

Post-Cycloaddition–Retroelectrocyclization Transformations of Polycyanobutadienes

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The thermal [2+2] cycloaddition–retroelectrocyclization (CA-RE) reaction between a range of alkynes, activated by electron-donating anilino (p-H₂NC₆H₄-) substituents, and the electron-deficient olefins tetracyanoethene (TCNE) and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) delivered anilino-substituted polycyanobutadienes (PCBDs). The aniline NH₂ groups provide a convenient handle for further transformations, yielding a new series of PCBDs without an electron-

donating group. Electrochemical investigations by rotating disk voltammetry and cyclic voltammetry revealed large anodic shifts in both the first and second reduction potentials as a result of the removal of the electron-donating functionality. This methodology allows for PCBD-containing substrates to be further elaborated, generating a new family of chromophores previously inaccessible by alternative synthetic methods.

Introduction

The click-type cycloaddition–retroelectrocyclization (CA-RE) reaction between electron-rich alkynes^[1] and tetra-,^[2] tri-,^[3] and dicyanoethenes^[3a,4] has been employed extensively in the rapid, high-yielding formation of polycy-anobutadienes (PCBDs; Scheme 1).^[5] In addition to intense intramolecular charge-transfer bands and high third-order nonlinear optical susceptibilities,^[6] members of this family of molecules possess exceptional, strongly anodically shifted electrochemical reduction potentials, despite the presence of the electron-donating group required to facilitate the CA-RE reaction. Such properties rank these easily assembled, thermally stable, cyano-based acceptors along-side state-of-the-art p-type dopants, and highlight their

potential application in optoelectronic devices such as organic light-emitting diodes and solar cells.^[7]

Previous reports on the chemical modification of the PCBD units resulting from the CA-RE reaction were limited to the spontaneous rearrangement of the cyanovinyl moiety,^[8] and no systematic studies into the chemical reactivity of this class of substrates have been carried out. As we have previously shown that PCBDs bearing weaker electron donors possess anodically shifted reduction potentials,^[2b] we became interested in developing a methodology by which the electron-donating group could be transformed into other functionalities after the CA-RE reaction. Such a strategy would enable us to systematically study the effect



Scheme 1. CA-RE reaction (EDG = electron-donating group).

of substituents on the properties of PCBDs and hence facilitate the rational design of novel, strong electron acceptors.

Herein, we report that the use of anilines 1-3 (see Table 1) as donors in the CA-RE reaction yields PCBDs 4-7 in which the anilino moiety is a platform for subsequent derivatization. For the first time, we have been able to synthesize a range of PCBDs 8-16 that lack an electron-donating group and investigate their physical properties. Further-

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more, we demonstrate that the new, strongly electron-accepting PCBDs are stable to a range of reaction conditions,

allowing the construction of previously inaccessible chromophores.

Table 1. Summary of the synthesis and post-CA-RE reactivity of 4-7.



[a] In MeCN, 25 °C, 1 h. [b] In MeCN, 80 °C, 5 h. [c] 50% H₂SO₄, NaNO₂, 1 h, 0 °C, then H₂PO₃, 25 °C, 18 h. [d] 50% H₂SO₄, NaNO₂, 1 h, 0 °C, then urea, KI, 3 h. [e] NaBO₃·4H₂O, AcOH, 60 °C, 10 h. [f] *t*BuONO, THF, 60 °C, 1 h. [g] *t*BuONO, I₂, MeCN, 25 °C, 3 h. [h] *p*-Toluenesulfonic acid monohydrate, NaNO₂, H₂O, KI, MeCN, 10–15 °C, 30 min.

Results and Discussion

Synthesis

We have previously reported the use of unsubstituted anilino groups (p-H₂NC₆H₄-) as activators in the CA-RE reaction of acetylenes with tetracyanoethene (TCNE) in the synthesis of PCBD **6**.^[2c] Accordingly, anilines **1** and **2** were treated with TCNE in acetonitrile at 25 °C for 1 h to deliver CA-RE products **4** and **5** in yields of 78 and 62%, respectively (Table 1). Meanwhile, the addition of 7,7,8,8-tetracyanoquinodimethane (TCNQ) to aniline **1** required heating at 80 °C for 5 h to furnish **7** in 85% yield.

We then submitted tetracyanobutadiene (TCBD) **4** to diazotization followed by Sandmeyer-type reaction in 50% aqueous H_2SO_4 to access phenyl and iodophenyl derivatives **8** and **9** in yields of 48 and 74%, respectively.^[9] The nitrophenyl analogue **10** was prepared in moderate yield by oxidation of **4** with NaBO₃ in acetic acid at 60 °C.^[10]

In contrast, submission of **5** and **6** to these aqueous diazotization conditions led only to decomposition,^[11] and poor solubility prevented the application of this methodology to TCNQ adduct **7**. As a result, we sought alternative conditions: It was found that heating substrates **5**–**7** at 60 °C with *tert*-butyl nitrite in THF transformed the aniline group into phenyl derivatives **11**, **13**, and **15**, respectively, in yields of 42–55%.^[12] Meanwhile, the corresponding aryl iodides **12**, **14**, and **16** were formed in yields of 31–62% upon iodination in acetonitrile.^[13] Unfortunately, none of anilines **5**–**7** could be oxidized by using the conditions outlined above, presumably because of the competing acetolysis of electrophilic substrates **5** and **6**,^[14] and low oxidation chemoselectivity in the case of expanded TCNQ derivative **7**.



The PCBD derivatives resulting from the CA-RE reactions are susceptible to nucleophilic attack due to the electrophilicity of the dicyanovinyl units. We expected that the reactivity of this new class of PCBD derivatives towards nucleophiles would be heightened as they no longer have electron-donating groups to attenuate their electrophilicity. This was supported by DFT calculations in which the substrates lacking electron donors were predicted to have lower-energy LUMOs (see the Supporting Information). Our hypothesis was also confirmed experimentally by ¹H NMR studies, which showed complete decomposition of **9** after just 1 h in CD₃CN in the presence of *n*-butylamine, whereas **4** only decomposed slowly under these conditions, even upon heating at 60 °C (see the Supporting Information).

Despite their relative chemical instability, we realized that the aryl iodide substrates gave us an excellent opportunity to explore the derivatization of molecules bearing the 1,1,4,4-tetracyanobuta-1,3-dienyl (TCBD) core. We found that 9 readily undergoes Suzuki and Sonogashira cross-coupling reactions to deliver the novel push-pull chromophores 18 and 20 in yields of 69 and 80%, respectively (Scheme 2).^[15] A subsequent second CA-RE reaction of the electron-rich alkyne 20 with TCNQ delivered the new chromophore 21 featuring both TCBD and expanded TCNQ electron-accepting moieties.^[16] These reactions are notable, because they significantly broaden the scope of substrates accessible in the CA-RE reaction to chromophores that are impossible to access by using the standard CA-RE protocol and furthermore pave the way for the incorporation of this versatile motif into more complex molecular architectures.



Scheme 2. Post-CA-RE transformations of aryl iodide 9.

