Article

Halogen bonding in *N*-alkyl-3-halogenopyridinium salts

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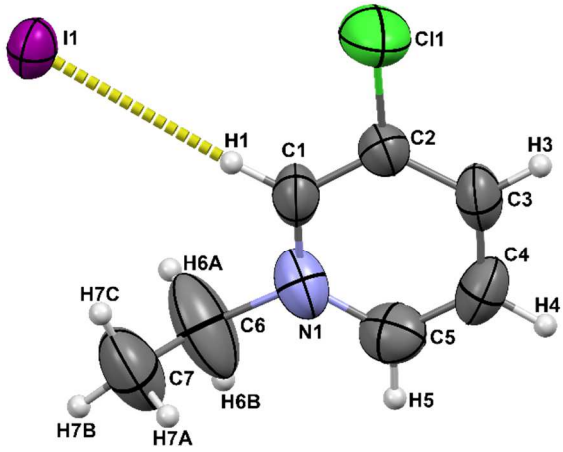

Figure S1. Molecular structure of [*N*-Et-**3-ClPy**]I showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

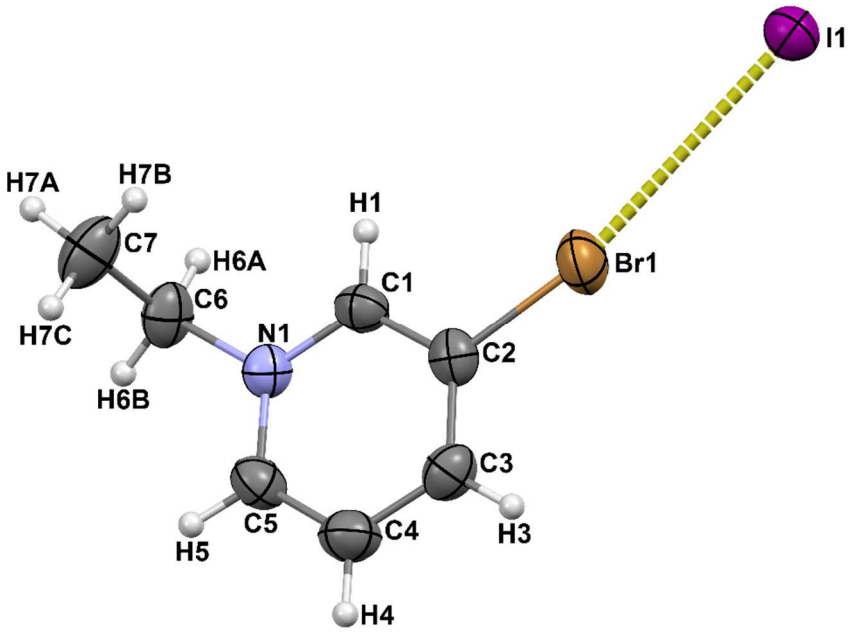

Figure S2. Molecular structure of [*N*-Et-**3-BrPy**]I showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

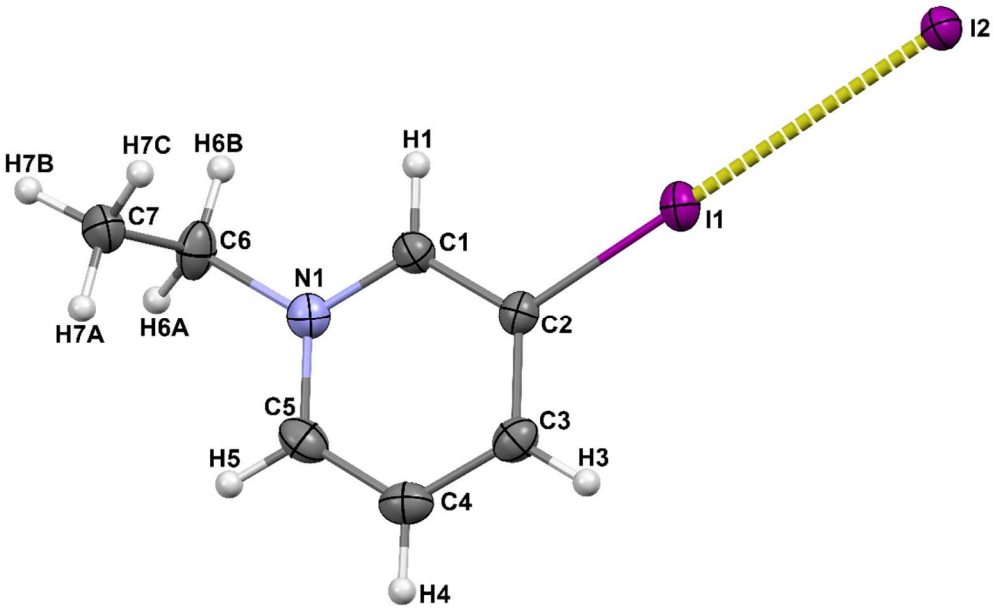

Figure S3. Molecular structure of **[***N*-Et-**3-IPy]**I showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

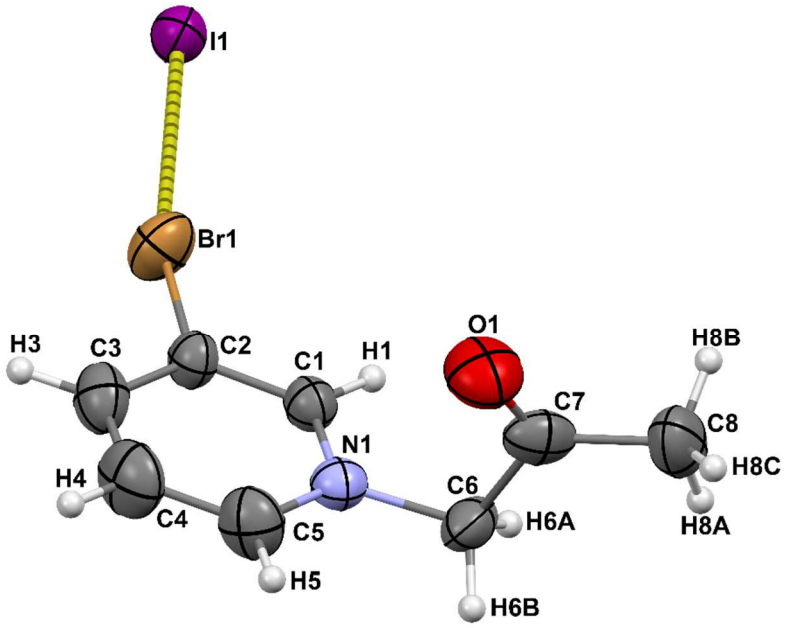

Figure S4. Molecular structure of [*N*-**Ace**-**3-ClPy**]I showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

