Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for:

Lewis acid activation of Weiss' Reagents ($[PhI(Pyr)_2]^{2+}$) with boranes and isolation of $[PhI(DMAP)]^{2+}$

Aseel Bakro,[a#] Lachlan Sharp-Bucknall,[a#] Tiffany B. Poynder,[a] Jack K. Clegg[b], David J. D. Wilson and Jason L. Dutton[a]*

[a] Department of Chemistry and Physics, La Trobe University, Melbourne, Victoria, Australia

[b] School of Chemistry and Molecular Biosciences, The University of Queensland, St Lucia, Queensland, Australia, 4072

# these authors contributed equally

j.dutton@latrobe.edu.au

Experimental:

General Experimental:

Solvents used were dried using an Innovative Technologies Solvent Purification System. The dried solvents were stored under a N_2 atmosphere over 3 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried by stirring for three days over CaH_2, distilled, and stored in the glovebox over 3 Å molecular sieves. 1Pyr,[1] 1DMAP,[1] pyr-BF_3,[2] and TMS-DMAP[3] were synthesized via literature procedure; all other reagents were supplied by Sigma Aldrich and used as received. All reactions were performed in an N_2-filled glove box or Schlenk line under dry N_2 gas.

X-ray Crystallography Details:

Single crystals were selected under n-paratone oil, mounted on nylon loops, and placed into a cold stream (172 K) of N_2 on an AXT Supernova CCD diffractometer using Cu Kα radiation. Structure solution and refinement were performed using the OLEX suite of software. CCDC Number 2103335 contains the supplementary crystallographic data for the structure of **2DMAP**

Synthesis of 2DMAP:

To a solution of $PhI(OAc)_2$ (69 mg, 0.21 mmol) in 1 mL CH_2Cl_2 was added TMS-OTf (82 µL, 0.45 mmol). The solution was then cooled to -35 °C and 4-DMAP (24 mg, 0.20 mmol) in 4 mL of cooled CH_2Cl_2 was added dropwise whilst stirring vigorously to produce a yellow solution with a yellow precipitate. The precipitate was collected via filtration and washed with CH_2Cl_2 (3 x 5 mL) to receive **2DMAP** as a yellow solid (80 mg, 63%). Single crystals suitable for X-ray crystallography were grown via vapor diffusion of diethyl ether into a saturated CH_2Cl_2 solution at -35 °C.

^{1}H NMR (500 MHz, CD_3CN) δ (ppm): 8.46 (d, 2H, *J* = 8.1 Hz), 8.38 (d, 2H, *J* = 7.6 Hz), 7.86 (t, 1H, *J* = 7.5 Hz), 7.71 (t, 2H, *J* = 7.9 Hz), 6.68 (d, 2H, *J* = 7.6 Hz), 3.15 (s, 6H)

^{13}C NMR (126 MHz, CD_3CN) δ (ppm): 147.88, 138.38, 136.45, 133.76, 131.45, 128.68, 111.45, 40.96

Synthesis of 2DMAP using TMS-DMAP:

To a solution of $PhI(OAc)_2$ (43 mg, 0.13 mmol) in 1 mL CH_2Cl_2 was added TMS-OTf (25 µL, 0.14 mmol) where the reaction was allowed to stir for 1 minute before TMS-DMAP (46.4 mg, 0.13 mmol) in 1 mL CH_2Cl_2 was added dropwise to receive a yellow solution. Two drops of Et_2O were then added to the solution to induce precipitation of a yellow solid, which was collected via filtration and washed with CH_2Cl_2 (3 x 3 mL) to receive **2DMAP** as a yellow solid. (59 mg, 70%).

Reaction of TMS-DMAP and PhI(OAc)(OTf) for *in situ* analysis:

PhI(OAc)(OTf) was generated via the addition of TMS-OTf (17 µl, 0.09 mmol) to a 1 mL CH_2Cl_2 solution of $PhI(OAc)_2$ (23 mg, 0.07 mmol), which was allowed to stir for 5 minutes. Volatiles were then removed *in vacuo* to give PhI(OAc)(OTf), with the residues redissolved in 0.5 mL CD_3CN. TMS-DMAP (24 mg, 0.07 mmol) in 0.5 mL CD_3CN was added dropwise to receive a yellow solution. The solution was then taken immediately for *in situ* ^{1}H NMR analysis.

General procedure for reactions between methyl substituted benzenes and 2DMAP:

In a typical experiment an NMR tube was charged with **2DMAP** (5 mg, 0.01 mmol) in CD_3CN, with the corresponding methyl substituted benzene subsequently added in excess (5 µl). The tube was then shaken and subjected to *in situ* ^{1}H-NMR analysis until all **2DMAP** was consumed. A small aliquot of the reaction mixture was then taken for mass spectrometry analysis. Volatiles were removed *in vacuo* from the remaining solution, with the residue then dissolved in $CDCl_3$ to confirm the presence of the corresponding $[Ph\text{-}I\text{-}Ar]^+$ species via ^{1}H NMR analysis.

General procedure for reactions between Weiss' reagents and $BF_3.Et_2O$ with and without benzene:

In a typical experiment one equivalent of $BF_3.Et_2O$ was added to **1L** (0.030 mmol) in 0.6 mL CD_3CN and the solution was stirred vigorously for 1 minute before being taken for NMR analysis. For reactions containing benzene, one equivalent of benzene was added to the

solution containing Weiss' reagent prior to the addition of $BF_3.Et_2O$, which was then stirred vigorously for 1 minute before being taken for NMR analysis. One drop of the above solutions were diluted in 1 mL of CH_3CN for mass spectral analysis.

