of substituted 3-pyrrolyl BODIPYs **11** and **12** along with α-formyl 3-pyrrolyl BODIPY **2** is shown in Figure 4b. The relevant fluorescence data are included in Table 1. Both diaryl-substituted BODIPYs **3**−**8** and substituted 3-pyrrolyl BODIPYs **9**−**14** showed bathochromically shifted fluorescence bands compared to their respective formylated BODIPYs **1** and **2**. The maximum red shifts in fluorescence bands were noted for aryl-substituted BODIPYs **6**−**8** and **12**−**14** due to extension of π-delocalization. Furthermore, the disubstituted BODIPYs **3**−**8** are strongly fluorescent with good quantum yields compared to diformyl BODIPY **1**. The photophysical data comparison of our compounds **6**[23] and **7**[24] with reported data on the same compounds indicated that the measured quantum yields in our case were lower, although all other photophysical parameters were in agreement. However, the substituted 3-pyrrolyl BODIPYs **9**−**14** are relatively more weakly fluorescent than α-formyl 3-pyrrolyl BODIPY **2** due to the flexible nature of compounds, which enhances the nonradiative decay pathways. In substituted BODIPYs **3**−**14**, the Stokes shifts are in the same range of their respective formylated BODIPYs **1** and **2**. The singlet state lifetimes were measured using the time-correlated single-photon counting (TCSPC) method. In general, all fluorescence decays were fitted to a single exponential (Supporting Information), and the fluorescence lifetimes varied between 3 and 7 ns. Thus, the fluorescence study indicated that the disubstituted BODIPYs **3**−**8** are highly fluorescent compounds, and the emission bands were shifted up to 700 nm with quantum yields of 0.3−0.7, supporting that the substituents presented directly at the BODIPY core assist in the enhancement in the fluorescence properties.

CONCLUSIONS

In summary, we used an alternate route to synthesize π-extended BODIPYs by treating BODIPYs containing formyl groups at the pyrrole carbons with alkyl/aryl ylides under simple room temperature with Wittig reaction conditions. These types of compounds were prepared earlier by Knoevenagel/Heck reaction by using BODIPYs containing methyl/halogen groups at the pyrrole carbons. The Wittig reaction requires mild reaction conditions and less reaction times and gives higher yields of products. We prepared a series of substituted conjugated BODIPYs including cholesterol-substituted BODIPYs under the Wittig reaction conditions. We hope that the Wittig method will be used in the future to synthesize π-extended BODIPYs for desired applications.

EXPERIMENTAL SECTION

General. All NMR spectra (δ values, ppm) were recorded with 300 or 400 MHz spectrometers. Tetramethylsilane (TMS) was used as an external reference for recording ^1H (of residual proton; δ = 7.26 ppm) and ^{13}C (δ = 77.0 ppm) spectra in $CDCl_3$. Chemical shift multiplicities are reported as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The HRMS spectra were recorded with a Bruker maxis impact 282001.00081 and Q-Tof micromass spectrometer using electron spray ionization method, TOF analyzer. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with an electrochemical system utilizing a three-electrode configuration consisting of a glassy carbon (working) electrode, platinum wire (auxiliary) electrode, and a saturated calomel (reference) electrode. The experiments were performed in dry CH_2Cl_2 with 0.1 M TBAP as the supporting electrolyte. Half-wave potentials were measured with DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated versus the saturated calomel electrode by the addition of ferrocene as an internal standard, taking $E_{1/2}$ (Fc/Fc^+) = 0.42 V vs SCE.[25] The quantum yields were calculated using sulforhodamine reference (Φ = 0.69 in ethanol, λ_{exc} = 530 nm).[26] All Φ values are corrected for changes in refractive index.

General Procedure for the Synthesis of Compounds 3, 4, 5, 9, 10, and 11. Samples of appropriate phosphine ylide (3 mmol) were added to the solution of compound **1** or **2** (1 mmol) in 30 mL of dichloromethane at 0 °C. The reaction mixture was allowed to stir at room temperature for 1 to 2 h. TLC analysis indicated the disappearance of the spot corresponding to starting precursor **1** or **2** and appearance of a new less polar spot corresponding to the desired product. The solvent was removed under reduced pressure, and the crude compound was purified by column chromatography on silica gel using petroleum ether/dichloromethane (80:20, v/v) to afford pure compounds as crystalline solids.

