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Azophosphonium Dyes

SPECIAL ISSUE

Facile Synthesis of Tuneable Azophosphonium Salts

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Dedicated to Koop Lammertsma and Edgar Niecke on the occasion of their 70th and 80th birthdays, respectively

Abstract: Azophosphonium salts have a facile synthesis and can be readily tuned at the *para* position of the aryl group and at the phosphorus position with the use of bulky phosphines, leading to a range of coloured compounds. A relation between the Hammett σ^{+}_{para} constant and the colour and ^{31}P NMR chemical shift was explored. The compounds were characterised by NMR spectroscopy, UV/Vis spectroscopy and single-crystal X-ray structure crystallography.

Introduction

Aryldiazonium salts $[ArN_2][X]$ are potent nitrogen-based Lewis acids that react as electrophiles in a plethora of transformations, of which the formation of azo dyes is one of the key applications.[1] For example, the commercially available Basic Red 51 (**A**, Figure 1) that is used for the dying of synthetic and natural fibres[2] is produced by the coupling of the corresponding diazonium salt with an imidazole, followed by alkylation.[3] Alternatively, N-coordination of diazonium salts to Lewis basic N-heterocyclic carbenes (NHCs) directly affords the strongly coloured azoimidazolium salts $[RN_2(NHC)][X]$, such as **B**.[4,5]

While the cationic NHC–diazonium Lewis adducts are of industrial relevance, the corresponding phosphine derivatives have received little attention. In 1953, Horner and Stöhr described the red azophosphonium chlorides **C** [R = H, Me, Cl, NO_2, CO_2H, OMe, OC(O)Me], with PPh_3 as the Lewis base, as unstable species.[6] Four decades later, Wokaun and co-workers observed a red colour upon addition of tris(dimethylamino)-phosphine to aromatic diazonium tetrafluoroborate salts and characterised the formed adducts (**D**) spectroscopically [R′ = $N(Me)_2$, R = *p*-Cl, *o*-Cl, *o*-CH_3 + *p*-Cl, *p*-C(O)OEt, *p*-SO_2NH_2, *p*-CN].[7] Subsequently, Flower and co-workers reported the $^{31}P\{^1H\}$ NMR chemical shift of **E** ($\delta^{31}P\{^1H\}$ = 40; R = 6-naphthalen-2-ol).[8] Very recently, the investigation of azophosphonium salts has picked up interest. Stephan and co-workers reported on the synthesis of **D** (R′ = Mes, *t*Bu, R = *p*-Cl) exhibiting red and purple colours, respectively.[9] Subsequent reduction of these compounds leads to the reversible formation of stable nitrogen-based radicals. Concurrently, we described the synthesis of the azophosphonium salts **D** [R′ = *t*Bu, *p*-R = NO_2, Br, H, OCH_3, $N(CH_3)_2$], displaying colours ranging from purple to red/brown.[10]

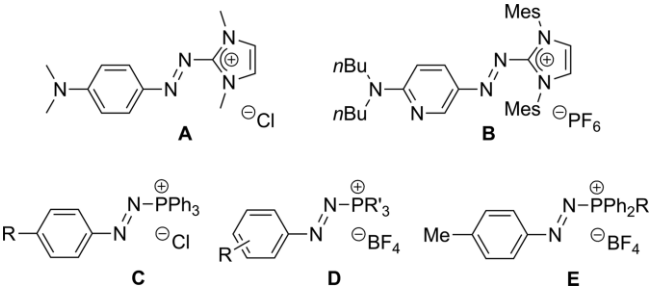

Figure 1. Reported azoimidazolium salts (**A**, **B**) and azophosphonium salts (**C**, **D**, **E**).

Herein, we extend these findings and target the synthesis of an array of azophosphonium salts by treatment of *para* substituted aryldiazonium salts with the sterically encumbered phosphines tBu_3P and Mes_3P. In addition, we sought to rationalise the effect of the aryl substituent on the physical properties of the products, including colour and ^{31}P NMR chemical shift. The Hammett σ_{para} value expresses the electron-donating or withdrawing ability of the *para* substituent on the aryl group. However, this parameter does not correlate well in systems where the substituent is conjugated with the reactive site (Figure 2), and the σ^{+}_{para} constant has been used previously to account for the resonance stabilisation of a positive charge.[11] We demonstrate that the σ^{+}_{para} constant correlates well with the colour and spectroscopic properties of a range of azophosphonium salts. This allows facile access to tuneable systems that can be used as dyes or precursors to stable nitrogen-based radicals.[9]

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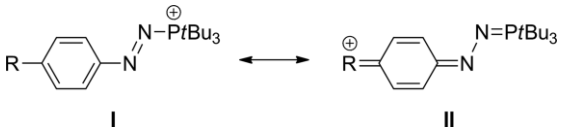
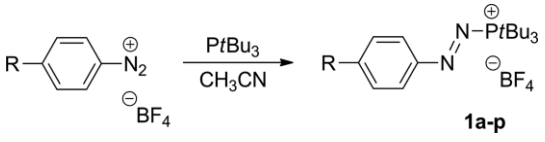


Figure 2. Resonance structures **I** and **II** of azophosphonium cations.

Results and Discussion

To explore the substituent effect on the ^{31}P NMR chemical shift as well as the colour of this novel class of azo dyes, we expanded the scope of the *para* substituted arylazophosphonium salts [(*p*-R-C_6H_4)N_2($PtBu_3$)][BF_4] **1** (Scheme 1).[10] Reaction of 16 *p*-substituted benzenediazonium salts with tri-*tert*-butylphosphine (1.1 equiv) in acetonitrile afforded many shades of intensely coloured phosphine–diazonium adducts [(*p*-R-C_6H_4)-N_2($PtBu_3$)][BF_4] **1a**–**p**, ranging from purple, to pink, red, and red/brown (Figure 3), which were isolated in moderate to good yields (55–97 %, Scheme 1, Table 1). Note that the purity of the diazonium salts used was crucial, as without prior recrystallisation we observed the formation of [tBu_3PH][BF_4], which results from protonation of the phosphine by remaining HBF_4 that was used in the synthesis of the diazonium salt.



Scheme 1. Synthesis of arylazophosphonium tetrafluoroborates **1**, R = NO_2 (**a**), CN (**b**), CF_3 (**c**), Br (**d**), Cl (**e**), H (**f**), F (**g**), C_6H_5 (**h**), $OC(O)CH_3$ (**i**), $C(CH_3)_3$ (**j**), CH_3 (**k**), OC_6H_5 (**l**), OCH_3 (**m**), $OCH(CH_3)_2$ (**n**), NH_2 (**o**), $N(CH_3)_2$ (**p**).

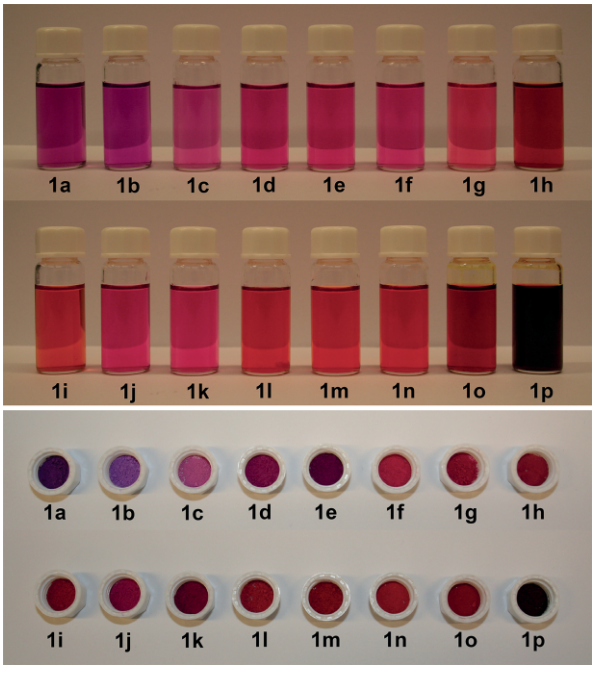


Figure 3. Colours of azophosphonium salts **1a**–**p** in solution (0.006 M in CH_3CN) and in the solid state.

Intriguingly, the electron-donating and withdrawing ability of the *para* substituent can be found in the computed bond lengths (Table 1) and follows the trend of the σ^+_{para} parameter. A greater contribution from resonance structure **II** (Figure 2) can be observed for the more electron-donating substituents as the N–N bond length elongates (N–N: **1a** 1.243, **1p** 1.268 Å) and shortening of the P–N and N–C bonds occurs (P–N: **1a** 1.742, **1p** 1.710 Å; N–C: **1a** 1.417, **1p** 1.371 Å; see Table S3 for further data). The same effect is also manifested in the greater alternation of C–C bond lengths (between long and short bonds) in the aryl ring. These data indicate a significant contribution from resonance form **II** for electron-donating *para* substituents.[14]

Table 1. σ^+ values for the *para*substituents, isolated yields, N–N distances and $^{31}P\{^1H\}$ chemical shifts for azophosphonium salts **1a**–**p**.

	p-R	σ^+_{para} value[a]	Yield [%]	N–N distance [Å][b]	$^{31}P\{^1H\}$ [ppm]
1a[c]	NO_2	0.79	94	1.243	73.5
1b	CN	0.66	96	1.244	73.0
1c	CF_3	0.61	56	1.244	72.2
1d[c]	Br	0.15	96	1.248	70.3
1e	Cl	0.11	83	1.249	70.1
1f[c]	H	0.00	95	1.248	69.4
1g	F	–0.07	71	1.249	69.4
1h	C_6H_5	–0.18	61	1.252	68.6
1i	$OC(O)CH_3$	–0.19	94	1.250	69.4
1j	$C(CH_3)_3$	–0.26	86	1.251	68.1
1k	CH_3	–0.31	82	1.251	68.0
1l	OC_6H_5	–0.50	55	1.257	67.9
1m[c]	OCH_3	–0.78	92	1.257	65.9
1n	$OCH(CH_3)_2$	–0.85	68	1.259	65.4
1o	NH_2	–1.30	97	1.264	59.4
1p[c]	$N(CH_3)_2$	–1.70	96	1.268	59.5

[a] See ref.[11] [b] Calculations performed at the ωB97X-D/6-311+G(d,p) level of theory. [c] See ref.[10]

UV/Vis spectroscopy for compounds **1a**–**p**, measured in CH_3CN, displays an intense absorption maximum ranging from λ_{max} = 300–464 nm corresponding to the $\pi\rightarrow\pi^*$ transition (Figure 4).[10] In general, a bathochromic shift can be observed for the position of the absorption going from electron-withdrawing (**1a**) to electron-donating (**1q**). A shift in the λ_{max} is observed for *para* substituent Ph (**1h**), OR (**1l**, **1m**, **1n**) and NR_2 (**1o**, **1p**) due to the mesomeric effect (+M) as the lone pair (or π-system) can be donated into the ring. This is strongest for the most electron-donating group, NR_2, resulting in the highest shift in λ_{max} (**1o** 435 nm, **1p** 464 nm). Compounds **1a**–**p** also show a weak absorption in the visible region from λ_{max} = 527–497 nm ($n\rightarrow\pi^*$).[14] Here the overall trend is a gradual hypsochromic shift from electron-withdrawing to the electron-donating *para* substituent in **1a**–**p** (Table 1). This is reflected in the colours of the compounds in solution, as various shades of purple, pink, red and lastly red/brown are seen (**1a** to **1p**, Figure 3), yet some outliers in the series can be observed (e.g. **1j** and **1k**). For **1h** and **1i** the mesomeric effect plays a crucial role, whereas this is not possible in the case of **1j** and **1k**.

