Supporting Information

Ligand Effect of Cyclometallated Iridium (III) Complexes on N-Alkylation of Amines in Hydrogen Borrowing Reactions

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I. Crystal data for **Cat. 1~7**

Table S1. Crystal data for **Cat. 1** ~ **Cat. 3**

Cat.	1	2	3
empirical formula	C_{42} H_{35} Cl_5 Ir N_2 P	C_{50} H_{45} Cl Ir N_2 O_3 P	C_{42} H_{32} Cl_5 F_3 Ir N_2 P
fw	968.14	980.50	1022.11
temp [K]	110(2)	296(2)	296(2)
radiated used (λ[Å])	0.71073	0.71073	0.71073
cryst size [mm^3]	0.66 x 0.56 x 0.54	0.200 x 0.100 x 0.100	0.200 x 0.100 x 0.100
cryst syst	Triclinic	Triclinic	Triclinic
space group	P -1	P-1	P-1
a [Å]	11.0738(5)	12.911(6)	11.250(13)
b [Å]	13.2326(6)	13.195(6)	13.317(16)
c [Å]	13.7902(5)	14.842(7)	14.035(17)
α [deg]	83.693(3)°	82.321(12)°	84.55(3)°.
β [deg]	70.637(3)°	72.051(10)°	74.18(3)°.
γ [deg]	82.745(4)°	63.435(10)°	83.10(3)°.
V [$Å^3$], Z	1886.19(14), 4	2151.4(18) ,2	2004(4) , 2
ρ_{calcd} [$g.cm^{-3}$]	1.705	1.514	1.694
μ [mm^{-1}]	3.970 mm^{-1}	3.247	3.752
F(000)	956	984	1004
scan rang θ [deg]	2.88 to 29.21°	1.442 to 26.000°.	1.511 to 25.998°.
no. of total refins	16612	42883	40353
no. of unique refins	8694 [R(int) = 0.0221]	8448 [R(int) = 0.1296]	7871 [R(int) = 0.1774]
no. of data/restraints/ params	8694 / 0 / 460	8448 / 1 / 523	7871 / 0 / 487
goodness-of-fit on F^2	0.986	0.940	0.973
R_1, wR_2 [I>σ2(I)]	0.0217 and 0.0474	R1 = 0.0451, wR2 = 0.0547	R1 = 0.0609, wR2 = 0.0736
R_1, wR_2 (all data)	0.0257 and 0.0479	R1 = 0.0881, wR2 = 0.0629	R1 = 0.1289, wR2 = 0.0882

Table S2. Selected bond distance (Å) and bond angles for **Cat. 1**~**3**.

Cat. 1			
Ir-C(22)	2.004(2)	Ir-N(1)	2.062(2)
Ir-C(11)	2.044(2)	Ir-P	2.4074(6)
Ir-N(2)	2.053(2)	Ir-Cl(1)	2.4919(6)
C(22)-Ir-C(11)	89.14(9)	N(2)-Ir-P	89.94(6)
C(22)-Ir-N(2)	80.64(9)	N(1)-Ir-P	98.60(6)
C(11)-Ir-N(2)	91.70(9)	C(22)-Ir-Cl(1)	172.90(7)
C(22)-Ir-N(1)	93.60(9)	C(11)-Ir-Cl(1)	86.98(7)
C(11)-Ir-N(1)	80.05(9)	N(2)-Ir-Cl(1)	93.53(6)
N(2)-Ir-N(1)	170.06(8)	N(1)-Ir-Cl(1)	91.58(6)
C(22)-Ir-P	94.17(6)	P-Ir-Cl(1)	89.85(2)
C(11)-Ir-P	176.51(7)		
Cat. 2			
Ir-C(22)	2.012(5)	Ir-N(1)	2.066(4)
Ir-C(11)	2.049(5)	Ir-P	2.4388(16)
Ir-N(2)	2.058(4)	Ir-Cl	2.4861(15)
C(22)-Ir-C(11)	89.91(18)	N(2)-Ir-P	91.12(12)
C(22)-Ir-N(2)	80.74(19)	N(1)-Ir-P	97.32(13)
C(11)-Ir-N(2)	91.65(18)	C(22)-Ir-Cl	172.91(15)
C(22)-Ir-N(1)	95.85(18)	C(11)-Ir-Cl	87.62(13)
C(11)-Ir-N(1)	80.00(19)	N(2)-Ir-Cl	92.68(12)
N(2)-Ir-N(1)	171.03(16)	N(1)-Ir-Cl	90.27(11)
C(22)-Ir-P	92.27(14)	P-Ir-Cl	90.49(6)
C(11)-Ir-P	176.71(14)		
Cat. 3			
Ir-C(12)	2.002(9)	Ir-N(2)	2.064(6)
Ir-C(11)	2.041(8)	Ir-P	2.419(3)
Ir-N(1)	2.064(6)	Ir-Cl(1)	2.499(3)
C(12)-Ir-C(11)	88.1(3)	N(1)-Ir-P	98.36(18)
C(12)-Ir-N(1)	94.2(3)	N(2)-Ir-P	90.42(18)
C(11)-Ir-N(1)	79.8(3)	C(12)-Ir-Cl(1)	172.1(2)
C(12)-Ir-N(2)	79.8(3)	C(11)-Ir-Cl(1)	87.3(2)

C(11)-Ir-N(2)	91.6(3)	N(1)-Ir-Cl(1)	91.29(17)
N(1)-Ir-N(2)	169.7(2)	N(2)-Ir-Cl(1)	93.9(2)
C(12)-Ir-P	94.1(2)	P-Ir-Cl(1)	90.76(8)
C(11)-Ir-P	177.2(3)		

Table S3. Crystal data for **Cat. 4** and **Cat. 5**

Cat.	**4**	**5**
empirical formula	C49 H41 Cl5 Ir N2 O5 P	C47 H35 Cl3 Ir N2 O5 P
fw	1138.26	1037.29
temp [K]	293(2)	296(2)
radiated used (λ[Å])	0.71073	0.71073
cryst size [mm^3]	0.800 x 0.300 x 0.200	0.500 x 0.500 x 0.500
cryst syst	Triclinic	Triclinic
space group	P-1	P-1
a [Å]	12.34(2)	12.499(3)
b [Å]	12.49(2)	14.154(3)
c [Å]	16.46(4)	16.193(3)
α [deg]	86.17(5)°.	85.480(6)°.
β [deg]	69.00(5)°.	87.279(6)°.
γ [deg]	88.19(5)°.	65.482(6)°.
V [$Å^3$], Z	2364(8) , 2	2597.9(9) , 2
ρ_{calcd} [$g.cm^{-3}$]	1.599	1.326
μ [mm^{-1}]	3.189	2.795
F(000)	1132	1028
scan rang θ [deg]	1.327 to 25.998°.	1.585 to 26.000°.
no. of total refins	9296	35372
no. of unique refins	9296 [R(int) = ?]	10226 [R(int) = 0.0793]
no. of data/restraints/ params	9296 / 0 / 563	10226 / 0 / 532
goodness-of-fit on F^2	1.060	1.031
R_1, wR_2 [I>σ2(I)]	R1 = 0.0526, wR2 = 0.1074	R1 = 0.0419, wR2 = 0.0914
R_1, wR_2 (all data)	R1 = 0.0804, wR2 = 0.1246	R1 = 0.0616, wR2 = 0.0998

Table S4. Crystal data for **Cat. 6** and **Cat. 7**

Cat.	**6**	**7**
empirical formula	C47.60 H38.80 Cl F4 Ir N2 O7.30 P	C47.25 H37.50 Cl3.50 Ir N2 O6 P
fw	1090.23	1076.54
temp [K]	297(2)	296(2) K
radiated used (λ[Å])	0.71073	0.71073 Å
cryst size [mm^3]	0.42 x 0.39 x 0.23	0.300 x 0.100 x 0.100
cryst syst	Orthorhombic	Triclinic
space group	P b c a	P-1
a [Å]	19.1611(8)	a = 13.2859(8)
b [Å]	20.4125(9)	b = 13.4065(8)
c [Å]	23.7193(10)	c = 15.6834(10)
α [deg]	90°.	= 103.2380(15)°
β [deg]	90°.	= 90.1227(16)°
γ [deg]	90°.	= 117.8150(14)°
V [$Å^3$], Z	9277.2(7) , 8	2385.7(3), 2
ρ_{calcd} [$g.cm^{-3}$]	1.561	1.499
μ [mm^{-1}]	3.039	3.075
F(000)	4334	1069
scan rang θ [deg]	1.69 to 26.01°.	1.747 to 26.000°.
no. of total refins	50639	33139
no. of unique refins	9119 [R(int) = 0.0427]	9373 [R(int) = 0.1131]
no. of data/restraints/ params	9119 / 0 / 640	9373 / 3 / 550
goodness-of-fit on F^2	1.047	1.005
R_1, wR_2 [$I>\sigma 2(I)$]	R1 = 0.0324, wR2 = 0.1027	R1 = 0.0602, wR2 = 0.1364
R_1, wR_2 (all data)	R1 = 0.0535, wR2 = 0.1171	R1 = 0.1096, wR2 = 0.1565

