

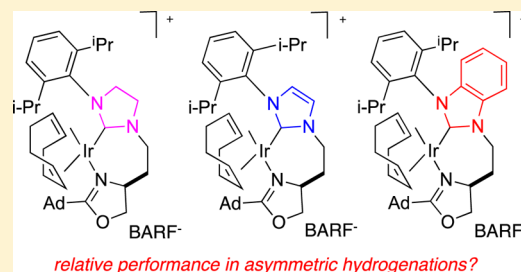
A Comparison between Oxazoline-imidazolinylidene, -imidazolylidene, -benzimidazolylidene Hydrogenation Catalysts

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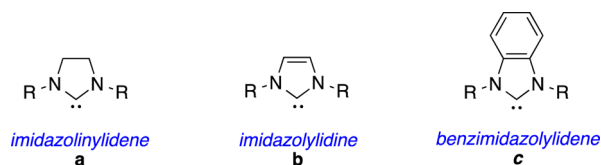
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S Supporting Information

ABSTRACT: Imidazolinylidene, imidazolylidene, benzimidazolylidene complexes **1a–c** were prepared and tested in asymmetric hydrogenations of a series of largely unfunctionalized alkenes. Similarities and differences in the catalytic performance of these complexes were rationalized in terms of the predicted mechanisms of these reactions, and their relative tendencies to generate protons under the hydrogenation conditions.



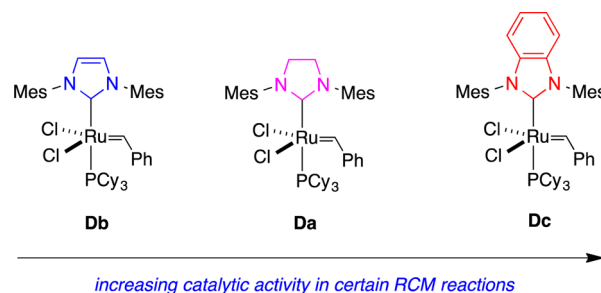
Stereoelectronic variation is to be expected within the series of *N*-heterocyclic carbene ligands **a–c**.^{1,2} With respect to size, even members of this series with the same *N*-aryl substituents may have various steric influences because they have different flexibilities; for instance, the planar systems **b** and **c** are less flexible than the saturated one **a**.¹ Flexibility in the ligands can also indirectly affect their electron donating properties. Direct donation of π -electrons from the *N*-aryl substituents to the metal in these systems can be significant,^{3,4} and it is bound to be orientation dependent. Consequently, differences in the carbene core that perturb the preferred orientations of the aryl groups also modulate the electron densities they donate to the metal.⁵ Moreover, the saturated imidazolinylidene **a** is the only member of this series that is not aromatic, and this has ill-defined impacts on its electron donating properties relative to the other two.⁶



Several strategies have been devised to gauge stereoelectronic differences in the series of ligands **a–c**. These approaches consider dimerization of the parent carbene,⁷ IR and Raman spectra⁸ of CO ligands in the same complex (sometimes interpreted in terms of the Tolman electronic parameter),⁹ electrochemical studies,⁴ and theoretical approaches.¹⁰ Overall, the most general conclusions from these studies are that all three ligands are stronger σ -donors than any phosphine, but electronic effects within the series tend to be small.^{1,10} For instance, carbonyl complexes containing ligands **a–c** may have IR absorbance within 3 cm^{-1} of each other, while others have almost identical REDOX potentials.⁴

Even if electronic variability in the series **a–c** is small, and the *N*-aryl groups are identical, substitution of one of these ligands

for another can have significant effects on *catalytic* performance. Evidence for this assertion comes from the Grubbs' metathesis catalysts. Early work had shown that ring closing metatheses mediated by the now widely appreciated Grubbs type II catalyst **Da** tended to proceed with superior reaction rates and overall conversions relative to **Db**.¹¹ Delaude and co-workers subsequently found that for favorable substrates the benzimidazolylidene complex **Dc** could give *faster* initial rates for ring-closing metathesis than **Da**.¹²

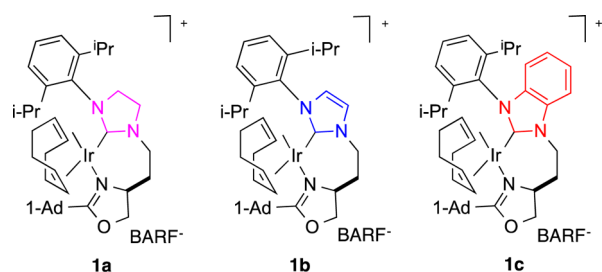


In total, the considerations above indicate there is no reliable way to extrapolate free ligand properties in the series **a–c** to the catalytic performance of complexes, and that even small stereoelectronic differences in the carbenes could have significant effects. Consequently, we were curious to test the series **1a–c** that includes our carbene catalyst **1b**. Complex **1b** and similar chiral analogs of Crabtree's catalyst are suitable for hydrogenation of trisubstituted alkenes without functional groups that typically coordinate to the metal in these complexes (CFGs).^{13–15} Consequently, this *Note* describes syntheses of the new complexes **1a** and **c** and use of these to hydrogenate some largely unfunctionalized alkenes. Enantioselectivities were the critical end-point parameter that we wished to measure

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because the overriding application of **1b** is in asymmetric catalysis.