The azophosphonium salts **1a**–**p** are ordered according to the Hammett σ^+_{para} values of their *para* substituent to highlight the substituent effect (Table 1). In our set of 16 tri-*tert*-butylphosphine–diazonium adducts, the σ^+_{para} constant ranges from 0.79 (**1a**) for the electron-withdrawing NO_2 group to –1.70 (**1p**)

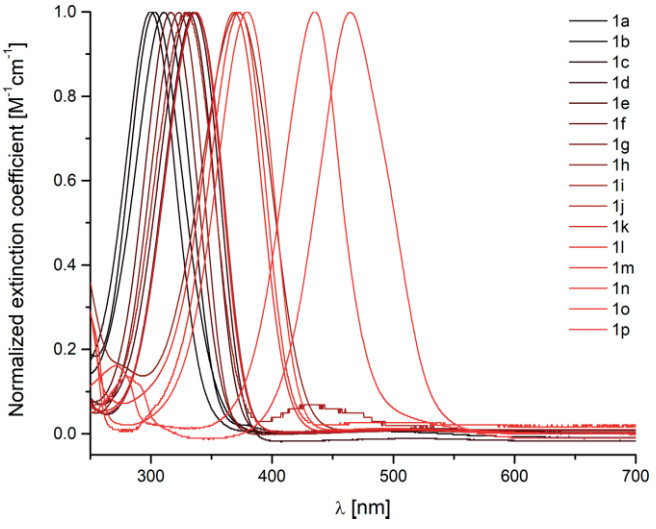


Figure 4. UV/Vis spectra of azophosphonium salts **1a**–**p**.

for the electron-donating $N(CH_3)_2$ substituent (Table 1).[11] Likewise, the $^{31}P\{^1H\}$ chemical shift ranges from 73.5 ppm (**1a**) to 59.5 ppm (**1p**), where the phosphorus resonance shifts upfield as the substituent becomes more electron-donating and thereby stabilises the positively charged phosphorus moiety to a greater extent via resonance. The Hammett plot of the σ^+_{para} value against the $^{31}P\{^1H\}$ NMR chemical shift of **1** shows a linear correlation (R^2 = 0.953; Figure 5), with only R = NH_2 (**1o**) as an outlier. This is likely due to the interaction of the coordinating solvent acetonitrile with the acidic protons on the NH_2 group, which stabilises resonance structure **II** (from Figure 2) to a greater extent and leads to a more upfield ^{31}P NMR resonance. As expected, comparing the $^{31}P\{^1H\}$ NMR chemical shifts with the non-corrected σ_{para} constant results in a poorer fitted linear correlation (R^2 = 0.882; see supporting information) with multiple outliers, highlighting the suitability of the σ^+_{para} parameters for these systems.

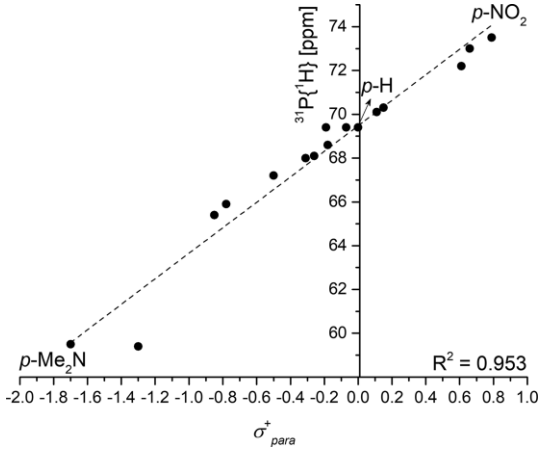


Figure 5. Hammett plot of the σ^+_{para} constants against the $^{31}P\{^1H\}$ chemical shift of azophosphonium salts **1a**–**p**.

To gain more insight into the dependence of the *para* substituent on the n→π* and π→π* excitations, we resorted to ωB97X-D/6-311+G(d,p) calculations. While the energy levels of n (HOMO) and π* (LUMO) decreases from **1a** (n: –12.6, π*: –4.9 eV; Table 2) to **1p** (n: –11.5, π*: –3.8 eV), the n→π* excitation gap remains the same (≈ 7.8 eV). For the π (HOMO-1) to π* (LUMO) excitation overall a slight decrease is observed (**1a**, n: –12.8, π*: –4.9 eV; **1p**, n: –10.3, π*: –3.8 eV), yet the π→π* excitation gap differs for all cases [from **1c**: 8.0 (biggest) to **1p**: 6.5 (smallest) eV], still, here too overall a decrease is observed from **1a** to **1p** (–7.9 to –6.5 eV, respectively). The energies obtained from the calculations are not accurate enough to correlate these to UV/Vis absorption bands,[12] for which time-dependent DFT calculations are required (see SI).[10]

Table 2. Optical properties and energies of the frontier orbitals for azophosphonium salts **1a**–**p**.

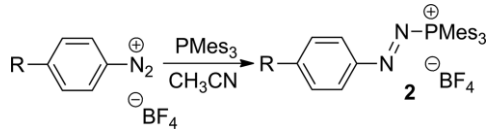
	λ_{abs} [nm][a] (log ξ_{max})	λ_{abs} [nm][b] (log ξ_{max})	HOMO-1 [eV]	HOMO [eV]	LUMO [eV]
1a[c]	303 (4.29)	523 (2.26)[d]	–12.8	–12.6	–4.9
1b	310 (4.15)	527 (3.10)	–12.4	–12.5	–4.8
1c	300 (4.12)	522 (3.02)	–12.6	–12.4	–4.6
1d[c]	336 (4.33)	517 (2.18)	–11.6	–12.2	–4.4
1e	331 (4.32)	516 (3.16)	–11.8	–12.2	–4.4
1f[c]	316 (4.21)	515 (2.16)	–12.2	–12.1	–4.3
1g	323 (4.22)	510 (3.10)	–12.1	–12.2	–4.4
1h	372 (4.38)	507 (3.46)	–10.8	–12.0	–4.2
1i	329 (3.59)	520 (3.19)	–11.7	–12.1	–4.2
1j	337 (4.35)	513 (3.23)	–11.6	–12.0	–4.1
1k	337 (4.31)	513 (3.19)	–11.8	–12.0	–4.2
1l	368 (4.43)	504 (3.42)	–11.1	–11.8	–4.0
1m[c]	373 (4.44)	500 (2.49)	–11.2	–11.9	–4.0
1n	379 (4.47)	497 (3.55)	–11.0	–11.8	–4.0
1o	435 (4.69)	–[e]	–10.7	–11.7	–3.9
1p[c]	464 (4.62)	–[e]	–10.3	–11.5	–3.8

[a] π→π* transition. [b] n→π* transition. [c] See ref.[10] [d] Data recorded after 1 day. For more information, see ref.[10] [e] n→π* transition not visible.

IR spectroscopy can also be used to probe the different resonance structures, as the N–N vibrations will be influenced by the different *para*-R groups. However, distinguishing experimentally between the vibrations proved to be difficult, therefore we resorted again to calculations at the ωB97X-D/6-311+G(d,p) level of theory. These calculations revealed an N_2 vibration that is coupled to the adjacent phenyl group due to the conjugated π-system.[14] A decrease in N–N stretching frequency is observed going from **1a** (1605 cm^{-1}) to **1q** (1538 cm^{-1}), owing to the weakening of the N=N double bond by the electron-donating groups.

We next investigated the influence of the substituents on phosphorus by using another bulky tertiary phosphine, namely trimesitylphosphine. For this we chose five different *para* substituents ranging from the most electron-donating to the most electron-withdrawing, namely NO_2, Br, H, OCH_3 and $N(CH_3)_2$. The reaction of *p*-substituted benzenediazonium tetrafluoroborate [(*p*-R-C_6H_4)N_2][BF_4] with $PMes_3$ (1.1 equiv) at 0 °C in acetonitrile resulted in coloured (from pale purple, to pale pink, to orange) arylazophosphonium salts [(*p*-R-C_6H_4)N_2($PMes_3$)][BF_4] **2a**,**d**,**f**,**m** in 79–98 % isolated yield (Scheme 2, Figure 6). However, treatment of *p*-dimethylaminobenzenediazonium tetrafluoroborate [{*p*-$(CH_3)_2$N-C_6H_4}N_2][BF_4] with $PMes_3$ in acetonitrile did not result in full conversion to the azophosphonium product **2p**. Yet, full conversion could be achieved by employing dichloromethane (DCM) as the solvent, in addition to a

small amount of $[HPMes_3][BF_4]$ impurity detectable in the ^{31}P NMR spectrum. The electron-donating $N(CH_3)_2$ group results in a less Lewis acidic diazonium salt, affording an equilibrium between bound $PMes_3$ and free $PMes_3$ in acetonitrile as here an interplay between solvated and thus stabilised diazonium salt vs. the donating ability of the phosphine is paramount. Stephan and co-workers previously demonstrated this lability for $[(p\text{-}ClC_6H_4)N_2(PMes_3)][BF_4]$, as the $PMes_3$ could be replaced by the addition of the stronger Lewis base $PtBu_3$.[9] Here too, for the most electron-donating *para* substituent more contribution of the resonance form **II** (Figure 2) is observed which can be seen in, among others, the N–N bond lengths as it elongates going from **2a** to **2p** (N–N: **2a** 1.233, **2p** 1.252 Å, see supporting information). DFT calculations at the ωB97X-D/6-311+G(d,p) level of theory concur with the less donating ability of $PMes_3$ (HOMO: $PMes_3$ –7.13 eV, $PtBu_3$ –7.69 eV). Likewise, the addition of $PMes_3$ leads to a slightly less thermodynamically stable product compared to the tri-*tert*-butylphosphine arylazophosphonium salt [**2f** ΔE = –48.2 kcal mol^{-1}, **1f** ΔE = –53.2 kcal mol^{-1} at the ωB97X-D/6-311+G(d,p) level of theory, respectively].



Scheme 2. Synthesis of arylazophosphonium tetrafluoroborates **2**, R = NO_2 (**a**), Br (**d**), H (**f**), MeO (**m**), Me_2N (**p**).

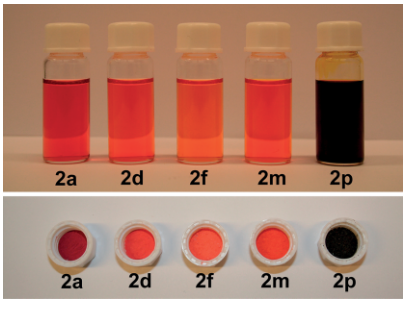


Figure 6. Colours of azophosphonium salts **2a**,**d**,**f**,**m**,**p** in solution (0.006 M in CH_3CN; **2p** in dry DCM) and in the solid state.

The colours of trimesitylphosphine–diazonium adducts **2** were quantified using UV/Vis spectroscopy and revealed an intense absorption maximum ranging from λ_{max} = 295–462 nm (π→π* transition), which displays a bathochromic shift from **2a** to **2p** (Table 3).[13] Here too, a weak absorption in the visible region is observed with λ_{max} = 472–500 nm (n→π* transition), which displays a hypsochromic shift from **2a** to **2p**. In addition, more intense absorption peaks (including shoulders) are observed which are attributed to absorptions related to the mesityl groups (Figure 7).[14] Comparing **1f** to **2f** reveals a hypsochromic shift for both absorptions (**1f**: π→π* λ_{abs} = 316, n→π* λ_{abs} = 512; **2f**: π→π* λ_{abs} = 304, n→π* λ_{abs} = 485 nm). This difference in colour in the arylazophosphonium salts is evidently also observed by eye, **1f** is pink whereas **2f** is pale pink (Figure 3, Figure 6).

Table 3. $^{31}P\{^1H\}$ NMR chemical shifts, optical properties and energies of the frontier orbitals for azophosphonium salts **2a**,**d**,**f**,**m**,**p**.

	$^{31}P\{^1H\}$ [ppm]	λ_{abs} [nm][a] (log ξ_{max})	λ_{abs} [nm][b] (log ξ_{max})	HOMO-1 [eV]	HOMO [eV]	LUMO [eV]
2a	46.9	295 (4.39)	500 (2.26)	–12.6	–12.2	–4.3
2d	45.2	332 (4.28)	488 (2.32)	–11.3	–12.0	–3.8
2f	44.7	304 (4.22)	485 (2.21)	–12.0	–11.9	–3.7
2m	42.7	312 (4.63)	472 (2.56)	–10.9	–11.8	–3.5
2p	39.9	462 (4.35)	–[c]	–9.9	–11.5	–3.3

[a] π→π* transition. [b] n→π* transition. [c] n→π* transition not visible.

