Synthesis of New Bioorganometallic Ir- and Rh-Complexes Having β-Lactam Containing Ligands

Jaime G. Muntaner, Luis Casarrubios* and Miguel A. Sierra*

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040, Madrid (Spain)
E-mail: (LC) luis_casarrubios@quim.ucm.es; (MAS) sierraor@ucm.es
web: http://http://www.ucm.es/info/biorgmet/

Supporting Information

1. Synthesis of 4-methyl-3-(pyridin-2-yl)benzaldehyde, 5c.

3-bromo-4-methylbenzaldehyde (0.75 g, 3.76 mmol), 2-(tri-n-butylstannyl)-pyridine (1.94 g, 5.30 mmol), and Pd(PPh₃)₄ (0.20 g, 0.19 mmol) were dissolved in anhydrous toluene (90 mL), the mixture was degassed by bubbling argon for 5 min and heated to 100°C for 36 h in a sealed tube. The solvent was removed under reduced pressure and the residue was purified by SiO₂ chromatography (Hex/EtOAc 8:2) to yield pure 5c (0.62 g, 3.14 mmol, 84%) as a brown oil. ¹H NMR (300 MHz, CDCl₃): δ= 9.99 (s, 1H), 8.70 (d, 1H, J = 4.8 Hz), 7.90 (d, 1H, J = 1.9 Hz), 7.84–7.71 (m, 2H), 7.42 (dd, 2H, J = 7.8, 3.5 Hz), 7.28–7.25 (m, 1H), 2.43 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ= 192.1, 158.8, 149.7, 143.8, 141.5, 136.8, 134.8, 131.9, 131.7, 129.3, 124.3, 122.5, 21.1. IR (CH₂Cl₂): ν= 1694 cm⁻¹. HRMS EI: m/z: [M]⁺ calcd. for C₁₃H₁₁NO: 196.0757, found 196.0766.

2. Synthesis of pyridineanilines

A three-neck round-bottom flask equipped with a stirbar was charged with isopropylmagnesium chloride (2.0 M in THF, 5.1 mL, 10.30 mmol). To this mixture was dropwise added neat 2-bromopyridine (1.44 g, 9.10 mmol) over 30 min. A water
bath was used to maintain the temperature below 30°C. After 3 h, zinc chloride (0.7 M in THF, 16.4 mL, 11.50 mmol) was dropwise added under 40 min (temperature must be also kept below 30°C during addition). After 1 h at room temperature, the mixture was cannulated to another flask containing Pd(PPh₃)₄ (0.08 g, 0.07 mmol, 0.8 mol%) and the corresponding iodoaniline (1.60 g, 7.30 mmol). The reaction was then refluxed for 24 h, cooled down to rt, quenched with saturated NH₄Cl solution (15 mL), extracted with EtOAc (3 x 30 mL), washed with 30 mL of saturated Na₂S₂O₃ solution and brine, dried over anhydrous MgSO₄ and evaporated. SiO₂ chromatography (Hex/EtOAc 9:1) yielded pure pyridinyl anilines 7b and 7c.

3-(pyridin-2-yl)aniline, 7b.

Following the general method, from 3-iodoaniline (1.60 g, 7.30 mmol), pure 7b (0.99 g, 5.90 mmol, 81%) was obtained as a reddish brown oil. ¹H NMR (300 MHz, CDCl₃): δ= 8.74 (d, 1H, J = 4.7 Hz), 7.74–7.70 (m, 2H), 7.46–7.38 (m, 2H), 7.31 (t, 1H, J = 7.7 Hz), 7.26–7.20 (m, 1H), 6.78 (d, 1H, J = 7.9 Hz), 3.42 (bs, 2H).

¹³C NMR (75 MHz, CDCl₃): δ= 157.5, 149.5, 147.2, 140.4, 136.8, 129.7, 122.2, 120.7, 117.1, 115.9, 113.6.

IR (CHCl₃): ν = 3300, 3150 cm⁻¹. HRMS ESI: m/z: [M+H]⁺ calcd. for C₁₁H₁₁N₂: 171.0917, found 171.0922.

4-(pyridin-2-yl)aniline, 7c. Following the general method, from 4-iodoaniline (1.60 g, 7.30 mmol), pure 7c (0.90 g, 5.29 mmol, 72%) was obtained as a brown solid. mp 96–98°C (EtOAc/Hex.). ¹H NMR (300 MHz, CDCl₃): δ= 8.64–8.61 (m, 1H), 7.87–7.82 (m, 2H), 7.70–7.59 (m, 2H), 7.14–7.08 (m, 1H), 6.77–6.72 (m, 2H), 3.82 (bs, 2H).

¹³C NMR (75 MHz, CDCl₃): δ= 157.7, 149.7, 147.8, 136.9, 129.9, 128.3, 121.2, 119.6, 115.4. IR (CHCl₃): ν = 3300, 3150 cm⁻¹. HRMS ESI: m/z: [M+H]⁺ calcd. for C₁₁H₁₁N₂: 171.0917, found 171.0920.
3. Synthesis of Imines 6, 8, and 9.

4-methoxy-N-(4-(pyridin-2-yl)benzylidene)aniline, 6b.

Following Method A, from 4-methoxyaniline (0.34 g, 2.70 mmol) and 4-(pyridin-2-yl)benzaldehyde (0.50 g, 2.70 mmol) in 8 mL of anhydrous CH₂Cl₂, pure 6b (0.72 g, 2.50 mmol, 95%) was obtained as a pale yellow solid. mp 143–145 ºC (EtOAc/Hex). ¹H NMR (300 MHz, CDCl₃): δ= 8.74 (bd, 1H, J = 4.7 Hz), 8.54 (s, 1H), 8.12 (d, 2H, J = 8.1 Hz), 8.00 (d, 2H, J = 8.1 Hz), 7.79 (bs, 2H), 7.30–7.27 (m, 3H), 6.95 (d, 2H, J = 8.6 Hz), 3.84 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ= 158.3, 157.7, 156.5, 149.7, 144.7, 141.5, 136.8, 128.9, 127.1, 122.5, 122.2, 120.7, 114.3, 55.4. IR (CH₂Cl₂): ν= 1619, 1580 cm⁻¹. HRMS EI: m/z calcd. for [M]⁺ (C₁₉H₁₆N₂O): 288.1257, found 288.1258.

(E)-4-methoxy-N-(4-methyl-3-(pyridin-2-yl)benzylidene)aniline, 6c.

Following Method A, from 4-methyl-3-(pyridin-2-yl)benzaldehyde 5c (0.16 g, 0.82 mmol) and 4-methoxyaniline (0.10 g, 0.82 mmol) in 2.0 mL of anhydrous CH₂Cl₂, pure 6c (0.24 g, 0.79 mmol, 97%) was obtained as a brown oil. ¹H NMR (300 MHz, CDCl₃): δ= 8.74–8.71 (m, 1H), 8.50 (s, 1H), 7.93 (d, 1H, J = 1.8 Hz), 7.85 (dd, 1H, J = 7.9, 1.9 Hz), 7.77 (td, 1H, J = 7.9, 1.9 Hz), 7.47 (dt, 1H, J = 7.9, 1.1 Hz), 7.39 (d, 1H, J = 7.9 Hz), 7.31–7.26 (m, 1H), 7.26–7.21 (m, 2H), 6.96–6.91 (m, 2H), 3.82 (s, 3H), 2.44 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ= 159.7, 158.5, 158.4, 149.6, 145.3, 141.2, 139.6, 136.6, 134.7, 131.6, 130.4, 128.5, 124.5, 122.5, 122.2, 114.7, 55.8, 20.8. IR (CH₂Cl₂): ν= 1623, 1585 cm⁻¹. HRMS EI: m/z calcd. for [M]⁺ (C₂₀H₁₈O₂N): 302.1414, found 302.1414.

N-(4-methoxybenzylidene)-3-(pyridin-2-yl)aniline, 8b.

Following Method A, from 3-(pyridin-2-yl)aniline 7b (0.18 g, 1.04 mmol) and 4-methoxybenzaldehyde (0.14 g, 1.04 mmol) in 2 mL of anhydrous CH₂Cl₂, pure 8b (0.29 g, 0.99 mmol, 95%) was obtained as a brown oil. ¹H NMR (300 MHz, CDCl₃): δ= 8.72
Following Method A, from 4-(pyridin-2-yl)aniline 7c (0.15 g, 0.88 mmol) and 4-(2-pyridyl)benzaldehyde (0.16 g, 0.88 mmol) in 2.0 mL of anhydrous CH$_2$Cl$_2$, pure 9 (0.28 g, 0.83 mmol, 95%) was obtained as a brown solid. mp 211–213ºC (EtOAc/Hex). 

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$= 8.75 (d, 1H, $J$ = 4.8 Hz), 8.71 (d, 1H, $J$ = 4.8 Hz), 8.58 (s, 1H), 8.15 (d, 2H, $J$ = 8.4 Hz), 8.06 (t, 4H, $J$ = 8.8 Hz), 7.85–7.72 (m, 4H), 7.37 (d, 2H, $J$ = 8.4 Hz), 7.32–7.17 (m, 2H). 

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$= 159.9, 156.8, 156.4, 152.5, 149.8, 149.6, 142.0, 137.1, 136.8, 136.7, 136.5, 129.3, 127.7, 127.2, 122.6, 121.9, 121.4, 120.8, 120.2. IR (CH$_2$Cl$_2$): $\nu$= 1582 cm$^{-1}$. MS EI: m/z calcd. for [M]$^+$ (C$_{23}$H$_{17}$N$_3$): 335.14, found 335.15.

**4. Synthesis of $\beta$-lactams.**

(±)-cis-1-(4-methoxyphenyl)-3-phenoxy-4-(4-(pyridin-2-yl)phenyl)azetidin-2-one, 11.

Following Method B, from imine 6b (0.40 g, 1.38 mmol), Et$_3$N (0.42 g, 4.14 mmol) and phenoxyacetyl chloride (0.22 g, 2.08 mmol), pure 11 (0.45 g, 1.08 mmol, 78%) was obtained as a single cis isomer after purification by SiO$_2$ chromatography (Hex/EtOAc 7:3) as a white solid. mp 162–164ºC (EtOAc/Hex). 

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$= 8.67 (d, 1H, $J$ = 4.9 Hz), 7.94 (d, 2H, $J$ = 8.3 Hz), 7.79–7.63 (m, 2H), 7.50 (d, 2H, $J$ = 8.3 Hz), 7.35–7.32 (m, 2H), 7.26–7.13 (m, 3H), 6.91 (t, 1H, $J$ = 7.2 Hz), 6.85–6.78 (m, 4H), 5.60 (d, 1H, $J$ = 4.8 Hz), 5.42 (d, 1H, $J$ = 4.8 Hz), 3.75 (s, 3H). 

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$= 162.3, 160.0, 157.1, 152.8, 149.6, 140.3, 136.8, 130.6, 129.5, 129.2, 124.1, 122.2, 121.9, 120.7, 119.0, 114.2, 55.4. IR (CH$_2$Cl$_2$): $\nu$= 1626, 1598 cm$^{-1}$. HRMS EI: m/z calcd. for [M]$^+$ (C$_{19}$H$_{16}$N$_2$O): 288.1257, found 288.1256.
MHz, CDCl$_3$): δ = 162.5, 157.0, 156.7, 156.6, 149.7, 139.8, 136.8, 133.6, 130.4, 129.3, 128.7, 127.0, 122.4, 122.3, 120.6, 119.0, 115.8, 114.4, 81.4, 62.0, 55.5. IR (CHCl$_3$): ν = 1740 cm$^{-1}$. HRMS ESI: m/z: [M+H]$^+$ calcd. for C$_{27}$H$_{23}$N$_2$O$_3$: 423.1703, found 423.1702. (+)-cis-(S)-3-[(3S,4R)-1-(4-methoxyphenyl)-2-oxo-4-(4-(pyridin-2-yl)phenyl)azetidin-3-yl]-4-phenyloxazolidin-2-one, 13.

