

**Stable Neutral Radical of Planar N₂O₂-type Dipyrrin Platinum Complex: Hybrid Radical of
Delocalized Organic π -orbital and Platinum d-orbital**

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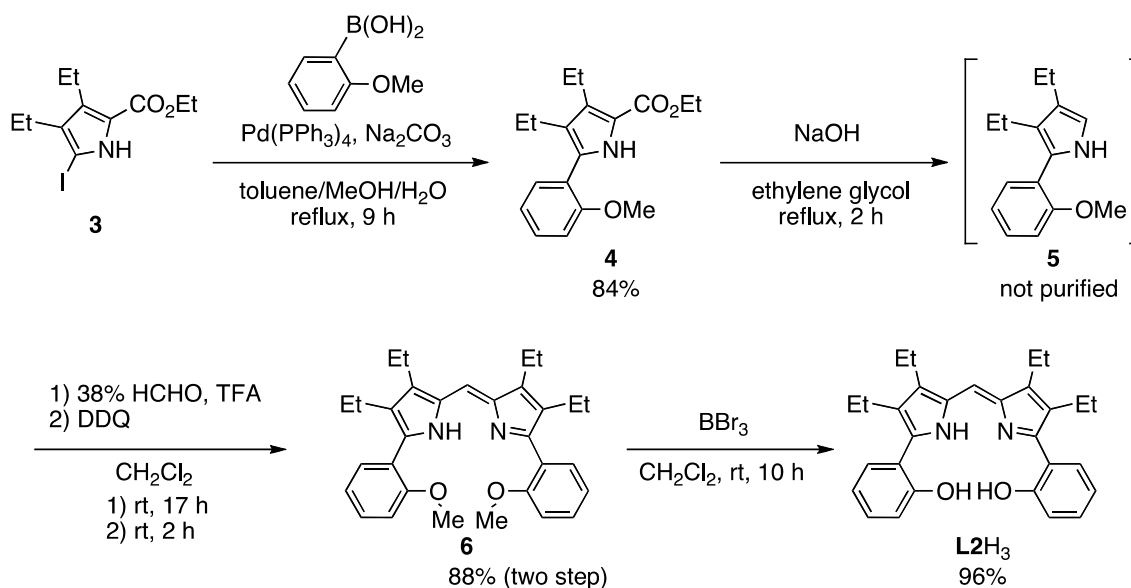
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(1) Synthetic Procedure

Compound **L1H₃** was synthesized according to literature.^{S1} Compound **L2H₃** was synthesized from **3**^{S2} (Scheme S1).



Scheme S1. Synthesis of **L2**.

Synthesis of ethyl 3,4-diethyl-2-(2-methoxyphenyl)-1H-pyrrole-2-carboxylate (**4**)

A toluene/methanol/water (30 mL/4 mL/6 mL) solution of **3** (1.50 g, 4.67 mmol), 2-methoxyphenylboronic acid (0.78 g, 5.14 mmol), Na₂CO₃ (0.99 g, 9.56 mmol), and Pd(PPh₃)₄ (270 mg, 0.234 mmol) was refluxed for 9 hours under a nitrogen atmosphere. The reaction mixture was extracted with ethyl acetate by three times. The combined organic phase was washed with distilled water and then dried over MgSO₄. After evaporation of solvent, crude products were separated by silica-gel column chromatography (ethyl acetate/hexane = 1:8) to give pale orange oil of **4** (1.18 g, 84%).

4: pale orange oil, ¹H NMR (400 MHz, CDCl₃): δ 9.38 (br, 1H), 7.42 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.31 (td, *J* = 7.8, 1.5 Hz, 1H), 7.02 (td, *J* = 7.8, 1.5 Hz, 1H), 6.98 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 2.81 (q, *J* = 7.5 Hz, 2H), 2.55 (q, *J* = 7.5 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.5 Hz, 3H), 1.15 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 14.55, 15.90, 15.95, 17.83, 18.43, 55.56, 59.71, 111.26, 117.72, 120.78, 121.05, 124.63, 128.88, 129.18, 130.17, 133.38, 156.63, 161.51; HRMS (ESI, positive): calcd for C₁₈H₂₃NO₃Na ([M+Na]⁺) 324.1575, found 324.1562.

