Contents

Experimental

1 General experimental methods

All manipulations were performed under an atmosphere of argon, using Schlenk and glove box techniques. Glassware was oven dried at 150ºC overnight and flamed under vacuum prior to use. Anhydrous CH_2Cl_2 and heptane (<0.005% H_2O) were purchased from ACROS or Aldrich and freeze-pump-thaw degassed three times before being placed under argon. CD_2Cl_2, d_3-MeCN and fluoroarenes (C_6H_5F, 1,2-$C_6H_4F_2$, 1,3,5-$C_6H_3F_3$, $C_6F_5CF_3$) were dried over CaH_2, vacuum distilled and the latter stored over thoroughly vacuum-dried 3 Å molecular sieves. C_6H_6, C_6D_6 and *cis*-cyclooctene (COE) were dried over Na and vacuum distilled. IBioxMe$_4$,[1] $[Ir(COE)_2Cl]_2$,[2] and Na[BAr$^F_4$][3] were synthesised using literature protocols. All other solvents and reagents are commercial products and were used as received. NMR spectra were recorded on Bruker DPX-400, AV-400, AV-500, AVIIIHD-500 and AVII-700 spectrometers at 298 K unless otherwise stated. ^{1}H NMR spectra recorded in 1,2-$C_6H_4F_2$ and C_6H_5F were referenced using the highest intensity peak of the highest (δ 6.87) and lowest (δ 6.86) frequency fluoroarene multiplets, respectively. ^{19}F NMR spectra recorded in 1,2-$C_6H_4F_2$ and C_6H_5F were referenced using the solvent peak at δ -138.75 (1,2-$C_6H_4F_2$) and δ -113.15 (C_6H_5F). An internal sealed capillary of C_6D_6 was used to lock and shim samples for acquisition of NMR data, and additionally reference ^{13}C{^{1}H} NMR spectra, at 298 K. An internal sealed capillary of d_6-acetone was used to lock and shim samples for acquisition of NMR data at 250 K. Chemical shirts are quoted in ppm and coupling constants in Hz. Microanalyses were performed by Stephan Boyer at London Metropolitan University.

2 Synthesis of new compounds

2.1 [Ir(IBioxMe$_4$)$_3$(2,3-$C_6H_3F_2$)(H)][BAr$^F_4$] (2)

Method 1: To a mixture of $[Ir(COE)_2Cl]_2$ (0.033 g, 0.037 mmol), IBioxMe$_4$ (0.050 g, 0.240 mmol) and Na[BArF$_4$] (0.069 g, 0.078 mmol) was added 1,2-$C_6H_4F_2$ (2.0 mL). The resulting suspension was shaken for 15 minutes at room temperature, diluted with heptane (2.0 mL) and filtered. The filtrate was layered with heptane to afford the product as bright orange crystals on diffusion at room temperature. Yield = 0.104 g (76%, orange-red crystals).

Method 2: To a mixture of **3** (0.150 g, 0.199 mmol), Na[BAr$^F_4$] (0.185 g, 0.209 mmol) and IBioxMe$_4$ (0.044 g, 0.209 mmol) was added 1,2-$C_6H_4F_2$ (10 mL). The orange-red solution was stirred at room temperature for one hour and then filtered. Layering the filtrate with heptane gave a solid upon diffusion, which was recrystallised from 1,2-$C_6H_4F_2$ – heptane to afford the orange-red crystalline product. Yield = 0.281 g (74%, orange-red crystals).

^{1}H NMR (1,2-$C_6H_4F_2$/C_6D_6, 700 MHz): δ 8.11 – 8.15 (m, 8H, Ar^F), 7.49 (br, 4H, Ar^F), 3.96 – 4.37 (m, 12H, OCH_2), 0.13 – 1.89 (δ 1.89, 1.87, 1.85, 1.82 (d, $^{1h}J_{FH}$ = 2.5), 1.78, 1.77, 1.70, 1.64, 1.61, 1.56 (d, $^{1h}J_{FH}$ = 1.5),

1.52, 1.49, 1.01, 0.98, 0.94, 0.85, 0.82, 0.77, 0.73, 0.28, 0.27, 0.18, 0.15; 36H, CH_3), -47.09 (d, $^{1h}J_{FH}$ = 3.7, 0.47H, *syn*-IrH), -48.67 (s, 0.53H, *anti*-IrH). The aryl fluoride resonances are obscured by the solvent.

^{19}F{^{1}H} NMR (1,2-$C_6H_4F_2$/C_6D_6, 377 MHz): δ -62.3 (s, 24F, Ar^F), -111.7 (dd, $^3J_{FF}$ = 27, $^{1h}J_{FH}$ = 4, 0.47F, *syn*-2,3-$C_6H_3F_2$), -115.2 (d, $^3J_{FF}$ = 28, 0.53F, *anti*-2,3-$C_6H_3F_2$), -139.5 (d, $^3J_{FF}$ = 28, 0.53F, *anti*-2,3-$C_6H_3F_2$). The *syn*-2,3-$C_6H_3F_2$ resonances is obscured by the solvent.

^{19}F{^{1}H} NMR (CD_2Cl_2, 377 MHz): δ -62.2 (s, Ar^F), -111.6 (dd, $^3J_{FF}$ = 27, $^{1h}J_{FH}$ = 4, 0.47F, *syn*-2,3-$C_6H_3F_2$), -114.9 (d, $^3J_{FF}$ = 28, 0.53F, *anti*-2,3-$C_6H_3F_2$), -139.4 (d, $^3J_{FF}$ = 27, 0.47F, *syn*-2,3-$C_6H_3F_2$), -139.9 (d, $^3J_{FF}$ = 28, 0.53F, *anti*-2,3-$C_6H_3F_2$).

^{13}C{^{1}H} NMR (1,2-$C_6H_4F_2$/C_6D_6, 176 MHz): δ 162.6 (q, $^1J_{BC}$ = 50, Ar^F), 158.4 (dd, $^1J_{FC}$ = 226, $^2J_{FC}$ = 9, $C_6H_3F_2$), 157.6 (dd, $^1J_{FC}$ = 230, $^2J_{FC}$ = 9, $C_6H_3F_2$), 153.1 (s, NCN), 152.9 (s, NCN), 152.5 (s, NCN), 152.4 (s, NCN), 135.1 (s, Ar^F), 129.7 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 128.0 (s, $\underline{C}OCH_2$), 127.9 (s, $\underline{C}OCH_2$), 127.8 (s, $\underline{C}OCH_2$), 127.3 (s, $\underline{C}OCH_2$), 127.2 (s, $\underline{C}OCH_2$), 127.2 (s, $\underline{C}OCH_2$), 126.5 (s, $\underline{C}OCH_2$), 126.5 (s, $\underline{C}OCH_2$), 126.3 (s, $\underline{C}OCH_2$), 126.1 (s, $\underline{C}OCH_2$), 124.9 (q, $^1J_{FC}$ = 272, Ar^F), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 88.1 (s, OCH_2), 87.8 (s, OCH_2), 87.8 (s, OCH_2), 87.7 (s, OCH_2), 87.3 (s, OCH_2), 87.1 (s, OCH_2), 86.8 (s, OCH_2), 86.8 (s, OCH_2), 86.3 (s, OCH_2), 67.7 (s, $\underline{C}(CH_3)_2$), 67.0 (s, $\underline{C}(CH_3)_2$), 67.0 (s, $\underline{C}(CH_3)_2$), 66.5 (s, $\underline{C}(CH_3)_2$), 65.1 (s, $\underline{C}(CH_3)_2$), 65.0 (s, $\underline{C}(CH_3)_2$), 64.9 (s, $\underline{C}(CH_3)_2$), 64.7 (s, $\underline{C}(CH_3)_2$), 63.7 (s, $\underline{C}(CH_3)_2$), 63.2 (s, $\underline{C}(CH_3)_2$), 62.2 (s, $\underline{C}(CH_3)_2$), 61.9 (s, $\underline{C}(CH_3)_2$), 30.3 (s, CH_3), 28.0 (d, $^{2h}J_{FC}$ = 11, CH_3), 27.4 (s, CH_3), 26.6 (s, CH_3), 24.8 (s, CH_3), 24.7 (s, CH_3), 24.5 (s, CH_3), 24.5 (s, CH_3), 24.1 (s, CH_3), 24.1 (s, CH_3), 24.0 (s, CH_3), 24.0 (s, CH_3), 23.9 (s, CH_3), 23.7 (s, CH_3), 23.7 (s, CH_3), 23.7 (s, CH_3), 23.6 (s, CH_3), 23.5 (s, CH_3), 23.4 (s, CH_3), 23.3 (s, CH_3), 21.8 (s, CH_3), 21.4 (d, $^{2h}J_{FC}$ = 2, CH_3), 18.8 (s, CH_3), 18.6 (s, CH_3). The aryl fluoride resonances are partially obscured by the solvent signals.

Anal. Calcd for $C_{71}H_{64}BF_{26}IrN_6O_6.(C_6H_4F_2)$ ([1794.32] 1908.41 $gmol^{-1}$): C, 48.46; H, 3.59; N, 4.40. Found: C, 48.55; H, 3.50; N, 4.48.

2.2 *trans*-[Ir(IBioxMe$_4$)$_2$(COE)Cl] (3)

To a suspension of $[Ir(COE)_2Cl]_2$ (0.210 g, 0.23 mmol) in 1,2-$C_6H_4F_2$ (12 mL) was added a solution of $IBioxMe_4$ (0.200 g, 0.96 mmol) in 1,2-$C_6H_4F_2$ (3 mL). The solution was stirred at room temperature for 3 hours, during which time a yellow precipitate formed. The suspension was then reduced to 3 mL and heptane (3 mL) added to aid precipitation. The product was isolated by filtration and washed with heptane (2 × 1 mL). Crystals suitable for X-ray analysis were grown from benzene – heptane. Yield = 0.330 g (94%, yellow microcrystalline solid).

^{1}H NMR (C_6D_6, 400 MHz): δ 3.91 (d, $^2J_{HH}$ = 7.9, 4H, OCH_2), 3.80 (d, $^2J_{HH}$ = 7.9, 4H, OCH_2), 2.51 – 2.59 (m, 2H, CH{COE}), 2.37 – 2.44 (m, 2H, $CHC\underline{H}_2${COE}), 2.03 (s, 12H, CH_3), 1.81 (s, 12H, CH_3), 1.54 – 1.67 (m, 4H, CH_2{COE}), 1.36 – 1.50 (m, 2H, $CHC\underline{H}_2${COE}), 1.00 – 1.09 (m, 4H, CH_2{COE}).

^{1}H NMR (1,2-$C_6H_4F_2$/C_6D_6, 400 MHz): δ 4.17 (d, $^2J_{HH}$ = 8.1, 4H, OCH_2), 4.14 (d, $^2J_{HH}$ = 8.1, 4H, OCH_2), 2.37 – 2.46 (m, 2H, CH{COE}), 2.23 – 2.31 (m, 2H, $CHC\underline{H}_2${COE}), 2.03 (s, 12H, CH_3), 1.96 (s, 12H, CH_3), 1.46 – 1.59

(m, 4H, CH_2{COE}), 1.30 – 1.42 (m, 2H, CHC$\underline{H}_2${COE}), 1.11 – 1.25 (m, 4H, CH_2{COE}).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.40 (d, $^2J_{HH}$ = 7.8, 4H, OCH_2), 4.36 (d, $^2J_{HH}$ = 7.8, 4H, OCH_2), 2.24 – 2.33 (m, 2H, CH{COE}), 2.11 – 2.19 (m, 2H, CHC$\underline{H}_2${COE}), 2.00 (s, 12H, CH_3), 1.98 (s, 12H, CH_3), 1.43 – 1.56 (m, 4H, CH_2{COE}), 1.14 – 1.36 (m, 4H, CH_2{COE}), 0.98 – 1.11 (m, 2H, CHC$\underline{H}_2${COE}).

^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 160.2 (s, NCN), 125.3 (s, $\underline{C}OCH_2$), 88.5 (s, OCH_2), 63.2 (s, $\underline{C}(CH_3)_2$), 38.4 (s, CH{COE}), 33.5 (s, CH$\underline{C}H_2${COE}), 31.2 (s, CH_2{COE}), 27.2 (s, CH_2{COE}), 26.8 (s, CH_3), 25.3 (s, CH_3).

Anal. Calcd for $C_{30}H_{46}IrN_4O_4.0.33(C_6H_6)$ ([754.39] 780.43 gmol^{-1}): C, 49.25; H, 6.20; N, 7.18. Found: C, 49.03; H, 6.49; N, 7.38. Benzene solvate was confirmed by dissolving in CD_2Cl_2.

2.3 *trans*-[Ir(IBioxMe$_4$)$_2$(2,2'-bipyridine)(C$_6$H$_3$F$_2$)(H)][BAr$^F{}_4$] (5)

To a mixture of **3** (0.050 g, 0.066 mmol), Na[BAr$^F{}_4$] (0.062 g, 0.070 mmol) and 2,2'-bipyridine (0.011 g, 0.073 mmol) was added 1,2-$C_6H_4F_2$ (4 mL). The bright orange-red solution was stirred at room temperature for one hour and then filtered. Layering the filtrate with heptane gave the crude product upon diffusion. Recrystallisation from CH_2Cl_2 – heptane afforded the analytically pure product. Yield = 0.095 g (82%, red crystals).

^{1}H NMR (1,2-$C_6H_4F_2$/C_6D_6, 400 MHz, selected data only): δ 8.10 – 8.16 (m, 8H, Ar^F), 7.50 (br, 4H, Ar^F), -19.28 (s, 0.45H, Ir$\underline{H}$(3,4-$C_6H_3F_2$)), -19.94 (br, 0.55H, Ir$\underline{H}$(2,3-$C_6H_3F_2$)).

