Supporting Information for

Ligand Exchange Among Iodine(I) Complexes

Shlin Yu*, Jas S. Ward

[1] University of Jyvaskyla, Department of Chemistry, Jyväskylä 40014, Finland

1. General Considerations 2
2. Synthesis of iodine(I) complex $[I(X)_2]PF_6$ 3
3. Synthesis of the asymmetrical iodine(I) complex $[I(X)(16)]PF_6$ 58
4. X-ray Crystallographic Studies 68
5. Computational Details.....70
6. References for Supplementary Information 75

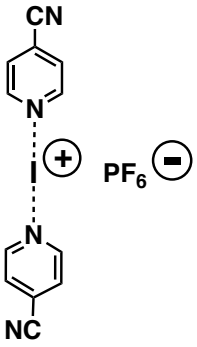
1. General Considerations

All reagents and solvents were purchased from commercial suppliers and used without further purification. [I(**16**)$_2$]PF_6 was synthesised according to literature procedure.[1] NMR spectra were recorded on a Bruker Avance III 500 MHz or Avance 300 MHz spectrometers. The ^{1}H-^{15}N NMR correlation spectra were recorded on a Bruker Avance III 500 MHz spectrometer at 30ºC in CD_2Cl_2 or CD_3CN. Chemical shifts are reported on the δ scale in ppm using the residual solvent signal as internal standard (CD_2Cl_2, δ_H 5.32; CD_3CN, δ_H 1.94), or for ^{1}H-^{15}N NMR spectroscopy, to an external d_3-$MeNO_2$ standard. Coupling constants are presented in Hz. For the ^{1}H-^{15}N HMBC spectroscopy, spectral windows of 4 ppm (^{1}H) and 600 ppm (^{15}N) were used with 1024 points in the direct dimension and 512 increments used in the indirect dimension resulting in a resolution of 1.2 ppm/point, however, a peak shape analysis was performed. Abbreviations of coupling patterns are as follows: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (*J*) are expressed in Hz.

Single crystals of a quality suitable for X-ray diffraction were obtained for the complexes by slow evaporation of a CD_2Cl_2 solution over several days.

2. Synthesis of iodine(I) complex $[I(X)_2]PF_6$

2.1 Synthesis of $[I(1)_2]PF_6$



To a solution of silver hexafluorophosphate (3.0 mg, 0.012 mmol, 1.0 eq) in CD_2Cl_2 (1 mL), a solution of 4-cyanopyridine (**1**) (2.5 mg, 0.024 mmol, 2.0 eq) in CD_2Cl_2 (0.85 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (3.0 mg, 0.012 mmol, 1.0 eq) in CD_2Cl_2 (0.15 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{1})_2]PF_6$ (78%, determined by ^{1}H NMR integration of the crude reaction mixture; and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 9.02 (d, *J* = 6.7 Hz, 2H), 7.88 (d, *J* = 6.8 Hz, 2H); **^{1}H-^{15}N correlation NMR** (500 MHz, CD_2Cl_2): δ -168.8.

NMR characterisation for ligand **1**: **^{1}H-^{15}N HMBC NMR** (500 MHz, CD_2Cl_2): δ -52.8.

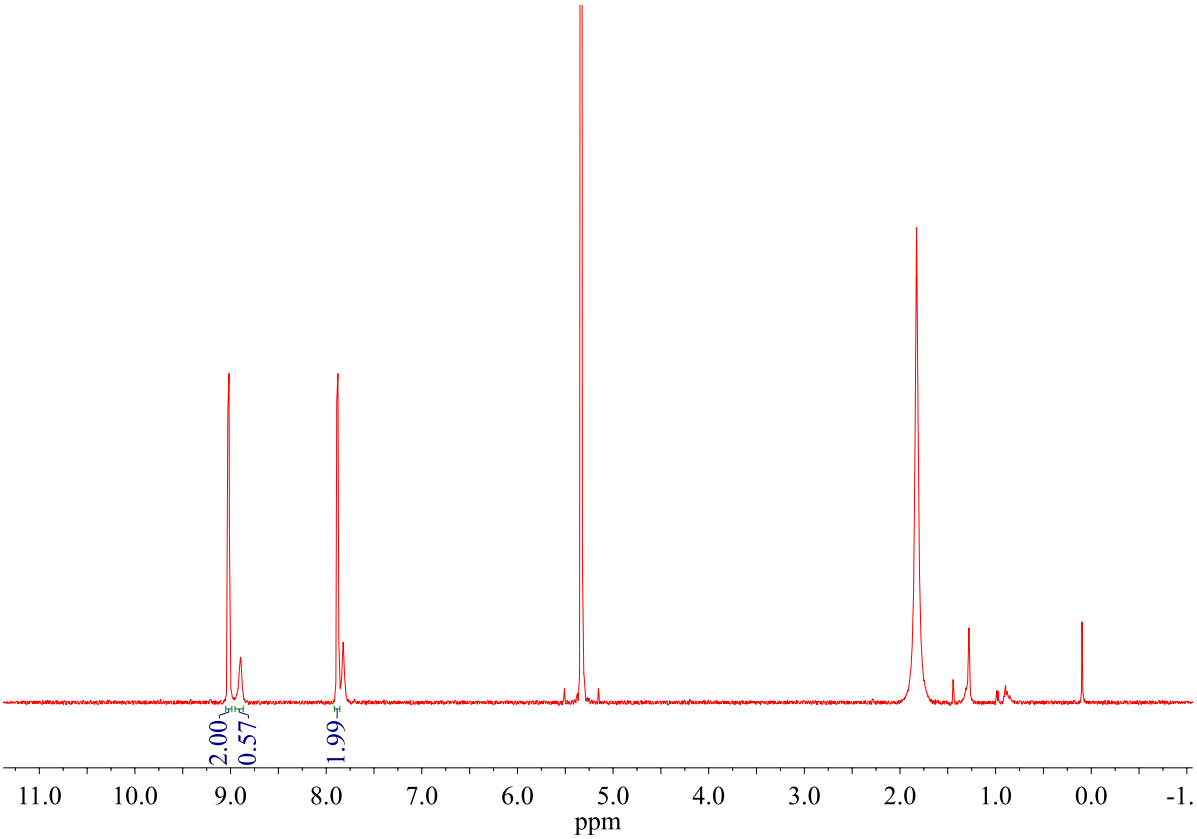


Figure S1. ^{1}H NMR spectrum of the crude mixture of reaction [I(**1**)$_2$]PF$_6$ (CD_2Cl_2, 500 MHz, 30 °C).

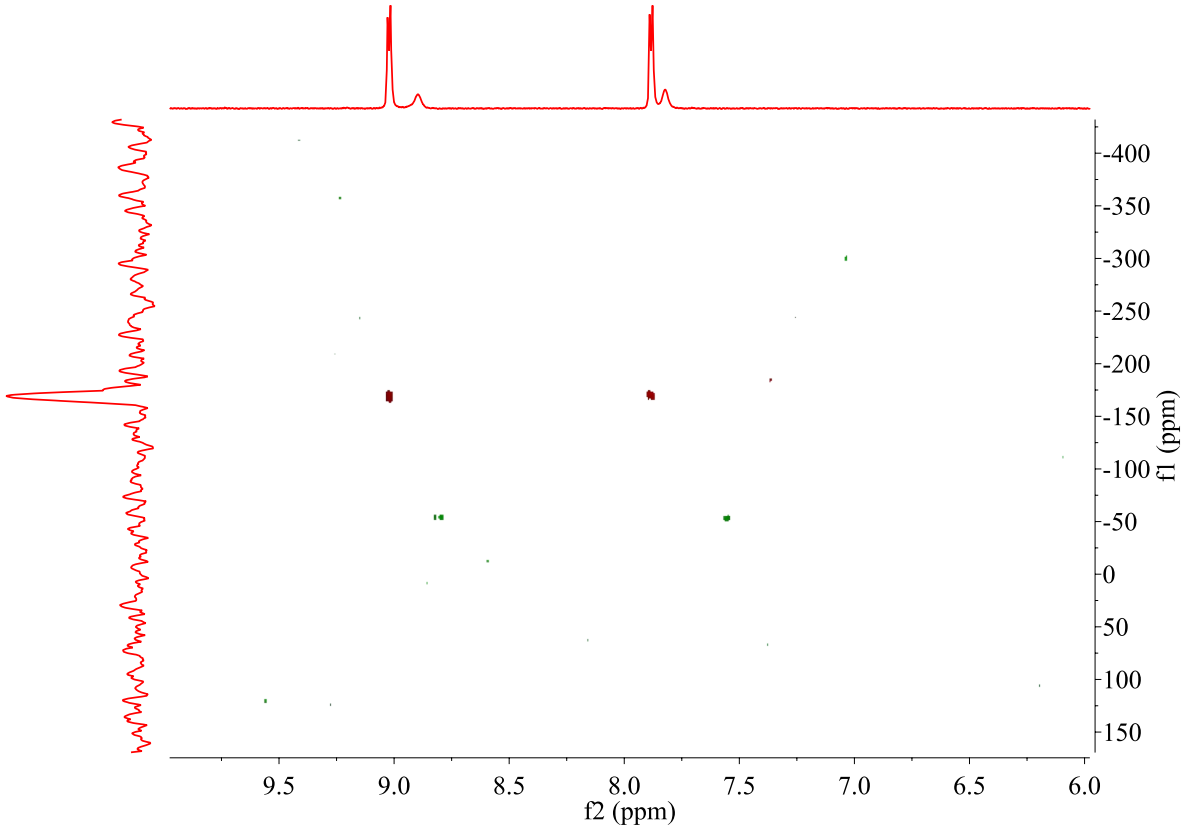


Figure S2. The stacked ^{1}H-^{15}N HMBC-NMR Spectra of ligand **1** in green and [N-I-N]$^{+}$ complex [I(**1**)$_2$]PF$_6$ in red, in CD_2Cl_2 at 30 °C.

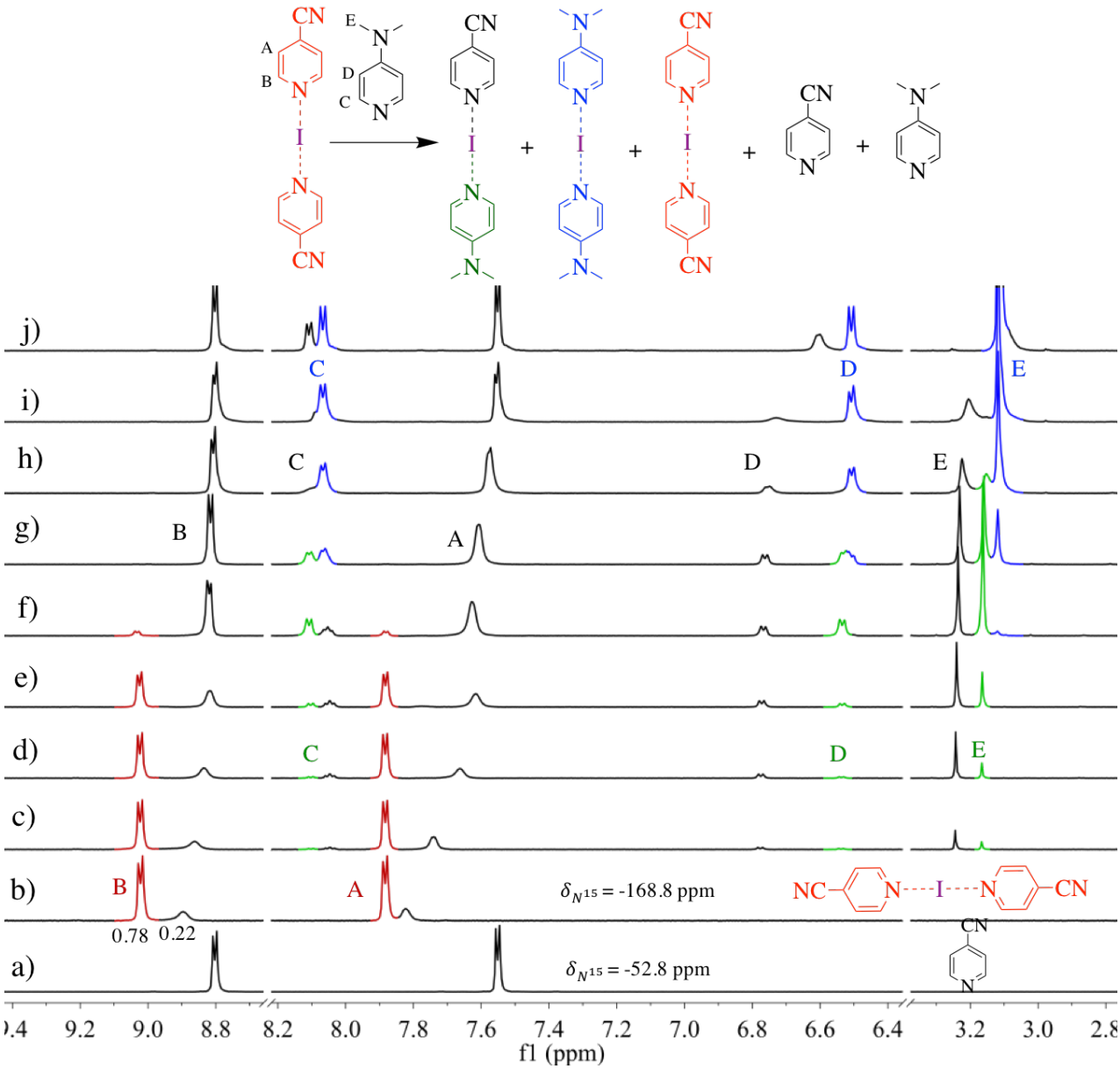
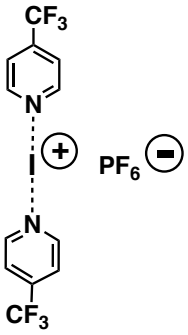


Figure S3. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **1** (a), the crude mixture of reaction $[I(\mathbf{1})_2]PF_6$ in the absence (b) and in the presence of 0.1 (c), 0.2 (d), 0.4 (e), 1.0 (f), 1.2 (g), 1.6 (h), 1.9 (i), and 2.5 equivalents (j) of **16**.

2.2 Synthesis of $[I(2)_2]PF_6$



To a solution of silver hexafluorophosphate (1.95 mg, 0.008 mmol, 1.0 eq) in CD_2Cl_2 (1 mL), a solution of 4-(trifluoromethyl)pyridine (**2**) (2.28 mg, 0.015 mmol, 2.0 eq) in CD_2Cl_2 (0.85 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (1.96 mg, 0.008 mmol, 1.0 eq) in CD_2Cl_2 (0.15 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{2})_2]PF_6$ (75%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 9.06 (d, *J* = 6.5 Hz, 2H), 7.89 (d, *J* = 6.6 Hz, 2H); **^{15}N NMR** (51 MHz, CD_2Cl_2): δ -168.5. The analytical data was in agreement with previously reported literature data.[2]

NMR characterisation for ligand **2**: **^{15}N NMR** (51 MHz, CD_2Cl_2): δ -54.8.

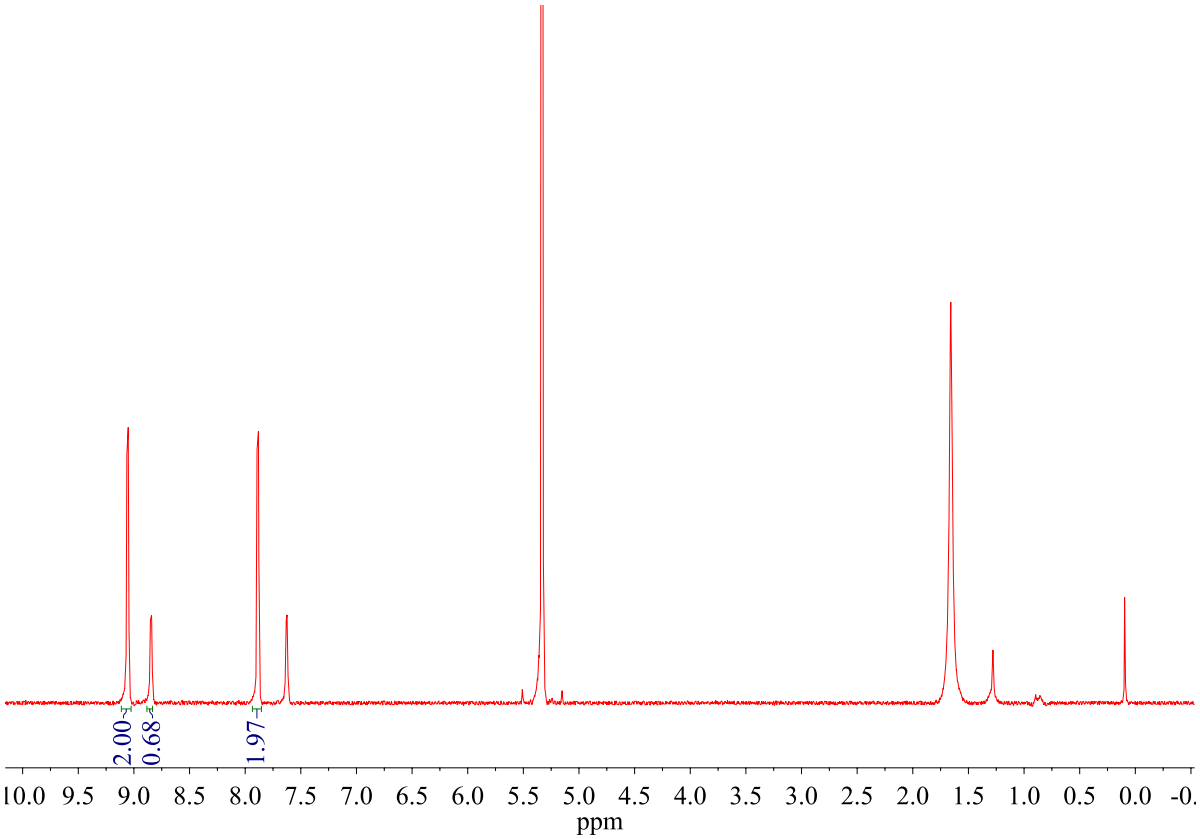


Figure S4. ^{1}H NMR spectrum of the crude mixture of reaction [I(**2**)$_2$]PF$_6$ (CD_2Cl_2, 500 MHz, 30 °C).

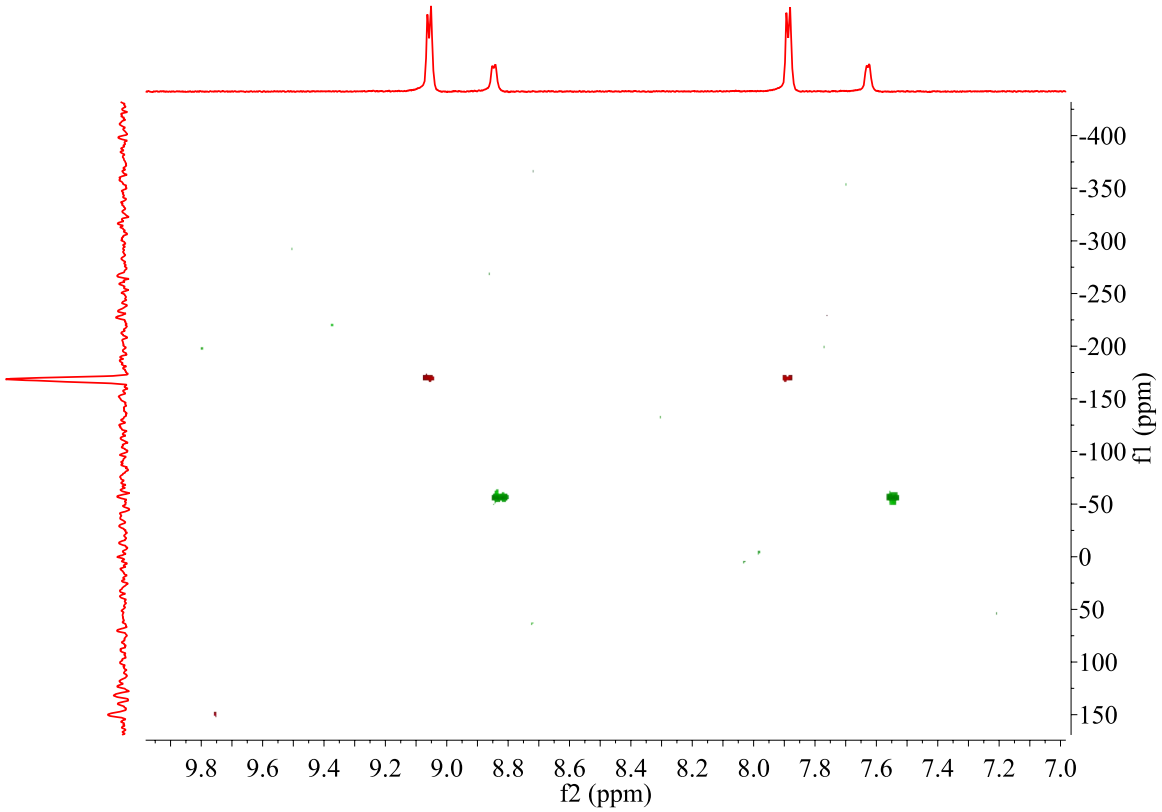


Figure S5. The stacked ^{1}H-^{15}N HMBC-NMR Spectra of ligand **2** in green and [N-I-N] complex [I(**2**)$_2$]PF$_6$ in red, in CD_2Cl_2 at 30 °C.

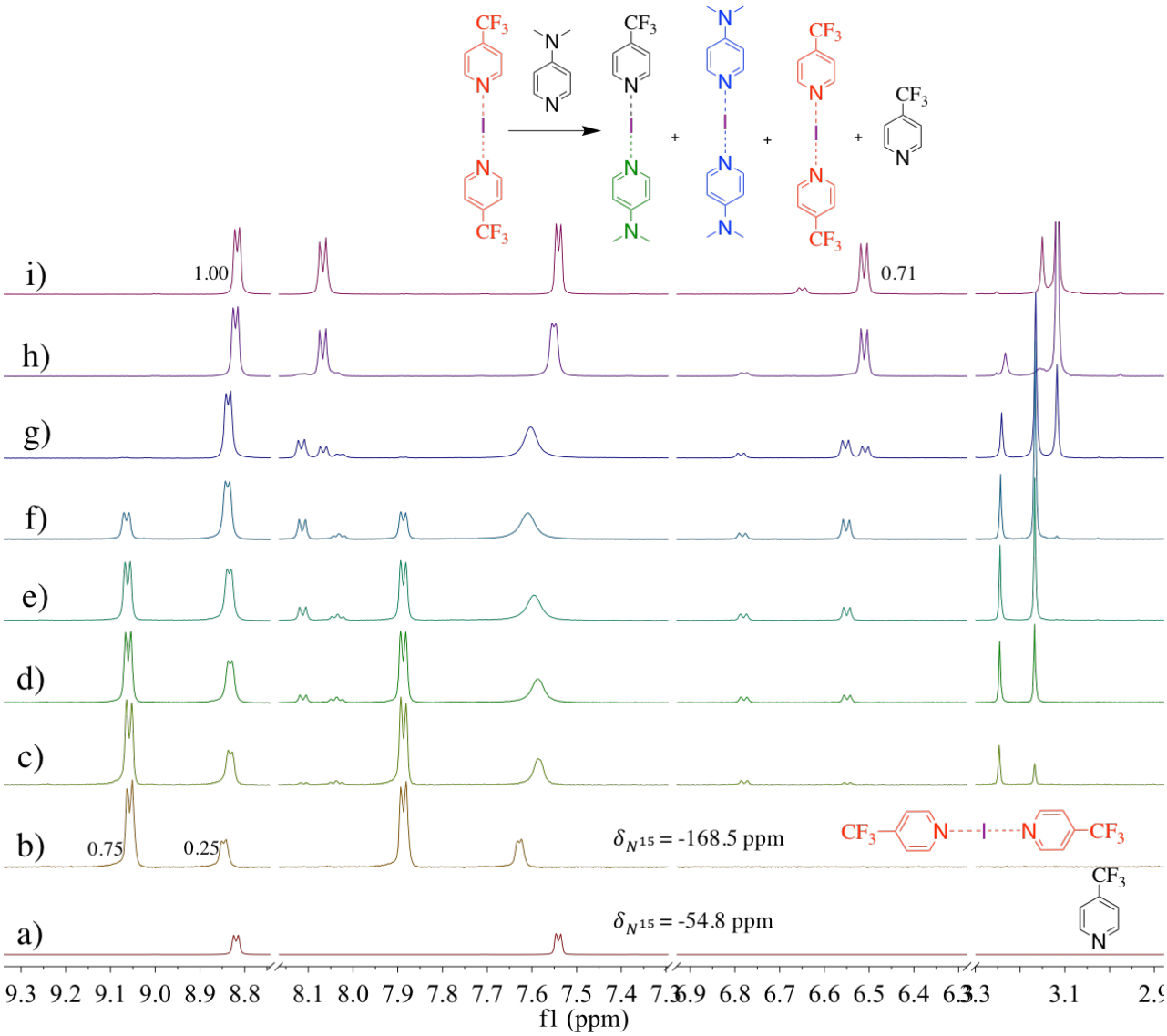
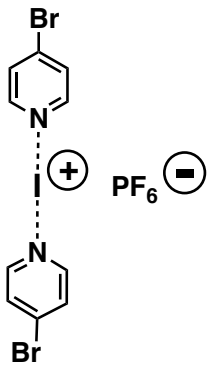


Figure S6. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **2** (a), the crude mixture of reaction $[I(\mathbf{2})_2]PF_6$ in the absence (b) and in the presence of 0.1 (c), 0.2 (d), 0.3 (e), 0.5 (f), 1.0 (g), 1.5 (h) and 1.7 equivalents (i) of **16**.

2.3 Synthesis of $[I(3)_2]PF_6$



To a solution of silver hexafluorophosphate (2.1 mg, 0.008 mmol, 1.0 eq) in CD_2Cl_2 (1 mL), a solution of 4-bromopyridine (**3**) (0.016 mmol, 2.0 eq) in CD_2Cl_2 (0.9 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (2.1 mg, 0.008 mmol, 1.0 eq) in CD_2Cl_2 (0.1 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{3})_2]PF_6$ (82%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.57 (d, J = 6.8 Hz, 2H), 7.79 (d, J = 6.8 Hz, 2H); **^{15}N NMR** (51 MHz, CD_2Cl_2): δ -180.8.

NMR characterisation for ligand **3**: **^{15}N NMR** (51 MHz, CD_2Cl_2): δ -71.3.

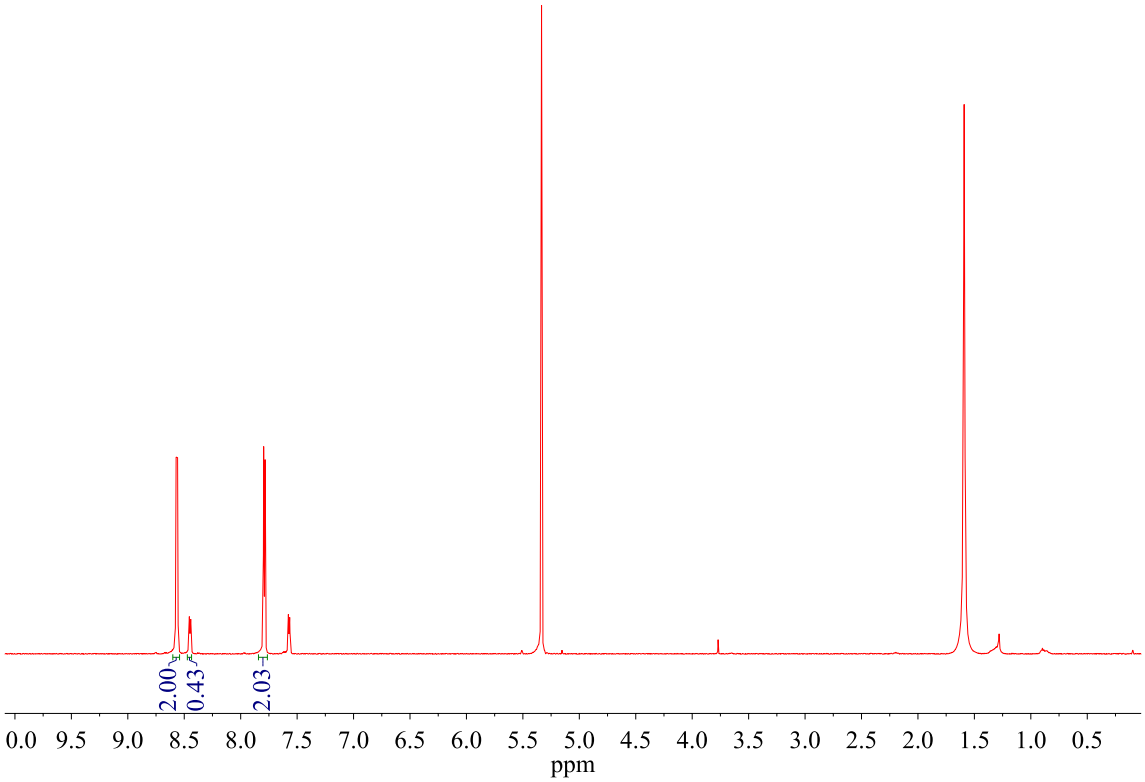


Figure S7. ^{1}H NMR spectrum of [I(**3**)$_2$]PF$_6$ (CD_2Cl_2, 500 MHz, 30 °C).

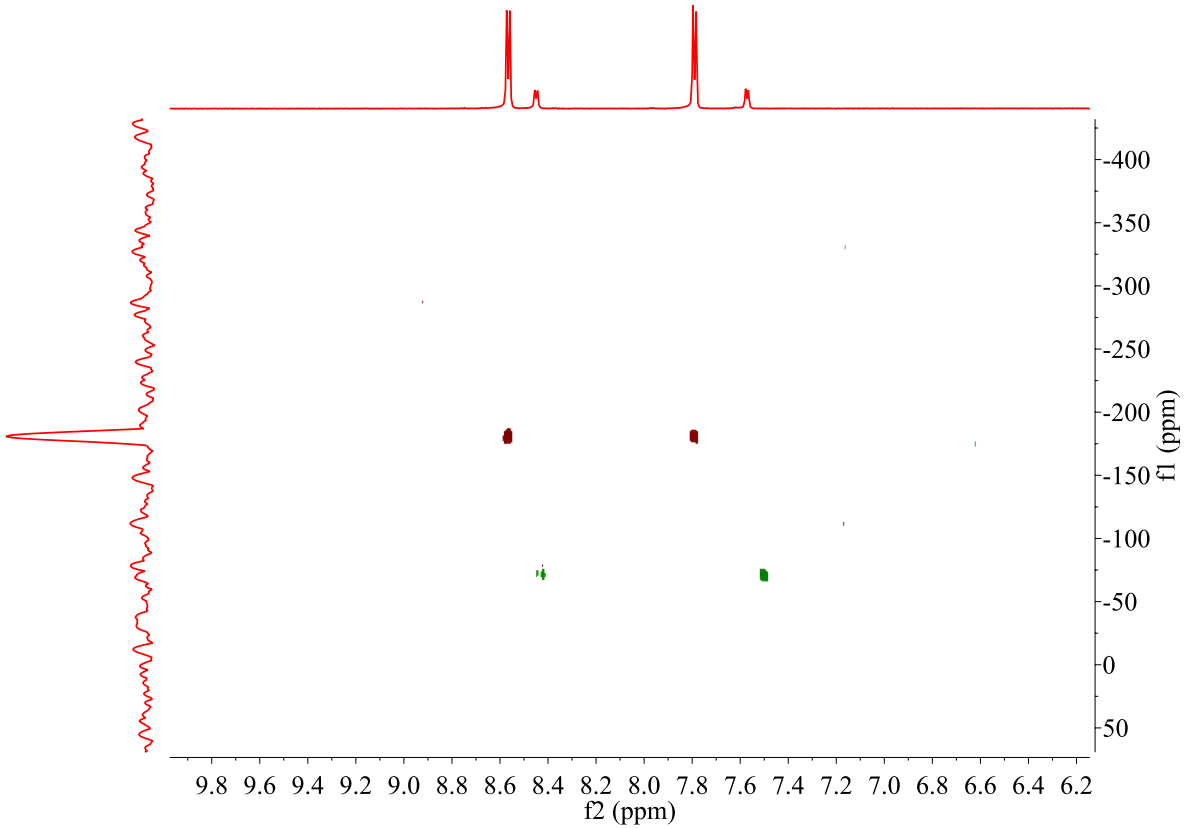


Figure S8. The stacked ^{1}H-^{15}N HMBC-NMR Spectra of ligand **3** in green and [N-I-N]$^{+}$ complex [I(**3**)$_2$]PF$_6$ in red, in CD_2Cl_2 at 30 °C.

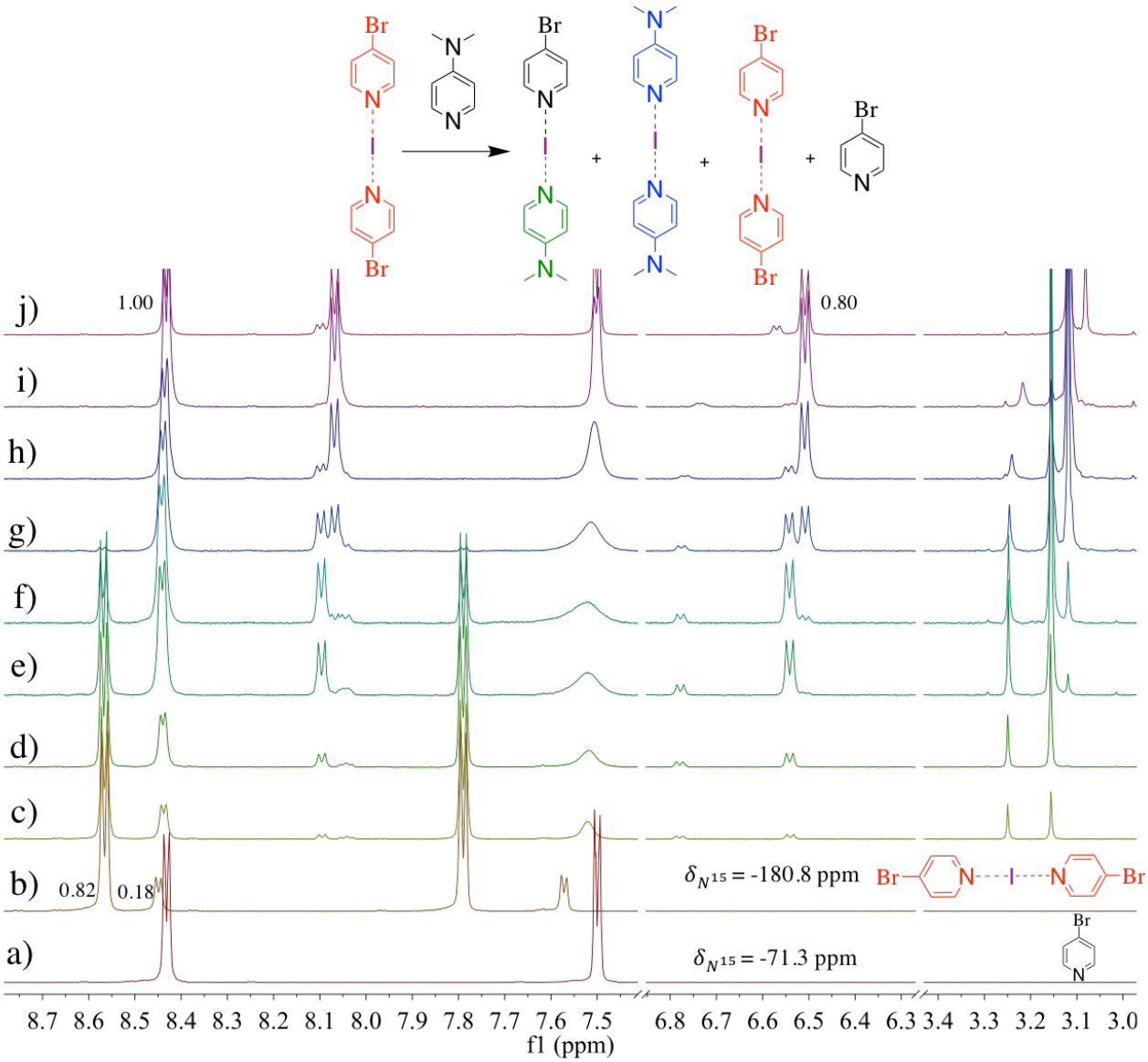
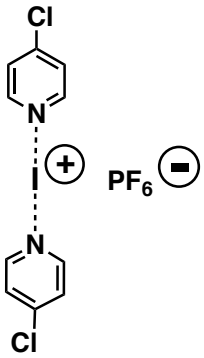


Figure S9. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **3** (a), the crude mixture of reaction $[I(\mathbf{3})_2]PF_6$ in the absence (b) and in the presence of 0.1 (c), 0.2 (d), 0.4 (e), 0.6 (f), 1.0 (g), 1.4 (h), 1.6 (i) and 1.8 equivalents (j) of **16**.

2.4 Synthesis of $[I(4)_2]PF_6$



To a solution of silver hexafluorophosphate (1.8 mg, 0.007 mmol, 1.0 eq) in CD_2Cl_2 (1.7 mL), a solution of 4-chloropyridine (**4**) (0.014 mmol, 2.0 eq) in CD_2Cl_2 (0.05 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (1.8 mg, 0.007 mmol, 1.0 eq) in CD_2Cl_2 (0.05 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{4})_2]PF_6$ (80%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.67 (d, J = 6.8 Hz, 2H), 7.62 (d, J = 6.8 Hz, 2H); **^{15}N NMR** (51 MHz, CD_2Cl_2): δ -182.0.