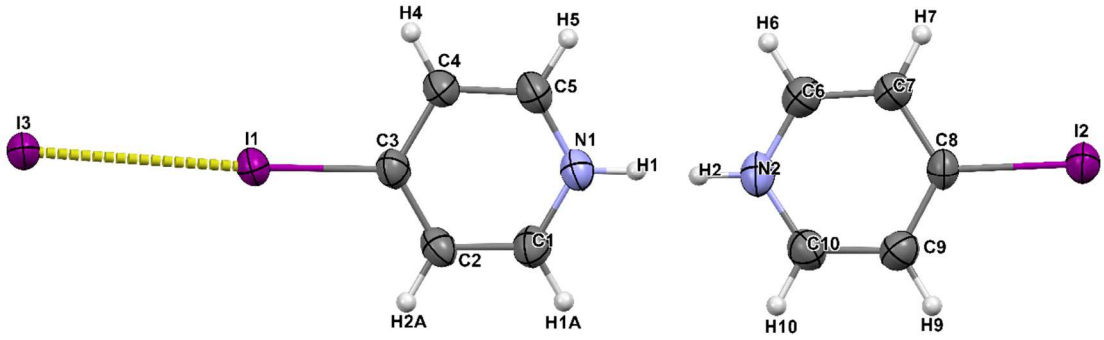

Figure S5. Molecular structure of [**4-IPy**]$_2$HI showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

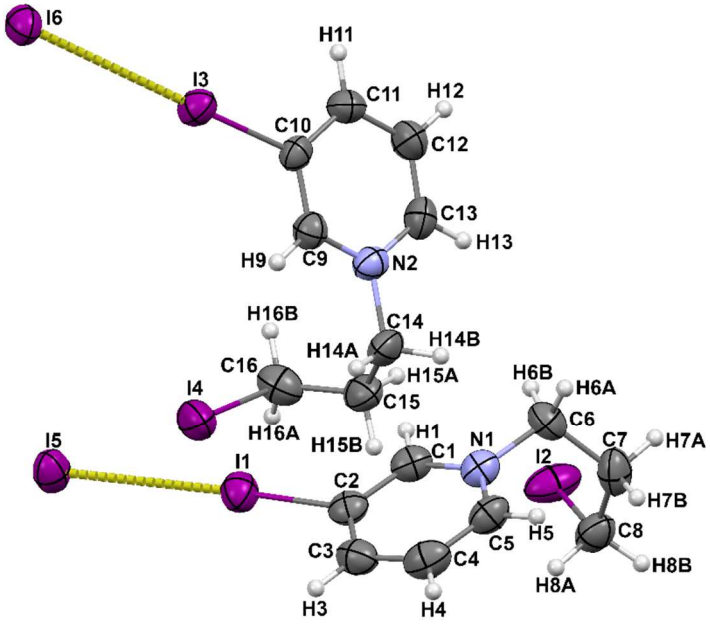

Figure S6. Molecular structure of **[***N*-**Prop**I-**3-IPy]**I showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

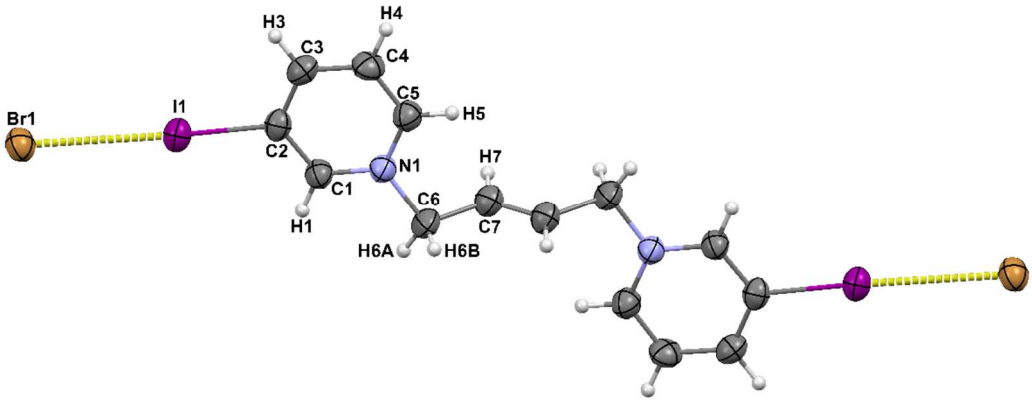

Figure S7. Molecular structure of **[*N*,*N*`-Buen-(3-IPy)**$_2$]Br$_2$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

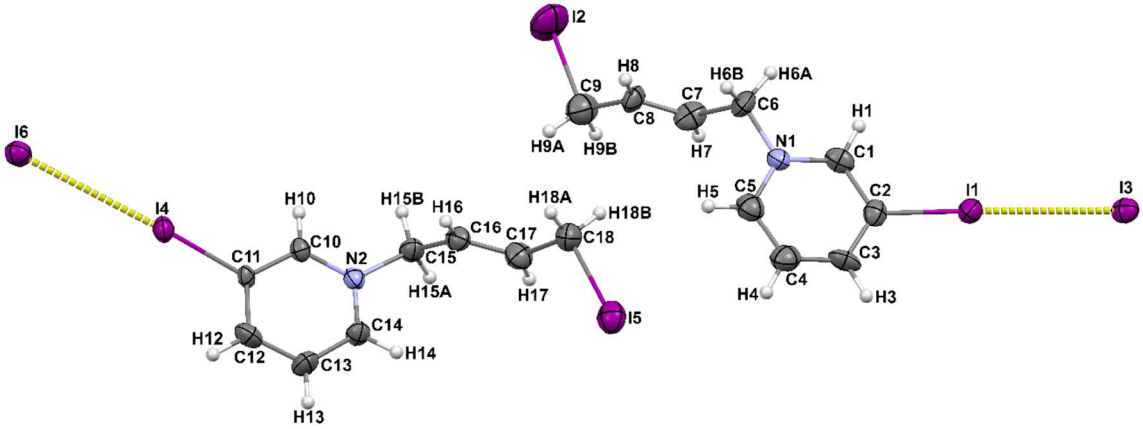

Figure S8. Molecular structure of [*N*-**BuenI-3-IPy**]I showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

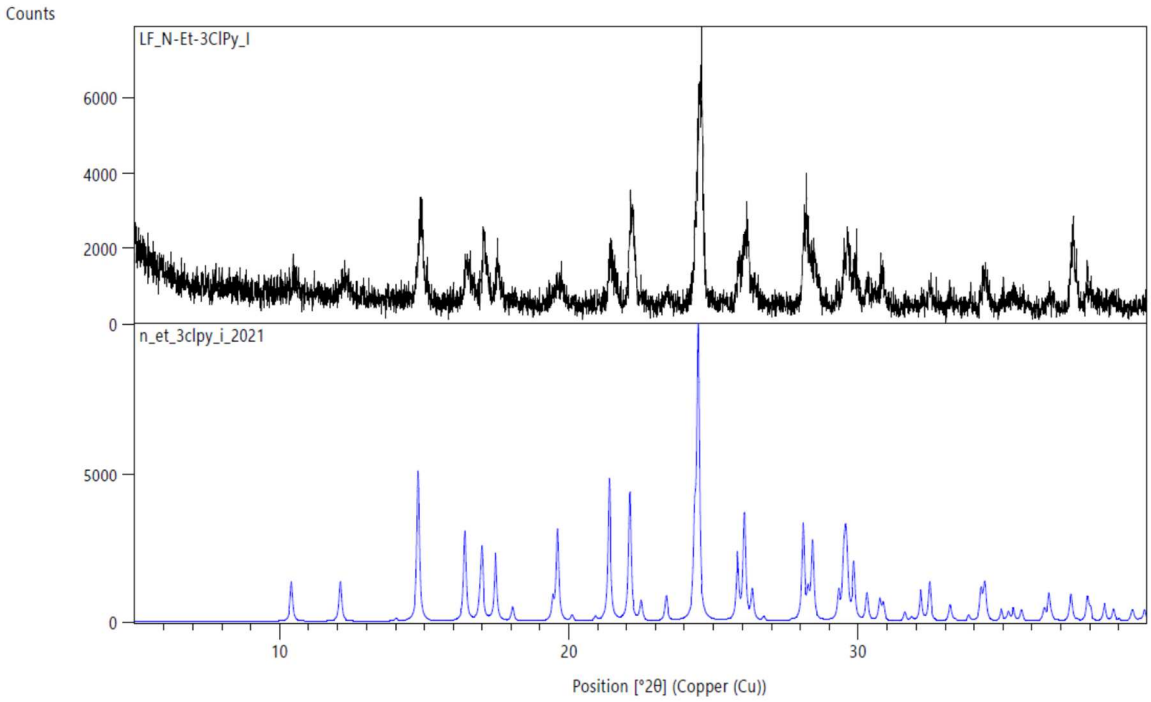

Figure S9. Measured (black) and calculated (blue) PXRD patterns of [*N*-Et-**3-ClPy**]I.

