

## *Supporting Information for:*

### **A 2,2'-bipyridine coordination complex of [ICl<sub>2</sub>]<sup>+</sup>**

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#### **Experimental Procedures:**

All manipulations involving ICl<sub>3</sub> or **5** were performed in an N<sub>2</sub> filled glovebox. Dichloromethane, MeCN, and Et<sub>2</sub>O, were obtained from Caledon Laboratories and dried using an Innovative Technologies Solvent Purification System with dual columns packed with solvent appropriate drying agents. The dried solvents were stored under an N<sub>2</sub> atmosphere over 3 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy (CDCl<sub>3</sub>, CD<sub>3</sub>CN) were purchased from Cambridge Isotope Laboratories and dried by stirring for three days over CaH<sub>2</sub>, distilled and stored in the glovebox over 3 Å molecular sieves. Reagents were purchased from Alfa Aesar, Precious Metals Online (Au powder) or Aldrich (ICl<sub>3</sub>) and used as received. Compound **7** was prepared via literature procedure, using tht-AuCl in place of Me<sub>2</sub>S-AuCl and 1,3-diisopropylbenzamidozolium iodide in place of 1,3-diisopropylbenzamidozolium bromide.<sup>1</sup> Compound **6**, for comparison to compound **5** in terms of spectroscopic and reaction properties, was prepared via literature procedure.<sup>2</sup>

**Synthesis of 5:** A solution of bpy (0.033 g, 0.214 mmol: 5 mL CH<sub>2</sub>Cl<sub>2</sub>) was added to a freshly prepared solution of ICl<sub>3</sub> (0.100 g, 0.429 mmol: 5 mL CH<sub>2</sub>Cl<sub>2</sub>), which resulted in the immediate precipitation of a bright yellow solid. The solution was cooled to -40° resulting in the precipitation of further amounts of yellow solid. The supernatant was decanted and the solids washed with Et<sub>2</sub>O (2 × 5ml), then dried *in vacuo*, which gave **5** as a bright yellow powder.

Yield: 0.075 g (56%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 8.94 (d,  $^3J_{\text{H-H}}$  5.5 Hz, 2 H), 8.13 (t,  $^3J_{\text{H-H}}$  7.5 Hz, 2 H), 7.75, (d,  $^3J_{\text{H-H}}$  8.0 Hz, 2 H), 7.55, (t,  $^3J_{\text{H-H}}$  5.5 Hz 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 155.3, 150.3, 139.4, 126.1, 125.5.

Generation of **8** using **5**: A solution of **7** (0.074 g, 0.160 mmol; 5 mL  $\text{CH}_2\text{Cl}_2$ ) was added to a slurry of **5** (0.05 g, 0.08 mmol; 5 mL  $\text{CH}_2\text{Cl}_2$ ) resulting in a red slurry. After 5 minutes the mixture was centrifuged and the solution transferred to a fresh vial. The volume of solution was reduced by half under vacuum, and then  $\text{Et}_2\text{O}$  (10 mL) was added giving an orange precipitate. The mixture was centrifuged, the supernatant was decanted and the solids were washed with  $\text{Et}_2\text{O}$  (3 x 5 mL). The orange solid was then dried under vacuum giving **8** as an orange powder. Yield: 0.061 g (75%).  $^1\text{H}$  NMR spectroscopic data were consistent with literature values,<sup>3</sup> and a unit cell analysis of single crystals grown from  $\text{CH}_2\text{Cl}_2$  solution gave identical parameters to the reported compound.

Generation of  $[\text{nBu}_4\text{N}][\text{ICl}_4]$ : A solution of  $[\text{nBu}_4\text{N}][\text{Cl}]$  (0.036 g, 0.133 mmol; 2 mL  $\text{CDCl}_3$ ) was added to a solution of  $\text{ICl}_3$  (0.031 g, 0.133 mmol; 2 mL  $\text{CDCl}_3$ ) resulting in an immediate colour change from orange to yellow. The solution was held at  $-40^\circ\text{C}$  resulting in the formation of single crystals, for which X-ray diffraction studies confirmed generation of  $[\text{nBu}_4\text{N}][\text{ICl}_4]$ . Solutions of  $[\text{nBu}_4\text{N}][\text{ICl}_4]$  generated *in situ* in  $\text{CDCl}_3$  as described above were used for the control oxidative chlorination experiments.

Reaction of  $[\text{nBu}_4\text{N}][\text{ICl}_4]$  with **7**

A solution of  $[\text{nBu}_4\text{N}][\text{ICl}_4]$  (0.120 mmol; 2 mL  $\text{CDCl}_3$ ) was added to a solution of **7** (0.052 g, 0.120 mmol) resulting in an immediate colour change to dark orange. After 30 minutes an aliquot was removed for  $^1\text{H}$  NMR spectroscopy which showed complete conversion to **8**.

Reaction of  $\text{ICl}_3$  with **7**

A solution of  $\text{ICl}_3$  (0.040 g 0.172 mmol; 2 mL  $\text{CDCl}_3$ ) was added to a solution of **7** (0.074 g, 0.172 mmol). After 30 minutes an aliquot was removed for  $^1\text{H}$  NMR spectroscopy which showed complete conversion to **8**.

#### Reaction of [<sup>n</sup>Bu<sub>4</sub>N][ICl<sub>4</sub>] with PhI

Neat PhI (0.325 mmol, 36 uL) was added to a solution of [<sup>n</sup>Bu<sub>4</sub>N][ICl<sub>4</sub>] (0.325 mmol; 4 mL CDCl<sub>3</sub>). After 30 minutes an aliquot was removed for <sup>1</sup>H NMR spectroscopy.

#### Reaction of ICl<sub>3</sub> with PhI

Neat PhI (0.236 mmol, 26 uL) was added to a solution of ICl<sub>3</sub> (0.055 g, 0.236 mmol; 3 mL CDCl<sub>3</sub>). After 30 minutes an aliquot was removed for <sup>1</sup>H NMR spectroscopy.

#### Reaction of **5** with PhI

Neat PhI (0.347 mmol, 39 uL) was added to a slurry of **5** (0.216 g, 0.347 mmol; 5 mL CDCl<sub>3</sub>). After 30 minutes an aliquot was removed for <sup>1</sup>H NMR spectroscopy.

#### Reaction of **6** with PhI

Neat PhI (0.173 mmol, 19 uL) was added to a solution of **6** (0.83 g, 0.173 mmol; 3 mL CDCl<sub>3</sub>). After 30 minutes an aliquot was removed for <sup>1</sup>H NMR spectroscopy.

### **X-ray crystallography**

Single crystals were selected under Paratone-N oil, mounted on nylon loops and placed into a cold stream (172 K) of N<sub>2</sub> on an Oxford CCD diffractometer using Mo K $\alpha$  radiation. Structure solution and refinement were performed using the SHELXTL suite of software. Structure and refinement information are found in Table 1.

**Table S1:** X-ray refinement details for single crystal X-ray structural determinations.

Compound	<b>5</b>	<b>[bipyH][ICl<sub>2</sub>]</b>	<b>[<sup>n</sup>Bu<sub>4</sub>N][ICl<sub>4</sub>]</b>
Empirical formula	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> I <sub>2</sub> Cl <sub>6</sub>	C <sub>10</sub> H <sub>9</sub> Cl <sub>2</sub> I <sub>1</sub> N <sub>2</sub>	C <sub>16</sub> H <sub>35</sub> Cl <sub>4</sub> I <sub>1</sub> N <sub>1</sub>
FW (g/mol)	622.8	354.99	510.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c	P2(1)/n
<i>a</i> (Å)	8.056(2)	11.666(2)	14.863(3)
<i>b</i> (Å)	13.093(3)	7.914(2)	8.754(2)
<i>c</i> (Å)	16.894(3)	13.981(3)	18.783(4)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	97.39(3)	97.62(3)	108.06(3)
$\gamma$ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1767.2	1279.4(4)	2323.4(8)
<i>Z</i>	4	4	4
<i>R</i> (int)	0.0254	0.0279	0.0476
<i>R</i> 1[ <i>I</i> >2 $\sigma$ ]	0.0273	0.0226	0.0401
<i>wR</i> 2( <i>F</i> <sup>2</sup> )	0.0557	0.0515	0.1049
GOF ( <i>S</i> )	1.044	1.082	1.037

## Computational details:

Unless noted, all calculations were carried out within Gaussian 09.<sup>4</sup> Geometries of all species were optimized with the B3LYP density functional<sup>5-7</sup> in conjunction with the def2-TZVP basis set,<sup>8</sup> which includes an effective core potential in the case of iodine. While relativistic effects are not treated explicitly, the def2-TZVP effective core potential for iodine implicitly accounts for relativistic effects. Stationary points were characterised as minima by calculating the Hessian matrix analytically at the same level of theory. Thermodynamic corrections were taken from these calculations (standard state of  $T = 298.15$  K and  $p = 1$  atm). Natural bond orbital (NBO) analysis was carried out with NBO 5.<sup>9</sup> at the B3LYP/def2-TZVP level of theory. EDA and EDA-NOCV calculations were performed using the ADF package<sup>10</sup> at the BP86/TZ2P level of theory, inclusive of ZORA relativistic effects.

