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Electronic Supplementary Information

Solvent effects on halogen bond symmetry

Anna-Carin C. Carlsson, Martin Uhrbom, Alavi Karim, Ulrika Brath, Jürgen Gräfenstein and Máté Erdélyi*

Department of Chemistry and Molecular Biology and the Swedish NMR Centre, University of Gothenburg, Kemivägen 10,
SE-412 96 Gothenburg, Sweden. E-mail: mate@chem.gu.se

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1 Synthesis of $[N\text{-}X\text{-}N]^+$ $^-$OTf Complexes

1.1 General Information

Unless otherwise stated, all reagents and solvent were purchased from commercial suppliers. CH_2Cl_2 was freshly distilled from CaH_2, and *n*-hexane was distilled from sodium metal/benzophenone ketyl prior to use. Pyridine was stored over KOH, and distilled from CaH_2. Pyridine-2-d_1 was supplied by QMX Laboratories. All glassware was dried at 150 °C in a heating oven overnight or at least for several hours prior to use and all reactions were performed under dry conditions using dry solvents, and under nitrogen or argon atmosphere. Centrifugations were carried out with a Heraeus Christ Labofuge A centrifuge. Melting points were recorded on a Büchi B-545 apparatus and are uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Varian VNMR-S 500 spectrometer at 25 °C in CD_2Cl_2 and CD_3CN. Chemical shifts are reported on the δ scale in ppm using residual solvent signal as internal standard; CD_3CN (δ_H 1.94, δ_C 118.26) and CD_2Cl_2 (δ_H 5.32, δ_C 54.00). For the ^{19}F NMR spectra, a sealed capillary filled with hexafluorobenzene (δ_F -164.4) was used as an internal standard. The numbering used for NMR assignment is shown in Fig. 3 in the main text. Diffusion NMR measurements were performed on a Varian 500 MHz VNMR-S spectrometer using the ONE-SHOT pulse sequence[1] as implemented in the software VNMRJ version 3.2. Four scans were acquired using 60 s relaxation delay (d1) , 2 ms diffusion-encoding/decoding gradient pulse duration and 25 ms diffusion delay. The z-gradient strengths were varied in 14 steps between 0 and 60 G/cm. Gradient strength was calibrated for the known diffusion coefficient of the residual water signal of a DMSO-d_6 sample.[2] Nitrogen chemical shifts were acquired using ^{1}H,^{15}N-gHMBCAD pulse sequence[3] on a 400 MHz Varian-MR spectrometer equipped with a OneNMR probe. Chemical shifts were referenced to nitromethane at 0 ppm (capillary).

High resolution mass spectroscopy (HRMS) data were obtained on a Q-TOF-MS at Stenhagen Analyslab AB, Gothenburg, Sweden, with detection in the positive ion mode. Standard autotune of masses was performed in the TOF-MS instruments before the experimental runs, and typical mass errors of 1-3 ppm were achieved in the calibration. The syntheses of $[N\text{-}X\text{-}N]^+$ $^-$OTf complexes **1** and **2** followed a previously published protocol.[4]

[1] Pelta, M. D., Morris, G. A., Stchedroff, J., Hammond, S. J. *Magn. Reson. Chem.*, 2002, **40**, S147.
[2] Packer, K. J., Tomlinson, D. J. *Trans. Faraday. Soc.*, 1971, **67**, 1302.
[3] (a) Bax, A., Summers, M. F. *J. Am. Chem. Soc.*, 1986, **108**, 2093. (b) Hurd, R. E., *J. Magn. Reson.*, 1990, **87**, 422. (c) Hadden, C. E., *Magn. Reson. Chem.* , 2005, **43**, 330.
[4] Carlsson, A.-C.C; Gräfenstein, J.; Laurila, J. L.; Bergquist, J.; Erdélyi, M. *Chem. Commun.*, 2012, **48**, 1458.

1.2 Bis(pyridine)bromonium triflate (1-d_0/1-d_1)

Pyridine (150 µL, 1.86 mmol), pyridine-2-d_1 (150 µL, 1.84 mmol), and silver triflate (453 mg, 1.76 mmol) were suspended in dry CH_2Cl_2 (6.0 mL) in a dried 20-mL vial sealed with a rubber septum (Biotage® high precision microwave vial) under stirring at room temperature below a nitrogen or argon atmosphere. When all solids were dissolved, and the mixture turned clear and colourless, a solution of bromine (0.58 M, 3.0 mL, 1.74 mmol) in dry CH_2Cl_2 was added dropwise using a syringe. Immediately, light yellow silver bromide precipitated. The reaction mixture was stirred vigorously for 15 min. The vial was then centrifuged for 7 min at 2000 rpm. The resulting yellow supernatant was transferred to another 20-mL vial, sealed with a rubber septum, and kept under nitrogen. Addition of dry *n*-hexane (12.0 mL) resulted in a light yellow precipitate. Precipitation was continued on an ice-bath for 50 min under nitrogen. Subsequently, the vial was centrifuged for 7 min at 2000 rpm. The supernatant was removed, and the remaining solid was washed twice with dry *n*-hexane (2 x 6.0 mL). Each washing step was followed by centrifugation for 7 min at 2000 rpm, and removal of the supernatant. After drying under vacuum, an isotopologue mixture of $[N\text{-}Br\text{-}N]^+$ complexes **1-d_0** and **1-d_1** (and **1-d_2**) was furnished as a white, crystalline solid (614 mg, 90 %). Complexes **1-d_0** and **1-d_1** were obtained in an approximate ratio of 1:1.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.73-8.76 (m, 3H, H–2, H–2', H-6 and H-6'), 8.21-8.26 (m, 2H, H–4 and H–4'), 7.72-7.78 (m, 4H, H–3, H-3', H–5 and H–5')(lit.[2] for **1-d_0**);
^{1}H NMR (500 MHz, CD_3CN) δ 8.71-8.74 (m, 3H, H–2, H–2', H-6 and H-6'), 8.24-8.29 (m, 2H, H–4 and H–4'), 7.72-7.77 (m, 4H, H–3, H-3', H–5 and H–5');
^{13}C NMR (125 MHz, CD_2Cl_2) δ 146.9 (C–2, C–6 and C–6'), 146.6 (t, J = 29.3 Hz, C–6'), 142.7 (C–4 and C–4'), 128.2 (C–3, C–5 and C–5'), 128.1, (C–3'), 121.6 (q, J = 321.1 Hz, CF_3);
^{13}C NMR (125 MHz, CD_3CN) δ 147.5 (C–2 and C–6), 147.4 (C–6'), 147.2 (t, J = 28.5 Hz, C–2'), 143.31 (C–4'), 143.29 (C–4), 128.7 (C–3, C–5 and C–5'), 128.6, (C–3'), 122.1 (q, J = 321 Hz, CF_3);
^{19}F NMR (376 MHz, CD_2Cl_2) δ -77.27 (s, CF_3); mp 89 – 93 °C (lit.[5] for **1-d_0** 87-89 °C).[2]

1.3 Bis(pyridine)iodonium triflate (2-d_0/2-d_1)

Pyridine (200 µL, 2.48 mmol), pyridine-2-d_1 (100 µL, 1.22 mmol), and silver triflate (460 mg, 1.79 mmol) were suspended in dry CH_2Cl_2 (7.0 mL) in a 20-mL vial (Biotage® high precision microwave vial), which was sealed with a rubber septum, under stirring at room temperature under nitrogen atmosphere. When all solids were dissolved a solution of iodine (457 mg, 1.80 mmol) in dry CH_2Cl_2 (8.0 mL) was added dropwise by syringe to the clear and colourless mixture. Immediately upon the addition, yellow silver iodide was precipitated. The reaction mixture was stirred vigorously for 15

[5] A. A. Neverov, H. X. Feng, K. Hamilton and R. S. Brown, Brown, *J. Org. Chem.*, 2003, **68**, 3802.

min. Thereafter, the vial was centrifuged for 10 min at 2000 rpm. The resulting orange supernatant was transferred to a round-bottomed flask, and concentrated under reduced pressure. The remaining orange solid was re-dissolved in dry CH_2Cl_2 (4.0 mL), and transferred to another 20-mL vial that was sealed with a rubber septum, and kept under nitrogen. Addition of dry *n*-hexane (18 mL) to the dark, orange solution resulted in formation of a yellow precipitate. Precipitation was continued on an ice-bath for 2 h under nitrogen. Subsequently, the vial was centrifuged for 10 min at 2000 rpm. The red supernatant was removed, and the remaining solid was washed twice with dry *n*-hexane (2 x 12.0 mL). After drying under vacuum, an isotopologue mixture of $[N\text{-}I\text{-}N]^+$ complexes **2-*d*$_0$** and **2-*d*$_1$** (and **2-*d*$_2$**) was furnished as a beige, crystalline solid (631 mg, 81 %). Complexes **2-*d*$_0$** and **2-*d*$_1$** were obtained in an approximate ratio of 2:1.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.78-8.81 (m, 3.5H, H–2, H–2', H-6 and H-6'), 8.20-8.25 (m, 2H, H–4 and H–4'), 7.62-7.66 (m, 4H, H–3, H–3', H–5 and H–5');
^{1}H NMR (500 MHz, CD_3CN) δ 8.74-8.83 (m, 3.5H, H–2, H–2', H-6 and H-6'), 8.21-8.29 (m, 2H, H–4 and H–4'), 7.58-7.68 (m, 4H, H–3, H-3', H–5 and H–5');
^{13}C NMR (125 MHz, CD_2Cl_2) δ 150.06 (C–2 and C–6), 150.03 (C–6'), 149.73 (t, *J* = 29.3 Hz, C–2'), 142.68 (C–4'), 142.66 (C–4), 128.49 (C–3, C–5 and C–5'), 128.34 (C–3'), 121.54 (q, *J* = 320.7 Hz, CF_3);
^{13}C NMR (125 MHz, CD_3CN, inverse gated ^{2}H decoupling) δ 150.64 (C–2 and C–6), 150.61 (C–6'), 150.3 (C–2'), 143.21 (C–4'), 143.21 (C–4), 128.8 (C–3, C–5 and C–5'), 128.7, (C–3'), 122.1 (q, *J* = 321 Hz, CF_3);
^{19}F NMR (376 MHz, CD_2Cl_2) δ -77.24 (s, CF_3); HRMS calcd for $(C_{10}H_{10}N_2INa)^+$ *m/z* 307.9786, found 307.9873; mp 84 – 88 °C.

1.4 Pyridine-pyridinium triflate (3-*d*$_0$/3-*d*$_1$)

The **3-*d*$_0$/3-*d*$_1$** sample was prepared by mixing pyridine, pyridine-2-*d*$_1$, and trifluoromethanesulfonic acid in CD_2Cl_2 or CD_3CN, adjusting the ^{13}C chemical shifts until the mixture contained pyridine/TfOH in an approximate 2:1 ratio, based on a previous titration of pyridine with TfOH in CD_2Cl_2 or CD_3CN at 25 °C.
^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.70-8.74 (m, 3.5H, H–2, H–2', H–6 and H–6'), 8.10-8.15 (m, 2H, H–4 and H–4'), 7.66-7.70 (m, 4H, H–3, H–3', H–5 and H–5');
^{1}H NMR (500 MHz, CD_3CN) δ 8.61-8.66 (m, 3H, H–2, H–2', H–6 and H–6'), 8.11-8.17 (m, 2H, H–4 and H–4'), 7.64-7.69 (m, 4H, H–3, H–3', H–5 and H–5');
^{13}C NMR (125 MHz, CD_2Cl_2) δ 146.30 (C–2 and C–6), 146.25 (C–6'), 145.97 (t, *J* = 28.3 Hz, C–2'), 141.92 (C–4'), 141.87 (C–4), 126.26 (C–5'), 126.24 (C–3 and C–5), 126.11 (C–3'), 121.05 (q, *J* = 319.4 Hz, $\underline{C}F_3$).

^{13}C NMR (125 MHz, CD_3CN, inverse gated ^{2}H decoupling) δ 146.8 (C–2 and C–6), 146.7 (C–6'), 146.4 (C–2'), 142.54 (C–4'), 142.49 (C–4), 126.62 (C–5'), 126.60 (C–3 and C–5), 126.5 (C–3'), 121.9 (q, J = 321 Hz, $\underline{C}F_3$).