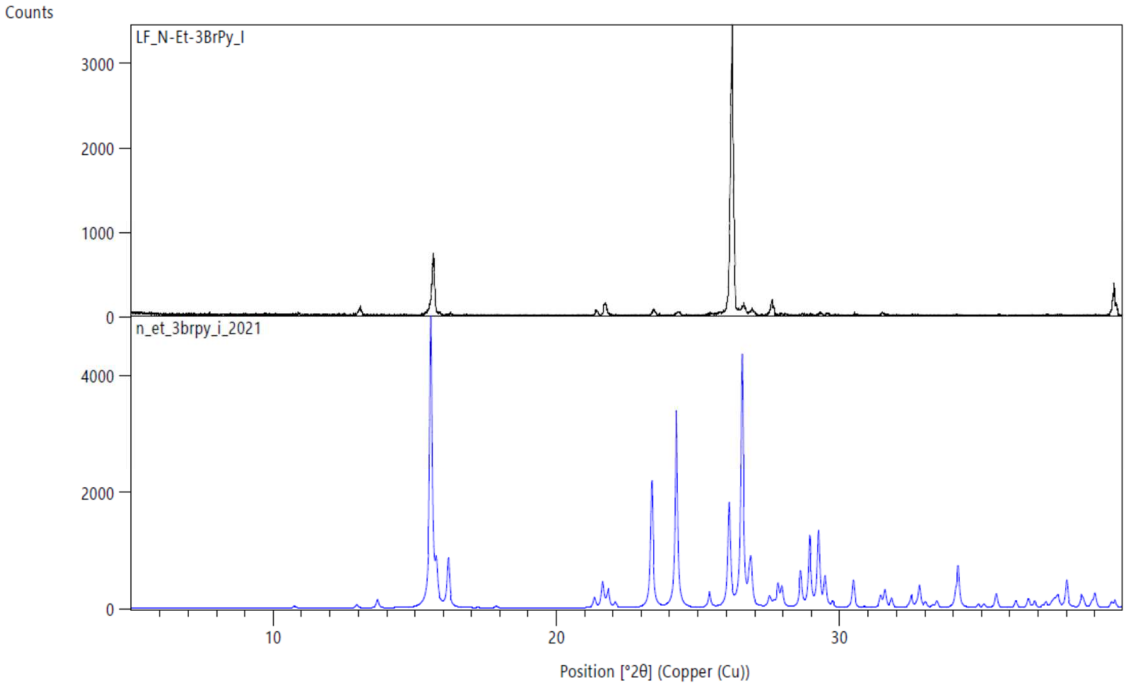

Figure S10. Measured (black) and calculated (blue) PXRD patterns of [*N*-Et-**3-BrPy**]I.

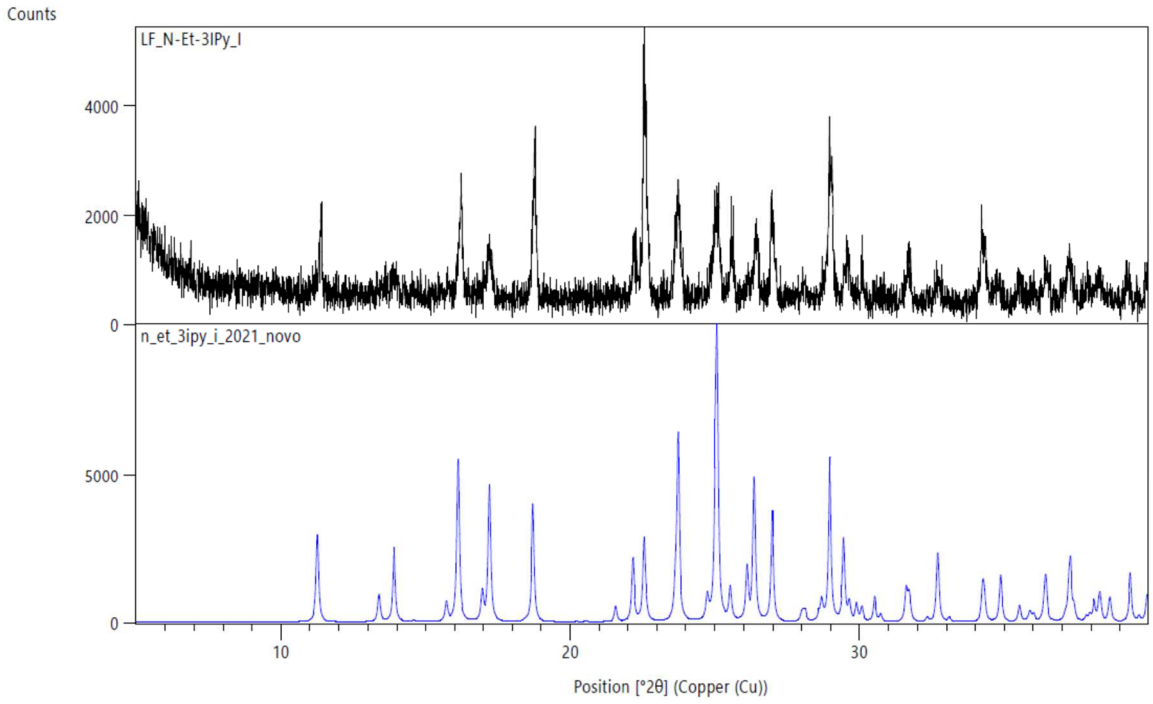

Figure S11. Measured (black) and calculated (blue) PXRD patterns of [*N*-Et-**3-IPy**]I.

