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

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

**Organic & Biomolecular Chemistry**

**ELECTRONIC SUPPLEMENTARY INFORMATION**

![Scheme](image)

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1) Materials

Demineralized water obtained from the Water Purification Facility at the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., was used unless otherwise stated. Demineralization was accomplished via filtration through ion exchange columns (Lewatit S100 for catex column, Lewatit MP500 for anex column) in a demineralization ion exchange station type ID-PP and IDKP (Kavalier, Votice, Czech Republic). Degassed solvents were obtained via the freeze-pump-thaw method. The solvent was frozen under Ar, and then thawed under vacuum. This process was repeated (3×). Finally the thawed solvent was purged with argon. Unless otherwise stated, all other starting materials and reagents were obtained from commercial suppliers and used without further purification.

d$_6$-Acetone (Merck, 99.9%, 100021)

Acetone, cyclohexane, dichloromethane, diethyl ether, ethyl acetate, hexanes, and toluene were purchased from Penta, Czech Republic (www.pentachemicals.eu)

Acetylene (Dissolved, Messer Technogas, UN1001)

1,2-Bis(diphenylphosphino)ethane (Aldrich, 97%, 1663-45-2)

[1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), [Pd(dppf)Cl$_2$], (Aldrich, 72287-26-4)

Bis(triphenylphosphine)nickel(0)dicarbonyl, [Ni(PPh$_3$)$_2$(CO)$_2$] (Fluka, ≥98.0%, 13007-90-4)

2-Bromo-1-methyl-1H-imidazole (Aldrich, 95%, 16681-59-7)

2-Bromopyridine (Alfa Aesar, 99%, 109-04-6)

2-Bromopyrimidine (Alfa Aesar, 98+, 4595-60-2)

2-Bromothiazole (Aldrich, 98%, 3034-53-5)

3-Butyn-1-ol (Alfa Aesar, 98+, 927-74-2)

Celite (Fluka, 512 medium, 91053-39-3)

2-Chlorobenzothiazole (Aldrich, 99%, 615-20-3)

Chloro(1,5-cyclooctadiene)iridium(I) dimer, [Ir(cod)Cl]$_2$, (Strem Chemicals, 99%, 12112-67-3)

Chloro(1,5-cyclooctadiene)(pentamethylcyclopentadienyl)ruthenium(II), [(Cp*Ru(cod)Cl] (Strem, 98%, 92390-26-6)

Chloro(pentamethylcyclopentadienyl)ruthenium(II) tetramer, [Cp*RuCl]$_4$, (Aldrich, 113860-07-4)

2-Chloroquinoline (Alfa Aesar, 99%, 612-62-4)
CuI (Aldrich, 99.999%, 7681-65-4)
Dicarbonylcyclopentadienyl cobalt(I), [CpCo(CO)₂] (Aldrich, 12078-25-0)
1,2-Dichloroethane (Aldrich, 107-06-2)
Dichlorobis(triphenylphosphine)palladium(II), [Pd(PPh₃)₂Cl₂] (Aldrich, 99.99%, 13965-03-2)
N,N-Dimethylformamide (Aldrich, 99.8%, 68-12-2)
Et₃N (Alfa Aesar, 99%, 121-44-8)
Ethynylbenzene (Aldrich, 98%, 536-74-3)
4-Ethynyl-N,N-dimethylaniline (Aldrich, 97%, 17573-94-3)
2-Ethynylpyridine (Aldrich, 98%, 1945-84-2)
EtOH (Riedel-de Haën, absolute, 64-17-5)
1-Hexyne (Alfa Aesar, 98+, 693-02-7)
4-Iodotoluene (Aldrich, 99%, 624-31-7)
Na₂SO₄ (Riedel-de Haën, anhydrous, 7757-82-6)
Tetrakis(triphenylphosphine)palladium(0), [Pd(PPh₃)₄] (Alfa Aesar, 99.8%, 14221-01-3)
3-Pentyn-1-ol (Fluka, 97+, 10229-10-4)
4-Phenyl-3-butyn-1-ol (prepared according to literature procedure[1])
Pyridine (Alfa Aesar, anhydrous 99.5+, 110-86-1)
3-Tetradecyn-1-ol (Alfa Aesar, 97%, 55182-74-6)
Trifluoromethanesulfonic anhydride (Alfa Aesar, 98%, 358-23-6)
Trifluoromethanesulfonic anhydride (Acros Organics, 98+, 358-23-6)
Tris(triphenylphosphine)rhodium(I)chloride, [Rh(PPh₃)₃Cl] (Fluka, 97+, 14694-95-2)
2) Procedures and analytical data - Sonogashira coupling

Based on a literature procedure[2].

