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HETEROCYCLE POLYCATIONS – SYNTHESES AND REACTIONS OF (OLIGO)PYRIDINIUM AND (OLIGO)IMIDAZOLIUM SALTS

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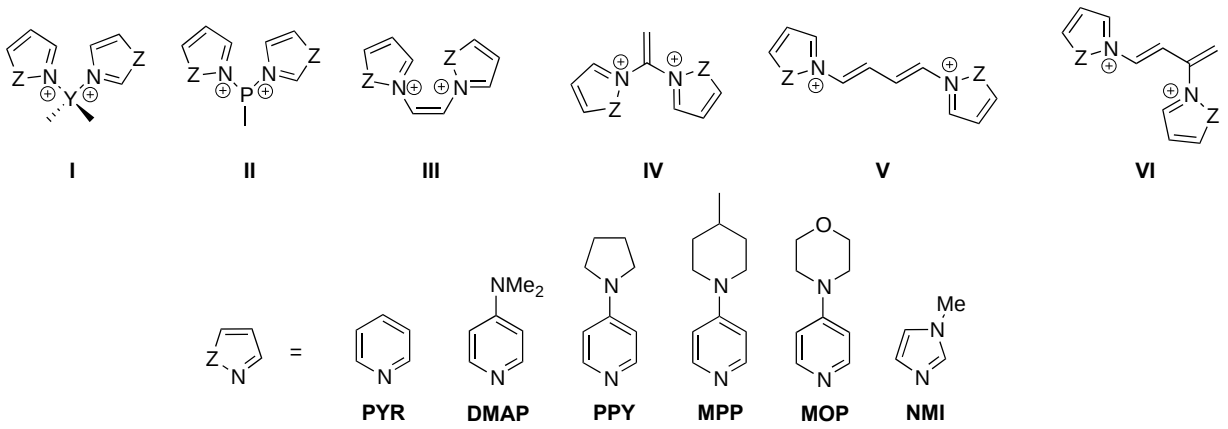
Abstract – The syntheses and chemical transformations of alkanes, phosphanes, alkenes, cycloalkenes, benzenes, naphthalenes, indolizines, pyridines, imidazoles, pyrimidines, pyrazines, pyridazines, purines, porphyrinazines, and porphyrins which are substituted by at least two pyridinium or imidazolium rings are reviewed up to 20-fold pyridinio-substituted systems.

CONTENTS

1. INTRODUCTION

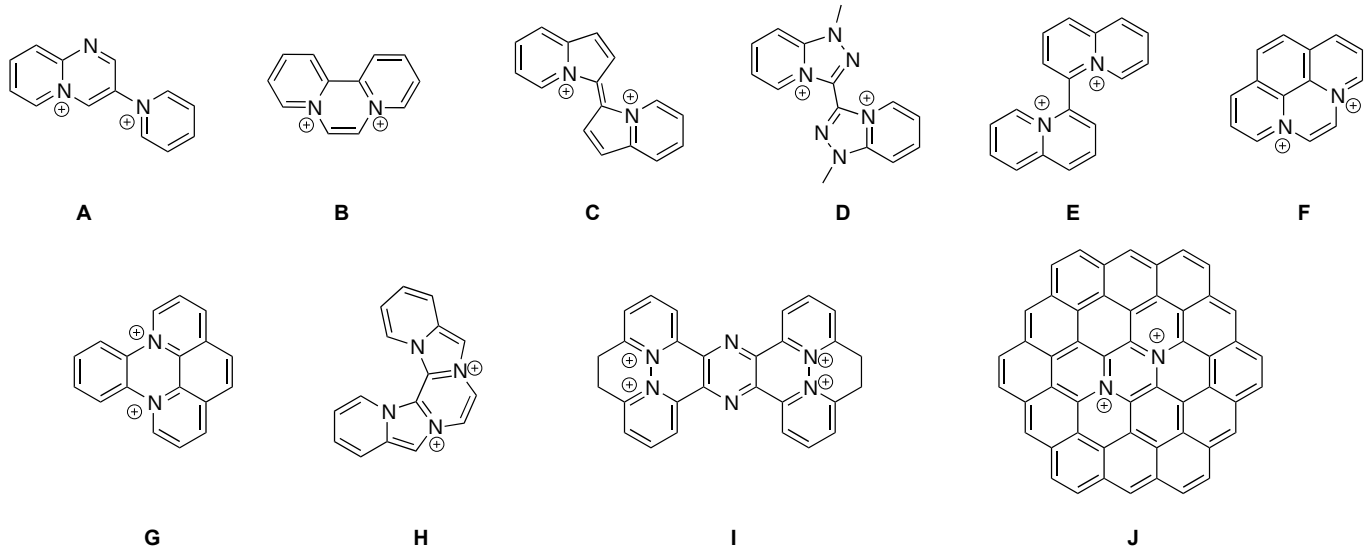
The unanticipated fun chemistry[1] of heterocycle polycations has developed considerably during the last decades and has given synthetic heterocylic chemistry, material science and pharmacology important impetus. Potential semiconductors and novel polymer precursors,[2] photosensitive systems,[3] polycationic oxidants,[4] biologically active compounds such as herbicides,[5] acetylcholinesterase reactivators,[6] and

cholinesterase inhibitors[7] are just few examples of morefold positively charged heteroaromatics with interesting properties. Halitoxin[8] and other polymeric pyridinium alkaloids,[9] cyclostellettamin C,[10] amphitoxin,[11] natural 3-alkylpyridinium polymers,[12] viscosamine,[13] viscosaline,[14] and the pachychalines A-C[15] are examples of heteroaromatic polycations possessing pyridinium rings which have been isolated from marine organisms and which prove that these compounds are relevant to biological processes, too. This review summarizes the syntheses and the chemical properties of heterocycle polycations from the viewpoint of heterocyclic chemistry. It covers di- to undecacationic systems possessing pyridinium and imidazolium rings with at least one of the structure elements **I** – **VI** as well as aza analogs, aromatic, and vinylogous derivatives thereof. Most representatives of this compound class possess hetarenium rings which originate from 4-(dimethylamino)pyridine (DMAP) and 1-methylimidazole (NMI), but pyridine (PYR), 4-(pyrrolidin-1-yl)pyridine (PPY), 4-(4-methylpyridin-1-yl)pyridine (MPP), and 4-(morpholin-1-yl)pyridine (MOP) substituents, among others, have been reported as well (Scheme 1).



Scheme 1

Catalytic chemistry via N-heterocyclic carbenes derived from oligocations as well as the chemistry of morefold charged di-, tri-, tetra-, penta- and higher ring systems such as the pyridinium substituted pyrido[1,2-*a*]pyrimidinium **A**,[16] dipyrido[1,2-*a*:2',1'-*c*]pyrazinediium **B**,[17] 3-(3*H*-indolizinium-3-ylidene)-3*H*-indolizinium **C**,[18] 3,3'-bi-1*H*-*s*-triazolo[4,3-*a*]pyridinium **D**,[19] 4,4'-biquinolizinium **E**,[20] pyrazino[1,2,3,4-*lmn*][1,10]phenanthrolinediium **F**,[21] dipyrido[3,2,1-*de*:1',2',3'-*mn*]phenazinediium **G**,[22] bispyrido-[1',2':3,4]imidazo[1,2-*a*:2',1'-c]pyrazine-6,9-diium **H**,[23] dipyrazino[1,2,3,4-*lmn*:1',2',3',4'-*l*'*m*'*n*']pyrazino-[2,3-*f*:5,6-*f*']di[1,10]phenanthroline-4,7,15,18-tetraium **I**,[24] 18t,18w-diazo-niatripyreno[2,1,10,9,8,7-*defghij*:2',1',10',9',8',7'-*nopqrst*:2",1",10",9",8",7"-*xyza*$_1$*b*$_1$*c*$_1$*d*$_1$]trinaphthylene **J**[25] (Scheme 2) and others is beyond the scope of this review which, nevertheless, cannot be comprehensive. A particular emphasis is placed on the studies of Streitwieser et al.,[1] Weiss et al., and of our group.

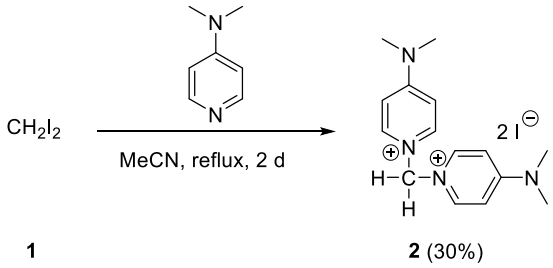


Scheme 2

2. SYNTHESES OF HETEROCYLE POLYCATIONS

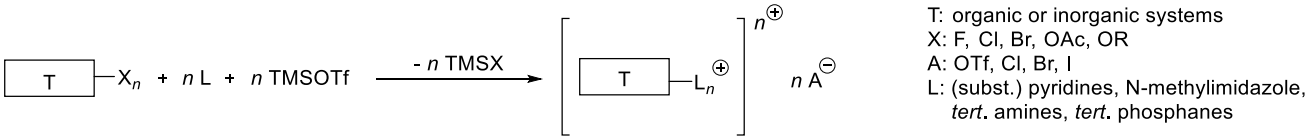
2.1. Syntheses from halogenated alkanes, alkenes and cycloalkenes

Heterocyle polycations are available by nucleophilic substitutions of selected halogenated precursors with nucleophilic heterocycles. Thus diiodomethane **1** reacted with 4-dimethylaminopyridine (DMAP) to give the bis-pyridinium salt **2** (Scheme 3).[26]



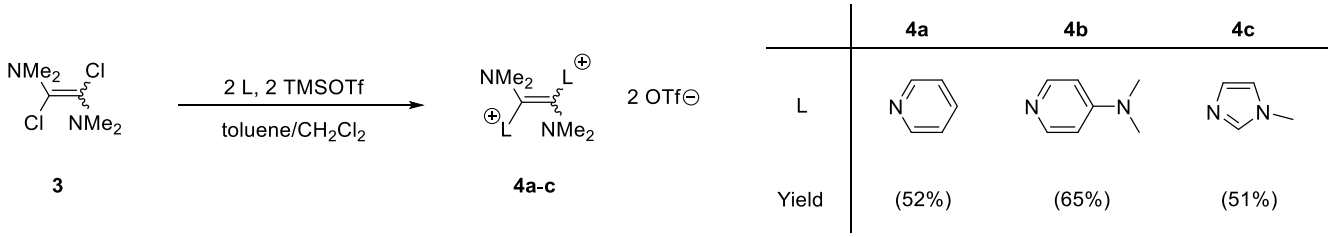
Scheme 3

Numerous interesting heteroaromatic polycations have been prepared applying the SASAPOS protocol developed by Weiss et al. SASAPOS stands for self-activated silyl-assisted polyonio substitution and is schematically depicted in Scheme 4. An organic or inorganic system, which bonds neutral ligands, undergoes a substitution with nucleophiles equivalent to the quantity of the bonding ligands in the presence of the same number of equivalents of trimethylsilyltriflate (TMSOTf). The TMSOTf serves as thermodynamic trap for the leaving groups.[27]



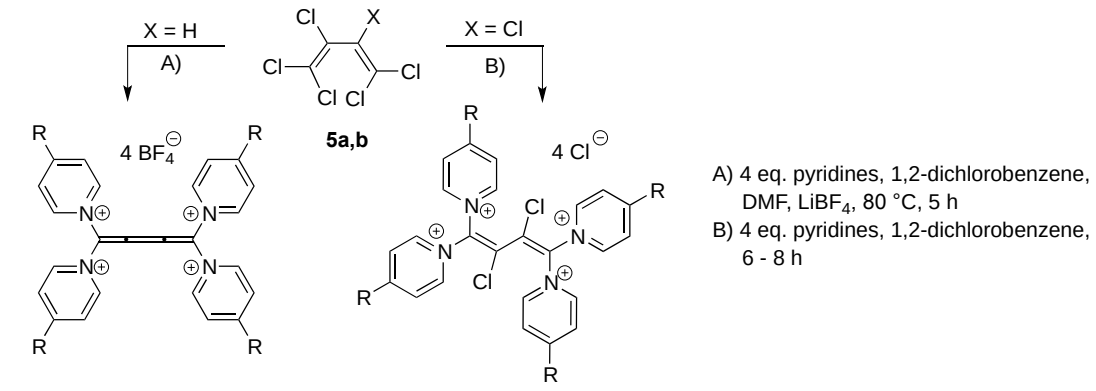
Scheme 4

As first example, the isomeric pair of the dihalogenated linear 1,2-bis(dimethylamino)ethene **3**, which was generated from dimethylformamide, reacted with two equivalents of hetarene and TMSOTf to give the corresponding substitution products **4** (Scheme 5) according to the SASAPOS protocol.[28]



Scheme 5

The syntheses of 1-vinylpyridinium salts including 1,2-di(pyridinium)ethene by an alternative route have been described as well.[29] These compounds have been prepared starting from 1,2-dibromo- and 1,2,3-tribromoalkanes and various pyridines in an SN_2-type reaction on an sp^3 carbon atom.[29] Pentachlorobuta-1,3-diene **5a** and hexachlorobuta-1,3-diene **5b** have been converted into the [3]cumulenes **6a-c** and the tetrakis-pyridinium substituted buta-1,3-dienes **7a-c**[30] which were applied to prepare 2,5-bis-pyridinium substituted 3,4-dichlorothiophenes (Scheme 6).[31]

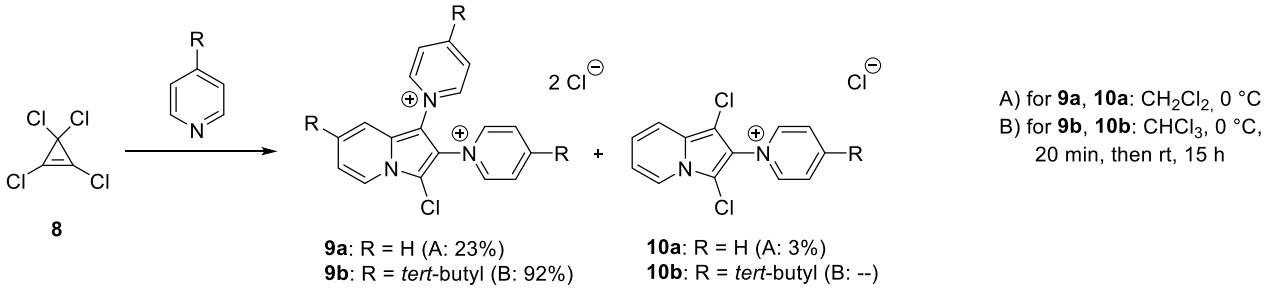


6a: R = NMe_2 (77%)
6b: R = pyrrolidin-1-yl (63%)
6c: R = morpholin-1-yl (69%)

7a: R = NMe_2 (75%)
7b: R = pyrrolidin-1-yl (61%)
7c: R = morpholin-1-yl (67%)

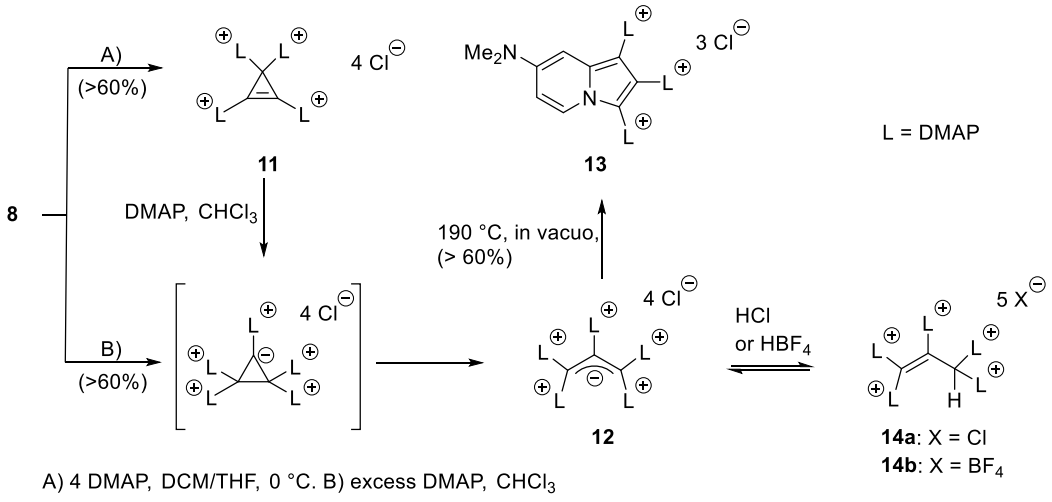
Scheme 6

Tetrachlorocyclopropene (TCCP) **8** reacted under relatively mild reaction conditions with pyridine to give a mixture of the pyridinium salts **9a** and **10a** (Scheme 7). The reaction proceeds through several steps of addition and elimination, followed by ring closure reactions. Analogous reactions were performed with 4-*tert*-butylpyridine, whereupon the bis-pyridinium indolizine **9b** was formed in considerably higher yields.[1,32] The reaction of tetrabromocyclopropene (TBCP) with pyridine resulted, in comparison to TCCP, in the formation of the corresponding bis-pyridinium indolizine as single product. Reduction of **9a** with hydrogen at approximately three bar on platinum dioxide gave a 72:28 mixture of the fully saturated and a partially reduced product possessing an aromatic pyrrole moiety.[1,32]



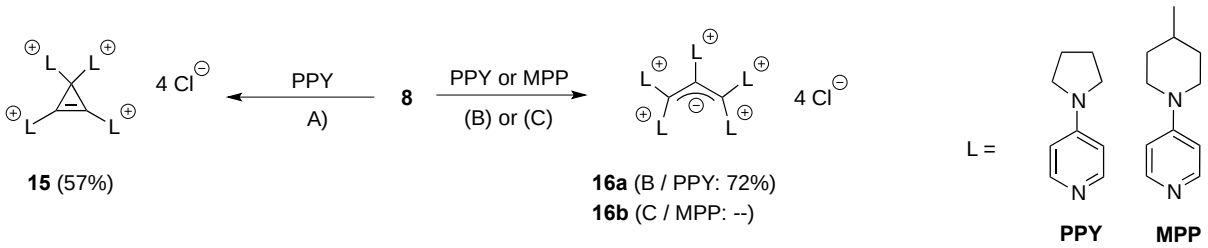
Scheme 7

TCCP **8** was also able to react with four equivalents of DMAP to give the fully substituted polycation **11**. If DMAP was used in excess, the dark red crystalline allylid **12** was formed by ring-cleavage. The latter was also obtained by reaction of **11** with additional DMAP. Furthermore, **12** was converted into a cyclic product **13** on warming, and into its colorless protonated form **14** by treatment with acid (Scheme 8).[33] TBCP reacted in analogy.



