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Facile Synthesis of Tuneable Azophosphonium Salts

Evi R. M. Habraken,[a] Lars J. C. van der Zee,[a] Koen N. A. van de Vrande,[a]

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 $\sigma^+_{para}$ 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 [ArN₂][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 [RN₂(NHC)][X], such as B.[4,5]

While the cationic NHC–diazonium Lewis adducts are industrially relevant, the corresponding phosphine derivatives have received little attention. In 1953, Horner and Stöhr described the red azophosphonium chlorides C [R = H, Me, Cl, NO₂, CO₂H, OMe, OC(O)Me], with PPh₃ 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-CH₃ + p-Cl, p-C(O)OEt, p-SO₂NH₂, p-CN].[7] Subsequently, Flower and co-workers reported the $^{31}$P(¹H) NMR chemical shift of E (δ$^{31}$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, tBu, 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' = tBu, p-R = NO₂, Br, H, OCH₃, N(CH₃)₂], displaying colours ranging from purple to red/brown.[10]

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 tBu₃P and Mes₃P. 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 $\nu_{para}$ 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 $\sigma^+_{para}$ 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]
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 azophosphonium salts $\left[[p-R-C_{6}H_{4}]_{2}N_{2}(P^{+}Bu_{3})\right][BF_{4}]^{-}$ (Scheme 1).$^\text{[10]}$ 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 $\left[[p-R-C_{6}H_{4}]_{2}N_{2}(P^{+}Bu_{3})\right][BF_{4}]^{-}$ 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 $\left[[Bu_{3}PH]\right][BF_{4}]^{-}$, which results from protonation of the phosphine by remaining HBF$_{4}$ that was used in the synthesis of the diazonium salt.

UV/Vis spectroscopy for compounds 1a–p, measured in CH$_{3}$CN, displays an intense absorption maximum ranging from $\lambda_{\text{max}}$ = 300–464 nm corresponding to the $\pi\rightarrow\pi^{*}$ transition (Figure 4).$^\text{[10]}$ In general, a bathochromic shift 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 1.417 Å; N–C: 1a 1.371 Å; see Table S3 for further data). The same effect is also manifested in the greater alternation of C–C bond lengths (Table 1) and follows the trend of the $\sigma^{+}$ value of their para substituents (Table 1).

The azophosphonium salts 1a–p are ordered according to the Hammett $\sigma^{+}$ values of their para substituent to highlight the substituent effect (Table 1).

![Image](https://example.com/image.png)

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

<table>
<thead>
<tr>
<th>$p$–R</th>
<th>$\sigma^{+}_{\text{para}}$ value$^\text{[a]}$</th>
<th>Yield [%]</th>
<th>N–N distance [Å]$^\text{[b]}$</th>
<th>$^{31}$P[1H] chemical shift [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a$^\text{[c]}$</td>
<td>NO$_{2}$</td>
<td>0.79</td>
<td>94</td>
<td>1.243</td>
</tr>
<tr>
<td>1b</td>
<td>CN</td>
<td>0.66</td>
<td>96</td>
<td>1.244</td>
</tr>
<tr>
<td>1c</td>
<td>CF$_{3}$</td>
<td>0.61</td>
<td>56</td>
<td>1.244</td>
</tr>
<tr>
<td>1d$^\text{[d]}$</td>
<td>Br</td>
<td>0.15</td>
<td>95</td>
<td>1.248</td>
</tr>
<tr>
<td>1e</td>
<td>Cl</td>
<td>0.11</td>
<td>83</td>
<td>1.249</td>
</tr>
<tr>
<td>1f$^\text{[e]}$</td>
<td>H</td>
<td>0.00</td>
<td>95</td>
<td>1.248</td>
</tr>
<tr>
<td>1g</td>
<td>F</td>
<td>-0.07</td>
<td>71</td>
<td>1.249</td>
</tr>
<tr>
<td>1h</td>
<td>C$<em>{6}H</em>{4}$</td>
<td>-0.18</td>
<td>61</td>
<td>1.252</td>
</tr>
<tr>
<td>1i</td>
<td>OC(O)CH$_{3}$</td>
<td>-0.19</td>
<td>94</td>
<td>1.250</td>
</tr>
<tr>
<td>1j</td>
<td>C(CH$<em>{3}$)$</em>{3}$</td>
<td>-0.26</td>
<td>86</td>
<td>1.251</td>
</tr>
<tr>
<td>1k</td>
<td>Cl$_{2}$</td>
<td>-0.31</td>
<td>82</td>
<td>1.251</td>
</tr>
<tr>
<td>1l</td>
<td>OC$<em>{3}$H$</em>{7}$</td>
<td>-0.50</td>
<td>55</td>
<td>1.257</td>
</tr>
<tr>
<td>1m$^\text{[f]}$</td>
<td>OCH$_{3}$</td>
<td>-0.78</td>
<td>92</td>
<td>1.257</td>
</tr>
<tr>
<td>1n</td>
<td>OCH$<em>{2}$CH$</em>{2}$</td>
<td>-0.85</td>
<td>68</td>
<td>1.259</td>
</tr>
<tr>
<td>1o</td>
<td>NH$_{2}$</td>
<td>-1.30</td>
<td>97</td>
<td>1.264</td>
</tr>
<tr>
<td>1p$^\text{[g]}$</td>
<td>N(CH$<em>{3}$)$</em>{2}$</td>
<td>-1.70</td>
<td>96</td>
<td>1.268</td>
</tr>
</tbody>
</table>