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.60 (d, $^3J_{HH}$ = 5.4, 0.55H, C^{a}H{bipy, 2,3-$C_6H_4F_2$}), 9.50 (d, $^3J_{HH}$ = 5.4, 0.45H, C^{a}H{bipy, 3,4-$C_6H_4F_2$}), 8.74 (d, $^3J_{HH}$ = 5.5, 0.55H, C^{b}H{bipy, 2,3-$C_6H_4F_2$}), 8.71 (d, $^3J_{HH}$ = 5.5, 0.45H, C^{b}H{bipy, 3,4-$C_6H_4F_2$}), 8.23 (d, $^3J_{HH}$ = 5.1, 0.55H, C^{c}H{bipy, 2,3-$C_6H_4F_2$}), 8.21 (d, $^3J_{HH}$ = 5.1, 0.45H, C^{c}H{bipy, 3,4-$C_6H_4F_2$}), 8.11 (d, $^3J_{HH}$ = 8.1, 1H, C^{d}H{bipy}), 8.01 (app br t, J = 8, 1H, C^{e}H{bipy}), 7.90 (app td, J = 8, J = 2, 1H, C^{f}H{bipy}), 7.89 (app td, J = 8, J = 2, 1H, C^{f}H{bipy}), 7.71 – 7.76 (m, 8H, Ar^F), 7.62 – 7.68 (m, 1H, C^{g}H{bipy}), 7.56 (br, 4H, Ar^F), 7.32 – 7.37 (m, 1H, C^{h}H{bipy}), 6.40 – 6.69 (m, 3H, $C_6H_3F_2$), 4.18 – 4.28 (m, ~4H, OCH_2), 3.93 – 4.08 (m, ~4H, OCH_2), 1.57 (s, 1.35H, CH_3{3,4-$C_6H_4F_2$}), 1.56 (s, 1.35H, CH_3{3,4-$C_6H_4F_2$}), 1.48 (s, 1.35H, CH_3{3,4-$C_6H_4F_2$}), 1.45 (s, 1.35H, CH_3{3,4-$C_6H_4F_2$}), 1.5 (vbr, 6.60H, CH_3{2,3-$C_6H_4F_2$}), 0.95 (s, 1.35H, CH_3{3,4-$C_6H_4F_2$}), 0.93 (s, 1.35H, CH_3{3,4-$C_6H_4F_2$}), 0.9 (vbr, 3.30H, CH_3{2,3-$C_6H_4F_2$}), -0.19 (s, 1.35H, CH_3{3,4-$C_6H_4F_2$}), -0.21 (s, 1.35H, CH_3{3,4-$C_6H_4F_2$}), -0.2 (vbr, 3.30H, CH_3{2,3-$C_6H_4F_2$}), -19.33 (s, 0.45H, Ir$\underline{H}$(3,4-$C_6H_3F_2$)), -19.99 (br, 0.55H, Ir$\underline{H}$(2,3-$C_6H_3F_2$)).

^{1}H NMR (CD_2Cl_2, 500 MHz, 200 K, selected data only): δ 7.71 – 7.75 (m, 8H, Ar^F), 7.53 (br, 4H, Ar^F), -19.17 (s, 0.20H, Ir$\underline{H}$(3,4-$C_6H_3F_2$)), -19.20 (s, 0.25H, Ir$\underline{H}$(3,4-$C_6H_3F_2$)), -19.55 (d, $^{1h}J_{FH}$ = 4.8, 0.23H, *syn*-Ir$\underline{H}$(2,3-$C_6H_3F_2$)), -20.12 (s, 0.32H, *anti*-Ir$\underline{H}$(2,3-$C_6H_3F_2$)).

^{19}F{^{1}H} NMR (CD_2Cl_2, 377 MHz): δ -62.8 (s, 24F, Ar^F), -118.3 (vbr, 0.23F, *syn*-$\underline{2}$,3-$C_6H_3F_2$), -119.8 (vbr, 0.32F, *anti*-$\underline{2}$,3-$C_6H_3F_2$), -141.6 (br d, $^3J_{FF}$ = 27, 0.55F, 2,$\underline{3}$-$C_6H_3F_2$), -143.2 (d, $^3J_{FF}$ = 21, 0.45F, 3,4-$C_6H_3F_2$), -151.3 (d, $^3J_{FF}$ = 21, 0.45F, 3,4-$C_6H_3F_2$).

^{19}F NMR (CD_2Cl_2, 377 MHz, 200 K): δ -62.1 (s, 24F, Ar^F), -117.9 (d, $^3J_{FF}$ = 27, 0.23F, *syn*-$\underline{2}$,3-$C_6H_3F_2$), -119.8 (d,

$^{3}J_{FF}$ = 29, 0.32F, *anti*-2,3-$C_6H_3F_2$), -141.4 (dm, $^{3}J_{FF}$ = 29, 0.32F, *anti*-2,3-$C_6H_3F_2$), -142.0 (dt, $^{3}J_{FF}$ = 27, J_{FH} = 8, 0.23F, *syn*-2,3-$C_6H_3F_2$), -142.8 (app quint, J = 11, 0.25F, 3,4-$C_6H_3F_2$), -143.9 (app quint, J = 11, 0.20F, 3,4-$C_6H_3F_2$), -151.5 (m, 0.20F, 3,4-$C_6H_3F_2$), -151.8 (m, 0.25F, 3,4-$C_6H_3F_2$).

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 126 MHz): δ 162.3 (q, $^{1}J_{BC}$ = 50, Ar^F), 160.3 (s, C{bipy}), 160.0 (s, NCN), 159.1 (br, NCN), 158.5 (s, C{bipy}), 156.3 (s, C^bH{bipy}), 156.2 (s, C^bH{bipy}), 152.9 (s, C^aH{bipy}), 150.4 (dd, $^{1}J_{FC}$ = 247, $^{2}J_{FC}$ = 20, $C_6H_3F_2$), 149.5 (dd, $^{1}J_{FC}$ = 246, $^{2}J_{FC}$ = 11, $C_6H_3F_2$), 147.0 (dd, $^{1}J_{FC}$ = 239, $^{2}J_{FC}$ = 13, $C_6H_3F_2$), 139.7 (s, C^eH{bipy}), 138.5 (s, C^fH{bipy}), 138.4 (s, C^fH{bipy}), 138.2 (d, J = 3, IrC{$C_6H_3F_2$}), 137.6 (s, IrC{$C_6H_3F_2$}), 135.4 (s, Ar^F), 133.1 (br d, J = 4, IrC{$C_6H_3F_2$}), 130.4 (d, $^{3}J_{FC}$ = 10, $C_6H_3F_2$), 129.4 (qq, $^{2}J_{FC}$ = 32, $^{3}J_{BC}$ = 3, Ar^F), 127.0 (s, $COCH_2$), 126.9 (s, $COCH_2$), 126.8 (s, C^hH{bipy}), 126.7 (br, $COCH_2$), 126.6 (s, C^hH{bipy}), 126.5 (s, C^gH{bipy}), 126.4 (s, C^gH{bipy}), 126.0 (s, $COCH_2$), 125.9 (s, $COCH_2$), 125.7 (br, $COCH_2$), 125.2 (q, $^{1}J_{FC}$ = 272, Ar^F), 125.2 (s, C^cH{bipy}), 125.0 (s, C^cH{bipy}), 124.1 (s, C^dH{bipy}), 123.8 (s, C^dH{bipy}), 123.7 (br, $C_6H_3F_2$), 118.1 (sept, $^{3}J_{FC}$ = 4, Ar^F), 115.8 (d, $^{2}J_{FC}$ = 14, $C_6H_3F_2$), 110.5 (d, $^{2}J_{FC}$ = 18, $C_6H_3F_2$), 86.8 – 87.1 (m, OCH_2), 66.8 (s, $C(CH_3)_2$), 66.8 (s, $C(CH_3)_2$), 65.0 (s, $C(CH_3)_2$), 64.9 (s, $C(CH_3)_2$), 26.2 (br, CH_3), 26.1 (s, CH_3), 26.1 (s, CH_3), 26.0 (s, CH_3), 24.3 (br, CH_3), 24.3 (s, CH_3), 24.2 (br, CH_3), 23.5 (br, CH_3), 23.4 (br, CH_3). We have not assigned/identified all of the signals of the three different isomers observed in this spectrum.

Anal. Calcd for $C_{70}H_{56}BF_{26}IrN_6O_4$ (1742.24 $gmol^{-1}$): C, 48.26; H, 3.24; N, 4.82. Found: C, 48.19; H, 3.13; N, 4.74.

2.4 [Ir(IBioxMe$_4$)$_3$(2-C_6H_4F)(H)][BAr^F_4] (6)

To a mixture of **3** (0.050 g, 0.066 mmol), Na[BAr^F_4] (0.062 g, 0.070 mmol) and IBioxMe$_4$ (0.015 g, 0.070 mmol) was added C_6H_5F (8 mL). The orange-red solution was stirred at room temperature for two hours and then filtered. Layering the filtrate with heptane gave a solid upon diffusion, which was recrystallised from C_6H_5F – heptane to afford the orange-red crystalline product. Yield = 0.081 g (66%, orange-red crystals).

^{1}H NMR (C_6H_5F/C_6D_6, 700 MHz): δ 8.29 – 8.32 (m, 8H, Ar^F), 7.62 (br, 4H, Ar^F), 3.80 – 4.12 (m, 12H, OCH_2), 0.06 – 1.74 (δ 1.72 (d, $^{1h}J_{FH}$ = 2.6), 1.70, 1.70, 1.65, 1.56, 1.54, 1.50, 1.47, 1.41 (d, $^{1h}J_{FH}$ = 2.0), 1.38, 1.38, 0.82, 0.79, 0.77, 0.69, 0.66, 0.62, 0.57, 0.18, 0.17, 0.11, 0.07; 36H, CH_3), -47.28 (d, $^{1h}J_{FH}$ = 3.4, 0.42H, *syn*-IrH), -48.94 (s, 0.58H, *anti*-IrH). The aryl fluoride resonances are obscured by the solvent.

$^{19}F\{^{1}H\}$ NMR (C_6H_5F/C_6D_6, 377 MHz): δ -62.4 (s, 24F, Ar^F), -84.7 (d, J_{FH} = 3, 0.42F, *syn*-2-C_6H_4F), -88.0 (s, 0.58F, *anti*-2-C_6H_4F).

$^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 377 MHz): δ -62.1 (s, Ar^F), -84.1 (s, *syn*-C_6H_4F), -87.0 (s, *anti*-C_6H_4F).

$^{13}C\{^{1}H\}$ NMR (C_6H_5F/C_6D_6, 176 MHz): δ 171.1 (d, $^{1}J_{FC}$ = 227, C_6H_4F), 170.4 (d, $^{1}J_{FC}$ = 232, C_6H_4F), 162.7 (q, $^{1}J_{BC}$ = 50, Ar^F), 151.7 (s, NCN), 150.0 (s, NCN), 135.3 (s, Ar^F), 129.7 (qq, $^{2}J_{FC}$ = 34, $^{3}J_{BC}$ = 3, Ar^F), 127.8 (s, $COCH_2$), 127.8 (s, $COCH_2$), 127.7 (s, $COCH_2$), 127.5 (s, $COCH_2$), 127.2 (s, $COCH_2$), 127.1 (s, $COCH_2$), 127.1 (s, $COCH_2$), 127.0 (s, $COCH_2$), 126.4 (s, $COCH_2$), 126.4 (s, $COCH_2$), 126.2 (s, $COCH_2$), 125.9 (s, $COCH_2$), 125.2 (q, $^{1}J_{FC}$ = 271,

Ar^F), 117.9 (sept, $^3J_{FC}$ = 4, Ar^F), 88.1 (s, OCH_2), 88.0 (s, OCH_2), 87.7 (s, OCH_2), 87.7 (s, OCH_2), 87.6 (s, OCH_2), 87.5 (s, OCH_2), 87.3 (s, OCH_2), 87.2 (s, OCH_2), 87.1 (s, OCH_2), 86.9 (s, OCH_2), 86.8 (s, OCH_2), 86.4 (s, OCH_2), 67.6 (s, $\underline{C}(CH_3)_2$), 67.0 (s, $\underline{C}(CH_3)_2$), 66.9 (s, $\underline{C}(CH_3)_2$), 66.4 (s, $\underline{C}(CH_3)_2$), 64.8 (s, $\underline{C}(CH_3)_2$), 64.7 (s, $\underline{C}(CH_3)_2$), 64.7 (s, $\underline{C}(CH_3)_2$), 64.4 (s, $\underline{C}(CH_3)_2$), 63.4 (s, $\underline{C}(CH_3)_2$), 62.9 (s, $\underline{C}(CH_3)_2$), 62.0 (s, $\underline{C}(CH_3)_2$), 61.7 (s, $\underline{C}(CH_3)_2$), 30.2 (s, CH_3), 27.9 (d, $^{2h}J_{FC}$ = 11, CH_3), 27.4 (s, CH_3), 26.7 (s, CH_3), 25.0 (s, CH_3), 24.9 (s, CH_3), 24.8 (s, CH_3), 24.7 (s, CH_3), 24.1 (s, CH_3), 24.1 (s, CH_3), 24.0 (s, CH_3), 24.0 (s, CH_3), 23.9 (s, CH_3), 23.6 (s, CH_3), 23.6 (d, $^{2h}J_{FC}$ = 11, CH_3), 23.5 (s, CH_3), 23.4 (s, CH_3), 21.8 (s, CH_3), 21.4 (d, $^{2h}J_{FC}$ = 2, CH_3), 18.8 (s, CH_3), 18.7 (s, CH_3). The aryl fluoride resonances are partially obscured by the solvent signals.

