PYRYLIUM SALTS OF γ-THIAPYRONES- A SIMPLE STEP TO PHOSPHONO-PHOSPHINO SUBSTITUTED PYRIDINES AND PYRIDINIUM SALTS

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Dedicated on the 70th birthday of Alan R. Katritzky, Department of Chemistry, University of Florida, Gainesville

Abstract- The phosphono-phoshino substituted γ-thiapyrones (**1**/**2**) are converted to pyrylium salts (**3**/**4**) with trimethyloxonium tetrafluoroborate (**5**) under mild conditions. Reactions of the pyrylium salts (**3**/**4**) with ammonia and primary amines (**10**) lead to phosphono-phosphino pyridines (**6**/**7**) and pyridinium salts (**8**/**9**).

INTRODUCTION

In our previous papers[1], we described the synthesis and chemical reactions of new phosphono-phosphino substituted γ-thiapyrones and other phosphono-phosphino substituted heterocyclic compounds. It is well known, that α-pyrones and γ-pyrones can be converted to pyrylium salts with a methylating agent.[2] The pyrylium salt chemistry is an old chemistry[3a,b] and there is only one step to synthesize these salts. Pyrylium salts form one of those classes of compounds whose surprising properties make organic chemistry such a fascinating subject to study[4,5] and which makes them suitable starting materials e.g. they are easily

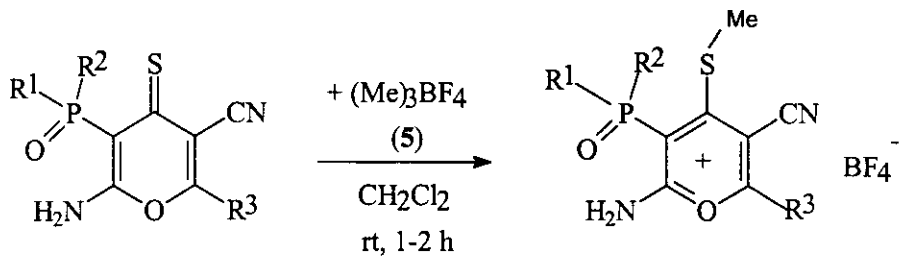
converted to 6-membered heterocycles (pyridines and pyridinium salts) by ammonia and primary amines.[6]

We were interested in the investigation of synthesis of phosphono-phosphino substituted pyrylium salts and of further transformation of this class of compounds, because the resulting phosphono-phosphino substituted pyridines and pyridinium salts should be important from a chemical and biological point of view.[7a-d]

In the present paper we describe the results of our studies concerning the preparation and reactions of phosphono-phosphino pyrylium salts of γ-thiapyrones (**3/4**).

RESULTS AND DISCUSSION

The reactions of phosphono-phosphino substituted γ-thiapyrones (**1/2**) with trimethyloxonium tetrafluoroborate (**5**) as a strong methylating agent lead to the phosphono-phosphino substituted pyrylium salts (**3/4**) (Scheme 1).



(1/2) (3/4)

Compound	R^1	R^2	R^3
3.1a	OMe	OMe	C_6H_5
3.1b	OEt	OEt	C_6H_5
3.2b	OEt	OEt	C_6H_4F
3.3b	OEt	OEt	C_6H_4Me
3.4c	OiPr	OiPr	C_6H_4Cl
3.5c	OiPr	OiPr	tBu

3.6c	OiPr	OiPr	C_4H_3O
4.1d	OEt	C_6H_5	C_6H_5
4.2d	OEt	C_6H_5	C_6H_4F

Scheme 1: Syntheses of phosphono-phosphino substituted pyrylium salts (**3/4**)

The structure of the pyrylium salts (**3/4**) was investigated by NMR spectroscopy. All these compounds were measured in CF_3COOD, because the solubility of the pyrylium salts in $CDCl_3$ was not high enough, but we measured the ^1H NMR spectra of 3.1b (32 scans) in $CDCl_3$ in order to localize the NH_2-protons [$\delta(H^A)$= 9.02 (br s, 1H) and $\delta(H^B)$= 10.38 (br s, 1H)].[1] The SCH_3-group of 3.1b is observed at 3.05 ppm as a sharp singlet, which shows us that the electrophilic attack of the methylating agent (**5**) took place at the sulfur atom, leading to the aromatic systems (**3/4**).

In our studies we could not observe an electrophilic attack of trimethyloxonium tetrafluoroborate at the nitrogen atom of the NH_2-group.

All the pyrylium salts show some characteristic signals in the ^{13}C NMR spectra. The SCH_3-group is localized at about 20 ppm. The C-3 atom of the pyrylium salt is given as a doublet at about 105-108 ppm ($^1J_{CP}$~ 185-195 Hz) and it is more downfield shifted than in the free γ-thiapyrones (**1/2**). But the CS-carbon signal is much more highfield shifted as it is located in the free γ-thiapyrones (**1/2**).[1] The signal is given as a doublet at about 172 ppm (20 ppm less than the CS double bond in the free γ-thiapyrones). This is another evidence for the aromatic systems (**3/4**).[8]

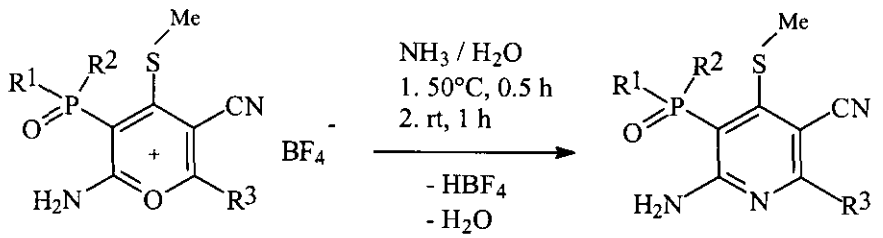
In the IR spectra the CO-group is observed at 1653-1663 cm^{-1} as a sharp band. It explains, that the positive charge is located in the pyrylium ring system. The BF_4 anion is observed at about 1080-1090 cm^{-1} as a sharp bright band, which is in agreement with the literature.[9a]

The UV spectra of the pyrylium salts (**3/4**) are also consistent with an aromatic

system.[4] There are two characteristic absorption bands at about 280-290 and 340-360 nm.[9b-d]

The various cationic species of the pyrylium salts (**3/4**) are observed with an intensity between 1-10% in the MS spectra. There are two characteristic fragments given in the spectra. One of them is the fragment of the phosphonate-phosphinate groups and the other one is reflected of the substituent R^3 (base peak).

The phosphono-phosphino substituted pyrylium salts (**3/4**) are converted to phosphono-phosphino substituted pyridines (**6/7**) by ammonia (Scheme 2). Nitrogen heterocyclic compounds are very important compounds, because there are many pyridines known as natural products, which show interesting aspects based on their biological activities.[10a,b]



3/4 **6/7**

Compound	R^1	R^2	R^3
6.7a	OMe	Ome	C_6H_4Br
6.1b	OEt	OEt	C_6H_5
6.1c	OiPr	OiPr	C_6H_5
6.2c	OiPr	OiPr	C_6H_4F
6.4c	OiPr	OiPr	C_6H_4Cl
7.5d	OEt	C_6H_5	tBu

Scheme 2: Syntheses of phophono-phosphino substituted pyridines (**6/7**)

Compared to the pyrylium salts (**3/4**) the SCH_3-group in the ^1H NMR spectra of the phosphono-phosphino pyridines (**6/7**) is located more highfield shifted around δ= 2.61-2.85 ppm as a singlet.

The C-3 atom of the pyridine system is still given as a doublet at around 111-115 ppm ($^1J_{CP}$= 193-196 Hz), but in contrast to the free γ-thiapyrones (**1/2**) the signal of the C-3 atom is more downfield shifted.[1] The other carbon atoms are observed in expected values.

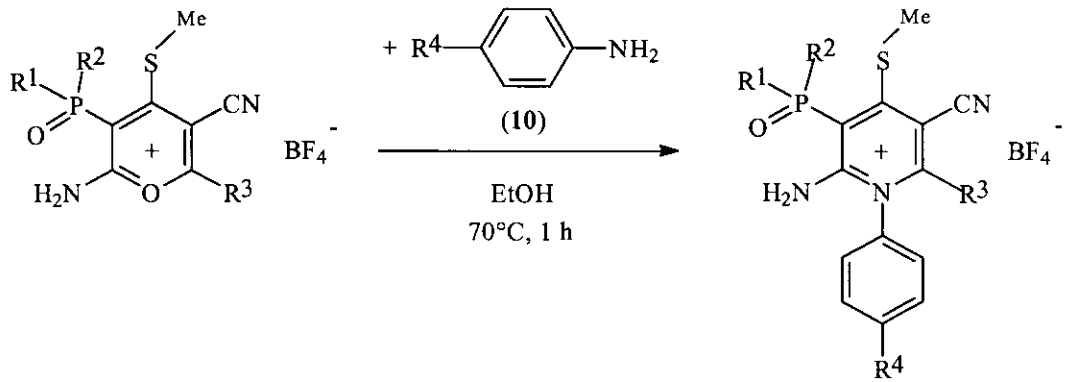
The C=N band of the pyridine system of the compounds (**6/7**) is observed at about 1520 cm^{-1} as a sharp band in the IR spectra, the stretching band of the CN-group at 2205 cm^{-1}. In contrast to the γ-thiapyrones (**1/2**) the stretching band of CN-group is located at 2230 cm^{-1}.[1]

The UV spectra of the phosphono-phosphino pyridines (**6/7**) are characteristic for aromatic compounds. The absorption bands between 240-248 nm and 280-290 nm represent the aromatic character of the pyridine system.[10b]

The molecular ions of the pyridines (**6/7**) are given between 10-20% intensity in MS spectra. Two fragments of the phosphonate group lead to the base peak, which represents the free acid of the phosphonopyridines and this is the major decomposition pathway. Furthermore the fragmentation shows the formation of very stable ions $[C_6H_5CO]^+$ (**6.1b, 6.1c**) and $[FC_6H_4CO]^+$ (**6.2c**), while these ions decompose by loss of carbon monoxide to give the ions with *m/z*= 77 and *m/z*= 95.

