Supporting Information

Mechanistic Studies on Dynamic Multi-Component Covalent Assemblies of Metal-Mediated Hemi-Aminal Ethers†

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Content

General Information:

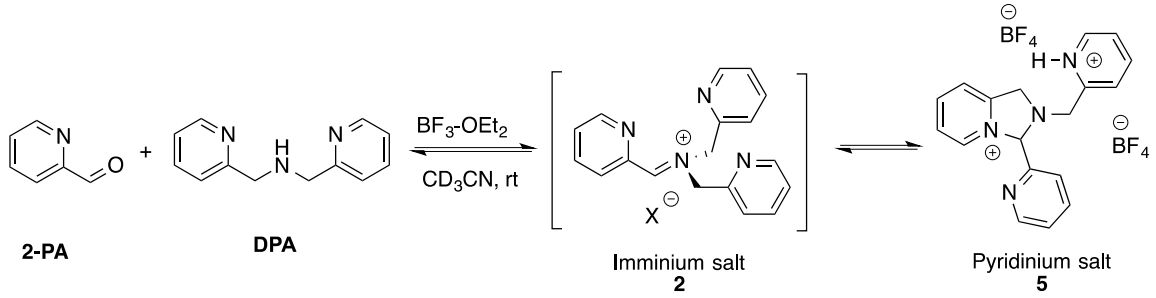
NMR spectra were recorded on Agilent MR 400 at The University of Texas at Austin NMR facility. ESI-mass spectra were obtained on Agilent 6100 at The University of Texas at Austin mass spectrometry facility. Circular dichroism (CD) spectra were recorded on a Jasco J-815 spectropolarimeter at The University of Texas facility.

Experimental Procedures:

General Procedures for Multi-component Assembly

All assembly reactions for kinetics and LEFR studies were performed *in situ* in acetonitrile without isolation and purification. Pyridine-2-carboxyaldehyde (**2-PA**, 35 mM, 1 equiv.), zinc triflate ($Zn(OTf)_2$, 35 mM, 1 equiv.), di-(2-picolyl)amine (**DPA**, 42mM, 1.2 equiv.), 4-penten-2-ol (ROH, 175 mM, 5 equiv. except for the alcohol dependence studies), and 4-(2-chloroethyl)morpholine hydrochloride (CEM-HCl, 35 mM, 1 equiv.) were stirred together in acetonitrile in the presence of 3Å activated molecular sieves. The mixture was stirred at room temperature.

Synthesis of Pyridinium Salt (5)



To pyridine-2-carboxaldehyde (**2-PA**, 3.21 mg, 0.03 mmol) in dry CD_3CN solution (60 mM), dipicolylamine (**DPA**, 7.17 mg, 0.036 mmol) was added. Then, BF_3-OEt_2 (5.11 μL, 0.036 mmol) was added dropwise. The reaction mixture was shaken for 3–5 min and then ^1H NMR, ^{13}C NMR, and mass spectrum were recorded.

Hammett Plot using σ^+:

X	K_{eq}	σ^+	log (k_X/k_H)
OH	16.9	-0.92	-0.21
Me	23.6	-0.31	-0.062
H	27.2	0	0
F	38.0	-0.07	0.14
alkyne	36.3	-	0.13
Cl	40.1	0.11	0.17
Br	39.7	0.15	0.16

Table S2. σ^+ values and corresponding log (k_X/k_H) values for encountered substituents.