X-ray Crystal Structures

Crystals of 4, 9, 15, and 20 suitable for X-ray diffraction studies were prepared by slow diffusion of diethyl ether or pentane into MeCN, THF, and $CHCl_3$ (see Supporting In-

formation), whereas **8** and **13** crystallized from CH₂Cl₂ and benzene, respectively (Figure 1). The PCBD units in each case are highly nonplanar, as previously reported,^[2a,2b] with a torsional angle θ between the two dicyanovinyl planes in the range 73–127° (Table 2). The corresponding torsional



Figure 1. ORTEP plots of **4**, **8**, **9**, **13**, **15**, and **20** with vibrational ellipsoids shown at the 50% probability level (T = 100 K). Arbitrary numbering. Selected bond lengths [Å] and torsional angles [°]: **4**: C16–C21 1.407(2), C16–C17 1.407(2), C17–C18 1.368(2), C18–C19 1.400(3), C19–C20 1.399(3), C20–C21 1.371(2), C2–C3–C4–C5 116.5(2); **8**: C3–C4 1.402(2), C3–C8 1.409(2), C4–C5 1.384(2), C5–C6 1.389(2), C6–C7 1.392(2), C7–C8 1.382(2), C2–C1–C1–C2 106.4(2); **9**: C9–C10 1.404(2), C9–C14, 1.400(2), C10–C11 1.391(2), C11–C12 1.396(2), C12–C13 1.388(2), C13–C14 1.385(2), C1–C2–C3–C4 –121.3(2); **13**: C11–C16 1.400(2), C11–C12 1.401(2), C12–C13 1.381(2), C13–C14 1.386(2), C14–C15 1.386(2), C15–C16 1.384(2), C1–C2–C3–C4 127.2(1); **15**, for one of the two different molecules in the unit cell: C12–C26 1.393(3), C26–C27 1.397(3), C27–C58 1.387(3), C47–C58 1.387(3), C47–C56 1.384(3), C12–C56 1.383(3), C14–C18 1.451(3), C11–C18 1.349(3), C1–C11 1.438(3), C1–C9 1.439(3), C9–C13 1.351(3), C13–C14 1.445(3), C14–C39–C44–C41 71.9(3); **20**: C4–C5 1.400(2), C5–C6 1.371(2), C6–C7 1.399(2), C9–C4 1.396(2), C4–C9 1.396(2), C8–C9 1.374(2), C12–C13 1.399(2), C12–C17 1.400(2), C13–C14 1.373(2), C14–C15 1.413(2), C15–C16 1.413(2), C16–C17 1.370(2), C1–C2–C3–C31 73.1(2). δr is the quinoid character of the ring, δr is 0 for benzene and 0.08–0.1 for fully quinoidal rings: $\delta r = \{[(a + a') - (b + b')]/2 + [(c + c') - (b + b')]/2\}/2$.

angle in the TCNQ adduct **15** is 72°, in accord with the value of 57° for the corresponding N,N-dimethylaniline derivative.^[4a]

Table 2	X-ray	data	analysis.
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	θ [°] ^[a]	$\delta r \ [\text{\AA}]^{[b]}$
4	116.5(2)	0.034(2)
8	106.4(2)	0.014(2)
9	121.3(2)	0.009(2)
13	127.2(1)	0.011(2)
15	71.9(3)	0.005(3) [0.097(3) for quinoid ring]
20	73.1(2)	0.035(2) (for both rings in spacer)

[a] θ = torsional angle between the two dicyanovinyl planes. [b] For definition, see caption to Figure 1.

We assessed the quinoidal character δr of the aromatic rings in each crystal structure (see caption to Figure 1 for definition) to analyze the extent of the ground-state donor– acceptor interactions for each substrate.^[17] Aniline-substituted intramolecular charge-transfer (ICT) adduct 4 has a δr value of 0.034(2), which is within the range of values previously reported for the corresponding dimethylaniline derivatives.^[2b] The expanded push–pull chromophore 20 also exhibits a δr value of 0.035(2) in both rings connecting the Me₂N donor to the TCBD acceptor, indicative of a ground-state charge-transfer interaction between the donor and acceptor moieties. Substrates 8, 9, 13, and 15, which lack electron-donating groups, have δr values of 0.01, which confirms that they have, as expected, no quinoidal character.

UV/Vis Spectroscopy

The UV/Vis spectra of the anilino-substituted PCBDs 4–7 feature intramolecular charge-transfer (ICT) absorptions in CH_2Cl_2 that are hypsochromically shifted relative to

those of the corresponding N,N-dimethylanilino substrates **22–25** (Table 3), which reflects the lower donating ability of the anilino relative to the N,N-dimethylanilino moiety.

Transformation of the anilino into phenyl, *p*-iodoaryl, or *p*-nitroaryl groups uniformly led to the disappearance of the ICT absorptions, leaving λ_{max} in the range 322–338 nm for TCNE adducts **8–10** (Figure 2) and 445–448 nm for TCNQ adducts **15** and **16**, respectively (see the Supporting Information).



Figure 2. UV/Vis spectra of 4 and 8–10 in CH_2Cl_2 at 25 °C. See the Supporting Information for the spectra of other novel PCBDs.

The novel chromophores 18 and 20, which result from the Sonogashira and Suzuki coupling reactions of aryl iodide 9, were compared with TCBD 22 to investigate how the introduction of the aryl and alkynyl linkers between the donor and acceptor affects the UV/Vis spectra. The introduction of the two different spacers has broadly the same

Table 3. UV/Vis data for ICT compounds in CH_2Cl_2 at a concentration of 10^{-5} M.

	$\lambda_{\max} \text{ [nm] } (E \text{ [eV]})$	$\varepsilon [\mathrm{M}^{-1}\mathrm{cm}^{-1}]$	
4	422 (2.94)	19500	
5	519 (2.39)	_[a]	
6 ^[2c]	542 (2.28)	3200	
7	575 (2.16)	26400	
18	508 (2.44)	13500	
20	486 (2.55)	13000	
21	630 (1.97)	19600	
22	470 (2.64)	23100	
23 ^[2b]	570 (2.18)	9500	
24 ^[2c]	643 (1.93)	3200	
25 ^[4a]	676 (1.84)	36300	

[a] Low solubility in CH₂Cl₂ prevented accurate determination of ε .



effect on the ICT absorption, λ_{max} is bathochromically shifted from 470 nm in **22** to 508 nm in **18** and 486 nm in **20**, whereas the molar extinction coefficient ε is reduced from 23100 to 13500 and 13000 M⁻¹ cm⁻¹, respectively. The shift to lower-energy and lower-intensity CT bands upon incorporation of additional linkers between the electron donor (D) and acceptor (A) in push–pull chromophores is indicative of weaker D–A coupling and has been observed previously.^[18] The UV/Vis spectrum of the double TCNE– TCNQ adduct **21** features λ_{max} at 630 nm, which is similar to the position of the CT band in the previously reported chromophore **25** ($\lambda_{\text{max}} = 676$ nm),^[4a] which indicates that the main ICT interaction is not significantly affected by the additional TCBD unit in the molecule.

