Electronic Supplementary Material (ESI) for Dalton Transactions.

Carbon dioxide cleavage across a tungsten-alkylidyne bearing a trianionic pincer-type ligand

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1. General Considerations.

Unless otherwise specified, all manipulations were performed under an inert atmosphere using glove-box techniques. Pentane, diethyl ether (Et_2O), tetrahydrofuran (THF) and benzene (C_6H_6) were dried using a GlassContour drying column. C_6D_6 (Cambridge Isotopes) was dried over sodium-benzophenone ketyl, distilled or vacuum transferred and stored over 4 Å molecular sieves. The ligand precursor [CF_3-ONO]H_3 (**1**) and its corresponding tungsten-alkylidyne [CF_3-ONO]W($\equiv$C^{t}Bu)(THF)$_2$ (**2**) were prepared according to published procedures.[1] ^{1}H and ^{13}C NMR spectra were obtained on Varian INOVA spectrometer (500 MHz), or a Mercury (400 MHz and 300 MHz) for proton. Chemical shifts, reported in δ (ppm), were referenced on the solvent, on the TMS scale for ^{1}H and ^{13}C. The ^{19}F{1H} spectra were acquired on a Varian Mercury Broad Band 300

MHz or Varian Mercury 300 MHz spectrometers. Elemental analyses were performed at Complete Analysis Laboratory Inc., Parsippany, New Jersey.

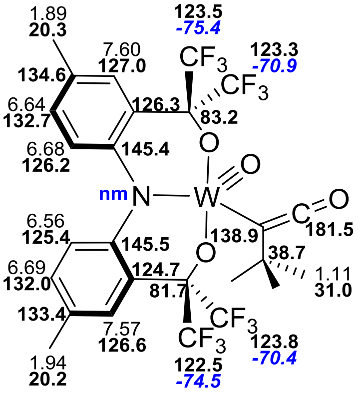
2. Synthesis of complex 6

2.1. Synthesis of complex 6

In an argon filled glove box, a J-Young NMR tube was charged with **1** (0.040 g, 0.043 mmol) in deuterated benzene, as a dark blue solution. 1 atm of CO_2 was admitted to this solution and heated at 60°C for 20h. A color change from dark blue to dark green is observed. The solvent was evaporated under reduced pressure to yield the tungsten oxo-ketene complex **6**. Yield (0.035g, 98%). For obtaining single crystals suitable for X-Ray diffraction complex **6** was dissolved in pentane and filtered to remove any impurity. The filtrate was reduced under vacuum and dissolved in a minimum amount of ether. Slow diffusion of pentane into this concentrated solution of **6** at -23°C results in single crystals. ^{1}H NMR (C_6D_6, 300 MHz) δ (ppm): δ 7.63 (s, 1H, Ar-*H*), 7.59 (s, 1H, Ar-*H*), 6.76-6.55 (m, 4H, Ar-*H*), 1.97 (s, 3H, Ar-C*H*$_3$), 1.92 (s, 3H, Ar-C*H'*$_3$), 1.16 (s, 9H, ^{t}Bu). ^{13}C determined by ^{1}H-^{13}C gHSQC and gHMBC experiments: (C_6D_6): δ = 181.5 (s, WC_α=C_β=O), 145.5 (s, Ar *C*), 145.4 (s, Ar *C*), 138.9 (s, WC_α=C_β=O), 134.6 (s, Ar *C*), 133.4 (s, Ar *C*), 132.7 (s, Ar *C*), 132.0 (s, Ar *C*), 127.0 (s, Ar *C*), 126.6 (s, Ar *C*), 126.3 (s, Ar C), 126.2 (s, Ar *C*), 125.4 (s, Ar *C*), 124.7 (s, Ar *C*), 123.8 (s, *C*F_3), 123.5 (s, *C*F_3'), 123.3 (s, *C*F_3''), 122.5 (s, *C*F_3'''), 83.2 (s, *C*$(CF_3)_2$), 81.7 (s, *C'*$(CF_3)_2$) 38.7 (s, W-C*C*$(CH_3)_3$), 31.0 (s, W-CC(*C*H_3)$_3$), 20.3 (s, Ar-*C*H_3), 20.2 (s, Ar-*C*H_3). ^{19}F NMR (C_6D_6, 300 MHz) δ (ppm): -70.4 (q, 3F,C*F*$_3$) , -70.9 (q, 3F,C*F*$_3$''), -74.7 (q, 3F,C*F*$_3$'''), -75.29 (q, 3F,C*F*$_3$'). IR: 2962, 2057, 1669, 1491, 1252, 1204, 1170, 1107, 961, 704 cm^{-1}. Elemental analysis calcd. (%) for $C_{26}H_{21}F_{12}NO_4W$ (823.28 g/mol): C 37.93, H 2.57, N 1.70; Found: C 38.01, H 2.63, N 1.96.

3. NMR Spectroscopic Data of Complex 6

3.1. NMR Spectroscopic Data of Complex 6



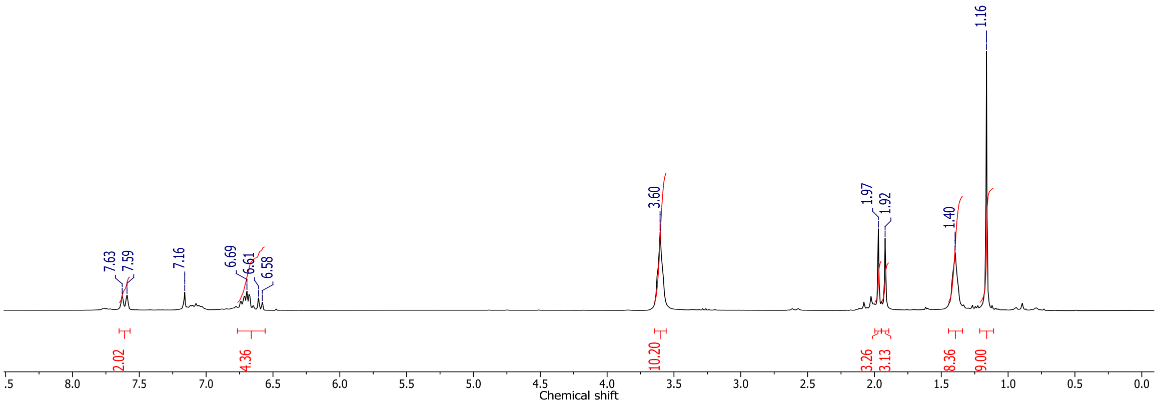


Figure S1. ^{1}H NMR spectrum of **6** in C_6D_6 (resonances at 3.60 and 1.40 ppm are THF).

