Supporting Information for:

Direct Synthesis of Palladium Porphyrins from Acyldipyrromethanes

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1. Order-of-Addition Effects

When a solution of KOH in ethanol is treated with a Pd(II) reagent or a Pd(IV) reagent, a black precipitate forms within 3-5 minutes. We designed a set of experiments to investigate the activity of both the black precipitate and the supernatant toward conversion of 1-acyldipyrromethane \(2a\) to the corresponding palladium porphyrin \(\text{Pd-4a}\).

**Experiment 1.** A sample of KOH (28 mg, 0.50 mmol, 500 mM) was dissolved in ethanol (1 mL), then \(\text{Pd(CH}_3\text{CN)}_2\text{Cl}_2\) (0.015 mg, 0.060 mmol, 60 mM) was added. The resulting orange mixture upon standing exposed to air for 2 min changed to dark brown, and particles of black material were observed at the bottom of the vial (3 min total elapsed time). Four minutes after the addition of the palladium reagent, a cloudy fine black precipitate filled the mixture. The black precipitate settled to the bottom of the flask. The mixture was filtered, affording the black filtered material and the filtrate. The filtrate was dried under vacuum, affording a light brown paste. The filtered material and the residue from the filtrate were examined in separate vials (1 and 2, respectively).

A sample of 1-acyldipyrromethane \(2a\) (0.10 mmol, 34 mg) was dissolved in a solution of KOH (28 mg, 0.50 mmol, 500 mM) in ethanol (1 mL). The resulting solution was added to vial 1 containing the filtered material. Vial 2, containing the filtrate, was treated identically. Each reaction was allowed to proceed with stirring at room temperature exposed to air (entry 1, Table S-1). The reactions were monitored by TLC, absorption spectroscopy, and LD-MS. After 1 h, no porphyrin was observed in either vial 1 or vial 2. However, the corresponding 1-acyldipyrrin \(6a\) was observed in each vial by TLC analysis (after 10 min) and was confirmed by LD-MS analysis. Upon stirring each vial for 18 h, 6-7 additional spots were present upon TLC analysis yet again there was no porphyrin formed.

**Experiment 2.** A sample of KOH (14 mg, 0.25 mmol, 500 mM) was dissolved in ethanol (0.5 mL) exposed to air, then \(\text{Pd(CH}_3\text{CN)}_2\text{Cl}_2\) (0.008 mg, 0.03 mmol, 60 mM) was added, affording a black precipitate. After 5 min, a sample of \(2a\) (17 mg, 0.050 mmol) was added to the resulting mixture. Upon stirring at room temperature for 10 min, the byproduct 1-acyldipyrrin \(6a\) was observed by TLC analysis. After stirring for 3 h, 4-5 spots were observed in addition to the 1-acyldipyrrin \(6a\) upon TLC analysis. UV-vis analysis of the reaction mixture showed the porphyrin in 2% yield (entry 2). The formation of 1-acyldipyrrin \(6a\) and porphyrin \(\text{Pd-4a}\) were also confirmed by LD-MS analysis. An experiment was performed under similar
conditions but after adding 2a, the mixture was heated at 75 °C. After 1 h the porphyrin was observed in 17% spectroscopic yield (entry 3).

It is known that a variety of PdX₂ species upon treatment with alkali yield a precipitate of Pd(OH)₂. The composition of the precipitate in these experiments is not known. However, Pd(OH)₂ was found to be inactive in the self-condensation of 1-acyldipyrromethane 2a (see entry 6, Table 1).

**Experiment 3.** Here the order-of-addition of reagents was changed. A sample of KOH (28 mg, 0.50 mmol, 500 mM) was dissolved in ethanol exposed to air, then 2a (0.10 mmol, 34 mg) was added, and lastly the Pd(CH₃CN)₂Cl₂ was added. After stirring at room temperature for 10 min, TLC and UV-vis analysis showed the formation of the porphyrin. The spectroscopic yield of porphyrin after 2 h was 25% (entry 4).

This series of experiments demonstrated the importance of the order-of-addition of reagents for the formation of palladium porphyrin in high yield. From a preparative standpoint, one must avoid the reaction of the palladium reagent with the solution of KOH in ethanol in the absence of the 1-acyldipyrromethane.

**Table S-1. Effect of the Order of Addition of Reagents**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Order of Addition of Reagents</th>
<th>Time</th>
<th>Yield of Pd-4a b</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>EtOH</td>
<td>KOH</td>
<td>Pd reagent</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3⁵,d</td>
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<tr>
<td>2</td>
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<td>2</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
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</table>

aThe standard conditions entail use of 2a (100 mM), KOH (500 mM), and Pd(CH₃CN)₂Cl₂ (60 mM) in ethanol at room temperature exposed to air. bYields were determined spectroscopically (see Section I.A in Experimental Section). cA solution of KOH in ethanol was treated with Pd(CH₃CN)₂Cl₂, and allowed to stand for 5 min to give a black precipitate. dThe black precipitate was filtered, and the filtrate was dried. eA solution of 2a (0.1 mmol, 100 mM) and KOH (0.5 mmol) in ethanol was added to the filtered material at room temperature. fDipyrrin was observed in TLC, LD-MS and UV-vis spectroscopic analysis. gA solution of 2a (0.1 mmol, 100 mM) and KOH (0.5 mmol) in ethanol was added to the dried filtrate at room temperature. hThis standard reaction was carried out at 75 °C.
2. Experiments Probing the Reaction Course and Intermediates

Omission of Palladium Reagent: 1-Acylldipyrrin Formation. A control experiment was conducted to probe the formation of 1-(4-methylbenzoyl)-5-phenylpyrrole (6a) from 1-(4-methylbenzoyl)-5-phenylpyrromethane (2a) in ethanolic KOH at 70 °C (in the absence of any palladium reagent). Accordingly, a solution of 2a (0.034 g, 0.10 mmol, 100 mM) in ethanol (1 mL) was treated with KOH (0.028 g, 0.50 mmol, 500 mM) at 70 °C exposed to air for 1 h. The reaction was monitored by periodic removal of aliquots and analysis by quantitative TLC and by UV-vis absorption spectroscopy. Three absorption bands were present in the UV-vis spectrum: a band at 316 nm corresponding to 2a, a broad band over 350 to 420 nm, and a third broad band with lower intensity over 420-540 nm. Given the overlapped absorption bands, it was difficult to observe the characteristic signature of 6a [typically \( \lambda_{\text{abs}} (\text{CH}_2\text{Cl}_2) 302 (\varepsilon = 15,300 \text{ M}^{-1}\text{cm}^{-1}) \), 432 (\( \varepsilon = 22,800 \text{ M}^{-1}\text{cm}^{-1}) \)]. TLC analysis showed the presence of several new products, including 6a by co-chromatography with an authentic sample. Quantitative TLC analysis\(^{S2}\) [silica, \( \text{CH}_2\text{Cl}_2/\text{ethyl acetate} (25:1) \)] was performed using an authentic sample of 6a at various concentrations (1 mM, 0.316 mM, 0.1 mM and 0.0316 mM) with visual inspection to estimate the concentration of 6a in the reaction mixture. The limit of detection of 6a was 0.01 mM, which corresponds to a yield of 6a of 0.01%. TLC analysis indicated that 6a is present in the reaction mixture at a concentration of \(~0.316 \text{ mM} \), corresponding to a yield of \(~0.3\% \).