2-(1-Hexynyl)pyridine (3)
CAS: 16344-82-4 (ref. 2, 3)

\[
\begin{align*}
\text{Br} & \quad \text{PdCl}_2(\text{PPh}_3)_2, \text{CuI} \\
\text{Et}_3\text{N} & \quad \text{PdCl}_2(\text{PPh}_3)_2 \quad \text{CuI} \\
\text{PdCl}_2(\text{PPh}_3)_2 (308 \text{ mg}, 0.44 \text{ mmol}, 5 \text{ mol %}) \text{ and CuI (84 mg, 0.44 mmol, 5 mol %) were} \\
\text{added in this order to a Schlenk flask. The flask was purged with Ar (3x). Freshly degassed} \\
\text{Et}_3\text{N (20 mL), 2-bromopyridine (840 }\mu\text{L, 8.80 mmol, 1 equiv) and 1-hexyne (1.5 mL,} \\
\text{13.14 mmol, 1.5 equiv) were added in this order. The mixture was stirred under Ar 1 min at} \\
\text{RT, and then 30 h at 80 °C. The reaction mixture was then filtered through Celite and the} \\
\text{filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was} \\
\text{concentrated in vacuo and the resultant residue was purified by flash chromatography on} \\
\text{silica gel (column diameter 6 cm, plug height 8 cm, hexane:ethyl acetate 6:1). Compound 3} \\
\text{was obtained as a brownish liquid in 94 % yield (1.32 g, 8.30 mmol).}
\end{align*}
\]

Analytical data for compound 3

\(\text{H NMR (600 MHz, (CD}_3\text{)_2CO): }\delta (\text{ppm}) = 0.98 \text{ (t, J = 7.3 Hz, 3H, H-12);} \)

\(1.49 - 1.57 \text{ (m, 2H, H-11); 1.60 - 1.66 \text{ (m, 2H, H-10); 2.49 \text{ (t, J = 7.1 Hz, 2H,} } \)

\(\text{H-9); 7.32 \text{ (ddd, J = 1.2, 4.8, 7.6 Hz, 1H, H-3); 7.45 \text{ (dt, J = 1.1, 7.9 Hz, 1H,} } \)

\(\text{H-5); 7.77 \text{ (dt, J = 1.8, 7.7 Hz, 1H, H-4); 8.56 \text{ (bd, J = 4.8 Hz, 1H, H-2).} } \)

\(\text{C NMR (151 MHz, (CD}_3\text{)_2CO): }\delta (\text{ppm}) = 13.81 \text{ (C-12), 19.15 \text{ (C-9), 22.56} } \)

\(\text{C-11), 31.25 \text{ (C-10), 81.62 \text{ (C-8), 90.61 \text{ (C-7), 123.28 \text{ (C-3), 127.61 \text{ (C-5),} } } \)

\(136.90 \text{ (C-4), 144.82 \text{ (C-6), 150.64 \text{ (C-2).} } \)

\(\text{IR (CCl}_4): }\tilde{\nu} (\text{cm}^{-1}) = 400 \text{ m, 629 w, 711 w, 886 w, 989 w, 1047 w, 1091 w,} \)
1148 m, 1269 m, 1329 w, 1380 s, 1428 vs, 1465 vs, 15 62 m, 2837 w, 2864 m, 2874 m, 2934 s, 2960 s, 3056 w, 3082 w.
MS (EI⁺) m/z (%): 159 [M⁺] (47), 144 (35), 130 (100), 117 (93), 89 (34), 63 (26), 51 (25), 39 (23).
HRMS (EI+) m/z: [M⁺] (C₁₁H₁₃N) calc.: 159.1048, found: 159.1050.

2-(p-Tolylethynyl)pyridine
CAS: 80221-14-3 (ref. 4)

4-Iodotoluene (115 mg, 0.53 mmol, 1.2 equiv), PdCl₂(PPh₃)₂ (16 mg, 0.02 mmol, 5.1 mol %) and CuI (9 mg, 0.05 mmol, 11.2 mol %) were added in this order to a reaction tube. The tube was purged with Ar (3x). 2-Ethynylpyridine (44 µL, 0.44 mmol, 1.0 equiv) and freshly distilled Et₃N (1.2 mL) were added in this order. The mixture was stirred under MW (100 W, 100 psi) 5 min at 60 °C. The reaction mixture was filtered through Celite and the filtercake was washed with a mixture of hexane: ethyl acetate 1:1. The filtrate was concentrated in vacuo and the resultant residue was purified by flash flash chromatography on silica gel (column diameter 1.5 cm, plug height 7 cm, hexane:ethyl acetate 7:1). 2-(p-Tolylethynyl)pyridine was obtained as a yellowish solid in 96 % yield (81 mg, 0.42 mmol).
Analytical data for 2-(p-tolylethynyl)pyridine

$^1$H NMR (600 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 2.41 (bs, 3H, H-13); 7.31 (m, 2H, H-11); 7.40 (ddddd, $J = 1.2, 4.9, 7.6$ Hz, 1H, H-3); 7.53 (m, 2H, H-10); 7.62 (dt, $J = 1.1, 7.8$ Hz, 1H, H-5); 7.85 (dt, $J = 1.8, 7.7$ Hz, 1H, H-4); 8.64 (ddd, $J = 1.0$, 1.8, 4.9 Hz, 1H, H-2).

$^{13}$C NMR (151 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 21.43 (C-13), 89.19 (C-8), 89.26 (C-7), 120.09 (C-9), 123.78 (C-3), 127.92 (C-5), 130.19 (C-11), 132.52 (C-10), 137.12 (C-4), 140.24 (C-12), 144.27 (C-6), 150.94 (C-2).

$^{15}$N NMR (61 MHz, (CD$_3$)$_2$CO): $\delta = 59.1$ (N-1).

