Supporting information

Chiral Cyclometalateda Iridium Complexes for Asymmetric Reduction Reactions

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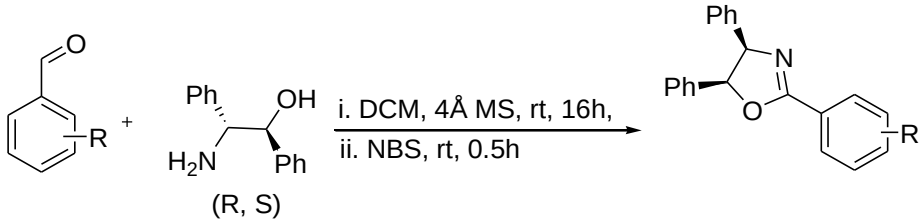
1. Experimental procedures

General information

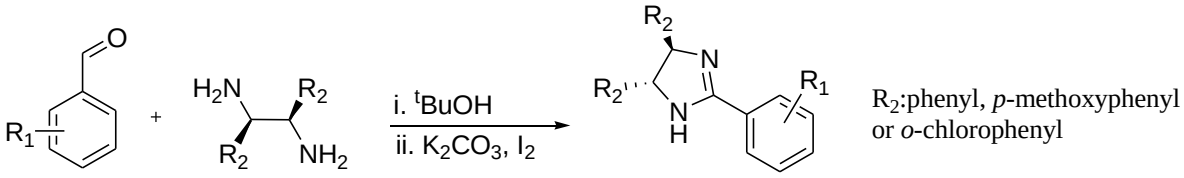
NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer, with TMS as internal standard. HPLC analysis was recorded on an Agilent 1260 Infinity equipped with Chiralpak IB-3or Chiralcel OJ-3 column. IPA, dichloromethane and toluene were dried on a MB-SPS 800. Methanol was dried over magnesium and iodine. 4Å MS were activated in an oven overnight. All other chemicals were obtained commercially and used without further purification.

General procedure for synthesis of oxazoline ligands[1]



A round bottom flask was charged with amino alcohol (1 eq), benzaldehyde (1 eq, 1 mmol), 4Å MS and a stirrer bar. DCM (5 mL) was added and the reaction was stirred at room temperature for 16 h. NBS (1 eq) was added slowly to the flask, producing an orange/yellow solution, which was stirred for a further 30 min. The reaction mixture was filtered and washed with aq $NaHCO_3$ (10 mL x 3) and water (10 mL). The organics were dried over $MgSO_4$ and concentrated under vacuum. The resulting residue was purified by column chromatography in 10% EtOAc in hexane.

General procedure forthe synthesis of imidazoline ligands[2]

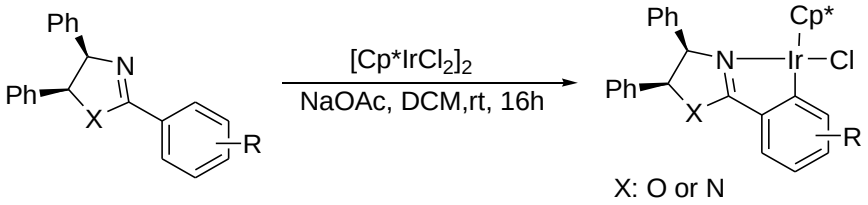


R_2:phenyl, *p*-methoxyphenyl or *o*-chlorophenyl

A reaction tube was charged with diamine (1 eq), benzaldehyde (1 eq, 1 mmol) and a stirrer bar. *t*BuOH (5 mL) was then added and the resulting mixture stirred at room temperature for 16 h. K_2CO_3 (3 eq) and I_2 (1.25 eq) were then added and the resulting dark orange solution was heated to 70 ^oC and stirred for 3 h. Once cooled the reaction was quenched by addition of saturated aq $Na_2S_2O_4$ (10 mL) and the organics extracted with EtOAc. The organic layer was

washed with water (10 mL x 3) and dried over $MgSO_4$. The solvent was then removed under vacuum and the residue purified by column chromatography in 50% EtOAc in hexane.

General procedure for preparation of cyclometalated complexes[3, 4, 5]



A glass vial was charged with $[IrCp^*Cl_2]_2$ (1 eq), ligand (2 eq), NaOAc (10 eq) and a stirrer bar. Dichloromethane was added and the resulting solution was left to stir at room temperature for 16 h. The reaction mixture was filtered through Celite and the solvent was removed under vacuum. The complex was recrystallised from DCM/hexane to yield iridacycles.

Due to the steric bulk, complex **4** formation required harsher cyclometalationconditions, heating to 50 ^oC under a sealed nitrogen atmosphere.

Standard procedure for DARA under FT conditions

A glass vial was charged with the iridium catalyst (1 mol%), amine (1.2 eq) and ketone (0.5 mmol) along with a stirring bar, IPA (2.5 mL) was added, followed by azeotropic formic acid-triethylamine (FT, 0.5 mL) to initiate the reaction. The glass vial was sealed and stirred at the stated temperature and time. After the reaction was complete, the reaction mixture was quenched by the addition of 1M NaOH and extracted into EtOAc. The organic phase was dried over MgSO4, filtered and evaporated under vacuum. The resulting residue was purified by column chromatography, in 15% EtOAc in hexane, upon which HPLC analysis was performed.

Standard procedure for DARA under aqueous conditions

A glass vial was charged with the iridium catalyst (1 mol%), amine (1.2 eq) and ketone (0.5 mmol) along with a stirring bar. 2-MeTHF (0.3 mL) was added, followedby an aqueous solution of sodium formate/formic acid (3 mL) to initiate the reaction. The glass vial was sealed and stirred at the stated temperature and time. After the reaction was complete, the reaction mixture was quenched by the addition of saturated aq K_2CO_3 and extracted into EtOAc. The organic phase was dried over $MgSO_4$, filtered and evaporated under vacuum. The resulting residue was

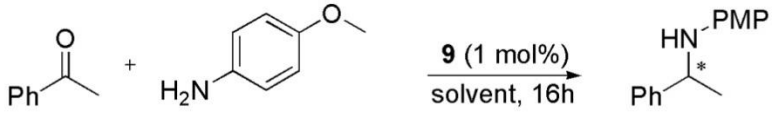
purified by column chromatography, in 15% EtOAc in hexane, upon which HPLC analysis was performed.

ATH of pyridinium salt

To a Schlenk tube charged with a stirrer bar, the benzyl protected pyridine (0.5 mmol) and an iridium complex (1 mol%) were loaded, followed by IPA (5 mL). The Schlenk tube was inserted into an Integrity 10 machine, pre-set to -10 ^{o}C. FT (1 mL) was injected into the Schlenk tube and the reaction mixture left to stir for 16 h. The reaction was quenched by the addition of aq NaOH solution (5 mL); the reaction mixture was warmed to room temperature. The organics were extracted with EtOAc x 3, dried over $MgSO_4$ and concentrated under vacuum. The resulting residue was purified by column chromatography, using an eluent of 20% EtOAc in hexane, upon which HPLC analysis was performed.

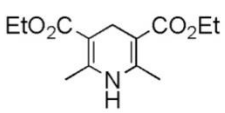
Optimisation of conditions for DARA with iridacycle 9*

Table S1. Optimisation Conditions for DARA with iridacycle **9**



Entry	Temp. (°C)	Solvent (mL/mL)	Additive	conv. (%)	ee (%)
1	r.t	IPA/FT (2.5/0.5)	-	78	56
2	r.t	FT (1)	-	0	27
3	r.t	IPA (2.5)	-	0	-
4[a]	r.t	PhMe/FT (2.5/0.5)	-	0	-
5[a]	r.t	MeCN (2.5/0.5)	-	0	-
6[a]	r.t	TFE (2.5/0.5)	-	25	-
7[a]	r.t	MeOH (2.5/0.5)	-	58	43
8[a]	r.t	t-amyl alcohol (2.5/0.5)	-	30	42
9[a]	r.t	t-butanol (2.5/0.5)	-	42	50
10[a]	r.t	PEG-200 (2.5/0.5)	-	57	53
11[a]	r.t	PEG-300 (2.5/0.5)	-	53	51
12[a]	r.t	PEG-400 (2.5/0.5)	-	47	50
13[a]	r.t	ethylene glycol (2.5/0.5)	-	80	44
14[a]	r.t	ethylene glycol- IPA (1/1)	-	73	48
15[b]	r.t	IPA/FT (2.5/0.5)	4Å MS (30 mg)	88	
16[b]	r.t	IPA/FT (2.5/0.5)	4Å MS (60 mg)	84	
17[b]	r.t	IPA/FT (2.5/0.5)	4Å MS (100 mg)	62	
18	**23**	**IPA/FT (2.5/0.5)**	**-**	**92**	**56**
19	15	IPA/FT (2.5/0.5)	-	78	56
20	5	IPA/FT (2.5/0.5)	-	70	54
21	-10	IPA/FT (2.5/0.5)	-	18	40
22[c]	20	H_2O (pH 4.5) with $NaCO_2H/HCO_2H$	-	100	40
23[d]	20	IPA with Hantszch ester	-	0	-
24[d]	20	PhMe with Hantszch ester	-	0	-

Reaction conditions; 0.5 mmol acetophenone, 0.6 mmol p-methoxy aniline
[a] room temperature was determined to be between 8 and 15 °C,
[b] ee values did not investigated,
[c] $NaCO_2H/HCO_2H$ was used as hydride source,
[d] Hantszch ester was used as hydride source

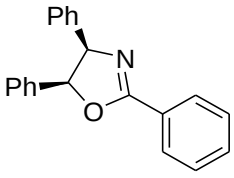


Hantszch ester

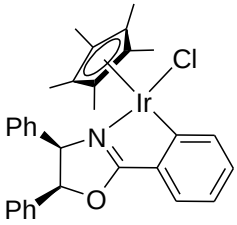
*The configuration of the amine product is *R* based on comparison with the literature HPLC data (*J. Am. Chem. Soc*. **2009**,*131,* 6967). We assume the configuration of other amines to be the same.

2. Analytic data

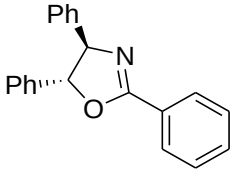
Analytic data for ligands and iridium complexes



(*4R,5S*)-2,4,5-Triphenyl-4,5-dihydrooxazole:[6] White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 8.19-8.17 (m, 2H), 7.59-7.55 (m, 1H), 7.52-7.48 (m, 2H), 7.09-7.00 (m, 6H), 6.99-6.92 (m, 4H), 6.02 (d, *J* = 10.0 Hz, 1H), 5.75 (d, *J* = 10.0 Hz ,1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 165.3, 138.1, 137.0, 132.2, 129.0, 128.9, 128.3, 128.1, 128.0, 127.9, 127.8, 127.4, 126.8, 85.7, 74.9; **HRMS** (ESI) for $C_{21}H_{17}NO$ $[M+H]^+$: m/z calc: 300.1383. Found: 300.1383.

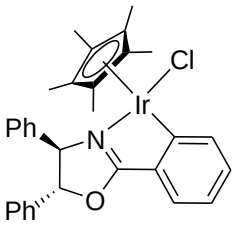


Complex 1: Orange crystals; A mixture of two isomers(2:1 ratio): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.86 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 0.5 Hz), 7.65 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.59 (dd, *J* = 7.4, 1.2 Hz, 0.5H), 7.40 (d, *J* = 6.6 Hz, 1H), 7.34-7.28 (m, 2H), 7.10-6.90 (m, 15H), 6.28 (d, *J* = 9.1 Hz, 1H), 6.23 (d, *J* = 10.0 Hz, 0.5H), 5.80 (d, *J* = 10.0 Hz, 0.5H), 5.42 (d, *J* = 9.1 Hz, 1H), 1.50 (s, 15H), 1.49 (s, 7.5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 181.6, 179.8, 177.3, 174.6, 163.8, 163.3, 162.4, 162.1, 158.8, 136.2, 135.8, 134.7, 132.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.5, 127.3, 126.7, 88.7, 88.0, 83.6, 77.6, 76.4, 72.5, 9.77, 9.54; **HRMS** (ESI) for $C_{31}H_{31}IrNO$ $[M-Cl]^+$: m/z calc: 626.2035. Found: 626.2042; **CHN** calculated: C 56.31, H 4.73, N 2.12. Found: C 56.38, H 4.69, N 2.14; Single crystal suitable for X-ray diffraction experiment was obtained by diffusion hexane into a solution of **1** in CH_2Cl_2.

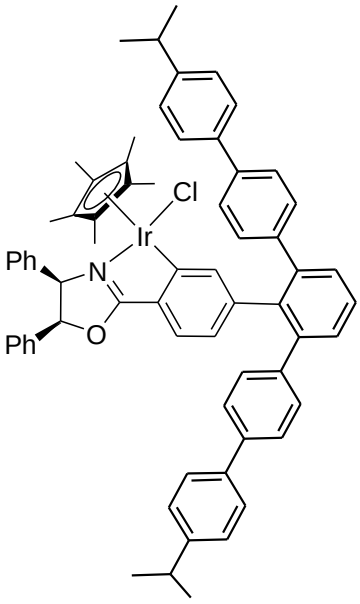


(*4R,5R*)-2,4,5-Triphenyl-4,5-dihydrooxazole:[7] **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 8.15-8.13 (m, 2H), 7.56-7.29 (m, 13H), 5.41 (d, *J* = 7.7 Hz, 1H), 5.22 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm): 164.5, 142.2, 140.9, 132.1, 129.4, 129.3, 129.1,

128.9, 128.8, 128.2, 127.9, 127.2, 126.1, 89.4, 79.5; **HRMS** (ESI) for $C_{21}H_{17}NO$ $[M+H]^+$: m/z calc: 300.1383. Found: 300.1385; **CHN** calculated: C 84.25, H 5.72, N 4.58. Found: C 84.60, H 5.77, N 4.61.

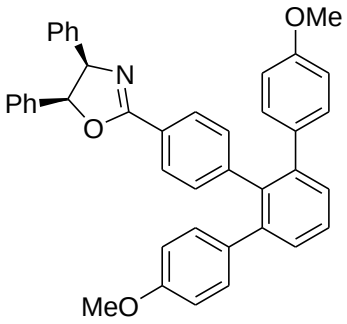


Complex 2: Orange crystals; A mixture of two isomers (1:1 ratio): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.85 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.59-7.54 (m, 4H), 7.46-7.27 (m, 20H), 7.08-7.03 (m, 2H), 5.54 (d, *J* = 7.0 Hz, 1H), 5.52 (d, *J* = 10.4 Hz, 1H), 5.18 (d, *J* = 7.0 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H), 1.51 (s, 15H), 1.46 (s, 15H). Single crystal suitable for X-ray diffraction experiment was obtained by diffusion hexane into a solution of **2** in CH_2Cl_2.

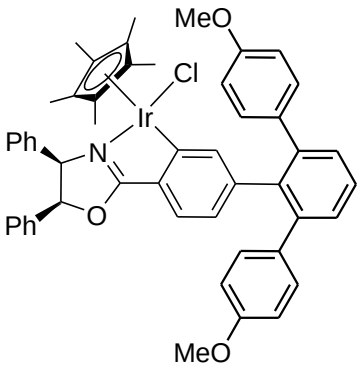


Complex 3: Yellow solid; A mixture of two isomers (2.3:1 ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.91-7.79 (m, 2H), 7.72-7.58 (m, 4H), 7.52-7.47 (m, 2H), 7.44-7.40 (m, 2H), 7.31-7.28 (m, 3H), 7.10-.08 (m, 8H), 7.06- 7.01 (m, 7H), 6.98-6.94 (m, 2H), 6.89 (bs, 2H), 6.28 (d, *J* = 9.1 Hz, 0.7H), 6.23 (d, *J* = 10.0 Hz, 0.3H), 5.80 (d, *J* = 10.0 Hz, 0.3H), 5.41 (d, *J* = 9.1 Hz, 0.7H), 1.75-1.68 (m, 2H), 1.52-1.47 (m, 23H), 1.39-1.37 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 181.2, 136.1, 135.7, 135.4, 134.8, 134.7, 134.3, 133.2, 132.4, 131.5, 129.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.6, 127.4,

127.3, 127.1, 126.9, 126.7, 126.3, 125.7, 125.6, 122.0, 121.9, 90.7, 88.4, 88.1, 87.7, 73.3, 72.0, 31.4, 9.5, 9.4, 9.3, 9.2; **MS** (ESI) for $C_{67}H_{63}ClIrNO$ $[M+H]^+$: m/z calc: 1126.4. Found: 1126.4.

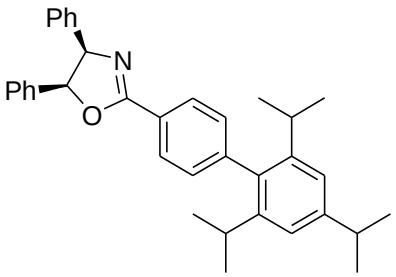


(*4R,5S*)-2-(4''-Methoxy-6'-(4-methoxyphenyl)-[1,1':2',1''-terphenyl]-4-yl)-4,5- diphenyl-4,5-dihydrooxazole: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.84-7.82 (m, 2H), 7.52-7.43 (m, 4H), 7.10-6.96 (m, 15H), 6.79-6.76 (m, 4H), 5.99 (d, *J* = 10.1 Hz, 1H), 5.72 (d, *J* = 10.1 Hz, 1H), 3.81 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 182.8, 165.1, 162.1,158.2, 144.0, 141.5, 137.8, 136.6, 134.1, 131.9, 131.0, 129.5, 127.9, 127.7, 127.6, 127.5, 127.4, 127.0, 126.4, 124.7, 113.3, 85.2, 74.4, 55.2; **HRMS** (ESI) for $C_{41}H_{33}NO_3$ $[M+H]^+$: m/z calc: 588.2533. Found: 588.2545.

