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Synthesis, NMR and X-ray characterisation of 6-substituted 4-amino-5-aryldiazenyl-1-arylpyridazinium salts

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Abstract—A new simple method has been used to prepare 6-substituted 4-(subst. amino)-5-aryldiazenyl-1-arylpyridazinium salts from *N*-methyl- or *N*-aryl-3-amino-1-phenylbut-2-en-1-ones and 4-aminopent-3-en-2-ones and substituted benzenediazonium tetrafluoroborates or hexafluorophosphates. The structure of selected derivatives was studied by means of ^{15}N NMR spectra and X-ray.

1. Introduction

In our previous paper,[1] we stated that the reaction of 1-phenyl-3-(2,4-dimethoxyphenylamino)but-2-en-1-one or 1-phenyl-3-methylaminobut-2-en-1-one with substituted benzenediazonium tetrafluoroborates produces, besides the expected products of attack of diazonium ion on methine carbon of enaminone, also the side products 4-(2,4-dimethoxyphenylamino)- or 4-methylamino-1-aryl-5-phenyldiazenylpyridazinium tetrafluoroborates in the yields of 17–22%. The mechanism for formation of these pyridazinium salts has not been reliably proven. The aim of the present paper is to explore the scope and limitations of this reaction, inclusive of the effect of the anion of the diazonium salt upon the yield of the pyridazinium salt, and to find out whether the reaction can also be applied to other enaminones than benzoylacetone derivatives.

2. Results and discussion

In contrast to our previous findings, now we have used benzenediazonium hexafluorophosphates instead of benzenediazonium tetrafluoroborates. This change in the anion approximately doubled the yield. The X-ray diffraction studies on a single crystal of product **10** (Figs. 1 and 2) unequivocally proved the presumed structure of the pyridazinium salt. The proton and carbon NMR spectra of the hexafluorophosphates are practically identical with those of the corresponding tetrafluoroborates (see Section 5).

The reaction of enaminone **1** with 4-methoxybenzenediazonium tetrafluoroborate did not give the respective

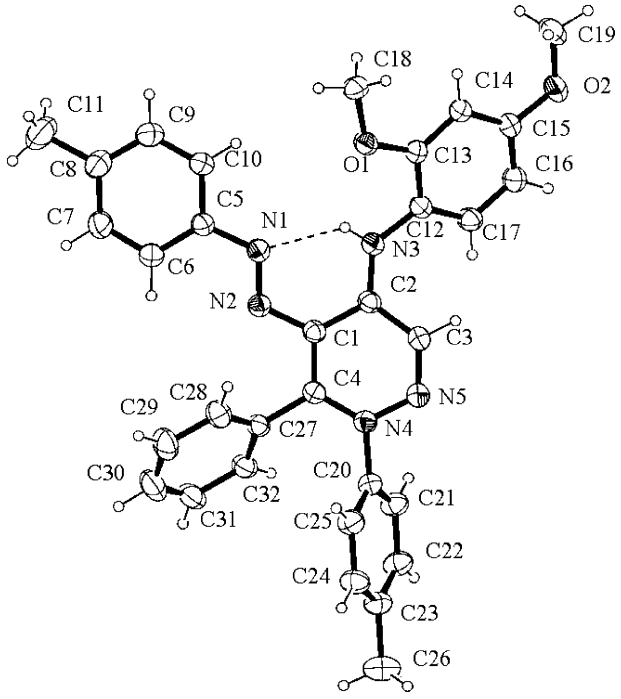

Figure 1. ORTEP view of the cation of compound **10**. Thermal ellipsoids are drawn at 30% probability level.

Keywords: Enaminones; Pyridazinium salts; Azo coupling; NMR; X-ray.
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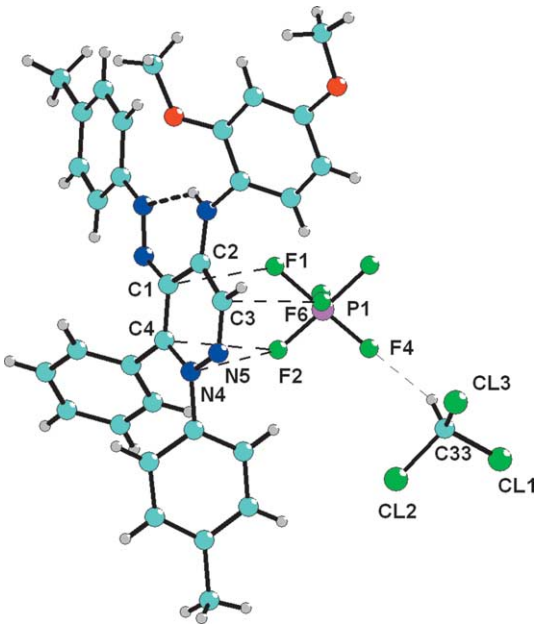


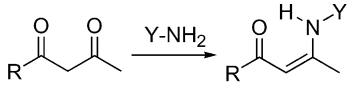
Figure 2. Crystal structure of compound **10** showing the most significant intermolecular interactions.

pyridazinium salts.[1] The increase in yield of pyridazinium salt **10** after replacement of the tetrafluoroborate by hexafluorophosphate of the diazonium salt led us to believe that it could be possible to prepare the 4-methoxy derivative too (Scheme 1). This turned out to be the case and 4-(2,4-dimethoxyphenylamino)-1-(4-methoxyphenyl)-5-(4-methoxyphenyldiazenyl)-6-phenylpyridazinium hexafluorophosphate (**12**) was obtained in a relatively good yield (40%) when the starting material molar ratios were 2:1.

The pyridazinium salts can only be prepared from diazonium salts with electropositive substituents (according to the Hammett σ constants up to the non-substituted benzenediazonium tetrafluoroborate). With hexafluorophosphates the reaction applicability expanded to the 4-Cl derivative. However, it was proved that the 4-nitro derivative is not formed even with the application of 4-nitrobenzenediazonium hexafluorophosphate.