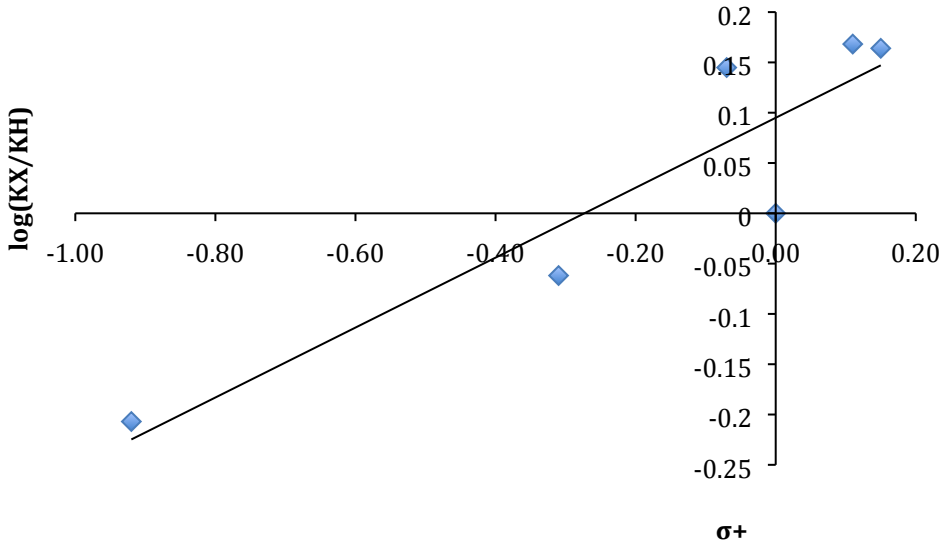


Figure S2. Hammett plot (σ^+) for four-component assembly with para substituted **2-PA**.

NMR and Mass Spectra:

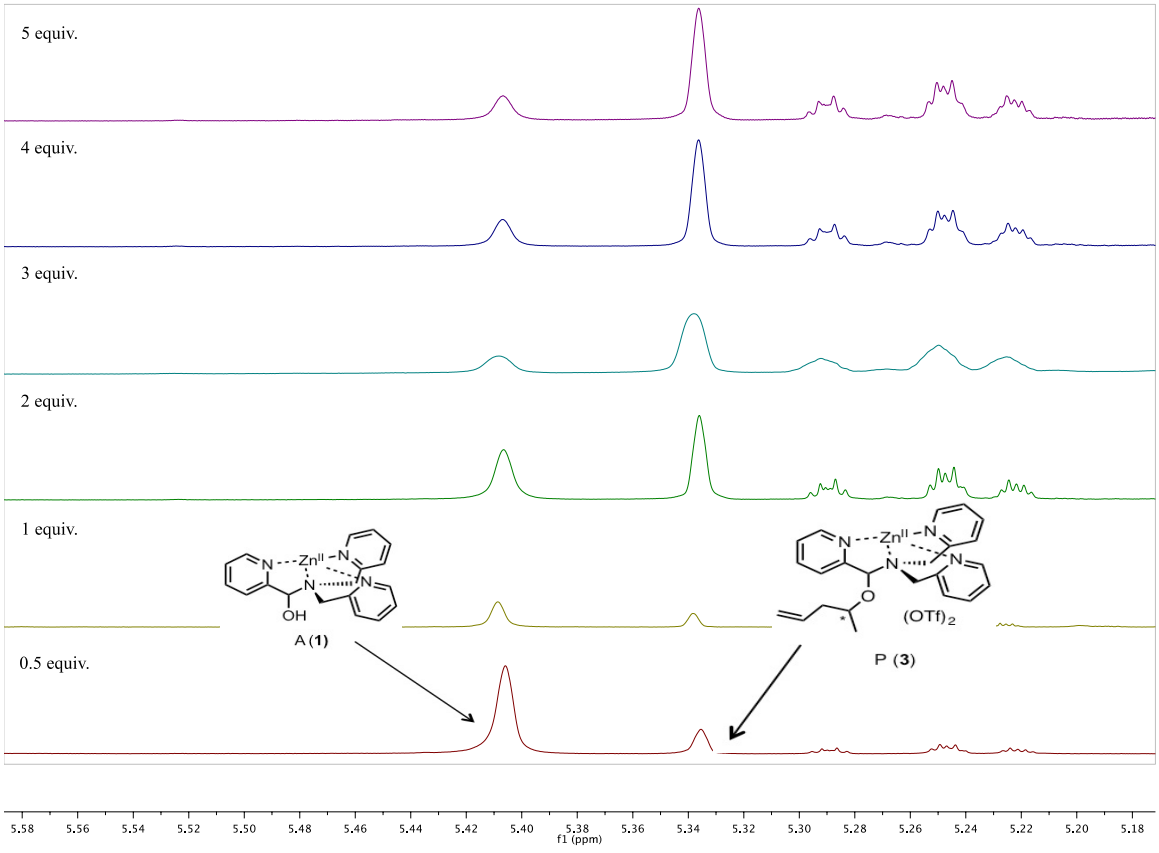


Figure S4. ^{1}H NMR of multi-component assembly varying the concentration of alcohol from 17.5 mM (0.5 equiv.) to 210 mM (6 equiv.). For alcohol, 4-penten-2-ol was chosen for all kinetic studies.

