Supporting Information

„Molecular-Level Characterization of the Structure and the Surface Chemistry of Periodic Mesoporous Organosilicates DNP-Surface Enhanced NMR Spectroscopy."

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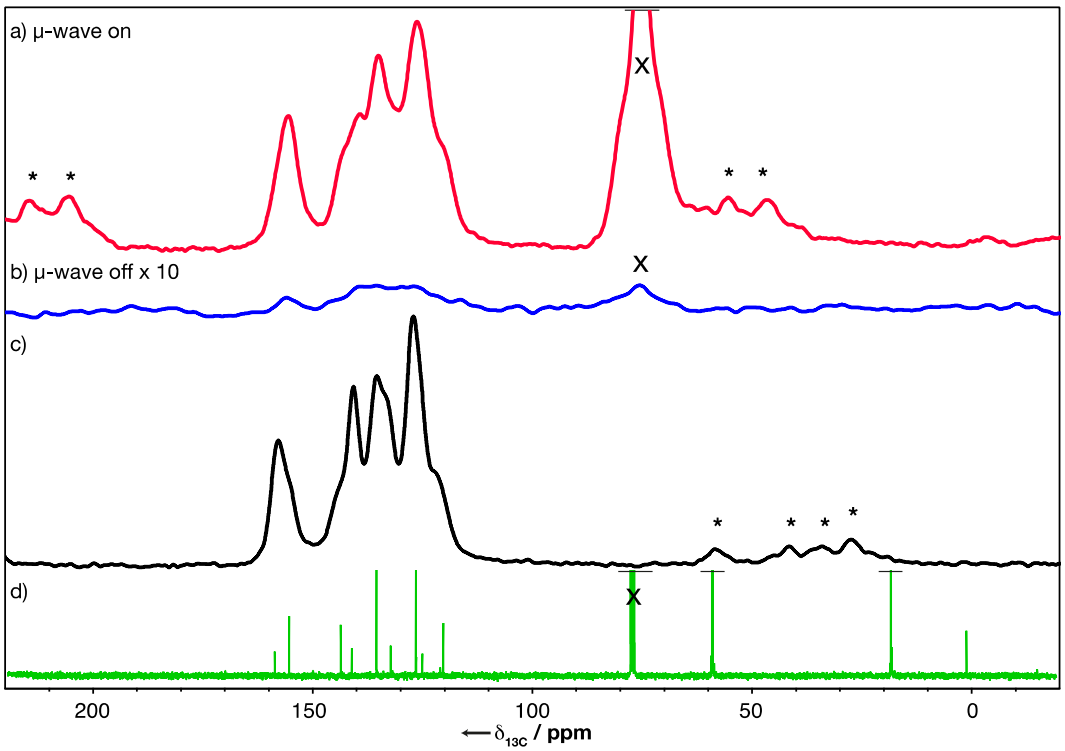


Figure S1: ^{13}C-NMR spectra: a) DNP-SENS µ-wave on spectrum of **ppy-PMO** (16 mM bCTbK / $C_2H_2Cl_4$, ν_{rot} = 8 kHz, 32 scans, S/N = 125); b) µ-wave off spectrum of **ppy-PMO** (16 mM bCTbK / $C_2H_2Cl_4$, ν_{rot} = 8 kHz, 256 scans); c) CP-MAS of **ppy-PMO** (neat, ν_{rot} = 10 kHz, 7888 scans, S/N = 96); d) **bTS-ppy** ($CDCl_3$, 1024 scans); X: solvent resonance, *: spinning-side-band

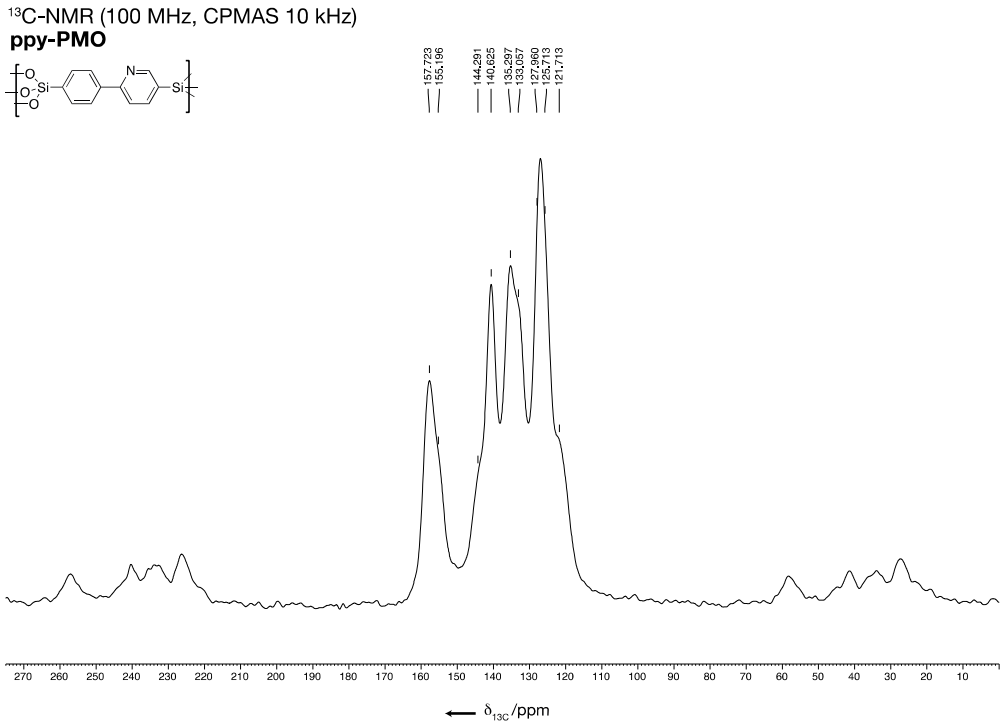


Figure S2: ^{13}C-NMR spectra: CP-MAS of **ppy-PMO** (neat, ν_{rot} = 10 kHz, 7888 scans τcp=2.5 ms, S/N = 96); full width of c) in Figure S1