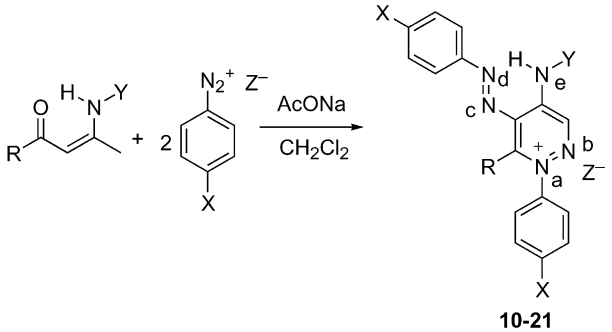
For a survey and characterization of the 6-arylpyridazinium hexafluorophosphates prepared, see Scheme 1, Table 1 and Section 5.

It was found that the reaction leading to formation of pyridazinium salts (Scheme 1) was not limited to enaminones derived from benzoylacetone alone. The reaction between 4-methylaminopent-3-en-2-one **5** and 4-methoxybenzenediazonium hexafluorophosphate also gave the respective 6-methylpyridazinium hexafluorophosphate (**17**), shown in Figures 3 and 4. Compound **17**, which is the first representative of 6-methyl derivatives, was also characterised by its ^{1}H and ^{13}C, ^{19}F, ^{31}P spectra (see Section 5 and Table 1) and ^{15}N NMR spectra (see Table 1 and Fig. 5). For more details about NMR of related compounds see Ref. 1. It was found that using this method is also possible to prepare related 6-methyl substituted pyridazinium hexafluorophosphates and tetrafluoroborates with various substituents at the amino group and aryl group,



1-9

R = C_6H_5, Y = 2,4-$(OCH_3)_2C_6H_3$ (**1**); R = C_6H_5, Y = 4-$(OCH_3)C_6H_4$ (**2**); R = Y = C_6H_5 (**3**); R = C_6H_5, Y = CH_3 (**4**); R = Y = CH_3 (**5**); R = CH_3, Y = 2,4-$(OCH_3)_2C_6H_3$ (**6**); R = CH_3, Y = CH_2-2,4-$(OCH_3)_2C_6H_3$ (**7**); R = CH_3, Y = 4-ClC_6H_5 (**8**); R = CH_3, Y = 4-$(CH_3)C_6H_5$ (**9**).



10-21

R = C_6H_5, Y = 2,4-$(OCH_3)_2C_6H_3$, X = CH_3, Z = PF_6^- (**10**); R = C_6H_5, Y = 2,4-$(OCH_3)_2C_6H_3$, X = H, Z = PF_6^- (**11**)
R = C_6H_5, Y = 2,4-$(OCH_3)_2C_6H_3$, X = OCH_3, Z = PF_6^- (**12**);
R = C_6H_5, Y = CH_3 , X = OCH_3, Z = PF_6^- (**13**); R = C_6H_5, Y = 2,4-$(OCH_3)_2C_6H_3$, X = Cl, Z = PF_6^- (**14**);
R = C_6H_5, Y = 4-$(OCH_3)C_6H_4$, X = CH_3, Z = BF_4^- (**15**); R = CH_3, Y = CH_3, X = OCH_3, Z = BF_4^- (**16**);
R = CH_3, Y = CH_3, X = OCH_3, Z = PF_6^- (**17**); R = CH_3, Y = CH_3, X = H, Z = BF_4^- (**18**);
R = CH_3, Y = CH_3, X = H, Z = PF_6^- (**19**); R = CH_3, Y = 2,4-$(OCH_3)_2C_6H_3$, X = OCH_3, Z = PF_6^- (**20**);
R = CH_3, Y = 4-$(CH_3)C_6H_4$, X = CH_3, Z = PF_6^- (**21**).

Scheme 1.

Table 1. ^{15}N, ^{19}F, ^{31}P and ^{11}B NMR parameters of the representative pyridazinium salts[a]

Compound	N_a	N_b	N_c	N_d	N_e	^{19}F[b]	^{31}P[c]	^{11}B
10 ($CDCl_3$)	−163.0	−32.5	[d]	107.7	−265.5	−73.90	−144.0	
16 (DMSO)	−164.7	−33.6	[d]	107.7	−276.0	−147.87[e] −147.93[f]		−1.82
17 (DMSO)	−164.7	−33.6	[d]	107.7	−276.2	−69.73	−143.1	

[a] For ^{1}H and ^{13}C see Section 5.
[b] Values of $^{1}J(^{19}F, ^{31}P)$: 713.4 Hz (**10**), 711.0 Hz (**17**).
[c] Values of $^{1}J(^{31}P, ^{19}F)$: 712.6 Hz (**10**), 711.3 Hz (**17**).
[d] Not detected.
[e] $^{19}F–^{10}B$.
[f] $^{19}F–^{11}B$.

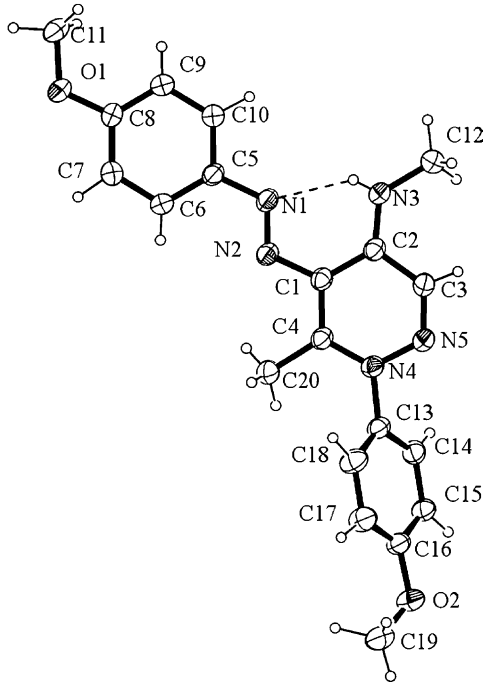


Figure 3. ORTEP view of the cation of compound **17**. Thermal ellipsoids are drawn at 30% probability level.

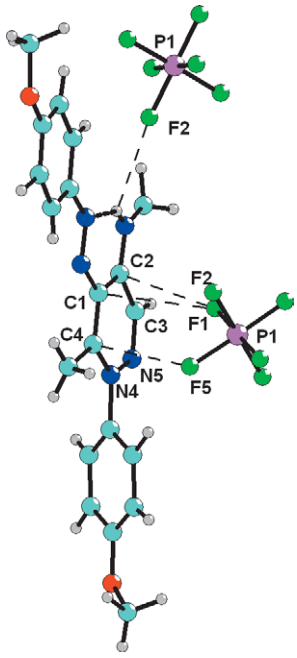


Figure 4. Crystal structure of compound **17** showing the most significant intermolecular interactions.

depending on the starting enaminone and diazonium salts (substances **16–21**).