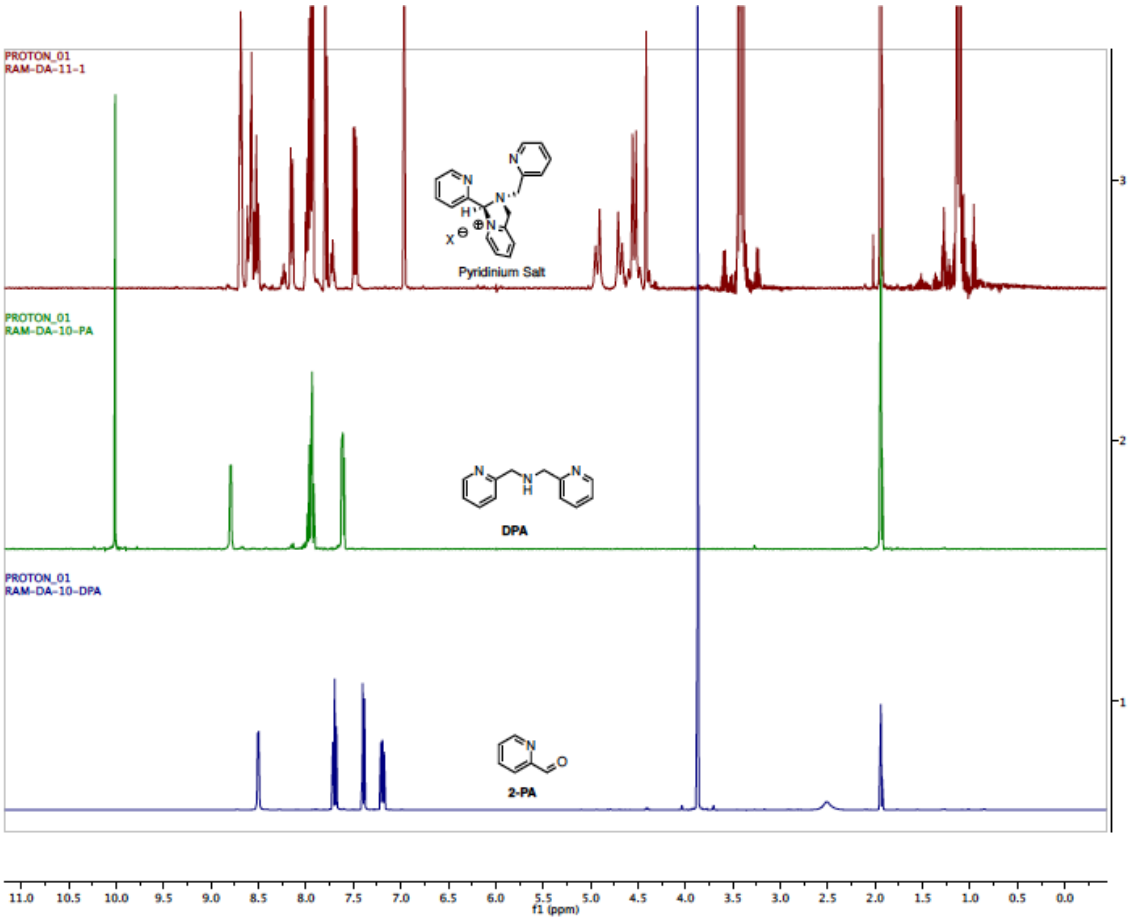


Figure S5. ^{1}H NMR of pyridinium salt (**5**) formed from **2-PA**(1.0 equiv.), **DPA** (1.2 equiv.), and BF_3-OEt_2 (1.2 equiv.) (top), ^{1}H NMR of **DPA** (middle) and ^{1}H NMR of **2-PA** (bottom). All nmrs recorded in CD_3CN.