Synthesis of 3,4-diethyl-2-(2-methoxyphenyl)-1H-pyrrole (**6**)

An ethylene glycol (20 mL) solution of **4** (1.18 g, 3.93 mmol) and NaOH (0.86 g, 21 mmol) was refluxed for 2 hours under an argon atmosphere. To the reaction mixture was added distilled water (40 mL), then the mixture was extracted with ethyl acetate by three times. The combined organic phase was washed with brine and then dried over MgSO₄. Evaporation of solvent gave pale brown

powder of **5** (897.3 mg, 99% if pure). A dichloromethane (20 mL) solution of **5** (251.0 mg, 1.095 mmol), 38% formalin (48.0 mg, 0.59 mmol), and trifluoroacetic acid (12.5 μ L, 0.164 mmol) was stirred at rt for 17 hours under a nitrogen atmosphere in the dark. To the mixture was added 2,3-dichloro-5,6-dicyano-*p*-quinone (123.7 mg, 0.545 mmol), and then the mixture was stirred further for 2 hours. The reaction mixture was filtered through alumina-padded column. After evaporation, chloroform (30 mL) and sat. NaHCO₃ (30 mL) was added. The aqueous phase was extracted with chloroform by three times. The combined organic phase was dried over MgSO₄. Evaporation of solvent gave orange powder of **6** (225.6 mg, 88%).

6: orange powder, ¹H NMR (400 MHz, CDCl₃): δ 7.49 (dd, $J = 7.9, 1.6$ Hz, 2H), 7.29 (td, $J = 7.9, 1.6$ Hz, 2H), 6.97 (td, $J = 7.9, 1.6$ Hz, 2H), 6.90 (dd, $J = 7.9, 1.6$ Hz, 2H), 6.84 (s, 1H), 3.69 (s, 6H), 2.66 (q, $J = 7.6$ Hz, 4H), 2.49 (q, $J = 7.6$ Hz, 4H), 1.24 (t, $J = 7.6$ Hz, 6H), 1.04 (t, $J = 7.6$ Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 15.28, 17.25, 17.95, 18.33, 55.31, 110.85, 116.94, 120.34, 124.38, 128.89, 130.20, 130.88, 137.47, 140.19, 150.84, 157.05; HRMS (ESI, positive): calcd for C₃₁H₃₇N₂O₂ ([M+H]⁺) 469.2855, found 469.2832.

Synthesis of L2H₃

To a dichloromethane (40 mL) solution of **6** (225.6 mg, 481 μ mol) was added BBr₃ (0.4 mL, 4.2 mmol) at 0 °C. The reaction mixture was stirred at rt for 10 hours and then methanol was added. After evaporation, the residue was dissolved into methanol (100 mL) and conc. HCl (10 mL). The reaction mixture was refluxed for 3 hours. To the mixture was added sat. NaHCO₃, then the mixture was extracted with ethyl acetate by four times. The combined organic phase was dried over MgSO₄. Evaporation of solvent gave purple powder of L2H₃ (203.5 mg, 96%).

L2H₃: purple powder, ¹H NMR (600 MHz, CDCl₃): δ 7.60 (dd, $J = 7.7, 1.6$ Hz, 2H), 7.09 (td, $J = 7.7, 1.6$ Hz, 2H), 6.95 (dd, $J = 7.7, 1.6$ Hz, 2H), 6.94 (s, 1H), 6.85 (dd, $J = 7.7, 1.6$ Hz, 2H), 2.73 (q, $J = 7.8$ Hz, 4H), 2.72 (q, $J = 7.8$ Hz, 4H), 1.28 (t, $J = 7.8$ Hz, 6H), 1.22 (t, $J = 7.8$ Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 15.24 (CH₃), 17.26 (CH₃), 17.89 (CH₂), 18.77 (CH₂), 116.00 (CH), 117.20 (CH), 118.59 (C), 119.38 (CH), 128.41 (CH), 129.89 (CH), 130.40 (C), 134.23 (C), 143.08 (C), 150.38 (C), 157.27 (C); Anal calcd for C₂₉H₃₂N₂O₂ C, 79.06; H, 7.32; N 6.36, found C, 78.93; H, 7.50; N 6.32.

