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Photochromism of dihydroindolizines. Part 12: synthesis and photochromism of novel π-conjugated rigid dihydroindolizines as potential molecular electronic devices

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ABSTRACT

Novel carbon-rich photochromic dihydroindolizine DHI derivatives and new spirocyclopropenes have been synthesized. Three alternative synthetic pathways for the synthesis of DHI **10** have been established. Different Sonogashira-mediated coupling reactions have been applied to optimize the reaction conditions and to obtain the best yields. Palladium-mediated Sonogashira coupling of DHIs with 4-(thioacetyl)iodobenzene **13** and iodobenzene **17** yielded coupling products, which have potential applications in molecular electronics. Irradiation of photochromic DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f** with polychromatic light leads to betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f**. The coloured betaine forms are obvious in CH_2Cl_2 solution with concentration of 1×10^{-5} mol/L at room temperature because of their slower 1,5-electrocyclization. All the absorption maxima of the coloured betaines were found to be in the visible region and lie between 524 (betaine **9a**) and 639 nm (betaine **15f**). The kinetics of the thermal 1,5-electrocyclization was studied using multichannel UV–vis spectrophotometry. The kinetic measurements showed that the half-lives of the coloured betaines are in the second domain and lie between 112 and 1379 s. A highly pronounced increase in the half-lives of betaines bearing dimethyl substituted pyridazine compared with non-substituted pyridazine betaines was monitored. A large increase in the photostability of both DHIs and betaines under investigation compared with the standard DHI was observed. The charged zwitterionic betaine structures were stabilized by increasing the solvent polarity due to the electrostatic interactions between them. The tuning of the absorption maxima and the kinetic properties by changing the substitution in the fluorene part (region A) and pyridazine part (region C) will help these compounds to find their applications.

1. Introduction

Molecules that respond to the application of external stimuli by undergoing reversible transformations between two distinct structures have the potential to significantly influence the development of numerous important materials science and structural biology technologies.[1,2] This potential is based on the fact that, because the molecules typically undergo dramatic changes in their electronic and topological characteristics, they can act as switching elements and other dynamic components in various optoelectronic devices and functional materials. Compounds that interconvert between different isomers having unique absorption spectra when stimulated with light are referred to as photochromic and the process is called photochromism. In these systems, the changes in the electronic patterns responsible for the changes in colour also result in variations in other practical physical properties such as luminescence,[3–7] electronic conductance,[8,9] refractive index,[10–13] optical rotation[14–16] and viscosity.[17,18] The photomodulation of these properties has the potential to significantly advance optoelectronic technologies such as waveguides,[19,20] read/write/erase optical information storage systems[21] and actuators.[22,23]

If organic photochromic compounds are to find widespread use in photonic device applications such as erasable memory media and optical switching, several mandatory properties must be met. Foremost are thermal irreversibility, photo-fatigue resistance and high efficiency in rapid photoconversion processes.[24] An additional factor that cannot be downplayed is the ability to tailor the physical and chemical properties of the photochromic backbone in a facile, flexible and modular manner. This can only be accomplished by designing photochromic compounds that possess many different locations on their molecular skeletons where functional groups can be anchored.[25]

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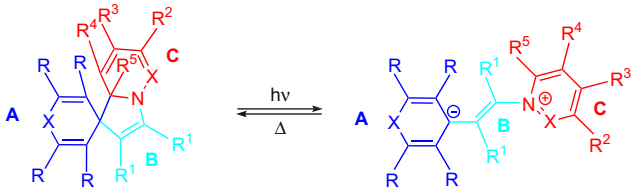
Photochromic dihydroindolizines were discovered and developed by Dürr[26,27] and are well-known photochromic materials that have been attracting much interest from the viewpoints of both fundamental elucidation of electrocyclization reactions (Scheme 1) and their potential applications in optical memories and switches.[28–32] These materials, based on the 1,5-electrocyclization between two distinct isomeric states: ring-open form (betaine form) and ring-closed form (DHI form), are promising candidates for optical storage media and electronic devices.[33,34]



Scheme 1. Schematic representation of the photo-induced ring opening of the DHI (the three regions **A**, **B** and **C** are represented) to the corresponding coloured betaine.

In the last decade, research on the synthesis of carbon-rich organic and organometallic compounds for widespread applications in the field of materials science has remarkably increased. In this context, the use of π-conjugated rigid fluorenyl chromophores and their derivatives offers exciting perspectives for the design of new molecular oligomeric and polymeric materials for various optoelectronic applications.[35] Molecular electronics is currently a topic of considerable interest among a diverse community of scientists and engineers as well as the general population and popular press.[35] Much effort and capital have been expended to improve and further miniaturize the components of computers. The methods currently used to make the microchips have been commercially scaled down to 0.13 μm (130 nm) feature size (interconnect metal line width, for instance). The lower limit is expected to be about 30 nm.[36] Experts in the semiconductor field estimate that this limit will be reached in 10–15 years.[36]

If electronics and computer components are to continue decreasing in size beyond the 30 nm limit, new technologies must be invented and explored. Molecular scale devices are logical approaches to reduce the size of current electronic devices. Self-assembled monolayers (SAMs) of molecular scale wires can achieve ordering of approximately 10^{14} molecules/cm^2, seven orders of magnitude greater. Also, one can manufacture 1 mol of these molecules in a large laboratory flask, which amounts to 6×10^{23} devices, or more than the number of transistors ever made in the history of the world.[37–42] It is for these reasons and others that work continues in the development of molecular electronic candidates. Of course, there are numerous problems that need to be solved before molecular computing is realized, including addressing single molecules in circuits and the need for heat dissipation at these packing levels.[38] Many molecular structures have been synthesized for use as molecular devices, including switches, wires, controllers and gates.[39–43]

Within contemporary acetylene chemistry[44] there is great interest in the synthesis of conjugated diyne and oligoyne molecules. They are fundamentally important carbon-rich building blocks[45] for molecular rods and cyclic frameworks and they are active components in optoelectronic devices (wires, switches, non-linear optics, etc.)[46] and the extent of intramolecular ð-conjugation within the diyne is a topic of experimental and theoretical debate.[47]

Recently, we succeeded in the design and synthesis of a carbon-rich photochromic dihydroindolizine by using many coupling reaction conditions.[48] The novel synthesized target molecules may have applications in the field of optoelectronics and non-linear optics. These results motivated us to explore the synthesis of more novel, rigid, carbon-rich fluorenyldihydroindolizines aiming to obtain new properties and applications. In continuation of our research on the synthesis and photochromic behaviour of photochromic dihydroindolizines (DHIs), this manuscript will shed more light on the synthesis and photophysical properties of carbon-rich fluorenyldihydroindolizine derivatives with molecular wire type substituents, which are designed to facilitate anchoring of the molecules to metal substrates and study their photochromic behaviour in solution.

2. Results and discussion

2.1. Synthesis of fluorenylacetylene spirocyclo-propene precursors

Spirocyclopropene **7a** (n=0) was previously synthesized by us[48] via five steps in 22% yield. Spirocyclopropenes **7b** (n=1) and **7c** (n=2) were accomplished also in five steps, starting with the literature conversion of fluorene to 2,7-dibromo-9*H*-fluoren-9-one in 56% yield over three steps[30] (Scheme 2). The following Sonogashira coupling of 2,7-dibromo-9*H*-fluoren-9-one with **2b** (n=1) and **2c** (n=2) in the presence of $Pd(PPh)_3Cl_2$ (5 wt %)/CuI/Et_2NH in THF at room temperature for 24 h afforded the coupling products **3b** (n=1) and **3c** (n=2) in 61 and 53% yield, respectively. Interestingly, condensation of compounds **3b**,**c** with hydrazine hydrate in boiling ethanol for 6 h leads not to the formation of the corresponding condensation products but to the condensation demethylsilylation products **4b** and **4c** in 41 and 39% yield, respectively.

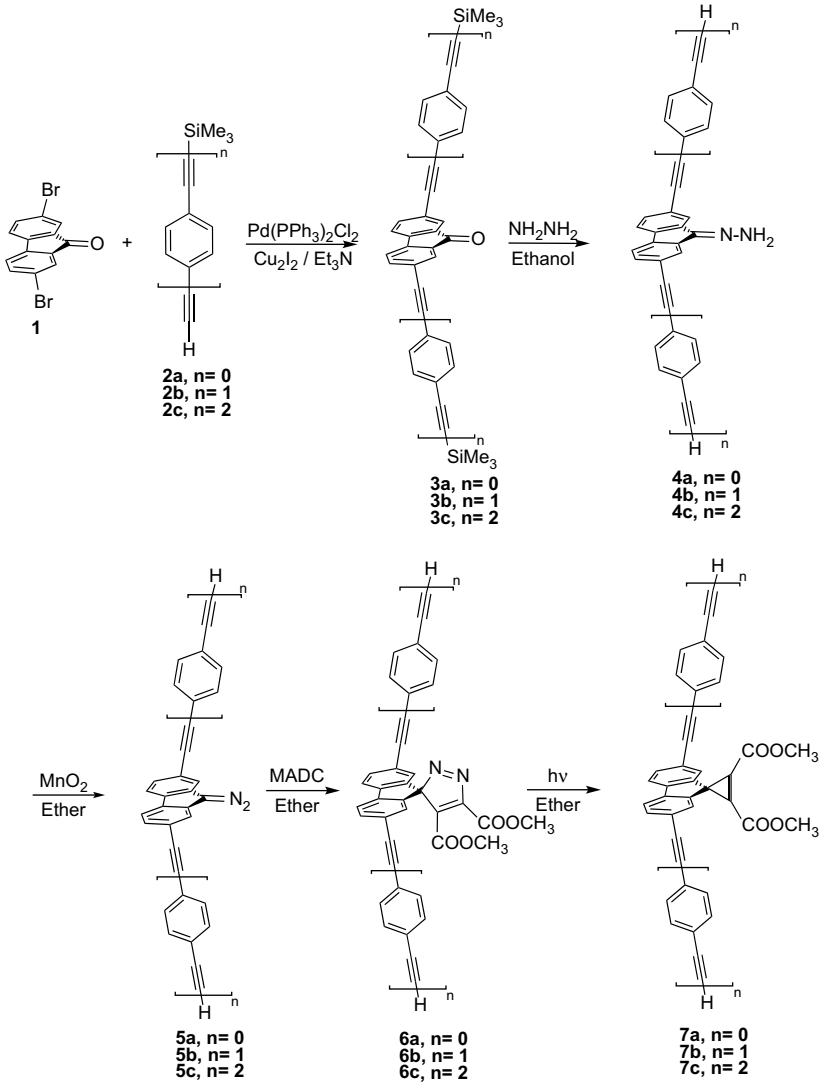
Oxidation of the hydrazone derivatives **4b**,**c** with manganese dioxide and/or mercuric oxide in dry ether at room temperature in the absence of light afforded fluorenes **5b**,**c** in moderate yield (53 and 51%, respectively). Addition of methyl acetylene-dicarboxylate (MADC) to the 9-diazofluorene derivatives **5b**,**c** in dry ether in dark condition for 24 h led to the formation of **6b** and **6c** in poor yield (33 and 29%, respectively).

Photolysis of the pyrazole derivatives **6b**,**c** with a high pressure mercury lamp (125 W) in dry ether solution for 2 h under a nitrogen atmosphere gave the target spirocyclopropene derivatives **7b** and **7c** in very low yield (15 and 13%, respectively).

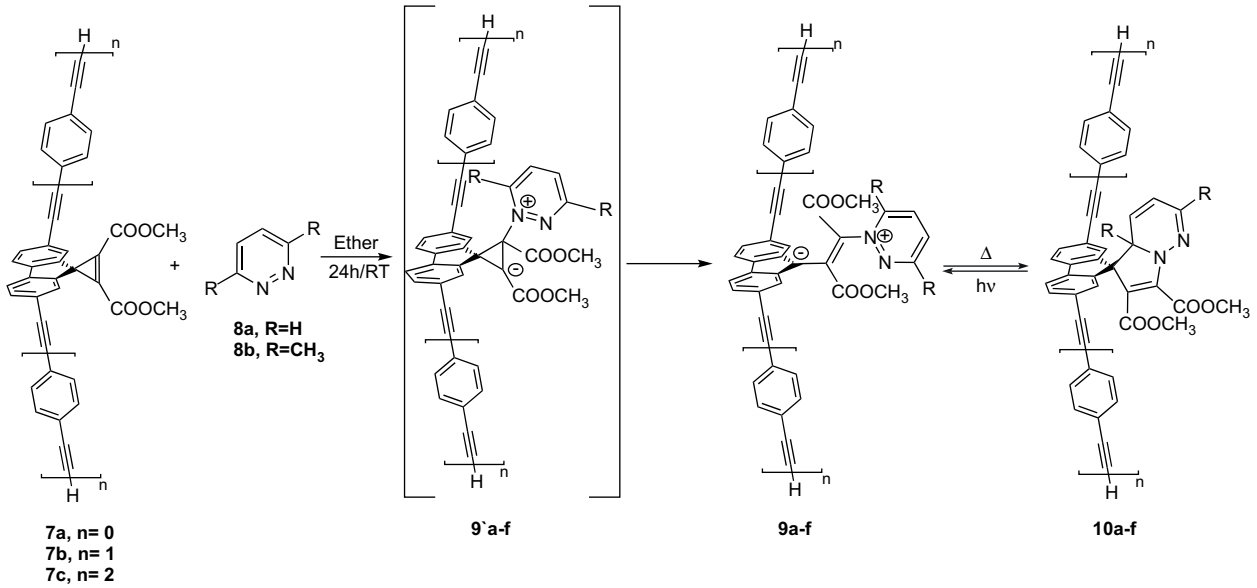
2.2. Different attempts for the synthesis of π-conjugated photochromic dihydroindolizines 10a–f

Photochromic DHI **10a** (R=H, n=0) was previously synthesized by us.[48] Nucleophilic addition of pyridazines **8a**,**b** to spirocyclopropenes **7b**,**c** using the cyclopropene route[26,30] (Scheme 3) in dry ether solution at room temperature under dry nitrogen in the absence of light (TLC controlled using CH_2Cl_2 as eluent) led to the formation of the photochromic dihydroindolizines (DHIs) **10b–f** in low yield (14–24%, method A, Table 1). The reaction occurred through electrophilic addition of the electron-deficient spirocyclopropenes **7b**,**c** to the nitrogen of the *N*-heterocyclic pyridazines **8a**,**b**, which led to ring opening via a cyclopropyl-allyl conversion **9′b–f** to the coloured betaines **9b–f** (Scheme 3). A subsequent ring closure to DHIs **10b–f** results in a partial slow thermal 1,5-electrocyclization back reaction (Scheme 3), which can be reversed upon exposure to light. Pure photochromic DHIs **10a–f** were obtained by column chromatography on silica gel using dichloromethane as the eluent.

Another successful alternative method for the synthesis of the target photochromic DHIs **10b–f** was achieved through the following synthesis (Scheme 4, Table 1). The Sonogashira coupling of **11a** and **11b** (which were previously prepared by us[30]) with **2a–c** in the presence of palladium diphenylphosphinedichloride (5%) and CuI/Et_3N in dry THF yielded the desired photochromic trimethylsilyl DHIs **12a–f** in 34–23% yield after purification by flash chromatography on silica gel and CH_2Cl_2 as eluent (method B).



Scheme 2. Preparation outline of spirocyclopropene precursors **7a**–**c**.



Scheme 3. Method (A) for preparation outline of photochromic DHIs **10a**–**f** from spirocyclopropenes **7b**,**c**.

