General Information

All chemicals were purchased from *ABCR*, *Acros Organics*, *Alfa Aesar*, *Carbolution*, *ChemPur*, *Sigma-Aldrich*, *TCI* or *VWR*. Commercially available chemicals were, unless mentioned otherwise, used without further purification. Dry dichloromethane, diethyl ether and tetrahydrofuran were received from a *MBRAUN MB SPS-800*. The solvents were distilled, dried over 4Å molecular sieve and finally dried on an Alox column. The moisture content of the solvents was determined with *Karl Fischer (Titroline®7500KF)* titration. Pentane, ethyl acetate, dichloromethane and acetone were used after single distillation. Dry $CDCl_3$ for NMR-catalysis experiments were stored under argon and over molecular sieve 3Å. Oxygen- or moisture-sensitive reactions were carried out under standard *Schlenk* technique with argon as inert gas. Reagents were injected via a rubber septum or added under argon counterflow.

Thin-layer chromatography (TLC) was performed by using *Merck* TLC aluminium sheets (silica gel 60, F254). Detection of the substances was obtained by fluorescence detection under UV light (λ = 254 nm), iodine stain or potassium permanganate stain. Column chromatography was performed with silica gel (grain size 0.04-0.063 cm, Merck Si60).

Isothermal titration calorimetry (ITC) experiments were performed on a *MicroCal VP-ITC* instrument.

Nuclear magnetic resonance (NMR) spectra were obtained on instruments of the type *DPX 250*, *DRX 400*, *AVIII 300* and *AVIII 400* from *Bruker* at 302 K. Chemical shifts (δ) are given as parts per million (ppm). Multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet) and m (multiplet).

Infrared (IR) spectra were obtained with a *Shimadzu IR Affinity - 1S* spectrometer equipped with a *Specac Quest ATR* through attenuated total reflection (ATR).

Mass spectra were recorded with a *Bruker Daltonics Esquire 6000* instrument (ESI) or a *VG Instruments Autospec / EBEE-Geometrie* (EI).

CHNS Elemental Analysis was performed with a *vario Micro cube* from *Elementar Analysentechnik*.

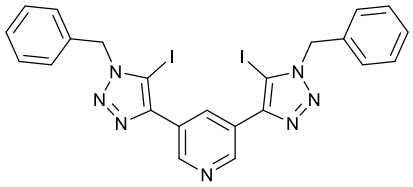
Synthesis of known precursors

1,3-Ph(I)^{Oct,Me}/OTf [1], octyl trifluoromethanesulfonate (Oct–OTf) [2], octyl azide [3], TBTA [4], 3,5-diethynylpyridine (**5**)[5], sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBArF), tetramethylammonium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate (TMA–BArF)[6]and 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)pyridine[7] were synthesized according to literature procedures.

3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)pyridine was purified by column chromatography (silica, CH_2Cl_2:THF 9:1)

1 F. Kniep, L. Rout, S. M. Walter, H. K. V. Bensch, S. H. Jungbauer, E. Herdtweck and S. M. Huber, *Chem. Commun.*, 2012, **48**, 9299.
2 W. K. Fife, P. Ranganathan, M. Zeldin, *J. Org. Chem.*, 1990, **55**, 5610.
3 S. Wang, K. Jia, J. Cheng, Y. Chen, Y. Yuan, *Tetrahedron Letters*, 2017, **58**, 3717.
4 M. von Delius, E. M. Geertsema, D. A. Leigh, *Nat. Chem.*, 2010, **2**, 96.
5 Y. Shin, G. E. Fryxell, C. A. Johnson II, and M. M. Haley, *Chem. Mat.*, 2008, **20** , 981-986
6 P. N. Bartlett, D. C. Cook, M. W. George, J. Ke, W. Levason, G. Reid, W. Sub, W. Zhanga, *Phys. Chem. Chem. Phys.*, 2010,**12**, 492.
7 S. W. Robinson, C. L. Mustoe, N. G. White, A. Brown, A. L. Thompson, P. Kennepohl and P. D. Beer, *J. Am. Chem. Soc.*, 2015, **137**, 499-507.

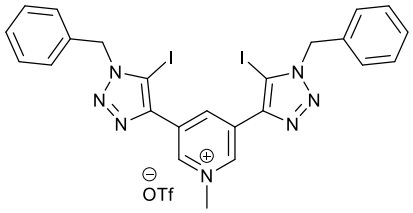
Synthesis of 3,5-bis(5-iodo-1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (3,5-Py(I)^{Bn}).



10 mL dry acetonitrile and 10 mL dry THF were degassed. Under an argon atmosphere, 209 mg benzyl azide (1.57 mmol), 943 mg sodium iodide (6.29 mmol) and 1.14 g copper(II) triflate (3.15 mmol) were added. After 5 min, 8.4 mg TBTA (15.7 µmol), 240 mg 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) (1.57 mmol) and 100 mg 3,5 diethynylpyridine (**5**) (0.78 mmol) were added. The reaction mixture was stirred in the dark at room temperature. After 3 days, the mixture was diluted with 20 mL dichloromethane and washed (10x) with 16% NH_4OH solution. The organic phase was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified with column chromatography (silica, ethyl acetate). The product was obtained as white solid in 41% yield (209 mg).

^{1}H NMR (200 MHz, CD_2Cl_2):	δ 9.2 (d, J = 2.1 Hz, 2H, C_1-H), 8.8 (t, J = 2.1 Hz, 1H, C_3-H), 7.6 – 7.2 (m, 10H, $C_{7\text{-}10}$), 5.7 (s, 4H, C_6-H).
^{13}C NMR (50 MHz, CD_2Cl_2):	δ 148.4, 147.9, 134.9, 133.1, 129.5, 129.1, 128.4, 126.9, 78.1.
FAB-MS (m/z):	645.8 [M^+]
CHNS elemental analysis:	calc.: N: 15,20, C: 42.81, H: 2.66
	found: N: 14.61, C: 43.08, H: 2.92
IR (ATR, cm^{-1}):	1590 (w), 1490 (w), 1445 (w), 1395 (m), 1321 (m), 1236 (m), 1122 (w), 1068 (w), 1023 (w), 976 (m), 894 (w), 816 (w), 757 (w), 709 (vs), 583 (w), 537 (w), 457 (w), 416 (w).
TLC:	R_f = 0.7 (Ethyl acetate)

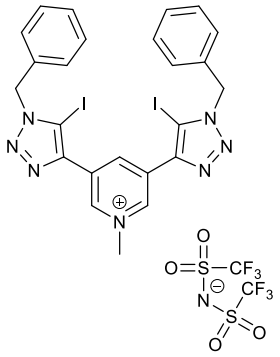
Synthesis of 3,5-bis(1-benzyl-5-iodo-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium trifluoromethanesulfonate (3,5-Py(I)^{Bn,Me}/OTf)



Under an argon atmosphere 184 mg 3,5-bis(5-iodo-1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (285 µmol) was dissolved in 20 mL dry dichloromethane and cooled at 0 °C. 56 mg methyl trifluoromethanesulfonate (342 µmol) was added dropwise. The mixture was slowly warmed up to room temperature and stirred for 24 h. The solvent was removed *in vacuo* and the residue was resolved in a little amount of acetonitrile. After addition of 100 mL diethyl ether, the precipitation was filtered and washed with cold diethyl ether. After drying under high vacuum, the product was obtained as white solid in 72% (163 mg) yield.

^{1}H NMR (200 MHz, CD_3CN)	δ 9.6 (t, J = 1.8 Hz, 1H, C_3H), 9.3 (d, J = 1.8 Hz, 2H, C_1H), 7.5 - 7.3 (m, 10H, $C_{Ar}H$), 5.8 (s, 4H, C_6H), 4.5 (s, 3H, NCH_3).
^{19}F NMR (235 MHz, CD_3CN)	δ -79.2 (CF_3).
^{13}C NMR (63 MHz, CD_3CN)	δ 144.4, 142.9, 137.8, 135.6, 132.6, 129.9, 129.5, 128.8, 83.0, 55.4, 50.2.
FAB-MS (m/z):	659.8 [M^+]
CHNS elemental analysis:	calc.: N: 12,11, C: 37.10, H: 2.49
	found: N: 11.95, C: 37.09, H: 2.45
IR (ATR, cm^{-1})	3100 (vw), 1597 (w), 1528 (w), 1494 (w), 1443 (w), 1405 (w), 1324 (w), 1269 (s), 1239 (vs), 1155 (m), 1077 (w), 1021 (s, C-I), 892 (w), 813 (w), 766 (w), 704 (s), 668 (w), 631 (s), 569 (w), 516 (m), 466 (w), 410 (w).

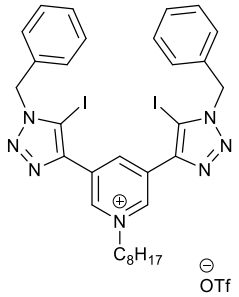
Synthesis of 3,5-bis(1-benzyl-5-iodo-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium bis((trifluoromethyl)sulfonyl)amide (3,5-Py(I)^{Bn,Me}/NTf$_2$)



In a microwave vessel 50 mg 3,5-bis(5-iodo-1-benzyl-1H-1,2,3-triazol-4-yl)pyridine was suspend in 2 mL dry toluene and 2 mL dry ethyl acetate. After flushing with argon, 57 mg *N*-methyl bis[(trifluoromethyl)sulfonyl]imide was added. The mixture was heated up to 130 °C under microwave radiation (180 W) for 1 h. After cooling down to room temperature, the solvent was removed *in vacuo.* The residue was resolved in small amount of acetonitrile and overlay with 20 mL pentane. After stirring for 1 h, the mixture was leaved untouched overnight. The top layer was removed carefully with a pipette and the solvent was removed *in vacuo.* The product was obtained as greenish sticky oil in 96% (70 mg) yield.

^{1}H NMR (250 MHz, CD_3CN)	δ 9.63 (t, J = 1.7 Hz, 1H, C_3-H), 9.25 (dd, J = 1.7 Hz, 2H, C_1-H), 7.47 – 7.29 (m, 10H, C_{Ar}H), 5.76 (s, 4H, C_6-H), 4.46 (s, 3H, NCH_3).
^{19}F NMR (235 MHz, CD_3CN)	δ -80.16 (SCF_3).
^{13}C NMR (75 MHz, $CDCl_3$)	δ 142.9, 141.0, 137.3, 133.4, 132.4, 129.3, 129.1, 128.1, 117.6, 80.6, 55.0, 50.2.
ESI-MS (m/z)	Positiv: 659.6 [M^+]; Negativ: 279.6 [NTf_2^-]
CHNS elemental analysis:	calc.: N: 11,38, C: 34.16, H: 4.10
	found: N: 11.58, C: 34.68, H: 2.80
IR (ATR, cm^{-1})	2924 (vw), 1607 (w), 1446 (w), 1344 (m, S=O), 1180 (vs, C-F), 1130 (s, S=O), 1049 (s, C-I), 892 (w), 820 (w), 786 (w), 716 (m), 670 (w), 606 (m), 566 (m), 505 (m).

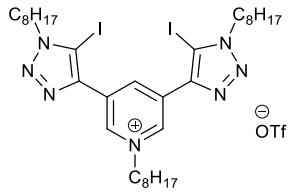
Synthesis of 3,5-bis(1-benzyl-5-iodo-1H-1,2,3-triazol-4-yl)-1-octylpyridin-1-ium trifluoromethanesulfonate (3,5-Py(I)^{Bn,Oct}/OTf)



Under an argon atmosphere 150 mg 3,5-bis(5-iodo-1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (244 µmol) was dissolved in 5 mL dry dichloromethane and cooled at 0 °C. 60 mg octyl trifluoromethanesulfonate (229 µmol) was added dropwise. The mixture was slowly warmed up to room temperature and stirred for 24 h. The solvent was removed *in vacuo* and the residue was resolved in a little amount of acetonitrile. After addition of 100 mL diethyl ether, the precipitation was filtered and washed with cold diethyl ether. After drying under high vacuum, the product was obtained as sticky oil in 98% yield (208 mg).

^{1}H NMR (250 MHz, $CDCl_3$)	δ 9.72 (t, J = 1.6 Hz, 1H, C_1-H), 9.36 (d, J = 1.7 Hz, 2H, C_3-H), 7.58 – 7.28 (m, 10H, C_{Ar}H), 5.62 (s, 4H, C_6-H) 4.84 (t, J = 7.5 Hz, 2H, $N_{py}C\mathbf{H}_2CH_2$), 2.10 (p, J = 7.5 Hz, 2H, $N_{py}CH_2C\mathbf{H}_2$), 1.52 – 1.14 (m, 10H, CH_2), 0.92 – 0.79 (br, 3H, CH_3).
^{19}F NMR (235 MHz, $CDCl_3$)	δ -77.96 (SCF_3)
^{13}C NMR (63 MHz, $CDCl_3$)	δ 142.8, 140.1, 135.8, 133.5, 132.6, 129.2, 129.0, 128.2, 82.7, 64.1, 54.9, 53.6, 31.8, 31.8, 29.1, 26.2, 22.7, 14.2.
ESI-MS (m/z)	Positive: 757.8 [M^+], Negative: 148.5 [OTf^-]
CHNS elemental analysis:	calc.: N: 10.80, C: 42.35, H: 3.78; (+1/3 H_2O): N: 10.73, C: 42.07, H: 3.83
	found: N: 11.73, C: 42.20, H: 3.83
IR (ATR, cm^{-1}):	3056 (w), 2923 (m), 2853 (m), 1605 (m), 1447 (m), 1408 (w), 1330 (w), 1242 (s), 1153 (s), 1073 (w), 1022 (s, C-I), 897 (w), 817 (m), 762 (w), 716 (s), 685 (m), 630 (s), 571 (m), 513 (m).

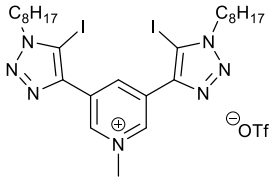
Synthesis of 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)-1-octylpyridin-1-ium trifluoromethanesulfonate (3,5-Py(I)^{Oct,Oct}/OTf)



Under an argon atmosphere 400 mg 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)pyridine (580 µmol) was dissolved in 20 mL dry dichloromethane and cooled at -78 °C. 152 mg octyl trifluoromethanesulfonate (609 µmol) was added dropwise. The mixture was slowly warmed up to room temperature and stirred for 24 h. The solvent was removed *in vacuo.* The residue was resolved in small amount of dichloromethane and overlay with 30 mL hexane. After stirring for 1 h, the mixture was leaved untouched overnight. The top layer was removed carefully with a pipette and the solvent was removed in vacuo. The product was obtained as yellowish sticky oil in 89% yield (283 mg).