Following Method B, from imine 6b (0.42 g, 1.44 mmol), Et$_3$N (0.44 g, 4.32 mmol) and (S)-(+)2-oxo-4-phenyl-3-oxazolidineacetyl chloride (0.52 g, 2.16 mmol), pure 13 (0.54 g, 1.09 mmol, 76%) was obtained as a single *cis* isomer after purification by SiO$_2$ chromatography (Hex/EtOAc 7:3) as a white solid. mp > 250 ºC (CHCl$_3$/Hex). [α]$_D^{25}$ = +80.0º (c = 1.6, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): δ = 8.73 (d, 1H, J = 4.5 Hz), 7.97 (d, 2H, J = 8.1 Hz), 7.85–7.73 (m, 2H), 7.37–7.25 (m, 8H), 7.21–7.16 (m, 2H), 6.81 (d, 2H, J = 9.0 Hz), 5.24 (d, 1H, J = 5.2 Hz), 4.82 (d, 1H, J = 5.2 Hz), 4.67 (dd, 1H, J = 8.9, 7.2 Hz), 4.35 (t, 1H, J = 8.9 Hz), 4.01 (dd, 1H, J = 8.9, 7.2 Hz), 3.76 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 160.0, 157.2, 156.6, 156.4, 149.6, 137.0, 136.8, 133.5, 130.8, 129.4, 129.2, 128.0, 127.6, 127.3, 122.4, 120.6, 118.6, 114.3, 70.6, 63.0, 61.1, 59.5, 55.4. IR (CHCl$_3$): ν = 1746 cm$^{-1}$. HRMS ESI: m/z: [M+H]$^+$ calcd. for C$_{30}$H$_{26}$N$_3$O$_4$: 492.1918, found 492.1942.

(±)-4-[(4-methoxyphenyl)-3-phenoxy-1-(4-(pyridin-2-yl)phenyl)azetidin-2-one, 17. Following Method B, from imine 8c (0.17 g, 0.59 mmol), Et$_3$N (0.18 g, 1.77 mmol) and phenoxyacetylchloride (0.10 g, 0.89 mmol), a crude 3.5:1 mixture of *cis*-17/trans-17 was obtained. Purification by SiO$_2$ chromatography (Hex/EtOAc 7:3) yielded pure *cis*-17 (0.14 g, 0.33 mmol, 56%) and trans-17 (0.02 g, 0.05 mmol, 8%) as white solids. 37 mg (0.09 mmol, 15%) of the *cis/trans* mixture were also recovered. *cis*-17. mp 199–202ºC (EtOAc/Hex). $^1$H NMR (300 MHz, CDCl$_3$): δ = 8.65 (bd, 1H, J = 5.0 Hz), 7.95–7.92 (m, 2H), 7.76–7.63 (m, 2H), 7.50–7.45 (m, 2H), 7.36–7.31 (m, 2H),
7.22–7.17 (m, 3H), 6.94 (t, 1H, \( J = 7.4 \) Hz), 6.86–6.81 (m, 4H), 5.59 (d, 1H, \( J = 4.8 \) Hz), 5.43 (d, 1H, \( J = 4.8 \) Hz), 3.77 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 163.2, 159.9, 157.0, 156.5, 149.6, 137.5, 136.7, 135.5, 129.4, 129.3, 127.7, 126.0, 124.2, 122.2, 122.0, 120.1, 117.9, 115.7, 113.9, 81.3, 61.8, 55.2. IR (CHCl\(_3\)): \( \nu = 1754 \) cm\(^{-1}\).

HRMS ESI: \( m/z \) calcd. for [M+H]\(^+\) (C\(_{27}\)H\(_{23}\)N\(_2\)O\(_3\)): 423.1703, found 423.1685. \textbf{trans-17.} mp 140–142ºC (EtOAc/Hex). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 8.64 \) (bd, 1H, \( J = 4.6 \) Hz), 7.91 (d, 2H, \( J = 8.6 \) Hz), 7.74–7.62 (m, 2H), 7.43 (d, 2H, \( J = 8.6 \) Hz), 7.36 (d, 2H, \( J = 8.6 \) Hz), 7.27 (t, 2H, \( J = 7.9 \) Hz), 7.22–7.16 (m, 1H), 7.02 (t, 1H, \( J = 7.4 \) Hz), 6.97 (d, 2H, \( J = 8.6 \) Hz), 6.89 (d, 2H, \( J = 8.2 \) Hz), 5.14 (d, 1H, \( J = 1.6 \) Hz), 5.04 (d, 1H, \( J = 1.6 \) Hz), 3.84 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 162.6, 160.2, 157.0, 156.4, 149.6, 137.3, 136.7, 135.5, 129.6, 127.8, 127.6, 127.1, 122.2, 121.9, 120.0, 117.9, 115.3, 114.8, 87.4, 63.8, 55.3. IR (CHCl\(_3\)): \( \nu = 1760 \) cm\(^{-1}\). HRMS EI: \( m/z \) calcd. for C\(_{27}\)H\(_{22}\)N\(_2\)O\(_3\): 422.1625, found 422.1626.

\((\pm)-\text{cis-1-(4-methoxyphenyl)-3-phenoxy-4-(3-(pyridin-2-yl)phenyl)azetidin-2-one},\) 24.

Following Method B, from imine 6a (0.13 g, 0.44 mmol), Et\(_3\)N (0.13 g, 1.32 mmol) and phenoxyacetyl chloride (0.07 g, 0.66 mmol), pure 24 (0.14 g, 0.33 mmol, 75%) was obtained as a single \textit{cis} isomer after purification by SiO\(_2\) chromatography (Hex/EtOAc 7:3) as a white solid. mp 166–169ºC (EtOAc/Hex). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 8.69 \) (d, 1H, \( J = 4.7 \) Hz), 8.01 (bs, 1H), 7.92 (dt, 1H, \( J = 7.1, 1.8 \) Hz), 7.74 (td, 1H, \( J = 7.7, 1.9 \) Hz), 7.66–7.59 (m, 1H), 7.49–7.40 (m, 2H), 7.40–7.31 (m, 2H), 7.28–7.20 (m, 1H), 7.19–7.10 (m, 2H), 6.88 (t, 1H, \( J = 7.4 \) Hz), 6.85–6.77 (m, 4H), 5.61 (d, 1H, \( J = 4.8 \) Hz), 5.47 (d, 1H, \( J = 4.8 \) Hz), 3.75 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 162.4, 156.8, 156.6, 156.4, 149.5, 139.4, 136.7, 133.3, 130.3, 129.2, 128.8, 128.5, 127.2,
126.7, 122.2, 122.0, 120.5, 118.8, 115.6, 114.3, 81.1, 62.0, 55.3. IR (CHCl₃): ν = 1752 cm⁻¹. HRMS ESI: m/z: [M+H]⁺ calcd. for C₂₇H₂₃N₂O₃: 423.1703, found 423.1723.

(+) cis-(S)-3-((3S,4R)-1-(4-methoxyphenyl)-2-oxo-4-(3-(pyridin-2-yl)phenyl)azetidin-3-yl)-4-phenyloxazolidin-2-one, 25.

Following Method B, from imine 6a (0.25 g, 0.87 mmol), Et₃N (0.26 g, 2.61 mmol) and (S)- (+)-2-oxo-4-phenyl-3-oxazolidineacetyl chloride (0.31 g, 1.30 mmol), pure 25 (0.31 g, 0.63 mmol, 73%) was obtained as a single cis isomer after purification by SiO₂ chromatography (Hex/EtOAc 7:3) as a white solid. mp 203–205ºC (CHCl₃/Hex). [α]D²⁵ = +100.6° (c = 1.8, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ= 8.69 (d, 1H, J = 4.7 Hz), 8.03 (d, 1H, J = 7.8 Hz), 7.96 (bs, 1H), 7.76–7.73 (m, 2H), 7.44 (t, 1H, J = 7.7 Hz), 7.35–7.12 (m, 9H), 6.75 (d, 2H, J = 8.8 Hz), 5.25 (d, 1H, J = 5.1 Hz), 4.73 (d, 1H, J = 5.1 Hz), 4.58 (dd, 1H, J = 8.8, 7.1 Hz), 4.24 (t, 1H, J = 8.8 Hz), 3.95 (dd, 1H, J = 8.8, 7.1 Hz), 3.72 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ= 159.9, 156.8, 156.4, 156.2, 149.4, 139.6, 136.9, 136.5, 133.1, 130.7, 129.3, 129.2, 129.1, 128.0, 127.3, 127.0, 125.9, 122.3, 120.8, 118.4, 114.1, 70.2, 62.7, 61.2, 59.5, 55.2. IR (CHCl₃): ν= 1753 cm⁻¹. HRMS ESI: m/z: [M+H]⁺ calcd. for C₃₀H₂₆N₃O₄: 492.1918, found 492.1941.

(±)-cis-4-(4-methoxyphenyl)-3-phenoxy-1-(3-(pyridin-2-yl)phenyl)azetidin-2-one, 26.

Following Method B, from imine 8b (0.07 g, 0.25 mmol), Et₃N (0.08 g, 0.75 mmol) 76 mg (0.75 mmol) and phenoxyacetyl chloride (0.05 g, 0.38 mmol), pure 26 (0.07 g, 0.17 mmol, 68%) was obtained as a single cis isomer after purification by SiO₂ chromatography (Hex/EtOAc 7:3) as a white solid. mp 173–176ºC (EtOAc/Hex). ¹H NMR (300 MHz, CDCl₃): δ= 8.67 (d, 1H, J = 4.7 Hz), 8.09 (bs, 1H), 7.79–7.69 (m, 2H), 7.65 (d, 1H, J = 8.1 Hz), 7.43–7.30 (m, 4H), 7.27–7.13 (m, 3H), 6.94 (t, 1H, J = 7.4 Hz), 6.83 (d, 4H, J = 8.6 Hz), 5.58 (d, 1H, J = 4.8 Hz), 5.47 (d, 1H, J = 4.8 Hz),
3.76 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 163.2, 159.8, 156.9, 156.5, 149.6, 140.5, 137.3, 136.7, 129.5, 129.4, 129.2, 124.2, 123.1, 122.4, 122.1, 120.7, 117.8, 116.1, 115.7, 113.8, 81.2, 61.7, 55.1. IR (CHCl$_3$): ν = 1754 cm$^{-1}$. HRMS ESI: m/z calcd. for [M+H]$^+$ (C$_{27}$H$_{23}$N$_2$O$_3$): 423.1703, found 423.1724.

(+)-cis-(S)-3-((2R,3S)-2-(4-methoxyphenyl)-4-oxo-1-(3-(pyridin-2-yl)phenyl)azetidin-3-yl)-4-phenyloxazolidin-2-one, cis-27.

