



Versatile synthetic methods for the engineering of thiophene-substituted *Bodipy* dyes

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ABSTRACT

Novel thienyl-borondiazapyrromethene (*Bodipy*) dyes have been prepared using boronic acids or boronate reagents as cross-coupling mediators. A key dichloro/bromo-*Bodipy* starting material appears to be a useful starting material for such coupling reactions, enabling the synthesis of various symmetrically and unsymmetrically substituted thienyl-dyes. An alternative means of introducing thienyl substituents is through Knoevenagel substitution in the 3 and 5 positions of *Bodipy* by reaction with a formyl-functionalized thiophene derivative, resulting in systems of extended delocalization. All these *Bodipy* derivatives are stable and exhibit pronounced fluorescence on irradiation in the $S_0 \rightarrow S_1$ transition.

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Thiophene derivatives have been found to exhibit a wide range of biological activities¹ and many are active compounds as chemotherapeutics,² while many have also been used in various materials science applications.³ Polythiophenes obtained both chemically and electrochemically display interesting optical and charge transport properties. Variation of substituents, geometries, and shapes has provided detailed insights into the structure–activity relationships that have been scrutinized in several excellent reviews.^{4,5} The use of oligothiophenethynylene⁶ for the construction of cyclic nanoarrays^{7,8} and linear scaffolds capped by various stoppers have also been investigated.^{9,10} Furthermore, thiophene-based functional polymers have attracted significant attention due to their application as conductive and active layers in OLEDs,¹¹ and their high conductivity provides them with excellent characteristics as organic thin film transistors.^{12,13} Based on a thorough understanding of structure–property relationships and the ingenuity of synthetic chemists, ambipolarity, tunability, high quantum efficiencies, and stability have all been achieved.¹³ Our findings have revealed that thiophenes are among the most promising units for use to connect chromophoric centers and to provide interesting optical properties.^{14,15}

In extending this work, we have recently found that the grafting of thiophene subunits onto difluoro-boradiaza-s-indacenes, commonly termed *Bodipy* (for boron dipyrromethene),^{16,17} results in

a bathochromic shift of the absorption and emission wavelengths. In some rare cases, near infra-red emission occurs. As a matter of fact, only a few such dyes have been prepared up to now, mostly due to the difficulty in preparation of the necessary thiophene functionalized starting materials.^{18–20}

Here, we disclose our attempts to selectively functionalize *Bodipy* with various thiophene residues in order to control the optical properties of the dyes. While various means of so-doing can be envisaged, we chose to use tri-substituted reactants shown in Chart 1, with the objective of selectively introducing thienyl units at the 3 and 5 positions.

These reactants were prepared by a conventional multistep synthesis from the corresponding substituted benzaldehydes and pyrrole. Halogenation of the intermediate dipyrromethane was performed by using NCS or NBS followed by DDQ oxidation and stabilization of the dipyrromethene with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in basic conditions.²¹ The X-ray crystal structures of the three compounds have been determined (Fig. 1). All three molecules have approximate

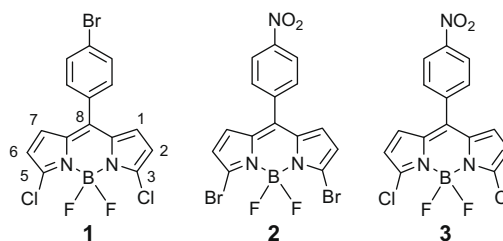


Chart 1.

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twofold rotational symmetry, though this is not crystallographically imposed. The *Bodipy* cores (12 atoms) are *quasi*-planar for each structure, but the rms deviation from the least-squares mean plane is significantly higher in compound **1** than those of the nitrophenyl compounds **2** and **3** (0.09 Å against 0.016 and 0.019 Å, respectively), owing to an apparent bend at the extremities and a distortion at the boron atom for compound **1**. The value of the dihedral angle of the substituted phenyl groups with respect to the *Bodipy* platforms increases from 55.2(2)° in **1** to 59.6(1)° in **2**, and then to 60.2(1)° in **3**. The average B–N and B–F bond lengths are, respectively, around 1.560(6) Å and 1.372(9) Å and the average N1–B1–N2, F1–B1–F2, and N–B–F, angles are 105.5(5)°, 111.0(3)°, and 109.9(3)°, closely similar to the literature values. Another recurrent observation is the pronounced double bond character for the C4–N1 and C5–N2 bonds [1.350(6) Å] in contrast with the longer C1–N1 and C8–N2 bond lengths [1.396(5) Å]. Molecules of compound **1** are all packed similarly in the crystalline state with the bromophenyl groups directed along the *b*-axis (with short Br···F and Cl···Cl intermolecular distances of 3.3 Å) and the core units lying in a plane *quasi*-parallel to *ab*, resulting in some instances of short contacts between adjacent molecules consistent with π – π interactions.