Table 1
Substituent patterns, yields and melting points of the target photochromic DHIs (**10a–f**) synthesized by three pathways A, B and C

DHI **10**	R	*n*	Method	Yield (%)	Mp (°C)
a	H	0	A	24	152–153
a	H	0	B	68	152
a	H	0	C	43	151–152
b	H	1	A	20	143
b	H	1	B	56	142–143
b	H	1	C	40	142
c	H	2	A	16	116
c	H	2	B	51	115–116
c	H	2	C	39	114–115
d	CH_3	0	A	18	122
d	CH_3	0	B	46	122
d	CH_3	0	C	36	121
e	CH_3	1	A	17	112
e	CH_3	1	B	45	111–112
e	CH_3	1	C	32	112
f	CH_3	2	A	14	98
f	CH_3	2	B	44	99–100
f	CH_3	2	C	30	98

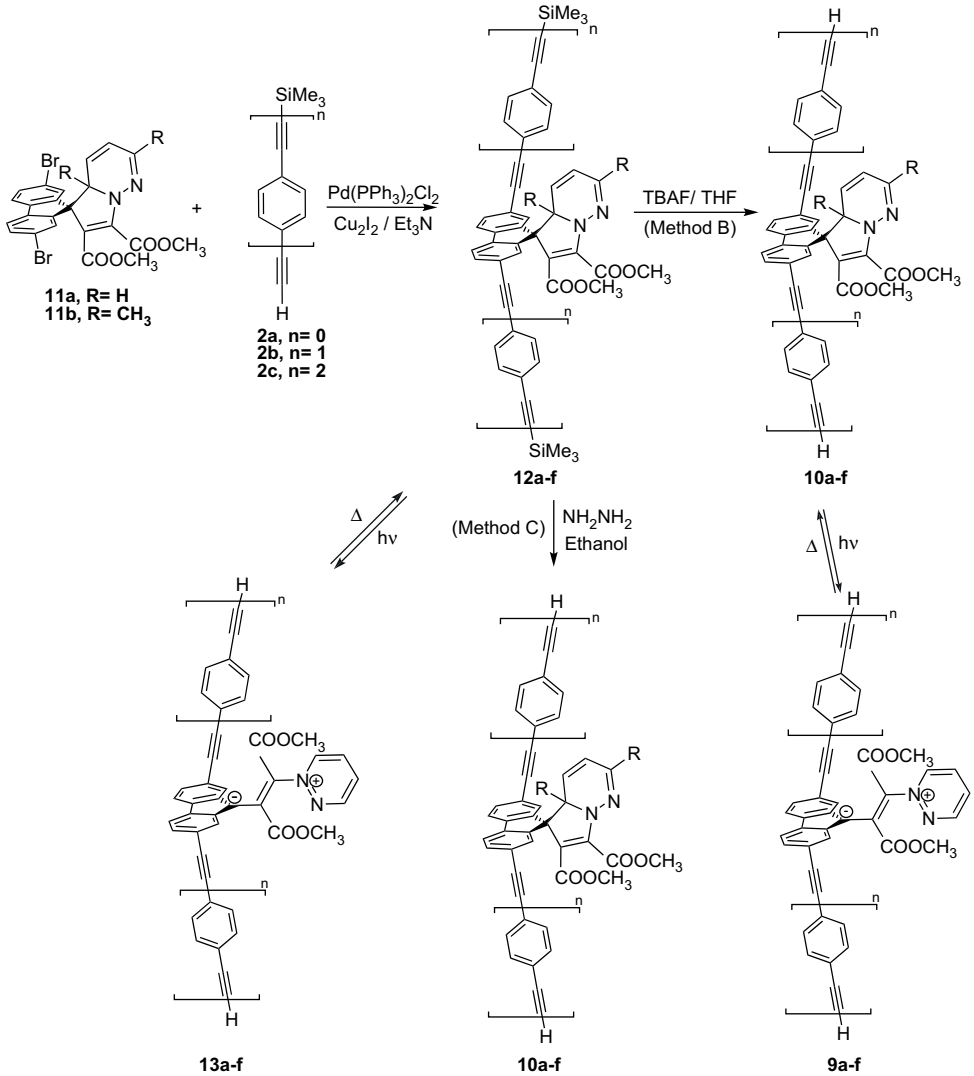
Treatment of DHIs **12a–f** with tetrabutyl ammonium fluoride (TBAF) in dry THF for 17 h afforded the desilylated products **10a–f** in 44–68% yield (Table 1).

Alternatively, deprotection could be achieved with hydrazine hydrate to give **10a–f** in 30–43% yield (method C, Table 1). Thus, rigid acetylenic bridged DHIs **10a–f** could be successfully prepared through three reactions pathways as shown in Scheme 4. The three products obtained from the different pathways showed the same analytical and exactly the same spectroscopic data as well as the same melting points (mp) and mixing melting points (mmp) (Table 1).

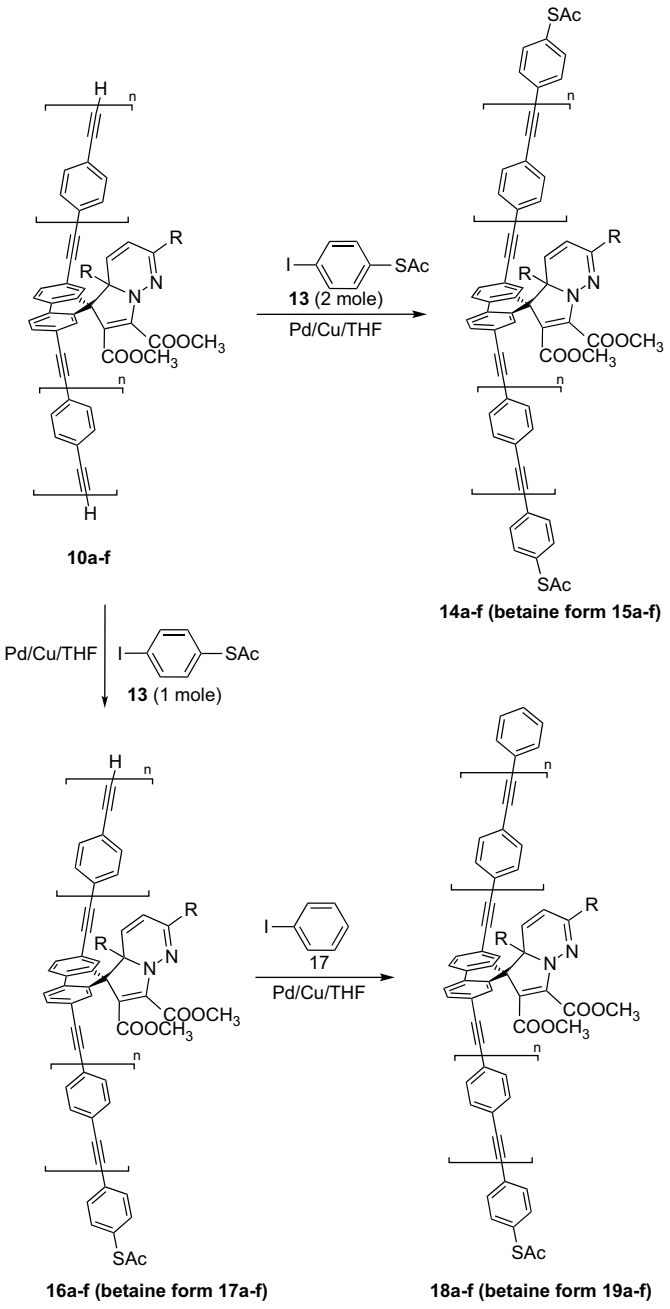
2.3. Palladium-mediated Sonogashira coupling of photochromic DHIs 10a–f with aryl halothioethers 13 and haloaryl 17 under different reaction conditions

The final coupling of the photochromic DHIs **10a–f** to thioester **13**[47] and iodobenzene **17** was planned via a palladium-mediated Sonogashira coupling (Scheme 5). Because of the strong affinity of sulfur containing groups, especially free thiols, for transition metals like palladium, the protection of the sulfur atoms is mandatory.[49] In the past, the coupling of alkynes with palladium in the presence of thioacetate functionalities was successfully achieved by several groups.[50,51]

Reaction of DHIs **10a–f** with 2 mol of 4-(thioacetyl)iodobenzene **13** under standard Sonogashira conditions (3% $Pd(PPh_3)Cl_2$, 10% PPh_3, 5% CuI/NEt_3, THF, 18 h at 45 °C, method A) gave low conversions to the coupling products **14a–f** (17–23% yield, method A). Alternative conditions for the Sonogashira coupling, using $Pd(OAc)_2$, triphenylphosphine and 10% CuI, NEt_3, toluene, DMF (3:1) for 12 h at 40 °C (method B) gave **14a–f** in better yields (27–38%). Aiming to



Scheme 4. Method (B,C) of the reaction pathways for the synthesis of the target photochromic DHIs **10a–f**.



Scheme 5. Palladium-mediated Sonogashira coupling of DHI **10a–f** with 4-(thioacetyl)iodobenzene **13** and iodobenzene **17**.

improve the coupling product yield of **14a–f**, the reaction conditions were changed to use bis(dibenzylideneacetone)palladium(0), 10% CuI, triphenylphosphine and DIEA in THF at 40 °C for 3 h (method C), which led to the formation of the coupling products **14a–f** in 43–52% yield. In addition, coupling of photochromic DHIs **10a–f** with 2 mol of 4-(thioacetyl)iodobenzene **13** using 1,0-phenathroline/NaI, CuI, DMF and TEA at 110 °C (method D) did not afford the coupling products **14a–f** (Table 2).

The above mentioned reaction conditions have been applied to the reaction of DHIs **10a–f** with 1 mol of 4-(thioacetyl)iodobenzene **13** in order to synthesize the desired monocoupling products **16a–f**. The best reaction conditions with the highest yield was found when using bis(dibenzylideneacetone)palladium(0), Cu_2I_2, triphenylphosphine and DIEA in THF at 40 °C for 3 h (method C), which led to the formation of the coupling products **16a–f** in 46–64% yield. Further coupling of DHIs **16a–f** with iodobenzene **17** under the above mentioned Sonogashira-coupling conditions (method C) led to the formation of the coupling products of the photochromic DHIs **18a–f** in 30–43% yield (Table 1). Analysis of **14c** through a NOESY experiment and MM2 (Fig. 1) suggests that the pyridazine moiety is perpendicular to the fluorene skeleton, which explained the coupling between the pyridazine and fluorene protons observed in this system.

Table 2
Substituents pattern, yields and melting points of the photochromic DHIs (**14a–f**, **16a–f** and **18a–f**) synthesized through palladium-mediated Sonogashira coupling

DHI	R	*n*	Method	Yield (%)	Mp (°C)
14a	H	0	A	23	112
14a	H	0	B	37	112–113
14a	H	0	C	52	113
14b	H	1	A	21	100
14b	H	1	B	38	99
14b	H	1	C	47	99–100
14c	H	2	A	20	86
14c	H	2	B	30	88
14c	H	2	C	47	87
14d	CH_3	0	A	18	102
14d	CH_3	0	B	29	102
14d	CH_3	0	C	45	101
14e	CH_3	1	A	18	84
14e	CH_3	1	B	27	82
14e	CH_3	1	C	44	80
14f	CH_3	2	A	17	72
14f	CH_3	2	B	27	71
14f	CH_3	2	C	43	71
16a	H	0	C	63	143
16b	H	1	C	64	136
16c	H	2	C	60	130
16d	CH_3	0	C	56	118
16e	CH_3	1	C	54	110
16f	CH_3	2	C	46	98
18a	H	0	C	40	129
18b	H	1	C	42	118
18c	H	2	C	43	102
18d	CH_3	0	C	39	113
18e	CH_3	1	C	35	90
18f	CH_3	2	C	30	83

2.4. Photophysical properties of the newly synthesized carbon-rich photochromic DHIs 10a–f, 12a–f, 14a–f, 16a–f and 18a–f, and their corresponding betaines 9a–f, 13a–f, 15a–f, 17a–f and 19a–f in dichloromethane solution at 23 °C

*2.4.1. Absorption spectra of DHIs **9**, **11**, **14**, **16** and **18**, and their corresponding betaines **8**, **12**, **15**, **17** and **19***

Photophysical data pertinent to their photochromic properties were obtained from the absorption features of photochromic DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f**. Electronic spectra of the newly synthesized DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f** were measured in dichloromethane solution using a UV–vis spectrophotometer with concentration of 1×10^{-5} mol/L at 23 °C. All studied DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f** are yellow in the solid state and in dichloromethane solution (Table 3). The intensities ($\log\varepsilon$) of these bands were found to be between 3.90 and 4.53 depending on the number of alkyne groups. The absorption of DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f** was observed in the far UV region and showed absorption maxima between 388 and 399 nm (Table 3). This absorption is dependent on the number of phenylethyne (*n*) substituents on the fluorene (region A). A pronounced bathochromic shift after coupling with 4-(thioacetyl)iodobenzene and iodobenzene as in DHIs **14a–f**, **16a–f** and **18a–f** by about 10 nm was recorded. This may be attributed to the increasing aromaticity of the conjugated DHI skeleton after coupling reaction. Methyl substituents in the pyridazine region could not influence the absorption maxima of the DHI system. As established previously,[26–34]

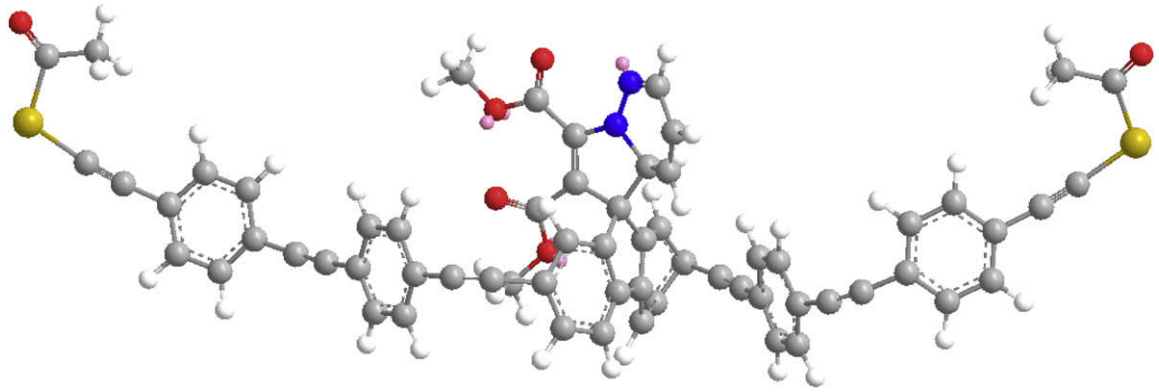


Figure 1. Representation of the optimized (MM2) structure of DHI **14c**.

these absorption bands can be assigned to the locally excited (LE) π–π^* transition located in the butadienyl-vinyl-amine chromophores[29–34] of DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f** (Table 3).