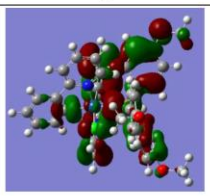
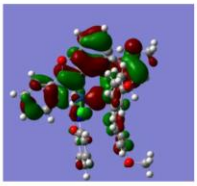
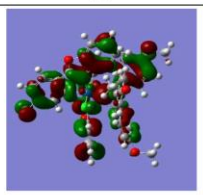
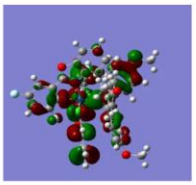
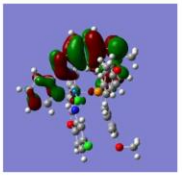
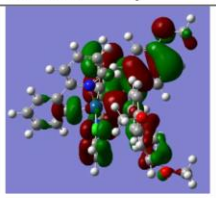
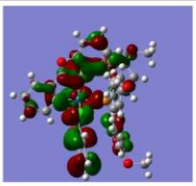
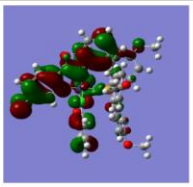
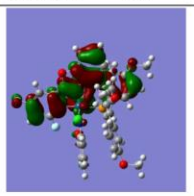
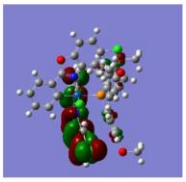
Table S5. Selected bond distance (Å) and bond angles for **Cat. 4**~**7**.

Cat. 4			
Ir-C(1)	2.050(8)	Ir-N(1)	2.095(6)
Ir-C(14)	2.084(9)	Ir-P(1)	2.427(4)
Ir-N(2)	2.091(7)	Ir-Cl(1)	2.463(4)
C(1)-Ir-C(14)	89.6(3)	N(2)-Ir-P(1)	100.2(2)
C(1)-Ir-N(2)	92.8(3)	N(1)-Ir-P(1)	90.9(2)
C(14)-Ir-N(2)	80.2(3)	C(1)-Ir-Cl(1)	174.6(2)
C(1)-Ir-N(1)	81.3(3)	C(14)-Ir-Cl(1)	87.3(2)
C(14)-Ir-N(1)	89.1(3)	N(2)-Ir-Cl(1)	91.10(19)
N(2)-Ir-N(1)	167.8(2)	N(1)-Ir-Cl(1)	94.14(19)
C(1)-Ir-P(1)	94.8(2)	P(1)-Ir-Cl(1)	88.17(11)
C(14)-Ir-P(1)	175.5(2)		
Cat. 5			
Ir-C(14)	2.018(5)	Ir-N(1)	2.226(4)
Ir-N(2)	2.080(4)	Ir-Cl(1)	2.3751(13)
Ir-C(1)	2.106(5)	Ir-P	2.3972(14)
C(14)-Ir-N(2)	80.17(17)	C(1)-Ir-Cl(1)	84.34(12)
C(14)-Ir-C(1)	89.94(18)	N(1)-Ir-Cl(1)	87.71(11)
N(2)-Ir-C(1)	92.07(15)	C(14)-Ir-P	89.93(14)
C(14)-Ir-N(1)	167.63(17)	N(2)-Ir-P	90.24(10)
N(2)-Ir-N(1)	95.63(14)	C(1)-Ir-P	177.63(12)
C(1)-Ir-N(1)	78.53(16)	N(1)-Ir-P	101.77(11)
C(14)-Ir-Cl(1)	95.67(15)	Cl(1)-Ir-P	93.31(5)
N(2)-Ir-Cl(1)	174.53(10)		
Cat. 6			
Ir-C(26)	2.047(4)	Ir-N(1)	2.081(4)
Ir-N(2)	2.049(4)	Ir-P	2.4145(14)
Ir-C(13)	2.080(5)	Ir-Cl	2.4465(12)
C(26)-Ir-N(2)	79.42(17)	C(13)-Ir-P	173.97(14)
C(26)-Ir-C(13)	89.23(19)	N(1)-Ir-P	99.40(11)
N(2)-Ir-C(13)	92.4(2)	C(26)-Ir-Cl	170.24(13)

C(26)-Ir-N(1)	96.53(17)	N(2)-Ir-Cl	94.08(12)
N(2)-Ir-N(1)	171.52(16)	C(13)-Ir-Cl	83.73(14)
C(13)-Ir-N(1)	80.07(19)	N(1)-Ir-Cl	88.93(11)
C(26)-Ir-P	96.80(13)	P-Ir-Cl	90.25(4)
N(2)-Ir-P	88.52(12)		

Cat. 7

Ir-C(13)	2.033(9)	Ir-N(2)	2.067(7)
Ir-N(1)	2.046(7)	Ir-P	2.416(2)
Ir-C(26)	2.062(10)	Ir-Cl(1)	2.480(2)
C(13)-Ir-N(1)	80.7(3)	C(26)-Ir-P	174.3(3)
C(13)-Ir-C(26)	88.3(4)	N(2)-Ir-P	100.5(2)
N(1)-Ir-C(26)	90.5(3)	C(13)-Ir-Cl(1)	171.6(3)
C(13)-Ir-N(2)	91.3(3)	N(1)-Ir-Cl(1)	93.4(2)
N(1)-Ir-N(2)	167.5(3)	C(26)-Ir-Cl(1)	85.8(3)
C(26)-Ir-N(2)	79.5(3)	N(2)-Ir-Cl(1)	93.40(19)
C(13)-Ir-P	97.3(3)	P-Ir-Cl(1)	88.58(8)
N(1)-Ir-P	90.2(2)		

Cat.	2	4	5	6	7
LUMO					
	Composition	Composition	Composition	Composition	Composition
	5.19% Ir	5.50% Ir	5.48% Ir	5.30% Ir	3.02% Ir
	35.65% Ph	22.64% Ph	29.09% Ph	32.06% Ph	19.47% Ph
	17.04% Py	17.47% Ox	18.94% Ox	18.21% Ox	20.50% Ox
HOMO					
	Composition	Composition	Composition	Composition	Composition
	5.19% Ir	4.75% Ir	4.19% Ir	3.97% Ir	3.33% Ir
	34.92% Ph	29.86% Ph	32.35% Ph	33.02% Ph	22.72% Ph
	16.86% C^N	21.72% Ox	24.05% Ox	17.71% Ox	27.43% Ox

Ph: The phenyl group of the C^N ligand
Py: The pyridyl of C^N ligands
Ox : The benzoxazole groups of C^N ligands

Figure S1. Theoretical calculation data of **Cat.2** and **4**-**7**, including the orbital distribution and composition of HOMO and LUMO

II. Structural Data of Benzoxazole Derivative Ligands

2-phenylbenzoxazole (pbo) (**L2**): 80% yield. 1H NMR (300 MHz, CDCl3, 298 K; δ (ppm)): 8.28−8.25 (m, 2H), 7.80−7.76 (m, 1H), 7.60−7.56 (m, 1H), 7.53−7.51 (m, 3H), 7.37−7.33 (m, 2H). 13C NMR (75 MHz, CDCl3, 298 K; δ (ppm)): δ163.2, 151.0, 142.3, 131.7, 129.1, 127.8, 127.4, 125.3, 124.8, 120.263, 110.8. Anal. Calcd for $C_{13}H_9NO$ (MW = 195.22): C, 79.98; H, 4.65; N, 7.18. Found: C, 79.99; H, 4.65; N, 7.20%. MS (FAB; m/z): 195.0686

2-(4-Chlorophenyl)benzoxazole (cpbo) (**L3**): 75% yield. 1H NMR (300 MHz, CDCl3, 298 K; δ (ppm)): 8.17 (d, J = 8.7 Hz, 2H), 7.77−7.74 (m, 1H), 7.57−7.54 (m, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.38−7.33 (m, 2H). 13C NMR (75 MHz, CDCl3, 298 K; δ (ppm)): 162.2, 150.9, 142.2, 137.9, 129.4, 129.0, 125.8, 125.5, 124.9, 120.3, 110.8. Anal. Calcd for $C_{13}H_8NOCl$ (MW = 229.67): C, 67.98; H, 3.51; N, 6.10. Found: C, 67.98; H, 3.53; N, 6.11%. MS (FAB; m/z):229.0303