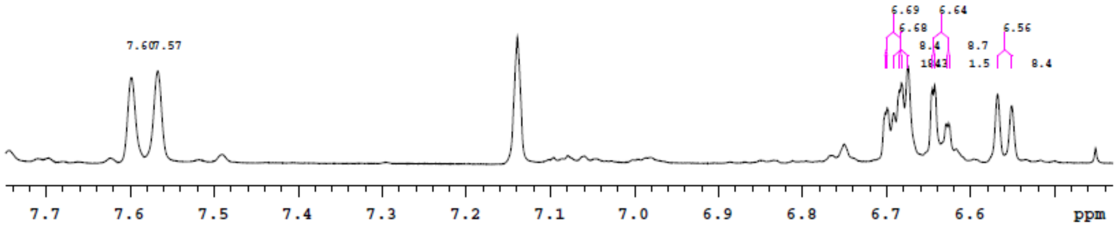


Figure S2. Expansion of ^{1}H NMR spectrum of **6** in C_6D_6.

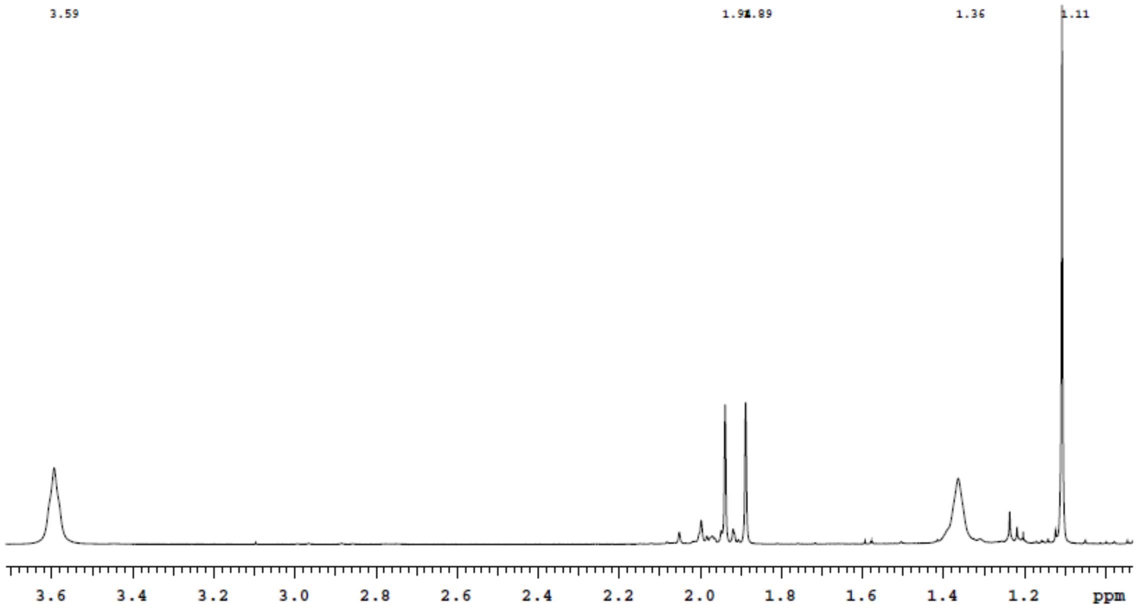


Figure S3. Expansion of ^{1}H NMR spectrum of **6** in C_6D_6.

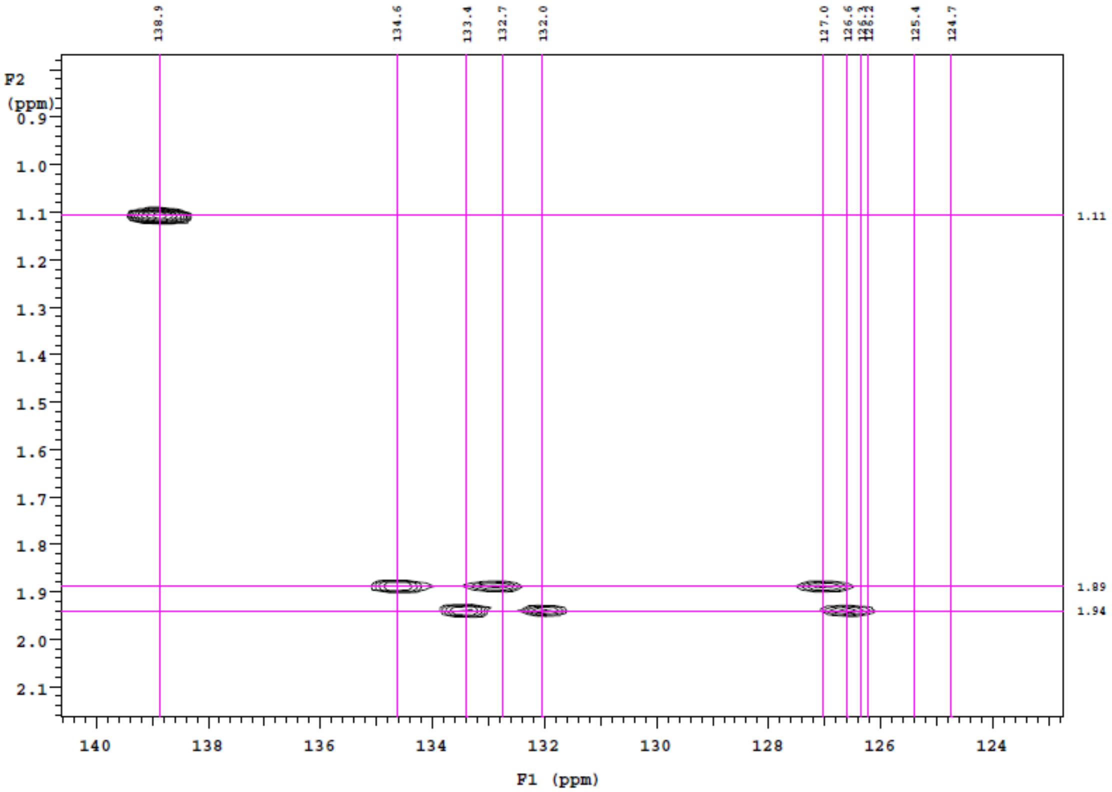


Figure S4. Expansion of ^{1}H-^{13}C gHMBC spectrum of **6** in C_6D_6.

