Supplementary Materials: Iridium-Catalyzed Asymmetric Ring-Opening of Oxabenzonorbornadienes with *N*-Substituted Piperazine Nucleophiles

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1. Crystal Structure and Data of (1*S*,2*S*)-2-[4-(4-fluoro-phenyl)-piperazin-1-yl]-1,2-dihydronaphthalen-1-ol (2i) (CCDC 1415336)



Figure S1. Crystal structure of 2i.

Identification Code	2i
Empirical formula	C20H21FN2O
Formula weight	324.39
Temperature	296 (2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
	<i>a</i> = 9.572 (3) A alpha = 90 deg.
Unit cell dimensions	<i>b</i> = 10.034 (3) A beta = 90 deg.
	<i>c</i> = 17.732 (5) A gamma = 90 deg.
Volume	1703.1 (9) A ³
Z, Calculated density	4, 1.265 Mg/m ³
Absorption coefficient	0.086 mm ⁻¹
F (000)	688
Crystal size	0.22 × 0.20 × 0.18 mm
Theta range for data collection	2.30 to 26.40 deg.
Limiting indices	$-11 \le 11, -12 \le k \le 12, -22 \le l \le 11$
Reflections collected/unique	9291/3432 [R(int) = 0.0357]
Completeness to theta = 26.40	98.5%
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	3432/1/218
Goodness-of-fit on F ²	1.037
Final R indices [I > 2sigma(I)]	R1 = 0.0583, wR2 = 0.1588
R indices (all data)	R1 = 0.1067, wR2 = 0.1882
Absolute structure parameter	1 (2)
Largest diff. peak and hole	0.357 and −0.205 e·A ⁻³

Table S1. Crystal data and structure refinement for 2i.

x	у	Z	U (eq)	
C (1)	-816 (5)	6098 (4)	5364 (2)	82 (1)
C (2)	413 (5)	6733 (4)	5210 (2)	83 (1)
C (3)	845 (4)	6884 (4)	4470 (2)	76 (1)
C (4)	21 (4)	6413 (3)	3877 (2)	65 (1)
C (5)	-1244 (4)	5778 (3)	4036 (2)	67 (1)
C (6)	-1654 (4)	5616 (4)	4786 (2)	78 (1)
C (7)	482 (4)	6457 (4)	3074 (2)	77 (1)
C (8)	-675 (4)	6622 (4)	2530 (2)	79 (1)
C (9)	-1806 (4)	5605 (4)	2699 (2)	75 (1)
C (10)	-2083 (4)	5292 (4)	3404 (2)	76 (1)
C (11)	309 (4)	5414 (4)	1437 (2)	86 (1)
C (12)	952 (4)	5605 (4)	663 (2)	84 (1)
C (13)	-530 (5)	7514 (4)	481 (2)	86 (1)
C (14)	-1147 (5)	7275 (4)	1241 (2)	89 (1)
C (15)	300 (3)	6263 (3)	-625 (2)	61 (1)
C (16)	860 (4)	5116 (4)	-963 (2)	71 (1)
C (17)	1098 (4)	5039 (5)	-1726 (2)	86 (1)
C (18)	762 (5)	6082 (6)	-2162 (2)	93 (1)
C (19)	216 (4)	7238 (5)	-1873 (2)	98 (1)
C (20)	7 (4)	7331 (4)	-1098 (2)	77 (1)
F (1)	1000 (4)	6028 (4)	-2928 (1)	150 (1)
N (1)	-144 (3)	6681 (3)	1753 (2)	77 (1)
N (2)	-23 (3)	6259 (3)	147 (2)	62 (1)
O (1)	1578 (2)	7409 (3)	2966 (1)	80 (1)

Table S2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters $(A^2 \times 10^3)$ for **2i**. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Symmetry transformations used to generate equivalent atoms:

Bonding Lengthes	Å
C(1)-C(2)	1.365 (6)
C(1)-C(6)	1.389 (5)
C(2)-C(3)	1.384 (5)
C(3)-C(4)	1.397 (5)
C(4)-C(5)	1.397 (5)
C(4)-C(7)	1.492 (5)
C(5)-C(6)	1.396 (5)
C(5)-C(10)	1.462 (5)
C(7)-O(1)	1.432 (4)
C(7)-C(8)	1.478 (5)
C(8)-N(1)	1.469 (4)
C(8)-C(9)	1.518 (5)
C(9)-C(10)	1.316 (5)
C(11)-N(1)	1.455 (5)
C(11)-C(12)	1.515 (5)
C(12)-N(2)	1.462 (4)
C(13)-N(2)	1.474 (5)
C(13)-C(14)	1.491 (5)
C(14)-N(1)	1.449 (5)

Table S3. Bond lengths [Å] and angles [deg] for 2i.

Table S3. Cont.

Bonding Lengthes	Å
C(15)-C(20)	1.390 (5)
C(15)-N(2)	1.403 (4)
C(15)-C(16)	1.404 (5)
C(16)-C(17)	1.375 (5)
C(17)-C(18)	1.340 (6)
C(18)-C(19)	1.372 (6)
C(18)-F(1)	1.378 (5)
C(19)-C(20)	1.392 (5)
C(2)-C(1)-C(6)	120.8 (4)
C(1)-C(2)-C(3)	119.9 (4)
C(2)-C(3)-C(4)	120.5(4)
C(3)-C(4)-C(5)	119.5 (3)
C(3)-C(4)-C(7)	122.8 (3)
C(5)-C(4)-C(7)	117.5(3)
C(6)-C(5)-C(4)	119.2 (3)
C(6)- $C(5)$ - $C(10)$	1225(3)
C(4)- $C(5)$ - $C(10)$	122.0(3)
C(1) - C(6) - C(5)	120.0(4)
O(1) - C(7) - C(8)	112.8 (3)
O(1) - C(7) - C(4)	111 4 (3)
C(8)-C(7)-C(4)	113.9 (3)
N(1)-C(8)-C(7)	110.9(3)
N(1) - C(8) - C(9)	117.3 (3)
C(7)-C(8)-C(9)	109.3 (3)
C(10)-C(9)-C(8)	119 4 (3)
C(9)- $C(10)$ - $C(5)$	122 6 (3)
N(1)-C(11)-C(12)	111.1 (3)
N(2)-C(12)-C(11)	111.4 (3)
N(2)-C(13)-C(14)	110.8 (3)
N(1)-C(14)-C(13)	111.7 (3)
C(20)-C(15)-N(2)	123.2 (3)
C(20)-C(15)-C(16)	116.8 (3)
N(2)-C(15)-C(16)	119.9 (3)
C(17)- $C(16)$ - $C(15)$	122.0 (4)
C(18)-C(17)-C(16)	119.0 (4)
C(17)- $C(18)$ - $C(19)$	122.4 (4)
C(17)-C(18)-F(1)	119.9 (5)
C(19)-C(18)-F(1)	117.7 (5)
C(18)-C(19)-C(20)	118.7(4)
C(19)-C(20)-C(15)	121 1 (4)
C(14)-N(1)-C(11)	1084(3)
C(14)-N(1)-C(8)	112.0 (3)
C(11)-N(1)-C(8)	115.4 (3)
C(15)-N(2)-C(12)	118.1 (3)
C(15)-N(2)-C(13)	117.5 (3)
C(12)-N(2)-C(13)	110.0 (3)

Symmetry transformations used to generate equivalent atoms:

U11	U22	U33	U23	U13	U12	
C (1)	97 (3)	85 (3)	66 (2)	-1 (2)	7 (2)	17 (2)
C (2)	100 (3)	78 (2)	71 (3)	-9 (2)	-14 (2)	11 (2)
C (3)	75 (2)	73 (2)	79 (3)	-1 (2)	-6 (2)	-6 (2)
C (4)	69 (2)	60 (2)	65 (2)	-1 (2)	-4 (2)	-2 (2)
C (5)	70 (2)	61 (2)	70 (2)	0 (2)	6 (2)	1 (2)
C (6)	79 (2)	71 (2)	85 (3)	3 (2)	9 (2)	6 (2)
C (7)	68 (2)	89 (3)	74 (2)	4 (2)	1 (2)	-20 (2)
C (8)	77 (2)	86 (3)	76 (2)	1 (2)	-2 (2)	-1 (2)
C (9)	67 (2)	80 (2)	77 (2)	-9 (2)	-1 (2)	-15 (2)
C (10)	58 (2)	83 (3)	86 (3)	-7 (2)	3 (2)	-12 (2)
C (11)	94 (3)	78 (2)	86 (2)	25 (2)	5 (2)	17 (2)
C (12)	90 (3)	90 (3)	73 (2)	18 (2)	0 (2)	13 (2)
C (13)	111 (3)	73 (2)	75 (2)	0 (2)	-4 (2)	15 (2)
C (14)	105 (3)	78 (3)	85 (3)	-9 (2)	-2 (2)	13 (2)
C (15)	55 (2)	65 (2)	64 (2)	5 (2)	-6 (2)	-5 (2)
C (16)	69 (2)	70 (2)	74 (2)	-6 (2)	-8 (2)	-2 (2)
C (17)	68 (2)	101 (3)	89 (3)	-21 (3)	-4 (2)	-7 (2)
C (18)	84 (3)	127 (4)	67 (3)	-5 (3)	2 (2)	-1 (3)
C (19)	84 (3)	122 (4)	87 (3)	39 (3)	-13 (2)	-7 (3)
C (20)	79 (2)	72 (2)	80 (3)	12 (2)	-6 (2)	-1 (2)
F (1)	153 (2)	229 (4)	69 (2)	0 (2)	3 (2)	-5 (3)
N (1)	78 (2)	77 (2)	75 (2)	6 (2)	2 (2)	-9 (2)
N (2)	64 (2)	56 (2)	67 (2)	3 (1)	-2 (1)	4 (1)
O (1)	79 (1)	79 (2)	81 (2)	10(1)	-2 (1)	-25 (1)

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

Table S5. Hydrogen coordinates	×104) and isotropic displacement	parameters ($A^2 \times 10^3$) for 2i .

x	у	Z	U (eq)	
H (1)	-1095	5988	5863	99
H (2)	959	7063	5601	99
H (3)	1690	7303	4367	91
H (6)	-2488	5185	4898	94
H (7)	893	5583	2967	92
H (8)	-1086	7498	2633	95
H (9)	-2300	5206	2308	90
H (10)	-2842	4741	3505	91
H (11A)	-485	4818	1399	103
H (11B)	990	5008	1770	103
H (12A)	1791	6140	708	101
H (12B)	1214	4744	459	101
H (13A)	-1229	7907	153	104
H (13B)	240	8138	525	104
H (14A)	-1470	8114	1449	107
H (14B)	-1948	6688	1192	107
H (16)	1077	4387	-661	85
H (17)	1486	4275	-1937	103
H (19)	-11	7946	-2189	117
H (20)	-333	8120	-894	92
H (1A)	1548	7695	2533	119

2. Copies of ¹H- and ¹³C-NMR Spectra of Compounds 1a–1b, 2a–2x and 3a–3i



Figure S2. ¹H-NMR Spectra of Compound 1a.



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

Figure S3. ¹³C-NMR Spectra of Compound 1a.











Figure S10. ¹H-NMR Spectra of Compound 2c.



Figure S13. ¹³C-NMR Spectra of Compound 2d.









Figure S17. ¹³C-NMR Spectra of Compound 2f.







20

PPM







Figure S23. ¹³C-NMR Spectra of Compound 2i.



Figure S24. ¹H-NMR Spectra of Compound 2j.







Figure S26. ¹H-NMR Spectra of Compound 2k.



Figure S28. ¹H-NMR Spectra of Compound 2l.



Figure S31. ¹³C-NMR Spectra of Compound 2m.







Figure S35. ¹³C-NMR Spectra of Compound 20.



Figure S36. ¹H-NMR Spectra of Compound 2p.







Figure S38. ¹H-NMR Spectra of Compound 2q.



Figure S39. ¹³C-NMR Spectra of Compound 2q.



Figure S40. ¹H-NMR Spectra of Compound 2r.











Figure S44. 1H-NMR Spectra of Compound 2t.