Scheme 8

The reaction of TCCP **8** with other N-nucleophiles such as 4-pyrrolidinopyridine (PPY) and 4-(4-methyl-1-piperidinyl)pyridine (MPP), respectively, yielded the fully substituted polycation **15** and the allylides **16a** and **16b** (Scheme 9).[26]



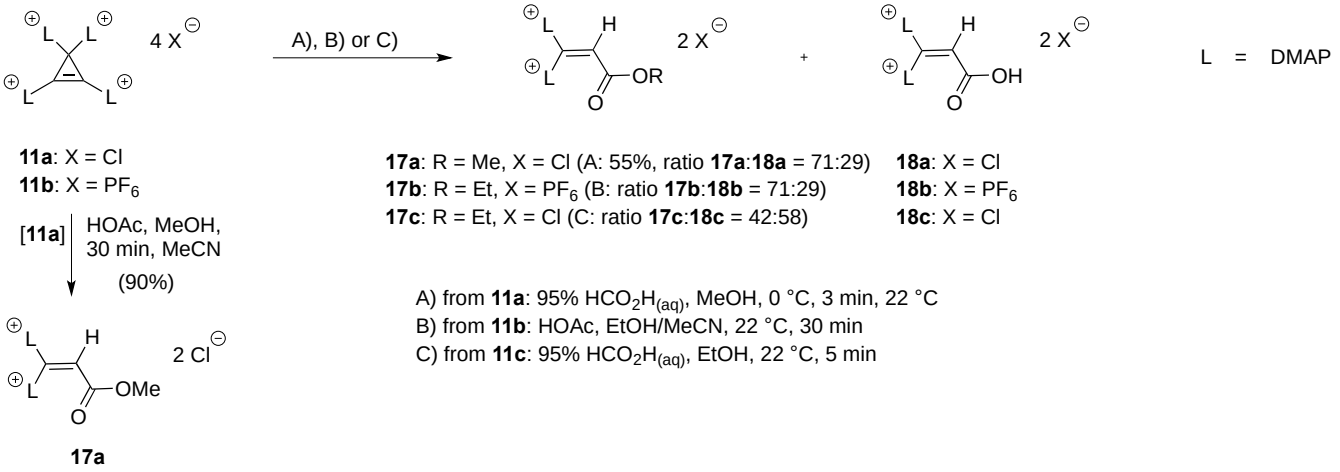
15 (57%)

16a (B / PPY: 72%)
16b (C / MPP: --)

A) PPY, Et_2O / CH_2Cl_2. B) for **16a**: PPY, $CHCl_3$ / Et_2O, 0 °C, N_2-atm., 10 min, rt, 12 h. C) for **16b**: MPP, TCM, 0 °C

Scheme 9

On reaction with the tetracationic cyclopropenes **11** formic acid or acetic acid in the presence of methanol or ethanol led to the formation of the dicationic propenoates **17** and acrylic acids **18**. Under optimized reaction conditions, no mixture was formed but the methyl propenoate **17a** was isolated as single product (Scheme 10).[34]



11a: X = Cl
11b: X = PF_6

[**11a**] HOAc, MeOH, 30 min, MeCN (90%)

2 Cl
OMe

17a

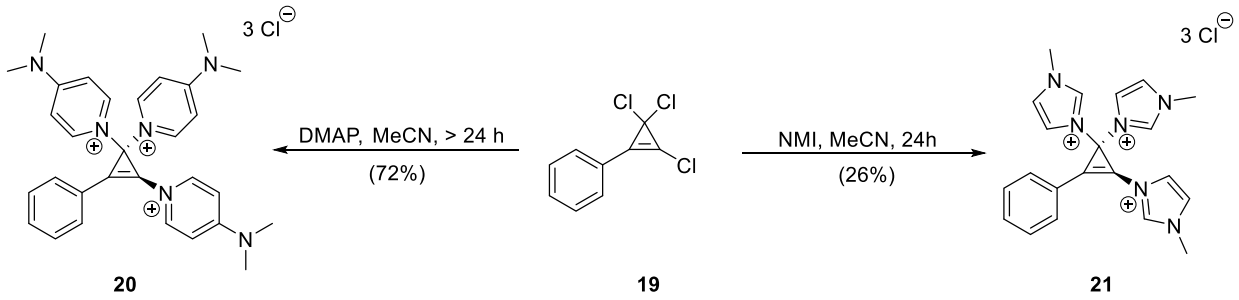
17a: R = Me, X = Cl (A: 55%, ratio **17a**:**18a** = 71:29)
17b: R = Et, X = PF_6 (B: ratio **17b**:**18b** = 71:29)
17c: R = Et, X = Cl (C: ratio **17c**:**18c** = 42:58)

18a: X = Cl
18b: X = PF_6
18c: X = Cl

A) from **11a**: 95% $HCO_2H_{(aq)}$, MeOH, 0 °C, 3 min, 22 °C
B) from **11b**: HOAc, EtOH/MeCN, 22 °C, 30 min
C) from **11c**: 95% $HCO_2H_{(aq)}$, EtOH, 22 °C, 5 min

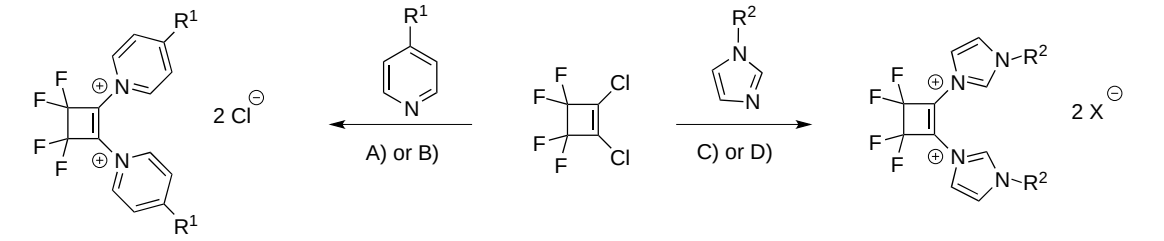
Scheme 10

4-Dimethylaminopyridine and 1-methylimidazole, respectively, substituted also all chlorine atoms of **19**. Ring opening to the corresponding allylids did not occur under the reaction conditions applied (Scheme 11).[35]



Scheme 11

The mixed halogenated cyclobutene **22** reacted with pyridines and imidazoles to give **23** and **24** which were isolated as yellow to off-white solids (Scheme 12).[36]



23a: R^1 = NMe_2 (A: 63%)
23b: R^1 = phenyl (B: 16%)

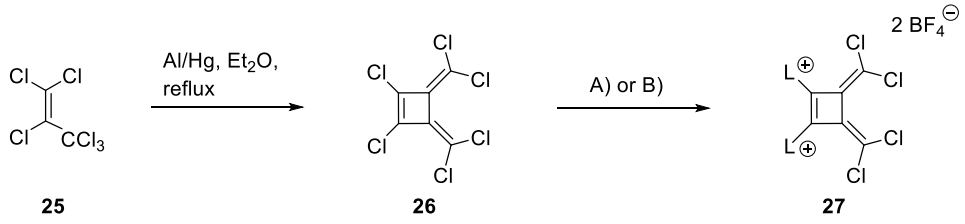
22

24a: R^2 = Me, X = Cl (C: 70%)
24b: R^2 = phenyl, X = BF_4 (D: 17%)

A) for **23a**: DCM, 3 h. B) for **23b**: MeCN, N_2 atm, 55 °C, 12 h. C) for **24a**: MeCN, N_2 atm, rt, 2 min
D) for **24b**: Et_2O / CH_2Cl_2, 0 °C, >1 h, $NaBF_4$(aq)

Scheme 12

1,2-Bis[(4-dimethylamino)pyridinium-1-yl]fluorocycloalkene dichlorides have been described and converted which can be transformed into the corresponding dioxo-, oxothioxo- and dithioxo-cyclofluoropyridinium betaines.[37] The dication **27a** (L = imidazolium), prepared via **25** and **26** as part of a series of dications **27a-c**, has been developed as precursor of a bis-carbene, the palladium complexes of which proved to be highly efficient catalysts for Suzuki-Miyaura reactions (Scheme 13).[38-42]



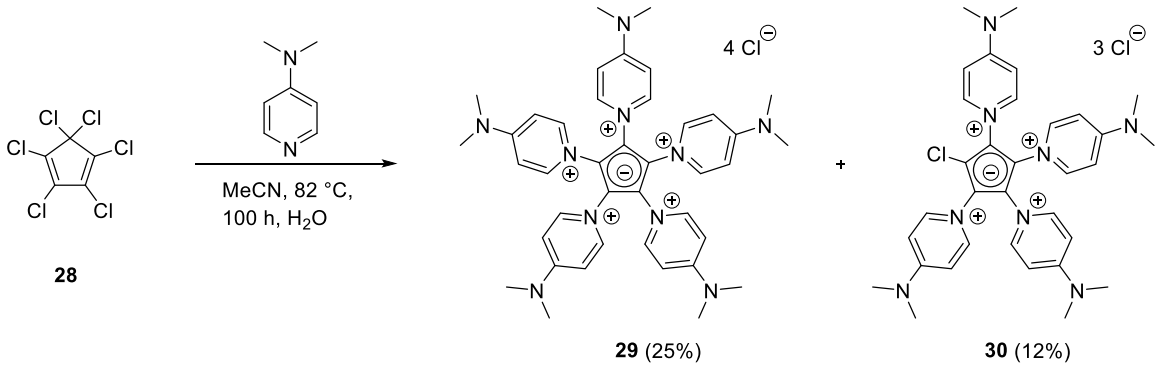
25 **26** **27**

A) 1,2-dichlorobenzene, 60 °C, 4 h, then $NaBF_4$, H_2O
B) 1,2-dichlorobenzene, 70 - 100 °C, 3 h

a: L = 3-methylimidazole, X = BF_4 (A: 73%)
b: L = DMAP, X = Cl (B: 76%)
c: L = 4-aminopyridine, X = Cl (B: 59%)

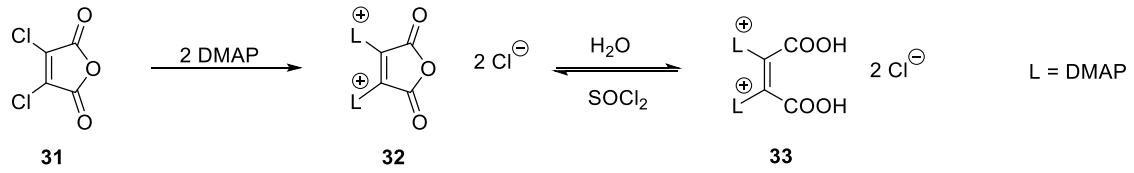
Scheme 13

Hexachlorocyclopentadiene **28** and excess DMAP reacted to form the penta- and tetra-onio substituted products **29** and **30** possessing a cyclopentadiene anion in the polycations (Scheme 14).[36] The corresponding bispyridinium and trispyridinium salts were described as water-soluble organometallic complexes.[43]



Scheme 14

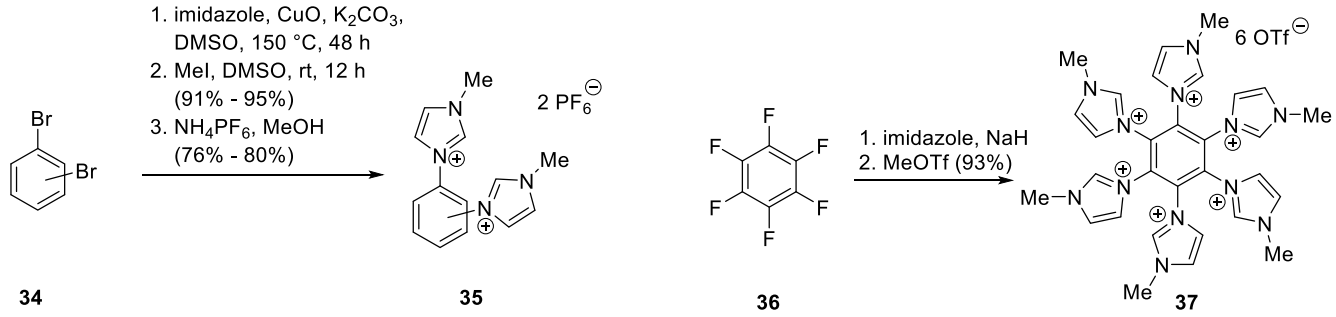
On reaction with dichloromaleic anhydride **31**, two equivalents of DMAP yielded the yellow disubstituted compound **32**. By addition of water, **32** hydrolyzed under ring-opening to the functionalized maleic acid **33**. This conversion could be reversed by treating **33** with thionyl chloride (Scheme 15).[44]



Scheme 15

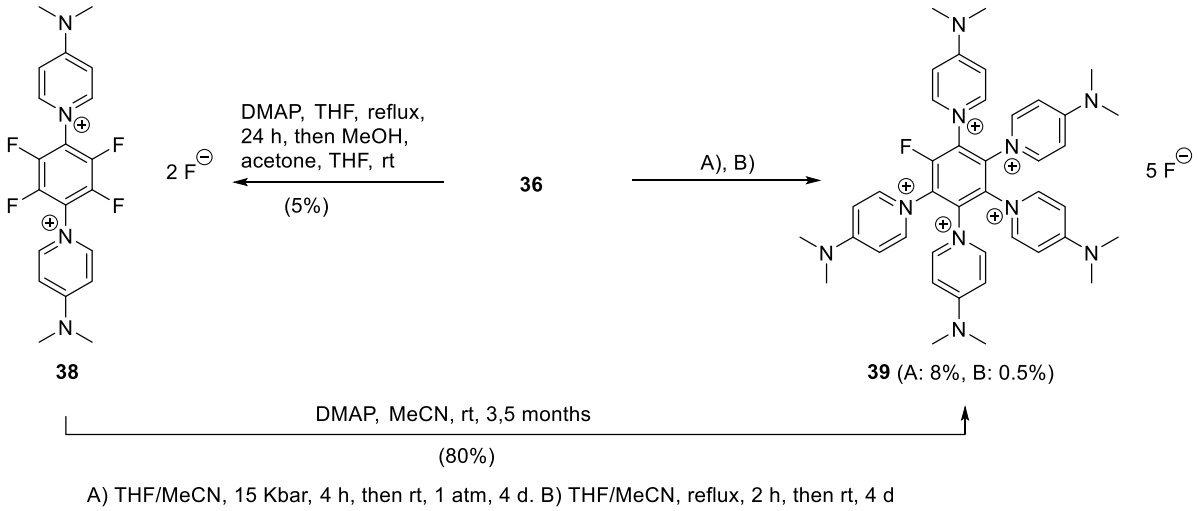
2.2. Syntheses from halogenated aromatics and heteroaromatics