Furthermore we try to convert the phospono-phosphino substituted pyrylium salts (**3/4**) to phosphono-phosphino substituted pyridinium salts (**8/9**) by using primary amines. The pyrylium salts (**3/4**) react with simple aromatic amines to give phosphono-phosphino substituted pyridinium salts (**8/9**) (Scheme 3). Pyridinium salts are very important intermediates, which on treatment of nucleophiles undergo nucleophilic displacement of the *N*-substituent on the pyridinium cation.[5] We choose *p*-substituted anilines (**10**) because there would be no problem to discuss the spectra of the resulting compounds, especially the ^1H and ^{13}C NMR

spectra.



3/4 8/9

Compound	R^1	R^2	R^3	R^4
8.1a	OMe	OMe	C_6H_5	Br
8.1b	OEt	OEt	C_6H_5	CH_3CO
8.2c	OiPr	OiPr	C_6H_4F	CH_3CO
8.4c	OiPr	OiPr	C_6H_4Cl	Br
9.5d	OEt	C_6H_5	tBu	Br

Scheme 3: Syntheses of phosphono-phosphino substituted pyridinium salts (**8/9**)

In the ^1H NMR spectra the CH_3-group of the acetyl ligand of the compounds (**8.1b**) and (**8.2c**) is located as a sharp singlet at about δ= 2.55-2.75 ppm and the SCH_3-group between 2.85-3.05 ppm. The CO-group of the acetyl ligand is observed at δ= 196-197 ppm in the ^{13}C NMR spectra and the characteristic doublet of the C-3 atom of the pyridinium ring system is in this class of compounds most downfield shifted compared to the pyrylium salts (**3/4**) and pyridine systems (**6/7**). The C-3 atom of the pyridinium salts (**8/9**) is given at about δ= 120-122 ppm.

In the UV spectra the compounds (**8/9**) show two characteristic absorption bands (λ_{max}= 250-254 and 328-334 nm), which are in agreement with the aromatic

character of this class of compounds.

The C=N band with the positive charge of the pyridinium ring system is located at 1660-1680 cm^{-1}, the CO-group of the acetyl ligand at 1690-1720 cm^{-1} as sharp bands and the stretching band of the CN-group at 2210-2220 cm^{-1}.

The MS spectra of the compounds (**8/9**) show that the cationic phosphono-phosphino substituted pyridinium systems are very stable, because the molecular ions are given in high intensity in the spectra. The further fragmentation of the pyridinium cations can be explained in the same manner as it is described for the pyrylium salts (**3/4**).

EXPERIMENTAL

All reactions were carried out under argon. The solvents were dried or used in abs. quality. Melting points were determined on a Reichert hot stage microscope and are uncorrected. IR spectra were measured with a Perkin-Elmer IR spectrophotometer 1600 (FT IR) and are given in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker WM-250 (^{1}H-NMR: 250.13 MHz, ^{13}C-NMR: 62.89 MHz), a Varian XL 300 (^{1}H-NMR: 299.95 MHz, ^{13}C-NMR: 75.43 MHz) and a Bruker WM-360 (^{1}H-NMR: 260 MHz, ^{13}C-NMR: 90.56 MHz) spectrometer in $CDCl_3$ and CF_3COOD. All chemical shifts are reported in ppm downfield from tetramethylsilane; coupling constants J are given in Hz. ^{31}P-NMR spectra were measured with a Bruker WM-360 (^{31}P-NMR: 145.79 MHz) spectrometer using H_3PO_4 (internal standard 85% H_3PO_4). EIMS spectra were recorded on a Varian MAT 311 A spectrometer (70 eV). UV spectra were measured with a Hewlett Packard 8452 A Diode Array spectrometer in acetonitrile. Element analyses were performed on a Heraus Vario EL CHNS apparatus.

General procedure for the preparation of phosphono-phosphino substituted pyrylium salts (**3/4**)

To a solution of 1 mmol of phosphono-phosphino substituted γ-thiapyrones (**1/2**)

in CH_2Cl_2 (15 mL) was added trimethyloxonium tetrafluoroborate (**5**) (222 mg, 1.5 mmol). The reaction mixture was stirred under argon for 1-2 h at rt. After evaporation of the solvent, the yellow residue was recrystallized (methylene chloride / ether) to give the phosphono-phosphino substituted pyrylium salts (**3**/**4**) as light yellow crystals.

2-Amino-5-cyano-6-phenyl-4-methylsulfanyl-4*H*-pyran-3-ylphosphonic acid dimethyl ester tetrafluoroborate (**3.1a**)

-355 mg (81%) of **3.1a** were obtained after recrystallization (methylene chloride / ether) as light yellow crystals, mp 162-163°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 3.09 (s, 3H, SCH_3), 3.95 (d_p, $^3J_{HP}$= 12 Hz, 6H, OCH_3), 7.56-7.78 (m, 3H, 3′-H, 4′-H, 5′-H), 8.08-8.11 (d, $^3J_{HH}$= 8.1 Hz, 2′-H, 6′-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 20.4 (s, SCH_3), 54.9 (d_p, $^2J_{CP}$= 6.5 Hz, OCH_3), 97.7 (d_p, $^3J_{CP}$= 12 Hz, C-5), 104.8 (d_p, $^1J_{CP}$= 193 Hz, C-3), 113.1 (s, CN), 126.0 (s, C-1′), 128.4, 129.7 (2*d, C-2′, C-3′, C-5′, C-6′), 133.4 (s, C-4′), 164.1 (d_p, $^2J_{CP}$= 21.4 Hz, C-2), 169.6 (s, C-6), 175.9 (d_p, $^2J_{CP}$= 5.1 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 12.58 (s). IR (KBr, tablet) ν= 3325 (w), 3111 (w), 2955 (w), 2855 (w), 2230 (w), 1662 (s), 1617 (m), 1582 (m), 1559 (m), 1507 (w), 1457 (w), 1423 (m), 1395 (w), 1290 (w), 1225 (m), 1190 (w), 1083 (br s), 1027 (br s), 848 (m), 769 (m), 723 (m), 688 (m), 648 (m), 587 (m), 533 (w), 483 (w), 448 (w), 427 (w), 415 (w), 406 (w). MS (70 eV, 115°C) m/z (%)= 351 (M^+, 11), 350 (21), 319 (12), 318 (55), 317 (31), 242 (3), 241 (2), 240 (3), 215 (5), 214 (2), 110 (5), 109 (7), 106 (4), 105 (76), 78 (8), 77 (100), 51 (13), 45 (2), 43 (2). UV (MeCN) λ_{max} (log ε)= 298 (4.25), 366 (4.18). Anal. Calcd for $C_{15}H_{16}N_2O_4BF_4PS$: C, 41.11; H, 3.68; N, 6.41; S, 7.31. Found: C, 40.83; H, 3.88; N, 6.02; S, 6.98.

2-Amino-5-cyano-6-phenyl-4-methylsulfanyl-4*H*-pyran-3-ylphosphonic acid diethyl ester tetrafluoroborate (**3.1b**)