Omission of Dipyrromethane: 1,9-Diacyldipyrrin Formation. A similar reaction of 1,9-diacyldipyrrromethane 3a with KOH in ethanol (in the absence of any palladium reagent) was performed to see whether the corresponding 1,9-diacyldipyrrin is formed. Accordingly, a mixture of 3a (100 mM) in ethanol exposed to air was treated with KOH (1 M) and the resulting red mixture was heated at reflux. The reaction was monitored by UV-vis absorption spectroscopy to see the presence of the signature peak (470 nm) for a 1,9-diacyldipyrrin (e.g., 5-mesityl-1,9-di-p-tolylidipyrrin 8 has \( \varepsilon_{470 \text{ nm}} = 28,000 \text{ M}^{-1}\text{cm}^{-1} \) in toluene, as determined herein). The absorption spectrum of the reaction mixture after 2 h did not show any signature peak for the 1,9-diacyldipyrrin. TLC examination showed only the presence of 3a.

Omission Experiments Probing Complex Formation. A reaction of 3a (in the absence of any dipyrromethane) in ethanolic KOH and \( \text{Pd} (\text{CH}_3\text{CN})_2\text{Cl}_2 \) was performed to see whether the corresponding bis(1,9-diacyldipyrrinato)palladium(II) complex is formed. Accordingly, a mixture of 3a (100 mM) in EtOH was treated with KOH (1 M) followed by \( \text{Pd} (\text{CH}_3\text{CN})_2\text{Cl}_2 \) (100 mM) and the resulting red mixture was heated at reflux exposed to air. The reaction was monitored by UV-vis absorption spectroscopy to see the presence of the anticipated peak (assumed \(~560 \text{ nm} \)) for a bis(1,9-diacyldipyrrinato)palladium(II) complex. The absorption spectrum of the reaction mixture (after 2 h) did not show any such peak. TLC examination showed the presence of 3a and some non-polar spots.

Also, a reaction of 2-benzoylpyrrole (7) in ethanolic KOH and \( \text{Pd} (\text{CH}_3\text{CN})_2\text{Cl}_2 \) was performed to see whether the corresponding palladium complex is formed. Accordingly, a mixture of 7 (100 mM) in EtOH was treated with KOH (500 M) followed by \( \text{Pd} (\text{CH}_3\text{CN})_2\text{Cl}_2 \) (50 mM) and the resulting mixture was heated at reflux exposed to air. The reaction was monitored by UV-vis absorption spectroscopy to see the presence of any peak (estimated at 380 nm on the basis of spectra for an analogous copper(II) complex of a 1-acyldipyrrromethane)\(^2\) for the palladium complex. The absorption spectrum of the reaction mixture (after 2 h) did not show any peak for such a complex. TLC examination showed only the presence of 7.
Analysis of the Formation of Palladium Dihydroporphyrin Pd-9. Samples of 2i (0.278 g, 1.00 mmol), KOH (0.280 g, 5.00 mmol) and Pd(CH$_3$CN)$_2$Cl$_2$ (0.155 g, 0.600 mmol) were placed in a flask and ethanol (10 mL) was added. The mixture was heated at 75 °C exposed to air for 1 h. The reaction was monitored by periodic removal of aliquots and analysis by TLC and UV-vis absorption spectroscopy. A band at 500 nm and a broad band from 510 to 540 nm were observed. Given the overlapped absorption bands, it was difficult to observe the characteristic signature of Pd-9 [λ$_{abs}$ in nm (log ε) 321 (4.25), 406 (4.39), 465 (4.53), 501 (4.72)]. TLC analysis showed the presence of several new products, including Pd-9 by co-chromatography with an authentic sample. Quantitative TLC analysis$^2$ [silica, CH$_2$Cl$_2$/hexanes (1:1)] was performed using an authentic sample of Pd-9 at various concentrations (3.16 mM, 1 mM, 0.316 mM and 0.1 mM) with visual inspection to estimate the concentration of Pd-9 in the reaction mixture. The limit of detection of Pd-9 was 0.0316 mM, which corresponds to a yield of Pd-9 of ~0.06%. TLC analysis indicated that Pd-9 is present in the reaction mixture at a concentration approximately corresponding to the standard sample at 0.316 mM of the authentic Pd-9, thus corresponding to a yield of ~0.6%. The formation of Pd-9 was also confirmed by MALDI-MS (POPOP), which showed a peak at m/z = 624.6.

3. Synthesis of $^{13}$C-labeled 1-Acylpyrromethanes

![Scheme S1](image_url)
The reaction of $^{13}$C-1-benzoic acid with 2,2'-dipyridyl disulfide and triphenylphosphine following a known procedure$^{1,17}$ afforded the isotopically labeled Mukaiyama reagent $^{13}$C-S-2-pyridyl benzothioate (5g) (Scheme S1). The Mukaiyama reagent was employed to form the desired $^{13}$C-labeled 1-acyldipyrromethanes. The reaction with 5-phenyldipyrromethane (1a) was carried out in the typical fashion,$^2$ using 9-BBN-triflate as a coordination aid. The intermediate complex 2j-BBN was obtained in 70% yield. Decomplexation by treatment with 1-pentanol in THF afforded the labeled 1-acyldipyrromethane 2j in 67% overall yield. The 1-methyldipyrromethane S-1, obtained by Wolff-Kishner reduction$^3$ of 1-formyldipyrromethane (2h) in 81% yield, also was treated with Mukaiyama reagent 5g. A stable 9-BBN complex was not obtained and the desired labeled 1-acyldipyrromethane 11 was obtained in 21% yield.

4. Synthesis of a Palladium Chlorin

The palladium porphyrin-forming conditions were examined for application to the formation of a palladium chlorin. The method employed for the formation of a chlorin employs the reaction of a tetrahydrodipyrrin bearing a geminal dimethyl group in the pyrroline ring (Western half) and a 1-bromo-9-carbinol-substituted dipyrromethane (Eastern half).$^{54}$ The reaction proceeds via acid-catalyzed condensation to give a tetrahydrobilene-a intermediate followed by metal-mediated oxidative cyclization to give the zinc chlorin. Demetalation and remetalation then provides access to a variety of metallochlorins. The Western half S-2 was synthesized following a known procedure.$^{54}$ Here we sought to examine whether a 1-bromo-9-acyl-substituted dipyrromethane (Eastern half precursor) could be used directly to give the palladium chlorin under basic conditions, thereby avoiding several reaction steps. Thus, treatment of Eastern half precursor (S-3) (100 mM) with Western half (S-2) (100 mM) in the presence of Pd(CH$_3$CN)$_2$Cl$_2$ (100 mM) and KOH (500 mM) gave the palladium porphyrin Pd-4a in 2% yield and palladium-chlorin S-Pd4 in 2.8% yield (Scheme S2). The palladium chlorin S-Pd4 was characterized by $^1$H NMR, and UV–vis spectroscopy and LD-MS analysis.