Anal. Calcd for $C_{71}H_{65}BF_{25}IrN_6O_6.(C_6H_5F)$ ([1776.32] 1872.43 $gmol^{-1}$): C, 49.39; H, 3.77; N, 4.49. Found: C, 49.28; H, 3.77; N, 4.54.

2.5 [Ir(IBioxMe$_4$)$_3$(2,4,6-$C_6H_2F_3$)(H)][BAr^F_4] (7)

To a mixture of **3** (0.050 g, 0.066 mmol), Na[BAr^F_4] (0.062 g, 0.070 mmol) and IBioxMe$_4$ (0.015 g, 0.070 mmol) was added 1,3,5-$C_6H_3F_3$ (8 mL). The orange-red suspension was stirred at room temperature for two hours and periodically sonicated. The supernatant was decanted and the remaining volatiles removed under vacuum, then the solid was dissolved in 1,2-$C_6H_4F_2$ and the solution filtered. Layering the filtrate with heptane afforded crystals upon diffusion. The crystals were re-suspended in 1,3,5-$C_6H_3F_3$ and the resulting suspension was sonicated and the solvent was decanted after 16 hours. The whole process was repeated and the microcrystalline solid was dried under high vacuum. Crystals suitable for X-ray analysis were grown from 1,2-$C_6H_4F_2$ – heptane. Yield = 0.103 g (80%, orange-red microcrystalline solid).

^{1}H NMR (1,2-$C_6H_4F_2$ – 1,3,5-$C_6H_3F_3$ (1:1)/C_6D_6, 700 MHz): δ 8.04 – 8.07 (m, 8H, Ar^F), 7.43 (br, 4H, Ar^F), 4.30 (d, $^2J_{HH}$ = 8.3, 1H, OCH_2), 4.17 – 4.24 (m, $^2J_{HH}$ = 8.3, 6H, OCH_2), 4.14 (d, $^2J_{HH}$ = 8.3, 1H, OCH_2), 4.13 (d, $^2J_{HH}$ = 8.5, 1H, OCH_2), 4.10 (d, $^2J_{HH}$ = 8.3, 1H, OCH_2), 4.09 (d, $^2J_{HH}$ = 8.3, 1H, OCH_2), 4.05 (d, $^2J_{HH}$ = 8.3, 1H, OCH_2), 1.89 (s, 3H, CH_3), 1.80 (d, $^{1h}J_{FH}$ = 3.4, 3H, CH_3), 1.79 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.59 (d, $^{1h}J_{FH}$ = 3.2, 3H, CH_3), 1.52 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 0.76 (s, 3H, CH_3), 0.33 (s, 3H, CH_3), 0.31 (s, 3H, CH_3), -48.06 (br, 1H, IrH). The aryl fluoride resonances are obscured by the solvent.

^{19}F{^{1}H} NMR (1,2-$C_6H_4F_2$ – 1,3,5-$C_6H_3F_3$ (1:1)/C_6D_6, 377 MHz): δ -62.6 (s, 24F, Ar^F), -78.5 (m, 1F, $\underline{2}$,4,$\underline{6}$-$C_6H_2F_3$), -82.1 (dd, $^4J_{FF}$ = 6, $^3J_{FH}$ = 3, 1F, $\underline{2}$,4,$\underline{6}$-$C_6H_2F_3$), -116.4 (t, $^4J_{FF}$ = 6, 1F, 2,$\underline{4}$,6-$C_6H_2F_3$).

^{19}F{^{1}H} NMR (CD_2Cl_2, 377 MHz): δ -62.3 (s, Ar^F), -77.8 (dd, $^4J_{FF}$ = 7, $^4J_{FF}$ = 3, $\underline{2}$,4,$\underline{6}$-$C_6H_2F_3$), -81.0 (dd, $^4J_{FF}$ = 7, $^4J_{FF}$ = 3, $\underline{2}$,4,$\underline{6}$-$C_6H_2F_3$), -116.6 (t, $^4J_{FF}$ = 7, $C_6H_2F_3$).

^{13}C{^{1}H} NMR (1,2-$C_6H_4F_2$ – 1,3,5-$C_6H_3F_3$ (1:1)/C_6D_6, 176 MHz): δ 170.5 (ddd, $^1J_{FC}$ = 228, $^3J_{FC}$ = 25, $^3J_{FC}$ = 14, $C_6H_2F_3$), 170.0 (ddd, $^1J_{FC}$ = 233, $^3J_{FC}$ = 25, $^3J_{FC}$ = 14, $C_6H_2F_3$), 162.6 (q, $^1J_{BC}$ = 50, Ar^F), 147.8 (s, NCN), 146.0 (s, NCN), 135.2 (s, Ar^F), 129.6 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 127.5 (s, $\underline{C}OCH_2$), 127.2 (s, $\underline{C}OCH_2$), 126.6 (s, $\underline{C}OCH_2$), 126.5 (s, $\underline{C}OCH_2$), 125.0 (q, $^1J_{FC}$ = 272, Ar^F), 117.4 (sept, $^3J_{FC}$ = 4, Ar^F), 88.3 (s, OCH_2), 87.9 (s, OCH_2), 87.8 (s, OCH_2), 87.2 (s, OCH_2), 87.2 (s, OCH_2), 86.7 (s, OCH_2), 67.4 (s, $\underline{C}(CH_3)_2$), 66.7 (s, $\underline{C}(CH_3)_2$), 65.4 (s, $\underline{C}(CH_3)_2$), 65.4

(s, $\underline{C}(CH_3)_2$), 63.8 (s, $\underline{C}(CH_3)_2$), 62.5 (s, $\underline{C}(CH_3)_2$), 27.9 (d, $^{2h}J_{FC}$ = 12, CH_3), 27.1 (s, CH_3), 25.0 (s, CH_3), 24.8 (s, CH_3), 24.1 (s, CH_3), 24.0 (s, CH_3), 23.8 (s, CH_3), 23.8 (d, $^{2h}J_{FC}$ = 12, CH_3), 23.8 (s, CH_3), 23.5 (s, CH_3), 21.7 (d, $^{2h}J_{FC}$ = 3, CH_3), 18.8 (s, CH_3). The aryl fluoride resonances are partially obscured by the solvent signals. **Anal.** Calcd for $C_{71}H_{63}BF_{27}IrN_6O_6.(C_6H_3F_3)$ ([1812.30] 1944.39 $gmol^{-1}$): C, 47.56; H, 3.42; N, 4.32. Found: C, 47.46; H, 3.37; N, 4.40.

2.6 [Ir(IBioxMe$_4$)$_3$(NCCH$_3$)][BAr$^F{}_4$] (8)

Complex **2** (0.040 g, 0.022 mmol) was dissolved in acetonitrile (5 mL). The solution was stirred at room temperature for 16 hours, during which the solution became bright yellow. The volatiles were removed in vacuo. Repeated suspension in heptane, sonication and filtration afforded yellow microcrystalline **4**. Crystals suitable for X-ray analysis were grown from C_6H_5F – heptane. Yield = 0.033 g (87%, yellow microcrystalline solid).

^{1}H NMR (C_6H_5F/C_6D_6, 400 MHz): δ 8.26 – 8.32 (m, 8H, Ar^F), 7.61 (br, 4H, Ar^F), 4.13 (d, $^2J_{HH}$ = 8.1, 2H, OCH_2), 3.99 – 4.08 (m, 8H, OCH_2), 3.92 (d, $^2J_{HH}$ = 8.0, 2H, OCH_2), 2.08 (s, 6H, CH_3), 1.92 (s, 6H, CH_3), 1.91 (s, 6H, CH_3), 1.53 (s, 6H, CH_3), 1.49 (s, 3H, CH_3CN), 0.80 (s, 6H, CH_3), 0.64 (s, 6H, CH_3).

^{1}H NMR (CD_3CN, 400 MHz): δ 7.68 – 7.71 (m, 8H, Ar^F), 7.67 (br, 4H, Ar^F), 4.35 – 4.45 (m, 10H, OCH_2), 4.20 (d, $^2J_{HH}$ = 8.2, 2H, OCH_2), 2.28 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 1.96 (s, 3H, $NCCH_3$), 1.68 (s, 6H, CH_3), 1.02 (s, 6H, CH_3), 0.77 (s, 6H, CH_3).

^{13}C{^{1}H} NMR (CD_3CN, 101 MHz): δ 162.6 (q, $^1J_{BC}$ = 50, Ar^F), 157.6 (s, NCN), 143.2 (s, NCN), 135.6 (s, Ar^F), 129.7 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 126.0 (s, $\underline{C}OCH_2$), 125.9 (s, $\underline{C}OCH_2$), 125.4 (q, $^1J_{FC}$ = 272, Ar^F), 118.7 (sept, $^3J_{FC}$ = 4, Ar^F), 89.8 (s, OCH_2), 89.7 (s, OCH_2), 87.8 (s, OCH_2), 65.8 (s, $\underline{C}(CH_3)_2$), 63.7 (s, $\underline{C}(CH_3)_2$), 62.3 (s, $\underline{C}(CH_3)_2$), 26.6 (s, CH_3), 26.2 (s, CH_3), 25.5 (s, CH_3), 25.0 (s, CH_3), 24.2 (s, CH_3), 21.9 (s, CH_3); coordinated CH_3CN signals not observed.

Anal. Calcd for $C_{67}H_{63}BF_{24}IrN_7O_6$ (1721.27 $gmol^{-1}$): C, 46.75; H, 3.69; N, 5.70. Found: C, 46.62; H, 3.74; N, 5.65.

3 NMR scale reaction details

3.1 [Ir(IBioxMe$_4$)$_3$(2,3-C$_6$H$_3$F$_2$)(H)][BAr$^F{}_4$] (2)

i. Solution stability was tested using a solution of **2** (0.0179 g, 0.0100 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) in a J Young's valve NMR tube. No significant change was observed after 24 hours at 293 K by ^{1}H and ^{19}F NMR spectroscopy.

ii. A solution of **2** (0.0179 g, 0.0100 mmol) in 1,2-$C_6H_4F_2$ (0.256 mL, 0.0026 mol) was prepared in a J Young's valve NMR tube and C_6H_5F (0.244 mL, 0.0026 mol) was added. The ensuing reaction was followed in situ by ^{1}H and ^{19}F NMR spectroscopy. After 2 hours at 298 K an equilibrium mixture of **2** and **6** was obtained corresponding to K = 6.

iii. A solution of **2** (0.0179 g, 0.0100 mmol) in CD_2Cl_2 (0.5 mL) was prepared in a J Young's valve NMR tube and the ensuing reaction followed in situ by ^{1}H and ^{19}F NMR spectroscopy at 298 K. Decomposition of **2** occurred with an apparent first order kinetics and an approximate half-life of 30 minutes (4 hours of data collected).

3.2 *trans*-[Ir(IBioxMe$_4$)$_2$(COE)Cl] (3)

i. Solution stability was tested using solutions of **3** (0.0100 g, 0.0133 mmol) in a J Young's valve NMR tube. No significant change was observed after 24 hours at 293 K by ^{1}H NMR spectroscopy in C_6D_6 (0.5 mL), 1,2-$C_6H_4F_2$ (0.5 mL) or CD_2Cl_2 (0.5 mL).

ii. A solution of **3** (0.0050 g, 0.0066 mmol) and IBioxMe$_4$ (0.0015 g, 0.0073 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was prepared in a J Young's valve NMR tube. Analysis of the solution by ^{1}H NMR spectroscopy indicated absence of any reaction after 24 hours at 293 K. No reaction was apparent by ^{1}H NMR spectroscopy after 3 hours at 333 K.

iii. A solution of **3** (0.0050 g, 0.0066 mmol) and 2,2'-bipyridine (0.0011 g, 0.0073 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was prepared in a J Young's valve NMR tube. Analysis of the solution by ^{1}H NMR spectroscopy indicated absence of any reaction after 24 hours at 293 K.

iv. A solution of **3** (0.0075 g, 0.0100 mmol) and Na[BAr$^F{}_4$] (0.0098 g, 0.0110 mmol) in pre-cooled 1,2-$C_6H_4F_2$ (0.5 mL, ca 250 K) was prepared in a J Young's valve NMR tube and the sample analysed immediately by ^{1}H and ^{19}F NMR spectroscopy at 250 K. The ^{1}H NMR spectrum showed the presence of uncoordinated COE alongside 4 different hydride species as the major organometallic products (> 80%). The ^{19}F NMR spectrum suggested these major species are the products of C–H bond activation of 1,2-$C_6H_4F_2$. An additional species, tentatively assigned to dimeric [{Ir(IBioxMe$_4$)$_2$(2,3-$C_6H_3F_2$)H}$_2$Cl]$^+$ (**9**) based on ^{19}F data, is also observed. This suggestion would account for the slightly higher amount of *trans*-[Ir(IBioxMe$_4$)$_2$(2,2'-bipyridine)(2,3-$C_6H_3F_2$)(H)][BAr$^F{}_4$] formed, in comparison to *trans*-[Ir(IBioxMe$_4$)$_2$(2,2'-bipyridine)(3,4-$C_6H_3F_2$)(H)][BAr$^F{}_4$], during the reaction of in situ generated **4** with 2,2'-bipyridine.

