

## Supporting Information

### **Phosphine-free Chiral Iridium Catalysts for Asymmetric Catalytic Hydrogenation of Simple Ketones**

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**Table S1.** Selected Crystallographic data for **2e**, **2c**, **2d**, **1a** and **1b**

	<b>2e</b>	<b>2c</b>	<b>2d</b>	<b>1a</b>	<b>1b</b>
Empirical formula	C <sub>24</sub> H <sub>31</sub> Ir N <sub>2</sub> O	C <sub>38</sub> H <sub>48</sub> Ir <sub>2</sub> N <sub>2</sub> O	C <sub>32</sub> H <sub>44</sub> Ir <sub>2</sub> N <sub>2</sub> O	C <sub>28</sub> H <sub>42</sub> Ir <sub>2</sub> N <sub>2</sub> O	C <sub>27</sub> H <sub>40</sub> Ir <sub>2</sub> N <sub>2</sub> O
Formula weight	555.71	933.18	857.09	807.04	793.01
Temperature	133(2) K	133(2) K	133(2) K	133(2) K	133(2) K
Wavelength	0.71069 Å	0.71069 Å	0.71069 Å	0.71069 Å	0.71069 Å
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	P2(1)2(1)2(1)	C2/c	P2(1)	P2(1)2(1)2(1)	P2(1)
Unit cell dimensions	a = 7.2300(2) Å b = 13.5480(5) c = 22.4250(7) β = 90.00°	a = 34.9260(6) Å b = 10.3380 (3)Å c = 23.4380(4) Å β = 131.149(3)°	a = 9.5720(4) Å b = 10.4280(4)Å c = 14.4780(7)Å β = 105.083(4) °	a = 23.1230(11) Å b = 9.6330(4) Å c = 11.8500(4) Å β = 90.00 °	a = 11.7050(5) Å b = 9.4170(4)Å c = 12.4450(5)Å β = 113.115(3)°
Volume	2196.57(12) Å <sup>3</sup>	6372.4(4) Å <sup>3</sup>	1395.36(10) Å <sup>3</sup>	2639.52(19) Å <sup>3</sup>	1261.64(9) Å <sup>3</sup>
Z	4	8	2	4	2
Density (g/cm <sup>3</sup> )	1.680	1.945	2.040	2.031	2.087
μ	6.094	8.379	9.556	10.096	10.559
F(000)	1096	3616	824	1544	756
Crystal size (mm <sup>3</sup> )	0.41 x 0.32 x 0.29	0.26 x 0.11x 0.09	0.21x 0.15x 0.12	0.23 x 0.21 x 0.09	0.19 x 0.19 x 0.11
Reflections collected	4141	6021	5276	4442	4712
Goodness-of-fit on F <sup>2</sup>	0.927	0.963	0.970	0.954	1.027
Final R indices [I > 2σ(I)]	R1 = 0.0208 wR2 = 0.0440	R1 = 0.0438, wR2 = 0.1068	R1 = 0.0615 , wR2 = 0.1541	R1 = 0.0399, wR2 = 0.0848	R1 = 0.0263, wR2 = 0.0600
R indices (all data)	R1 = 0.0231, wR2 = 0.0443	R1 = 0.0533, wR2 = 0.1106	R1 = 0.0720 , wR2 = 0.1609	R1 = 0.0497, wR2 = 0.0878	R1 = 0.0284, wR2 = 0.0605

**Table S2.** Asymmetric Hydrogenation of  $\alpha$ -Methylpropiophenone Catalyzed by binuclear Iridium Complexes **1a,1a** and **2c,2d**

Entry	Pre-catalyst <sup>a</sup>	Acetone/ $\alpha$ -Methylpropiophenone	Conv.[%] <sup>b</sup>	ee[%] <sup>b</sup>
1	1a	-	24	11
2	1a	2:1	40	24
3	1b	-	16	7
4	1b	2:1	23	11
5	2c	-	20	5
6	2c	2:1	35	8
7	2d	-	12	nil
8	2d	2:1	16	2

<sup>a</sup> Reaction conditions : 0.05 mol% **pre-catalyst**; <sup>b</sup> Conversion and ee were determined by GC.