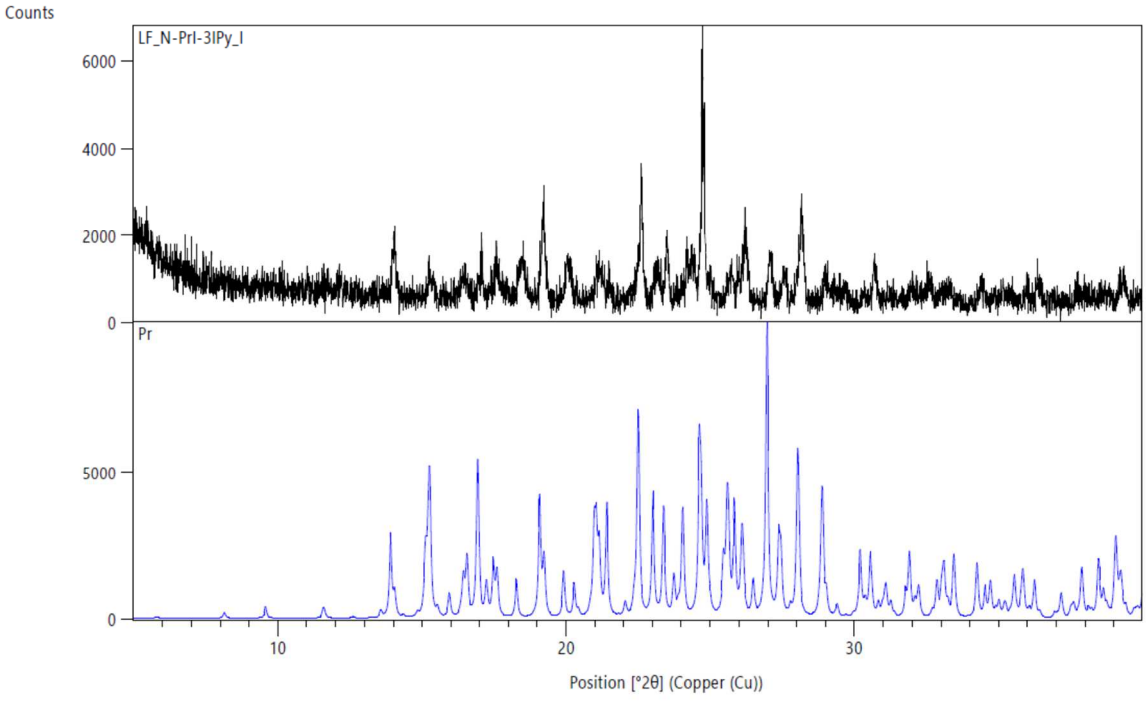

Figure S12. Measured (black) and calculated (blue) PXRD patterns of [*N*-**Prop**I-**3-IPy**]Br.

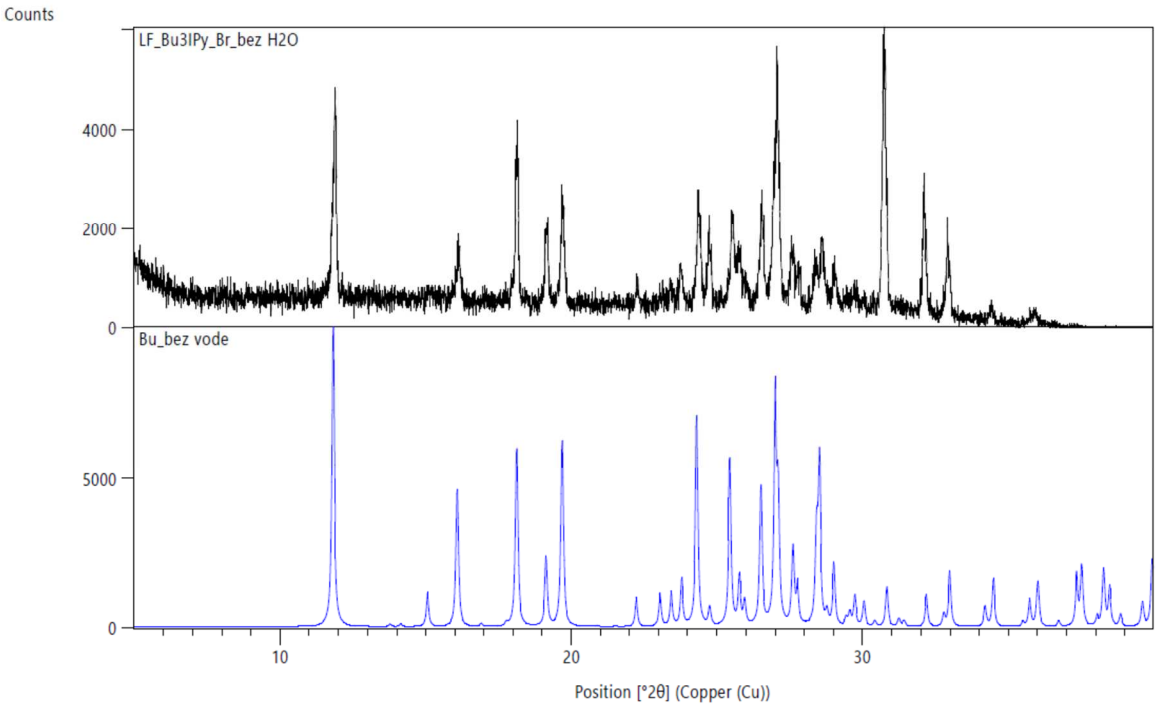

Figure S13. Measured (black) and calculated (blue) PXRD patterns of [*N*,*N*`-**Buen**-(**3-IPy**)$_2$]Br$_2$.

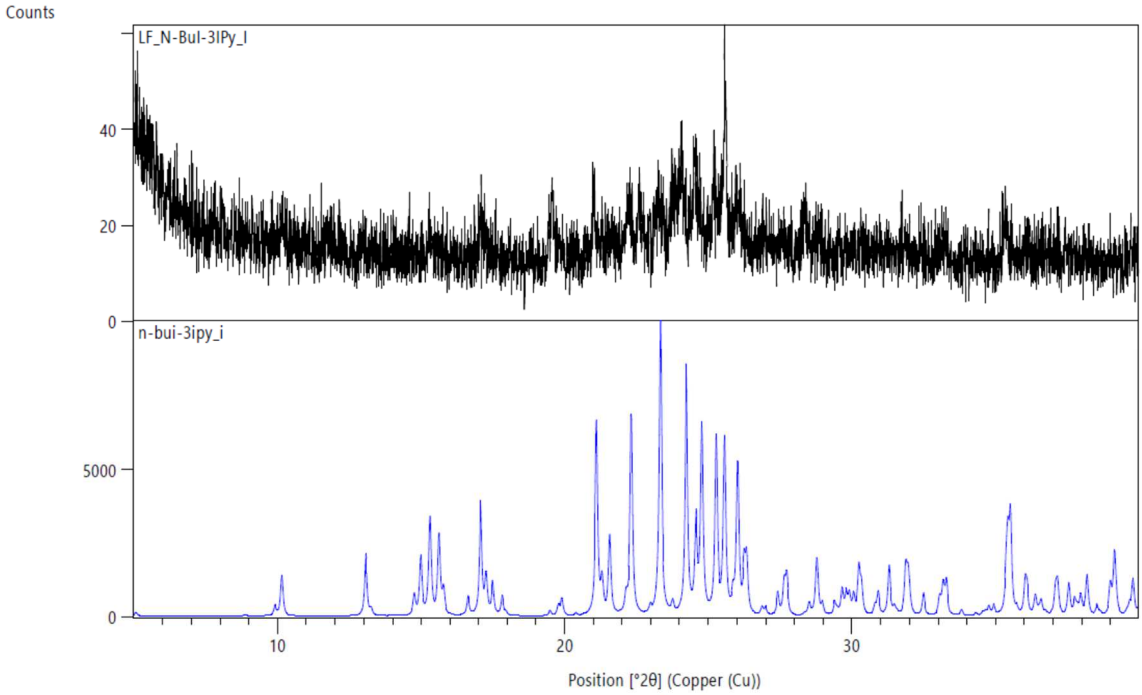

Figure S14. Measured (black) and calculated (blue) PXRD patterns of [*N*-**Buen**I-**3-IPy**]I.