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4. Yield: 15.9 mg (71%). Mp 224 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.38 (t, J = 7.15 Hz, 6 H), 2.48 (s, 3 H), 4.31 (q, J = 7.09 Hz, 4 H), 6.58 (d, J = 16.14 Hz, 2 H), 6.91 (q, J = 4.40 Hz, 4 H), 7.34 (d, J = 7.78 Hz, 2 H), 7.42 (d, J = 8.04 Hz, 2 H), 8.15 (d, J = 16.14 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 14.3, 22.9, 61.2, 118.4, 125.6, 128.6, 128.8, 129.5, 130.7, 130.9, 131.3, 132.3, 133.3, 137.5, 152.6, 166.1. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −138.17 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm): 1.00 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{26}H_{25}BF_2N_2NaO_4$ 501.1772 (M + Na)$^+$, found 501.1768 (M + Na)$^+$.

3. Yield: 17 mg (80%). Mp 233 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.38 (t, J = 7.15 Hz, 6 H), 2.24 (s, 6 H), 2.46 (s, 3 H), 4.33 (q, J = 7.09 Hz, 4 H), 6.85 (d, J = 4.52 Hz, 2 H), 6.94 (d, J = 4.52 Hz, 2 H), 7.34 (d, J = 7.84 Hz, 2 H), 7.44 (d, J = 8.10 Hz, 2 H), 8.23 (s, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 14.4, 15.6, 21.6, 61.6, 121.6, 128.1, 129.4, 130.8, 130.9, 131.1, 134.4, 136.7, 141.3, 144.6, 152.7, 168.1. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −140.25 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm): 1.12 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{28}H_{29}BF_2N_2NaO_4$ 529.2086 (M + Na)$^+$, found 529.2081 (M + Na)$^+$.

5. Yield: 38 mg (74%). Mp 262.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.6−2.4 (m, 89 H), 6.52 (d, J 16.06 Hz, 2 H),6.90 (q, J = 4.27 Hz, 4 H),7.33 (d, J = 7.88 Hz, 2 H),7.42 (d, J = 8.03 Hz, 2 H),8.13 (d, J = 16.06 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 21.7, 22.5, 22.8, 22.9, 23.0, 24.0, 24.5, 28.0, 28.2, 28.4, 29.6, 29.8, 29.9, 32.1, 32.1, 36.0, 36.4, 36.8, 37.2, 38.3, 39.7, 39.9, 42.5, 50.2, 56.3, 56.9, 75.0, 118.4, 122.9, 126.0, 129.5, 130.7, 131.2, 133.2, 137.5, 139.8, 165.5. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −138.21 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.14 MHz, $CDCl_3$, δ ppm): 0.99 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{76}H_{105}BF_2N_2KO_4$ 1197.7779 (M + K)$^+$, found 1197.7761 (M + K)$^+$.

9. Yield: 18 mg (75%). Mp 207 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.36 (t, J = 6.97 Hz, 3 H), 4.29 (q, J = 6.85 Hz, 2 H), 6.30 (d, J = 15.89 Hz, 1 H), 6.50−6.52 (m, 1 H), 6.62−6.65 (m, 1 H), 6.75 (d, J = 2.69 Hz, 1 H), 6.89−7.02 (m, 3 H), 7.47−7.64 (m, 6 H), 7.79 (s, 1 H), 10.72 (br t, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 14.5, 60.8, 115.9, 116.1, 117.2, 119.1, 121.2, 126.9, 127.1, 128.5, 130.3, 130.7, 132.8, 132.9, 134.1, 134.4, 134.9, 137.9, 139.0, 141.3, 149.4. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −138.16 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.14 MHz, $CDCl_3$, δ ppm): 1.21 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{24}H_{20}BFN_3O_2$ 412.1633 (M − F)$^+$, found 412.1627 (M − F)$^+$.

10. Yield: 20 mg (81%). Mp 205 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.38 (t, J = 7.15 Hz, 3 H), 2.24 (s, 3 H), 4.30 (q, J = 7.31 Hz, 2 H), 6.50 (dd, J = 3.81, 2.23 Hz, 1 H), 6.66 (dd, J = 3.81, 2.23 Hz, 1H), 6.73 (d, J = 3.81 Hz, 1 H), 6.93−6.99 (q, J = 4.68 Hz, 2 H), 7.05 (dd, J = 3.81, 2.54 Hz, 1 H), 7.50−7.60 (m, 6 H), 7.75 (s, 1 H), 10.8 (br t, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 14.5, 14.6, 61.2, 116.8, 116.9, 119.4, 121.3, 126.3, 126.4, 127.3, 128.5, 130.2, 130.6, 132.9, 133.9, 134.5, 136.1, 138.0, 138.2, 140.6, 149.8, 168.5. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −140.36 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.14 MHz, $CDCl_3$, δ ppm): 1.03 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{25}H_{22}BFN_3O_2$ 426.1789 (M − F)$^+$, found 426.1790 (M − F)$^+$.