IR (CHCl$_3$): $\tilde{\nu}$ (cm$^{-1}$) = 400 w, 517 m, 541 w, 889 vw, 947 vw, 992 w, 1021 w, 1045 w, 1090 w, 1118 vw, 1156 m, 1184 vw, 1282 w, 1314 w, 1380 vw, 1409 vw, 1429 s, 1464 vs, 1511 s, 1584 vs, 1607 vw, 2223 m, 3033 w, 3056 w, 3084 w

MS (ESI) m/z (%): 194 [M+H$^+$] (100).

HRMS (ESI) m/z: [M+H$^+$] (C$_{14}$H$_{12}$N) calc.: 194.0964, found: 194.0962.

m.p. = 66-67 °C

2-(1-Hexynyl)quinoline

CAS: 70437-01-3 (ref. 3)

PdCl$_2$(PPh$_3$)$_2$ (38 mg, 0.06 mmol, 6.0 mol %), CuI (11 mg, 0.06 mmol, 6.1 mol %) and 2-chloroquinoline (150 mg, 0.91 mmol, 1 equiv) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). 1-Hexyne (150 µL, 1.31 mmol, 1.4 equiv) and freshly degassed Et$_3$N (3.5 mL) were added in this order. The mixture was stirred under Ar 1 min at
RT, and then 23 h at 70 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate 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, hexane:ethyl acetate 13:1). 2-(1-Hexynyl)quinoline was obtained as a yellow liquid in 91 % yield (174 mg, 0.83 mmol).

**Analytical data for 2-(1-hexynyl)quinoline**

\[
\text{\textsuperscript{1}H NMR (600 MHz, (CD\textsubscript{3})\textsubscript{2}CO): } \delta (\text{ppm}) = 1.01 (t, J = 7.3 Hz, 3H, H-16); 1.54 – 1.60 (m, 2H, H-15); 1.65 – 1.71 (m, 2H, H-14); 2.56 (t, J = 7.1 Hz, 2H, H-13); 7.55 (d, J = 8.4 Hz, 1H, H-3); 7.62 (ddd, J = 1.2, 6.8, 8.1 Hz, 1H, H-6); 7.80 (ddd, J = 1.4, 6.8, 8.5 Hz, 1H, H-7); 7.97 (ddt, J = 0.6, 1.4, 8.1 Hz, 1H, H-5); 8.01 (ddt, J = 0.8, 1.2, 8.5 Hz, 1H, H-8); 8.32 (dd, J = 1.1, 8.4 Hz, 1H, H-4).
\]

\[
\text{\textsuperscript{13}C NMR (151 MHz, (CD\textsubscript{3})\textsubscript{2}CO): } \delta (\text{ppm}) = 13.82 (\text{C-16}), 19.26 (\text{C-13}), 22.61 (\text{C-15}), 31.20 (\text{C-14}), 82.23 (\text{C-11}), 91.72 (\text{C-12}), 125.08 (\text{C-3}), 127.62 (\text{C-6}), 127.83 (\text{C-9}), 128.56 (\text{C-5}), 129.73 (\text{C-8}), 130.67 (\text{C-7}), 136.87 (\text{C-4}), 144.90 (\text{C-2}), 149.03 (\text{C-10}).
\]

IR (CHCl\textsubscript{3}): \(\tilde{\nu} (\text{cm}^{-1}) = 477 \text{ m}, 617 \text{ w}, 831 \text{ vs}, 870 \text{ w}, 974 \text{ w}, 955 \text{ w}, 1024 \text{ w}, 1120 \text{ m}, 1142 \text{ w}, 1237 \text{ m}, 1260 \text{ m}, 1276 \text{ m}, 1307 \text{ m}, 1323 \text{ m}, 1355 \text{ w}, 1355 \text{ w}, 1379 \text{ w}, 1425 \text{ s}, 1460 \text{ m}, 1466 \text{ m}, 1501 \text{ vs}, 1555 \text{ m}, 1596 \text{ vs}, 1618 \text{ m}, 2227 \text{ m}, 3042 \text{ w}, 3064 \text{ w}, 3088 \text{ vw}, 3104 \text{ vw}.

MS (El\textsuperscript{+}) m/z (%): 209 [M\textsuperscript{+}] (61), 208 (50), 194 (30), 180 (100), 167 (90), 140 (30).

HRMS (El\textsuperscript{+}) m/z: [M\textsuperscript{+}] (C\textsubscript{15}H\textsubscript{15}N) calc.: 209.1204, found: 209.1208.
2-(Phenylethynyl)quinoline