2 IPE NMR Experiments

2.1 General Experimental Information

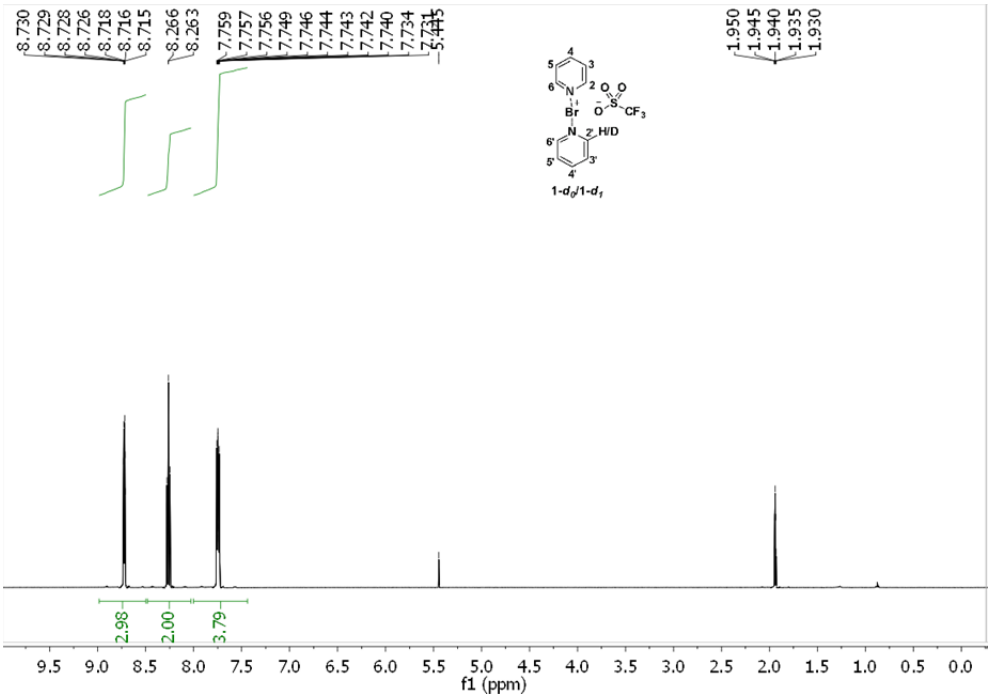
Isotopic perturbation of equilibrium (IPE) NMR experiments were recorded on a Varian VNMR-S 500 MHz spectrometer equipped with an X{HF} probe using ^{13}C detection with simultaneous broadband ^{1}H and inverse-gated ^{2}H decoupling. Dry NMR samples were prepared using pre-dried CD_3CN, by storing the solvent over molecular sieves overnight followed by ultrasonication in the presence of CaH_2 for one hour; CaH_2 was subsequently removed by ultracentrifugation. The NMR tubes were dried under high vacuum for several hours before use. Spectra of mixtures of the nondeuterated and monodeuterated compounds **1-*d*$_0$**/**1-*d*$_1$**, **2-*d*$_0$**/**2-*d*$_1$**, **3-*d*$_0$**/**3-*d*$_1$** and pyridine-d_0/pyridine-d_1, were recorded for CD_2Cl_2 solutions as described earlier,[4] and for CD_3CN solutions for the temperature interval -30 to +70 °C. To obtain high quality spectra for determination of small variations in isotopic shifts ($^{n}\Delta_{obs}$) ^{13}C spectra have been recorded with 32768 points and were zero-filled to 262144 points for processing. The spectral quality and the estimated chemical shift uncertainty are discussed in detail in the ESI of reference 4. The pyridine-d_0/pyridine-d_1 sample consisted of a mixture of pyridine with pyridine-2-d_1, the nondeuterated compound being in excess. Supplemented NMR spectra (^{1}H and ^{13}C with ^{2}H decoupling, section 2.2) were recorded at 25°C.

2.2 ^{1}H and ^{13}C NMR Spectra in CD_3CN

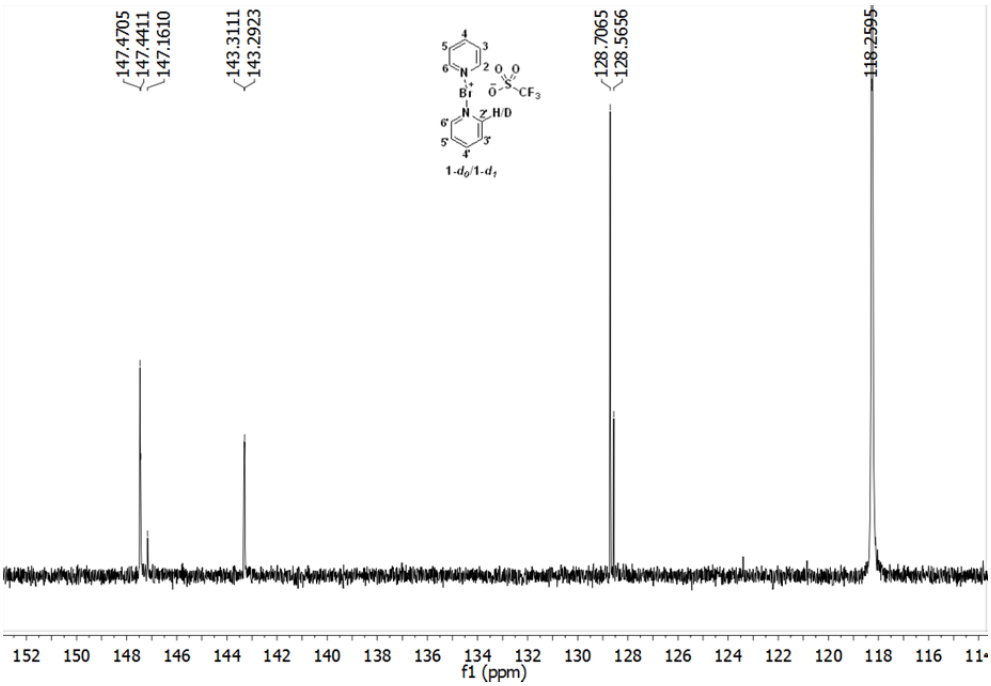
The ^{1}H and ^{13}C NMR spectra of the compounds obtained for CD_2Cl_2 solutions are given in reference 4.

2.2.1 Bis(pyridine)bromonium triflate (1-d_0/1-d_1)

^{1}H NMR spectrum (500 MHz, CD_3CN)

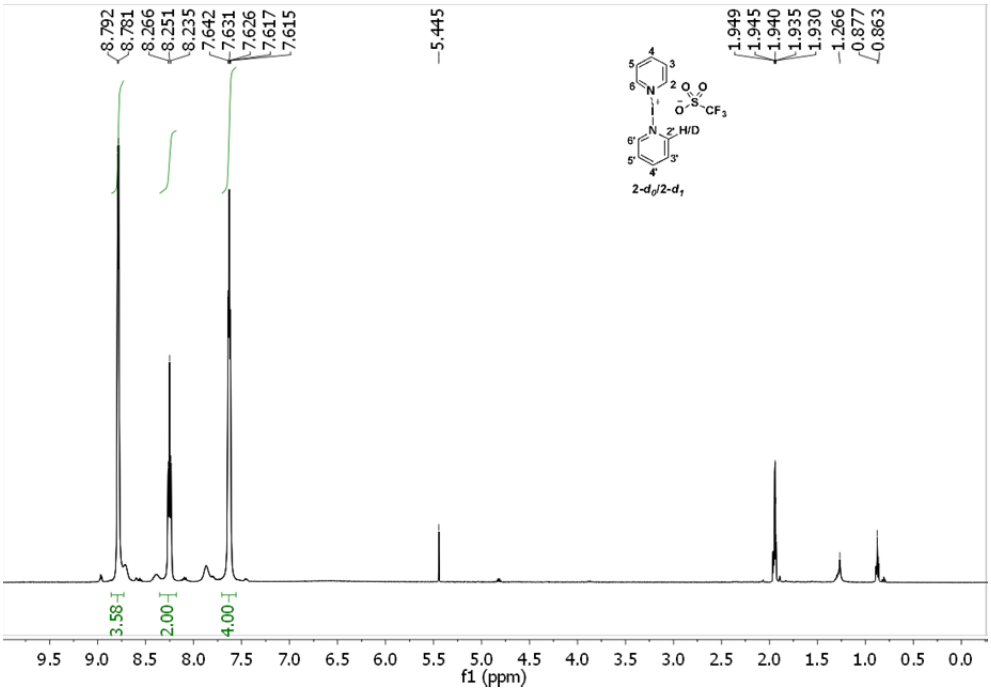


^{13}C NMR spectrum (125 MHz, CD_3CN, inverse gated ^{2}H decoupling)

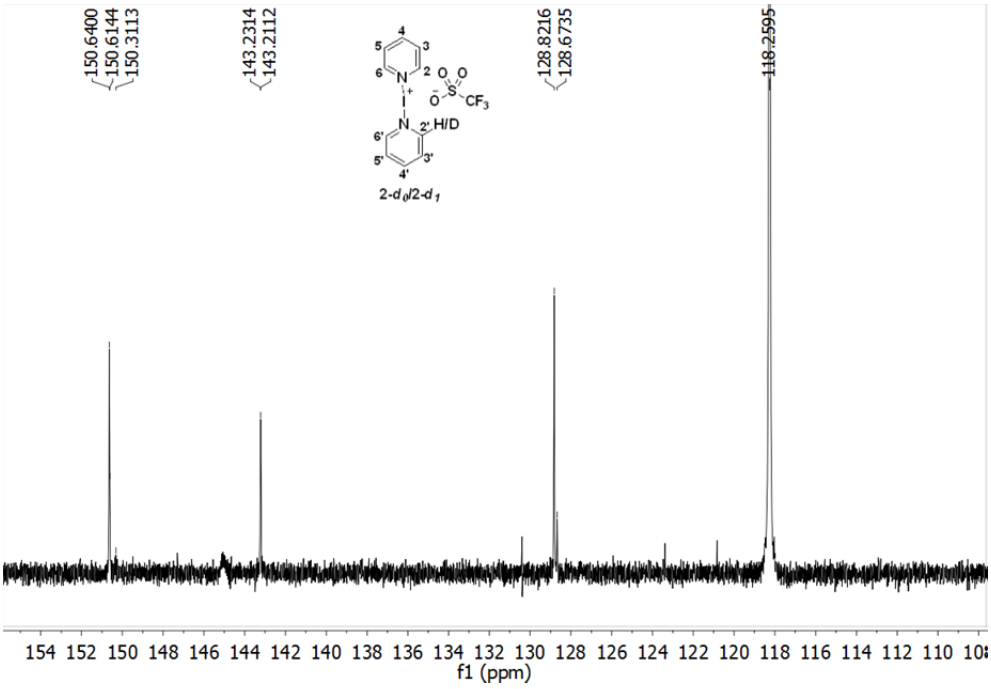


2.2.2 Bis(pyridine)iodonium triflate (2-d_0/2-d_1)

^{1}H NMR spectrum (500 MHz, CD_3CN)