11. Yield: 29.4 mg (92%). Mp 230 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.6−2.4 (m, 43 H), 4.70−4.77 (m, 1H), 5.42 (d, J = 3.76 Hz, 1 H), 6.28 (d, J = 16.06 Hz, 1 H), 6.51 (dd, J = 3.89, 2.13 Hz, 1 H), 6.63 (dd, J = 3.89, 2.13 Hz, 1 H), 6.74 (d, J = 3.76 Hz, 1 H), 6.89−6.92 (m, 1 H), 6.93−6.98 (m, 3 H), 7.49−7.56 (m, 5 H), 7.59 (s, 1 H), 7.79 (s, 1 H), 10.71 (t, J = 10.04 Hz, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 12.0, 18.9, 19.5, 21.2, 22.7, 23.0, 24.0, 24.5, 28.1, 28.2, 28.4, 32.0, 32.1, 36.0, 36.4, 36.8, 37.2, 38.4, 39.7, 39.9, 42.5, 50.2, 56.3, 56.8, 74.3, 115.9, 116.6, 117.1, 119.2, 121.2, 122.9, 126.9, 127.0, 128.5, 130.3, 130.6, 132.7, 132.9, 134.1, 134.4, 135.0, 138.0, 138.9, 139.9, 141.2, 149.5, 166.5. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −140.28 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.14 MHz, $CDCl_3$, δ ppm): 1.22 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{49}H_{60}BF_2N_3O_2Na$ 794.4647 (M + Na)$^+$, found 794.4658 (M + Na)$^+$.

General Procedure for the Synthesis of Compounds 6, 7, 8, 12, 13, and 14. Sample of phosphonium salt (3 mmol) was dissolved in 20 mL of tetrahydrofuran (THF), and butyllithium (2.5 mmol) was added slowly at 0 °C under nitrogen atmosphere, and the reaction mixture turned from a white turbid color to red. The reaction mixture was allowed to stir for 30 min at the same temperature. The appropriate formylated BODIPY compound **1** or **2** (1 mmol) was added to the reaction mixture at 0 °C. The progress of the reaction was monitored by TLC, which showed the disappearance of the spot corresponding to the formylated BODIPY compound **1** or **2** and the appearance of one major spot corresponding to the desired compound. The solvent was removed on a rotary evaporator under vacuum. The crude compound was purified by silica gel chromatography with petroleum ether/ethyl acetate (95/5) and afforded the desired pure product as crystalline solids.

6. Yield: 15.9 mg (74%). Mp 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.47 (s, 3 H) 6.85 (d, J = 4.03 Hz, 2 H), 6.94 (d, J = 4.40 Hz, 2 H), 7.29−7.38 (m, 5 H), 7.39−7.48 (m, 6 H), 7.66 (d, J = 7.34 Hz, 4 H), 7.80 (d, J = 16.51 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 21.2, 116.4, 119.4, 127.7, 129.0, 129.2, 129.2, 129.6, 130.6, 131.6, 136.5, 136.8, 140.1, 140.3, 154.6. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −139.62 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm): 1.50 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{32}H_{25}BF_2N_2Na$ 509.1977 (M + Na)$^+$, found 509.1967 (M + Na)$^+$.

7. Yield: 16 mg (65%). Mp 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.46 (s, 3 H), 3.86 (s, 6 H), 6.80 (d, J = 4.36 Hz, 2 H), 6.89 (d, J = 4.40 Hz, 2 H), 6.94 (d, J = 8.64 Hz, 4 H), 7.27−7.30 (m, 6 H), 7.41 (d, J = 7.84 Hz, 2 H), 7.60 (d, J = 8.64 Hz, 4 H), 7.65 (d, J = 16.17 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 21.6, 55.6, 114.5, 116.0, 117.6, 129.2, 129.3, 129.5, 129.7, 130.6, 131.9, 136.2, 138.9, 140.1, 154.8, 160.7. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −139.99 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm): 1.48 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{34}H_{29}BF_2N_2O_2Na$ 569.2188 (M + Na)$^+$, found 569.2186 (M + Na)$^+$.