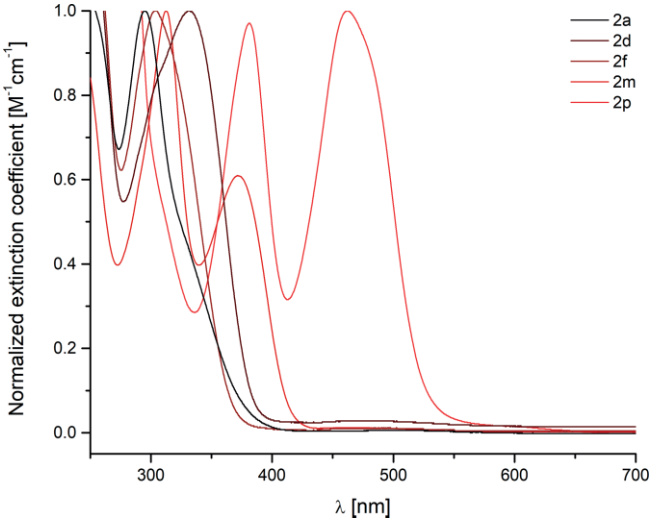


Figure 7. UV/Vis spectra of azophosphonium salts. **2a**,**d**,**f**,**m** (0.006M in CH_3CN; **2p** in dry DCM).

We resorted again to DFT calculations at the ωB97X-D/6-311+G(d,p) level of theory and here the same trend as for **1a** to **1p** is observed. A decrease in the value of n (HOMO) to π* (LUMO) (**2a** n: –12.2, π*: –4.3 eV, **2p** n: –11.5, π*: –3.3 eV) with a similar excitation gap of around 8.2 kcal mol^{-1} is revealed. For the π→π* excitation (HOMO-1 to LUMO) the same holds, overall a decrease is observed from **2a** to **2p** (**2a** π: –12.6, π*: –4.3 eV, Δ –8.3; **2p** π: –9.9.3, π*: –3.8 eV, Δ –6.6) probing the effect of the *para* R-group on the molecular orbitals.

The molecular structures **2d**, **2f**, **2m** obtained by single-crystal X-ray structure determinations (Figure 8) show in all cases the *trans* arylazophosphonium moiety. The N–N bond lengths for **2d** (1.249(2) Å), **2f** (1.2437(17) Å) and Stephan's $[(p\text{-}ClC_6H_4)N_2(PMes_3)][BF_4]$ (1.244(2) Å) are within 3σ of each other and so are not significantly different.[9] Previously, we reported on the single-crystal X-ray structure of **1f** (with a different borate counterion, $[BPh_4]^-$),[10] which allows a comparison of bond metrics between azophosphonium salts with different substituents on the phosphorus centre ($PMes_3$ (**2f**) vs. $PtBu_3$ (**1f**)). The pertinent bond distances are statistically similar for both species: N–N [**2f** 1.2437(17), **1f** 1.245(6) Å], C–N [**2f** 1.4316(19), **1f** 1.437(7) Å] and P–N [**2f** 1.7545(12), **1f** 1.742(5) Å]. However, a change in planarity is found in the P1–N2–N1–C1 angle {**2f** –178.18(9)° vs. **1f** 173.4(7) [–167.3(11)° (second disorder component)]}.

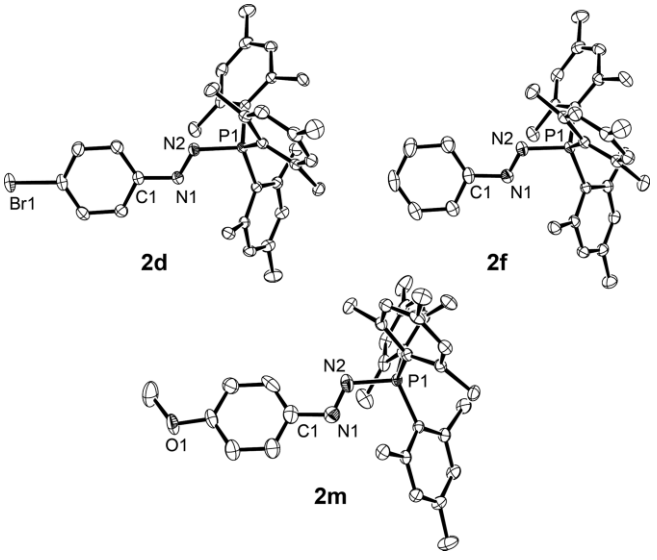


Figure 8. Molecular structures of **2d**,**f**,**m** [*p*-R-(C_6H_5)N_2($PMes_3$)][BF_4] (displacement ellipsoids are set at 30 % probability, hydrogen atoms, disordered solvent molecules and noncoordinating BF_4 anion are omitted for clarity). Selected bond length [Å] and torsion angles [°] for **2d**: P1–N2 1.7544(14), N2–N1 1.249(2), N1–C1 1.424(2); P1–N2–N1–C1 –176.60(11). **2f**: P1–N2 1.7545(12), N2–N1 1.2437(17), N1–C1 1.4316(19); P1–N2–N1–C1 –178.18(9). **2m**: P1–N2 1.736(2), N2–N1 1.214(3), N1–C1 1.432(3); P1–N2–N1–C1 –177.86(17).

Conclusions

The tuneability of the azophosphonium salts, on both the aryl ring and phosphine, has been extended, showing the ease and tolerance of this synthetic protocol. The physical properties of the arylazophosphonium salts [(*p*-R-C_6H_4)N_2(PR'_3)][BF_4] have been rationalised using the σ^+_{para} Hammett constant and probed using ^{31}P NMR spectroscopy, UV/Vis spectroscopy and density functional methods. We anticipate this chemistry is a versatile entry point for the design of highly tuneable diazo compounds that can find application as dyes or as one-electron acceptors for the synthesis of stabilised radicals.

Experimental Section

All manipulations regarding the preparation of air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 500 NEO or a Bruker AV300-II and internally referenced to the residual solvent resonances ($CDCl_3$: ^1H δ = 7.26 ppm, $^{13}C\{^1H\}$ δ = 77.16 ppm; CD_3CN: ^1H δ = 1.94 ppm, $^{13}C\{^1H\}$ δ = 1.32, 118.26 ppm; $(CD_3)_2SO$: ^1H δ = 2.50 ppm). $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 500 NEO and externally referenced (BF_3·OEt_2, 85 % H_3PO_4, respectively). ^{19}F NMR spectra were recorded on a Bruker AV300-II and externally referenced ($CFCl_3$). Chemical shifts are reported in ppm. Melting points were measured on samples in open capillaries on a Büchi M-565 melting point apparatus and are uncorrected. High resolution mass spectra were recorded on a Bruker MicroTOF with ESI nebuliser (ESI) or were recorded on an AccuTOF GC v 4g, JMS-T100GCV, Mass spectrometer (JEOL, Japan) with a FD Emitter, Carbotec GmbH (Germany), FD 13 µm. Current rate 51.2 mA/min over 1.2 min and typical measurement conditions are: counter electrode –10kV, Ion source 37 V. IR spectra of air-stable compounds were recorded in air on a Bruker Alpa-P. UV/Vis spectra were recorded on a UV-2600 Shimadzu spectrometer in a cell with a 2 mm path length. All reagents were purchased from commercial resources and used without further purification. To dissolve P*t*Bu_3 in acetonitrile, sometimes a bit of heat was applied. **1a**, **1d**, **1f**, **1m** and **1p** were prepared according to literature procedures.[10] All diazonium salts were stored under nitrogen at 4 °C or –20 °C.

Synthesis of *p*-Acetoxy Aniline: [*p*-CH_3(O)CO-$PhNH_2$] was prepared according to Manna et al.[15] *p*-Nitrophenyl acetate (200.7 mg, 1.108 mmol, 1.0 equiv) was dissolved in ethyl acetate (4 mL) and Pd/C (10 %, 5.8 mg, 0.005 mmol) was added. The mixture was stirred under an hydrogen atmosphere and the reaction progress was checked with TLC (petroleum ether/ethyl acetate = 3:1.1). After full conversion (47 h), the mixture was filtered, washed with ethyl acetate (2 × 1 mL) and the solvents evaporated to dryness to give [*p*-CH_3(O)CO-$PhNH_2$] as a brown oil in 98 % yield (164.0 mg, 1.085 mmol). ^1H NMR (300.1 MHz, $CDCl_3$, 295 K) δ = 6.86 (d, $^3J_{H,H}$ = 8.8 Hz, 2H; Ph*H*), 6.66 (d, $^3J_{H,H}$ = 8.7 Hz, 2H; Ph*H*), 3.63 (br. s, 2H; NH_2), 2.26 (s, 3H; CH_3(O)CO).

Aryldiazonium Salt Synthesis: Method A: To the *para* substituted aniline (2.0 mmol, 1.0 equiv) in water (1 mL) was added 50 wt.-% aq. HBF_4 (0.68 mL). The mixture was cooled in an ice bath and a solution of $NaNO_2$ (2.0 mmol, 1.0 equiv) in water (0.4 mmol) was added dropwise. The mixture was stirred for 45 min at 0 °C after which the precipitate was collected by filtration, washed with diethyl ether (4 × 20 mL) and dried in vacuo to afford the desired crude *para* substituted diazonium salt [*p*-R-PhN_2][BF_4].[16,17]

Aryldiazonium Salt Synthesis: Method B: To the *para* substituted aniline (2.0 mmol, 1.0 equiv) in ethanol (1 mL) was added 50 wt.-% aq. HBF_4 (4.0 mmol, 2.0 equiv). The mixture was cooled in an ice bath and *tert*-butyl nitrite (4.0 mmol, 2.0 equiv) was added dropwise. The mixture was stirred for 1 h at 0 °C after which the precipitate was collected by filtration, washed with diethyl ether (3 × 20 mL) and dried in vacuo to afford the desired crude *para* substituted diazonium salt [*p*-R-PhN_2][BF_4].[18] If no precipitate had formed diethyl ether was added resulting in the formation of solids.

Purification of the Aryldiazonium Salt: Method A: The crude product was dissolved in a minimal amount of acetonitrile, filtered if necessary, and recrystallised by addition of diethyl ether until no more precipitate formed, after which the solids were filtered, washed with diethyl ether (4 × 20 mL) and dried in vacuo to afford the *para* substituted diazonium salt [*p*-R-PhN_2][BF_4].

Purification of the Aryldiazonium Salt: Method B: The crude product was dissolved in a minimal amount of acetone, filtered if necessary, and recrystallised by addition of diethyl ether until no more precipitate formed, after which the solids were filtered, washed with diethyl ether (4 × 20 mL) and dried in vacuo to afford the *para* substituted diazonium salt [*p*-R-PhN_2][BF_4].

Synthesis of *p*-Cyanobenzenediazonium Tetrafluoroborate [*p*-NC-PhN_2][BF_4]:[16,17] [*p*-NC-PhN_2][BF_4] was synthesised using method A starting with 4-aminobenzonitrile (237.3 mg, 2.0 mmol, 1.0 equiv), which afforded the crude product as a white powder in 64 % (279.2 mg, 1.287 mmol). Purification by method A afforded [*p*-NC-PhN_2][BF_4] as a white powder in 45 % yield (194.0 mg, 0.894 mmol). ^1H NMR (300.0 MHz, $(CD_3)_2SO$, 299 K): δ = 8.84 (d, $^3J_{H,H}$ = 8.4 Hz, 2H; Ph*H*), 8.46 (d, $^3J_{H,H}$ = 8.5 Hz, 2H; Ph*H*).