NMR characterisation for ligand **4**: **^{15}N NMR** (51 MHz, CD_2Cl_2): δ -72.2.

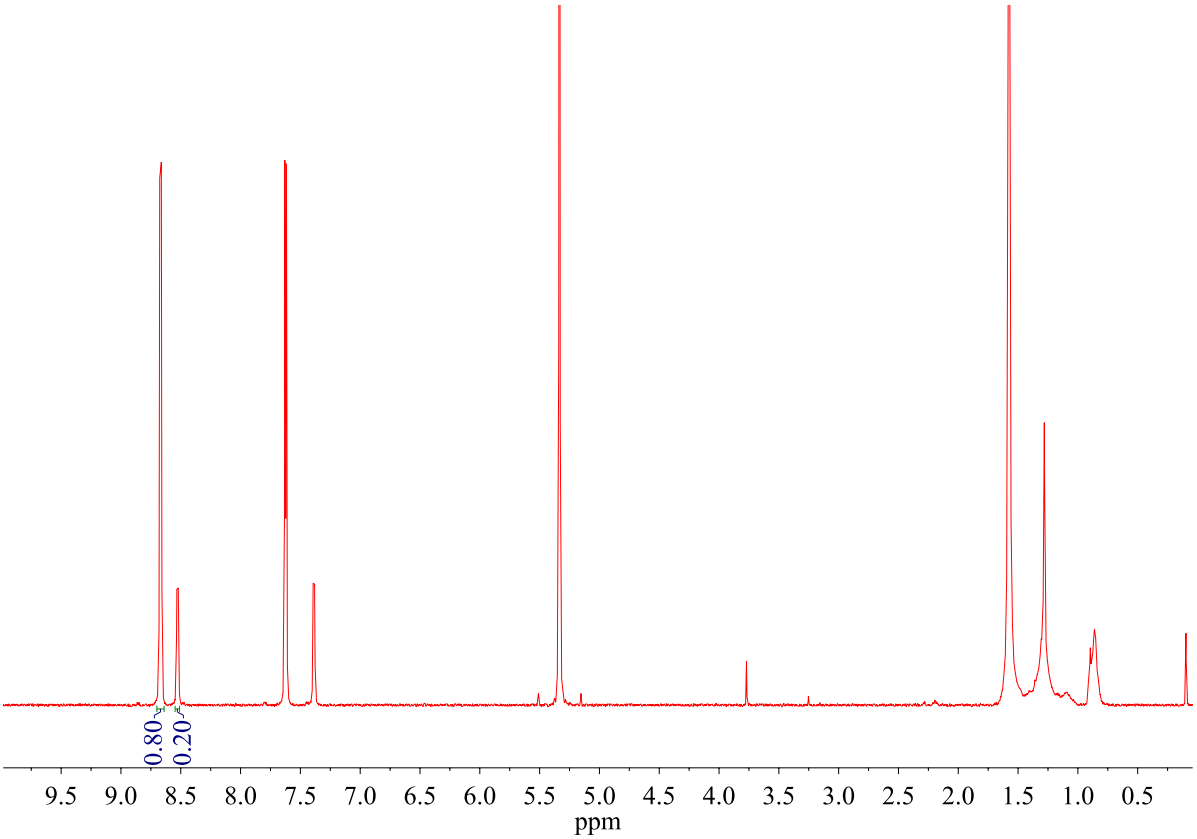


Figure S10. ^{1}H NMR spectrum of the crude mixture of reaction [I(**4**)$_2$]PF$_6$ (CD_2Cl_2, 500 MHz, 30 °C).

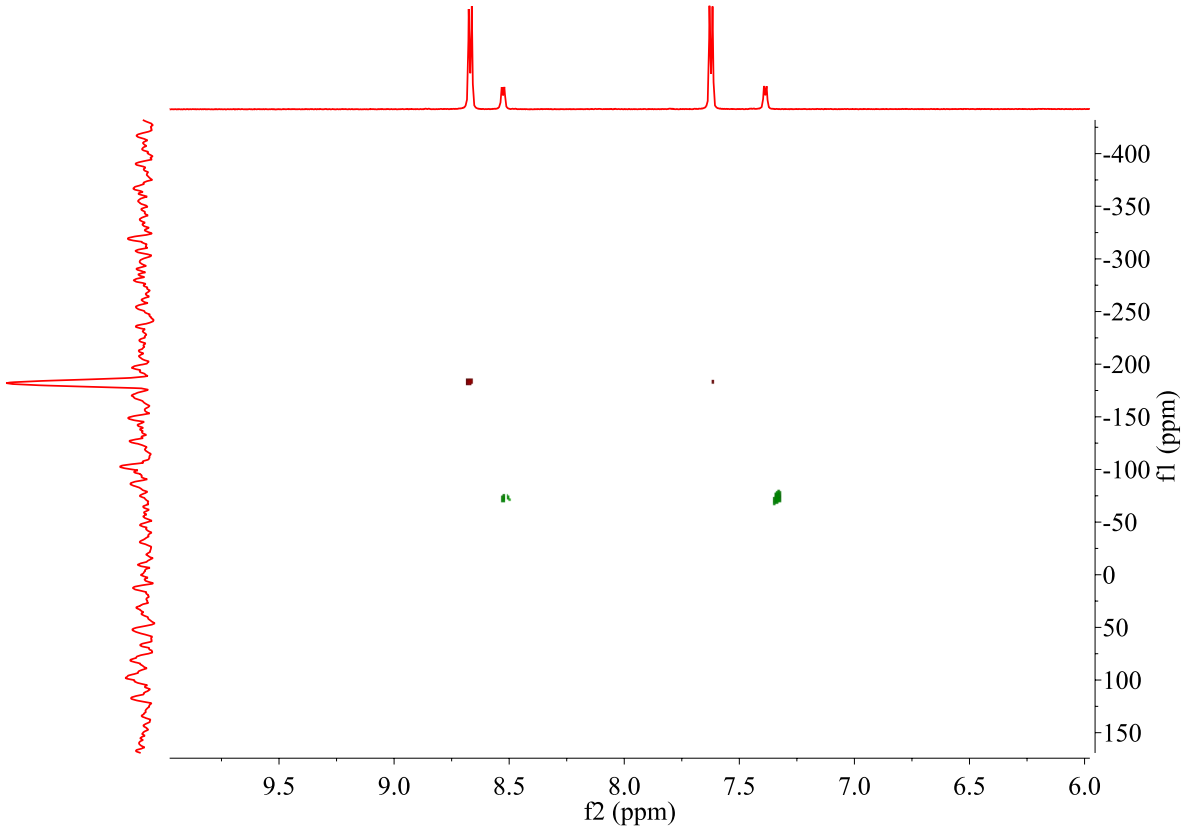


Figure S11. The stacked ^{1}H-^{15}N HMBC-NMR Spectra of ligand **4** in green and [N-I-N]$^{+}$ complex [I(**4**)$_2$]PF$_6$ in red, in CD_2Cl_2 at 30 °C.

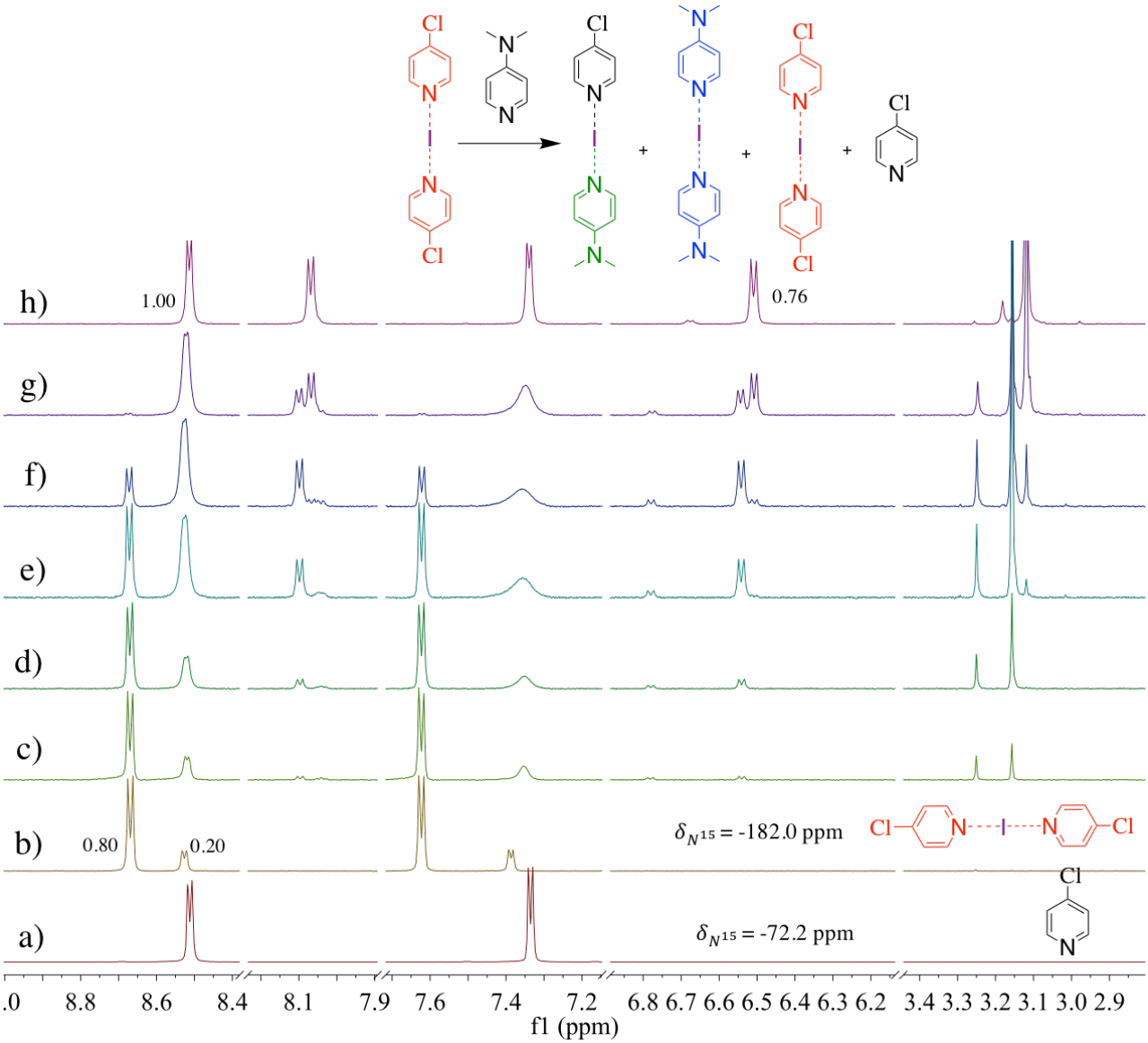
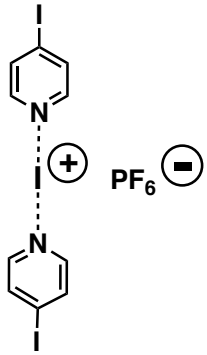


Figure S12. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **4** (a), the crude mixture of reaction $[I(\mathbf{4})_2]PF_6$ in the absence (b) and in the presence of 0.1 (c), 0.2 (d), 0.4 (e), 0.6 (f), 1.0 (g) and 1.4 equivalents (h) of **16**.

2.5 Synthesis of $[I(5)_2]PF_6$



To a solution of silver hexafluorophosphate (3.1 mg, 0.012 mmol, 1.0 eq) in CD_2Cl_2 (2.0 mL), a solution of 4-iodopyridine (**5**) (5.0 mg, 0.024 mmol, 2.0 eq) in CD_2Cl_2 (0.9 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (3.1 mg, 0.012 mmol, 1.0 eq) in CD_2Cl_2 (0.1 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{5})_2]PF_6$ (83%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.36 (d, J = 6.6 Hz, 2H), 8.00 (d, J = 6.6 Hz, 2H).

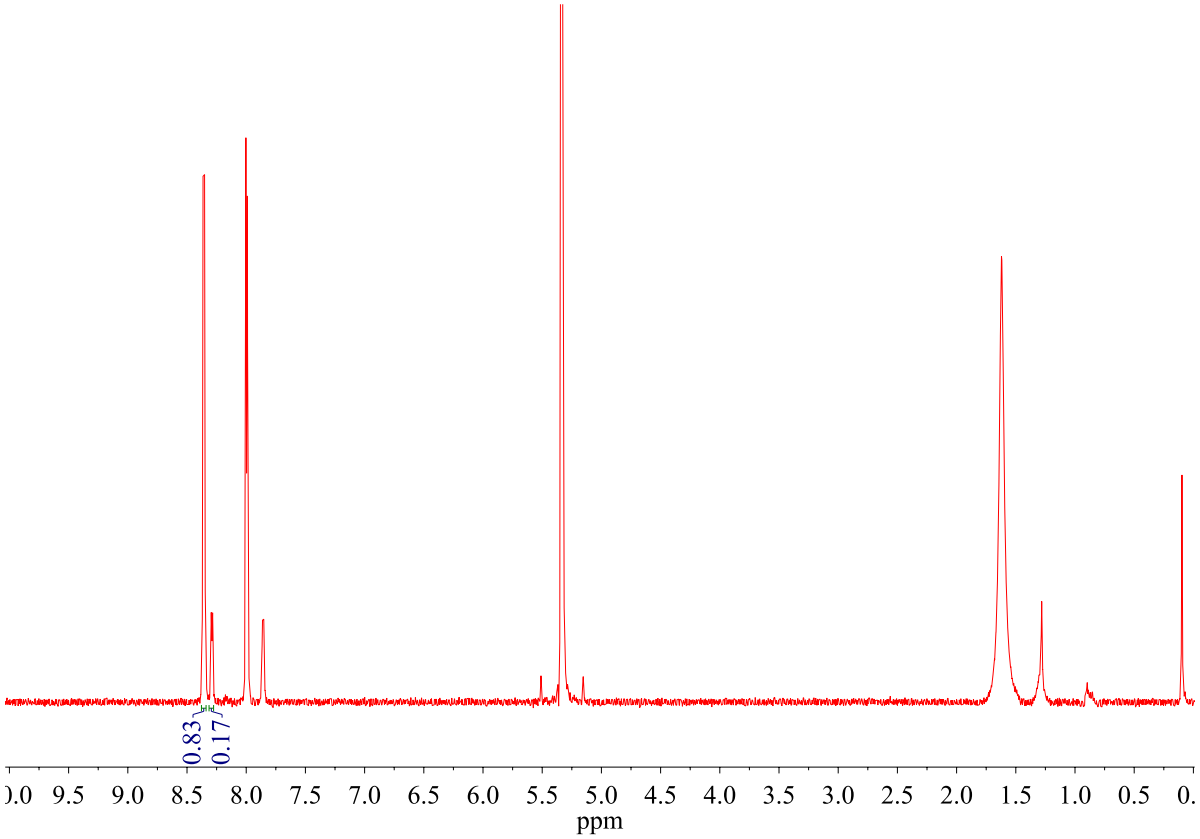


Figure S13. ^{1}H NMR spectrum of the crude mixture of reaction $[I(\mathbf{5})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

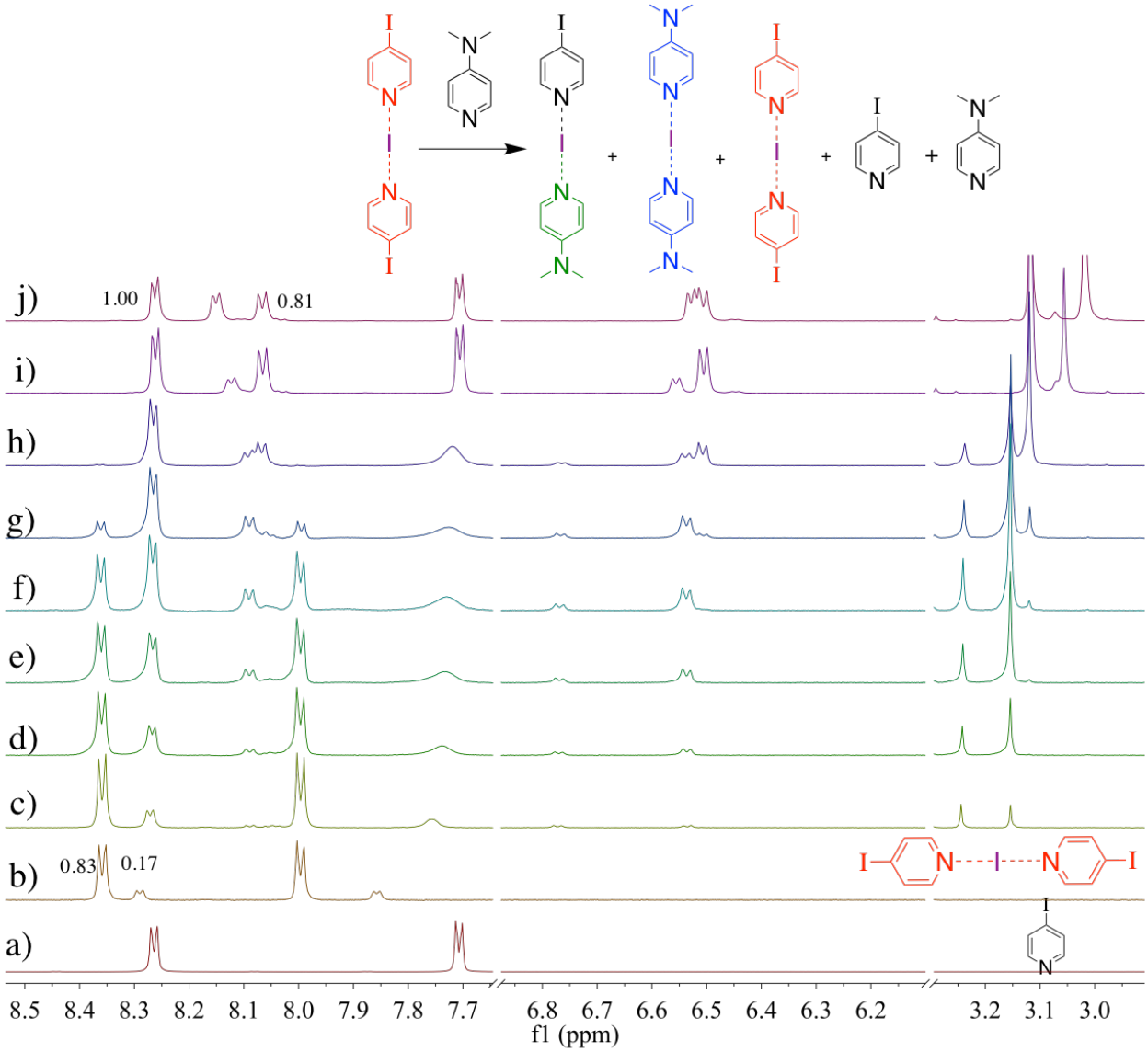
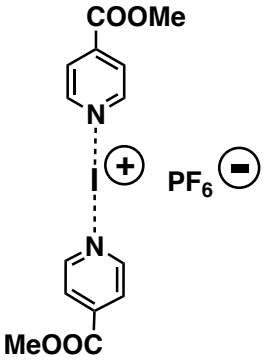


Figure S14. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **5** (a), the crude mixture of reaction $[I(\mathbf{5})_2]PF_6$ in the absence (b) and in the presence of 0.1 (c), 0.2 (d), 0.3 (e), 0.4 (f), 0.6 (g), 1.0 (h), 1.5 (i) and 2.0 equivalents (j) of **16**.

2.6 Synthesis of $[I(6)_2]PF_6$



To a solution of silver hexafluorophosphate (9.1 mg, 0.036 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of methyl isonicotinate (**6**) (9.9 mg, 0.072 mmol, 2.0 eq) in CD_2Cl_2 (0.65 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (9.2 mg, 0.036 mmol, 1.0 eq) in CD_2Cl_2 (0.35 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{6})_2]PF_6$ (88%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.95 (d, J = 6.6 Hz, 4H), 8.13 (d, J = 6.6 Hz, 4H), 4.04 (s, 6H).

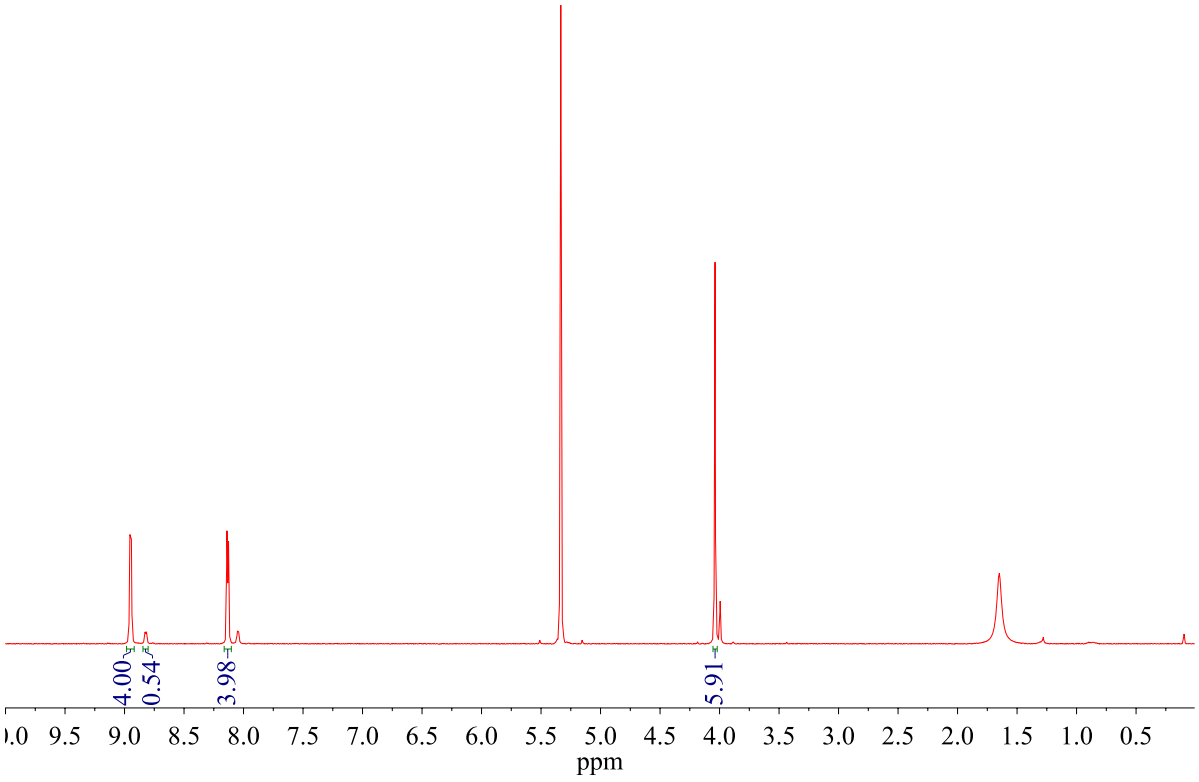


Figure S15. ^{1}H NMR spectrum of the crude mixture of reaction $[I(\mathbf{6})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

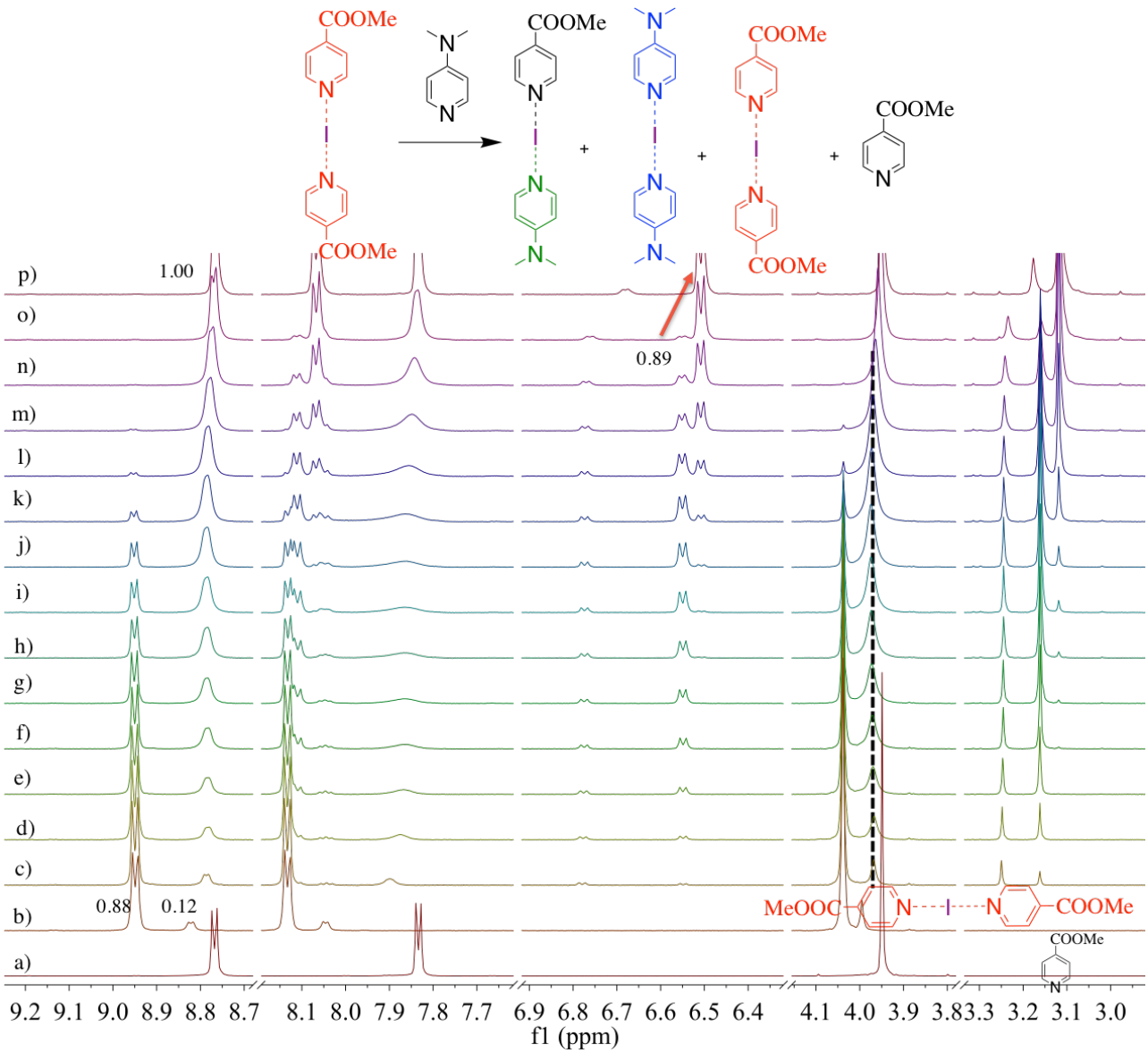
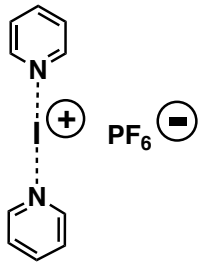


Figure S16. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **6** (a), the crude mixture of reaction $[I(\mathbf{6})_2]PF_6$ in the absence (b) and in the presence of 0.1 (b), 0.2 (c), 0.3 (d), 0.4 (e), 0.5 (f), 0.6 (g), 0.7 (h), 0.8 (i), 0.9 (j), 1.0 (k), 1.2 (l), 1.4 (m), 1.6 (n), 1.8 (o) and 2.0 equivalents (p) of **16**.

2.7 Synthesis of $[I(7)_2]PF_6$



To a solution of silver hexafluorophosphate (9.7 mg, 0.038 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of pyridine (**7**) (6.1 mg, 0.076 mmol, 2.0 eq) in CD_2Cl_2 (0.55 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (9.8 mg, 0.038 mmol, 1.0 eq) in CD_2Cl_2 (0.45 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(7)_2]PF_6$ (95%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.77 (d, J = 5.0 Hz, 4H), 8.24 (t, J = 7.8 Hz, 2H), 7.64 (t, J = 7.1 Hz, 4H). The analytical data was in agreement with previously reported literature data.[1]

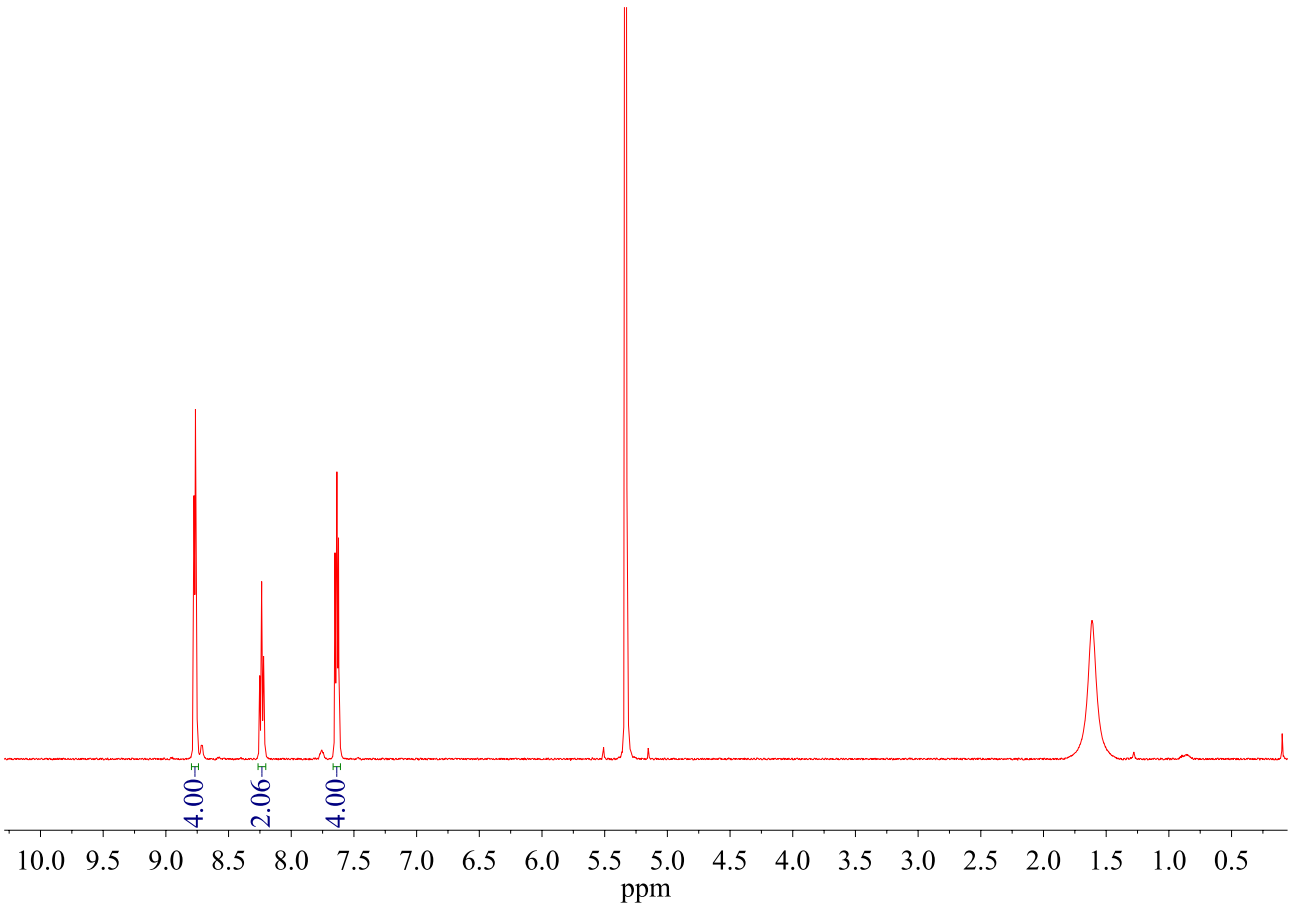


Figure S17. ^{1}H NMR spectrum of $[I(7)_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

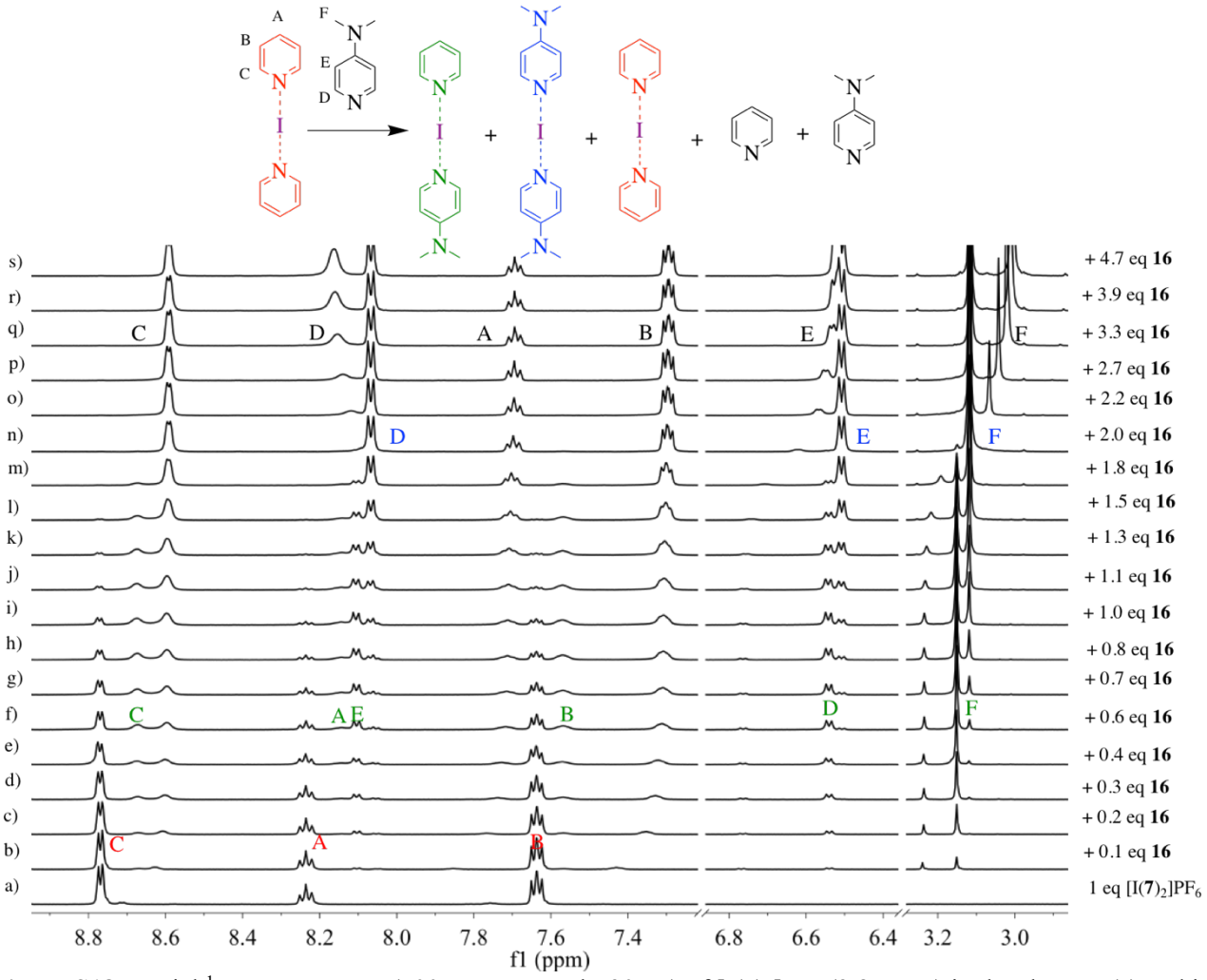
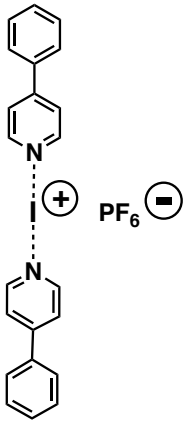


Figure S18. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of $[I(\mathbf{7})_2]PF_6$ (3.85 mM) in the absence (a) and in the presence of 0.1 (b), 0.2 (c), 0.3 (d), 0.4 (e), 0.6 (f), 0.7 (g), 0.8 (h), 1.0 (i), 1.1 (j), 1.3 (k), 1.5 (l), 1.8 (m), 2.0 (n), 2.2 (o), 2.7 (p),3.3 (q), 3.9 (r), and 4.7 equivalents (s) of **16**.

2.9 Synthesis of $[I(8)_2]PF_6$



To a solution of silver hexafluorophosphate (10.1 mg, 0.040 mmol, 1.0 eq) in CD_2Cl_2 (2.0 mL), a solution of 4-phenylpyridine (**8**) (12.4 mg, 0.080 mmol, 2.0 eq) in CD_2Cl_2 (0.60 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (10.2 mg, 0.040 mmol, 1.0 eq) in CD_2Cl_2 (0.40 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{8})_2]PF_6$ (89%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.77 (d, *J* = 5.4 Hz, 4H), 7.82 (d, *J* = 5.3 Hz, 4H), 7.79-7.74 (m, 4H), 7.64-7.58 (m, 6H).

