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Fluorenes |*Hot Paper*|

Structurally Diverse π-Extended Conjugated Polycarbo- and Heterocycles through Pd-Catalyzed Autotandem Cascades

Raquel Barroso,[a] María-Paz Cabal,[a] Rosana Badía-Laiño,[b] and Carlos Valdés*[a]

Abstract: The Pd-catalyzed reaction between 2,2′-dibromobiphenyls and related systems with tosylhydrazones gives rise to new π-extended conjugated polycarbo- and heterocycles through an autotandem process involving a cross-coupling reaction followed by an intramolecular Heck cyclization. The reaction shows wide scope regarding both coupling partners. Cyclic and acyclic tosylhydrazones can participate in the process. Additionally, a variety of aromatic and heteroaromatic dibromoderivatives have been employed, leading to an array of diverse scaffolds featuring a fluorene or acridine central nucleus, and containing binaphthyl, thiophene, benzothiophene and indole moieties. The application to appropriate tetrabrominated systems led to greater structural complexity through two consecutive autotandem cascades. The photophysical properties of selected compounds were studied through their absorption and emission spectra. Fluorescence molecules featuring very high quantum yields were identified, showing the potential of this methodology in the development of molecules with interesting optoelectronic properties.

Introduction

Polycyclic aromatic molecules with extended π-conjugation have attracted great interest over the last decades because of their vast array of applications as advanced materials[1] and key components of electronic devices. Organic synthesis have provided tools to incorporate a large diversity of π-conjugated molecular frameworks[2] allowing for the tuning of the electronic and photophysical properties.[3] Among the different structural subunits present in organic functional materials, the fluorene system stands as an ubiquitous moiety in π-extended conjugated systems with applications in organic photovoltaics[4] and electroluminescent materials.[5] Moreover, the fluorene structure is also present in molecules with biological activity[6] and in ligands for organometallic chemistry.[7] For these reasons, the synthesis of fluorenes and structurally related aromatic molecules has attracted a great deal of attention recently.[8]

In the last few years we have been devoted to the development of new synthetic methodologies based on the employment of sulfonylhydrazones in metal-catalyzed and uncatalyzed reactions.[9] In particular, in 2007 we reported the Pd-catalyzed cross-coupling reactions between tosylhydrazones and aryl halides as a very reliable method for the synthesis of substituted alkenes.[9a] In these reactions the tosylhydrazone acts as a carbene precursor and behaves as the nucleophilic component of the cross-coupling. From a mechanistic point of view, the differencial steps of this transformation include the formation of a palladium carbene complex and the migratory insertion reaction. Since our initial contribution, and as a result of the efforts of several research groups, the application of sulfonylhydrazones and diazo compounds in metal-catalyzed processes involving metal carbenes and migratory insertion reactions has undergone remarkable development.[10] More recently, we have incorporated the Pd-catalyzed cross-coupling with tosylhydrazones in autotandem reactions, that is, processes in which the same Pd-catalyst is able to promote more than one independent bond-forming catalytic step.[11] Thus, cascade reactions that combine the C–C bond-forming reaction of tosylhydrazones with a C–N bond-forming reaction have been developed to obtain quite complex heterocyclic systems from simple starting materials (Scheme 1b).[12] Moreover, the concatenation of the tosylhydrazone cross-coupling followed a C–H functionalization on an azole has led to a straightforward synthesis of pyrroloisoquinolines through an autotandem process with the creation two C–C bonds (Scheme 1c).[13]

Pd-catalyzed autotandem processes have been particularly attractive in the synthesis of heterocyclic molecules by combining C–C and C–N cross-coupling reactions.[14–16] These approaches generally rely on the employment of complementary and preorganized bifunctional coupling partners. For instance, in the examples presented in Scheme 1, *ortho*-dihalobenzene derivatives behave as bis-electrophiles, whereas the β-aminotosylhydrazone (Scheme 1b) and the α-*N*-azoletosylhydrazone (Scheme 1c) are the ambidentate nucleophilic partners, respectively. Alternatively, two coupling partners, both featuring an

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[a] *R. Barroso, Prof. M.-P. Cabal, Prof. C. Valdés*
Departamento de Química Orgánica e Inorgánica and
Instituto Universitario de Química Organometálica
"Enrique Moles", Universidad de Oviedo
c/Julián Clavería 8, Oviedo 33066 (Spain)
E-mail: acvg@uniovi.es

[b] *Prof. R. Badía-Laiño*
Departamento de Química Física y Analítica
Universidad de Oviedo
c/Julián Clavería 8, Oviedo 33066 (Spain)

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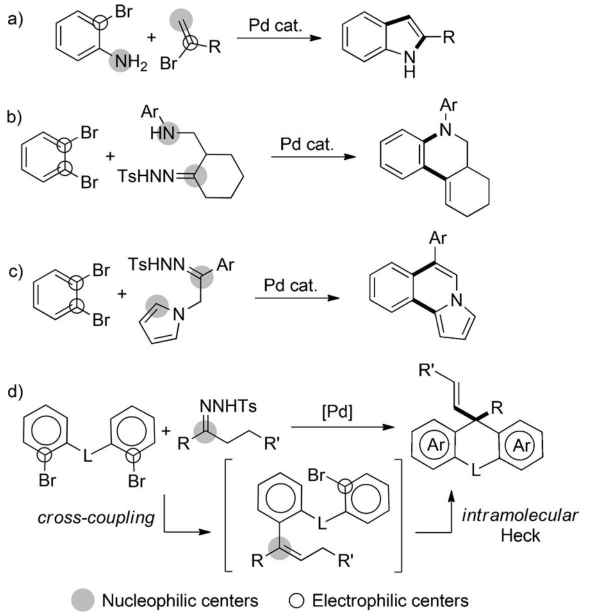


Scheme 1. Examples of typical Pd-catalyzed autotandem reactions: a) with complementary bifunctional coupling partners; b) C–C/C–N and c) C–C/C–C cascades of ambidentate electrophiles with functionalized tosylhydrazones; d) this work's approach (new bonds are represented in bold).