In line with push–pull chromophores resulting previously from the CA-RE reaction, the longest-wavelength absorptions originating from ICT disappear completely on protonation with TFA, to be regenerated upon treatment with Et₃N.^[2b] Furthermore, these ICT substrates also exhibit positive solvatochromism in hexane/CH₂Cl₂ mixtures.^[2b,19] The most pronounced effect was observed with TCNQ adduct 7, which changed from $\lambda_{max} = 525$ nm in 95:5 hexane/ CH₂Cl₂ to $\lambda_{max} = 575$ nm in CH₂Cl₂, whereas the TCNE adducts 4, 5, 18, 20, and 22 exhibited shifts in λ_{max} in the range of 11–31 nm in the same solvents (see the Supporting Information).

Electrochemistry

The redox potentials of substrates 4–16, 18, and 20–22 were measured by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) against the ferricinium/ferrocene couple in CH_2Cl_2 with 0.1 M nBu_4NPF_6 as the electrolyte (Table 4). All of the substrates studied gave well-resolved, reversible, one-electron reductions for each dicvanovinyl moiety, and 10 also exhibited a reversible reduction centered on the nitro group. For the first time, we were able to systematically assess the influence of the electronic character of the substituents on the reduction potentials of arylated PCBDs (Figure 3) and, as expected, there is a strong positive correlation between the first reduction potential and the Hammett value of the *para* substituent σ_{p} .^[20] This delivers a 0.34 V anodic shift in the first reduction potential on moving from N,N-dimethylaniline-substituted TCBD 22 to nitro derivative 10. There is also a weaker positive correlation for the second reduction potentials (see the Supporting Information).

However, it is clear that the identity of the alkyne, and the cyanoolefin with which it reacts, is also of great importance in determining the reduction potentials of the resultant PCBDs. In line with previous observations, the first reductions of all the TCBD derivatives were shifted to more positive potentials by 0.18–0.23 V when the starting material for their synthesis was varied from internal diarylalkyne 1 to terminal alkyne 2.^[2b] The anodic shift of pentacyanobutadienes 6, 13, and 14, which result from the CA-RE of cyanoalkyne 3 and subsequent derivatization, was

Table 4. Cyclic voltammetry and rotating disk voltammetry data recorded in $CH_2Cl_2 + 0.1 \text{ M } nBu_4NPF_6$.^[a]

	CV		RDV		
	$E^{\circ} [V]^{[b]}$	$\Delta E_{\rm p} [{\rm mV}]^{[c]}$	$E_{\rm p} [V]^{[d]}$	$E_{1/2} [V]^{[e]}$	Slope [mV] ^[f]
4			+1.09	+1.05 (1e ⁻)	60
	-0.85	100		-0.87 (1e ⁻)	90
	-1.20	100		-1.27 (1e ⁻)	80
5			+1.05	$+1.03 (1e^{-})$	60
	-0.64	100		-0.64 (1e ⁻)	60
<[7]	-1.25	110		-1.32 (1e ⁻)	100
6 ^[8]	0.07	100	+1.14	0.07 (1)	60
	-0.27	100		$-0.2/(1e^{-})$	60
-	-0.86	100	10.50	-0.86 (1e)	65
1	0.65	80	+0.50	+0.52 (1e)	60 65
	-0.03	80		-0.00 (1e)	03
0	-0.78	125		-0.81 (1e)	70
0	-0.74	123		-0.70 (1e ⁻)	70
0	-1.10 -0.65	70		-0.67 (1e ⁻)	60
,	-1.10	70		-1.12 (1e ⁻)	60
10	-0.55	60		-0.55 (1e ⁻)	60
10	-0.99	75		-1.01 (1e ⁻)	70
	-1.71	70		-1.76 (1e ⁻)	65
11	-0.51	60		-0.49 (1e ⁻)	60
	-1.20	100		-1.26 (1e ⁻)	100
12	-0.47	80		-0.49 (1e ⁻)	60
	-1.14	90		-1.18 (1e ⁻)	70
13	-0.16	80		-0.16 (1e ⁻)	60
	-0.81	95		-0.85 (1e ⁻)	75
14	-0.07	60		–0.07 (1e [–])	60
	-0.74	70		–0.75 (1e [–])	70
15	-0.54	70		-0.56 (1e ⁻)	60
	-0.68	65		$-0.70 (1e^{-})$	70
16	-0.53	70		-0.55 (1e ⁻)	60
10	-0.67	70		-0.69 (1e ⁻)	60
18	+0.48	60		$+0.50 (1e^{-})$	60
	-0./5	65		-0.//(1e)	65
20	-1.13	00	+0.50	-1.13 (1e) ± 0.48 (1e ⁻)	60 50
20	0.67	70	+0.50	+0.46 (1c)	50
	_1.09	80		-0.07 (1c ⁻)	60
21	1.09	00	+0.45	$+0.46 (1e^{-})$	50
	-0.55	60	. 0.15	-0.54 (1e ⁻)	60
	-0.69	60		-0.68 (1e ⁻)	60
	-0.85	60		-0.84 (1e ⁻)	60
	-1.20	70		-1.20 (1e ⁻)	100
22	+0.92	70		+0.91 (1e ⁻)	60
	-0.89	70		-0.90 (1e ⁻)	60
	-1.22	80		-1.19 (1e ⁻)	65
23 ^[h]	+0.86	80		+0.87 (1e ⁻)	70
	-0.69	80		$-0.70 (1e^{-})$	70
• 4[m]	-1.26	80		-1.38 (1e ⁻)	140
24 ^[8]	+1.00	90		+1.00 (1e ⁻)	65
	-0.30	90		-0.30 (1e ⁻)	05
25 [i]	-0.83	100	+0.42	-0.83 (1e) ± 0.42 (1a)	100
43.1	_0.68	70	±0.42	$-0.67(1e^{-})$	50 60
	-0.08	70		-0.81 (1e ⁻)	60
	0.02	, .			00

[a] CV scan rate, $\nu = 0.1 \text{ V s}^{-1}$. All potentials are given vs. the ferricinium/ferrocene couple used as an internal standard. [b] $E^{\circ} = (E_{\rm pc} + E_{\rm pa})/2$, in which $E_{\rm pc}$ and $E_{\rm pa}$ correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_{\rm p} = E_{\rm ox} - E_{\rm red}$. [d] $E_{\rm p} = i$ rreversible peak potential. [e] $E_{1/2} =$ half-wave potential. [f] Logarithmic analysis of the wave obtained by plotting *E* vs. log[*I*/(*I*_{lim} – *I*)]. [g] Data taken from ref.^[2c] [h] Data taken from ref.^[2b] [i] Data



Figure 3. Relationship between the first reduction potential and the Hammett constant of the *para* substituent for different classes of PCBDs. The lines given are lines of best fit as calculated by Microsoft Excel. $\sigma_p(NMe_2) = -0.83$, $\sigma_p(NH_2) = -0.66$, $\sigma_p(H) = 0.00$, $\sigma_p(I) = 0.17$, and $\sigma_p(NO_2) = 0.78$.

uniformly shifted by 0.6 V relative to the corresponding TCBDs arising from the reactions of internal alkyne $1^{[2c]}$ Furthermore, changing from the TCNE to TCNQ adducts (compare **4**, **8**, **9**, and **22** with **7**, **15**, **16**, and **25**), also leads to a shift to more positive potentials of 0.12–0.21 V for the first reduction.^[4a] Different trends are apparent in the second reduction potentials, in which the substrates derived from terminal alkynes **5**, **11**, and **12** exhibit the cathodically most shifted reduction potentials in the range –1.14 to –1.25 V, whereas the TCNQ adducts **7**, **15**, and **16**, which are able to more effectively separate the two charges, are the anodically most shifted in the range –0.67 to –0.78 V.