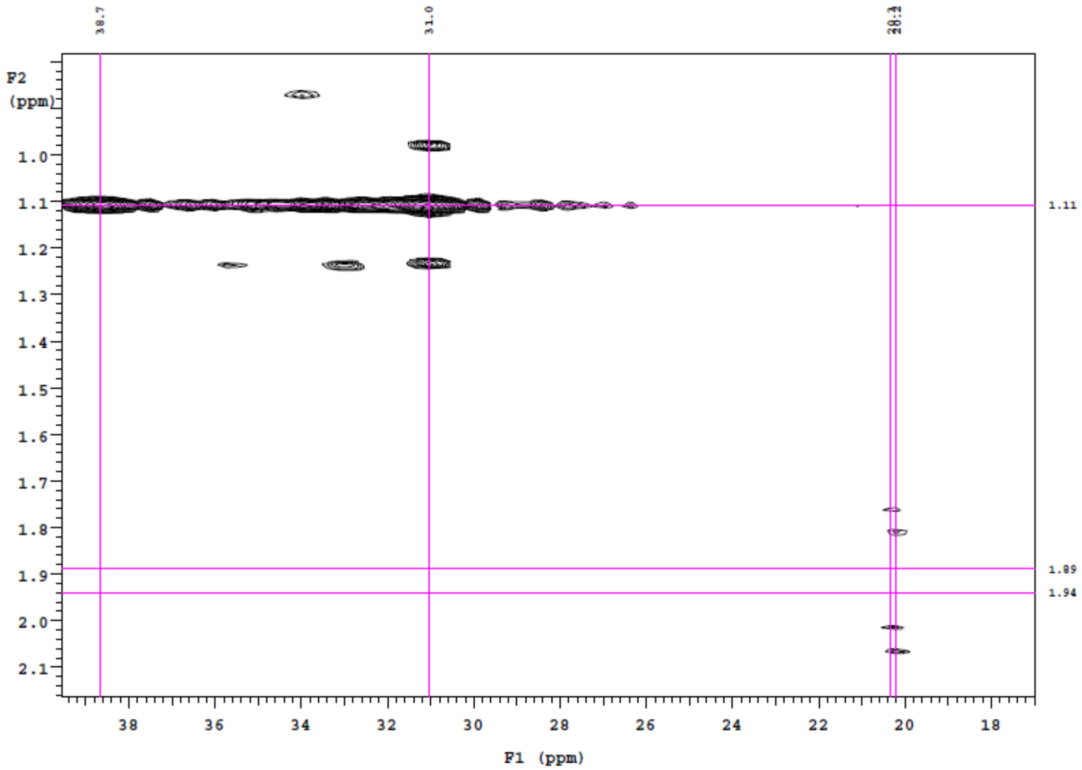


Figure S5. Expansion of ^{1}H-^{13}C gHMBC spectrum of **6** in C_6D_6.

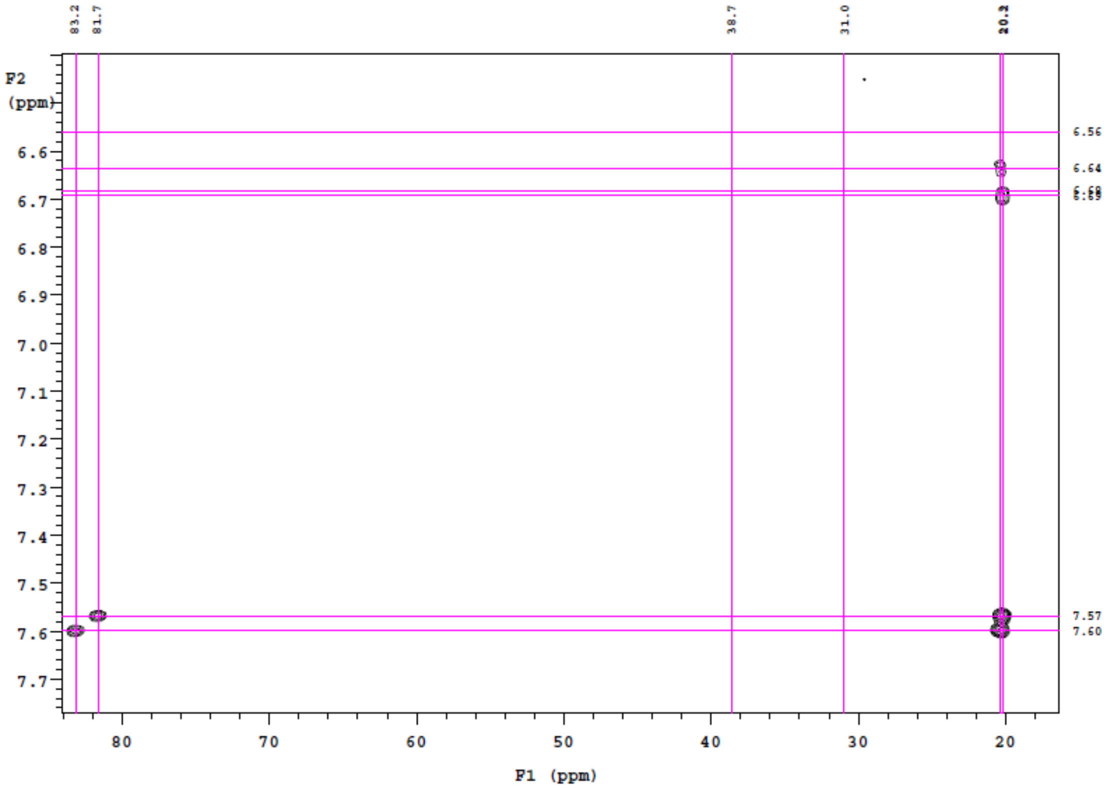


Figure S6. Expansion of ^{1}H-^{13}C gHMBC spectrum of **6** in C_6D_6.