Synthesis of *p*-Trifluorobenzenediazonium Tetrafluoroborate [*p*-F_3C-PhN_2][BF_4]:[17,18] [*p*-F_3C-PhN_2][BF_4] was synthesised using method A starting with 4-(trifluoromethyl)aniline (0.25 mL, 2.0 mmol, 1.0 equiv), which afforded the crude product as a yellow

powder in 53 % (273.9 mg, 1.053 mmol). Purification by method A afforded [*p*-CF_3-PhN_2][BF_4] as a white powder in 34 % yield (176.0 mg, 0.677 mmol). ^{1}H NMR (300.0 MHz, CD_3CN, 293 K): δ = 8.69 (d, $^3J_{H,H}$ = 8.5 Hz, 2H; Ph*H*), 8.23 (d, $^3J_{H,H}$ = 8.5 Hz, 2H; Ph*H*).

Synthesis of *p*-Chlorobenzenediazonium Tetrafluoroborate [*p*-Cl-PhN_2][BF_4]:[16–18] [*p*-Cl-PhN_2][BF_4] was synthesised using method A starting with 4-chloroaniline (255.9 mg, 2.0 mmol, 1.0 equiv), which afforded the crude product as a white powder in 73 % (331.8 mg, 1.47 mmol). Purification by method A afforded [*p*-Cl-PhN_2][BF_4] as a white powder in 58 % yield (261.5 mg, 1.16 mmol). ^{1}H NMR (300.1 MHz, CD_3CN, 299 K): δ = 8.46 (d, $^3J_{H,H}$ = 8.8 Hz, 2H; Ph*H*), 7.94 (d, $^3J_{H,H}$ = 8.7 Hz, 2H; Ph*H*).

Synthesis of *p*-Fluorobenzenediazonium Tetrafluoroborate [*p*-F-PhN_2][BF_4]:[17,18] [*p*-F-PhN_2][BF_4] was synthesised using method A starting with 4-fluoroaniline (239.3 mg, 2.2 mmol, 1.0 equiv), which afforded the crude product as a white powder in 49 % (221.8 mg, 1.056 mmol). Purification by method A afforded [*p*-F-PhN_2][BF_4] as a white powder in 43 % yield (195.0 mg, 0.929 mmol). ^{1}H NMR (300.0 MHz, CD_3CN, 299 K): δ = 8.71–8.40 (m, 2H; Ph*H*), 7.69–7.55 (m, 2H; Ph*H*). Synthesis of *p*-phenylbenzenediazonium tetrafluoroborate [*p*-C_6H_5-PhN_2][BF_4].[18]

[*p*-Ph-PhN_2][BF_4] was synthesised using method B starting with 4-aminobiphenyl (370.8 mg, 2.2 mmol, 1.0 equiv), which afforded the crude product as a slightly brownish powder in 70 % (410.3 mg, 1.531 mmol). Purification by method B afforded [*p*-Ph-PhN_2][BF_4] as a pale red powder in 59 % yield (344.1 mg, 1.284 mmol). ^{1}H NMR (300.1 MHz, CD_3CN, 298 K) δ = 8.52 (d, $^3J_{H,H}$ = 8.5 Hz, 2H; N_2Ph*H*), 8.18 (d, $^3J_{H,H}$ = 8.6 Hz, 2H; N_2Ph*H*), 7.83 (m, 2H; Ph*H*), 7.60 (m, 3H; Ph*H* and *p*-Ph*H*).

Synthesis of *p*-Acetoxybenzenediazonium Tetrafluoroborate [*p*-CH_3(O)CO-PhN_2][BF_4]:[16] [*p*-CH_3(O)CO-PhN_2][BF_4] was synthesised using method A starting with *p*-aminophenyl acetate (160.5 mg, 1.022 mmol, 1.0 equiv), which afforded the crude product as a slightly purple powder in 55 % (146.3 mg, 0.585 mmol). Purification by method B afforded [*p*-CH_3(O)CO-PhN_2][BF_4] as a slightly yellow powder in 39 % yield (103.9 mg, 0.416 mmol). ^{1}H NMR (300.1 MHz, CD_3CN, 293 K) δ = 8.53 (d, $^3J_{H,H}$ = 9.2 Hz, 2H; Ph*H*), 7.69 (d, $^3J_{H,H}$ = 9.3 Hz, 2H; Ph*H*), 2.35 (s, 3H; CH_3(O)CO).

Synthesis of *p*-*tert*-Butylbenzenediazonium Tetrafluoroborate [*p*-$(CH_3)_3$C-PhN_2][BF_4]:[17,18] [*p*-$(CH_3)_3$-PhN_2][BF_4] was synthesised using method A starting with 4-*tert*-butylaniline (347.8 mg, 2.3 mmol, 1.0 equiv), which afforded the crude product as a white powder in 80 % (461.6 mg, 1.861 mmol). Purification by method B afforded [*p*-$(CH_3)_3$-PhN_2][BF_4] as a white powder in 63 % yield (361.8 mg, 1.459 mmol). ^{1}H NMR (300.1 MHz, CD_3CN, 294 K): δ = 8.39 (d, $^3J_{H,H}$ = 9.0 Hz, 2H; Ph*H*), 7.96 (d, $^3J_{H,H}$ = 9.1 Hz, 2H; Ph*H*), 1.38 (s, 9H; C(CH_3)$_3$).

Synthesis of *p*-Methylbenzenediazonium Tetrafluoroborate [*p*-CH_3-PhN_2][BF_4]:[17,18] [*p*-CH_3-PhN_2][BF_4] was synthesised using method A starting with *p*-toluidine (214.3 mg, 2.0 mmol, 1.0 equiv), which afforded the crude product as a white powder in 62 % (196.0 mg, 0.952 mmol). Purification by method B afforded [*p*-CH_3-PhN_2][BF_4] as a white powder in 47 % yield (196 mg, 0.952 mmol). ^{1}H NMR (300.1 MHz, CD_3CN, 294 K): δ = 8.35 (d, $^3J_{H,H}$ = 8.4 Hz, 2H; Ph*H*), 7.73 (d, $^3J_{H,H}$ = 8.4 Hz, 2H; Ph*H*), 2.61 (s, 3H; CH_3).

Synthesis of *p*-Phenoxybenzenediazonium Tetrafluoroborate [*p*-C_6H_5O-PhN_2][BF_4]:[18] [*p*-PhO-PhN_2][BF_4] was synthesised using method B starting with 4-phenoxyaniline (376.6 mg, 2.0 mmol, 1.0 equiv), which afforded the crude product as a purple powder in 100 % (578.3 mg, 2.036 mmol). Purification by method B afforded [*p*-PhO-PhN_2][BF_4] as a white powder in 82 % yield (473.4 mg, 1.667 mmol). ^{1}H NMR (300.1 MHz, CD_3CN, 295 K) δ = 8.41 (d, $^3J_{H,H}$ = 9.4 Hz, 2H; N_2Ph*H*), 7.56 (t, $^3J_{H,H}$ = 7.7 Hz, 2H; *m*-OPh*H*), 7.42 (t, $^3J_{H,H}$ = 7.5 Hz, 1H; *p*-OPh*H*), 7.28 (d, $^3J_{H,H}$ = 9.4 Hz, 2H; *o*-OPh*H*), 7.23 (d, $^3J_{H,H}$ = 7.4 Hz, 2H; N_2Ph*H*).

Synthesis of *p*-Isopropoxybenzenediazonium Tetrafluoroborate [*p*-$(CH_3)_2$HCO-PhN_2][BF_4]:[19] [*p*-*i*PrO-PhN_2][BF_4] was synthesised using method A starting with 4-isopropoxyaniline (0.35 mL, 2.4 mmol, 1.0 equiv), which afforded the crude product as a slightly purple powder in 93 % (555.9 mg, 2.224 mmol). During the synthesis an additional 1.5 mL of water was added to improve stirring. Purification by method B afforded [*p*-*i*PrO-PhN_2][BF_4] as a white powder in 86 % yield (518.0 mg, 2.072 mmol). ^{1}H NMR (300.1 MHz, CD_3CN, 293 K) δ = 8.36 (d, $^3J_{H,H}$ = 9.1 Hz, 2H; Ph*H*), 7.28 (d, $^3J_{H,H}$ = 9.1 Hz, 2H; Ph*H*), 4.94 (sept, $^3J_{H,H}$ = 6.0 Hz, 1H; $(CH_3)_2CH$), 1.40 (d, $^3J_{H,H}$ = 6.0 Hz, 6H; $(CH_3)_2$CH).

Synthesis of *p*-Aminobenzenediazonium Tetrafluoroborate [*p*-H_2N-PhN_2][BF_4]: [*p*-H_2N-PhN_2][BF_4] was prepared according to a modified literature procedure of Y. Yagci et al.[20] under inert conditions. 50 wt.-% HBF_4 (0.97 mL, 7.7 mmol, 1.1 equiv) was added to a solution of *p*-phenylenediamine (759.3 mg, 7.0 mmol, 1.0 equiv) in acetone (10 mL) at 0 °C and a colour change from light pink to green/yellow was observed. After 10 min, *tert*-butyl nitrite (0.97 mL, 8.4 mmol, 1.2 equiv) was added dropwise and the colour changed to brown. The reaction mixture was stirred for 15 min. after which diethyl ether (30 mL) was added and brown solids precipitated, which were filtered, washed with diethyl ether (6 × 20 mL) and dried in vacuo resulting in the isolation of a brown powder in 93 % yield (1353.8 mg, 6.542 mmol). Subsequently, the crude product was dissolved in a minimal amount of acetonitrile (10 mL), filtered and precipitated by the addition of diethyl ether (60 mL) after which the solids were filtered, washed with diethyl ether (6 × 20 mL) and dried in vacuo to give [*p*-H_2N-PhN_2][BF_4] as a brown powder in 85 % yield (1230.0 mg, 5.944 mmol). ^{1}H NMR (300.0 MHz, $(CD_3)_2SO$, 299 K): δ = 8.50–7.80 (m, 4H; Ph*H*), 6.82 (s, 2H; NH_2).

General Procedure for the Synthesis of the Arylazophosphonium Salts 1a to 1p: These reactions were performed in the dark using aluminium foil wrapping to protect the reaction mixture from exposure to sunlight. A solution of P*t*Bu_3 (0.440 mmol, 1.1 equiv) in acetonitrile (2 mL) was added dropwise to a solution of the corresponding *para* substituted diazonium tetrafluoroborate [*p*-R-PhN_2][BF_4] (0.400 mmol, 1.0 equiv) in acetonitrile (2 mL) at 0 °C. The solution was stirred for 5 min at 0 °C and then warmed to room temperature in 1 h after which all volatiles were removed in vacuo. The product was purified by addition of DCM (0.5 mL), subsequent addition of *n*-pentane (15 mL) and stirring for 10 min. resulted in the precipitation of solids. These solids were collected by filtration, washed with *n*-pentane (2 × 5 mL) and the solvents evaporated to dryness to afford the desired arylazophosphonium compound.

Note: the syntheses of **1a**, **1d**, **1f**, **1m** and **1p** are described in reference 10. To compare all $^{31}P\{^1H\}$ data the following compounds were measured on a 500 MHz NMR ($^{31}P\{^1H\}$: 202.6 MHz). **1a** $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 299 K): δ = 73.4 (s; no impurity observed). **1d** $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 299 K): δ = 72.9 (s; no impurity observed). **1f** $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 299 K): δ = 69.4 (s; no impurity observed). **1m** $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 299 K): δ = 65.9 (s; no impurity observed). **1p** $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 299 K): δ = 59.5 (s; product, 97 %), 50.3 (s; impurity [*t*Bu_3PH][BF_4], 3 %).