Irradiation of DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f** with polychromatic light leads to ring open betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f** (Fig. 2). The coloured betaine forms **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f** varied from red to blue-green; their colouration is obvious in CH_2Cl_2 solution with a concentration of 1×10^{-5} mol/L at room temperature because of their slower 1,5-electrocyclization, which refers to the stabilization of the charged zwitterionic betaines affected by the heterocyclic pyridazine moiety. All the absorption maxima of the coloured betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f** were found to be in the visible region and lie between 524 (betaine **9a**) and 639 nm (betaine **15f**). The UV spectra of the coloured betaines containing a pyridazine as a heterocyclic moiety in region C (i.e., **9a–c**, **13a–c**, **14a–c**, **17a–c** and **19a–c**) (Fig. 2) exhibit a red colour and show only one absorption maximum ranged between 524 and 537 nm. On the other hand, the betaine forms, which contain a dimethyl pyridazine substituents in region C (i.e., **9d–f**, **13d–f**, **14d–f**, **17d–f** and **19d–f)** exhibit a green-blue colour and show three absorption maxima between three isosbestic points (Table 3). The existence of the three isosbestic points proves that the thermal back reaction of the coloured betaines follows the first order reaction. Interestingly, a bathochromic shift of the absorption of the betaines containing non-substituted pyridazines **9a–c**, **13a–c**, **14a–c17a–c** and **19a–c** by more than 100 nm in the visible region compared with the betaines with dimethyl substituted pyridazines **9d–f**, **13d–f**, **14d–f**, **17d–f** and **19d–f** was recorded. This big shift led to the change of the coloured forms from red to green-blue and can be attributed to the electron donating abilities of the two methyl groups. These stabilized the zwitterionic betaines, hence causing the bathochromic shift of the coloured betaine absorptions in the visible region[30] (Table 3). Furthermore, a noticeable bathochromic shift of about 5–7 nm was observed upon increasing the number of bridged phenyl acetylenic groups from n=0 to n=3 with no dependency on the substituted or non-

Table 3
UV–vis absorption DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f**, and their corresponding betaines **8**, **12**, **15**, **17** and **19**, and kinetic data of betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f** in the *s* range (recorded by UV spectrophotometer) in CH_2Cl_2 solution (23 °C, $c=1\times10^{-5}$ mol/L)

DHI/betaine	λ_{max} (DHI) [nm]	log ε	λ_{max} (betaine) [nm]	$k\times10^{-3}$ (s^{-1})	$t_{1/2}$ (s)	Colour of betaine
10a/9a	388	3.90	524	6.19	112	Red
10b/9b	392	3.93	527	4.85	143	Red
10c/9c	397	4.07	530	3.50	198	Red
10d/9d	393	4.10	352, 447,627	0.99	698	Blue-green
10e/9e	395	4.15	356, 447,629	0.71	980	Blue-green
10f/9f	398	4.19	350, 445,631	0.62	1112	Blue-green
12a/13a	390	3.91	525	5.98	116	Red
12b/13b	392	3.94	528	4.65	149	Red
12c/13c	393	4.00	532	3.71	187	Red
12d/13d	394	4.14	353, 448,628	0.97	712	Green
12e/13e	398	4.17	358, 448,629	0.95	998	Green
12f/13f	398	4.19	353, 446,632	0.57	1202	Green
14a/15a	390	4.12	529	4.15	167	Red
14b/15b	394	4.22	533	3.54	196	Red
14c/15c	398	4.27	538	2.85	243	Red
14d/15d	395	4.14	357, 448,633	0.86	806	Green-blue
14e/15e	397	4.19	358, 448,634	0.74	937	Green-blue
14f/15f	398	4.25	353, 446,639	0.50	1379	Green-blue
16a/17a	388	3.92	526	4.95	140	red
16b/17b	395	3.97	528	4.15	167	red
16c/17c	397	4.09	529	3.50	198	red
16d/17d	394	4.10	354, 442,630	0.99	703	Green-blue
16e/17e	396	3.96	358, 446,632	0.88	786	Green-blue
16f/17f	398	4.09	352, 447,636	0.70	984	Green-blue
18a/19a	388	4.16	528	4.25	163	Red
18b/19b	388	3.94	532	3.54	196	Red
18c/19c	390	3.99	537	2.85	243	Red
18d/19d	394	4.09	355, 447,632	0.86	806	Green-blue
18e/19e	396	4.12	357, 447,633	0.74	937	Green-blue
18f/19f	397	4.22	358, 448,635	0.50	1379	Green-blue

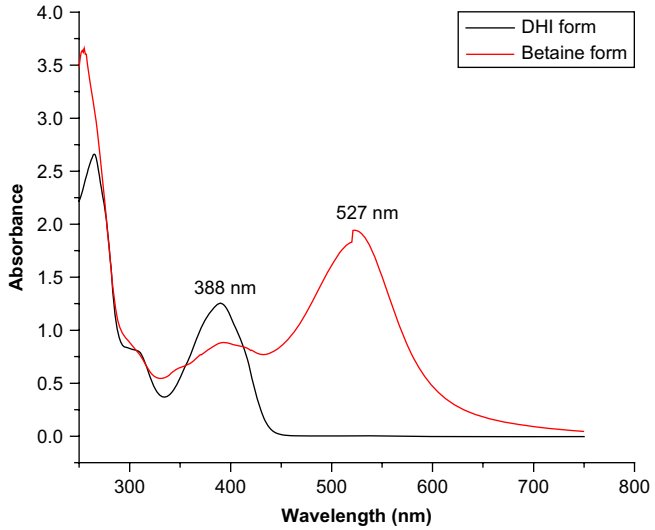


Figure 2. UV–vis of photochromic DHI **18c** and the corresponding betaine form **19c** after UV irradiation in CH_2Cl_2 ($c=1\times10^{-5}$ mol/L) at ambient temperature.

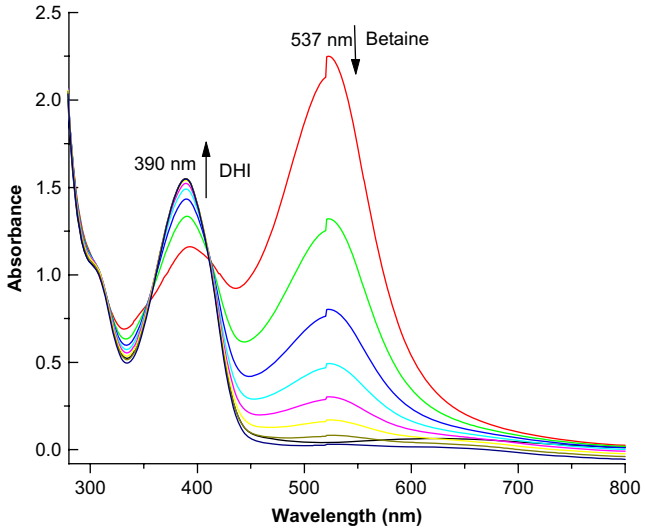


Figure 4. Kinetic FT-UV–vis spectrum of the thermal fading of betaine **19c** to DHI **18c** (cycle time=90 s, run time=900 s) in CH_2Cl_2 ($c=1\times10^{-5}$ mol/L at 253 K).

substituted pyridazine. This may be attributed to the increasing aromaticity of the fluorene unit conjugated with the aromatic phenyl rings through the bridged acetylenic bond. More spectroscopic data about the UV–vis measurements of the coloured betaines under investigation are listed in Table 3.

The kinetics of the thermal 1,5-electrocyclization was studied by using multichannel FT-UV–vis spectrophotometry (Figs. 3–5). The kinetic measurements showed that the half-lives of the coloured betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f** are in the second domain and lie between 112 and 1379 s (Table 3, Figs. 3–5). A highly pronounced increase in the half-lives of the betaines bearing a dimethyl substituted pyridazine (**9d–f**, **13d–f**, **14d–f**, **17d–f** and **19d–f**) by approximately a factor of 6 was observed compared with the half-lives of the betaines bearing a non-substituted pyridazine (**9a–c**, **13a–c**, **14a–c**, **17a–c** and **19a–c**). This increase in the half-lives may be attributed to the stabilization of the electrostatic charges on the betaines by the electron donating methyl groups. An increase of the half-lives of the betaines by increasing the number of acetylenic bridges from one to three acetylenic bridges in the fluorene part by approximately a factor of 1.25 was recorded. This may be attributed to the bulky sterically hindered phenyl rings substituted by the fluorene moiety. Also, a noticeable increase in the half-lives of the betaines coupled with thioacetyl groups as in **15a–f**, **17a–f** and **19a–f** compared with non-coupled betaines was observed. This tuning of the absorption maxima and the kinetic properties by changing the fluorene substitution (region A) as well as in the pyridazine (region C) will help this family of compounds to find many applications particularly in the area of molecular electronics.

*2.4.2. Photo-fatigue resistance of photochromic DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f**, and their corresponding betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f** in dichloromethane solution ($c=1\times10^{-5}$) at 253 K*

In studying the quality of a photochromic system the problem of carrying out a large number of colourization–decolourization cycles arises frequently. The gradual loss of the ability to change colour by exposure to visible or ultraviolet light in this context has been termed fatigue.[1] *Gautron*[51] has advanced a quantitative approach to measure the fatigue in photochromic systems.

Due to the slow thermal bleaching process of the betaines to DHIs, a temperature FT-UV–vis measurement was used in this case.

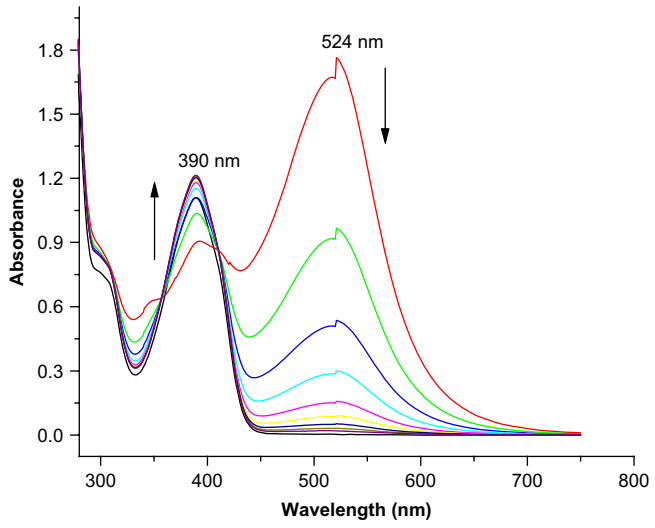


Figure 3. Kinetic FT-UV–vis spectrum of the thermal fading of betaine **13a** to DHI **12a** (cycle time=60 s, run time=600 s) in CH_2Cl_2 ($c=1\times10^{-5}$ mol/L at 253 K).

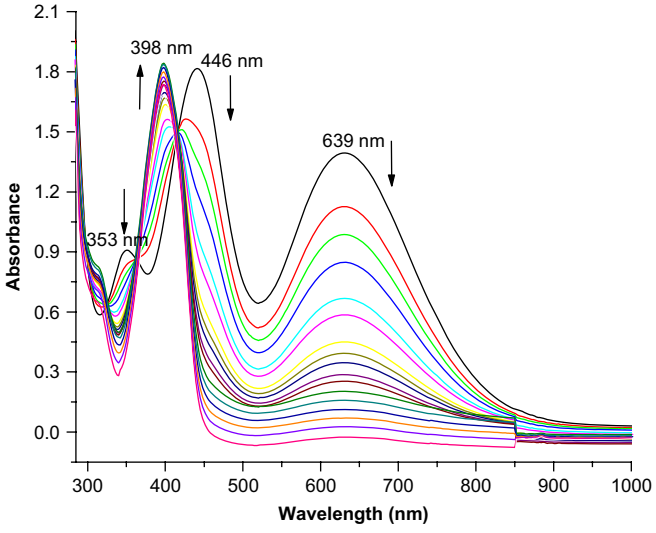


Figure 5. Kinetic FT-UV–vis spectrum of the thermal fading of betaine **15f** to DHI **14f** (cycle time=90 s, run time=3600 s) in CH_2Cl_2 ($c=1\times10^{-5}$ mol/L at 253 K).

Table 4
Photodegradation data of some selected betaines **9a–f**, **15a–f**, **17a–f** and **19a–f** in dichloromethane solution (c=1×10^{-5} mol/L) at 23 °C

Betaines	t_{30}-Betaine/DHI (min)	F	Betaines	t_{30}-Betaine/DHI (min)	F
9a	471	**1.94**	**17a**	589	2.42
9b	423	**1.74**	**17b**	542	2.23
9c	359	**1.48**	**17c**	513	2.11
9d	521	**2.14**	**17d**	675	2.78
9e	486	**2.00**	**17e**	624	2.57
9f	412	**1.70**	**17f**	525	2.16
15a	475	**1.95**	**19a**	599	2.47
15b	458	**1.88**	**19b**	546	2.25
15c	424	**1.74**	**19c**	534	2.20
15d	493	**2.03**	**19d**	698	2.87
15e	476	**1.96**	**19e**	664	2.73
15f	453	**1.86**	**19f**	603	2.48
Standard	**243**	**1.00**	**243**	**243**	**1.00**

Irradiation of degassed dichloromethane solution of DHIs **10a–f**, **12a–f**, **14a–f**, **16a–f** and **18a–f** at room temperature (23 °C) with polychromatic light (λ=200–400 nm) produced the coloured betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f**. Upon continued irradiation they decomposed after sometime. However, if oxygen is excluded, these systems are noticeably more stable. It is possible that in the presence of oxygen, betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f** act as sensitizers towards singlet oxygen.[1]

The photodegradation data represented in Table 4 and Figure 6 show that most of the selected betaines under investigation showed a higher photo-fatigue resistance than the standard dicyano-pyridazine *DHI* (t_{30}=243 min) by a factor of 1.48 in the case of betaine **9c**, and 2.87 in the case of betaine **19d**. A noticeable decrease of the t_{30} values by increasing the number of acetylenic bridges in both betaines bearing two methyl groups and the non-substituted pyridazine was recorded. A highly pronounced increase of the t_{30} values of the betaines incorporating dimethyl pyridazine as in betaines **9d–f**, **15d–f**, **17d–f** and **19d–f** compared with the betaines incorporating non-substituted pyridazine as in betaines **9a–c**, **15a–c**, **17a–c** and **19a–c** by factor of about 0.4 has been observed. Interestingly, betaines **15a–f** and **19a–f**, which have potential molecular electronic applications, showed the highest t_{30} values compared with other betaines under investigation. Betaine **19d** (t_{30}=698 min), substituted with two methyl groups in the pyridazine moiety, showed the highest photo-fatigue resistance by a factor of about 0.3 amongst the other studied betaines and also by a factor of 1.87 compared with the standard betaine (t_{30}=243 min). This betaine can now be used as the new standard in the photodegradation measurements in the photochromic dihydroindolizines family.

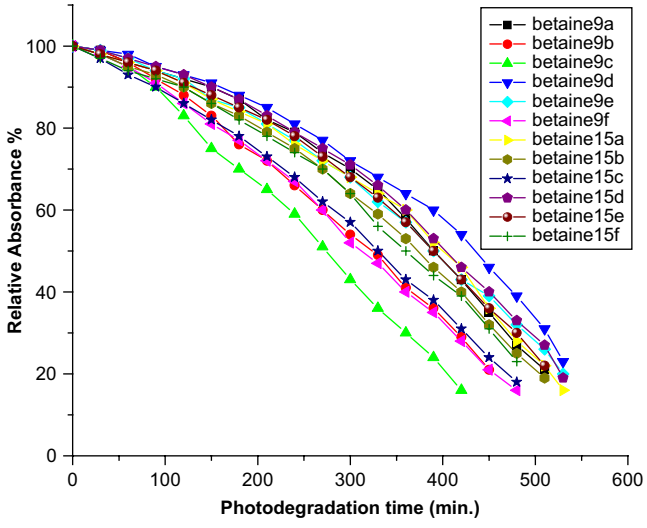


Figure 6. Time-relative absorbance relationship of the photodegradation experiment for determination of the t_{30} value of selected betaines **9a–f** and **15a–f** in CH_2Cl_2 (c=1×10^{-5} mol/L) at ambient temperature.

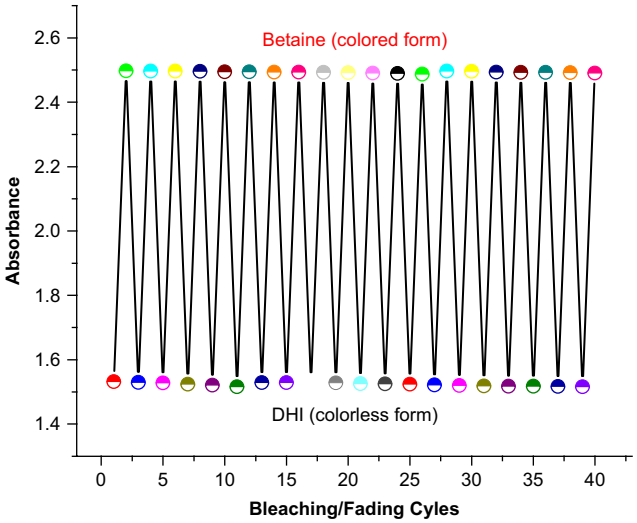


Figure 7. Cycling of the bleaching and fading of DHI **18b** and betaine **19b** (irradiation/thermal fading/irradiation cycles) in CH_2Cl_2 (c=1×10^{-5} mol/L) at ambient temperature.