2-(3.5-Difluorophenyl)benzoxazole (fpbo) (**L4**): 88% yield. 1H NMR (300 MHz, CDCl3, 298 K; δ (ppm)): 7.80−7.74 (m, 3H), 7.59−7.56 (m, 1H), 7.41−7.36 (m, 2H), 7.00−6.96 (m, 1H). 13C NMR (75 MHz, CDCl3, 298 K; δ (ppm)): 165.1, 164.9, 161.8, 161.7, 160.9, 151.0, 141.9, 130.4, 130.3, 130.1, 126.1, 125.2, 120.6, 110.9, 110.8, 110.7, 110.6, 107.3, 107.0, 106.7. Anal. Calcd for $C_{13}H_7NO\ F_2$ (MW = 231.20): C, 67.53; H, 3.05; N, 6.06. Found: C, 67.50; H, 3.08; N, 5.99%. MS (FAB; m/z): 231.0496

2-Phenyl-5-chlorobenzoxazole (pcbo) (**L5**): 75% yield. 1H NMR (300 MHz, CDCl3, 298 K; δ (ppm)): 8.23−8.20 (m, 2H), 7.66 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 1.8 Hz, 1H), 7.55−7.49 (m, 3H), 7.32 (dd, J = 8.7, 1.8 Hz, 1H). 13C NMR (75 MHz,

CDCl3, 298 K; δ (ppm)): 163.9, 151.1, 141.1, 132.0, 130.9, 129.2, 127.8, 126.9, 125.5, 120.7, 111.4. Anal. Calcd for $C_{13}H_8NOCl$ (MW = 229.67): C, 67.98; H, 3.51; N, 6.10. Found: C, 67.91; H, 3.52; N, 6.09%. MS (FAB; m/z): 229.0300

III. Structural Data of Dinuclear Iridium Precursors $(C^N)_2Ir(\mu\text{-}Cl)_2Ir(C^N)_2$ (D1~D5)

$(pp)_2Ir(\mu\text{-}Cl)_2Ir(pp)_2$ (**D**1): 85% yield. 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 8.39−8.35 (m, 4H), 8.18−8.14 (m, 4H), 7.53−7.47 (m, 4H) , 7.44−7.35 (m, 6H) , 7.16−8.12 (m, 2H) , 6.93−6.87 (m, 2H). Anal. Calcd for $C_{44}H_{22}N_4Cl_2Ir_2$ (MW = 1072.09): C, 49.29; H, 3.01; N, 5.23%. Found: C, 49.67; H, 3.08; N, 5.31%. MS (FAB; m/z): 1070.9610

$(pbo)_2Ir(\mu\text{-}Cl)_2Ir(pbo)_2$ (**D2**): 90% yield. 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 7.78−7.76 (m, 4H), 7.75−7.73 (m, 10H), 7.52−7.49 (m, 4H), 7.43−7.41 (m, 4H), 7.40−7.36 (m, 10H). Anal. Calcd for $C_{52}H_{32}N_4O_4Cl_2Ir_2$ (MW = 1232.17): C, 50.69; H, 2.61; N, 4.55%. Found: C, 50.67; H, 2.63; N, 4.51%. MS (FAB; m/z): 1231.8585

$(cpbo)_2Ir(\mu\text{-}Cl)_2Ir(cpbo)_2$ (**D3**): 88% yield. 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 8.76−8.73 (m, 2H), 8.09−8.54 (m, 4H), 7.95 (d, J = 8.4 Hz, 2H), 7.84−7.60 (m, 8H), 7.48 (dd, J = 8.2, 2.1 Hz, 2H), 7.38 (t, J = 8.4 Hz, 2H), 7.14 (t, J = 8.4 Hz, 2H), 7.03 (dd, J = 8.1, 1.8 Hz, 2H), 6.40 (d, J = 7.8 Hz, 2H), 6.0 (d, J = 2.1 Hz, 2H). Anal. Calcd for $C_{52}H_{28}N_4O_4Cl_6Ir_2$ (MW = 1369.98): C, 45.59; H, 2.06; N, 4.09%. Found: C, 45.67; H, 2.10; N, 4.11%. MS (FAB; m/z): 1367.9515

$(fpbo)_2Ir(\mu\text{-}Cl)_2Ir(fpbo)_2$ (**D4**): 78% yield. 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 8.18 (d, J = 8.18, 8.1 Hz, 4H), 7.31 (dd, J = 7.6, 2.7 Hz, 4H), 7.22−7.12 (m, 8H),

6.99 (dt, J = 7.1, 1.5 Hz, 4H), 6.14 (dt, J = 9.6, 2.7 Hz, 4H). 13C NMR (75 MHz, CDCl3, 298 K; δ (ppm)): 174.9, 169.2, 169.1, 167.5, 167.4, 160.3, 160.2, 158.7, 158.6, 149.1, 140.8, 133.6, 133.5, 133.4, 133.3, 125.1, 124.4, 118.0, 115.3, 115.0, 110.9, 108.6, 108.4, 107.2, 107.0, 106.8, 31.8, 31.1, 22.8, 14.3. Anal. Calcd for $C_{52}H_{24}N_4O_4Cl_2F_8Ir_2$ (MW = 1376.12): C, 45.38; H, 1.76; N, 4.07%. Found: C, 45.80; H, 1.80; N, 4.03%. MS (FAB; m/z): 1376.0319.

$(pcbo)_2Ir(\mu\text{-}Cl)_2Ir(pcbo)_2$ (**D5**): 80% yield. 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 8.22 (d, J = 1.8 Hz, 4H), 7.65 (dd, J = 7.8, 1.2 Hz, 4H), 7.36 (d, J = 9 Hz, 4H), 7.1 (dd, J = 8.7, 2.1 Hz, 4H), 6.87 (dt, J = 7.4, 1.2 Hz, 4H), 6.68 (dt, J = 7.4, 1.2 Hz, 4H), 6.17 (d, J = 7.8 Hz, 4H). Anal. $C_{52}H_{28}N_4O_4Cl_6Ir_2$ (MW = 1369.98): C, 45.59; H, 2.06; N, 4.09%. Found: C, 45.38; H, 2.08; N, 4.05%. MS (FAB; m/z): 1367.9504.

IV. Structural Data of Catalysts $(C^N)_2Ir(Cl)$ (TPP) (Cat.1~7)

$(pp)_2Ir(Cl)(TPP)$ (**Cat. 1**): 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 9.194(d, J=6Hz, 1H), 8.849(d, J=5.4Hz, 1H), 7.883(d, J=7.8Hz, 1H), 7.565(d, J=7.8Hz, 1H), 7.083(t, J=6.9Hz, 4H), 6.832(t, J=7.2Hz, 1H), 6.803(t, J=5.7Hz, 1H), 6.693(t, J=5.7Hz, 1H), 5.888(d, J=7.8Hz, 1H), 5.835(d, J=6.75Hz, 1H). Anal. Calcd for $C_{40}H_{31}N_2ClPIr$ (MW = 798.3282): C, 60.18; H, 3.91; N, 3.51%. Found: C, 60.67; H, 3.85; N, 3.49%. HMS (FAB; m/z): 798.2241

$(pp)_2Ir(Cl)(TMPP)$ (**Cat. 2**): 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 9.306(d, J=5.4Hz, 1H), 8.523(d, J=5.4Hz, 1H), 7.878(d, J=8.4Hz, 1H), 7.563(d, J=8.4Hz, 1H), 7.535(d, J=7.8Hz, 1H), 7.473(t, J=7.8Hz,, 1H), 7.428(d, J=7.2Hz, 1H), 7.129(t, J=9Hz, 3H), 6.836~6.792(m, 1H), 6.611(d, J=7.2Hz, 3H), 5.929(d, J=7.8Hz, 1H) Anal. Calcd

for $C_{43}H_{37}N_2O_3ClPIr$ (MW = 888.4043): C, 58.13; H, 4.20; N, 3.15%. Found: C, 58.67; H, 4.30; N, 3.17%. HMS (FAB; m/z): 888.2559

$(pp)_2Ir(Cl)(TFPP)$ (**Cat. 3**): 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 8.715(d, J=5.4Hz, 1H), 7.907(d, J=8.4Hz, 1H), 7.725(t, J=7.8Hz, 1H), 7.576(d, J=9.6Hz, 1H), 7.529(t, J=7.8Hz, 1H), 7.496(d, J=4.2Hz, 1H), 7.240~7.180(m, 4H), 6.576(t, J=8.1Hz, 1H), 5.819(t, J=6.6Hz, 1H) Anal. Calcd for $C_{40}H_{28}N_2ClF_3PIr$ (MW = 852.2999): C, 56.37; H, 3.31; N, 3.29%. Found: C, 56.67; H, 3.30; N, 3.31%. HMS (FAB; m/z): 852.1959.