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

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 $\sigma^{+}$ 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 arylamino ring. These data indicate a significant contribution from resonance form II for electron-donating para substituents.$^\text{[14]}$

![Image](https://example.com/image.png)

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

![Image](https://example.com/image.png)

**Figure 3. Colours of azophosphonium salts 1a–p in solution (0.006 M in CH$_{3}$CN) and in the solid state.**

![Image](https://example.com/image.png)

**Figure 4.** UV/Vis absorption spectrophotometry for compounds 1.
As expected, comparing the $^{31}$P{1H} NMR chemical shifts with the non-corrected $\sigma^*_{\text{para}}$ value against the $^{31}$P{1H} NMR chemical shift of 1 shows a linear correlation ($R^2 = 0.953$; Figure 5), with only $R = \text{NH}_2$ ($1o$) as an outlier. This is likely due to the interaction of the coordinating solvent acetonitrile with the acidic protons on the NH₂ 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 $\sigma^*_{\text{para}}$ constant results in a poorer fitted linear correlation ($R^2 = 0.882$; see supporting information) with multiple outliers, highlighting the suitability of the $\sigma^*_{\text{para}}$ parameters for these systems.

To gain more insight into the dependence of the $\sigma^*_{\text{para}}$ against the $^{31}$P{1H} chemical shift of azophosphonium salts 1a-p.

![Figure 5. Hammett plot of the $\sigma^*_{\text{para}}$ constants against the $^{31}$P{1H} chemical shift of azophosphonium salts 1a-p.](image)

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

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\epsilon_{\text{max}}$</th>
<th>HOMO-1 [eV]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 (4.29)</td>
<td>523 (2.26)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>310 (4.15)</td>
<td>527 (3.10)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>300 (4.12)</td>
<td>522 (3.02)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>336 (4.33)</td>
<td>517 (2.18)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>331 (4.32)</td>
<td>516 (3.16)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>316 (4.21)</td>
<td>515 (2.16)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>323 (4.22)</td>
<td>510 (3.10)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>372 (4.38)</td>
<td>507 (3.46)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>329 (3.59)</td>
<td>520 (3.19)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>337 (4.35)</td>
<td>513 (3.23)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>337 (4.31)</td>
<td>513 (3.19)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>368 (4.43)</td>
<td>504 (3.42)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>373 (4.44)</td>
<td>500 (2.49)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>379 (4.47)</td>
<td>497 (3.55)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>435 (4.69)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
<tr>
<td>464 (4.62)</td>
<td>$\sigma^* \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
<td>$\pi \rightarrow \pi^*$ transition.</td>
</tr>
</tbody>
</table>

[a] $\pi \rightarrow \pi^*$ transition. [b] $\pi \rightarrow \pi^*$ transition. [c] $\pi \rightarrow \pi^*$ transition. [d] $\pi \rightarrow \pi^*$ transition. [e] $\pi \rightarrow \pi^*$ transition. [f] Data recorded after 1 day. For more information, see ref.[10] [g] $\pi \rightarrow \pi^*$ 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 $\omega$B97X-D/6-311+G(d,p) level of theory. These calculations revealed an N₂ vibration that is coupled to the adjacent phenyl group due to the conjugated $\pi$-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 NO₂, Br, H, OCH₃ and N(CH₃)₂. The reaction of $[\text{p-R-C}_6\text{H}_4\text{N}_2\text{PMe}_3]\text{BF}_4$ with PMes₃ (1.1 equiv) at 0 °C in dichloromethane (DCM) as the solvent, in addition to a
small amount of [HPMes3][BF4] impurity detectable in the $^{31}$P NMR spectrum. The electron-donating N(CH2)2 group results in a less Lewis acidic diazonium salt, affording an equilibrium between bound PMes3 and free PMes3 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-Cl-C6H4)N2(PMes3)][BF4], as the PMes3 could be replaced by the addition of the stronger Lewis base PrBu3.\[9\] 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(dp) level of theory concur with the less donating ability of PMes3 (HOMO: PMes3 –7.13 eV, PrBu3 –7.69 eV). Likewise, the addition of PMes3 leads to a slightly less thermodynamically stable product compared to the tri-tert-butylphosphine arylazophosphonium salt [2f $\Delta$E = –48.2 kcal mol$^{-1}$, 1f $\Delta$E = –53.2 kcal mol$^{-1}$ at the ωB97X-D/6-311+G(dp) level of theory, respectively].