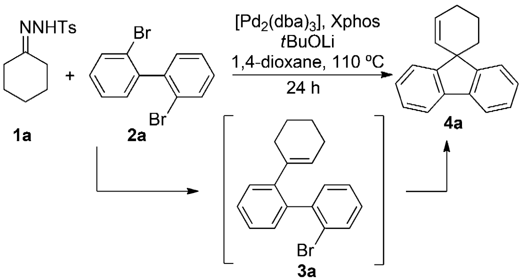
electrophilic and a nucleophilic reacting point could be combined for the construction of cyclic structures through the autotandem cascade (Scheme 1a).[15b]

Continuing with our interest in Pd-catalyzed autotandem processes employing tosylhydrazones, we designed a conceptually different approach, in which the functionality formed in the first Pd-catalyzed step would react in a subsequent Pd-catalyzed C–C bond-forming reaction. Considering that a new double bond is formed in the Pd-catalyzed cross-couplings with tosylhydrazones, we envisioned that it might then react in an intramolecular Heck reaction, to provide cyclic systems through a C–C/C–C autotandem sequence. This approach turned out to be successful, and in a preliminary communication we reported the preparation of spirofluorene and spiroacridine derivatives employing this methodology.[17]

Encouraged by our preliminary results on these tandem reactions as a new methodology for the synthesis of new π-extended materials, we decided to investigate the scope of the transformation in more detail. Herein, we present a full account of our results that show that this chemistry can be applied to the generation of a diversity of polycarbo- and heterocycles with extended π-conjugation with promising optoelectronic properties. Moreover, some photophysical properties and potential applications of selected π-extended systems are also discussed. In this paper, we wish to report a detailed description of the progress of our work.

Results and Discussion

Our initial experiments were carried out employing 2,2′-dibromobiphenyl **2a** as the ambidentate electrophile and the tosylhydrazone of cyclohexanone **1a**. We expected that, after the initial cross-coupling reaction to give cyclohexenone **3a**, a 5-*exo*-trig intramolecular Heck-type cyclization[18] might occur, giving rise to spirofluorene **4a** (Scheme 2). We selected symmetrical coupling partners to avoid the formation of regioisomers, hence simplifying analysis of the results.



$[Pd_2(dba)_3]$	1a/2a	3a/4a	Isolated yield 4a
2 mol %	1: 1	70: 30	24%
2 mol %	2: 1	55: 45	43%
4 mol %	2: 1	0: 100	93%

Scheme 2. Initial C–C/C–C Pd-catalyzed auto-tandem reaction considered and some optimization results

As starting point to develop suitable experimental conditions, we selected the standard reaction conditions that we had developed for the cross-coupling reactions with tosylhydrazones and aryl bromides, that is, $[Pd_2(dba)_3]$ (dba = dibenzalacetone) as the Pd-source, Xphos as the ligand, LiO*t*Bu as the base in dioxane as the solvent. The initial experiments employing a 1:1 ratio of both coupling partners and 2 mol% of $[Pd_2(dba)_3]$ led to a mixture of the cross-coupling product **3a** and the desired spirocycle **4a**. To drive the reaction to the exclusive formation of the spirocyclic compound **4a**, we increased the catalyst loading as well as the **1a/2a** ratio. Thus, employing 4 mol% of $[Pd_2(dba)_3]$ and tosylhydrazone **1a** in excess, the spirocyclic compound **4a** derived from the autotandem reaction was isolated in an excellent yield of 93%. The structure **4a** could be assigned based on the ^{13}C, ^{1}H NMR, and MS spectra. In particular, the presence of two dt at 5.35 (^{3}J = 9.9 Hz, ^{4}J = 2.1 Hz), and 6.12 ppm (^{3}J = 9.9 Hz, ^{3}J = 3.8 Hz) in the ^{1}H NMR spectrum was a clear indication of the presence of the endocyclic double bond. Moreover, the spirocyclic structure was later confirmed by X-ray crystallographic analysis in another member of this family of spiro compounds (Figure 1). Interestingly, during the autotandem reaction, the unusual formation of two $C-C_{Ar}$ bonds on the same carbon atom has taken place.[6b, 19, 20]

The formation of **4a** can be explained by considering two independent processes catalyzed by the same Pd species. As represented in Scheme 3, a first catalytic cycle involves the formation of **3a** through oxidative addition of the Pd^0 species to one of the C–Br bonds of **2a** to form arylpalladium complex **A**, generation of the Pd-carbene intermediate **B**, migratory insertion to give the alkylpalladium complex **C**, and β-hydride elimination, that releases the intermediate alkene **3a**. Then, alkene **3a** will be incorporated to a second catalytic cycle that involves an intramolecular Heck reaction, which ultimately leads

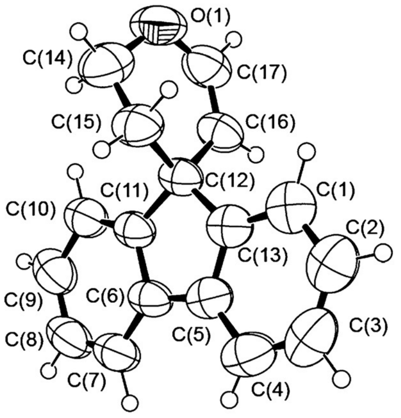
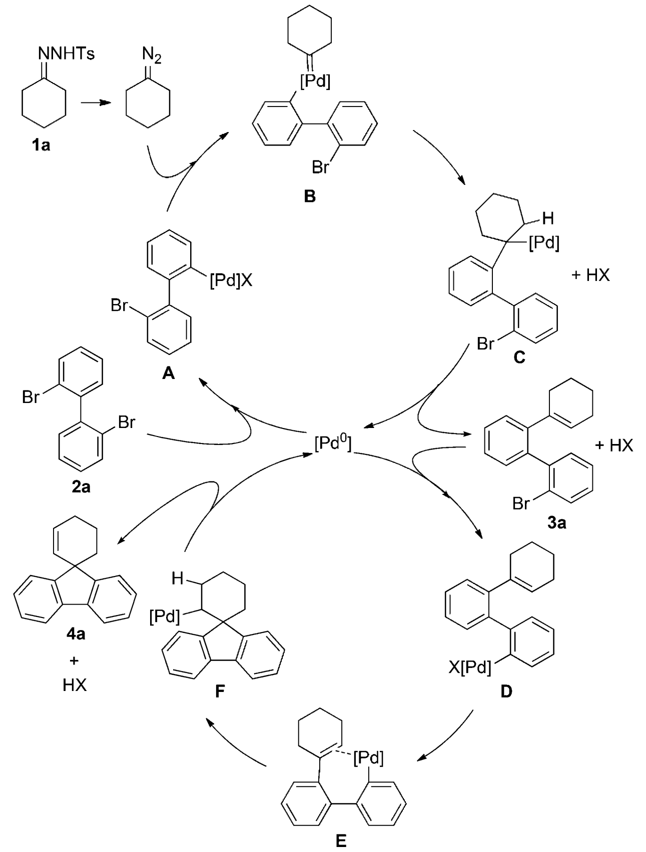


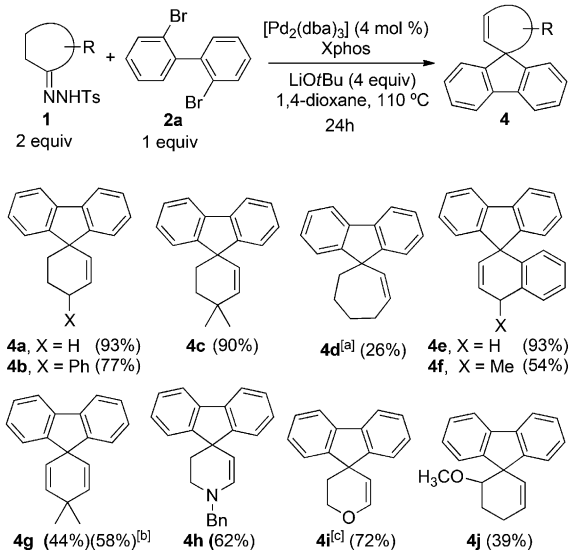
Figure 1. ORTEP representation of the molecular structure of **4i** determined by X-ray crystallographic analysis.[17]



Scheme 3. Mechanism proposed for the Pd-catalyzed autotandem process.

