*Electronic Supplementary material.*

# Remote Control: Stereoselective Coordination of Electron-Deficient 2,2'-bipyridine Ligands to Re(I) and Ir(III) Cores

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## Contents

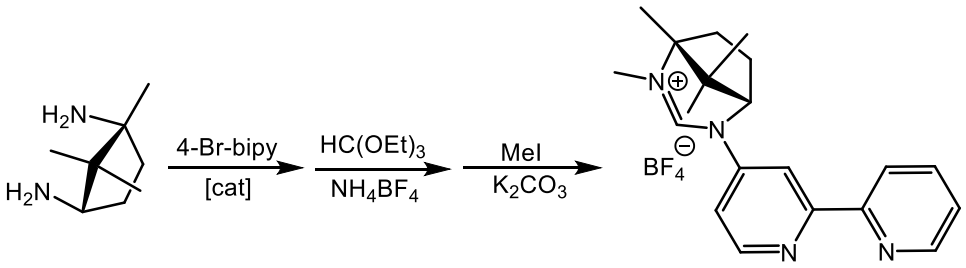
## 1.1 Materials and analytical methods

All chemicals were purchased from commercial sources and used without further purification unless otherwise stated. NMR spectra were recorded on Bruker Fourier 300, DPX 400 and Avance 500 or 600 MHz NMR spectrometers. $^{1}$H and $^{13}$C{$^{1}$H} NMR chemical shifts were referenced relative to the residual solvent resonances in the deuterated solvent. Mass spectra (ESI) were recorded on a Waters LCT premier XE spectrometer. A Chirascan spectrometer (Applied Photophysics, Leatherhead, U.K.) was used to measure both linear dichroism (LD) and circular dichroism (CD) spectra using a 1 cm path length quartz cuvette.

Single-crystal XRD data were collected on an Agilent SupaNova Dual Atlas diffractometer with a mirror monochromator using either Cu (λ = 1.5418 Å) or Mo (λ = 0.7107 Å) radiation. Sample temperature was controlled using an Oxford Cryosystems cooling apparatus. Crystal structures were solved and refined using SHELXS and refined using SHELXL.[1] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in idealized positions, and a riding model was used with Uiso set at 1.2 or 1.5 times the value of Ueq for the atom to which they are bonded.

## 2. Synthetic procedures

2.1. [4-L$^{Me}$H]BF$_4$, **4$^{Me}$**.




The bipy functionalised diamine precursor was prepared in a similar way to the pyridine derivative reported by Wilhelm et al.[2] A mixture of (1*R*,3*S*)-1,3-diamino-1,2,2-trimethylcyclopentane (1.05 g, 7.4 mmol), 4-bromobipyridine (1.73 g, 7.4 mmol), $Pd_2(dba)_3$ (0.1 g, 0.12 mmol), BINAP (0.3 g, 0.48 mmol) and NaO$^t$Bu (2.0 g, 20.1 mmol) in toluene was heated at 100 °C for 48 hrs. After cooling, the mixture was passed through a Celite plug which was washed with $CH_2Cl_2$ (3 x 25 ml). The solvents were removed in vacuo and the residue portioned between 12M HCl (20 ml) and $CH_2Cl_2$ (50 ml). The aqueous phase was isolated and made basic (care!) by the addition of solid NaOH with cooling and constant agitation. The basic solution was subsequently extracted into $CH_2Cl_2$ (3 x 50 ml) and the organic extracts dried over $MgSO_4$, filtered and taken to dryness to yield a viscous oil. The crude diamine was dissolved in $HC(OEt)_3$ (25 ml), solid $NH_4BF_4$ (0.78 g, 7.4 mmol) added thereto and the whole mix heated to 100 °C for 2 hours whereupon a cream precipitate formed. After cooling the solid was filtered and washed with $Et_2O$ (3 x 20 ml) and air-dried. A portion of the solid (1.0 g, 2.5 mmol) was dissolved in dry MeCN (40 ml) to which MeI (0.2 ml, 3.2 mmol) and $K_2CO_3$ (0.93 g, 7.5 mmol) were added. The mixture was stirred at RT for 72 hours, filtered and the volatiles removed in vacuo to yield a pale yellow solid. This proved to be a mixture of [4-L$^{Me}$H]BF$_4$ and [4-L$^{Me}$H]I. To convert fully to the $BF_4^-$ salt the solid was dissolved in $CH_2Cl_2$ (20 ml) and shaken with a sat. aq. solution of $NH_4BF_4$ (2 x 10 ml). The organic phase was dried over $MgSO_4$, filtered and the solvents removed in vacuo to give [4-L$^{Me}$H]BF$_4$ as a white solid. Yield (based on the starting diamine) = 72%.

$^{1}$H ($d_6$-acetone, 300 MHz): 8.82 (s, 1H), 8.63 (d, 5.3 Hz, 1H), 8.58 (d, 4.5 Hz, 1H), 8.37 (d, 7.9 Hz, 1H), 8.33 (s, 1H), 7.86 (t, 7.8 Hz, 1H), 7.50 (m, 1H), 7.37 (m, 1H), 4.36 (s br, 1H), 3.44 (s, 3H), 2.73 (m, 1H), 2.41 (m, 2H), 2.13 (m, 1H), 1.44 (s, 3H), 1.25 (s, 3H), 1.19 (s, 3H) ppm. $^{13}$C{$^{1}$H} ($d_6$-acetone, 100 MHz): 158.0 (C), 154.6 (C), 153.6 (C), 151.3 (CH), 149.3 (CH), 148.6 (CH), 137.4 (CH), 124.8 (CH), 121.2 (CH), 115.1 (CH), 111.2 (CH), 72.3 (C), 68.3 (CH), 41.7 (C), 38.8 ($CH_2$), 38.0 ($CH_3$), 31.1 ($CH_2$), 20.9 ($CH_3$), 16.1 ($CH_3$), 13.2 ($CH_3$) ppm. HRMS (ES): m/z 321.2083 (calc. 321.2079) $[L]^+$, 100%.

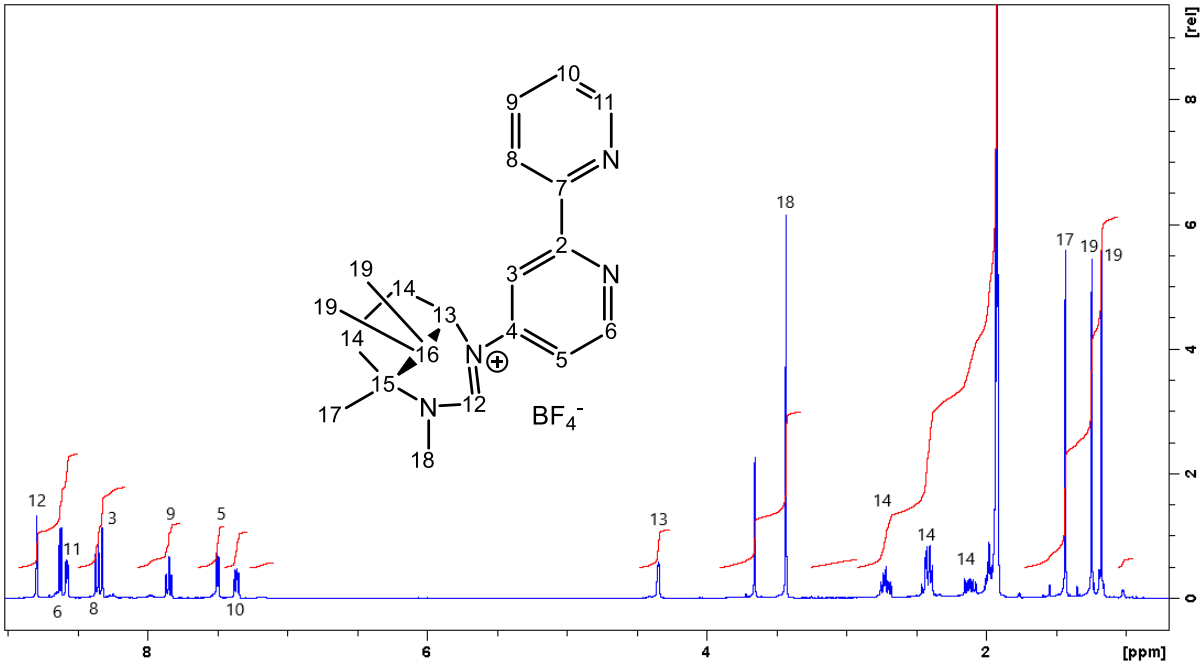



**Figure S1.** $^{1}$H NMR ($d_6$-acetone, 298 K, 300 MHz) spectrum of [4-L$^{Me}$H]$BF_4$, **4$^{Me}$**.

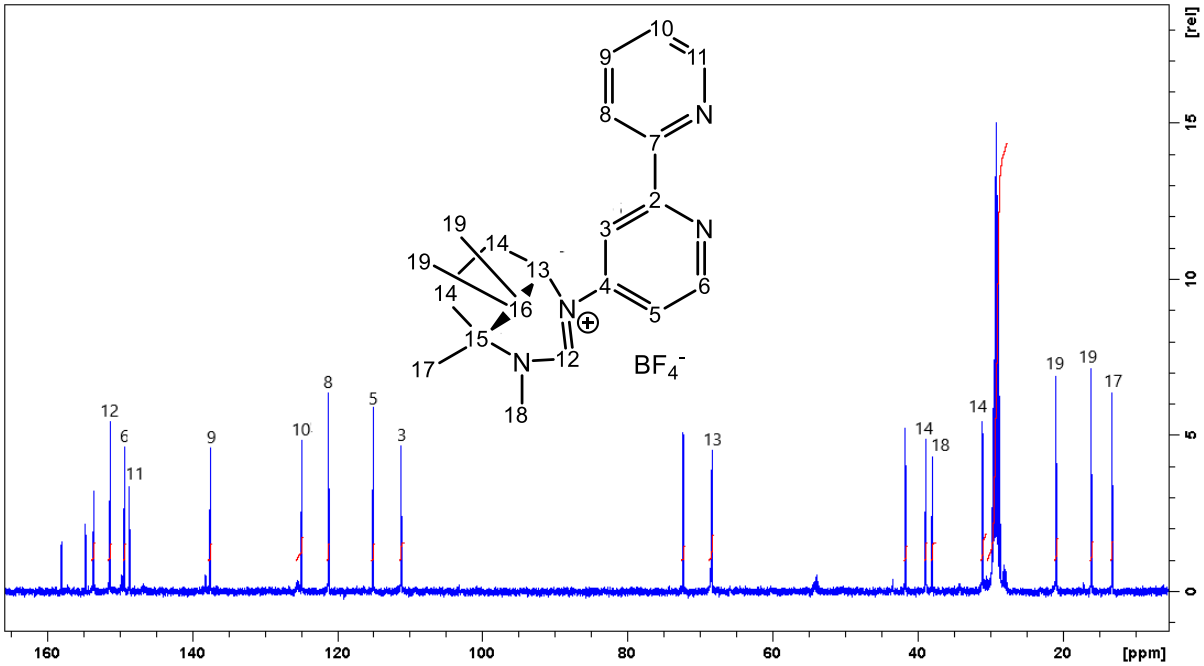



**Figure S2.** $^{13}$C{$^{1}$H} NMR ($d_6$-acetone, 298 K, 100 MHz) spectrum of [4-L$^{Me}$H]$BF_4$, **4$^{Me}$**.

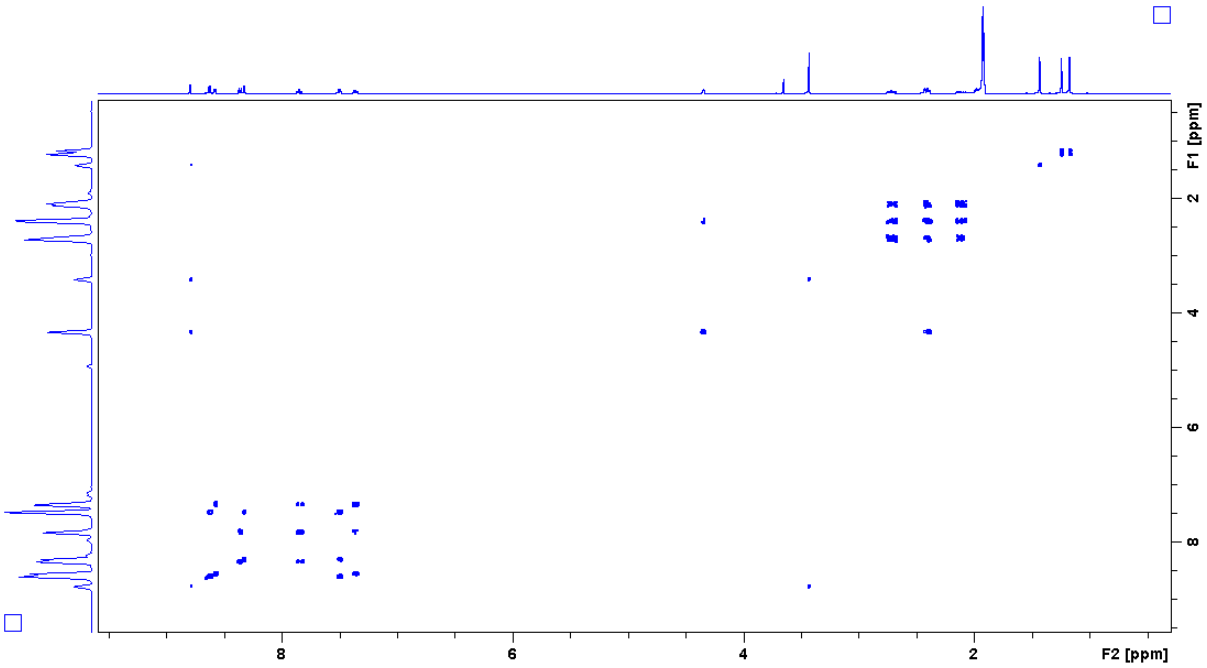



**Figure S3.** $^{1}H/^{1}H$ COSY NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of [4-$L^{Me}H$]$BF_4$, **4$^{Me}$**.

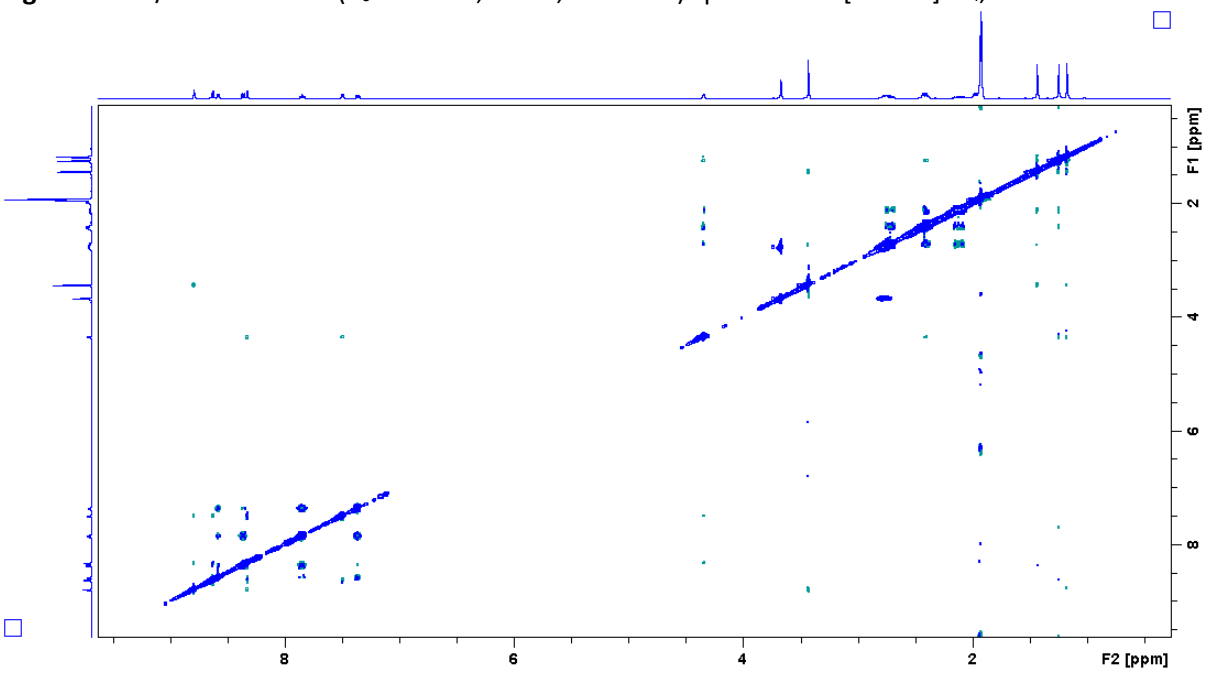



**Figure S4.** $^{1}H/^{1}H$ NOESY NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of [4-$L^{Me}H$]$BF_4$, **4$^{Me}$**.

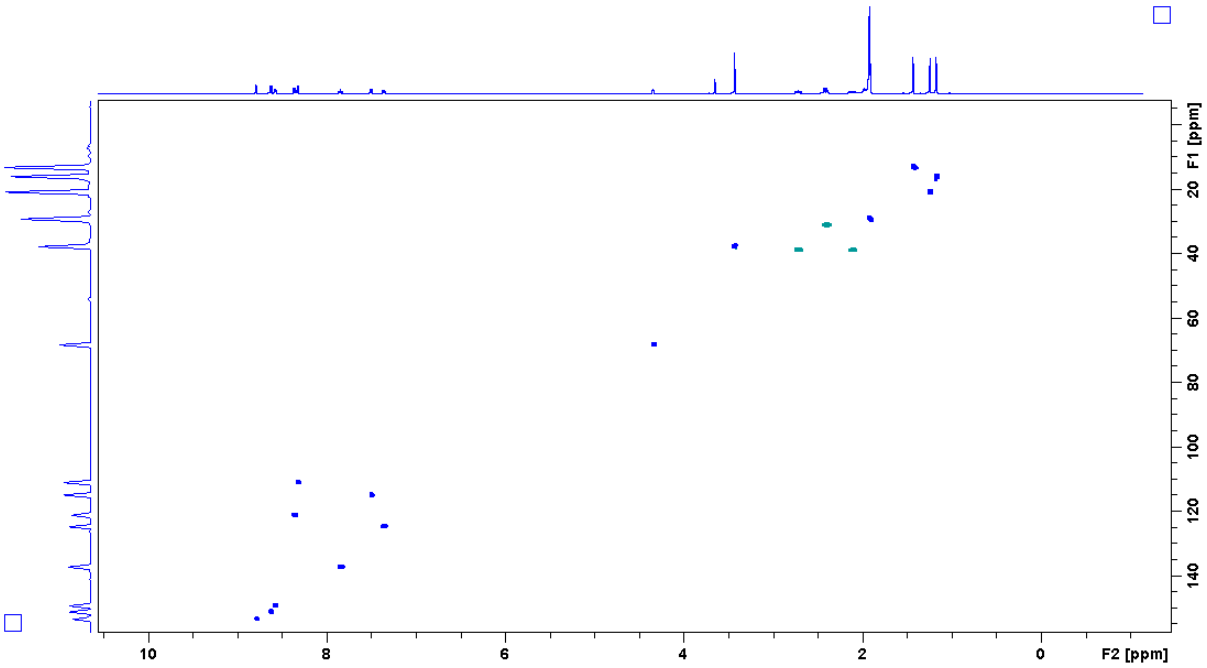
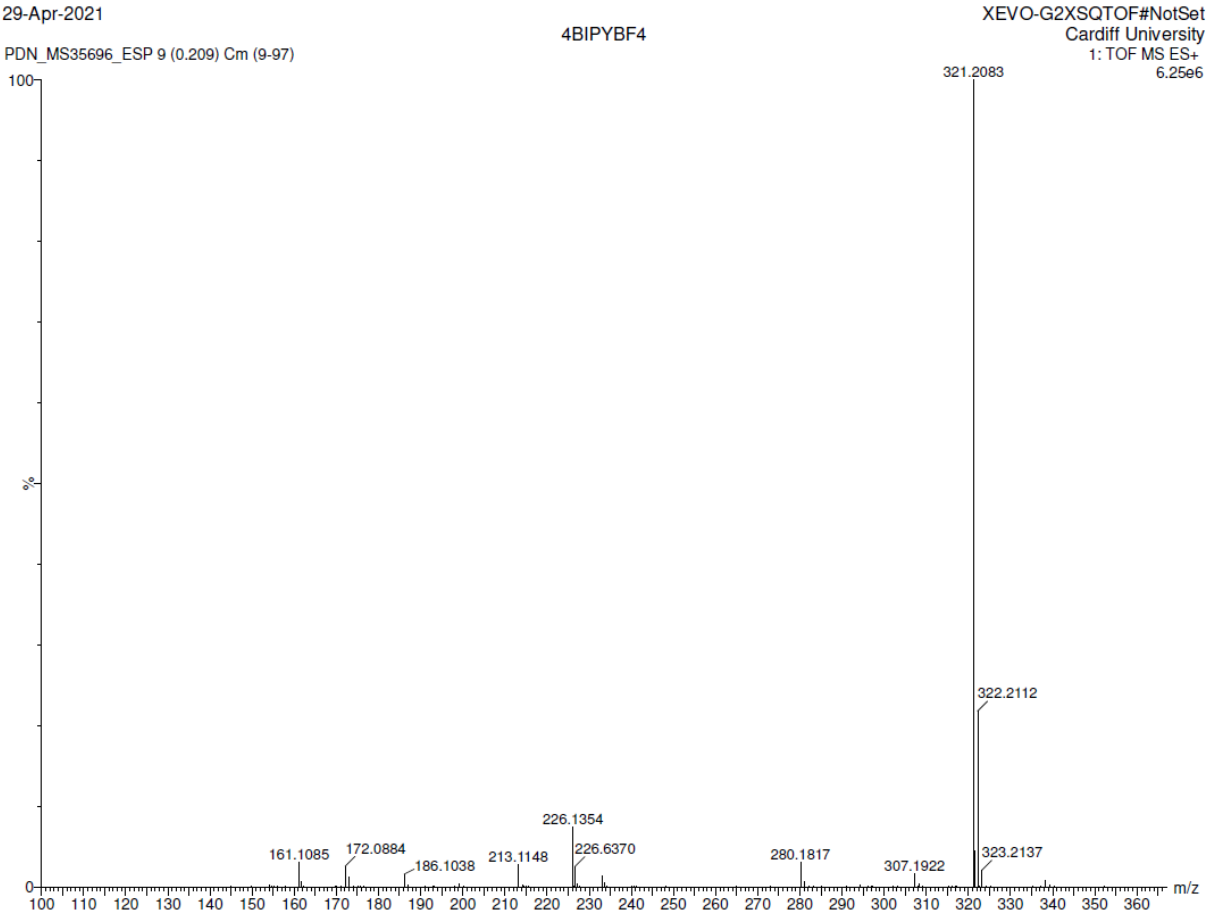


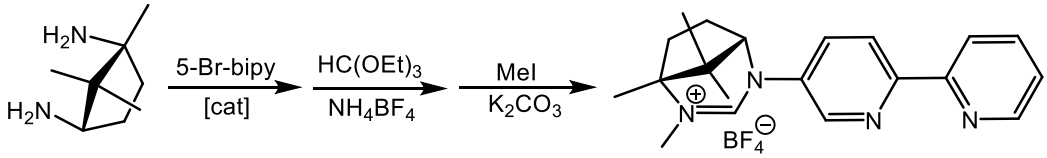

**Figure S5.** $^{1}H/^{13}C$ HSQC NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of [4-$L^{Me}$H]$BF_4$, **4$^{Me}$**.



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 5.0 | 5.0 | 100.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 321.2083 | 321.2079 | 0.4 | 1.2 | 10.5 | 1089.1 | n/a | n/a | C20 H25 N4 |

**Figure S6.** HRMS spectrum and data for [4-L$^{Me}$H]BF$_4$, **4$^{Me}$**.

2.2. [5-L$^{Me}$H]BF$_4$, **5$^{Me}$**.




This was prepared in the same way as defined for [4-L$^{Me}$H]BF$_4$. Yield = 82%.

$^1$H (d$_6$-acetone/d$_6$-dmso, 400 MHz): 8.76 (dd, 2.7, 0.6 Hz, 1H), 8.57 (ddd, 4.7, 1.8, 0.9 Hz, 1H), 8.56 (s 1H), 8.43 (dd, 8.7, 0.5 Hz, 1H), 8.31 (dt, 8.0, 0.9 Hz, 1H), 8.01 (dd, 8.7, 2.8 Hz, 1H), 7.82 (td, 7.8, 1.9 Hz, 1H), 7.37 (ddd, 7.6, 4.8, 0.5 Hz, 1H), 4.19 (d, 5.0 Hz, 1H), 3.37 (s, 3H), 2.73 (m, 1H), 2.71 (m, 1H), 2.43 (m, 1H), 2.33 (m, 1H), 2.09 (m, 1H), 1.41 (s, 3H), 1.22 (s, 6H) ppm. $^{13}$C{$^1$H} (d$_6$-acetone/d$_6$-dmso, 100 MHz): 155.0 (C), 154.7 (C), 153.6 (CH), 149.6 (CH), 142.9 (CH), 137.8 (C), 137.3 (CH), 130.6 (CH), 124.5 (CH), 121.2 (CH), 120.8 (CH), 71.6 (C), 69.6 (CH), 41.5 (C), 39.0 (CH$_2$), 37.5 (CH$_3$), 31.2 (CH$_2$), 20.9 (CH$_3$), 16.2 (CH$_3$), 13.3 (CH$_3$) ppm. HRMS (ES): m/z 321.2084 (calc. 321.2079) [L]$^+$, 100%.

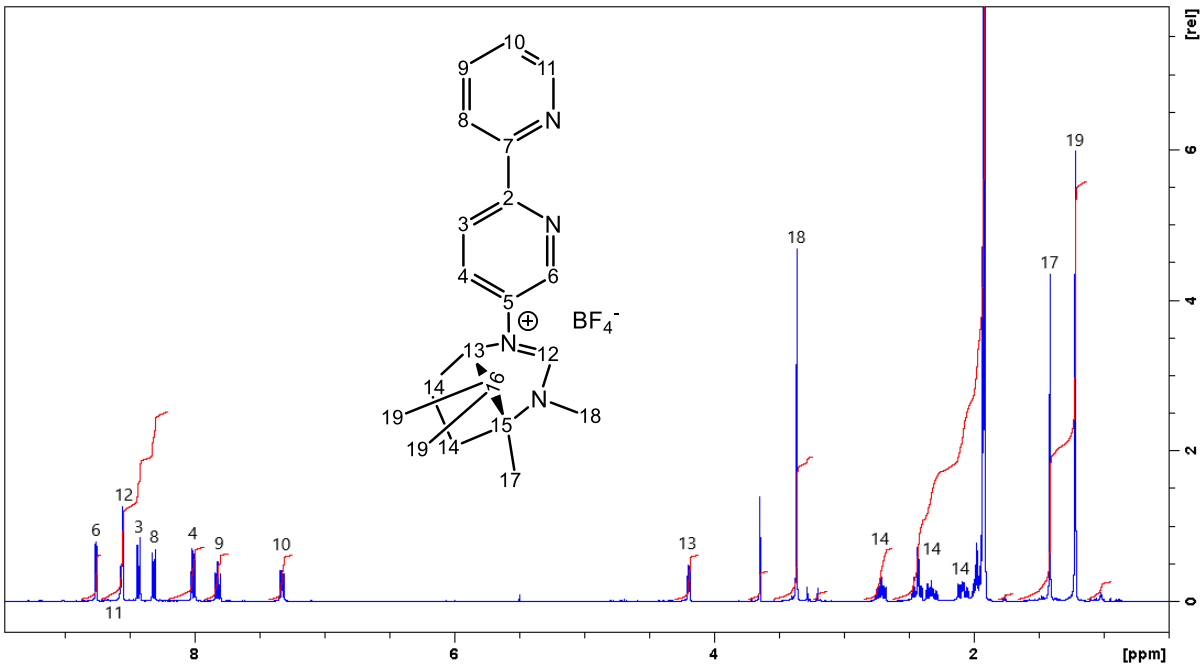



**Figure S7.** $^1$H NMR (d$_6$-acetone/d$_6$-dmso, 298 K, 400 MHz) spectrum of [5-L$^{Me}$H]BF$_4$, **5$^{Me}$**.

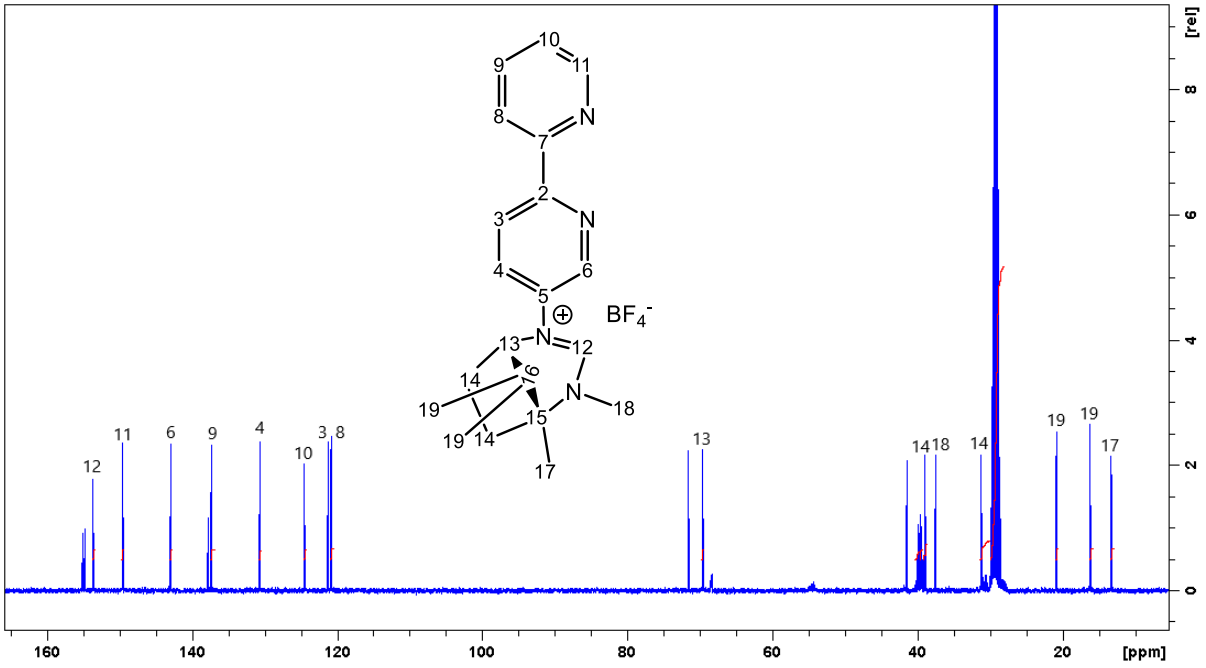



**Figure S8.** $^{13}C\{^{1}H\}$ NMR ($d_6$-acetone/$d_6$-dmso, 298 K, 100 MHz) spectrum of [5-$L^{Me}$H]$BF_4$, **5$^{Me}$**.

