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PAPER

Nitrogen heteroaromatic cations by [2+2+2] cycloaddition†‡

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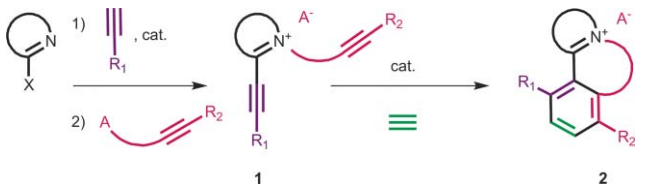
A modular approach to the construction of monocationic quaternary N-heteroaromatic frameworks was developed capitalizing on a direct pyridine-type nitrogen quaternization followed by metal-catalyzed [2+2+2] cycloaddition with gaseous acetylene. The flexibility of the route is demonstrated on 12 diverse scaffolds based on pyridinium, quinolinium, thiazolium, benzothiazolium, imidazolium, and pyrimidinium. Electrochemical study revealed a quinolinium redox system with two electrochemically distinct forms that are interconverted by a homogeneous chemical reaction triggered by fast electron transfers (reduction at –0.7 V and oxidation at –0.05 V).

Introduction

N-Heteroaromatic cations, *i.e.* species with quaternary pyridine-type nitrogen atoms, are of considerable interest due to their rich application potential.[1] In particular, the wide-ranging bioactivities and fluorescent properties of natural[1c–e] (*e.g.* berberine) and non-natural[1f–h] (*e.g.* ethidium) members of this family find widespread use. For this reason, novel, flexible, and expedient synthetic routes to this class of compounds are valuable. In this context, it is notable that syntheses of N-heteroaromatic cations most frequently employ quaternization as the last step in the synthetic sequence.[2] Although this approach has proved to be widely useful and opened access to many interesting cationic compounds, it considerably limits the structural features of accessible N-heteroaromatic cations. By contrast, access to N-heteroaromatic cations *via* organometallic transformation, that comes after the pyridine-type nitrogen quaternization step, might represent a marked advantage in terms of step economy,[3] modularity, and target structural features. This undoubtedly underexplored approach integrates the N-quaternization step as a strategic skeleton-building operation. By taking advantage of olefin metathesis Vaquero, Cuadro *et al.*[4] have recently shown such a complementary approach to be a useful tool in the construction of novel cationic structures. In our recent synthesis of helquats, a novel class of helicene–viologen hybrids, we introduced the first examples of metal-catalyzed [2+2+2] cycloaddition of cationic N-heteroaromatic substrates.[5] We then speculated that a modular assembly of diynes **1** followed by a complexity-generating [2+2+2] cycloaddition[6] would offer an exceptionally flexible and direct route to polycyclic monocationic scaffolds **2** (Scheme 1).



Scheme 1 Assembly of N-heterocyclic cations *via* Sonogashira coupling–N-quaternization–[2+2+2] cycloaddition.

Herein we present the results of a synthetic study towards diverse monocationic N-heteroaromatic tricycles relying on [2+2+2] cycloaddition of cationic diynes with gaseous acetylene.[7,8]

Results and discussion

1. Synthesis

At the outset, we prepared diyne **4** by N-quaternization of known pyridine **3** (ref. 9) with 3-butynyl triflate (Table 1).[4a,5a] The diyne **4**, a room-temperature ionic liquid (RTIL), was prepared in excellent purity without the need for chromatography after the N-quaternization step.[10] Next we focused on the key transformation of the cationic substrate **4** with gaseous acetylene under various [2+2+2] cycloaddition conditions (Table 1). Use of Wilkinson's catalyst[11] $[Rh(PPh_3)_3Cl]$ (10 mol %) in degassed DMF at 80 °C led to the smooth formation of tricyclic benzo[a]3,4-dihydroquinolizinium **5** (ref. 12) in 93% isolated yield, (entry 8). Notably, catalytic system $[Ir(cod)Cl]_2$/dppe also afforded product **5** in good yield (79%, entry 4). To the best of our knowledge, the

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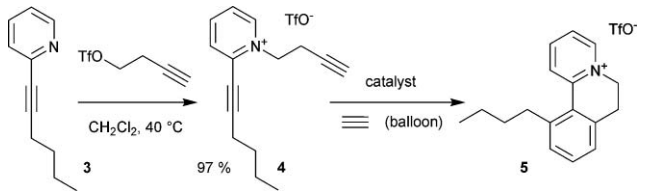
† Dedicated to Professor Antonín Holý on the occasion of his 74th birthday.

‡ Electronic supplementary information (ESI) available: Experimental procedures for compounds **3**, **24**, and **27**; precursors of compounds **6–13**, spectroscopic characterization data, NMR scans, X-ray crystallographic data of **8**, **12**, **16**, **24**, **25**, electrochemical experiments. CCDC reference numbers 736009–736013. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00507j

Table 1 Synthesis of tricycle **5** *via* diyne **4** and optimization of [2+2+2] cycloaddition reaction **4**→**5**[a]



entry[a]	catalyst	solvent (°C/h)	yield (%)[b]
1	[Cp*Ru(cod)Cl]	DMF (140/20)	40
2	[Cp*RuCl]$_4$	DMF (130/24)	43
3	[Ir(cod)Cl]$_2$/dppe	1,4-dioxane (25/20)	58
4	[Ir(cod)Cl]$_2$/dppe	DMF (80/24)	79
5	[Ni(PPh$_3$)$_2$(CO)$_2$]	DMF (130/20)	24
6	[CpCo(CO)$_2$]	DMF (153/1.5)	30
7	[Rh(PPh$_3$)$_3$Cl]	EtOH (80/24)	85
8	[Rh(PPh$_3$)$_3$Cl]	DMF (80/1.5)	93

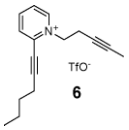
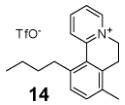
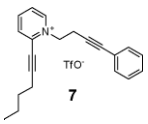
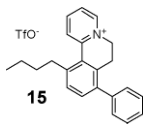
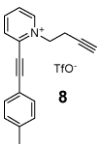
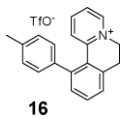
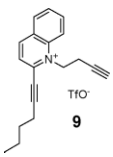
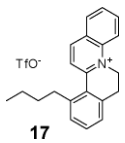
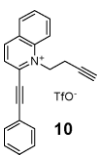
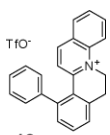
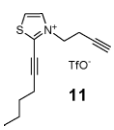
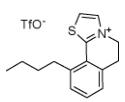
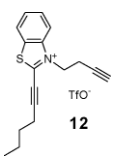
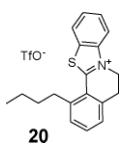
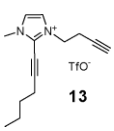
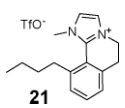
[a] Reaction conditions: **4** (0.15 mmol), catalyst (0.015 mmol), solvent (4 ml), acetylene (balloon). [b] Isolated yields after chromatography. dppe = 1,2-bis(diphenylphosphino)ethane.

successful use of a catalytic system based on [Ir(cod)Cl]$_2$ has never been reported before in the context of [2+2+2] cycloaddition with gaseous acetylene.[13]

Following this introductory study, we turned to a diverse set of cationic diynes in order to validate the usefulness and generality of this approach. A series of N-quaternization experiments analogous to transformation **3**→**4** were conducted using a variety of N-heteroaromatic substrates and triflates generated from their corresponding alcohol precursors. This protocol secures convenient access to the cationic diynes **6–13** (Table 2, left column).[14] Notably, all diynes prepared were liquids (RTIL) with the exception of compounds **8** and **12** that were isolated as a greenish crystalline solid and pink powder, respectively.[15] The scope of the key rhodium-catalyzed [2+2+2] cycloaddition was evaluated with respect to the structure of diyne (Table 2). Substrate **6** bearing two internal alkyne units undergoes slow [2+2+2] cycloaddition with [Rh(PPh$_3$)$_3$Cl] as catalyst (**6**→**14**, entry 1). In this case, a catalytic system based on [Ir(cod)Cl]$_2$ leads to faster conversion and higher yield of tricycle **14**. An aryl substituent capping the pendant alkyne functionality is compatible with the key cyclization, affording azonia *m*-terphenyl derivative **15** (entry 2). The related azonia *o*-terphenyl system **16** can also be conveniently accessed (entry 3). Significantly, incorporation of various heterocyclic moieties is feasible as exemplified by successful syntheses of quinolinium, thiazolium, benzothiazolium, and imidazolium systems **17–21** (entries 4–8). In the cyclization of the imidazolium system **13** (entry 8) the use of [Ir(cod)Cl]$_2$/dppe proved to be crucial as conversion to product **21** was negligible with Wilkinson's catalyst. The identities of compounds **8**, **12**, and **16** were unambiguously confirmed by X-ray crystal structure analysis (Fig. 1).[15]