Figure 7 represents an interesting property of the bleaching/fading of the DHI **18b** and betaine **19b**. These cycles of DHI/betaine showed that after irradiation and thermal fading, no decomposition product could be observed by UV–vis measurements. This result is corroborated by NMR measurements, which showed similar NMR spectra (coupling, δ values and integration) of the DHI before irradiation and after 20 cycles of irradiation with no detection of any decomposed products.

2.4.3. Solvatochromism

It is known that the UV–vis-absorption spectra of chemical compounds may be influenced by the surrounding medium and that solvents can bring about a change in the position, intensity and shape of absorption.[52,53]

Generally, a strong effect of the solvent polarity on the λ_{max} and half-lives of betaines **9a–f**, **13a–f**, **15a–f**, **17a–f** and **19a–f** was observed. For example, changing the solvent from tetrahydrofuran to methanol leads to a hypsochromic shift ranged between $\Delta\nu \cong +790$ and $\Delta\nu \cong +1120$ cm^{-1} in absorption in the visible region. These two

Table 5
Half-lives ($t_{1/2}$) of thermal 1,5-electrocyclization of selected betaines **9a**, **13f**, **15c**, **15e**, **17c**, **17d**, **19a**, **19d** and **19f**, and E_T(30) values of 10 different solvents recorded by kinetic UV–vis technique (c=1×10^{-5} mol/L) at ambient temperature

Solvents	Betaines $t_{1/2}$ (s)									E_T (30)
	9a	**13f**	**15c**	**15e**	**17c**	**17d**	**19a**	**19d**	**19f**	
n-Pentane	45	927	182	745	162	556	134	635	1087	32
Toluene	90	981	212	769	174	580	139	674	1139	34
Dioxane	103	1039	214	824	183	627	145	701	1201	36
Tetrahydrofuran	107	1099	222	836	187	639	149	734	1247	37
Chloroform	110	1164	237	887	191	673	154	787	1323	39
Dichloromethane	112	1202	243	937	198	712	168	811	1387	41
Acetonitrile	130	1301	298	1067	218	797	189	928	1537	46
2-Propanol	136	1464	301	1118	234	844	192	976	1664	49
Ethanol	151	1575	307	1173	256	887	212	1017	1737	52
Methanol	160	1687	329	1294	284	951	229	1113	1898	56

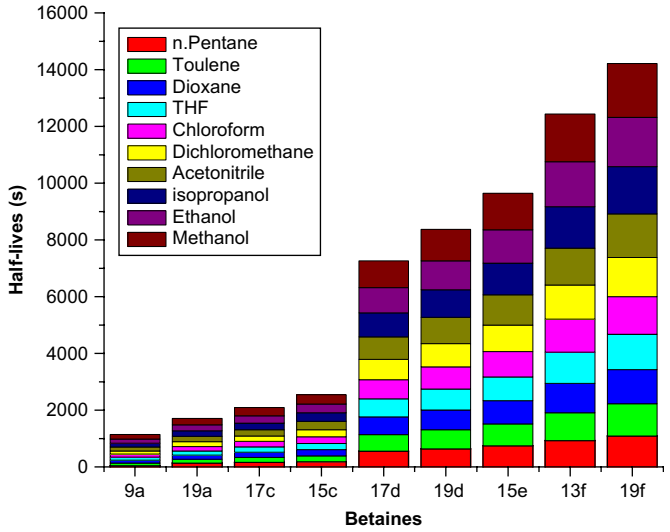


Figure 8. Representative diagram showing the influence of differing solvent polarity on the half-lives ($t_{1/2}$) of betaines **9a**, **13f**, **15c**, **15e**, **17c**, **17d**, **19a**, **19d** and **19f** recorded by millisecond flash photolysis technique (c=1×10^{-5} mol/L) at 23 °C.

solvatochromic shifts are ascribable to π–π* transitions in the visible region.

A pronounced solvent influence on the half-lives ($t_{1/2}$) of the selected betaines **9a**, **13f**, **15c**, **15e**, **17c**, **17d**, **19a**, **19d** and **19f** was determined using UV–vis techniques at room temperature in 10 different solvents (Table 5). A large increase in the half-lives with increasing solvent polarity was recorded in all studied betaines **9a**, **13f**, **15c**, **15e**, **17c**, **17d**, **19a**, **19d** and **19f** (Fig. 8). This is mainly attributed to the partial charge transfer from the betaine form to the solvent and vice versa, as a result of a weak Coulombic-exchange effect. Therefore, the charged zwitterionic betaine structure was stabilized by increasing the solvent polarity due to the electrostatic interactions between them. The tunability of the half-lives in the different media polarities exhibits the importance of correct solvent selection for specific applications.

3. Conclusion

Carbon-rich molecules based on photochromic dihydroindolizine (DHI) derivatives have been successfully synthesized via Sonogashira-coupling reactions. The coupling reactions between fluorenes (region A) and acetylenic bridges resulted in target molecules with extended photochromism. In addition, new spirocyclopropenes for present and future designing of photochromic DHIs have been synthesized by both chemical and photochemical reaction methods. Different attempts towards suitable conditions for Sonogashira-mediated coupling of the DHI skeleton with 4-(thioacetyl)iodobenzene and iodobenzene have been discussed. Interesting photochromic properties have been observed by tuning the chemical structure of the photochromic DHI by changing the number of acetylenic bridges in the fluorene part and the substitution in the pyridazine region. This pronounced influence of the substitutions in both regions A and C showed strong effects on the UV–vis absorption of DHIs and betaines as well as their kinetic properties (half-lives). Interestingly, the photochromic DHIs and their corresponding betaines showed a very strong resistance to photodegradation through direct irradiation or by cycling between coloured and closed forms. A pronounced effect of 10 solvents with different polarities on the photochromism of the synthesized DHIs and their corresponding betaines has been observed. These broad spectrum photochromic properties of the new DHIs and their corresponding betaines will help to find their suitable applications. Further studies by supporting of these compounds onto the surface of metals such as gold, silicon and titanium will be discussed in detail in the forthcoming paper.

4. Experimental

4.1. General

Spirocyclopropene derivatives **7a**–**c** were obtained via photolysis of the corresponding pyrazoles prepared according to the reported procedures.[54] Photolysis was carried out in the photochemical reactor of Schenck[55] made from Pyrex (λ >290 nm). The source of irradiation was a high pressure mercury lamp Philips HPK 125 W. Dihydroindolizines **11a**,**b** were previously prepared by us.[30a–d] Trimethylsilyl acetylene derivatives **2a**–**c** were prepared following the reaction procedures published by Rodriguez et al.[35b] Full characterization of spirocyclopropenes **7a**–**c** will be given in detail in the forthcoming paper.[56] Prior to photolysis, solutions were flushed with dry nitrogen for 30 min before switching on the UV lamp. The progress of the reaction and the purity of the products isolated were monitored using TLC. Separation and purification of all the synthesized photochromic materials were carried out using column chromatography (80 cm length×2 cm diameter) on silica gel and CH_2Cl_2 as eluent. Melting points were determined on an Electrothermal Eng. Ltd melting point apparatus and are uncorrected. All NMR spectra were collected on a Brüker DRX 400 spectrometer (400 MHz) in $CDCl_3$ using TMS as the internal standard. Chemical shifts (δ) are reported in parts per million. FTIR measurements were performed using a Perkin Elmer Paragon 1000 instrument. Mass spectra were recorded on a VG AutoSpec apparatus using electronic impact at 70 eV. MALDI-MS spectra were recorded in the positive mode by using a 2,5-dihydroxy-benzoic acid in dioxane as matrix. IR spectra were measured on a BIO-Rad Excalibur series, FTS 3000. UV spectra were recorded on an FT-UV/VIS JASCO V-570 computerized spectrophotometer. Experimental details, procedures and full characterizations of the new synthesized DHIs **10a**–**f**, **12a**–**f**, **14a**–**f**, **16a**–**f** and **18a**–**f** are described below.

4.2. Dimethyl (2,7-diphenylethynyl)$_n$-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-*b*]pyridazine]-6′,7′-dicarboxylates 10a–f: general procedure

Method A. A mixture of spirocyclopropenes **7a**–**c** (1 mmol) in dry ether (50 mL) and pyridazine **8a** (2 mmol) and/or 2,6-dimethyl pyridazine (2 mmol) were stirred at room temperature under dry N_2 with exclusion of light for 24 h. Ether was removed under reduced pressure and the residue was chromatographed twice on silica gel (dichloromethane). The pure product was obtained after recrystallization from the appropriate solvents to afford the products as pale yellow crystals.

Method B. To a solution of 2,7-dibromo pyridazine DHIs **11a**,**b** (1.1 mmol) and trimethylacetylene (0.35 mL, 2.5 mmol) in dry THF (20 mL) and freshly distilled triethylamine (50 mL) under an argon atmosphere at 50 °C were added dichloro bis(triphenylphosphine)palladium (39 mg, 0.052 mmol, 5%) and copper iodide (2.1 mg, 0.015 mmol). The mixture was stirred for 5 h and then the amine and THF were removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution with a little amount of KCN (1% solution, 20 mL) and extracted with dichloromethane. The extracts were dried over anhydrous sodium sulfate and after filtration, the solvent was removed to give a brown solid, which was purified by silica gel column chromatography to afford the trimethylated DHIs **12a**–**f**. DHIs **12a**–**f**

(0.28 mmol) were stirred in freshly distilled dry THF (20 mL) with a mixture of tetrabutyl ammonium fluoride (TBAF, 0.300 g, 2.2 mmol) in freshly distilled THF solution (5 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 12 h and then water (20 mL) was added. The mixture was extracted with ethyl acetate (3×20 mL) and the residue was purified by column chromatography using dichloromethane as eluent to afford the required compounds **10a–f** as yellow solids.

Method C. A solution of DHIs **12a–f** (0.5 mmol) and hydrazine hydrate (99%, 0.1 mL, 2 mmol) in absolute ethanol (20 mL) was cooled to 0 °C and stirred at this temperature for 2 h. The solvent was removed and the product was extracted with ethyl acetate (3×20 mL) and the residue was purified by column chromatography using dichloromethane as eluent to afford the required compounds **10a–f** as yellow solids.

4.2.1. Dimethyl 2,7-diethynyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***10a***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J=2.2 Hz, 1H, CH-arom.), 7.30–7.39 (m, 4H, CH-arom.), 7.26 (d, J=0.88 Hz, 1H, CH-arom.), 6.98 (dd, J=1.76, 1.98 Hz, 1H, 6′-CH), 5.45–5.49 (m, 1H, 7′-CH), 4.95 (t, J=2.2 Hz, 1H, 8a′-CH), 4.72 (dt, J=9.60, 1.76 Hz, 8′-CH), 4.02 (s, 2H, acetylenic-H), 3.90 (s, 3H, 3′-CH_3), 3.42 (s, 3H, 2′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.67 (3′-CO), 161.36 (2′-CO), 149.70, 148.47, 142.61, 138.99, 138.94, 138.12, 133.87, 133.18, 129.27, 128.76, 125.23, 124.98, 124.14, 121.22, 120.87, 118.97, 104.93, 82.42 (acetylenic-C), 81.40 (acetylenic-C), 65.36 (8′a-C), 63.39 (spiro-C), 53.45 (3′-CH_3), 51.37 (2′-CH_3) ppm; IR (KBr): ν=3107–3070 (C–H, arom.), 2832–2969 (C–H, aliph.), 2167 (acetylenic bond),1747 (3′-C=O), 1697 (2′-C=O), 1591 (C=N), 1440 (C=C), 1333, 1249, 1194, 1087, 957, 889, 773 cm^{-1}; MS-EI m/e (%) 434.13 [M$^+$]. Elemental analysis for $C_{27}H_{18}N_2O_4$: C, 74.64; H, 4.18; N, 6.45. Found %: C, 74.65; H, 4.17; N, 6.45.

4.2.2. Dimethyl 2,7-bis((4-ethynylphenyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***10b***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J=7.86 Hz, 4H, arom.), 7.54 (d, J=7.86 Hz, 4H, arom.), 7.31 (d, J=2.2 Hz, 1H, CH-arom.), 7.27–7.36 (m, 4H, CH-arom.), 6.97 (d, J=0.88 Hz, 1H, CH-arom.), 7.77 (dd, J=1.76, 1.98 Hz, 1H, 6′-CH), 5.49–5.51 (m, 1H, 7′-CH), 4.94 (t, J=2.2 Hz, 1H, 8a′-CH), 4.74 (dt, J=9.60, 1.76 Hz, 8′-CH), 4.08 (s, 2H, acetylenic-H), 3.94 (s, 3H, 3′-CH_3), 3.44 (s, 3H, 2′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.63 (3′-CO), 161.34 (2′-CO), 149.74, 148.47, 142.64, 138.97, 138.97, 138.13, 133.84, 133.18, 131.93, 129.28, 128.77, 125.20, 124.95, 124.10, 122.43, 121.27, 120.87, 118.95, 104.97, 93.39 (acetylenic-C), 91.67 (acetylenic-C), 82.47 (acetylenic-C), 81.45 (acetylenic-C), 65.32 (8′a-C), 63.45 (spiro-C), 53.48 (3′-CH_3), 51.33 (2′-CH_3) ppm; IR (KBr): ν=3138–3062 (C–H, arom.), 2837–2978 (C-H, aliph.), 2158 (acetylenic bond), 1756 (3′-C=O), 1685 (2′-C=O), 1597 (C=N), 1449 (C=C), 1342, 1257, 1192, 1098, 952, 882, 773 cm^{-1}; MS-EI m/e (%) 634.19 [M$^+$]. Elemental analysis for $C_{43}H_{26}N_2O_4$: C, 81.37; H, 4.13; N, 4.41. Found %: C, 81.36; H, 4.15; N, 4.42.

4.2.3. Dimethyl 2,7-bis((4-((4-ethynylphenyl)ethynyl)phenyl)-ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***10c***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J=7.86 Hz, 4H, arom.), 7.57 (d, J=7.86 Hz, 4H, arom.), 7.54 (d, J=7.86 Hz, 4H, arom.), 7.51 (d, J=7.86 Hz, 4H, arom.), 7.35 (d, J=2.2 Hz, 1H, CH-arom.), 7.32–7.38 (m, 4H, CH-arom.), 6.96 (d, J=0.88 Hz, 1H, CH-arom.), 7.73 (dd, J=1.76, 1.97 Hz, 1H, 6′CH), 5.50–5.52 (m, 1H, 7′-CH), 4.92 (t, J=2.2 Hz, 1H, 8a′-CH), 4.74 (dt, J=9.60,1.76 Hz, 8′-CH), 4.05 (s, 2H, acetylenic-H), 3.92 (s, 3H, 3′-CH_3), 3.44 (s, 3H, 2′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.61 (3′-CO), 161.37 (2′-CO), 149.78, 148.42, 142.61, 138.97, 138.93, 138.10, 133.84, 133.27, 131.81, 129.29, 128.74, 125.28, 124.95, 124.08, 122.47, 121.26, 120.84, 118.90, 104.98, 93.38 (acetylenic-C), 91.61 (acetylenic-C), 82.42 (acetylenic-C), 81.42 (acetylenic-C), 65.36 (8′a-C), 63.42 (spiro-C), 53.44 (3′-CH_3), 51.37 (2′-CH_3) ppm; IR (KBr): ν=3128–3067 (C-H, arom.), 2830–2987 (C-H, aliph.), 2152 (acetylenic bond), 1754 (3′-C=O), 1683 (2′-C=O), 1598 (C=N), 1457 (C=C), 1348, 1256, 1190, 1097, 954, 889, 773 cm^{-1}; MS-EI m/e (%) 834.25 [M$^+$]. Elemental analysis for $C_{59}H_{34}N_2O_4$: C, 84.87; H, 4.10; N, 3.36. Found %: C, 84.88; H, 4.11; N, 3.35.