^{1}H NMR (250 MHz, $CDCl_3$)	δ 9.81 (d, J = 1.6 Hz, 1H, C_3-H), 9.38 (d, J = 1.6 Hz, 2H, C_1-H), 4.86 (t, J = 7.5 Hz, 2H, C_7-H), 4.43 (t, J = 7.4 Hz, 4H, C_6-H), 2.14 (p, J = 7.5 Hz, 2H, $N_{py}CH_2C\mathbf{H}_2$), 1.93 (p, J = 7.3 Hz, 4H, $N_{tri}CH_2C\mathbf{H}_2$), 1.52 – 1.20 (br, 30H), 0.94 – 0.79 (br, 9H).
^{19}F NMR (235 MHz, $CDCl_3$)	δ -77.97 (CF_3).
^{13}C NMR (63 MHz, $CDCl_3$)	δ 142.3, 139.9, 135.5, 132.9, 82.3, 64.1, 51.6, 31.8, 31.8, 29.9, 29.2, 29.1, 29.1, 26.6, 26.5, 26.3, 22.7, 22.7, 14.2, 14.2.
ESI-MS (m/z):	Positive: 802.1 [M^+], Negative: 148.5 [OTf^-]
CHNS elemental analysis:	calc.: N: 10.30, C: 42.90, H: 5.72
	found: N: 10.51, C: 43.22, H: 5.58
IR (ATR, cm^{-1})	3050 (w), 2923 (s, C_{sp3}H), 2855 (s, C_{sp3}H), 1604 (w), 1458 (m), 1409 (w), 1373 (w), 1332 (w),1242 (vs), 1158 (s), 1024 (s), 900 (w), 808 (w), 721 (w), 685 (w), 632 (s), 571 (w), 515 (m)

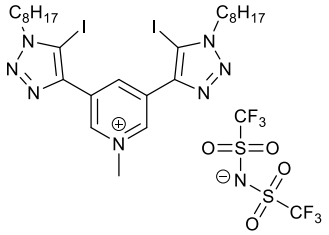
Synthesis of 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium trifluoromethanesulfonate (3,5-Py(I)^{Oct,Me}/OTf)



Under an argon atmosphere 500 mg 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)pyridine (725 µmol) was dissolved in 25 mL dry dichloromethane and cooled at -78 °C. 131 mg methyl trifluoromethanesulfonate (797 µmol) was added dropwise. The mixture was slowly warmed up to room temperature and stirred for 24 h. The solvent was removed in vacuo and the residue was resolved in a little amount of acetonitrile. After addition of 150 mL diethyl ether, the precipitation was filtered and washed with cold diethyl ether. After drying under high vacuum, the product was obtained as white solid in 90% (559 mg) yield.

^{1}H NMR (200 MHz, $CDCl_3$)	δ 9.70 (t, J = 1.6 Hz, 1H, C_3-H), 9.40 (d, J = 1.6 Hz, 2H, C_1-H), 4.70 (s, 3H, C_7-H), 4.40 (t, J = 7.4 Hz, 4H, C_6-H), 2.29 – 1.63 (m, 4H, CH_2), 1.55 – 1.14 (m, 20H, CH_2), 1.00 – 0.62 (m, 3H, CH_3).
^{19}F NMR (235 MHz, CD_3CN)	δ -79.30.
^{13}C NMR (50 MHz, $CDCl_3$)	δ 142.4, 141.3, 135.6, 132.4, 120.5 (q, J = 320 Hz, CF_3), 81.8, 51.6, 50.3, 31.8, 29.9, 29.2, 29.1, 26.5, 22.7, 14.2.
ESI-MS (m/z)	Positive: 703.9 [M^+]; Negative: 148.5 [OTf^-]
CHNS elemental analysis:	calc.: N: 11.49, C: 37.99, H: 4.72
	found: N: 11.35, C: 37.76, H: 4.70
IR (ATR, cm^{-1})	3098 (w), 2923 (s, C_{sp3}H), 2855 (m, C_{sp3}H), 1594 (m), 1524 (w), 1459 (w), 1412 (w), 1371 (w), 1330 (w), 1277 (s), 1234 (vs), 1164 (s), 1022 (s, C-I), 921 (w), 894 (w), 802 (w), 760 (w), 721 (w), 669 (w), 633 (s), 572 (w), 515 (m).

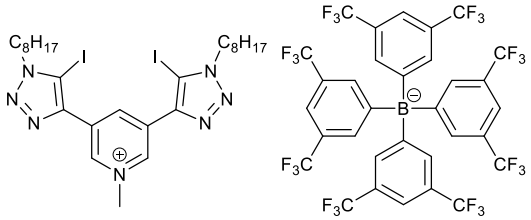
Synthesis of 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium bis((trifluoromethyl)sulfonyl)amide (3,5-Py(I)^{Oct,Me}/NTf$_2$)



In a microwave vessel 400 mg (580 µmol) 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)pyridine was suspend in 5 mL dry toluene and 5 mL dry ethyl acetate. After flushing with argon, 188 mg (638 µmol) N-methyl bis[(trifluoromethyl)sulfonyl]imide was added. The mixture was heated up to 130 °C under microwave radiation (180 W) for 1 h. After cooling down to room temperature, the solvent was removed in vacuo. The residue was resolved in small amount of acetonitrile and overlay with 25 mL pentane. After stirring for 1 h, the mixture was leaved untouched overnight. The top layer was removed carefully with a pipette and the solvent was removed in vacuo. The product was obtained as brownish sticky oil in 98% (560 mg) yield.

^{1}H NMR (250 MHz, $CDCl_3$)	δ 9.77 (t, J = 1.6 Hz, 1H, C_3-H), 9.30 (d, J = 1.6 Hz, 2H, C_1-H), 4.65 (s, 3H, $N_{py}CH_3$), 4.50 (t, J = 7.4 Hz, 4H, C_6-H), 1.98 (p, J = 7.2 Hz, 4H, $NCH_2C\mathbf{H}_2$), 1.47 – 1.23 (br, 20H), 0.95 – 0.79 (br, 6H, $CH_2C\mathbf{H}_3$).
^{19}F NMR (235 MHz, $CDCl_3$)	δ -78.66 (SCF_3).
^{13}C NMR (63 MHz, $CDCl_3$)	δ 142.3, 140.9, 137.0, 132.3, 122.2, 117.1, 80.0, 51.5, 50.0, 31.7, 29.7, 29.0, 28.9, 26.4, 22.6, 14.0.
ESI-MS (m/z)	Positive: 703.9 [M^+], Negative: 279.6 [NTf_2^-]
CHNS elemental analysis:	calc.: N: 11.38, C: 34.16, H: 4.10
	found: N: 11.36, C: 34.36, H: 4.08
IR (ATR, cm^{-1})	3083 (w), 2926 (m), 2857 (m), 1608 (w), 1534 (w), 1460 (w), 1345 (s), 1182 (vs), 1133 (s), 1051 (s, C-I), 895 (w), 790 (w), 736 (w), 654 (w), 608 (s), 569 (s), 508 (s), 401 (w).

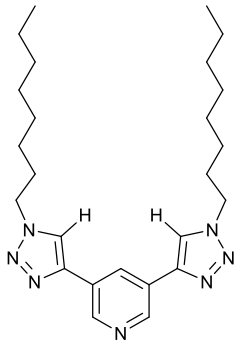
Synthesis of 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ((3,5-Py(I)^{Oct,Me}/BAr$^{F}_{4}$)



200 mg 3,5-bis(5-iodo-1-octyl-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium trifluoromethanesulfonate (234 µmol) and 285,5 mg tetramethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate were dissolved in 4.7 mL dry chloroform and stirred for 24 h at room temperature. The solvent was removed *in vacuo* and resuspended in 5 mL cold diethyl ether. The precipitation was filtered, and the solvent of the filtrate was removed. The residue was resolved in a small amount of chloroform, after the addition of cold diethyl ether, the precipitation was filtered *via* a syringe filter. The solvent was removed *in vacuo* and dried under high vacuum. The product was obtained as yellowish powder in 97% yield (360 mg).

^{1}H NMR (300 MHz, $CDCl_3$):	δ 9.90 (d, *J* = 1.4 Hz, 1H), 9.20 (t, *J* = 1.4 Hz, 2H), 7.79 – 7.60 (s, 8H), 7.49 (s, 4H), 4.48 (t, *J* = 7.4 Hz, 4H), 4.40 (s, 3H), 1.97 (p, *J* = 7.4 Hz, 4H), 1.51 – 1.09 (m, 20H), 0.98 – 0.51 (m, 6H).
^{19}F NMR (235 MHz, $CDCl_3$):	δ -62.32.
^{13}C NMR (75 MHz, $CDCl_3$):	δ 161.8 (dd, *J* = 99.6, 49.7 Hz), 141.4, 139.8 , 136.4 , 134.9 , 133.6 , 130.1 , 129.8 – 128.0 (m), 126.4 , 122.8 , 119.2 , 117.6 , 79.3 , 51.8 , 49.7 , 31.8 , 29.8 , 29.1 , 29.0 , 26.4 , 22.7 , 14.1 .
IR (ATR, cm^{-1}):	2931 (w), 2860 (w), 1610 (m), 1506 (w), 1487 (w), 1417 (w), 1354 (s), 1271 (vs), 1112 (vs), 947 (m), 931 (w), 885 (s), 839 (s), 744 (m), 711 (s), 680 (s), 669 (s), 638 (w), 580 (w), 516 (w), 447 (m), 406 (w)
ESI-MS (m/z):	Positive: 704.0 [M^+]; Negative: 863.1 [$BAr^{F}_{4}{}^-$]
CHNS elemental analysis:	calc.: N: 6.25, C: 44.44, H: 3.34
	found: N: 5,57, C: 44,40, H: 3.22

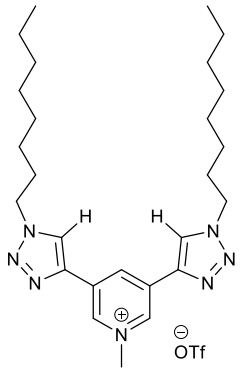
Synthesis of 3,5-bis(1-octyl-1H-1,2,3-triazol-4-yl)pyridine (3,5-Py(H)^{Oct})



19.6 mg Copper(II) sulfate pentahydrate (78.6 µmol), 200 mg 3,5 diethynylpyridine (1.57 mmol), 418.9 mg octyl azide (3.15 mmol), 16.7 mg TBTA (31.5 µmol) and 46.7 mg Sodium ascorbate were dissolved in 5 mL Water and 5 mL dichloromethane. The mixture was stirred vigorously for 5 days. The mixture was diluted with 30 mL dichloromethane and washed (10x) with 16% NH_4OH solution. The organic phase was dried over Na_2SO_4. The solvent was evaporated, and the crude product purified with column chromatography (silica, CH_2CL_2 with 3% MeOH). The product was obtained as white solid in 68% yield (470 mg).

^{1}H NMR (250 MHz, $CDCl_3$):	δ 9.03 (d, J = 2.1 Hz, 2H, C_1-H), 8.61 (t, J = 2.1 Hz, 1H, C_3-H), 7.90 (s, 2H, C_5-H), 4.44 (t, J = 7.2 Hz, 4H, C_6-H), 1.98 (p, J = 7.2 Hz, 4H), 1.48 – 1.19 (m, 20H), 0.95 – 0.77 (m, 6H).
^{13}C NMR (63 MHz, $CDCl_3$):	δ 146.4, 144.6, 129.8, 127.0, 120.3, 50.8, 31.8, 30.4, 29.1, 29.1, 26.6, 22.7, 14.2.
IR (ATR, cm^{-1}):	2955 (m), 2918 (s), 2852 (m), 1608 (w), 1545 (w), 1464 (m), 1401 (w), 1374 (w), 1347 (w), 1227 (m), 1179 (w), 1151 (w), 1121 (w), 1083 (w), 1050 (m), 968 (w), 928 (w), 884 (w), 800 (s), 753 (w), 702 (m), 652 (m), 520 (w), 462 (w), 439 (w).
ESI-MS (m/z):	438.1 [M^+]
CHNS elemental analysis:	calc.: N: 22.40, C: 68.61, H: 8.98
	found: N: 22.25, C: 68.40, H: 9.00

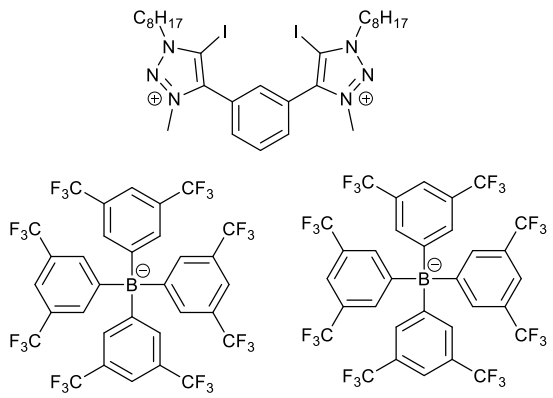
Synthesis of 1-methyl-3,5-bis(1-octyl-1H-1,2,3-triazol-4-yl)pyridin-1-ium trifluoromethanesulfonate (3,5-Py(H)^{Oct,Me}/OTf)



Under an argon atmosphere 200 mg 3,5-bis(1-octyl-1H-1,2,3-triazol-4-yl)pyridine (457 µmol) was dissolved in 20 mL dry dichloromethane and cooled at 0 °C. 75 mg methyl trifluoromethanesulfonate (457 µmol) was added dropwise. The mixture was slowly warmed up to room temperature and stirred for 24 h. The solvent was removed *in vacuo* and the residue was resolved in a little amount of acetonitrile. After addition of 100 mL diethyl ether, the precipitation was filtered and washed with cold diethyl ether. After drying under high vacuum, the product was obtained as white solid in 92% (255 mg) yield.

^{1}H NMR (250 MHz, CD_3CN)	δ 9.14 (t, J = 1.6 Hz, 1H, C_3-H), 9.11 (d, J = 1.6 Hz, 2H, C_1-H), 8.52 (s, 2H, C_5-H), 4.47 (t, J = 7.1 Hz, 4H, C_6-H), 4.42 (s, 3H, NC**H**$_3$), 1,99 (br, 4H, CH_2)1.40 – 1.19 (m, 20H, CH_2), 0.96 – 0.82 (m, 6H, CH_2C**H**$_3$).
^{19}F NMR (235 MHz, CD_3CN)	δ -79.34.
^{13}C NMR (63 MHz, CD_3CN)	δ 141.4, 141.0, 136.8, 133.3, 124.9, 51.6, 49.8, 32.5, 30.7, 29.8, 29.6, 27.0, 23.3, 14.4.
IR (ATR, cm^{-1})	3125 (w), 3074 (w), 2925 (m), 2858 (m), 1613 (w), 1554 (w), 1464 (w), 1376 (w), 1249 (vs), 1160 (s), 1052 (w), 1026 (m), 908 (w), 840 (w), 804 (w), 754 (w), 727 (w), 676 (w), 634 (s), 571 (w), 516 (m).
ESI-MS (m/z):	452.3 [M$^+$]
CHNS elemental analysis:	calc.: N: 11.38, C: 34.16, H: 4.10
	found: N: 11.36, C: 34.36, H: 4.08

Synthesis of 4,4'-(1,3-phenylene)bis(5-iodo-3-methyl-1-octyl-1H-1,2,3-triazol-3-ium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (1,3-Ph(I)^{Oct,Me}/BAr$^{F}_{4}$)



2 g sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (2,26 mmol) was dissolved in 25 mL methanol. To the solution, 1 g *Amberlite* IRA958 Cl Resin was added and stirred carefully for 1 h. The "BAr$^{F}_{4}$ loaded" Resin was transfer into a thin column (d = 0,8 cm, l = 30 cm) and washed with 250 mL methanol. 200 mg 4,4'-(1,3-phenylene)bis(5-iodo-3-methyl-1-octyl-1H-1,2,3-triazol-3-ium) trifluoromethanesulfonate (**1,3 Ph(I)^{Oct,Me}/OTf**) (197 µmol) was dissolved in 100 mL methanol and added to the column. The drop rate of the column was around 1 drop pro 10 s. The procedure was repeated three times. The solvent was removed *in vacuo* and the product was obtained as yellowish solid 62% yield (297 mg).