3. Crystallography

ORTEP[2] diagrams of compounds **10** and **17** are shown in Figures 1 and 3, respectively. The structures of both organic cations are very similar to those recently published.[1] The pyridazinium rings are essentially planar and display extended conjugation with the positive charge mainly located on nitrogen N4. Both compounds form short intramolecular N–H···N hydrogen bond assisted by resonance between the aminic N3–H group and the nitrogen N1 of the diazenyl moiety. The N1···N3 distances of 2.625(2) and 2.645(3) Å in **10** and **17**, respectively, are in agreement with those of analogue structures recently reported.[1] In compound **17** the N3–H aminic group forms also a bifurcated weak hydrogen bond with a fluorine atom (F2) of the PF_6^- anion [N3···F2 = 3.083(4) Å]. In both structures the PF_6^- anions are involved in short electrostatic interactions with pyridazinium rings as shown in Figures 2 and 4 and in Table 3.

4. Conclusions

The described way of preparation of pyridazinium salts is simple: the reaction proceeds under mild conditions and the separation of product being easy, too. The reaction can be

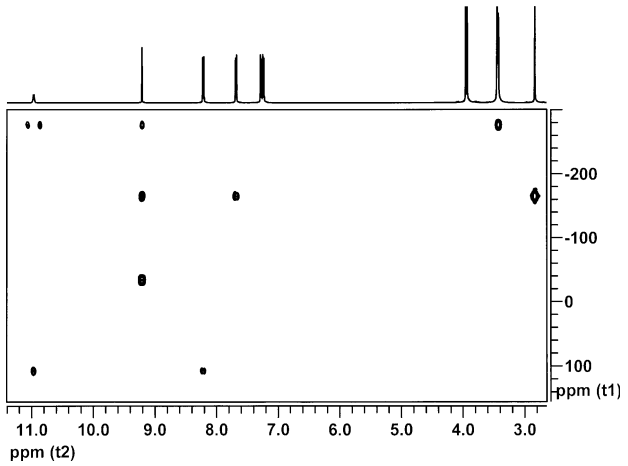


Figure 5. 500 MHz $^{1}H–^{15}N$ gs HMBC spectrum of the compound **17** in DMSO-d_6 optimised for 5 Hz. One of azo nitrogens has not been detected at the natural abundance.

applied to both diazonium tetrafluoroborates and diazonium hexafluorophosphates: the latter gave higher yields in the majority of cases. The method can be used to prepare various 1-(substituted aryl)-4-(substituted amino)pyridazinium salts substituted at 6-position by a phenyl or methyl group. The reaction is affected by substituent type both in the diazonium salt and in the amino group of the starting enaminone. Electron-donating substituents in diazonium salts are usually more appropriate for the formation of the pyridazinium salt, but exceptions were also observed in the reactions of *N*-arylenaminones with diazonium tetrafluoroborates. The reaction is restricted to enaminones with a secondary amino group; the compounds with a primary amino group only give products of a single azo coupling, and the enaminones with a tertiary amino groups show double azo coupling.[3]

5. Experimental

5.1. General

The NMR spectra were measured at 298 K with a Bruker AVANCE 500 spectrometer equipped with a 5 mm broadband probe with a gradient of magnetic field in the direction of z axis at the frequencies of 500.13 MHz (^{1}H), 125.77 MHz (^{13}C), 50.69 MHz (^{15}N), 470.56 MHz (^{19}F), 202.46 MHz (^{31}P) and with a Bruker AMX 360 spectrometer at the frequency of 360.14 MHz (^{1}H), 90.57 MHz (^{13}C), 115.55 MHz (^{11}B). The ^{1}H NMR spectra were calibrated in $CDCl_3$ on hexamethyldisiloxane (δ 0.05) and in DMSO-d_6 on the central signal of the solvent multiplet (δ 2.55). The ^{13}C NMR spectra were calibrated on the central signal of the solvent multiplet (δ 39.6 for DMSO and δ 76.9 for $CDCl_3$). The carbon NMR spectra were measured in standard way and by means of the APT pulse sequence (spectral width 26.455 kHz, acquisition time 1.238 s, zero filling to 64 K and line broadening 1 Hz prior Fourier transformation). The ^{15}N NMR spectra were calibrated on external neat ^{15}N nitromethane placed in a coaxial capillary (δ 0.0). The ^{11}B NMR spectra were calibrated on external $B(OCH_3)_3$ placed in a co-axial capillary (δ 18.1). In order to suppress the signals of ^{11}B nuclei from NMR tube glass, the measurements were carried out in teflon sample tube liners (Aldrich) inserted into 5 mm tubes whose bottom part of about 25 mm length was cut off. The ^{19}F NMR spectra were calibrated on internal $CFCl_3$ (δ 0.0, central signal of multiplet of the standard) and were measured using 5 mm ^{1}H/^{19}F dual probehead with proton noise decoupling. The $\delta(^{15}N)$ values were measured with the help of techniques with inversion detection (^{1}H–^{15}N HMBC) processed in the magnitude mode. The gradient ratios were 70:30:50.1. Experiments were performed with the NH one-bond coupling 90 Hz, and NH long-range coupling 5 Hz, 2k$\times$160k zero filled to 2k$\times$1k, sinebell squared in both dimensions.

Melting points were determined with a Kofler hot stage microscope and were not corrected. The elemental analyses were carried out with a FISONS EA 1108 automatic analyser.

Dichloromethane was pre-dried by standing with anhydrous calcium chloride and subsequent distillation with phosphorus pentoxide. The anhydrous sodium acetate was fused on a porcelain dish and left to cool in a desiccator. The diazonium tetrafluoroborates used were prepared by procedures described elsewhere[4] and diazonium hexafluorophosphates were prepared in the same manner as corresponding tetrafluoroborates with using sodium hexafluorophosphate instead of sodium tetrafluoroborate.