Imidazole **E**, required to make catalyst **1a**, is known and was prepared via the literature procedure.¹⁶ Benzimidazole **F** is also a known compound,¹⁷ but we synthesized it using a different method, *i.e.* reaction of the corresponding 1,2-benzenediamine with trimethyl orthoformate under acidic conditions as indicated in the Experimental Section. Scheme 1 shows how these two nucleophiles were reacted with the appropriate iodo-oxazoline¹⁸ to give the corresponding carbene precursors that were converted to the iridium complexes under identical conditions. Complex **1a** is yellow, whereas **1b** and **c** are orange. ¹³C NMR chemical shifts of the coordinated carbene in this series **1a–c** are very similar: 178.4, 179.5, and 187.2 ppm, respectively.

Scheme 1

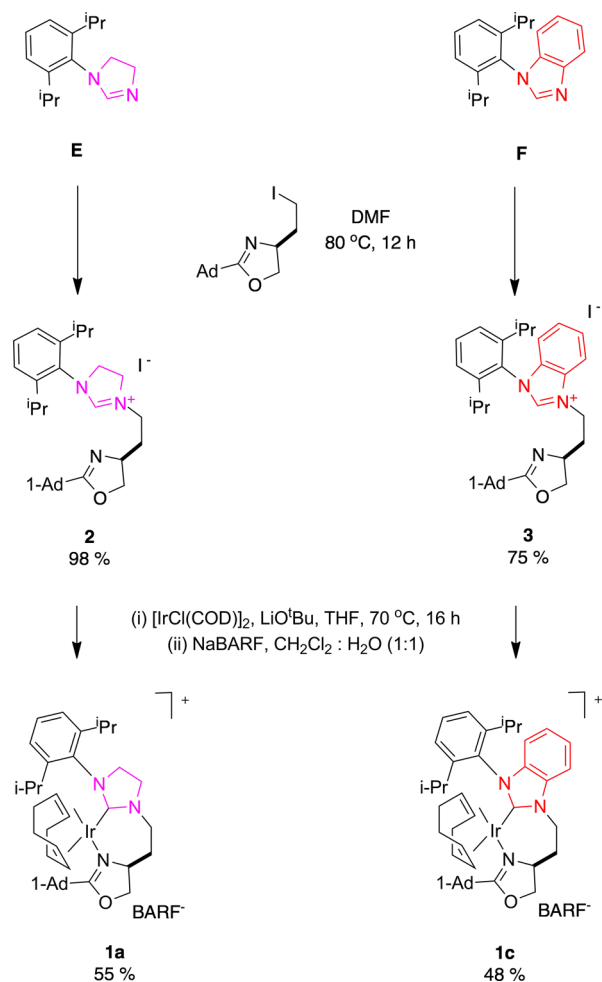


Table 1. Stereoselective Hydrogenations Using the Featured Catalysts

Entry	alkenes	alkanes		
		Stereoselectivity ^a		
		1a	1b	1c
1		93	99	95
2		12	5	15
3		57	63	55
4		77	83	75
5		70	65	66
6		93	96	95
7		91	93	93
8		94	95	94
9 ^{b,c}		49:1.0	49:1.0	48:1.0

^aEnantioselectivity unless it stated. ^bDiastereoselectivity. ^cReactions using 2 mol % of **1a–c**.

Table 1 shows comparative data for a series of hydrogenations using catalysts **1a–1c**. The stilbene derivative in entry 1 was included because it is the most widely studied substrate for asymmetric hydrogenations using chiral Crabtree's catalyst analogs.¹³ The endocyclic alkene in entry 2 was chosen because substrates of that kind are not reduced with high stereoselectivities using catalyst **1b**. The other substrates shown in Table 1 are relevant to our studies on hydrogenations to form fragments of polyketide-derived natural products and other useful chirons.^{19,20}

All the experiments summarized in Table 1 gave 100% conversions under the conditions indicated. Stereoselectivities in these reactions were almost identical in almost every case; variation of the catalyst carbene feature had no significant effect.