$(pbo)_2Ir(Cl)(TMPP)$ (**Cat. 4**): 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 8.585(d, J=8.4Hz, 1H), 7.739(d, J=7.8Hz, 1H), 7.637(d, J=8.4Hz, 1H), 7.559(d, J=7.8Hz, 1H), 7.349(d, J=8.4Hz, 1H), 7.301(t, J=8.1Hz, 1H), 7.111(t, J=7.8Hz, 1H), 7.067(d, J=7.8Hz, 1H), 6.815(t, J=7.5Hz, 1H), 6.699(t, J=6.4Hz, 1H), 6.479(d, J=7.2Hz, 3H). Anal. Calcd for $C_{47}H_{37}N_2O_5ClPIr$ (MW = 968.4451): C, 58.29; H, 3.85; N, 2.89%. Found: C, 58.67; H, 3.80; N, 2.81%. HMS (FAB; m/z): 968.2458

$(cpbo)_2Ir(Cl)(TMPP)$ (**Cat. 5**): 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 7.711(d, J=8.4Hz, 1H), 7.688(d, J=1.8Hz, 1H), 7.674(d, J=1.8Hz, 1H), 7.456(d, J=7.8Hz, 1H), 7.104(t, J=7.8Hz, 1H), 7.067(d, J=4.2Hz, 1H), 6.968(t, J=8.1Hz, 1H), 6.942(t, J=8.1Hz, 1H), 6.883(d, J=4.2Hz, 1H), 6.507(d, J=8.1Hz, 3H), 6.286(d, J=3.9Hz, 1H), 6.042(d, J=7.8Hz, 1H). Anal. Calcd for $C_{47}H_{35}N_2O_5Cl_3PIr$ (MW = 1037.3355): C, 54.42; H, 3.40; N, 2.70%. Found: C, 54.67; H, 3.30; N, 2.75%. HMS (FAB; m/z): 1037.1667

$(fpbo)_2Ir(Cl)(TMPP)$ (**Cat. 6**): 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 8.529(d,

J=7.8Hz, 1H), 7.626(d, J=8.4Hz, 1H), 7.428(d, J=3.6Hz, 1H), 7.305(t, J=7.5Hz, 2H), 7.150(d, J=5.1Hz, 1H), 7.063(t, J=7.5Hz, 2H), 6.512(s, 3H), 6.297~6.260(m, 2H) Anal. Calcd for $C_{47}H_{33}N_2O_5ClF_4PIr$ (MW = 1040.4074): C, 54.26; H, 3.20; N, 2.69%. Found: C, 54.37; H, 3.18; N, 2.71%. HMS (FAB; m/z): 1040.2081

(pcbo)$_2$Ir(Cl)(TMPP) (**Cat. 7**): 1H NMR (300 MHz, DMSO-d6, 298 K; δ (ppm)): 8.490 (d, J=1.8Hz, 1H), 7.745(d, J=7.8Hz, 1H), 7.620(d, J=3.9Hz, 1H), 7.577(d, J=9Hz, 1H), 7.348(s, 1H), 7.302~7.240(m, 3H), 6.968(t, J=7.5Hz, 2H), 6.764~6.739(m, 5H) Anal. Calcd for $C_{47}H_{35}N_2O_5Cl_3PIr$ (MW = 1037.3355): C, 54.42; H, 3.40; N, 2.70%. Found: C, 54.47; H, 3.50; N, 2.65%. MS (FAB; m/z): 1037.2559

V. Structural Data of N-alkylation Products.

***N*-benzylaniline (P$_1$)**:^{1}H NMR (d-chloroform, 600MHz) = 7.38-7.33 (m, Ar, 4H), 7.28-7.25 (m, Ar, 1H), 7.19-7.16 (m, Ar, 2H), 6.73-6.68 (t, Ar, 1H), 6.65-6.63 (d, Ar, 2H, JHH = 7.8Hz), 4.33 (s, CH2, 2H), 4.02 (br. s, NH, 1H). ^{13}C NMR (d-Chloroform, 150MHz) = 148.2, 139.4, 129.3, 128.7, 127.5, 127.3, 117.6, 112.8, 48.3. MS (ESI/CI): m/z =183.02, Calculated for C13H13N: 183.26 g/mol.

***N*-(*p*-chlorobenzyl)aniline (P$_2$)**: ^{1}H NMR (d-chloroform, 600MHz) = 7.29 (s, 3H, Ar), 7.17-7.11 (m, 2H, Ar), 6.73-6.68 (m, 1H, Ar), 6.58-6.59 (m, 2H, Ar), 4.28 (d, 2H, JHH = 5.4Hz), 4.05 (br. s, NH, 1H). ^{13}C NMR (d-Chloroform, 150MHz) = 147.8, 137.8, 132.9, 129.3,128.8, 128.7, 117.8, 112.9, 47.506. MS (ESI/CI): m/z = 216.98, Calculated for

$C_{13}H_{12}NCl^{+}$ $[M]^{+}$: 217.68 g/mol.

***N*-(4-methoxybenzyl)aniline (P_3):** ^{1}H NMR (d-chloroform, 600MHz) = 7.29-7.27 (d, JHH = 8.4Hz, 2H, Ar), 7.18-7.15 (m, 2H, Ar), 6.88-6.86 (m, 2H, Ar), 6.72-6.69 (t, 1H, Ar), 6.63-6.62 (m, 2H, Ar), 4.24 (br. s, NH, 1H), 3.91 (d, JHH = 13.2Hz, 1H) , 3.79 (s, 3H). .^{13}C NMR (d-Chloroform, 150MHz) = 158.9, 148.2, 131.4, 129.3, 128.8, 117.5, 113.8, 112.8, 55.3, 47.8. MS (ESI/CI): m/z = 213.21, Calculated for $C_{14}H_{15}NO^{+}$ $[M]^{+}$: 213.28 g/mol.

***N*-benzyl, *N*-(4-chlorophenyl)amine (P4) :** ^{1}H NMR (d-chloroform, 600MHz) = 7.34-7.20 (m, Ar, 4H), 7.11-7.07 (m, Ar, 2H), 6.55-6.5102 (m, Ar, 2H), 4.62 (s, 1H), 4.30, 4.29 (d, CH2 ,2H, JHH = 6.0Hz), 4.05(br. s, NH, 1H). ^{13}C NMR (d-Chloroform, 150MHz) = 146.7, 138.8, 128.9, 128.7, 127.5, 127.4, 127.1, 126.6, 122.1, 113.9 ,54.5, 48.4. MS (ESI/CI): m/z = 217.14, Calculated for $C_{13}H_{12}NCl^{+}$ $[M]^{+}$: 217.70 g/mol.

***N*-(4-chlorobenzyl), *N*-(4-chlorophenyl)amine (P5)**

^{1}H NMR (d-chloroform, 600MHz) = 7.39 (d, JHH = 9Hz, 2H, Ar), 7.31 (d, JHH = 9Hz, 2H, Ar), 7.03 (d, JHH = 9Hz, 2H, Ar), 6.57 (d, JHH = 9Hz, 2H, Ar), 4.32 (s, 2H). ^{13}C NMR (d-Chloroform, 150MHz) = 147.2, 138.9, 132.3, 129.0, 128.8, 128.1, 121.8, 114.9, 47.1. MS (ESI/CI): m/z = 253.21, Calculated for $C_{13}H_{11}NCl_2^{+}$ $[M]^{+}$: 252.14 g/mol.

_N_-(4-methoxybenzyl), _N_-(4-chlorophenyl)amine (P6)

^{1}H NMR (d-chloroform, 600MHz) =7.13 (d, JHH = 9Hz, 2H, Ar), 7.04 (d, JHH = 9Hz, 2H, Ar), 6.89 (d, JHH = 9Hz, 2H, Ar), 6.58(d, JHH = 9Hz, 2H, Ar), 4.32 (s, 2H), 3.79 (s, -OCH_3, 3H). ^{13}C NMR (d-Chloroform, 150MHz) = 160.1, 147.3 132.4, 129.0, 128.4, 121.8, 114.9, 114.2, 56.1, 47.1. MS (ESI/CI): m/z = 248.21, Calculated for $C_{14}H_{14}NOCl^{+}$ $[M]^{+}$: 247.72 g/mol.

