SASAPOS Cascades of Perfluorinated Aromatic Carboxylic Acids: Low-Temperature Decarboxylation Triggered by Electrostatic Effects of Polycationic Ligand Sets

Frank G. Pühlhofer*[a] and Robert Weiss[a]

Keywords: Polycations / Decarboxylation / Electrostatic effects / Nucleophilic substitution / Ion clusters

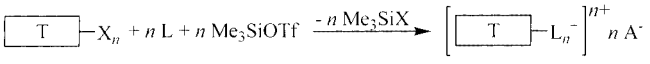
Polycationically substituted derivatives of benzoic and phthalic acids were synthesized for the first time via SASAPOS cascades of the corresponding perfluoro(di)carboxylic acids or acyl chlorides (SASAPOS: ***s***elf-***a***ctivated ***s***ilyl-***a***ssisted ***p***oly-***o***nio ***s***ubstitution). The carboxylic acids decarboxylate with extreme ease (e.g. at room temperature or below) via the corresponding carboxylates. Electrostatically highly stabilized phenylanion derivatives figure as potent electrofuges in these reactions.

Introduction

During the last decade we have developed a general method to replace formally neutral ligand sets in both organic and inorganic compounds by poly- and per-cationic ligand sets.[1−9] This can be achieved by ***s***elf-***a***ctivated ***s***ilyl-***a***ssisted ***p***oly-***o***nio ***s***ubstitution cascades: the SASAPOS protocol, as outlined in general form in Scheme 1.

Such an exchange sequence within the ligand sphere of the central unit T exerts a pronounced effect on the properties of the latter, which is generally proportional to the type and number of cationic ligands introduced. In particular the electrostatically induced lowering of the central template's LUMO leads to a marked increase in electron affinity and electrophilicity of the system. In previous work we had shown that P-nucleophiles are transformed into excellent nucleofuges via SASAPOS cascades on the phosphorus center ("cationic leaving groups").[10] We reasoned that quite generally organic and inorganic systems should develop nucleofugic character while undergoing a SASAPOS transformation, if at least one substituent of potentially electrofugic character is attached to the central template. Qualitatively, this tendency should increase with the number of onio-ligands introduced within a specific SASAPOS cascade. We subsequently describe SASAPOS cascades on perfluorinated aromatic carboxylic acids, the course of which is in line with these expectations.

The experiments and results described below act as prototypes for the introduction of polycationically substituted benzene derivatives into (organic) syntheses as systems that may figure as highly stabilized polycationic leaving groups and as salt-like substituents which provide electrostatic and steric stabilization for formally anionic reaction sites in future applications.

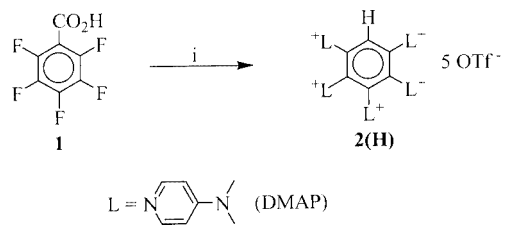


T: organic or inorganic system
X: F, Cl, Br, I, OAc, OR
A: OTf, Cl, Br, I
L: (subst.) pyridines, *N*-methylimidazole, *tert.* amines, nucl. carbenes, *tert.* phosphanes, tetramethylthiocarbamide, dimethylthioformamide

Scheme 1. The general SASAPOS protocol

Results and Discussion

In a first model reaction the SASAPOS protocol was applied to pentafluorobenzoic acid (**1**). With 4-(dimethylamino)-pyridine (DMAP) as the nucleophile L and Me_3SiOTf as the thermodynamic trap for the F^--ions the pentakis(onio)



Scheme 2. SASAPOS protocol applied to pentafluorobenzoic acid (**1**); i) + 5 DMAP, + 5 Me_3SiOTf; − 5 Me_3SiF, − CO_2; Ph−Cl, Δ, 1 d; 97%

[a] Institut für Organische Chemie, Universität Erlangen-Nürnberg,
Henkestraße 42, 91054 Erlangen, Germany
Fax: (internat.) + 49-(0)9131-85-25876
E-mail: frank.puehlhofer@chemie.uni-erlangen.de

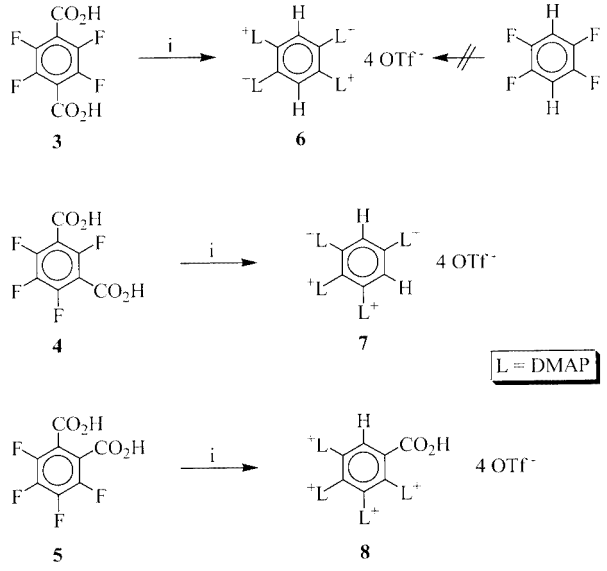
  DOI: 10.1002/ejoc.200300598

substitution product **2(H)** was generated in virtually quantitative yield (Scheme 2).

2(H) was identical with a product we had obtained in earlier work, in which pentafluorobenzene had been exposed to the SASAPOS protocol.[5]

Thus it was evident that CO_2 had been expelled as an electrofuge from the emerging ion cluster at some stage of the SASAPOS sequence. This provides support for our initial assumption concerning facile elimination of electrofuges in the course and as a result of SASAPOS cascades (we refer to this point further below).

This reaction scheme could be extended to structurally related dicarboxylic acids, as exemplified for the three isomeric phthalic acid derivatives **3**−**5** in Scheme 3.



Scheme 3. SASAPOS protocol applied to phthalic acid derivatives **3**−**5**; i) + 4 DMAP, + 4 Me_3SiOTf; − 4 Me_3SiF, − 1, 2 respectively CO_2; Ph−Cl, Δ, 1 d; >95%

Under the same reaction conditions as detailed in Scheme 2 the corresponding SASAPOS cascades of dicarboxylic acids **3**−**5** are also accompanied by decarboxylation. While the *p*- and *m*-dicarboxylic acids **3** and **4**, respectively, lost **both** carboxylic acid functions in the process, the representative of the *o*-series, **5**, selectively released only **one** equivalent CO_2 during the corresponding SASAPOS cascade. This latter observation can be plausibly explained by noting that along the SASAPOS cascade the carboxylic acid function in the *o*-series can have at most one cationic neighbour, whereas there are two for each of the carboxylic acid functions in the other two cases.