^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.93 (t, J = 1.8 Hz, 1H), 7.76 – 7.60 (m, 11H), 7.48 (d, J = 2.0 Hz, 4H), 4.54 (t, J = 7.6 Hz, 4H), 4.07 (s, 6H), 2.03 (h, J = 7.7, 6.9 Hz, 4H), 1.47 – 1.20 (m, 20H), 0.93 – 0.76 (m, 6H).
^{19}F NMR (235 MHz, $CDCl_3$)	δ -62.40.
^{13}C NMR (75 MHz, $CDCl_3$)	δ 161.8 (dd, J = 99.4, 49.9 Hz), 145.4, 134.9, 133.6, 132.8, 131.5, 130.0, 129.0 (q, J = 30.4 Hz), 126.4, 124.5, 122.8, 119.2, 117.6, 100.2, 55.6, 38.9, 31.7, 29.4, 29.0, 28.9, 26.3, 22.6.
IR (ATR, cm^{-1})	2931 (w), 2860 (w), 1610 (w), 1558 (w), 1506 (w), 1471 (w), 1354 (s), 1273 (vs), 1112 (vs), 931 (m), 885 (m), 839 (m), 813 (w), 744 (w), 711 (s), 680 (s), 669 (s), 449 (m).
CHNS elemental analysis:	calc.: N: 3.44, C: 45.20, H: 2.80
	found: N: 5.29, C: 44.39, H: 2.88

^{1}H-NMR-Experiments

All ^{1}H-NMR-Experiments were performed on the *Bruker AVII-300* spectrometer. $CDCl_3$ (*Eurisotop*, without silver) was dried over 3 Å molecular sieves and stored under argon. All NMR-tubes were used oven dry. *Hamilton gas tight* syringes were used for the preparation of the stock solutions of the activator (halogen bond donor or reference compound), 1,3,5-trimethoxybenzene and benzhydryl bromide. At first, 3.3 mg Cs_2CO_3 was added in the NMR tube, then 300 µl dry $CDCl_3$, 100 µl (100 mM) 1,3,5-trimethoxybenzene (**2**) solution and 100 µl (100 mM) activator solution. The mixture was mixed by inversion and sonication for 5 mins. At last, 100 µL (100 mM) benzhydryl bromide (**1**) solution was added and mixed by inversion. The samples were directly transferred and submitted to the NMR spectrometer. All samples were measured in parallel. The first spectra were measured after approximated 1 h and every fourth hour an additional spectrum was recorded by using the periodic experiment script of the *Bruker* Software. The acquisition time were given in the fid data file and was read out with *MestReNova* version 9.0.1-13254.

The conversion was determined by integration of the methoxy signals (3.77 ppm) of 1,3,5-trimethoxybenzene (**2**) against the two methoxy signals (3.80 ppm and 3.58 ppm) in the product ((2,4,6-trimethoxyphenyl)methylene)dibenzene (**3**).[8] 1,3,5-trimethoxybenzene (**2**) was chosen as relative standard and the integral was defined as 1. The conversation is equal 100% divided through the sum of all integrals and multiplied by the respective integral.

[8] In some cases, the twofold substitution occured and ((2,4,6-trimethoxy-1,3-phenylene)bis(methanetriyl))tetrabenzene (methoxy signals at 3.41 ppm and 3.03 ppm) was formed as minor product (<5 % after 17 h in the case of 3,5-Py(I)^{Oct,Me}/OTf as activator).

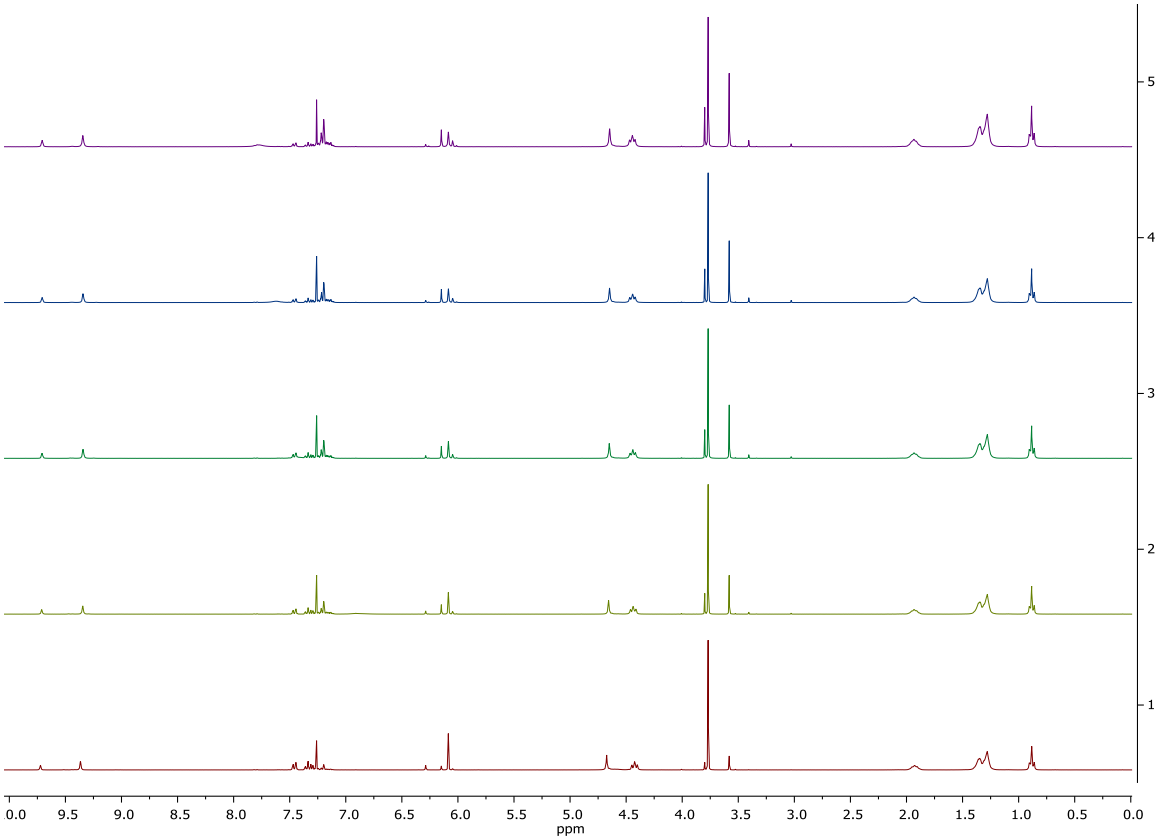


Figure 1: Example for a stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide activated by 3,5-Py(I)$^{Oct,\ Me}$/OTf is depicted. Spectra recording after 1 h, 5 h, 9 h, 13 h and 17 h.

NMR-Spectra of new compounds

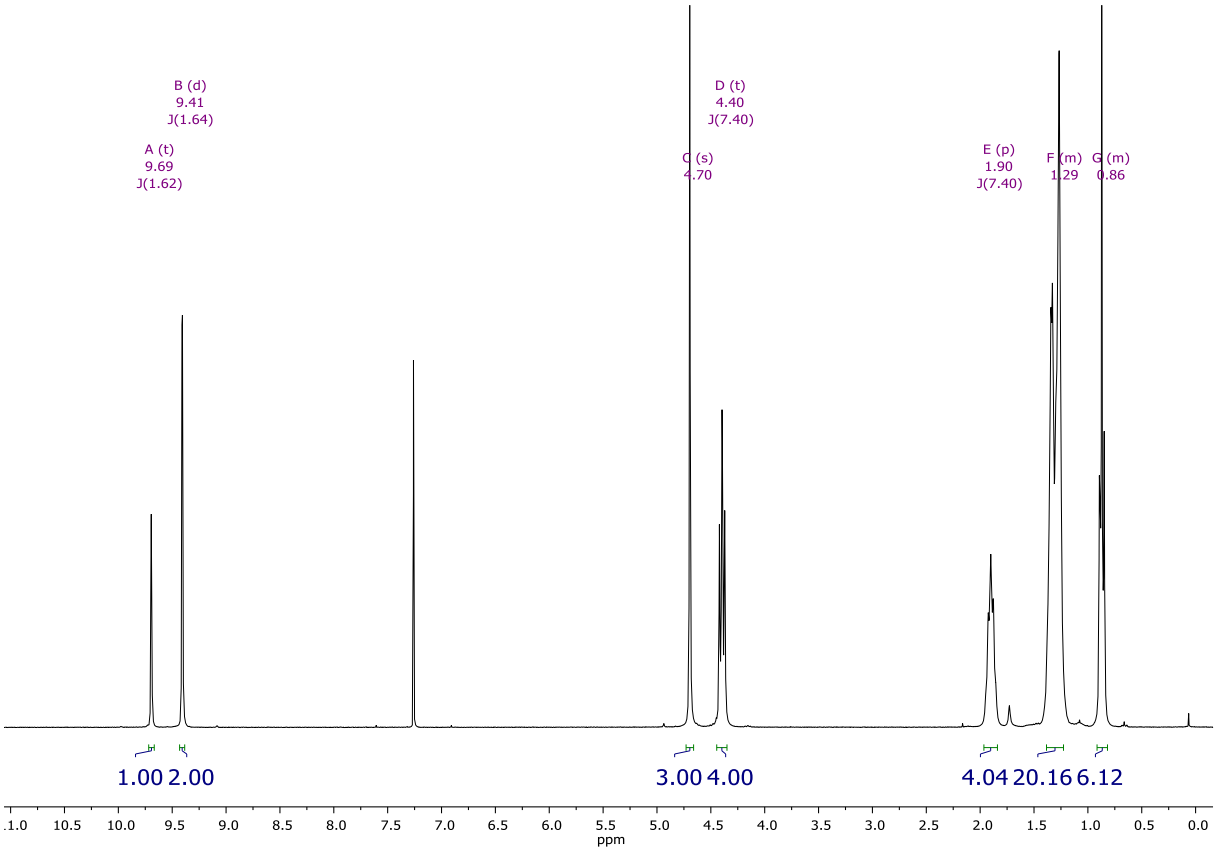


Figure 2: ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/OTf.

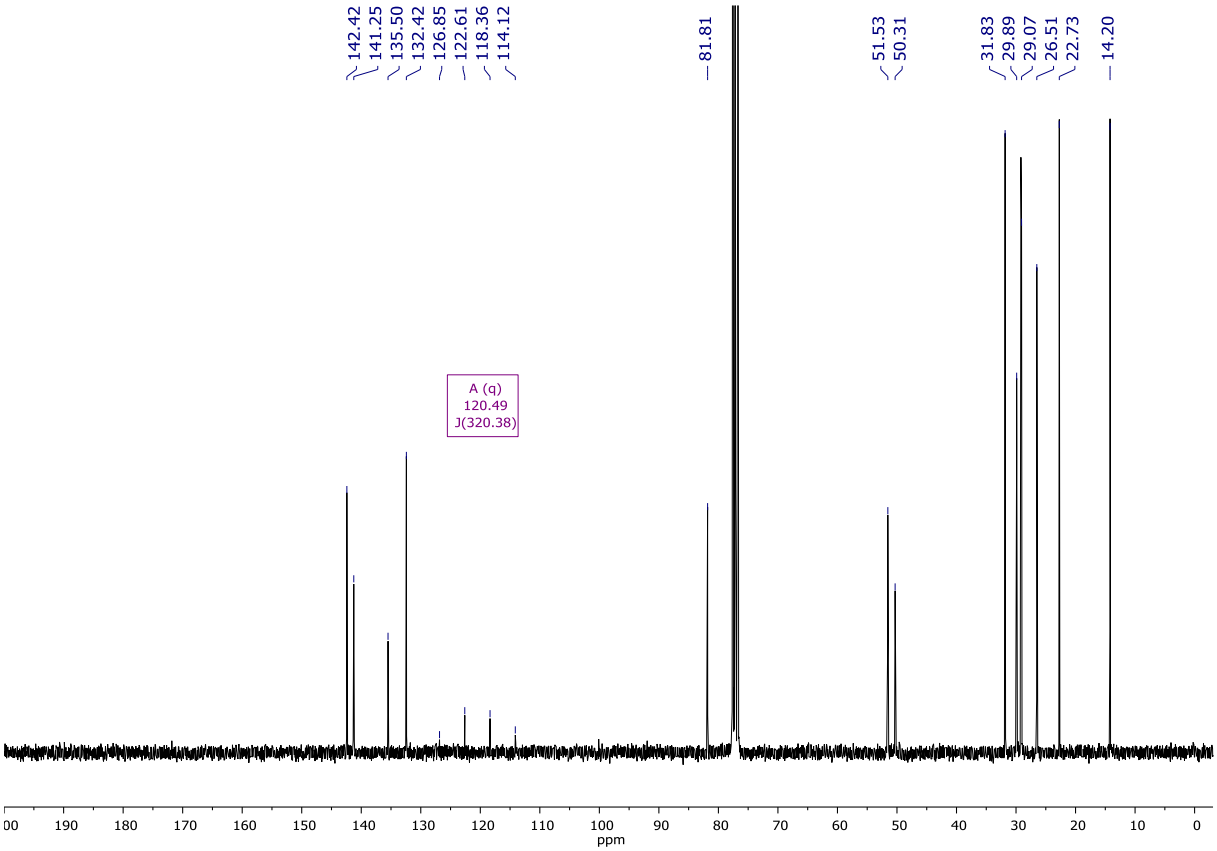


Figure 3: ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/OTf.

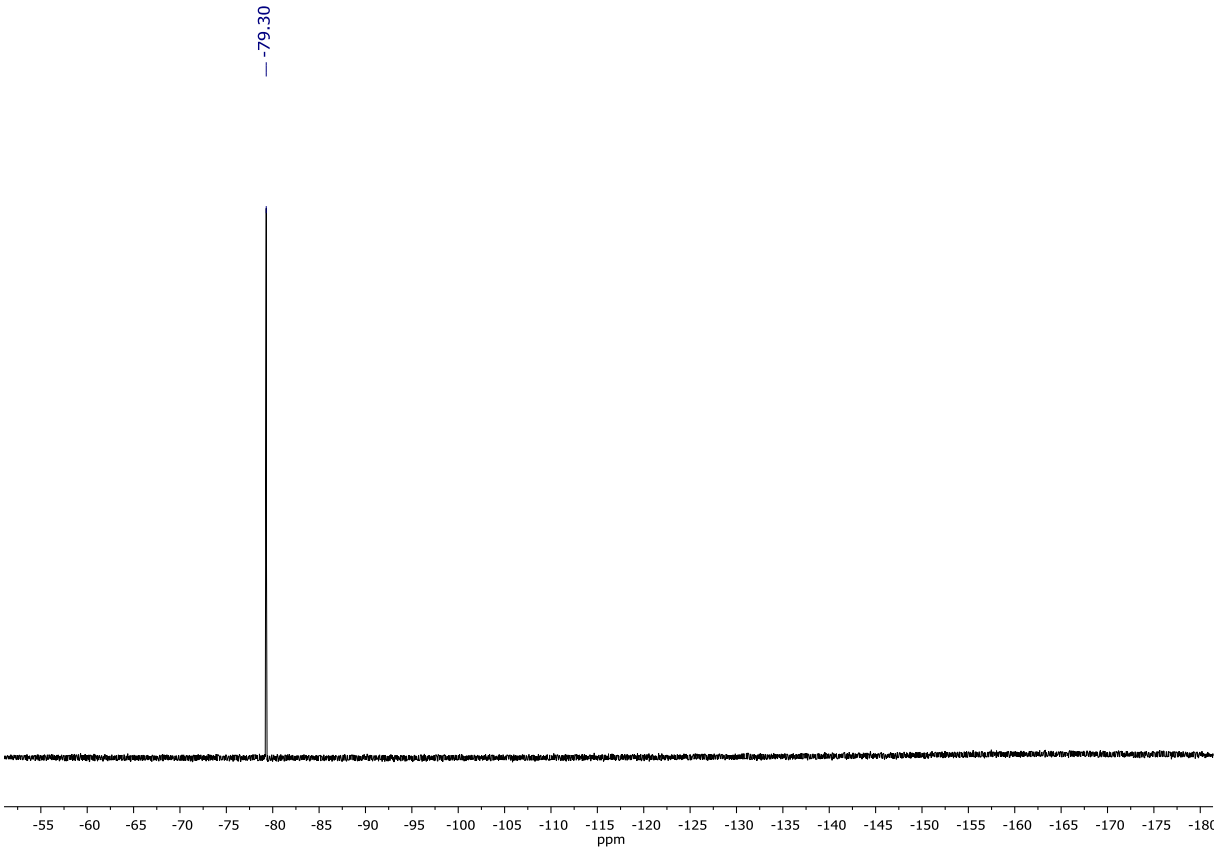


Figure 4: ^{19}F-NMR spectrum (235 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/OTf.

