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One-Pot Rh(III)-Catalyzed Twofold C–H Activation/Oxidative Annulation of *N*-Arylpyrroles with Alkynes to Fluorescent Ullazines

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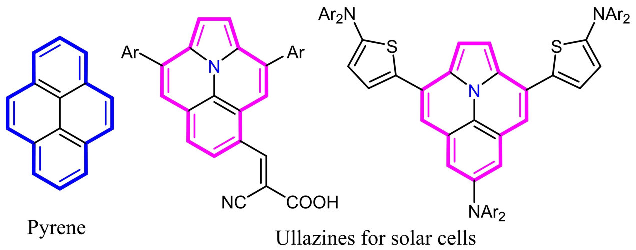
Abstract: A range of densely functionalized ullazines have been synthesized by a one-pot Rh(III)-catalyzed twofold C–H activation/oxidative annulation of *N*-arylpyrroles with alkynes. Electrophilic bromination at 5- or 5,7- positions of the EWG-substituted ullazine core offers an interesting single or double entry for further extended functionalization. Mechanistic considerations suggest two complementary paths, EWG-assisted and S_EAr, for the C–H activations. All ullazines exhibit strong fluorescence emissions. Ullazines bearing thiophene and triarylamine units at 5- and 5,7- positions show a significant bathochromic shift in their emission spectra, attributed to the more extended electronic circuits present.

Keywords: C–H Activation; Fluorescence, Pyrroles; Rhodium; Ullazines

Introduction

Pyrene, a polycyclic aromatic hydrocarbon (PAH) that contains four fused benzene rings, is well recognized by its unique optical properties, good stability and hole transporting ability that makes very attractive for applications in organic electronic devices (Figure 1).[1] Their planar isoelectronic *N*-doped cyclopenta[*c*,*d*]phenalene derivatives, ullazines, have received extensive interest in the field of dye-sensitized and perovskite solar cells (DSSCs and PSCs)[2] for their excellent performance as light harvesting moieties and electron donor abilities (Figure 1).[3]

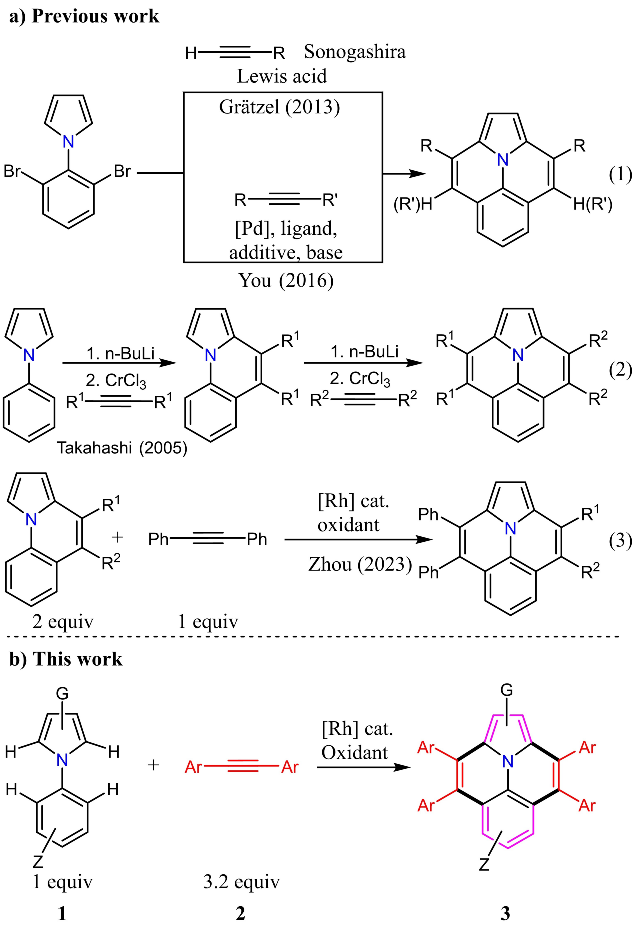


Pyrene

Ullazines for solar cells

Figure 1. Pyrene and Ullazines.

Most typical synthetic routes to ullazines[2b,4] often rely on the use of halogenated *N*-arylpyrroles[2b,4c–e,j] (Scheme 1a, eq 1) but, however, these methods present limitations in substrate scope and difficulties in achieving densely functionalized ullazines, underscoring the need for improved synthetic strategies. On the contrary, synthetic routes based on metal-catalyzed C–H activation/oxidative annulation of non-halogenated *N*-arylpyrroles have been scarcely developed. A pioneering stepwise chromium-mediated synthesis of ullazines from *N*-arylpyrroles and alkynes has been described by Takahashi (Scheme 1a, eq 2).[4a] Zhou recently reported the synthesis of a little number of ullazines by Rh(III)-catalyzed oxidative annulation of pyrroloquinolines with diphenylacetylene[5] based on early described Dong/Chen's conditions for single



- ✓ One-pot twofold C-H activation/oxidative annulation
- ✓ EDG and EWG substituents tolerated
- ✓ Access to novel substitution patterns

Scheme 1. Synthetic routes to ullazines.

C–H activation/oxidative annulation of *N*-arylpyrroles to pyrroloquinolines (Scheme 1a, eq 3).[6] It is worth to mention that an excess of valuable *N*-arylpyrrole partners were required for these successful cycloadditions. To the best of our knowledge, one-pot synthesis of ullazines starting from *N*-arylpyrroles has not yet been developed.

Herein, we report a novel route to functionalized ullazines based on a one-pot Rh(III)-catalyzed twofold C–H activation/oxidative annulation of *N*-arylpyrroles with alkynes. The reaction is tolerant with arylalkynes and *N*-arylpyrroles bearing EDG and EWG groups including halogens (Cl, Br, F) in different positions of the ullazine skeleton available for synthetic manipulations at specific sites (Scheme 1b).

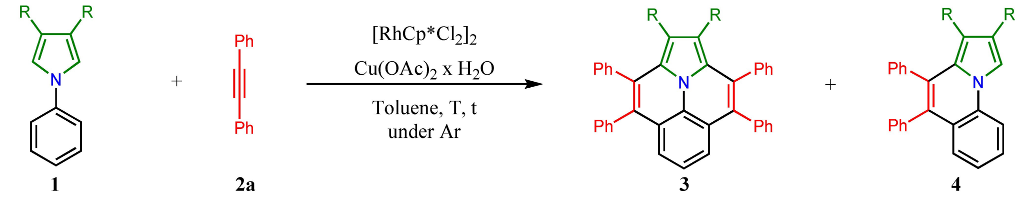
Results and Discussion

The ester derivative 3,4-dimethoxycarbonyl *N*-phenylpyrrole **1a**[7] was chosen as the initial substrate for reaction development. Under previously reported conditions for single annulations,[6] only traces of the desired double annulated ullazine **3aa** could be detected being the pyrroloquinoline **4aa** obtained in a very low 14% yield (Table 1, entry 1).[8] On changing several factors such as ratio of partners, reaction duration and concentration led to the desired ullazine **3aa** albeit in a low 20% yield (Table 1, entry 2), that could be increased to 47% raising the temperature to 135 °C (Table 1, entry 3).[9] Catalyst loading at different temperatures was next explored. To our delight, using $[RhCp^*Cl_2]_2$ (10% mol) at 135 °C for 72 h led to the isolation of **3aa** in 64% yield (Table 1, entry 4), which means a remarkable 80% yield for each one of the annulations.[10] In a separate experiment, this last result was firmly confirmed since the second annulation to obtain ullazine **3aa** from pyrroloquinoline **4aa** could be achieved in 70% yield using 5% Rh under the same reaction conditions (Table 1, entry 5).[8]

Concentration of the reaction was then analyzed. Interestingly, more concentrated reactions (0.4 M and 0.8 M) are well tolerated giving similar yields of ullazine **3aa** under optimized conditions (Table 1, entries 6 and 7). On the other hand, in a MW experiment, ullazine **3aa** could be isolated in 54% yield from pyrrole **1a** and alkyne **2a** using 10% Rh catalyst in only 24 h of reaction (Table 1, entry 8).[8] The nature of the alkyl ester, **1a** or **1b**, has no influence on the course of the reaction (Table 1, entries 4 and 9). Influence of refreshing the catalyst loading during the long reaction times using the more easily available *N*-phenylpyrrole **1b** was then explored.[11] In a 72 h test reaction, using an initial 5% Rh catalyst followed by a refreshing of another 5% Rh loading after 36 h afforded ullazine **3ba** in a very good 67% yield (Table 1, entry 10). Gratifyingly, even using only a 2.5% Rh catalyst and another 2.5% Rh at the refreshing point led to **3ba** in fairly good yield (Table 1, entry 11).

