

Supplementary information for

**Synthesis of Bis(σ -aryl)dirhodium(III) Caprolactamates by
Oxidative Arylation With Arylboronic Acids**

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General: All reagents and solvents were used without further purification. Yields reported are those obtained after chromatography on silica gel (SiliCycle, 60A, 40-63 mesh), unless otherwise noted. The preparation of dirhodium(II) caprolactamate $[\text{Rh}_2(\text{cap})_4(\text{CH}_3\text{CN})_2]$ has been previously described.¹ ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker DRX-400 NMR as solutions in CDCl_3 unless otherwise noted. Chemical shifts are reported in parts per million (ppm, δ) downfield from Me_4Si (TMS); coupling constants are reported in Hertz (Hz). UV/Visible spectra were obtained on a Varian Cary 50 spectrophotometer using a xenon flash lamp. IR spectra were recorded on a JASCO FT/IR 4100 spectrometer. Mass spectra were recorded at high resolution with either a VG Micromass 70/70H or VG ZAB-E spectrometer.

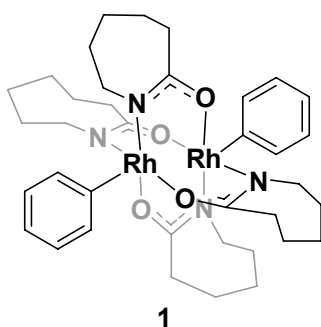
Experimental procedure:

General procedure A: $\text{Rh}_2(\text{cap})_4(\text{MeCN})_2$ (20.0 mg, 0.027 mmol) and $[\text{Cu}(\text{OTf})_2]\cdot\text{C}_6\text{H}_6$ (1.5 mg, 3.0 μmol) were dissolved in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1.5 mL, 4:1) and sonicated for 5 min. This purple solution was then added dropwise to a stirring solution of boronic acid (0.15 – 0.30 mmol) and NaOMe (16.2 mg, 0.30 mmol) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1.5 mL, 4:1). An additional 2 mL of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (4:1) was used to transfer the purple solution and bring the final reaction volume to 5 mL. After

having stirred at room temperature for 10 min, the color of the generated reaction solution changed from purple to green (or orange). With continued stirring for 8–18 h, the reaction was complete (determined by TLC using CH₂Cl₂ or CH₂Cl₂/acetone = 98:2). The solvent was removed under reduced pressure to yield a green (or orange) residue. The residue was purified by chromatography on silica gel. The products were identified spectroscopically.

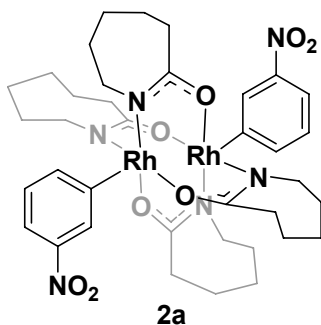
General procedure B: CuSO₄·5H₂O (0.75 mg, 3 μmol) was dissolved in 1 mL MeOH, and this solution was added to the mixture of Rh₂(cap)₄(MeCN)₂ (22.1 mg, 0.03 mmol), NaOMe (16.2 mg, 0.30 mmol) and arylboronic acid (0.15 – 0.30 mmol) in 4 mL CH₂Cl₂. The generated purple reaction solution was stirred at room temperature for 6–20 hrs to complete the reaction (determined by TLC, CH₂Cl₂ or CH₂Cl₂/acetone = 98:2). The solvents were then removed under reduced pressure, and the green solid residue was purified by chromatography on silica gel using CH₂Cl₂ or CH₂Cl₂/acetone as the eluent. The products were identified spectroscopically.

***Bis-σ*-(phenyl) tetrakis-μ**-(caprolactamato)dirhodium(III) (**1**):²



Green solid. ¹H NMR (400 MHz, CDCl₃): δ 7.54 (comp, 4H), 7.12 (comp, 6H), 3.10–3.00 (comp, 8H), 2.53–2.38 (comp, 8H), 1.83 (comp, 4H), 1.70–1.45 (comp, 20H). ¹³C NMR (100 MHz, CDCl₃): δ 183.7, 148.0 (d, *J* = 37.0 Hz), 137.1, 126.1, 124.0, 51.4, 38.6, 30.7, 29.8, 24.3.