The face-to-face distances range from 3.506(3) Å to 3.932(3) Å. The two other structures adopt the same space group, $P2_1/c$. The nitro groups interact with one of the X = Br, Cl atoms with O–X distances ranging from 3.101 to 3.251 Å, together with double F–X interactions (with an F–Cl distance of 3.165 Å and F–Br 3.219 Å) aligning the molecules along the [2 0 1] direction, but without developing π – π stacking interactions.

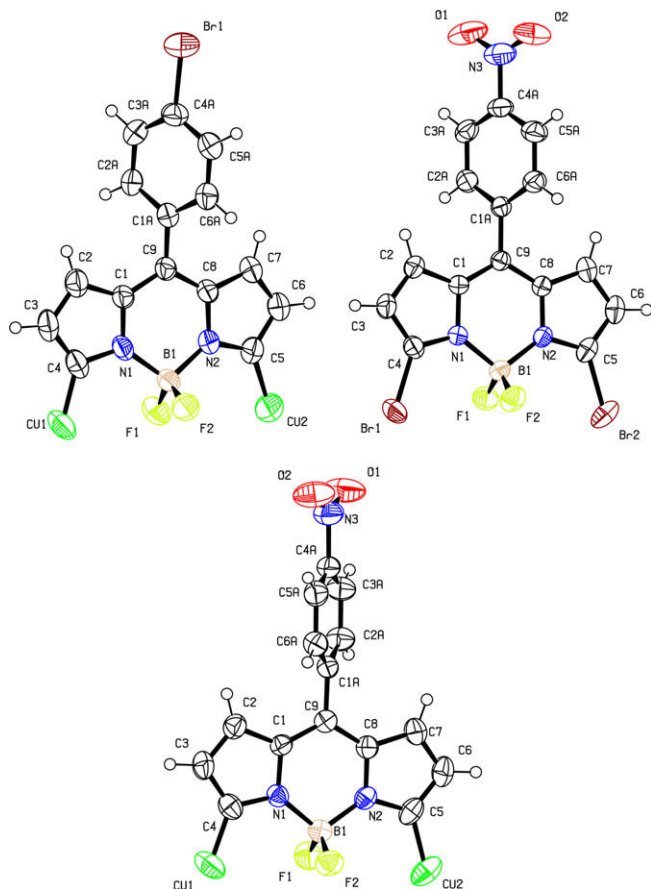


Figure 1. ORTEP view of **1** (top left), **2** (top right), and **3** (bottom). Displacement ellipsoids are drawn at the 30% probability level.

It has previously been suggested that both chloro groups in dye **1** are potentially reactive toward nucleophiles in S_NAr reactions.²² In our case, the reaction of thienyl magnesium bromide²³ with **1** at –40 °C provided an intractable mixture of compounds. After some experimentation, it became obvious that a simpler strategy would be to use cross-coupling reactions. The first attempt to functionalize derivative **1** was made with 3.6 equiv of tolylboronic acid under conventional conditions [toluene, Pd(PPh₃)₄, with aqueous K₂CO₃ at 110 °C] providing in 15 min the trisubstituted compound **4** in 56% yield (Chart 2). The reaction with thienylboronic acid in the same conditions led to a different scenario. The grafting of thiophene fragments was then relatively selective in the 3 and 5 positions, affording compound **5** in modest yield (29%).

Both experiments were considered quite promising in regard to producing functionalized *Bodipy* dyes which emit in the near infrared. However, it was found that both thienylboronic acid and the dichloro derivative **1** were not stable under the harsh Suzuki cross-coupling reactions. Thus, to explore possible improvements, changes were made in the nature of the thienylboronate derivative, the nature of the base, and the temperature. The essential outcomes are summarized in Table 1 and Scheme 1.

