

Supporting Information

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

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1. EXPERIMENTAL SECTION

I. Experimental Details

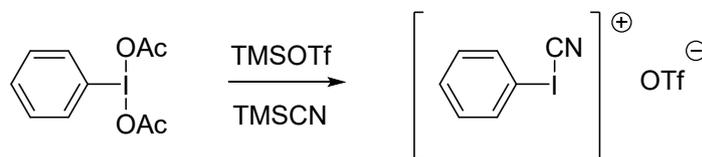
All reagents were purchased from Sigma Aldrich and used as received. Glovebox solvents were dried using an Innovative Technologies Solvent Purification System. The dried solvents were stored under N₂ atmosphere over 3 Å molecular sieves in the glovebox. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried by stirring for three days over CaH₂, 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.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 N₂ (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

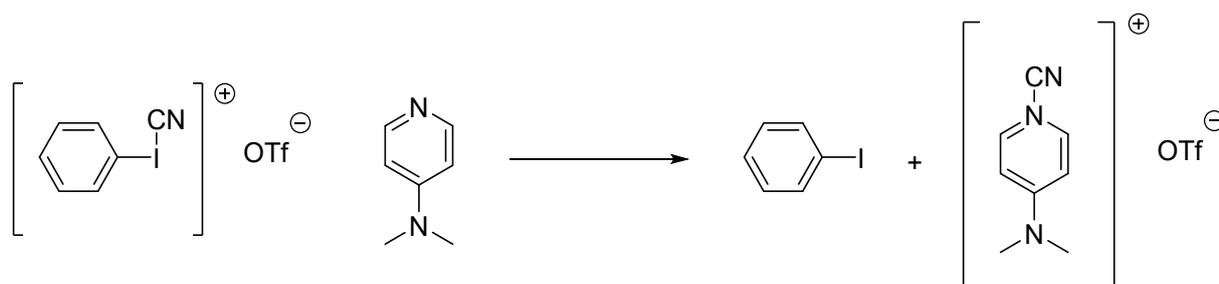
a. Synthesis of Stang's reagent



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 CH₂Cl₂ 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:Et₂O) at -35 °C.

¹H NMR (400 MHz, CDCl₃) 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); ¹⁹F NMR (CDCl₃): -77.7

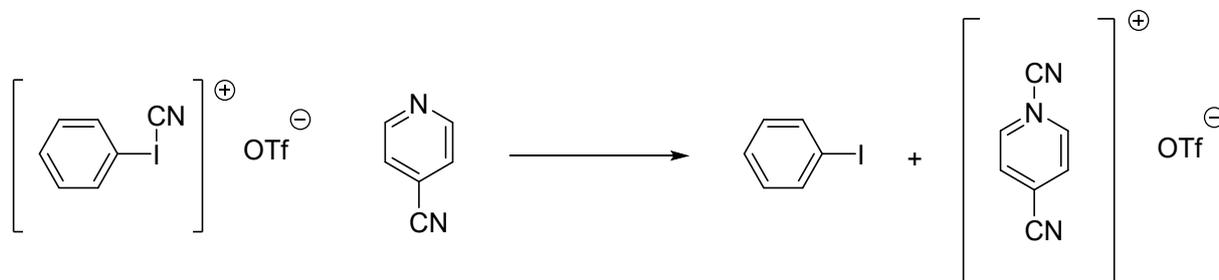
b. Synthesis of CDAP OTf



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. Et₂O (3 mL) was added to form a precipitate. The precipitate was washed with Et₂O (3 x 1 mL) and dried in vacuo to afford a white solid (5.8 mg, 74 % yield).

^1H NMR (400 MHz, CD_3CN) δ (ppm): 9.32 (d, $J = 8.34$ Hz, 2H), 7.14 (d, $J = 8.34$ Hz, 2H); ^{19}F NMR (CD_3CN): -79.3

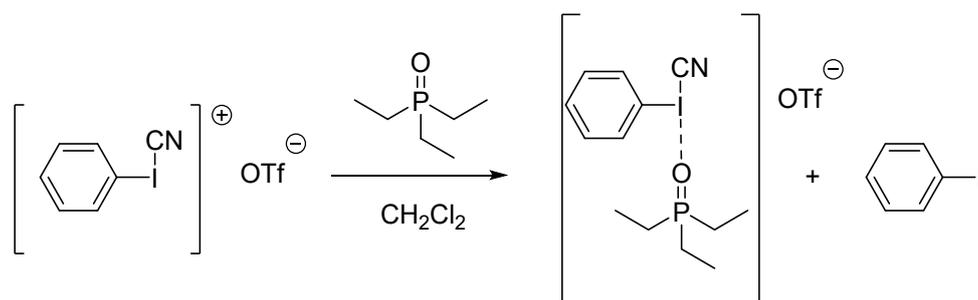
c. Synthesis of the 4-cyanopyridine derivative of CDAP OTf



To a stirred solution of Stang's reagent (10 mg, 0.0264 mmol, 1 eq) in MeCN (0.5 mL) was added 4-cyanopyridine (2.7 mg, 0.0264 mmol, 1 eq). The solution immediately turned yellow and was further stirred for 5 minutes. Et_2O (1 mL) was added, and the resultant precipitate was washed with additional Et_2O (3 x 1 mL). The volatiles were removed to afford a crystalline brown solid (5.2 mg, 73 % yield). Single crystals suitable for X-Ray crystallography were obtained via vapour diffusion ($\text{MeCN}:\text{Et}_2\text{O}$) at -35 $^\circ\text{C}$.