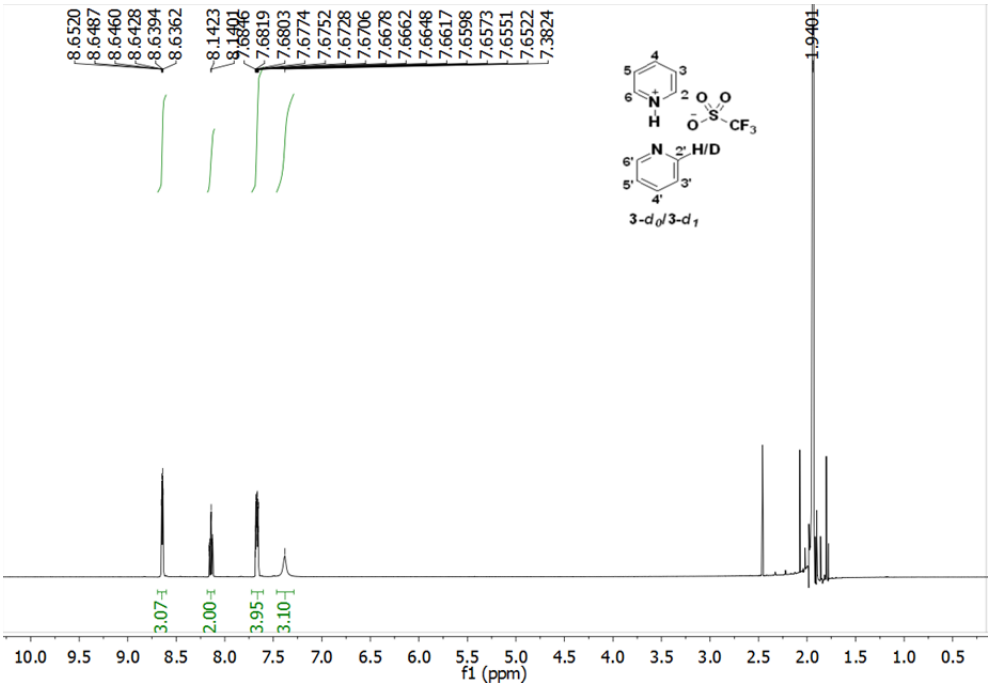


^{13}C NMR spectrum (125 MHz, CD_3CN, inverse gated ^{2}H decoupling)

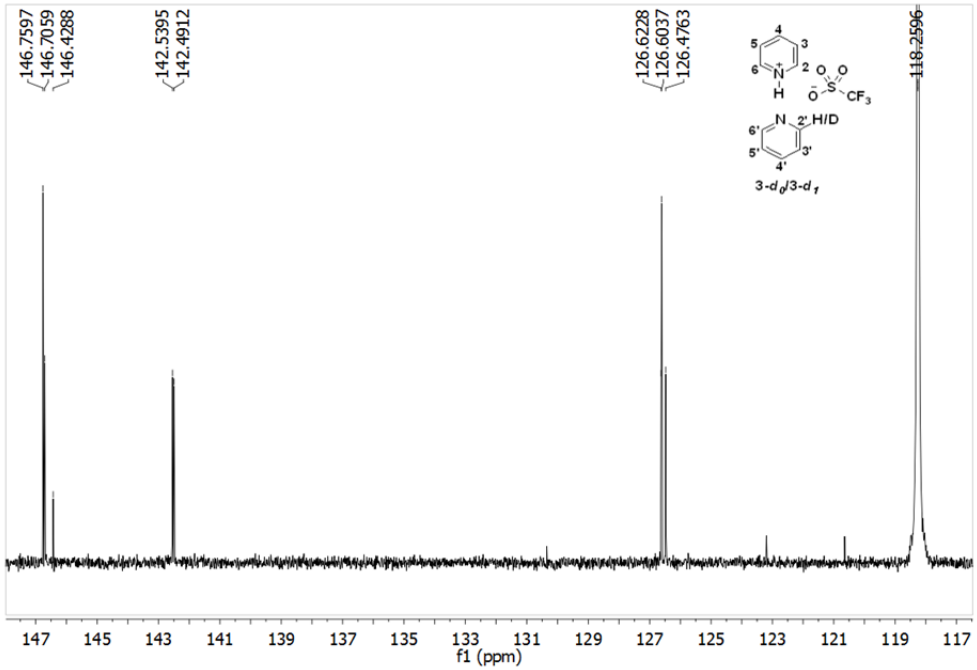


2.2.3 Pyridine-pyridinium triflate (3-d_0/3-d_1)

^{1}H NMR spectrum (500 MHz, CD_3CN)

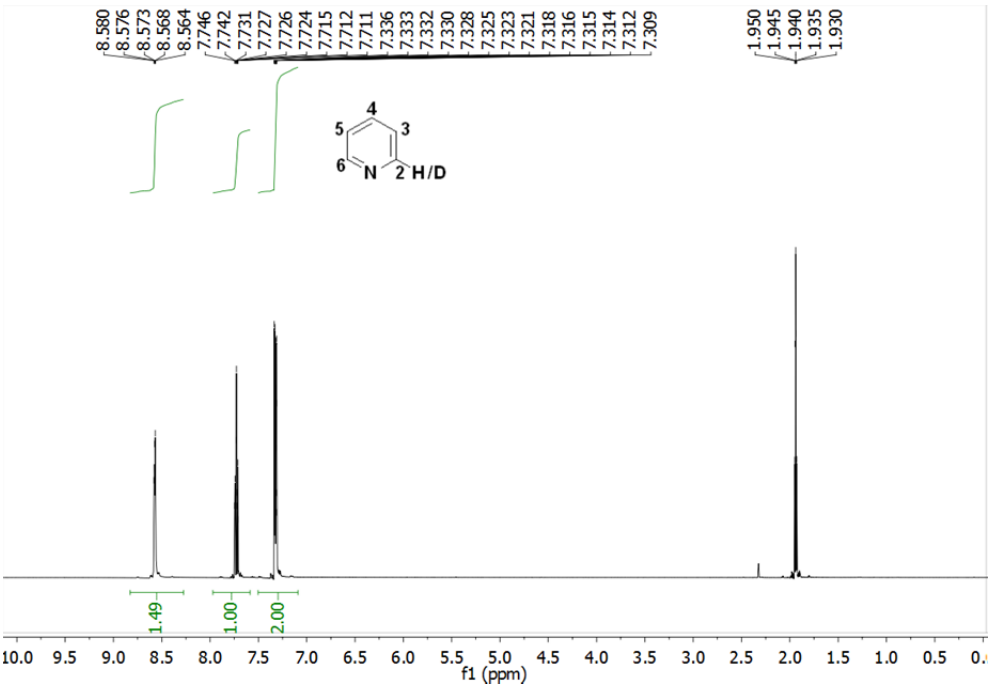


^{13}C NMR spectrum (125 MHz, CD_3CN, inverse gated ^{2}H decoupling)

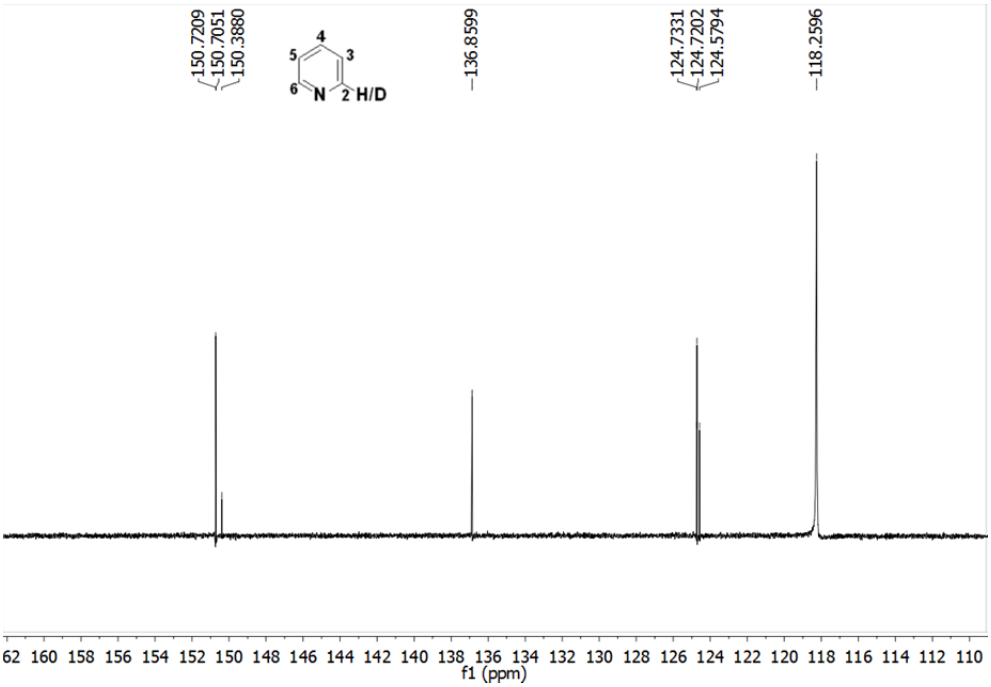


2.2.4 Pyridine-d_0/Pyridine-d_1

^{1}H NMR spectrum (500 MHz, CD_3CN)

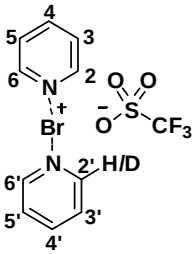


^{13}C NMR spectrum (125 MHz, CD_3CN, inverse gated ^{2}H decoupling)



2.3. ^{13}C NMR Chemical Shifts, Observed Isotope Shift, and Temperature Coefficients

Bis(pyridine)bromonium triflate (1-d_0/1-d_1)



1-d_0/1-d_1

Table S1. The chemical shifts of bis(pyridine)bromonium triflate (**1-d_0**/**1-d_1**) given in ppm.

Temp. (°C)	δ $C2_H,6_H$	δ $C6_D$	δ $C2_D$	δ $C4_H$	δ $C4_D$	δ $C3_H,5_H$	δ $C5_D$	δ $C3_D$
70	147.9741	147.9478	147.6680	143.6526	143.6713	129.0701	129.0701	128.9357
50	147.7513	147.7229	147.4424	143.4963	143.5130	128.9148	128.9148	128.7781
25	147.4686	147.4379	147.1593	143.2912	143.3093	128.7057	128.7057	128.5646
0	147.2024	147.1790	146.8915	143.0804	143.0893	128.4900	128.4900	128.3457
-20	147.0155	146.9838	146.7027	142.8694	142.8929	128.3154	128.3154	128.1687
-25	146.9948	146.9636	146.6808	142.8514	142.8685	128.3030	128.3030	128.1556
-30	146.9417	146.9103	146.6281	142.8112	142.8299	128.2594	128.2594	128.1115

Table S2. The temperature dependence of the isotope shifts observed for bis(pyridine)bromonium triflate (**1-d_0**/**1-d_1**), given in ppm.

Temp. (°C)	$^1\Delta_{obs}$ δ_{C2D}-δ_{C2H}	$^3\Delta_{obs}$ δ_{C6D}-δ_{C6H}	$^3\Delta_{obs}$ δ_{C4D}-δ_{C4H}	$^2\Delta_{obs}$ δ_{C3D}-δ_{C3H}	$^4\Delta_{obs}$ δ_{C5D}-δ_{C5H}
70	-0.3061	-0.0263	0.0187	-0.1344	0.0000
50	-0.3089	-0.0284	0.0167	-0.1367	0.0000
25	-0.3093	-0.0307	0.0181	-0.1411	0.0000
0	-0.3109	-0.0234	0.0089	-0.1443	0.0000
-20	-0.3128	-0.0317	0.0235	-0.1467	0.0000
-25	-0.3140	-0.0312	0.0171	-0.1474	0.0000
-30	-0.3136	-0.0314	0.0187	-0.1479	0.0000