As shown in Table 1, replacing the 2-thienylboronic acid by the more stable 2-thienylboronic acid pinacol ester enabled the use of a stoichiometric quantity of boronate to obtain **5** and **6** in a shorter time. Additionally, the presence of water (possible nucleophilic species for S_NAr reaction) was avoided by using anhydrous Cs₂CO₃ instead of aqueous K₂CO₃ aq. Despite these two modifications, the yield of compound **5** remained approximatively the same, around 33%, at 110 °C. The solution for the problem of instability of compound **1** was found by changing the temperature. The yield of **5** was increased to 62% by decreasing the temperature to 90 °C. A balance between reaction time and progress of the reaction to obtain the mono-substituted derivative **6** in acceptable yield was not found, however. Like the dichloro compound **1**, the monochloro derivatives **6** and **7** are heat sensitive. However, the faster rate of the reaction with tolylboronic acid at 110 °C allowed **7** to be isolated in 56% yield (Scheme 2).

Compounds **6** and **7** are interesting as precursors to unsymmetrically substituted *Bodipy* dyes such as compound **8** bearing one thienyl and one tolyl residue. This dual substitution pattern allows fine tuning of the emission channel of the dye (vide infra).

The X-ray structure of the bis-thiophene derivative **5** was also determined and its features were compared to the previous structures. The dihedral angle between the Br-phenyl and the *Bodipy* units is 50.3(3)°, which is less than that in the previous complexes. The *Bodipy* core deviates from the planarity by a rms value of 0.059° with a slight twist observed at the remote rings, up and down with respect to the least-squares mean plane. The thiophene rings are tilted outwards from the *Bodipy* core by almost the same angle, 25.2(4) and 21.6(4)°, leaving the sulfur atoms on the edges

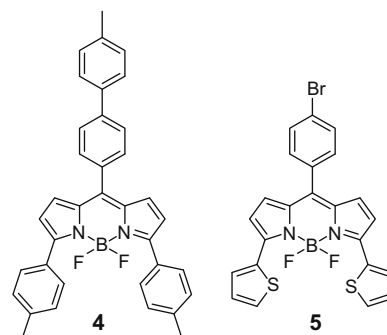


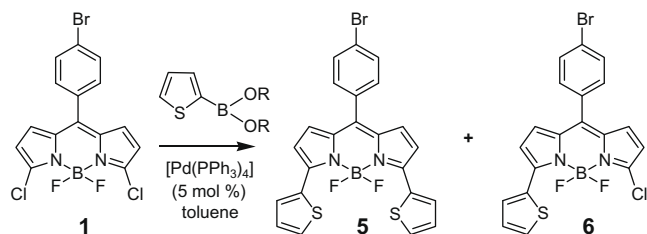
Chart 2.

Table 1
Reactivity of thienylboronate derivatives with dichloroBodipy **1**

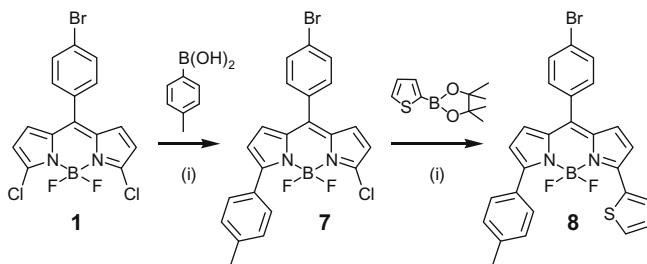
Reagent	Base	Equiv	Time (h)	T (°C)	Yield ^a (%)	
					5	6
	K ₂ CO ₃ aq	(2 + 5.2 ^b) (1 + 9 ^b)	60	110	29	12
			35	110	9	10
	Cs ₂ CO ₃ anhydrous	2.2	4	110	33	tr
	Cs ₂ CO ₃ anhydrous	2.2	1.5	90	62	tr
	Cs ₂ CO ₃ anhydrous	0.9	18	110	tr	16
	Cs ₂ CO ₃ anhydrous	0.9	2	90	tr	20

^a Isolated yield, tr for trace amounts.

^b Added in between three and five portions.



Scheme 1. Suzuki cross-coupling reactions of compound **1**. For specific conditions see Table 1.



Scheme 2. Reagents and conditions: (i) [Pd(PPh₃)₄] (5 mol %), toluene, aqueous K₂CO₃ 5 equiv, 1 equiv of boronate derivative; 110 °C. Compound **7** obtained after 30 min in 56% and compound **8** after 6 h in 34%.

turned out. No π – π stacking interactions are observed between molecules, which are seemingly linked by C–H...F hydrogen bonds in the crystal (Fig. 2).