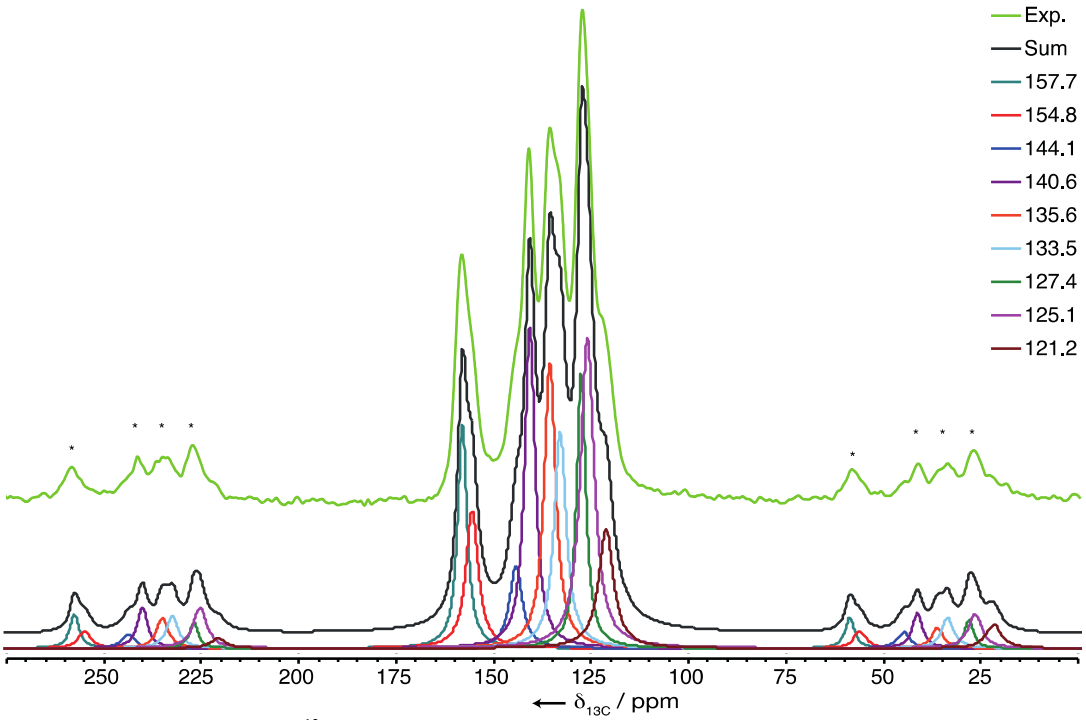


Figure S3: Decompostion of ^{13}C-NMR of **ppy-PMO**; the experimental spectrum (Fig S2) (light green) was fitted with nine individual sites using dmfit

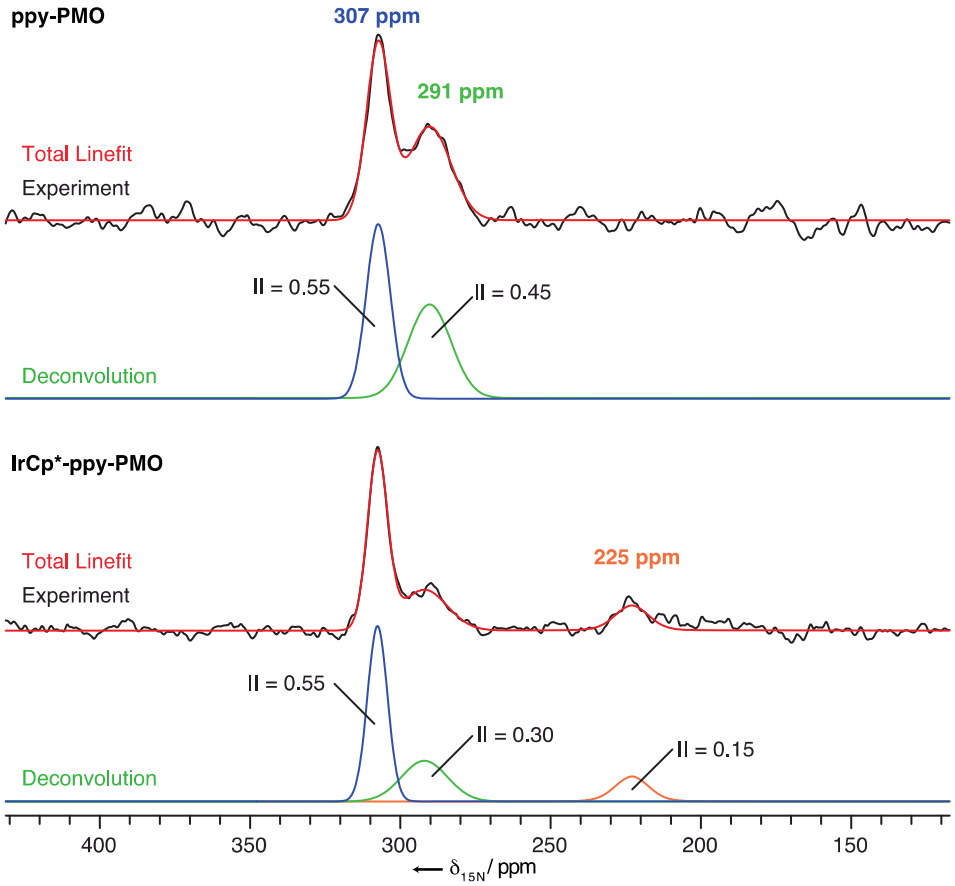


Figure S4: Deconvolution of ^{15}N CPMAS DNP SENS spectra of **ppy-PMO** (top) and **IrCp*-ppy-PMO** (bottom). Integrated intensities (II) for each of the sites are given.