^1H NMR (400 MHz, CD_3CN) δ (ppm): 9.42 (d, $J = 7.26$ Hz, 2H), 8.64 (d, $J = 7.26$, 2H); ^{13}C NMR (CD_3CN): 150.7, 133.1, 121.1, 114.2; ^{19}F NMR (CD_3CN): -79.3

d. Reaction of Stang's reagent with Et_3PO



To a solution of Stang's reagent (10 mg, 0.02638 mmol) in CDCl_3 (0.5 ml) was added $\text{Et}_3\text{P}=\text{O}$ (3.5 mg, 0.02638 mmol). The reaction immediately turned clear and was stirred for 5 minutes, and then NMR experiments were taken for analysis including ^{31}P NMR to determine Lewis acidity by the Gutmann-Beckett method. This method determines the acceptor number (AN) by subtracting the ^{31}P NMR shift of $\text{Et}_3\text{P}=\text{O}$ (41 ppm) from the target species ^{31}P NMR shift ($\text{AN} = 2.21(\delta_{\text{sample}} - 41)$).

IV. NMR Spectra

a. Stang's reagent

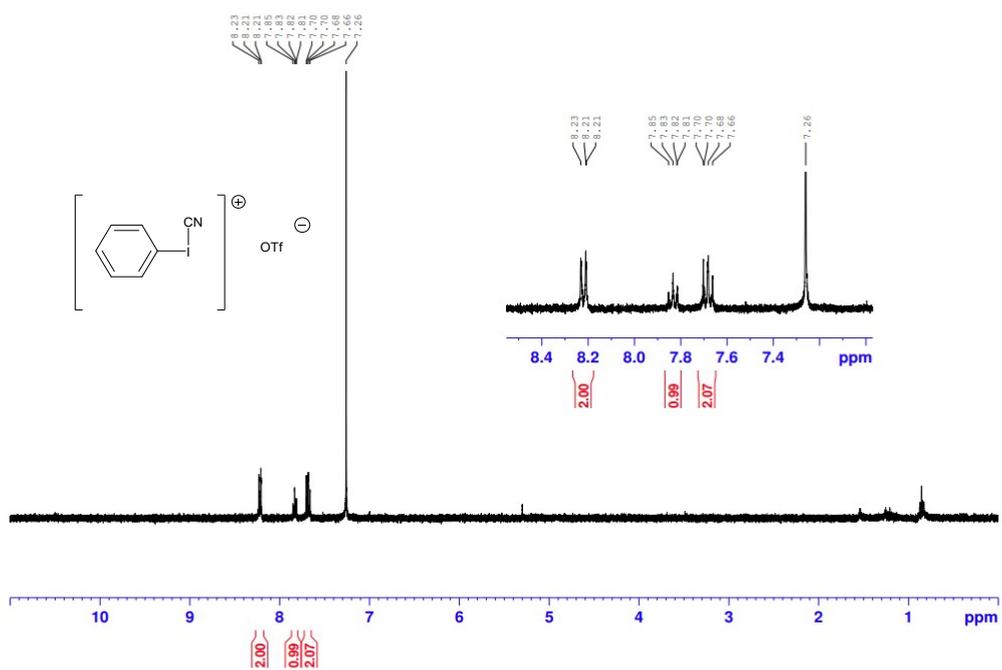


Figure S 1: ^1H NMR of Stang's reagent in CDCl_3

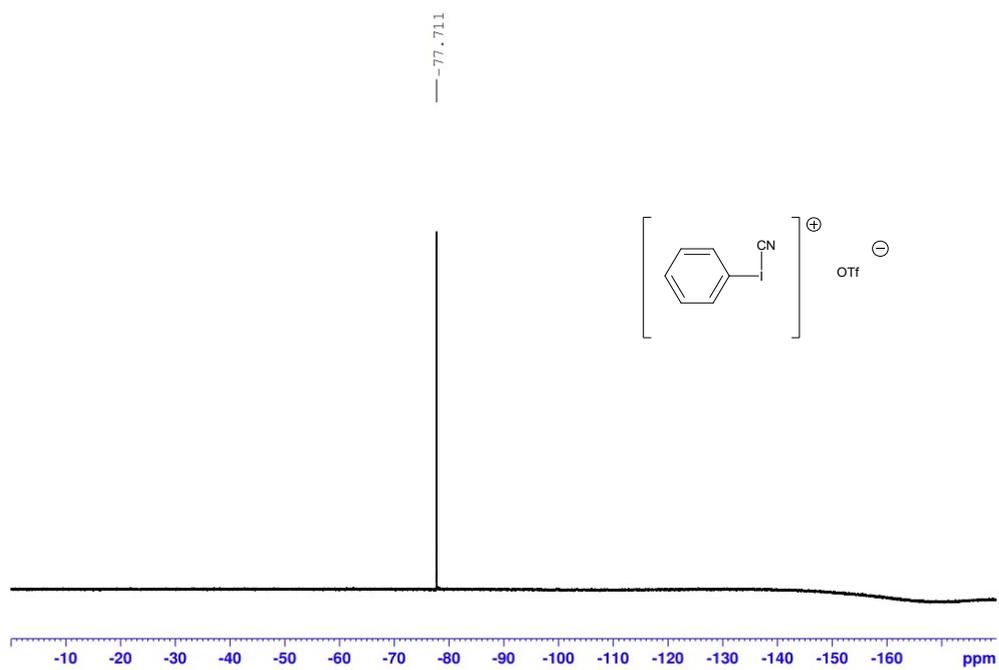


Figure S 2: ^{19}F NMR of Stang's reagent in CDCl_3

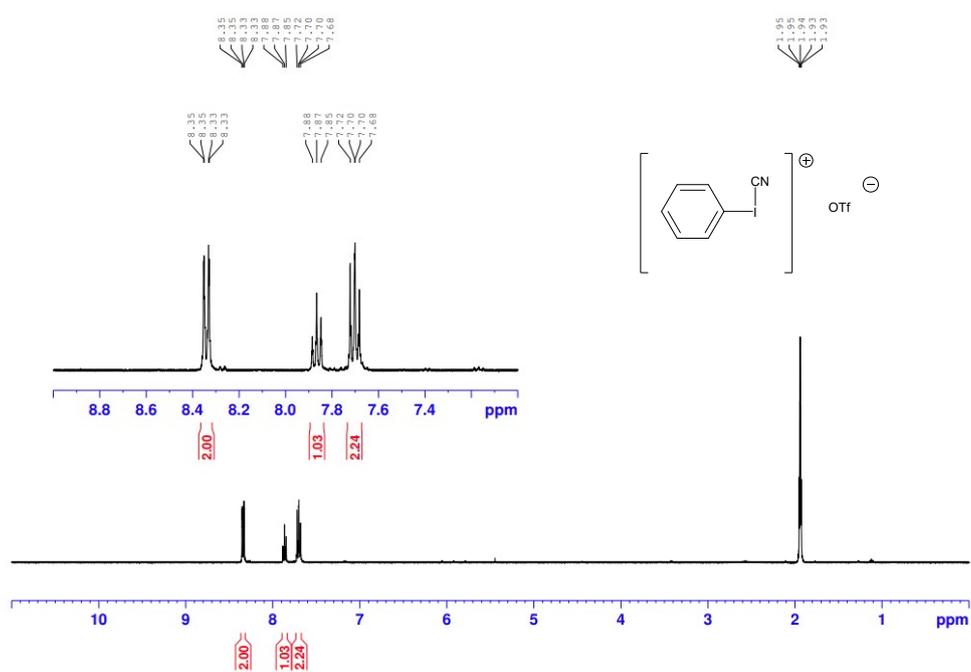


Figure S 3: ^1H NMR of Stang's reagent in CD_3CN

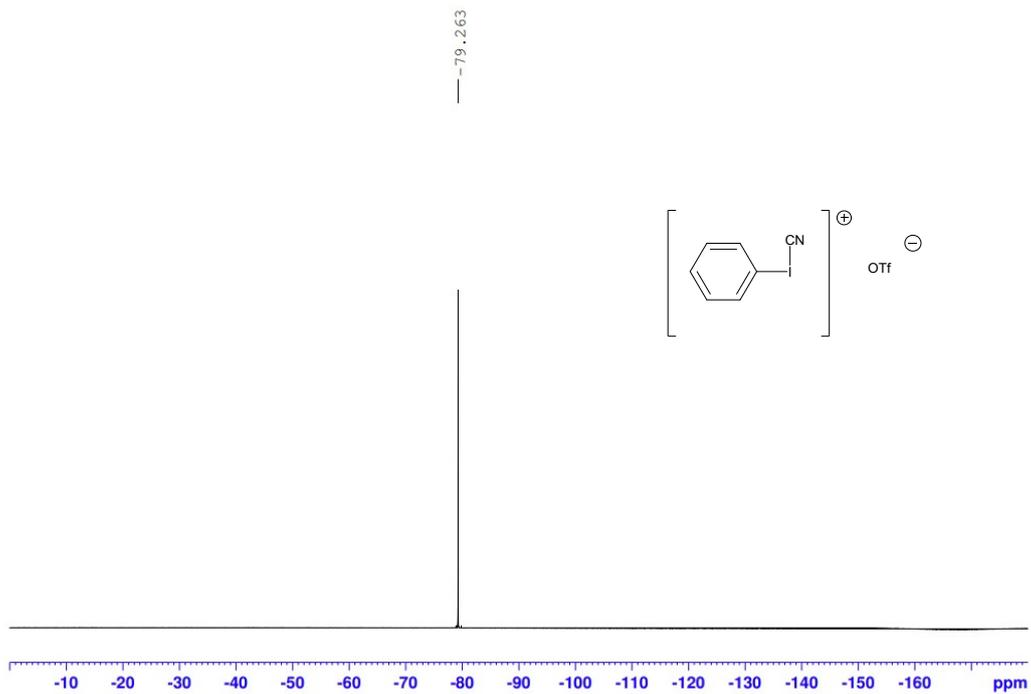


Figure S 4: ^{19}F NMR of Stang's reagent in CD_3CN

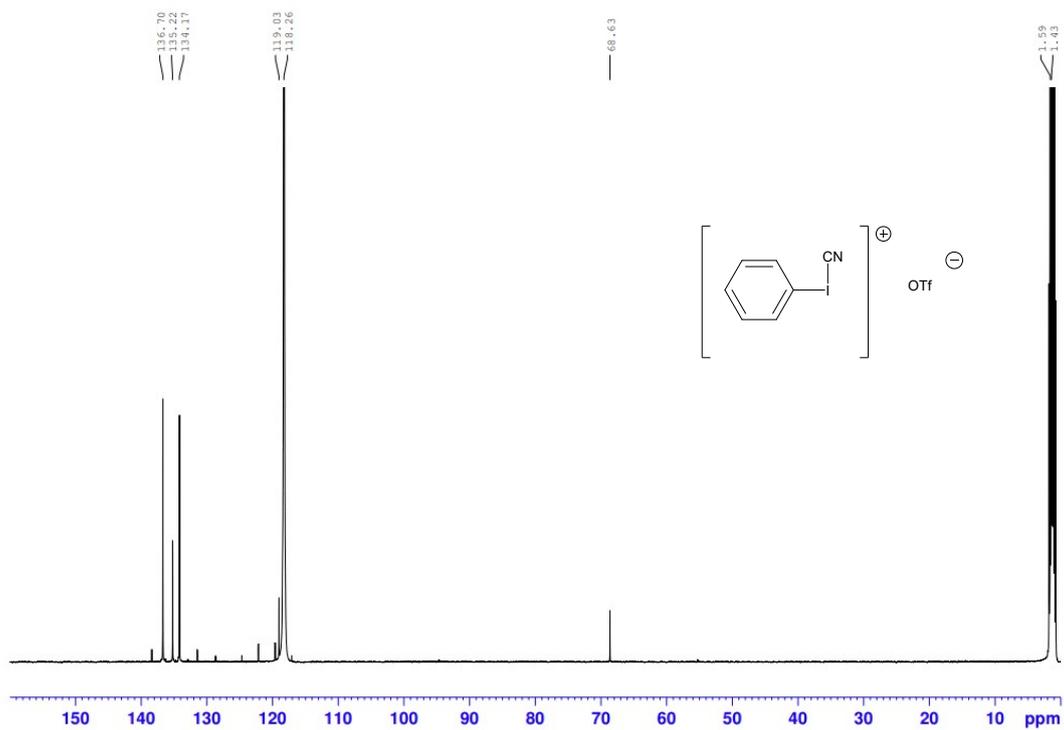