The crystal data for compounds **10** and **17** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo K_α radiation and corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR97[5]) and refined using full-matrix least-squares. In compound **10** all non-hydrogen atoms were refined anisotropically and hydrogens included on calculated positions, riding on their

Table 2. Crystal data

Compound	**10**	**17**
Formula	$(C_{32}H_{30}N_5O_2)^+\cdot(PF_6)^-\cdot CHCl_3$	$(C_{20}H_{22}N_5O_2)^+\cdot(PF_6)^-$
M	780.95	509.40
System	Orthorhombic	Monoclinic
Space group	$Pna2_1$	Cc
a (Å)	30.1530(3)	11.8255(3)
b (Å)	14.4669(1)	23.3472(7)
c (Å)	8.2887(1)	9.3110(2)
α (°)	90	90
β (°)	90	117.684(2)
γ (°)	90	90
U (Å^3)	3615.7(1)	2276.4(1)
Z	4	4
D_c (g cm^{-3})	1.435	1.486
T (K)	295	295
μ (cm^{-1})	3.667	1.978
θ_{min}–θ_{max} (°)	3.9–28.0	1.7–30.0
Unique reflections	8324	6067
R_{int}	0.041	0.056
Observed reflections [$I>2\sigma(I)$]	6986	4193
R (observed reflections)	0.0624	0.0499
wR (all reflections)	0.1828	0.1437
S	1.023	1.028
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	0.38; −0.45	0.34; −0.22

carrier atoms except for N3–H hydrogen, which was refined isotropically. The PF_6^- anion was found disordered and the six fluorine atoms were refined with two independent orientations with occupancies of 0.6 and 0.4, respectively. The asymmetric unit contains also a molecule of solvent $CHCl_3$. In compound **17** all non-hydrogen atoms were refined anisotropically and hydrogens isotropically.

All the calculations were performed using SHELXL-97[6] and PARST[7] implemented in WINGX[8] system of programs. The crystal data and refinement parameters are summarized in Table 2. Selected bond and short contact distances are given in Table 3 and hydrogen bond parameters are shown in Table 4.

CCDC-266954 and 266955 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk] (Table 4).

5.1.1. 3-(2,4-Dimethoxyphenylamino)-1-phenylbut-2-en-1-one (1). Compound **1** was prepared according to the procedure described in Ref. 1.

5.1.2. 3-(4-Methoxyphenylamino)-1-phenylbut-2-en-1-one (2). Compound **2** was prepared by the same method as **1**. Crystallisation from toluene, yield 77%; mp 106–107 °C. ^{1}H NMR (360.14 MHz, $CDCl_3$) 2.00 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 5.83 (s, 1H, =CH), 6.83 (m, 2H, Ar), 7.05 (m, 2H, Ar), 7.39 (m, 3H, Ar), 7.89 (m, 2H, Ar), 12.94 (br s, 1H, NH). ^{13}C NMR (90.57 MHz, $CDCl_3$) 19.89 (CH_3), 55.11 (OCH_3), 93.42 (=CH), 114.02 (CH Ar), 126.19 (CH Ar), 126.72 (CH Ar), 127.95 (CH Ar), 130.46 (CH Ar), 131.08 (C_q Ar), 139.82 (C_q Ar), 157.51 (C_q Ar), 162.81 (=C–N), 187.47 (C=O). Anal. Calcd for $C_{17}H_{17}NO_2$ (267.33): C, 76.38; H, 6.41; N, 5.24. Found: C, 76.34; H, 6.60; N, 5.47.

Table 3. Selected bond and short contact distances (Å)

	10	17
N1–N2	1.268(3)	1.266(3)
N2–C1	1.395(3)	1.405(3)
C1–C2	1.431(3)	1.426(3)
N3–C2	1.330(3)	1.322(4)
C1–C4	1.401(3)	1.400(4)
N4–C4	1.346(3)	1.361(3)
N4–N5	1.348(3)	1.352(3)
N5–C3	1.298(3)	1.303(4)
C2–C3	1.415(3)	1.424(4)
N4···F2	3.130(11)	
C1···F1	3.196(8)	
C3···F6	3.149(12)	
C4···F2	3.128(11)	
C1···F1		3.194(5)
C2···F1		3.187(5)
C4···F5		3.193(6)

5.1.3. 3-Phenylamino-1-phenylbut-2-en-1-one (3). Compound has been prepared according to method described in Ref. 9. Yield 85%; mp 107–108.5 °C (Ref. 9; mp 110.5–111.5 °C). ^{1}H NMR (360.14 MHz, $CDCl_3$) 2.10 (s, 3H, CH_3), 5.87 (s, 1H, =CH), 7.14 (m, 2H, Ar), 7.20 (m, 1H, Ar), 7.33 (m, 2H, Ar), 7.40 (m, 3H, Ar), 7.90 (m, 2H, Ar), 13.09 (br s, 1H, NH). ^{13}C NMR (90.57 MHz) 20.21 (CH_3), 94.45 (=CH), 124.55 (CH Ar), 125.57 (CH Ar), 126.87 (CH Ar), 128.08 (CH Ar), 128.97 (CH Ar), 130.70 (CH Ar), 138.46 (C_q Ar), 139.84 (C_q Ar), 162.00 (=C–N), 188.47 (C=O).

5.1.4. 3-Methylamino-1-phenylbut-2-en-1-one (4). Compound **4** was prepared according to the procedure described in Ref. 10.

5.1.5. 4-Methylaminopent-3-en-2-one (5). Compound **5** was prepared according to procedure described in Ref. 11.

5.1.6. 4-(2,4-Dimethoxyphenylamino)pent-3-en-2-one (6). A mixture of acetylacetone (0.1 mol) and 2,4-dimethoxyaniline (0.1 mol) was heated in 50 ml toluene to boiling. The water formed in reaction was distilled off as an azeotrope with toluene. The toluene thus removed was replenished by adding fresh toluene. After the reaction, the solvent was distilled off, and the residue was submitted to vacuum distillation. Yield 84%, bp 165 °C/5 mBar. ^{1}H NMR (360.14 MHz, $CDCl_3$): 1.87 (s, 3H, CH_3), 2.07 (s, 3H, CH_3CO), 3.79 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.15 (s, 1H, =CH), 6.42 (dd, 1H, CH_{Ar}, J=8.6, 2.7 Hz), 6.48 (d, 1H, CH_{Ar}, J=2.6 Hz), 7.00 (d, 1H, CH_{Ar}, J=8.6 Hz), 12.04 (br s, 1H, NH). ^{13}C NMR (90.57 MHz, $CDCl_3$): 19.43, 28.91 (2×CH_3), 55.35, 55.55 (2×OCH_3), 96.69, 99.08, 103.62, 120.80, 126.75 (5×CH), 154.50, 158.73, 161.70 (3×C_q), 195.48 (C=O). Anal. Calcd for $C_{13}H_{17}NO_3$ (235.28): C, 66.36; H, 7.28; N, 5.95. Found: C, 66.47; H, 7.23; N, 5.99.