_N_-benzyl, _N_-(4-methoxyphenyl)amine (P7): ^{1}H NMR (d-chloroform, 600MHz) = 7.37-7.32 (m, Ar, 4H), 7.27-7.25 (t, Ar, 1H), 6.77-6.76 (m, Ar, 2H), 6.59-6.60 (m, Ar, 2H), 4.27 (s, CH2, 2H), 3.73 (s, CH3, 3H).^{13}C NMR ($CDCl_3$, 150MHz) δ (ppm) = 152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.1, 55.8, 49.3. MS (ESI/CI): m/z = 213.05, Calculated for $C_{14}H_{15}NO^{+}$ $[M]^{+}$: 213.28g/mol.

_N_-(4-chlorobenzyl), _N_-(4-methoxyphenyl)amine (P8)

^{1}H NMR (d-chloroform, 600MHz) =7.38 (d, JHH = 9Hz, 2H, Ar), 7.30(d, JHH = 9Hz, 2H, Ar), 6.76 (d, JHH = 9Hz, 2H, Ar), 6.68(d, JHH = 9Hz, 2H, Ar), 4.31 (s, 2H), 3.78 (s, -OCH_3, 3H). ^{13}C NMR (d-Chloroform, 150MHz) = 152.7, 141.6, 138.9, 132.4, 128.8, 128.1, 115.4, 115.1, 56.1, 47.1. MS (ESI/CI): m/z = 248.61, Calculated for $C_{14}H_{14}NOCl^{+}$ $[M]^{+}$:

247.72 g/mol.

***N*-(4-methoxybenzyl), *N*-(4-methoxyphenyl)amine (P9)**

^{1}H NMR (d-chloroform, 600MHz) =7.12 (d, JHH = 9Hz, 2H, Ar), 6.88 (d, JHH = 9Hz, 2H, Ar), 6.78 (d, JHH = 9Hz, 2H, Ar), 6.70(d, JHH = 9Hz, 2H, Ar), 4.32 (s, 2H), 3.90 (s, -OCH_3, 3H) , 3.78 (s, -OCH_3, 3H). ^{13}C NMR (d-Chloroform, 150MHz) = 160.1, 152.7, 141.6 132.4, 128.4, 115.4, 115.1, 114.2, 57.5, 56.1, 47.1. MS (ESI/CI): m/z = 242.21, Calculated for $C_{15}H_{17}NO_2^+$ $[M]^+$: 243.30g/mol.

***N*-hexylaniline (P10):** ^{1}H NMR (d-chloroform, 600MHz) = 7.17-7.14 (m, Ar, 2H), 6.68-6.66 (m, Ar, 1H), 6.59-6.58 (m, Ar, 2H), 3.57 (br. s, NH, 1H), 3.11-3.0718 (t, 2H), 1.62-1.55 (m, 2H), 1.45-1.39 (m, 2H), 0.96-0.93 (t, 3H). ^{13}C NMR (d-Chloroform, 150MHz) = 148.6, 129.2, 117.7, 112.7, 43.7, 31.7, 28.8, 27.4, 23.3, 134.0. MS (ESI/CI): m/z = 177.17, Calculated for $C_{12}H_{19}N^+$ $[M]^+$: 177.29 g/mol.

***N*-hexyl, *N*-(4-chlorophenyl) amine (P11):**

^{1}H NMR (d-chloroform, 600MHz) =7.03 (d, JHH = 9Hz, 2H, Ar), 6.58 (d, JHH = 9Hz, 2H, Ar), 3.08 (m,1H,), 1.86(m, 2H), 1.60 (m, 2H), 1.25 (m, 2H), 1.12 (m, 2H), ^{13}C NMR (d-Chloroform, 150MHz) = 147.9, 129.1 119.7, 114.5, 52.6, 33.4, 25.9, 24.7. MS (ESI/CI):

m/z = 210.21, Calculated for $C_{12}H_{16}NCl^{+}$ $[M]^{+}$: 209.71 g/mol.

_N_-hexyl, _N_-(4-methoxyphenyl) amine (P12):

^{1}H NMR (d-chloroform, 600MHz) =6.77 (d, JHH = 9Hz, 2H, Ar), 6.69 (d, JHH = 9Hz, 2H, Ar), 3.79 (s,1H,), 3.37(m, 1H), 1.60 (m, 2H), 1.46 (m, 2H), 1.16 (m, 4H), ^{13}C NMR (d-Chloroform, 150MHz) = 151.8, 142.0 115.3, 114.3, 56.1, 52.6, 33.4, 25.9, 24.7. MS (ESI/CI): m/z = 206.21, Calculated for $C_{13}H_{19}NO^{+}$ $[M]^{+}$: 205.29g/mol.

_N_-Benzylpyrrolidine (P13):

^{1}H NMR (d-chloroform, 600MHz) =7.23 (m, 5H, Ar), 3.66 (s, 2H), 2.51 (m,4H,), 1.68(m, 4H). ^{13}C NMR (d-Chloroform, 150MHz) = 138.6, 128.7, 128.2, 127.2, 63.3, 54.4, 24.9. MS (ESI/CI): m/z = 162.21, Calculated for $C_{11}H_{15}N^{+}$ $[M]^{+}$: 161.24 g/mol.

_N_-(4-Chlorobenzyl)pyrrolidine (P14):

^{1}H NMR (d-chloroform, 600MHz) =7.39 (d, JHH = 6Hz, 2H, Ar), 7.32 (d, JHH = 6Hz, 2H, Ar), 3.66 (s,2H,), 2.51(m, 4H), 1.68 (m, 4H). ^{13}C NMR (d-Chloroform, 150MHz) = 137.7, 131.7, 129.8, 128.2, 68.6, 54.4, 24.9. MS (ESI/CI): m/z = 195.21, Calculated for $C_{11}H_{14}NCl^{+}$ $[M]^{+}$: 195.69 g/mol.

_N_-(4-Methoxybenzyl)pyrrolidine (P15):

^{1}H NMR (d-chloroform, 600MHz) =7.13 (d, JHH = 9Hz, 2H, Ar), 6.89 (d, JHH = 9Hz, 2H, Ar), 3.79 (s,3H,), 3.66(s, 2H), 2.51 (m, 4H), 1.68 (m, 4H). ^{13}C NMR (d-Chloroform, 150MHz) = 160.4, 130.2, 129.1, 114.1, 63.6, 56.1, 54.4, 24.9. MS (ESI/CI): m/z = 192.21, Calculated for $C_{12}H_{17}NO^{+}$ $[M]^{+}$: 191.27 g/mol.

Benzylpiperazine (P16): ^{1}H NMR ($CDCl_3$, 600MHz) δ (ppm) = 7.29-7.22 (m, Ar, 5H), 3.56-3.40 (m, 4H), 2.89-2.86 (m, 4H), 2.41 (br. s, NH , 1H). ^{13}C NMR ($CDCl_3$, 150MHz) δ (ppm) = 137.8, 129.2, 128.1, 127.0, 64.0, 54.1, 45.8. HRMS (ESI/APCI): *m/z* = 177.2642 g/mol, calc'd. for $C_{11}H_{17}N_2^{+}$ $[M]^{+}$: 177.2644g/mol.

(4-Chlorobenzyl) piperazine (P17):

^{1}H NMR (d-chloroform, 600MHz) =7.40 (d, JHH = 9Hz, 2H, Ar), 7.32 (d, JHH = 9Hz, 2H, Ar), 3.66 (s,2H,), 2.68 (m, 4H), 2.34 (m, 4H). ^{13}C NMR (d-Chloroform, 150MHz) = 137.7, 131.7, 129.4, 128.3, 63.4, 53.5, 46.7. MS (ESI/CI): m/z = 210.21, Calculated for $C_{11}H_{14}N_2Cl^{+}$ $[M]^{+}$: 209.69 g/mol.

(4-Methoxybenzyl) piperazine (P18)

^{1}H NMR (d-chloroform, 600MHz) =7.13 (d, JHH = 9Hz, 2H, Ar), 6.89 (d, JHH = 9Hz, 2H,

Ar), 3.79 (s,3H,), 3.66 (s, 2H), 2.68 (m, 4H), 2.34 (m, 4H). ^{13}C NMR (d-Chloroform, 150MHz) = 160.4, 130.2, 129.1, 114.35, 68.4, 56.1, 52.5, 45.7. MS (ESI/CI): m/z = 204.21, Calculated for $C_{12}H_{17}N_2O^+$ $[M]^+$: 205.27 g/mol.