## Cartesian coordinates of optimized geometries

### 5 (bpy-ICl<sub>2</sub><sup>+</sup>)

B3LYP/def2-TZVP optimized geometry (Å).

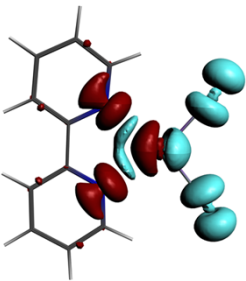
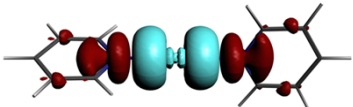
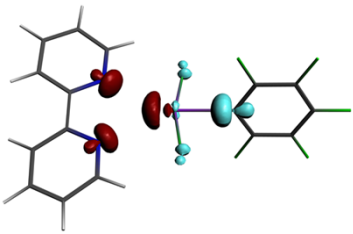
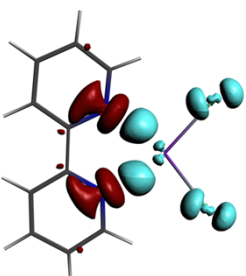
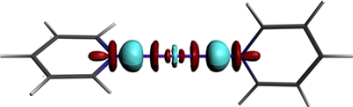
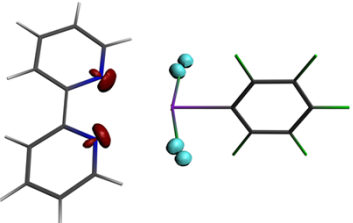
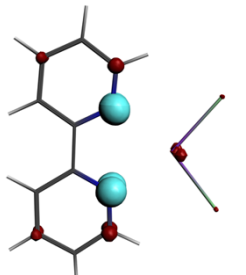
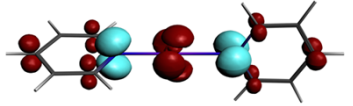
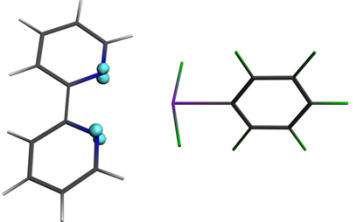
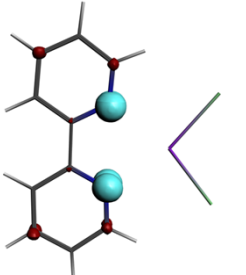
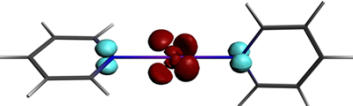
1	1		
7	0.000000	1.364654	-0.784001
6	0.000000	2.696757	-0.699917
6	0.000000	3.497874	-1.829884
6	0.000000	2.882744	-3.073074
6	0.000000	1.497821	-3.148690
6	0.000000	0.740546	-1.978666
6	0.000000	-0.740546	-1.978666
6	0.000000	-2.696757	-0.699917
6	0.000000	-3.497874	-1.829884
6	0.000000	-2.882744	-3.073074
6	0.000000	-1.497821	-3.148690
1	0.000000	-1.017234	-4.114725
1	0.000000	-3.473192	-3.979601
1	0.000000	-4.573711	-1.726752
1	0.000000	-3.119244	0.296738
1	0.000000	1.017234	-4.114725
1	0.000000	3.473192	-3.979601
1	0.000000	4.573711	-1.726752
1	0.000000	3.119244	0.296738
7	0.000000	-1.364654	-0.784001
53	0.000000	0.000000	1.223118
17	0.000000	1.863062	2.763595
17	0.000000	-1.863062	2.763595

### C<sub>6</sub>F<sub>6</sub>-IF<sub>2</sub>-ICl<sub>2</sub> complex

B3LYP/def2-TZVP optimized geometry (Å).

0	1		
53	0.000000	0.000000	0.010119
9	0.000000	2.002367	-0.278150
9	0.000000	-2.002367	-0.278150
9	-2.347328	-0.297913	-2.172959
9	-2.336217	-0.298250	-4.869383
9	0.000000	0.000000	-6.219728
9	2.336217	0.298250	-4.869383
9	2.347328	0.297913	-2.172959
6	0.000000	0.000000	-2.103573
6	-1.183557	-0.151436	-2.809438
6	-1.193502	-0.153228	-4.197000
6	0.000000	0.000000	-4.889308
6	1.193502	0.153228	-4.197000
6	1.183557	0.151436	-2.809438
7	0.112126	1.363714	2.655986
7	-0.112126	-1.363714	2.655986
6	0.362684	2.670821	2.611460
1	0.309214	3.120721	1.628049
6	0.678778	3.420455	3.738206
1	0.873659	4.480673	3.650106
6	0.746577	2.768840	4.960054
1	1.006696	3.307498	5.862503
6	0.483318	1.408791	5.011467
1	0.553169	0.883571	5.952688
6	0.154481	0.728891	3.834989
6	-0.154481	-0.728891	3.834989
6	-0.483318	-1.408791	5.011467
1	-0.553169	-0.883571	5.952688
6	-0.746577	-2.768840	4.960054
1	-1.006696	-3.307498	5.862503
6	-0.678778	-3.420455	3.738206
1	-0.873659	-4.480673	3.650106
6	-0.362684	-2.670821	2.611460
1	-0.309214	-3.120721	1.628049