Decarboxylation in all these cases will in all likelihood proceed via a polyoniosubstituted carboxylate, which will fragment into CO_2 and an electrostatically stabilized phenylanion. The degree of stabilization of this species depends on the number and relative positions of the cationic substituents. Finally the phenylanion intermediate is trapped by a proton (potentially also by other electrophiles, see below). At what precise stage of the SASAPOS cascade the electrofuge is expelled is unknown at present. In principle, decarboxylation could even precede the polyonio substitution, because polyfluorinated aromatic carboxylic acids are most likely also decarboxylated under the reaction conditions chosen (temperature of refluxing chlorobenzene; presence of a base).[11−13] At least in the case of **3** this can be excluded, as the hypothetical decarboxylation product of **3**, 1,2,5,6-tetrafluorobenzene, does not react at all under SASAPOS conditions to give **6** (cf. Scheme 3). Obviously the carboxylic acid functions, their anions, or the corresponding silyl esters are instrumental for the primary stages of the SASAPOS cascades.

In consequence, we tried to independently synthesize the pentakis-$DMAP^+$-substituted carboxylate **10** via the corresponding acid **9** (cf. Scheme 4). To inhibit decarboxylation during the SASAPOS cascade such a synthesis has to be performed under mild reaction conditions (e.g. room temperature). This necessitates an activation of the aromatic template for S_NAr reactions to achieve $F/DMAP^+$ exchange. As we reported recently, such an activation is provided by acylonio substituents.[7] For a detailed study of the reaction sequence in Scheme 2, we applied this latter activation method to pentafluorobenzoyl chloride (**11**) to synthesize a precursor **13** for **9** and **10**, respectively (Scheme 4).

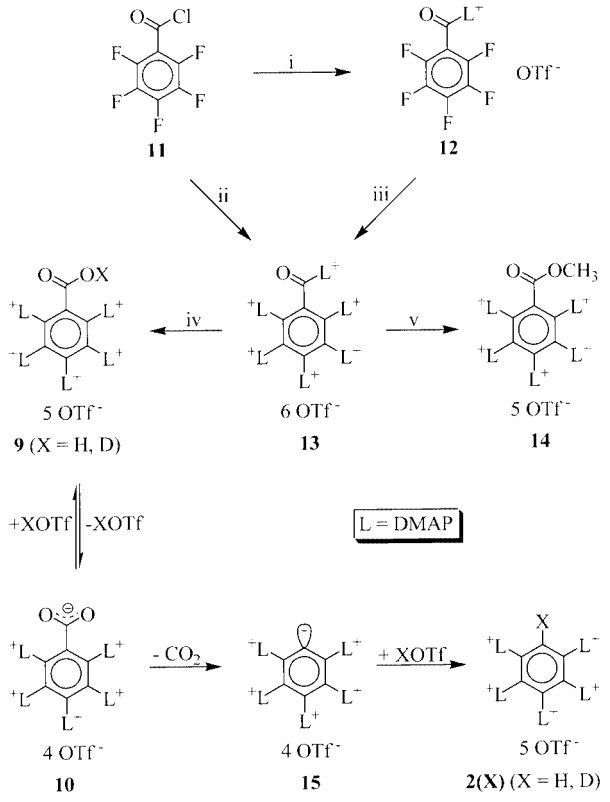
As shown in Scheme 4, precursor **13** can be synthesized directly from **11** or via isolation of the acylonio-activated species **12**. Since **13** is extremely labile towards hydrolysis we were unable to obtain NMR data from pure **13**. FAB-MS spectra of **13** include a peak at m/z = 1577, representing $[\mathbf{13} - OTf]^+$. IR spectra show an intense C=O stretching at 1762 cm^{-1}.

It is well known that acylonio functions $-C(O)L^+$ react with H−Nu under mild conditions to yield −C(O)Nu derivatives.[7] This behaviour was exploited for further stabilization and derivatization of **13** by reacting it with H_2O, D_2O, and CH_3OH (Scheme 4). We expected formation of the (deuterated) carboxylic acid **9** or its methyl ester **14** under these conditions. As shown in Scheme 4, only the latter expectation was fulfilled, while reactions with X_2O (X = H, D) led to formation of the decarboxylation products **2(H)** (X = H) and **2(D)** (X = D). These last two reactions profit from the intermediacy of the highly stabilized phenylanion derivative **15**.

2(H) and **2(D)** were fully characterized by FAB-MS, NMR, and EA. Further hydrolysis experiments showed that CO_2 evolution starts at temperatures as low as −30 °C.

A corresponding behaviour has never been reported for pentafluorobenzoic acid (**1**). Hence, the effect of this particular type of cationic ligand on the decarboxylation of aromatic carboxylic acids is even stronger than the corresponding effect of fluorine substituents. The reaction sequence in Scheme 4 can thus be described as an electrostatically triggered decarboxylation.

As reported previously, the electrostatic activation provided by cationic ligands depends on the number of such substituents, their pole strength, and the distance between

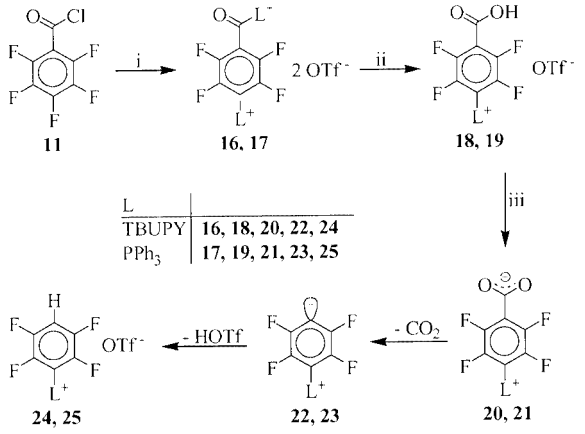


Scheme 4. Synthesis and reactions of the hexacationic precursor system **13**; i) + DMAP, + Me_3SiOTf; − 0.95 Me_3SiCl; CH_2Cl_2, room temp., 12 h; 92%; ii) + 6 DMAP, + 6 Me_3SiOTf; − Me_3SiCl, − 5 Me_3SiF; CH_2Cl_2, room temp., 12 h; 87%; iii) + 5 DMAP, + 5 Me_3SiOTf; − 5 Me_3SiF; CH_2Cl_2, room temp., 12 h; 63%; iv) + excess X_2O (X = H, D); − $DMAPX^+$ OTf^-; CH_3CN, room temp., 0.5 h; 73% (X = H), 95% (X = D); v) + CH_3OH; − $DMAPH^+$ OTf^-; CH_3CN, room temp., 12 h; 81%

positive pole and template.[6] We reasoned therefore that the electrostatic activation exerted by the polycationic ligand set in **9** could also be approximated by a set of cationic ligands fewer in number but higher in pole strength.