The colours of trimesitylphosphine–diazonium adducts 2 were quantified using UV/Vis spectroscopy and revealed an intense absorption maximum ranging from $\lambda_{\text{max}} = 295–462$ nm (π→π* transition), which displays a bathochromic shift from 2a to 2p (Table 3).\[11\] Here too, a weak absorption in the visible region is observed with $\lambda_{\text{max}} = 472–500$ 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* $\lambda_{\text{abs}} = 316$, n→π* $\lambda_{\text{abs}} = 512$; 2f: π→π* $\lambda_{\text{abs}} = 304$, n→π* $\lambda_{\text{abs}} = 485$ 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).

We resorted again to DFT calculations at the ωB97X-D/6-311+G(dp) 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: π* = –12.2, π*: –4.3 eV, 2p: π* = –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, 2p: π*: –4.3 eV, Δ = –8.3; 2f: π*: –9.9, 2p: 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-Cl-C6H4)N2(PMes3)][BF4] (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, [BPh4]−),\[10\] which allows a comparison of bond metrics between arylazophosphonium salts with different substituents on the phosphorus centre (PMes3 (2f) vs. PrBu3 (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 1.7425(5) Å]. However, a change in planarity is found in the P1–N2–C1 angle (2f –178.18(9)° vs. 1f 173.4(7)° [–167.3(11)° (second disorder component)]).

![Figure 6. Colours of azophosphonium salts 2a,d,f,m,p in solution (0.006 M in CH2CN; 2p in dry DCM)](image)

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

<table>
<thead>
<tr>
<th>$^{31}$P{1H}[ppm]</th>
<th>$\lambda_{\text{abs}}$[nm][a]</th>
<th>$\lambda_{\text{abs}}$[nm][b]</th>
<th>ΔHOMO-1</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>46.9</td>
<td>295 (4.39)</td>
<td>500 (2.26)</td>
<td>–12.6</td>
<td>–12.2</td>
</tr>
<tr>
<td>2d</td>
<td>45.2</td>
<td>332 (4.28)</td>
<td>488 (2.32)</td>
<td>–11.3</td>
<td>–12.0</td>
</tr>
<tr>
<td>2f</td>
<td>44.7</td>
<td>304 (4.22)</td>
<td>485 (2.21)</td>
<td>–12.0</td>
<td>–11.9</td>
</tr>
<tr>
<td>2m</td>
<td>42.7</td>
<td>312 (4.63)</td>
<td>472 (2.56)</td>
<td>–10.9</td>
<td>–11.8</td>
</tr>
<tr>
<td>2p</td>
<td>39.9</td>
<td>462 (4.35)</td>
<td>–9.9</td>
<td>–11.5</td>
<td>–3.3</td>
</tr>
</tbody>
</table>

[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 CH2CN; 2p in dry DCM)](image)
Figure 8. Molecular structures of 2d.f.m [p-(R-CH3)2PhN2][BF4] (displace-
ment ellipsoids are set at 30 % probability, hydrogen atoms, disordered sol-
vent molecules and noncoordinating BF4 anion are omitted for clarity). Se-
lected bond length [Å] and torsion angles [°] for 2d: P1–N2 1.7544(14), N2–
N1 1.2492(14), N1–C1 1.4242(14); 2f: P1–N2 1.7545(12), N2–N1 1.2437(17),
N1–C1 1.4316(19); 2m: P1–N2 1.7362(16), N2–N1 1.2143(16), N1–C1 1.4323(13);
P1–N2–N1–C1 –178.18(9).