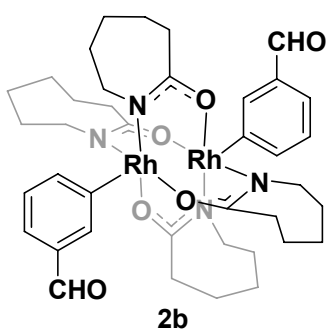
***Bis-σ*-(3-nitrophenyl)-tetrakis-μ**-(caprolactamato)dirhodium(III) (**2a**):



Green solid. ¹H NMR (400 MHz, CDCl₃): δ 8.38 (s, 2H), 8.04 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 3.05–2.94 (comp, 8H), 2.54–2.41 (comp,

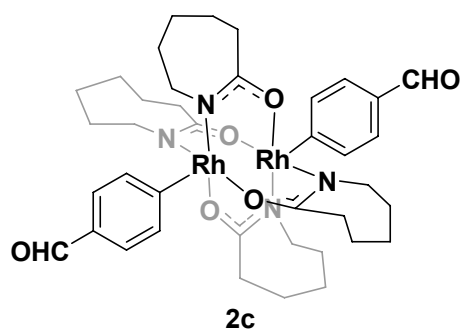
8H), 1.88 (comp, 4H), 1.79–1.53 (comp, 12H), 1.56–1.43 (comp, 8H). ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{MeOD}$, 4:1): δ 184.6, 145.6, 143.4, 141.4 (d, $J = 14.2$ Hz), 131.2, 126.1, 119.9, 51.9, 39.0, 30.7, 29.6, 24.4. UV/Visible (CH_2Cl_2): 423 nm ($\epsilon = 6440 \text{ M}^{-1}\text{cm}^{-1}$). IR (neat): 1340, 1512, 1584 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{36}\text{H}_{49}\text{N}_6\text{O}_8\text{Rh}_2$ ($[\text{M}+\text{H}]^+$): 899.1722; found: 899.1691.

Bis- σ -(3-formylphenyl)-tetrakis- μ -(caprolactamato)dirhodium (III) (2b):



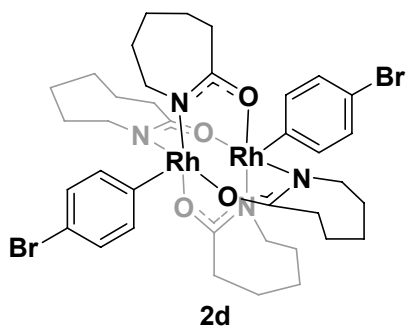
Green solid. ^1H NMR (400 MHz, CDCl_3): δ 10.00 (s, 2H), 8.08 (s, 2H), 7.87 (d, $J = 7.6$ Hz, 2H), 7.67 (d, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 3.02–2.93 (comp, 8H), 2.53–2.42 (comp, 8H), 1.88 (comp, 4H), 1.67–1.46 (comp, 20H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.8, 184.5, 148.3 (d, $J = 37.0$ Hz), 143.9, 139.2, 127.1, 126.0, 52.1, 39.2, 31.1, 30.2, 24.8. UV/Visible (CH_2Cl_2): 425 nm ($\epsilon = 4090 \text{ M}^{-1}\text{cm}^{-1}$). IR (neat): 1589 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{38}\text{H}_{50}\text{N}_4\text{O}_6\text{Rh}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 887.1738; found: 887.1263.

Bis- σ -(4-formylphenyl)-tetrakis- μ -(caprolactamato)dirhodium(III) (2c):



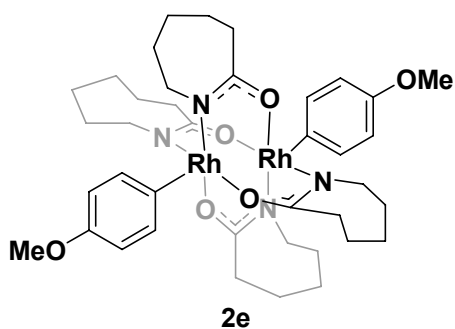
Green solid. ^1H NMR (400 MHz, CDCl_3): δ 10.03 (s, 2H), 7.80 (d, $J = 8.4$ Hz, 4H), 7.61 (d, $J = 8.4$ Hz, 4H), 2.90 (comp, 8H), 2.53–2.38 (comp, 8H), 1.85 (comp, 4H), 1.68–1.43 (comp, 20H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.1, 184.1, 161.4 (d, $J = 37.0$ Hz), 137.6, 133.6, 126.4, 51.5, 38.6, 30.5, 29.6, 24.2. UV/Visible (CH_2Cl_2): 422 nm ($\epsilon = 7890 \text{ M}^{-1}\text{cm}^{-1}$). IR (neat): 1564, 1690 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{38}\text{H}_{51}\text{N}_4\text{O}_6\text{Rh}_2$ ($[\text{M}+\text{H}]^+$): 865.1919; found: 865.1931.