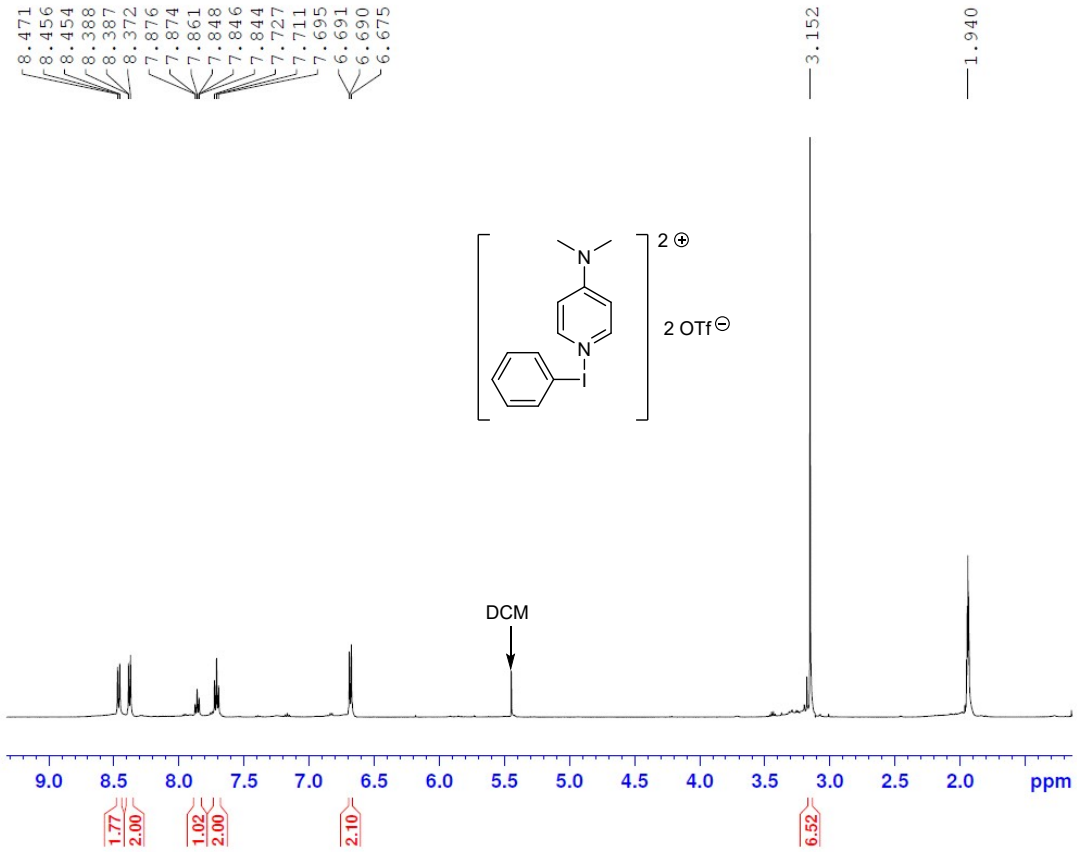

Figure S1. ^{1}H NMR spectrum of **2DMAP**.

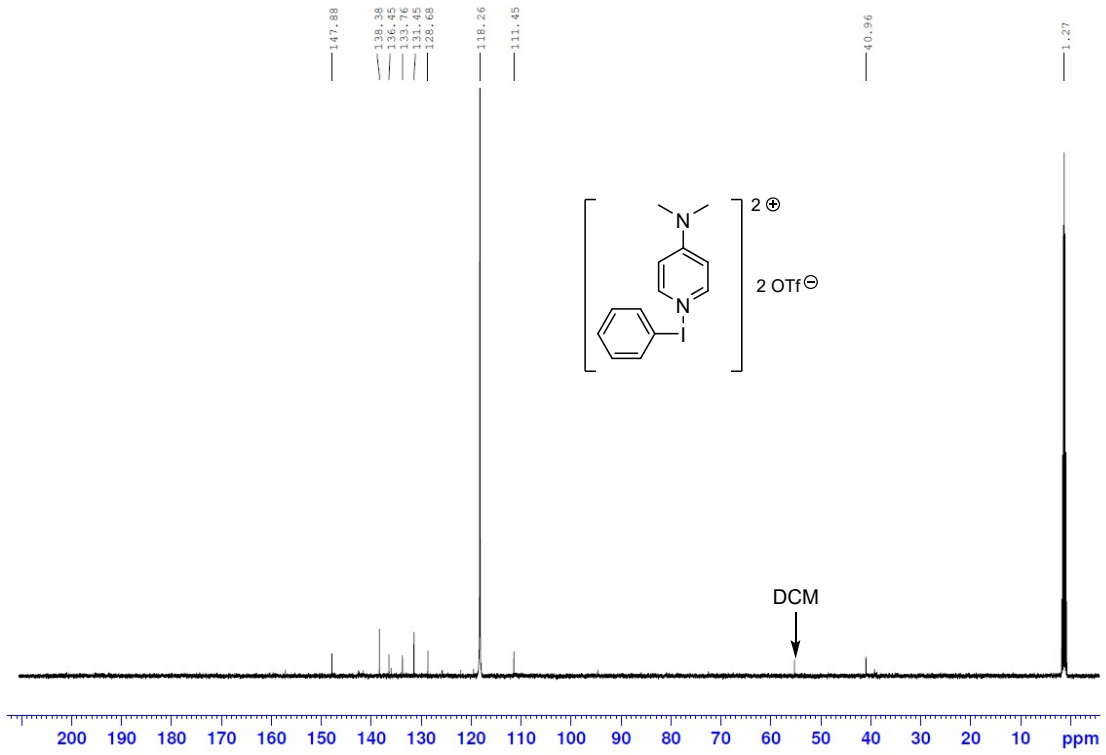

Figure S2. ^{13}C NMR spectrum of **2DMAP**.

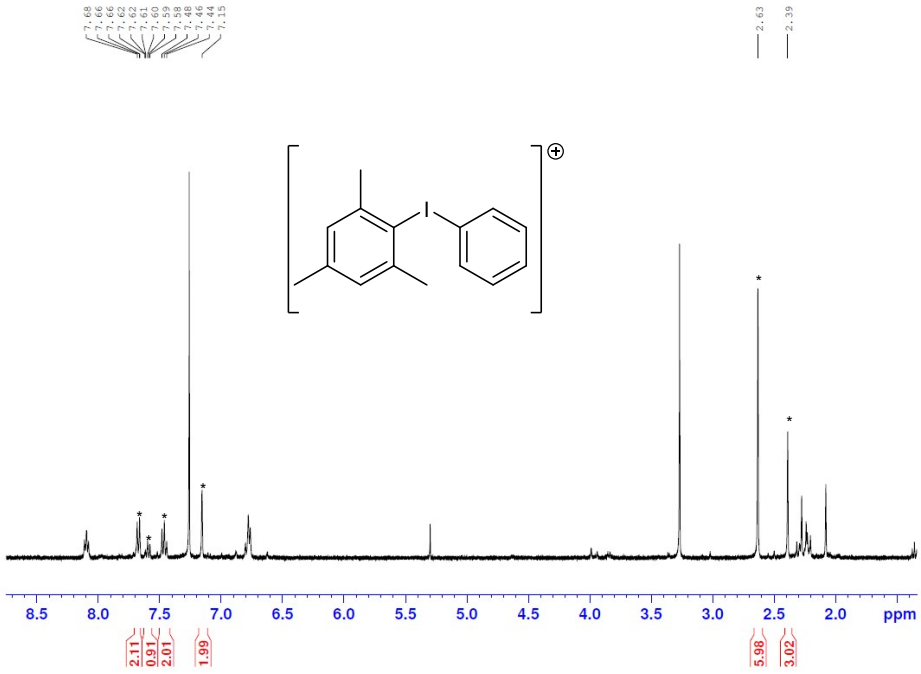

Figure S3. 1H NMR of reaction between **2DMAP** and toluene where * indicates shifts of $[Ph\text{-}I\text{-}Mes]^+$.

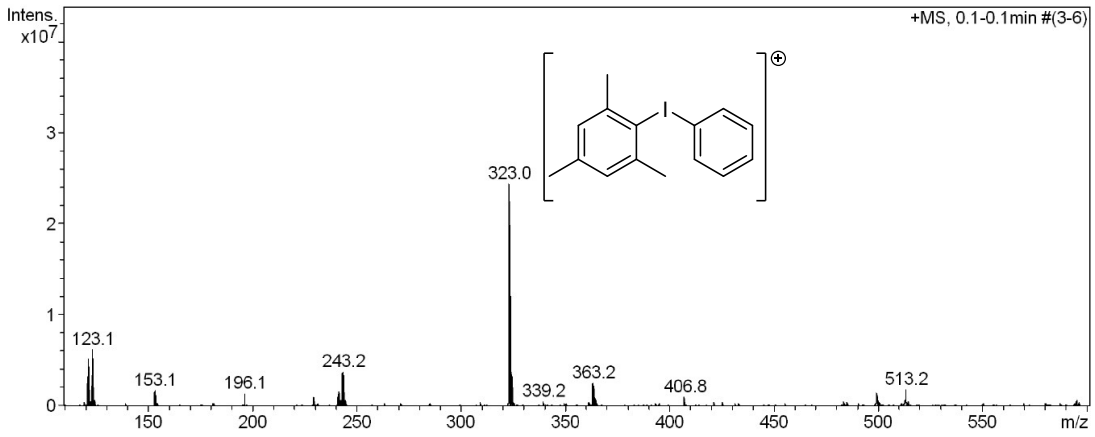

Figure S4. Mass spectrum of reaction between **2DMAP** and mesitylene.