Conclusions
The tuneability of the azophosphonium salts, on both the aryl ring and phoshine, has been extended, showing the ease and tolerance of this synthetic protocol. The physical properties of the azarylphosphonium salts [p-(R-CH3)2PhN2][PR3][BF4] have been rationalised using the σ para Hammett constant and probed using 31P 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 com-
ounds 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 proce-
dures.1H and 13C[1H] NMR spectra were recorded on a Bruker 500
NEO or a Bruker AV300-II and internally referenced to the residual solvent resonances (CDCl3: 1H δ = 7.26 ppm, 13C[1H] δ = 77.16 ppm;
CD3CN: 1H δ = 1.94 ppm, 13C[1H] δ = 1.32, 118.26 ppm; (CD3)2SO: 1H δ = 2.50 ppm).19F NMR spectra were recorded on a Bruker AV300-II and externally referenced (CFCI3). Chemical shifts are re-
ported in ppm. Melting points were measured on samples in open capillaries on a Büchi M-565 melting point apparatus and are uncor-
rected. 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 Alpha-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 PtBu3 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-CH3(O)CO-PhN2H2] was pre-
pared according to Manna et al.13p-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).11 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-CH3(O)CO-PhN2H2] as a brown oil in 98 % yield (164.0 mg, 1.085 mmol).1H NMR (300.1 MHz, CDCl3, 295 K): δ = 6.86 (d, 3JH,H = 8.8 Hz, 2H; PhHδ), 6.66 (d, 3JH,H = 8.7 Hz, 2H; PhHδ), 3.63 (br. s, 2H; NH2), 2.26 (s, 3H; CH3(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. HBF4 (0.68 mL). The mixture was cooled in an ice bath and a solution of NaN32O (2.0 mmol, 1.0 equiv) in water (0.4 mmol) was added dropwise. The mixture was stirred for 40 min at 0 °C after which the precipitate was collected by filtration, washed with di-
ethyl ether (4 × 20 mL) and dried in vacuo to afford the desired crude para substituted diazonium salt [p-R-PhN2][BF4].

 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. HBF4 (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 drop-
wise. The mixture was stirred for 1 h at 0 °C after which the precipi-
tate 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-PhN2][BF4]. 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 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-PhN2][BF4].

 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-PhN2][BF4].

Synthesis of p-Cyanobenzenediazonium Tetrafluoroborate [p-NC-PhN2][BF4] 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 yellow
powder in 53 % (273.9 mg, 1.053 mmol). Purification by method A afforded [p-CF3PhN]BF4 as a white powder in 34 % yield (176.0 mg, 0.677 mmol). 1H NMR (300.0 MHz, CD3CN, 293 K): δ = 8.69 (d, 3JH-H = 8.5 Hz; 2H; PhH). 8.23 (d, 3JH-H = 8.5 Hz; 2H; PhH).

Synthesis of p-Chlorobenzenediazonium Tetrafluoroborate [p-Cl-PhN]BF4 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]BF4 as a white powder in 58 % yield (261.5 mg, 1.16 mmol). 1H NMR (300.1 MHz, CD3CN, 299 K): δ = 8.46 (d, 3JH-H = 8.8 Hz; 2H; PhH). 7.94 (d, 3JH-H = 8.7 Hz; 2H; PhH).

Synthesis of p-Fluorobenzenediazonium Tetrafluoroborate [p-F-PhN]BF4 was synthesised using method B starting with 4-fluoroaniline (239.3 mg, 2.2 mmol, 1.0 equiv), which afforded the crude product as a white powder in 43 % yield (195.0 mg, 0.929 mmol). 1H NMR (300.1 MHz, CD3CN, 294 K): δ = 8.8 Hz, 2H; N2Ph 8.18 (d, 3JH-H = 6.0 Hz; 6H; (CH3)2C). 7.69–7.55 (m, 2H; PhH). Synthesis of p-phenylbenzenediazonium tetrafluoroborate [p-C6H5-PhN]BF4 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 white powder in 62 % (261.5 mg, 1.459 mmol). 1H NMR (300.1 MHz, CD3CN, 293 K): δ = 8.46 (d, 3JH-H = 9.1 Hz; 2H; PhH). 7.23 (d, 3JH-H = 6.0 Hz; 6H; (CH3)2CH).

Synthesis of p-Aminoanilinediazonium Tetrafluoroborate [p-H2N-PhN]BF4 was synthesised according to a modified literature procedure of Y. Yagi et al.[20] under inert conditions. 50 wt.-% HBF4 (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 aceton (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 (1355.8 mg, 6.542 mmol). Subsequently, the crude product was dissolved in a minimal amount of acetonitrile (10 mL), filtered and precipitated with 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-H2N-PhN]BF4 as a white powder in 85 % yield (1230.0 mg, 5.944 mmol). 1H NMR (300.0 MHz, CD3)2SO, 299 K): δ = 8.50–7.80 (m, 4H; PhH); 6.82 (s, 2H; NH2).

General Procedure for the Synthesis of the Arylazophos- phonium 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 PhBu3 (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-PN]BF4 (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 31P{1H} data the following compounds were measured on a 500 MHz NMR (31P{1H}: 202.6 MHz): 1a 31P{1H} NMR (202.4 MHz, CDCl3, 299 K): δ = 73.4 (s; no impurity observed). 1d 31P{1H} NMR (202.4 MHz, CDCl3, 299 K): δ = 72.9 (s; no impurity observed). 1f 31P{1H} NMR (202.4 MHz, CDCl3, 299 K): δ = 69.4 (s; no impurity observed). 1m 31P{1H} NMR (202.4 MHz, CDCl3, 299 K): δ = 65.9 (s; no impurity observed). 1p 31P{1H} NMR (202.4 MHz, CDCl3, 299 K): δ = 59.5 (s; product 97 %), 50.3 (s; impurity [Bu3P][BF4], 3 %).