![Scheme S2](image-url)
5. Experimental Section

General. $^1$H NMR (400 MHz), and $^{13}$C NMR (100 MHz) were collected routinely in CDCl$_3$ unless noted otherwise. Melting points are uncorrected. Absorption spectra were collected in toluene unless noted otherwise. Silica gel (40 µm average particle size) or alumina (80-200 mesh) was used for column chromatography. THF was distilled from sodium under argon with benzophenone/ketyl as indicator. Diethyl ether was anhydrous. All other chemicals were reagent grade and were used as received. Absolute ethanol was used in all porphyrin-forming studies.

Noncommercial Compounds. Dipyrrromethanes 1a-c were prepared as described in the literature and analyzed for purity by gas chromatography. 1-Acyl-dipyrrromethane-boron complexes 2a-BBN and 2f-BBN,$^2$ 1-acyldipyrrromethanes 2a,$^2$ 2f,$^2$ 2g,$^9$ and 2h,$^20$ 1,9-diacyldipyrrromethane 3a,$^12$ the Mukaiyama reagents 5a-c,$^12$ and 5d,$^2$ 2-benzoylpyrrole ($7$),$^{24}$ and 1,9-diacyldipyrrrin 8$^{25}$ were prepared as described in the literature. Known compounds 1d,$^{29,30}$ 2d,$^{31}$ 5e,$^{18}$ 5f,$^{11}$ and 9$^{32}$ were prepared as described below.

Anaerobic Experiment with a Pd(0) Reagent. A Schlenk flask was charged with 2a (0.17 g, 0.50 mmol), Pd(PPh$_3$)$_4$ (0.35 g, 0.30 mmol) and KOH (0.14 g, 2.5 mmol). The mixture was subjected to several cycles of freeze-pump degassing with argon. Degassed ethanol was then added via cannula and the reaction mixture was heated to 70 °C for 1 h. There was no porphyrin formation according to UV–vis spectroscopy.

Anaerobic Experiment with a Pd(4) Reagent. A Schlenk flask was charged with 2a (0.17 g, 0.50 mmol), Na$_2$PdCl$_6$ (0.11 g, 0.30 mmol) and KOH (0.14 g, 2.5 mmol). The mixture was subjected to several cycles of freeze-pump-thaw degassing with argon. Degassed ethanol was then added via cannula and the reaction mixture was heated to 70 °C. After 1 h, the mixture was concentrated. The residue was dissolved in CH$_2$Cl$_2$ and chromatographed (alumina, CH$_2$Cl$_2$). The resulting porphyrin-containing solution was concentrated to give an orange-purple solid. The solid was triturated with methanol and dried in vacuo, affording a crystalline orange-purple solid (0.013 g, 7%): LD-MS obsd 746.1; FABMS obsd 746.1706, calcd 746.1662 (C$_{46}$H$_{32}$N$_4$Pd). $\lambda_{abs}$ 416, 523 nm.

5,5-Dimethyl dipyrromethane (1d). Following a standard procedure,$^{10}$ a solution of acetone (5.80 g, 100 mmol) in pyrrole (692 mL) was degassed for 20 min. Then InCl$_3$ (2.21 g, 10.0 mmol) was added. After 2 h of stirring at room temperature under argon, NaOH (12 g, 0.30 mol, 20–40 mesh beads) was added, and the stirring was continued for 45 min. The mixture was filtered. The filtrate was concentrated under high vacuum. The resulting oil was triturated with hexanes (100 mL) and the mixture was concentrated. This procedure was repeated four times, affording a pale white solid. Crystallization from 120 mL of ethanol/water (4:1) afforded colorless crystals (13.2 g, 76%): mp 54–56 °C; (lit.$^{30}$ 56 °C; lit.$^{29}$ 59 °C). The $^1$H NMR spectral data are consistent with reported values:$^{30}$ $^1$H NMR $\delta$ 1.63 (s, 6H), 6.07–6.10 (m, 2H), 6.12–6.14 (m, 2H), 6.56–6.63 (m, 2H), 7.54–7.80 (br, 2H); $^{13}$C NMR $\delta$ 29.5, 35.4, 104.0, 107.7, 117.4, 139.3. Anal. Calcd for C$_{11}$H$_{14}$N$_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.80; H, 8.21; N, 16.05.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-methoxybenzoyl)-5-phenyldipyrrromethane (2b-BBN). Following a standard acylation-complexation procedure,$^{8}$ a solution of EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) was added slowly to a solution of 1a (2.22 g, 10.0 mmol) in THF (10 mL) under argon. The mixture was stirred at room temperature for 10 min and then cooled to −78 °C. A solution of 5b (2.45 g, 10.0 mmol) in THF (10 mL) was added. The solution was
stirred at −78 °C for 10 min and then warmed to room temperature. After standard workup, the crude product (a red-orange oil) thus obtained was dissolved in CH$_2$Cl$_2$ (20 mL) and treated with TEA (3.35 mL, 24.0 mmol) followed by 9-BBN-OTf (40.0 mL, 20.0 mmol, 0.5 M in hexanes) with stirring at room temperature. After 1 h, the mixture was passed through a pad of silica (CH$_2$Cl$_2$), affording a yellow solid (2.96 g, 62%): mp 178–180 °C; $^1$H NMR δ 0.62–0.73 (m, 2H), 1.62–1.84 (m, 6H), 1.86–2.31 (m, 6H), 3.92 (s, 3H), 5.83–5.88 (m, 1H), 6.02 (s, 1H), 6.13–6.18 (m, 1H), 6.39 (d, $J = 4.2$ Hz, 1H), 6.69–6.75 (m, 1H), 7.05 (d, $J = 8.8$ Hz, 2H), 7.13–7.37 (m, 6H), 7.78–7.94 (br, 1H), 8.21 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR δ 24.0, 25.2, 26.0, 26.5, 30.6, 30.9, 34.6, 34.7, 44.8, 55.8, 108.1, 108.6, 114.7, 117.5, 117.8, 120.6, 123.5, 127.1, 128.5, 128.7, 132.0, 132.6, 134.6, 142.4, 151.3, 164.4, 174.0. Anal. Calcd for C$_3$H$_7$N$_2$O: C, 78.15; H, 6.98; N, 5.73. Found: C, 78.07; H, 7.00; N, 5.73. $\lambda_{abs}$ 386 nm.

1-(4-Methoxybenzoyl)-5-phenyldipyrromethane (2b). Following a standard procedure, a sample of 2b-BBN (2.38 g, 5.00 mmol) in THF (8.0 mL) and 1-pentanol (2.0 mL) was refluxed for 1.5 h. The mixture was concentrated. The residue was dissolved in a small volume of CH$_2$Cl$_2$ (2.0 mL) and treated with hexanes, affording an oily precipitate. The solvent was decanted and the residue was dried in vacuo, washed thoroughly with hexanes, and dried to afford a pale brown amorphous powder (1.45 g, 81%): mp 55–56 °C; $^1$H NMR δ 3.88 (s, 3H), 5.88 (m, 1H), 6.05–6.12 (m, 1H), 6.14–6.18 (m, 1H), 6.67–6.72 (m, 1H), 7.28–7.32 (m, 1H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.90–7.98 (m, 5H), 8.04 (d, $J = 8.8$ Hz, 2H), 8.11–8.13 (m, 1H), 9.59–9.73 (br, 1H); $^{13}$C NMR δ 44.3, 55.6, 107.9, 108.5, 110.6, 113.7, 118.0, 120.4, 127.3, 128.5, 128.8, 130.9, 131.1, 131.3, 141.1, 141.5, 162.8, 183.8; FABMS obsd 356.1524, calcd 356.1549 (C$_3$H$_7$N$_2$O$_2$).