CAS: 70437-00-2 (ref. 5)

\[
\begin{align*}
\text{Cl} & \quad \text{PdCl}_2(\text{PPh}_3)_2, \text{CuI} \\
+ & \quad \text{Et}_3\text{N}
\end{align*}
\]

\[\text{C}_{17}\text{H}_{11}\text{N} \quad 229.276\]

\[\text{PdCl}_2(\text{PPh}_3)_2 (38 \text{ mg, 0.05 mmol, 5.7 mol %), CuI (13 mg, 0.07 mmol, 7 mol %) and 2-}
\text{chloroquinoline (155 mg, 0.95 mmol, 1 equiv)} \text{ were added in this order to a Schlenk flask.}
\]

\[\text{The flask was purged with Ar (3x). Ethynylbenzene (120 \mu\text{L}, 1.09 mmol, 1.2 equiv) and}
\text{freshly degassed Et}_3\text{N (4 mL) were added in this order. The mixture was stirred under Ar}
\text{1 min at RT, and then 18 h at 80 °C and consequently 2 h at 100 °C. The reaction mixture was}
\text{then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl}
\text{acetate 1:1. The filtrate was concentrated in vacuo and the resultant residue was purified by}
\text{flash chromatography on silica gel (column diameter 2.5 cm, plug height 8 cm, hexane:ethyl}
\text{acetate 9:1). 2-(Phenylethynyl)quinoline was obtained as a yellowish liquid in 79 % yield}
\text{(171 mg, 0.75 mmol).}
\]

\text{Analytical data for 2-(phenylethynyl)quinoline}

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (600 MHz, (CD}_3\text{)_2CO):} & \quad \delta (\text{ppm}) = 7.52 - 7.55 (\text{m, 3H, H-15, H-16}); \\
& \quad 7.68 (\text{ddd, J = 1.5, 6.9, 8.2 Hz, 1H, H-5}); \\
& \quad 7.72 - 7.74 (\text{m, 2H, H-14}); \\
& \quad 7.74 (\text{d, J = 8.4 Hz, 1H, H-9}); \\
& \quad 7.85 (\text{ddd, J = 1.5, 6.9, 8.5 Hz, 1H, H-4}); \\
& \quad 8.02 (\text{ddt, J = 0.6, 1.5, 8.2 Hz, 1H, H-6}); \\
& \quad 8.08 (\text{ddt, J = 0.8, 1.5, 8.5 Hz, 1H, H-3}); \\
& \quad 8.41 (\text{dd, J = 1.2, 8.4 Hz, 1H, H-8}).
\end{align*}
\]

\[
\begin{align*}
\text{\textsuperscript{13}C NMR (151 MHz, (CD}_3\text{)_2CO):} & \quad \delta (\text{ppm}) = 89.60 (\text{C-12}), \\
& \quad 90.37 (\text{C-11}), \\
& \quad 122.95 (\text{C-13}), \\
& \quad 125.16 (\text{C-9}), \\
& \quad 128.06 (\text{C-5}), \\
& \quad 128.06 (\text{C-7}), \\
& \quad 128.68 (\text{C-6}), \\
& \quad 129.60 (\text{C-15}), \\
& \quad 129.92 (\text{C-16}), \\
& \quad 130.24 (\text{C-3}), \\
& \quad 130.93 (\text{C-4}), \\
& \quad 132.79 (\text{C-14}), \\
& \quad 137.14 (\text{C-8}), \\
& \quad 144.23 (\text{C-10}), \\
& \quad 149.20 (\text{C-2}).
\end{align*}
\]
IR (CHCl$_3$): $\tilde{\nu}$ (cm$^{-1}$) = 477 w, 549 w, 620 w, 690 s, 831 vs, 870 w, 918 w, 955 w, 974 w, 1000 w, 1028 w, 1017 w, 1070 w, 1115 m, 1147 m, 1180 vw, 1312 m, 1338 w, 1375 w, 1425 m, 1444 m, 1459 w, 1491 m, 1501 vs, 1553 m, 1572 w, 1594 vs, 1617 m, 2195 w, 2211 m, 2222 m, 2245 w, 3040 w, 3063 w, 3085 w, 3102 w.

MS (ESI) m/z (%): 230 [M+H$^+$] (100).

HRMS (ESI) m/z: [M+H$^+$] (C$_{17}$H$_{12}$N) calc.: 230.0964, found: 230.0965.

2-(1-Hexynyl)thiazole

CAS: 174184-05-5 (ref. 2, 6)

CuI (7 mg, 0.04 mmol, 3.3 mol %) and Pd(dppf)Cl$_2$ (20 mg, 0.03 mmol, 2.2 mol %) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Freshly degassed Et$_3$N (5.5 mL), 2-bromothiazole (100 µL, 1.12 mmol, 1 equiv) and 1-hexyne (190 µL, 1.65 mmol, 1.5 equiv) were added in this order. The mixture was stirred under Ar 5 min at RT, and then 6 h at 70 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with hexane. The filtrate was concentrated $\textit{in vacuo}$ and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 4 cm, hexane:ethyl acetate 10:1). 2-(1-Hexynyl)thiazole was obtained as a yellowish liquid in 80 % yield (148 mg, 0.89 mmol).
Analytical data for 2-(1-hexynyl)thiazole

$^1$H NMR (600 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 0.95 (t, $J = 7.3$ Hz, 3H, H-11); 1.46-1.53 (m, 2H, H-10); 1.59-1.64 (m, 2H, H-9); 2.51 (t, $J = 7.1$ Hz, 2H, H-8); 7.62 (d, $J = 3.3$ Hz, 1H, H-3); 7.80 (d, $J = 3.3$ Hz, 1H, H-2).

$^{13}$C NMR (151 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 13.75 (C-11), 19.30 (C-8), 22.56 (C-10), 30.85 (C-9), 74.89 (C-6), 96.34 (C-7), 121.50 (C-3), 144.10 (C-2), 149.49 (C-5).