Synthesis of p-Isopropylenzymediazonium Tetrafluoroborate [p-iPrO-PhN]BF4 was synthesised using method A starting with 4-isopropyloxyaniline (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-iPrO-PhN]BF4 as a white powder in 86 % yield (518.0 mg, 2.072 mmol). 1H NMR (300.1 MHz, CD3CN, 293 K): δ = 8.36 (d, 3JH-H = 9.1 Hz; 2H; PhH). 7.28 (d, 3JH-H = 9.1 Hz; 2H; PhH). 4.94 (sept, 3JH-H = 6.0 Hz, 1H; (CH3(CH)2)CH). 1.40 (d, 3JH-H = 6.0 Hz, 6H; (CH3(CH)2)CH).

Synthesis of p-Arylazoacetonitrile [p-Ph-PhN]BF4 was synthesised using method A starting with 4-tert-butylaniline (347.8 mg, 2.2 mmol, 1.0 equiv), which afforded the crude product as a slightly brownish powder in 70 % (410.3 mg, 1.861 mmol). Purification by method B afforded [p-Ph-PhN]BF4 as a white 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-Ph-PhN]BF4 as a white powder in 93 % yield (518.0 mg, 2.072 mmol). 1H NMR (300.1 MHz, CD3CN, 293 K): δ = 8.41 (d, 3JH-H = 9.4 Hz; 2H; N2PhH). 7.56 (t, 3JH-H = 7.7 Hz, 2H; m-OPhH). 7.42 (t, 3JH-H = 7.5 Hz, 1H; p-OPhH). 7.28 (d, 3JH-H = 9.4 Hz, 2H; o-OPhH). 7.23 (d, 3JH-H = 7.4 Hz, 2H; N2PhH).
lated as a purple powder in 96% yield (186.5 mg, 0.445 mmol). M.p. (open capillary): 121–129 °C (decomposition). 1H NMR (500.0 MHz, CDCl3, 298 K): δ = 8.14, 8.12, 7.96, 7.94 (AB-type, 4H; PhH); 1.71 (d, JCP = 14.9 Hz, 27H, C(CH3)3). 11B{1H} NMR (160.4 MHz, CDCl3, 298 K): δ = −1.0 (s). 13C NMR (125.7 MHz, CDCl3, 298 K): δ = 155.5 (d, 2JCP = 39.5 Hz, ipso-PhN2), 134.2 (s; ipso-PhN2), 124.3 (s; m-PhC-N2), 119.1 (s; CN), 117.5 (s; p-PhC-N2), 42.7 (d, JCP = 21.5 Hz, Ph(CH3)2), 29.7 (s; PC(CH3)3). 19F NMR (282.4 MHz, CDCl3, 298 K): δ = −152.2 (d, JCF = −153.1 Hz). 31P{1H} NMR (202.4 MHz, CDCl3, 298 K): δ = 27.9 (s; product, 98%); 51.8 (s; impurity [Bu3P][BF4]2, 2%).

HR-MS (ESI): calcd for C64H42N2O2P(−BF4)3: 353.1924, found 353.1925 (M − BF4) [M+BF4]−, 391.1925, found 391.1925 (2M − BF4)2[M+2BF4]−, 429.1926, found 429.1927 (3M − BF4)3[M+3BF4]−. IR (cm−1): v = 2982 (w), 1590 (w), 1487 (w), 1450 (w), 1414 (w), 1380 (w), 1319 (w), 1283 (m), 1233 (m), 1175 (w), 1138 (m), 1045 (s), 1025 (s), 993 (m), 930 (w), 877 (w), 854 (m), 816 (w), 800 (w), 757 (m), 635 (m), 585 (w), 519 (w), 486 (w), 459 (w), 420 (w).

