

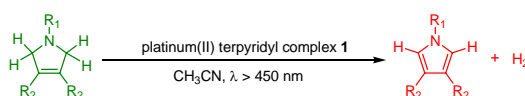
## Supporting Information for

# Facile Preparation of 3,4-Diarylpyrroles and Hydrogen by Platinum(II) Terpyridyl Complex

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### Instrumentation and Materials:

Acetonitrile for spectroscopic measurements and photochemical reaction was purified by the reported procedure.<sup>1</sup> <sup>1</sup>H NMR spectra were recorded on a Bruker Avance dpx 400 MHz instruments using TMS as an internal standard. Mass spectra were recorded with Trio-2000 GC-MS spectrometers. The UV-Vis absorption spectra were recorded using a Shimadzu 1601PC spectrophotometer. The photoluminescence spectra were determined on a Hitachi 4500 spectrophotometer. The time-resolved emission and nanosecond transient absorption spectroscopy were carried out on Edinburgh LP 920. The quantum yields of the photocatalytic reaction were determined by using 532 nm monochromatic light (Millennia Nd:YVO<sub>4</sub> laser) and the light power was recorded by a power meter EPM2000.

Complex **1** was prepared by the reaction of [Pt(trpy)Cl]Cl (trpy = 4'-(4-methoxyphenyl)-2,2':6',2''-terpyridine) with HC≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>5</sub>-4, according to the literature method.<sup>2</sup>

Complex **1**: <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ ppm: 3.92 (s, 3H), 7.22 (d, 2H, *J* = 8.85 Hz), 7.46 (m, 3H), 7.52 (m, 4H), 7.59 (m, 2H), 7.91 (t, 2H, *J* = 6.64 Hz), 8.19 (d, 2H, *J* = 8.81 Hz), 8.53 (t, 2H, *J* = 8.13 Hz), 8.85 (d, 2H, *J* = 8.02 Hz), 8.97 (s, 2H), 9.12 (d, 2H, *J* = 5.50 Hz); FAB-MS: *m/z* 835 (*M*<sup>+</sup>). Anal. Calcd for C<sub>38</sub>H<sub>26</sub>ClN<sub>3</sub>O<sub>5</sub>Pt·0.5H<sub>2</sub>O: C, 54.07; H, 3.22; N, 4.98; O, 10.42. Found: C, 53.84; H, 2.94; N, 4.81; O, 10.38.

3,4-Diaryl-2,5-dihydropyrroles (**2a-2e**) were synthesized from very cheap starting materials by McMurry coupling of dicarbonyl compounds with TiCl<sub>4</sub>/Zn.<sup>3</sup> 3,4-Diarylpyrroles **3a-3e** were obtained in high isolated yield by the photocatalytic reaction and identified by <sup>1</sup>H NMR and MS.

**2a**: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 1.92 (s, 6H, CH<sub>3</sub>), 2.40 (s, 6H, CH<sub>3</sub>), 4.42 (s, 4H, CH<sub>2</sub>), 6.50 (d, 2H, *J* = 8.5 Hz, phenyl), 6.52 (s, 2H, thienyl), 7.22 (d, 2H, *J* = 8.5 Hz, phenyl); MS (EI) *m/z* 399 (*M*<sup>+</sup>, 100).

**3a**: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 2.15 (s, 6H), 2.37 (s, 6H), 6.41 (s, 2H), 7.02 (s, 2H), 7.34 (d, 2H, *J* = 8.6 Hz), 7.39 (d, 2H, *J* = 8.6 Hz); MS (EI): *m/z* 397 (*M*<sup>+</sup>, 100).

**2b**: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 1.93 (s, 6H, CH<sub>3</sub>), 2.40 (s, 6H, CH<sub>3</sub>), 4.47 (s, 4H, CH<sub>2</sub>), 6.53 (s, 2H, thienyl), 6.62 (d, 2H, *J* = 7.0 Hz, phenyl), 6.75 (t, 1H, phenyl), 7.30 (t, 2H, phenyl); MS (EI) *m/z* 365 (*M*<sup>+</sup>, 100).