(2) ^1H and ^{13}C NMR Spectra

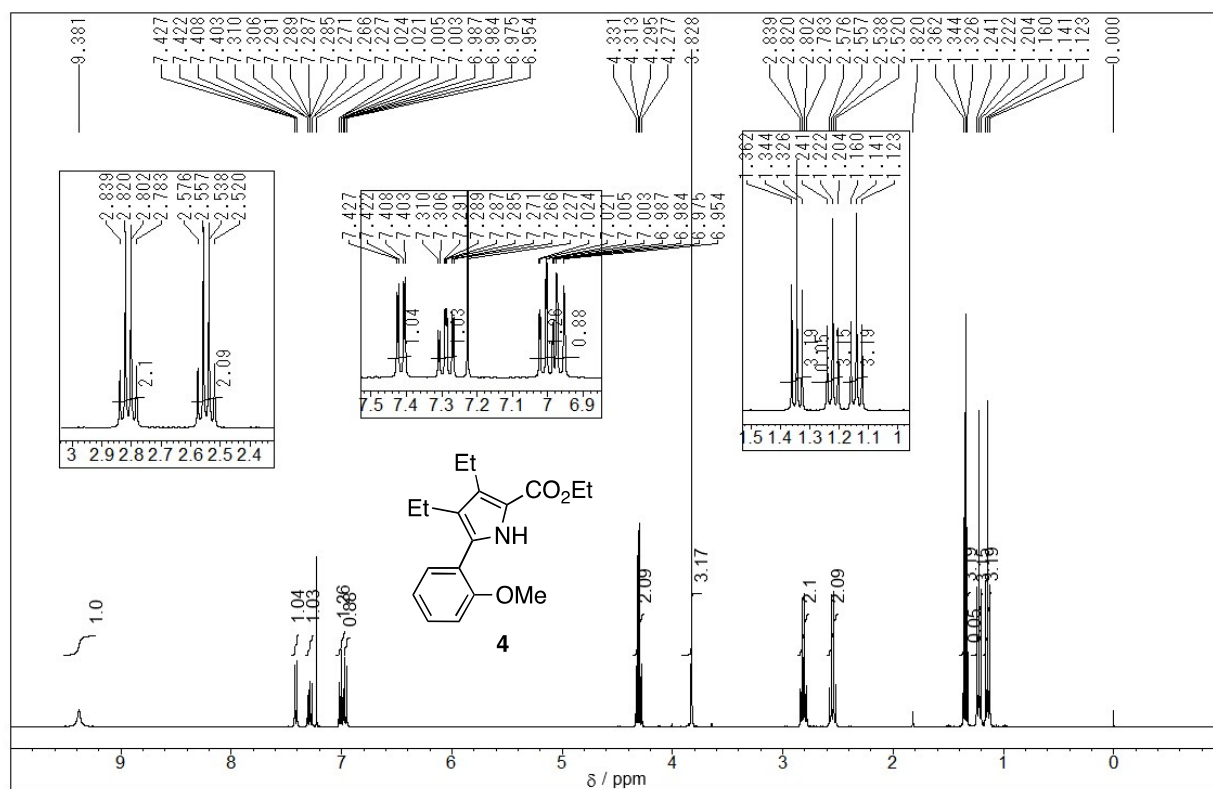


Figure S1. ^1H NMR spectrum of **4** (400 MHz, CDCl_3).