Finally, in an effort to gain an insight into the reaction mechanism,[12] we run the reaction with the preformed $RhCp^*(OAc)_2$ catalyst but, however, ullazine **3ba** could only be isolated in a low 34% yield (Table 2, entry 1), that might suggest the involvement of an electrophilic-type mechanism. To support this plausible operating mechanism, the nature of the directing group and the electronic richness of the pyrrole was then analyzed. Thus, when using the secondary dicarboxamide **1c**[13] the double annulation chemoselectively occurred to give the ullazine **3ca** in 55% yield, indicating that the C–H activation/annulation through the phenyl ring is favoured against the previously observed alternative annulation that led to a pyrroloisoquinolone (Table 2, entry 2).[14] Regarding the more challenging monosubstituted and disubstituted derivatives, the 3-methoxycarbonyl *N*-phenylpyrrole **1d** gave a mixture of the single annulated pyrroloquinoline **4da** (29% yield)[15] and the double

Table 1. Optimization of the reaction.[a]

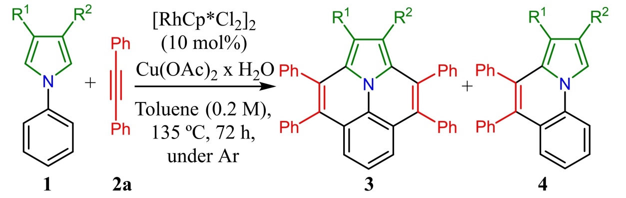


1a, R = CO_2Me
1b, R = CO_2Et

Entry	Pyrrole	$[RhCp^*Cl_2]_2$ (mol %)	T (°C)	t (h)	[M]	Yield (%)[b]
1[c]	**1 a**	5	110	24	0.1	**4 aa**, 14
2	**1 a**	5	110	72	0.2	**3 aa**, 20
3	**1 a**	5	135	72	0.2	**3 aa**, 47
4[d]	**1 a**	10	135	72	0.2	**3 aa**, 64
5	**4 aa**	5	135	72	0.2	**3 aa**, 70
6	**1 a**	10	135	72	0.4	**3 aa**, 62
7	**1 a**	10	135	72	0.8	**3 aa**, 60
8	**1 a**	10	135 (MW)	24	0.2	**3 aa**, 54
9[d]	**1 b**	10	135	72	0.2	**3 ba**, 62
10[e]	**1 b**	5 + 5	135	72	0.2	**3 ba**, 67
11[e]	**1 b**	2.5 + 2.5	135	72	0.2	**3 ba**, 60

[a] Typical reaction conditions: **1 a** (1 equiv.), **2 a** (3.2 equiv.), $Cu(OAc)_2 \times H_2O$ (2.2 equiv.).
[b] Isolated yields.
[c] Dong/Chen's conditions: **1 a** (2 equiv.), **2 a** (1 equiv.), $Cu(OAc)_2 \times H_2O$ (1.2 equiv.).
[d] Pyrroloquinolines **4 aa** (9% yield) or **4 ba** (10% yield) were also isolated and **1 a** (10% yield) or **1 b** (12%) were recovered, respectively.
[e] Refreshing at 36 h.

Table 2. Experiments with mechanistic implications.[a]



1b, R^1, R^2 = CO_2Et
1c, R^1, R^2 = CONHMe
1d, R^1 = H, R^2 = CO_2Me
1e, R^1 = Me, R^2 = CO_2Et

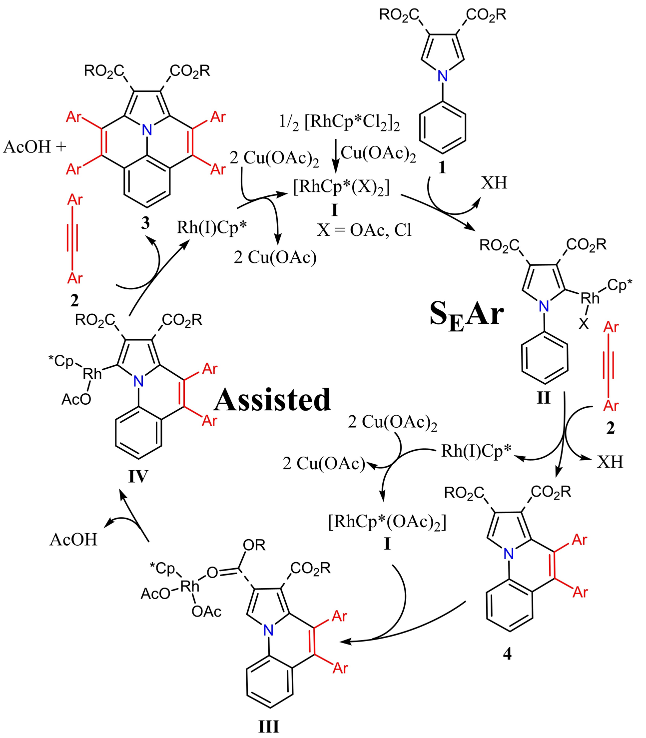
Entry	Pyrrole	Yield **3** (%)[b]	Yield **4** (%)[b]
1[c]	**1 b**	**3 ba**, 34	**4 ba**, 8
2	**1 c**	**3 ca**, 55	**4 ca**, 10
3	**1 d**	**3 da**, 44	**4 da**, 29
4	**1 e**	**3 ea**, 16	**4 ea**, 24

[a] Typical reaction conditions: **1** (1 equiv.), **2 a** (3.2 equiv.), $Cu(OAc)_2 \times H_2O$ (2.2 equiv.).
[b] Isolated yields.
[c] 20 mol% of $RhCp^*(OAc)_2$ as catalyst.

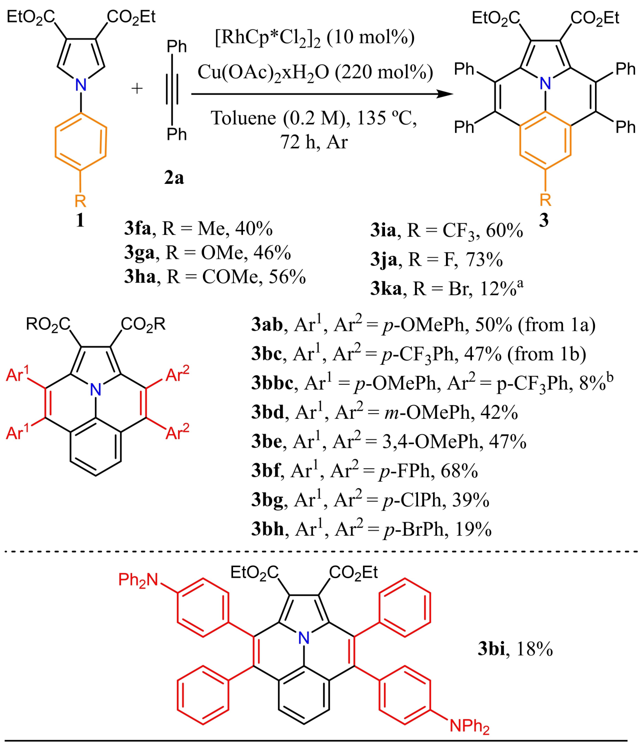
annulated ullazine **3 da** in 44% yield (Table 2, entry 3). A similar trend was observed when the disubstituted 3-ethoxycarbonyl-4-methyl *N*-phenylpyrrole **1 e**, bearing EWG and EDG groups, gave a mixture of the single annulated pyrroloquinoline **4 ea** (24% yield)[15] and the double annulated ullazine **3 ea** in 16% yield (Table 2, entry 4).

These results might suggest that the twofold C–H activation processes take place through two complementary mechanistic paths (Scheme 2): i) initial C–H bond activation would happen via a S_EAr process in the most nucleophilic position of the pyrrole ring. The initial catalytically active Rh(III) species **I** would afford species **II**, followed by alkyne coordination, insertion into Rh–C bond, C–H activation on the aryl ring and reductive elimination would afford the pyrroloquinoline **4** with concomitant regeneration of the catalytic active Rh(III) species;[16] ii) a second C–H activation on the pyrrole ring would now take place most likely by an EWG-assisted (coordination) CMD process, thus showing the crucial balance between the electronic richness and steric hindrance of the substituents of pyrrole ring during the annulations,[17] to afford, following a similar sequence of steps, the final double annulated ullazine **3**.

Scope and limitations of both reaction partners were then explored (Scheme 3). *p*-Substituted *N*-arylpyrroles with electron-donating (EDG) and electron-withdrawing (EWG) substituents were well tolerated giving the corresponding ullazines **3 fa**–**3 ja** in fairly good yields (40%-73%), being slightly favoured



Scheme 2. Mechanistic proposal.



Scheme 3. Scope of the reaction. Typical reaction conditions: **1** (1 equiv.), **2** (3.2 equiv.), isolated yields.[a] Ullazine **3ba** was also obtained in 62% yield.[b] Overall yield for two consecutive single annulations.

the annulations on electron-poor substrates. An exception is the case of the *p*-Br *N*-arylpyrrole **1k** in which an inseparable mixture of the parent ullazine **3ba** (62% yield) and the expected brominated ullazine **3ka** (12% yield) was obtained. Electronically distinct *p*-substituted diphenylacetylenes **2b** (Ar^1, Ar^2 = *p*-OMe) and **2c** (Ar^1, Ar^2 = *p*-CF_3) were also well tolerated giving rise to the corresponding ullazines **3ab** and **3bc** in rather good yields. Interestingly, electronically distinct left and right aryls were also installed, **3bbc**, in two consecutive single annulations although in relatively low overall yield. *Meta*- and double substituted diphenylacetylenes were also well accommodated giving rise to ullazines, **3bd** and **3be**, in reasonable yields. In the case of the synthetically useful halogenated diarylacetylenes, the corresponding ullazines **3bf–3bh** could be isolated in 19%-68% yields. Curiously, the highly polarized diarylacetylene bearing the electron-rich *N*-Ph_2 substituent regioselectively afforded the ullazine **3bi** albeit in a low 18% yield.[18]

The structure of ullazine **3aa** (crystals grown in DCM) was confirmed by X-Ray diffraction analysis in which the presence of the planar azapyrene core was firmly established (Figure 2).[19] To our surprise, X-Ray diffraction analysis of ullazine **3ca** (crystals grown in $CHCl_3$) showed the incorporation of an unexpected chlorine atom in position 5 of the *N*-aryl ring as $\mathbf{3ca_{5\text{-}Cl}}$ (Figure 2).[19]