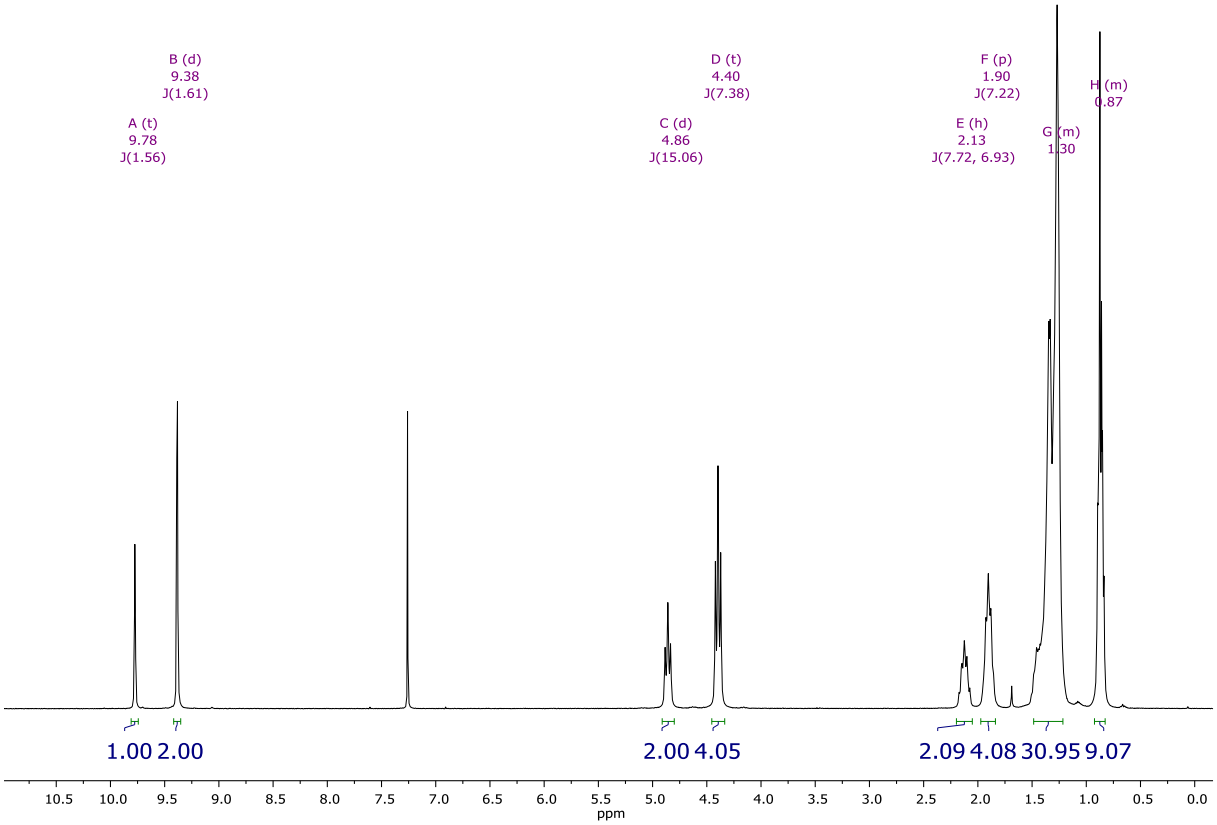


Figure 5: ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Oct}/OTf.

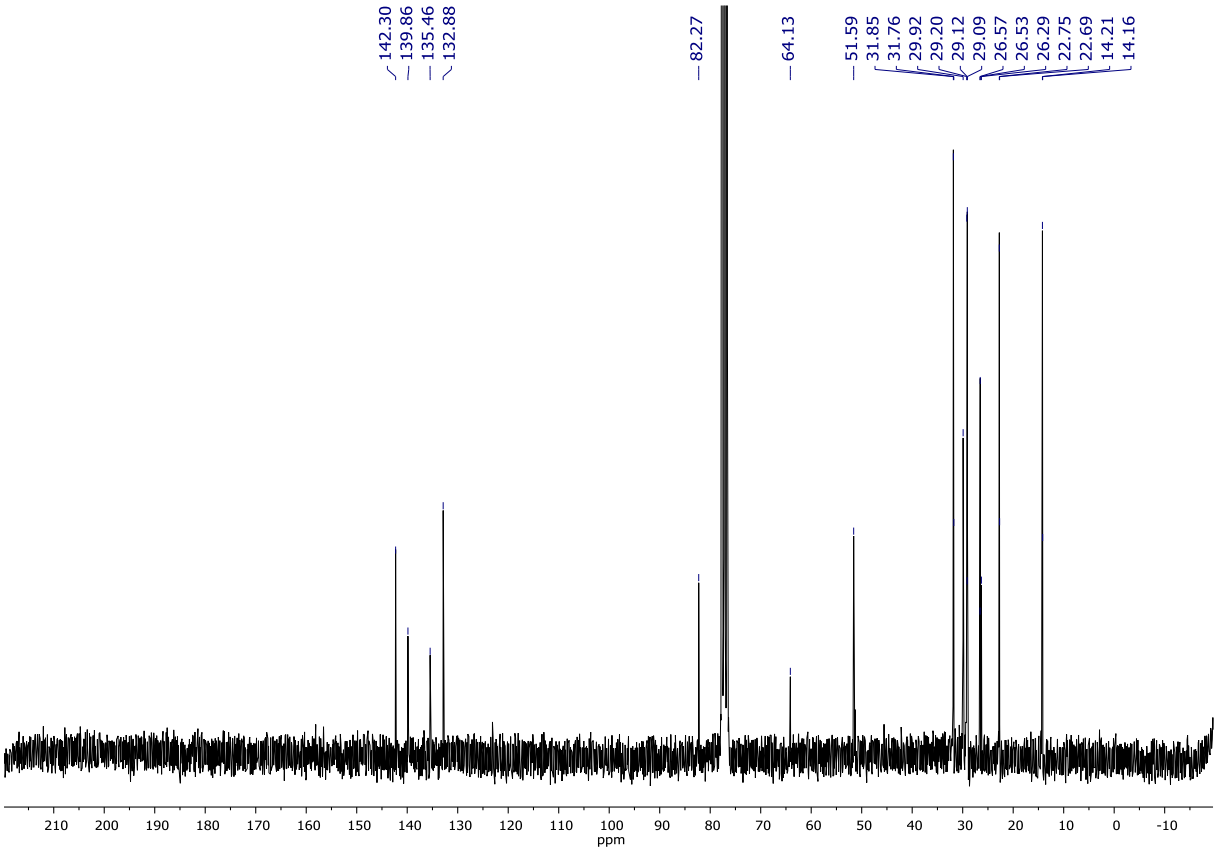


Figure 6: ^{13}C-NMR spectrum (63 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Oct}/OTf.

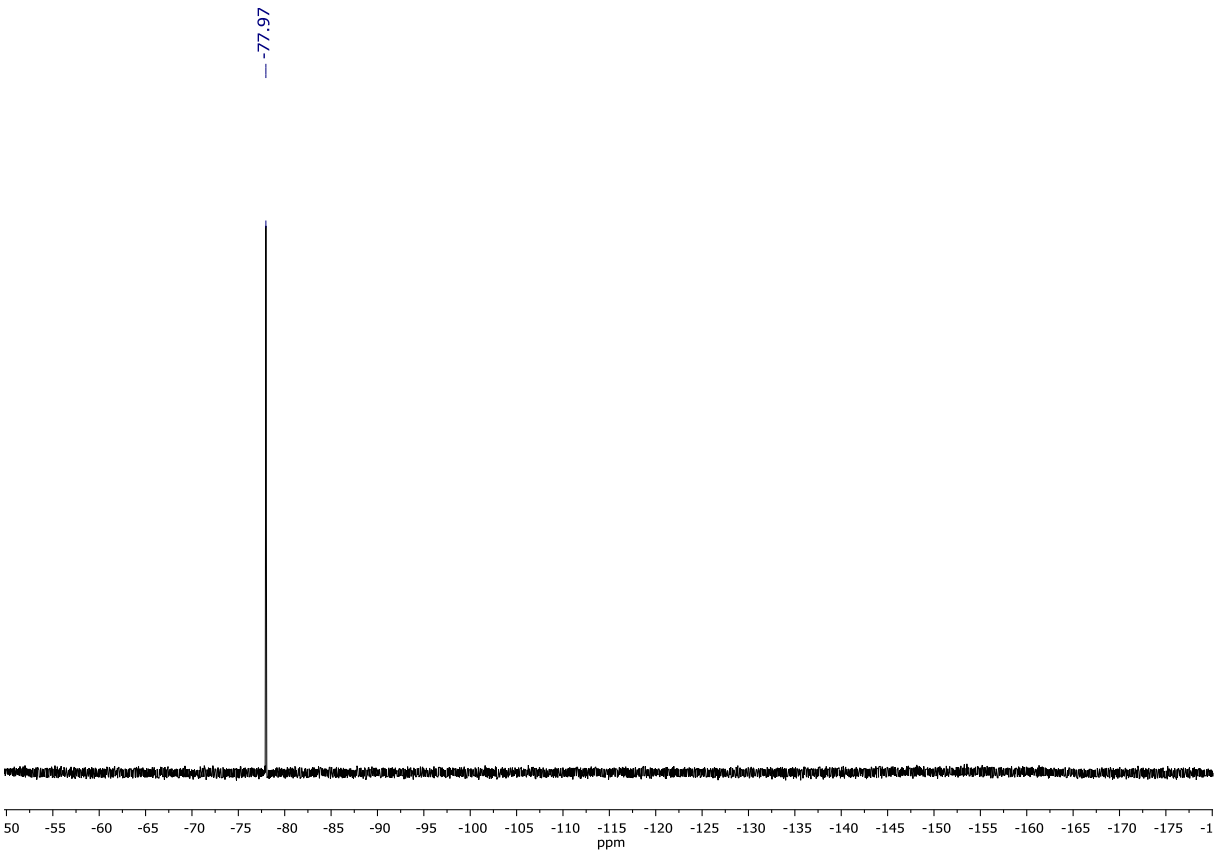


Figure 7: ^{19}F-NMR spectrum (235 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Oct}/OTf.

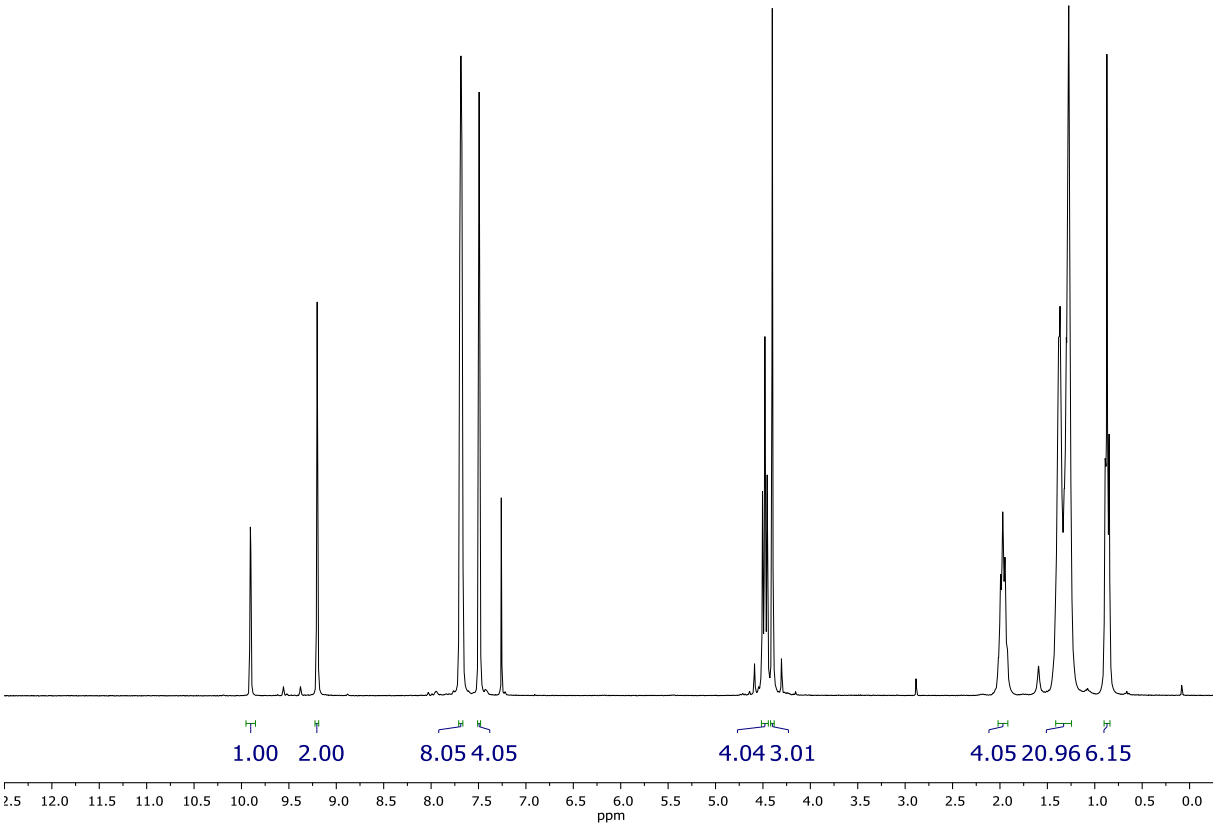


Figure 8: ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/BAr^{F}.