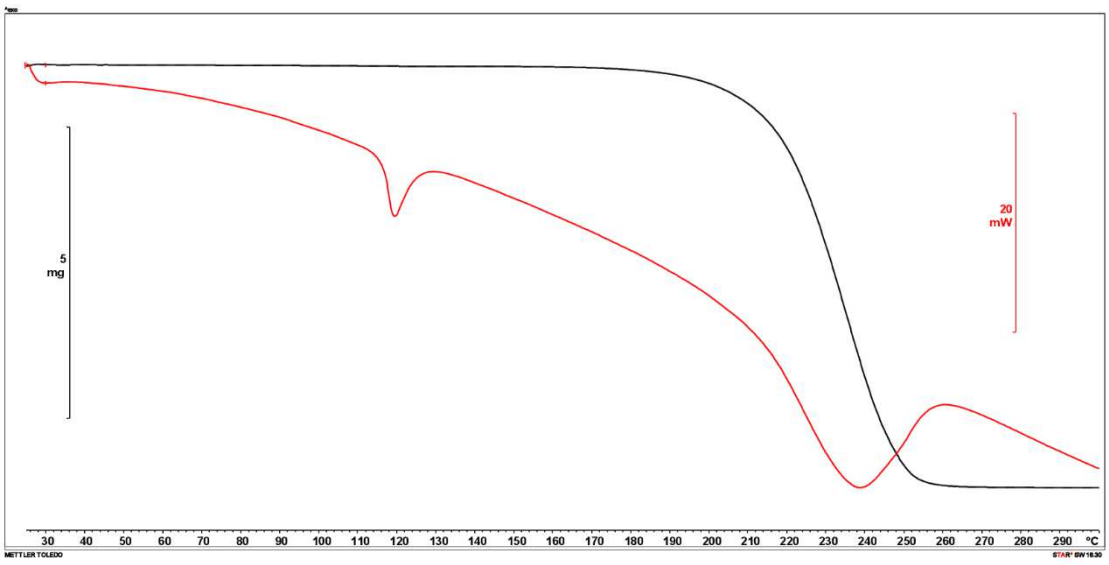

Figure S15. TG (black) and DSC (red) thermograms of [*N*-Et-**3-ClPy**]I.

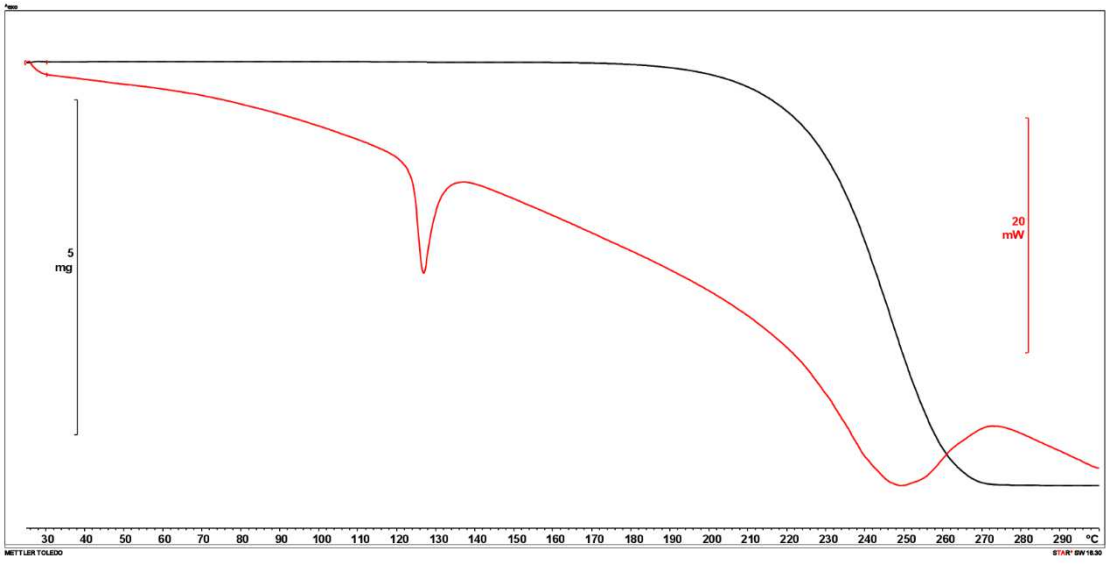

Figure S16. TG (black) and DSC (red) thermograms of [*N*-Et-**3-BrPy**]I.

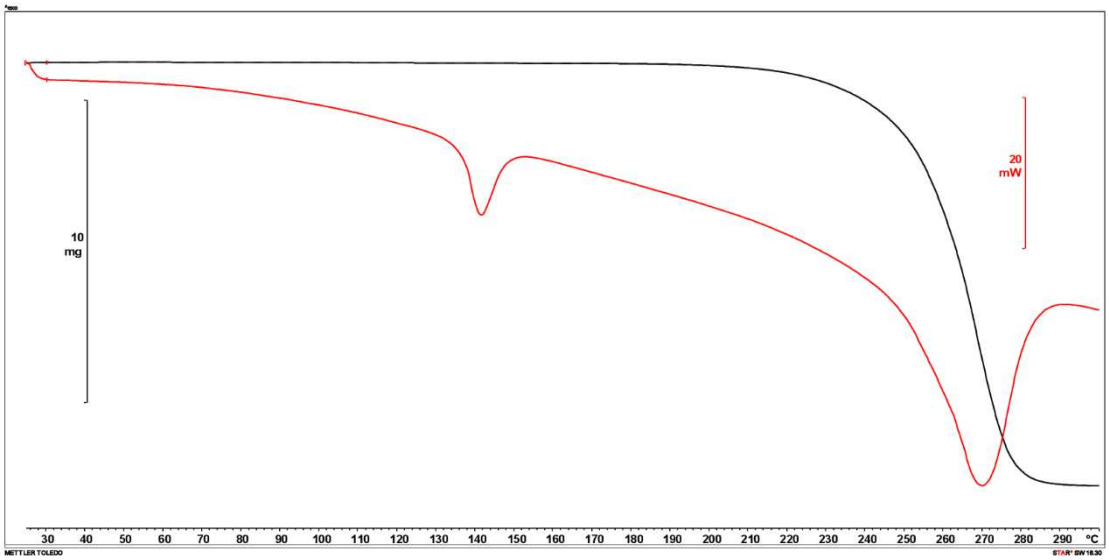

Figure S17. TG (black) and DSC (red) thermograms of [*N*-Et-**3-IPy**]I.