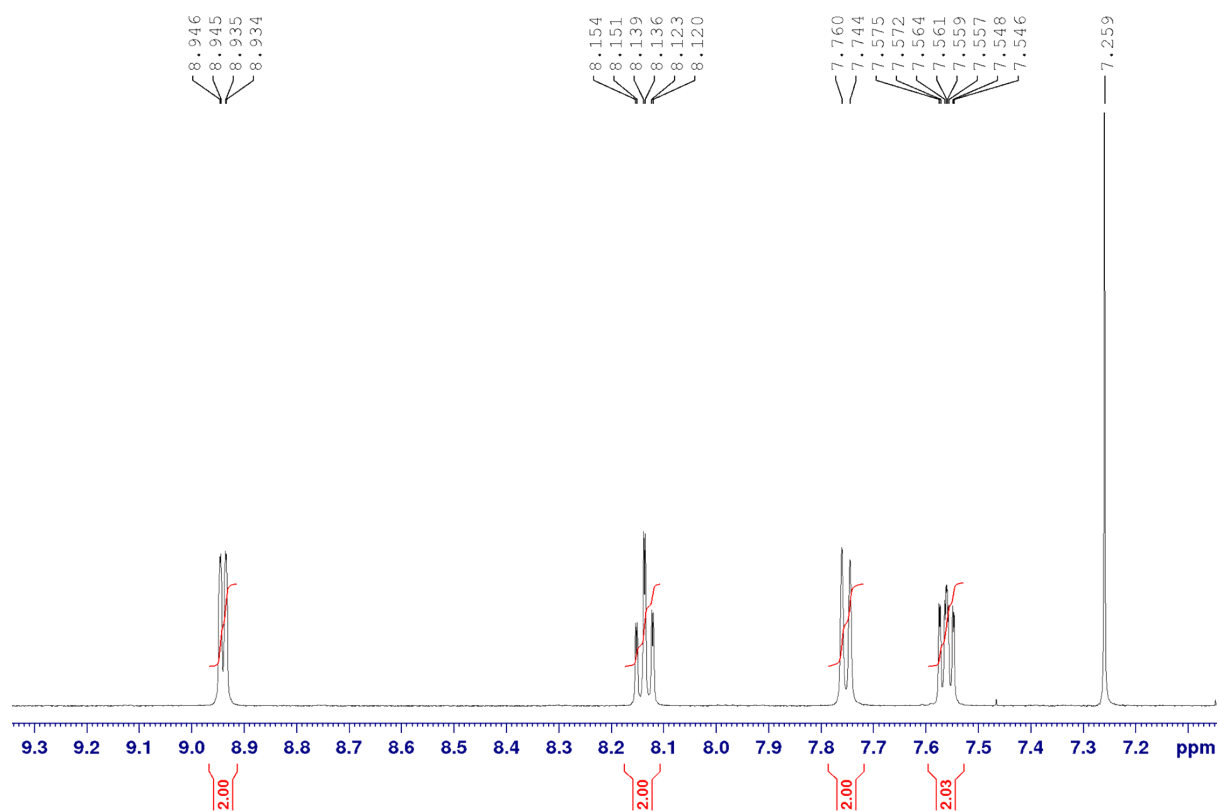
**EDA-NOCV analysis.** Deformation densities  $\Delta\rho$  associated with the most important orbital interactions in 5, [pyr-I-pyr]<sup>+</sup> and C<sub>6</sub>F<sub>5</sub>IF<sub>2</sub>-bpy. The direction of the charge flow is red→blue. The B3LYP/TZ2P energy of interaction (kJ/mol) and the percentage contribution to the total orbital interaction ( $\Delta E_{\text{orb}}$ ) are given.

	5	[IPyr <sub>2</sub> ] <sup>+</sup>	C <sub>6</sub> F <sub>5</sub> IF <sub>2</sub> -bpy
$\Delta\rho_1$	 -202.1 kJ/mol (43.2%)	 -428.3 kJ/mol (63.3%)	 -37.2 kJ/mol (49.5%)
$\Delta\rho_2$	 -154.5 kJ/mol (33.0%)	 -93.0 kJ/mol (13.8%)	 -17.9 kJ/mol (23.8%)
$\Delta\rho_3$	 -25.5 kJ/mol (5.4%)	 -31.3 kJ/mol (9.3%) <sup>a</sup>	
$\Delta\rho_4$	 -20.9 kJ/mol (4.5%)	 -15.3 kJ/mol (4.5%) <sup>a</sup>	

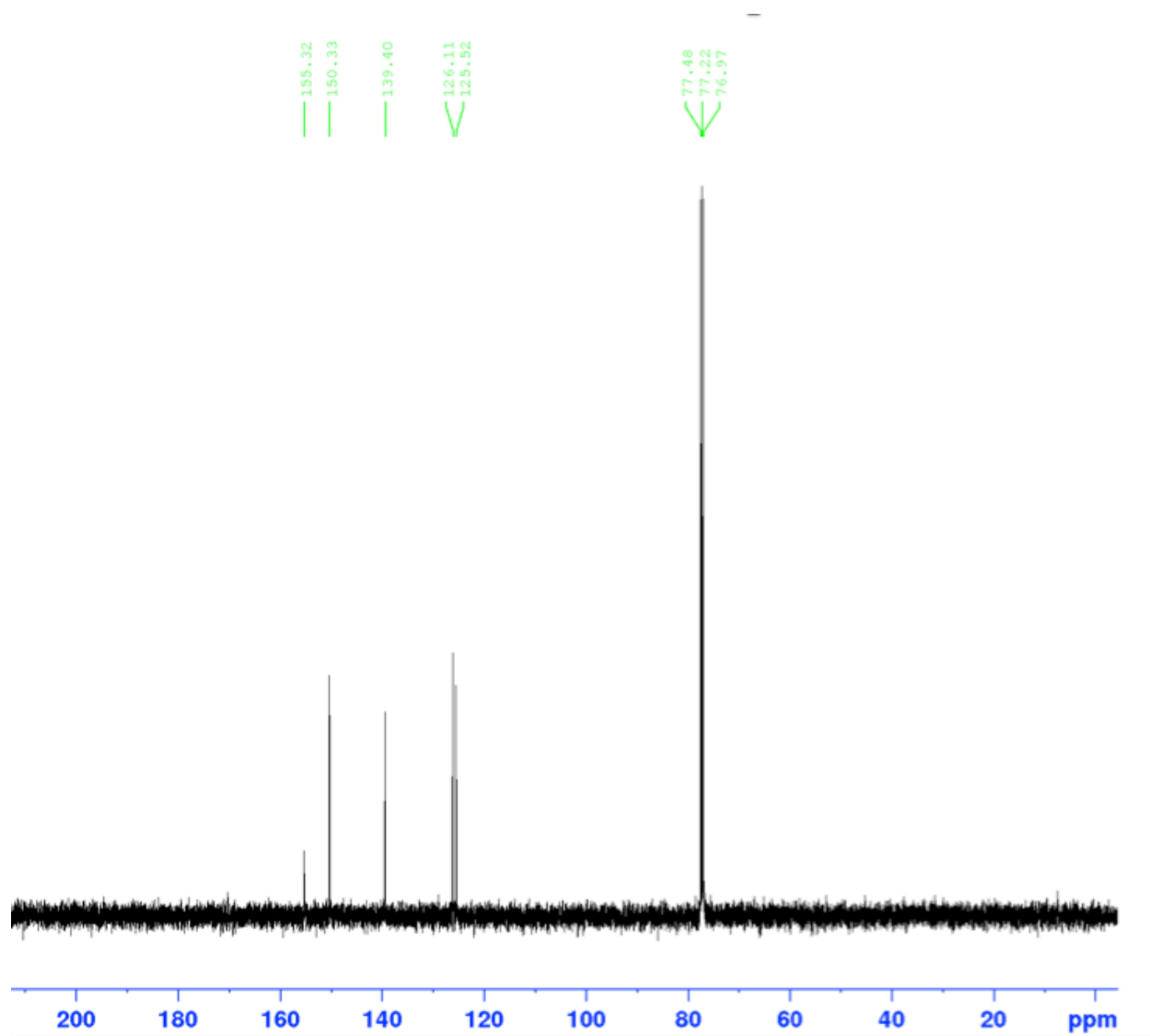
<sup>a</sup> Degenerate interactions are overlaid on the one plot, with the percentage including both degenerate interactions.