Synthesis of [p-C5H4PhN2(PBu3)][BF4] (1h): [p-Ph3P=PhN2(−BF4)3] was synthesised from p-phenylbenzenediazonium tetrafluoroborate [p-Ph3P=PhN2][BF4] (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). 1H NMR (500.0 MHz, CDCl3, 298 K): δ = 8.05, 8.03, 7.90, 7.88 (AB-type, 4H; PhH); 7.69 (d, 2JH = 7.1 Hz, 2H, o-PhH), 7.51 (t, 2JH = 7.3 Hz, 2H, m-PhH), 7.48–7.41 (m, 1H, p-PhH), 1.74 (d, 2JCP = 14.4 Hz, 27H, C(CH3)3). 11B{1H} NMR (160.4 MHz, CDCl3, 298 K): δ = −0.9 (s). 13C NMR (125.7 MHz, CDCl3, 298 K): δ = 154.6 (d, 2JCP = 39.8 Hz, ipso-PhC-N2), 150.3 (s; ipso-PhC), 138.7 (s; p-PhC-N2), 129.6 (s; p-PhC-N2), 129.4 (s; m-PhC-N2), 128.8 (s; o-PhC-N2), 127.6 (s; o-PhC), 124.7 (s; m-PhC-N2), 142.6 (d, 2JCP = 23.4 Hz, Ph(−C3H3)), 29.8 (s; PC(CH3)3). 19F NMR (282.4 MHz, CDCl3, 299 K): δ = −153.2 (d, JCF = −153.2 Hz). 31P{1H} NMR (202.4 MHz, CDCl3, 298 K): δ = 68.6 (s; product, 98%); 51.0 (s; impurity [Bu3P][BF4]2, 2%). HR-MS (ESI): calcd for C64H42N2O2P(−BF4)3: 383.2616, found 383.2632 ([p-Ph3P=PhN2][BF4]+). IR (cm−1): v = 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 (w), 701 (m), 704 (m), 632 (m), 616 (m), 555 (m), 519 (w), 491 (m), 488 (w), 433 (w).

Synthesis of [p-C6H5OICO-PPh4][BF4] (1i): [p-CH3ICO-PPh4][BF4] was synthesised from p-acetoxybenzenediazonium tetrafluoroborate [p-CH3ICO-PPh4][BF4] (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). 1H NMR (500.0 MHz, CDCl3, 301 K): δ = 8.03, 8.01, 7.44, 7.43 (AB-type, 4H; PhH), 2.37 (s, 3H, CH3(O)CO), 1.72 (d, 2JCP = 14.5 Hz, 27H, C(CH3)3). 11B{1H} NMR (160.4 MHz, CDCl3, 297 K): δ = −0.9 (s). 13C NMR (125.7 MHz, CDCl3, 297 K): δ = 168.6 (s; CH3(O)CO), 157.8 (s; p-PhC-N2), 153.0 (d, 2JCP = 39.7 Hz, ipso-PhC-N2), 125.6 (s; m-PhC-N2), 123.7 (s; o-PhC-N2), 42.6 (d, 2JCP = 23.1 Hz, PC(CH3)3), 29.8 (s; PC(CH3)3), 21.3 (s; CH3(O)CO). 19F NMR (282.4 MHz, CDCl3, 299 K): δ = −153.2 (s, −153.2 Hz). 31P{1H} NMR (202.4 MHz, CDCl3, 297 K): δ = 69.4 (s) (no impurity observed). HR-MS (ESI): calcd for C64H42N2O2P(−BF4)3: 365.2358, found 365.2360 ([CH3ICO-PPh4][BF4]+)2. IR (cm−1): v = 3001 (w), 1754 (w), 1587 (w), 1494 (w), 1477 (w), 1449 (w), 1413 (w), 1371 (w), 1313 (w), 1283 (w), 1180 (s), 1138 (s), 1098 (m), 1056 (s), 1025 (s), 908 (s), 939 (w), 910 (m), 875 (m), 847 (w), 803 (m), 764 (m), 718 (w), 633 (m), 577 (w), 546 (w), 519 (w), 498 (w), 487 (w), 477 (w), 421 (w).

Synthesis of [p-C6H5C=Ph-N=Ph-PBu3][BF4] (1j): [p-CH3C=Ph-N=Ph-PBu3][BF4] was synthesised from p-tert-butylbenzenediazonium tetrafluoroborate [p-CH3C=Ph-N=Ph-PBu3][BF4] (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). 1H NMR (500.0 MHz, CDCl3, 300 K): δ = 7.89, 7.88, 7.66, 7.66 (AB-type, 4H; PhH), 7.11 (d, 2JCP = 14.4 Hz, 27H, C(CH3)3). 11B{1H} NMR (160.4 MHz, CDCl3, 300 K): δ = −0.9 (s). 13C NMR (125.7 MHz, CDCl3, 299 K): δ = 162.5 (s; p-PhC-N2), 153.9 (d, 2JCP = 39.6 Hz, ipso-PhC-N2), 127.4 (s; o-PhC-N2), 123.9 (s; m-PhC-
N2), 42.5 (d, J_{1,3C} = 23.7 Hz; PC(i-C6H5)3), 36.0 (s; p-C(i-C6H5)2Ph), 31.0 (s; p-C(i-C6H5)2Ph), 29.8 (s; PC(i-C6H5)3). 19F NMR (282.4 MHz, CDCl3, 294 K) δ = −153.4 (s), −153.4 (s). 31P{1H} NMR (202.4 MHz, CDCl3, 298 K) δ = 68.1 (s; product, 99 %), 51.3 (s; impurity [Bu2Ph(PhF)]1), 1% HR-MS (FD): calcd for C_{33}H_{37}P_{1}N_{3}O_{2}F_{1} (M – BF4) 538.2623, found 538.2646. 1H NMR (500.0 MHz, CDCl3, 298 K): δ = 5.1 (m, 6H; CH2), 2.16 (s, 9H; (CH3)3), 2.02 (d, 3J_{1,3J} = 14.3 Hz, 2H; PC(i-C6H5)3), 1.40 (d, 3J_{1,3J} = 6.1 Hz, 3H; (CH3)2CH). 13C NMR (125.7 MHz, CDCl3, 298 K) δ = 128.7 (w), 125.3 (w), 118.5 (w), 115.1 (w), 112.5 (w), 110.4 (m), 109.0 (m), 104.7 (s), 101.0 (s), 93.0 (s), 85.5 (m), 799 (s), 784 (m), 741 (w), 689 (w), 627 (w), 577 (w), 561 (w), 519 (w), 484 (w).