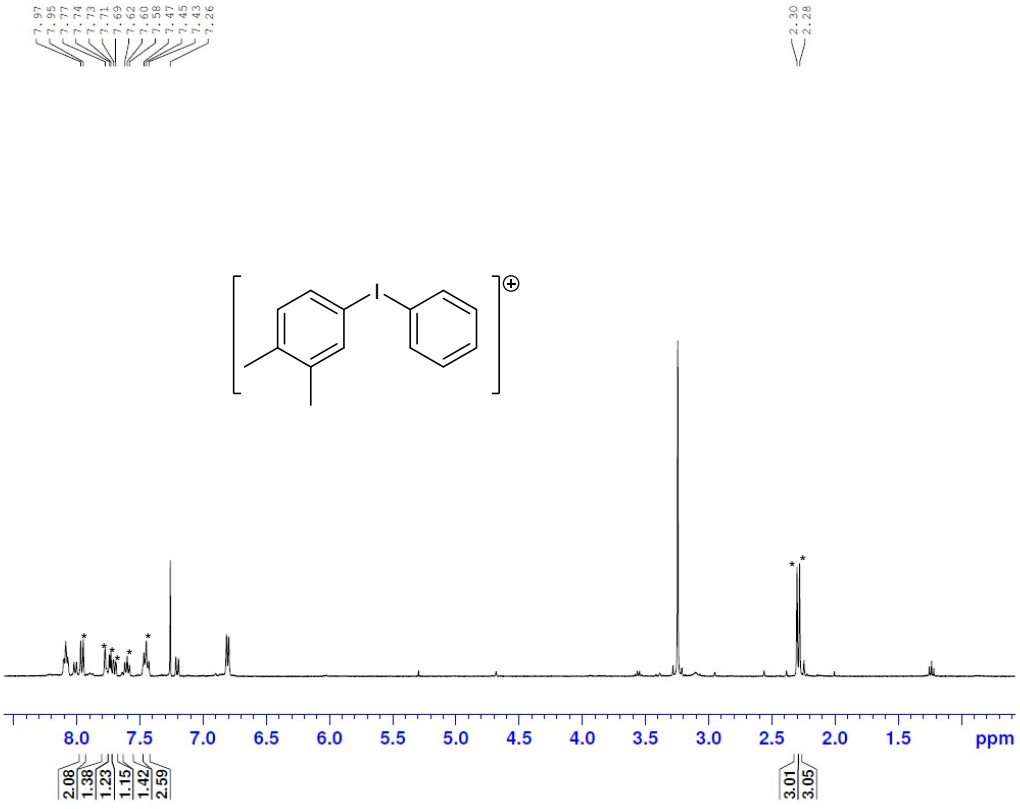

Figure S5. 1H NMR of reaction between **2DMAP** and 1,2-xylene where * indicates shifts of [Ph-I-3,4-dimethylbenzene]$^{+}$.

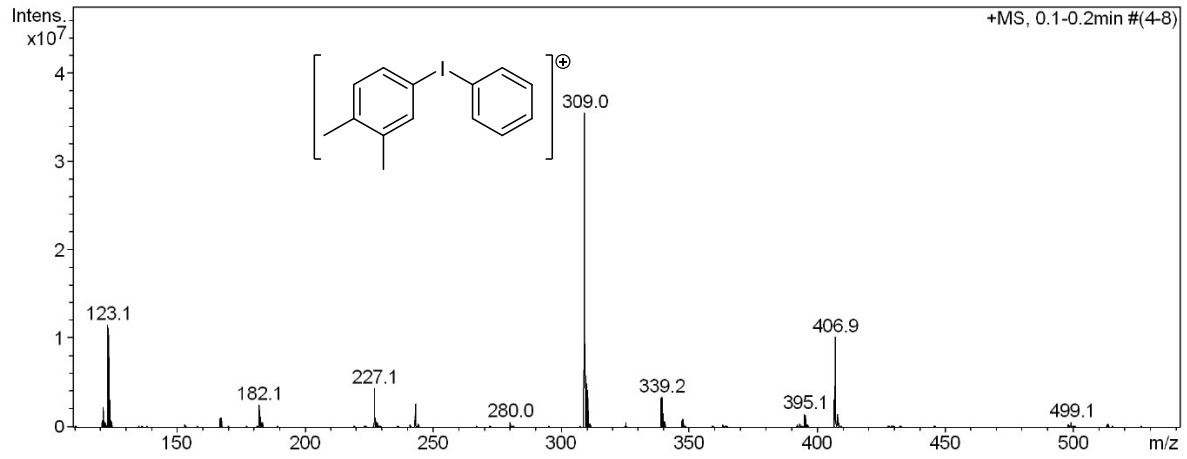

Figure S6. Mass spectrum of reaction between **2DMAP** and 1,2-xylene.

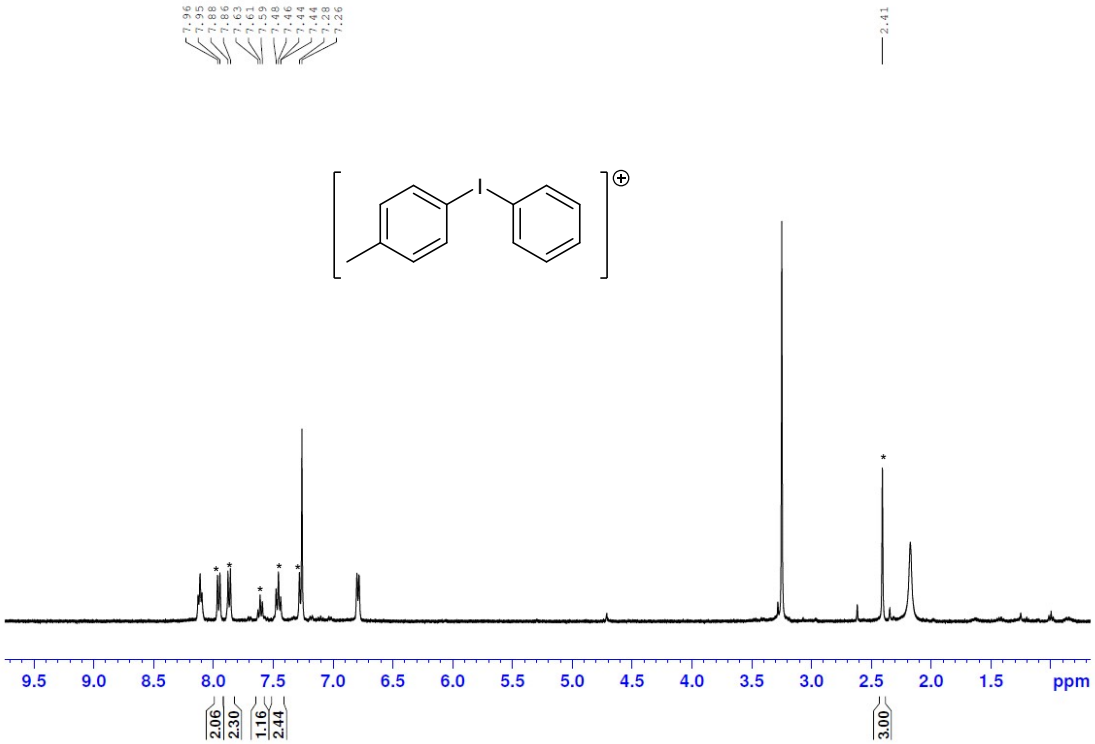

Figure S7. 1H NMR of reaction between **2DMAP** and mesitylene where * indicates shifts of [Ph-I-*p*-tol]$^+$.