$^{15}$N NMR (61 MHz, (CD$_3$)$_2$CO): $\delta = 48.7$ (N-1).

IR (CCl$_4$): $\tilde{\nu}$ (cm$^{-1}$) = 620 s, 719 vs, 874 m, 885 m, 1050 m, 1059 s, 1132 vs, 1318 m, 1325 m, 1380 m, 1415 m, 1481 vs, 1602 w, 2233 s, 3088 w, 3122 w.

MS (ESI) m/z (%): 166 [M+H$^+$] (100).

HRMS (ESI) m/z: [M+H$^+$] (C$_9$H$_{12}$NS) calc.: 166.0685, found: 166.0682.

2-(1-Hexynyl)benzothiazole

CAS: 330436-78-7 (ref. 6)

PdCl$_2$(PPh$_3$)$_2$ (15 mg, 0.02 mmol, 5.4 mol %) and CuI (5 mg, 0.02 mmol, 6.3 mol %) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Freshly degassed (1.5 mL), 2-chlorobenzothiazole (50 µL, 0.38 mmol, 1 equiv) and 1-hexyne (66 µL, 0.58 mmol, 1.5 equiv) were added in this order. The mixture was stirred under Ar 1 min at RT, and then 26 h at 80 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with mixture hexane/EtOAc 1:1. The filtrate was concentrated in vacuo and the resultant residue was purified by flash chromatography on silica gel (column diameter

SI 10
2.5 cm, plug height 7 cm, hexane:ethyl acetate 14:1). 2-(1-Hexynyl)benzothiazole was obtained as a yellow liquid in 67 \% yield (56 mg, 0.26 mmol).

**Analytical data for 2-(1-hexynyl)benzothiazole**

\[
1^1H \text{ NMR (600 MHz, (CD}_3\text{)}_2\text{CO): } \delta (\text{ppm}) = 1.00 (t, J = 7.4 \text{ Hz, 3H, H-14}); 1.52 – 1.60 (m, 2H, H-13); 1.66 – 1.72 (m, 2H, H-12); 2.62 (t, J = 7.1 \text{ Hz, 2H, H-11}); 7.54 (ddd, J = 1.3, 7.2, 8.0 Hz, 1H, H-5); 7.60 (ddd, J = 1.3, 7.2, 8.2 Hz, 1H, H-6); 8.03 (ddd, J = 0.7, 1.3, 8.2 Hz, 1H, H-7); 8.08 (ddd, J = 0.7, 1.3, 8.0 Hz, 1H, H-4).
\]

\[
1^3C \text{ NMR (151 MHz, (CD}_3\text{)}_2\text{CO): } \delta (\text{ppm}) = 13.75 \text{ (C-14), 19.42 (C-11), 22.59 (C-13), 30.72 (C-12), 75.30 (C-10), 99.26 (C-9), 122.51 (C-4), 124.01 (C-7), 127.04 (C-5), 127.54 (C-6), 135.80 (C-3), 149.43 (C-2), 153.85 (C-8).}
\]

IR (CHCl\textsubscript{3}): \( \tilde{\nu} \ (\text{cm}^{-1}) = 441 \text{ m, 611 w, 689 w, 854 vw, 874 w, 927 m, 938 m, 972 w, 997 m, 1015 w, 1106 w, 1127 w, 1161 w, 1245 m, 1283 w, 1313 s, 1365 w, 1381 w, 1433 vs, 1487 s, 1520 vw, 1557 w, 1581 vw, 1592 w, 2230 vs, 3067 w. \)

MS (ESI) m/z (%): 216 [M+H\textsuperscript{+}] (100).

HRMS (ESI) m/z: [M+H\textsuperscript{+}] (C\textsubscript{13}H\textsubscript{14}NS) calc.: 216.0841, found: 216.0841.

**2-(1-Hexynyl)-1-methylimidazole**

CAS: 192063-28-8 (ref. 7)

\[
\text{PdCl}_2(\text{PPh}_3)_2, \text{CuI} \quad \text{Et}_3\text{N} \quad \text{C}_{10}\text{H}_{14}\text{N}_2 \quad 162.232
\]

\text{PdCl}_2(\text{PPh}_3)_2 (21 mg, 0.03 mmol, 4.8 mol \%) and CuI (7 mg, 0.04 mmol, 6.2 mol \%) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). 2-Bromo-1-methylimidazole (60 \text{ \mu L}, 0.62 mmol, 1 equiv), 1-hexyne (85 \text{ \mu L}, 0.74 mmol, 1.2 equiv) and freshly degassed Et\textsubscript{3}N (2 mL) were added in this order. The mixture was stirred under Ar 1
min at RT, and then 40 h at 80 °C. The reaction mixture was then filtered through Celite and 
the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was 
concentrated in vacuo and the resultant residue was purified by flash chromatography on 
silica gel (column diameter 2.5 cm, plug height 8 cm, hexane:ethyl acetate 3:1). 2-(1-
Hexynyl)-1-methylimidazole was obtained as a yellow liquid in 69 % yield (69 mg, 0.42 
mmol).