5.1.7. 2,4-Dimethoxybenzaldoxime. A 250 ml three-necked flask equipped with a reflux condenser, thermometer and dropping funnel was charged with a solution of 2, 4-dimethoxy-benzaldehyde (16.6 g, 0.1 mol) in 75 ml ethanol, and a solution of hydroxylamine hydrochloride (7 g, 0.1 mol) in 20 ml water. The mixture was stirred, and a solution of anhydrous sodium carbonate (5.3 g, 0.05 mol) in 20 ml water was added drop by drop from the funnel. After addition of all the carbonate, the mixture was refluxed 5 h, whereupon it was cooled in ice bath, and the separated

Table 4. Hydrogen bond parameters (Å and degrees)

D–H···A	D–H	H···A	D···A	D–H···A
Compound **10**				
N3–H···N1	0.75(4)	2.04(3)	2.625(2)	135(3)
C33–H33[a]···F4	0.98	2.18	3.084(12)	153
Compound **17**				
N3–H···N1	0.70(3)	2.08(3)	2.645(3)	140(4)
N3–H···F2($x,-y,z-1/2$)	0.70(3)	2.68(4)	3.083(4)	119(3)

[a] Calculated hydrogen.

product was collected by suction and dried in air. Yield 10.8 g (60%); mp 103–105 °C (Ref. 12; mp 104–105 °C).

5.1.8. 2,4-Dimethoxybenzylamine. 2,4-Dimethoxybenzaldoxime (10.8 g) was hydrogenated at atmospheric pressure in ethyl acetate with RaneyNi as catalyst for 48 h. The solvent was removed by distillation, and the evaporation residue was distilled in vacuum to give 4.5 g (45%) liquid, bp 110–120 °C/10 mBar (Ref. 13, bp 142–143 °C/20 mBar). ^{1}H NMR (500.13 MHz, $CDCl_3$): 3.73 (s, 2H, CH_2), 3.78 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.41 (dd, 1H, CH_{Ar}, $J=8.1$, 2.4 Hz), 6.44 (d, 1H, CH_{Ar}, $J=2.3$ Hz), 7.08 (d, 1H, CH_{Ar}, $J=8.1$ Hz). ^{13}C NMR (125.77 MHz, $CDCl_3$): 42.02 (CH_2), 55.00, 5.19 (2×OCH_3), 98.42, 103.44 (2×CH_{Ar}), 124.38 (C_q), 128.83 (CH_{Ar}), 158.22, 159.76 (2×C_q).

5.1.9. 4-(2,4-Dimethoxybenzylamino)pent-3-en-2-one (7). A 100 ml three-necked flask equipped with azeotropic distillation head was charged with acetylacetone (29 mmol), 2,4-dimethoxybenzylamine (29 mmol), 30 ml toluene and 4-methylbenzenesulphonic acid (1 mmol). The mixture was heated to boiling on an oil bath while intermittently removing the toluene–water azeotrope, until the distillate was clear toluene. Then a part of toluene was distilled off and the residue was cooled. The separated crystals were collected by suction. The product was purified by vacuum distillation (173–176 °C/6–7 mBar). Yield 66%. ^{1}H NMR (360.14 MHz, $CDCl_3$): 1.93 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 4.33 (d, 2H, CH_2, $J=6.4$ Hz), 4.96 (s, 1H, =CH), 6.40–6.44 (m, 2H, CH_{Ar}), 7.06 (d, 1H, CH_{Ar}, $J=8.4$ Hz), 11.03 (br s, 1H, NH). ^{13}C (90.57 MHz, $CDCl_3$): 18.60 (CH_3), 28.65 (CH_3), 41.74 (CH_2), 55.20, 55.23 (2×OCH_3), 95.23, 98.43, 103.83 (3×CH_{Ar}), 118.57 (C_q), 128.54 (CH_{Ar}), 157.85, 160.30, 162.84 (3×C_q), 194.57 (C=O). Anal. Calcd for $C_{14}H_{19}NO_3$ (249.31): C, 67.45; H, 7.68; N, 5.62. Found: C, 67.69; H, 7.51; N, 5.64.

5.1.10. 4-(4-Chlorophenylamino)pent-3-en-2-one (8). This compound has been prepared according to procedure described in Ref. 14. Product has been purified by vacuum distillation, (bp 123–132 °C/4 mBar) and by crystallization from *n*-hexane; mp 55.5–57 °C (Ref. 14; mp 60–61 °C). ^{1}H NMR (360.14 MHz, $CDCl_3$): 1.95 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 5.18 (s, 1H, =CH), 6.98–7.05 (m, 2H, AA′), 7.25–7.28 (m, 2H, XX′), 12.43 (br s, 1H, NH). ^{13}C (90.57 MHz, $CDCl_3$): 19.44, 28.89 (2×CH_3), 97.86 (=CH), 125.46, 128.88 (2×CH), 130.60, 137.06 (3×C_q), 159.34 (=C–N), 196.15 (C=O).

5.1.11. 4-(4-Methylphenylamino)pent-3-en-2-one (9). Compound has been prepared according to procedure described in Ref. 14. Product has been purified by crystallisation from *n*-hexane; mp 63.5–64.5 °C (Ref. 14 68–69 °C). ^{1}H NMR (360.14 MHz, $CDCl_3$): 1.93 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 5.14 (s, 1H, =CH), 6.97 (m, 2H, AA′), 7.11 (m, 2H, XX′), 12.38 (br s, 1H, NH). ^{13}C (90.57 MHz, $CDCl_3$): 19.64, 20.79, 29.00 (3×CH_3), 97.11 (=CH), 124.74, 129.55 (2×CH_{Ar}), 135.37, 135.97 (2×C_q), 160.56 (=C–N), 195.77 (C=O).