The 3,3'-(phenylene)bis[1-methyl-1*H*-imidazolium] salts **35** and **37** have been prepared by Ullmann reactions and S_NAr reaction starting from **34** and **36**, respectively. The corresponding biscarbenes formed Au, Ag, Cu, Ir, Ru, Rh, and Pd complexes (Scheme 16).[45-52] Three and four-fold imidazolium substituted benzenes and their complexes have been described as well.[53,54] The hexaimidazolium salt, prepared starting from hexafluorobenzene, has been converted into silver and gold carbene complexes.[55]



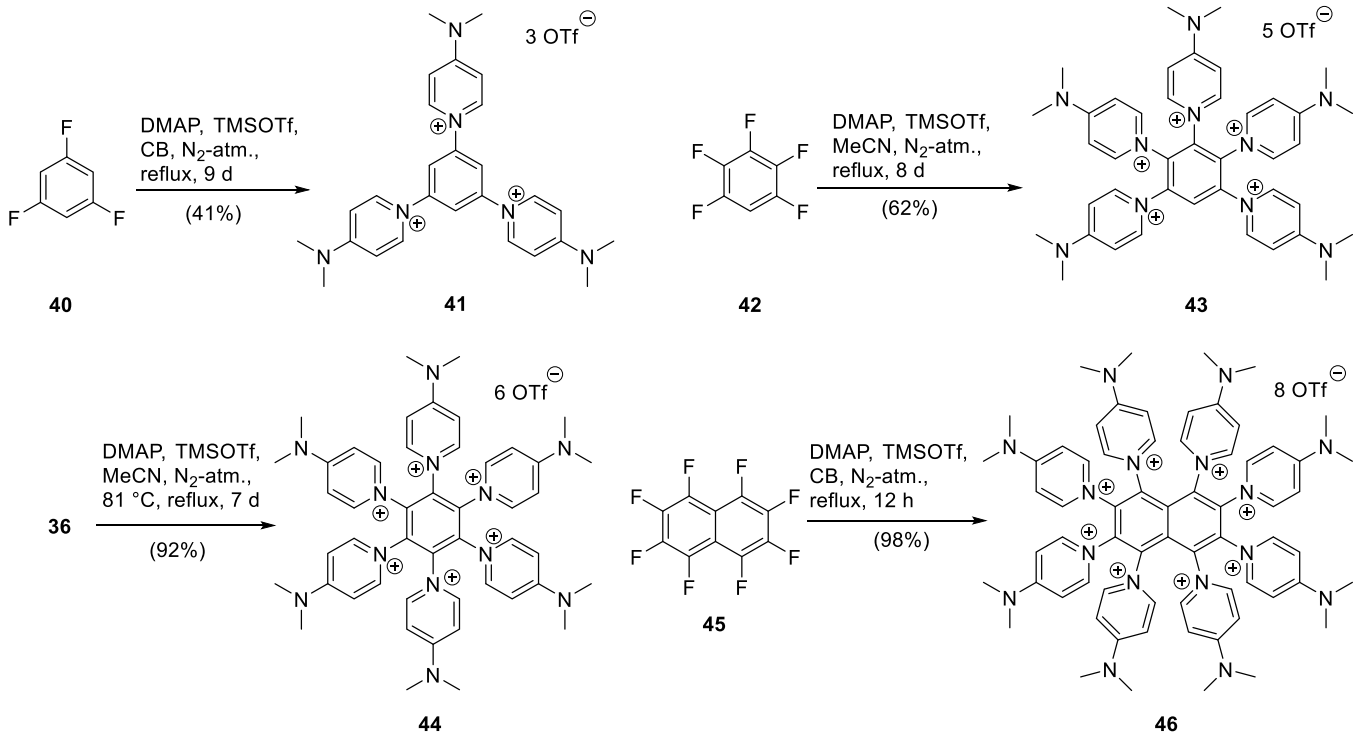
Scheme 16

Hexafluorobenzene **36** reacted with five equivalents of DMAP at reflux temperature to give di- or pentasubstituted products in low yields after purification. Under high pressure, the dication **38** was obtained in a higher yield. Furthermore, the dication **38** was converted into the pentacation **39** by reaction with DMAP over a period of 3,5 months (Scheme 17), and this compound is also available from **36**.[36]



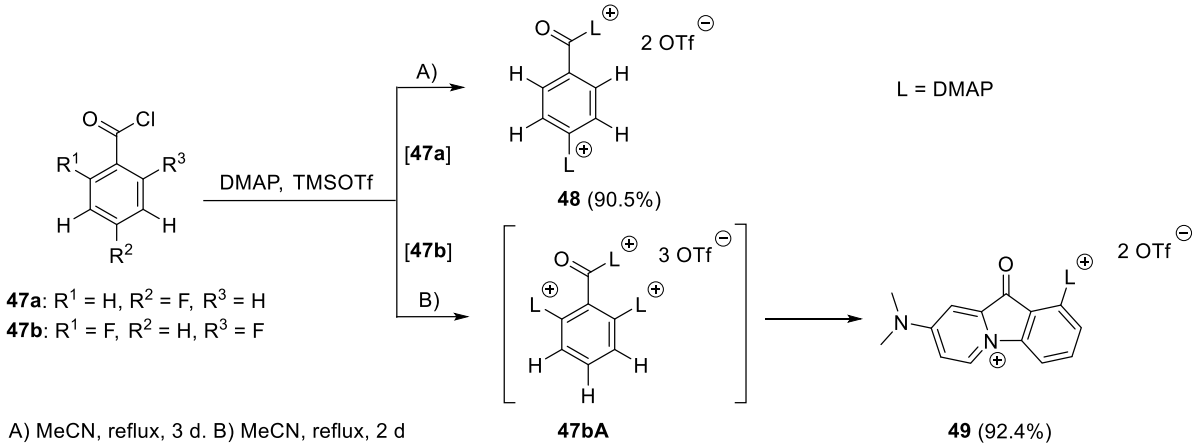
Scheme 17

Reactions of the fluorinated benzenes **36**, **40**, **42**, and perfluoronaphthalene **45** yielded, in the presence of a slight excess of DMAP and TMSOTf, relative to the respective number of bonded fluorine atoms, the tri- to octasubstituted heteroaromatic polycations **41**, **43**, **44**, and **46** as triflates, respectively (Scheme 18). It is noteworthy, that without SASAPOS only the pentafunctionalized product **39** was synthesized from **36** in low yield even under extreme reaction conditions (cf. Scheme 17).[36,56,57]



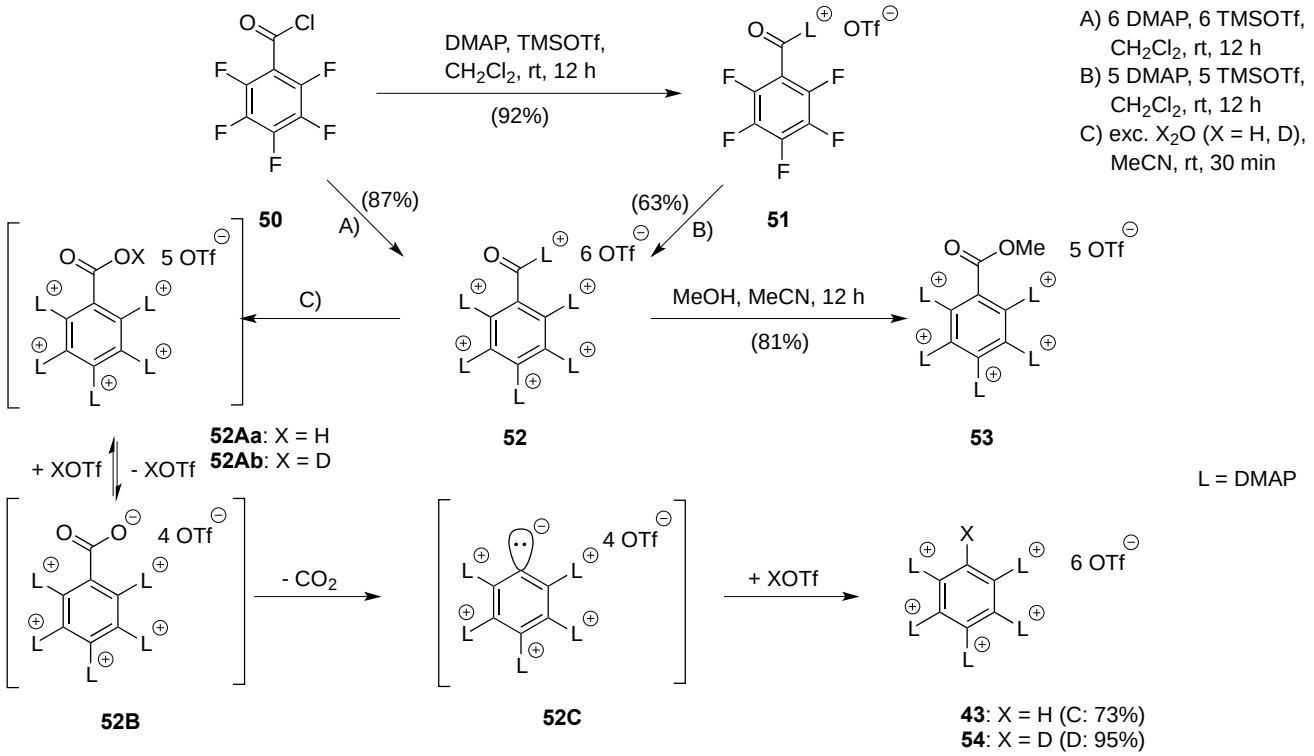
Scheme 18

The fluorobenzoyl chlorides **47a,b** reacted with excess DMAP and TMSOTf to give the dicationic products **48** and **49**, respectively. Initially, an acyl hetarenium salt was formed, followed by substitution of the fluorine atoms attached to the benzene ring. At this stage, the reaction from **47a** ended with the formation of **48**, whereas the reaction from **47b** continued *via* intermediate **47bA**. Subsequently, 5-ring closure occurred under elimination of DMAP triflate to give **49** (Scheme 19).[58] On reaction with pentafluorobenzoyl chloride *tert*-butylpyridine (TBUPY) and TMSOTf yielded the tetrafluoro analog of **48** after 1 h in dichloromethane.[59]



Scheme 19

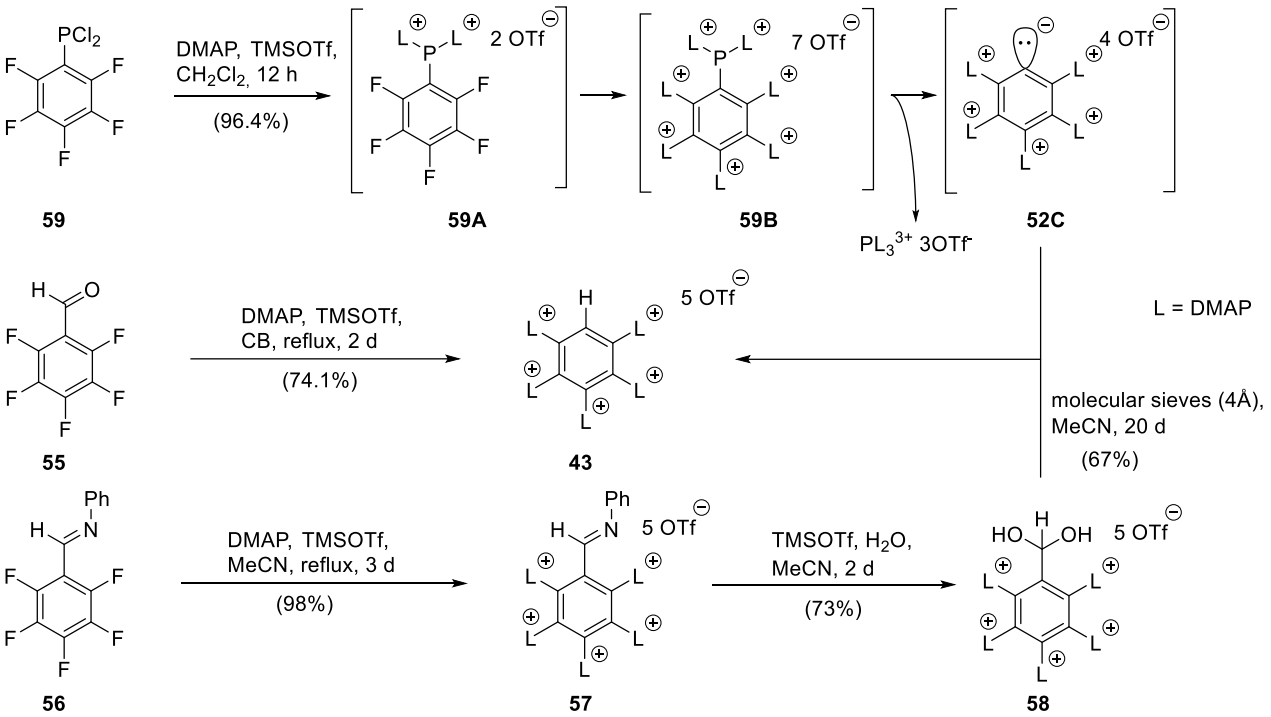
Depending on the amount of DMAP and TMSOTf starting material **50** was converted under SASAPOS conditions into **51** or **52**. Alternatively, **52** could also be generated from **51**. As shown, the hexasubstituted triflate **52** served as precursor for the synthesis of additional polycationic compounds. On the one hand, it reacted with methanol to its colorless methyl ester **53**. On the other hand, treatment with water or deuterated water led to the formation of the colorless products **43** and **54**. This reaction proceeded through three intermediates, containing hydrolysis to the acid species **52Aa,b**, followed by deprotonation to **52B** and subsequent decarboxylation to the phenyl anion **52C**, which was finally converted into **43** or **54** by triflic acid (Scheme 20).[59]



Scheme 20

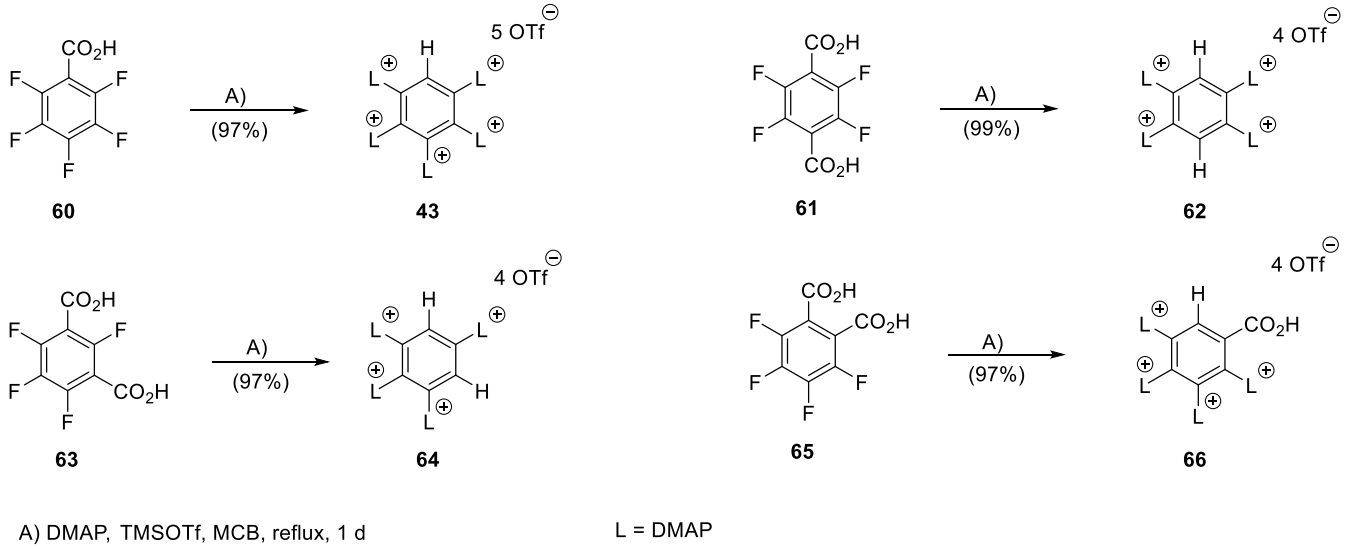
The pentacation **43** was also synthesized from pentafluorobenzaldehyde **55**, phenyl imine **56** or dichloro pentafluorophenyl phosphane **59** (Scheme 21). In the first case, **55** reacted with DMAP and TMSOTf, whereupon the product **43** was formed. In the second case, the reaction starting from **56** with DMAP and TMSOTf initially yielded the pentasubstituted imine **57**, the acid-catalyzed hydrolysis of which led to the geminal diol **58**. Finally, treatment of this compound with molecular sieves resulted in the formation of **43**. In the third case, **59** reacted with DMAP under SASAPOS conditions *via* three intermediates. At first, only the two chlorine atoms bonding on the phosphorus were substituted so that **59A** was formed, as evidenced by ^{1}H NMR spectroscopy. Second, all fluorine atoms attached to the benzene ring were

likewise substituted by further reaction with DMAP and TMSOTf resulting in the polycationic intermediate **59B**. Reaction with an additional molecule of the nucleophilic compound led to an inseparable mixture containing the phenyl anion **52C** and the tricationic phosphane. Hydrolysis of **52C** finally resulted in the formation of **43** (Scheme 21).[60]