Following Method B, from imine 8b (0.34 g, 1.18 mmol), Et$_3$N (0.36 g, 3.54 mmol) and (S)(+)-2-oxo-4-phenyl-3-oxazolidineacetyl chloride (0.42 g, 1.77 mmol), pure cis-27 (0.36 g, 0.73 mmol, 62%) was obtained as a single cis isomer after purification by SiO$_2$ chromatography (Hex/EtOAc 1:1) as a white solid. mp 231–233ºC (CHCl$_3$/Hex). [α]$_D$ = +8.0º (c = 0.15, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): δ = 8.64 (d, 1H, $J$ = 4.2 Hz), 8.00 (bs, 1H), 7.77–7.70 (m, 2H), 7.65 (d, 1H, $J$ = 7.9 Hz), 7.39–7.16 (m, 10H), 6.87 (d, 2H, $J$ = 8.7 Hz), 5.28 (d, 1H, $J$ = 5.2 Hz), 4.74 (d, 1H, $J$ = 5.2 Hz), 4.60 (dd, 1H, $J$ = 8.8, 7.1 Hz), 4.35 (t, 1H, $J$ = 8.8 Hz), 4.03 (dd, 1H, $J$ = 8.8, 7.1 Hz), 3.83 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 160.8, 159.6, 157.1, 156.6, 149.6, 140.5, 137.7, 136.8, 136.7, 129.5, 129.4, 129.2, 128.8, 127.5, 124.1, 123.1, 122.4, 120.8, 117.6, 115.8, 114.2, 70.5, 62.8, 60.9, 59.6, 55.2. IR (CHCl$_3$): ν = 1753 cm$^{-1}$. HRMS ESI: m/z calcd. for [M+H]$^+$ (C$_{30}$H$_{26}$N$_2$O$_4$): 492.1918, found 492.1930.

(+)-trans-(S)-3-((2S,3S)-2-(4-methoxyphenyl)-4-oxo-1-(3-(pyridin-2-yl)phenyl)azetidin-3-yl)-4-phenyloxazolidin-2-one, trans-27.

Following Method A, from imine 8b (0.16 g, 0.56 mmol), Et$_3$N (0.17 g, 1.68 mmol) and (S)(+)-2-oxo-4-phenyl-3-oxazolidineacetyl chloride (0.21 g, 0.90 mmol), pure trans-27 (0.23 g, 0.47 mmol, 83%) was obtained as a single trans isomer after purification by SiO$_2$ chromatography (Hex/EtOAc 7:3) as a white solid. mp 235–237ºC (CHCl$_3$/Hex). [α]$_D$ = +51.8º (c = 0.4, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): δ = 8.67 (d, 1H, $J$ = 4.7 Hz), 8.00 (bs, 1H), 7.89–7.80 (m, 2H), 7.70–7.65 (m, 2H), 7.40–7.15 (m, 10H), 6.87 (d, 2H, $J$ = 8.7 Hz), 5.28 (d, 1H, $J$ = 5.2 Hz), 4.74 (d, 1H, $J$ = 5.2 Hz), 4.60 (dd, 1H, $J$ = 8.8, 7.1 Hz), 4.35 (t, 1H, $J$ = 8.8 Hz), 4.03 (dd, 1H, $J$ = 8.8, 7.1 Hz), 3.83 (s, 3H).
Hz), 7.89 (bs, 1H), 7.77–7.70 (m, 2H), 7.59 (d, 1H, J = 7.9 Hz), 7.47–7.19 (m, 7H), 7.09 (d, 2H, J = 8.6 Hz), 6.86–6.76 (m, 3H), 5.07 (dd, 1H, J = 9.0, 6.4 Hz), 4.88 (d, 1H, J = 2.4 Hz), 4.77 (t, 1H, J = 9.0 Hz), 4.38 (dd, 1H, J = 9.0, 6.4 Hz), 4.24 (d, 1H, J = 2.4 Hz), 3.77 (s, 3H).

13C NMR (75 MHz, CDCl3): δ = 162.3, 159.9, 157.1, 156.5, 149.7, 140.4, 137.9, 136.8, 136.7, 129.7, 129.5, 129.3, 127.6, 127.5, 127.2, 123.2, 122.4, 120.6, 117.5, 116.5, 114.6, 70.2, 68.7, 60.6, 59.0, 55.3. IR (CHCl3): ν = 1755 cm⁻¹.

HRMS ESI: m/z calcd. for [M+H]⁺ (C30H26N3O4): 492.1918, found 492.1926.

(±)-cis-1-(4-methoxyphenyl)-4-(4-methyl-3-(pyridin-2-yl)phenyl)-3-phenoxyazetidin-2-one, 32.

Following Method B, from imine 6c (0.16 g, 0.52 mmol), Et3N (0.16 g, 1.56 mmol) and phenoxyacetyl chloride (0.13 g, 0.78 mmol), pure 32 (0.16 g, 0.36 mmol, 70%) was obtained as a single cis isomer after purification by SiO2 chromatography (Hex/EtOAc 7:3) as a white solid. mp 144–146ºC (EtOAc/Hex). ¹H NMR (300 MHz, CDCl3): δ= 8.66 (d, 1H, J = 4.0 Hz), 7.70 (td, 1H, J = 7.8, 1.9 Hz), 7.41–7.29 (m, 4H), 7.26–7.11 (m, 5H), 6.92 (t, 1H, J = 7.4 Hz), 6.84 (d, 2H, J = 7.9 Hz), 6.79 (d, 2H, J = 8.9 Hz), 3.73 (s, 3H), 2.31 (s, 3H). 13C NMR (75 MHz, CDCl3): δ= 162.8, 159.8, 157.3, 156.8, 149.3, 140.6, 136.9, 136.6, 131.3, 130.7, 130.5, 129.9, 129.6, 128.1, 124.4, 122.4, 122.1, 119.3, 116.1, 114.7, 81.4, 62.2, 55.7, 20.4. IR (CHCl3): ν = 1752 cm⁻¹. HRMS ESI: m/z: [M+H]⁺ calcd. for C28H24N3O3: 437.1860, found 437.1873.

(±)-cis-3-phenoxy-1,4-bis(4-(pyridin-2-yl)phenyl)azetidin-2-one, 34. Following Method B, from imine 9 (0.09 g, 0.27 mmol), Et3N (0.08 g, 0.81 mmol) and phenoxyacetyl chloride (0.04 g, 0.40 mmol), a crude 9:1 mixture of cis/trans 34 was obtained. Purification by SiO2 chromatography (Hex/EtOAc 7:3) yielded pure cis-34 (0.10 g, 0.21 mmol, 79%) as a white solid and 0.02 g (0.04 mmol, 15%) of the cis/trans mixture. mp 145-148ºC (EtOAc/Hex). ¹H NMR (300 MHz, CDCl3): δ= 8.67 (m, 2H),
7.99–7.90 (m, 4H), 7.73–7.67 (m, 4H), 7.55–7.48 (m, 4H), 7.27–7.16 (m, 4H), 6.93 (t, 1H, J = 7.3 Hz), 6.85 (d, 2H, J = 8.1 Hz), 5.66 (d, 1H, J = 4.7 Hz), 5.53 (d, 1H, J = 4.7 Hz). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ= 163.1, 156.9, 156.6, 156.3, 149.6, 149.5, 139.7, 137.4, 136.9, 136.8, 135.5, 133.3, 129.3, 128.6, 127.8, 127.0, 122.3, 122.0, 120.6, 120.2, 117.9, 115.7, 81.4, 62.0. IR (CHCl\(_3\)): ν = 1743 cm\(^{-1}\). HRMS ESI: m/z: [M+H]+ calcd. for C\(_{31}\)H\(_{24}\)N\(_3\)O\(_2\): 470.1863, found 470.1883.

5. Synthesis of Cyclometallated Complexes.

Rhodium complex 14b.

Following general procedure, from β-lactam 11 (20.0 mg, 47 µmol), [RhCp*Cl\(_2\)]\(_2\) (14.6 mg, 23 µmol) and NaOAc (9.3 mg, 113 µmol) in 2.5 mL of CH\(_2\)Cl\(_2\) and after precipitation, a 1.7:1 diastereomeric mixture of 14b (29.9 mg, 43 µmol, 92%) was obtained as an orange solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ= 8.72 (d, 2H, [M+m], J = 5.5 Hz), 7.89 (d, 1H, [m], J = 1.7 Hz), 7.82 (d, 1H, [M], J = 1.7 Hz), 7.77–7.65 (m, 4H, [M+m]), 7.60–7.47 (m, 2H, [M+m]), 7.44–7.31 (m, 4H, [M+m]), 7.25–7.05 (m, 8H, [M+m]), 7.01–6.86 (m, 6H, [M+m]), 6.80–6.76 (m, 4H, [M+m]), 5.68 (d, 1H, [M], J = 4.9 Hz), 5.56 (d, 1H, [m], J = 4.9 Hz), 5.46 (d, 1H, [M], J = 4.9 Hz), 5.41 (d, 1H, [m], J = 4.9 Hz), 3.73 (s, 3H, [m]), 3.72 (s, 3H, [M]), 1.58 (s, 15H, [m]), 1.51 (s, 15H, [M]). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ= 178.7 (d, J(C, Rh) = 32.1 Hz), 164.8, 164.7, 164.7, 164.6, 162.9, 162.7, 157.5, 157.4, 156.5, 156.3, 151.3, 151.2, 144.1, 144.0, 137.1, 137.0, 136.6, 135.9, 134.3, 134.0, 130.4, 129.3, 129.0, 123.3, 123.2, 123.1, 122.3, 122.2, 121.9, 119.3, 119.2, 119.2, 119.0, 116.2, 115.6, 114.4, 114.3, 95.9 (d, J(C, Rh) = 6.3 Hz), 95.8 (d, J(C, Rh) = 6.1 Hz), 82.1, 81.1, 62.9, 62.3, 55.4, 55.3, 9.1, 9.0. IR (CHCl\(_3\)): ν = 1750 cm\(^{-1}\). HRMS ESI: m/z: [M-Cl]+ calcd. for C\(_{37}\)H\(_{36}\)N\(_3\)O\(_3\)Rh: 659.1775, found 659.1784.
Iridium complex 15a.

Following general procedure, from β-lactam 12 (10.0 mg, 27 µmol), [IrCp*Cl₂]₂ (11.0 mg, 13 µmol) and NaOAc (5.0 mg, 61 µmol) in 1.5 mL of CH₂Cl₂ and after precipitation, a 1.2:1 diastereomeric mixture of 15a (20.0 mg, 26 µmol, 95%) was obtained as a yellow solid. ¹H NMR (300 MHz, CDCl₃):  δ= 8.70 (d, 2H, J = 5.8 Hz, [M+m]), 7.90–7.74 (m, 4H, [M+m]), 7.74–7.54 (m, 4H, [M+m]), 7.34 (d, 4H, J = 8.6 Hz, [M+m]), 7.17–6.96 (m, 4H, [M+m]), 6.89–6.68 (m, 4H, [M+m]), 5.24 (d, 1H, J = 4.8 Hz, [M]), 5.20 (d, 1H, J = 4.5 Hz, [M]), 4.90 (d, 1H, J = 4.8 Hz, [M]), 4.85 (d, 1H, J = 4.5 Hz, [M]), 3.73 (s, 6H, [M+m]), 3.27 (s, 3H, [M]), 3.18 (s, 3H, [M]), 1.62 (s, 15H, [M]).

¹³C NMR (75 MHz, CDCl₃):  δ= 166.7, 163.9, 163.9, 163.4, 163.3, 156.3, 156.2, 151.3, 144.6, 144.5, 137.0, 137.0, 135.5, 135.3, 135.2, 135.2, 130.9, 130.8, 123.8, 123.7, 122.5, 121.9, 121.4, 119.1, 118.9, 114.3, 88.6, 88.5, 85.1, 85.0, 62.4, 61.9, 60.4, 58.4, 58.3, 55.4, 55.4, 8.8. IR (CHCl₃): ν= 1745 cm⁻¹. HRMS ESI: m/z: [M-Cl]⁺ calcd. for C₃₂H₃₄IrN₂O₃: 687.2195 found 687.2229.