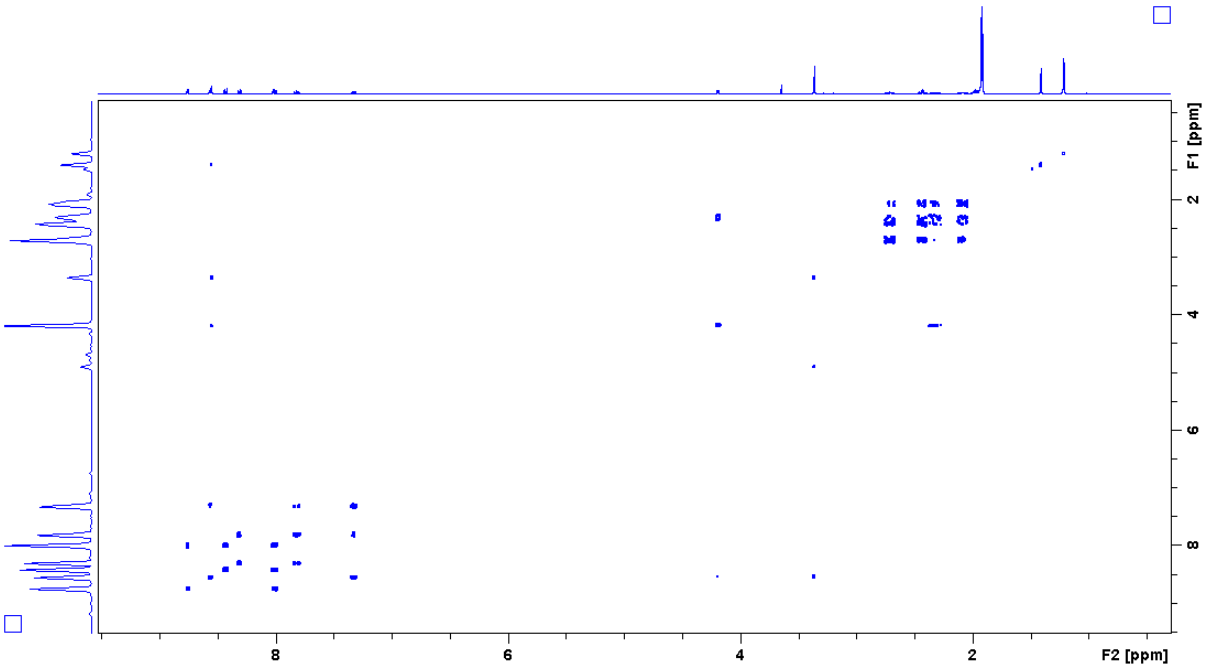



**Figure S9.** $^{1}H/^{1}H$ COSY NMR ($d_6$-acetone/$d_6$-dmso, 298 K, 400 MHz) spectrum of [5-$L^{Me}$H]$BF_4$, **5$^{Me}$**.

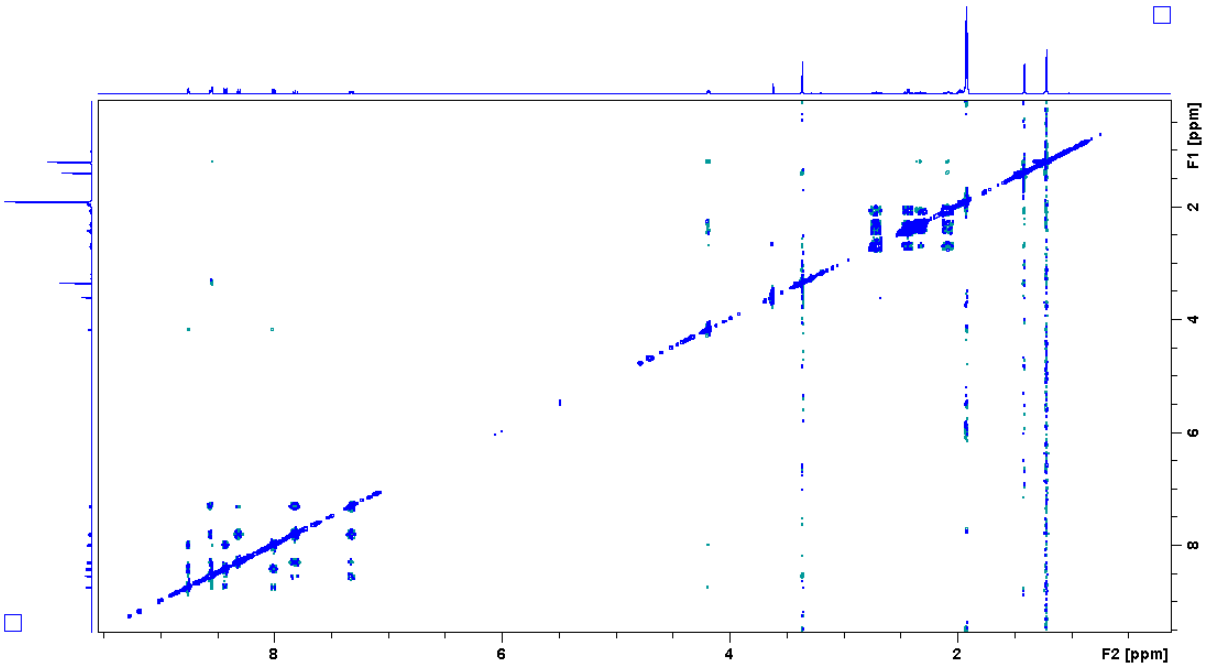



**Figure S10.** $^{1}H/^{1}H$ NOESY NMR ($d_6$-acetone/$d_6$-dmso, 298 K, 400 MHz) spectrum of [5-$L^{Me}H$]$BF_4$, **5$^{Me}$**.

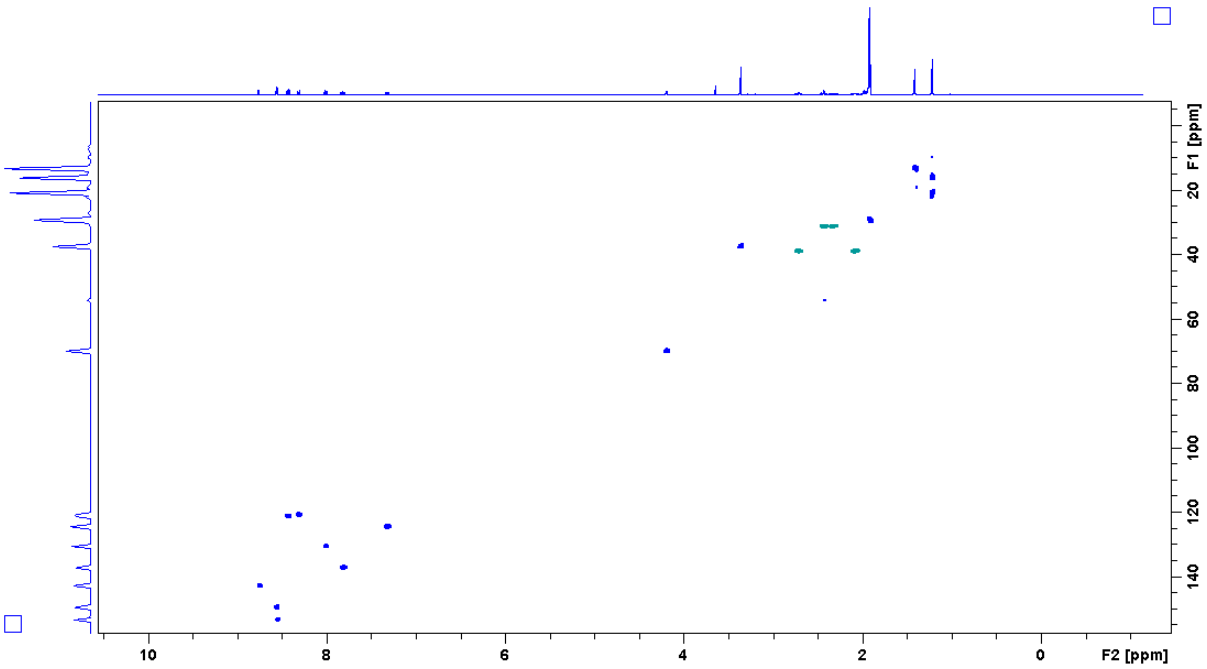
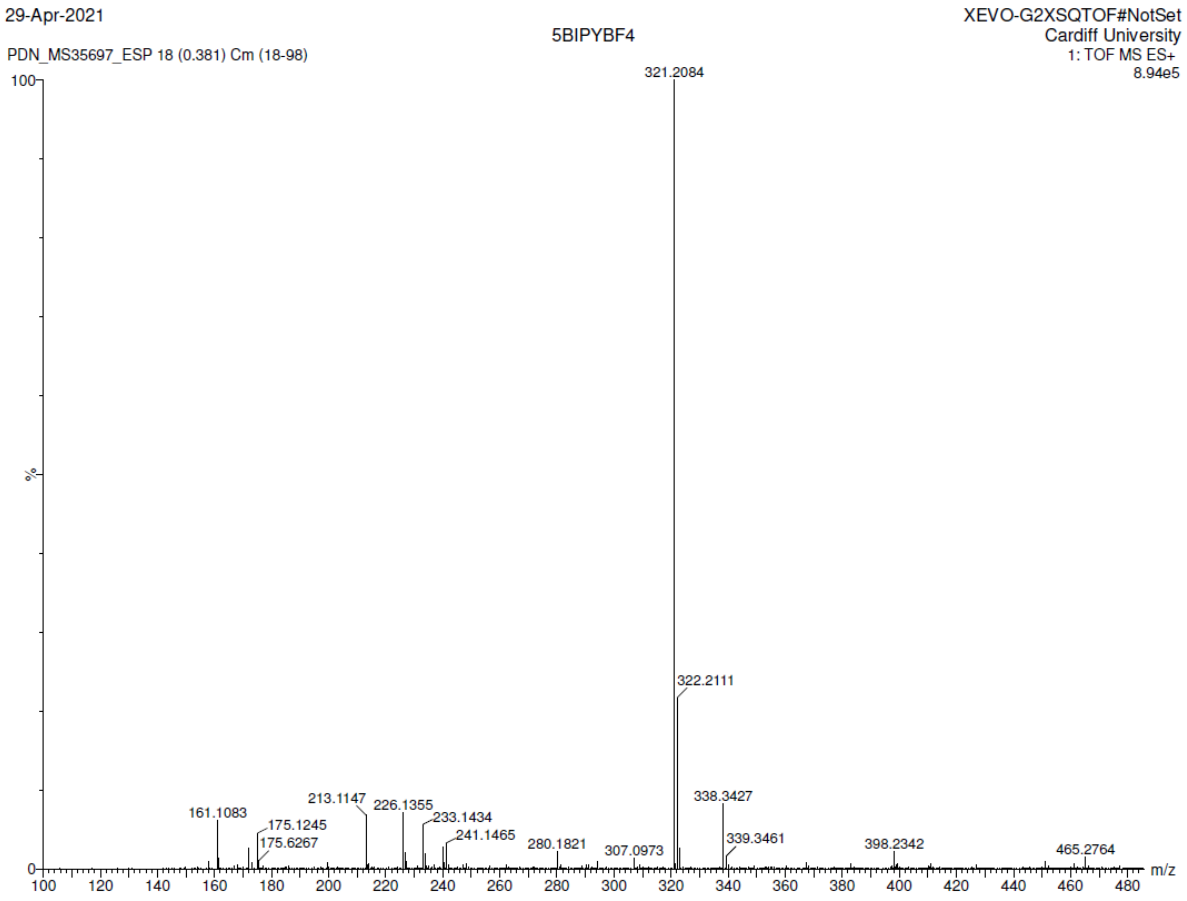


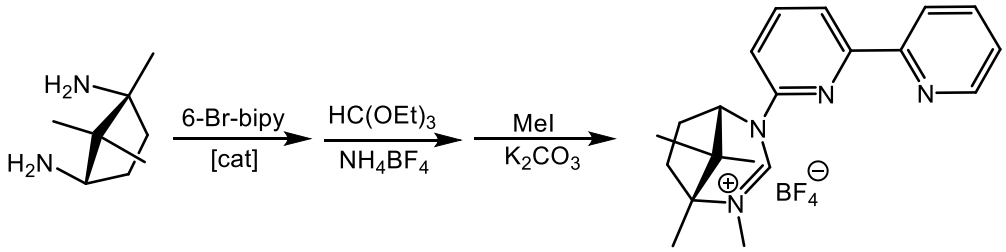

**Figure S11.** $^{1}H/^{13}C$ HSQC NMR ($d_6$-acetone/$d_6$-dmso, 298 K, 400 MHz) spectrum of [5-$L^{Me}H$]$BF_4$, **5$^{Me}$**.




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 5.0 | 5.0 | 100.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 321.2084 | 321.2079 | 0.5 | 1.6 | 10.5 | 965.4 | n/a | n/a | C20 H25 N4 |

**Figure S12.** HRMS spectrum and data for [5-L$^{Me}$H]BF$_4$, **5$^{Me}$**.

2.3. [6-L$^{Me}$H]BF$_4$, **6$^{Me}$**.




This was prepared in the same way as defined for [4-L$^{Me}$H]BF$_4$. Yield = 85%.

$^1$H ($CDCl_3$, 400 MHz): 8.91 (s, 1H), 8.69 (d, 4.8 Hz, 1H), 8.37 (dd, 7.4, 1.7 Hz 1H), 8.34 (dt, 8.0, 1.0 Hz 1H), 7.99 (td, 8.2, 1.9 Hz, 1H), 7.88 (tt, 7.8, 1.8 Hz, 1H), 7.58 (dd, 8.0, 1.4 Hz, 1H), 7.36 (m, 1H), 4.61 (d, 4.2 Hz, 1H), 3.49 (s, 3H), 2.75 (m, 1H), 2.44 (m, 2H), 2.09 (m, 1H), 1.46 (s, 3H), 1.31 (s, 3H), 1.19 (s, 3H) ppm. $^{13}$C{$^1$H} ($CDCl_3$, 100 MHz): 155.3 (C), 154.6 (C), 151.8 (CH), 149.9 (C), 149.5 (CH), 141.0 (CH), 137.1 (CH), 124.4 (CH), 121.3 (CH), 120.0 (CH), 114.2 (CH), 72.1 (C), 65.4 (CH), 41.5 (C), 39.2 ($CH_2$),

38.7 ($CH_3$), 31.2 ($CH_2$), 22.1 ($CH_3$), 17.1 ($CH_3$), 14.4 ($CH_3$) ppm. HRMS (ES): m/z 321.2087 (calc. 321.2079) $[L]^+$, 100%.

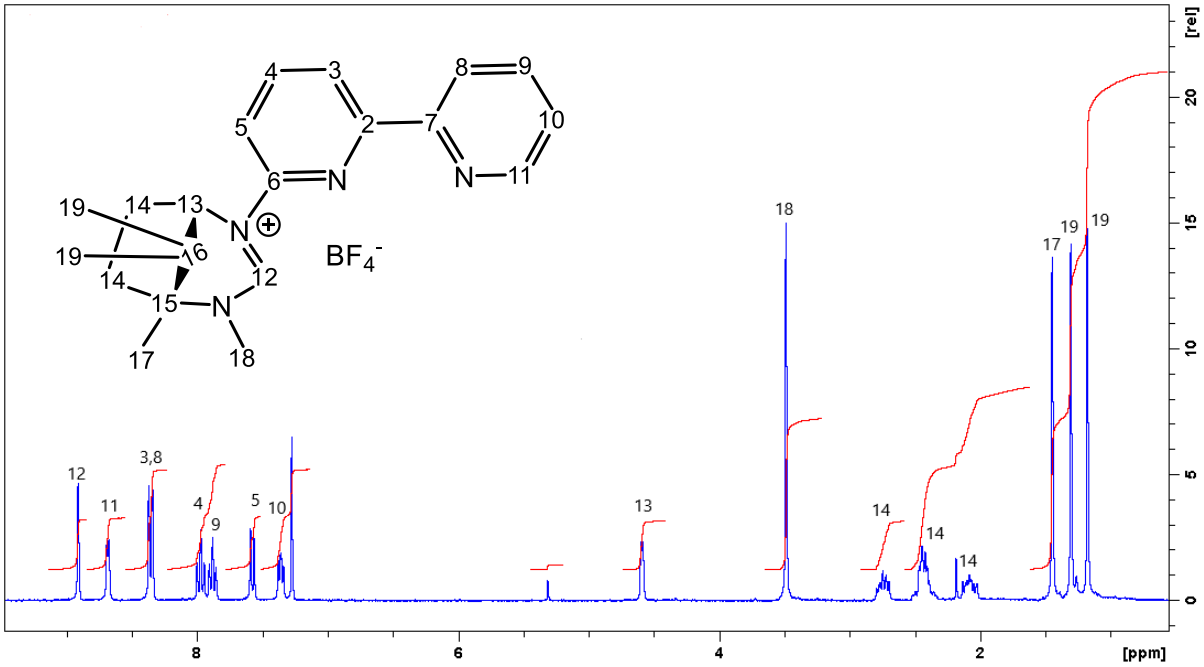



**Figure S13.** $^1$H NMR ($CDCl_3$, 298 K, 400 MHz) spectrum of [6-L$^{Me}$H]$BF_4$, **6$^{Me}$**.

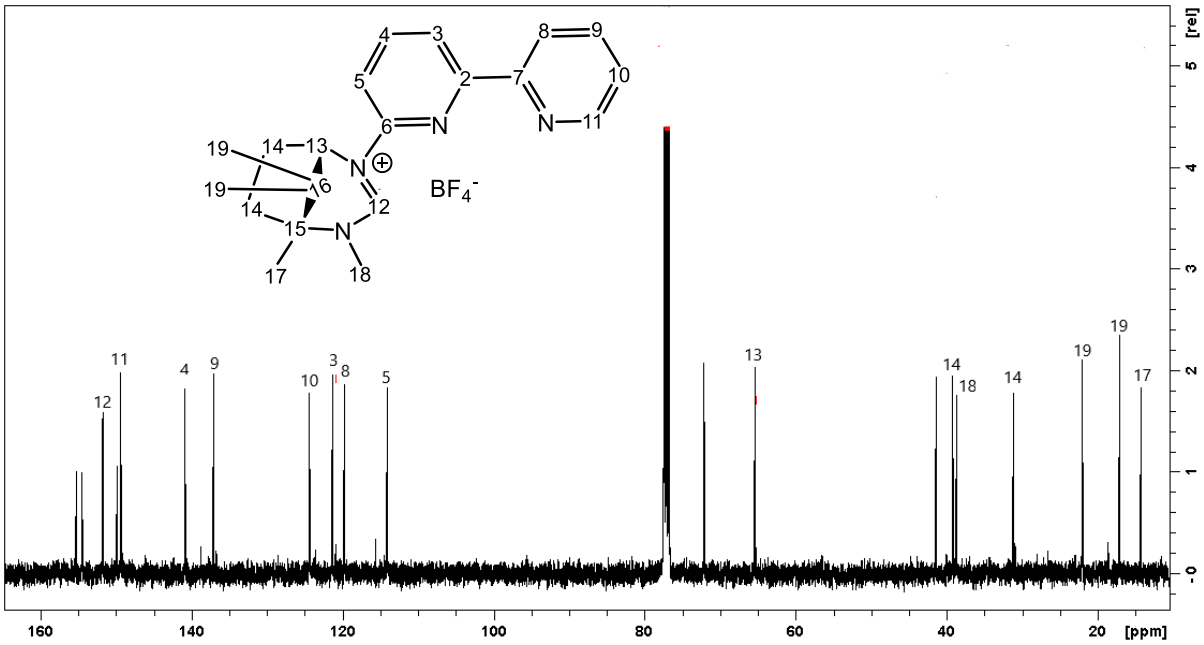



**Figure S14.** $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 400 MHz) spectrum of [6-L$^{Me}$H]$BF_4$, **6$^{Me}$**.

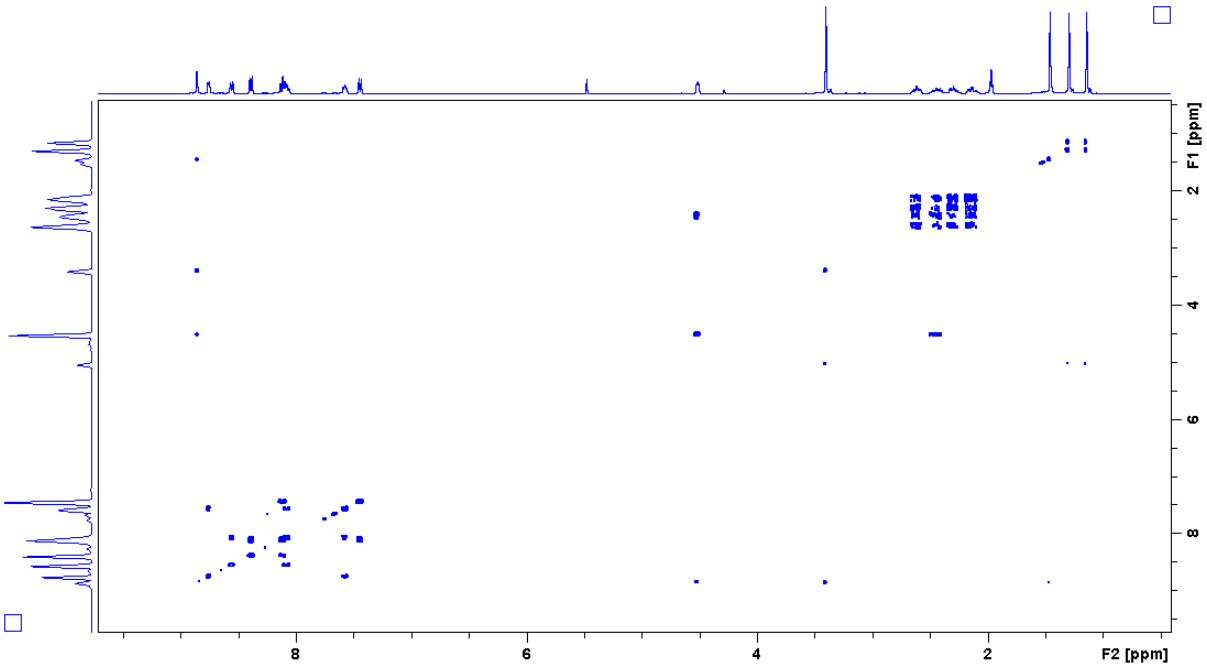



**Figure S15.** $^{1}H/^{1}H$ COSY NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of [6-$L^{Me}H$]$BF_4$, **$6^{Me}$**.

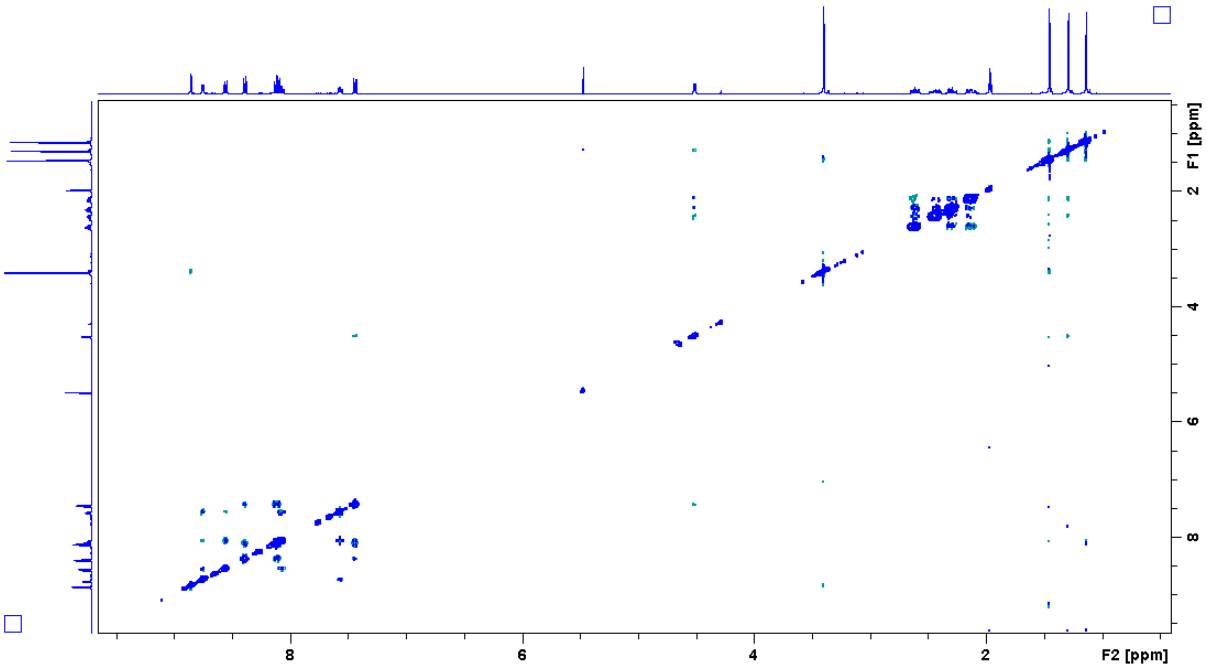



**Figure S15.** $^{1}H/^{1}H$ NOESY NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of [6-$L^{Me}H$]$BF_4$, **$6^{Me}$**.

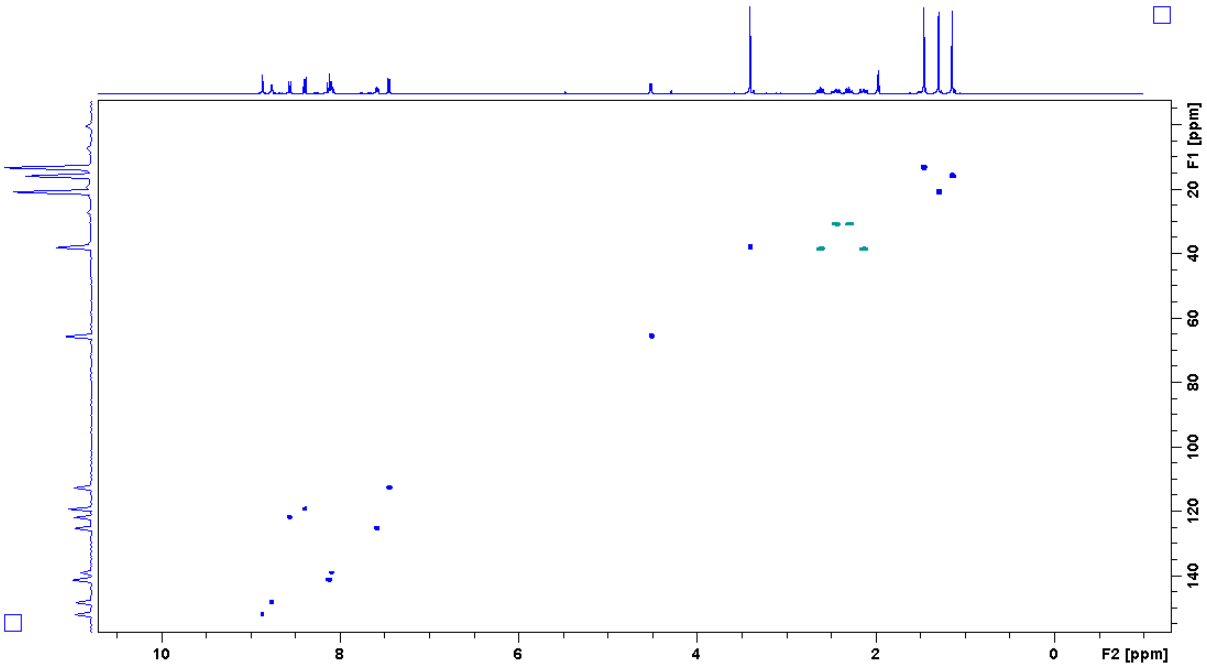
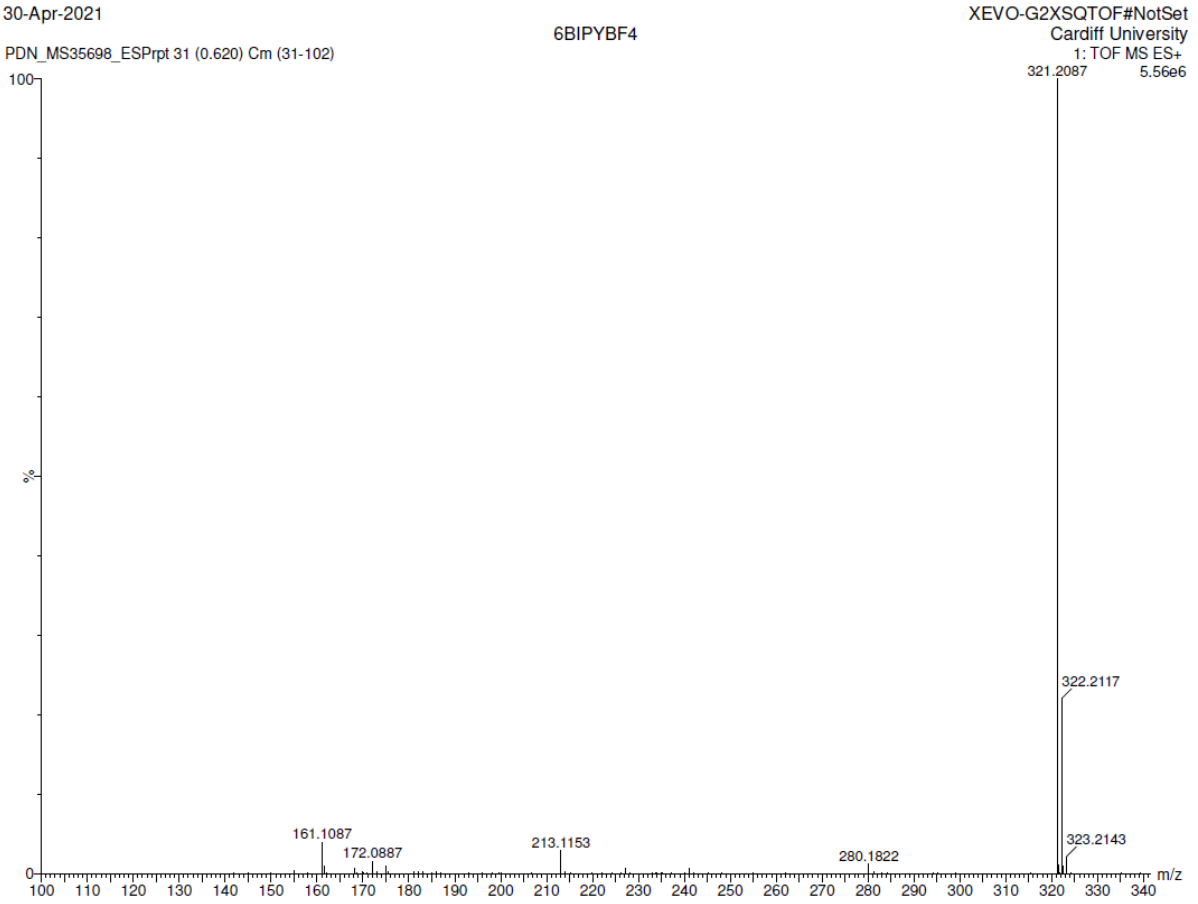


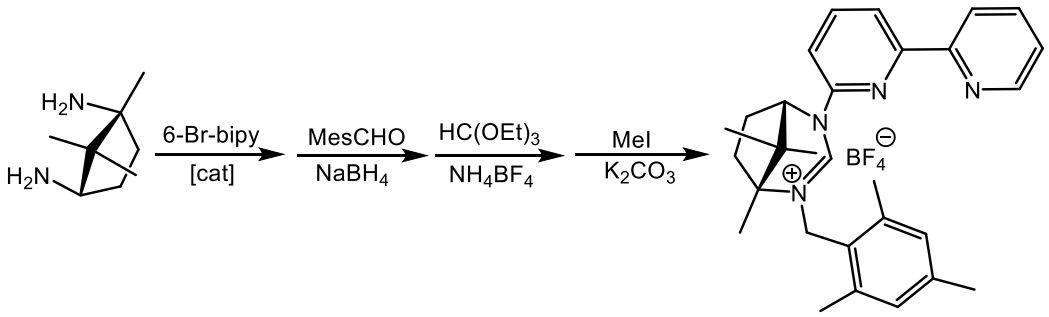

**Figure S16.** $^{1}H/^{13}C$ HSQC NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of [6-L$^{Me}$H]$BF_4$, **6$^{Me}$**.