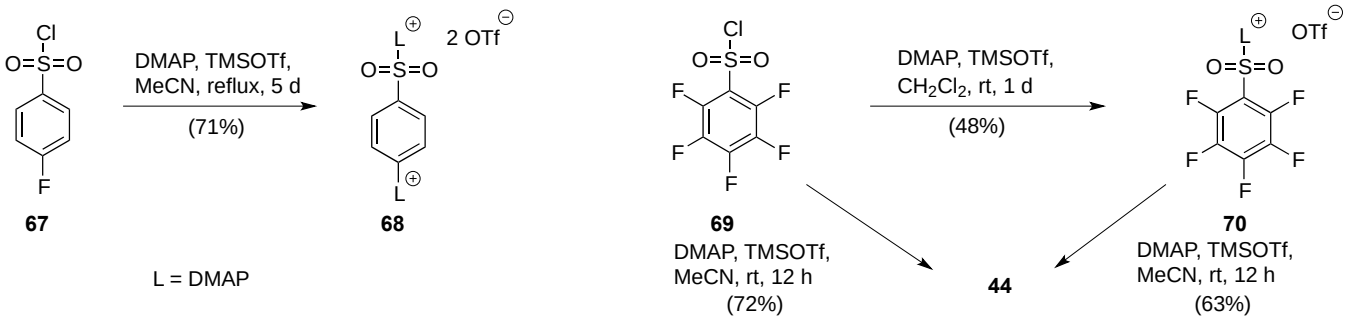
Scheme 21

The fluorinated benzoic acid **60** reacted with DMAP and TMSOTf under decarboxylation to give the aforementioned product **43**. Related polycationic compounds were also generated by reaction of the fluorinated phthalic acids **61**, **63** and **65** with DMAP and TMSOTf. Thus the two tetrasubstituted benzenes **62** and **64** as well as the tetrafunctionalized benzoic acid **66** were obtained. Due to decarboxylation two hydrogen atoms remained in the original 1- and 4-position or 1- and 3-position of the terephthalic acid **61** or the isophthalic acid **63**, respectively. By contrast, the phthalic acid **65** eliminated only one equivalent of carbon dioxide (Scheme 22).[59,60]



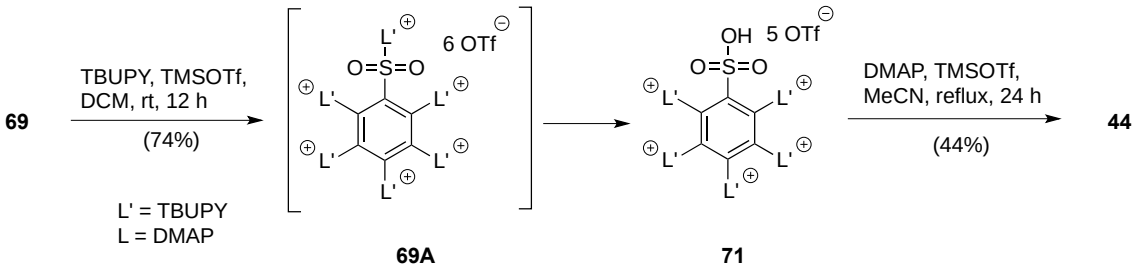
Scheme 22

A heteroaromatic polycation, which contains a sulfonyl group, was synthesized from 4-fluorobenzenesulfonyl chloride **67**. Its reaction with DMAP under SASAPOS conditions yielded the colorless dicationic triflate **68** in which both halogen atoms were substituted by the N-nucleophile (Scheme 23).[45] On reaction with the sulfonylic dication **68**, pyrrolidine replaced the chloride of the sulfonyl chloride group.[61] The pentafluorinated species **69** was converted into the colorless monocation **70** or into the completely substituted benzene derivative **44** by reaction with DMAP and TMSOTf. The latter mentioned product was also obtained from the reaction of **69** with additional DMAP/TMSOTf.[61]



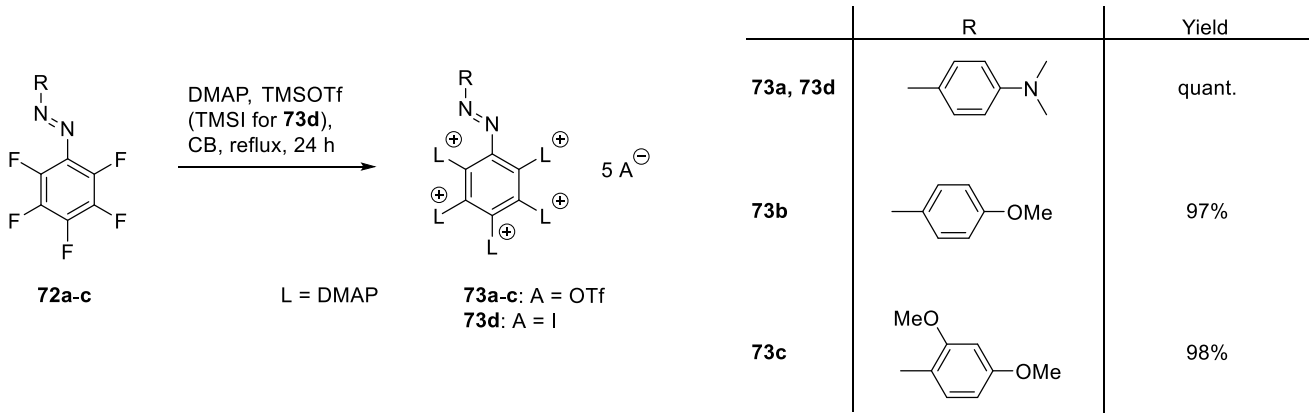
Scheme 23

The reaction of starting material **69** with 4-*tert*-butylpyridine (TBUPY) and TMSOTf led to the formation of the pentafunctionalized benzenesulfonic acid **71**. Initially, all halogen atoms were substituted by the N-nucleophile, whereupon the intermediate **69A** was formed which instantly hydrolyzed with traces of water (Scheme 24). Transformation to **44** by ligand exchange with DMAP was possible.



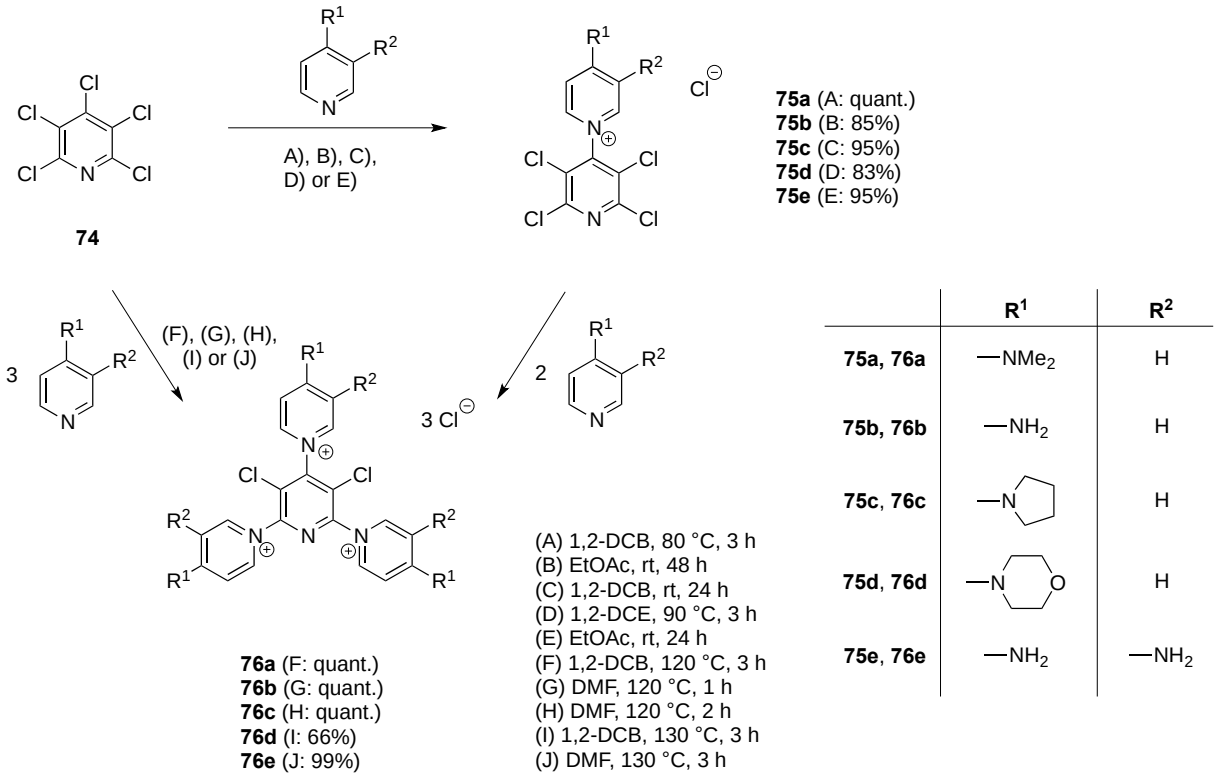
Scheme 24

Furthermore, the pentafluorophenylazo dyes **72a-c** reacted with DMAP and TMSOTf or TMSI, respectively, to give the corresponding pentasubstituted polycations **73** (Scheme 25). Bathochromic effects occurred because of the expansion of the conjugated π-electron system by implementing the DMAP substituents to the phenyl ring.[62] Similar reactions from corresponding aldimine and stilbene dyes resulted analogously in the formation of the pentafunctionalized compounds.[61]



Scheme 25

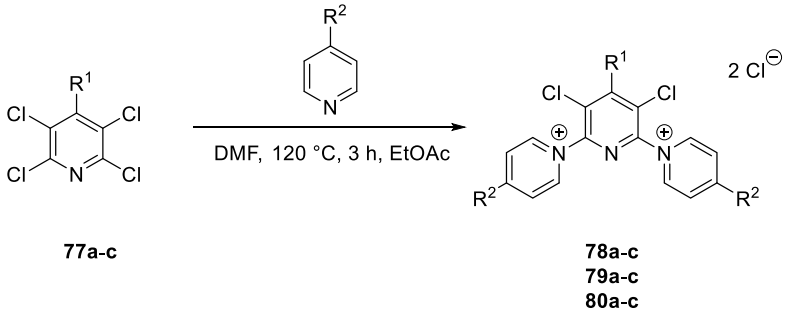
Three equivalents of various nucleophiles converted pentachloropyridine **74** into the trications **76a-e** which were obtained as yellow solids. By using only one equivalent of the corresponding N-nucleophile, the monocationic salts **75a-e** were formed (Scheme 26).[63-65]



	R^1	R^2
75a, 76a	—NMe_2	H
75b, 76b	—NH_2	H
75c, **76c**	—N	H
75d, **76d**	—N O	H
75e, **76e**	—NH_2	—NH_2

Scheme 26

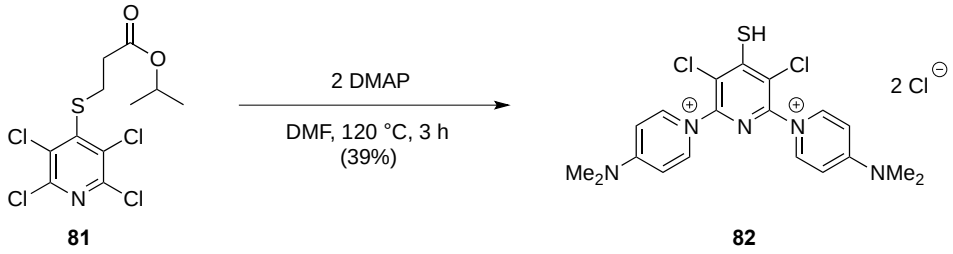
4-Substituted pyridines **77a-c** gave dicationic systems such as **78a-c** – **80a-c** (Scheme 27).[66]



	R^1	R^2	Yield
78a	S-Et		(54%)
78b	S-*i*Pr	—NH_2	(61%)
78c	H		(73%)
79a	S-Et		(90%)
79b	S-*i*Pr	—NMe_2	(89%)
79c	H		(95%)
80a	S-Et		(65%)
80b	S-*i*Pr	—N	(66%)
80c	H		(99%)

Scheme 27

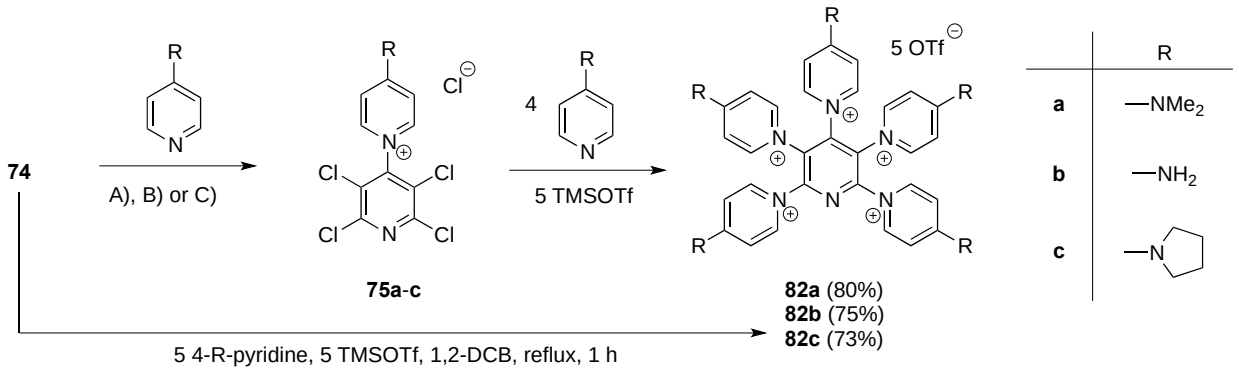
On reaction with pyridine-4-thioether **81**, which can be generated from a multistep synthesis based on **75a** and 3-sulfanylpropionic acid, two equivalents of DMAP yielded the yellow dicationic pyridine-4-thiol **82** (Scheme 28). Efforts to synthesize this product by reaction of the 4-thiol derivative of **81** with DMAP failed.[64]



81 **82**

Scheme 28

Pentachloropyridine **74**, which has already been mentioned before, also reacted under SASAPOS conditions. With five equivalents of the selected N-nucleophiles and TMSOTf all chlorine atoms were substituted so that the pentafunctionalized polycations **82** were obtained as pale grey to yellow triflates. Alternatively, the products were also synthesized from the monocations **75a-c** (Scheme 29) as well as from pentafluoropyridine.[63,65]



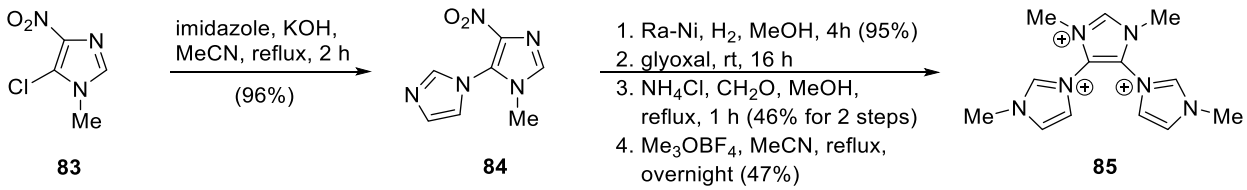
75a-c

82a (80%)
82b (75%)
82c (73%)