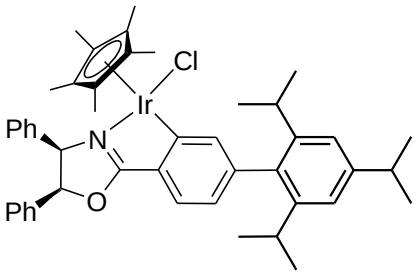


Complex 4: Yellow solid; A mixture of two isomers (2:1 ratio): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.50-7.41 (m, 4.5H), 7.39 (dd, *J* = 6.7, 1.1 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.25-7.18 (m, 3H), 7.14-6.97 (m, 15H), 6.94-6.84 (m, 3H), 6.82-6.69 (m, 6H), 6.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.59 (dd, *J* = 7.8, 1.4 Hz, 0.5H), 6.26 (d, *J* = 9.3 Hz, 1H), 6.15 (d, *J* = 9.9 Hz, 0.5H), 5.75 (d, *J* = 9.9 Hz, 0.5H), 5.37 (d, *J* = 9.3 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 1.5H), 3.76 (s, 3H), 3.75 (s, 1.5H), 1.25 (s, 15H), 1.24 (s, 7.5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 181.8, 181.1, 162.1, 158.1, 158.0, 157.9, 145.0, 143.8, 142.2, 140.9, 140.5, 140.0, 139.7, 139.4, 139.2, 126.4, 135.1, 134.8, 134.5, 133.8, 131.3, 131.1, 130.9, 129.4, 129.3, 129.3, 129.2, 129.1, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.6, 127.4, 126.9, 126.3, 126.0,

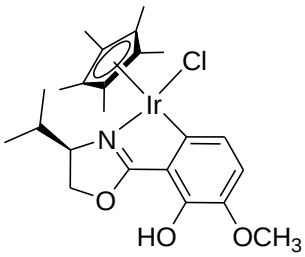
125.8, 125.7, 125.4, 113.5, 113.3, 113.2, 90.5, 88.0, 87.2, 73.1, 72.0, 55.3, 55.3, 55.3, 55.2, 9.2, 8.9; **MS** (ESI) for $C_{51}H_{47}ClIrNO_3$ $[M+H]^+$: m/z calc: 950.3. Found: 950.4; **CHN** calculated: C 64.51, H4.99, N 1.48. Found: C 64.00, H 4.96, N 1.33.



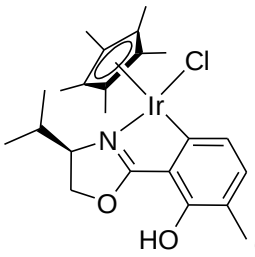
***(4R,5S)*-4,5-Diphenyl-2-(2',4',6'-triisopropyl-[1,1'-biphenyl]-4-yl)-4,5-dihydrooxazole:**[8] White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 8.20 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 9.2 Hz, 2H), 7.08-6.97 (m, 12H), 6.05 (d, *J* = 10.1 Hz, 1H), 5.78 (d, *J* = 10.1 Hz, 1H), 2.95 (septet, *J* = 6.9 Hz, 1H), 2.63 (septet, *J* = 6.9 Hz, 2H), 1.32 (d, *J* = 6.9 Hz, 6H), 1.11 (d, *J* = 6.9 Hz, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 165.0, 148.3, 146.3, 145.0, 137.8, 136.7, 136.2, 130.2, 128.3, 128.0, 127.7, 127.7, 127.4, 127.0, 126.4, 125.7, 120.7, 85.4, 74.6, 23.3, 30.4, 24.2, 24.1. **HRMS** (ESI) for $C_{36}H_{39}NO$ $[M+H]^+$: m/z calc: 502.3104. Found: 502.3109.



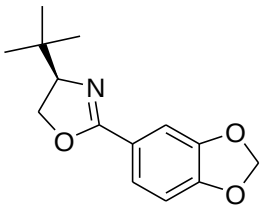
Complex 5:[8] Yellow solid; A mixture of two isomers (2.3:1 ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.68 (d, *J* = 7.7 Hz, 0.7H), 7.62 (s, 0.7H), 7.58 (d, *J* = 7.7 Hz, 0.3H) 7.56 (s, 0.3H), 7.42 (d, *J* = 7.2 Hz, 0.7H) 7.35 (d, *J* = 7.2 Hz, 0.3H), 7.12-7.02 (m, 11H) 6.90 (d, *J* = 7.7 Hz, 0.7H), 6.87 (d, *J* = 7.7 Hz, 0.3H), 6.30 (d, *J* = 9.2 Hz, 0.7H), 6.27 (d, *J* = 10.4 Hz, 0.3H), 5.80 (d, *J* = 10.4 Hz, 0.3H), 5.47 (d, *J* = 9.2 Hz, 0.7H), 3.03-2.69 (m, 3H), 1.58 (s, 3H), 1.50 (s, 12H), 1.36 (d, *J* = 6.8 Hz, 6H), 1.20-1.09 (m, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 181.1, 163.2, 147.5, 145.9, 137.8, 137.3, 136.2, 134.4, 128.1, 128.0, 127.8, 126.3, 123.7, 120.7, 120.2, 90.7, 88.2, 87.5, 72.1, 34.2, 30.5, 30.2, 25.0, 24.6, 24.0, 23.9, 9.4, 9.1; **CHN** calculated: C 63.98, H6.19, N 1.62. Found: C 63.78, H 6.27, N 1.45.



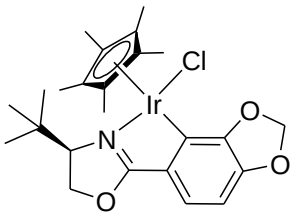
Complex 6: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.14 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 7.1 Hz, 1H), 4.49-4.36 (m, 1H), 4.36-4.16 (m, 2H), 3.78 (s, 3H), 2.76-2.58 (m, 1H), 1.58 (s, 15H), 0.92 (d, *J* = 7.1Hz, 3H), 0.84 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 159.5, 152.9, 120.8, 114.9, 113.2, 109.7, 84.5, 73.9, 87.9, 56.5, 29.6, 19.5, 9.2, 9.0. **MS** (ESI) for $C_{23}H_{31}ClIrNO_3$ $[M]^+$: 597.2. Found: 597.3. **CHN** calculated: C 46.26, H 5.23, N 2.35. Found: C 45.46, H 5.27, N 1.69.



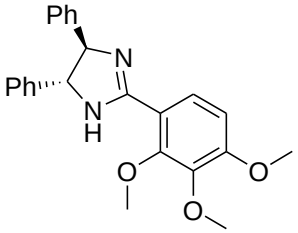
Complex 7: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.38 (d, *J* = 7.0 Hz, 1H), 7.12 (d, *J* =7.0 Hz, 1H), 4.46-4.43 (m, 1H), 4.30-4.19 (m, 2H), 2.68-2.56 (m, 1H), 2.93 (s, 3H), 1.61 (s, 15H), 0.91 (dd, *J* = 24.1, 7.7 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 160.8, 133.6, 131.0, 126.5, 113.4, 108.2, 84.3, 74.2, 67.4, 29.7, 19.5, 17.8, 14.8, 9.0; **MS** (ESI) for $C_{23}H_{31}ClIrNO_2$ $[M+H]^+$: m/z calc: 582.2. Found: 582.5; **CHN** calculated: C 47.53, H 5.38, N 2.41. Found: C 45.92, H 5.38, N 1.82.



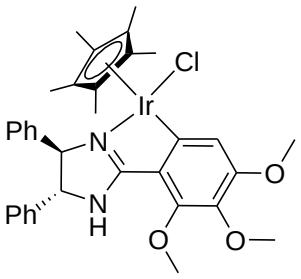
(*R*)-2-(Benzo[d][1,3]dioxol-5-yl)-4-(*tert*-butyl)-4,5-dihydrooxazole: White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.50 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H), 4.33-4.28 (m, 1H), 4.20 (t, *J* = 8.1 Hz, 1H), 4.01 (dd, *J* = 10, 7.6 Hz, 1H), 0.94 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 162.7, 150.0, 147.5, 123.0, 121.9, 108.5, 107.9, 101.4, 76.0, 68.7, 34.0, 25.8; **HRMS** (ESI) for $C_{14}H_{17}NO_3$ $[M+H]^+$: m/z calc: 248.1281. Found: 248.1285; **CHN** calculated: C 68.00, H 6.93, N 5.66. Found: C 67.43, H 6.87, N 5.55.



Complex 8: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.05 (d, *J* = 7.9 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 6.02 (d, *J* = 1.5 Hz, 1H), 5.97 (d, *J* = 1.5 Hz, 1H), 4.77 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.55 (t, *J* = 8.8 Hz, 1H), 3.96 (dd, *J* = 9.4, 4.0 Hz, 1H), 1.75 (s, 15H), 1.09 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 179.5, 162.1, 150.7, 149.5, 141.4, 138.9, 124.9, 122.8, 103.3, 100.0, 99.4, 87.8, 72.3, 70.9, 58.6, 35.8, 25.7, 9.6; **MS** (ESI) for $C_{24}H_{31}ClIrNO_3$ $[M]^+$: m/z calc: 609.2. Found: 609.3; **CHN** calculated: C 47.32, H 5.18, N 2.30. Found: C 46.26, H 5.06, N 1.72.

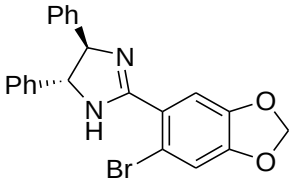


***(4R,5R)*-4,5-Diphenyl-2-(2,3,4-trimethoxyphenyl)-4,5-dihydro-1*H*-imidazole:** Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 8.04 (d, *J* = 8.9 Hz, 1H), 7.36-7.25 (m, 11H $CDCl_3$ included), 6.78 (d, *J* = 8.9 Hz, 1H), 4.86 (s, 2H), 3.97 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 161.6, 155.9, 152.9, 144.0, 142.0, 128.7, 127.4, 126.6, 126.1, 116.1, 107.9, 61.8, 61.0. 56.2; **HRMS** (ESI) for $C_{24}H_{24}N_2O_3$ $[M+H]^+$: m/z calc: 389.1860. Found: 389.1868.

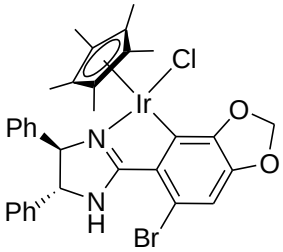


Complex 9: Yellow solid; A mixture of two isomer (2:1 ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.51 (d, *J* = 6.9Hz, 1H), 7.41-7.28 (m, 9H, including $CDCl_3$), 7.1 (m, 1H), 6.61 (s, 1H), 4.97 (d, *J* = 6.0 Hz, 0.33H), 4.92-4.84 (m, 1.32H), 4.71 (d, *J* = 6.0 Hz, 0.33H), 4.04 (s, 2H), 4.01 (s, 1H), 4.00 (s, 2H), 3.99 (s, 1H), 3.83 (s, 1H), 3.79 (s, 2H), 1.46 (s, 10H), 1.44 (s, 5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 176.7, 175.7, 161.4, 160.2, 156.7, 156.2, 151.5, 151.4, 144.1, 142.4, 140.4, 139.7, 136.0, 135.8, 128.9, 128.7, 128.3, 128.2, 128.1,

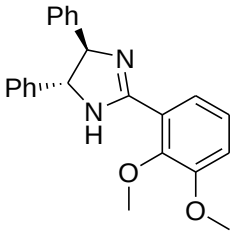
128.0, 127.5, 127.3, 120.1, 118.9, 113.9, 113.4, 87.6, 87.1, 78.5, 78.0, 72.3, 72.1, 61.2, 61.1, 60.4, 55.8, 9.5, 9.2; **HRMS** (ESI) for $C_{34}H_{38}ClIrN_2O_3$ $[M]^+$: m/z calc: 750.2200. Found: 750.2206; **CHN** calculated: C 54.42, H 5.10, N 3.73. Found: C 53.92, H 5.34, N 3.33.



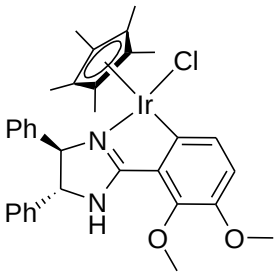
(*4R,5R*)-2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazole: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.35-7.26 (m, 11H plus $CHCl_3$), 7.01 (s, 1H), 5.99 (s, 1H), 4.82 (s, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 162.8, 149.8, 147.4, 143.3, 128.7, 127.5, 126.8, 125.7, 113.3, 111.1, 102.3, 75.3; **HRMS** (ESI) for $C_{22}H_{17}BrN_2O_2$ $[M+H]^+$: m/z calc: 421.0552 and 423.0531. Found: 421.0546 and 423.0529; **CHN** calculated: C 62.72, H 4.07, N 6.65. Found: C 63.17, H 4.06, N 6.71.



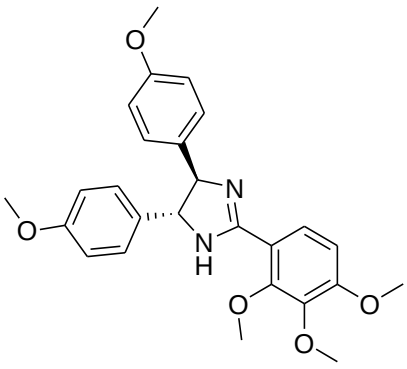
Complex 10: Yellow solid; A mixture of two isomers (2:1 ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.47-7.40 (m, 8H), 7.34-7.30 (m, 7H), 6.78 (s, 0.5H), 6.76 (s, 1H), 6.13 (s, 1H), 6.01 (s, 1H), 5.98 (s, 1H), 5.01 (d, *J* = 5.6 Hz, 0.5H), 4.93-4.86 (m, 2H), 4.70 (d, *J* = 5.6 Hz, 0.5H), 1.51 (s, 15H), 1.47 (s, 7.5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 175.8, 175.0, 151.3, 150.9, 148.7, 148.1, 144.1, 143.7, 141.8, 140.4, 139.4, 129.0, 128.9, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.6, 127.3, 127.2, 126.6, 113.7, 113.4, 108.8, 108.7, 100.2, 99.9, 88.9, 88.3, 79.1, 78.2, 72.1, 71.2, 9.8, 9.5; **HRMS** (ESI) for $C_{32}H_{31}BrClIrN_2O_2$ $[M]^+$: m/z calc: 782.0881. Found: 782.0875; **CHN** calculated: C 49.07, H 3.99, N 3.58. Found: C 48.58, H 4.10, N 3.54.



(*4R,5R*)-2-(2,3-Dimethoxyphenyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazole: Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.85 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.37-7.28 (m, 10H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 8.1, 1.5 Hz, 1H), 4.89 (s, 2H), 3.92 (s, 3H), 3.91 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 161.9, 152.9, 148.1, 143.9, 128.7, 126.6, 124.5, 123.6, 122.7, 114.7, 61.6, 56.0; **HRMS** (ESI) for $C_{23}H_{22}N_2O_2$ $[M+H]^+$ m/z calc: 359.1754. Found: 359.1750.

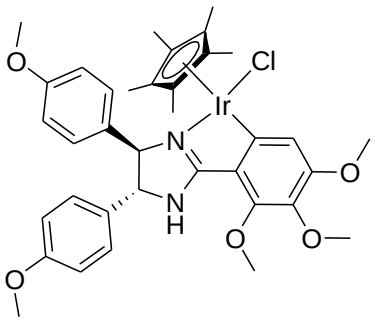


Complex 11: Yellow solid; A mixture of two isomers (2:1 ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.52 (d, *J* = 6.8 Hz, 2H), 7.48-7.27(m, 13H), 7.00 (t, *J* = 8.1 Hz, 1.5H), 6.78 (s, 1H), 6.73 (s, 0.5H), 4.99 (d, *J* = 6.1 Hz, 0.5H) 4.96-4.86 (m, 2H), 4.74 (d, *J* = 6.1 Hz, 0.5H), 3.98 (s, 3H), 3.96 (s, 1.5H), 3.86 (s, 1.5H), 3.85 (s, 3H), 1.45 (s, 15H), 1.43 (s, 7.5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 176.8, 175.9, 155.9, 147.7, 146.9, 140.5, 139.6, 130.7, 130.3, 128.9, 128.8, 128.4, 128.2, 128.1, 127.6, 127.3, 126.9, 119.1, 118.2, 87.5, 87.0, 78.8, 78.3, 72.2, 71.9, 61.2, 56.6, 53.5, 9.4, 9.2; **HRMS** (ESI) for $C_{33}H_{36}ClIrN_2O_2$ $[M+H]^+$: m/z calc: 721.2167. Found: 721.2127; **CHN** calculated: C 55.03, H 5.04, N 3.89. Found: C 52.33, H 4.86, N 2.92.