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 5.0 | 5.0 | 100.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 321.2087 | 321.2079 | 0.8 | 2.5 | 10.5 | 1141.6 | n/a | n/a | C20 H25 N4 |

**Figure S17.** HRMS spectrum and data for [6-L$^{Me}$H]$BF_4$, **6$^{Me}$**.

2.4. [6-L$^{Mes}$H]$BF_4$, **6$^{Mes}$**.




The C-N coupling reaction was performed as detailed for [4-L$^{Me}$H]$BF_4$. The product (1.0 g, 3.37 mmol) was dissolved in EtOH (50 ml) and mesitaldehyde (0.5g, 3.37 mmol) added thereto. The solution was heated to 70 °C for one hour, allowed to cool and the volatiles removed in vacuo. The residue was taken up into fresh EtOH (50 ml) to which solid sodium borohydride (0.25 g, 6.6 mmol) was added in portions. The mixture was left to stir overnight at RT before being quenched by the addition of conc. HCl (0.5 ml). After removal of the volatiles in vacuo, the residue was dissolved in water (50 ml) which was made basic by the addition of solid NaOH. The basic solution was extracted with $CH_2Cl_2$ (3 x 40 ml) and the organic phase dried over $MgSO_4$, filtered and taken to dryness to yield an oil which was used without further purification in the final two steps which were performed as detailed in 2.1. above. Yield = 67%.

$^1$H ($CD_3CN$, 400 MHz): 8.59 (dm, 4.9 Hz, 1H), 8.32 (s, 1H), 8.22 (d, 8.0 Hz 1H), 8.00 (t, 8.1 Hz 1H), 7.92 (td, 7.8, 1.5 Hz, 1H), 7.51 (dt, 7.9, 0.8 Hz, 1H), 7.45 (d, 8.3 Hz, 1H), 7.42 (ddd, 7.5, 4.7, 1.0 Hz, 1H), 7.10 (s, 2H), 5.04 (d, 14.0 Hz, 1H), 4.79 (d, 14.0 Hz, 1H), 4.56 (d, 3.7 Hz, 1H), 2.54 (m, 1H), 2.39-2.12 (m, 3H), 1.71 (s, 3H), 1.29 (s, 3H), 1.14 (s, 3H) ppm. $^{13}$C{$^1$H} ($CD_3CN$, 100 MHz): 155.4 (C), 154.5 (C), 150.3 (C), 150.2 (CH), 148.6 (CH), 141.7 (C), 141.0 (C), 139.9 (CH), 137.7 (CH), 130.5 (CH), 125.3 (CH), 124.8 (C), 120.7 (CH), 119.5 (CH), 111.9 (CH), 74.1 (C), 66.4 (CH), 48.6 ($CH_2$), 42.3 ($CH_2$), 31.5 ($CH_2$), 21.5 ($CH_3$), 21.0 ($CH_3$), 19.5 ($CH_3$), 16.7 ($CH_3$), 13.7 ($CH_3$) ppm. HRMS (ES): m/z 439.2874 (calc. 439.2862) $[L]^+$, 100%.

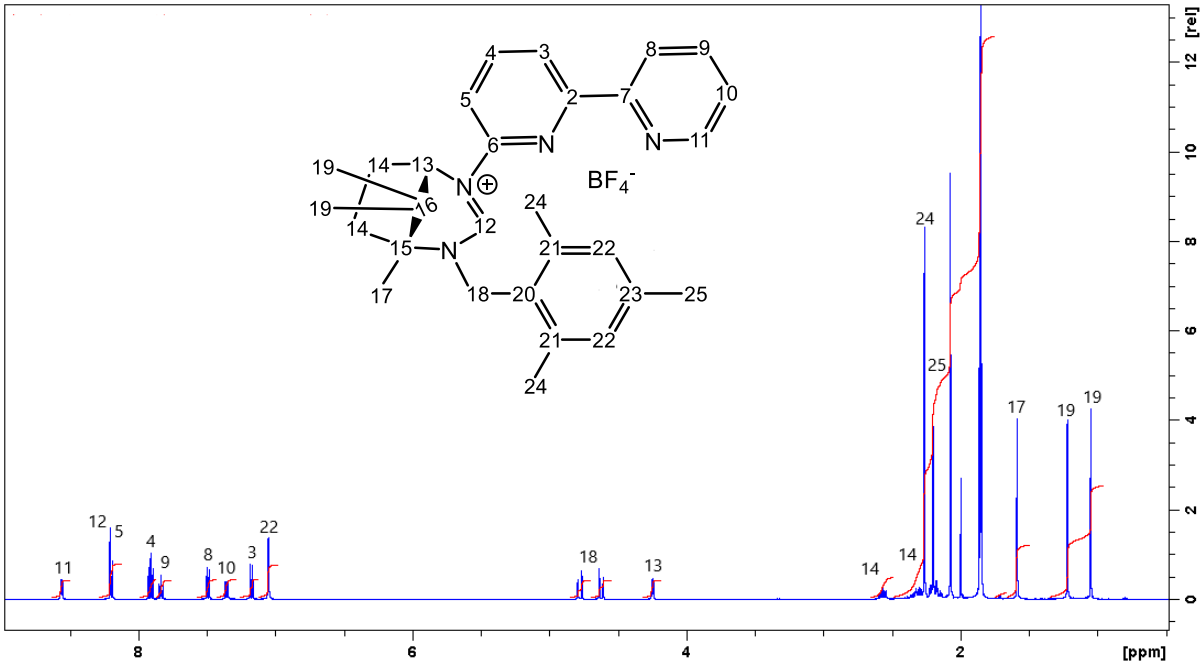



**Figure S18.** $^{1}$H NMR ($CD_3CN$, 298 K, 400 MHz) spectrum of [6-L$^{Mes}$H]$BF_4$, **6$^{Mes}$**.

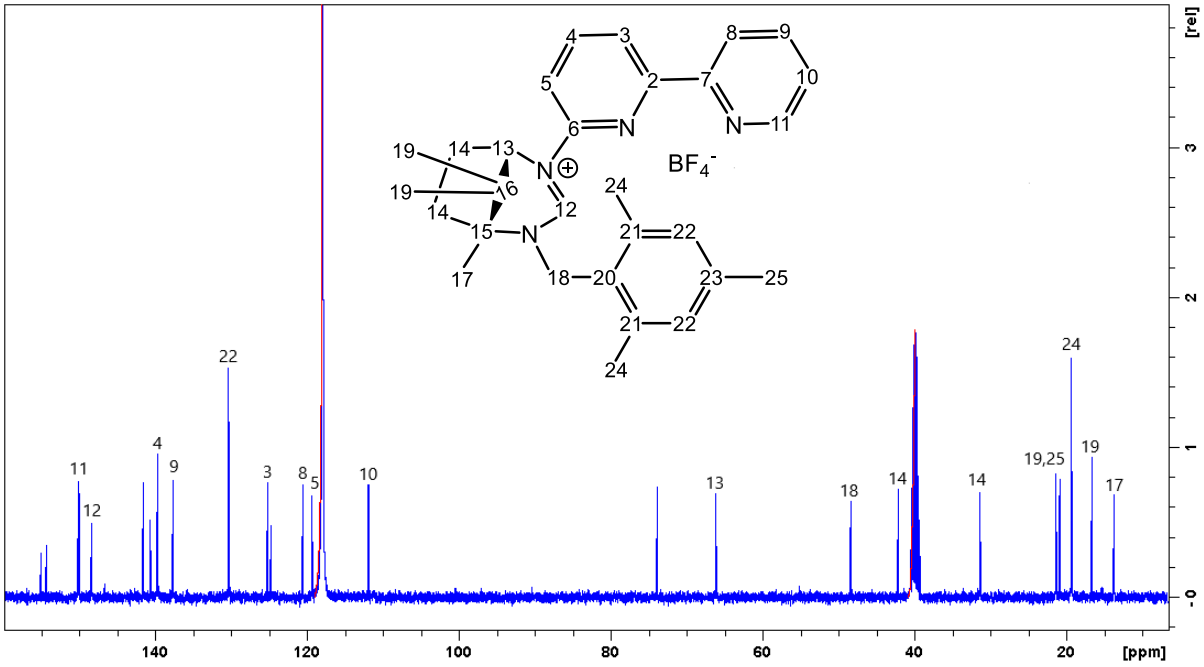



**Figure S19.** $^{13}$C{$^{1}$H} NMR ($CD_3CN$, 298 K, 100 MHz) spectrum of [6-L$^{Mes}$H]$BF_4$, **6$^{Mes}$**.

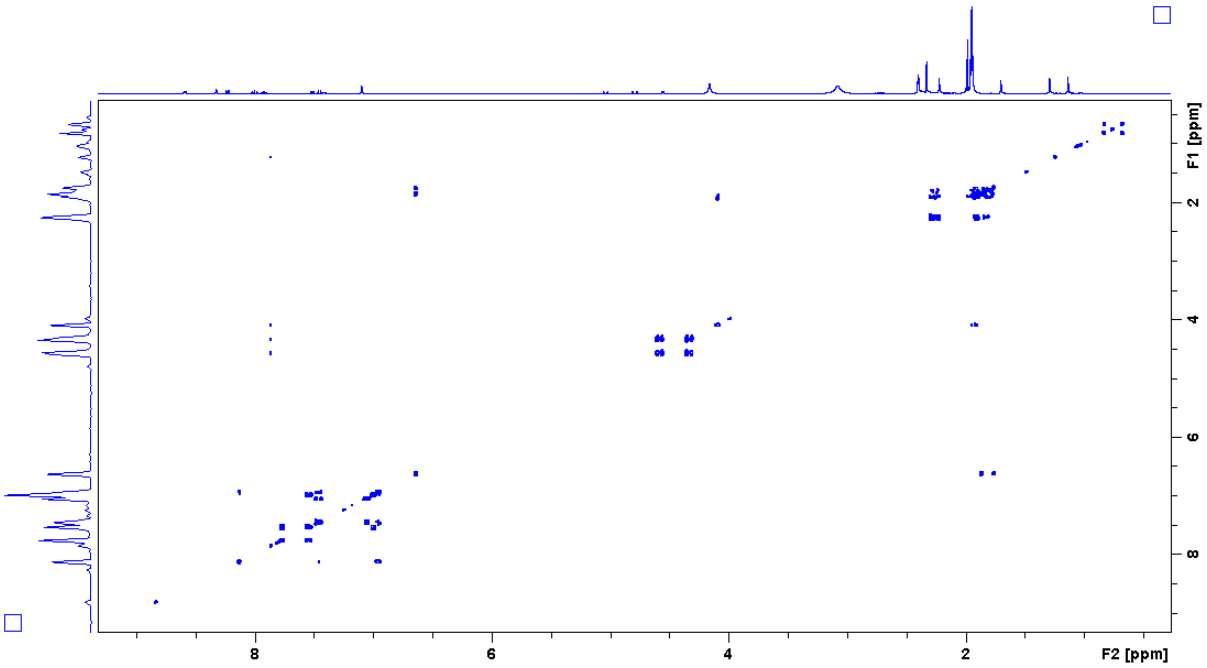



**Figure S20.** $^{1}H/^{1}H$ COSY NMR ($CD_3CN$, 298 K, 400 MHz) spectrum of [6-$L^{Mes}H$]$BF_4$, **6$^{Mes}$**.

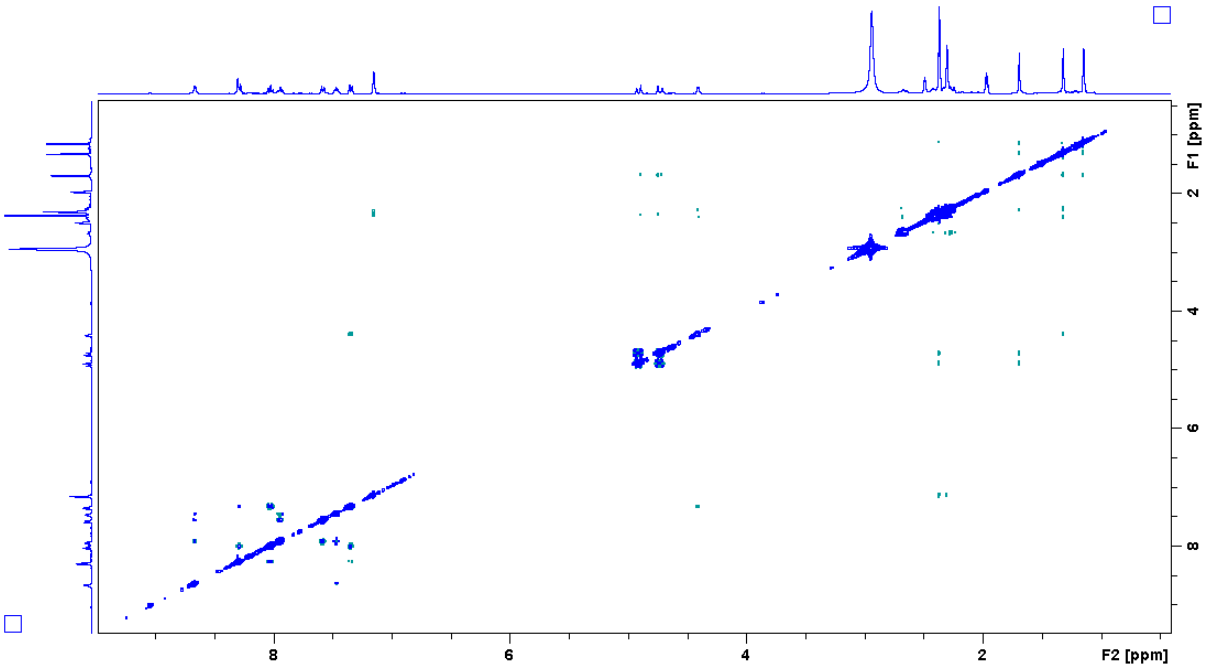



**Figure S21.** $^{1}H/^{1}H$ NOESY NMR ($CD_3CN$, 298 K, 400 MHz) spectrum of [6-$L^{Mes}H$]$BF_4$, **6$^{Mes}$**.

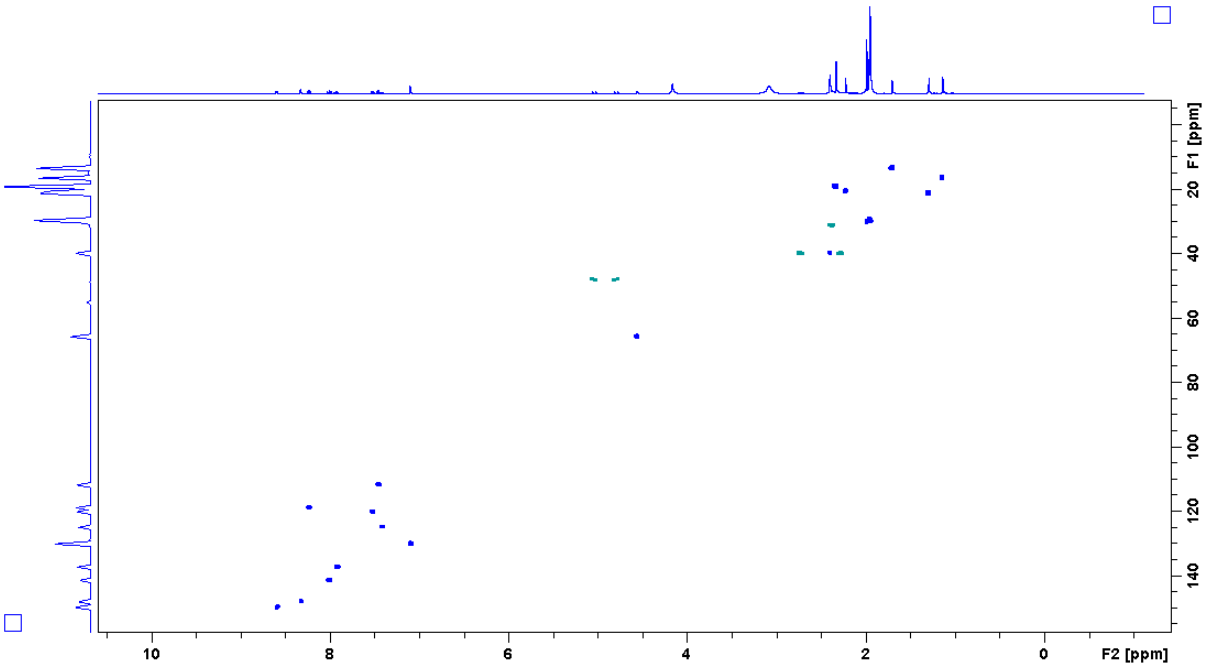
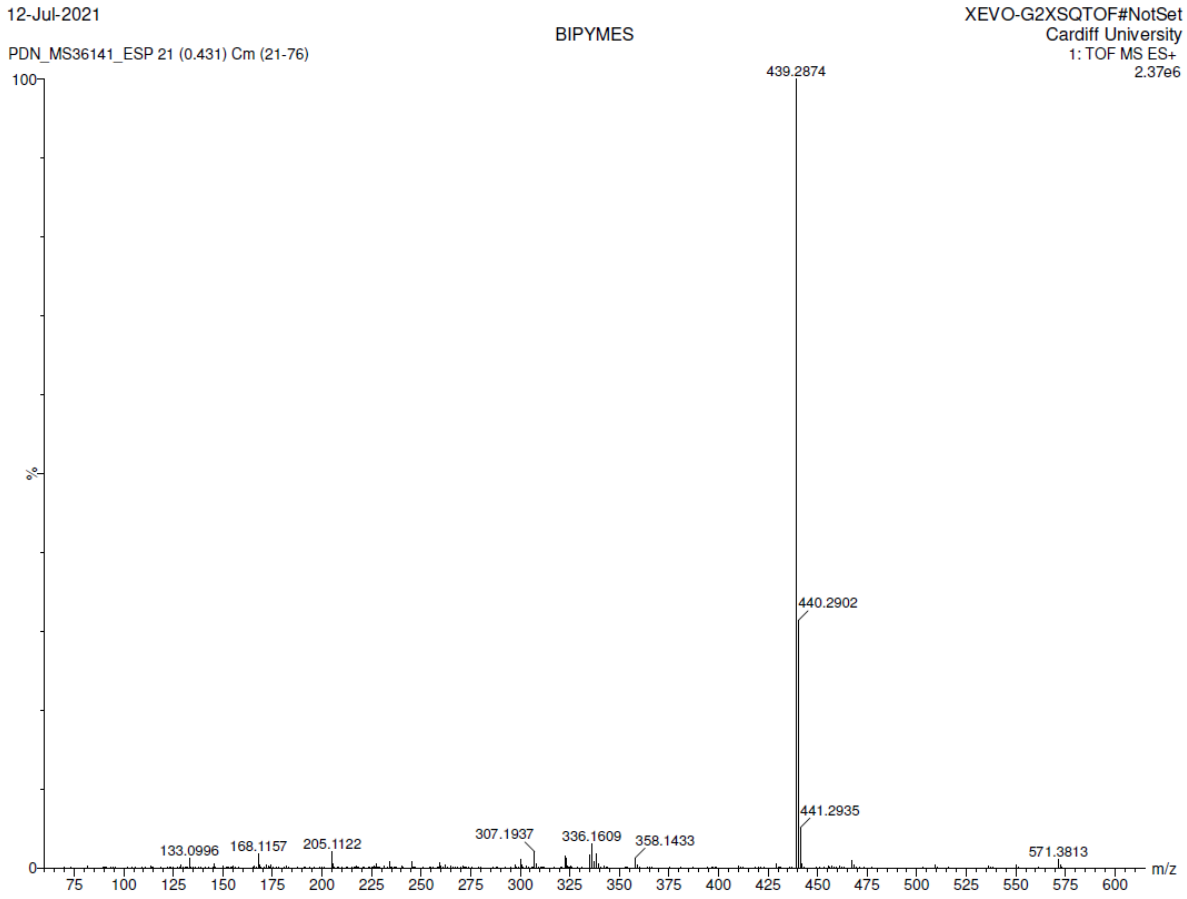


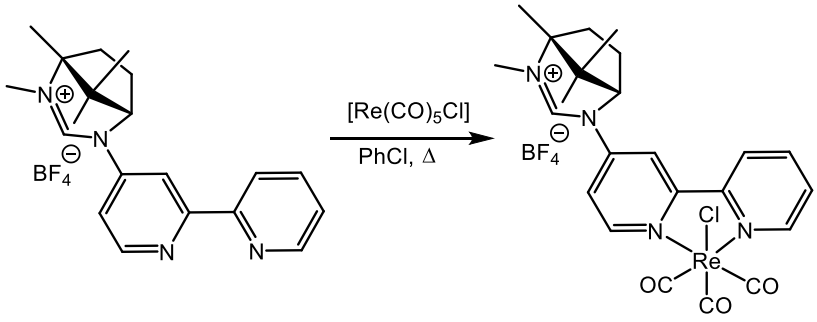

**Figure S22.** $^{1}H/^{13}C$ HSQC NMR ($CD_3CN$, 298 K, 400 MHz) spectrum of [6-$L^{Mes}H$]$BF_4$, **$6^{Mes}$**.



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 5.0 | 5.0 | 100.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 439.2874 | 439.2862 | 1.2 | 2.7 | 14.5 | 1042.2 | n/a | n/a | C29 H35 N4 |

**Figure S23.** HRMS spectrum and data for [6-L$^{Mes}$H]BF$_4$, **6$^{Mes}$**.

2.5. *C*-[Re(CO)$_3$(4-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-4$^{Me}$**.




A solution of [Re(CO)$_5$Cl] (100 mg, 2.76 x 10$^{-4}$ mol) and [4-L$^{Me}$H]BF$_4$ (113 mg, 2.76 x 10$^{-4}$ mol) in chlorobenzene (7 ml) was heated to 100 °C for two hours whereupon a yellow-precipitate formed. After cooling, the solid was filtered, washed with diethyl ether and air-dried. Yield = 157 mg (80%). A second crop could be isolated from the mother liquor on standing. Yield = 11%.

$^1$H (d$_6$-dmso, 400 MHz): 8.86 (obs, 1H), 8.85 (s, 1H), 8.82 (dd, 6.2, 1.0 Hz 1H), 8.64 (d, 8.0 Hz 1H), 8.47 (t, 2.3 Hz, 1H), 8.24 (tt, 7.9, 1.2 Hz, 1H), 7.62 (m, 2H), 4.34 (t, 4.6 Hz, 1H), 3.22 (s, 3H), 2.36 (m, 1H), 2.20-2.00 (m, 2H), 1.89 (m, 1H), 1.21 (s, 3H), 1.03 (s, 3H), 0.90 (s, 3H) ppm. $^{13}$C{$^1$H} (d$_6$-dmso, 100 MHz): 198.2 (CO), 198.1 (CO), 190.4 (CO), 157.3 (C), 155.2 (CH), 154.5 (C), 154.1 (C), 153.6 (CH), 149.7 (CH), 140.7 (CH), 128.9 (CH), 125.3 (CH), 117.5 (CH), 114.6 (CH), 72.8 (C), 67.2 (CH), 42.0 (C), 39.0 (CH$_2$), 38.6 (CH$_3$), 30.8 (CH$_2$), 21.6 (CH$_3$), 16.7 (CH$_3$), 13.7 (CH$_3$) ppm. HRMS (ES): m/z 627.1183 (calc. 627.1173) [L]$^+$, 100%.

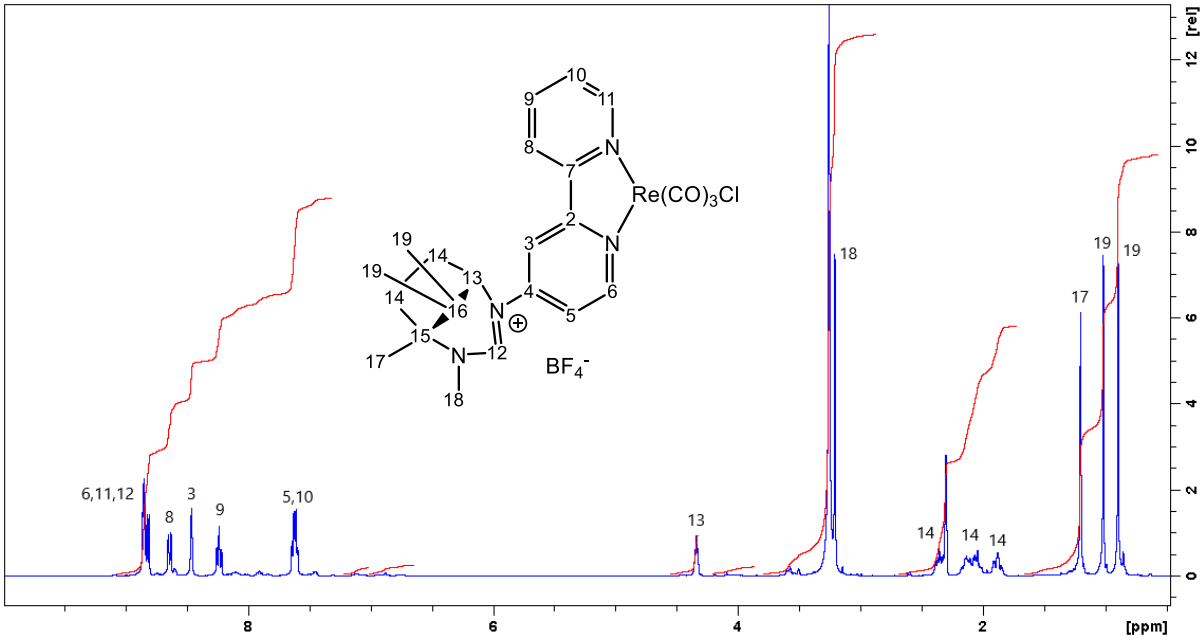



**Figure S24.** $^{1}$H NMR (d$_6$-dmso, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(4-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-4$^{Me}$**.

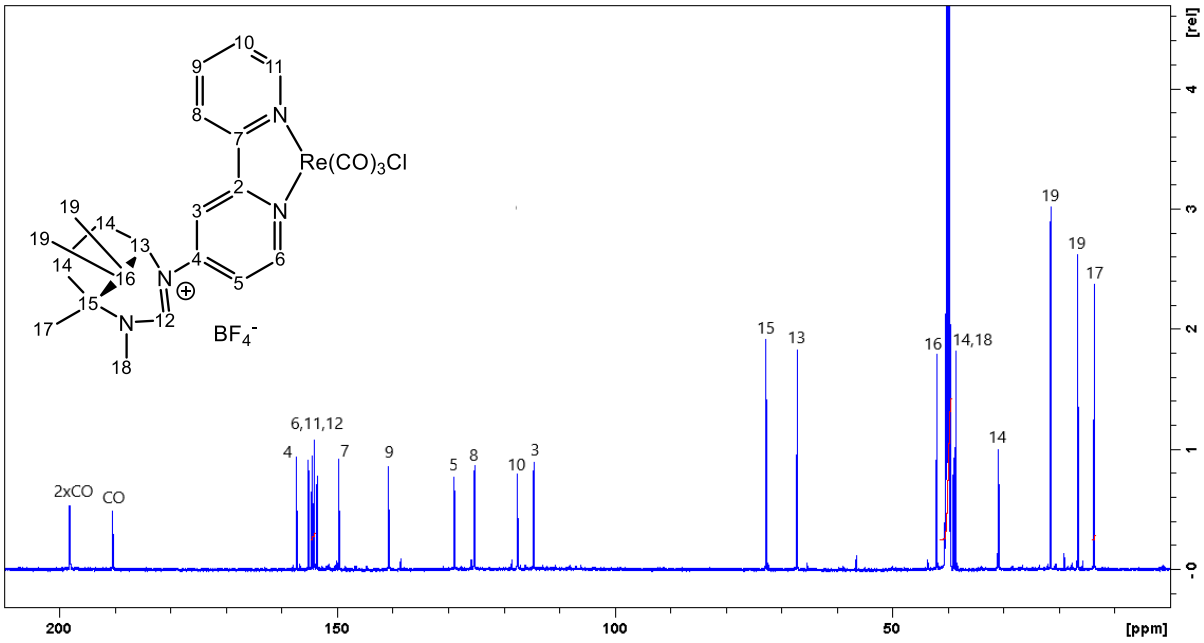



**Figure S25.** $^{13}$C{$^{1}$H} NMR (d$_6$-dmso, 298 K, 100 MHz) spectrum of *C*-[Re(CO)$_3$(4-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-4$^{Me}$**.

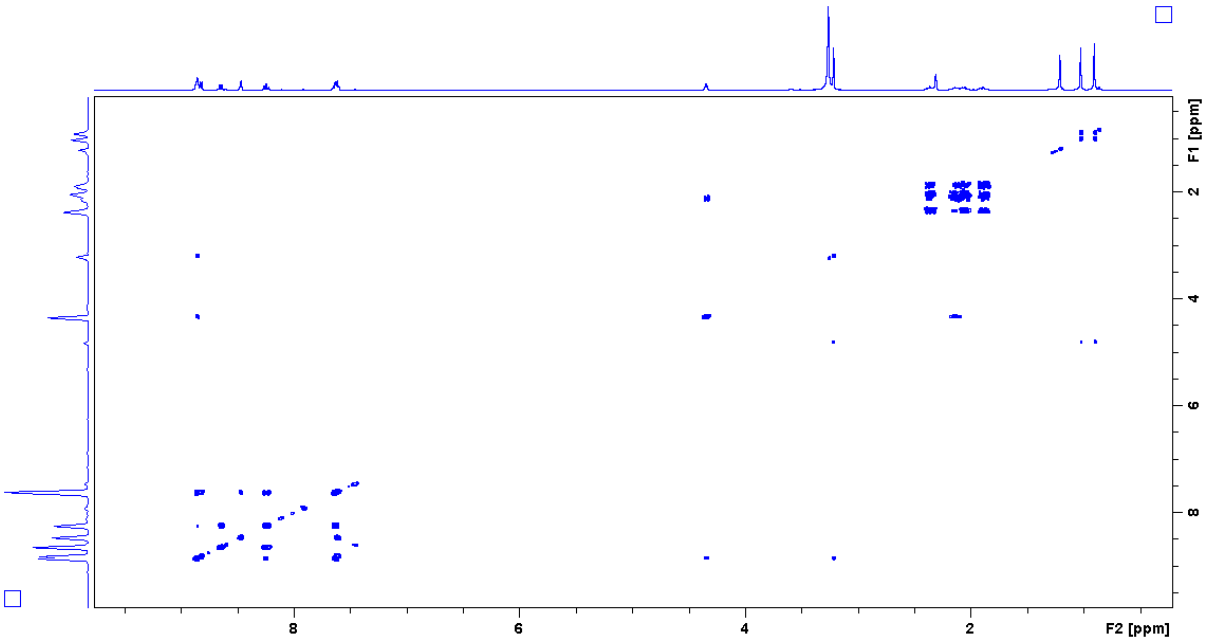



**Figure S26.** $^{1}H/^{1}H$ COSY NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of *C*-$[Re(CO)_3(4\text{-}L^{Me}H)Cl]BF_4$, ***C*-Re-4$^{Me}$**.

