Exploring the chemistry and photophysics of substituted picolinates positional isomers in iridium(III)bisphenylpyridine complexes

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S1. NMR spectra of reported compounds

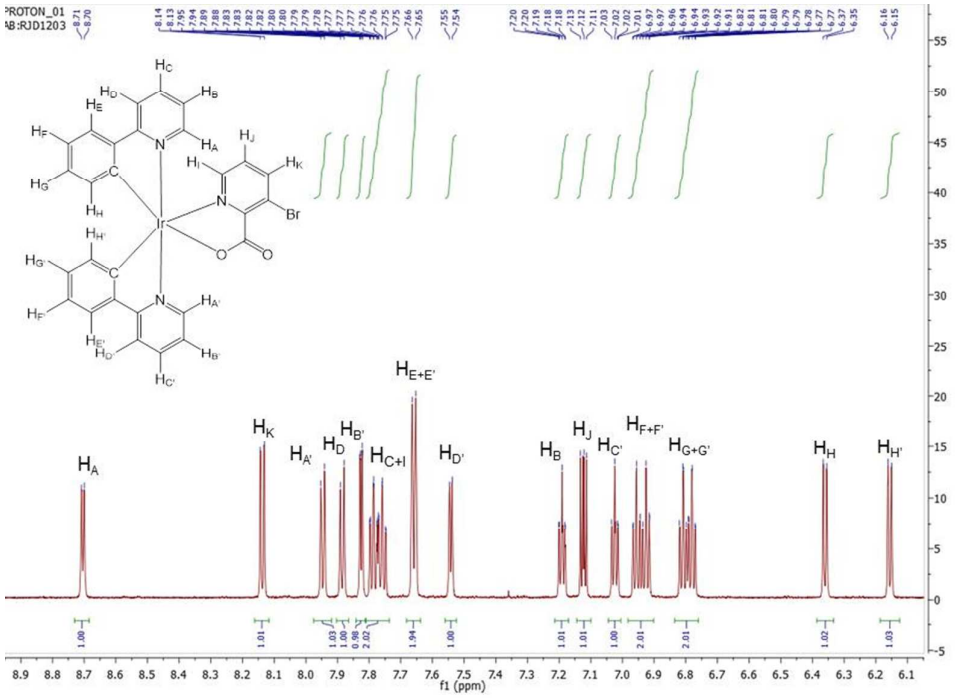

Figure S1. ^{1}H NMR spectrum of **1**, recorded in CD_2Cl_2.

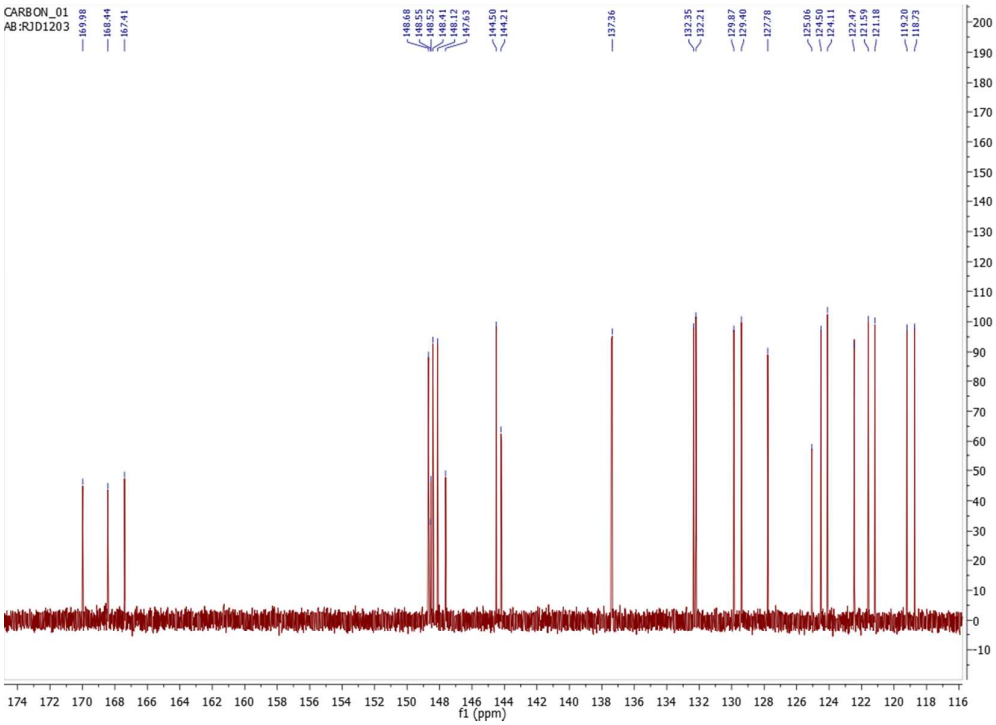

Figure S2. ^{13}C NMR spectrum of **1**, recorded in CD_2Cl_2.

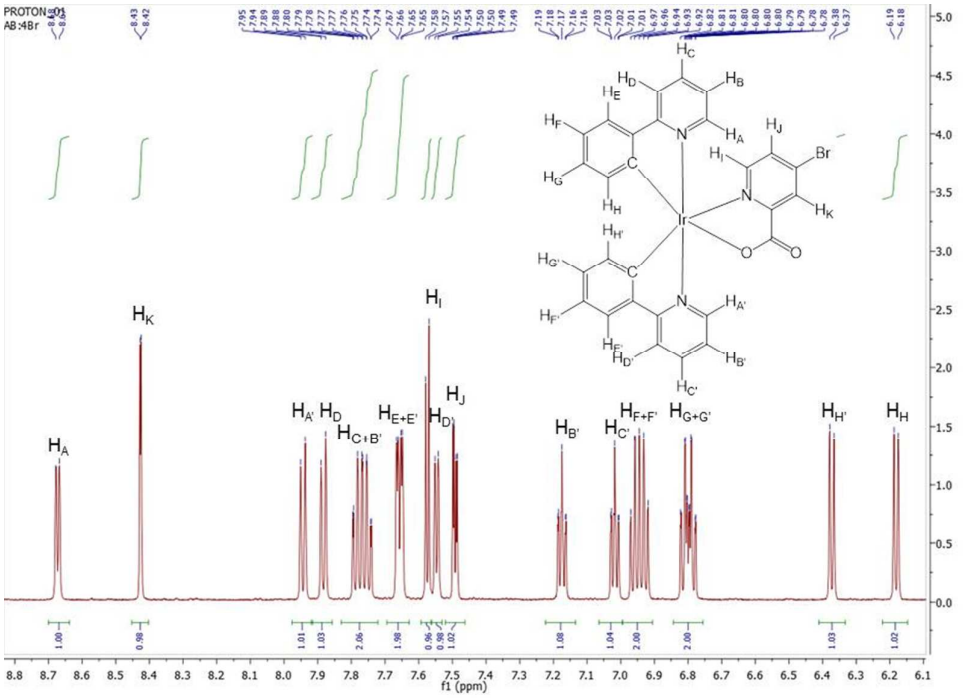

Figure S3. ^{1}H NMR spectrum of **2**, recorded in CD_2Cl_2.

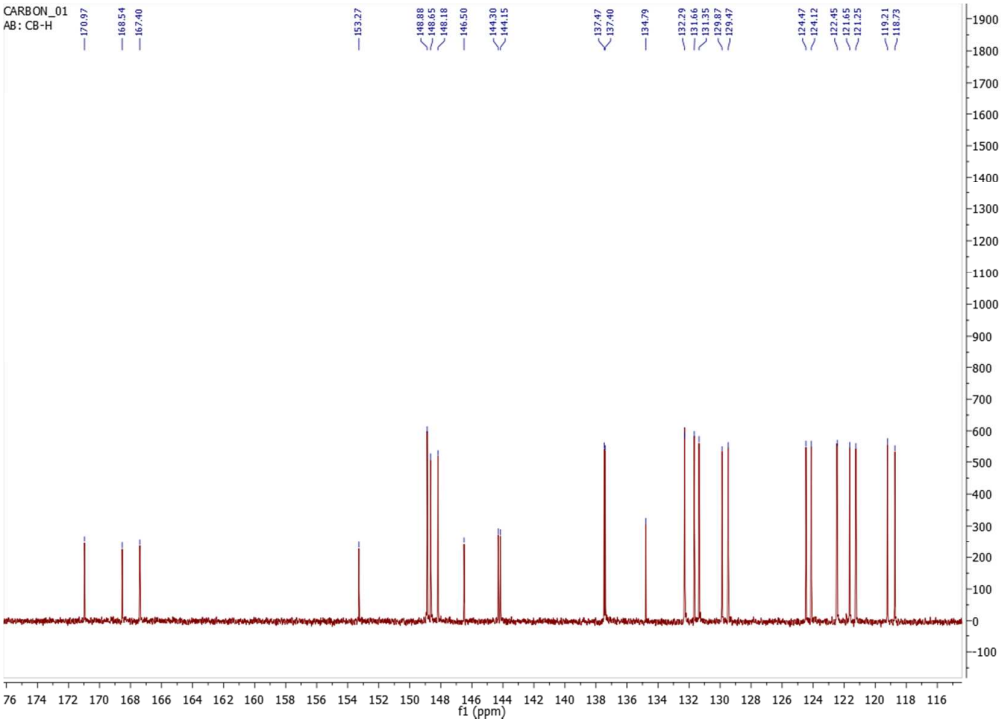

Figure S4. ^{13}C NMR spectrum of **2**, recorded in CD_2Cl_2.

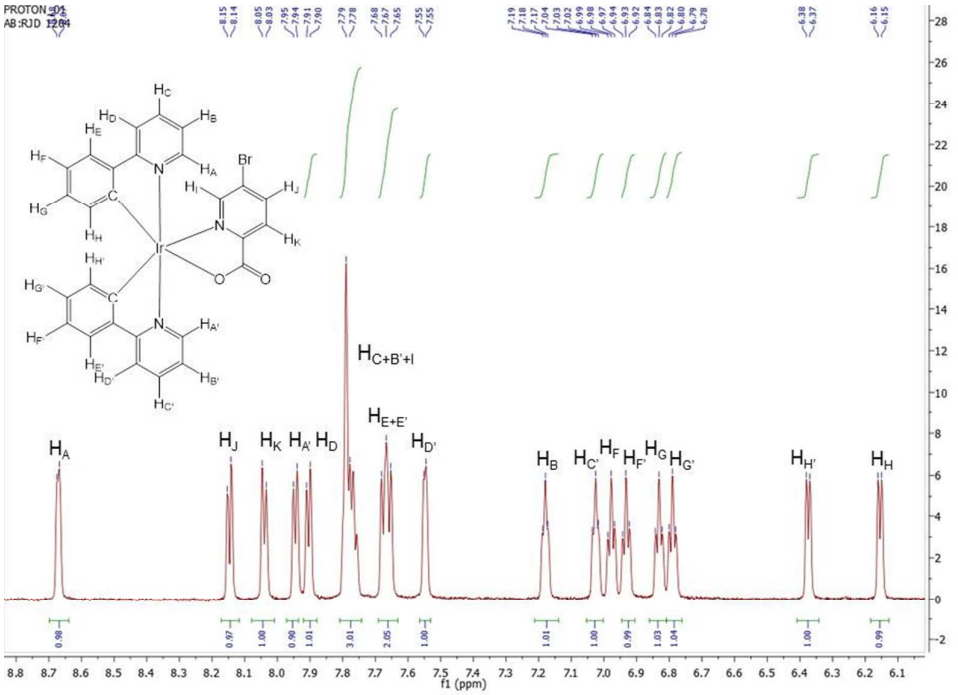

Figure S5. ^{1}H NMR spectrum of **3**, recorded in CD_2Cl_2.

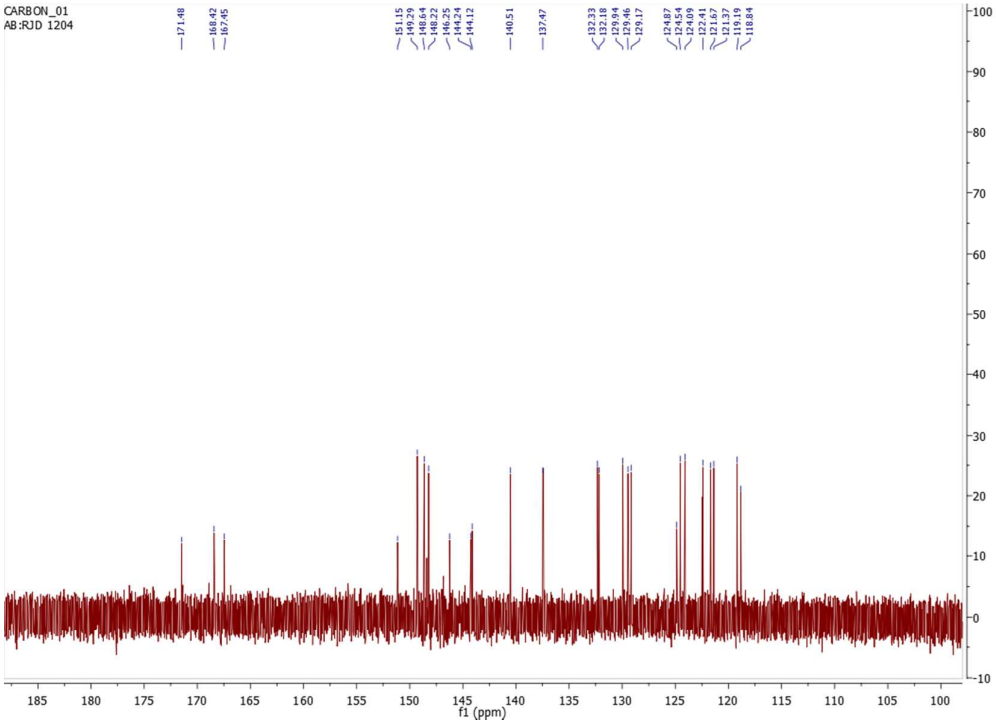

Figure S6. ^{13}C NMR spectrum of **3**, recorded in CD_2Cl_2.

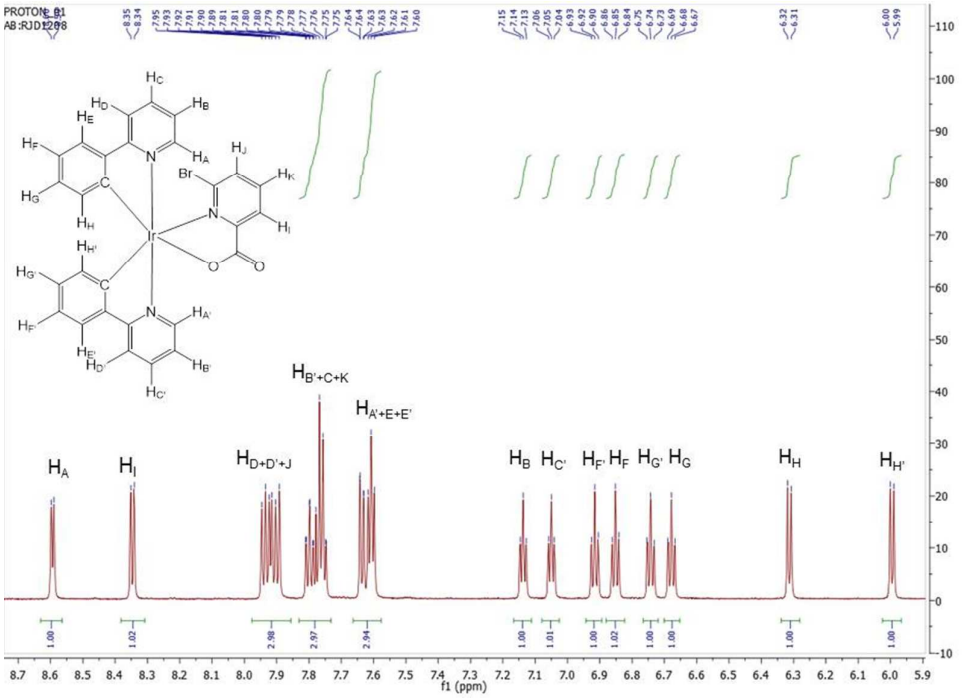

Figure S7. ^{1}H NMR spectrum of **4**, recorded in CD_2Cl_2.

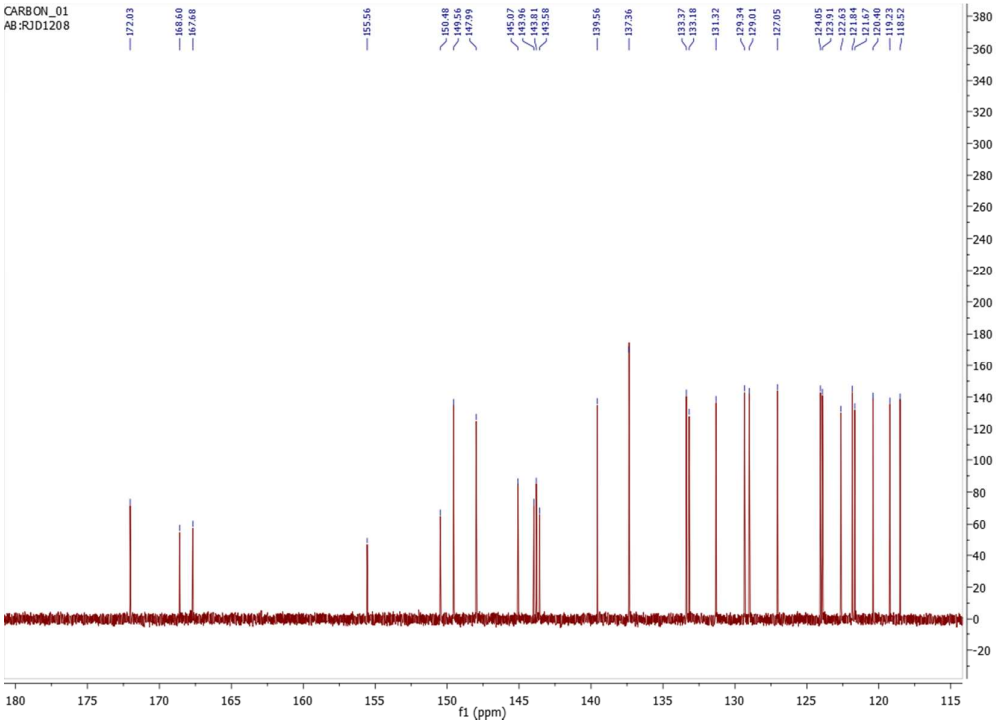

Figure S8. ^{13}C NMR spectrum of **4**, recorded in CD_2Cl_2.

