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Phosphorescent Emitters from Natural Products: Cinchonine-Derived Iridium(III) Complexes

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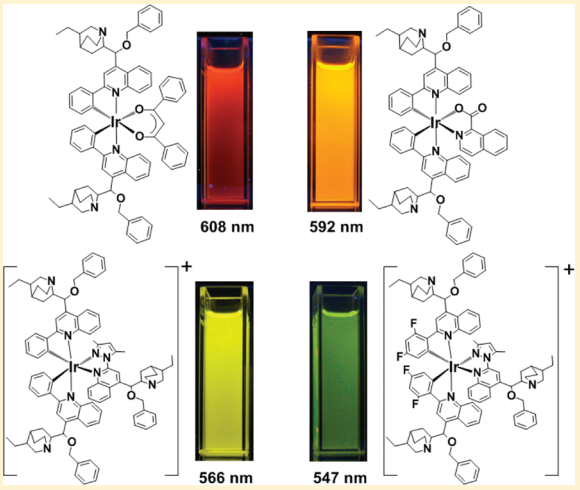
Supporting Information

ABSTRACT: The natural product cinchonine is readily converted into novel cyclometalating and coordinating ligands that can be used to prepare phosphorescent Ir(III) complexes. These phosphorescent emitters are very soluble in organic solvents and exhibit relatively high quantum efficiencies.



INTRODUCTION

Cinchona alkaloids have a long therapeutic history and are enjoying renewed interest as synthetic targets,[1] efficient organocatalysts,[2] and chiral resolution reagents.[3] Appropriately placed donor atoms make them inexpensive chelating ligands for chiral metal catalysts.[4] We reasoned that, with relatively straightforward synthetic modifications, *Cinchona* alkaloid derivatives could also be a novel source of cyclometalating and coordinating ligands for phosphorescent metal complexes with potential applications as emitters in organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs).[5] The bulky 1-azabicyclo[2.2.2]octane moiety could impart improved solubility in solvents or in a polymer host, reducing aggregation and thereby reducing quenching of the luminescence through triplet−triplet annihilation.[6] Herein, we report the synthesis and photophysical properties of phosphorescent iridium complexes of the three cinchonine-derived ligands **L1**−**L3** (Chart 1).

Neutral Ir(III) complexes were prepared from **L1** or **L2** as cyclometalating ligands in combination with a variety of ancillary ligands. The combination of **L1** or **L2** and coordinating ligand **L3** yields ionic Ir(III) complexes (Chart 2). The steric bulk of the cinchonine-derived ligand protects the emissive core of the complex and improves the solubility of the complex, in much the same way as the dendritic environments elegantly engineered by Burn and co-workers.[7]

RESULTS AND DISCUSSION

A five-step modification of inexpensive cinchonine provided 2′-chloro-9-*O*-benzyl-10,11-dihydrocinchonine (28% overall yield), from which ligands **L1** and **L2** were prepared by a Suzuki−Miyaura coupling with the corresponding arylboronic acid and **L3** was prepared by S_NAr displacement with hydrazine followed by condensation with acetylacetone (Scheme 1). Alternatively, **L1** could be directly synthesized from 9-*O*-benzyl-10,11-dihydrocinchonine or 9-*O*-benzyl-10,11-dihydrocinchonine *N*′-oxide as starting materials and phenyllithium or phenylmagnesium bromide. Reaction of $IrCl_3 \cdot xH_2O$ with 3 equiv of **L1** or **L2** by the well-established Nonoyama route[8] provided the dinuclear complexes $[Ir(\mathbf{L1})_2Cl]_2$ (**1**) and $[Ir(\mathbf{L2})_2Cl]_2$ (**2**) in 44% and 24% yields, respectively. Subsequent treatment of **1** with the ancillary ligands acetylacetone (acacH), dibenzoylmethane (dbm), 2-picolinic acid (pic), and isoquinoline-1-carboxylic acid (iq) in the presence of base yielded the four neutral complexes $Ir(\mathbf{L1})_2(acac)$ (**3**), $Ir(\mathbf{L1})_2(dbm)$ (**4**), $Ir(\mathbf{L1})_2(pic)$

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(**5**), and Ir(**L1**)$_2$(iq) (**6**) (Chart 2).[9] Treatment of **1** with **L3** followed by anion exchange with NH_4PF_6 gave rise to two diastereomeric, ionic complexes [Ir(**L1**)$_2$(**L3**)][PF_6] (**7a**,**b**), which were separated by chromatography on neutral alumina. The analogous reaction of **2** with **L3** provided the fluorine-substituted [Ir(**L2**)$_2$(**L3**)][PF_6] (**8**) as a mixture of diastereomers which were not separated. All of these complexes could be prepared in moderate to high yield. Complexes **1**−**8** were highly soluble in CH_2Cl_2, DMF, and DMSO and readily soluble in other common solvents such as $CHCl_3$, MeCN, and MeOH.

Molecular ions $[M + H]^+$ (M = neutral complexes) or $[M]^+$ (M = charged complexes) were observed in the ESI mass spectra at *m*/*z* 1214.6 (**3**), 1339.0 (**4**), 1238.3 (**5**), 1288.5 (**6**), 1595.7 (**7a**,**b**), and 1668.5 (**8**). The corresponding cationic fragments [Ir(**L1**)$_2$]$^+$ and [Ir(**L2**)$_2$]$^+$ (**3**−**8**) and dicationic species [M + 2H]$^{2+}$ (**3**−**6**), [Ir(**L1**)$_2$+H]$^{2+}$ (**7**), and [Ir(**L2**)$_2$+H]$^{2+}$ (**8**) were also diagnostic. ^{1}H and ^{13}C NMR spectra were complex, but the protons ortho to the cyclometalated carbon appeared characteristically at ca. 6.5 ppm.[10] Complexes **3**−**8** were further characterized by FT-IR spectra and their bulk purity confirmed by elemental analyses. Unfortunately, single crystals suitable for X-ray diffraction studies have so far proved elusive.