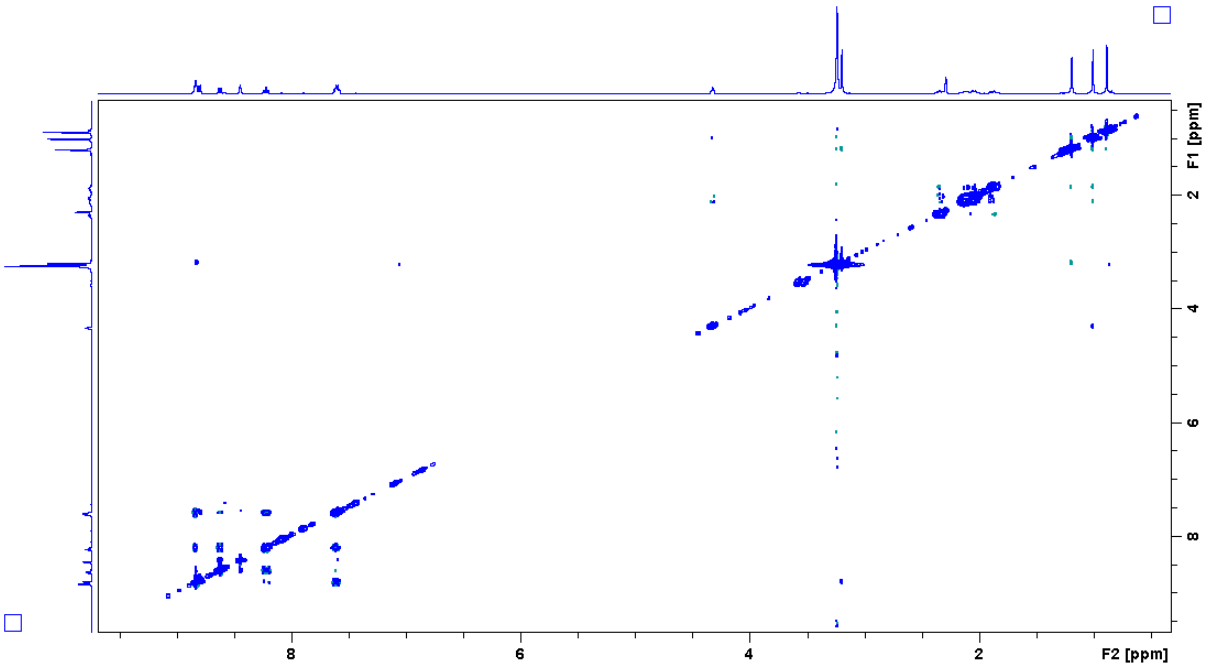



**Figure S27.** $^{1}H/^{1}H$ NOESY NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of *C*-$[Re(CO)_3(4\text{-}L^{Me}H)Cl]BF_4$, ***C*-Re-4$^{Me}$**.

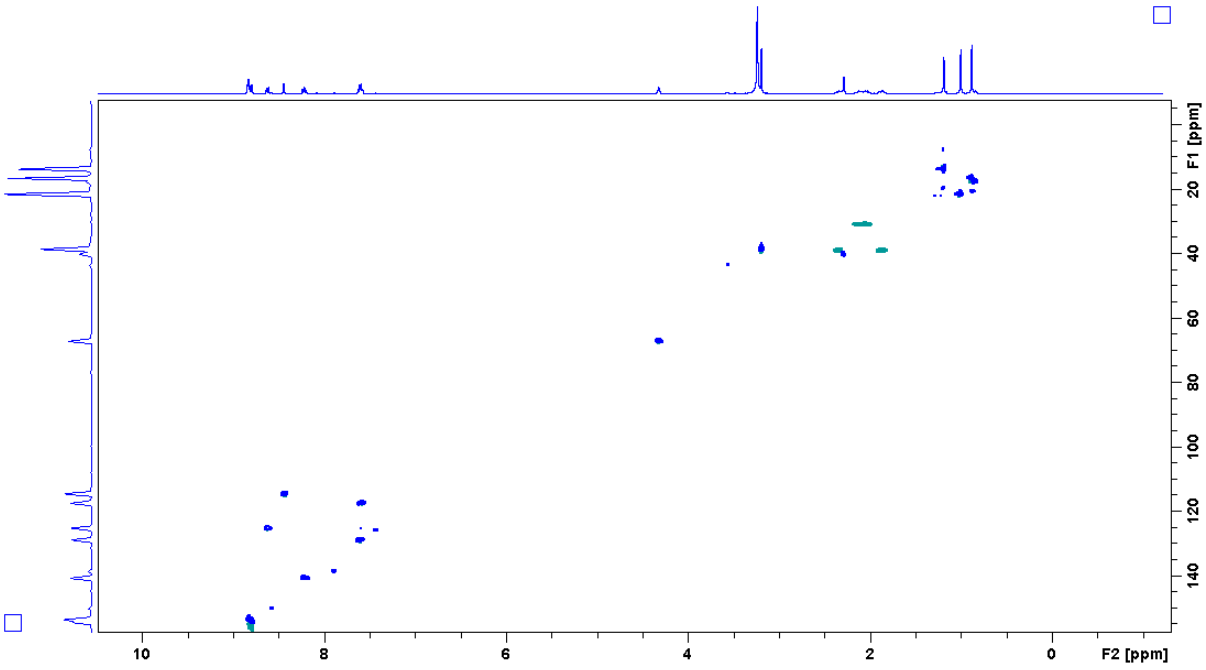
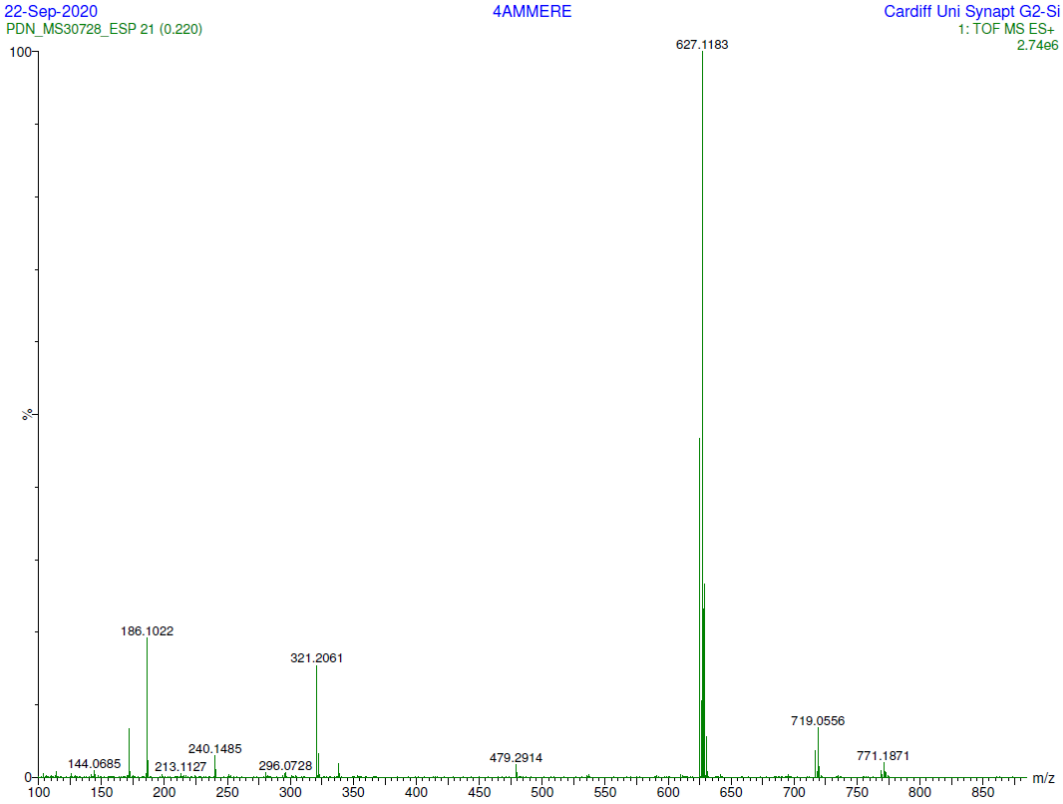
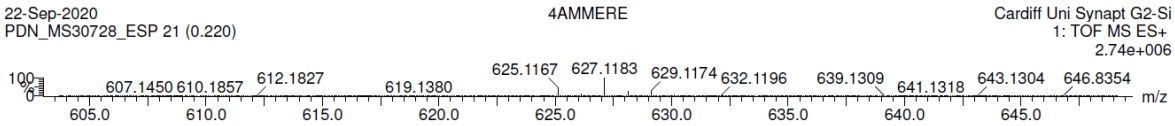



**Figure S28.** $^{1}H/^{13}C$ HSQC NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(4-L$^{Me}$H)Cl]BF$_4$, ***C*-Re-4$^{Me}$**.



Monoisotopic Mass, Odd and Even Electron Ions
74 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-25 N: 0-4 O: 0-3 Cl: 0-1 187Re: 0-1




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 20.0 | 10.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 627.1183 | 627.1173 | 1.0 | 1.6 | 13.0 | 638.3 | n/a | n/a | C23 H25 N4 O3 Cl 187Re |

**Figure S29.** HRMS spectrum and data for *C*-[Re(CO)$_3$(4-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-4$^{Me}$**.

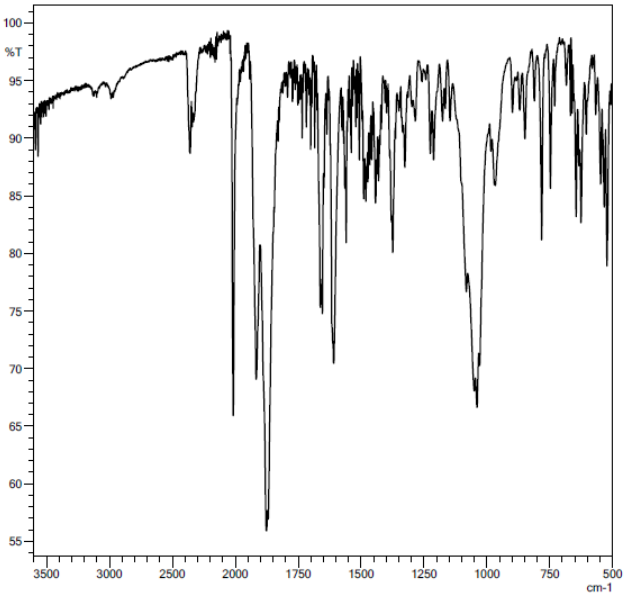
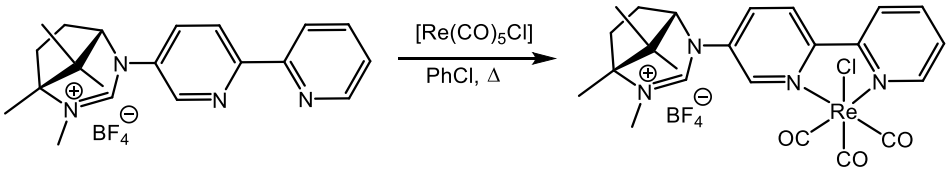



**Figure S30.** Solid-state IR spectrum of *C*-[Re(CO)$_3$(4-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-4$^{Me}$**.

2.6. *C*-[Re(CO)$_3$(5-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-5$^{Me}$**.




This was prepared in the same manner as described for the [4-L$^{Me}$H]BF$_4$ derivative. The complex was crystallised upon slow evaporation of a saturated solution in acetone to give acicular crystals. Yield = 61%.

$^1$H (d$_6$-acetone, 400 MHz): 9.48 (s, 1H), 9.22 (dd, 5.3, 0.8 Hz, 1H), 8.97 (d, 7.9 Hz 1H), 8.90 (d, 8.3 Hz 1H), 8.60 (t, 8.0 Hz, 1H), 8.46 (d obs, 7.9 Hz, 1H), 8.45 (td obs, 8.0, 1.5 Hz, 1H), 7.96 (ddd, 7.7, 5.4, 1.0 Hz, 1H), 4.97 (d, 4.0 Hz, 1H), 3.58 (s, 3H), 2.92 (m, 1H), 2.65-2.55 (m, 2H), 2.31 (m, 1H), 1.64 (s, 3H), 1.50 (s, 3H), 1.49 (s, 3H) ppm. $^{13}$C{$^1$H} (d$_6$-dmso, 100 MHz): 198.0 (2 x CO), 197.7 (CO), 197.5 (CO), 190.4 (2 x CO), 154.8 (C), 154.7 (C), 154.3 (CH), 154.0 (C), 153.8 (C), 153.6 (CH), 146.2 (CH), 145.2 (CH), 140.8 (CH), 139.9 (C), 139.8 (C), 133.3 (CH), 132.4 (CH), 130.8 (C), 128.9(CH), 128.5 (C), 128.4

(C), 125.2 (CH), 72.0 (C), 71.8 (C), 68.7 (CH), 68.4(CH), 41.9 (C), 41.7 (C), 39.1 ($CH_2$), 39.0 ($CH_2$), 38.0 (2 x $CH_3$), 21.4 ($CH_3$), 21.3 ($CH_3$), 16.8 (2 x $CH_3$), 13.7 (2 x $CH_3$) ppm. HRMS (ES): m/z 627.1177 (calc. 627.1173) $[L]^+$, 100%.

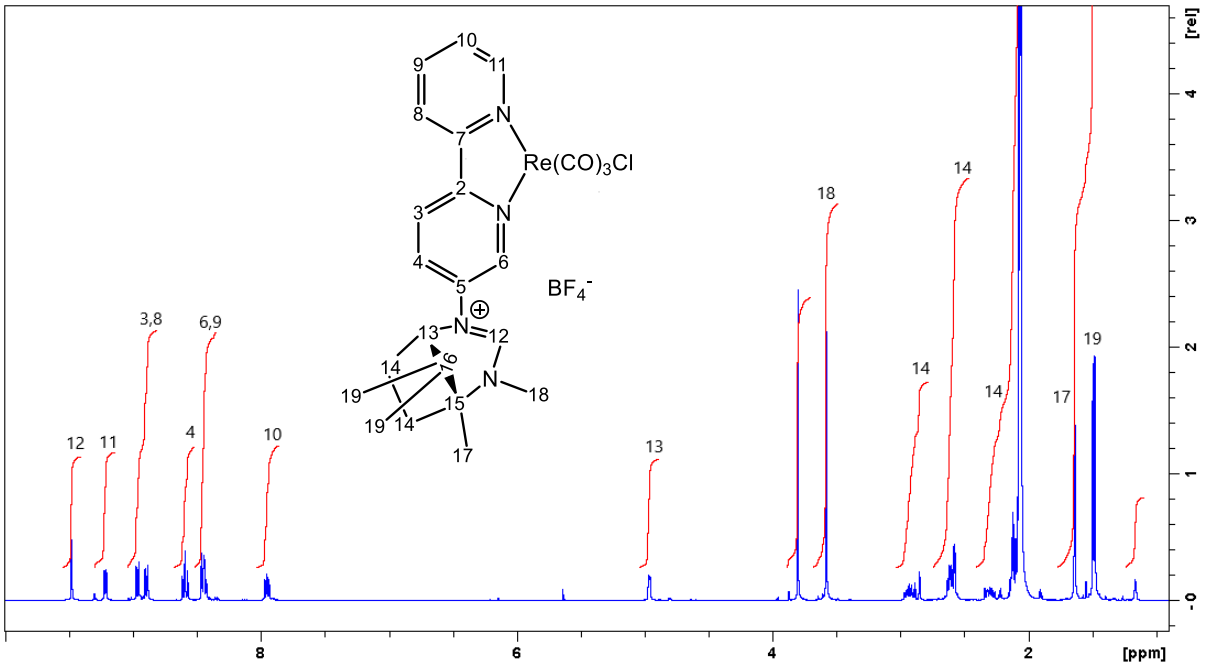



**Figure S31.** $^1$H NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(5-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-5$^{Me}$**.

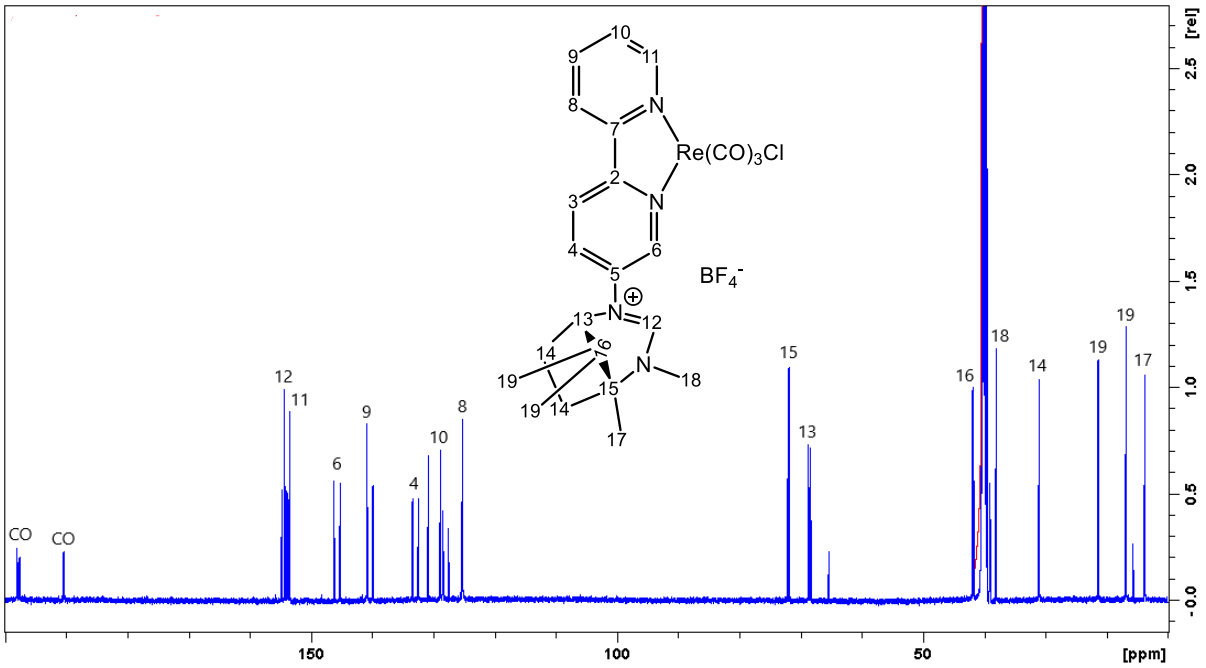



**Figure S32.** $^{13}$C{$^1$H} NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(5-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-5$^{Me}$**.

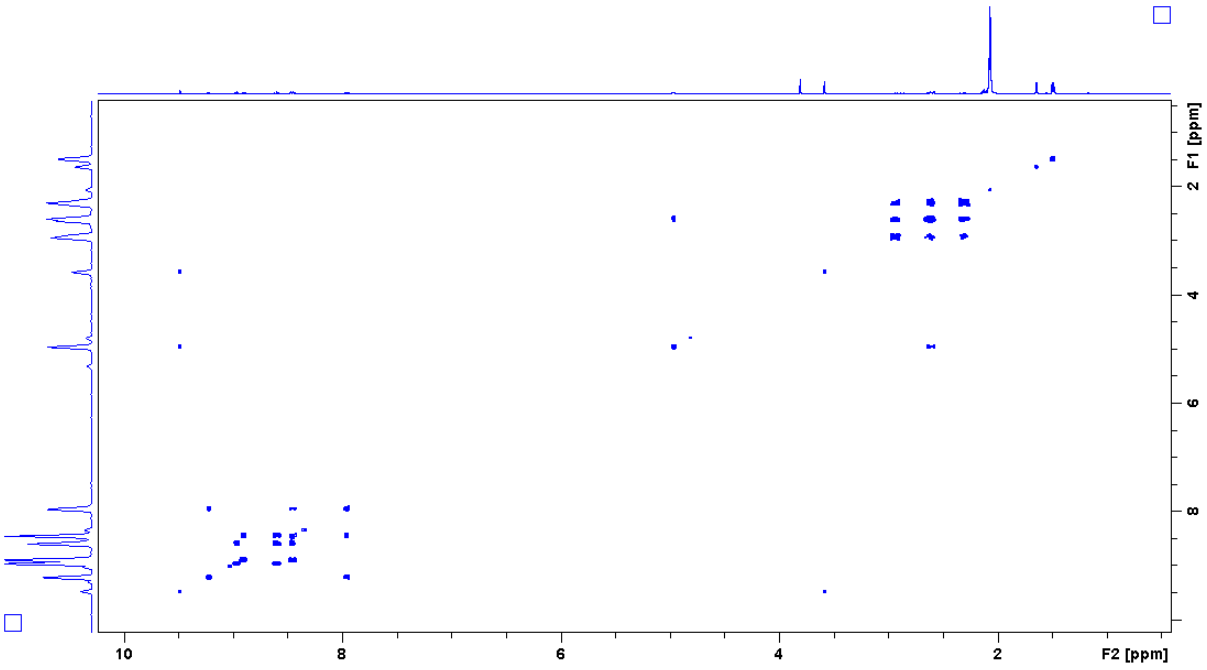



**Figure S33.** $^{1}$H NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(5-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-5$^{Me}$**.

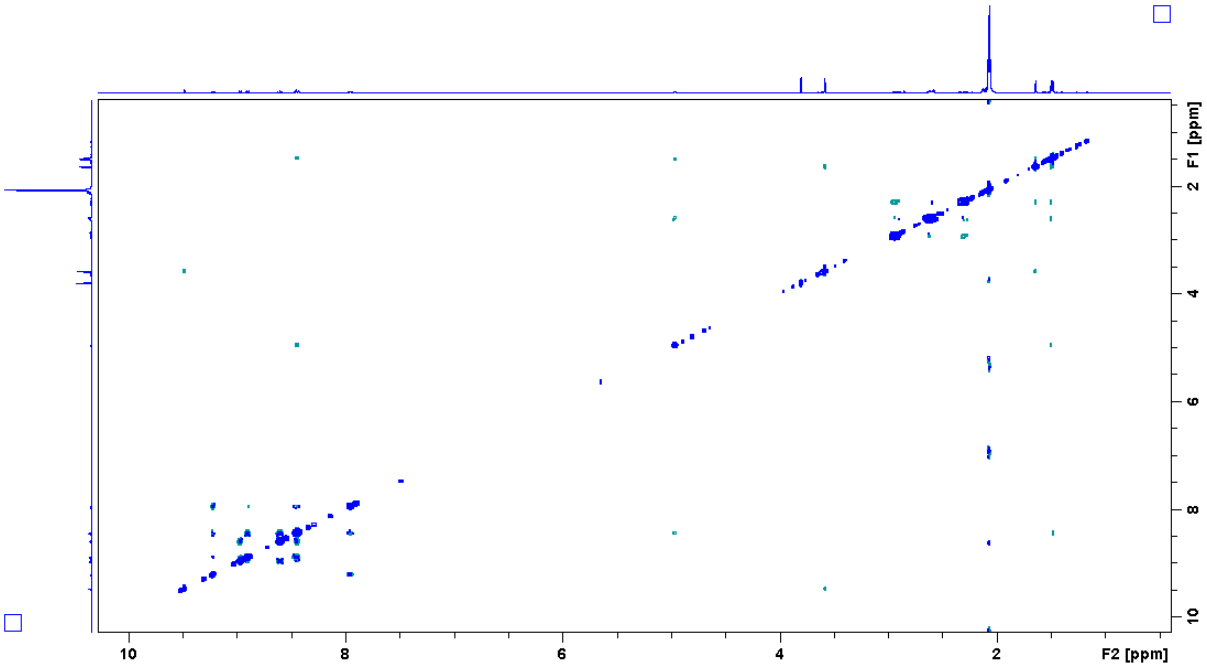



**Figure S34.** $^{1}$H/$^{1}$H NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(5-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-5$^{Me}$**.

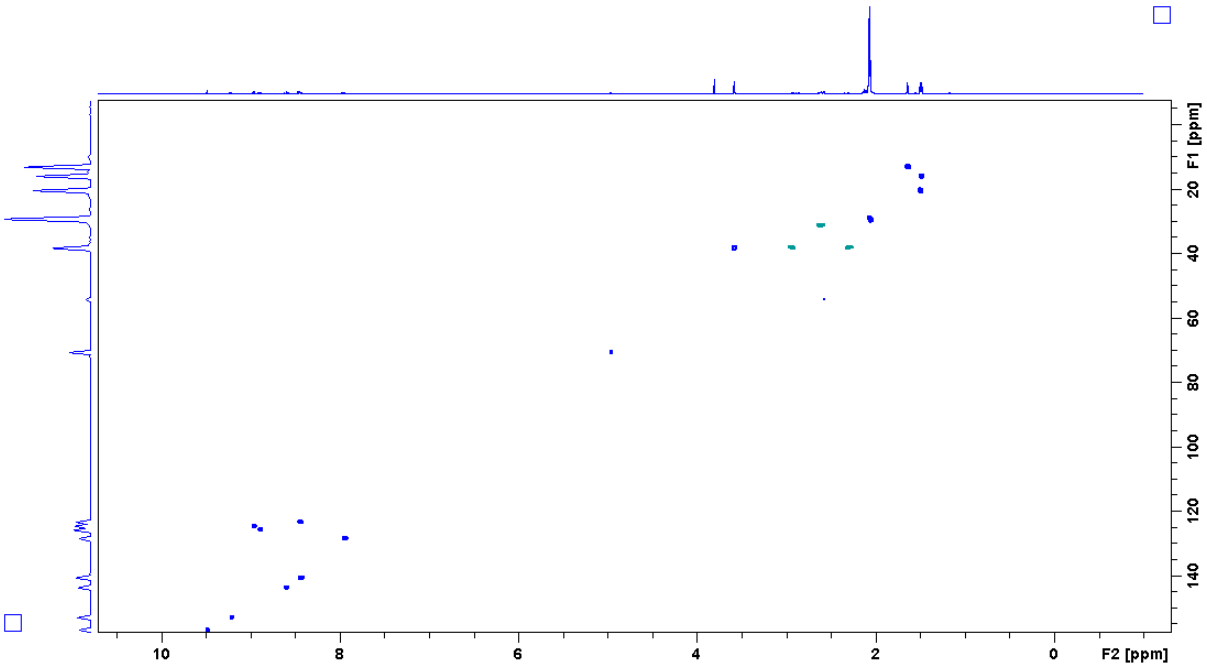
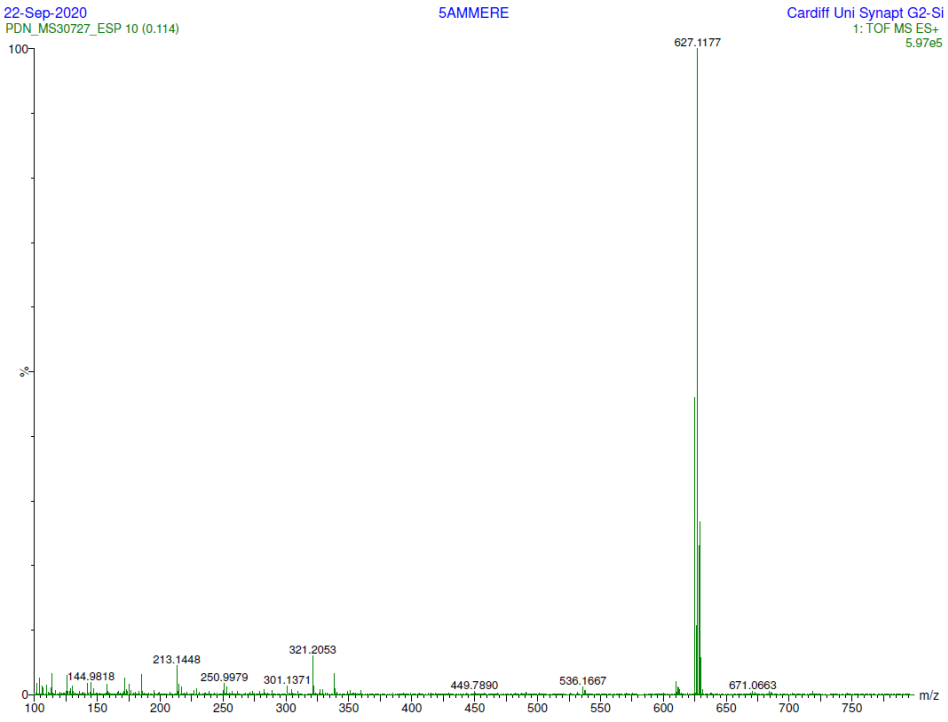



**Figure S35.** $^{1}H/^{13}C$ NMR ($d_6$-acetone, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(5-L$^{Me}$H)Cl]BF$_4$, ***C*-Re-5$^{Me}$**.



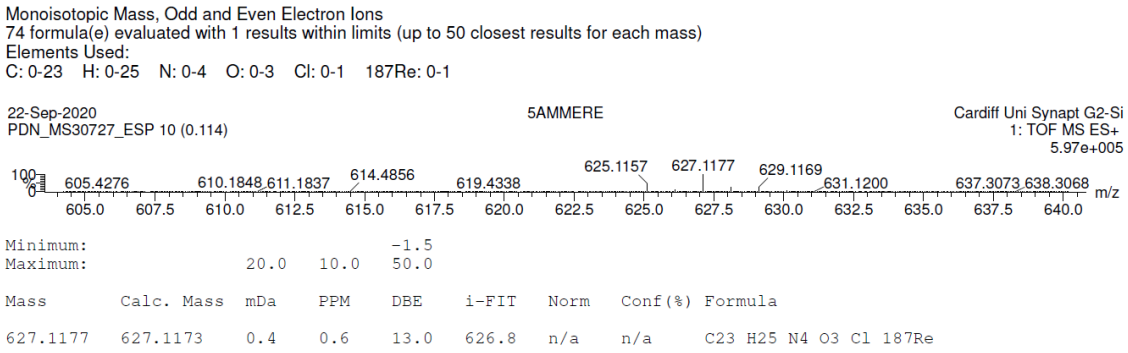



**Figure S36.** HRMS spectrum and data for *C*-[Re(CO)$_3$(5-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-5$^{Me}$**.

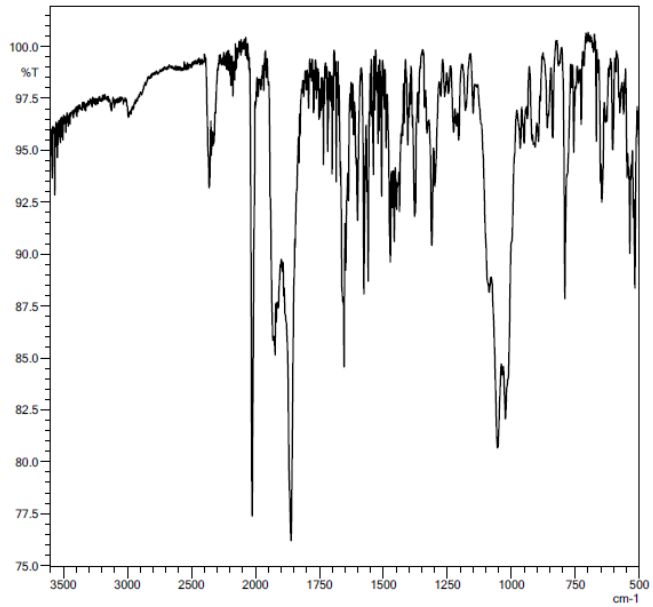
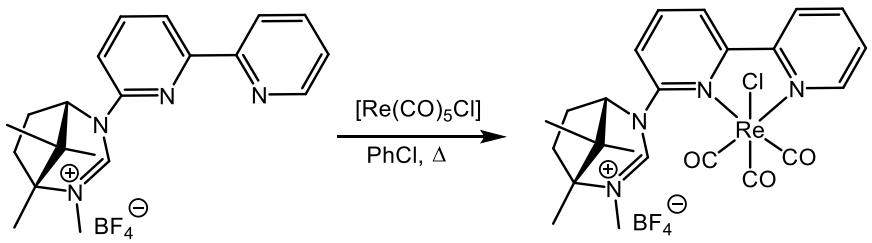



**Figure S37.** Solid-state IR spectrum of *C*-[Re(CO)$_3$(5-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-5$^{Me}$**.