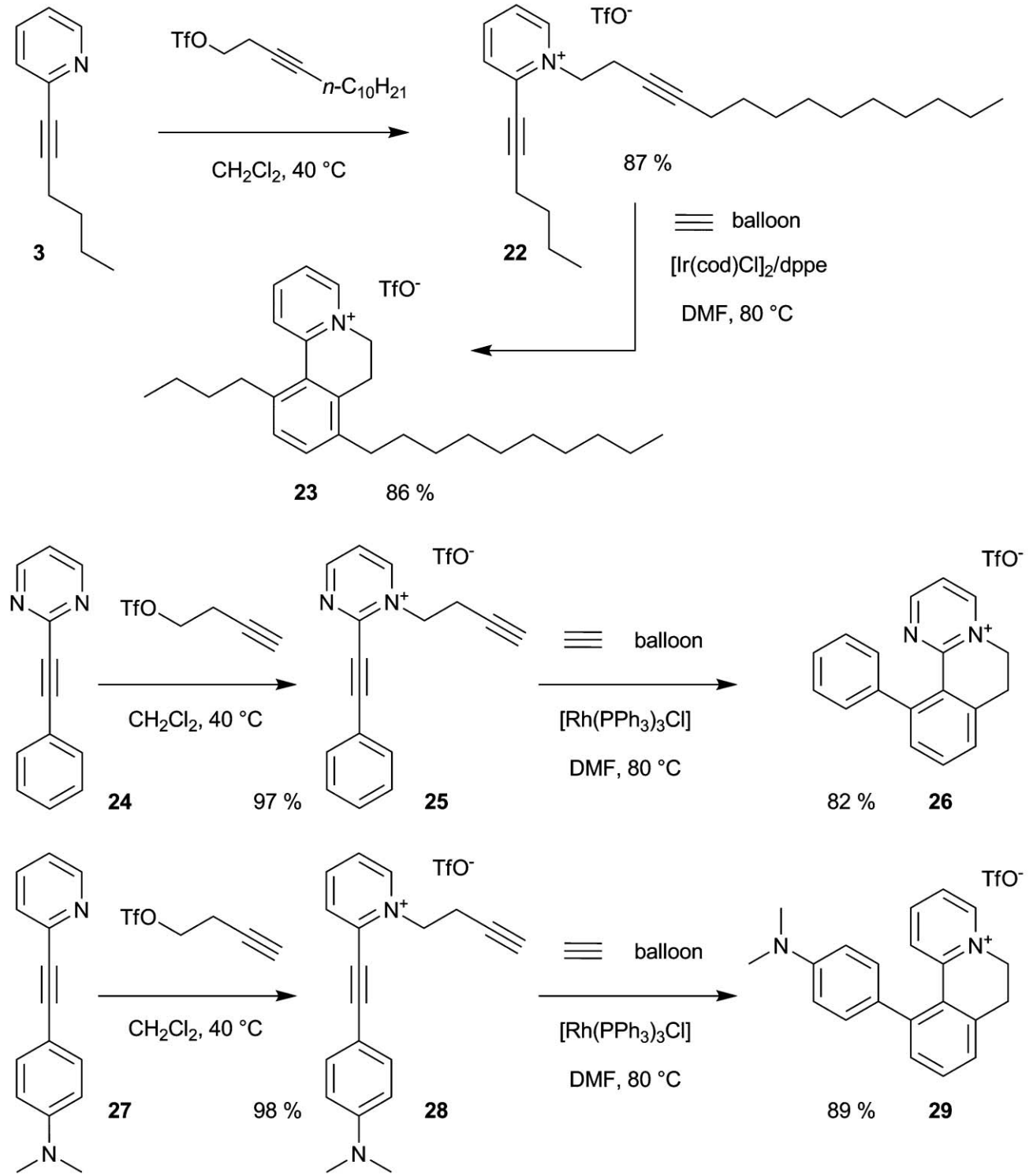
Next, we examined the possibility of tuning the polarity of the targeted organic cations by introduction of a lipophilic side chain. Scheme 2 shows that the species **23** can be easily synthesized in high yield.[16] By contrast to cations **4–21**, both species **22** and **23** exhibit no solubility in water and excellent solubility in diethyl ether. To demonstrate the broader utility and flexibility of the described synthetic route, two systems bearing additional nitrogen

Table 2 Scope of [2+2+2] cycloaddition of cationic diynes with acetylene gas[a]

entry	diyne	catalyst (h)	product	yield (%)[b]
1	 **6**	B (19)	 **14**	60
2	 **7**	A (48)	 **15**	85[c]
3	 **8**	A (2)	 **16**	88
4	 **9**	A (48)	 **17**	72[d]
5	 **10**	A (20)	 **18**	79[d]
6	 **11**	A (24)	 **19**	74[e]
7	 **12**	A (20)	 **20**	59
8	 **13**	B (19)	 **21**	87

[a] Reaction conditions: diyne (0.06–0.32 mmol), DMF, acetylene (balloon), 80 °C, catalyst A: [Rh(PPh$_3$)$_3$Cl] (10 mol %) or B: [Ir(cod)Cl]$_2$ (5 mol %), dppe (10 mol %). [b] Isolated yields after chromatography. [c] Reaction was run with 5 mol % of catalyst A, 80 °C, 24 h; then another portion of catalyst A (5 mol %) was added, 100 °C, 24 h. [d] Reaction temperature was 90 °C. [e] 5 mol % of catalyst A, EtOH was used instead of DMF.

functionality were prepared: a pyrimidinium containing system **26** and compound **29** containing a peripheral dimethylamino group (Scheme 2). A noteworthy feature common to both routes is the exclusive monoquaternization of one nitrogen atom only (**24**→**25**, **27**→**28**).[17] Significantly, the additional nitrogen functionalities are well tolerated in the key rhodium-catalyzed



Scheme 2 Synthesis of lipophilic cation **23** and systems **26** and **29** with additional nitrogen functionalities.

[2+2+2] cycloadditions. An important class of dyes comprise a push–pull chromophore based on a pyridinium type moiety that is in conjugation with an electron-rich dialkylamino functionality. To this end, the second route (**27**→**28**→**29**) opens a straightforward synthetic pathway to novel systems that bear structural similarity to these push–pull chromophores.

2. Electrochemistry

We set out to study the electrochemical properties of selected N-heteroaromatic cations as there is an established correlation between redox parameters and bioactivity.[1h] Benzothiazolium **20** showed reversible behavior (Fig. 2, curve 1), whereas quinolinium

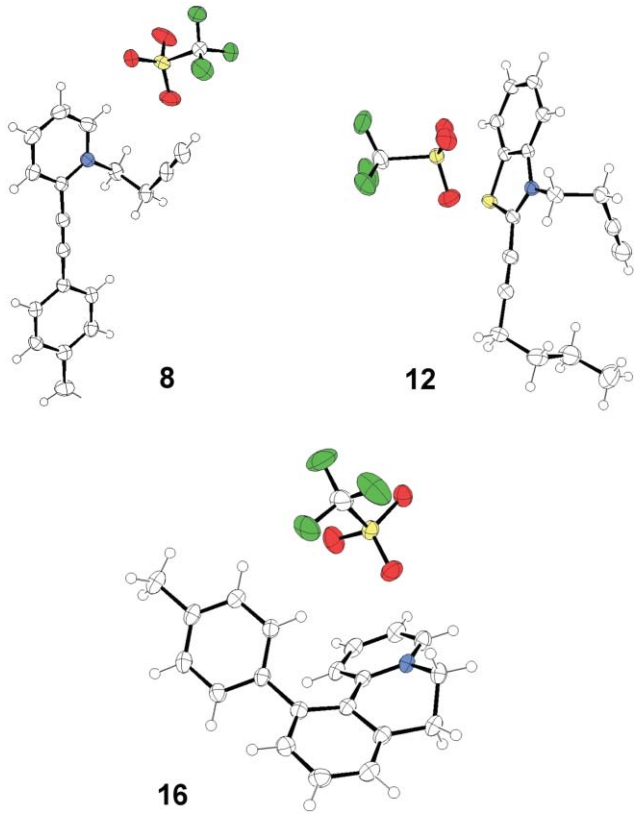


Fig. 1 Single-crystal X-ray structures of **8**, **12**, and **16**.[15]

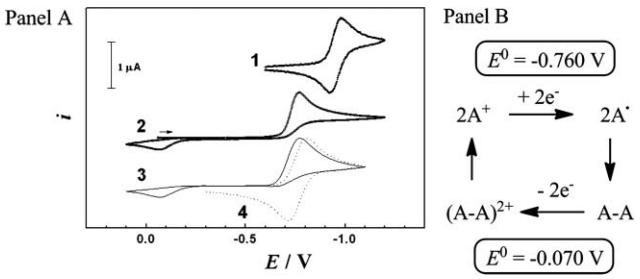


Fig. 2 Panel A: cyclic voltammograms of **20** (curve 1), **17** (curve 2), and numerical simulations considering an EC mechanism (curve 3) and simple electron transfer (curve 4) for **17**[18]; Panel B: dimerization scheme for system **17**.

17 revealed a feature rarely found in organic redox systems (Fig. 2, curve 2).[19] Specifically, system **17** yields a voltammogram corresponding to an irreversible one-electron reduction, which at the same time has a peak shape characteristic of a reversible electron transfer. The back scan of the voltammogram (Fig. 2, curve 2) shows an oxidation peak, which also has a peak shape corresponding to a fast electron transfer. However, the potential difference of the reduction and oxidation peaks ΔE_p = 0.7 V is very large. Whereas voltammograms with $\Delta E_p > RT/nF$ (n is the number of transferred electrons) usually indicate a slow electron transfer, the electrochemical impedance spectroscopy with **17** estimates the heterogeneous rate constant to be fast (ca k^0 = 0.007 cm s^{-1}). Also, DC polarogram (not shown) has a reversible shape corresponding to a fast electron transfer. These data lead to the conclusion that the irreversibility of the redox system based on **17** must be of a chemical nature. This led us to a hypothesis that the reduction yields a radical rapidly forming a dimer[20] (Fig. 2, panel B). The dimer undergoes oxidation at a considerably less negative potential as evidenced by the observed anodic voltammetric peak. The oxidation of the dimer is also characterized by a fast electron transfer and a fast decomposition to the original oxidized form of **17** cation. This explanation is also consistent with the less intense anodic peak current as the dimer can diffuse away from the electrode surface leading to the diminished value of the reduction peak. The suggested explanation is confirmed by digital simulations of voltammograms (curve 3 *vs.* 4 in Fig. 2).[21] Using the experimentally determined formal redox potentials E^0s and heterogeneous rate constant, the experimental voltammogram is reproduced well by simulation using the dimerization scheme (curve 3), not a simple electron transfer (curve 4).