We have previously reported evidence that the carbene-containing catalyst **1b** is significantly less prone to generate protons in hydrogenation reactions than corresponding complexes that have phosphorus-based ligands in place of the carbene.²¹ Calculations in that work indicated that the carbene complexes gave intermediates that are of the order of 10⁷ times less acidic than similar P-containing complexes.²¹ For the current study, similar calculations were undertaken for the series **1a–c**, and the data obtained are outlined in Table 2. Relative σ -donor and π -acceptor properties deduced from similar calculations are also shown. In the event, calculated pK_a

Table 2. σ -Donor and π -Acceptor Potentials and pK_a of Complexes 1a–c

	σ -donor (eV)	π -acceptor (eV)	pK_a complex 1
, a	-4.690	-0.119	18.0
, b	-4.865	0.063	17.4
, c	-5.080	-1.337	15.8

values for the complexes are within a 2.2 unit range. Similarly, the calculated σ -donor and π -acceptor potentials for the free carbenes were within relatively tight ranges: ± 0.2 and ± 0.7 eV, respectively. These observations are consistent with Figure 1, which shows the HOMOs from these calculations are all relatively similar in shape.

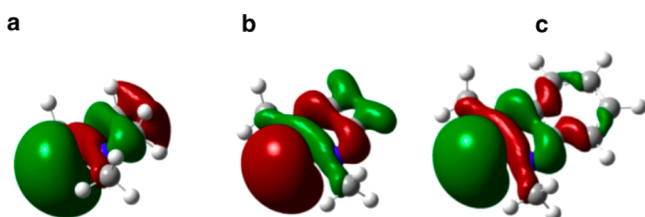


Figure 1. HOMO of carbene electron from imidazoline (a), imidazole (b), and benzimidazole (c).

Experimental validation of the calculated pK_a trends discussed above was obtained by performing the hydrogenation shown in Figure 2 and then adding a pH indicator. Whereas, we have shown previously that N,P-complexes tend to give red solutions (similar to the control in Figure 2a), all three complexes **1a–c** gave light yellow solutions indicating the reaction medium is not acidic.

Our hypothesis regarding the mechanism of hydrogenation with **1b**, based on calculations, indicated²² a strong *trans*-effect orients the alkene ligand opposite to the carbene in intermediate **G** as indicated in Figure 3. These calculations also indicate transformation of **G** into the transition state **H** was predicted to be the rate-limiting step in the catalytic cycle. We propose all the carbene ligands (abbreviated to C in Figure 3) maintain that strong *trans*-effect in the catalysis, and there are insufficient steric differences to perturb the enantioselectivities.

One of the referees for this paper suggested calculations should be performed to explain the relatively poor performance for catalyst **1b** with endocyclic substrates, as in entry 2 of Table 1. Our calculations corresponding to use of catalyst **1b** in entry 1, as reported previously, involved evaluating the energies of three species. Specifically these were (i) the intermediate **G** in Figure 3 before the turnover limiting step; (ii) the transition state that relates **G** and **H**; and (iii) the energy of the intermediate **H** after the turnover limiting step. These studies proved that the energy of that intermediate **H** is closely related

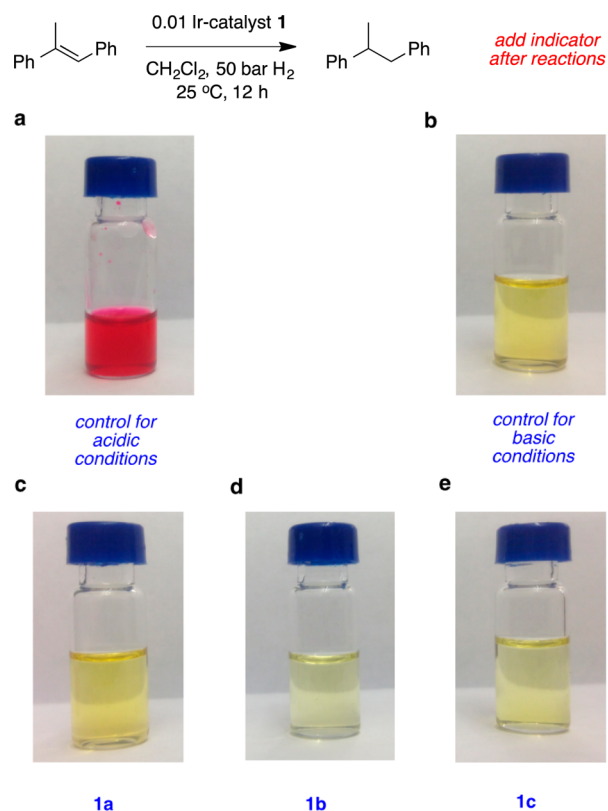


Figure 2. Hydrogenation with catalyst **1**: (a) Methyl red with acetic acid in CH_2Cl_2 (control for acid); (b) methyl red with Et_3N in CH_2Cl_2 (control for base); (c) **1a** with methyl red; (d) **1b** with methyl red; and (e) **1c** with methyl red.