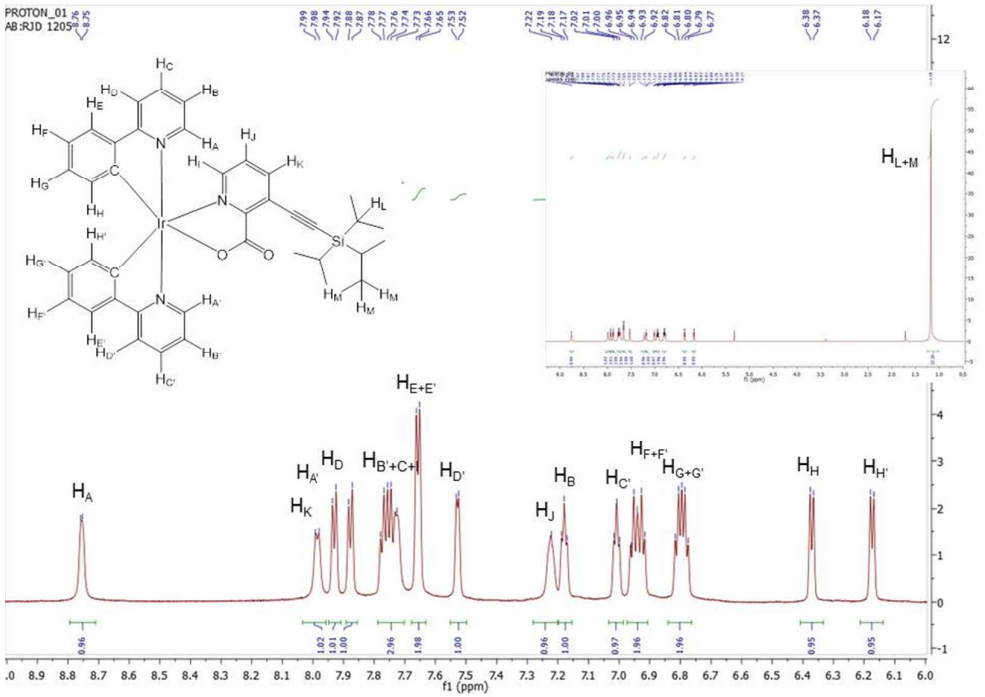

Figure S9. ^{1}H NMR spectrum of **5**, recorded in CD_2Cl_2.

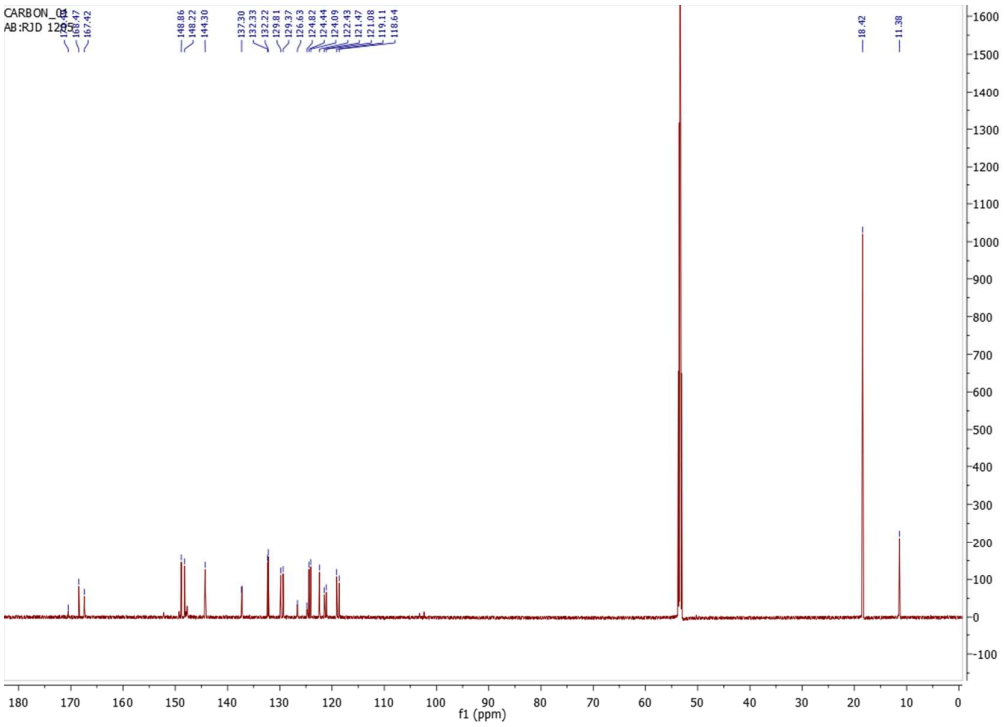

Figure S10. ^{13}C NMR spectrum of **5**, recorded in CD_2Cl_2.

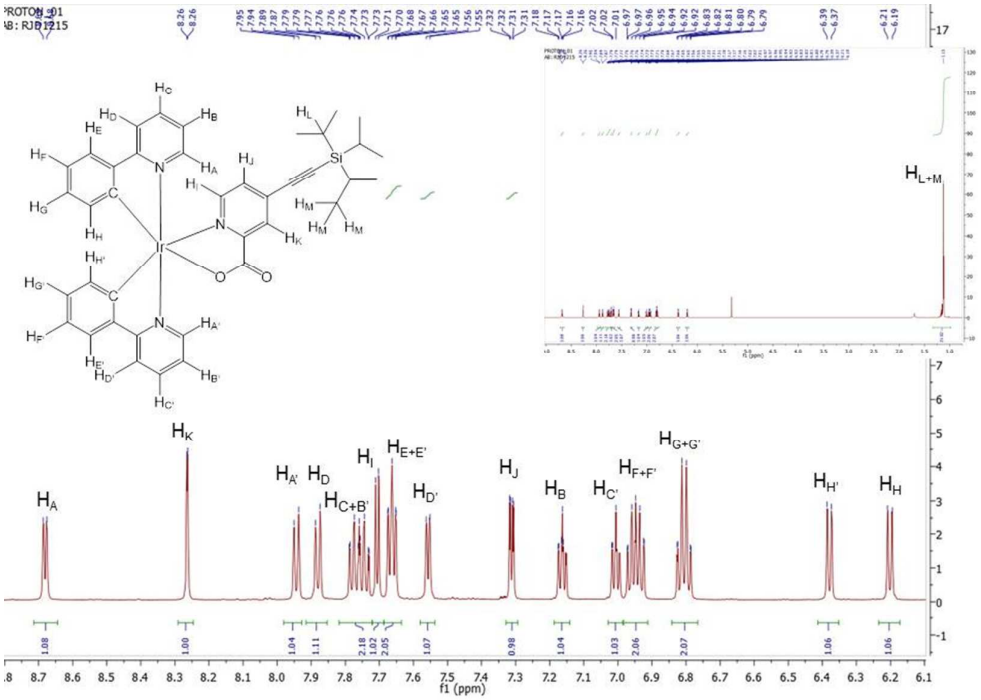

Figure S11. ^{1}H NMR spectrum of **6**, recorded in CD_2Cl_2.

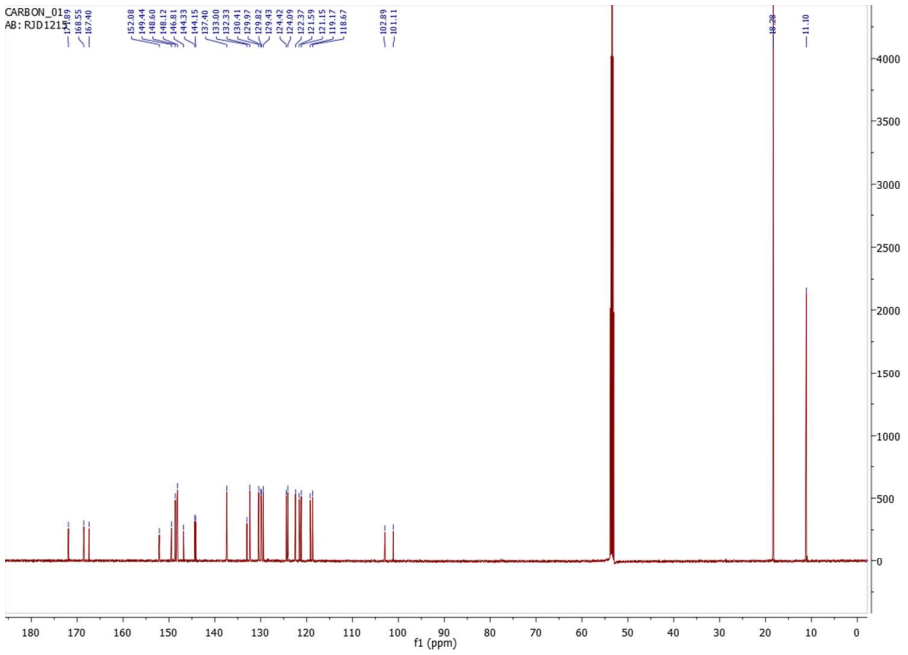

Figure S12. ^{13}C NMR spectrum of **6**, recorded in CD_2Cl_2.

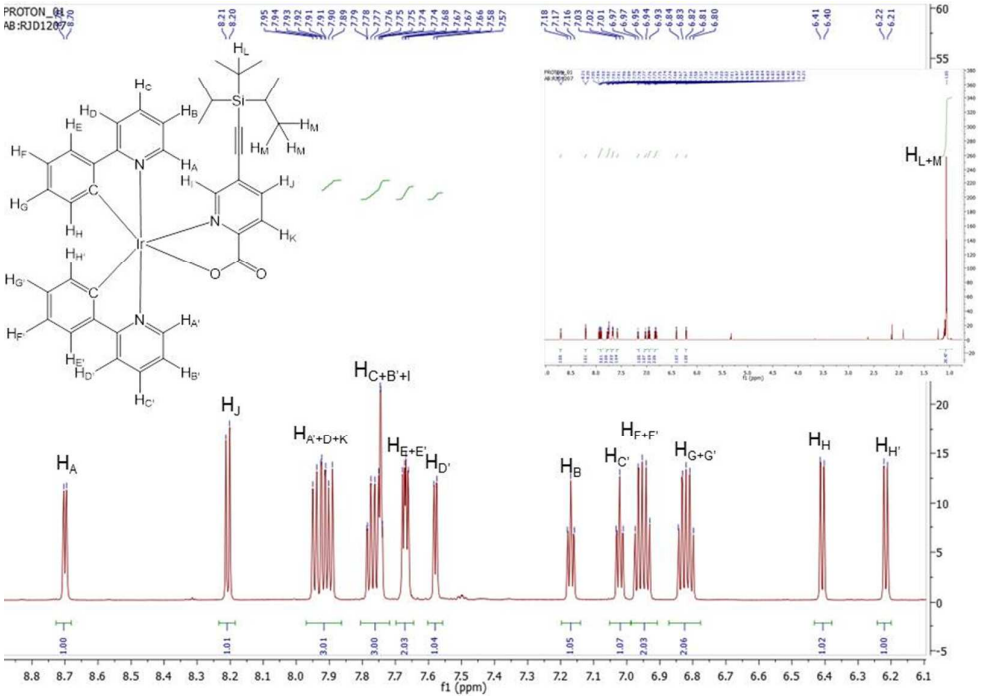

Figure S13. ^{1}H NMR spectrum of **7**, recorded in CD_2Cl_2.

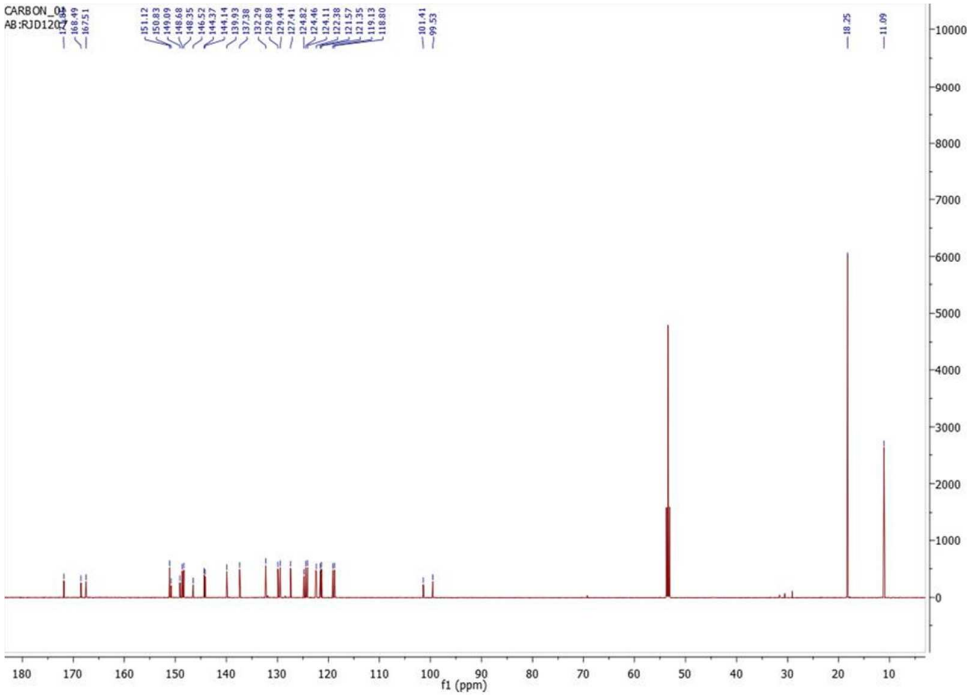

Figure S14. ^{13}C NMR spectrum of **7**, recorded in CD_2Cl_2.

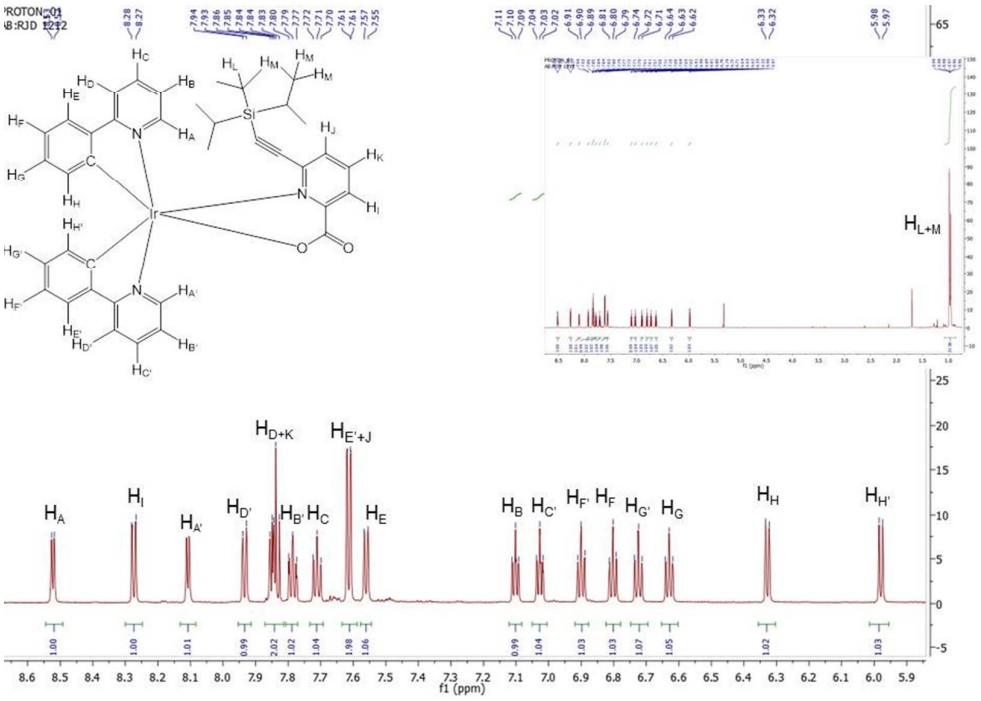

Figure S15. ^{1}H NMR spectrum of **8**, recorded in CD_2Cl_2.

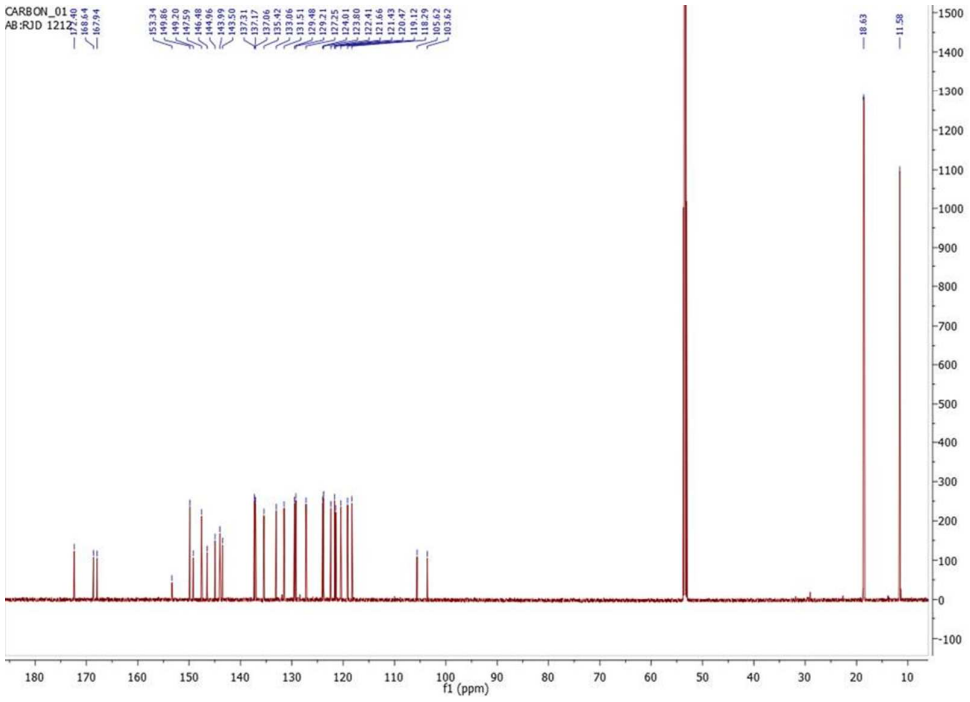

Figure S16. ^{13}C NMR spectrum of **8**, recorded in CD_2Cl_2.