4.2.4. Dimethyl 2,7-diethynyl-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***10d***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=1.45 Hz, 1H, CH-arom.), 7.60 (d, J=8.13 Hz, 2H, CH-arom.), 7.50 (dd, J=1.55, 2.12 Hz, 1H, CH-arom.), 7.46–725 (m, 2H, CH-arom.), 5.54 (d, J=9.73 Hz, 1H, 7′-CH), 5.04 (d, J=9.71 Hz, 1H, 8′-CH), 4.07 (s, 2H, acetylenic-H), 3.95 (s, 3H, 3′-CH_3), 3.37 (s, 3H, 2′-CH_3), 2.05 (s, 3H, 6′-CH_3), 1.48 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.62 (3′-CO), 161.56 (2′-CO), 149.37, 147.34, 144.87, 139.87, 138.07, 132.79, 131.77, 131.51, 129.87, 127.86, 121.28, 121.34, 120.95, 118.94, 100.88, 82.48 (acetylenic-C), 81.47 (acetylenic-C), 66.79 (8′a-C), 66.41 (spiro-C), 53.41 (3′-CH_3), 51.08 (2′-CH_3), 22.41 (6′-CH_3), 21.18 (8′-CH_3) ppm; IR (KBr): ν=3079 (C–H, arom.), 2932–2977 (C-H, aliph.), 2182 (acetylenic bond), 1741 (3′-C=O), 1691 (2′-C=O), 1608 (C=N), 1537 (C=C), 1426, 1379, 1287, 1168, 1068, 945, 879, 762 cm^{-1}; MS-EI m/e (%) 462.16 [M$^+$]. Elemental analysis for $C_{29}H_{22}N_2O_4$: C, 75.31; H, 4.79; N, 6.06. Found %: C, 75.32; H, 4.78; N, 6.07.

4.2.5. Dimethyl 2,7-bis((4-ethynylphenyl)ethynyl)-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***10e***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=1.45 Hz, 1H, CH-arom.), 7.63 (d, J=7.86 Hz, 4H, arom.), 7.60 (d, J=8.13 Hz, 2H, CH-arom.), 7.51 (d, J=7.86 Hz, 4H, arom.), 7.48 (dd, J=1.55, 1.97 Hz, 1H, CH-arom.), 7.42–7.50 (m, 2H, CH-arom.), 5.53 (d, J=9.73 Hz, 1H, 7′-CH), 5.10 (d, J=9.71 Hz, 1H, 8′-CH), 4.22 (s, 2H, acetylenic-H), 3.97 (s, 3H, 3′-CH_3), 3.32 (s, 3H, 2′-CH_3), 2.09 (s, 3H, 6′-CH_3), 1.57 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.96 (3′-CO), 161.54 (2′-CO), 149.39, 147.31, 144.88, 139.73, 138.64, 132.87, 131.74, 131.57, 129.81, 127.86, 121.35, 121.23, 120.87, 118.87, 100.80, 93.39 (acetylenic-C), 91.67 (acetylenic-C), 82.57 (acetylenic-C), 81.44 (acetylenic-C), 66.87 (8′a-C), 66.57 (spiro-C), 53.47 (3′-CH_3), 51.11 (2′-CH_3), 22.51 (6′-CH_3), 21.27 (8′-CH_3) ppm; IR (KBr): ν=3087 (C–H, arom.), 2980 (C–H, aliph.), 2178 (acetylenic bond), 1743 (3′-C=O), 1697 (2′-C=O), 1612 (C=N), 1537 (C=C), 1434, 1384, 1281, 1197, 1070, 941, 889, 760 cm^{-1}; MS-EI m/e (%) 662.22 [M$^+$]. Elemental analysis for $C_{45}H_{30}N_2O_4$: C, 81.55; H, 4.56; N, 4.23. Found %: C, 81.55; H, 4.55; N, 4.24.

4.2.6. Dimethyl 2,7-bis((4-((4-ethynylphenyl)ethynyl)phenyl)-ethynyl)-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***10f***

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J=7.86 Hz, 4H, arom.), 7.63 (d, J=7.86 Hz, 4H, arom.), 7.59 (d, J=7.86 Hz, 4H, arom.), 7.54 (d, J=7.86 Hz, 4H, arom.), 7.68 (d, J=1.45 Hz, 1H, CH-arom.), 7.56 (d, J=8.20 Hz, 2H, CH-arom.), 7.47–7.49 (dd, J=1.55, 1.98 Hz, 1H, CH-arom.), 7.42–7.46 (m, 2H, CH-arom.), 5.42 (d, J=9.60 Hz, 1H, 7′-CH), 5.08 (d, J=9.71 Hz, 1H, 8′-CH), 4.27 (s, 2H, acetylenic-H), 3.92 (s, 3H, 3′-CH_3), 3.37 (s, 3H, 2′-CH_3), 2.18 (s, 3H, 6′-CH_3), 1.67 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.76 (3′-CO), 161.65 (2′-CO), 149.27, 147.37, 144.80, 139.77, 138.61, 132.88, 131.84, 131.63, 129.79, 127.38, 121.30, 121.24, 120.90, 118.97, 100.80, 93.45 (acetylenic-C), 91.85 (acetylenic-C), 82.50 (acetylenic-C), 81.47 (acetylenic-C), 66.76 (8′a-C), 66.67 (spiro-C), 53.43 (3′-CH_3), 51.17 (2′-CH_3), 22.59 (6′-CH_3), 21.36 (8′-CH_3) ppm; IR (KBr): ν=3120 (C–H, arom.),

2963 (C–H, aliph.), 2199 (acetylenic bond), 1749 (3′-C═O), 1692 (2′-C═O), 1604 (C═N), 1539 (C═C), 1434, 1381, 1287, 1210, 1077, 946, 887, 766 cm^{-1}; MS-EI *m*/*e* (%) 862.28 [M^+]. Elemental analysis for $C_{61}H_{38}N_2O_4$: C, 84.90; H, 4.44; N, 3.25. Found %: C, 84.91; H, 4.43; N, 3.25.

4.2.7. Dimethyl 2,7-bis((trimethylsilyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **12a**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.21–7.28 (m, 4H, CH-arom.), 7.04 (d, *J*=0.88 Hz, 1H, CH-arom.), 7.71 (dd, *J*=1.76, 1.99 Hz, 1H, 6′-CH), 5.37–5.39 (m, 1H, 7′-CH), 4.93 (t, *J*=2.2 Hz, 1H, 8a′-CH), 4.69 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.92 (s, 3H, 3′-CH_3), 3.40 (s, 3H, 2′-CH_3), 0.28 (s, 18H, $Si(CH_3)_3$) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.62 (3′-CO), 161.45 (2′-CO), 149.78, 148.44, 142.62, 139.08, 138.87, 138.01, 133.89, 133.22, 129.29, 128.67, 125.45, 124.92, 124.10, 121.27, 120.68, 118.99, 104.84, 80.10 (acetylenic-C), 79.38 (acetylenic-C), 64.34 (8′a-C), 62.97 (spiro-C), 51.46 (3′-CH_3), 50.67 (2′-CH_3), 13.69 ($Si(CH_3)_3$) ppm; IR (KBr): ν=3149–3023 (C–H, arom.), 2849–2984 (C–H, aliph.), 2146 (acetylenic bond), 1741 (3′-C═O), 1694 (2′-C═O), 1591 (C═N), 1442 (C═C), 1367, 1234, 1187, 1072, 955, 893, 778 cm^{-1}; MS-EI *m*/*e* (%) 578.21 [M^+]. Elemental analysis for $C_{33}H_{34}N_2O_4Si_2$: C, 68.48; H, 5.92; N, 4.84. Found %: C, 68.49; H, 5.93; N, 4.82.

4.2.8. Dimethyl 2,7-bis((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **12b**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J*=7.86 Hz, 4H, arom.), 7.57 (d, *J*=7.86 Hz, 4H, arom.), 7.36 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.29–7.34 (m, 4H, CH-arom.), 6.96 (d, *J*=0.88 Hz, 1H, CH-arom.), 7.74 (dd, *J*=1.76, 1.96 Hz, 1H, 6′-CH), 5.50–5.53 (m, 1H, 7′-CH), 4.93 (t, *J*=2.2 Hz, 1H, 8a′-CH), 4.75 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.88 (s, 3H, 3′-CH_3), 3.41 (s, 3H, 2′-CH_3), 0.26 (s, 18H, $Si(CH_3)_3$) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.72 (3′-CO), 161.17 (2′-CO), 149.76, 148.44, 142.73, 138.81, 138.67, 138.22, 133.87, 133.27, 131.96, 129.36, 128.82, 125.36, 125.13, 124.64, 122.38, 121.21, 120.79, 118.76, 104.84, 93.32 (acetylenic-C), 90.99 (acetylenic-C), 81.67 (acetylenic-C), 80.44 (acetylenic-C), 64.79 (8′a-C), 62.98 (spiro-C), 52.98 (3′-CH_3), 51.02 (2′-CH_3), 13.97 ($Si(CH_3)_3$) ppm; IR (KBr): ν=3138–3095 (C–H, arom.), 2867–2980 (C–H, aliph.), 2146 (acetylenic bond), 1754 (3′-C═O), 1687 (2′-C═O), 1580 (C═N), 1457 (C═C), 1347, 1269, 1190, 1067, 957, 873, 795 cm^{-1}; MS-EI *m*/*e* (%) 778.27 [M^+]. Elemental analysis for $C_{49}H_{42}N_2O_4Si_2$: C, 75.54; H, 5.43; N, 3.60. Found %: C, 75.53; H, 5.44; N, 3.60.

4.2.9. Dimethyl 2,7-bis((4-((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **12c**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J*=7.86 Hz, 4H, arom.), 7.52 (d, *J*=7.86 Hz, 4H, arom.), 7.58 (d, *J*=7.86 Hz, 4H, arom.), 7.56 (d, *J*=7.86 Hz, 4H, arom.), 7.35 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.36–7.39 (m, 4H, CH-arom.), 6.93 (d, *J*=0.88 Hz, 1H, CH-arom.), 7.73 (dd, *J*=1.76, 1.98 Hz, 1H, 6′-CH), 5.53–5.54 (m, 1H, 7′-CH), 4.92 (t, *J*=2.2 Hz, 1H, 8a′-CH), 4.72 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.86 (s, 3H, 3′-CH_3), 3.37 (s, 3H, 2′-CH_3), 0.24 (s, 18H, $Si(CH_3)_3$) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.61 (3′-CO), 162.43 (2′-CO), 149.83, 148.47, 142.66, 138.82, 138.86, 138.37, 133.76, 133.10, 131.79, 129.64, 128.75, 125.37, 124.87, 124.13, 122.67, 121.36, 120.79, 118.87, 104.64, 93.36 (acetylenic-C), 90.67 (acetylenic-C), 81.79 (acetylenic-C), 80.39 (acetylenic-C), 65.46 (8′a-C), 63.75 (spiro-C), 53.95 (3′-CH_3), 51.64 (2′-CH_3), 13.97 ($Si(CH_3)_3$) ppm; IR (KBr): ν=3136–3079 (C–H, arom.), 2837–2990 (C–H, aliph.), 2162 (acetylenic bond), 1750 (3′-C═O), 1687 (2′-C═O), 1598 (C═N), 1474 (C═C), 1356, 1247, 1136, 1080, 957, 899, 774 cm^{-1}; MS-EI *m*/*e* (%) 978.33 [M^+]. Elemental analysis for $C_{65}H_{50}N_2O_4Si_2$: C, 79.72; H, 5.15; N, 2.86. Found %: C, 79.71; H, 5.14; N, 2.86.

4.2.10. Dimethyl 2′,4a′-dimethyl-2,7-bis((trimethylsilyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **12d**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J*=1.45 Hz, 1H, CH-arom.), 7.64 (d, *J*=8.13 Hz, 2H, CH-arom.), 7.54 (dd, *J*=1.55, 1.98 Hz, 1H, CH-arom.), 7.44–7.47 (m, 2H, CH-arom.), 5.52 (d, *J*=9.73 Hz, 1H, 7′-CH), 5.12 (d, *J*=9.71 Hz, 1H, 8′-CH), 3.78 (s, 3H, 3′-CH_3), 3.33 (s, 3H, 2′-CH_3), 2.15 (s, 3H, 6′-CH_3), 1.42 (s, 3H, 8′-CH_3), 0.24 (s, 18H, $Si(CH_3)_3$) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 136.63 (3′-CO), 161.66 (2′-CO), 149.46, 147.37, 144.90, 139.96, 138.16, 132.79, 131.96, 131.51, 129.67, 127.67, 121.34, 121.95, 120.34, 118.85, 100.86, 82.42 (acetylenic-C), 81.31 (acetylenic-C), 66.67 (8′a-C), 66.67 (spiro-C), 53.67 (3′-CH_3), 51.19 (2′-CH_3), 22.46 (6′-CH_3), 21.23 (8′-CH_3), 13.12 ($Si(CH_3)_3$) ppm; IR (KBr): ν=3087 (C–H, arom.), 2960–2989 (C–H, aliph.), 2164 (acetylenic bond), 1743 (3′-C═O), 1697 (2′-C═O), 1613 (C═N), 1540 (C═C), 1427, 1380, 1267, 1189, 1076, 947, 873, 749 cm^{-1}; MS-EI *m*/*e* (%) 606.24 [M^+]. Elemental analysis for $C_{35}H_{38}N_2O_4Si_2$: C, 69.27; H, 6.31; N, 4.62. Found %: C, 69.28; H, 6.32; N, 4.60.

4.2.11. Dimethyl 2′,4a′-dimethyl-2,7-bis((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **10e**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J*=1.45 Hz, 1H, CH-arom.), 7.60 (d, *J*=7.86 Hz, 4H, arom.), 7.56 (d, *J*=8.13 Hz, 2H, CH-arom.), 7.57 (d, *J*=7.86 Hz, 4H, arom.), 7.48 (dd, *J*=1.55, 1.97 Hz, 1H, CH-arom.), 7.41–7.53 (m, 2H, CH-arom.), 5.60 (d, *J*=9.73 Hz, 1H, 7′-CH), 5.13 (d, *J*=9.71 Hz, 1H, 8′-CH), 3.82 (s, 3H, 3′-CH_3), 3.39 (s, 3H, 2′-CH_3), 2.03 (s, 3H, 6′-CH_3), 1.46 (s, 3H, 8′-CH_3), 0.24 (s, 18H, $Si(CH_3)_3$) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.69 (3′-CO), 162.01 (2′-CO), 149.46, 147.37, 144.76, 139.71, 138.64, 132.64, 131.25, 131.46, 129.97, 127.67, 121.37, 121.64, 120.97, 118.98, 100.23, 93.46 (acetylenic-C), 91.67 (acetylenic-C), 82.46 (acetylenic-C), 81.79 (acetylenic-C), 66.37 (8′a-C), 66.48 (spiro-C), 53.37 (3′-CH_3), 51.46 (2′-CH_3), 22.79 (6′-CH_3), 21.38 (8′-CH_3), 13.36 ($Si(CH_3)_3$) ppm; IR (KBr): ν=3081 (C–H, arom.), 2995 (C–H, aliph.), 2167 (acetylenic bond), 1740 (3′-C═O), 1693 (2′-C═O), 1613 (C═N), 1597 (C═C), 1433, 1394, 1287, 1182, 1046, 976, 879, 763 cm^{-1}; MS-EI *m*/*e* (%) 806.30 [M^+]. Elemental analysis for $C_{51}H_{46}N_2O_4Si_2$: C, 75.90; H, 5.74; N, 3.47. Found %: C, 75.89; H, 5.73; N, 3.47.