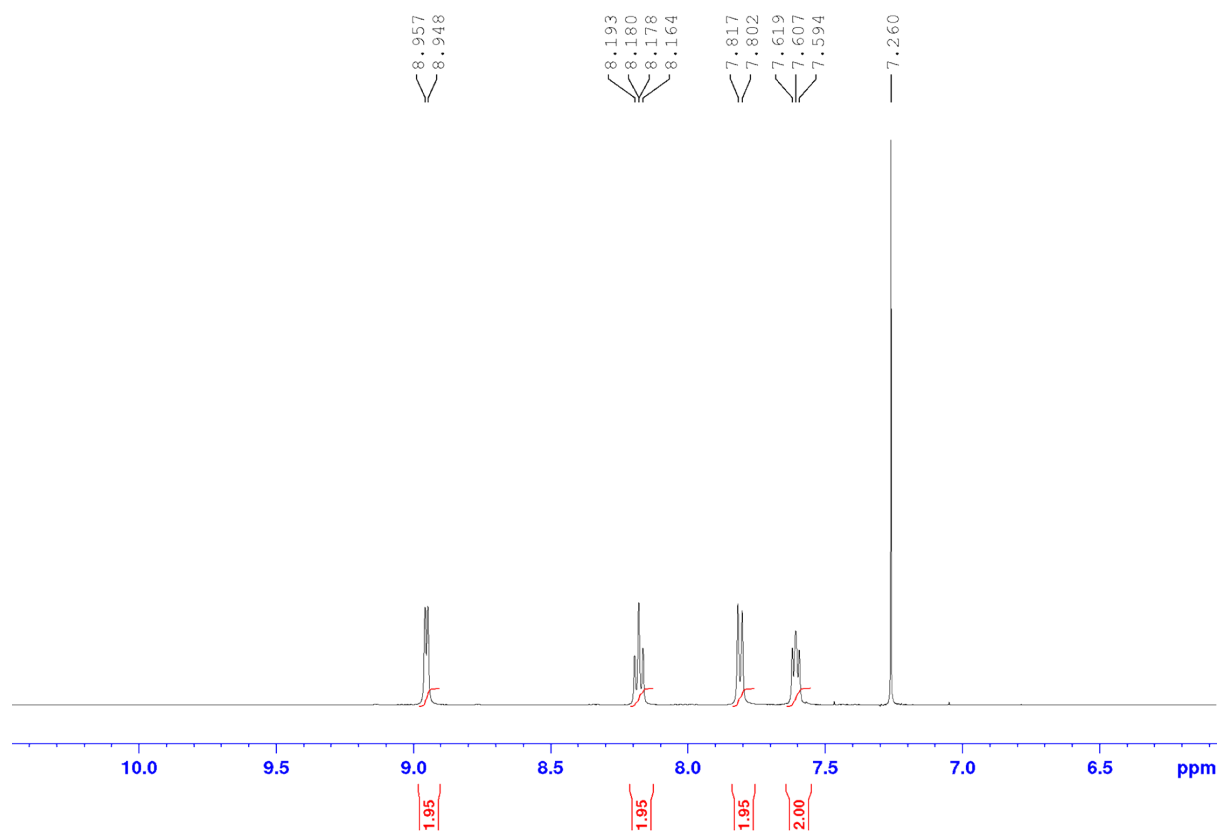
**Figure S1.** Proton-NMR spectrum (CDCl<sub>3</sub>) of **5**.



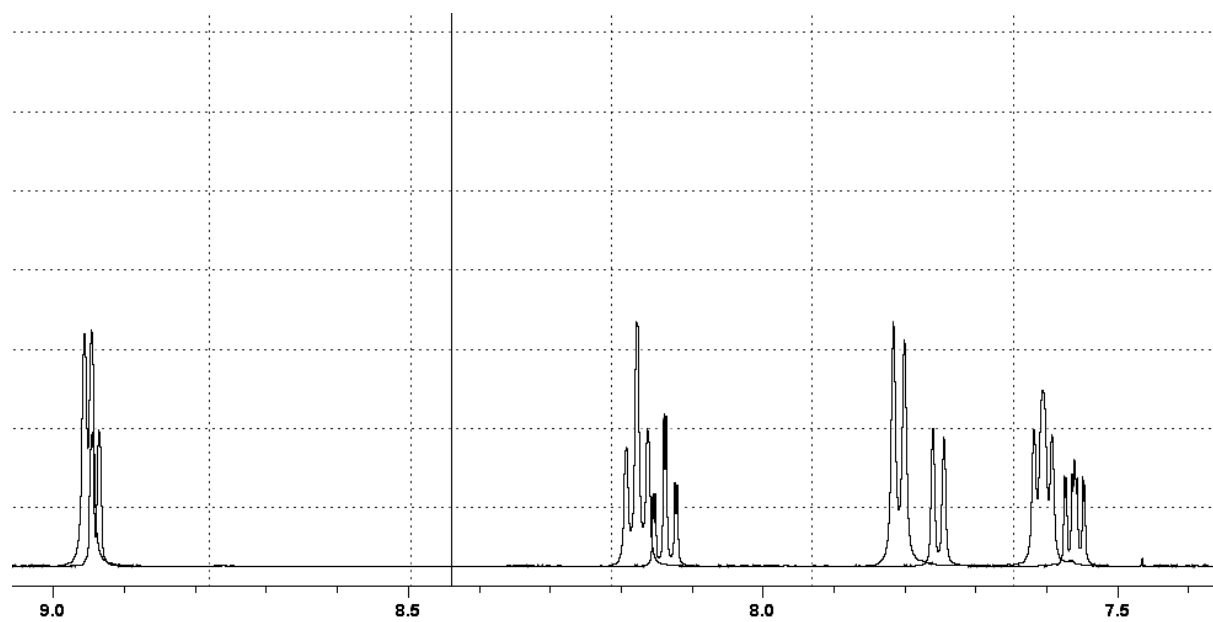
**Figure S2.** Carbon-13 NMR spectrum (CDCl<sub>3</sub>) of **5**.



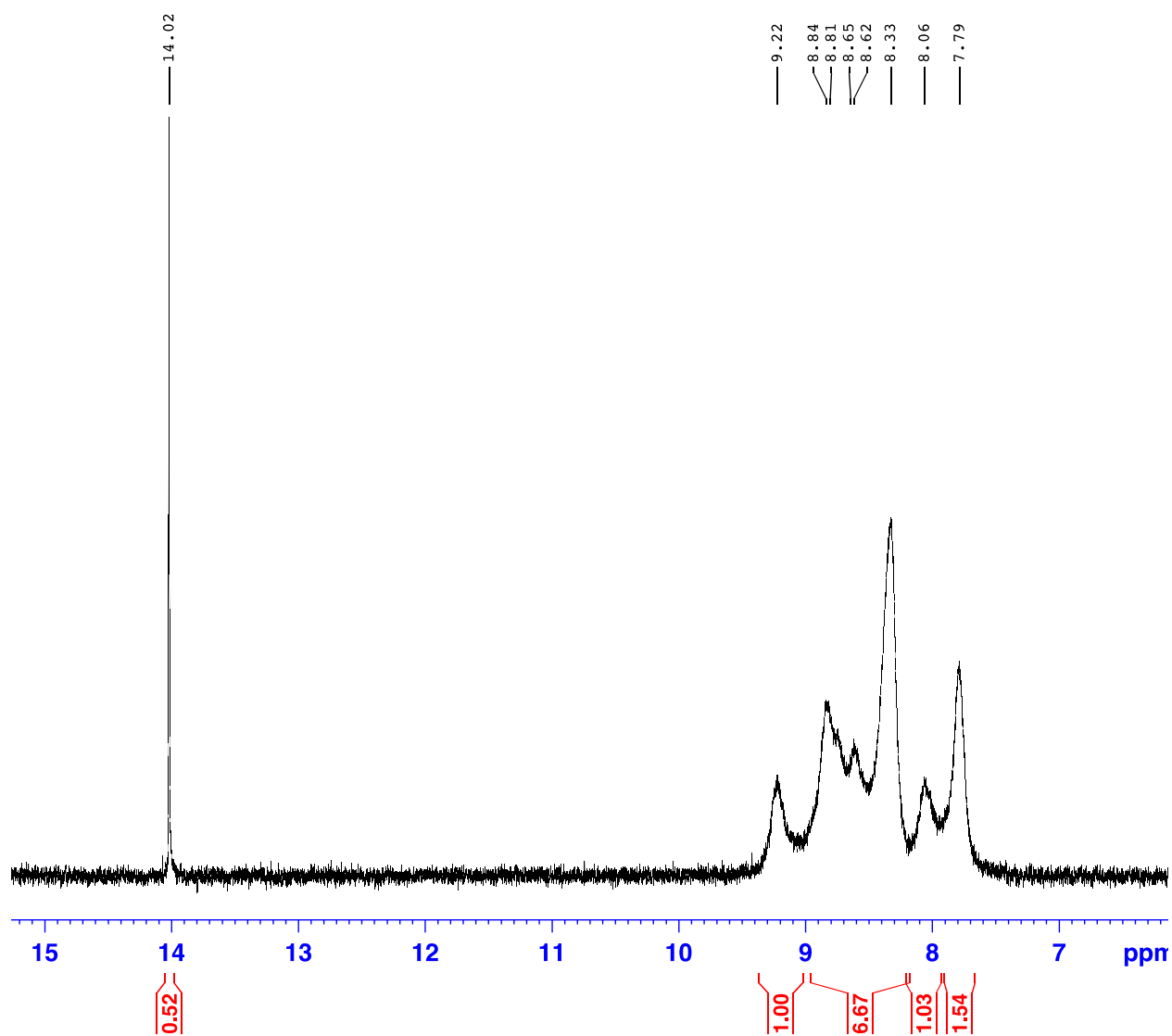
**Figure S3.** Proton NMR spectrum (CDCl<sub>3</sub>) of **6**.