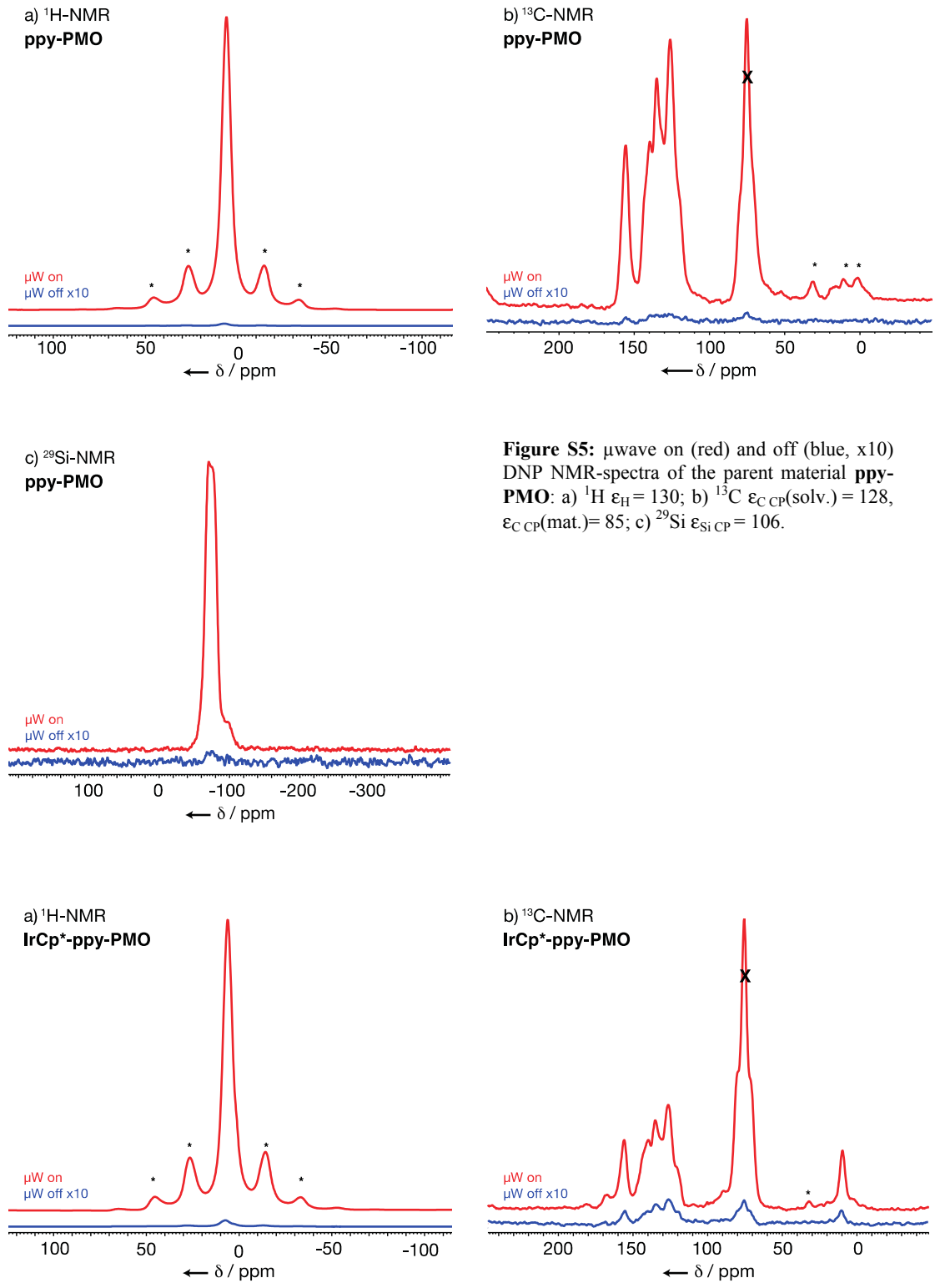


Figure S5: μwave on (red) and off (blue, x10) DNP NMR-spectra of the parent material **ppy-PMO**: a) $^{1}H\ \varepsilon_{H} = 130$; b) $^{13}C\ \varepsilon_{C\ CP}(solv.) = 128$, $\varepsilon_{C\ CP}(mat.) = 85$; c) $^{29}Si\ \varepsilon_{Si\ CP} = 106$.

Figure S6: μwave on (red) and off (blue, x10) DNP NMR-spectra of **IrCp*-ppy-PMO** a) $^{1}H\ \varepsilon_{H} = 46$; b) $^{13}C\ \varepsilon_{C\ CP}(solv.) = 100$, $\varepsilon_{C\ CP}(mat.) = 32$.

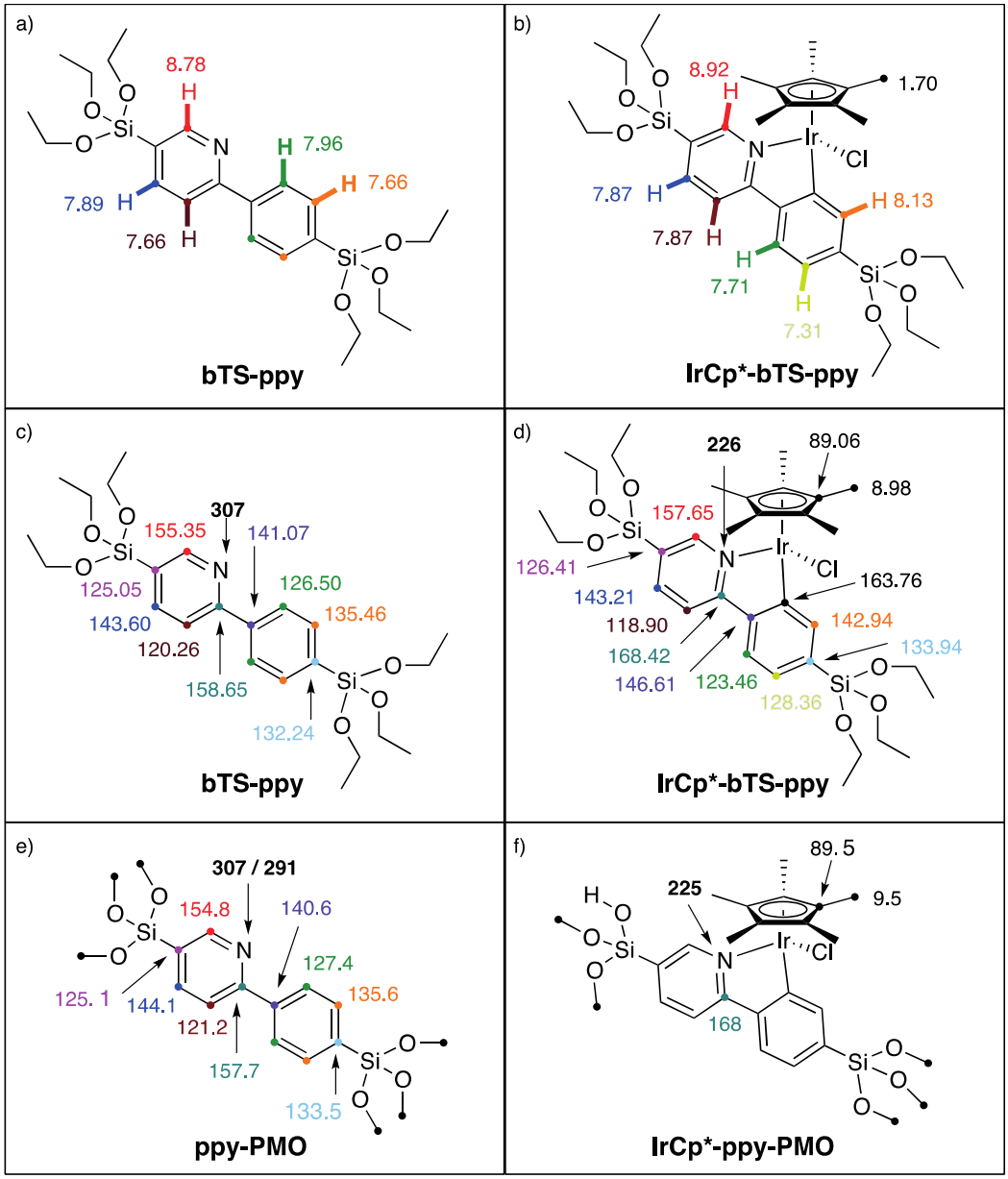


Figure S7: Assignment of the chemical shifts in the aromatic core and metal complexes a) ^{1}H **bTS-ppy,** b) ^{1}H **IrCp*-bTS-ppy,** c) ^{13}C & ^{15}N **bTS-ppy,** d) ^{13}C & ^{15}N **IrCp*-bTS-ppy,** e) ^{13}C & ^{15}N **ppy-PMO**, f) ^{13}C & ^{15}N **IrCp*-ppy-PMO** other resonances are coverd **by ppy-PMO**.