This was tested by substituting 4-*tert*-butylpyridine (TBUPY) and triphenylphosphane (PPh_3) for DMAP in SASAPOS cascades applied to pentafluorobenzoyl chloride (**11**) as substrate (Scheme 5). For reasons discussed elsewhere the reaction cascades stopped at the disubstitution stage to give the salts **16** and **17**.[14,15] Hydrolysis of these salts under acidic conditions (H_2O/CF_3SO_3H) yielded the corresponding onio substituted carboxylic acids **18** and **19**, which were fully characterized (Scheme 5). Addition of catalytic amounts of L to suspensions of **18** and **19** in acetonitrile at room temperature gave high yields of the cationically substituted tetrafluorobenzene derivatives **24** and **25** (Scheme 5). These reaction sequences provide strong evidence for the corresponding 4-onio substituted phenylanion derivatives **22** and **23** as intermediates.

Steps ii and iii in Scheme 5 might be combined as hydrolyses under basic conditions, but work-up gets inconvenient since **24** (**25**) need to be separated from protonated TBUPY (PPh_3) by column chromatography.



Scheme 5. Synthesis of cationically substituted tetrafluorobenzene derivatives; i) + 2 L, + 2 Me_3SiOTf; − Me_3SiCl, − Me_3SiF; CH_2Cl_2, room temp., 1 h (TBUPY), 12 h (PPh_3); 89% (TBUPY), 74% (PPh_3); ii) + excess H_2O/CF_3SO_3H (10%); − LH^+ OTf^-; CH_3CN, Δ, 0.5 h; 96% (TBUPY), room temp., 1 h; 94% (PPh_3); iii) + cat. L; CH_3CN, room temp., 7 h; 72% (TBUPY), 12 h; 92% (PPh_3)

Conclusion

The reported results give strong evidence that the decarboxylation sequences of perfluorinated aromatic carboxylic acids proceed via electrostatically stabilized phenylanion derivatives as intermediates. These intermediates act as highly stabilized polycationic leaving groups. The characterization of their electrofugic potential in related reactions and their isolation are the subjects of current investigations.

Experimental Section

General Remarks: All reactions were carried out under N_2 in dry solvents.

Pentakis[4-(dimethylamino)-1-pyridinio]benzene Pentakis(trifluoromethanesulfonate) [2(H)] from 1: Me_3SiOTf (1.29 mL, 7.14 mmol) was added to a suspension of DMAP (997 mg, 8.16 mmol) and pentafluorobenzoic acid (**1**) (217 mg, 1.02 mmol) in chlorobenzene (25 mL), whereupon the suspension cleared. The reaction mixture was stirred under reflux for one day, and a colourless precipitate started to form after 2 h. The precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield 1418 mg (97%) of **2(H)** as a colourless powder. ^1H NMR (400 MHz, CD_3CN): δ = 3.18 (s, 6 H, CH_3), 3.20 (s, 12 H, CH_3), 3.24 (s, 12 H, CH_3), 6.87 (d, $^3J_{H,H}$ = 8.25 Hz, 2 H, H3/5 DMAP), 6.90 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H3/5 DMAP), 6.99 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H3/5 DMAP), 8.01 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H2/6 DMAP), 8.05 (d, $^3J_{H,H}$ = 7.69 Hz, 2 H, H2/6 DMAP), 8.12 (d, $^3J_{H,H}$ = 8.25 Hz, 4 H, H2/6 DMAP), 8.64 (s, 1 H, benzene) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 41.36 (s, CH_3), 41.43 (s, CH_3), 109.80 (s, C3/5 DMAP), 110.56 (s, C3/5 *p*-DMAP), 110.65 (s, C3/5 DMAP), 121.79 (q, $|^1J_{C,F}|$ = 320.4 Hz, CF_3), 132.86 (s, C6 benzene), 137.93 (s, C1/5 benzene), 138.29 (s, C3 benzene), 140.96 (s, C2/6 DMAP), 141.42 (s, C2/6 DMAP), 142.37 (s, C2/4 benzene), 157.40 (s, C4 *p*-DMAP), 157.45 (s, C4 DMAP), 157.80 (s, C4 DMAP) ppm. FAB-MS (NBA): *m/z* = 1279 $[M - OTf]^+$, 1129 $[M - HOTf - OTf]^+$. $C_{46}H_{51}F_{15}N_{10}O_{15}S_5$ (1429.24): calcd. C 38.66, H 3.60, N 9.80; found C 38.95, H 3.85, N 9.38.

General Procedure for the Syntheses of the Tetracationically Substituted Aromatics 6−8: Me_3SiOTf (6 equiv.) was added to a suspension of DMAP (7 equiv.) and tetrafluoro phthalic acid **3**−**5** (1 equiv.) in chlorobenzene (25 mL), whereupon the suspension cleared. The reaction mixture was stirred under reflux for one day, and a colourless precipitate started to form after 2 h. The precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield a colourless powder.

1,2,4,5-Tetrakis[4-(dimethylamino)-1-pyridinio]benzene Tetrakis(trifluoromethanesulfonate) (6): Yield 99% of **6** as a colourless powder. ^{1}H NMR (400 MHz, CD_3CN): δ = 3.24 (s, 24 H, CH_3), 6.98 (d, $^3J_{H,H}$ = 8.06 Hz, 8 H, H3/5 DMAP), 8.12 (d, $^3J_{H,H}$ = 8.06 Hz, 8 H, H2/6 DMAP), 8.21 (s, 2 H, benzene) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 41.26 (s, CH_3), 109.60 (s, C3/5 DMAP), 120.30 (q, $|^1J_{C,F}|$ = 322.3 Hz, CF_3), 131.11 (s, C3/6 benzene), 139.84 (s, C1/2/4/5 benzene), 141.98 (s, C2/6 DMAP), 157.75 (s, C4 DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1009 [M − OTf]$^+$, 859 [M − HOTf − OTf]$^+$. $C_{38}H_{42}F_{12}N_8O_{12}S_4$ (1159.02) + 2H_2O: calcd. C 38.19, H 3.88, N 9.38 S 10.73; found C 38.05, H 3.85, N 9.21 S 10.58.