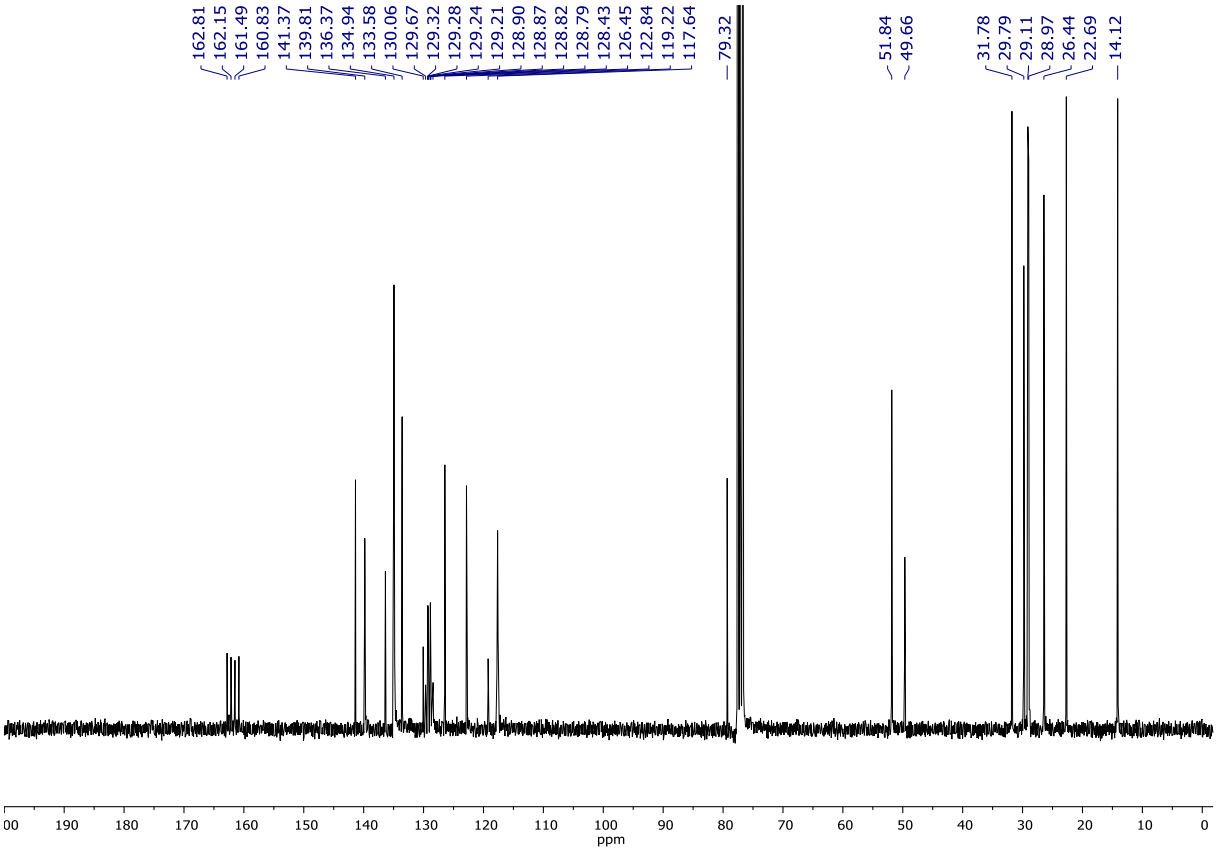


Figure 9: ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/BAr^{F}.

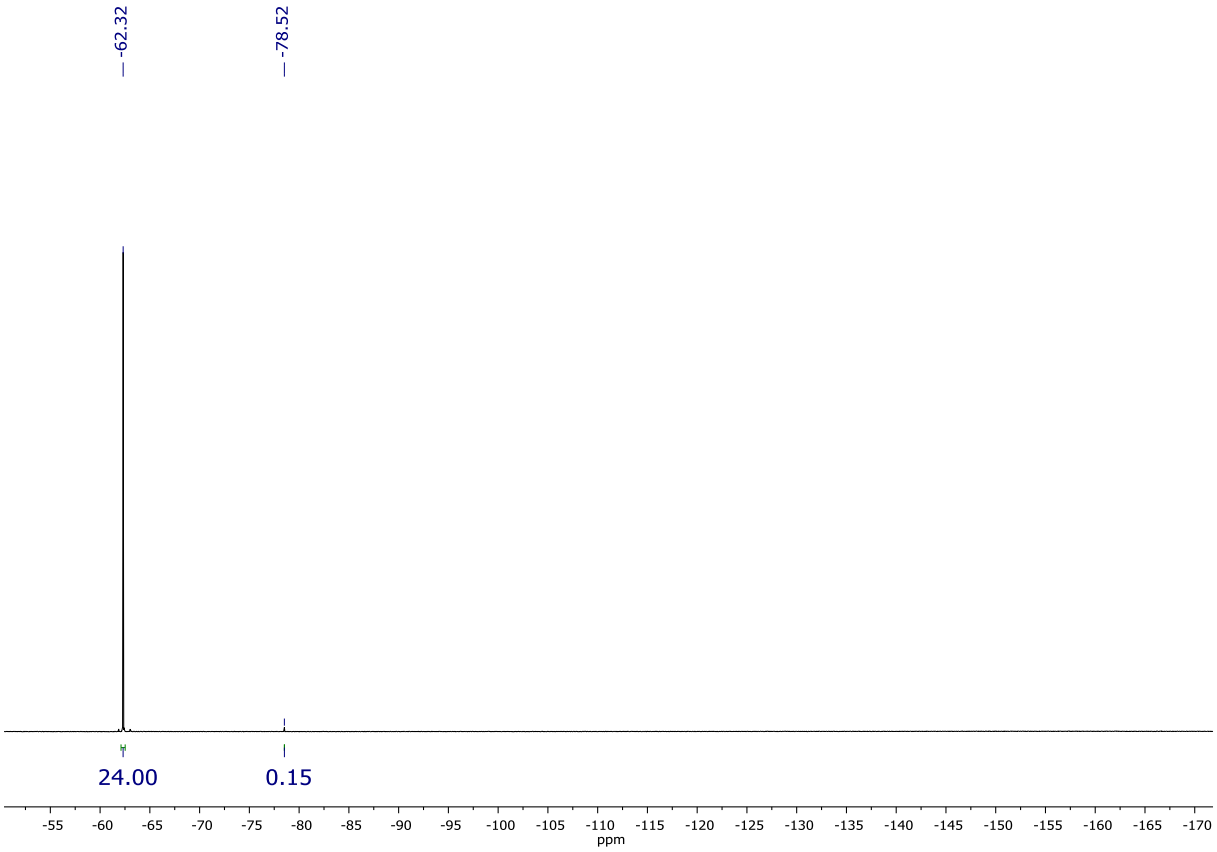


Figure 10: ^{19}F-NMR spectrum (235 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/BAr^F.

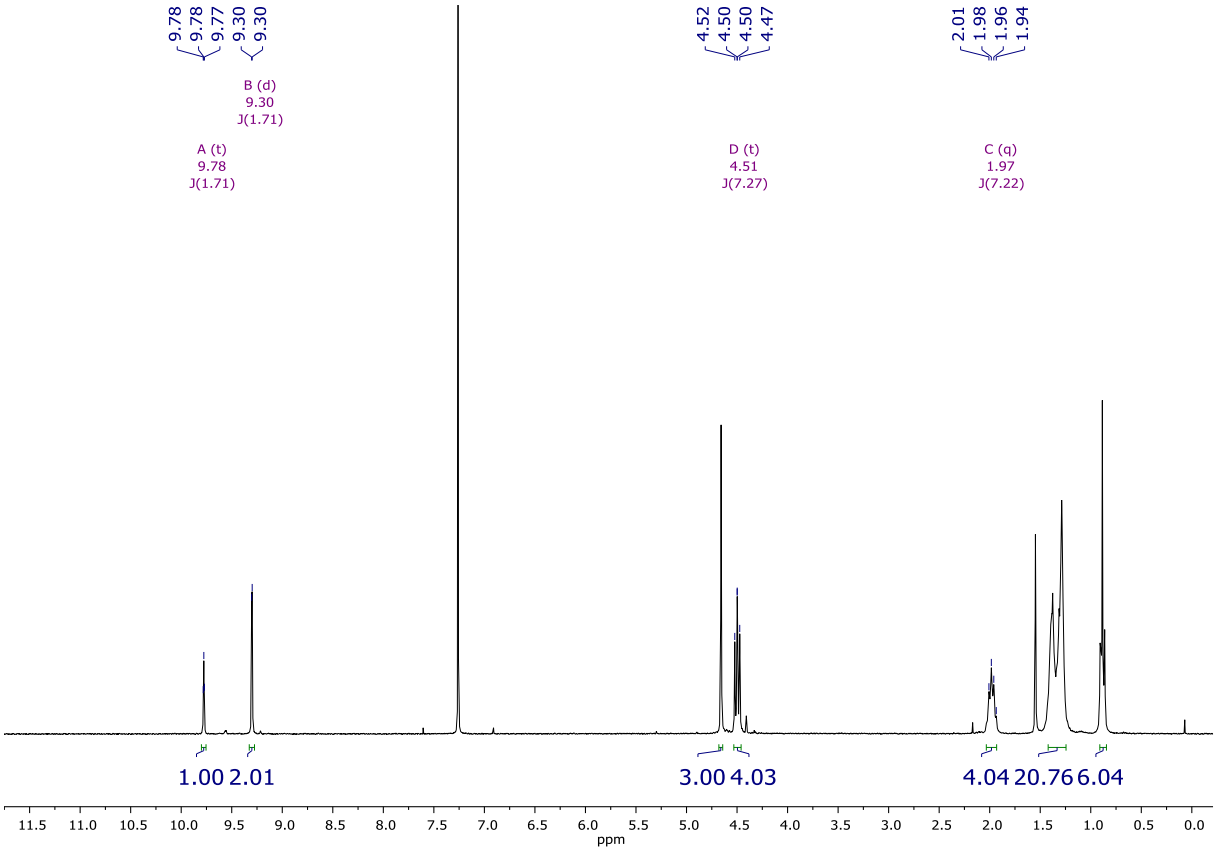


Figure 11: ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/NTf_2.

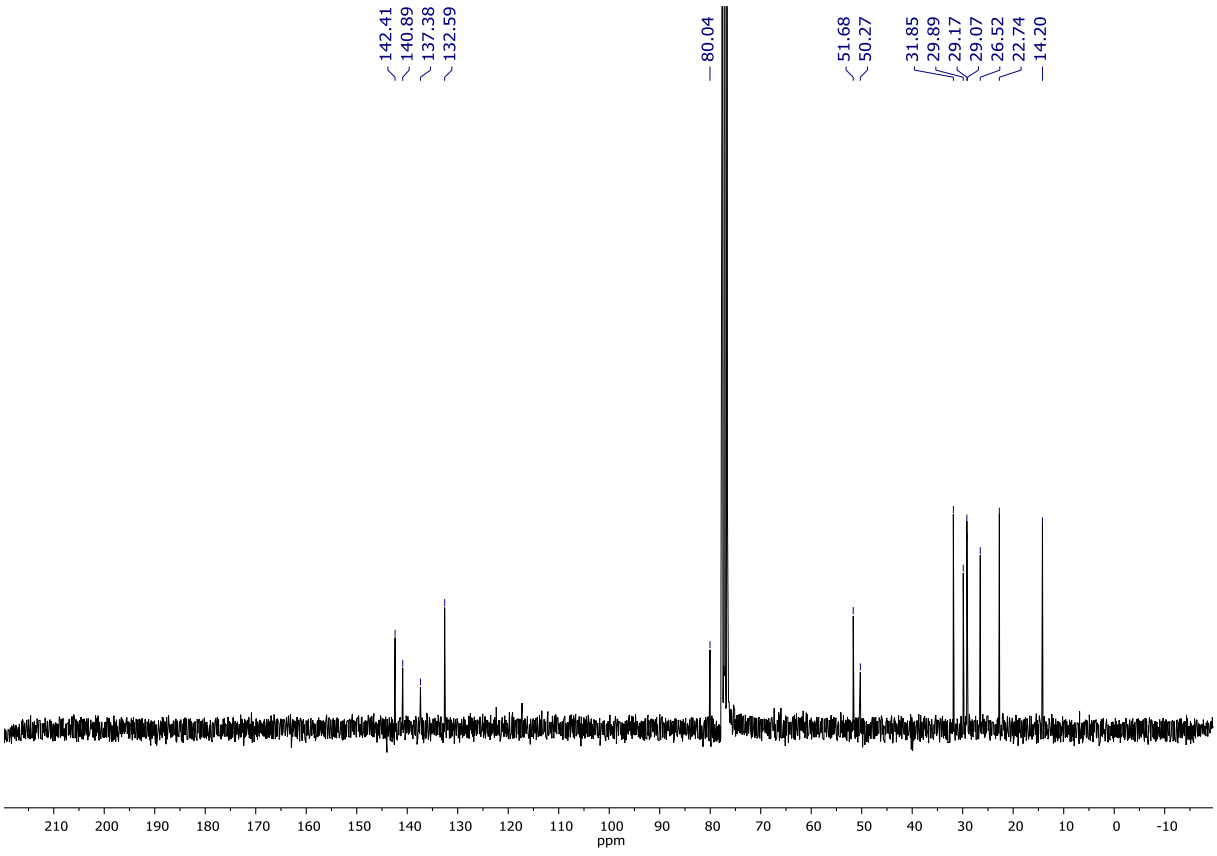


Figure 12: ^{13}C-NMR spectrum (63 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/NTf_2.