-340 mg (73%) of **3.1b** were obtained after recrystallization (methylene chloride /

ether) as light yellow crystals, mp 106-107°C. ^{1}H-NMR (299.95 MHz, CF_3COOD) δ= 1.40 (d_pt, $^3J_{HH}$= 6.9 Hz, 6H, $OCH_2C\underline{H}_3$), 3.04 (s, 3H, SCH_3), 4.17-4.25 (m, 4H, $OC\underline{H}_2CH_3$), 7.55-7.76 (m, 3H, 3′-H, 4′-H, 5′-H), 8.16-8.20 (d, $^3J_{HH}$= 8.1 Hz, 2′-H, 6′-H). ^{13}C-NMR (75.43 MHz, CF_3COOD) δ= 16.3 (d_pt, $^3J_{CP}$= 6.8 Hz, $OCH_2\underline{C}H_3$), 20.1 (s, SCH_3), 64.7 (d_pq, $^2J_{CP}$= 5.7 Hz, $O\underline{C}H_2CH_3$), 93. 0 (d_p, $^3J_{CP}$= 11.9 Hz, C-5), 104.5 (d_p, $^1J_{CP}$= 194 Hz, C-3), 112.5 (s, CN), 126.6 (s, C-1′), 128.6, 129.4 (2*d, C-2′, C-3′, C-5′, C-6′), 133.5 (s, C-4′), 155.7 (s, C-6), 163.2 (d_p, $^2J_{CP}$= 22.7 Hz, C-2), 172.6 (d_p, $^2J_{CP}$= 5.2 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 8.95 (s). IR (KBr, tablet) ν= 3422 (w), 3361 (w), 3111 (w), 2925 (w), 2876 (w), 2230 (w), 1662 (s), 1616 (m), 1584 (m), 1559 (m), 1506 (w), 1457 (m), 1447 (m), 1394 (w), 1313 (w), 1216 (m), 1084 (br s), 1015 (br s), 851 (m), 799 (w), 742 (m), 689 (m), 583 (w), 521 (w), 481 (w), 450 (w), 418 (w), 408 (w), 405 (w). MS (70 eV, 145°C) m/z (%)= 379 (M^+, 10), 378 (17), 353 (11), 352 (8), 333 (3), 332 (5), 216 (18), 215 (27), 106 (7), 105 (100), 77 (81), 51 (10), 47 (9), 45 (6), 43 (3). UV (MeCN) λ_{max} (log ε)= 288 (4.24), 354 (4.22). Anal. Calcd for $C_{17}H_{20}N_2O_4BF_4PS$: C, 43.79; H, 4.32; N, 6.03; S, 6.87. Found: C, 43.51; H, 4.14; N, 5.81; S, 6.63.

2-Amino-5-cyano-6- (4′-fluorophenyl) -4-methylsulfanyl- 4*H*- pyran-3-ylphosphonic acid diethyl ester tetrafluoroborate (**3.2b**)

-375 mg (78%) of **3.2b** were obtained after recrystallization (methylene chloride / ether) as light yellow crystals, mp 165-167°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.52 (d_pt, $^3J_{HH}$= 7 Hz, 6H, $OCH_2C\underline{H}_3$), 3.18 (s, 3H, SCH_3), 4.44-4.53 (m, 4H, $OC\underline{H}_2CH_3$), 7.37-7.42 (t, $^3J_{HF}$= 7.7 Hz, 2H, 3′-H, 5′-H), 8.28-8.32 (dd, $^4J_{HF}$= 4.8 Hz, 2H, 2′-H, 6′-H). ^{13}C-NMR (62.89 MHz, CF_3COOD) δ= 16.7 (d_pt, $^3J_{CP}$= 6 Hz, $OCH_2\underline{C}H_3$), 21.6 (s, SCH_3), 68.8 (d_pq, $^2J_{CP}$= 6.7 Hz, $O\underline{C}H_2CH_3$), 99.0 (d_p, $^3J_{CP}$= 12.7 Hz, C-5), 108.5 (d_p, $^1J_{CP}$= 197 Hz, C-3), 114.4 (s, CN), 119.5 (dd, $^2J_{CF}$= 23.1 Hz, C-3′, C-5′), 124.1 (d, $^4J_{CF}$= 3 Hz, C-1′), 135.5 (d, $^3J_{CF}$= 10.5 Hz, C-2′, C-6′), 162.9 (s, C-4′), 164.3 (s, C-6), 166.5 (d_p, $^2J_{CP}$= 21.9 Hz, C-2),

179.0 (d_p, $^2J_{CP}$= 5.1 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 9.03 (s). IR (KBr, tablet) ν= 3421 (w), 3266 (m), 3142 (m), 2989 (w), 2922 (w), 2233 (w), 1661 (s), 1598 (s), 1559 (m), 1508 (m), 1432 (m), 1305 (m), 1247 (s), 1215 (m), 1170 (s), 1088 (br s), 1038 (br s), 850 (m), 771 (m), 668 (w), 611 (m), 568 (w), 504 (w), 468 (w), 421 (w), 412 (w), 407 (w). MS (70 eV, 160°C) m/z (%)= 397 (M^+, 17), 396 (13), 351 (11), 350 (40), 323 (10), 322 (33), 260 (4), 259 (6), 124 (8), 123 (100), 96 (5), 95 (58), 75 (20), 49 (17), 45 (10), 44 (3), 43 (4). UV (MeCN) λ_{max} (log ε)= 288 (4.21), 352 (4.23). Anal. Calcd for $C_{17}H_{19}N_2O_4BF_5PS$: C, 42.16; H, 3.95; N, 5.80; S, 6.62. Found: C, 41.76; H, 4.30; N, 5.78; S, 6.53.

2-Amino-5-cyano-6-*p*-tolyl-4-methylsulfanyl-4*H*-pyran-3-ylphosphonic acid diethyl ester tetrafluoroborate (**3.3b**)

-360 mg (75%) of **3.3b** were obtained after recrystallization (methylene chloride / ether) as light yellow crystals, mp 167-169°C. ^{1}H-NMR (299.95 MHz, CF_3COOD) δ= 1.37 (d_pt, $^3J_{HH}$= 6.9 Hz, 6H, $OCH_2C\underline{H}_3$), 2.46 (s, 3H, $C_6H_4C\underline{H}_3$), 3.02 (s, 3H, SCH_3), 4.14-4.28 (m, 4H, $OC\underline{H}_2CH_3$), 7.33-7.36 (d, $^3J_{HH}$= 8.4 Hz, 2H, 3´-H, 5´-H), 8.08-8.11 (d, $^3J_{HH}$= 8.4 Hz, 2H, 2´-H, 6´-H). ^{13}C-NMR (75.43 MHz, CF_3COOD) δ= 16.1 (d_pt, $^3J_{CP}$= 6.6 Hz, $OCH_2\underline{C}H_3$), 20.2 (s, SCH_3), 21.3 (s, $C_6H_4\underline{C}H_3$), 64.5 (d_pq, $^2J_{CP}$= 5.8 Hz, $O\underline{C}H_2CH_3$), 93.2 (d_p, $^3J_{CP}$= 12.1 Hz, C-5), 104.3 (d_p, $^1J_{CP}$= 192 Hz, C-3), 112.6 (s, CN), 126.8 (s, C-1´), 128.5, 129.4 (2 *d, C-2´, C-3´, C-5´, C-6´), 143.9 (s, C-4´), 155.9 (s, C-6), 163.4 (d_p, $^2J_{CP}$= 23.1 Hz, C-2), 172.7 (d_p, $^2J_{CP}$= 5.4 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 8.98 (s). IR (KBr, tablet) ν= 3315 (m), 3112 (w), 3005 (w), 2984 (w), 2920 (w), 2229 (w), 1652 (s), 1607 (m), 1576 (m), 1558 (m), 1506 (m), 1436 (w), 1394 (w), 1216 (m), 1083 (br s), 1017 (br s), 824 (m), 788 (w), 668 (w), 607 (w), 567 (w), 523 (w), 480 (w), 447 (w), 423 (w), 413 (w), 403 (w). MS (70 eV, 184°C) m/z (%)= 393 (M^+, 4), 392 (8), 348 (7), 347 (19), 318 (44), 317 (64), 254 (8), 120 (7), 119 (96), 92 (10), 91 (100), 65 (39), 47 (11), 45 (14), 43 (4), 41 (4). UV (MeCN) λ_{max} (log ε)= 288 (4.41), 350 (3.81). Anal. Calcd for $C_{18}H_{22}N_2O_4BF_4PS$: C, 45.01; H,

4.62; N, 5.85; S, 6.67. Found: C, 44.85; H, 5.02; N, 5.87; S, 6.62.

2-Amino-5-cyano-6-(4-chlorophenyl)-4-methylsulfanyl-4*H*-pyran-3-ylphosphonic acid diisopropyl ester tetrafluoroborate (**3.4c**)

-450 mg (85%) of **3.4c** were obtained after recrystallization (methylene chloride / ether) as light yellow crystals, mp 92-93°C. ^{1}H-NMR (299.95 MHz, CF_3COOD) δ= 1.37, 1.45 (2*d_p, $^3J_{HH}$= 6.2 Hz, 12H, OCH($C\underline{H}_3$)$_2$), 3.02 (s, 3H, SCH_3), 4.76-4.82 ($d_p$sept,$^2J_{HP}$= 7.5 Hz, $^3J_{HH}$= 6.2 Hz, 2H, OC$\underline{H}$(CH_3)$_2$), 7.50-7.54 (d, $^3J_{HH}$= 8.1 Hz, 2H, 3′-H, 5′-H), 8.13-8.17 (d, $^3J_{HH}$= 8.1 Hz, 2H, 2′-H, 6′-H). ^{13}C-NMR (62.89 MHz, CF_3COOD) δ= 20.4 (s, SCH_3), 23.8 (d_pq, $^3J_{CP}$= 5 Hz), 23.9 (d_pq, $^3J_{CP}$= 4 Hz, OCH($\underline{C}H_3$)$_2$), 76.5 (d_pd, $^2J_{CP}$= 6 Hz, O$\underline{C}$H(CH_3)$_2$), 98.5 (d_p, $^3J_{CP}$= 12.5 Hz, C-5), 106.7 (d_p, $^1J_{CP}$= 184 Hz, C-3), 113.7 (s, CN), 125.0 (s, C-1′), 128.9, 129.6 (2*d, C-2′, C-3′, C-5′, C-6′), 142.3 (s, C-4′), 161.0 (s, C-6), 164.3 (d_p, $^2J_{CP}$= 24.8 Hz, C-2), 173.0 (d_p, $^2J_{CP}$=6.9 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 9.20 (s). IR (KBr, tablet) ν= 3318 (m), 3007 (w), 2982 (w), 2919 (w), 2231 (w), 1653 (s), 1623 (m), 1576 (m), 1559 (m), 1496 (w), 1436 (w), 1387 (m), 1216 (m), 1083 (br s), 1037 (br s), 839 (m), 710 (w), 668 (w), 592 (w), 522 (w), 487 (w), 436 (w), 419 (w), 405 (w). MS (70 eV, 199°C) m/z (%)= 441 (M^+, 2), 440 (3), 398 (2), 397 (3), 339 (38), 337 (41), 276 (12), 274 (12), 140 (8), 139 (100), 111 (47), 76 (3), 75 (10), 49 (30), 47 (34), 43 (50), 41 (69). UV (MeCN) λ_{max} (log ε)= 290 (4.36) 356 (3.99). Anal. Calcd for $C_{19}H_{23}N_2O_4ClBF_4PS$: C, 43.15;H, 4.38; N, 5.31; S, 6.06. Found: C, 42.95; H, 4.69; N, 5.43; S, 5.79.