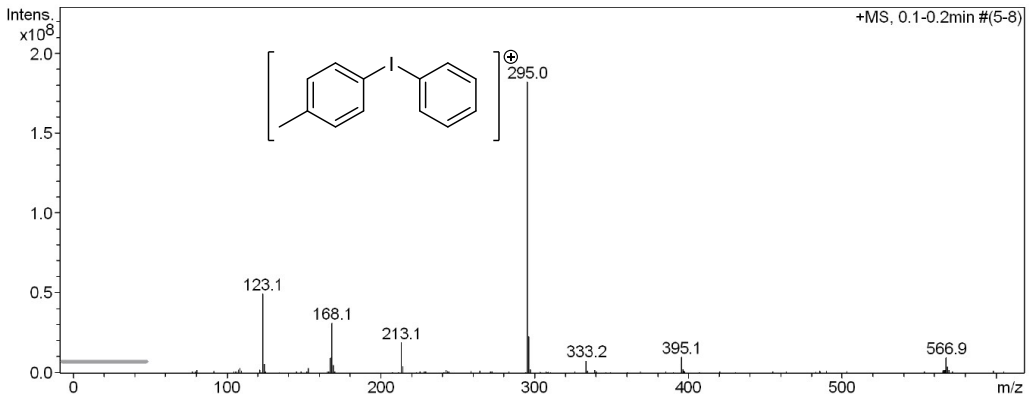

Figure S8. Mass spectrum for reaction between **2DMAP** and toluene.

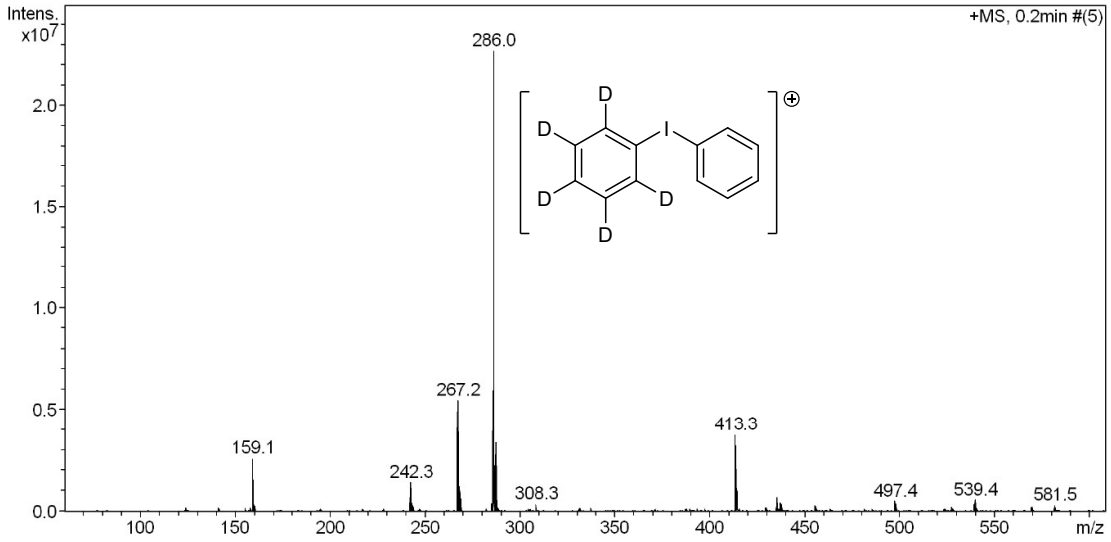

Figure S9. Mass spectrum for reaction between **1Pyr** and $BF_3.OEt_2$ in C_6D_6.

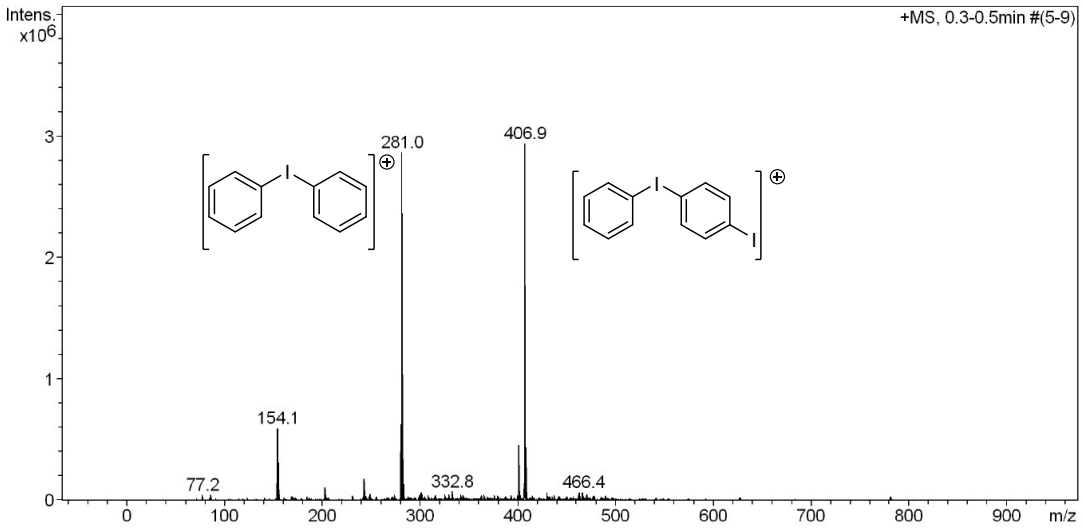

Figure S10. Mass spectrum for reaction between **1Pyr**, $BF_3.OEt_2$ and C_6H_6.

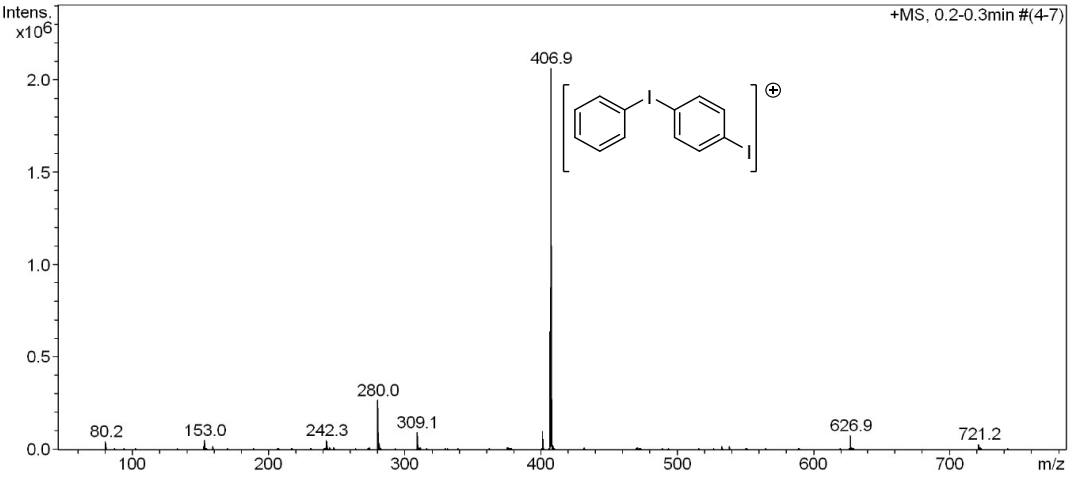

Figure S11. Mass spectrum for reaction between **1Pyr** and $BF_3.OEt_2$.