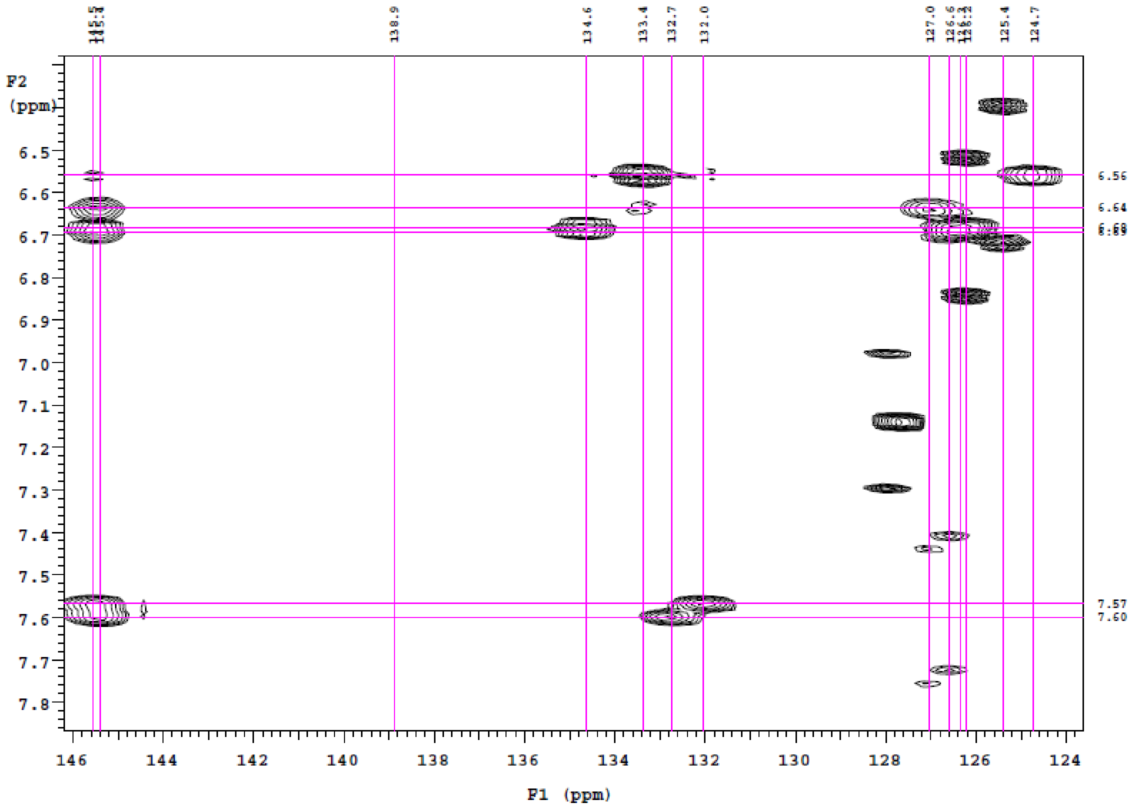


Figure S7. Expansion of ^{1}H-^{13}C gHMBC spectrum of **6** in C_6D_6.

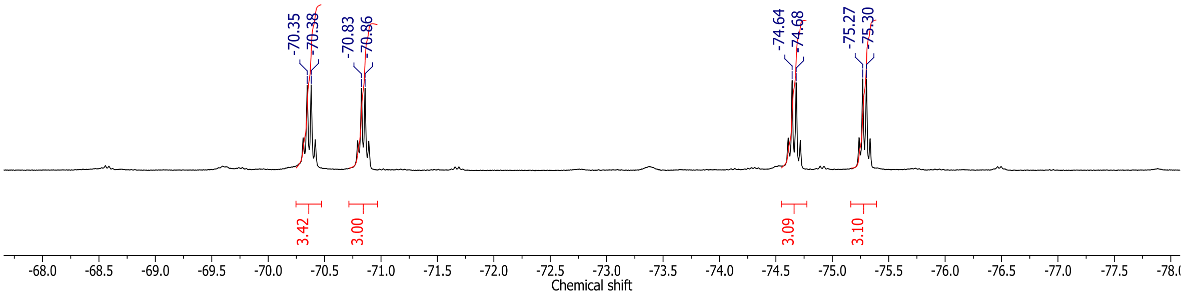


Figure S8. ^{19}F NMR spectrum of **6** in C_6D_6.

