

# Eco-friendly K-10 Clay-Mediated [3 + 3] Spiroannulation of Morita–Baylis–Hillman Adduct of Isatin with Anthracene: Synthesis of Green Fluorophore Compounds

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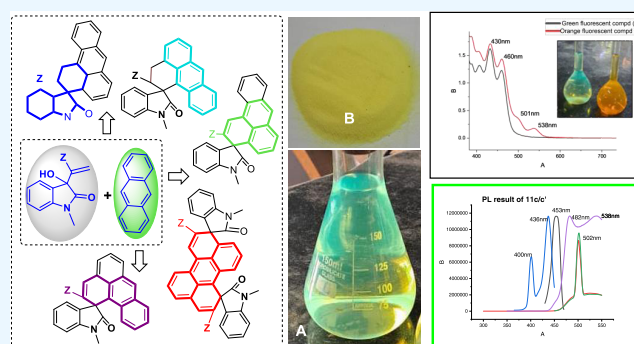
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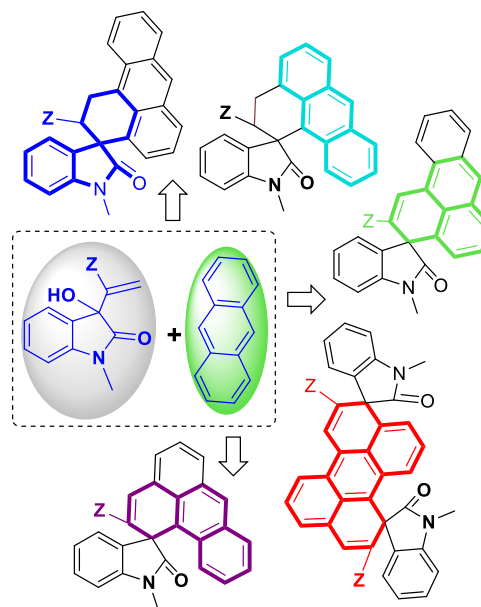
**ABSTRACT:** An easy and simple spiroannulation of the Morita–Baylis–Hillman adduct of isatin derivatives with anthracene was achieved in moderate-to-good yields (37–75%). The spiroderivatives synthesized in this work exhibited green fluorescence properties. The reaction occurred in metal-free eco-friendly K-10 clay-mediated conditions. The final products have multiple structural features such as 3-spirooxindole, fluorophoric anthracene, phenanthracene, phenalene, and perylene cores.



## 1. INTRODUCTION

Contributions of organic fluorescent materials<sup>1</sup> and their related findings play important roles in the advancement and applications of chemical and biological research.<sup>2</sup> The novel synthesis of an organic fluorophore molecule<sup>1</sup> is relevantly observed with attention focused on modern technological developments such as organic light-emitting diodes, organic thin-film transistors,<sup>3</sup> and electroluminescent, polymeric, optoelectronic, and semiconductive devices.<sup>4</sup>

The existence of spirooxindoles in a large number of natural products and pharmaceutically important molecules has been clearly highlighted in several synthetic organic chemistry reports.<sup>5</sup> Notably, from its discovery in 1832 to the present modern days, the chemistry of anthracene<sup>6</sup> has grown for a wide range of applications. The Morita–Baylis–Hillman chemistry<sup>7</sup> is significantly suitable to establish synthetically important core structures and useful transformations, which garner the attention of organic chemists. Because of our field of interest in the area of MBH chemistry, a novel attempt for the derivatization of anthracene using Morita–Baylis–Hillman adducts of isatin was deduced to achieve compounds with featured electrochemical and photophysical functionalities. Thus, we planned to establish an interesting new methodology for the construction of 3-spirooxindole fluorescent derivatives applying the [3 + 3] spiroannulation reaction in metal-free eco-friendly Mont. K-10 clay-mediated facile conditions, with the aim to achieve structural features such as 3-spirooxindole, fluorophoric anthracene, phenanthracene, phenalene, and perylene cores, as highlighted in [Figure 1](#).



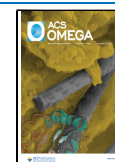
**Figure 1.** Multiple structural features of the targeted products.