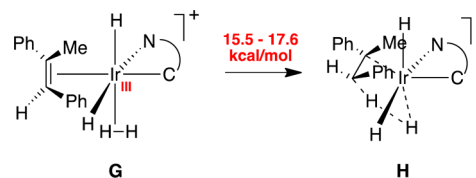


Figure 3. Transformation of **G** to **H** is predicted to be rate-limiting in the catalytic hydrogenation of *trans*-1,2-diphenylpropene mediated by complex **1b**.

to the transition state energy.²² Those studies also showed four pathways should be considered. These are two for each enantioface of the alkene and, for each enantioface, pathways corresponding to two different π -complex rotamers related by 180° rotation around the metal to π -bond in the starting intermediates **G**. These correspond to putting each of the two inequivalent phenyl groups of the complexed alkene between the smaller pocket between the bulky 2,6-di-isopropylphenyl and adamantyl substituents. The conclusion from this study is that the pathway from intermediate **G** to **H** (based on the relative energies of these two intermediates) for hydrogenation of the alkene in Table 1, entry 1, to give the (*S*)-product was 5.91 kcal/mol more stable than any of the two pathways leading to the (*R*)-enantiomer.

In the current study, calculations were performed using exactly the same procedures as before to assess the energies of the same four types of pathways for the endocyclic substrate in entry 2. Figure 4 shows two of the four key intermediates (analogous to **H**) and their relative energy differences from the starting π -complexes (analogous to **G**); all the values are

normalized relative to the most favorable pathway identified. That most favorable pathway corresponds to production of the (*R*)-enantiomer, but there is another calculated to be only 0.21 kcal/mol higher in energy that leads to the (*S*)-enantiomer. Thus these calculations explain the poor enantioselectivities for endocyclic alkenes like **J**: in both intermediates shown the edge-fused ring system stacks above the (*i*Pr)₂C₆H₃ ligand aryl substituent.

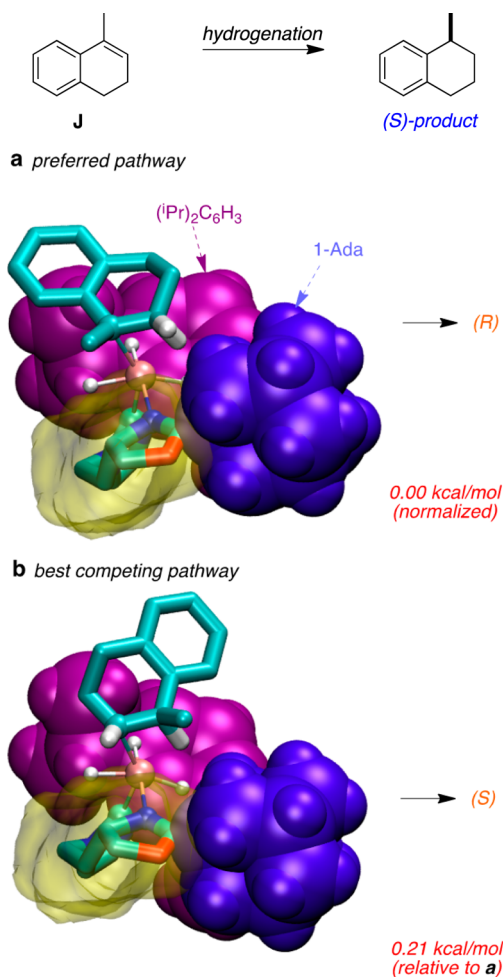


Figure 4. Intermediates in the two most preferred pathways for hydrogenation of substrate **J** leading to different enantiomers have the same energies (within error limits for these calculations).

There are two conclusions from this study. First, though we cannot rule out the possibility that differences will emerge for catalytic reactions mediated by complexes **1a–c**, there are negligible differences between them in the asymmetric hydrogenation reactions shown in Table 1. Second, poor enantioselectivities in the hydrogenations of endocyclic substrates like **J** seem to arise because hydrogenation pathways for the two enantiofaces of this substrate proceed through energetically similar turnover limiting steps as illustrated in Figure 4.

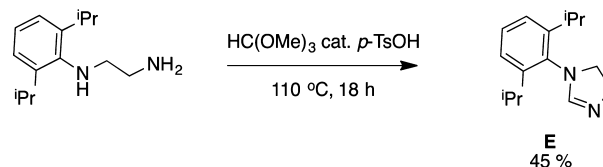
EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an inert atmosphere (nitrogen, or argon where stated) with dry solvents under anhydrous conditions. Glassware for anhydrous reactions was dried in an oven at 140 °C for a minimum of 6 h prior to use. Dry solvents

were obtained by passing the previously degassed solvents through activated alumina columns. Reagents were purchased at a high commercial quality (typically 97% or higher) and used without further purification, unless otherwise stated. High field NMR spectra were recorded at 300 MHz for ¹H and 75 MHz for ¹³C. Chemical shifts of ¹H and ¹³C spectra were referenced to the NMR solvents. Flash chromatography was performed using silica gel (230–600 mesh). Thin layer chromatography was performed using glass plates coated with silica gel 60 F254. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dq = double quartet, m = multiplet, br = broad.