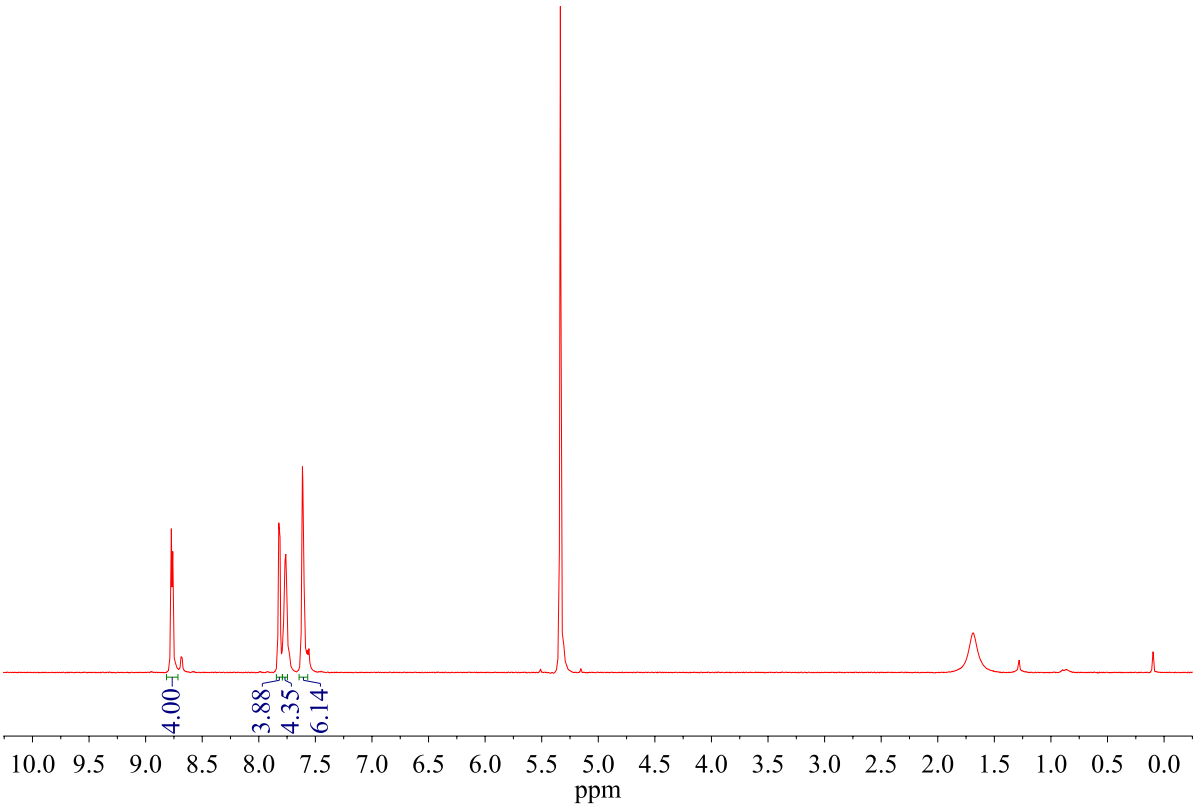


Figure S19. ^{1}H NMR spectrum of the iodine(I) complex $[I(\mathbf{8})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

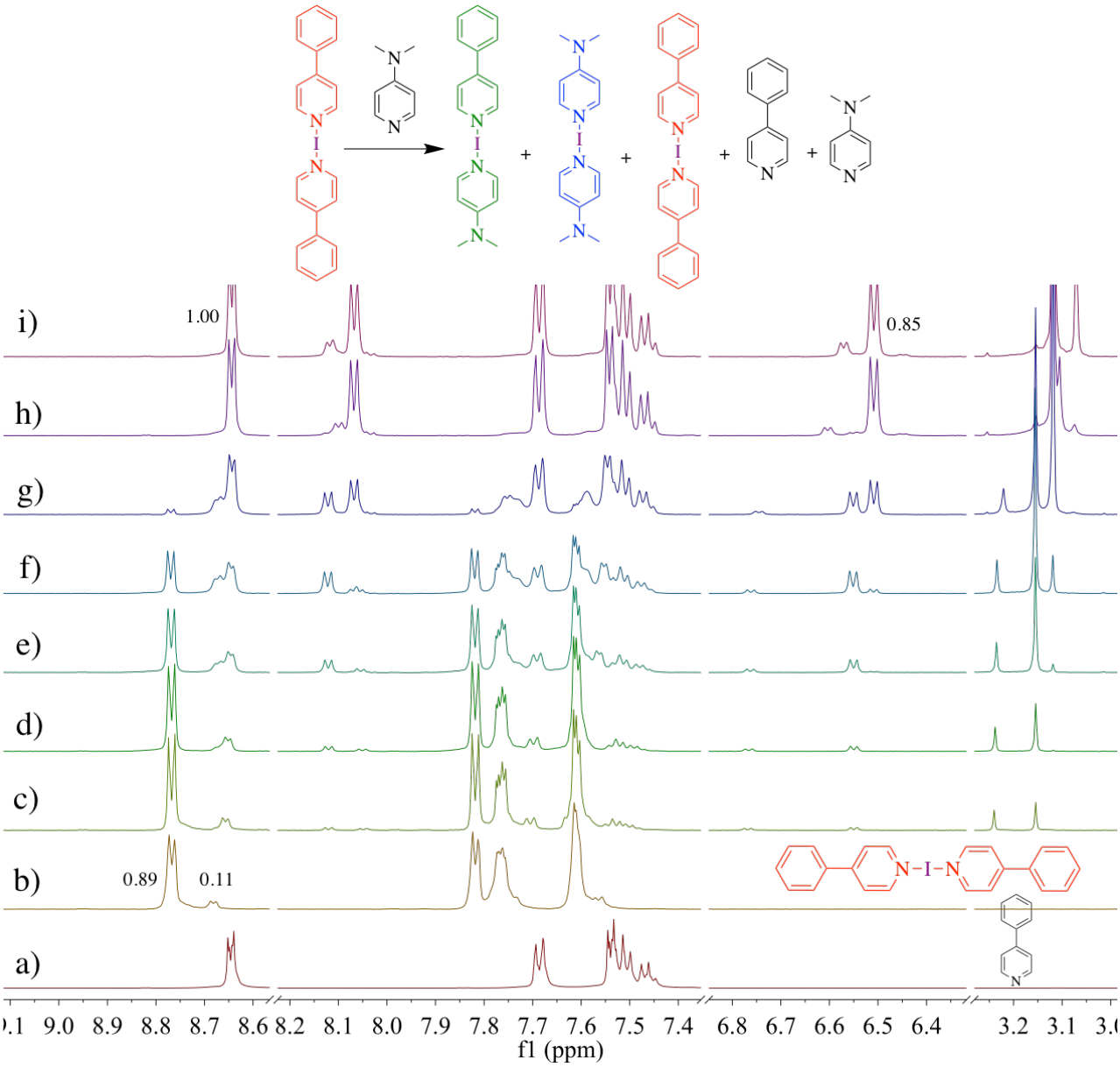
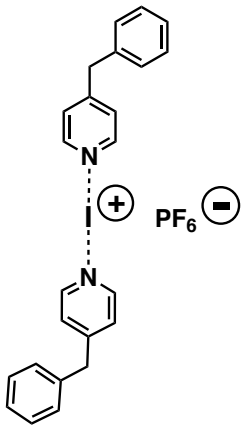


Figure S20. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **8** (a), the iodine(I) complex $[I(\mathbf{8})_2]PF_6$ in the absence (b) and in the presence of 0.1 (c), 0.2 (d), 0.3 (e), 0.5 (f),), 1.0 (g), 1.5 (h) and 1.6 equivalents (i) of **16**.

2.9 Synthesis of $[I(9)_2]PF_6$



To a solution of silver hexafluorophosphate (9.0 mg, 0.036 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of 4-benzylpyridine (**9**) (12.1 mg, 0.071 mmol, 2.0 eq) in CD_2Cl_2 (1.0 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (9.1 mg, 0.036 mmol, 1.0 eq) in CD_2Cl_2 (0.40 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{9})_2]PF_6$ (>95%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.57 (d, J = 6.7 Hz, 4H), 7.41-7.28 (m, 10H), 7.20 (d, J = 7.0 Hz, 4H), 4.14 (s, 4H).

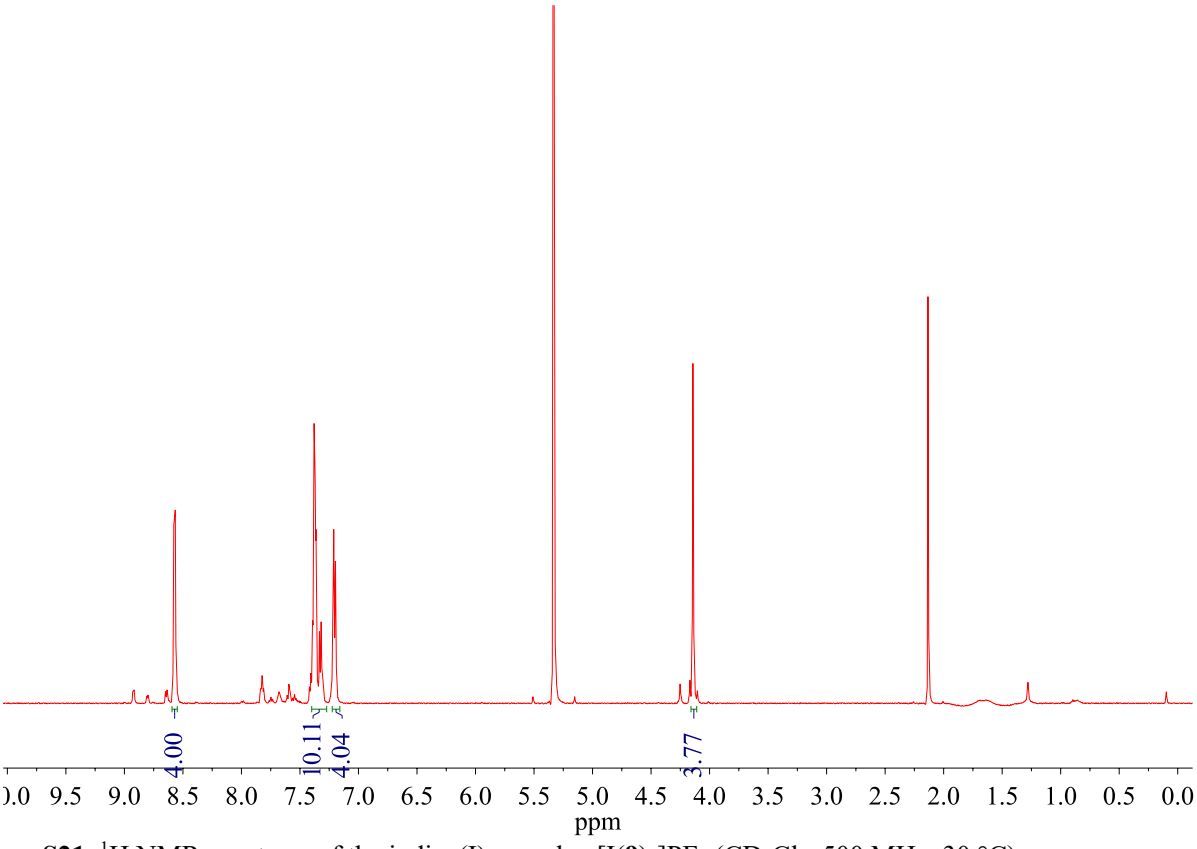


Figure S21. ^{1}H NMR spectrum of the iodine(I) complex $[I(\mathbf{9})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

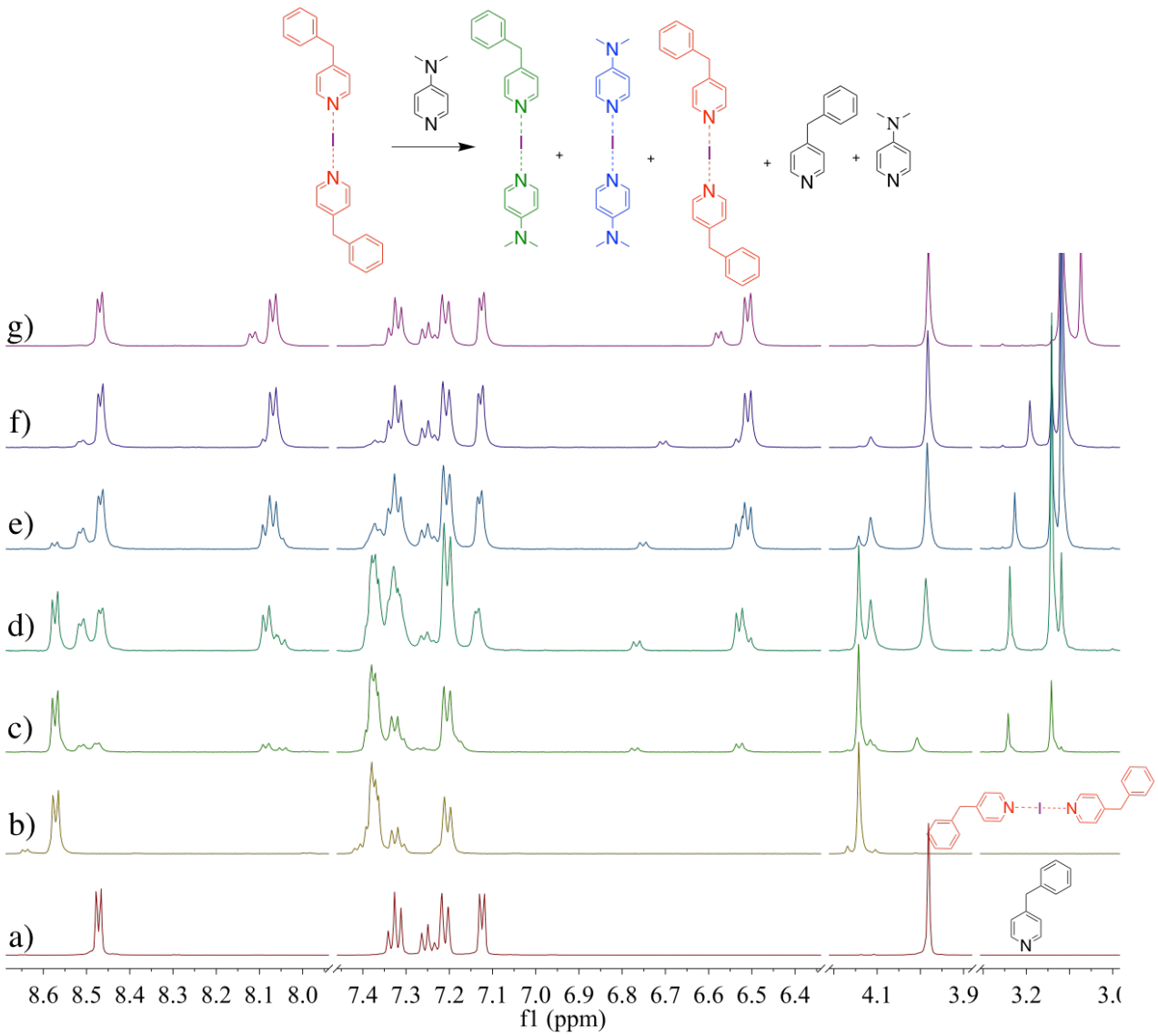
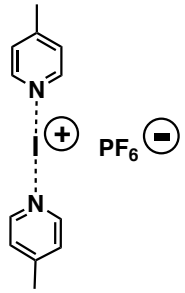


Figure S22. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **9** (a), the iodine(I) complex $[I(\mathbf{9})_2]PF_6$ in the absence (b) and in the presence of 0.5 (c), 1.0 (d), 1.6 (e), 2.0 (f) and 2.6 equivalents (g) of **16**.

2.10 Synthesis of $[I(10)_2]PF_6$



To a solution of silver hexafluorophosphate (10.1 mg, 0.040 mmol, 1.0 eq) in CD_2Cl_2 (2.0 mL), a solution of 4-methylpyridine (**10**) (7.5 mg, 0.080 mmol, 2.0 eq) in CD_2Cl_2 (0.6 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (10.2 mg, 0.040 mmol, 1.0 eq) in CD_2Cl_2 (0.40 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{10})_2]PF_6$ (97%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.56 (d, J = 6.5 Hz, 4H), 7.40 (d, J = 5.8 Hz, 4H), 2.55 (s, 6H).

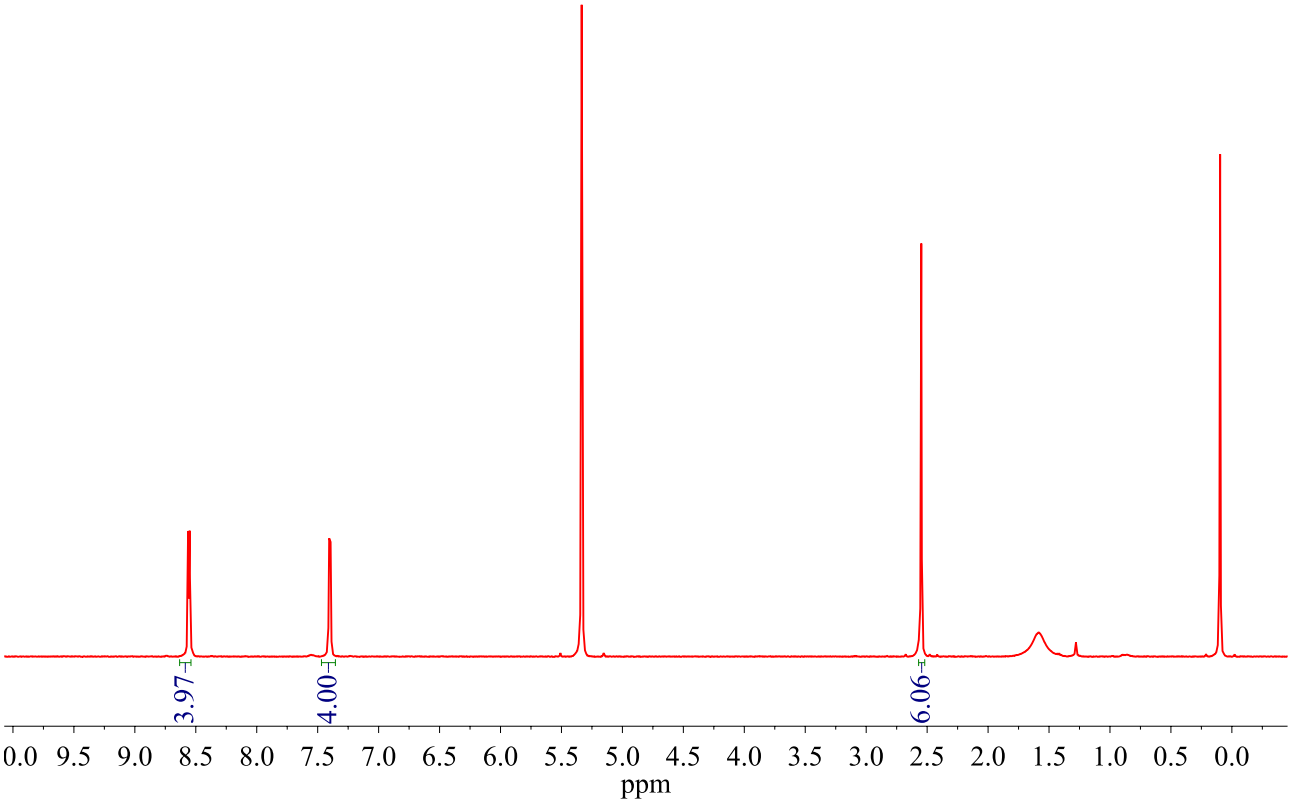


Figure S23. ^{1}H NMR spectrum of the iodine(I) complex $[I(\mathbf{10})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

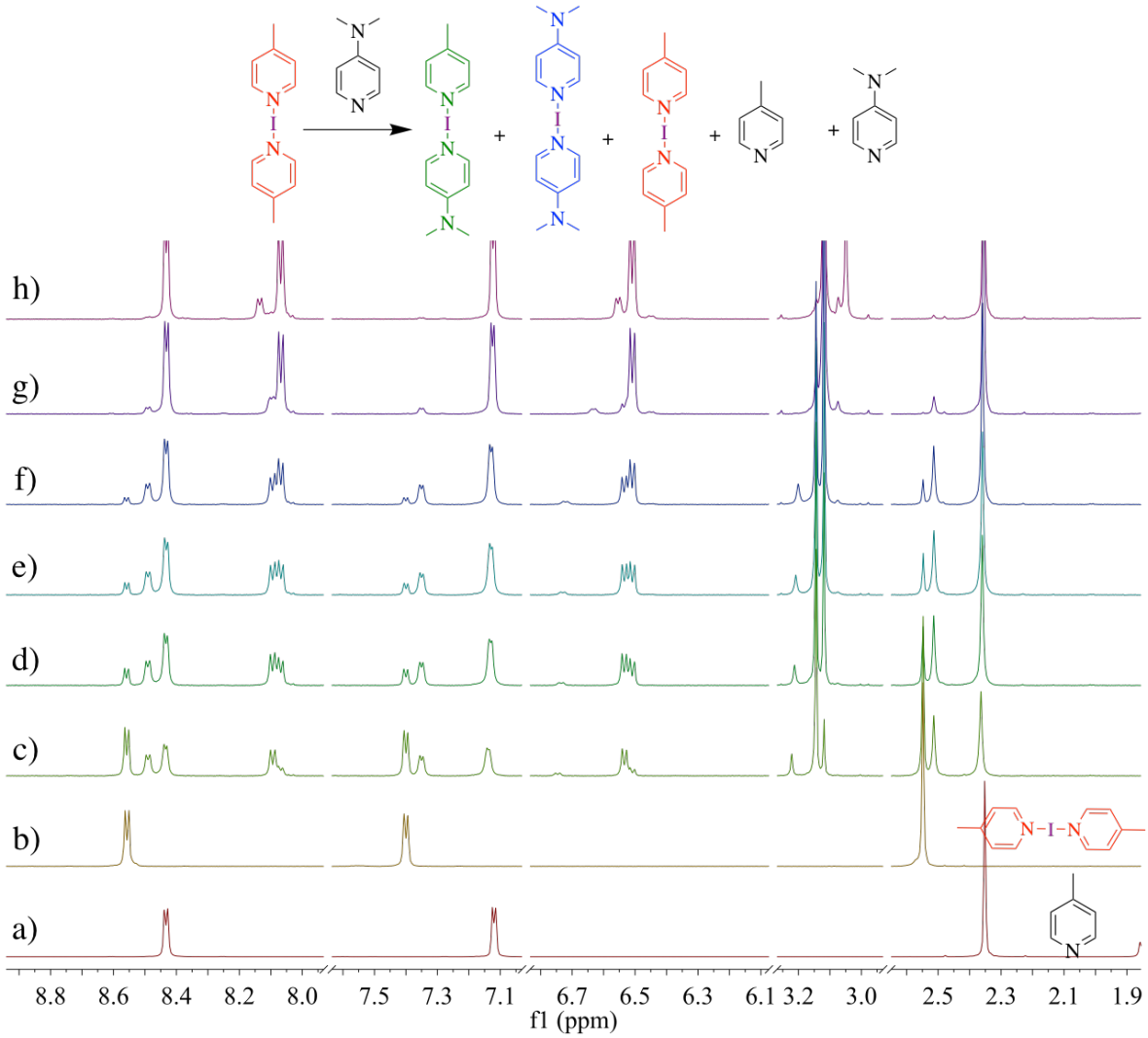


Figure S24. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **10** (a), the iodine(I) complex [I(**10**)$_2$]PF_6 in the absence (b) and in the presence of 0.6 (c), 1.0 (d), 1.2 (e), 1.5 (f), 1.8 (g) and 2.0 equivalents (h) of **16**.

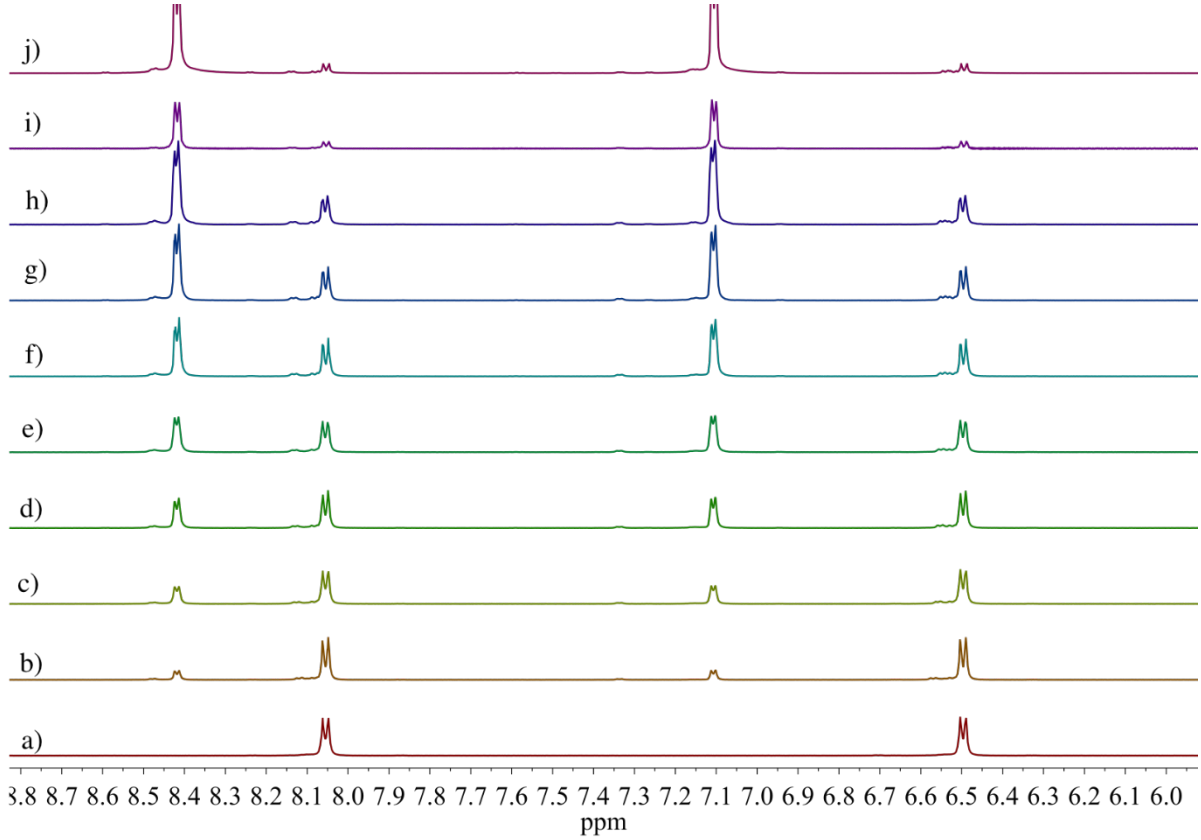
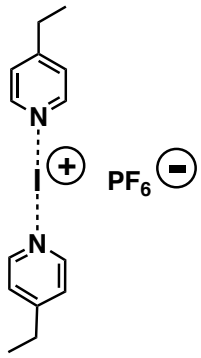


Figure S25. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of the crude mixture of reaction [I(**16**)$_2$]PF_6 (8 mM **16**) in the absence (a) and in the presence of 0.2 (b), 0.4 (c), 0.6 (d), 1.0 (e), 1.5 (f), 2.0 (g), 4.0 (h), 6.0 (i), 10.0 (j), 15.0 (k) and 20.0 equivalents (l) of **10**.

2.11 Synthesis of $[I(11)_2]PF_6$



To a solution of silver hexafluorophosphate (7.5 mg, 0.030 mmol, 1.0 eq) in CD_2Cl_2 (2.0 mL), a solution of 4-ethylpyridine (**11**) (6.4 mg, 0.060 mmol, 2.0 eq) in CD_2Cl_2 (0.65 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (7.6 mg, 0.030 mmol, 1.0 eq) in CD_2Cl_2 (0.35 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{11})_2]PF_6$ (96%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.59 (d, J = 6.5 Hz, 4H), 7.42 (d, J = 5.8 Hz, 4H), 2.84 (q, J = 7.6 Hz, 4H), 1.32 (q, J = 7.6 Hz, 6H). The analytical data was in agreement with previously reported literature data.[1]

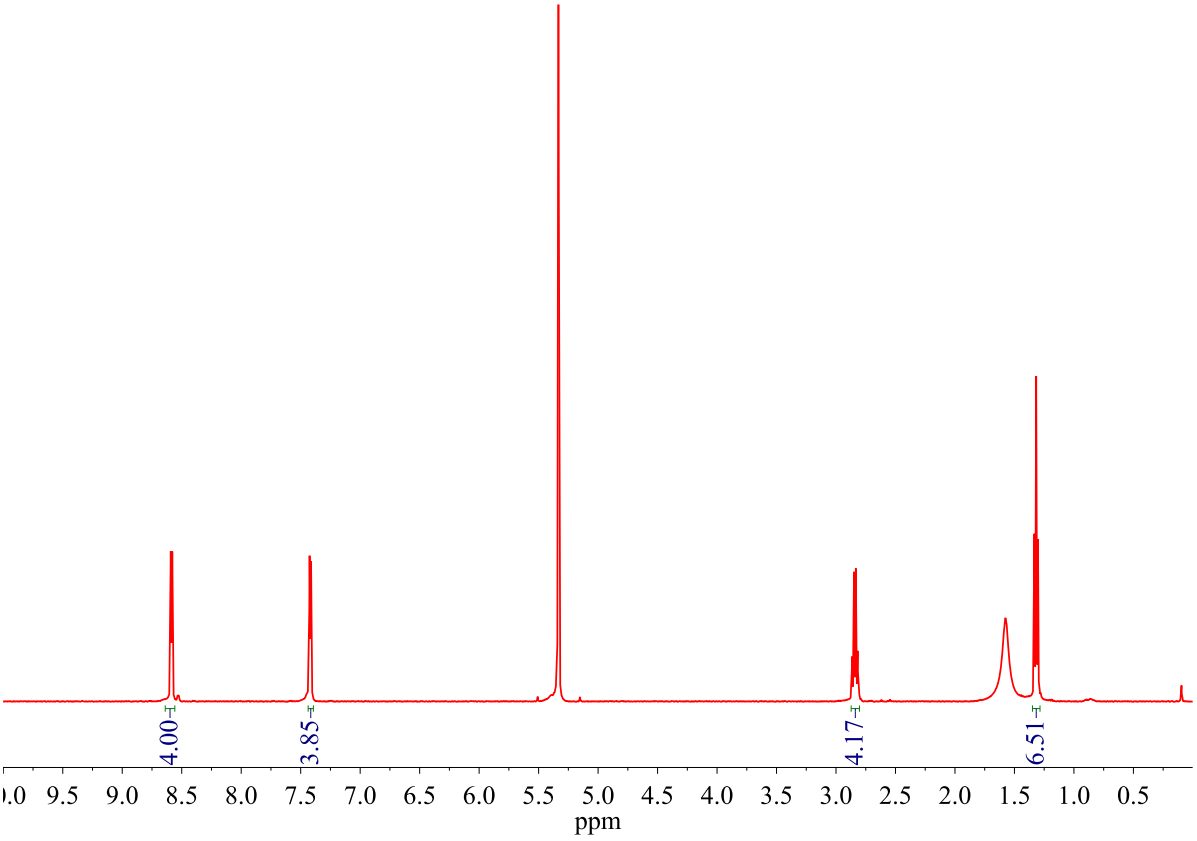


Figure S26. ^{1}H NMR spectrum of the iodine(I) complex $[I(\mathbf{11})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

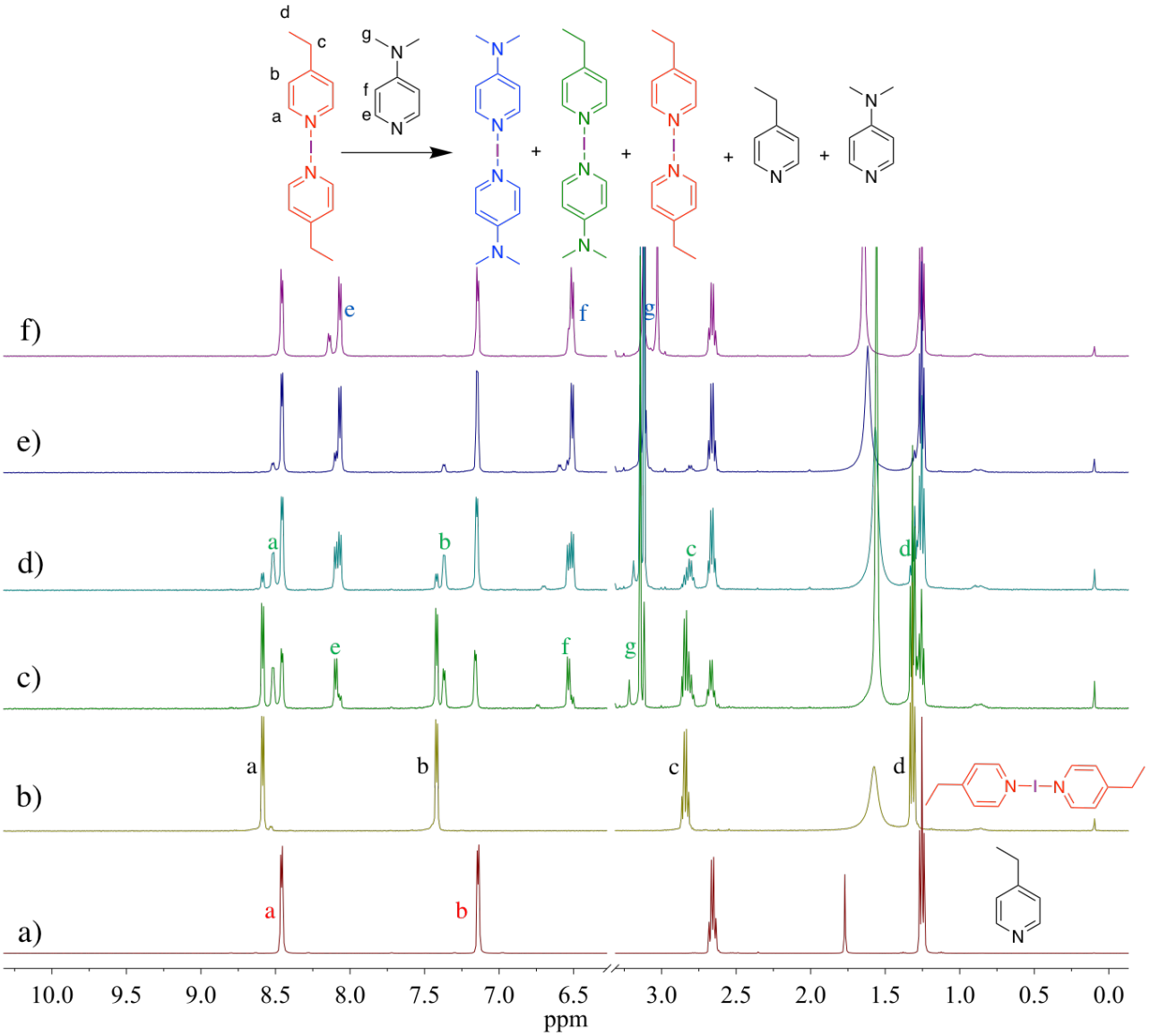
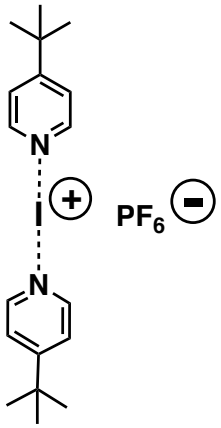


Figure S27. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **11** (a), the iodine(I) complex [I(**11**)$_2$]PF_6 in the absence (b) and in the presence of 0.5 (c), 1.0 (d), 1.5 (e) and 2.0 equivalents (f) of **16**.

2.12 Synthesis of $[I(12)_2]PF_6$



To a solution of silver hexafluorophosphate (9.7 mg, 0.038 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of 4-*tert*-butylpyridine (**12**) (10.4 mg, 0.077 mmol, 2.0 eq) in CD_2Cl_2 (0.6 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (9.8 mg, 0.038 mmol, 1.0 eq) in CD_2Cl_2 (0.4 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{12})_2]PF_6$ (92%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.61 (d, J = 6.8 Hz, 4H), 7.57 (d, J = 6.8 Hz, 4H), 1.38 (s, 18H); **^{15}N NMR** (51 MHz, CD_2Cl_2): δ -181.4. NMR characterisation for ligand **12**: **^{15}N NMR** (51 MHz, CD_2Cl_2): δ -74.7.

