Supporting Information

Aryne Insertion into P=O Bond: One-pot Synthesis of Quaternary Phosphonium Triflates

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Copies of NMR, HRMS spectra and single crystal X-ray analysis of 3aa
$^{1}$H and $^{13}$C NMR spectra of 3aa

![NMR Spectra of 3aa](image)

1H NMR spectrum

13C NMR spectrum
$^{31}$P NMR spectrum of 3aa

![NMR spectrum](image)

HRMS spectrum of 3aa

![HRMS spectrum](image)
$^1$H and $^{13}$C NMR spectra of 3ab
$^{31}$P NMR spectrum of 3ab

S spectrum of 3ab
$^{1}$H and $^{13}$C NMR spectra of 3ac
$^{31}$P NMR spectrum of 3ac

HRMS spectrum of 3ac
$^1$H and $^{13}$C NMR spectra of 3ad
$^{31}$P NMR spectrum of 3ad

HRMS spectrum of 3ad
$^1$H and $^{13}$C NMR spectra of 3ae

3ae
$^{31}$P NMR spectrum of 3ae

HR

MS spectrum of 3ae
$^1$H and $^{13}$C NMR spectra of 3af
$^{31}$P NMR spectrum of 3af

HRMS spectrum of 3af
$^1$H and $^{13}$C NMR spectra of 3ag

![NMR spectra diagram]
$^{31}$P NMR spectrum of 3ag

HRMS spectrum of 3ag
$^1$H and $^{13}$C NMR spectra of 3ah
$^{31}$P NMR spectrum of 3ah

RMS spectrum of 3ah
$^{1}$H and $^{13}$C NMR spectra of 3ba

![NMR Spectra Image]

The image shows the $^{1}$H and $^{13}$C NMR spectra of 3ba, with detailed spectral data provided in the figure. The spectra are labeled with chemical shifts in ppm, ranging from 0.0 to 8.0 for $^{1}$H and from 0.0 to 160.0 for $^{13}$C.
$^{31}P$ NMR spectrum of 3ba

HRMS spectrum of 3ba
$^{1}\text{H}$ and $^{13}\text{C}$ NMR spectra of 3bb
$^{31}$P NMR spectrum of 3bb

[Image of $^{31}$P NMR spectrum]

HRMS spectrum of 3bb

[Image of HRMS spectrum]
$^1$H and $^{13}$C NMR spectra of 3bc
$^{31}$P NMR spectrum of 3bc

HRMS spectrum of 3bc
$^1$H and $^{13}$C NMR spectra of 3bd

![NMR Spectra Diagram]
$^{31}$P NMR spectrum of 3bd

HRMS spectrum of 3bd
$^{1}$H and $^{13}$C NMR spectra of 3be

3be

C NMR spectra of 3be
$^{31}$P NMR spectrum of 3be

HRMS spectrum of 3be
$^1$H and $^{13}$C NMR spectra of 3bf

![NMR Spectra Image]
$^{31}$P NMR spectrum of 3bf

HRMS spectrum of 3bf
$^1$H and $^{13}$C NMR spectra of 3bg
$^{31}$P NMR spectrum of 3bg

HRMS spectrum of 3bg
$^1$H and $^{13}$C NMR spectra of 3bh
$^{31}$P NMR spectrum of 3bh

HRMS spectrum of 3bh
$^1$H and $^{13}$C NMR spectra of the mixture of 3ca, 3ca', 3c’a and 3c’a’
$^3$P NMR spectra of the mixture of 3ca, 3ca', 3c'a and 3c'a'

HRMS spectrum of 3ca
$^{1}$H and $^{13}$C NMR spectra of 3db

S36
$^{31}P$ NMR spectrum of 3db

MS spectrum of 3db
$^1$H and $^{13}$C NMR spectra of 3dg
$^{31}$P NMR spectrum of 3dg
MS spectrum of 3dg

$^1$H and $^{13}$C NMR spectra of 3dh
$^{31}$P NMR spectrum of 3dh

S41
HRMS spectrum of 3dh
$^1$H and $^{13}$C NMR spectra of 3ea

![NMR Spectra Diagram](image-url)
$^{31}$P NMR spectrum of 3ea

HRMS spectrum of 3ea
HRMS spectrum of 3aa-D
Sample preparation and crystal structure determination of 3aa

The pure compound 3aa as obtained from column chromatography was crystallized from ethyl acetate.