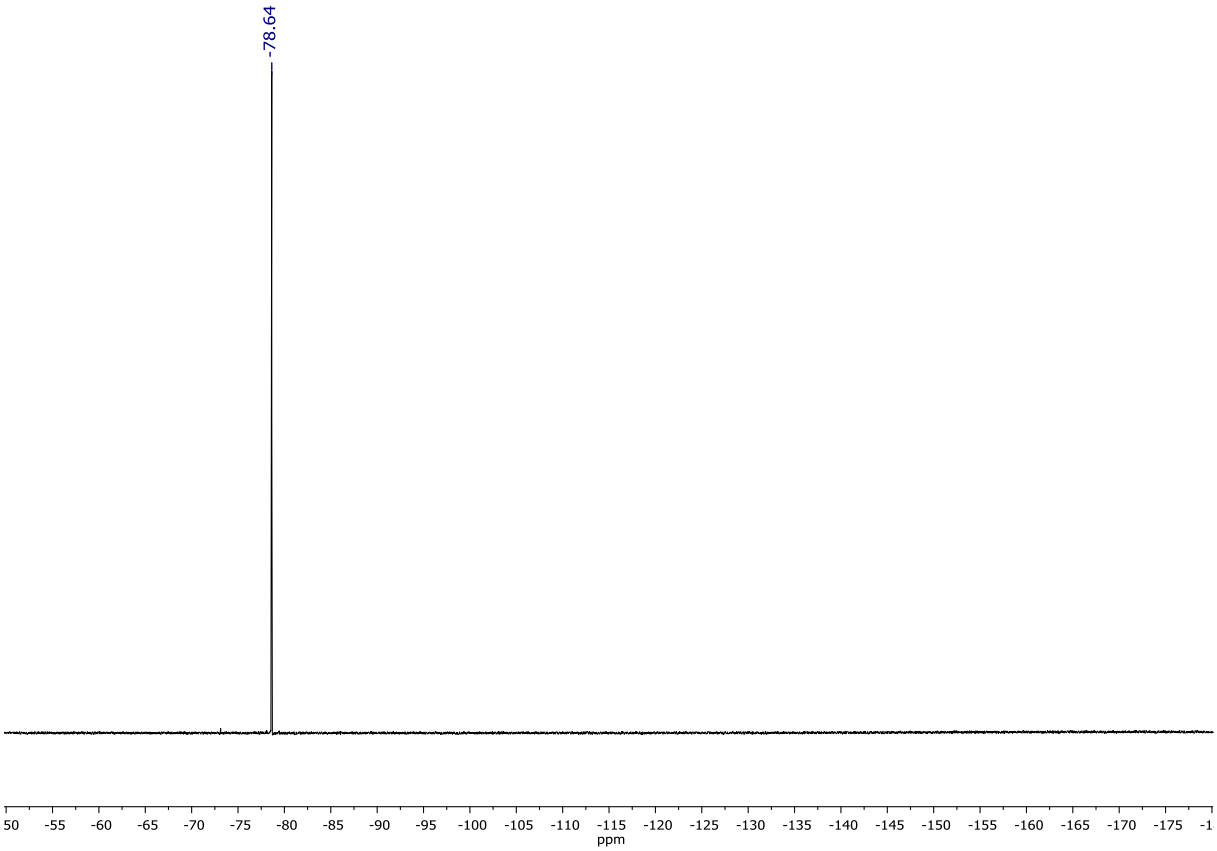


Figure 13: ^{19}F-NMR spectrum (235 MHz, $CDCl_3$) of 3,5-Py(I)^{Oct,Me}/NTf_2

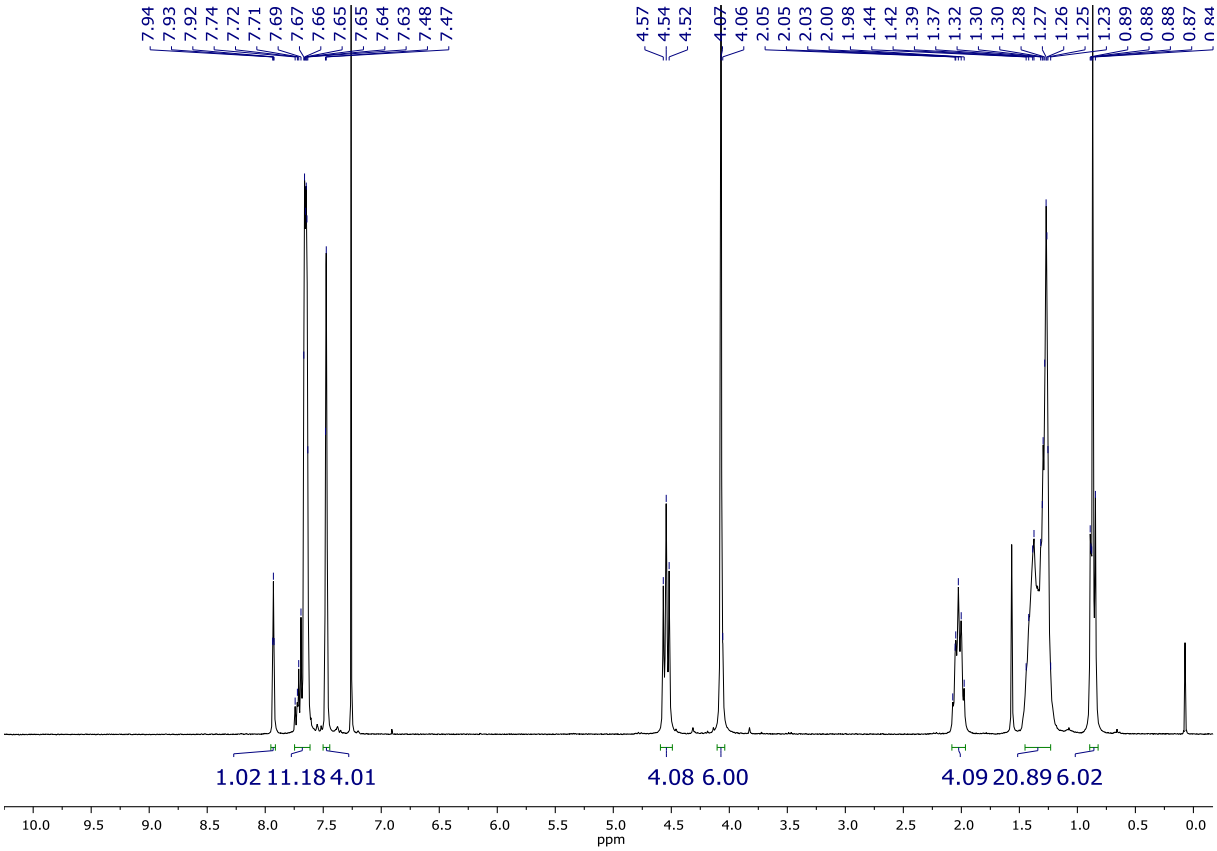


Figure 14: ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of 1,3-Ph(I)^{Oct,Me}/BAr$^{F}_4$.

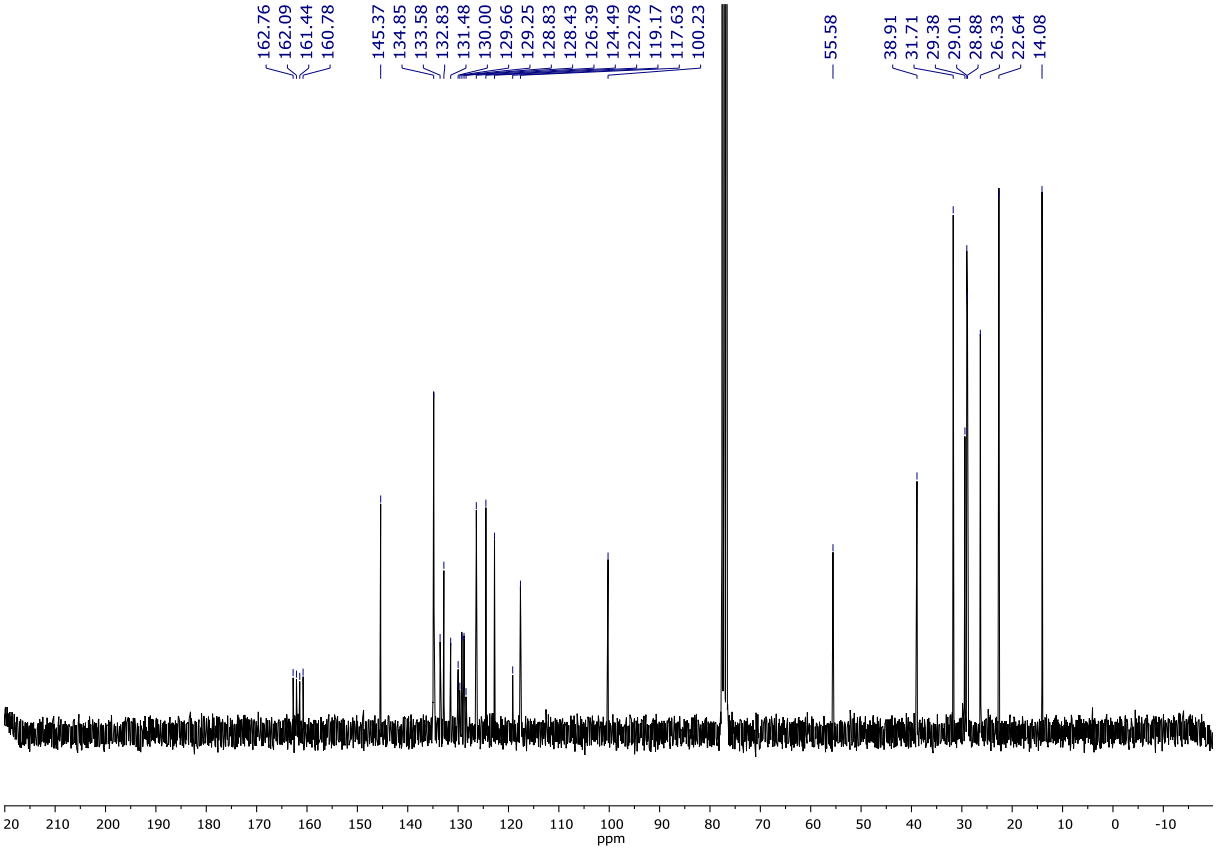


Figure 15: ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of 1,3-Ph(I)^{Oct,Me}/BAr$^{F}_4$.

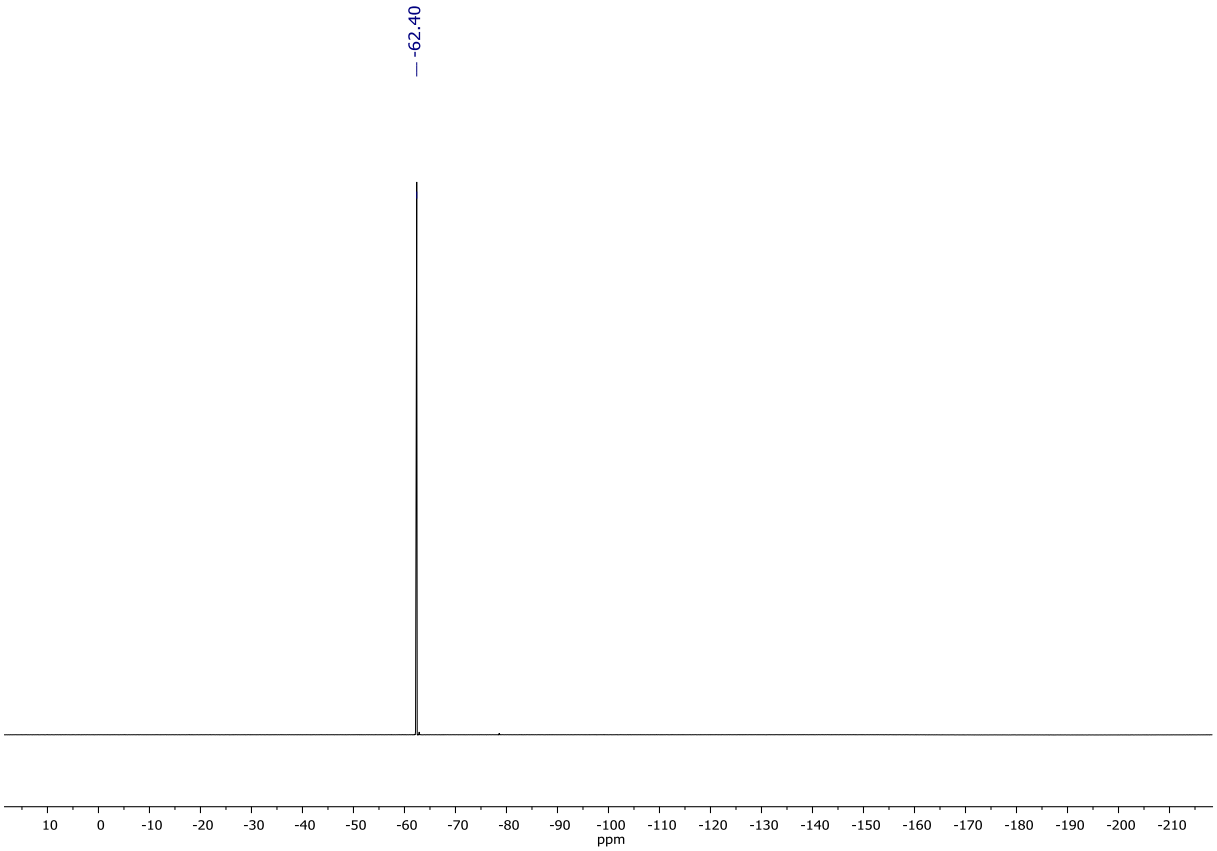


Figure 16: ^{19}F-NMR spectrum (235 MHz, $CDCl_3$) of 1,3-Ph(I)^{Oct,Me}/BAr^F_4.

ITC data

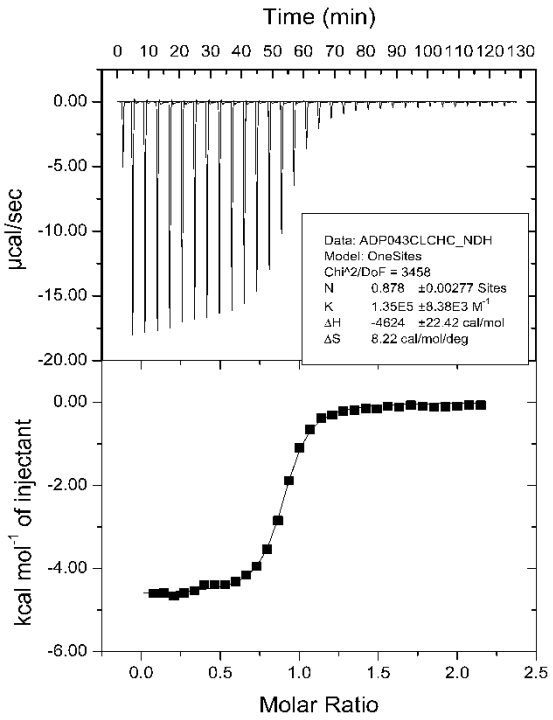


Figure 17: TOA-Cl (10 mM) into 3,5-Py(I)$^{Oct,\ Me}$/OTf (1 mM) in dry $CHCl_3$.

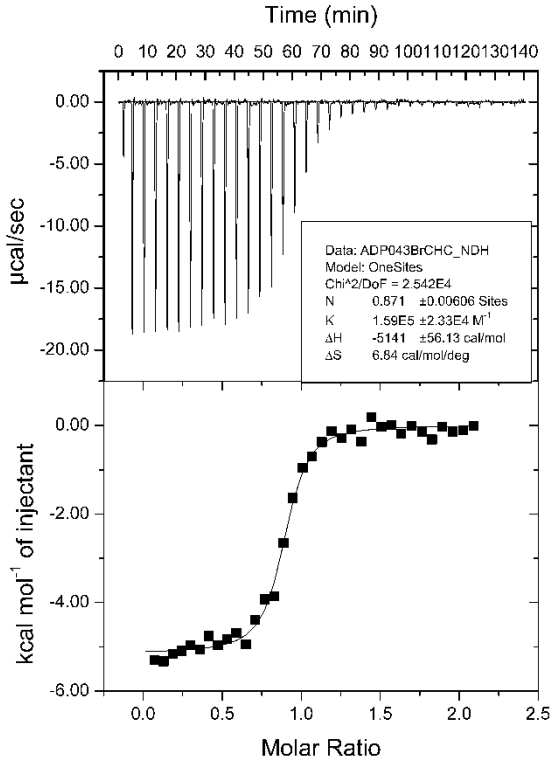


Figure 18: TOA-Br (10 mM) into 3,5-Py(I)$^{Oct, Me}$/OTf (1 mM) in dry $CHCl_3$.

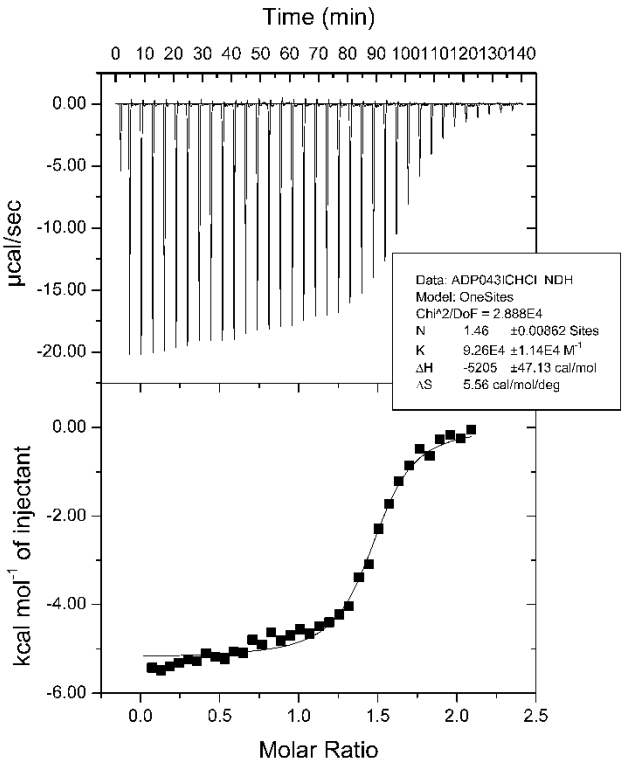


Figure 19*:* TOA-I (10 mM) into 3,5-Py(I)$^{Oct, Me}$/OTf (1 mM) in dry $CHCl_3$.