Figure S 5: ^{13}C NMR of Stang's reagent in CD_3CN

b. CDAP OTf

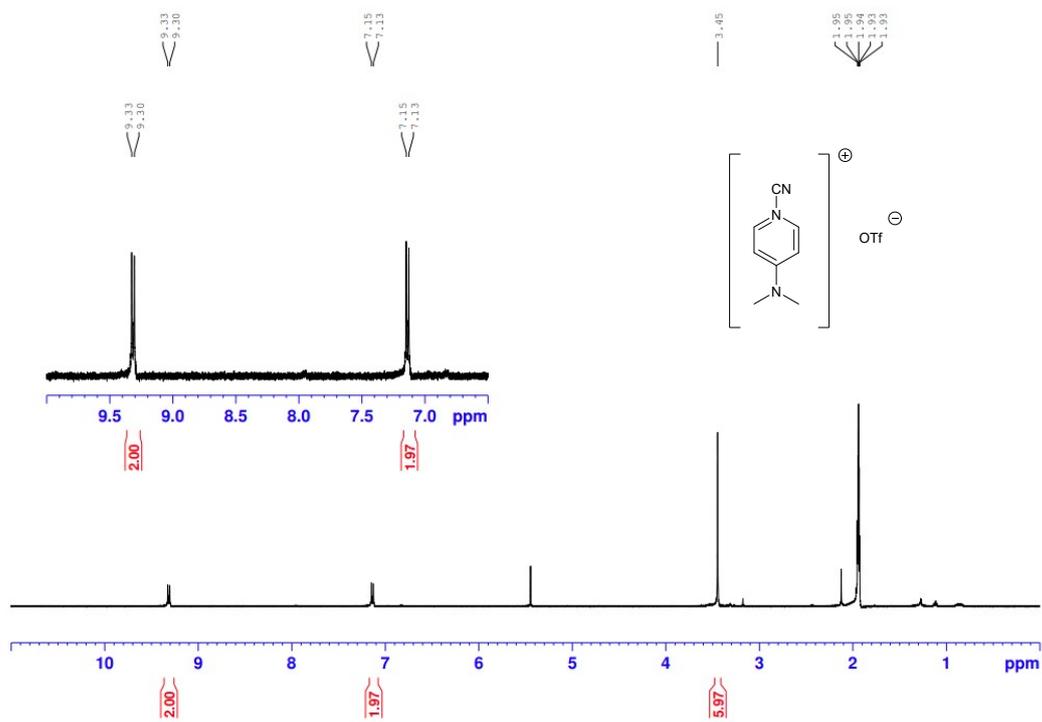


Figure S 6: ¹H NMR of CDAP OTf in CD₃CN

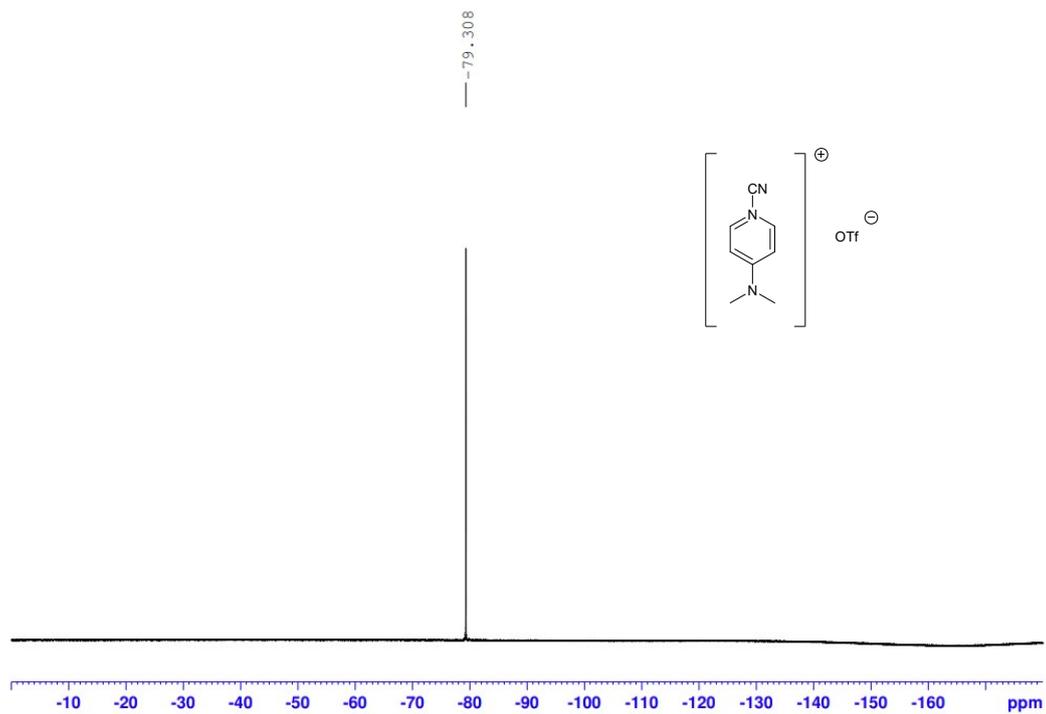


Figure S 7: ¹⁹F NMR of CDAP OTf in CD₃CN

d. 4-cyanopyridine derivative of CDAP OTf

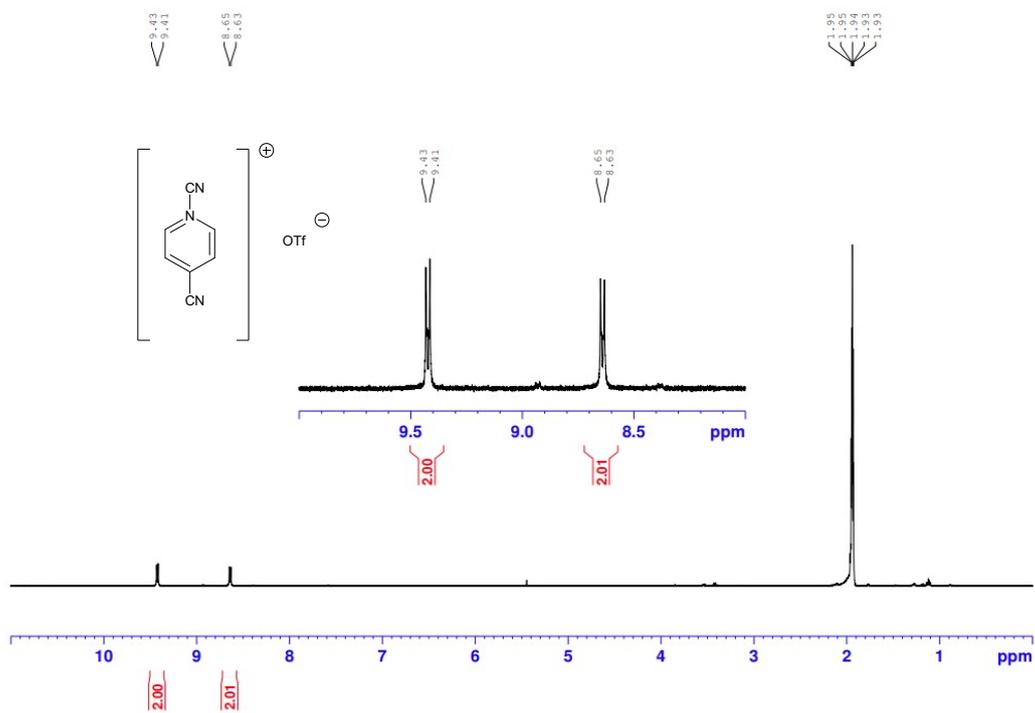


Figure S 10: ^1H NMR of the 4-cyanopyridine derivative of CDAP OTf in CD_3CN