Finally, another useful way to fine-tune the optical properties of such dyes is to extend the conjugation in the 3 and 5-position using styryl-based modules.²⁴ This scenario has previously been used to promote solid state-gas sensors.²⁵ The molecules **11** and **12** were designed such that polarity would be imparted by a short polyethyleneglycol chain carried by the thiophene subunit. Compound **10** was prepared by a two-step protocol from commercially available 2-methanolthiophene (according to Scheme 3). The first step consists of the alkylation of the alcohol using a polyethyleneglycoltosylate and the second a Vilsmeier reaction using standard reaction conditions.²⁶ The mono- and distyryl compounds **11** and **12** were synthesized from a tetramethylBodipy derivative by a Knoevenagel condensation.²⁵ Both dyes were conveniently separated by column chromatography, thanks to the presence of the polyethyleneglycol side chains. As previously observed for similar dyes, substitution of the fluoro groups on the boron is a convenient way to improve the stability and processability of the dyes.²⁷ The use of alkynyl Grignard reagents is an efficient way to substitute the fluoro groups on the boron center and dyes **13** and **14** were iso-

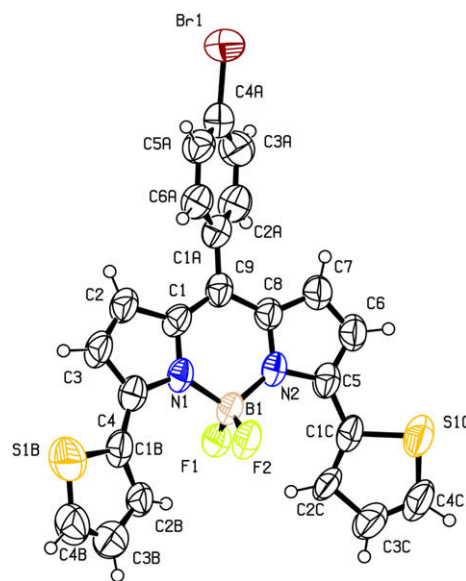
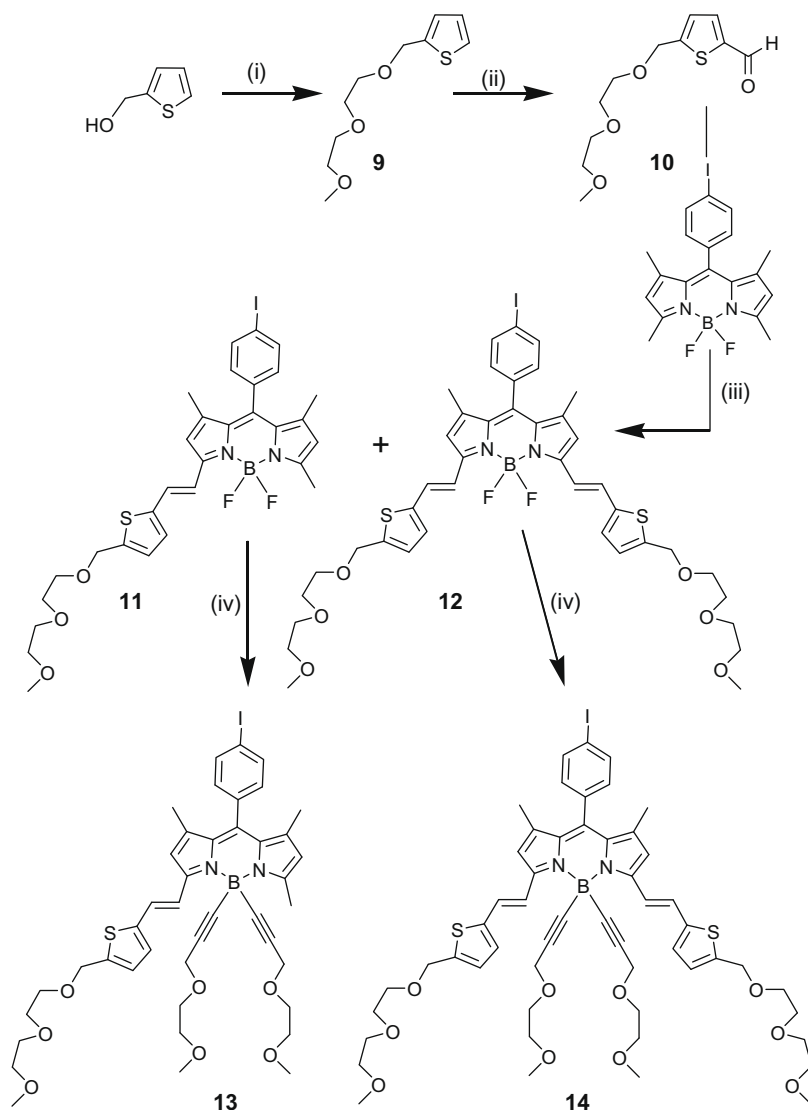


Figure 2. ORTEP view of **5**. Displacement ellipsoids are drawn at the 30% probability level.

lated in reasonably good yields (43% and 65% isolated yields, respectively).