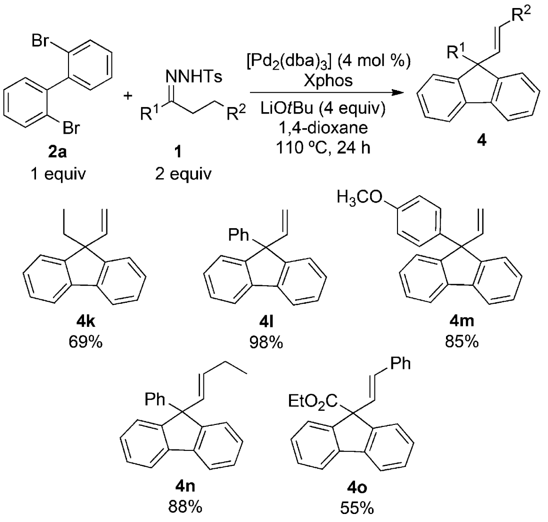
to the formation of **4a** after the second β-hydride elimination from the alkylpalladium complex **F**. Importantly, a requirement for tosylhydrazones to participate in this tandem reaction would be to feature hydrogen atoms that could be eliminated at both the α and β positions. Moreover, for the reaction to be successful, the intramolecular cyclization must be favored against the incorporation of a second molecule of tosylhydrazone from intermediate **D**. This is the case for 5-*exo*-trig cyclizations, and for 6-*exo*-trig Heck reactions, however, it failed for reactions involving the formation of seven-membered rings (see later, Schemes 9 and 10).

With this initial result in hand, and taking into consideration the mechanistic proposal, we set out to study the scope of this reaction. We considered the preparation of spirofluorene derivatives, a type of structure that is currently employed in the development of electroluminescent and optoelectronic materials.[21] First, the scope of the reaction was examined regarding the structure of the tosylhydrazone. As presented in Scheme 4 the synthesis of spirofluorenes **4** could be accomplished by employing a variety of tosylhydrazones **1** derived from cyclic ketones. The reaction proceeded successfully with tosylhydrazones of 4-substituted cyclohexanones and cycloheptanone to give spirofluorenes **4a–c**, and **4d**, respectively, but failed with cyclopentanone. Moreover, tetralone tosylhydrazone was also an appropriate substrate for the reaction leading to the interesting spiro derivatives **4e** and **4f** which feature and additional aromatic ring. Similarly, the reaction with the hydrazone of 4,4,-dimethylcyclohexenone led to the symmetric spirofluorene **4g** featuring two unconjugated double bonds. Interestingly, the cascade reaction could also be achieved with the tosylhydrazones of *N*-benzyl-4-piperidone and 4-piranone, which led to the corresponding spiro derivatives **4h** and **4i** featuring enamine and enol ether functionalities, respectively. In particular, the structure of **4i** was confirmed by X-ray crystallographic analysis (Figure 1).[17] Finally, the reaction with the hydrazone of 2-methoxycyclohexanone furnished spiro compound **4j** in a completely regioselective manner.[9d]



Scheme 4. Synthesis of spirofluorenes **4** by reaction between cyclic *N*-tosylhydrazones **1** and 2,2′-dibromobiphenyl **2a**. Yields of the isolated product obtained after column chromatography. [a] Reaction time 48 h. [b] Yield determined by ^{1}H NMR spectroscopy employing triphenylmethane as internal reference. [c] Structure confirmed by X-ray diffraction.

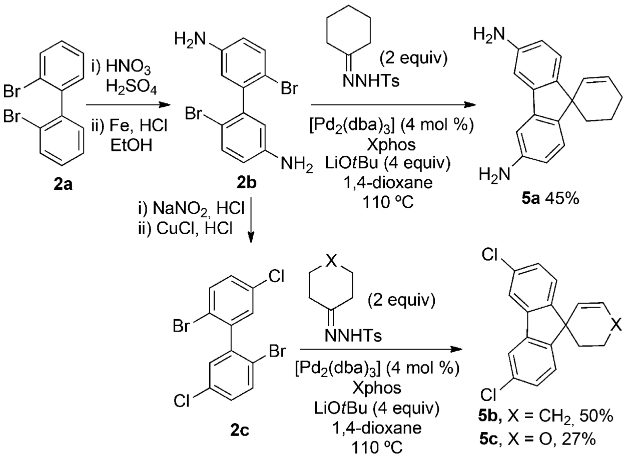
We next turned our attention to the employment of tosylhydrazones derived from acyclic ketones. Indeed, under similar reaction conditions, the autotandem reaction proceeded successfully for an array of acyclic systems, if the precursor ketone features hydrogens at the vicinal α and β positions. Thus, the reactions with hydrazones of ethyl ketones, such as 3-pentanone and propiophenones led to 9-vinylsubstituted fluorenes **4k**, **4l** and **4m**, respectively (Scheme 5). On the other hand, the reactions with a hydrazone substituted with longer alkyl group provided the alkene with the expected *trans* stereochemistry **4n**. Noteworthy, the reaction tolerates the presence of the ester functionality as represented in **4o**. Thus, this set of examples shows the wide applicability of this methodology as a general synthesis of functionalized 9,9-disubstituted fluorenes.



Scheme 5. Synthesis of 9,9-disubstituted fluorenes by reaction between acyclic *N*-tosylhydrazones **1** and 2,2′-dibromobiphenyl **2a**.