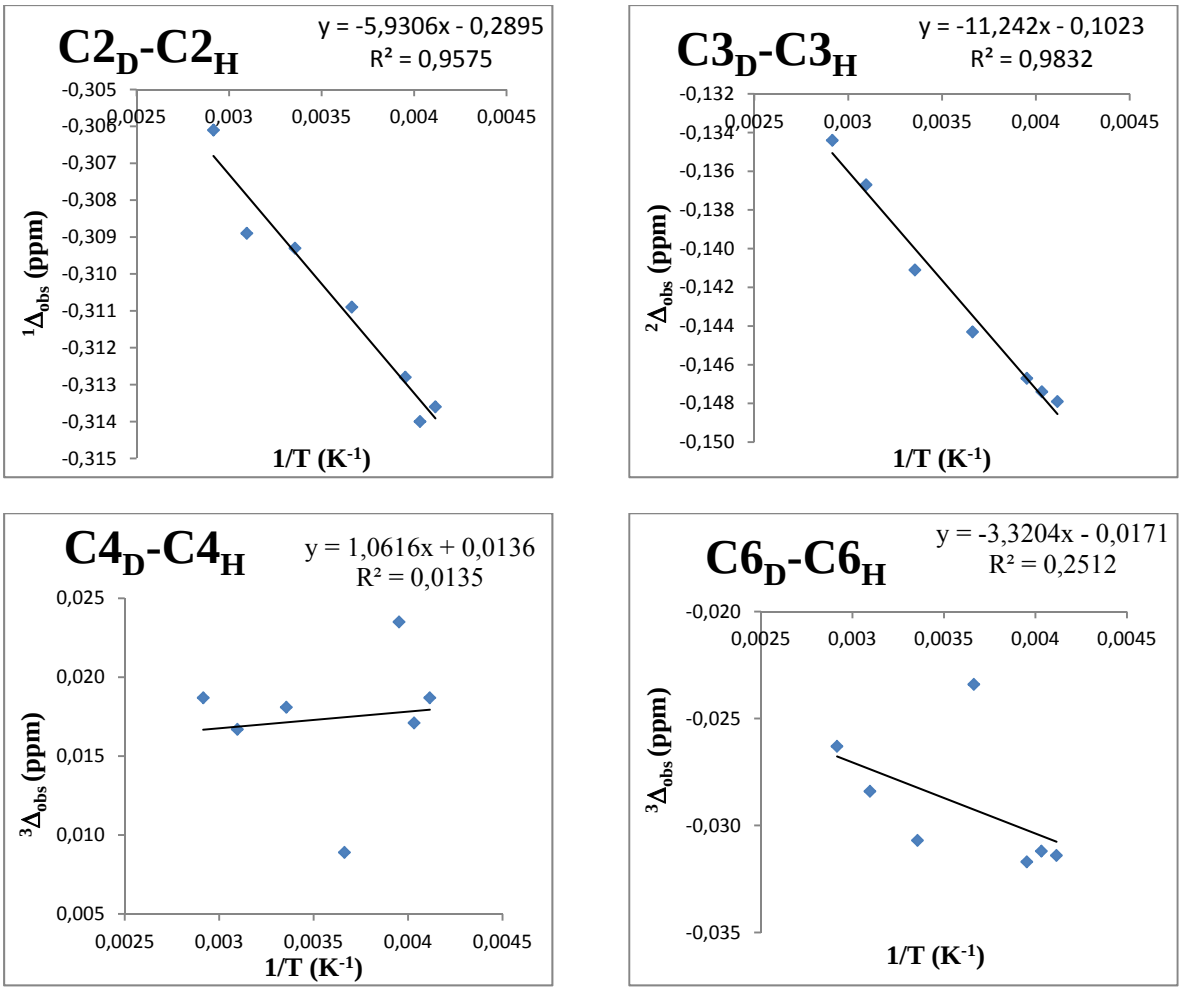
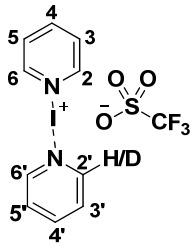


Figure S3. The temperature dependence of the isotope shifts of bis(pyridine)bromonium triflate (**1-*d*$_0$**/**1-*d*$_1$**), shown for each carbon separately.

Bis(pyridine)iodonium triflate (2-d_0/2-d_1)



2-d_0 /2-d_1

Table S3. The chemical shifts of bis(pyridine)iodonium triflate (**2-d_0/2-d_1**) given in ppm.

Temp. (°C)	δ $C2_H$,6_H	δ $C6_D$	δ $C2_D$	δ $C4_H$	δ $C4_D$	δ $C3_H$,5_H	δ $C5_D$	δ $C3_D$
40	150.7854	150.7211	150.4587	143.3353	143.3524	128.9446	128.9446	128.7988
25	150.6400	150.6144	150.3113	143.2112	143.2314	128.8216	128.8216	128.6735
10	150.4790	150.4495	150.1466	143.0813	143.1022	128.6829	128.6829	128.5330
0	150.3740	150.3435	150.0401	142.9986	143.0188	128.5920	128.5920	128.4413
-10	150.2692	150.2386	149.9340	142.9162	142.9378	128.5004	128.5004	128.3485
-15	150.2150	150.1838	149.8798	142.8740	142.8959	128.4527	128.4527	128.3002
-20	150.1627	150.1318	149.8272	142.8334	142.8551	128.4058	128.4058	128.2527
-25	150.0816	150.0500	149.7466	142.7641	142.7860	128.3317	128.3317	128.1779
-30	150.0528	150.0213	149.7171	142.7470	142.7685	128.3089	128.3089	128.1547

Table S4. The temperature dependence of the isotope shifts for bis(pyridine)iodonium triflate (**2-d_0/2-d_1**), given in ppm.

Temp. (°C)	$^1\Delta_{obs}$ δ_{C2D}-δ_{C2H}	$^3\Delta_{obs}$ δ_{C6D}-δ_{C6H}	$^3\Delta_{obs}$ δ_{C4D}-δ_{C4H}	$^2\Delta_{obs}$ δ_{C3D}-δ_{C3H}	$^4\Delta_{obs}$ δ_{C5D}-δ_{C5H}
40	-0.3267	-0.0643	0.0171	-0.1458	0.0000
25	-0.3287	-0.0256	0.0202	-0.1481	0.0000
10	-0.3324	-0.0295	0.0209	-0.1499	0.0000
0	-0.3339	-0.0305	0.0202	-0.1507	0.0000
-10	-0.3352	-0.0306	0.0216	-0.1519	0.0000
-15	-0.3352	-0.0312	0.0219	-0.1525	0.0000
-20	-0.3355	-0.0309	0.0217	-0.1531	0.0000
-25	-0.3350	-0.0316	0.0219	-0.1538	0.0000
-30	-0.3357	-0.0315	0.0215	-0.1542	0.0000

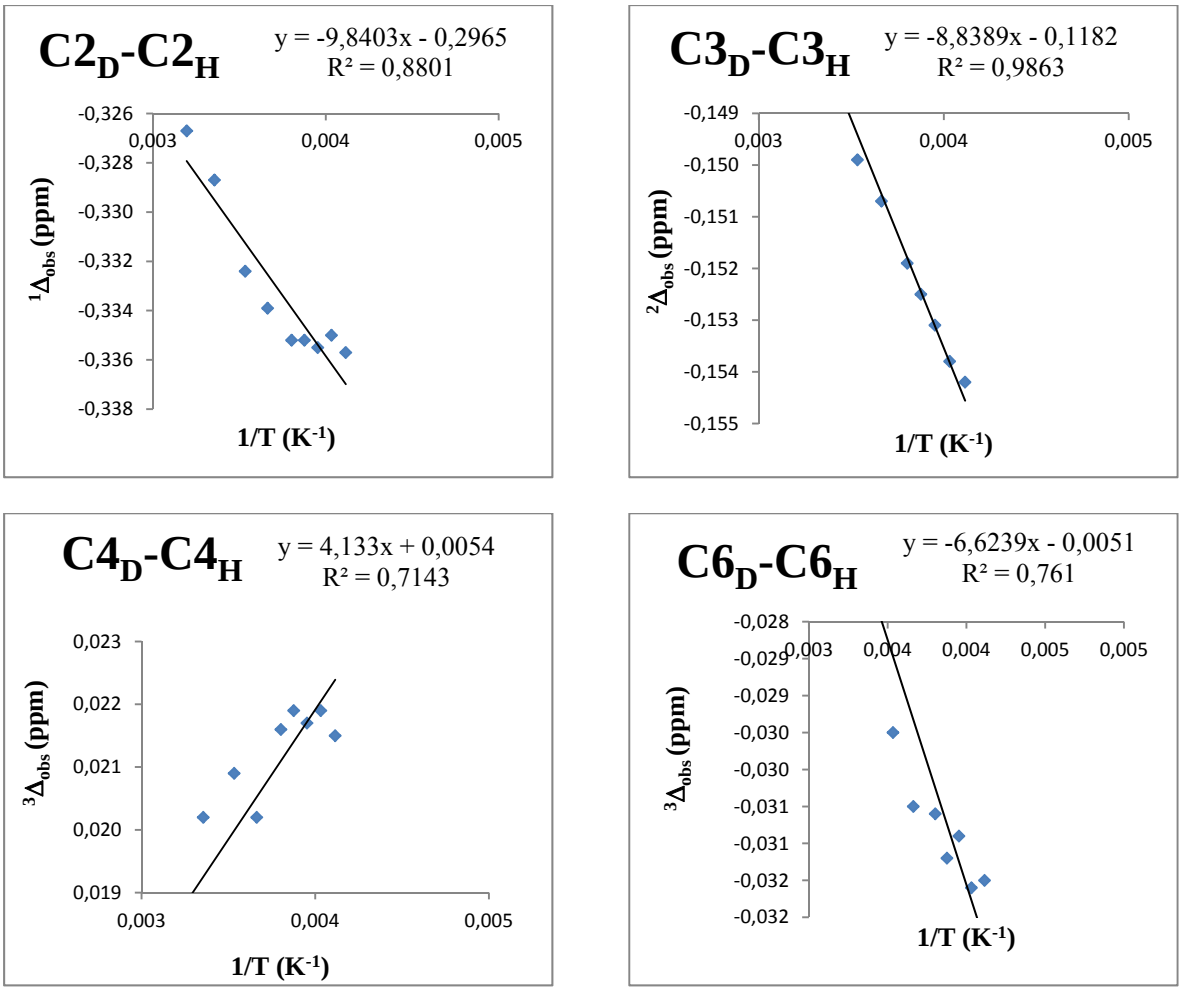
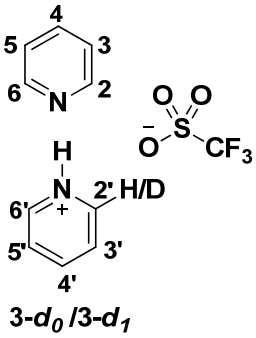


Figure S4. The temperature dependence of the isotope shifts of bis(pyridine)iodonium triflate (**2-*d*$_0$**/**2-*d*$_1$**), shown for each carbon separately.

Pyridine-pyridinium triflate (3-d_0/3-d_1)



3-d_0 /3-d_1

Table S5. The chemical shifts of pyridine-pyridinium triflate (**3-d_0/3-d_1**) given in ppm.

Temp. (°C)	δ $C2_H$,6_H	δ $C6_D$	δ $C2_D$	δ $C4_H$	δ $C4_D$	δ $C3_H$,5_H	δ $C5_D$	δ $C3_D$
33	146.8613	146.8082	146.5317	142.5409	142.5887	126.6766	126.6958	126.5502
23	146.7597	146.7059	146.4288	142.4912	142.5395	126.6037	126.6228	126.4763
-10	146.4109	146.3562	146.0798	142.3611	142.4085	126.3763	126.3951	126.2446
-15	146.3509	146.2960	146.0198	142.3466	142.3935	126.3416	126.3602	126.2093
-20	146.2883	146.2336	145.9579	142.3326	142.3795	126.3063	126.3245	126.1732
-25	146.2213	146.1664	145.8900	142.3189	142.3653	126.2689	126.2874	126.1362
-33	146.1606	146.1056	145.8299	142.3076	142.3538	126.2358	126.2539	126.1011

Table S6. The temperature dependence of the isotope shifts for pyridine-pyridinium triflate (**3-d_0/3-d_1**), given in ppm.