The UV−vis absorption and emission data for complexes **3**−**6**, **7a**, and **8** are recorded in Table 1 and Figures 1 and 2. The diastereomeric complexes **7a**,**b** exhibited identical UV/vis absorption and emission profiles, quantum yields, and lifetimes. The intense bands for all complexes in the high-energy portion of the spectra between 230 and 350 nm can be assigned to the spin-allowed $^1(\pi-\pi^*)$ transitions of the ligands. The weaker and low-energy bands at wavelengths longer than 440 nm suggests substantial mixing of spin-forbidden ^{3}MLCT and higher lying ^{1}MLCT transitions facilitated by the strong spin−orbit coupling of the Ir(III) center.[11] It should be noted that the spectra observed for all these complexes are similar, suggesting that the dominant absorptions are due to the "(**L1**)$_2$Ir" or "(**L2**)$_2$Ir" fragment.

Complexes **3**−**8** gave emissions in a broad color range from green (547 nm, **8**) to red (608 nm, **4**) (Figure 3), with phosphorescence quantum yields between 0.05 and 0.51 and lifetimes in the range of 4.2−11.5 μs for degassed CH_2Cl_2 solutions at room temperature. By way of comparison, complex **3** has a UV/vis absorption and emission profile almost identical with that reported for the simple analogue Ir(QN)$_2$(acac) (QN = 2-phenylquinolyl-*N*,*C*) but exhibits a higher quantum efficiency (0.19 versus 0.1).[12] The triplet levels of the acac ligand of **3** lie above the energies of **L1** and MLCT excited states, and the luminescence is thus dominated by the **L1** and MLCT transitions. The longer emission wavelength and relatively low quantum efficiency of **4** can be attributed to the lower triplet-state energy of dbm relative to **L1** or the ^{1}MLCT in this complex. The emission spectra of complexes **7a** and **8** are blue-shifted relative to **3**−**6**, suggesting that for these cationic Ir(III) complexes, the HOMO consists mainly of a mixture of Ir d and phenyl π orbitals, while the LUMO has significant chelating ligand character, as previously calculated for cationic complexes with a bipyridyl auxiliary ligand.[13,14] The emission of **8** is blue-shifted by 19 nm relative to **7a**, because of the influence of the electron-withdrawing fluorine atoms on the HOMO located predominantly on the cyclometalating ligand.

Chart 1

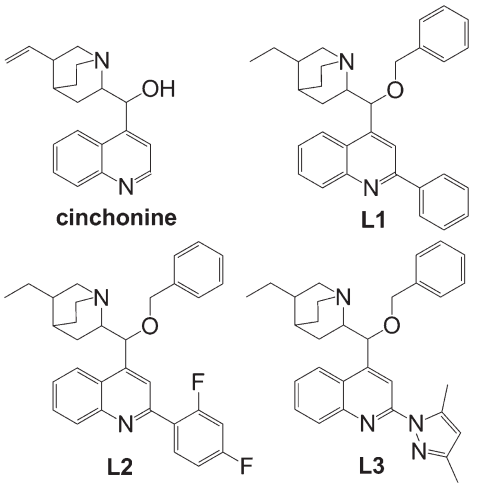
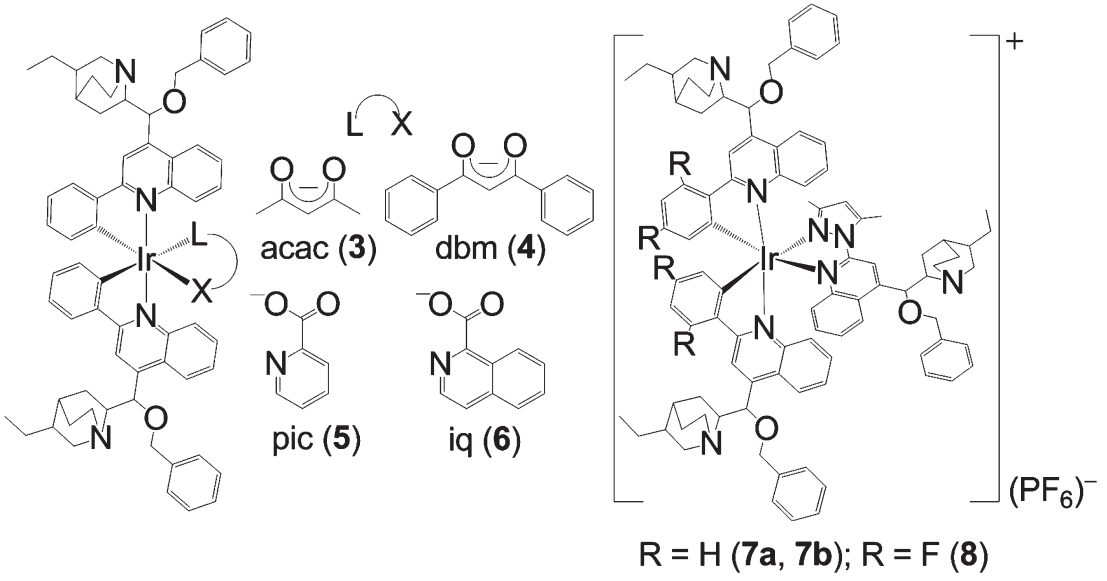


Chart 2



Scheme 1. Synthetic Procedures for L1−L3

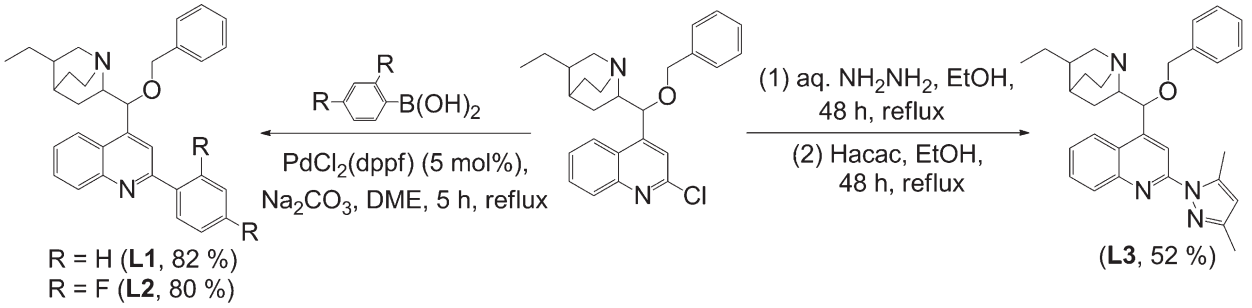


Table 1. Photophysical Data of of 3−6, 7a, and 8 in Degassed CH_2Cl_2 at Room Temperature

	UV−vis (nm)	λ_{max} (nm)	Φ [a]	τ (μs)
3	230, 272, 348, 431, 472	597	0.19	4.2
4	231, 271, 347, 429, 473	608	0.05	4.3
5	231, 274, 346, 408, 463	580	0.20	4.6
6	230, 279, 343, 413, 464	592	0.51	4.6
7a	232, 276, 244, 444	566	0.06	10.1
8	224, 260, 280, 336, 439	547	0.29	11.5

[a] With respect to Rhodamine 6G (Φ = 0.95 in ethanol).