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## Scheme 1. Initial Study of Fluorescent Product Formation

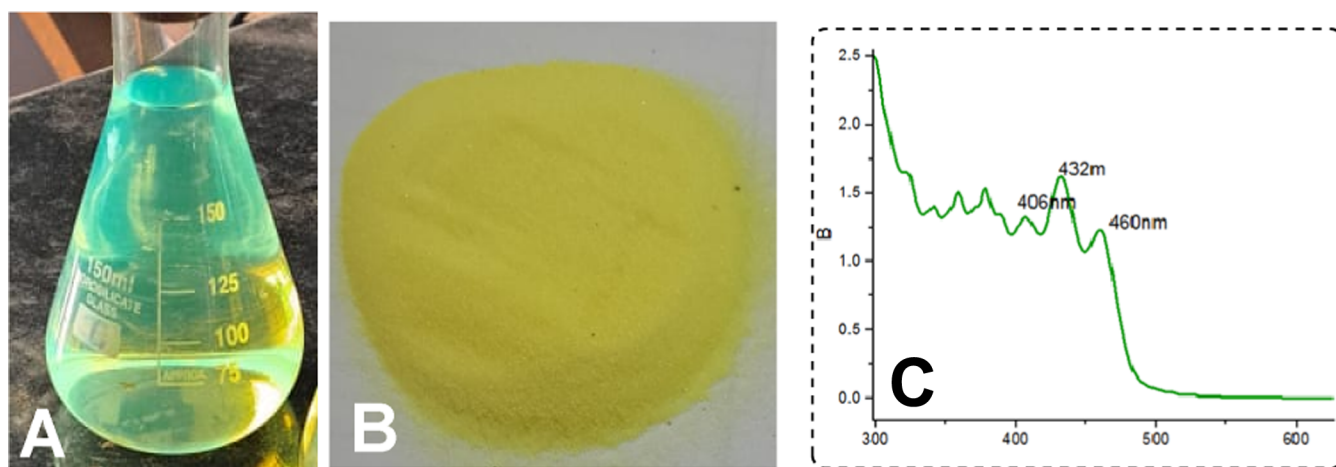
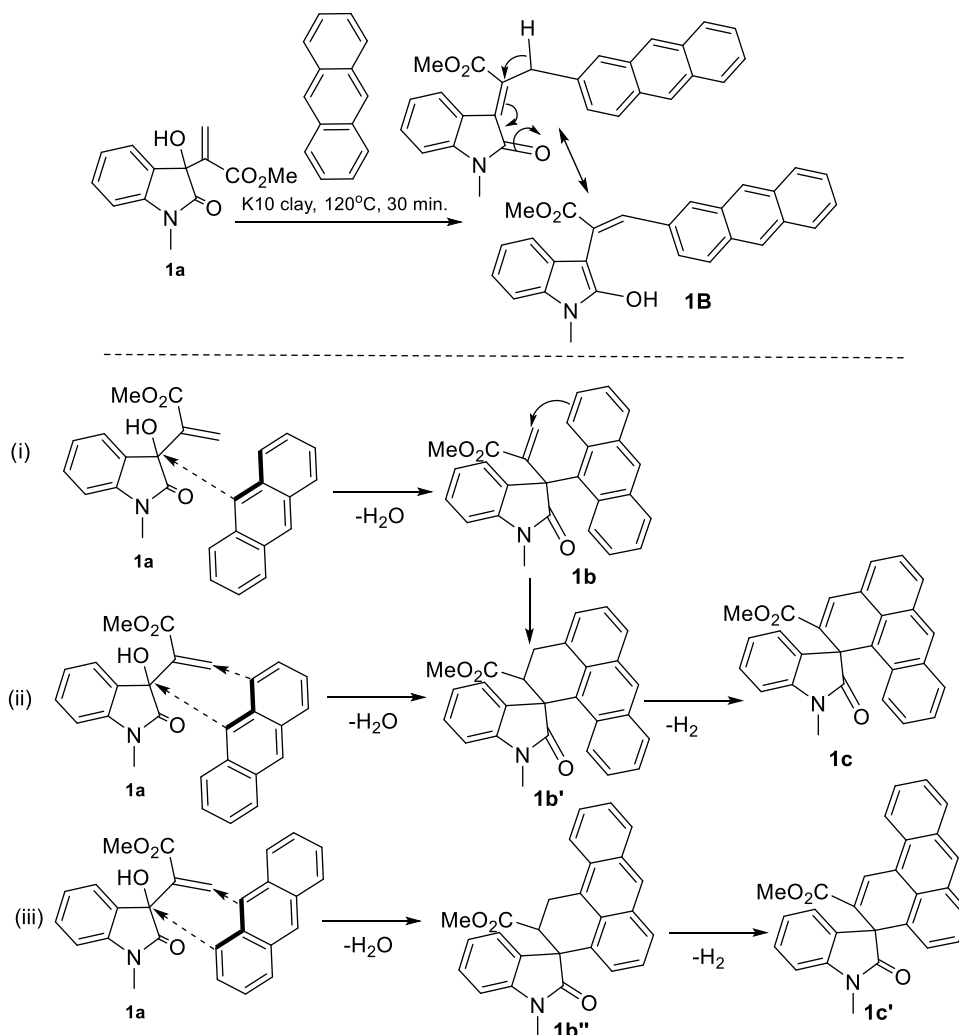