Temp. (°C)	$^1\Delta_{obs}$ δ_{C2D}-δ_{C2H}	$^3\Delta_{obs}$ δ_{C6D}-δ_{C6H}	$^3\Delta_{obs}$ δ_{C4D}-δ_{C4H}	$^2\Delta_{obs}$ δ_{C3D}-δ_{C3H}	$^4\Delta_{obs}$ δ_{C5D}-δ_{C5H}
33	-0.3296	-0.0531	0.0478	-0.1264	0.0192
23	-0.3309	-0.0538	0.0483	-0.1274	0.0191
-10	-0.3311	-0.0547	0.0474	-0.1317	0.0188
-15	-0.3311	-0.0549	0.0469	-0.1323	0.0186
-20	-0.3304	-0.0547	0.0469	-0.1331	0.0182
-25	-0.3313	-0.0549	0.0464	-0.1327	0.0185
-33	-0.3307	-0.0550	0.0462	-0.1347	0.0181

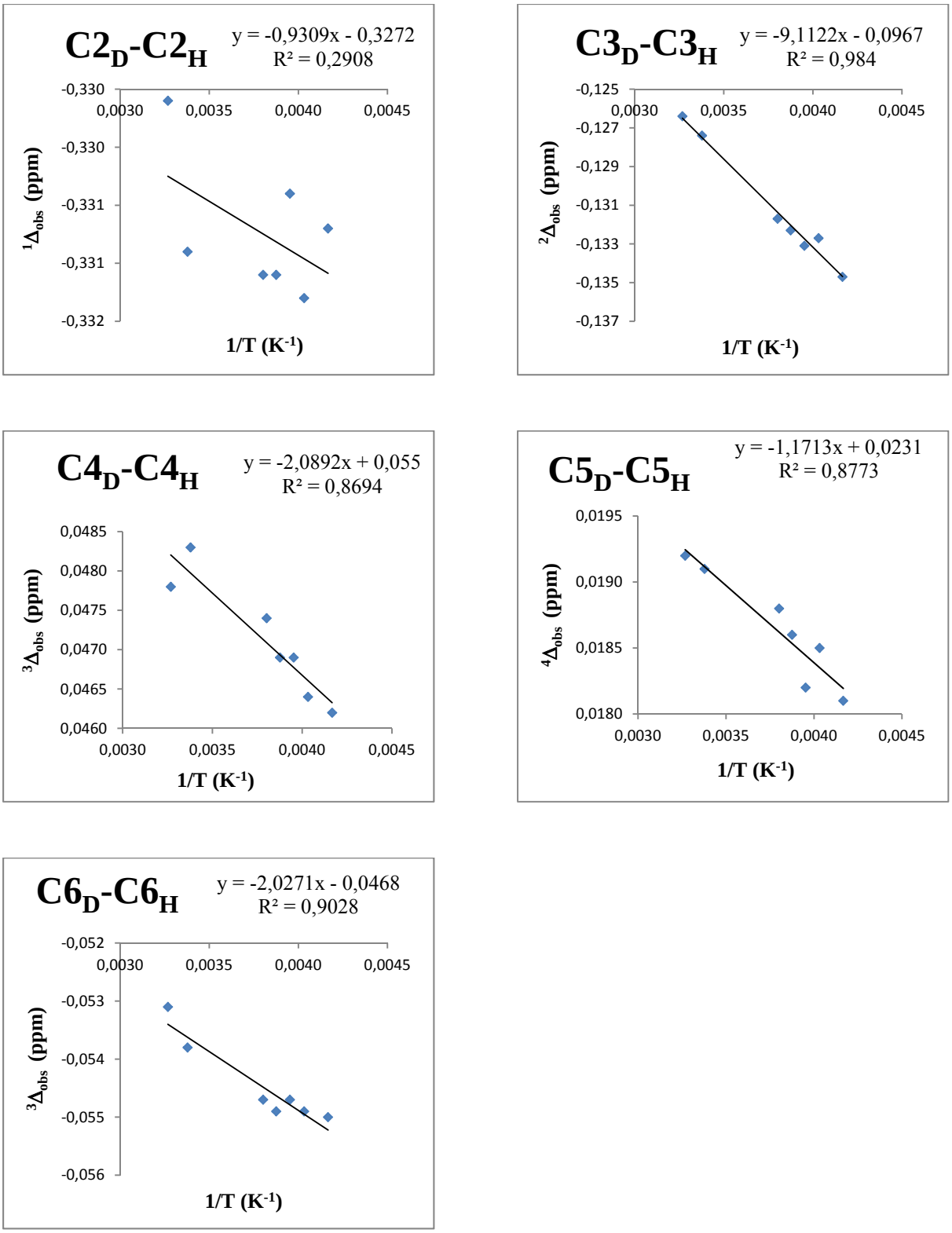


Figure S5. The temperature dependence of the isotope shifts of pyridine-pyridinium triflate (**3-*d*$_0$**/**3-*d*$_1$**), shown for each carbon separately.

Pyridine-d_0/Pyridine-d_1

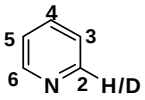


Table S7. The chemical shifts of pyridine/pyridine-d_1 given in ppm.

Temp. (°C)	δ $C2_H$,6_H	δ $C6_D$	δ $C2_D$	δ $C4_H$	δ $C4_D$	δ $C3_H$,5_H	δ $C5_D$	δ $C3_D$
70	151.1473	151.1331	150.8185	137.1297	137.1297	125.0374	125.0505	124.9014
55	151.0073	150.9921	150.6785	137.0433	137.0433	124.9343	124.9457	124.7974
40	150.8697	150.8542	150.5384	136.9587	136.9587	124.8333	124.8444	124.6939
25	150.7291	150.7133	150.3962	136.8721	136.8721	124.7292	124.7414	124.5882
10	150.5938	150.5774	150.2597	136.7903	136.7903	124.6282	124.6409	124.4859
0	150.4998	150.4828	150.1651	136.7333	136.7333	124.5600	124.5732	124.4159
-10	150.4030	150.3857	150.0672	136.6756	136.6756	124.4886	124.5020	124.3436
-15	150.3558	150.3382	150.0186	136.6479	136.6479	124.4537	124.4670	124.3079
-30	150.2078	150.1901	149.8713	136.5606	136.5606	124.3447	124.3587	124.1977

Table S8. The temperature dependence of the isotope shifts for pyridine/pyridine-d_1 given in ppm.

Temp. (°C)	$^1\Delta_{obs}$ δ_{C2D}-δ_{C2H}	$^3\Delta_{obs}$ δ_{C6D}–δ_{C6H}	$^3\Delta_{obs}$ δ_{C4D}-δ_{C4H}	$^2\Delta_{obs}$ δ_{C3D}-δ_{C3H}	$^4\Delta_{obs}$ δ_{C5D}-δ_{C5H}
70	-0.3288	-0.0142	0.0000	-0.1360	0.0131
55	-0.3288	-0.0152	0.0000	-0.1369	0.0114
40	-0.3313	-0.0155	0.0000	-0.1394	0.0111
25	-0.3329	-0.0158	0.0000	-0.1410	0.0122
10	-0.3341	-0.0164	0.0000	-0.1425	0.0125
0	-0.3347	-0.0170	0.0000	-0.1441	0.0132
-10	-0.3358	-0.0173	0.0000	-0.1450	0.0134
-15	-0.3372	-0.0176	0.0000	-0.1458	0.0133
-30	-0.3365	-0.0177	0.0000	-0.1470	0.0140

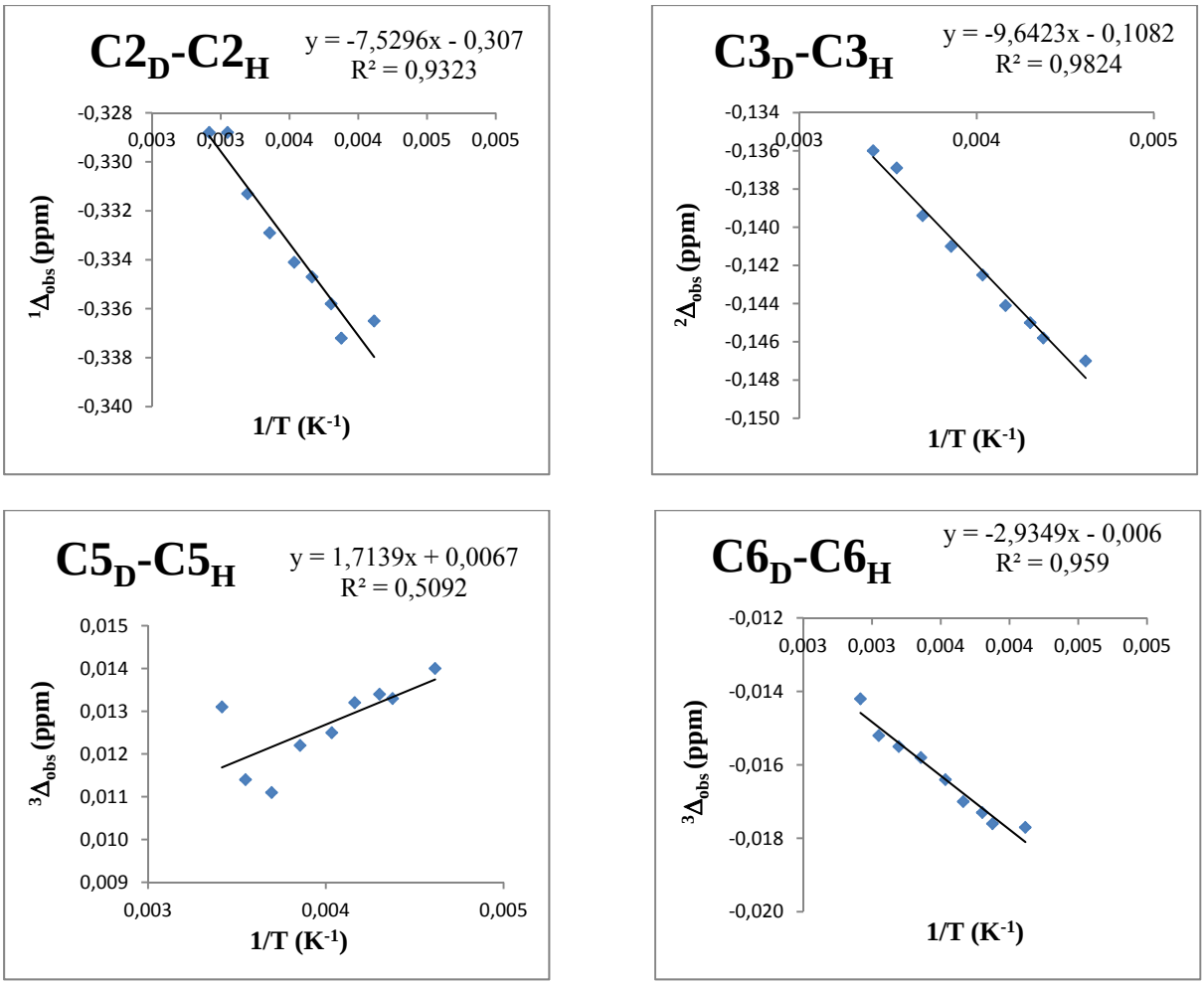


Figure S6. The temperature dependence of the isotope shifts of pyridine/pyridine-d_1 shown for each carbon separately.

3 Computational Details: Geometry Optimization and Thermochemistry

All calculations in this work were performed with the Gaussian09 program package.[6] The computational protocol was kept identical to that in Refs. 7 and 8 as far as possible. Geometries were optimized with density functional theory (DFT) using the B3LYP exchange and correlation functional[9] and the LANL08 basis set[10] and LANL2DZ effective core potential (ECP)[11] for I and Br, Pople's 6-311++G(d,p) basis set[12,13,14] for N and the H atom in the N-H-N bond of **3**, and Pople's 6-311G(d,p)[12,13] basis set otherwise. This construction of the basis set ensures that the basis set (i) is of triple-zeta quality including polarization functions for all atoms, (ii) provides diffuse functions for all atoms involved in hydrogen or halogen bonds. At the same time, the size of the basis set is still tractable. However, the 6-311+G(d,p) basis set was used for all atoms in the triflate moiety to account for the anionic character of the triflate ion. Solvent effects were taken into account by the polarisable continuum model (PCM)[15] with CH_2Cl_2 (ε = 8.93) and CH_3CN (ε = 35.69). To ensure proper convergence of the SCRF calculations in all cases, the cavity had to be constructed as solvent-excluded surface (Gaussian 09 keyword: `Surface=SES`) with atomic radii from the all-atom universal force field (Gaussian 09 keyword: `Radii=UA0`), in distinction from the protocol used in Refs. 7 and 8. Hence, the results presented here for solution in CH_2Cl_2 differ slightly from those in Refs. 7 and 8. Natural atomic populations (NAP) were calculated with the natural-bond orbital (NBO) analysis package[16] as implemented in Gaussian 09.