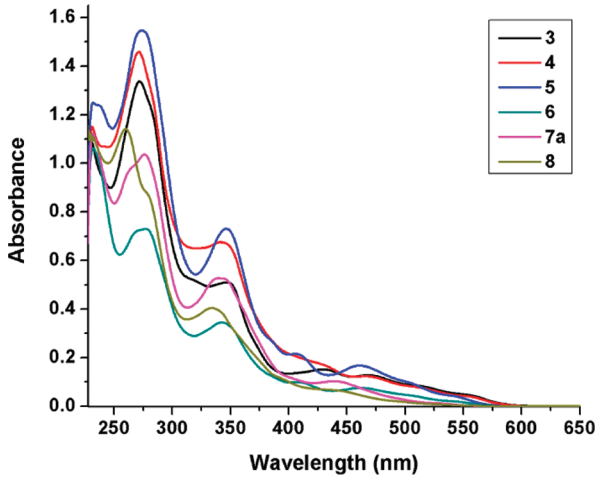


Figure 1. UV−vis spectra of **3**−**6**, **7a**, and **8** recorded in degassed CH_2Cl_2 solutions at room temperature.

In summary, we have demonstrated that the abundant natural product cinchonine is readily converted to novel cyclometalating and coordinating ligands that can be used to prepare phosphorescent Ir(III) complexes. These phosphorescent emitters are very soluble in organic solvents and exhibit relatively high quantum efficiencies. Some emission color tuning is possible by variation of the auxiliary ligands. We propose that these changes in solubility and photophysical properties relative to simple cyclometalated Ir(III) complexes are the result of the extraneous bulk of the natural product and benzyl protecting group, both of which increase solubility and partially encapsulate the emitting core, reducing intermolecular quenching of the phosphorescence. Future work will focus on dispersion of these emitters on solid supports or in a polymer host.

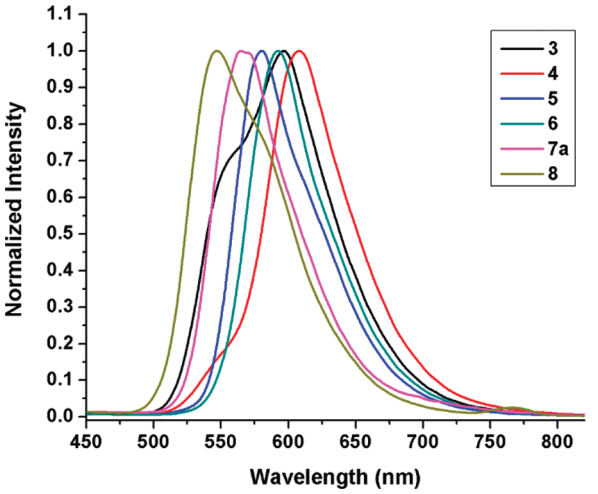


Figure 2. Luminescence spectra of **3**−**6**, **7a**, and **8** recorded in degassed CH_2Cl_2 solutions at room temperature.

EXPERIMENTAL SECTION

General Considerations. All synthetic procedures involving $IrCl_3 \cdot xH_2O$ and other Ir(III) species were carried out in the dark and under a N_2 atmosphere using standard Schlenk techniques. Elemental analyses were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 500 MHz spectrometer, and their chemical shifts were referenced to Me_4Si (TMS). The ^{19}F NMR spectra were recorded on a Bruker ACF 300 spectrometer. IR spectra were recorded on a Bruker IFS 48 FTIR spectrometer using KBr as pellets. UV−vis spectra were recorded on a UVIKON spectrometer. Electrospray mass spectra were obtained in positive-ion mode with a Finnigan/MAT LCQ mass spectrometer. Peaks were assigned from the m/z values and the isotope distribution patterns. Photoluminescence was measured using a Perkin-Elmer LS55 luminescence spectrometer, and the quantum yield was determined using Rhodamine 6G (quantum yield 0.96 in ethanol) as reference at room temperature using degassed CH_2Cl_2 or EtOH solvents.[15] The phosphorescence lifetime was measured using an Edinburgh FL920P lifetime spectrometer.

Synthesis of 2′-Phenyl-9-*O*-benzyl-10,11-dihydrocinchonine (L1). *Method A.* Phenyllithium was prepared by adding bromobenzene (3.74 g, 24 mmol) in anhydrous Et_2O (30 mL) to lithium metal

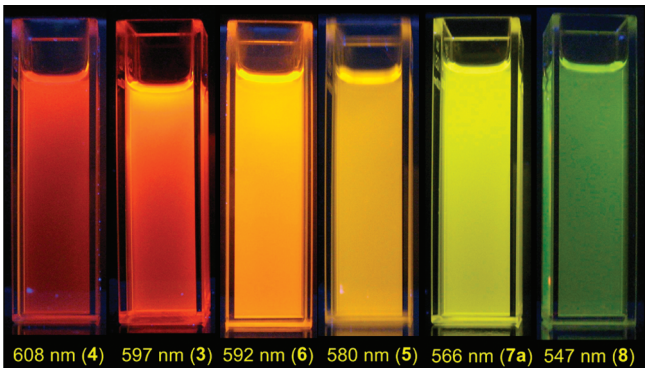


Figure 3. Emission photos of **3**−**6**, **7a**, and **8** recorded in degassed CH_2Cl_2 solutions at room temperature.