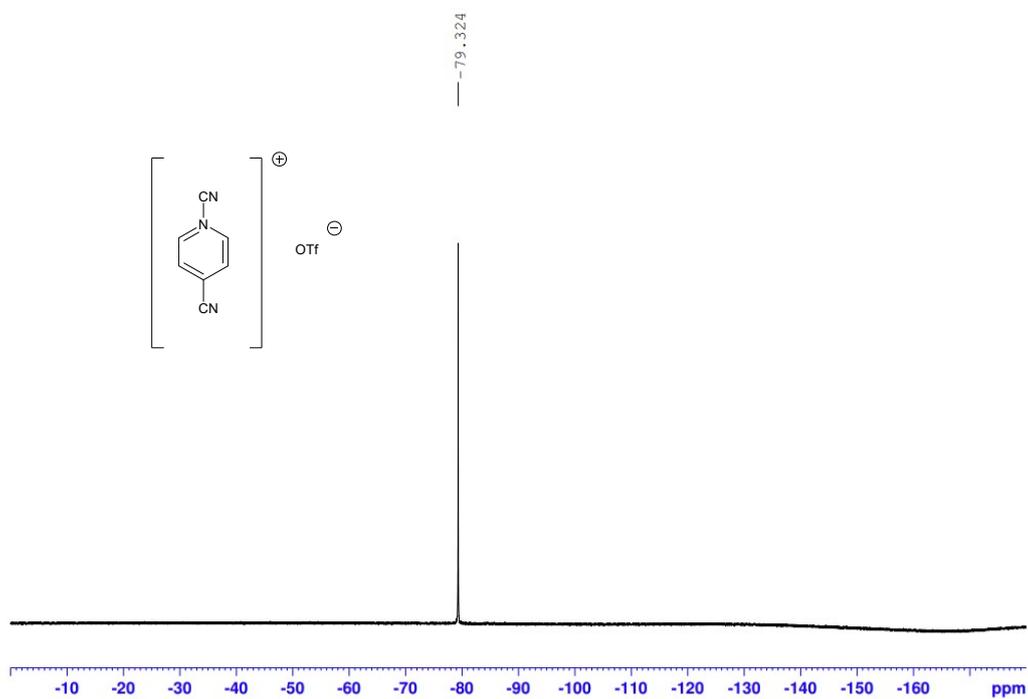


Figure S 11: ^{19}F NMR of the 4-cyanopyridine derivative of CDAP OTf in CD_3CN

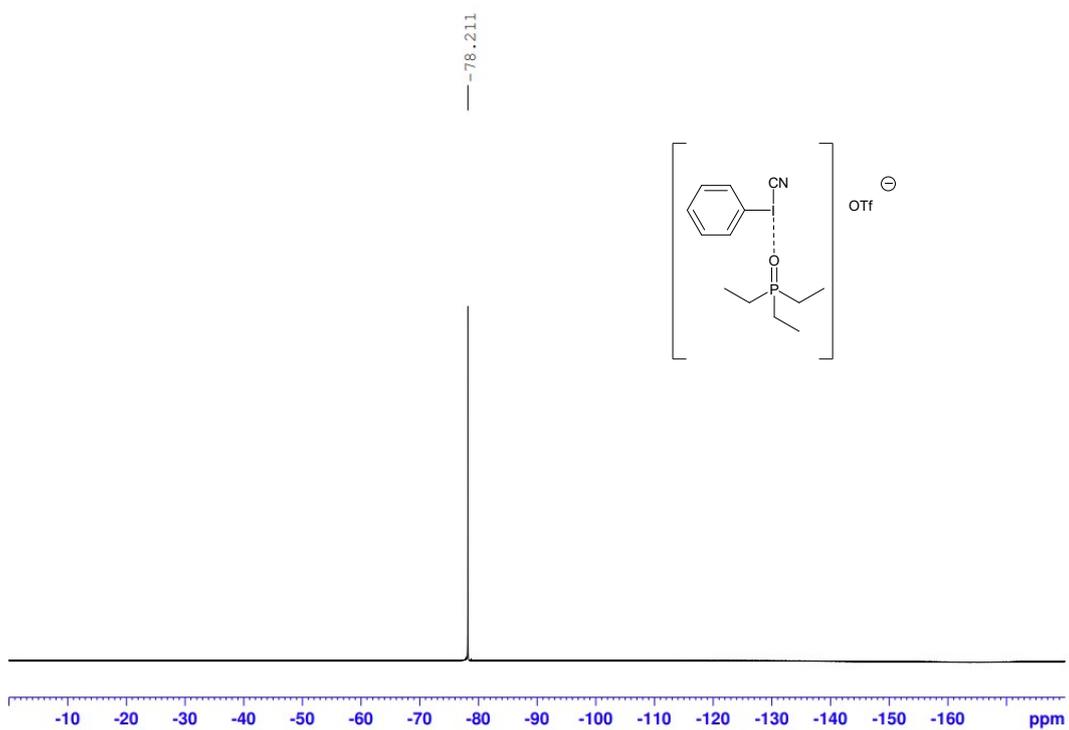


Figure S 14: ^{19}F NMR of the crude reaction of Stang's reagent and Et_3PO in CDCl_3

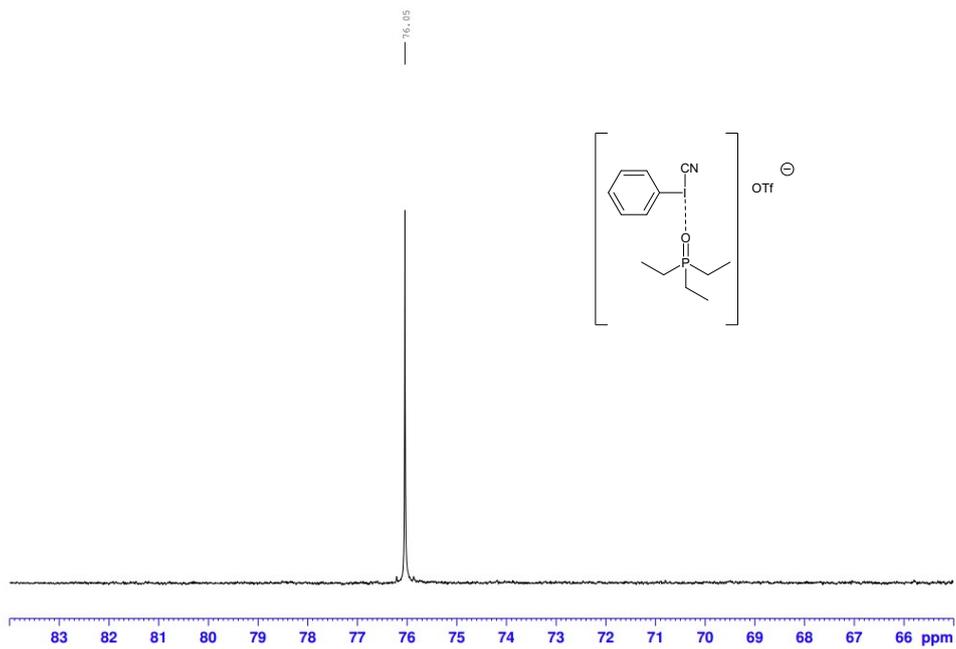


Figure S 15: ^{31}P NMR of the crude reaction of Stang's reagent and Et_3PO in CDCl_3