Rhodium complex 15b.

Following general procedure, from β-lactam 12 (18.0 mg, 50 µmol), [RhCp*Cl₂]₂ (15.4 mg, 30 µmol) and NaOAc (9.7 mg, 100 µmol) in 1.5 mL of CH₂Cl₂ and after precipitation, a 1:1 diastereomeric mixture of 15b (28.5 mg, 40 µmol, 90%) was obtained as an orange solid. ¹H NMR (300 MHz, CDCl₃):  δ= 8.74 (d, 2H, J = 5.6 Hz), 7.84 (dd, 2H, J = 6.7, 1.7 Hz), 7.80–7.66 (m, 4H), 7.60 (dd, 2H, J = 9.1, 8.0 Hz), 7.42–7.29 (m, 4H), 7.20–7.00 (m, 4H), 6.75–6.72 (m, 4H), 5.25 (d, 1H, J = 4.8 Hz), 5.21 (d, 1H, J = 4.7 Hz), 4.92 (d, 1H, J = 4.8 Hz), 4.86 (d, 1H, J = 4.7 Hz), 3.73 (s, 3H), 3.72 (s, 3H), 3.29 (s, 3H), 3.19 (s, 3H), 1.62 (s, 15H), 1.57 (s, 15H). ¹³C NMR (75 MHz, CDCl₃):  δ= 178.5 (d, J(C, Rh) = 32.3 Hz), 178.4 (d, J(C, Rh) = 32.3 Hz), 164.7, 163.9, 163.8, 156.3, 156.2, 151.3, 144.1, 144.0, 137.1, 137.1, 136.4, 136.3, 134.9, 134.7,
130.8, 130.7, 123.3, 123.2, 122.6, 122.2, 122.1, 119.3, 118.9, 114.3, 95.9, (d, J(C, Rh) = 6.3 Hz), 95.9 (d, J(C, Rh) = 6.3 Hz), 85.1, 85.0, 62.4, 61.9, 58.5, 58.4, 55.4, 55.4, 9.0.

IR (CHCl₃): ν = 1746 cm⁻¹. HRMS ESI: m/z: [M-Cl]+ calcd. for C₃₂H₃₄N₂O₃Rh: 597.1619 found 597.1638.

**Iridium complex 16a.**

Following general procedure, from β-lactam 13 (30.0 mg, 61 µmol), [IrCp*Cl₂]₂ (24.3 mg, 30 µmol) and NaOAc (11.6 mg, 142 µmol) in 3.0 mL of CH₂Cl₂ and after precipitation, a 3.3:1 diastereomeric mixture of 16a (49.0 mg, 57 µmol, 94%) was obtained as a yellow solid. ¹H NMR (300 MHz, benzene-d₆, 25ºC): δ= 8.50 (d, 1H, [m], J = 5.9 Hz), 8.45 (d, 1H, [M], J = 5.7 Hz), 8.17 (d, 1H, [m], J = 1.7 Hz), 7.79 (bs, 1H, [M]), 7.68 (d, 2H, [M], J = 9.0 Hz), 7.49–7.35 (m, 5H, [M+m]), 7.33–7.21 (m, 3H, [M+m]), 7.20–7.00 (m, 7H, [M+m]), 6.98–6.91 (m, 3H, [m]), 6.87 (t, 2H, [M+m], J = 7.8 Hz), 6.71 (d, 2H, [M], J = 9.0 Hz), 6.62 (d, 2H, [m], J = 9.0 Hz), 6.50–6.36 (m, 2H, [M+m]), 4.73 (t, 1H, [M], J = 8.4 Hz), 4.68 (d, 1H, [m], J = 5.2 Hz), 4.60 (d, 1H, [M], J = 5.2 Hz), 4.56 (bd, 1H, [m], J = 5.2 Hz), 4.32 (bd, 2H, [M+m], J = 5.2 Hz), 4.06 (t, 2H, [M+m], J = 8.5 Hz), 3.45–3.37 (m, 2H, [M+m]), 3.28 (s, 3H, [M]), 3.24 (s, 3H, [m]), 1.51 (s, 15H, [M]), 1.48 (s, 15H, [m]). ¹³C NMR (75 MHz, benzene-d₆, 25ºC): δ= 167.1, 164.6, 163.5, 160.6, 160.1, 158.0, 157.0, 156.7, 156.6, 151.7, 151.4, 145.4, 138.5, 138.5, 138.0, 137.4, 137.4, 136.2, 135.6, 135.6, 135.3, 132.8, 132.3, 129.4, 128.1, 124.6, 124.4, 122.6, 122.4, 122.3, 122.0, 119.4, 119.1, 119.0, 114.8, 114.7, 88.8, 88.7, 70.6, 70.3, 64.7, 63.7, 61.9, 61.7, 59.8, 55.1, 8.9. IR (CHCl₃): n= 1758 cm⁻¹. HRMS ESI: m/z: [M-Cl]+ calcd. for C₄₀H₃₉IrN₂O₄: 818,2567 found 818,2624.

**Iridium complex cis-19a.**

Following general procedure, from β-lactam cis-17 (20.0 mg, 47 µmol), [IrCp*Cl₂]₂ (18.8 mg, 23 µmol) and NaOAc (9.0 mg, 110 µmol) in 2.3 mL of CH₂Cl₂ and after
precipitation, a 2.6:1 diastereomeric mixture of cis-19a (35.0 mg, 44 µmol, 94%) was obtained as a yellow solid. $^1$H NMR (300 MHz, benzene-$d_6$, 50°C): δ = 8.94 (d, 1H, [m], J = 2.0 Hz), 8.49 (d, 1H, [m], J = 5.7 Hz), 8.44 (d, 1H, [M], J = 5.6 Hz), 8.19 (dd, 1H, [M], J = 8.4, 2.1 Hz), 7.49 (d, 1H, [M], J = 8.5 Hz), 7.42 (bs, 1H, [m]), 7.35 (d, 1H, [M], J = 2.1 Hz), 7.31–7.10 (m, 7H, [M+m]), 7.02–6.96 (m, 4H, [M+m]), 6.91–6.80 (m, 6H, [M+m]), 6.74 (t, 2H, [M+m], J = 7.3 Hz), 6.65–6.59 (m, 4H, [M+m]), 6.40–6.34 (m, 2H, [M+m]), 5.16 (d, 2H, [M+m], J = 5.0 Hz), 4.82 (d, 1H, [m], J = 5.0 Hz), 4.59 (d, 1H, [M], J = 5.0 Hz), 3.20 (s, 3H, [M]), 3.17 (s, 3H, [M]), 1.56 (s, 15H, [M]), 1.29 (s, 15H, [M]). $^{13}$C NMR (75 MHz, benzene-$d_6$, 50°C): δ = 167.2, 165.9, 165.4, 163.7, 163.3, 160.2, 160.2, 158.0, 151.4, 151.3, 141.3, 141.1, 139.8, 139.3, 136.9, 130.1, 129.9, 129.5, 128.9, 126.4, 126.3, 125.2, 123.9, 122.0, 121.5, 121.3, 118.7, 118.6, 116.2, 116.1, 114.1, 113.3, 111.1, 88.8, 88.5, 81.8, 81.7, 62.1, 61.4, 54.7, 54.6, 8.9, 8.6. IR (CHCl$_3$): ν = 1753 cm$^{-1}$. HRMS ESI: m/z: [M-Cl]$^+$ calcd. for C$_{37}$H$_{36}$IrN$_2$O$_3$: 749.2352, found 749.2381.

Iridium complex trans-19a.

Following general procedure, from β-lactam trans-17 (17.0 mg, 40 µmol), [IrCp*Cl$_2$]$_2$ (15.9 mg, 20 µmol) and NaOAc (7.8 mg, 95 µmol) in 2.0 mL of CH$_2$Cl$_2$ and after precipitation, a 4:1 diastereomeric mixture of trans-19a (29.8 mg, 38 µmol, 95%) was obtained as a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): δ = 8.62 (bd, 2H, [M+m], J = 5.2 Hz), 7.94 (d, 1H, [m], J = 2.1 Hz), 7.73–7.68 (m, 2H, [M+m]), 7.64–7.56 (m, 4H, [M+m]), 7.55–7.51 (m, 2H, [M+m]), 7.46–7.39 (m, 4H, [M+m]), 7.35–7.23 (m, 5H, [M+m]), 7.07–6.96 (m, 8H, [M+m]), 6.94–6.87 (m, 4H, [M+m]), 5.12 (d, 1H, [M], J = 1.7 Hz), 5.11 (d, 1H, [m], J = 1.7 Hz), 5.09 (d, 1H, [M], J = 1.7 Hz), 5.00 (d, 1H, [m], J = 1.7 Hz), 3.85 (s, 3H, [m]), 3.83 (s, 3H, [M]), 1.65 (s, 15H, [m]), 1.50 (s, 15H, [M]). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 166.8, 164.8, 163.4, 163.3, 160.6, 160.6, 157.6, 151.6,
151.5, 141.4, 141.2, 139.3, 138.7, 137.4, 137.3, 130.0, 128.6, 128.4, 128.2, 124.9, 124.7, 124.1, 122.6, 119.1, 115.9, 115.2, 112.9, 89.1, 88.1, 87.7, 64.8, 55.8, 9.3, 9.1. IR (CHCl\(_3\)): \(\nu = 1756\) cm\(^{-1}\). HRMS ESI: \(m/z: [M-Cl]^+\) calcd. for C\(_{37}\)H\(_{36}\)IrN\(_2\)O\(_3\): 749.2352, found 749.2380.

Rhodium complex \(\textit{cis-20b}\).

Following general procedure, from \(\beta\)-lactam \(\textit{cis-18}\) (22.3 mg, 45 \(\mu\)mol), \([\text{RhCp*Cl}_2]_2\) (14.0 mg, 23 \(\mu\)mol) and NaOAc (8.9 mg, 109 \(\mu\)mol) in 2.5 mL of CH\(_2\)Cl\(_2\) and after precipitation, a 3.7:1 diastereomeric mixture of \(\textit{cis-20b}\) (31.0 mg, 40 \(\mu\)mol, 89\%) was obtained as an orange solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.68\) (d, 1H, [m], \(J = 5.6\) Hz), 8.63 (d, 1H, [M], \(J = 5.6\) Hz), 8.28 (d, 1H, [m], \(J = 2.1\) Hz), 7.72–7.60 (m, 6H, [M+m]), 7.55 (d, 1H, [M], \(J = 8.4\) Hz), 7.44–7.32 (m, 11H, [M+m]), 7.28–7.21 (m, 3H, [M+m]), 7.18 (d, 1H, [M], \(J = 2.0\) Hz), 7.12–7.03 (m, 2H, [M+m]), 6.95–6.85 (m, 4H, [M+m]), 6.53 (d, 1H, [m], \(J = 8.3\) Hz), 5.29 (d, 1H, [M], \(J = 5.2\) Hz), 5.15 (d, 1H, [m], \(J = 5.2\) Hz), 4.66 (d, 1H, [m], \(J = 5.2\) Hz), 4.62–4.57 (m, 1H, [m]), 4.59 (d, 1H, [M], \(J = 5.2\) Hz), 4.48 (dd, 1H, [M], \(J = 8.8, 6.9\) Hz), 4.37–4.22 (m, 1H, [m]), 4.28 (t, 1H, [M], \(J = 8.8\) Hz), 4.00 (dd, 2H, [M+m], \(J = 8.8, 6.9\) Hz), 3.83 (s, 3H, [m]), 3.82 (s, 3H, [M]), 1.63 (s, 15H, [m]), 1.37 (s, 15H, [M]). \(^{13}\)C NMR (75 MHz, CDCl\(_3\), [M]): \(\delta = 179.4\) (d, \(J(C, \text{Rh}) = 32.8\) Hz), 164.6, 164.4, 169.8, 160.7, 159.8, 159.4, 157.1, 156.9, 151.0, 140.1, 138.0, 137.0, 137.0, 136.6, 129.4, 129.3, 129.1, 128.9, 128.1, 127.7, 127.5, 127.4, 127.3, 125.0, 124.8, 124.1, 123.5, 121.5, 118.9, 114.2, 114.0, 113.6, 111.7, 96.1 (d, \(J(C, \text{Rh}) = 6.2\) Hz), 95.8 (d, \(J(C, \text{Rh}) = 6.2\) Hz), 70.4, 70.3, 62.7, 62.6, 61.6, 61.0, 59.7, 59.5, 55.3, 55.2, 9.1, 8.8. IR (CHCl\(_3\)): \(\nu = 1754\) cm\(^{-1}\). HRMS ESI: \(m/z: [M-Cl]^+\) calcd. for C\(_{40}\)H\(_{39}\)N\(_3\)O\(_4\)Rh: 728.1990 found 728.1997.
Rhodium complex trans-20b.