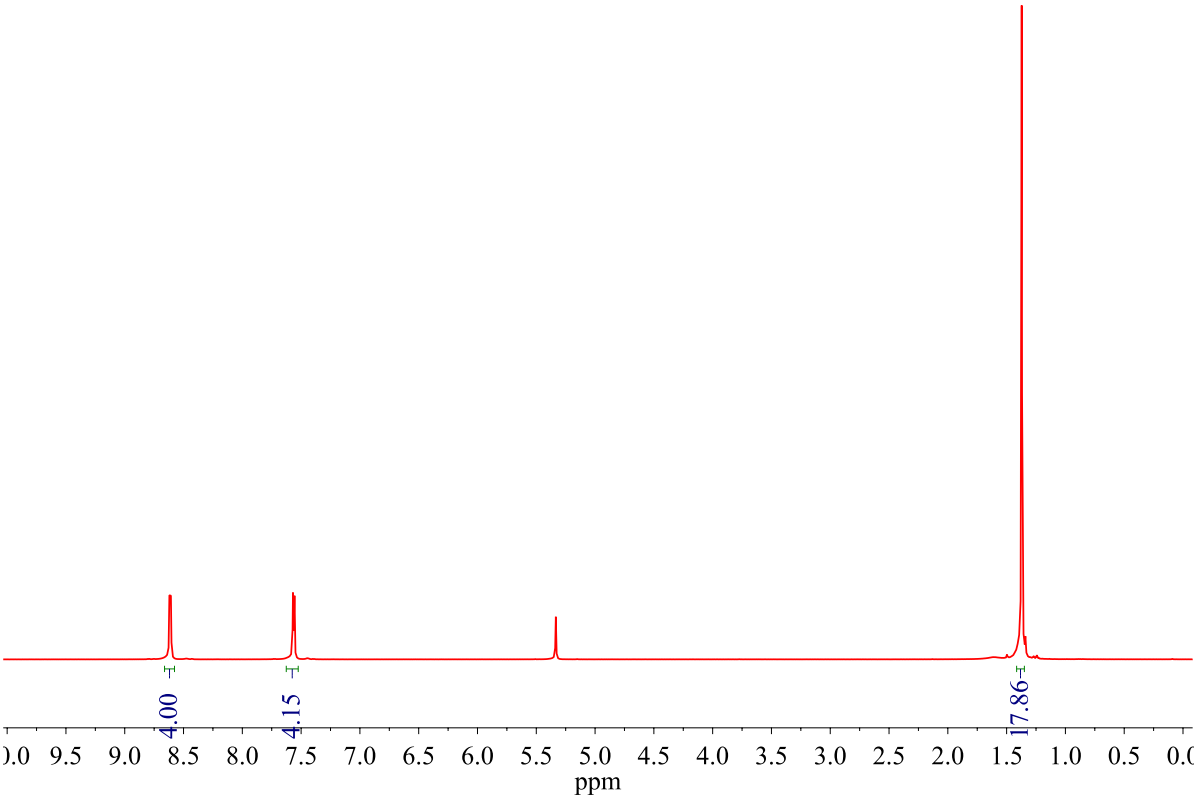


Figure S28. ^{1}H NMR spectrum of the iodine(I) complex [I(**12**)$_2$]PF$_6$ (CD_2Cl_2, 500 MHz, 30 °C).

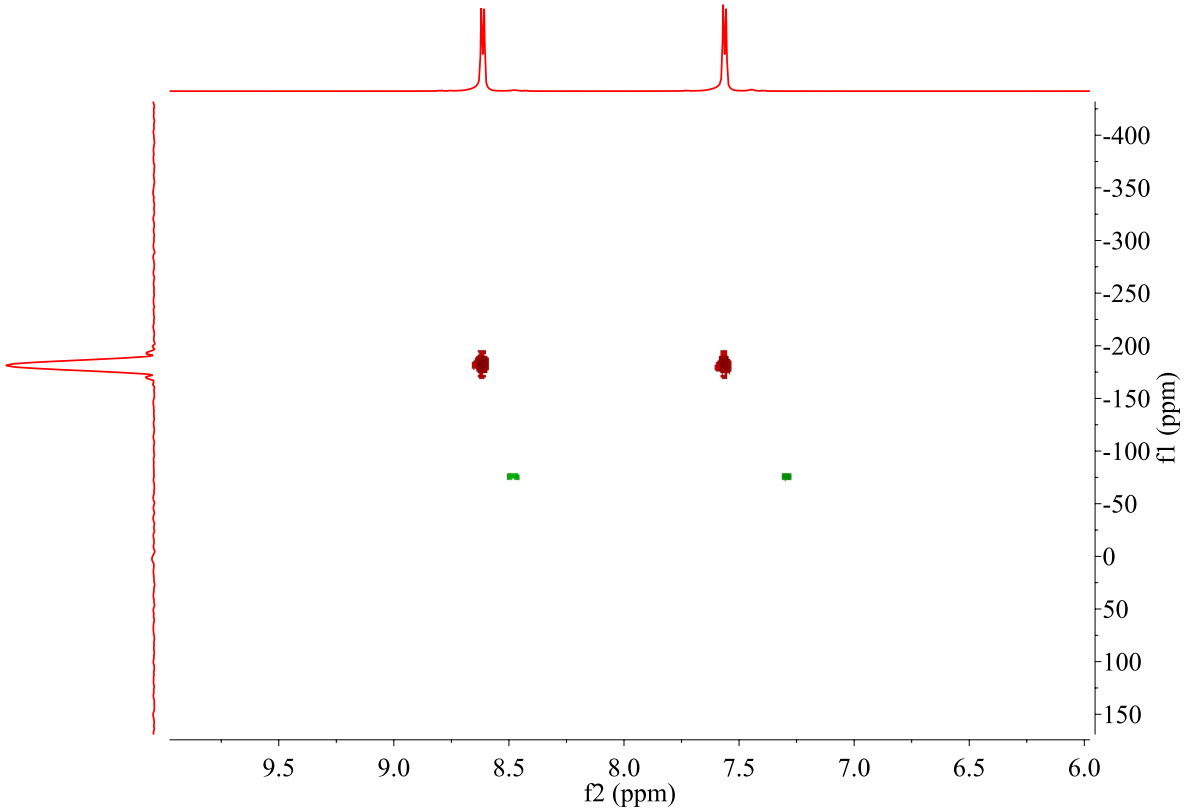


Figure S29. The stacked ^{1}H-^{15}N HMBC-NMR Spectra of ligand **12** in green and [N-I-N]$^{+}$ complex [I(**12**)$_2$]PF$_6$ in red, in CD_2Cl_2 at 30 °C.

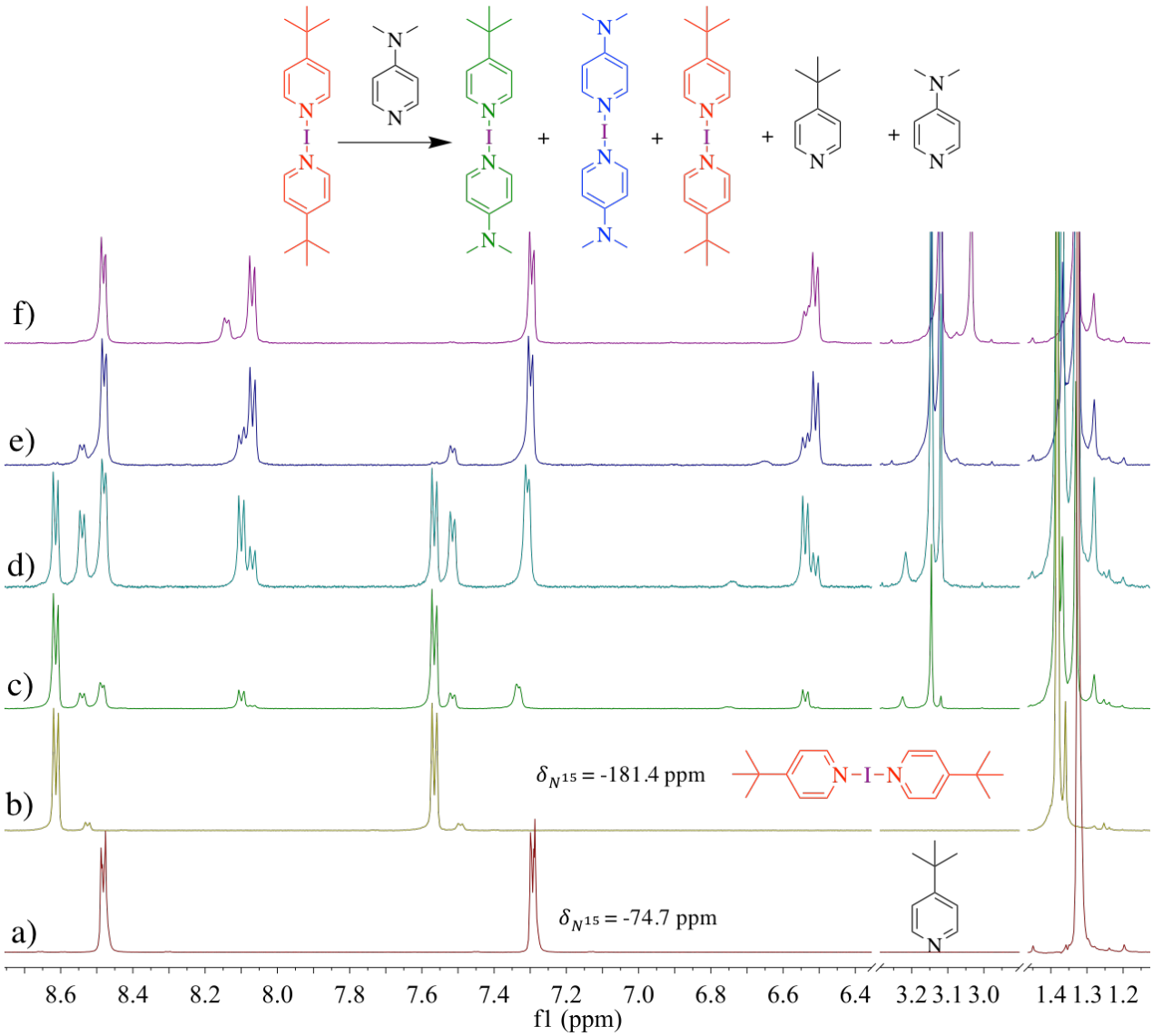
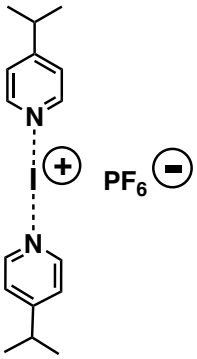


Figure S30. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **12** (a), the iodine(I) complex [I(**12**)$_2$]PF_6 in the absence (b) and in the presence of 0.4 (c), 1.0 (d), 2.0 (e) and 3.0 equivalents (f) of **16**.

2.13 Synthesis of $[I(13)_2]PF_6$



To a solution of silver hexafluorophosphate (9.57 mg, 0.038 mmol, 1.0 eq) in CD_2Cl_2 (2.0 mL), a solution of 4-isopropylpyridine (**13**) (9.21 mg, 0.076 mmol, 2.0 eq) in CD_2Cl_2 (0.6 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (9.64 mg, 0.038 mmol, 1.0 eq) in CD_2Cl_2 (0.4 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{13})_2]PF_6$ (94%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.60 (d, J = 6.8 Hz, 4H), 7.44 (d, J = 6.7 Hz, 4H), 3.08 (m, 2H), 1.32 (d, J = 7.0 Hz, 12H). The analytical data was in agreement with previously reported literature data.[3]

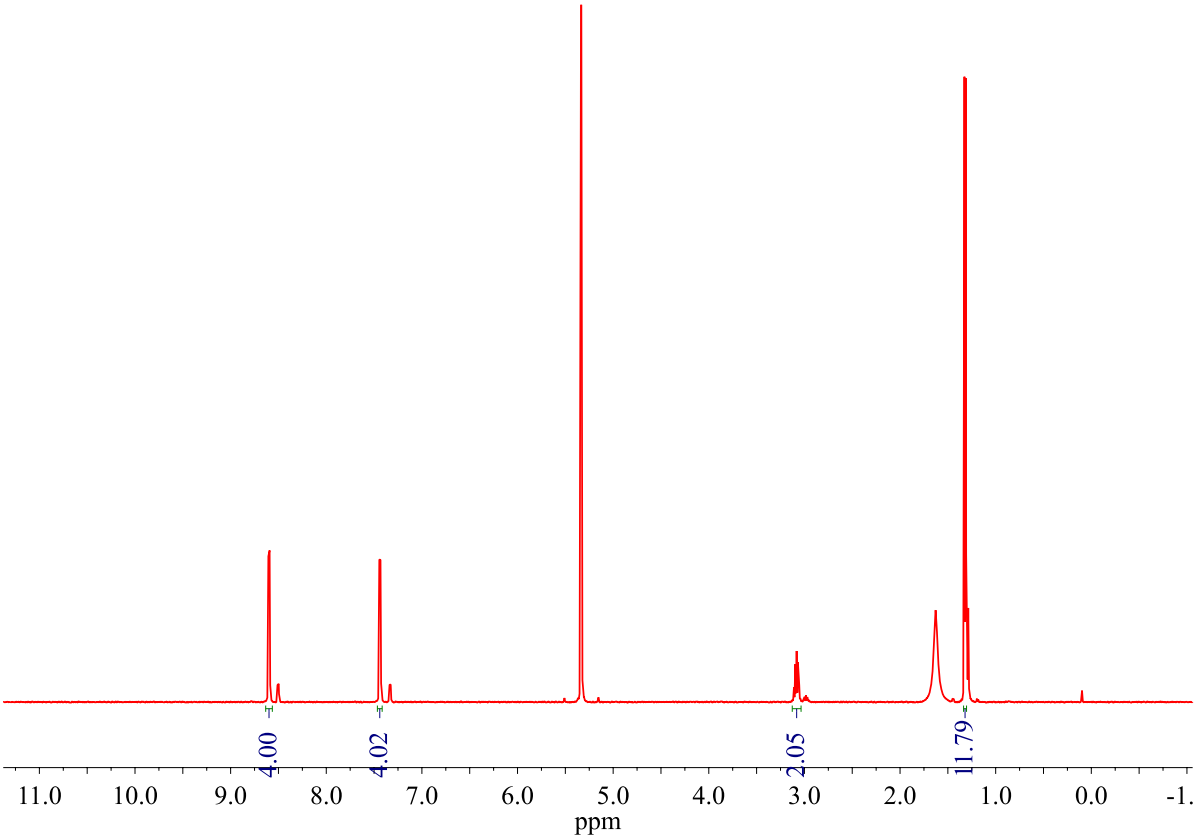


Figure S31. ^{1}H NMR spectrum of the iodine(I) complex $[I(\mathbf{13})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

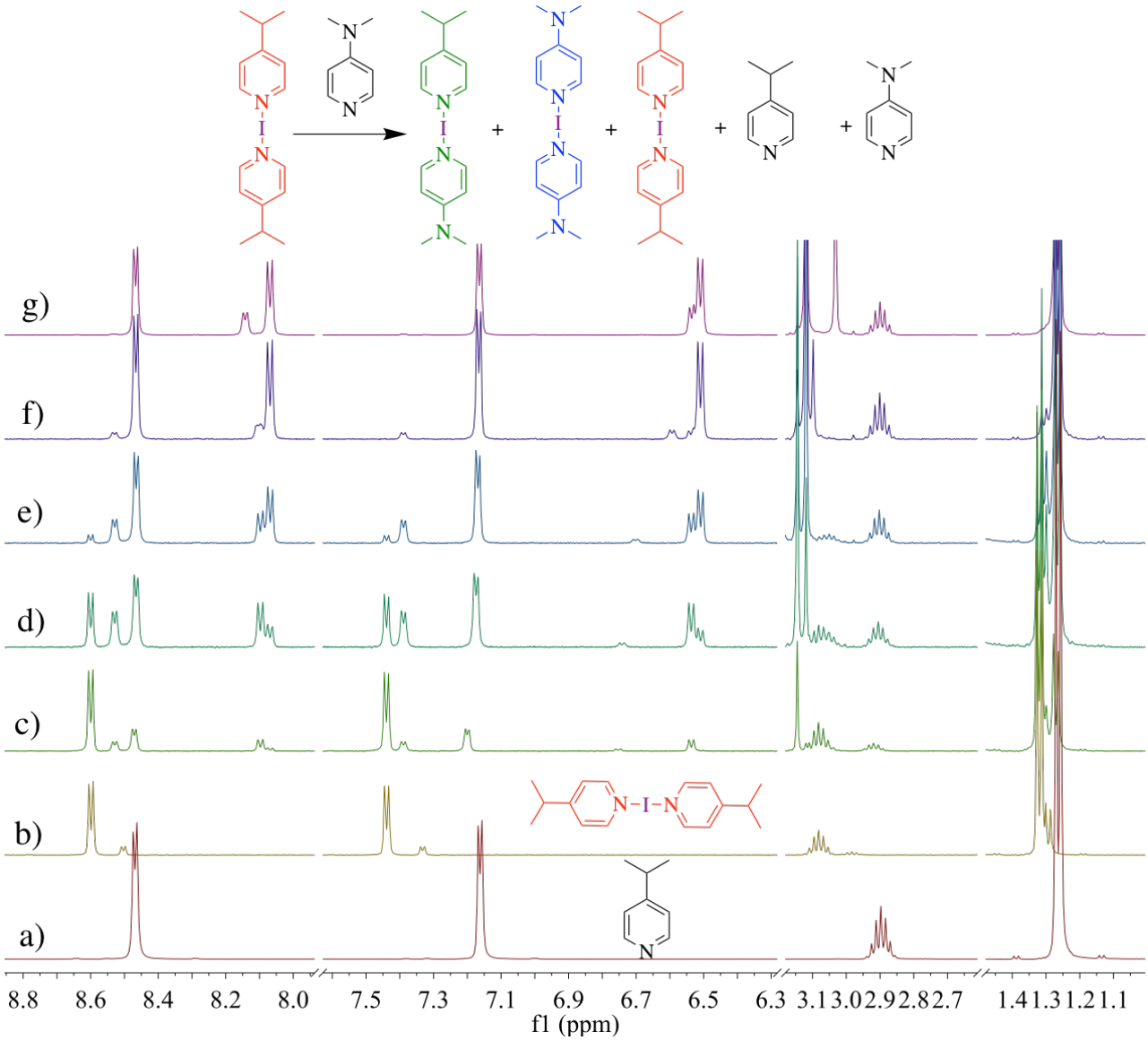
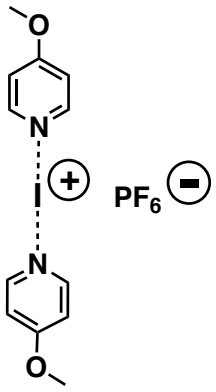


Figure S32. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **13** (a), the iodine(I) complex [I(**13**)$_2$]PF_6 in the absence (b) and in the presence of 0.4 (c), 1.0 (d), 1.5 (e), 2.0 (f) and 2.6 equivalents (g) of **16**.

2.14 Synthesis of $[I(14)_2]PF_6$



To a solution of silver hexafluorophosphate (9.0 mg, 0.036 mmol, 1.0 eq) in CD_2Cl_2 (2.0 mL), a solution of 4-methoxypyridine (**14**) (7.8 mg, 0.071 mmol, 2.0 eq) in CD_2Cl_2 (0.65 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (9.1 mg, 0.036 mmol, 1.0 eq) in CD_2Cl_2 (0.35 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{14})_2]PF_6$ (96%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.48 (d, J = 7.1 Hz, 4H), 7.02 (d, J = 7.1 Hz, 4H), 4.01 (s, 6H).

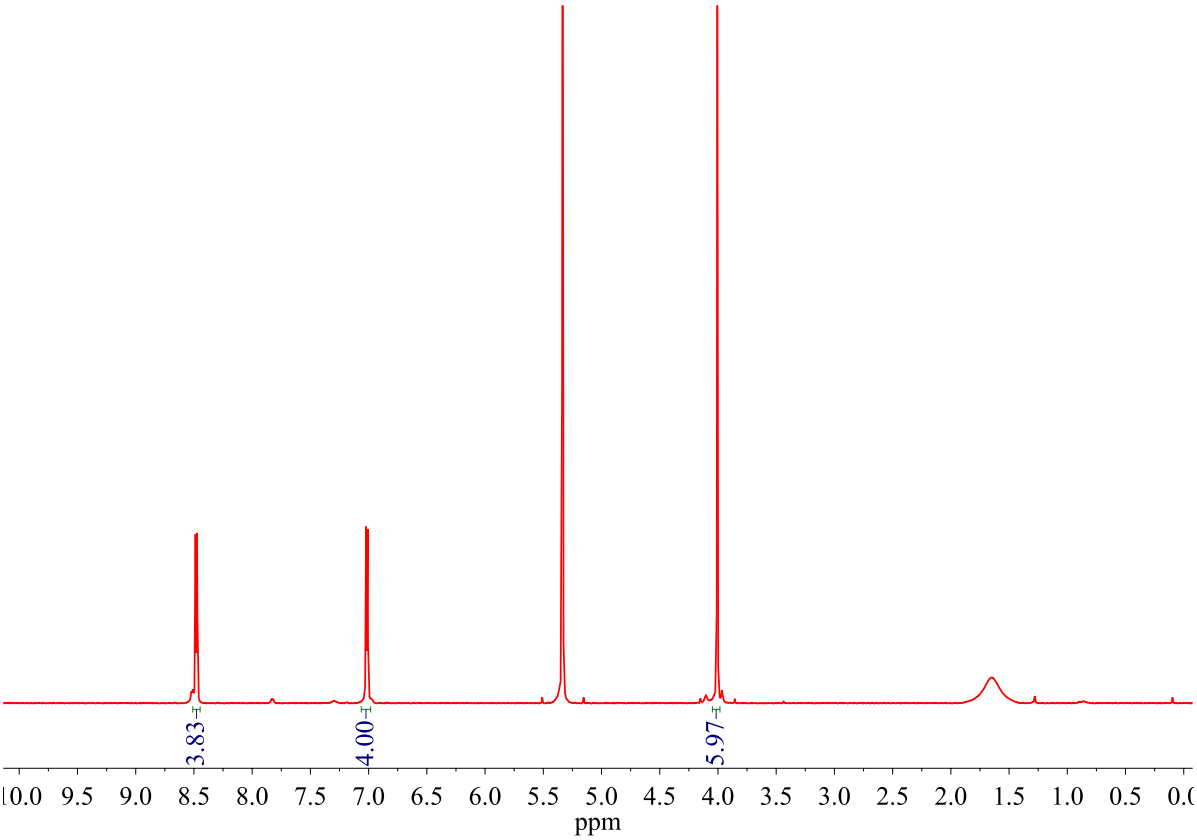


Figure S33. ^{1}H NMR spectrum of the iodine(I) complex $[I(\mathbf{14})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

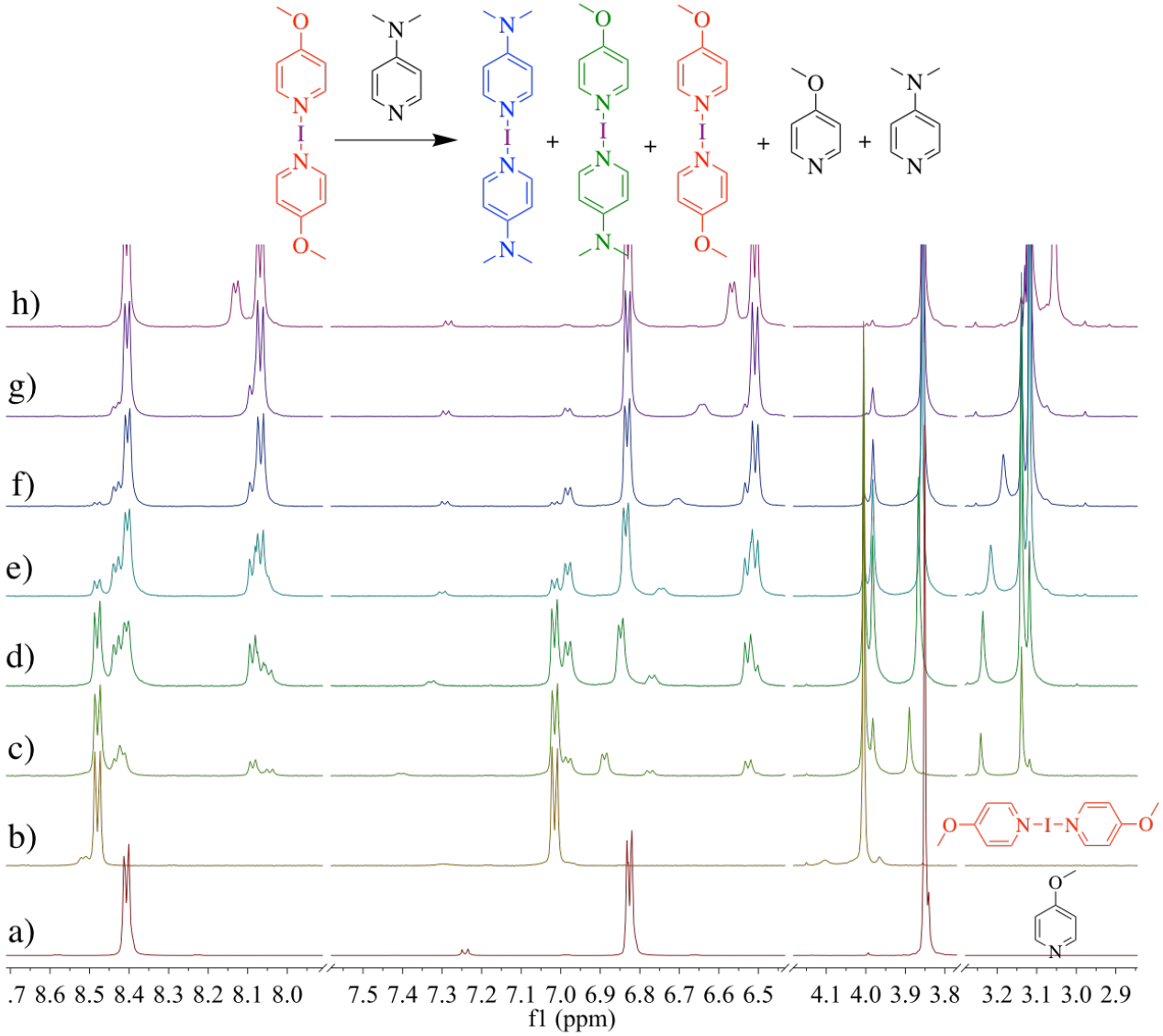
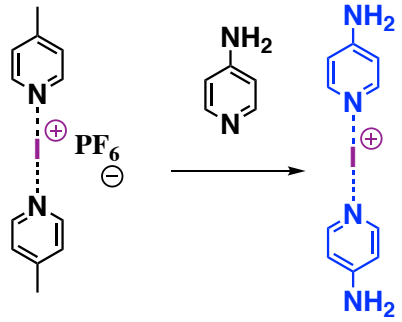


Figure S34. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **14** (a), the iodine(I) complex [I(**14**)$_2$]PF_6 in the absence (b) and in the presence of 0.5 (c), 1.0 (d), 1.6 (e), 2.0 (f), 2.4 (g) and 3.0 equivalents (h) of **16**.

2.15 Synthesis of $[I(15)_2]PF_6$



$[I(\mathbf{15})_2]PF_6$ was prepared by the ligand exchange reaction of [$I(\mathbf{10})_2]PF_6$ and 4-aminopyridine (**15**), then proved by the following titrations **16** of into the crude mixture of reaction $[I(\mathbf{15})_2]PF_6$.

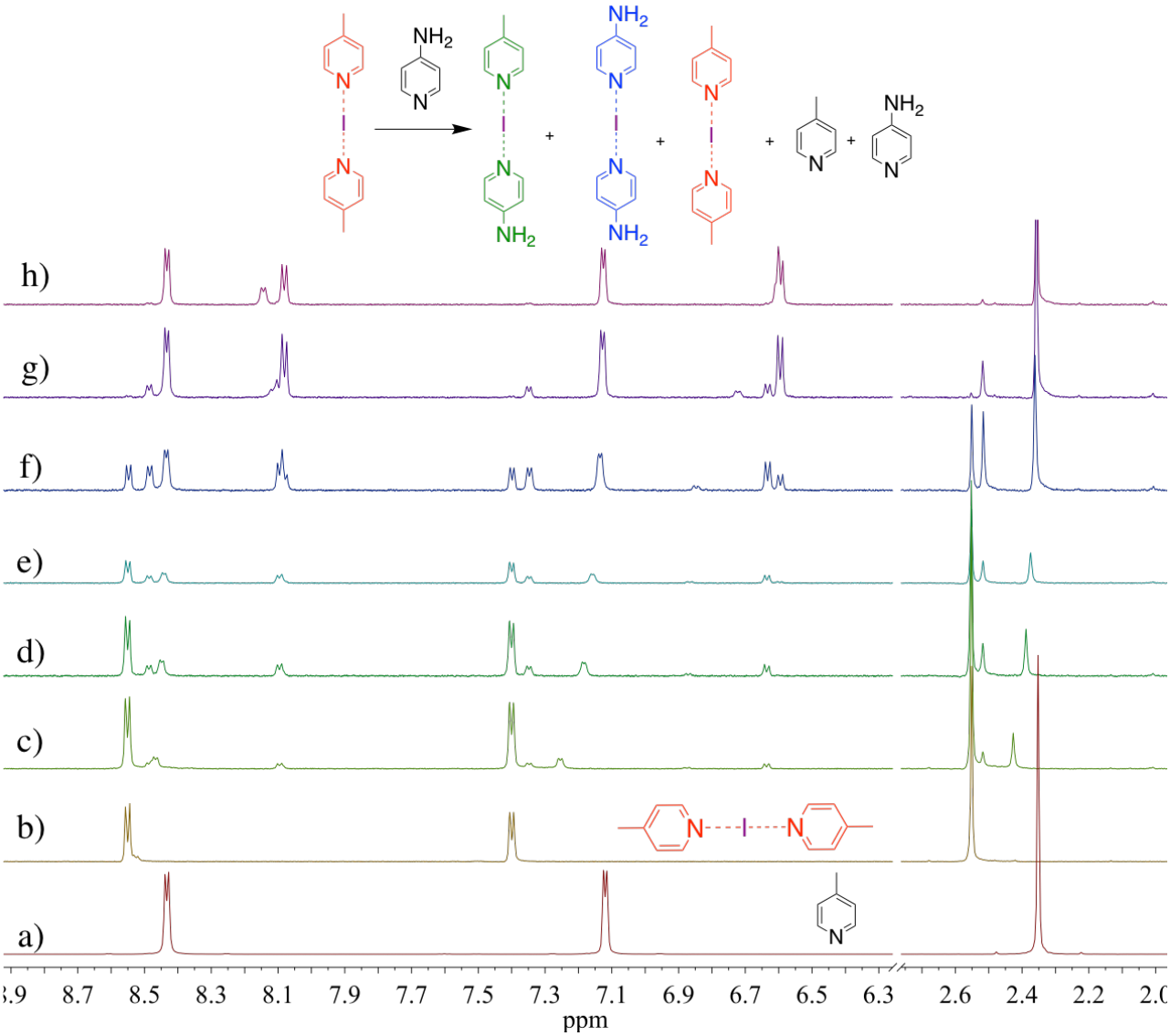


Figure S35. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **10** (a), 1 mM $[I(\mathbf{10})_2]PF_6$ in the absence (b) and in the presence of 0.2 (c), 0.4 (d), 0.6 (e), 1.0 (f), 1.8 (g) and 2.6 equivalents (h) of **15**.

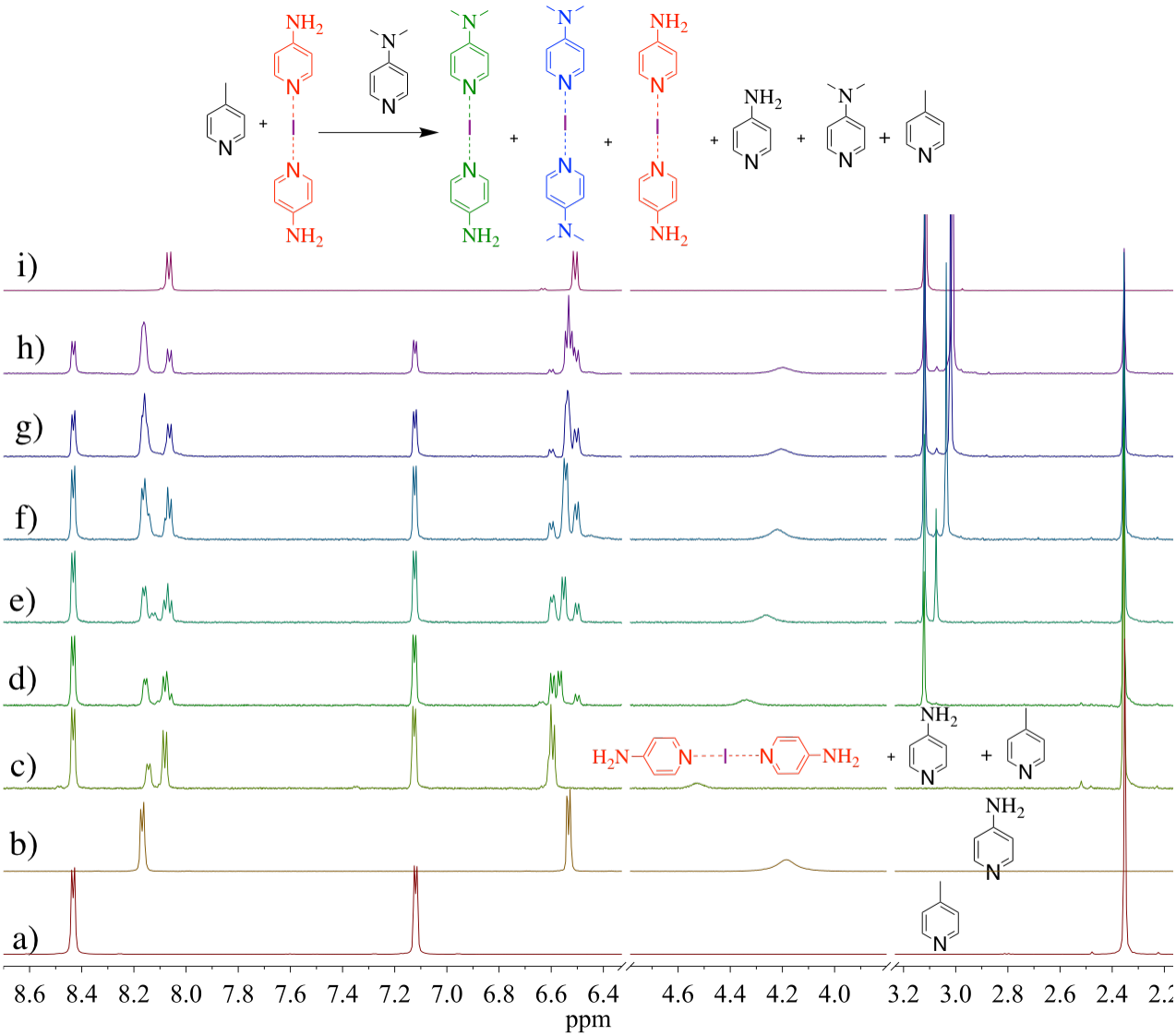
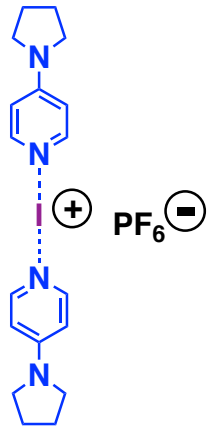


Figure S36. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **10** (a), pure **15** (b), the crude mixture of reaction [I(**15**)$_2$]PF_6 in the absence (c) and in the presence of 0.4 (d), 0.8 (e), 1.6 (f), 2.4 (g) and 3.2 equivalents (h) of **16**, and pure [I(**16**)$_2$]PF_6 (i).

2.16 Synthesis of $[I(17)_2]PF_6$



To a solution of silver hexafluorophosphate (9.8 mg, 0.039 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of 4-pyrrolidinopyridine (**17**) (6.5 mg, 0.078 mmol, 2.0 eq) in CD_2Cl_2 (0.6 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (9.9 mg, 0.039 mmol, 1.0 eq) in CD_2Cl_2 (0.4 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{17})_2]PF_6$ (72%, determined by ^{1}H NMR integration of the crude reaction mixture) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.04 (d, *J* = 7.2 Hz, 4H), 6.39 (d, *J* = 6.8 Hz, 4H), 3.45-3.36 (m, 8H), 2.12-2.07 (m, 8H).