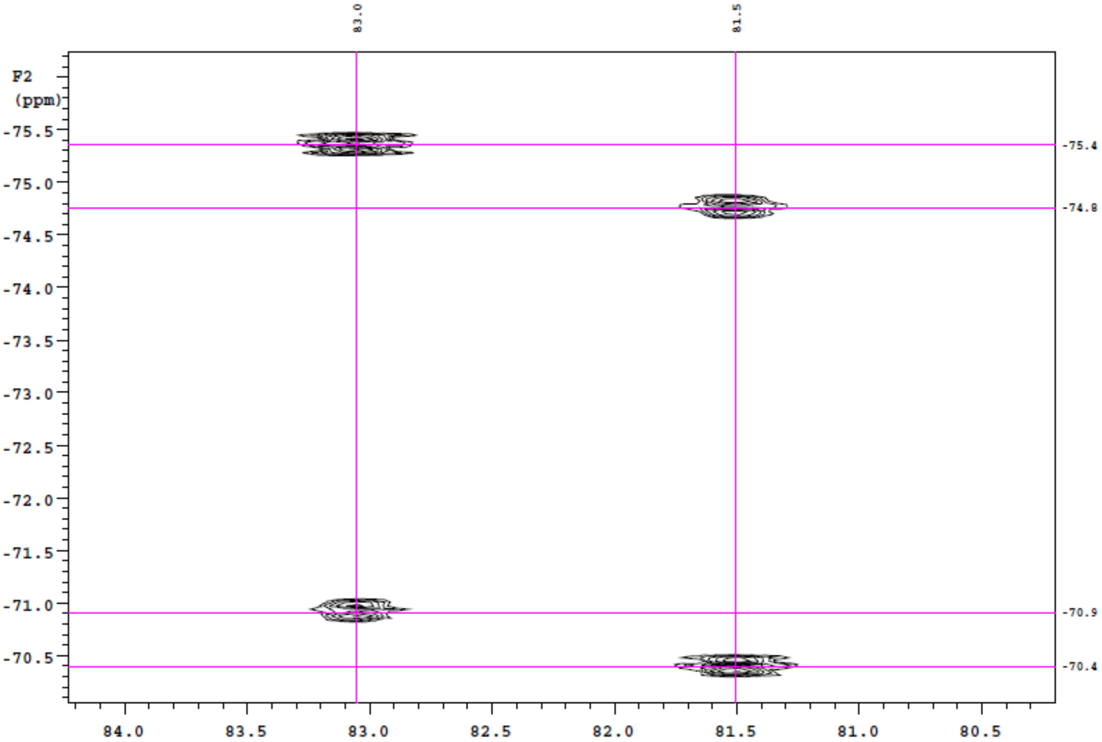


Figure S9. Expansion of ^{19}F-^{13}C gHMBC spectrum of **6** in C_6D_6.

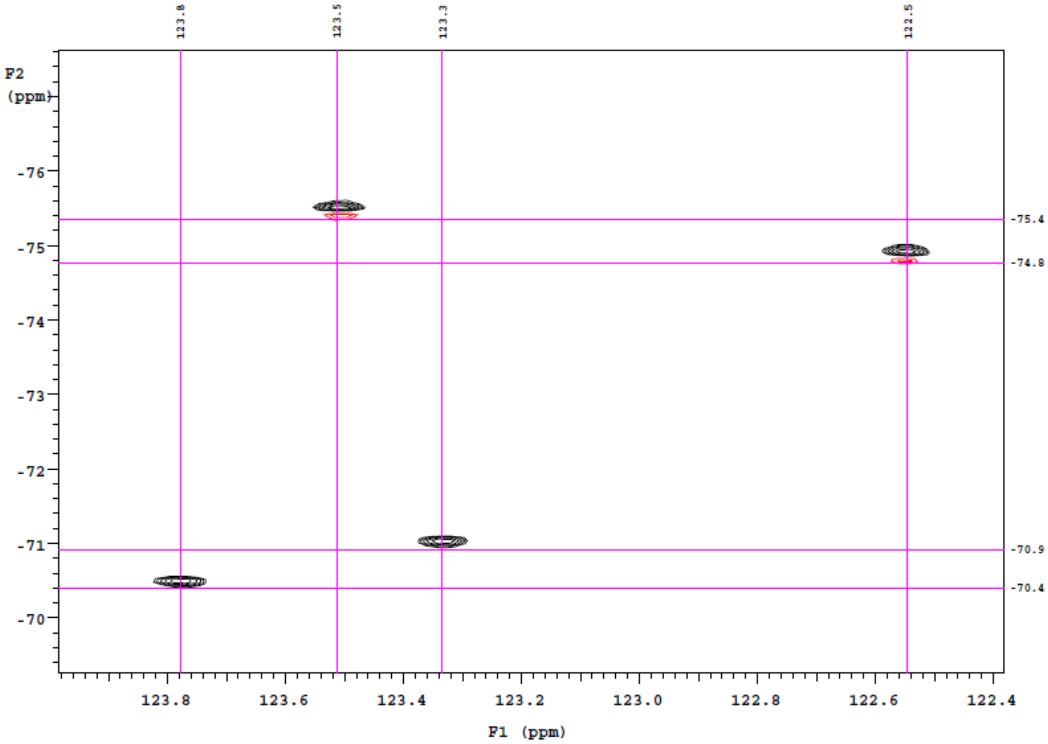


Figure S10. Expansion of ^{19}F-^{13}C gHSQC spectrum of **6** in C_6D_6.

4. IR Spectroscopic Data of Complex 6

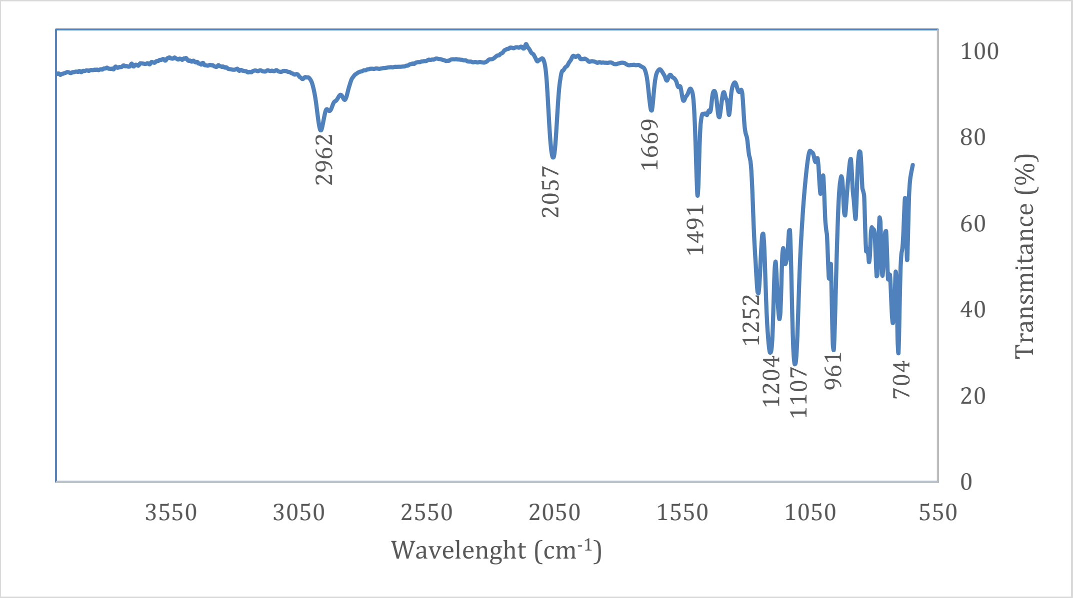


Figure S11. IR spectrum of complex **6**.