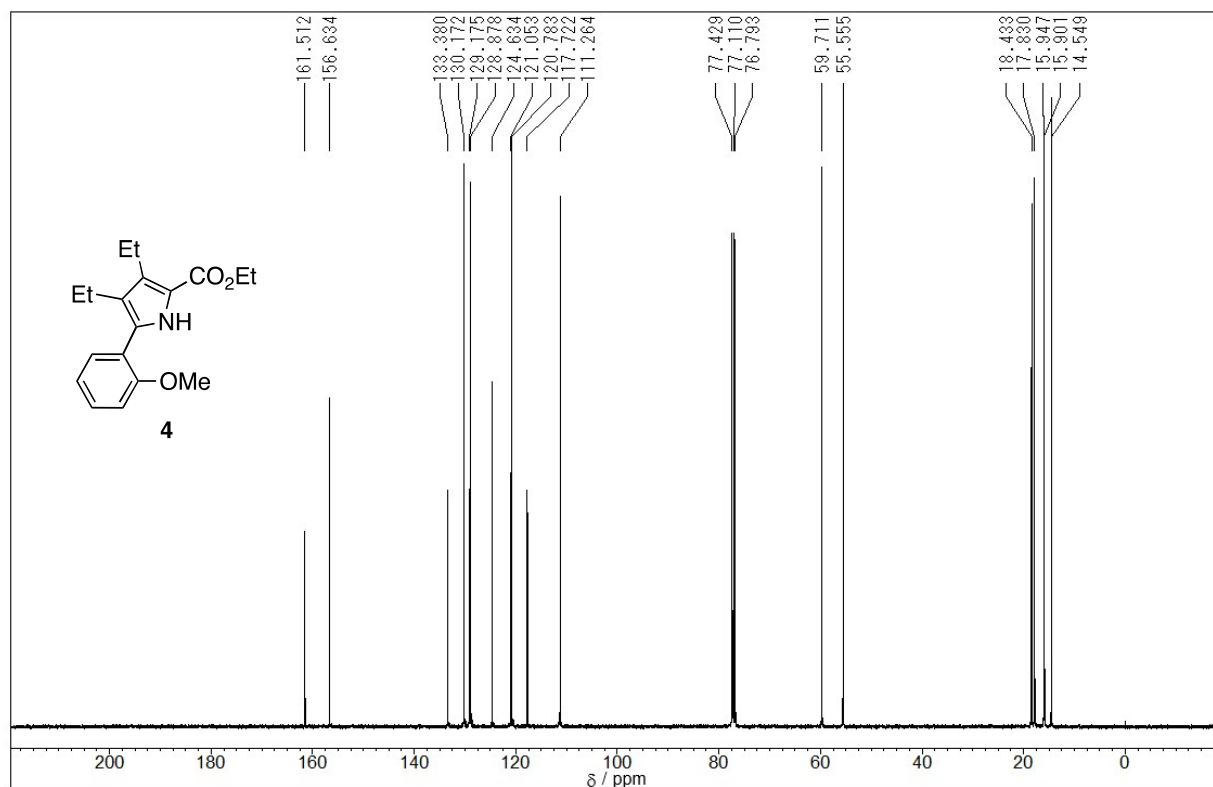


Figure S2. ^{13}C NMR spectrum of **4** (100 MHz, CDCl_3).