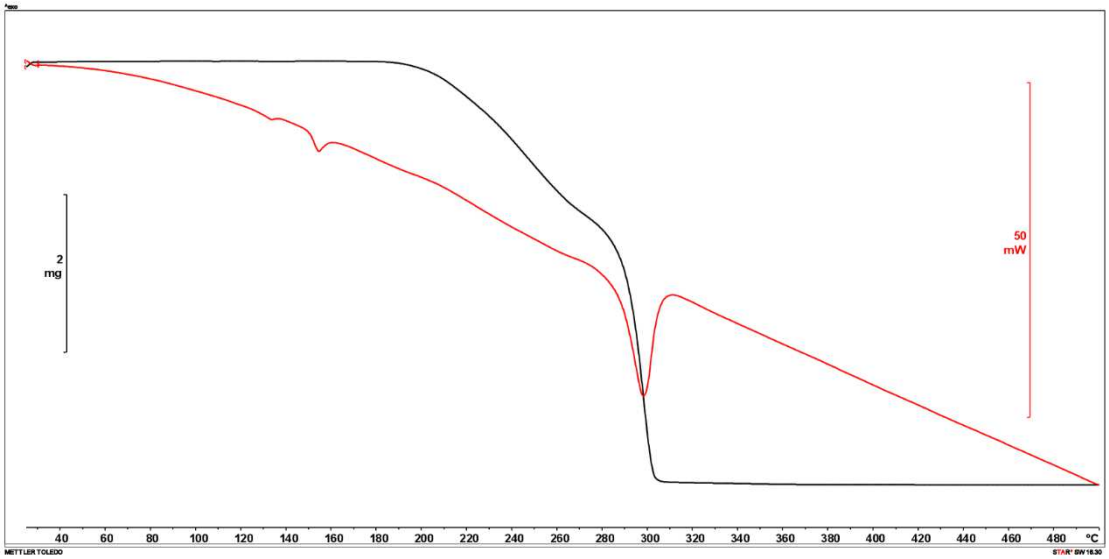

Figure S18. TG (black) and DSC (red) thermograms of [*N*-**Prop**I-**3-IPy**]I.

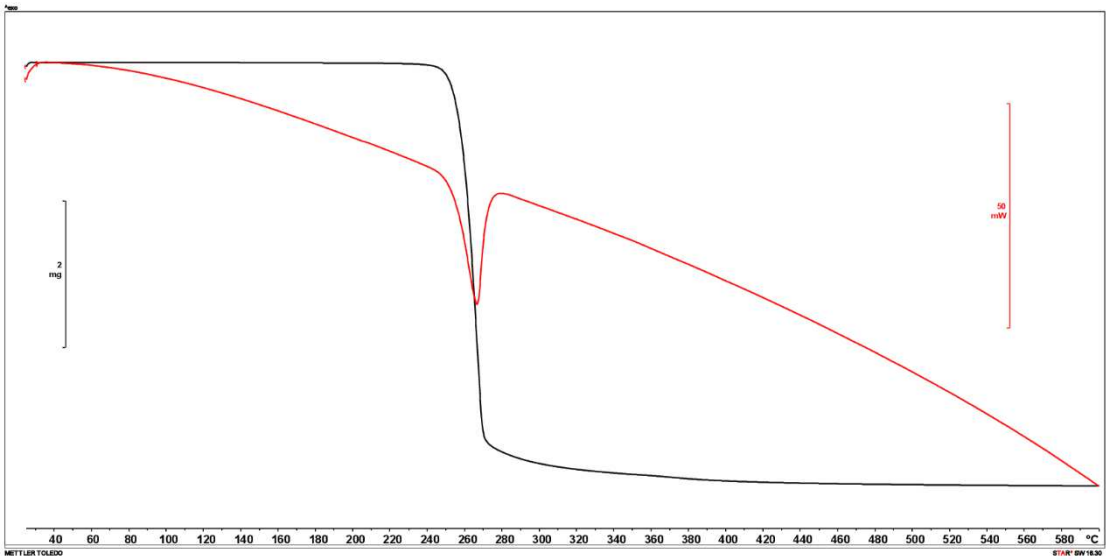

Figure S19. TG (black) and DSC (red) thermograms of **[*N*,*N*`-Buen**-(**3-IPy**)$_2$]Br$_2$.

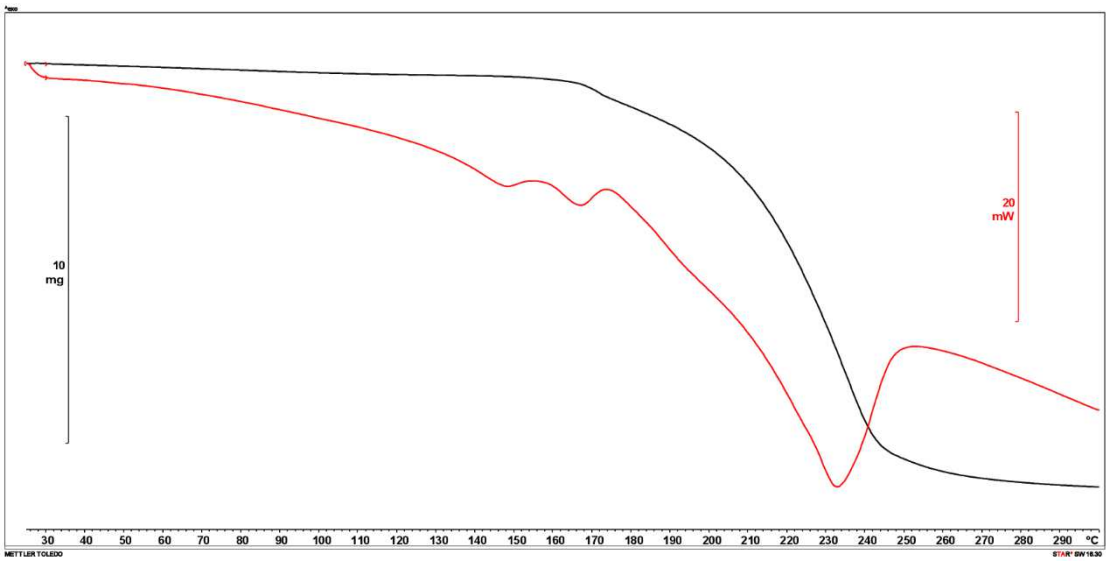

Figure S20. TG (black) and DSC (red) thermograms of [*N*-**Buen**I-**3-IPy**]I.

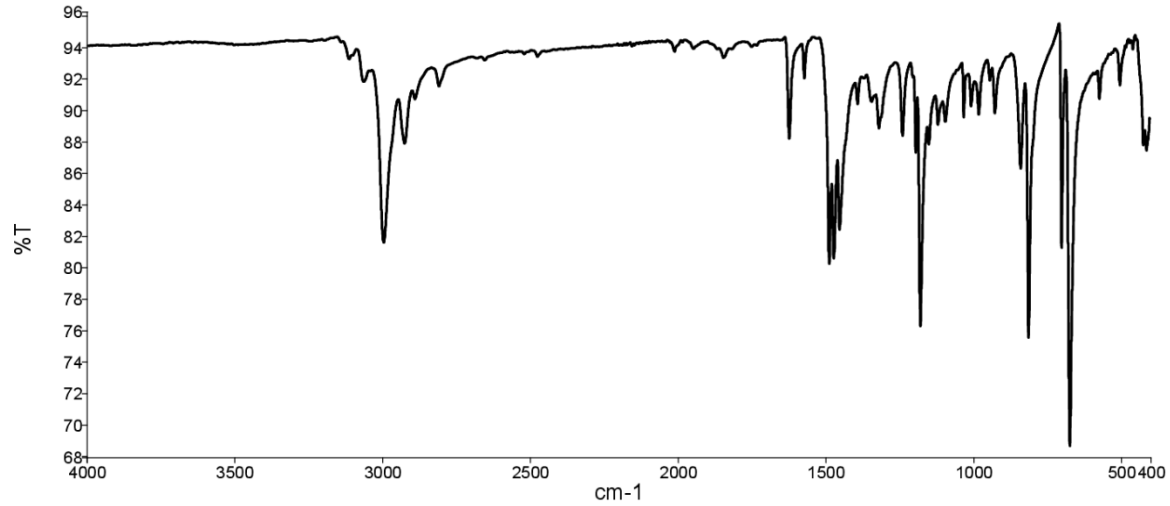

Figure S21. IR spectrum (ATR) of [*N*-Et-**3-ClPy**]I.