1,2,3,5-Tetrakis[4-(dimethylamino)-1-pyridinio]benzene Tetrakis(trifluoromethanesulfonate) (7): Yield 97% of **7** as a colourless powder. ^{1}H NMR (400 MHz, CD_3CN): δ = 3.20 (s, 6 H, CH_3), 3.24 (s, 12 H, CH_3), 3.30 (s, 6 H, CH_3), 6.86 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H3/5 DMAP), 6.97 (d, $^3J_{H,H}$ = 8.05 Hz, 4 H, H3/5 DMAP1/3), 7.12 (d, $^3J_{H,H}$ = 8.05 Hz, 2 H, H3/5 DMAP), 8.00 (d, $^3J_{H,H}$ = 7.81 Hz, 2 H, H2/6 DMAP), 8.12 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H2/6 DMAP1/3), 8.30 (s, 2 H, benzene), 8.38 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H2/6 DMAP) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 41.24 (s, CH_3), 41.31 (s, CH_3), 109.40 (s, C3/5 DMAP), 109.46 (s, C3/5 DMAP1/3), 110.30 (s, C3/5 DMAP), 121.92 (q, $|^1J_{C,F}|$ = 321.1 Hz, CF_3), 127.56 (s, C4/6 benzene), 134.54 (s, C2/5 benzene), 140.83 (s, C1/3 benzene), 141.50 (s, C2/6 DMAP), 141.74 (s, C2/6 DMAP), 142.07 (s, C2/6 DMAP1/3), 145.41 (s, C2/5 benzene), 157.44 (s, C4 DMAP), 157.75 (s, C4 DMAP1/3), 158.06 (s, C4 DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1009 [M − OTf]$^+$, 859 [M − HOTf − OTf]$^+$. $C_{38}H_{42}F_{12}N_8O_{12}S_4$ (1159.02) + 2H_2O: calcd. C 38.19, H 3.88, N 9.38 S 10.73; found C 37.94, H 3.81, N 9.35 S 10.55.

2,3,4,5-Tetrakis[4-(dimethylamino)-1-pyridinio]benzoic Acid Tetrakis(trifluoromethanesulfonate) (8): Yield 97% of **8** as a colourless powder. ^{1}H NMR (400 MHz, CD_3NO_2): δ = 3.26 (s, 6 H, CH_3), 3.27 (s, 6 H, CH_3), 3.33 (s, 6 H, CH_3), 3.35 (s, 6 H, CH_3), 6.95 (d, $^3J_{H,H}$ = 8.30 Hz, 2 H, H3/5 DMAP), 6.97 (d, $^3J_{H,H}$ = 8.30 Hz, 2 H, H3/5 DMAP), 7.01 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H3/5 DMAP), 7.07 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H3/5 DMAP), 8.18 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H2/6 DMAP), 8.19 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H2/6 DMAP), 8.22 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H2/6 DMAP), 8.24 (d, $^3J_{H,H}$ = 8.05 Hz, 2 H, H2/6 DMAP), 8.87 (s, 1 H, benzene) ppm. ^{13}C NMR (100 MHz, CD_3NO_2): δ = 41.17 (s, CH_3), 41.28 (s, CH_3), 41.32 (s, CH_3), 41.39 (s, CH_3), 109.24 (s, C3/5 DMAP), 109.81 (s, C3/5 DMAP), 110.23 (s, C3/5 DMAP), 110.47 (s, C3/5 DMAP), 122.07 (q, $|^1J_{C,F}|$ = 319.9 Hz, CF_3), 134.64 (s, C1/2/3/4/5 benzene), 135.88 (s, C6 benzene), 138.89 (s, C1/2/3/4/5 benzene), 139.31 (s, C1/2/3/4/5 benzene), 141.76 (s, C1/2/3/4/5 benzene), 141.82 (s, C2/6 DMAP), 142.11 (s, C1/2/3/4/5 benzene), 142.22 (s, C2/6 DMAP), 142.84 (s, C2/6 DMAP), 157.69 (s, C4 DMAP), 157.75 (s, C4 DMAP), 158.22 (s, C4 DMAP), 162.77 (s, CO) ppm. FAB-MS (NBA): *m*/*z* = 1053 [M − OTf]$^+$, 1009 [M − CO_2 − OTf]$^+$, 859 [M − CO_2 − HOTf − OTf]$^+$, 709 [M − CO_2 − 2HOTf − OTf]$^+$, 587 [M − CO_2 − DMAP − 2HOTf − OTf]$^+$. $C_{39}H_{42}F_{12}N_8O_{14}S_4$ (1203.03) + 3H_2O: calcd. C 37.26, H 3.85, N 8.91 S 10.20; found C 37.38, H 3.55, N 8.67 S 10.42.

{[4-(Dimethylamino)-1-pyridinio]carbonyl}pentafluorobenzene Trifluoromethanesulfonate (12): DMAP (242 mg, 1.98 mmol) and Me_3SiOTf (0.36 mL, 1.98 mmol) were added to a solution of pentafluorobenzoyl chloride **11** (0.3 mL, 2.08 mmol) in CH_2Cl_2 (20 mL). The resulting pale-yellow reaction mixture was stirred for 12 h at room temperature. Addition of diethyl ether (50 mL) yielded a colourless precipitate, which was filtered and washed with diethyl ether (7 × 5 mL). Drying in high vacuum yielded 895 mg (92%) of **12** as a colourless powder. IR (nujol): ṽ = 3094, 1752, 1650, 1603, 1510, 1259, 1175, 1107, 1030, 992, 839, 828, 750, 730, 638 cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN): δ = 3.37 (s, 6 H, CH_3), 7.01 (d, $^3J_{H,H}$ = 8.30 Hz, 2 H, H3/5 DMAP), 8.43 (d, $^3J_{H,H}$ = 8.30 Hz, 2 H, H2/6 DMAP) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 42.28 (s, CH_3), 106.64 (t, $|J_{C,F}|$ = 3.7 Hz, C1 benzene), 109.18 (s, C3/5 DMAP), 122.11 (q, $|^1J_{C,F}|$ = 319.9 Hz, CF_3), 137.81 (s, C2/6 DMAP), 139.51 (dm, $|^1J_{C,F}|$ = 257.4 Hz, C−F benzene), 146.08 (dm, $|^1J_{C,F}|$ = 262.9 Hz, C−F benzene), 158.79 (s, CO), 159.68 (s, C4 DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1249 [3M − OTf]$^+$, 783 [2M − OTf]$^+$, 317 [M − OTf]$^+$. $C_{15}H_{10}F_8N_2O_4S_1$ (466.30): calcd. C 38.64, H 2.16, N 6.01; found C 38.45, H 2.47, N 5.99.