In the series 18 and 20–22, the first reduction potentials are shifted from -0.89 V in the parent compound 22, to -0.75 and -0.67 upon insertion of the aryl (18) and aryl-ethynyl (20) spacers, respectively. This anodic shift corroborates earlier findings in suggesting that the extra linkers act to insulate the donor moiety from the acceptor, leading to a more electron-deficient, easily reduced acceptor.^[2b,18]

Only the aniline or dimethylaniline derivatives exhibit oxidations: aniline TCNE adducts **4**–6 give single-electron irreversible oxidations in the range ± 1.14 to ± 1.05 V, whereas the TCNQ adducts **7** and **21** are oxidized irreversibly at ± 0.50 and ± 0.45 V, respectively. In the series of novel chromophores assembled with cross-coupling chemistry, parent dimethylaniline **22** undergoes a reversible single-electron transfer at ± 0.92 V, whereas oxidation occurs at ± 0.48 and ± 0.50 V for homologated derivatives **18** and **20**, respectively. These observations reinforce the previous conclusions that weaker donor–acceptor coupling accompanies the incorporation of the aryl and arylethynyl linkers into the molecules.^[18]

Conclusions

We have developed protocols that allow, for the first time, the systematic chemical modification of the products of the CA-RE reaction. We then applied this methodology to the synthesis of a series of PCBDs not substituted with electron-donating groups. The properties of this novel class of substrates were investigated by X-ray diffraction, UV/Vis spectroscopy, and electrochemical methods. We observed an inverse correlation between the strength of the donor substituent and the reduction potentials of the substrates, which points the way towards the future design of even more powerful electron acceptors.

Furthermore, we have been able to demonstrate that aryl iodide derivatives provide a flexible platform for the further derivatization of PCBDs, allowing the synthesis of previously inaccessible push-pull chromophores. The current focus of our research is the development of further reaction conditions compatible with the PCBD cores, and the application of these in the synthesis of complex molecular architectures.

Experimental Section

General: The procedures for the synthesis of **4**, **5**, and **7–22** are reported herein. 4-Ethynylaniline **2** is commercially available, and 4-(phenylethynyl)aniline (1),^[21] 3-(4-aminophenyl)buta-1,3-diene-1,1,2,4,4-pentacarbonitrile (6),^[2c] and *N*,*N*-dimethyl-4-(phenyl-ethynyl)aniline^[22] were prepared according to literature procedures. All other details can be found in the Supporting Information.

General Procedure (GPA) for the CA-RE Reaction with TCNE: Alkynylaniline and TCNE (1 equiv.) were dissolved in MeCN

(30 mL/mmol), and the resulting dark-red solution was stirred at 25 °C under Ar until TLC analysis indicated complete consumption of the starting material. The solvent was removed in a rotary evaporator under reduced pressure (in vacuo) and the residue purified by flash column chromatography (FC) on SiO₂.

General Procedure (GP B) for the CA-RE Reaction with TCNQ: Alkynylaniline and TCNQ (1 equiv.) were dissolved in MeCN (30 mL/mmol), and the resulting dark-green solution was stirred at the given temperature under Ar. Workup was carried out as in General Procedure A.

General Procedure (GP C) for the Transformation of Aniline Moieties into Phenyl Derivatives: A solution of the aniline derivative and *tert*-butyl nitrite (2 equiv.) in THF (10 mL/mmol) was heated at 60 °C under Ar. TLC analysis indicated that the reaction is normally complete within 1 h. The reaction was quenched by addition of 1 m Na₂S₂O₃ solution (10 mL/mmol) and the mixture extracted with CH₂Cl₂ (3×10 mL/mmol). The combined organic layers were dried with Na₂SO₄, filtered, and the solvents removed in vacuo, before purification by FC on SiO₂.

General Procedure (GP D) for the Transformation of Anilines into Iodoaryl Derivatives: A solution of the aniline derivative in MeCN (5 mL/mmol) was added to a solution of *tert*-butyl nitrite (1.5 equiv.) and iodine (3 equiv.) in MeCN (10 mL/mmol), and the mixture was stirred at 25 °C under Ar. TLC analysis indicated that the reaction was normally complete within 3 h. The reaction was quenched by addition of a 1 M Na₂S₂O₃ solution (10 mL/mmol) and the mixture extracted with CH₂Cl₂ (3×10 mL/mmol). The combined organic layers were dried with Na₂SO₄, filtered, and the solvents removed in vacuo before purification by FC on SiO₂.

4: 4-(Phenylethynyl)aniline (1;^[21] 1.11 g, 5.73 mmol) was treated according to GPA. Purification by FC (SiO₂; $CH_2Cl_2 \rightarrow CH_2Cl_2/$ MeCN, 97:3) gave **4** as a red solid (1.44 g, 4.48 mmol, 78%). $R_{\rm f}$ = 0.2 (SiO₂, CH₂Cl₂). M.p. 219–222 °C. ¹H NMR (400 MHz, CD₃CN): δ = 5.64 (s, 2 H), 6.76 (d, J = 9.0 Hz, 2 H), 7.64–7.57 (m, 2 H), 7.73-7.67 (m, 1 H), 7.74 (d, J = 9.0 Hz, 2 H), 7.84-7.78(m, 2 H) ppm. ¹³C NMR (101 MHz, CD₃CN): δ = 75.92, 88.28, 111.77, 112.28, 113.60, 114.19, 114.28, 118.31, 129.45, 129.68, 131.94, 133.14, 134.22, 155.43, 163.96, 168.66 ppm. IR (neat): $\tilde{v} =$ 3482 (w), 3380 (m), 2219 (s), 1626 (s), 1602 (s), 1543 (m), 1525 (w), 1488 (s), 1451 (s), 1337 (s), 1301 (m), 1259 (s), 1198 (m), 1182 (s), 1028 (w), 999 (m), 965 (m), 882 (m), 834 (s) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 328 (13400), 422 nm (19500 m⁻¹ cm⁻¹). HRMS (ESI): calcd. for $C_{20}H_{12}N_5^+$ 322.1087; m/z (%) = 322.1089 (2) [MH]⁺, 217.1190 (100). C₂₀H₁₁N₅ (321.1014): calcd. C 74.76, H 3.45, N 21.79; found C 74.80, H 3.60, N 21.63.