Bis- σ -(4-bromophenyl)-tetrakis- μ -(caprolactamato)dirhodium(III) (2d):



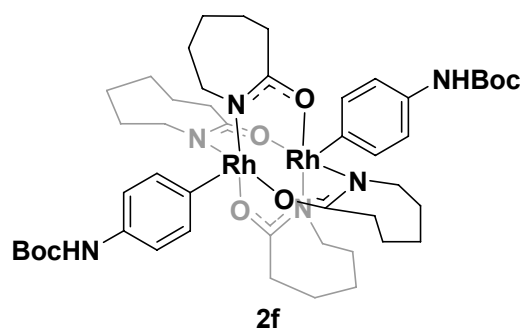
Green solid. This compound was insoluble in all NMR solvents to the extent that NMR spectra were not obtained. UV/Visible (CH₂Cl₂): 432 nm ($\epsilon = 7970 \text{ M}^{-1}\text{cm}^{-1}$). IR (neat): 1340, 1512, 1584 cm⁻¹. HRMS (ESI): Calcd for C₃₆H₄₈Br₂N₄O₄Rh₂Na ([M+Na]⁺): 989.0030; found: 988.9886.

Bis-σ-(4-methoxyphenyl)-tetrakis-μ-(caprolactamato)dirhodium(III) (2e):



Green solid. ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, $J = 8.8 \text{ Hz}$, 4H), 6.82 (d, $J = 8.8 \text{ Hz}$, 4H), 3.86 (s, 6H), 3.08–2.95 (comp, 8H), 2.50–2.37 (comp, 8H), 1.84 (comp, 4H), 1.62–1.55 (comp, 12H), 1.55–1.42 (comp, 8H). ¹³C NMR (100 Hz, CDCl₃): δ 183.4, 157.7, 136.8, 134.2 (d, $J = 38.7 \text{ Hz}$), 112.0, 55.2, 51.3, 38.5, 30.6, 29.7, 24.3. UV/Visible (CH₂Cl₂): 452 nm ($\epsilon = 6220 \text{ M}^{-1}\text{cm}^{-1}$). IR (neat): 1231, 1588 cm⁻¹. HRMS (ESI): Calcd for C₃₈H₅₅N₄O₆Rh₂ ([M+H]⁺): 869.2232; found: 869.2226.

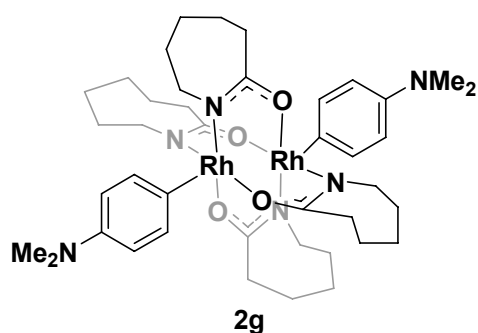
Bis-σ-{4-(tert-butylcarbamato)phenyl}-tetrakis-μ-(caprolactamato)-dirhodium(III) (2f):



Yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, $J = 8.4 \text{ Hz}$, 4H), 7.17 (d, $J = 8.4 \text{ Hz}$, 4H), 6.44 (s, 2H), 3.06–2.92 (comp, 8H), 2.47–2.35 (comp, 8H), 1.80 (comp, 4H), 1.65–1.37 (comp, 38H). ¹³C NMR (100 MHz, CDCl₃): δ 183.4, 152.7, 138.2 (d, $J = 39.0 \text{ Hz}$), 136.2, 134.7, 117.1, 79.6, 51.1, 38.4, 30.3, 29.3, 28.0, 24.0.

