Supporting Information

Structural verification and new reactivity for Stang’s reagent [PhI(CN)][OTf]

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1. EXPERIMENTAL SECTION

I. Experimental Details

All reagents were purchased from Sigma Aldrich and used as received. Glovebox solvents were dried using an Innovative Technologies Solvent Purification System. The dried solvents were stored under N\textsubscript{2} atmosphere over 3 Å molecular sieves in the glovebox. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried by stirring for three days over CaH\textsubscript{2}, distilled prior to use, and stored in the glovebox over 3 Å molecular sieves. Stang’s reagent was synthesised using a modified synthesis from Holt and Gaunt using PIDA instead of PIFA.\textsuperscript{1} All other reagents were purchased from Sigma Aldrich and used as received. All experiments were completed under inert conditions utilising Schleck line and glovebox techniques unless stated otherwise. Glassware was dried in an oven at 120 °C overnight and transferred to the glovebox port or Schlenk line where it was subjected to three vacuum cycles over 30 minutes prior to use. NMR spectra for all experiments were recorded using Bruker Ultrashield Plus 500 MHz and Ascend 400 MHz spectrometers.

II. X-ray Crystallography Details

Single crystals were selected under paratone-n oil, mounted on nylon loops and placed into a cold stream of N\textsubscript{2} (175 K for the crystal of Stang’s reagent and 220 K for the 4-cyanopyridine analogue of CDAP) on a Rigaku SuperNova CCD diffractometer using Cu Ka radiation. Structure solution and refinement were performed using the SHELXTL suite of software.
III. Syntheses

a. Synthesis of Stang’s reagent

To a stirred solution of PIDA (20.0 mg, 0.0621 mmol, 1 eq) and TMSOTf (13.8 mg, 0.0621 mmol, 1 eq) in CH$_2$Cl$_2$ was added TMSCN (9.2 mg, 0.0931 mmol, 1.5 eq). An immediate precipitate formed that was washed with hexane (3 x 1 mL), and the volatiles removed to afford a white powder (19 mg, 81% yield). Single crystals suitable for X-Ray crystallography were obtained via vapour diffusion (MeCN:Et$_2$O) at -35 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.23-8.21 (d, J = 8 Hz, 2H), 7.83 (t, J = 16 Hz, 1H), 7.68 (t, J = 16 Hz, 2H); $^{19}$F NMR (CDCl$_3$): -77.7

b. Synthesis of CDAP OTf

To a solution of Stang’s reagent (10 mg, 0.0264 mmol, 1 eq) in MeCN (0.5 mL) was added 4-dimethylaminopyridine (3.20 mg, 0.0264 mmol, 1 eq). The reaction immediately turned yellow and was stirred for 5 minutes. Et$_2$O (3 mL) was added to form a precipitate. The precipitate was washed with Et$_2$O (3 x 1 mL) and dried in vacuo to afford a white solid (5.8 mg, 74 % yield).
c. Synthesis of the 4-cyanopyridine derivative of CDAP OTf

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\begin{align*}
&\text{To a stirred solution of Stang’s reagent (10 mg, 0.0264 mmol, 1 eq) in MeCN (0.5 mL) was added 4-}
\text{cyanopyridine (2.7 mg, 0.0264 mmol, 1 eq). The solution immediately turned yellow and was further}
\text{stirred for 5 minutes. Et}_2\text{O (1 mL) was added, and the resultant precipitate was washed with additional}
\text{Et}_2\text{O (3 x 1 mL). The volatiles were removed to afford a crystalline brown solid (5.2 mg, 73 % yield).}
\text{Single crystals suitable for X-Ray crystallography were obtained via vapour diffusion (MeCN:Et}_2\text{O) at -}
35 \text{°C.}
\end{align*}
\]

\[^1\text{H NMR (400 MHz, CD}_3\text{CN) } \delta \text{ (ppm): 9.42 (d, J = 7.26 Hz, 2H), 8.64 (d, J = 7.26, 2H); }\]