2-Amino-5-cyano-6-*tert*-butyl-4-methylsulfanyl-4*H*-pyran-3-ylphosponic acid diisopropyl ester tetrafluoroborate (**3.5c**)

-330 mg (70%) of **3.5c** were obtained after recrystallization (methylene chloride / ether) as light yellow crystals, mp 95-97°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ=

1.38, 1.44 (2*d_p, $^3J_{HH}$= 6.2 Hz, 12H, OCH(C<u>H</u>$_3$)$_2$), 1.59 (s, 9H, (C<u>H</u>$_3$)$_3$C), 2.89 (s, 3H, SCH$_3$), 4.80-4.88 ($d_p$sept, $^2J_{HP}$= 7.4 Hz, $^3J_{HH}$= 6.2 Hz, 2H, OC<u>H</u>(CH$_3$)$_2$). ^{13}C-NMR (90.56 MHz, CF$_3$COOD) δ= 20.5 (s, SCH$_3$), 23.8 (d_pq, $^3J_{CP}$= 5 Hz), 23.9 (d_pq, $^3J_{CP}$= 4 Hz, OCH(<u>C</u>H$_3$)$_2$), 27.7 (s, (<u>C</u>H$_3$)$_3$C), 37.5 (s, (CH$_3$)$_3$<u>C</u>), 76.4 (d_pd, $^2J_{CP}$= 6.1 Hz, O<u>C</u>H(CH$_3$)$_2$), 98.7 (d_p, $^3J_{CP}$= 12.4 Hz, C-5), 106.9 (d_p, $^1J_{CP}$= 190 Hz, C-3), 113.2 (s, CN), 160.7 (s, C-6), 163.8 (d_p, $^2J_{CP}$= 24.6 Hz, C-2), 171.8 (d_p, $^2J_{CP}$= 6.8 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF$_3$COOD) δ= 9.11 (s). IR (KBr, tablet) ν= 3283 (m), 3150 (w), 2984 (w), 2939 (w), 2891 (w), 2230 (w), 1663 (s), 1576 (m), 1559 (m), 1490 (m), 1473 (m), 1425 (w), 1388 (m), 1376 (m), 1225 (m), 1069 (br s), 1008 (br s), 898 (w), 769 (m), 668 (w), 590 (m), 550 (m), 486 (w), 451 (w), 424 (w), 412 (w), 404 (w). MS (70 eV, 106°C) m/z (%)= 387 (M^+, 8), 386 (1), 305 (3), 304 (6), 288 818), 286 (13), 220 (10), 219 (10), 195 (17), 194 (6), 124 (2), 75 (20), 58 (4), 57 (100), 45 (20), 43 (33), 41 (25). UV (MeCN) λ_{max} (log ε)= 280 (4.26), 348 (3.85). Exact MS calcd for $C_{17}H_{28}N_2O_4BF_4PS$: 387.1506. Found: 387.1505.

<u>2-Amino-5-cyano-6-furoyl-4-methylsulfanyl-4*H*-pyran-3-ylphosphonic acid diisopropyl ester tetrafluoroborate (**3.6c**)</u>

-390 mg (81%) of **3.6c** were obtained after recrystallization (methylene chloride / ether) as light yellow crystals, mp 89-91°C. ^{1}H-NMR (299.95 MHz, CF$_3$COOD) δ = 1.36, 1.44 (2*d, $^3J_{HH}$= 6.2 Hz, 12H, OCH(C<u>H</u>$_3$)$_2$), 2.99 (s, 3H, SCH$_3$), 4.76-4.85 ($d_p$sept, $^2J_{HP}$= 7.5 Hz, $^3J_{HH}$= 6.2 Hz, 2H, OC<u>H</u>(CH$_3$)$_2$), 6.81 (d, $^3J_{HH}$= 3.2 Hz, 1H, 5′-H), 7.94, 8.21 (2*d, $^3J_{HH}$= 4.8 Hz, 2H, 3′-H, 4′-H). ^{13}C-NMR (90.56 MHz, CF$_3$COOD) δ= 20.1 (s, SCH$_3$), 23.8 (d_pq, $^3J_{CP}$= 5 Hz), 23.9 (d_pq, $^3J_{CP}$= 4 Hz, OCH(<u>C</u>H$_3$)$_2$), 74.9 (d_pd, $^2J_{CP}$= 6 Hz, O<u>C</u>H(CH$_3$)$_2$), 93.0 (d_p, $^3J_{CP}$= 11.7 hz, C-5), 105.1 (d_p, $^1J_{CP}$= 192 Hz, C-3), 112.3 (s, CN), 113.7 (C-3′), 121.2 (s, C-4′), 142.5 (s, C-2′), 148.7 (s, C-5′), 156.1 (s, C-6), 163.5 (d_p, $^2J_{CP}$= 23.2 Hz, C-2), 172.8 (d_p, $^2J_{CP}$= 4.8 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF$_3$COOD) δ= 9.30 (s). IR (KBr, tablet) ν= 3310 (m), 3018 (w), 2991 (w), 2916 (w), 2230 (w), 1653

(s), 1616 (m), 1569 (m), 1506 (w), 1457 (m), 1387 (m), 1300 (w), 1205 (m), 1084 (br s), 1003 (br s), 886 (w), 835 (m), 735 (w), 668 (w), 533 (w), 472 (w), 434 (w), 420 (w), 410 (w), 401 (w). MS (70 eV, 134°C) m/z (%)= 397 (M^+, 2), 396 (7), 336 (10), 312 (34), 311 (5), 232 (16), 231 (4), 124 (3), 96 (5), 95 (100), 68 (4), 49 (25), 47 (31), 45 (36), 43 (34), 41 (40). UV (MeCN) λ_{max} (log ε)= 290 (4.23), 356 (4.20). Exact MS calcd for $C_{17}H_{22}N_2O_5BF_4PS$: 397.0644. Found: 397.0642.

2-Amino-5-cyano-6-phenyl-4-methylsulfanyl-4*H*-pyran-3-ylphenylphosphinic acid ethyl ester tetrafluoroborate (**4.1d**)

- 280 mg (56%) of **4.1d** were obtained after recrystallization (methylene chloride / ether) as light yellow crystals, mp 153-155°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.24 (t_p, $^3J_{HH}$= 7.1 Hz, 3H, $OCH_2\underline{C}H_3$), 3.03 (s, 3H, SCH_3), 4.09-4.28 (m, 2H, $OCH_2\underline{C}H_3$), 7.32-7.89 [(2*m, 10H, 2´-H, 3´-H, 4´-H, 5´-H, 6´-H); PC_6H_5]. ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 16.4 (t_p, $^3J_{CP}$= 7.5 Hz, $OCH_2\underline{C}H_3$), 20.2(s, SCH_3), 64.5 (d_p, $^2J_{CP}$= 5.8 Hz, $O\underline{C}H_2CH_3$), 98.6 (d_p, $^1J_{CP}$= 148 Hz, C-3), 109.1 (d_p, $^3J_{CP}$= 8.9 Hz, C-5), 114.1 (s, CN), 127.7 (s, C-1´a), 128.4 (s, C-1´), 129.0, 129.4 (2*d, C-2´, C-3´, C-5´, C-6´), 131.0, 131.7 (2*d, C-2´a, C-3´a, C-5´a, C-6´a), 132.7 (s, C-4´a), 133.3 (s, C-4), 159.3 (s, C-6), 163.8 (d_p, $^2J_{CP}$= 22.8 Hz, C-2), 173.0 (d_p, $^2J_{CP}$= 5.4 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD)= 25.43 (s). IR (KBr, tablet) ν= 3329 (m), 3066 (w), 2966 (w), 2922 (w), 2233 (w), 1663 (s), 1600 (m), 1590 (m), 1559 (m), 1476 (m), 1458 (m), 1386 (w), 1261 (m), 1196 (m), 1123 (m), 1083 (br s), 1022 (br s), 972 (w), 802 (m), 720 (m), 693 (m), 648 (w), 569 (m), 542 (w), 479 (w), 450 (w), 423 (w), 410 (w), 405 (w). MS (70 eV, 156°C) m/z (%)= 365 (9), 364 (M^+- SCH_3, 46), 363 (21), 262 (3), 215 (8), 142 (3), 141 (10), 105 (60), 78 (19), 77 (100), 51 (15), 48 (11), 47 (31), 45 (19), 43 (16), 41 (5). UV (MeCN) λ_{max} (log ε)= 300 (4.17), 404 (4.20). Exact MS calcd for $C_{21}H_{20}N_2O_3BF_4PS$: 411.0668. Found: 411.0666.