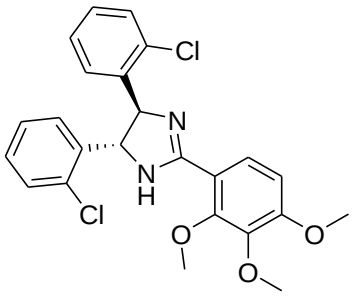


(*4R,5R*)-4,5-bis(4-methoxyphenyl)-2-(2,3,4-rimethoxyphenyl)-4,5-dihydro-1*H*-imidazole: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ

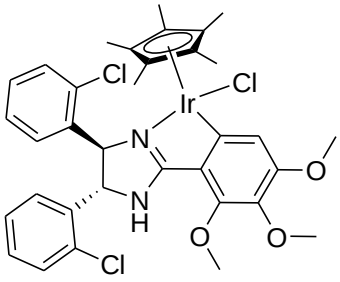
(ppm) 8.02 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 4H), 6.87 (d, *J* = 8.6 Hz, 4H), 4.77 (s, 2H), 3.96 (s, 3H), 3.92 (s, 3H), 3.89 (s, 3H), 3.85 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 161.4, 159.0, 156.0, 152.9, 142.0, 136.0, 127.7, 126.1, 114.1, 114.0, 107.9, 61.9, 61.0, 56.1, 55.3.



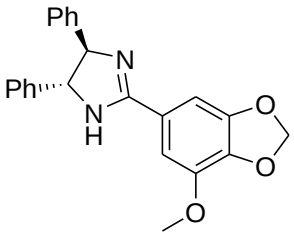
Complex 12: Yellow solid; A mixture of two isomers (6.5:1 ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.44-6.82 (m, 9H, including $CDCl_3$), 6.59-6.38 (m, 1.35H), 5.64-5.51 (m, 1H), 5.13-5.04 (m, 0.15H), 4.90 (d, *J* = 10.5 Hz, 0.15H), 4.83-4.53 (m, 1H), 4.02-3.46 (m, 16H), 3.27-3.15 (m, 1.25H), 1.46 (s, 15H), 1.40 (s, 2.3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 176.4, 159.0, 156.7, 151.5, 135.8, 132.4, 132.0, 130.0, 128.6, 128.4, 114.1, 113.9, 113.3, 88.2, 87.6, 87.2, 88.0, 78.0, 71.7, 61.1, 60.7, 55.8, 55.4, 55.3, 55.0, 53.5, 9.5, 9.3, 9.3; **HRMS** (ESI) for $C_{36}H_{42}ClIrN_2O_5$ [M]: m/z calc: 810.2411. Found: 810.2417.



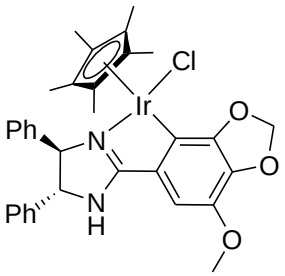
(*4R*,*5R*)-4,5-bis(2-chlorophenyl)-2-(2,3,4-trimethoxyphenyl)-4,5-dihydro-1*H*-imidazole: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 8.04 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 6.5 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.3-7.26 (m, 2H, plus $CHCl_3$), 7.23-7.19 (m, 2H), 6.80 (d, *J* = 8.9 Hz, 1H), 5.42 (bs, 2H), 3.93 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 162.2, 156.1, 152.9, 142.1, 141.1, 133.0, 129.5, 128.5, 127.3, 126.0, 115.8, 107.9, 61.8, 61.0, 56.2; **HRMS** (CI) for $C_{24}H_{22}Cl_2N_2O_3$ $[M+H]^+$: m/z calc: 457.1080. Found: 457.1095.



Complex 13: Yellow solid; A mixture of two isomers (1.5:1 ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.69 (d, *J* = 7.8 Hz, 1H), 7.42-7.29 (m, 5H), 7.24-7.17 (m, 2H), 7.11 (s, 0.4H), 7.07 (s, 0.6H), 6.52 (s, 1H), 5.62 (d, *J* = 10.7 Hz, 0.6H), 5.52 (d, *J* = 4.5 Hz, 0.4H), 5.43 (d, *J* = 10.7 Hz, 0.6H), 5.27 (d, *J* = 4.5 Hz, 0.4H), 4.02 (s, 2H), 4.01 (m, 3H), 3.99 (s, 1H), 3.82 (s, 1H), 3.79 (s, 2H), 1.49 (s, 9H), 1.48 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 177.0, 176.2, 161.6, 133.0, 132.7, 130.1, 129.9, 129.3, 129.0, 128.9, 128.7, 128.3, 128.3, 127.4, 127.2, 113.9, 113.4, 87.8, 87.1, 73.2, 67.8, 61.2, 60.8, 55.8, 53.4, 9.3, 9.1; **HRMS** (ESI) for $C_{34}H_{36}Cl_3IrN_2O_3$ $[M]^+$: m/z calc: 818.1421. Found: 818.1422.

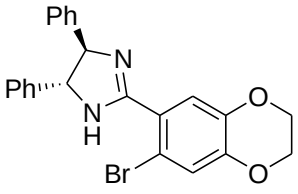


(*4R,5R*)-2-(7-Methoxybenzo[*d*][1,3]dioxol-5-yl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazole: Yellow solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.35-7.27 (m, 11H), 7.06 (s, 1H), 6.04 (s, 2H), 4.88 (s, 2H), 3.95 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 171.1, 162.9, 148.9, 143.7, 143.2, 137.9, 128.8, 127.6, 126.6, 107.8, 102.1, 101.7, 56.9. **MS** (ESI) for $C_{23}H_{20}N_2O_3$ $[M+H]^+$: m/z calc: 373.2. Found: 373.2.

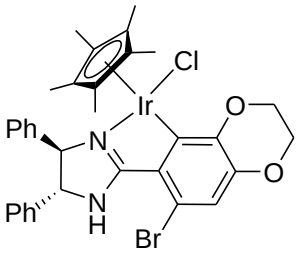


Complex 14: Yellow solid; A mixture of two isomers (2.9:1 ratio); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.57-7.07 (m, 15H plus $CDCl_3$), 6.83 (s, 1H), 6.76 (s, 0.35H), 6.09 (bs, 1H), 5.97 (bs, 1.7H), 5.08 (bs, 0.35H), 4.93 (d, *J* = 10.8 Hz, 1H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.62 (bs, 0.35H), 3.78 (s, 4.05H, minor+major isomers), 1.46 (bs, 20.25H, minor+major isomers); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 177.4, 171.2, 151.5, 140.5, 140.0, 139.8, 137.3, 131.2, 129.0, 128.9, 128.7, 128.4, 128.2, 128.1, 127.4, 106.9, 100.0, 88.2, 87.5, 79.6, 71.6, 56.5,

9.9, 9.6, 9.4; **HRMS** (ESI) for $C_{33}H_{34}ClIrN_2O_3[M]^+$: m/z calc: 734.1882. Found: 734.1880; **CHN** calculated: C 53.98, H 4.67, N 3.81. Found: C 53.08, H 4.66, N 3.42.

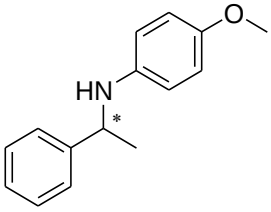


(*4R,5R*)-2-(7-bromo-2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-4,5-diphenyl-4,5- dihydro-1*H*-imidazole: White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.46 (s, 1H), 7.36-7.32 (m, 10H), 7.14 (s, 1H), 4.88 (s, 2H), 4.41-4.39 (m, 1H), 4.29-4.26 (m, 3H); **HRMS** (ESI) for $C_{23}H_{19}BrN_2O_2$ $[M+H]^+$: m/z calc: 435.0703. Found: 435.0702.



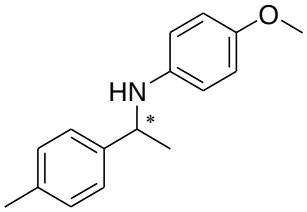
Complex 15: Yellow solid; A mixture of two isomers (2.5:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.47-7.36 (m, 7H), 7.35-7.23 (m, 7H), 7.08 (s, 0.4H), 6.81 (s, 1H), 5.05-4.97 (m, 0.4H), 4.95-4.83 (m, 2H), 4.70-4.64 (m, 0.4H), 4.40-4.19(m, 5.6H), 1.47 (s, 15H), 1.43 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 176.1, 158.8, 146.1, 144.9, 141.9, 140.7, 139.5, 129.1, 129.0, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.5, 127.1, 127.0, 124.7, 117.1, 111.8, 88.9, 88.7, 88.2, 87.9, 87.4, 82.9, 78.8. 78.0, 72.1, 71.0, 70.8, 64.5, 64.4, 63.8, 63.7, 53.5, 9.9, 9.5.

Analytic data for Amine Products

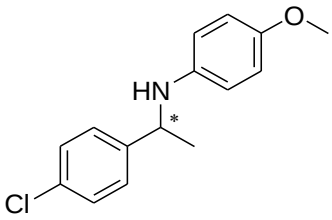


4-Methoxy-*N*-(1-phenylethyl)aniline:[9] White solid isolated in 90% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.37-7.29 (m, 4H), 7.23-7.20 (m, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 8.4 Hz, 2H), 4.21 (q, *J* = 6.6 Hz, 1H), 3.69 (s, 3H), 1.51 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 152.1, 145.2, 141.2, 128.6, 126.9, 126.0, 114.9, 114.8, 55.7, 54.5, 25.0; **HRMS** (CI) for $C_{15}H_{17}NO$ $[M+H]^+$: m/z calc: 228.1383. Found:

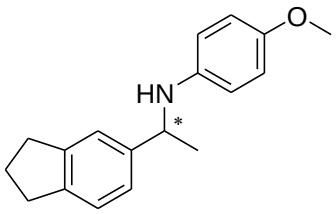
228.1386; **CHN** calculated: C 79.26, H 7.54, N 6.16. Found: C 79.42, H 7.50, N 5.95; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 7.14 min (major) and 8.61 min.



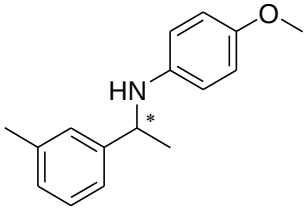
4-Methoxy-*N*-(1-(*p*-tolyl)ethyl)aniline:[10] White solid isolated in 95% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.24 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 4.38 (q, *J* = 6.7 Hz, 1H), 3.69 (s, 3H), 3.32 (s, 3H), 1.48 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 142.5, 141.7, 136.3, 129.3, 128.5, 125.8, 114.8, 114.6, 55.8, 54.0, 25.1, 21.1; **HRMS** (CI) for $C_{16}H_{19}NO$ $[M+H]^+$ calc: 242.1539. Found: 242.1544; **CHN** calculated: C 79.63, H 7.94, N 5.80. Found: C 79.88, H 7.81, N 4.7; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 11.16 min and 11.99 min (major).



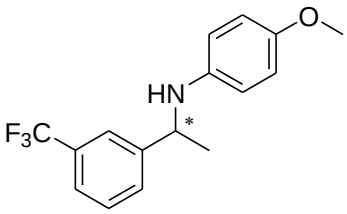
***N*-(1-(4-Chlorophenyl)ethyl)-4-methoxyaniline:**[10] Orange oil isolated in 94% yield (in the organic system) and 80% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.31-7.25 (m, 4H), 6.69 (d, *J* = 8.9 Hz, 2H), 6.43 (d, *J* = 8.9 Hz, 2H), 4.37 (q, *J* = 6.7 Hz, 1H), 3.69 (s, 3H), 1.47 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 152.1, 144.0, 141.1, 132.3, 128.8, 127.3, 114.8, 114.7, 55.7, 53.8, 25.1; **HRMS** (CI) for $C_{15}H_{16}ClNO$ $[M+H]^+$: m/z calc: 262.0993. Found: 262.0992; **CHN** calculated: C 68.83, H 6.16, N 5.35. Found: C 69.73, H 6.33, N 5.12; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 17.23 min and 18.83 min (major).



***N*-(1-(2,3-Dihydro-*1H*-inden-5-yl)ethyl)-4-methoxyaniline:** Orange oil isolated in 80% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.22 (s, 1H), 7.13 (q, *J* = 7.7 Hz, 2H), 6.69 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 8.9 Hz, 2H), 4.38 (q, *J* = 6.7 Hz, 1H), 3.69 (s, 3H), 2.87 (t, *J* = 7.7 Hz, 4H), 2.05 (quin, *J* = 7.5 Hz, 2H), 1.48 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 151.9, 144.7, 143.4, 142.9, 124.4, 123.8, 121.8, 114.8, 114.6, 55.8, 54.3, 32.9, 32.5, 25.5, 25.3; **HRMS** (CI) for $C_{18}H_{21}NO$ $[M+H]^+$: m/z calc: 268.1696. Found: 268.1706; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^{o}C, 254 nm) 10.85 min and 11.80 min (major).

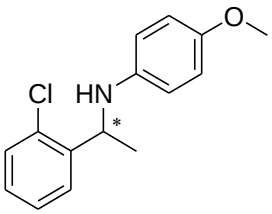


4-Methoxy-*N*-(1-(*m*-tolyl)ethyl)aniline:[11] Yellow oil isolated in 96% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.21-7.14 (m, 3H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 8.9 Hz, 2H), 4.36 (q, *J* = 6.7 Hz, 1H), 3.69 (s, 3H), 2.33 (s, 3H), 1.48 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 152.0, 145.4, 141.5, 138.2, 128.5, 127.7, 126.6, 123.0, 114.8, 114.7, 55.8, 54.4, 25.0, 21.5. **HRMS** (CI) for $C_{16}H_{19}NO$ $[M+H]^+$: m/z calc: 242.1539. Found: 242.1536; **CHN** calculated: C 79.63, H 7.94, N 5.80. Found: C 80.43, H 7.98, N 5.57; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^{o}C, 254 nm) 11.12 min and 12.25 min (major).

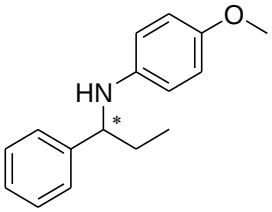


4-Methoxy-*N*-(1-(3-(trifluoromethyl)phenyl)ethyl)aniline:[11] Yellow oil isolated in 95% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.63 (bs, 1H), 7.55 (d, *J* = 6.4 Hz, 1H), 7.48 (d, *J* = 6.4 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 1H), 6.69 (d, *J* = 6.9 Hz, 2H), 6.43 (d, *J* = 7.0 Hz, 2H), 4.45 (m, 1H), 3.69 (s, 3H), 1.49 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 152.2, 146.8, 141.1, 129.3, 129.1, 123.8, 123.8, 122.8, 122.8, 114.8, 114.6,

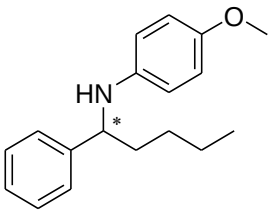
55.7, 54.2, 25.2; **HRMS** (CI) for $C_{16}H_{16}F_3NO$ $[M+H]^+$: m/z calc: 296.1257. Found: 296.1267; **CHN** calculated: C 65.08, H 5.46, N 4.74. Found: C 65.78, H 5.52, N 4.33; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 15.81 min and 20.08 min (major).



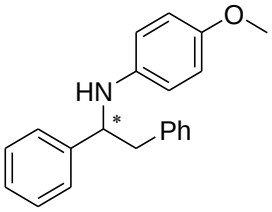
***N*-(1-(2-Chlorophenyl)ethyl)-4-methoxyaniline:**[11] Orange oil isolated in 88% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.45 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.34 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.20-7.12 (m, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 8.8 Hz, 2H), 4.83 (q, *J* = 6.6 Hz, 1H),3.86 (bs, 1H), 3.68 (s, 3H), 1.48 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 152.0, 142.3, 141.0, 132.5, 129.7, 128.0, 127.2, 126.8, 114.8, 114.3, 55.7, 50.9, 23.0; **HRMS** (CI) for $C_{15}H_{16}ClNO$ $[M+H]^+$: m/z calc: 262.0993. Found: 262.1002; **CHN** calculated: C 68.83, H 6.16, N 5.35. Found: C 68.75, H 6.20, N 4.94; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 10.38 min (major) and 11.56 min.



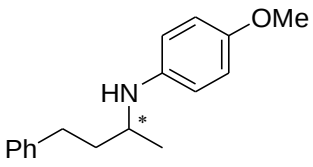
4-Methoxy-*N*-(1-phenylpropyl)aniline:[11] Orange oil isolated in 88% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.34-7.28 (m, 4H), 7.23-7.20 (m, 1H), 6.70-6.66 (m, 2H), 6.79-6.45 (m, 2H), 4.15 (t, *J* = 6.7 Hz, 1H), 3.68 (s, 3H), 1.80 (dq, *J* = 16.1, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 151.8, 144.2, 141.8, 128.5, 126.8, 126.6, 114.8, 114.4, 60.6, 55.8, 31.7, 10.9; **HRMS** (CI) for $C_{16}H_{19}NO$ $[M+H]^+$: m/z calc: 242.1539. Found: 242.1547; **CHN** $C_{16}H_{19}NO$ calculated C 79.63, H 7.94, N 5.80. Found: C 80.94, H 8.03, N 5.58; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 8.57 min and 9.21 min (major).