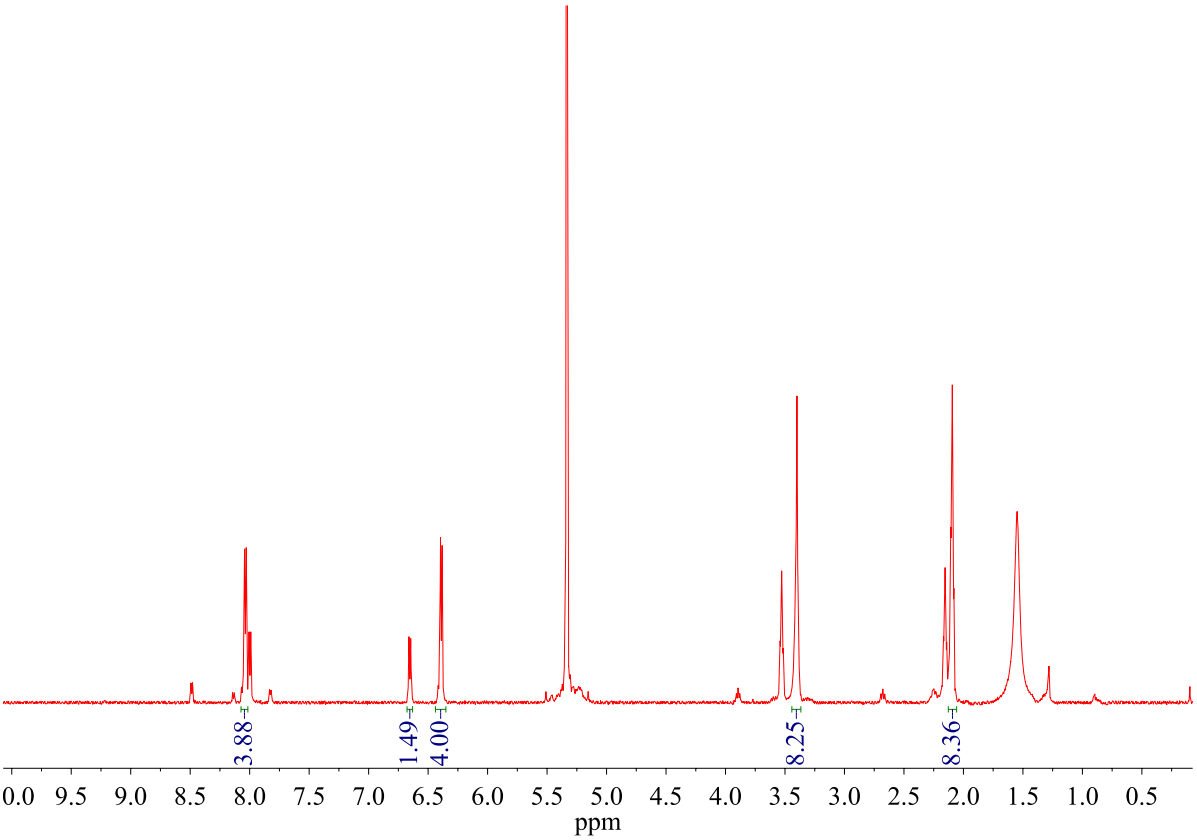


Figure S37. ^{1}H NMR spectrum of the crude mixture of reaction $[I(\mathbf{17})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

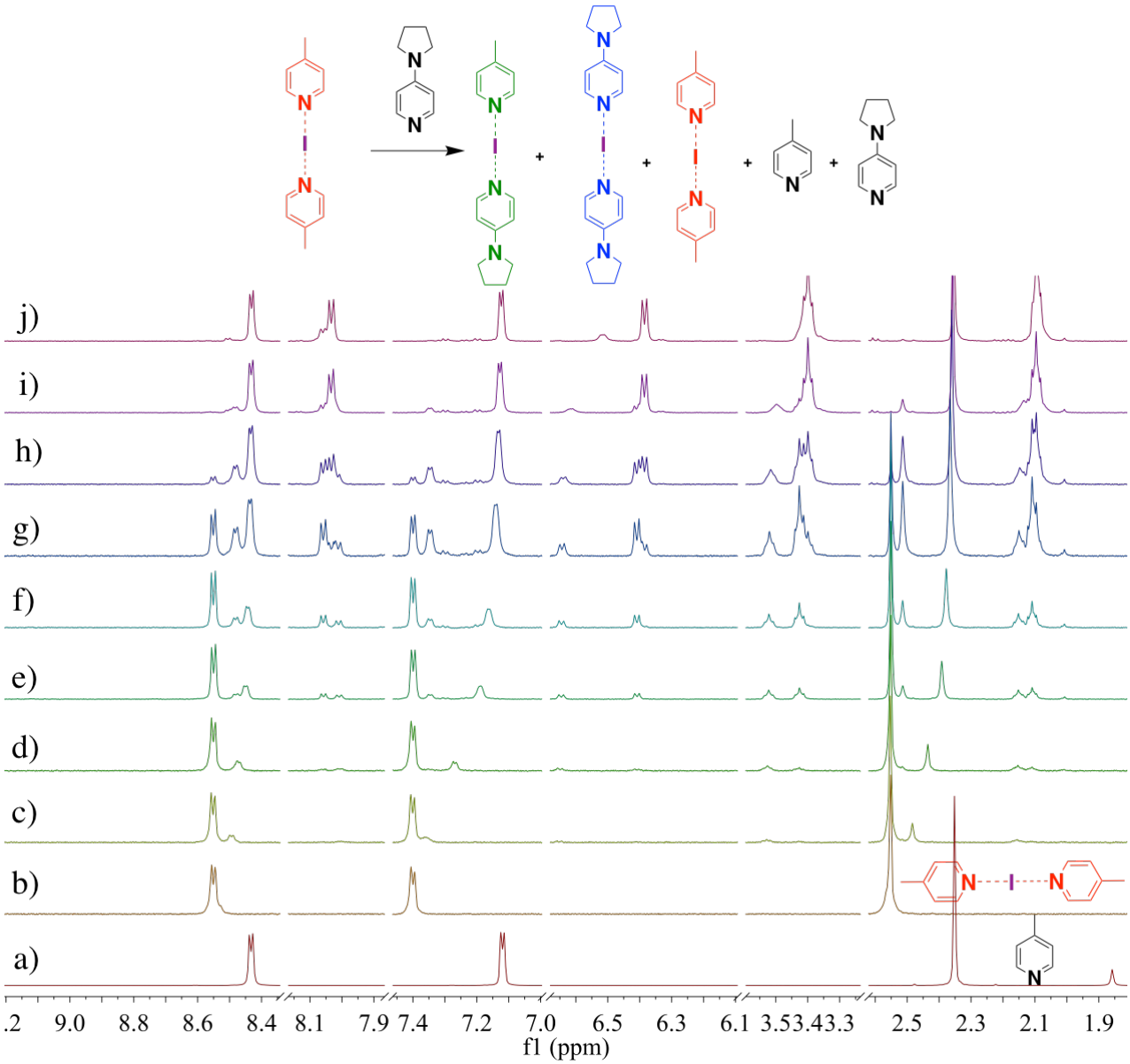
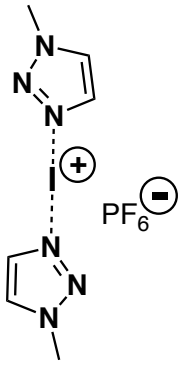


Figure S38. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **10** (a), 1 mM [I(**10**)$_2$]PF_6 in the absence (b) and in the presence of 0.1 (c), 0.2 (d), 0.4 (e), 0.6 (f), 1.0 (g), 1.5 (h), 2.0 (i) and 2.5 equivalents (j) of **17**.

2.17 Synthesis of $[I(18)_2]PF_6$



To a solution of silver hexafluorophosphate (9.8 mg, 0.039 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of 1-methyl-1,2,4-triazole (**18**) (6.5 mg, 0.078 mmol, 2.0 eq) in CD_2Cl_2 (0.6 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (9.9 mg, 0.039 mmol, 1.0 eq) in CD_2Cl_2 (0.4 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{18})_2]PF_6$ (93%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.02 (s, 2H), 7.90 (s, 2H), 4.27 (s, 6H). The analytical data was in agreement with previously reported literature data.[4]

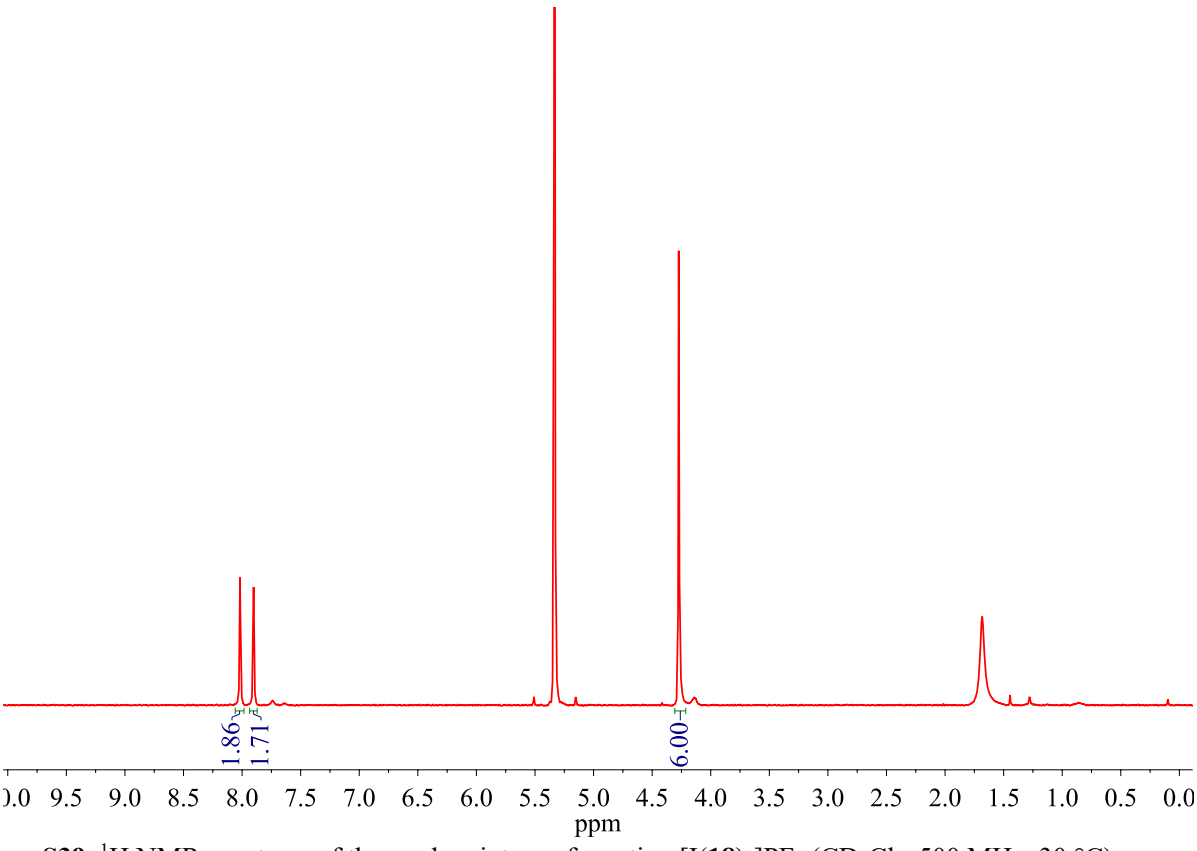


Figure S39. ^{1}H NMR spectrum of the crude mixture of reaction $[I(\mathbf{18})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

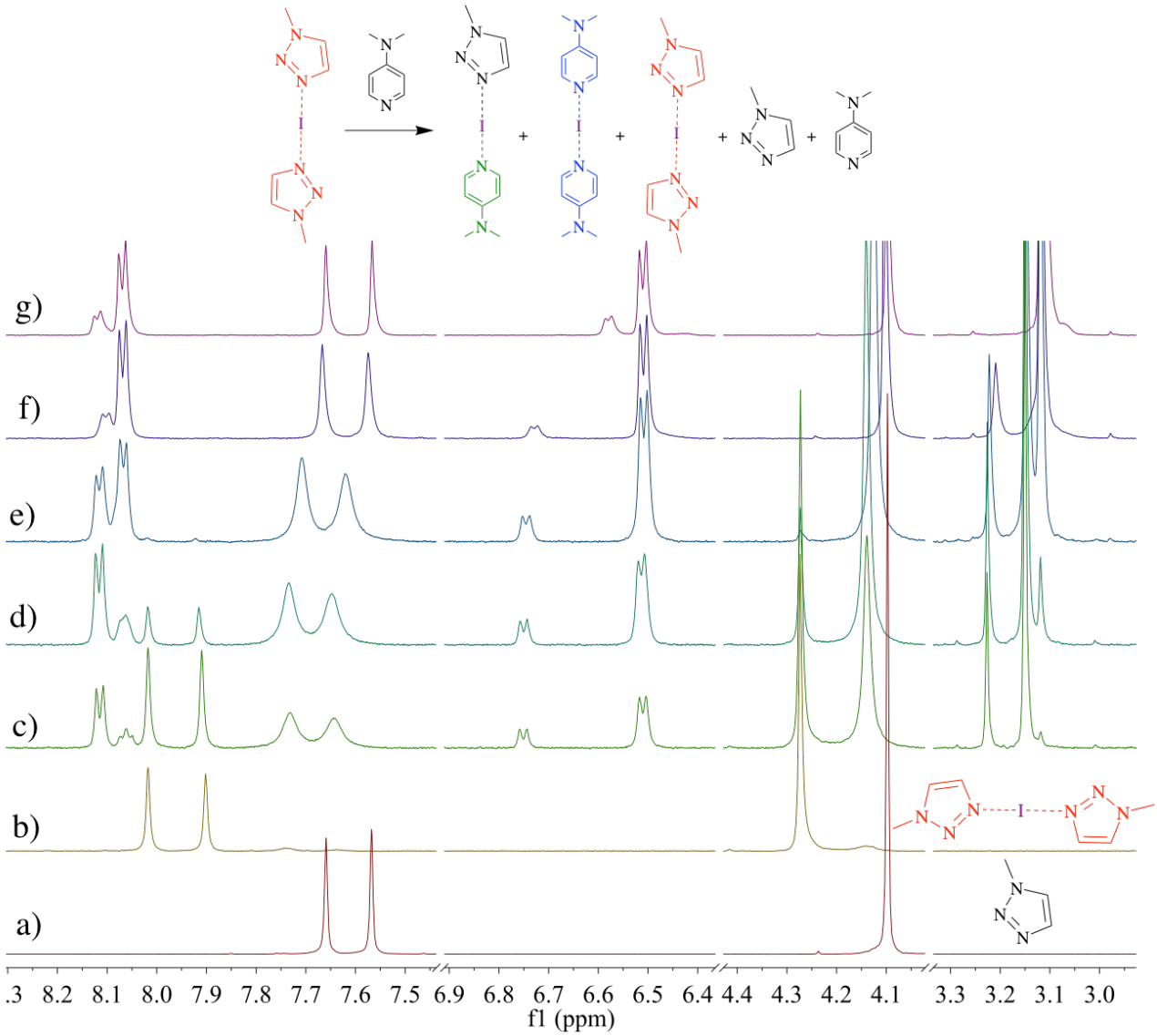
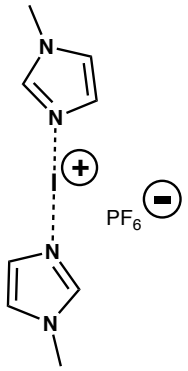


Figure S40. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **18** (a), the crude mixture of reaction [I(**18**)$_2$]PF_6 in the absence (b) and in the presence of 0.5 (c), 0.8 (d), 1.2 (e), 1.6 (f) and 2.0 equivalents (g) of **16**.

2.18 Synthesis of $[I(19)_2]PF_6$



To a solution of silver hexafluorophosphate (5.7 mg, 0.023 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of 1-methylimidazole (**19**) (3.7 mg, 0.045 mmol, 2.0 eq) in CD_2Cl_2 (0.8 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (5.7 mg, 0.023 mmol, 1.0 eq) in CD_2Cl_2 (0.2 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{19})_2]PF_6$ (96%, determined by ^1H NMR integration of the crude reaction mixture and proved by ^1H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^1H NMR** (500 MHz, CD_2Cl_2): δ 7.87 (s, 2H), 7.15 (s, 2H), 6.97 (s, 2H), 3.83 (s, 6H). The analytical data was in agreement with previously reported literature data.

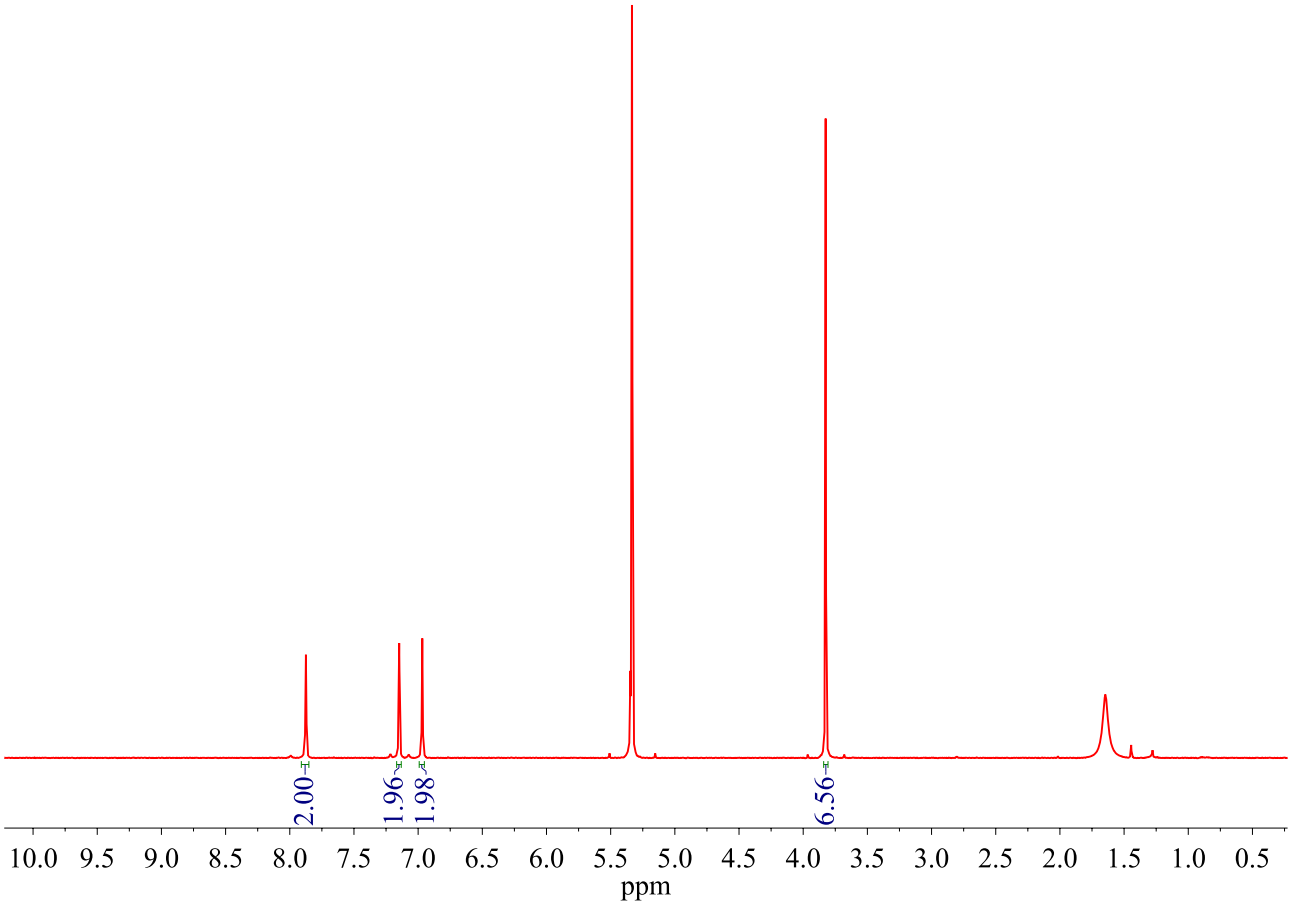


Figure S41. ^{1}H NMR spectrum of the crude mixture of reaction [I(**19**)$_2$]PF_6 (CD_2Cl_2, 500 MHz, 30 °C).

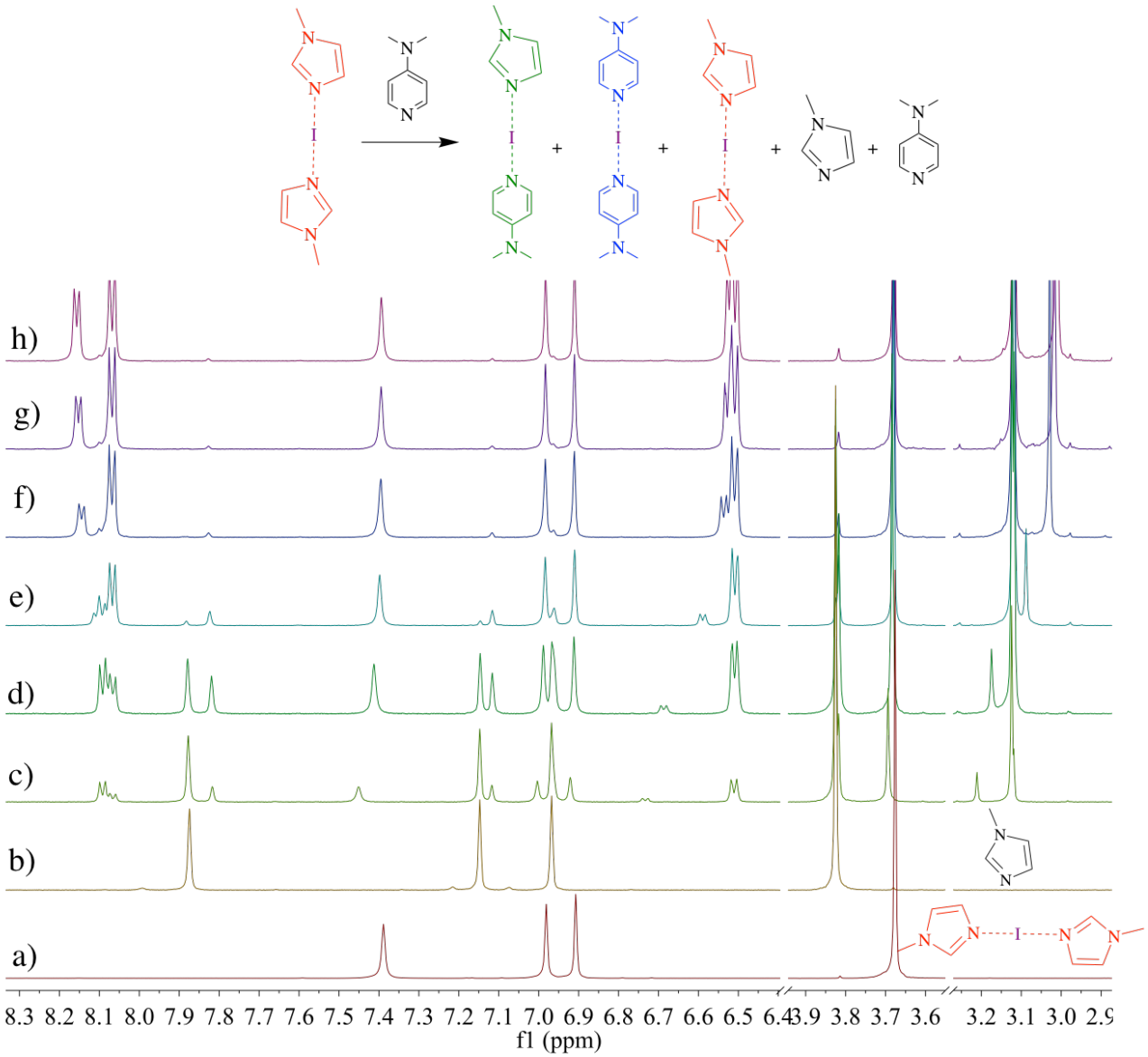
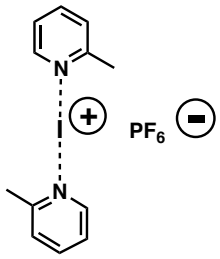


Figure S42. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **19** (a), the crude mixture of reaction $[I(\mathbf{19})_2]PF_6$ in the absence (b) and in the presence of 0.5 (c), 1.0 (d), 2.0 (e), 3.0 (f), 3.5 (g) and 4.0 equivalents (h) of **16**.

2.19 Synthesis of $[I(20)_2]PF_6$



To a solution of silver hexafluorophosphate (4.9 mg, 0.019 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of 2-methylpyridine (**20**) (3.6 mg, 0.039 mmol, 2.0 eq) in CD_2Cl_2 (0.8 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (4.9 mg, 0.019 mmol, 1.0 eq) in CD_2Cl_2 (0.2 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{20})_2]PF_6$ (77%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.89 (dd, J = 5.6, 1.6 Hz, 2H), 8.08 (td, J = 7.7, 1.6 Hz, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 6.6 Hz, 2H), 2.85 (s, 6H).

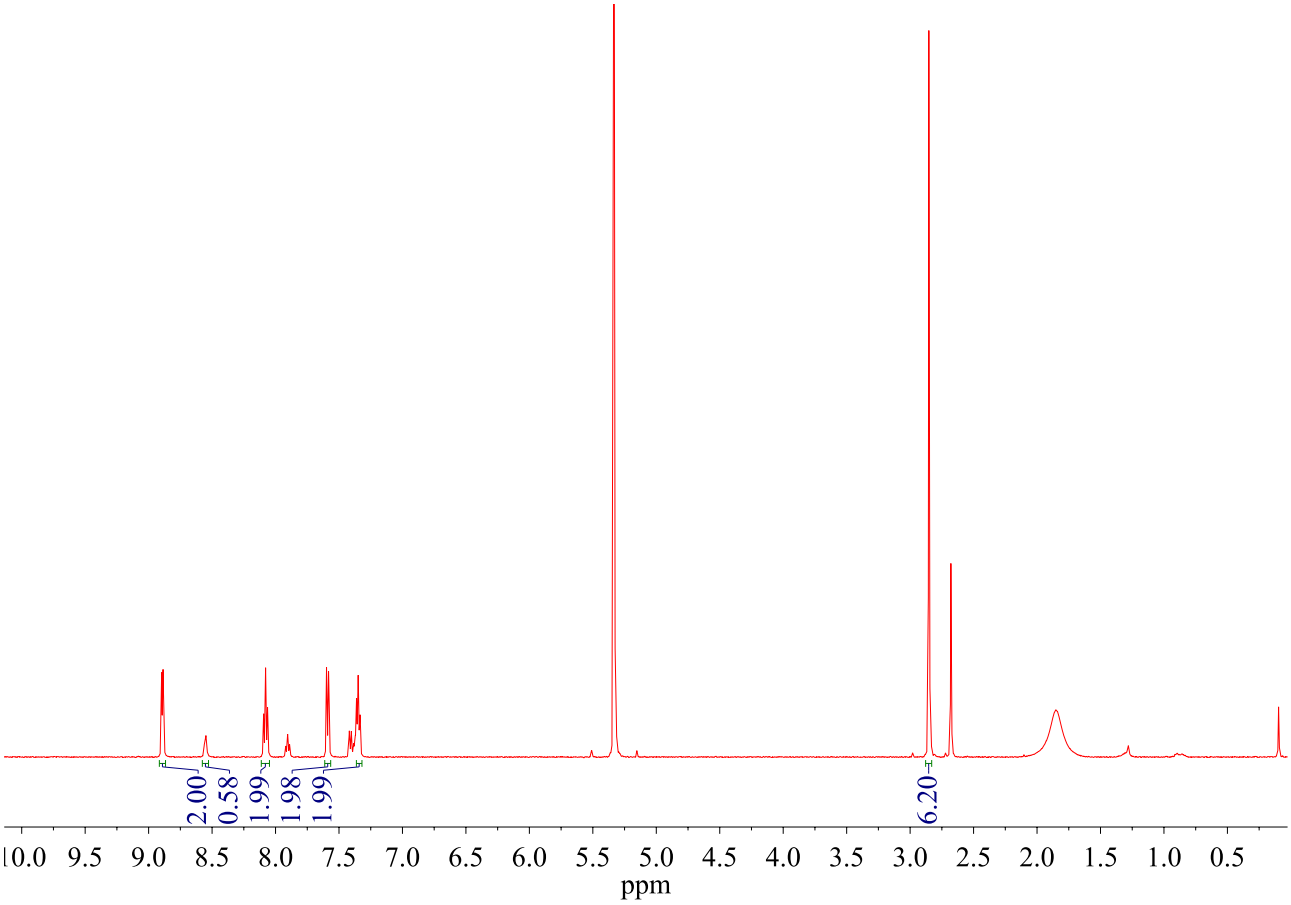


Figure S43. ^{1}H NMR spectrum of the crude mixture of reaction $[I(\mathbf{20})_2]PF_6$ (CD_2Cl_2, 500 MHz, 30 °C).

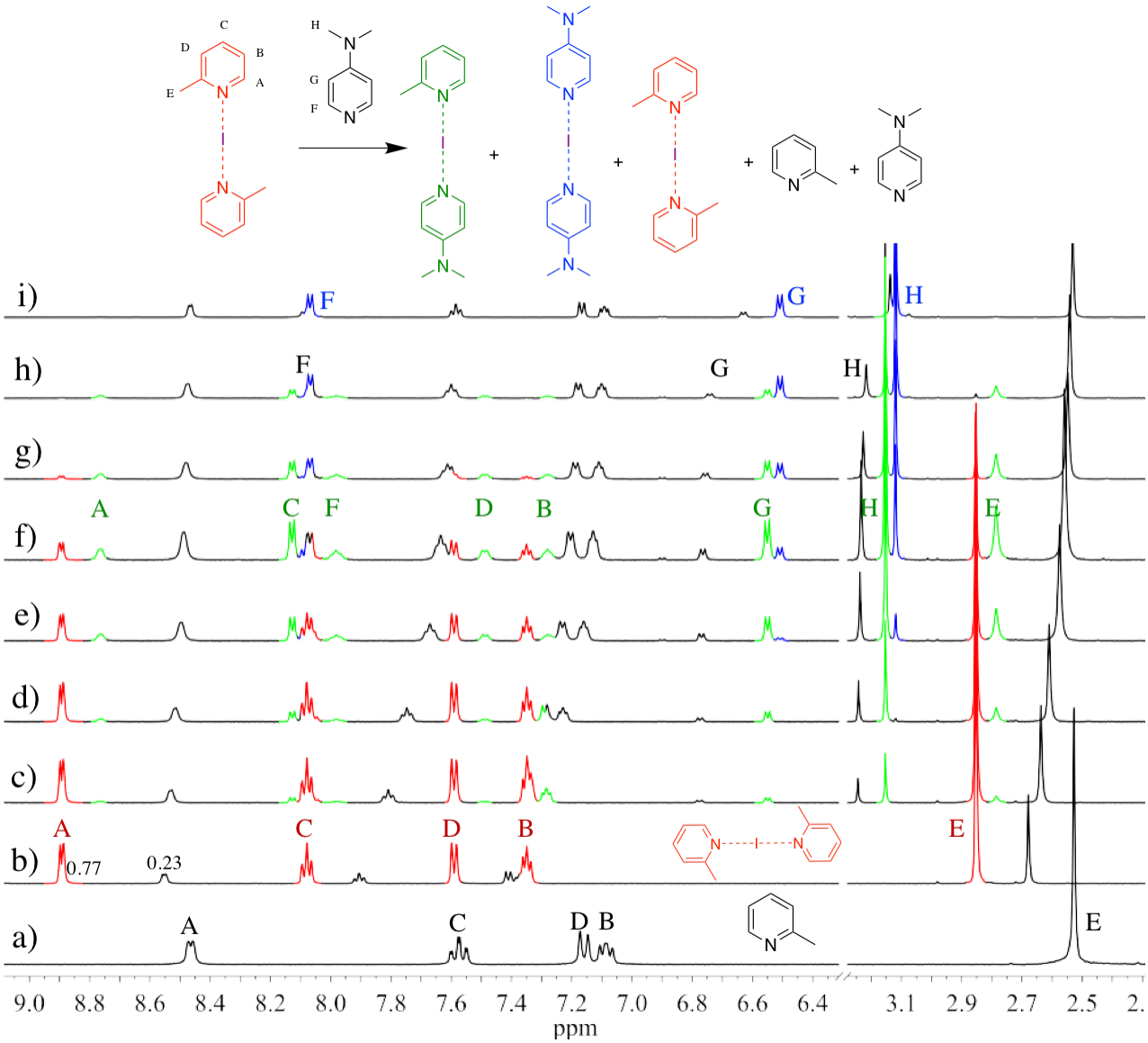
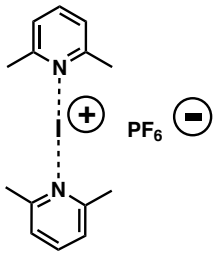


Figure S44. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **20** (a), the crude mixture of reaction $[I(\mathbf{20})_2]PF_6$ in the absence (b) and in the presence of 0.1 (c), 0.2 (d), 0.4 (e), 0.6 (f), 0.8 (g), 1.0 (h) and 1.5 equivalents (i) of **16**.

2.20 Synthesis of $[I(21)_2]PF_6$



To a solution of silver hexafluorophosphate (2.0 mg, 0.008 mmol, 1.0 eq) in CD_2Cl_2 (1.0 mL), a solution of 2,6-lutidine (**21**) (1.7 mg, 0.016 mmol, 2.0 eq) in CD_2Cl_2 (0.9 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (2.0 mg, 0.008 mmol, 1.0 eq) in CD_2Cl_2 (0.1 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{21})_2]PF_6$ (about 12%, determined by ^1H NMR integration of the crude reaction mixture and proved by ^1H NMR titration experiments) was stored in a 4 mL vial in the fridge.

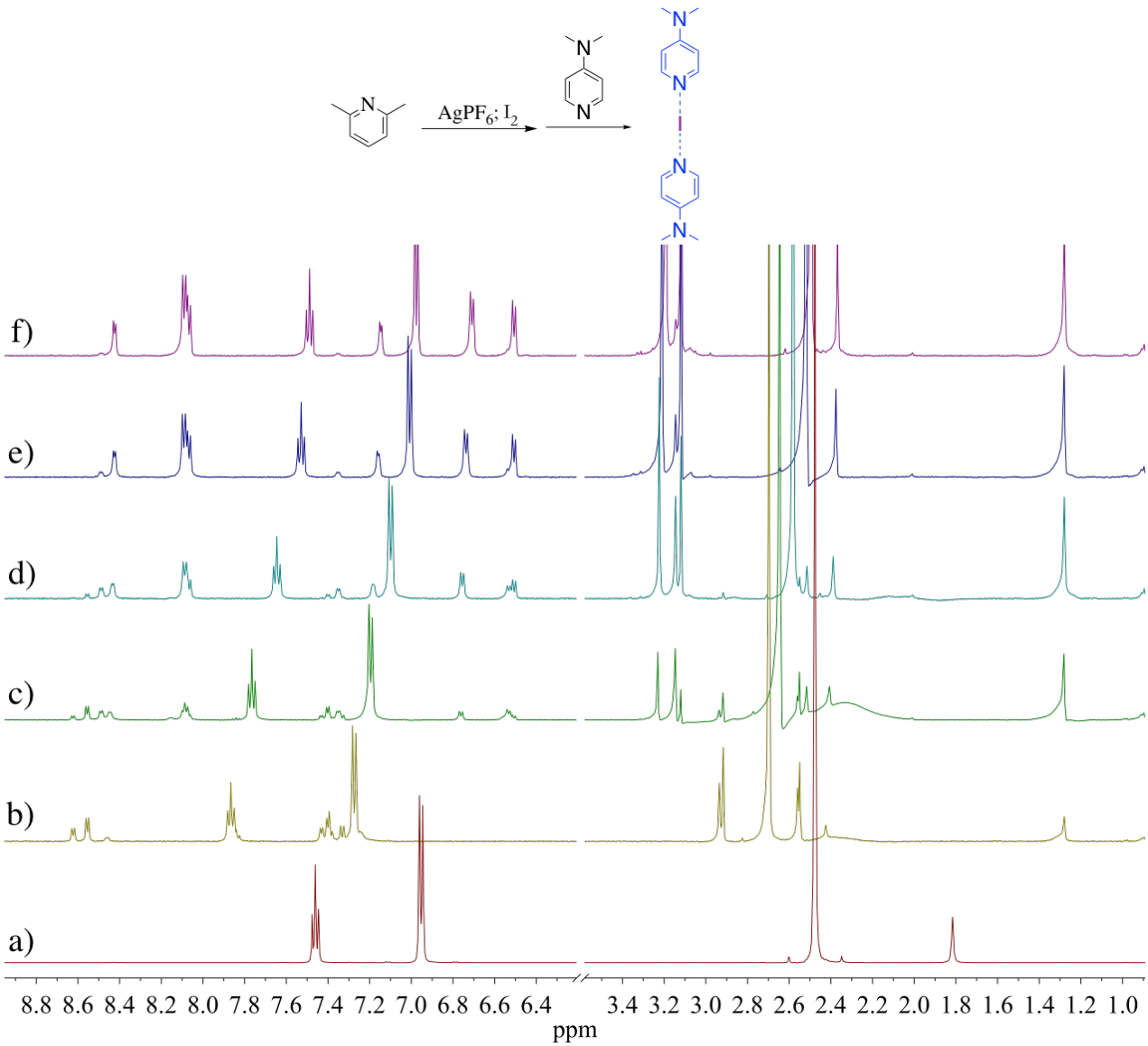
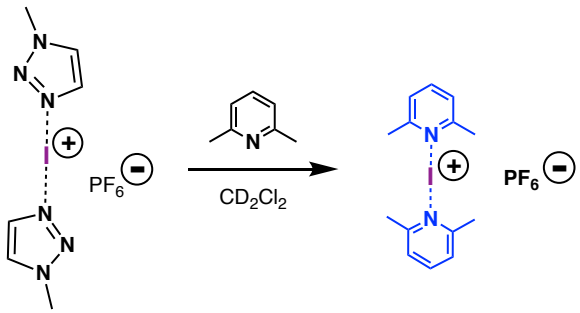


Figure S45. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **21** (a), the crude mixture of reaction $[I(\mathbf{21})_2]PF_6$ in the absence (b) and in the presence of 0.5 (c), 1.0 (d), 1.5 (e) and 1.8 equivalents (g) of **16**.



To a solution of $[I(\mathbf{18})_2]PF_6$ (48.0 mg, 0.11 mmol, 1.0 eq.) in dichloromethane (1.0 mL), a solution of **21** (32.0 mg, 0.30 mmol, 2.7 eq.) in dichloromethane (0.5 mL) was added. The reaction mixture was stirred for 5 minutes, concentrated to ~1 mL under reduced pressure and upon the addition of

Et_2O (20 mL), the desired product was precipitated from solution as a white solid, which was filtered and washed with Et_2O. The product was dried under reduced pressure to obtain [I(**21**)$_2$]PF_6 (44.4 mg, 83%). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 7.87 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 4H), 2.93 (s, 12H); **^{15}N NMR** (51 MHz, CD_3CN): δ -154.9.

NMR characterisation for **21**: **^{15}N NMR** (51 MHz, CD_3CN): δ -67.8.