2-Amino-5-cyano-6-(4-fluorophenyl)-4-methylsulfanyl-4*H*-pyran-3-ylphenyl-phos-

phinic acid ethyl ester tetrafluoroborate (**4.2d**)

- 53 mg (53%) of **4.2d** were obtained after recrystallization (methylene chloride / ether) as light yellow crystals, mp 133-134°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.23 (t_p, $^3J_{HH}$= 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 3.04 (s, 3H, SCH_3), 4.07-4.25 (m, 2H, $OC\underline{H}_2CH_3$), 7.33-7.68 (m, 5H, PC_6H_5), 7.70-7.74 (t, $^3J_{HF}$= 7.8 Hz, 2H, 3´-H, 5´-H), 8.25-8.29 (dd, $^4J_{HF}$= 5.1 Hz, 2H, 2´-H, 6´-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 16.3 (t_p, $^3J_{CP}$= 7.6 Hz, $OCH_2\underline{C}H_3$), 20.3 (s, SCH_3), 64.6 (d_p, $^2J_{CP}$= 5.9 Hz, $O\underline{C}H_2CH_3$), 98.7 (d_p, $^1J_{CP}$= 149 Hz, C-3), 109.1 (d_p, $^3J_{CP}$= 8.8 Hz, C-5), 114.2 (s, CN), 119.5 (dd, $^2J_{CF}$= 23.0 Hz, C-3´, C-5´), 124.3 (d, $^4J_{CF}$= 3.2 Hz, C-1´), 127.7 (d, C-1´a), 131.1, 131.8 (2*d, C-2´a, C-3´a, C-5´a, C-6´a), 132.8 (s, C-4´a), 135.6 (d, $^3J_{CF}$= 10.6 Hz, C-2´, C-6´), 159.4 (s, C-6), 163.9 (d_p, $^2J_{CP}$= 23.6 Hz, C-2), 173.1 (d_p, $^2J_{CP}$= 5.6 hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD)= 25.39 (s). IR (KBr, tablet) ν= 3363 (m), 3211 (m), 3077 (w), 2966 (w), 2924 (w), 2233 (w), 1661 (s), 1601 (s), 1569 (m), 1507 (m), 1472 (m), 1437 (m), 1247 (m), 1137 (m), 1083 (br s), 1035 (br s), 919 (w), 847 (m), 750 (w), 693 (w), 668 (w), 597 (w), 559 (w), 522 (w), 472 (w), 449 (w), 441 (w), 419 (w), 407 (w). MS (70 eV, 166°C) m/z (%)= 429 (M^+, 3), 428 (14), 384 (2), 383 (12), 382 (63), 381 (19), 260 (3), 171 (4), 142 (5), 141 (19), 124 (9), 123 (100), 96 (3), 95 (61), 78 (5), 77 (25), 49 (30), 47 (12), 44 (12), 43 (3). UV (MeCN) λ_{max} (log ε)= 302 (4.05), 404 (4.08). Exact MS calcd for $C_{21}H_{19}N_2O_3BF_5PS$: 429.0838. Found: 429.0836.

General procedure for the preparation of phosphono-phosphino substituted pyridines (**6/7**)

A solution of 0.5 mmol of phosphono-phosphino substituted pyrylium salts (3/4) in EtOH (20 mL) was added dropwise to an ammonia solution (20 mL of conc. ammonia and 20 mL of water) at 50°C. The solution was stirred at 50°C for 0.5 h and 1 h at rt. The solution was acidified with concentrated hydrogen chloride (pH

3). The resulting solution was extracted with ether (50 mL) and the extract was dried over K_2CO_3. After evaporation of the solvent, the residue was stirred with ether / n-hexane (1:1) to give the phosphono-phosphino substituted pyridines (**6/7**) as light yellow crystals.

2-Amino-5-cyano-6-(4-bromophenyl)-4-methylsulfanylpyridin-3-ylphosphonic acid dimethyl ester (**6.7a**)

-100 mg (47%) of **6.7a** were obtained as light yellow crystals, mp 171-173°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 2.63 (s, 3H, SCH_3), 3.84 (d_p, $^3J_{HP}$= 12 Hz, OCH_3), 7.50-7.54 (d, $^3J_{HH}$= 8.1 Hz, 2H, 3′-H, 5′-H), 7.92-7.96 (d, $^3J_{HH}$= 8.1 Hz, 2H, 2′-H, 6′-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 19.9 (s, SCH_3), 53.4 (d_p, $^2J_{CP}$= 5.8 Hz, OCH_3), 95.6 (d_p, $^3J_{CP}$= 14.4 Hz, C-5), 112.0 (d_p, $^1J_{CP}$= 196 Hz, C-3), 119.1 (s, CN), 128.3 (C-1′), 129.1, 130.2 (2*d, C-2′, C-3′, C-5′, C-6′), 137.9 (s, C-4′), 159.1 (d_p, $^2J_{CP}$= 6.6 Hz, C-2), 164.9 (s, C-6), 172.5 (d_p, $^2J_{CP}$= 7.8 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 17.68 (s). IR (KBr, tablet) ν= 3361 (w), 3123 (w), 3056 (w), 2956 (w), 2922 (w), 2209 (m), 1594 (w), 1568 (m), 1523 (br s), 1496 (w), 1442 (s), 1390 (m), 1374 (m), 1220 (m), 1171 (w), 1032 (br s), 996 (w), 896 (w), 820 (m), 777 (w), 723 (w), 668 (w), 621 (w), 578 (w), 523 (w), 496 (w), 471 (w), 431 (w), 415 (w), 405 (w). MS (70 eV, 187°C) m/z (%)= 429 (61), 428 (m^+, 16), 427 (64), 386 (20), 384 (24), 264 (61), 262 (66), 185 (39), 183 (46), 157 (32), 155 (48), 109 (53), 80 (23), 79 (74), 57 (57), 44 (48), 43 (100), 41 (67). UV (MeCN) λ_{max} (log ε)= 242 (4.20), 284 (4.08), 352 (3.82). Exact MS calcd for $C_{15}H_{15}N_3O_3BrPS$: 428.1128. Found: 428.1127.

2-Amino-5-cyano-6-phenyl-4-methylsulfanylpyridin-3-ylphosphonic acid diethyl ester (**6.1b**)

-75 mg (40%) of **6.1b** were obtained as light yellow crystals, mp 97-99°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.42 (d_pt, $^3J_{HH}$= 6.2 Hz, 6H, $OCH_2C\underline{H}_3$),

2.85 (s, 3H, SCH_3), 4.22-4.36 (m, 4H, OCH_2CH_3), 7.54-7.76 (m, 5H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 16.1 (d_pt, $^3J_{CP}$= 7.1 Hz, OCH_2CH_3), 20.3 (s, SCH_3), 64.7 (d_pq, $^2J_{CP}$= 6.2 Hz, OCH_2CH_3), 98.3 (d_p, $^3J_{CP}$= 15.1 Hz, C-5), 113.1 (s, CN), 115.4 (d_p, $^1J_{CP}$= 193 Hz, C-3), 128.5 (s, C-1′), 129.6, 130.6 (2*d, C-2′, C-3′, C-4′, C-5′, C-6′), 157.9 (s, C-6), 162.4 (d_p, $^2J_{CP}$= 12.8 Hz, C-2), 166.5 (d_p, $^2J_{CP}$= 6.8 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 15.86 (s). IR (KBr, tablet) ν= 3422 (m), 3125 (m), 3066 (w), 2981 (w), 2933 (w), 2212 (m), 1570 (m), 1527 (s), 1496 (m), 1458 (m), 1437 (m), 1218 (m), 1111 (w), 1021 (br s), 971 (m), 784 (m), 714 (m), 668 (w), 592 (w), 458 (w), 416 (w), 411 (w), 407 (w). MS (70 eV, 137°C) m/z (%)= 378 (35), 377 (M^+, 61), 349 (23), 321 (19), 304 (13), 303 (59), 242 (9), 241 (12), 140 (7), 106 (4), 105 (100), 77 (20), 65 (10), 45 (15), 43 (69), 41 (1). UV (MeCN) λ_{max} (log ε)= 260 (4.11), 276 (4.07), 320 (3.78). Anal. Calcd for $C_{17}H_{20}N_3O_3PS$: C, 54.08; H, 5.33; N, 11.17; S, 8.49. Found: C, 53.79; H, 5.09; N, 10.88; S, 8.36.