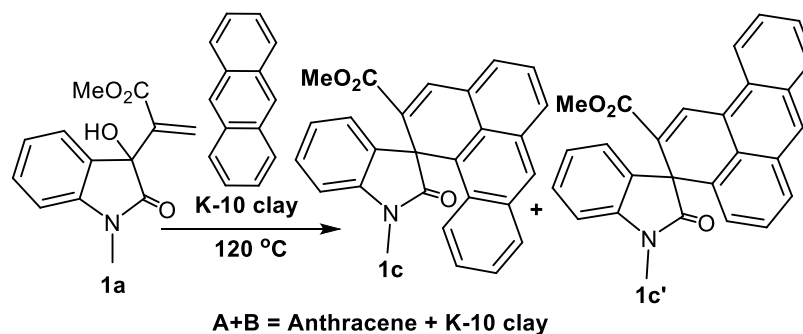
Figure 2. (A) Column fraction in 20% EtOAc/hexane; (B) silica gel slurry; (C) UV-visible spectrum of green fluorescent compound **1c**.

## 2. RESULTS AND DISCUSSION

As shown in Scheme 1, we began the initial study by treating the Morita-Baylis-Hillman adduct **1a** with anthracene and 50% w/w Mont. K-10 clay in a sealed tube to heat over an oil bath at 120 °C for 30 min to afford an interesting green fluorescent product after silica gel column purification. The

UV-visible spectral analysis showed characteristic absorption bands at 406, 432, and 460 nm, as shown in Figure 2. Based on the results of our previous studies,<sup>7n</sup> it was suspected that the allylic arylation followed by allylic proton shift **1B** may be responsible for the fluorescent nature of the product. However, this was not supported by the NMR and mass spectral

Table 1. Optimization Study for Fluorescent Product Formation



entry	(A+B) (amount)	condition	time (h)	% yield of 1c/c' <sup>a</sup>
1	2 equiv. + (50% w/w)	120 °C, neat conventional	1	23
2	2 equiv. + (50% w/w)	neat, 70%PL, MW irradiation	0.5	35
3	2 equiv. + (100% w/w)	120 °C in Cl-C <sub>6</sub> H <sub>5</sub> conventional	1.5	65
4	1.2 equiv. + (0% w/w)	120 °C, neat conventional	2	0
5	1.2 equiv. + (0% w/w)	120 °C, in Cl-C <sub>6</sub> H <sub>5</sub> conventional	2	0
6	1.2 equiv. + (100% w/w)	120 °C, in Cl-C <sub>6</sub> H <sub>5</sub> conventional	2	75
7	2 equiv. + (100% w/w)	70%PL, MW in Cl-C <sub>6</sub> H <sub>5</sub>	0.5	45

<sup>a</sup>Combined yield of inseparable mixtures based on proton NMR.

analyses. Especially, the mass peak supposed to appear at  $m/z$  407 and  $m/z$  408( $m+1$ ) was absent, and only a peak with respect to a spiro-derivative was seen at  $m/z$  406, which matched the  $m+1$  peak of a spiroannulated product **1c**.