**Synthesis of [p-C6H4-PhN2(pBu2)][BF4]** (1k): [p-C6H4-PhN2-(pBu2)][BF4] was synthesised from 2-p-toluenediazonium tetrafluoroborate [p-C6H4-PhN2][BF4] (86.6 mg, 0.42 mmol, 1.0 equiv) and isolated as a pink powder in 82 % yield (140.9 mg, 0.435 mmol). M.p. (open capillary): 92–98 °C (decomposition). 1H NMR (500.0 MHz, CDCl3, 298 K): δ = 8.4 (s; 3H, Ph), 7.46 (d, 3J_{1,3J} = 8.6 Hz, 2H; o-PhH-N), 7.46 (t, 3J_{1,3J} = 7.6 Hz, 7H; p-OPhH), 7.17–7.11 (m, 4H; m-PhH-N, o-OPhH), 1.71 (d, 3J_{1,3J} = 14.3, 27H; PC(i-C6H5)3). 19F NMR (160.4 MHz, CDCl3, 298 K) δ = −0.9 (s). 13C NMR (125.7 MHz, CDCl3, 298 K) δ = 153.1 (s; p-PhH-N), 150.3 (d, 2J_{1,2J} = 40.2 Hz; ipso-PhH-CN), 130.6 (s; m-OPhH), 126.9 (s; o-PhH-CN), 126.1 (s; Ph-CN), 124.2 (d, 3J_{1,3J} = 24.4 Hz; PC(i-C6H5)3), 29.9 (s; PC(i-C6H5)3). 19F NMR (282.4 MHz, CDCl3, 293 K) δ = −153.3 (s), −153.3 (s). 31P{1H} NMR (202.4 MHz, CDCl3, 298 K) δ = 41.7 (d, 1J_{1,3J} = 39.7 Hz; P(i-C6H5)3), 21.9 (s; (CH3)3). HR-MS (ESI): calcd for C_{33}H_{37}P_{1}N_{3}O_{2}F_{1} (M – BF4) 322.2412, found 322.2414. IR (cm–1): ν = 1666 (w), 1596 (w), 1497 (w), 1441 (w), 1330 (w), 1249 (s), 1193 (m), 1177 (w), 1135 (m), 1113 (w), 1098 (s), 1041 (d, 3J_{1,3J} = 270 Hz; Ph-CN), 918 (s; PC(i-C6H5)3), the remaining Ph-CN signal was not observed. 19F NMR (282.4 MHz, CDCl3, 298 K) δ = 31.9 (s; p-PhH-CN), 149.9 (d, 2J_{1,2J} = 41.7 Hz; ipso-PhH-CN), 115.4 (br. s; Ph-CN), 41.7 (d, 3J_{1,3J} = 29.4 Hz; PC(i-C6H5)3), 29.8 (s; PC(i-C6H5)3), the remaining Ph-CN signal was not observed. 19F NMR (282.4 MHz, CDCl3, 298 K) δ = 153.1 (s; p-PhH-CN), 150.3 (d, 2J_{1,2J} = 40.2 Hz; ipso-PhH-CN), 130.6 (s; m-OPhH), 126.9 (s; o-PhH-CN), 124.2 (d, 3J_{1,3J} = 24.4 Hz; PC(i-C6H5)3), 29.9 (s; PC(i-C6H5)3). Remaining Ph-CN signal was not observed. 19F NMR (282.4 MHz, CDCl3, 298 K) δ = 153.1 (s; p-PhH-CN), 150.3 (d, 2J_{1,2J} = 40.2 Hz; ipso-PhH-CN), 130.6 (s; m-OPhH), 126.9 (s; o-PhH-CN), 124.2 (d, 3J_{1,3J} = 24.4 Hz; PC(i-C6H5)3), 29.9 (s; PC(i-C6H5)3). Remaining Ph-CN signal was not observed. 19F NMR (282.4 MHz, CDCl3, 298 K) δ = 153.1 (s; p-PhH-CN), 150.3 (d, 2J_{1,2J} = 40.2 Hz; ipso-PhH-CN), 130.6 (s; m-OPhH), 126.9 (s; o-PhH-CN), 124.2 (d, 3J_{1,3J} = 24.4 Hz; PC(i-C6H5)3), 29.9 (s; PC(i-C6H5)3). Remaining Ph-CN signal was not observed. 19F NMR (282.4 MHz, CDCl3, 298 K) δ = 153.1 (s; p-PhH-CN), 150.3 (d, 2J_{1,2J} = 40.2 Hz; ipso-PhH-CN), 130.6 (s; m-OPhH), 126.9 (s; o-PhH-CN), 124.2 (d, 3J_{1,3J} = 24.4 Hz; PC(i-C6H5)3), 29.9 (s; PC(i-C6H5)3). Remaining Ph-CN signal was not observed.