UV/Visible (CH₂Cl₂): 450 nm ($\epsilon = 12600 \text{ M}^{-1}\text{cm}^{-1}$). IR (neat): 2923, 1727, 1586, 1496 cm⁻¹. HRMS (ESI): Calcd for C₄₆H₆₉N₆O₈Rh₂ ([M+H]⁺): 1039.3209; found: 1039.3290.

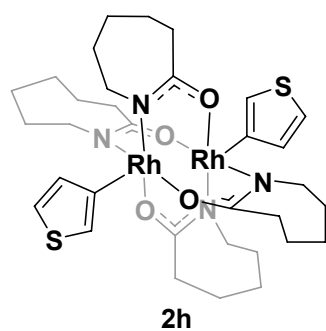
***Bis- σ* -{4-(*N,N*-dimethylanimo)phenyl}-*tetrakis- μ* -(caprolactamato)dirhodium(III) (2g):**



Purple solid. ¹H NMR (400 MHz, CDCl₃): δ 7.35 (d, $J = 8.8$ Hz, 4H), 6.72 (d, $J = 8.8$ Hz, 4H), 3.12–2.96 (comp, 8H), 2.98 (s, 12 H), 2.46–2.36 (comp, 8H), 1.82 (comp, 4H), 1.61–1.37 (comp, 20H). ¹³C NMR (100 MHz, CDCl₃): δ 183.6, 148.8, 136.4, 131.4 (d, $J = 37.6$ Hz), 112.9, 51.5,

41.6, 38.9, 30.8, 29.9, 24.5. UV/Visible (CH₂Cl₂): 485 nm ($\epsilon = 3050 \text{ M}^{-1}\text{cm}^{-1}$). IR (neat): 1589 cm⁻¹. HRMS (ESI): Calcd for C₄₀H₆₁N₆O₄Rh₂ ([M+H]⁺): 895.2864; found: 895.2848.

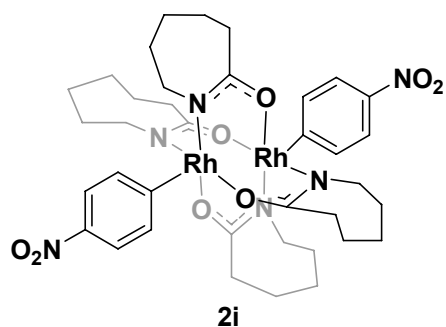
***Bis- σ* -(3-thienyl)-*tetrakis- μ* -(caprolactamato)dirhodium(III) (2h).**



Yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, $J = 4.8$ Hz, 2H), 7.33 (dd, $J = 4.8, 3.2$ Hz, 2H), 7.11 (d, $J = 3.2$ Hz, 2H), 3.08–2.97 (comp, 8H), 2.53–2.37 (comp, 8H), 1.86 (comp, 4H), 1.63–1.55 (comp, 12H), 1.54–1.39 (comp, 8H). ¹³C NMR (100 MHz, CDCl₃/MeOD, 4:1): δ 184.2, 133.3, 127.8 (d, $J = 39.2$ Hz), 120.5, 119.8, 52.1,

39.3, 31.2, 30.2, 24.9. UV/Visible (CH₂Cl₂): 457 nm ($\epsilon = 5890 \text{ M}^{-1}\text{cm}^{-1}$). IR (neat): 442, 1585 cm⁻¹. HRMS (ESI): Calcd for C₃₂H₄₇N₄O₄S₂Rh₂ ([M+H]⁺): 821.1149; found: 821.1181.

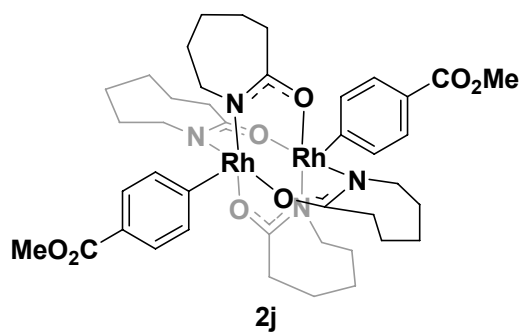
***Bis- σ* -(4-nitrophenyl)-*tetrakis- μ* -(caprolactamato)dirhodium(III) (2i):**



Green solid. ^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, $J = 8.8$ Hz, 4H), 7.76 (d, $J = 8.8$ Hz, 4H), 2.93 (comp, 8H), 2.51–2.37 (comp, 8H), 1.83 (comp, 4H), 1.65–1.38 (comp, 20H). This compound was insoluble in all NMR solvents to the extent that its ^{13}C NMR spectrum was not obtained. UV/Visible (CH_2Cl_2): 415 nm ($\epsilon = 8850 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (ESI): Calcd for $\text{C}_{36}\text{H}_{48}\text{N}_6\text{O}_8\text{Rh}_2$ (M^+): 898.1644; found: 898.1675.