2-Amino-5-cyano-6-phenyl-4-methylsulfanylpyridin-3-ylphosphonic acid diisopropyl ester (**6.1c**)

-100 mg (50%) of **6.1c** were obtained as light yellow crystals, mp 125-127°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ 1.17, 1.20 (2*d_p, $^3J_{HH}$= 6.2 Hz, 12H, $OCH(CH_3)_2$), 2.61 (s, 3H, SCH_3), 4.53-4.61 ($d_p$sept, $^2J_{HP}$= 7.4 Hz, $^3J_{HH}$= 6.2 Hz, 2H, $OCH(CH_3)_2$), 7.29-7.36 (m, 3H, 3′-H, 4′-H, 5′-H), 7.56-7.59 (d, $^3J_{HH}$= 8.1 Hz, 2H, 2′-H, 6′-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 19.9 (s, SCH_3), 23.7 (d_pq, $^3J_{CP}$= 5 Hz), 23.8 (d_pq, $^3J_{CP}$= 4 Hz, $OCH(CH_3)_2$), 71.1 (d_pd, $^2J_{CP}$= 6.2 Hz, $OCH(CH_3)_2$), 95.5 (d_p, $^3J_{CP}$= 14 Hz, C-5), 111.6 (d_p, $^1J_{CP}$= 196 Hz, C-3), 119.5 (s, CN), 128.1 (s, C-1′), 128.8, 129.7 (2*d, C-2′, C-3′, C-4′, C-5′, C-6′), 158.6 (d_p, $^2J_{CP}$= 6.3 Hz, C-2), 166.2 (s, C-6), 172.6 (d_p, $^2J_{CP}$= 8 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 13.27 (s). IR (KBr, tablet) ν= 3446 (w), 3274 (m), 3055 (w), 2978 (m), 2928 (w), 2866 (w), 2204 (m), 1588 (m), 1544 (m), 1520 (br s), 1456 (s), 1435 (m), 1384 (m), 1219 (m), 1102 (m), 999 (br s), 885 (w), 804

(w), 779 (m), 706 (m), 667 (m), 601 (w), 536 (w), 458 (w), 422 (w), 410 (w), 401 (w). MS (70 eV, 156°C) m/z (%)= 405 (M^+, 19), 364 (4), 363 (7), 322 (32), 321 (100), 241 (4), 239 (3), 140 (3), 105 (20), 104 (6), 77 (9), 45 (3), 43 (18), 41 (20). UV (MeCN) λ_{max} (log ε)= 240 (4.17), 284 (4.10), 354 (3.79). Anal. Calcd for $C_{19}H_{24}N_3O_3PS$: C, 56.26; H, 5.96; N, 10.39; S, 7.90. Found: C, 56.02; H, 5.83; N, 10.14; S, 7.68.

2-Amino-5-cyano-6-(4-fluorophenyl)-4-methylsulfanylpyridin-3-ylphosphonic acid diisopropyl ester (**6.2c**)

-90 mg (43 %) of **6.2c** were obtained as light yellow crystals, mp 141-143°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.17, 1.21 (2*d_p, $^3J_{HH}$= 6.2 Hz, 12 H, OCH($C\underline{H}_3$)$_2$), 2.61 (s, 3H, SCH_3), 4.50-4.62 ($d_p$sept, $^2J_{HP}$= 7.2 Hz, $^3J_{HH}$= 6.2 Hz, 2H, OC$\underline{H}$(CH_3)$_2$), 6.90-7.02 (t, $^3J_{HF}$= 7.8 Hz, 2H, 3´-H, 5´-H), 7.58-7.62 (dd, $^4J_{HF}$= 4.8 Hz, 2H, 2´-H, 6´-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 19.9 (s, SCH_3), 23.7 (d_pq, $^3J_{CP}$= 5 Hz), 23.9 (d_pq, $^3J_{CP}$= 4 Hz, OCH($C\underline{H}_3$)$_2$), 71.4 (d_pd, $^2J_{CP}$= 6.2 Hz, O$\underline{C}$H(CH_3)$_2$), 96.1 (d_p, $^3J_{CP}$= 14.4 Hz, C-5), 111.5 (d_p, $^1J_{CP}$= 196 Hz, C-3), 119.3 (dd, $^2J_{CF}$= 21.6 Hz, C-3´, C-5´), 119.3 (s, CN), 130.7 (dd, $^3J_{CF}$= 8.4 Hz, C-2´, C-6´), 134.4 (s, C-1´), 159.0 (d_p, $^2J_{CP}$= 6.1 Hz, C-2), 162.3 (s, C-4´), 165.3 (s, C-6), 172.4 (d_p, $^2J_{CP}$= 8.9 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 13.34 (s). IR (KBr, tablet) ν= 3429 (w), 3270 (m), 3077 (w), 2978 (w), 2923 (w), 2206 (m), 1604 (m), 1559 (m), 1521 (s), 1456 (m), 1385 (m), 1323 (w), 1223 (m), 1157 (m), 1103 (m), 988 (br s), 886 (w), 822 (m), 800 (m), 721 (w), 668 (w), 523 (w), 463 (w), 426 (w), 413 (w), 403 (w). MS (70 eV, 203°C) m/z (%)= 423 (M^+, 11), 382 (5), 381 (22), 340 (18), 339 (100), 260 (12), 259 (12), 158 (2), 123 (2), 122 (8), 95 (2), 75 (1), 43 (24), 42 (10), 41 (23). UV (MeCN) λ_{max} (log ε)= 242 (4.11), 284 (4.10), 352 (3.79). Exact MS calcd for $C_{19}H_{23}N_3O_3FPS$: 423.2240. Found: 423.2238.

2-Amino-5-cyano-6-(4-chlorophenyl)-4-methylsulfanylpyridin-3-ylphosphonic acid

diisopropyl ester (**6.4c**)

-100 mg (45%) of **6.4c** were obtained as light yellow crystals, mp 138-140°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.21, 1.24 (2*d_p, $^3J_{HH}$= 6.2 Hz, 12H, OCH($C\underline{H}_3$)$_2$), 2.61 (s, 3H, SCH_3), 4.58-4.68 ($d_p$sept, $^2J_{HP}$= 7.4 Hz, $^3J_{HH}$= 6.2 Hz, 2H, OC$\underline{H}$(CH_3)$_2$), 7.27-7.30 (d, $^3J_{HH}$= 8.1 Hz, 2H, 3′-H, 5′-H), 7.57-7.60 (d, $^3J_{HH}$= 8.1 Hz, 2H, 2′-H, 6′-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 19.9 (s, SCH_3), 23.8 (d_pq, $^3J_{CP}$= 5 Hz), 23.9 (d_pq, $^3J_{CP}$= 4 Hz, OCH($\underline{C}H_3$)$_2$), 71.4 (d_pd, $^2J_{CP}$= 6.2 Hz, O$\underline{C}$H(CH_3)$_2$), 95.7 (d_p, $^3J_{CP}$= 14.2 Hz, C-5), 111.9 (d_p, $^1J_{CP}$= 195 Hz, C-3), 119.2 (s, CN), 128.5 (s, C-1′), 128.9, 129.7 (2*d, C-2′, C-3′, C-5′, C-6′), 136.1 (s, C-4′), 159.0 (d_p, $^2J_{CP}$= 6.5 Hz, C-2), 165.0 (s, C-6), 172.6(d_p, $^2J_{CP}$= 8.1 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 13.36 (s). IR (KBr, tablet) ν= 3447 (w), 3268 (m), 3123 (w), 2987 (m), 2930 (w), 2207 (m), 1570 (m), 1521 (br s), 1448 (s), 1391 (m), 1374 (w), 1221 (m), 1141 (w), 1090 (m), 998 (br s), 803 (m), 778 (w), 668 (w), 607 (m), 539 (w), 491 (w), 447 (w), 419 (w), 409 (w), 404 (w). MS (70 eV, 160°C) m/z (%)= 439 (M^+, 12), 357 (38), 355 (100), 339 (25), 337 (34), 276 (12), 141 (4), 139 (17), 111 (4), 57 (3), 44 (10), 41 (149. UV (MeCN) λ_{max} (log ε)= 246 (4.04), 282 (3.90), 354 (3.61). Anal. Calcd for $C_{19}H_{23}N_3O_3ClPS$: C, 51.86; H, 5.26; N, 9.58; S, 7.28. Found: C, 51.63; H, 5.09; N, 9.31; S, 7.07.