The possible and preferred attacks of anthracene on the MBH adduct of isatin are shown in Scheme 1. To increase product formation and to determine the reaction pathway alternative to neat reaction conditions, chlorobenzene was used as a solvent. In the chlorobenzene heating, intermediates **1b**, **1b'**, and **1b''** were identified by NMR and mass analyses.

For the optimization of the methodology, the reactions were performed, as shown in Table 1. Thus, the MBH adduct **1a** (50 mg, 0.202 mmol) with 2 equiv of anthracene using 50% w/w freshly activated K-10 clay was taken in a sealed tube, and the tube conventionally heated at 120 °C to yield the desired fluorescent compound (3-spiro-oxindalone) **1c/c'** in 23% yield (Table 1, entry 1). In microwave irradiation conditions, the reaction was tested, and a slightly improved yield of 35% was found, as shown in Table 1 (entry 2). Further, to increase the formation of the target molecule, the amount of K-10 clay was increased to 100% w/w, and the reaction mixture was immersed in chlorobenzene to heat over an oil bath at 120 °C. Interestingly, the yield improved to 55% (Table 1, entry 3). To assess the progress of the reaction in the absence of K-10 clay, only the MBH adduct and 1.5 equiv of anthracene were heated for the period of 2 h in neat conditions and in the presence of chlorobenzene. No fluorescent product formation was observed (Table 1, entries 4 and 5). The use of 1.2 equiv of anthracene and 100% w/w K-10 clay in chlorobenzene under conventional heating for 2 h was found to be the optimum conditions for fluorescent compound formation (Table 1, entries 6 and 7).

Encouraged by the optimized study, different MBH adducts **2a–16a** were tried with anthracene to assess the generality of the methodology (Table 2). All reactions proceeded smoothly with moderate-to-good yields. Thus, the simple isatin-derived MBH adducts **2a** and **3a** afforded the green fluorescent compounds **2(cc')** and **3(cc')** in moderate yields. 1-Methyl, 1,5-dimethyl, and 1-ethyl isatin-derived MBH adducts **4a–10a**

underwent [3 + 3]-spiroannulation in 42–68% yields. Similarly, *N*-propargyl and *N*-benzyl isatin-derived adducts **11a–16a** afforded products **11(cc')–16(cc')** in 43–72% yields. While performing the generality study, UV–visible spectral comparisons between anthracene and fluorescent products were performed to determine the progress of the reactions, as shown in Figure 3. Thus, the absorption band intensity decreased between 300 and 390 nm of anthracene, and the appearance followed by enhancement of bands between 400–470 nm confirmed the formation of green fluorescent compounds.