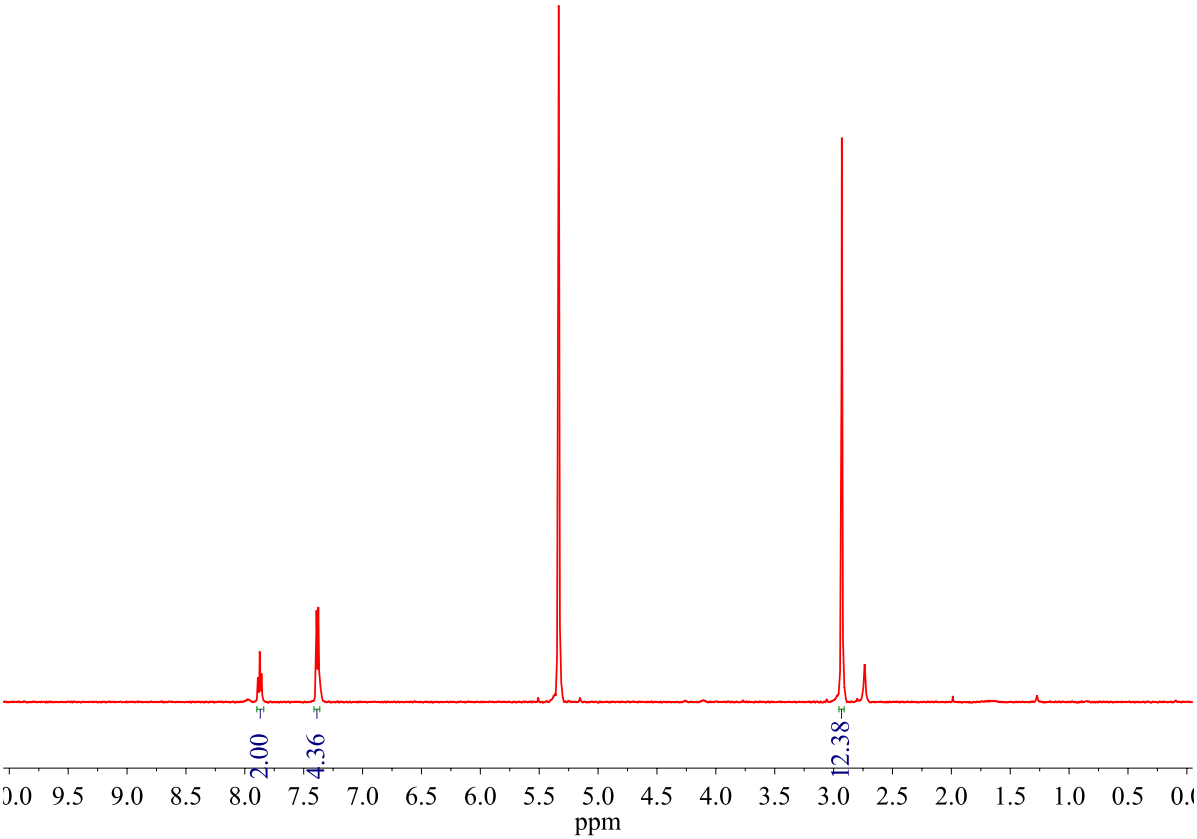


Figure S46. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 30 °C) of [I(**21**)$_2$]PF_6.

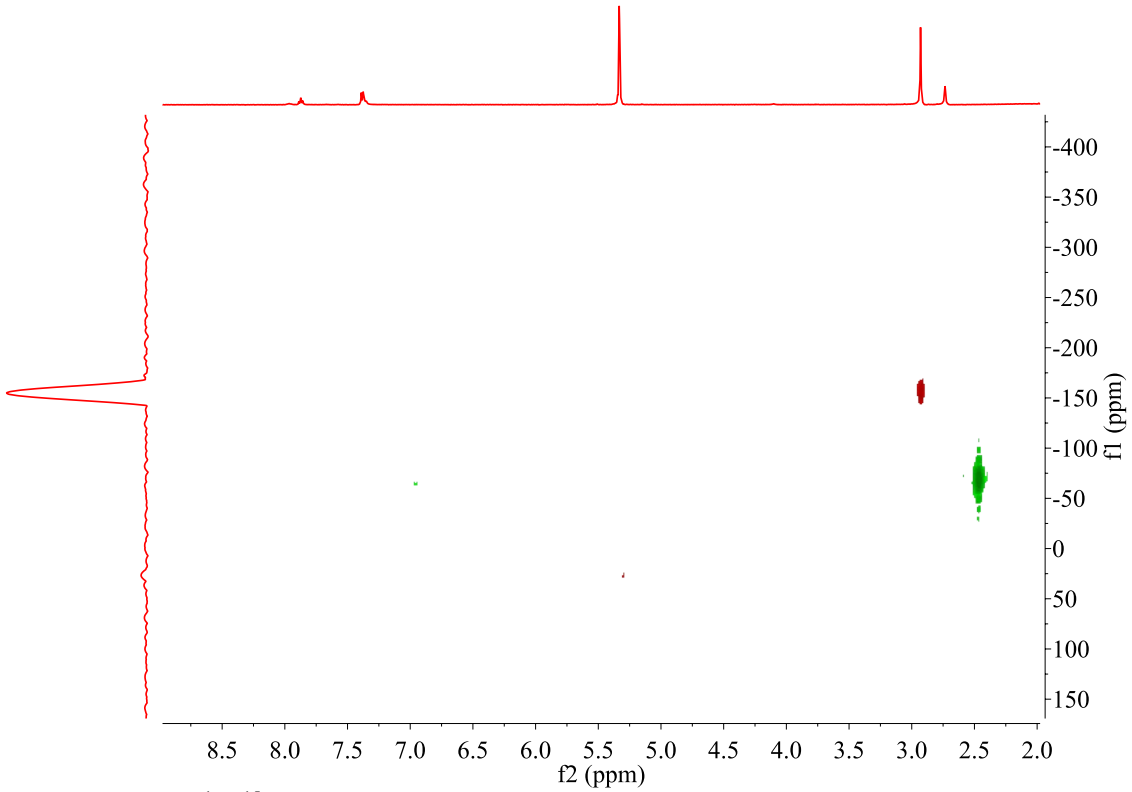


Figure S47. The stacked ^{1}H-^{15}N-HMBC spectra of ligand **21** in green and [N-I-N]$^{+}$ complex [I(**21**)$_2$]PF$_6$ in red, in CD_2Cl_2 at 30 °C.

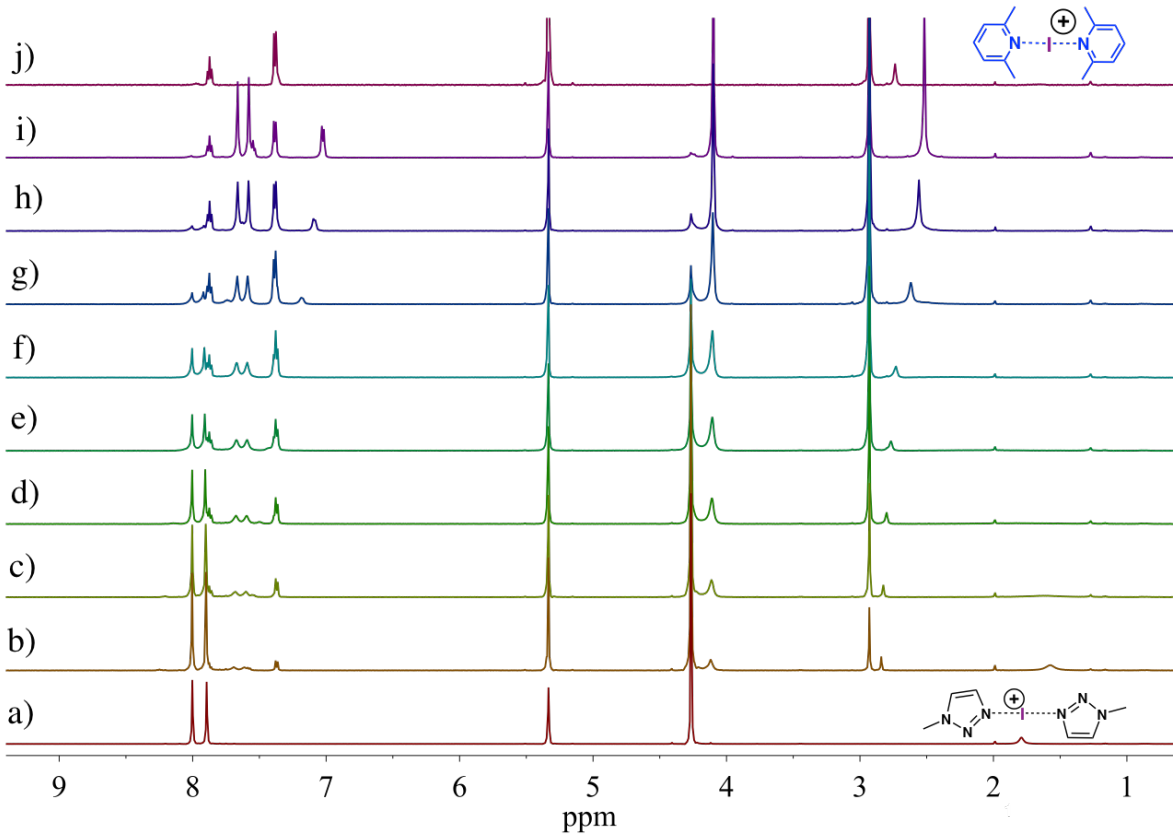
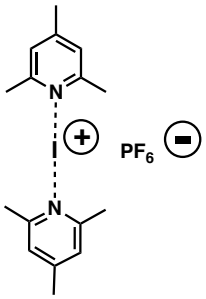


Figure S48. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of [I(**18**)$_2$]PF$_6$ in the absence (a) and in the presence of 0.2 (b), 0.4 (c), 0.6 (d), 0.8 (e), 1.0 (f), 1.5 (g), 2.0 (h), 2.5 (i) equivalents of **21** and pure [I(**21**)$_2$]PF$_6$ (j).

2.21 Synthesis of $[I(22)_2]PF_6$



To a solution of silver hexafluorophosphate (3.2 mg, 0.013 mmol, 1.0 eq) in CD_2Cl_2 (2.0 mL), a solution of 2,4,6-trimethylpyridine (**22**) (3.1 mg, 0.025 mmol, 2.0 eq) in CD_2Cl_2 (0.9 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (3.2 mg, 0.013 mmol, 1.0 eq) in CD_2Cl_2 (0.1 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of $[I(\mathbf{22})_2]PF_6$ (43%, determined by ^{1}H NMR integration of the crude reaction mixture and proved by ^{1}H NMR titration experiments) was stored in a 4 mL vial in the fridge.

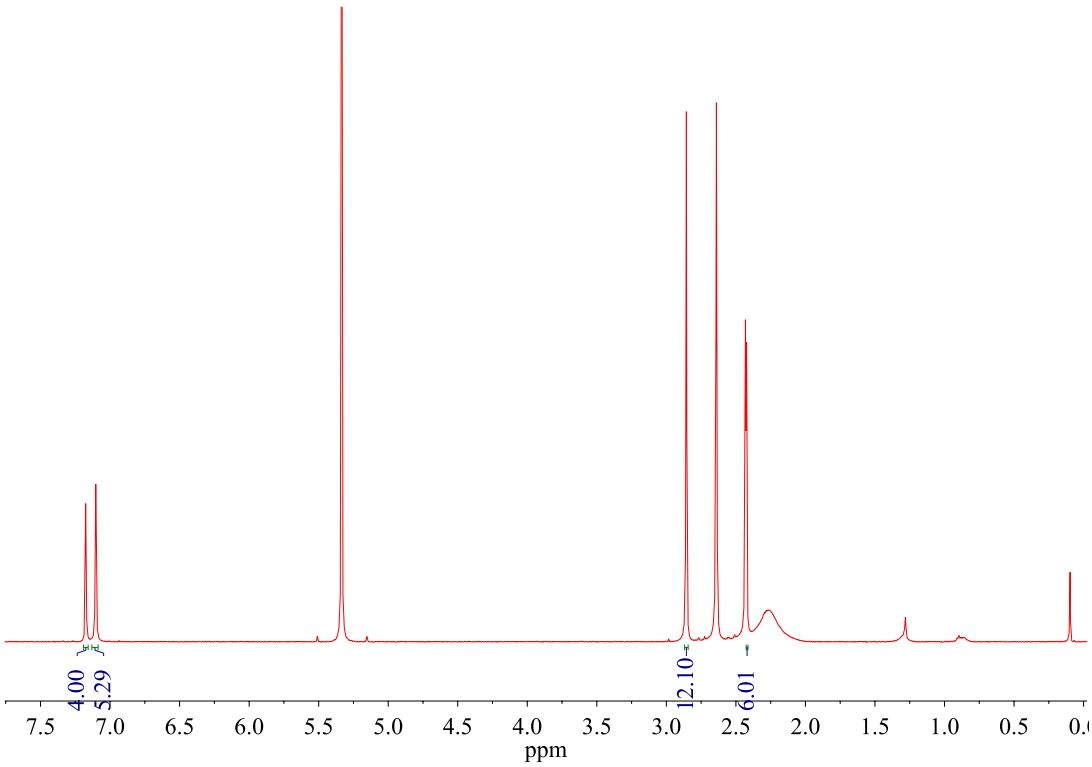


Figure S49. ^{1}H NMR spectrum of the crude mixture of reaction $[I(\mathbf{22})_2]PF_6$ by the $[N\cdots Ag^+\cdots N] \rightarrow [N\cdots I^+\cdots N]$ cation exchange reaction (CD_2Cl_2, 500 MHz, 30 °C).

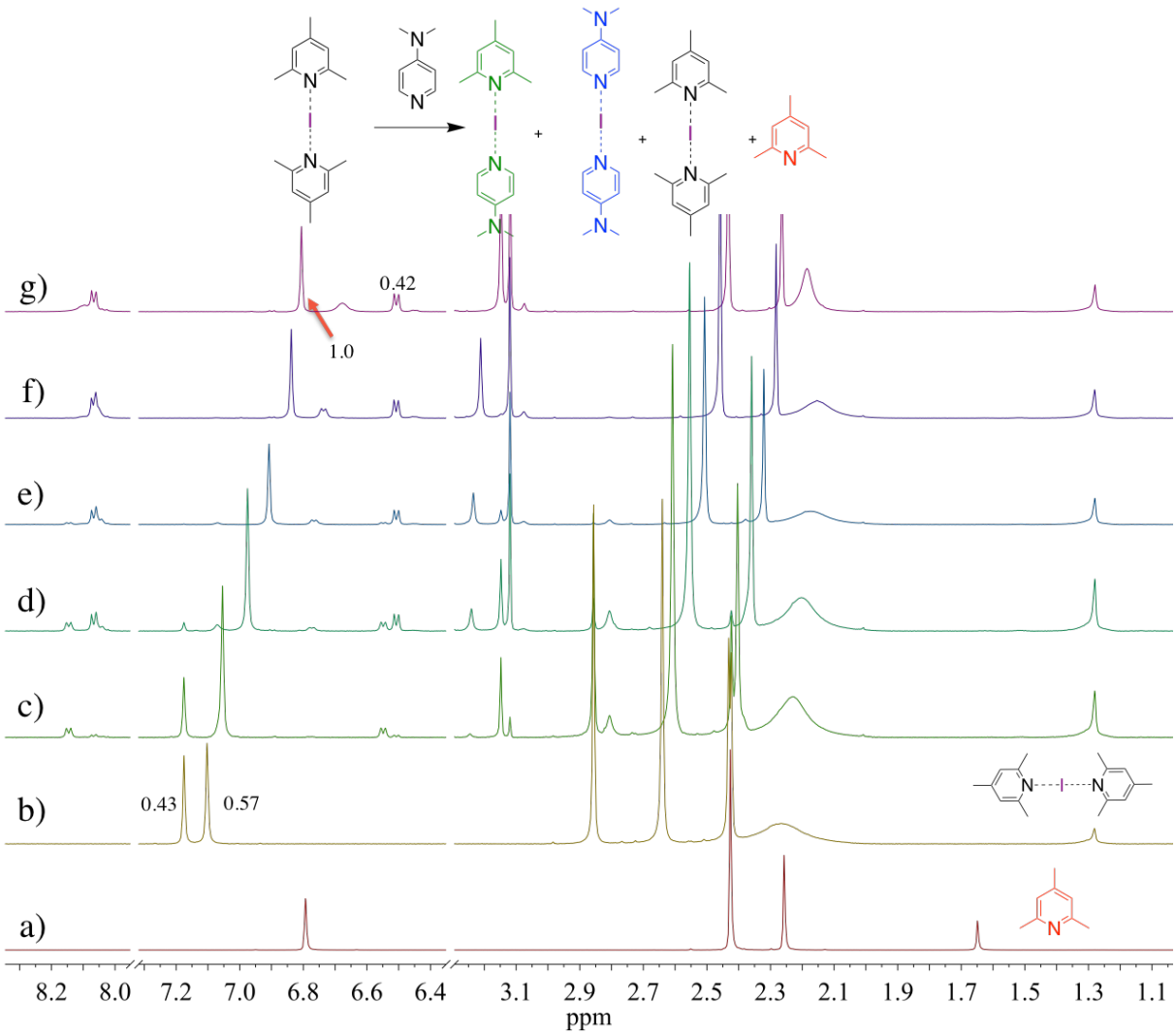
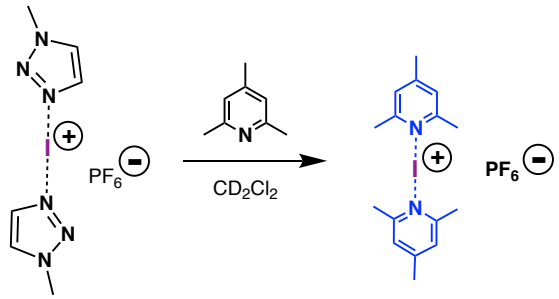


Figure S50. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of pure **22** (a), the crude mixture of reaction [I(**22**)$_2$]PF_6 in the absence (b) and in the presence of 0.2 (c), 0.6 (d), 1.0 (e), 1.4 (f) and 1.8 equivalents (g) of **16**.



To a solution of [I(**18**)$_2$]PF_6 (45.0 mg, 0.10 mmol, 1.0 eq.) in dichloromethane (1 mL), a solution of **22** (31.5 mg, 0.26 mmol, 2.6 eq.) in dichloromethane (0.5 mL) was added. The reaction mixture was stirred for 5 minutes, concentrated to ~1 mL under reduced pressure and upon the addition of Et_2O (20 mL), the desired product was precipitated from solution as a white solid, which was filtered and washed with Et_2O. The product was dried under reduced pressure to obtain [I(**22**)$_2$]PF_6 (44.7 mg,

87%). **^{1}H NMR** (500 MHz, CD_3CN): δ 7.17 (s, 4H), 2.85 (s, 12H), 2.42 (s, 6H); **^{13}C NMR** (125 MHz, CD_3CN): X; **^{15}N NMR** (51 MHz, CD_3CN): δ -173.3.

NMR characterisation for **22**: **^{15}N NMR** (51 MHz, CD_3CN): δ -67.8.

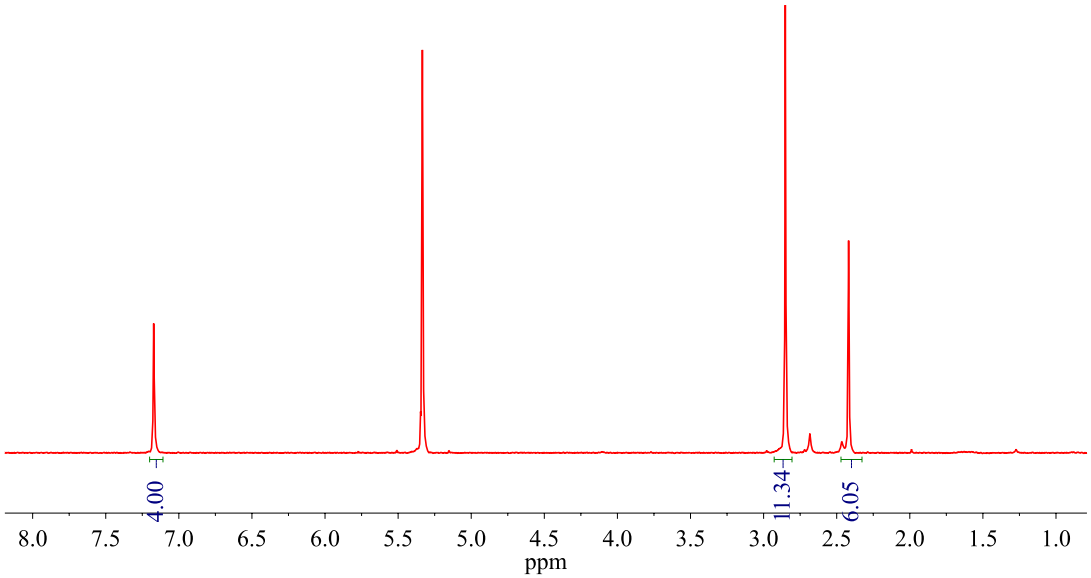


Figure S51. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 30 °C) of $[I(\mathbf{22})_2]PF_6$.

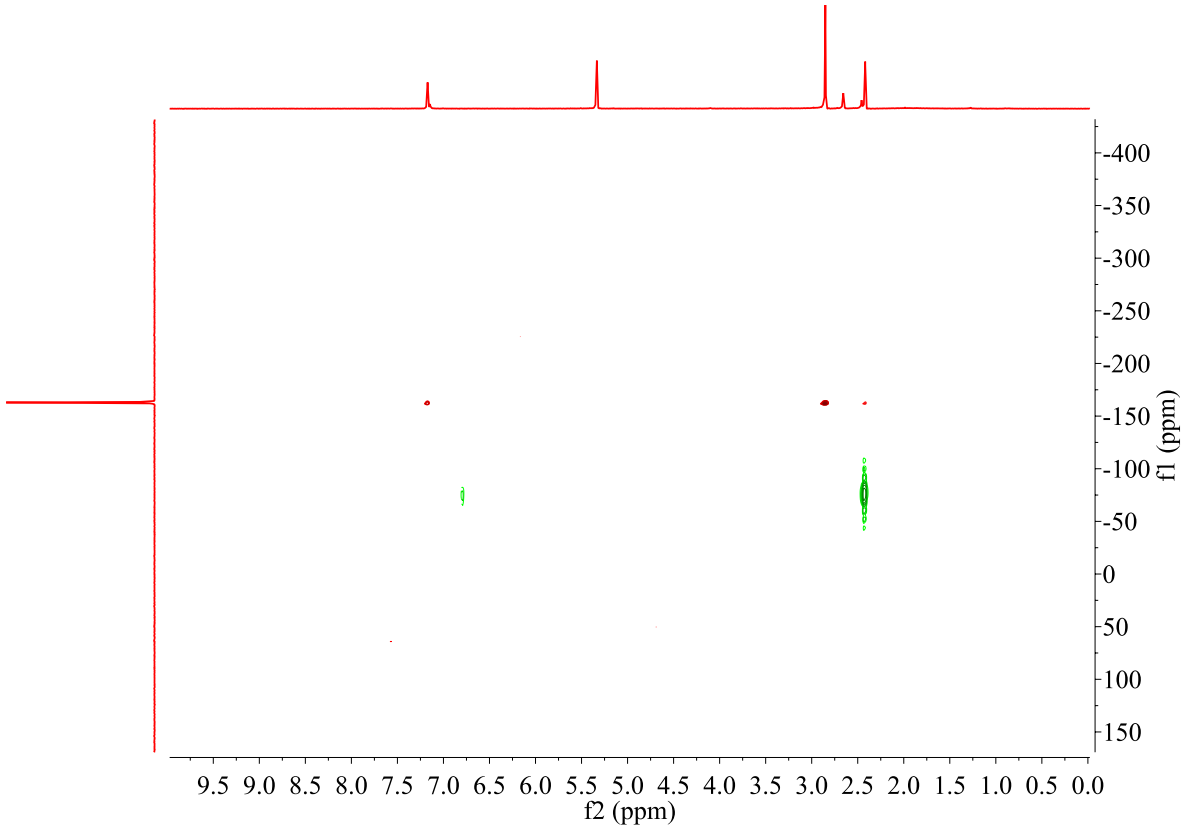


Figure S52. The stacked ^{1}H-^{15}N-HMBC spectra of ligand **22** in green and $[N\text{-}I\text{-}N]^+$ complex $[I(\mathbf{22})_2]PF_6$ in red, in CD_2Cl_2 at 30 °C.

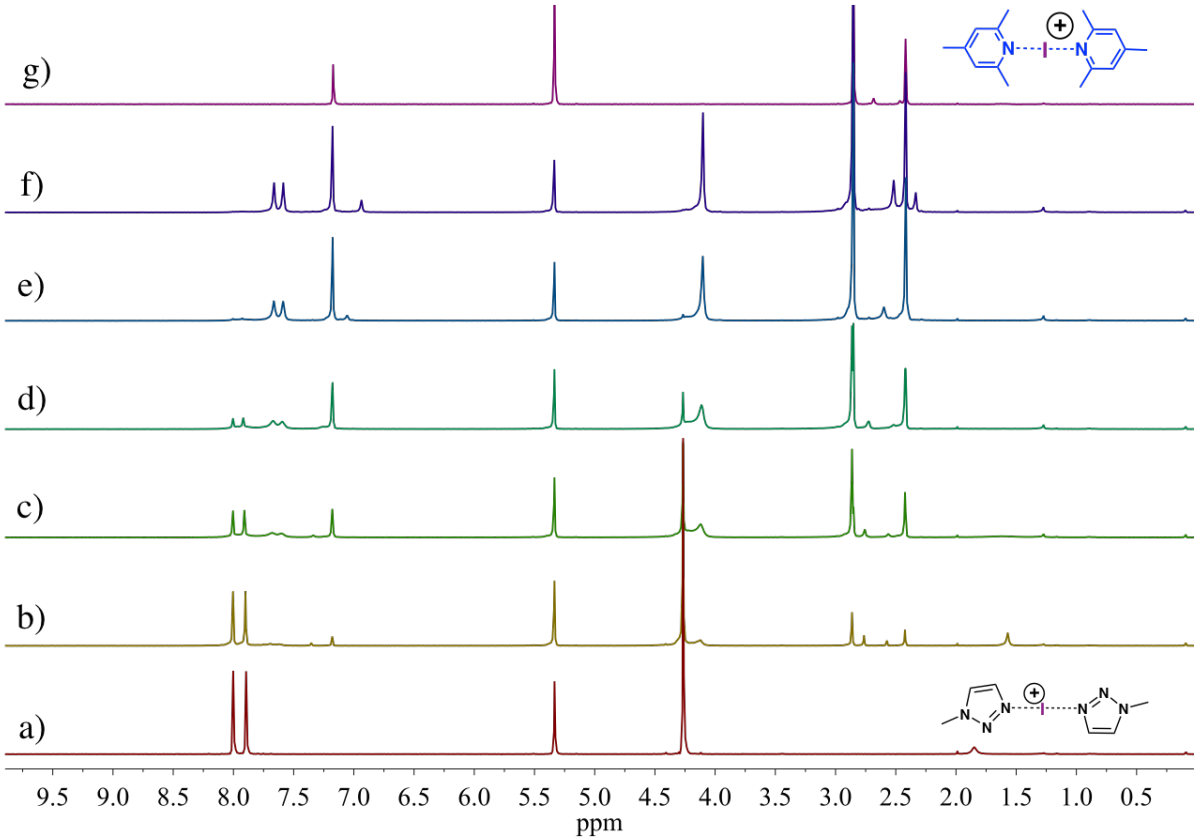
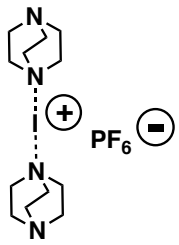


Figure S53. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 30 °C) of [I(**18**)$_2$]PF_6 in the absence (a) and in the presence of 0.2 (b), 0.6 (c), 1.0 (d), 1.5 (e), 1.8 (f) equivalents of **22** and pure [I(**22**)$_2$]PF_6 (g).

2.22 Synthesis of [I(23)$_2$]PF_6



To a solution of silver hexafluorophosphate (5.8 mg, 0.023 mmol, 1.0 eq) in CD_3CN (1.8 mL), a solution of 1,4-diazabicyclo[2.2.2]octane (**23**) (5.2 mg, 0.046 mmol, 2.0 eq) in CD_2Cl_2 (0.1 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (5.8 mg, 0.023 mmol, 1.0 eq) in CD_2Cl_2 (0.1 mL) was added. The mixture was centrifuged for 5 minutes and was filtered, then the solution of [I(**22**)$_2$]PF_6 was stored in a 4 mL vial in the fridge. ^{1}H NMR analysis (**Fig. S54**) showed complicated and broad peaks, indicating the reaction doesn't go well.

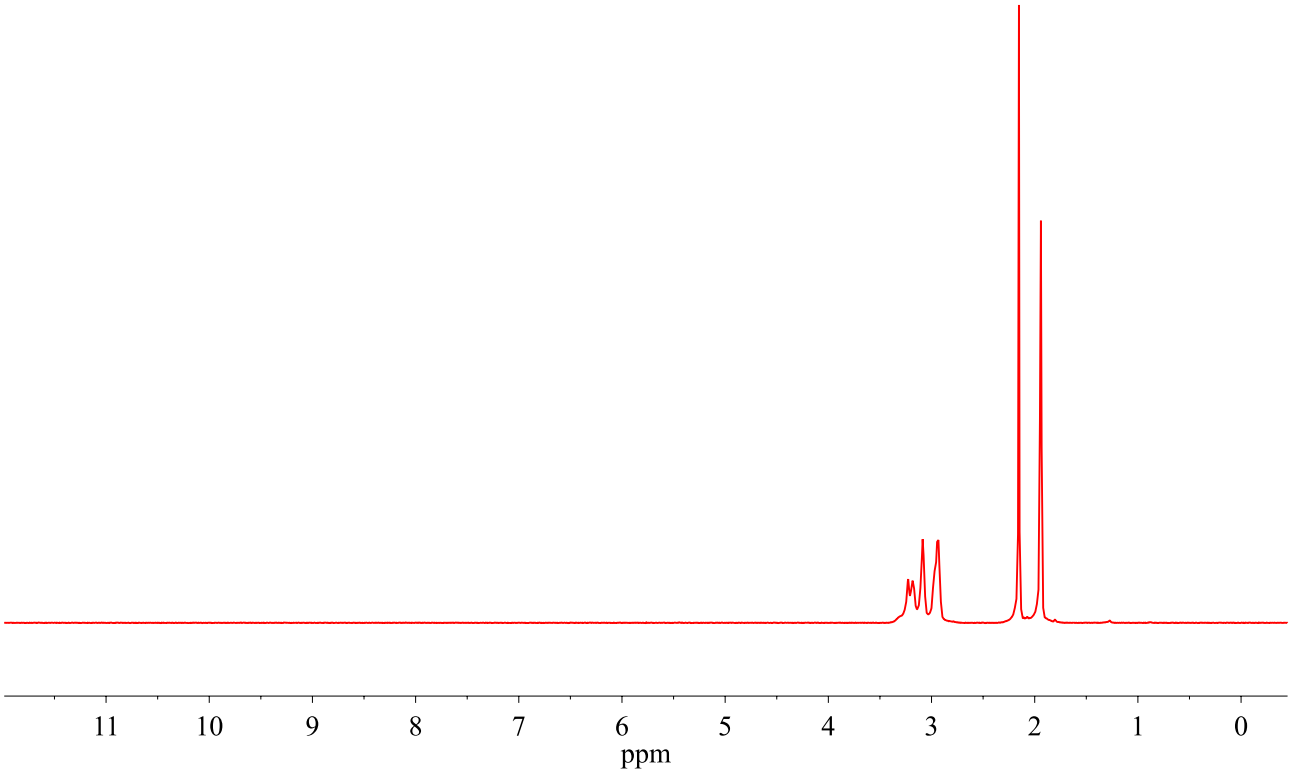
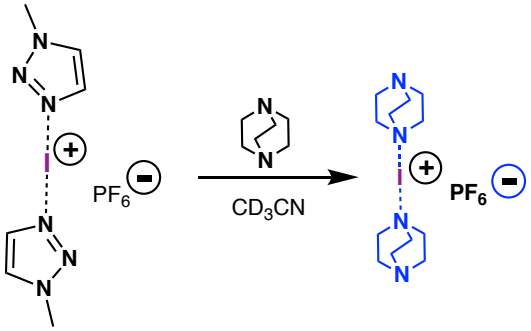


Figure S54. ^{1}H NMR spectrum of the crude mixture of reaction [I(**23**)$_2$]PF$_6$ by the [N···Ag···N]$^+$ → [N···I···N]$^+$ cation exchange reaction (CD$_3$CN, 500 MHz, 30 °C).



To a solution of [I(**18**)$_2$]PF$_6$ (116.0 mg, 0.26 mmol, 1.0 eq.) in acetonitrile (1.0 mL), a solution of **23** (59.4 mg, 0.53 mmol, 2.0 eq.) in acetonitrile (0.5 mL) was added. The reaction mixture was stirred for 5 minutes, concentrated to ~0.5 mL under reduced pressure and upon the addition of Et$_2$O (20 mL), the desired product was precipitated from solution as a white solid, which was filtered and washed with Et$_2$O. The product was dried under reduced pressure to obtain [I(**23**)$_2$]PF$_6$ (92.0 mg, 70%). **^{1}H NMR** (500 MHz, CD$_3$CN): δ 3.11-3.05 (m, 12H), 2.95-2.89 (m, 12H).

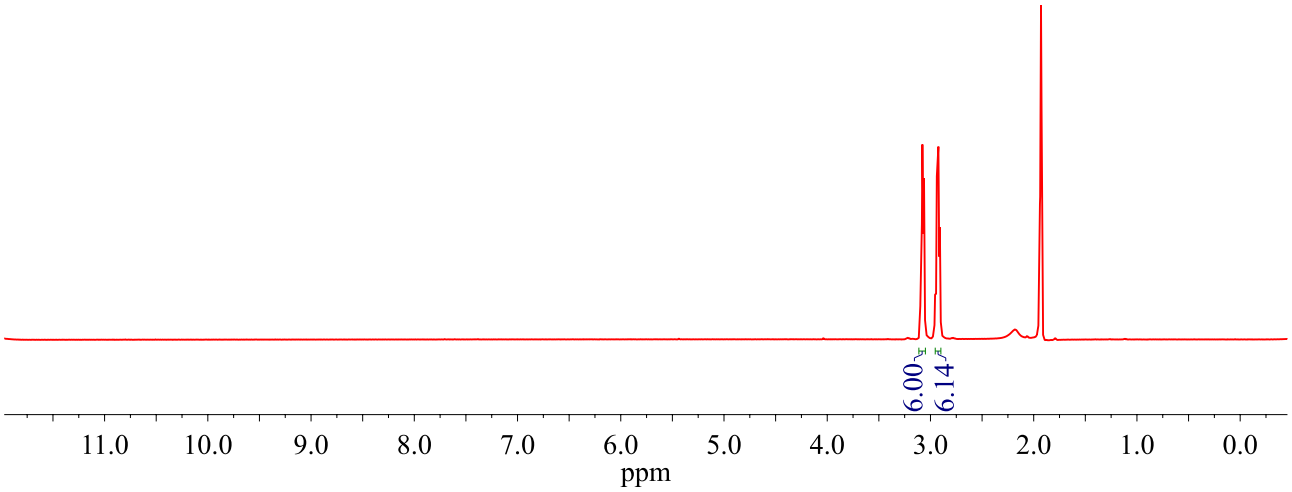


Figure S55. ^{1}H NMR spectrum (500 MHz, CD_3CN, 30 °C) of $[I(\mathbf{23})_2]PF_6$.