***N*-phenylpyrrolidine (P19):** ^{1}H NMR (d-chloroform, 600MHz) = 7.26 (m, 2H), 7.12 (m, 1H), 6.84(m, 1H), 3.19–3.18 (m, 4H), 2.33 (s, 3H), 1.94-1.92 (m,4H). ^{13}C NMR (d-Chloroform, 150MHz) = 148.6, 129.7, 115.8, 111.97, 47.9, 26.0. MS (ESI/CI): m/z =147.13, Calculated for C13H13N: 147.23 g/mol.

***N*-phenylpiperidine (P20):** ^{1}H NMR (d-chloroform, 600MHz) = 7.45 (t, 2H, J=7.4 Hz), 6.99 (d, 2H, J=7.8 Hz), 6.73 (t, 1H, J=7.3 Hz), 3.36 (t, 4H, J=6.7 Hz), 1.81 (m, 4H), 1.62 (t, 2H, J=4.8 Hz). ^{13}C NMR ($CDCl_3$, 150MHz) δ (ppm) = 152.6, 129.9, 119.7, 117.3, 60.12, 26.6, 24.9. MS (ESI/CI): m/z = 161.12, Calculated for $C_{11}H_{15}N^+$ $[M]^+$: 161.25 g/mol.

***N*-phenylcycloheptamine (P21)**

^{1}H NMR (d-chloroform, 600MHz) =7.30 (m, 2H, Ar), 6.91 (m, 2H, Ar), 6.71 (m, 1H, Ar), 3.36 (m, 4H), 1.78(m, 4H), 1.66 (m, 4H). ^{13}C NMR (d-Chloroform, 150MHz) = 150.1, 130.3, 117.3, 114.4, 51.3, 27.6, 27.5. MS (ESI/CI): m/z = 174.81, Calculated for

$C_{12}H_{17}N^{+}$ $[M]^{+}$: 175.27 g/mol.

N-Methyl-N'-phenylpiperazine (P22): ^{1}H NMR (d-chloroform, 600MHz) = 8.21 (dd, 1H),7.66 (ddd, 1H), 6.88 – 6.78 (m, 2H), 3.74 –3.66 (m, 4H), 3.22 – 3.13 (m, 4H). ^{13}C NMR (d-Chloroform, 150MHz) = 160.4, 147.9, 137.6, 110.1, 107.2, 46.1, 45.8. MS (ESI/CI): m/z = 177.23, Calculated for $C_{11}H_{16}N_2^{+}$ $[M]^{+}$: 176.25 g/mol.

N-(4-Chlorophenyl), N'-methylpiperazine (**P23**): ^{1}H NMR (d-chloroform, 600MHz) =7.13 (d, JHH = 9Hz, 2H, Ar), 6.72 (d, JHH = 9Hz, 2H, Ar), 3.44 (m,4H,), 2.35 (m, 4H), 2.20 (s, 3H. ^{13}C NMR (d-Chloroform, 150MHz) = 149.0, 129.5, 123.1, 116.8, 52.7, 50.3, 46.1. MS (ESI/CI): m/z = 210.92, Calculated for $C_{11}H_{15}N_2Cl^{+}$ $[M]^{+}$: 210.70g/mol.

N-(4-Methoxyphenyl), N'-methylpiperazine (**P24**):^{1}H NMR (d-chloroform, 600MHz) =6.74 (d, JHH = 9Hz, 2H, Ar), 6.65 (d, JHH = 9Hz, 2H, Ar), 3.79 (s,3H,), 3.41(m, 4H), 2.35 (m, 4H), 2.20 (s, 3H). ^{13}C NMR (d-Chloroform, 150MHz) = 152.6, 143.4, 117.5, 115.5, 56.1, 52.6, 50.1, 46.1. MS (ESI/CI): m/z = 205.92, Calculated for $C_{12}H_{18}N_2O^{+}$ $[M]^{+}$: 206.28 g/mol.

VI. The Atomic Coordinates of **Cat. 1~7**

Table S6. The Atomic Coordinates (angstroms) of **Cat. 1**

Element	Coordinates (Angstroms)		
	X	Y	Z
Ir	0.765	0.7634	0.6258
P	0.6883	0.7259	0.8096
Cl(1)	0.9909	0.7284	0.6273
N(1)	0.7717	0.9187	0.6236
N(2)	0.7515	0.6147	0.6045
C(1)	0.7221	0.9773	0.7042
C(2)	0.7366	1.0795	0.6972
C(3)	0.8057	1.1259	0.6032
C(4)	0.8507	1.0683	0.5194
C(5)	0.8307	0.9655	0.5291
C(6)	0.8667	0.8996	0.4436
C(7)	0.9211	0.9357	0.3408
C(8)	0.9509	0.8693	0.2639
C(9)	0.9259	0.7678	0.2891
C(10)	0.8709	0.7322	0.3908
C(11)	0.8403	0.7974	0.4706
C(12)	0.8456	0.5381	0.596
C(13)	0.8314	0.4409	0.5781
C(14)	0.7156	0.4199	0.5703
C(15)	0.6181	0.498	0.5798
C(16)	0.6371	0.5958	0.596
C(17)	0.5445	0.686	0.6023
C(18)	0.4203	0.6827	0.5994
C(19)	0.34	0.7719	0.6022
C(20)	0.3845	0.8647	0.6061
C(21)	0.5077	0.868	0.6102
C(22)	0.5891	0.7786	0.6118
C(23)	0.7911	0.752	0.8821
C(24)	0.8763	0.8272	0.8458
C(25)	0.9488	0.85	0.9033
C(26)	0.939	0.7974	0.9979

C(27)	0.8552	0.723	1.0351
C(28)	0.7818	0.6998	0.9783
C(29)	0.6707	0.5895	0.8416
C(30)	0.7795	0.5227	0.8379
C(31)	0.7732	0.4185	0.8545
C(32)	0.6577	0.3779	0.8731
C(33)	0.5508	0.4426	0.8743
C(34)	0.5559	0.5477	0.8601
C(35)	0.5323	0.7898	0.8829
C(36)	0.5192	0.8484	0.9643
C(37)	0.402	0.9006	1.0151
C(38)	0.2955	0.8935	0.9865
C(39)	0.3063	0.8351	0.9066
C(40)	0.4236	0.7845	0.8538
Cl(2)	0.3794	1.0782	0.786
Cl(3)	0.4363	1.2851	0.706
C(41)	0.4157	1.1654	0.6765
Cl(4)	0.8422	0.5053	1.2666
Cl(5)	0.8084	0.4252	1.0898
C(42)	0.8725	0.4002	1.1902

Table S7. The Atomic Coordinates (angstroms) of **Cat. 2**

Element	Coordinates (Angstroms)		
	X	Y	Z
Ir	0.8964	0.8514	0.8235
Cl	0.9558	1.007	0.757
P	1.0623	0.7218	0.7016
O(1)	1.2618	0.2354	0.824
O(2)	1.5173	0.7842	0.5464
O(3)	0.864	0.7686	0.3754
N(1)	0.9888	0.8191	0.9234
N(2)	0.7804	0.8932	0.7414
C(1)	1.0997	0.7353	0.9208
C(2)	1.1567	0.7247	0.987
C(3)	1.1004	0.8008	1.0607
C(4)	0.9867	0.8836	1.067
C(5)	0.9294	0.892	0.9989
C(6)	0.8055	0.9717	1.002
C(7)	0.7294	1.0521	1.0752
C(8)	0.6112	1.118	1.0781
C(9)	0.5673	1.1062	1.0079
C(10)	0.6422	1.0305	0.934
C(11)	0.7641	0.9621	0.928
C(12)	0.7548	0.9813	0.6837
C(13)	0.6752	1.0053	0.63
C(14)	0.6223	0.9342	0.6364
C(15)	0.6464	0.844	0.6974
C(16)	0.7258	0.8233	0.7513
C(17)	0.7538	0.7347	0.8214
C(18)	0.708	0.6534	0.8419
C(19)	0.7345	0.5764	0.9117
C(20)	0.8042	0.5804	0.9646
C(21)	0.8515	0.659	0.9459
C(22)	0.8297	0.7366	0.8721
C(23)	1.1298	0.5714	0.7327
C(24)	1.0568	0.5122	0.7655
C(25)	1.1051	0.4003	0.7935