A) 1,2-DCB, 80 °C, 3 h. B) EtOAc, rt, 48 h. C) 1,2-DCB, rt, 24 h

Scheme 29

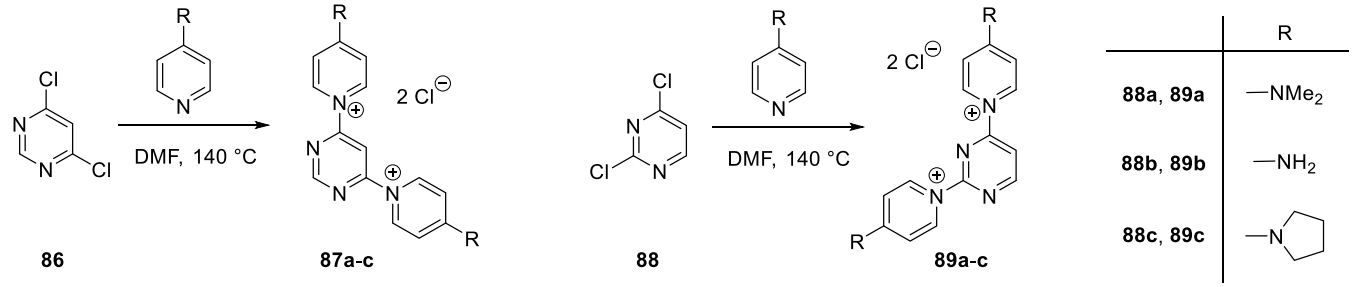
Concerning diazoles, the tricationic imidazolium derivative **85** has been synthesized starting from **83** via **84** to gain access to pincer-CNC mononuclear, dinuclear and heterodinuclear Au(III) and Pt(II) complexes,[67] Ir, Rh and Pd complexes as catalysts,[68] and dipalladium complexes (Scheme 30).[69]



83 **84** **85**

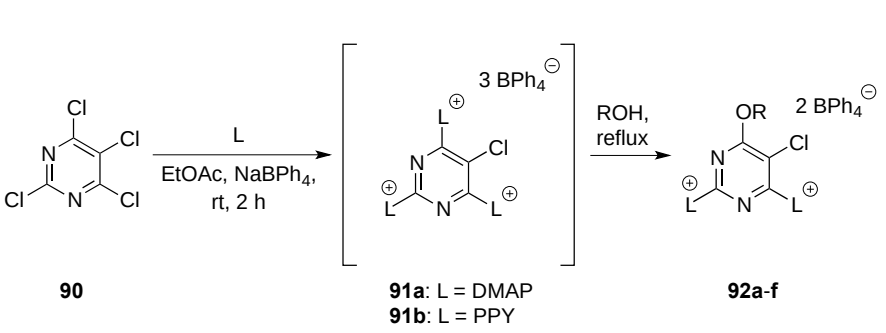
Scheme 30

Concerning diazines, the two dichlorinated pyrimidines **86** and **88** reacted with DMAP, 4-aminopyridine or PPY under analogous conditions as mentioned before in the pyridine series of heterocycle polycations to give the disubstituted products **87a-c** and **89a-c** (Scheme 31).[70]



Scheme 31

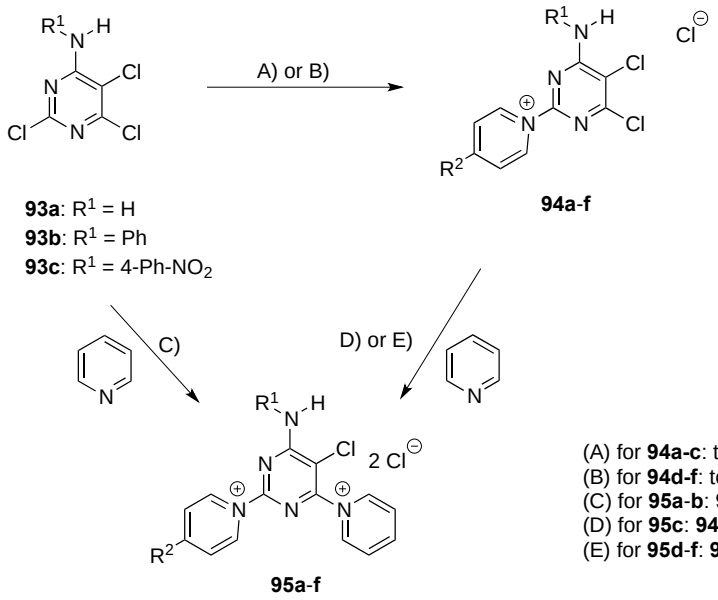
Tetrachloropyrimidine **90** reacted with DMAP and PPY in the presence of sodium tetraphenylborate (to replace the hygroscopic chloride toward the tetraphenylborate anion) to give the trications **91a,b** which reacted with alcohols to give the O-alkylated species **92a-f** (Scheme 32).



	L	R	Yield
92a	DMAP	Et	(80%)
92b	DMAP	Me	(65%)
92c	DMAP	*i*-Pr	(45%)
92d	PPY	Et	(85%)
92e	PPY	Me	(24%)
92f	PPY	*i*-Pr	(18%)

Scheme 32

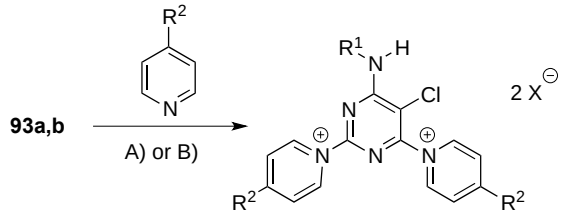
Water gives positively charged pyrimidin-4-olates as tripolar substances.[71] The 4-amino-2,5,6-trichloropyrimidines **93a-c** formed the dipyridinium salts **95a-f**, in part *via* monocations **94a-f** (Scheme 33).[72] The aforementioned compounds **93a,b** reacted with DMAP or PPY dependent on the reaction conditions applied to the disubstituted chlorides or tetraphenylborates **96-99** (Scheme 34).[73] Furthermore, the 1-methylimidazolium salts **100** were available from **93a** and **93c** (Scheme 35).[73]



	R^1	R^2	Yield
94a, **95a**	H	H	(61%), (77%)
94b, **95b**	Ph	H	(73%), (80%)
94c, **95c**	4-Ph-NO_2	H	(78%), (44%)
94d, **95d**	H	pyridin-4-yl	(54%), (56%)
94e, **95e**	Ph	pyridin-4-yl	(37%), (47%)
94f, **95f**	4-Ph-NO_2	pyridin-4-yl	(90%), (43%)

(A) for **94a-c**: toluene, pyridine, reflux, 3 h
(B) for **94d-f**: toluene, 4,4'-bipyridine, reflux, 3 h
(C) for **95a**-**b**: **93a** or **93b**, pyridine, 80 °C
(D) for **95c**: **94f**, pyridine, reflux, 4 h
(E) for **95d**-**f**: **94c**-**f**, pyridine, 70-80 °C, 1 h

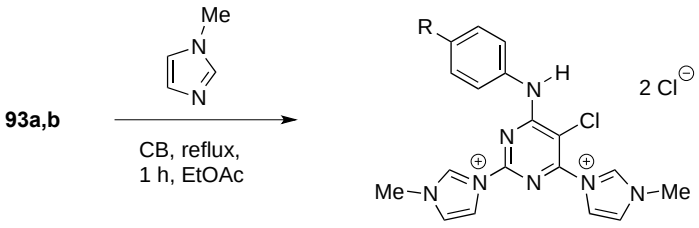
Scheme 33



	R^1	R^2	X	Yield
96a	H	NMe_2	Cl	(77%)
96b	H		BPh_4	(63%)
97a	Ph		Cl	(54%)
97b	Ph		BPh_4	(61%)
98a	H		Cl	(53%)
98b	H		BPh_4	(59%)
99a	Ph		Cl	(77%)
99b	Ph		BPh_4	(54%)

A) for **a**: CB, reflux, 1 h
B) for **b**: anhydrous EtOAc, $NaBPh_4$, reflux, 1 h

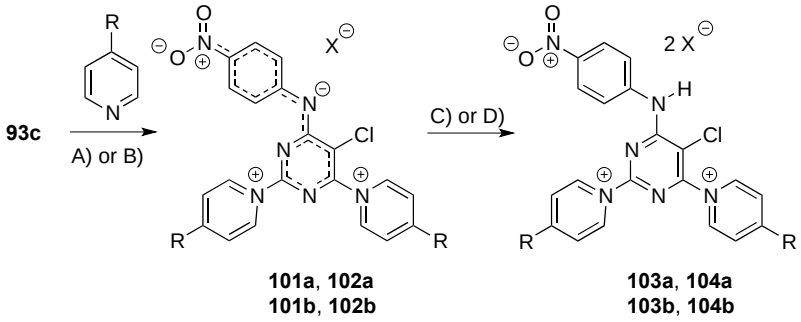
Scheme 34



100a: R = H (56%)
100b: R = NO_2 (49%)

Scheme 35

Moreover, the reaction of compound **93c** with DMAP or PPY initially led, dependent on the reaction conditions applied, to the tripolar disubstituted monocationic chlorides or tetraphenylborates **101** and **102**, in which the amino N-atom is deprotonated (Scheme 36). These could further be converted into the corresponding dications **103**, **104** by protonation of the amino N-atom with hydrochloric acid.[73]

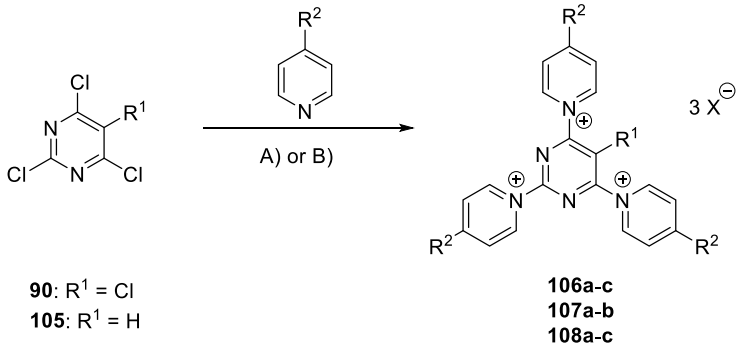


	X	R	Yields (2 steps)
101a	Cl	NMe_2	(45% / 95%)
101b	BPh_4		(52% / 94%)
102a	Cl		(78% / 89%)
102b	BPh_4		(64% / 81%)

A) for **101a**, **102a**: CB, reflux, 1 h. B) for **101b**, **102b**: anhydrous EtOAc, $NaBPh_4$, reflux, 1 h
C) for **103a**, **104a**: EtOH, 10% HCl. D) for **103b**, **104b**: EtOH, 10% HCl, EtOAc, $NaBPh_4$

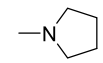
Scheme 36

The chloropyrimidines **90** and **105** reacted with selected N-nucleophiles to give the trisubstituted trications **106-108**, whereby substitutions occur only at the α- and γ-position of the pyrimidine (Scheme 37).[70]



90: R^1 = Cl
105: R^1 = H

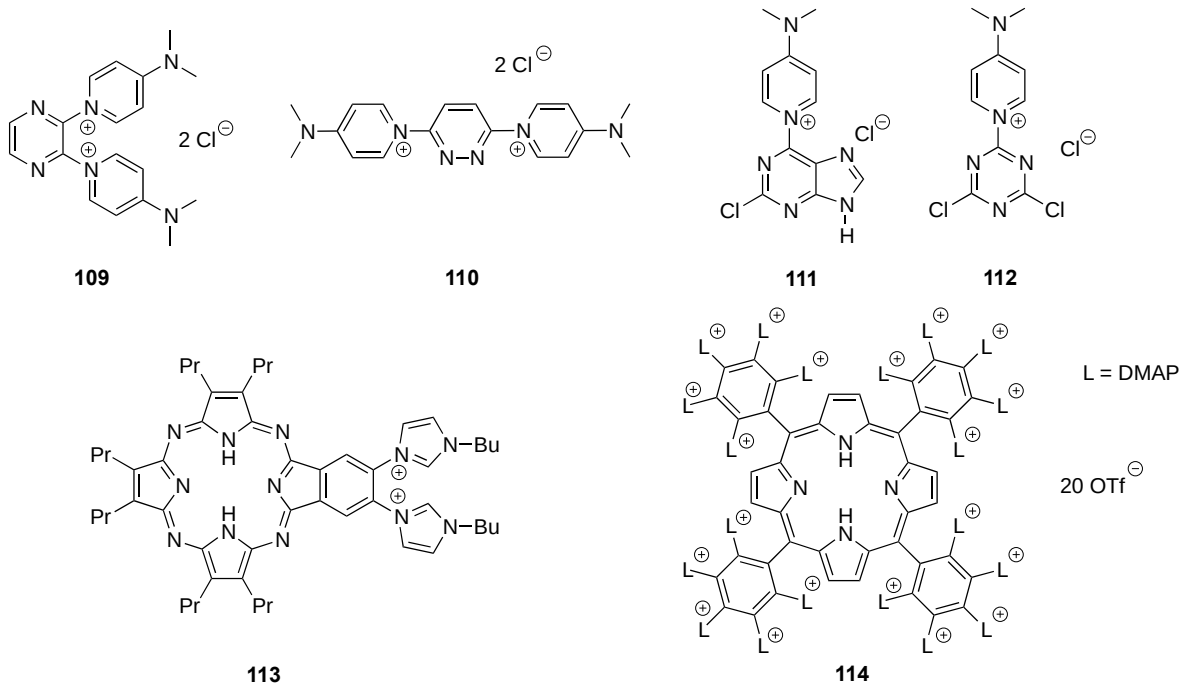
A) for **106a-108a**, **106b-108b**: DMF, 140 °C, 1 h
B) for **106c**,**108c**: 1,2-DCB, TMSOTf, reflux, 3 h

	R^1	R^2	X
106a	H	$-NMe_2$	Cl
106b	Cl		Cl
106c	Cl		OTf
107a	H	$-NH_2$	Cl
107b	Cl		Cl
108a	H		Cl
108b	Cl		Cl
108c	Cl		OTf

Scheme 37

DMAP-substituted pyrazines, pyridazines, purines, and 1,3,5-triazines have been described as well. They have been prepared starting from the corresponding chlorinated precursors either by refluxing in 1,2-dichlorbenzene over a period of 1 h to 4 h (**109-111**) or by refluxing in acetone for 30 minutes (**112**).[76] A porphyrinazine with 1,2-bisimidazolium structure element **113** has been described which

supplements the smaller core elements mentioned before. It has been used as highly pigmented ligand in catalytic systems with palladium.[74] A heteroaromatic polycation, which is 20-fold positively charged, was available from the reaction of the corresponding fluorinated porphyrin derivate with DMAP and TMSOTf. The product **114** was isolated as intensely violet colored triflate in nearly quantitative yield (Scheme 38).[47]

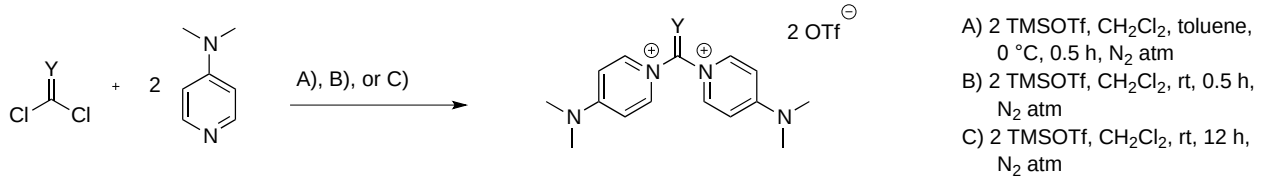


109 **110** **111** **112** **113** **114**

Scheme 38

2.3. Syntheses from halogenated carbonyls and their thio as well as aza analogs

The reaction of phosgene and its derivates **115a-c** with DMAP gave the geminal disubstituted products **116** (Scheme 39).[77]

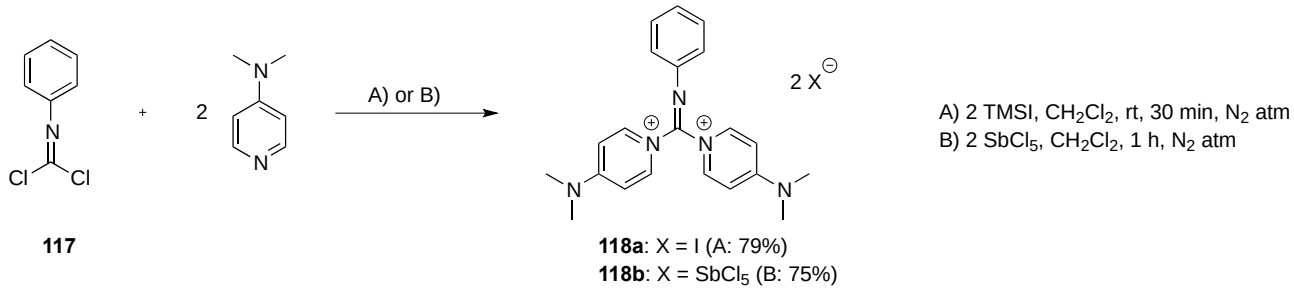


115a: Y = O
115b: Y = S
115c: Y = $N^+Me_2Cl^-$

116a: Y = O (A: 75%)
116b: Y = S (B: 66%)
116c: Y = $N^+Me_2Cl^-$ (C: 75%)