4-Methoxy-*N*-(1-phenylpentyl)aniline:[12] Yellow oil isolated in 75% yield (in the organic system) and 84% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.34-7.20 (m, 5H), 6.68-6.62(m, 4H), 4.2 (t, *J* = 7.0 Hz, 1H), 3.68 (s, 3H), 1.96-1.87 (m, 2H), 1.31-1.21 (m, 4H), 0.84 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 141.6, 128.6, 127.3, 127.0, 116.7, 114.6, 55.7, 45.7, 37.4, 28.4, 22.5, 14.7, 14.0, 6.6; **HRMS** (CI) for $C_{18}H_{23}NO$ $[M+H]^+$: m/z calc: 270.1852. Found: 270.1863; **CHN** calculated: C 80.26, H 8.61, N 5.20. Found: C 81.26, H 8.64, N 4.78; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 °C, 254 nm) 7.60 min and 8.16 min (major).

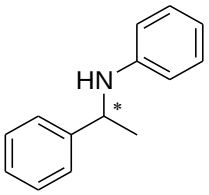


***N*-(1,2-Diphenylethyl)-4-methoxyaniline:**[13] Yellow oil isolated in 38% yield (in the organic system) and 76% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 8.02-7.97 (m, 2H), 7.55-7.44 (m, 3H), 7.32-7.30 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 8.8 Hz, 2H), 4.50 (dd, *J* = 8.0, 5.9 Hz, 1H), 3.11 (dd, *J* = 13.9, 5.9 Hz, 1H), 3.66 (s, 3H), 2.99 (dd, *J* = 14.0, 8.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 129.9, 129.5, 129.2, 129.0, 128.7, 128.6, 128.5, 127.0, 126.7, 126.5, 114.9, 114.7, 60.1, 55.7, 45.3; **HRMS** (CI) for $C_{21}H_{21}NO$ $[M+H]^+$: m/z calc: 304.1696. Found: 304.1709; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 °C, 254 nm) 10.51 min and 13.99 min (major).

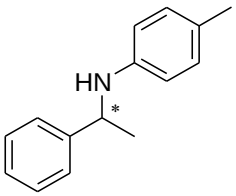


4-Methoxy-*N*-(4-phenylbutan-2-yl)aniline:[10] Yellow oil isolated in 97% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.30-7.28 (m, 2H), 7.19-7.17 (m, 3H), 6.78-6.74 (m, 2H), 6.53-6.50 (m, 2H), 3.74 (s, 3H), 3.42-3.37 (m, 1H), 2.78-2.70 (m, 2H), 1.89-1.71 (m, 2H), 1.19 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 151.9, 142.1, 141.7, 128.5, 128.4, 126.1, 125.8, 115.0, 114.8, 55.8, 49.0, 38.9, 32.5, 20.9; **HRMS** (CI) for $C_{17}H_{21}NO$

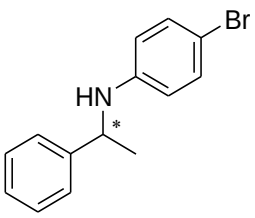
$[M+H]^+$: m/z calc: 256.1696. Found: 256.1703; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 11.84 min and 12.39 min.



***N*-(1-Phenylethyl)aniline:**[10] Yellow oil isolated in 37% yield (in the organic system) and 82% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.38-7.30 (m, 4H), 7.24-7.20 (m, 1H), 7.11-7.06 (m, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.52-6.50 (m, 2H), 4.48 (q, *J* = 6.7 Hz, 1H), 1.52 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 129.1, 129.0, 128.7, 128.4, 126.9, 125.9, 119.4, 113.3, 53.5, 25.0; **HRMS** (CI) for $C_{14}H_{15}N$ $[M+H]^+$: m/z calc: 198.1277. Found: 198.1280; **CHN** calculated: C 85.24, H 7.66, N 7.10. Found: C 86.33, H7.91, N 7.25; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 8.25 min (major) and 9.57 min.

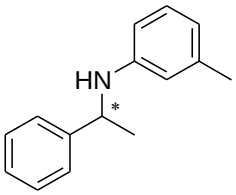


4-Methyl-*N*-(1-phenylethyl)aniline:[10] White solid isolated in 37% yield (in the organic system) and 84% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.37-7.29 (m, 4H), 7.23-7.20 (m, 1H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.43 (d, *J* = 8.2 Hz, 2H), 4.45 (q, *J* = 6.7 Hz, 1H), 2.18 (s, 3H), 1.50 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 129.6, 129.5, 128.6, 127.1, 126.8, 125.8, 119.4, 113.5, 53.7, 25.1, 20.4; **HRMS** (CI) for $C_{15}H_{17}N$ $[M+H]^+$: m/z calc: 212.1434. Found: 212.1442; **CHN** $C_{15}H_{17}N$ calculated C 85.26, H 8.11, N 6.63. Found: C 85.01, H 8.19, N 6.60; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 7.96 min and 8.73 min (major).

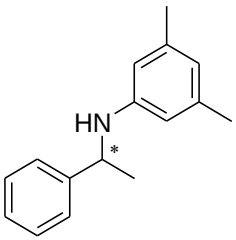


4-Bromo-*N*-(1-phenylethyl)aniline:[10] Yellow oil isolated in 8% yield (in the organic system) and 42% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.32-7.29 (m, 4H), 7.23-7.21 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.36 (d, *J* = 8.5 Hz, 2H),

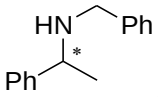
4.42 (q, *J* = 6.7 Hz, 1H), 1.50 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 146.2, 144.6, 131.8, 128.8, 127.1, 125.8, 114.9, 108.9, 55.5, 25.0; **HRMS** (CI) for $C_{14}H_{14}BrN$ $[M+H]^+$: m/z calc: 276.0382. Found: 276.0382; **CHN** calculated: C 60.89, H 5.11, N 5.07. Found: C 61.59, H 5.43, N 4.77; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 9.77 min and 11.59 min (major).



3-Methyl-*N*-(1-phenylethyl)aniline:[14] Orange oil isolated in 47% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.38-7.31 (m, 4H), 7.24-7.22 (m, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7. Hz, 1H), 6.36 (s, 1H), 6.3 (dd, *J* = 8, 2.2 Hz, 1H), 4.47 (q, *J* = 6.7 Hz, 1H), 2.21 (s, 3H), 1.50 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 147.3, 145.4, 138.9, 129.0, 128.6, 126.8, 125.9, 118.2, 114.1, 110.3, 53.4, 25.0, 21.6; **HRMS** (CI) for $C_{15}H_{17}N$ $[M+H]^+$: m/z calc: 212.1434. Found: 212.1443; **CHN** calculated: C 85.26, H 8.11, N 6.63. Found: C 85.19, H 8.27, N 6.79; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 7.24 min (major) and 8.66 min.

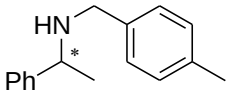


3,5-Dimethyl-*N*-(1-phenylethyl)aniline:[15] Yellow oil isolated in 50% yield (in the organic system) and 65% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.37-7.29 (m, 4H), 7.23-7.20 (m, 1H), 6.31 (s, 1H), 6.16 (s, 2H), 4.47 (q, *J* = 6.7 Hz, 1H), 2.16 (s, 6H), 1.48 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 147.4, 145.5, 138.8, 128.6, 126.8, 125.9, 119.3, 111.2, 53.3, 25.0, 21.5; **HRMS** (CI) for $C_{16}H_{19}N$ $[M+H]^+$: m/z calc: 226.1590. Found: 226.1591; **HPLC** (Chiralpak IB-3, 98:2 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 6.21 min (major) and 6.84 min.

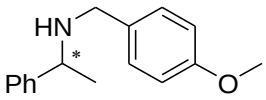


***N*-Benzyl-1-phenylethanamine:**[9] Yellow oil isolated in 80 yield (in the organic system) and 97% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.36-

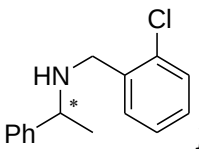
7.21 (m, 10H), 3.81 (q, *J* = 6.6 Hz, 1H), 3.62 (q, *J* = 13.1 Hz, 2H), 1.63 (bs, 1H), 1.37 (d, *J* = 6.6 Hz, 3H) ;**^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 145.6, 140.6, 128.5, 128.4, 128.2, 127.0, 126.9, 126.7, 57.5, 51.7, 24.6; **HRMS** (CI) for $C_{15}H_{17}N$ $[M+H]^+$: m/z calc: 212.1434. Found: 212.1444; **HPLC** (Chiralpak IB-3, 99:1 Hex:IPA + 0.1% $HNEt_2$, 1 mL/min, 25 ^oC, 254 nm) 5.65 min (major) and 6.09 min.



***N*-(4-Methylbenzyl)-1-phenylethanamine:**[16] Yellow oil isolated in 66% yield (in the organic system) and 94% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.35-7.34 (m, 4H), 7.6-7.26 (m, 1H), 7.17-7.10 (m, 4H), 3.80 (q, *J* = 6.6 Hz, 1H), 3.58 (q, *J* = 13.0 Hz, 2H), 2.33 (s, 3H), 1.60 (bs, 1H), 1.35 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 145.6, 137.6, 136.4, 129.1, 128.5, 128.1, 126.9, 126.8, 57.4, 51.4, 24.5, 21.3; **HRMS** (CI) for $C_{16}H_{19}N$ $[M+H]^+$: m/z calc: 226.1590. Found: 226.1596; **HPLC** (Chiralpak IB-3, 99.8:0.2 Hex:IPA (+ 0.1% $HNEt_2$), 0.5 mL/min, 25 ^oC, 254 nm) 16.83 min (major) and 17.72 min.



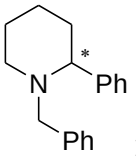
***N*-Benzyl-1-(4-nitrophenyl)ethanamine:**[17] Yellow oil isolated in 77% yied (in the organic system) and 93% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.35-7.33 (m, 4H), 7.26-7.25 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.82-3.77 (m, 4H), 3.56 (q, *J* = 12.9 Hz, 2H), 1.36 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 158.6, 145.7, 132.8, 129.3, 128.5, 126.9, 126.7, 113.8, 57.4, 55.3, 51.1, 24.6; **HRMS** (CI) for $C_{16}H_{19}NO$ $[M+H]^+$: m/z calc: 242.1539. Found: 242.1545; **HPLC** (Chiralpak IB-3, 99.8:0.2 Hex:IPA (+ 0.1% $HNEt_2$), 0. 5 mL/min, 25 ^oC, 254 nm) 25.69 min (major) and 27.27 min.



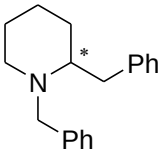
***N*-(2-Chlorobenzyl)-1-phenylethanamine:**[18] Yellow oil isolated in 90% yield (in the organic system) and 93% yield (in the aqueous system); **^{1}H NMR** ($CDCl_3$, 400 MHz,) δ (ppm) 7.39-7.30 (m, 6H), 7.26-7.23 (m, 1H), 7.22-7.16 (m, 2H), 3.82-3.67 (m, 3H), 1.8 (bs,

1H), 1.37 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 145.3, 137.8, 133.8, 130.5, 129.5, 128.5, 128.3, 127.0, 126.8, 57.4, 49.3, 24.6; **HRMS** (CI) for $C_{15}H_{16}ClN$ $[M+H]^+$: m/z calc: 246.1044. Found: 246.1055; **HPLC** (Chiralpak IB-3, 99.8:0.2 Hex:IPA (+ 0.1% $HNEt_2$), 0.5 mL/min, 25 ^oC, 254 nm) 17.63 min (major) and 18.77 min.

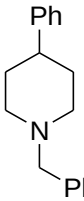
Analytic data for piperidine products



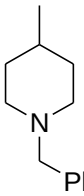
1-Benzyl-2-phenylpiperidine:[19] White solid isolated in 97% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.45 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.27-7.18 (m, 6H), 3.76 (d, *J* = 13.6 Hz, 1H), 3.10 (dd, *J* = 11.0, 2.6 Hz, 1H), 2.96 (d, *J* = 11.5 Hz, 1H), 2.80 (d, *J* = 13.5 Hz, 1H), 1.96-1.90 (m, 1H), 1.77 (d, *J* = 12.5 Hz, 2H),1.62-1.56 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 148.73, 139.82, 128.70, 128.49, 128.00, 127.46, 126.87, 126.51, 69.20, 59.79, 53.36, 37.01, 26.00, 25.25; **HRMS** (CI) for $C_{18}H_{21}N$ $[M+H]^+$: m/z calc: 252.1747. Found: 252.1753; **HPLC** (Chiracel OJ-3, 100% EtOH, 1 mL/min, 25 ^oC, 220 nm) 1.31 min and 1.66 min.



1,2-Dibenzylpiperidine:[19] White solid isolated in 75% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.37-7.27 (m, 5H), 7.24-7.13 (m, 5H), 4.05 (d, *J* = 13.6 Hz, 1H), 3.49 (d, *J* = 13.6 Hz, 1H), 3.70 (d, *J* = 9.7 Hz, 1H), 2.8-2.74 (m, 1H), 2.68-2.59 (m, 2H), 2.22 (dt, *J* = 11.7, 6.0 Hz, 1H), 1.66- 1.61 (m, 1H), 1.54-1.5 (m, 3H), 1.36-1.26 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 129.4, 129.3, 128.8, 128.3, 128.2, 128.1, 128.0, 61.71, 58.5, 50.8, 36.5, 29.3, 25.4, 22.4; **HRMS** (ESI) for $C_{19}H_{23}N$ $[M+H]^+$: m/z calc: 266.1903. Found: 266.1910; **HPLC** (Chiracel OJ-3, 100% EtOH, 1 mL/min, 25 ^oC, 220 nm) 1.41 min and 1.99 min.



1-Benzyl-4-phenylpiperidine:[20,21] White solid isolated in 75% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.39-7.30 (m, 9H), 7.24-7.20 (m, 1H), 6.06 (dt, *J* = 3.4, 1.8 Hz, 1H), 3.64 (s, 2H), 3.18 (q, *J* = 2.8 Hz, 2H), 2.72 (t, *J* = 5.8 Hz, 2H), 2.58-2.55 (m, 2H), 1.83-1.80 (m, 1H), 1.58-1.56 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 135.00, 129.26, 128.29, 128.27, 127.12, 124.92, 121.93, 62.76, 53.35, 49.99, 28.06; **HRMS** (CI) for $C_{18}H_{21}N$ $[M+H]^+$: m/z calc: 252.1747. Found: 252.1753.

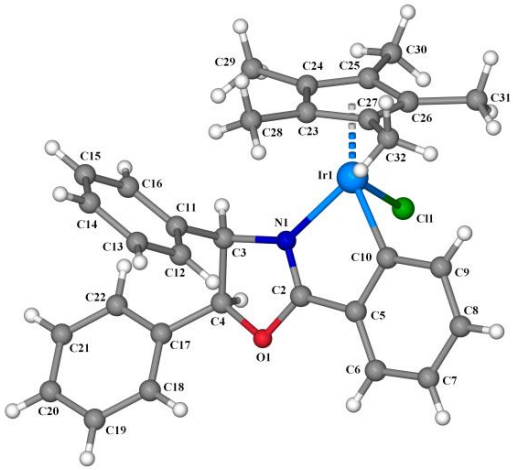


1-Benzyl-4-methylpiperidine:[21] White solid isolated in 80% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ (ppm) 7.32-7.29 (m, 4H), 7.24-7.22 (m, 1H), 3.48 (s, 2H), 2.93 (quin, *J* = 2.05 Hz, 1H), 2.83 (dt, *J* = 11.9 3.0 Hz, 2H), 2.55 (t, *J* = 5.8 Hz, 1H), 1.93 (td, *J* = 11.5, 2.4 Hz, 2H), 1.67 (d, *J* = 1.2 Hz, 1H), 1.58 (dd, *J* = 12.6, 1.6 Hz, 2H), 0.91 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ (ppm) 129.24, 128.19, 128.10, 126.82, 63.59, 53.98, 53.98, 34.39, 30.81, 21.94; **HRMS** (CI) for $C_{13}H_{19}N$ $[M+H]^+$: m/z calc: 190.1590. Found: 190.1594.