4.2.12. Dimethyl 2′,4a′-dimethyl-2,7-bis((4-((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **10f**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J*=7.86 Hz, 4H, arom.), 7.72 (d, *J*=7.86 Hz, 4H, arom.), 7.64 (d, *J*=7.86 Hz, 4H, arom.), 7.57 (d, *J*=7.86 Hz, 4H, arom.), 7.52 (d, *J*=1.45 Hz, 1H, CH-arom.), 7.48 (d, *J*=8.20 Hz, 2H, CH-arom.), 7.45 (dd, *J*=1.55, 1.98 Hz, 1H, CH-arom.), 7.40–7.42 (m, 2H, CH-arom.), 5.52 (d, *J*=9.60 Hz, 1H, 7′-CH), 5.26 (d, *J*=9.71 Hz, 1H, 8′-CH), 3.85 (s, 3H, 3′-CH_3), 3.32 (s, 3H, 2′-CH_3), 2.23 (s, 3H, 6′-CH_3), 1.72 (s, 3H, 8′-CH_3), 0.28 (s, 18H, $Si(CH_3)_3$) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 163.81 (3′-CO), 161.80 (2′-CO), 149.36, 147.34, 144.79, 139.64, 138.57, 132.38, 131.57, 131.61, 129.37, 127.82, 121.64, 121.15, 120.60, 119.32, 100.67, 93.98 (acetylenic-C), 90.87 (acetylenic-C), 81.67 (acetylenic-C), 80.96 (acetylenic-C), 67.34 (8′a-C), 66.47 (spiro-C), 53.64 (3′-CH_3), 51.28 (2′-CH_3), 22.67 (6′-CH_3), 21.46 (8′-CH_3), 13.36 ($Si(CH_3)_3$) ppm; IR (KBr): ν=3099 (C–H, arom.), 2895 (C–H, aliph.), 2184 (acetylenic bond), 1739 (3′-C═O), 1697 (2′-C═O), 1600 (C═N), 1549 (C═C), 1467, 1389, 1275, 1216, 1078, 969, 885, 767 cm^{-1}; MS-EI *m*/*e* (%) 1006.36 [M^+]. Elemental analysis for $C_{67}H_{54}N_2O_4Si_2$: C, 79.89; H, 5.40; N, 2.78. Found %: C, 79.90; H, 5.41; N, 2.77.

4.3. Sonogashira-mediated coupling for the synthesis of photochromic DHIs dimethyl 2,7-bis((4-(acetylthio)phenyl)-ethynyl)$_n$-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-*b*]pyridazine]-6′,7′-dicarboxylates 14a–f: general procedure

To an oven-dried screw cap tube or a round bottom flask equipped with a water cooled condenser and a magnetic stir bar were added 4-iodoacetyl-1-iodobenzene **13** (1.66 g, 6 mmol), bis (dibenzylideneacetone)palladium(0) (172 mg, 0.3 mmol), copper(I) iodide (114 mg, 0.6 mmol) and triphenylphosphine (314 mg, 0.12 mmol) to the terminal alkynes DHIs **12a–f** (2.99 mmol). The vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). A co-solvent system of freshly distilled THF (40 mL) followed by DIEA (4.2 mL, 24 mmol) was added. The reaction mixture was stirred in a 40 °C oil bath for 3 h until the reaction was complete. The reaction vessel was cooled to room temperature and the mixture quenched with a saturated solution of NH_4Cl (20 mL). The organic layer was diluted with CH_2Cl_2 and washed with a saturated solution of NH_4Cl (3×20 mL). The combined aqueous layers were extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent removed in vacuo. The crude products were then purified by column chromatography on silica gel with CH_2Cl_2 as eluent. The pure products were obtained as yellow needles. Full characterizations of the coupling products **14a–f** are cited below:

4.3.1. Dimethyl 2,7-bis((4-(acetylthio)phenyl)ethynyl)-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***14a***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–815 (d, J=1.6 Hz, 4H, arom.), 8.09 (d, J=8.1 Hz, 4H, arom.), 7.92–7.94 (d, J=2.2 Hz, 1H, CH-arom.), 7.76–7.82 (m, 4H, CH-arom.), 7.77 (dd, J=1.76, 1.98 Hz, 1H, 6′-CH), 7.14–7.16 (d, J=0.88 Hz, 1H, CH-arom.), 5.53–5.57 (m, 1H, 7′-CH), 4.83–4.86 (t, J=2.2 Hz, 1H, 8a′-CH), 4.70–4.73 (dt, J=9.60, 1.76 Hz, 8′-CH), 3.86 (s, 3H, 3′-CH_3), 3.31 (s, 3H, 2′-CH_3), 2.43 (s, 6H, 2CO–CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 189.15 (CO–CH_3), 163.75 (3′-CO), 162.69 (2′-CO), 150.20, 149.67, 148.21, 142.98, 138.97, 138.35, 138.13, 133.64, 133.38, 131.10, 129.41, 128.78, 125.78, 125.84, 124.58, 122.34, 121.38, 120.78, 118.36, 104.87, 98.26 (acetylenic-C), 96.47 (acetylenic-C), 65.37 (8′a-C), 63.22 (spiro-C), 53.98 (3′-CH_3), 51.00 (2′-CH_3), 30.84 (CO–CH_3) ppm; IR (KBr): ν=3010–3098 (C–H, arom.), 2898–2987 (C–H, aliph.), 2207 (acetylenic bond), 1756 (3′-C=O), 1709 (CO–CH_3), 1695 (2′-C=O), 1586 (C=N), 1454 (C=C), 1347, 1263, 1187, 1102, 958, 887, 776 cm^{-1}; MS-EI m/e (%) 734.15 [M$^+$]. Elemental analysis for $C_{43}H_{30}N_2O_6S_2$: C, 70.28; H, 4.11; N, 3.81; S, 8.73. Found %: C, 70.28; H, 4.10; N, 3.82; S, 8.75.

4.3.2. Dimethyl 2,7-bis((4-((4-(acetylthio)phenyl)ethynyl)-phenyl)ethynyl)-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-b]-pyridazine]-6′,7′-dicarboxylate ***14b***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J=7.86 Hz, 4H, arom.), 8.30 (d, J=7.86 Hz, 4H, arom.), 8.11 (d, J=7.86 Hz, 4H, arom.), 7.83 (d, J=7.86 Hz, 4H, arom.), 7.71 (d, J=2.2 Hz, 1H, CH-arom.), 7.38–7.45 (m, 4H, CH-arom.), 7.92 (d, J=0.88 Hz, 1H, CH-arom.), 7.60 (dd, J=1.76, 1.99 Hz, 1H, 6′-CH), 5.50–5.53 (m, 1H, 7′-CH), 4.86 (t, J=2.2 Hz, 1H, 8a′-CH), 4.77 (dt, J=9.60, 1.76 Hz, 8′-CH), 3.94 (s, 3H, 3′-CH_3), 3.44 (s, 3H, 2′-CH_3), 2.39 (s, 6H, 2CO–CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ191.87 (CO–CH_3), 164.13 (3′-CO), 162.64 (2′-CO), 150.23, 149.22, 148.97, 142.14, 138.78, 138.36, 138.20, 133.79, 133.36, 131.84, 129.20, 128.81, 125.36, 124.87, 124.16, 122.98, 121.64, 120.93, 118.76, 104.82, 96.43 (acetylenic-C), 94.61 (acetylenic-C), 83.36 (acetylenic-C), 80.99 (acetylenic-C), 65.79 (8′a-C), 63.42 (spiro-C), 53.63 (3′-CH_3), 51.78 (2′-CH_3), 30.62 (CO-CH_3) ppm; IR (KBr): ν=3089–3100 (C–H, arom.), 2887–2989 (C–H, aliph.), 2236 (acetylenic bond), 1743 (3′-C=O), 1706 (CO–CH_3), 1692 (2′-C=O), 1582 (C=N), 1457 (C=C), 1357, 1264, 1190, 1112, 963, 876, 736 cm^{-1}; MS-EI m/e (%) 934.22 [M$^+$]. Elemental analysis for $C_{59}H_{38}N_2O_6S_2$: C, 75.78; H, 4.10; N, 3.00; S, 6.86. Found %: C, 75.77; H, 4.11; N, 3.01; S, 6.86.

4.3.3. Dimethyl 2,7-bis((4-((4-((4-(acetylthio)phenyl)ethynyl)-phenyl)ethynyl)phenyl)ethynyl)-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***14c***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J=7.56 Hz, 4H, arom.), 8.07 (d, J=7.86 Hz, 4H, arom.), 7.98 (d, J=7.86 Hz, 4H, arom.), 7.74 (d, J=7.86 Hz, 4H, arom.), 7.62 (d, J=7.86 Hz, 4H, arom.), 7.47 (d, J=7.86 Hz, 4H, arom.), 7.41 (d, J=2.2 Hz, 1H, CH-arom.), 7.28–7.34 (m, 4H, CH-arom.), 7.17 (d, J=1.00 Hz, 1H, CH-arom.), 7.11 (dd, J=1.76, 1.86 Hz, 1H, 6′-CH), 5.43–5.45 (m, 1H, 7′-CH), 4.97 (t, J=2.2 Hz, 1H, 8a′-CH), 4.71 (dt, J=9.60, 1.76 Hz, 8′-CH), 3.88 (s, 3H, 3′-CH_3), 3.36 (s, 3H, 2′-CH_3), 2.38 (s, 6H, 2CO-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.28 (CO–CH_3), 163.14 (3′-CO), 162.49 (2′-CO), 152.27, 151.31, 149.36, 148.89, 142.73, 138.46, 138.87, 138.36, 133.75, 133.10, 131.54, 129.48, 128.36, 125.17, 124.80, 124.19, 122.97, 121.16, 120.84, 118.67, 104.90, 94.77 (acetylenic-C), 93.60 (acetylenic-C), 84.68 (acetylenic-C), 82.36 (acetylenic-C), 64.79 (8′a-C), 62.99 (spiro-C), 52.46 (3′-CH_3), 50.99 (2′-CH_3), 31.99 (CO-CH_3) ppm; IR (KBr): ν=3099–3110 (C–H, arom.), 2849–2936 (C–H, aliph.), 2209 (acetylenic bond), 1746 (3′-C=O), 1704 (CO–CH_3), 1692 (2′-C=O), 1603 (C=N), 1469 (C=C), 1352, 1263, 1181, 1136, 957, 880, 759 cm^{-1}; MS-EI m/e (%) 1134.28 [M$^+$]. Elemental analysis for $C_{75}H_{46}N_2O_6S_2$: C, 79.34; H, 4.08; N, 2.47; S, 5.65. Found %: C, 79.34; H, 4.10; N, 2.48; S, 5.64.

4.3.4. Dimethyl 2,7-bis((4-(acetylthio)phenyl)ethynyl)-2′,4a′-dimethyl-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***14d***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J=1.6 Hz, 4H, arom.), 8.13 (d, J=8.1 Hz, 4H, arom.), 8.03 (d, J=1.45 Hz, 1H, CH-arom.), 7.59 (d, J=8.13 Hz, 2H, CH-arom.), 7.43 (dd, J=1.55, 1.96 Hz, 1H, CH-arom.), 7.44–7.49 (m, 2H, CH-arom.), 5.60 (d, J=9.56 Hz, 1H, 7′-CH), 5.00 (d, J=9.71 Hz, 1H, 8′-CH), 3.82 (s, 3H, 3′-CH_3), 3.47 (s, 3H, 2′-CH_3), 2.30 (CO–CH_3), 2.10 (s, 3H, 6′-CH_3), 1.49 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 190.12 (CO–CH_3), 163.62 (3′-CO), 162.20 (2′-CO), 151.36, 149.69, 147.34, 144.95, 139.69, 138.13, 133.67, 131.97, 131.64, 129.78, 127.30, 121.48, 121.67, 120.92, 118.73, 101.36, 83.00 (acetylenic-C), 80.97 (acetylenic-C), 66.65 (8′a-C), 66.32 (spiro-C), 53.12 (3′-CH_3), 51.57 (2′-CH_3), 31.82 (CO–CH_3), 22.43 (6′-CH_3), 21.18 (8′-CH_3) ppm; IR (KBr): ν=3022–3098 (C–H, arom.), 2912–2945 (C–H, aliph.), 2209 (acetylenic bond), 1745 (3′-C=O), 1706 (CO–CH_3), 1694 (2′-C=O), 1619 (C=N), 1535 (C=C), 1423, 1377, 1283, 1170, 1078, 939, 876, 765 cm^{-1}; MS-EI m/e (%) 762.19 [M$^+$]. Elemental analysis for $C_{45}H_{34}N_2O_6S_2$: C, 70.85; H, 4.49; N, 3.67; S, 8.41. Found %: C, 70.86; H, 4.48; N, 3.68; S, 8.42.

4.3.5. Dimethyl 2,7-bis((4-((4-(acetylthio)phenyl)ethynyl)-phenyl)ethynyl)-2′,4a′-dimethyl-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***14e***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J=7.86 Hz, 4H, arom.), 8.40 (d, J=7.86 Hz, 4H, arom.), 8.33 (d, J=7.86 Hz, 4H, arom.), 7.93 (d, J=7.86 Hz, 4H, arom.), 7.70 (d, J=2.2 Hz, 1H, CH-arom.), 7.36–7.39 (m, 4H, CH-arom.), 7.91 (d, J=0.88 Hz, 1H, CH-arom.), 7.68 (dd, J=1.76, 1.96 Hz, 1H, 6′-CH), 5.59–5.60 (m, 1H, 7′-CH), 4.38 (dt, J=9.60, 1.76 Hz, 8′-CH), 3.90 (s, 3H, 3′-CH_3), 3.39 (s, 3H, 2′-CH_3), 2.32 (s, 6H, 2CO–CH_3), 2.18 (s, 3H, 6′-CH_3), 1.43 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 190.36 (CO–CH_3), 163.28 (3′-CO), 161.99 (2′-CO), 151.26, 150.68, 149.32, 143.26, 139.36, 138.52, 138.33, 134.79, 133.67, 131.87, 129.39, 128.75, 125.47, 124.78, 124.13, 122.49, 120.96, 120.34, 118.60, 104.79, 96.34 (acetylenic-C), 93.98 (acetylenic-C), 82.36 (acetylenic-C), 80.32 (acetylenic-C), 65.46 (8′a-C), 63.98 (spiro-C), 53.74

(3′-CH_3), 51.47 (2′-CH_3), 30.27 (CO–CH_3), 22.41 (6′-CH_3), 21.23 (8′-CH_3) ppm; IR (KBr): ν=3009–3098 (C–H, arom.), 2890–2974 (C–H, aliph.), 2205 (acetylenic bond), 1741 (3′-C=O), 1709 (CO–CH_3), 1689 (2′-C=O), 1578 (C=N), 1454 (C=C), 1336, 1274, 1182, 1116, 967, 874, 738 cm^{-1}; MS-EI *m*/*e* (%) 962.25 [M^+]. Elemental analysis for $C_{61}H_{42}N_2O_6S_2$: C, 76.07; H, 4.40; N, 2.91; S, 6.66. Found %: C, 76.07; H, 4.41; N, 2.92; S, 6.87.