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[6] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

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[8] A. C. Carlsson, J. Grafenstein, A. Budnjo, J. L. Laurila, J. Bergquist, A. Karim, R. Kleinmaier, U. Brath and M. Erdelyi, *J. Am. Chem. Soc.*, 2012, **134**, 5706.

[9] (a) A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37,** 785; (c) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys*., 1980, **58**, 1200; (d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98,** 11623.

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[11] (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 27; (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 284;(c) P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 299.

[12] (a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.,* 1980, **72**, 650.
(b) M. M. Francl, W. J. Petro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.

[13] R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys*., 1980, **72**, 650.

[14] T. Clark, J. Chandrasekhar, G.W. Spitznagel and P.v. R. Schleyer, *J. Comp. Chem*., 1983, **4**, 294.

[15] (a) B. Mennucci and J. Tomasi, *J. Chem. Phys.,* 1997, **106**, 5151; (b) M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.,* 2002, **117**, 43.

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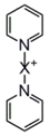
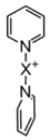
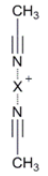
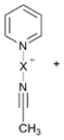
DFT description of the three-center four-electron bonds in **1** and **2** is subtle due to the incomplete coverage of non-dynamic electron on the one hand and the self-interaction error on the other hand.[17,18] The reliability of the applied DFT method for **1** and **2** was previously confirmed7 using second-order Møller-Plesset (MP2) perturbation theory[19] and the same basis set as described in the previous paragraph, the details being given in reference 4.

3.1 Equilibrium Geometries and Selected Charges

Table S7. Computationally predicted N-X and N-N distances [Å] for the equilibrium geometries of **1**, **2**, and **3**.[a]

Structure		X	$d_{N\text{-}X}(1)$	$d_{N\text{-}X}(2)$	$d_{N\text{-}N}$	$d_{N\text{-}X}(1)$	$d_{N\text{-}X}(2)$	$d_{N\text{-}N}$
Solvent			**CH_2Cl_2**			**CH_3CN**		
	-	Br	1.894 *1.893*			1.893		
		I	2.093 *2.092*			2.092		
		H	1.024 *1.015*			1.027		
	1	Br	2.139 *2.139*	2.139 *2.139*	4.278 *4.278*	2.139	2.139	4.278
	2	I	2.301 *2.302*	2.301 *2.302*	4.602 *4.604*	2.301	2.301	4.602
	3	H	1.078 *1.069*	1.678 *1.733*	2.755 *2.802*	1.076	1.689	2.765
	1	Br	2.140 *2.140*	2.140 *2.140*	4.280 *4.279*	2.140	2.140	4.280
	2	I	2.302 *2.302*	2.302 *2.302*	4.604 *4.605*	2.304	2.304	4.607
	3	H	1.084 *1.082*	1.646 *1.648*	2.730 *2.730*	1.081	1.657	2.738
		Br				2.060	2.060	4.120
		I				2.228	2.228	4.456
		Br				1.940	2.470	4.410
		I				2.180	2.450	4.630

(a) Values in italics are from Ref. 7, the differences are due to the different construction of the cavity in the PCM calculations.

[17] See e.g. A. D. Becke, *J. Chem. Phys.*, 2003, **119,** 2972.
[18] See e.g. J. Gräfenstein and D. Cremer, *Theor. Chem. Accounts*, 2009, **123**, 171.
[19] C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.

3.2 Cartesian Coordinates, Thermochemistry Data, and Selected Vibrational Frequencies

Energies are given in Hartree units unless otherwise stated, coordinates in Ångström, vibrational frequencies in cm^{-1}. E(e) denotes the electronic energy (without ZPE), E(298), H(298), and G(298) the energy (including vibrational corrections), enthalpy, and Gibbs free energy at 298.15 K and 1 atm.

Only selected vibrational frequencies are given, in particular: all imaginary frequencies, small frequencies that indicate the geometric stability of a compound, and the frequencies for the N–X–N stretching vibrations. For complexes with symmetric N–X–N geometry, the frequencies are labeled as (s) = symmetric or (a) = antisymmetric.

For a number of compounds, several geometries are given, referring to non-global minima or transition state. For the compounds used in the thermochemical calculations, the headline of the data block is underlined.

3.2.1 Acetonitrile

pyridine C2v SCRF DFT

```
Charge = 0   Multiplicity = 1
N         0.000000     0.000000     1.417595
C         0.000000     1.144718     0.720561
C         0.000000     1.197233    -0.671396
C         0.000000     0.000000    -1.382054
C         0.000000    -1.197233    -0.671396
C         0.000000    -1.144718     0.720561
H         0.000000     2.062091     1.303839
H         0.000000     2.154664    -1.180600
H         0.000000     0.000000    -2.467301
H         0.000000    -2.154664    -1.180600
H         0.000000    -2.062091     1.303839

  E(e)             =          -248.3558104620
  ZPE              =             0.088257
                   =           231.718916      kJ/mol
  E(298)           =          -248.263274
  H(298)           =          -248.262330
  G(298)           =          -248.294301
```

1 D2d SCRF DFT

```
Charge = 1   Multiplicity = 1
Br        0.000000     0.000000     0.000000
N         0.000000     0.000000     2.139320
C         0.000000     1.168486     2.799239
C         0.000000     1.201986     4.185624
C         0.000000     0.000000     4.889330
C         0.000000    -1.201986     4.185624
C         0.000000    -1.168486     2.799239
N         0.000000     0.000000    -2.139320
C         1.168486     0.000000    -2.799239
C         1.201986     0.000000    -4.185624
C         0.000000     0.000000    -4.889330
C        -1.201986     0.000000    -4.185624
C        -1.168486     0.000000    -2.799239
H         0.000000     2.069700     2.196072
H         0.000000     2.157927     4.696052
H         0.000000     0.000000     5.974145
H         0.000000    -2.157927     4.696052
H         0.000000    -2.069700     2.196072
H         2.069700     0.000000    -2.196072
H         2.157927     0.000000    -4.696052
H         0.000000     0.000000    -5.974145
H        -2.157927     0.000000    -4.696052
H        -2.069700     0.000000    -2.196072

  E(e)             =          -509.7052870590
  ZPE              =             0.180392
                   =           473.619637      kJ/mol
  E(298)           =          -509.513126
  H(298)           =          -509.512182
  G(298)           =          -509.564785

    Frequencies:
      B2                   161.6342 (a)
      A1                   173.0364 (s)
```

1 D2h SCRF DFT

```
Charge = 1   Multiplicity = 1
Br         0.000000     0.000000     0.000000
N          0.000000     0.000000     2.138772
C          0.000000     1.168437     2.798622
C          0.000000     1.201974     4.184989
C          0.000000     0.000000     4.888733
C          0.000000    -1.201974     4.184989
C          0.000000    -1.168437     2.798622
N          0.000000     0.000000    -2.138772
C          0.000000    -1.168437    -2.798622
C          0.000000    -1.201974    -4.184989
C          0.000000     0.000000    -4.888733
C          0.000000     1.201974    -4.184989
C          0.000000     1.168437    -2.798622
H          0.000000     2.069692     2.195424
H          0.000000     2.157929     4.695387
H          0.000000     0.000000     5.973541
H          0.000000    -2.157929     4.695387
H          0.000000    -2.069692     2.195424
H          0.000000    -2.069692    -2.195424
H          0.000000    -2.157929    -4.695387
H          0.000000     0.000000    -5.973541
H          0.000000     2.157929    -4.695387
H          0.000000     2.069692    -2.195424

  E(e)            =          -509.7052866990
  ZPE             =             0.180378
                  =           473.582650      kJ/mol
  E(298)          =          -509.513136
  H(298)          =          -509.512192
  G(298)          =          -509.564795

    Frequencies:
      B1U                  161.8916 (a)
      AG                   172.7634 (s)
```

---

2 C2v twisted SCRF DFT

```
Charge = 1   Multiplicity = 1
N          2.303548     0.000000     0.000000
C          2.972076    -0.830482     0.819046
C          4.358090    -0.854957     0.843218
C          5.063061     0.000000     0.000000
C          4.358090     0.854957    -0.843218
C          2.972076     0.830482    -0.819046
H          2.374635    -1.474837     1.454482
H          4.867205    -1.536071     1.514992
H          6.147858     0.000000     0.000000
H          4.867205     1.536071    -1.514992
H          2.374635     1.474837    -1.454482
I         -0.000013     0.000000     0.000000
N         -2.303530     0.000000     0.000000
C         -2.972060     0.830452     0.819075
C         -4.358074     0.854924     0.843251
C         -5.063045     0.000000     0.000000
C         -4.358074    -0.854924    -0.843251
C         -2.972060    -0.830452    -0.819075
H         -2.374619     1.474787     1.454531
H         -4.867188     1.536012     1.515052
H         -6.147842     0.000000     0.000000
H         -4.867189    -1.536012    -1.515052
H         -2.374619    -1.474787    -1.454531

  E(e)            =          -507.9394097090
  ZPE             =             0.180209
                  =           473.137222      kJ/mol
  E(298)          =          -507.747253
  H(298)          =          -507.746309
  G(298)          =          -507.802356

    Frequencies:
      A                      4.8134
      A                    163.2099 (a)
      A                    165.4807 (s)
```

2 D2d SCRF DFT

```
Charge = 1   Multiplicity = 1
I         0.000000     0.000000     0.000000
N         0.000000     0.000000     2.302262
C         0.000000     1.166606     2.970701
C         0.000000     1.200948     4.356767
C         0.000000     0.000000     5.061639
C         0.000000    -1.200948     4.356767
C         0.000000    -1.166606     2.970701
N         0.000000     0.000000    -2.302262
C         1.166606     0.000000    -2.970701
C         1.200948     0.000000    -4.356767
C         0.000000     0.000000    -5.061639
C        -1.200948     0.000000    -4.356767
C        -1.166606     0.000000    -2.970701
H         0.000000     2.071818     2.373573
H         0.000000     2.157450     4.866176
H         0.000000     0.000000     6.146456
H         0.000000    -2.157450     4.866176
H         0.000000    -2.071818     2.373573
H         2.071818     0.000000    -2.373573
H         2.157450     0.000000    -4.866176
H         0.000000     0.000000    -6.146456
H        -2.157450     0.000000    -4.866176
H        -2.071818     0.000000    -2.373573

  E(e)             =          -507.9392567900
  ZPE              =             0.180075
                   =           472.787147      kJ/mol
  E(298)           =          -507.748132
  H(298)           =          -507.747188
  G(298)           =          -507.797724

    Frequencies:
      B1                    -8.4456
      B2                   161.4689 (a)
      A1                   165.1209 (s)
```

2 D2h SCRF DFT

```
Charge = 1   Multiplicity = 1
I         0.000000     0.000000     0.000000
N         0.000000     0.000000     2.301714
C         0.000000     1.166568     2.970093
C         0.000000     1.200939     4.356139
C         0.000000     0.000000     5.061049
C         0.000000    -1.200939     4.356139
C         0.000000    -1.166568     2.970093
N         0.000000     0.000000    -2.301714
C         0.000000    -1.166568    -2.970093
C         0.000000    -1.200939    -4.356139
C         0.000000     0.000000    -5.061049
C         0.000000     1.200939    -4.356139
C         0.000000     1.166568    -2.970093
H         0.000000     2.071831     2.372966
H         0.000000     2.157460     4.865512
H         0.000000     0.000000     6.145860
H         0.000000    -2.157460     4.865512
H         0.000000    -2.071831     2.372966
H         0.000000    -2.071831    -2.372966
H         0.000000    -2.157460    -4.865512
H         0.000000     0.000000    -6.145860
H         0.000000     2.157460    -4.865512
H         0.000000     2.071831    -2.372966

  E(e)             =          -507.9392742810
  ZPE              =             0.180067
                   =           472.764678      kJ/mol
  E(298)           =          -507.748156
  H(298)           =          -507.747212
  G(298)           =          -507.797750

    Frequencies:
      AU                    -8.8677
      B1U                  161.7143 (a)
```

```
      AG                   164.9372 (s)
```