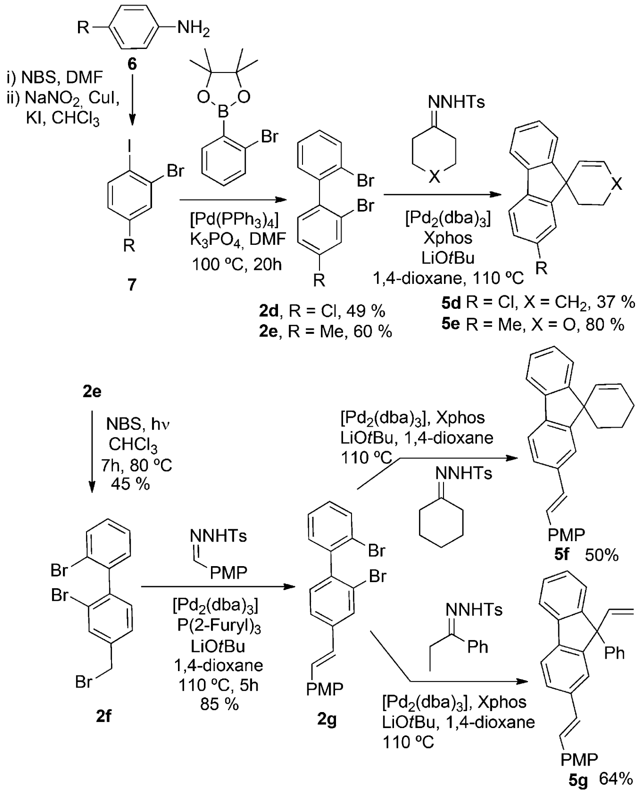
Considering that substituted fluorenes are structural constituents of molecules with interesting photophysical properties, and also might be original scaffolds in medicinal chemistry, we decided to explore the versatility and scope of the autotandem reaction towards the synthesis of structurally diverse spirofluorene derivatives by employing substituted dibrominated scaffolds. Thus, we selected a series of symmetrically substituted [5,5′-diamino- (**2b**);[22] 5,5′-dichloro- (**2c**);[21] and unsymmetrically substituted [4-chloro- (**2d**) and 4-methyl-2,2′dibromobiphenyl (**2e**)[23]]2,2′-dibromobiphenyls.

Direct manipulation of commercial 2,2′-dibromobiphenyl led to symmetrically substituted derivatives **2b** and **2c**. An autotandem reaction on 2,2′-dibromo-5,5′-dichlorobiphenyl **2c** led to the desired substituted spirofluorenes **5b** and **5c**, albeit with moderate to poor yields (Scheme 6). Importantly, although chloroarenes can also react in cross-couplings with tosylhydrazones, the formation of the spirofluorene occurred selectively. The reaction with 2,2′-dibromo-5,5′-diaminobiphenyl **2b** provided also the spirocyclic compound **5a** (Scheme 6). This time the autotandem reaction takes place in the presence of the free NH_2 groups. Noteworthy, both classes of substituted fluorenes feature appropriate functionalities to be further elaborated or incorporated into oligomeric structures.



Scheme 6. Synthesis of symmetrically substituted spirofluorenes **5a**–**c** by reaction between cyclic *N*-tosylhydrazones **1** and 5,5′disubstituted-2,2′-dibromobiphenyls **2b**,**c**.

The unsymmetrical 2,2′-dibromides **2d** and **2e** were prepared from commercially available *para*-substituted anilines **6**, by aromatic bromination with *N*-bromosuccinimide (NBS) followed by Sandmeyer reaction to yield the corresponding 2-bromo-1-iodo-4-substituted benzenes **7** (Scheme 7).[24] Next, the palladium-catalyzed Suzuki–Miyaura cross-coupling reac-

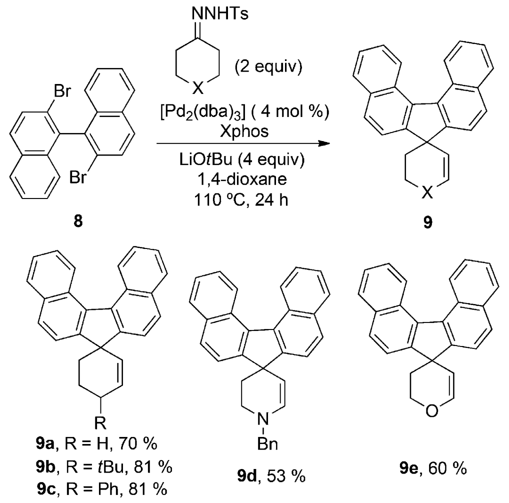


Scheme 7. Synthesis of unsymmetrically substituted spirofluorenes **5d**–**g** by reaction between *N*-tosylhydrazones **1** and 5,5′disubstituted-2,2′-dibromobiphenyls **2d**, **2e**, and **2f**.

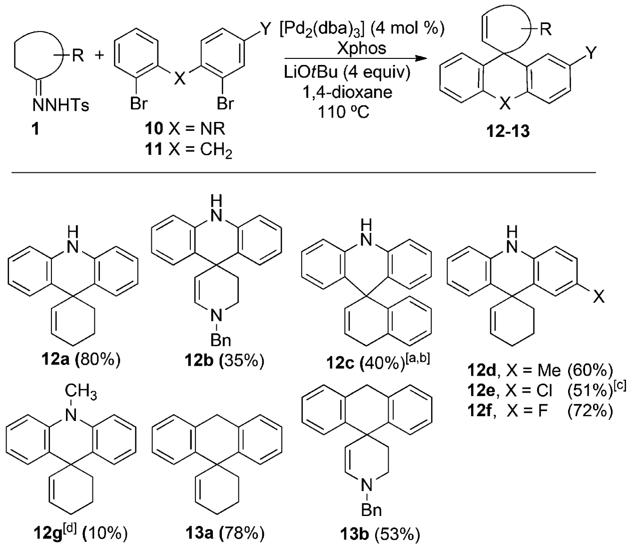
tion with 2-(2-bromophenyl)-1,3,2-dioxaborinane in the presence of $K_3PO_4 \cdot 7H_2O$ in DMF produced 2,2′-dibromo-4-substituted-biphenyl **2d** and **2e**.[25] Then, the autotandem reactions under typical conditions afforded, as desired, the substituted spirofluorenes **5d**,**e** (Scheme 7).

Additionally, benzyl bromination of **2e** led to tribromide **2f**, which was converted into the new dibromide **2g** by cross-coupling with the tosylhydrazone of *p*-methoxybenzaldehyde, employing a modification of the conditions reported by Wang.[26] As expected, under the standard reaction conditions, the new dibromide **2g** provided the fluorenes **5f** and **5g**, featuring additional conjugation (Scheme 7). Interestingly, two sequential Pd-catalyzed cross-couplings with tosylhydrazones are employed in the synthesis of these highly conjugated materials.

The process is also very efficient for the preparation of spirodibenzofluorenes **9** from the corresponding commercially available 2,2′-dibromobinaphthyl **8**, with yields very similar to those of the reactions with the biphenyl derivatives. Again, both carbo- and heterocyclic tosylhydrazones were compatible with this cascade reaction (Scheme 8). These new structures are particularly appealing because of their very extended π-conjugation.[27] The presence of the five-membered ring enforces a very rigid structure that enables conjugation of the two naphthalene moieties. A discussion on fluorescence and potential applications of these molecules will be discussed later in the paper.