The solubility of these novel dyes appeared to be good to excellent for all compounds including alcohols and no degradations in the solid state and the solution was observed within a given time.

The electronic absorption spectra of the new dyes are depicted in Figure 3 and exhibit the characteristic $S_0 \rightarrow S_n$ transitions for substituted Bodipy units. The weak absorptions in the 330–430 nm window are typical of $S_0 \rightarrow S_2$ transitions, while in some cases there are strong intramolecular charge-transfer (ICT) bands, as well as a strong absorption between 510 and 630 nm which is typical of a $S_0 \rightarrow S_1$ transition with a shoulder at the high-energy side and which is attributed to the first vibrational band of the same transition. All features are consistent with the absorption spectroscopic behavior of standard Bodipy chromophores. As would be expected from the design and previous measurements,²⁸ the progressive substitution of the chloro groups in **1** by a phenyl or thienyl group resulted in bathochromic shifts of 27 and 54 nm, respectively. Substitution of the remaining chloro by the same substituent enhanced this shift to 45 and 106 nm, respectively, for compounds **4** and **5**. Interestingly, for the hybrid dye **8** bearing one phenyl and one thienyl fragment an intermediate shift of 77 nm is found, allowing for control of the absorption and emission channels (Table 2).



Scheme 3. Reagents and conditions: (i) NaH (1.4 equiv), THF, rt, MeO(CH₂CH₂O)₂OTs (1 equiv), 12 h, 75%; (ii) POCl₃ (1.6 equiv), DMF (2 equiv), dichloroethane, 80°C, 2h, 46%; (iii) toluene, piperidine, Bodipy (1 equiv), aldehyde (1.5 equiv), 140°C, 10% for **11** and 13% for **12**; (iv) THF, HC≡CCH₂OCH₂CH₂OMe (6.6 equiv), EtMgBr (5.6 equiv), 60°C, 2h, 43% for **13** and 65% for **14**.

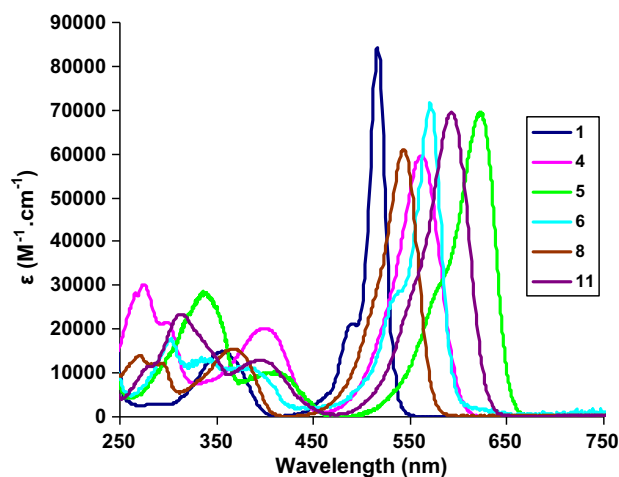


Figure 3. Absorption spectra for the substituted dyes in CH₂Cl₂ at rt. Inset correspond to the color code and compound labeling.

Excitation of these dyes in the lower energy transition produced strong fluorescence within the 520–620 wavelength range (Fig. 4). The short lifetime (nanosecond range) and the high quantum yield (Table 2) are in line with a singlet emitter. For each compound, there is reasonably good mirror symmetry between the fluorescence and (lowest-energy) absorption spectral patterns while the excitation spectra match well with the absorption spectra over the entire wavelength range. Stokes' shifts tend to be rather small (Table 2), indicating that the geometry does not change significantly upon excitation. Furthermore, the change in emission maximum tracks the shifts noted for the absorption band and λ_{em} moves progressively toward lower energy on increasing the effective size of the ancillary substituent. In all cases, the interplay between short excited state lifetimes, the symmetry in a mirror between the absorption and emission band and the relatively high quantum yields determined at rt in fluid solution are in keeping with a singlet excited state. No evidences for the population of a low lying triplet excited state were obtained so far.