Single crystal X-ray crystallographic data of the colourless block shaped crystals of 3aa was collected at 296 K with Mo Kα radiation (λ = 0.71073 Å) using a Bruker SMART CCD diffractometer equipped with graphite monochromators. The BRUKER SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using BRUKER SAINT software. The structures were solved by direct methods and refined by full-matrix least-square calculations using SHELXL 2014/7 software. All the non-H atoms were refined in the anisotropic approximation against F² of all reflections. Crystal data and details of the final refinement parameters are summarized below.

Crystal data for 3aa: C₃₁H₂₄F₃O₄PS, M = 580.53 gmol⁻¹, Monoclinic, space group P 2₁/n, a = 9.5734(4) Å, b = 15.0468(7) Å, c = 19.4977(9) Å, β (°) = 92.992(3), V = 2804.8(2) Å³, Z = 4, F000 = 1200, μ = 0.228 mm⁻¹, T = 296 (2) K, 30535 reflections collected, 4938 unique reflections (Rint = 0.0491), 3084 observed reflections [I > 2σ(I)], R₁(obs) = 0.0725, wR₁(obs) = 0.1785, R₂(all) = 0.1100, wR₂(all) = 0.2035, 361 parameters refined, Final GOF= 0.982. Completeness to 2θ = 99.9%.

Crystallographic data for the structure reported in this paper have been deposited with the CCDC as supplementary publication no. CCDC-1888261. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].
Figure 1: X-ray crystal of structure of 3aa. Thermal ellipsoids are drawn at the 30% probability.

**CIF check Report of 3aa:**

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F000' 1201.57
h,k,lmax 11,17,23 11,17,23
Nref 4941 4938
Tmin,Tmax 0.947,0.971
Tmin' 0.938

Correction method= Not given

Data completeness= 0.999
Theta(max)= 24.999
R(reflections)= 0.0725( 3084)
wR2(reflections)= 0.2035( 4938)
S = 0.982
Npar= 361

The following ALERTS were generated. Each ALERT has the format
\textbf{test-name\_ALERT\_alert-type\_alert-level}.
Click on the hyperlinks for more details of the test.

\textbf{Alert level C}
PLAT094\_ALERT\_2\_C Ratio of Maximum / Minimum Residual Density .... 2.32
Report
PLAT231\_ALERT\_4\_CHirshfeld Test (Solvent) S1 --O4 . 8.5
s.u.
PLAT231\_ALERT\_4\_CHirshfeld Test (Solvent) S1 --C31 . 6.2
s.u.
PLAT244\_ALERT\_4\_C Low 'Solvent' Ueq as Compared to Neighbors of
Check
S1
PLAT260\_ALERT\_2\_C Large Average Ueq of Residue Including S1 0.164
Check
PLAT331\_ALERT\_2\_C Small Aver Phenyl C-C Dist C1 --C6 . 1.37
Ang.
PLAT340\_ALERT\_3\_C Low Bond Precision on C-C Bonds ............... 0.00673
Ang.
PLAT906\_ALERT\_3\_C Large K Value in the Analysis of Variance ...... 5.409
Check
PLAT911\_ALERT\_3\_C Missing FCF ReflBetweenThmin&STh/L= 0.595 3
Report

\textbf{Alert level G}
PLAT244\_ALERT\_4\_G Low 'Solvent' Ueq as Compared to Neighbors of C31
Check
PLAT883\_ALERT\_1\_G No Info/Value for _atom_sites_solution_primary . Please
Do!
PLAT978\_ALERT\_2\_G Number C-C Bonds with Positive Residual Density.1 Info

0 \textbf{ALERT level A} = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
9 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check