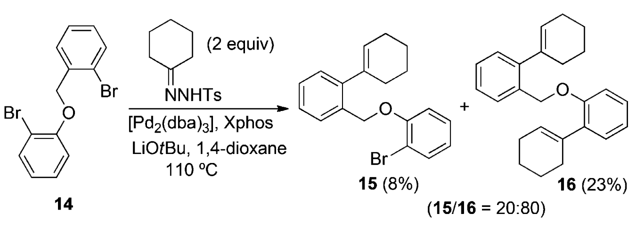
Scheme 8. Synthesis of spirodibenzofluorenes **9** by reaction between *N*-tosylhydrazones and 2,2′-dibromobinaphthyl **8**.



Scheme 9. Synthesis of spiroacridines **12** and spirodihydroanthracenes **13** by autotandem reactions. [a] Tosylhydrazone (4 equiv) was employed. [b] Reaction time 48 h. [c] Tosylhydrazone (3 equiv) and LiO*t*Bu (5 equiv) were employed. [d] *N*-Methylcarbazole derived from an intramolecular cyclization of aniline **10** was isolated as major compound.

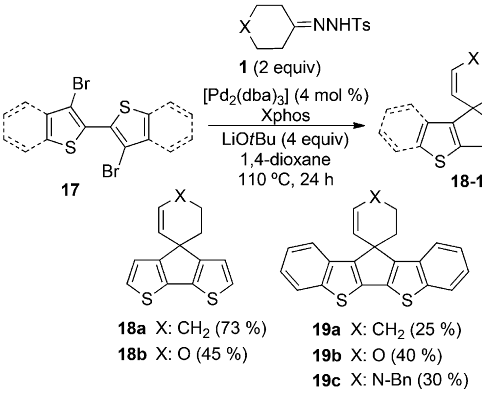
To expand the applicability of the autotandem cascade, the process was also examined employing other brominated scaffolds such as bis(2-bromophenyl)amines **10**, and bis(2-bromophenyl)methane **11** (Scheme 9). These reactions were expected to afford the corresponding spiro compounds **12** and **13**, featuring a central six-membered ring through a 6-*exo*-trig cyclization. Although the initial experiments were carried out under the same reaction conditions, these cascade processes turned out to be more challenging. Indeed, under the standard conditions, the diarylanilines showed some tendency to cyclize and form carbazoles.[16b] Nevertheless, it was found that employing a larger excess of the tosylhydrazone, the spiroacridines could be synthesized in preparatively useful yields. Interestingly, the autotandem reaction under these conditions proceeded successfully with the N–H-free anilines, leading to the spiroacridines **12**, valuable structures for the development of molecules with optoelectronic properties, that could be further elaborated through the free N–H.[28] However, the *N*-methylated analogue **10b**, showed a higher tendency to cyclize to the carbazole even in the presence of a large excess of tosylhydrazone, and the spirocompound **12g** could be isolated only in very poor yield. Finally, the reactions with bis(2-bromophenyl)methane **11** occurred uneventfully providing the spirodihydroanthracenes **13** with fairly good yields.

On the other hand, the reaction with benzyl ether **14** failed to provide the spirocyclic compound. In this case, we obtained a mixture of compounds **15** and **16**, derived from the mono- and dialkenylation reaction, respectively, (Scheme 10). Clearly, the formation of a seven-membered ring through a 7-*exo*-trig cyclization is not a favored process.



Scheme 10. Reaction with dibromide **14**, which did not afford the spirocyclic structure.

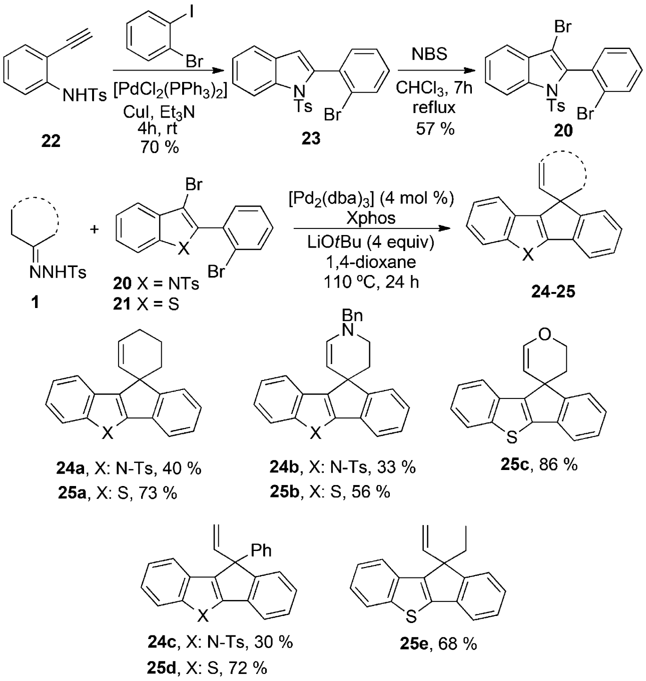
To explore the robustness and further applications of this cascade transformation, more elaborated scaffolds were examined. Thus, we turned our attention to the incorporation of heterocycles, considering that the new heterocyclic structures might be of interest in medicinal chemistry as well as in the development of molecules with optoelectronic properties. Our initial effort was directed towards thiophene and benzothiophene derivatives that would lead to polycyclic structures, which are widely present in functional organic materials.[29] Thus, for our study we chose the 3,3′-dibromo-2,2′-bithiophene **17a**[30] and the 3,3′-2,2′-dibenzodithiophene **17b**.[31] Delightfully, the autotandem cascade reactions with **17a** proceeded as expected to yield spirodithiophenes[32] **18** with moderate to good yields (Scheme 11). It is worth noting that molecules **18** are unprecedented 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes, structures that are employed as monomers in conductive polymers with applications in organic photovoltaics.[29] This reaction represents a new entry into spiro- and functionalized derivatives of these systems. Moreover, the reactions with the bis(benzothiophene) **17b** provided another class of unknown spirocyclic structures **19** (Scheme 11) with doubtless interest in the development of molecules with optoelectronic properties. A preliminary study on the fluorescence properties of some members of this family of compounds is discussed below.



Scheme 11. Synthesis of spirocyclic derivatives of cyclopentadithiophenes **18** and cyclopentadibenzothiophenes **19**.

Next, we considered using dibromide scaffolds combining two different aromatic rings that might provide unsymmetrical spirobenzofluorene analogues. For our study we chose 3-bromo-2-(2-bromophenyl)-1-tosyl-1*H*-indole **20** and 3-bromo-2-(2-bromophenyl)benzo[*b*]thiophene **21** (Scheme 12). The required dibrominated indole **20**[33] was readily prepared by reaction of *N*-tosyl-2-ethynylaniline **22** with 1-bromo-2-iodobenzene[34] under typical Sonogashira conditions, which afforded the corresponding indole derivative **23**, followed by bromination with NBS (Scheme 12). The benzothiophene analogue **21** was prepared following a known procedure by selective Suzuki cross-coupling of 2,3-dibromothiophene with *o*-bromophenylboronic acid.[35]

The cascade reactions under typical reaction conditions led to the expected indeno[1,2-*b*]indoles **24**[36] and benzo[*b*]indeno[2,1-*d*]thiophene derivatives **25** (Scheme 12). The reactions are not restricted to the preparation of the spirocyclic derivatives; tosylhydrazones derived from acyclic ketones can be also incorporated, leading to functionalized indenoindoles **24c** and indenobenzothiophene **25d** and **e**, the latter usually with higher overall yields.



