

Communication

One-Pot Synthesis of Push–Pull Butadienes from 1,3-Diethyl-2-thiobarbituric Acid and Propargylic Alcohols

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Abstract: A new synthetic procedure for obtaining two previously reported donor-acceptor butadiene dyes, namely 5-(3,3-bis(4-methoxyphenyl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione and 5-(3,3-bis(4-(dimethylamino)phenyl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, based on the InCl₃-catalyzed coupling 1,3-diethyl-2-thiobarbituric acid with 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol and 1,1-bis(4-(dimethylamino)phenyl)prop-2-yn-1-ol, respectively, is presented. The reactions, which cleanly proceed in water under MW irradiation, involve the initial generation of the corresponding enals by Meyer-Schuster rearrangement of the alkynols and their subsequent Knoevenagel condensation with the 2-thiobarbituric acid derivative. By following the same approach, the novel butadiene 5-(3,3-bis(4-(1,1'-biphenyl)-4-yl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, which was characterized by ¹H and ¹³C{¹H} NMR, IR, UV-Vis, elemental analysis and HRMS, was synthesized in 79% yield.

Keywords: push–pull molecules; butadienes; indium chloride; propargylic alcohols; Meyer–Schuster rearrangement; Knoevenagel condensation; barbituric acid; microwave-assisted reactions



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1. Introduction

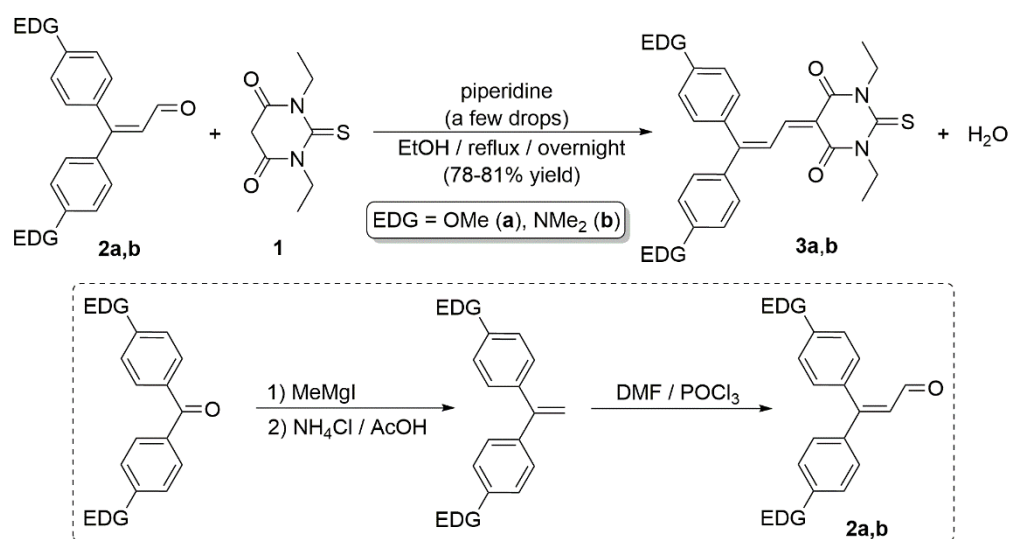
Push–pull chromophores, in which electron donor and electron acceptor groups are connected through a π -conjugated system (Figure 1), are the subject of considerable research interest in material science due to their unique properties (color, electrochemical, photochemical and solvatochromic behavior, nonlinear optical (NLO) properties, etc.) [1–5].



Figure 1. Simplified representation of a push–pull molecule.