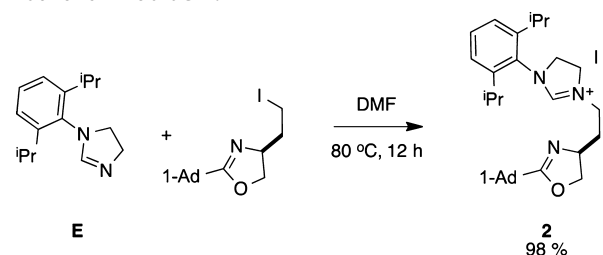
Calculations were performed as previously described.^{21,22}

Preparation of 1-(2,6-Diisopropylphenyl)-4,5-dihydro-imidazole **E**.



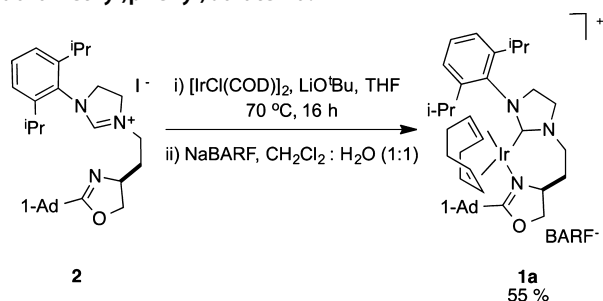
N-(2,6-Diisopropylphenyl)ethane-1,2-diamine (2.20 g, 10 mmol) was dissolved in 10 mL of trimethyl orthoformate. A catalytic amount of *p*-toluenesulfonic acid (0.10 g, 0.5 mmol) was added to the solution, and then the mixture was refluxed using an air condenser to allow methanol to escape until completion (18 h). Solvent was removed under reduced pressure, and the residue was purified by recrystallization (CH₂Cl₂/hexane) to obtain **E** (1.04 g, 4.5 mmol, 45%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.16 (3H, m), 6.82 (1H, s), 4.06 (2H, t, *J* = 8.7 Hz), 3.58 (2H, t, *J* = 10.2 Hz), 3.11–3.04 (2H, m), 1.23 (6H, d, *J* = 6.9 Hz), 1.18 (6H, d, *J* = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 163.0, 156.2, 155.9, 148.2, 134.1, 128.6, 124.1, 55.0, 51.6, 28.3, 28.0, 25.3, 24.5, 23.9, 23.5. IR (Thin film, cm⁻¹) 3364, 3206, 3063, 3024, 2963, 2928, 2866, 1678, 1605, 1585, 1458, 1381, 1366, 1327, 1265, 1204, 1180, 1107, 1053, 961, 933, 887. HRMS (ESI, TOF): Exact mass calcd for C₁₅H₂₂N₂ *i.e.* [M+H]⁺ 231.1861. Found 231.1835.

Preparation of (*S*)-3-(2-(2-(Adamantan-1-yl)-4,5-dihydrooxazol-4-yl)ethyl)-1-(2,6-diisopropylphenyl)-4,5-dihydroimidazolium iodide **2**.

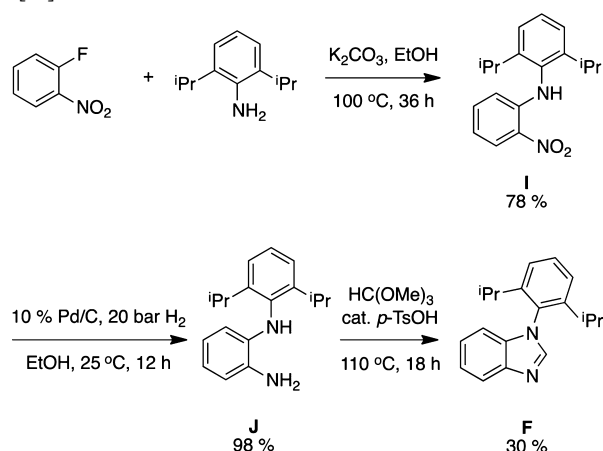


(*S*)-2-(Adamantan-1-yl)-4-(2-iodoethyl)-4,5-dihydrooxazole (1.80 g, 5 mmol) and 1-(2,6-diisopropylphenyl)-4,5-dihydroimidazole **E** (1.15 g, 5 mmol) were dissolved in 10 mL of DMF under an Ar atmosphere. The mixture was heated to 80 °C for 12 h. The solvent was removed under reduced pressure, and the residue was washed with Et₂O (5 × 5 mL) to yield compound **2** (2.89 g, 4.9 mmol, 98%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 9.0 (1H, s), 8.05–8.01 (1H, m), 7.49–7.40 (2H, m), 7.31–7.20 (1H, m), 3.79 (2H, m), 3.57–3.46 (3H, m), 3.45–3.23 (1H, m), 2.92–2.70 (3H, m), 2.37 (1H, s), 1.91–1.54 (15H, m), 1.27–1.00 (14H, m); ¹³C NMR (75 MHz, CDCl₃) δ 183.6, 166.1, 162.8, 161.9, 147.0, 144.5, 143.9, 142.7, 142.3, 129.6, 124.4, 123.4, 122.5, 73.4, 50.7, 47.2, 20.3, 38.9, 38.6, 37.3, 36.4, 28.2, 28.0, 27.4, 25.1, 24.1, 23.5, 22.3. IR (Thin film, cm⁻¹) 3066, 2978, 2922, 2844, 1610, 1602, 1458, 1352, 1268, 1161, 1131, 998, 931. HRMS (ESI, TOF): Exact mass calcd for C₃₀H₄₄N₃O⁺ *i.e.* [M]⁺ 462.3479. Found 462.3487.