2.7. *C*-[Re(CO)$_3$(6-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-6$^{Me}$**.




This was prepared in the same manner as described for the [4-L$^{Me}$H]BF$_4$ derivative. The complex was crystallised as needle-like crystals upon vapour diffusion of pentane into an acetone solution of the complex. Yield = 67%. A second crop was obtained upon continued vapour diffusion. Yield = 8%.

$^1$H ($CD_3CN$, 400 MHz): 9.28 (s, 1H), 9.13 (ddd, 5.6, 1.6, 0.8, Hz, 1H), 8.51 (dd, 7.9, 1.0 Hz 1H), 8.47 (dt, 8.3, 0.8 Hz 1H), 8.39 (t, 8.2 Hz, 1H), 8.29 (td, 7.9, 1.5 Hz, 1H), 7.80 (dd, 8.3, 0.8 Hz, 1H), 7.78 (ddd, 7.7, 5.5, 1.1 Hz, 1H), 4.44 (d, 5.4 Hz, 1H), 3.40 (s, 3H), 2.83 (m, 1H), 2.55-2.40 (m, 2H), 2.15 (m, 1H), 1.47

(s, 3H), 1.33 (s, 3H), 1.23 (s, 3H) ppm. $^{13}C\{^1H\}$ ($d_6$-acetone/$d_6$-dmso, 100 MHz): 196.7 (CO), 195.1 (CO), 188.4 (CO), 156.9 (CH), 156.5 (C), 156.1 (C), 155.5 (C), 153.0 (CH), 143.6 (CH), 140.8 (CH), 128.6 (CH), 125.8 (CH), 124.4(CH), 123.0 (CH), 73.6 (C),70.8 (CH), 41.6 (C), 38.3 ($CH_2$), 38.2 ($CH_3$), 31.2 ($CH_2$), 20.4 ($CH_3$), 15.9 ($CH_3$), 13.0 ($CH_3$) ppm. HRMS (ES): m/z 627.1174 (calc. 627.1173) $[L]^+$, 100%.

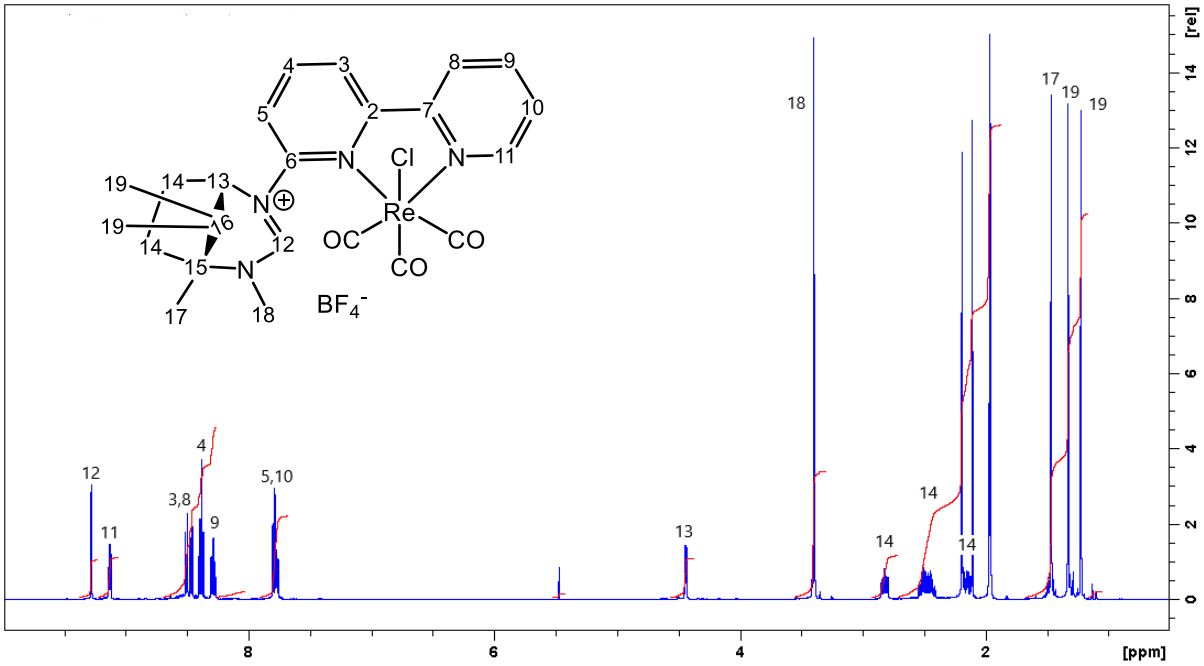



**Figure S38.** $^1H$ NMR ($CD_3CN$, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(6-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-6$^{Me}$**.

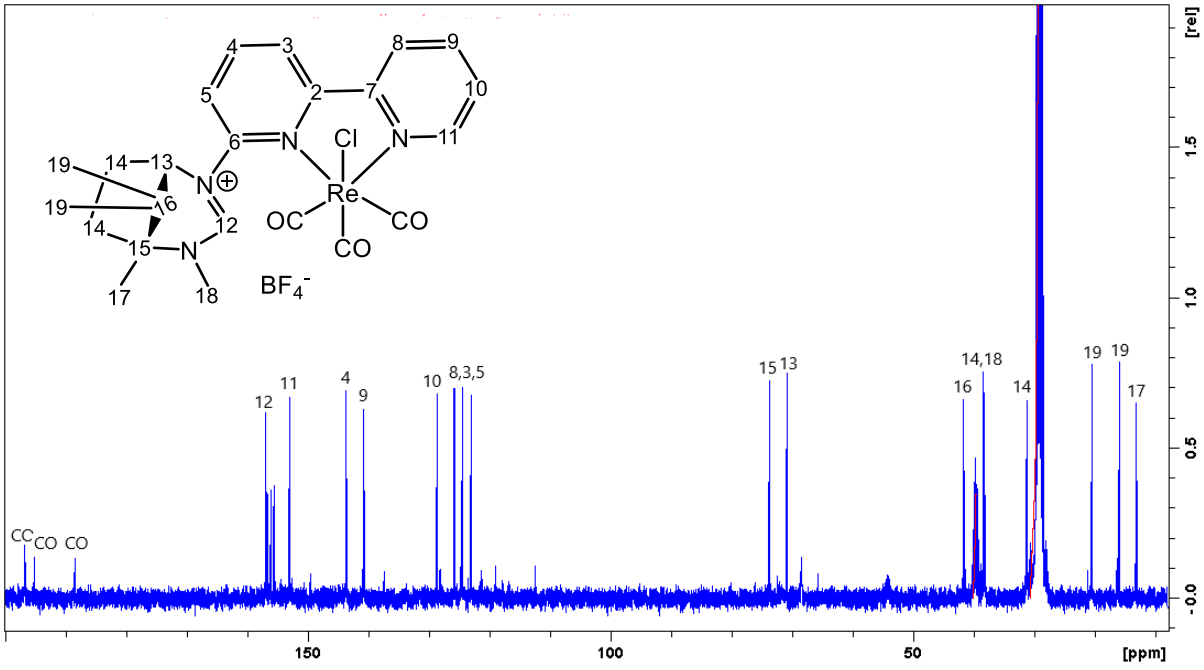



**Figure S39.** $^{13}C\{^1H\}$ NMR ($d_6$-acetone/$d_6$-dmso, 298 K, 100 MHz) spectrum of *C*-[Re(CO)$_3$(6-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-6$^{Me}$**.

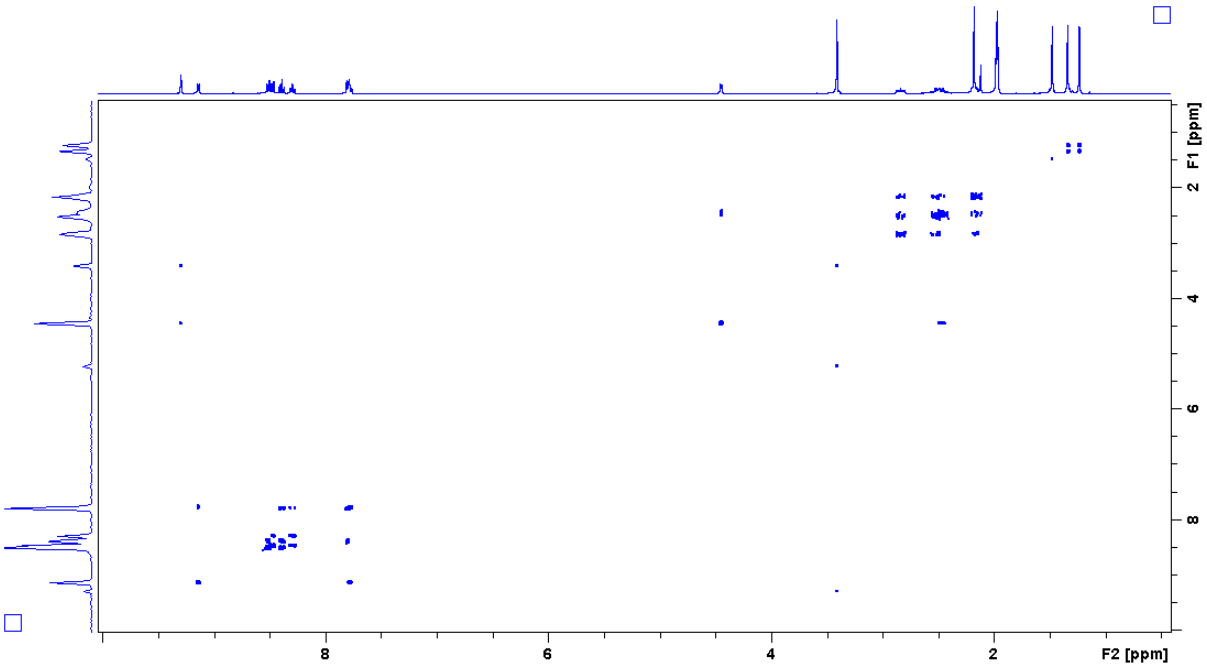



**Figure S40.** $^{1}H/^{1}H$ COSY NMR ($CD_3CN$, 298 K, 400 MHz) spectrum of *C*-$[Re(CO)_3(6\text{-}L^{Me}H)Cl]BF_4$, ***C*-Re-6$^{Me}$**.

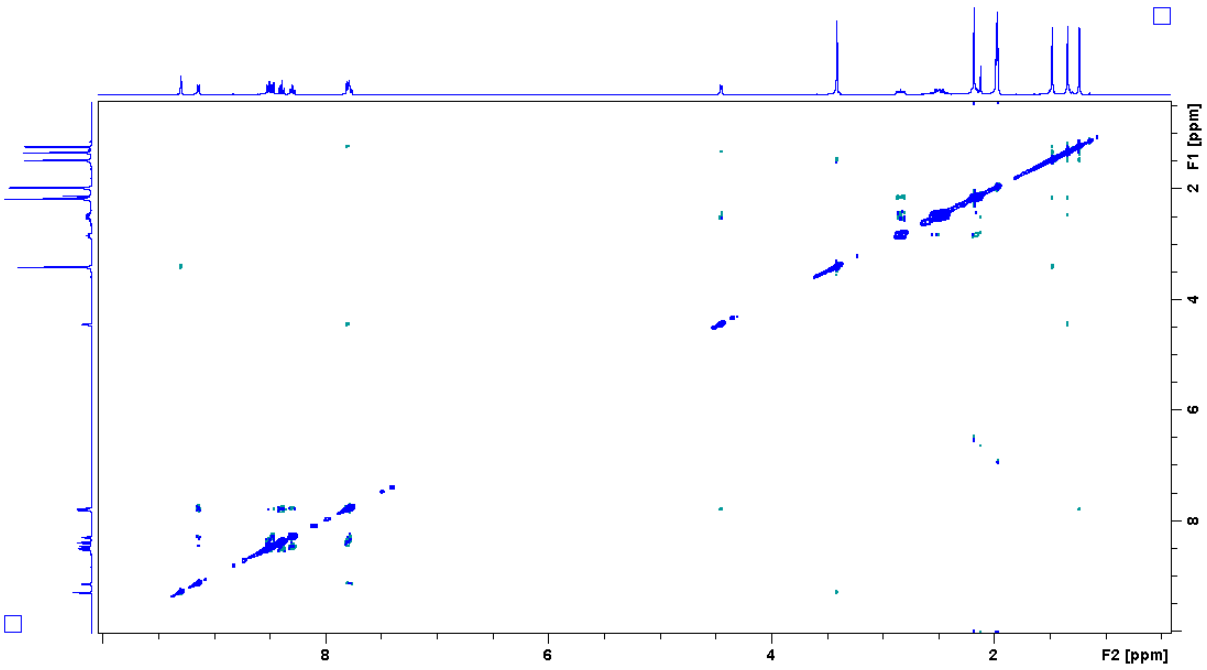



**Figure S41.** $^{1}H/^{1}H$ NOESY NMR ($CD_3CN$, 298 K, 400 MHz) spectrum of *C*-$[Re(CO)_3(6\text{-}L^{Me}H)Cl]BF_4$, ***C*-Re-6$^{Me}$**.

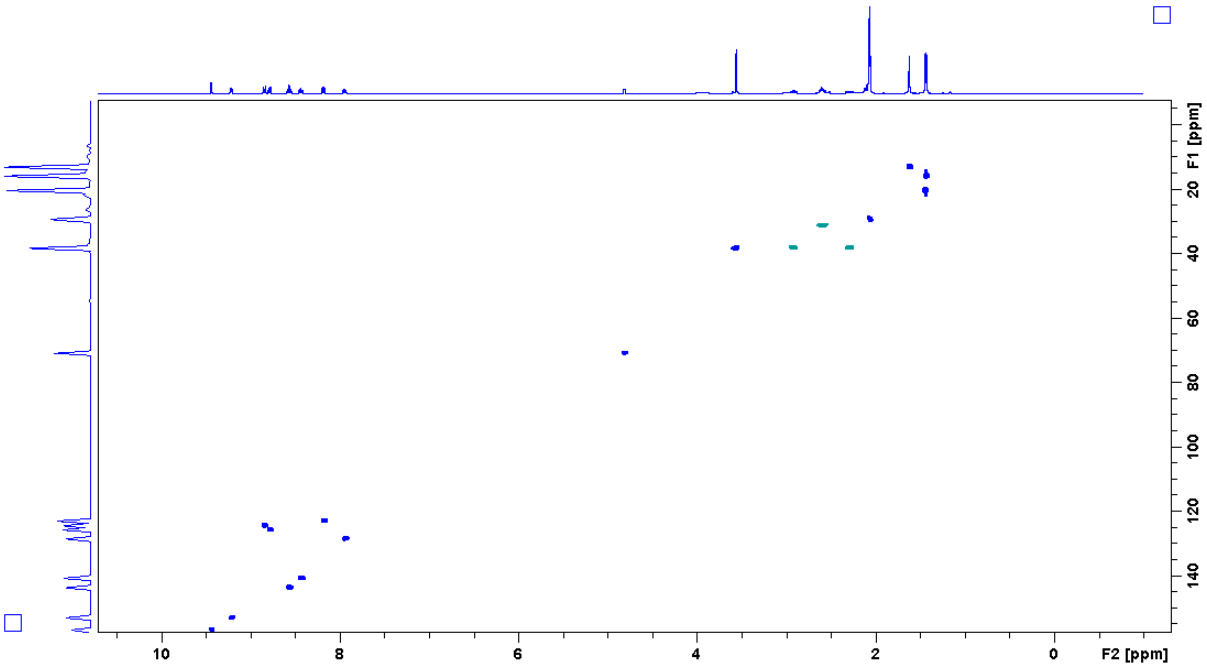
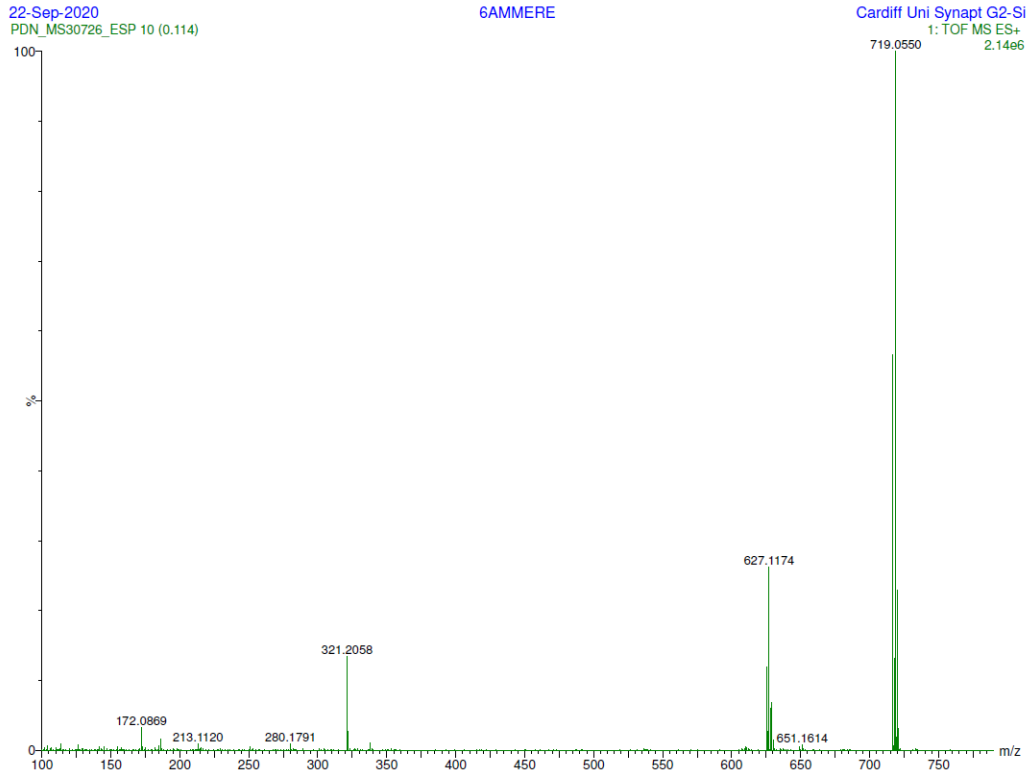
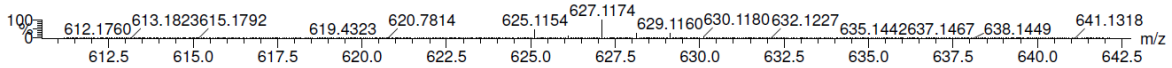



**Figure S42.** $^{1}H/^{13}C$ HSQC NMR ($d_6$-acetone + one drop $d_6$-dmso, 298 K, 400 MHz) spectrum of *C*-$[Re(CO)_3(6\text{-}L^{Me}H)Cl]BF_4$, *C*-**Re-6$^{Me}$**.



Monoisotopic Mass, Odd and Even Electron Ions
74 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-25 N: 0-4 O: 0-3 Cl: 0-1 187Re: 0-1

22-Sep-2020 6AMMERE Cardiff Uni Synapt G2-Si
PDN_MS30726_ESP 10 (0.114) 1: TOF MS ES+
5.59e+005




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 20.0 | 10.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 627.1174 | 627.1173 | 0.1 | 0.2 | 13.0 | 624.9 | n/a | n/a | C23 H25 N4 O3 Cl 187Re |

**Figure S43.** HRMS spectrum and data for *C*-[Re(CO)$_3$(6-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-6$^{Me}$**.

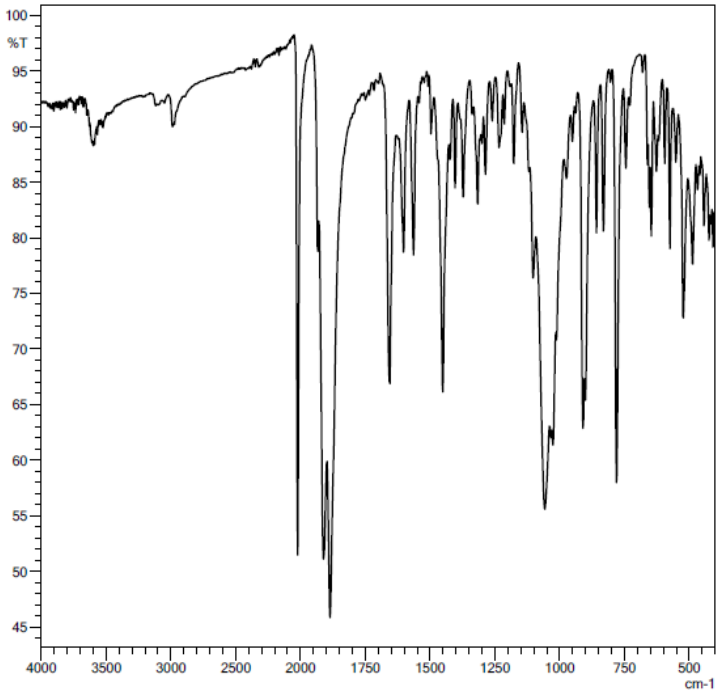
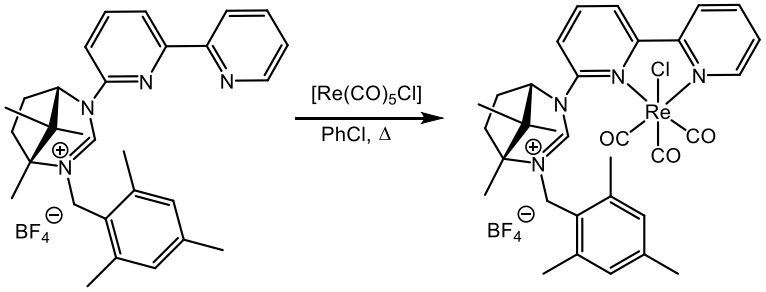



**Figure S44.** Solid-state IR spectrum of *C*-[Re(CO)$_3$(6-L$^{Me}$H)Cl]BF$_4$, *C*-**Re-6$^{Me}$**.

2.8. *C*-[Re(CO)$_3$(6-L$^{Mes}$H)Cl]BF$_4$, *C*-**Re-6$^{Mes}$**.




This was prepared in the same manner as described for *C*-[Re(CO)$_3$(4-L$^{Mes}$H)Cl]BF$_4$, *C*-**Re-4$^{Mes}$**. Recrystallisaton was affected from acetone/pentane by vapour diffusion. Yield = 71%.

$^{1}$H ($CD_2Cl_2$, 400 MHz): 8.95 (d, 5.3 Hz, 1H), 8.40 (t, 7.9 Hz, 1H), 8.34 (d, 8.0 Hz 1H), 8.28 (s, 1H), 8.23 (d, 8.2 Hz, 1H), 8.09 (t, 7.9 Hz, 1H), 7.79 (d, 7.7 Hz, 1H), 7.56 (t, 6.6 Hz, 1H), 6.79 (s, 2H), 4.88 (d, 15.1 Hz, 1H), 4.70 (d, 15.1 Hz, 1H), 4.31 (d, 4.1 Hz, 1H), 3.01 (m, 1H), 2.71 (m, 1H), 2.41 (m, 1H), 2.15 (m, 1H), 1.51 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H) ppm. $^{13}$C{$^{1}$H} ($CD_2Cl_2$, 150 MHz): 197.5 (CO), 195.1 (CO), 188.0 (CO), 156.8 (C), 155.6 (C), 155.0 (CH), 154.6 (C), 152.6 (CH), 144.2 (CH), 140.0 (CH), 138.5 (C), 130.8 (C), 130.6 (CH), 128.0 (CH), 125.2 (CH), 124.9 (C), 124.7 (CH), 75.4 (C), 73.2 (CH), 49.9 ($CH_2$), 41.5 (C), 39.2 ($CH_2$), 31.7 ($CH_2$), 21.2 ($CH_3$), 20.6 ($CH_3$), 20.3 ($CH_3$), 17.9 ($CH_3$), 14.9 ($CH_3$) ppm. HRMS (ES): m/z 745.1945 (calc. 745.1955) $[L]^{+}$, 100%.

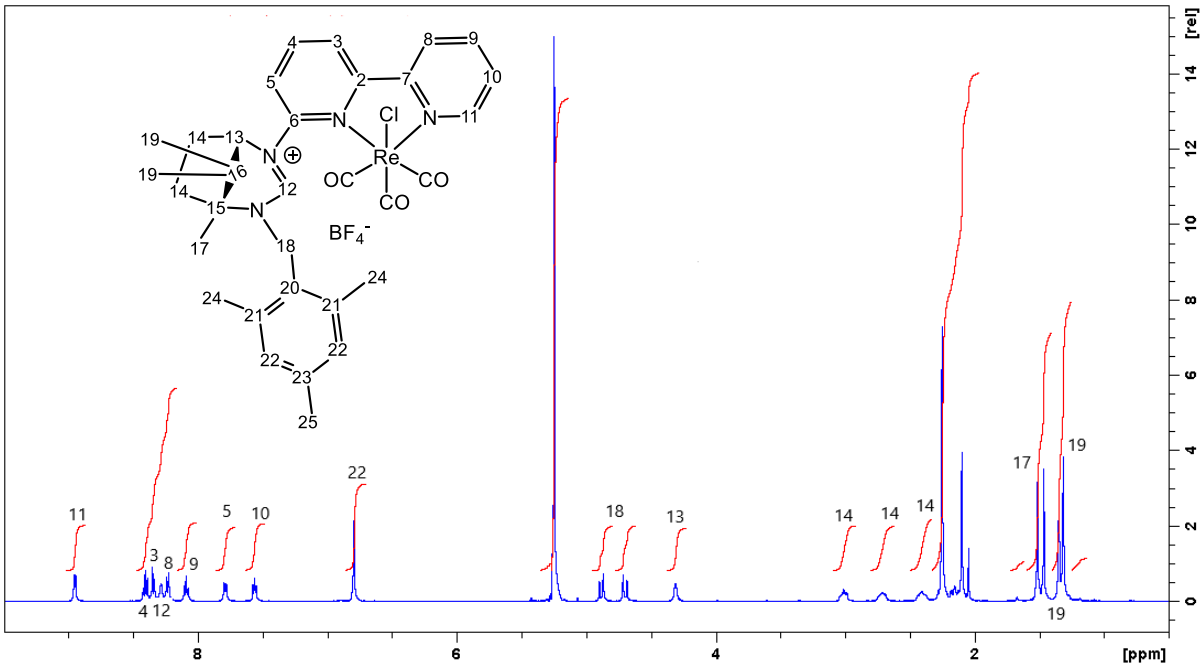



**Figure S45.** $^{1}$H NMR ($CD_2Cl_2$, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(6-L$^{Mes}$H)Cl]BF$_4$, *C*-**Re-6$^{Mes}$**.

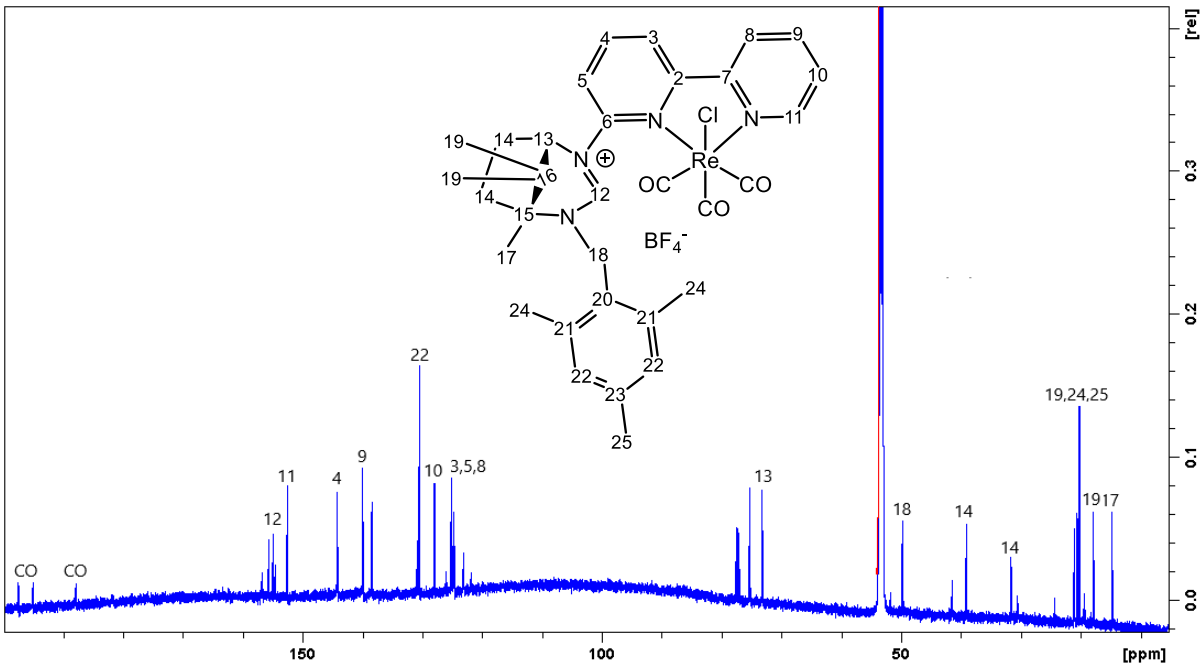


**Figure S46.** $^{13}C\{^{1}H\}$ NMR ($CD_2Cl_2$, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(6-L$^{Mes}$H)Cl]BF$_4$, *C*-**Re-6$^{Mes}$**.

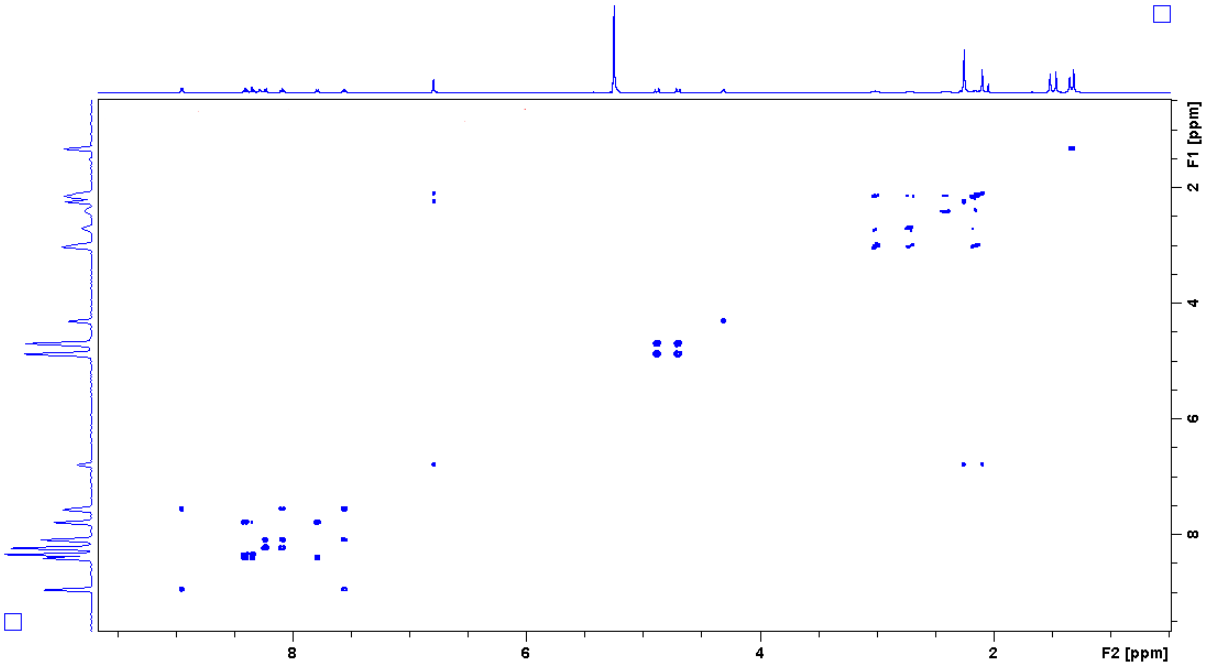



**Figure S47.** $^{1}H/^{1}H$ COSY NMR ($CD_2Cl_2$, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(6-L$^{Mes}$H)Cl]BF$_4$, *C*-**Re-6$^{Mes}$**.