Conclusions

In conclusion, the three-step sequence of Sonogashira coupling, N-quaternization, and [2+2+2] cycloaddition opens short, flexible, and atom-economic access to a series of novel monocationic tricycles based on pyridinium, quinolinium, thiazolium, benzothiazolium, imidazolium, and pyrimidinium. The demonstrated strategy manifests the value of pathways based on skeleton-building N-quaternization followed by a key organometallic complexity-generating step for the rapid assembly of elaborate organic cationics. To this end, we anticipate that the use of pyridine-type nitrogen as a functionalization handle will also serve for the benefit of other organometallic C–C bond forming strategies and thus the preparative power of organometallic chemistry will be harnessed in exploiting novel intriguing nitrogen-containing carbon frameworks. Electrochemical studies with the quinolinium system **17** revealed an interesting bistable behavior indicating a reversible dimer formation triggered by electron transfer. Such a phenomenon is rarely encountered in organic redox systems and warrants further investigation.[22]

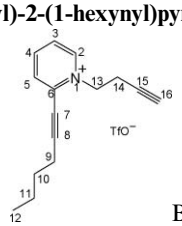
Experimental

General details

Liquids and solutions were transferred *via* needle and syringe under inert atmosphere unless otherwise stated. Melting points were determined on a Wagner & Munz PolyTherm A micro melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) analysis was performed on silica gel plates (Silica gel 60 F_{254}-coated aluminium sheets, Merck, cat. no. 1.05554.0001) and visualized by UV (UV lamp 254/365 nm, Spectroline® Model ENF – 240C/FE) and/or chemical staining with $KMnO_4$ [$KMnO_4$ (1% aq.), Na_2CO_3 (2% aq.)]. Flash chromatography was performed on silica gel 60 (Fluka, cat. no. 60741) with the indicated eluent. NMR spectra were measured on a Bruker Avance 600 (600 MHz for ^{1}H, 151 MHz for ^{13}C), Bruker Avance 500 (500 MHz for ^{1}H, 125.7 MHz for ^{13}C) or Bruker Avance 400 (400 MHz for ^{1}H, 100.6 MHz for ^{13}C) NMR spectrometer in acetone referenced to the CHD_2COCD_3 peak (δ_H = 2.09 ppm), CD_3COCD_3 (δ_C = 29.80 ppm. ^{14}N NMR spectra were referenced

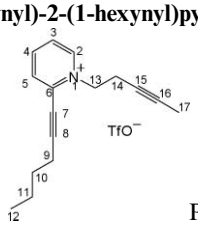
to the nitromethane peak ($\delta_N = 0$ ppm). Chemical shifts are given in δ-scale as parts per million (ppm); coupling constants (J) are given in Hertz. Where indicated, the signal assignments in the NMR spectra are unambiguous; the numbering scheme is arbitrary and is shown in the inserts. Where assigned, all ^{1}H and ^{13}C resonance assignments are based on analysis of H,H-COSY; H,H-ROESY; H,C-HSQC and H,C-HMBC spectra. IR spectra were recorded on a Bruker EQUINOX55 (IFS55) spectrometer in $CHCl_3$, or CCl_4 (cuvette width 0.1 mm), or as KBr pellets. Abbreviation for intensities of IR bands are as follows: s for strong, vs for very strong, m for medium, w for weak, vw for very weak, br for broad, sh for shoulder. Mass spectral data were obtained at the Mass Spectrometry Facility operated by the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i. EI MS spectra were measured at an electron energy of 70 eV; m/z values are given along with their relative intensities (%). ESI mass spectra were recorded using a Thermo Scientific LCQ Fleet mass spectrometer equipped with an electrospray ion source and controlled by Xcalibur software. The mobile phase consisted of methanol–water (9 : 1), flow rate of 200 μL min^{-1}. The sample was dissolved, diluted with the mobile phase and injected using a 5 μL loop. Spray voltage, capillary voltage, tube lens voltage and capillary temperature were 5.5 kV, 5 V, 80 V and 275 °C, respectively. HR MS spectra were obtained with the EI or ESI instruments.

1-(3-Butynyl)-2-(1-hexynyl)pyridinium trifluoromethanesulfonate (4).



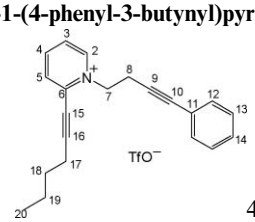
But-3-ynyl trifluoromethanesulfonate (2.95 g, 14.58 mmol, 2.6 equiv) was added dropwise at room temperature to a solution of compound **3** (905 mg, 5.68 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (15 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 22 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **4** was obtained as a brownish liquid in 97% yield (1.99 g, 5.51 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.00 (t, J = 7.4 Hz, 3H, H-12); 1.54–1.61 (m, 2H, H-11); 1.73–1.79 (m, 2H, H-10); 2.72 (t, J = 2.7 Hz, 1H, H-16); 2.81 (t, J = 7.1 Hz, 2H, H-9); 3.15 (dt, J = 2.7, 6.7 Hz, 2H, H-14); 5.13 (t, J = 6.7 Hz, 2H, H-13); 8.25 (dt, J = 1.5, 6.3, 7.9 Hz, 1H, H-3); 8.36 (bdd, J = 1.6, 8.2 Hz, 1H, H-5); 8.75 (dt, J = 1.5, 7.9 Hz, 1H, H-4); 9.24 (ddd, J = 0.5, 1.5, 6.3 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.73 (C-12), 19.97 (C-9), 20.20 (C-14), 22.69 (C-11), 30.20 (C-10), 59.06 (C-13), 72.71 (C-7), 74.52 (C-16), 78.85 (C-15), 112.15 (C-8), 127.44 (C-3), 133.22 (C-5), 138.79 (C-6), 146.71 (C-4), 147.57 (C-2). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 w, 638 vs, 1031 vs, 1113 w, 1165 s, 1275 vs, 1329 w, 1343 w, 1382 w, 1462 m, 1509 s, 1573 m, 1619 m, 2124 vw, 2226 s, 3061 w, 3090 w, 3308 m. MS (ESI) m/z (%): 212 [(M-OTf)$^+$] (100). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{15}H_{18}N$) calc.: 213.1434, found: 212.1432.

1-(3-Pentynyl)-2-(1-hexynyl)pyridinium trifluoromethanesulfonate (6).



Pent-3-ynyl trifluoromethanesulfonate (119 mg, 0.55 mmol, 2.1 equiv) was added dropwise at room temperature to a solution of compound **3** (42 mg, 0.26 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (2.5 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 20 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **6** was obtained as a brownish liquid in 82% yield (81 mg, 0.22 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.01 (t, J = 7.4 Hz, 3H, H-12); 1.55–1.62 (m, 2H, H-11); 1.74–1.79 (m, 2H, H-10); 1.75 (t, J = 2.7 Hz, 3H, H-17); 2.81 (t, J = 7.1 Hz, 2H, H-9); 3.05 (tq, J = 2.7, 6.6 Hz, 2H, H-14); 5.08 (t, J = 6.6 Hz, 2H, H-13); 8.25 (ddd, J = 1.6, 6.2, 7.8 Hz, 1H, H-3); 8.36 (ddd, J = 0.6, 1.6, 8.1 Hz, 1H, H-5); 8.74 (dt, J = 1.5, 7.9 Hz, 1H, H-4); 9.22 (ddd, J = 0.6, 1.5, 6.2 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 3.03 (C-17), 13.73 (C-12), 19.94 (C-9), 20.66 (C-14), 22.68 (C-11), 30.23 (C-10), 59.65 (C-13), 72.67 (C-7), 73.68 (C-15), 81.36 (C-16), 111.86 (C-8), 127.28 (C-3), 133.13 (C-5), 138.68 (C-6), 146.57 (C-4), 147.47 (C-2). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 m, 638 vs, 1031 vs, 1165 s, 1273 vs, 1382 w, 1509 s, 1573 m, 1619 s, 2226 s, 3061 w, 3091 w. MS (ESI) m/z (%): 226 [(M-OTf)$^+$] (100). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{16}H_{20}N$) calc.: 226.1590, found: 226.1590.

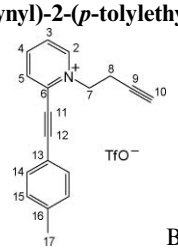
2-(1-Hexynyl)-1-(4-phenyl-3-butynyl)pyridinium trifluoromethanesulfonate (7).



4-Phenylbut-3-ynyl trifluoromethanesulfonate (245 mg, 0.88 mmol, 2.5 equiv) was added dropwise at room temperature to a solution of compound **3** (55 mg, 0.35 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (3.0 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 16 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **7** was obtained as a brownish liquid in 84% yield (128 mg, 0.29 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.93 (t, J = 7.3 Hz, 3H, H-20); 1.49–1.56 (m, 2H, H-19); 1.68–1.74 (m, 2H, H-18); 2.79 (t, J = 7.1 Hz, 2H, H-17); 3.35 (t, J = 6.5 Hz, 2H, H-8); 5.21 (t, J = 6.5 Hz, 2H, H-7); 7.32 - 7.38 (m, 5H, H-12, H-13, H-14); 8.25 (ddd, J = 1.6, 6.3, 7.8 Hz, 1H, H-3); 8.35 (ddd, J = 0.6, 1.6, 8.0 Hz, 1H, H-5); 8.72 (dt, J = 1.5, 7.9 Hz, 1H, H-4); 9.30 (ddd, J = 0.6, 1.5, 6.3 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.73 (C-20), 19.99 (C-17), 21.28 (C-8), 22.69 (C-19), 30.21 (C-18), 59.21 (C-7), 72.80 (C-15), 84.42 (C-10), 85.23 (C-9), 112.09 (C-16), 123.35 (C-11), 127.45 (C-3), 129.34

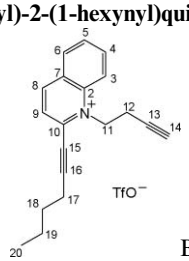
(C-13), 129.38 (C-14), 132.22 (C-12), 133.22 (C-5), 138.91 (C-6), 147.48 (C-2), 148.74 (C-4). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 m, 638 vs, 1031 vs, 1165 s, 1273 vs, 1382 w, 1509 s, 1573 m, 1619 s, 2226 s, 3061 w, 3091 w. MS (ESI) *m/z* (%): 288 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{21}H_{22}N$) calc.: 288.1744, found: 288.1747.

1-(3-Butynyl)-2-(*p*-tolylethynyl)pyridinium trifluoromethanesulfonate (8).



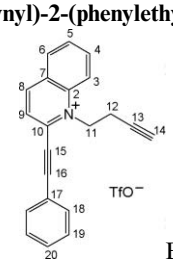
But-3-ynyl trifluoromethanesulfonate (223 mg, 1.10 mmol, 2.3 equiv) was added dropwise at room temperature to a solution of 2-(*p*-tolylethynyl)pyridine (95 mg, 0.49 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (4.5 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 24 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **8** was obtained as a greenish solid in 99% yield (193 mg, 0.49 mmol). mp 166–168 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 2.48 (t, J = 0.8 Hz, 3H, H-17); 2.78 (t, J = 2.7 Hz, 1H, H-10); 3.26 (dt, J = 2.7, 6.6 Hz, 2H, H-8); 5.29 (t, J = 6.6 Hz, 2H, H-7); 7.44–7.46 (m, 2H, H-15); 7.77–7.79 (m, 2H, H-14); 8.30 (ddd, J = 1.5, 6.2, 8.0 Hz, 1H, H-3); 8.53 (ddd, J = 0.6, 1.5, 8.1 Hz, 1H, H-5); 8.82 (ddd, J = 1.5, 8.0 Hz, 1H, H-4); 9.31 (ddd, J = 0.6, 1.5, 6.2 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 20.32 (C-8), 21.71 (C-17), 59.24 (C-7), 74.66 (C-10), 78.95 (C-11), 80.23 (C-9), 108.05 (C-12), 117.00 (C-13), 127.57 (C-3), 130.68 (C-15), 133.14 (C-5), 133.55 (C-14), 138.65 (C-6), 143.78 (C-16), 146.66 (C-4), 147.67 (C-2). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 430 vw, 518 m, 573 w, 636 s, 648 w, 669 vw, 707 w, 735 w, 756 w, 784 m, 824 m, 862 w, 1017 w, 1031 vs, 1108 w, 1158 s, 1170 s, 1225 s, 1261 vs, 1274 vs, 1287 s, 1319 w, 1385 w, 1409 w, 1501 w, 1518 s, 1570 m, 1602 m, 1617 m, 2123 vw, 2222 s, 3041 w, 3060 w, 3080 w, 3093 w, 3249 m. MS (ESI) *m/z* (%): 246 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{18}H_{16}N$) calc.: 246.1277, found: 246.1277.