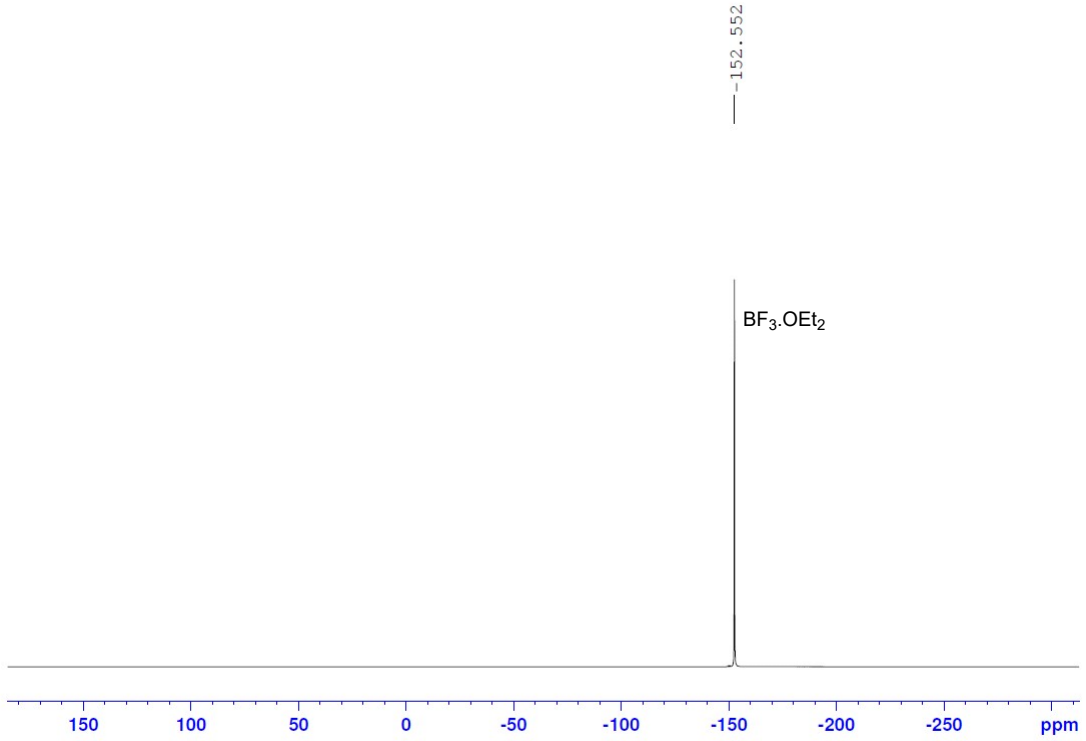

Figure S12. ^{19}F NMR of $BF_3.OEt_2$ in CD_3CN.

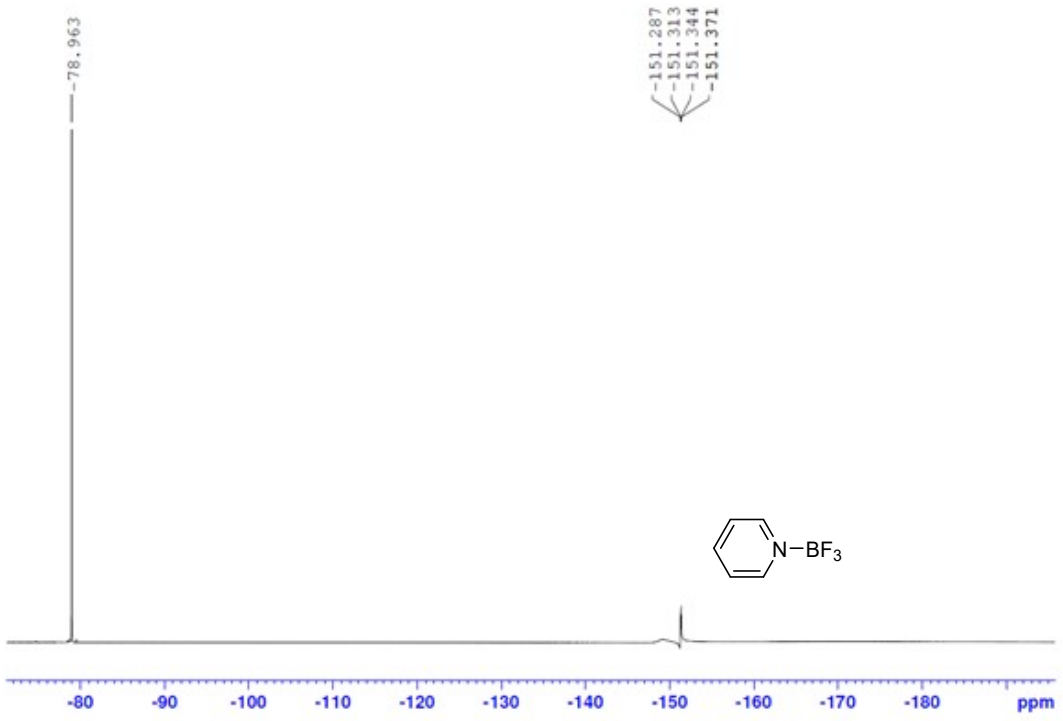

Figure S13. ^{19}F NMR from reaction between **1Pyr** and $BF_3.OEt_2$.