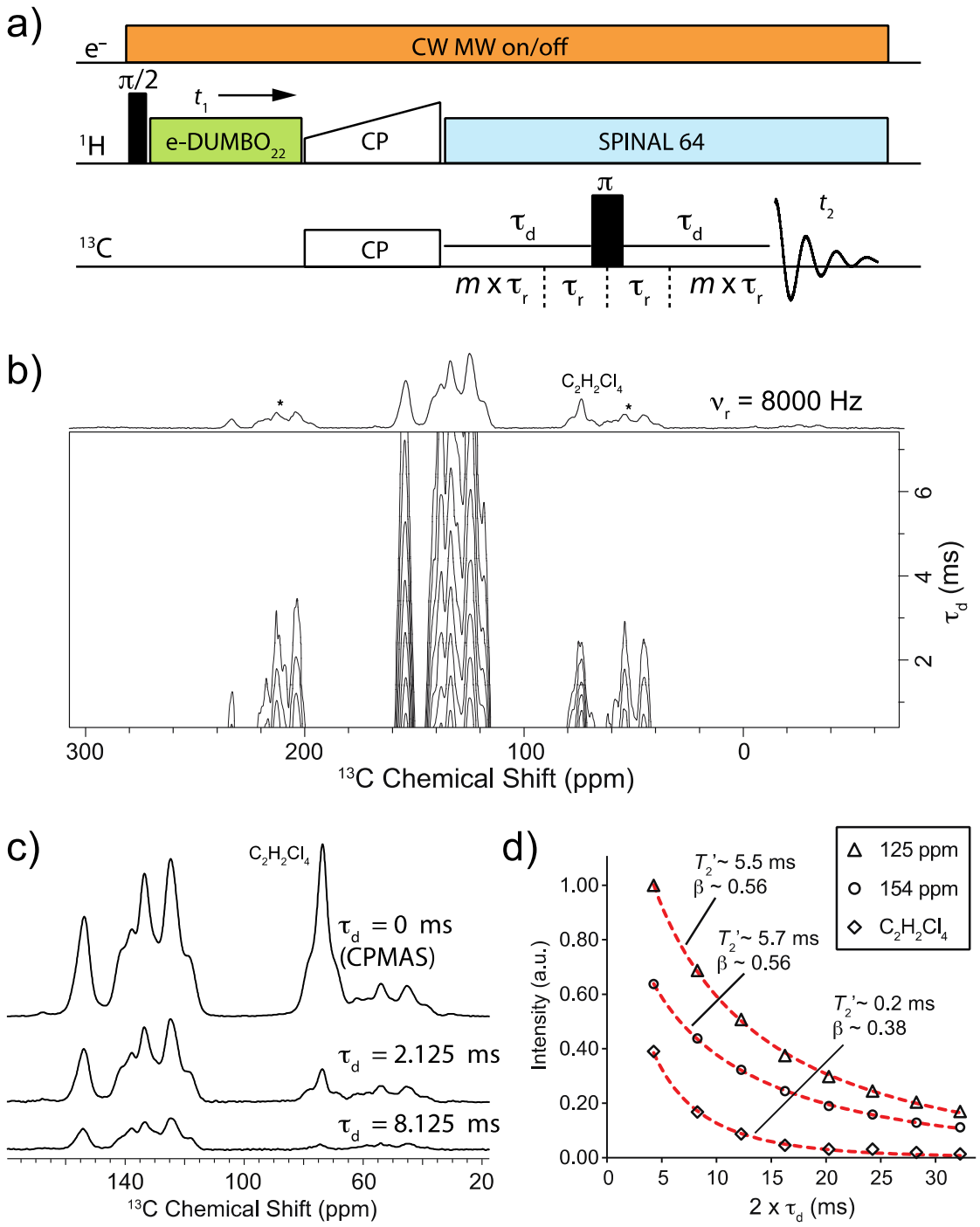


Figure S8: a) ^{1}H-^{13}C CPMAS echo detected HETCOR pulse sequence. For the acquisition of one dimensional spectra the e-DUMBO$_{22}$ block on ^{1}H was excluded. b) Pseudo-2D spectrum showing the intensity of the echo detected 13C CPMAS spectra as a function of the echo delay (τ_d) acquired with microwave irradiation. c) Comparison of standard ^{13}C CPMAS spectrum (upper) and echo detected spectra acquired with τ_d = 2.125 ms (middle) and τ_d = 8.125 ms (lower). d) The intensity of the several different carbon resonances in the echo detected spectra as a function of $2\tau_d$ (open points). Red dashed lines represent fits to stretched exponential functions of the form, $I(t) = \exp(-(t/T_2')^{\beta})$. The 1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$) possesses a short $T_2'(^{13}C)$ which enables efficient suppresion of the solvent resonances with minimal signal losses.

b) Experimental Details

General

Chemicals were of reagent grade or better and purchased from, ABCR, Acros Organics, Sigma-Aldrich or TCI and used without further purification. All air or water sensitive manipulations were carried out under argon using Schlenk-techniques or gloveboxes. Elemental analysis was performed by Mikroanalytisches Labor Pascher (Remagen, Germany). Nitrogen sorption experiments were performed on a BELsorp-mini II. Powder X-ray experiments were performed on a STOE Padi Diffractometer in Debye-Scherrer Mode (2 θ) with a dectris Mythen 1K area detector using Cu K-α (ν = 1.54 Å) radiation.

Liquid-state NMR Experiments

^{1}H, ^{13}C, ^{15}N, and ^{29}Si-NMR spectra were recorded on Bruker DRX 200, DRX 300, and DRX 400 spectrometers. The samples were measured as solutions in the given solvent at room temperature in non-spinning mode. ^{1}H, ^{13}C chemical shifts are referenced relative to residual solvent peak; ^{15}N chemical shifts were referenced to external NH_3; ^{29}Si chemical shifts were referenced to external tetramethylsilane. Chemical shifts for ^{15}N were determined by measurement of ^{1}H-^{15}N HMBC and spectra. ^{29}Si spectra were acquire using inverse gated decoupling pulse sequences. The multiplicities of the signals are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet. The assignment of ^{1}H and ^{13}C chemical shifts was aided by standard ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and ^{1}H-^{1}H COSY experiments. To establish close contacts ^{1}H-^{1}H NOESY and spectra were recorded. ^{1}H-^{15}N HMBC spectra were acquired on a Bruker DRX 300 or spectrometer equipped with a multinuclear inverse probe. A relaxation delay of 2.0 s was applied and a defocusing delay of 100 ms was chosen, corresponding to a coupling constant of 5 Hz. The number of scans per increment was 32 (2k data points), and 128 experiments were acquired in the second dimension. ^{1}H-^{1}H NOESY spectra were acquired on Bruker DRX 400 spectrometer equipped with a multinuclear inverse probe. A relaxation delay of 4.0 s was applied and the mixing time was 1.7 s. The number of scans per increment was 32 (2k data points) and 256 experiments were acquired in the second dimension.