This serendipitous finding led us to analyze in detail the electrophilic bromination of ullazines **3** since the Vilsmeier-Haack formylation is so far the most typical functionalization in this position for the preparation of Grätzel cells.[20] To our delight, bromination of ullazine **3ba** with 1eq of NBS at 4 °C afforded the 5-bromoullazine **5** in a fairly good 78% yield while bromination with 4 eq of NBS, under the same conditions, gave the 5,7-dibromoullazine **6** in an excellent 85% yield (Scheme 4). Subsequent Sonogashira reactions of **5**, **6** and **3ka** with 2-ethynylthiophene afforded 5- and 6-(tiophen-2-ylethynyl) ullazines **7** and **9** (54% and 38% yields) respectively, and 5,7-bis(tiophen-2-ylethynyl) ullazine **8** (70% yield),[19] interesting functionalized ullazines with more extended

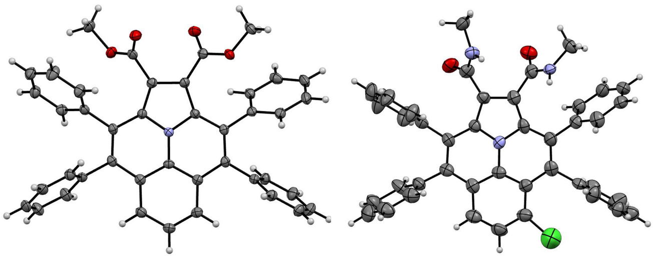
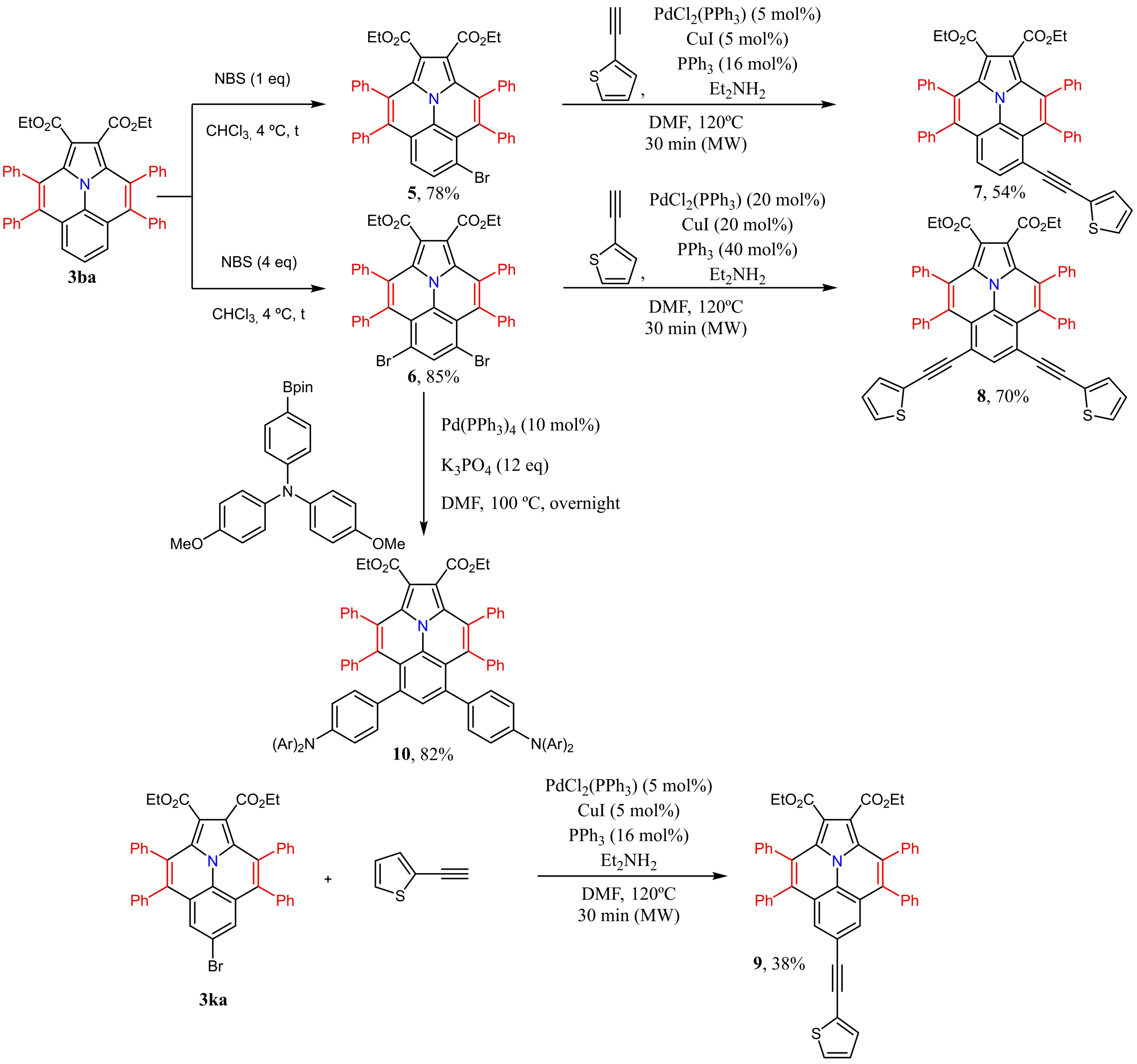


Figure 2. ORTEP drawing of **3aa** (left) and $\mathbf{3ca_{5\text{-}Cl}}$ (right) showing thermal ellipsoids at the 50% probability level.



Scheme 4. Bromination of ullazine **3 ba**, Sonogashira reactions to (thien-2-ylethynyl) ullazines **7**, **8** and **9** and Suzuki reaction to ullazine **10**.

electronic structures (Figure 3).[2a,c,d] In addition, triarylamino ullazine **10** was obtained by the corresponding Suzuki coupling of dibromoullazine **6** in 82% yield.

Absorption and emission spectra for selected ullazines, showed absorptions from 270 nm to 396 nm with λ_{max} from 389 nm to 396 nm independently of the substitution in any aryl ring of ullazines **3**.[8] By contrast, ullazines **7** and **8**, show a significant λ_{max} bathochromically shifted to 432 nm and 482 nm, respectively, due to the more extended electronic circuits (Figure 4), that disappear in ullazine **9** that bears, however, the tiophen-2-ylethynyl moiety at position 6. On the other hand, the triarylamine-

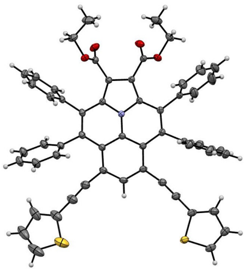


Figure 3. ORTEP drawing of **8** showing thermal ellipsoids at the 50% probability level.

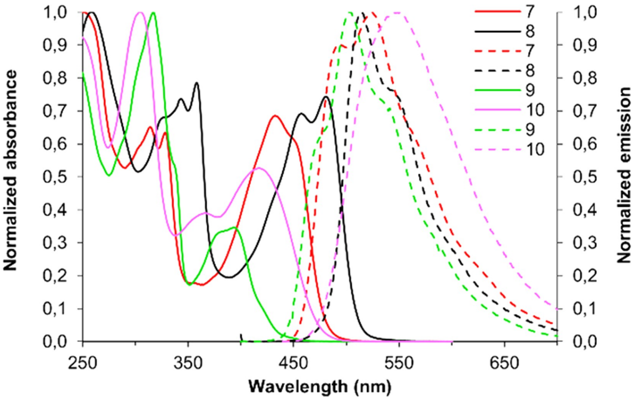


Figure 4. Normalized absorption and emission spectra of ullazines **7**, **8**, **9** and **10**.

substituted ullazine **10** shows a blue shift to 417 nm respect to ullazine **8**. All ullazines have strong fluorescence emission with maxima from 497 nm to 551 nm.

Conclusion

In summary, we have developed a synthetic route to densely functionalized ullazines by a one-pot Rh(III)-catalyzed twofold C–H activation/double annulation of *N*-arylpyrroles with diarylalkynes. The reaction tolerates EDG and EWG substituents in both partners including halogens (F, Cl, Br) that allow further manipulations. Mechanistic investigations suggest two complementary paths, EWG-assisted and S_EAr, for the C–H activations on the pyrrole ring. A family of ullazines **7**–**9**, characterized by possessing thienylethynyl units at 5-, 6- and 7-positions, and ullazine **10**, with triarylamine substituents at 5- and 7-positions, have been prepared and their electronic properties feature as good candidates for use as HTMs in PSCs.

Experimental Section

General Information

All reactions were performed under an inert atmosphere of argon and with anhydrous solvents in glassware oven or flame dried at 80 °C unless otherwise stated. All the chemicals and solvents were purchased from Acros Organics Ltd., Aldrich Chemical Co. Ltd., Alfa Aesar, Fluorochem Ltd., Strem Chemicals Inc. or TCI Europe N.V. chemical companies and used without further purification, unless otherwise stated. For microwave assisted reactions a CEM Discover 2.0 was used. Analytical thin layer chromatography was carried out on silica-coated aluminum plates (silica gel 60 F254 Merck) using UV light as visualizing agent (254 nm) and $KMnO_4$ (solution of 1.5 g of potassium permanganate, 10 g of potassium bicarbonate and 1.25 mL of 10% sodium hydroxide in 200 mL of water) with heat as developing agents. Flash column chromatography separations were performed on silica gel 60 (Merck, 230–400 mesh) with the indicated eluent. All the synthesised compounds were named following IUPAC guidelines as applied by ChemDraw Professional (version 22.0). ^1H and ^{13}C nuclear magnetic resonance experiments were carried out using a Varian Inova 500 MHz, a Varian Inova 400 MHz, a Varian Mercury 300 MHz or a Bruker DPX 250 or a Bruker Avance 300 NMR spectrometers. All chemical shifts are reported in parts per million (ppm) and referenced to residual solvent peaks. Coupling constants J are given in Hertz (Hz). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or as a combination of them. Multiplicities of ^{13}C NMR signals were determined by DEPT experiments. Mass spectrometry was carried out on a Bruker micro TOF spectrometer. X-ray crystallographic analysis was performed at the CACTUS facility of the University of Santiago de Compostela.