**3b**: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 2.16 (s, 6H), 2.37 (s, 6H), 6.43 (s, 2H), 7.23-7.46 (m, 5H), 7.07 (s, 2H); MS (EI): *m/z* 363 (*M*<sup>+</sup>, 100).

**2c:** <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>) δ ppm: 1.92 (s, 6H, CH<sub>3</sub>), 2.29 (s, 3H, CH<sub>3</sub>), 2.39 (s, 6H, CH<sub>3</sub>), 4.45 (s, 4H, CH<sub>2</sub>), 6.51 (s, 2H, thienyl), 6.61 (d, 2H, *J* = 7.6 Hz, phenyl), 7.1 (d, 2H, *J* = 7.6 Hz, phenyl); MS (EI) *m/z* 379 (*M*<sup>+</sup>, 100).

**3c:** <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 2.16 (s, 6H), 2.37 (s, 3H), 2.38 (s, 6H), 6.43 (s, 2H), 7.24 (d, 2H, *J* = 8.2 Hz), 7.03 (s, 2H), 7.30 (d, 2H, *J* = 8.2 Hz); MS (EI): *m/z* 377 (*M*<sup>+</sup>, 100).

**2d:** <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>) δ ppm: 1.92 (s, 6H, CH<sub>3</sub>), 2.39 (s, 6H, CH<sub>3</sub>), 3.79 (s, 3H, OCH<sub>3</sub>), 4.42 (s, 4H, CH<sub>2</sub>), 6.51 (s, 2H, thienyl), 6.52 (d, 2H, *J* = 8.3 Hz, phenyl), 6.90 (d, 2H, *J* = 8.3 Hz, phenyl); MS (EI) *m/z* 395 (*M*<sup>+</sup>, 100).

**3d:** <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 2.19 (s, 6H), 2.39 (s, 6H), 3.86 (s, 3H), 6.5 (s, 2H), 6.98 (d, 2H, *J* = 8.4 Hz), 7.00 (s, 2H), 7.37 (d, 2H, *J* = 8.4 Hz); MS (EI): *m/z* 393 (*M*<sup>+</sup>, 100).

**2e:** <sup>1</sup>H-NMR (400MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ ppm: 3.69 (s, 3H, OCH<sub>3</sub>), 4.54 (s, 4H, CH<sub>2</sub>), 6.61 (d, 2H, phenyl), 6.87 (d, 2H, phenyl), 7.30-7.27 (m, 10H, phenyl); MS (EI) *m/z* 327(*M*<sup>+</sup>, 100).

**3e:** <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 3.81(s, 3H), 7.05-7.02 (d, 2H), 7.32-7.17 (m, 12H), 7.57-7.54 (d, 2H); MS (EI): *m/z* 325 (*M*<sup>+</sup>, 100).

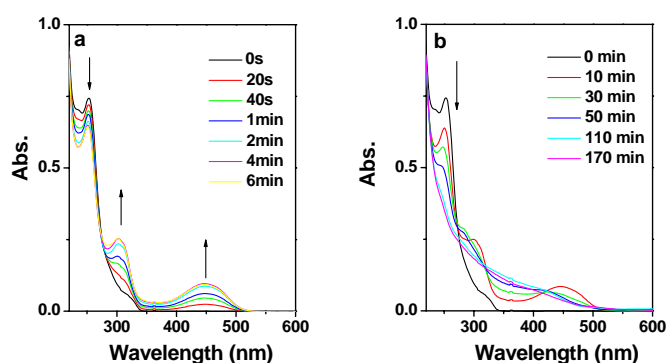
(1) Perrin, D. D.; Armarego, W. L. F. Purification of Laboratory Chemicals, 3<sup>rd</sup> ed.; Pergamon: Oxford, **1988**.

(2) Zhang, D.; Wu, L.-Z.; Zhou, L.; Han, X.; Yang, Q. Z.; Zhang, L. P.; Tung, C. H. *J. Am. Chem. Soc.* **2004**, *126*, 3440–3441.