DNP- Solid-State NMR Experiments

Standard cross-polarization (CP) was used for 1D carbon-13 and silicon-29 spectra. ^{13}C and ^{29}Si solid-state NMR experiments were performed on a 9.4 T Bruker Avance

III DNP spectrometer. For ^{13}C CPMAS The ^{1}H $\pi/2$ pulse length was 2.5 μs (100 kHz). A linear amplitude ramp (from 50% to 100% of the nominal RF field strength) was used for the ^{1}H channel, with a 3.0 ms contact time and a nominal RF field amplitude of ν_1 = 68 kHz for ^{1}H and 50 kHz for ^{13}C. SPINAL-64[1] proton decoupling was applied during the acquisition of the ^{13}C signal with an RF field amplitude of ν_1 = 100 kHz. The ^{13}C acquisition time was 10 ms with 992 complex points.

For ^{29}Si CPMAS the ^{1}H $\pi/2$ pulse length was 2.5 μs (100 kHz). A linear amplitude ramp (from 50% to 100% of the nominal RF field strength) was used for the ^{1}H channel, with a 2.0 ms contact time and a nominal RF field amplitude of ν_1 = 65 kHz for ^{1}H and 50 kHz for ^{29}Si. SPINAL-64 proton decoupling was applied during the acquisition of the ^{29}Si signal with an RF field amplitude of ν_1 = 100 kHz. The ^{29}Si acquisition time was 10 ms with 992 complex points.

^{15}N CPMAS spectra were acquired on a 14.1 T Bruker Avance III DNP spectrometer. The ^{1}H $\pi/2$ pulse length was 2.5 μs (100 kHz). A linear amplitude ramp (from 50% to 100% of the nominal RF field strength) was used for the ^{1}H channel with a nominal RF field amplitude of ν_1 = 65 kHz for ^{1}H and 50 kHz for ^{15}N. The ^{15}N spectrum of **ppy-PMO** was acquired with a 12500 Hz sample spinning rate and a delay of 8 s in between each of 192 scans. A 1.5 ms contact time was used. The ^{15}N spectrum of **IrCp*-ppy-PMO** was obtained by summing three individual spectra acquired with a 4 s recycle delay in between each of the 2048 scans, a 12500 Hz sample spinning rate and three different contact times. The three spectra were acquired with contact times of 1.5 ms, 2.5 ms and 4.0 ms to check for any variation in the relative intensity of the individual nitrogen resonances. However, the relative intensities did not vary with the contact time so the spectra were summed in order to improve the signal to noise ratio.

DNP enhancements

DNP enhancements were obtained by scaling the μwave-on spectrum to the same number of scans as the μwave-off spectrum and subsequent determination of the scaling factor to reach the same relative intensity. ε_H was measured on the solvent resonance at 6.3 ppm; carbon enhancements were measured on the solvent $\varepsilon_{C\,CP}$(solv.) and the aromatic carbon resonance $\varepsilon_{C\,CP}$(mat.) respectively; silicon-29 enhancement $\varepsilon_{Si\,CP}$ was measured on the T-site resonance

Synthesis of **ppy-PMO**

In a 250 ml beaker stearyltrimethylammonium chloride (1.25 g, 3.6 mmol) was dissolved in water (78 mL) and sodium hydroxide (6 M, 1.3 mL), the resulting solution was stirred for 20 minutes Then 5-(triethoxysilyl)-2-(4-triethoxysilylphenyl)-pyridine (1.36 g, 2.83 mmol) was added under rapid stirring, the resulting solution was stirred for 24 hours and then heated to 97°C under static conditions for 24 hours. The reslting white solid was then filtered and washed with water (35 mL x 3) and acetone (75 mL x 2). The resulting white powder was dried at 85°C under vacuum (10^{-5} mbar) for 16 hours. The material was suspended in ethanol (190 mL) and hydrochloric acid (2 M, 3.5 mL) and was stirred for 24 hours. After filtration the soldi was washed with water (100 mL), aqueous sodium hydroxide (0.03 M, 50 mL), water (100 mL x 2), methanol (20 mL), and acetone (20 mL x3). The material was dried at 85°C under vacuum (10^{-5} mbar) for 16 hours to give **ppy-PMO** (559 mg) as white powder. Elemental Analysis calculated for $C_{11}H_7NSi_2O_3$: C 51.3%, H 2.7%, N 5.4% Si 21.8%, O 18.7%; found: C 48.0%, H 2.8%, N 5.3%, Si 20.3%, O 18.2%. BET surface area (N_2, 77 K) 873 m^2/g.

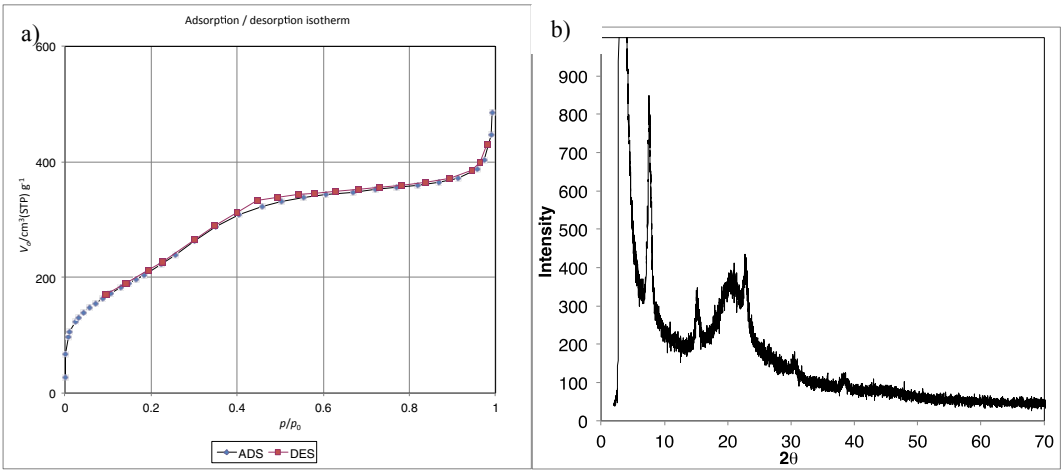
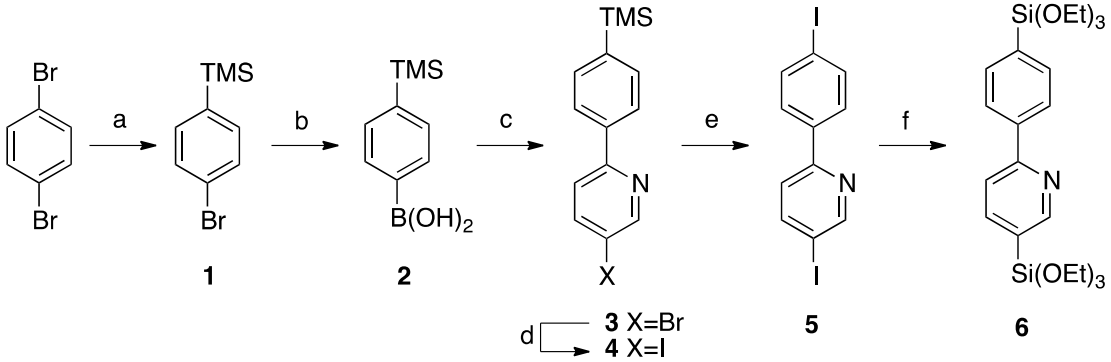