Following general procedure, from β-lactam trans-18 (7.8 mg, 16 μmol), [RhCp*Cl₂]₂ (4.9 mg, 8 μmol) and NaOAc (3.1 mg, 37 μmol) in 1.0 mL of CH₂Cl₂ and after precipitation, a 3.4:1 diastereomeric mixture of trans-20b (11.3 mg, 15 μmol, 89%) was obtained as an orange solid. ¹H NMR (300 MHz, CDCl₃): δ= 8.72–8.65 (m, 2H, [M+M]), 7.99 (d, 1H, [M], J = 2.0 Hz), 7.72–7.66 (m, 3H, [M+M]), 7.65–7.55 (m, 2H, [M]), 7.53 (d, 1H, [M], J = 8.4 Hz), 7.50–7.43 (m, 3H, [M+M]), 7.42–7.33 (m, 6H, [M+M]), 7.32–7.24 (m, 2H, [M+M]), 7.15–7.02 (m, 6H, [M+M]), 6.89 (d, 1H, [M], J = 2.1 Hz), 6.87–6.78 (m, 4H, [M+M]), 6.38 (dd, 1H, [M], J = 8.4, 2.1 Hz), 5.12 (dd, 1H, [M], J = 9.0, 6.2 Hz), 5.06 (dd, 1H, [M], J = 9.0, 6.2 Hz), 4.97 (d, 1H, [M], J = 2.4 Hz), 4.92 (d, 1H, [M], J = 2.3 Hz), 4.77 (t, 2H, [M+M], J = 9.0 Hz), 4.45 (dd, 1H, [M], J = 9.0, 6.2 Hz), 4.38 (dd, 1H, [M], J = 9.0, 6.2 Hz), 4.06 (d, 1H, [M], J = 2.4 Hz), 3.96 (d, 1H, [M], J = 2.3 Hz), 3.78 (s, 3H, [M]), 3.75 (s, 3H, [M]), 1.61 (s, 15H, [M]), 1.38 (s, 15H, [M]). ¹³C NMR (75 MHz, CDCl₃): δ= 179.5 (d, J(C, Rh) = 32.7 Hz), 164.5, 164.5, 162.4, 162.3, 160.0, 159.9, 157.3, 157.0, 151.1, 151.0, 140.3, 140.2, 137.9, 137.8, 137.0, 136.6, 136.6, 130.5, 130.0, 129.7, 129.6, 128.3, 128.2, 127.6, 127.5, 127.3, 127.1, 125.6, 124.7, 123.8, 123.4, 121.7, 118.9, 118.8, 114.7, 113.6, 96.1 (d, J(C, Rh) = 6.3 Hz), 95.9 (d, J(C, Rh) = 6.3 Hz), 70.2, 69.9, 69.2, 68.6, 60.0, 58.8, 58.7, 55.4, 55.4, 9.1, 8.8. IR (CH₂Cl₂): ν = 1755 cm⁻¹. HRMS ESI: m/z: [M-Cl]⁺ calcd. for C₄₀H₃₀N₇O₄Rh: 728.1990 found 728.2000.

Iridium complex 23a.

Following general procedure, from β-lactam 21 (15.9 mg, 38 μmol), [IrCp*Cl₂]₂ (15.0 mg, 19 μmol) and NaOAc (7.4 mg, 90 μmol) in 1.9 mL of CH₂Cl₂ and after precipitation, a 4.1:1 diastereomeric mixture of 23a (28.0 mg, 35 μmol, 94%) was
obtained as a yellow solid. Suitable crystals for X-Ray analysis were obtained by CH₂Cl₂/hex crystallization (Figure S1).

**Figure S1.** ORTEP Diagram of 23a. Hydrogen atoms and crystallization CH₂Cl₂ are omitted for clarity. A single molecule extracted from the CIF file is shown. Selected bond distances (Å): Ir(1)–N(2) 2.09(1), Ir(1)–C(9) 2.04(1), Ir(1)–Cl(1) 2.403(5), N(2)–C(14) 1.35(1), C(14)–C(15) 1.46(2), C(9)–C(15) 1.42(2).

¹H NMR (300 MHz, benzene-ᴅ₆, 50ºC): δ = 8.60 (d, 2H, [M+m], J = 5.7 Hz), 8.30 (d, 1H, [m], J = 8.6 Hz), 7.96 (bd, 1H, [M], J = 8.3 Hz), 7.83–7.80 (m, 2H, [M+m]), 7.12–7.01 (m, 10H, [M+m]), 7.00–6.90 (m, 6H, [M+m]), 6.86–6.79 (m, 3H, [M+m]), 6.67–6.62 (m, 1H, [M]), 6.56 (bd, 3H, [M+m], J = 8.2 Hz), 6.51–6.41 (m, 3H, [M+m]), 5.31 (d, 1H, [m], J = 1.6 Hz), 5.15 (s, 2H, [M]), 4.95 (d, 1H, [m], J = 1.6 Hz), 3.24 (s, 3H, [M]), 3.23 (s, 3H, [m]), 1.37 (s, 30H, [M+m]).¹³C NMR (75 MHz, benzene-ᴅ₆, 50ºC):
\[ \delta = 167.5, 166.1, 163.7, 163.6, 160.7, 160.5, 158.3, 158.1, 152.5, 152.3, 137.6, 137.1, 136.9, 135.1, 132.7, 132.2, 130.6, 130.1, 129.9, 129.6, 128.9, 122.7, 122.5, 121.9, 116.6, 116.4, 114.9, 88.9, 88.7, 88.0, 66.5, 54.9, 54.8, 8.7, 8.6 \]

IR (CHCl\(_3\)):
\[ \nu = 1765 \text{ cm}^{-1} \]

HRMS ESI: \( m/z: [M-Cl]^+ \) calcd. for C\(_{37}\)H\(_{36}\)IrN\(_2\)O\(_3\): 749.2356, found 749.2311.

Iridium complex 28a.

Following general procedure, from \( \beta \)-lactam 24 (16.0 mg, 38 \( \mu \)mol), [IrCp*Cl\(_2\)]\(_2\) (15.0 mg, 19 \( \mu \)mol) and NaOAc (7.4 mg, 90 \( \mu \)mol) in 2.0 mL of CH\(_2\)Cl\(_2\) and after precipitation, a 1:1 diastereomeric mixture of 28a (28.2 mg, 36 \( \mu \)mol, 95%) was obtained as a yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)):
\[ \delta = 8.69–8.62 (m, 2H), 7.76–7.56 (m, 8H), 7.42–7.34 (m, 4H), 7.23 (dd, 1H, \( J = 7.9, 1.9 \) Hz), 7.14–7.02 (m, 7H), 6.87–6.69 (m, 10H), 5.58 (d, 2H, \( J = 4.5 \) Hz), 5.38 (d, 1H, \( J = 4.5 \) Hz), 5.35 (d, 1H, \( J = 4.5 \) Hz), 3.73 (s, 3H), 3.72 (s, 3H), 1.59 (s, 15H), 1.54 (s, 15H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)):
\[ \delta = 167.0, 166.9, 165.6, 165.4, 162.9, 162.8, 157.1, 157.0, 156.9, 156.8, 151.9, 151.8, 144.7, 144.4, 137.5, 137.4, 136.2, 136.0, 131.8, 131.0, 130.9, 130.5, 129.4, 126.1, 125.9, 124.4, 122.9, 122.8, 122.7, 122.1, 119.6, 119.5, 119.1, 116.1, 115.8, 114.8, 114.7, 89.0, 88.9, 81.4, 81.1, 62.9, 62.8, 55.8, 9.2, 9.1. \] IR (CHCl\(_3\)):
\[ \nu = 1750 \text{ cm}^{-1} \]

HRMS ESI: \( m/z: [M-Cl]^+ \) calcd. for C\(_{37}\)H\(_{36}\)IrN\(_2\)O\(_3\): 749.2352, found 749.2319.

Rhodium complex 28b.

Following general procedure, from \( \beta \)-lactam 24 (20.2 mg, 48 \( \mu \)mol), [RhCp*Cl\(_2\)]\(_2\) (14.8 mg, 24 \( \mu \)mol) and NaOAc (9.3 mg, 110 \( \mu \)mol) in 2.5 mL of CH\(_2\)Cl\(_2\) and after precipitation, a 1.5:1 diastereomeric mixture of 28b (29.9 mg, 43 \( \mu \)mol, 91%) was obtained as an orange solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)):
\[ \delta = 8.73–8.65 (m, 2H, [M+m]), 7.78–7.62 (m, 7H, [M+m]), 7.56 (d, 1H, [M], \( J = 2.0 \) Hz), 7.52 (d, 1H, [m], \( J\]
= 1.9 Hz), 7.43–7.32 (m, 4H, [M+m]), 7.31–7.26 (m, 1H, [m]), 7.19–7.02 (m, 7H, [M+m]), 6.88–6.68 (m, 9H, [M+m]), 5.58 (d, 2H, [M+m], J = 4.6 Hz), 5.39 (d, 1H, [M], J = 4.6 Hz), 5.36 (d, 1H, [m], J = 4.6 Hz), 3.73 (s, 6H, [M+m]), 1.50 (s, 15H, [M]), 1.45 (s, 15H, [M]).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 180.8 (d, $J(C, Rh)$ = 32.1 Hz), 180.7 (d, $J(C, Rh)$ = 32.0 Hz), 164.6, 162.3, 162.3, 156.6, 156.5, 156.4, 151.4, 151.3, 143.7, 143.4, 137.2, 137.1, 136.8, 136.6, 130.8, 130.7, 130.4, 130.4, 129.3, 129.0, 128.9, 126.6, 126.4, 123.5, 122.1, 122.1, 121.6, 119.4, 119.1, 118.9, 115.4, 115.1, 114.4, 114.3, 96.0 (d, $J(C, Rh)$ = 6.2 Hz), 95.9 (d, $J(C, Rh)$ = 6.2 Hz), 80.7, 80.5, 62.4, 55.4, 9.0, 8.9. IR (CHCl$_3$): $\nu$ = 1751 cm$^{-1}$. HRMS ESI: $m/z$: [M-Cl]$^+$ calcd. for C$_{37}$H$_{36}$N$_2$O$_3$Rh: 659.1775, found 659.1787.