2-Amino-5-cyano-6-*tert*-butyl-4-methylsulfanylpyridin-3-ylphosphinic acid ethyl ester (**7.5d**)

- 66 mg (34%) of **7.5d** were obtained as light yellow crystals, mp 148-149°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.23 (t_p, $^3J_{HH}$= 6.8 Hz, 3H, $OCH_2C\underline{H}_3$), 1.52 (s, 9H, ($C\underline{H}_3$)$_3$C), 2.89 (s, 3H, SCH_3), 4.20-4.32 (m, 2H, $OC\underline{H}_2CH_3$), 7.36-7.73 (m, 5H, 2′a-H, 3′a-H, 4′a-H, 5′a-H, 6′a-H). ^{13}C-NMR (90.56 MHz, CF_3COOD)δ= 16.4 (t_p, $^3J_{CP}$= 7.4 Hz, $OCH_2\underline{C}H_3$), 20.5 (s, S$\underline{C}H_3$), 27.9 (s, ($\underline{C}H_3$)$_3$C), 37.8 (s, (CH_3)$_3\underline{C}$), 98.5 (d_p, $^3J_{CP}$= 15.4 Hz, C-5), 110.4 (d_p, $^1J_{CP}$= 150 Hz, C-3), 113.4

(s, CN), 127.9 (d, C-1´a), 131.0, 131.8 (2*d, C-2´a, C-3´a, C-5´a, C-6´a), 133.5 (d, C-4´a), 157.5 (s, C-6), 162.4 (d_p, $^2J_{CP}$= 22.9 Hz, C-2), 167.0 (d_p, $^2J_{CP}$= 6.7 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 32.82 (s). IR (KBr, tablet) ν= 3418 (m), 3128 (w), 3066 (w), 2981 (w), 2923 (w), 2221 (m), 1574 (m), 1529 (s), 1496 (w), 1451 (m), 1433 (m), 1394 (s), 1371 (s), 1316 (w), 1219 (m), 1160 (w), 1111 (w), 1020 (br s), 969 (w), 857 (w), 804 (w), 780 (m), 712 (m), 668 (w), 650 (w), 591 (w), 540 (w), 457 (w), 423 (w), 412 (w), 404 (w). MS (70 eV, 158°C) m/z (%)= 390 (28), 389 (M^+, 52), 361 (27), 304 (4), 303 (2), 267 (10), 223 (5), 222 (7), 186 (8), 141 (11), 113 (4), 78 (10), 77 (90), 58 (8), 57 (100), 45 (30), 44 (29), 43 (10), 41 (60). UV (MeCN) λ_{max} (log ε)= 250 (4.22), 278 (4.11), 322 (3.82, sh). Exact MS calcd for $C_{19}H_{24}N_3O_2PS$: 389.2242. Found: 389.2241.

General procedure for the preparation of phosphono-phosphino substituted pyridinium salts (**8/9**)

A solution of 0.5 mmol of phosphono-phosphino substituted pyrylium salts (**3/4**) and 0.55 mmol of *p*-substituted anilines (**10**) in EtOH (20 mL) was heated at 70°C under argon for 1 h. The solvent was evaporated and the residue was dissolved in chloroform (30 mL) and the organic layer was dried over anhydrous $MgSO_4$ and filtered. The chloroform solution was concentrated and stirred with ether / n-hexane (1:1) to give the phosphono-phosphino substituted pyridinium salts (**8/9**) as yellow crystals.

2-Amino-5-cyano-6-phenyl-4-methylsulfanyl-1-(4-bromophenyl)pyridinium-3-yl-phosphonic acid dimethyl ester tetrafluoroborate (**8.1a**)

-135 mg (45%) of **8.1a** were obtained as yellow crystals, mp 153-154°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 2.84 (s, 3H, SCH_3), 3.76, 3.80 (2*d_p, $^3J_{HP}$= 12 Hz, 6H, OCH_3), 6.85-6.89 (d, $^3J_{HH}$= 8.1 Hz, 2H, 9´-H, 11´-H), 7.23-7.41 (m, 5H, 2´-H, 3´-H, 4´-H, 5´-H, 6´-H), 7.44-7.47 (d, $^3J_{HH}$= 8.1 Hz, 2H, 8´-H, 12´-H). ^{13}C-NMR

(90.56 MHz, CF_3COOD) δ= 20.1 (s, SCH_3), 53.2 (d_p, $^2J_{HP}$= 6.6 Hz, OCH_3), 98.2 (d_p, $^3J_{CP}$= 16.1 Hz, C-5), 114.6 (s, CN), 121.9 (d_p, $^1J_{CP}$= 197 Hz, C-3), 126.4 (s, C-1′), 128.4, 129.2 (2*d, C-2′, C-3′, C-4′, C-5′, C-6′), 129.0, 129.8 (2*d, C-8′, C-9′, C-11′, C-12′), 136.8 (s, C-7′), 140.3 (s, 10′), 158.4 (d_p, $^2J_{CP}$= 20 Hz, C-2), 159.4 (s, C-6), 161.5 (d_p, $^2J_{CP}$= 6.8 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 12.38 (s). IR (KBr, tablet) ν= 3369 (w), 3017 (w), 2962 (m), 2905 (w), 2208 (m), 1671 (s), 1595 (s), 1555 (s), 1489 (s), 1446 (w), 1400 (w), 1386 (m), 1215 (s), 1083 (br s), 1032 (br s), 865 (w), 821 (m), 762 (m), 730 (m), 638 (m), 555 (s), 480 (w), 441 (w), 420 (w), 409 (w), 402 (w). MS (70 eV, 177°C) m/z (%)= 506 (M^+, 11), 505 (28), 504 (9), 503 (28), 495 (45), 494 (28), 493 (100), 492 (16), 261 (10), 260 (54), 259 (10), 268 (56), 157 (24), 155 (30), 105 (39), 77 (43), 47 (13), 43 (5), 41 (4). UV (MeCN) λ_{max} (log ε)= 250 (4.28), 328 (3.99). Anal. Calcd for $C_{21}H_{23}N_3O_3BBrF_4PS$: C, 42.36; H, 3.89; N, 7.08; S, 5.38. Found: C, 42.09; H, 3.81; N, 6.93; S, 5.21.

2- Amino-5- cyano-6- phenyl-4-methylsulfanyl-1- (4-acetylphenyl)pyridinium-3- yl-phosphonic acid diethyl ester tetrafluoroborate (**8.1b**)

-115 mg (40%) of **8.1b** were obtained as yellow crystals, mp 148-149°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.40 (d_pt, $^3J_{HH}$= 7 Hz, 6H, $OCH_2\underline{C}H_3$), 2.52 (s, 3H, $COCH_3$), 2.82 (s, 3H, SCH_3), 4.25-4.37 (m, 4H, $OC\underline{H}_2CH_3$), 7.09-7.26 (m, 5H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 7.29-7.32 (d, $^3J_{HH}$= 7.6 Hz, 2H, 9′-H, 11′-H), 7.81-7.84 (d, $^3J_{HH}$=7.6 Hz, 2H, 8′-H, 12′-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 16.2 (d_pq, $^3J_{CP}$= 6.4 Hz, $OCH_2\underline{C}H_3$), 20.2 (s, SCH_3), 26.5 (s, $CO\underline{C}H_3$), 63.3 (d_pq, $^2J_{CP}$= 6.2 Hz, $O\underline{C}H_2CH_3$), 98.2 (d_p, $^3J_{CP}$= 16.5 Hz, C-5), 115.1 (s, CN), 122.2 (d_p, $^1J_{CP}$= 202 Hz, C-3), 128.7, 129.9 (2*d, C-8′, C-9′, C-11′, C-12′), 129.0, 130.8 (2*d, C-2′, C-3′, C-4′,C-5′, C-6′), 131.0 (s, C-1′), 136.9 (s, C-7′), 140.8 (s, C-10′), 158.7 (d_p, $^2J_{CP}$= 19.2 Hz, C-2), 159.0 (s, C-6), 161.2 (d_p, $^2J_{CP}$= 6.7 Hz, C-4), 196.6 (s, $\underline{C}OCH_3$). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 8.48 (s). IR (KBr, tablet) ν= 3321 (m), 3069 (w), 2983 (w), 2930 (w), 2220 (m),

1729 (s), 1675 (s), 1601 (m), 1544 (s), 1476 (s), 1447 (m), 1374 (m), 1244 (s), 1059 (br s), 1023 (br s), 955 (m), 872 (w), 821 (m), 710 (m), 693 (m), 590 (m), 552 (s), 525 (m), 485 (w), 431 (w), 411 (w), 402 (w). MS (70 eV, 200°C) m/z (%)= 496 (M^+, 50), 495 (100), 440 (3), 439 (10), 359 (3), 223 (4), 222 (23), 179 (4), 122 (3), 104 (4), 77 (15), 76 (10), 47 (3), 44 (2), 43 (63). UV (MeCN) λ_{max} (log ε)= 254 (4.30), 330 (3.98). Exact MS calcd for $C_{25}H_{27}N_3O_4BF_4PS$: 496.1459. Found: 496.1458.