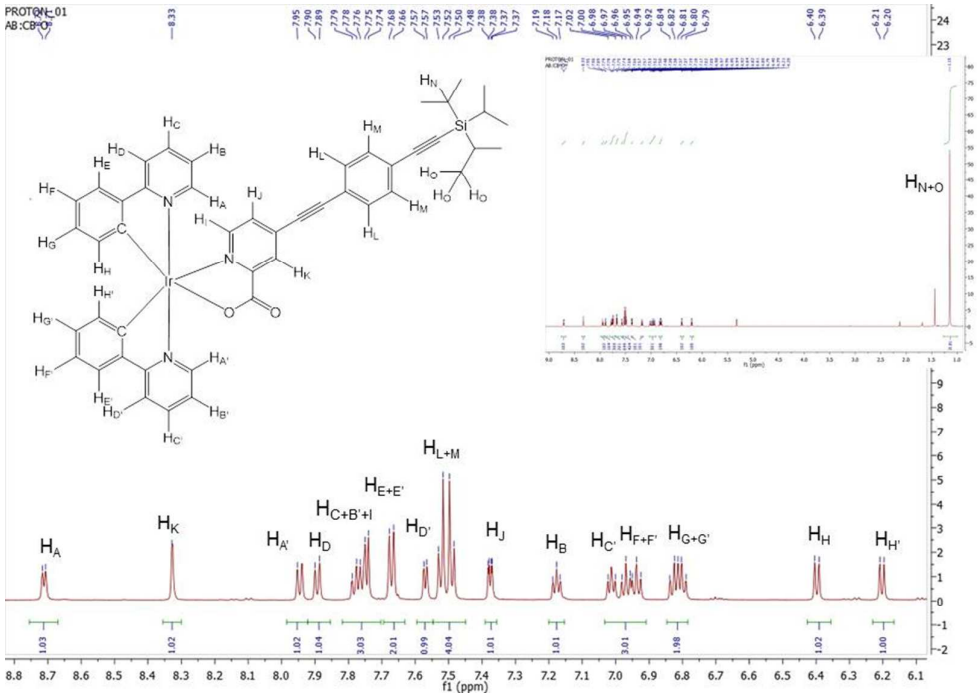

Figure S17. ^{1}H NMR spectrum of **9**, recorded in CD_2Cl_2.

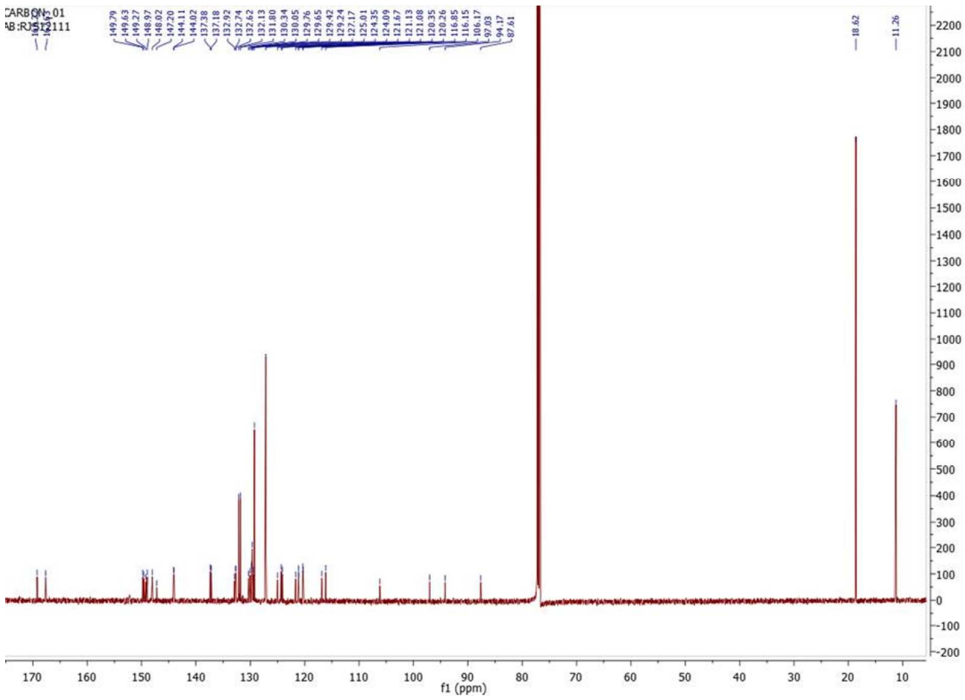

Figure S18. ^{13}C NMR spectrum of **9**, recorded in CD_2Cl_2.

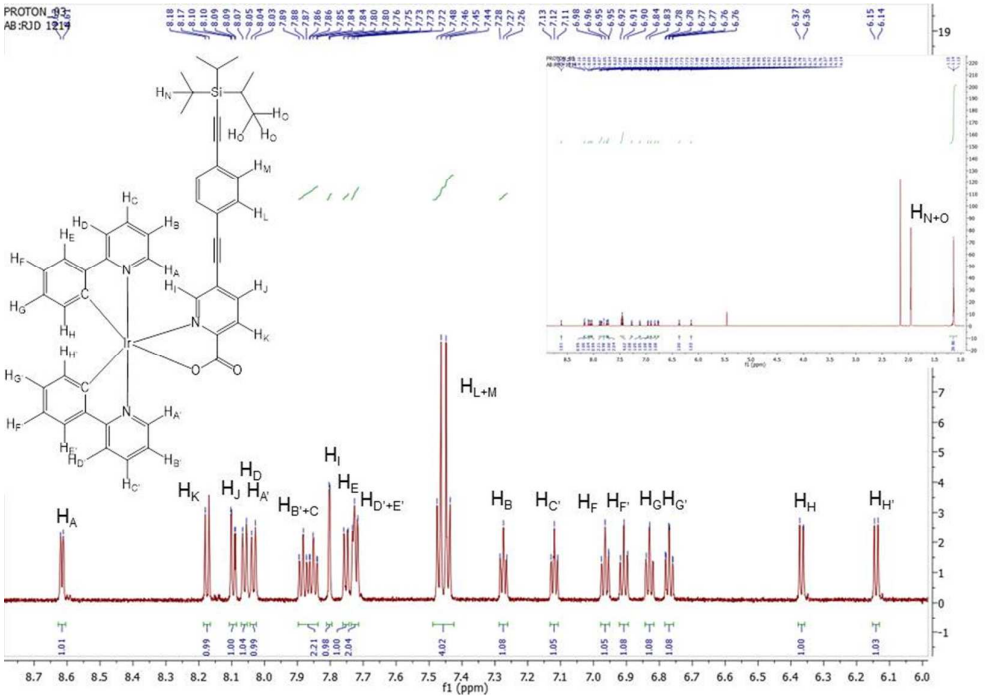

Figure S19. ^{1}H NMR spectrum of **10**, recorded in CD_3CN.

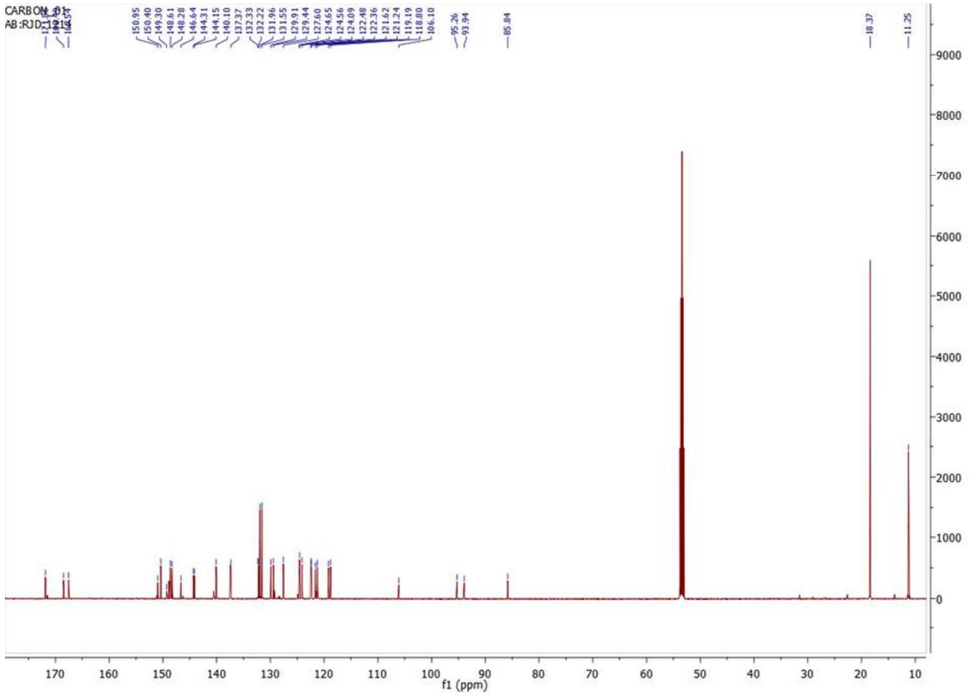

Figure S20. ^{13}C NMR spectrum of **10**, recorded in CD_2Cl_2.

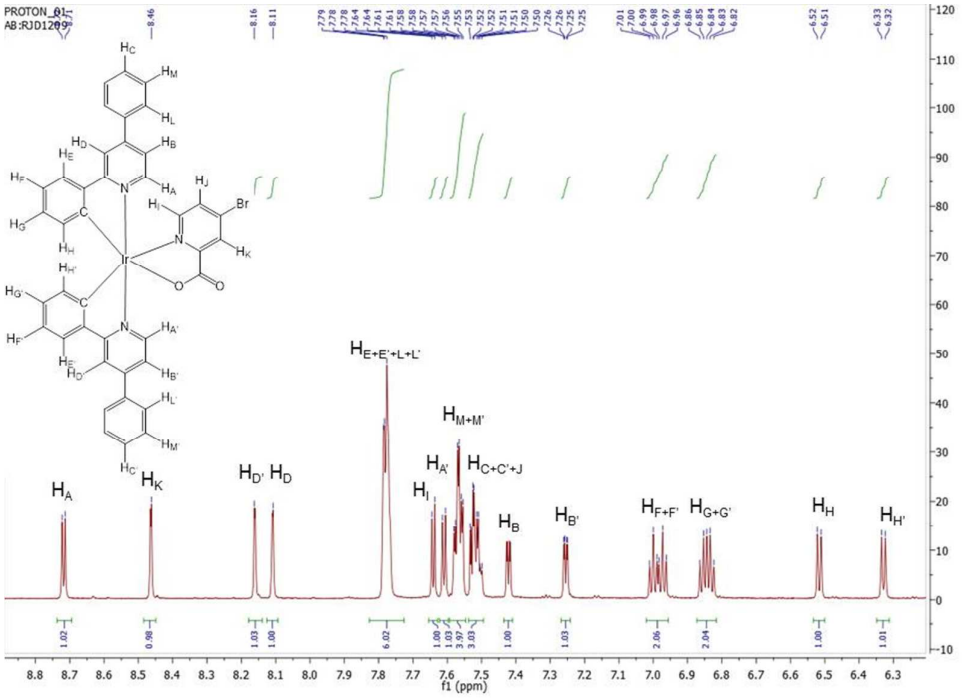

Figure S21. ^{1}H NMR spectrum of **11**, recorded in CD_2Cl_2.

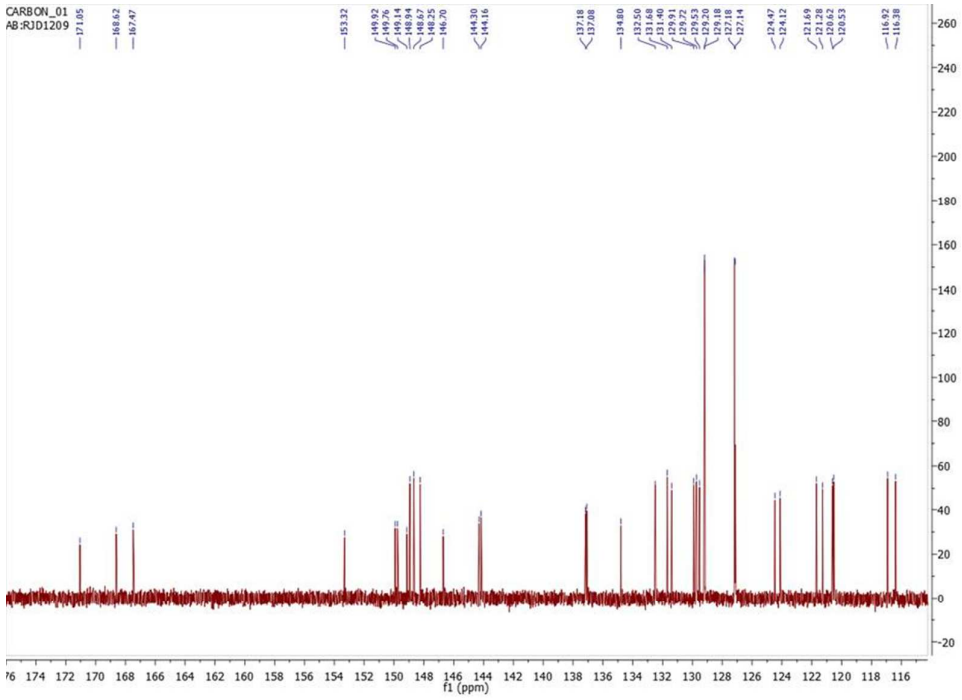

Figure S22. ^{13}C NMR spectrum of **11**, recorded in CD_2Cl_2.

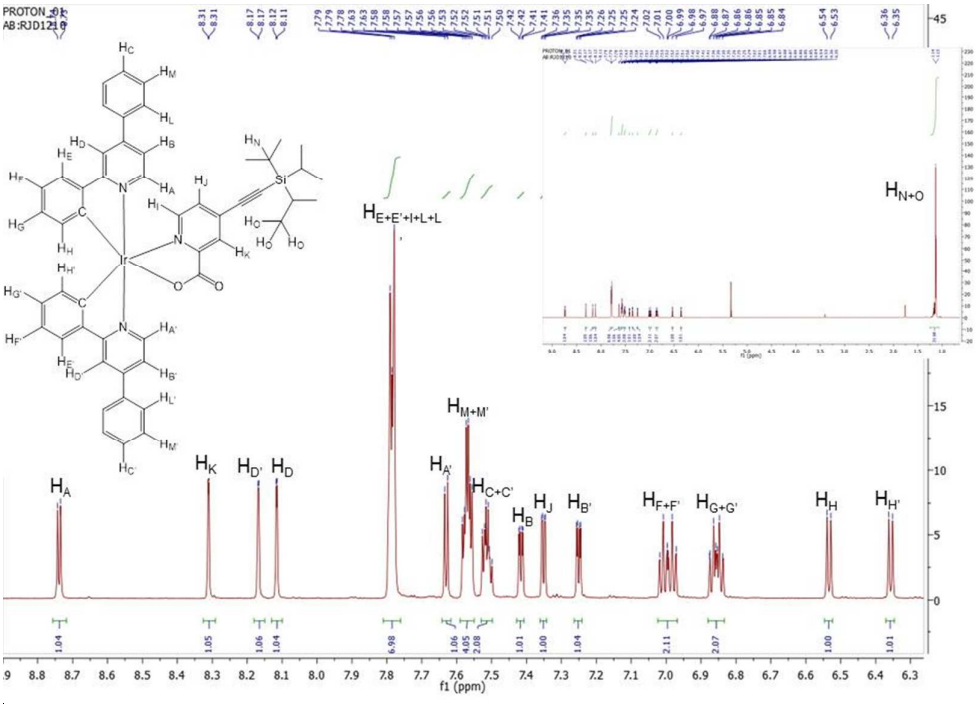

Figure S23. ^{1}H NMR spectrum of **12**, recorded in CD_2Cl_2.

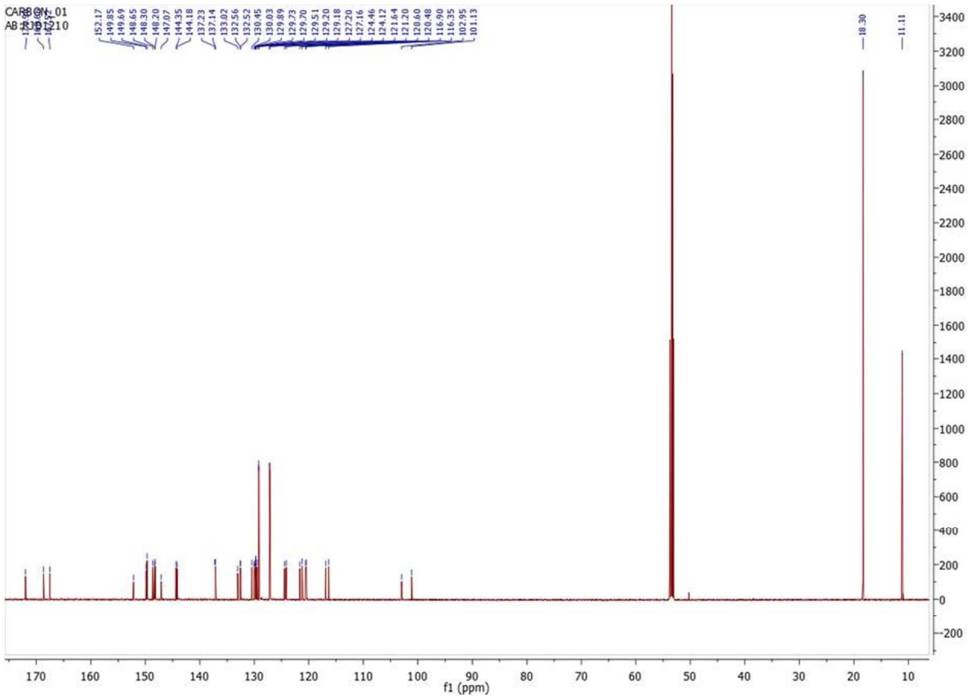

Figure S24. ^{13}C NMR spectrum of **12**, recorded in CD_2Cl_2.