General Procedures for the Synthesis of Ullazines 3

A sealed tube equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (12.4 mg, 0.02 mmol, 10 mol%), *N*-arylpyrrole **1** (0.20 mmol, 1 eq), alkyne **2** (0.64 mmol, 3.2 eq), $Cu(OAc)_2xH_2O$ (87.8 mg, 0.44 mmol, 2.2 eq) and toluene (1 mL). The suspension was heated in an oil bath at 135 °C for 72 h under an Argon atmosphere. The reaction mixture was quenched with NaCl(aq) solution and extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using appropriate solvents as eluents to afford the products.

*Dimethyl 3,4,8,9-tetraphenylindolizino[6,5,4,3-ija]quinoline-1,2-dicarboxylate (***3 aa***) and Dimethyl 4,5-diphenylpyrrolo[1,2-a]quinoline-2,3-dicarboxylate (***4 aa***)*: Solvents used: Hex/DCM/EtOAc (8:1:1). Amount of **3 aa** obtained: 78.9 mg (64% yield), yellow solid. ^1H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.44–7.33 (m, 5H), 7.33–7.19 (m, 18H), 3.19 (s, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.4 (CO), 135.9 (C), 135.8 (C), 133.7 (C), 130.4 (C), 129.8 (C), 129.5 (CH), 129.1 (CH), 127.4 (CH), 126.7 (CH), 126.3 (CH), 126.2 (CH), 125.1 (C), 123.6 (C), 123.5 (CH), 120.4 (CH), 113.0 (C), 50.9 (CH_3).HRMS (APCI) calculated for $C_{42}H_{29}NO_4$ $[M]^+$: 611.2091, found 611.2089. Amount of **4 aa** obtained: 8.1 mg (9% yield), yellow solid. ^1H-NMR (500 MHz, $CDCl_3$) δ (ppm): 8.48 (s, 1H), 8.05–8.00 (m, 1H), 7.63–7.56 (m, 1H), 7.39–7.28 (m, 2H), 7.27–7.13 (m, 8H), 7.11–7.04 (m, 2H), 3.86 (s, 3H), 3.23 (s, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 166.1 (CO), 163.9 (CO), 136.6 (C), 135.8 (C), 133.1 (C), 131.8 (C), 130.9 (CH), 130.5 (CH), 130.2 (C), 129.0 (C), 128.7 (CH), 128.6 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 127.1(CH), 125.2 (CH), 125.0 (C), 117.7 (C), 115.9 (CH), 114.5 (CH), 112.3 (C), 52.1 (CH_3), 51.8 (CH_3). HRMS (APCI) calculated for $C_{28}H_{22}NO_4$ $[M+H]^+$: 436.1543, found 436.1541. Amount of pyrrole **1 a** recovered: 5.4 mg (10%).

*Diethyl 3,4,8,9-tetraphenylindolizino[6,5,4,3-ija]quinoline-1,2-dicarboxylate (***3 ba***)*: Solvents used: Hex/DCM/EtOAc (8:1:1). Amount of **3 ba** obtained: 79.1 mg (62% yield), yellow solid. ^1H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.36–7.29 (m, 5H), 7.27–7.14 (m, 18H), 3.57 (q, $J = 7.1$ Hz, 4H), 1.00 (t, $J = 7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 165.0 (CO), 136.9 (2xC), 134.5 (C), 131.5 (C), 130.8 (C), 130.5 (CH), 130.1 (CH), 128.4 (CH), 127.7 (CH), 127.3 (CH), 127.2 (CH), 126.1 (C), 124.4 (CH), 124.3 (C), 121.3 (CH), 114.4 (C), 61.1 (CH_2), 13.8 (CH_3). HRMS (APCI) calculated for $C_{44}H_{34}NO_4$ $[M+H]^+$: 640.2482, found 640.2483. Amount of **4 ba** obtained: 9.5 mg (10% yield), yellow solid. Amount of pyrrole **1 b** recovered: 7.1 mg (12%).

Gram Scale

A sealed tube equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (61.8 mg, 0.1 mmol, 10 mol%), *N*-arylpyrrole **1 b** (287.3 mg, 1 mmol, 1 eq), diphenylacetylene (570.3 mg, 3.2 mmol, 3.2 eq), $Cu(OAc)_2xH_2O$ (439.2 mg, 2.2 mmol, 2.2 eq) and toluene (5 mL). The suspension was heated in an oil bath at 135 °C for 72 h under an Argon atmosphere. The reaction mixture was quenched with NaCl(aq) solution and extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using a mixture of Hex/DCM/EtOAc (8:1:1) as eluent to afford **3 ba** as a yellow solid in a 50% yield (319.2 mg). Amount of **4 ba** obtained: 38.6 mg (8% yield). Amount of pyrrole **1 b** recovered: 51.9 mg (18%).

Refreshing Catalyst Loading Experiments

A sealed tube equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (5 or 2.5 mol%), *N*-arylpyrrole **1 b** (57.5 mg, 0.2 mmol, 1 eq), diphenylacetylene (141.1 mg, 0.64 mmol, 3.2 eq), $Cu(OAc)_{2\times}H_2O$ (87.8 mg, 0.44 mmol, 2.2 eq) and toluene (1 mL). The suspension was heated in an oil bath at 135 °C for 36 h under an Argon atmosphere. The reaction mixture was stopped at this time and 5 mol% (Table 1, entry 10) or 2.5 mol% (Table 1, entry 11) of the catalyst complex was added under argon atmosphere and heated at 135 °C for another 36 h. Once finished, the reaction mixture was quenched with NaCl(aq) solution and extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using a mixture of Hex/DCM/EtOAc (8:1:1) as eluent to afford **3 ba** (85.9 mg, 67%, entry 10 and 77.4 mg, 60%, entry 11) as a yellow solid. Amount of **4 ba** obtained: 5.7 mg, 6%, entry 10 and 8.7 mg, 9%, entry 11. Amount of pyrrole **1 b** recovered: 3.1 mg, 5%, entry 10 and 4.7 mg, 8%, entry 11.

*N^1,N^2-dimethyl-3,4,8,9-tetraphenylindolizino[6,5,4,3-ija]quinoline-1,2-dicarboxamide (**3 ca**):* Solvents used: EtOAc. Amount of **3 ca** obtained: 66.9 mg (55% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.33–7.29 (m, 4H), 7.26–7.14 (m, 19H), 2.27 (d, J = 4.9 Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.7 (CO), 135.9 (C), 135.5 (C), 132.8 (C), 129.6 (C), 129.5 (CH), 129.3 (C), 129.0 (CH), 127.4 (CH), 126.9 (CH), 126.5 (CH), 126.2 (CH), 125.0 (C), 123.2 (CH), 122.3 (C), 119.9 (CH), 116.1 (C), 25.6 (CH_3). HRMS (APCI) calculated for $C_{42}H_{32}N_3O_2$ $[M+H]^+$: 610.2489, found 610.2490.

*Methyl 3,4,8,9-tetraphenylindolizino[6,5,4,3-ija]quinoline-1-carboxylate (**3 da**) and methyl 4,5-diphenylpyrrolo[1,2-a]quinoline-2-carboxylate (**4 da**):* Solvents used: Hex/DCM/EtOAc (9:0.5:0.5). Amount of **3 da** obtained: 48.8 mg (44% yield), yellow solid. R_f 0.5. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.42–7.27 (m, 19H), 7.25–7.20 (m, 4H), 7.18 (s, 1H), 3.20 (s, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 166.0 (CO), 138.4 (C), 137.4 (C), 137.1 (C), 136.6 (C), 134.4 (C), 131.9 (C), 131.3 (C), 131.2 (C), 131.1 (C), 130.7 (CH), 130.6 (CH), 130.2 (CH), 129.9 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.54 (CH), 127.46 (CH), 127.3 (CH), 127.12 (C), 127.06 (CH), 126.8 (CH), 126.6 (C), 126.2 (C), 126.0 (C), 124.1 (CH), 120.7 (CH), 120.5 (CH), 112.7 (C), 110.0 (CH), 51.5 (CH_3). HRMS (APCI) calculated for $C_{40}H_{28}NO_2$ $[M+H]^+$: 554.2115, found 554.2116. Amount of **4 da** obtained: 22.2 mg (29% yield), yellow solid. R_f 0.3. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 8.55 (d, $J = 1.7$ Hz, 1H), 8.05 (dd, $J = 8.3$, 1.2 Hz, 1H), 7.59 (ddd, $J = 8.4$, 7.1, 1.5 Hz, 1H), 7.46 (dd, $J = 8.2$, 1.4 Hz, 1H), 7.35–7.26 (m, 9H), 7.22–7.16 (m, 2H), 6.66 (d, $J = 1.7$ Hz, 1H), 3.92 (s, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 165.4 (CO), 137.0 (C), 136.9 (C), 132.5 (C), 132.3 (C), 131.3 (CH), 131.0 (C), 130.1 (CH), 129.9 (C), 128.4 (CH), 128.1 (CH), 127.9 (2xCH), 127.3 (CH), 127.0 (CH), 125.4 (C), 124.7 (CH), 119.2 (C), 116.1 (CH), 114.4 (CH), 105.2 (CH), 51.5 (CH_3). HRMS (APCI) calculated for $C_{26}H_{20}NO_2$ $[M+H]^+$: 378.1489, found 378.1501.