5. X-Ray Crystallography for complex 6

5.1. Experimental procedure for structure of complex 6

X-Ray Intensity data were collected at 100 K on a Bruker **DUO** diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector.

Raw data frames were read by program SAINT[2] and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in SHELXTL2013, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. In the final cycle of refinement, 6377 reflections (of which 5888 are observed with $I > 2\sigma(I)$) were used to refine 402 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 2.05%, 4.38% and 1.162, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

5.2. **Crystal structure of complex 6**

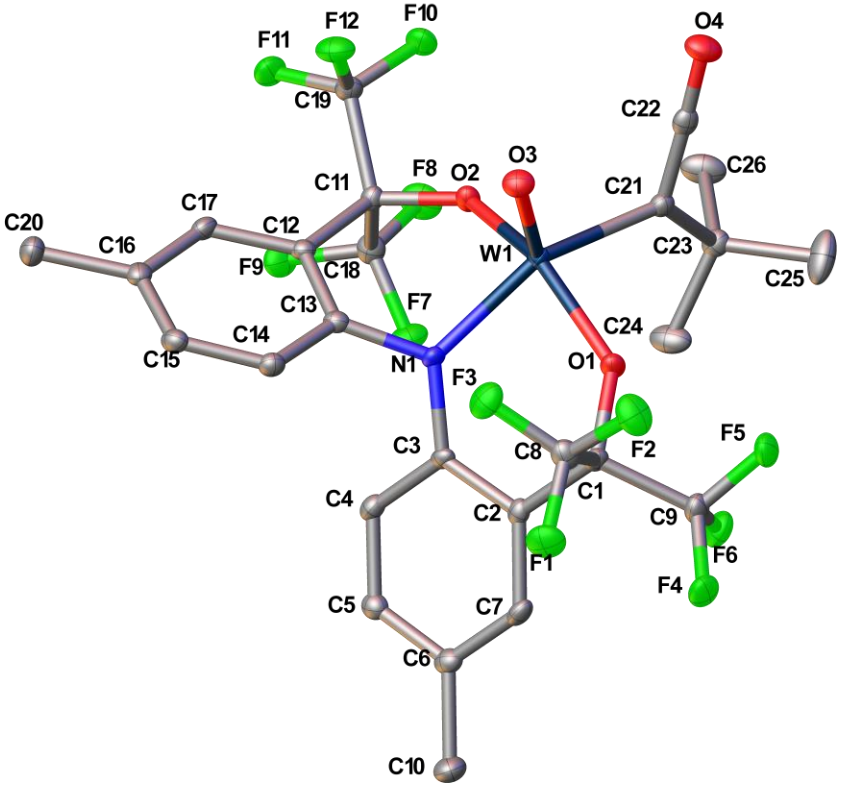


Figure S12. Molecular structure of **6**. Ellipsoids shown at 50% probability level and hydrogens removed for clarity.

Table S1. Crystal data and structure refinement for complex **6**.

Identification code	face	
Empirical formula	C26 H21 F12 N O4 W	
Formula weight	823.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 22.3171(17) Å	α= 90°.
	b = 9.1000(7) Å	β= 96.6553(15)°.
	c = 27.541(2) Å	γ = 90°.
Volume	5555.5(7) Å^3	
Z	8	
Density (calculated)	1.969 Mg/m^3	
Absorption coefficient	4.274 mm^{-1}	
F(000)	3184	
Crystal size	0.259 x 0.142 x 0.087 mm^3	
Theta range for data collection	1.489 to 27.497°.	
Index ranges	$-28\leq h\leq 27$, $-11\leq k\leq 11$, $-35\leq l\leq 35$	
Reflections collected	48404	
Independent reflections	6377 [R(int) = 0.0432]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Analytical	
Max. and min. transmission	0.8408 and 0.5877	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6377 / 0 / 402	
Goodness-of-fit on F^2	1.162	
Final R indices [I>2sigma(I)]	R1 = 0.0205, wR2 = 0.0438 [5888]	
R indices (all data)	R1 = 0.0236, wR2 = 0.0446	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.406 and -1.285 e.Å^{-3}	

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	1121(1)	6283(1)	1364(1)	11(1)
F(1)	2546(1)	4552(2)	210(1)	25(1)
F(2)	1904(1)	3139(2)	503(1)	28(1)
F(3)	1650(1)	5331(2)	276(1)	23(1)
F(4)	3200(1)	3587(2)	1024(1)	25(1)
F(5)	2479(1)	2790(2)	1409(1)	24(1)
F(6)	3027(1)	4598(2)	1704(1)	24(1)
F(7)	1670(1)	10006(2)	1838(1)	22(1)
F(8)	968(1)	10338(2)	2302(1)	27(1)
F(9)	1063(1)	11840(2)	1709(1)	24(1)
F(10)	-117(1)	9102(2)	1990(1)	21(1)
F(11)	-158(1)	11093(2)	1571(1)	25(1)
F(12)	-356(1)	9013(2)	1212(1)	24(1)
O(1)	1816(1)	5084(2)	1284(1)	15(1)
O(2)	788(1)	8001(2)	1641(1)	14(1)
O(3)	534(1)	5578(2)	992(1)	18(1)
O(4)	109(1)	3863(2)	1978(1)	23(1)
N(1)	1556(1)	7742(2)	992(1)	13(1)
C(1)	2310(1)	5121(3)	1016(1)	13(1)
C(2)	2574(1)	6663(3)	985(1)	13(1)
C(3)	2190(1)	7885(3)	980(1)	12(1)
C(4)	2440(1)	9292(3)	952(1)	15(1)
C(5)	3043(1)	9487(3)	908(1)	16(1)
C(6)	3429(1)	8284(3)	897(1)	16(1)
C(7)	3188(1)	6891(3)	942(1)	16(1)
C(8)	2102(1)	4522(3)	494(1)	18(1)
C(9)	2761(1)	4018(3)	1290(1)	18(1)
C(10)	4087(1)	8494(3)	840(1)	23(1)
C(11)	676(1)	9441(3)	1489(1)	13(1)
C(12)	794(1)	9741(3)	962(1)	12(1)

C(13)	1198(1)	8870(3)	738(1)	13(1)
C(14)	1276(1)	9133(3)	247(1)	15(1)
C(15)	990(1)	10301(3)	-2(1)	15(1)
C(16)	618(1)	11243(3)	224(1)	16(1)
C(17)	519(1)	10929(3)	702(1)	15(1)
C(18)	1095(1)	10420(3)	1844(1)	18(1)
C(19)	3(1)	9677(3)	1568(1)	16(1)
C(20)	327(1)	12562(3)	-40(1)	21(1)
C(21)	1067(1)	5255(3)	2022(1)	13(1)
C(22)	560(1)	4502(3)	2004(1)	15(1)
C(23)	1484(1)	5457(3)	2508(1)	15(1)
C(24)	2024(1)	6417(4)	2415(1)	25(1)
C(25)	1698(2)	3949(3)	2697(1)	35(1)
C(26)	1125(1)	6243(4)	2873(1)	26(1)

Table S3. Bond lengths [Å] and angles [°] for complex **6**.