**Ir(1dium complex 29a.**

Following general procedure, from $\beta$-lactam 25 (20.0 mg, 40 $\mu$mol), [IrCp$^*$Cl$_2$]$_2$ (16.2 mg, 20 $\mu$mol) and NaOAc (7.8 mg, 95 $\mu$mol) in 2.0 mL of CH$_2$Cl$_2$ and after precipitation, a 1:1 diastereomeric mixture of 29a (32.4 mg, 38 $\mu$mol, 95%) was obtained as a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.68 (d, 2H, $J$ = 5.7 Hz), 7.88 (d, 1H, $J$ = 7.7 Hz), 7.84 (d, 1H, $J$ = 7.7 Hz), 7.76 (d, 1H, $J$ = 8.1 Hz), 7.70–7.60 (m, 4H), 7.51 (bs, 1H), 7.39–7.32 (m, 5H), 7.31–7.07 (m, 13H), 6.82–6.76 (m, 4H), 5.19 (d, 1H, $J$ = 5.1 Hz), 5.14 (d, 1H, $J$ = 4.9 Hz), 4.75 (d, 1H, $J$ = 5.1 Hz), 4.66 (d, 1H, $J$ = 4.9 Hz), 4.62–4.54 (m, 1H), 4.28 (dd, 1H, $J$ = 8.9, 6.9 Hz), 4.19 (t, 1H, $J$ = 8.9 Hz), 4.12 (t, 1H, $J$ = 8.9 Hz), 3.93 (dd, 1H, $J$ = 8.9, 7.5 Hz), 3.83 (dd, 1H, $J$ = 8.9, 6.9 Hz), 3.74 (s, 3H), 3.74 (s, 3H), 1.70 (s, 15H), 1.70 (s, 15H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 166.6, 166.5, 164.5, 164.3, 160.2, 160.1, 157.5, 157.2, 156.2, 156.2, 151.1, 145.2, 144.9, 137.4, 137.3, 136.7, 136.5, 136.1, 135.9, 131.2, 131.1, 130.0, 129.4, 129.3, 129.2, 129.0, 128.9, 127.6, 127.5, 126.1, 125.9, 122.8, 122.7, 122.6, 122.5, 119.6, 118.7, 118.7, 114.2, 114.1, 88.5, 88.5, 77.0, 70.2, 70.1, 63.2, 62.8, 61.4, 61.3, 59.6,
59.4, 55.4, 8.9, 8.9. IR (CHCl$_3$): $\nu$ = 1755 cm$^{-1}$. HRMS ESI: $m/z$: [M-Cl]$^+$ calcd. for C$_{40}$H$_{39}$Ir$_3$N$_3$O$_4$: 818.2567, found 818.2608.

**Rhodium complex 29b.**

Following general procedure, from $\beta$-lactam 25 (20.0 mg, 40 $\mu$mol), [RhCp*Cl$_2$]$_2$ (12.4 mg, 20 $\mu$mol) and NaOAc (7.8 mg, 95 $\mu$mol) in 2.0 mL of CH$_2$Cl$_2$ and after precipitation, a 1:1 diastereomeric mixture of 29b (27.5 mg, 36 $\mu$mol, 90%) was obtained as an orange solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.72 (d, 2H, $J = 5.5$ Hz), 7.86 (dd, 2H, $J = 9.0, 7.8$ Hz), 7.72–7.48 (m, 6H), 7.52 (bs, 1H), 7.38–7.22 (m, 10H), 7.20–7.06 (m, 8H), 6.79 (d, 2H, $J = 9.1$ Hz), 6.78 (d, 2H, $J = 9.1$ Hz), 5.17 (d, 1H, $J = 5.0$ Hz), 5.14 (d, 1H, $J = 5.0$ Hz), 4.68 (d, 1H, $J = 5.0$ Hz), 4.64 (d, 1H, $J = 5.0$ Hz), 4.60–4.56 (m, 1H), 4.32 (dd, 1H, $J = 8.9, 7.0$ Hz), 4.19 (t, 1H, $J = 8.9$ Hz), 4.11 (t, 1H, $J = 8.9$ Hz), 3.94 (dd, 1H, $J = 8.0, 8.7$ Hz), 3.83 (dd, 1H, $J = 8.9, 7.0$ Hz), 3.73 (s, 6H), 1.64 (s, 15H), 1.64 (s, 15H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 179.9 (d, $J(C, \text{Rh}) = 32.4$ Hz), 179.8 (d, $J(C, \text{Rh}) = 32.4$ Hz), 164.7, 164.6, 160.1, 157.4, 157.1, 156.3, 156.2, 151.1, 144.5, 144.3, 137.4, 137.1, 136.9, 136.6, 136.3, 131.1, 131.0, 129.4, 129.3, 129.2, 129.1, 128.9, 128.8, 127.7, 127.5, 127.1, 126.8, 122.5, 122.4, 122.3, 121.9, 119.8, 119.7, 118.7, 114.2, 114.1, 95.9 (d, $J(C, \text{Rh}) = 6.3$ Hz), 95.8 (d, $J(C, \text{Rh}) = 6.3$ Hz), 70.2, 70.1, 63.1, 62.7, 61.3, 61.2, 59.7, 59.4, 55.4, 9.2, 9.1. IR (CHCl$_3$): $\nu$ = 1751 cm$^{-1}$. HRMS ESI: $m/z$: [M-Cl]$^+$ calcd. for C$_{40}$H$_{39}$N$_3$O$_4$Rh: 728.1990, found 728.2017.

**Iridium complex 30a.**

Following general procedure, from $\beta$-lactam 26 (15.9 mg, 38 $\mu$mol), [IrCp*Cl$_2$]$_2$ (15.0 mg, 19 $\mu$mol) and NaOAc (7.4 mg, 90 $\mu$mol) in 1.9 mL of CH$_2$Cl$_2$ and after precipitation, a 1:1 diastereomeric mixture of 30a (28.0 mg, 35 $\mu$mol, 94%) was obtained as a yellow solid. $^1$H NMR (300 MHz, benzene-$d_6$, 25$^\circ$C): $\delta$ = 8.92 (d, 1H, $J = 2.1$ Hz), 8.44 (dd, 1H, $J = 5.8, 1.4$ Hz), 8.41 (dd, 1H, $J = 5.7, 1.4$ Hz), 8.03 (dd, 1H, $J =$
8.2, 2.1 Hz), 7.95 (d, 1H, J = 8.2 Hz), 7.77 (d, 1H, J = 8.1 Hz), 7.73 (d, 1H, J = 2.1 Hz), 7.66 (d, 1H, J = 8.0 Hz), 7.49–7.43 (m, 3H), 7.33 (d, 2H, J = 8.7 Hz), 7.11–6.84 (m, 11H), 6.76–6.70 (m, 2H), 6.57 (d, 2H, J = 8.7 Hz), 6.54 (d, 2H, J = 8.7 Hz), 6.50–6.40 (m, 2H), 5.31 (d, 1H, J = 4.9 Hz), 5.29 (d, 1H, J = 4.9 Hz), 5.26 (d, 1H, J = 4.9 Hz), 5.13 (d, 1H, J = 4.9 Hz), 3.08 (s, 3H), 3.04 (s, 3H), 1.37 (s, 15H), 1.32 (s, 15H).

$^{13}$C NMR (75 MHz, benzene-$d_6$, 25°C): δ = 166.9, 163.2, 162.9, 160.1, 160.0, 159.4, 159.3, 158.0, 157.9, 151.4, 151.2, 145.8, 145.2, 137.7, 137.2, 136.7, 136.5, 133.9, 133.6, 130.1, 129.9, 129.6, 129.5, 126.2, 125.7, 122.5, 122.4, 122.1, 121.9, 121.2, 119.6, 119.2, 116.1, 114.6, 114.1, 112.9, 88.4, 88.3, 81.7, 81.6, 62.0, 61.5, 54.5, 54.4, 8.8, 8.8. IR (CHCl$_3$): ν = 1748 cm$^{-1}$. HRMS ESI: m/z: [M-Cl]$^+$ calcd. for C$_{37}$H$_{36}$IrN$_2$O$_3$: 749.2352, found 749.2375.

**Rhodium complex 30b.**

Following general procedure, from β-lactam 26 (14.0 mg, 33 µmol), [RhCp*Cl$_2$]$_2$ (10.2 mg, 16 µmol) and NaOAc (6.2 mg, 75 µmol) in 1.5 mL of CH$_2$Cl$_2$ and after precipitation, a 1.3:1 diastereomeric mixture of 30b (21.3 mg, 30 µmol, 93%) was obtained as an orange solid. Suitable crystals for X-Ray analysis were obtained by CH$_2$Cl$_2$/hex crystallization (Figure S2).
**Figure S2.** ORTEP diagram of 30b. Selected bond distances (Å) and angles (°): Rh–N(1) 2.065(4), Rh–Cl(1) 2.405(1), Rh–C(11) 1.973(8), C(6)–C(11) 1.415(9), C(5)–C(6) 1.470(9), C(5)–N(1) 1.36(1), H(2)–C(12)–C(13)–H(13) 6.2(8).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.72 (d, 2H, [M+m], $J$ = 5.6 Hz), 7.96 (d, 1H, [M], $J$ = 2.2 Hz), 7.87 (d, 1H, [m], $J$ = 2.2 Hz), 7.78–7.58 (m, 6H, [M+m]), 7.35 (t, 4H, [M+m], $J$ = 8.5 Hz), 7.24–7.11 (m, 7H, [M+m]), 7.07 (dd, 1H, [m], $J$ = 8.3, 2.3 Hz), 6.99 (dd, 1H, [M], $J$ = 8.3, 2.3 Hz), 6.92 (t, 2H, [M+m], $J$ = 7.4 Hz), 6.87–6.76 (m, 7H, [M+m]), 5.52 (d, 1H, [m], $J$ = 4.7 Hz), 5.51 (d, 1H, [M], $J$ = 4.7 Hz), 5.37 (d, 1H, [M], $J$ = 4.7 Hz), 5.35 (d, 1H, [m], $J$ = 4.7 Hz), 3.77 (s, 3H, [m]), 3.75 (s, 3H, [M]), 1.60 (s, 30H, [M+m]). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 174.3 (d, $J$(C, Rh) = 32.6 Hz), 174.2 (d, $J$(C, Rh) = 32.9 Hz), 164.5, 164.5, 162.9, 162.8, 159.8, 159.7, 157.0, 151.2, 151.2, 144.0, 143.8, 137.2, 137.2, 136.9, 136.8, 133.2, 133.0, 129.5, 129.5, 129.2, 124.9, 124.6, 122.4, 122.0, 119.6, 119.5, 119.3, 115.7, 113.8, 113.8, 113.5, 113.1, 95.9 (d, $J$(C, Rh) =
6.2 Hz), 81.1, 81.0, 61.9, 61.7, 55.2, 9.1. IR (CHCl$_3$): $\nu$= 1749 cm$^{-1}$. HRMS ESI: $m/z$: [M-Cl]$^+$ calcd. for C$_{17}$H$_{36}$N$_2$O$_3$Rh: 659.1775, found 659.1808.