*Ethyl 2-methyl-3,4,8,9-tetraphenylindolizino[6,5,4,3-ija]quinoline-1-carboxylate (**3 ea**) and Ethyl 3-methyl-4,5-diphenylpyrrolo[1,2-a]quinoline-2-carboxylate (**4 ea**):* Solvents used: Hex/DCM (7:3). Amount of **3 ea** obtained: 18 mg (16% yield), yellow solid. R_f 0.6. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.37–7.26 (m, 12H), 7.26–7.17 (m, 10H), 7.11 (dd, $J = 7.8$, 1.1 Hz, 1H), 3.51 (q, $J = 7.1$ Hz, 2H), 1.82 (s, 3H), 1.00 (t, $J = 7.1$ Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 166.7 (CO), 137.8 (C), 137.5 (C), 137.3 (C), 137.2 (C), 132.9 (C), 132.22 (C), 132.19 (C), 131.6 (C), 130.71 (CH), 130.68 (CH), 130.5 (CH), 130.09 (CH), 130.07 (C), 128.4 (CH), 128.37 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 127.0 (2xCH), 126.9 (CH), 126.6 (C), 125.8 (C), 124.1 (C), 123.6 (CH), 123.4 (C), 119.9 (CH), 119.8 (CH), 117.8 (C), 114.5 (C), 60.7 (CH_2), 14.0 (CH_3), 11.1 (CH_3). HRMS (APCI) calculated for $C_{42}H_{32}NO_2$ $[M+H]^+$: 582.2428, found 582.2439. Amount of **4 ea** obtained: 19.1 mg (24% yield), yellow solid. R_f 0.4. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 8.51 (s, 1H), 7.99 (d, $J = 8.3$ Hz, 1H), 7.50 (ddd, $J = 8.5$, 5.2, 3.4 Hz, 1H), 7.28–7.06 (m, 12H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.78 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 165.5 (CO), 137.7 (C), 137.3 (C), 132.4 (C), 132.0 (C), 131.2 (CH), 130.4 (CH), 130.0 (C), 128.2 (CH), 127.8 (C), 127.77 (CH), 127.7 (CH), 127.6 (CH), 127.0 (CH), 126.7 (CH), 125.3 (C), 124.4 (CH), 118.5 (C), 116.3 (C), 116.1 (CH), 114.1 (CH), 59.8 (CH_2), 14.5 (CH_3), 11.2 (CH_3). HRMS (APCI) calculated for $C_{28}H_{24}NO_2$ $[M+H]^+$: 406.1802, found 406.1807.

*Diethyl 6-methyl-3,4,8,9-tetraphenylindolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (**3 fa**):* Solvents used: Hex/EtOAc (9:1). Amount of **3 fa** obtained: 62.5 mg (40% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.27–7.07 (m, 20H), 6.97 (s, 2H), 3.51 (q, $J = 7.1$ Hz, 4H), 2.25 (s, 3H), 0.93 (t, $J = 7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 165.0 (CO), 136.98 (C), 136.95 (C), 134.29 (C), 134.27 (C), 130.8 (C), 130.5 (CH), 130.1 (CH), 129.9 (C), 128.4 (CH), 127.7 (CH), 127.21 (CH), 127.18 (CH), 126.1 (C), 124.1 (C), 121.8 (CH), 114.2 (C), 61.0 (CH_2), 22.0 (CH_3), 13.8 (CH_3).

HRMS (APCI) calculated for $C_{45}H_{36}NO_4$ $[M+H]^+$: 654.2639, found 654.2657.

*Diethyl 6-methoxy-3,4,8,9-tetraphenylindolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 ga***):* Solvents used: Hex/DCM/EtOAc (8:1:1). Amount of **3 ga** obtained: 61.9 mg (46% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.30 (dd, $J=8.1$, 6.7 Hz, 4H), 7.26–7.13 (m, 16H), 6.77 (s, 2H), 3.61 (s, 3H), 3.57 (q, $J=7.1$ Hz, 4H), 0.99 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 165.0 (CO), 156.5 (C), 136.9 (C), 136.8 (C), 134.1 (C), 131.3 (C), 130.4 (CH), 130.1 (CH), 128.5 (CH), 127.7 (CH), 127.6 (C), 127.29 (CH), 127.27 (CH), 127.0 (C), 123.8 (C), 114.4 (C), 106.8 (CH), 61.0 (CH_2), 54.4 (CH_3), 13.8 (CH_3). HRMS (APCI) calculated for $C_{45}H_{36}NO_5$ $[M+H]^+$: 670.2588, found 670.2605.

*Diethyl 6-acetyl-3,4,8,9-tetraphenylindolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 ha***):* Solvents used: Hex/DCM/EtOAc (8:1:1). Amount of **3 ha** obtained: 76.5 mg (56% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.90 (s, 2H), 7.41–7.18 (m, 20H), 3.63 (q, $J=7.1$ Hz, 4H), 2.45 (s, 3H), 1.04 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 197.8 (CO), 164.7 (CO), 136.5 (C), 136.2 (C), 134.7 (C), 133.5 (C), 133.2 (C), 131.6 (C), 130.4 (CH), 130.1 (CH), 128.6 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 126.2 (C), 124.6 (C), 121.1 (CH), 115.3 (C), 61.2 (CH_2), 26.7 (CH_3), 13.8 (CH_3). HRMS (APCI) calculated for $C_{46}H_{36}NO_5$ $[M+H]^+$: 682.2588, found 682.2602.

*Diethyl 3,4,8,9-tetraphenyl-6-(trifluoromethyl) indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 ia***):* Solvents used: Hex/DCM/EtOAc (8:1:1). Amount of **3 ia** obtained: 83.8 mg (60% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.53 (s, 2H), 7.42–7.16 (m, 20H), 3.63 (q, $J=7.1$ Hz, 4H), 1.05 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.6 (CO), 136.3 (C), 135.9 (C), 134.2 (C), 132.6 (C), 132.1 (C), 130.3 (CH), 130.0 (CH), 128.7 (CH), 128.2 (C). 128.1 (C), 127.8 (CH), 127.7 (CH), 127.6 (CH), 126,7 (q, $J=32.4$ Hz, C), 126.5 (C), 124.4 (C), 124.1 (q, $J=272.8$ Hz, CF_3), 117.5 (q, $J=3.9$ Hz, CH), 115.5 (C), 61.3 (CH_2), 13.8 (CH_3). ^{19}F-NMR (471 MHz, $CDCl_3$) δ (ppm): −61.3. HRMS (APCI) calculated for $C_{45}H_{33}F_3NO_4$ $[M+H]^+$: 708.2356, found 708.2384.

*Diethyl 6-fluoro-3,4,8,9-tetraphenylindolizino[6,5,4,3-ija]quinoline-1,2-dicarboxylate (***3 ja***):* Solvents used: Hex/DCM/EtOAc (8:1:1). Amount of **3 ja** obtained: 95.8 mg (73% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.40–7.26 (m, 12H), 7.26–7.17 (m, 8H), 6.98 (d, $J=10.1$ Hz, 2H), 3.63 (q, $J=7.1$ Hz, 4H), 1.05 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.9 (CO), 159.8 (d, $J=241.2$ Hz, C), 136.7 (C), 136.5 (C), 134.1 (d, $J=3.6$ Hz, C), 132.1 (C), 130.5 (CH), 130.2 (CH), 128.8 (CH), 128.4 (C), 128.2 (d, $J=9.9$ Hz, C), 127.9 (CH), 127.7 (CH), 127.6 (CH), 124.1 (C), 115.1 (C), 107.7 (d, $J=26.3$ Hz, CH), 61.3 (CH_2), 13.9 (CH_3). ^{19}F-NMR (471 MHz, $CDCl_3$) δ (ppm): −114.10. HRMS (APCI) calculated for $C_{44}H_{33}FNO_4$ $[M+H]^+$: 658.2388, found 658.2390.

*Diethyl 6-chloro-3,4,8,9-tetraphenylindolizino[6,5,4,3-ija]quinoline-1,2-dicarboxylate (***3 ka***):* Reactants: diethyl 1-(4-(bromophenyl)-1H-pyrrole-3,4-dicarboxylate **1 k** (73.2 mg, 0.20 mmol, 1 eq), diphenylacetylene **2 a** (114.1 mg, 0.64 mmol, 3.2 eq). 96 mg of an inseparable mixture of **3 ba** and **3 ka** in a 5:1 ratio was obtained. *Second run: 110 °C, 24 h, ratio **3 ba**/**3 ka** obtained 2:1. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.42–7.26 (m, 17.48H), 7.26–7.17 (m, 9.90H), 3.63 (q, $J=7.1$ Hz, 4.79H), 1.05 (td, $J=7.1$, 2.4 Hz, 7.20H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) of **3 ba** δ (ppm): 165.0 (CO), 136.9 (2xC), 134.5 (C), 131.5 (C), 130.8 (C), 130.5 (CH), 130.1 (CH), 128.4 (CH), 127.7 (CH), 127.3 (CH), 127.2 (CH), 126.1 (C), 124.4 (CH), 124.3 (C), 121.3 (CH), 114.4 (C), 61.1 (CH_2), 13.8 (CH_3). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) of **3 ka** δ (ppm): 164.7 (CO), 136.5 (C), 136.1 (C), 133.5 (C), 132.5 (C), 131.9 (C), 130.4 (CH), 130.0 (CH), 128.7 (CH), 127.9 (C), 127.7 (CH), 127.6 (CH), 127.5 (CH), 124.1 (C), 123.3 (CH), 115,2 (C), 61.2 (CH_2), 13.8 (CH_3). HRMS (APCI) of **3 ka** calculated for $C_{44}H_{32}BrNO_4$ $[M]^+$: 717.1509, found 717.1500.