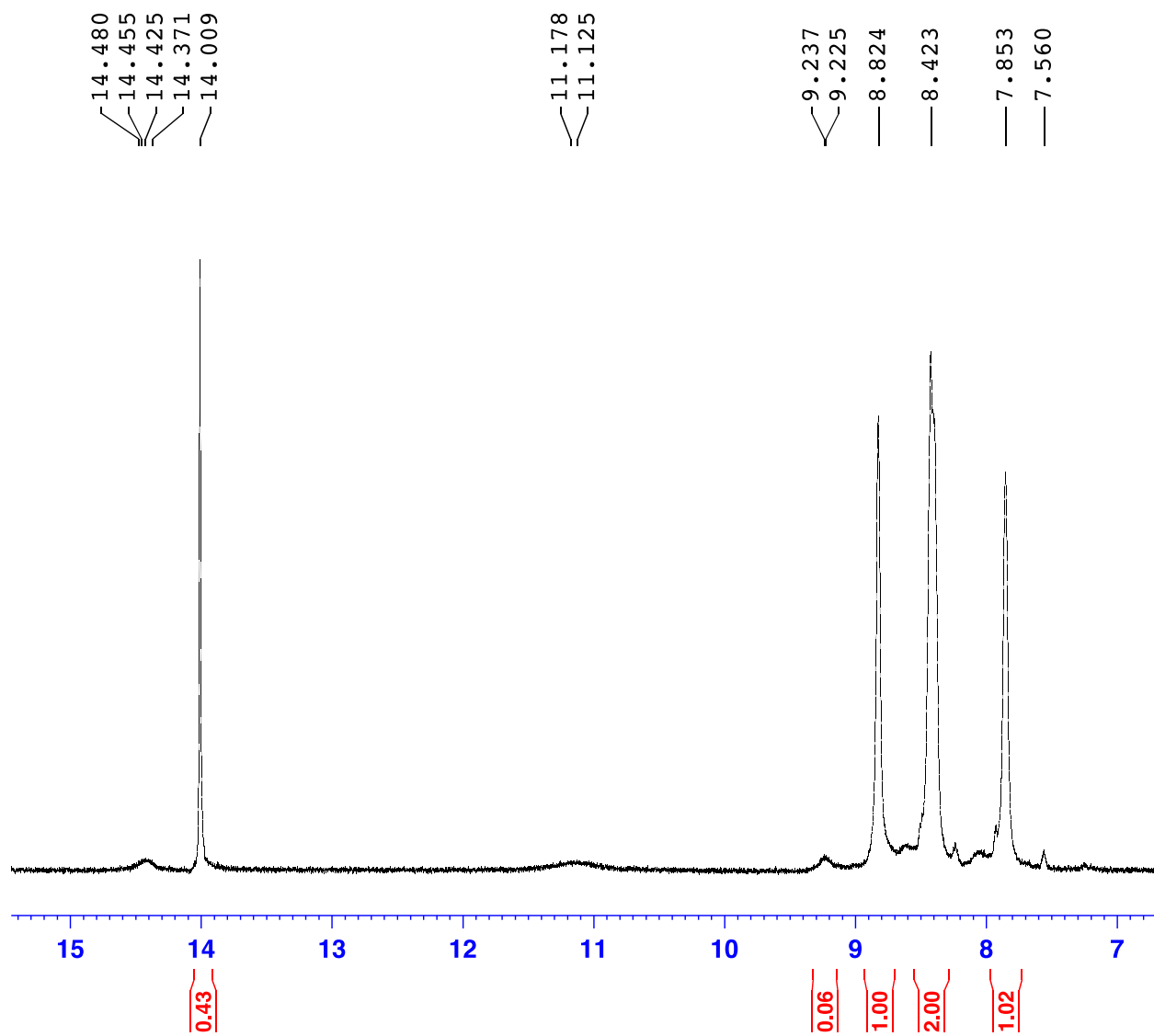
**Figure S4.** Superimposed <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of **5** and **6**.