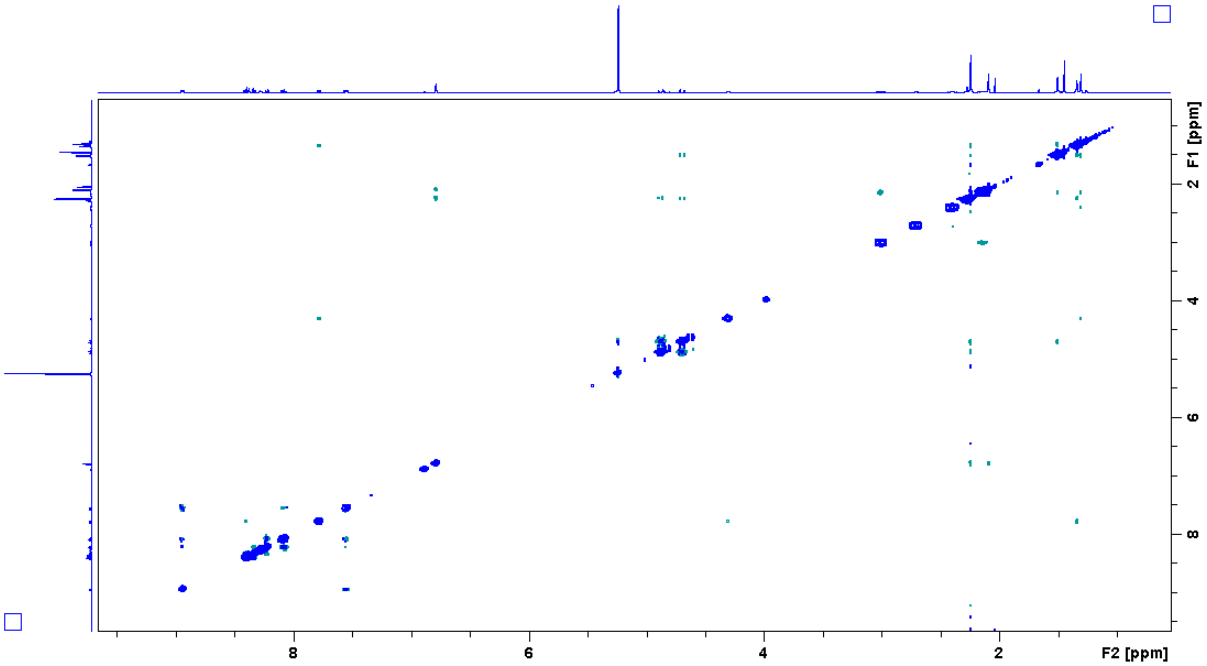



**Figure S48.** $^{1}H/^{1}H$ NOESY NMR ($CD_2Cl_2$, 298 K, 400 MHz) spectrum of *C*-[Re(CO)$_3$(6-L$^{Mes}$H)Cl]BF$_4$, *C*-**Re-6$^{Mes}$**.

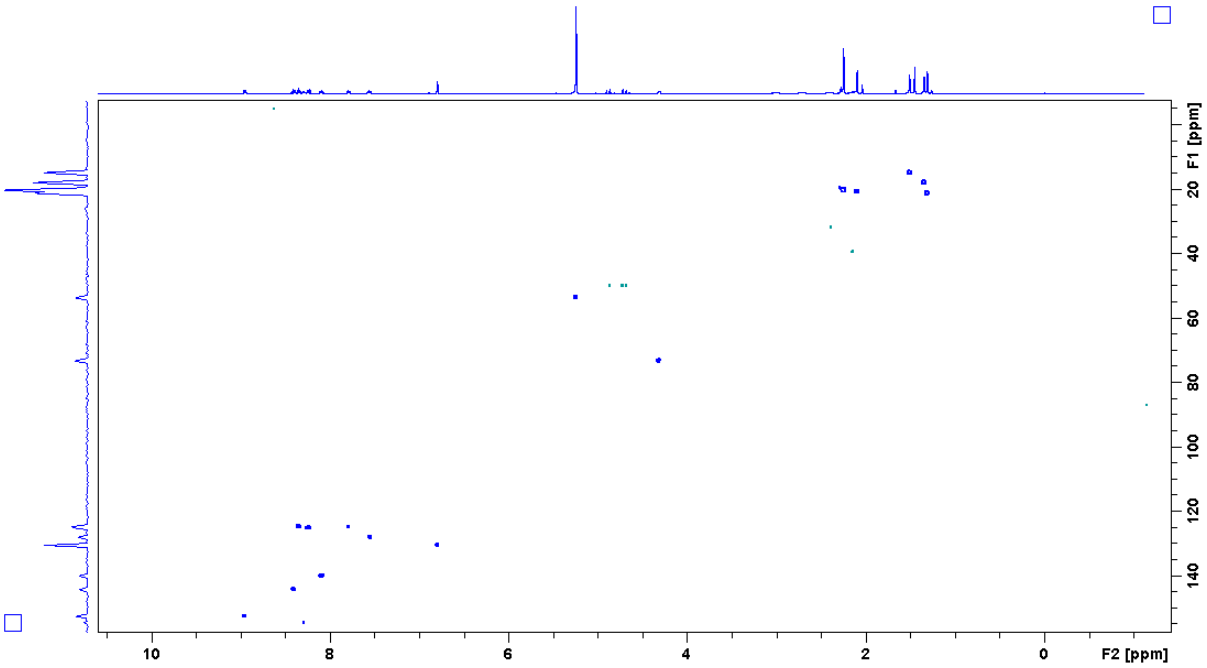
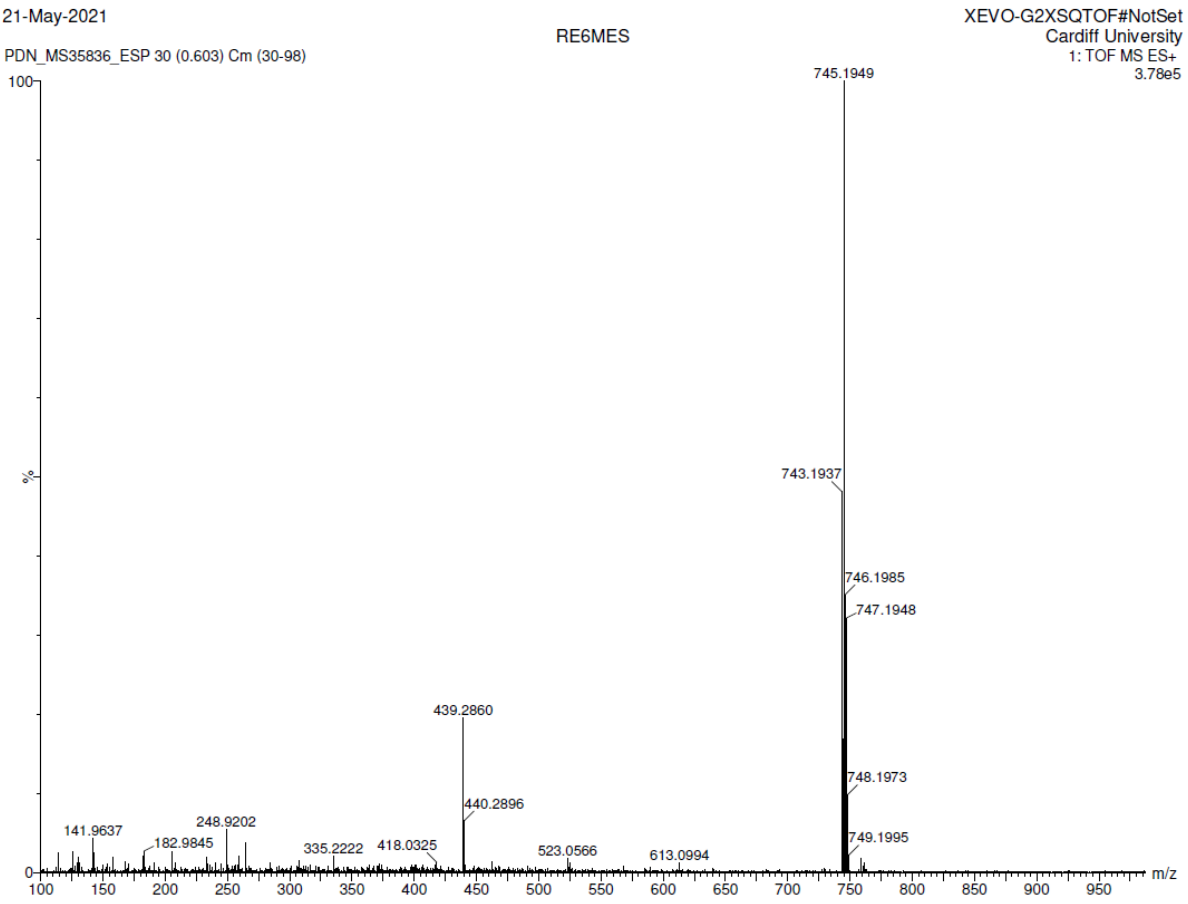



**Figure S49.** $^{1}H/^{13}C$ HSQC NMR ($CD_2Cl_2$, 298 K, 400 MHz) spectrum of *C*-$[Re(CO)_3(6\text{-}L^{Mes}H)Cl]BF_4$, ***C*-Re-6$^{Mes}$**.



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 5.0 | 5.0 | 100.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 745.1949 | 745.1955 | -0.6 | -0.8 | 17.0 | 657.4 | n/a | n/a | C32 H35 N4 O3 Cl 187Re |

**Figure S50.** HRMS spectrum and data for *C*-[Re(CO)$_3$(6-L$^{Mes}$H)Cl]BF$_4$, *C*-**Re-6$^{Mes}$**.

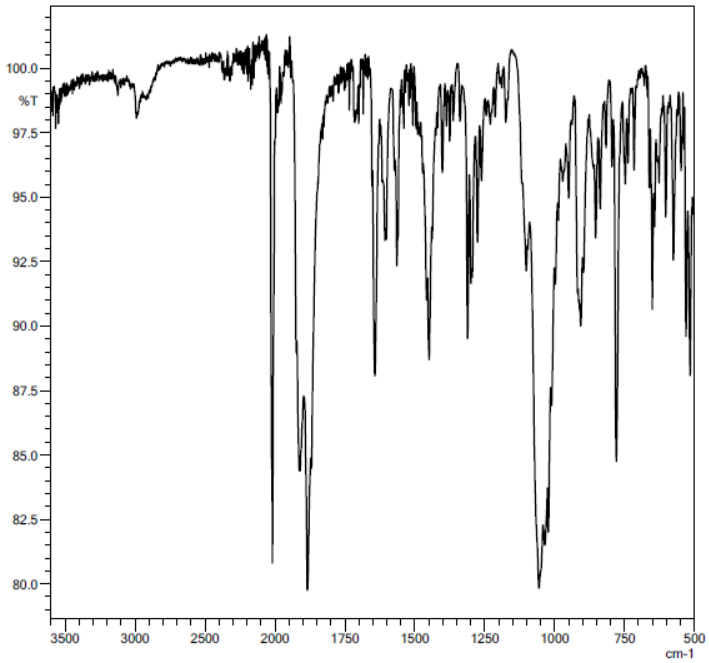
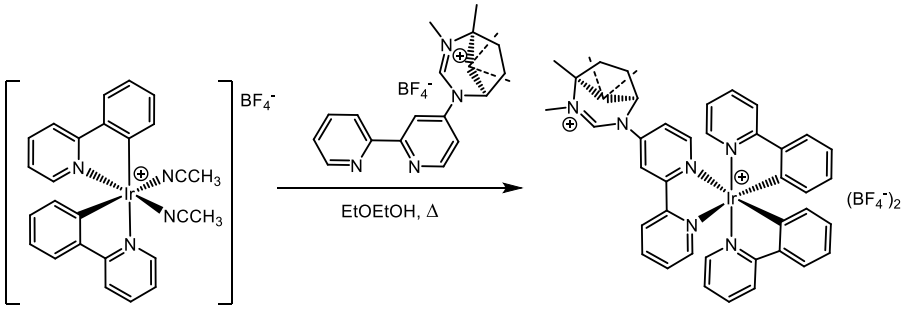



**Figure S51.** Solid-state IR spectrum of *C*-[Re(CO)$_3$(6-L$^{Mes}$H)Cl]BF$_4$, *C*-**Re-6$^{Mes}$**.

2.9. Δ-[Ir(Phpy)$_2$(4-L$^{Me}$H)](BF$_4$)$_2$.EtOEtOH, Δ-**Ir-4$^{Me}$**




A mixture of [Ir(Phpy)$_2$(MeCN)$_2$](BF$_4$) (100 mg, 1.49 x 10$^{-4}$ mmol) and [4-L$^{Me}$H]BF$_4$ (61 mg, 1 mol eq.) were heated in EtOEtOH (8 ml) at 100 °C under N$_2$ for 15 hrs. The cooled mixture was left to stand on the bench whereupon the compound precipitated as an orange solid. Yield = 115mg (71%). A second crystalline crop was obtained from the mother liquor on standing. Yield = 27mg (17%).

$^1$H (d$_6$-dmso, 400 MHz): 8.94 (s, 1H), 8.94 (obs, 1H), 8.81 (s, 1H), 8.39 (t, 7.9 Hz 1H), 8.29 (t, 7.3 Hz 2H), 8.00-7.90 (m, 5H), 7.81-7.75 (m, 3H), 7.71 (d, 5.6 Hz, 1H), 7.63 (d, 5.7 Hz, 1H), 7.19 (m, 2H), 7.05 (t, 7.4 Hz, 2H), 6.93 (m, 2H), 6.21 (dd, 7.5, 3.9 Hz, 2H), 4.39 (d, 4.3 Hz, 1H), 3.38 (s, 3H), 2.23 (m, 2H), 2.07 (m, 1H), 1.40 (s, 3H), 1.20 (s, 3H), 1.09 (s, 3H) ppm. $^{13}$C{$^1$H} (d$_6$-dmso, 100 MHz): 167.4 (C), 167.3

(C), 157.4 (C), 155.2 (C), 154.1 (CH), 151.0 (C), 150.6 (CH), 149.4 (CH), 144.2 (CH), 140.1 (C), 139.4 (CH), 131.5 (CH), 130.8 (CH), 129.8 (C), 125.6 (CH), 124.6 (CH), 124.3 (CH), 122.9 (CH), 120.6 (CH), 119.0 (CH), 115.5 (CH), 72.6 (C), 67.4 (CH), 41.9 (C), 39.0 ($CH_2$), 38.6 ($CH_3$), 31.0 ($CH_2$), 21.6 ($CH_3$), 16.7 ($CH_3$), 13.7 ($CH_3$) ppm. HRMS (ES): m/z 819.2920 (calc. 819.2931) $[L]^+$, 100%.

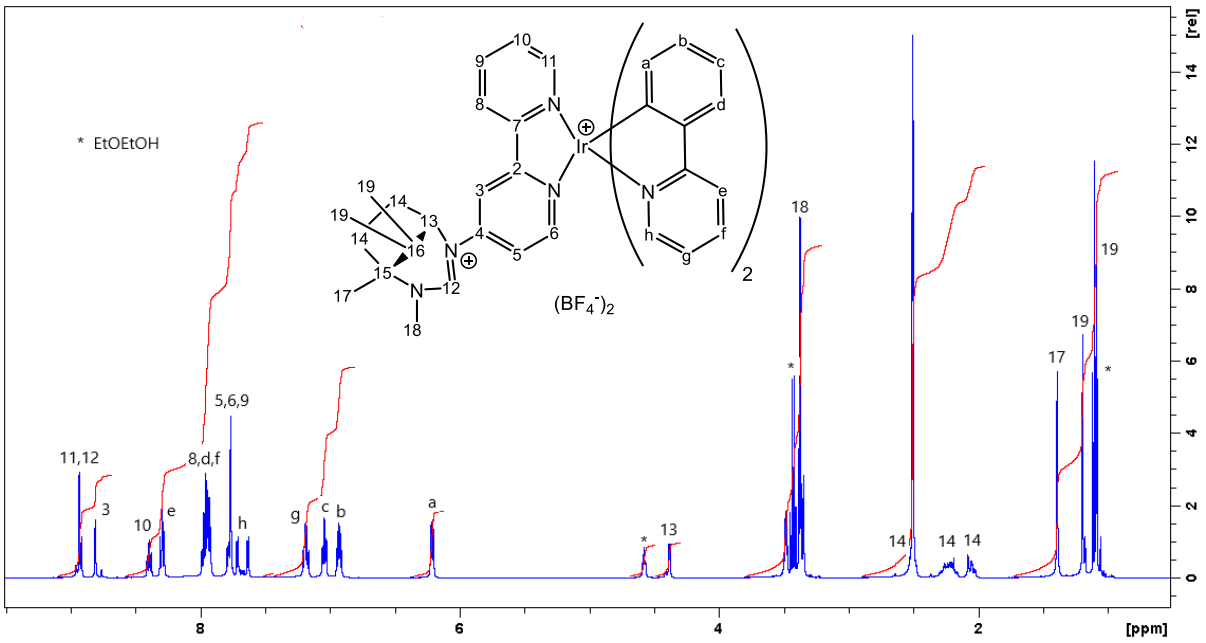



**Figure S52.** $^1$H NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of Δ-[Ir(Phpy)$_2$(4-L$^{Me}$H)](BF$_4$)$_2$, Δ-**Ir-4$^{Me}$**.

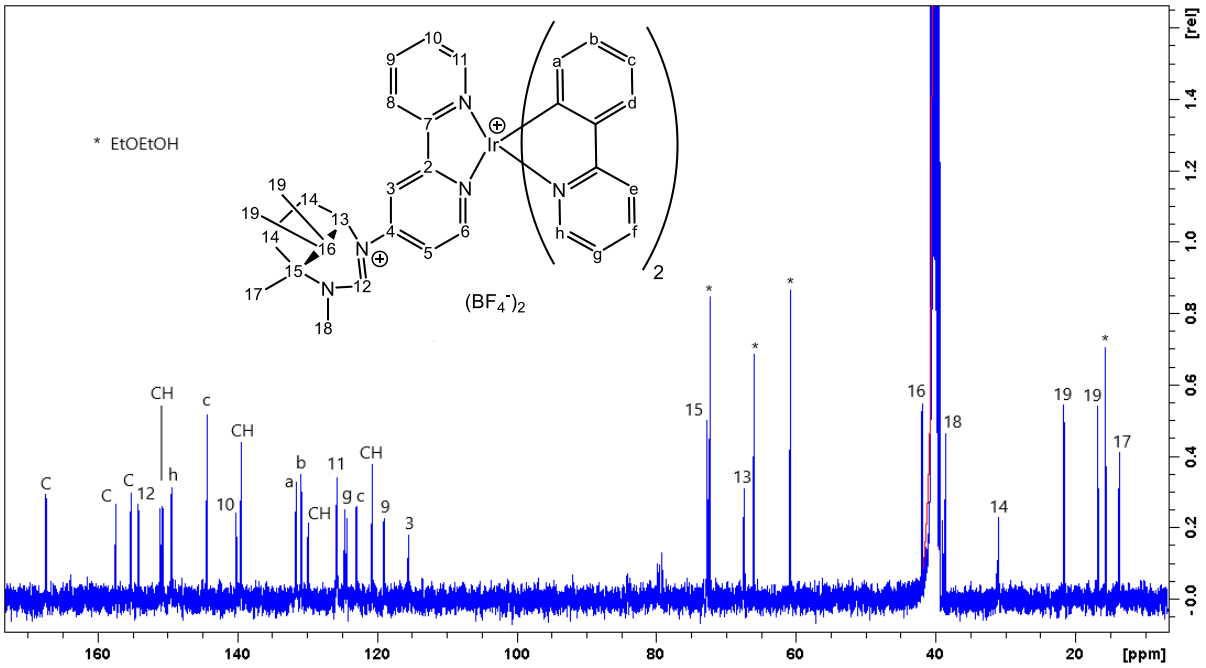



**Figure S53.** $^{13}$C{$^1$H} NMR ($d_6$-dmso, 298 K, 100 MHz) spectrum of Δ-[Ir(Phpy)$_2$(4-L$^{Me}$H)](BF$_4$)$_2$, Δ-**Ir-4$^{Me}$**.

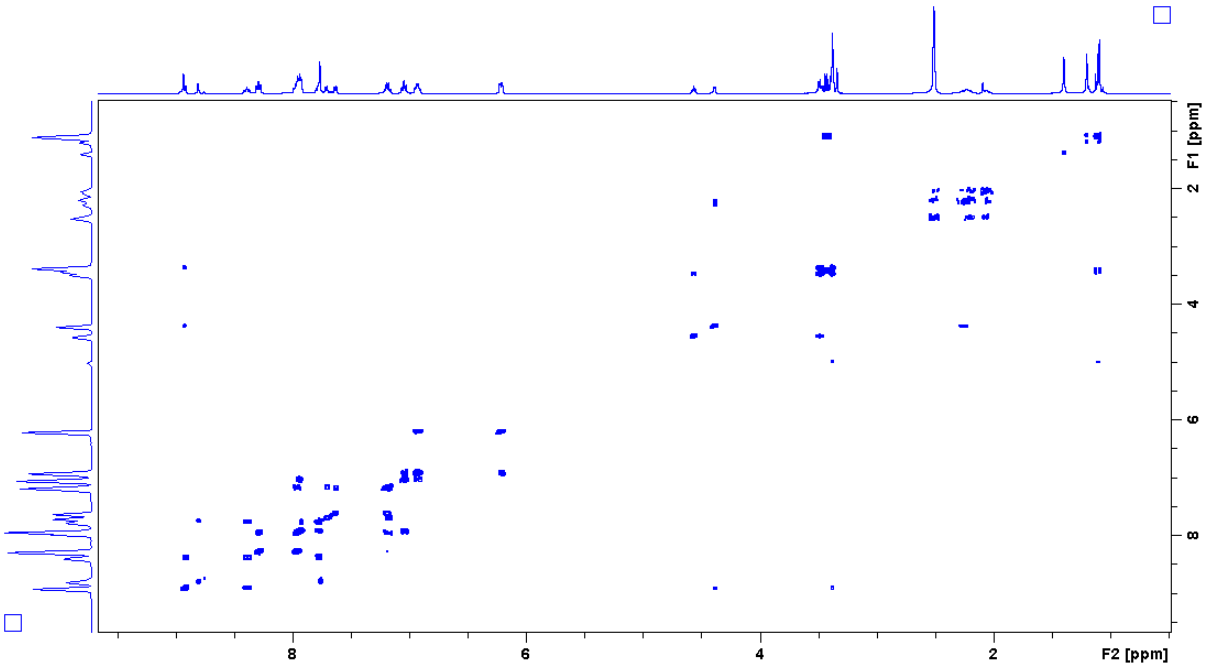



**Figure S54.** $^{1}H/^{1}H$ COSY NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of Δ-[Ir(Phpy)$_2$(4-L$^{Me}$H)](BF$_4$)$_2$, Δ-**Ir-4$^{Me}$**.

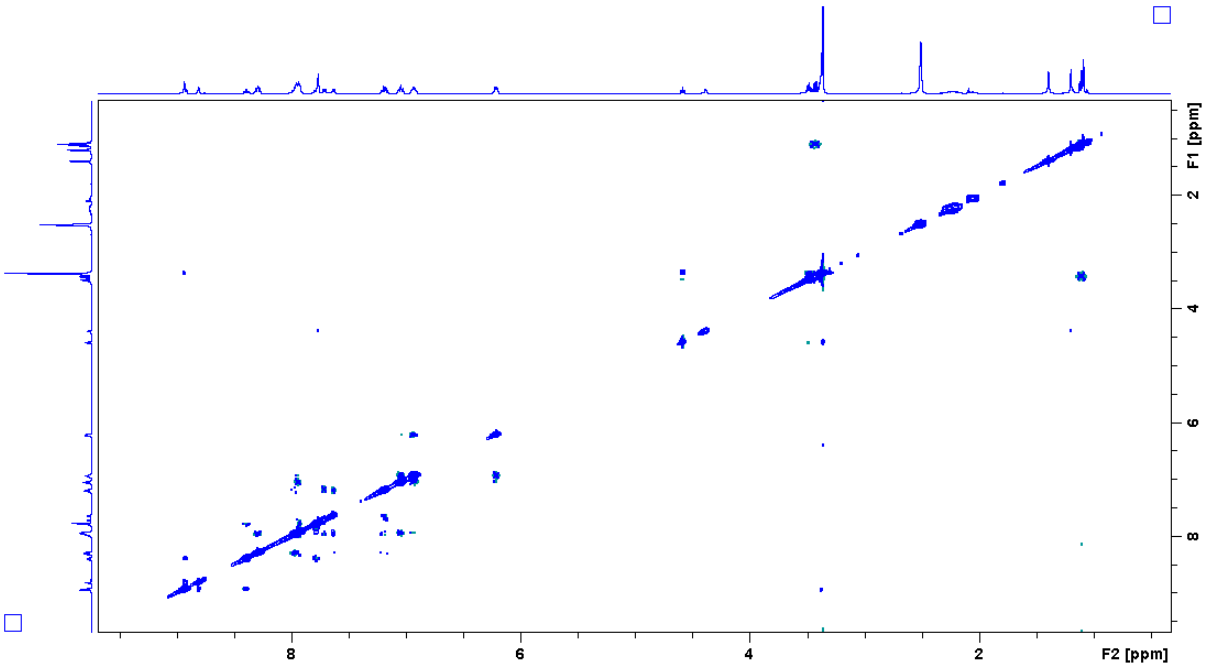



**Figure S55.** $^{1}H/^{1}H$ NOESY NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of Δ-[Ir(Phpy)$_2$(4-L$^{Me}$H)](BF$_4$)$_2$, Δ-**Ir-4$^{Me}$**.

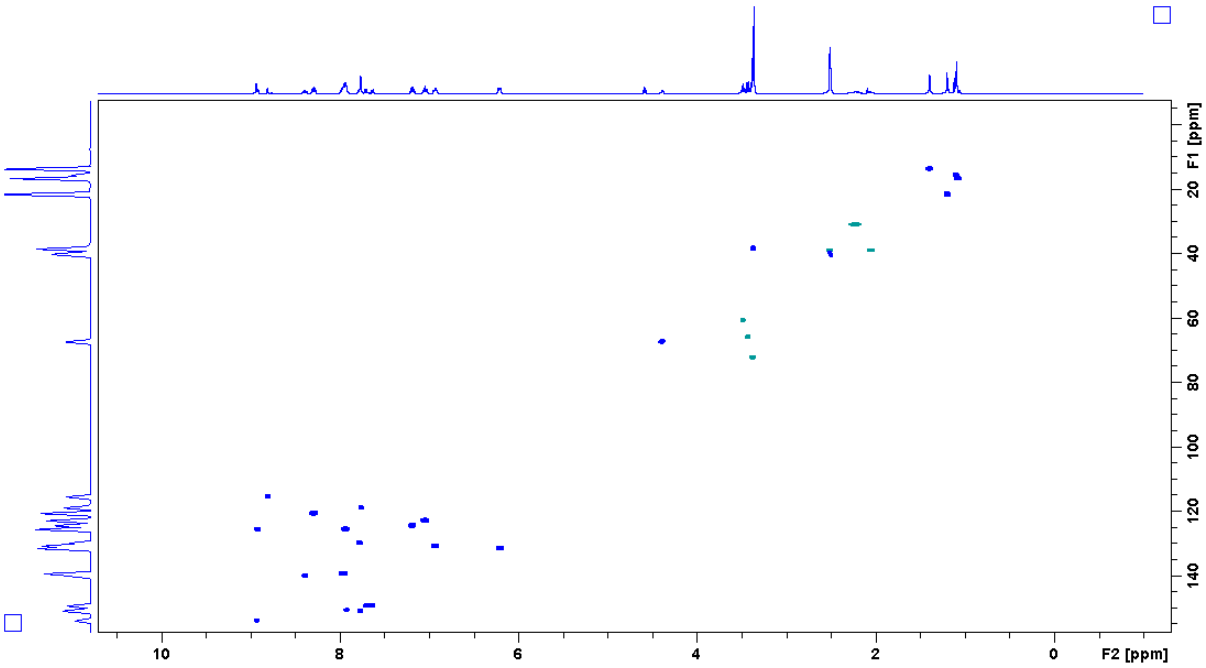
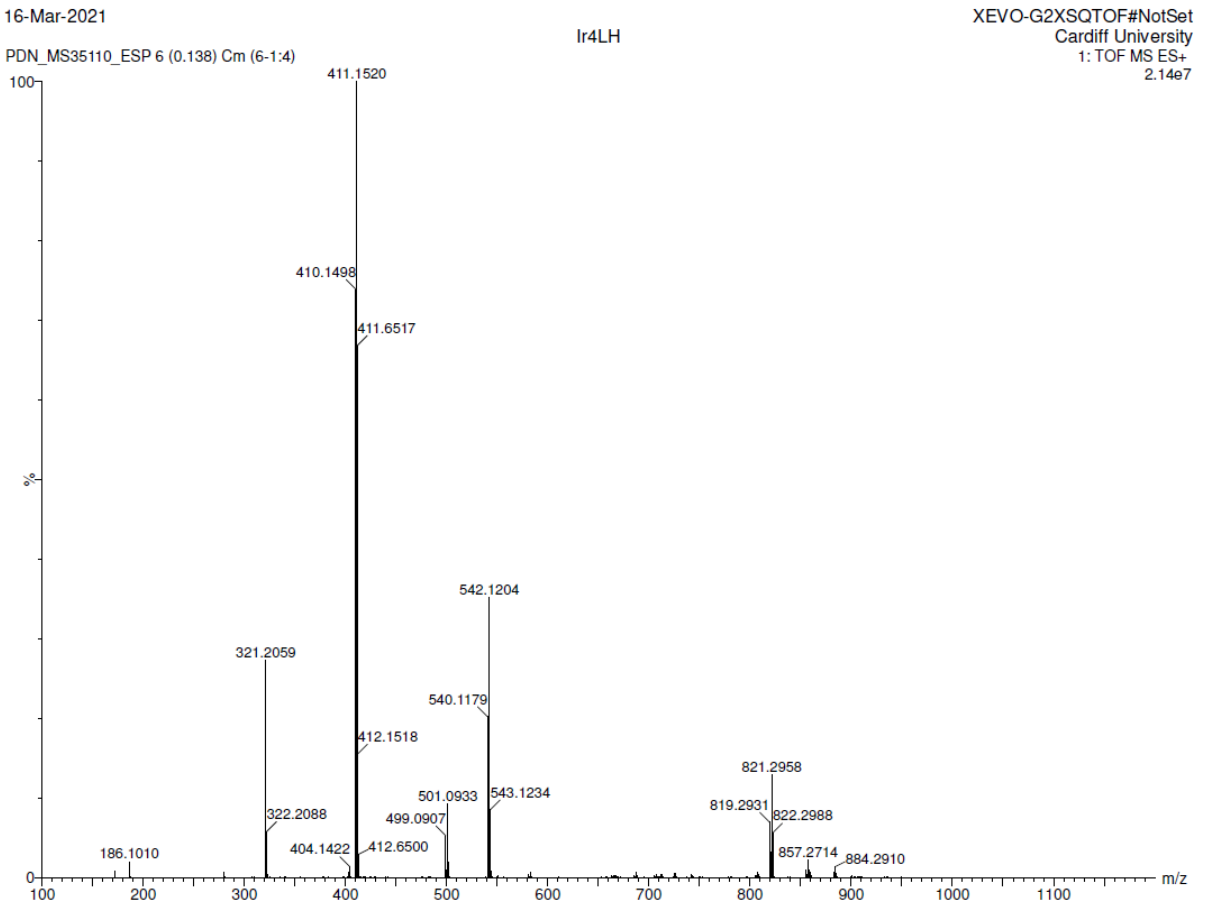
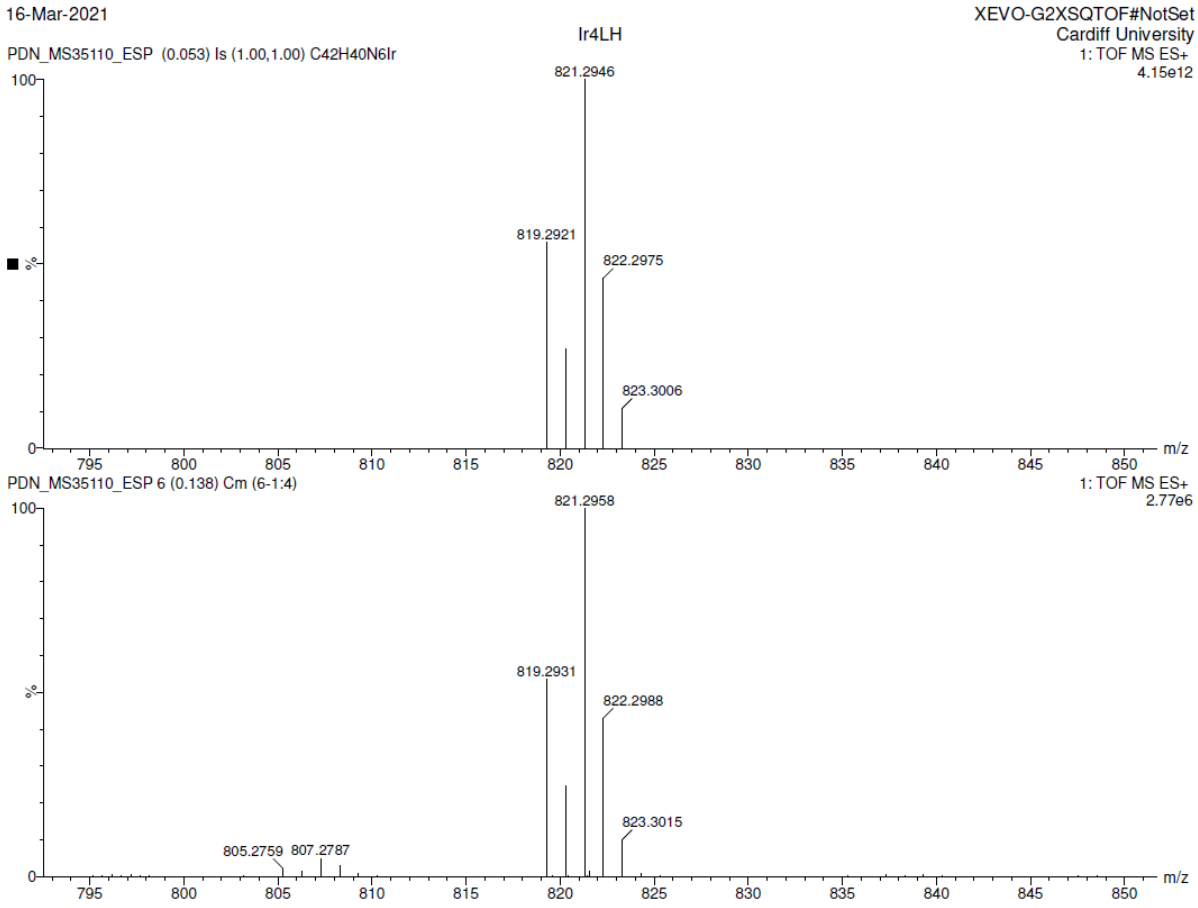



**Figure S56.** $^{1}H/^{13}C$ HSQC NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of Δ-[Ir(Phpy)$_2$(4-L$^{Me}$H)](BF$_4$)$_2$, Δ-**Ir-4$^{Me}$**.