2.38 (s, 9H; p 774 (m), 751 (w), 732 (m), 703 (w), 686 (w), 654 (s), 614 (w), 573 (w), as anti-solvent. M.p. (open capillary): 91–153 °C (decomposition). 1H NMR (500.0 MHz, CDCl3, 298 K): δ = 7.77, 7.75, 7.67, 7.66 (AB-type, 4H; BrPh2), 7.13 (s, 3H; m-Ph), 7.11 (s, 3H; m-Mes), 2.38 (s, 9H; p-mesCH3), 2.13 (s, 9H; o-mesCH3), 1.99 (s, 9H; o-mesCH3). 11B{1H} NMR (160.4 MHz, CDCl3, 298 K): δ = −0.9 (s). 13C NMR (125.7 MHz, CDCl3, 298 K): δ = 151.2 (d, 1J_{C,B} = 52.3 Hz; isop-PhC), 146.9 (s; p-Mes), 145.2 (d, 1J_{C,P} = 70.0 Hz; o-Mes), 144.7 (d, 1J_{C,P} = 11.8 Hz; o-Mes), 133.9 (s; o-Ph), 133.7 (d, 1J_{C,P} = 121.1 Hz; m-MesCH3), 133.1 (d, 1J_{C,P} = 11.7 Hz; m-MesCH3), 132.4 (s; p-MesCH3), 125.7 (s; p-MePh), 115.2 (d, 1J_{C,B} = 82.6 Hz; isop-PhC), 24.4 (s; o-MesCH3), 21.4 (s; p-MesCH3). 19F NMR (282.4 MHz, CDCl3, 299 K): δ = −154.2 (s), −154.3 (s). 31P{1H} NMR (202.4 MHz, CDCl3, 298 K): δ = 45.2 (s; product, 96 %), −27.9 (s; impurity presumably [Mes3PH][BF4], 4 %). HR-MS (ESI): calcd for C33H37Br1N2P1 (M – BF4) 573.1863, found 573.1857. 19F NMR (282.4 MHz, CDCl3, 294 K): δ = −154.2 (s), −154.3 (s). 31P{1H} NMR (202.4 MHz, CDCl3, 299 K): δ = 42.7 (s; product, 96 %), −27.8 (s; impurity presumably [Mes3PH][BF4], 4 %). HR-MS (ESI): calcd for C35H43N3P1 (M – BF4) 523.2878, found 523.2882. 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-Kα radiation (λ = 0.15418 Å). Dual space methods (SHELXL)[22] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F2). Hydrogen atoms were located by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied. In 2m the BF4 anion and in 2f the solvent CH2Cl2 are disordered (see cif-files for details).
2d: Red crystals, $C_{31}H_{39}BrN_2P^+$, $\alpha = 78.334(2)\degree$, $\beta = 75.402(2)\degree$, $\gamma = 11.4682(5)\,\text{Å}$, $V = 1709.44(15)\,\text{Å}^3$, $Z = 2$, $\rho = 1.446\,\text{Mg/m}^3$, $\mu(\text{Cu-K})_\alpha = 3.934\,\text{mm}^{-1}$, $F(000) = 766$, $2\theta_{\text{max}} = 144.4\degree$, 32836 reflections, of which 6510 were independent ($R_{	ext{int}} = 0.030$), 423 parameters, $R_1 = 0.035$ (for 6011 $I > 2\sigma(I)$), $wR_2 = 0.173$ (all data), $S = 1.09$, largest diff. peak/hole $= 1.812$ (see cif-file for details).

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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13[13] $\lambda_{\text{max}}$ is measured in dry DCM, a small bathochromic shift of $\lambda_{\text{max}}$ is expected, for more information see reference 10.

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