5.2. General procedure of azo coupling reactions

Re-melted sodium acetate (30 mmol) and the respective benzenediazonium tetrafluoroborate or hexafluorophosphate (10 mmol) were added to a solution of enaminone (5 mmol) in 30 ml dichloromethane with stirring. The reaction mixture was stirred at room temperature 72 h, whereupon the solids were collected by suction on a sintered-glass filter and the filter cake was washed with dichloromethane. The filtrate was evaporated in vacuum, and the evaporation residue was either recrystallized or submitted to column chromatography (in the case of compounds **13** and **16–19** and **21** washing by ethylacetate was performed instead of column chromatography). The following compounds were prepared by the procedure described.

5.2.1. 4-(2,4-Dimethoxyphenylamino)-1-(4-methylphenyl)-5-(4-methylphenyldiazenyl)-6-phenylpyridazinium hexafluorophosphate (10). This compound was obtained as red crystalline solid after crystallization of evaporation residue from ethanol. Yield 43%; mp 243–245 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): 2.26 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 6.58 (dd, 1H, CH_{Ar}, $J=2.6$, 8.7 Hz), 6.61 (d, 1H, CH_{Ar}, $J=2.5$ Hz), 7.04–7.05 (m, 2H, AA′), 7.18–7.20 (m, 2H, AA′), 7.24–7.26 (m, 2H, XX′), 7.28–7.32 (m, 2H, CH_{Ar}), 7.35–7.42 (m, 5H, CH_{Ar}), 7.63 (d, 1H, CH_{Ar}, $J=8.7$ Hz), 8.81 (s, 1H, CH), 12.83 (s, 1H, NH). ^{13}C NMR (125.77 MHz, $CDCl_3$): 20.99 (CH_3), 21.55 (CH_3), 55.69 (OCH_3), 56.04 (OCH_3), 99.59, 105.35 (2×CH_{Ar}), 115.70 (C_q), 123.34, 126.20, 126.24, 127.72 (4×CH_{Ar}), 128.74, 128.89 (2×C_q), 129.59, 130.10, 130.13, 130.69 (4×CH_{Ar}), 139.28, 139.85, 140.32 (3×C_q), 141.33 (CH), 144.35, 149.71, 154.02, 158.04, 161.27 (5×C_q). ^{31}P NMR (202.45 MHz, $CDCl_3$): −143.99 (sp, $J=712.6$ Hz). ^{19}F NMR (470.56 MHz): −73.88 (d, $J=713.4$ Hz). Anal. Calcd for $C_{32}H_{30}F_6N_5O_2P$ (661.58): C, 58.10; H, 4.57; N, 10.59. Found: C, 58.01; H, 4.72; N, 10.31.

5.2.2. 4-(2,4-Dimethoxyphenylamino)-1-phenyl-5-phenyldiazenyl-6-phenylpyridazinium hexafluorophosphate (11). This compound was obtained as red crystalline solid after column chromatography (silica/chloroform/ethylacetate 3:1) and recrystallization from ethanol. Yield 38%; mp 236–240 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): 3.85 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 6.61–6.63 (m, 2H, CH_{Ar}), 7.28–7.32 (m, 5H, CH_{Ar}), 7.36–7.46 (m, 8H, CH_{Ar}), 7.48–7.5 (m, 2H, CH_{Ar}), 7.69 (d, 1H, CH_{Ar}, $J=8.72$ Hz), 8.86 (s, 1H, CH_{Ar}), 12.87 (br s, 1H, NH). ^{13}C NMR (125.77 MHz, $CDCl_3$): 55.73 (OCH_3), 56.04 (OCH_3), 99.75, 105.21 (2×CH_{Ar}), 115.66 (C_q), 123.34, 126.44, 126.57, 127.79 (4×CH_{Ar}), 128.57, 128.81 (2×C_q), 129.11, 129.40, 129.64, 130.29, 130.75, 133.03 (6×CH_{Ar}), 139.42 (C_q), 141.61 (CH), 142.64, 151.43, 153.98, 158.45, 161.36 (5×C_q). Anal. Calcd for $C_{30}H_{26}F_6N_5O_2P$ (633.53): C, 56.88; H, 4.14; N, 11.05. Found: C, 57.04; H, 4.15; N, 10.92.

5.2.3. 4-(2,4-Dimethoxyphenylamino)-1-(4-methoxyphenyl)-5-(4-methoxyphenyldiazenyl)-6-phenylpyridazinium hexafluorophosphate (12). This compound was obtained as red crystalline solid after column chromatography (silica/chloroform/ethylacetate 4:1) and recrystallization

from ethanol. Yield 40%; mp 129–134 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): 3.73 (s, 3H, OCH_3), 3.84 (s, 6H, 2×OCH_3), 3.84 (s, 3H, OCH_3), 6.58–6.60 (m, 2H, 2×CH_{Ar}), 6.74–6.75 (m, 2H, AA′), 6.87–6.89 (m, 2H, AA′), 7.27–7.30 (m, 2H, XX′), 7.30–7.33 (m, 3H, CH_{Ar}), 7.35–7.40 (m, 4H, CH_{Ar}), 7.45–7.48 (m, 2H, XX′), 7.63 (d, 1H, CH_{Ar}, J=9 Hz), 8.79 (s, 1H, CH), 12.80 (br s, 1H, NH). ^{13}C NMR (125.77 MHz, $CDCl_3$): 55.40 (OCH_3), 55.70 (2×OCH_3), 56.02 (OCH_3), 99.64, 105.20, 114.08, 114.75 (4×CH_{Ar}), 115.84 (C_q), 125.61, 126.14, 127.74, 127.77 (4×CH_{Ar}), 128.93, 129.11 (2×C_q), 130.05, 130.63 (2×CH_{Ar}), 135.70, 139.28 (2×C_q), 140.98 (CH), 145.96, 153.95, 157.58, 159.93, 161.13, 163.90 (6×C_q). Anal. Calcd for $C_{32}H_{30}F_6N_5O_4P$ (693.58): C, 55.42; H, 4.36; N, 10.10. Found: C, 55.71; H, 4.25; N, 9.91.