(0.18 g, 26 mmol) in anhydrous Et_2O under nitrogen. This was carried out by adding a small aliquot of the bromobenzene solution (2 mL) with heating to initiate the reaction. A white suspension indicated that initiation had occurred, and then the remaining bromobenzene solution was added dropwise and the reaction mixture stirred for 3 h. 9-*O*-Benzyl-10,11-dihydrocinchonine (3.87 g, 10 mmol) was added to Et_2O (40 mL) and the solution vigorously stirred. The suspension was transferred to the preformed lithium reagent and the reaction mixture stirred overnight. The mixture was added to ice water, acidified with dilute HCl, and extracted using $CHCl_3$. The product was purified by chromatography on silica (EA/MeOH 15/1 as eluent). Yield: 0.74 g (16%).

Method B. Phenylmagnesium bromide was prepared from bromobenzene (3.12 g, 20 mmol) and magnesium turnings (0.48 g, 20 mmol) in freshly distilled THF (20 mL). 9-*O*-Benzyl-10,11-dihydrocinchonine *N*′-oxide (4.03 g, 10 mmol) was dissolved in dry THF (40 mL) and slowly added to the Grignard reagent. The resulting mixture was stirred for 1 h, quenched with ice water, and acidified with HCl. $CHCl_3$ (60 mL) was added and stirred for 15 min. The organic layer was separated, filtered, washed with water, concentrated, and purified by chromatography on silica (EA/MeOH 15/1 as eluent). Yield: 2.77 g (60%).

Method C. 9-*O*-Benzyl-2′-chloro-10,11-dihydrocinchonine (2.1 g, 5.0 mmol) and phenylboronic acid (0.58 g, 5.5 mmol) were dissolved in 1, 2-dimethoxyethane (50 mL), and the solution was degassed. $PdCl_2$-(dppf) (0.18 g, 0.025 mmol) was added and the mixture degassed again. Finally, degassed aqueous Na_2CO_3 (5.3 g in 10 mL of water) was injected via syringe and the solution refluxed for 5 h. After the mixture was cooled to room temperature, the solvent was removed and CH_2Cl_2 (50 mL) added. The organic layer was washed with brine (3 × 50 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed, and the crude product was purified by chromatography on silica using EA/MeOH 15/1 as eluent to give a brown oil (1.90 g, 82%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 8.3 Hz, 1H), 8.15−8.20 (m, 3H), 8.04 (s, 1H), 7.74−7.76 (m, 1H), 7.53−7.59 (m, 3H), 7.46−7.49 (m, 1H), 7.36−7.38 (m, 4H), 7.32−7.34 (m, 1H), 5.43 (br, 1H), 4.47−4.55 (AB quartet, 2H), 3.09−3.12 (m, 2H), 2.90−2.95 (m, 1H), 2.83−2.88 (m, 1H), 2.71−2.77 (m, 1H), 2.10−2.14 (m, 1H), 1.41−1.54 (m, 6H), 1.26−1.30 (m, 1H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.6, 149.4, 147.8, 140.4, 138.6, 131.4, 130.0, 129.9, 129.4, 129.0, 128.6, 128.4, 128.2, 126.9, 126.2, 123.7, 117.0, 81.8, 72.2, 61.2, 51.6, 50.8, 38.2, 28.0, 27.1, 25.9, 22.4, 12.6. MS (ESI): 463.3 $[M + H]^+$. Anal. Calcd for $C_{32}H_{34}N_2O$: C, 83.08; H, 7.41; N, 6.06. Found: C, 74.38; H, 6.66; N, 4.64; corresponding to **L1** + 2EA.

Synthesis of 2′-(2,4-Difluorophenyl)-9-*O*-benzyl-10,11-dihydrocinchonine (L2). Ligand **L2** was prepared using the Suzuki reaction described for **L1**. The crude product was purified by chromatography on silica (EA/MeOH 20/1) to give a brown oil (2.0 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23−8.24 (m, 1H), 8.13−8.20 (m, 2H), 8.01 (s, 1H), 7.73−7.76 (m, 1H), 7.57−7.60 (m, 1H), 7.34−7.38 (m, 4H), 7.28−7.32 (m, 1H), 7.03−7.07 (m, 1H), 6.94−6.98 (m, 1H), 5.38 (br, 1H), 4.41−4.56 (AB quartet, 2H), 3.12 (br, 1H), 3.03 (br, 1H), 2.80−2.91 (m, 2H), 2.69−2.75 (m, 1H), 2.07−2.09 (m, 1H), 1.31−1.51 (m, 7H), 0.85 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.6, 165.1 (d, J_{C-F} = 12.0 Hz), 163.1 (d, J_{C-F} = 12.0 Hz), 162.5 (d, J_{C-F} = 12.0 Hz), 160.5 (d, J_{C-F} = 12.0 Hz), 153.3, 149.4, 147.4, 138.4, 133.2−133.4 (q), 131.2, 130.0, 128.9, 128.7, 128.3, 127.3, 126.2, 125.0−125.2 (dd, J = 3.7 Hz, 12.0 Hz), 123.8, 120.4, 112.5−112.7 (dd, J = 3.5 Hz, 21.1 Hz), 104.8−105.2 (m), 81.7, 72.2, 61.2, 51.5, 50.8, 38.1, 28.0, 27.0, 25.9, 12.6. ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −32.7 (d, J = 8.7 Hz, 1F), −36.5 (d, J = 8.7 Hz, 1F). MS (ESI): 499.2 $[M + H]^+$. Anal. Calcd for $C_{32}H_{32}F_2N_2O$: C, 77.08; H, 6.47; N, 5.62. Found: C, 74.85; H, 6.02; N, 5.22; corresponding to **L2** + 0.5EA.

Synthesis of 2′-(3,5-Dimethylpyrazole)-9-*O*-benzyl-10,11-dihydrocinchonine (L3). 9-*O*-Benzyl-2′-chloro-10,11-dihydrocinchonine (0.84 g, 2 mmol) and NH_2NH_2 (4.27 g, 60% aqueous solution, 40 equiv) were dissolved in EtOH (50 mL). After reflux under N_2 for 48 h, the mixture was cooled to room temperature and the solvent removed under vacuum. Ethyl acetate (50 mL) was added, and the organic phase was successively washed with water (3 × 50 mL) and brine (50 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent removed to give an orange, oily crude product (0.73 g), which was dried under vacuum and used without further purification.