10-(Dibutylboryl)-1-(pentafluorobenzoyl)-5-phenyldipyrromethane (2c-BBu$_2$). Following a standard acylation-complexation procedure, a solution of EtMgBr (5.0 mL, 5.0 mmol, 1.0 M in THF) was added slowly to a solution of 1a (0.222 g, 1.00 mmol) in THF (1 mL) under argon. The mixture was stirred at room temperature for 10 min and then cooled to −78 °C. A solution of 5c (0.304 g, 1.00 mmol) in THF (1 mL) was added. The solution was stirred at −78 °C for 10 min and then warmed to room temperature. After standard workup, the crude product (a red-orange oil) thus obtained was dissolved in CH$_2$Cl$_2$ (2 mL) and treated with TEA (0.35 mL, 2.4 mmol) followed by BBu$_3$-OTf (2 mL, 2 mmol, 1.0 M in CH$_2$Cl$_2$) with stirring at room temperature. After 1 h, the mixture was passed through a pad of silica (CH$_2$Cl$_2$), affording a brownish-yellow paste (0.295 g, 55%): $^1$H NMR δ 0.38–0.54 (m, 2H), 0.59–0.69 (m, 6H), 0.70–1.26 (m, 10H), 5.59 (s, 1H), 5.85–5.91 (m, 1H), 6.14–6.16 (m, 1H), 6.52 (d, $J = 4.4$ Hz, 1H), 6.68–6.73 (m, 1H), 7.03–7.09 (m, 1H), 7.21–7.39 (m, 5H), 7.75–7.86 (br, 1H); $^{13}$C NMR δ 14.2, 14.3, 22.2, 22.4, 26.0, 26.1, 26.9, 27.3, 44.5, 108.2, 109.0, 117.8, 120.0, 121.8, 127.7, 128.8, 129.1, 131.1, 131.3, 131.6, 140.6, 154.8, 164.4; FABMS obsd 541.2444, calcd 541.2450 (C$_{30}$H$_{30}$BF$_3$N$_2$O). $\lambda_{abs}$ 315 nm.

1-Pentafluorobenzoyl-5-phenyldipyrromethane (2c). Following a standard procedure, a sample of 2c-BBu$_2$ (0.230 g, 0.425 mmol) in 1-pentanol (1 mL) was heated at 70–75 °C. After 4 h the boron complex was still present in reaction mixture, as proven by TLC. The reaction mixture was stirred overnight at room temperature. The mixture was concentrated, and the residue was dissolved in a small volume of CH$_2$Cl$_2$ (2.0 mL) and treated with hexanes, affording an oily precipitate. The product was chromatographed (silica, CH$_2$Cl$_2$), affording a pale golden-brown amorphous powder (295 mg, 55%): mp 48–56 °C; $^1$H NMR δ 5.55 (s, 1H), 5.96–6.00 (m, 1H), 6.11–6.12 (m, 1H), 6.14–6.16 (m, 1H), 6.63–6.67 (m, 1H), 6.68–6.72 (m,
110.7, 117.8, 120.9, 127.3, 128.1, 128.3, 130.6, 131.1, 136.4 (m), 138.9 (m), 140.3, 141.2 (m), 142.8 (m), 143.7 (m), 145.3, 171.9; FABMS obsd 416.0965, calcd 416.0948 (C$_2$H$_3$F$_3$N$_2$O). Anal. Calcd for C$_2$H$_3$F$_3$N$_2$O: C, 63.47; H, 3.15; N, 6.73. Found: C, 63.78; H, 3.46; N, 6.53.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-hexanoyl-5-phenylpyrromethane (2d-BBN). Following a standard acylation-complexation procedure, a solution of EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) was added slowly to a solution of 1a (2.22 g, 10.0 mmol) in THF (10 mL) under argon. The mixture was stirred at room temperature for 10 min and then cooled to −78 °C. A solution of 5d (2.09 g, 10.0 mmol) in THF (10 mL) was added. The solution was stirred at −78 °C for 10 min and then warmed to room temperature. After standard workup, the crude product (a red-orange oil) thus obtained was dissolved in CH$_2$Cl$_2$ (20 mL) and treated with TEA (3.35 mL, 24.0 mmol) followed by 9-BBN-OTf (40.0 mL, 20.0 mmol, 0.5 M in hexanes) with stirring at room temperature. After 1 h, the mixture was passed through a pad of silica (CH$_2$Cl$_2$), affording a yellow paste (1.95 g, 42%): $^1$H NMR δ 0.55–0.58 (m, 2H), 0.86–1.00 (m, 3H), 1.28–1.43 (m, 4H), 1.60–2.20 (m, 14H), 2.80–2.87 (m, 2H), 5.80–5.84 (m, 1H), 5.94 (s, 1H), 6.09–6.15 (m, 1H), 6.28–6.33 (m, 1H), 6.66–6.71 (m, 1H), 7.05–7.06 (m, 1H), 7.12–7.18 (m, 2H), 7.19–7.39 (m, 3H), 7.78–7.83 (br 1H); $^{13}$C NMR δ 14.1, 22.5, 23.9, 25.0, 25.5, 25.6, 26.3, 30.6, 30.9, 31.5, 31.9, 34.2, 34.3, 44.8, 108.1, 108.6, 117.1, 117.5, 119.9, 127.1, 128.5, 132.4, 136.9, 142.2, 152.3, 185.3; FABMS obsd 440.3012, calcd 440.2999 (C$_{29}$H$_{37}$BN$_2$O). λ$_{abs}$ 338 nm.

1-Hexanoyl-5-phenylpyrromethane (2d). Following a standard procedure, a sample of 2d-BBN (1.95 g, 4.20 mmol) in THF (6.3 mL) and 1-pentanol (2.2 mL) was refluxed for 2 h. The mixture was concentrated. The residue was dissolved in a small volume of CH$_2$Cl$_2$ (2.0 mL) and treated with hexanes, affording an oily precipitate. The solvent was decanted and the residue was dried in vacuo, washed thoroughly with hexanes, and dried again to afford a brown oil (0.96 g, 30%): $^1$H NMR δ 0.83–0.91 (m, 3H), 1.24–1.40 (m, 4H), 1.58–1.72 (m, 2H), 2.56–2.72 (m, 2H), 5.49 (s, 1H), 5.94–5.96 (m, 1H), 5.98–6.04 (m, 1H), 6.12–6.18 (m, 1H), 6.68–6.73 (m, 1H), 6.80–6.86 (m, 1H), 7.13–7.34 (m, 5H), 8.15–8.20 (br, 1H), 9.40–9.45 (br, 1H); $^{13}$C NMR δ 14.1, 22.7, 25.4, 31.9, 37.9, 44.3, 107.9, 108.7, 110.2, 117.2, 117.9, 127.5, 128.5, 129.0, 131.2, 131.7, 140.6, 141.0, 191.2; FABMS obsd 320.1906, calcd 320.1889 (C$_{21}$H$_{24}$N$_2$O). The characterization data are consistent with reported values for the product from the synthesis via a different route. 31