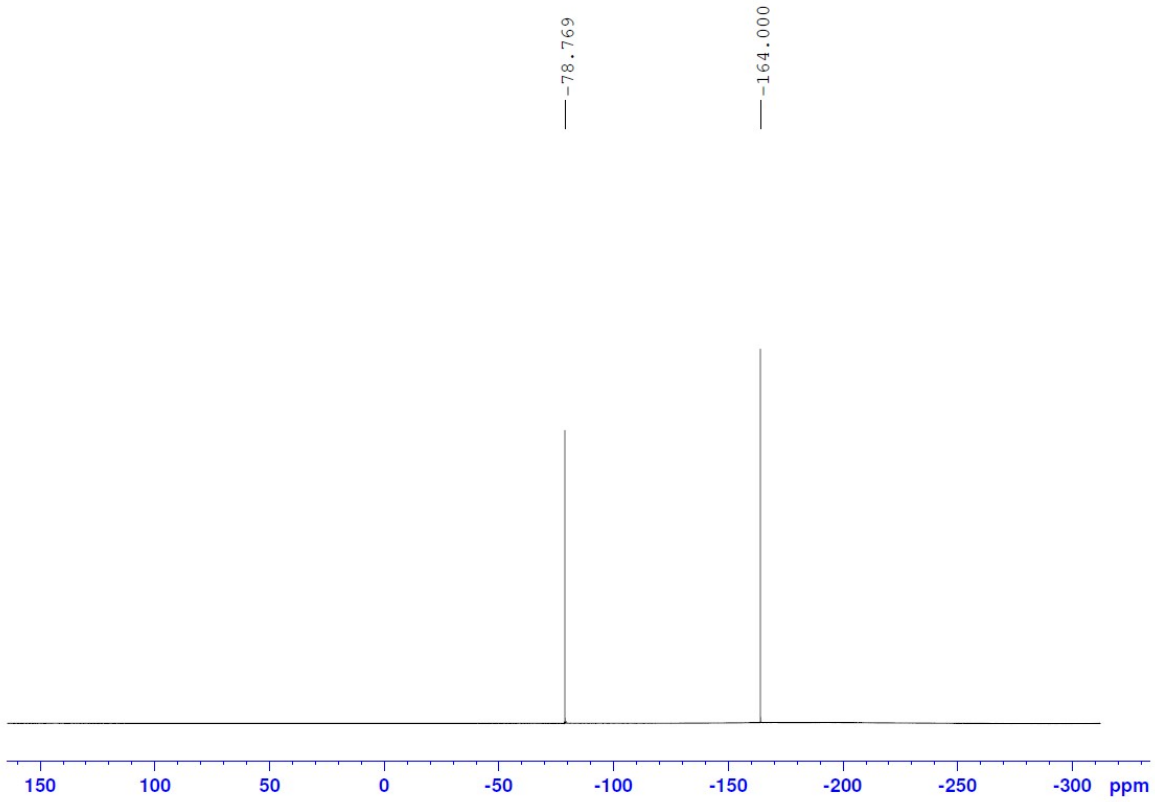

Figure S14. ^{19}F NMR of TBA-OTf in CD_3CN with C_6F_6 as internal standard calibrated to –164 ppm.

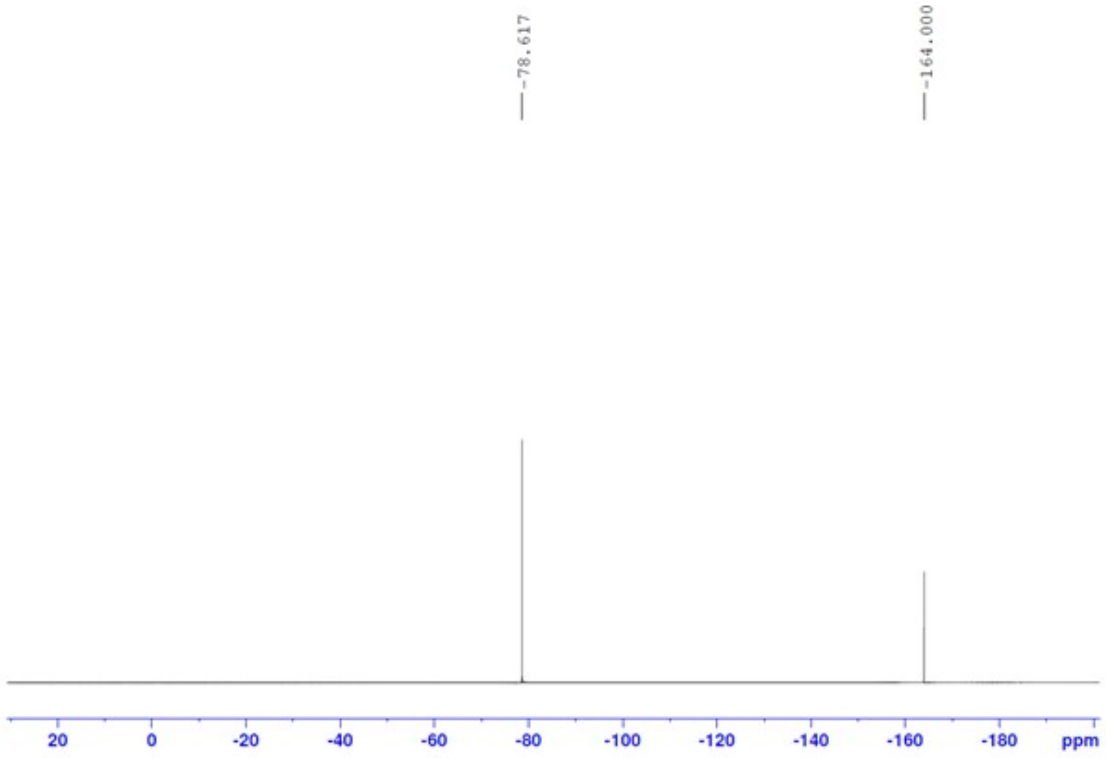

Figure S15. ^{19}F NMR of **2DMAP** in CD_3CN with C_6F_6 as internal standard calibrated to –164 ppm.

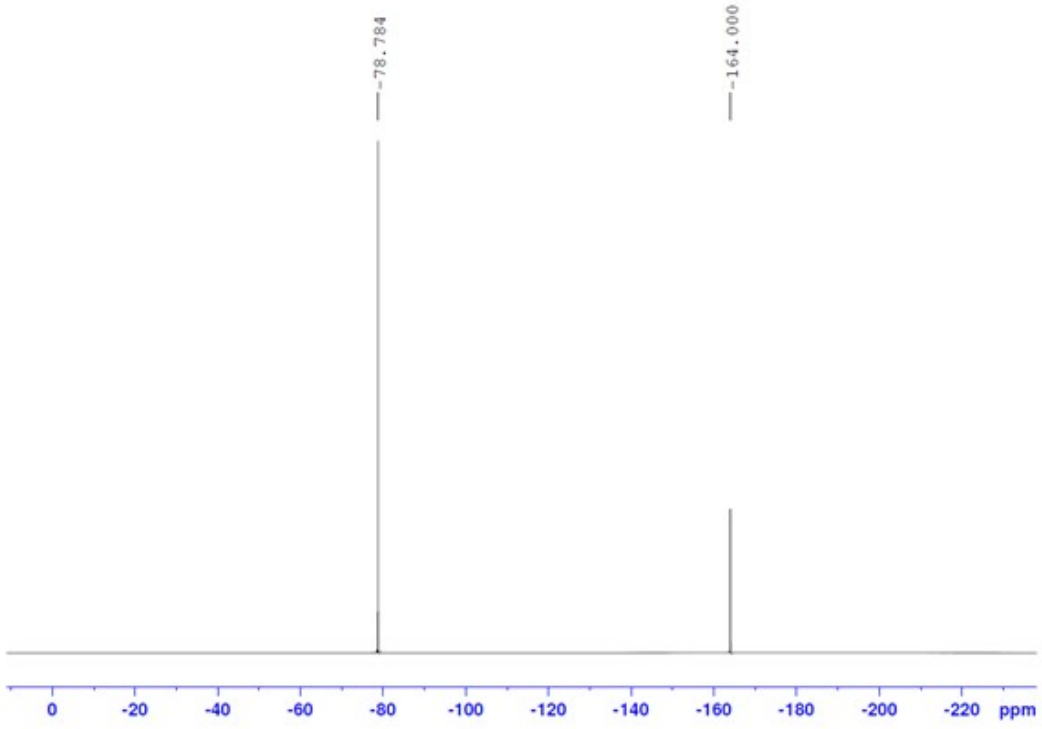

Figure S16. ^{19}F NMR of **1DMAP** in CD_3CN with C_6F_6 as internal standard calibrated to –164 ppm.