^{1}H NMR (1,2-$C_6H_4F_2$/d_6-acetone, 400 MHz, 250 K, selected data only): δ 8.16 – 8.28 (m, 8H, Ar^F), 7.41 (br, 4H, Ar^F), 5.47 (br, 2H, CH{free COE}), -44.91 (br, 0.24H, IrH{**4**}), -46.37 (br, 0.25H, IrH{**4**}), -46.45 (br, 0.09H, IrH{**9**}), -46.48 (br, 0.17H, IrH{**4**}), -46.61 (br, 0.14H, IrH{**4**}). **^{19}F NMR** (1,2-$C_6H_4F_2$/d_6-acetone, 377 MHz, 250 K): δ -62.2 (s, 24F, Ar^F), -117.2 (d, $^3J_{FF}$ = 25, 0.25F, 2,3-$C_6H_3F_2${**4**}), -117.6 (m, 0.07F), -118.1 (m, 0.10F), -118.2 (m, 0.15F, 2,3-$C_6H_3F_2${**4**}), -140.4 (d, $^3J_{FF}$ = 25, 0.25F, 2,3-$C_6H_3F_2${**4**}), -140.7 (m, 0.14F, 3,4-$C_6H_3F_2${**4**}), -140.9 (m, 0.25F, 3,4-$C_6H_3F_2${**4**}), -147.1 (m, 0.14F, 3,4-$C_6H_3F_2${**4**}), -147.3 (m, 0.25F, 3,4-$C_6H_3F_2${**4**}). Presumably, the solvent obscures a number of the aryl fluoride resonances.

v. A solution of **3** (0.0075 g, 0.0100 mmol) and Na[BAr^F_4] (0.0098 g, 0.0110 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was prepared in a J Young's valve NMR tube and after 5 minutes at 293 K, $IBioxMe_4$ (0.0023 g, 0.0110 mmol) was added. Analysis of the solution by ^{1}H and ^{19}F NMR spectroscopy indicated quantitative formation of **2** (< 15 min).

vi. A solution of **3** (0.0075 g, 0.0100 mmol) and Na[BAr^F_4] (0.0098 g, 0.0110 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was prepared in a J Young's valve NMR tube and after 5 minutes at 293 K, 2,2'-bipyridine (0.0017 g, 0.0110 mmol) was added. Analysis the solution by ^{1}H and ^{19}F NMR spectroscopy indicated quantitative formation of **5** (< 15 min).

3.3 *trans*-[Ir($IBioxMe_4$)$_2$(2,2'-bipyridine)($C_6H_3F_2$)(H)][BAr^F_4] (5)

i. Solution stability was tested using a solution of **5** (0.0200 g, 0.0115 mmol) in CD_2Cl_2 (0.5 mL) in a J Young's valve NMR tube. No change was observed after 24 hours at 293 K by ^{1}H NMR spectroscopy.

ii. A solution of **5** (0.010 g, 0.0057 mmol) in C_6H_5F (0.5 mL) was prepared in a J Young's valve NMR tube. Analysis of the solution by ^{1}H and ^{19}F NMR spectroscopy indicated the absence of any reaction after 24 hours at 293 K.

iii. A solution of **5** (0.010 g, 0.0057 mmol) in a 1:1 mixture of 1,2-$C_6H_4F_2$ and 1,3,5-$C_6H_3F_3$ (0.5 mL) was prepared in a J Young's valve NMR tube. Analysis of the solution by ^{1}H and ^{19}F NMR spectroscopy indicated the absence of any reaction after 24 hours at 293 K.

3.4 [Ir($IBioxMe_4$)$_3$(2-C_6H_4F)(H)][BAr^F_4] (6)

i. Solution stability was tested using a solution of **6** (0.0089 g, 0.0050 mmol) in C_6H_5F (0.5 mL) in a J Young's valve NMR tube. No significant change was observed after 24 hours at 293 K by ^{1}H and ^{19}F NMR spectroscopy.

ii. A solution of **6** (0.0178 g, 0.0100 mmol) in CD_2Cl_2 (0.5 mL) was prepared in a J Young's valve NMR tube and the ensuing reaction followed in situ by ^{1}H and ^{19}F NMR spectroscopy. Decomposition of **2** occurred with an apparent first order kinetics and an approximate half-life of 2 minutes (40 minutes of data collected).

iii. A suspension of **6** (0.0089 g, 0.005 mmol) in $C_6F_5CF_3$ (0.5 mL) was prepared in a J Young's valve NMR tube and the ensuing reaction followed in situ by ^1H and ^{19}F NMR spectroscopy. The ^1H NMR spectrum after 20 min showed formation of transient cationic species of apparent D_3 symmetry alongside one equivalent of fluorobenzene (Figure S21). Fluorobenzene and $[BAr^F_4]^-$ are observed in the $^{19}F\{^1H\}$ NMR spectrum; no other significant fluorine containing species could be delinated.

^{1}H NMR ($C_6F_5CF_3/C_6D_6$, 400 MHz): δ 7.56 – 7.61 (m, 8H, Ar^F), 7.21 (br, 4H, Ar^F), 4.28 (s, 12H, OCH_2), 1.62 (s, 18H, CH_3), 1.30 (v br, 18H, CH_3).

3.5 [Ir(IBioxMe$_4$)$_3$(2,4,6-C$_6$H$_2$F$_3$)(H)][BAr$^F_4$] (7)

i. Solution stability was tested using a solution of **7** (0.0091 g, 0.0050 mmol) in a 1:1 mixture of 1,2-$C_6H_4F_2$ and 1,3,5-$C_6H_3F_3$ (0.5 mL) in a J Young's valve NMR tube. No significant change was observed after 24 hours by ^1H and ^{19}F NMR spectroscopy at 293 K.

ii. A solution of **7** (0.0181 g, 0.0100 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was prepared in a J Young's valve NMR tube and the ensuing reaction followed in situ by ^1H and ^{19}F NMR spectroscopy. After 16 days, the concentration of **7** was not changing significantly within the error of integration. By integration of the hydride signals, an approximate value for arene exchange was calculated (K = 1/106).

iii. A solution of **7** (0.0181 g, 0.0100 mmol) in CD_2Cl_2 (0.5 mL) was prepared in a J Young's valve NMR tube and the ensuing reaction followed in situ by ^1H and ^{19}F NMR spectroscopy. Decomposition of **7** occurred with an apparent first order kinetics and an approximate half-life of 6 days at 293 K (25 days of data collected).

3.6 [Ir(IBioxMe$_4$)$_3$(NCCH$_3$)][BAr$^F_4$] (8)

i. A solution of **8** (0.0172 g, 0.0100 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was prepared in a J Young's valve NMR tube. Analysis of the solution by ^1H and ^{19}F NMR spectroscopy indicated partial conversion to **2** (24%) after 14 hours at 298 K. Subsequent removal of the volatiles under high vacuum and re-dissolution of the solid in 1,2-$C_6H_4F_2$ (0.5 mL) allowed higher conversion; after 6 cycles, a yield of 70% was reached.

4 Selected NMR spectra

4.1 [Ir(IBioxMe$_4$)$_3$(2,3-C$_6$H$_3$F$_2$)(H)][BAr$^F{}_4$] (2)

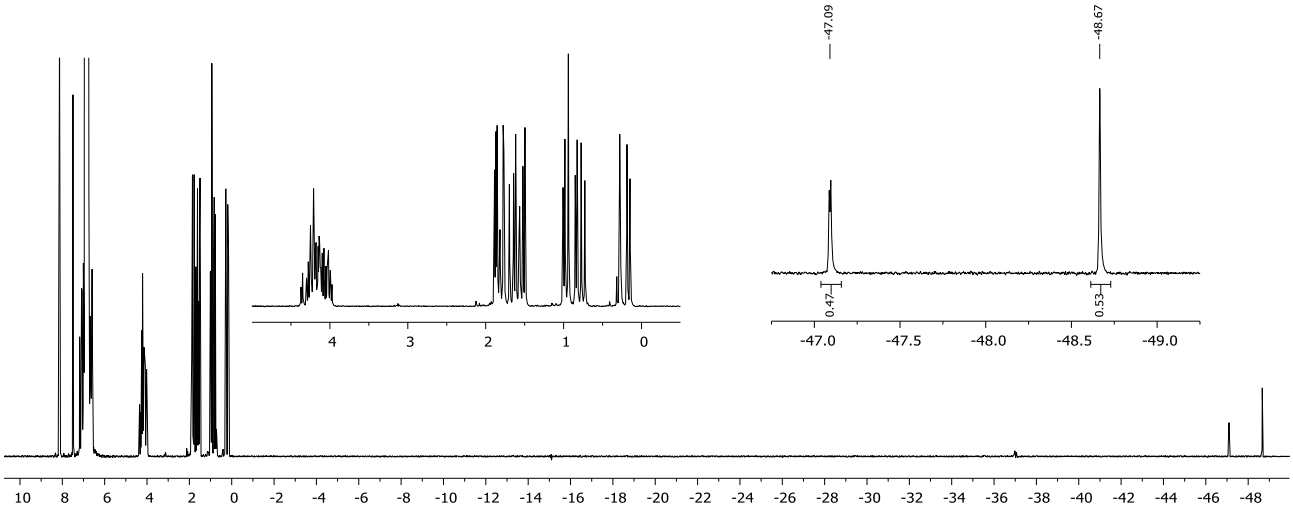

Figure S1: ^{1}H NMR spectrum in 1,2-C$_6$H$_4$F$_2$ (C$_6$D$_6$ capillary; 400 MHz, 298 K).

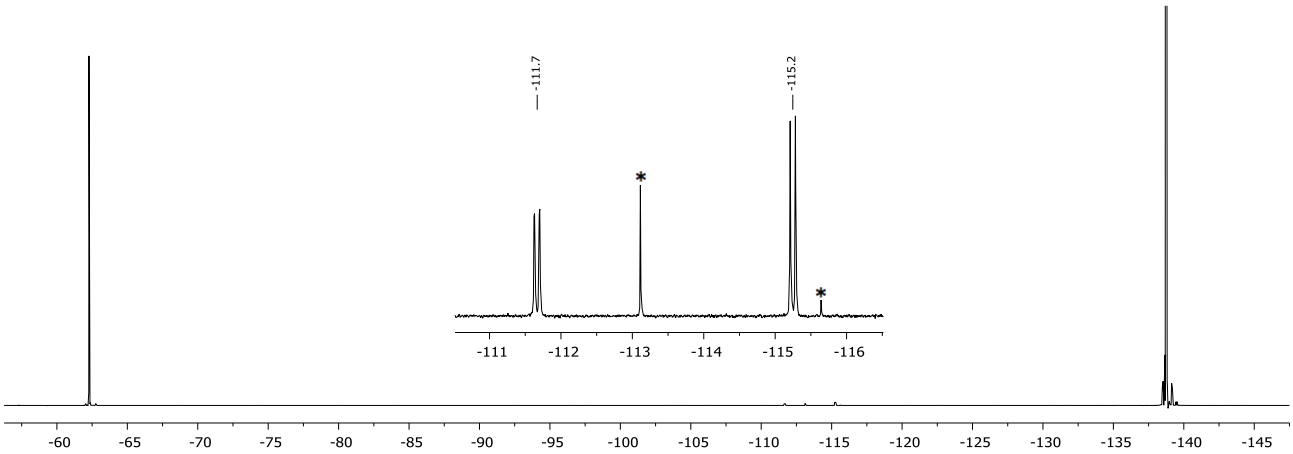

Figure S2: ^{19}F{^{1}H} NMR spectrum in 1,2-C$_6$H$_4$F$_2$ (C$_6$D$_6$ capillary; 377 MHz, 298 K). * Impurities in 1,2-C$_6$H$_4$F$_2$.

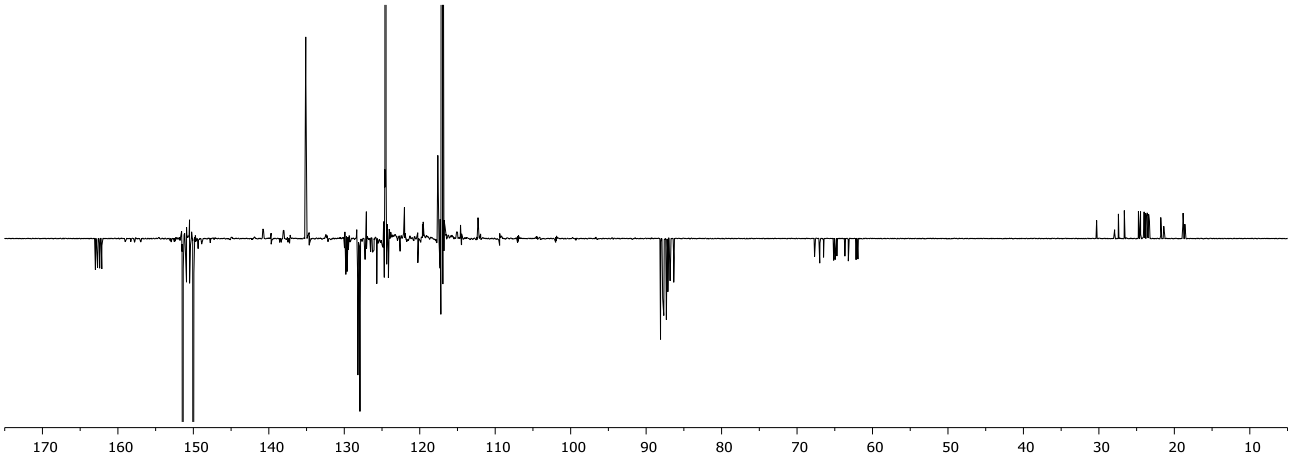

Figure S3: ^{13}C{^{1}H} APT NMR spectrum in 1,2-C$_6$H$_4$F$_2$ (C$_6$D$_6$ capillary; 176 MHz, 298 K).