1-(3-Butynyl)-2-(1-hexynyl)quinolinium trifluoromethanesulfonate (9).



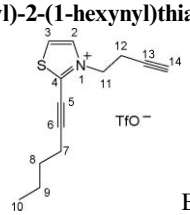
But-3-ynyl trifluoromethanesulfonate (357 mg, 1.77 mmol, 2.5 equiv) was added dropwise at room temperature to a solution of 2-(1-hexynyl)quinoline (150 mg, 0.72 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (6.5 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 19 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **9** was obtained as a brownish liquid in 97% yield (286 mg, 0.70 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.03 (t, J = 7.3 Hz, 3H, H-20); 1.60–1.67 (m, 2H, H-19); 1.81–1.87 (m, 2H, H-18); 2.69 (t, J = 2.7 Hz, 1H, H-14); 2.93 (t, J = 7.0 Hz, 2H, H-17); 3.24 (dt, J = 2.7, 7.2 Hz, 2H, H-12); 5.66 (t, J = 7.2 Hz, 2H, H-11); 8.13 (ddd, J = 0.9, 7.0, 8.2 Hz, 1H, H-5); 8.35 (d, J = 8.6 Hz, 1H, H-9); 8.41 (ddd, J = 1.5, 7.0, 9.1 Hz, 1H, H-4); 8.56 (dt, J = 0.6, 1.5, 8.2 Hz, 1H, H-6); 8.80 (dq, J = 0.8, 9.1 Hz, 1H, H-3); 9.31 (dd, J = 1.1, 8.6 Hz, 1H, H-8). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.76 (C-20), 19.27 (C-12), 20.43 (C-17), 22.77 (C-19), 30.18 (C-18), 53.61 (C-11), 74.28 (C-14), 75.58 (C-15), 79.17 (C-13), 116.59 (C-16), 119.93 (C-3), 127.31 (C-9), 129.94 (C-7), 131.03 (C-5), 131.83 (C-6), 137.36 (C-4), 139.80 (C-2), 143.01 (C-10), 147.47 (C-8). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 m, 638 vs, 838 m, 870 w, 1031 vs, 1164 s, 1274 vs, 1379 m, 1438 m, 1521 s, 1575 s, 1600 s, 1619 m, 2125 vw, 2223 s, 3088 w. MS (ESI) *m/z* (%): 262 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{19}H_{20}N$) calc.: 262.1590, found: 262.1590.

1-(3-Butynyl)-2-(phenylethynyl)quinolinium trifluoromethanesulfonate (10).



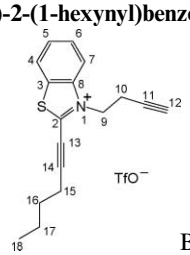
But-3-ynyl trifluoromethanesulfonate (135 mg, 0.67 mmol, 2.9 equiv) was added dropwise at room temperature to a solution of 2-(phenylethynyl)quinoline (53 mg, 0.23 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (2.2 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 19 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. It was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 8 cm, CH_2Cl_2–MeOH 10 : 1). The compound **10** was obtained as a brownish liquid in 41% yield (41 mg, 0.10 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 2.71 (t, J = 2.7 Hz, 1H, H-14); 3.35 (dt, J = 2.7, 7.0 Hz, 2H, H-12); 5.80 (t, J = 7.0 Hz, 2H, H-11); 7.66–7.70 (m, 2H, H-19); 7.74–7.78 (m, 1H, H-20); 7.99–8.01 (m, 2H, H-18); 8.17 (ddd, J = 1.1, 7.0, 8.1 Hz, 1H, H-5); 8.44 (ddd, J = 1.5, 7.0, 9.0 Hz, 1H, H-4); 8.55 (d, J = 8.6 Hz, 1H, H-9); 8.59 (ddt, J = 0.6, 1.5, 8.1 Hz, 1H, H-6); 8.86 (dq, J = 0.8, 9.0 Hz, 1H, H-3); 9.38 (dd, J = 1.1, 8.6 Hz, 1H, H-8). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 18.64 (C-12), 53.11 (C-11), 73.65 (C-14), 78.52 (C-13), 82.57 (C-15), 110.34 (C-16), 119.12 (C-3), 119.19 (C-17), 126.42 (C-9), 129.31 (C-19), 129.33 (C-7), 130.40 (C-5), 131.08 (C-6), 132.54 (C-20), 133.20 (C-18), 136.69 (C-4), 139.18 (C-2), 141.78 (C-10), 146.65 (C-8). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 w, 638 vs, 686 m, 836 w, 922 w, 999 w, 1030 vs, 1057 w, 1153 s, 1160 s, 1269 vs, 1346 m, 1377 w, 1437 w, 1445 w, 1472 w, 1493 w, 1523 m, 1573 s, 1594 s, 1602 s, 1618 m, 2204 vs, 3086 w, 3307 m. MS (ESI) *m/z* (%): 282 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{21}H_{16}N$) calc.: 282.1277, found: 282.1277.

1-(3-Butynyl)-2-(1-hexynyl)thiazolium trifluoromethanesulfonate (11).



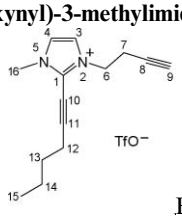
But-3-ynyl trifluoromethanesulfonate (240 mg, 1.19 mmol, 2.8 equiv) was added dropwise at room temperature to a solution of 2-(1-hexynyl)thiazole (70 mg, 0.42 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (5 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 16 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **11** was obtained as a brownish liquid in 89% yield (139 mg, 0.38 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.00 (t, J = 7.4 Hz, 3H, H-10); 1.54–1.61 (m, 2H, H-9); 1.74–1.80 (m, 2H, H-8); 2.72 (t, J = 2.7 Hz, 1H, H-14); 2.88 (t, J = 7.1 Hz, 2H, H-7); 3.10 (dt, J = 2.7, 6.6 Hz, 2H, H-12); 4.97 (t, J = 6.6 Hz, 2H, H-11); 8.45 (d, J = 4.0 Hz, 1H, H-3); 8.67 (d, J = 4.0 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.68 (C-10), 20.04 (C-12), 20.35 (C-7), 22.64 (C-9), 30.31 (C-8), 53.32 (C-11), 67.62 (C-6), 74.05 (C-14), 79.18 (C-13), 118.47 (C-5), 125.48 (C-3), 137.92 (C-2), 152.40 (C-4). ^{15}N NMR (61 MHz, $(CD_3)_2CO$): δ = 162.0 (*N*-1). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 w, 638 vs, 1030 vs, 1165 s, 1263 vs, 1278 vs, 1322 w, 1345 w, 1382 w, 1428 w, 1459 w, 1545 m, 1604 w, 2126 vw, 2222 s, 3108 w, 3135 w, 3308 m. MS (ESI) *m*/*z* (%): 218 [(M-OTf)$^+$] (100). HRMS (ESI) *m*/*z*: [(M-OTf)$^+$] ($C_{13}H_{16}NS$) calc.: 218.0998, found: 218.0998.

3-(3-Butynyl)-2-(1-hexynyl)benzothiazolium trifluoromethanesulfonate (12).



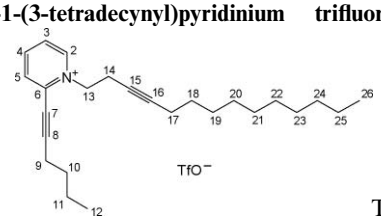
But-3-ynyl trifluoromethanesulfonate (320 mg, 1.59 mmol, 2.8 equiv) was added dropwise at room temperature to a solution of 2-(1-hexynyl)benzothiazole (123 mg, 0.57 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (5.5 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 21 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **12** was obtained as an orange solid in 99% yield (236 mg, 0.57 mmol). mp 90–92 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.02 (t, J = 7.4 Hz, 3H, H-18); 1.62 (tq, J = 6.1, 7.4 Hz, 2H, H-17); 1.84 (tt, J = 6.1, 7.1 Hz, 2H, H-16); 2.67 (t, J = 2.7 Hz, 1H, H-12); 2.99 (t, J = 7.1 Hz, 2H, H-15); 3.19 (dt, J = 2.7, 6.7 Hz, 2H, H-10); 5.31 (t, J = 6.7 Hz, 2H, H-9); 8.02 (ddd, J = 1.1, 7.3, 8.2 Hz, 1H, H-5); 8.10 (ddd, J = 1.2, 7.3, 8.6 Hz, 1H, H-6); 8.56 (ddd, J = 0.7, 1.2, 8.2 Hz, 1H, H-4); 8.57 (dt, J = 0.9, 8.6 Hz, 1H, H-7). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.71 (C-18), 19.20 (C-10), 20.78 (C-17), 22.75 (C-15), 29.88 (C-16), 50.79 (C-9), 69.29 (C-13), 74.34 (C-12), 79.34 (C-11), 118.28 (C-4), 122.94 (C-14), 125.58 (C-7), 130.62 (C-5), 130.68 (C-3), 131.60 (C-6), 140.64 (C-8), 155.52 (C-2). ^{15}N NMR (61 MHz, $(CD_3)_2CO$): δ = 176.00 (*N*-1). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 441 w, 517 m, 574 w, 638 vs, 997 vw, 1030 vs, 1051 w, 1083 vw, 1105 vw, 1165 s, 1201 m, 1265 vs, 1340 m, 1382 w, 1427 w, 1441 m, 1465 m, 1502 w, 1579 w, 2125 vw, 2222 s, 3074 w, 3100 w, 3308 m. MS (ESI) *m*/*z* (%): 268 [(M-OTf)$^+$] (100). HRMS (ESI) *m*/*z*: [(M-OTf)$^+$] ($C_{17}H_{18}NS$) calc.: 268.1154, found: 2681150.