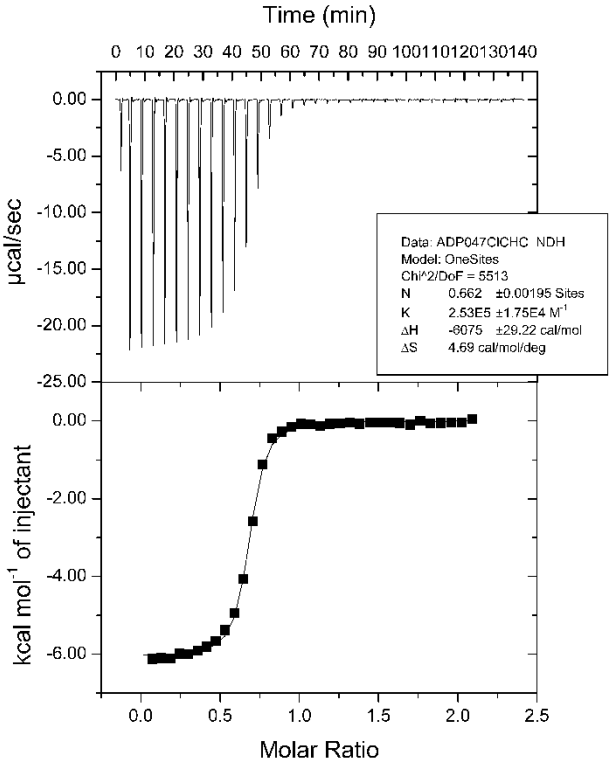


Figure 20: TOA-Cl(10 mM) into 3,5-Py(I)$^{Oct, Me}$/NTf_2 (1 mM) in dry $CHCl_3$.

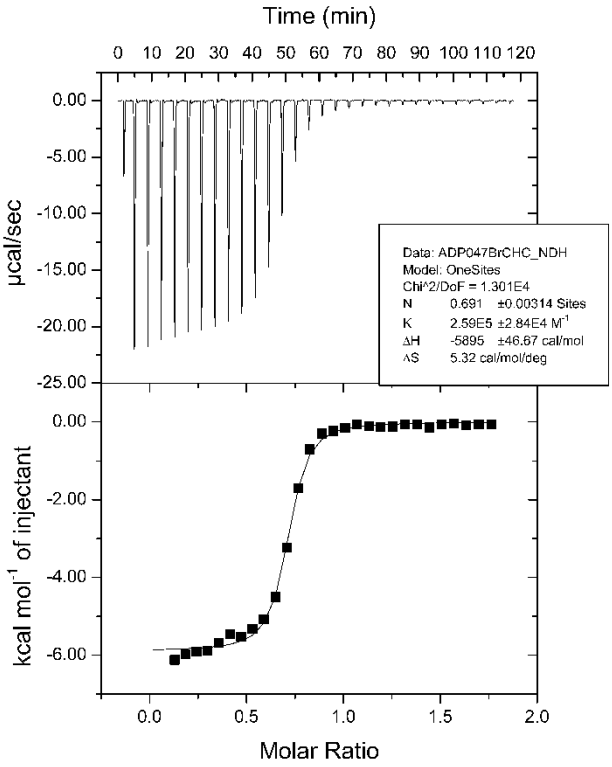


Figure 21: TOA-Br (10 mM) into 3,5-Py(I)$^{Oct, Me}$/NTf_2 (1 mM) in dry $CHCl_3$.

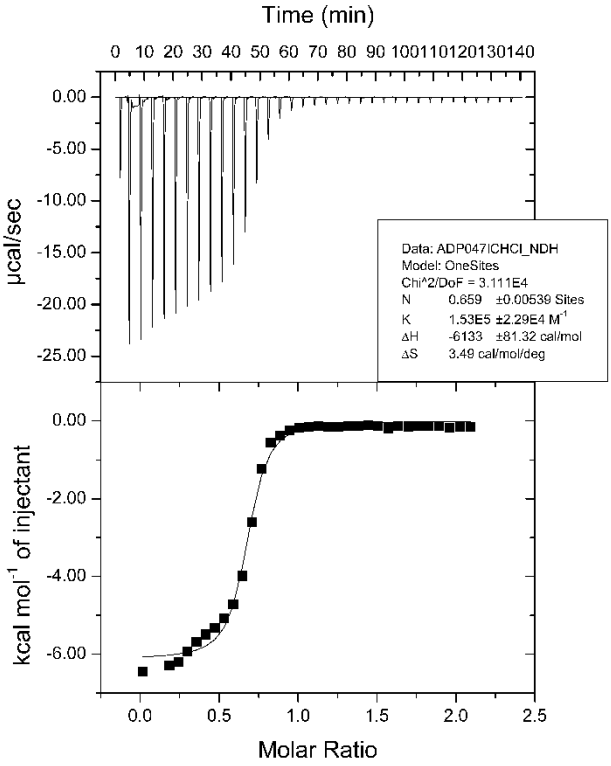


Figure 22: TOA-I (10 mM) into 3,5-Py(I)$^{Oct, Me}$/NTf_2 (1 mM) in dry $CHCl_3$.

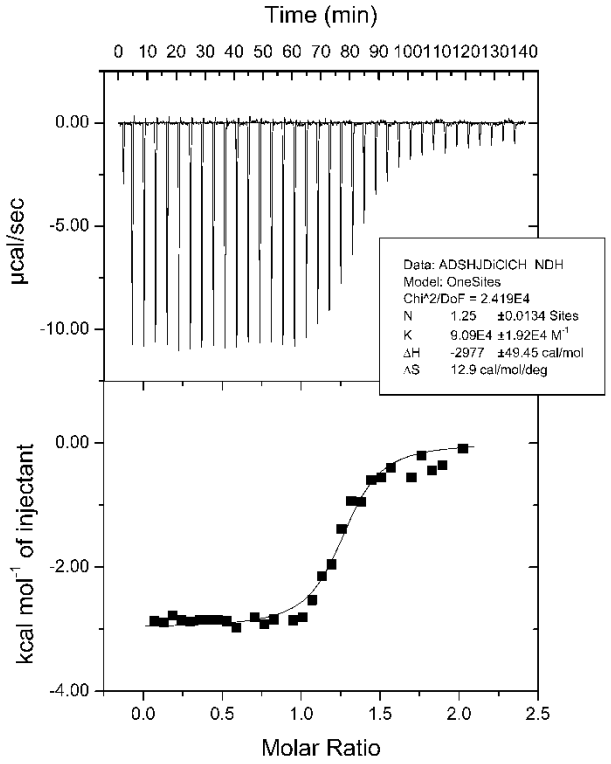


Figure 23: TOA-Cl (10 mM) into 1,3-Ph(I)^{Oct,Me}/OTf (1 mM) in dry $CHCl_3$.

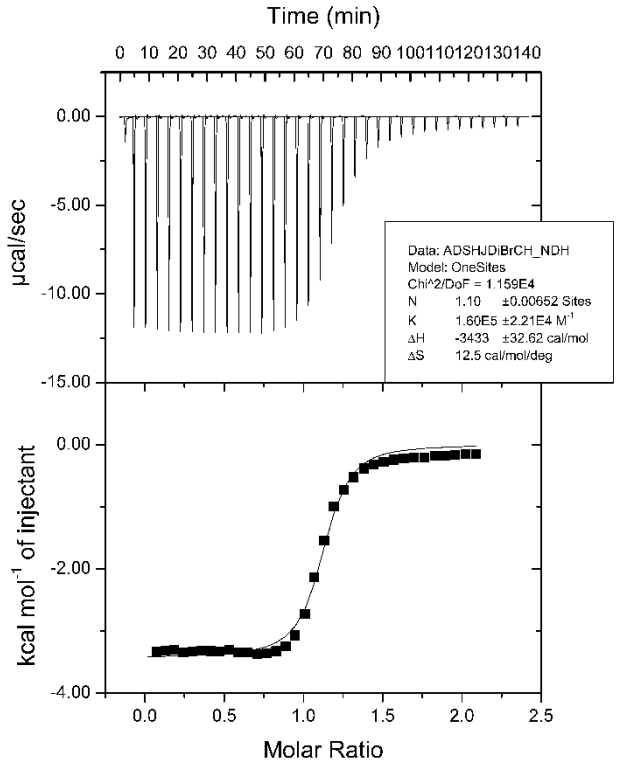


Figure 24: TOA-Br (10 mM) into 1,3-Ph(I)^{Oct,Me}/OTf (1 mM) in dry $CHCl_3$.

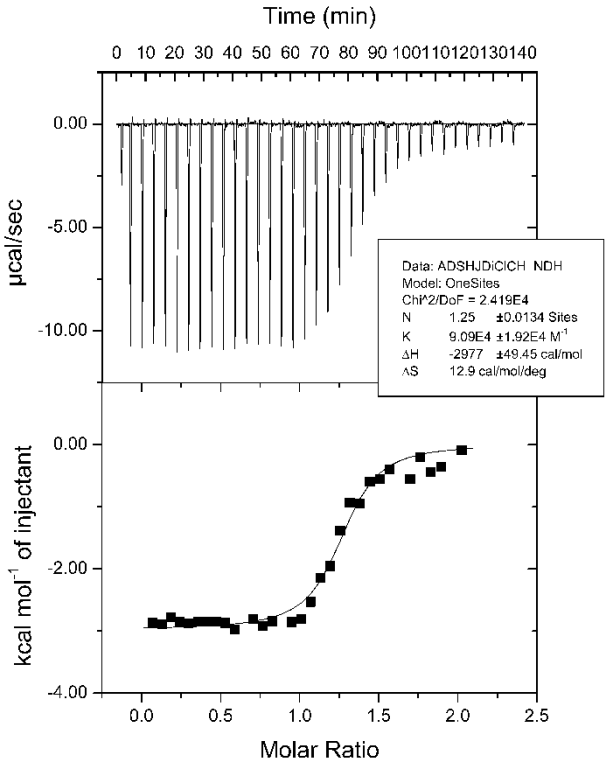


Figure 18: TOA-Br (10 mM) into 1,3-Ph(I)^{Oct,Me}/OTf (1 mM) in dry $CHCl_3$.

XRD Measurements

XRD measurements were performed on a single crystal-X-ray-diffractometer Stoe IPDSI. The crystal structures were solved using WinGX[9], SHELXT[10] and evaluated using shelxle64[11] and SHELXL. Visualizations were generated using Diamond 3.[12]

[9] L. J. Farrugia, J. Appl. Crystallogr., 1999, 32, 837.
[10] G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112.
[11] C. B. Hübschle, G. M. Sheldrick and B. Dittrich, J. Appl. Cryst. 2011, 44, 1281.
[12] a) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, Towler and van der Streek, J. Appl. Crystallogr., 2006, 39, 453-457 b) Diamond - Crys-tal and Molecular Structure Visualization, Crystal Impact - Dr. H. Putz & Dr. K. Bran-denburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, http://www.crystalimpact.com/diamond

Table 1: Crystallographic data of **3,5- Py(I)^{Bn,Me}/OTf** and **3,5-Py(I)^{Bn,Oct}/Br**

structure	**3,5-Py(I)^{Bn,Me}/OTf**	**3,5-Py(I)^{Bn,Oct}/Br**
CCDC-No.	1817655	1817656
sum formula	C25 H20 F3 I2 N7 O3 S	C33 H37 Br I2 N8
molar mass [g/mol]	809,34	879.11
crystal system	monoclinic	
space group	P 21/c (14)	
lattice constant [Å]		
a	14.2649(18)	15.479(5)
b	8.5985(7)	16.978(5)
c	22.850(3)	13.102(5)
β [°]	95.100(15)°	99.204(5)
density [g/cm^3]	1,93	1,72
cell volume [Å^3]	2791.61(50)	3398.91(200)
number of formula units	4	4
temperature [K]	170(2)	
used radiation	0.71073 Å (Mo-Kα, Graphite Monochromator)	
F(000)	1568,0	1728,0
abs. coefficient [mm^{-1}]	2,39	3,062
abs. correction	numerical	
measuring range	2.8 - 25.0°	2.5 - 25.0°
index area	$-16 \leq h \leq 16$	$-18 \leq h \leq 18$
	$-9 \leq k \leq 9$	$-18 \leq k \leq 19$
	$-27 \leq l \leq 27$	$-15 \leq l \leq 15$
reflexes measured	24138	23120
independent	4658	5803
observed	3752	44778
rint	0,032	0,052
solution/refinement	SHELXT / SHELXL	
R1 (observed/all)	0.021/0.030	0.026/0.035
wR2 (observed/all)	0.047/0.050	0.062/0.065
GooF = S	1,006	0,957
residual electron density max./min [e-/Å^3]	0.671/-0.504	0.972/-0.530

Table 2: Fractional Coordinates and Isotropic Thermal Parameters of **3,5-Py(I)^{Bn,Me}/OTf**.