1-(2,4,6-Trimethylbenzoyl)-5-phenylpyrromethane (2e). Following a standard procedure, a solution of 1a (2.22 g, 10.0 mmol) in THF (10 mL) at room temperature under Ar was treated with EtMgBr (25 mL, 25 mmol, 1.0 M solution in THF) for 10 min. The solution was cooled to −78 °C. Then a solution of 5e (2.57 g, 10.0 mmol) in THF (10.0 mL) was added. The reaction mixture was stirred at −78 °C for 10 min and at room temperature for 20 min. Standard workup and chromatography [silica, CH$_2$Cl$_2$/ethyl acetate (9:1)] afforded a colorless solid (2.48 g, 67%): mp 200–202 °C; $^1$H NMR δ 2.16 (s, 6H), 2.30 (s, 3H), 5.52 (s, 1H), 5.94–6.01 (m, 2H), 6.15–6.20 (m, 1H), 6.34–6.44 (br, 1H), 6.68–6.72 (m, 1H), 6.85 (s, 2H), 7.21–7.39 (m, 5H), 7.96–8.12 (br, 1H), 9.21–9.35 (br, 1H); $^{13}$C NMR δ 19.3, 21.1, 44.2, 107.7, 108.3, 110.7, 117.8, 120.9, 127.3, 128.1, 128.3, 128.8, 130.6, 132.1, 134.47, 134.50, 136.5, 138.2, 140.6, 142.0, 188.9. Anal. Calcd for C$_{23}$H$_{24}$N$_2$O: C, 81.49; H, 6.57; N, 7.60. Found: C, 81.44; H, 6.57; N, 7.67.

1-Benzoyl-5,5-dimethylpyrromethane (2i). Following a standard procedure, a solution of 1d (1.74 g, 10.0 mmol) in THF (10 mL) at room temperature under argon was treated
with EtMgBr (25 mL, 25 mmol, 1.0 M solution in THF) for 10 min. The solution was cooled to –78 °C. Then a solution of 5f (2.15 g, 10.0 mmol) in THF (10.0 mL) was added. The reaction mixture was stirred at reflux exposed to air. After 8 h, the mixture was cooled to –78 °C for 10 min and at room temperature for 20 min. Standard workup and chromatography [silica, CH₂Cl₂/ethyl acetate (9:1)] afforded the crude carbinol as an orange oil.

Following a known procedure, a solution of EtMgBr (10 mL, 10 mmol, 1.0 M in THF) was carefully added to a stirred solution of 5-phenyldipyrrmethane (1a) (1.22 g, 4.90 mmol) in THF (5 mL) under argon. The mixture was stirred at room temperature for 10 min and then cooled to –78 °C. A solution of 5g (1.06 g, 4.90 mmol) in THF (5 mL) was then added over 1 min. The solution was maintained at –78 °C for 10 min, then the orange mixture was allowed to warm to room temperature. After standard workup, the crude product obtained was dissolved in CH₂Cl₂ (10 mL) and treated with TEA (1.6 mL, 12 mmol) and 9-BBN-OTf (20 mL, 10 mmol, 0.5 M hexanes) while stirring at room temperature. After 1 h, the reaction mixture was passed through a silica pad (CH₂Cl₂), affording a yellow solid (1.54 g, 70%): mp 175–180 °C; ¹H NMR δ 0.64–0.76 (m, 2H), 1.64–1.88 (m, 6H), 1.92–2.30 (m, 6H), 5.84–5.86 (m, 1H), 6.02 (s, 1H), 6.13–6.18 (m, 1H), 6.42–6.46 (m, 1H), 6.70–6.76 (m, 1H), 7.15–7.20 (m, 2H), 7.23–7.37 (m, 4H), 7.54–7.60 (m, 2H), 7.62–7.68 (m, 1H), 7.82–7.90 (br, 1H), 8.18–8.24 (m, 2H); ¹³C NMR δ 23.9, 25.2, 25.7, 30.7, 30.8, 34.5, 34.6, 44.8, 108.2, 108.7, 117.6, 118.6, 118.7, 121.2, 121.3, 127.2, 128.6, 128.8, 129.2, 129.3, 129.76, 129.79, 133.9, 142.1, 174.4; FABMS obsd 447.2551, calcd 447.2563 (C₂₉H₁₈N₂O). \( \lambda_{abs} \) 332 nm.

1-(Benzoyl-carbonyl)-¹³C]-10-(9-borabicyclo[3.3.1]nona-9-yl)-5-phenyldipyrrmethane (2j-OB). Following a known procedure, a solution of 2j-BBN (1.54 g, 3.50 mmol) in THF (5.5 mL) and 1-pentanol (2.6 mL) was refluxed for 3.5 h. The reaction was cooled to room temperature and concentrated. The crude product was treated with hexanes (30 mL), heated until completely dissolved and was cooled to room temperature. The resulting precipitate was separated, dissolved in CH₂Cl₂ and dried to give a pale-brown amorphous powder (1.07 g, 67%): mp 56–62 °C; ¹H NMR δ 5.56 (s, 1H), 5.97–6.00 (m, 1H), 6.08–6.10 (m, 1H), 6.12–6.16 (m, 1H), 6.62–6.65 (m, 1H), 6.78–6.82 (m, 1H), 7.16–7.30 (m, 5H), 7.44 (d, J = 7.6 Hz, 2H), 7.50–7.58 (m, 1H), 7.74–7.80 (m, 2H), 8.35–8.42 (br, 1H), 10.10–10.15 (br, 1H); ¹³C NMR δ 44.4, 108.0, 108.8, 110.7, 110.8, 118.0, 120.7, 120.8, 127.6, 128.4, 128.5, 128.6, 129.0, 129.1, 131.9, 140.8, 169.4, 184.7; FABMS obsd 327.1467, calcd 327.1453 (C₂₁H₁₈N₂O).

1-(α-Hydroxy)benzyl-methyl-¹³C]-5-phenyldipyrrmethane (2j-OH). Following a known procedure, a sample of NaBH₄ (116 mg, 3.06 mmol) was added in small portions to a stirred solution of 2j (40 mg, 0.12 mmol) in THF/methanol (3:1, 2.5 mL). After 20 min the usual workup afforded the crude carbinol as an orange oil. ¹³C NMR spectroscopy of the crude 2j-OH (mixture of diastereomers) showed the carbinol resonance at 70.36 and 70.45 ppm for the ¹³C-labeled carbon.

[5,15-Bis(4-methylphenyl)-10,20-diphenylporphinato]copper(II) (Cu-4a). A mixture of 2a (85 mg, 0.25 mmol), KOH (140 mg, 2.50 mmol) and Cu(OAc)₂·H₂O (50 mg, 0.25 mmol) in ethylene glycol (3 mL) was stirred at reflux exposed to air. After 8 h, the mixture was cooled...
to room temperature and diluted with CHCl₃. The mixture was then passed through a pad of silica (CHCl₃). The reddish fractions were collected and concentrated to afford a red-purple solid (11 mg, 13%): LD-MS obsd 703.6; FABMS obsd 703.1930, calcd 703.1923 (C₄₆H₃₂CuN₄). λ<sub>abs</sub> 415, 538 nm.