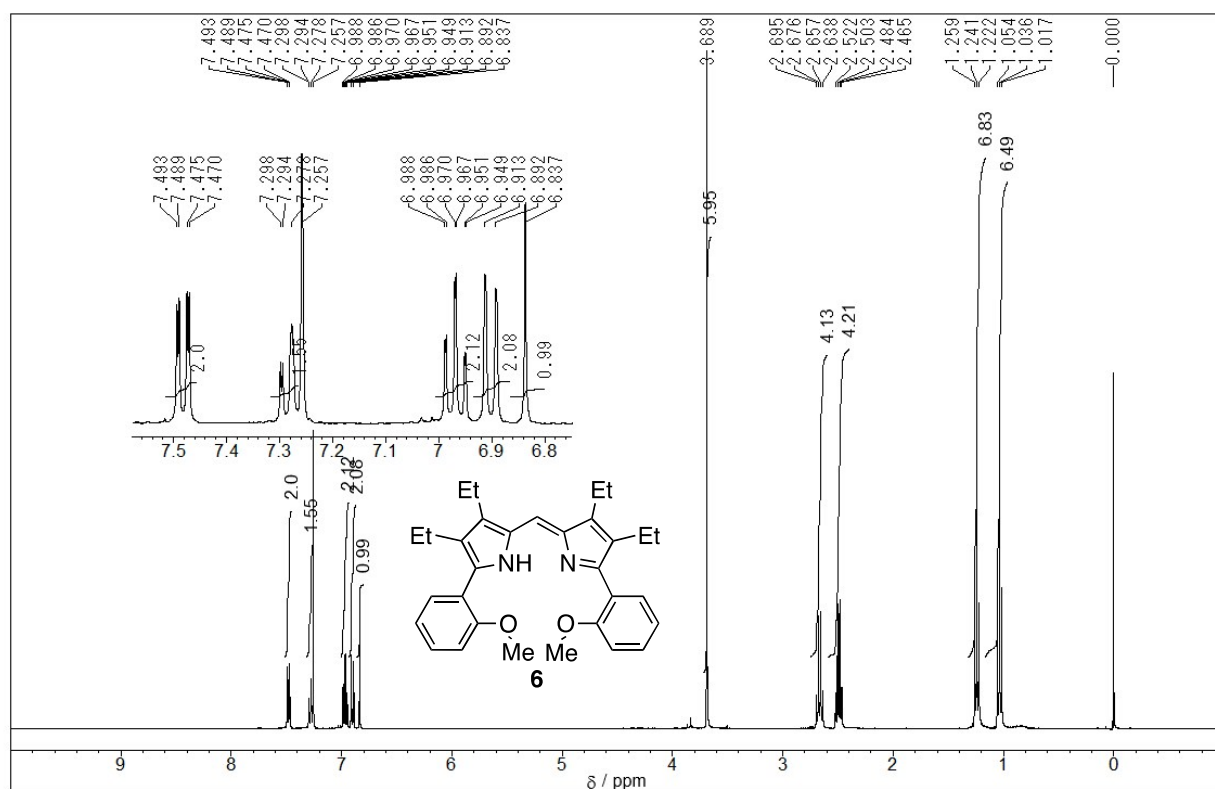


Figure S3. ¹H NMR spectrum of **6** (400 MHz, CDCl₃).