3. Single crystal X-ray diffraction details

Crystallographic data of complex 1

CCDC number: CCDC 2031296

[Ir(Cl)($C_{21}H_{16}ON$)($C_{10}H_{15}$)]	
M = 661.22	
orange prism,	
0.40 x 0.30 x 0.20 mm^3	
monoclinic, space group $P2_1$ (No. 4)	
a = 11.3621(9) Å	
b = 11.4447(9) Å	
c = 11.5177(9) Å	
β = 119.266(1)°	
V = 1306.54(2) $Å^3$	
Z = 2	
D_c = 1.681 g/cm^3	
T = 100(2)K	
$2\theta_{max}$ = 55.0°	
7488 reflections collected,	
5218 unique	
Multiscan absorption correction	
R_{int} = 0.0210	
Final *GooF* = 0.748	
R1 = 0.0197	
wR2 = 0.0442	
327 parameters, 1 restraint	
Flack parameter = 0.013(5)	
μ = 5.236 mm^{-1}	

Data collection, structure solution and refinement

The crystals were large, good quality orange prisms. A suitably sized crystal with well defined habit was selected for the analysis. The crystal was mounted on a glass fibre and placed in a cold stream at 100K. Single crystal X-ray data were collected on a Bruker D8 diffractometer with an APEX CCD detector, and 1.5 kW graphite monochromated Mo radiation. The detector to crystal distance was 5.985 cm. Exposure times of 10 s per frame and scan widths of 0.3º were used throughout the data collection. The data collection was performed using two ω scans with different φ values yielding data in the θ range 4.10 to 27.5° with an average completeness of 97%. The frames were integrated with the SAINT v7.45a (Bruker, 2005).[1] A multi-scan correction was carried out using the program SADABS V2008-1 (Bruker, 2008)[2].

The structure was solved and refined with X-SEED,[3] a graphical interface to SHELX (Sheldrick, 2008).[4] The hydrogen atoms were placed in geometrically idealized positions and were refined freely. In the final cycles of refinement all non-hydrogen atoms were refined anisotropically.

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1 Bruker (2009). SAINT V7.68a, BRUKER AXS Inc., Madison, WI, USA.

2 Bruker (2008), SADABS V2008-1, BRUKER AXS Inc., Madison, WI, USA.

3 Barbour, L. J. "X-Seed – A software tool for supramolecular crystallography" *J. Supramol. Chem.* **2001**, *1*, 189-191.

4 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	C_{31} H_{31} Cl Ir N O	
Formula weight	661.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 11.3621(9) Å	α= 90°.
	b = 11.4447(9) Å	β= 119.2660(10)°.
	c = 11.5177(9) Å	γ = 90°.
Volume	1306.54(18) $Å^3$	
Z	2	
Density (calculated)	1.681 Mg/m^3	
Absorption coefficient	5.236 mm^{-1}	
F(000)	652	
Crystal size	0.40 x 0.30 x 0.20 mm^3	
Theta range for data collection	2.70 to 27.48°.	
Index ranges	-14<=h<=14, -13<=k<=14, -10<=l<=14	
Reflections collected	7488	
Independent reflections	5218 [R(int) = 0.0210]	
Completeness to theta = 27.48°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4207 and 0.2285	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5206 / 1 / 327	
Goodness-of-fit on F^2	0.748	
Final R indices [I>2sigma(I)]	R1 = 0.0197, wR2 = 0.0442	
R indices (all data)	R1 = 0.0206, wR2 = 0.0445	
Absolute structure parameter	0.013(5)	
Largest diff. peak and hole	1.078 and -1.196 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	7319(1)	1855(1)	4684(1)	9(1)
Cl(1)	6997(1)	2382(1)	6528(1)	14(1)
O(1)	3303(3)	2890(2)	2780(3)	14(1)
N(1)	5217(2)	1858(5)	3583(2)	11(1)
C(2)	4669(4)	2852(4)	3336(5)	13(1)
C(3)	4136(4)	949(4)	3031(4)	9(1)
C(4)	2947(3)	1689(4)	2948(3)	12(1)
C(5)	5494(4)	3884(3)	3598(4)	12(1)
C(6)	5011(4)	5027(3)	3314(4)	16(1)
C(7)	5923(4)	5921(3)	3593(4)	15(1)
C(8)	7296(4)	5662(3)	4170(4)	14(1)
C(9)	7769(4)	4517(4)	4483(4)	14(1)
C(10)	6881(4)	3587(3)	4191(4)	11(1)
C(11)	3930(4)	511(3)	1700(4)	13(1)
C(12)	3971(4)	1271(4)	771(4)	17(1)
C(13)	3804(4)	848(4)	-427(4)	22(1)
C(14)	3608(4)	-326(4)	-719(4)	26(1)
C(15)	3555(4)	-1092(4)	185(5)	26(2)
C(16)	3716(4)	-673(4)	1390(4)	19(1)
C(17)	1533(4)	1399(3)	1899(4)	12(1)
C(18)	701(4)	2218(3)	976(4)	17(1)
C(19)	-629(3)	1943(7)	64(3)	20(1)
C(20)	-1122(4)	837(4)	71(4)	22(1)
C(21)	-289(4)	15(4)	989(4)	19(1)
C(22)	1036(4)	281(4)	1906(4)	16(1)
C(23)	7984(4)	715(3)	3629(4)	12(1)
C(24)	7968(4)	3(4)	4669(4)	13(1)
C(25)	8875(4)	505(3)	5909(4)	13(1)
C(26)	9458(4)	1566(3)	5670(4)	14(1)
C(27)	8946(3)	1640(3)	4258(4)	11(1)
C(28)	7300(4)	403(4)	2179(4)	16(1)
C(29)	7149(4)	-1076(4)	4450(4)	18(1)
C(30)	9201(4)	83(4)	7251(4)	18(1)
C(31)	10499(4)	2317(4)	6762(4)	19(1)

C(32)	9380(4)	2478(3)	3537(4)	17(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

Ir(1)-Cl(1)	2.4016(10)
Ir(1)-N(1)	2.085(2)
Ir(1)-C(10)	2.055(4)
Ir(1)-C(23)	2.156(4)
Ir(1)-C(24)	2.247(5)
Ir(1)-C(25)	2.251(4)
Ir(1)-C(26)	2.147(5)
Ir(1)-C(27)	2.146(4)
O(1)-C(2)	1.360(6)
O(1)-C(4)	1.472(5)
N(1)-C(2)	1.261(7)
N(1)-C(3)	1.494(6)
C(2)-C(5)	1.445(6)
C(3)-C(4)	1.557(6)
C(3)-C(11)	1.518(6)
C(4)-C(17)	1.501(6)
C(5)-C(6)	1.394(5)
C(5)-C(10)	1.419(7)
C(6)-C(7)	1.378(6)
C(7)-C(8)	1.396(7)
C(8)-C(9)	1.395(6)
C(9)-C(10)	1.390(6)
C(11)-C(12)	1.397(6)
C(11)-C(16)	1.392(6)
C(12)-C(13)	1.385(6)
C(13)-C(14)	1.377(6)
C(14)-C(15)	1.385(7)
C(15)-C(16)	1.393(7)
C(17)-C(18)	1.386(5)
C(17)-C(22)	1.400(6)
C(18)-C(19)	1.391(6)
C(19)-C(20)	1.386(9)
C(20)-C(21)	1.386(6)
C(21)-C(22)	1.386(7)
C(23)-C(24)	1.456(6)
C(23)-C(27)	1.437(5)
C(23)-C(28)	1.501(6)

C(24)-C(25)	1.412(6)
C(24)-C(29)	1.492(7)
C(25)-C(26)	1.472(6)
C(25)-C(30)	1.483(6)
C(26)-C(27)	1.437(6)
C(26)-C(31)	1.505(6)
C(27)-C(32)	1.501(6)
C(3)-H(3)	1.0000
C(4)-H(4)	1.0000
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
Cl(1)-Ir(1)-N(1)	85.02(7)

Cl(1)-Ir(1)-C(10)	83.19(12)
Cl(1)-Ir(1)-C(23)	153.78(10)
Cl(1)-Ir(1)-C(24)	115.83(11)
Cl(1)-Ir(1)-C(25)	91.73(11)
Cl(1)-Ir(1)-C(26)	101.13(11)
Cl(1)-Ir(1)-C(27)	138.71(11)
N(1)-Ir(1)-C(10)	77.3(2)
N(1)-Ir(1)-C(23)	105.73(16)
N(1)-Ir(1)-C(24)	106.2(2)
N(1)-Ir(1)-C(25)	134.21(19)
N(1)-Ir(1)-C(26)	170.29(17)
N(1)-Ir(1)-C(27)	136.02(13)
C(10)-Ir(1)-C(23)	122.17(16)
C(10)-Ir(1)-C(24)	160.71(17)
C(10)-Ir(1)-C(25)	147.69(17)
C(10)-Ir(1)-C(26)	110.69(17)
C(10)-Ir(1)-C(27)	99.60(17)
C(23)-Ir(1)-C(24)	38.55(15)
C(23)-Ir(1)-C(25)	63.47(15)
C(23)-Ir(1)-C(26)	65.58(16)
C(23)-Ir(1)-C(27)	39.04(15)
C(24)-Ir(1)-C(25)	36.58(14)
C(24)-Ir(1)-C(26)	64.38(15)
C(24)-Ir(1)-C(27)	64.36(16)
C(25)-Ir(1)-C(26)	39.02(15)
C(25)-Ir(1)-C(27)	64.15(16)
C(26)-Ir(1)-C(27)	39.11(16)
C(2)-O(1)-C(4)	103.4(3)
Ir(1)-N(1)-C(2)	115.5(4)
Ir(1)-N(1)-C(3)	135.8(4)
C(2)-N(1)-C(3)	108.7(3)
O(1)-C(2)-N(1)	117.3(4)
O(1)-C(2)-C(5)	123.1(4)
N(1)-C(2)-C(5)	119.5(5)
N(1)-C(3)-C(4)	99.0(3)
N(1)-C(3)-C(11)	110.4(4)
C(4)-C(3)-C(11)	114.6(3)
O(1)-C(4)-C(3)	103.3(3)
O(1)-C(4)-C(17)	110.8(3)

C(3)-C(4)-C(17)	119.0(3)
C(2)-C(5)-C(6)	125.3(4)
C(2)-C(5)-C(10)	111.1(3)
C(6)-C(5)-C(10)	123.7(4)
C(5)-C(6)-C(7)	118.5(4)
C(6)-C(7)-C(8)	119.4(3)
C(7)-C(8)-C(9)	121.5(4)
C(8)-C(9)-C(10)	121.0(4)
Ir(1)-C(10)-C(5)	115.2(3)
Ir(1)-C(10)-C(9)	128.5(3)
C(5)-C(10)-C(9)	115.9(3)
C(3)-C(11)-C(12)	121.4(3)
C(3)-C(11)-C(16)	120.1(4)
C(12)-C(11)-C(16)	118.5(4)
C(11)-C(12)-C(13)	120.4(4)
C(12)-C(13)-C(14)	120.8(4)
C(13)-C(14)-C(15)	119.7(4)
C(14)-C(15)-C(16)	119.9(4)
C(11)-C(16)-C(15)	120.8(4)
C(4)-C(17)-C(18)	121.9(4)
C(4)-C(17)-C(22)	118.3(4)
C(18)-C(17)-C(22)	119.8(4)
C(17)-C(18)-C(19)	120.6(4)
C(18)-C(19)-C(20)	119.7(5)
C(19)-C(20)-C(21)	119.8(4)
C(20)-C(21)-C(22)	121.0(4)
C(17)-C(22)-C(21)	119.2(4)
Ir(1)-C(23)-C(24)	74.1(3)
Ir(1)-C(23)-C(27)	70.1(2)
Ir(1)-C(23)-C(28)	129.6(3)
C(24)-C(23)-C(27)	108.0(3)
C(24)-C(23)-C(28)	125.1(4)
C(27)-C(23)-C(28)	126.1(4)
Ir(1)-C(24)-C(23)	67.3(2)
Ir(1)-C(24)-C(25)	71.9(2)
Ir(1)-C(24)-C(29)	127.0(3)
C(23)-C(24)-C(25)	107.9(4)
C(23)-C(24)-C(29)	125.6(4)
C(25)-C(24)-C(29)	126.5(4)

Ir(1)-C(25)-C(24)	71.6(3)
Ir(1)-C(25)-C(26)	66.7(2)
Ir(1)-C(25)-C(30)	126.6(3)
C(24)-C(25)-C(26)	108.6(4)
C(24)-C(25)-C(30)	127.5(4)
C(26)-C(25)-C(30)	123.9(4)
Ir(1)-C(26)-C(25)	74.3(3)
Ir(1)-C(26)-C(27)	70.4(2)
Ir(1)-C(26)-C(31)	125.3(3)
C(25)-C(26)-C(27)	106.9(3)
C(25)-C(26)-C(31)	123.8(4)
C(27)-C(26)-C(31)	129.1(4)
Ir(1)-C(27)-C(23)	70.8(2)
Ir(1)-C(27)-C(26)	70.5(3)
Ir(1)-C(27)-C(32)	127.3(3)
C(23)-C(27)-C(26)	108.3(3)
C(23)-C(27)-C(32)	124.5(4)
C(26)-C(27)-C(32)	127.1(3)
N(1)-C(3)-H(3)	111.00
C(4)-C(3)-H(3)	111.00
C(11)-C(3)-H(3)	111.00
O(1)-C(4)-H(4)	108.00
C(3)-C(4)-H(4)	108.00
C(17)-C(4)-H(4)	108.00
C(5)-C(6)-H(6)	121.00
C(7)-C(6)-H(6)	121.00
C(6)-C(7)-H(7)	120.00
C(8)-C(7)-H(7)	120.00
C(7)-C(8)-H(8)	119.00
C(9)-C(8)-H(8)	119.00
C(8)-C(9)-H(9)	120.00
C(10)-C(9)-H(9)	120.00
C(11)-C(12)-H(12)	120.00
C(13)-C(12)-H(12)	120.00
C(12)-C(13)-H(13)	120.00
C(14)-C(13)-H(13)	120.00
C(13)-C(14)-H(14)	120.00
C(15)-C(14)-H(14)	120.00
C(14)-C(15)-H(15)	120.00

C(16)-C(15)-H(15)	120.00
C(11)-C(16)-H(16)	120.00
C(15)-C(16)-H(16)	120.00
C(17)-C(18)-H(18)	120.00
C(19)-C(18)-H(18)	120.00
C(18)-C(19)-H(19)	120.00
C(20)-C(19)-H(19)	120.00
C(19)-C(20)-H(20)	120.00
C(21)-C(20)-H(20)	120.00
C(20)-C(21)-H(21)	119.00
C(22)-C(21)-H(21)	120.00
C(17)-C(22)-H(22)	120.00
C(21)-C(22)-H(22)	120.00
C(23)-C(28)-H(28A)	109.00
C(23)-C(28)-H(28B)	109.00
C(23)-C(28)-H(28C)	109.00
H(28A)-C(28)-H(28B)	109.00
H(28A)-C(28)-H(28C)	110.00
H(28B)-C(28)-H(28C)	110.00
C(24)-C(29)-H(29A)	109.00
C(24)-C(29)-H(29B)	109.00
C(24)-C(29)-H(29C)	109.00
H(29A)-C(29)-H(29B)	109.00
H(29A)-C(29)-H(29C)	109.00
H(29B)-C(29)-H(29C)	110.00
C(25)-C(30)-H(30A)	110.00
C(25)-C(30)-H(30B)	109.00
C(25)-C(30)-H(30C)	110.00
H(30A)-C(30)-H(30B)	109.00
H(30A)-C(30)-H(30C)	109.00
H(30B)-C(30)-H(30C)	109.00
C(26)-C(31)-H(31A)	109.00
C(26)-C(31)-H(31B)	109.00
C(26)-C(31)-H(31C)	109.00
H(31A)-C(31)-H(31B)	109.00
H(31A)-C(31)-H(31C)	109.00
H(31B)-C(31)-H(31C)	110.00
C(27)-C(32)-H(32A)	109.00
C(27)-C(32)-H(32B)	109.00

C(27)-C(32)-H(32C)	109.00
H(32A)-C(32)-H(32B)	109.00
H(32A)-C(32)-H(32C)	109.00
H(32B)-C(32)-H(32C)	110.00

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	10(1)	10(1)	9(1)	0(1)	6(1)	1(1)
Cl(1)	16(1)	16(1)	12(1)	-2(1)	9(1)	0(1)
O(1)	10(1)	15(2)	16(2)	0(1)	6(1)	1(1)
N(1)	11(1)	14(1)	11(1)	2(2)	6(1)	-2(2)
C(2)	10(2)	21(2)	9(2)	1(2)	5(2)	-1(2)
C(3)	12(2)	7(2)	10(2)	-2(2)	7(2)	-1(2)
C(4)	13(2)	14(3)	8(2)	0(2)	5(1)	1(2)
C(5)	14(2)	13(2)	10(2)	-2(1)	7(2)	0(1)
C(6)	18(2)	15(2)	15(2)	0(2)	8(2)	4(2)
C(7)	24(2)	10(2)	12(2)	2(1)	10(2)	3(2)
C(8)	19(2)	13(2)	15(2)	-3(2)	11(2)	-3(2)
C(9)	15(2)	17(2)	13(2)	0(2)	9(2)	2(2)
C(10)	17(2)	10(2)	10(2)	1(1)	10(2)	0(2)
C(11)	8(2)	22(2)	8(2)	0(2)	3(2)	1(2)
C(12)	17(2)	21(2)	13(2)	0(2)	8(2)	3(2)
C(13)	20(2)	35(3)	12(2)	4(2)	10(2)	1(2)
C(14)	24(2)	38(3)	18(2)	-10(2)	12(2)	-2(2)
C(15)	32(3)	25(2)	26(3)	-13(2)	19(2)	-10(2)
C(16)	21(2)	20(2)	17(2)	-4(2)	11(2)	-7(2)
C(17)	13(2)	18(2)	10(2)	-2(1)	9(2)	-1(1)
C(18)	20(2)	22(2)	12(2)	0(1)	9(2)	1(1)
C(19)	16(2)	31(2)	11(2)	1(3)	5(1)	4(3)
C(20)	14(2)	41(3)	11(2)	-8(2)	6(2)	-4(2)
C(21)	22(2)	21(2)	18(2)	-7(2)	13(2)	-5(2)
C(22)	13(2)	22(2)	15(2)	1(2)	9(2)	0(2)
C(23)	9(2)	16(2)	11(2)	3(1)	7(2)	4(1)
C(24)	14(2)	14(2)	12(2)	2(2)	8(2)	6(2)
C(25)	11(2)	15(2)	16(2)	0(2)	8(2)	6(2)
C(26)	9(2)	17(3)	17(2)	2(1)	6(2)	3(1)
C(27)	7(2)	10(3)	17(2)	1(1)	6(1)	3(1)
C(28)	17(2)	22(2)	12(2)	-3(2)	9(2)	0(2)
C(29)	21(2)	13(2)	22(2)	3(2)	12(2)	-1(2)
C(30)	23(2)	17(2)	16(2)	5(2)	12(2)	7(2)
C(31)	14(2)	25(2)	18(2)	-4(2)	8(2)	2(2)