**Figure S5.** Proton NMR spectrum of **5** five minutes after being dissolved in CD<sub>3</sub>CN.

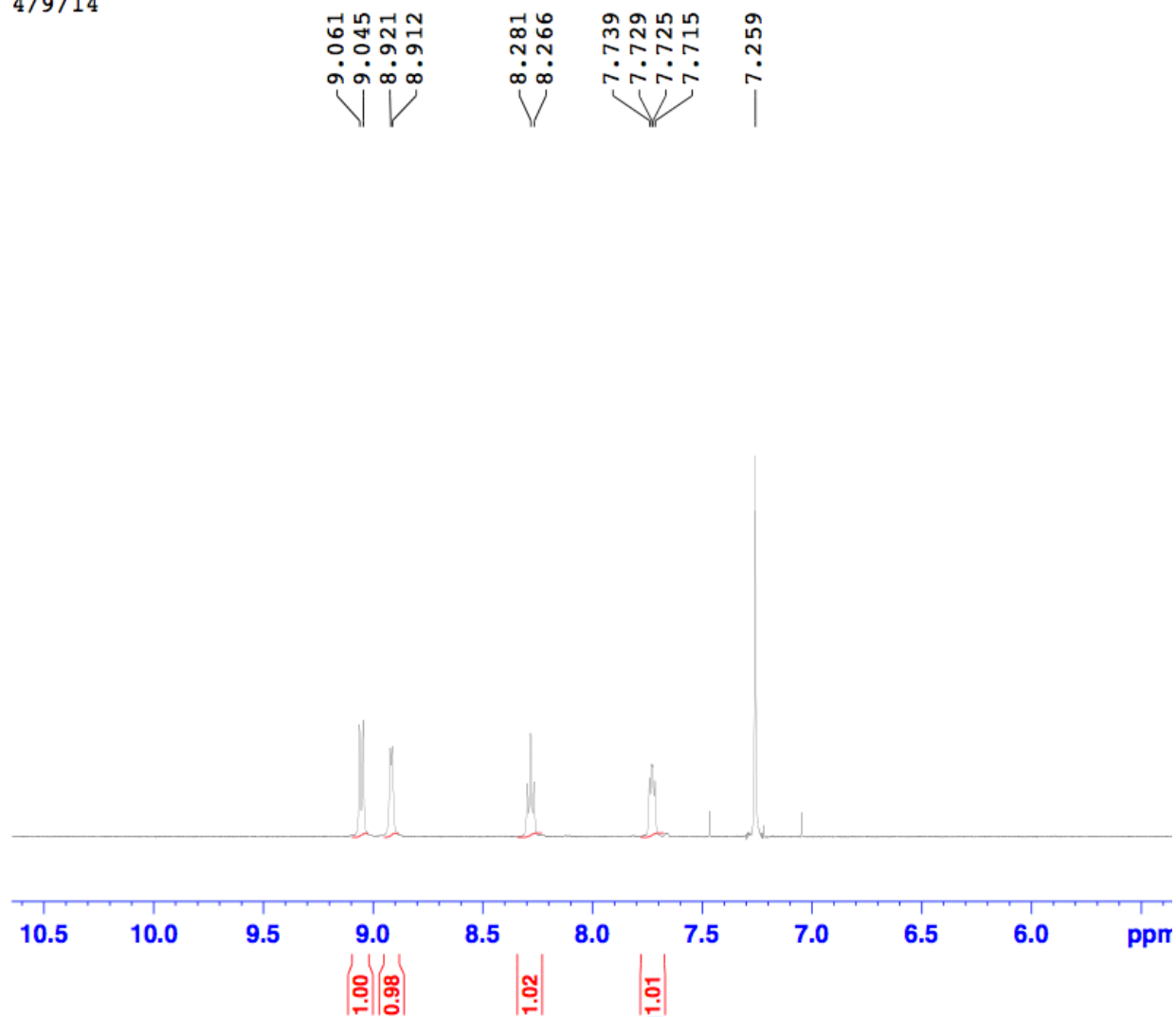


**Figure S6.** Proton NMR spectrum of **5** one hour after being dissolved in CD<sub>3</sub>CN.

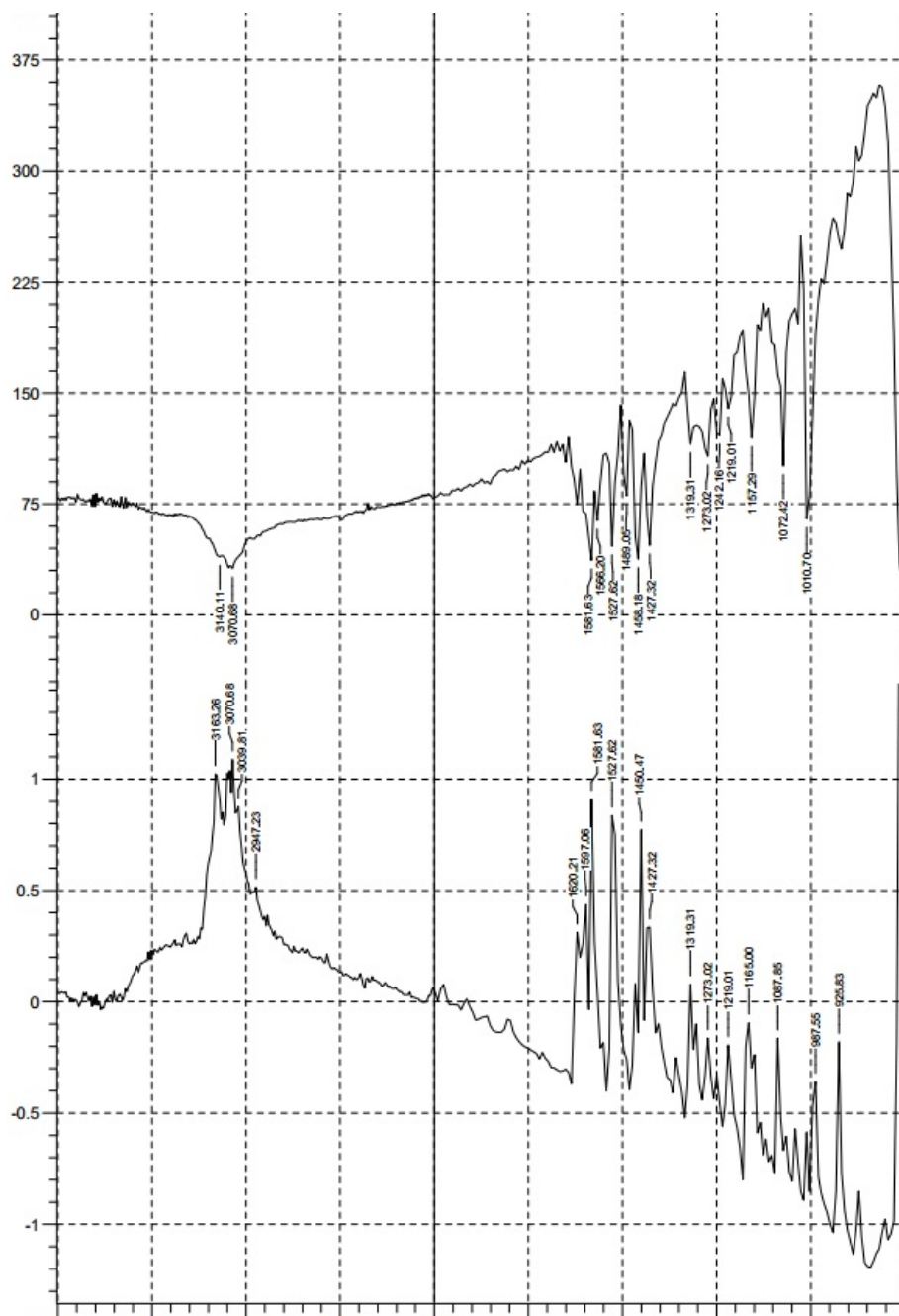


**Figure S7.** Proton NMR spectrum (CDCl<sub>3</sub>) of [Hbpy][Cl], generated from bipyridine and one equivalent of ethereal HCl.

hcl + bipy, white solid  
4/9/14



**Figure S8.** FT-IR spectra (KBr pellets) of **5** prepared under N<sub>2</sub> (top) and prepared in the ambient atmosphere resulting in 5 minutes of exposure to air (bottom).



**Table S2.** Raw FT-IR peak table for sample of **5** prepared under N<sub>2</sub>.

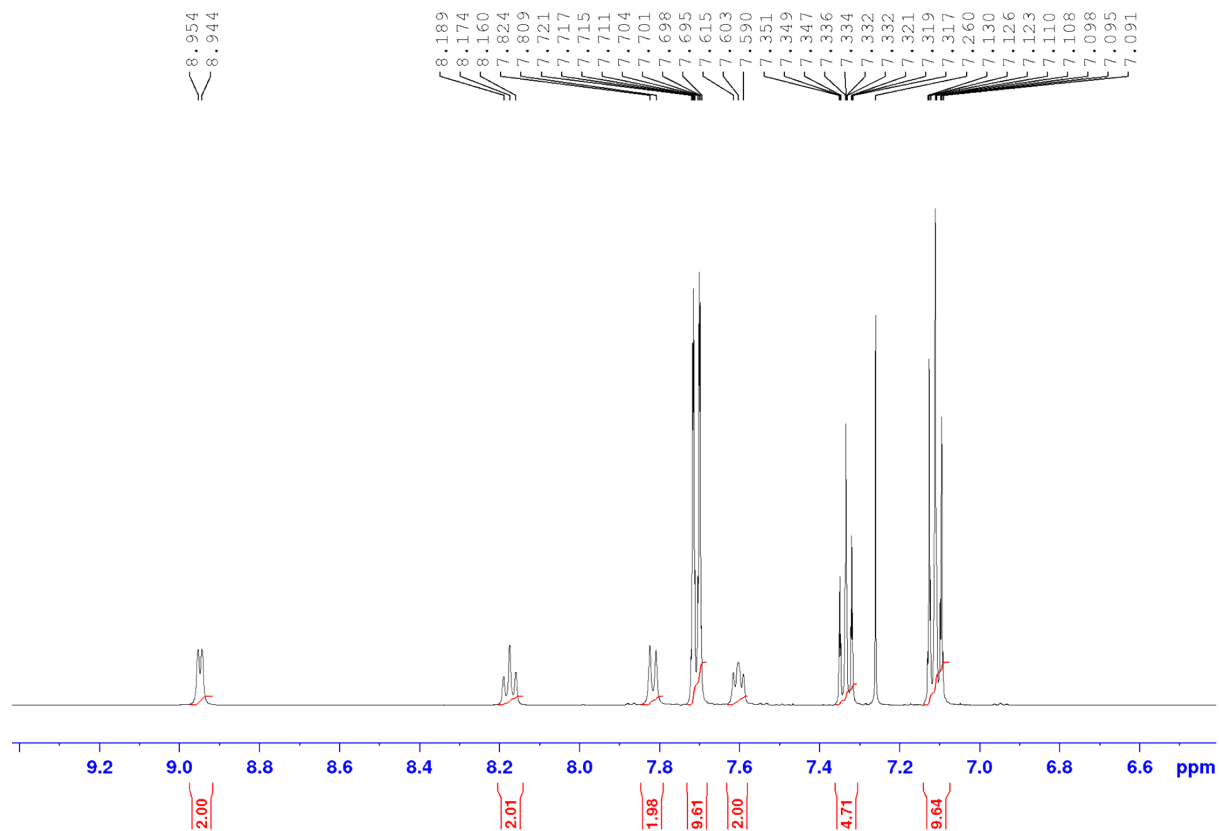
	<b>Peak</b>	<b>Intensity</b>	<b>Corr. Inte</b>	<b>Base (H)</b>	<b>Base (L)</b>	<b>Area</b>	<b>Corr. Are</b>
1	1010.7	64.9812	182.9953	1026.13	972.12	-9.1201	11.545
2	1072.42	100.8014	106.5585	1111	1041.56	-16.2278	5.7668
3	1157.29	119.5909	75.0724	1180.44	1141.86	-7.189	3.9334
4	1219.01	139.6862	29.4402	1234.44	1180.44	-11.6598	1.5052
5	1242.16	121.3621	34.0323	1257.59	1234.44	-2.7604	1.5133
6	1273.02	107.1293	33.0758	1303.88	1257.59	-4.291	2.0124
7	1319.31	115.4908	30.7155	1334.74	1303.88	-3.6349	1.3505
8	1427.32	47.0796	68.9394	1442.75	1365.6	-0.6456	6.8324
9	1458.18	37.6585	80.6011	1481.33	1442.75	4.4738	7.5257
10	1489.05	80.7302	54.4162	1504.48	1481.33	-0.1515	2.995
11	1527.62	46.5626	75.6965	1543.05	1504.48	1.8626	5.5292
12	1566.2	63.7159	26.4797	1573.91	1543.05	1.7685	1.1761
13	1581.63	36.8965	49.8567	1612.49	1573.91	8.3244	6.7022
14	3070.68	31.391	13.1218	3124.68	2985.81	56.5082	9.3733
15	3140.11	39.3346	1.9268	3302.13	3132.4	46.1677	-2.3794