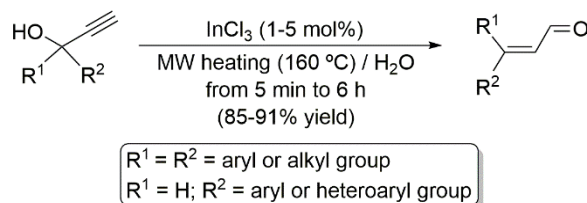
A wide variety of donor and acceptor units, as well as π -conjugated spacers, have been combined during the last decades for the construction of push–pull molecules. In this context, the pseudoaromatic 2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione ring of thiobarbituric acid and its *N*-alkylated derivatives has been extensively employed as an electron-withdrawing moiety in push–pull chromophores [6–9]. Representative examples are dyes **3a,b**, recently described by Dumur and co-workers, featuring *p*-methoxyphenyl and *p*-dimethylaminophenyl donor groups connected to the barbituric acid skeleton through a 1,3-butadiene chain spacer (Scheme 1), which showed a marked solvatochromic behavior in solution [10,11]. As shown in Scheme 1, compounds **3a,b** were obtained by Knoevenagel condensation of commercially available 1,3-diethyl-2-thiobarbituric acid **1** with the corresponding α,β -unsaturated aldehyde **2a,b** in refluxing ethanol under basic conditions. For the preparation of enals **2a,b**, Dumur and co-workers followed a classical synthetic

route involving the initial olefination of the respective 4,4'-disubstituted benzophenone, and subsequent Vilsmeier formylation of the resulting 1,1-diarylethylenes (see Scheme 1).



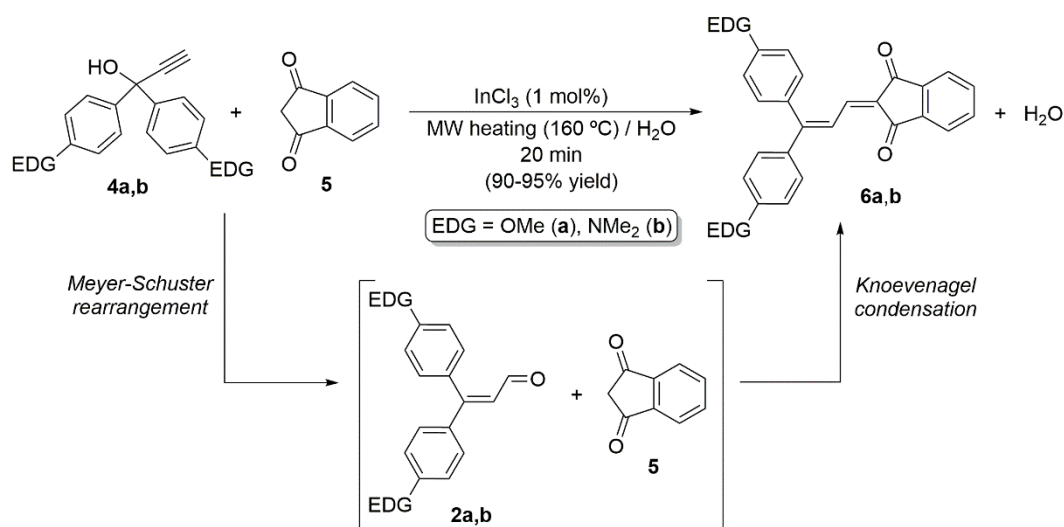
Scheme 1. Synthesis of dyes **3a,b** reported by Dumur and co-workers.

It is well known that α,β -unsaturated carbonyl compounds (both enals and enones) can be accessed, in a straightforward and atom-economical manner, through the catalytic Meyer–Schuster rearrangement of propargylic alcohols [12–14]. In this context, we developed some years ago an efficient, general and environmentally benign protocol for the Meyer–Schuster conversion of terminal propargylic alcohols into enals employing inexpensive InCl_3 as the catalyst, water as solvent, and microwaves (MW) irradiation as the heating source (Scheme 2) [15].



Scheme 2. MW-assisted InCl_3 -catalyzed Meyer–Schuster rearrangement of terminal propargylic alcohols in water.