Analytical data for 2-(1-hexynyl)-1-methylimidazole

\[ ^1H \text{NMR (600 MHz, (CD}_3\text{)}_2\text{CO):}\ \delta (ppm) = 0.95 (t, J = 7.3 Hz, 3H, H-10); 1.47-
1.52 (m, 2H, H-9); 1.58-1.63 (m, 2H, H-8); 2.48 (t, J = 7.0 Hz, 2H, H-7); 3.71 
(s, 3H, H-3); 6.90 (bs, 1H, H-2); 7.10 (bs, 1H, H-1). \]

\[ ^13C \text{NMR (151 MHz, (CD}_3\text{)}_2\text{CO):}\ \delta (ppm) = 13.77 (C-10), 19.18 (C-7), 22.53 
(C-9), 31.18 (C-8), 33.41 (C-3), 71.63 (C-5), 93.98 (C-6), 122.25 (C-1), 129.29 
(C-2), 133.46 (C-4). \]

IR (CCl\textsubscript{4}): $\tilde{\nu}$ (cm$^{-1}$) = 704 vs, 809 w, 913 w, 1140 m, 1286 s, 1324 w, 1380 w, 
1409 m, 1474 s, 1513 m, 1582 w, 2243 w, 3115 w.

MS (ESI) m/z (%): 163 [M+H\textsuperscript{+}] (100).

HRMS (ESI) m/z: [M+H\textsuperscript{+}] (C\textsubscript{10}H\textsubscript{15}N\textsubscript{2}) calc.: 163.1230, found: 163.1228.

2-(Phenylethynyl)pyrimidine (24)
CAS: 69696-00-0 (ref. 8)

\[
\begin{align*}
\text{(Br)} & + \text{Ph} & \xrightarrow{\text{PdCl}_2(\text{PPh}_3)_2, \text{CuI}} & \text{Et}_3\text{N} & \text{N} \\
& & & & \text{24}
\end{align*}
\]

C\textsubscript{12}H\textsubscript{8}N\textsubscript{2}
180.205
PdCl$_2$(PPh$_3$)$_2$ (75 mg, 0.11 mmol, 5.1 mol %), CuI (21 mg, 0.11 mmol, 5.4 mol %) and 2-bromopyrimidine (334 mg, 2.10 mmol, 1 equiv) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Ethynylbenzene (230 µL, 2.09 mmol, 1 equiv) and freshly degassed Et$_3$N (3 mL) were added in this order. The mixture was stirred under Ar 1 min at RT, and then 8 h at 80 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was concentrated in vacuo and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 9 cm, hexane:ethyl acetate 3:1). Compound 24 was obtained as a yellowish solid in 76 % yield (288 mg, 1.60 mmol).

**Analytical data for compound 24**

$^1$H NMR (600 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 7.51 (t, $J$ = 4.9 Hz, 1H, H-3); 7.51 - 7.57 (m, 3H, H-10, H-11); 7.70 - 7.72 (m, 2H, H-9); 8.87 (d, $J$ = 4.9 Hz, 2H, H-2, H-4).

$^{13}$C NMR (151 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 86.86 (C-7), 89.31 (C-6), 121.19 (C-3), 122.26 (C-8), 129.65 (C-10), 130.64 (C-11), 133.01 (C-9), 153.86 (C-5), 158.35 (C-2,4).

IR (CHCl$_3$): $\tilde{\nu}$ (cm$^{-1}$) = 544 w, 641 w, 689 s, 807 m, 919 w, 1000 w, 1027 w, 1070 w, 1174 m, 1255 m, 1280 vw, 1329 vw, 1401 w, 1415 vs, 1444 w, 1493 s, 1555 vs, 1566 s, 1578 w, 1600 w, 2188 w, 2204 w, 2230 s, 2279 w, 3041 w, 3086 w.

MS (El$^+$) m/z (%): 180 [M$^+$] (100), 127 (90).

HRMS (El$^+$) m/z: [M$^+$] (C$_{12}$H$_8$N$_2$) calc.: 180.0687, found: 180.0694.

m.p. = 74-76 °C
N,N-Dimethyl-4-(2-pyridinylethynyl)aniline (27)

PdCl$_2$(PPh$_3$)$_2$ (48 mg, 0.07 mmol, 9.4 mol %), CuI (13 mg, 0.07 mmol, 9.4 mol %) and 4-ethynyl-N,N-dimethylaniline (115 mg, 0.79 mmol, 1.1 equiv) were added in this order to a Schlenk flask. The flask was purged with Ar (3x). Freshly degassed Et$_3$N (20 mL) and 2-bromopyridine (70 µL, 0.73 mmol, 1 equiv) were added in this order. The mixture was stirred under Ar 1 min at RT, and then 18 h at 80 °C. The reaction mixture was then filtered through Celite and the filtercake was washed with a mixture of hexane:ethyl acetate 1:1. The filtrate was concentrated *in vacuo* and the resultant residue was purified by flash chromatography on silica gel (column diameter 2.5 cm, plug height 8 cm, hexane:ethyl acetate 3:1). Compound 27 was obtained as a yellow solid in 41 % yield (66 mg, 0.30 mmol).