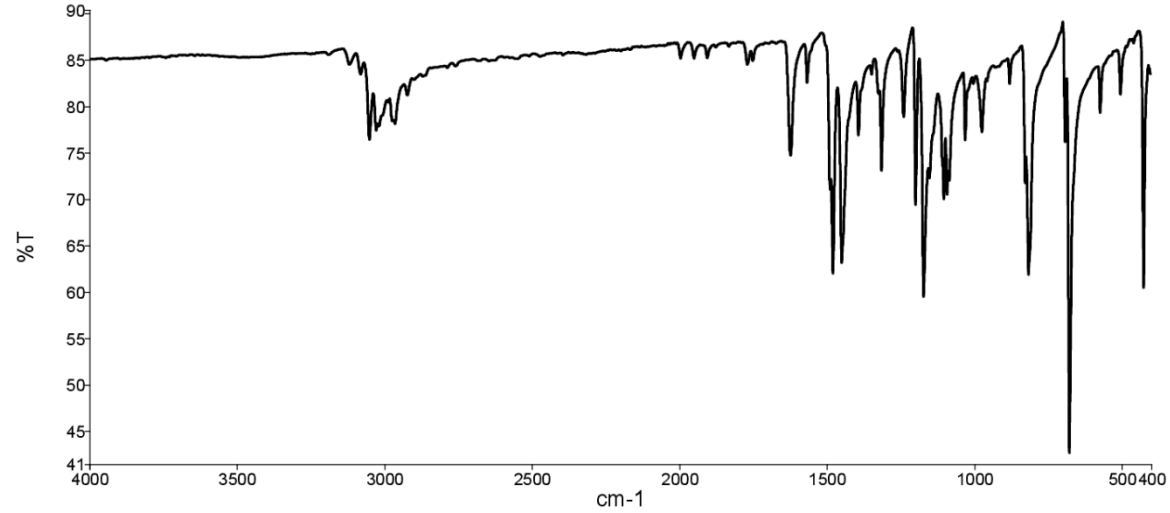

Figure S22. IR spectrum (ATR) of [*N*-Et-**3-BrPy**]I.

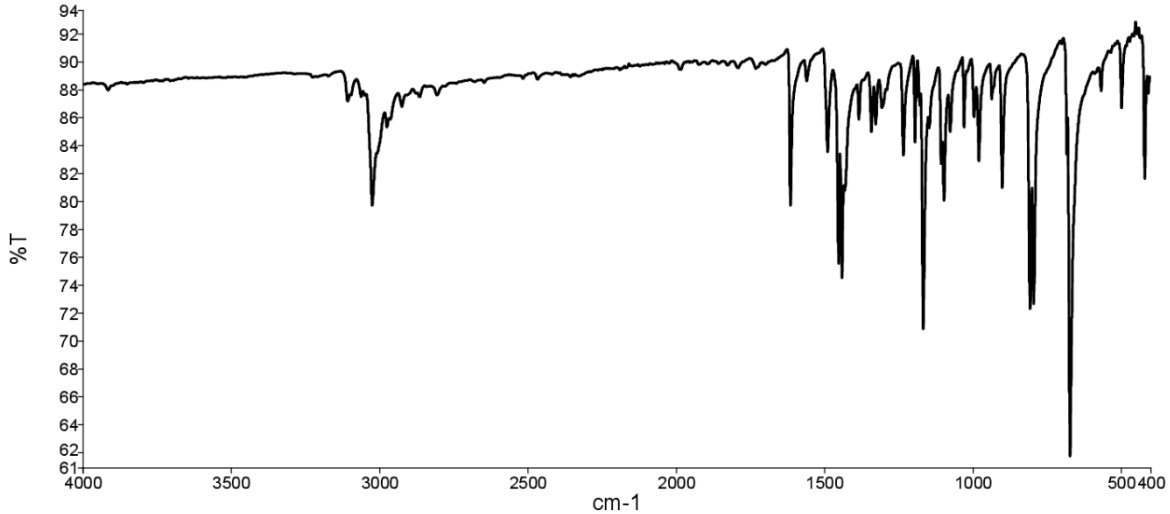

Figure S23. IR spectrum (ATR) of [*N*-Et-**3-IPy**]I.

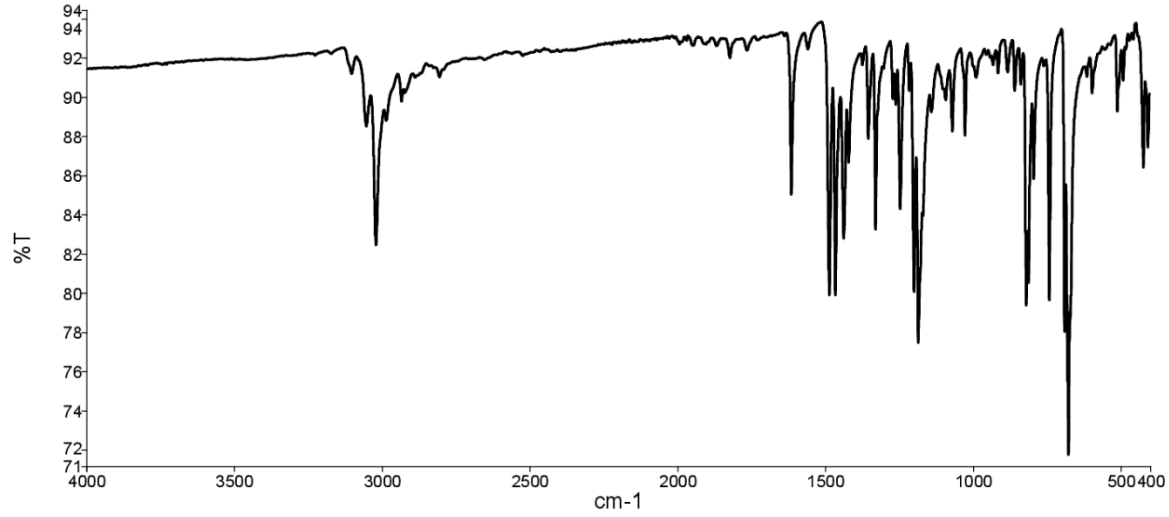

Figure S24. IR spectrum (ATR) of [*N*-**Prop**I-**3-IPy**]I.