C(26)	1.2241	0.3457	0.7941
C(27)	1.2966	0.402	0.7639
C(28)	1.2492	0.5127	0.7334
C(29)	1.1986	0.7465	0.6504
C(30)	1.2769	0.7006	0.5626
C(31)	1.383	0.7117	0.5244
C(32)	1.4144	0.7682	0.5748
C(33)	1.3392	0.8136	0.6628
C(34)	1.2315	0.8044	0.6996
C(35)	1.0152	0.7264	0.5965
C(36)	0.9982	0.8207	0.5385
C(37)	0.9506	0.8387	0.4626
C(38)	0.9152	0.7594	0.4455
C(39)	0.933	0.6648	0.502
C(40)	0.982	0.6482	0.5755
C(41)	1.378	0.1789	0.8403
C(42)	1.6002	0.7363	0.456
C(43)	0.8274	0.8713	0.3266
C(44)	0.4886	0.4874	0.8491
C(45)	0.5581	0.3703	0.8623
C(46)	0.6621	0.2973	0.804
C(47)	0.7201	0.3369	0.7246
C(48)	0.6563	0.4548	0.7055
C(49)	0.5508	0.5147	0.7673
C(50)	0.7246	0.4914	0.6265

Table S8. The Atomic Coordinates (angstroms) of **Cat. 3**

Element	Coordinates (Angstroms)		
	X	Y	Z
Ir	0.725	0.7304	0.8709
Cl(1)	0.5027	0.7644	0.8677
P	0.7921	0.7724	0.6941
F(1)	0.4696	0.6998	0.4418
F(2)	0.8192	1.2165	0.6362
F(3)	1.2715	0.5571	0.481
N(1)	0.7196	0.5765	0.8666
N(2)	0.7384	0.8774	0.8988
C(1)	0.761	0.5227	0.7858
C(2)	0.751	0.4193	0.7881
C(3)	0.6968	0.3698	0.8771
C(4)	0.6592	0.4222	0.9597
C(5)	0.6728	0.5266	0.9558
C(6)	0.6423	0.5881	1.0406
C(7)	0.596	0.5496	1.1374
C(8)	0.5678	0.6125	1.2152
C(9)	0.5873	0.7146	1.1946
C(10)	0.633	0.7524	1.0984
C(11)	0.662	0.691	1.0188
C(12)	0.897	0.7162	0.8884
C(13)	0.978	0.6261	0.8913
C(14)	1.096	0.6303	0.8992
C(15)	1.1415	0.7207	0.9039
C(16)	1.0651	0.8092	0.9048
C(17)	0.9417	0.808	0.8997
C(18)	0.8504	0.8975	0.9071
C(19)	0.871	0.9934	0.9236
C(20)	0.7755	1.0705	0.9352
C(21)	0.6604	1.0504	0.929
C(22)	0.6446	0.9553	0.9078
C(23)	0.6891	0.7517	0.6196
C(24)	0.6053	0.6793	0.6471
C(25)	0.5325	0.6612	0.5866

C(26)	0.5437	0.7174	0.4991
C(27)	0.6239	0.7881	0.4685
C(28)	0.6973	0.8076	0.526
C(29)	0.8088	0.9079	0.6668
C(30)	0.7014	0.9729	0.6796
C(31)	0.7047	1.0766	0.6691
C(32)	0.8141	1.1132	0.645
C(33)	0.9239	1.0543	0.6286
C(34)	0.9224	0.9486	0.6397
C(35)	0.9413	0.7099	0.6244
C(36)	0.9509	0.6576	0.5413
C(37)	1.0621	0.6076	0.4932
C(38)	1.1605	0.6081	0.527
C(39)	1.1591	0.6576	0.6083
C(40)	1.0454	0.7105	0.658
C(41)	1.6527	1.0955	0.3002
Cl(2)	1.7119	1.0798	0.3969
Cl(3)	1.6722	0.9931	0.2304
C(42)	0.9263	0.6755	0.1729
Cl(4)	0.9438	0.7938	0.1981
Cl(5)	0.8887	0.594	0.2764

Table S9. The Atomic Coordinates (angstroms) of **Cat. 4**

Element	Coordinates (Angstroms)		
	X	Y	Z
Ir	0.511	0.7363	0.7205
Cl(1)	0.561	0.5513	0.7569
P(1)	0.315	0.7038	0.822
O(1)	0.5651	0.9519	0.8824
O(2)	0.5915	0.6509	0.4673
O(3)	-0.0817	0.9722	0.7878
O(4)	0.1251	0.2567	0.8572
O(5)	0.3272	0.7889	1.175
N(1)	0.5561	0.8024	0.8176
N(2)	0.4954	0.6897	0.6055
C(1)	0.482	0.8949	0.6936
C(2)	0.4478	0.9425	0.6282
C(3)	0.4283	1.0527	0.6249
C(4)	0.4419	1.1172	0.6866
C(5)	0.4785	1.0735	0.7509
C(6)	0.5005	0.9622	0.7544
C(7)	0.5393	0.9057	0.8178
C(8)	0.5984	0.7737	0.884
C(9)	0.6335	0.6772	0.9122
C(10)	0.6704	0.6785	0.9833
C(11)	0.6689	0.771	1.0258
C(12)	0.6348	0.8684	0.9973
C(13)	0.6022	0.8652	0.925
C(14)	0.6829	0.7521	0.6363
C(15)	0.779	0.7845	0.6565
C(16)	0.8868	0.7846	0.592
C(17)	0.9056	0.7458	0.5118
C(18)	0.8118	0.7105	0.4927
C(19)	0.7032	0.7136	0.5553
C(20)	0.5976	0.6821	0.5427
C(21)	0.4137	0.6636	0.5679
C(22)	0.295	0.6601	0.5995
C(23)	0.2409	0.6253	0.5441

C(24)	0.3049	0.5957	0.46
C(25)	0.4227	0.6005	0.4284
C(26)	0.4753	0.6361	0.4833
C(27)	0.1929	0.7858	0.8114
C(28)	0.2064	0.8969	0.7964
C(29)	0.1172	0.9616	0.7881
C(30)	0.0118	0.9161	0.7953
C(31)	-0.0631	1.081	0.7537
C(32)	-0.0037	0.8068	0.8113
C(33)	0.0854	0.741	0.8194
C(34)	0.2578	0.5665	0.8354
C(35)	0.1726	0.5284	0.9131
C(36)	0.126	0.4253	0.9227
C(37)	0.1634	0.3594	0.8535
C(38)	0.0363	0.2166	0.9351
C(39)	0.2472	0.3963	0.776
C(40)	0.2945	0.498	0.7678
C(41)	0.3106	0.7262	0.9331
C(42)	0.2761	0.8246	0.9711
C(43)	0.2823	0.8422	1.0513
C(44)	0.3235	0.7635	1.0962
C(45)	0.3597	0.666	1.0594
C(46)	0.3534	0.6497	0.9785
C(47)	0.3606	0.7064	1.2258
C(48)	0.2499	0.952	0.4606
Cl(2)	0.1969	0.89	0.401
Cl(3)	0.1779	0.9466	0.5697
C(49)	1.1155	0.4654	0.277
Cl(4)	1.0567	0.5453	0.3624
Cl(5)	1.0936	0.5062	0.184

Table S10. The Atomic Coordinates (angstroms) of **Cat. 5**

Element	Coordinates (Angstroms)		
	X	Y	Z
Ir	-0.0006	0.199	0.2292
Cl(1)	0.076	0.2524	0.3393
Cl(2)	0.4901	0.0055	0.1231
Cl(3)	0.2126	0.4665	0.0853
P	-0.1923	0.3377	0.2416
O(1)	0.0945	-0.0768	0.3828
O(2)	-0.0768	0.1732	-0.0091
O(3)	-0.2687	0.7823	0.2496
O(4)	-0.49	0.308	-0.0233
O(5)	-0.4317	0.3383	0.5706
N(1)	-0.0148	0.076	0.3176
N(2)	-0.0537	0.1517	0.1261
C(1)	0.1704	0.0802	0.2217
C(2)	0.2637	0.0813	0.1735
C(3)	0.3734	0.0027	0.185
C(4)	0.3958	-0.0778	0.2441
C(5)	0.3041	-0.0805	0.2932
C(6)	0.1917	-0.0016	0.2815
C(7)	0.0901	0.001	0.3281
C(8)	-0.0885	0.0457	0.3704
C(9)	-0.0193	-0.0482	0.4105
C(10)	-0.0609	-0.1024	0.4682
C(11)	-0.1796	-0.0575	0.4853
C(12)	-0.2516	0.0365	0.4446
C(13)	-0.2084	0.0888	0.3867
C(14)	0.0418	0.2848	0.1388
C(15)	0.1038	0.3469	0.1448
C(16)	0.1359	0.3901	0.0734
C(17)	0.111	0.3753	-0.0047
C(18)	0.0513	0.3148	-0.0134
C(19)	0.0187	0.2695	0.0576
C(20)	-0.0364	0.1985	0.0576
C(21)	-0.1071	0.0887	0.1065