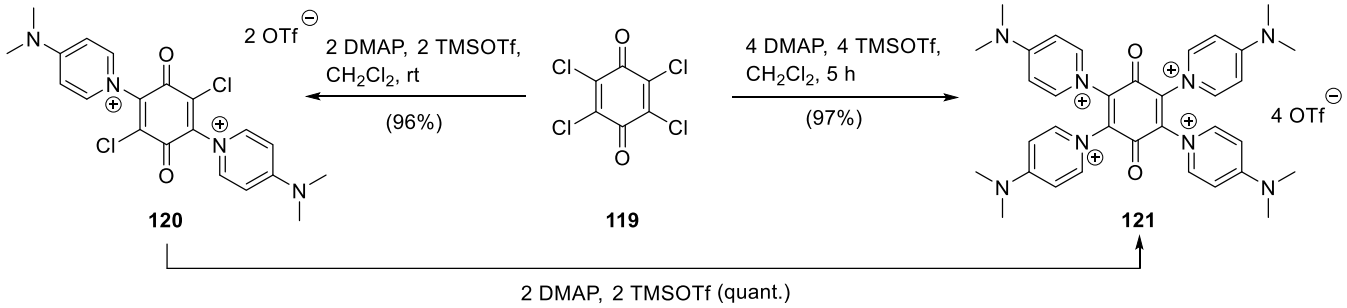
Scheme 39

The reaction of the phosgene derivate **117** with DMAP yielded the dicationic iodides and antimony pentachlorides **118** (Scheme 40).[77]



Scheme 40

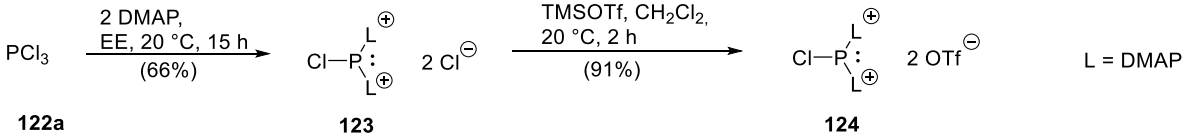
p-Chloranil **119** is another chemical compound which can be converted into a polycationic form. Depending on the number of equivalents of DMAP and TMSOTf applied, the 2,5-disubstituted species **120** or the tetrasubstituted product **121** can be obtained. The latter was also generated from **120** with two additional equivalents of DMAP and TMSOTf (Scheme 41). The products are red in color and display an approximately equal to higher reversible redox potential in comparison to DDQ, what possibly makes them to interesting oxidizing agents in organic chemistry. The tetracationically substituted hydroquinone and the analogously functionalized 1,4-diethoxybenzene can be prepared through reaction of the tetracationic quinone derivate **121** with hydroquinone or tetraethoxyethylene, respectively.[78]



Scheme 41

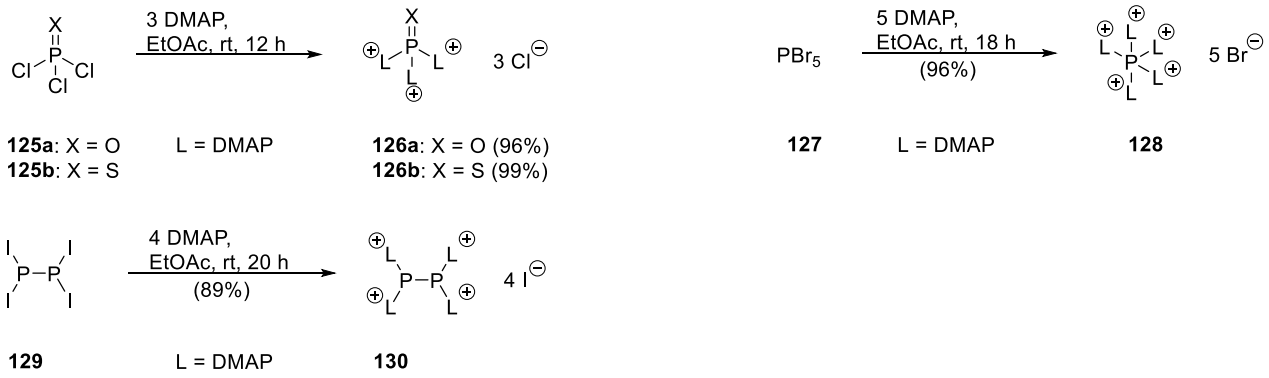
2.4. Syntheses starting from phosphanes and hypervalent iodine compounds

Weiss et al. also examined polycationic phosphorus compounds. Phosphorus trichloride **122a** reacted with two equivalents of DMAP to give the disubstituted dication **123**, the counterions of which could be exchanged to triflate to give **124** (Scheme 42).[79]



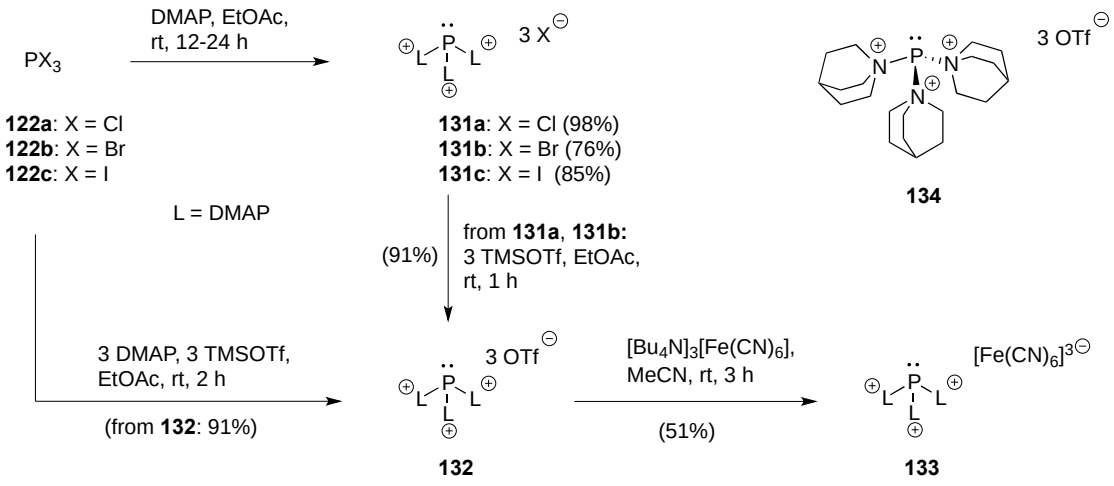
Scheme 42

The reaction of phosphoryl chloride **125a** or thiophosphoryl chloride **125b** with three equivalents of DMAP yielded the corresponding trication **126a,b** in which all chlorine atoms are substituted by the N-nucleophile (Scheme 43). The pentafunctionalized phosphorus compound **128** was obtained from phosphorus pentabromide **127** with five equivalents of DMAP. On reaction with diphosphorus tetraiodide **129**, four equivalents of DMAP yielded the tetracation **130**.[80]



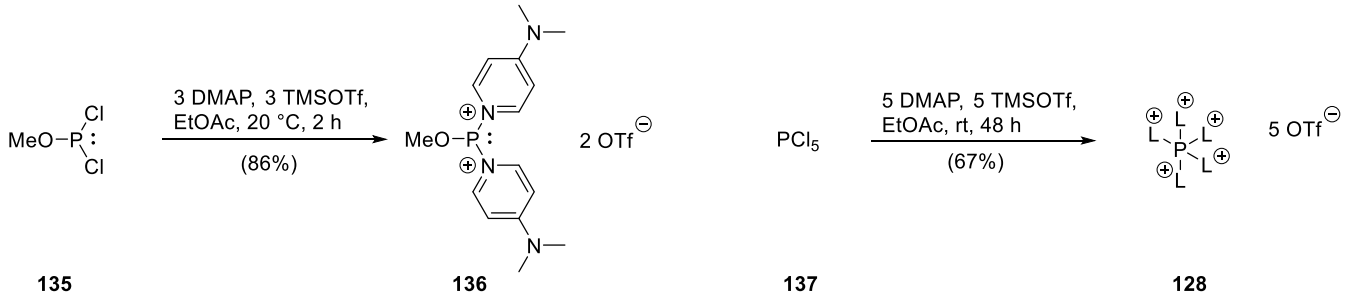
Scheme 43

Halogenated phosphorus(III) compounds also reacted with DMAP in the presence of TMSOTf to give substituted polycations. In this case, the fully substituted trication **132** was available from phosphorus(III)trichloride **122**. Alternatively, **132** was synthesized by a two-step procedure via the halides **131**. Subsequently, the tristriflate was treated with tris(tetrabutylammonium)hexacyanoferrate(III), whereupon the anion exchanged species **133** was formed (Scheme 44).[80] Analogously, phosphorous trichloride **122** reacted with quinuclidine to give the sterically crowed polycation **134**.[80]



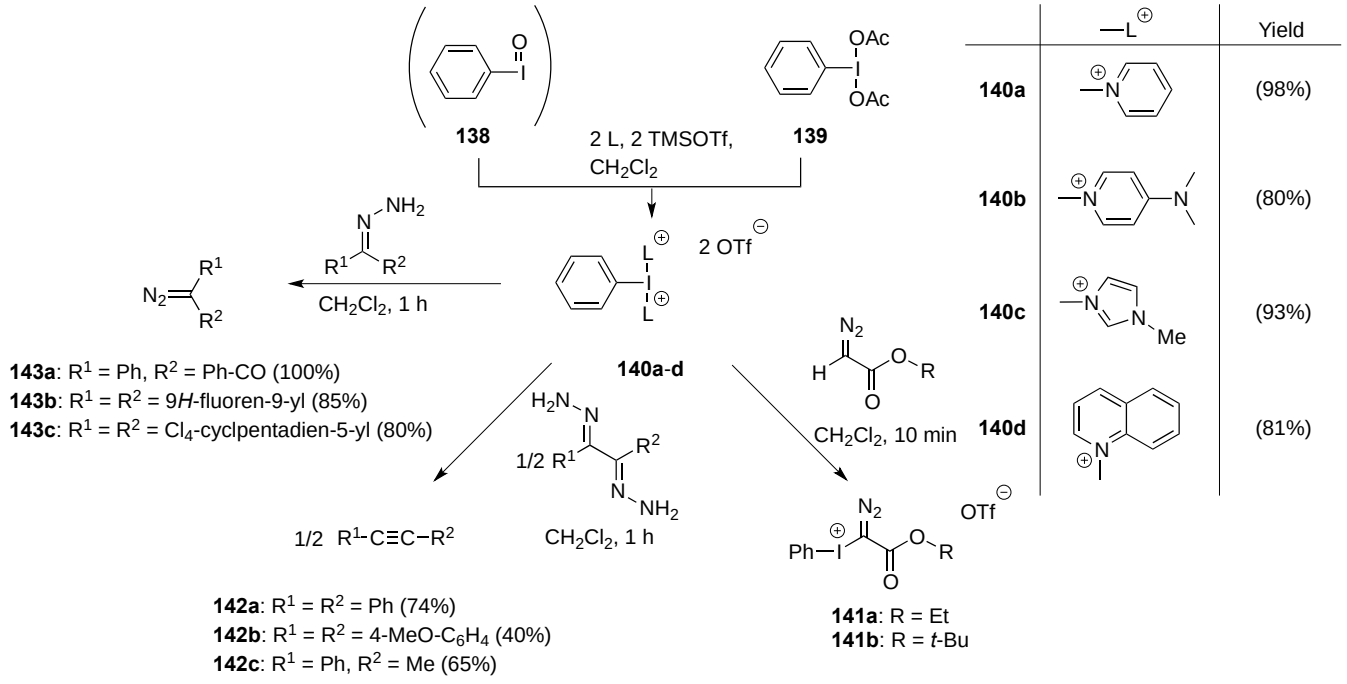
Scheme 44

Furthermore, efforts to substitute the chlorine atoms of methyl dichlorophosphite **135** with DMAP resulted in the formation of the dicationic salt **136** (Scheme 45).[80] Investigations on phosphorus pentachloride **137** showed that it reacts with DMAP similar to phosphorus trichloride. Yet consequently, to obtain the fully substituted product **128** as triflate salt, five equivalents of the N-nucleophile and TMSOTf had to be used.[80]



Scheme 45

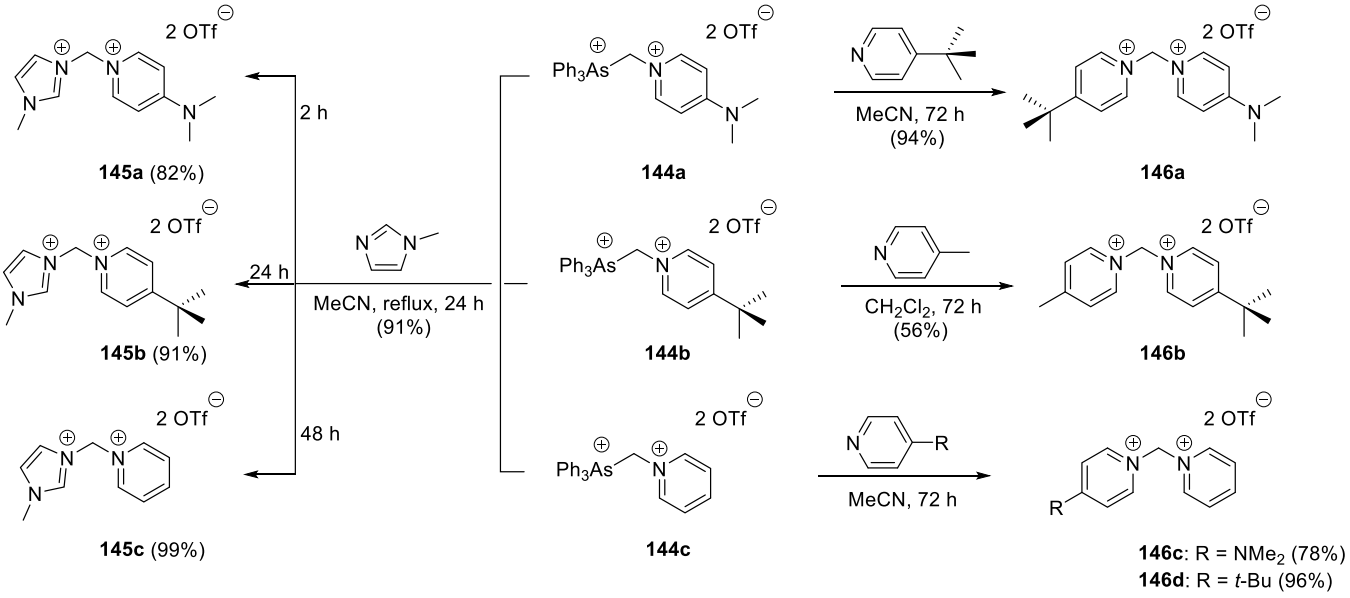
The polysubstituted cationic aryliodine(III) salts **140a-d**, in which the hypervalent iodine atom bonds a phenyl ring and two N-heteroaromatics, are available from the reaction of the polymeric iodosobenzene **138** or the diacetate **139** with selected N-nucleophiles (Scheme 46).[81] From the reaction of the dicationically substituted aryliodine(III) salt **140a** with selected diazoacetate compounds, the corresponding yellow colored α-aryliodonio(III) diazo products **141** can be obtained.[82] The same educt **140a** dehydrogenates monohydrazones to diazo compounds **143** and oxidizes 1,2-bishydrazones to alkynes **142**.[81]



Scheme 46

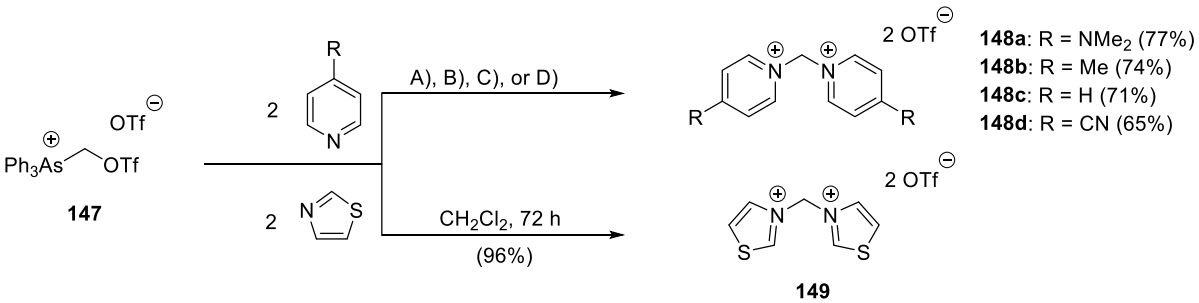
2.5. Syntheses starting from salts

Geminal disubstituted heteroaromatic polycations were obtained on treatment of the 2-fold positively charged compounds **144a-c** with one equivalent of N-nucleophile, respectively. Thereby, the mixed substituted dications **145a-c** and **146a-d** were formed under elimination of triphenylarsine (Scheme 47). The charged educts were generated by multistep reaction based on *t*-butyl diazoacetate, followed by a nucleophilic substitution with pyridine, DMAP or TBUPY.[83]