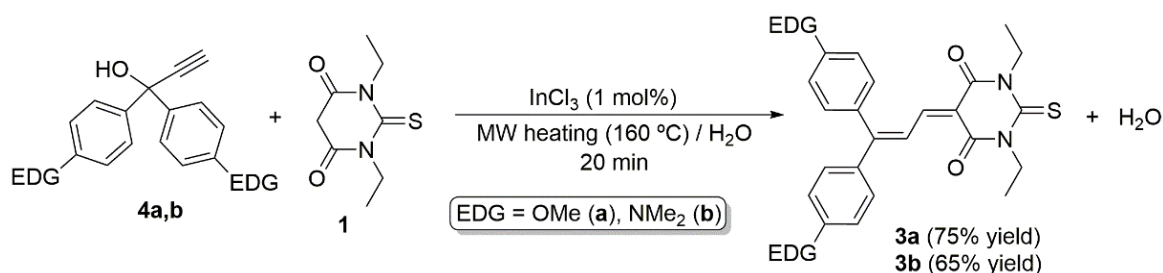
Additionally, in line with the interest of our group in the design of push–pull molecules [16,17], we demonstrated the utility of this MW-assisted InCl_3 -catalyzed reaction in the field with the high-yield synthesis of the donor–acceptor butadienes **6a,b**, structurally related to **3a,b**, by coupling of the corresponding propargylic alcohols **4a,b** with indan-1,3-dione **5** [18]. As shown in Scheme 3, under the reaction conditions employed, the Meyer–Schuster and Knoevenagel reactions run smoothly and successively in a one-pot manner. Taking advance of this previous work, herein we would like to communicate that Dumur’s dyes **3a,b** can also be generated by direct MW-assisted InCl_3 -catalyzed coupling 1,3-diethyl-2-thiobarbituric acid **1** with alkynols **4a,b**. In addition, the synthesis and spectroscopic characterization of the novel butadiene 5-(3,3-bi([1,1'-biphenyl]-4-yl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione **3c** will be presented.



Scheme 3. MW-assisted InCl₃-catalyzed synthesis of the push-pull butadienes **6a,b**.

2. Results and Discussion

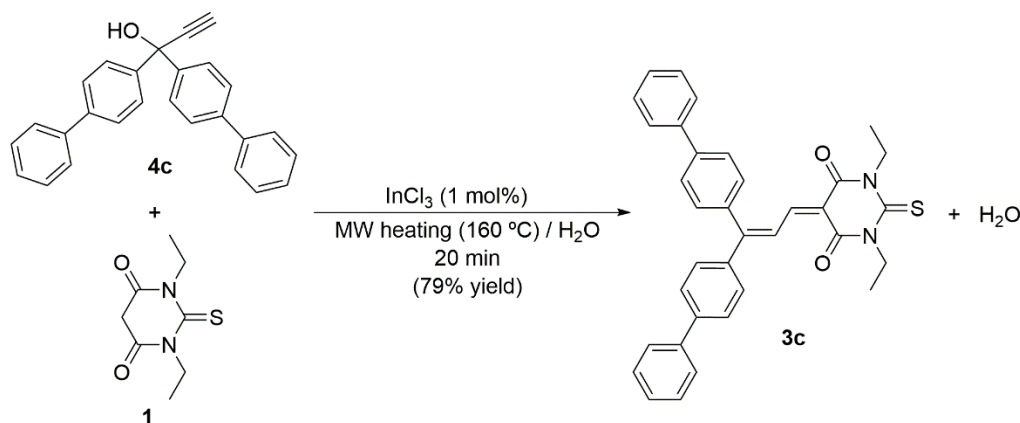
As shown in Scheme 4, we found that by applying the same reaction conditions previously employed in the preparation of the indan-1,3-dione-based dyes **6a,b**, the push-pull butadienes **3a,b** can be accessed in 75 and 65% yield, respectively. A notable aspect of this new synthetic route is the ease reaction work-up procedure to isolate the products since, after the MW-irradiation period (20 min at 160 °C) and cooling of the mixture to room temperature, both derivatives appear as precipitated solids. In this way, a simple decantation and consecutive washing with water, methanol and diethyl ether delivered **3a,b** in pure form. The recorded IR, NMR (¹H and ¹³C{¹H}) and HRMS spectra were in full agreement with the characterization data reported by Dumur and co-workers (full details are given in the Materials and Methods section and copies of the spectra included in the Supplementary Materials) [10,11].



Scheme 4. MW-assisted InCl₃-catalyzed synthesis of butadienes **3a,b** from 1,3-diethyl-2-thiobarbituric acid **1** and propargylic alcohols **4a,b**.