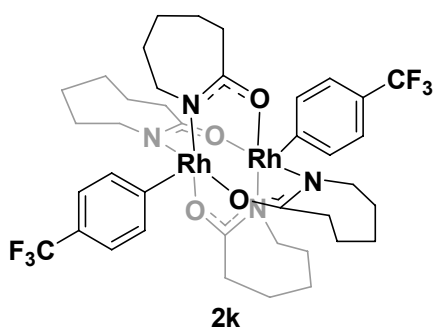
Bis-σ-(4-methoxycarbonylphenyl)-tetrakis-μ-(caprolactamato)dirhodium(III)

(2j):



Green solid. ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 8.4$ Hz, 4H), 7.65 (d, $J = 8.4$ Hz, 4H), 3.91 (s, 6H), 2.92 (comp, 8H), 2.42 (comp, 8H), 1.80 (comp, 4H), 1.58–1.39 (comp, 20H). ^{13}C NMR (100 MHz, CDCl_3): δ 184.3, 168.1, 157.6 (d, $J = 36.6$ Hz), 136.9, 126.9, 126.4, 51.8, 51.6, 38.9, 30.7, 29.8, 24.4. UV/Visible (CH_2Cl_2): 425 nm ($\epsilon = 8170 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (ESI): Calcd for $\text{C}_{40}\text{H}_{54}\text{N}_4\text{O}_8\text{Rh}_2$ (M^+): 924.2050; found: 924.2090.

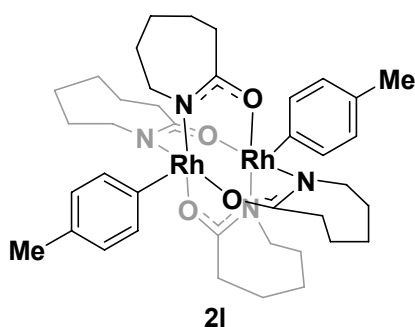
Bis-σ-(4-trifluoromethylphenyl)-tetrakis-μ-(caprolactamato)dirhodium(III) (2k):



Green solid. ^1H NMR (400 MHz, CDCl_3): δ 7.65 (d, $J = 8.4$ Hz, 4H), 7.35 (d, $J = 8.4$ Hz, 4H), 2.95 (comp, 8H), 2.51–2.35 (comp, 8H), 1.81 (comp, 4H), 1.62–1.38 (comp, 20H). ^{13}C

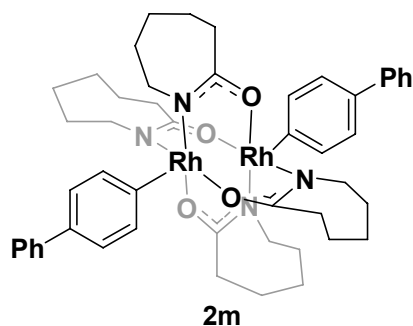
NMR (100 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$, 1:1): δ 184.0, 167.9 (d, $J = 23.3$ Hz), 154.5, 142.9, 137.4, 121.8 (q, $J = 3.2$ Hz), 51.4, 38.2, 30.6, 29.9, 29.8. UV/Visible (CH_2Cl_2): 420 nm ($\epsilon = 4160 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (ESI): Calcd for $\text{C}_{38}\text{H}_{49}\text{F}_6\text{N}_4\text{O}_4\text{Rh}_2$ ($[\text{M}+\text{H}]^+$): 945.1768; found: 945.1784.