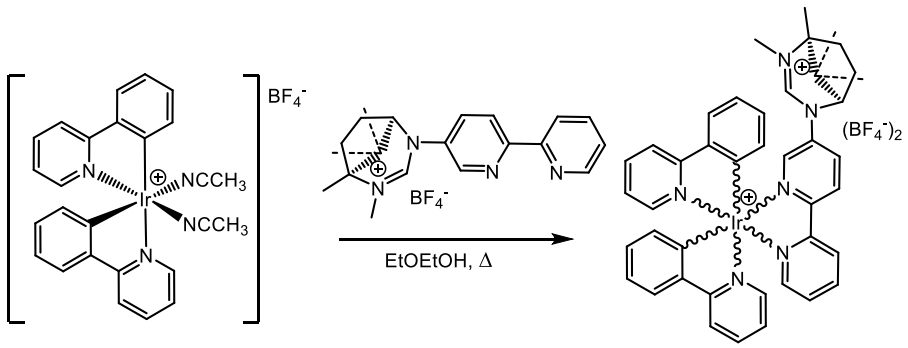





| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 5.0 | 5.0 | 100.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 819.2931 | 819.2920 | 1.1 | 1.3 | 27.0 | 384.4 | n/a | n/a | C42 H40 N6 191Ir |

**Figure S57.** HRMS spectrum and data for Δ-[Ir(Phpy)$_2$(4-L$^{Me}$H)](BF$_4$)$_2$, Δ-**Ir-4$^{Me}$**.

## 2.10. Δ,Λ-[Ir(Phpy)$_2$(5-L$^{Me}$H)](BF$_4$)$_2$, Δ,Λ-**Ir-5$^{Me}$**



A mixture of $[Ir(Phpy)_2(MeCN)_2](BF_4)$ (100 mg, 1.49 x $10^{-4}$ mmol) and $[5\text{-}L^{Me}H]BF_4$ (61 mg, 1 mol eq.) were heated in EtOEtOH (8 ml) at 100 °C under $N_2$ for 15 hrs. The cooled mixture was left to stand on the bench whereupon a small amount of an orange-red solid deposited. Yield = 21 mg (13%). A crop was obtained from the mother liquor on standing. Yield = 30 mg (19%). The majority of the solid was precipitated as an orange solid upon the addition of water to the remaining mother liquor. Yield = 102 mg (63%).

$^1H$ ($d_6$-dmso, 400 MHz): 9.02 (dd, 8.9, 3.5 Hz, 1H), 8.89 (dd, 8.1, 4.6 Hz, 1H), 8.56 (s, 1H), 8.41 (td, 9.1, 2.2 Hz 1H), 8.31 (m, 2H), 8.00-7.80 (m, 5H), 7.73 (m, 1H), 7.69 (t, 4.8 Hz, 1H), 7.63 (d, 4.7 Hz, 1H), 7.58 (t, 3.2 Hz, 1H), 7.20 (m, 2H), 7.07 (m, 2H), 6.96 (m, 2H), 6.31 (m, 1H), 6.20 (t, 7.1 Hz, 1H), 3.57 (d, 4.5 Hz, 1H), 3.35 (d, 5.3 Hz, 1H), 3.17 (s, 3H), 3.14 (s, 3H), 2.34 (m, 1H), 1.87 (m, 2H), 1.59 (m, 1H), 1.23 (s, 6H), 0.98 (s, 3H), 0.93 (s, 6H), 0.74 (s, 3H) ppm. $^{13}C\{^1H\}$ ($d_6$-dmso, 100 MHz): 167.2 (C), 167.1 (C), 154.9 (C), 154.8 (C), 154.4 (CH), 154.3 (C), 153.9 (C), 153.6 (C), 150.7 (C), 150.6 (C), 150.5 (CH), 150.4 (CH), 150.1 (CH), 149.6 (CH), 144.6 (C), 144.5 (C), 144.3 (CH), 142.6 (CH), 141.5 (CH), 141.0 (CH), 140.7 (CH), 140.3 (CH), 139.5 (CH), 139.3 (CH), 132.0 (CH), 131.6 (CH), 130.7 (CH), 129.3 (C), 129.2 (C), 125.9 (CH), 125.7 (CH), 125.6 (CH), 125.5 (CH), 124.7 (CH), 124.5 (CH), 123.0 (CH), 122.9 (CH), 120.7 (CH), 120.5 (CH), 72.3 (C), 72.0 (C), 68.9 (CH), 68.3 (CH), 41.8 (C), 41.4 (C), 38.9 ($CH_2$), 38.7 ($CH_2$), 38.0 ($CH_3$), 30.9 ($CH_2$), 30.5 ($CH_2$), 21.5 ($CH_3$), 21.4 ($CH_3$), 16.7 ($CH_3$), 16.5 ($CH_3$), 13.7 ($CH_3$), 13.6 ($CH_3$) ppm. HRMS (ES): m/z 819.2939 (calc. 819.2931) $[L]^+$, 100%.

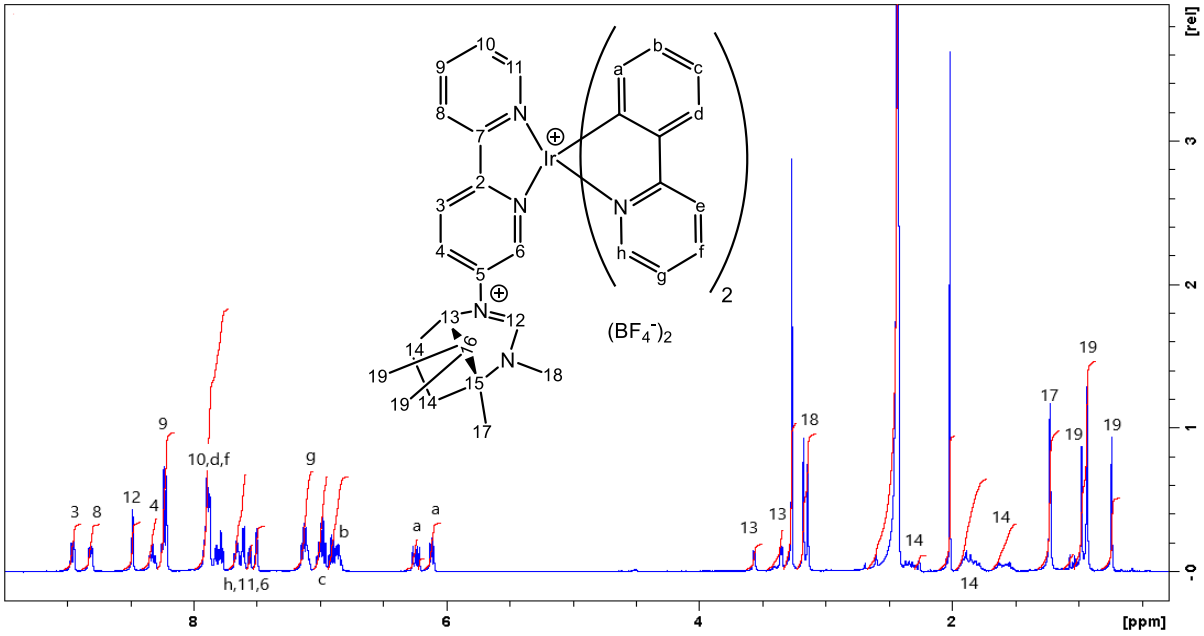



**Figure S58.** $^1H$ NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of Δ,Λ-$[Ir(Phpy)_2(5\text{-}L^{Me}H)](BF_4)_2$, Δ,Λ-**Ir-5$^{Me}$**.

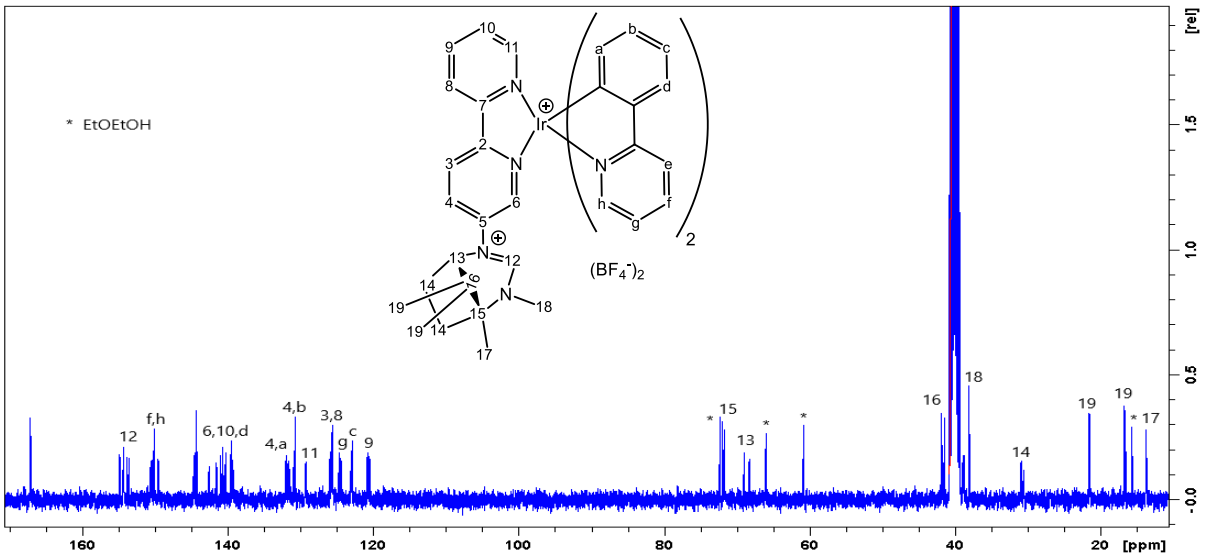



**Figure S59.** $^{13}C\{^{1}H\}$ NMR ($d_6$-dmso, 298 K, 100 MHz) spectrum of Δ,Λ-[Ir(Phpy)$_2$(5-L$^{Me}$H)](BF$_4$)$_2$, Δ,Λ-**Ir-5$^{Me}$**.

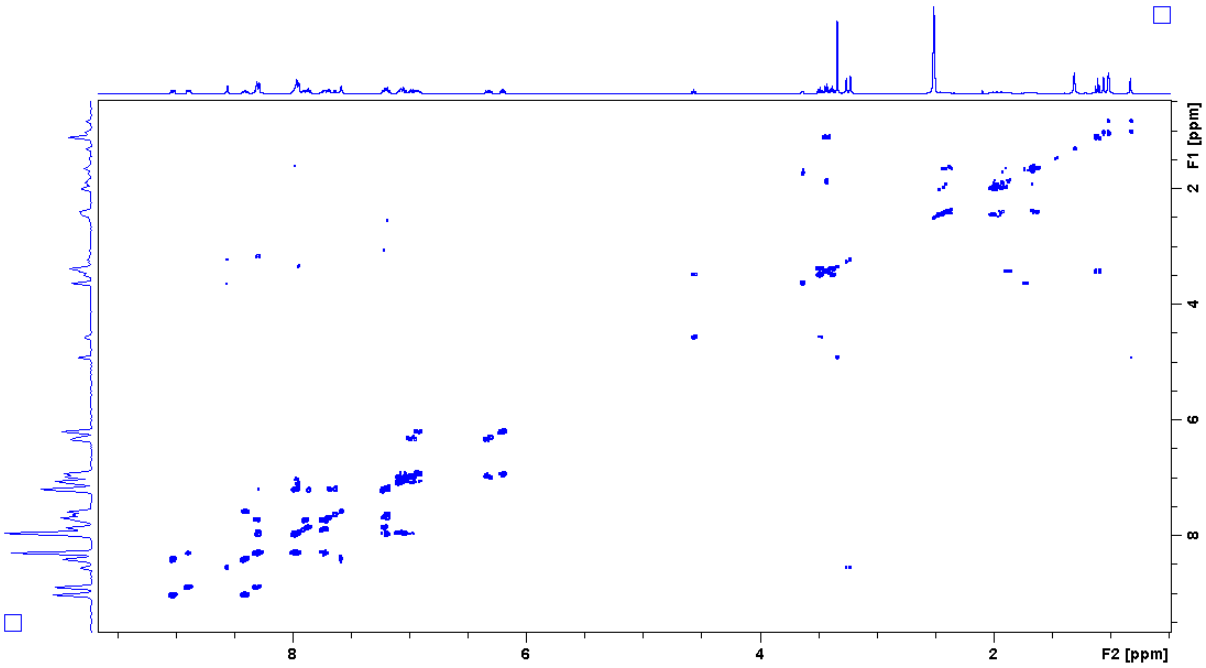



**Figure S60.** $^{1}H/^{1}H$ COSY NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of Δ,Λ-[Ir(Phpy)$_2$(5-L$^{Me}$H)](BF$_4$)$_2$, Δ,Λ-**Ir-5$^{Me}$**.

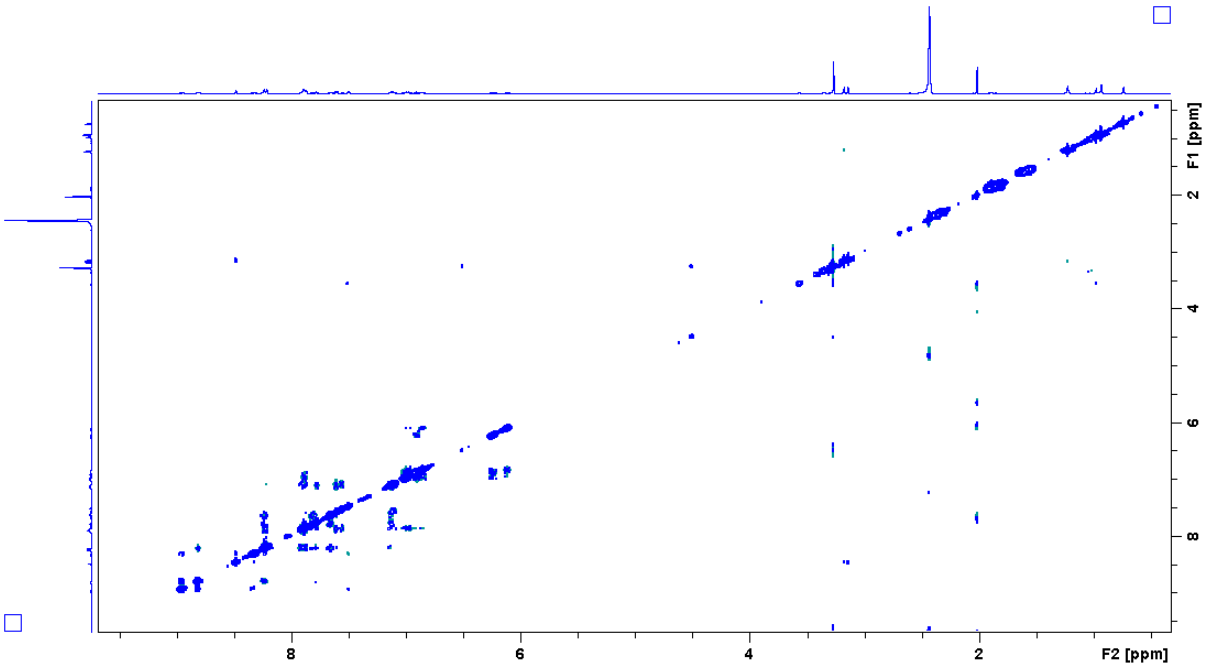



**Figure S61.** $^{1}H/^{1}H$ NOESY NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of Δ,Λ-[Ir(Phpy)$_2$(5-L$^{Me}$H)](BF$_4$)$_2$, Δ,Λ-**Ir-5$^{Me}$**.

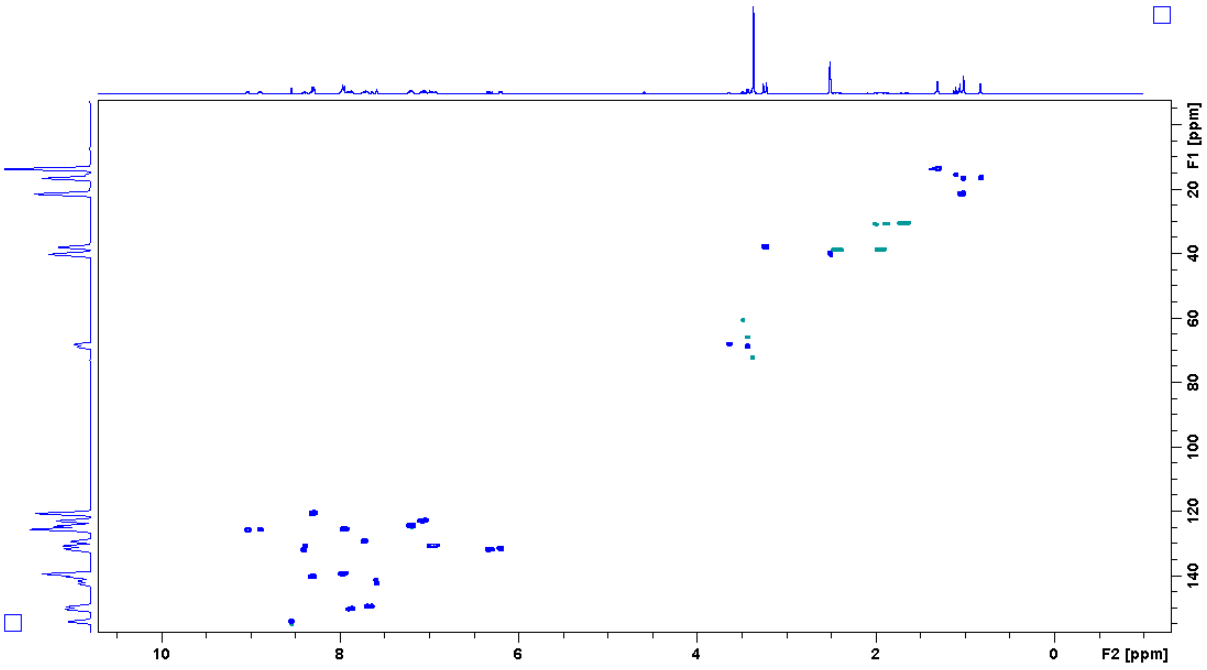
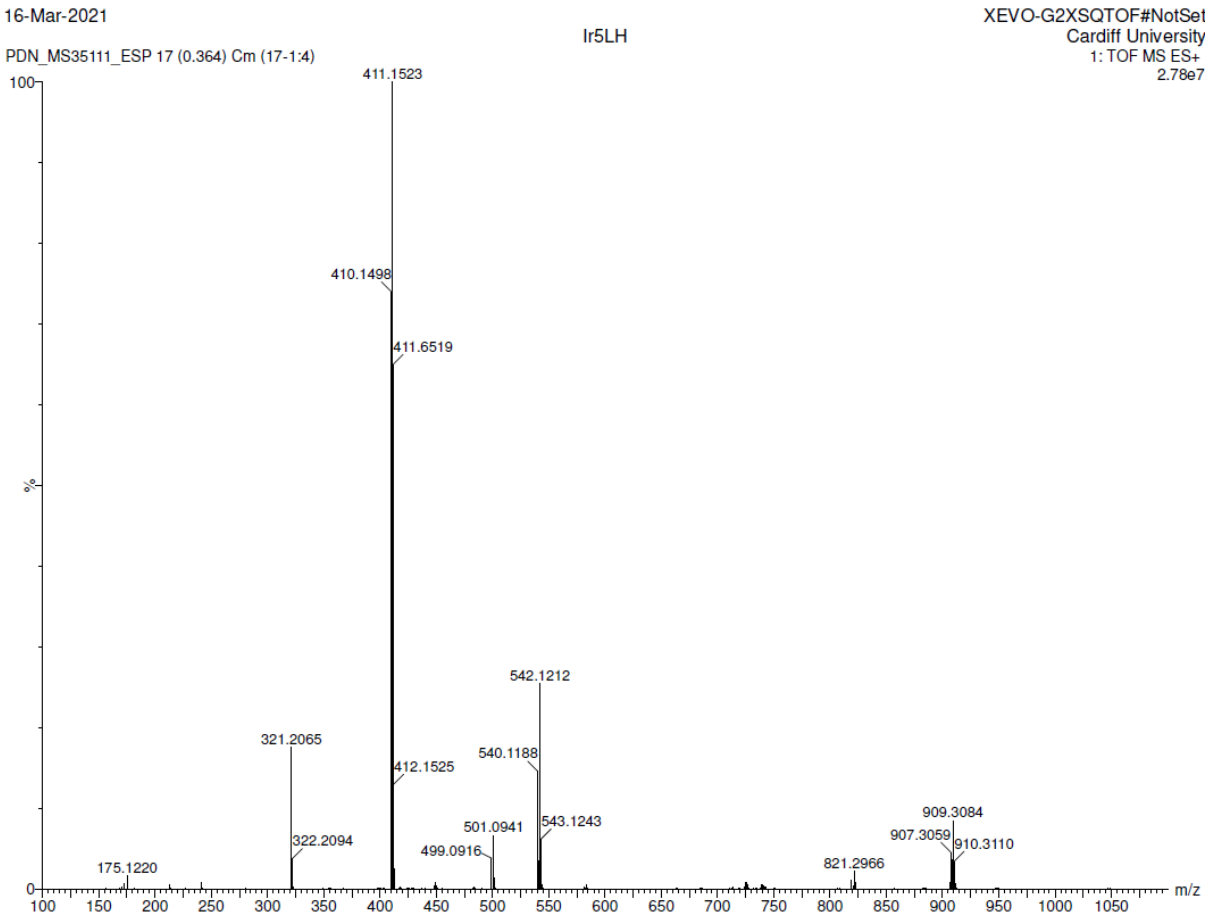
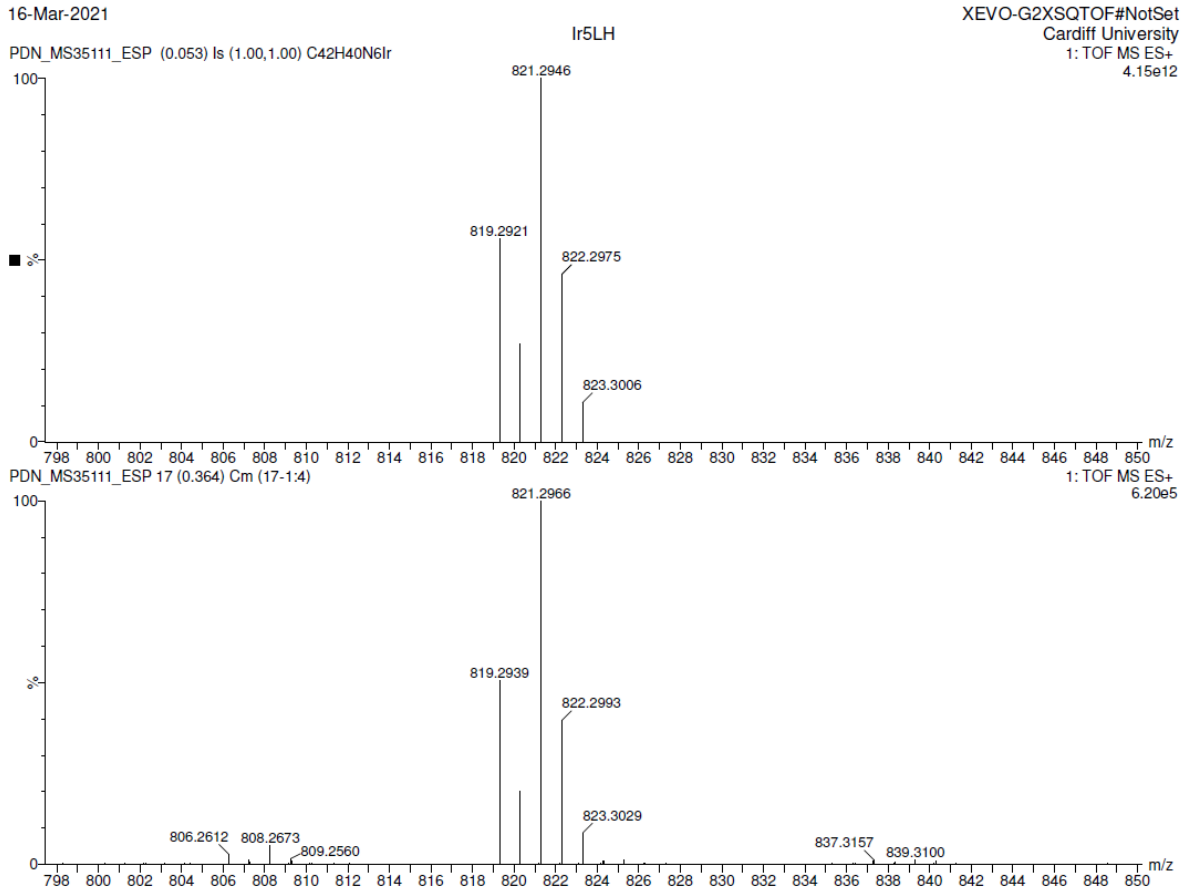



**Figure S62.** $^{1}H/^{13}C$ HSQC NMR ($d_6$-dmso, 298 K, 400 MHz) spectrum of Δ,Λ-[Ir(Phpy)$_2$(5-L$^{Me}$H)](BF$_4$)$_2$, Δ,Λ-**Ir-5$^{Me}$**.


16-Mar-2021
Ir5LH
XEVO-G2XSQTOF#NotSet
Cardiff University
1: TOF MS ES+
2.78e7
PDN_MS35111_ESP 17 (0.364) Cm (17-1:4)
100
%
0
411.1523
410.1498
411.6519
542.1212
321.2065
540.1188
412.1525
501.0941
543.1243
909.3084
907.3059
910.3110
322.2094
499.0916
175.1220
821.2966
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 5.0 | 5.0 | 100.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 819.2939 | 819.2920 | 1.9 | 2.3 | 27.0 | 190.0 | n/a | n/a | C42 H40 N6 191Ir |

**Figure S63.** HRMS spectrum and data for Δ,Λ-[Ir(Phpy)$_2$(5-L$^{Me}$H)](BF$_4$)$_2$, Δ,Λ-**Ir-5$^{Me}$**.

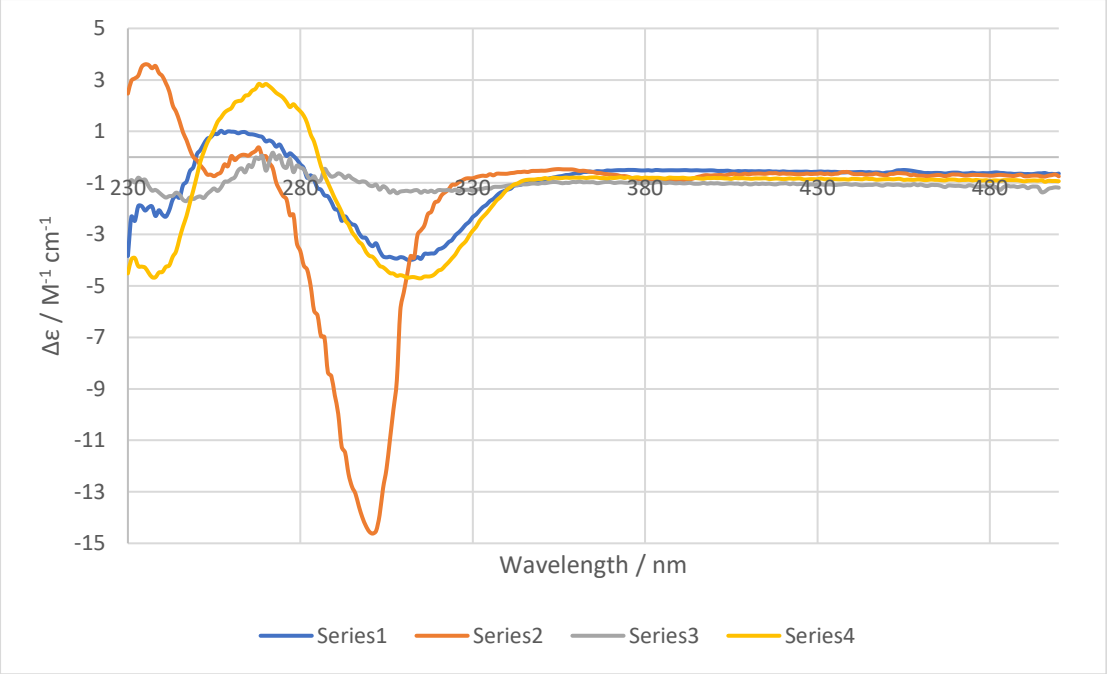



**Figure S64.** CD spectra of the ligands recorded in $CH_2Cl_2$. Series 1 (blue): [6-$L^{Me}$H]BF4; Series 2 (orange): [5-$L^{Me}$H]BF4; Series 3 (grey): [4-$L^{Me}$H]$BF_4$; Series 4 (yellow): [6-$L^{Mes}$H]$BF_4$.