The synthetic utility of this MW-assisted InCl₃-catalyzed process was further demonstrated with the preparation of the novel butadiene 5-(3,3-bi([1,1'-biphenyl]-4-yl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione **3c** starting from stoichiometric amounts of 1,3-diethyl-2-thiobarbituric acid **1** and 1,1-di([1,1'-biphenyl]-4-yl)prop-2-yn-1-ol **4c** (Scheme 5). Compound **3c** was isolated as a red solid in 79% yield and characterized by ¹H and ¹³C{¹H} NMR, IR, elemental analysis and HRMS, with all data being fully consistent with the proposed formulation (full details are given in the Materials and Methods section and copies of the spectra included in the Supplementary Materials). Thus, its IR spectrum showed characteristic C=O vibrations appearing as a strong and broad absorption band at 1667 cm⁻¹. The generation of a butadiene >C=CH-CH=C< unit was clearly reflected in the ¹H NMR spectrum by the appearance of two doublet signals at 8.30 and 8.73 ppm

($^3J_{\text{HH}} = 12.3$ Hz), the spectrum also showing the typical signals for the two inequivalent ethyl groups of the *N*-alkylated thiobarbituric acid skeleton, i.e., two quartets at δ_{H} 4.54 and 4.62 ppm and two triplets at δ_{H} 1.31 and 1.38 ppm for the CH_2 and CH_3 units, respectively ($^3J_{\text{HH}} = 6.9$ Hz). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3c** also showed the expected signals, with the most quickly identifiable being that of the $\text{C}=\text{S}$ unit, which appears as the most deshielded one in the spectrum (δ_{C} 178.9 ppm).



Scheme 5. MW-assisted InCl_3 -catalyzed synthesis of the novel butadiene **3c**.

Finally, the optical properties of the novel butadiene **3c** were briefly investigated by means of UV-Vis spectroscopy in heptane and methyl sulfoxide (DMSO) solution (see Table 1; copies of the spectra are included in the Supplementary Materials file). As expected, the spectra displayed an intense absorption band in the visible region, hypsochromically shifted when compared to that of compounds **3a,b** due to the lower electron-donor capability of the biphenyl units vs. the *p*-methoxyphenyl and *p*-dimethylaminophenyl ones. In addition, similarly to the case of **3a,b**, **3c** also features a positive solvatochromic behavior, its absorption maximum undergoing a red shift on going from the non-polar heptane solvent to the highly polar DMSO one ($\Delta\lambda_{\text{max}} = 29$ nm).

Table 1. λ_{max} values of butadienes **3a–c** in heptane and dimethyl sulfoxide solution.

Compound	λ_{max} in Heptane	λ_{max} in DMSO	$\Delta\lambda_{\text{max}}$
3a *	456 nm	478 nm	22 nm
3b **	549 nm	609 nm	60 nm
3c ***	419 nm	448 nm	29 nm

* Data from reference [10]. ** Data from reference [11]. *** Spectra recorded using 6×10^{-5} M solutions.

3. Materials and Methods

Indium(III) chloride and 1,3-diethyl-2-thiobarbituric acid **1** were obtained from Merck KGaA (Darmstadt, Germany) and used as received. The propargylic alcohols **4a,b** [19] and **4c** [20] were synthesized following the methods reported in the literature. Organic solvents were dried by standard methods and distilled under argon before use [21]. NMR spectra were recorded on a Bruker DPX-300 (Billerica, MA, USA) spectrometer. The residual signal of the deuterated solvent (CDCl_3) was employed as reference for the chemical shifts. The PerkinElmer 1720-XFT and Lambda 25 spectrometers (Waltham, MA, USA) were used for IR and UV-Vis measurements, respectively. HRMS data were provided by the General Services of the University of Oviedo employing a QTOF Bruker Impact II mass spectrometer. Elemental analyses were provided by the Analytical Service of the Instituto de Investigaciones Químicas (IIQ-CSIC) of Seville using a LECO TruSpec CHN analyzer (St. Joseph, MI, USA).