4.2 *trans*-[Ir(IBioxMe$_4$)$_2$(COE)Cl] (3)

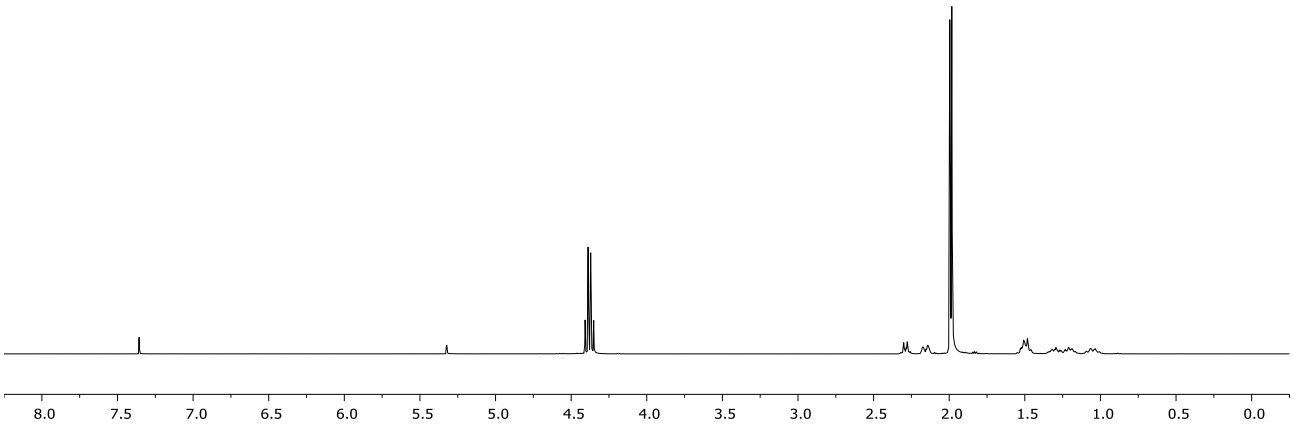

Figure S4: ^{1}H NMR spectrum in CD_2Cl_2 (400 MHz, 298 K).

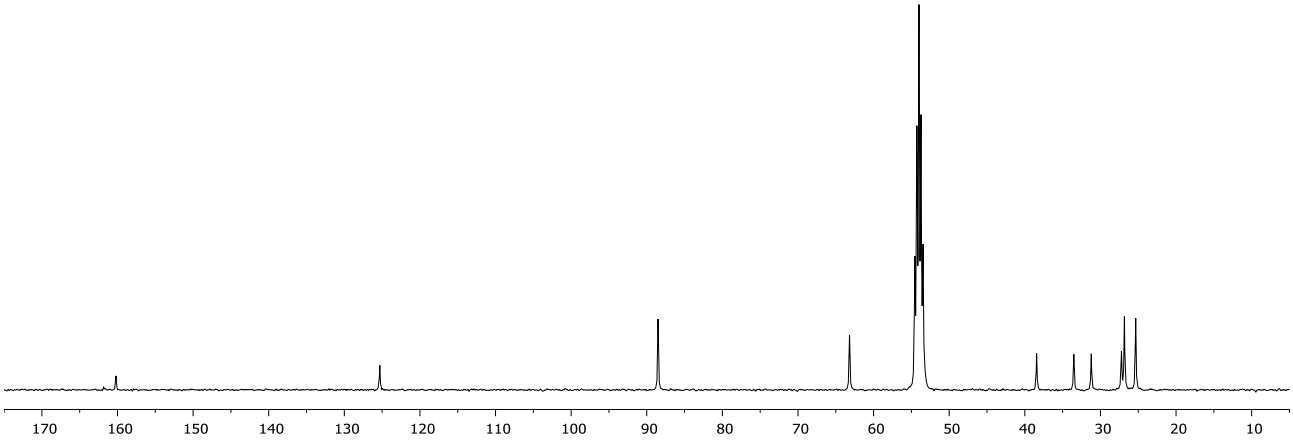

Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum in CD_2Cl_2 (101 MHz, 298 K).

4.3 *trans*-[Ir(IBioxMe$_4$)$_2$(2,3-C$_6$H$_3$F$_2$)(H)][BAr$^F{}_4$] (4)

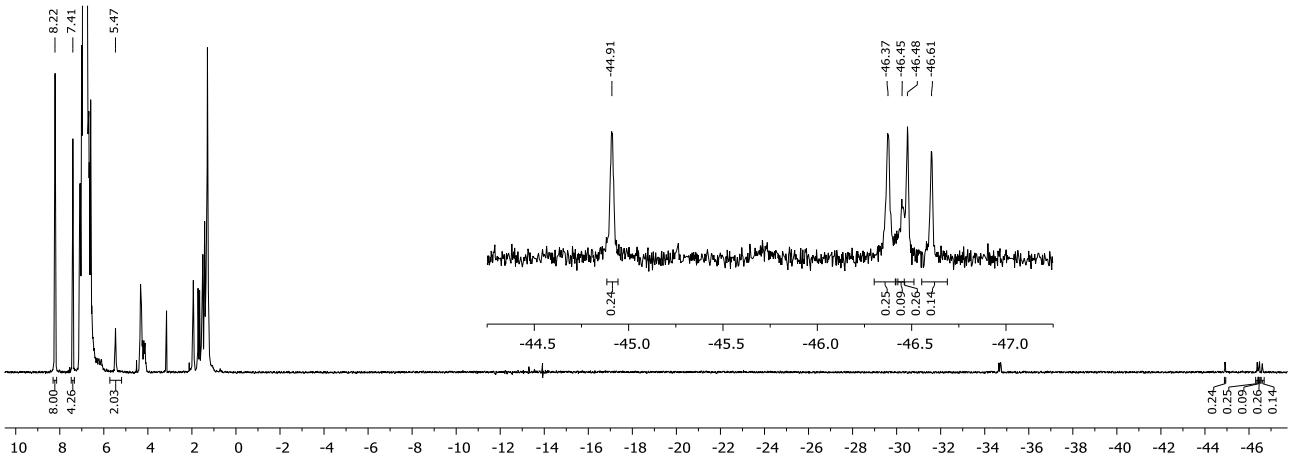

Figure S6: ^{1}H NMR spectrum in 1,2-C$_6$H$_4$F$_2$ (d$_6$-acetone capillary; 400 MHz, 250 K).

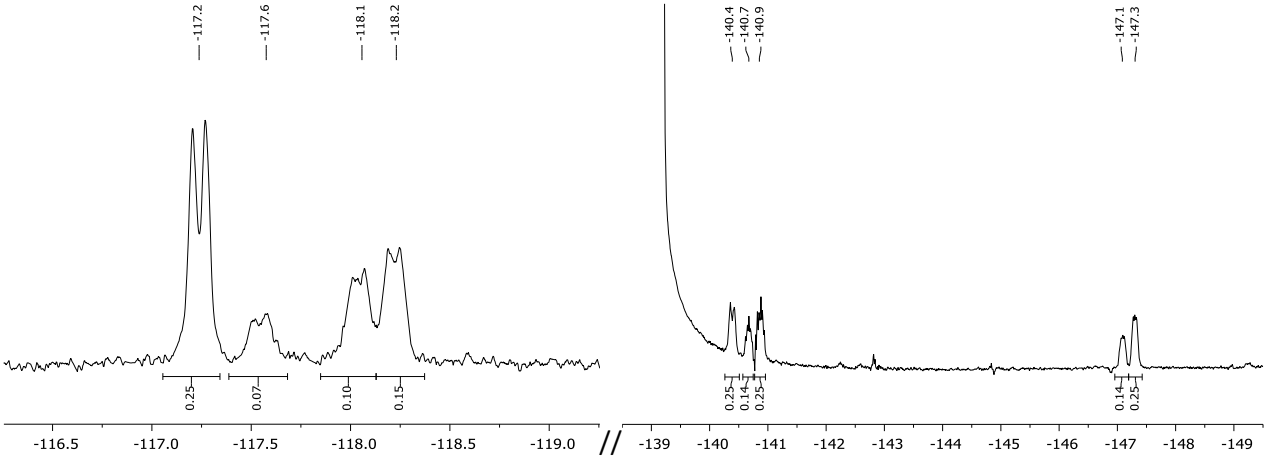

Figure S7: Selected regions of the ^{19}F NMR spectrum in 1,2-C$_6$H$_4$F$_2$ (d$_6$-acetone capillary; 377 MHz, 250 K).

4.4 *trans*-[Ir(IBioxMe$_4$)$_2$(2,2'-bipyridine)(C$_6$H$_3$F$_2$)(H)][BAr$^F{}_4$] (5)

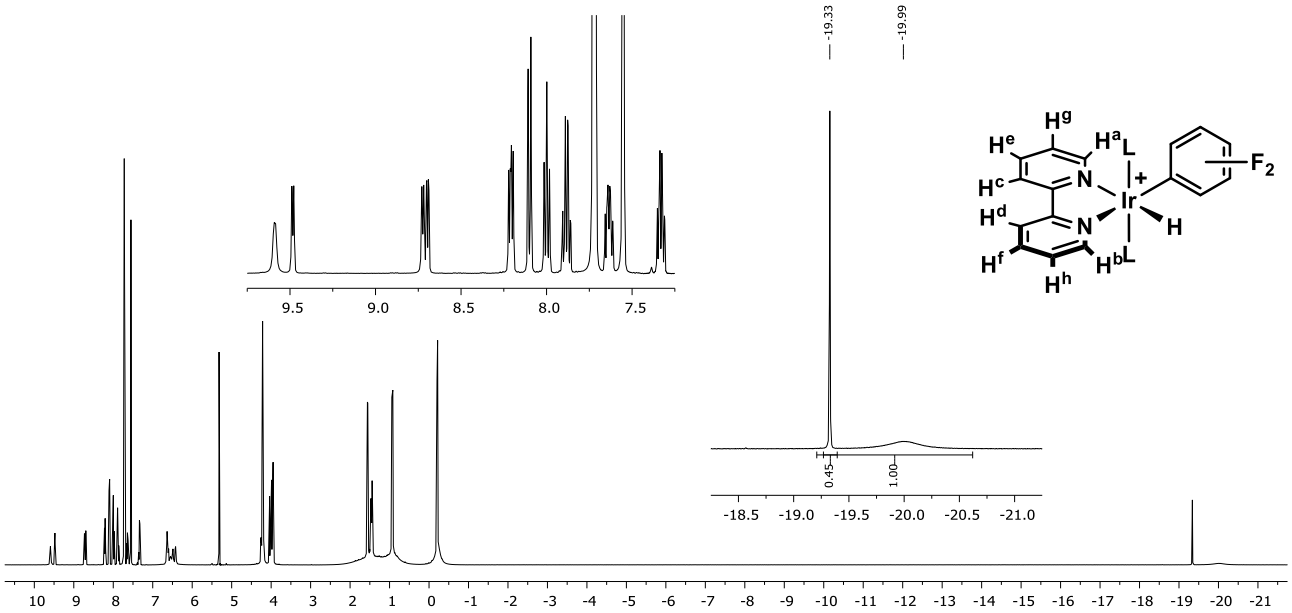

Figure S8: ^{1}H NMR spectrum in CD_2Cl_2 (500 MHz, 298 K; L = IBioxMe$_4$).

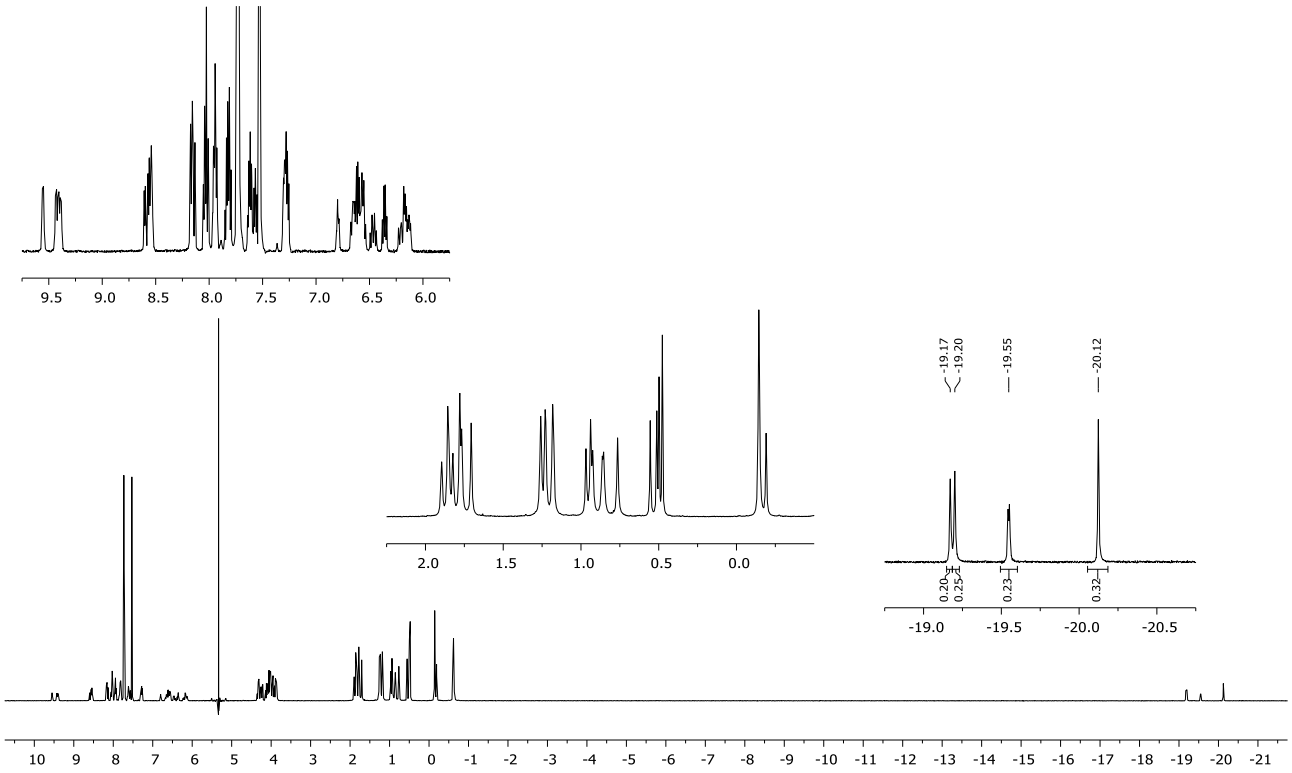

Figure S9: ^{1}H NMR spectrum in CD_2Cl_2 (500 MHz, 200 K).