5.2.4. 1-(4-Methoxyphenyl)-4-methylamino-5-(4-methoxyphenyldiazenyl)-6-phenylpyridazinium hexafluorophosphate (13). This compound was obtained as orange solid after recrystallization from ethanol. Yield 33%; mp 215–218 °C. ^{1}H NMR (500.13 MHz, DMSO-d_6): 3.51 (d, 3H, NCH_3, J=5.5 Hz), 3.78 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3) 6.99–7.00 (m, 2H, AA′), 7.11–7.14 (m, 2H, AA′), 7.44–7.52 (m, 7H, CH_{Ar}), 7.74–7.77 (m, 2H, XX′), 9.39 (s, 1H, CH), 10.97 (q, 1H, NH, J=5.5 Hz). ^{13}C NMR (125.77 MHz, DMSO-d_6): 30.95 (NCH_3), 55.82, 56.18 (2×OCH_3), 114.42, 115.21, 125.60, 127.96, 128.41 (5×CH_{Ar}), 129.01, 129.85 (2×C_q), 130.30, 130.84 (2×CH_{Ar}), 136.17, 141.33 (2×C_q), 141.46 (CH), 146.50, 156.72, 159.92, 163.71 (4×C_q). ^{31}P NMR (202.45 MHz, DMSO-d_6): −143.14 (sp, J=711.5 Hz). ^{19}F NMR (470.56 MHz, DMSO-d_6): −69.72 (d, J=711.8 Hz). Anal. Calcd for $C_{25}H_{24}F_6N_5O_2P$ (571.46): C, 52.55; H, 4.23; N, 12.26. Found: C, 52.79; H, 4.42; N, 12.19.

5.2.5. 4-(2,4-Dimethoxyphenylamino)-1-(4-chlorophenyl)-5-(4-chlorophenyldiazenyl)-6-phenylpyridazinium hexafluorophosphate (14). This compound was obtained as dark purple solid after column chromatography (silica/$CHCl_3$) and recrystallization from ethanol. Yield 32%; mp 245–249 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): 3.83 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.57–6.59 (m, 2H, CH_{Ar}), 7.21–7.23 (2H, m, CH_{Ar}), 7.31–7.41 (m, 11H, CH_{Ar}), 7.64 (d, 1H, CH_{Ar}, J=9.5 Hz), 8.83 (s, 1H, =CH), 12.75 (br s, 1H, NH). ^{13}C NMR (125.77 MHz, $CDCl_3$): 55.69, 56.05 (2×OCH_3), 99.65, 105.23 (2×CH_{Ar}), 115.43 (C_q), 124.38, 126.08, 127.91, 127.96 (4×CH_{Ar}), 128.27, 128.77 (2×C_q), 129.25, 129.73, 130.54, 130.62 (4×CH_{Ar}), 135.73, 139.24, 139.26, 140.99 (4×C_q), 141.75 (CH), 149.77, 153.89, 158.47, 161.42 (4×C_q). Anal. Calcd for $C_{30}H_{24}Cl_2F_6N_5O_2P$ (702.42): C, 51.30; H, 3.44; N, 9.97. Found: C, 51.05; H, 3.40; N, 9.65.

5.2.6. 4-(4-Methoxyphenylamino)-1-(4-methylphenyl)-5-(4-methylphenyldiazenyl)-6-phenylpyridazinium tetrafluoroborate (15). This compound was obtained as orange solid after column chromatography (silica/$CHCl_3$/ethylacetate 3:2) and washing by hot ethylacetate. Yield 9%; mp 207–215 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): 2.20 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 6.92–6.94 (m, 2H, AA′), 6.95–6.97 (m, 2H, AA′), 7.13–7.14 (m, 2H, AA′), 7.23–7.26 (m, 2H, CH_{Ar}), 7.30–7.32 (m, 3H, CH_{Ar}), 7.34–7.36 (m, 2H, XX′), 7.45–7.46 (m, 2H, CH_{Ar}), 7.47–7.49 (m, 2H, XX′), 8.69 (s, 1H, CH), 12.71 (br s, 1H, NH). ^{13}C NMR (125.77 MHz, $CDCl_3$): 20.88, 21.44, 55.41 (3×CH_3), 115.30, 123.20 (2×CH_{Ar}), 126.18 (C_q), 126.33, 126.79, 127.44 (3×CH_{Ar}), 128.55, 128.79 (2×C_q), 129.31, 129.81, 129.88, 130.65 (4×CH_{Ar}), 139.52, 140.21, 140.37 (3×C_q), 141.05 (CH), 144.00, 149.62, 158.35, 159.72 (4×C_q). Anal. Calcd for $C_{31}H_{28}BF_4N_5O$ (573.40): C, 64.94; H, 4.92; N, 12.21. Found: C, 64.97; H, 4.87; N, 12.10.

5.2.7. 1-(4-Methoxyphenyl)-4-methylamino-5-(4-methoxyphenyldiazenyl)-6-methylpyridazinium tetrafluoroborate (16). This compound was obtained as orange solid after recrystallization from methanol. Yield 20%; mp 210–213.5 °C. ^{1}H NMR (360.14 MHz, DMSO-d_6): 2.82 (s, 3H, CH_3), 3.41 (d, 3H, NCH_3, J=5.4 Hz), 3.92 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 7.20–7.28 (m, 4H, 2×AA′), 7.65–7.70 (m, 2H, XX′), 8.18–8.22 (m, 2H, XX′), 9.18 (s, 1H, =CH), 10.97 (br q, 1H, NH, J=5.4 Hz). ^{13}C NMR (90.57 MHz, DMSO-d_6): 17.04 (CH_3), 30.53 (NCH_3), 55.07, 56.24 (2×OCH_3), 115.18, 115.27, 125.88, 127.82 (4×CH_{Ar}), 128.21, 135.38, 140.23 (3×C_q), 140.82 (CH), 146.50, 157.18, 160.75, 163.71 (4×C_q). Anal. Calcd for $C_{20}H_{22}F_4N_5O_2B$ (451.23): C, 53.24; H, 4.91; N, 15.52. Found: C, 53.41; H, 4.96; N, 15.27.