A mixture of crude 2′-hydrazine-9-*O*-benzyl-10,11-dihydrocinchonine (0.73 g, 1.76 mmol) and acetylacetone (0.2 g, 2 mmol) was added to EtOH (50 mL), and the mixture was refluxed under N_2 for 48 h. The solvent was removed to give an orange, oily product, which was dried under vacuum. The product was purified by chromatography on silica (EA/MeOH 20/1 (v/v)) to give a yellowish oil (0.50 g, 52% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.19 (br, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.60−7.63 (m, 1H), 7.45−7.48 (m, 1H), 7.36−7.38 (m, 2H), 7.29−7.32 (m, 2H), 7.23−7.25 (m, 1H), 5.99 (s, 1H), 5.35 (br, 1H), 4.37−4.53 (AB quartet, 2H), 3.18 (br, 1H), 2.99 (br, 1H), 2.85−2.89 (m, 1H), 2.80 (br, 4H), 2.64−2.70 (m, 1 H), 2.32 (s, 3H), 2.03−2.08 (m, 1H), 1.25−1.44 (m, 7H), 0.80 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 152.7, 150.2, 149.2, 147.5, 142.5, 138.2, 129.9, 129.8, 128.7, 128.1, 126.1, 125.1, 124.0, 113.4, 110.0, 81.4, 72.0, 60.9, 51.0, 50.3, 37.8, 27.6, 26.7, 25.6, 22.6, 15.6, 14.2, 12.3. MS (ESI): 481.4 $[M + H]^+$. Anal. Calcd for $C_{31}H_{36}N_4O$: C, 77.47; H, 7.55; N, 11.66. Found: C, 73.79; H, 6.00; N, 9.65; corresponding to **L3** + EA.

Synthesis of 1. $IrCl_3 \cdot xH_2O$ (0.30 g, 1 mmol) and **L1** (1.20 g, 2.6 mmol) were mixed in a double-necked flask, and the system was flushed with N_2 three times. A mixture of 2-ethoxyethanol and water (12 mL, 3/1 v/v) was deoxygenated with a N_2 stream for 3 min and injected into the flask. The mixture was refluxed at 140 °C for 60 h in the dark. The mixture was then cooled to room temperature, and CH_2Cl_2 (200 mL) and brine (50 mL) were added. The CH_2Cl_2 phase was separated, washed with brine (3 × 50 mL), and dried over anhydrous Na_2SO_4. The solvent was removed and the crude product purified by chromatography on neutral Al_2O_3 (ethyl acetate/methanol, 50/1 v/v) to give thr dark red product **1** (0.51 g, 44% based on Ir). Mp: 142 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.69−8.73 (m, 2H), 8.26−8.36 (m, 4H), 7.91−7.94 (m, 2H), 7.39−7.70 (m, 16H), 7.00−7.03 (m, 2H), 6.66−6.69 (m, 2H), 6.36−6.38 (m, 2H), 5.36−5.57 (m, 2H), 4.46−4.76 (m, 4H), 3.46−3.58 (m, 1H), 3.25−3.35 (m, 2H), 2.74−2.99 (m, 9H), 2.46 (br, 3H), 2.04−2.17 (m, 2H), 1.37−1.83 (m, 19H), 0.97−1.02 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 186.2, 168.9, 150.8, 148.6, 148.3, 146.5, 146.5, 145.7, 138.3, 134.8, 130.7, 129.3, 128.7, 128.5, 128.1, 127.1, 126.7, 126.4, 123.9, 121.6, 120.9, 114.5, 80.0, 72.2, 62.0, 61.4, 51.3, 50.3, 50.2, 37.9, 27.7, 26.7, 25.8, 25.7, 24.8, 23.5, 12.1 ppm. MS (ESI, CH_2Cl_2): m/z 558.7 $[Ir(\mathbf{L1})_2 + H]^{2+}$; 1115.8 $[Ir(\mathbf{L1})_2]^+$. Anal. Calcd for $C_{128}H_{132}Cl_2Ir_2N_8O_4$: C, 66.79; H, 5.78; N, 4.87. Found: C, 66.39; H, 5.73; N, 4.66.

Synthesis of 2. Complex **2** was synthesized using the same procedure described for **1**. The crude product was purified by chromatography on neutral Al_2O_3 (acetate/methanol, 100/1 v/v). Yield: 0.35 g (24% based on Ir). Mp: 146 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.75 (br, 1H), 8.67 (br, 1H), 8.53−8.56 (br, 3H), 8.38−8.39 (m, 1H), 7.69−7.72 (m, 4H), 7.37−7.51 (m, 12H), 6.55−6.59 (m, 2H), 5.85−5.90 (m, 2H), 5.70 (br, 1H), 5.53 (br, 1H), 4.61−4.74 (m, 4H), 3.48 (br, 1H), 3.34 (br, 2H), 2.79−3.02 (m, 10H), 2.15−2.16 (m, 2H), 1.83 (br, 2H), 1.35−1.66 (m, 21H), 0.93−0.96 (m, 9H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 187.0, 168.9, 165.9, 165.8, 165.7, 165.6, 163.2, 163.1, 162.6, 162.5, 161.2, 161.1, 160.5, 160.4, 150.8, 150.4, 148.6, 148.5, 148.5, 148.4, 147.8, 147.6, 137.8, 130.8, 130.7, 130.6, 128.5, 128.4, 128.3, 128.3, 127.9, 127.8, 126.9, 126.8, 126.3, 126.0, 124.6, 123.9, 116.8, 116.7, 98.2, 98.0, 97.8, 72.1, 72.0, 61.4, 60.9, 50.9, 50.5, 49.9, 49.9, 37.4, 29.7, 27.0, 27.0, 26.4, 26.4, 25.4, 25.3, 24.4, 24.3, 22.7, 11.7 ppm. ^{19}F{^{1}H} NMR (282 MHz, CD_2Cl_2): δ −32.96 (−33.03) (m, 2F), −33.53 (−33.68) (m, 2F). MS (ESI, CH_2Cl_2): m/z 1187.5 $[Ir(\mathbf{L2})_2]^+$. Anal. Calcd for $C_{128}H_{124}Cl_2F_8Ir_2N_8O_4$: C, 62.86; H, 5.11; N, 4.58. Found: C, 62.64; H, 5.44; N, 4.27.