Scheme 47

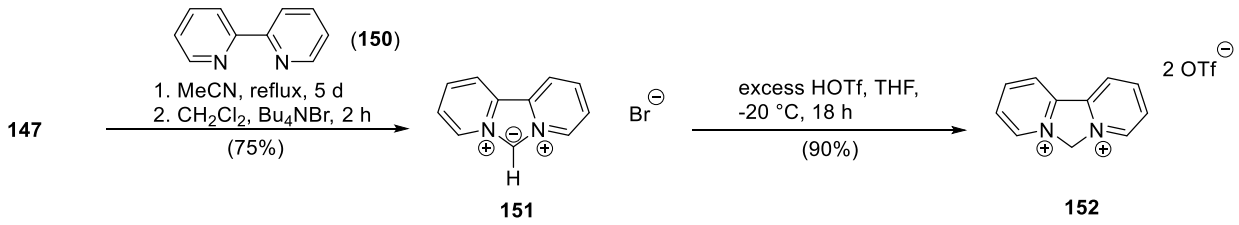
Similar products were prepared by reaction of trifluoromethanesulfonic acid ester **147**, which is the precursor of **144**, with thiazole and selected pyridine derivatives. Thereby, the geminal equally disubstituted compounds **148a-d** and **149** were formed under elimination of triphenylarsine and the triflate, whereby the latter serves as second counterion (Scheme 48).[84]



A) MeCN, reflux, 40 h. B) CH_2Cl_2, 23 h. C) MeCN, reflux, 72 h. D) MeCN, reflux, 48 h

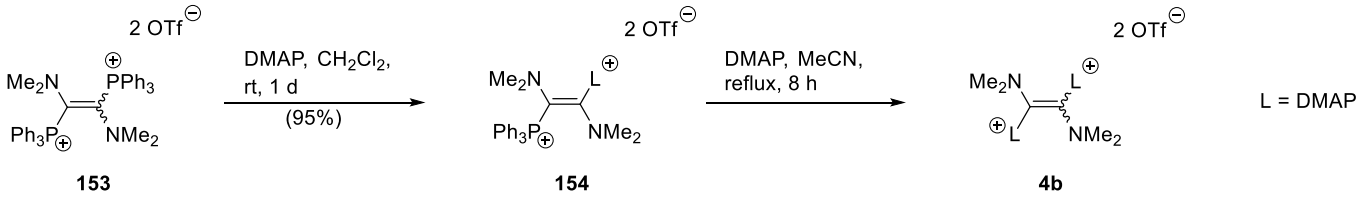
Scheme 48

On reaction with 2,2'-bipyridine (**150**), **147** initially yielded the dark yellow monocationic bromide **151** after anion exchange. Followed by treatment with an excess of trifluoromethanesulfonic acid, its protonated form was obtained as white dicationic triflate **152**. Caused by the bidenticity of the 2,2'-bipyridine, this product consists, in comparison to the aforementioned ones, of three coupled ring units (Scheme 49).[83,84]



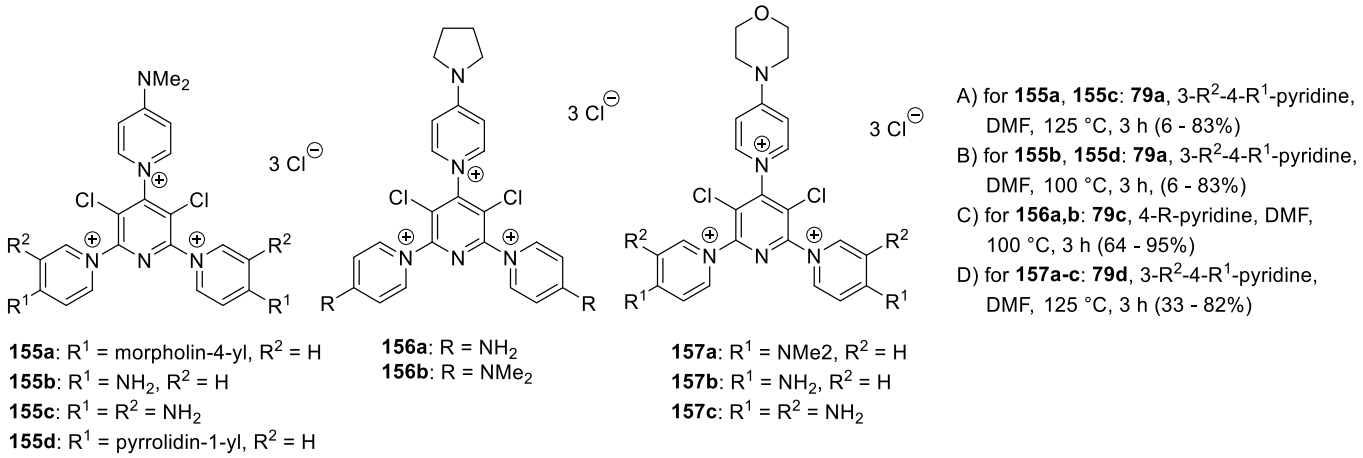
Scheme 49

The difunctionalized ethene derivate **4b** (cf. Scheme 5) was prepared from the reaction of the starting material **153** with DMAP. The triphenylphosphonium groups were successively substituted by the N-nucleophile, so that the mixed substituted dication **154** was formed primarily. Subsequently, the latter was converted into product **4b** only under elevated reaction temperatures (Scheme 50).[28]



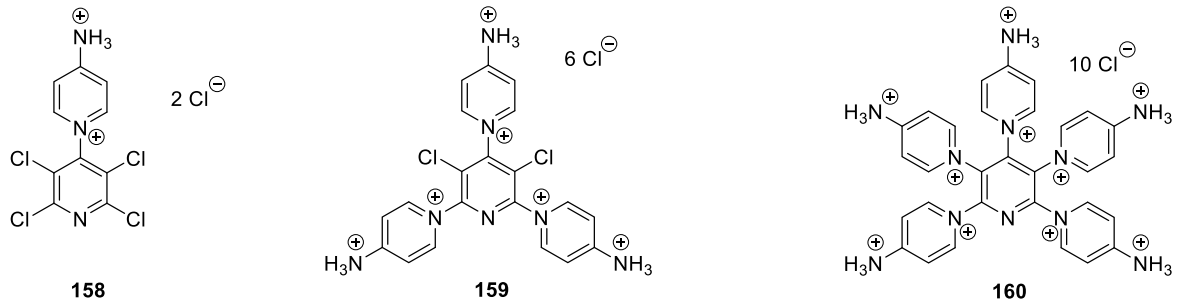
Scheme 50

Other mixed heteroaromatic polycations, which contain two different types of heteroaromatic ligands, are available from the reaction of the monofunctionalized monocations **75a**, **75c** and **75d** with selected N-nucleophiles. Thereby only the two chlorine atoms in α-position, relative to the nitrogen atom, were substituted so that the tricationic products **155-157** were formed (Scheme 51).[63,64]



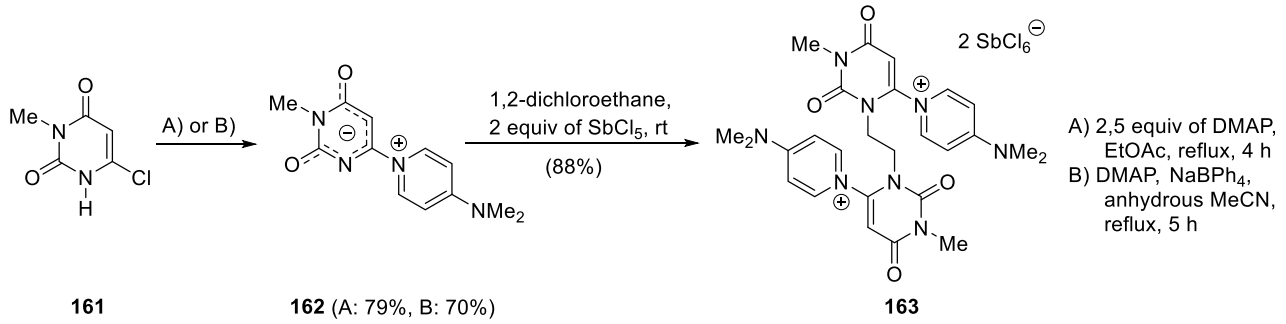
Scheme 51

The protonation of amino groups is another possibility to synthesize heteroaromatic polycations. Thus the monocation **75b**, substituted by 4-aminopyridine, was protonated to give the colorless dication **158** (Scheme 29).[63] Different reactions with acids are shown in the scheme below. In this two cases, the amino groups of the cationic educts **76b** and **80b** were protonated to give the 6- or 10-fold heteroaromatic cation **159** or **160**, respectively (Scheme 52).[63]



Scheme 52

6-Chlorouracil **161** has also been used to synthesize heteroaromatic polycations. Although a partial aromatic character has been attributed to uracil,[85] its structure sets this molecule apart from the aforementioned systems. DMAP was able to induce a nucleophilic substitution followed by a deprotonation so that the mesomeric betaine **162** was formed that was converted into the lemon yellow dication **163** by alkylation with 1,2-dichloroethane in the presence of antimony pentachloride (Scheme 53).[86]

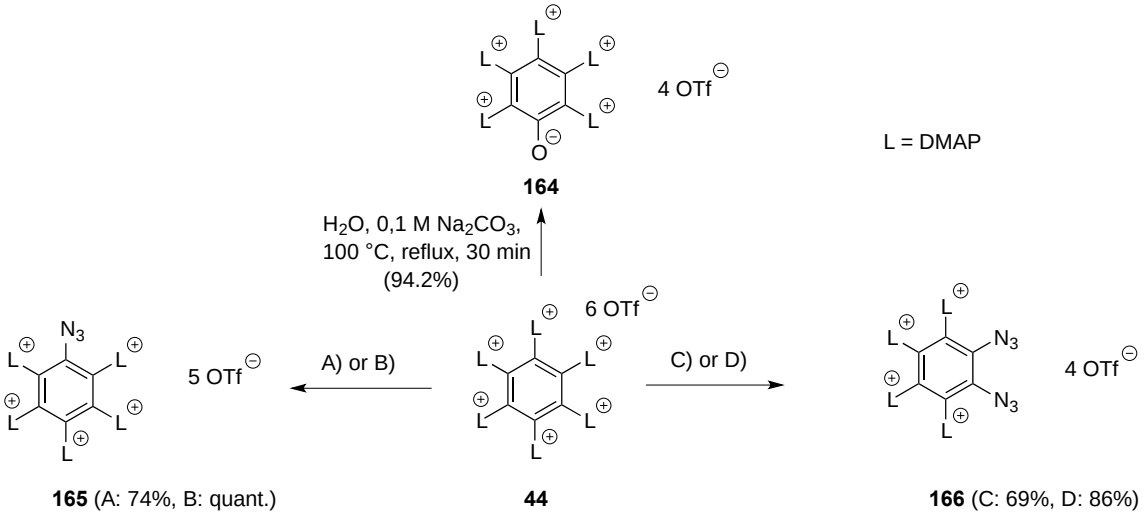


Scheme 53

3. REACTIONS OF HETEROCYCLE POLYCATIONS

3.1. Nucleophilic substitutions

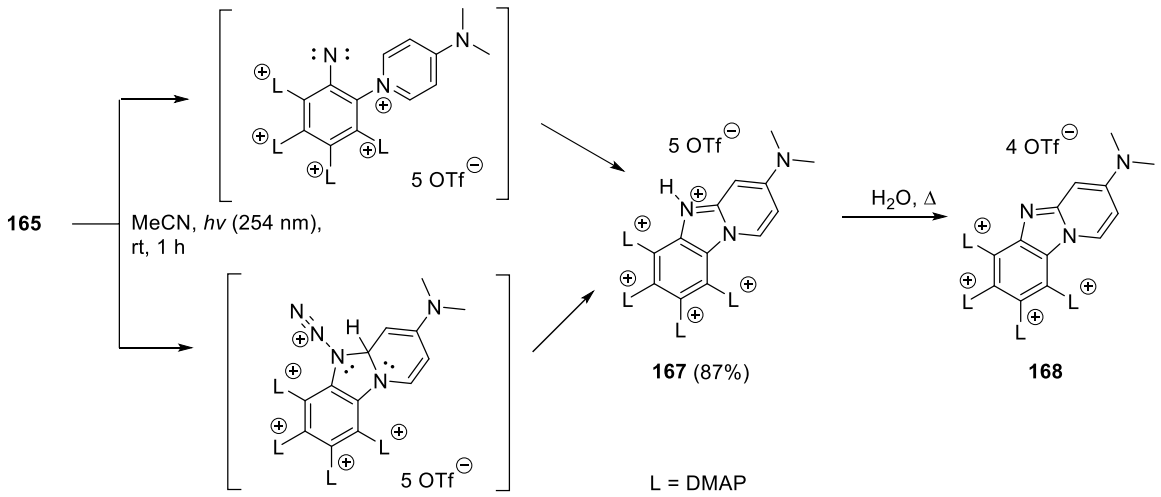
One of the outstanding features of heteroaromatic polycations is their cabability to substitute one or more of the hetarenium rings by other nucleophiles. Often, these procedures gained access to hitherto unknown substitution patterns of the core element. Thus the cationic aromatic **44** reacted with water to give the olate **164** in which one of the cationic groups is substituted by an olate group.[6,58] Based on the hexacation **44**, one or two DMAP ligands were substituted by azido groups, so that the nearly colorless products **165a**,**b** or **166c**,**d** were formed. These substitutions were carried out with sodium azide or guanidinium azide (TMGA) as azide source, whereby the reactions with the latter one led to higher yields (Scheme 54).[62] The same educt **44** reacted with TMGA in the presence of triphenylphosphane to yield iminophosphoranes which were transformed into other products, including amines.[62]



A) $NaN_{3(aq)}$, MeCN, rt, 3 h, NaCl, CH_2Cl_2, 12 h. B) TMGA, MeCN, 2 h, CH_2Cl_2, 1 h
C) NaN_3, MeCN, rt, 3 h, H_2O, NaCl, CH_2Cl_2, 12 h, CH_2Cl_2. D) TMGA, MeCN, 2 h, CH_2Cl_2, 3 h

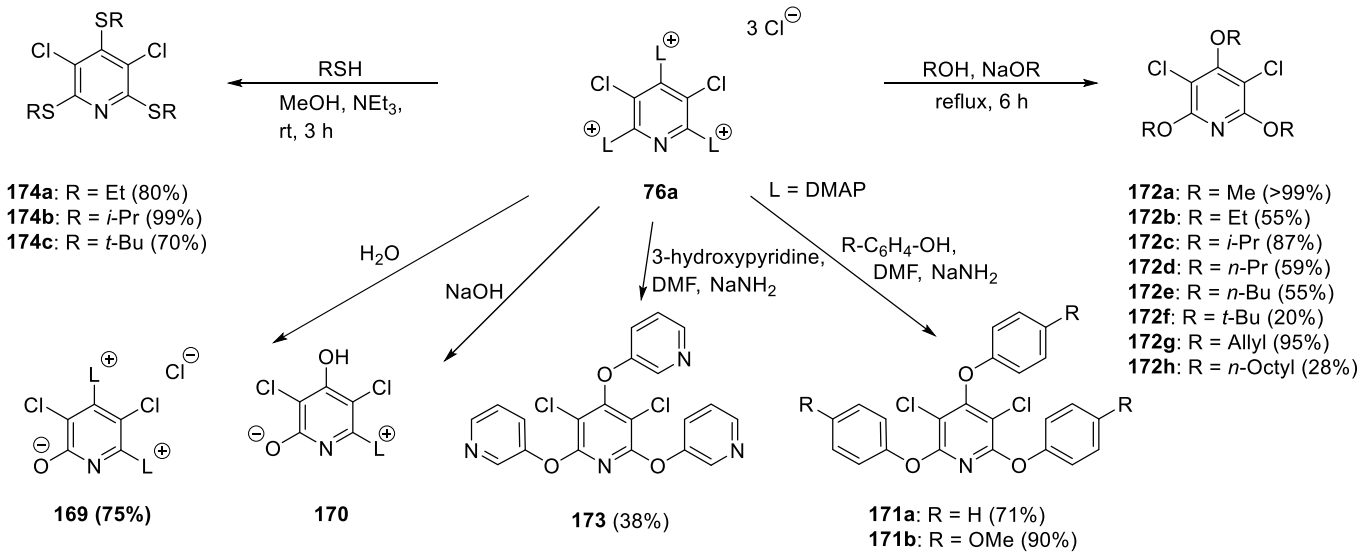
Scheme 54

By irradiation of the azidobenzene **165** at a wavelength of 254 nm, an internal 5-ring closure occurred, so that the cyclized product **167** was obtained. This reaction proceeded through two possible pathways under loss of a nitrogen molecule. Subsequently, the product was converted into its deprotonated form **168** by recrystallization from hot water (Scheme 55).[62]