Scheme 12. Synthesis of spirocyclic derivatives of indeno[1,2-*b*]indoles **24** and benzo[*b*]indeno[2,1-*d*]thiophenes **25**.

These results show clearly the versatility of this approach in the synthesis of heterocycle-containing π-extended polycyclic systems. By combining cross-coupling reactions to access the required dibromides with the cascade cyclization, a wide variety of structurally diverse spirocyclic or disubstituted analogues of fluorenes could be efficiently prepared.

Finally, continuing with our idea of employing this autotandem reaction in the synthesis of new fluorene-based structures with extended π-conjugation, we selected tetrabrominated scaffolds **26**, **27**, and **28** (Figure 2), expecting that in each case, two independent autotandem reactions might occur, giving rise to new flat polyaromatic structures.

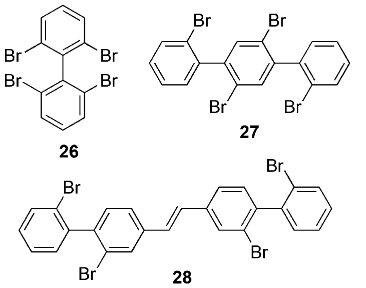
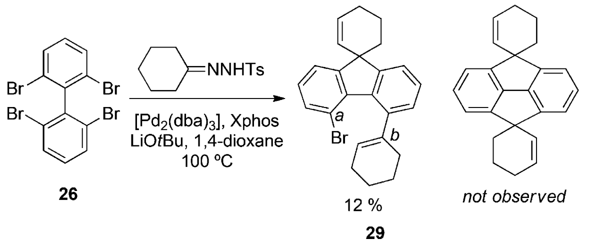


Figure 2. Tetrabrominated scaffolds selected for double autotandem reactions.

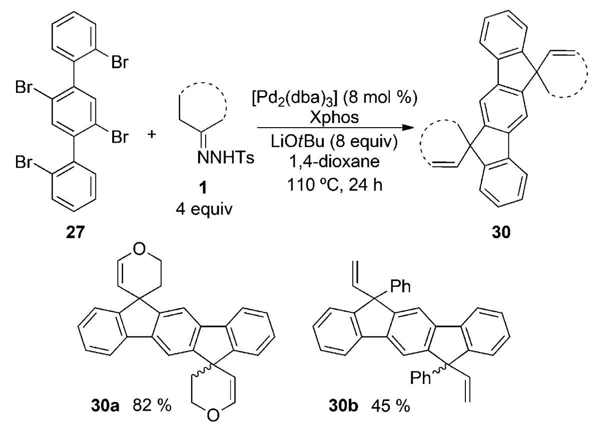
The double autotandem processes were studied, employing the corresponding excess of tosylhydrazone. The treatment of 2,2′,6,6′-tetrabromobiphenyl **26**[37] with cyclohexanone tosylhydrazone failed to give the product derived from a double cascade reaction. Instead, a mixture of compounds was obtained, from which the intermediate **29** (that incorporates two cyclohexene subunits, but in which only one cascade reaction has taken place) could be isolated, although with very poor yield (Scheme 13). Clearly, after the formation of the first spirofluorene, a distortion in the bond angles occurs as a result of the formation of the five-membered ring, leaving carbon atoms *a* and *b* far apart, and a second 5-*exo*-trig cyclization would be disfavored. Nevertheless, the formation of **29**, although in very poor yield, indicates that the formation of spirofluorenes substituted at 4′ and 5′ positions is feasible. We plan to investigate on those intriguing class of structures in the future.



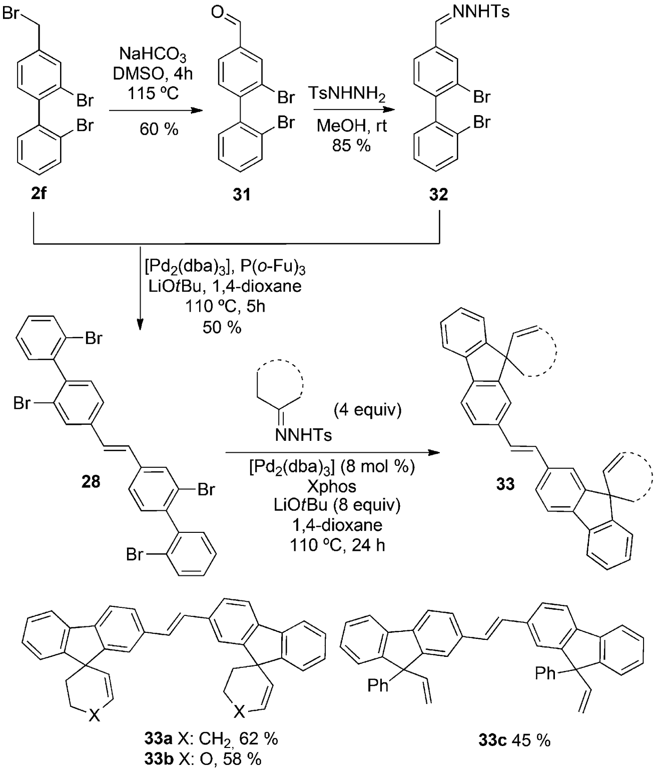
Scheme 13. Pd-Catalyzed reaction of tosylhydrazone **1a** with tetrabromide **26**.

We next turned our attention to tetrabromide **27**, a scaffold that had been previously employed in the synthesis of functional organic materials with heterocyclic ladderane structures.[23,38] Unlike the reactions with **26**, the autotandem processes with tetrabromide **27** proceeded successfully, giving rise to 6,12-dihydroindeno[1,2-*b*]fluorenes **30**. Noteworthy, these molecules feature an all-carbon ladderane structure, which has been employed as building block for blue emitters,[39] and molecules with other organic electronics applications.[40] The tosylhydrazones of 4-pyranone and propiophenone were employed this time as representatives of cyclic and acyclic tosylhydrazones, respectively (Scheme 14).