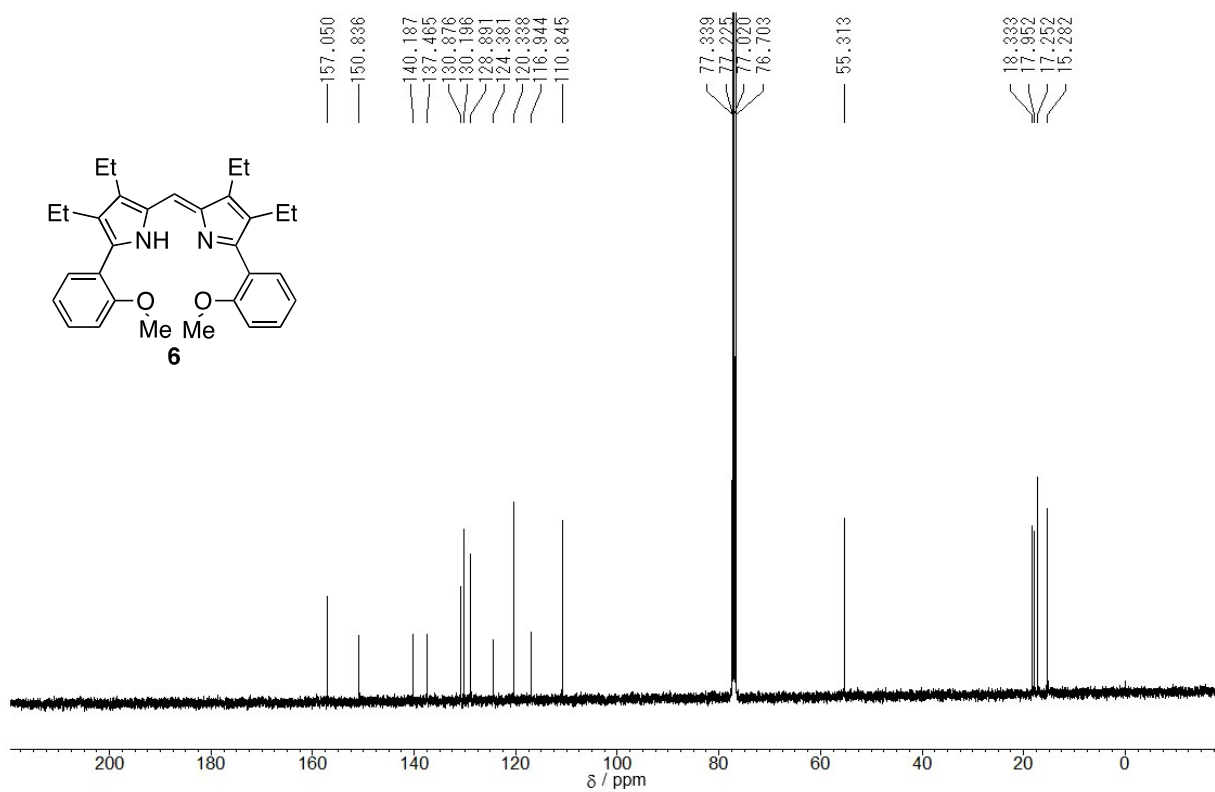


Figure S4. ¹³C NMR spectrum of **6** (100 MHz, CDCl₃).

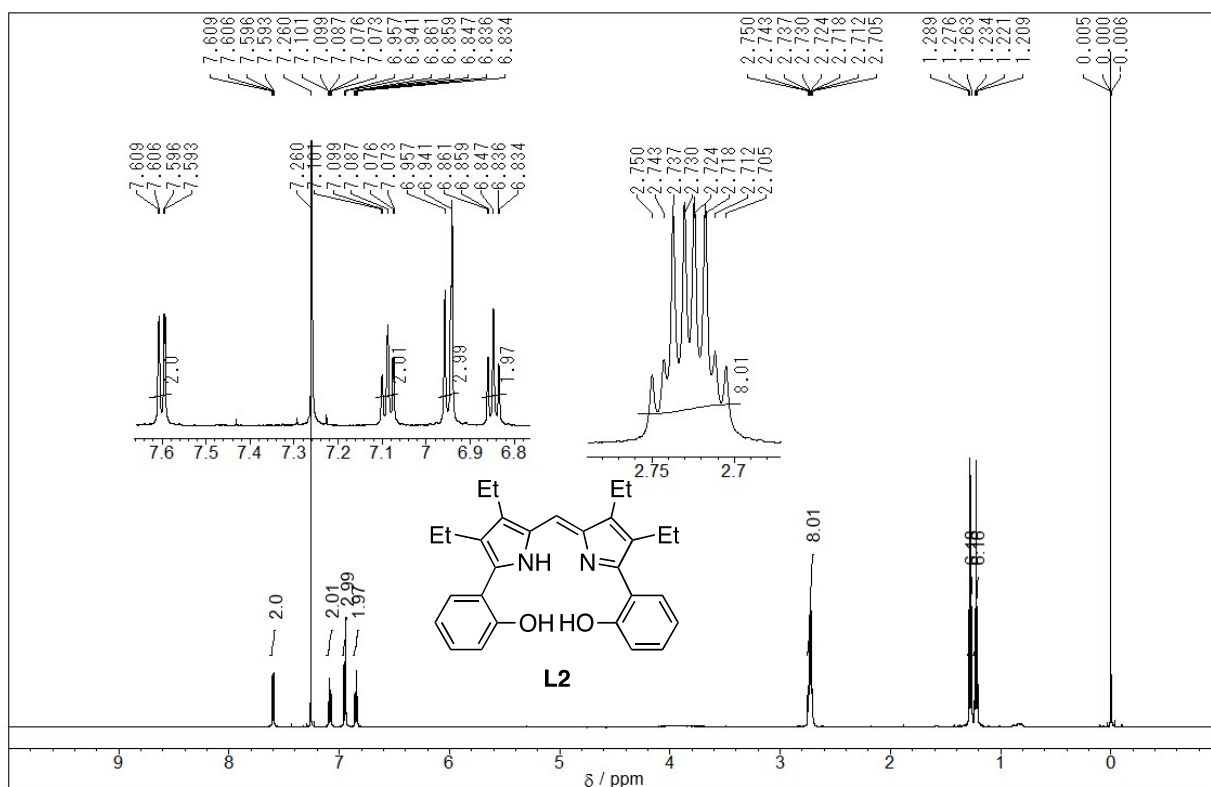


Figure S5. ^1H NMR spectrum of L2H_3 (600 MHz, CDCl_3).