Pentakis[4-(dimethylamino)-1-pyridinio]-{[4-(dimethylamino)-1-pyridinio]carbonyl}benzene Hexakis(trifluoromethanesulfonate) (13) from 11: DMAP (636 mg, 5.21 mmol) and Me_3SiOTf (0.82 mL, 4.81 mmol) were added to a solution of pentafluorobenzoyl chloride (**11**, 0.1 mL, 0.69 mmol) in CH_2Cl_2 (20 mL). The resulting pale-yellow reaction mixture was stirred at room temperature for 12 h, and a colourless precipitate started to form after 10 min. The precipitate was filtered, washed with CH_2Cl_2 (7 × 5 mL), and dried in high vacuum to yield 1032 mg (87%) of **13** as a colourless powder. IR (nujol): ṽ = 1762 (C=O) cm^{-1}. FAB-MS (NBA): *m*/*z* = 1577 [M − OTf]$^+$.

Pentakis[4-(dimethylamino)-1-pyridinio]-{[(4-dimethylamino)-1-pyridinio]carbonyl}benzene Hexakis(trifluoromethanesulfonate) (13) from 12: DMAP (535 mg, 4.38 mmol) and Me_3SiOTf (0.73 mL, 4.02 mmol) were added to a solution of **12** (342 mg, 0.73 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at room temperature for 12 h, and a colourless precipitate started to form after 2 min. The precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL) and dried in high vacuum to yield 791 mg (63%) of **13** as a colourless powder; for characterization see above.

Pentakis[(4-dimethylamino)-1-pyridinio]benzoic Acid Methyl Ester Pentakis(trifluoromethanesulfonate) (14): Methanol (0.1 mL) was added to solid **13** (423 mg, 0.24 mmol) and CH_3CN (15 mL) was added after 2 min. The resulting yellow solution was stirred for 12 h and then evaporated to dryness. CH_2Cl_2 (30 mL) was added to the residue and stirred for 12 h to remove formed protonated DMAP. The remaining colourless precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield 289 mg (81%) of **14** as a colourless powder. IR (nujol): ṽ = 3066, 1746, 1652, 1592, 1264, 1148, 1064, 1030, 825, 637 cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN/CF_3COOD): δ = 3.17 (s, 6 H, CH_3 *p*-DMAP), 3.17 (s, 12 H, CH_3), 3.22 (s, 12 H, CH_3), 3.61 (s, 3 H, OCH_3), 6.84 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H3/5 *p*-DMAP), 6.85 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H3/5 DMAP), 6.94 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H3/5 DMAP), 8.05 (d, $^3J_{H,H}$ = 7.08 Hz, 2 H, H2/6 *p*-DMAP), 8.06 (d, $^3J_{H,H}$ = 7.81 Hz, 4 H, H2/6 DMAP), 8.15 (d, $^3J_{H,H}$ = 8.05 Hz, 4 H, H2/6 DMAP) ppm. ^{13}C NMR (100 MHz, CD_3CN/CF_3COOD): δ = 41.60 (s, CH_3), 41.66 (s, CH_3), 56.11 (s, OCH_3) 110.13 (s, C3/5 DMAP), 110.90 (s, C3/5 DMAP), 110.97 (s, C3/5 *p*-DMAP), 121.56 (q, $|^1J_{C,F}|$ = 318.1 Hz, CF_3), 136.46 (s, benzene), 140.55 (s, benzene), 140.70 (s, benzene), 141.07 (s, C2/6 *p*-DMAP), 141.28 (s, C2/6 DMAP), 141.69 (s, benzene), 142.03 (s, C2/6 DMAP), 157.82

(s, C4 DMAP), 158.09 (s, C4 DMAP), 160.94 (s, CO) ppm. FAB-MS (NBA): *m/z* = 1336 [M − HOTf]$^+$, 1278 [M − $COOCH_3$ − OTf]$^+$, 1008 [M + H − $COOCH_3$ − 2OTf]$^+$.

Pentakis[4-(dimethylamino)-1-pyridinio]benzene Pentakis(trifluoromethanesulfonate) [2(H)] from 11: DMAP (550 mg, 4.50 mmol) and Me_3SiOTf (0.76 mL, 4.20 mmol) were added to a solution of pentafluorobenzoyl chloride (**11**, 0.1 mL, 0.69 mmol) in CH_2Cl_2 (25 mL). After stirring for 12 h the formed precipitate (**13**) was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum. The dry primary product (**13**) was dissolved in CH_3CN (10 mL) and H_2O (1 mL) was added. The solvent was removed in high vacuum after 30 min. The protonated DMAP formed was removed by adding CH_2Cl_2 (30 mL) and stirring for 12 h. The remaining colourless precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield 718 mg (73%) of **2(H)** as a colourless powder. ^{1}H NMR (400 MHz, CD_3CN): δ = 3.16 (s, 6 H, CH_3), 3.21 (s, 12 H, CH_3), 3.25 (s, 12 H, CH_3), 6.88 (d, $^3J_{H,H}$ = 8.64 Hz, 2 H, H3/5 DMAP), 6.90 (d, $^3J_{H,H}$ = 8.25 Hz, 4 H, H3/5 DMAP), 7.00 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H3/5 DMAP), 8.02 (d, $^3J_{H,H}$ = 8.25 Hz, 4 H, H2/6 DMAP), 8.07 (d, $^3J_{H,H}$ = 8.24 Hz, 2 H, H2/6 DMAP), 8.13 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H2/6 DMAP), 8.64 (s, 1 H, benzene) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 41.36 (s, CH_3), 41.42 (s, CH_3), 109.79 (s, C3/5 DMAP), 110.53 (s, C3/5 *p*-DMAP), 110.62 (s, C3/5 DMAP), 121.80 (q, $|^1J_{C,F}|$ = 319.9 Hz, CF_3), 132.86 (s, C6 benzene), 137.94 (s, C1/5 benzene), 138.28 (s, C3 benzene), 140.96 (s, C2/6 DMAP), 141.40 (s, C2/6 DMAP), 142.36 (s, C2/4 benzene), 157.40 (s, C4 *p*-DMAP), 157.45 (s, C4 DMAP), 157.77 (s, C4 DMAP) ppm. FAB-MS (NBA): *m/z* = 1279 [M − OTf]$^+$, 1129 [M − HOTf − OTf]$^+$. $C_{46}H_{51}F_{15}N_{10}O_{15}S_5$ (1429.24): calcd. C 38.66, H 3.60, N 9.80; found C 38.92, H 3.89, N 9.33.