C(22)	-0.1227	0.1041	0.0214
C(23)	-0.1772	0.0565	-0.0209
C(24)	-0.2153	-0.0094	0.0269
C(25)	-0.1999	-0.026	0.1109
C(26)	-0.1435	0.0218	0.1527
C(27)	-0.2064	0.4732	0.2322
C(28)	-0.1215	0.4974	0.2613
C(29)	-0.1382	0.5994	0.2681
C(30)	-0.242	0.6786	0.2441
C(31)	-0.3245	0.6561	0.2127
C(32)	-0.312	0.5554	0.2073
C(33)	-0.2036	0.8107	0.3026
C(34)	-0.2884	0.3341	0.1639
C(35)	-0.2982	0.3863	0.0863
C(36)	-0.3652	0.3765	0.0256
C(37)	-0.4252	0.3128	0.0396
C(38)	-0.4145	0.2579	0.1142
C(39)	-0.3464	0.2692	0.1743
C(40)	-0.5448	0.238	-0.0113
C(41)	-0.2734	0.3434	0.3405
C(42)	-0.3935	0.3765	0.3464
C(43)	-0.4494	0.3758	0.4229
C(44)	-0.3854	0.3445	0.4932
C(45)	-0.2659	0.3153	0.4885
C(46)	-0.2118	0.3145	0.4135
C(47)	-0.5547	0.3649	0.5782

Table S11. The Atomic Coordinates (angstroms) of **Cat. 6**

Element	Coordinates (Angstroms)		
	X	Y	Z
Ir	-0.4923	0.2622	0.5172
Cl	-0.6112	0.3043	0.5079
P	-0.4891	0.2389	0.4174
F(1)	-0.5436	0.3746	0.7576
F(2)	-0.5403	0.1875	0.644
F(3)	-0.2251	0.1061	0.5802
F(4)	-0.3221	0.3098	0.5361
O(1)	-0.446	0.4514	0.5655
O(2)	-0.4938	0.0655	0.5547
N(1)	-0.4557	0.3583	0.516
N(2)	-0.5237	0.1676	0.5307
C(1)	-0.4237	0.4052	0.4812
C(2)	-0.3968	0.4037	0.4276
C(3)	-0.3696	0.4607	0.4058
C(4)	-0.3683	0.5191	0.4385
C(5)	-0.3926	0.5206	0.4931
C(6)	-0.4194	0.4627	0.5121
C(7)	-0.4664	0.3882	0.5644
C(8)	-0.4929	0.3549	0.613
C(9)	-0.5051	0.3847	0.6645
C(10)	-0.5293	0.347	0.7067
C(11)	-0.5424	0.281	0.6999
C(12)	-0.5287	0.2524	0.6478
C(13)	-0.5052	0.2867	0.6017
C(14)	-0.5855	0.13	0.5338
C(15)	-0.6558	0.1442	0.5241
C(16)	-0.7017	0.0924	0.5298
C(17)	-0.6804	0.0297	0.5452
C(18)	-0.6115	0.0151	0.5549
C(19)	-0.5657	0.067	0.5488
C(20)	-0.4732	0.1272	0.5434
C(21)	-0.4028	0.1507	0.5474
C(22)	-0.3462	0.1113	0.5616

C(23)	-0.2828	0.1422	0.566
C(24)	-0.2744	0.2088	0.5584
C(25)	-0.3334	0.2447	0.5445
C(26)	-0.3989	0.2192	0.537
C(27)	-0.5047	0.3066	0.3683
C(28)	-0.5492	0.3565	0.3817
C(29)	-0.5598	0.4091	0.345
C(30)	-0.5258	0.4114	0.2945
C(31)	-0.481	0.3614	0.2803
C(32)	-0.4712	0.3093	0.3163
C(34)	-0.4089	0.2008	0.3898
C(35)	-0.4094	0.1546	0.3474
C(36)	-0.3465	0.1281	0.328
C(37)	-0.2839	0.1478	0.3501
C(38)	-0.2832	0.195	0.3901
C(39)	-0.3449	0.2216	0.4101
C(41)	-0.5573	0.1803	0.3984
C(42)	-0.6216	0.2006	0.3782
C(43)	-0.6744	0.155	0.3683
C(44)	-0.6626	0.0899	0.3767
C(45)	-0.5994	0.0689	0.3954
C(46)	-0.5479	0.113	0.4071
O(6)	-0.2601	0.2966	0.2326
C(48)	-0.3277	0.2685	0.2081
O(7)	-0.2796	0.3926	0.2342
O(8)	-0.2157	0.363	0.2925
O(3)	-0.5484	0.466	0.2586
O(4)	-0.2114	0.1296	0.3373
O(5)	-0.7096	0.0383	0.3721
C(33)	-0.5156	0.4656	0.206
C(40)	-0.2127	0.0799	0.2918
C(47)	-0.7839	0.0557	0.3716
O(3')	-0.526	0.465	0.2666
O(4')	-0.2312	0.1171	0.328
O(5')	-0.723	0.0504	0.3594
C(33')	-0.481	0.47	0.208
C(40')	-0.1648	0.1397	0.3239
C(47')	-0.79	0.075	0.35

Table S12. The Atomic Coordinates (angstroms) of **Cat. 7**

Element	Coordinates (Angstroms)		
	X	Y	Z
Ir	0.6904	0.9199	0.7672
Cl(1)	0.5279	0.932	0.7012
Cl(2)	0.5174	0.8252	0.3538
Cl(3)	0.8799	1.3686	1.1086
P	0.816	1.1163	0.7572
O(1)	0.8313	0.7762	0.5767
O(2)	0.5436	0.8778	0.9966
O(3)	0.858	1.0872	0.3739
O(4)	1.2978	1.36	0.9435
O(5)	0.6406	1.4579	0.8615
N(1)	0.7265	0.8541	0.6473
N(2)	0.6503	0.9534	0.8942
C(1)	0.6947	0.828	0.5568
C(2)	0.6181	0.8416	0.509
C(3)	0.6118	0.8096	0.4182
C(4)	0.6815	0.7671	0.3761
C(5)	0.7558	0.7505	0.4225
C(6)	0.7606	0.7811	0.5125
C(7)	0.8045	0.8202	0.6554
C(8)	0.8559	0.8331	0.7397
C(9)	0.9374	0.7994	0.7538
C(10)	0.9762	0.8156	0.84
C(11)	0.9347	0.8636	0.9103
C(12)	0.858	0.9011	0.8946
C(13)	0.8138	0.8864	0.809
C(14)	0.6864	1.0425	0.9713
C(15)	0.771	1.1583	0.9954
C(16)	0.7788	1.2226	1.0781
C(17)	0.7054	1.1749	1.1382
C(18)	0.6258	1.0607	1.1186
C(19)	0.6182	0.9957	1.0339
C(20)	0.5681	0.8593	0.9116
C(21)	0.5182	0.7489	0.85

C(22)	0.4294	0.646	0.8626
C(23)	0.3931	0.5444	0.7948
C(24)	0.4399	0.5469	0.7191
C(25)	0.5287	0.6516	0.7063
C(26)	0.57	0.7541	0.7713
C(27)	0.8352	1.1175	0.642
C(28)	0.9206	1.1014	0.5991
C(29)	0.9244	1.0906	0.5099
C(30)	0.8453	1.0993	0.4604
C(31)	0.7599	1.1173	0.5008
C(32)	0.7545	1.1251	0.59
C(33)	0.7778	1.0909	0.3177
C(34)	0.9627	1.1919	0.8148
C(35)	1.0127	1.3036	0.8723
C(36)	1.1212	1.3535	0.9139
C(37)	1.1874	1.2966	0.8988
C(38)	1.1395	1.1846	0.8422
C(39)	1.0295	1.1334	0.802
C(40)	1.3677	1.3101	0.9357
C(41)	0.7667	1.2244	0.7916
C(42)	0.8211	1.3307	0.7713
C(43)	0.7848	1.4131	0.7958
C(44)	0.6878	1.3871	0.8372
C(45)	0.6334	1.2813	0.8589
C(46)	0.6708	1.2001	0.8351
C(47)	0.6939	1.5701	0.8419
C(48)	0.662	1.396	0.454
Cl(4)	0.7296	1.3613	0.5318
Cl(5)	0.6172	1.4754	0.538
O(6')	0.888	1.568	0.324
O(6)	0.924	1.564	0.397