Synthesis of [*p*-NC-PhN_2(P*t*Bu_3)][BF_4] (1b): [*p*-NC-PhN_2(P*t*Bu_3)]-[BF_4] was synthesised from *p*-cyanobenzenediazonium tetrafluoroborate [*p*-NC-PhN_2][BF_4] (101 mg, 0.466 mmol, 1.0 equiv) and iso-

lated as a purple powder in 96 % yield (186.5 mg, 0.445 mmol). M.p. (open capillary): 121–129 °C (decomposition). ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K): δ = 8.14, 8.12, 7.96, 7.94 (AB-type, 4H; Ph*H*), 1.71 (d, $^3J_{H,P}$ = 14.9 Hz, 27H; C(*CH*$_3$)$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, $CDCl_3$, 298 K): δ = –1.0 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K): δ = 155.5 (d, $^3J_{C,P}$ = 39.5 Hz; *ipso*-Ph*C*-N$_2$), 134.2 (s; *o*-Ph*C*-N$_2$), 124.3 (s; *m*-Ph*C*-N$_2$), 119.1 (s; *C*N), 117.5 (s; *p*-Ph*C*-N$_2$), 42.7 (d, $^1J_{C,P}$ = 21.5 Hz; P*C*(CH$_3$)$_3$), 29.7 (s; PC(*CH*$_3$)$_3$). ^{19}F NMR (282.4 MHz, $CDCl_3$, 298 K): δ = –152.5 (s), –152.2 (s). ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 298 K): δ = 72.9 (s; product, 98 %), 51.8 (s; impurity [*t*Bu$_3$PH][BF$_4$], 2 %). HR-MS (ESI): calcd for $C_{19}H_{31}N_3P_1$ (M – BF_4) 332.2256, found 332.2249 [*p*-CN-PhN$_2$(P*t*Bu$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2985 (w), 2229 (w), 1467 (w), 1404 (w), 13778 (w), 1307 (w), 1288 (w), 1174 (w), 1147 (w), 1048 (s), 1027 (s), 933 (w), 865 (w), 848 (m), 802 (w), 791 (w), 716 (w), 644 (w), 628 (w), 554 (w), 519 (w), 494 (m), 439 (w).

Synthesis of [*p*-F$_3$C-PhN$_2$(P*t*Bu$_3$)][BF$_4$] (1c): [*p*-F$_3$C-PhN$_2$(P*t*Bu$_3$)][BF$_4$] was synthesised from *p*-(trifluoromethyl)benzenediazonium tetrafluoroborate [*p*-F$_3$C-PhN$_2$][BF$_4$] (81.4 mg, 0.313 mmol, 1.0 equiv) and isolated as a purple powder in 56 % yield (81.4 mg, 0.176 mmol). M.p. (open capillary): 109–119 °C (decomposition). ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K): δ = 8.13, 812, 7.92, 7.90 (AB-type, 4H; Ph*H*), 1.71 (d, $^3J_{H,P}$ = 14.8 Hz, 27H; C(*CH*$_3$)$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, $CDCl_3$, 299 K): δ = –1.0 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K): δ = 156.0 (d, $^3J_{C,P}$ = 39.5 Hz; *ipso*-Ph*C*-N$_2$), 137.1 (q, $^2J_{C,F}$ = 32.1 Hz; *p*-Ph*C*-N$_2$), 127.5 (s; *m*-Ph*C*- N$_2$), 124.1 (s; *o*-Ph*C*-N$_2$), 123.2 (q, $^1J_{C,F}$ = 273.4 Hz; *C*F$_3$), 42.7 (d, $^1J_{C,P}$ = 21.7 Hz; P*C*(CH$_3$)$_3$), 29.7 (s; PC(*CH*$_3$)$_3$). ^{19}F NMR (282.4 MHz, $CDCl_3$, 299 K): –63.2 (s; *CF*$_3$), –152.8 (s; B*F*$_4$), –152.9 (s; B*F*$_4$). ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 299 K): δ = 72.2 (s; product, 99 %), 51.6 (s; impurity [*t*Bu$_3$PH][BF$_4$], 1 %). HR-MS (ESI): calcd for $C_{19}H_{31}F_3N_2P_1$ (M – BF_4) 375.2177, found 375.2170 [*p*-CF$_3$-PhN$_2$(P*t*Bu$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2983 (w), 1612 (w), 1470 (w), 1403 (w), 1378 (w), 1320 (m), 1175 (m), 1154 (w), 1136 (m), 1047 (s), 1027 (s), 1008 (m), 931 (w), 854 (m), 798 (m), 737 (w), 650 (m), 624 (w), 595 (w), 519 (w), 485 (w), 419 (w).

Synthesis of [*p*-Cl-PhN$_2$(P*t*Bu$_3$)][BF$_4$] (1e): [*p*-Cl-PhN$_2$(P*t*Bu$_3$)][BF$_4$] was synthesised from *p*-chlorobenzenediazonium tetrafluoroborate [*p*-Cl-PhN$_2$][BF$_4$] (89.1 mg, 0.394 mmol, 1.0 equiv) and isolated as a dark pink powder in 83 % yield (140.8 mg, 0.328 mmol). M.p. (open capillary): 116–122 °C (decomposition). ^{1}H NMR (500.0 MHz, $CDCl_3$, 299 K): δ = 7.95, 7.93, 7.63, 7.62 (AB-type, 4H; Ph*H*), 1.69 (d, $^3J_{H,P}$ = 14.7 Hz, 27H; C(*CH*$_3$)$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, $CDCl_3$, 299 K): δ = –1.0 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 299 K): δ = 153.6 (d, $^3J_{C,P}$ = 39.8 Hz; *ipso*-Ph*C*-N$_2$), 144.6 (s; *p*-Ph*C*-N$_2$), 130.7 (s; *o*-Ph*C*-N$_2$), 125.1 (s; *m*-Ph*C*-N$_2$), 42.5 (d, $^1J_{C,P}$ = 22.9 Hz; P*C*(CH$_3$)$_3$), 29.7 (s; PC(*CH*$_3$)$_3$). ^{19}F NMR (282.4 MHz, $CDCl_3$, 298 K): δ = –152.9 (s), –153.0 (s). ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 299 K): δ = 70.1 (s; product, 98 %), 51.6 (s; impurity [*t*Bu$_3$PH][BF$_4$], 2 %). HR-MS (ESI): calcd for $C_{18}H_{31}Cl_1N_2P_1$ (M – BF_4) 341.1913, found 341.1906 [*p*-Cl-PhN$_2$(P*t*Bu$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2982 (w), 1573 (w), 1475 (m), 1448 (w), 1402 (w), 1376 (w), 1300 (w), 1283 (w), 1173 (w), 1149 (w), 1084 (m), 1048 (s), 1026 (s), 1007 (m), 932 (w), 862 (w), 838 (m), 800 (w), 786 (w), 680 (m), 631 (w), 518 (w), 494 (w), 482 (m), 441 (w), 424 (w).

Synthesis of [*p*-F-PhN$_2$(P*t*Bu$_3$)][BF$_4$] (1g): [*p*-F-PhN$_2$(P*t*Bu$_3$)][BF$_4$] was synthesised from *p*-fluorobenzenediazonium tetrafluoroborate [*p*-F-PhN$_2$][BF$_4$] (78.6 mg, 0.374 mmol, 1.0 equiv) and isolated as a dark pink powder in 71 % yield (109.1 mg, 0.265 mmol). M.p. (open capillary): 105–118 °C (decomposition). ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K): δ = 8.06 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,F}$ = 5.1 Hz, 2H; *o*-Ph*H*), 7.36 (t, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,F}$ = 8.3 Hz, 2H; *m*-Ph*H*), 1.72 (d, $^3J_{H,P}$ = 14.6 Hz; C(*CH*$_3$)$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, $CDCl_3$, 298 K): δ = –1.0 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K): δ = 168.3 (d, $^1J_{C,F}$ = 263.1 Hz; *p*-Ph*C*-N$_2$), 152.3 (d, $^3J_{C,P}$ = 39.8 Hz; *ipso*-Ph*C*-N$_2$), 126.9 (d, $^3J_{C,F}$ = 10.5 Hz; *o*-Ph*C*-N$_2$), 117.7 (d, $^2J_{C,F}$ = 23.4 Hz; *m*-Ph*C*-N$_2$), 42.5 (d, $^1J_{C,P}$ = 23.2 Hz; P*C*(CH$_3$)$_3$), 29.7 (s; PC(*CH*$_3$)$_3$). ^{19}F NMR (282.4 MHz, $CDCl_3$, 293 K): δ = 69.4 (s; *p*-*F*-Ph), –153.1 (s; B*F*$_4$), –153.2 (s; B*F*$_4$). ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 298 K): δ = 69.4 (s; product, 99 %), 51.6 (s; impurity [*t*Bu$_3$PH][BF$_4$], 1 %). HR-MS (ESI): calcd for $C_{18}H_{31}F_1N_2P_1$ (M – BF_4) 325.2209, found 325.2198 [*p*-F-PhN$_2$(P*t*Bu$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2982 (w), 1590 (w), 1487 (w), 1450 (w), 1414 (w), 1402 (w), 1380 (w), 1319 (w), 1283 (w), 1233 (m), 1175 (w), 1138 (m), 1045 (s), 1025 (s), 999 (m), 930 (w), 877 (w), 854 (m), 816 (w), 800 (w), 757 (m), 635 (w), 585 (w), 519 (w), 486 (w), 459 (w), 420 (w).

Synthesis of [*p*-C$_6$H$_5$-PhN$_2$(P*t*Bu$_3$)][BF$_4$] (1h): [*p*-Ph-PhN$_2$(P*t*Bu$_3$)][BF$_4$] was synthesised from *p*-phenylbenzenediazonium tetrafluoroborate [*p*-Ph-PhN$_2$][BF$_4$] (66.1 mg, 0.247 mmol, 1.0 equiv) and isolated as a red powder in 61 % yield (71.0 mg, 0.151 mmol). M.p. (open capillary): 119–123 °C (decomposition). ^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K) δ = 8.05, 8.03, 7.90, 7.88 (AB-type, 4H; Ph*H*-N$_2$), 7.69 (d, $^3J_{H,H}$ = 7.1 Hz, 2H; *o*-Ph*H*), 7.51 (t, $^3J_{H,H}$ = 7.3 Hz, 2H; *m*-Ph*H*), 7.48–7.41 (m, 1H; *p*-Ph*H*), 1.74 (d, $^3J_{H,P}$ = 14.4 Hz, 27H; PC(*CH*$_3$)$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, $CDCl_3$, 298 K) δ = –0.9 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K) δ = 154.6 (d, $^3J_{C,P}$ = 39.8 Hz; *ipso*-Ph*C*-N$_2$), 150.3 (s; *ipso*-Ph*C*), 138.7 (s; *p*-Ph*C*-N$_2$), 129.6 (s; *p*-Ph*C*), 129.4 (s; *m*-Ph*C*), 128.8 (s; *o*-Ph*C*-N$_2$), 127.6 (s; *o*-Ph*C*), 124.7 (s; *m*-Ph*C*-N$_2$), 42.6 (d, $^1J_{C,P}$ = 23.4 Hz; P*C*(CH$_3$)$_3$), 29.8 (s; PC(*CH*$_3$)$_3$). ^{19}F NMR (282.4 MHz, $CDCl_3$, 299 K) δ = –153.2 (s), –153.2 (s). ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 298 K) δ = 68.6 (s; product, 98 %), 51.0 (s; impurity [*t*Bu$_3$PH][BF$_4$], 2 %). HR-MS (ESI): calcd for $C_{24}H_{36}N_2P$ (M – BF_4) 383.2616, found 383.2632 [*p*-Ph-PhN$_2$(P*t*Bu$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2984 (w), 1597 (w), 1479 (m), 1436 (m), 1401 (m), 1376 (w), 1309 (w), 1284 (w), 1204 (w), 1175 (w), 1150 (m), 1048 (s), 1026 (s), 1005 (s), 931 (w), 872 (m), 852 (m), 790 (m), 773 (s), 731 (w), 704 (m), 632 (m), 616 (m), 555 (w), 519 (w), 491 (m), 488 (w), 433 (w).