C(32)	19(2)	17(2)	18(2)	0(2)	12(2)	-2(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1**.

	x	y	z	U(eq)
H(3)	4358	287	3672	24(8)
H(4)	2985	1643	3833	24(8)
H(6)	4074	5185	2938	15(5)
H(7)	5620	6707	3393	15(5)
H(8)	7922	6279	4354	15(5)
H(9)	8711	4371	4901	15(5)
H(12)	4114	2083	962	22(6)
H(13)	3826	1374	-1055	22(6)
H(14)	3510	-610	-1537	22(6)
H(15)	3408	-1902	-16	22(6)
H(16)	3680	-1201	2008	22(6)
H(18)	1041	2975	967	24(6)
H(19)	-1197	2510	-562	24(6)
H(20)	-2029	643	-551	24(6)
H(21)	-632	-742	989	24(6)
H(22)	1601	-288	2531	24(6)
H(28A)	7170	1111	1651	27(7)
H(28B)	6421	48	1921	27(7)
H(28C)	7861	-152	2019	27(7)
H(29A)	7673	-1760	4459	31(4)
H(29B)	6322	-1027	3587	31(4)
H(29C)	6914	-1151	5160	31(4)
H(30A)	8540	-508	7168	31(4)
H(30B)	9171	741	7782	31(4)
H(30C)	10106	-261	7691	31(4)
H(31A)	11380	1929	7150	31(4)
H(31B)	10245	2434	7453	31(4)
H(31C)	10552	3075	6394	31(4)
H(32A)	9763	3180	4081	31(4)
H(32B)	8598	2695	2686	31(4)
H(32C)	10062	2106	3374	31(4)

Table 6. Torsion angles [°] for **1**.

Cl(1)-Ir(1)-N(1)-C(2)	73.1(3)
Cl(1)-Ir(1)-N(1)-C(3)	-103.7(3)
C(10)-Ir(1)-N(1)-C(2)	-11.0(3)
C(10)-Ir(1)-N(1)-C(3)	172.2(3)
C(23)-Ir(1)-N(1)-C(2)	-131.3(3)
C(23)-Ir(1)-N(1)-C(3)	52.0(3)
C(24)-Ir(1)-N(1)-C(2)	-171.4(3)
C(24)-Ir(1)-N(1)-C(3)	11.8(3)
C(25)-Ir(1)-N(1)-C(2)	160.7(3)
C(25)-Ir(1)-N(1)-C(3)	-16.1(4)
C(27)-Ir(1)-N(1)-C(2)	-101.7(3)
C(27)-Ir(1)-N(1)-C(3)	81.5(4)
Cl(1)-Ir(1)-C(10)-C(5)	-77.3(3)
Cl(1)-Ir(1)-C(10)-C(9)	95.5(4)
N(1)-Ir(1)-C(10)-C(5)	9.1(3)
N(1)-Ir(1)-C(10)-C(9)	-178.1(4)
C(23)-Ir(1)-C(10)-C(5)	109.8(3)
C(23)-Ir(1)-C(10)-C(9)	-77.4(4)
C(25)-Ir(1)-C(10)-C(5)	-159.7(3)
C(25)-Ir(1)-C(10)-C(9)	13.1(6)
C(26)-Ir(1)-C(10)-C(5)	-176.7(3)
C(26)-Ir(1)-C(10)-C(9)	-3.9(4)
C(27)-Ir(1)-C(10)-C(5)	144.3(3)
C(27)-Ir(1)-C(10)-C(9)	-42.9(4)
Cl(1)-Ir(1)-C(23)-C(24)	15.1(4)
Cl(1)-Ir(1)-C(23)-C(27)	-101.3(3)
Cl(1)-Ir(1)-C(23)-C(28)	137.8(3)
N(1)-Ir(1)-C(23)-C(24)	-96.5(3)
N(1)-Ir(1)-C(23)-C(27)	147.1(2)
N(1)-Ir(1)-C(23)-C(28)	26.2(4)
C(10)-Ir(1)-C(23)-C(24)	178.9(3)
C(10)-Ir(1)-C(23)-C(27)	62.4(3)
C(10)-Ir(1)-C(23)-C(28)	-58.5(4)
C(24)-Ir(1)-C(23)-C(27)	-116.4(3)
C(24)-Ir(1)-C(23)-C(28)	122.7(5)
C(25)-Ir(1)-C(23)-C(24)	35.5(3)
C(25)-Ir(1)-C(23)-C(27)	-80.9(2)

C(25)-Ir(1)-C(23)-C(28)	158.2(4)
C(26)-Ir(1)-C(23)-C(24)	78.9(3)
C(26)-Ir(1)-C(23)-C(27)	-37.5(2)
C(26)-Ir(1)-C(23)-C(28)	-158.4(4)
C(27)-Ir(1)-C(23)-C(24)	116.4(3)
C(27)-Ir(1)-C(23)-C(28)	-120.9(5)
Cl(1)-Ir(1)-C(24)-C(23)	-172.6(2)
Cl(1)-Ir(1)-C(24)-C(25)	-53.4(3)
Cl(1)-Ir(1)-C(24)-C(29)	69.0(4)
N(1)-Ir(1)-C(24)-C(23)	95.0(3)
N(1)-Ir(1)-C(24)-C(25)	-145.7(3)
N(1)-Ir(1)-C(24)-C(29)	-23.3(4)
C(23)-Ir(1)-C(24)-C(25)	119.2(4)
C(23)-Ir(1)-C(24)-C(29)	-118.3(4)
C(25)-Ir(1)-C(24)-C(23)	-119.2(4)
C(25)-Ir(1)-C(24)-C(29)	122.4(5)
C(26)-Ir(1)-C(24)-C(23)	-82.3(3)
C(26)-Ir(1)-C(24)-C(25)	36.9(3)
C(26)-Ir(1)-C(24)-C(29)	159.4(4)
C(27)-Ir(1)-C(24)-C(23)	-38.7(3)
C(27)-Ir(1)-C(24)-C(25)	80.5(3)
C(27)-Ir(1)-C(24)-C(29)	-157.1(4)
Cl(1)-Ir(1)-C(25)-C(24)	133.7(3)
Cl(1)-Ir(1)-C(25)-C(26)	-105.6(2)
Cl(1)-Ir(1)-C(25)-C(30)	10.2(4)
N(1)-Ir(1)-C(25)-C(24)	49.0(3)
N(1)-Ir(1)-C(25)-C(26)	169.6(2)
N(1)-Ir(1)-C(25)-C(30)	-74.5(4)
C(10)-Ir(1)-C(25)-C(24)	-146.3(3)
C(10)-Ir(1)-C(25)-C(26)	-25.7(4)
C(10)-Ir(1)-C(25)-C(30)	90.2(5)
C(23)-Ir(1)-C(25)-C(24)	-37.4(3)
C(23)-Ir(1)-C(25)-C(26)	83.2(3)
C(23)-Ir(1)-C(25)-C(30)	-160.9(4)
C(24)-Ir(1)-C(25)-C(26)	120.7(4)
C(24)-Ir(1)-C(25)-C(30)	-123.5(5)
C(26)-Ir(1)-C(25)-C(24)	-120.7(4)
C(26)-Ir(1)-C(25)-C(30)	115.8(4)
C(27)-Ir(1)-C(25)-C(24)	-81.2(3)

C(27)-Ir(1)-C(25)-C(26)	39.5(2)
C(27)-Ir(1)-C(25)-C(30)	155.4(4)
Cl(1)-Ir(1)-C(26)-C(25)	78.8(2)
Cl(1)-Ir(1)-C(26)-C(27)	-166.37(18)
Cl(1)-Ir(1)-C(26)-C(31)	-41.8(4)
C(10)-Ir(1)-C(26)-C(25)	165.7(2)
C(10)-Ir(1)-C(26)-C(27)	-79.5(2)
C(10)-Ir(1)-C(26)-C(31)	45.1(4)
C(23)-Ir(1)-C(26)-C(25)	-77.4(2)
C(23)-Ir(1)-C(26)-C(27)	37.5(2)
C(23)-Ir(1)-C(26)-C(31)	162.0(4)
C(24)-Ir(1)-C(26)-C(25)	-34.6(2)
C(24)-Ir(1)-C(26)-C(27)	80.2(2)
C(24)-Ir(1)-C(26)-C(31)	-155.3(4)
C(25)-Ir(1)-C(26)-C(27)	114.8(3)
C(25)-Ir(1)-C(26)-C(31)	-120.6(5)
C(27)-Ir(1)-C(26)-C(25)	-114.8(3)
C(27)-Ir(1)-C(26)-C(31)	124.6(4)
Cl(1)-Ir(1)-C(27)-C(23)	138.96(19)
Cl(1)-Ir(1)-C(27)-C(26)	20.5(3)
Cl(1)-Ir(1)-C(27)-C(32)	-101.8(3)
N(1)-Ir(1)-C(27)-C(23)	-48.8(3)
N(1)-Ir(1)-C(27)-C(26)	-167.3(3)
N(1)-Ir(1)-C(27)-C(32)	70.4(4)
C(10)-Ir(1)-C(27)-C(23)	-130.5(2)
C(10)-Ir(1)-C(27)-C(26)	111.1(2)
C(10)-Ir(1)-C(27)-C(32)	-11.2(4)
C(23)-Ir(1)-C(27)-C(26)	-118.5(3)
C(23)-Ir(1)-C(27)-C(32)	119.3(4)
C(24)-Ir(1)-C(27)-C(23)	38.2(2)
C(24)-Ir(1)-C(27)-C(26)	-80.2(2)
C(24)-Ir(1)-C(27)-C(32)	157.5(4)
C(25)-Ir(1)-C(27)-C(23)	79.0(2)
C(25)-Ir(1)-C(27)-C(26)	-39.4(2)
C(25)-Ir(1)-C(27)-C(32)	-161.7(4)
C(26)-Ir(1)-C(27)-C(23)	118.5(3)
C(26)-Ir(1)-C(27)-C(32)	-122.3(4)
C(4)-O(1)-C(2)-N(1)	13.1(5)
C(4)-O(1)-C(2)-C(5)	-169.5(4)

C(2)-O(1)-C(4)-C(17)	-153.8(4)
C(2)-O(1)-C(4)-C(3)	-25.3(4)
C(3)-N(1)-C(2)-O(1)	6.3(5)
Ir(1)-N(1)-C(2)-O(1)	-171.4(3)
C(2)-N(1)-C(3)-C(11)	99.3(4)
Ir(1)-N(1)-C(2)-C(5)	11.2(5)
C(3)-N(1)-C(2)-C(5)	-171.2(4)
Ir(1)-N(1)-C(3)-C(11)	-83.8(4)
Ir(1)-N(1)-C(3)-C(4)	155.7(2)
C(2)-N(1)-C(3)-C(4)	-21.3(4)
N(1)-C(2)-C(5)-C(10)	-3.2(6)
O(1)-C(2)-C(5)-C(6)	-0.5(7)
O(1)-C(2)-C(5)-C(10)	179.5(4)
N(1)-C(2)-C(5)-C(6)	176.9(4)
N(1)-C(3)-C(4)-O(1)	27.6(3)
C(11)-C(3)-C(4)-C(17)	33.5(5)
N(1)-C(3)-C(11)-C(12)	-39.5(6)
N(1)-C(3)-C(11)-C(16)	139.5(5)
C(4)-C(3)-C(11)-C(12)	71.2(6)
C(4)-C(3)-C(11)-C(16)	-109.9(5)
N(1)-C(3)-C(4)-C(17)	150.9(3)
C(11)-C(3)-C(4)-O(1)	-89.8(4)
O(1)-C(4)-C(17)-C(18)	-3.6(6)
O(1)-C(4)-C(17)-C(22)	179.4(4)
C(3)-C(4)-C(17)-C(18)	-123.1(5)
C(3)-C(4)-C(17)-C(22)	59.9(5)
C(2)-C(5)-C(6)-C(7)	-178.4(4)
C(10)-C(5)-C(6)-C(7)	1.6(6)
C(2)-C(5)-C(10)-Ir(1)	-6.5(5)
C(2)-C(5)-C(10)-C(9)	179.8(4)
C(6)-C(5)-C(10)-Ir(1)	173.5(3)
C(6)-C(5)-C(10)-C(9)	-0.2(6)
C(5)-C(6)-C(7)-C(8)	-1.2(6)
C(6)-C(7)-C(8)-C(9)	-0.6(6)
C(7)-C(8)-C(9)-C(10)	2.1(6)
C(8)-C(9)-C(10)-Ir(1)	-174.3(3)
C(8)-C(9)-C(10)-C(5)	-1.6(6)
C(3)-C(11)-C(12)-C(13)	178.9(5)
C(16)-C(11)-C(12)-C(13)	-0.1(7)

C(3)-C(11)-C(16)-C(15)	-178.6(5)
C(12)-C(11)-C(16)-C(15)	0.4(7)
C(11)-C(12)-C(13)-C(14)	-0.6(7)
C(12)-C(13)-C(14)-C(15)	1.1(8)
C(13)-C(14)-C(15)-C(16)	-0.8(8)
C(14)-C(15)-C(16)-C(11)	0.0(8)
C(4)-C(17)-C(18)-C(19)	-176.3(4)
C(22)-C(17)-C(18)-C(19)	0.7(7)
C(4)-C(17)-C(22)-C(21)	176.7(4)
C(18)-C(17)-C(22)-C(21)	-0.4(7)
C(17)-C(18)-C(19)-C(20)	-0.6(7)
C(18)-C(19)-C(20)-C(21)	0.3(7)
C(19)-C(20)-C(21)-C(22)	0.0(7)
C(20)-C(21)-C(22)-C(17)	0.0(7)
Ir(1)-C(23)-C(24)-C(25)	-60.7(3)
Ir(1)-C(23)-C(24)-C(29)	120.2(5)
C(27)-C(23)-C(24)-Ir(1)	62.3(3)
C(27)-C(23)-C(24)-C(25)	1.7(5)
C(27)-C(23)-C(24)-C(29)	-177.4(4)
C(28)-C(23)-C(24)-Ir(1)	-127.6(5)
C(28)-C(23)-C(24)-C(25)	171.7(4)
C(28)-C(23)-C(24)-C(29)	-7.4(8)
Ir(1)-C(23)-C(27)-C(26)	60.8(3)
Ir(1)-C(23)-C(27)-C(32)	-122.6(4)
C(24)-C(23)-C(27)-Ir(1)	-64.9(3)
C(24)-C(23)-C(27)-C(26)	-4.1(5)
C(24)-C(23)-C(27)-C(32)	172.4(4)
C(28)-C(23)-C(27)-Ir(1)	125.1(4)
C(28)-C(23)-C(27)-C(26)	-174.1(4)
C(28)-C(23)-C(27)-C(32)	2.5(7)
Ir(1)-C(24)-C(25)-C(26)	-56.4(3)
Ir(1)-C(24)-C(25)-C(30)	122.5(5)
C(23)-C(24)-C(25)-Ir(1)	57.8(3)
C(23)-C(24)-C(25)-C(26)	1.4(5)
C(23)-C(24)-C(25)-C(30)	-179.7(4)
C(29)-C(24)-C(25)-Ir(1)	-123.1(5)
C(29)-C(24)-C(25)-C(26)	-179.5(5)
C(29)-C(24)-C(25)-C(30)	-0.6(8)
Ir(1)-C(25)-C(26)-C(27)	-63.3(3)

Ir(1)-C(25)-C(26)-C(31)	122.3(5)
C(24)-C(25)-C(26)-Ir(1)	59.4(3)
C(24)-C(25)-C(26)-C(27)	-3.9(5)
C(24)-C(25)-C(26)-C(31)	-178.3(4)
C(30)-C(25)-C(26)-Ir(1)	-119.5(4)
C(30)-C(25)-C(26)-C(27)	177.2(4)
C(30)-C(25)-C(26)-C(31)	2.8(7)
Ir(1)-C(26)-C(27)-C(23)	-61.0(3)
Ir(1)-C(26)-C(27)-C(32)	122.5(4)
C(25)-C(26)-C(27)-Ir(1)	65.9(3)
C(25)-C(26)-C(27)-C(23)	4.9(5)
C(25)-C(26)-C(27)-C(32)	-171.5(4)
C(31)-C(26)-C(27)-Ir(1)	-120.1(5)
C(31)-C(26)-C(27)-C(23)	178.9(4)
C(31)-C(26)-C(27)-C(32)	2.4(7)

Table 7. Hydrogen bonds for **1** [Å and °].