	Atomic parameters			
Atom	x/a	y/b	z/c	Uiso/eq
Br	-0.29439(2)	-0.26895(2)	-0.07279(3)	0.0256(1)
C1	-0.7391(2)	0.1486(2)	-0.1755(3)	0.0203(8)
C10	-0.5564(2)	0.0164(2)	-0.2207(2)	0.0172(7)
C11	-0.5562(2)	-0.0367(2)	-0.1407(3)	0.0193(7)
C12	-0.6169(2)	-0.0306(2)	-0.0723(2)	0.0178(7)
C13	-0.6766(2)	0.0307(2)	-0.0878(3)	0.0199(8)
C2	-0.8250(2)	0.1278(2)	-0.2440(3)	0.0213(8)
C21	-0.4951(2)	0.0153(2)	-0.2953(3)	0.0195(8)
C22	-0.4269(2)	-0.0350(2)	-0.3092(3)	0.0196(7)
C23	-0.3306(2)	-0.0375(3)	-0.4485(3)	0.0269(9)
C24	-0.2400(2)	-0.0060(2)	-0.4123(3)	0.0229(8)
C25	-0.2252(3)	0.0660(3)	-0.3633(3)	0.0310(9)
C26	-0.1411(3)	0.0956(3)	-0.3405(3)	0.0373(10)
C27	-0.0712(3)	0.0534(3)	-0.3654(3)	0.0401(11)
C28	-0.0853(3)	-0.0187(3)	-0.4125(3)	0.0359(10)
C29	-0.1696(2)	-0.0485(3)	-0.4364(3)	0.0281(9)
C3	-0.8879(2)	0.1979(2)	-0.2489(3)	0.0240(8)
C31	-0.6195(2)	-0.0829(2)	0.0169(2)	0.0173(7)
C32	-0.5742(2)	-0.1497(2)	0.0538(3)	0.0174(7)
C33	-0.5796(2)	-0.2302(2)	0.2171(3)	0.0272(9)
C34	-0.6524(2)	-0.2881(2)	0.2225(3)	0.0224(8)
C35	-0.7017(3)	-0.2831(3)	0.3011(3)	0.0302(9)
C36	-0.7698(3)	-0.3348(3)	0.3061(3)	0.0393(11)
C37	-0.7898(3)	-0.3923(3)	0.2314(4)	0.0415(11)
C38	-0.7404(3)	-0.3986(3)	0.1539(3)	0.0416(11)
C39	-0.6720(3)	-0.3466(3)	0.1489(3)	0.0324(9)
C4	-0.9224(3)	0.2115(3)	-0.1474(3)	0.0305(9)
C5	-0.9920(2)	0.2749(2)	-0.1541(3)	0.0289(9)
C6	-1.0191(3)	0.2935(3)	-0.0503(3)	0.0343(10)
C7	-1.0554(3)	0.2249(3)	0.0038(3)	0.0355(10)
C8	-1.1356(3)	0.1889(4)	-0.0574(4)	0.0562(15)
C9	-0.6186(2)	0.0764(2)	-0.2312(2)	0.0175(7)
C90	-0.0233(5)	-0.0336(4)	-0.1251(4)	0.0727(18)
C91	-0.1160(3)	-0.0505(4)	-0.1270(5)	0.0671(17)
H11	-0,5151	-0,07716	-0,13215	0,023
H13	-0,71788	0,03607	-0,04392	0,024
H1A	-0,71311	0,19357	-0,20482	0,024
H1B	-0,75079	0,1636	-0,1076	0,024
H23A	-0,34708	-0,02553	-0,52137	0,032
H23B	-0,32942	-0,09434	-0,44122	0,032
H25	-0,27188	0,09452	-0,34556	0,037
N4	-0.39752(18)	-0.00599(19)	-0.3928(2)	0.0218(7)

N5	-0.67584(18)	-0.06428(19)	0.0838(2)	0.0222(7)
N6	-0.6669(2)	-0.1153(2)	0.1588(2)	0.0252(7)
N7	-0.60508(18)	-0.16757(19)	0.1408(2)	0.0209(7)
N90	0.0546(5)	-0.0200(4)	-0.1196(5)	0.095(2)

Table 3: Anisotropic Displacement Parameters of **3,5-Py(I)^{Bn,Me}/OTf.**

Anisotropic displacement parameters, in Å^2

Atom	U11	U22	U33	U12	U13	U23
Br	0.02486(18)	0.00852(15)	0.00295(15)	-0.00167(15)	0.00020()	0.0002()
C1	0.0220(17)	0.0042(14)	0.0058(14)	-0.0016(14)	0.0018()	0.0020()
C10	0.0184(16)	-0.0023(13)	0.0001(13)	-0.0045(14)	0.0016()	0.0020()
C11	0.0218(17)	0.0022(14)	0.0006(14)	-0.0018(14)	0.0017()	0.0020()
C12	0.0139(15)	-0.0012(14)	-0.0013(13)	0.0007(14)	0.0017()	0.0020()
C13	0.0197(17)	-0.0010(14)	0.0035(14)	-0.0011(14)	0.0017()	0.0020()
C2	0.0206(17)	0.0002(15)	0.0043(14)	-0.0027(14)	0.0018()	0.0020()
C21	0.0182(17)	-0.0018(14)	-0.0005(13)	0.0041(14)	0.0017()	0.0020()
C22	0.0224(17)	0.0004(14)	0.0015(14)	-0.0005(14)	0.0016()	0.0020()
C23	0.0273(19)	-0.0001(16)	0.0084(15)	-0.0072(16)	0.0019()	0.0030()
C24	0.0191(17)	-0.0036(16)	0.0075(14)	0.0016(15)	0.0018()	0.0020()
C25	0.033(2)	-0.0013(17)	0.0134(17)	-0.0092(18)	0.0020()	0.0030()
C26	0.037(2)	-0.015(2)	0.012(2)	-0.0120(19)	0.0030()	0.0030()
C27	0.048(3)	-0.011(2)	0.0052(19)	-0.002(2)	0.0020()	0.0030()
C28	0.053(3)	-0.0008(18)	0.0097(18)	0.001(2)	0.0020()	0.0030()
C29	0.037(2)	0.0001(16)	0.0085(16)	-0.0034(17)	0.0019()	0.0020()
C3	0.031(2)	0.0044(15)	-0.0001(15)	0.0010(16)	0.0018()	0.0020()
C31	0.0148(16)	-0.0021(14)	0.0002(13)	-0.0007(14)	0.0016()	0.0020()
C32	0.0204(17)	0.0006(13)	0.0001(13)	-0.0027(14)	0.0015()	0.0020()
C33	0.0252(19)	0.0021(16)	-0.0039(16)	0.0091(16)	0.0020()	0.0020()
C34	0.0213(18)	0.0081(15)	0.0035(15)	0.0054(14)	0.0019()	0.0020()
C35	0.025(2)	0.0091(18)	0.0083(17)	0.0046(16)	0.0020()	0.0030()
C36	0.043(2)	0.013(2)	0.0196(19)	0.020(2)	0.0020()	0.0030()
C37	0.058(3)	-0.0008(19)	0.006(2)	0.018(2)	0.0020()	0.0030()
C38	0.042(2)	-0.002(2)	-0.001(2)	-0.004(2)	0.0030()	0.0030()
C39	0.027(2)	0.0050(19)	0.0105(18)	-0.0010(17)	0.0020()	0.0030()
C4	0.032(2)	0.0074(17)	0.0029(16)	0.0025(17)	0.0020()	0.0030()
C5	0.038(2)	0.0030(16)	0.0055(17)	0.0010(17)	0.0020()	0.0020()
C6	0.039(2)	-0.0006(18)	0.0085(17)	-0.0061(19)	0.0020()	0.0030()
C7	0.030(2)	0.0007(19)	0.0096(18)	0.0007(18)	0.0020()	0.0030()
C8	0.042(3)	-0.028(3)	0.009(2)	-0.002(3)	0.0030()	0.0040()
C9	0.0162(16)	-0.0029(14)	0.0023(13)	0.0036(13)	0.0017()	0.0020()
C90	0.054(3)	0.007(4)	0.020(3)	0.011(3)	0.0050()	0.0050()
C91	0.076(4)	-0.001(3)	-0.002(3)	0.021(3)	0.0030()	0.0050()
I1	0.02896(13)	0.00234(9)	0.00384(9)	-0.00185(9)	0.00012(0)	0.00015(0)
I2	0.02180(12)	0.00491(9)	0.00060(9)	-0.00001(9)	0.00012(0)	0.00015(0)
N1	0.0181(14)	0.0018(12)	0.0038(12)	-0.0006(12)	0.0014()	0.0018()
N2	0.0224(15)	0.0022(13)	0.0053(12)	0.0055(13)	0.0015()	0.0020()
N3	0.0270(17)	0.0017(14)	0.0085(13)	0.0058(14)	0.0016()	0.0020()
N4	0.0222(15)	0.0013(13)	0.0058(12)	0.0017(13)	0.0015()	0.0020()
N5	0.0221(15)	0.0002(13)	0.0062(12)	0.0016(13)	0.0015()	0.0019()

Table 4: Fractional Coordinates and Isotropic Thermal Parameters of **3,5-Py(I)^{Bn,Oct}/Br**.

	Atomic parameters			
Atom	x/a	y/b	z/c	Uiso/eq
C1	0.0857(3)	0.1376(5)	0.48950(16)	0.0409(9)
C10	0.4696(2)	0.2581(4)	0.39378(13)	0.0202(6)
C11	0.5043(2)	0.3048(4)	0.34145(13)	0.0216(6)
C12	0.6195(2)	0.4300(4)	0.28517(13)	0.0291(7)
C13	0.6364(2)	0.4190(4)	0.39252(13)	0.0221(7)
C14	0.6057(2)	0.3767(4)	0.44639(12)	0.0198(6)
C15	0.5214(2)	0.2969(4)	0.44651(12)	0.0201(6)
C16	0.6661(2)	0.4253(4)	0.49953(13)	0.0213(7)
C17	0.6615(2)	0.4028(4)	0.55901(13)	0.0199(6)
C18	0.7686(2)	0.5097(4)	0.64675(13)	0.0256(7)
C19	0.8436(2)	0.3980(4)	0.67139(13)	0.0227(7)
C2	0.0169(3)	0.2424(6)	0.5021(2)	0.0522(12)
C20	0.8245(2)	0.2889(5)	0.71293(14)	0.0332(8)
C21	0.8950(3)	0.1912(5)	0.73688(16)	0.0405(9)
C22	0.9851(3)	0.2016(5)	0.71941(16)	0.0413(9)
C23	1.0038(3)	0.3094(5)	0.67740(18)	0.0433(10)
C24	0.9335(2)	0.4074(5)	0.65304(16)	0.0334(8)
C25	0.2531(2)	0.1332(5)	0.68080(14)	0.0300(8)
C3	-0.0479(3)	0.2950(5)	0.4590(2)	0.0564(13)
C4	-0.0446(3)	0.2428(6)	0.4029(2)	0.0551(12)
C5	0.0254(3)	0.1400(5)	0.38883(17)	0.0413(9)
C6	0.0909(2)	0.0860(4)	0.43250(15)	0.0291(8)
C7	0.1655(2)	-0.0277(4)	0.41741(14)	0.0279(7)
C8	0.3265(2)	0.1062(4)	0.42979(13)	0.0215(7)
C9	0.3804(2)	0.1723(4)	0.38894(12)	0.0206(7)
F1	0.22958(14)	0.2037(3)	0.72901(9)	0.0506(6)
F2	0.19265(15)	0.0196(3)	0.66906(12)	0.0583(7)
F3	0.24109(16)	0.2350(3)	0.63686(9)	0.0477(6)
H1	0,12866	0,10163	0,51943	0,049
H11	0,47063	0,28186	0,30576	0,026
H12A	0,60516	0,35013	0,25642	0,044
H12B	0,68638	0,44588	0,29021	0,044
H12C	0,5891	0,52503	0,27213	0,044
H13	0,69267	0,4732	0,39134	0,027
H15	0,49907	0,26878	0,48205	0,024
H18A	0,71479	0,50205	0,66977	0,031
H18B	0,79281	0,61492	0,65082	0,031
H2	0,0147	0,27761	0,54047	0,063
H20	0,76404	0,28085	0,72492	0,04
H21	0,88166	0,11808	0,76494	0,049
H22	1,03245	0,13654	0,73581	0,05

Table 5: Anisotropic Displacement Parameters of **3,5-Py(I)^{Bn,Oct}/Br**.

Anisotropic displacement parameters, in Å^2

Atom	U11	U22	U33	U12	U13	U23
C1	0.0349(19)	-0.0079(18)	0.0114(15)	-0.0045(18)	0.0019()	0.0030()
C10	0.0226(15)	0.0057(12)	0.0017(11)	-0.0003(12)	0.0014()	0.0019()
C11	0.0203(14)	0.0044(13)	0.0012(11)	-0.0005(12)	0.0015()	0.0019()
C12	0.0182(15)	-0.0037(15)	0.0102(13)	0.0031(14)	0.0018()	0.0020()
C13	0.0239(15)	0.0025(12)	0.0065(12)	0.0006(12)	0.0015()	0.0019()
C14	0.0188(14)	0.0062(12)	0.0009(11)	0.0014(12)	0.0015()	0.0019()
C15	0.0157(13)	0.0047(12)	0.0035(11)	0.0031(12)	0.0016()	0.0018()
C16	0.0228(15)	-0.0012(12)	0.0045(11)	-0.0072(13)	0.0014()	0.0019()
C17	0.0219(15)	0.0025(12)	0.0028(11)	0.0022(12)	0.0015()	0.0019()
C18	0.0239(15)	-0.0006(14)	0.0013(12)	-0.0079(14)	0.0016()	0.0020()
C19	0.0185(15)	-0.0005(13)	0.0002(12)	-0.0096(12)	0.0016()	0.0020()
C2	0.053(3)	-0.011(2)	0.028(2)	-0.020(2)	0.00200(	0.0030()
C20	0.0268(17)	-0.0027(16)	0.0078(14)	-0.0043(15)	0.0018()	0.0020()
C21	0.0283(18)	0.0092(18)	0.0013(15)	0.0081(16)	0.0020()	0.0030()
C22	0.0323(19)	0.0123(18)	-0.0103(15)	-0.0030(17)	0.0020()	0.0030()
C23	0.049(2)	0.0045(17)	0.0031(15)	0.0010(19)	0.0018()	0.0030()
C24	0.0353(19)	-0.0021(15)	0.0041(14)	-0.0014(15)	0.0018()	0.0020()
C25	0.0241(16)	0.0032(15)	0.0005(13)	0.0011(14)	0.0018()	0.0020()
C3	0.088(4)	0.002(2)	0.034(2)	0.005(2)	0.0020()	0.0030()
C4	0.068(3)	0.011(2)	0.010(2)	0.012(2)	0.0020()	0.0030()
C5	0.039(2)	0.0007(18)	0.0047(16)	-0.0006(17)	0.0020()	0.0030()
C6	0.0339(18)	-0.0105(14)	0.0101(13)	0.0003(14)	0.0016()	0.0020()
C7	0.0253(16)	-0.0090(14)	0.0044(13)	-0.0024(13)	0.0017()	0.0020()
C8	0.0188(15)	0.0047(12)	0.0010(12)	-0.0022(11)	0.0016()	0.0020()
C9	0.0131(13)	0.0032(13)	0.0029(11)	0.0016(11)	0.0016()	0.0019()
F1	0.0314(11)	0.0183(11)	0.0065(9)	-0.0135(11)	0.0011()	0.0020()
F2	0.0804(18)	-0.0125(11)	-0.0126(11)	-0.0006(13)	0.0012()	0.0019()
F3	0.0393(12)	0.0213(11)	0.0058(10)	0.0158(10)	0.0013()	0.0017()
I1	0.01752(10)	-0.00018(8)	0.00314(7)	0.00239(8)	0.00011(0)	0.00013(0)
I2	0.0183(1)	-0.00078(8)	0.00376(7)	0.00108(8)	0.00011(0)	0.00013(0)
N1	0.0216(13)	-0.0018(11)	0.0036(10)	-0.0024(11)	0.0014()	0.0017()
N2	0.0202(13)	-0.0029(13)	0.0003(11)	-0.0006(12)	0.0015()	0.0019()
N3	0.0201(13)	-0.0005(12)	0.0018(10)	-0.0008(11)	0.0014()	0.0018()
N4	0.0182(12)	0.0046(11)	0.0052(10)	0.0023(10)	0.0014()	0.0017()
N5	0.0230(13)	-0.0020(12)	0.0025(11)	0.0014(11)	0.0013()	0.0018()
N6	0.0271(14)	-0.0028(12)	0.0042(12)	0.0017(12)	0.0015()	0.0020()
N7	0.0209(13)	0.0005(11)	0.0024(10)	-0.0008(11)	0.0013()	0.0017()

O1	0.0235(12)	0.0013(11)	0.0018(9)	0.0107(10)	0.0013()	0.0017()
O2	0.0451(14)	-0.0032(11)	0.0106(11)	0.0066(11)	0.0013()	0.0017()
O3	0.0220(12)	0.0234(13)	0.0040(11)	-0.0011(11)	0.0017()	0.0018()
S1	0.0173(4)	0.0044(3)	0.0041(3)	0.0031(3)	0.0004()	0.0005()