2-Amino-5-cyano-6-4-fluorophenyl)-4-methylsulfanyl-1-(4-acetylphenyl)pyridinium-3-ylphosphonic acid diisopropyl ester tetrafluoroborate (**8.2c**)

-130 mg (41%) of **8.2c** were obtained as yellow crystals, mp 191-192°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.52, 1.58 (2*d_p, $^3J_{HH}$= 6.1 Hz, 12H, OCH($C\underline{H}_3$)$_2$), 2.73 (s, 3H, $COCH_3$), 3.09 (s, 3H, SCH_3), 5.07-5.19 ($d_p$sept, $^2J_{HP}$= 7.4 Hz, $^3J_{HH}$= 6.1 Hz, 2H, O$\underline{C}$H(CH_3)$_2$), 7.05-7.12 (d, $^3J_{HF}$= 7.7 Hz, 2H, 3′-H, 5′-H), 7.33-7.41 (2*d, $^3J_{HH}$= 8.1 Hz, 4H, 8′-H, 9′-H, 11′-H, 12′-H), 8.08-8.11 (dd, $^4J_{HF}$= 4.8 Hz, 2H, 2′-H, 6′-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 20.5 (s, S$\underline{C}$H$_3$), 23.7 (d_pq, $^3J_{CP}$= 5 Hz), 23.9 (d_pq, $^3J_{CP}$= 4 Hz, OCH($\underline{C}$H$_3$)$_2$), 73.4 (d_pd, $^2J_{CP}$= 6.6 Hz, O$\underline{C}$H(CH_3)$_2$), 99.1 (d_p, $^3J_{CP}$= 16.5 Hz, C-5), 115.3 (s, CN), 121.8 (d_p, $^1J_{CP}$= 199 Hz, C-3), 127.6 (s, C-1′), 128.9, 129.2 (2*d, C-8′, C-9′, C-11′, C-12′), 129.9, 130.9 (2*d, C-2′, C-3′, C-5′, C-6′), 137.4 (s, C-7′), 140.5 (s, C-10′), 160.3 (s, C-4′), 160.8 (d_p, $^2J_{CP}$= 17.8 Hz, C-2), 161.3 (s, C-6), 162.3 (d_p, $^2J_{CP}$= 6.2 Hz, C-4), 197.3 (s, $\underline{C}$OCH$_3$). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 12.49 (s). IR (KBr, tablet) ν= 3325 (w), 3077 (w), 2929 (w), 2219 (m), 1718 (s), 1660 (s), 1604 (s), 1548 (s), 1513 (m), 1476 (s), 1383 (w), 1304 (w), 1239 (s), 1164 (w), 1088 (br s), 998 (s), 978 (s), 823 (m), 778 (m), 682 (w), 599 (m), 555 (s), 489 (w), 458 (w), 421 (w), 411 (w), 402 (w). MS (70 ev, 178°C) m/z (%)= 542 (M^+, 13), 541 (38), 459 (10), 458 (31), 441 (12), 439 (25), 241 (2), 240 (13), 121 (5), 91 (8), 77 (2), 44 (4), 43 (22), 41 (2). UV (MeCN) λ_{max} (log ε)= 254 (4.35), 332 (4.04). Exact MS calcd for $C_{27}H_{30}N_3O_4BF_5PS$: 542.1678. Found: 542.1677.

2-Amino-5-cyano-6-(4-chlorophenyl)-4-methylsulfanyl-1-(4-bromophenyl)pyridinium-3-ylphosphonic acid diisopropyl ester tetrafluoroborate (**8.4c**)

-150 mg (44%) of **8.4c** were obtained as yellow crystals, mp 166-168°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.33, 1.38 (2*d_p, $^3J_{HH}$= 6.1 Hz, 12H, OCH($C\underline{H}_3$)$_2$), 2.82 (s, 3H, SCH_3), 4.83-4.92 ($d_p$sept, $^2J_{HP}$= 7.4 Hz, $^3J_{HH}$= 6.1 Hz, 2H, OC$\underline{H}$(CH_3)$_2$), 6.83-6.87 (d, $^3J_{HH}$= 8.2 Hz, 2H, 9′-H, 11′-H), 7.09-7.12 (d, $^3J_{HH}$= 8.2 Hz, 2H, 3′-H, 5′-H), 7.27-7.30 (d, $^3J_{HH}$= 8.2 Hz, 2H, 2′-H, 6′-H), 7.39-7.42 (d, $^3J_{HH}$= 8.2 Hz, 2H, 8′-H, 12′-H). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 20.1 (s, SCH_3), 23.7 (d_pq, $^3J_{CP}$= 5 Hz), 23.9 (d_pq, $^3J_{CP}$= 4 Hz), OCH($\underline{C}H_3$)$_2$), 73.2 (d_pd, $^2J_{CP}$= 6 Hz, O$\underline{C}$H(CH_3)$_2$), 98.0 (d_p, $^3J_{CP}$= 16.4 Hz, C-5), 114.9 (s, CN), 121.8 (d_p, $^1J_{CP}$= 198 Hz, C-3), 128.3 (s, C-1′), 129.0, 129.9 (2*d, C-8′, C-9′, C-11′, C-12′), 129.8, 130.6 (2*d, C-2′, C-3′, C-5′, C-6′), 136.2 (s, C-4′), 137.0 (s, C-7′), 140.9 (s, C-10′), 158.6 (d_p, $^2J_{CP}$= 19.8 Hz, C-2), 159.2 (s, C-6), 161.4 (d_p, $^2J_{CP}$= 6.6 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 12.41 (s). IR (KBr, tablet) ν= 3419 (w), 3186 (m), 3077 (w), 2981 (m), 2923 (w), 2214 (m), 1674 (s), 1635 (m), 1595 (m), 1569 (m), 1545 (s), 1500 (m), 1486 (s), 1474 (s), 1398 (m), 1382 (m), 1235 (s), 1175 (m), 1104 (m), 1080 (br s), 1011 (s), 989 (s), 833 (m), 817 (m), 776 (m), 668 (w), 640 (m), 556 (s), 507 (w), 444 (w), 422 (w), 408 (w), 402 (w). MS (70 eV, 179°C) m/z (%)= 596 (9), 595 (M^+, 25), 594 (6), 593 (18), 512 (97), 510 (27), 431 (8), 429 (4), 296 (6), 294 (26), 157 (25), 155 (30), 125 (32), 99 (100), 76 (17), 75 (16), 45 (17), 42 (54), 41 (89). UV (MeCN) λ_{max} (log ε)= 250 (4.16), 330 (3.85). Anal. Calcd for $C_{25}H_{27}N_3O_3BBrClF_4PS$: C, 43.96; H, 3.98; N, 6.17; S, 4.69. Found: C, 43.74; H, 3.81; N, 6.01; S, 4.48.

2-Amino-5-cyano-6-*tert*-butyl-4-methylsulfanyl-1-(4-bromophenyl)pyridinium-3-ylphenylphosphinic acid ethyl ester tetrafluoroborate (**9.5d**)

- 117 mg (37%) of **9.5d** were obtained as yellow crystals, mp 110-112°C. ^{1}H-NMR (250.13 MHz, CF_3COOD) δ= 1.24 (t_p, $^3J_{HH}$= 6.9 Hz, 3H, $OCH_2C\underline{H}_3$), 1.52

(s, 9H, $(C\underline{H}_3)_3C$), 2.86 (s, 3H, SCH_3), 4.07-4.25 (m, 2H, $OC\underline{H}_2CH_3$), 6.88-6.92 (d, $^3J_{HH}$= 8.1 Hz, 2H, 9´-H, 11´-H), 7.36-7.40 (d, $^3J_{HH}$= 8.1 Hz, 2H, 8´-H, 12´-H), 7.42-7.87 (m, 5H, PC_6H_5). ^{13}C-NMR (90.56 MHz, CF_3COOD) δ= 16.3 (t_p, $^3J_{CP}$= 7.2 Hz, $OCH_2\underline{C}H_3$), 20.1 (s, SCH_3), 27.8 (s, $(\underline{C}H_3)_3C$), 37.8 (s, $(CH_3)_3\underline{C}$), 64.4 (d_pt, $^2J_{CP}$= 7.1 Hz, $O\underline{C}H_2CH_3$), 98.6 (d_p, $^3J_{CP}$= 15.6 Hz, C-5), 113.8 (s, CN), 120.9 (d_p, $^1J_{CP}$= 149 Hz, C-3), 127.6 (d, C-1´s), 129.2, 130.1 (2*d, C-8´, C-9´, C-11´, C-12´), 131.3, 131.8 (2*d, C-2´a, C-3´a, C-5´a, C-6´a), 133.3 (d, C-4´a), 137.3 (s, C-7´), 140.4 (s, C-10´), 158.6 (d_p, $^2J_{CP}$= 20.1 Hz, C-2), 159.4 (s, C-6), 162.8 (d_p, $^2J_{CP}$= 6.6 Hz, C-4). ^{31}P-NMR (145.79 MHz, CF_3COOD) δ= 32.14 (s). IR (KBr, tablet) ν= 3231 (m), 3125 (m), 3022 (w), 2901 (w), 2200 (m), 1623 (m), 1593 (m), 1517 (s), 1487 (s), 1438 (m), 1419 (m), 1323 (m), 1282 (m), 1184 (s), 1069 (br s), 1014 (br s), 811 (s), 769 (m), 693 (w), 599 (w), 521 (m), 482 (s), 425 (w), 418 (w), 405 (w). MS (70 eV, 155°C) m/z (%)= 546 (4), 545 (14), 544 (M^+, 8), 543 (12), 499 (12), 498 (20), 497 (11), 496 (15), 470 (10), 468 (14), 366 (13), 364 (2), 302 (1), 300 (3), 198 (2), 126 (2), 99 (46), 98 (40), 78 (8), 77 (100), 58 (4), 57 (89), 51 (16), 47 (8), 45 (2), 43 (3), 41 (1). UV (MeCN) λ_{max} (log ε)= 248 (4.40), 302 (3.70). Exact MS calcd for $C_{25}H_{28}N_3O_2BBrF_4PS$: 545.4264. Found: 545.4263.

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