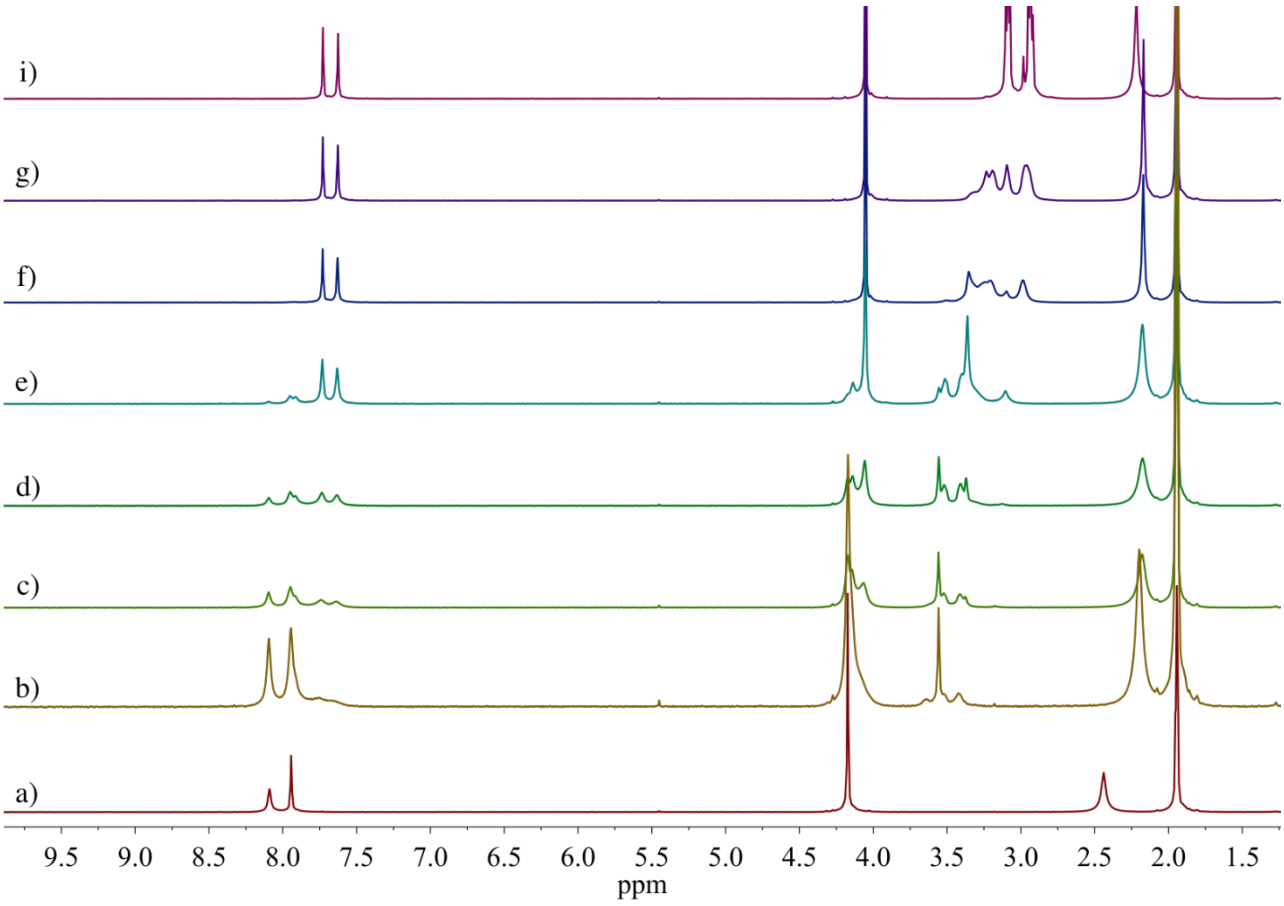
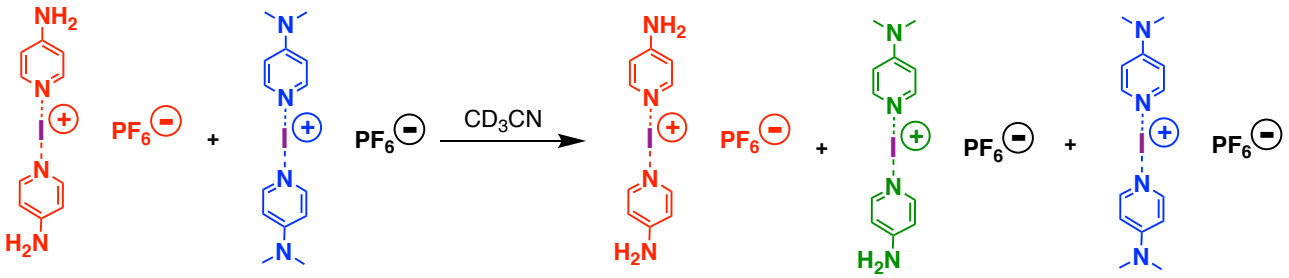


Figure S56. ^{1}H NMR spectra (500 MHz, CD_3CN, 30 °C) of $[I(\mathbf{18})_2]PF_6$ in the absence (a) and in the presence of 0.2 (b), 0.4 (c), 0.6 (d), 1.0 (e), 1.5 (f), 2.0 (g) and 2.5 (h) equivalents of **23**.

3. Synthesis of the asymmetrical iodine(I) complex [I(X)(16)]PF_6

3.1 The study of 1:1 mixture of [I(15)$_2$]PF_6 and [I(16)$_2$]PF_6



Due to the bad solubility of [I(**15**)$_2$]PF_6 in CD_2Cl_2, the study of a 1:1 mixture of [I(**15**)$_2$]PF_6 and [I(**16**)$_2$]PF_6 was conducted in CD_3CN. To a 2 mL vial, 0.5 mL of 40 mM I(**15**)$_2$]PF_6 in CD_3CN and 0.5 mL of 40 mM [I(**16**)$_2$]PF_6 in CD_3CN were added and the mixture was studied by NMR spectroscopy. The molar ratios of [I(**15**)$_2$]$^+$, [I(**15**)(**16**)]$^+$ and [I(**16**)$_2$]$^+$ in the mixture was calculated to be 1:2:1 by integration of the corresponding ^{15}N NMR signals.

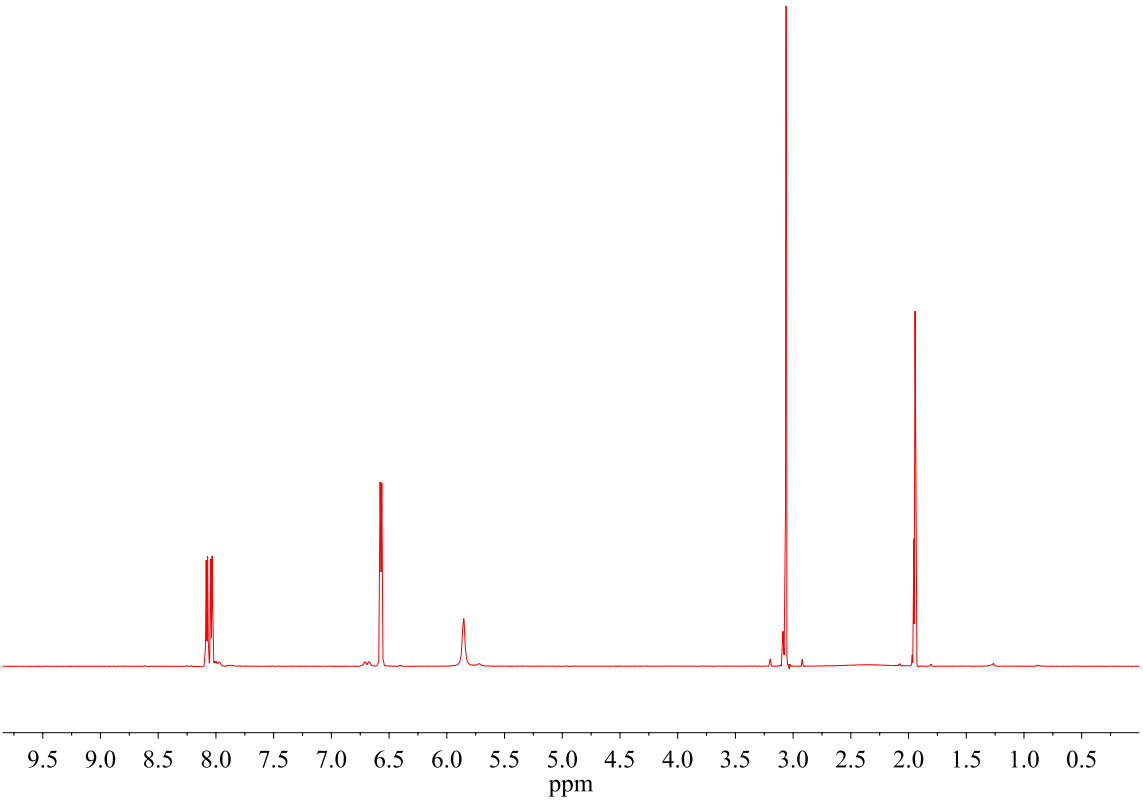


Figure S57. ^{1}H NMR spectrum of 1:1 mixture of [I(**15**)$_2$]PF_6 and [I(**16**)$_2$]PF_6 in CD_3CN at 30 °C.

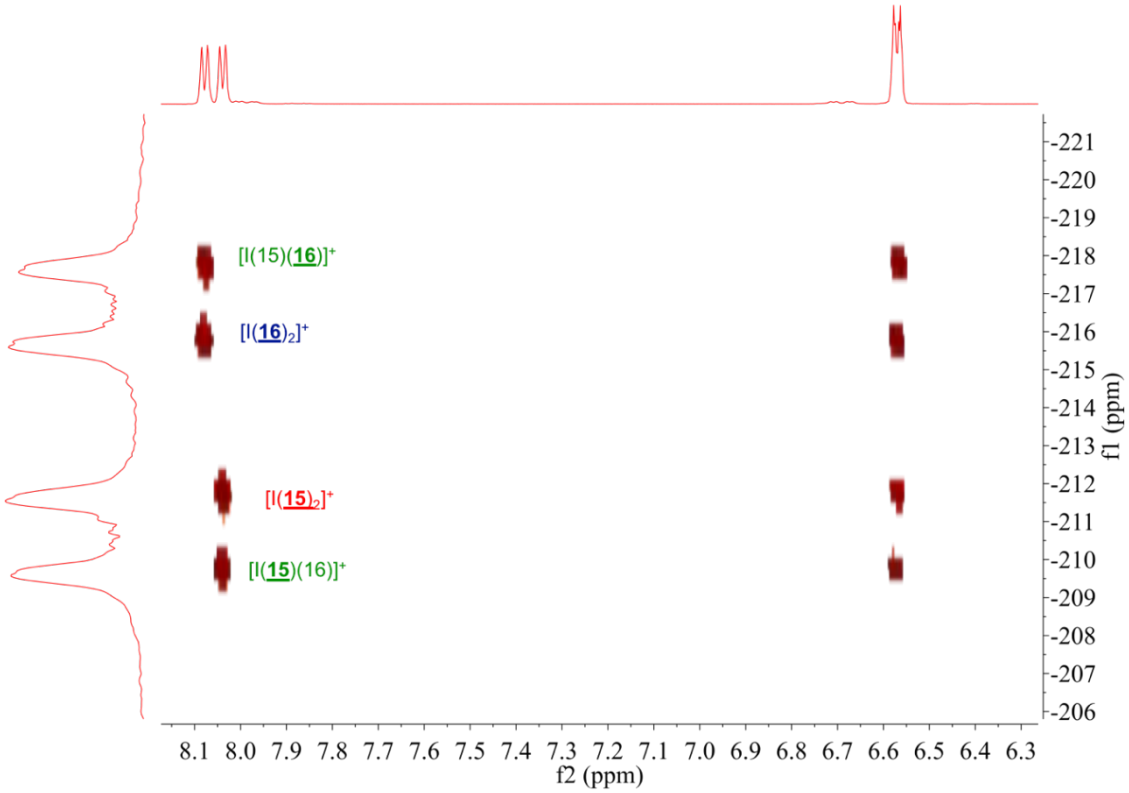


Figure S58. ^{1}H-^{15}N-HMBC NMR spectrum of 1:1 mixture of [I(**15**)$_2$]PF$_6$ and [I(**16**)$_2$]PF$_6$ in CD$_3$CN at 30 °C. [I(**15**)$_2$]$^+$: (δ^{15}N = –211.5); [I(**16**)$_2$]$^+$: (δ^{15}N = –217.6); [I(**15**)(**16**)]$^+$: (δ^{15}N(**15**) = –209.6, (δ^{15}N(**16**) = –215.6).

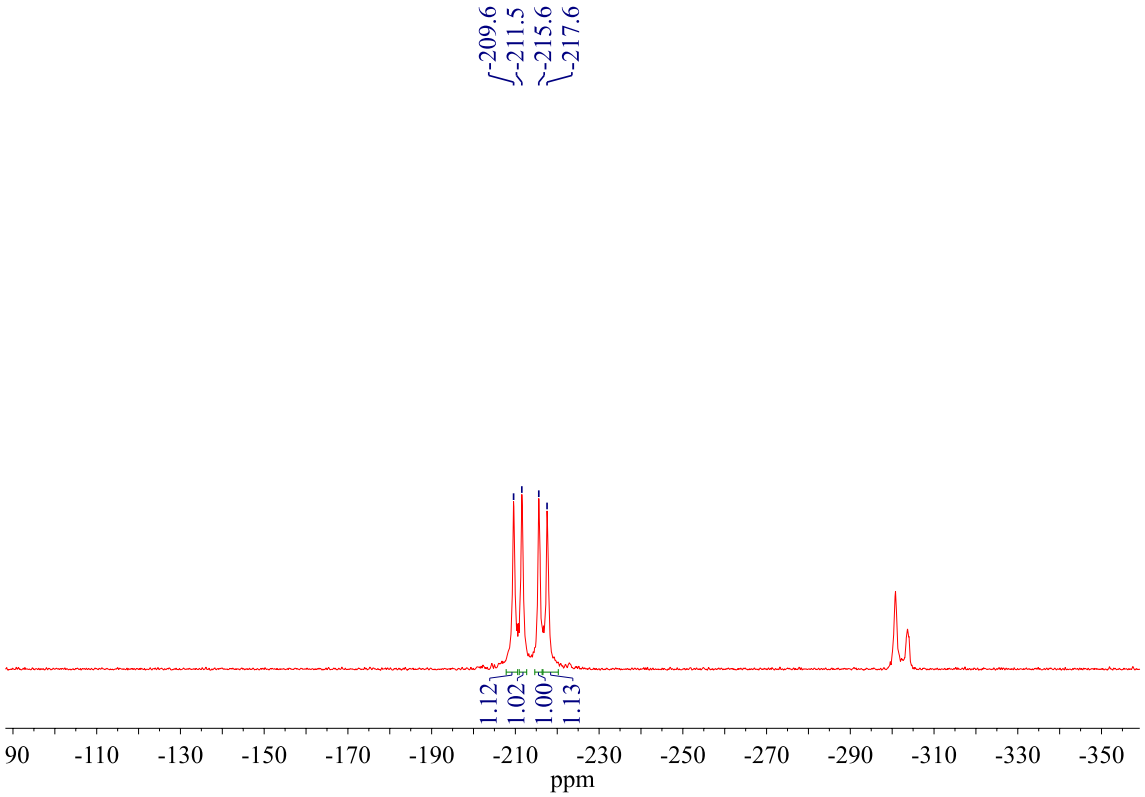


Figure S59. ^{15}N NMR spectrum of 1:1 mixture of [I(**15**)$_2$]PF$_6$ and [I(**16**)$_2$]PF$_6$, projected from the related ^{1}H-^{15}N-HMBC NMR spectrum.

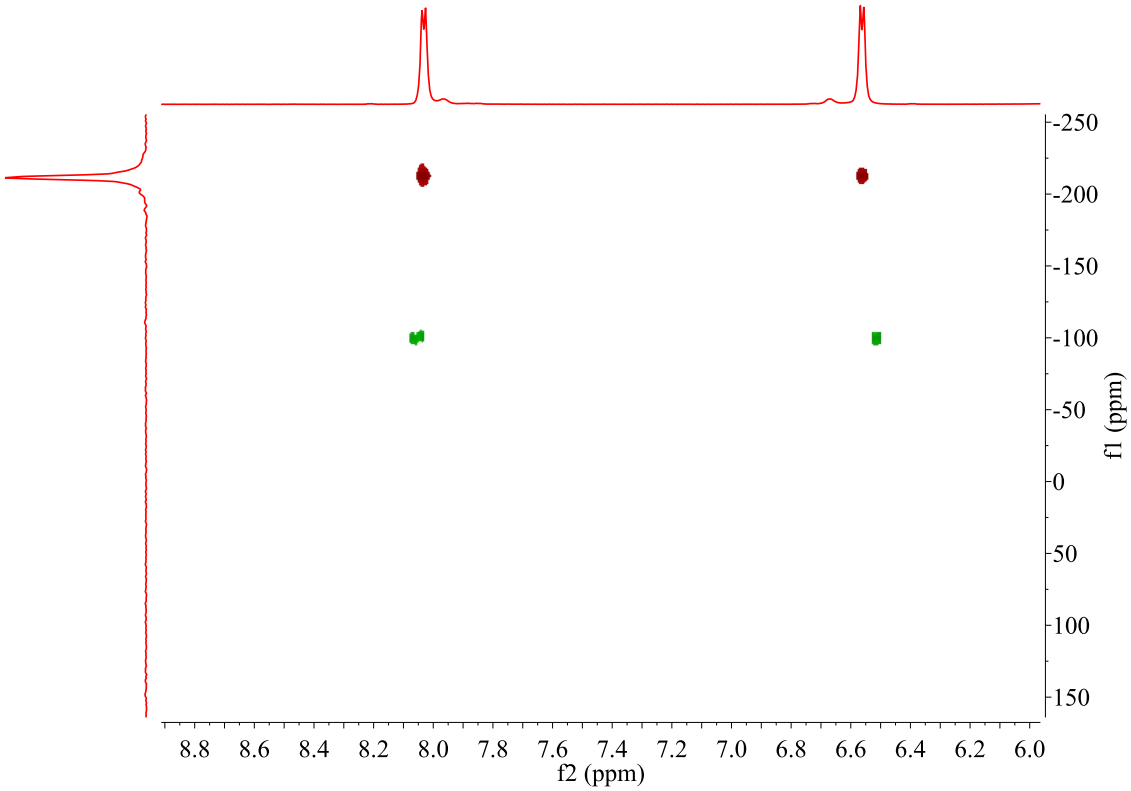
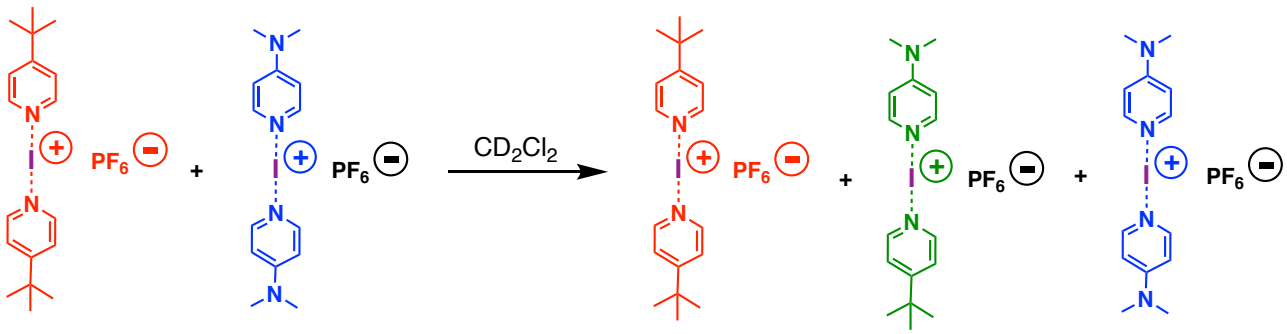


Figure S60. The stacked ^{1}H-^{15}N HMBC-NMR Spectra of ligand **15** in green and $[N\text{-}I\text{-}N]^{+}$ complex $[I(\mathbf{15})_2]PF_6$ in red, in CD_2CN at 30 °C.

3.2 The study of 1:1 mixture of $[I(12)_2]PF_6$ and $[I(16)_2]PF_6$



To a 2 mL vial, 0.5 mL of 40 mM $I(\mathbf{12})_2]PF_6$ in CD_2Cl_2 and 0.5 mL of 40 mM $[I(\mathbf{16})_2]PF_6$ in CD_2Cl_2 were added and the mixture was studied by NMR spectroscopy. The molar ratios of $[I(\mathbf{12})_2]^{+}$, $[I(\mathbf{12})(\mathbf{16})]^{+}$ and $[I(\mathbf{16})_2]^{+}$ in the mixture was calculated to be 1:3.2:1 by integration of the corresponding ^{1}H NMR signals.

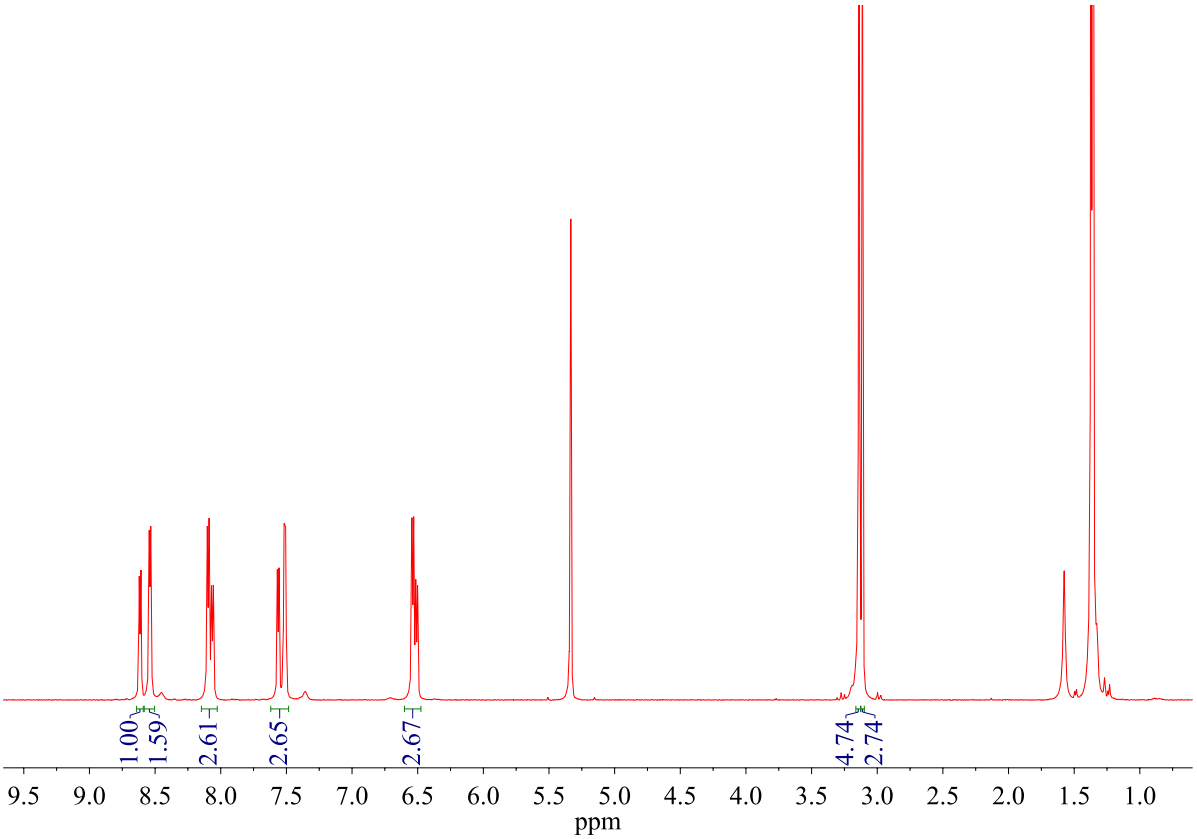


Figure S61. ^{1}H NMR spectrum of 1:1 mixture of [I(**12**)$_2$]PF$_6$ and [I(**16**)$_2$]PF$_6$ in CD_2Cl_2 at 30 °C.

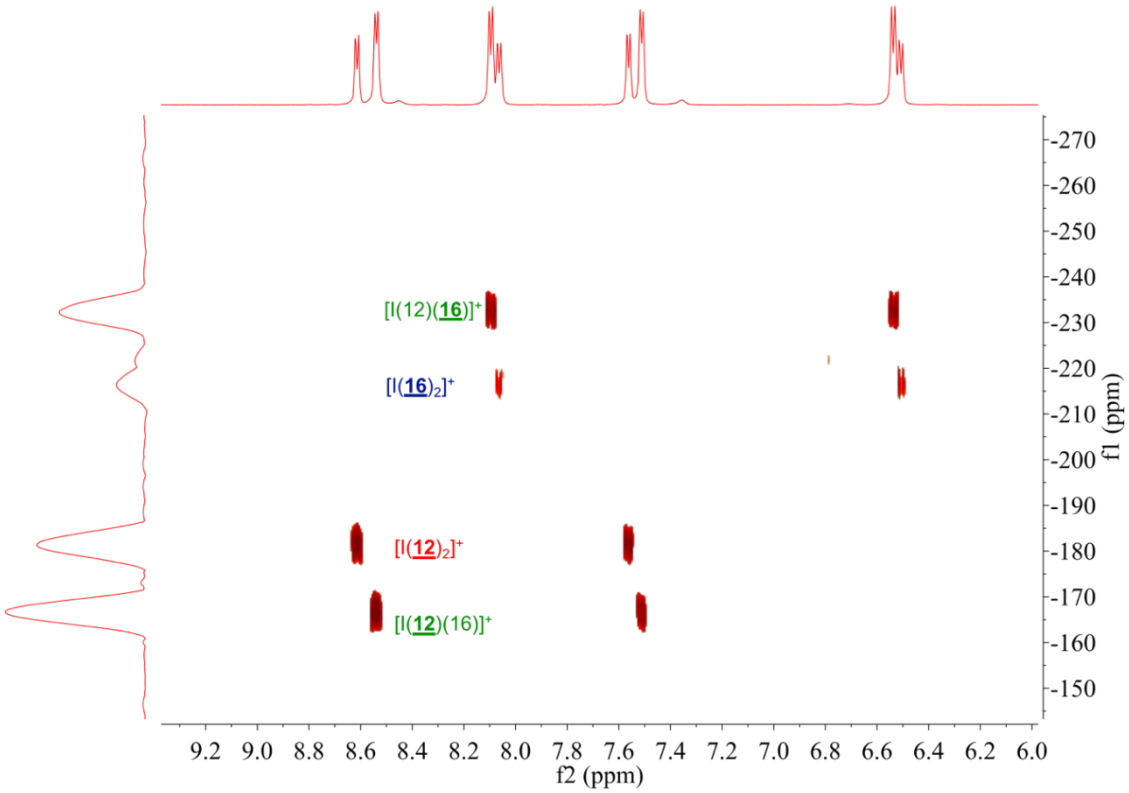
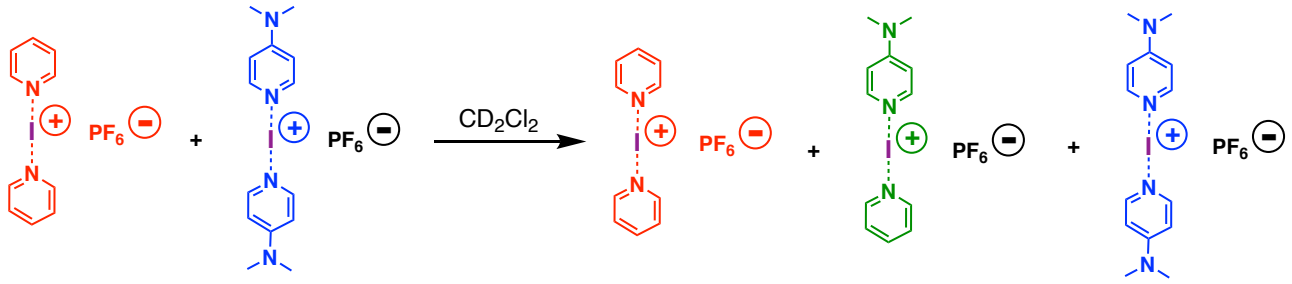


Figure S62. ^{1}H-^{15}N-HMBC NMR spectrum of 1:1 mixture of [I(**12**)$_2$]PF$_6$ and [I(**16**)$_2$]PF$_6$ in CD_2Cl_2 at 30 °C. [I(**12**)$_2$]$^+$: (δ^{15}N = –181.4); [I(**16**)$_2$]$^+$: (δ^{15}N = –216.3); [I(**12**)(**16**)]$^+$: (δ^{15}N(**12**) = –166.7, (δ^{15}N(**16**) = –232.2).

3.3 The study of 1:1 mixture of $[I(7)_2]PF_6$ and $[I(16)_2]PF_6$



To a 2 mL vial, 0.5 mL of 40 mM $I(\mathbf{7})_2]PF_6$ in CD_2Cl_2 and 0.5 mL of 40 mM $[I(\mathbf{16})_2]PF_6$ in CD_2Cl_2 were added and the mixture was studied by NMR spectroscopy. The molar ratios of $[I(\mathbf{7})_2]^+$, $[I(\mathbf{7})(\mathbf{16})]^+$ and $[I(\mathbf{16})_2]^+$ in the mixture was calculated to be about 1:4.8:1 by integration of the corresponding ^{1}H NMR signals.

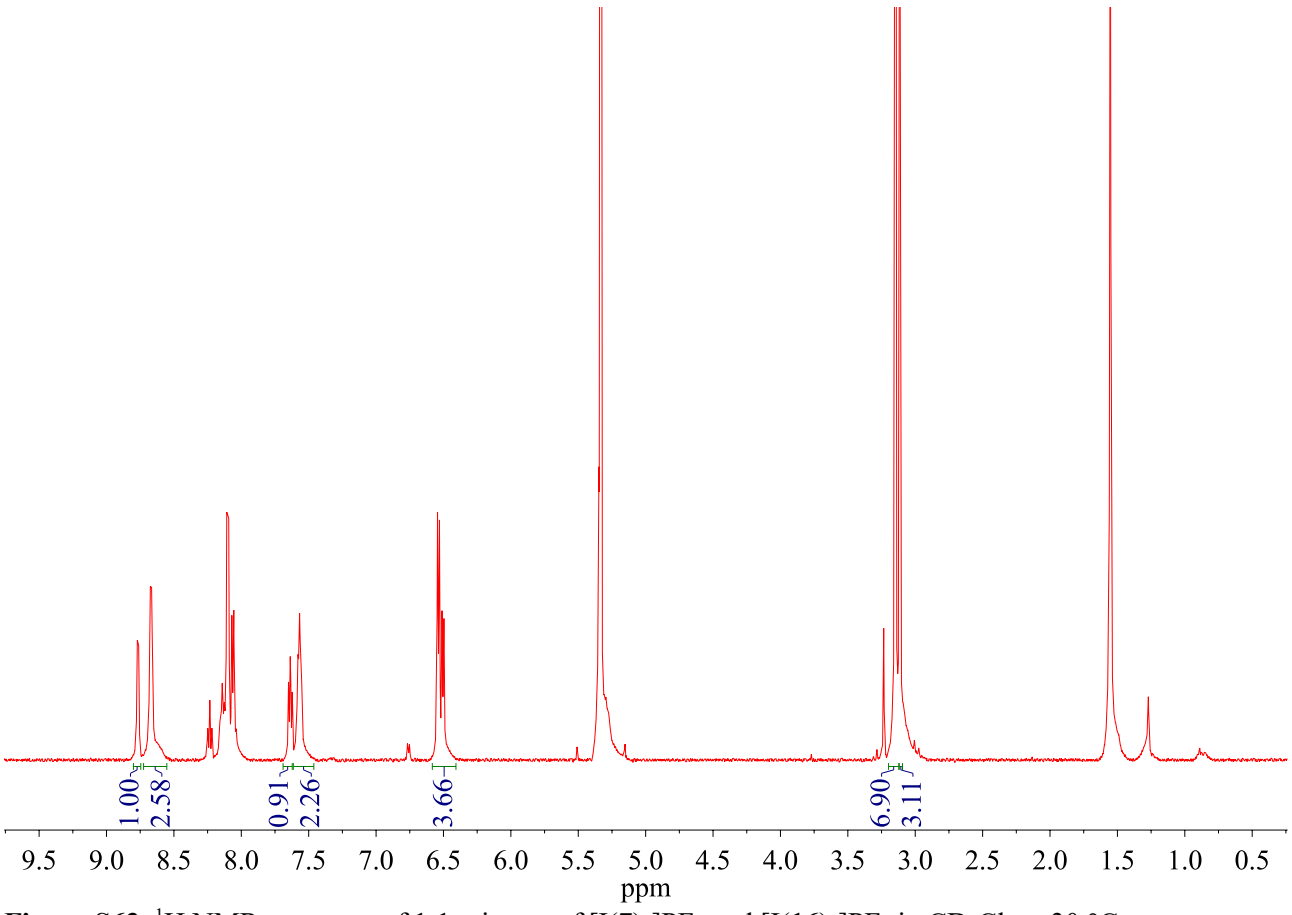


Figure S63. ^{1}H NMR spectrum of 1:1 mixture of $[I(\mathbf{7})_2]PF_6$ and $[I(\mathbf{16})_2]PF_6$ in CD_2Cl_2 at 30 °C.

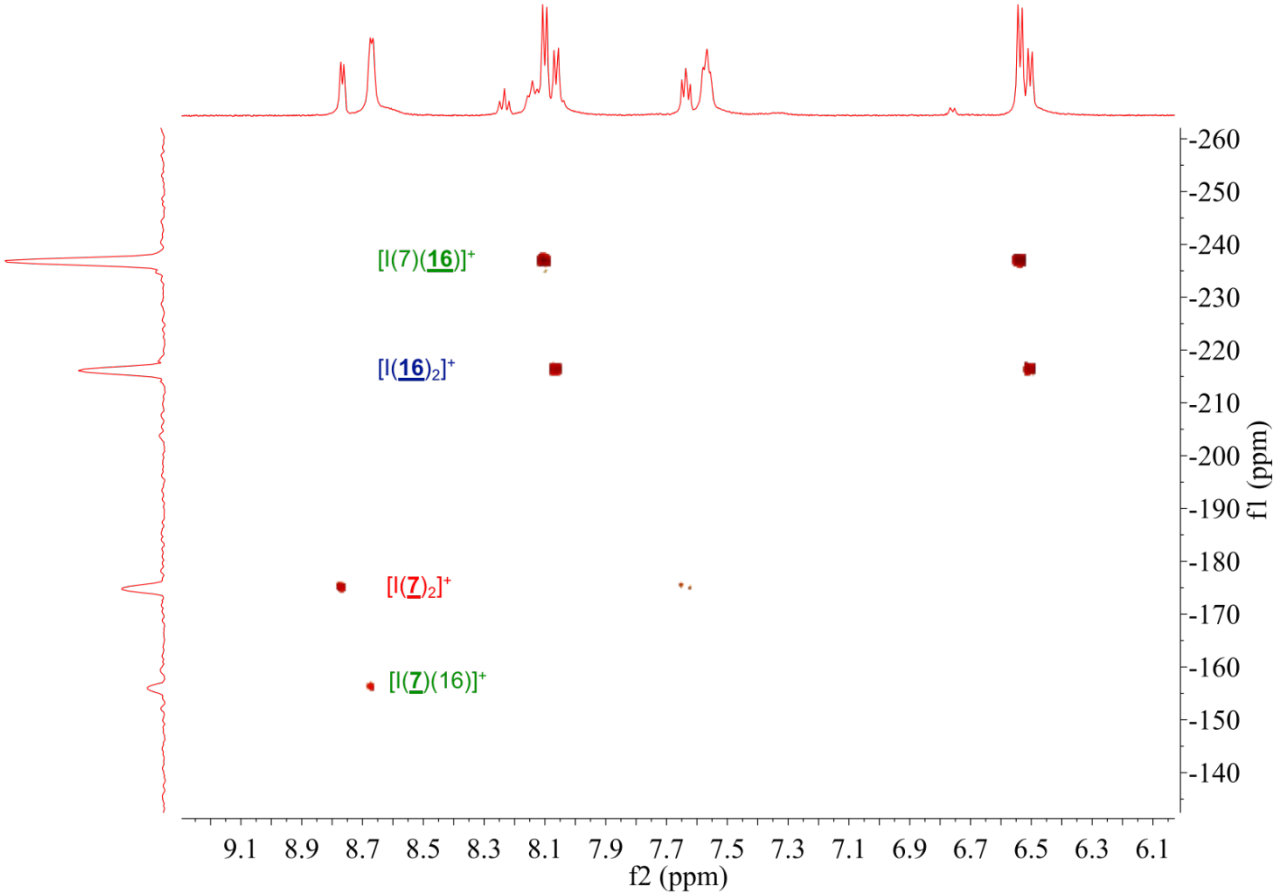
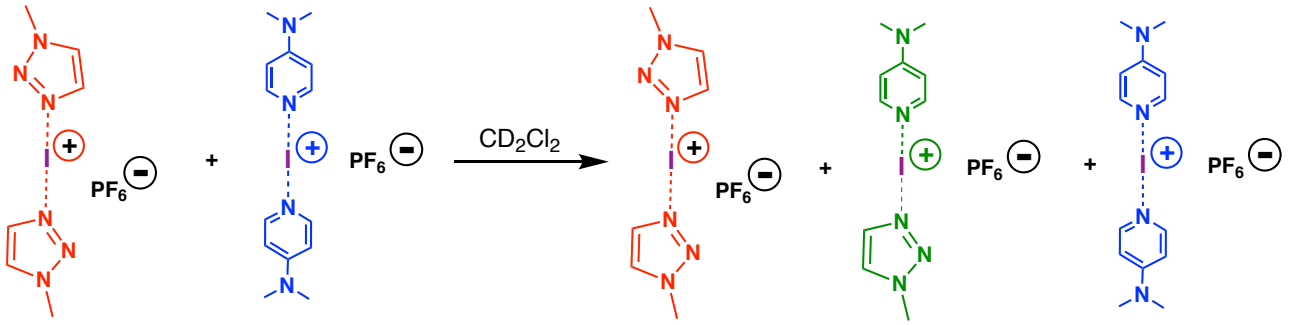


Figure S64. ^{1}H-^{15}N-HMBC NMR spectrum of 1:1 mixture of $[I(\mathbf{7})_2]PF_6$ and $[I(\mathbf{16})_2]PF_6$ in CD_2Cl_2 at 30 °C. $[I(\mathbf{7})_2]^+$: ($\delta^{15}N = -174.7$); $[I(\mathbf{16})_2]^+$: ($\delta^{15}N = -216.3$); $[I(\mathbf{7})(\mathbf{16})]^+$: ($\delta^{15}N(\mathbf{7})$ = not detectable, ($\delta^{15}N(\mathbf{16}) = -236.9$).

3.4 The study of 1:1 mixture of $[I(\mathbf{18})_2]PF_6$ and $[I(\mathbf{16})_2]PF_6$



To a 2 mL vial, 0.5 mL of 40 mM $I(\mathbf{18})_2]PF_6$ in CD_2Cl_2 and 0.5 mL of 40 mM $[I(\mathbf{16})_2]PF_6$ in CD_2Cl_2 were added and the mixture was studied by NMR spectroscopy. The molar ratios of $[I(\mathbf{18})_2]^+$, $[I(\mathbf{18})(\mathbf{16})]^+$ and $[I(\mathbf{16})_2]^+$ in the mixture was calculated to be about 1:9.5:1 by integration of the corresponding ^{1}H NMR signals.