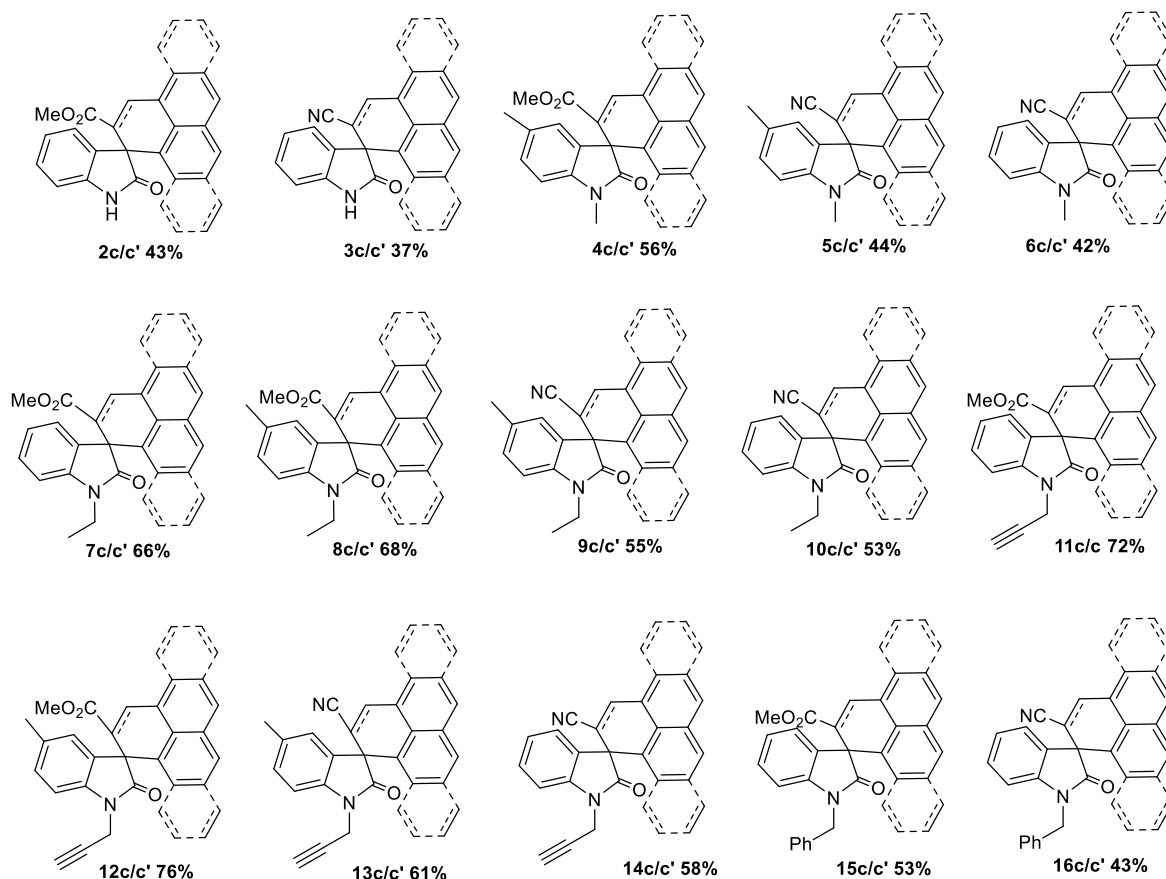
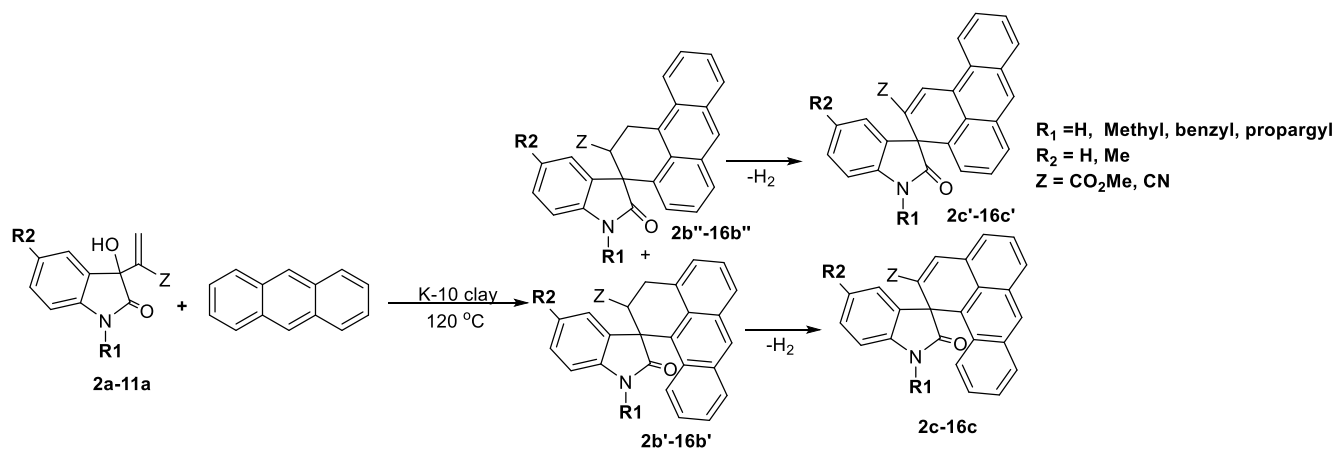
It was noticed that the reaction between *N*-propargylisatin methyl acrylate MBH adduct **11a** and anthracene provided interesting evidence for the regio- and stereochemistry aspects of [3 + 3] the spiroannulation product formation in proton NMR analysis.