1-(3-Butynyl)-2-(1-hexynyl)-3-methylimidazolium trifluoromethanesulfonate (13).



But-3-ynyl trifluoromethanesulfonate (146 mg, 0.72 mmol, 2.1 equiv) was added dropwise at room temperature to a solution of 2-(1-hexynyl)-1-methylimidazole (57 mg, 0.35 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (3.5 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 21 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **13** was obtained as a red liquid in 94% yield (120 mg, 0.33 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.00 (t, J = 7.4 Hz, 3H, H-15); 1.54–1.61 (m, 2H, H-14); 1.73–1.79 (m, 2H, H-13); 2.66 (t, J = 2.7 Hz, 1H, H-9); 2.82 (t, J = 7.0 Hz, 2H, H-12); 2.95 (dt, J = 2.7, 6.6 Hz, 2H, H-7); 4.10 (s, 3H, H-16); 4.59 (t, J = 6.6 Hz, 2H, H-6); 7.85 (d, J = 2.1 Hz, 1H, H-4); 7.92 (d, J = 2.1 Hz, 1H, H-3). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.68 (C-15), 19.72 (C-12), 20.18 (C-7), 22.56 (C-14), 30.31 (C-13), 36.54 (C-16), 48.79 (C-6), 62.76 (C-10), 73.44 (C-9), 79.71 (C-8), 111.88 (C-11), 123.41 (C-3), 124.64 (C-4), 130.87 (C-1). ^{15}N NMR (61 MHz, $(CD_3)_2CO$): δ = 196.2 (*N*-2), 203.8 (*N*-5). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 w, 638 vs, 700 m, 914 w, 1031 vs, 1080 w, 1165 s, 1269 vs, 1321 w, 1342 w, 1382 w, 1421 w, 1466 w, 1510 m, 1582 m, 2127 vvw, 2239, 3308 m. MS (ESI) *m*/*z* (%):215 [(M-OTf)$^+$] (93), 171 (100), 163 (32), 156 (35), 133 (42). HRMS (ESI) *m*/*z*: [(M-OTf)$^+$] ($C_{14}H_{19}N_2$) calc.: 215.1543, found: 215.1549.

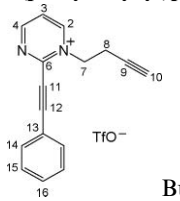
2-(1-Hexynyl)-1-(3-tetradecynyl)pyridinium trifluoromethanesulfonate (22).



Tetradec-3-ynyl trifluoromethanesulfonate (515 mg, 1.50 mmol, 2.1 equiv) was added dropwise at room temperature to a solution of compound **3** (115 mg, 0.72 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (5.5 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 19 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*.

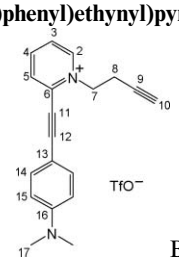
It was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 8 cm, CH_2Cl_2–MeOH 10 : 1). The compound **22** was obtained as a brownish liquid in 87% yield (315 mg, 0.63 mmol). By contrast to cations **4–21**, compound **22** exhibits no solubility in water and excellent solubility in diethyl ether. ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.91 (t, J = 7.0 Hz, 3H, H-12); 1.01 (t, J = 7.3 Hz, 3H, H-26); 1.28–1.37 (m, 14H, H-18, H-19, H-20, H-21, H-22, H-23, H-24); 1.42–1.47 (m, 2H, H-25); 1.55–1.62 (m, 2H, H-11); 1.74–1.80 (m, 2H, H-10); 2.16 (tt, J = 2.4, 7.1 Hz, 2H, H-17); 2.82 (t, J = 7.1 Hz, 2H, H-9); 3.10 (tt, J = 2.4, 6.6 Hz, 2H, H-14); 5.10 (t, J = 6.6 Hz, 2H, H-13); 8.27 (ddd, J = 1.6, 6.2, 7.8 Hz, 1H, H-3); 8.37 (ddd, J = 0.6, 1.6, 8.0 Hz, 1H, H-5); 8.76 (dt, J = 1.5, 7.9 Hz, 1H, H-4); 9.23 (ddd, J = 0.6, 1.5, 6.2 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.75 (C-26), 14.30 (C-12), 18.87 (C-17), 19.97 (C-9), 20.68 (C-14), 22.70 (C-11), 23.27 (C-25), 29.33 (C-19), 29.47 (C-20), 29.99 (C-21), 30.23 (C-22), 30.24 (C-10), 30.27 (C-23), 30.30 (C-24), 32.57 (C-18), 59.61 (C-13), 72.74 (C-7), 74.52 (C-15), 85.88 (C-16), 111.93 (C-8), 127.30 (C-3), 133.13 (C-5), 138.78 (C-6), 146.55 (C-4), 147.45 (C-2). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 w, 638 vs, 1030 vs, 1165 s, 1275 vs, 1380 w, 1431 w, 1445 w, 1462 m, 1509 s, 1573 m, 1619 m, 2226 s, 2857 s, 2930 vs, 2960 s, 3091 w. MS (ESI) m/z (%): 352 [(M-OTf)$^+$] (100). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{25}H_{38}N$) calc.: 352.2999, found: 352.2999.

1-(3-Butynyl)-2-(phenylethynyl)pyrimidinium trifluoromethanesulfonate (25).



But-3-ynyl trifluoromethanesulfonate (246 mg, 1.22 mmol, 2.7 equiv) was added dropwise at room temperature to a solution of compound **24** (83 mg, 0.46 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (4.5 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 18 h at 40 °C. The reaction mixture was cooled to room temperature and solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **25** was obtained as an orange solid in 97% yield (169 mg, 0.44 mmol). mp 97–99 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 2.82 (t, J = 2.7 Hz, 1H, H-10); 3.31 (dt, J = 2.7, 6.7 Hz, 2H, H-8); 5.31 (t, J = 6.7 Hz, 2H, H-7); 7.64–7.68 (m, 2H, H-15); 7.75–7.79 (m, 1H, H-16); 7.96–7.99 (m, 2H, H-14); 8.44 (dd, J = 4.8, 6.4 Hz, 1H, H-3); 9.65 (dd, J = 1.9, 4.8 Hz, 1H, H-4); 9.68 (dd, J = 1.9, 6.4 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 19.97 (C-8), 58.67 (C-7), 75.01 (C-10), 78.97 (C-9), 81.52 (C-11), 105.38 (C-12), 119.19 (C-13), 123.11 (C-3), 130.15 (C-15), 133.55 (C-16), 134.22 (C-14), 147.17 (C-6), 154.82 (C-2), 166.03 (C-4). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 w, 575 w, 639 s, 686 w, 815 w, 872 vw, 924 vw, 999 w, 1030 vs, 1069 vw, 1168 m, 1175 m, 1263 s, 1279 vs, 1428 w, 1445 w, 1474 m, 1500 s, 1557 s, 1606 m, 2128 vw, 2198 m, 2208 s, 2220 m, 2236 m, 3066 w, 3089 w, 3306 w. MS (ESI) m/z (%): 233 [(M-OTf)$^+$] (100). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{16}H_{13}N_2$) calc.: 233.1073, found: 233.1073.

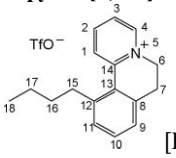
1-(3-Butynyl)-2-((4-(dimethylamino)phenyl)ethynyl)pyridinium trifluoromethanesulfonate (28).



But-3-ynyl trifluoromethanesulfonate (30 mg, 0.15 mmol, 0.9 equiv) was added dropwise at room temperature to a solution of compound **27** (37 mg, 0.17 mmol, 1 equiv) in freshly distilled CH_2Cl_2 (2 mL) prepared in a round bottomed flask pre-purged with Ar (3x). The mixture was stirred under Ar for 1 min at room temperature, and then 18 h at room temperature. Solvent was evaporated *in vacuo*. The crude product was washed with Et_2O (3x) and dried *in vacuo*. The compound **28** was obtained as a red solid in 98% yield (70 mg, 0.17 mmol). mp 187–188 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 2.75 (t, J = 2.7 Hz, 1H, H-10); 3.15 (s, 6H, H-17); 3.23 (dt, J = 2.7, 6.7 Hz, 2H, H-8); 5.17 (t, J = 6.7 Hz, 2H, H-7); 6.88–6.90 (m, 2H, H-15); 7.68–7.70 (m, 2H, H-14); 8.12 (ddd, J = 1.5, 6.3, 7.7 Hz, 1H, H-3); 8.35 (ddd, J = 0.7, 1.5, 8.1 Hz, 1H, H-5); 8.68 (ddd, J = 1.5, 7.7, 8.1 Hz, 1H, H-4); 9.15 (ddd, J = 0.7, 1.5, 6.3 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 20.03 (C-8), 40.01 (C-17), 58.82 (C-7), 74.44 (C-10), 79.04 (C-9), 81.28 (C-11), 104.79 (C-12), 112.65 (C-15), 112.96 (C-13), 125.76 (C-3), 131.95 (C-5), 135.40 (C-14), 139.46 (C-16), 145.81 (C-4), 146.84 (C-2), 153.53 (C-6). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 w, 573 w, 638 m, 822 m, 943 w, 1010 w, 1029 s, 1066 w, 1145 s, 1162 m, 1175 m, 1258 s, 1270 s, 1282 s, 1317 w, 1378 m, 1416 vw, 1444 w, 1503 w, 1531 m, 1562 s, 1603 s, 1619 w, 2174 vs, 2203 w, 3077 w, 3231 w, 3308 w. MS (ESI) m/z (%): 275 [(M-OTf)$^+$] (38), 259 (70), 221 (100), 207 (63), 158 (18). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{19}H_{19}N_2$) calc.: 275.1543, found: 275.1539.

[2+2+2] Cycloaddition

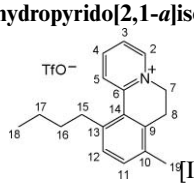
11-Butyl-6,7-dihydropyrido[2,1-*a*]isoquinolinium trifluoromethanesulfonate (5).