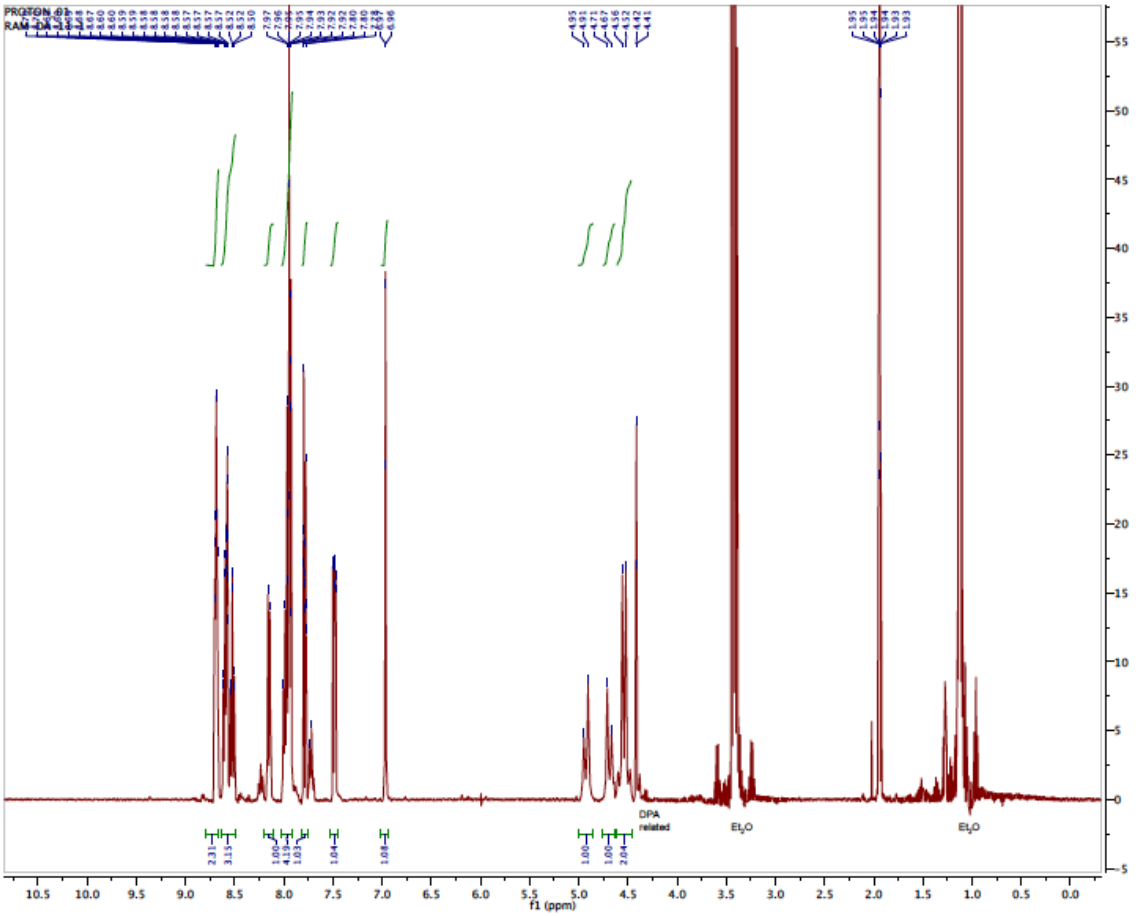


Figure S6. ^{1}H NMR of pyridinium salt (**5**) formed from **2-PA**(1.0 equiv.), **DPA** (1.2 equiv.), and BF_3-OEt_2 (1.2 equiv.) in CD_3CN.