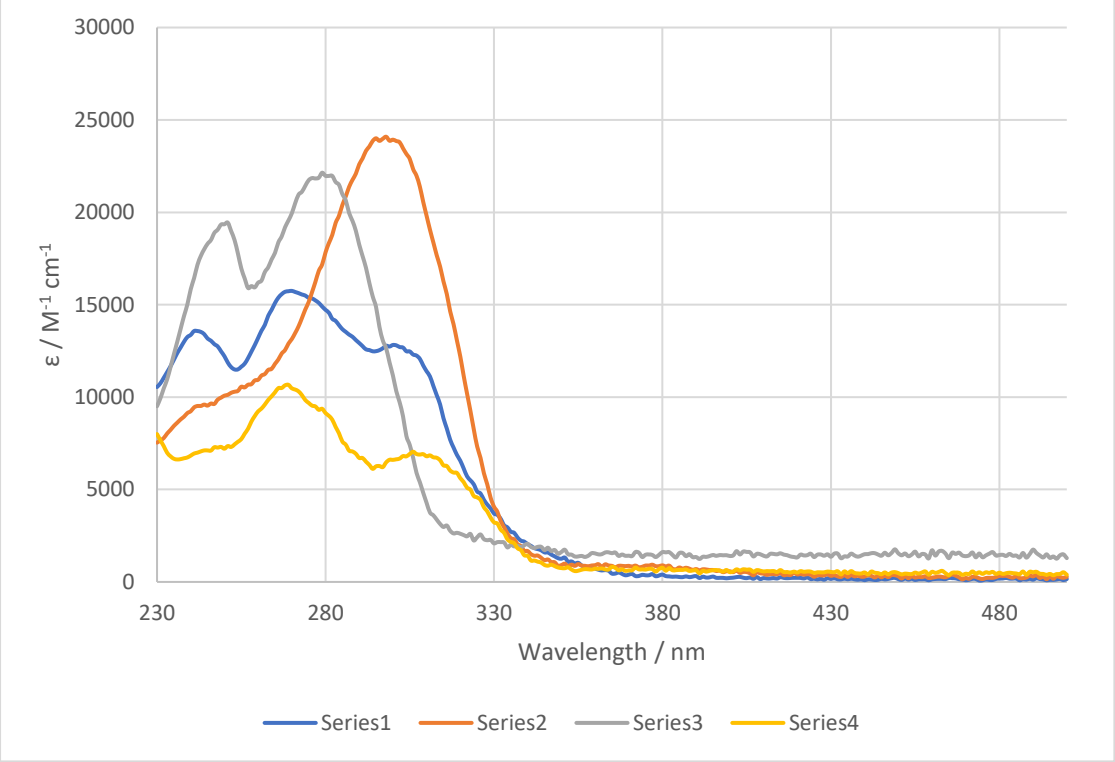



**Figure S65.** Electronic spectra of the ligands recorded in $CH_2Cl_2$. Series 1 (blue): [6-$L^{Me}$H]$BF_4$; Series 2 (orange): [5-$L^{Me}$H]$BF_4$; Series 3 (grey): [4-$L^{Me}$H]$BF_4$; Series 4 (yellow): [6-$L^{Mes}$H]$BF_4$.

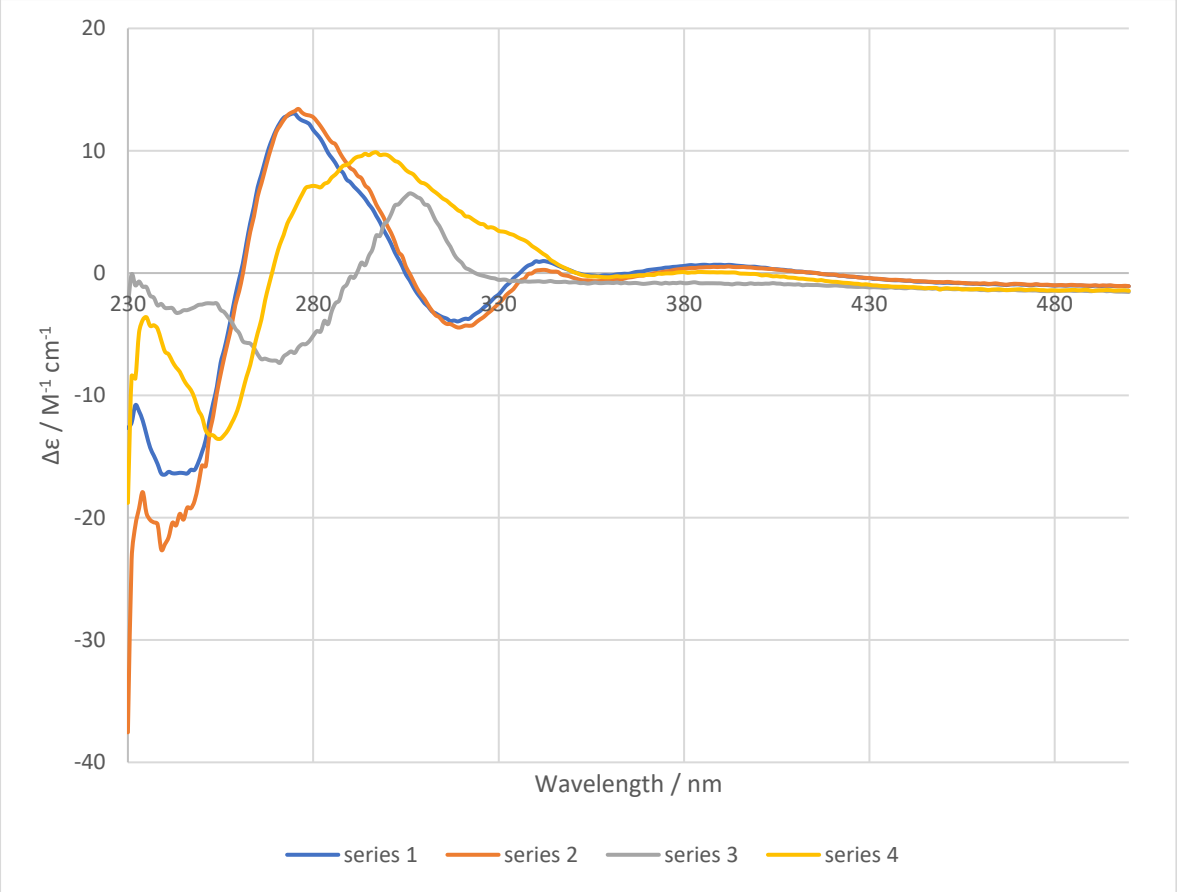



**Figure S66.** CD spectra of $[Re(CO)_3(6\text{-}L^{Me}H)Cl]BF_4$ (series 1, blue), $[Re(CO)_3(5\text{-}L^{Me}H)Cl]BF_4$ (series 2, orange), $[Re(CO)_3(4\text{-}L^{Me}H)Cl]BF_4$ (series 3, grey) and $[Re(CO)_3(6\text{-}L^{Mes}H)Cl]BF4$ (series 4, yellow) recorded in $CH_2Cl_2$.

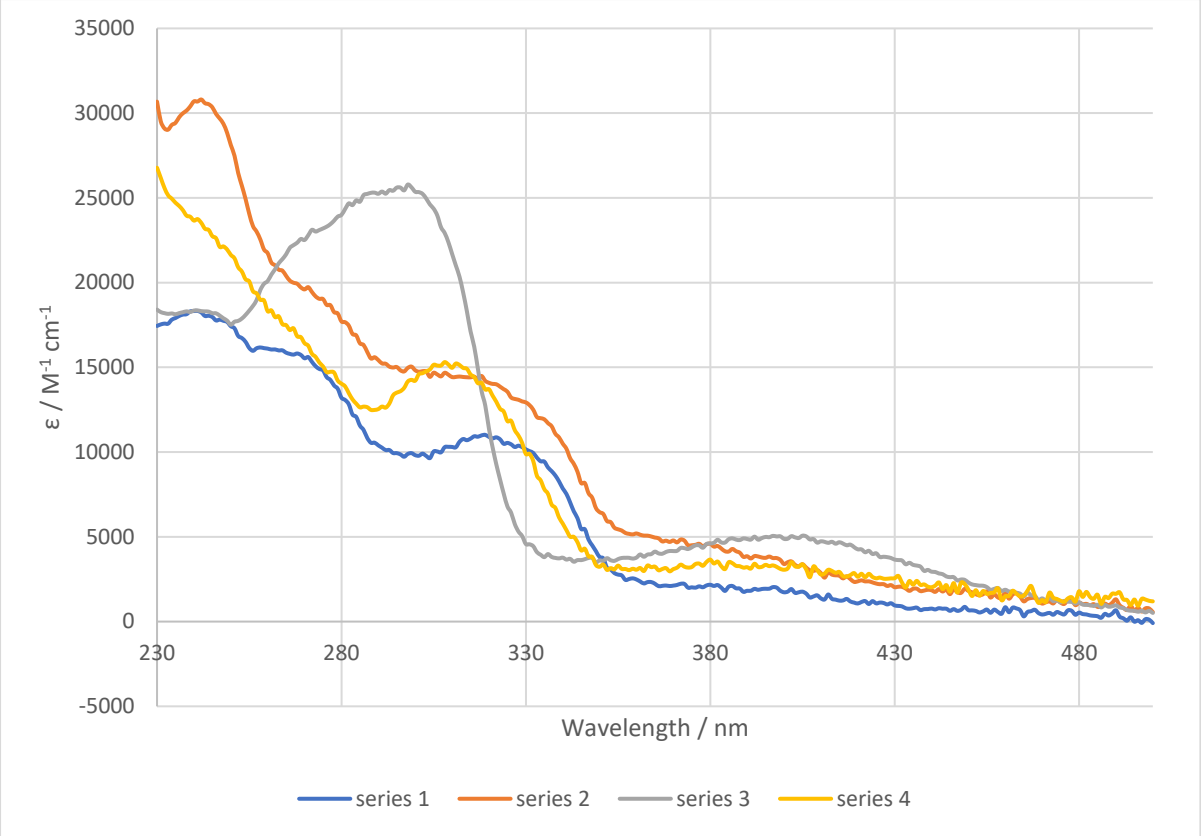



**Figure S67.** Electronic spectra of the rhenium complexes recorded in $CH_2Cl_2$. Series 1 (blue): $[Re(CO)_3(6\text{-}L^{Me}H)Cl]BF_4$; Series 2 (orange): $[Re(CO)_3(5\text{-}L^{Me}H)Cl]BF_4$; Series 3 (grey): $[Re(CO)_3(4\text{-}L^{Me}H)Cl]BF_4$; Series 4 (yellow): $[Re(CO)_3(6\text{-}L^{Mes}H)Cl]BF_4$.

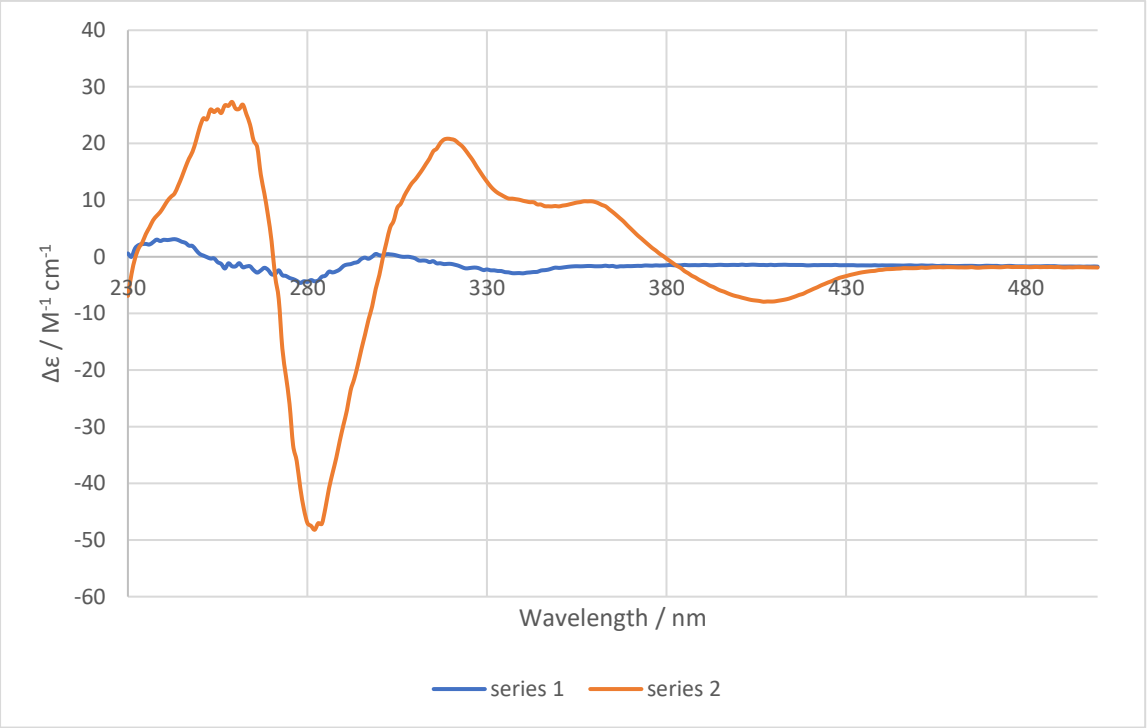


**Figure S68.** CD spectra of the iridium complexes recorded in $CH_2Cl_2$. Series 1 (blue): Δ,Λ-[Ir(Phpy)$_2$(5-$L^{Me}$H)](BF$_4$)$_2$; Series 2 (orange): Δ-[Ir(Phpy)$_2$(4-$L^{Me}$H)](BF$_4$)$_2$.

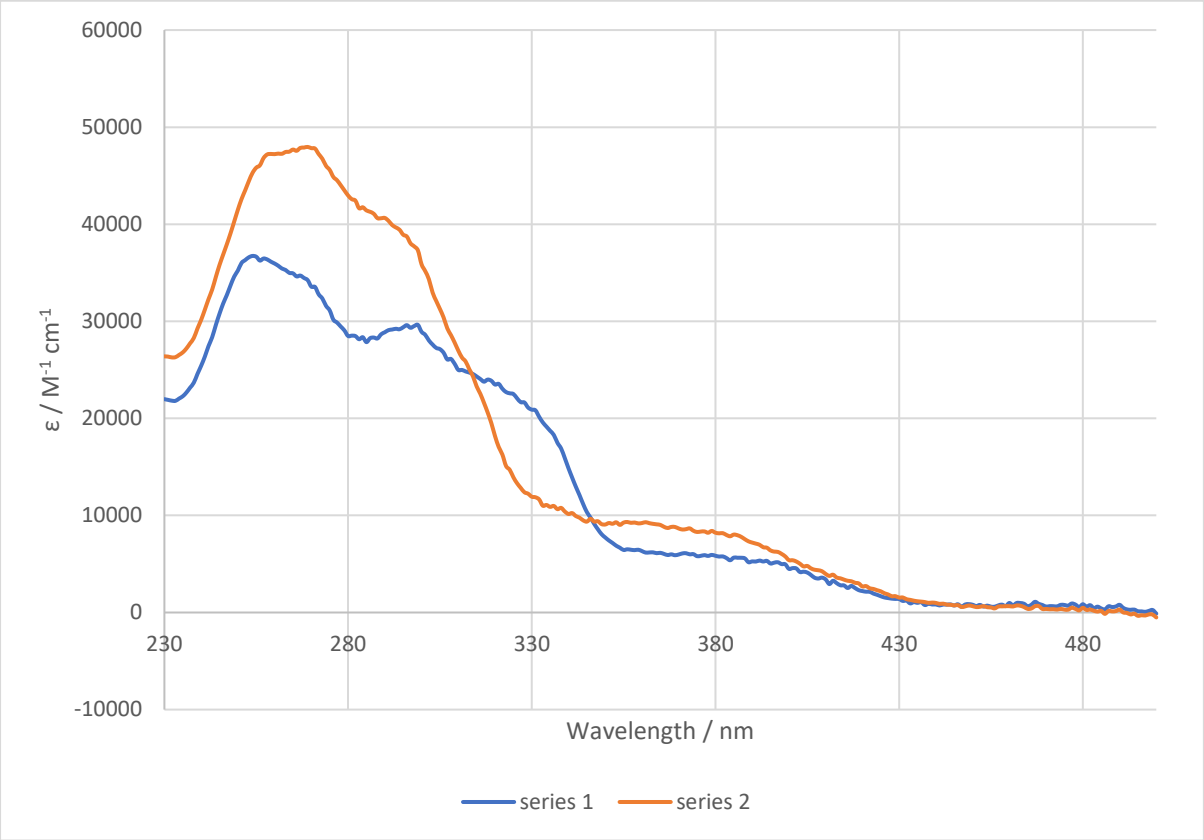



**Figure S69.** Electronic spectra of the iridium complexes recorded in $CH_2Cl_2$. Series 1 (blue): Δ,Λ-[Ir(Phpy)$_2$(5-$L^{Me}$H)](BF$_4$)$_2$; Series 2 (orange): Δ-[Ir(Phpy)$_2$(4-$L^{Me}$H)](BF$_4$)$_2$.

**Table S1.** Crystal data and structure refinement for *C*-$[Re(CO)_3(6\text{-}L^{Me}H)Cl_{0.9}I_{0.1}]I$, *C*-$[Re(CO)_3(6\text{-}L^{Me}H)Cl](Cl)_{0.64}.(BF_4)_{0.36}$ and Δ-$[Ir(Phpy)_2(4\text{-}L^{Me}H)](BF_4)_2$.

| Compound (Identification code) | *C*-$[Re(CO)_3(6\text{-}L^{Me}H)Cl_{0.9}I_{0.1}]I$ | *C*-$[Re(CO)_3(6\text{-}L^{Me}H)Cl](Cl)_{0.64}.(BF_4)_{0.36}$ | Δ-$[Ir(Phpy)_2(4\text{-}L^{Me}H)](BF_4)_2$ |
|---|---|---|---|
| CCDC reference | 2098556 | 2098557 | 2098558 |
| Empirical formula | $C_{23}H_{29}Cl_{0.9}N_4O_5I_{1.1}Re$ | $C_{38}H_{47}B_{0.36}F_{1.44}N_4O_5Cl_{1.64}Re$ | $C_{46}H_{53}B_2F_8N_6O_3Ir$ |
| Formula weight | 799.65 | 915.56 | 1103.76 |
| Temperature /K | 298(2) | 293(2) | 296(2) |
| Wavelength /Å | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | P $2_1$ | P $2_1$ | P $2_1$ |
| a/Å | 9.9804(3) | 9.5272(3) | 8.58820(10) |
| b/Å | 10.6322(3) | 11.1664(3) | 13.3127(2) |
| c/Å | 12.5079(4) | 19.1835(5) | 20.2920(3) |
| α/° | 90 | 90 | 90 |
| β/° | 92.751(3) | 97.194(3) | 90.6720(10) |
| γ/° | 90 | 90 | 90 |
| Volume/$Å^3$ | 1325.73(7) | 2024.76(10) | 2319.87(6) |
| Z | 4 | 4 | 2 |
| Density (calculated)/ $Mgm^{-3}$ | | 1.502 | 1.580 |
| Absorption coefficient/ $mm^{-1}$ | 6.000 | 3.161 | 6.258 |
| S1Crystal size/ $mm^3$ | 0.194x0.081x0.061 | 0.460x0.092x0.063 | 0.192 x 0.152 x 0.139 |
| Reflections collected | 13244 | 33296 | 23557 |
| Independent reflections | 6236 | 10036 | 9669 |
| R(int) | 0.0276 | 0.0407 | 0.0317 |
| Data / restraints / parameters | 6236 / 25 / 330 | 10036 / 356 / 544 | 9669 / 488 / 694 |
| Goodness-of-fit on $F^2$ | 1.044 | 1.095 | 1.043 |
| R1, wR2 [I>2σ(I)] | 0.0299, 0.0538 | 0.0410, 0.1036 | 0.0286, 0.0735 |
| R1, wR2 (all data) | 0.0354, 0.0565 | 0.0479, 0.1084 | 0.0300, 0.0748 |
| Absolute structure parameter | -0.028(4) | -0.006(5) | -0.031(4) |
| Largest diff. peak and hole e.$Å^{-3}$ | 1.024 and -1.115 | 1.749 and -0.818 | 1.556 and -0.756 |

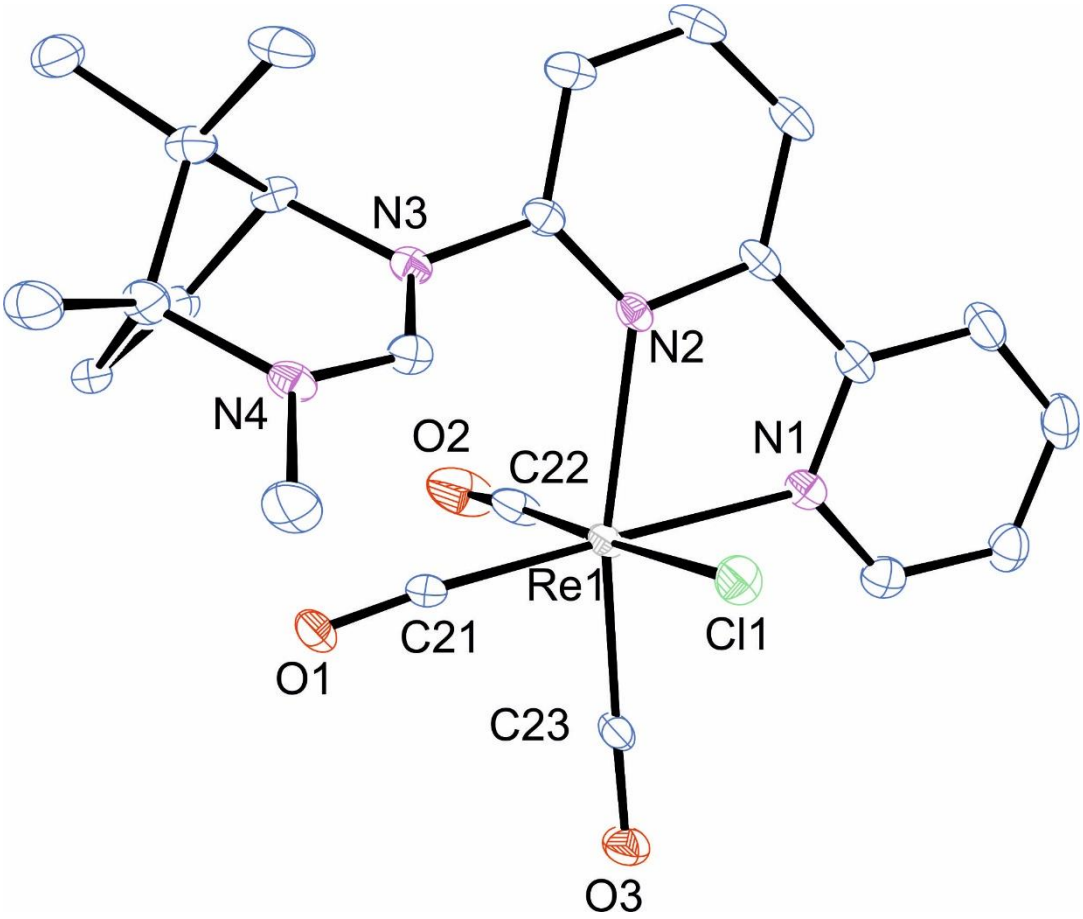



**Figure S70.** A 50% probability Ortep[3] representation of the molecular structure of *C*-[Re(CO)$_3$(6-L$^{Me}$H)Cl$_{0.9}$I$_{0.1}$]$^+$ with hydrogen atoms, solvent molecules and counterion omitted.

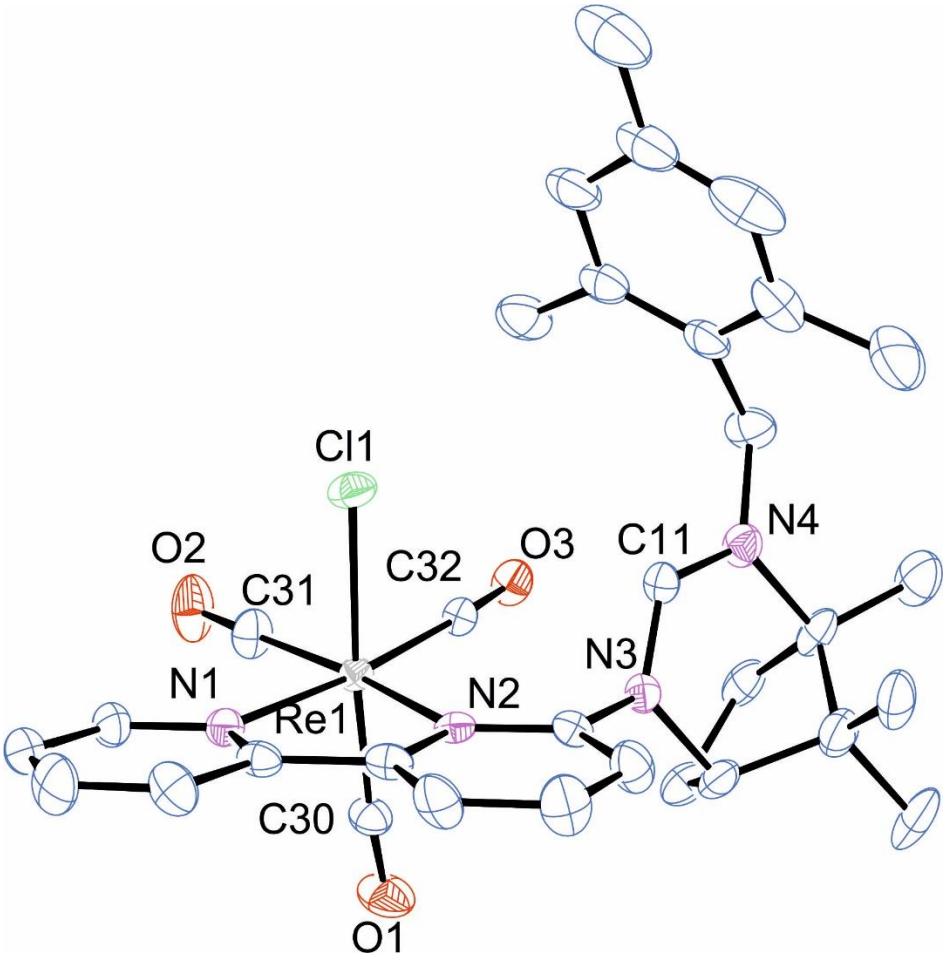



**Figure S71.** A 50% probability Ortep[3] representation of the molecular structure of *C*-[Re(CO)$_3$(6-L$^{Mes}$H)Cl]$^+$ with hydrogen atoms, solvent molecules and counterions omitted.

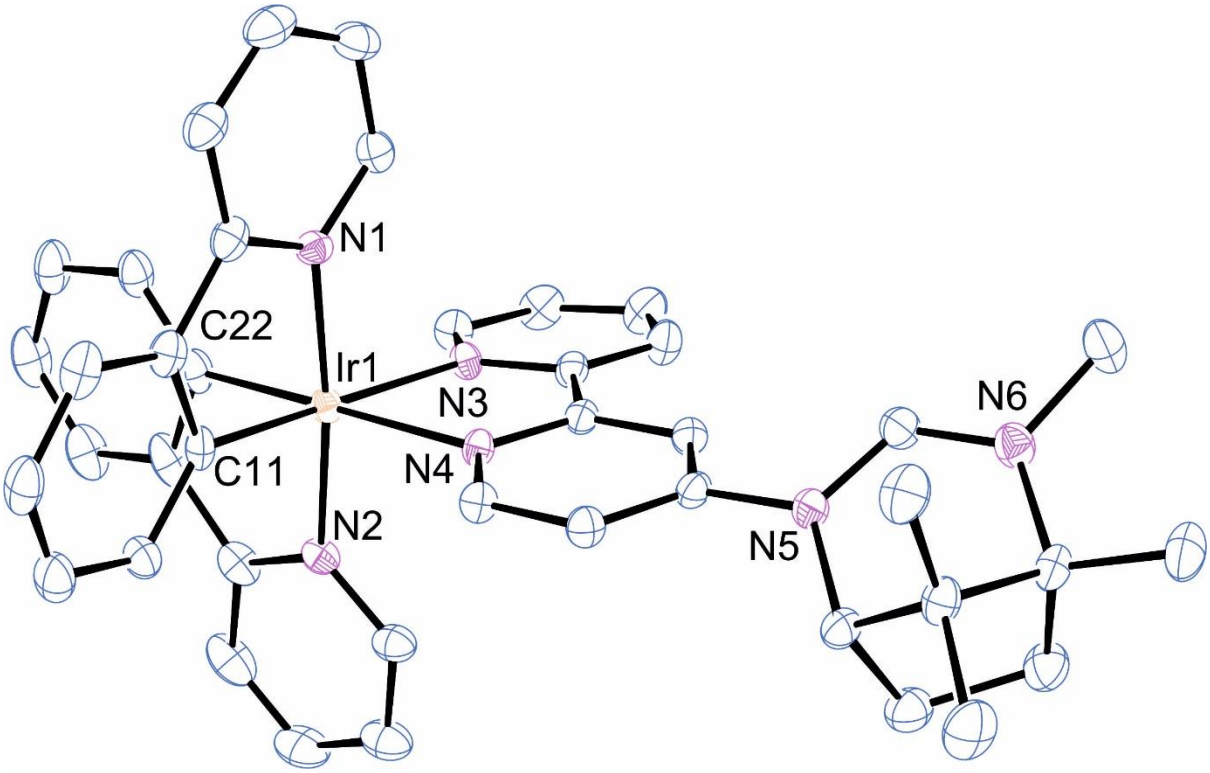



**Figure S72.** A 50% probability Ortep[3] representation of the molecular structure of Δ-[Ir(Phpy)$_2$(4-L$^{Me}$H)]$^{2+}$ with hydrogen atoms, solvent molecules and counterions omitted.

## References

1) Sheldrick, G. M. A short history of SHELX *Acta Crystallogr. A* 2008, **64**, 112-122.

2) M. Uzarewicz-Baig, M. Koppenwallner, S. Tabassum and R. Wilhelm, *Appl. Organometal. Chem.*, 2014, **28**, 552-558.

3) L. J. Farrugia, *J. Appl. Cryst.* 2012, **45**, 849-854.