Synthesis of [*p*-CH$_3$(O)CO-PhN$_2$(P*t*Bu$_3$)][BF$_4$] (1i): [*p*-CH$_3$(O)CO-PhN$_2$(P*t*Bu$_3$)][BF$_4$] was synthesised from *p*-acetoxybenzenediazonium tetrafluoroborate [*p*-CH$_3$(O)CO-PhN$_2$][BF$_4$] (86.6 mg, 0.346 mmol, 1.0 equiv) and isolated as a red powder in 94 % yield (147.1 mg, 0.325 mmol). M.p. (open capillary): 102–104 °C (decomposition). ^{1}H NMR (500.0 MHz, $CDCl_3$, 301 K) δ = 8.03, 8.01, 7.44, 7.43 (AB-type, 4H; Ph*H*), 2.37 (s, 3H; *CH*$_3$C(O)O), 1.72 (d, $^3J_{C,P}$ = 14.5 Hz, 27H; PC(*CH*$_3$)$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, $CDCl_3$, 297 K) δ = –0.9 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 297 K) δ = 168.6 (s; CH$_3$(O)*C*O), 157.8 (s; *p*-Ph*C*-N$_2$), 153.0 (d, $^3J_{C,P}$ = 39.7 Hz; *ipso*-Ph*C*-N$_2$), 125.6 (s; *m*-Ph*C*-N$_2$), 123.7 (s; *o*-Ph*C*-N$_2$), 42.6 (d, $^1J_{C,P}$ = 23.1 Hz; P*C*(CH$_3$)$_3$), 29.8 (s; PC(*CH*$_3$)$_3$), 21.3 (s; *C*H$_3$(O)CO). ^{19}F NMR (282.4 MHz, $CDCl_3$, 299 K) δ = –153.2 (s), –153.2 (s). ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$, 297 K) δ = 69.4 (s) (no impurity observed). HR-MS (ESI): calcd for $C_{20}H_{34}N_2O_2P$ (M – BF_4) 365.2358, found 365.2360 [*p*-CH$_3$(O)CO-PhN$_2$(P*t*Bu$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 3001 (w), 1754 (w), 1587 (w), 1494 (w), 1477 (w), 1449 (w), 1414 (w), 1403 (w), 1371 (w), 1313 (w), 1283 (w), 1180 (s), 1138 (s), 1098 (m), 1056 (s), 1025 (s), 1008 (s), 939 (w), 910 (m), 875 (m), 847 (w), 803 (m), 764 (m), 718 (w), 633 (w), 577 (w), 546 (w), 519 (w), 498 (w), 487 (w), 477 (w), 421 (w).

Synthesis of [*p*-(CH$_3$)$_3$C-PhN$_2$(P*t*Bu$_3$)][BF$_4$] (1j): [*p*-(CH$_3$)$_3$-PhN$_2$-(P*t*Bu$_3$)][BF$_4$] was synthesised from *p*-*tert*-butylbenzenediazonium tetrafluoroborate [*p*-(CH$_3$)$_3$-PhN$_2$][BF$_4$] (80.6 mg, 0.325 mmol, 1.0 equiv) and isolated as a red powder in 86 % yield (125.9 mg, 0.280 mmol). M.p. (open capillary): 123–126 °C (decomposition). ^{1}H NMR (500.0 MHz, $CDCl_3$, 300 K) δ = 7.89, 7.88, 7.68, 7.66 (AB-type, 4H; Ph*H*), 1.71 (d, $^3J_{H,P}$ = 14.4 Hz, 27H; PC(*CH*$_3$)$_3$), 1.38 (s, 9H; *p*-C(*CH*$_3$)$_3$Ph). ^{11}B{^{1}H} NMR (160.4 MHz, $CDCl_3$, 300 K) δ = –0.9 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 299 K) δ = 162.5 (s; *p*-Ph*C*-N$_2$), 153.9 (d, $^3J_{C,P}$ = 39.6 Hz; *ipso*-Ph*C*-N$_2$), 127.4 (s; *o*-Ph*C*-N$_2$), 123.9 (s; *m*-Ph*C*-

N_2), 42.5 (d, $^1J_{C,P}$ = 23.7 Hz; $PC(CH_3)_3$), 36.0 (s; *p*-$C(CH_3)_3Ph$), 31.0 (s; *p*-$C(CH_3)_3Ph$), 29.8 (s; $PC(CH_3)_3$). ^{19}F NMR (282.4 MHz, $CDCl_3$, 294 K) δ = –153.4 (s), –153.4 (s). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 298 K) δ = 68.1 (s; product, 99 %), 51.3 (s; impurity [*t*Bu_3PH][BF_4], 1 %). HR-MS (FD): calcd for $C_{22}H_{40}N_2P$ (M – BF_4) 363.2929, found 363.2935 [*p*-$(CH_3)_3$-PhN_2(P*t*Bu_3)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2964 (w), 1596 (w), 1497 (w), 1475 (w), 1446 (w), 1402 (w), 1370 (w), 1318 (w), 1271 (w), 1214 (w), 1173 (w), 1150 (w), 1091 (m), 1048 (s), 1025 (s), 930 (w), 855 (m), 799 (w), 784 (m), 741 (w), 689 (w), 627 (w), 577 (w), 561 (w), 519 (w), 484 (w).

Synthesis of [*p*-CH_3-PhN_2(P*t*Bu_3)][BF_4] (1k): [*p*-CH_3-PhN_2-(P*t*Bu_3)][BF_4] was synthesised from *p*-methylbenzenediazonium tetrafluoroborate [*p*-CH_3-PhN_2][BF_4] (86.6 mg, 0.420 mmol, 1.0 equiv) and isolated as a pink powder in 82 % yield (140.9 mg, 0.435 mmol). M.p. (open capillary): 95–114 °C (decomposition). ^1H NMR (500.0 MHz, $CDCl_3$, 298 K): δ = 7.84, 7.83, 7.46, 7.44 (AB-type, 4H; Ph*H*), 2.50 (s, 3H; CH_3), 1.70 (d, $^3J_{H,P}$ = 14.4, 27H; $PC(CH_3)_3$). $^{11}B\{^1H\}$ NMR (160.4 MHz, $CDCl_3$, 298 K): δ = –0.9 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K): δ = 154.1 (d, $^3J_{C,P}$ = 39.7 Hz; *ipso*-Ph*C*-N_2), 149.9 (s; *p*-Ph*C*-N_2), 131.0 (s; *o*-Ph*C*-N_2), 124.0 (s; *m*-Ph*C*-N_2), 42.4 (d, $^1J_{C,P}$ = 23.9 Hz; $PC(CH_3)_3$), 29.8 (s; $PC(CH_3)_3$), 22.3 (s; CH_3). ^{19}F NMR (282.4 MHz, $CDCl_3$, 293 K): δ = –153.5 (s), –153.5 (s). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 298 K): δ = 68.0 (s; no impurity observed). HR-MS (ESI): calcd for $C_{19}H_{34}N_2P_1$ (M – BF_4) 321.2460, found 321.2457 [*p*-CH_3-PhN_2(P*t*Bu_3)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 3001 (w), 2978 (w), 1596 (w), 1478 (w), 1433 (m), 1403 (m), 1372 (w), 1313 (w), 1300 (w), 1283 (w), 1262 (w), 1204 (w), 1175 (w), 1148 (m), 1094 (m), 1048 (s), 1027 (s), 933 (w), 870 (m), 847 (w), 832 (m), 800 (s), 750 (m), 708 (m), 637 (w), 625 (w), 546 (w), 519 (w), 496 (w), 484 (m), 460 (w), 423 (w).

Synthesis of [*p*-C_6H_5O-PhN_2(P*t*Bu_3)][BF_4] (1l): [*p*-PhO-PhN_2-(P*t*Bu_3)][BF_4] was synthesised from *p*-phenoxybenzenediazonium tetrafluoroborate [*p*-PhO-PhN_2][BF_4] (72.0 mg, 0.254 mmol, 1.0 equiv) and isolated as a red powder in 55 % yield (67.8 mg, 0.139 mmol). M.p. (open capillary): 114–118 °C (decomposition). ^1H NMR (500.0 MHz, $CDCl_3$, 298 K) δ = 7.95 (d, $^3J_{H,H}$ = 8.6 Hz, 2H; *o*-Ph*H*-N_2), 7.46 (t, $^3J_{H,H}$ = 7.8 Hz, 2H; *m*-OPh*H*), 7.29 (t, $^3J_{H,H}$ = 7.6 Hz, 1H; *p*-OPh*H*), 7.17–7.11 (m, 4H; *m*-Ph*H*-N_2, *o*-OPh*H*), 1.71 (d, $^3J_{H,P}$ = 14.3, 27H; $PC(CH_3)_3$). $^{11}B\{^1H\}$ NMR (160.4 MHz, $CDCl_3$, 298 K) δ = –0.9 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K) δ = 166.4 (s; *p*-Ph*C*-N_2), 154.3 (s; *ipso*-OPh*C*), 151.5 (d, $^3J_{C,P}$ = 40.2 Hz; *ipso*-Ph*C*-N_2), 130.6 (s; *m*-OPh*C*), 126.9 (s; *o*-Ph*C*-N_2), 126.1 (s; *p*-OPh*C*), 120.9 (s; *o*-OPh*C*), 118.2 (s; *m*-Ph*C*-N_2), 42.4 (d, $^1J_{C,P}$ = 24.4 Hz; $PC(CH_3)_3$), 29.9 (s; $PC(CH_3)_3$). ^{19}F NMR (282.4 MHz, $CDCl_3$, 293 K) δ = –153.3 (s), –153.3 (s). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 298 K) δ = 67.2 (s; product, 99 %), 50.8 (s; impurity [*t*Bu_3PH][BF_4], 1 %). HR-MS (FD): calcd for $C_{24}H_{36}N_2OP$ (M – BF_4) 399.2565, found 399.2545 [*p*-PhO-PhN_2(P*t*Bu_3)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2981 (w), 1603 (w), 1576 (m), 1481 (m), 1441 (w), 1401 (m), 1330 (w), 1284 (w), 1249 (s), 1193 (m), 1177 (w), 1136 (s), 1092 (m), 1048 (s), 1026 (s), 939 (w), 881 (w), 853 (w), 796 (s), 781 (s), 748 (m), 695 (m), 630 (m), 589 (w), 520 (w), 491 (m), 469 (m), 422 (w).

Synthesis of [*p*-$(CH_3)_2$HCO-PhN_2(P*t*Bu_3)][BF_4] (1n): [*p*-*i*PrO-PhN_2(P*t*Bu_3)][BF_4] was synthesised from *p*-isopropoxybenzenediazonium tetrafluoroborate [*p*-*i*PrO-PhN_2][BF_4] (76.1 mg, 0.304 mmol, 1.0 equiv) at –20 to –25 °C and isolated as a red powder in 68 % yield (94.2 mg, 0.208 mmol). Note that for the work-up 35 mL of *n*-pentane was used instead of 10 mL. M.p. (open capillary): 112–116 °C (decomposition). ^1H NMR (500.0 MHz, $CDCl_3$, 298 K) δ = 7.94, 7.92, 7.09, 7.07 (AB-type, 4H; Ph*H*), 4.80 (sept, $^3J_{H,H}$ = 6.0 Hz, 1H; $(CH_3)_2CH$), 1.68 (d, $^3J_{H,P}$ = 14.3 Hz, 27H; $PC(CH_3)_3$), 1.40 (d, $^3J_{H,H}$ = 6.1 Hz, 6H; $(CH_3)_2CH$). $^{11}B\{^1H\}$ NMR (160.4 MHz, $CDCl_3$, 298 K) δ = –0.9 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K) δ = 166.8 (s; *p*-Ph*C*-N_2), 150.8 (d, $^3J_{C,P}$ = 40.6 Hz; *ipso*-Ph*C*-N_2), 127.4 (br. s; *m*-Ph*C*-N_2), 116.7 (s; *o*-Ph*C*-N_2), 71.9 (s; $(CH_3)_2CH$), 42.2 (d, $^1J_{C,P}$ = 25.6 Hz; $PC(CH_3)_3$), 29.8 (s; $PC(CH_3)_3$), 21.9 (s; $(CH_3)_2CH$). ^{19}F NMR (282.4 MHz, $CDCl_3$, 294 K) δ = –153.5 (s), –153.6 (s). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 298 K) δ = 65.4 (s; product, 96.4 %), 51.3 (s; impurity [*t*Bu_3PH][BF_4], 0.4 %). HR-MS (ESI): calcd for $C_{21}H_{38}N_2OP$ (M – BF_4) 365.2722, found 365.2708 [*p*-*i*PrO-PhN_2(P*t*Bu_3)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2982 (w), 1596 (w), 1572 (w), 1487 (w), 1387 (m), 1328 (w), 1300 (w), 1255 (m), 1215 (w), 1175 (w), 1136 (s), 1117 (w), 1098 (s), 1048 (s), 1024 (s), 942 (m), 874 (w), 842 (m), 792 (s), 754 (m), 633 (m), 608 (w), 531 (w), 519 (w), 495 (s), 420 (w).