Peaks corresponding to pyridinium salt (**5**): ^{1}H NMR (400 MHz, CD_3CN) δ 8.72–8.66 (m, 2H), 8.62–8.50 (m, 3H), 8.15 (d, J = 8.0 Hz, 1H), 8.00–7.91 (m, 4H), 7.79 (d, J = 8.0 Hz, 1H), 7.48 (m, 1H), 6.97 (s, 1H), 4.93 (d, J = 16.8 Hz, 1H), 4.69 (d, J = 16.8 Hz, 1H), 4.58 (d, J = 16.8 Hz, 1H), 4.50 (d, J = 16.8 Hz, 1H).

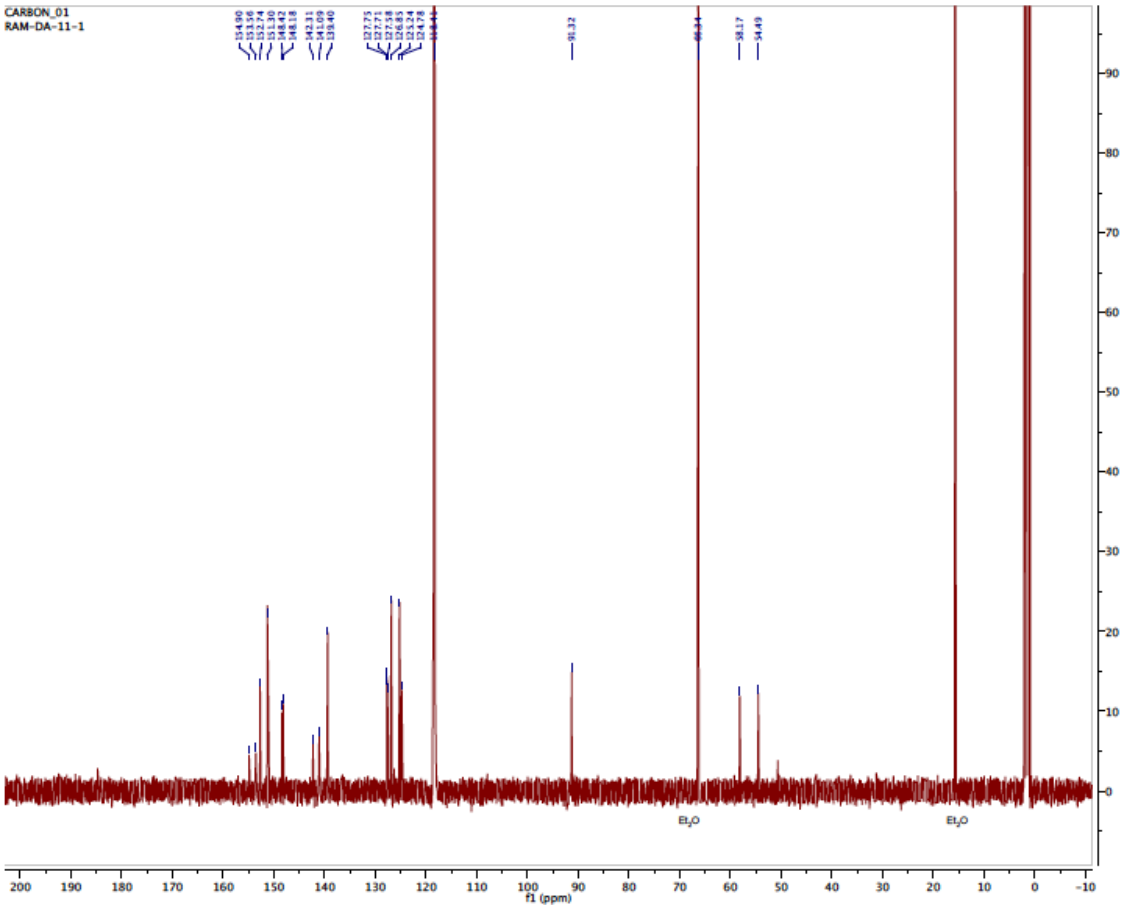


Figure S7. ^{13}C NMR of pyridinium salt (**5**) formed from **2-PA**(1.0 equiv.), **DPA** (1.2 equiv.), and BF_3-OEt_2 (1.2 equiv.) in CD_3CN.