Synthesis of 3. A mixture of **1** (0.23 g, 0.1 mmol), acetylacetone (0.034 g, 0.34 mmol), and K_2CO_3 (0.14 g, 1.0 mmol) were dissolved in 1,2-dichloroethane (30 mL), and this mixture was then degassed, flushed with N_2 three times, and refluxed under N_2 for 8 h. The mixture was then cooled to room temperature, the solvent removed, and the resulting red residue redissolved in CH_2Cl_2 (100 mL). The organic phase was washed with brine (3 × 50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed, and the crude product was dried under vacuum and purified by chromatography on neutral Al_2O_3 using ethyl acetate as eluent to give a dark red solid (**3**). Yield: 0.19 g (78% based on Ir). Mp: 152 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.36−8.40 (m, 2H), 8.01−8.14 (m, 3H), 7.73−7.79 (m, 2H), 7.20−7.41 (m, 12H), 6.84−6.87 (m, 2H), 6.45−6.56 (m, 3H), 5.35 (s, 1H), 4.64−4.64 (m, 1H), 4.43−4.56 (m, 3H), 3.06 (br, 1H), 2.75−2.89 (m, 4H), 2.53−2.69 (m, 4H), 2.27 (br, 1H), 1.88−2.00 (m, 2H), 1.60−1.63 (m, 2H), 1.22−1.45 (m, 18H), 0.78−0.82 (m, 6H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 186.2, 186.0, 169.6, 149.9, 149.8, 149.6, 149.3, 149.2, 147.7, 147.6, 138.1, 138.0, 136.1, 136.0, 130.2, 130.1, 128.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.2, 127.1, 126.3, 126.2, 126.0, 125.9, 125.8, 123.7, 121.1, 100.3, 100.2, 71.9, 71.7, 61.4, 51.1, 51.0, 50.2, 50.1, 37.8, 37.7, 28.0, 27.9, 27.6, 27.5, 26.7, 26.6, 25.5, 25.4, 11.9. MS (ESI, CH_2Cl_2, 180 °C): m/z 558.6 $[Ir(\mathbf{L1})_2 + H]^{2+}$; 608.5 $[\mathbf{3} + 2H]^{2+}$; 1115.6 $[Ir(\mathbf{L1})_2]^+$; 1214.6 $[\mathbf{3} + H]^+$. Anal. Calcd for $C_{69}H_{73}IrN_4O_4$: C, 68.23; H, 6.06; N, 4.61. Found: C, 68.67; H, 6.21; N, 4.63.

Synthesis of 4. Compound **4** was prepared using the method as described for **3**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate as eluent to give a dark red solid. Yield: 0.21 g (78% based on Ir). Mp: 178 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.68−8.70 (m, 2H), 8.42−8.47 (m, 2H), 8.11−8.17 (m, 3H), 8.05−8.06 (m, 2H), 7.22−7.59 (m, 28H), 7.13−7.16 (m, 2H), 6.81−6.83 (m, 4H), 6.02−6.04 (m, 2H), 5.57 (br, 1H), 5.47 (br, 1H), 4.74−4.58 (m, 3H), 4.44−4.47 (m, 1H), 3.32−3.35 (m, 1H), 3.16 (br, 2H), 2.97−3.07 (m, 3H), 2.70−2.88 (m, 5H), 2.10−2.25 (m, 3H), 1.85 (br, 1H), 1.76 (br, 1H), 1.40−1.64 (m, 13H), 1.22−1.40 (m, 3H), 1.01−1.04 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 181.3, 181.1, 169.7, 169.5, 150.2, 150.1, 149.3, 149.2, 147.8, 147.7, 141.3, 141.2, 138.1, 138.0, 136.2, 130.3, 130.2, 130.0, 129.9, 128.8, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.2, 127.1, 126.4, 126.3, 126.3, 126.1, 125.9, 125.8, 125.6, 123.7, 121.2, 95.4, 95.3, 71.9, 71.6, 61.6, 60.8, 60.3, 51.1, 50.2, 50.1, 37.8, 37.7, 27.6, 27.4, 26.7, 26.6, 25.4, 11.9. MS (ESI, CH_2Cl_2, 180 °C): m/z 557.7: $[Ir(\mathbf{L1})_2 + H]^{2+}$; 670.5 $[\mathbf{4} + 2H]^{2+}$; 1115.6 $[Ir(\mathbf{L1})_2]^+$; 1339.0 $[\mathbf{4} + H]^+$. Anal. Calcd for $C_{79}H_{77}IrN_4O_4$: C, 70.88; H, 5.80; N, 4.19. Found: C, 70.53; H, 5.65; N, 4.04.

Synthesis of 5. Compound **5** was prepared in a fashion similar to that for **3**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate/methanol (75/1 v/v) as eluent. Yield: 0.12 g (49% based on Ir). Mp: 227 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.82−8.84 (m, 1H), 8.35−8.37 (m, 2H), 7.97−8.20 (m, 6H), 7.81−7.83 (m, 1H), 7.68−7.72 (m, 1H), 7.41−7.61 (m, 14H), 7.29−7.34 (m, 1H), 7.09−7.19 (m, 2H), 6.93−7.00 (m, 2H), 6.77−6.87 (m, 2H), 6.44−6.47 (m, 1H), 5.36−5.49 (m, 2H), 4.43−4.78 (m, 4H), 3.25−3.31 (m, 1H), 2.67−3.06 (m, 8H), 2.48 (br, 2H), 2.15 (br, 2H), 1.81 (br, 2H), 1.52−1.65 (m, 13H), 0.96−1.00 (m, 6H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 171.4, 170.0, 168.7, 152.8, 150.5, 150.4, 150.2, 148.3, 147.9, 147.4, 146.5, 145.9, 145.9, 138.1, 138.0, 137.7, 135.9, 134.8, 131.0, 129.8, 129.4, 129.3, 128.5, 128.4, 128.4, 128.3, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.3, 127.0, 126.7, 126.5, 126.4, 126.4, 126.4, 126.2, 125.5, 124.7, 123.6, 122.0, 121.2, 72.0, 72.0, 71.8, 71.6, 61.6, 61.4, 61.2, 60.9, 60.3, 51.0, 51.0, 50.1, 50.1, 37.7, 27.6, 27.5, 26.6, 25.4, 25.4, 11.9. MS (ESI, CH_2Cl_2, 180 °C): m/z 557.6 $[Ir(\mathbf{L1})_2 + H]^{2+}$; 620.0 $[\mathbf{5} + 2H]^{2+}$; 1115.6 $[Ir(\mathbf{L1})_2]^+$; 1238.4 $[\mathbf{5} + H]^+$. Anal. Calcd for $C_{70}H_{70}IrN_5O_4$: C, 67.94; H, 5.70; N, 5.66. Found: C, 62.77; H, 5.52; N, 5.28.