**Iridium complex cis-31a.**

Following general procedure, from $\beta$-lactam cis-27 (15.0 mg, 30 $\mu$mol), [IrCp*Cl$_2$]$_2$ (12.1 mg, 15 $\mu$mol) and NaOAc (5.8 mg, 71 $\mu$mol) in 1.5 mL of CH$_2$Cl$_2$ and after precipitation, a 1:1 diastereomeric mixture of cis-31a (24.0 mg, 28 $\mu$mol, 94%) was obtained as a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$= 8.70–8.66 (m, 2H), 7.98 (d, 1H, $J$ = 2.1 Hz), 7.84 (d, 1H, $J$ = 2.2 Hz), 7.79 (bd, 1H, $J$ = 8.1 Hz), 7.72–7.60 (m, 5H), 7.34–7.30 (m, 6H), 7.21–7.05 (m, 10H), 7.01 (dd, 1H, $J$ = 8.2, 2.2 Hz), 6.88–6.79 (m, 5H), 5.20 (t, 2H, $J$ = 5.5 Hz), 4.80 (d, 1H, $J$ = 5.1 Hz), 4.74 (d, 1H, $J$ = 5.1 Hz), 4.71–4.60 (m, 2H), 4.42–4.33 (m, 2H), 4.06–3.99 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 1.64 (s, 15H), 1.64 (s, 15H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$= 166.5, 166.4, 160.3, 160.3, 159.4, 159.4, 159.1, 159.0, 157.5, 157.5, 151.3, 151.3, 144.5, 144.4, 137.1, 137.0, 136.9, 135.7, 132.9, 132.6, 129.3, 129.3, 129.1, 129.1, 128.8, 128.7, 128.7, 127.6, 127.6, 124.8, 124.6, 122.8, 122.7, 120.0, 119.5, 119.5, 119.3, 114.2, 114.1, 113.7, 113.1, 88.5, 88.5, 70.7, 70.6, 62.9, 62.8, 60.8, 60.7, 59.5, 59.4, 55.2, 8.9, 8.8. IR (CHCl$_3$): $\nu$= 1755 cm$^{-1}$. HRMS ESI: $m/z$: [M-Cl]$^+$ calcd. for C$_{40}$H$_{39}$IrN$_3$O$_4$: 818.2567, found 818.2596.

**Rhodium complex cis-31b.**

Following general procedure, from $\beta$-lactam cis-27 (20.6 mg, 42 $\mu$mol), [RhCp*Cl$_2$]$_2$ (12.9 mg, 21 $\mu$mol) and NaOAc (8.1 mg, 99 $\mu$mol) in 2.0 mL of CH$_2$Cl$_2$ and after precipitation, a 1:1 diastereomeric mixture of cis-31b (29.7 mg, 39 $\mu$mol, 93%) was obtained as an orange solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$= 8.75–8.70 (m, 2H), 7.96 (bs, 1H), 7.80 (d, 1H, $J$ = 2.2 Hz), 7.77–7.60 (m, 6H), 7.36–7.29 (m, 6H), 7.22–7.10 (m, 10H), 7.05 (dd, 1H, $J$ = 8.2, 2.2 Hz), 6.90–6.78 (m, 5H), 5.21 (d, 1H, $J$ = 5.1 Hz), 5.18 (d, 1H, $J$ = 5.1 Hz), 4.79 (d, 1H, $J$ = 5.1 Hz), 4.74 (d, 1H, $J$ = 5.1 Hz), 4.72–4.60 (m,
2H), 4.42–4.32 (m, 2H), 4.07–3.99 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 1.59 (s, 15H), 1.58 (s, 15H). $^1$C NMR (75 MHz, CDCl$_3$): $\delta =$ 174.0 (d, $J$(C, Rh)= 32.7 Hz), 173.9 (d, $J$(C, Rh)= 32.7 Hz), 164.6, 164.6, 164.5, 164.5, 160.4, 160.4, 159.4, 159.4, 157.3, 157.3, 151.2, 151.2, 143.8, 143.8, 137.2, 136.9, 136.8, 136.7, 133.6, 133.3, 129.3, 129.3, 129.1, 128.8, 128.7, 127.5, 127.5, 124.6, 124.4, 122.3, 119.6, 119.5, 119.3, 119.0, 114.1, 114.1, 113.2, 112.7, 95.9 (d, $J$(C, Rh)= 6.2 Hz), 70.6, 70.5, 62.8, 62.8, 60.9, 60.7, 59.5, 59.4, 55.2, 9.1, 9.1. IR (CH$_2$Cl$_2$): $\nu =$ 1768, 1753 cm$^{-1}$. HRMS ESI: $m/z$: [M-Cl]$^+$ calcd. for C$_{40}$H$_{39}$N$_3$O$_4$Rh: 728.1990, found 728.2004.

Iridium complex trans-31a.

Following general procedure, from $\beta$-lactam trans-27 (15.0 mg, 30 $\mu$mol), [IrCp*Cl$_2$)$_2$ (12.1 mg, 15 $\mu$mol) and NaOAc (5.8 mg, 71 $\mu$mol) in 1.5 mL of CH$_2$Cl$_2$ and after precipitation, a 1.3:1 diastereomeric mixture of trans-31a (24.0 mg, 28 $\mu$mol, 94%) was obtained as a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 8.68 (d, 2H, [M+m], $J$ = 5.5 Hz), 7.79 (d, 1H, [M], $J$ = 2.2 Hz), 7.72–7.63 (m, 5H [M+m]), 7.56 (d, 1H [m], $J$ = 8.2 Hz), 7.56 (d, 1H [M], $J$ = 8.2 Hz), 7.45–7.39 (m, 4H, [M+m]), 7.37–7.32 (m, 6H, [M+m]), 7.14–7.04 (m, 6H, [M+m]), 6.85–6.79 (m, 4H, [M+m]), 6.58 (dd, 1H, [m], $J$ = 8.2, 2.2 Hz), 6.49 (dd, 1H, [M], $J$ = 8.2, 2.2 Hz), 5.03 (m, 2H, [M+m]), 4.86 (d, 1H, [m], $J$ = 2.3 Hz), 4.79–4.73 (m, 2H, [M+m]), 4.78 (d, 1H, [M], $J$ = 2.3 Hz), 4.38–4.32 (m, 2H, [M+m]), 4.29 (d, 1H, [M], $J$ = 2.3 Hz), 4.16 (d, 1H, [m], $J$ = 2.3 Hz), 3.77 (s, 3H, [m]), 3.76 (s, 3H, [M]), 1.65 (s, 15H, [M]), 1.64 (s, 15H, [m]). $^1$C NMR (75 MHz, CDCl$_3$): $\delta =$ 166.5, 161.8, 161.8, 159.9, 159.8, 159.3, 159.3, 157.2, 157.1, 151.3, 144.4, 144.3, 138.1, 138.0, 137.1, 137.1, 135.6, 135.5, 131.8, 131.7, 129.6, 129.6, 129.4, 128.0, 127.8, 127.5, 127.5, 127.3, 127.3, 122.7, 120.2, 119.8, 119.3, 119.2, 114.6, 114.5, 114.2, 113.7, 88.5, 88.5, 70.3, 68.6, 68.4, 60.4, 60.3, 59.1, 58.9, 55.3, 8.9, 8.8. IR
(CHCl₃): n = 1754 cm⁻¹. HRMS ESI: m/z: [M-Cl]⁺ calcd. for C₄₀H₃₉Ir₃N₄O₄: 818.2567, found 818.2598.

**Rhodium complex trans-31b.**

Following general procedure, from β-lactam trans-27 (30.8 mg, 63 µmol), [RhCp*Cl₂]₂ (19.1 mg, 31 µmol) and NaOAc (12.0 mg, 147 µmol) in 2.0 mL of CH₂Cl₂ and after precipitation, a 1.3:1 diastereomeric mixture of **trans-31b** (44.3 mg, 57 µmol, 92%) was obtained as an orange solid. ¹H NMR (300 MHz, CDCl₃): δ = 8.72 (d, 2H, [M+m], J = 5.6 Hz), 7.81 (d, 1H, [M], J = 2.2 Hz), 7.77–7.65 (m, 3H, [M+m]), 7.64–7.58 (m, 2H, [M+m]), 7.55 (d, 1H, [m], J = 8.2 Hz), 7.54 (d, 1H, [M], J = 8.2 Hz), 7.46–7.29 (m, 10H, [M+m]), 7.20–7.10 (m, 2H, [M+m]), 7.06 (d, 4H, [M+m], J = 8.5 Hz), 6.82 (m, 4H, [M+m]), 6.64 (dd, 1H, [M], J = 8.2, 2.2 Hz), 6.47 (dd, 1H, [M], J = 8.2, 2.2 Hz), 5.07–4.99 (m, 2H, [M+m]), 4.85 (d, 1H, [m], J = 2.3 Hz), 4.75 (t, 2H, [M+m], J = 9.0 Hz), 4.74 (d, 1H, [M], J = 2.4 Hz), 4.37–4.30 (m, 2H, [M+m]), 4.33 (d, 1H, [M], J = 2.4 Hz), 4.19 (d, 1H, [m], J = 2.3 Hz), 3.77 (s, 3H, [m]), 3.75 (s, 3H, [M]), 1.59 (s, 15H, [M]), 1.58 (s, 15H, [m]). ¹³C NMR (75 MHz, CDCl₃): δ = 174.2 (d, J(C, Rh) = 32.7 Hz), 164.6, 164.5, 164.5, 164.4, 162.0, 161.9, 159.9, 159.8, 157.2, 157.0, 151.3, 151.2, 143.8, 143.6, 138.1, 137.9, 137.2, 137.1, 136.7, 136.6, 136.3, 132.6, 132.4, 129.6, 129.6, 129.4, 129.2, 127.9, 127.7, 127.5, 127.4, 127.3, 127.2, 122.3, 119.6, 119.5, 119.3, 119.1, 114.6, 114.5, 113.8, 113.1, 95.8 (d, J(C, Rh) = 6.0 Hz), 70.3, 70.2, 68.6, 68.3, 60.4, 60.3, 59.2, 58.9, 55.3, 53.4, 9.1, 9.1. IR (CH₂Cl₂): ν = 1742 cm⁻¹. HRMS EI: m/z: [M]⁺ calcd. for C₄₀H₃₉N₃O₄RhCl: 763.1679, found 763.1684.

**Iridium complex 33.**

Following general procedure, from β-lactam 32 (21.9 mg, 50 µmol), [IrCp*Cl₂]₂ (20.0 mg, 25 µmol) and NaOAc (9.7 mg, 118 µmol) in 2.5 mL of CH₂Cl₂ and after precipitation, a 20:1 diastereomeric mixture of **33** (36.0 mg, 45 µmol, 90%) was
obtained as a yellow solid. Pure major isomer (30 mg, 37 µmol, 74%) was obtained by MeOH disgregation of the mixture and collection of the solid by filtration. mp > 250ºC (CH₂Cl₂/Hex). ¹H NMR (300 MHz, CDCl₃, [M]): δ= 8.78 (dd, 1H, J = 5.7, 1.6 Hz), 8.02 (d, 1H, J = 8.3 Hz), 7.75–7.61 (m, 3H), 7.39–7.21 (m, 5H), 7.17–7.06 (m, 1H), 7.10–6.99 (m, 1H), 6.86 (d, 1H, J = 7.8 Hz), 6.65 (d, 2H, J = 9.0 Hz), 6.12 (d, 1H, J = 5.1 Hz), 5.62 (d, 1H, J = 5.1 Hz), 3.61 (s, 3H), 2.66 (s, 3H), 1.50 (s, 15H).

⁴C NMR (75 MHz, CDCl₃, [M]): δ= 168.8, 167.2, 164.2, 157.9, 156.0, 152.8, 143.7, 137.2, 136.3, 135.0, 130.2, 130.0, 129.5, 127.2, 122.0, 121.8, 121.4, 120.3, 116.3, 113.7, 89.2, 81.4, 65.0, 55.2, 23.7, 8.8. IR (CH₂Cl₂, [M]): ν= 1739 cm⁻¹. HRMS EI: m/z calcd. for [M]⁺ (C₃₇H₃₈ClIrN₂O₃): 798.2195, found 798.2199.