4.3.6. Dimethyl 2-((4-((4-((4-(acetylthio)phenyl)ethynyl)-phenyl)ethynyl)phenyl)ethynyl)-7-((4-((4-((4-(acetylthiomethyl)-phenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***14f***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J*=7.56 Hz, 4H, arom.), 8.14 (d, *J*=7.86 Hz, 4H, arom.), 7.99 (d, *J*=7.86 Hz, 4H, arom.), 7.74 (d, *J*=7.86 Hz, 4H, arom.), 7.58 (d, *J*=7.86 Hz, 4H, arom.), 7.48 (d, *J*=7.86 Hz, 4H, arom.), 7.47 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.30–7.37 (m, 4H, CH-arom.), 7.20 (d, *J*=1.00 Hz, 1H, CH-arom.), 5.44–5.46 (m, 1H, 7′-CH), 4.73 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.73 (s, 3H, 3′-CH_3), 3.42 (s, 3H, 2′-CH_3), 2.39 (s, 6H, 2CO–CH_3), 2.14 (s, 3H, 6′-CH_3), 1.46 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.27 (CO–CH_3), 163.17 (3′-CO), 162.46 (2′-CO), 152.36, 151.49, 149.22, 148.79, 142.64, 138.34, 138.79, 138.38, 133.67, 133.15, 131.56, 129.50, 128.46, 125.76, 124.34, 124.18, 122.76, 121.36, 120.49, 118.75, 104.61, 94.78 (acetylenic-C), 93.79 (acetylenic-C), 84.36 (acetylenic-C), 82.47 (acetylenic-C), 64.87 (8′a-C), 62.94 (spiro-C), 52.41 (3′-CH_3), 50.48 (2′-CH_3), 31.36 (CO–CH_3), 22.47 (6′-CH_3), 21.34 (8′-CH_3) ppm; IR (KBr): ν=3000–3095 (C–H, arom.), 2898–2964 (C–H, aliph.), 2201 (acetylenic bond), 1741 (3′-C=O), 1707 (CO–CH_3), 1689 (2′-C=O), 1610 (C=N), 1461 (C=C), 1355, 1267, 1183, 1140, 960, 884, 787 cm^{-1}; MS-EI *m*/*e* (%) 1176.33 [M^+]. Elemental analysis for $C_{78}H_{52}N_2O_6S_2$: C, 79.57; H, 4.45; N, 2.38; S, 5.45. Found %: C, 79.56; H, 4.46; N, 2.37; S, 5.47.

4.4. Sonogashira-mediated coupling for the synthesis of photochromic DHIs (5′*S*)-dimethyl 2-((4-(acetylthio)phenyl)-ethynyl)$_n$-7-ethynyl-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-*b*]pyridazine]-6′,7′-dicarboxylates 16a–f: general procedure

To an oven-dried screw cap tube or a round bottom flask equipped with a water cooled west condenser and a magnetic stir bar were added 4-iodoacetyl-1-iodobenzene **13**[47] (0.831 g, 2.99 mmol), bis(dibenzylideneacetone)palladium(0) (0.086 mg, 0.149 mmol), copper(I) iodide (0.057 mg, 0.30 mmol) and triphenylphosphine (0.157 mg, 0.060 mmol) to the terminal alkynes DHIs **12a–f** (2.99 mmol). The vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen (3×). A co-solvent system of freshly distilled THF (20 mL) followed by DIEA (2.1 mL, 12 mmol) was added. The reaction mixture was stirred in a 40 °C oil bath for 3 h (TLC controlled) until the reaction was complete. The reaction vessel was cooled to room temperature and the mixture quenched with water or a saturated solution of NH_4Cl. The organic layer was diluted with CH_2Cl_2 and washed with a saturated solution of NH_4Cl (3×30 mL). The combined aqueous layers were extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent removed in vacuo. The crude products were then purified twice by column chromatography on silica gel and CH_2Cl_2 as eluent. The pure products were obtained in high purity as yellow needles. Full characterizations of the coupling products **16a–f** are cited below:

4.4.1. Dimethyl 2-((4-(acetylthio)phenyl)ethynyl)-7-ethynyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***16a***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J*=1.6 Hz, 2H, arom.), 8.13 (d, *J*=8.1 Hz, 2H, arom.), 7.87 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.74–7.78 (m, 4H, CH-arom.), 7.77 (dd, *J*=1.76, 1.89 Hz, 1H, 6′-CH), 7.17 (d, *J*=1.20 Hz, 1H, CH-arom.), 5.62–5.64 (m, 1H, 7′-CH), 4.83 (t, *J*=2.2 Hz, 1H, 8a′-CH), 4.79 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 4.13 (s, 1H, acetylenic-H), 3.76 (s, 3H, 3′-CH_3), 3.38 (s, 3H, 2′-CH_3), 2.32 (s, 3H, CO-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 190.06 (CO–CH_3), 163.77 (3′-CO), 162.67 (2′-CO), 149.66, 149.98, 142.62, 138.93, 138.79, 138.36, 133.79, 133.38, 131.36, 129.98, 128.20, 125.75, 125.83, 124.46, 122.67, 121.64, 120.82, 118.64, 104.36, 97.60 (acetylenic-C), 95.98 (acetylenic-C), 81.85 (acetylenic-CH), 65.37 (8′a-C), 63.84 (spiro-C), 53.63 (3′-CH_3), 50.67 (2′-CH_3), 30.31 (CO–CH_3) ppm; IR (KBr): ν=3005–3034 (C–H, arom.), 2860–2957 (C–H, aliph.), 2236 (acetylenic bond), 1749 (3′-C=O), 1703 (CO–CH_3), 1687 (2′-C=O), 1588 (C=N), 1446 (C=C), 1339, 1267, 1172, 1163, 957, 886, 778 cm^{-1}; MS-EI *m*/*e* (%) 584.14 [M^+]. Elemental analysis for $C_{35}H_{24}N_2O_5S$: C, 71.90; H, 4.14; N, 4.79; S, 5.48. Found %: C, 71.89; H, 4.13; N, 4.80; S, 5.47.

4.4.2. Dimethyl 2-((4-((4-(acetylthio)phenyl)ethynyl)phenyl)-ethynyl)-7-((4-ethynylphenyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***16b***

^{1}H NMR (400 MHz, CDCl3) δ 8.27 (d, *J*=7.56 Hz, 2H, arom.), 8.02 (d, *J*=7.86 Hz, 2H, arom.), 7.97 (d, *J*=8.15 Hz, 2H, arom.), 7.78 (d, *J*=8.15 Hz, 2H, arom.), 7.45 (d, *J*=7.86 Hz, 4H, arom.), 7.32 (d, *J*=7.86 Hz, 4H, arom.), 7.24 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.18–7.21 (m, 4H, CH-arom.), 7.13 (d, *J*=1.25, 1.89 Hz, 1H, CH-arom.), 7.07 (dd, *J*=1.76, 1.97 Hz, 1H, 6′-CH), 5.36–5.42 (m, 1H, 7′-CH), 4.93 (t, *J*=2.2 Hz, 1H, 8a′-CH), 4.72 (dt, *J*=8.25, 1.76 Hz, 8′-CH), 4.12 (s, 1H, acetylenic-H), 3.95 (s, 3H, 3′-CH_3), 3.43 (s, 3H, 2′-CH_3), 2.20 (s, 3H, CO–CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 190.98 (CO–CH_3), 162.25 (3′-CO), 161.52 (2′-CO), 150.28, 149.30, 148.97, 142.85, 138.52, 138.49, 138.73, 132.20, 131.95, 131.03, 129.27, 128.69, 125.27, 124.87, 124.36, 121.38, 120.67, 120.31, 119.97, 105.91, 94.85 (acetylenic-C), 92.99 (acetylenic-C), 85.67 (acetylenic-C), 82.03 (acetylenic-C), 64.67 (8′a-C), 62.62 (spiro-C), 52.74 (3′-CH_3), 51.23 (2′-CH_3), 32.06 (CO-CH_3) ppm; IR (KBr): ν=3016–3100 (C–H, arom.), 2910–2978 (C–H, aliph.), 2211 (acetylenic bond), 1741 (3′-C=O), 1700 (CO–CH_3), 1689 (2′-C=O), 1600 (C=N), 1475 (C=C), 1349, 1253, 1173, 1138, 965, 878, 746 cm^{-1}; MS-EI *m*/*e* (%) 784.20 [M^+]. Elemental analysis for $C_{51}H_{32}N_2O_5S$: C, 78.04; H, 4.11; N, 3.57; S, 4.09. Found %: C, 78.04; H, 4.10; N, 3.58; S, 4.08.

4.4.3. Dimethyl 2,7-bis((4-((4-((4-(acetylthio)-phenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-4a′H-spiro-[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***16c***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32–8.40 (m, 8H, arom.), 8.21–8.24 (m, 4H, arom.), 8.11 (d, *J*=1.6 Hz, 4H, arom.), 8.09 (d, *J*=8.1 Hz, 4H, arom.), 8.04 (d, *J*=1.45 Hz, 1H, CH-arom.), 7.63 (d, *J*=8.16 Hz, 2H, CH-arom.), 7.42 (dd, *J*=1.55, 1.98 Hz, 1H, CH-arom.), 7.41–7.42 (m, 2H, CH-arom.), 5.63 (d, *J*=9.56 Hz, 1H, 7′-CH), 5.09 (d, *J*=9.71 Hz, 1H, 8′-CH), 5.06 (s, 1H, acetylenic-H), 3.80 (s, 3H, 3′-CH_3), 3.41 (s, 3H, 2′-CH_3), 2.29 (CO–CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.90 (CO–CH_3), 163.02 (3′-CO), 162.98 (2′-CO), 150.39, 149.46, 148.76, 142.34, 138.74, 138.30, 138.78, 131.13, 130.97, 130.28, 130.89, 128.64, 125.27, 124.87, 124.70, 120.69, 120.30, 120.01, 119.35, 106.39, 93.99 (acetylenic-C), 91.76 (acetylenic-C), 82.63 (acetylenic-C), 81.98 (acetylenic-C), 63.70 (8′a-C), 63.09 (spiro-C), 51.71 (3′-CH_3), 51.69 (2′-CH_3), 32.16 (CO–CH_3) ppm; IR (KBr): ν=3004–3098 (C–H, arom.), 2923–2985 (C–H, aliph.), 2207 (acetylenic bond), 1747 (3′-C=O), 1706 (CO–CH_3), 1695 (2′-C=O), 1607 (C=N), 1463 (C=C), 1363, 1243, 1160, 1178, 979, 864, 741 cm^{-1}; MS-EI *m*/*e* (%) 984.27 [M^+]. Elemental analysis for $C_{67}H_{40}N_2O_5S$: C, 81.69; H, 4.09; N, 2.84; S, 3.25. Found %: C, 81.70; H, 4.08; N, 2.84; S, 3.24.

4.4.4. Dimethyl 2-((4-(acetylthio)phenyl)ethynyl)-7-ethynyl-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***16d***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J*=1.6 Hz, 2H, arom.), 8.07 (d, *J*=8.1 Hz, 2H, arom.), 8.02 (d, *J*=1.65 Hz, 1H, CH-arom.), 7.87 (d,

J=8.13 Hz, 2H, CH-arom.), 7.54 (dd, *J*=1.60, 1.99 Hz, 1H, CH-arom.), 7.49–7.52 (m, 2H, CH-arom.), 5.66 (d, *J*=9.56 Hz, 1H, 7′-CH), 5.28 (d, *J*=9.71 Hz, 1H, 8′-CH), 4.01 (s, 1H, acetylenic-H), 3.79 (s, 3H, 3′-CH_3), 3.36 (s, 3H, 2′-CH_3), 2.24 (CO–CH_3), 2.16 (s, 3H, 6′-CH_3), 1.34 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.32 (CO–CH_3), 162.98 (3′-CO), 161.67 (2′-CO), 150.17, 149.37, 147.30, 145.02, 139.37, 139.03, 134.21, 132.00, 131.69, 129.76, 127.57, 121.62, 121.78, 120.31, 118.85, 101.84, 85.61 (acetylenic-C), 84.37 (acetylenic-C), 83.61 (acetylenic-C), 80.20 (acetylenic-C), 66.21 (8′a-C), 65.69 (spiro-C), 52.99 (3′-CH_3), 50.60 (2′-CH_3), 31.49 (CO–CH_3), 22.27 (6′-CH_3), 20.98 (8′-CH_3) ppm; IR (KBr): ν=3009–3078 (C–H, arom.), 2896–2978 (C–H, aliph.), 2214 (acetylenic bond), 1742 (3′-C=O), 1701 (CO–CH_3), 1685 (2′-C=O), 1607 (C=N), 1534 (C=C), 1436, 1349, 1237, 1174, 1101, 946, 868, 766 cm^{-1}; MS-EI *m*/*e* (%) 612.17 [M$^+$]. Elemental analysis for $C_{37}H_{28}N_2O_5S$: C, 72.53; H, 4.61; N, 4.57; S, 5.23. Found %: C, 72.52; H, 4.62; N, 4.55; S, 5.22.

*4.4.5. Dimethyl 2-((4-((4-(acetylthio)phenyl)ethynyl)phenyl)-ethynyl)-7-((4-ethynylphenyl)ethynyl)-2′,4a′-dimethyl-4a′H-spiro-[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **16e***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J*=7.56 Hz, 2H, arom.), 8.25 (d, *J*=7.86 Hz, 2H, arom.), 8.20 (d, *J*=7.86 Hz, 4H, arom.), 7.86 (d, *J*=7.86 Hz, 4H, arom.), 7.78 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.49–7.57 (m, 4H, CH-arom.), 7.85 (d, *J*=0.88 Hz, 1H, CH-arom.), 7.62 (dd, *J*=1.76, 1.88 Hz, 1H, 6′-CH), 5.46–5.50 (m, 1H, 7′-CH), 4.51 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 4.12 (s, 1H, acetylenic-H), 3.92 (s, 3H, 3′-CH_3), 3.42 (s, 3H, 2′-CH_3), 2.28 (s, 3H, CO–CH_3), 2.23 (s, 3H, 6′-CH_3), 1.39 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.36 (CO–CH_3), 162.89 (3′-CO), 160.56 (2′-CO), 150.78, 150.30, 149.54, 143.31, 139.68, 138.74, 138.69, 134.85, 133.36, 132.25, 130.67, 128.95, 125.34, 124.75, 124.36, 122.97, 118.48, 104.97, 95.37 (acetylenic-C), 93.21 (acetylenic-C), 82.45 (acetylenic-C), 80.85 (acetylenic-C), 65.30 (8′a-C), 63.78 (spiro-C), 53.26 (3′-CH_3), 51.48 (2′-CH_3), 30.20 (CO–CH_3), 22.42 (6′-CH_3), 21.36 (8′-CH_3) ppm; IR (KBr): ν=3025–3110 (C–H, arom.), 2839–2945 (C–H, aliph.), 2213 (acetylenic bond), 1746 (3′-C=O), 1712 (CO–CH_3), 1680 (2′-C=O), 1563 (C=N), 1450 (C=C), 1330, 1268, 1173, 1164, 956, 878, 730 cm^{-1}; MS-EI *m*/*e* (%) 812.23 [M$^+$]. Elemental analysis for $C_{53}H_{36}N_2O_5S$: C, 78.31; H, 4.46; N, 3.45; S, 3.94. Found %: C, 78.32; H, 4.45; N, 3.44; S, 3.92.