Peaks corresponding to pyridinium salt (**5**): ^{13}C NMR (100 MHz, CD_3CN) δ 154.9, 153.6, 152.7, 151.3, 148.4, 148.2, 142.3, 141.1, 139.4, 127.8, 127.7, 127.6, 126.9, 125.2, 124.5, 91.3, 58.2, 54.5.

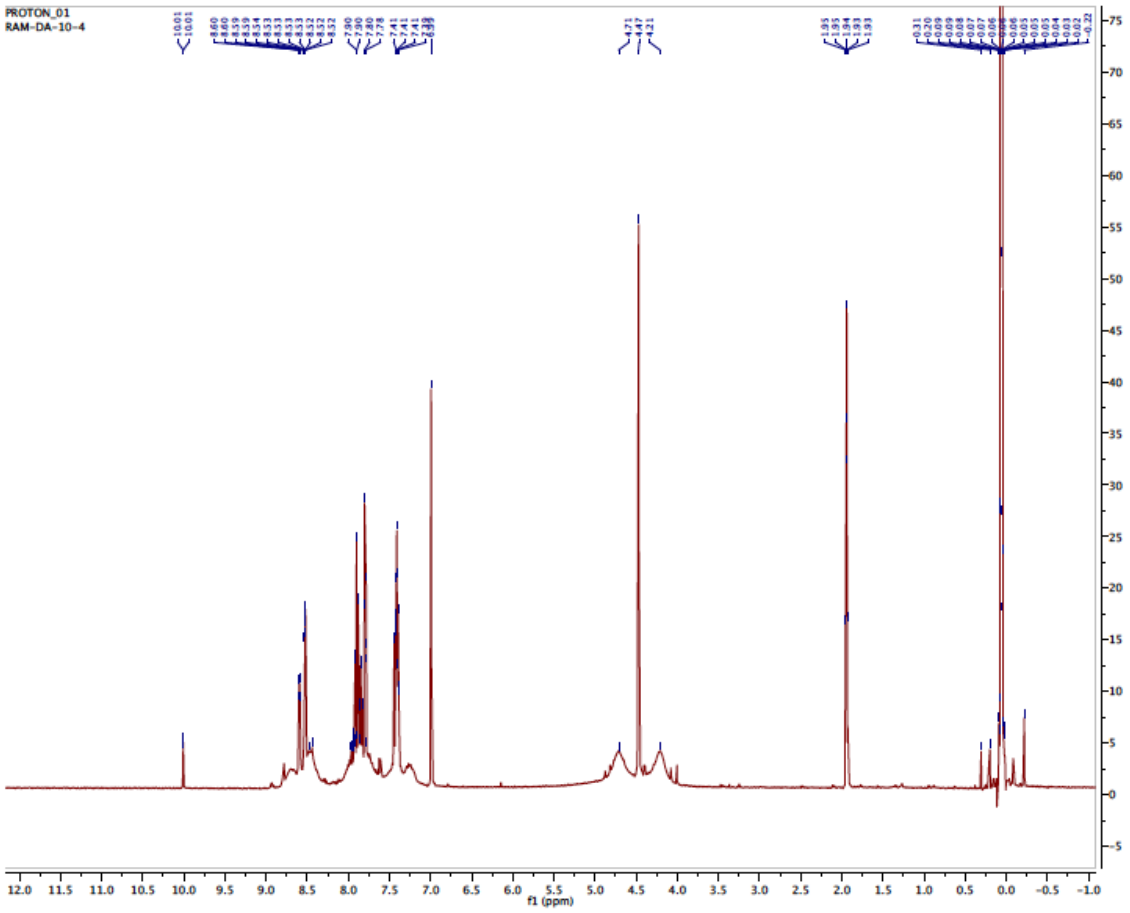


Figure S8. ^{1}H NMR of pyridinium salt (**5**) formed from **2-PA** (1.0 equiv.), **DPA** (1.2 equiv.) and TMS-OTf (1.2 equiv.) in CD_3CN.