**Table S3.** Raw FT-IR peak table for sample of **5** prepared in ambient atmosphere.

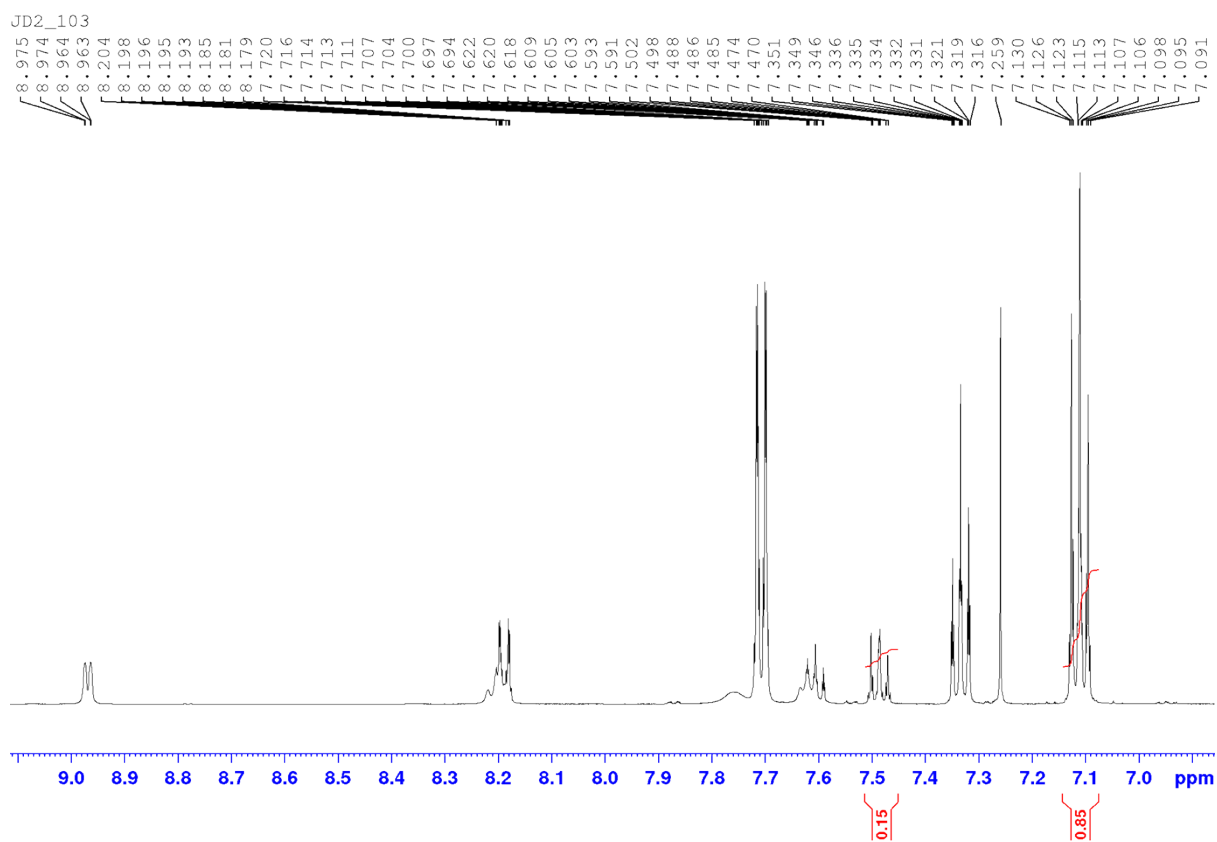
	<b>Peak</b>	<b>Intensity</b>	<b>Corr. Inte</b>	<b>Base (H)</b>	<b>Base (L)</b>	<b>Area</b>	<b>Corr. Are</b>
1	763.81	2.066	1.5964	779.24	748.38	24.1101	34.6271
2	925.83	-0.1804	0.8845	941.26	887.26	-45.711	12.9158
3	987.55	-0.3591	0.5396	1002.98	941.26	-48.3671	9.9549
4	1087.85	-0.1657	0.5691	1095.57	1072.42	-10.7961	5.8227
5	1165	-0.0949	0.3704	1180.44	1157.29	-6.5164	6.1829
6	1219.01	-0.1954	0.4336	1234.44	1180.44	-26.3535	10.3652
7	1273.02	-0.1638	0.2746	1288.45	1257.59	-9.7621	3.7668
8	1319.31	0.0781	0.3937	1334.74	1311.59	-5.1176	3.3752
9	1427.32	0.3346	0.4467	1442.75	1411.89	4.7038	8.1646
10	1450.47	0.7713	0.8823	1458.18	1442.75	5.0935	6.8075
11	1527.62	0.8354	0.5964	1535.34	1481.33	5.4251	22.5592
12	1581.63	0.9104	0.9888	1589.34	1558.48	8.4649	12.2144
13	1597.06	0.437	0.394	1612.49	1589.34	6.0099	4.1094
14	1620.21	0.3116	0.3015	1635.64	1612.49	1.8076	3.7676
15	2947.23	0.5147	0.071	2970.38	2916.37	24.5328	1.3855
16	3039.81	0.877	0.1024	3055.24	2978.09	50.6836	1.466
17	3070.68	1.0886	0.179	3078.39	3055.24	22.2522	1.9196
18	3163.26	1.0232	0.394	3263.56	3116.97	96.9181	17.7626