Synthesis of (η⁴-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4,5-dihydrooxazolyl)ethyl]-3-(2,6-diisopropylphenyl)-4,5-

dihydroimidazolin-2-ylidene)iridium(I) Tetrakis(3,5-bis(tri-fluoromethyl)phenyl)borate 1a.

(*S*)-3-(2-(2-(Adamantan-1-yl)-4,5-dihydrooxazol-4-yl)ethyl)-1-(2,6-diisopropylphenyl)-4,5-dihydroimidazolium iodide **2** (1 mmol) was added to a round-bottom flask along with 1.5 equiv of lithium *tert*-butoxide and 0.5 equiv of [Ir(COD)Cl]₂ under Ar. THF was syringed in to make the solution 0.03 M in imidazolium salt. The mixture was heated to 70 °C in an oil bath and stirred for 16 h. After cooling to room temperature, the volatiles were removed under reduced pressure and 1.5 equiv of NaBARF in 5 mL of CH₂Cl₂ was added. Water (5 mL) was added, and the mixture was stirred vigorously for 15 min. The organic layer was removed, and the aqueous layer was washed with an additional 5 mL of CH₂Cl₂. The organic layers were combined and dried (Na₂SO₄), and the volatiles were removed in *vacuo*. The residue was chromatographed using a short silica column and 10% hexane/CH₂Cl₂ as the eluent to obtain compound **1a** (55%). Mp 79.8–80.4 (decompose). ¹H NMR (300 MHz, CDCl₃) δ 7.74 (8H, s), 7.57 (4H, s), 7.41–7.39 (1H, m), 7.28–7.20 (2H, m), 4.73–4.68 (1H, m), 4.41–4.29 (2H, m), 4.16–4.12 (1H, m), 3.97–3.58 (6H, m), 3.46–3.38 (1H, m), 3.25–3.21 (1H, m), 2.95–2.89 (1H, m), 2.68–2.59 (1H, m), 2.17–1.59 (20H, m), 1.45–1.15 (16H, m), 0.95–0.84 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ 178.4, 177.5, 174.5, 163.6, 162.7, 162.0, 161.3, 160.7, 146.7, 136.3, 134.9, 134.8, 130.0, 129.2, 129.1, 128.7 (2 peaks), 128.6, 126.4, 124.8, 122.7, 117.5, 85.5, 62.1, 55.7, 39.3, 36.1, 29.1, 28.7, 27.4, 26.9, 25.4, 23.9, 22.9. IR (Thin film, cm⁻¹) 3067, 2967, 2916, 2851, 1609, 1606, 1458, 1354, 1277, 1161, 1126, 999, 929, 887. HRMS (ESI, TOF): Exact mass calcd for C₃₈H₅₅IrN₃O⁺ *i.e.* [M]⁺ 762.3969. Found 762.3954 and C₃₂H₁₂BF₂₄⁻ *i.e.* [M]⁻ 863.0654. Found 863.0632.



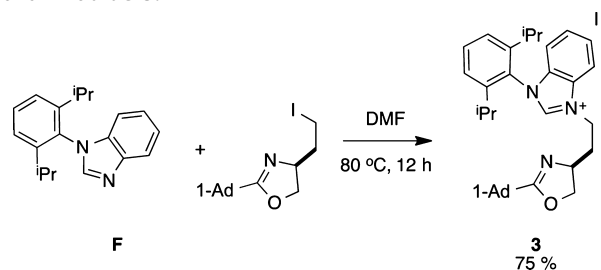
Preparation of 2,6-Diisopropyl-*N*-(2-nitrophenyl)aniline 1. 2-Fluoronitrobenzene (1.41 g, 10 mmol) was added into a solution of K₂CO₃ (2.76 g, 20 mmol) and 2,6-diisopropylaniline (4.43 g, 20 mmol) in 30 mL of ethanol. The mixture was refluxed until completion (36 h). The mixture was allowed to cool to ambient temperature and then filtered through Celite. Solvent was removed under reduced pressure, and the crude products were chromatographed using 5% CH₂Cl₂/hexane to yield **1** (2.27 g, 7.6 mmol, 76%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.10 (2H, d, *J* = 7.8 Hz), 6.98 (1H, t, *J* = 7.5 Hz), 6.70–6.45 (4H, m), 3.65 (1H, br), 3.05–2.96 (2H, m), 1.34 (12H, d, *J* = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 145.6, 143.0, 141.3, 126.3, 124.5, 123.8, 120.4, 118.6, 118.0,

116.6, 115.8, 114.3, 79.6, 29.1. HRMS (ESI, TOF): Exact mass calcd for C₁₈H₂₂N₂O₂ *i.e.* [M+H]⁺ 299.1760. Found 299.1733.