Pentakis[4-(dimethylamino)-1-pyridinio]deuteriobenzene Pentakis(trifluoromethanesulfonate) [2(D)]: DMAP (599 mg, 4.90 mmol) and Me_3SiOTf (0.82 mL, 4.55 mmol) were added to a solution of pentafluorobenzoyl chloride (**11**, 0.1 mL, 0.69 mmol) in CH_2Cl_2 (25 mL). After 12 h of stirring D_2O (1 mL) was added and the solvent removed in high vacuum after 10 min. The protonated DMAP formed was removed by adding CH_2Cl_2 (30 mL) and stirring for 12 h. The remaining colourless precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield 939 mg (95%) of **2(D)** as a colourless powder. ^{1}H NMR (400 MHz, CD_3CN): δ = 3.18 (s, 6 H, CH_3), 3.20 (s, 12 H, CH_3), 3.24 (s, 12 H, CH_3), 6.87 (d, $^3J_{H,H}$ = 8.64 Hz, 2 H, H3/5 DMAP), 6.89 (d, $^3J_{H,H}$ = 8.25 Hz, 4 H, H3/5 DMAP), 7.00 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H3/5 DMAP), 8.00 (d, $^3J_{H,H}$ = 8.25 Hz, 4 H, H2/6 DMAP), 8.04 (d, $^3J_{H,H}$ = 8.24 Hz, 2 H, H2/6 DMAP), 8.11 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H2/6 DMAP) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 41.34 (s, CH_3), 41.42 (s, CH_3), 109.79 (s, C3/5 DMAP), 110.54 (s, C3/5 *p*-DMAP), 110.64 (s, C3/5 DMAP), 121.77 (q, $|^1J_{C,F}|$ = 319.9 Hz, CF_3), 132 (br. m, C6 benzene), 137.90 (s, C1/5 benzene), 138.25 (s, C3 benzene), 140.93 (s, C2/6 DMAP), 141.39 (s, C2/6 DMAP), 142.30 (s, C2/4 benzene), 157.39 (s, C4 *p*-DMAP), 157.43 (s, C4 DMAP), 157.77 (s, C4 DMAP) ppm. FAB-MS (NBA): *m/z* = 1280 [M − OTf]$^+$, 1130 [M − HOTf − OTf]$^+$. $C_{46}H_{50}D_1F_{15}N_{10}O_{15}S_5$ (1430.24) + 0.5H_2O: calcd. C 38.42, H 3.64, N 9.74 S 11.15; found C 38.42, H 3.51, N 9.43 S 11.36.

4-[4-(*tert*-Butyl)-1-pyridinio]-1-{[4-(*tert*-butyl)-1-pyridinio]carbonyl}-2,3,5,6-tetrafluorobenzene Bis(trifluoromethanesulfonate) (16): 4-*tert*-Butylpyridine (3.08 mL, 20.85 mmol) and Me_3SiOTf (2.51 mL, 13.90 mmol) were added to a solution of pentafluorobenzoyl chloride (**11**, 1.0 mL, 6.95 mmol) in CH_2Cl_2 (25 mL). Formation of a colourless precipitate started after 5 min. After 1 h of stirring the precipitate was filtered, washed with CH_2Cl_2 (5 × 10 mL), and dried in high vacuum to yield 4578 mg (89%) of **16** as a colourless powder. IR (nujol): $\tilde{\nu}$ = 3132, 3056, 1793, 1636, 1609, 1251, 1225, 1152, 1029, 1002, 860, 803, 719, 664, 638 cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.38 (s, 9 H, CH_3), 1.46 (s, 9 H, CH_3), 8.03 (d, $^3J_{H,H}$ = 6.60 Hz, 2 H, H3/5 pyridine), 8.32 (d, $^3J_{H,H}$ = 7.15 Hz, 2 H, H3/5 pyridine), 8.58 (d, $^3J_{H,H}$ = 6.60 Hz, 2 H, H2/6 pyridine), 8.77 (d, $^3J_{H,H}$ = 7.14 Hz, 2 H, H2/6 pyridine) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 29.99 (s, CH_3), 30.17 (s, CH_3), 37.78 [s, $C(CH_3)_3$], 38.66 [s, $C(CH_3)_3$], 121.54 (q, $|^1J_{C,F}|$ = 318.9 Hz, CF_3), 127.85 (s, C3/5 pyridine), 127.91 (s, C3/5 pyridine), 146.61 (s, C2/6 pyridine), 146.70 (s, C2/6 pyridine), 159.56 (s, CO), 174.83 (s, C4 pyridine), 178.03 (s, C4 pyridine) ppm. $C_{27}H_{26}F_{10}N_2O_7S_2$ (744.62): calcd. C 43.55, H 3.52, N 3.76; found C 43.47, H 3.47, N 3.57.

4-Triphenylphosphonio-1-[(triphenylphosphonio)carbonyl]-2,3,5,6-tetrafluorobenzene Bis(trifluoromethanesulfonate) (17): Triphenylphosphane (364 mg, 1.39 mmol) and Me_3SiOTf (0.25 mL, 1.39 mmol) were added to a solution of pentafluorobenzoyl chloride (**11**, 0.1 mL, 0.69 mmol) in CH_2Cl_2 (20 mL). Addition of diethyl ether (50 mL) after 12 h of stirring yielded a colourless precipitate, which was filtered, washed with diethyl ether (7 × 5 mL), and dried in high vacuum to yield 507 mg (74%) of **17** as a colourless powder. IR (nujol): $\tilde{\nu}$ = 1826, 1739, 1693, 1652, 1587, 1525, 1261, 1224, 1154, 1106, 1030, 987, 875, 750, 723, 689, 637 cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.83 (m, phenyl) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 116.76 (d, $|^1J_{C,P}|$ = 86.4 Hz, C1 phenyl), 117.20 (d, $|^1J_{C,P}|$ = 91.9 Hz, C1 phenyl), 122.03 (q, $|^1J_{C,F}|$ = 319.9 Hz, CF_3), 131.37 (d, $|^3J_{C,P}|$ = 12.9 Hz, C3/5 phenyl), 131.50 (d, $|^3J_{C,P}|$ = 12.9 Hz, C3/5 phenyl), 131.55 (d, $|J_{C,P}|$ = 11.9 Hz, C1/4 benzene), 135.23 (d, $|^2J_{C,P}|$ = 12.9 Hz, C2/6 phenyl), 135.49 (d, $|^2J_{C,P}|$ = 12.0 Hz, C2/6 phenyl), 135.55 (d, $|J_{C,P}|$ = 11.1 Hz, C1/4 benzene), 136.57 (s, C4 phenyl), 146.48 (dm $|^1J_{C,F}|$ = 294.1 Hz, C2/3/5/6 benzene), 149.20 (dm, $|^1J_{C,F}|$ = 259.3 Hz, C2/3/5/6 benzene), 159.10 (s, CO) ppm. ^{31}P NMR (162 MHz, CD_3CN): δ = 21.7 (s), 17.33 (s) ppm. FAB-MS (NBA): *m/z* = 849 [M − OTf]$^+$, 410 [M − CO − PPh_3 − 2OTf]$^+$. $C_{45}H_{30}F_{10}O_7P_2S_2$ (998.78) + 2H_2O: calcd. C 52.22, H 3.31; found C 52.52, H 3.41.