*Dimethyl 3,4,8,9-tetrakis (4-methoxyphenyl)indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 ab***):* Solvents used: Hex/EtOAc/DCM (7:2:1). Amount of **3 ab** obtained: 71.2 mg (49% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.35 (dd, $J=8.6$, 7.0 Hz, 1H), 7.28 (d, $J=1.0$ Hz, 2H), 7.12 (d, $J=8.6$ Hz, 4H), 7.07 (d, $J=8.6$ Hz, 4H), 6.91–6.84 (m, 4H), 6.82–6.73 (m, 4H), 3.83 (s, 6H), 3.79 (s, 6H), 3.23 (s, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.6 (CO), 157.54 (C), 157.51 (C), 133.4 (C), 130.6 (CH), 130.3 (C), 130.2 (CH), 129.6 (C), 128.5 (C), 128.1 (C), 125.5 (C), 123.9 (C), 123.3 (CH), 120.1 (CH), 112.9 (CH), 112.7 (C), 112.2 (CH), 54.2 ($2xCH_3$), 51.0 (CH_3). HRMS (APCI) calculated for $C_{46}H_{37}NO_8$ $[M]^+$: 731.2514, found 731.2509.

*Diethyl 3,4,8,9-tetrakis (4-(trifluoromethyl) phenyl) indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 bc***):* Solvents used: Hex/EtOAc gradient (95:5 to 85:15). Amount of **3 bc** obtained: 86.1 mg (47% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.62 (d, $J=7.9$ Hz, 4H), 7.51 (d, $J=7.9$ Hz, 4H), 7.42 (t, $J=8.0$ Hz, 1H), 7.34 (d, $J=7.9$ Hz, 4H), 7.29 (d, $J=7.9$ Hz, 4H), 7.20 (d, $J=8.0$ Hz, 2H), 3.59 (q, $J=7.1$ Hz, 4H), 1.00 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.3 (CO), 139.9 (C), 139.8 (C), 133.5 (C), 131.7 (C), 130.8 (CH), 130.5 (CH), 130.1 (q, $J=32.7$ Hz, C), 130.0 (q, $J=32.7$ Hz, C), 129.9 (C), 125.8 (q, $J=3.8$ Hz, CH), 125.4 (C), 125.1 (CH), 125.0 (q, $J=3.8$ Hz, CH), 123.9 (q, $J=272.2$ Hz, $2xCF_3$), 123.8 (C), 121.8 (CH), 115.0 (C), 61.4 (CH_2), 13.7 (CH_3). ^{19}F-NMR (471 MHz, $CDCl_3$) δ (ppm): −62.7, −62.8. HRMS (APCI) calculated for $C_{48}H_{29}F_{12}NO_4$ $[M]^+$: 911.1899, found 911.1908.

*Diethyl 3,4,8,9-tetrakis (3-methoxyphenyl) indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 bd***):* Solvents used: Hex/EtOAc (8:2). Amount of **3 bd** obtained: 64 mg (42% yield), yellow solid. ^{1}H-NMR (500 MHz, mm_$C_2D_2Cl_4$) δ (ppm): 7.36 (dd, $J=8.9$, 6.8 Hz, 1H), 7.30 (d, $J=8.5$ Hz, 2H), 7.24 (t, $J=7.9$ Hz, 2H), 7.12 (t, $J=7.9$ Hz, 2H), 6.79 (ddd, $J=35.6$, 8.3, 2.5 Hz, 12H), 3.69 (bs, 16H), 1.03 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, mm_$C_2D_2Cl_4$) δ (ppm): 164.7 (CO), 160.0 (C), 159.4 (C), 138.3 (C), 138.1 (C), 134.1 (C), 131.7 (C), 130.7 (C), 129.4 (CH), 128.6 (CH), 126.1 (C), 124.5 (CH), 124.2 (C), 123.1 (CH), 122.9 (CH), 121.4 (CH), 116.4 (CH), 115.9 (CH), 114.8 (C), 114.1 (CH), 113.7 (CH), 60.9 (CH_2), 55.5 (CH_3), 55.4 (CH_3), 13.8 (CH_3). HRMS (APCI) calculated for $C_{48}H_{42}NO_8$ $[M+H]^+$: 760.2905, found 760.2909.

*Diethyl 3,4,8,9-tetrakis(3-methoxyphenyl)indolizino[6,5,4,3-ija]quinoline-1,2-dicarboxylate (***3 be***):* Solvents used: Hex/EtOAc (1:1). Amount of **3 be** obtained: 80.5 mg (46% yield), yellow solid. ^{1}H-NMR (500 MHz, mm_$C_2D_2Cl_4$) δ (ppm): 7.35 (p, J = 5.0 Hz, 3H), 6.90–6.69 (m, 12H), 3.86 (s, 6H), 3.82 (s, 6H), 3.68 (bs, 16H), 1.03 (t, J = 7.1 Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, mm_$C_2D_2Cl_4$) δ (ppm): 164.9 (CO), 149.9 (C), 149.2 (C), 148.94 (C), 148.90 (C), 134.1 (C), 131.7 (C), 130.7 (C), 130.2 (C), 130.0 (C), 126.4 (C), 124.5 (CH), 124.4 (C), 123.3 (CH), 122.9 (CH), 121.1 (CH), 115.7 (CH), 115.4 (CH), 114.7 (C), 112.9 (CH), 112.2 (CH), 61.0 (CH_2), 56.5 (2xCH_3), 56.4 (CH_3), 56.3 (CH_3), 13.8 (CH_3). HRMS (APCI) calculated for $C_{52}H_{50}NO_{12}$ $[M+H]^+$: 880.3328, found 880.3352.

*Diethyl 3,4,8,9-tetrakis (4-bromophenyl) indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 bf***):* Solvents used: Hex/EtOAc/DCM (8:1:1). Amount of **3 bf** obtained: 96.8 mg (68% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.38 (dd, J = 8.3, 7.5 Hz, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.19–7.14 (m, 4H), 7.10 (ddt, J = 8.2, 5.1, 2.4 Hz, 4H), 7.07–7.00 (m, 4H), 6.97–6.89 (m, 4H), 3.69 (q, J = 7.1 Hz, 4H), 1.05 (t, J = 7.1 Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.7 (CO), 162.0 (d, J = 247.3 Hz, C), 161.9 (d, J = 247.3 Hz, C), 133.9 (C), 132.6 (d, J = 3.7 Hz, C), 132.4 (d, J = 3.7 Hz, C), 132.1 (d, J = 8.2 Hz, CH), 131.8 (d, J = 8.2 Hz, CH), 131.5 (C), 130.3 (C), 126.0 (C), 124.7 (CH), 124.3 (C), 121.4 (CH), 115.8 (d, J = 21.4 Hz, CH), 114.9 (d, J = 21.4 Hz, CH), 114.4 (C), 61.3 (CH_2), 13.9 (CH_3). ^{19}F-NMR (471 MHz, $CDCl_3$) δ (ppm): −113.94, −113.98. HRMS (APCI) calculated for $C_{44}H_{29}F_4NO_4$ $[M]^+$: 711.2027, found 711.2030.

*Diethyl 3,4,8,9-tetrakis (4-chlorophenyl) indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 bg***):* Solvents used: Hex/EtOAc/DCM (8:1:1). Amount of **3 bg** obtained: 60.4 mg (39% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.37 (dd, J = 8.4, 7.6 Hz, 1H), 7.34–7.31 (m, 4H), 7.24–7.19 (m, 6H), 7.16–7.10 (m, 4H), 7.10–7.05 (m, 4H), 3.68 (q, J = 7.1 Hz, 4H), 1.05 (t, J = 7.1 Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.6 (CO), 134.9 (C), 134.8 (C), 133.64 (2xC), 133.55 (C), 131.8 (CH), 131.5 (C), 131.4 (CH), 130.0 (C), 129.1 (CH), 128.2 (CH), 125.8 (C), 124.8 (CH), 124.1 (C), 121.5 (CH), 114.6 (C), 61.4 (CH_2), 13.8 (CH_3). HRMS (APCI) calculated for $C_{44}H_{29}Cl_4NO_4$ $[M]^+$: 775.0845, found 775.0842.

*Diethyl 3,4,8,9-tetrakis (4-bromophenyl) indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***3 bh***):* Solvents used: Hex/EtOAc/DCM (9:0.5:0.5). Amount of **3 bh** obtained: 36.5 mg (19% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.51–7.45 (m, 4H), 7.39–7.35 (m, 5H), 7.21 (d, J = 8.0 Hz, 2H), 7.11–7.03 (m, 4H), 7.03–6.99 (m, 4H), 3.67 (q, J = 7.1 Hz, 4H), 1.05 (t, J = 7.2 Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.6 (CO), 135.3 (C), 135.2 (C), 133.4 (C), 132.05 (CH), 132.04 (CH), 131.7 (CH), 131.5 (C), 131.2 (CH), 129.9 (C), 125.7 (C), 124.8 (CH), 123.9 (C), 121.9 (C), 121.8 (C), 121.5 (CH), 114.7 (C), 61.4 (CH_2), 13.8 (CH_3). HRMS (APCI) calculated for $C_{44}H_{29}Br_4NO_4$ $[M]^+$: 950.8825, found 950.8818.