Scheme 55

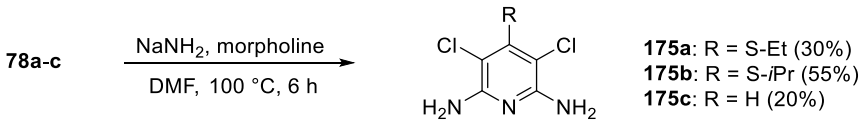
Water converted the trication of pyridine **76a** into the tripole **169**.[65] Sodium hydroxide gave the betaine **170**. Thereby, the cationic groups in γ-position and one in α-position were substituted by a hydroxyl group and a negatively charged oxygen atom, respectively (Scheme 56).[65] Alcoholysis as well as thioalcoholysis provided an elegant approach to a series of substituted pyridines. Some examples are depicted below. An exception can be observed in the reaction of the pyridine derivates **79a** and **79b** with



Scheme 56

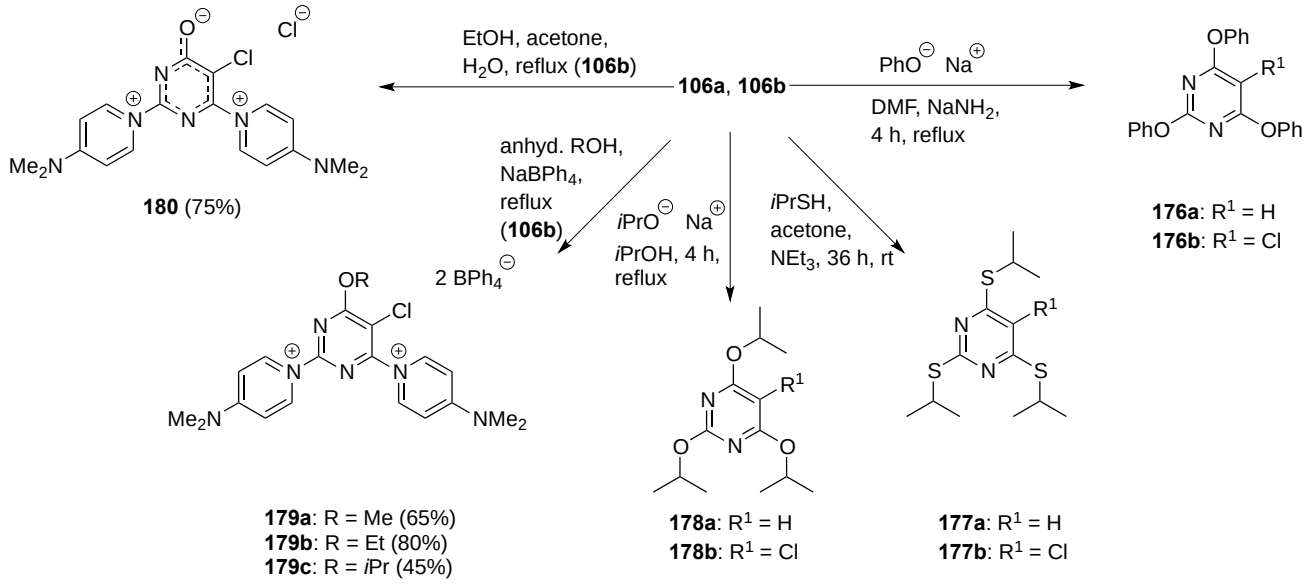
n-butanethiol, because the thioalkyl group bonded in γ position was also substituted by the thio-n-butyl group.[65,66,70,87,88] Dications of pyridine reacted accordingly.

On reaction with the dications **78a-c**, the strong base sodium amide yielded the yellow uncharged products **175** in the presence of morpholine, whereby the cationic DMAP ligands were substituted by amino groups (Scheme 57).[66]



Scheme 57

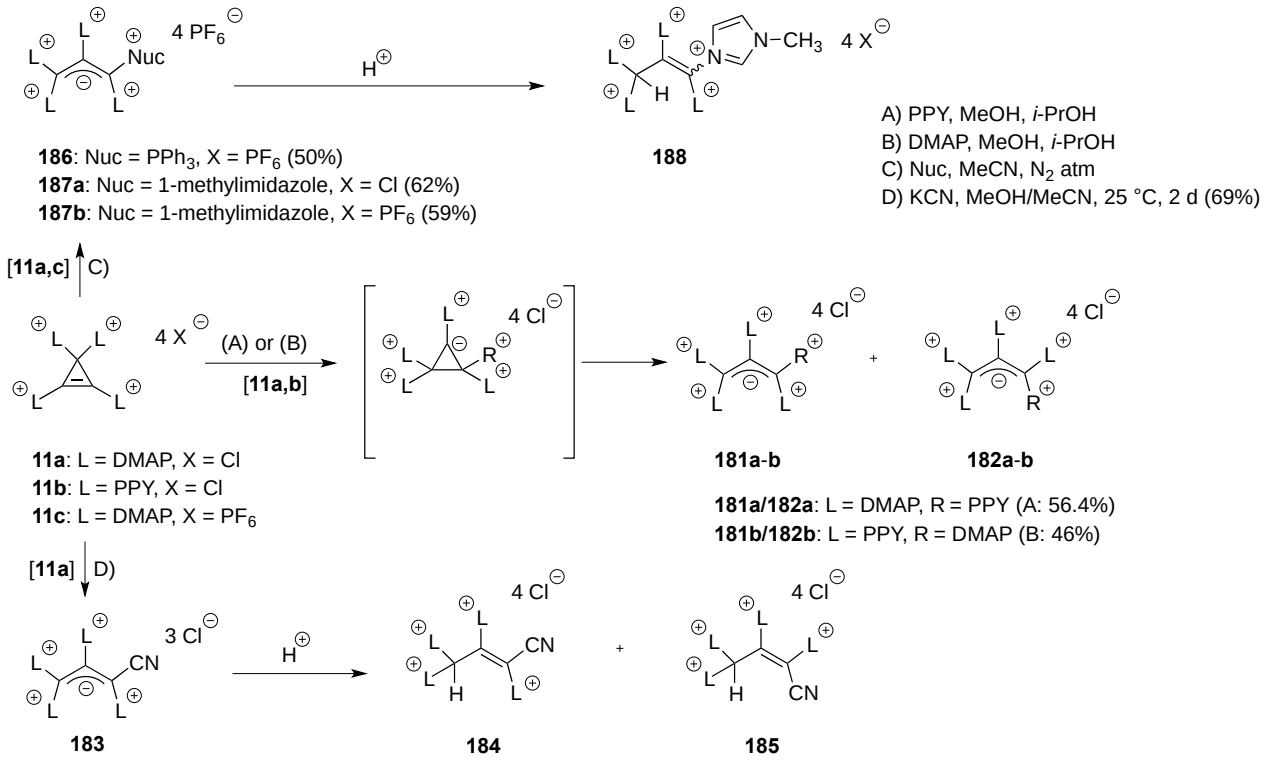
Pyrimidines reacted to novel substituted pyrimidines as depicted in Scheme 58. Thus, dicationic systems (**179**), tripoles (**180**) as well as neutral functionalized pyrimidines were obtained (**176-178**).



Scheme 58

3.2. Nucleophilic additions

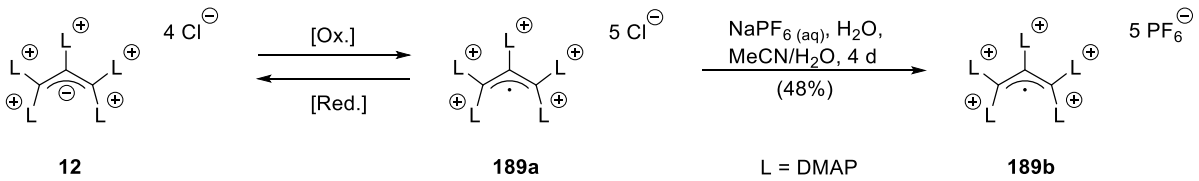
A different addition pattern follows from the reaction of the already substituted TCCP **11a-c** with nucleophiles. Therein, the charged allylides **181-183**, and **186-187** are formed, which exist, depending on the deployed nucleophile, as an isomeric pair or as single stereochemical products. Subsequent protonation of the allylides **183** and **187**, yields a mixture of the corresponding (E)- and (Z)-isomeric propenes **184**/**185** or **188**, respectively (Scheme 59).[26,35]



Scheme 59

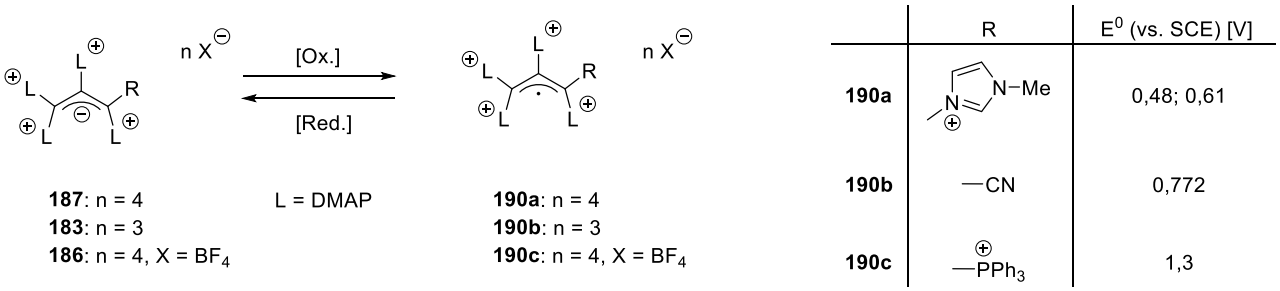
3.3. Oxidations and reductions

The black crystalline allyl radical **189b** can be prepared from the dark red allylide **12** by chemical oxidation with chlorine gas and subsequent treatment with an aqueous solution of sodium hexafluorophosphate. The oxidation is reversible, whereby the standard potential of the allylide, measured against the saturated calomel electrode (SCE), amounts to +0,44 V (Scheme 60).[89]



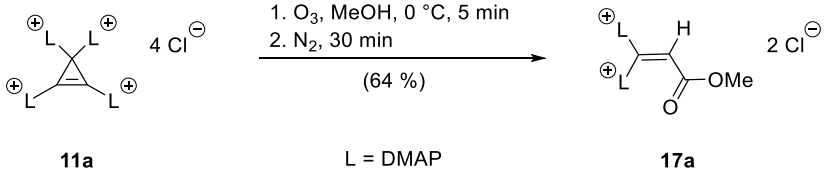
Scheme 60

The mixed allylides **187**, **183**, and **186**, which consist of two different ligand sets, can be similarly oxidized to the corresponding allyl radicals **190a-c**. Within these product list, the triphenylphosphonium allyl radical **190c** displayed the highest standard potential (Scheme 61).[35]



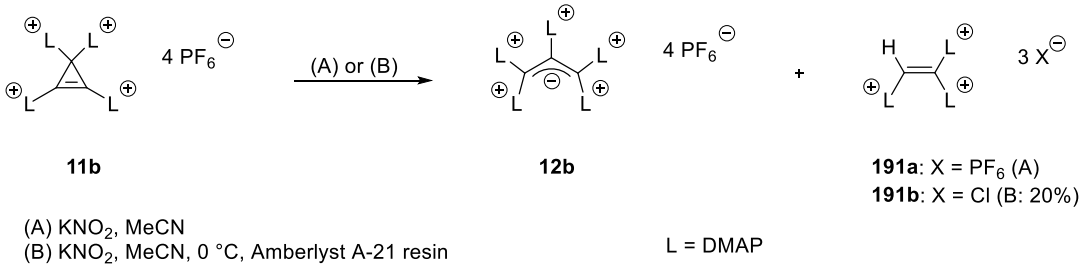
Scheme 61

On reaction with the tetracationically substituted cyclopropene **11a**, ozone yields the methyl propenoate **17a** (Scheme 62).[34] This product can also be synthesized via different paths mentioned before.



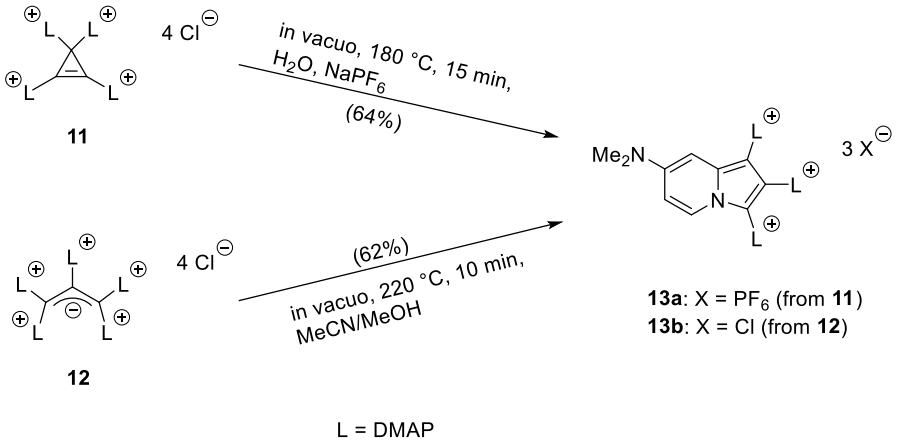
Scheme 62

The reaction of **11b** (PF_6^- salt) with potassium nitrite led in the formation of a 1:1 mixture of deep ruby red plates of the allylide **12b** and pale orange prisms of the tricationic ethylene derivate **191** in the presence of traces of water. The latter could also be synthesized as chloride by application of an ion exchanger (Scheme 63).[35]



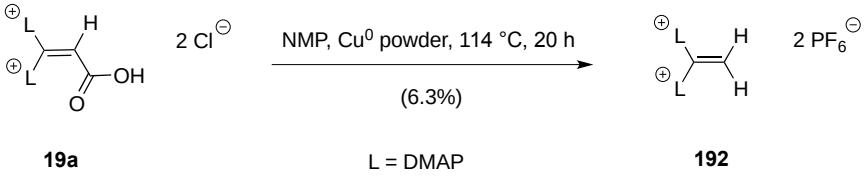
Scheme 63

The tetracationic substituted cyclopropene **11** as well as its corresponding allylide **12** can be converted into the cyclic products **13** on warming (Scheme 64).[26]



Scheme 64

At elevated temperature and in the presence of elemental copper, the dicationically functionalized acrylic acid **19a** decarboxylates to the ethylene compound **192** (Scheme 65).[34]



Scheme 65

4. CONCLUSIONS

Pyridine and imidazole can serve to construct polycationic molecules possessing alkanes, alkenes, cycloalkenes, as well as aromatics and heteroaromatics such as benzene, pyridine, pyrimidine, pyrazine, imidazole as core structure elements. Nucleophilic substitutions on halogenated precursors constitute the major avenue to these polycationic systems. Oligo- and per-hetarenio substituted pyridines and pyrimidines are versatile starting materials for the preparation of functionalized heteroaromatics.

List of abbreviations

CB	chlorobenzene
cf.	*confer* (Latin): compare
DCB	dichlorobenzene
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMAP	4-(dimethylamino)pyridine

DMF	dimethylformamide
DMSO	dimethyl sulfoxide
e.g.	*exempli gratia* (Latin): for example
i.e.	*id est* (Latin): that is to say
MeCN	acetonitrile
MOP	4-(morpholin-1-yl)pyridine
MPP	4-(4-methylpyridin-1-yl)pyridine
NMI	1-methylimidazole
NMP	*N*-methylpyrrolidone
PPY	4-(pyrrolidin-1-yl)pyridine
PYR	pyridine
SASAPOS	self-activated silyl-assisted polyonio substitution
SCE	saturated calomel electrode
TBCP	tetrabromocyclopropene
TBUPY	*tert*-butylpyridine
TCCP	tetrachlorocyclopropene
TGMA	guanidinium azide
THF	tetrahydrofuran
TMSI	trimethylsilyl iodide
TMSOTf	trimethylsilyl triflate

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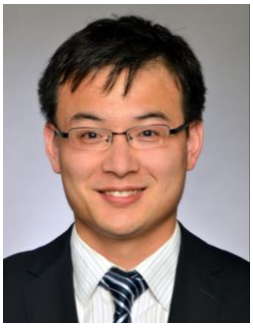

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