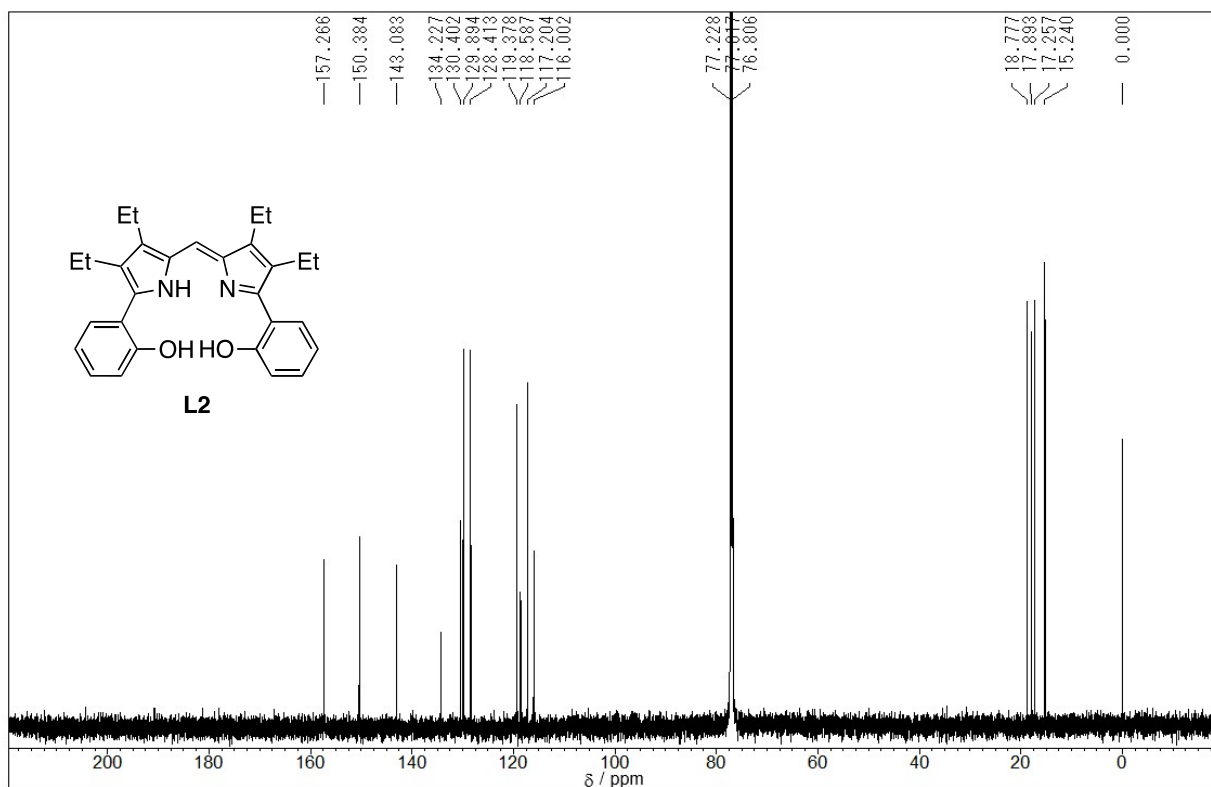


Figure S6. ^{13}C NMR spectrum of L2H_3 (150 MHz, CDCl_3).

(3) References

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S2 J. Setsune, M. Kawama, T. Nishinaka, *Tetrahedron Lett.* **2011**, 52, 1773.