The synthesis of tetrabromide **28** was accomplished from tribromide **2f** (Scheme 15). On one side, compound **2g** was transformed into the tosylhydrazone **32** through aldehyde **31**. Next, the Pd-catalyzed cross-coupling reaction between **2g** and **32** occurs chemoselectively through the benzylic position of the tribromide, leading to tetrabromide **28** as a single diastereoisomer. Then, the cascade reactions with an excess of the appropriate tosylhydrazone led to the new π-extended structures **33**, which include the fluorene and vinylphenylene fragments, very common moieties in functional organic materials (Scheme 15). Again, both cyclic and acyclic tosylhydrazones can be employed in the coupling reaction, leading to structurally diverse polyaromatic structures (Scheme 15). It must be noted that compounds **30** and **33** are expected to be formed as a mixture of two diastereoisomers, which have shown identical ^{1}H and ^{13}C NMR spectra in all cases.

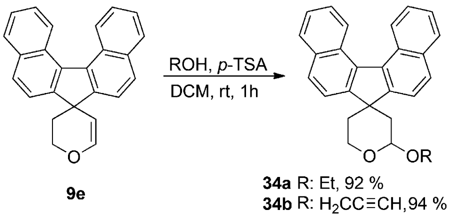


Scheme 14. Synthesis of 6,12-dihydroindeno[1,2-*b*]fluorenes **30** through a double autotandem cascade.



Scheme 15. Synthesis of spirofluorene-vinylphenylene hybrids **33** through a double autotandem cascade.

Notably, the polycyclic compounds obtained through the autotandem reactions discussed along this paper feature an additional double bond that comes from the final β-hydride elimination in the catalytic cycle. The presence of this functionality might be useful to accomplish further modifications, such as oxidations, ring openings, or eventually to attach these fragments to other molecules through addition reactions or cross-metathesis. So far, we have concentrated in a quite simple transformation on the derivatives obtained from the 4-oxanone tosylhydrazone, which feature a dihydropyran moiety. Treatment of the binaphthyl derivative **9e** with an alcohol in acidic media leads to the formation of the corresponding acetal **34**, emulating the reactivity of dihydropyran, a very commonly used protective group for alcohols.[41] As an example, a terminal triple bond, that could be later elongated through click chemistry was attached to the fluorescence spirobinaphthyl to yield the functionalized derivative **34 b** (Scheme 16). This very simple reaction might enable the modification of these structures to tune their physical properties, such as solubility or aggregation in solid phase, or to attach the fluorophore structures to polymers, solid supports or monolayers, as well as open the door to the employment of these molecules as fluorescence tags that can be introduced and cleaved under the same conditions as the THP protective group.



Scheme 16. Attachment of alcohols to fluorescence spirobinaphthyl **9** taking advantage of the enol ether functionality.

Photophysical properties

Most of the molecules described along this work feature unprecedented structures with extended π-conjugation. To evaluate the potential interest of these classes of molecules in the development of functional organic materials and luminescent devices, we carried out a study of the photophysical properties of some selected compounds by means of their UV/Vis absorption and fluorescence spectra. Thus, thiophene- and benzothiophene-containing spirocompounds (**18**, **19**, and **25**), spiro dibenzofluorenes (**9** and **34**) and bisfluorenes (**33**) were studied. A summary of the results is presented in Table 1.

From our point of view, the data obtained from spirodibenzofluorenes **9** and **34** are quite appealing. Their absorption spectra in CH_2Cl_2 highly dilute solution feature $\pi \rightarrow \pi^*$ transitions at about $\lambda_{max} = 353$ and 370 nm, showing a large bathochromic shift when compared with the absorption spectra reported for 1,1′-binaphthyl ($\lambda_{max} = 280$ and 295 nm).[42] Interestingly, whereas in typical 2,2′-binaphthyls there is no conjugation between the two napthyl rings because of the steric repulsions between the substituents at positions 8 and 8′, the geometrical distortion created by the formation of the five-membered ring enforces a rigid structure in which both naphthyl rings are arranged in a situation closer to planarity, therefore promoting effective conjugation between the rings. In fact, DFT molecular modeling studies predict a structure in which both naphthalene rings are slightly bent (torsion angle of 21°) to avoid the steric interaction between the hydrogens at the internal positions (Figure 3). Nevertheless, despite the distortion from planarity, conjugation between both naphthalene fragments occurs: the graphical representations of HOMO and LUMO orbitals clearly show the extension of the π-conjugation along both aromatic structures.[43] Interestingly, these compounds turned out to be highly fluorescent, showing an emission band at about 403 nm with also high quantum yields.

Regarding the thiophene-containing spiroderivatives, the simplest 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene **18** showed an absorption band at $\lambda_{max} = 318$ nm, but no significant emission bands. The non-symmetric compound **25 a** presented an emission band at 357 nm, although with a modest quantum yield. However, the benzocondensed analogues **19 a** and **19 c** featured significant emission bands at 407 and 383 nm, respectively. These results indicate the potential interest of these previously unknown structures in the design of new electroluminescent materials by modifying the aromatic backbones attached at the spirocyclic central core.

Finally, the UV/Vis spectra of bisfluorenes **33** show an absorption band at $\lambda_{max} = 367$ nm. The importance of the presence of the fluorene structure to enforce the extended π-conjugation is shown by comparing these data with the spectra of the tetrabromide precursor **28**, which features absorption at $\lambda_{max} = 320$ nm (Figure 4). Moreover, compounds **33** are strongly fluorescence in CH_2Cl_2 solution, with sharp emission bands at 399 and 423 nm, and very high quantum yields (Figure 4 and Table 1). The type of substitution at C9 on the fluorene moieties has no significant influence on the position of the absorption and emission bands, nevertheless, the determined quantum yields differ slightly (Table 1) but consistently maintaining very high values.

Table 1. Absorption and emission spectral data for selected compounds.[e]

	λ_{abs} [nm][a]	$(\varepsilon \pm s^{[b]}) \times 10^4$ [$L\,mol^{-1}\,cm^{-1}$]	λ_{em} [nm][a]	$\Phi^{[d]} \pm s^{[b]}$ [%]
9 e	250	4.1 ± 0.1	385 sh, 403	60 ± 10
34 a	250	2.15 ± 0.1	385 sh, 401	110 ± 20
34 b	250	2.15 ± 0.06	385 sh, 402	60 ± 10
18 b	318 (315)	2.8 ± 0.1	399 (372)	1.0 ± 0.1 (0.3)
25 a[c]	316 (305 sh, 315)	1.7 ± 0.1 (0.97 ± 0.01)	357	16 ± 2 (11.8 ± 0.4)
25 c[c]	315	1.0 ± 0.2	356	17 ± 2
19 a[c]	355 (350)	1.2 ± 0.1 (0.28 ± 0.01)	407 (404)	24 ± 3 (49 ± 3)
19 c[c]	334, 351 (333 347)	0.1 (0.77 ± 0.3)	383, 403 (377 398)	18 ± 3 (25 ± 1)
28	326	2.3 ± 0.2	379	
33 a	366	3.18 ± 0.08	399–422	68 ± 9
33 b	366	0.98 ± 0.06	399–423	98 ± 6
33 c	366	1.0 ± 0.1	399–422	100 ± 10

[a] Measured in CH_2Cl_2 (1×10^{-5} M) at RT. [b] Standard deviation. [c] Measurements carried out in hexanes are indicated in brackets. [d] Fluorescence quantum yields relative to quinine sulfate 0.1 N in H_2SO_4 ($\Phi = 0.55$ at 360 nm). [e] More detail is provided in the Supporting Information.