Figure 9: a) ad-/desorption isotherm of ppy-PMO b) powder-XRD of ppy-PMO.

Precursor Synthesis



Scheme 1: Synthetic route to precursor **6**: a) 1) *n*-BuLi, -78°C; 2) TMSCl -78°C to 25°C; quant.; b) 1) *n*-BuLi, -78°C, 2) $B(OMe)_3$, -78° to 25°C, 49%; c) 2,5-dibromopyridine, $Pd(PPh_3)_4$, K_2CO_3, PhMe, H_2O, 83%; d) 1) *n*-BuLi, -78°C, 2) I_2, -78° to 25°C, quant.; e) ICl, Et_2O, CH_2Cl_2, 0°C, 98%; f) $(EtO)_3SiH$, $[Rh(cod)(NCMe)_2]BF_4$, NBu_4I, NEt_3, DMF, 80°C, 24h
52%

Synthesis of 4-trimethylsilylbromobenzene **1**

A 500 mL two neck flask under argon was charged with 1,4-dibromobenzene (37.7 g, 160 mmol, 1.0 equiv.) and Et_2O (300 mL) was added. The resulting solution was cooled to -78°C (acetone, CO_2(s)) and *n*-butyllithium (1.6 M in hexanes, 100 mL, 160 mmol, 1.0 equiv.) was added dropwise over 10 minutes. The solution was stirred for 4 hours at -78°C before trimethylsilylchloride (23 mL, 176 mmol, 1.1 equiv.) was added The solution was allowed to reach room temperature overnight and was then poured into water (400 mL). The phases were separated, the organic phase was washed with water (100 mL) and the combined aqueous phases were extracted with Et_2O (100 mL x 3). The organic phases were combined and dried over $MgSO_4$. Removal of the solvent yielded **1** (36.7 g, quant.) as colorless powder, which was used without further purification. ^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 7.55-7.49 (m, *2H*), 7.44-7.38 (m, *2H*), 0.28 (s, *9H*); ^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 139.37, 135.06, 131.00, 123.69, -1.08.

Synthesis of 4-trimethylsilylphenylboronicacid **2**

1 (36.7 g, 160 mmol, 1.0 equiv.) was dissolved in THF (800 mL) and cooled to -78°C (acetone, CO_2(s)). *n*-Butyllithium (1.6 M in hexanes, 100 mL, 160 mmol, 1.0 equiv.) was added dropwise and the solution stirred for 1.5 h. Then trimethylborate (20 mL, 176 mmol, 1.1 equiv.) was added over the course of 10 minutes and stirring was continued for 30 minutes at -78°C before the solution was allowed to reach room temperature overnight. It was then cooled to 0°C and aqueous HCl (1M, 500 mL) and EtOAc (200 mL) were added. Phases were separated and the aqueous phase was

extracted with EtOAc (200 mL x 3). The organic phases were combined and dried over $MgSO_4$. The solvent was removed and the resulting solid recrystallized from pentane to give **2** (15.2 g, 49%) as colorless needles. ^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 8.20 (d, *2H, J* = 7.8 Hz), 7.68 (d, *2H, J* = 7.8 Hz), 0.35 (s, *9H*).

Synthesis of 5-bromo-2-(4-trimethylsilylphenyl)pyridine **3**

A 2 L 2-neck flask was charged with toluene (1.1 L) and water (0.2 L) the solvents were then degassed by a stream of Ar for 30 minutes. 2 (15.1 g, 80.0 mmol, 1.0 equiv.) and 2,5-dibromopyridine (18.9 g, 80.0 mmol, 1.0 equiv.) were added. To the resulting solution K_2CO_3 (46.0 g, 320 mmol, 4.0 equiv.) and $Pd(PPh_3)$ (4.61 g, 4.00 mmol, 0.05 equiv.) the solution was heated to 80°C and stirred for 3 days. After cooling to room temperature the phases were separated; the organic phase was washed with water (200 mL x 2) and then dried over $MgSO_4$. The solvent was removed in *vacuo* and the resulting yellow solid was purified by flash column chromatography (cyclohexane/ CH_2Cl_2 2:1) followed by column chromatography (cyclohexane/ CH_2Cl_2 gradient: 1:0→ 3:1→ 1:1→ 1:2→ 0:1) to give **3** (20.2 g, 83%) as colorless powder. ^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 8.74 (d, *1H*, *J*/Hz = 2.4), 7.97-7.92 (m, *3H*), 7.86 (dd, *1H*, *J*/Hz = 8.5, 2.4), 7.66-7.60 (m, *2H*), 0.31 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ/ppm = 156.09, 150.89, 142.20, 139.40, 138.64, 134.01, 126.07, 121.77, 119.48, -1.03.