---

3 C2v twisted SCRF DFT

```
Charge = 1   Multiplicity = 1
H         0.000000     0.000000     0.301911
N         0.000000     0.000000     1.383083
C         0.000000     1.177067     2.032802
C         0.000000     1.206557     3.415696
C         0.000000     0.000000     4.114708
C         0.000000    -1.206557     3.415696
C         0.000000    -1.177067     2.032802
N         0.000000     0.000000    -1.354899
C         1.153609     0.000000    -2.040439
C         1.199677     0.000000    -3.429573
C         0.000000     0.000000    -4.136829
C        -1.199677     0.000000    -3.429573
C        -1.153609     0.000000    -2.040439
H         0.000000     2.068433     1.415521
H         0.000000     2.158987     3.931754
H         0.000000     0.000000     5.199731
H         0.000000    -2.158987     3.931754
H         0.000000    -2.068433     1.415521
H         2.065564     0.000000    -1.450161
H         2.155820     0.000000    -3.940187
H         0.000000     0.000000    -5.221888
H        -2.155820     0.000000    -3.940187
H        -2.065564     0.000000    -1.450161

  E(e)             =          -497.1744979390
  ZPE              =             0.190524
                   =           500.220798      kJ/mol
  E(298)           =          -496.973581
  H(298)           =          -496.972637
  G(298)           =          -497.022392

    Frequencies:
      A1                   127.2338
      A1                   611.0440
```

---

3 C2v planar SCRF DFT

```
Charge = 1   Multiplicity = 1
H         0.000000     0.000000     0.321471
N         0.000000     0.000000     1.397362
C         0.000000     1.177040     2.048494
C         0.000000     1.206123     3.431082
C         0.000000     0.000000     4.130350
C         0.000000    -1.206123     3.431082
C         0.000000    -1.177040     2.048494
N         0.000000     0.000000    -1.367777
C         0.000000    -1.152237    -2.056653
C         0.000000    -1.198834    -3.445783
C         0.000000     0.000000    -4.153837
C         0.000000     1.198834    -3.445783
C         0.000000     1.152237    -2.056653
H         0.000000     2.069982     1.433921
H         0.000000     2.158730     3.946801
H         0.000000     0.000000     5.215365
H         0.000000    -2.158730     3.946801
H         0.000000    -2.069982     1.433921
H         0.000000    -2.066540    -1.470125
H         0.000000    -2.155482    -3.955495
H         0.000000     0.000000    -5.238888
H         0.000000     2.155482    -3.955495
H         0.000000     2.066540    -1.470125

  E(e)             =          -497.1730487440
  ZPE              =             0.190665
                   =           500.591751      kJ/mol
  E(298)           =          -496.972945
  H(298)           =          -496.972001
  G(298)           =          -497.018376

    Frequencies:
      A2                   -51.3630
```

```
      A1                   146.2439 (a)
      A1                   611.7396 (s)
```

Acetonitrile C3v SCRF DFT

```
Charge = 0   Multiplicity = 1
N         0.000000     0.000000     1.432336
C         0.000000     0.000000     0.279074
C         0.000000     0.000000    -1.175586
H         0.000000     1.026082    -1.549091
H         0.888613    -0.513041    -1.549091
H        -0.888613    -0.513041    -1.549091

  E(e)             =          -132.8030090700
  ZPE              =             0.045103
                   =           118.416865      kJ/mol
  E(298)           =          -132.754315
  H(298)           =          -132.753371
  G(298)           =          -132.780867

    Frequencies:
      E                    393.1575
```

---

pyridine-bromonium-acetonitrile complex D3h SCRF DFT

```
Charge = 1   Multiplicity = 1
N         0.000000     0.000000     2.060100
C         0.000000     0.000000     3.207055
C         0.000000     0.000000     4.652604
H         0.000000     1.030531     5.015760
H        -0.892466    -0.515266     5.015760
H         0.892466    -0.515266     5.015760
Br        0.000000     0.000000     0.000000
N         0.000000     0.000000    -2.060100
C         0.000000     0.000000    -3.207055
C         0.000000     0.000000    -4.652604
H         0.000000     1.030531    -5.015760
H         0.892466    -0.515266    -5.015760
H        -0.892466    -0.515266    -5.015760

  E(e)             =          -278.5362776150
  ZPE              =             0.092942
                   =           244.019081      kJ/mol
  E(298)           =          -278.432712
  H(298)           =          -278.431768
  G(298)           =          -278.481130
```

---

pyridine-iodonium-acetonitrile complex D3h SCRF DFT

```
Charge = 1   Multiplicity = 1
N         0.000000     0.000000     2.227939
C         0.000000     0.000000     3.375806
C         0.000000     0.000000     4.821272
H         0.000000     1.030273     5.185199
H        -0.892243    -0.515137     5.185199
H         0.892243    -0.515137     5.185199
I         0.000000     0.000000     0.000000
N         0.000000     0.000000    -2.227939
C         0.000000     0.000000    -3.375806
C         0.000000     0.000000    -4.821272
H         0.000000     1.030273    -5.185199
H         0.892243    -0.515137    -5.185199
H        -0.892243    -0.515137    -5.185199

  E(e)             =          -276.7822751010
  ZPE              =             0.092891
                   =           243.886406      kJ/mol
  E(298)           =          -276.678786
  H(298)           =          -276.677841
  G(298)           =          -276.727405
```

---

pyridine-protium-acetonitrile complex D3h SCRF DFT

```
Charge = 1   Multiplicity = 1
H       -0.001253     0.446929     0.000000
N       -0.001437    -0.590479     0.000000
C       -0.001433    -1.235319     1.181528
C       -0.001433    -2.616956     1.207435
C       -0.001426    -3.314810     0.000000
C       -0.001433    -2.616956    -1.207435
C       -0.001433    -1.235319    -1.181528
H       -0.001412    -0.615066     2.070329
H       -0.001418    -3.133575     2.159478
H       -0.001394    -4.399857     0.000000
H       -0.001418    -3.133575    -2.159478
H       -0.001412    -0.615066    -2.070329
N        0.000157     2.284314     0.000000
C        0.002130     3.435414     0.000000
C        0.005038     4.887339     0.000000
H        1.033091     5.255595     0.000000
H       -0.507941     5.258708    -0.889631
H       -0.507941     5.258708     0.889631

  E(e)            =          -381.6140869970
  ZPE             =             0.147904
                  =           388.322647      kJ/mol
  E(298)          =          -381.456237
  H(298)          =          -381.455293
  G(298)          =          -381.505692
```

OTf- Cs SCRF DFT

```
Charge = -1   Multiplicity = 1
S       -0.410103    -0.823814     0.000000
C        0.430493     0.864227     0.000000
O       -1.847724    -0.483556     0.000000
F        1.769013     0.737293     0.000000
F        0.083511     1.575575     1.086795
F        0.083511     1.575575    -1.086795
O        0.083511    -1.445742     1.245736
O        0.083511    -1.445742    -1.245736

  E(e)            =          -961.8140800790
  ZPE             =             0.026215
                  =            68.827679      kJ/mol
  E(298)          =          -961.780593
  H(298)          =          -961.779649
  G(298)          =          -961.820534
```

BrOTf Cs SCRF DFT

```
Charge = 0   Multiplicity = 1
S        0.753084    -0.345152     0.000000
C        1.469507     1.424580     0.000000
O       -0.799885     0.199273     0.000000
F        2.790943     1.296432     0.000000
F        1.076880     2.068708     1.086958
F        1.076880     2.068708    -1.086958
O        1.076880    -0.977480     1.262020
O        1.076880    -0.977480    -1.262020
Br      -2.177135    -1.082405     0.000000

  E(e)            =          -974.7286406070
  ZPE             =             0.027086
                  =            71.113858      kJ/mol
  E(298)          =          -974.692114
  H(298)          =          -974.691169
  G(298)          =          -974.739765
```

IOTf Cs SCRF DFT

```
Charge = 0   Multiplicity = 1
S         1.126947    -0.153104     0.000000
C         1.854963     1.604171     0.000000
O        -0.406530     0.358601     0.000000
F         3.177999     1.472259     0.000000
F         1.469292     2.256748     1.086966
F         1.469292     2.256748    -1.086966
O         1.469292    -0.783311     1.260619
O         1.469292    -0.783311    -1.260619
I        -1.971068    -0.969490     0.000000

  E(e)             =          -972.9666481320
  ZPE              =             0.027043
                   =            71.000137      kJ/mol
  E(298)           =          -972.930123
  H(298)           =          -972.929179
  G(298)           =          -972.978516
```

HOTf C1 SCRF DFT

```
Charge = 0   Multiplicity = 1
S        -0.867610    -0.141546     0.046766
C         1.018475     0.008743    -0.002440
O        -1.283584     1.265480    -0.604480
F         1.542080    -1.092635     0.527243
F         1.398619     1.069452     0.705451
F         1.427795     0.139927    -1.258916
O        -1.253290    -0.207044     1.442450
O        -1.237008    -1.160537    -0.909633
H        -1.354481     1.978398     0.075695

  E(e)             =          -962.2303614940
  ZPE              =             0.036911
                   =            96.910477      kJ/mol
  E(298)           =          -962.185505
  H(298)           =          -962.184560
  G(298)           =          -962.227177
```

HOTf Cs SCRF DFT

```
Charge = 0   Multiplicity = 1
S        -0.273679    -0.837104     0.000000
C         0.457166     0.908601     0.000000
O        -1.801479    -0.334510     0.000000
F         1.781600     0.780307     0.000000
F         0.071972     1.565945     1.086846
F         0.071972     1.565945    -1.086846
O         0.071972    -1.468568     1.259735
O         0.071972    -1.468568    -1.259735
H        -2.433750    -1.094544     0.000000

  E(e)             =          -962.2279368350
  ZPE              =             0.036129
                   =            94.857012      kJ/mol
  E(298)           =          -962.184329
  H(298)           =          -962.183385
  G(298)           =          -962.224826

    Frequencies:
      A"                  -130.8856
```

3.2.2. Dichloromethane

pyridine C2v SCRF DFT

```
Charge = 0   Multiplicity = 1
N         0.000000     0.000000     1.417467
C         0.000000     1.144215     0.720587
C         0.000000     1.197075    -0.671414
C         0.000000     0.000000    -1.382101
C         0.000000    -1.197075    -0.671414
C         0.000000    -1.144215     0.720587
H         0.000000     2.061206     1.304259
H         0.000000     2.154393    -1.180533
H         0.000000     0.000000    -2.467197
H         0.000000    -2.154393    -1.180533
H         0.000000    -2.061206     1.304259

  E(e)             =          -248.3548683070
  ZPE              =             0.088293
                   =           231.813516      kJ/mol
  E(298)           =          -248.262296
  H(298)           =          -248.261352
  G(298)           =          -248.293322
```

1 D2d SCRF DFT

```
Charge = 1   Multiplicity = 1
Br        0.000000     0.000000     0.000000
N         0.000000     0.000000     2.139530
C         0.000000     1.168333     2.799603
C         0.000000     1.201910     4.185950
C         0.000000     0.000000     4.889670
C         0.000000    -1.201910     4.185950
C         0.000000    -1.168333     2.799603
N         0.000000     0.000000    -2.139530
C         1.168333     0.000000    -2.799603
C         1.201910     0.000000    -4.185950
C         0.000000     0.000000    -4.889670
C        -1.201910     0.000000    -4.185950
C        -1.168333     0.000000    -2.799603
H         0.000000     2.069266     2.196490
H         0.000000     2.157615     4.696386
H         0.000000     0.000000     5.974275
H         0.000000    -2.157615     4.696386
H         0.000000    -2.069266     2.196490
H         2.069266     0.000000    -2.196490
H         2.157615     0.000000    -4.696386
H         0.000000     0.000000    -5.974275
H        -2.157615     0.000000    -4.696386
H        -2.069266     0.000000    -2.196490

  E(e)             =          -509.6998061030
  ZPE              =             0.180505
                   =           473.914484      kJ/mol
  E(298)           =          -509.507503
  H(298)           =          -509.506559
  G(298)           =          -509.560786

    Frequencies:
      B1                        3.4691
      B2                      164.8693 (a)
      A1                      173.1980 (s)
```