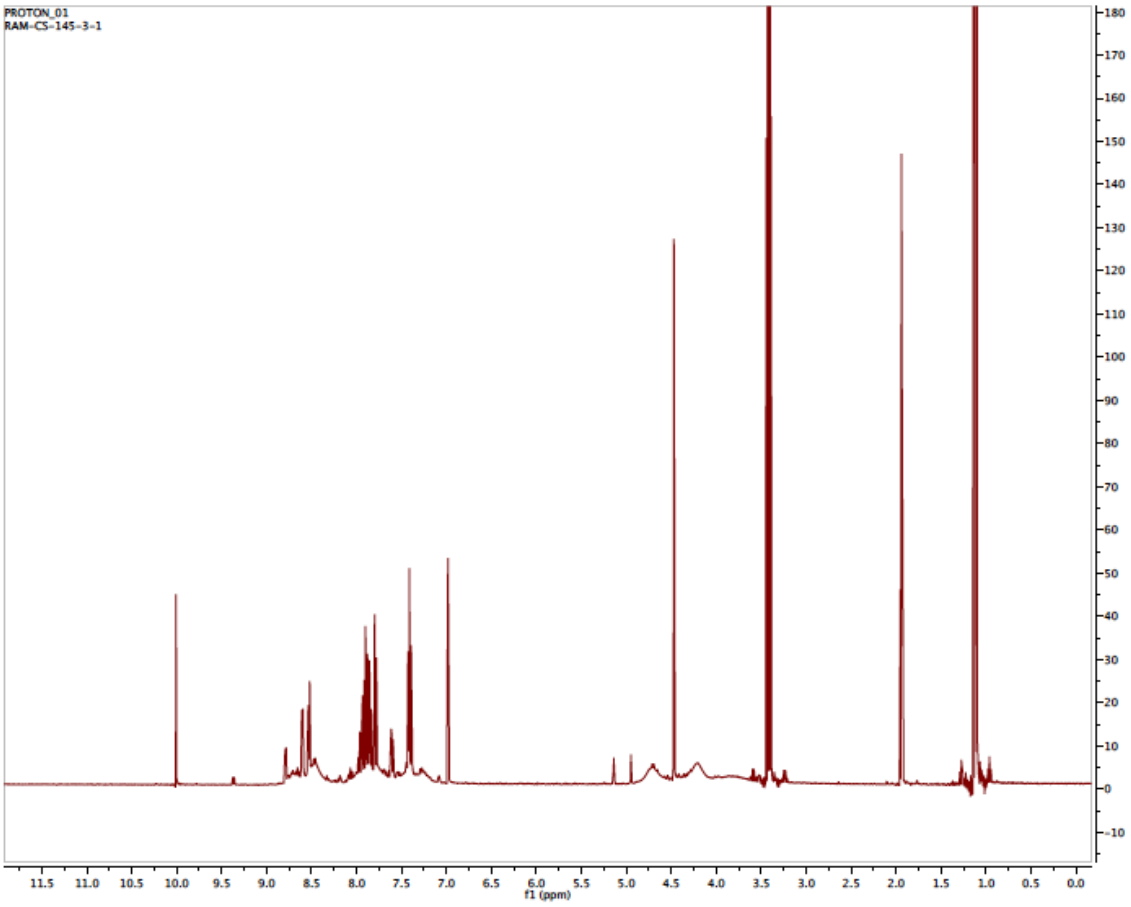


Figure S9. ^{1}H NMR of pyridinium salt (**5**) formed from **2-PA** (1.0 equiv.), **DPA** (1.0 equiv.) and BF_3-OEt_2 (1.0 equiv.) in CD_3CN.