5: Compound **2** (109 mg, 0.85 mmol) was treated according to GP A. FC (SiO₂; CH₂Cl₂ → CH₂Cl₂/MeCN, 97:3) gave **5** as a darkpurple solid (130 mg, 0.53 mmol, 62%). $R_{\rm f} = 0.17$ (SiO₂, CH₂Cl₂). M.p. 185–189 °C. ¹H NMR (400 MHz, CD₃CN): $\delta = 5.41$ (s, 2 H), 6.78 (d, J = 8.9 Hz, 2 H), 7.49 (d, J = 8.9 Hz, 2 H), 8.25 (s, 1 H) ppm. ¹³C NMR (101 MHz, CD₃CN): $\delta = 80.42$, 96.86, 109.76, 112.08, 112.97, 113.85, 114.04, 119.00, 132.69, 154.59, 157.29, 160.99 ppm. IR (neat): $\tilde{v} = 3473$ (w), 3353 (m), 3028 (m), 2214 (s), 1623 (s), 1607 (s), 1484 (s), 1452 (s), 1354 (s), 1338 (s), 1289 (s), 1179 (s), 993 (w), 826 (s) cm⁻¹. UV/Vis (CH₂Cl₂): $\lambda_{\rm max}$ (ε) = 308 (15800), 435 (5280), 519 nm (5700 м⁻¹ cm⁻¹).^[23] HRMS (EI): calcd. for C₁₄H₇N₅⁺ 245.0701; *m/z* (%) = 245.0696 (100) [M]⁺.

7: 4-(Phenylethynyl)aniline (1; 300 mg, 1.55 mmol) was treated according to GP B at 80 °C for 5 h. FC (SiO₂; CH₂Cl₂ \rightarrow CH₂Cl₂/MeCN 97:3) afforded 7 as a blue-black solid (521 mg, 1.31 mmol, 85%). $R_{\rm f} = 0.1$ (SiO₂, CH₂Cl₂). M.p. 130–132 °C. ¹H NMR

(400 MHz, CD₂Cl₂): δ = 4.44 (s, 2 H), 6.70 (d, *J* = 8.8 Hz, 2 H), 7.07 (dd, *J* = 9.7, 2.0 Hz, 1 H), 7.15–7.24 (m, 3 H), 7.28 (dd, *J* = 9.7, 2.0 Hz, 1 H), 7.45–7.52 (m, 3 H), 7.53–7.61 (m, 1 H), 7.60– 7.68 (m, 2 H) ppm. ¹³C NMR (101 MHz, CD₂Cl₂): δ = 74.18, 87.68, 112.34, 112.91, 114.12, 114.16, 114.88, 124.82, 125.43, 125.72, 129.49, 129.56, 132.95, 133.37, 134.23, 134.41, 134.60, 135.67, 150.97, 151.52, 154.11, 172.11 ppm. IR (neat): \tilde{v} = 3353 (w), 2200 (m), 1619 (w), 1580 (s), 1523 (m), 1445 (m), 1375 (m), 1323 (s), 1294 (s), 1255 (m), 1170 (s), 878 (m), 832 (s), 812 (s) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 317 (19600), 422 (13000), 575 nm (26400 m⁻¹ cm⁻¹). HRMS (ESI): calcd. for C₂₆H₁₆N₅⁺ 398.1400; *m/z* (%) = 398.1406 (100) [MH]⁺. C₂₆H₁₅N₅·CH₂Cl₂ (482.09): calcd. C 67.23, H 3.55, N 14.52; found C 67.33, H 3.73, N 14.27.

8: A 2 M solution of sodium nitrite (0.64 mL, 1.28 mmol) was added dropwise to a solution of 4 (200 mg, 0.624 mmol) in 50% aqueous H_2SO_4 (44 mL), while maintaining the temperature at 0 °C. After stirring at 0 °C for 1 h, a 50% aqueous solution of H₃PO₂ (0.572 mL, 5.93 mmol) was added dropwise, and the resulting yellow solution was warmed to 25 °C and stirred for 18 h, before being neutralized by the dropwise addition of a saturated solution of NaHCO₃. The resulting brown, heterogeneous mixture was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layers were separated, dried with Na₂SO₄, and filtered. The solvent was removed in vacuo and FC (SiO₂; hexane/CH₂Cl₂, 1:1 \rightarrow CH₂Cl₂) provided 8 as a cream solid (91 mg, 0.297 mmol, 48%).^[9a] $R_{\rm f} = 0.2$ (SiO₂, CH₂Cl₂). M.p. 232–235 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.54–7.62 (m, 4 H), 7.64–7.72 (m, 6 H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 87.86, 111.02, 111.46, 129.27, 130.14, 131.01, 134.69, 167.13 ppm. IR (neat): $\tilde{v} = 3057$ (w), 2207 (s), 1602 (m), 1539 (m), 1480 (w), 1420 (s), 1348 (w), 1312 (m), 1280 (m), 1247 (m), 1181 (s), 1093 (w), 1079 (m), 1027 (w), 998 (m), 914 (w), 835 (s), 808 (m) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 322 nm $(13200 \text{ m}^{-1} \text{ cm}^{-1})$. HRMS (MALDI-TOF, 3-HPA): calcd. for $C_{20}H_{10}N_4^+$ 306.0900; *m*/*z* (%) = 306.0899 (1) [M]⁺, 233.0557 (100).

9: A 2 M solution of sodium nitrite (3.31 mL, 6.62 mmol) was added dropwise to a solution of 4 (1.00 g, 3.12 mmol) in 50% aqueous H₂SO₄ (218 mL), while maintaining the temperature at 0 °C. The resulting solution was stirred at 0 °C for 1 h before the addition of urea (210 mg, 3.50 mmol) in a single portion. The yellow solution was added dropwise, through a cannula, to a solution of KI (2.63 g, 15.8 mmol) in H₂O (218 mL), while maintaining the temperature of both solutions at 0 °C. The resulting brown, heterogeneous mixture was stirred at 0 °C for 3 h before extraction with CH_2Cl_2 (3×150 mL). A 1 M solution of $Na_2S_2O_3$ (30 mL) was added to the combined organic layers, which were subsequently separated, dried with Na₂SO₄, and filtered. The solvent was removed in vacuo, and FC (SiO₂; hexane/CH₂Cl₂, $1:1 \rightarrow CH_2Cl_2$) gave 9 as a yellow solid (990 mg, 2.30 mmol, 74%).^[9b] $R_{\rm f} = 0.76$ (SiO₂, CH₂Cl₂). M.p. 195–198 °C. ¹H NMR (400 MHz, CD₃CN): δ = 7.51 (d, J = 8.8 Hz, 2 H), 7.57–7.64 (m, 2 H), 7.66–7.73 (m, 1 H), 7.74–7.80 (m, 2 H), 7.98 (d, J = 8.8 Hz, 2 H) ppm. ¹³C NMR (101 MHz, CD₃CN): δ = 89.59, 89.67, 101.70, 111.46, 111.51, 111.85, 111.95, 129.58, 129.81, 130.78, 130.86, 131.28, 134.33, 139.07, 165.41, 165.88 ppm. IR (neat): $\tilde{v} = 2230$ (m), 1594 (w), 1577 (s), 1557 (m), 1482 (m), 1445 (m), 1397 (m), 1328 (w), 1305 (w), 1270 (w), 1247 (m), 1183 (m), 1062 (m), 1003 (s), 956 (w), 932 (w), 881 (w), 831 (s), 824 (m) cm⁻¹. UV/Vis (CH₂Cl₂); λ_{max} (ε) = 338 nm $(13700 \text{ m}^{-1} \text{ cm}^{-1})$. HRMS (ESI): calcd. for C₂₀H₁₀IN₄⁺ 432.9945; m/z (%) = 432.9949 (100) [MH]⁺. C₂₀H₉IN₄ (431.99): calcd. C 55.58, H 2.10, N 12.96, I 29.36; found C 55.82, H 2.29, N 12.86, I 29.12.