$[Rh(PPh_3)_3Cl]$ (33 mg, 0.04 mmol, 9.8 mol %) and compound **4** (131 mg, 0.36 mmol, 1 equiv) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Freshly degassed DMF (9 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 1 h at 80 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 13 cm, CH_2Cl_2–MeOH 7 : 1). The compound **5** was obtained as a brownish liquid in 93% yield (131 mg, 0.34 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.96 (t, J = 7.3 Hz, 3H, H-18); 1.45 (m, 2H, H-17); 1.76–1.82 (m, 2H, H-16); 3.08 (m, 2H, H-15); 3.39 (m, 2H, H-7); 4.95 (m, 2H, H-6); 7.45 (ddt, J = 1.0, 1.6, 7.2 Hz, 1H, H-9); 7.60 (ddt, J = 1.6, 7.8 Hz, 1H, H-11); 7.63 (dd, J = 7.2, 7.8 Hz, 1H, H-10); 8.15 (ddd, J = 1.4, 6.1,

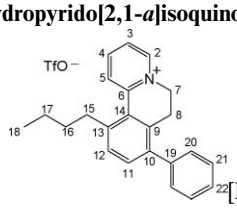
7.6 Hz, 1H, H-3); 8.48 (dd, J = 1.4, 8.2 Hz, 1H, H-1); 8.77 (ddd, J = 1.5, 7.6, 8.2 Hz, 1H, H-2); 9.23 (ddq, J = 0.7, 1.5, 6.1 Hz, 1H, H-4). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 14.00 (C-18), 23.26 (C-17), 28.81 (C-7), 33.99 (C-15), 34.10 (C-16), 56.26 (C-6), 126.20 (C-3), 126.65 (C-9), 127.24 (C-13), 128.96 (C-1), 131.35 (C-11), 133.36 (C-10), 139.58 (C-8), 143.63 (C-12), 146.15 (C-2), 146.68 (C-4), 149.49 (C-14). ^{15}N NMR (61 MHz, $(CD_3)_2CO$): δ = 175.3 (*N*-5). IR ($CHCl_3$): ṽ (cm^{-1}) = 518 m, 574 w, 638 vs, 694 vw, 1030 vs, 1106 w, 1163 s, 1170 s, 1263 vs, 1275 vs, 1300 s, 1381 w, 1437 w, 1475 w, 1509 s, 1569 w, 1584 m, 1598 w, 1627 m, 3090 w. MS (ESI) m/z (%): 238 [(M-OTf)$^+$] (100). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{17}H_{20}N$) calc.: 238.1590, found: 238.1588.

11-Butyl-8-methyl-6,7-dihydropyrido[2,1-*a*]isoquinolinium trifluoromethanesulfonate (14).



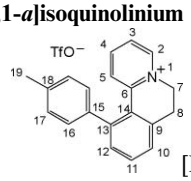
$[Ir(cod)Cl]_2$ (11 mg, 0.02 mmol, 5.5 mol %), dppe (14 mg, 0.03 mmol, 11.2 mol %) and compound **6** (115 mg, 0.31 mmol, 1 equiv) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Freshly degassed DMF (3 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 19 h at 80 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 7 cm, CH_2Cl_2–MeOH 12 : 1). The compound **14** was obtained as a brownish liquid in 60% yield (74 mg, 0.18 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.94 (t, J = 7.4 Hz, 3H, H-18); 1.39–1.45 (m, 2H, H-17); 1.73–1.79 (m, 2H, H-16); 2.43 (s, 3H, H-19); 3.03–3.06 (m, 2H, H-15); 3.32–3.35 (m, 2H, H-8); 4.95 (bt, J = 6.3 Hz, 2H, H-7); 7.50 (d, J = 8.0 Hz, 1H, H-12); 7.52 (d, J = 8.0 Hz, 1H, H-11); 8.14 (ddd, J = 1.4, 6.2, 7.6 Hz, 1H, H-3); 8.43 (dd, J = 1.4, 8.5 Hz, 1H, H-5); 8.75 (ddd, J = 1.5, 7.6, 8.5 Hz, 1H, H-4); 9.23 (ddq, J = 0.7, 1.5, 6.2 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 14.00 (C-18), 18.90 (C-19), 23.26 (C-17), 25.65 (C-8), 33.86 (C-15), 34.21 (C-16), 55.76 (C-7), 126.02 (C-3), 127.41 (C-14), 129.12 (C-5), 130.74 (C-12), 134.15 (C-10), 135.02 (C-11), 138.22 (C-9), 141.04 (C-13), 145.91 (C-4), 146.25 (C-2), 149.94 (C-6). IR ($CHCl_3$): ṽ (cm^{-1}) = 518 m, 574 w, 638 vs, 690 vw, 901 vw, 1030 vs, 1108 w, 1165 s, 1265 vs, 1275 vs, 1382 w, 1403 w, 1457 m, 1486 m, 1510 s, 1555 w, 1574 m, 1589 w, 1627 m, 3089 w. MS (ESI) m/z (%): 252 [(M-OTf)$^+$] (7), 208 (20), 174 (17), 167 (25), 158 (23), 128 (18), 126 (100), 117 (55), 112 (70), 103 (37). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{18}H_{22}N$) calc.: 252.1747, found: 252.1745.

11-Butyl-8-phenyl-6,7-dihydropyrido[2,1-*a*]isoquinolinium trifluoromethanesulfonate (15).



$[Rh(PPh_3)_3Cl]$ (9 mg, 0.01 mmol, 5.5 mol %) and compound **7** (77 mg, 0.18 mmol, 1 equiv) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (5 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 24 h at 80 °C. Another portion of $[Rh(PPh_3)_3Cl]$ (8.5 mg, 0.009 mmol, 5.2 mol %) was added as a solution in degassed DMF (1 mL) and the reaction mixture was stirred another 24 h at 100 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 12 cm, CH_2Cl_2–MeOH 12 : 1). The compound **15** was obtained as a brownish liquid in 85% yield (70 mg, 0.15 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.98 (t, J = 7.3 Hz, 3H, H-18); 1.47 (m, 2H, H-17); 1.82–1.87 (m, 2H, H-16); 3.13 (m, 2H, H-15); 3.32 (bt, J = 6.2 Hz, 2H, H-8); 4.86 (m, 2H, H-7); 7.45–7.51 (m, 3H, H-20, H-22); 7.54–7.57 (m, 2H, H-21); 7.66 (d, J = 8.0 Hz, 1H, H-11); 7.71 (bt, J = 8.0 Hz, 1H, H-12); 8.19 (ddd, J = 1.4, 6.1, 7.7 Hz, 1H, H-3); 8.54 (bdd, J = 1.4, 8.3 Hz, 1H, H-5); 8.81 (ddd, J = 1.6, 7.7, 8.3 Hz, 1H, H-4); 9.26 (ddt, J = 0.7, 1.5, 6.1 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 14.03 (C-18), 23.33 (C-17), 27.61 (C-8), 33.98 (C-15), 34.19 (C-16), 56.13 (C-7), 126.35 (C-3), 128.09 (C-14), 128.75 (C-22), 129.38 (C-5), 129.46 (C-20), 130.09 (C-21), 131.09 (C-12), 134.35 (C-11), 137.20 (C-10), 139.62 (C-9), 139.96 (C-19), 142.83 (C-13), 146.04 (C-4), 146.29 (C-2), 149.90 (C-6). IR ($CHCl_3$):ṽ (cm^{-1}) = 518 m, 574 m, 638 vs, 703 s, 919 vw, 1030 vs, 1076 w, 1112 w, 1165 s, 1274 vs, 1381 w, 1399 w, 1444 m, 1458 m, 1476 m, 1509 s, 1560 w, 1573 m, 1593 vw, 1627 m, 3062 w, 3087 w. MS (ESI) m/z (%): 314 [(M-OTf)$^+$] (100), 280 (11). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{23}H_{24}N$) calc.: 314.1903, found: 314.1903.

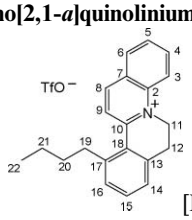
11-*p*-Tolyl-6,7-dihydropyrido[2,1-*a*]isoquinolinium trifluoromethanesulfonate (16).



$[Rh(PPh_3)_3Cl]$ (14 mg, 0.02 mmol, 11 mol %) and compound **8** (56 mg, 0.14 mmol, 1 equiv) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (4 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 2 h at 80 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 8.5 cm, CH_2Cl_2–MeOH 10 : 1). The compound **16** was obtained as a brownish solid in 88% yield (52 mg, 0.12 mmol). mp 125–127 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 2.42 (t, J = 0.8 Hz, 3H, H-19); 3.53 (m, 2H, H-8); 5.13 (m, 2H, H-7); 7.30–7.32 (m, 2H, H-17); 7.38–7.40 (m, 2H, H-16); 7.53 (ddd, J = 0.5, 1.4, 8.4 Hz, 1H, H-5); 7.53 (ddt, J = 0.9, 1.3, 7.5 Hz, 1H, H-10); 7.58 (ddt, J = 0.6, 1.3, 7.7 Hz, 1H, H-12); 7.77 (t, J = 7.6 Hz, 1H, H-11); 7.98 (ddd, J = 1.4, 6.2, 7.6 Hz, 1H, H-3); 8.25 (ddd, J = 1.5, 7.6, 8.4 Hz, 1H, H-4); 9.16 (ddq, J = 0.7, 1.5, 6.2 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 21.13 (C-19), 28.57 (C-8), 56.24 (C-7), 125.87 (C-14), 125.94 (C-3), 128.22 (C-10), 129.96 (C-5), 130.13 (C-16), 130.80

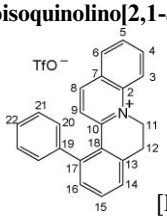
(C-17), 132.23 (C-12), 133.72 (C-11), 137.98 (C-15), 139.33 (C-18), 140.33 (C-9), 143.57 (C-13), 144.50 (C-4), 146.14 (C-2), 150.28 (C-6). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 487 w, 517 w, 574 w, 638 s, 660 vw, 722 w, 752 w, 764 w, 799 m, 828 w, 935 vw, 1031 s, 1115 w, 1154 s, 1263 vs, 1274 vs, 1387 vw, 1405 vw, 1446 w, 1456 w, 1473 w, 1510 m, 1570 w, 1585 w, 1592 w, 1609 vw, 1627 w, 3025 m, 3053 m, 3090 m. MS (ESI) *m/z* (%): 272 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{20}H_{18}N$) calc.: 272.1434, found: 272.1434.