**Analytical data for compound 27**

$^1$H NMR (600 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 3.05 (s, 6H, H-13); 6.78 - 6.80 (m, 2H, H-11); 7.33 (ddd, J = 1.2, 4.8, 7.5 Hz, 1H, H-3); 7.45 - 7.47 (m, 2H, H-10); 7.55 (dt, J = 1.1, 7.9 Hz, 1H, H-5); 7.80 (dt, J = 1.8, 7.8 Hz, 1H, H-4); 8.60 (ddd, J = 1.0, 1.8, 4.8 Hz, 1H, H-2).

$^{13}$C NMR (151 MHz, (CD$_3$)$_2$CO): $\delta$ (ppm) = 40.10 (C-13), 88.21 (C-7), 91.01 (C-8), 109.29 (C-9), 112.64 (C-11), 123.00 (C-3), 127.39 (C-5), 133.73 (C-10), 136.91 (C-4), 145.06 (C-6), 150.78 (C-2), 151.68 (C-12).

IR (CHCl$_3$): $\tilde{v}$ (cm$^{-1}$) = 400 w, 497 vw, 524 m, 540 w, 628 w, 819 s, 887 vv, 946 m, 991 w, 1006 w, 1046 w, 1064 w, 1091 w, 1130 m, 1152 vs, 1175 w, 1235
m, 1281 w, 1324 w, 1364 s, 1412 vs, 1428 m, 1446 s, 1523 vs, 1561 m, 1583 vs, 1607 vs, 2121 s, 2810 w, 3054 w, 3084 w.

MS (ESI) m/z (%): 223 [M+H]+ (100).

HRMS (ESI) m/z: [M+H]+ (C_{15}H_{15}N_{2}) calc.: 223.1230, found: 223.1230.

m.p. = 92-93 °C

3) Procedures and analytical data - Preparation of triflates from alcohols

The preparation of alkynyl trifluoromethanesulfonates is based on literature procedures\textsuperscript{[9,10]}

**General procedure for preparation of alkynyl trifluoromethanesulfonates**

\[
\text{HO-} \text{R} \xrightarrow{\text{TfO}_{2} \text{pyridine}} \text{R} \text{TiO-} \text{CH}_2\text{Cl}_2
\]

A solution of alkyn-1-ol (1 equiv) and dry pyridine (1 equiv) in freshly distilled CH\textsubscript{2}Cl\textsubscript{2} (1 mL per 1 mmol of the alcohol used) was added dropwise via syringe and needle to a stirring solution of triflic anhydride (1 equiv) in freshly distilled CH\textsubscript{2}Cl\textsubscript{2} (1 mL per 1 mmol of the alcohol used) prepared in a separate Schlenk tube prepurged with Ar (3x) and cooled to 0 °C. The reaction mixture was stirred for a further 1 h at 0 °C. The reaction mixture was warmed to RT and extracted with H\textsubscript{2}O (3x). CH\textsubscript{2}Cl\textsubscript{2} layer was dried with Na\textsubscript{2}SO\textsubscript{4} and filtered through a plug of anhydrous Na\textsubscript{2}SO\textsubscript{4}. The filtercake was washed with CH\textsubscript{2}Cl\textsubscript{2}. The filtrate was concentrated in vacuo at 100 mbar at 25 °C. The triflates were obtained as brownish liquids.

**But-3-ynyl trifluoromethanesulfonate**

**CAS: 32264-79-2 (ref. 11)**

\[\text{TiO-} \text{C} \xrightarrow{\text{CH}_2\text{Cl}_2} \text{R}\]

\[\text{TfO-} \text{C} \xrightarrow{\text{CH}_2\text{Cl}_2} \text{R}\]

\[\text{R} = \text{H, Me, Ph, n-C}_{10}\text{H}_{21}\]

\[^{1}H\text{ NMR (400 MHz, CDCl}_{3}\): } \delta (ppm) = 2.11 (t, J = 2.7 Hz, 1H); 2.73 (td, J = 2.7, 6.7 Hz, 2H); 4.57 (tq, J = 0.5, 6.7 Hz, 2H).

\[^{13}C\text{ NMR (100 MHz, CDCl}_{3}\): } \delta (ppm) = 19.89, 71.77, 73.50, 76.86, 118.61.

B.p. = 55 °C at 2 mbar
d = 1.33
Pent-3-ynyl trifluoromethanesulfonate  
**CAS: 54106-83-1 (ref. 12)**

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta \text{ (ppm)} = 1.78 \text{ (t, J = 2.5 Hz, 3H); 2.67 (tq, J = 2.5, 6.9 Hz, 2H); 4.53 (t, J = 6.9 Hz, 2H).} \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{): } \delta \text{ (ppm)} = 3.28, 20.19, 71.67, 74.41, 79.41, 118.62. \]