The appearance of four triplet peaks in the alkyne proton chemical shift range of 2.0–2.5 ppm and a geminal and vicinal coupled doublet of doublet (dd) pattern in the chemical shift range of 2.7–2.9 ppm were indicative of possible diastereo- and regioisomer formation in the [3 + 3] spiroannulation (Figure 4).

It was observed that the perylene core formation was due to the possibility of a reaction between the MBH adduct and anthracene in a 2:1 ratio, as shown in Scheme 2. While performing column purification of the reaction mixtures obtained in the cases of adducts **1a**, **7a**, and **11a**, orange-colored products **1d**, **7d**, and **11d** were collected by column purification. The mass and UV–visible spectra of the orange products supported the perylene core.

Thus, the perylene core appeared in the mass spectral analysis as a peak at  $m/z$  661( $m+1$ ) found for the orange fluorescent fraction **7d**. The UV–visible spectral comparison between green (**1c**) and orange (**1d**) fluorescent products was recorded. The appearance of red-shifted additional new absorption bands at 501 and 538 nm was seen for the orange fraction, as shown in Figure 5.

The representative UV–visible and photoluminescence (PL) spectra for compound **11c/c'** were recorded in CHCl<sub>3</sub>.

Table 2. Generality of the Method for Fluorescent Product Formation<sup>a</sup>

<sup>a</sup>All regioisomers reported as combined yield (c/c' inseparable mixtures with ~1:1 ratio based on <sup>1</sup>H NMR spectroscopy)

The PL spectral study showed emission peaks at 482, 502, and 540 nm, as shown in Figure 6.

### 3. CONCLUSIONS

In conclusion, we developed a novel synthetic transformation of the MBH adduct of isatin with anthracene to identify a green fluorescent derivative. The newly formed compounds were characterized by preliminary UV–vis spectroscopy, mass spectrometry, and NMR spectroscopy analyses. Further studies using these results are in progress in our laboratory.

### 4. EXPERIMENTAL PROCEDURE

**4.1. General Considerations.** NMR spectra were recorded at 400 (<sup>1</sup>H) and 100.6 (<sup>13</sup>C) MHz on a Bruker Avance 400 MHz NMR spectrometer using chloroform-d<sub>1</sub> as the solvent. Chemical shifts are given in the  $\delta$ -scale with tetramethylsilane as the internal standard. Coupling constants (*J*) are reported in hertz (Hz). Yields refer to quantities obtained after chromatography. IR spectra were recorded on a Nicolet (Impact 400D FT-IR) spectrophotometer or a Bomem MB-series FT-IR spectrophotometer. Abbreviations used in <sup>1</sup>H NMR are as follows: s, singlet; d, doublet; dd, doublet of a

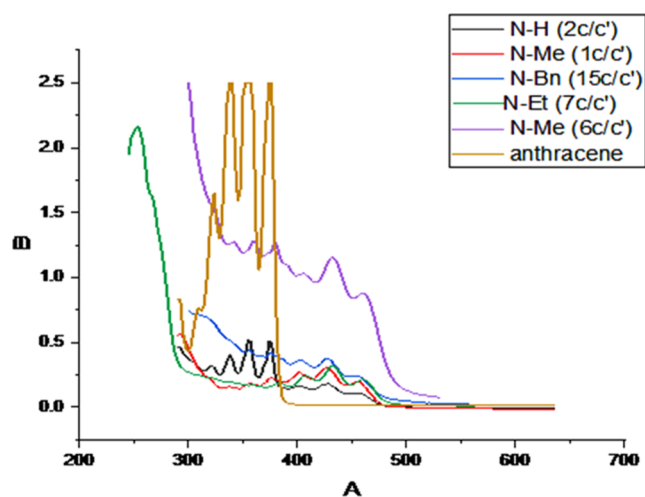
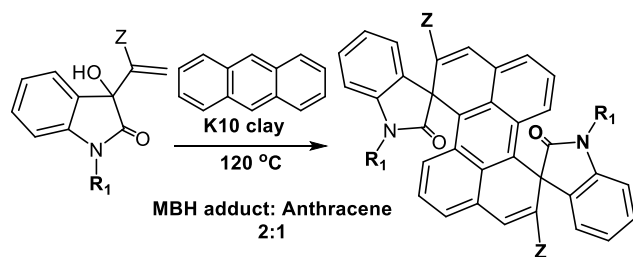