4-[4-(*tert*-Butyl)-1-pyridinio]-2,3,5,6-tetrafluorobenzoic Acid Trifluoromethanesulfonate (18): An aqueous solution of trifluoromethanesulfonic acid (10%, 1.0 mL) was added to a suspension of **16** (8718 mg, 11.71 mmol) in acetonitrile (25 mL), which cleared after 30 sec. The solution was stirred under reflux for 30 min and the solvent was removed completely. CH_2Cl_2 (50 mL) was added to the colourless residue and stirred for 12 h to dissolve protonated 4-*tert*-butylpyridine. The remaining precipitate was filtered, washed with CH_2Cl_2 (5 × 15 mL), and dried in high vacuum to yield 5382 mg (96%) of **18** as a colourless powder. IR (nujol): $\tilde{\nu}$ = 3129, 3069, 1737, 1638, 1378, 1284, 1223, 1177, 1160, 1029, 1008, 856, 696, 637 cm^{-1}. ^{1}H NMR (400 MHz, CD_3NO_2/CF_3COOD): δ = 1.55 (s, 9 H, CH_3), 8.46 (d, $^3J_{H,H}$ = 7.08 Hz, 2 H, H3/5 pyridine), 8.86 (d, $^3J_{H,H}$ = 6.10 Hz, 2 H, H2/6 pyridine) ppm. ^{13}C NMR (100 MHz, CD_3NO_2/CF_3COOD): δ = 30.08 (s, CH_3), 38.89 [s, $C(CH_3)_3$], 116.89 (t, $|^2J_{C,F}|$ = 15.7 Hz, C4 benzene), 121.44 (q, $|^1J_{C,F}|$ = 318.0 Hz, CF_3), 125.10 (m, C1 benzene), 128.13 (s, C3/5 pyridine), 143.52 (dm, $|^1J_{C,F}|$ = 259 Hz, C2/3/5/6 benzene), 146.73 (s, C2/6 pyridine), 147.15 (dm, $|^1J_{C,F}|$ = 263 Hz, C2/3/5/6 benzene), 160.43 (s, CO_2H), 179.00 (s, C4 pyridine) ppm. FAB-MS (NBA): *m/z* = 805 [2M − OTf]$^+$, 328 [M − OTf]$^+$, 284 [M − CO_2 − OTf]$^+$. $C_{17}H_{14}F_7N_1O_5S_1$ (477.35): calcd. C 42.78, H 2.96, N 2.93 S 6.72; found C 42.61, H 2.95, N 2.77 S 6.30.

4-(Triphenylphosphonio)-2,3,5,6-tetrafluorobenzoic Acid Trifluoromethanesulfonate(19): An aqueous solution of trifluoromethanesulfonic acid (10%, 1.0 mL) was added to a yellow solution of **17** (2252 mg, 2.26 mmol) in acetonitrile (25 mL). The solution was stirred for 1 h at room temperature and the solvent was removed completely. $CHCl_3$ (50 mL) was added to the colourless residue and stirred for 12 h to dissolve protonated triphenylphosphane. The remaining precipitate was filtered, washed with $CHCl_3$ (5 × 5 mL), and dried in high vacuum to yield 1276 mg (94%) of **19** as a colourless powder. IR (nujol): $\tilde{\nu}$ = 1744 (CO) cm^{-1}. ^1H NMR (400 MHz, CD_3NO_2): δ = 7.9 (m, phenyl) ppm. ^{13}C NMR (100 MHz, CD_3NO_2): δ = 103.59 (d, $|^1J_{C,P}|$ = 86.9 Hz, C4 benzene), 117.62 (d, $|^1J_{C,P}|$ = 91.6 Hz, C1 phenyl), 122.12 (q, $|^1J_{C,F}|$ = 320.0 Hz, CF_3), 122.46 (s, C1 benzene), 131.93 (d, $|^3J_{C,P}|$ = 13.9 Hz, C3/5 phenyl), 135.77 (d, $|^2J_{C,P}|$ = 11.1 Hz, C2/6 phenyl), 137.56 (d, $|^4J_{C,P}|$ = 3.7 Hz, C4 phenyl), 150 (2 × m, CF benzene), 159.72 (s, COOH) ppm. ^{31}P NMR (162 MHz, CD_3NO_2): δ = 18.1 (s) ppm. FAB-MS (NBA): *m/z* = 1059 $[2M - OTf]^+$, 455 $[M - OTf]^+$, 411 $[M - CO_2 - OTf]^+$. $C_{26}H_{16}F_7O_5P_1S_1$ (604.43): calcd. C 51.76, H 2.67 S 5.30; found C 51.49, H 3.04 S 5.58.