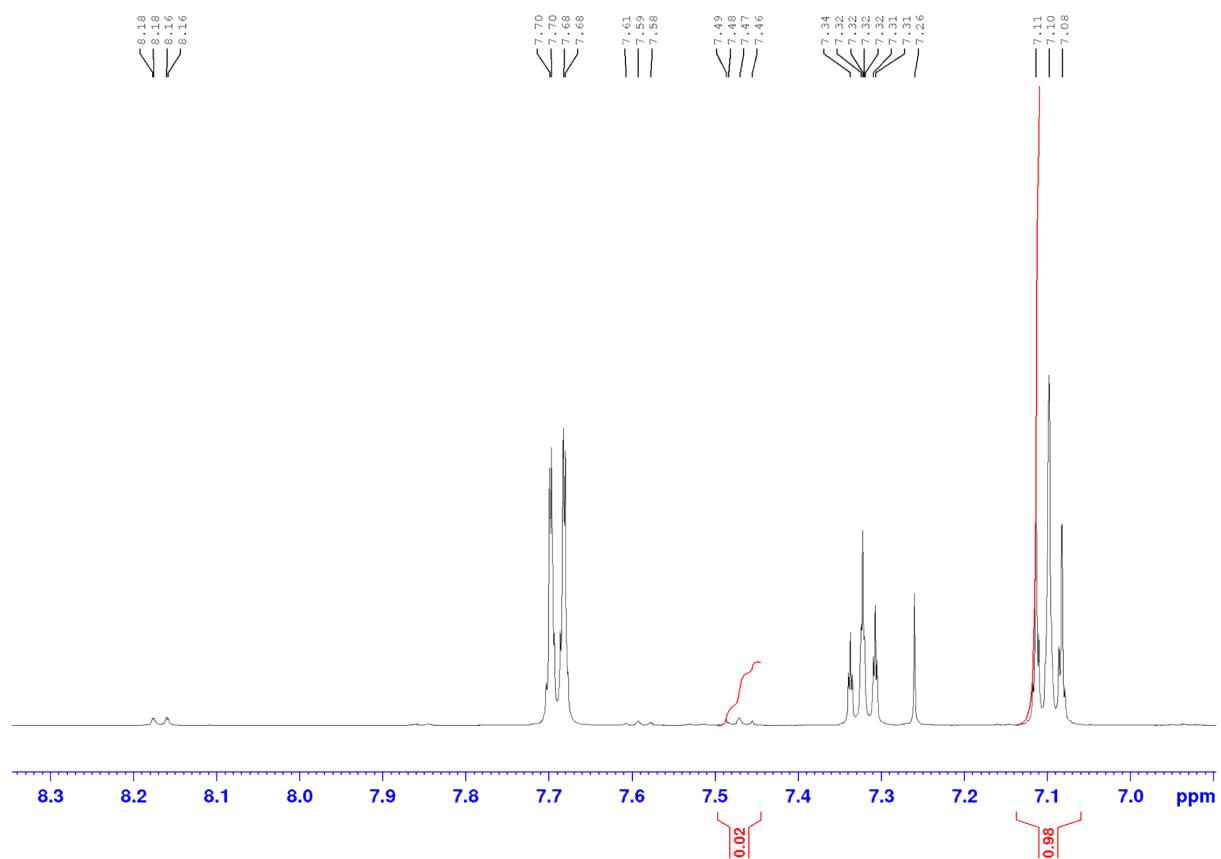
**Figure S9.** Proton NMR spectrum (CDCl<sub>3</sub>) of the reaction mixture of **6** and PhI.



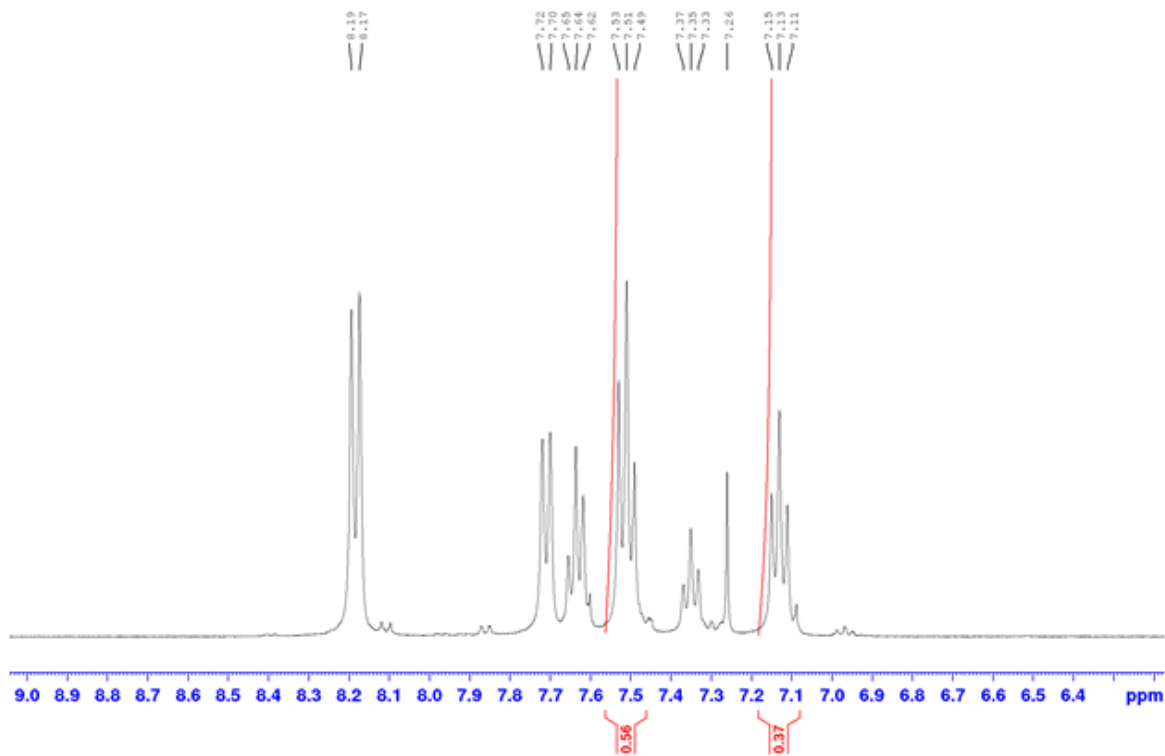
**Figure S10.** Proton NMR spectrum (CDCl<sub>3</sub>) of the reaction mixture of **5** and PhI.



**Figure S11.** Proton NMR spectrum (CDCl<sub>3</sub>) of the reaction mixture of [nBu<sub>4</sub>N][ICl<sub>4</sub>] and PhI.



**Figure S12.** Proton NMR spectrum (CDCl<sub>3</sub>) of the reaction mixture of ICl<sub>3</sub> and PhI.



## References

- (1) Jothibasu, R.; Huynh, H. V.; Koh, L. L. *J. Organomet. Chem.* **2008**, *693*, 374.
- (2) Batsanov, A. S.; Howard, J. A. K.; Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. *Eur. J. Org. Chem.* **2005**, 1876.
- (3) Sivaram, H.; Tan, J.; Huynh, H. V. *Organometallics* **2012**, *31*, 5875.
- (4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.;

- Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian 09, Revision A.1, Gaussian, Inc.: Wallingford CT, 2009.
- (5) Becke, A. D. *Phys. Rev. A: Gen. Phys.* **1988**, *38*, 3098.
- (6) Becke, A. D. *Journal of Chemical Physics* **1993**, *98*, 5648.
- (7) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.
- (8) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- (9) E. D. Glendening; J. K. Badenhoop; A. E. Reed; J. E. Carpenter; J. A. Bohmann; C. M. Morales; Weinhold, F.; NBO 5.9. see <http://www.chem.wisc.edu/~nbo5>: Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2011.
- (10) E.J. Baerends; T. Ziegler; J. Autschbach; D. Bashford; A. Bérces; F.M. Bickelhaupt; C. Bo; P.M. Boerrigter; L. Cavallo; D.P. Chong; L. Deng; R.M. Dickson; D.E. Ellis; M. van Faassen; L. Fan; T.H. Fischer; C. Fonseca Guerra; A. Ghysels; A. Giammona; S.J.A. van Gisbergen; A.W. Götz; J.A. Groeneveld; O.V. Gritsenko; M. Grüning; S. Gusarov; F.E. Harris; P. van den Hoek; C.R. Jacob; H. Jacobsen; L. Jensen; J.W. Kaminski; G. van Kessel; F. Kootstra; A. Kovalenko; M.V. Krykunov; E. van Lenthe; D.A. McCormack; A. Michalak; M. Mitoraj; J. Neugebauer; V.P. Nicu; L. Noodleman; V.P. Osinga; S. Patchkovskii; P.H.T. Philipsen; D. Post; C.C. Pye; W. Ravenek; J.I. Rodríguez; P. Ros; P.R.T. Schipper; G. Schreckenbach; J.S. Seldenthuis; M. Seth; J.G. Snijders; M. Solà; M. Swart; D. Swerhone; G. te Velde; P. Vernooijs; L. Versluis; L. Visscher; O. Visser; F. Wang; T.A. Wesolowski; E.M. van Wezenbeek; G. Wiesenekker; S.K. Wolff; T.K. Woo; Yakovlev, A. L. ADF2012, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>.