Iridium complex 37a. Following the general procedure, from 16a (50.0 mg, 58 µmol) and methyl 2-hexynoate (9.6 mg, 76 µmol), a crude 1:1 mixture of diastereomers 37aa and 37ab was obtained. After washing with hexanes and purification by SiO₂ chromatography (Hex/EtOAc 2:3), pure 37aa (18 mg, 18 µmol, 31%) and 37ab (22 mg, 22 µmol, 39%) were obtained as yellow solids. Additionally, a fraction containing both isomers (12 mg, 12 µmol, 21%) was also recovered.

37aa. mp > 250ºC (CH₂Cl₂/Hex). [α]D²⁵ = -120° (c = 0.5, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ= 9.46 (d, 1H, J= 5.9 Hz), 7.76 (td, 1H, J = 7.7, 1.7 Hz), 7.59 (d, 1H, J = 1.9 Hz), 7.50–7.40 (m, 4H), 7.36–7.15 (m, 6H), 7.02 (d, 1H, J = 8.0 Hz), 6.78 (d, 2H, J = 9.0 Hz), 5.25 (d, 1H, J = 5.2 Hz), 4.65 (d, 1H, J = 5.2 Hz), 4.59 (t, 1H, J = 8.3 Hz), 4.29 (t, 1H, J = 8.8 Hz), 4.05 (t, 1H, J = 8.3 Hz), 3.75 (s, 3H), 3.68 (s, 3H), 2.96–2.80 (m, 1H), 2.66–2.51 (m, 1H), 1.28 (s, 15H), 1.23–1.09 (m, 2H), 0.69 (t, 3H, J = 7.3 Hz). ⁴C NMR (75 MHz, CDCl₃): δ= 163.6, 159.9, 156.7, 156.4, 155.5, 146.0, 143.7, 139.4,
137.9, 136.1, 133.8, 133.5, 130.7, 129.7, 128.3, 127.5, 126.8, 125.1, 124.0, 118.5, 114.2, 88.0, 70.4, 62.5, 61.1, 60.3, 55.5, 49.6, 40.1, 23.5, 13.7, 8.5.

IR (CHCl$_3$): $\nu$= 1756, 1690 cm$^{-1}$. HRMS ESI: $m/z$: [M-Cl]$^{+}$ calcd. for C$_{47}$H$_{49}$N$_3$O$_6$Ir: 944.3248 found 944.3291.

37ab. mp > 250ºC (CH$_2$Cl$_2$/Hex). $[\alpha]_D^{25} = +182^\circ$ (c = 0.3 in CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$= 9.47 (d, 1H, $J = 5.9$ Hz), 7.78–7.69 (m, 1H), 7.64 (d, 1H, $J = 1.9$ Hz), 7.51–7.35 (m, 6H), 7.33–7.22 (m, 3H), 7.22–7.16 (m, 1H), 7.12 (d, 1H, $J = 7.9$ Hz), 6.83–6.76 (m, 2H), 5.22 (d, 1H, $J = 5.2$ Hz), 4.67–4.57 (m, 2H), 4.37 (t, 1H, $J = 8.8$ Hz), 4.08 (dd, 1H, $J = 8.8, 7.3$ Hz), 3.76 (s, 3H), 3.64 (s, 3H), 2.97–2.82 (m, 1H), 2.39–2.27 (s, 1H), 1.21 (s, 15H), 1.18–1.02 (m, 2H), 0.64 (t, 3H, $J = 7.3$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$= 163.8, 160.1, 156.5, 156.3, 155.5, 139.4, 137.6, 136.4, 133.8, 133.6, 130.9, 130.4, 129.8, 129.7, 129.2, 128.8, 127.4, 126.7, 124.8, 123.9, 118.8, 114.4, 88.0, 70.3, 62.6, 61.5, 60.4, 55.5, 39.3, 23.7, 13.5, 8.5. IR (CHCl$_3$): $\nu$= 1756, 1690 cm$^{-1}$.

HRMS ESI: $m/z$: [M-Cl]$^{+}$ calcd. for C$_{47}$H$_{49}$N$_3$O$_6$Ir: 944.3248 found 944.3291.

Rhodium complex 37b.

Following the general procedure, from 16b (37.0 mg, 48 mmol) and methyl-2-hexynoate (7.9 mg, 63 µmol), a crude 1.5:1 mixture of diastereomers 37ba and 37bb was obtained. After washing with hexanes and purification by SiO$_2$ chromatography (Hex/EtOAc 2:3), pure 37ba (20 mg, 22 µmol, 46%) and 37bb (18 mg, 20 µmol, 41%) were obtained as orange solids.

37ba. mp>250ºC (CH$_2$Cl$_2$/Hex). $[\alpha]_D^{25} = -154.1^\circ$ (c = 0.8, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$= 9.56 (bd, 1H, $J = 5.9$ Hz), 7.78 (td, 1H, $J = 7.7, 1.7$ Hz), 7.63 (d, 1H, $J = 1.9$ Hz), 7.50–7.40 (m, 4H), 7.36–7.29 (m, 2H), 7.29–7.22 (m, 3H), 7.19 (bd, 1H, $J = 8.0$ Hz), 7.08 (d, 1H, $J = 8.0$ Hz), 6.78 (d, 2H, $J = 9.0$ Hz), 5.27 (d, 1H, $J = 5.2$ Hz), 4.68 (d, 1H, $J = 5.2$ Hz), 4.61 (t, 1H, $J = 8.2$ Hz), 4.31 (t, 1H, $J = 8.9$ Hz), 4.06 (dd, 1H, $J = 9.0$, 8.9 Hz).
7.8 Hz), 3.75 (s, 3H), 3.67 (s, 3H), 2.79–2.69 (m, 1H), 2.68–2.55 (m, 1H), 1.28 (s, 15H), 1.22–1.01 (m, 2H), 0.64 (t, 3H, J = 7.3 Hz). 13C NMR (75 MHz, CDCl3): δ = 163.1, 159.9, 156.7, 156.4, 155.5, 155.1, 144.4, 138.8, 137.7, 137.1, 136.1, 133.9, 133.6, 130.6, 129.7, 128.5, 127.6, 126.6, 125.2, 123.3, 118.5, 114.3, 95.8 (d, J(C, Rh)= 6.8 Hz), 70.4, 62.5, 61.0, 60.3, 55.5, 49.8, 40.6, 22.8, 13.6, 8.7. IR (CHCl3): ν = 1757, 1692 cm⁻¹. HRMS ESI: m/z: [M-Cl]⁺ calcd. for C47H49N3O6Rh: 854.2671, found 854.2695. 37bb. mp>250ºC (CH2Cl2/Hex). [α]D²⁵ = +325.6º (c = 0.5, CHCl3). 1H NMR (300 MHz, CDCl3): δ = 9.57 (bd, 1H, J = 6.0 Hz), 7.76 (td, 1H, J = 7.7, 1.6 Hz), 7.71 (d, 1H, J = 1.8 Hz), 7.52–7.35 (m, 6H), 7.32–7.21 (m, 4H), 7.19 (d, 1H, J = 8.0 Hz), 6.80 (d, 2H, J = 9.0 Hz), 5.23 (d, 1H, J = 5.2 Hz), 4.66–4.55 (m, 2H), 4.36 (t, 1H, J = 8.8 Hz), 4.08 (dd, 1H, J = 8.9, 7.2 Hz), 3.75 (s, 3H), 3.62 (s, 3H), 2.85–2.69 (m, 1H), 2.45–2.29 (m, 1H), 1.19 (s, 15H), 1.03–0.92 (m, 2H), 0.60 (t, 3H, J = 7.3 Hz). 13C NMR (75 MHz, CDCl3): δ = 163.3, 160.2, 156.6, 156.4, 155.3, 145.2, 138.9, 137.6, 136.5, 133.9, 133.7, 130.4, 129.9, 129.8, 129.5, 127.5, 126.7, 125.2, 123.4, 119.0, 114.5, 95.8 (d, J(C, Rh)= 6.7 Hz), 70.4, 62.7, 61.5, 60.5, 55.6, 49.8, 39.9, 23.2, 13.5, 8.8. IR (CHCl3): ν = 1757, 1692 cm⁻¹. HRMS ESI: m/z: [M-Cl]⁺ calcd. for C47H49N3O6Rh: 854.2671, found 854.2676.

Iridium complex 38a.

Following the general procedure, a methanolic (8.0 mL) solution of 16a (29.0 mg, 34 µmol) was bubbled with CO at rt for 15 min and then stirred for 10 h. Evaporation of the solvent yielded a 1.6:1 mixture of diastereomers (29.1 mg, 33 µmol, 97%). Attempts to purify these mixtures were unsuccessful. 1H NMR (300 MHz, CDCl3): δ= 8.93 (d, 1H, J = 5.3 Hz, [m]), 8.84 (d, 1H, J = 5.3 Hz, [M]), 8.39 (d, 1H, J = 7.8 Hz, [M]), 8.26–8.04 (m, 4H, [M+m]), 7.90 (d, 1H, J = 7.9 Hz, [m]), 7.81 (bs, 1H, [M]), 7.76–7.65 (m,
2H, [M+m]), 7.60 (bs, 1H, [m]), 7.48–7.19 (m, 16H, [M+m]), 6.92–6.65 (m, 4H, [M+m]), 5.50 (d, 1H, J = 5.4 Hz, [m]), 5.26 (d, 1H, J = 5.1 Hz, [M]), 5.05 (dd, 1H, J = 8.8, 6.2 Hz, [m]), 4.84 (d, 1H, J = 5.4 Hz, [m]), 4.61 (bs, 1H, [M]), 4.41 (m, 2H, [M+m]), 4.17 (t, 1H, J = 8.5 Hz, [M]), 4.02 (dd, 1H, J = 8.8, 6.3 Hz, [m]), 3.93 (t, 1H, J = 8.1 Hz, [M]), 3.76 (s, 3H, [m]), 3.73 (s, 3H, [M]), 1.94 (s, 15H, [m]), 1.75 (s, 15H, [M]).

**Rhodium complex 38b.**

Following the general procedure, a methanolic (9.0 mL) solution of 16b (35.6 mg, 46 µmol) was bubbled with CO at rt for 15 min and then stirred for 10 h. Evaporation of the solvent yielded a 2:1 mixture of diastereomers (35 mg, 44 µmol, 95%). Attempts to purify these mixtures were unsuccessful. 

$^1$H NMR (300 MHz, CDCl$_3$): δ = 8.81 (bs, 1H, [m]), 8.69 (d, 1H, J = 5.1 Hz, [M]), 8.36 (d, 1H, J = 7.9 Hz, [M]), 8.21–8.07 (m, 4H, [M+m]), 7.91–7.47 (m, 6H, [M+m]), 7.48–7.25 (m, 13H), 7.22–7.05 (m, 2H, [M+m]), 6.82 (d, 4H, J = 8.6 Hz, [M+m]), 5.51 (d, 1H, J = 5.4 Hz, [m]), 5.29 (d, 1H, J = 5.2 Hz, [M]), 5.09 (dd, 1H, J = 8.9, 6.1 Hz, [m]), 4.89 (d, 1H, J = 5.3 Hz, [m]), 4.60 (bs, 1H, [M]), 4.50–4.37 (m, 2H, [M+m]), 4.24–4.08 (m, 1H, [M]), 4.08–3.99 (m, 1H, [m]), 3.92 (t, 1H, J = 8.1 Hz), 3.75 (s, 3H, [m]), 3.74 (s, 3H, [M]), 1.85 (s, 15H, [m]), 1.64 (s, 15H, [M]).

**References and Notes.**

---