3.1. General Procedure for the Preparation of Butadienes 3a–c

A pressure-resistant septum-sealed glass vial was charged with 1,3-diethyl-2-thiobarbituric acid (**1**; 0.101 g, 0.5 mmol), the corresponding propargylic alcohol (**4a–c**; 0.5 mmol), InCl_3 (0.001 g, 0.005 mmol), a magnetic stirrer bar and water (0.5 mL). The vial was then placed inside the cavity of a CEM Discover[®] S-Class microwave synthesizer (Matthews, NC, USA) and power was held at 300 W until the desired temperature was reached (160 °C). Microwave power was automatically regulated for the remainder of the experiment to maintain the temperature (monitored by a built-in infrared sensor). The internal pressure during the reaction ranged between 10 and 70 psi. After 20 min of irradiation, the vial was cooled to room temperature, the reaction mixture transferred to a flask, and the solid precipitate washed with water (1 × 5 mL), methanol (1 × 5 mL) and diethyl ether (1 × 5 mL). Characterization data for the resulting compounds **3a–c** are as follows.

3.2. 5-(3,3-Bis(4-methoxyphenyl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**3a**)

Red solid. Yield: 0.168 g (75%). ¹H NMR (300 MHz, CDCl_3): δ = 8.52 (d, 1H, J_{HH} = 12.7 Hz), 8.20 (d, 1H, J_{HH} = 12.7 Hz), 7.47 (d, 2H, J_{HH} = 8.9 Hz), 7.23 (d, 2H, J_{HH} = 8.7 Hz), 7.02 (d, 2H, J_{HH} = 8.7 Hz), 6.92 (d, 2H, J_{HH} = 8.9 Hz), 4.58 (q, 2H, J_{HH} = 7.0 Hz), 4.52 (q, 2H, J_{HH} = 7.0 Hz), 3.91 (s, 3H), 3.88 (s, 3H), 1.35 (t, 3H, J_{HH} = 7.0 Hz), 1.29 (t, 3H, J_{HH} = 7.0 Hz) ppm. ¹³C{¹H} NMR (75 MHz, CDCl_3): δ = 179.0, 166.6, 162.4, 161.5, 161.1, 160.1, 157.1, 133.5, 133.2, 132.1, 130.1, 122.9, 114.1, 113.9, 113.6, 55.5, 55.4, 43.6, 43.1, 12.5, 12.4 ppm. IR (KBr): ν = 2969 (w), 2930 (w), 2837 (w), 1683 (m), 1660 (s), 1604 (s), 1533 (s), 1451 (w), 1423 (m), 1382 (s), 1335 (s), 1281 (s), 1256 (s), 1236 (s), 1212 (s), 1172 (s), 1139 (m), 1107 (s), 1078 (m), 1025 (m), 887 (m), 832 (m), 785 (m), 661 (w), 554 (w), 491 (w) cm^{-1} . HRMS (ESI): m/z 451.168272 [$\text{M} + \text{H}^+$] (calcd. for $\text{C}_{25}\text{H}_{27}\text{O}_4\text{N}_2\text{S}$: 451.168605).

3.3. 5-(3,3-Bis(4-(dimethylamino)phenyl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**3b**)

Purple solid. Yield: 0.154 g (65%). ¹H NMR (300 MHz, CDCl_3): δ = 8.48 (d, 1H, J_{HH} = 13.2 Hz), 8.23 (d, 1H, J_{HH} = 13.2 Hz), 7.50 (d, 2H, J_{HH} = 9.0 Hz), 7.25 (d, 2H, J_{HH} = 9.0 Hz), 6.76 (d, 2H, J_{HH} = 9.0 Hz), 6.67 (d, 2H, J_{HH} = 9.0 Hz), 4.62 (q, 2H, J_{HH} = 6.9 Hz), 4.53 (q, 2H, J_{HH} = 6.9 Hz), 3.10 (s, 6H), 3.09 (s, 6H), 1.36 (t, 3H, J_{HH} = 6.9 Hz), 1.30 (t, 3H, J_{HH} = 6.9 Hz) ppm. ¹³C{¹H} NMR (75 MHz, CDCl_3): δ = 178.8, 171.0, 161.8, 160.6, 158.1, 152.9, 152.4, 134.3, 133.5, 128.4, 125.7, 120.9, 111.4, 111.3, 109.4, 43.4, 42.9, 40.1, 12.6, 12.5 ppm. IR (KBr): ν = 2976 (w), 2927 (w), 1651 (s), 1592 (s), 1508 (s), 1433 (m), 1361 (s), 1283 (s), 1263 (m), 1239 (s), 1189 (s), 1142 (m), 1105 (s), 992 (w), 947 (m), 898 (m), 858 (w), 819 (m), 782 (m), 750 (w), 731 (w), 550 (w), 488 (w), 478 (w), 411 (w) cm^{-1} . HRMS (ESI): m/z 477.231418 [$\text{M} + \text{H}^+$] (calcd. for $\text{C}_{27}\text{H}_{33}\text{N}_4\text{O}_2\text{S}$: 477.231874).