*4.4.6. Dimethyl 2-((4-((4-((4-(acetylthio)phenyl)ethynyl)phenyl)-ethynyl)phenyl)ethynyl)-7-((4-((4-ethynylphenyl)ethynyl)-phenyl)ethynyl)-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **16f***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J*=7.60 Hz, 2H, arom.), 8.22 (d, *J*=7.60 Hz, 2H, arom.), 8.14 (d, *J*=7.60 Hz, 4H, arom.), 8.10 (d, *J*=7.86 Hz, 4H, arom.), 7.97 (d, *J*=7.86 Hz, 4H, arom.), 7.66 (d, *J*=7.86 Hz, 4H, arom.), 7.41 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.36–7.39 (m, 4H, CH-arom.), 7.25 (d, *J*=1.15 Hz, 1H, CH-arom.), 5.42–5.49 (m, 1H, 7′-CH), 4.69 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 4.20 (s, 1H, acetylenic-H), 3.69 (s, 3H, 3′-CH_3), 3.46 (s, 3H, 2′-CH_3), 2.40 (s, H, CO–CH_3), 2.11 (s, 3H, 6′-CH_3), 1.37 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.46 (CO–CH_3), 163.48 (3′-CO), 162.69 (2′-CO), 152.78, 151.62, 149.37, 148.21, 142.36, 138.78, 138.49, 138.15, 133.97, 133.25, 130.98, 130.48, 129.20, 125.32, 124.10, 124.48, 122.79, 121.54, 120.78, 119.63, 104.25, 94.74 (acetylenic-C), 92.82 (acetylenic-C), 83.46 (acetylenic-C), 88.63 (acetylenic-C), 64.89 (8′a-C), 63.87 (spiro-C), 52.32 (3′-CH_3), 50.46 (2′-CH_3), 30.89 (CO–CH_3), 22.36 (6′-CH_3), 21.47 (8′-CH_3) ppm; IR (KBr): ν=3024–3100 (C–H, arom.), 2869–2932 (C–H, aliph.), 2219 (acetylenic bond), 1746 (3′-C=O), 1702 (CO–CH_3), 1690 (2′-C=O), 1615 (C=N), 1465 (C=C), 1354, 1263, 1185, 1144, 967, 888, 786 cm^{-1}; MS-EI *m*/*e* (%) 1012.30 [M$^+$]. Elemental analysis for $C_{69}H_{44}N_2O_5S$: C, 81.80; H, 4.38; N, 2.76; S, 3.16. Found %: C, 81.81; H, 4.38; N, 2.77; S, 3.15.

*4.4.7. Sonogashira-mediated coupling for the synthesis of photochromic DHIs dimethyl 2,7-bis((4-(acetylthio)phenyl)-ethynyl)$_n$-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylates **18a–f***

These compounds prepared by following the general procedure mentioned for **16a–f**. The pure products were obtained with highly purity as yellow needles. Full characterizations of the coupling products **18a–f** are cited below:

*4.4.8. Dimethyl 2-((4-(acetylthio)phenyl)ethynyl)-7-(phenylethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]-pyridazine]-6′,7′-dicarboxylate **18a***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J*=1.6 Hz, 4H, arom.), 8.13 (d, *J*=8.1 Hz, 4H, arom.), 8.03 (t, *J*=5.6 Hz, 1H, CH-arom.), 7.96 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.72–7.78 (m, 4H, CH-arom.), 7.74 (dd, *J*=1.76, 2.01 Hz, 1H, 6′-CH), 7.24 (d, *J*=0.88 Hz, 1H, CH-arom.), 5.61 (m, 1H, 7′-CH), 4.90 (t, *J*=2.2 Hz, 1H, 8a′-CH), 4.74 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.80 (s, 3H, 3′-CH_3), 3.33 (s, 3H, 2′-CH_3), 2.40 (s, 3H, CO-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 190.03 (CO–CH_3), 162.74 (3′-CO), 161.99 (2′-CO), 150.26, 150.13, 149.46, 142.33, 138.57, 138.96, 138.22, 133.46, 133.78, 131.36, 129.67, 128.36, 125.46, 125.58, 125.23, 124.36, 122.67, 120.69, 118.34, 104.78, 98.62 (acetylenic-C), 95.56 (acetylenic-C), 65.36 (8′a-C), 62.99 (spiro-C), 54.21 (3′-CH_3), 52.32 (2′-CH_3), 31.54 (CO–CH_3) ppm; IR (KBr): ν=3000–3102 (C–H, arom.), 2862–2934 (C–H, aliph.), 2211 (acetylenic bond), 1751 (3′-C=O), 1701 (CO-CH_3), 1694 (2′-C=O), 1587 (C=N), 1464 (C=C), 1353, 1251, 1178, 1111, 957, 881, 784 cm^{-1}; MS-EI *m*/*e* (%) 660.17 [M$^+$]. Elemental analysis for $C_{41}H_{28}N_2O_5S$: C, 74.53; H, 4.27; N, 4.24; S, 4.85. Found %: C, 74.54; H, 4.27; N, 4.23; S, 8.83.

*4.4.9. Dimethyl 2-((4-((4-(acetylthio)phenyl)ethynyl)-phenyl)ethynyl)-7-((4-(phenylethynyl)phenyl)ethynyl)-4a′H-spiro-[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **18b***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J*=7.60 Hz, 4H, arom.), 8.26 (d, *J*=7.60 Hz, 4H, arom.), 8.15–8.18 (m, 5H, arom.), 7.94 (d, *J*=7.86 Hz, 4H, arom.), 7.87 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.36–7.43 (m, 4H, CH-arom.), 7.91 (d, *J*=0.88 Hz, 1H, CH-arom.), 7.66 (dd, *J*=1.60, 1.96 Hz, 1H, 6′-CH), 5.51–5.54 (m, 1H, 7′-CH), 4.84 (t, *J*=2.2 Hz, 1H, 8a′-CH), 4.72 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.90 (s, 3H, 3′-CH_3), 3.46 (s, 3H, 2′-CH_3), 2.31 (s, 3H, CO–CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.82 (CO–CH_3), 164.46 (3′-CO), 162.20 (2′-CO), 150.67, 150.00, 148.84, 142.36, 138.64, 139.22, 139.27, 133.36, 133.20, 131.40, 129.67, 128.81, 125.93, 124.78, 124.28, 123.00, 122.64, 121.93, 119.67, 104.52, 96.64 (acetylenic-C), 94.96 (acetylenic-C), 82.01 (acetylenic-C), 80.98 (acetylenic-C), 64.97 (8′a-C), 63.35 (spiro-C), 53.85 (3′-CH_3), 50.99 (2′-CH_3), 30.84 (CO–CH_3) ppm; IR (KBr): ν=3036–3098 (C–H, arom.), 2868–2973 (C–H, aliph.), 2216 (acetylenic bond), 1740 (3′-C=O), 1701 (CO–CH_3), 1663 (2′-C=O), 1585 (C=N), 1464 (C=C), 1358, 1274, 1192, 1110, 967, 873, 735 cm^{-1}; MS-EI *m*/*e* (%) 860.23 [M$^+$]. Elemental analysis for $C_{57}H_{36}N_2O_5S$: C, 79.52; H, 4.21; N, 3.25; S, 3.72. Found %: C, 79.52; H, 4.20; N, 3.24; S, 3.70.

*4.4.10. Dimethyl 2-((4-((4-((4-(acetylthio)phenyl)ethynyl)-phenyl)ethynyl)phenyl)ethynyl)-7-((4-((4-(phenylethynyl)phenyl)-ethynyl)phenyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **18c***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J*=7.56 Hz, 4H, arom.), 8.12 (d, *J*=7.86 Hz, 4H, arom.), 7.96–8.01 (m, 5H, arom.), 7.71 (d, *J*=7.86 Hz, 4H, arom.), 7.54 (d, *J*=7.86 Hz, 4H, arom.), 7.51 (d, *J*=7.86 Hz, 4H, arom.), 7.42 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.30–7.35 (m, 4H, CH-arom.), 7.18 (d, *J*=1.00 Hz, 1H, CH-arom.), 7.13 (dd, *J*=1.76, 1.88 Hz, 1H, 6′-CH), 5.40–5.43 (m, 1H, 7′-CH), 5.01 (t, *J*=2.2 Hz, 1H, 8a′-CH), 4.76 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.81 (s, 3H, 3′-CH_3), 3.35 (s, 3H, 2′-CH_3), 2.32 (s, 3H, CO–CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 192.36 (CO–CH_3), 164.13 (3′-CO), 161.99 (2′-CO), 151.06, 150.78, 150.39, 148.64, 142.36, 138.78, 138.46, 138.12, 133.23, 133.15, 131.57, 129.79, 128.64,

125.01, 124.67, 124.57, 122.39, 121.78, 120.64, 118.82, 104.67, 94.32 (acetylenic-C), 92.98 (acetylenic-C), 83.87 (acetylenic-C), 82.20 (acetylenic-C), 64.67 (8′a-C), 62.65 (spiro-C), 52.47 (3′-CH_3), 50.87 (2′-CH_3), 31.23 (CO–CH_3) ppm; IR (KBr): ν=3039–3100 (C–H, arom.), 2858–2997 (C–H, aliph.), 2202 (acetylenic bond), 1739 (3′-C=O), 1701 (CO–CH_3), 1693 (2′-C=O), 1600 (C=N), 1467 (C=C), 1357, 1245, 1178, 1196, 967, 886, 734 cm^{-1}; MS-EI *m*/*e* (%) 1060.30 [M^+]. Elemental analysis for $C_{73}H_{44}N_2O_5S$: C, 82.62; H, 4.18; N, 2.64; S, 3.02. Found %: C, 82.63; H, 4.17; N, 2.64; S, 3.01.

4.4.11. Dimethyl 2-((4-(acetylthio)phenyl)ethynyl)-2′,4a′-dimethyl-7-(phenylethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***18d***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J*=1.6 Hz, 4H, arom.), 8.24 (d, *J*=8.1 Hz, 4H, arom.), 8.12 (d, *J*=1.45 Hz, 1H, CH-arom.), 7.59–7.62 (m, 3H, CH-arom.), 7.44 (dd, *J*=1.55, 1.87 Hz, 1H, CH-arom.), 7.43–7.47 (m, 2H, CH-arom.), 5.62 (d, *J*=9.56 Hz, 1H, 7′-CH), 5.11 (d, *J*=9.71 Hz, 1H, 8′-CH), 3.80 (s, 3H, 3′-CH_3), 3.43 (s, 3H, 2′-CH_3), 2.33 (CO–CH_3), 2.17 (s, 3H, 6′-CH_3), 1.52 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.13 (CO–CH_3), 162.87 (3′-CO), 161.99 (2′-CO), 150.92, 149.39, 147.37, 144.85, 139.67, 138.37, 133.58, 131.27, 131.98, 129.47, 127.25, 121.53, 121.46, 120.87, 118.58, 101.36, 83.25 (acetylenic-C), 81.02 (acetylenic-C), 66.25 (8′a-C), 66.43 (spiro-C), 52.12 (3′-CH_3), 51.53 (2′-CH_3), 31.85 (CO–CH_3), 22.21 (6′-CH_3), 21.20 (8′-CH_3) ppm; IR (KBr): ν=3036–3058 (C–H, arom.), 2912–2958 (C–H, aliph.), 2247 (acetylenic bond), 1746 (3′-C=O), 1702 (CO–CH_3), 1691 (2′-C=O), 1620 (C=N), 1537 (C=C), 1426, 1378, 1286, 1178, 1075, 932, 871, 767 cm^{-1}; MS-EI *m*/*e* (%) 688.20 [M^+]. Elemental analysis for $C_{43}H_{32}N_2O_5S$: C, 74.98; H, 4.68; N, 4.07; S, 4.66. Found %: C, 74.98; H, 4.68; N, 4.07; S, 4.66.

4.4.12. Dimethyl 2-((4-((4-(acetylthio)phenyl)ethynyl)phenyl)-ethynyl)-2′,4a′-dimethyl-7-(phenylethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***18e***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J*=7.86 Hz, 4H, arom.), 8.34 (d, *J*=7.86 Hz, 4H, arom.), 8.32 (d, *J*=7.86 Hz, 4H, arom.), 7.90 (t, *J*=4.56 Hz, 1H, arom.), 7.72 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.40–7.43 (m, 4H, CH-arom.), 7.92 (d, *J*=0.88 Hz, 1H, CH-arom.), 7.65 (dd, *J*=1.76, 1.96 Hz, 1H, 6′-CH), 5.63–5.65 (m, 1H, 7′-CH), 4.34 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.95 (s, 3H, 3′-CH_3), 3.32 (s, 3H, 2′-CH_3), 2.28 (s, 3H, CO–CH_3), 2.23 (s, 3H, 6′-CH_3), 1.42 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 190.48 (CO–CH_3), 163.48 (3′-CO), 161.95 (2′-CO), 151.27, 150.46, 149.37, 143.24, 140.79, 139.36, 138.89, 135.52, 132.90, 131.69, 129.78, 128.26, 125.36, 124.48, 124.16, 122.85, 120.43, 120.39, 118.78, 104.28, 96.15 (acetylenic-C), 93.62 (acetylenic-C), 82.48 (acetylenic-C), 80.23 (acetylenic-C), 65.47 (8′a-C), 63.69 (spiro-C), 53.28 (3′-CH_3), 51.48 (2′-CH_3), 30.36 (CO–CH_3), 22.45 (6′-CH_3), 21.15 (8′-CH_3) ppm; IR (KBr): ν=3002–3091 (C-H, arom.), 2886–2984 (C-H, aliph.), 2212 (acetylenic bond), 1746 (3′-C=O), 1703 (CO–CH_3), 1682 (2′-C=O), 1575 (C=N), 1463 (C=C), 1334, 1285, 1173, 1162, 965, 871, 730 cm^{-1}; MS-EI m/e (%) 788.23 [M^+]. Elemental analysis for $C_{51}H_{36}N_2O_5S$: C, 77.64; H, 4.60; N, 3.55; S, 4.06. Found %: C, 77.64; H, 4.60; N, 3.54; S, 4.04.

4.4.13. Dimethyl 2-((4-((4-((4-(acetylthio)phenyl)ethynyl)phenyl)-ethynyl)phenyl)ethynyl)-2′,4a′-dimethyl-7-((4-((4-(phenyl-ethynyl)phenyl)ethynyl)phenyl)ethynyl)-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate ***18f***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J*=7.60 Hz, 4H, arom.), 8.22 (d, *J*=7.86 Hz, 4H, arom.), 8.01 (d, *J*=7.86 Hz, 4H, arom.), 7.85–7.90 (m, 5H, arom.), 7.59 (d, *J*=7.86 Hz, 4H, arom.), 7.46 (d, *J*=7.56 Hz, 4H, arom.), 7.58 (d, *J*=2.2 Hz, 1H, CH-arom.), 7.31–7.42 (m, 4H, CH-arom.), 7.24 (d, *J*=1.00 Hz, 1H, CH-arom.), 5.43–5.45 (m, 1H, 7′-CH), 4.65 (dt, *J*=9.60, 1.76 Hz, 8′-CH), 3.63 (s, 3H, 3′-CH_3), 3.39 (s, 3H, 2′-CH_3), 2.28 (s, 3H, CO–CH_3), 2.18 (s, 3H, 6′-CH_3), 1.41 (s, 3H, 8′-CH_3) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 192.00 (CO–CH_3), 164.16 (3′-CO), 161.98 (2′-CO), 151.39, 150.48, 149.32, 148.48, 141.36, 138.65, 138.36, 138.30, 133.28, 133.17, 131.39, 129.20, 128.78, 125.64, 124.38, 124.58, 122.37, 121.30, 120.85, 118.61, 104.74, 94.82 (acetylenic-C), 92.77 (acetylenic-C), 85.00 (acetylenic-C), 81.78 (acetylenic-C), 64.38 (8′a-C), 62.84 (spiro-C), 52.48 (3′-CH_3), 50.74 (2′-CH_3), 31.61 (CO–CH_3), 22.75 (6′-CH_3), 21.21 (8′-CH_3) ppm; IR (KBr): ν=3006–3078 (C–H, arom.), 2886–2961 (C–H, aliph.), 2217 (acetylenic bond), 1745 (3′-C=O), 1701 (CO–CH_3), 1686 (2′-C=O), 1600 (C=N), 1468 (C=C), 1354, 1262, 1187, 1142, 961, 883, 772 cm^{-1}; MS-EI *m*/*e* (%) 1088.33 [M^+]. Elemental analysis for $C_{75}H_{48}N_2O_5S$: C, 82.70; H, 4.44; N, 2.57; S, 2.94. Found %: C, 82.71; H, 4.43; N, 2.57; S, 2.93.

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