Bis- σ -(4-methylphenyl)-tetrakis- μ -(caprolactamato)dirhodium(III) (2l):



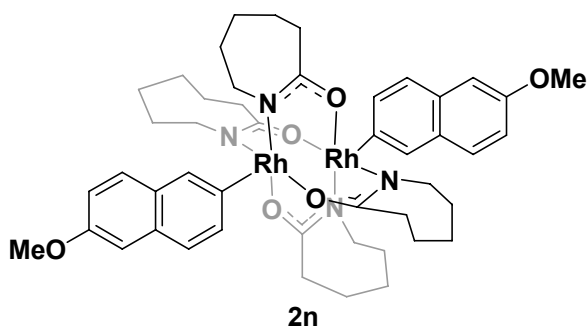
Green solid. ^1H NMR (400 MHz, CDCl_3): δ 7.37 (d, $J = 8.4$ Hz, 4H), 6.94 (d, $J = 8.4$ Hz, 4H), 3.08–2.90 (comp, 8H), 2.47–2.38 (comp, 14H), 1.80 (comp, 4H), 1.65–1.36 (comp, 20H). ^{13}C NMR (100 MHz, CDCl_3): δ 183.8, 142.8 (d, $J = 37.0$ Hz), 136.6, 133.4, 127.3, 51.5, 38.8, 30.8, 29.8, 24.4, 20.6. UV/Visible (CH_2Cl_2): 440 nm ($\epsilon = 8060 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (ESI): Calcd for $\text{C}_{38}\text{H}_{55}\text{N}_4\text{O}_4\text{Rh}_2$ ($[\text{M}+\text{H}]^+$): 837.2333; found: 837.2370.

Bis- σ -(4-phenylphenyl)-tetrakis- μ -(caprolactamato)dirhodium(III) (2m):



Green solid. ^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J = 7.2$ Hz, 4H), 7.61 (d, $J = 8.4$ Hz, 4H), 7.43 (t, $J = 7.2$ Hz, 4H), 7.36 (d, $J = 8.4$ Hz, 4H), 7.29 (t, $J = 7.2$ Hz, 2H), 3.05 (comp, 8H), 2.45 (comp, 8H), 1.83 (comp, 4H), 1.68–1.42 (comp, 20H). ^{13}C NMR (100 MHz, CDCl_3): δ 184.0, 156.2, 146.6 (d, $J = 37.0$ Hz), 143.7, 137.3, 127.8, 126.5, 125.1, 113.9, 51.7, 38.9, 30.8, 29.7, 24.5. UV/Visible (CH_2Cl_2): 440 nm ($\epsilon = 130 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (ESI): Calcd for $\text{C}_{48}\text{H}_{59}\text{N}_4\text{O}_4\text{Rh}_2$ ($[\text{M}+\text{H}]^+$): 961.2646; found: 961.2693.

Bis- σ -(6-methoxynaphthalen-2-yl)-tetrakis- μ -(caprolactamato)dirhodium(III) (2n):



Green solid. ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, $J = 1.2$ Hz, 2H), 7.74–7.70 (comp, 4H), 7.51 (d, $J = 1.2$ Hz, 2H), 7.18 (d, $J = 2.4$ Hz, 2H), 7.07 (dd, $J = 8.8, 2.4$ Hz, 2H), 3.93 (s, 6H), 3.10–2.90 (comp, 8H), 2.45 (comp, 8H),

1.83 (comp, 4H), 1.72–1.41 (comp, 20H). ^{13}C NMR (100 MHz, CDCl_3): δ 184.0, 156.5, 135.8, 134.5, 132.8 (d, $J = 36.9$ Hz), 128.5, 127.8, 123.8, 117.3, 113.9, 105.5, 55.3, 51.6, 38.9, 30.8, 29.7, 24.5. UV/Visible (CH_2Cl_2): 455 nm ($\epsilon = 6120 \text{ M}^{-1}\text{cm}^{-1}$). HRMS (ESI): Calcd for $\text{C}_{46}\text{H}_{59}\text{N}_4\text{O}_6\text{Rh}_2$ ($[\text{M}+\text{H}]^+$): 969.2545; found: 969.2552.

References:

1. M. P. Doyle, L. J. Westrum, W. N. E. Wolthuis, M. M. See, W. P. Boone, V. Bagheri, and M. M. Pearson, *J. Am. Chem. Soc.* 1993, **115**, 958.
2. J. M. Nichols, J. Wolf, P. Zavalij, B. Varughese and M. P. Doyle, *J. Am. Chem. Soc.*, 2007, **129**, 3504.