10: NaBO₃· $4H_2O$ (120 mg, 0.78 mmol) was added in a single portion to a suspension of **4** (50 mg, 0.156 mmol) in glacial acetic acid

(2 mL). The mixture was heated at 60 °C under Ar for 5 h before cooling to 25 °C. A further loading of NaBO₃·4H₂O (120 mg, 0.78 mmol) was added and the mixture heated at 60 °C under Ar for 5 h, by which time the solution had become light-yellow. The reaction was quenched by the addition of a 1 M Na₂S₂O₃ solution (2 mL), and the resulting mixture was extracted with CH₂Cl₂ $(3 \times 10 \text{ mL})$. The combined organic layers were dried with Na₂SO₄ and filtered. The solvents were removed in vacuo, and FC (SiO₂; hexane/CH₂Cl₂, 1:1 \rightarrow CH₂Cl₂) afforded 10 as a cream solid (25 mg, 0.071 mmol, 46%).^[10] $R_{\rm f} = 0.83$ (SiO₂, CH₂Cl₂). M.p. 168– 170 °C. ¹H NMR (400 MHz, C_6D_6): $\delta = 6.72$ (d, J = 8.9 Hz, 2 H), 6.78-6.85 (m, 2 H), 6.85-6.91 (m, 1 H), 6.97-7.02 (m, 2 H), 7.39 (d, J = 8.9 Hz, 2 H) ppm. ¹³C NMR (101 MHz, C₆D₆): $\delta = 88.82$, 91.43, 110.47, 110.64, 111.00, 111.21, 124.23, 128.74, 129.40, 129.61, 130.49, 133.98, 135.44, 149.62, 164.04, 164.95 ppm. IR (neat): $\tilde{v} = 3109$ (w), 2924 (w), 2231 (m), 1602 (m), 1523 (s), 1445 (m), 1406 (w), 1348 (s), 1327 (s), 1254 (m), 1181 (s), 1108 (m), 1012 (m), 1000 (m), 861 (s), 846 (s) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 338 nm (12500 M^{-1} cm⁻¹). HRMS (ESI): calcd. for C₂₀H₁₀N₅O₂⁺¹ $352.0829; m/z (\%) = 352.0838 (100) [MH]^+.$

11: Compound **5** (100 mg, 0.408 mmol) was treated according to GP C, and FC (SiO₂; hexane/CH₂Cl₂, 1:1 → CH₂Cl₂) delivered **11** as a pale-yellow solid (40 mg, 0.173 mmol, 42%). $R_{\rm f} = 0.55$ (SiO₂, CH₂Cl₂). M.p. 141–143 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.42$ (d, J = 7.0 Hz, 2 H), 7.59–7.66 (m, 2 H), 7.72 (ddt, J = 8.4, 7.0, 1.3 Hz, 1 H), 8.02 (s, 1 H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 93.31$, 98.14, 108.12, 110.51, 110.98, 111.73, 128.79, 129.77, 130.24, 133.92, 151.45, 162.33 ppm. IR (neat): $\tilde{v} = 3046$ (m), 2922 (w), 2233 (m), 1574 (w), 1542 (s), 1487 (m), 1445 (s), 1351 (m), 1330 (w), 1317 (w), 1179 (w), 1160 (w), 1074 (w), 1027 (w), 939 (w), 921 (s), 888 (w) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 357 nm (4290 M⁻¹ cm⁻¹). HRMS (EI): calcd. for C₁₄H₆N₄⁺ 230.0592; *m*/*z* (%) = 230.0587 (100) [M]⁺.

12: Compound **5** (100 mg, 0.408 mmol) was treated according to GP D, and FC (SiO₂; hexane/CH₂Cl₂, 1:1 → CH₂Cl₂) gave **12** as a pale-yellow solid (62 mg, 0.175 mmol, 43%). $R_{\rm f} = 0.56$ (SiO₂, CH₂Cl₂). M.p. 195–199 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.14$ (d, J = 8.5 Hz, 2 H), 7.98 (s, 1 H), 7.99 (d, J = 8.5 Hz, 2 H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 93.35$, 98.25, 101.73, 108.24, 110.39, 110.88, 111.55, 128.93, 129.89, 139.60, 150.98, 161.30 ppm. IR (neat): $\tilde{v} = 3046$ (m), 2922 (w), 2853 (w), 2233 (m), 1918 (w), 1660 (w), 1584 (s), 1540 (s), 1481 (m), 1392 (s), 1360 (w), 1335 (w), 1304 (w), 1263 (w), 1185 (w), 1153 (w), 1112 (s), 1059 (m), 1007 (s), 935 (s), 838 (w), 823 (s) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 374 nm (4590 m⁻¹ cm⁻¹). HRMS (EI): calcd. for C₁₄H₅IN₄⁺ 355.9559; *m/z* (%) = 355.9554 (100) [M]⁺. C₁₄H₅IN₄ (355.96): calcd. C 47.22, H 1.42, N 15.73, I 35.63; found C 47.07, H 1.61, N 15.51, I 35.58.

13: Compound **6** (25 mg, 0.093 mmol) was treated according to GP C. Instead of being subjected to an aqueous workup, the solvent was removed in a stream of N₂. Purification by preparative recycling GPC using a JAIGEL-1H column (Japan Analytics Industries Co. Ltd.), eluting with CHCl₃ at 4 mLmin⁻¹, gave **13** as a yellow solid (13 mg, 0.051 mmol, 55%). $R_{\rm f}$ not determined due to rapid decomposition on silica and alumina. M.p. 130–132 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.60–7.65 (m, 2 H), 7.65–7.73 (m, 2 H), 7.76–7.83 (m, 1 H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 90.80, 105.36, 107.86, 108.68, 110.17, 110.35, 110.39, 129.13, 129.35, 130.64, 135.78, 136.38, 157.85 ppm. IR (neat): \tilde{v} = 2235 (m), 1593 (w), 1577 (m), 1562 (m), 1541 (s), 1490 (w), 1445 (s), 1327 (m), 1314 (m), 1235 (w), 1189 (s), 1139 (m), 1105 (w), 1080 (w), 999 (m), 933 (w), 897 (w), 846 (w), 801 (w) cm⁻¹. UV/Vis



(CH₂Cl₂); λ_{max} (ε) = 376 nm (3820 m⁻¹ cm⁻¹). HRMS (EI): calcd. for C₁₅H₅N₅⁺ 255.0545; *m*/*z* (%) = 255.0540 (100) [M]⁺.