V. Low Resolution ESI MS

a. CDAP OTf

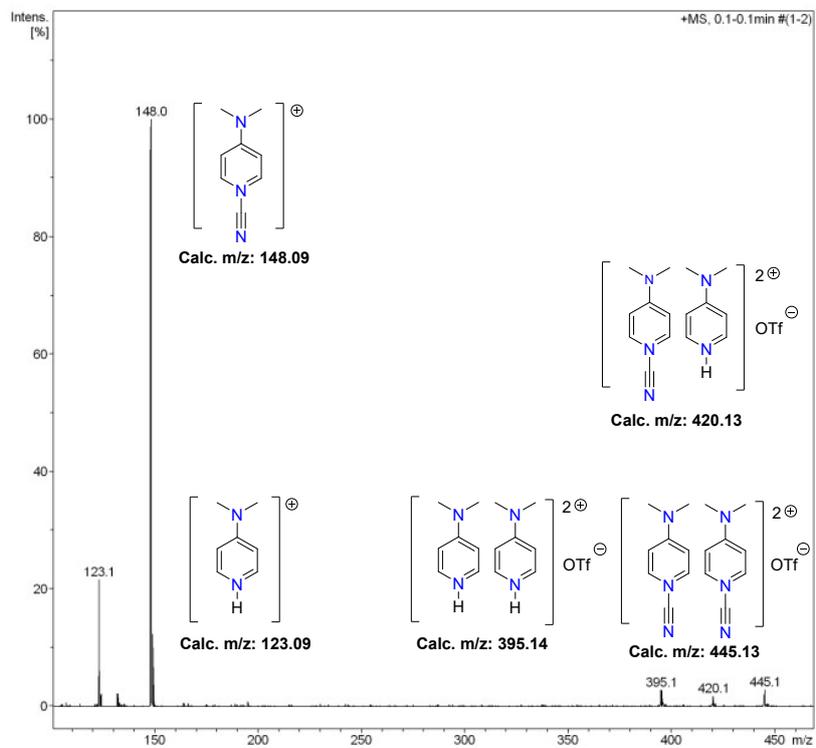


Figure S 16: Low resolution ESI-MS of CDAP OTf

b. Stang's reagent and pyridine

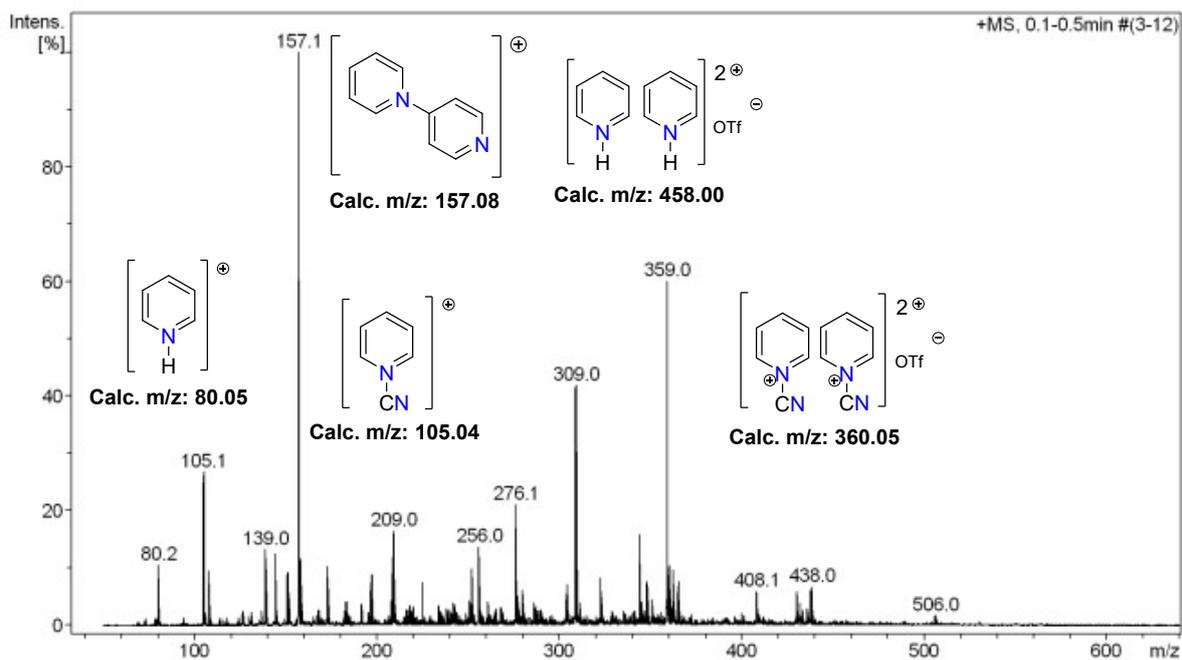


Figure S 17: Low resolution ESI-MS of Stang's reagent and pyridine

c. 4-cyanopyridine derivative of CDAP OTf

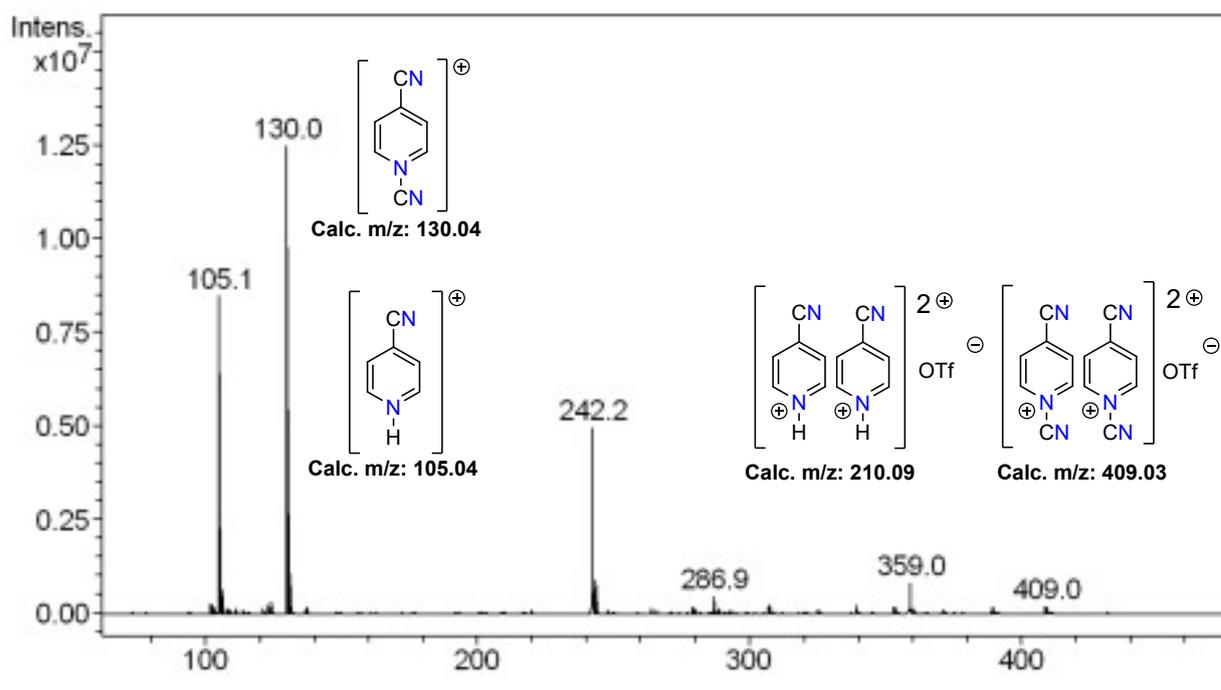


Figure S 18: Low resolution ESI-MS of the 4-cyanopyridine derivative of CDAP

VI. Electrochemical Conductivity Measurements