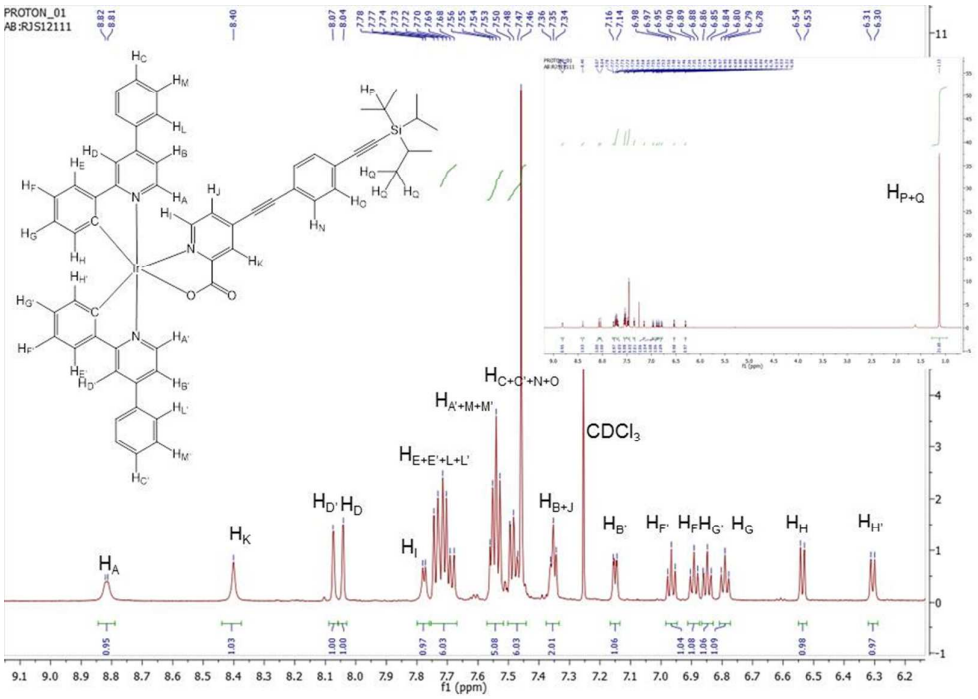

Figure S25. ^{1}H NMR spectrum of **12**, recorded in $CDCl_3$.

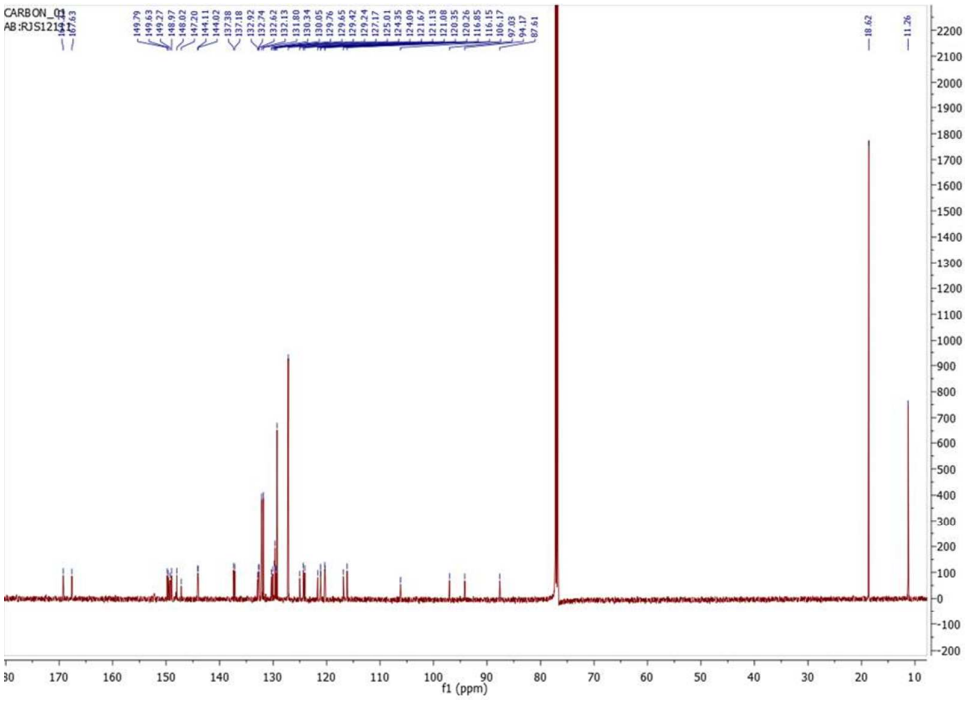

Figure S26. ^{13}C NMR spectrum of **13**, recorded in $CDCl_3$.

S2. Crystallographic data

Table S1. Crystal and Refinement Data for $(2)_2 \cdot 6CH_2Cl_2$, 3, and $4 \cdot CH_3OH$.

Compound	$(2)_2 \cdot 6CH_2Cl_2$	**3**	$4 \cdot CH_3OH$
Code	15srv042	15srv061	15srv086
Empirical formula	$C_{28}H_{19}BrIrN_3O_2$ x $3CH_2Cl_2$	$C_{28}H_{19}BrIrN_3O_2$	$C_{28}H_{19}BrIrN_3O_2$ x CH_3OH
Formula weight	956.35	701.57	733.61
Temperature/K	120.0	120.0	120.0
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pna2_1$	$P2_1/c$
a/Å	27.6191(17)	15.5416(2)	17.2087(8)
b/Å	9.2062(5)	15.89863(20)	9.3633(4)
c/Å	27.7085(16)	9.59745(17)	16.1960(7)
α/°	90.00	90.00	90.00
β/°	108.067(6)	90.00	106.5986(15)
γ/°	90.00	90.00	90.00
Volume/$Å^3$	6698.0(7)	2371.44(6)	2500.92(19)
Z	8	4	4
$\rho_{calc}g/cm^3$	1.897	1.965	1.948
μ/mm^{-1}	5.693	7.347	6.974
F(000)	3696.0	1344.0	1416.0
Crystal size/mm^3	0.49 × 0.06 × 0.03	0.19 × 0.15 × 0.05	0.33 × 0.15 × 0.13
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3 to 56	3.66 to 61	4.94 to 60
Index ranges	$-36 \le h \le 36$, $-12 \le k \le 12$, $-36 \le l \le 36$	$-22 \le h \le 22$, $-22 \le k \le 22$, $-13 \le l \le 13$	$-24 \le h \le 24$, $-13 \le k \le 13$, $-22 \le l \le 22$
Reflections collected	87958	38325	53763
Independent reflections	16165 [R_{int} = 0.1868, R_{sigma} = 0.1532]	7213 [R_{int} = 0.0613, R_{sigma} = 0.0462]	7289 [R_{int} = 0.0318, R_{sigma} = 0.0191]
Data/restraints/parameters	16165/288/777	7213/1/316	7289/0/337
Goodness-of-fit on F^2	1.045	1.036	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0796, wR_2 = 0.1486	R_1 = 0.0287, wR_2 = 0.0539	R_1 = 0.0161, wR_2 = 0.0315
Final R indexes [all data]	R_1 = 0.1266, wR_2 = 0.1687	R_1 = 0.0382, wR_2 = 0.0577	R_1 = 0.0202, wR_2 = 0.0325
Largest diff. peak/hole / e $Å^{-3}$	1.99/-1.23	0.94/-0.78	1.05/-0.58

Table S2. Crystal and Refinement Data for 5, 6 and 8·3C_6H_6

Compound	**5**	**6**	**8**·3C_6H_6
Code	15srv068	15srv125	15srv179
Empirical formula	$C_{39}H_{40}IrN_3O_2Si$	$C_{39}H_{40}IrN_3O_2Si$	$C_{39}H_{40}IrN_3O_2Si$ x 3 C_6H_6
Formula weight	803.03	803.03	1037.35
Temperature/K	120.0	120.0	120.0
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	$P2_1/c$
a/Å	9.2178(2)	9.2875(5)	15.2001(7)
b/Å	13.2251(3)	13.2704(7)	9.6279(4)
c/Å	14.8047(3)	14.7165(8)	33.3532(15)
α/°	86.803(2)	95.698(2)	90.00
β/°	81.390(2)	93.6752(19)	95.5780(10)
γ/°	72.436(2)	108.3362(18)	90.00
Volume/$Å^3$	1701.15(7)	1704.44(16)	4858.0(4)
Z	2	2	4
$\rho_{calc}g/cm^3$	1.568	1.565	1.418
μ/mm^{-1}	3.998	3.990	2.818
F(000)	804.0	804.0	2112.0
Crystal size/mm^3	0.26 × 0.22 × 0.09	0.2 × 0.13 × 0.035	0.52 × 0.14 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71000)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.24 to 60	4.54 to 59	3.46 to 55
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-20 \le l \le 20$	$-12 \le h \le 12$, $-18 \le k \le 18$, $-20 \le l \le 20$	$-19 \le h \le 19$, $-12 \le k \le 12$, $-43 \le l \le 43$
Reflections collected	40683	36431	59527
Independent reflections	9907 [R_{int} = 0.0531, R_{sigma} = 0.0462]	9522 [R_{int} = 0.0306, R_{sigma} = 0.0314]	11162 [R_{int} = 0.0359, R_{sigma} = 0.0263]
Data/restraints/parameters	9907/66/418	9522/7/420	11162/125/514
Goodness-of-fit on F^2	1.077	1.028	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0626	R_1 = 0.0220, wR_2 = 0.0449	R_1 = 0.0402, wR_2 = 0.1101
Final R indexes [all data]	R_1 = 0.0351, wR_2 = 0.0650	R_1 = 0.0285, wR_2 = 0.0468	R_1 = 0.0486, wR_2 = 0.1172
Largest diff. peak/hole / e $Å^{-3}$	1.21/-0.71	1.08/-0.93	3.90/-2.49

Table S3. Crystal and Refinement Data for 9·3CH_3OH, 11 and 12·CH_2Cl_2

Compound	**9**·3CH_3OH	**11**	**12**·CH_2Cl_2
Code	15srv055	15srv088	15srv087
Empirical formula	$C_{46}H_{44}IrN_4O_2Si$ x $3CH_3OH$	$C_{40}H_{27}BrIrN_3O_2$	$C_{51}H_{48}IrN_3O_2Si$ x CH_2Cl_2
Formula weight	1001.27	853.76	1040.14
Temperature/K	120.0	120.0	120.0
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a/Å	27.1144(13)	20.2273(11)	10.8708(7)
b/Å	9.3146(5)	8.8519(5)	12.7251(8)
c/Å	18.7080(9)	20.0716(11)	18.2903(11)
α/°	90.00	90.00	106.298(2)
β/°	99.9930(10)	95.974(2)	90.817(2)
γ/°	90.00	90.00	108.688(2)
Volume/$Å^3$	4653.2(4)	3574.3(3)	2285.3(2)
Z	4	4	2
$\rho_{calc}g/cm^3$	1.429	1.587	1.512
μ/mm^{-1}	2.944	4.891	3.109
F(000)	2036.0	1664.0	1048.0
Crystal size/mm^3	0.17 × 0.08 × 0.04	0.17 × 0.17 × 0.02	0.34 × 0.19 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.42 to 58	4.36 to 58	4.38 to 58
Index ranges	-36 ≤ h ≤ 36, -12 ≤ k ≤ 12, -25 ≤ l ≤ 25	-29 ≤ h ≤ 29, -13 ≤ k ≤ 13, -29 ≤ l ≤ 29	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24
Reflections collected	86094	63135	46896
Independent reflections	12352 [R_{int} = 0.0684, R_{sigma} = 0.0490]	9489 [R_{int} = 0.0848, R_{sigma} = 0.0882]	12111 [Rint = 0.0510, Rsigma = 0.0549]
Data/restraints/parameters	12352/87/495	9489/0/424	12111/0/556
Goodness-of-fit on F^2	1.247	1.061	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1101	R_1 = 0.0487, wR_2 = 0.1069	R1 = 0.0319, wR2 = 0.0641
Final R indexes [all data]	R_1 = 0.0801, wR_2 = 0.1162	R_1 = 0.0786, wR_2 = 0.1158	R1 = 0.0447, wR2 = 0.0677
Largest diff. peak/hole / e $Å^{-3}$	1.43/-3.78	2.21/-2.59	1.36/-1.02

Table S4. Selected bond lengths for $(\mathbf{2})_2 \cdot 6CH_2Cl_2$.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.162(10)		N1A	C1A	1.356(18)
Ir1	N1	2.044(12)		N1A	C5A	1.346(17)
Ir1	N2	2.047(11)		N3A	C23A	1.347(16)
Ir1	N3	2.145(12)		N3A	C27A	1.335(19)
Ir1	C7	1.977(15)		N21	C12A	1.321(19)
Ir1	C18	1.993(14)		N21	C16A	1.37(2)
Br1	C25	1.861(14)		N22	C17A	1.48(2)
O1	C28	1.309(16)		N22	C19A	1.385(19)
O2	C28	1.215(15)		C1A	C2A	1.35(2)
N1	C1	1.335(17)		C2A	C3A	1.34(2)
N1	C5	1.385(19)		C3A	C4A	1.40(2)
N2	C12	1.324(17)		C4A	C5A	1.41(2)
N2	C16	1.354(16)		C5A	C6A	1.44(2)
N3	C23	1.323(16)		C6A	C7A	1.38(2)
N3	C27	1.350(18)		C6A	C11A	1.43(2)
C1	C2	1.38(2)		C7A	C8A	1.43(2)
C2	C3	1.38(2)		C8A	C9A	1.36(2)
C3	C4	1.42(2)		C9A	C10A	1.40(2)
C4	C5	1.34(2)		C10A	C11A	1.35(2)
C5	C6	1.43(2)		C12A	C13A	1.40(2)
C6	C7	1.44(2)		C13A	C14A	1.43(3)
C6	C11	1.43(2)		C14A	C15A	1.34(2)
C7	C8	1.380(19)		C15A	C16A	1.40(2)
C8	C9	1.41(2)		C16A	C17A	1.52(2)
C9	C10	1.39(2)		C17A	C22A	1.34(2)
C10	C11	1.36(2)		C19A	C20A	1.39(2)
C12	C13	1.372(19)		C20A	C21A	1.39(2)
C13	C14	1.35(2)		C21A	C22A	1.35(2)
C14	C15	1.39(2)		C23A	C24A	1.36(2)
C15	C16	1.393(19)		C23A	C28A	1.53(2)
C16	C17	1.512(19)		C24A	C25A	1.41(2)
C17	C18	1.406(19)		C25A	C26A	1.38(2)
C17	C22	1.364(19)		C26A	C27A	1.41(2)
C18	C19	1.37(2)		Cl1	C1S	1.781(17)
C19	C20	1.41(2)		Cl2	C1S	1.769(16)
C20	C21	1.40(2)		Cl3	C2S	1.763(18)
C21	C22	1.40(2)		Cl4	C2S	1.760(17)
C23	C24	1.390(19)		Cl5	C3S	1.750(18)
C23	C28	1.52(2)		Cl6	C3S	1.800(19)
C24	C25	1.37(2)		Cl7	C4S	1.741(11)
C25	C26	1.39(2)		Cl7	C4SA	1.741(11)
C26	C27	1.433(19)		Cl8	C4S	1.741(11)
Ir2	O1A	2.171(10)		Cl8	C4SA	1.742(11)
Ir2	N1A	2.046(11)		Cl9	C5SA	1.741(11)
Ir2	N3A	2.116(12)		Cl9	C5SB	1.741(11)
Ir2	N21	1.989(14)		Cl10	C5SB	1.743(11)
Ir2	N22	1.963(14)		Cl20	C5SA	1.741(11)
Ir2	C7A	1.987(14)		Cl11	C6SA	1.740(11)
Br2	C25A	1.879(15)		Cl12	C6SA	1.741(11)
O1A	C28A	1.288(16)		Cl21	C6S	1.741(11)
O2A	C28A	1.229(16)		Cl22	C6S	1.742(11)