*Diethyl 3,9-bis (4-(diphenylamino) phenyl)-4,8-diphenylindolizino [6,5,4,3-ija]quinoline-1,2-dicarboxylate (***3 bi***)*: Solvents used: Hex/DCM/EtOAc (9:0.5:0.5). Amount of **3 bi** obtained: 34.9 mg (18% yield), yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.47–7.26 (m, 9H), 7.26–7.15 (m, 12H), 7.09–6.95 (m, 18H), 6.93–6.86 (m, 2H), 3.83 (q, J = 7.1 Hz, 2H), 3.61 (q, J = 7.1 Hz, 2H), 1.11 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H). ^{13}C-NMR, DEPT δ (ppm): 165.1 (CO), 164.9 (CO), 147.7 (C), 147.7 (C), 146.8 (C), 146.7 (C), 137.2 (C), 137.1 (C), 134.7 (C), 134.4 (C), 131.6 (C), 131.5 (C), 131.5 (CH), 131.1 (CH), 131.1 (C), 130.7 (CH), 130.7 (C), 130.3 (CH), 129.2 (CH), 129.1 (CH), 128.4 (CH), 127.7 (CH), 127.2 (CH), 127.1 (CH), 126.1 (C), 126.1 (C), 124.6 (C), 124.4 (CH), 124.4 (C), 124.1 (CH), 124.0 (CH), 123.96 (CH), 123.6 (CH), 122.8 (CH), 122.7 (CH), 121.22 (CH), 121.2 (CH), 114.2 (C), 114.1 (C), 61.1 (CH_2), 61.0 (CH_2), 14.1 (CH_3), 13.9 (CH_3). HRMS (APCI) calculated for $C_{68}H_{51}N_3O_4$ $[M]^+$: 973.3874, found 973.3874.

*Synthesis of diethyl 4,5-bis (4-(trifluoromethyl) phenyl) pyrrolo [1,2-a] quinoline-2,3-dicarboxylate (***4 bc***):* A sealed tube equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (12.4 mg, 0.02 mmol, 5 mol%), diethyl 1-phenyl-pyrrole-3,4-dicarboxylate **1 b** (114.9 mg, 0.40 mmol, 1 eq), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne **2 c** (276.5 mg, 0.88 mmol, 2.2 eq), $Cu(OAc)_2xH_2O$ (95.8 mg, 0.48 mmol, 1.2 eq) and toluene (1 mL). The suspension was heated at 110 °C for 24 h under an Argon atmosphere. The reaction mixture was quenched with NaCl(aq) solution and extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using a gradient of Hex/EtOAc (95:5 to 85:15) as eluent to afford **4 bc** (57.3 mg, 24% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 8.52 (s, 1H), 8.06 (dd, J = 8.5, 1.1 Hz, 1H), 7.64 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.35 (ddd, J = 8.3, 7.2, 1.1 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.24–7.20 (m, 3H), 4.33 (q, J = 7.1 Hz, 2H), 3.55 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.07 (t, J = 7.1 Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 165.6 (CO), 163.3 (CO), 140.1 (C), 139.1 (C), 131.9 (C), 131.7 (C), 131.2 (CH), 131.0 (CH), 130.0 (q, J = 32.7 Hz, C), 129.8 (q, J = 32.7 Hz, C), 129.4 (CH), 129.2 (C), 128.2 (CH), 127.6 (C), 125.6 (CH), 125.1 (q, J = 3.7 Hz, CH), 124.7 (q, J = 3.7 Hz, CH), 124.1 (C), 123.9 (q, J = 272.4 Hz, CF_3), 123.8 (q, J = 272.4 Hz, CF_3), 118.5 (C), 116.4 (CH), 114.8 (CH), 113.1 (C), 61.3 (CH_2), 60.7 (CH_2), 14.3 (CH_3), 13.6 (CH_3). ^{19}F-NMR (471 MHz, $CDCl_3$) δ (ppm): −62.67, −62.85. HRMS (APCI) calculated for $C_{32}H_{23}F_6NO_4$ $[M+H]^+$: 599.1526, found 599.1526.

*Synthesis of diethyl 3,4-bis (4-methoxyphenyl)-8,9-bis (4-(trifluoromethyl) phenyl)indolizino [6,5,4,3-ija]quinoline-1,2-dicarboxylate (***3 bbc***):* A sealed tube equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 5 mol%), diethyl 4,5-bis(4-(trifluoromethyl)phenyl)pyrrolo[1,2-a]quinoline-2,3-dicarboxylate **4 bc** (60 mg, 0.10 mmol, 1 eq), 1,2-bis(4-methoxyphenyl)ethyne **2 b** (38.1 mg, 0.16 mmol, 1.6 eq), $Cu(OAc)_2xH_2O$ (24 mg, 0.12 mmol, 1.2 eq) and toluene (0.5 mL). The suspension was heated at 135 °C for 72 h under an Argon atmosphere. The reaction mixture was extracted with NaCl(aq) solution and DCM (3x). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using Hex/EtOAc (85:15) as eluent to afford **3 bbc** (26.4 mg, 32% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.62–7.58 (m, 2H), 7.51–7.48 (m, 2H), 7.38–7.31 (m, 4H), 7.30–7.27 (m, 2H), 7.14–7.09 (m, 3H), 7.08–7.04 (m, 2H), 6.89–6.84 (m, 2H), 6.78–6.74 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.65 (q, $J=7.1$ Hz, 2H), 3.58 (q, $J=7.1$ Hz, 2H), 1.04 (t, $J=7.1$ Hz, 3H), 0.99 (t, $J=7.1$ Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, CDCl$_3$) δ (ppm): 165.0 (CO), 164.5 (CO), 158.75 (C), 158.67 (C), 140.4 (C), 134.6 (C), 133.1 (C), 131.5 (CH), 131.2 (CH), 131.0 (CH), 130.9 (C), 130.5 (CH), 129.9 (q, $J=32.9$ Hz, C), 129.8 (q, $J=32.9$ Hz, C), 129.6 (C), 129.0 (C), 128.8 (C), 127.2 (C), 126.7 (C), 125.7 (q, $J=3.7$ Hz, CH), 125.3 (C), 125.0 (C), 124.9 (q, $J=3.7$ Hz, CH), 124.7 (CH), 123.9 (q, $J=273.0$ Hz, 2xCF$_3$), 123.4 (C), 122.9 (C), 122.0 (CH), 120.8 (CH), 115.0 (C), 114.1 (C), 114.0 (CH), 113.3 (CH), 61.4 (CH$_2$), 61.2 (CH$_2$), 55.2 (2xCH$_3$), 13.80 (CH$_3$), 13.77 (CH$_3$). ^{19}F-NMR (471 MHz, CDCl$_3$) δ (ppm): −62.64, −62.75. HRMS (APCI) calculated for $C_{48}H_{35}F_6NO_6$ [M]$^+$: 835.2363, found 835.2365.

Derivatizations

*Synthesis of diethyl 5-bromo-3,4,8,9-tetraphenylindolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (**5**):* A 0.1 M solution of NBS (64.1 mg, 0.36 mmol, 1.2 eq) in CHCl$_3$ (3.6 mL) was added dropwise to a solution of **3ba** (191.9 mg, 0.30 mmol, 1 eq) in CHCl$_3$ (4.5 mL) under an Argon atmosphere. The mixture was stirred for 40 h at 4 °C in a cooled room. After addition of a portion of silica gel the mixture was concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using Hex/EtOAc/DCM (9:0.5:0.5) as eluent to afford the monobromo ullazine **5** (168,4 mg, 78% yield) as a dark yellow solid. ^{1}H-NMR (500 MHz, CDCl$_3$) δ (ppm): 7.73 (d, $J=8.6$ Hz, 1H), 7.41–7.26 (m, 6H), 7.26–7.13 (m, 15H), 3.63 (dq, $J=8.4$, 7.1 Hz, 4H), 1.09 (t, $J=7.1$ Hz, 3H), 1.04 (t, $J=7.1$ Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, CDCl$_3$) δ (ppm): 164.8 (CO), 164.5 (CO), 137.7 (C), 136.7 (C), 136.6 (C), 136.2 (C), 134.5 (C), 134.0 (C), 133.4 (C), 133.2 (C), 132.5 (CH), 132.1 (CH), 130.9 (C), 130.54 (CH), 130.48 (CH), 130.0 (CH), 128.6 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 127.34 (CH), 127.29 (CH), 127.1 (CH), 127.06 (CH), 126.0 (C), 125.1 (C), 123.8 (C), 123.3 (C), 122.0 (CH), 115.3 (C), 114.59 (C), 114.55 (C), 61.3 (CH$_2$), 61.1 (CH$_2$), 13.81 (CH$_3$), 13.78 (CH$_3$). HRMS (APCI) calculated for $C_{44}H_{33}BrNO_4$ [M+H]$^+$: 718.1587, found 718.1601.

*Synthesis of diethyl 5,7-dibromo-3,4,8,9-tetraphenylindolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (**6**):* A 0.1 M solution of NBS (810.1 mg, 4.551 mmol, 4 eq) in CHCl$_3$ (23 mL) was added dropwise to a solution of **3ba** (696.0 mg, 1.0 mmol, 1 eq) in CHCl$_3$ (16.2 mL) under an Argon atmosphere. The mixture was stirred for 24 h at 4 °C in a cooled room. After addition of a portion of silica gel the mixture was concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using Hex/EtOAc/DCM (8:1:1) as eluent to afford the dibromo ullazine **6** (773.0 mg, 89% yield) as a dark yellow solid. ^{1}H-NMR (500 MHz, CDCl$_3$) δ (ppm): 8.10 (s, 1H), 7.20–7.11 (m, 17H), 7.09–7.05 (m, 3H), 3.55 (q, $J=7.1$ Hz, 4H), 1.00 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, CDCl$_3$) δ (ppm): 164.3 (CO), 139.3 (CH), 137.4 (C), 136.0 (C), 134.6 (C), 134.0 (C), 133.4 (C), 132.1 (CH), 130.5 (CH), 127.42 (CH), 127.37 (CH), 127.23 (CH), 127.18 (CH), 124.6 (C), 123.3 (C), 115.5 (C), 114.4 (C), 61.3 (CH$_2$), 13.8 (CH$_3$).HRMS (APCI) calculated for $C_{44}H_{31}Br_2NO_4$ [M]$^+$: 795.0614, found 795.0607.