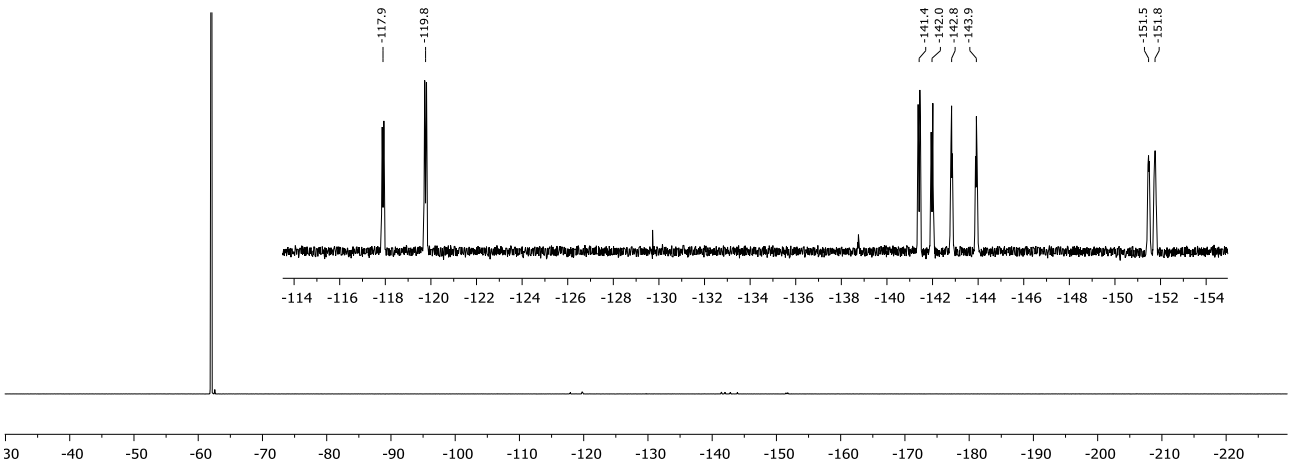

Figure S10: ^{19}F NMR spectrum in CD_2Cl_2 (377 MHz, 200 K).

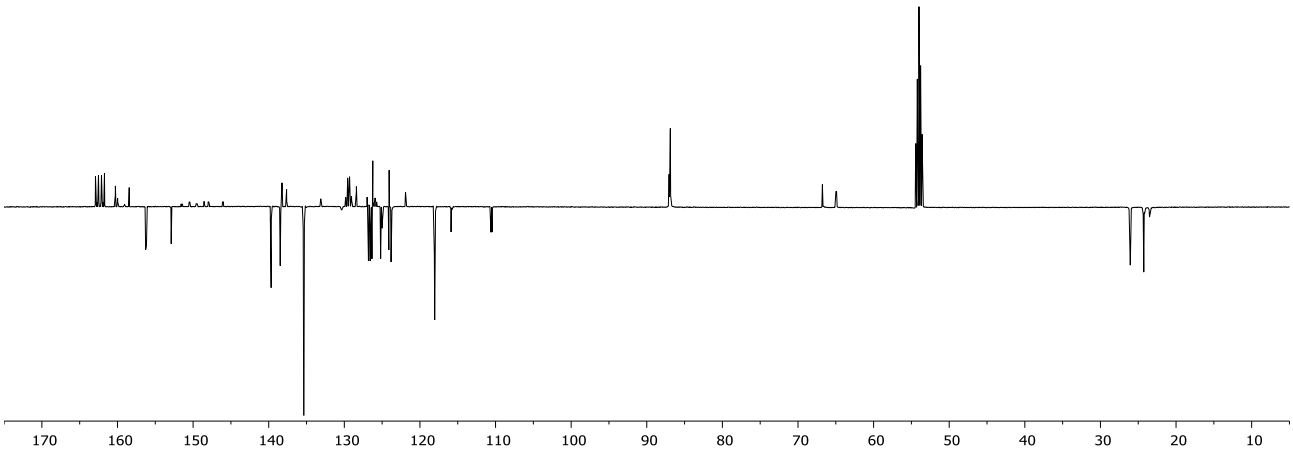

Figure S11: $^{13}C\{^1H\}$ APT NMR spectrum in CD_2Cl_2 (126 MHz, 298 K).

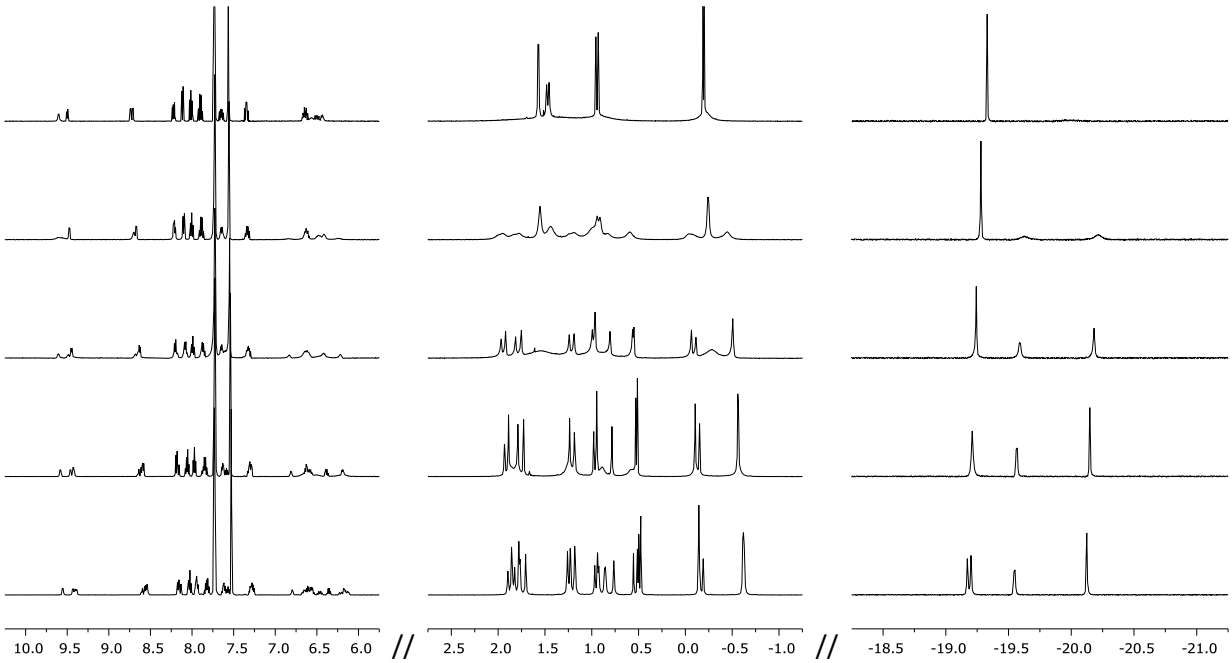

Figure S12: ^1H NMR spectra in CD_2Cl_2 (500 MHz, from top to bottom: 298; 273; 250; 225; 200 K).

4.5 [Ir(IBioxMe$_4$)$_3$(2-C$_6$H$_4$F)(H)][BAr$^F{}_4$] (6)

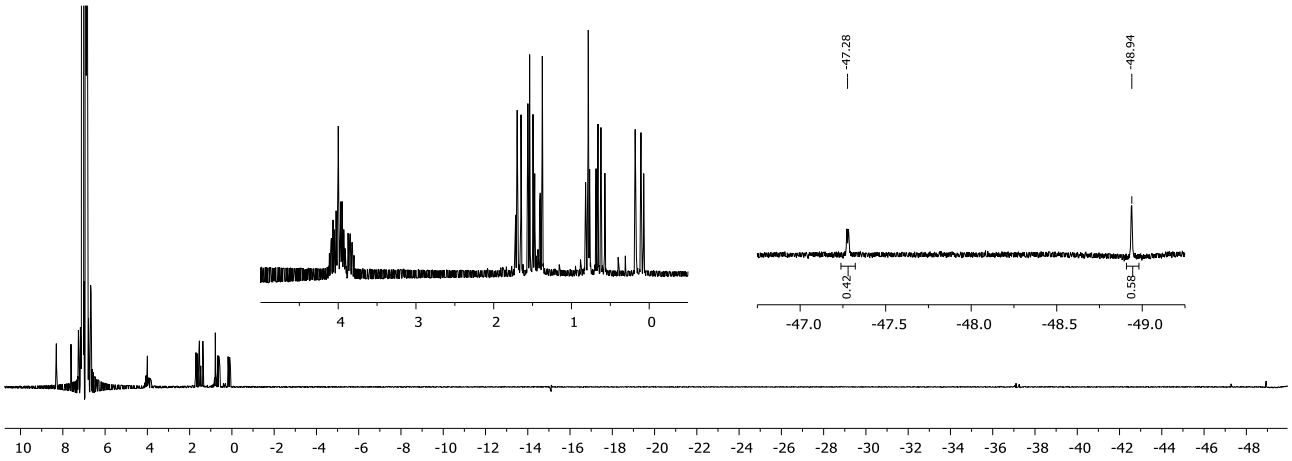

Figure S13: ^{1}H NMR spectrum in C_6H_5F (C_6D_6 capillary; 400 MHz, 298 K).

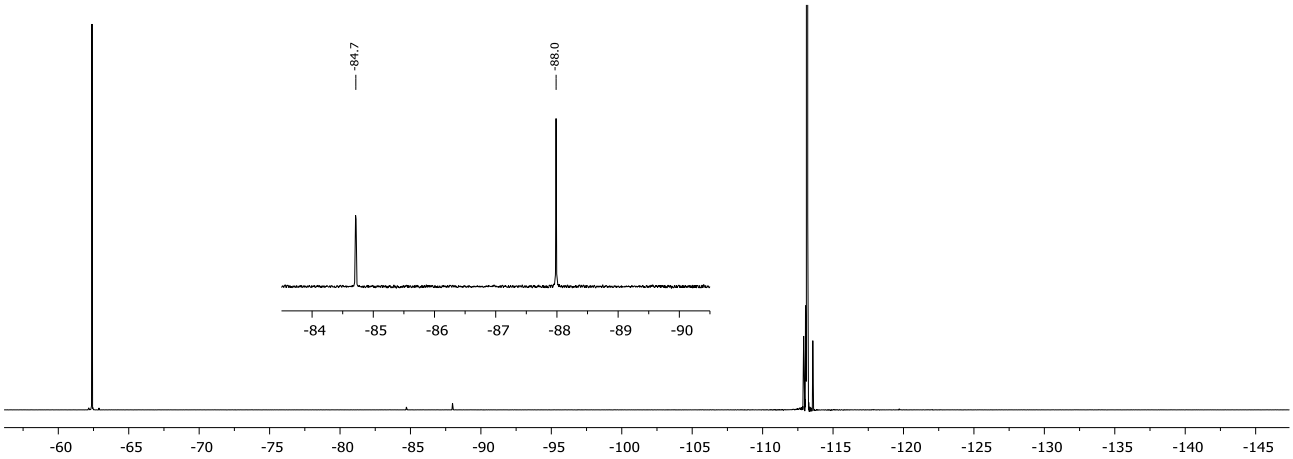

Figure S14: ^{19}F{^{1}H} NMR spectrum in C_6H_5F (C_6D_6 capillary; 377 MHz, 298 K).

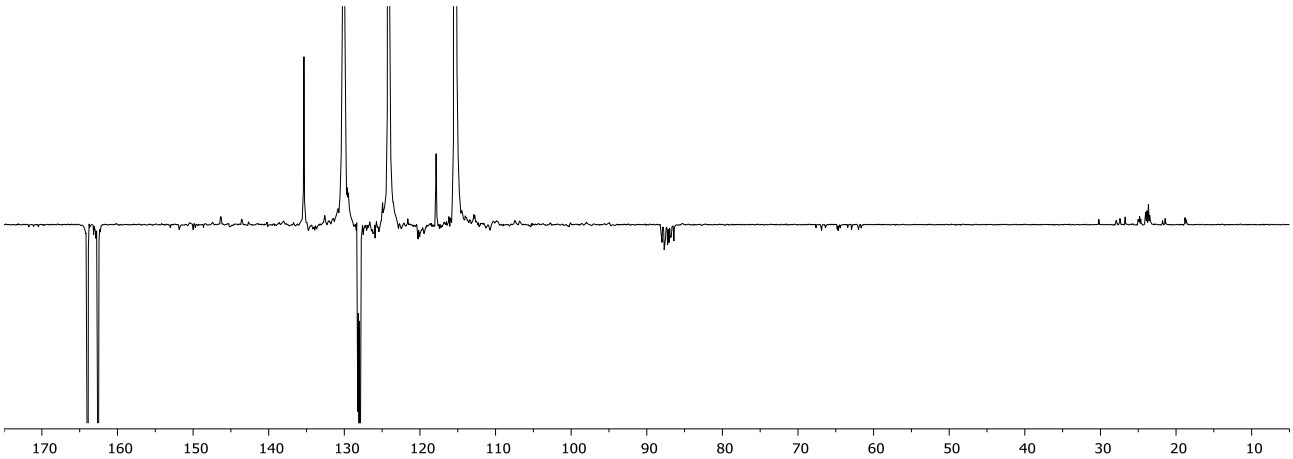

Figure S15: ^{13}C{^{1}H} APT NMR spectrum in C_6H_5F (C_6D_6 capillary; 176 MHz, 298 K).