4-[4-(*tert*-Butyl)-1-pyridinio]-2,3,5,6-tetrafluorobenzene Trifluoromethanesulfonate (24): 4-*tert*-Butylpyridine (0.32 mL, 2.15 mmol) was added to a suspension of **18** (5139 mg, 10.77 mmol) in acetonitrile (30 mL). The suspension was stirred for 7 h and cleared after 15 min. After removal of the solvent in high vacuum the oily residue was dissolved in CH_2Cl_2 (20 mL). Addition of diethyl ether (100 mL) led to formation of a colourless precipitate, which was filtered, washed with diethyl ether (5 × 10 mL), and dried in high vacuum to yield 3340 mg (72%) of **24** as a colourless powder. IR (nujol): $\tilde{\nu}$ = 3127, 3073, 1637, 1544, 1512, 1276, 1261, 1152, 1030, 947, 852, 637 cm^{-1}. ^1H NMR (400 MHz, CD_3CN/CF_3COOD): δ = 1.47 (s, 9 H, CH_3), 7.77 (tt, $|^3J_{H,F}|$ = 10.25 Hz, $|^4J_{H,F}|$ = 7.45 Hz, 1 H, H4 benzene), 8.32 (dt, $^3J_{H,H}$ = 7.08 Hz, $|^6J_{H,F}|$ = 2.08 Hz, 2 H, H3/5 pyridine), 8.79 (dt, $^3J_{H,H}$ = 7.33 Hz, $|^5J_{H,F}|$ = 0.98 Hz, 2 H, H2/6 pyridine) ppm. ^{13}C NMR (100 MHz, CD_3CN/CF_3COOD): δ = 30.00 (s, CH_3), 38.48 [s, $C(CH_3)_3$], 111.40 (t, $|^2J_{C,F}|$ = 23.0 Hz, C4 benzene), 120.23 (q, $|^1J_{C,F}|$ = 321.7 Hz, CF_3), 124.18 (m, C1 benzene), 127.69 (s, C3/5 pyridine), 142.98 (dm, $|^1J_{C,F}|$ = 257 Hz, C2/3/5/6 benzene), 146.86 (s, C2/6 pyridine), 147.60 (dm, $|^1J_{C,F}|$ = 242 Hz, C2/3/5/6 benzene), 177.55 (s, C4 pyridine) ppm. FAB-MS (NBA): *m/z* = 1584 $[4M - OTf]^+$, 1150 $[3M - OTf]^+$, 717 $[2M - OTf]^+$, 284 $[M - OTf]^+$. $C_{16}H_{14}F_7N_1O_3S_1$ (433.34) + 0.5H_2O: calcd. C 43.44, H 3.42, N 3.17 S 7.25; found C 43.19, H 3.26, N 3.00 S 7.36.

4-(Triphenylphosphonio)-2,3,5,6-tetrafluorobenzene Trifluoromethanesulfonate (25): Triphenylphosphane (50 mg, 0.19 mmol) was added to a solution of **19** (1144 mg, 1.89 mmol) in acetonitrile (20 mL). The resulting solution was stirred for 12 h at room temperature. After removal of the solvent in high vacuum, diethyl ether (100 mL) was added to the residue. The resulting colourless precipitate was filtered, washed with diethyl ether (5 × 5 mL), and dried in high vacuum to yield 972 mg (92%) of **25** as a colourless powder. IR (nujol): $\tilde{\nu}$ = 1630, 1276, 1272, 1158, 1034 cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ = 7.8 (m, phenyl, benzene) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 101.01 (d, $|^1J_{C,P}|$ = 88.3 Hz, C4 benzene), 116.64 (t, $|^2J_{C,F}|$ = 23 Hz, C1 benzene), 117.63 (d, $|^1J_{C,P}|$ = 91.6 Hz, C1 phenyl), 122.19 (q, $|^1J_{C,F}|$ = 320.9 Hz, CF_3), 131.47 (d, $|^3J_{C,P}|$ = 13.9 Hz, C3/5 phenyl), 135.46 (d, $|^2J_{C,P}|$ = 11.6 Hz, C2/6 phenyl), 136.99 (d, $|^4J_{C,P}|$ = 3.2 Hz, C4 phenyl), 149 (2 × m, CF benzene) ppm. ^{31}P NMR (162 MHz, CD_3NO_2): δ = 16.85 (s) ppm. FAB-MS (NBA): *m/z* = 971 $[2M - OTf]^+$, 411 $[M - OTf]^+$. $C_{25}H_{16}F_7O_3P_1S_1$ (560.42): calcd. C 53.58, H 2.88 S 5.72; found C 53.47, H 2.91 S 5.52.

Acknowledgments

This research was supported by the Deutsche Forschungsgemeinschaft.

[1] R. Weiss, N. J. Salomon, G. E. Miess, R. Roth, *Angew. Chem.* **1986**, *98*, 925−926; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 917−919.
[2] R. Weiss, R. Roth, *J. Chem. Soc., Chem. Commun.* **1987**, 317−318.
[3] R. Weiss, R. Roth, *Synthesis* **1987**, 870−872.
[4] R. Weiss, J. Seubert, F. Hampel, *Angew. Chem.* **1994**, *106*, 900−901; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1952−1953.
[5] R. Weiss, B. Pomrehn, F. Hampel, W. Bauer, *Angew. Chem.* **1995**, *107*, 1446−1448; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1319−1321.
[6] R. Weiss, R. May, B. Pomrehn, *Angew. Chem.* **1996**, *108*, 1319−1321; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1232−1234.
[7] R. Weiss, F. Pühlhofer, F. Hampel, *Z. Naturforsch., Teil B* **2001**, *56*, 1209−1216.
[8] R. Weiss, F. Pühlhofer, *Z. Naturforsch., Teil B* **2001**, *56*, 1360−1368.
[9] R. Weiss, F. Pühlhofer, N. Jux, K. Merz, *Angew. Chem.* **2002**, *114*, 3969−3971; *Angew. Chem. Int. Ed.* **2002**, *41*, 3815−3817.
[10] R. Weiss, S. Engel, *Angew. Chem.* **1992**, *104*, 239−240; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 216−217.
[11] K. J. Theriot, N. L. Krystowczyk, Y.-D. Chen, E. A. Burt, L. H. Shepherd (Albemarle Corporation), US 5,329,054, **1994**.
[12] S. R. Korn, M. S. Howarth, G. Jamieson (Zeneca Limited), PCT/GB95/00335, **1995**.
[13] Y. Okumura, I.-k. Toride-shi, O. Kaieda, I.-k. Tsuchiura-shi (Nippon Shokubai Co., Ltd.), EP 0767157A1, **1997**.
[14] F. Pühlhofer, Dissertation, Universität Erlangen-Nürnberg, **2001**.
[15] It was found that further SASAPOS reactions of benzene derivatives that include cationic substituents in the 1,4-positions are hindered.[14] This hindrance is due to the formation of ion clusters. Those are formed by chelating coordination of two anions towards the dicationic benzene derivatives so that the anions figure as bridges between the cationic substituents in the 1,4-positions. Hence the anions are fixed below and above the plane of the benzene ring (X-ray data for comparable systems is given in ref.[14]) and block further attack of nucleophiles on the benzene moiety. As explained above, TBUPY and PPh_3 provide increased pole strength compared to DMAP. Therefore the ion clusters **16** and **17** (Scheme 5) would need increased activation to undergo further SASAPOS as was found for compound **12**. In the case of **16** the application of corresponding reactions conditions (e.g. polar solvent, high temperature) led to formation of dark brown-red, oily products that could not be characterized.

Received September 25, 2003