B.p. = 65 °C at 2 mbar  
d = 1.28

4-Phenylbut-3-ynyl trifluoromethanesulfonate  
**CAS: 87639-40-5 (ref. 13)**

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta \text{ (ppm)} = 2.97 \text{ (t, J = 6.8 Hz, 2H); 4.66 (tq, J = 0.5, 6.8 Hz, 2H); 7.38 - 7.45 (m, 5H).} \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{): } \delta \text{ (ppm)} = 20.85, 73.84, 82.04, 83.69, 118.64, 122.56, 128.31, 128.41, 131.68. \]

d = 1.34

Tetradec-3-ynyl trifluoromethanesulfonate  

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta \text{ (ppm)} = 0.88 \text{ (t, J = 6.8 Hz, 3H); 1.17 - 1.40 (m, 14 H); 1.42-1.53 (m, 2H); 2.14 (tt, J = 2.3, 7.1 Hz, 2H); 2.69 (tt, J = 2.3, 6.9 Hz, 2H); 4.53 (tq, J = 0.5, 6.9 Hz, 2H).} \]

\[ \text{C NMR (151 MHz, (CD}_3\text{)}_2\text{CO): } \delta \text{ (ppm)} = 14.31, 18.94, 20.51, 23.28, 29.42, 29.45, 29.83, 30.01, 30.22, 30.25, 32.57, 74.54, 77.28, 83.67, 118.92. \]

d = 1.09
4) X-ray analysis

X-ray analysis of
1-(3-Butynyl)-2-(p-tolylethynyl)pyridinium trifluoromethanesulfonate (8)
CCDC 736009

Crystallization is effected via the slow diffusion of diethylether into a solution of the compound 8 in CH₂Cl₂.
C₁₉H₁₆F₃NO₃S, MW = 395.40, m.p. = 166-168 °C.
Unit cell parameters: Space group P2₁/c, a = 7.4866 (2) Å, b = 14.3369 (2) Å, c = 17.3851 (3) Å, β = 100.0166 (9)°.

X-ray analysis of
3-(3-Butynyl)-2-(1-hexynyl)benzothiazolium trifluoromethanesulfonate (12)
CCDC 736010
Crystallization is effected via the slow diffusion of cyclohexane into a solution of the compound 12 in ethylacetate.

C_{18}H_{18}F_{3}NO_{3}S_{2}, MW = 417.47, m.p. = 90-92 °C.
Unit cell parameters: Space group Pca21, a = 12.1750 (2) Å, b = 10.9843 (2) Å, c = 14.5988 (2) Å.

X-ray analysis of 11-p-Tolyl-6,7-dihydropyrido[2,1-a]isoquinolinium trifluoromethanesulfonate (16)
CCDC 736011

Crystallization is effected via the slow diffusion of CCl\textsubscript{4} into a solution of the compound 16 in CH\textsubscript{2}Cl\textsubscript{2}.

C_{21}H_{18}F_{3}NO_{3}S, MW = 421.43, m.p. = 125-127 °C.
Unit cell parameters: Space group C2/c, a = 23.1671 (5) Å, b = 10.5994 (2) Å, c = 15.6896 (3) Å, β = 92.5160 (13)°.
X-ray analysis of
2-(Phenylethynyl)pyrimidine (24)
CCDC 736012

Crystallization is effected via the slow diffusion of hexane into a solution of the compound 24 in diethylether.
C_{12}H_8N_2, MW = 180.21, m.p. = 74-76 °C.
Unit cell parameters: Space group Pna21, a = 23.3925 (2) Å, b = 6.2169 (4) Å, c = 13.0456 (8) Å.

X-ray analysis of
1-(3-Butynyl)-2-(phenylethynyl)pyrimidinium trifluoromethanesulfonate (25)
CCDC 736013

Crystallization is effected via the slow diffusion of diethylether into a solution of the compound 25 in THF.
C_{17}H_{13}F_3N_2O_3S, MW = 382.36, m.p. = 97-99 °C.
Unit cell parameters: Space group P-1, a = 7.4977 (2) Å, b = 10.5242 (2) Å, c = 11.7581 (3) Å, α = 81.4639 (15)°, β = 79.5813 (13)°, γ = 75.5501 (15)°.
5) Electrochemical experiments

Tetrabutylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) and acetonitrile were supplied by Sigma-Aldrich. The indifferent electrolyte n-Bu$_4$NPF$_6$ was re-crystallized and dried under vacuum. Acetonitrile was dried over activated 4Å molecular sieves. Electrochemical measurements were performed using a system for DC polarography, cyclic voltammetry, phase-sensitive AC polarography, AC voltammetry and electrochemical impedance spectroscopy (EIS). It consisted of a fast rise-time potentiostat, a lock-in amplifier (Stanford Research, model SRS830) and a frequency response analyzer (Stanford Research, model SRS760). The instruments were interfaced to a personal computer via an IEEE–interface card (PC–Lab, AdvanTech Model PCL–848) and a data acquisition card (PCL–818) using 12–bit precision for both A/D and D/A conversion. A three-electrode electrochemical cell was used. The reference electrode, Ag|AgCl|1M LiCl, was separated from the test solution by a salt bridge. The potential of the ferrocene/ferrocenium redox couple measured vs our reference electrode was 0.471 V. The working electrode was a valve–operated static mercury electrode (SMDE2, Laboratorní Přístroje, Prague) with an area $2.30 \times 10^{-3}$ cm$^2$ and a computer controlled drop time. The auxiliary electrode was the cylindrical platinum net. Oxygen was removed from the solution by passing a stream of argon saturated with vapors of the solvent. Numerical simulations of voltammograms by the finite difference method were done by means of a freeware program$^{[14]}$

6) References


[14] Nervi, C. Electrochemical Simulation Package, University of Turin,
http://lem.ch.unito.it/chemistry/electrochemistry.html
7) $^1$H and $^{13}$C NMR spectra

![NMR spectra diagram](image)