14: Compound 6 (100 mg, 0.37 mmol) was treated according to GP D using 0.5 equiv. of I₂. Instead of being subjected to an aqueous workup, the solvent was removed in a stream of N2. Purification by preparative recycling GPC using a JAIGEL-1H column (Japan Analytics Industries Co. Ltd.), eluting with CHCl₃ at 4 mL min⁻¹, gave 14 as a yellow foam (44 mg, 0.12 mmol, 31%). $R_{\rm f}$ not determined due to rapid decomposition on silica and alumina. ¹H NMR (400 MHz, CDCl₃): δ = 7.33 (d, J = 8.8 Hz, 2 H), 8.04 (d, J = 8.8 Hz, 2 H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 90.85$, 104.67, 105.63, 107.85, 108.58, 110.10, 110.27, 110.31, 128.22, 130.04, 135.81, 140.06, 156.89 ppm. IR (neat): $\tilde{v} = 2924$ (w), 2232 (w), 1577 (s), 1536 (m), 1482 (m), 1397 (s), 1322 (m), 1299 (m), 1262 (w), 1187 (m), 1138 (w), 1062 (s), 1005 (s), 895 (w), 830 (s) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 374 nm (3840 M⁻¹ cm⁻¹). HRMS (EI): calcd. for $C_{15}H_4IN_4^+$ 380.9511; m/z (%) = 380.9506 (92) [M]⁺, 254.0464 (100).

15: Compound 7 (40 mg, 0.100 mmol) was treated according to GP C and purified by FC (SiO₂; hexane/CH₂Cl₂, $1:1 \rightarrow$ CH₂Cl₂) to give 15 as a dark-red solid (18 mg, 0.046 mmol, 47%). $R_{\rm f} = 0.51$ (SiO₂, CH₂Cl₂). M.p. 115–117 °C. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.19 (dd, J = 10.0, 1.9 Hz, 1 H), 7.26–7.33 (m, 4 H), 7.33–7.38 (m, 1 H), 7.40–7.51 (m, 5 H), 7.53–7.62 (m, 3 H) ppm. ¹³C NMR $(101 \text{ MHz}, \text{ CD}_2\text{Cl}_2): \delta = 78.66, 87.33, 112.40, 112.58, 113.22,$ 126.84, 126.93, 129.24, 129.49, 129.56, 131.00, 131.24, 133.50, 133.59, 133.88, 134.63, 134.84, 134.89, 149.77, 153.81, 171.09 ppm (one carbon signal missing as a signal of two CN groups is present at $\delta = 113.22$). IR (neat): $\tilde{v} = 2922$ (w), 2213 (s), 1979 (s), 1605 (m), 1573 (m), 1535 (m), 1482 (s), 1443 (s), 1387 (m), 1345 (m), 1321 (m), 1273 (m), 1187 (s), 1073 (m), 1059 (m), 1029 (s), 1003 (m), 905 (s), 834 (s) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 445 nm (23500 M⁻¹ cm⁻¹). HRMS (MALDI-TOF, 3-HPA): calcd. for $C_{26}H_{14}N_4^+$ 382.1213; m/z (%) = 382.1214 (1) [M]⁺, 242.0754 (100).

16: Compound 7 (62 mg, 0.156 mmol) was added to a solution of p-toluenesulfonic acid monohydrate (88 mg, 0.468 mmol) in MeCN (1 mL), and the resulting suspension of amine salt was cooled to 10 °C. A solution of NaNO₂ (22 mg, 0.312 mmol) and KI (65 mg, 0.39 mmol) in H₂O (0.3 mL) was gradually added. The mixture was stirred at this temperature for 10 min, allowed to warm to 25 °C, and stirred for a further 30 min. A 1 M Na₂S₂O₃ solution (5 mL) was added and the resulting mixture extracted with CH₂Cl₂ $(3 \times 10 \text{ mL})$. The combined organic layers were dried with Na₂SO₄ and filtered. The solvents were removed in vacuo, and FC (SiO₂; hexane/CH₂Cl₂, $1:1 \rightarrow$ CH₂Cl₂) gave 16 as a dark-red film (49 mg, 0.096 mmol, 62%).^[13b] $R_{\rm f} = 0.49$ (SiO₂, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ = 6.98 (d, J = 8.5 Hz, 2 H), 7.13 (d, J = 10.4 Hz, 1 H), 7.29-7.37 (m, 3 H), 7.45-7.54 (m, 2 H), 7.55-7.64 (m, 3 H), 7.78 (d, J = 8.5 Hz, 2 H) ppm. ¹³C NMR (101 MHz, $CDCl_3$): $\delta = 79.59, 87.29, 98.68, 112.20, 112.30, 112.99, 113.02,$ 127.29, 127.33, 129.42, 129.89, 132.06, 133.22, 133.51, 133.92, 133.96, 134.21, 134.85, 138.72, 148.23, 153.54, 170.57 ppm. IR (neat): $\tilde{v} = 3057$ (w), 2207 (s), 1602 (m), 1532 (m), 1480 (w), 1420 (s), 1348 (w), 1265 (w), 1229 (w), 1181 (s), 1093 (w), 1079 (m), 1026 (m), 999 (m), 976 (w), 913 (w), 835 (m), 808 (m) cm⁻¹. UV/Vis (CH_2Cl_2) : λ_{max} (ε) = 309 (13300), 449 nm (24000 M⁻¹ cm⁻¹). HRMS (MALDI-TOF, 3-HPA): calcd. for $C_{26}H_{13}IN_4^-$ 508.0190; *m*/*z* (%) = 508.0185 (100) [M]⁻.

18: A 1:1 mixture of benzene/water (10 mL) was deoxygenated by bubbling Ar through the solution for 20 min, and the air in a two-necked flask fitted with a condenser containing 9 (125 mg, 0.290 mmol), [4-(dimethylamino)phenyl]boronic acid (17; 96 mg,

0.58 mmol), Na₂CO₃ (62 mg, 0.58 mmol), and [Pd(PPh₃)₄] (10 mg, 0.009 mmol) was exchanged with Ar by performing three evacuation/refilling cycles. The purged benzene/water mixture was transferred, through a syringe, to the two-necked flask, and the resulting mixture was heated at 90 °C for 12 h. The mixture was extracted with CH_2Cl_2 (3×10 mL/mmol), and the combined organic layers were dried with Na₂SO₄ and filtered. The solvents were removed in vacuo, and FC (SiO₂; hexane/CH₂Cl₂, $1:1 \rightarrow$ CH₂Cl₂) gave 18 as a dark-red solid (85 mg, 0.20 mmol, 69%).^[15a] $R_{\rm f} = 0.39$ (SiO₂, hexanes/ethyl acetate, 7:3). M.p. 171–175 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.05 (s, 6 H), 6.79 (d, J = 9.0 Hz, 2 H), 7.54–7.62 (m, 4 H), 7.64–7.70 (m, 1 H), 7.70–7.78 (m, 4 H), 7.79 (d, J = 8.8 Hz, 2 H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 40.24, 83.65, 87.66, 111.16, 111.72, 111.83, 112.41, 112.45, 125.06, 126.67, 127.66, 128.18, 129.39, 130.04, 130.29, 131.40, 134.61, 147.95, 151.28, 165.79, 167.89 ppm. IR (neat): $\tilde{v} = 2920$ (w), 2224 (m), 1615 (w), 1590 (s), 1538 (s), 1520 (s), 1500 (s), 1444 (s), 1367 (s), 1294 (s), 1255 (m), 1234 (m), 1212 (s), 1170 (s), 1060 (m), 999 (m), 946 (m), 906 (w), 848 (m), 812 (s) cm⁻¹. UV/Vis (CH₂Cl₂): $\lambda_{max} (\varepsilon) = 508 \text{ nm}$ (13500 $\text{M}^{-1} \text{ cm}^{-1}$). HRMS (ESI): calcd. for C₂₈H₂₀N₅⁺ 426.1713; *m*/*z* $(\%) = 426.1075 (100) [MH]^+$.