1 D2h SCRF DFT

```
Charge = 1   Multiplicity = 1
Br         0.000000     0.000000     0.000000
N          0.000000     0.000000     2.139191
C          0.000000     1.168206     2.799298
C          0.000000     1.201864     4.185614
C          0.000000     0.000000     4.889388
C          0.000000    -1.201864     4.185614
C          0.000000    -1.168206     2.799298
N          0.000000     0.000000    -2.139191
C          0.000000    -1.168206    -2.799298
C          0.000000    -1.201864    -4.185614
C          0.000000     0.000000    -4.889388
C          0.000000     1.201864    -4.185614
C          0.000000     1.168206    -2.799298
H          0.000000     2.069226     2.196287
H          0.000000     2.157582     4.696020
H          0.000000     0.000000     5.973984
H          0.000000    -2.157582     4.696020
H          0.000000    -2.069226     2.196287
H          0.000000    -2.069226    -2.196287
H          0.000000    -2.157582    -4.696020
H          0.000000     0.000000    -5.973984
H          0.000000     2.157582    -4.696020
H          0.000000     2.069226    -2.196287

  E(e)            =          -509.6997020410
  ZPE             =             0.180480
                  =           473.849297      kJ/mol
  E(298)          =          -509.507413
  H(298)          =          -509.506469
  G(298)          =          -509.561678

    Frequencies:
      AU                      1.2428
      B1U                   164.8975 (a)
      AG                    172.8800 (s)
```

---

2 D2 SCRF DFT

```
Charge = 1   Multiplicity = 1
N          0.000000     0.000000     2.140010
C          0.000000     1.168267     2.799639
C          0.000408     1.201922     4.185997
C          0.000000     0.000000     4.889663
C         -0.000408    -1.201922     4.185997
C          0.000000    -1.168267     2.799639
H         -0.001143     2.068906     2.196198
H          0.000358     2.157705     4.696269
H          0.000000     0.000000     5.974234
H         -0.000358    -2.157705     4.696269
H          0.001143    -2.068906     2.196198
Br         0.000000     0.000000     0.000196
N          0.000000     0.000000    -2.139589
C          0.873848     0.775373    -2.799876
C          0.898598     0.797889    -4.186194
C          0.000000     0.000000    -4.889961
C         -0.898598    -0.797889    -4.186194
C         -0.873848    -0.775373    -2.799876
H          1.548192     1.373287    -2.197213
H          1.613283     1.432491    -4.696527
H          0.000000     0.000000    -5.974524
H         -1.613283    -1.432491    -4.696527
H         -1.548192    -1.373287    -2.197213

  E(e)            =          -509.6997498610
  ZPE             =             0.180538
                  =           474.001887      kJ/mol
  E(298)          =          -509.507436
  H(298)          =          -509.506491
  G(298)          =          -509.559904

    Frequencies:
      B                     146.7364 (a)
      A                     164.5953 (s)
```

2 D2d SCRF DFT

```
Charge = 1   Multiplicity = 1
I         0.000000     0.000000     0.000000
N         0.000000     0.000000     2.302432
C         0.000000     1.166491     2.971000
C         0.000000     1.200887     4.357022
C         0.000000     0.000000     5.061888
C         0.000000    -1.200887     4.357022
C         0.000000    -1.166491     2.971000
N         0.000000     0.000000    -2.302432
C         1.166491     0.000000    -2.971000
C         1.200887     0.000000    -4.357022
C         0.000000     0.000000    -5.061888
C        -1.200887     0.000000    -4.357022
C        -1.166491     0.000000    -2.971000
H         0.000000     2.071444     2.373956
H         0.000000     2.157146     4.866454
H         0.000000     0.000000     6.146495
H         0.000000    -2.157146     4.866454
H         0.000000    -2.071444     2.373956
H         2.071444     0.000000    -2.373956
H         2.157146     0.000000    -4.866454
H         0.000000     0.000000    -6.146495
H        -2.157146     0.000000    -4.866454
H        -2.071444     0.000000    -2.373956

  E(e)             =          -507.9337813400
  ZPE              =             0.180198
                   =           473.109566      kJ/mol
  E(298)           =          -507.742524
  H(298)           =          -507.741580
  G(298)           =          -507.792266

    Frequencies:
      B1                   -22.3086
      B2                   162.1558 (a)
      A1                   164.7295 (s)
```

2 D2h SCRF DFT

```
Charge = 1   Multiplicity = 1
I         0.000000     0.000000     0.000000
N         0.000000     0.000000     2.301933
C         0.000000     1.166394     2.970495
C         0.000000     1.200853     4.356488
C         0.000000     0.000000     5.061406
C         0.000000    -1.200853     4.356488
C         0.000000    -1.166394     2.970495
N         0.000000     0.000000    -2.301933
C         0.000000    -1.166394    -2.970495
C         0.000000    -1.200853    -4.356488
C         0.000000     0.000000    -5.061406
C         0.000000     1.200853    -4.356488
C         0.000000     1.166394    -2.970495
H         0.000000     2.071416     2.373532
H         0.000000     2.157130     4.865885
H         0.000000     0.000000     6.146005
H         0.000000    -2.157130     4.865885
H         0.000000    -2.071416     2.373532
H         0.000000    -2.071416    -2.373532
H         0.000000    -2.157130    -4.865885
H         0.000000     0.000000    -6.146005
H         0.000000     2.157130    -4.865885
H         0.000000     2.071416    -2.373532

  E(e)             =          -507.9337230510
  ZPE              =             0.180187
                   =           473.080947      kJ/mol
  E(298)           =          -507.742473
  H(298)           =          -507.741529
  G(298)           =          -507.792227

    Frequencies:
      AU                   -23.3495
```

```
      B1U                   162.2789 (a)
      AG                    164.5005 (s)
```

---

3 C2v twisted SCRF DFT

```
Charge = 1   Multiplicity = 1
H         0.000000     0.000000     0.295007
N         0.000000     0.000000     1.379317
C         0.000000     1.176840     2.029673
C         0.000000     1.206470     3.412491
C         0.000000     0.000000     4.111525
C         0.000000    -1.206470     3.412491
C         0.000000    -1.176840     2.029673
N         0.000000     0.000000    -1.351256
C         1.153611     0.000000    -2.037245
C         1.199525     0.000000    -3.426051
C         0.000000     0.000000    -4.133293
C        -1.199525     0.000000    -3.426051
C        -1.153611     0.000000    -2.037245
H         0.000000     2.068051     1.412613
H         0.000000     2.158576     3.928733
H         0.000000     0.000000     5.196327
H         0.000000    -2.158576     3.928733
H         0.000000    -2.068051     1.412613
H         2.065681     0.000000    -1.447497
H         2.155499     0.000000    -3.936564
H         0.000000     0.000000    -5.218132
H        -2.155499     0.000000    -3.936564
H        -2.065681     0.000000    -1.447497

  E(e)             =          -497.1684564410
  ZPE              =             0.190633
                   =           500.507067      kJ/mol
  E(298)           =          -496.967449
  H(298)           =          -496.966505
  G(298)           =          -497.016190

    Frequencies:
      A1                   131.8475
      A1                   610.2048
```

---

3 C2v planar SCRF DFT

```
Charge = 1   Multiplicity = 1
H         0.000000     0.000000     0.314183
N         0.000000     0.000000     1.392700
C         0.000000     1.176707     2.044308
C         0.000000     1.206070     3.426908
C         0.000000     0.000000     4.126247
C         0.000000    -1.206070     3.426908
C         0.000000    -1.176707     2.044308
N         0.000000     0.000000    -1.363321
C         0.000000    -1.152093    -2.052413
C         0.000000    -1.198741    -3.441271
C         0.000000     0.000000    -4.149283
C         0.000000     1.198741    -3.441271
C         0.000000     1.152093    -2.052413
H         0.000000     2.069853     1.430720
H         0.000000     2.158396     3.942715
H         0.000000     0.000000     5.211043
H         0.000000    -2.158396     3.942715
H         0.000000    -2.069853     1.430720
H         0.000000    -2.066776    -1.466940
H         0.000000    -2.155159    -3.950959
H         0.000000     0.000000    -5.234111
H         0.000000     2.155159    -3.950959
H         0.000000     2.066776    -1.466940

  E(e)             =          -497.1667097120
  ZPE              =             0.190864
                   =           501.111781      kJ/mol
  E(298)           =          -496.966477
  H(298)           =          -496.965533
  G(298)           =          -497.011624

    Frequencies:
```

```
      A1                   169.6880
      A1                   610.6769
```

OTf- Cs SCRF DFT

```
Charge = -1   Multiplicity = 1
S       -0.410982    -0.826133     0.000000
C        0.429764     0.862811     0.000000
O       -1.847843    -0.483459     0.000000
F        1.769430     0.739655     0.000000
F        0.083970     1.576850     1.086417
F        0.083970     1.576850    -1.086417
O        0.083970    -1.445705     1.246079
O        0.083970    -1.445705    -1.246079

  E(e)            =          -961.8065028330
  ZPE             =             0.026252
                  =            68.925166      kJ/mol
  E(298)          =          -961.772978
  H(298)          =          -961.772034
  G(298)          =          -961.812923
```

BrOTf Cs SCRF DFT

```
Charge = 0   Multiplicity = 1
S        0.753217    -0.346234     0.000000
C        1.468711     1.423849     0.000000
O       -0.799946     0.199640     0.000000
F        2.790292     1.296317     0.000000
F        1.076620     2.068505     1.086953
F        1.076620     2.068505    -1.086953
O        1.076620    -0.977215     1.262533
O        1.076620    -0.977215    -1.262533
Br      -2.176625    -1.081857     0.000000

  E(e)            =          -974.7278116170
  ZPE             =             0.027158
                  =            71.303226      kJ/mol
  E(298)          =          -974.691226
  H(298)          =          -974.690282
  G(298)          =          -974.738845
```

IOTf Cs SCRF DFT

```
Charge = 0   Multiplicity = 1
S        1.126947    -0.153104     0.000000
C        1.854963     1.604171     0.000000
O       -0.406530     0.358601     0.000000
F        3.177999     1.472259     0.000000
F        1.469292     2.256748     1.086966
F        1.469292     2.256748    -1.086966
O        1.469292    -0.783311     1.260619
O        1.469292    -0.783311    -1.260619
I       -1.971068    -0.969490     0.000000

  E(e)            =          -972.9666481320
  ZPE             =             0.027043
                  =            71.000137      kJ/mol
  E(298)          =          -972.930123
  H(298)          =          -972.929179
  G(298)          =          -972.978516
```

HOTf C1 SCRF DFT

```
Charge = 0   Multiplicity = 1
S       -0.867617    -0.143175     0.051103
C        1.018136     0.007292    -0.002977
O       -1.279157     1.245784    -0.648546
F        1.544389    -1.072960     0.564844
F        1.394430     1.093706     0.669162
F        1.428764     0.097581    -1.262252
O       -1.253661    -0.151699     1.448041
```

```
O       -1.238520    -1.192884    -0.869031
H       -1.364480     1.972495     0.010712

  E(e)            =          -962.2282615740
  ZPE             =             0.037153
                  =            97.543810      kJ/mol
  E(298)          =          -962.183210
  H(298)          =          -962.182266
  G(298)          =          -962.224416
```

HOTf Cs SCRF DFT

```
Charge = 0   Multiplicity = 1
S       -0.271059    -0.837771     0.000000
C        0.457213     0.909313     0.000000
O       -1.802291    -0.334673     0.000000
F        1.781631     0.782047     0.000000
F        0.070847     1.565509     1.086889
F        0.070847     1.565509    -1.086889
O        0.070847    -1.468685     1.260258
O        0.070847    -1.468685    -1.260258
H       -2.431479    -1.092779     0.000000

  E(e)            =          -962.2258136930
  ZPE             =             0.036320
                  =            95.357628      kJ/mol
  E(298)          =          -962.182011
  H(298)          =          -962.181066
  G(298)          =          -962.222553

    Frequencies:
      A"                 -158.3285
```