Table S5. Selected bond angles for $(\mathbf{2})_2 \cdot 6CH_2Cl_2$.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	90.4(4)		N22	Ir2	O1A	96.5(5)
N1	Ir1	N2	174.0(4)		N22	Ir2	N1A	92.3(5)
N1	Ir1	N3	96.9(5)		N22	Ir2	N3A	172.9(5)
N2	Ir1	O1	93.1(4)		N22	Ir2	N21	82.7(6)
N2	Ir1	N3	88.8(4)		N22	Ir2	C7A	89.9(6)
N3	Ir1	O1	77.0(4)		C7A	Ir2	O1A	172.2(5)
C7	Ir1	O1	95.8(5)		C7A	Ir2	N1A	79.5(6)
C7	Ir1	N1	80.6(6)		C7A	Ir2	N3A	97.0(5)
C7	Ir1	N2	94.1(5)		C7A	Ir2	N21	97.5(6)
C7	Ir1	N3	172.3(5)		C28A	O1A	Ir2	116.1(9)
C7	Ir1	C18	92.1(6)		C1A	N1A	Ir2	123.4(10)
C18	Ir1	O1	170.9(5)		C5A	N1A	Ir2	115.3(10)
C18	Ir1	N1	95.4(5)		C5A	N1A	C1A	121.0(13)
C18	Ir1	N2	81.8(5)		C23A	N3A	Ir2	116.3(10)
C18	Ir1	N3	95.3(5)		C27A	N3A	Ir2	126.8(9)
C28	O1	Ir1	116.1(8)		C27A	N3A	C23A	116.8(12)
C1	N1	Ir1	123.8(11)		C12A	N21	Ir2	127.7(12)
C1	N1	C5	120.0(13)		C12A	N21	C16A	115.1(14)
C5	N1	Ir1	116.2(9)		C16A	N21	Ir2	117.1(10)
C12	N2	Ir1	126.0(9)		C17A	N22	Ir2	115.0(10)
C12	N2	C16	118.8(12)		C19A	N22	Ir2	132.7(12)
C16	N2	Ir1	115.2(9)		C19A	N22	C17A	112.1(13)
C23	N3	Ir1	114.1(10)		C2A	C1A	N1A	121.2(14)
C23	N3	C27	120.1(13)		C3A	C2A	C1A	121.8(15)
C27	N3	Ir1	125.3(9)		C2A	C3A	C4A	117.4(14)
N1	C1	C2	121.1(14)		C3A	C4A	C5A	120.9(14)
C3	C2	C1	120.4(14)		N1A	C5A	C4A	117.6(14)
C2	C3	C4	117.1(15)		N1A	C5A	C6A	114.6(13)
C5	C4	C3	121.2(16)		C4A	C5A	C6A	127.7(14)
N1	C5	C6	112.3(12)		C7A	C6A	C5A	114.4(13)
C4	C5	N1	120.0(14)		C7A	C6A	C11A	122.9(14)
C4	C5	C6	127.7(15)		C11A	C6A	C5A	122.7(14)
C5	C6	C7	116.4(14)		C6A	C7A	Ir2	116.0(11)
C11	C6	C5	122.2(13)		C6A	C7A	C8A	115.6(13)
C11	C6	C7	121.0(13)		C8A	C7A	Ir2	128.4(11)
C6	C7	Ir1	113.9(10)		C9A	C8A	C7A	122.0(15)
C8	C7	Ir1	130.0(12)		C8A	C9A	C10A	120.3(16)
C8	C7	C6	115.8(13)		C11A	C10A	C9A	120.9(15)
C7	C8	C9	122.8(14)		C10A	C11A	C6A	118.2(15)
C10	C9	C8	120.1(13)		N21	C12A	C13A	127.0(17)
C11	C10	C9	120.2(15)		C12A	C13A	C14A	114.9(16)
C10	C11	C6	119.8(14)		C15A	C14A	C13A	120.4(16)
N2	C12	C13	122.8(14)		C14A	C15A	C16A	119.3(17)
C14	C13	C12	119.0(14)		N21	C16A	C15A	123.1(15)
C13	C14	C15	120.1(14)		N21	C16A	C17A	113.6(13)
C14	C15	C16	118.0(13)		C15A	C16A	C17A	123.3(14)
N2	C16	C15	121.2(13)		N22	C17A	C16A	111.4(12)
N2	C16	C17	113.7(11)		C22A	C17A	N22	124.3(14)
C15	C16	C17	125.1(12)		C22A	C17A	C16A	124.1(14)
C18	C17	C16	114.6(12)		N22	C19A	C20A	123.4(15)
C22	C17	C16	122.9(12)		C19A	C20A	C21A	120.3(15)
C22	C17	C18	122.5(13)		C22A	C21A	C20A	119.7(15)
C17	C18	Ir1	114.2(10)		C17A	C22A	C21A	120.1(16)
C19	C18	Ir1	128.8(11)		N3A	C23A	C24A	123.4(14)

Table S5 continued. Selected bond angles for $(\mathbf{2})_2 \cdot 6CH_2Cl_2$.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C19	C18	C17	116.7(13)		N3A	C23A	C28A	114.9(12)
C18	C19	C20	121.9(15)		C24A	C23A	C28A	121.7(12)
C21	C20	C19	120.7(15)		C23A	C24A	C25A	118.5(13)
C20	C21	C22	117.1(14)		C24A	C25A	Br2	119.3(11)
C17	C22	C21	121.0(14)		C26A	C25A	Br2	120.5(13)
N3	C23	C24	122.8(13)		C26A	C25A	C24A	120.2(14)
N3	C23	C28	117.5(12)		C25A	C26A	C27A	115.6(15)
C24	C23	C28	119.6(12)		N3A	C27A	C26A	125.2(13)
C25	C24	C23	119.9(13)		O1A	C28A	C23A	115.8(12)
C24	C25	Br1	122.5(11)		O2A	C28A	O1A	126.5(14)
C24	C25	C26	117.6(14)		O2A	C28A	C23A	117.7(13)
C26	C25	Br1	119.9(12)		Cl2	C1S	Cl1	110.3(9)
C25	C26	C27	120.5(15)		Cl4	C2S	Cl3	110.9(10)
N3	C27	C26	119.0(13)		Cl5	C3S	Cl6	111.4(11)
O1	C28	C23	114.4(11)		C4SA	Cl7	C4S	34.1(16)
O2	C28	O1	124.5(13)		C4S	Cl8	C4SA	34.1(16)
O2	C28	C23	121.1(13)		Cl7	C4S	Cl8	114.6(12)
N1A	Ir2	O1A	95.9(4)		Cl7	C4SA	Cl8	114.5(11)
N1A	Ir2	N3A	90.1(4)		C5SB	Cl9	C5SA	46.6(19)
N3A	Ir2	O1A	76.6(4)		Cl20	C5SA	Cl9	126(2)
N21	Ir2	O1A	87.6(5)		Cl9	C5SB	Cl10	108.4(11)
N21	Ir2	N1A	174.2(5)		Cl11	C6SA	Cl12	96.5(12)
N21	Ir2	N3A	95.2(5)		Cl21	C6S	Cl22	102.9(11)

Table S6. Selected bond lengths for **3**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.159(3)		C7	C12	1.419(6)
Ir1	N1	2.032(3)		C8	C9	1.407(7)
Ir1	N2	2.050(4)		C9	C10	1.385(7)
Ir1	N3	2.156(4)		C10	C11	1.384(7)
Ir1	C7	1.997(5)		C11	C12	1.401(7)
Ir1	C27	2.008(3)		C13	C14	1.390(5)
Br2	C14	1.864(6)		C14	C15	1.397(9)
O1	C18	1.280(5)		C15	C16	1.388(7)
O2	C18	1.230(5)		C16	C17	1.385(6)
N1	C1	1.351(5)		C17	C18	1.506(6)
N1	C5	1.360(6)		C21	C22	1.384(6)
N2	C21	1.349(6)		C22	C23	1.379(7)
N2	C25	1.362(5)		C23	C24	1.384(7)
N3	C13	1.343(5)		C24	C25	1.397(6)
N3	C17	1.351(6)		C25	C26	1.465(6)
C1	C2	1.363(6)		C26	C27	1.416(7)
C2	C3	1.400(7)		C26	C31	1.393(6)
C3	C4	1.373(6)		C27	C28	1.394(6)
C4	C5	1.403(6)		C28	C29	1.407(6)
C5	C12	1.482(6)		C29	C30	1.386(7)
C7	C8	1.398(6)		C30	C31	1.371(7)

Table S7. Selected bond angles for **3**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	93.76(14)		C10	C9	C8	120.4(5)
N1	Ir1	N2	174.61(14)		C11	C10	C9	119.9(5)
N1	Ir1	N3	87.80(13)		C10	C11	C12	119.4(5)
N2	Ir1	O1	89.13(14)		C7	C12	C5	114.7(4)
N2	Ir1	N3	97.29(13)		C11	C12	C5	122.9(4)
N3	Ir1	O1	77.01(13)		C11	C12	C7	122.4(4)
C7	Ir1	O1	173.63(14)		N3	C13	C14	122.1(5)
C7	Ir1	N1	80.77(16)		C13	C14	Br2	120.7(5)
C7	Ir1	N2	96.59(16)		C13	C14	C15	118.9(5)
C7	Ir1	N3	99.40(15)		C15	C14	Br2	120.3(3)
C7	Ir1	C27	90.9(2)		C16	C15	C14	118.4(4)
C27	Ir1	O1	92.9(2)		C17	C16	C15	119.9(5)
C27	Ir1	N1	94.79(18)		N3	C17	C16	121.3(4)
C27	Ir1	N2	80.51(18)		N3	C17	C18	116.9(4)
C27	Ir1	N3	169.7(2)		C16	C17	C18	121.8(4)
C18	O1	Ir1	116.0(3)		O1	C18	C17	116.3(4)
C1	N1	Ir1	125.1(3)		O2	C18	O1	125.2(4)
C1	N1	C5	118.2(4)		O2	C18	C17	118.4(4)
C5	N1	Ir1	116.7(3)		N2	C21	C22	122.5(4)
C21	N2	Ir1	125.1(3)		C23	C22	C21	118.2(5)
C21	N2	C25	119.5(4)		C22	C23	C24	120.0(4)
C25	N2	Ir1	115.4(3)		C23	C24	C25	119.7(4)
C13	N3	Ir1	127.4(3)		N2	C25	C24	119.7(4)
C13	N3	C17	119.3(4)		N2	C25	C26	114.3(4)
C17	N3	Ir1	113.2(3)		C24	C25	C26	126.0(4)
N1	C1	C2	123.5(5)		C27	C26	C25	115.0(4)
C1	C2	C3	118.2(4)		C31	C26	C25	123.3(4)
C4	C3	C2	119.8(4)		C31	C26	C27	121.7(4)
C3	C4	C5	118.9(4)		C26	C27	Ir1	114.3(3)
N1	C5	C4	121.3(4)		C28	C27	Ir1	128.5(4)
N1	C5	C12	113.2(4)		C28	C27	C26	117.0(4)
C4	C5	C12	125.4(4)		C27	C28	C29	120.7(4)
C8	C7	Ir1	129.2(4)		C30	C29	C28	120.8(4)
C8	C7	C12	116.1(4)		C31	C30	C29	119.5(4)
C12	C7	Ir1	114.6(3)		C30	C31	C26	120.3(5)
C7	C8	C9	121.6(5)					

Table S8. Selected bond lengths for **4·CH$_3$OH**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.1571(12)		C7	C8	1.400(2)
Ir1	N1	2.0380(15)		C8	C9	1.395(3)
Ir1	N2	2.0425(15)		C9	C10	1.388(3)
Ir1	N3	2.2346(15)		C10	C11	1.384(3)
Ir1	C7	1.9975(17)		C12	C13	1.387(3)
Ir1	C27	1.9924(18)		C13	C14	1.380(3)
Br1	C12	1.8849(18)		C14	C15	1.388(3)
O1	C17	1.272(2)		C15	C16	1.379(3)
O2	C17	1.242(2)		C16	C17	1.514(2)
N1	C1	1.347(2)		C21	C22	1.376(3)
N1	C5	1.367(2)		C22	C23	1.390(3)
N2	C21	1.344(2)		C23	C24	1.379(3)
N2	C25	1.365(2)		C24	C25	1.399(3)
N3	C12	1.336(2)		C25	C26	1.453(3)
N3	C16	1.366(2)		C26	C27	1.416(2)
C1	C2	1.379(3)		C26	C31	1.405(3)
C2	C3	1.390(3)		C27	C28	1.399(3)
C3	C4	1.378(3)		C28	C29	1.388(3)
C4	C5	1.394(3)		C29	C30	1.387(3)
C5	C6	1.465(3)		C30	C31	1.378(3)
C6	C7	1.411(2)		O3	C1S	1.402(3)
C6	C11	1.399(3)				

Table S9. Selected bond angles for **4·CH$_3$OH**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Ir1	N3	75.82(5)		C8	C7	Ir1	128.28(14)
N1	Ir1	O1	86.87(5)		C8	C7	C6	117.30(16)
N1	Ir1	N2	174.76(6)		C9	C8	C7	121.09(18)
N1	Ir1	N3	97.71(6)		C10	C9	C8	120.60(18)
N2	Ir1	O1	95.26(5)		C11	C10	C9	119.68(18)
N2	Ir1	N3	87.46(6)		C10	C11	C6	119.90(18)
C7	Ir1	O1	92.57(6)		N3	C12	Br1	117.94(13)
C7	Ir1	N1	80.75(7)		N3	C12	C13	124.73(17)
C7	Ir1	N2	94.35(7)		C13	C12	Br1	117.23(14)
C7	Ir1	N3	168.37(6)		C14	C13	C12	118.10(18)
C27	Ir1	O1	175.87(6)		C13	C14	C15	118.76(18)
C27	Ir1	N1	97.22(7)		C16	C15	C14	119.22(18)
C27	Ir1	N2	80.61(7)		N3	C16	C15	122.94(17)
C27	Ir1	N3	104.01(6)		N3	C16	C17	116.24(15)
C27	Ir1	C7	87.62(7)		C15	C16	C17	120.73(16)
C17	O1	Ir1	117.74(11)		O1	C17	C16	116.48(15)
C1	N1	Ir1	125.26(13)		O2	C17	O1	125.36(17)
C1	N1	C5	119.23(16)		O2	C17	C16	118.14(16)
C5	N1	Ir1	115.37(12)		N2	C21	C22	122.53(18)
C21	N2	Ir1	124.65(12)		C21	C22	C23	118.68(19)
C21	N2	C25	119.55(16)		C24	C23	C22	119.42(18)
C25	N2	Ir1	115.70(12)		C23	C24	C25	119.77(18)
C12	N3	Ir1	132.32(12)		N2	C25	C24	120.04(18)
C12	N3	C16	115.90(15)		N2	C25	C26	113.83(16)
C16	N3	Ir1	110.69(11)		C24	C25	C26	126.09(17)
N1	C1	C2	122.31(18)		C27	C26	C25	115.29(16)
C1	C2	C3	118.97(19)		C31	C26	C25	123.51(17)
C4	C3	C2	119.09(18)		C31	C26	C27	121.19(18)
C3	C4	C5	120.05(18)		C26	C27	Ir1	114.51(13)
N1	C5	C4	120.27(17)		C28	C27	Ir1	128.39(14)
N1	C5	C6	113.72(15)		C28	C27	C26	117.10(16)
C4	C5	C6	126.01(17)		C29	C28	C27	121.32(18)
C7	C6	C5	115.15(16)		C30	C29	C28	120.69(19)
C11	C6	C5	123.44(17)		C31	C30	C29	119.84(18)
C11	C6	C7	121.41(17)		C30	C31	C26	119.84(18)
C6	C7	Ir1	114.25(13)					

Table S10. Selected bond lengths for **5**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.162(2)		C10	C11	1.384(5)
Ir1	N1	2.038(3)		C12	C13	1.377(4)
Ir1	N2	2.041(2)		C13	C14	1.385(5)
Ir1	N3	2.166(3)		C14	C15	1.402(4)
Ir1	C7	1.987(3)		C15	C16	1.405(4)
Ir1	C27	1.994(3)		C15	C18	1.440(4)
Si1	C19	1.844(3)		C16	C17	1.521(4)
Si1	C32	2.002(8)		C18	C19	1.207(5)
Si1	C32A	1.838(6)		C21	C22	1.383(4)
Si1	C35	1.940(9)		C22	C23	1.387(5)
Si1	C35A	1.800(7)		C23	C24	1.378(5)
Si1	C38	1.776(7)		C24	C25	1.402(4)
Si1	C38A	2.028(7)		C25	C26	1.459(4)
O1	C17	1.285(4)		C26	C27	1.423(4)
O2	C17	1.225(4)		C26	C31	1.401(4)
N1	C1	1.355(4)		C27	C28	1.410(4)
N1	C5	1.370(4)		C28	C29	1.389(5)
N2	C21	1.347(4)		C29	C30	1.387(5)
N2	C25	1.374(4)		C30	C31	1.388(5)
N3	C12	1.347(4)		C32	C33	1.536(3)
N3	C16	1.346(4)		C32	C34	1.537(4)
C1	C2	1.371(4)		C32A	C33A	1.537(3)
C2	C3	1.392(5)		C32A	C34A	1.536(3)
C3	C4	1.392(5)		C35	C36	1.535(4)
C4	C5	1.393(4)		C35	C37	1.536(4)
C5	C6	1.462(4)		C35A	C36A	1.536(3)
C6	C7	1.420(4)		C35A	C37A	1.536(3)
C6	C11	1.399(4)		C38	C39	1.536(3)
C7	C8	1.407(4)		C38	C40	1.536(3)
C8	C9	1.396(4)		C38A	C39A	1.536(3)
C9	C10	1.386(5)		C38A	C40A	1.536(3)

Table S11. Selected bond angles for **5**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Ir1	N3	75.99(9)		C6	C7	Ir1	114.6(2)
N1	Ir1	O1	94.96(9)		C8	C7	Ir1	128.7(2)
N1	Ir1	N2	175.45(10)		C8	C7	C6	116.7(3)
N1	Ir1	N3	83.34(10)		C9	C8	C7	121.4(3)
N2	Ir1	O1	89.49(9)		C10	C9	C8	120.4(3)
N2	Ir1	N3	98.68(10)		C11	C10	C9	120.2(3)
C7	Ir1	O1	172.45(10)		C10	C11	C6	119.7(3)
C7	Ir1	N1	80.60(11)		N3	C12	C13	121.1(3)
C7	Ir1	N2	95.07(11)		C12	C13	C14	119.0(3)
C7	Ir1	N3	97.33(11)		C13	C14	C15	120.3(3)
C7	Ir1	C27	88.83(11)		C14	C15	C16	117.6(3)
C27	Ir1	O1	97.87(10)		C14	C15	C18	117.7(3)
C27	Ir1	N1	97.71(11)		C16	C15	C18	124.7(3)
C27	Ir1	N2	80.72(11)		N3	C16	C15	120.8(3)
C27	Ir1	N3	173.85(10)		N3	C16	C17	115.5(3)
C19	Si1	C32	103.9(2)		C15	C16	C17	123.7(3)
C19	Si1	C35	107.5(3)		O1	C17	C16	115.4(3)
C19	Si1	C38A	98.0(2)		O2	C17	O1	125.9(3)
C32	Si1	C38A	142.5(3)		O2	C17	C16	118.7(3)
C32A	Si1	C19	106.8(2)		C19	C18	C15	172.2(3)
C32A	Si1	C32	35.8(3)		C18	C19	Si1	176.6(3)
C32A	Si1	C35	132.7(3)		N2	C21	C22	122.7(3)
C32A	Si1	C38A	108.5(2)		C21	C22	C23	118.9(3)
C35	Si1	C32	104.0(3)		C24	C23	C22	119.2(3)
C35	Si1	C38A	97.9(2)		C23	C24	C25	120.3(3)
C35A	Si1	C19	111.9(2)		N2	C25	C24	119.8(3)
C35A	Si1	C32	88.2(3)		N2	C25	C26	113.8(3)
C35A	Si1	C32A	118.2(3)		C24	C25	C26	126.4(3)
C35A	Si1	C35	15.8(3)		C27	C26	C25	114.9(3)
C35A	Si1	C38A	111.4(3)		C31	C26	C25	123.5(3)
C38	Si1	C19	115.3(2)		C31	C26	C27	121.6(3)
C38	Si1	C32	114.3(3)		C26	C27	Ir1	114.7(2)
C38	Si1	C32A	81.8(3)		C28	C27	Ir1	129.0(2)
C38	Si1	C35	111.1(3)		C28	C27	C26	116.2(3)
C38	Si1	C35A	119.2(3)		C29	C28	C27	121.9(3)
C38	Si1	C38A	28.3(3)		C30	C29	C28	120.7(3)
C17	O1	Ir1	117.36(18)		C29	C30	C31	119.4(3)
C1	N1	Ir1	125.3(2)		C30	C31	C26	120.2(3)
C1	N1	C5	119.2(3)		C33	C32	Si1	110.9(5)
C5	N1	Ir1	115.10(19)		C33	C32	C34	107.3(7)
C21	N2	Ir1	125.1(2)		C34	C32	Si1	113.3(6)
C21	N2	C25	119.1(3)		C33A	C32A	Si1	108.4(5)
C25	N2	Ir1	115.8(2)		C34A	C32A	Si1	111.3(4)
C12	N3	Ir1	123.3(2)		C34A	C32A	C33A	112.1(6)
C16	N3	Ir1	114.58(19)		C36	C35	Si1	114.1(6)
C16	N3	C12	121.1(3)		C36	C35	C37	109.0(8)
N1	C1	C2	122.6(3)		C37	C35	Si1	108.3(6)
C1	C2	C3	118.6(3)		C36A	C35A	Si1	115.1(5)
C4	C3	C2	119.6(3)		C36A	C35A	C37A	109.5(6)
C3	C4	C5	119.4(3)		C37A	C35A	Si1	114.4(5)
N1	C5	C4	120.4(3)		C39	C38	Si1	113.2(5)
N1	C5	C6	113.6(3)		C39	C38	C40	110.4(6)
C4	C5	C6	125.9(3)		C40	C38	Si1	116.1(5)
C7	C6	C5	114.6(3)		C39A	C38A	Si1	111.4(4)