[5,15-Bis(4-methoxyphenyl)-10,20-diphenylporphinato]palladium(II) (Pd-4b). Self-condensation of 2b (0.356 g, 1.00 mmol) in the presence of KOH (0.280 g, 5.00 mmol) and Pd(CH₃CN)₂Cl₂ (0.155 g, 0.600 mmol) in ethanol (10.0 mL) following the procedure described for Pd-4a gave a purple solid. The solid was triturated with methanol and dried in vacuo affording a crystalline purple solid (0.148 g, 38%): ¹H NMR δ 4.08 (s, 6H), 7.23–7.31 (m, 4H), 7.69–7.81 (m, 6H), 8.04–8.11 (m, 4H), 8.18–8.20 (m, 4H), 8.80 (d, J = 5.1 Hz, 4H), 8.84 (d, J = 5.1 Hz, 4H); ¹³C NMR δ 55.8, 112.4, 121.7, 121.8, 126.9, 127.9, 131.1, 131.2, 134.3, 135.3, 141.7, 142.0, 142.1, 159.6; LD-MS obsd 778.1; FABMS obsd 778.1611, calcd 778.1560 (C₄₆H₃₂N₄O₂Pd). λ<sub>abs</sub> in nm (log ε) 419 (5.45), 465 (3.36), 486 (3.46), 525 (4.41), 554 (3.33).

[5,15-Bis(4-ethoxy-2,3,5,6-tetrafluorophenyl)-10,20-diphenylporphinato]palladium(II) (Pd-4c). Self-condensation of 2c (0.380 g, 1.00 mmol) in the presence of KOH (0.280 g, 5.00 mmol) and Pd(CH₃CN)₂Cl₂ (0.155 g, 0.600 mmol) in ethanol (10.0 mL) following the procedure described for Pd-4a gave a purple solid. The solid was triturated with methanol and dried in vacuo affording a crystalline purple solid (0.138 g, 29%): ¹H NMR δ 1.65 (t, J = 7.0 Hz, 6H), 4.64 (q, J = 4.6 Hz, 4H), 7.74–7.81 (m, 6H), 8.17–8.19 (m, 4H), 8.80 (d, J = 4.8 Hz, 4H), 8.89 (d, J = 5.1 Hz, 4H); ¹³C NMR δ 16.0, 29.9, 122.8, 127.1, 128.3, 129.8, 132.7, 134.4, 141.4, 141.4, 142.4; LD-MS obsd 952.1; FABMS obsd 950.1174, calcd 950.119 (C₄₆H₂₈F₈N₄O₃Pd). λ<sub>abs</sub> in nm (log ε) 414 (5.35), 485 (3.63), 522 (4.38), 555 (4.14).

[5,15-Dipentyl-10,20-diphenylporphinato]palladium(II) (Pd-4d). Self-condensation of 2d (0.320 g, 1.00 mmol) in the presence of KOH (0.280 g, 5.00 mmol) and Pd(CH₃CN)₂Cl₂ (0.155 g, 0.600 mmol) in ethanol (10.0 mL) following the procedure described for Pd-4a gave an orange-purple solid. The solid was triturated with methanol and dried in vacuo affording a crystalline purple solid (0.172 g, 49%): ¹H NMR δ 0.96 (t, J = 7.3 Hz, 6H), 1.49–1.59 (m, 4H), 1.72–1.82 (m, 4H), 2.44–2.53 (m, 4H), 4.85–4.93 (m, 4H), 7.72–7.80 (m, 6H), 8.14–8.18 (m, 4H), 8.83 (d, J = 5.1 Hz, 4H), 9.40 (d, J = 5.1 Hz, 4H); ¹³C NMR δ 14.4, 23.0, 32.9, 35.5, 38.2, 120.8, 121.4, 126.9, 127.9, 128.0, 131.5, 134.3, 140.9, 141.7, 142.3; LD-MS obsd 706.0; FABMS obsd 706.2338, calcd 706.2288 (C₄₂H₄₀N₄Pd). λ<sub>abs</sub> in nm (log ε) 419 (5.23), 467 (3.10), 489 (3.29), 527 (4.20), 560 (3.17).

[meso-Tetrakis(4-methoxyphenyl)porphinato]palladium(II) (Pd-4f). Self-condensation of 2f (0.386 g, 1.00 mmol) in the presence of KOH (0.280 g, 5.00 mmol) and Pd(CH₃CN)₂Cl₂ (0.155 g, 0.600 mmol) in ethanol (10.0 mL) following the procedure described for Pd-4a gave a purple crystalline solid. The solid was triturated with methanol and dried in vacuo affording a crystalline purple solid (0.185 g, 44%): ¹H NMR δ 4.09 (s, 12H), 7.24–7.31 (m, 8H), 8.07 (d, J = 8.6 Hz, 8H), 8.83 (s, 8H); ¹³C NMR δ 55.8, 112.4, 121.6, 131.1, 134.4, 135.3, 142.7, 159.6; LD-MS obsd 838.2; FABMS obsd 838.1815, calcd 838.1771 (C₄₆H₃₆N₄O₄Pd). λ<sub>abs</sub> in nm (log ε) 420 (5.55), 485 (3.57), 525 (4.47), 560 (3.56). A different route to this compound has been reported.²²

[5,15-Diphenylporphinato]palladium(II) (Pd-4h). Self-condensation of 2h (0.250 g, 1.00 mmol) in the presence of KOH (0.280 g, 5.00 mmol) and Pd(CH₃CN)₂Cl₂ (0.155 g, 0.600
mmol) in ethanol (10.0 mL) following the procedure described for Pd-4a gave an orange-purple solid. The solid was triturated with methanol and dried in vacuo affording a crystalline orange-purple solid (0.162 g, 57%). $^1$H NMR $\delta$ 7.74–7.77 (m, 6H), 8.18–8.27 (m, 4H), 9.01 (d, $J = 4.8$ Hz, 4H), 9.30 (d, $J = 4.8$ Hz, 4H); $^13$C NMR $\delta$ 107.3, 109.4, 127.0, 128.0, 131.2, 131.7, 134.5, 141.3, 141.5, 141.8; LD-MS obsd 565.3; FABMS obsd 566.0746, calcd 566.0722 (C$_{32}$H$_{20}$N$_4$Pd). $\lambda_{abs}$ (in CH$_2$Cl$_2$) in nm (log $\varepsilon$) 405 (5.39), 476 (3.39), 513 (4.35), 544 (3.94).

**[meso-(5,15-$^{13}$C)Tetraphenylporphinato]palladium(II) (Pd-4j).** A sample of 2j (0.326 g, 1.00 mmol) in the presence of KOH (0.280 g, 5.00 mmol) and Pd(CH$_3$CN)$_2$Cl$_2$ (0.155 g, 0.600 mmol) in ethanol (10 mL) following the procedure described for Pd-4a gave a crystalline purple solid (0.152 g, 42%): $^1$H NMR $\delta$ 7.70–7.80 (m, 12H), 8.16–8.20 (m, 8H), 8.81 (s, 8H); $^13$C NMR $\delta$ 121.9, 126.9, 128.0, 131.19, 131.24, 134.3, 141.4, 141.70, 141.74, 141.8, 142.0, 142.1, 142.3; LD-MS obsd 720.0; FABMS obsd 720.1442, calcd 720.1416 (C$_{42}$H$_{28}$N$_4$Pd). $\lambda_{abs}$ in nm (log $\varepsilon$) 417 (5.33), 484 (3.50), 488 (3.48), 524 (4.42), 553 (3.42).