Synthesis of 6. Compound **6** was prepared in a fashion similar to that for **3**. The crude product was purified by chromatography on neutral Al_2O_3 using ethyl acetate/methanol (50/1 v/v) as eluent. Yield: 0.21 g (81% based on Ir). Mp: 200 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.59−9.62 (m, 1H), 8.74−8.76 (m, 1H), 8.18−8.21 (m, 2H), 7.79−7.99 (m, 5H), 7.55−7.64 (m, 2H), 7.39−7.51 (m, 5H), 7.19−7.36 (m, 10H), 7.11−7.15 (m, 1H), 7.00−7.03 (m, 1H), 6.91−6.95 (m, 1H), 6.76−6.77 (m, 1H), 6.67−6.70 (m, 2H), 6.59−6.61 (m, 1H), 6.24−6.28 (m, 1H), 5.30−5.33 (m, 1H), 4.38−4.52 (m, 3H), 3.94 (s, 1H), 3.03−3.13 (m, 1H), 2.42−2.90 (m, 8H), 2.19 (br, 2H), 1.88−2.01 (m, 2H), 1.61−1.65 (br, 1H), 1.54 (br, 1H), 1.17−1.42 (m, 14H), 0.76−0.81 (m, 9H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 172.4, 170.2, 170.1, 169.3, 169.2, 152.1, 152.0, 151.3, 150.9, 150.8, 150.6, 150.1, 150.0, 150.0, 148.7, 148.6, 147.9, 147.9, 147.6, 147.5, 146.9, 141.9, 138.5, 138.3, 138.3, 138.3, 137.2, 136.9, 136.1, 135.0, 131.7, 131.7, 131.2, 131.2, 131.1, 130.8, 130.0, 129.7, 129.7, 129.5, 129.4, 129.3, 129.2, 129.2, 129.0, 128.9, 128.7, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.4, 127.1, 126.9, 126.7, 126.7, 126.6, 126.4, 126.4, 126.2, 126.0, 125.8, 124.2, 122.2, 121.4, 72.3, 72.2, 72.1, 71.8, 61.1, 53.0, 51.3, 50.4, 50.3, 50.3, 39.1, 38.0, 37.9, 30.7, 30.0, 29.3, 27.7, 27.6, 26.9, 26.9, 26.9, 25.7, 25.6, 24.1, 23.1, 14.1, 12.2, 12.1, 11.1. MS (ESI, CH_2Cl_2, 180 °C): m/z 558.7 $[Ir(\mathbf{L1})_2 + H]^{2+}$; 645.2 $[\mathbf{6} + 2H]^{2+}$; 1115.7 $[Ir(\mathbf{L1})_2]^+$; 1288.4 $[\mathbf{6} + H]^+$. Anal. Calcd for $C_{74}H_{72}IrN_5O_4$: C, 69.03; H, 5.64; N, 5.44. Found: C, 69.53; H, 6.10; N, 5.57.

Synthesis of 7a,b. A mixture of **1** (0.23 g, 0.1 mmol) and **L3** (0.096 g, 0.2 mmol) in a two-necked flask was flushed with N_2 three times. A CH_2Cl_2/MeOH mixture (20 mL/10 mL) was added under N_2 and the mixture refluxed for 12 h. The reaction mixture was cooled to room temperature, and NH_4PF_6 (0.16 g, 1 mmol) in MeOH (5 mL) was added under N_2. The mixture was stirred for another 5 h and the solvent evaporated. The resulting red residue was dried under vacuum, and CH_2Cl_2 (5 mL) was added. NH_4Cl was removed by filtration. The solvent was evaporated and the product purified by chromatography on neutral Al_2O_3 using ethyl acetate/hexane (4/1 v/v) and ethyl acetate/MeOH (10/1 v/v) as eluents. Two red bands, **7a**,**b**, were collected. Yield: 0.18 g (51.7%) (**7a**) and 0.078 g (22.4%) (**7b**). Mp: 160 °C (**7a**), 165 °C (**7b**). ^{1}H NMR (500 MHz, CD_2Cl_2) for **7a**: δ 8.27−8.40 (m, 2H), 8.05−8.12 (m, 1H), 7.91−7.93 (m, 1H), 7.79−7.86 (m, 2H), 7.64−7.74 (m, 1H), 7.16−7.55 (m, 18H), 7.02−7.10 (m, 2H), 6.68−6.90 (m, 2H), 6.29−6.42 (m, 1H), 5.93−6.19 (m, 1H), 5.31−5.38 (m, 2H), 5.08−5.15 (m, 2H), 4.57−4.62 (m, 2H), 4.44−4.51 (m, 1H), 3.73−3.87 (m, 1H), 2.51−3.04 (m, 15H), 1.16−1.95 (m, 26H), 0.75−0.95 (m, 9H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) for **7a**: δ 169.9, 169.7, 169.5, 169.2, 156.3, 155.8, 154.6, 152.6, 151.8, 151.2, 150.2, 149.8, 149.1, 148.9, 148.0, 147.3, 146.9, 146.7, 146.1, 146.0, 145.9, 144.9, 144.6, 144.0, 143.2, 137.7, 137.7, 137.6, 137.3, 137.2, 136.9, 133.4, 132.8, 132.3, 132.1, 131.8, 131.3, 131.1, 130.9, 130.9, 130.8, 130.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.1, 126.9, 126.7, 126.7, 126.6, 126.5,