\[^{19}\text{F NMR (CD}_3\text{CN): -79.3}\]

d. Reaction of Stang’s reagent with Et\textsubscript{3}PO

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\begin{align*}
&\text{To a solution of Stang’s reagent (10 mg, 0.02638 mmol) in CDCl}_3 \text{ (0.5 ml) was added Et}_3\text{P=O (3.5 mg,}
\text{ 0.02638 mmol). The reaction immediately turned clear and was stirred for 5 minutes, and then NMR}
\text{experiments were taken for analysis including }^{31}\text{P NMR to determine Lewis acidity by the Gutmann-}
\text{Beckett method. This method determines the acceptor number (AN) by subtracting the }^{31}\text{P NMR shift of}
\text{Et}_3\text{P=O (41 ppm) from the target species }^{31}\text{P NMR shift (AN = 2.21(}\delta\text{sample – 41)).}
\end{align*}
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IV. NMR Spectra

a. Stang’s reagent

Figure S 1: $^1$H NMR of Stang’s reagent in CDCl$_3$
Figure S 2: $^{19}$F NMR of Stang’s reagent in CDCl$_3$

Figure S 3: $^1$H NMR of Stang’s reagent in CD$_3$CN
Figure S 4: $^{19}$F NMR of Stang’s reagent in CD$_3$CN

Figure S 5: $^{13}$C NMR of Stang’s reagent in CD$_3$CN

b. CDAP OTf
Figure S 6: $^1$H NMR of CDAP OTf in CD$_3$CN

Figure S 7: $^{19}$F NMR of CDAP OTf in CD$_3$CN
c. Reaction of Stang’s reagent and pyridine

Figure S 8: $^1$H NMR of the crude reaction of Stang’s reagent and pyridine in CD$_3$CN

Figure S 9: $^{19}$F NMR of the crude reaction of Stang’s reagent and pyridine in CD$_3$CN
d. 4-cyanopyridine derivative of CDAP OTf

Figure S 10: $^1$H NMR of the 4-cyanopyridine derivative of CDAP OTf in CD$_3$CN

Figure S 11: $^{19}$F NMR of the 4-cyanopyridine derivative of CDAP OTf in CD$_3$CN
Figure S 12: $^{13}$C NMR of the 4-cyanopyridine derivative of CDAP OTf in CD$_3$CN

e. Reaction of Stang’s reagent and Et$_3$PO

Figure S 13: $^1$H NMR of the crude reaction of Stang’s reagent and Et$_3$PO in CDCl$_3$
Figure S 14: $^{19}$F NMR of the crude reaction of Stang’s reagent and Et$_3$PO in CDCl$_3$.

Figure S 15: $^{31}$P NMR of the crude reaction of Stang’s reagent and Et$_3$PO in CDCl$_3$. 
V. Low Resolution ESI MS

a. CDAP OTf

![Diagram of CDAP OTf with calculated m/z values]

Figure S 16: Low resolution ESI-MS of CDAP OTf

b. Stang’s reagent and pyridine
c. 4-cyanopyridine derivative of CDAP OTf
VI. Electrochemical Conductivity Measurements

Using a CH Instruments 660E potentiostat, electrochemical impedance spectroscopy (EIS) was performed on neat MeCN (1 mL), 0.1 M Phl(OAc)$_2$ (PIDA), and 0.1 M Stang’s reagent in MeCN. This was performed using a 3 mm glassy carbon working electrode, a solid carbon plate counter electrode, and Ag wire separated from the solution by porous sheath as the reference electrode.

Using an initial voltage of 1 mV and 5 mV amplitude, the frequency response was scanned from 1 Hz to 1 MHz. For assessing the ohmic resistance of the three samples, data acquired between 20-100 KHz was plotted to observe the x intercepts, indicating ohmic resistance of ~530 (MeCN), 270 (PIDA), and 40 Ω (Stang’s reagent).

2. REFERENCES