Table S11 continued. Selected bond angles for **5**.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C11	C6	C5	123.7(3)		C40A	C38A	Si1	112.0(4)
C11	C6	C7	121.7(3)		C40A	C38A	C39A	109.5(5)

Table S12. Selected bond lengths for **6**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.1731(15)		C9	C10	1.397(4)
Ir1	N1	2.0413(18)		C10	C11	1.374(4)
Ir1	N2	2.0407(18)		C12	C13	1.378(3)
Ir1	N3	2.122(2)		C13	C14	1.395(3)
Ir1	C7	2.004(2)		C14	C15	1.398(3)
Ir1	C27	1.997(2)		C14	C18	1.431(3)
Si1	C19	1.849(3)		C15	C16	1.371(3)
Si1	C32	1.877(3)		C16	C17	1.524(3)
Si1	C35	1.873(4)		C18	C19	1.196(4)
Si1	C38	1.921(4)		C21	C22	1.373(3)
Si1	C38A	1.908(5)		C22	C23	1.391(4)
O1	C17	1.277(3)		C23	C24	1.384(4)
O2	C17	1.228(3)		C24	C25	1.388(3)
N1	C1	1.353(3)		C25	C26	1.464(3)
N1	C5	1.366(3)		C26	C27	1.411(3)
N2	C21	1.345(3)		C26	C31	1.394(3)
N2	C25	1.363(3)		C27	C28	1.396(3)
N3	C12	1.349(3)		C28	C29	1.395(3)
N3	C16	1.353(3)		C29	C30	1.382(3)
C1	C2	1.374(3)		C30	C31	1.382(3)
C2	C3	1.377(4)		C32	C33	1.519(4)
C3	C4	1.381(4)		C32	C34	1.535(4)
C4	C5	1.399(3)		C35	C36	1.526(4)
C5	C6	1.457(3)		C35	C37	1.503(6)
C6	C7	1.414(3)		C38	C39	1.565(4)
C6	C11	1.401(3)		C38	C40	1.592(5)
C7	C8	1.398(3)		C38A	C39A	1.575(5)
C8	C9	1.381(3)		C38A	C40A	1.592(5)

Table S13. Selected bond angles for **6**.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
N1	Ir1	O1	88.49(7)		C9	C8	C7	121.5(2)
N1	Ir1	N3	95.90(7)		C8	C9	C10	120.6(2)
N2	Ir1	O1	93.91(7)		C11	C10	C9	119.4(2)
N2	Ir1	N1	177.58(7)		C10	C11	C6	120.2(2)
N2	Ir1	N3	84.92(7)		N3	C12	C13	122.1(2)
N3	Ir1	O1	76.61(6)		C12	C13	C14	119.8(2)
C7	Ir1	O1	99.46(7)		C13	C14	C15	117.5(2)
C7	Ir1	N1	80.39(8)		C13	C14	C18	121.2(2)
C7	Ir1	N2	98.93(8)		C15	C14	C18	121.2(2)
C7	Ir1	N3	174.74(8)		C16	C15	C14	119.7(2)
C27	Ir1	O1	171.17(7)		N3	C16	C15	122.3(2)
C27	Ir1	N1	97.27(8)		N3	C16	C17	115.79(19)
C27	Ir1	N2	80.38(8)		C15	C16	C17	121.9(2)
C27	Ir1	N3	96.07(8)		O1	C17	C16	115.47(19)
C27	Ir1	C7	88.14(8)		O2	C17	O1	127.0(2)
C19	Si1	C32	108.29(12)		O2	C17	C16	117.5(2)
C19	Si1	C35	105.95(14)		C19	C18	C14	175.5(3)
C19	Si1	C38	102.79(15)		C18	C19	Si1	178.1(3)
C19	Si1	C38A	113.9(2)		N2	C21	C22	122.1(2)
C32	Si1	C38	106.18(15)		C21	C22	C23	119.1(2)
C32	Si1	C38A	119.0(2)		C24	C23	C22	118.9(2)
C35	Si1	C32	114.32(14)		C23	C24	C25	120.0(2)
C35	Si1	C38	118.35(18)		N2	C25	C24	120.2(2)
C35	Si1	C38A	94.2(3)		N2	C25	C26	113.32(19)
C38A	Si1	C38	24.2(3)		C24	C25	C26	126.4(2)
C17	O1	Ir1	116.71(14)		C27	C26	C25	115.19(19)
C1	N1	Ir1	124.89(16)		C31	C26	C25	123.1(2)
C1	N1	C5	119.1(2)		C31	C26	C27	121.6(2)
C5	N1	Ir1	115.91(15)		C26	C27	Ir1	113.83(16)
C21	N2	Ir1	124.80(15)		C28	C27	Ir1	128.82(17)
C21	N2	C25	119.63(19)		C28	C27	C26	117.3(2)
C25	N2	Ir1	115.05(14)		C29	C28	C27	120.8(2)
C12	N3	Ir1	126.40(15)		C30	C29	C28	120.7(2)
C12	N3	C16	118.3(2)		C29	C30	C31	119.9(2)
C16	N3	Ir1	115.29(15)		C30	C31	C26	119.6(2)
N1	C1	C2	122.9(2)		C33	C32	Si1	113.79(19)
C1	C2	C3	118.4(2)		C33	C32	C34	109.3(3)
C2	C3	C4	119.8(2)		C34	C32	Si1	112.5(2)
C3	C4	C5	120.0(2)		C36	C35	Si1	113.8(3)
N1	C5	C4	119.7(2)		C37	C35	Si1	115.6(2)
N1	C5	C6	114.00(19)		C37	C35	C36	109.8(3)
C4	C5	C6	126.3(2)		C39	C38	Si1	110.2(3)
C7	C6	C5	115.0(2)		C39	C38	C40	105.4(4)
C11	C6	C5	123.8(2)		C40	C38	Si1	106.9(3)
C11	C6	C7	121.2(2)		C39A	C38A	Si1	107.1(6)
C6	C7	Ir1	114.62(16)		C39A	C38A	C40A	88.8(7)
C8	C7	Ir1	128.36(17)		C40A	C38A	Si1	112.5(5)
C8	C7	C6	117.0(2)					

Table S14. Selected bond lengths for **8**·3C_6H_6.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.137(3)		C23	C24	1.384(8)
Ir1	N1	2.037(3)		C24	C25	1.395(6)
Ir1	N2	2.039(4)		C25	C26	1.460(7)
Ir1	N3	2.199(4)		C26	C27	1.418(6)
Ir1	C7	1.999(4)		C26	C31	1.403(7)
Ir1	C27	1.997(4)		C27	C28	1.398(7)
Si1	C19	1.850(7)		C28	C29	1.391(7)
Si1	C32	1.934(7)		C29	C30	1.388(8)
Si1	C35	1.927(10)		C30	C31	1.383(8)
Si1	C38	1.813(11)		C32	C33	1.528(14)
Si1A	C19A	1.848(7)		C32	C34	1.550(13)
Si1A	C32A	1.938(6)		C35	C36	1.522(13)
Si1A	C35A	1.937(7)		C35	C37	1.576(11)
Si1A	C38A	1.932(7)		C38	C39	1.555(13)
O1	C17	1.278(5)		C38	C40	1.544(12)
O2	C17	1.229(5)		C32A	C33A	1.4721
N1	C1	1.352(6)		C32A	C34A	1.5741
N1	C5	1.372(6)		C35A	C36A	1.480(16)
N2	C21	1.345(6)		C35A	C37A	1.559(16)
N2	C25	1.369(6)		C38A	C39A	1.509(17)
N3	C12	1.352(6)		C38A	C40A	1.569(16)
N3	C16	1.354(6)		C21S	C22S	1.388(11)
C1	C2	1.377(6)		C21S	C23S^{1}	1.372(12)
C2	C3	1.400(7)		C22S	C23S	1.371(10)
C3	C4	1.376(7)		C23S	C21S^{1}	1.372(12)
C4	C5	1.390(6)		C1S	C6S	1.3900
C5	C6	1.456(6)		C1S	C2S	1.3900
C6	C7	1.411(6)		C6S	C5S	1.3900
C6	C11	1.397(6)		C5S	C4S	1.3900
C7	C8	1.404(6)		C4S	C3S	1.3900
C8	C9	1.388(7)		C3S	C2S	1.3900
C9	C10	1.391(8)		C16S	C11S	1.3900
C10	C11	1.378(8)		C16S	C15S	1.3900
C12	C13	1.404(7)		C11S	C12S	1.3900
C12	C18	1.378(9)		C12S	C13S	1.3900
C12	C18A	1.531(9)		C13S	C14S	1.3900
C13	C14	1.375(8)		C14S	C15S	1.3900
C14	C15	1.384(7)		C34S	C35S	1.3900
C15	C16	1.377(6)		C34S	C33S	1.3900
C16	C17	1.527(6)		C35S	C36S	1.3900
C18	C19	1.193(9)		C36S	C31S	1.3900
C18A	C19A	1.191(9)		C31S	C32S	1.3900
C21	C22	1.377(7)		C32S	C33S	1.3900
C22	C23	1.384(8)				

Table S15. Selected bond angles for **8**·3C_6H_6.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Ir1	N3	76.93(12)		C15	C16	C17	119.1(4)
N1	Ir1	O1	95.59(13)		O1	C17	C16	115.8(4)
N1	Ir1	N2	175.58(14)		O2	C17	O1	125.7(4)
N1	Ir1	N3	86.25(14)		O2	C17	C16	118.5(4)
N2	Ir1	O1	87.33(13)		C19	C18	C12	165.9(13)
N2	Ir1	N3	97.67(14)		C19A	C18A	C12	166.2(12)
C7	Ir1	O1	175.37(16)		C18	C19	Si1	163.0(11)
C7	Ir1	N1	80.53(17)		C18A	C19A	Si1A	173.1(10)
C7	Ir1	N2	96.39(16)		N2	C21	C22	123.1(5)
C7	Ir1	N3	105.20(16)		C21	C22	C23	118.6(5)
C27	Ir1	O1	91.24(14)		C24	C23	C22	119.2(5)
C27	Ir1	N1	95.46(17)		C23	C24	C25	120.2(5)
C27	Ir1	N2	81.13(17)		N2	C25	C24	119.9(4)
C27	Ir1	N3	168.16(15)		N2	C25	C26	113.6(4)
C27	Ir1	C7	86.64(17)		C24	C25	C26	126.5(4)
C19	Si1	C32	104.6(5)		C27	C26	C25	115.8(4)
C19	Si1	C35	109.1(5)		C31	C26	C25	123.2(4)
C35	Si1	C32	108.0(5)		C31	C26	C27	121.0(5)
C38	Si1	C19	107.2(5)		C26	C27	Ir1	113.9(3)
C38	Si1	C32	108.8(5)		C28	C27	Ir1	128.3(3)
C38	Si1	C35	118.2(5)		C28	C27	C26	117.6(4)
C19A	Si1A	C32A	105.1(5)		C29	C28	C27	121.0(4)
C19A	Si1A	C35A	108.1(8)		C30	C29	C28	120.7(5)
C19A	Si1A	C38A	107.6(8)		C31	C30	C29	120.0(5)
C35A	Si1A	C32A	100.5(5)		C30	C31	C26	119.8(5)
C38A	Si1A	C32A	121.2(5)		C33	C32	Si1	108.3(8)
C38A	Si1A	C35A	113.5(9)		C33	C32	C34	113.3(10)
C17	O1	Ir1	117.8(3)		C34	C32	Si1	107.7(8)
C1	N1	Ir1	124.8(3)		C36	C35	Si1	110.8(9)
C1	N1	C5	119.4(4)		C36	C35	C37	109.7(10)
C5	N1	Ir1	115.7(3)		C37	C35	Si1	109.8(7)
C21	N2	Ir1	125.3(3)		C39	C38	Si1	115.4(8)
C21	N2	C25	119.0(4)		C40	C38	Si1	112.9(8)
C25	N2	Ir1	115.6(3)		C40	C38	C39	108.5(10)
C12	N3	Ir1	130.0(3)		C33A	C32A	Si1A	107.46(17)
C12	N3	C16	117.2(4)		C33A	C32A	C34A	112.195(2)
C16	N3	Ir1	112.0(3)		C34A	C32A	Si1A	114.26(15)
N1	C1	C2	122.5(4)		C36A	C35A	Si1A	121.4(15)
C1	C2	C3	118.3(5)		C36A	C35A	C37A	121.3(18)
C4	C3	C2	119.4(4)		C37A	C35A	Si1A	106.8(16)
C3	C4	C5	120.4(4)		C39A	C38A	Si1A	110.4(19)
N1	C5	C4	119.9(4)		C39A	C38A	C40A	114.8(19)
N1	C5	C6	113.9(4)		C40A	C38A	Si1A	107.3(13)
C4	C5	C6	126.2(4)		C23S[1]	C21S	C22S	120.2(7)
C7	C6	C5	115.0(4)		C23S	C22S	C21S	120.0(8)
C11	C6	C5	123.3(4)		C22S	C23S	C21S[1]	119.7(7)
C11	C6	C7	121.7(4)		C6S	C1S	C2S	120.0
C6	C7	Ir1	114.8(3)		C1S	C6S	C5S	120.0
C8	C7	Ir1	128.1(3)		C4S	C5S	C6S	120.0
C8	C7	C6	116.8(4)		C3S	C4S	C5S	120.0
C9	C8	C7	121.4(5)		C2S	C3S	C4S	120.0
C8	C9	C10	120.4(5)		C3S	C2S	C1S	120.0
C11	C10	C9	119.8(4)		C11S	C16S	C15S	120.0
C10	C11	C6	119.8(5)		C16S	C11S	C12S	120.0

Table S15 continued. Selected bond angles for **8**·3C_6H_6.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N3	C12	C13	121.0(4)		C13S	C12S	C11S	120.0
N3	C12	C18	125.9(7)		C12S	C13S	C14S	120.0
N3	C12	C18A	117.9(6)		C15S	C14S	C13S	120.0
C13	C12	C18A	120.8(6)		C14S	C15S	C16S	120.0
C18	C12	C13	112.9(7)		C35S	C34S	C33S	120.0
C18	C12	C18A	12.3(7)		C34S	C35S	C36S	120.0
C14	C13	C12	120.6(5)		C35S	C36S	C31S	120.0
C13	C14	C15	118.4(5)		C36S	C31S	C32S	120.0
C16	C15	C14	118.6(5)		C33S	C32S	C31S	120.0
N3	C16	C15	124.2(4)		C32S	C33S	C34S	120.0
N3	C16	C17	116.7(4)					

Table S16. Selected bond lengths for **9**·3CH_3OH.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.167(4)		C21	C22	1.361(9)
Ir1	N1	2.036(5)		C23	C24	1.389(8)
Ir1	N2	2.037(5)		C24	C25	1.396(9)
Ir1	N3	2.131(5)		C25	C26	1.396(9)
Ir1	C7	2.001(6)		C25	C28	1.452(17)
Ir1	C18	1.984(6)		C25	C28A	1.439(18)
Si1	C37	1.848(15)		C26	C27	1.376(8)
Si1	C38	1.878(7)		C28	C29	1.20(2)
Si1	C41	1.877(7)		C28A	C29A	1.18(2)
Si1	C44	1.878(7)		C29	C30	1.405(17)
Si2	C37A	1.843(17)		C29A	C30A	1.452(19)
Si2	C38A	1.879(7)		C30	C31	1.3900
Si2	C41A	1.876(7)		C30	C35	1.3900
Si2	C44A	1.878(7)		C31	C32	1.3900
O1	N4	1.289(7)		C32	C33	1.3900
O2	N4	1.237(7)		C33	C34	1.3900
N1	C1	1.346(8)		C33	C36	1.451(15)
N1	C5	1.371(8)		C34	C35	1.3900
N2	C12	1.350(8)		C30A	C31A	1.3900
N2	C16	1.356(7)		C30A	C35A	1.3900
N3	C23	1.350(8)		C31A	C32A	1.3900
N3	C27	1.334(7)		C32A	C33A	1.3900
N4	C23	1.506(9)		C33A	C34A	1.3900
C1	C2	1.366(9)		C33A	C36A	1.444(15)
C2	C3	1.385(10)		C34A	C35A	1.3900
C3	C4	1.374(9)		C36	C37	1.190(19)
C4	C5	1.382(9)		C36A	C37A	1.19(2)
C5	C6	1.467(8)		C38	C39	1.528(7)
C6	C7	1.421(8)		C38	C40	1.528(7)
C6	C11	1.398(8)		C38A	C39A	1.528(7)
C7	C8	1.391(8)		C38A	C40A	1.527(7)
C8	C9	1.386(8)		C41	C42	1.527(7)
C9	C10	1.383(9)		C41	C43	1.527(7)
C10	C11	1.393(9)		C41A	C42A	1.528(7)
C12	C13	1.383(8)		C41A	C43A	1.527(7)
C13	C14	1.378(9)		C44	C45	1.529(7)
C14	C15	1.380(9)		C44	C46	1.529(7)
C15	C16	1.399(8)		C44A	C45A	1.528(7)
C16	C17	1.455(8)		C44A	C46A	1.528(7)
C17	C18	1.409(8)		O3	C47	1.428(8)
C17	C22	1.413(8)		O4	C48	1.427(8)
C18	C19	1.406(8)		O5	C49	1.428(8)
C19	C20	1.390(9)		O5A	C49A	1.428(8)
C20	C21	1.392(10)				