**S-2-Pyridyl 2,4,6-trimethylbenzothioate (5e).** Following a standard procedure,$^{12}$ a solution of 2-mercaptopypyridine (3.33 g, 30.0 mmol) in THF (30 mL) was treated with p-mesityloxy chloride (5.48 g, 30.0 mmol) at room temperature with stirring for 30 min. The standard workup followed by precipitation afforded a pale yellow solid (6.32 g, 82%): mp 48–50 °C (lit.$^{18}$ 54–55 °C): $^1$H NMR $\delta$ 2.30 (s, 3H), 2.40 (s, 6H), 6.88 (s, 2H), 7.29–7.35 (m, 1H), 7.76–7.83 (m, 2H), 8.64–8.69 (m, 1H); $^13$C NMR $\delta$ 19.2, 21.3, 123.7, 128.6, 130.0, 133.9, 137.0, 137.3, 139.9, 150.6, 152.1, 195.3. Anal. Calcd for C$_{15}$H$_{15}$NOS: C, 70.01; H, 5.87; N, 5.44. Found: C, 70.10; H, 5.95; N, 5.38. The title compound has been prepared via a different route; the reported H NMR spectral data ($^1$H NMR spectrum) are consistent with those observed here.$^{18}$

**S-2-Pyridyl benzothioate (5f).** Following a standard procedure,$^{12}$ a solution of 2-mercaptopypyridine (3.33 g, 30.0 mmol) in THF (30 mL) was treated with benzoyl chloride (4.21 g, 30.0 mmol) at room temperature with stirring for 30 min. The standard workup followed by precipitation afforded a pale yellow solid (5.67 g, 88%): mp 48–50 °C. $^1$H NMR spectral data are consistent with reported values: $^{11}$ $^1$H NMR $\delta$ 7.31–7.37 (m, 1H), 7.46–7.53 (m, 2H), 7.59–7.65 (m, 1H), 7.71–7.78 (m, 1H), 7.81 (dt, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H), 8.00–8.06 (m, 2H), 8.66–8.71 (m, 1H); $^13$C NMR $\delta$ 123.7, 127.6, 128.9, 131.0, 134.0, 136.6, 137.3, 150.6, 151.4, 189.4. Anal. Calcd for C$_{12}$H$_{15}$NOS: C, 66.95; H, 4.21; N, 6.51. Found: C, 66.63; H, 4.12; N, 6.57.

**1-(Benzoyl-carbonyl-$^{13}$C)-5-phenyldipyrrin (6j).** Following the procedure described for 6a, a solution of 2j (32.7 mg, 0.10 mmol) in THF (32 mL) was treated dropwise with a solution of DDQ (22.7 mg, 0.10 mmol) in THF (32 mL). After stirring for 1 h at room temperature, the solvent was evaporated. The reaction mixture was dissolved in CH$_2$Cl$_2$ and purified by column chromatography [silica, CH$_2$Cl$_2$/ethyl acetate (25:1)] affording a brown amorphous powder (21
mg, 65%): mp 119–122 °C; $^1$H NMR $\delta$ 6.38 (d, $J = 4.0$ Hz, 1H), 6.58 (d, $J = 4.4$ Hz, 1H), 6.80–6.85 (m, 2H), 7.45–7.52 (m, 7H), 7.58–7.62 (m, 1H), 7.91–8.0 (m, 2H), 8.10 (s, 1H), 13.1–13.3 (br, 1H); $^{13}$C NMR $\delta$ 119.3, 119.4, 122.14, 122.18, 125.7, 128.1, 126.6, 129.3, 129.4, 129.5, 131.0, 132.4, 135.3, 136.6, 138.1, 138.7, 139.3, 140.9, 150.9, 185.8; FABMS obsd 7361.5, 129.4, 129.5, 131.0, 132.4, 135.3, 136.6, 138.1, 138.7, 139.3, 140.9, 150.9, 160.1, 185.8; FABMS obsd 326.1393, calcd 326.1374. $\lambda_{\text{abs}}$ (CH$_2$Cl$_2$) 304 nm, 431 nm.

5,5,15,15-Tetramethyl-10,20-diphenylporphodimethene (9). A sample of NaBH$_4$ (0.945 g, 25.0 mmol) was added in small portions to a stirred solution of 1-acyldipyrromethane 2i (0.278 g, 1.00 mmol) in THF/methanol (3:1, 20 mL). The progress of the reduction was monitored by TLC analysis [alumina, hexanes/ethyl acetate (9:1)] of reaction aliquots. After the reaction was complete (about 20 min), the reaction mixture was poured into a stirred mixture of saturated aqueous NH$_4$Cl and CH$_2$Cl$_2$. The organic phase was separated, washed with water, dried (Na$_2$SO$_4$), and concentrated under reduced pressure to afford the monocarbinol as a yellow paste. The monocarbinol (1.00 mmol, assuming quantitative reduction) was dissolved in reagent-grade CH$_2$Cl$_2$ (200 mL). Yb(OTf)$_3$ (0.040 g, 0.064 mmol, 0.32 mM) was added. The reaction was monitored by absorption spectroscopy [by injecting a 50-µL reaction aliquot into a solution of DDQ (300 µL, 0.01 M in toluene); then 50 µL of the resulting oxidized mixture was dissolved in CH$_2$Cl$_2$/EtOH (3:1, 3 mL), and the absorption spectrum was recorded]. After acid-catalyzed condensation for 4 h, DDQ (0.227 g, 1.00 mmol) was added. The reaction mixture was stirred at 45 °C for 30 min. The reaction mixture was poured into a stirred mixture of saturated aqueous NH$_4$Cl and CH$_2$Cl$_2$. The organic phase was separated, washed with water, dried (Na$_2$SO$_4$), and concentrated under reduced pressure to afford the title compound as a crystalline reddish purple solid (0.105 g) and 10 as a crystalline orange solid (0.075 g). $^1$H NMR spectral data are consistent with those of the reported values.32 Data for the title compound 9: $^1$H NMR $\delta$ 1.95 (s, 12H), 6.23 (dd, $J_1 = 4.3$ Hz, $J_2 = 0.9$ Hz, 4H), 6.32 (dd, $J_1 = 4.3$ Hz, $J_2 = 0.9$ Hz, 4H), 7.35–7.47 (m, 10H), 14.18 (s, 2H); $^{13}$C NMR $\delta$ 29.1, 38.4, 114.4, 127.6, 128.5, 128.8, 130.9, 137.3, 140.5, 140.6, 165.5; LD-MS obsd 520.7; FABMS obsd 521.2717, calcd 521.2705 [(M+H$^+$)] (M = C$_{36}$H$_{32}$N$_4$); $\lambda_{\text{abs}}$ (CH$_2$Cl$_2$) 322, 423 nm. Data for 10: $^1$H NMR $\delta$ 1.79 (s, 18H), 6.34 (d, $J = 4.2$ Hz, 6H), 6.49 (d, $J = 4.2$ Hz, 6H), 7.35–7.48 (m, 15H), 13.13 (s, 3H); $^{13}$C NMR $\delta$ 27.6, 39.3, 115.5, 127.7, 128.7, 129.1, 130.7, 137.5, 139.8, 139.9, 162.6; LD-MS obsd 782.1; FABMS obsd 781.4067, calcd 781.4019 [(M+H$^+$)] (M = C$_{54}$H$_{48}$N$_6$); $\lambda_{\text{abs}}$ (CH$_2$Cl$_2$) 274, 441 nm.