Figure S45. ¹³C-NMR Spectra of Compound 2t.



Figure S46. ¹H-NMR Spectra of Compound 2u.



Figure S47. ¹³C-NMR Spectra of Compound 2u.



Figure S48. ¹H-NMR Spectra of Compound 2v.















Figure S55. ¹³C-NMR Spectra of Compound 3a.



Figure S56. ¹H-NMR Spectra of Compound 3b.



Figure S57. ¹³C-NMR Spectra of Compound 3b.



Figure S58. ¹H-NMR Spectra of Compound 3c.







Figure S62. ¹H-NMR Spectra of Compound 3e.



Figure S63. ¹³C-NMR Spectra of Compound 3e.











Figure S68. ¹H-NMR Spectra of Compound 3h.



Figure S69. ¹³C-NMR Spectra of Compound 3h.







Figure S71. ¹³C-NMR Spectra of Compound 3i.

3. The Parts of Copies of HPLC of 2a, 2c, 2g–2h, 2i–2k, 2m–2o, 2q–2r, 2u–2x, and 3b



Figure S72. HPLC trace for racemic-2a.



Peak No.	Time (min)	Area (mV × s)	Area (%)
1	18.983	30,127,222	75.35
2	20.858	8,637,715	21.6

Figure S73	. HPLC	trace for	enantien	riched- 2a	(ee =	54%).
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Figure S74. HPLC trace for racemic-2c.



Figure S75. HPLC trace for enantienriched-2c (*ee* = 67%).



Figure 76. HPLC trace for racemic-2g.



Figure S77.	HPLC trace	for enantien:	riched- 2g	(ee = 50%).



Figure S78. HPLC trace for racemic-2h.



Figure S79. HPLC trace for enantienriched-**2h** (*ee* = 54%).



Figure S80. HPLC trace for racemic-2j.



1	32.506	27,526,003	71.29
2	36.390	8,157,145	21.13

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Figure S81. HPLC trace for enantienriched-**2***j* (*ee* = 54%).



Figure S82. HPLC trace for racemic-2k.



Реак No.	l'ime (min)	Area (mv × s)	Area (%)
1	13.750	22,130,480	66.58
2	14.269	10,407,103	31.31

Figure S83. HPLC trace for enantienriched-2k (ee =	= 36%).
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Figure S84. HPLC trace for racemic-2m.



Figure S85.	HPLC trace	for enantienri	ched-2m	(ee = 47%).



Figure S86. HPLC trace for racemic-2n.



Figure S87. HPLC trace for enantienriched-**2n** (*ee* = 54%).



Figure S88. HPLC trace for racemic-20.



Figure S89. HPLC trace for enantienriched-20 (*ee* = 58%).



reak no.	Time (min)	Area (m v × s)	Area (%)
1	21.709	9,459,897	43.64
2	27.107	9,146,611	42.2

Figure S90. HPLC trace for racemic-2q.



Figure S91. HPLC trace for enantienriched-**2q** (*ee* = 57%).



Figure S92. HPLC trace for racemic-2r.



Figure S93. HPLC trace for enantienriched-2r (ee	e = 59%).
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Figure S94. HPLC trace for racemic-2u.



Figure S95. HPLC trace for enantienriched-**2u** (*ee* = 51%).



Figure S96. HPLC trace for racemic-2v.

4,108,356

39.23

37.174

2



Figure	S97.	HPLC	trace	for	enantie	nrich	ed-2v	(ee =	54%).
riguie	397.	TH LC	trace	101	enanne	ennen	leu-2v	(<i>ee</i> –	54 /0).



Figure S98. HPLC trace for racemic-2w.



I Eak INU.	Time (mm)	Alea ($\Pi V \land S$)	Alea (70)
1	13.679	11,962,356	75.53
2	15.493	3,336,627	21.07

Figure S9	9. HPLC	trace for	enantienri	ched- 2w	(ee = 56%).
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Figure S100. HPLC trace for racemic-2x.



Figure S101. HPLC trace for enantienriched-**2x** (*ee* = 39%).



Figure S102. HPLC trace for racemic-3b.



Figure S103. HPLC trace for enantienriched-**3b** (*ee* = 49%).