3.4. 5-(3,3-Di([1,1'-biphenyl]-4-yl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (**3c**)

Red solid. Yield: 0.214 g (79%). ¹H NMR (300 MHz, CDCl_3): δ = 8.73 (d, 1H, J_{HH} = 12.3 Hz), 8.30 (d, 1H, J_{HH} = 12.3 Hz), 7.78–7.40 (m, 18H), 4.62 (q, 2H, J_{HH} = 6.9 Hz), 4.54 (q, 2H, J_{HH} = 6.9 Hz), 1.38 (t, 3H, J_{HH} = 6.9 Hz), 1.31 (t, 3H, J_{HH} = 6.9 Hz) ppm. ¹³C{¹H} NMR (75 MHz, CDCl_3): δ = 178.9, 165.0, 160.8, 160.0, 156.0, 143.8, 140.0, 139.5, 136.4, 131.9, 130.5, 129.0, 128.9, 128.1, 127.9, 127.3, 127.2, 127.1, 124.6, 115.3, 43.8, 43.3, 12.5, 12.4 ppm. IR (KBr): ν = 3027 (w), 2972 (w), 2930 (w), 1697 (w), 1692 (m), 1667 (s), 1598 (m), 1548 (s), 1485 (m), 1434 (m), 1386 (s), 1337 (s), 1282 (s), 1236 (m), 1212 (s), 1107 (s), 1095 (s), 1004 (m), 969 (w), 887 (w), 848 (m), 787 (w), 765 (w), 733 (w), 693 (m), 493 (w) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{35}\text{H}_{30}\text{N}_2\text{O}_2\text{S}$: C 77.46, H 5.57, N 5.16; found: C 77.29, H 5.59, N 5.25. HRMS (ESI): m/z 543.210255 [$\text{M} + \text{H}^+$] (calcd. for $\text{C}_{35}\text{H}_{31}\text{N}_2\text{O}_2\text{S}$: 543.210076).

4. Conclusions

Based on the ability of InCl_3 to promote the tandem Meyer–Schuster/Knoevenagel condensation of terminal propargylic alcohols with 1,3-dicarbonyl compounds in water under

MW irradiation [18], a new synthesis of the previously reported butadiene dyes **3a,b** has been developed. In addition, applying the same MW-assisted InCl_3 -catalyzed protocol, the related butadiene 5-(3,3-bi([1,1'-biphenyl]-4-yl)allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione **3c** could also be synthesized for the first time, and fully characterized, starting from 1,3-diethyl-2-thiobarbituric acid and 1,1-di([1,1'-biphenyl]-4-yl)prop-2-yn-1-ol.

Supplementary Materials: The following supporting information can be downloaded online, Figures S1–S5: ^1H , $^{13}\text{C}\{^1\text{H}\}$, DEPT-1,3,5, IR and HRMS spectra obtained for compound **3a**; Figures S6–S10: ^1H , $^{13}\text{C}\{^1\text{H}\}$, DEPT-1,3,5, IR and HRMS spectra obtained for compound **3b**; Figures S11–S15: ^1H , $^{13}\text{C}\{^1\text{H}\}$, DEPT-1,3,5, IR and HRMS spectra obtained for compound **3c**; Figures S16 and S17: UV-Vis spectrum of compound **3c** recorded in heptane and DMSO solution.

Author Contributions: Conceptualization, V.C.; synthesis and characterization of compounds **3a–c**, J.F. Both authors contributed to the discussion of the experimental results as well as the writing and editing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples of the compounds **3a–c** are not available from the authors.

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