Figure 3. UV-visible spectral comparisons.

doublet; and m, multiplet. Analytical thin layer chromatography (TLC) was performed on glass plates coated with silica gel (Merck) containing 13% calcium sulfate as a binder. Column chromatography was performed using 100-(200)

## Scheme 2. Formation of the Perylene Core



SM	R <sub>1</sub>	Z	perylene core	% yield
1a	Me	CO <sub>2</sub> Me	1d	15%
7a	Et	CO <sub>2</sub> Me	7d	17%
11a	Propargly	CO <sub>2</sub> Me	11d	16%

mesh silica gel, and an appropriate mixture of petroleum ether (60–80 °C) and ethyl acetate was used as the solvent system for elution unless otherwise specified. The solvents were removed (under reduced pressure where necessary) using a Heidolph or Buchi rotary evaporator. All solvents were distilled before use, and reactions requiring dry conditions were carried

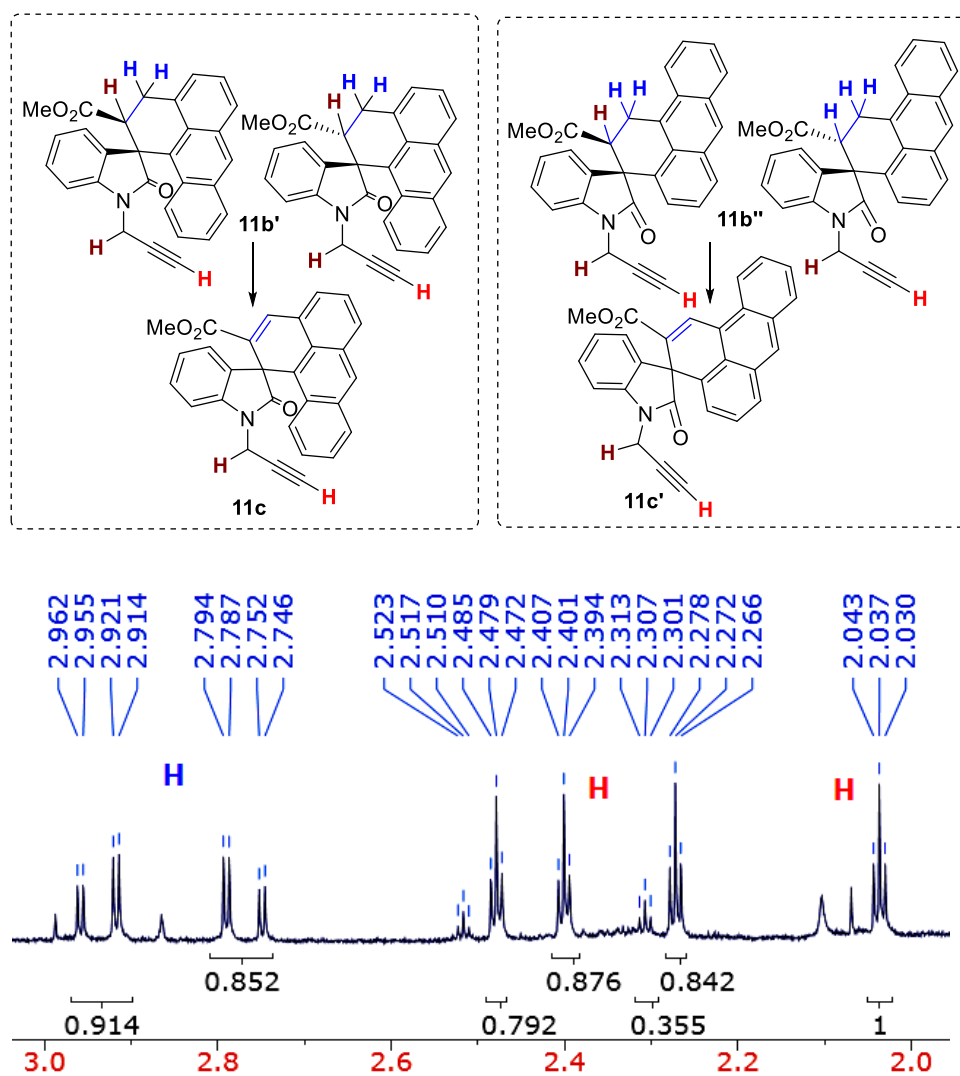
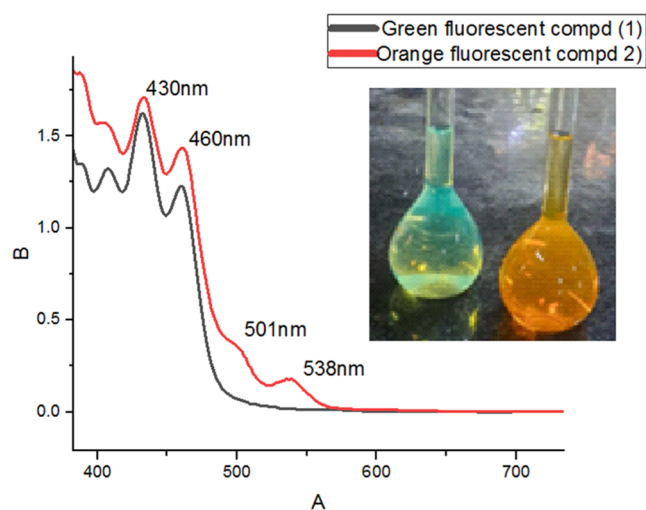
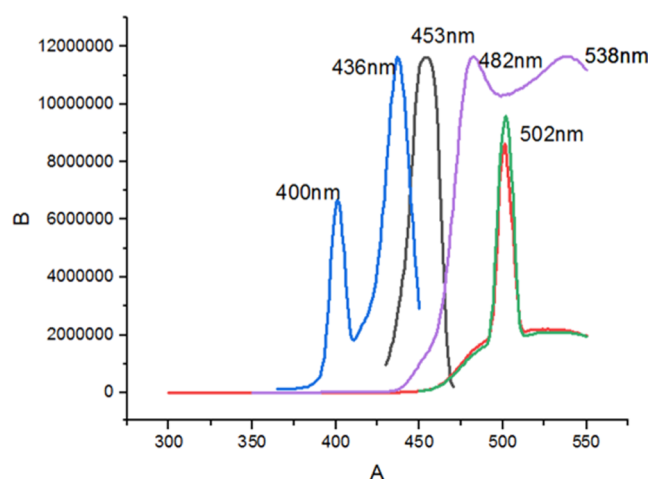