Using a CH Instruments 660E potentiostat, electrochemical impedance spectroscopy (EIS) was performed on neat MeCN (1 mL), 0.1 M PhI(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).

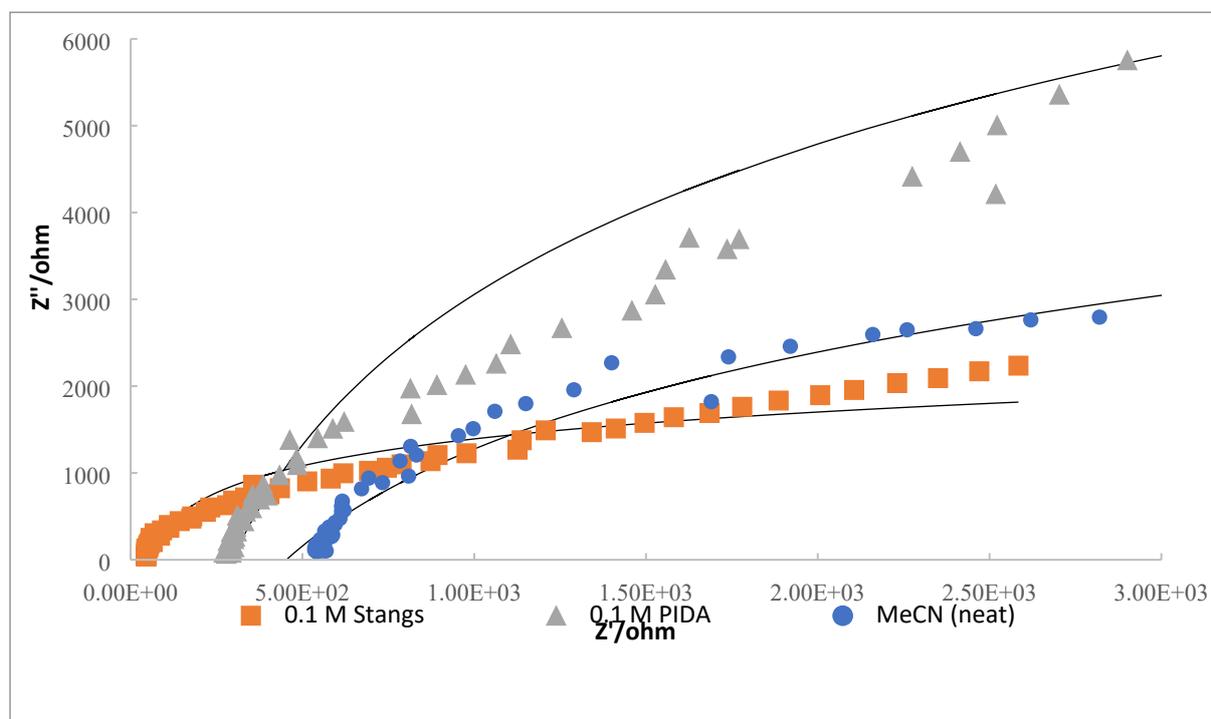


Figure S 19: Electrochemical impedance spectroscopy plots

2. REFERENCES

1. Holt, D.; Gaunt, M. J., Copper-Catalyzed Oxy-Alkenylation of Homoallylic Alcohols to Generate Functional syn-1,3-Diol Derivatives. *Angew. Chem. Int. Ed.* **2015**, *127* (27), 7968-7972.