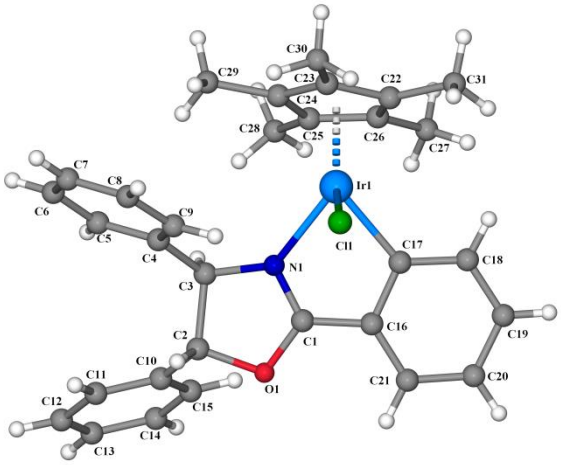
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(16)-H(16)...Cl(1)#1	0.9500	2.7100	3.642(5)	168.00
C(18)-H(18)...O(1)	0.9500	2.3900	2.765(6)	103.00

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+1

Crystallographic data of complex 2

CCDC number: CCDC 2031297

[Ir(Cl)(2*R*,3*R*-$C_{21}H_{16}ON$)($C_{10}H_{15}$)] *M* = 661.22 orange prism, 0.35 x 0.25 x 0.10 mm^3 orthorhombic, space group $P2_12_12_1$ (No. 19) *a* = 7.7357(5) Å *b* = 14.3256(9) Å *c* = 22.7397(14) Å *V* = 2520.0(3) $Å^3$ *Z* = 4 D_c = 1.743 g/cm^3 *T* = 100(2)K $2\theta_{max}$ = 56.6º 19464 reflections collected, 6247 unique Numerical absorption correction R_{int} = 0.0210 Final *GooF* = 0.748 *R1* = 0.0197 *wR2* = 0.0442 327 parameters, 1 restraint Flack parameter = 0.013(5) μ = 5.236 mm^{-1}	

Data collection, structure solution and refinement

The crystals were large, good quality orange prisms. A suitably sized crystal with well defined habit was selected for the analysis. The crystal was mounted on a glass fibre and placed in a cold stream at 100K. Single crystal X-ray data were collected on a Bruker D8 diffractometer with an APEX CCD detector, and 1.5 kW graphite monochromated Mo radiation. The detector to crystal distance was 5.985 cm. Exposure times of 10 s per frame and scan widths of 0.3º were used throughout the data collection. The faces of the crystal were indexed, and the distances of the faces from the centre of the crystal were measured for a numerical absorption correction. The data collection was performed using three ω scans with different φ values yielding data in the θ range 1.68 to 28.3° with an average completeness of 99.7%. The frames were integrated with the SAINT v7.45a (Bruker, 2005).[5] A numerical absorption correction based on the size and shape of the crystal was carried out using the program SADABS V2008-1 (Bruker, 2008)[6].

The structure was solved and refined with X-SEED,[7] a graphical interface to SHELX (Sheldrick, 2008).[8] The hydrogen atoms were located from difference maps and were refined with a mixture of constraints and restraints. In the final cycles of refinement all non-hydrogen atoms were refined anisotropically.

Table 1. Crystal data and structure refinement for **2**.

5 Bruker (2009). SAINT V7.68a, BRUKER AXS Inc., Madison, WI, USA.

6 Bruker (2008), SADABS V2008-1, BRUKER AXS Inc., Madison, WI, USA.

7 Barbour, L. J. "X-Seed – A software tool for supramolecular crystallography" *J. Supramol. Chem.* **2001**, *1*, 189-191.

8 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Identification code	**2**	
Empirical formula	C_{31} H_{31} Cl Ir N O	
Formula weight	661.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 7.7357(5) Å	α= 90°.
	b = 14.3256(9) Å	β= 90°.
	c = 22.7397(14) Å	γ = 90°.
Volume	2520.0(3) $Å^3$	
Z	4	
Density (calculated)	1.743 Mg/m^3	
Absorption coefficient	5.430 mm^{-1}	
F(000)	1304	
Crystal size	0.35 x 0.25 x 0.10 mm^3	
Theta range for data collection	1.68 to 28.28°.	
Index ranges	-9<=h<=10, -19<=k<=19, -27<=l<=30	
Reflections collected	19464	
Independent reflections	6247 [R(int) = 0.0216]	
Completeness to theta = 28.28°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.6128 and 0.2523	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6247 / 0 / 352	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0146, wR2 = 0.0332	
R indices (all data)	R1 = 0.0154, wR2 = 0.0334	
Absolute structure parameter	-0.013(4)	
Largest diff. peak and hole	0.788 and -0.396 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Ir(1)	5407(1)	588(1)	1130(1)	10(1)
Cl(1)	8237(1)	819(1)	716(1)	15(1)
O(1)	8225(2)	103(1)	2665(1)	16(1)
N(1)	6584(2)	751(1)	1957(1)	12(1)
C(1)	7430(3)	31(2)	2142(1)	13(1)
C(2)	7956(3)	1068(2)	2860(1)	15(1)
C(3)	6575(3)	1459(2)	2426(1)	12(1)
C(4)	6949(3)	2444(2)	2233(1)	13(1)
C(5)	6285(3)	3178(2)	2571(1)	17(1)
C(6)	6623(3)	4092(2)	2416(1)	19(1)
C(7)	7643(3)	4293(2)	1928(1)	20(1)
C(8)	8309(3)	3563(2)	1596(1)	19(1)
C(9)	7949(3)	2641(2)	1742(1)	15(1)
C(10)	7468(3)	1073(2)	3500(1)	15(1)
C(11)	8018(3)	1798(2)	3861(1)	17(1)
C(12)	7557(3)	1814(2)	4450(1)	19(1)
C(13)	6567(3)	1092(2)	4688(1)	22(1)
C(14)	6020(4)	373(2)	4331(1)	23(1)
C(15)	6445(3)	360(2)	3738(1)	19(1)
C(16)	7351(3)	-827(2)	1811(1)	13(1)
C(17)	6299(3)	-739(2)	1307(1)	13(1)
C(18)	6040(3)	-1558(2)	982(1)	14(1)
C(19)	6772(3)	-2402(2)	1157(1)	17(1)
C(20)	7799(3)	-2457(2)	1659(1)	18(1)
C(21)	8120(3)	-1659(2)	1986(1)	17(1)
C(22)	3748(3)	528(2)	374(1)	15(1)
C(23)	4200(3)	1509(2)	454(1)	17(1)
C(24)	3590(3)	1810(2)	1006(1)	17(1)
C(25)	2764(3)	1018(2)	1290(1)	15(1)
C(26)	2791(3)	247(2)	887(1)	15(1)
C(27)	1890(3)	-663(2)	983(1)	20(1)
C(28)	1805(3)	1072(2)	1861(1)	23(1)
C(29)	3643(4)	2788(2)	1244(1)	23(1)
C(30)	5162(4)	2087(2)	15(1)	24(1)

C(31)	3977(4)	-20(2)	-182(1)	22(1)

Table 3. Bond lengths [Å] and angles [°] for **2**.

Ir(1)-Cl(1)	2.4056(6)
Ir(1)-N(1)	2.1011(18)
Ir(1)-C(17)	2.062(2)
Ir(1)-C(22)	2.148(2)
Ir(1)-C(23)	2.232(2)
Ir(1)-C(24)	2.263(2)
Ir(1)-C(25)	2.166(2)
Ir(1)-C(26)	2.154(2)
O(1)-C(1)	1.344(3)
O(1)-C(2)	1.466(3)
N(1)-C(1)	1.292(3)
N(1)-C(3)	1.471(3)
C(1)-C(16)	1.443(3)
C(2)-C(3)	1.558(3)
C(2)-C(10)	1.505(4)
C(3)-C(4)	1.505(3)
C(4)-C(5)	1.401(3)
C(4)-C(9)	1.388(3)
C(5)-C(6)	1.381(3)
C(6)-C(7)	1.393(4)
C(7)-C(8)	1.388(4)
C(8)-C(9)	1.390(3)
C(10)-C(11)	1.391(3)
C(10)-C(15)	1.401(3)
C(11)-C(12)	1.386(4)
C(12)-C(13)	1.396(4)
C(13)-C(14)	1.377(4)
C(14)-C(15)	1.389(4)
C(16)-C(17)	1.411(3)
C(16)-C(21)	1.390(3)
C(17)-C(18)	1.401(3)
C(18)-C(19)	1.394(3)
C(19)-C(20)	1.392(4)
C(20)-C(21)	1.388(4)
C(22)-C(23)	1.461(4)
C(22)-C(26)	1.440(3)
C(22)-C(31)	1.498(4)

C(23)-C(24)	1.409(4)
C(23)-C(30)	1.495(4)
C(24)-C(25)	1.453(3)
C(24)-C(29)	1.502(4)
C(25)-C(26)	1.435(3)
C(25)-C(28)	1.499(4)
C(26)-C(27)	1.494(3)
C(2)-H(2)	1.0000
C(3)-H(3)	1.0000
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800

Cl(1)-Ir(1)-N(1)	86.58(5)
Cl(1)-Ir(1)-C(17)	84.18(7)
Cl(1)-Ir(1)-C(22)	103.65(6)
Cl(1)-Ir(1)-C(23)	91.70(6)
Cl(1)-Ir(1)-C(24)	114.20(6)
Cl(1)-Ir(1)-C(25)	152.29(7)
Cl(1)-Ir(1)-C(26)	141.80(7)
N(1)-Ir(1)-C(17)	77.48(8)
N(1)-Ir(1)-C(22)	168.42(8)
N(1)-Ir(1)-C(23)	137.08(8)
N(1)-Ir(1)-C(24)	107.16(8)
N(1)-Ir(1)-C(25)	103.16(8)
N(1)-Ir(1)-C(26)	131.43(8)
C(17)-Ir(1)-C(22)	108.57(9)
C(17)-Ir(1)-C(23)	145.02(9)
C(17)-Ir(1)-C(24)	160.99(9)
C(17)-Ir(1)-C(25)	123.06(9)
C(17)-Ir(1)-C(26)	98.90(9)
C(22)-Ir(1)-C(23)	38.90(9)
C(22)-Ir(1)-C(24)	63.91(9)
C(22)-Ir(1)-C(25)	65.26(9)
C(22)-Ir(1)-C(26)	39.11(9)
C(23)-Ir(1)-C(24)	36.54(9)
C(23)-Ir(1)-C(25)	63.40(9)
C(23)-Ir(1)-C(26)	64.18(9)
C(24)-Ir(1)-C(25)	38.23(9)
C(24)-Ir(1)-C(26)	63.90(9)
C(25)-Ir(1)-C(26)	38.81(9)
C(1)-O(1)-C(2)	105.96(18)
Ir(1)-N(1)-C(1)	114.98(16)
Ir(1)-N(1)-C(3)	136.25(14)
C(1)-N(1)-C(3)	108.46(19)
O(1)-C(1)-N(1)	117.3(2)
O(1)-C(1)-C(16)	123.2(2)
N(1)-C(1)-C(16)	119.3(2)
O(1)-C(2)-C(3)	104.17(18)
O(1)-C(2)-C(10)	109.37(19)
C(3)-C(2)-C(10)	116.08(19)
N(1)-C(3)-C(2)	102.02(18)

N(1)-C(3)-C(4)	115.75(19)
C(2)-C(3)-C(4)	112.88(19)
C(3)-C(4)-C(5)	118.3(2)
C(3)-C(4)-C(9)	122.1(2)
C(5)-C(4)-C(9)	119.6(2)
C(4)-C(5)-C(6)	120.2(2)
C(5)-C(6)-C(7)	120.5(2)
C(6)-C(7)-C(8)	119.2(2)
C(7)-C(8)-C(9)	120.9(2)
C(4)-C(9)-C(8)	119.8(2)
C(2)-C(10)-C(11)	119.9(2)
C(2)-C(10)-C(15)	120.8(2)
C(11)-C(10)-C(15)	119.3(2)
C(10)-C(11)-C(12)	120.2(2)
C(11)-C(12)-C(13)	120.2(2)
C(12)-C(13)-C(14)	119.6(2)
C(13)-C(14)-C(15)	120.6(2)
C(10)-C(15)-C(14)	119.9(2)
C(1)-C(16)-C(17)	111.9(2)
C(1)-C(16)-C(21)	124.2(2)
C(17)-C(16)-C(21)	123.8(2)
Ir(1)-C(17)-C(16)	115.66(16)
Ir(1)-C(17)-C(18)	128.43(17)
C(16)-C(17)-C(18)	115.9(2)
C(17)-C(18)-C(19)	121.1(2)
C(18)-C(19)-C(20)	121.0(2)
C(19)-C(20)-C(21)	119.7(2)
C(16)-C(21)-C(20)	118.4(2)
Ir(1)-C(22)-C(23)	73.65(14)
Ir(1)-C(22)-C(26)	70.68(13)
Ir(1)-C(22)-C(31)	128.76(18)
C(23)-C(22)-C(26)	106.9(2)
C(23)-C(22)-C(31)	125.5(2)
C(26)-C(22)-C(31)	126.8(2)
Ir(1)-C(23)-C(22)	67.45(13)
Ir(1)-C(23)-C(24)	72.93(14)
Ir(1)-C(23)-C(30)	125.41(18)
C(22)-C(23)-C(24)	109.0(2)
C(22)-C(23)-C(30)	124.7(2)

C(24)-C(23)-C(30)	126.4(2)
Ir(1)-C(24)-C(23)	70.53(14)
Ir(1)-C(24)-C(25)	67.28(13)
Ir(1)-C(24)-C(29)	131.25(18)
C(23)-C(24)-C(25)	107.7(2)
C(23)-C(24)-C(29)	126.7(2)
C(25)-C(24)-C(29)	125.4(2)
Ir(1)-C(25)-C(24)	74.49(13)
Ir(1)-C(25)-C(26)	70.15(13)
Ir(1)-C(25)-C(28)	128.84(17)
C(24)-C(25)-C(26)	108.2(2)
C(24)-C(25)-C(28)	124.2(2)
C(26)-C(25)-C(28)	126.9(2)
Ir(1)-C(26)-C(22)	70.21(13)
Ir(1)-C(26)-C(25)	71.05(13)
Ir(1)-C(26)-C(27)	126.83(17)
C(22)-C(26)-C(25)	108.0(2)
C(22)-C(26)-C(27)	127.0(2)
C(25)-C(26)-C(27)	124.9(2)
O(1)-C(2)-H(2)	109.00
C(3)-C(2)-H(2)	109.00
C(10)-C(2)-H(2)	109.00
N(1)-C(3)-H(3)	109.00
C(2)-C(3)-H(3)	109.00
C(4)-C(3)-H(3)	109.00
C(4)-C(5)-H(5)	120.00
C(6)-C(5)-H(5)	120.00
C(5)-C(6)-H(6)	120.00
C(7)-C(6)-H(6)	120.00
C(6)-C(7)-H(7)	120.00
C(8)-C(7)-H(7)	120.00
C(7)-C(8)-H(8)	120.00
C(9)-C(8)-H(8)	120.00
C(4)-C(9)-H(9)	120.00
C(8)-C(9)-H(9)	120.00
C(10)-C(11)-H(11)	120.00
C(12)-C(11)-H(11)	120.00
C(11)-C(12)-H(12)	120.00
C(13)-C(12)-H(12)	120.00

C(12)-C(13)-H(13)	120.00
C(14)-C(13)-H(13)	120.00
C(13)-C(14)-H(14)	120.00
C(15)-C(14)-H(14)	120.00
C(10)-C(15)-H(15)	120.00
C(14)-C(15)-H(15)	120.00
C(17)-C(18)-H(18)	119.00
C(19)-C(18)-H(18)	119.00
C(18)-C(19)-H(19)	120.00
C(20)-C(19)-H(19)	119.00
C(19)-C(20)-H(20)	120.00
C(21)-C(20)-H(20)	120.00
C(16)-C(21)-H(21)	121.00
C(20)-C(21)-H(21)	121.00
C(26)-C(27)-H(27A)	109.00
C(26)-C(27)-H(27B)	110.00
C(26)-C(27)-H(27C)	109.00
H(27A)-C(27)-H(27B)	109.00
H(27A)-C(27)-H(27C)	110.00
H(27B)-C(27)-H(27C)	109.00
C(25)-C(28)-H(28A)	109.00
C(25)-C(28)-H(28B)	109.00
C(25)-C(28)-H(28C)	109.00
H(28A)-C(28)-H(28B)	110.00
H(28A)-C(28)-H(28C)	110.00
H(28B)-C(28)-H(28C)	109.00
C(24)-C(29)-H(29A)	110.00
C(24)-C(29)-H(29B)	109.00
C(24)-C(29)-H(29C)	109.00
H(29A)-C(29)-H(29B)	109.00
H(29A)-C(29)-H(29C)	109.00
H(29B)-C(29)-H(29C)	110.00
C(23)-C(30)-H(30A)	109.00
C(23)-C(30)-H(30B)	109.00
C(23)-C(30)-H(30C)	109.00
H(30A)-C(30)-H(30B)	110.00
H(30A)-C(30)-H(30C)	109.00
H(30B)-C(30)-H(30C)	109.00
C(22)-C(31)-H(31A)	109.00

C(22)-C(31)-H(31B)	109.00
C(22)-C(31)-H(31C)	109.00
H(31A)-C(31)-H(31B)	109.00
H(31A)-C(31)-H(31C)	109.00
H(31B)-C(31)-H(31C)	109.00

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

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

C(31)	28(1)	25(1)	13(1)	-1(1)	-5(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2**.

	x	y	z	U(eq)
H(2)	9056	1425	2808	20(8)
H(3)	5422	1446	2624	14(6)
H(5)	5601	3047	2908	13(6)
H(6)	6157	4587	2644	13(7)
H(7)	7880	4922	1822	11(7)
H(8)	9020	3695	1266	20(8)
H(9)	8386	2147	1506	17(7)
H(11)	8711	2285	3704	20(8)
H(12)	7916	2318	4692	15(7)
H(13)	6272	1096	5093	25(9)
H(14)	5346	-118	4493	25(10)
H(15)	6042	-132	3494	21(8)
H(18)	5355	-1538	635	18(7)
H(19)	6566	-2949	932	11(7)
H(20)	8279	-3038	1776	19(8)
H(21)	8847	-1680	2323	15(7)
H(27A)	1996	-845	1396	19(10)
H(27B)	2419	-1143	734	19(11)
H(27C)	666	-598	880	13(10)
H(28A)	1448	444	1981	20(11)
H(28B)	781	1468	1813	28(9)
H(28C)	2560	1341	2163	25(8)
H(29A)	4642	3118	1080	26(8)
H(29B)	3743	2767	1674	26(9)
H(29C)	2580	3116	1135	21(8)
H(30A)	4348	2340	-274	23(8)
H(30B)	6020	1698	-186	19(10)
H(30C)	5748	2602	217	23(10)
H(31A)	3888	-688	-95	16(7)
H(31B)	5116	114	-350	21(10)
H(31C)	3076	156	-464	18(10)

Table 6. Torsion angles [°] for **2**.