5.2.8. 1-(4-Methoxyphenyl)-4-methylamino-5-(4-methoxyphenyldiazenyl)-6-methylpyridazinium hexafluorophosphate (17). This compound was obtained as orange solid after recrystallization from ethanol. Yield 26%; mp 217–221 °C. ^{1}H NMR (360.14 MHz, DMSO-d_6): 2.84 (s, 3H, CH_3), 3.43 (d, 3H, NCH_3, J=5.4 Hz), 3.93 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.23–7.25 (m, 2H, AA′), 7.26–7.29 (m, 2H, AA′), 7.67–7.70 (m, 2H, XX′), 8.21–8.23 (m, 2H, XX′), 9.22 (s, 1H, =CH), 10.97 (br q, 1H, NH, J=5.4 Hz). ^{13}C NMR (90.57 MHz, DMSO-d_6): 16.94 (CH_3), 30.44 (NCH_3), 55.82, 56.02 (2×OCH_3), 115.03, 125.65, 127.55 (3×CH_{Ar}), 128.07 (C_q), 135.18 (CH_{Ar}), 139.79, 139.95 (2×C_q), 140.78 (CH), 146.30, 156.99, 160.48, 163.54 (4×C_q). Anal. Calcd for $C_{20}H_{22}F_6N_5O_2P$ (509.39): C, 47.16; H, 4.35; N, 13.75. Found: C, 47.17; H, 4.43; N, 13.98.

5.2.9. 1-Phenyl-4-methylamino-5-phenyldiazenyl-6-methylpyridazinium tetrafluoroborate (18). This compound was obtained as orange solid after recrystallization from ethanol. Yield 3%; mp 220.5–224 °C. ^{1}H NMR (360.14 MHz, DMSO-d_6): 2.86 (s, 3H, CH_3), 3.43 (d, 3H, NCH_3, J=5.5 Hz), 7.68–7.70 (m, 3H, CH_{Ar}), 7.76–7.77 (m, 5H, CH_{Ar}), 8.17–8.20 (m, 2H, CH_{Ar}), 9.24 (s, 1H, CH), 11.08 (br q, 1H, NH, J=5.4 Hz). ^{13}C NMR (90.57 MHz, DMSO-d_6): 17.16 (CH_3), 30.75 (NCH_3), 123.53, 126.48 (2×CH), 128.09 (C_q), 130.04, 130.42, 131.13, 133.36 (4×CH), 140.23, 142.40, 152.16, 157.93 (4×C_q). Anal. Calcd for $C_{18}H_{18}F_4N_5BF_4$ (391.18): C, 55.27; H, 4.64; N, 17.90. Found: C, 55.24; H, 4.53; N, 17.92.

5.2.10. 1-Phenyl-4-methylamino-5-phenyldiazenyl-6-methylpyridazinium hexafluorophosphate (19). This compound was obtained as orange solid and were not recrystallized. Yield 54%; mp 210–214.5 °C. ^{1}H NMR (360.14 MHz, DMSO-d_6): 2.86 (s, 3H, CH_3), 3.45 (d, 3H, NCH_3, J=5.5 Hz), 7.67–7.71 (m, 3H, CH_{Ar}), 7.74–7.78 (m, 5H, CH_{Ar}), 8.18–8.21 (m, 2H, CH_{Ar}), 9.26 (s, 1H,

=CH), 11.09 (br q, 1H, NH, $J=5.4$ Hz). ^{13}C NMR (90.57 MHz, DMSO-d_6): 17.04 (CH_3), 30.67 (NCH_3), 123.44, 126.36 ($2\times CH_{Ar}$), 127.98 (C_q), 129.90, 130.32, 131.01, 133.24 ($4\times CH_{Ar}$), 140.12 (C_q), 141.55 (CH), 142.31, 152.06, 157.79 ($3\times C_q$). Anal. Calcd for $C_{18}H_{18}F_6N_5P$ (449.34): C, 48.12; H, 4.04; N, 15.59. Found: C, 48.33; H, 4.26; N, 15.81.

5.2.11. 1-(4-Methoxyphenyl)-4-(2,4-dimethoxyphenylamino)-5-(4-methoxyphenyldiazenyl)-6-methylpyridazinium hexafluorophosphate (20). This compound was obtained as dark red solid after column chromatography (silica/chloroform/ethylacetate 4:1) and recrystallization from ethanol. Yield 37%; mp 126–131 °C. ^{1}H NMR (360.14 MHz, $CDCl_3$): 2.89 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.90 (s, 6H, $2\times OCH_3$), 6.56–6.59 (m, 2H, CH_{Ar}), 7.00–7.06 (m, 4H, $2\times AA'$), 7.46–7.50 (m, 3H, $XX'+CH_{Ar}$), 7.84–7.86 (m, 2H, XX'), 8.59 (s, 1H, =CH), 12.75 (br s, 1H, NH). ^{13}C NMR (90.57 MHz, $CDCl_3$): 16.71 (CH_3), 55.51, 55.57, 55.69, 55.91 ($4\times OCH_3$), 99.30, 105.21, 114.80, 114.84 ($4\times CH_{Ar}$), 115.48 (C_q), 125.49, 125.61, 126.97 ($3\times CH_{Ar}$), 128.71, 134.70, 137.94 ($3\times C_q$), 140.29 (CH), 145.76, 153.89, 157.85, 160.73, 160.96, 164.00 ($6\times C_q$). Anal. Calcd for $C_{27}H_{28}F_6N_5O_4P$ (631.51): C, 51.35; H, 4.47; N, 11.09. Found: C, 51.51; H, 4.19; N, 10.97.

5.2.12. 1-(4-Methylphenyl)-4-(4-methylphenylamino)-5-(4-methylphenyldiazenyl)-6-methylpyridazinium hexafluorophosphate (21). This compound was obtained as orange solid after recrystallization from ethanol. Yield 34%; mp 223–227 °C. ^{1}H NMR (360.14 MHz, $CDCl_3$): 2.35 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.86 (s, 3H, NCH_3), 7.20–7.31 (m, 8H, CH_{Ar}), 7.39–7.42 (m, 2H, XX'), 7.69–7.72 (m, 2H, XX'), 8.51 (s, 1H, CH), 12.78 (br s, 1H, NH). ^{13}C NMR (90.57 MHz, $CDCl_3$): 16.70, 20.96, 21.05, 21.51 ($4\times CH_3$), 123.23, 125.10, 125.44 ($3\times CH_{Ar}$), 128.31 (C_q), 130.07, 130.35, 130.82 ($3\times CH$), 130.83, 138.93, 139.23, 139.52 ($4\times C_q$), 140.30 (CH), 140.90, 144.41, 149.64, 158.72 ($4\times C_q$). Anal. Calcd for $C_{26}H_{26}F_6N_5P$ (553.49): C, 56.42; H, 4.73; N, 12.65. Found: C, 56.60; H, 4.82; N, 12.62.

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