General Procedure for Sonogashira Coupling of 5 and 3ba/3ka with 2-Ethynylthiophene

Diethylamine (0.23 mL, 2.2 mmol, 22 eq) and DMF (0.4 mL) were introduced in a dry 10 mL microwave vial. The vial was cooled at 0 °C (ice bath) and then degassed by argon bubbling for 30 minutes. The corresponding bromoullazine **5** (71.9 mg, 0.1 mmol, 1 eq) or 220 mg of a 2/1 mixture of **3ba**/**3ka**, PdCl$_2$(PPh$_3$)$_2$ (3.5 mg, 5.0 μmol, 5 mol%), CuI (1.0 mg, 5.0 μmol, 5 mol%), triphenylphosphine (4.2 mg, 0.016 mmol, 0.16 eq) and 2-ethynylthiophene (0.012 mL, 0.120 mmol, 1.2 eq) were introduced and the reaction vessel was sealed with a teflon cap. After microwave irradiation the temperature being ramped to 120 °C and heated during 25 minutes. The mixture was then allowed to reach room temperature and diluted with DCM and extracted with NaCl$_{(aq)}$. The combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using the appropriate mixture of solvents to afford the cross-coupling products.

*Diethyl 3,4,8,9-tetraphenyl-5-(thiophen-2-ylethynyl) indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (**7**):* Solvents used: Hex/EtOAc (9:1). Amount of **7** obtained: 40.0 mg (54% yield), dark orange solid. ^{1}H-NMR (500 MHz, CDCl$_3$) δ (ppm): 7.63 (d, $J=8.5$ Hz, 1H), 7.36 (dd, $J=8.0$, 6.5 Hz, 2H), 7.33–7.27 (m, 1H), 7.25–7.16 (m, 19H), 6.88 (dd, $J=5.2$, 3.6 Hz, 1H), 6.83 (dd, $J=3.7$, 1.1 Hz, 1H), 3.60 (qd, $J=7.1$, 3.7 Hz, 4H), 1.05 (t, $J=7.1$ Hz, 3H), 1.02 (t, $J=7.1$ Hz, 3H). ^{13}C-NMR, DEPT (125 MHz, CDCl$_3$) δ (ppm): 164.8 (CO), 164.7 (CO), 137.5 (C), 136.8 (C), 136.6 (C), 136.4 (C), 134.64 (C), 134.60 (C), 132.9 (C), 132.7 (CH), 132.4 (CH), 132.2 (C), 131.6 (CH), 131.4 (C), 130.5 (CH), 130.4 (CH), 130.1 (CH), 128.6 (CH), 128.0 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 126.6 (CH), 126.3 (C), 125.0 (C), 124.9 (C), 124.2 (C), 123.7 (C), 120.9 (CH), 115.2 (C), 115.1 (C), 114.8 (C), 93.1 (C), 91.8 (C), 61.2 (CH$_2$), 61.1 (CH$_2$), 13.83 (CH$_3$), 13.81 (CH$_3$).HRMS (APCI) calculated for $C_{50}H_{36}NO_4S$ [M+H]$^+$: 746.2360, found 746.2358.

*Diethyl 3,4,8,9-tetraphenyl-6-(thiophen-2-ylethynyl) indolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (**9**):* Solvents used: Hex/EtOAc (9:1). Amount of **9** obtained: 28.4 mg (38% yield), yellow solid. ^{1}H-NMR (500 MHz, CDCl$_3$) δ (ppm): 7.45 (s, 2H), 7.43–7.18 (m, 22H), 7.00 (dd, $J=5.1$, 3.7 Hz, 1H), 3.63 (q, $J=7.1$ Hz, 4H), 1.05 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, CDCl$_3$) δ (ppm): 164.8 (CO), 136.6 (C), 136.4 (C), 133.9 (C), 132.2 (CH), 131.6 (C), 131.0 (C), 130.5 (CH), 130.1 (CH), 128.6 (CH), 127.7 (CH), 127.5 (CH), 127.4 (2xCH), 127.0 (CH), 126.3 (C), 124.3 (C), 124.0 (CH), 122.9 (C), 119.1 (C), 115.0 (C), 93.2 (C), 82.5 (C), 61.2 (CH$_2$), 13.8 (CH$_3$). HRMS (APCI) calculated for $C_{50}H_{35}NO_4S$ [M]$^+$: 745.2281, found 745.2308.

*Synthesis of diethyl 3,4,8,9-tetraphenyl-5,7-bis(thiophen-2-ylethynyl)indolizino[6,5,4,3-ija]quinoline-1,2-dicarboxylate (**8**):* Diethylamine (0.6 mL, 5.8 mmol, 58 eq) and DMF (1.4 mL) were introduced in a 10 mL microwave vial. The vial was cooled at 0 °C (ice bath) and then degassed by argon bubbling for 30 minutes. 5,7-dibromoullazine **6** (79.8 mg, 0.1 mmol, 1 eq), PdCl$_2$(PPh$_3$)$_2$ (4.0 mg, 0.02.0 mmol, 0.2 eq), CuI (3.8 mg, 0.02.0 mmol, 0.2 eq), triphenylphosphine (10.5 mg, 0.04 mmol, 0.4 eq) and 2-thiopheneacetylene (0.025 mL, 0.25 mmol, 2.5

eq) were introduced and the reaction vessel was sealed with a teflon cap. After microwave irradiation the temperature being ramped to 120 °C and heated during 25 minutes. The mixture was then allowed to reach room temperature and diluted with DCM and extracted with $NaCl_{(aq)}$. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by column chromatography through a silica gel pad using Hex/EtOAc/DCM (8:1:1) as eluent to afford 5,7-bis(thiophen-2-ylethynyl) ullazine **8** (60.0 mg, 70% yield) as a red solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.93 (s, 1H), 7.25–7.12 (m, 22H), 6.87 (dd, $J=5.2$, 3.6 Hz, 2H), 6.84 (dd, $J=3.6$, 1.2 Hz, 2H), 3.56 (q, $J=7.1$ Hz, 4H), 1.01 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.5 (CO), 140.4 (CH), 137.3 (C), 136.2 (C), 134.7 (C), 133.3 (C), 133.2 (C), 132.6 (CH), 131.6 (CH), 130.4 (CH), 128.1 (CH), 127.4 (CH), 127.3 (2xCH), 127.2 (CH), 126.6 (CH), 124.9 (C), 124.8 (C), 123.5 (C), 115.5 (C), 115.1 (C), 92.2 (C), 92.1 (C), 61.3 (CH_2), 13.8 (CH_3). HRMS (APCI) calculated for $C_{56}H_{38}NO_4S_2$ $[M+H]^+$: 852.2237, found 852.2212.

*Synthesis of diethyl 5,7-bis 4-(bis (4-methoxyphenyl) amino) phenyl)-3,4,8,9-tetraphenylindolizino [6,5,4,3-ija] quinoline-1,2-dicarboxylate (***10***):* A solution of 5,7-dibromoullazine 6 (239.3 mg, 0.3 mmol, 1 eq), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*,*N*-bis(4-methoxyphenyl)aniline (323.5 mg, 0.75 mmol, 2.5 eq) and $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 0.1 eq) in dry DMF (15.0 mL) under Argon atmosphere was prepared in a 100 mL round-bottomed flask. After degassing the mixture for 30 min, K_3PO_4 (764.2 mg, 3.6 mmol, 12 eq) was added in one portion and the reaction heated at 100 °C overnight. Once the reaction mixture reached room temperature was quenched with H_2O (20 mL). The resulting precipitate was filtered off and sequentially washed with H_2O (10 mL) and MeOH (10 mL). Then, the precipitate was redissolved in DCM, the solvent removed under reduced pressure. The resulting crude residue was purified by flash chromatography through a silica gel pad using Hex/EtOAc/DCM (7:2:1) as eluent to afford the triarylamino ullazine 10 (306.9 mg, 82% yield) as an orange solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.31 (s, 1H), 7.18–7.07 (m, 10H), 6.97–6.86 (m, 10H), 6.85–6.78 (m, 16H), 6.77–6.73 (m, 4H), 6.56–6.51 (m, 4H), 3.79 (s, 12H), 3.56 (q, $J=7.1$ Hz, 4H), 1.00 (t, $J=7.1$ Hz, 6H). ^{13}C-NMR, DEPT (125 MHz, $CDCl_3$) δ (ppm): 164.9 (CO), 155.5 (C), 146.7 (C), 141.3 (C), 139.0 (C), 136.8 (C), 135.8 (C), 135.3 (C), 134.32 (C), 134.27 (C), 133.9 (CH), 132.6 (C), 131.8 (CH), 130.8 (CH), 130.2 (CH), 127.2 (CH), 127.0 (CH), 126.8 (CH), 125.9 (CH), 125.7 (CH), 125.0 (C), 122.5 (C), 120.7 (CH), 114.5 (CH), 114.3 (C), 61.0 (CH_2), 55.5 (CH_3), 13.8 (CH_3). HRMS (APCI) calculated for $C_{84}H_{67}N_3O_8$ $[M]^+$: 1245.4923, found 1245.4908.

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[17] 3-Monoakyl- and 3,4-dialkyl substituted *N*-arylpyrroles gave complex mixtures in which only traces of the corresponding single annulated products were observed.

[18] However, aliphatic alkynes failed to react.

[19] Deposition numbers 2301671 (for **3ca$_{5\text{-Cl}}$**), 2301672 (for **3aa**), and 2301673 (for **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service (http://www.ccdc.cam.ac.uk/structures).

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