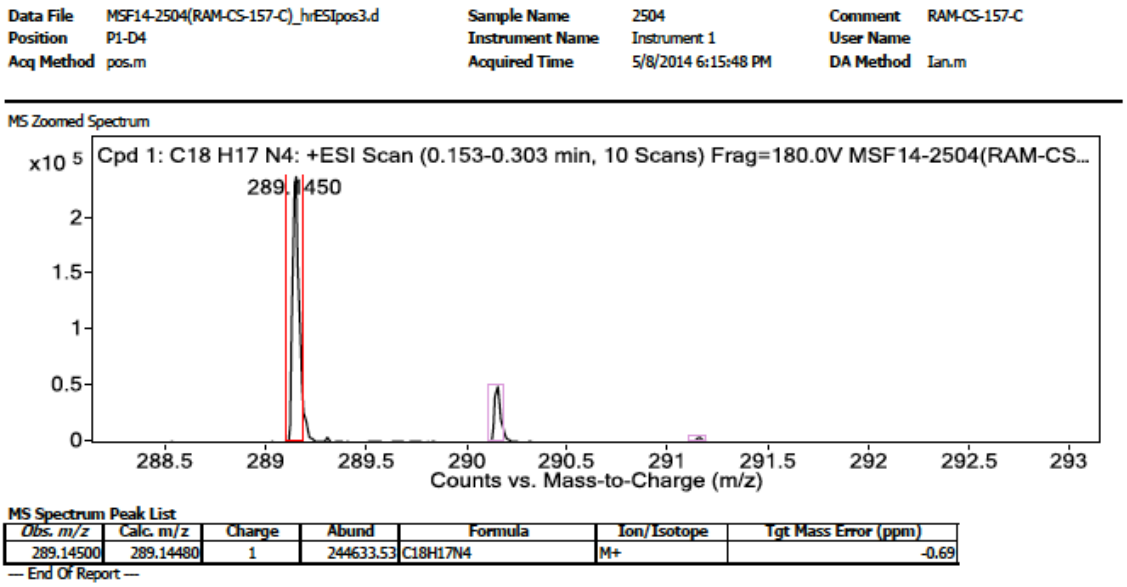
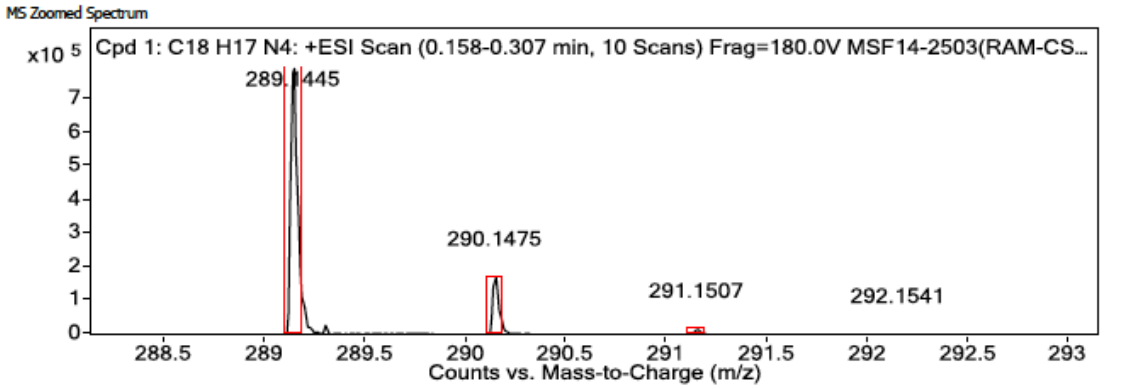


Figure S10. Mass spectrum of pyridinium salt (**5**) generated from **2-PA**, **DPA** and BF_3-OEt_2. HRMS calcd for $C_{18}H_{17}N_4^+$ (M^+) 289.1448. Found 289.1450.

Data File	MSF14-2503(RAM-CS-157-A)_hrESIpos1.d	**Sample Name**	2503	**Comment**	RAM-CS-157-A
Position	P1-D3	**Instrument Name**	Instrument 1	**User Name**	
Acq Method	pos.m	**Acquired Time**	5/8/2014 5:59:58 PM	**DA Method**	Ian.m



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
289.14450	289.14480	1	816216.9	C18H17N4	M+	1.01
290.14750	290.14770	1	171349.73	C18H17N4	M+	0.92
291.15070	291.15060	1	16915.33	C18H17N4	M+	-0.31
292.15410	292.15350	1	1405.73	C18H17N4	M+	-2.12
343.15280			855700.24			

— End Of Report —

Figure S11. Mass spectrum of pyridinium salt generated from **2-PA**, **DPA** and TMS-OTf. HRMS calcd for $C_{18}H_{17}N_4^+$ (M^+) 289.1448. Found 289.1445.