W(1)-O(3)	1.6936(18)
W(1)-O(2)	1.9269(17)
W(1)-O(1)	1.9301(17)
W(1)-N(1)	1.997(2)
W(1)-C(21)	2.054(2)
F(1)-C(8)	1.332(3)
F(2)-C(8)	1.335(3)
F(3)-C(8)	1.334(3)
F(4)-C(9)	1.346(3)
F(5)-C(9)	1.342(3)
F(6)-C(9)	1.332(3)
F(7)-C(18)	1.338(3)
F(8)-C(18)	1.326(3)
F(9)-C(18)	1.345(3)
F(10)-C(19)	1.330(3)
F(11)-C(19)	1.338(3)
F(12)-C(19)	1.334(3)
O(1)-C(1)	1.396(3)
O(2)-C(11)	1.389(3)
O(4)-C(22)	1.158(3)
N(1)-C(3)	1.425(3)
N(1)-C(13)	1.432(3)
C(1)-C(2)	1.527(3)
C(1)-C(9)	1.554(3)
C(1)-C(8)	1.555(3)
C(2)-C(3)	1.403(3)
C(2)-C(7)	1.405(4)
C(3)-C(4)	1.402(4)
C(4)-C(5)	1.377(4)
C(5)-C(6)	1.395(4)
C(6)-C(7)	1.389(4)
C(6)-C(10)	1.506(4)
C(11)-C(12)	1.531(3)

C(11)-C(18)	1.553(3)
C(11)-C(19)	1.557(3)
C(12)-C(13)	1.396(3)
C(12)-C(17)	1.399(3)
C(13)-C(14)	1.404(3)
C(14)-C(15)	1.381(3)
C(15)-C(16)	1.391(4)
C(16)-C(17)	1.388(3)
C(16)-C(20)	1.511(3)
C(21)-C(22)	1.319(4)
C(21)-C(23)	1.551(3)
C(23)-C(25)	1.525(4)
C(23)-C(24)	1.533(4)
C(23)-C(26)	1.535(4)

O(3)-W(1)-O(2)	103.89(8)
O(3)-W(1)-O(1)	106.99(8)
O(2)-W(1)-O(1)	148.92(8)
O(3)-W(1)-N(1)	109.21(9)
O(2)-W(1)-N(1)	84.08(8)
O(1)-W(1)-N(1)	82.62(8)
O(3)-W(1)-C(21)	103.97(9)
O(2)-W(1)-C(21)	87.47(8)
O(1)-W(1)-C(21)	88.49(8)
N(1)-W(1)-C(21)	146.81(9)
C(1)-O(1)-W(1)	137.83(15)
C(11)-O(2)-W(1)	135.29(14)
C(3)-N(1)-C(13)	115.0(2)
C(3)-N(1)-W(1)	128.02(16)
C(13)-N(1)-W(1)	116.68(15)
O(1)-C(1)-C(2)	112.7(2)
O(1)-C(1)-C(9)	103.58(19)
C(2)-C(1)-C(9)	112.9(2)
O(1)-C(1)-C(8)	108.1(2)
C(2)-C(1)-C(8)	110.21(19)
C(9)-C(1)-C(8)	109.2(2)

C(3)-C(2)-C(7)	118.8(2)
C(3)-C(2)-C(1)	119.4(2)
C(7)-C(2)-C(1)	121.8(2)
C(4)-C(3)-C(2)	118.6(2)
C(4)-C(3)-N(1)	119.2(2)
C(2)-C(3)-N(1)	122.2(2)
C(5)-C(4)-C(3)	121.4(2)
C(4)-C(5)-C(6)	120.9(2)
C(7)-C(6)-C(5)	117.8(2)
C(7)-C(6)-C(10)	121.2(2)
C(5)-C(6)-C(10)	121.0(2)
C(6)-C(7)-C(2)	122.3(2)
F(1)-C(8)-F(3)	107.4(2)
F(1)-C(8)-F(2)	107.4(2)
F(3)-C(8)-F(2)	107.0(2)
F(1)-C(8)-C(1)	111.9(2)
F(3)-C(8)-C(1)	110.6(2)
F(2)-C(8)-C(1)	112.2(2)
F(6)-C(9)-F(5)	107.2(2)
F(6)-C(9)-F(4)	107.5(2)
F(5)-C(9)-F(4)	106.3(2)
F(6)-C(9)-C(1)	111.0(2)
F(5)-C(9)-C(1)	111.1(2)
F(4)-C(9)-C(1)	113.3(2)
O(2)-C(11)-C(12)	114.11(19)
O(2)-C(11)-C(18)	106.09(19)
C(12)-C(11)-C(18)	109.8(2)
O(2)-C(11)-C(19)	103.3(2)
C(12)-C(11)-C(19)	112.47(19)
C(18)-C(11)-C(19)	110.8(2)
C(13)-C(12)-C(17)	118.8(2)
C(13)-C(12)-C(11)	120.6(2)
C(17)-C(12)-C(11)	120.6(2)
C(12)-C(13)-C(14)	119.1(2)
C(12)-C(13)-N(1)	123.0(2)
C(14)-C(13)-N(1)	117.8(2)