Table S17. Selected bond angles for **9**·3CH_3OH.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	90.55(18)		C22	C17	C16	123.4(5)
N1	Ir1	N2	173.9(2)		C17	C18	Ir1	114.4(4)
N1	Ir1	N3	95.24(19)		C19	C18	Ir1	128.3(5)
N2	Ir1	O1	93.83(18)		C19	C18	C17	116.9(5)
N2	Ir1	N3	89.96(18)		C20	C19	C18	121.1(6)
N3	Ir1	O1	76.45(17)		C19	C20	C21	120.7(6)
C7	Ir1	O1	97.89(19)		C22	C21	C20	119.9(6)
C7	Ir1	N1	80.9(2)		C21	C22	C17	120.1(6)
C7	Ir1	N2	94.3(2)		N3	C23	N4	116.1(5)
C7	Ir1	N3	173.2(2)		N3	C23	C24	121.9(6)
C18	Ir1	O1	169.2(2)		C24	C23	N4	122.1(6)
C18	Ir1	N1	95.8(2)		C23	C24	C25	119.2(6)
C18	Ir1	N2	80.5(2)		C24	C25	C26	117.8(6)
C18	Ir1	N3	94.2(2)		C24	C25	C28	117.0(9)
C18	Ir1	C7	91.8(2)		C24	C25	C28A	127.7(9)
C37	Si1	C38	105.2(6)		C26	C25	C28	125.0(9)
C37	Si1	C41	106.6(7)		C26	C25	C28A	114.0(9)
C37	Si1	C44	107.9(6)		C28A	C25	C28	14.6(9)
C41	Si1	C38	110.4(6)		C27	C26	C25	119.6(6)
C41	Si1	C44	110.6(6)		N3	C27	C26	122.5(6)
C44	Si1	C38	115.6(7)		C29	C28	C25	168.0(18)
C37A	Si2	C38A	102.9(7)		C29A	C28A	C25	177(2)
C37A	Si2	C41A	107.4(7)		C28	C29	C30	176.2(18)
C37A	Si2	C44A	106.9(8)		C28A	C29A	C30A	173(2)
C41A	Si2	C38A	118.2(7)		C31	C30	C29	122.0(9)
C41A	Si2	C44A	109.5(6)		C31	C30	C35	120.0
C44A	Si2	C38A	111.1(6)		C35	C30	C29	118.0(9)
N4	O1	Ir1	116.5(4)		C30	C31	C32	120.0
C1	N1	Ir1	125.6(4)		C33	C32	C31	120.0
C1	N1	C5	118.3(5)		C32	C33	C34	120.0
C5	N1	Ir1	116.1(4)		C32	C33	C36	120.3(8)
C12	N2	Ir1	124.2(4)		C34	C33	C36	119.7(8)
C12	N2	C16	119.8(5)		C35	C34	C33	120.0
C16	N2	Ir1	115.9(4)		C34	C35	C30	120.0
C23	N3	Ir1	115.2(4)		C31A	C30A	C29A	121.6(9)
C27	N3	Ir1	125.9(4)		C31A	C30A	C35A	120.0
C27	N3	C23	118.9(5)		C35A	C30A	C29A	118.4(9)
O1	N4	C23	115.7(5)		C30A	C31A	C32A	120.0
O2	N4	O1	124.5(6)		C33A	C32A	C31A	120.0
O2	N4	C23	119.8(6)		C32A	C33A	C34A	120.0
N1	C1	C2	123.1(6)		C32A	C33A	C36A	120.3(8)
C1	C2	C3	118.6(6)		C34A	C33A	C36A	119.7(8)
C4	C3	C2	119.3(6)		C33A	C34A	C35A	120.0
C3	C4	C5	120.0(6)		C34A	C35A	C30A	120.0
N1	C5	C4	120.6(6)		C37	C36	C33	177.8(15)
N1	C5	C6	113.4(5)		C37A	C36A	C33A	177.6(16)
C4	C5	C6	126.0(6)		C36	C37	Si1	175.9(14)
C7	C6	C5	115.3(5)		C36A	C37A	Si2	175.0(15)
C11	C6	C5	123.1(6)		C39	C38	Si1	117.4(12)
C11	C6	C7	121.6(6)		C40	C38	Si1	113.1(10)
C6	C7	Ir1	114.2(4)		C40	C38	C39	107.6(15)
C8	C7	Ir1	129.7(5)		C39A	C38A	Si2	116.7(10)
C8	C7	C6	116.1(5)		C40A	C38A	Si2	114.0(12)
C9	C8	C7	122.4(6)		C40A	C38A	C39A	109.3(14)

Table S17 continued. Selected bond angles for **9**·3CH_3OH.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C10	C9	C8	120.9(6)		C42	C41	Si1	112.6(10)
C9	C10	C11	118.8(6)		C43	C41	Si1	113.3(13)
C10	C11	C6	120.1(6)		C43	C41	C42	107.5(16)
N2	C12	C13	121.6(6)		C42A	C41A	Si2	113.7(10)
C14	C13	C12	119.1(6)		C43A	C41A	Si2	110.6(9)
C13	C14	C15	119.7(6)		C43A	C41A	C42A	108.3(12)
C14	C15	C16	119.4(6)		C45	C44	Si1	111.9(10)
N2	C16	C15	120.3(5)		C45	C44	C46	107.8(14)
N2	C16	C17	113.5(5)		C46	C44	Si1	115.4(12)
C15	C16	C17	126.2(5)		C45A	C44A	Si2	113.0(10)
C18	C17	C16	115.2(5)		C45A	C44A	C46A	110.2(14)
C18	C17	C22	121.3(6)		C46A	C44A	Si2	112.3(10)

Table S18. Selected bond lengths for **11**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.180(4)		C12	C17	1.401(8)
Ir1	N1	2.027(5)		C13	C14	1.383(8)
Ir1	N2	2.038(4)		C14	C15	1.376(9)
Ir1	N3	2.131(4)		C15	C16	1.383(10)
Ir1	C7	1.988(5)		C16	C17	1.387(9)
Ir1	C27	2.009(5)		C21	C22	1.370(8)
Br1	C40	1.880(6)		C22	C23	1.409(7)
O1	C43	1.280(7)		C23	C24	1.385(7)
O2	C43	1.238(7)		C23	C32	1.470(8)
N1	C1	1.352(7)		C24	C25	1.386(8)
N1	C5	1.361(7)		C25	C26	1.454(8)
N2	C21	1.341(7)		C26	C27	1.394(7)
N2	C25	1.375(6)		C26	C31	1.402(7)
N3	C38	1.335(7)		C27	C28	1.395(7)
N3	C42	1.350(7)		C28	C29	1.398(7)
C1	C2	1.360(8)		C29	C30	1.372(9)
C2	C3	1.383(8)		C30	C31	1.380(8)
C3	C4	1.385(8)		C32	C33	1.383(8)
C3	C12	1.476(8)		C32	C37	1.379(8)
C4	C5	1.392(8)		C33	C34	1.384(9)
C5	C6	1.476(7)		C34	C35	1.374(9)
C6	C7	1.404(8)		C35	C36	1.364(9)
C6	C11	1.391(8)		C36	C37	1.390(10)
C7	C8	1.403(7)		C38	C39	1.352(8)
C8	C9	1.382(8)		C39	C40	1.379(8)
C9	C10	1.382(9)		C40	C41	1.380(8)
C10	C11	1.385(8)		C41	C42	1.379(8)
C12	C13	1.399(8)		C42	C43	1.507(7)

Table S19. Selected bond angles for **11**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Ir1	O1	95.22(17)		C17	C12	C3	120.9(6)
N1	Ir1	N2	173.91(17)		C14	C13	C12	121.3(6)
N1	Ir1	N3	88.74(17)		C15	C14	C13	119.9(6)
N2	Ir1	O1	86.08(16)		C14	C15	C16	120.0(6)
N2	Ir1	N3	97.36(17)		C15	C16	C17	120.3(6)
N3	Ir1	O1	76.60(15)		C16	C17	C12	120.6(7)
C7	Ir1	O1	172.30(18)		N2	C21	C22	124.2(5)
C7	Ir1	N1	80.3(2)		C21	C22	C23	119.9(5)
C7	Ir1	N2	99.0(2)		C22	C23	C32	123.0(5)
C7	Ir1	N3	96.92(18)		C24	C23	C22	115.5(5)
C7	Ir1	C27	87.0(2)		C24	C23	C32	121.6(5)
C27	Ir1	O1	99.57(18)		C23	C24	C25	123.0(5)
C27	Ir1	N1	93.44(19)		N2	C25	C24	119.9(5)
C27	Ir1	N2	80.47(19)		N2	C25	C26	113.8(5)
C27	Ir1	N3	175.77(19)		C24	C25	C26	126.3(5)
C43	O1	Ir1	115.8(3)		C27	C26	C25	115.7(5)
C1	N1	Ir1	123.9(4)		C27	C26	C31	121.5(5)
C1	N1	C5	119.0(5)		C31	C26	C25	122.7(5)
C5	N1	Ir1	116.9(4)		C26	C27	Ir1	114.5(4)
C21	N2	Ir1	127.0(4)		C26	C27	C28	117.1(5)
C21	N2	C25	117.6(5)		C28	C27	Ir1	128.4(4)
C25	N2	Ir1	115.3(3)		C27	C28	C29	121.4(5)
C38	N3	Ir1	127.0(4)		C30	C29	C28	120.4(5)
C38	N3	C42	117.9(4)		C29	C30	C31	119.7(5)
C42	N3	Ir1	115.0(3)		C30	C31	C26	119.9(5)
N1	C1	C2	121.6(5)		C33	C32	C23	122.2(5)
C1	C2	C3	121.1(5)		C37	C32	C23	120.3(5)
C2	C3	C4	117.4(5)		C37	C32	C33	117.6(6)
C2	C3	C12	121.2(5)		C32	C33	C34	121.2(6)
C4	C3	C12	121.3(5)		C35	C34	C33	120.7(6)
C3	C4	C5	120.3(5)		C36	C35	C34	118.6(6)
N1	C5	C4	120.6(5)		C35	C36	C37	121.0(6)
N1	C5	C6	112.6(5)		C32	C37	C36	120.9(6)
C4	C5	C6	126.8(5)		N3	C38	C39	124.2(5)
C7	C6	C5	114.8(5)		C38	C39	C40	117.8(6)
C11	C6	C5	123.3(5)		C39	C40	Br1	119.9(5)
C11	C6	C7	121.8(5)		C39	C40	C41	119.9(5)
C6	C7	Ir1	115.2(4)		C41	C40	Br1	120.2(4)
C8	C7	Ir1	127.8(4)		C42	C41	C40	118.5(5)
C8	C7	C6	116.9(5)		N3	C42	C41	121.7(5)
C9	C8	C7	121.4(5)		N3	C42	C43	116.0(5)
C8	C9	C10	120.5(6)		C41	C42	C43	122.4(5)
C9	C10	C11	119.8(6)		O1	C43	C42	116.6(5)
C10	C11	C6	119.6(6)		O2	C43	O1	126.5(5)
C13	C12	C3	121.4(5)		O2	C43	C42	117.0(5)
C13	C12	C17	117.7(6)					

Table S20. Selected bond lengths for **12·CH_2Cl_2**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ir1	O1	2.151(2)		C16	C17	1.388(5)
Ir1	N1	2.039(2)		C21	C22	1.375(4)
Ir1	N2	2.039(2)		C22	C23	1.401(4)
Ir1	N3	2.164(2)		C23	C24	1.390(4)
Ir1	C7	2.001(3)		C23	C32	1.485(4)
Ir1	C27	1.994(3)		C24	C25	1.389(4)
Si1	C45	1.851(3)		C25	C26	1.462(4)
Si1	C46	1.887(3)		C26	C27	1.414(4)
Si1	C49	1.887(3)		C26	C31	1.388(4)
Si1	C52	1.874(4)		C27	C28	1.401(4)
O1	C43	1.270(3)		C28	C29	1.384(4)
O2	C43	1.233(3)		C29	C30	1.389(4)
N1	C1	1.343(4)		C30	C31	1.375(4)
N1	C5	1.363(4)		C32	C33	1.392(5)
N2	C21	1.343(4)		C32	C37	1.394(5)
N2	C25	1.357(4)		C33	C34	1.390(5)
N3	C38	1.341(4)		C34	C35	1.377(5)
N3	C42	1.348(4)		C35	C36	1.380(5)
C1	C2	1.374(4)		C36	C37	1.386(5)
C2	C3	1.397(4)		C38	C39	1.374(4)
C3	C4	1.386(4)		C39	C40	1.392(4)
C3	C12	1.484(4)		C40	C41	1.393(4)
C4	C5	1.382(4)		C40	C44	1.435(4)
C5	C6	1.460(4)		C41	C42	1.378(4)
C6	C7	1.411(4)		C42	C43	1.512(4)
C6	C11	1.395(4)		C44	C45	1.200(4)
C7	C8	1.395(4)		C46	C47	1.540(5)
C8	C9	1.385(4)		C46	C48	1.521(5)
C9	C10	1.390(4)		C49	C50	1.534(5)
C10	C11	1.375(4)		C49	C51	1.532(5)
C12	C13	1.395(4)		C52	C53	1.536(5)
C12	C17	1.395(4)		C52	C54	1.519(6)
C13	C14	1.386(4)		Cl1	C1S	1.766(5)
C14	C15	1.381(5)		Cl2	C1S	1.739(5)
C15	C16	1.378(5)				

Table S21. Selected bond angles for **12·CH_2Cl_2**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Ir1	N3	75.76(8)		C16	C15	C14	119.9(3)
N1	Ir1	O1	89.88(8)		C15	C16	C17	120.3(3)
N1	Ir1	N2	172.04(9)		C16	C17	C12	120.8(3)
N1	Ir1	N3	100.79(9)		N2	C21	C22	122.1(3)
N2	Ir1	O1	96.97(9)		C21	C22	C23	120.3(3)
N2	Ir1	N3	84.89(9)		C22	C23	C32	121.7(3)
C7	Ir1	O1	94.50(9)		C24	C23	C22	116.6(3)
C7	Ir1	N1	80.31(11)		C24	C23	C32	121.7(3)
C7	Ir1	N2	95.06(11)		C25	C24	C23	121.3(3)
C7	Ir1	N3	170.15(10)		N2	C25	C24	120.3(3)
C27	Ir1	O1	174.02(9)		N2	C25	C26	114.0(3)
C27	Ir1	N1	92.81(11)		C24	C25	C26	125.7(3)
C27	Ir1	N2	80.76(11)		C27	C26	C25	115.1(3)
C27	Ir1	N3	98.48(10)		C31	C26	C25	123.5(3)
C27	Ir1	C7	91.22(11)		C31	C26	C27	121.4(3)
C45	Si1	C46	106.13(15)		C26	C27	Ir1	114.0(2)
C45	Si1	C49	104.99(15)		C28	C27	Ir1	129.1(2)
C45	Si1	C52	108.65(15)		C28	C27	C26	116.7(3)
C46	Si1	C49	115.17(16)		C29	C28	C27	121.5(3)
C52	Si1	C46	112.00(16)		C28	C29	C30	120.6(3)
C52	Si1	C49	109.43(16)		C31	C30	C29	119.3(3)
C43	O1	Ir1	117.96(18)		C30	C31	C26	120.5(3)
C1	N1	Ir1	125.47(19)		C33	C32	C23	120.6(3)
C1	N1	C5	118.5(2)		C33	C32	C37	118.3(3)
C5	N1	Ir1	115.78(19)		C37	C32	C23	121.1(3)
C21	N2	Ir1	125.0(2)		C34	C33	C32	120.7(3)
C21	N2	C25	119.4(3)		C35	C34	C33	120.1(3)
C25	N2	Ir1	115.5(2)		C34	C35	C36	119.9(3)
C38	N3	Ir1	126.5(2)		C35	C36	C37	120.1(3)
C38	N3	C42	117.7(2)		C36	C37	C32	120.7(3)
C42	N3	Ir1	114.19(18)		N3	C38	C39	123.1(3)
N1	C1	C2	122.7(3)		C38	C39	C40	119.5(3)
C1	C2	C3	120.3(3)		C39	C40	C41	117.6(3)
C2	C3	C12	122.3(3)		C39	C40	C44	120.5(3)
C4	C3	C2	116.3(3)		C41	C40	C44	121.8(3)
C4	C3	C12	121.4(3)		C42	C41	C40	119.5(3)
C5	C4	C3	121.8(3)		N3	C42	C41	122.6(3)
N1	C5	C4	120.5(3)		N3	C42	C43	115.8(2)
N1	C5	C6	114.1(2)		C41	C42	C43	121.5(3)
C4	C5	C6	125.4(3)		O1	C43	C42	115.0(2)
C7	C6	C5	114.6(3)		O2	C43	O1	125.7(3)
C11	C6	C5	123.9(3)		O2	C43	C42	119.3(3)
C11	C6	C7	121.5(3)		C45	C44	C40	177.1(3)
C6	C7	Ir1	114.9(2)		C44	C45	Si1	174.7(3)
C8	C7	Ir1	128.1(2)		C47	C46	Si1	115.0(2)
C8	C7	C6	116.8(3)		C48	C46	Si1	112.2(2)
C9	C8	C7	121.6(3)		C48	C46	C47	109.5(3)
C8	C9	C10	120.3(3)		C50	C49	Si1	112.7(2)
C11	C10	C9	119.8(3)		C51	C49	Si1	114.4(2)
C10	C11	C6	119.9(3)		C51	C49	C50	110.6(3)
C13	C12	C3	120.7(3)		C53	C52	Si1	111.4(3)
C13	C12	C17	118.0(3)		C54	C52	Si1	113.9(3)
C17	C12	C3	121.3(3)		C54	C52	C53	111.9(4)
C14	C13	C12	121.1(3)		Cl2	C1S	Cl1	111.2(3)

Table S21 continued. Selected bond angles for **12·CH_2Cl_2**.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C15	C14	C13	120.0(3)					

S3. DFT model validation

Table S22. Bond length comparison of SDD and LANL2DZ/6-31G(d) basis sets, MAD values.