Synthesis of 5-iodo-2-(4-trimethylsilylphenyl)pyridine **4**

3 (20.2 g, 66.0 mmol, 1.0 equiv.) was dissolved in Et_2O (300 mL) and cooled to -78°C (acetone, CO_2 (s)) then *n*-butyllithium (1.6 M in hexanes, 42 mL, 66.0 mmol, 1.0 equiv.) was added dropwise and the resulting solution was stirred for 2.5 h. Subsequently I_2 (20.1 g, 79.2 mmol, 1.2 equiv.) in Et_2O (125 mL) was added at -78°C and the solution was allowed to reach room temperature overnight. The solution was then poured into water (500 mL) and $Na_2S_2O_5$ (1.5 g) in water (200 mL) was added. The phases were separated and the organic phase was washed with water (200 mL). The aqueous phases were combined and the pH was adjusted to 8; followed by extraction with CH_2Cl_2 (100 mL x 3). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford **4** (23.3 g, quant.) as light beige powder that was used without further purification. ^{1}H-NMR (300 MHz, $CDCl_3$) δ/ppm = 8.89 (d, *1H*, *J*/Hz = 2.2), 8.04 (dd, *1H*, *J*/Hz = 8.4, 2.2)

7.97-7.92 (m, *2H*), 7.86 (dd, *1H*, *J*/Hz = 8.5, 2.4), 7.66-7.60 (m, *2H*), 7.54 (d, *1H*, *J*/Hz = 8.4), 0.30 (s, 9H).

Synthesis of 5-iodo-2-(4-iodophenyl)pyridine **5**

4 (23.3 g, 66.0 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (750 mL) and cooled to 0°C. ICl (14 mL, 280 mmol, 4.2 equiv.) in CH_2Cl_2 (250 mL) was added dropwise over 30 minutes. The solution was stirred for 19 h before the addition of NaOH (aq) (8 M, 660 mL) and $N_2S_2O_5$ (12 g, in 100 mL H_2O). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (300 mL x 3). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure to give a brown powder. That was recrystallized from CH_2Cl_2 to give **5** (21.0 g, 80%) as shiny beige flakes. ^{1}H-NMR (200 MHz, $CDCl_3$) δ/ppm = 8.91 (d, *1H*, *J*/Hz = 2.2), 8.09 (dd, *1H*, *J*/Hz = 8.4, 2.2) 7.90-7.81 (m, *2H*), 7.79-7.70 (m, *2H*), 7.86 (dd, *1H*, *J*/Hz = 8.5, 2.4), 7.54 (dd, *1H*, *J*/Hz = 8.4, 0.7).

Synthesis of 5-triethoxysilyl-2-(4-triethoxysilylphenyl)pyridine **bTS-ppy**

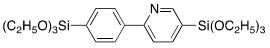
A 2 L 2-neck round-bottom-flask under argon was charged with **5** (12.2 g 30.0 mmol, 1.0 equiv.), $[Rh(cod)(NCMe)_2]BF_4$ (0.584 g, 1.54 mmol, 0.05 equiv.) and tetrabutylammonium iodide (25.5 g, 68.9 mmol, 2.3 equiv.) and subsequently DMF (800 mL) was added. To the resulting solution NEt_3 (25 mL, 180 mmol, 6.0 equiv) and triethoxysilane (25 mL, 135 mmol, 4.5 equiv.) were added and the solution was heated to 80°C for 22 h. The solvent was then removed in *vacuo* and the resulting slurry was dispersed in Et_2O (800 mL) and filtered through a pad of celite and activated charcoal. Removal of the solvent and *Kugelrohr* distillation (250°C, 10^{-5} mbar) afforded **6** (7.4 g, 50%) as yellow liquid. ^{1}H-NMR (300 MHz, CD_2Cl_2) δ/ppm = 8.91 (s, *1H*, 6-Py), 8.0 (s, *1H*, 3-Ph), 7.87 (m, *2H*, 4,5-Py), 7.71 (d, *1H*,), 7.31 (d, *1H*, 5-Ph), 3.99-3.79 (m, *12H*, $SiOC\boldsymbol{H_2}CH_3)_3$), 1.3-1.2 m, *18H*, $Si(OCH_2C\boldsymbol{H_3})_3$); ^{13}C-NMR (75 MHz, CD_2Cl_2) δ/ppm = 168.4 (2-Py), 163.8 (2-Ph), 157.7 (6-Py), 146.6 (1-Ph), 143.2 (4-Py), 142.9 (3-Ph), 133.9 (4-Ph), 128.4 (5-Ph), 126.4 (5-Py), 118.9 (3-Py), (Py-$Si(O\boldsymbol{C}H_2CH_3)_3$), ($Si(O\boldsymbol{C}H_2CH_3)_3$), ($Si(OCH_2\boldsymbol{C}H_3)_3$); ^{15}N-NMR (^{1}H-^{15}N HMBC,$CDCl_3$) δ/ppm = 307; ^{29}Si-NMR (60 MHz, $CDCl_3$) -58.37, 59.23. HR-MS (MALDI/ESI) m/z = 480.2234 (calc. $[M+H^+]$ 480.2232)

Synthesis of Iridium(**bTS-ppy**)Cp*Cl **IrCp*-bTS-ppy**

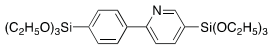
A young-style NMR-tube was charged with $[IrCp^*Cl_2]_2$ (16 mg, 0.02 mmol, 1.0 equiv.), **6** (16 µL, 0.04 mmol, 2.0 equiv.) and NaOAc (4.6 mg, 0.06 mmol, 2.8 equiv.) and CD_2Cl_2 (~0.5 mL) was added *via* vacuum transfer. The solution was stirred for 24h when the reaction was complete. ^{1}H-NMR (300 MHz, CD_2Cl_2) δ/ppm = 8.92 (s, *1H*, 6-Py), 8.12 (s, *1H*, 3-Ph), 7.87 (m, *2H*, 4,5-Py), 7.71 (d, *1H*, 6-Ph), 7.31 (d, *1H*, 5-Ph), 3.99-3.79 (m, *12H*, SiO*C**H**$_2$*$CH_3)_3$), 1.70 (s, *15H*, C_5(*C**H**$_3$*)$_5$), 1.3-1.2 (m, *18H*, Si(OCH_2*C**H**$_3$*)$_3$); ^{13}C-NMR (75 MHz, CD_2Cl_2) δ/ppm = 168.4 (2-Py), 163.8 (2-Ph), 157.7 (6-Py), 146.6 (1-Ph), 143.2 (4-Py), 142.9 (3-Ph), 133.9 (4-Ph), 128.4 (5-Ph), 126.4 (5-Py), 123.5 (6-Ph), 118.9 (3-Py), 89.1 (**C**$_5$($CH_3)_5$), 59.5 (Py-Si(O**C**$H_2$$CH_3)_3$), 59.1 (Ph-Si(O**C**$H_2$$CH_3)_3$), 18.5 (Si($OCH_2$**C**$H_3)_3$), 9.0 ($C_5$(**C**$H_3)_5$); ^{15}N-NMR (^{1}H-^{15}N HMBC, CD_2Cl_2) δ/ppm = 225. HR-MS (MALDI/ESI) m/z = 841.2572 (calc. [M^+] 841.2559)