20: Toluene (15 mL) was deoxygenated by bubbling Ar through the solution for 20 min, and the air in a Schlenk tube containing 9 (125 mg, 0.289 mmol), 4-ethynyl-N,N-dimethylaniline (19; 43.6 mg, 0.301 mmol), P(2-furyl)₃ (8.1 mg, 0.035 mmol), CuI (3.3 mg, 0.017 mmol), and PdCl₂ (3.0 mg, 0.017 mmol) was exchanged with Ar by performing three evacuation/refilling cycles. The toluene was transferred, through a syringe, to the Schlenk tube, and diisopropylamine (34.2 µL, 0.347 mmol) was added. The solution was heated at 50 °C for 3 h (TLC analysis) and the mixture extracted with CH_2Cl_2 (3×20 mL/mmol). The combined organic layers were dried with Na₂SO₄, filtered, and the solvents removed in vacuo before FC (SiO₂; hexane/CH₂Cl₂, 1:1 \rightarrow CH₂Cl₂) delivered **20** as a dark-green solid (104 mg, 0.231 mmol, 80%).^[15b] $R_{\rm f} = 0.47$ (SiO₂, hexanes/ethyl acetate, 7:3). M.p. 189-191 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.03 (s, 6 H), 6.66 (d, J = 8.9 Hz, 2 H), 7.43 (d, J = 8.9 Hz, 2 H), 7.54–7.63 (m, 4 H), 7.64–7.71 (m, 5 H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 40.13, 85.72, 87.33, 87.90, 99.01, 108.23, 111.03, 111.41, 111.55, 111.70, 111.87, 128.83, 129.31, 129.41, 130.11, 131.20, 131.89, 132.27, 133.44, 134.69, 150.85, 165.72, 167.31 ppm. IR (neat): $\tilde{v} = 3061$ (w), 2202 (s), 2164 (w), 1592 (s), 1531 (m), 1510 (m), 1480 (m), 1413 (s), 1370 (w), 1348 (w), 1324 (m), 1263 (m), 1230 (w), 1181 (s), 1131 (m), 1093 (m), 1069 (m), 1026 (m), 999 (m), 977 (w), 945 (w), 910 (w), 834 (s), 806 (s) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 486 nm (13000 m⁻¹ cm⁻¹). HRMS (ESI): calcd. for $C_{30}H_{20}N_5^+$ 450.1713; m/z (%) = 450.1722 (100) [MH]⁺.

21: Compound **20** (16 mg, 0.036 mmol) was treated according to GP B for 1 h, and FC (SiO₂; hexane/CH₂Cl₂, 1:1 \rightarrow CH₂Cl₂) gave **21** as a dark-blue solid (21 mg, 0.032 mmol, 91%). $R_{\rm f} = 0.17$ (SiO₂, CH₂Cl₂). M.p. 215–217 °C. ¹H NMR (600 MHz, CDCl₃): $\delta = 3.15$ (s, 6 H), 6.72 (d, J = 9.1 Hz, 2 H), 6.91 (dd, J = 9.5, 2.0 Hz, 1 H), 7.17 (dd, J = 9.5, 2.0 Hz, 1 H), 7.22 (d, J = 9.1 Hz, 2 H), 7.29 (dd, J = 9.6, 2.0 Hz, 1 H), 7.47 (dd, J = 9.6, 2.0 Hz, 1 H), 7.68–7.74 (m, 3 H), 7.77 (d, J = 8.9 Hz, 2 H) ppm. ¹³C NMR (151 MHz, CDCl₃): $\delta = 40.35$, 73.09, 88.21, 90.51, 90.58, 110.56, 110.93, 111.11, 111.26, 111.66, 112.33, 112.92, 114.58, 114.61, 122.78, 125.63, 125.97, 129.33, 130.10, 130.46, 130.56, 130.82, 132.33, 133.73, 134.45, 134.53, 135.36, 135.67, 139.76, 149.69, 153.19, 153.83, 164.91, 165.92, 169.92 ppm. IR (neat): $\tilde{v} = 2201$ (s), 1607 (w), 1576 (s), 1406 (w), 1347 (s), 1162 (s), 940 (m), 905 (m), 823 (s) cm⁻¹. UV/Vis (CH₂Cl₂): $\lambda_{\rm max}(\varepsilon) = 335$

(38300), 630 nm (19600 m⁻¹ cm⁻¹). HRMS (MALDI-TOF, DCTB): calcd. for $C_{42}H_{23}N_9^+$ 653.2071; *m/z* (%) = 653.2073 (100) [M]⁺.

22: N,N-Dimethyl-4-(phenylethynyl)aniline^[22] (150 mg. 0.679 mmol) was treated according to GPA, and FC (SiO2; hexane/CH₂Cl₂, 1:1 \rightarrow CH₂Cl₂) gave 22 as a dark-red solid (220 mg, 0.630 mmol, 93%). $R_{\rm f} = 0.46$ (SiO₂, CH₂Cl₂). M.p. 214–217 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.17 (s, 6 H), 6.74 (d, J = 9.4 Hz, 2 H), 7.54 (d, J = 8.0 Hz, 2 H), 7.62 (m, 1 H), 7.70–7.76 (m, 2 H), 7.79 (d, J = 9.4 Hz, 2 H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta =$ 40.20, 74.28, 87.21, 111.31, 112.05, 112.28, 113.38, 114.30, 117.93, 129.48, 129.76, 131.94, 132.53, 134.29, 154.46, 163.22, 169.34 ppm. IR (neat): $\tilde{v} = 2925$ (w), 2229 (w), 2209 (s), 1605 (s), 1577 (w), 1550 (m), 1477 (s), 1434 (s), 1387 (s), 1353 (s), 1304 (m), 1290 (m), 1265 (m), 1232 (w), 1212 (s), 1174 (s), 1062 (m), 1031 (m), 999 (m), 942 (m), 904 (m), 842 (w), 819 (s), 804 (m) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 312 (13000), 420 (13600, sh), 470 nm (23100 m⁻¹ cm⁻¹). HRMS (ESI): calcd. for $C_{22}H_{16}N_5^+$ 350.1400; m/z (%) = 350.1406 (100) [MH]⁺. C₂₂H₁₅N₅ (349.13): calcd. C 75.63, H 4.33, N 20.04; found C 75.50, H 4.47, N 19.92.

Supporting Information (see footnote on the first page of this article): Materials and general methods, UV/Vis, electrochemical, computational, and X-ray diffraction data, and ¹H and ¹³C NMR spectra for all new compounds.

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