Preparation of *N*-(2,6-Diisopropylphenyl)benzene-1,2-diamine J. 10 % Pd/C (0.02 g, 0.02 mmol) was added to a solution of 2,6-diisopropyl-*N*-(2-nitrophenyl)aniline **1** (0.65 g, 2 mmol) in 15 mL of EtOH. The mixture was then placed into a steel pressure bomb and then flushed with H₂. The reaction was stirred under 20 bar of H₂ for 12 h. The mixture was passed through Celite, and the solvent was removed under reduced pressure to yield compound **J** (0.52 g, 1.96 mmol, 98%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.36–7.29 (3H, m), 6.88–6.76 (3H, m), 6.29–6.26 (1H, m), 5.01 (1H, br), 3.60 (2H, br), 3.21–3.12 (2H, m), 1.37–1.23 (12H, m); ¹³C NMR (75 MHz, CDCl₃) δ 145.6, 137.2, 136.5, 134.4, 126.2, 123.8, 120.4, 119.6, 116.5, 114.2, 28.0, 14.2. HRMS (ESI, TOF): Exact mass calcd for C₁₈H₂₄N₂ *i.e.* [M+2H]²⁺ 135.1043. Found 135.1054.

Preparation of 1-(2,6-Diisopropylphenyl)-benzo[*d*]imidazole F. *N*-(2,6-Diisopropylphenyl)benzene-1,2-diamine **J** (0.60 g, 2.3 mmol) was dissolved in 5 mL of trimethyl orthoformate. A catalytic amount of *p*-toluenesulfonic acid (0.002 g, 0.01 mmol) was added to the solution, and then the mixture was refluxed using an air condenser to allow methanol to escape until completion (18 h). Solvent was removed under reduced pressure, and the residue was purified by recrystallization (CH₂Cl₂/hexane) to obtain **F** (0.19 g, 0.69 mmol, 30%) as a brown solid. ¹H NMR (300 MHz, CDCl₃) δ 7.93 (1H, s), 7.55–7.53 (1H, m), 7.38–7.24 (5H, m), 7.08–7.05 (1H, m), 2.34–2.25 (2H, m), 1.13 (6H, d, *J* = 6.9 Hz), 1.06 (6H, d, *J* = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 147.5, 143.7, 143.1, 130.6, 130.2, 124.2, 123.6, 122.4, 120.3, 110.3, 28.3, 24.7, 23.9. IR (Thin film, cm⁻¹) 3429, 3075, 2963, 2928, 2870, 1643, 1612, 1593, 1485, 1462, 1385, 1366, 1308, 1281, 1223, 1142, 1057, 1007, 976, 934, 887. HRMS (ESI, TOF): Exact mass calcd for C₁₉H₂₂N₂ *i.e.* [M+H]⁺ 279.1861. Found 279.1863.

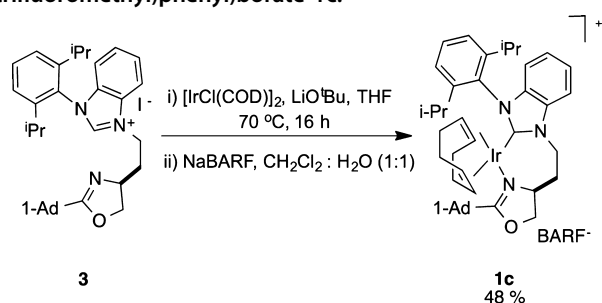
Preparation of (*S*)-3-(2-(2-(Adamantan-1-yl)-4,5-dihydrooxazol-4-yl)ethyl)-1-(2,6-diisopropylphenyl)benzo[*d*]imidazolium iodide 3.