11-Butyl-6,7-dihydroisoquinolino[2,1-*a*]quinolinium trifluoromethanesulfonate (17).



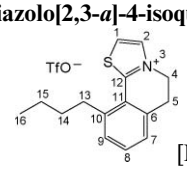
[Rh(PPh$_3$)$_3$Cl] (22 mg, 0.02 mmol, 9.8 mol %) and compound **9** (101 mg, 0.25 mmol, 1 equiv) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (5 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 48 h at 90 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 11 cm, CH_2Cl_2–MeOH 10 : 1). The compound **17** was obtained as a brownish liquid in 72% yield (77 mg, 0.18 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.89 (t, J = 7.4 Hz, 3H, H-22); 1.38 (m, 2H, H-21); 1.72–1.78 (m, 2H, H-20); 3.08 (m, 2H, H-19); 3.44 (t, J = 6.3 Hz, 2H, H-12); 5.28 (bt, J = 6.3 Hz, 2H, H-11); 7.49 (bdd, J = 1.6, 8.1 Hz, 1H, H-14); 7.63 (bdd, J = 1.6, 7.6 Hz, 1H, H-16); 7.68 (t, J = 7.8 Hz, 1H, H-15); 8.06 (ddd, J = 0.9, 7.0, 8.1 Hz, 1H, H-5); 8.31 (ddd, J = 1.6, 7.0, 9.1 Hz, 1H, H-4); 8.47 (d, J = 8.8 Hz, 1H, H-9); 8.49 (bdd, J = 1.6, 8.1 Hz, 1H, H-6); 8.79 (bdq, J = 0.7, 9.1 Hz, 1H, H-3); 9.26 (bd, J = 8.8 Hz, 1H, H-8). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.97 (C-22), 23.31 (C-21), 28.50 (C-12), 34.18 (C-19), 34.29 (C-20), 48.91 (C-11), 119.46 (C-3), 124.81 (C-9), 126.21 (C-14), 128.74 (C-18), 129.37 (C-7), 130.34 (C-5), 131.29 (C-6), 131.53 (C-16), 134.40 (C-15), 136.23 (C-4), 139.71 (C-13), 140.47 (C-2), 144.67 (C-17), 146.05 (C-8), 153.58 (C-10). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 485 vw, 518 w, 546 vw, 574 w, 638 s, 688 vw, 712 vw, 838 w, 871 w, 1030 vs, 1057 vw, 1154 m, 1165 m, 1272 vs, 1320 vw, 1379 w, 1438 w, 1468 w, 1479 w, 1524 m, 1567 w, 1589 w, 1600 m, 1621 w, 2864 w, 2875 w, 2934 w, 2962 w. MS (ESI) *m/z* (%): 288 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{21}H_{22}N$) calc.: 288.1747, found: 288.1748.

11-Phenyl-6,7-dihydroisoquinolino[2,1-*a*]quinolinium trifluoromethanesulfonate (18).



[Rh(PPh$_3$)$_3$Cl] (6 mg, 0.01 µmol, 9.7 mol %) and compound **10** (30 mg, 0.07 mmol, 1 equiv) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (2 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 20 h at 90 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 10 cm, CH_2Cl_2–MeOH 10 : 1). The compound **18** was obtained as a brownish liquid in 79% yield (25 mg, 0.06 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 3.61 (t, J = 6.3 Hz, 2H, H-12); 5.51 (t, J = 6.3 Hz, 2H, H-11); 7.44–7.54 (m, 5H, H-20, H-21, H-22); 7.55 (d, J = 8.8 Hz, 1H, H-9); 7.70 (ddt, J = 0.7, 1.3, 7.7 Hz, 1H, H-14); 7.75 (dq, J = 0.9, 7.5 Hz, 1H, H-16); 7.88 (t, J = 7.6 Hz, 1H, H-15); 8.05 (ddd, J = 0.8, 7.0, 8.1 Hz, 1H, H-5); 8.33 (ddd, J = 1.5, 7.0, 9.1 Hz, 1H, H-4); 8.36 (ddt, J = 1.5, 8.1 Hz, 1H, H-6); 8.74 (bdd, J = 0.7, 8.8 Hz, 1H, H-8); 8.85 (dq, J = 0.8, 9.1 Hz, 1H, H-3). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 28.28 (C-12), 48.85 (C-11), 119.56 (C-3), 125.74 (C-9), 127.40 (C-18), 128.00 (C-16), 129.11 (C-7), 129.59 (C-22), 130.11 (C-20), 130.43 (C-5), 130.59 (C-21), 131.15 (C-6), 132.35 (C-14), 134.70 (C-15), 136.01 (C-4), 140.28 (C-2), 140.89 (C-13), 140.89 (C-19), 144.06 (C-8), 144.53 (C-17), 153.96 (C-10). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 482 vw, 518 w, 545 w, 574 w, 638 s, 686 w, 703 m, 835 w, 865 w, 1001 vw, 1030 vs, 1052 vw, 1075 vw, 1155 s, 1165 s, 1273 vs, 1322 w, 1429 w, 1439 w, 1452 w, 1466 w, 1477 w, 1497 vw, 1523 m, 1566 w, 1577 w, 1592 m, 1604 m, 1620 w, 3063 w. MS (ESI) *m/z* (%): 308 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{23}H_{18}N$) calc.: 308.1434, found: 308.1432.

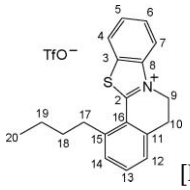
10-Butyl-5,6-dihydrothiazolo[2,3-*a*]-4-isoquinolinium trifluoromethanesulfonate (19).



[Rh(PPh$_3$)$_3$Cl] (14 mg, 0.02 mmol, 4.8 mol %) and compound **11** (118 mg, 0.32 mmol, 1 equiv.) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Freshly distilled EtOH (9 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 24 h at 80 °C. The reaction mixture was concentrated *in vacuo*. The resultant residue was dissolved in EtOAc and extracted with H_2O (3x). H_2O layers were combined and solvent was evaporated. The compound **19** was obtained as a brownish liquid in 74% yield (94 mg, 0.24 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.02 (t, J = 7.4 Hz, 3H, H-16); 1.59 (m, 2H, H-15); 1.73–1.79 (m, 2H, H-14); 3.16 (m, 2H, H-13); 3.54 (m, 2H, H-5); 4.93 (m, 2H, H-4); 7.53 (dq, J = 1.0, 7.5 Hz, 1H, H-7); 7.57 (ddt, J = 0.7, 1.3, 7.8 Hz, 1H, H-9); 7.70 (t, J = 7.7 Hz, 1H, H-8); 8.48 (d, J = 3.9 Hz, 1H, H-1), 8.63 (ddt, J = 3.9 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 14.04 (C-16), 23.25 (C-15), 28.48 (C-5), 32.98 (C-14), 35.02 (C-13), 49.61 (C-4), 122.96 (C-1), 123.53 (C-11), 127.87 (C-7), 131.34 (C-9), 134.88 (C-8), 137.34 (C-6), 137.68 (C-2), 143.42 (C-10), 164.18 (C-12). ^{15}N NMR (61 MHz, $(CD_3)_2CO$): δ = 175.24 (*N*-3). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 534 w, 574 w, 638 s, 694 vw, 1030 vs, 1165 s, 1265 vs, 1276 vs, 1381 w, 1435 w, 1449 w, 1474 w, 1547 m, 1582 w, 1596 w, 3113 w, 3139 w. MS (ESI) *m/z* (%): 244 [(M-OTf)$^+$] (100),

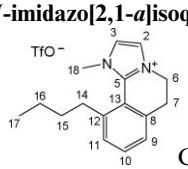
224 (6), 193 (6). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{15}H_{18}NS$) calc.: 244.1154, found: 244.1154.

1-Butyl-5,6-dihydro-11-thia-6a-azoniabenzo[*a*]fluorene trifluoromethanesulfonate (20).



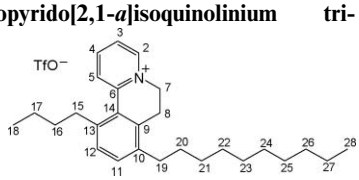
$[Rh(PPh_3)_3Cl]$ (7 mg, 0.01 mmol, 10.9 mol %) and compound **12** (27 mg, 0.06 mmol, 1 equiv) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (2 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 20 h at 80 °C. Progress of the reaction was checked by NMR. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 12 cm, CH_2Cl_2–MeOH 14 : 1). The compound **20** was obtained as a red liquid in 59% yield (17 mg, 0.04 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 1.03 (t, J = 7.4 Hz, 3H, H-20); 1.62 (m, 2H, H-19); 1.80–1.86 (m, 2H, H-18); 3.30 (m, 2H, H-17); 3.68–3.71 (m, 2H, H-10); 5.13 (m, 2H, H-9); 7.62 (dq, J = 1.1, 7.5 Hz, 1H, H-14); 7.64 (ddt, J = 0.6, 1.3, 7.8 Hz, 1H, H-12); 7.80 (t, J = 7.6 Hz, 1H, H-13); 7.96 (ddd, J = 1.0, 7.2, 8.2 Hz, 1H, H-5); 8.07 (ddd, J = 1.2, 7.2, 8.6 Hz, 1H, H-6); 8.50 (dt, J = 0.8, 8.6 Hz, 1H, H-7); 8.59 (ddd, J = 0.7, 1.2, 8.2 Hz, 1H, H-4). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 14.09 (C-20), 23.30 (C-19), 28.12 (C-10), 33.46 (C-18), 35.17 (C-17), 46.14 (C-9), 117.39 (C-7), 123.67 (C-16), 124.91 (C-4), 128.04 (C-14), 129.62 (C-5), 130.49 (C-3), 130.93 (C-6), 131.89 (C-12), 136.16 (C-13), 138.86 (C-11), 141.13 (C-8), 145.15 (C-15), 167.79 (C-2). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 426 w, 496 vw, 517 m, 574 w, 638 vs, 722 w, 998 vw, 1030 vs, 1058 vw, 1082 vw, 1105 w, 1163 s, 1200 m, 1271 vs, 1346 m, 1381 w, 1421 w, 1435 w, 1444 m, 1455 m, 1469 m, 1498 m, 1585 m, 1597 m, 3069 w, 3097 w. MS (ESI) *m/z* (%): 294 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{19}H_{20}NS$) calc.: 294.1311, found: 294.1311.

10-Butyl-1-methyl-5,6-dihydro-1*H*-imidazo[2,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (21).