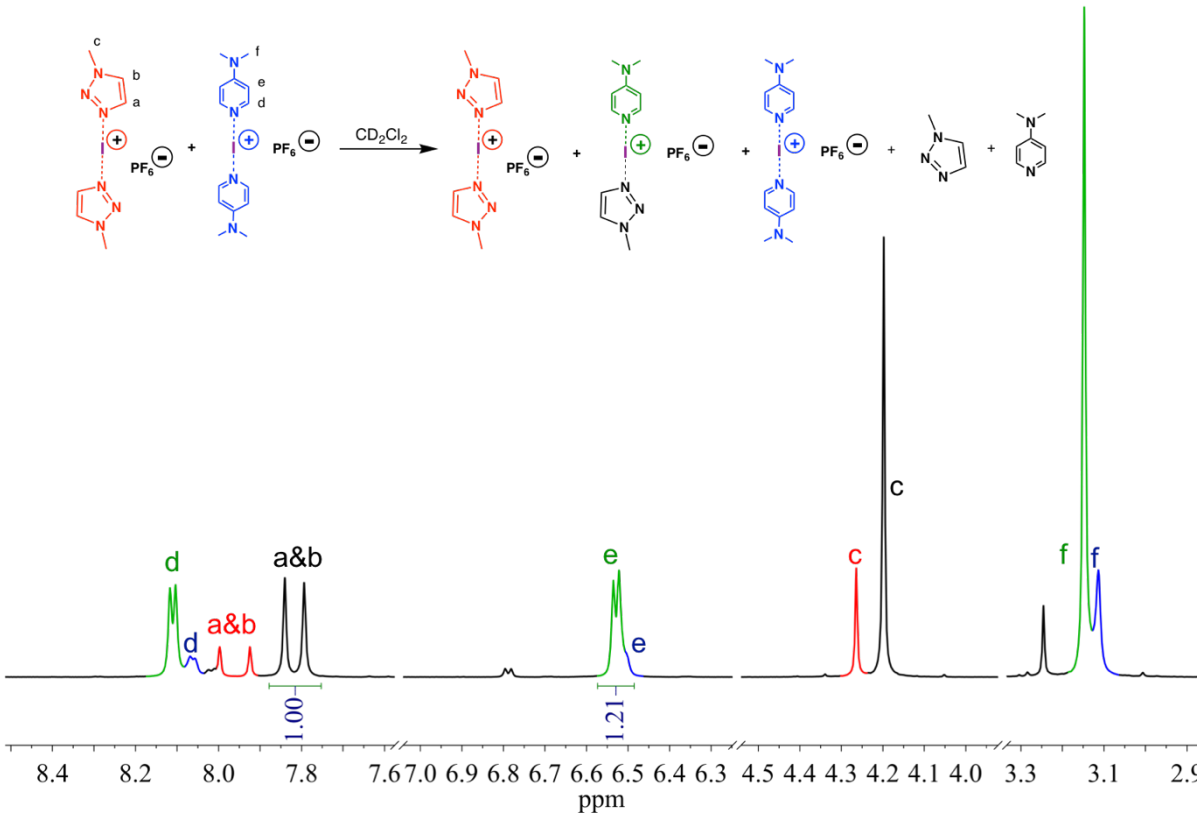


Figure S65. Partial ^{1}H NMR spectrum of 1:1 mixture of [I(**18**)$_2$]PF$_6$ and [I(**16**)$_2$]PF$_6$ in CD_2Cl_2 at 30 °C.

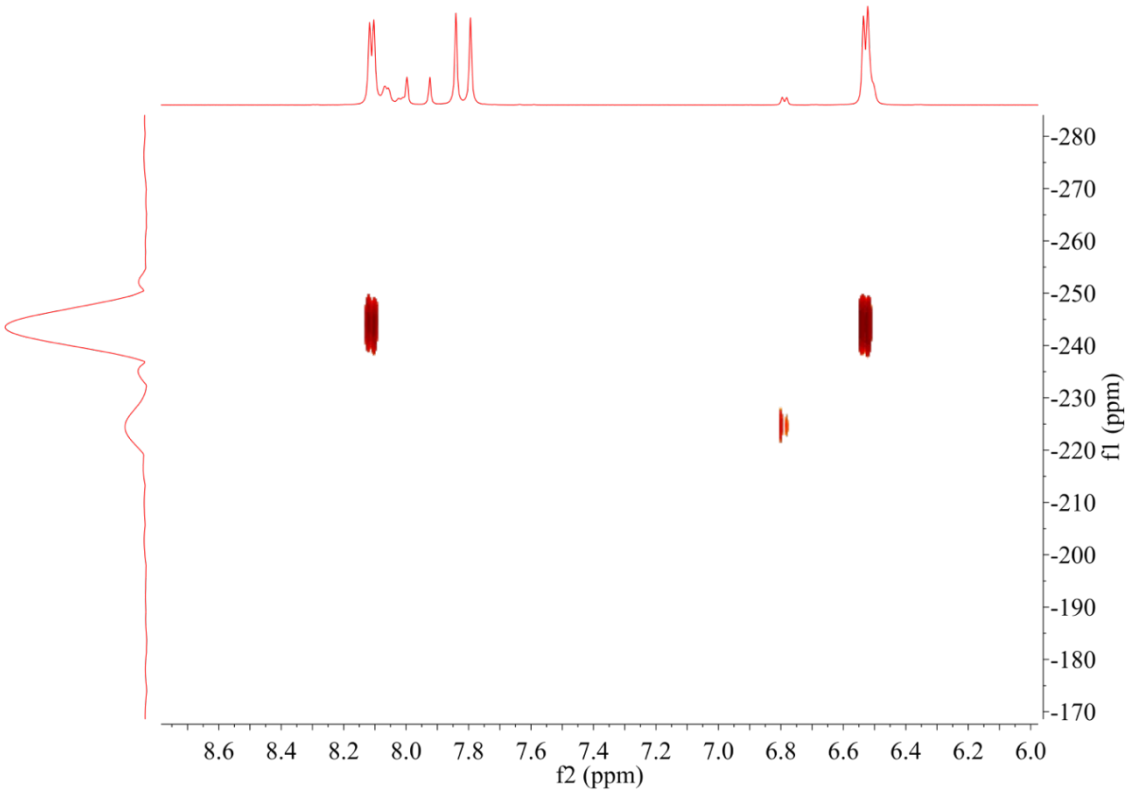
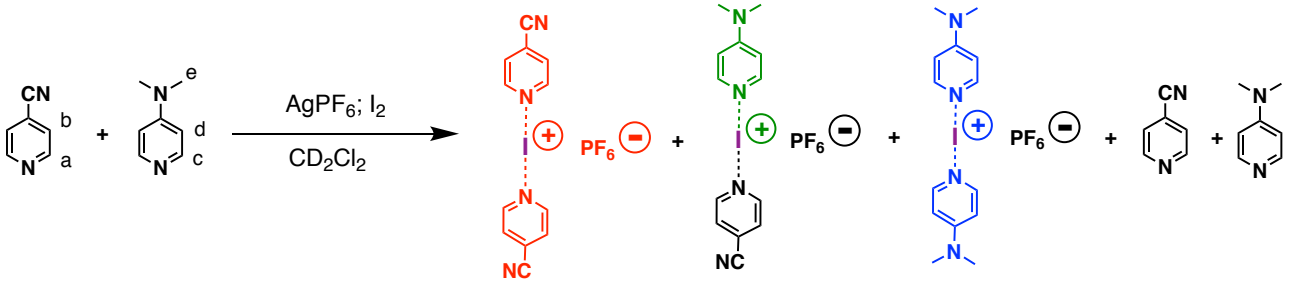


Figure S66. ^{1}H-^{15}N-HMBC NMR spectrum of 1:1 mixture of [I(**18**)$_2$]PF$_6$ and [I(**16**)$_2$]PF$_6$ in CD_2Cl_2 at 30 °C. [I(**16**)$_2$]$^+$: (δ^{15}N = –216.3); [I(**18**)(**16**)]$^+$: (δ^{15}N(**18**) = not detectable, (δ^{15}N(**16**) = –243.6).

3.5 The Study of asymmetrical iodine(I)complex [I(1)(16)]PF_6



The iodine(I) complex [I(**1**)$_2$]PF_6 cannot be obtained purely (Figure S1), Thus the asymmetrical iodine(I) complex [I(**1**)(**16**)]PF_6 were attempted from the ligands **1** and **16** directly. To a solution of silver hexafluorophosphate (6.0 mg, 0.024 mmol, 1.0 eq) in CD_2Cl_2 (1 mL), a solution of 4-cyanopyridine (**1**) (2.5 mg, 0.024 mmol, 1.0 eq) and 4-(dimethylamino)pyridine (**16**) (2.9 mg, 0.024 mmol, 1.0 eq) in CD_2Cl_2 (0.85 mL) was added. After the solution was stirred for 3 minutes at room temperature, the elemental I_2 (6.0 mg, 0.024 mmol, 1.0 eq) in CD_2Cl_2 (0.15 mL) was added. The mixture was centrifuged for 1 minute and filtered, then the reaction mixture of [I(**1**)(**16**)]PF_6 was studied by NMR spectroscopy. Probably due to the reactivity of [I(**1**)(**16**)]$^+$ and [I(**1**)$_2$]$^+$, free ligands **1** and **16** were observed in the mixture, the amounts of which cannot be ignored. The molar ratios of [I(**1**)$_2$]$^+$, [I(**1**)(**16**)]$^+$ and [I(**16**)$_2$]$^+$ in the mixture was calculated to be about 1:23.5:1.2 by integration of the corresponding ^{1}H NMR signals.

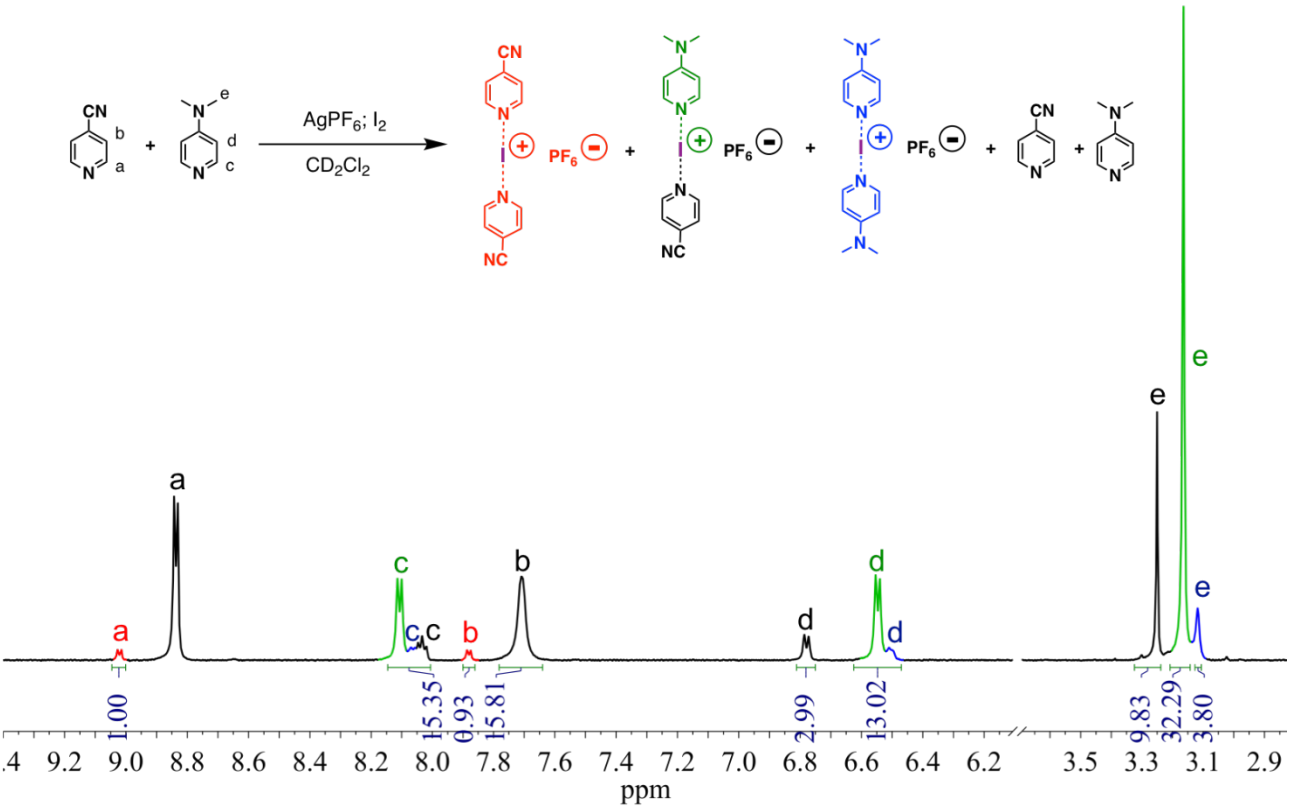


Figure S67. Partial ^{1}H NMR spectrum of the reaction mixture of [I(**1**)(**16**)]PF_6 in CD_2Cl_2 at 30 °C.

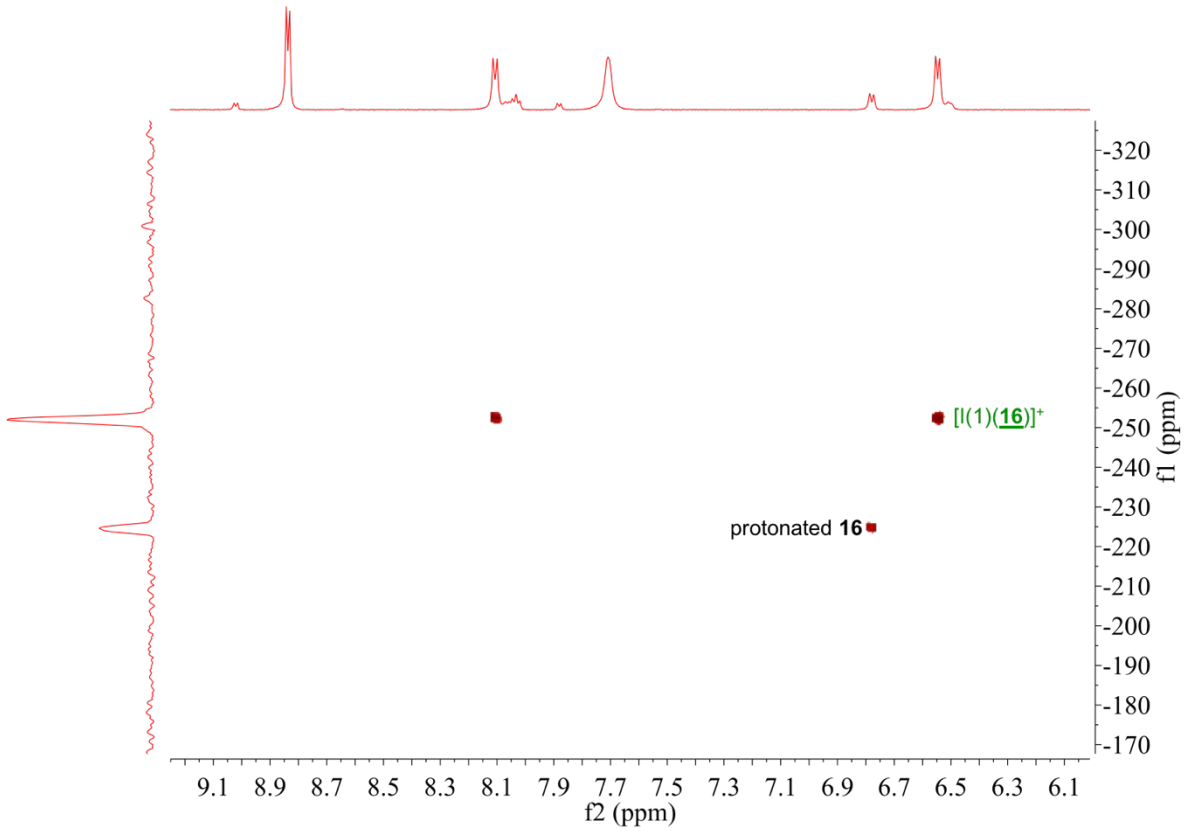


Figure S68. ^{15}N NMR spectrum of the reaction mixture of [I(**1**)(**16**)]PF_6 in CD_2Cl_2 at 30 °C. $[I(\mathbf{16})_2]^+$: (δ^{15}N = –216.2); $[I(\mathbf{1})(\mathbf{16})]^+$: ($\delta^{15}$N(**1**) = not detectable, (δ^{15}N(**16**) = –252.0).

Table S1. The ^{15}N chemical shift (δ_N), $\Delta\delta_N$, $\Delta\Delta\delta_N$ values for ligands **16**, **15**, **12**, **18**, **1**, and relative complexes.

Comp*	δ_N [a]	$\Delta\delta_N$ [b]	$\Delta\Delta\delta_N$ [c]
16	-108.6 (-104.9) [d]	--	--
$[I(\mathbf{16})_2]^+$	-216.2 (-215.6) [d]	-107.6 (-110.7) [d]	--
15	-99.1 [d]	--	--
$[I(\mathbf{15})_2]^+$	-211.4 [d]	-112.3 [d]	--
$[I(\mathbf{15})(\mathbf{16})]^+$	**15**: -209.6 [d]	**15**: -110.5 [d]	**15**: +1.8 [d]
	16: -217.6 [d]	**16**: -112.7 [d]	**16**: -2.0 [d]
12	-74.7	--	--
$[I(\mathbf{12})_2]^+$	-181.4	-106.7	--
$[I(\mathbf{12})(\mathbf{16})]^+$	**15**: -166.7	**15**: -92.0	**15**: +14.7
	16: -232.2	**16**: -123.6	**16**: -16.3
7	-66.8	--	--
$[I(\mathbf{7})_2]^+$	-174.7	-107.9	--
$[I(\mathbf{7})(\mathbf{16})]^+$	**7**: -156.0	**7**: -89.2	**7**: +18.7
	16: -236.9	**16**: -128.3	**16**: -21.0
18	-31.1	--	--
$[I(\mathbf{18})_2]^+$	-142.4	-111.3	--
$[I(\mathbf{18})(\mathbf{16})]^+$	**18**: --	**18**: --	**18**: --
	16: -243.6	**16**: -135.0	**16**: -27.4
1	-52.8	--	--
$[I(\mathbf{1})_2]^+$	-168.8	-116.0	--
$[I(\mathbf{1})(\mathbf{16})]^+$	**1**: --	**1**: --	**1**: --
	16: -252.0	**16**: -143.4	**16**: -35.8

[a] δ_N is the **^{15}N** chemical shift of pyridinic nitrogen of [N-I-N] complexes or free ligands [b] $\Delta\delta_N$ are The ^{15}N NMR chemical shift change of pyridinic nitrogen of DMAP upon complexation; [c] $\Delta\Delta\delta_N$ are the chemical shift differences of δ_N between the asymmetrical complex and the analogue symmetrical one, $\Delta\Delta\delta_N = \Delta\delta_N$(asymm.) - $\Delta\delta_N$(symm.); [d] performed in CD_3CN.

4. X-ray Crystallographic Studies

The single crystal X-ray data for [I(**23**)$_2$]PF$_6$ and [I(**18**)(**16**)]PF$_6$ were collected at 120 K using an Agilent SuperNova dual wavelength diffractometer with an Atlas detector using mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The program CrysAlisPro[5] was used for the data collection and reduction on the SuperNova diffractometer, and the intensities were absorption corrected using a gaussian face index absorption correction method. All structures were solved by intrinsic phasing (SHELXT)[6] and refined by full-matrix least squares on F^2 using the Olex2,[7] utilising the SHELXL-2015 module.[8] Anisotropic displacement parameters were assigned to non-H atoms and isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with $U_{iso}(H) = 1.2\ U_{eq}$ (aromatic) or $1.5\ U_{eq}$ (alkyl) of their respective parent atoms. The X-ray single crystal data and CCDC numbers of all new structures are included below.

CCDC 2127227-2127228 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Crystal data for [I(**23**)$_2$]PF$_6$: CCDC-2127228, [$C_{12}H_{24}IN_4$][PF_6], M = 496.22, colourless plate, 0.26 × 0.10 × 0.05 mm^3, Orthorhombic, space group $P2_12_12_1$, a = 10.3407(1) Å, b = 17.5114(3) Å, c = 20.2383(3) Å, V = 3664.75(9) Å^3, Z = 8, D_{calc} = 1.799 gcm^{-3}, F000 = 1968, μ = 15.14 mm^{-1}, T = 120 K, θ_{max} = 72.1°, 7153 total reflections, 6777 with $I_o > 2\sigma(I_o)$, R_{int} = 0.034, 7153 data, 434 parameters, 21 restraints, GooF = 1.04, 0.44 < dΔρ < –0.75 eÅ^{-3}, R[$F^2 > 2\sigma(F^2)$] = 0.029, *w*R(F^2) = 0.064.

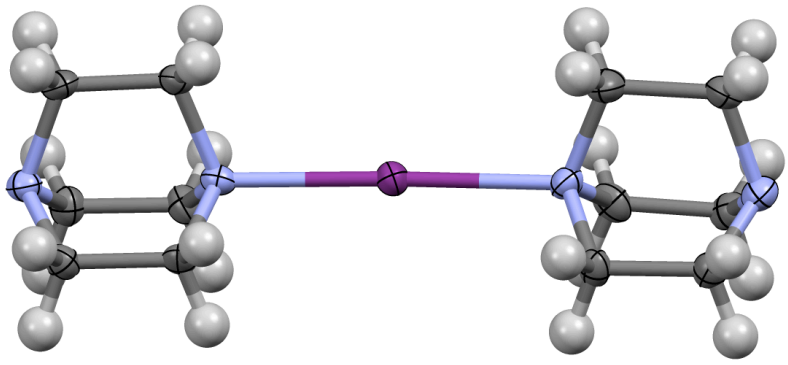


Figure S69. The crystal structure of [I(**23**)$_2$]PF$_6$ (thermal ellipsoids at 50% probability; PF_6 anion omitted for clarity). A second crystallographically independent molecule of [[I(**23**)$_2$]PF$_6$ has been omitted for clarity.

Crystal data for [I(**18**)(**16**)]PF$_6$: CCDC-2127227, [$C_{10}H_{15}IN_5$][PF_6], M = 477.14, colourless plate, 0.18 × 0.16 × 0.02 mm^3, Orthorhombic, space group $Pca2_1$, a = 10.7960(3) Å, b = 20.9622(5) Å, c = 14.3983(3) Å, V = 3258.45(14) Å^3, Z = 8, D_{calc} = 1.945 gcm^{-3}, F000 = 1856, μ = 17.02 mm^{-1}, T = 120 K, θ_{max} = 72.1°, 4634 total reflections, 4184 with $I_o > 2\sigma(I_o)$, R_{int} = 0.049, 4634 data, 422 parameters, 56 restraints, GooF = 1.03, 4.23 < dΔρ < –0.80 eÅ^{-3}, R[$F^2 > 2\sigma(F^2)$] = 0.061, *w*R(F^2) = 0.136.

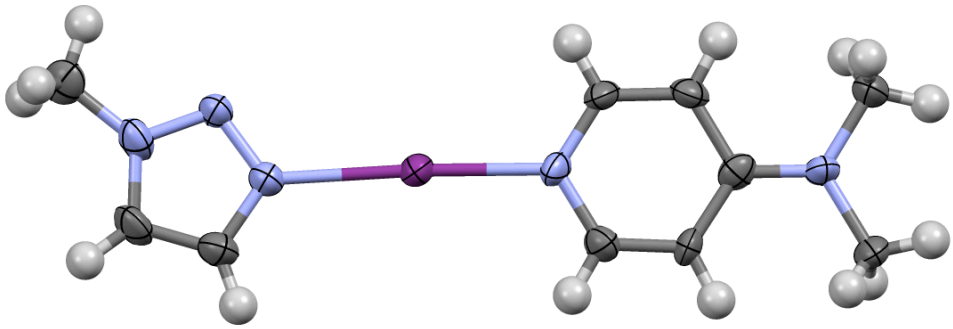


Figure S70. The crystal structure of [I(**18**)(**16**)]PF_6 (thermal ellipsoids at 50% probability; PF_6 anion omitted for clarity). A second crystallographically independent molecule of [I(**18**)(**16**)]PF_6 has been omitted for clarity.

5. Computational Details

General Considerations

The geometry calculations for complexes were done at the M06-2X/def2-TZVP level of theory6 using the SPARTAN20 program[9] with dichloromethane (dielectric = 8.82) as the solvent using the conductor like polarizable continuum model (C-PCM).[10,11] The initial models were built using SPARTAN20 and optimized at the MM-level before the DFT calculations. The complexes $[I(\mathbf{L})(\mathbf{16})]^+$ (**L** = **16**, **15**, **12**, **7**, **18**, **1**) were built up from the corresponding MM-level optimized DMAP (**16**) and pyridine **L** so that the N···N distance was ca. 4.50 Å and the N–I–N angle ca. 180º and then optimized with the given DFT method.

Table S2: Computational (DFT) Bond Lengths and Angles for complexes$[I(\mathbf{16})_2]^+$ and $[I(\mathbf{L})(\mathbf{16})]^+$ (**L** = **15**, **12**, **7**, **18**; in order of decreasing Lewis basicity from top to bottom) (The available experimental results are also included).

Complex*	N_L–I [Å] (DFT/**XRD**)	I–N_{16} [Å] (DFT/**XRD**)	N_L–I–N_{16} [°] (DFT/**XRD**)	
$[I(\mathbf{16})_2]^+$	2.243/**2.236(3)**	2.245/**2.251(3)**	179.32/**179.9(1)**	3.05/2.92
$[I(\mathbf{15})(\mathbf{16})]^+$	2.252	2.240	179.53	3.25/3.06
$[I(\mathbf{12})(\mathbf{16})]^+$	2.286	2.209	179.44	
$[I(\mathbf{7})(\mathbf{16})]^+$	2.301	2.201	179.92	3.38/3.02
$[I(\mathbf{18})(\mathbf{16})]^+$	2.317/**2.335(8)** **2.340(8)**	2.181/**2.187(8)** **2.163(8)**	179.49/**178.1(4)** **177.0(4)**	
$[I(\mathbf{1})(\mathbf{16})]^+$	2.343	2.168	179.55	2.82/2.71

Cartesian Coordinates

$[I(\mathbf{16})_2]^+$

LUMO/HOMO (ev) 3.05/2.92

H	-1.989000	-2.388000	0.562000
C	-1.085000	-2.954000	0.378000
C	1.254000	-4.265000	-0.108000
N	0.020000	-2.242000	0.109000
C	-1.094000	-4.323000	0.420000
C	0.103000	-5.043000	0.175000
C	1.165000	-2.900000	-0.129000
H	-2.022000	-4.826000	0.639000
H	2.034000	-2.291000	-0.343000
H	2.210000	-4.725000	-0.307000
H	-0.030000	2.439000	2.024000
C	-0.057000	2.983000	1.088000
C	-0.121000	4.238000	-1.329000
N	-0.070000	2.243000	-0.031000
C	-0.074000	4.352000	1.074000
C	-0.107000	5.044000	-0.163000
C	-0.102000	2.875000	-1.215000
H	-0.061000	4.877000	2.016000
H	-0.112000	2.245000	-2.096000
H	-0.147000	4.672000	-2.317000
N	-0.124000	6.382000	-0.227000
C	-0.111000	7.172000	0.995000
H	0.791000	6.975000	1.578000
H	-0.983000	6.951000	1.613000

H	-0.130000	8.225000	0.732000
C	-0.151000	7.050000	-1.519000
H	-0.156000	8.123000	-1.359000
H	-1.046000	6.778000	-2.083000
H	0.728000	6.790000	-2.112000
I	-0.031000	0.000000	0.051000
N	0.145000	-6.381000	0.207000
C	-1.059000	-7.145000	0.499000
H	-1.829000	-6.969000	-0.255000
H	-1.461000	-6.879000	1.478000
H	-0.812000	-8.201000	0.503000
C	1.389000	-7.079000	-0.082000
H	1.210000	-8.148000	-0.030000
H	2.162000	-6.819000	0.644000
H	1.751000	-6.834000	-1.082000

[I(**15**)(**16**)]$^{+}$
LUMO/HOMO (ev) 3.25/3.06

H	-0.496000	2.014000	-1.047000
C	-0.308000	1.111000	-1.614000
C	0.185000	-1.226000	-2.926000
N	-0.028000	0.008000	-0.902000
C	-0.359000	1.118000	-2.981000
C	-0.111000	-0.077000	-3.703000
C	0.213000	-1.136000	-1.561000
H	-0.589000	2.045000	-3.484000
H	0.436000	-2.004000	-0.953000
H	0.388000	-2.181000	-3.384000
H	-1.957000	0.062000	3.755000
C	-1.028000	0.085000	4.312000
C	1.377000	0.141000	5.594000
N	0.102000	0.096000	3.588000
C	-1.027000	0.100000	5.681000
C	0.201000	0.129000	6.372000
C	1.280000	0.124000	4.229000
H	-1.963000	0.090000	6.223000
H	2.166000	0.132000	3.607000
H	2.350000	0.163000	6.066000
N	0.248000	0.145000	7.711000
I	0.031000	0.059000	1.337000
N	-0.153000	-0.119000	-5.041000
C	-0.463000	1.083000	-5.800000
H	0.278000	1.864000	-5.616000
H	-1.450000	1.468000	-5.538000
H	-0.455000	0.841000	-6.858000
C	0.101000	-1.369000	-5.740000
H	0.007000	-1.199000	-6.808000
H	-0.618000	-2.136000	-5.445000
H	1.109000	-1.735000	-5.533000
H	-0.595000	0.138000	8.259000
H	1.128000	0.167000	8.199000

[I(**12**)(**16**)]$^{+}$
LUMO/HOMO (ev) 3.03/2.93

H	-1.954000	0.701000	3.048000

C	-1.063000	0.456000	3.613000
C	1.242000	-0.188000	4.919000
N	0.016000	0.093000	2.900000
C	-1.059000	0.520000	4.979000
C	0.120000	0.195000	5.698000
C	1.144000	-0.223000	3.556000
H	-1.965000	0.819000	5.484000
H	1.991000	-0.511000	2.946000
H	2.183000	-0.455000	5.375000
H	0.467000	1.914000	-1.764000
C	0.214000	1.018000	-2.316000
C	-0.437000	-1.294000	-3.592000
N	-0.097000	-0.063000	-1.591000
C	0.213000	0.990000	-3.693000
C	-0.117000	-0.186000	-4.373000
C	-0.416000	-1.196000	-2.213000
H	0.473000	1.892000	-4.228000
H	-0.660000	-2.043000	-1.583000
H	-0.704000	-2.243000	-4.033000
I	-0.049000	0.022000	0.693000
N	0.172000	0.249000	7.034000
C	-1.003000	0.647000	7.796000
H	-1.832000	-0.042000	7.626000
H	-1.322000	1.655000	7.521000
H	-0.755000	0.638000	8.852000
C	1.401000	-0.100000	7.732000
H	1.240000	0.006000	8.800000
H	2.219000	0.558000	7.434000
H	1.688000	-1.133000	7.524000
C	-0.112000	-0.214000	-5.894000
C	-0.522000	-1.580000	-6.444000
H	0.165000	-2.365000	-6.124000
H	-0.506000	-1.542000	-7.533000
H	-1.533000	-1.851000	-6.131000
C	-1.095000	0.845000	-6.414000
H	-0.816000	1.848000	-6.089000
H	-2.108000	0.637000	-6.065000
H	-1.095000	0.830000	-7.505000
C	1.305000	0.114000	-6.388000
H	2.023000	-0.621000	-6.021000
H	1.625000	1.104000	-6.060000
H	1.320000	0.097000	-7.479000

$[I(\mathbf{7})(\mathbf{16})]^{+}$

LUMO/HOMO (ev) 3.38/3.02

H	2.052000	0.000000	4.210000
C	1.149000	0.000000	4.808000
C	-1.206000	-0.000000	6.187000
N	-0.008000	0.000000	4.142000
C	1.187000	0.000000	6.189000
C	-0.010000	0.000000	6.890000
C	-1.166000	-0.000000	4.805000
H	2.140000	0.000000	6.698000
H	-0.011000	0.000000	7.972000
H	-2.068000	-0.000000	4.207000
H	-2.160000	-0.000000	6.695000

H	0.001000	-2.064000	-0.456000
C	0.002000	-1.156000	-1.045000
C	0.005000	1.204000	-2.411000
N	0.001000	-0.000000	-0.360000
C	0.005000	-1.204000	-2.411000
C	0.006000	-0.000000	-3.162000
C	0.002000	1.156000	-1.045000
H	0.005000	-2.171000	-2.890000
H	0.001000	2.064000	-0.456000
H	0.005000	2.171000	-2.890000
N	0.009000	-0.000000	-4.499000
C	0.008000	-1.259000	-5.230000
H	-0.882000	-1.846000	-4.995000
H	0.893000	-1.851000	-4.989000
H	0.013000	-1.046000	-6.294000
C	0.008000	1.259000	-5.230000
H	0.013000	1.046000	-6.294000
H	0.893000	1.851000	-4.989000
H	-0.882000	1.846000	-4.995000
I	-0.005000	-0.000000	1.841000

[I(**18**)(**16**)]$^{+}$

LUMO/HOMO (ev) 3.29/3.17

H	-1.656000	1.302000	0.314000
C	-1.553000	0.239000	0.492000
C	-1.157000	-2.428000	0.906000
N	-0.328000	-0.282000	0.306000
C	-2.623000	-0.515000	0.884000
C	-2.461000	-1.906000	1.111000
C	-0.146000	-1.598000	0.513000
H	-3.576000	-0.027000	1.013000
H	0.855000	-1.976000	0.352000
H	-0.937000	-3.473000	1.053000
I	1.327000	0.994000	-0.319000
N	-3.479000	-2.682000	1.498000
C	-4.801000	-2.106000	1.698000
H	-5.177000	-1.664000	0.774000
H	-4.779000	-1.337000	2.473000
H	-5.482000	-2.892000	2.010000
C	-3.269000	-4.103000	1.730000
H	-4.206000	-4.550000	2.044000
H	-2.526000	-4.264000	2.514000
H	-2.932000	-4.602000	0.819000
C	3.907000	3.104000	-0.216000
H	3.846000	3.118000	0.858000
C	4.751000	3.750000	-1.079000
H	5.567000	4.435000	-0.929000
N	4.358000	3.351000	-2.304000
N	3.346000	2.517000	-2.240000
N	3.073000	2.366000	-0.980000
C	4.917000	3.740000	-3.592000
H	5.970000	3.472000	-3.618000
H	4.797000	4.812000	-3.723000
H	4.371000	3.202000	-4.361000

[I(**1**)(**16**)]$^{+}$

LUMO/HOMO (ev) 2.82/2.71

H	-0.503000	2.015000	-0.810000
C	-0.313000	1.114000	-1.378000
C	0.190000	-1.224000	-2.691000
N	-0.030000	0.007000	-0.669000
C	-0.360000	1.120000	-2.744000
C	-0.108000	-0.074000	-3.467000
C	0.217000	-1.140000	-1.328000
H	-0.592000	2.047000	-3.245000
H	0.442000	-2.006000	-0.720000
H	0.399000	-2.178000	-3.149000
H	-1.950000	0.078000	3.983000
C	-1.024000	0.096000	4.544000
C	1.388000	0.139000	5.835000
N	0.108000	0.100000	3.839000
C	-1.020000	0.113000	5.925000
C	0.210000	0.135000	6.574000
C	1.288000	0.121000	4.457000
H	-1.949000	0.109000	6.477000
H	2.170000	0.124000	3.828000
H	2.355000	0.156000	6.316000
I	0.030000	0.058000	1.498000
N	-0.149000	-0.114000	-4.802000
C	-0.452000	1.090000	-5.562000
H	0.290000	1.868000	-5.373000
H	-1.440000	1.476000	-5.302000
H	-0.441000	0.849000	-6.619000
C	0.117000	-1.362000	-5.505000
H	0.019000	-1.190000	-6.572000
H	-0.595000	-2.134000	-5.208000
H	1.129000	-1.717000	-5.300000
C	0.264000	0.154000	8.011000
N	0.310000	0.172000	9.156000

6. References for Supplementary Information

1 J. S. Ward, G. Fiorini, A. Frontera and K. Rissanen, *Chem. Commun.*, 2020, **56**, 8428–8431.
2 A.-C. C. Carlsson, K. Mehmeti, M. Uhrbom, A. Karim, M. Bedin, R. Puttreddy, R. Kleinmaier, A. A. Neverov, B. Nekoueishahraki, J. Gräfenstein, K. Rissanen and M. Erdélyi, *J. Am. Chem. Soc.*, 2016, **138**, 9853–9863.
3 J. S. Ward, A. Frontera and K. Rissanen, *Chem. Commun.*, 2021, **57**, 5094–5097.
4 S. Yu, P. Kumar, J. S. Ward, A. Frontera and K. Rissanen, *Chem*, 2021, **7**, 948–958.
5 Agilent Technologies Ltd, 2014.
6 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.*, 2015, **71**, 3–8.
7 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
8 G. M. Sheldrick, *Acta Crystallogr. Sect. C, Struct. Chem.*, 2015, **71**, 3–8.
9 Spartan'20, Wavefunction Inc., Irvine CA, USA.
10 X. Zhang and J. M. Herbert, *J. Phys. Chem. B*, 2014, **118**, 7806–7817.
11 A. W. Lange and J. M. Herbert, *Chem. Phys. Lett.*, 2011, **509**, 77–87.