Synthesis of [*p*-H_2N-PhN_2(P*t*Bu_3)][BF_4] (1o): [*p*-H_2N-PhN_2-(P*t*Bu_3)][BF_4] was synthesised from *p*-aminobenzenediazonium tetrafluoroborate [*p*-H_2N-PhN_2][BF_4] (97.2 mg, 0.470 mmol, 1.0 equiv) and isolated as a red powder in 97 % yield (186.2 mg, 0.455 mmol). M.p. (open capillary): 126–140 °C (decomposition). ^1H NMR (500.0 MHz, $CDCl_3$, 298 K): δ = 7.67 (br. s, 2H; Ph*H*), 6.84 (d, $^3J_{H,H}$ = 7.9 Hz, 2H; Ph*H*), 6.15 (br. s, 2H; NH_2), 1.60 (d, $^3J_{H,P}$ = 13.6 Hz, 27 H; $C(CH_3)_3$). $^{11}B\{^1H\}$ NMR (160.4 MHz, $CDCl_3$, 298 K): δ = –0.8 (s; no impurity observed). ^{13}C NMR (125.7 MHz, $CDCl_3$, 299 K): δ = 159.1 (s; *p*-Ph*C*-N_2), 149.9 (d, $^3J_{C,P}$ = 41.7 Hz; *ipso*-Ph*C*-N_2), 115.4 (br. s; Ph*C*-N_2), 41.7 (d, $^1J_{C,P}$ = 29.4 Hz; $PC(CH_3)_3$), 29.8 (s; $PC(CH_3)_3$), the remaining Ph*C*-N_2 signal was not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$, 299 K): δ = –151.9 (s), –152.0 (s). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 298 K): δ = 59.4 (s). HR-MS (ESI): calcd for $C_{18}H_{33}N_3P_1$ (M – BF_4) 322.2412, found 322.2414 [*p*-NH_2-PhN_2(P*t*Bu_3)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 3454 (w), 3360 (m), 3245 (w), 2977 (w), 1648 (m), 1604 (m), 1517 (w), 1485 (w), 1473 (w), 1399 (w), 1379 (w), 1321 (m), 1286 (s), 1178 (w), 1142 (m), 1054 (s), 1017 (s), 938 (w), 868 (w), 849 (m), 820 (m), 802 (m), 778 (s), 731 (w), 635 (w), 591 (w), 549 (w), 516 (w), 499 (w), 485 (w), 458 (m), 421 (w).

Note: for the following compounds (**2a**,**d**,**f**,**m**,**p**) in all cases DCM was still present in the end product. Leaving the compound on vacuum at 1x10^{-3} mbar for a longer time did not result in the decrease of the amount of DCM.

Synthesis of [*p*-O_2N-PhN_2($PMes_3$)][BF_4] (2a): [*p*-O_2N-PhN_2-($PMes_3$)][BF_4] was synthesised following the general procedure for arylazo-phosphonium salts from 4-nitrobenzenediazonium tetrafluoroborate [*p*-O_2N-PhN_2][BF_4] (72.0 mg, 0.304 mmol, 1.0 equiv) and trimesitylphosphine and was isolated as a pale purple powder in 94 % yield (178.0 mg, 0.285 mmol). Crystals were grown by vapour diffusion of a saturated solution of **2a** in DCM with *n*-pentane as anti-solvent; due to the formation of multiple twins publishable data is precluded. M.p. (open capillary): 92–98 °C (decomposition). ^1H NMR (500.0 MHz, $CDCl_3$, 298 K): δ = 8.46, 8.45, 8.01, 7.99 (AB-type, 4H; NO_2Ph*H*), 7.18 (s, 3H; *m*-Mes*H*), 7.14 (s, 3H; *m*-Mes*H*), 2.40 (s, 9H; *p*-MesCH_3), 2.16 (s, 9H; *o*-MesCH_3), 2.02 (s, 9H; *o*-MesCH_3). $^{11}B\{^1H\}$ NMR (160.4 MHz, $CDCl_3$, 298 K): δ = –0.9 (s). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K): δ = 154.4 (d, $^1J_{C,P}$ = 52.0 Hz; *ipso*-Ph*C*), 151.6 (s; *p*-Ph*C*), 147.3 (s; *p*-Mes*C*), 145.3 (d, $^2J_{C,P}$ = 5.5 Hz; *o*-Mes*C*), 144.9 (d, $^2J_{C,P}$ = 12.2 Hz; *o*-Mes*C*), 133.9 (d, $^3J_{C,P}$ = 11.2 Hz; *m*-Mes*C*), 133.3 (d, $^3J_{C,P}$ = 10.4 Hz; *m*-Mes*C*), 125.9 (s; *o*-Ph*C*), 125.3 (s; *m*-Ph*C*), 114.6 (d, $^1J_{C,P}$ = 81.7 Hz; *ipso*-Mes*C*), 24.4 (s; *o*-MesCH_3), 21.5 (s; *p*-MesCH_3). ^{19}F NMR (282.4 MHz, $CDCl_3$, 294 K): δ = –153.9 (s), –154.0 (s). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 298 K): δ = 46.9 (s; product, 88 %), –27.8 (s; impurity presumably [Mes_3PH][BF_4], 8 %), 95.4 (s, impurity, 2 %), 90.8 (s; impurity, 2 %). HR-MS (ESI): calcd for $C_{33}H_{37}N_3O_2P_1$ (M – BF_4) 538.2623, found 538.2646. [*p*-NO_2-PhN_2($PMes_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2965 (w), 2931 (w), 1601 (w), 1552 (m), 1531 (w), 1488 (m),1449 (w), 1399 (w), 1384 (w), 1347 (w), 1319 (m), 1287 (w), 1253 (w), 1185 (w), 1151 (w), 1090 (w), 1052 (s), 1035 (s),

1007 (m), 958 (w), 926 (w), 868 (m), 839 (m), 750 (w), 733 (m), 700 (w), 654 (s), 568 (w), 554 (w), 514 (w), 473 (w), 461 (w), 440 (m), 412 (w).

Synthesis of [*p*-Br-PhN$_2$(PMes$_3$)][BF$_4$] (2d): [*p*-Br-PhN$_2$(PMes$_3$)][BF$_4$] was synthesised from 4-bromobenzenediazonium tetrafluoroborate [*p*-Br-PhN$_2$][BF$_4$] (60.1 mg, 0.222 mmol, 1.0 equiv) and trimesitylphosphine and was isolated as a pale pink powder in 91 % yield (132.8 mg, 0.201 mmol). X-ray quality crystals were grown by vapour diffusion of a saturated solution of **2d** in DCM with *n*-pentane as anti-solvent. M.p. (open capillary): 91–153 °C (decomposition). ^{1}H NMR (500.0 MHz, CDCl$_3$, 298 K): δ = 7.77, 7.75, 7.67, 7.66 (AB-type, 4H; BrPh*H*), 7.13 (s, 3H; *m*-Mes*H*), 7.11 (s, 3H; *m*-Mes*H*), 2.38 (s, 9H; *p*-MesC*H*$_3$), 2.13 (s, 9H; *o*-MesC*H*$_3$), 1.99 (s, 9H; *o*-MesC*H*$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, CDCl$_3$, 298 K): δ = –0.9 (s). ^{13}C NMR (125.7 MHz, CDCl$_3$, 298 K): δ = 151.2 (d, $^1J_{C,P}$ = 52.3 Hz; *ipso*-PhC), 146.9 (s; *p*-MesC), 145.2 (d, $^2J_{C,P}$ = 7.0 Hz; *o*-MesC), 144.7 (d, $^2J_{C,P}$ = 11.8 Hz; *o*-MesC), 133.9 (s; *o*-PhC), 133.7 (d, $^3J_{C,P}$ = 12.1 Hz; *m*-MesCH), 133.1 (d, $^3J_{C,P}$ = 11.7 Hz; *m*-MesCH), 132.4 (s; *p*-PhC), 125.7 (s; *m*-PhC), 115.2 (d, $^1J_{C,P}$ = 82.6 Hz; *ipso*-MesC), 24.4 (s; *o*-MesCH$_3$), 21.4 (s; *p*-MesCH$_3$). ^{19}F NMR (282.4 MHz, CDCl$_3$, 299 K): δ = –154.2 (s), –154.3 (s). ^{31}P{^{1}H} NMR (202.4 MHz, CDCl$_3$, 298 K): δ = 45.2 (s; product, 96 %), –27.9 (s; impurity presumably [Mes$_3$PH][BF$_4$], 4 %). HR-MS (ESI): calcd for C$_{33}$H$_{37}$Br$_1$N$_2$P$_1$ (M – BF$_4$) 573.1863, found 573.1845 [*p*-Br-PhN$_2$(PMes$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2970 (w), 2921 (w), 1602 (m), 1584 (w), 1572 (w), 1553 (w), 1477 (w), 1448 (m), 1399 (w), 1381 (w), 1303 (w), 1286 (w), 1270 (w), 1191 (w), 1149 (w), 1050 (s), 1034 (s), 1002 (s), 959 (w), 923 (w), 863 (m), 841 (m), 762 (w), 730 (m), 700 (w), 654 (s), 643 (s), 565 (w), 552 (m), 519 (w), 510 (w), 476 (m), 446 (s), 411 (w).

Synthesis of [*p*-H-PhN$_2$(PMes$_3$)][BF$_4$] (2f): *p*-H-PhN$_2$(PMes$_3$)][BF$_4$] was synthesised from benzenediazonium tetrafluoroborate [*p*-H-PhN$_2$][BF$_4$] (59.0 mg, 0.307 mmol, 1.0 equiv) and trimesitylphosphine and was isolated as a pale pink powder in 98 % yield (175.6 mg, 0.303 mmol). X-ray quality crystals were grown by vapour diffusion of a saturated solution of **2f** in DCM with *n*-pentane as anti-solvent. M.p. (open capillary): 107–160 °C (decomposition). ^{1}H NMR (500.0 MHz, CD$_3$CN, 300 K): δ = 7.82 (d, $^3J_{H,H}$ = 7.4 Hz, H; *o*-Ph*H*), 7.78 (t, $^3J_{H,H}$ = 7.5 Hz, 1H; *p*-Ph*H*), 7.65 (t, $^3J_{H,H}$ = 7.8 Hz, 2H; *m*-Ph*H*), 7.20 (br. s, 6H; *m*-Mes*H*), 2.38 (s, 9H; *p*-MesC*H*$_3$), 2.14 (s, 9H; *o*-MesC*H*$_3$), 2.01 (s, 9H; *o*-MesC*H*$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, CDCl$_3$, 299 K): δ = –0.9 (s). ^{13}C NMR (125.7 MHz, CD$_3$CN, 300 K): δ = 153.7 (d, $^1J_{C,P}$ = 52.3 Hz; *ipso*-PhC), 147.5 (s; *p*-MesC), 146.5 (d, $^2J_{C,P}$ = 4.4 Hz; *o*-MesC), 145.9 (d, $^2J_{C,P}$ = 11.8 Hz; *o*-MesC), 137.5 (s; *p*-PhC), 134.1 (d, $^3J_{C,P}$ = 11.5 Hz; *m*-MesC), 133.7 (d, $^3J_{C,P}$ = 11.2 Hz; *m*-MesC), 131.2 (s; *m*-PhC), 125.3 (s; *o*-PhC), 116.3 (d, $^1J_{C,P}$ = 82.5 Hz; *ipso*-MesC), 24.6 (s; *o*-MesCH$_3$), 21.3 (s; *p*-MesCH$_3$). ^{19}F NMR (282.4 MHz, CDCl$_3$, 293 K): δ = –154.1 (s), –154.2 (s). ^{31}P{^{1}H} NMR (202.4 MHz, CD$_3$CN, 300 K): δ = 44.7 (s; product, 84 %) –27.5 (s; impurity presumably [Mes$_3$PH][BF$_4$], 16 %). HR-MS (ESI): calcd for C$_{33}$H$_{38}$N$_2$P$_1$ (M – BF$_4$) 493.2773, found 493.2793 [*p*-H-PhN$_2$(PMes$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2971 (w), 2929 (w), 1601 (w), 1552 (w), 1483 (w), 1444 (m), 1400 (w), 1384 (w), 1311 (w), 1286 (w), 1272 (w), 1190 (w), 1146 (m), 1093 (s), 1051 (s), 1036 (w), 998 (w, 959 (w), 938 (w), 924 (w), 856 (w), 774 (m), 751 (w), 732 (m), 703 (w), 686 (w), 654 (s), 614 (w), 573 (w), 553 (m), 519 (w), 475 (m), 443 (m), 427 (m).