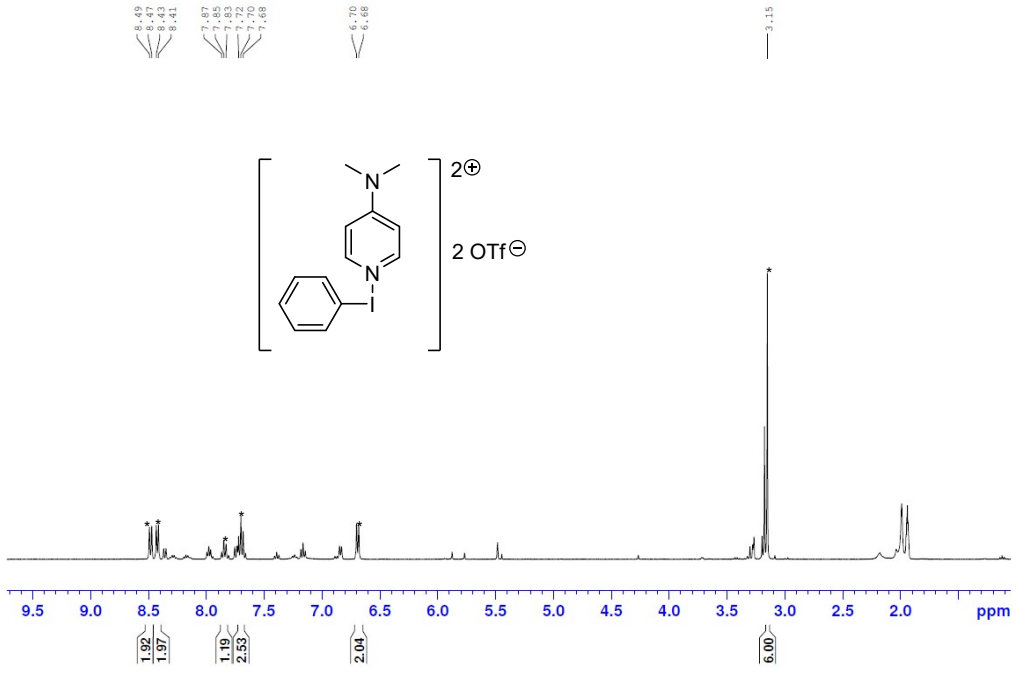

Figure S17. *In situ* ^1H NMR of reaction between PhI(OAc)(OTf) and TMS-DMAP, where * indicates shifts of **2DMAP**.

Theoretical Calculations

Unless noted, all calculations were carried out with Orca 5.0.1.[4-5] Geometries were optimised using the B3LYP functional[6-7] inclusive of D3(BJ) empirical dispersion[8] together with the def2-TZVPPD basis set[9-10] and associated ECPs for heavier atoms. Solvation was included in geometry optimizations with the CPCM solvation model[11-12] with parameters for dichloromethane solvent. All calculations utilised the RIJCOSX.[13] Harmonic frequency calculations were carried out analytically to confirm that optimized geometries were minima. Natural bond orbital (NBO) analysis was carried out with NBO 6.0[14] coupled to Orca 5.0.1.

Cartesian Coordinates of Optimized Geometries (Å)

B3LYP-D3(BJ)/def2-TZVPPD (CPCM, dichloromethane)

1DMAP
$[PhI(DMAP)_2]^{2+}$

I	-0.756364	0.000385	-0.006075
N	-0.657408	-2.221404	-0.002243
N	-0.655047	2.222080	-0.011037
N	-0.442287	6.356603	-0.025973
N	-0.443642	-6.355894	0.005115
C	-0.604492	2.908977	1.151937
H	-0.624430	2.326081	2.061820
C	1.355771	-0.000648	0.019556
C	-0.639436	-2.903672	1.164451
H	-0.684457	-2.317041	2.071033
C	2.024863	0.005588	-1.195016
H	1.492580	0.010653	-2.134576
C	-0.567373	-4.266373	1.208940
H	-0.557854	-4.746374	2.173357
C	-0.531284	4.271830	1.188944
H	-0.496301	4.755618	2.150877
C	-0.509243	-5.019907	0.002897
C	-0.507781	5.020615	-0.021255
C	3.415768	0.004926	-1.163415
H	3.965952	0.009611	-2.094178
C	-0.438216	-7.096033	1.265049
H	0.432149	-6.834363	1.869119
H	-0.401661	-8.157254	1.046546
H	-1.341730	-6.891352	1.841419
C	-0.388568	7.100674	1.230549
H	-1.283614	6.921981	1.828669
H	-0.327011	8.159678	1.007050
H	0.488265	6.817576	1.814955
C	4.090486	-0.001920	0.053466
H	5.171701	-0.002420	0.066869
C	-0.631457	2.901946	-1.179022
H	-0.671427	2.313371	-2.084587
C	-0.600475	-2.905876	-1.166347
H	-0.615680	-2.321044	-2.075087
C	1.994561	-0.007479	1.250303
H	1.439260	-0.012052	2.176476
C	-0.526746	-4.268635	-1.205825
H	-0.486343	-4.750380	-2.168559
C	-0.559848	4.264599	-1.225980
H	-0.545648	4.742582	-2.191328
C	3.385833	-0.008124	1.253204
H	3.912824	-0.013353	2.197285
C	-0.383271	-7.097214	-1.252731
H	0.498142	-6.815054	-1.830721
H	-0.326081	-8.156886	-1.031276
H	-1.273881	-6.914826	-1.856282
C	-0.433397	7.094149	-1.287406
H	-1.335300	6.888274	-1.865901
H	-0.397360	8.155809	-1.070993
H	0.438648	6.831252	-1.888498

1pyr
$[PhI(pyr)_2]^{2+}$

I	-0.873303	-0.000253	-0.005630
N	-0.778977	-2.252368	-0.005533
N	-0.778965	2.251958	-0.005448
C	-0.752205	2.909496	1.164619
H	-0.778555	2.313694	2.065433
C	1.236575	0.000042	0.005603
C	-0.756150	-2.909745	1.164766
H	-0.785023	-2.313835	2.065426
C	1.893590	0.002884	-1.215988
H	1.354041	0.004859	-2.151329
C	-0.695554	-4.289379	1.194222
H	-0.677084	-4.799045	2.146016
C	-0.690854	4.289139	1.193691
H	-0.669234	4.798853	2.145394

C	-0.660695	-4.988734	-0.006633
C	-0.659416	4.988292	-0.007320
C	3.284186	0.003204	-1.192939
H	3.828063	0.005346	-2.127272
C	3.966437	0.000775	0.019941
H	5.047676	0.001078	0.025620
C	-0.752206	2.907953	-1.176461
H	-0.778367	2.310899	-2.076444
C	-0.748859	-2.908531	-1.176328
H	-0.771902	-2.311509	-2.076423
C	1.880711	-0.002489	1.234016
H	1.331502	-0.004836	2.163735
C	-0.688158	-4.288191	-1.206885
H	-0.663879	-4.796793	-2.159117
C	-0.690981	4.287549	-1.207412
H	-0.669421	4.796050	-2.159763
C	3.271486	-0.002053	1.225562
H	3.805536	-0.003920	2.165543
H	-0.611327	6.068258	-0.008038
H	-0.613115	-6.068723	-0.007022