Cl(1)-Ir(1)-N(1)-C(1)	-77.33(15)
Cl(1)-Ir(1)-N(1)-C(3)	109.99(19)
C(17)-Ir(1)-N(1)-C(1)	7.46(16)
C(17)-Ir(1)-N(1)-C(3)	-165.2(2)
C(23)-Ir(1)-N(1)-C(1)	-166.14(16)
C(23)-Ir(1)-N(1)-C(3)	21.2(2)
C(24)-Ir(1)-N(1)-C(1)	168.38(16)
C(24)-Ir(1)-N(1)-C(3)	-4.3(2)
C(25)-Ir(1)-N(1)-C(1)	128.93(16)
C(25)-Ir(1)-N(1)-C(3)	-43.8(2)
C(26)-Ir(1)-N(1)-C(1)	98.35(18)
C(26)-Ir(1)-N(1)-C(3)	-74.3(2)
Cl(1)-Ir(1)-C(17)-C(16)	80.31(17)
Cl(1)-Ir(1)-C(17)-C(18)	-97.5(2)
N(1)-Ir(1)-C(17)-C(16)	-7.46(17)
N(1)-Ir(1)-C(17)-C(18)	174.7(2)
C(22)-Ir(1)-C(17)-C(16)	-177.21(17)
C(22)-Ir(1)-C(17)-C(18)	5.0(2)
C(23)-Ir(1)-C(17)-C(16)	164.94(16)
C(23)-Ir(1)-C(17)-C(18)	-12.9(3)
C(25)-Ir(1)-C(17)-C(16)	-105.15(19)
C(25)-Ir(1)-C(17)-C(18)	77.0(2)
C(26)-Ir(1)-C(17)-C(16)	-138.10(18)
C(26)-Ir(1)-C(17)-C(18)	44.1(2)
Cl(1)-Ir(1)-C(22)-C(23)	-75.38(13)
Cl(1)-Ir(1)-C(22)-C(26)	169.49(12)
Cl(1)-Ir(1)-C(22)-C(31)	47.4(2)
C(17)-Ir(1)-C(22)-C(23)	-163.75(13)
C(17)-Ir(1)-C(22)-C(26)	81.12(15)
C(17)-Ir(1)-C(22)-C(31)	-41.0(2)
C(23)-Ir(1)-C(22)-C(26)	-115.1(2)
C(23)-Ir(1)-C(22)-C(31)	122.8(3)
C(24)-Ir(1)-C(22)-C(23)	35.15(13)
C(24)-Ir(1)-C(22)-C(26)	-79.98(15)
C(24)-Ir(1)-C(22)-C(31)	157.9(3)
C(25)-Ir(1)-C(22)-C(23)	77.64(14)
C(25)-Ir(1)-C(22)-C(26)	-37.49(14)

C(25)-Ir(1)-C(22)-C(31)	-159.6(3)
C(26)-Ir(1)-C(22)-C(23)	115.1(2)
C(26)-Ir(1)-C(22)-C(31)	-122.1(3)
Cl(1)-Ir(1)-C(23)-C(22)	109.83(12)
Cl(1)-Ir(1)-C(23)-C(24)	-130.45(13)
Cl(1)-Ir(1)-C(23)-C(30)	-7.6(2)
N(1)-Ir(1)-C(23)-C(22)	-163.37(12)
N(1)-Ir(1)-C(23)-C(24)	-43.65(18)
N(1)-Ir(1)-C(23)-C(30)	79.2(2)
C(17)-Ir(1)-C(23)-C(22)	27.6(2)
C(17)-Ir(1)-C(23)-C(24)	147.28(16)
C(17)-Ir(1)-C(23)-C(30)	-89.9(2)
C(22)-Ir(1)-C(23)-C(24)	119.72(19)
C(22)-Ir(1)-C(23)-C(30)	-117.4(3)
C(24)-Ir(1)-C(23)-C(22)	-119.72(19)
C(24)-Ir(1)-C(23)-C(30)	122.9(3)
C(25)-Ir(1)-C(23)-C(22)	-82.84(14)
C(25)-Ir(1)-C(23)-C(24)	36.88(14)
C(25)-Ir(1)-C(23)-C(30)	159.7(2)
C(26)-Ir(1)-C(23)-C(22)	-39.38(13)
C(26)-Ir(1)-C(23)-C(24)	80.34(15)
C(26)-Ir(1)-C(23)-C(30)	-156.8(2)
Cl(1)-Ir(1)-C(24)-C(23)	56.51(14)
Cl(1)-Ir(1)-C(24)-C(25)	176.36(12)
Cl(1)-Ir(1)-C(24)-C(29)	-65.7(2)
N(1)-Ir(1)-C(24)-C(23)	150.53(13)
N(1)-Ir(1)-C(24)-C(25)	-89.62(14)
N(1)-Ir(1)-C(24)-C(29)	28.4(3)
C(22)-Ir(1)-C(24)-C(23)	-37.39(14)
C(22)-Ir(1)-C(24)-C(25)	82.46(15)
C(22)-Ir(1)-C(24)-C(29)	-159.6(3)
C(23)-Ir(1)-C(24)-C(25)	119.9(2)
C(23)-Ir(1)-C(24)-C(29)	-122.2(3)
C(25)-Ir(1)-C(24)-C(23)	-119.9(2)
C(25)-Ir(1)-C(24)-C(29)	118.0(3)
C(26)-Ir(1)-C(24)-C(23)	-81.16(15)
C(26)-Ir(1)-C(24)-C(25)	38.69(14)
C(26)-Ir(1)-C(24)-C(29)	156.7(3)
Cl(1)-Ir(1)-C(25)-C(24)	-7.2(2)

Cl(1)-Ir(1)-C(25)-C(26)	109.23(17)
Cl(1)-Ir(1)-C(25)-C(28)	-128.9(2)
N(1)-Ir(1)-C(25)-C(24)	101.11(14)
N(1)-Ir(1)-C(25)-C(26)	-142.51(14)
N(1)-Ir(1)-C(25)-C(28)	-20.6(2)
C(17)-Ir(1)-C(25)-C(24)	-175.40(13)
C(17)-Ir(1)-C(25)-C(26)	-59.02(17)
C(17)-Ir(1)-C(25)-C(28)	62.9(2)
C(22)-Ir(1)-C(25)-C(24)	-78.60(15)
C(22)-Ir(1)-C(25)-C(26)	37.79(14)
C(22)-Ir(1)-C(25)-C(28)	159.7(3)
C(23)-Ir(1)-C(25)-C(24)	-35.28(14)
C(23)-Ir(1)-C(25)-C(26)	81.11(15)
C(23)-Ir(1)-C(25)-C(28)	-157.0(3)
C(24)-Ir(1)-C(25)-C(26)	116.4(2)
C(24)-Ir(1)-C(25)-C(28)	-121.8(3)
C(26)-Ir(1)-C(25)-C(24)	-116.4(2)
C(26)-Ir(1)-C(25)-C(28)	121.9(3)
Cl(1)-Ir(1)-C(26)-C(22)	-16.66(19)
Cl(1)-Ir(1)-C(26)-C(25)	-134.76(12)
Cl(1)-Ir(1)-C(26)-C(27)	105.3(2)
N(1)-Ir(1)-C(26)-C(22)	170.32(13)
N(1)-Ir(1)-C(26)-C(25)	52.22(18)
N(1)-Ir(1)-C(26)-C(27)	-67.8(2)
C(17)-Ir(1)-C(26)-C(22)	-108.56(15)
C(17)-Ir(1)-C(26)-C(25)	133.34(14)
C(17)-Ir(1)-C(26)-C(27)	13.4(2)
C(22)-Ir(1)-C(26)-C(25)	-118.1(2)
C(22)-Ir(1)-C(26)-C(27)	121.9(3)
C(23)-Ir(1)-C(26)-C(22)	39.17(14)
C(23)-Ir(1)-C(26)-C(25)	-78.93(15)
C(23)-Ir(1)-C(26)-C(27)	161.1(2)
C(24)-Ir(1)-C(26)-C(22)	79.98(15)
C(24)-Ir(1)-C(26)-C(25)	-38.12(14)
C(24)-Ir(1)-C(26)-C(27)	-158.1(2)
C(25)-Ir(1)-C(26)-C(22)	118.1(2)
C(25)-Ir(1)-C(26)-C(27)	-120.0(3)
C(2)-O(1)-C(1)-N(1)	-3.8(3)
C(2)-O(1)-C(1)-C(16)	-178.0(2)

C(1)-O(1)-C(2)-C(3)	11.2(2)
C(1)-O(1)-C(2)-C(10)	135.94(19)
Ir(1)-N(1)-C(1)-O(1)	179.21(15)
Ir(1)-N(1)-C(1)-C(16)	-6.4(3)
C(3)-N(1)-C(1)-O(1)	-6.1(3)
C(3)-N(1)-C(1)-C(16)	168.3(2)
Ir(1)-N(1)-C(3)-C(2)	-174.59(15)
Ir(1)-N(1)-C(3)-C(4)	-51.6(3)
C(1)-N(1)-C(3)-C(2)	12.4(2)
C(1)-N(1)-C(3)-C(4)	135.4(2)
O(1)-C(1)-C(16)-C(17)	174.1(2)
O(1)-C(1)-C(16)-C(21)	-1.8(4)
N(1)-C(1)-C(16)-C(17)	0.0(3)
N(1)-C(1)-C(16)-C(21)	-175.9(2)
O(1)-C(2)-C(3)-N(1)	-14.1(2)
O(1)-C(2)-C(3)-C(4)	-138.95(19)
C(10)-C(2)-C(3)-N(1)	-134.4(2)
C(10)-C(2)-C(3)-C(4)	100.8(2)
O(1)-C(2)-C(10)-C(11)	145.4(2)
O(1)-C(2)-C(10)-C(15)	-35.4(3)
C(3)-C(2)-C(10)-C(11)	-97.1(3)
C(3)-C(2)-C(10)-C(15)	82.1(3)
N(1)-C(3)-C(4)-C(5)	153.7(2)
N(1)-C(3)-C(4)-C(9)	-27.5(3)
C(2)-C(3)-C(4)-C(5)	-89.2(3)
C(2)-C(3)-C(4)-C(9)	89.6(3)
C(3)-C(4)-C(5)-C(6)	178.9(2)
C(9)-C(4)-C(5)-C(6)	0.1(4)
C(3)-C(4)-C(9)-C(8)	-177.6(2)
C(5)-C(4)-C(9)-C(8)	1.2(4)
C(4)-C(5)-C(6)-C(7)	-0.8(4)
C(5)-C(6)-C(7)-C(8)	0.3(4)
C(6)-C(7)-C(8)-C(9)	1.0(4)
C(7)-C(8)-C(9)-C(4)	-1.7(4)
C(2)-C(10)-C(11)-C(12)	179.2(2)
C(15)-C(10)-C(11)-C(12)	0.0(3)
C(2)-C(10)-C(15)-C(14)	179.5(2)
C(11)-C(10)-C(15)-C(14)	-1.3(4)
C(10)-C(11)-C(12)-C(13)	1.3(4)

C(11)-C(12)-C(13)-C(14)	-1.4(4)
C(12)-C(13)-C(14)-C(15)	0.1(4)
C(13)-C(14)-C(15)-C(10)	1.3(4)
C(1)-C(16)-C(17)-Ir(1)	6.5(3)
C(1)-C(16)-C(17)-C(18)	-175.4(2)
C(21)-C(16)-C(17)-Ir(1)	-177.55(19)
C(21)-C(16)-C(17)-C(18)	0.6(4)
C(1)-C(16)-C(21)-C(20)	173.5(2)
C(17)-C(16)-C(21)-C(20)	-1.9(4)
Ir(1)-C(17)-C(18)-C(19)	178.59(18)
C(16)-C(17)-C(18)-C(19)	0.8(3)
C(17)-C(18)-C(19)-C(20)	-0.7(4)
C(18)-C(19)-C(20)-C(21)	-0.8(4)
C(19)-C(20)-C(21)-C(16)	2.0(4)
Ir(1)-C(22)-C(23)-C(24)	-61.39(17)
Ir(1)-C(22)-C(23)-C(30)	118.4(2)
C(26)-C(22)-C(23)-Ir(1)	63.26(16)
C(26)-C(22)-C(23)-C(24)	1.9(3)
C(26)-C(22)-C(23)-C(30)	-178.3(2)
C(31)-C(22)-C(23)-Ir(1)	-126.3(3)
C(31)-C(22)-C(23)-C(24)	172.3(2)
C(31)-C(22)-C(23)-C(30)	-7.9(4)
Ir(1)-C(22)-C(26)-C(25)	61.32(16)
Ir(1)-C(22)-C(26)-C(27)	-121.8(2)
C(23)-C(22)-C(26)-Ir(1)	-65.25(16)
C(23)-C(22)-C(26)-C(25)	-3.9(3)
C(23)-C(22)-C(26)-C(27)	173.0(2)
C(31)-C(22)-C(26)-Ir(1)	124.5(3)
C(31)-C(22)-C(26)-C(25)	-174.2(2)
C(31)-C(22)-C(26)-C(27)	2.7(4)
Ir(1)-C(23)-C(24)-C(25)	-57.12(16)
Ir(1)-C(23)-C(24)-C(29)	127.5(3)
C(22)-C(23)-C(24)-Ir(1)	58.01(16)
C(22)-C(23)-C(24)-C(25)	0.9(3)
C(22)-C(23)-C(24)-C(29)	-174.5(2)
C(30)-C(23)-C(24)-Ir(1)	-121.8(3)
C(30)-C(23)-C(24)-C(25)	-178.9(2)
C(30)-C(23)-C(24)-C(29)	5.7(4)
Ir(1)-C(24)-C(25)-C(26)	-62.48(16)

Ir(1)-C(24)-C(25)-C(28)	126.8(2)
C(23)-C(24)-C(25)-Ir(1)	59.13(17)
C(23)-C(24)-C(25)-C(26)	-3.4(3)
C(23)-C(24)-C(25)-C(28)	-174.1(2)
C(29)-C(24)-C(25)-Ir(1)	-125.4(2)
C(29)-C(24)-C(25)-C(26)	172.1(2)
C(29)-C(24)-C(25)-C(28)	1.4(4)
Ir(1)-C(25)-C(26)-C(22)	-60.79(16)
Ir(1)-C(25)-C(26)-C(27)	122.2(2)
C(24)-C(25)-C(26)-Ir(1)	65.31(16)
C(24)-C(25)-C(26)-C(22)	4.5(3)
C(24)-C(25)-C(26)-C(27)	-172.5(2)
C(28)-C(25)-C(26)-Ir(1)	-124.2(2)
C(28)-C(25)-C(26)-C(22)	175.0(2)
C(28)-C(25)-C(26)-C(27)	-2.0(4)

Table 7. Hydrogen bonds for **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9)...Cl(1)	0.9500	2.6200	3.506(3)	156.00
C(27)-H(27C)...Cl(1)#1	0.9800	2.7900	3.586(2)	139.00

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z

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