4.6 [Ir(IBioxMe$_4$)$_3$(2,4,6-C$_6$H$_2$F$_3$)(H)][BAr$^F{}_4$] (7)

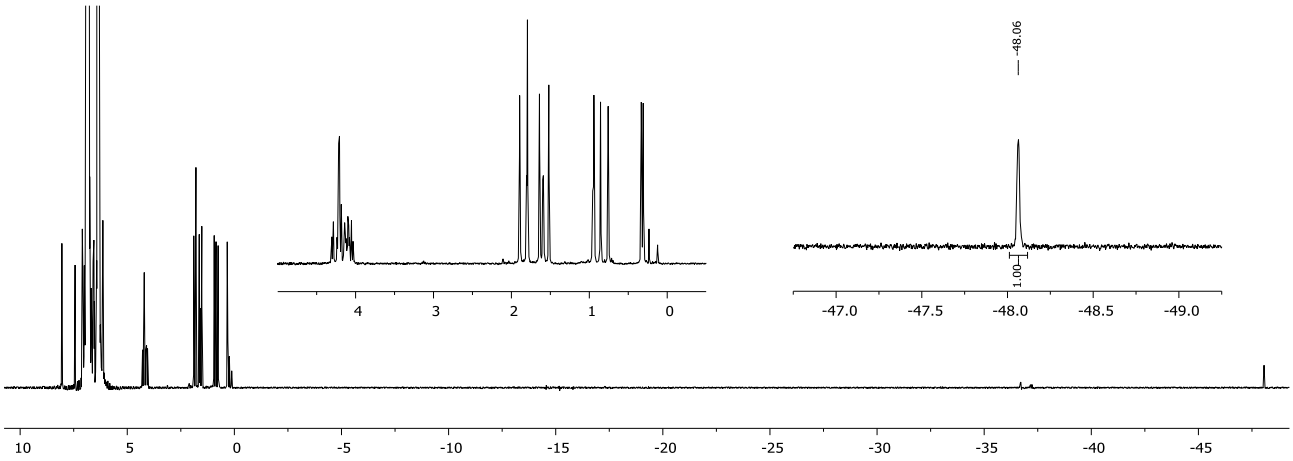

Figure S16: ^{1}H NMR spectrum in 1,2-C$_6$H$_4$F$_2$ – 1,3,5-C$_6$H$_3$F$_3$ (1:1, C$_6$D$_6$ capillary; 400 MHz, 298 K).

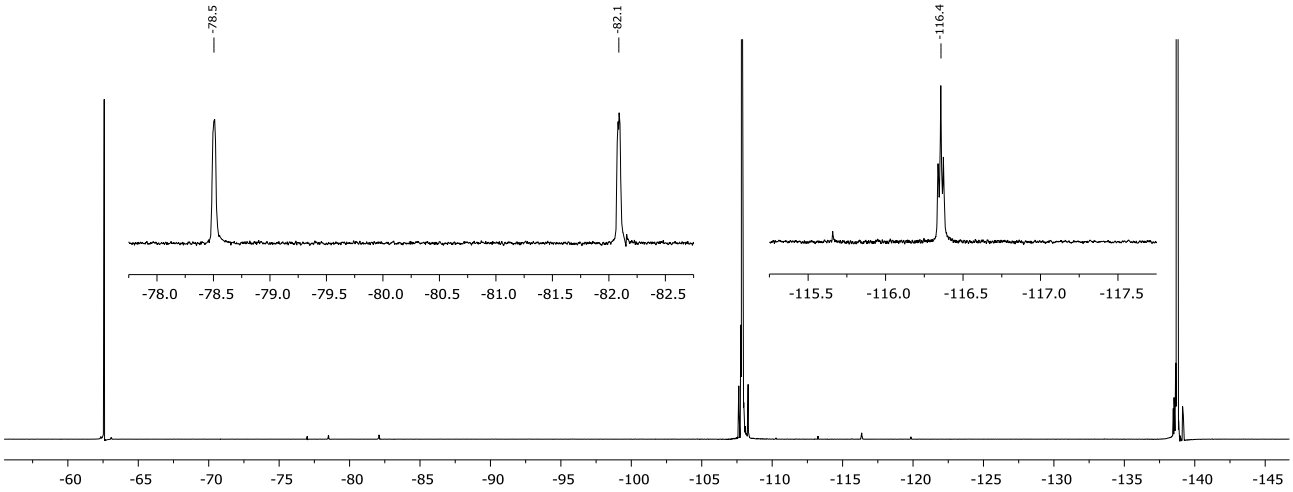

Figure S17: ^{19}F{^{1}H} NMR spectrum in 1,2-C$_6$H$_4$F$_2$ – 1,3,5-C$_6$H$_3$F$_3$ (1:1, C$_6$D$_6$ capillary; 377 MHz, 298 K).

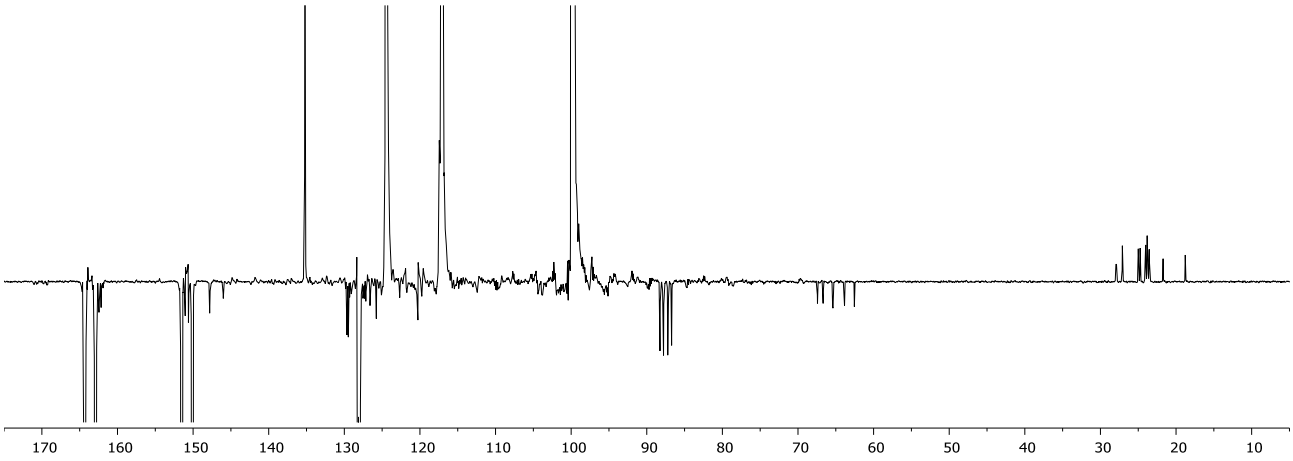

Figure S18: ^{13}C{^{1}H} APT NMR spectrum in 1,2-C$_6$H$_4$F$_2$ – 1,3,5-C$_6$H$_3$F$_3$ (1:1, C$_6$D$_6$ capillary; 176 MHz, 298 K).

4.7 $[Ir(IBioxMe_4)_3(NCCH_3)][BAr^F_4]$ (8)

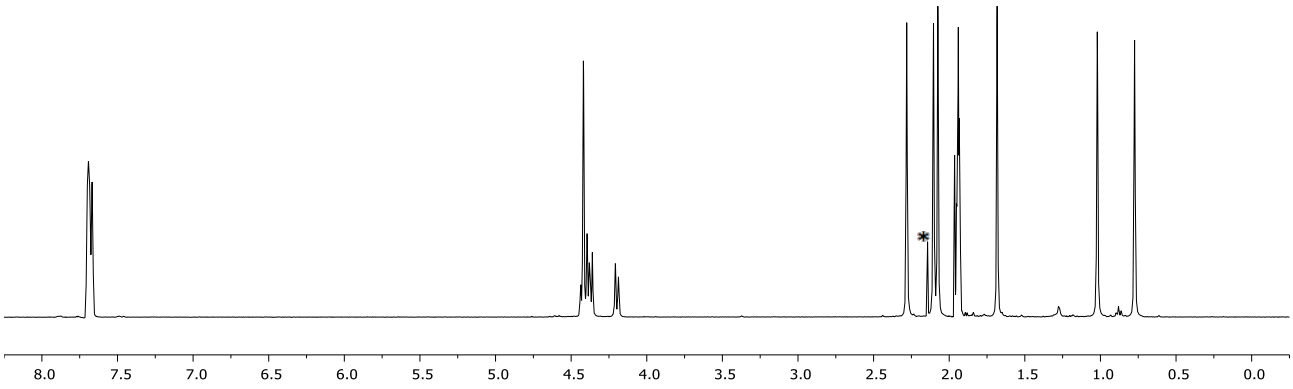

Figure S19: ^{1}H NMR spectrum in CD_3CN (400 MHz, 298 K). * Residual H_2O.

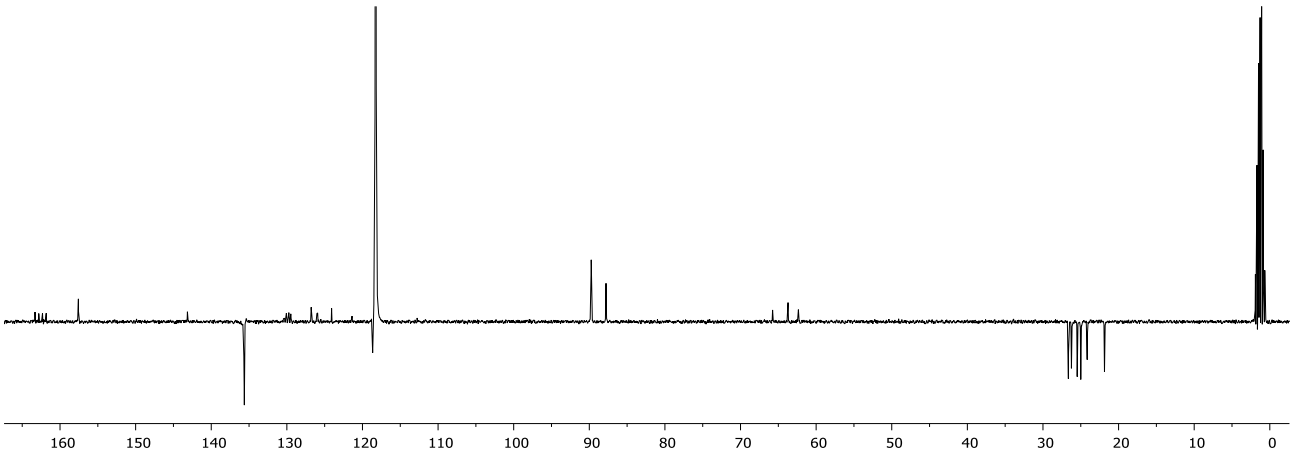

Figure S20: $^{13}C\{^1H\}$ APT NMR spectrum in CD_3CN (101 MHz, 298 K).

4.8 Stability of 6 in perfluorotoluene – attempted preparation of 1

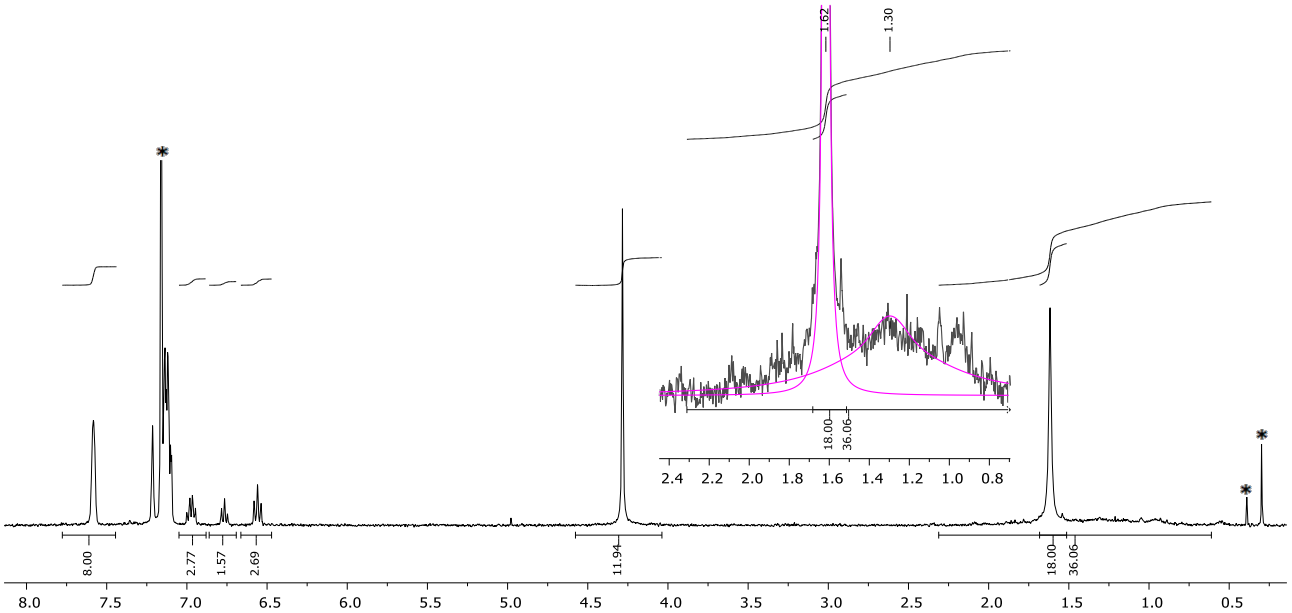

Figure S21: ^{1}H NMR spectrum of **6** dissolved in $C_6F_5CF_3$ recorded after 20 minutes (C_6D_6 capillary; 400 MHz, 298 K). * Signals from C_6D_6 capillary (residual C_6H_6, H_2O and grease).