Compound	Basis set (MAD values, Å)	
	SDD	LANL2DZ/6-31G(d)
2	0.031	0.039
3	0.030	0.033
4	0.035	0.038
5	0.030	0.033
6	0.032	0.035

Table S23. Comparison of simulated and measured infrared vibrational frequencies for SDD and LANL2DZ/6-31G(d) basis sets, MAD

Compound	Basis set (MAD values, cm^{-1})	
	SDD	LANL2DZ/6-31G(d)
2	34.6	67.3
3	22.2	59.7
4	15.6	50.7
5	35.2	41.2
6	24.7	50.5

S4 Orbital Contributions

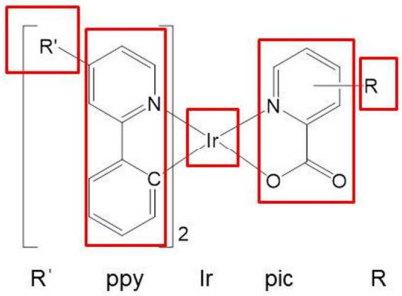

Figure S27. Molecular components of complexes **1**-**13**;where R' = -H or -Ph and R = -Br, -C≡C-Tips or -C≡C-C_6H_4-C≡C-Tips.

Table S24. Orbital contributions for complex **1**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
135	L+10	0.47	3	94	3	0
134	L+9	0.05	7	92	1	0
133	L+8	-0.04	97	6	0	0
132	L+7	-0.10	10	88	1	0
131	L+6	-0.99	0	2	44	54
130	L+5	-1.23	1	98	0	0
129	L+4	-1.29	2	87	11	0
128	L+3	-1.72	1	39	58	2
127	L+2	-1.78	3	70	27	1
126	L+1	-1.85	4	93	3	0
125	LUMO	-2.28	1	2	97	0
124	HOMO	-5.47	44	52	4	0
123	H-1	-6.07	63	21	16	0
122	H-2	-6.28	50	45	4	0
121	H-3	-6.37	20	73	7	1
120	H-4	-6.61	7	90	3	0
119	H-5	-6.73	6	77	15	2
118	H-6	-6.90	0	28	61	11
117	H-7	-7.50	8	38	52	2
116	H-8	-7.61	1	2	52	45
115	H-9	-7.74	11	21	65	3
114	H-10	-7.83	14	61	24	1

Table S25. Orbital contributions for complex **2**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
135	L+10	0.46	4	93	4	0
134	L+9	0.04	9	90	1	0
133	L+8	-0.02	98	4	0	0
132	L+7	-0.12	8	91	1	0
131	L+6	-1.05	0	0	45	55
130	L+5	-1.23	1	98	0	0
129	L+4	-1.31	2	89	9	0
128	L+3	-1.74	1	34	64	1
127	L+2	-1.79	3	73	24	0
126	L+1	-1.86	4	93	3	0
125	LUMO	-2.30	1	2	95	2
124	HOMO	-5.48	43	53	4	0
123	H-1	-6.11	62	24	14	0
122	H-2	-6.29	56	38	5	1
121	H-3	-6.40	16	79	5	0
120	H-4	-6.62	7	91	2	0
119	H-5	-6.76	5	91	4	0
118	H-6	-7.17	0	15	85	0
117	H-7	-7.52	8	37	54	1
116	H-8	-7.73	9	15	73	4
115	H-9	-7.82	13	59	25	2
114	H-10	-8.04	12	29	25	33

Table S26. Orbital contributions for complex **3**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
135	L+10	0.45	4	90	5	1
134	L+9	0.04	8	91	1	0
133	L+8	-0.04	98	6	0	-1
132	L+7	-0.11	10	88	1	0
131	L+6	-1.07	0	3	44	54
130	L+5	-1.23	2	98	0	0
129	L+4	-1.30	2	89	9	0
128	L+3	-1.75	1	35	63	1
127	L+2	-1.80	3	73	24	0
126	L+1	-1.86	4	92	4	0
125	LUMO	-2.30	1	2	95	1
124	HOMO	-5.49	43	53	4	0
123	H-1	-6.11	62	24	14	0
122	H-2	-6.30	52	44	4	0
121	H-3	-6.40	20	75	5	0
120	H-4	-6.62	7	91	2	0
119	H-5	-6.76	6	90	4	0
118	H-6	-7.14	0	15	85	0
117	H-7	-7.51	8	35	56	1
116	H-8	-7.63	3	8	61	28
115	H-9	-7.77	7	14	66	12
114	H-10	-7.83	14	59	25	2

Table S27. Orbital contributions for complex **4**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
135	L+10	0.52	12	83	1	4
134	L+9	0.08	11	85	2	2
133	L+8	-0.01	31	66	1	2
132	L+7	-0.06	68	31	0	2
131	L+6	-1.00	3	9	39	50
130	L+5	-1.21	2	97	0	1
129	L+4	-1.30	2	90	8	1
128	L+3	-1.65	0	8	89	3
127	L+2	-1.75	4	94	2	0
126	L+1	-1.83	4	94	2	1
125	LUMO	-2.29	1	2	97	0
124	HOMO	-5.47	44	53	3	0
123	H-1	-6.05	65	21	14	0
122	H-2	-6.24	17	81	2	1
121	H-3	-6.33	51	43	5	1
120	H-4	-6.58	10	88	1	1
119	H-5	-6.69	6	90	3	1
118	H-6	-7.10	1	17	82	1
117	H-7	-7.50	4	17	69	10
116	H-8	-7.56	5	18	58	19
115	H-9	-7.77	26	42	17	15
114	H-10	-7.83	9	18	64	9

Table S28. Orbital contributions for complex **5**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
182	L+10	0.53	5	16	7	72
181	L+9	0.49	4	89	3	4
180	L+8	0.08	8	91	1	0
179	L+7	0.00	95	4	0	1
178	L+6	-0.08	9	89	1	1
177	L+5	-1.20	2	98	0	0
176	L+4	-1.29	2	95	2	1
175	L+3	-1.74	4	94	2	0
174	L+2	-1.82	3	95	2	0
173	L+1	-1.95	1	4	81	14
172	LUMO	-2.15	1	3	90	7
171	HOMO	-5.42	44	52	4	0
170	H-1	-6.02	63	21	16	0
169	H-2	-6.23	59	35	6	1
168	H-3	-6.33	10	79	8	2
167	H-4	-6.58	5	83	8	4
166	H-5	-6.63	4	35	34	26
165	H-6	-6.76	1	65	10	23
164	H-7	-6.81	3	11	21	65
163	H-8	-7.16	0	6	29	65
162	H-9	-7.43	7	35	51	6
161	H-10	-7.46	1	2	25	73

Table S29. Orbital contributions for complex **6**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
182	L+10	0.31	3	14	54	29
181	L+9	0.26	1	1	8	91
180	L+8	0.06	8	89	2	1
179	L+7	-0.01	98	3	0	0
178	L+6	-0.09	7	91	2	0
177	L+5	-1.21	1	98	0	0
176	L+4	-1.27	1	85	13	1
175	L+3	-1.66	0	19	78	3
174	L+2	-1.75	4	93	3	0
173	L+1	-1.83	3	94	2	0
172	LUMO	-2.40	2	1	81	16
171	HOMO	-5.44	43	52	4	0
170	H-1	-6.06	62	23	15	0
169	H-2	-6.22	61	28	7	4
168	H-3	-6.35	9	86	4	1
167	H-4	-6.59	6	92	2	1
166	H-5	-6.73	4	90	5	1
165	H-6	-7.07	4	5	18	73
164	H-7	-7.08	0	13	79	8
163	H-8	-7.15	0	1	3	96
162	H-9	-7.46	7	35	54	3
161	H-10	-7.64	7	12	63	17

Table S30. Orbital contributions for complex **7**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
182	L+10	0.23	1	6	9	84
181	L+9	0.16	1	5	57	37
180	L+8	0.06	8	85	4	3
179	L+7	-0.01	96	3	0	1
178	L+6	-0.09	8	89	2	1
177	L+5	-1.21	2	98	0	0
176	L+4	-1.28	2	87	10	1
175	L+3	-1.65	1	16	80	3
174	L+2	-1.76	4	90	6	0
173	L+1	-1.82	3	96	1	0
172	LUMO	-2.38	1	2	84	14
171	HOMO	-5.44	43	52	4	0
170	H-1	-6.06	63	22	15	0
169	H-2	-6.25	58	37	5	0
168	H-3	-6.36	13	82	5	0
167	H-4	-6.59	7	91	2	0
166	H-5	-6.73	5	89	6	1
165	H-6	-6.90	1	2	27	70
164	H-7	-7.07	0	15	73	12
163	H-8	-7.17	0	1	13	85
162	H-9	-7.46	7	36	55	2
161	H-10	-7.58	2	4	30	64

Table S31. Orbital contributions for complex **8**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
182	L+10	0.51	3	23	51	23
181	L+9	0.30	7	46	5	41
180	L+8	0.10	26	70	0	3
179	L+7	0.03	70	29	0	1
178	L+6	-0.20	12	45	3	41
177	L+5	-1.17	2	98	0	0
176	L+4	-1.26	1	96	3	1
175	L+3	-1.70	4	95	1	0
174	L+2	-1.78	3	95	1	0
173	L+1	-1.92	0	3	84	12
172	LUMO	-2.18	1	1	86	12
171	HOMO	-5.40	45	52	3	0
170	H-1	-5.98	65	21	14	0
169	H-2	-6.18	34	63	2	1
168	H-3	-6.24	32	60	5	2
167	H-4	-6.51	9	85	2	3
166	H-5	-6.64	5	90	3	3
165	H-6	-6.91	2	3	33	62
164	H-7	-7.02	1	18	79	2
163	H-8	-7.10	1	4	2	93
162	H-9	-7.45	6	27	61	6
161	H-10	-7.54	2	5	31	62

Table S32. Orbital contributions for complex **9**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
208	L+10	0.07	8	90	1	0
207	L+9	-0.01	98	3	0	0
206	L+8	-0.09	7	91	1	0
205	L+7	-0.75	0	0	0	100
204	L+6	-1.18	1	32	37	30
203	L+5	-1.21	2	95	2	2
202	L+4	-1.34	1	64	11	24
201	L+3	-1.74	2	41	47	10
200	L+2	-1.76	3	72	22	3
199	L+1	-1.84	3	85	10	2
198	LUMO	-2.64	2	1	57	40
197	HOMO	-5.44	43	52	4	0
196	H-1	-6.06	60	22	14	3
195	H-2	-6.14	46	14	9	31
194	H-3	-6.34	3	87	3	6
193	H-4	-6.45	22	24	6	49
192	H-5	-6.60	8	87	2	3
191	H-6	-6.74	6	87	5	2
190	H-7	-7.04	0	0	0	100
189	H-8	-7.08	0	15	84	0
188	H-9	-7.24	1	1	7	91
187	H-10	-7.45	7	35	55	2

Table S33. Orbital contributions for complex **10**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)			
			Ir	ppy	pic	R
208	L+10	0.06	8	91	1	0
207	L+9	-0.01	99	2	0	0
206	L+8	-0.09	7	91	2	0
205	L+7	-0.75	0	0	0	100
204	L+6	-1.20	1	59	24	16
203	L+5	-1.22	2	82	10	7
202	L+4	-1.39	1	53	16	29
201	L+3	-1.73	3	57	32	8
200	L+2	-1.79	3	44	44	9
199	L+1	-1.83	3	94	2	1
198	LUMO	-2.60	0	1	61	37
197	HOMO	-5.44	43	52	4	0
196	H-1	-6.06	63	22	15	0
195	H-2	-6.23	32	16	11	40
194	H-3	-6.30	25	24	6	46
193	H-4	-6.37	15	79	5	1
192	H-5	-6.60	7	91	2	0
191	H-6	-6.74	6	89	5	0
190	H-7	-7.05	0	0	0	100
189	H-8	-7.08	0	16	83	1
188	H-9	-7.18	0	0	13	87
187	H-10	-7.46	8	36	55	1

Table S34. Orbital contributions for complex **11**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	ppy	pic	R	R'
175	L+10	-0.27	2	42	0	0	55
174	L+9	-0.30	3	48	1	0	48
173	L+8	-0.58	1	3	0	0	96
172	L+7	-0.60	1	3	0	0	96
171	L+6	-1.05	0	0	45	55	0
170	L+5	-1.35	1	91	0	0	8
169	L+4	-1.44	1	75	15	0	9
168	L+3	-1.76	1	16	82	1	1
167	L+2	-2.01	4	73	1	0	23
166	L+1	-2.05	4	74	2	0	21
165	LUMO	-2.29	1	3	94	2	0
164	HOMO	-5.47	43	53	4	0	0
163	H-1	-6.05	61	22	12	0	5
162	H-2	-6.21	59	27	5	1	8
161	H-3	-6.37	5	90	3	0	1
160	H-4	-6.60	4	93	1	0	2
159	H-5	-6.74	2	91	3	0	4
158	H-6	-7.01	5	19	13	0	62
157	H-7	-7.09	11	17	12	1	59
156	H-8	-7.18	1	15	73	0	10
155	H-9	-7.26	0	0	0	0	100
154	H-10	-7.27	0	0	0	0	100

Table S35. Orbital contributions for complex **12**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	ppy	pic	R	R'
222	L+10	-0.04	4	85	1	1	9
221	L+9	-0.25	2	42	1	0	55
220	L+8	-0.28	4	47	1	0	47
219	L+7	-0.57	0	3	0	0	97
218	L+6	-0.59	1	3	0	0	96
217	L+5	-1.32	1	90	0	0	8
216	L+4	-1.39	1	67	24	1	8
215	L+3	-1.67	0	24	71	3	1
214	L+2	-1.99	3	73	1	0	23
213	L+1	-2.02	4	74	1	0	21
212	LUMO	-2.39	2	2	80	16	0
211	HOMO	-5.43	43	52	4	0	0
210	H-1	-6.00	61	21	13	0	5
209	H-2	-6.14	60	23	6	3	7
208	H-3	-6.34	4	92	3	0	1
207	H-4	-6.58	4	93	1	0	2
206	H-5	-6.71	2	90	4	0	3
205	H-6	-6.97	1	11	12	41	35
204	H-7	-6.98	4	18	22	0	55
203	H-8	-7.08	0	14	71	6	9
202	H-9	-7.15	0	1	3	95	0
201	H-10	-7.16	12	10	6	39	33

Table S36. Orbital contributions for complex **13**.

Molecular Orbital		Energy (eV)	Molecular Components Contributions (%)				
			Ir	ppy	pic	R	R'
248	L+10	-0.27	3	48	1	0	48
247	L+9	-0.57	0	3	0	0	97
246	L+8	-0.58	1	3	0	0	96
245	L+7	-0.75	0	0	0	100	0
244	L+6	-1.21	1	6	45	46	1
243	L+5	-1.32	1	90	0	0	8
242	L+4	-1.44	0	73	8	11	8
241	L+3	-1.76	0	11	74	13	1
240	L+2	-1.99	3	73	1	0	23
239	L+1	-2.02	3	75	1	0	21
238	LUMO	-2.64	2	1	57	40	0
237	HOMO	-5.43	43	52	4	0	0
236	H-1	-6.00	60	21	13	1	5
235	H-2	-6.08	49	16	7	22	5
234	H-3	-6.33	2	89	3	6	1
233	H-4	-6.41	13	15	7	61	4
232	H-5	-6.58	4	91	1	1	2
231	H-6	-6.71	2	90	3	0	4
230	H-7	-6.98	4	18	20	0	57
229	H-8	-7.04	0	0	0	100	0
228	H-9	-7.05	6	15	32	8	39
227	H-10	-7.11	3	16	48	6	26

S5. Physical Measurements

Instrumentation. All the photophysical measurements of iridium complexes were performed using DCM as the solvent.

The UV-Visible spectra were measured on a Unicam UV2-100 spectrometer operated with the Unicam Vison software in quartz cuvettes with path length l = 1 cm.

Excitation and emission photoluminescence spectra were recorded on a Horiba Jobin Yvon SPEX Fluorolog 3-22 spectrofluorometer. Samples were degassed by repeated freeze-pump-thaw cycles using a turbomolecular pump until the pressure was stable in quartz cuvettes, l = 1 cm. The solutions had absorbance below 0.15 to minimise inner filter effects. PLQYs were measured following our previously reported method.[1]

Emission lifetimes were determined by using a custom spectrometer; measured by time-correlated single photon counting (TCSPC) using a pulsed diode laser (371 nm), made by IBH Ltd, running at 1 MHz. The fluorescence emission was collected at right angles to the excitation source. The emission wavelength was selected using a Horiba Jobin Yvon Triax 190 monochromator and detected by a cooled IBH TBX-04 PMT. Timing was achieved using an Ortec 567 time-to-amplitude converter and an E. G. & G Trumpcard pulse height analyser (PHA), and data was recorded using Maestro (ver.510) software. The data were transferred to a PC and analysed using non-linear regression to a single exponential decay, and the quality of fit established by reduced χ^2 and random residuals. The samples were degassed by repeated freeze-pump-thaw cycles in duplicates. The decay data were fitted to a single exponential function.

Electrochemical analyses of the iridium complexes were carried out using a PalmSens EmStat^2 potentiometer, with platinum working, platinum counter and platinum pseudo

reference electrodes, from solutions in DCM containing 0.1 M supporting electrolyte (tetrabutylammonium hexafluorophospate, $TBAPF_6$), scan rate = 100 mV s^{-1}. The ferrocene/ferrocinium couple was used as the internal reference.

IR data was collected using a Perkin Elmer Spectrum Two IR spectrometer.

References

1. Davidson, R.; Hsu, Y.-T.; Batchelor, T.; Yufit, D.; Beeby, A., *Dalton Trans.* **2016,** *45*, 11496-11507.