Synthesis of [*p*-CH$_3$O-PhN$_2$(PMes$_3$)][BF$_4$] (2m): [*p*-CH$_3$O-PhN$_2$-(PMes$_3$)][BF$_4$] was synthesised from 4-methoxybenzenediazonium tetrafluoroborate [*p*-CH$_3$O-PhN$_2$][BF$_4$] (70.4 mg, 0.317 mmol, 1.0 equiv) and trimesityl-phosphine which and isolated as an orange powder in 79 % yield (153.0 mg, 0.251 mmol). X-ray quality crystals were grown by vapour diffusion of a saturated solution of **2m** in DCM with *n*-pentane as anti-solvent. M.p. (open capillary): 109–122 °C (decomposition). ^{1}H NMR (500.0 MHz, CDCl$_3$, 300 K): δ = 7.79 (d, $^3J_{H,H}$ = 7.9 Hz, 2H; *o*-Ph*H*), 7.15–7.04 (m, 8H; *m*-Ph*H* and *m*-Mes*H*), 3.97 (s, 3H; OC*H*$_3$), 2.39 (s, 9H; *p*-MesC*H*$_3$), 2.12 (s, 9H; *o*-MesC*H*$_3$), 2.03 (s, 9H; *o*-MesC*H*$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, CDCl$_3$, 299 K): δ = –0.9 (s). ^{13}C NMR (125.7 MHz, CDCl$_3$, 300 K): δ = 167.4 (s; *p*-PhC), 147.9 (d, $^1J_{C,P}$ = 53.0 Hz; *ipso*-PhC), 146.3 (s; *p*-MesC), 145.5 (d, $^2J_{C,P}$ = 6.9 Hz; *o*-MesC), 144.4 (d, $^2J_{C,P}$ = 9.4 Hz; *o*-MesC), 133.4 (d, $^3J_{C,P}$ = 8.9 Hz; *m*-MesC), 133.0 (d, $^3J_{C,P}$ = 9.3 Hz; *m*-MesC), 127.9 (s; *o*-PhC), 116.3 (d, $^1J_{C,P}$ = 83.0 Hz; *ipso*-MesC), 115.9 (s; *m*-PhC), 56.6 (s; OCH$_3$), 24.5 (s; *o*-MesCH$_3$), 24.4 (s; *o*-MesCH$_3$), 21.5 (s; *p*-MesCH$_3$). ^{19}F NMR (282.4 MHz, CDCl$_3$, 294 K): δ = –154.2 (s), –154.3 (s). ^{31}P{^{1}H} NMR (202.4 MHz, CDCl$_3$, 299 K): δ = 42.7 (s; product, 96 %), –27.8 (s; impurity presumably [Mes$_3$PH][BF$_4$], 4 %). HR-MS (ESI): calcd for C$_{34}$H$_{40}$N$_2$OP$_1$ (M – BF$_4$) 523.2878, found 523.2882 [*p*-CH$_3$O-PhN$_2$(PMes$_3$)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 2924 (w), 2252 (w), 1599 (m), 1555 (w), 1499 (w), 1446 (m), 1401 (m), 1322 (w), 1273 (m), 1215 (w), 1183 (w), 1140 (m), 1114 (w), 1091 (m), 1050 (s), 1014 (s), 959 (w), 928 (w), 870 (w), 843 (m), 811 (w), 791 (w), 733 (m), 722 (m), 654 (s), 601 (w), 576 (w), 554 (w), 509 (m), 488 (w), 455 (m), 416 (w).

Synthesis of [*p*-(CH$_3$)$_2$N-PhN$_2$(PMes$_3$)][BF$_4$] (2p): The following reaction was performed in the dark using aluminium foil. A solution of trimesitylphosphine (106.5 mg, 1.0 mmol, 1.0 equiv) in DCM (2 mL) was added dropwise to a solution of 4-(dimethylamino)-benzenediazonium tetrafluoroborate [*p*-(CH$_3$)$_2$N-PhN$_2$][BF$_4$] (64.3 mg, 1.0 mmol, 1.0 equiv) in DCM (2 mL) at 0 °C. The solution was stirred for 5 min at 0 °C, and then warmed to room temperature in 30 min. after which all volatiles were removed in vacuo to afford **2p** as an orange/brown powder in a near quantitative yield. Note that performing this reaction in acetonitrile does not lead to full conversion, as an equilibrium is formed between the electron-rich diazonium salt and the phosphine. Furthermore, once the product is formed in DCM, isolated, and then dissolved in acetonitrile, pentane or CDCl$_3$ the compound is not stable. Slow degradation of the compound in air is observed over time. Growing crystals in DCM has thus far not been successful. ^{1}H NMR (500.0 MHz, CD$_2$Cl$_2$, 300 K): δ = 7.65 (br. s, 2H; Ph*H*), 7.07 (s, 3H; *m*-Mes*H*), 7.07 (s, 3H; *m*-Mes*H*), 6.76 (d, $^3J_{H,H}$ = 9.1 Hz, 2H; Ph*H*), 3.20 (s, 6H; N(C*H*$_3$)$_2$), 2.37 (s, 9H; *p*-MesC*H*$_3$), 2.07 (br. s, 18H; *o*-MesC*H*$_3$). ^{11}B{^{1}H} NMR (160.4 MHz, CD$_2$Cl$_2$, 300 K): δ = –1.1 (s). ^{13}C NMR (125.7 MHz, CD$_2$Cl$_2$, 301 K): δ = 157.0 (s; *p*-PhC), 146.1–145.4 (m; *ipso*-PhC, *o*-MesC, *p*-MesC), 133.1 (d, $^3J_{C,P}$ = 34.2 Hz; *m*-MesC), 118.4 (d, $^1J_{C,P}$ = 83.7 Hz; *ipso*-MesC), 112.3 (br. s; PhC, observed with HSQC), 40.9 (s; N(C*H*$_3$)$_2$), 24.7 (s; *o*-MesCH$_3$), 24.4 (s; *o*-MesCH$_3$), 21.4 (s; *p*-MesCH$_3$), the remaining PhC signal was not observed. ^{19}F NMR (282.4 MHz, CD$_2$Cl$_2$, 295 K): δ = –153.2 (s), –153.2 (s). ^{31}P{^{1}H} NMR (202.4 MHz, CD$_2$Cl$_2$, 300 K): δ = 39.92 (s; product, 90 %), –27.5 (s; impurity presumably [Mes$_3$PH][BF$_4$], 10 %). HR-MS (ESI): calcd for C$_{35}$H$_{43}$N$_3$P$_1$ (M – BF$_4$) 536.3195, found 536.3190 [*p*-(CH$_3$)$_2$N-PhN$_2$(PMes$_3$)]$^+$. IR (cm^{-1}; recorded in air): 2960 (w), 2919 (w), 2160 (w), 1590 (m), 1547 (w), 1444 (w), 1391 (w), 1354 (w), 1326 (m), 1302 (m), 1286 (m), 1254 (w), 1145 (m), 1121 (m), 1048 (s), 1031 (s), 934 (m), 848 (w), 825 (m), 762 (m), 716 (m), 706 (w), 650 (m), 630 (m), 598 (w), 573 (w), 553 (m), 519 (w), 508 (m), 455 (w), 440 (w), 426 (w).

X-ray Crystal Structure Determinations: The single-crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-K_α radiation (λ = 1.54178 Å). Dual space methods (SHELXT)[21] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2).[22] Hydrogen atoms were localised by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied. In **2m** the BF$_4$ anion and in **2f** the solvent CH$_2$Cl$_2$ are disordered (see cif-files for details).

2d: Red crystals, $C_{33}H_{37}BrN_2P^+ \cdot BF_4^- \cdot CH_2Cl_2$, M_r = 744.26, crystal size 0.16 × 0.10 × 0.08 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 11.5869(6) Å, b = 12.1061(6) Å, c = 14.2286(7) Å, α = 71.661(2)°, β = 72.304(2)°, γ = 67.307(2)°, V = 1709.44(15) Å^3, Z = 2, ρ = 1.446 Mg/m^{-3}, μ(Cu-K_α) = 3.934 mm^{-1}, F(000) = 764, $2\theta_{max}$ = 144.4°, 32836 reflections, of which 6717 were independent (R_{int} = 0.027), 415 parameters, R_1 = 0.030 (for 6544 $I > 2\sigma(I)$), wR_2 = 0.078 (all data), S = 1.05, largest diff. peak/hole = 0.673/–0.461 e Å^{-3}.

2f: Red crystals, $C_{33}H_{38}N_2P^+ \cdot BF_4^- \cdot CH_2Cl_2$, M_r = 665.36, crystal size 0.16 × 0.10 × 0.05 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 11.4682(5) Å, b = 11.6754(5) Å, c = 14.1121(7) Å, α = 78.334(2)°, β = 75.402(2)°, γ = 65.327(2)°, V = 1651.48(13) Å^3, Z = 2, ρ = 1.338 Mg/m^{-3}, μ(Cu-K_α) = 2.643 mm^{-1}, F(000) = 696, $2\theta_{max}$ = 144.6°, 35516 reflections, of which 6510 were independent (R_{int} = 0.030), 423 parameters, 7 restraints, R_1 = 0.035 (for 6011 $I > 2\sigma(I)$), wR_2 = 0.094 (all data), S = 1.03, largest diff. peak/hole = 0.400/–0.524 e Å^{-3}.

2m: Orange crystals, $C_{34}H_{40}N_2OP^+ \cdot BF_4^-$, M_r = 610.46, crystal size 0.22 × 0.16 × 0.14 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 8.0843(4) Å, b = 12.8764(6) Å, c = 15.5236(8) Å, α = 97.390(2)°, β = 94.542(2)°, γ = 95.878(2)°, V = 1587.10(14) Å^3, Z = 2, ρ = 1.277 Mg/m^{-3}, μ(Cu-K_α) = 1.216 mm^{-1}, F(000) = 644, $2\theta_{max}$ = 144.6°, 20298 reflections, of which 6189 were independent (R_{int} = 0.025), 417 parameters, 147 restraints, R_1 = 0.065 (for 5794 $I > 2\sigma(I)$), wR_2 = 0.173 (all data), S = 1.09, largest diff. peak/hole = 1.812 (see cif-file for details)/–0.620 e Å^{-3}.

CCDC 1866247 (for **2m**), 1866248 (for **2d**), and 1866249 (for **2f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Diazonium salts · Donor–acceptor systems · Lewis acids · Phosphines · Dyes/Pigments

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