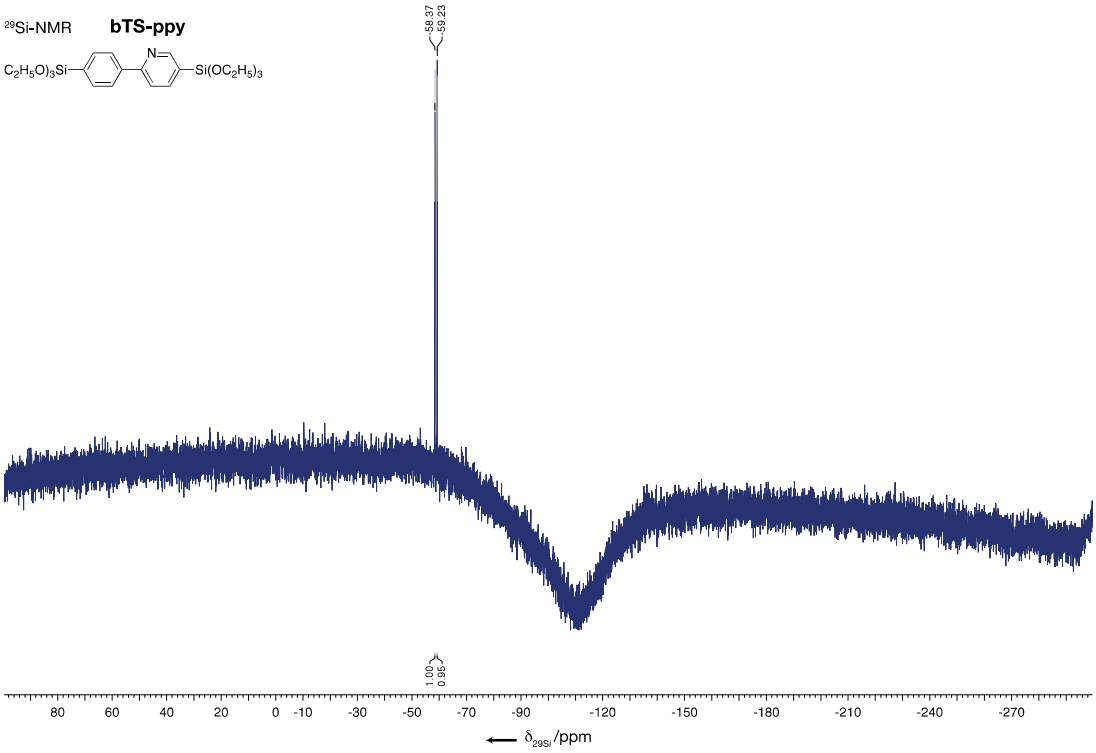
c) Spectra

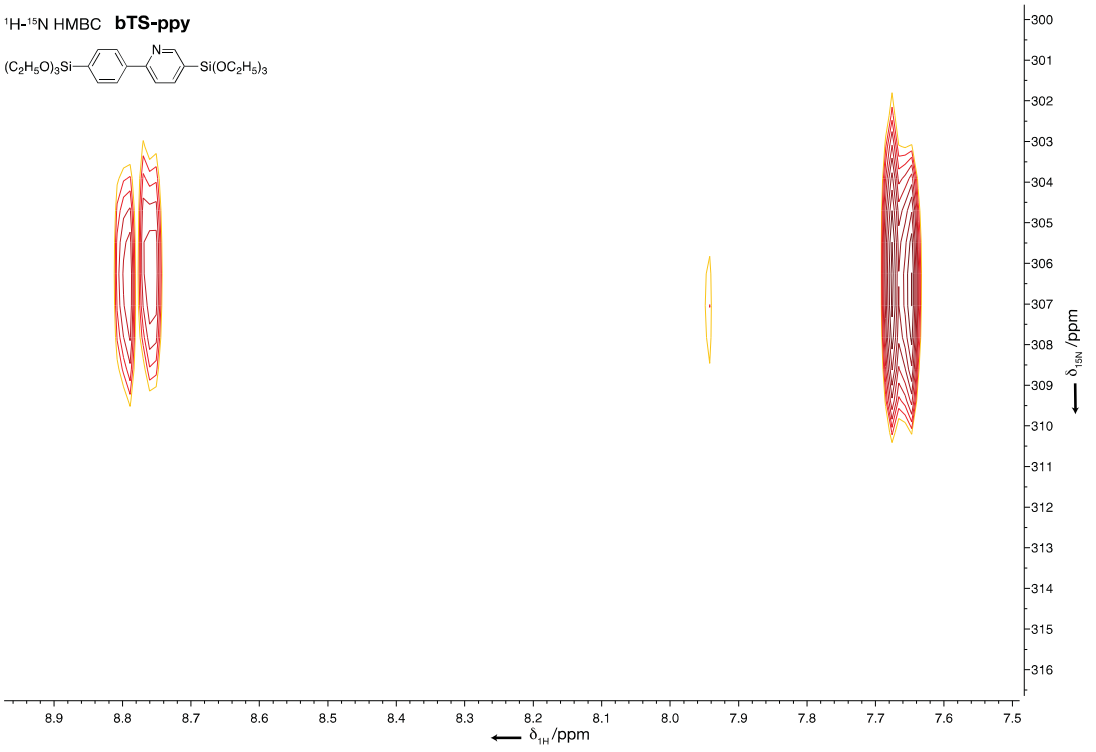
^{1}H-NMR **bTS-ppy**



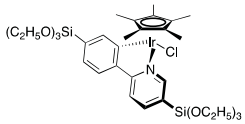
^{13}C-NMR **bTS-ppy**



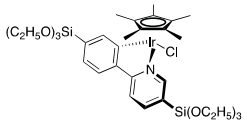

29Si-NMR
bTS-ppy
(C2H5O)3Si
N
Si(OC2H5)3
58.37
59.23
1.00
0.95
80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180 -210 -240 -270
δ29Si/ppm


1H-15N HMBC
bTS-ppy
(C2H5O)3Si
N
Si(OC2H5)3
300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316
δ15N/ppm
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5
δ1H/ppm

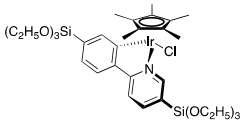
^{1}H-NMR (400 MHz, CD_2Cl_2)
IrCp*-bTS-ppy



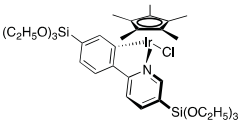
^{13}C-NMR (100 MHz, CD_2Cl_2)
IrCp*-bTS-ppy



^{1}H-^{15}N HMBC **IrCp*-bTS-ppy**



^{1}H-^{1}H NOESY **IrCp*-bTS-ppy**



References

1. B. M. Fung, A. K. Khitrin and K. Ermolaev, *J. Magn. Reson.*, 2000, **142**, 97-101.