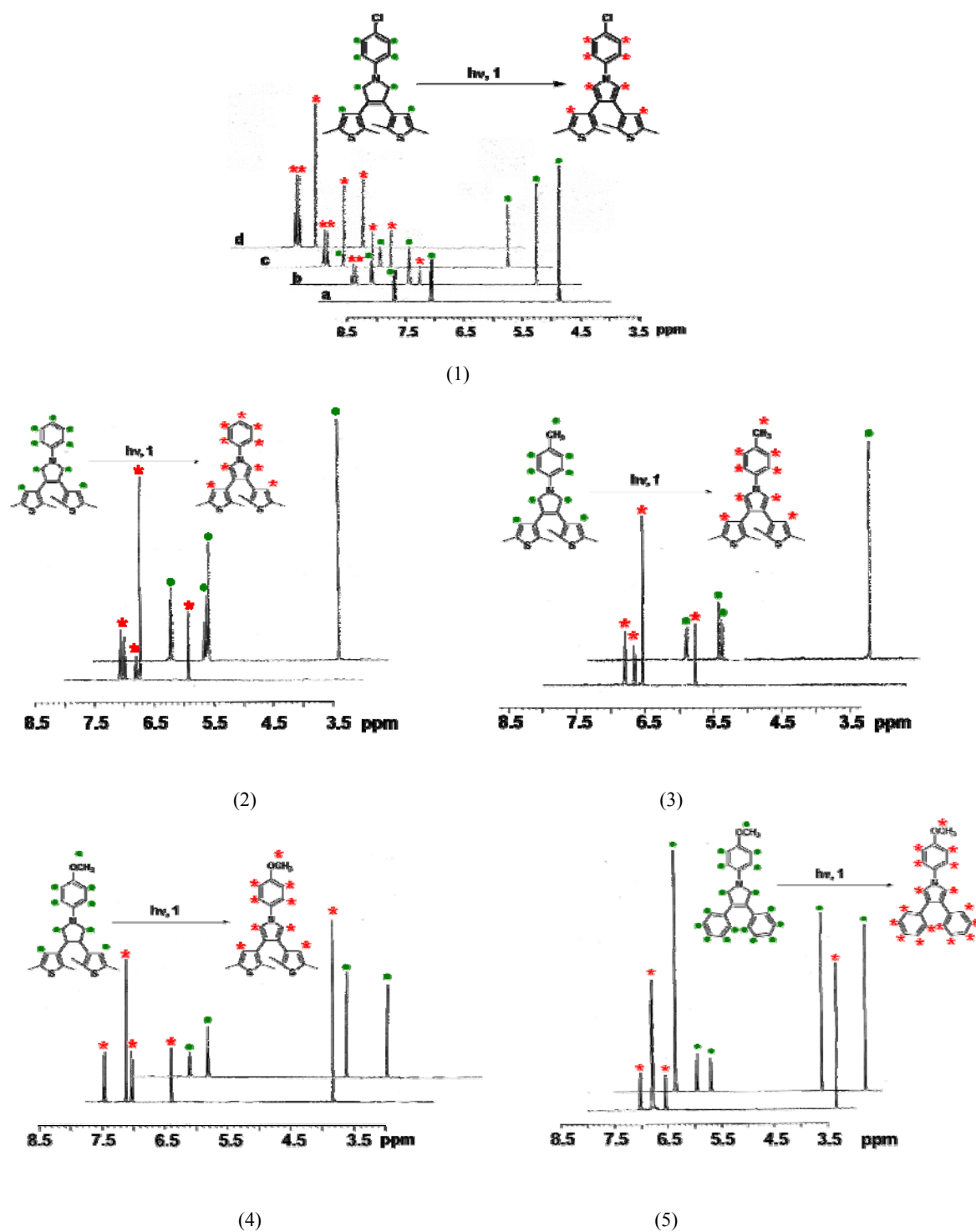
(3) Chen Y.; Zeng, D. X.; Xie, N.; Dang, Y. Z. *J. Org. Chem.* **2005**, *70*, 5001-5005.