Figure 4. <sup>1</sup>H NMR spectra confirming the possible regio- and stereo- isomers formations.





**Figure 5.** UV-vis spectral comparison of the green and orange fluorescent compounds **1c** and **1d**.



**Figure 6.** PL spectrum for compound **11c/c'**.

out using dry solvents, which were dried according to the literature procedure.

#### 4.2. General Experimental Procedure for [3 + 3] Spiroannulation of the MBH Adduct of Isatin with Anthracene using K-10 Clay.

- (a) *Neat conditions*: A mixture of 50 mg of MBH adduct (0.20 mmol), 1.5 equiv of anthracene, and 100%w/w K-10 clay was ground in a mortar/pestle in solvent-free conditions at room temperature (3 min). The mixture was taken in a sealed tube to heat over an oil bath at 120 °C for 1 h. The crude mixture was purified by silica gel column chromatography using EtOAc/hexane (20:80) as the eluent to afford the desired green fluorescent compound as a semisolid.
- (b) *Using chlorobenzene as solvent conditions*: A mixture of 50 mg of MBH adduct (0.20 mmol), 1.2 equiv of anthracene, and 100%w/w K-10 clay was ground in a mortar/pestle in solvent-free conditions at room temperature (3 min). The mixture was taken in a sealed tube and mixed with 2 mL of chlorobenzene to heat over an oil bath at 120 °C for 2 h. The crude mixture was purified by silica gel column chromatography using

EtOAc/hexane (20:80) as the eluent to afford the desired green fluorescent compound as a semisolid.

### ■ ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c07084>.

<sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS, IR, and UV-visible spectra of synthesized compounds (PDF)

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#### Notes

The authors declare no competing financial interest.

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