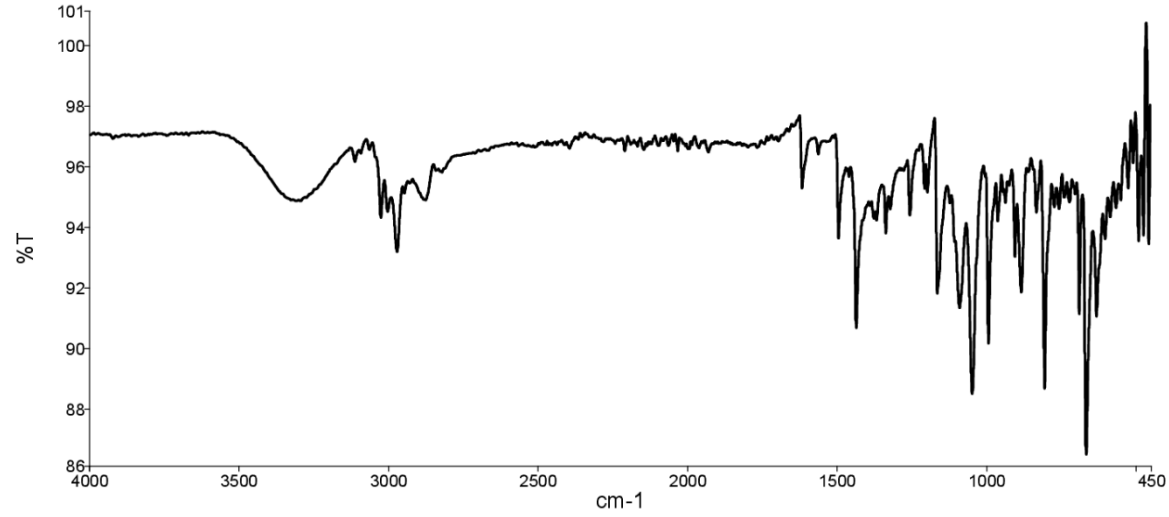

Figure S25. IR spectrum (ATR) of [*N*,*N*`-**Buen**-(**3-IPy**)$_2$]Br$_2$.

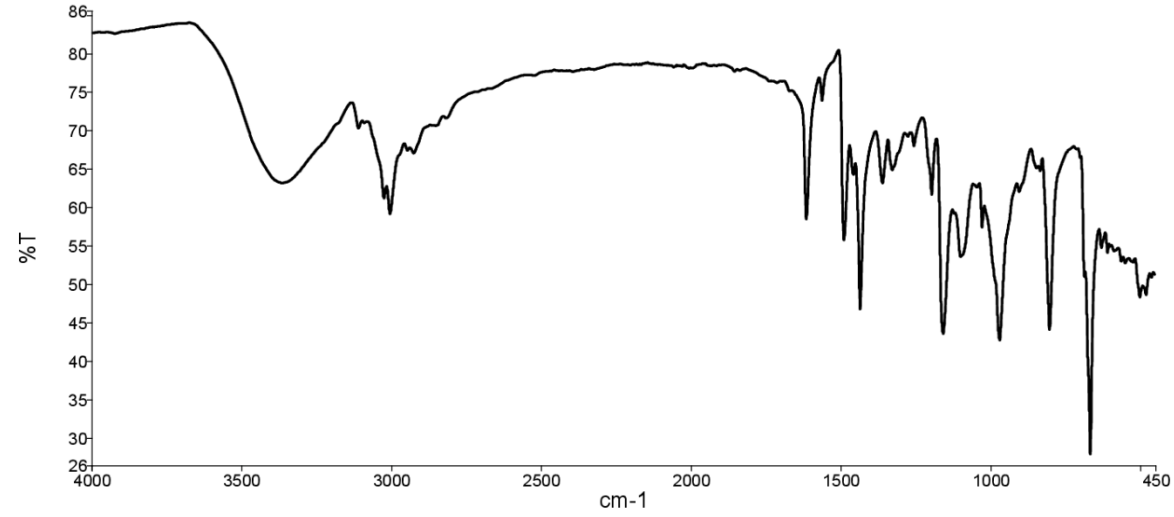

Figure S26. IR spectrum (ATR) of [*N*-**Buen**I-**3-IPy**]I.

Table S1. An overview and crystallographic data of the prepared compounds.

	[*N*-Et-**3-ClPy**]I	[*N*-Et-**3-BrPy**]I	[*N*-Et-**3-IPy**]I	[*N*-**Ace-3-IPy**]I
Molecular formula	C_7H_9ClIN	C_7H_9BrIN	$C_7H_9I_2N$	C_8H_9ONIBr
M_r	269.5	314.0	361.0	342.0
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\,2_1/c$	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/n$
Crystal data:				
a / Å	6.3486(3)	6.8018(4)	7.88120(10)	8.8788(6)
b / Å	10.4216(5)	10.2748(5)	12.1185(2)	7.0447(4)
c / Å	14.7025(7)	13.8404(8)	10.2971(2)	17.4511(9)
α / °	90	90	90	90
β / °	96.626(4)	99.623(5)	91.892(2)	95.905(5)
γ / °	90	90	90	90
V / Å^3	966.26(5)	953.66(8)	982.92(1)	504.55(5)
Z	4	4	4	4
D_{calc} / g cm^{-3}	1.85	2.19	2.44	2.09
λ(MoK_α) / Å	0.71073	0.71073	0.71073	0.71073
T / K	295	295	295	295
Crystal size / mm^3	0.15 x 0.04 x 0.03	0.14 x 0.02 x 0.01	0.14 x 0.14 x 0.12	0.08 x 0.08 x 0.09
μ / mm^{-1}	3.524	7.481	6.334	6.587
F(000)	512	584	656	640
Refl. collected/unique	6548 / 1878	6712 / 2069	34119 / 2860	5525 / 2116
Data parameters	92	93	93	118
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	1.029; –2.368	1.948; –1.726	0.700; –0.685	0.491; –1.043
$R[F^2 > 4\sigma(F^2)]$	0.056	0.044	0.023	0.035
w$R(F^2)$	0.131	0.125	0.051	0.076
Goodness-of-fit, S	1.097	1.095	1.089	0.939

Table S1. Continued.

	[**4-IPy**]$_2$HI	[*N*-**Prop**I-**3-IPy**]I	[*N*,*N*'-**Buen**-(**3-IPy**)2]Br_2	[*N*-**Buen**I-**3-IPy**]I
Molecular formula	$C_{10}H_9I_3N_2$	$C_8H_{10}I_3N$	$C_{14}H_{14}Br_2I_2N_2$	$C_9H_{10}I_3N$
M_r	537.9	1001.8	623.9	618.18
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/n$	P n a 2_1
Crystal data:				
a / Å	6.8903(4)	7.2177(2)	7.7257(13)	34.8020(14)
b / Å	17.6755(10)	30.4077(11)	11.5890(18)	10.3728(4)
c / Å	13.2376(11)	11.6116(4)	9.7976(18)	7.3369(3)
α / °	90	90	90	90
β / °	100.199(7)	93.483(3)	93.698(16)	90
γ / °	90	90	90	90
V / Å^3	1361.24(15)	2543.73(5)	875.38(9)	2648.58(2)
Z	4	8	2	8
D_{calc} / g cm^{-3}	2.322	2.62	2.37	2.57
λ(MoK_α) / Å	0.71073	0.71073	0.71073	0.71073
T / K	170	295	295	295
Crystal size / mm^3	0.06 x 0.04 x 0.01	0.02 x 0.02 x 0.11	0.07 x 0.02 x 0.005	0.10 x 0.12 x 0.14
μ / mm^{-1}	6.861	7.330	8.149	7.044
F(000)	968	1792	986	1840
Refl. collected/unique	3031 / 1576	106756 / 106756	12567 / 1916	16254 / 5018
Data parameters	136	218	91	235
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.391; –1.074	1.882; –1.556	0.659; –0.895	1.327; –1.380
$R[F^2 > 4\sigma(F^2)]$	0.072	0.041	0.030	0.044
w$R(F^2)$	0.066	0.077	0.073	0.102
Goodness-of-fit, S	1.057	0.970	0.993	1.059