2DMAP
[PhI(DMAP)]$^{2+}$

I	1.444358	-1.342908	-0.041232
N	0.715192	0.571124	-0.025278
N	-0.736650	4.416772	0.002012
C	-0.356246	-2.394108	-0.010555
C	0.499332	1.204056	1.169823
H	0.730574	0.651579	2.067350
C	-0.936795	-2.733024	-1.231002
H	-0.473736	-2.469986	-2.170524
C	0.016748	2.469632	1.202592
H	-0.132563	2.922943	2.168435
C	-0.276113	3.174453	-0.006494
C	-2.140196	-3.422591	-1.192785
H	-2.621228	-3.702253	-2.119430
C	-0.955494	5.124503	1.267019
H	-1.687915	4.598394	1.879077
H	-1.330458	6.116886	1.047879
H	-0.021507	5.215761	1.821972
C	-2.720401	-3.752805	0.030314
H	-3.658137	-4.290899	0.046559
C	0.443738	1.200316	-1.210876
H	0.632663	0.644704	-2.116278
C	-0.904339	-2.715406	1.229506
H	-0.416517	-2.439176	2.152602
C	-0.039805	2.465707	-1.225457
H	-0.232708	2.916087	-2.184917
C	-2.108559	-3.404537	1.232841
H	-2.565268	-3.670241	2.175767
C	-1.020123	5.117640	-1.254065
H	-1.767863	4.577577	-1.834374
H	-1.404098	6.103600	-1.021634
H	-0.111456	5.223501	-1.847353

2pyr
[PhI(pyr)]$^{2+}$

I	1.385136	-0.017217	-0.169667
N	0.017058	1.580027	-0.097836
C	0.037973	-1.584152	-0.069051
C	-0.157070	2.217097	1.080959
H	0.417360	1.871632	1.926490
C	-0.427768	-2.120575	-1.271974
H	-0.101256	-1.737015	-2.227300
C	-1.050353	3.263235	1.151066
H	-1.183017	3.769080	2.095959
C	-1.755347	3.638496	0.012609
C	-1.330519	-3.168710	-1.189779
H	-1.715088	-3.611103	-2.097766
C	-1.736909	-3.648017	0.054933
H	-2.440962	-4.467140	0.104927
C	-0.646173	1.919015	-1.225659
H	-0.438861	1.351382	-2.120205
C	-0.343280	-2.044526	1.193007
H	0.048856	-1.603624	2.097432
C	-1.550177	2.957218	-1.182774
H	-2.079009	3.222547	-2.086256
C	-1.247436	-3.092993	1.237381
H	-1.567323	-3.478388	2.195056
H	-2.459096	4.457695	0.056564

[PhI(DMAP)(OTf)]$^{+}$

I	-0.193350	-0.452785	-0.399518
O	-2.836739	-0.084489	1.638224
O	-4.343496	1.138378	0.099345
O	-2.430588	-0.093653	-0.780740
N	1.907094	-0.645037	-0.133016
N	5.993149	-0.898255	0.395783
S	-3.436684	0.048037	0.333394
F	-3.655647	-2.580402	0.192722
F	-5.012708	-1.504043	-1.116700
F	-5.394999	-1.578272	1.020931
C	-0.074956	1.639026	-0.183230
C	4.673585	-0.817860	0.225094
C	2.431044	-0.683028	1.119596
H	1.731513	-0.638782	1.941105
C	-0.246168	2.173835	1.085164
H	-0.447584	1.547126	1.940689
C	6.889677	-0.940155	-0.759146
H	6.696603	-1.823938	-1.368804
H	6.766880	-0.049663	-1.376400
H	7.913306	-0.978680	-0.404956
C	2.732021	-0.690680	-1.211406
H	2.264365	-0.655951	-2.184139
C	6.566828	-0.948171	1.740456
H	6.331314	-0.040382	2.297691
H	6.188263	-1.810344	2.290497
H	7.643804	-1.035413	1.656620
C	0.165181	2.399836	-1.318352
H	0.283011	1.944831	-2.290561
C	3.773132	-0.766604	1.328824
H	4.127127	-0.792535	2.345882
C	-4.441118	-1.502510	0.089979
C	4.083071	-0.778160	-1.071521
H	4.683639	-0.815610	-1.964919
C	-0.162282	3.556135	1.213650
H	-0.293280	4.005514	2.188197
C	0.244452	3.778978	-1.160174
H	0.428915	4.401150	-2.024912
C	0.082251	4.351431	0.098126
H	0.142361	5.425356	0.209287

[PhI(pyr)(OTf)]$^+$

I	11.770139	4.445258	13.252055
S	13.126057	5.195585	10.307474
F	10.620445	5.139146	9.479233
O	14.386231	4.897271	9.689955
O	12.713805	4.086322	11.261939
N	10.969824	4.709591	15.277359
F	11.939172	3.773238	8.423667
F	12.036646	5.904992	8.020690
O	12.902676	6.503136	10.866568
C	13.716335	4.754847	13.987505
C	9.972167	5.035695	17.802697
C	10.742928	5.953366	15.736367
H	10.970716	6.773320	15.071152
C	14.214507	6.049906	13.988650
H	13.628231	6.883430	13.633229
C	10.717180	3.622232	16.027300
H	10.927919	2.659119	15.586555
C	14.433750	3.645380	14.412430
H	14.010350	2.652406	14.385707
C	10.241868	6.144074	17.007930
H	10.066514	7.149615	17.360064
C	11.845903	4.986739	8.968457
C	10.212886	3.760492	17.304579
H	10.016027	2.876538	17.892596
C	15.512273	6.233061	14.452525
H	15.933236	7.228692	14.465166
C	15.729365	3.859492	14.868729
H	16.318186	3.017020	15.203793
C	16.263054	5.144878	14.887541
H	17.273474	5.299047	15.240308
H	9.577742	5.164448	18.800800

References:

1. R. Weiss, J. Seubert, *Angew. Chem. Int. Ed*. **1994**, 33, 891-893.
2. E. Chénard, A. Sutrisno, L. Zhu, R. S. Assary, J. A. Kowalski, J. L. Barton, J. A. Bertke, D. L. Gray, F. R. Brushett, L. A. Curtiss, J. S. Moore, *J. Phys. Chem*. **2016**, 120, 16, 8461–8471.
3. A. P. Robertson, S. S. Chitnis, S. Chhina, H.J. Cortes S, B. O. Patrick, H. A. Jenkins, N. Burford. *Can. J. Chem*. **2016**, 94(4), 424-429.
4. F. Neese, *WIREs Comp. Mol. Sci.*, **2012**, 2, 73–78
5. F. Neese, *WIREs Comp. Mol. Sci.*, **2018**, 8, e1327
6. A. D. Becke, *J. Chem. Phys*. **1993**, 98, 5648-5652.
7. C. Lee, W. Yang, R. G. Parr, Phys. Rev. B **1988**, 37, 785-789.
8. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem*. **2011**, 32, 1456-1465.
9. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
10. D. Rappoport, F. Furche, *J. Chem. Phys.* **2010**, *133*, 134105.
11. V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995-2001.
12. M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669-681.
13. F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.*, **2009**, 356, 98.
14. E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem*. 2013, 34, 1429-1437