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126.3, 126.3, 126.2, 125.8, 125.5, 125.4, 125.3, 125.1, 125.0, 124.6, 124.4, 123.6, 123.2, 123.0, 122.9, 122.6, 114.2, 113.8, 108.7, 80.5, 80.0, 72.1, 72.1, 72.0, 71.9, 71.7, 61.9, 61.8, 61.6, 61.2, 51.0, 51.0, 50.9, 50.2, 50.1, 37.6, 37.5, 37.3, 27.5, 27.4, 27.4, 27.3, 27.3, 26.5, 26.5, 26.3, 26.2, 25.4, 25.3, 25.2, 25.2, 25.1, 22.0, 21.8, 14.8, 13.5, 12.3, 12.1, 11.8, 11.8, 11.7, 11.7, 11.6. ^{1}H NMR (500 MHz, CD_2Cl_2) for **7b**: δ 8.28−8.40 (m, 2H), 8.05−8.13 (m, 1H), 7.80−7.93 (m, 3H), 7.54−7.74 (m, 1H), 7.18−7.51 (m, 14H), 7.04−7.10 (m, 2H), 6.68−6.90 (m, 2H), 5.93−6.42 (m, 2H), 5.10−5.41 (m, 2H), 4.44−4.62 (m, 2H), 3.73−4.29 (m, 2H), 2.52−3.28 (m, 12H), 1.18−2.05 (m, 24H), 0.76−0.93 (m, 7H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) for **7b**: δ 169.7, 169.5, 156.3, 155.8, 150.2, 149.7, 148.0, 147.3, 146.7, 146.0, 144.9, 144.6, 144.0, 143.2, 137.7, 137.5, 137.3, 137.2, 136.9, 132.8, 132.2, 131.3, 131.1, 130.9, 130.7, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.8, 127.8, 127.6, 127.1, 126.9, 126.8, 126.7, 126.6, 126.5, 126.2, 125.5, 125.3, 125.1, 124.4, 123.6, 123.3, 123.0, 122.9, 122.6, 114.2, 108.7, 72.2, 72.1, 71.7, 61.8, 61.5, 50.1, 50.1, 37.6, 37.4, 37.3, 27.4, 27.2, 26.4, 26.4, 25.4, 25.1, 25.1, 14.8, 13.6, 12.3, 12.1, 11.8, 11.7, 11.6. MS (ESI, CH_2Cl_2) for **7a,b**: *m/z* 799.1 $[Ir(\mathbf{L1})_2(\mathbf{L3}) + H]^{2+}$; 1115.8 $[Ir(\mathbf{L1})_2]^+$; $[Ir(\mathbf{L1})_2(\mathbf{L3})]^+$. Anal. Calcd for $C_{95}H_{102}F_6IrN_8O_3P$: C, 65.54; H, 5.91; N, 6.44. Found for **7a**: C, 64.17; H, 5.12; N, 6.36. Found for **7b**: C, 64.15; H, 5.05; N, 6.28.

Synthesis of 8. Complex **8** was synthesized from **2** (0.24 g, 0.1 mmol) and **L3** (0.096 g, 0.2 mmol) using the same reaction conditions described for the synthesis of **7**. Purification by chromatography on a neutral Al_2O_3 column using ethyl acetate/hexane (4/1 v/v) as eluent provided **8** as a mixture of diastereomers which were not separated Yield: 0.12 g (33%). Mp: 190 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 10.39−10.46 (m, 1H), 8.81−8.87 (m, 3H), 8.42−8.50 (m, 5H), 8.23−8.33 (m, 5H), 7.77−7.95 (m, 9H), 7.26−7.63 (m, 61H), 6.63−6.83 (m, 6H), 6.32−6.34 (m, 2H), 6.02−6.05 (m, 2H), 5.58−5.59 (m, 1H), 5.17−5.43 (m, 9H), 4.25−4.73 (m, 14H), 3.83−3.95 (m, 2H), 3.31−3.34 (m, 1H), 2.27−3.10 (m, 51H), 1.27−2.06 (m, 104 H), 0.83−0.99 (m, 40H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 167.1, 167.0, 166.9, 166.8, 166.7, 166.6, 166.6, 164.2, 156.4, 156.2, 155.8, 155.2, 153.7, 153.5, 152.9, 152.9, 152.8, 152.2, 152.1, 152.0, 151.9, 150.2, 149.8, 148.9, 147.9, 147.0, 146.9, 146.8, 146.6, 146.6, 146.3, 145.3, 144.7, 144.6, 137.6, 137.6, 137.5, 137.2, 136.8, 132.3, 131.6, 131.4, 131.3, 131.1, 130.5, 130.4, 130.3, 130.2, 129.8, 128.7, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.6, 127.3, 127.1, 127.1, 126.6, 126.4, 126.3, 126.1, 126.1, 125.9, 125.8, 125.5, 125.4, 125.3, 125.0, 124.7, 124.5, 124.0, 114.8, 114.1, 100.1, 100.0, 100.0, 99.8, 99.6, 99.5, 99.3, 99.3, 99.2, 99.0, 80.2, 72.2, 72.0, 71.9, 71.8, 71.7, 71.7, 69.3, 62.5, 61.7, 61.7, 61.4, 61.3, 51.0, 50.9, 50.7, 50.6, 50.2, 50.1, 50.0, 49.9, 49.9, 49.8, 37.6, 37.5, 37.4, 37.4, 37.3, 31.9, 31.6, 29.7, 29.4, 29.1, 29.0, 27.5, 27.4, 27.2, 26.5, 26.4, 26.3, 26.3, 26.2, 25.4, 25.3, 25.2, 25.1, 21.6, 21.4, 14.9, 13.9, 13.7, 13.5, 13.4, 12.7, 11.8, 11.7, 11.7, 11.6 ppm. ^{19}F{^{1}H} NMR (282 MHz, CD_2Cl_2): δ 3.47, 0.95, −28.48 (d), −29.49 (d), −29.72 (d), −30.71 (d), −31.84 (d), −32.15 (d), −32.54 (d), −33.41, −33.75 ppm. MS (ESI, CH_2Cl_2): *m/z* 834.6 $[Ir(\mathbf{L2})_2(\mathbf{L3})+H]^{2+}$; 1187.5 $[Ir(\mathbf{L2})_2]^+$; 1668.5 $[Ir(\mathbf{L2})_2(\mathbf{L3})]^+$. Anal. Calcd for $C_{95}H_{98}F_{10}IrN_8O_3P$: C, 62.93; H, 5.45; N, 6.18. Found: C, 62.06; H, 5.65; N, 5.86.

■ ASSOCIATED CONTENT

Supporting Information. Text giving the synthetic procedure for 2′-chloro-9-*O*-benzyl-10,11-dihydrocinchonine and figures giving ESI, ^{1}H NMR, ^{13}C NMR spectra for all complexes and decoupled ^{19}F NMR spectra for **L2**, **2**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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