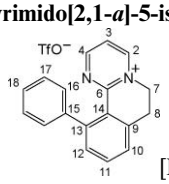
Compound **13** (30 mg, 0.08 mmol, 1 equiv.), $[IrCl(cod)]_2$ (3 mg, 0.01 mmol, 5.5 mol %) and dppe (3 mg, 0.01 mmol, 9.3 mol %) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (2.2 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 19 h at 80 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 5 cm, CH_2Cl_2–MeOH 10 : 1). The compound **21** was obtained as a yellow liquid in 87% yield (27 mg, 0.07 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.87 (t, J = 7.3 Hz, 3H, H-17); 1.28 (m, 2H, H-16); 1.60–1.67 (m, 2H, H-15); 3.23–3.27 (m, 4H, H-7, H-14); 4.06 (s, 3H, H-18); 4.30–4.73 (bs, 2H, H-6); 7.49 (ddt, J = 1.0, 1.3, 7.2 Hz, 1H, H-9); 7.63 (ddt, J = 0.6, 1.6, 7.9 Hz, 1H, H-11); 7.66 (dd, J = 7.2, 7.9 Hz, 1H, H-10); 7.86 (d, J = 2.1 Hz, 1H, H-3); 7.96 (d, J = 2.1 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 13.99 (C-17), 22.92 (C-16), 30.92 (C-7), 34.33 (C-14), 34.49 (C-15), 38.69 (C-18), 46.15 (C-6), 120.44 (C-13), 122.95 (C-2), 125.12 (C-3), 127.00 (C-9), 130.18 (C-11), 133.32 (C-10), 140.63 (C-12), 142.40 (C-8), 143.63 (C-5). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 518 m, 574 w, 638 vs, 707 m, 1031 vs, 1093 w, 1100 w, 1164 s, 1274 vs, 1381 w, 1423 w, 1437 w, 1465 m, 1521 m, 1576 m, 1586 w, 1597 w, 3133 w. MS (ESI) *m/z* (%): 241 [(M-OTf)$^+$] (75), 197 (100), 183 (57). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{16}H_{21}N_2$) calc.: 241.1699, found: 241.1696.

11-Butyl-8-decyl-6,7-dihydropyrido[2,1-*a*]isoquinolinium trifluoromethanesulfonate (23).



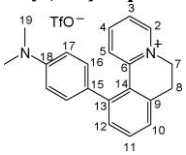
$[Ir(cod)Cl]_2$ (3 mg, 0.01 mmol, 8 mol %), dppe (3 mg, 0.01 mmol, 13 mol %) and compound **22** (28 mg, 0.06 mmol, 1 equiv.) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (1.6 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 20 h at 80 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.0 cm, plug height 8 cm, CH_2Cl_2–MeOH 15 : 1). The product was dissolved in Et_2O and filtered. The solvent was evaporated. The compound **23** was obtained as a brownish liquid in 86% yield (25 mg, 0.05 mmol). By contrast to cations **4**–**21**, compound **23** exhibits no solubility in water and excellent solubility in diethyl ether. ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 0.90 (t, J = 7.2 Hz, 3H, H-28); 0.94 (t, J = 7.4 Hz, 3H, H-18); 1.27–1.36 (m, 12H, H-21, H-22, H-23, H-24, H-25, H-26, H-27); 1.39–1.47 (m, 2H, H-17); 1.62–1.68 (m, 2H, H-20); 1.74–1.80 (m, 2H, H-16); 2.78–2.82 (m, 2H, H-19); 3.02–3.06 (m, 2H, H-15); 3.38–3.40 (m, 2H, H-8); 4.94 (bt, J = 6.2 Hz, 2H, H-7); 7.54 (s, 1H, H-11); 7.54 (s, 1H, H-12); 8.14 (ddd, J = 1.4, 6.2, 7.7 Hz, 1H, H-3); 8.43 (bdd, J = 1.4, 8.3 Hz, 1H, H-5); 8.75 (ddd, J = 1.5, 7.7, 8.3 Hz, 1H, H-4); 9.24 (ddq, J = 0.7, 1.5, 6.2 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 14.01 (C-18), 14.30 (C-28), 23.26 (C-17), 23.27 (C-27), 25.44 (C-8), 29.99 (C-26), 30.13 (C-25), 30.13 (C-24), 30.27 (C-23), 30.27 (C-22), 31.13 (C-21), 32.56 (C-20), 33.25 (C-19), 33.89 (C-15), 34.21 (C-16), 55.89 (C-7), 126.01 (C-3), 127.60 (C-14), 129.21 (C-5), 130.81 (C-12), 134.42 (C-11), 137.69 (C-10), 138.83 (C-9), 141.15 (C-13), 145.89 (C-4), 146.19 (C-2), 150.01 (C-6). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 414 vw, 518 m, 543 vw, 574 w, 638 s, 690 w, 842 vw, 1030 vs, 1166 s, 1263 vs, 1275 vs, 1380 w, 1407 vw, 1485 w, 1600 vw, 1510 m, 1574 m, 1626 m, 2857 m, 2873 m, 2929 s, 2959 m, 3087 w. MS (ESI) *m/z* (%): 378 [(M-OTf)$^+$] (100). HRMS (ESI) *m/z*: [(M-OTf)$^+$] ($C_{27}H_{40}N$) calc.: 378.3155, found: 378.3153.

11-Phenyl-6,7-dihydropyrimido[2,1-*a*]-5-isoquinolinium trifluoromethanesulfonate (26).



$[Rh(PPh_3)_3Cl]$ (15 mg, 0.02 mmol, 9.7 mol %) and compound **25** (61 mg, 0.16 mmol, 1 equiv.) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (7 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 20 h at 80 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 9 cm, CH_2Cl_2–MeOH 10 : 1). The compound **26** was obtained as a brownish liquid in 82% yield (54 mg, 0.13 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 3.60–3.63 (m, 2H, H-8); 5.19–5.22 (m, 2H, H-7); 7.37–7.43 (m, 5H, H-16, H-17, H-18); 7.58 (ddt, J = 0.6, 1.3, 7.7 Hz, 1H, H-10); 7.66 (ddt, J = 0.8, 1.3, 7.6 Hz, 1H, H-12); 7.85 (t, J = 7.6 Hz, 1H, H-11); 8.06 (dd, J = 4.7, 6.3 Hz, 1H, H-3); 9.00 (dd, J = 2.0, 4.7 Hz, 1H, H-4); 9.49 (ddt, J = 0.8, 2.0 6.3 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 27.71 (C-8), 55.96 (C-7), 121.72 (C-3), 125.73 (C-14), 128.14 (C-12), 128.23 (C-18), 129.04 (C-16), 129.58 (C-17), 132.56 (C-10), 135.05 (C-11), 141.93 (C-15), 142.20 (C-13), 145.89 (C-9), 153.74 (C-2), 158.01 (C-6), 164.33 (C-4). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 482 vw, 518 w, 542 vw, 575 w, 623 w, 639 s, 702 m, 810 w, 1001 vw, 1030 vs, 1076 vw, 1094 vw, 1166 s, 1260 vs, 1273 vs, 1319 w, 1423 w, 1436 w, 1455 w, 1471 w, 1484 s, 1498 w, 1556 s, 1576 w, 1593 m, 1619 m, 3066 w, 3083 w. MS (ESI) m/z (%): 259 [(M-OTf)$^+$] (100). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{18}H_{15}N_2$) calc.: 259.1230, found: 259.1229.

11-(4-(Dimethylamino)phenyl)-6,7-dihydropyrido[2,1-*a*]isoquinolinium trifluoromethanesulfonate (29).



$[Rh(PPh_3)_3Cl]$ (11 mg, 0.01 mmol, 10.2 mol %) and compound **28** (47 mg, 0.11 mmol, 1 equiv.) were added to a Schlenk tube. The tube was sealed with a septum, and the system was purged with Ar (3x). Degassed DMF (3 mL) was added *via* needle and syringe. A balloon with acetylene was connected to the Schlenk tube, and argon atmosphere was changed to atmosphere of acetylene. The reaction mixture was stirred for 24 h at 80 °C. The reaction mixture was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 1.5 cm, plug height 10 cm, CH_2Cl_2–MeOH 10 : 1). The compound **29** was obtained as an orange liquid in 89% yield (44 mg, 0.10 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) = 2.90 (s, 6H, H-19); 3.48 (bt, J = 6.8 Hz, 2H, H-8); 5.10 (bt, J = 6.8 Hz, 2H, H-7); 6.80–6.82 (m, 2H, H-17); 7.29–7.32 (m, 2H, H-16); 7.54 (ddt, J = 1.0, 1.3, 7.6 Hz, 1H, H-12); 7.55 (ddt, J = 0.7, 1.3, 7.6 Hz, 1H, H-10); 7.61 (bdd, J = 1.4, 8.4 Hz, 1H, H-5); 7.71 (t, J = 7.6 Hz, 1H, H-11); 7.94 (ddd, J = 1.4, 6.2, 7.6 Hz, 1H, H-3); 8.26 (ddd, J = 1.6, 7.6, 8.4 Hz, 1H, H-4); 9.12 (ddq, J = 0.7, 1.6, 6.2 Hz, 1H, H-2). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) = 28.72 (C-8), 40.23 (C-19), 56.18 (C-7), 113.41 (C-17), 125.45 (C-14), 125.61 (C-3), 127.22 (C-12), 127.75 (C-15), 129.75 (C-5), 131.05 (C-16), 131.87 (C-10), 133.60 (C-11), 140.23 (C-9), 144.12 (C-13), 144.19 (C-4), 145.88 (C-2), 150.97 (C-6), 151.62 (C-18). IR ($CHCl_3$): $\tilde{\nu}$ (cm^{-1}) = 476 vw, 518 m, 544 vw, 561 vw, 574 m, 638 vs, 823 m, 948 w, 1005 vw, 1030 vs, 1064 w, 1135 m, 1163 s, 1170 s, 1264 vs, 1276 vs, 1363 m, 1428 w, 1445 m, 1473 m, 1508 s, 1526 s, 1552 w, 1567 m, 1580 m, 1593 m, 1610 s, 1626 m, 2811 w, 3091 w. MS (ESI) m/z (%): 301 [(M-OTf)$^+$] (100). HRMS (ESI) m/z: [(M-OTf)$^+$] ($C_{21}H_{21}N_2$) calc.: 301.1699, found: 301.1699.

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14 Experimental details in ESI‡.

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