(*S*)-2-(Adamantan-1-yl)-4-(2-iodoethyl)-4,5-dihydrooxazole (1.80 g, 5 mmol) and 1-(2,6-diisopropylphenyl)benzo[*d*]imidazole **F** (1.39 g, 5 mmol) were dissolved in 10 mL of DMF under an Ar atmosphere. The mixture was heated to 80 °C for 12 h. The solvent was removed under reduced pressure, and the residue was washed with Et₂O (5 × 5 mL) to yield compound **3** (2.39 g, 3.8 mmol, 75%) as a brown solid. ¹H NMR (300 MHz, CDCl₃) δ 8.06 (1H, s), 8.06–7.99 (1H, m), 7.57–7.22 (5H, m), 7.06–7.03 (1H, m), 4.15–4.08 (1H, m), 2.97–2.90 (2H, m), 2.29–1.74 (14H, m), 1.37–1.21 (5H, m), 1.12 (6H, d, *J* = 6.9 Hz), 1.04 (6H, d, *J* = 6.9 Hz), 0.94–0.84 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ 182.9, 147.4, 146.7, 143.9, 135.6, 132.8, 130.4, 124.2, 123.9, 122.9, 120.1, 117.7, 110.5, 60.0, 51.8, 49.6, 49.1, 46.3, 40.5, 38.8, 36.5, 28.3, 27.9, 24.7, 23.9, 22.5, 22.4. IR (Thin film, cm⁻¹) 3065, 2977, 2915, 2853, 1615, 1605, 1454, 1352, 1267, 1161, 998, 934, 889. HRMS (ESI, TOF): Exact mass calcd for C₃₄H₄₄N₃O⁺ *i.e.* [M]⁺ 510.3479. Found 510.3499.

Synthesis of (η⁴-1,5-Cyclooctadiene)(1-[(4*S*)-(2-(1-adamantyl)-4-5-dihydrooxazolyl)-ethyl]-3-(2,6-diisopropyl-

phenyl)benzo[d]imidazol-2-ylidene)iridium(I) Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate **1c**.



(*S*)-3-(2-(2-(Adamantan-1-yl)-4,5-dihydrooxazol-4-yl)ethyl)-1-(2,6-diisopropylphenyl)-benzo[d]imidazol-3-ium iodide **3** (1 mmol) was added to a round-bottom flask along with 1.5 equiv of lithium *tert*-butoxide and 0.5 equiv of [Ir(COD)Cl]₂ under Ar. THF was syringed in to make the solution 0.03 M in imidazolium salt. The mixture was heated to 70 °C in an oil bath and stirred for 16 h. After cooling to room temperature, the volatiles were removed under reduced pressure and 1.5 equiv of NaBARF in 5 mL of CH₂Cl₂ was added. Water (5 mL) was added, and the mixture was stirred vigorously for 15 min. The organic layer was removed, and the aqueous layer was washed with an additional 5 mL of CH₂Cl₂. The organic layers were combined and dried (Na₂SO₄), and the volatiles were removed *in vacuo*. The residue was chromatographed using a short silica column and 10% hexane/CH₂Cl₂ as the eluent to obtain **1c** (43%). Mp 145.5–146.4 (decompose). ¹H NMR (300 MHz, CDCl₃) δ 7.72 (8H, s), 7.52 (4H, s), 7.46–7.40 (3H, m), 7.28–7.26 (2H, m), 7.18–7.10 (1H, m), 6.92–6.89 (1H, m), 4.65–4.50 (1H, m), 4.38 (2H, s), 3.78–3.71 (3H, m), 3.39–3.25 (2H, m), 2.87–2.70 (1H, m), 2.30–1.60 (7H, m), 1.56–1.17 (18H, m), 1.17–1.11 (2H, m), 0.95 (6H, d, *J* = 6.9 Hz), 0.90 (6H, d, *J* = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 187.2, 162.7, 162.0, 161.3, 160.7, 146.4, 142.5, 139.1, 134.8, 134.5, 131.7, 129.1, 129.0 (2 peaks), 128.6, 128.5, 128.3, 126.5, 126.3, 125.1, 124.8, 122.7, 117.9, 117.5, 117.4, 112.1, 70.5, 61.8, 36.2, 31.7, 29.7, 28.6, 24.3, 23.4, 22.7, 14.1. IR (Thin film, cm⁻¹) 3067, 2967, 2916, 2851, 1609, 1458, 1354, 1277, 1161, 1126, 995, 949, 934, 887, 837. HRMS (ESI, TOF): Exact mass calcd for C₄₂H₅₅IrN₃O *i.e.* [M]⁺ 810.3974. Found 810.3998 and C₃₂H₁₂BF₂₄⁻ *i.e.* [M]⁻ 863.0654. Found 863.0634.

Catalytic Hydrogenation Conditions. The corresponding alkenes (0.25 mmol) and Ir-catalyst (1–2 mol %) were dissolved in CH₂Cl₂ (0.5 M). The resulting mixture was degassed by three cycles of freeze–pump–thaw and then transferred to a Parr Bomb. The bomb was pressurized to 50 bar with hydrogen and the mixture was stirred at 300 rpm for 16 h. The bomb was then vented and solvent was evaporated. The crude product was passed through a short silica plug using 10–30% EtOAc/hexane as the eluent. The enantiomeric ratio was then measured through chiral GC or HPLC analysis.

■ ASSOCIATED CONTENT

■ Supporting Information

¹H and ¹³C NMR spectra for compounds **1–3**, **E–F**, **I–J**, GC and HPLC traces for stereoselectivity determination after hydrogenation, ν_{CO} IR absorbances for simple carbenes and shape of carbenes electron for π -acceptor. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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