Our design opens up the possibility of engineering new sophisticated dyes bearing thiophene residues at the periphery. The effi-

Table 2
Selected spectroscopic data for the new dyes^a

Dyes	λ_{abs} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{exc} (nm)	λ_{em} (nm)	Φ^b	Stokes' shifts (cm ⁻¹)
1	516	79,200	356	527	0.36	400
4	561	59,600	525	591	0.15	900
5	622	69,700	338	643	0.82	525
6	570	71,500	535	587	0.40	508
7	543	60,200	513	569	0.08	842
8	593	73,000	554	622	0.68	786
11	580	98,400	560	593	0.82	380
12	657	118,000	648	672	0.37	230
13	576	108,300	562	587	0.81	240
14	658	83,400	640	670	0.33	270

^a Measured in dichloromethane except for compounds **12**, **13**, and **14** in ethanol at rt.

^b Quantum yields are determined using cresyl violet ($\Phi_{\text{ref}} = 0.51$, $\lambda_{\text{exc}} = 623$ nm) as the standard.²⁹

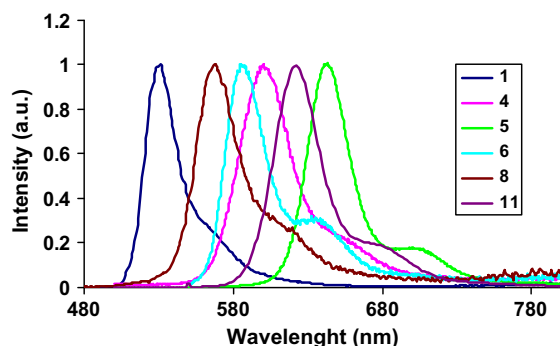


Figure 4. Emission spectra for the substituted dyes in CH₂Cl₂ at rt, in each case the excitation wavelength correspond to the maximum of the S₀→S₂ transition. Inset correspond to the color code and compound labeling.

ciency of the substitution reactions depends on the reaction time, temperature, and nature of the mineral base. Hybrid dyes bearing thienyl and phenyl were also prepared along with 2-thienylvinyl-based molecules. The mono- substituted and di-substituted thiophene dyes were easily separated thanks to the presence of short polyethyleneglycol chains which could be incorporated either as side chain on the thiophene or as ethynyl modules on the boron. All dyes exhibit intense fluorescence spanning from 527 to 672 nm. Current work is focused on increasing the water solubility and increasing the versatility by introducing additional useful substituents.

Supplementary data

CCDC 735530–735533 contain the supplementary crystallographic data for the four crystal structures of this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, United Kingdom; Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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- Typical preparation for compound **2**: A solution of 5-(4-nitrophenyl)dipyrromethane: Rohand, T.; Dolusic, E.; Ngo, T. H.; Maes, W.; Dehaen, W. *Arkivoc*, **2007**, 10, 307, (100 mg, 0.374 mmol) in 6 mL of THF was cooled to –78 °C under argon. NBS (133 mg, 0.748 mmol) was added in two portions over 30 min period. Once all NBS had dissolved, DDQ (85 mg, 0.374 mmol) in 1.5 mL THF was added over 10 min. The reaction mixture was warmed to rt. Triethylamine (8 mL, 4.61 mmol) and boron trifluoride diethyletherate (1.3 mL, 10.28 mmol) were added dropwise successively. The mixture was stirred at room temperature until the complete consumption of the starting material and water was added. The organic extracts were washed with water and brine. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel eluting with petroleum ether/dichloromethane (60:40) to give 67 mg (38%) of **2**: ¹H NMR (CDCl₃) δ 6.64 (AB, 4H, ^{AB}J = 4.2 Hz, ν_{AB} = 23.1 Hz); 8.05 (AB, 4H, ^{AB}J = 8.0 Hz, ν_{AB} = 141.2 Hz). ¹H NMR for **3**: (CDCl₃) δ 6.62 (AB, 4H, ^{AB}J = 4.3 Hz, ν_{AB} = 54.4 Hz); 8.04 (AB, 4H, ^{AB}J = 8.9 Hz, ν_{AB} = 141.9 Hz). ¹H NMR for **1**: (CDCl₃) δ 6.63 (AB, 4H, ^{AB}J = 4.4 Hz, ν_{AB} = 109.3 Hz); 7.50 (AB, 4H, ^{AB}J = 8.4 Hz, ν_{AB} = 92.9 Hz).
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