### UV-irradiation reactions

We also repeated the UV-irradiation of 3,4-diaryl-2,5-dihydropyrroles in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> and have the following results: when direct UV-irradiation of **2** in degassed CH<sub>3</sub>CN without a photocatalyst was carried out, a typical photochromic behavior was obtained in the first 10 min as shown in **Figure S1**. Two new absorption bands resulted from the ring-closed isomer appeared at longer wavelengths of 300 and 450 nm along with a decreased band at around 250 nm. After that a remarkable degradation was detected (**Figure S1**). The isolated yield of product was less than 20% when **2c** ( $5 \times 10^{-3}$  M) was UV-irradiated for 3 h in degassed acetonitrile. Indeed, 3,4-diarylpyrroles could be prepared by direct irradiation of 3,4-diaryl-2,5-dihydropyrroles with UV light in dichloromethane solution. However, no hydrogen could be obtained during the UV-irradiation reaction, indicating that the reaction pathway is different from the photocatalytic reaction in this work.



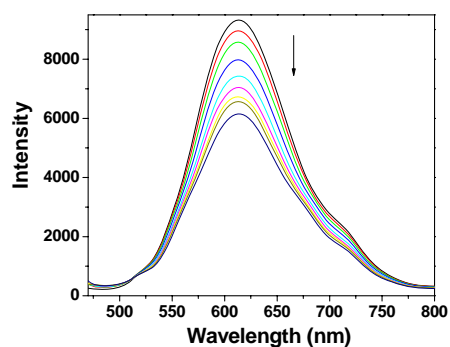
**Figure S1.** Absorption spectral changes of **2c** ( $2.4 \times 10^{-5}$  M) in degassed CH<sub>3</sub>CN upon irradiation at 254 nm. a: Irradiation periods between 0-6 min; b: Irradiation periods between 10-170 min.



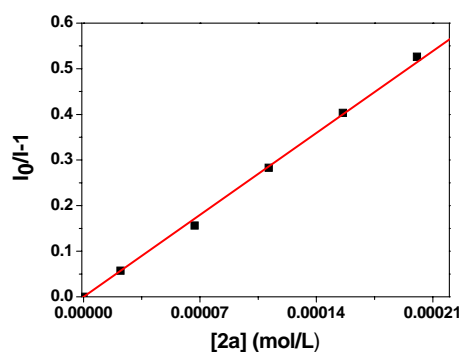
**Figure S2.** (1)  $^1\text{H}$ -NMR spectral changes of **1** and **2a** in  $\text{CD}_3\text{CN}$  with irradiation at  $\lambda > 450$  nm for a) 0 min; b) 10 min; c) 30 min; d) 90 min. For the trace amount of **1**, the spectra only show the disappearance of **2a** (●) and the appearance of **3a** (\*); (2)  $^1\text{H}$  NMR spectra before (●) and after (\*) the photo-irradiation of **2b** and **1** in  $\text{CD}_3\text{CN}$ ; (3)  $^1\text{H}$  NMR spectra before (●) and after (\*) the photo-irradiation of **2c** and **1** in  $\text{CD}_3\text{CN}$ ; (4)  $^1\text{H}$  NMR spectra before (●) and after (\*) the photo-irradiation of **2d** and **1** in  $\text{CD}_3\text{CN}$ ; (5)  $^1\text{H}$  NMR spectra before (●) and after (\*) the photo-irradiation of **2e** and **1** in  $\text{CD}_3\text{CN}$ .

## Luminescence quenching

Complex **1** exhibits moderately intense photoluminescence with  $\lambda_{\text{max}}$  at 628 nm in acetonitrile at room temperature, which is readily quenched by 3,4-diaryl-2,5-dihydropyrrole **2**. **Figure S3a** shows the luminescence spectra of **1** as a function of **2a**. The quenching process follows Stern-Volmer kinetics (**Figure S3b**). The quenching constants ( $k_q$ ) are consistent with those obtained from dynamic quenching and data are listed in **Table S1**.



a



b

**Figure S3.** a: Emission spectra of complex **1** in degassed CH<sub>3</sub>CN as a function of concentration of **2a**;  
b: Stern-Volmer plot for luminescence intensity quenching of **1** by **2a**; [**1**] = 1.2 × 10<sup>-5</sup> M.

**Table S1.** The quenching constants for all 3,4-diaryl-2,5-dihydropyrrole **2** studied in this work:  $I/I_0 - 1 = k_q \cdot \tau_0 \cdot [2]$

Substrate	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>2e</b>
$k_q (\times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1})$	12.4	11.1	7.8	10.3	10.2