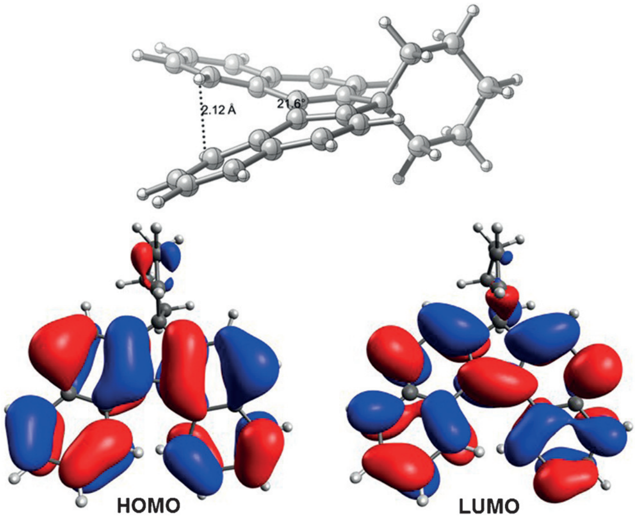


Figure 3. Above: Three-dimensional optimized structure[44] (b3 Lyp/6-31+G**) for the spirobinaphthyl parent structure. A dihedral angle of 21.6° between the two naphthyl moieties facilitates the conjugation over the whole aromatic surface. Below: Representation of the HOMO and LUMO molecular orbitals that show the delocalization over the whole aromatic surface.

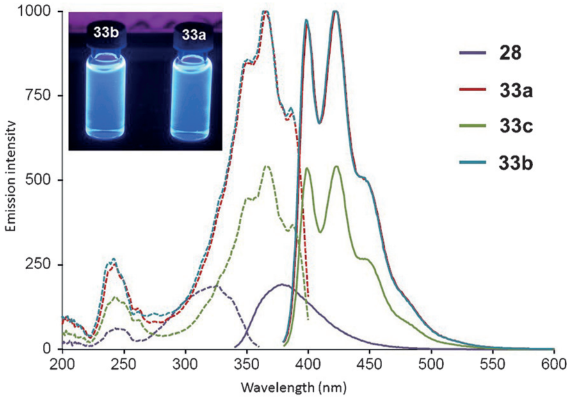


Figure 4. Fluorescence spectra for compounds **28** and **33 a–c** 1×10^{-5} M solutions in CH$_2$Cl$_2$). -----: excitation spectra; solid lines: emission spectra. The inserted picture corresponds to solutions of **33 a** and **33 b** in CH$_2$Cl$_2$ upon UV irradiation at 365 nm.

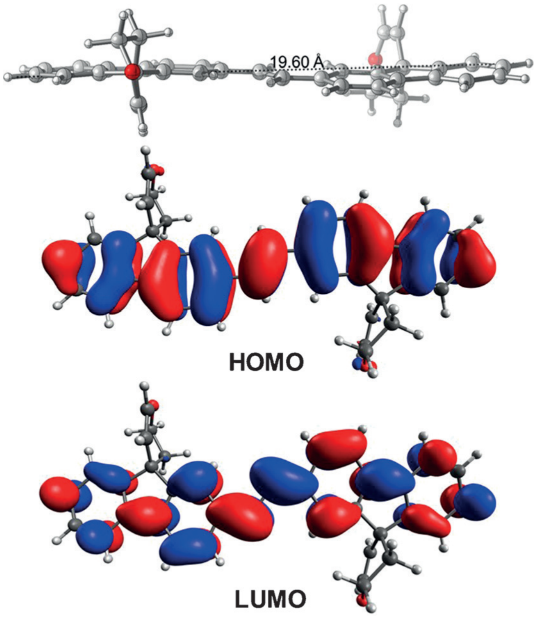


Figure 5. Three-dimensional optimized structure (b3Lyp/6-31+G**) for the spirofluorene-vinylphenylene hybrid **33 b**. A 2 nm-long planar structure is predicted. Representation of the HOMO and LUMO molecular orbitals that show the delocalization over the whole π-surface.

DFT-based molecular modeling studies on **33 b** shows a totally planar structure for these fluorene-vinylphenylene hybrids, which enables the efficient conjugation of the all-carbon-π-extended system responsible for the blue emission properties observed (Figure 5). Noteworthy, the nearly 2 nm long planar structure was synthesized from simple materials through two consecutive cross-couplings based on tosylhydrazones (Scheme 15). Interestingly, these structures resulted in very efficient blue-emitting molecules in solution (Figure 4).

These results clearly show the versatility of our methodology for the generation of structurally diverse small molecules with extended π-conjugation and interesting photophysical properties. Although we have not attempted so far to optimize the conjugated structures into any particular application, we have already discovered new structures with promising properties as blue-light emitters.[45] Moreover, the modular nature of our methodology might allow for the combination of different aromatic structures with suitable substitutions and different hydrazones, offering the opportunity of tuning the physical properties as well as the absorption and emission properties of the molecules.

Conclusion

We have shown that the autotandem Pd-catalyzed reaction between tosylhydrazones and 2,2′-dibromobiphenyls and related systems represents a very versatile method for the synthesis of π-extended conjugated molecules. The method allows for the introduction of a variety of structures, substituents, and functional groups around the basic fluorene structure, enabling the tuning of the electronic properties of the materials. As a proof-of-concept, we have already developed a very straightforward method for the preparation of highly fluorescence blue-emitting molecules through a synthetic route that involves two consecutive Pd-catalyzed reactions with tosylhydrazones.

Experimental Section

General procedure for the Pd-catalyzed auto-tandem reaction between tosylhydrazones 1 and dibromides

Synthesis of polycyclic aromatic molecules with extended π-conjugation: A carousel reaction tube was charged under nitrogen atmosphere with the corresponding *N*-tosylhydrazone (2 equiv), biaryldibromide compound (0.2 mmol, 1 equiv), tris(dibenzylideneacetone)dipalladium(0) (4 mol %), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (Xphos) (8 mol %), lithium *tert*-butoxide (0.8 mmol, 4 equiv) and 1,4-dioxane (2 mL).The reaction mixture was stirred at 110 °C for 24 h. After cooling to room temperature, the 1,4-dioxane was removed under reduced pressure. The reaction crude was dissolved in CH_2Cl_2 and filtered through Celite. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using hexane, pentane or a mixture of hexane/ethyl acetate, pentane/diethyl ether or hexane/CH_2Cl_2 as eluent.

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