8. Yield: 20.1 mg (68%). Mp 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.52 (s, 3 H), 6.99 (d, J = 4.52 Hz, 2 H), 7.19 (d, J = 4.52 Hz, 2 H), 7.39 (d, J = 7.78 Hz, 2 H), 7.41−7.50 (m, 8 H), 7.52 (d, J = 7.78 Hz, 2 H), 7.66 (d, J = 16.31 Hz, 2 H), 7.98 (d, J = 7.78 Hz, 4 H), 8.27 (d, J = 16.56 Hz, 2 H), 8.35−8.42 (m, 6 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 21.7, 53.6, 116.4, 125.5, 125.8, 126.4, 128.0, 128.2, 128.9, 129.3, 129.9, 130.1, 130.7, 131.3, 131.6, 131.7, 133.1, 136.4, 140.6, 154.6. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −139.39 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm): 1.36 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{48}H_{33}BF_2N_2Na$ 709.2605 (M + Na)$^+$, found 709.2624 (M + Na)$^+$.

12. Yield: 19.9 mg (83%). Mp 193 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.48 (dd, J = 3.89, 2.13 Hz, 1 H), 6.56 (dd, J = 3.89, 2.13 Hz, 1 H), 6.65 (d, J = 3.51 Hz, 1 H), 6.91−6.96 (m, 2 H), 7.03−7.07 (m, 3 H), 7.30 (d, J = 7.28 Hz, 1 H), 7.38 (t, J = 7.53 Hz, 2 H), 7.49−7.58 (m, 8 H), 7.73 (s, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 112.3, 115.9, 117.7, 120.8, 121.7, 124.6, 126.7, 128.2, 128.4, 128.9, 129.5, 129.9, 130.6, 132.8, 136.3, 136.8, 138.3, 138.4, 139.4, 150.3. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −140.70 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm): 1.39 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{27}H_{20}BFN_3$ 416.1734 (M − F)$^+$, found 416.1734 (M − F)$^+$.

13. Yield: 22 mg (85%). Mp 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.85 (s, 3 H), 6.46−6.48 (m, 1 H), 6.52−6.54 (m, 1 H), 6.64 (d, J = 2.51 Hz, 1 H), 6.89−6.97 (m, 4 H), 7.04 (d, J = 15.81 Hz, 2 H), 7.44−7.60 (m, 7 H), 7.71 (s, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 55.3, 111.9, 114.5, 115.7, 115.8, 121.1, 121.8, 124.2, 124.3, 128.2, 128.5, 129.5, 129.6, 129.8, 130.6, 132.8, 133.7, 134.9, 135.9, 137.9, 138.4, 140.2, 150.3. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −140.70 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm): 1.41 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{28}H_{22}BFON_3$ 446.1840 (M − F)$^+$, found 446.1808 (M − F)$^+$.

14. Yield: 22.5 mg (76%). Mp 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.46 (dd, J = 3.85, 2.12 Hz, 1 H), 6.67 (t, J = 4.17 Hz, 2 H), 6.95 (d, J = 16.61 Hz, 1 H), 7.12 (dd, J = 3.93, 2.36 Hz, 1 H), 7.46−7.60 (m, 9 H), 7.69 (s, 1 H), 7.96 (d, J = 16.52 Hz, 1 H), 8.01−8.06

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(m, 2 H), 8.38−8.45 (m, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 112.4, 116.2, 120.4, 121.6, 124.8, 125.0, 125.5, 125.5, 126.0, 126.6, 127.2, 128.5, 129.9, 130.0, 130.7, 131.7, 131.9, 132.9, 133.8, 134.8, 136.8, 138.3, 138.9, 150.4. ^{19}F NMR (376.5 MHz, $CDCl_3$, δ ppm): −140.65 (q, ^3J(B,F) = 64.0 Hz). ^{11}B NMR (128.4 MHz, $CDCl_3$, δ ppm): 1.48 (t, ^3J(B,F) = 32.0 Hz). HRMS calcd for $C_{35}H_{25}BF_2N_3$ 536.2110 $(M + H)^+$, found 536.2107 $(M + H)^+$.

■ ASSOCIATED CONTENT

Supporting Information

Characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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