C(15)-C(14)-C(13)	120.6(2)
C(14)-C(15)-C(16)	121.1(2)
C(17)-C(16)-C(15)	117.8(2)
C(17)-C(16)-C(20)	120.9(2)
C(15)-C(16)-C(20)	121.3(2)
C(16)-C(17)-C(12)	122.3(2)
F(8)-C(18)-F(7)	107.9(2)
F(8)-C(18)-F(9)	107.9(2)
F(7)-C(18)-F(9)	106.7(2)
F(8)-C(18)-C(11)	112.8(2)
F(7)-C(18)-C(11)	109.8(2)
F(9)-C(18)-C(11)	111.5(2)
F(10)-C(19)-F(12)	107.4(2)
F(10)-C(19)-F(11)	106.9(2)
F(12)-C(19)-F(11)	107.7(2)
F(10)-C(19)-C(11)	111.2(2)
F(12)-C(19)-C(11)	110.0(2)
F(11)-C(19)-C(11)	113.4(2)
C(22)-C(21)-C(23)	121.3(2)
C(22)-C(21)-W(1)	110.01(17)
C(23)-C(21)-W(1)	128.04(18)
O(4)-C(22)-C(21)	178.1(3)
C(25)-C(23)-C(24)	110.4(2)
C(25)-C(23)-C(26)	111.2(2)
C(24)-C(23)-C(26)	108.9(2)
C(25)-C(23)-C(21)	108.7(2)
C(24)-C(23)-C(21)	109.3(2)
C(26)-C(23)-C(21)	108.3(2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for complex **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W(1)	11(1)	12(1)	10(1)	0(1)	2(1)	1(1)
F(1)	26(1)	33(1)	18(1)	-5(1)	10(1)	2(1)
F(2)	39(1)	20(1)	26(1)	-4(1)	5(1)	-6(1)
F(3)	25(1)	29(1)	15(1)	-2(1)	-2(1)	6(1)
F(4)	24(1)	22(1)	31(1)	4(1)	11(1)	12(1)
F(5)	27(1)	16(1)	30(1)	8(1)	8(1)	5(1)
F(6)	24(1)	28(1)	19(1)	4(1)	-2(1)	8(1)
F(7)	14(1)	26(1)	27(1)	-6(1)	-1(1)	0(1)
F(8)	31(1)	35(1)	15(1)	-8(1)	5(1)	-5(1)
F(9)	26(1)	15(1)	30(1)	-4(1)	3(1)	0(1)
F(10)	21(1)	26(1)	19(1)	4(1)	10(1)	3(1)
F(11)	22(1)	22(1)	33(1)	3(1)	12(1)	9(1)
F(12)	14(1)	34(1)	22(1)	-3(1)	3(1)	-3(1)
O(1)	16(1)	15(1)	16(1)	2(1)	7(1)	4(1)
O(2)	17(1)	14(1)	13(1)	1(1)	6(1)	3(1)
O(3)	16(1)	21(1)	16(1)	-3(1)	1(1)	-2(1)
O(4)	19(1)	22(1)	29(1)	-3(1)	7(1)	-6(1)
N(1)	10(1)	14(1)	15(1)	2(1)	4(1)	4(1)
C(1)	12(1)	14(1)	13(1)	0(1)	4(1)	4(1)
C(2)	15(1)	14(1)	9(1)	1(1)	1(1)	3(1)
C(3)	10(1)	18(1)	8(1)	1(1)	3(1)	3(1)
C(4)	14(1)	17(1)	13(1)	0(1)	1(1)	4(1)
C(5)	15(1)	18(1)	13(1)	2(1)	1(1)	-1(1)
C(6)	13(1)	23(1)	12(1)	2(1)	1(1)	2(1)
C(7)	14(1)	19(1)	14(1)	1(1)	2(1)	8(1)
C(8)	22(1)	17(1)	16(1)	-1(1)	6(1)	1(1)
C(9)	20(1)	15(1)	20(1)	3(1)	5(1)	5(1)
C(10)	14(1)	26(2)	28(1)	4(1)	3(1)	2(1)
C(11)	14(1)	13(1)	11(1)	1(1)	2(1)	3(1)
C(12)	9(1)	15(1)	13(1)	0(1)	2(1)	-1(1)
C(13)	11(1)	15(1)	13(1)	0(1)	2(1)	-1(1)

C(14)	13(1)	16(1)	15(1)	0(1)	4(1)	1(1)
C(15)	13(1)	20(1)	14(1)	2(1)	3(1)	0(1)
C(16)	11(1)	17(1)	19(1)	3(1)	1(1)	-1(1)
C(17)	11(1)	15(1)	20(1)	1(1)	3(1)	3(1)
C(18)	21(1)	19(1)	14(1)	-1(1)	3(1)	2(1)
C(19)	14(1)	18(1)	16(1)	1(1)	4(1)	2(1)
C(20)	20(1)	20(1)	22(1)	7(1)	4(1)	5(1)
C(21)	12(1)	14(1)	14(1)	0(1)	3(1)	2(1)
C(22)	18(1)	15(1)	12(1)	-1(1)	4(1)	5(1)
C(23)	16(1)	18(1)	12(1)	-1(1)	1(1)	2(1)
C(24)	18(1)	41(2)	16(1)	-3(1)	1(1)	-6(1)
C(25)	50(2)	22(2)	26(2)	1(1)	-17(1)	8(2)
C(26)	23(1)	36(2)	20(1)	-12(1)	8(1)	-6(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for complex **6**.

	x	y	z	U(eq)
H(4A)	2188	10129	964	17
H(5A)	3198	10453	884	19
H(7A)	3447	6063	944	19
H(10A)	4246	7595	706	34
H(10B)	4311	8707	1159	34
H(10C)	4131	9315	617	34
H(14A)	1527	8501	85	18
H(15A)	1049	10464	-334	18
H(17A)	255	11544	858	18
H(20A)	343	13402	183	31
H(20B)	-95	12336	-156	31
H(20C)	543	12802	-320	31
H(24A)	2280	6581	2724	37
H(24B)	1879	7363	2278	37
H(24C)	2259	5919	2184	37
H(25A)	1970	4065	3000	52
H(25B)	1913	3458	2452	52
H(25C)	1349	3355	2760	52
H(26A)	1381	6378	3184	39
H(26B)	772	5649	2928	39
H(26D)	991	7204	2742	39

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