[5,5,15,15-Tetramethyl-10,20-diphenylporphodimethenate]palladium(II) (Pd-9). A mixture of 9 (52 mg, 0.10 mmol, 50 mM) and Pd(O$_2$CCF$_3$)$_2$ (66.5 mg, 0.200 mmol) in 1,2-dichloroethane/methanol (4:1, 2 mL) was stirred at 45 °C for 30 min. The reaction mixture was concentrated. The residue was dissolved in CHCl$_3$ and passed through a pad of alumina [hexanes/CH$_2$Cl$_2$ (2:1)]. The fraction containing the title compound was concentrated to give a red solid. The solid was triturated with methanol and dried in vacuo, affording a crystalline red solid (14 mg, 22%): $^1$H NMR $\delta$ 1.94 (s, 12H), 6.37 (d, $J = 4.4$ Hz, 4H), 6.47 (d, $J = 4.4$ Hz, 4H), 7.36–7.47 (m, 10H); $^{13}$C NMR $\delta$ 31.4, 40.7, 114.2, 127.5, 128.5, 130.6, 131.5, 135.2, 137.8, 145.4, 164.3; MALDI-MS (POPOP) obsd 623.6; FABMS obsd 624.1561, calcd 624.1505 (C$_{50}$H$_{30}$N$_4$Pd); $\lambda_{\text{abs}}$ in nm (log $\varepsilon$) 321 (4.25), 406 (4.39), 465 (4.53), 501 (4.72).

1-Methyl-5-phenylpyrromethane (S-1). Following a standard procedure,33 a mixture of 2h (5.00 g, 20.0 mmol) and KOH (3.86 g, 68.8 mmol) in ethylene glycol (30 mL) was treated with hydrazine hydrate (2.65 g, 82.8 mmol) and refluxed for 1 h. The reaction mixture was
cooled to room temperature, diluted with CH₂Cl₂, and washed with water. The organic layer was dried (Na₂SO₄), concentrated, and chromatographed (silica, CH₂Cl₂) to afford a brown paste (3.85 g, 81%). ¹H NMR δ 2.19 (s, 3H), 5.41 (s, 1H), 5.70–5.76 (m, 1H), 5.77–5.81 (m, 1H), 5.90–5.93 (m, 1H), 6.12–6.18 (m, 1H), 6.69 (d, J = 1.3 Hz, 1H), 7.17–7.36 (m, 5H), 7.59 (br, 1H), 7.94 (br, 1H); ¹³C NMR δ 13.2, 44.2, 106.1, 107.2, 107.5, 108.5, 117.3, 127.0, 127.5, 128.6, 128.7, 131.2, 132.8, 142.4; FABMS obsd 236.1303, calcd 236.1313 (C₁₁H₁₄O₂).

1-(Benzyol-carbonyl-¹³C)-9-methyl-5-phenyldipyrrromethane (11). Following a standard procedure,¹¹ a solution of S-I (2.36 g, 10.0 mmol) in THF (10 mL) at room temperature under argon was treated with EtMgBr (25 mL, 25 mmol, 1.0 M solution in THF) for 10 min. The solution was cooled to –78 °C. Then a solution of 5g (2.16 g, 10.0 mmol) in THF (10.0 mL) was added. The reaction mixture was stirred at –78 °C for 10 min and at room temperature for 20 min. Standard workup and chromatography [silica, CH₂Cl₂/ethyl acetate (9:1)] afforded a light brown amorphous solid (0.72 g, 21%): mp 183 °C (dec); ¹H NMR δ 2.16 (s, 3H), 5.49 (s, 1H), 5.80–5.81 (m, 1H), 5.82–5.87 (m, 1H), 6.07–6.11 (m, 1H), 6.77–6.84 (m, 1H), 7.20–7.37 (m, 5H), 7.40–7.58 (m, 3H), 7.75–7.87 (m, 3H), 9.62 (s, 1H); ¹³C NMR (THF-d₈) δ 13.2, 45.3, 106.1, 108.4, 110.7, 110.8, 119.88, 119.94, 127.4, 128.0, 128.97, 129.00, 129.05, 129.5, 129.73, 129.75, 131.4, 132.0, 132.1, 140.1, 140.7, 143.4, 143.7, 184.0; FABMS obsd 341.1603, calcd 341.1609 (C₁₂H₁₄N₂O₂).

1-Bromo-5-phenyl-(4-methylbenzoyl)dipyrrromethane (S-3). Following a general procedure,¹¹ a solution of 2a (0.340 g, 1.00 mmol) in 10 mL of dry THF was cooled to –78 °C under argon. NBS (0.179 g, 1.00 mmol) was added and the reaction mixture was stirred at –78 °C. After 1 h, hexanes (10 mL) and water (10 mL) was added and the mixture was allowed to warm to room temperature. The organic phase was extracted with CH₂Cl₂, dried (Na₂SO₄) and concentrated under reduced pressure without heating. Column chromatography [silica, CH₂Cl₂/ethyl acetate (3:1)] afforded a pale brown powder (0.312 g, 75%): mp 68 °C (dec.); ¹H NMR δ 2.43 (s, 3H), 5.49 (s, 1H), 5.85–5.90 (m, 1H), 6.03–6.12 (m, 2H), 6.78–6.82 (m, 1H), 7.17–7.34 (m, 7H), 8.28–8.35 (br, 1H), 9.70–9.92 (br, 1H); ¹³C NMR δ 21.8, 44.4, 98.0, 109.9, 110.6, 111.0, 121.1, 127.6, 128.4, 129.0, 129.2, 129.4, 131.2, 132.7, 135.7, 140.4, 141.0, 142.7, 184.9; FABMS obsd 418.0654; calcd 418.0681 (C₁₃₂H₁₉BrN₂O).

[17,18-Dihydro-18,18-dimethyl-5-phenyl-10-(4-methylbenzoyl)porphinato]-palladium(II) (S-Pd4). A solution of S-3 (105 mg, 0.250 mmol) and S-2 (47 mg, 0.25 mmol) in ethanol (2.5 mL) was treated with Pd(CH₃CN)₂Cl₂ (65 mg, 0.25 mmol) and KOH (70.0 mg, 1.25 mmol) at room temperature. Then the reaction mixture was heated at reflux. After 4 h, the reaction mixture was concentrated and chromatographed [silica, CH₂Cl₂/hexanes (1:1)] to afford Pd-4a (first band, 1.9 mg, ¹H NMR, UV–vis spectral data and LD-MS analysis are consistent with that of the product obtained from self-condensation of 2a) and title compound (4.3 mg, 2.8%): ¹H NMR δ 2.01 (s, 6H), 2.65 (s, 3H), 4.59 (s, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.64–7.69 (m, 3H), 7.90 (d, J = 7.6 Hz, 2H), 8.00–8.03 (m, 2H), 8.34–8.42 (m, 2H), 8.49–8.60 (m, 4H), 8.62 (s, 1H), 8.72 (s, 1H); LD-MS obsd 610.1; FABMS obsd 610.1404, calcd 610.1349 (C₃₅H₂₈N₄Pd); λ₂₈₀ 401, 591 nm.
SI References.