5 Reaction kinetics

5.1 Kinetic scheme for arene substitution reactions

The kinetics for the substitution reaction between **A** and **b** to afford **B** and **a** is modelled using the following four equations, involving the intermediate presence of a species **X**:

$$(1)\ \ \mathbf{A} \xrightarrow{k_1} \mathbf{X} + \mathbf{a} \qquad (2)\ \ \mathbf{X} + \mathbf{a} \xrightarrow{k_2} \mathbf{A} \qquad (3)\ \ \mathbf{X} + \mathbf{b} \xrightarrow{k_3} \mathbf{B} \qquad (4)\ \ \mathbf{B} \xrightarrow{k_4} \mathbf{X} + \mathbf{b}$$

Application of the steady state approximation for **X** affords leads to equation 5, where $[\mathbf{A}]_0$ is the initial concentration of **A**, which can be simplified to equations 6 and 7.

$$(5)\quad \frac{\mathrm{d}[\mathbf{A}]}{\mathrm{dt}} = \frac{-k_1[\mathbf{A}] + \frac{k_2[\mathbf{a}]}{k_3[\mathbf{b}]} k_4([\mathbf{A}]_0 - [\mathbf{A}])}{\frac{k_2[\mathbf{a}]}{k_3[\mathbf{b}]} + 1}$$

$$(6)\quad \frac{\mathrm{d}[\mathbf{A}]}{\mathrm{dt}} = \frac{-k_1[\mathbf{A}]}{\frac{k_2[\mathbf{a}]}{k_3[\mathbf{b}]} + 1} \ \{\text{when } k_1 \gg k_4\}$$

$$(7)\quad \frac{\mathrm{d}[\mathbf{A}]}{\mathrm{dt}}|_{t=0} = -k_1[\mathbf{A}]_0 \ \ \{\text{when } [\mathbf{b}] \gg [\mathbf{a}]\}$$

5.2 Substitution reactions of 2 with 1,3,5-$C_6H_3F_3$

A solution of **2** (0.0179 g, 0.0100 mmol) in 1,2-$C_6H_4F_2$ (0.448 mL) was prepared in a J Young's valve NMR tube and 50 equivalents of 1,3,5-$C_6H_3F_3$ (0.052 mL) added. The ensuing reaction was followed in situ by ^{1}H and ^{19}F{^{1}H} NMR spectroscopy. The reaction was repeated with 100, 150, 200 and 250 equivalents of 1,3,5-$C_6H_3F_3$, keeping the total volume of the solution constant (0.5 mL, see Figure S22). In each case, quantitative formation of **7** was observed. The measured first order rate constants are given in Table S1.

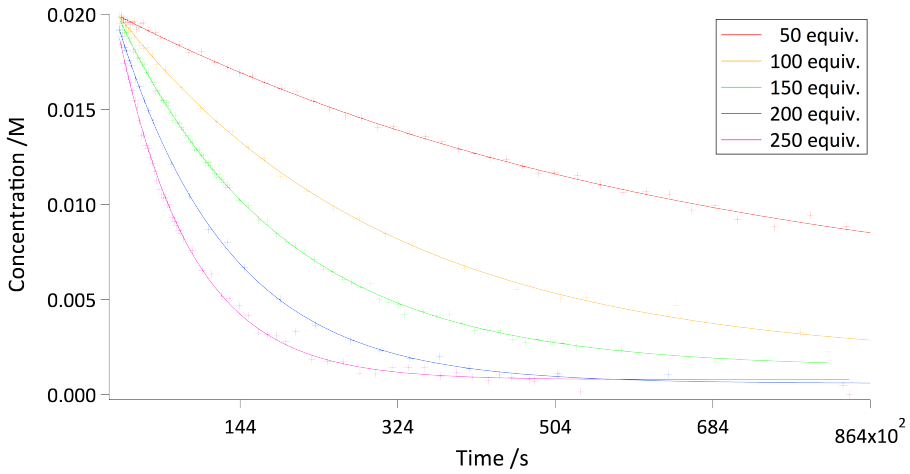

Figure S22: Concentration of **2** on dissolution in mixtures of 1,2-$C_6H_4F_2$ and 1,3,5-$C_6H_3F_3$ (50, 100, 150, 200, 250 equiv./**2**) at 298 K

Table S1: Observed rate constants for substitution reactions of **2** with 1,3,5-$C_6H_3F_3$ at 298 K[4]

equiv. 1,3,5-$C_6H_3F_3$ / **2**	R^2 (fit)	k_{obs} /10^{-3} s^{-1}	error /10^{-3} s^{-1}	data collected /h
50	0.999	0.01218	0.00014	24
100	0.999	0.0326	0.0005	65
150	0.999	0.0530	0.0005	23
200	0.999	0.0788	0.0011	45
250	0.998	0.120	0.002	23

In the presence of an excess of 1,3,5-$C_6H_3F_3$, this substitution reaction can be considered irreversible – the measured equilibrium constant at 298 K for the exchange of 1,2-$C_6H_4F_2$ with 1,3,5-$C_6H_3F_3$ is very large (K > 100, i.e. $k_1 >> k_4$). Rate constants for the processes were determined from a fit of the data using equation 6 (R^2 = 0.998, Figure S23). The resulting rate constants are: k_1 = (1.5 ± 0.9) × 10^{-3} s^{-1} and k_2/k_3 = 12 ± 7.[4]

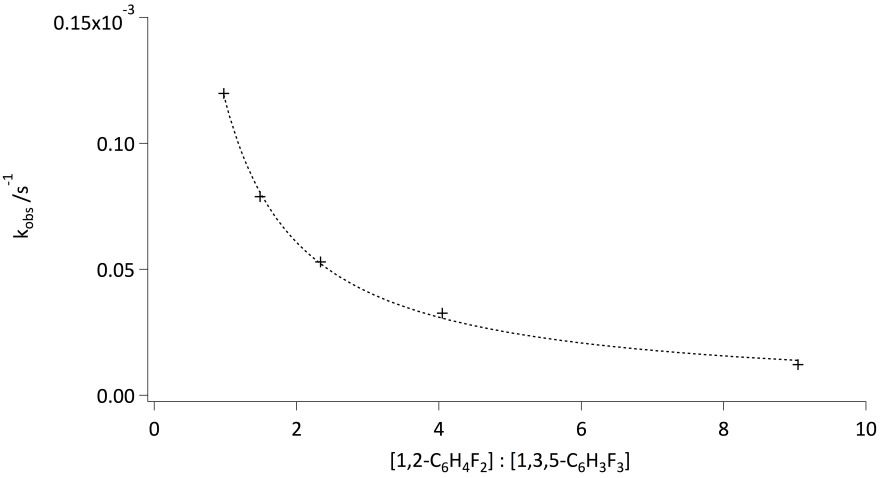

Figure S23: Observed rate constants for substitution reactions of **2** at 298 K as a function of the solution composition.

5.3 Substitution reaction of 6 with 1,2-$C_6H_4F_2$

A solution of **6** (0.0089 g, 0.0050 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was prepared in a J Young's valve NMR tube. Analysis of the solution by ^1H and ^{19}F NMR spectroscopy indicated the quantitative formation of **2** within 10 minutes at 298 K. Assuming the substitution proceeds with pseudo first order reaction kinetics (i.e. $k_1 >> k_4$ and [**b**] >> [**a**] in equation 5) and is complete after approximately 3×$t_{1/2}$, the rate constant for arene dissociation (k_1) has a lower bound of 3 × 10^{-3} s^{-1}.

5.4 Substitution reaction of 7 with 1,2-$C_6H_4F_2$

A solution of **7** (0.0181 g, 0.0100 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was prepared in a J Young's valve NMR tube and the ensuing reaction followed in situ by ^1H and ^{19}F NMR spectroscopy. Complex **2** was formed slowly, with the initial rate for the decrease in [**7**] measured allowing the calculation of the rate constant for arene dissociation (k_1) = (1.96 ± 0.15) × 10^{-6} s^{-1} (using equation 7; 11 days of data collected).[4]

5.5 Substitution reactions of 2, 6 and 7 with acetonitrile

Solutions of the aryl hydride complexes (0.0100 mmol) in d_3-MeCN (0.5 mL) were prepared in a J Young's valve NMR tube and the ensuing reactions followed in situ by ^{1}H and ^{19}F NMR spectroscopy at 298 K. In each case pseudo first order (i.e. $k_1 >> k_4$ and [**b**] >> [**a**] in equation 5) and quantitative formation of **8** was observed (Table S2).

Table S2: Observed rate constants for the formation of **8** in d_3-MeCN at 298 K[4]

complex	R^2 (fit)	k_{obs} /10^{-3} s^{-1}	error /10^{-3} s^{-1}	data collected /h
2	0.995	0.120	0.007	10
6	0.999	2.7	0.3	0.5
7	0.988	0.000384	0.000013	744

6 Crystallography

6.1 Crystallographic data

Crystallographic data for **2**, **5**, **6**, **7**, and **8** are summarised in Table S3. Data were collected on an Oxford Diffraction Gemini Ruby CCD diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation and a low-temperature device [150(2) K]. Data were collected and reduced using CrysAlisPro.[5] All non-hydrogen atoms were refined anisotropically using SHELXL,[6] through the Olex2 interface.[7] Hydride ligands could not be reliably located in the solutions of **2**, **5**, **6**, and **7**; all other hydrogen atoms were placed in calculated positions using the riding model. Full crystallographic details are documented in CIF format and have been deposited with the Cambridge Crystallographic Data Centre (see Table S3). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S3: Crystallographic data.

	2.$^1/_2$($C_6H_4F_2$)	**5**.CH_2Cl_2	**6**.C_6H_5F	**7**	**8**
CCDC	1037606	1037607	1037610	1037611	1037618
Formula	$C_{74}H_{66}BF_{27}IrN_6O_6$	$C_{71}H_{58}BCl_2F_{26}IrN_6O_4$	$C_{77}H_{70}BF_{26}IrN_6O_6$	$C_{71}H_{63}BF_{27}IrN_6O_6$	$C_{67}H_{63}BF_{24}IrN_7O_6$
M	1851.33	1827.14	1872.40	1812.28	1721.25
Crystal System	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/c$	*P*-1	$P2_1/c$
a [Å]	14.29260(15)	19.5682(4)	20.7249(5)	14.3353(2)	13.7820(2)
b [Å]	17.57617(19)	18.7483(3)	22.1162(3)	17.5209(2)	20.0926(2)
c [Å]	30.9787(4)	20.3900(5)	18.7709(4)	30.9758(4)	25.2535(3)
α [deg]	96.4495(9)	90	90	95.9306(10)	90
β [deg]	91.4551(9)	104.772(2)	116.331(3)	91.1596(11)	91.1355(12)
γ [deg]	106.0089(9)	90	90	106.1582(12)	90
V [Å^3]	7420.03(14)	7233.2(3)	7711.1(3)	7423.00(18)	6991.72(16)
Z	4 (*Z*' = 2)	4	4	4 (*Z*' = 2)	4
Density [gcm^{-3}]	1.657	1.678	1.613	1.622	1.635
μ (mm^{-1})	1.925	2.041	1.851	1.922	2.030
θ range [deg]	$2.9 \le \theta \le 25.7°$	$3.3 \le \theta \le 25.7°$	$3.3 \le \theta \le 25.7°$	$3.3 \le \theta \le 27.9°$	$3.4 \le \theta \le 27.9°$
Reflns collected	140009	84388	53806	173726	57568
R_{int}	0.0475	0.0566	0.0605	0.0656	0.0618
Completeness	99.8%	99.8%	99.8%	99.8%	99.8%
No. of data/restr/ param	28177/2984/2493	13701/663/1154	14602/1905/1368	35340/1830/2313	16651/360/1024
R_1 [$I > 2\sigma(I)$]	0.0400	0.0543	0.0500	0.0379	0.0410
wR_2 [all data]	0.0897	0.1423	0.1247	0.0957	0.0967
GoF	1.060	1.043	1.049	1.035	1.015
Largest diff. pk and hole [eÅ^{-3}]	1.41/-1.23	6.09/-1.56	4.11/-2.13	1.18/-0.64	1.44/-1.33

7 References

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[2] J. L. Herde, J. C. Lambert, C. V. Senoff, M. A. Cushing, *Inorg. Synth.*, 1974, **15**, 18–20.

[3] W. E. Buschmann, J. S. Miller, K. Bowman-James, C. N. Miller, *Inorg. Synth.*, 2002, **33**, 83–91.

[4] Errors calculated from data fit.

[5] Oxford Diffraction Ltd, Abingdon, England, 2014.

[6] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.

[7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, H. *J. Appl. Cryst.*, 2009, **42**, 339–341.